ORGANIC
LETTERS

2009
Vol. 11, No. 11
2337−2340

Synthesis of Condensed Heteroaromatic Compounds by Palladium-Catalyzed Oxidative Coupling of Heteroarene Carboxylic Acids with Alkynes

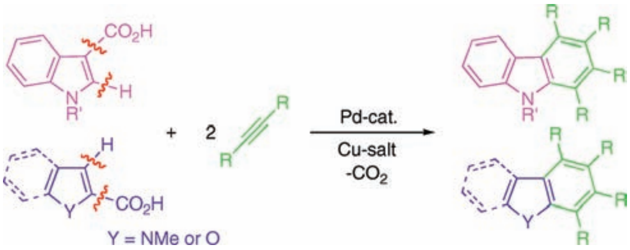
Mana Yamashita, Koji Hirano, Tetsuya Satoh,* and Masahiro Miura*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

satoh@chem.eng.osaka-u.ac.jp; miura@chem.eng.osaka-u.ac.jp

Received April 7, 2009

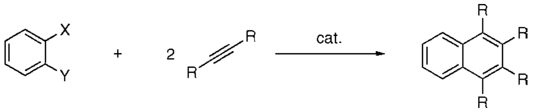
ABSTRACT



The palladium-catalyzed oxidative coupling of indole-3-carboxylic acids with alkynes effectively proceeds in a 1:2 manner accompanied by decarboxylation to produce the corresponding 1,2,3,4-tetrasubstituted carbazoles, some of which exhibit solid-state fluorescence. Pyrrole-, benzofuran-, and furancarboxylic acids also undergo the decarboxylative coupling to afford highly substituted indole, dibenzofuran, and benzofuran derivatives, respectively.

Polycyclic aromatic and heteroaromatic compounds have attracted considerable attention due to their electro- and photochemical and optoelectronic properties and their utility as π-conjugated functional materials such as organic semiconductors and luminescent materials.[1] Highly substituted derivatives with condensed aromatic cores are of particular interest because of their stability, solubility, enhanced ability to transport charge, and their fluorescent properties in the solid state.[2] Among modern potential strategies to prepare polysubstituted, condensed aromatics is the transition-metal-catalyzed homologation, such as benzene to naphthalene and naphthalene to anthracene, by the coupling of a given aromatic substrate with two alkyne molecules (Scheme 1).[3]

Scheme 1



Thus, the catalytic transformations of di- (X ≠ H, Y ≠ H)[3,4] and more readily available monofunctionalized aromatic substrates (X ≠ H, Y = H)[5] have been developed. The latter reaction involving regioselective C−H bond cleavage is also attractive from the atom-economic point of view.[6] In particular, the decarboxylative coupling of benzoic acids with

---

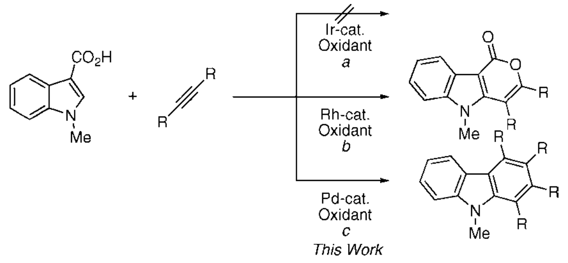
[1] Selected reviews: (a) Anthony, J. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 452. (b) Watson, M. D.; Fethtenkötter, A.; Müllen, K. *Chem. Rev.* **2001**, *101*, 1267. (c) Mitschke, U.; Bäuerle, P. *J. Mater. Chem.* **2000**, *10*, 1471. (d) Harvey, R. G. *Polycyclic Aromatic Hydrocarbons*; Wiley-VCH: New York, 1996.

[2] For recent example, see: (a) Kaur, I.; Stein, N. N.; Kopreski, R. P.; Miller, G. P. *J. Am. Chem. Soc.* **2009**, *131*, 3424. (b) Ahmed, E.; Briseno, A. L.; Xia, Y.; Jenekhe, S. A. *J. Am. Chem. Soc.* **2008**, *130*, 1118. (c) Paraskar, A. S.; Reddy, A. R.; Patra, A.; Wijsboom, Y. H.; Gidron, O.; Shimon, L. J. W.; Leitus, G.; Bendikov, M. *Chem.—Eur. J.* **2008**, *14*, 10639. (d) Cicoira, F.; Santato, C. *Adv. Funct. Mater.* **2007**, *17*, 3421.

