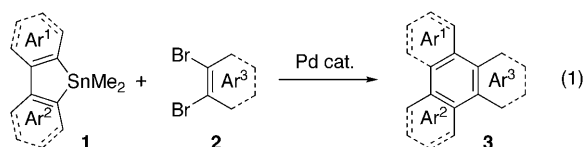


# 9-Stannafluorenes: 1,4-Dimetal Equivalents for Aromatic Annulation by Double Cross-Coupling\*\*

Ikuhiro Nagao, Masaki Shimizu,\* and Tamejiro Hiyama

In the field of organic materials science, the design and characterization of polycyclic aromatic hydrocarbons (PAHs), which exhibit superior electronic, optical, and/or self-assembling properties, has been studied intensely.<sup>[1]</sup> Hence, efficient synthetic methods leading to functionalized PAHs are expected to assist the rapid developments of PAH-based functional materials.<sup>[2]</sup> The transition-metal-catalyzed cross-coupling reactions of organometals with organic halides are an efficient method for regio- and stereospecific formation of C(sp<sup>2</sup>)-C(sp<sup>2</sup>) bond.<sup>[3]</sup> As a result, double cross-coupling reactions of organodimetallic reagents and dihalides would provide a straightforward and promising method for designing PAHs if the annulation reaction takes place efficiently in preference to the possible oligomerization and/or polymerization. However, the examples of such annulations are limited.<sup>[4]</sup>

Herein, we report that the palladium-catalyzed double cross-coupling reaction of 9-stannafluorenes **1** with 1,2-dihaloarenes **2** serves as a new entry to aromatic annulation and provides a variety of triply annulated benzene derivatives **3** in good to excellent yields [Eq. (1)]. Moreover, the approach is applicable to the synthesis of twisted PAHs<sup>[5]</sup> such as phenanthro[9,10-*b*]triphenylenes and diphenanthro[9,10-*b*:9',10'-*d*]thiophene through double annulation with tetrabromoarenes, and the reaction can be extended to annulation with 1,1-dibromoalkenes leading to the production of dibenzofulvenes.

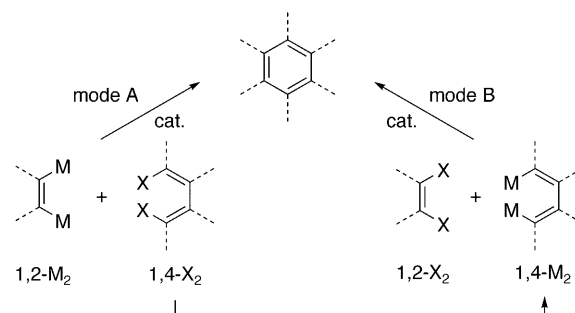


[\*] I. Nagao, Prof. Dr. M. Shimizu, Prof. Dr. T. Hiyama  
Department of Material Chemistry, Graduate School of Engineering  
Kyoto University, Kyoto University Katsura  
Nishikyo-ku, Kyoto 615-8510 (Japan)  
Fax: (+81) 75-383-2445  
E-mail: m.shimizu@hs2.ecs.kyoto-u.ac.jp  
Homepage: <http://npc05.kuic.kyoto-u.ac.jp/e-index.htm>

[\*\*] This work was supported by Grants-in-Aid for Creative Scientific Research (grant no. 16GS0209) from the Ministry of Education, Culture, Sports, Science, and Technology (Japan) and The Asahi Glass Foundation.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.200903779>.

Our research group has recently demonstrated that the palladium-catalyzed double cross-coupling reaction of *vic*-bis(pinacolatoboryl)alkenes and -phenanthrenes is a versatile synthetic method for the preparation of functionalized phenanthrenes and dibenzo[*g,p*]chrysenes.<sup>[4*ij*]</sup> As illustrated in Scheme 1, the annulation reaction can be categorized as the



**Scheme 1.** Modes of [4+2]-type aromatic annulation using dimetal reagents and dihalogenated compounds.

coupling of 1,2-dimetal reagents 1,2-M<sub>2</sub> and 1,4-dihaloarenes 1,4-X<sub>2</sub> (mode A). To expand the synthetic utility of palladium-catalyzed aromatic annulation using dimetal reagents, we were interested in the combination of 1,2-dihaloarenes 1,2-X<sub>2</sub> and 1,4-dimetal reagents 1,4-M<sub>2</sub> (umpolung of mode A) as an alternative approach (mode B). Considering that 1,4-M<sub>2</sub> can be readily prepared from the corresponding 1,4-X<sub>2</sub> and, in particular, the structural variation of available 1,2-X<sub>2</sub> is much broader than that of 1,2-M<sub>2</sub>: thus mode B-type annulation could greatly expand the repertoire of accessible PAHs. However, the precedents of mode B-type annulation were limited to only the reactions of 2,2'-diborylbiphenyls,<sup>[4*a*]</sup> zirconacyclopentadienes,<sup>[4*b-d*]</sup> [Zr(2,2'-biphenyldiyl)<sub>3</sub>][Li·(THF)<sub>4</sub>]<sub>2</sub>,<sup>[4*e-g*]</sup> 2,2'-distannylbinaphthyl,<sup>[4*h*]</sup> and 1,4-dilithiobutadienes<sup>[4*i*]</sup> with 1,2-dihaloarenes, and there is still much room for improvement in the scope of the substrates and reagents, yields, and reaction conditions.

