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Regioselective C−H Bond Cleavage/Alkyne Insertion under Ruthenium Catalysis

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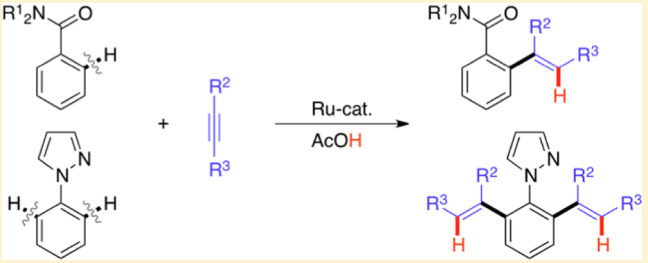
Supporting Information

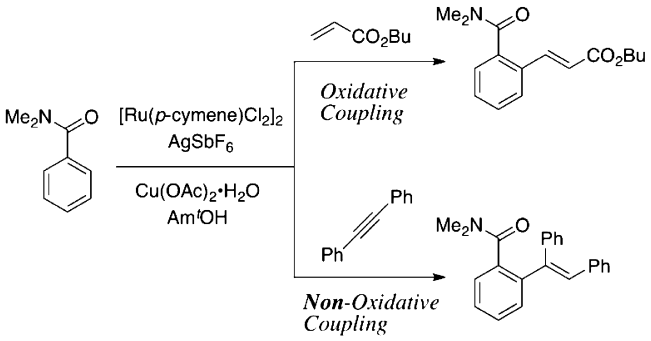
ABSTRACT: The ruthenium-catalyzed coupling reactions of benzamides with alkynes in the presence of acetic acid as a promoter smoothly proceeded regio- and stereoselectively through a directed C−H bond cleavage to produce the corresponding *ortho*-alkenylated products. Phenylpyrazoles and related substrates also underwent a similar coupling to give dialkenylated products selectively. Several competitive experiments were performed to obtain mechanistic insight into both the mono- and dialkenylation reactions.



INTRODUCTION

Since alkenylarene structures can be seen in numerous organic functional materials, methods for their construction have been widely investigated and developed. The direct alkenylation reactions of arenes through regioselective C−H bond activation with the aid of directing groups have attracted much attention as atom- and step-economical methods for their precise syntheses.[1] As early examples, we have demonstrated that 2-phenylphenols, *N*-sulfonyl-2-phenylanilines, and benzoic acids undergo oxidative coupling with alkenes in the presence of a Pd or Rh catalyst and an appropriate oxidant to afford *ortho*-alkenylated products.[2,3] After the discovery, a number of related oxidative alkenylation reactions of a wide range of aromatic substrates have been reported by us[4] and others.[5] More recently, we have succeeded in finding that heteroarene carboxylic acids,[6] phenylazoles,[7] and benzamides[7] undergo similar alkenylation under ruthenium catalysis. The ruthenium-catalyzed reactions seem to be attractive because of their relatively lower catalyst cost than Pd and Rh. One such reaction is depicted in Scheme 1, in which *N*,*N*-dimethylbenzamide undergoes the oxidative coupling with butyl acrylate in the presence of a Ru/Ag catalyst system[8] and a copper salt oxidant to form an *ortho*-alkenylated product almost quantitatively.[8a] We next examined the reaction of the amide employing alkynes in place of alkenes under the same oxidative conditions. As a result, the corresponding oxidative coupling product could not be obtained at all: instead, C−H bond cleavage and alkyne insertion took place to give an alkenylarene as a nonoxidative coupling product. It was then confirmed that this reaction proceeds more efficiently in the absence of any oxidant. Furthermore, the reaction system was found to be applicable to the alkenylation of phenylazoles. The detailed results obtained with respect to these coupling reactions are described herein.[9]

Scheme 1. Ruthenium-Catalyzed Alkenylation of *N*,*N*-Dimethylbenzamide



Recently, similar C−H bond cleavage/alkyne insertion processes using rhodium,[10,11] iridium,[12] palladium,[13] rhenium,[14] nickel,[15] and cobalt[16] catalysts have been disclosed, but the substrate scope still remains limited.

RESULTS AND DISCUSSION

As described above, *N*,*N*-dimethylbenzamide (**1a**) (0.25 mmol) reacted with diphenylacetylene (**2a**) (0.5 mmol) in the presence of $[Ru(p\text{-cymene})Cl_2]_2$ (0.0125 mmol), $AgSbF_6$ (0.05 mmol), and $Cu(OAc)_2{\cdot}H_2O$ (0.5 mmol) in Am^tOH (3 mL) at 100 °C under N_2 to produce (*E*)-2-(1,2-diphenylethenyl)-*N*,*N*-dimethylbenzamide (**3a**) in 45% yield (Scheme 1 and entry 1 in Table 1). It was confirmed that both the ruthenium catalyst and the silver cocatalyst are essential for the present reaction: without each one of them, **3a** could not be

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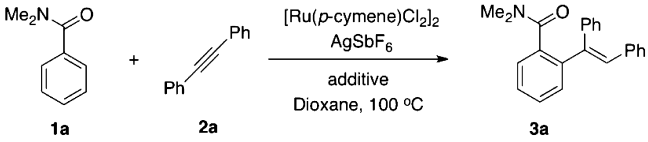
Table 1. Reaction of *N,N*-Dimethylbenzamide (1a) with Diphenylacetylene (2a)[a]



1a 2a 3a

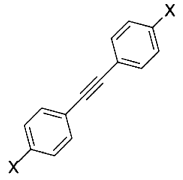
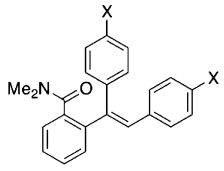
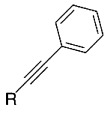
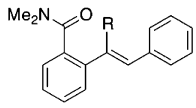
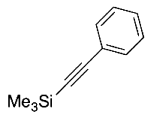
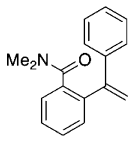
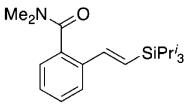
entry	additive (mmol)	solvent	time (h)	yield of **3a** (%)[b]
1	$Cu(OAc)_2·H_2O$ (0.5)	Am^{t}OH	4	47 (45)
2[c]	$Cu(OAc)_2·H_2O$ (0.5)	Am^{t}OH	4	0
3[d]	$Cu(OAc)_2·H_2O$ (0.5)	Am^{t}OH	4	0
4	$Cu(OAc)_2·H_2O$ (0.5)	DMF	4	tr
5	$Cu(OAc)_2·H_2O$ (0.5)	dioxane	4	90
6	$Cu(OAc)_2·H_2O$ (0.5)	diglyme	4	88
7[e]	$Cu(OAc)_2·H_2O$ (0.5)	dioxane	4	88
8		dioxane	5	43
9	AcOH (1)	dioxane	5	96 (81)
10	AcOH (0.1)	dioxane	5	55
11	H_2O (1)	dioxane	5	0
12	KOAc (1)	dioxane	5	0
13[f]	AcOH (1)	dioxane	5	82

[a]Reaction conditions: [**1a**]/[**2a**]/[{Ru(*p*-cymene)Cl_2}$_2$]/[$AgSbF_6$] = 0.25:0.5:0.0125:0.05 (in mmol), in solvent (3 mL) at 100 °C for 5 h under N_2. [b]GC yield based on the amount of **1a** used. Value in parentheses indicates yield after purification. [c]Without [Ru(*p*-cymene)Cl_2]$_2$. [d]Without $AgSbF_6$. [e]At 120 °C. [f][**2a**] = 0.3 mmol.

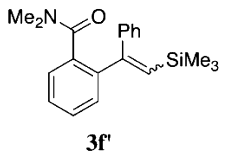
obtained at all (entries 2 and 3, Table 1). While the reaction was sluggish in DMF (entry 4), the product yield was significantly improved in dioxane and diglyme up to 90% and 88% yields, respectively (entries 5 and 6). At 120 °C, a comparable result was obtained (entry 7). In all cases described above, no oxidative coupling product was detected despite the oxidative conditions using $Cu(OAc)_2·H_2O$. However, the reaction efficiency severely decreased without the copper species (entry 8). Afterward, it was found that it acts as an AcOH source rather than oxidant. Thus, the reaction was remarkably promoted by addition of AcOH (1 mmol) to afford **3a** in 96% yield (entry 9). Decreasing the amount of AcOH to 0.1 mmol reduced the yield (entry 10). Under conditions using H_2O or KOAc in place of AcOH, **3a** was not formed at all (entries 11 and 12). Even with a slight excess (0.3 mmol) of **2a**, the alkenylated product **3a** was formed in 82% yield (entry 13).