10.1021/ol900736s CCC: $40.75

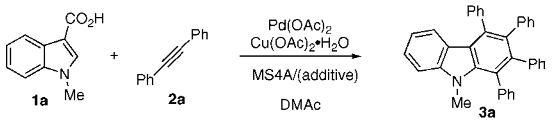
alkyne molecules under iridium catalysis (X = CO_2H, Y = H), which we recently succeeded in developing,[5g] seems to be of considerable interest because of wide availability of the acids as aryl sources.[7]

Scheme 2



During our further study of the scope of this reaction, it was found that heteroarene carboxylic acids such as 1-methylindole-3-carboxylic acid hardly underwent the Ir-catalyzed coupling with alkynes (Scheme 2, path *a*). Under rhodium catalysis, meanwhile, a lactone was obtained as a 1:1 oxidative coupling product (path *b*).[8] To our delight, the desired 1:2 coupling has been observed to proceed efficiently by the use of a palladium catalyst to produce the corresponding 1,2,3,4-tetrasubstituted carbazole derivative selectively (path *c*). Highly substituted carbazoles have been attractive synthesis targets in medicinal chemistry and materials field, because of their biological activities as well as photophysical and optoelectronic properties.[9] Expectedly, some of carbazoles obtained by this procedure have been found to show solid-state fluorescence. The results obtained with the new coupling reactions of not only indolecarboxylic acids but also pyrrole-, benzofuran-, and furancarboxylic acids are described herein.

Table 1. Reaction of 1-Methylindole-3-carboxylic Acid (**1a**) with Diphenylacetylene (**2a**)[a]



entry	**1a** (mmol)	additive	*T* (°C)	time (h)	% yield of **3a**[b]
1[c]	0.8	LiOAc	140	2	34
2[c]	0.8	LiCl	140	4	21
3[c]	0.8	Cs_2CO_3	140	2	4
4[c]	0.8	NaOAc	140	2	24
5	0.8	LiOAc	140	2	64 (60)
6	0.8	LiOAc	120	6	99 (80)
7	0.8	LiOAc	100	8	61
8[d]	0.8	LiOAc	120	6	86
9	0.6	LiOAc	120	9	99
10[e]	0.6	LiOAc	120	8	71

[a] Reaction conditions: [**2a**]/[$Pd(OAc)_2$]/[$Cu(OAc)_2{\cdot}H_2O$]/[additive] = 0.8:0.02:0.8:1.2 (in mmol), MS4A (400 mg) in DMAc (2.5 mL) under N_2. [b] GC yield based on the amount of **2a** used. Value in parentheses indicates yield after purification. [c] In DMAc (10 mL). [d] In DMF (2.5 mL). [e] 1-Methylindole-2-carboxylic acid (**1b**) was used in place of **1a**.

We recently reported that 1-methylindole-3-carboxylic acid (**1a**) smoothly underwent the oxidative coupling with alkenes such as acrylates in the presence of $Pd(OAc)_2$, $Cu(OAc)_2{\cdot}H_2O$, and LiOAc as catalyst, oxidant, and additive, respectively.[10] In an initial attempt, the reaction of **1a** (0.8 mmol) with diphenylacetylene (**2a**) (0.8 mmol) was conducted under similar conditions, using $Pd(OAc)_2$ (0.02 mmol), $Cu(OAc)_2{\cdot}H_2O$ (0.8 mmol), LiOAc (1.2 mmol), and molecular sieves (MS4A, 400 mg) in DMAc (10 mL) at 140 °C for 2 h under N_2 to afford 9-methyl-1,2,3,4-tetraphenyl-9*H*-carbazole (**3a**) in 34% yield (entry 1 in Table 1). Other additives such as LiCl, Cs_2CO_3, and NaOAc were found to be less effective than LiOAc (entries 2−4). In these cases, significant amounts

---

(3) (a) Takahashi, T.; Li, S.; Huang, W.; Kong, F.; Nakajima, K.; Shen, B.; Ohe, T.; Kanno, K.-I. *J. Org. Chem.* **2006**, *71*, 7967. (b) Takahashi, T.; Li, Y.; Stepnicka, P.; Kitamura, M.; Liu, Y.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **2002**, *124*, 576. (c) Takahashi, T.; Kitamura, M.; Shen, B.; Nakajima, K. *J. Am. Chem. Soc.* **2000**, *122*, 12876.

