JOC Article

Waste-Free Synthesis of Condensed Heterocyclic Compounds by Rhodium-Catalyzed Oxidative Coupling of Substituted Arene or Heteroarene Carboxylic Acids with Alkynes

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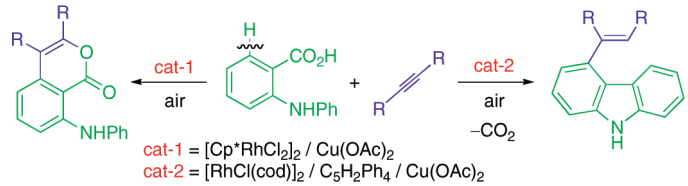
Received February 23, 2009

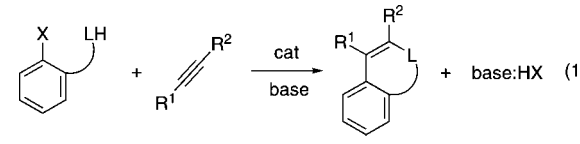


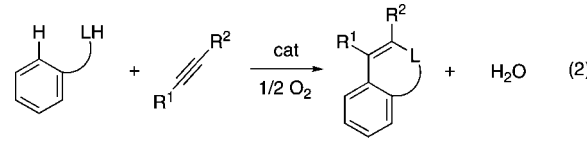
The direct oxidative coupling of 2-amino- and 2-hydroxybenzoic acids with internal alkynes proceeds efficiently in the presence of a rhodium/copper catalyst system under air to afford the corresponding 8-substituted isocoumarin derivatives, some of which exhibit solid-state fluorescence. Depending on conditions, 4-ethenylcarbazoles can be synthesized selectively from 2-(arylamino)benzoic acids. The oxidative coupling reactions of heteroarene carboxylic acids as well as aromatic diacids with an alkyne are also described.

Introduction

The intermolecular coupling of aromatic substrates with alkynes by transition-metal catalysis is now recognized to be a powerful tool to construct π-conjugated molecules.[1] Particularly, the palladium-catalyzed annulation by the coupling of aryl halides bearing an oxygen or nitrogen nucleophile (−LH in eq 1) with alkynes is a versatile way to produce condensed heteroaromatics.[2] In such processes, however, there is a substantial problem of forming stoichiometric amounts of salt wastes (base:HX) as byproducts.

One of the most promising methods to avoid the salt formation is the aerobic oxidative coupling using nonhalogenated aromatic substrates via C−H bond cleavage, in which no wastes are formed except for water (eq 2).[3,4] The oxygen- or nitrogen-containing substituent (−LH) can also act as a directing group in the initial C−H bond cleaving step to result in regioselective ring construction. Needless to say, compared with disubstituted aromatic substrates in eq 1, the parent monosubstituted ones in eq 2 are readily available. To date, however, the latter approach has not been extensively explored.[5,6]





As one of the rare examples, we demonstrated that benzoic acids can directly couple with alkynes under air in the presence of an Rh/Cu catalyst system to form isocoumarin derivatives (path *a* in Scheme 1, Z = H).[5a,b] The isocoumarin framework can be found in various natural products[7] and especially 8-amino- and 8-hydroxy isocoumarins are known to exhibit a broad range of interesting biological and photochemical properties.[7a,8] However, as we reported previously, the coupling of 2-substituted benzoic acids with alkynes to produce 8-substituted isocoumarins was sluggish, and consequently, significant amounts of 1:2 coupling products, naphthalene derivatives, were also formed as byproducts accompanied by decarboxylation.[5b] During our further study of this environmentally benign reaction, we have succeeded to conduct the coupling of 2-substituted benzoic acids such as anthranilic- and

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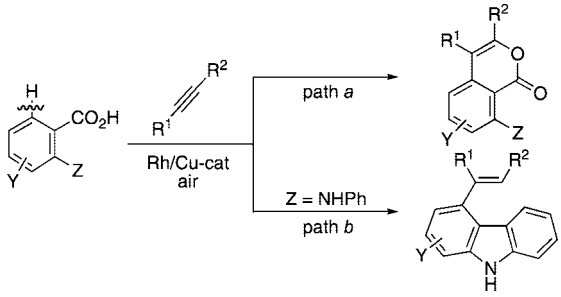
(2) For recent reviews, see: (a) Larock, R. C. *Top. Organomet. Chem.* **2005**, *14*, 147. (b) Zeni, G.; Larock, R. C. *Chem. Rev.* **2006**, *106*, 4644.