Under the conditions employed for entry 9 in Table 1, the reactions of **1a** with various alkynes **2a**−**2g** were examined (Table 2). Methyl (**2b**) and chloro (**2c**) substituted diphenylacetylenes reacted smoothly to form the corresponding coupling products **3b** and **3c**, respectively (entries 1 and 2). Unsymmetrical alkylphenylacetylenes, 1-phenylpropyne (**2d**) and 1-phenylhexyne (**2e**), coupled with **1a** to smoothly produce **3d** and **3e**, respectively (entries 3 and 4). It should be noted that no regio- and stereoisomers could be detected at all. The reaction of 1-phenyl-2-(trimethylsilyl)acetylene (**2f**) proceeded efficiently through C−H bond cleavage/alkyne insertion/desilylation to produce a 1,1-diarylethene derivative **3f** in 63% yield, along with a minor amount of normal product **3f′** (entry 5). Using a terminal alkyne, triisopropylsilylacetylene (**2g**), the expected coupling product **3g** was obtained, albeit with a low yield (entry 6). The reaction efficiency was not improved by using various acids in place of AcOH (entries 7−9). A more sterically hindered alkyne, 1-phenyl-2-(triisopropylsilyl)acetylene, did not react with **2a** at all.

Table 2. Reaction of *N,N*-Dimethylbenzamide (1a) with Alkynes 2[a,b,c,d,e,f]

entry	2	product, % yield
		
1	**2b**: X = Me	**3b**: X = Me, 65
2	**2c**: X = Cl	**3c**: X = Cl, 73
		
3	**2d**: R = Me	**3d**: R = Me, 77
4	**2e**: R = Bu	**3e**: R = Bu, 68
		
5	**2f**	**3f**, 63[b]
		
6	**2g**	**3g**, 19
7[c]		**3g**, 0
8[d]		**3g**, (5)[e]
9[f]		**3g**, 0

[a]Reaction conditions: [**1a**]/[**2**]/[{Ru(*p*-cymene)Cl_2}$_2$]/[$AgSbF_6$]/[AcOH] = 0.25:0.5:0.0125:0.05:1 (in mmol), in dioxane (3 mL) at 100 °C for 5 h under N_2. [b]A separable byproduct, *N,N*-dimethyl-2-(1-phenyl-2-(trimethylsilyl)vinyl)benzamide (**3f′**), was also formed (17%). [c]CF_3CO_2H (1 mmol) was employed in place of AcOH. [d]2,6-$Me_2C_6H_3CO_2H$ (1 mmol) was employed in place of AcOH. [e]GC yield. [f]4-$MeC_6H_4SO_3H$ (1 mmol) was employed in place of AcOH.



3f′

Table 3 summarizes the results for the coupling of a number of benzamides **1b**−**1h** with **2a**. A series of *N,N*-disubstituted benzamides having cyclic-, diisopropyl- and diphenylamino groups, **1b**−**1e**, reacted with **2a** to form products **3h**−**3k**, respectively (entries 1−4). 4-Methyl-, methoxy-, and chlorobenzamides **1f**−**1h** also underwent coupling with **2a** smoothly to form products **3l**−**3n** in 77−87% yields (entries 5−7).

One of the possible pathways for the reaction of **1** with **2** is illustrated in Scheme 2. Coordination of an amide function to the Ru center seems to trigger *ortho* C−H bond cleavage to give a five-membered ruthenacycle intermediate **I** accompanied by loss of a proton.[17] Alkyne insertion into the resulting Ru−C

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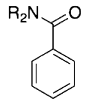
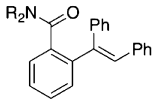
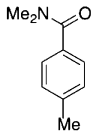
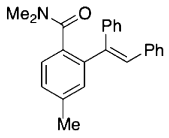
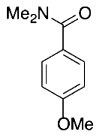
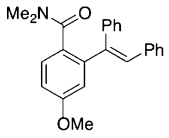
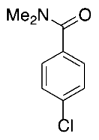
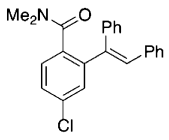
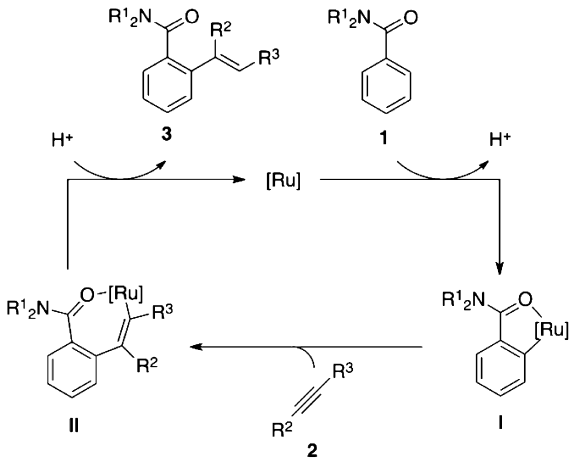
Table 3. Reaction of Benzamides 1 with Diphenylacetylene (2a)[a]

entry	1	product, % yield
		
1	**1b**, $R_2 = (CH_2)_4$	**3h**, $R_2 = (CH_2)_4$, 79
2	**1c**, $R_2 = (CH_2)_5$	**3i**, $R_2 = (CH_2)_5$, 56
3	**1d**, R = Pr^i	**3j**, R = Pr^i, 72
4	**1e**, R = Ph	**3k**, R = Ph, 47
		
5	**1f**	**3l**, 77
		
6	**1g**	**3m**, 84
		
7	**1h**	**3n**, 87

[a]Reaction conditions: [**1**]/[**2a**]/[{Ru(*p*-cymene)Cl_2}$_2$]/[$AgSbF_6$]/[AcOH] = 0.25:0.5:0.0125:0.05:1 (in mmol), in dioxane (3 mL) at 100 °C for 5 h under N_2.

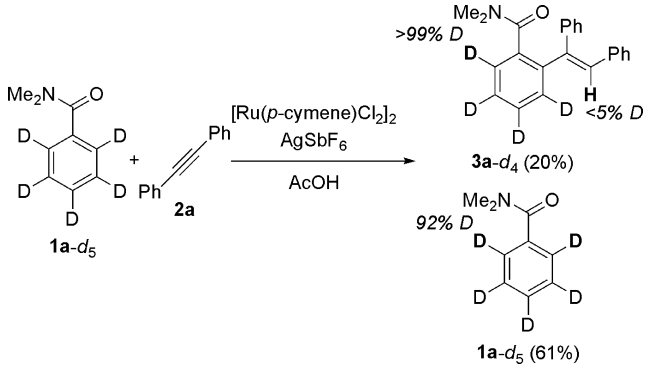
Scheme 2. Plausible Mechanism for the Reaction of 1 with 2



bond then occurs to form a seven-membered species **II**. Subsequent protonolysis may take place to produce **3**. In cases using unsymmetrical alkynes **2d**−**2g**, the regioselectivity of the insertion step from **I** to **II** seems to be governed by steric factors.

For providing further mechanistic information, deuterated *N*,*N*-dimethylbenzamide (**1a**-d_5) was treated with **2a** under standard reaction conditions (Scheme 3). In the early stage (15 min), deuterium incorporation in the olefinic position of the product could not be detected by ^{1}H NMR. This observation may exclude the possibility of the reaction pathway involving initial oxidative addition of the *ortho* C−H bond, which leads to deuterium incorporation at the position.[16a,d] Meanwhile, no significant D−H exchange at the *ortho* positions of recovered **1a**-d_5 as well as at the 6-position of product **3a**-d_4 was observed. This result indicates that the amide-directed C−H bond cleavage step to form intermediate **I** is likely irreversible.