(4) X = Y = halogen: (a) Huang, W.; Zhou, X.; Kanno, K.-I.; Takahashi, T. *Org. Lett.* **2004**, *6*, 2429. X = OTf, Y = $SiMe_3$: (b) Yoshikawa, E.; Radhakrishnan, K. V.; Yamamoto, Y. *J. Am. Chem. Soc.* **2000**, *122*, 7280. (c) Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. *J. Org. Chem.* **2000**, *65*, 6944. (d) Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. *J. Am. Chem. Soc.* **1999**, *121*, 5827. (e) Peña, D.; Escudero, S.; Pérez, D.; Guitián, E.; Castedo, L. *Angew. Chem., Int. Ed.* **1998**, *37*, 2659.

(5) X = $CrPh_2$, Y = H: (a) Whitesides, G. M.; Ehmann, W. J. *J. Am. Chem. Soc.* **1970**, *92*, 5625. (b) Herwig, W.; Metlesics, W.; Zeiss, H. *J. Am. Chem. Soc.* **1959**, *81*, 6203. X = I, Y = H: (c) Kawasaki, S.; Satoh, T.; Miura, M; Nomura, M. *J. Org. Chem.* **2003**, *68*, 6836. (d) Wu, G.; Rheingold, A. L.; Feib, S. L.; Heck, R. F. *Organometallics* **1987**, *6*, 1941. (e) Sakakibara, T.; Tanaka, Y.; Yamasaki, T.-I. *Chem. Lett.* **1986**, 797. X = COCl, Y = H: (f) Yasukawa, T.; Satoh, T.; Miura, M.; Nomura, M. *J. Am. Chem. Soc.* **2002**, *124*, 12680. X = CO_2H, Y = H: (g) Ueura, K.; Satoh, T.; Miura, M. *J. Org. Chem.* **2007**, *72*, 5362. X = CR_2OH, Y = H: (h) Uto, T.; Shimizu, M.; Ueura, K.; Tsurugi, H.; Satoh, T.; Miura, M. *J. Org. Chem.* **2008**, *73*, 298. X = Y = H: (i) Umeda, N.; Tsurugi, H.; Satoh, T.; Miura, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 4019. (j) Wu, Y.-T.; Huang, K.-H.; Shin, C.-C.; Wu, T.-C. *Chem.—Eur. J.* **2008**, *14*, 6697.

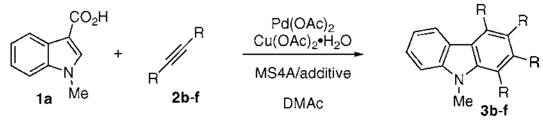
(6) Selected reviews: (a) Kakiuchi, F.; Kochi, T. *Synthesis* **2008**, 3013. (b) Lewis, J. C.; Bergman, R. G.; Ellman, J. A. *Acc. Chem. Res.* **2008**, *41*, 1013. (c) Ferreira, E. M.; Zhang, H.; Stoltz, B. M. *Tetrahedron* **2008**, *64*, 5987. (d) Park, Y. J.; Park, J.-W.; Jun, C.-H. *Acc. Chem. Res.* **2008**, *41*, 222. (e) Herrerias, C. I.; Yao, X.; Li, Z.; Li, C.-J. *Chem. Rev.* **2007**, *107*, 2546. (f) Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev.* **2007**, *107*, 174. (g) Godula, K.; Sames, D. *Science* **2006**, *312*, 67. (h) Satoh, T.; Miura, M. *J. Synth. Org. Chem.* **2006**, *64*, 1199. (i) Conley, B. L.; Tenn, W. J., III; Young, K. J. H.; Ganesh, S. K.; Meier, S. K.; Ziatdinov, V. R.; Mironov, O.; Oxgaard, J; Gonzales, J.; Goddard, W. A., III; Periana, R. A. *J. Mol. Catal. A* **2006**, *251*, 8. (j) Miura, M.; Satoh, T. *Top. Organomet. Chem.* **2005**, *14*, 55. (k) Kakiuchi, F.; Chatani, N. *Adv. Synth. Catal.* **2003**, *345*, 1077. (l) Ritleng, V.; Sirlin, C.; Pfeffer, M. *Chem. Rev.* **2002**, *102*, 1731. (m) Miura, M.; Nomura, M. *Top. Curr. Chem.* **2002**, *219*, 211. (n) Kakiuchi, F.; Murai, S. *Acc. Chem. Res.* **2002**, *35*, 826. (o) Dyker, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 1698. (p) Kakiuchi, F.; Murai, S. *Top. Organomet. Chem.* **1999**, *3*, 47. (q) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879.