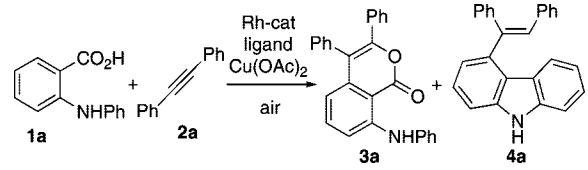
10.1021/jo900396z CCC: $40.75
Published on Web 04/03/2009

SCHEME 1. Coupling of 2-Substituted Benzoic Acids with Alkynes



salicylic acids with alkynes efficiently without decarboxylation under appropriate conditions to furnish the corresponding 8-amino- and 8-hydroxyisocoumarin derivatives selectively in good yields (path *a* in Scheme 1, Z = NHR or OH). Actually, most 8-aminoisocoumarins obtained have been found to show solid-state fluorescence, while the parent 8-unsubstituted ones were not fluorescent. Furthermore, by using another selected Rh/Cu catalyst system in the reaction of *N*-phenylanthranilic acids, 4-ethenylcarbazoles can be synthesized predominantly (path *b* in Scheme 1).[9] Carbazoles have been attractive synthesis targets in medicinal chemistry and materials field, because of their biological activities as well as photophysical and optoelectronic applications.[10] The results obtained for the reactions of these 2-substituted benzoic acids as well as heteroarene carboxylic acids and dicarboxylic acids are described herein.

TABLE 1. Reaction of *N*-Phenylanthranilic Acid (1a) with Diphenylacetylene (2a)[a]



entry	Rh-cat	ligand	solvent	temp (°C)	time (h)	% yield[b] 3a	% yield[b] 4a
1	[(Cp*RhCl$_2$)$_2$]	−	DMF	120	4	41	0
2	[(Cp*RhCl$_2$)$_2$]	−	o-xylene	120	2	94 (85)	0
3	[{RhCl(cod)}$_2$]	$C_5H_2Ph_4$	o-xylene	120	3	9	53
4	[{RhCl(cod)}$_2$]	$C_5H_2Ph_4$	DMF	120	2	18 (17)	79 (73)
5	[{RhCl(cod)}$_2$]	$C_5H_2Ph_4$	DMF	140	1	14	80
6	[{RhCl(cod)}$_2$]	$C_5H_2Ph_4$	DMF	100	2	5	58
7	[{RhCl(cod)}$_2$]	$C_5H_2Ph_4$	DMF	80	8	5	37
8	[{RhCl(cod)}$_2$]	−	DMF	120	2	0	0
9	[{RhCl(cod)}$_2$]	$C_5H_3Ph_3$	DMF	120	2	6	67

[a] Reaction conditions: [**1a**]:[**2a**]:[Rh-cat]:[ligand]:[Cu(OAc)$_2$] = 0.5:0.5:0.005:0.02:0.025 (in mmol), in solvent (2.5 mL) under air. [b] GC yield based on the amount of **1a** used. Value in parentheses indicates yield after purification.

Results and Discussion

In an initial attempt to carry out the desired coupling, *N*-phenylanthranilic acid (**1a**, 0.5 mmol) was treated with diphenylacetylene (**2a**, 0.5 mmol) under conditions similar to those employed for the coupling of benzoic acid with **2a**.[5a,b] In the presence of [{Cp*RhCl$_2$}$_2$] (0.005 mmol) and Cu(OAc)$_2$ (monohydrate, 0.025 mmol) in DMF at 120 °C (bath temperature) under air, 8-(*N*-phenylamino)-3,4-diphenylisocoumarin (**3a**) was formed in 41% yield (entry 1 in Table 1, Cp* = η^5-pentamethylcyclopentadienyl). In contrast to the case with either 2-methyl- or 2-phenylbenzoic acid,[5b] no 1:2 coupling product was detected, and 51% of **2a** was recovered. Interestingly, when the reaction was carried out in *o*-xylene, **2a** was completely consumed to give **3a** in 94% yield (entry 2).

Meanwhile, the use of another rhodium catalyst system, [{RhCl(cod)}$_2$]/$C_5H_2Ph_4$, which was effective for the oxidative coupling of salicylaldehydes with alkynes,[5d] dramatically affected the reaction ($C_5H_2Ph_4$ = 1,2,3,4-tetraphenyl-1,3-cyclopentadiene). Thus, the reaction with this catalyst in DMF proceeded through double C−H bond cleavage and decarboxylation to afford 4-(1,2-diphenylethenyl)-9*H*-carbazole (**4a**) in 79% yield along with a minor amount of **3a** (18%) (entry 4).