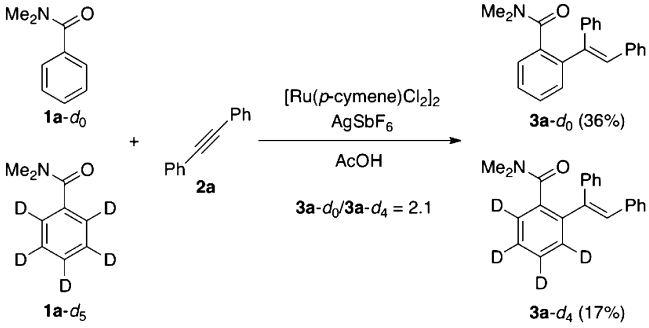
Scheme 3. Reaction of 1a-d_5 with 2a in Dioxane at 100 °C for 15 min[a]



[a]Reaction conditions: [**1a**-d_5]/[**2a**]/[{Ru(*p*-cymene)Cl_2}$_2$]/[$AgSbF_6$]/[AcOH] = 0.25:0.5:0.0125:0.05:1 (in mmol).

Next, an intermolecular competition reaction of **1a**-d_0/**1a**-d_5 with **2a** was examined. As shown in Scheme 4, a considerable primary kinetic isotope effect (KIE) of 2.1 was observed. Two parallel reactions using **1a**-d_0 and **1a**-d_5 were also performed separately and showed a similar KIE value of 2.0 (see the Experimental Section). These facts suggest that the rate-determining step involves C−H(D) bond cleavage.

Scheme 4. Competitive Reaction of 1a-d_0/1a-d_5 in Dioxane at 100 °C for 20 min[a]



[a]Reaction conditions: [**1a**-d_0]/[**1a**-d_5]/[**2a**]/[{Ru(*p*-cymene)Cl_2}$_2$]/[$AgSbF_6$]/[AcOH] = 0.125:0.125:0.5:0.0125:0.05:1 (in mmol).

On the other hand, an intermolecular competition experiment between methyl (**1f**) and chloro (**1h**) substituted benzamides was conducted (Scheme 5). Treatment of equimolar amounts of **1f** and **1h** with **2a** under standard conditions for 10 min gave a mixture of **3l** and **3n** with negligible preference for their formation (54:46). The observed vanishingly small substituent effect, in combination with the KIE effect observed, may suggest that the C−H bond cleavage step does not proceed via a simple S_EAr mechanism, but possibly involves an acetate-assisted deprotonation.[18]

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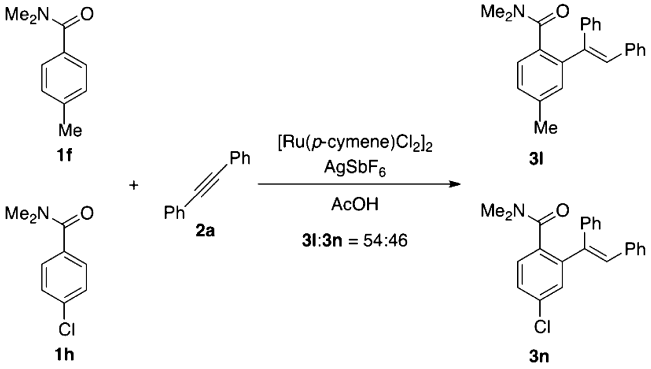
Scheme 5. Competitive Reaction of 1f and 1h in Dioxane at 100 °C for 10 min[a]



[a]Reaction conditions: [**1f**]/[**1h**]/[**2a**]/[{Ru(*p*-cymene)Cl_2}$_2$]/[$AgSbF_6$]/[AcOH] = 0.125:0.125:0.5:0.0125:0.05:1 (in mmol).

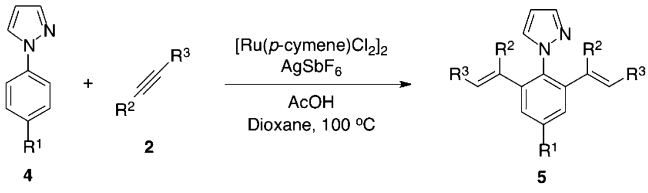
Next, the reactions of 1-phenylpyrazoles **4** with **2** were examined by using the same catalyst system. When 1-phenylpyrazole (**4a**) (0.25 mmol) was treated with **2a** (0.625 mmol) in the presence of [Ru(*p*-cymene)Cl_2]$_2$ (0.0125 mmol), $AgSbF_6$ (0.05 mmol), and AcOH (1 mmol) in dioxane (3 mL) at 100 °C under N_2 for 5 h, the coupling reaction took place efficiently in a 1:2 manner to selectively afford dialkenylated product **5a** in 85% yield (entry 1 in Table 4). Substituted diphenylacetylenes **2b**, **2c**, and **2h** also underwent 1:2 coupling to give the corresponding products **5b**−**5d** (entries 2−4). The reaction of unsymmetrical **2d** gave 1-[2,6-bis(1-phenylprop-1-en-2-yl)phenyl]pyrazole (**5e**) in 85% yield (entry 5). In this case, however, minor amounts (<5%) of isomers were also detected by GC-MS. Meanwhile, 1-(4-substituted phenyl)-pyrazoles **4b**−**4d** reacted with **2a** stereoselectively to form **5f**−**5h** in good yields (entries 6−8).

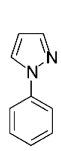
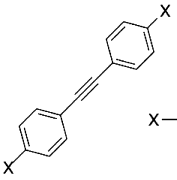
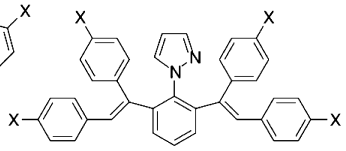
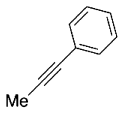
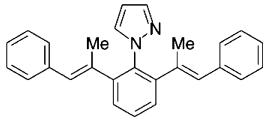
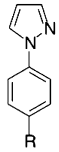
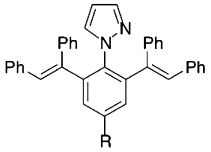
Under similar conditions, treatment of 2-phenylimidazole (**6a**) with **2a** also resulted in the selective formation of dialkenylated product **7a** in 79% yield (Scheme 6). In contrast, somewhat sterically more hindered 1-methyl-2-phenylimidazole (**6b**) reacted with **2a** in a 1:1 manner to produce **7b** selectively.[4] In this case, dialkenylated product could not be detected at all. Probably, the *ortho*-metalation of **7b** seems to be suppressed due to the steric repulsion between the methyl group on the N1 and the 1,2-diphenylethenyl group.

An intermolecular competition reaction of **4a**-d_0/**4a**-d_5 with **2a** was conducted to investigate the reaction mechanism (Scheme 7). In contrast to the case of **1a**-d_0/**1a**-d_5 (Scheme 4), no significant KIE was observed. Two parallel reactions using **4a**-d_0 and **4a**-d_5 also showed a small KIE value (see the Experimental Section).

In another competition experiment between methyl (**4b**) and chloro (**4d**) substituted phenylprazoles (Scheme 8), the larger difference of reactivities of electron-rich and electron-poor substrates, compared to that in benzamides (**1f**/**1h** in Scheme 5), was observed. These facts seem to be reasonable if an S_EAr-like mechanism is assumed to be operative at the C−H bond cleavage step. The difference of the C−H bond cleavage pathways in the reactions of bezamides and phenylpyrazoles may be brought about by the balance of electron densities of their aromatic rings and C−H acidities.

Table 4. Reaction of 1-Phenylpyrazoles 4 with Alkynes 2[a,b]



entry	4	2	product(s), % yield
			
1	**4a**	**2a**, X = H	**5a**, X = H, 85
2		**2b**, X = Me	**5b**, X = Me, 83
3		**2c**, X = Cl	**5c**, X = Cl, 77
4		**2h**, X = OMe	**5d**, X = OMe, 87
			
5	**4a**	**2d**	**5e**, 85[b]
			
6	**4b**, R = Me	**2a**	**5f**, R = Me, 87
7	**4c**, R = OMe		**5g**, R = OMe, 89
8	**4d**, R = Cl		**5h**, R = Cl, 84

[a]Reaction conditions: [**4**]/[**2**]/[{Ru(*p*-cymene)Cl_2}$_2$]/[$AgSbF_6$]/[AcOH] = 0.25:0.625:0.0125:0.05:1 (in mmol), in dioxane (3 mL) at 100 °C for 5 h under N_2. [b]Minor amounts (<5%) of isomers were also detected by GCMS.