(7) For recent examples of the catalytic decarboxylation as well as decarboxylative coupling reactions of carboxylic acids, see: (a) Miyasaka, M.; Fukushima, A.; Satoh, T.; Hirano, K.; Miura, M. *Chem.—Eur. J.* **2009**, *15*, 3674. (b) Huang, X.-C.; Wang, F.; Liang, Y.; Li, J.-H. *Org. Lett.* **2009**, *11*, 1139. (c) Duan, Z.; Ranjit, S.; Zhang, P.; Liu, X. *Chem.—Eur. J.* **2009**, *15*, 3666. (d) Bi, H.-P.; Zhao, L.; Liang, Y.-M.; Li, C.-J. M. *Angew. Chem., Int. Ed.* **2009**, *48*, 792. (e) Sharma, A.; Kumar, R.; Sharma, N.; Kumar, V.; Sinha, A. K. *Adv. Synth. Catal.* **2008**, *350*, 2910. (f) Goossen, L. J.; Rodríguez, N.; Linder, C. *J. Am. Chem. Soc.* **2008**, *130*, 15248. (g) Goossen, L. J.; Zimmermann, B.; Knauber, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 7103. (h) Voutchkova, A.; Coplin, A.; Leadbeater, N. E.; Crabtree, R. H. *Chem. Commun.* **2008**, 6312. (i) Becht, J.-M.; Le Drian, C. *Org. Lett.* **2008**, *10*, 3161. (j) Nakano, M.; Tsurugi, H.; Satoh, T.; Miura, M. *Org. Lett.* **2008**, *10*, 1851. For a recent review, see: (k) Goossen, L. J.; Rodríguez, N.; Goossen, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 3100.

(0.36−0.49 mmol) of 1-methylindole were also formed by simple decarboxylation. However, under concentrated conditions using DMAc (2.5 mL), the formation of 1-methylindole was suppressed (0.16 mmol) and the yield of **3a** was improved to 64% (entry 5). At 120 °C, to our delight, **3a** was obtained almost quantitatively (entry 6), while the yield was significantly reduced at 100 °C (entry 7). In DMF, the yield decreased slightly (entry 8). Decreasing the amount of **1a** to 0.6 mmol did not affect the reaction efficency (entry 9). Under similar conditions, 1-methylindole-2-carboxylic acid (**1b**) also reacted with **2a**, but the yield of **3a** was considerably lower (71%, entry 10).

The reactions of **1a** using various internal alkynes in place of **2a** were next examined. Under optimized conditions in Table 1 (entry 6, condtions A), methyl- (**2b**), methoxy- (**2c**), and chloro-substituted diphenylacetylenes (**2d**) underwent the coupling with **1a** to afford the corresponding 1,2,3,4-tetraaryl-9- methylcarbazoles **3b**−**d** in good yields (entries 1−3 in Table 2). Compared to these diarylacetylenes, 4-octyne (**2e**) was found to be less reactive. Thus, under conditions A, 9- methyl-1,2,3,4-tetrapropyl-9*H*-carbazole (**3e**) was formed in 32% yield (entry 4). Some screening experiments for reaction conditions led to the establishment of conditions B, which are suitable for the reaction with dialkylacetylenes. Thus, using an excess amount of **2e** (**1a**/**2e** = 1:4) in the presence of LiOH•H_2O (1.2 mmol) as well as LiOAc (2.4 mmol) as additive at 100 °C under air, **3e** was obtained in 62% yield (entry 5). The reactions of **1a** with 8-hexadecyne (**2f**) proceeded similarly under conditions B to give 1,2,3,4-tetraheptyl-9-methylcarbazole (**3f**) in 70% yield (entry 6).