We focused our attention on 9-stannafluorene derivatives as equivalents of 1,4-dimetal reagents, which are available from the corresponding 2,2'-dihaloarenes and are often used as precursors of 9-borafluorenes<sup>[6]</sup> but never employed for the synthesis of PAHs.<sup>[7]</sup> We anticipated that the cyclic form would have a beneficial effect on the reactivity toward the first coupling of the annulation owing to the strain.<sup>[8]</sup> In addition, the use of 9-stannafluorenes is favorable for lowering metal waste as compared with the corresponding 2,2'-distannylbiphenyls.

Initially, we chose 9,9-dimethyl-9-stannafluorene (**1a**) and 1,2-dibromobenzene (**2a**) as the coupling partners. After conducting extensive experiments,<sup>[9]</sup> we found that the expected product triphenylene (**3aa**) was isolated in 90% yield when the reaction was conducted in the presence of [Pd(PtBu<sub>3</sub>)<sub>2</sub>] (5 mol%) in THF at 60 °C (Table 1, entry 1).<sup>[10]</sup>

**Table 1:** Palladium-catalyzed annulation of **1a–1b** with **2a–2c** leading to **3aa**.<sup>[a]</sup>

| Entry | <b>1</b>           | <b>2</b>             | Additive (equiv)   | <b>3</b> Yield [%] <sup>[b]</sup> |
|-------|--------------------|----------------------|--------------------|-----------------------------------|
| 1     | <b>1a</b> (R = Me) | <b>2a</b> (X = Br)   | –                  | 87 (90) <sup>[c]</sup>            |
| 2     | <b>1a</b>          | <b>2a</b>            | CsF (5)            | 84                                |
| 3     | <b>1a</b>          | <b>2a</b>            | CuI (0.1)          | 68                                |
| 4     | <b>1a</b>          | <b>2a</b>            | CsF (5), CuI (0.1) | 8                                 |
| 5     | <b>1a</b>          | <b>2a'</b> (X = I)   | –                  | 0                                 |
| 6     | <b>1a</b>          | <b>2a'</b>           | CsF (5)            | 87                                |
| 7     | <b>1a</b>          | <b>2a''</b> (X = Cl) | –                  | 0                                 |
| 8     | <b>1a</b>          | <b>2a''</b>          | CsF (5)            | 21                                |
| 9     | <b>1b</b> (R = Bu) | <b>2a</b>            | –                  | 0                                 |
| 10    | <b>1b</b>          | <b>2a</b>            | CsF (5)            | 90                                |

[a] Reaction conditions: **1** (0.050 mmol), **2** (0.050 mmol), [Pd(PtBu<sub>3</sub>)<sub>2</sub>] (2.5 μmol, 5 mol%), additive as shown in Table, THF, 60 °C. [b] Yield based on <sup>1</sup>H NMR spectroscopy. [c] The value in parentheses is the yield of the isolated product.

No formation of oligomeric or polymeric by-products was observed. The addition of CsF or CuI was found to be less effective for the annulation reaction (Table 1, entries 2 and 3), whereas using these two additives simultaneously resulted in far from satisfactory results (Table 1, entry 4). This outcome sharply contrasts to those of Baldwin and co-workers, who reported the palladium-catalyzed reaction of arylstannanes with aryl halides.<sup>[11]</sup> The presence of CsF was essential in the case of 1,2-diiodobenzene (**2a'**; compare Table 1, entries 5 and 6), whereas the reaction with dichlorobenzene (**2a''**) was unsuccessful both in the absence and presence of CsF (Table 1, entries 7 and 8). Dibutylstannafluorene **1b** underwent the annulation reaction efficiently when CsF was added as in the case of **2a** (compare Table 1, entries 9 and 10). Bulkier atoms/substituents such as iodine and the butyl group appeared to slow down the transmetalation process, while the addition of fluorides probably accelerates the transmetalation process by generating stannates.<sup>[12]</sup>

The scope of the present annulation reaction is summarized in Table 2. Substituted dibromobenzenes **2b–2e** reacted with **1a** to produce triphenylenes **3ab–3ae** in high to excellent yields (Table 2, entries 1–4). Both electron-withdrawing and -donating substituents on **2** were tolerated. The annulation reaction carried out with dibromothiophenes **2f** and **2g** proceeded smoothly at the 2,3- and 3,4-positions to produce benzo[*b*]phenanthro[9,10-*d*]thiophene (**3af**) and phenanthro[9,10-*c*]thiophene (**3ag**) in 78–98% yield (Table 2, entries 5–7). Thus, the fusion mode of a thiophene ring was easily