CONCLUSIONS

In summary, we have demonstrated that the ruthenium-catalyzed coupling reactions of benzamides and phenylazoles with alkynes can be performed efficiently in 1:1 and 1:2 manners, respectively. The 1:1 and 1:2 selectivities may be governed by steric factors. A number of competitive experiments suggest that the different mechanisms, which possibly involve a rate-determining C−H bond cleavage and an S_EAr-like metalation, are operative in these reactions.

EXPERIMENTAL SECTION

General. ^1H and ^{13}C NMR spectra were recorded at 400 and 100 MHz for $CDCl_3$ solutions. HRMS data were obtained by EI using a double focusing mass spectrometer, unless noted. GC analysis was carried out using a silicon OV-17 column (i.d. 2.6 mm × 1.5 m). GC-MS analysis was carried out using a CBP-1 capillary column (i.d. 0.25 mm × 25 m). The structures of all products listed below were unambiguously determined by ^1H and ^{13}C NMR with the aid of NOE, COSY, HMQC, and HMBC experiments.

Diarylacetylenes **2b**, **2c**, and **2h**,[19] benzamides **1b**−**1h**,[11b] 1-phenylpyrazoles **4b**−**4d**,[20] and 1-methyl-2-phenylimidazole (**6b**)[21] were prepared according to published procedures. Other starting materials and reagents were commercially available.

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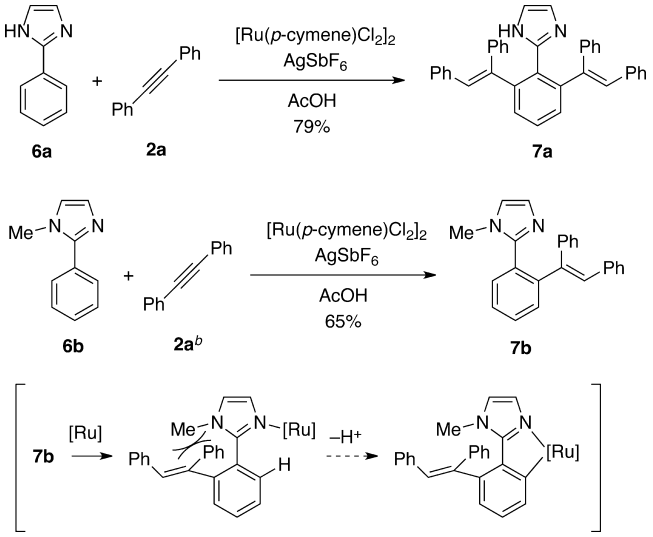
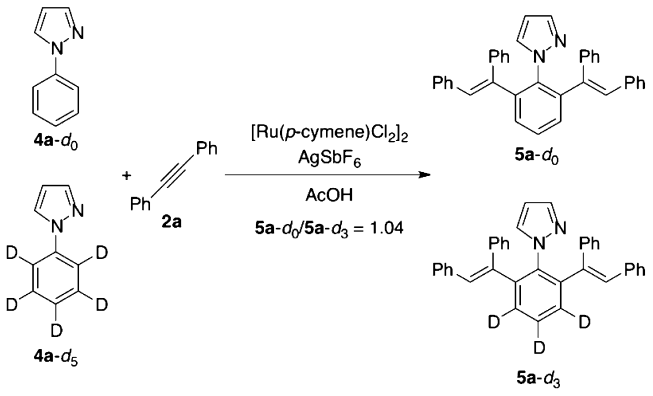
Scheme 6. Reaction of 2-Phenylimidazoles 6 with 2a in Dioxane at 100 °C for 5 h[a,b]



[a]Reaction conditions: [**6**]/[**2a**]/[{Ru(*p*-cymene)Cl_2}$_2$]/[$AgSbF_6$]/[AcOH] = 0.25:0.625:0.0125:0.05:1 (in mmol). [b]**2a** (0.5 mmol) was employed.

Scheme 7. Competitive Reaction of 4a-d_0/4a-d_5 in Dioxane at 100 °C for 20 min[a]

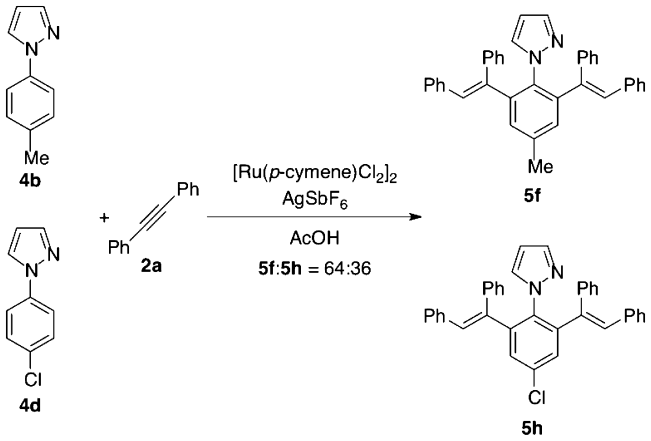


[a]Reaction conditions: [**4a**-d_0]/[**4a**-d_5]/[**2a**]/[{Ru(*p*-cymene)Cl_2}$_2$]/[$AgSbF_6$]/[AcOH] = 0.125:0.125:0.625:0.0125:0.05:1 (in mmol).

General Procedure for Coupling of Benzamides with Alkynes. To a 20 mL two-neck flask with a reflux condenser, a balloon, and a rubber cup were added benzamide **1** (0.25 mmol), alkyne **2** (0.5 mmol), [Ru(*p*-cymeme)Cl_2]$_2$ (0.0125 mmol, 7.6 mg), $AgSbF_6$ (0.05 mmol, 17 mg), AcOH (1 mmol, 60 mg), 1,4-diphenylethane (ca. 30 mg) as internal standard, and dioxane (3 mL). The resulting mixture was then stirred under nitrogen at 100 °C for 5 h. After cooling, the reaction mixture was poured into ethyl acetate (100 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 (1:1, v/v) as eluant.

Procedure for Reaction of Deuterated Benzamides with Diphenylacetylene. To a 20 mL two-neck flask with a reflux condenser, a balloon, and a rubber cup were added *N*,*N*-dimethylbenzamide-d_5 (**1a**-d_5) (0.25 mmol, 39 mg), diphenylacetylene (**2a**) (0.5 mmol, 89 mg), [Ru(*p*-cymeme)Cl_2]$_2$ (0.0125 mmol, 7.6 mg), $AgSbF_6$ (0.05 mmol, 17 mg), AcOH (1 mmol, 60 mg), 1,4-diphenylethane (ca. 30 mg) as internal standard, and dioxane (3 mL). The resulting mixture was stirred under N_2 at 100 °C for 15 min. After cooling, the reaction mixture was poured into water (100 mL), extracted with ethyl acetate (100 mL), washed with water (100 mL, three times), and dried over Na_2SO_4. Produced **3a**-d_4 and recovered **1a**-d_5 were isolated by column chromatography on silica gel using hexane−ethyl acetate (1:1) as eluant. Recovered **1a**-d_5 (23.4 mg, 61%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.98 (s, 3H), 3.11 (s, 3H), 7.41 (s, 0.2H). Produced **3a**-d_4 (16.7 mg, 20%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.57 (s, 3H), 2.66 (s, 3H), 6.79 (s, 0.96H), 7.03−7.06 (m, 2H), 7.10−7.16 (m, 5H), 7.22−7.25 (m, 3H).

Scheme 8. Competitive Reaction of 4b and 4d in Dioxane at 100 °C for 20 min[a]



[a]Reaction conditions: [**4b**]/[**4d**]/[**2a**]/[{Ru(*p*-cymene)Cl_2}$_2$]/[$AgSbF_6$]/[AcOH] = 0.125:0.125:0.625:0.0125:0.05:1 (in mmol).