Table 2. Reaction of 1-Methylindole-3-carboxylic Acid (**1a**) with Alkynes **2**[a]



entry	2	R	conditions	time (h)	3, % yield[b]
1	**2b**	4-MeC_6H_4	A	8	**3b**, 98 (82)
2	**2c**	4-$MeOC_6H_4$	A	8	**3c**, (75)
3	**2d**	4-ClC_6H_4	A	12	**3d**, (62)
4	**2e**	Pr	A	6	**3e**, 32
5	**2e**	Pr	B	10	**3e**, 62 (58)
6	**2f**	heptyl	B	10	**3f**, 70 (55)

[a] Reaction conditions: (A) [**1a**]/[**2**]/[$Pd(OAc)_2$]/[$Cu(OAc)_2$•H_2O]/[LiOAc] = 0.6:0.8:0.02:0.8:1.2 (in mmol), MS4A (400 mg) in DMAc (2.5 mL) at 120 °C under N_2; (B) [**1a**]/[**2**]/[$Pd(OAc)_2$]/[$Cu(OAc)_2$•H_2O]/[LiOAc]/[LiOH•H_2O] = 0.4:1.6:0.02:0.8:2.4:1.2 (in mmol), MS4A (400 mg) in DMAc (2.5 mL) at 100 °C under air. [b] GC yield based on the amount of **2** (conditions A) or **1a** (conditions B) used. Value in parentheses indicates yield after purification.

Some of tetraarylcarbazoles obtained above showed solid-state fluorescence in a range of 380−450 nm (see the Supporting Information). Notably, **3b** exhibited a relatively strong emmission compared to a typical blue emitter, anthracene, by a factor of 3.7 (λ_{emis} 393, 414 nm, A versus B in Figure 1).

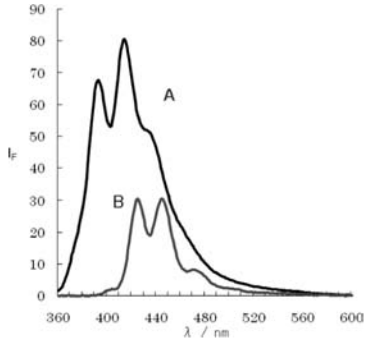
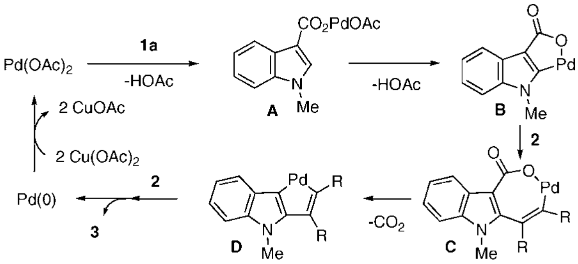


Figure 1. Fluorescence spectra of **3b** (A) and anthracene (B) in the solid-state upon excitation at 350 nm.

The reaction of **1a** with **2** seems to be initiated via fundamentally similar steps to those proposed for the oxidative coupling of **1a** with alkenes using $Pd(OAc)_2$/$Cu(OAc)_2$•H_2O/LiOAc system.[10] Thus, as depicted in Scheme 3, coordination of the carboxyl oxygen to $Pd(OAc)_2$ with liberation of AcOH gives a palladium(II) carboxylate **A** and directed palladation at the C2-position forms a palladacycle intermediate **B**. Subsequent alkyne insertion and decarboxylation occur to produce a five-membered palladacycle intermediate **D**.[11] Then, the second alkyne insertion and reductive elimination steps take place to form carbazole **3**. The resulting Pd(0) species may be oxidized in the presence

Scheme 3



---

(8) Shimizu, M.; Hirano, K.; Satoh, T.; Miura, M. *J. Org. Chem.* **2009**, *74*, 3478.