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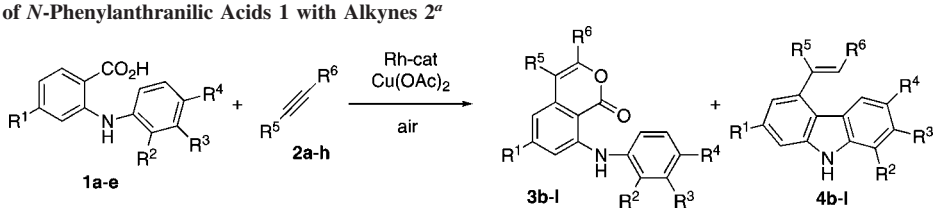
(10) For recent examples, see: (a) Kuwahara, A.; Nakano, K.; Nozaki, K. *J. Org. Chem.* **2005**, *70*, 413. (b) Liégault, B.; Lee, D.; Huestis, M. P.; Stuart, D. R.; Fagnou, K. *J. Org. Chem.* **2008**, *73*, 5022. (c) Tsang, W. C. P.; Munday, R. H.; Brasche, G.; Zheng, N.; Buchwald, S. L. *J. Org. Chem.* **2008**, *73*, 7603. (d) Jordan-Hore, J. A; Johansson, C. C. C.; Gulias, M; Beck, E. M.; Gaunt, M. J. *J. Am. Chem. Soc.* **2008**, *130*, 16184. For review, see: (e) Knölker, H.-J.; Reddy, K. R. *Chem. Rev.* **2002**, *102*, 4303.

TABLE 2. Reaction of *N*-Phenylanthranilic Acids 1 with Alkynes 2[a]



entry	1	R^1	R^2	R^3	R^4	2	R^5	R^6	conditions	time (h)	product(s), % yield[b]
1	**1b**	Cl	H	H	H	**2a**	Ph	Ph	A	2	**3b**, 75
2									B	2	**3b**, 8; **4b**, 75
3	**1c**	H	H	H	Me	**2a**	Ph	Ph	A	2	**3c**, 90 (89)
4									B	2	**3c**, 13; **4c**, 66
5	**1d**	H	H	H	OMe	**2a**	Ph	Ph	A	2	**3d**, 87
6									B	4	**3d**, 15; **4d**, 54
7	**1e**	H	Me	Me	H	**2a**	Ph	Ph	A	2	**3e**, 82
8									B	2	**3e**, 18; **4e**, 59
9	**1a**	H	H	H	H	**2b**	Pr	Pr	A	2	**3f**, 88
10									B	2	**3f**, 47; **4f**, 35
11	**1a**	H	H	H	H	**2c**	C_7H_{15}	C_7H_{15}	B	2	**3g**, 40; **4g**, 42
12	**1a**	H	H	H	H	**2d**	4-MeC_6H_4	4-MeC_6H_4	A	2	**3h**, 89
13									B	2	**3h**, 25; **4h**, 63
14	**1a**	H	H	H	H	**2e**	4-$MeOC_6H_4$	4-$MeOC_6H_4$	A	2	**3i**, 91
15									B	2	**3i**, 3; **4i**, 76
16	**1a**	H	H	H	H	**2f**	4-ClC_6H_4	4-ClC_6H_4	A	2	**3j**, 77
17									B	3	**3j**, 2; **4j**, 71
18	**1a**	H	H	H	H	**2g**	2-thienyl	2-thienyl	C	2	**3k**, 86
19									B	4	**3k**, 6; **4k**, 63
20	**1a**	H	H	H	H	**2h**	Me	Ph	A	2	**3l**, 84[c]
21									B	2	**4l**, 46[d]

[a] Reaction conditions A: [**1**]:[**2**]:[[(Cp*$RhCl_2)_2$]]:[$Cu(OAc)_2$] = 0.5:0.5:0.005:0.025 (in mmol), in o-xylene (2.5 mL) at 120 °C under air; B: [**1**]:[**2**]:[[{$RhCl(cod)\}_2$]]:[$C_5H_2Ph_4$]:[$Cu(OAc)_2$] = 0.5:0.5:0.005:0.02:0.025 (in mmol), in DMF (2.5 mL) at 120 °C under air; C: [**1**]:[**2**]:[[(Cp*$RhCl_2)_2$]]:[$Cu(OAc)_2$] = 0.5:0.5:0.005:1 (in mmol), in o-xylene (2.5 mL) at 120 °C under N_2. [b] Isolated yield based on the amount of 1 used. [c] Small amount (6%) of a regioisomer was also formed. [d] Contaminated with at least two isomers. **3l** was also formed in 21% GC yield.