Procedure for Competitive Reaction of 1a-d_0 and 1a-d_5. To a 20 mL two-neck flask with a reflux condenser, a balloon, and a rubber cup were added *N*,*N*-dimethylbenzamide (**1a**-d_0) (0.125 mmol, 19 mg), *N*,*N*-dimethylbenzamide-d_5 (**1a**-d_5) (0.125 mmol, 20 mg), diphenylacetylene (**2a**) (0.5 mmol, 89 mg), [Ru(*p*-cymeme)Cl_2]$_2$ (0.0125 mmol, 7.6 mg), $AgSbF_6$ (0.05 mmol, 17 mg), AcOH (1 mmol, 60 mg), 1,4-diphenylethane (ca. 30 mg) as internal standard, and dioxane (3 mL). The resulting mixture was stirred under N_2 at 100 °C for 20 min. After cooling, the reaction mixture was poured into water (100 mL), extracted with ethyl acetate (100 mL), washed with water (100 mL, three times), and dried over Na_2SO_4. The product was isolated by column chromatography on silica gel using hexane−ethyl acetate (1:1) as eluant (43.9 mg, 53%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.56 (s, 3H), 2.66 (s, 3H), 6.79 (s, 1H), 7.03−7.06 (m, 2H), 7.10−7.16 (m, 5H), 7.20−7.25 (m, 3.68H), 7.30−7.34 (m, 0.68H), 7.35−7.41 (m, 1.36H). The kinetic isotope effect was determined by ^{1}H NMR: k_H/k_D = 0.68/0.32 = 2.1.

Parallel Reactions of 1a-d_0 and 1a-d_5 (Scheme 9). To a 20 mL two-neck flask were added *N*,*N*-dimethylbenzamide-d_0 or -d_5 (**1a**-d_0 or **1a**-d_5) (0.25 mmol), diphenylacetylene (**2a**) (0.5 mmol, 89 mg), [Ru(*p*-cymeme)Cl_2]$_2$ (0.0125 mmol, 7.6 mg), $AgSbF_6$ (0.05 mmol, 17 mg), AcOH (1 mmol, 60 mg), 1,4-diphenylethane (ca. 30 mg) as internal standard, and dioxane (3 mL). The resulting mixture was stirred under N_2 at 100 °C for 10 min. GC and GC-MS analyses of the mixture confirmed formation of **3a**-d_0 (51%) or **3a**-d_4 (26%): k_H/k_D = 2.0.

Procedure for Competitive Reaction of 1f and 1h. To a 20 mL two-neck flask with a reflux condenser, a balloon, and a rubber cup were added *N*,*N*,4-trimethylbenzamide (**1f**) (0.125 mmol, 20 mg), 4-chloro-*N*,*N*-dimethylbenzamide (**1h**) (0.125 mmol, 23 mg), diphenylacetylene (**2a**) (0.5 mmol, 89 mg), [Ru(*p*-cymeme)Cl_2]$_2$ (0.0125 mmol, 7.6 mg), $AgSbF_6$ (0.05 mmol, 17 mg), AcOH (1 mmol, 60 mg), 1,4-diphenylethane (ca. 30 mg) as internal standard, and dioxane (3 mL). The resulting mixture was stirred under N_2 at 100 °C for 10 min. GC and GC-MS analyses of the mixture confirmed formation of **3l** (81%) and **3n** (68%).

General Procedure for Coupling of 1-Phenylpyrazoles with Alkynes. To a 20 mL two-neck flask with a reflux condenser, a balloon, and a rubber cup were added 1-phenylpyrazole **4** (0.25

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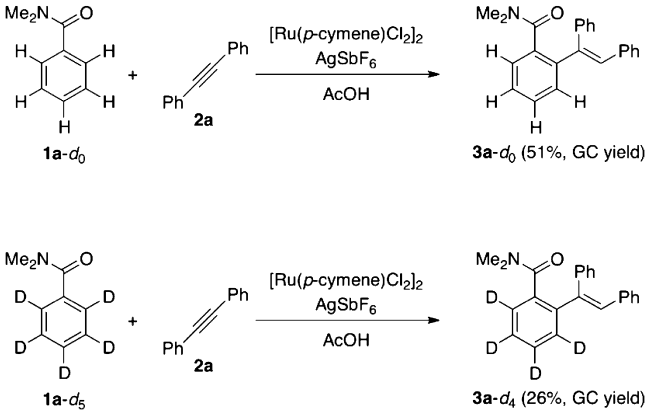
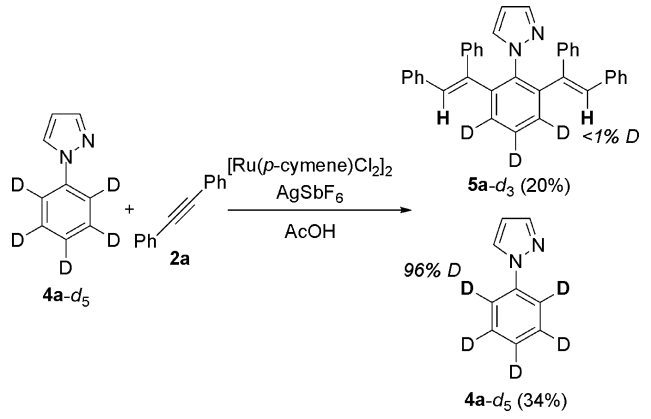
Scheme 9. Parallel Reactions Using 1a-d_0 and 1a-d_5 in Dioxane at 100 °C for 10 min[a]



[a]Reaction conditions: [**1a**-d_0 or **1a**-d_5]/[**2a**]/[{Ru(*p*-cymene)Cl_2}$_2$]/[$AgSbF_6$]/[AcOH] = 0.25:0.5:0.0125:0.05:1 (in mmol).

mmol), alkyne **2** (0.625 mmol), [Ru(*p*-cymeme)Cl_2]$_2$ (0.0125 mmol, 7.6 mg), $AgSbF_6$ (0.05 mmol, 17 mg), AcOH (1 mmol, 60 mg), 1,4-diphenylethane (ca. 30 mg) as internal standard, and dioxane (3 mL). The resulting mixture was then stirred under nitrogen at 100 °C for 5 h. After cooling, the reaction mixture was poured into ethyl acetate (100 mL). The organic layer was washed with water (100 mL, three times), and dried over Na_2SO_4. Product **5** was isolated by column chromatography on silica gel using hexane−ethyl acetate (5:1, v/v) as eluant.

Scheme 10. Reaction of 4a-d_5 with 2a in Dioxane at 100 °C for 10 min[a]

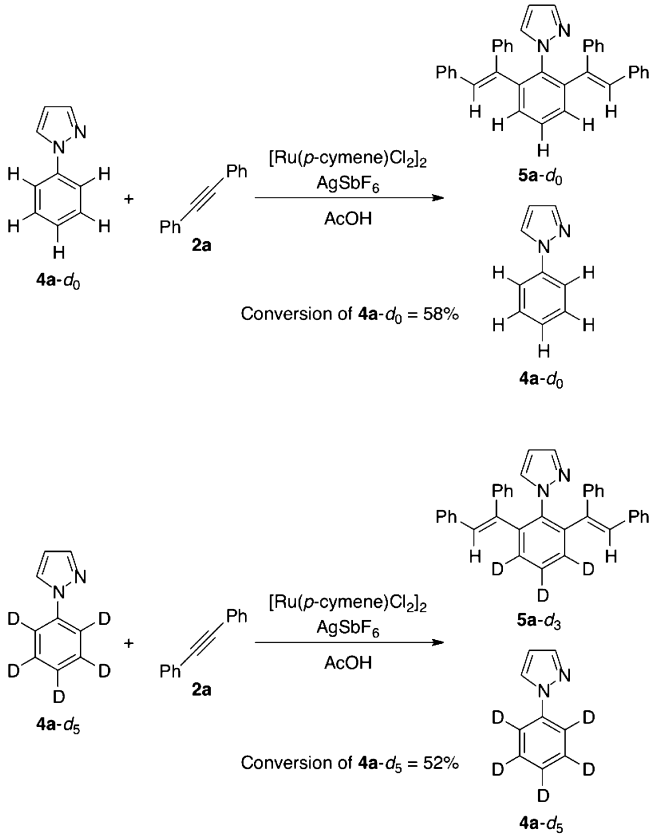


[a]Reaction conditions: [**4a**-d_5]/[**2a**]/[{Ru(*p*-cymene)Cl_2}$_2$]/[$AgSbF_6$]/[AcOH] = 0.25:0.625:0.0125:0.05:1 (in mmol).