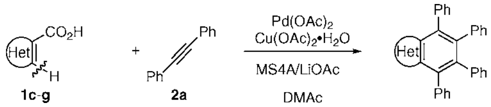
(9) For recent examples, see: (a) Adhikari, R. M.; Neckers, D. C.; Shah, B. K. *J. Org. Chem.* **2009**, *74*, 3341. (b) Jordan-Hore, J. A.; Johansson, C. C. C.; Gulias, M.; Beck, E. M.; Gaunt, M. J. *J. Am. Chem. Soc.* **2008**, *130*, 16184. (c) Tsuchimoto, T.; Matsubayashi, H.; Kaneko, M.; Nagase, Y.; Miyamura, T.; Shirakawa, E. *J. Am. Chem. Soc.* **2008**, *130*, 15823. (d) Janosik, T.; Wahlström, N.; Bergman, J. *Tetrahedron* **2008**, *64*, 9159. (e) Song, Y.; Di, C.; Wei, Z.; Zhao, T.; Xu, W.; Liu, Y.; Zhang, D.; Zhu, D. *Chem.—Eur. J.* **2008**, *14*, 4731. (f) Tsang, W. C. P.; Munday, R. H.; Brasche, G.; Zheng, N.; Buchwald, S. L. *J. Org. Chem.* **2008**, *73*, 7603. (g) Liégault, B.; Lee, D.; Huestis, M. P.; Stuart, D. R.; Fagnou, K. *J. Org. Chem.* **2008**, *73*, 5022. (h) Kuwahara, A.; Nakano, K.; Nozaki, K. *J. Org. Chem.* **2005**, *70*, 413. (i) Qiao, X.; Ho, D. M.; Pascal, R. A., Jr. *J. Org. Chem.* **1996**, *61*, 6748. (j) For review, see: (k) Knölker, H.-J.; Reddy, K. R. *Chem. Rev.* **2002**, *102*, 4303.

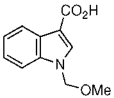
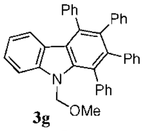
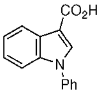
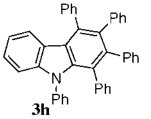
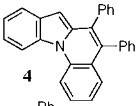
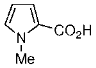
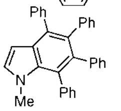
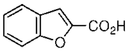
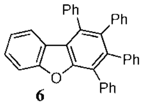
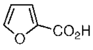
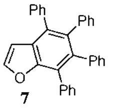
of the copper(II) salt to regenerate $Pd(OAc)_2$. During palladium-catalyzed oxidative reactions, in general, the regeneration of Pd(II) from Pd(0) is considered to be the crucial step to determine catalyst efficiency.[12] One of the possible roles of added LiOAc is to provide acetate anions as ligand to prevent the deactivation of Pd(0) to metallic species.[13]

In the cases using dialkylacetylenes, the addition of $LiOH{\cdot}H_2O$ besides LiOAc improved the reaction efficiency. Without this base, formation of 1:1 oxidative coupling products together with **3** was detected by GC−MS. One of its possible roles appears to be the trap of acids formed during the reaction, which may induce ring-opening of palladacycle intermediates such as **C** and **D** to form acyclic vinylpalladium species. The latter are known to undergo β-hydrogen elimination to produce allene derivatives.[14]

Table 3 summarizes the results for the coupling reactions of a series of heteroarene carboxylic acids with **2a** using the catalyst system of $Pd(OAc)_2/Cu(OAc)_2{\cdot}H_2O$/LiOAc. Expectedly, 1-(methoxymethyl)indole-3-carboxylic acid (**1c**) underwent the coupling with **2a** to produce the corresponding carbazole **3g** selectively in 80% yield (entry 1). In contrast, the reaction of 1-phenylindole-3-carboxylic acid (**1d**) with **2a** gave a mixture of 1:2 and 1:1 coupling products. Thus, when these substrates were treated using $Pd(OAc)_2$ (0.04 mmol) for 12 h, not only the expected homologation product, 1,2,3,4,9-pentaphenyl-9*H*-carbazole (**3h**) (21%) but also a tetracyclic compound **4** were formed (36%) by vinyl bridging (entry 2). From the reaction of 1-methylpyrrole-2-carboxylic acid (**1e**), a highly substituted indole derivative **5** was obtained in 63% yield (entry 3). In this case, increasing in the amounts of the substrate **1e** (0.8 mmol) and LiOAc (2.4 mmol) resulted in a better product yield.