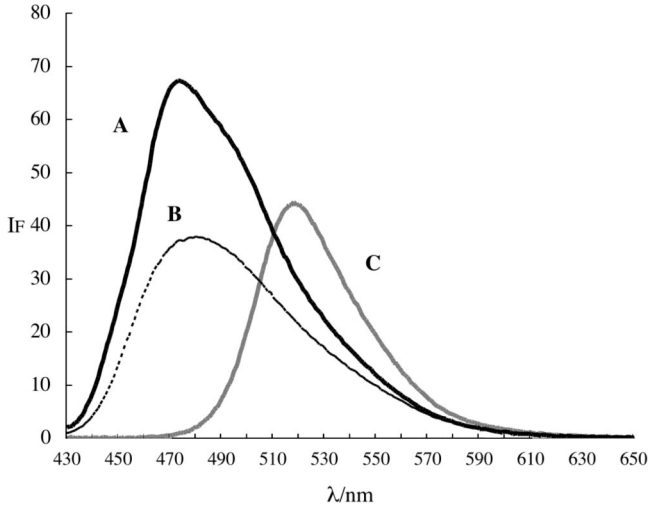


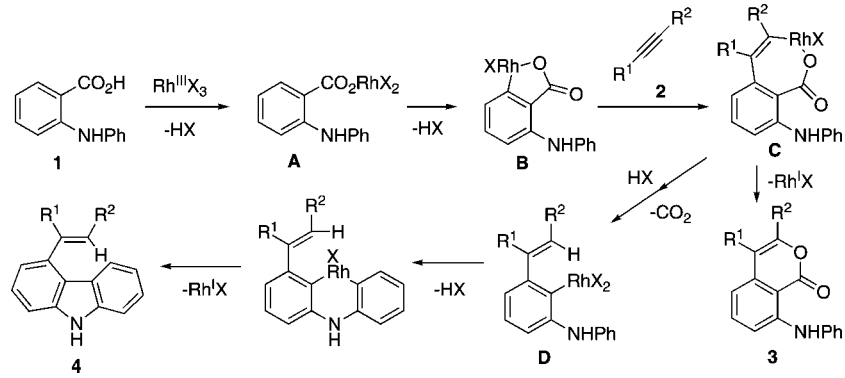
FIGURE 1. Fluorescence spectra of **3a** (A), **4i** (B), and Coumarin 153 (C) in the solid state upon excitation at 421 nm.

At 140 °C, a comparable result was obtained, while the yield of **4a** decreased at 100 or 80 °C (entries 5−7). Without $C_5H_2Ph_4$, the reaction did not proceed at all (entry 8). $C_5H_3Ph_3$ was somewhat less effective than $C_5H_2Ph_4$ (entry 9, $C_5H_3Ph_3$ = 1,2,4-triphenyl-1,3-cyclopentadiene).

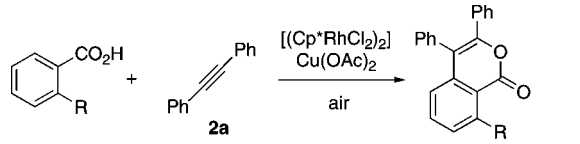
Table 2 summarizes the results for the synthesis of a series of 8-(arylamino)isocoumarins **3** and 4-ethenylcarbazoles **4** via the aerobic oxidative coupling of various anthranilic acids **1** and alkynes **2** in the presence of [{$Cp^*RhCl_2\}_2$] (conditions A) or [{$RhCl(cod)\}_2$]/$C_5H_2Ph_4$ (conditions B). Chloro-, methyl- and methoxy- substituted *N*-phenylanthranilic acids **1b**−**e** reacted with **2a** smoothly under both conditions A and B to produce the corresponding **3b**−**e** and **4b**−**e**, respectively (entries 1−8). Dialkylacetylenes such as 4-octyne (**2b**) underwent the coupling with **1a** under conditions A efficiently to give **3** (entry 9). Under conditions B, however, separable mixtures of **3** and **4** were obtained in comparable amounts (entries 10 and 11). The reactions of **1a** with substituted diphenylacetylenes **2d**−**f** effectively took place to afford **3h**−**j** or **4h**−**j** selectively in good yields, depending on the conditions (entries 12−17). The aerobic oxidative coupling of **1a** with bis(2-thienyl)acetylene (**2g**) was found to be sluggish under conditions A, the yield of 8-(*N*-phenylamino)-3,4-bis(2-thienyl)-isocoumarin (**3k**) being 46% even after 4 h. However, when the reaction was conducted in the presence of a stoichiometric amount of $Cu(OAc)_2$ (1 mmol) under N_2 (conditions C), **3k** was obtained in 92% yield (entry 18). 1-Phenylpropyne (**2h**) reacted with **1a** under conditions A to give 8-(*N*-phenylamino)-4-methyl-3-phenylisocoumarin (**3l**) in 89% yield, along with a small amount (6%) of an unidentified isomer (entry 20). The corresponding carbazole **4l** formed in the reaction of these substrates under conditions B was also contaminated with at least two isomers, detected by GC and GC-MS (entry 21).