Procedure for Reaction of 4a-d_5 with 2a (Scheme 10). To a 20 mL two-neck flask with a reflux condenser, a balloon, and a rubber cup were added 1-phenylpyrazole-d_5 (**4a**-d_5) (0.25 mmol, 37 mg), diphenylacetylene (**2a**) (0.625 mmol, 111 mg), [Ru(*p*-cymeme)Cl_2]$_2$ (0.0125 mmol, 7.6 mg), $AgSbF_6$ (0.05 mmol, 17 mg), AcOH (1 mmol, 60 mg), 1,4-diphenylethane (ca. 30 mg) as internal standard, and dioxane (3 mL). The resulting mixture was stirred under N_2 at 100 °C for 10 min. After cooling, the reaction mixture was poured into water (100 mL), extracted with ethyl acetate (100 mL), washed with water (100 mL, three times), and dried over Na_2SO_4. Produced **5a**-d_3 and recovered **4a**-d_5 were isolated by column chromatography on silica gel using hexane−ethyl acetate (5:1) as eluant. Recovered **4a**-d_5 (12.7 mg, 34%): ^{1}H NMR (400 MHz, $CDCl_3$) δ6.46−6.48 (m, 1H), 7.70 (s, 0.08H), 7.73−7.74 (m, 1H), 7.92−7.93 (m, 1H). Produced **5a**-d_3 (25.3 mg, 20%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.71−5.72 (m, 1H), 6.57 (s, 2H), 6.79−6.80 (m, 1H), 6.87−6.94 (m, 8H), 7.03−7.11 (m, 12H), 7.17−7.18 (m, 1H).

Procedure for Competitive Reaction of 4a-d_0 and 4a-d_5. To a 20 mL two-neck flask with a reflux condenser, a balloon, and a rubber cup were added 1-phenylpyrazole (**4a**-d_0) (0.125 mmol, 18 mg), 1-phenylpyrazole-d_5 (**4a**-d_5) (0.125 mmol, 19 mg), diphenylacetylene (**2a**) (0.625 mmol, 111 mg), [Ru(*p*-cymeme)Cl_2]$_2$ (0.0125 mmol, 7.6 mg), $AgSbF_6$ (0.05 mmol, 17 mg), AcOH (1 mmol, 60 mg), 1,4-diphenylethane (ca. 30 mg) as internal standard, and dioxane (3 mL). The resulting mixture was stirred under N_2 at 100 °C for 20 min. After cooling, the reaction mixture was poured into water (100 mL), extracted with ethyl acetate (100 mL), washed with water (100 mL, three times), and dried over Na_2SO_4. The product was isolated by column chromatography on silica gel using hexane−ethyl acetate (5:1) as eluant (40 mg, 32%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.71−5.72 (m, 1H), 6.58 (s, 2H), 6.79−6.80 (m, 1H), 6.88−6.94 (m, 8H), 7.06−7.11 (m, 12H), 7.18−7.19 (m, 1H), 7.43 (m, 1.54H). The kinetic isotope effect was determined by ^{1}H NMR: k_H/k_D = 0.51/0.49 = 1.04.

Scheme 11. Parallel Reactions Using 4a-d_0 and 4a-d_5 in Dioxane at 100 °C for 10 min[a]



[a]Reaction conditions: [**4a**-d_0 or **4a**-d_5]/[**2a**]/[{Ru(*p*-cymene)Cl_2}$_2$]/[$AgSbF_6$]/[AcOH] = 0.25:0.625:0.0125:0.05:1 (in mmol).

Parallel Reactions of 4a-d_0 and 4a-d_5 (Scheme 11). To a 20 mL two-neck flask were added 1-phenylpyrazole-d_0 or -d_5 (**4a**-d_0 or **4a**-d_5) (0.25 mmol), diphenylacetylene (**2a**) (0.625 mmol, 111 mg), [Ru(*p*-cymeme)Cl_2]$_2$ (0.0125 mmol, 7.6 mg), $AgSbF_6$ (0.05 mmol, 17 mg), AcOH (1 mmol, 60 mg), 1,4-diphenylethane (ca. 30 mg) as internal standard, and dioxane (3 mL). The resulting mixture was stirred under N_2 at 100 °C for 10 min. GC and GC-MS analyses of the mixture confirmed conversion of **4a**-d_0 (58%) or **4a**-d_5 (52%): k_H/k_D = 1.1.

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Procedure for Competitive Reaction of 4b and 4d. To a 20 mL two-neck flask with a reflux condenser, a balloon, and a rubber cup were added 1-(4-methylphenyl)pyrazole (**4b**) (0.125 mmol, 20 mg), 1-(4-chlorophenyl)pyrazole (**4d**) (0.125 mmol, 22 mg), diphenylacetylene (**2a**) (0.625 mmol, 111 mg), $[Ru(p\text{-cymeme})Cl_2]_2$ (0.0125 mmol, 7.6 mg), $AgSbF_6$ (0.05 mmol, 17 mg), AcOH (1 mmol, 60 mg), 1,4-diphenylethane (ca. 30 mg) as internal standard, and dioxane (3 mL). The resulting mixture was stirred under N_2 at 100 °C for 20 min. A mixture of **5f** and **5h** was obtained by column chromatography on silica gel using hexane−ethyl acetate (5:1) as eluant (61 mg). ^{1}H NMR analysis of the mixture confirmed the ratio of **5f** and **5h** (64:36).

(*E*)-2-(1,2-Diphenylethenyl)-*N*,*N*-dimethylbenzamide (3a):[9] Oil, 66 mg (81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.56 (s, 3H), 2.66 (s, 3H), 6.79 (s, 1H), 7.03−7.06 (m, 2H), 7.10−7.16 (m, 5H), 7.20−7.25 (m, 4H), 7.30−7.41 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.2, 38.6, 126.9, 127.0, 127.4, 127.5, 127.9, 128.0, 128.8, 129.5, 130.38, 130.40, 130.8, 136.3, 137.2, 139.5, 141.5, 141.8, 170.7; HRMS m/z calcd for $C_{23}H_{21}NO$ (M^+), 327.1623; found, 327.1622.

(*E*)-2-[1,2-Bis(4-methylphenyl)ethenyl]-*N*,*N*-dimethylbenzamide (3b): Oil, 57 mg (65%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 3H), 2.33 (s, 3H), 2.61 (s, 3H), 2.68 (s, 3H), 6.71 (s, 1H), 6.92−6.95 (m, 4H), 7.04 (s, 4H), 7.21−7.22 (m, 1H), 7.29−7.35 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 21.3, 34.3, 38.7, 127.1, 127.3, 128.6, 128.7, 128.8, 129.3, 130.2, 130.3, 130.4, 134.5, 136.2, 136.6, 136.7, 137.0, 140.5, 142.1, 170.8; HRMS m/z calcd for $C_{25}H_{25}NO$ (M^+), 355.1936; found, 355.1935.

(*E*)-2-[1,2-Bis(4-chlorophenyl)ethenyl]-*N*,*N*-dimethylbenzamide (3c):[9] Oil, 73 mg (73%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.59 (s, 3H), 2.68 (s, 3H), 6.76 (s, 1H), 6.96 (d, J = 8.2 Hz, 2H), 7.07 (d, J = 7.5 Hz, 2H), 7.11 (d, J = 7.2 Hz, 2H), 7.20−7.23 (m, 3H), 7.32−7.38 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.3, 38.8, 127.1, 127.9, 128.3, 128.4, 129.0, 129.9, 130.4, 130.7, 131.8, 132.8, 133.5, 135.3, 136.2, 137.7, 141.1, 141.2, 170.4; HRMS m/z calcd for $C_{23}H_{19}Cl_2NO$ (M^+), 395.0844; found, 395.0845.

(*E*)-2-(1-Methyl-2-phenylethenyl)-*N*,*N*-dimethylbenzamide (3d):[9] Oil, 51 mg (77%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.23 (s, 3H), 2.82 (s, 3H), 3.06 (s, 3H), 6.57 (s, 1H), 7.23−7.26 (m, 1H), 7.31−7.41 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.1, 34.8, 38.6, 126.7, 127.1, 127.3, 128.0, 128.2, 128.95, 128.97, 130.2, 135.1, 136.9, 137.8, 142.6, 171.6; HRMS m/z calcd for $C_{18}H_{19}NO$ (M^+), 265.1467; found, 265.1470.