Table 3. Reaction of Heteroarenecarboxylic Acids **1c-g** with **2a**[a]



entry	1	atmosphere	time (h)	product(s)	% yield[b]
1	 **1c**	N_2	8	 **3g**	80 (72)
2[c]	 **1d**	N_2	12	 **3h** +	21 (14)
				 **4**	36 (32)
3[d,e]	 **1e**	N_2	10	 **5**	63 (61)
4[d,f]	 **1f**	air	10	 **6**	72 (70)
5[d,g,h]	 **1g**	air	6	 **7**	45 (44)

[a] Reaction conditions: [**1**]/[**2a**]/[$Pd(OAc)_2$]/[$Cu(OAc)_2{\cdot}H_2O$]/[LiOAc] = 0.6:0.8:0.02:0.8:1.2 (in mmol), MS4A (400 mg) in DMAc (2.5 mL) at 120 °C. [b] GC yield based on the amount of **2a** used. Value in parentheses indicates yield after purification. [c] $Pd(OAc)_2$ (0.04 mmol) was used. [d] **1** (0.8 mmol) was used. [e] LiOAc (2.4 mmol) was used. [f] $LiOH{\cdot}H_2O$ (1.2 mmol) and 2,2-dimethylsuccinic acid (2.4 mmol) were used in place of LiOAc. [g] $Cu(OAc)_2{\cdot}H_2O$ (0.05 mmol) was used. [h] Pivalic acid (2.4 mmol) was used in place of LiOAc.

Meanwhile, the reactions of benzofuran- (**1f**) and furan-2-carboxylic acids (**1g**) with **2a** were found to proceed effectively under air with the addition of an appropriate acid. The reaction of **1f** using $LiOH{\cdot}H_2O$ (1.2 mmol) and 2,2-dimethylsuccinic acid (2.4 mmol) as additives in place of LiOAc afforded 1,2,3,4-tetraphenyldibenzofuran (**6**) in 72% yield (entry 4). In the reaction of **1g**, once produced 1,2,3,4-tetraphenylbenzofuran (**7**) was decomposed under the standard oxidative conditions. Therefore, the amount of $Cu(OAc)_2{\cdot}H_2O$ was decreased to 0.05 mmol and pivalic acid (2.4 mmol) was added in place of LiOAc. Under such modified conditions, **7** was obtained with a substantial yield (entry 5).

In summary, we have demonstrated that the palladium-catalyzed oxidative coupling of indole-3-carboxylic acids with two molecules of alkynes proceeds efficiently via directed C−H bond cleavage and decarboxylation to give the corresponding 1,2,3,4-tetrasubstituted carbazoles. Other related heteroarenecarboxylic acids also undergo the aromatic homologation. In these reactions, the carboxyl function effectively acts as a unique, removable directing group.[5g,7a,j,8,10,15] Work is underway toward further development of relevant reactions around the key functional group.

Acknowledgment. This work was partly supported by Grants-in-Aid from the Ministry of Education, Culture, Sports, Science and Technology, Japan, and the Kurata Memorial Hitachi Science and Technology Foundation.

Supporting Information Available: Standard experimental procedure and characterization data of products. This material is available free of charge via the Internet at http://pubs.acs.org.

OL900736S

---

(10) Maehara, A.; Tsurugi, H.; Satoh, T.; Miura, M. *Org. Lett.* **2008**, *10*, 1159.

(11) However, the participation of another sequence involving decarboxylation on a copper carboxylate cannot be excluded (see ref 7k).

(12) Stahl, S. S. *Angew. Chem., Int. Ed.* **2004**, *43*, 3400.

(13) Amatore, C.; Jutand, A. *J. Organomet. Chem.* **1999**, *576*, 254, and references therein.

(14) For example, see: Pivsa-Art, S.; Satoh, T.; Miura, M.; Nomura, M. *Chem. Lett.* **1997**, 823.

(15) For recent examples of *ortho*-arylation, see: (a) Chiong, H. A.; Pham, Q.-N.; Daugulis, O. *J. Am. Chem. Soc.* **2007**, *129*, 9879. (b) Giri, R.; Maugel, N.; Li, J.-J.; Wang, D.-H.; Breazzano, S. P.; Saunders, L. B.; Yu, J.-Q. *J. Am. Chem. Soc.* **2007**, *129*, 3510.