Expectedly, most 8-(arylamino)isocoumarins **3** obtained above showed solid-state fluorescence in a range of 450−500 nm (see the Supporting Information). In contrast, the parent 3,4-diphenylisocoumarin did not show fluorescence at all, confirming that the substitution of the isocoumarin core with an amino group at the 8-position is essential for the fluorescence properties. Notably, **3a** exhibited a relatively strong emission compared to a typical emitter, Coumarin 153 (2,3,6,7-tetrahydro-9-(trifluoromethyl)-1*H*,5*H*,11*H*-[1]benzopyrano[6,7,8-*ij*]quinolizin-11-one), by a factor of 2.0 (λ_{emis} 473 nm, A versus C in Figure 1). Meanwhile, among 4-ethenyl-

SCHEME 2. Plausible Mechanism for the Coupling of *N*-Phenylanthranilic Acid (1a) with Alkynes 2



SCHEME 3. Reaction of *o*-Substituted Benzoic Acids with Diphenylacetylene (2a), in DMF (2.5 mL) under Air at 120 °C for 2 h[a]



1f: R = NHMe
1g: R = NHAc
5: R = OH
7: R = COPh

product, % yield[b]

3m: R = NHMe, 80 (79)
3n: R = NHAc, 91 (88)
6: R = OH, 87 (74)
8: R = COPh, (78)

[a] Reaction conditions: [$ArCO_2H$]:[**2a**]:[[$(Cp^*RhCl_2)_2$]]:[$Cu(OAc)_2$] = 0.5:0.5:0.005:0.025 (in mmol). [b] GC yield. Value in parentheses indicates yield after purification.

carbazoles obtained, **4i** was found to be more luminescent (λ_{emis} 480 nm) than Coumarin 153 by a factor of 1.3 (B versus C).

A plausible mechanism for the reaction of *N*-phenylanthranilic acid (**1a**) with alkynes **2** is illustrated in Scheme 2, in which neutral ligands are omitted for clarity. Coordination of the carboxylic oxygen atom to an $Rh^{III}X_3$ species gives a rhodium(III) benzoate **A**. In the case using [{Cp^*RhCl_2}$_2$] as catalyst, subsequent *ortho*- rhodation to form a rhodacycle intermediate **B**,[11] alkyne insertion, and reductive elimination from **C** occur to produce **3**. On the other hand, in the reaction employing [{RhCl(cod)}$_2$]/$C_5H_2Ph_4$, the intermediate **C** may undergo decarboxylation and protonation to form *ortho*-ethenylated arylrhodium intermediate **D**, which then followed by cyclorhodation on its aminophenyl group and reductive elimination to construct the carbazole framework of **4**.[12] However, the origin of the ligand effect, which determines the preferable pathway from the intermediate **C** to **3** or **4**, is not clear at the present stage. In both cases, the resulting Rh^IX species may be oxidized by a copper(II) salt to regenerate $Rh^{III}X_3$. Under air, Cu^I species may also be reoxidized to Cu^{II}.

N-Methyl- (**1f**) and *N*-acetylanthranilic acids (**1g**) reacted with **2a** to afford the corresponding 8-aminoisocoumarins **3m** and **3n**, respectively, in good yields (Scheme 3). These reactions proceeded smoothly in DMF rather than in *o*-xylene, which is preferable solvent for the reaction of *N*-arylanthranilic acids as described above. From salicylic acid (**5**), 8-hydroxy-3,4-diphenylisocoumarin (**6**) was produced in 87% yield. 2-Benzoylbenzoic acid (**7**) underwent the coupling with **2a** to form isocoumarin **8**.