(*E*)-2-(1-Butyl-2-phenylethenyl)-*N*,*N*-dimethylbenzamide (3e):[9] Oil, 53 mg (68%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80 (t, J = 7.2 Hz, 3H), 1.22−1.34 (m, 4H), 2.57 (t, J = 6.9 Hz, 2H), 2.85 (s, 3H), 3.05 (s, 3H), 6.48 (s, 1H), 7.23−7.40 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 22.7, 30.9, 31.3, 34.8, 38.9, 126.6, 126.9, 127.2, 128.2, 128.7, 128.8, 129.1, 129.8, 135.4, 137.8, 141.3, 143.3, 171.5; HRMS m/z calcd for $C_{21}H_{25}NO$ (M^+), 307.1936; found, 307.1935.

(*E*)-2-(1-Phenylethenyl)-*N*,*N*-dimethylbenzamide (3f):[9] Oil, 40 mg (63%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.80 (s, 3H), 3.17 (s, 3H), 7.10 (s, 2H), 7.24−7.41 (m, 6H),7.47−7.49 (m, 2H),7.69 (d, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.8, 38.6, 125.1, 125.5, 126.6, 126.7, 127.7, 128.0, 128.7, 129.1, 131.2, 134.0, 135.9, 137.0, 171.1; HRMS m/z calcd for $C_{17}H_{17}NO$ (M^+), 251.1310; found, 251.1315.

2-[1-Phenyl-2-(trimethylsilyl)ethenyl]-*N*,*N*-dimethylbenzamide (3f′):[9] Oil, 14 mg (17%); ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.04 (s, 9H, major), 0.11 (s, 9H, minor), 2.87 (s, 3H, major), 2.88 (s, 3H, minor), 3.16 (s, 3H, major), 3.17 (s, 3H, minor), 6.76−6.78 (m, 1H, minor), 6.91−6.96 (m, 2H, minor), 7.10−7.11 (m, 2H), 7.16 (s, 1H, major), 7.18−7.23 (m, 2H), 7.27−7.37 (m, 6H), 7.38−7.42 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −1.6, 0.7, 34.65, 34.70, 38.4, 38.5, 125.8, 125.9, 126.1, 127.0, 127.4, 127.8, 127.9, 128.0, 128.3, 128.5, 129.2, 129.6, 136.32, 136.34, 141.8, 147.0, 148.7, 170.8; HRMS m/z calcd for $C_{20}H_{25}NOSi$ (M^+), 323.1705; found, 323.1709.

(*E*)-2-[2-(Triisopropylsilyl)ethenyl]-*N*,*N*-dimethylbenzamide (3g):[9] Oil, 16 mg (19%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07 (d, J = 6.8 Hz, 18H), 1.12−1.20 (m, 3H), 2.76 (s, 3H), 3.11 (s, 3H), 6.39 (d, J = 19.5 Hz, 1H), 6.95 (d, J = 19.5 Hz, 1H), 7.22−7.38 (m, 3H), 7.59 (d, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.9, 18.6, 34.6, 38.4, 125.4, 126.2, 127.7, 128.0, 128.9, 135.5, 135.6, 142.4, 171.2; HRMS m/z calcd for $C_{20}H_{33}NOSi$ (M^+), 331.2331; found, 331.2333.

{2-[(1*E*)-1,2-Diphenylethenyl]phenyl}-1-pyrrolidinylmethanone (3h):[9] Oil, 70 mg (79%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.52−1.64 (m, 4H), 2.97−3.15 (m, 4H), 6.81 (s, 1H), 7.02−7.04 (m, 2H), 7.10−7.11 (m, 3H), 7.14−7.25 (m, 6H), 7.29−7.38 (m, 2H) 7.42 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.2, 25.6, 45.0, 48.1, 126.78, 126.82, 127.3, 127.5, 127.9, 128.0, 128.9, 129.4, 130.48, 130.50, 130.7, 137.2, 137.3, 139.5, 141.6, 141.7, 169.0; HRMS m/z calcd for $C_{25}H_{23}NO$ (M^+), 353.1780; found, 353.1775.

{2-[(1*E*)-1,2-Diphenylethenyl]phenyl}-1-piperidinylmethanone (3i):[9] Oil, 51 mg (56%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37−1.59 (m, 6H), 2.74−2.81 (m, 1H), 2.95−3.01 (m, 1H), 3.18−3.21 (m, 1H), 3.68−3.71 (m, 1H), 6.80 (s, 1H), 7.02−7.05 (m, 2H), 7.08−7.17 (m, 5H), 7.22−7.26 (m, 4H), 7.28−7.39 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.4, 25.2, 26.0, 41.9, 47.9, 126.8, 126.9, 127.39, 127.43, 127.9, 128.2, 128.6, 129.5, 130.4, 130.5, 130.9, 136.4, 137.2, 139.8, 141.2, 141.6, 169.3; HRMS m/z calcd for $C_{26}H_{25}NO$ (M^+), 367.1936; found, 367.1935.

(*E*)-2-(1,2-Diphenylethenyl)-*N*,*N*-diisopropylbenzamide (3j): mp 170−171 °C, 69 mg (72%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 (d, J = 6.8 Hz, 3H), 1.11−1.16 (m, 6H), 1.51 (d, J = 6.8 Hz, 3H), 3.30−3.37 (m, 1H), 3.90−3.96 (m, 1H), 6.89 (s, 1H), 7.02−7.13 (m, 6H), 7.19−7.30 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.1, 20.5, 20.6, 20.9, 45.7, 50.8, 126.3, 126.7 127.2, 127.4, 127.85, 127.90, 128.4, 129.5, 130.5, 130.7, 130.9, 137.2, 138.3, 140.6, 140.7, 140.9, 170.4; HRMS m/z calcd for $C_{27}H_{29}NO$ (M^+), 383.2249; found, 383.2248.

(*E*)-2-(1,2-Diphenylethenyl)-*N*,*N*-diphenylbenzamide (3k):[9] mp 161−162 °C, 53 mg (47%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.59−6.61 (m, 2H), 6.79−6.88 (m, 6H), 7.10−7.23 (m, 15H), 7.32 (dt, J = 1.0, 7.6 Hz, 1H), 7.61 (dd, J = 1.2, 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.1, 127.4, 127.6, 128.0 (overlapped), 128.1, 128.8 (overlapped), 129.2, 129.6 (overlapped), 130.1, 130.4, 130.99, 131.04(overlapped), 136.5, 137.2, 139.4, 140.6, 141.2, 143.2, 171.1; HRMS m/z calcd for $C_{33}H_{25}NO$ (M^+), 451.1936; found, 451.1938.

(*E*)-2-(1,2-Diphenylethenyl)-*N*,*N*-dimethyl-4-methylbenzamide (3l): Oil, 66 mg (77%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 2.56 (s, 3H), 2.64 (s, 3H), 6.77 (s, 1H), 7.03−7.09 (m, 2H), 7.10−7.16 (m, 7H), 7.20−7.24 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 34.2, 38.7, 126.8, 127.0, 127.4, 127.9, 128.0, 128.1, 129.5, 130.4, 130.5, 131.0, 133.5, 137.2, 138.7, 139.5, 141.7, 141.8, 170.9; HRMS m/z calcd for $C_{24}H_{23}NO$ (M^+), 341.1780; found, 341.1775.

(*E*)-2-(1,2-Diphenylethenyl)-*N*,*N*-dimethyl-4-methoxybenzamide (3m): mp 111−112 °C, 75 mg (84%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.57 (s, 3H), 2.63 (s, 3H), 3.83 (s, 3H), 6.80 (s, 1H), 6.85 (dd, J = 2.5, 8.3 Hz, 1H), 6.94 (d, J = 2.6 Hz, 1H), 7.04−7.06 (m, 2H), 7.11−7.16 (m, 6H), 7.21−7.23 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.3, 38.8, 55.4, 112.7, 115.9, 126.9, 127.4, 127.9, 128.0, 128.5, 128.9, 129.5, 130.4, 130.7, 137.1, 139.2, 141.6, 143.6, 159.7, 170.7; HRMS m/z calcd for $C_{24}H_{23}NO_2$ (M^+), 357.1729; found, 357.1727.

(*E*)-2-(1,2-Diphenylethenyl)-*N*,*N*-dimethyl-4-chlorobenzamide (3n): mp 110−111 °C, 79 mg (87%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.54 (s, 3H), 2.64 (s, 3H), 6.80 (s, 1H), 7.02−7.05 (m, 2H), 7.11−7.16 (m, 6H), 7.24−7.26 (m, 3H), 7.31 (dd, J = 2.0, 8.2 Hz, 1H), 7.42 (d, J = 1.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.3, 38.6, 127.2, 127.5, 127.7, 128.0, 128.2, 128.4, 129.5, 130.3, 130.4, 131.7, 134.6, 134.7, 136.7, 138.8, 140.3, 143.7, 169.7; HRMS m/z calcd for $C_{23}H_{20}ClNO$ (M^+), 361.1233; found, 361.1238.