It has also been found that the present procedure is applicable to the synthesis of not only isocoumarins but also their heteroaryl analogs.[13] Thus, treatment of 1-methyl-1*H*-indole-2-carboxylic acid (**9a**) with **2a** under conditions A′ (similar to conditions A in Table 2 but in DMF) for 2 h gave 9-methyl-3,4-diphenylpyrano[3,4-*b*]indol-1(9*H*)-one (**10a**) in 96% yield (entry 1 in Table 3). Meanwhile, other heteroarene carboxylic acids containing an indole, pyrrole, benzothiophene, thiophene, or furan ring underwent the oxidative coupling with **2a** more smoothly under the conditions using a stoichiometric amount of $Cu(OAc)_2$ in DMF (conditions C′). In the reaction of benzofuran-2-carboxylic acid (**9h**) with **2a**, comparable amounts of product **10h** were obtained under both conditions A' and C' (entries 14 and 15).

For the synthesis of further complicated heterocyclic systems, the reactions of aromatic diacids were next examined. Diphenic acid (**11**) and terephthalic acid (**13**) efficiently reacted with **2b** to selectively produce 1:2 coupling products, 3,3′,4,4′-tetrapropyl[8,8′-bi-1*H*-2-benzopyran]-1,1′-dione (**12**) and 3,4,8,9-tetrapropylbenzo[1,2-*c*:4,5-*c*′]dipyran-1,6-dione (**14**),[14] respectively, in good yields (Scheme 4). In these cases, the use of stoichiometric amounts of Ag_2CO_3 as the oxidant was essential for the efficient coupling. In the cases using $Cu(OAc)_2$, no desired products were detected.

In summary, we have demonstrated that highly substituted isocoumarins and their heteroaryl analogs, 4-ethenylcarbazoles, and benzodipyrandione frameworks can be constructed efficiently by the direct coupling of (hetero)arene carboxylic acids with internal alkynes in the presence of a rhodium catalyst and an appropriate oxidant. Some of the condensed heterocyclic products exhibit intense fluorescence in the solid state.

Experimental Section

General Procedure for Aerobic Oxidative Coupling of 2-Substituted Benzoic Acids with Internal Alkynes under Conditions A. To a 20 mL two-necked flask were added benzoic

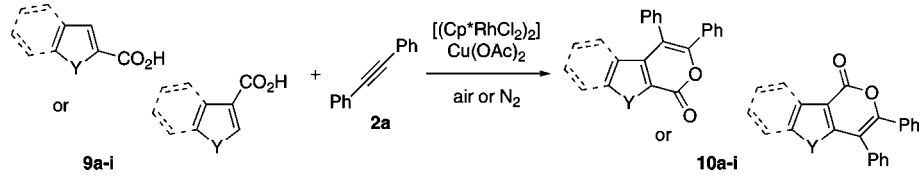
(11) For stoichiometric *ortho*-rhodation of a Cp*Rh benzoate, see: Kisenyi, J. M.; Sunley, G. J.; Cabeza, J. A.; Smith, A. J.; Adams, H.; Salt, N. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1987**, 2459.

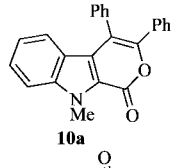
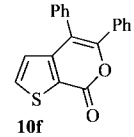
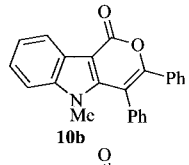
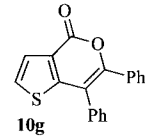
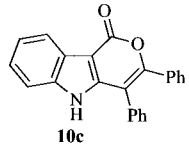
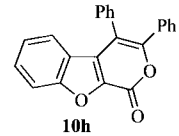
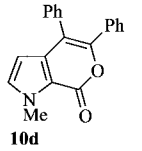
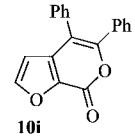
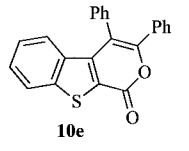
(12) A similar mechanism involving metal migration on diphenylamine systems was reported. See ref 9.

(13) (a) Freter, K. *J. Org. Chem.* **1972**, *37*, 2010. (b) Kita, Y.; Mohri, S.-I.; Tsugoshi, T.; Maeda, H.; Tamaru, Y. *J. Org. Chem.* **1985**, *33*, 4723. (c) Ram, V. J.; Goel, A.; Shukla, P. K.; Kapil, A. *Bioorg. Med. Chem. Lett.* **1997**, *7*, 3101. (d) Calvo, L.; González-Ortega, A.; Navarro, R.; Pérez, M.; Sañudo, M. C. *Synthesis* **2005**, 3152. (e) Raju, S.; Batchu, V. R.; Swamy, N. K.; Dev, R. V.; Sreekanth, B. R.; Babu, J. M.; Vyas, K.; Kumar, P. R.; Mukkanti, K.; Annamalai, P.; Pal, M. *Tetrahedron* **2006**, *62*, 9554. (f) Hellal, M.; Bourguignon, J.-J.; Bihel, F. J.-J. *Tetrahedron Lett.* **2008**, *49*, 62. (g) Patankar, J. A.; Khombare, R. T.; Khanwelkar, R. R.; Shet, J. B. *J. Chem. Res.* **2008**, 129.

(14) This is a partial structure of ladder-type conjugated polymers: Kim, I; Kim, T.-H.; Kang, Y; Lim, Y.-B *Tetrahedron Lett.* **2006**, *47*, 8689.

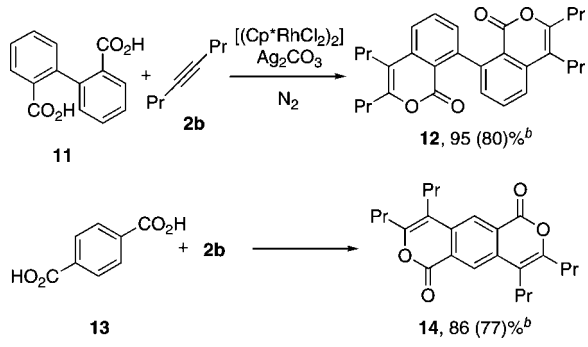
TABLE 3. Reaction of Heteroarene Carboxylic Acids 9 with Diphenylacetylene (2a)[a]



entry	10	conditions	% yield[b]	entry	10	conditions	% yield[b]
1[c]	 **10a**	A′	96 (89)	10	 **10f**	A′	52 (45)
				11		C′	88 (82)
2	 **10b**	A′	25	12	 **10g**	A′	55
3[c]		C′	88 (85)	13		C′	71 (60)
4[c]	 **10c**	A′	45	14[d]	 **10h**	A′	66 (58)
5[d]		C′	88 (77)	15[d]		C′	64
6	 **10d**	A′	69	16[d]	 **10i**	A′	21
7		C′	87 (75)	17		C′	43 (31)
8[d]	 **10e**	A′	77				
9[d]		C′	90 (73)				

[a] Reaction conditions A′: [**9**]:[**2a**]:[[(Cp*RhCl$_2$)$_2$]]:[Cu(OAc)$_2$] = 0.5:0.5:0.005:0.025 (in mmol), in DMF (2.5 mL) at 120 °C for 2 h under air; C′: [**9**]:[**2a**]:[[(Cp*RhCl$_2$)$_2$]]:[Cu(OAc)$_2$] = 0.5:0.5:0.005:1 (in mmol), in DMF (2.5 mL) at 120 °C for 2 h under N$_2$. [b] GC yield based on the amount of **2a** used. Value in parentheses indicates yield after purification. [c] **9** (0.6 mmol) was used. [d] At 140 °C.

SCHEME 4. Reaction of Aromatic Diacids with 4-Octyne (2b), in DMF (3 mL) under N$_2$ at 140 °C for 2 h[a]



[a] Reaction conditions: [diacid]:[**2b**]:[[(Cp*RhCl$_2$)$_2$]]:[Ag$_2$CO$_2$] = 0.5:1:0.005:1 (in mmol). [b] GC yield. Value in parentheses indicates yield after purification.

acid **1**, **5**, or **7** (0.5 mmol), alkyne **2** (0.5 mmol), (Cp*RhCl$_2$)$_2$ (0.005 mmol, 3 mg), Cu(OAc)$_2$ (0.025 mmol, 5 mg), 1-methylnaphthalene (ca. 50 mg) as internal standard, and *o*-xylene (2.5 mL). The resulting mixture was stirred under air at 120 °C. GC and GC-MS analyses of the mixtures confirmed formation of isocoumarin **3**, **6**, or **8**. Then, the mixture was cooled to room temperature and extracted with EtOAc (100 mL). Then the organic layer was washed by water (100 mL, twice) and dried over sodium sulfate. After evaporation of the solvents under vacuum, the residue was washed by hexane (10 mL, three times) to give crystals of the isocoumarin product.

8-(*N*-Phenylamino)-3,4-diphenylisocoumarin (3a) (entry 4 in Table 1). mp 196−200 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.36 (d, J = 7.7 Hz, 1H), 7.13−7.41 (m, 17H), 10.25 (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 104.1, 111.0, 113.8, 117.8, 123.8, 124.6, 127.8, 127.9, 128.8, 128.9, 129.1, 129.5, 131.3, 132.9, 135.0, 135.5, 140.1, 140.8, 149.4, 150.1, 164.1; MS *m*/*z* 389 (M$^+$). Anal. Calcd for C$_{27}$H$_{19}$NO$_2$: C, 83.27; H, 4.92; N, 3.60. Found: C, 83.09; H, 4.96; N, 3.68.