1-[2,6-Bis[(1*E*)-1,2-diphenylethenyl]phenyl]pyrazole (5a):[9] Oil, 106 mg (85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.71−5.72 (m, 1H), 6.57 (s, 2H), 6.80 (d, J = 2.2, 1H), 6.87−6.94 (m, 8H), 7.04−7.11 (m, 12H), 7.18−7.19 (m, 1H), 7.42−7.43 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 105.7, 126.7, 126.9, 127.78, 127.81, 128.5, 129.3, 129.4, 130.5, 130.7, 131.6, 137.1, 137.4, 139.2, 139.3, 139.7, 143.1; HRMS m/z calcd for $C_{37}H_{28}N_2$ (M^+), 500.2252; found, 500.2249.

1-[2,6-Bis[(1*E*)-1,2-bis(4-methylphenyl)ethenyl]phenyl]-pyrazole (5b): Oil, 116 mg (83%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.22 (s, 6H), 2.25 (s, 6H), 5.73−5.74 (m, 1H), 6.47 (s, 2H), 6.78−

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6.89 (m, 17H), 7.19 (d, J = 1.7 Hz, 1H), 7.35−7.38 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 21.2, 105.5, 128.3, 128.49, 128.53, 129.1, 129.2, 130.1, 130.2, 131.7, 134.4, 136.3, 136.4, 136.6, 137.3, 138.7, 139.0, 143.4; HRMS m/z calcd for $C_{41}H_{36}N_2$ (M^+), 556.2878; found, 556.2877.

1-[2,6-Bis[(1*E*)-1,2-bis(4-chlorophenyl)ethenyl]phenyl]-pyrazole (5c): Oil, 122 mg (77%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75−5.76 (m, 1H), 6.56 (s, 2H), 6.72−6.75 (m, 4H), 6.78 (d, J = 2.4 Hz, 1H), 6.85−6.87 (m, 4H), 6.99−7.08 (m, 8H), 7.12 (d, J = 1.8 Hz, 1H), 7.44−7.50 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 106.1, 128.1, 128.2, 128.9, 130.0, 130.5 (overlapped), 130.9, 131.6, 132.8, 133.0, 135.0, 137.0, 137.2, 139.3, 139.4, 142.5; HRMS m/z calcd for $C_{37}H_{24}Cl_4N_2$ (M^+), 636.0694; found, 636.0693.

1-[2,6-Bis[(1*E*)-1,2-bis(4-methoxyphenyl)ethenyl]phenyl]-pyrazole (5d): Oil, 135 mg (87%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.72 (s, 6H), 3.74 (s, 6H), 5.73−5.74 (m, 1H), 6.44 (s, 2H), 6.59−6.63 (m, 8H), 6.80−6.82 (m, 5H), 6.88−6.90 (m, 4H), 7.18 (d, J = 1.3 Hz, 1H), 7.37−7.40 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.1 (overlapped), 105.5, 113.20, 113.23, 128.3, 129.4, 130.0, 130.3, 130.4, 130.5, 131.6, 132.1, 137.3, 137.6, 139.0, 143.4, 158.2, 158.3; HRMS m/z calcd for $C_{41}H_{36}N_2O_4$ (M^+), 620.2675; found, 620.2681.

1-[2,6-Bis[(1*E*)-1-methyl-2-phenylethenyl]phenyl]pyrazole (5e): mp 78−80 °C, 80 mg (85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.70 (s, 6H), 6.36−6.37 (m, 1H), 6.46 (s, 2H), 7.19−7.23 (m, 6H), 7.30,-7.34 (m, 4H), 7.38−7.45 (m, 3H), 7.55 (d, J = 2.1 Hz, 1H), 7.66−7.67 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.2, 106.4, 126.5, 128.1, 128.3, 128.7, 128.8, 128.9, 129.9, 132.3, 137.0, 137.7, 139.7, 143.5; HRMS m/z calcd for $C_{27}H_{25}N_2$ ($M + H^+$), 377.2012; found, 377.2019.

1-[2,6-Bis[(1*E*)-1,2-diphenylethenyl]-4-methylphenyl]-pyrazole (5f): mp 171−172 °C, 112 mg (87%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.42 (s, 3H), 5.69−5.70 (m, 1H), 6.56 (s, 2H), 6.77 (d, J = 2.2 Hz, 1H), 6.88−6.93 (m, 8H), 7.05−7.08 (m, 12H), 7.16 (d, J = 1.7 Hz, 1H), 7.23 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 105.5, 126.6, 126.8, 127.75, 127.77, 129.2, 129.4, 130.4, 131.0, 131.7, 135.0, 137.1, 138.3, 139.0, 139.3, 139.8, 142.8; HRMS m/z calcd for $C_{38}H_{30}N_2$ (M^+), 514.2409; found, 514.2411.

1-[2,6-Bis[(1*E*)-1,2-diphenylethenyl]-4-methoxyphenyl]-pyrazole (5g): mp 160−161 °C, 118 mg (89%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85 (s, 3H), 5.67−5.68 (m, 1H), 6.59 (s, 2H), 6.71 (d, J = 2.1 Hz, 1H), 6.87−6.95 (m, 10H), 7.03−7.10 (m, 12H), 7.15 (d, J = 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.6, 105.4, 115.5, 126.7, 126.9, 127.77, 127.80, 129.3 (overlapped), 130.6, 130.8, 131.9, 137.0, 138.9, 139.1, 139.8, 144.4, 158.8; HRMS m/z calcd for $C_{38}H_{30}N_2O$ (M^+), 530.2358; found, 530.2357.

1-[2,6-Bis[(1*E*)-1,2-diphenylethenyl]-4-chlorophenyl]-pyrazole (5h): mp 146−147 °C, 112 mg (84%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.71−5.72 (m, 1H), 6.58 (s, 2H), 6.77 (d, J = 2.4 Hz, 1H), 6.86−6.93 (m, 8H), 7.06−7.12 (m, 12H), 7.17 (d, J = 1.8 Hz, 1H), 7.43 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 106.0, 127.0, 127.2, 127.8, 127.9, 129.3 (overlapped), 130.1, 131.4, 131.6, 134.1, 136.0, 136.6, 138.57, 138.59, 139.5, 144.7; HRMS m/z calcd for $C_{37}H_{27}ClN_2$ (M^+), 534.1863; found, 534.1864.

2-[2,6-Bis[(1*E*)-1,2-diphenylethenyl]phenyl]-1*H*-imidazole (7a): Oil, 98 mg (79%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.33 (s, 1H), 6.63 (s, 2H), 6.70 (s, 1H), 6.80−6.82(m, 4H), 6.95−6.97 (m, 4H), 7.03−7.07 (m, 12H), 7.45−7.46 (m, 3H), 7.73 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 115.2, 126.7, 126.8, 127.8, 128.2, 128.9, 129.3, 129.4, 129.7, 130.1, 130.5, 137.2, 140.1, 142.2, 144.1, 146.4; HRMS m/z calcd for $C_{37}H_{28}N_2$ (M^+), 500.2252; found, 500.2249.

(*E*)-2-[(1,2-Diphenylethenyl)phenyl]-1-methyl-1*H*-imidazole (7b):[9] Oil, 55 mg (65%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.10 (s, 3H), 6.55 (s, 1H), 6.69 (s, 1H), 6.83−6.86 (m, 2H), 6.87−6.88(m, 1H), 6.97−7.00 (m, 2H), 7.05−7.09 (m, 6H), 7.30−7.32 (m, 1H), 7.36−7.39 (m,1H), 7.44−7.50 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.0, 120.0, 126.7, 126.8, 127.3, 127.80, 127.84, 128.2, 129.1, 129.26, 129.31, 130.2, 130.45, 130.53, 131.2, 137.2, 140.0, 142.1, 145.7, 147.1; HRMS m/z calcd for $C_{24}H_{20}N_2$ (M^+), 336.1626; found, 336.1628.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra of products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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