General Procedure for Aerobic Oxidative Coupling of *N*-Arylanthranilic Acids with Internal Alkynes under Conditions B. To a 20 mL two-necked flask were added *N*-arylanthranilic acid **1** (0.5 mmol), alkyne **2** (0.5 mmol), [RhCl(cod)]$_2$ (0.005 mmol, 3 mg), C$_5$H$_2$Ph$_4$ (0.02 mmol, 7 mg), Cu(OAc)$_2$ (0.025 mmol, 5 mg), 1-methylnaphthalene (ca. 50 mg) as internal standard, and DMF (2.5 mL). The resulting mixture was stirred under air at 120 °C. GC and GC−MS analyses of the mixtures confirmed formation of 4-ethenylcarbazole **4** and **3**. Then, the mixture was cooled to room temperature and Et$_2$O (100 mL) and diluted hydrochloric acid (ca. 20 wt%, 100 mL) were added. The color of the organic layer turned from green to yellow during the extraction

process. After it was washed by water (100 mL, twice) and dried over sodium sulfate, the solvents were evaporated under vacuum. The product was isolated by column chromatography on silica gel using hexane-ethyl acetate (90:10, v/v) as eluant.

4-(1,2-Diphenylethenyl)-9H-carbazole (4a) (entry 4 in Table 1).[9] mp 121−126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95−7.06 (m, 3H), 7.16−7.37 (m, 14H), 8.02 (s, 1H), 8.29 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 104.4, 110.4, 119.3, 121.1, 121.5, 122.7, 123.1, 125.4, 125.6, 126.9, 127.3, 128.2, 128.3, 129.5, 129.9, 130.8, 137.4, 139.8, 140.0, 140.1, 140.4, 141.0; HRMS m/z Calcd for $C_{26}H_{19}N$ (M^+) 345.1517, found 345.1534.

General Procedure for Oxidative Coupling of Aromatic Diacids with Internal Alkynes. To a 20 mL two-necked flask were added diacid **11** or **13** (0.5 mmol), 4-octyne (**2b**) (1 mmol, 110 mg), $(Cp^*RhCl_2)_2$ (0.005 mmol, 3 mg), Ag_2CO_3 (1 mmol, 275 mg), 1-methylnaphthalene (ca. 50 mg) as internal standard, and DMF (3 mL). The resulting mixture was stirred under N_2 at 140 °C. GC and GC-MS analyses of the mixtures confirmed formation of **12** or **14**. Then, the mixture was cooled to room temperature and extracted with EtOAc (100 mL). Then the organic layer was washed by water (100 mL, twice) and dried over sodium sulfate. After evaporation of the solvents under vacuum, the residue was washed by hexane (10 mL, three times) to give crystals of the product.

3,3′,4,4′-Tetrapropyl[8,8′-bi-1H-2-benzopyran]-1,1′-dione (12) (Scheme 4). mp 181−186 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (t, J = 7.3 Hz, 6H), 1.06 (t, J = 7.3 Hz, 6H), 1.60−1.74 (m, 8H), 2.50−2.54 (m, 4H), 2.60−2.66 (m, 4H), 7.14 (d, J = 7.3 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 7.69 (t, J = 7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 14.2, 21.0, 22.8, 28.6, 32.6, 112.1, 118.6, 121.9, 127.7, 133.2, 138.7, 146.1, 154.0, 161.4; MS m/z 458 (M^+). Anal. Calcd for $C_{30}H_{34}O_4$: C, 78.57; H, 7.47. Found: C, 78.29; H, 7.31.

3,4,8,9-Tetrapropylbenzo[1,2-c:4,5-c′]dipyran-1,6-dione (14) (Scheme 4). mp 161−168 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00−1.08 (m, 12H), 1.58−1.68 (m, 4H), 1.72−1.82 (m, 4H), 2.60 (t, J = 7.7 Hz, 4H), 2.68 (t, J = 7.9 Hz, 4H), 8.47 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 14.1, 21.1, 22.9, 28.1, 32.7, 112.2, 124.8, 125.5, 135.7, 154.5, 162.1; MS m/z 382 (M^+). Anal. Calcd for $C_{24}H_{30}O_4$: C, 75.36; H, 7.91. Found: C, 75.09; H, 7.78.

Acknowledgment. This work was partly supported by a Grant-in-Aid from the Ministry of Education, Culture, Sports, Science and Technology, Japan and the General Sekiyu Research Foundation.

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

JO900396Z