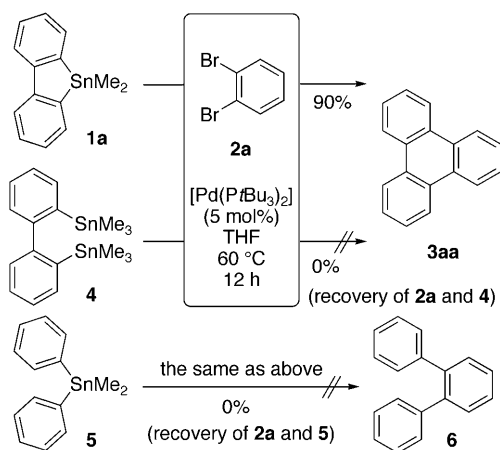
**Table 2:** Pd-catalyzed annulation of **1** with dibromoarenes **2**.<sup>[a]</sup>

| Entry            | <b>1</b>                                                                               | <b>2</b>                                                          | <b>3</b> (yield [%]) <sup>[b]</sup> |
|------------------|----------------------------------------------------------------------------------------|-------------------------------------------------------------------|-------------------------------------|
| 1                | <b>1a</b>                                                                              | <b>2b</b> (R <sup>5</sup> = CF <sub>3</sub> ; R <sup>6</sup> = H) | <b>3ab</b> (99)                     |
| 2                | <b>1a</b>                                                                              | <b>2c</b> (R <sup>5</sup> , R <sup>6</sup> = F)                   | <b>3ac</b> (85)                     |
| 3 <sup>[c]</sup> | <b>1a</b>                                                                              | <b>2d</b> (R <sup>5</sup> = OMe; R <sup>6</sup> = H)              | <b>3ad</b> (95)                     |
| 4 <sup>[d]</sup> | <b>1a</b>                                                                              | <b>2e</b> (R <sup>5</sup> , R <sup>6</sup> = Me)                  | <b>3ae</b> (85)                     |
| 5                | <b>1a</b>                                                                              | <b>2f</b>                                                         | <b>3af</b> (78)                     |
| 6 <sup>[d]</sup> | <b>1a</b>                                                                              | <b>2f</b>                                                         | <b>3af</b> (80)                     |
| 7                | <b>1a</b>                                                                              | <b>2g</b>                                                         | <b>3ag</b> (98)                     |
| 8                | <b>1a</b>                                                                              | <b>2h</b>                                                         | <b>3ah</b> (71)                     |
| 9                | <b>1c</b> (R <sup>1</sup> , R <sup>4</sup> = H; R <sup>2</sup> , R <sup>3</sup> = OMe) | <b>2a</b> (R <sup>5</sup> , R <sup>6</sup> = H)                   | <b>3ca</b> (99)                     |
| 10               | <b>1d</b> (R <sup>1</sup> , R <sup>2</sup> , R <sup>3</sup> , R <sup>4</sup> = Me)     | <b>2a</b> (R <sup>5</sup> , R <sup>6</sup> = H)                   | <b>3da</b> (77)                     |
| 11               | <b>1e</b> (R <sup>1</sup> , R <sup>2</sup> = OMe; R <sup>3</sup> , R <sup>4</sup> = H) | <b>2c</b> (R <sup>5</sup> , R <sup>6</sup> = F)                   | <b>3ec</b> (97)                     |
| 12               | <b>1f</b>                                                                              | <b>2a</b>                                                         | <b>3fa</b> (74)                     |
| 13               | <b>1a</b> (R <sup>2</sup> = H)                                                         | <b>2i</b> (R <sup>7</sup> = OnC <sub>10</sub> H <sub>21</sub> )   | <b>3ai</b> (80)                     |
| 14               | <b>1g</b> (R <sup>2</sup> = OnC <sub>6</sub> H <sub>13</sub> )                         | <b>2j</b> (R <sup>7</sup> = H)                                    | <b>3gj</b> (66)                     |
| 15               | <b>1a</b>                                                                              | <b>2k</b>                                                         | <b>3ak</b> (85)                     |

[a] Reaction conditions: **1** (1.0 mmol), **2** (1.0 mmol), [Pd(PtBu<sub>3</sub>)<sub>2</sub>] (50 μmol, 5 mol%), THF, 60 °C, 12 h. [b] Yield of isolated product. [c] **1** (1.0 mmol), **2** (1.0 mmol), [Pd(PtBu<sub>3</sub>)<sub>2</sub>] (50 μmol, 5 mol%), CsF (5 mmol), 1,4-dioxane, 130 °C, 12 h. [d] CsF (5 mmol) was used as the additive.

controlled. Dibenzo[*f,h*]quinoline (**3ah**) was obtained in 71 % yield from **1a** and 2,3-dibromopyridine (**2h**; Table 2, entry 8).<sup>[13]</sup> Substituted 9-stannafluorenes **1c–1e** also participated in the annulation reaction to give symmetrical triphenylenes **3ca** and **3da** as well as an unsymmetrical one **3ec** in high to excellent yields (Table 2, entries 9–11). Dithienostannole **1f** also underwent the double cross-coupling reaction as the equivalent of 2,2'-dimetalbithiophene with **2a** to produce **3fa** in 74 % yield (Table 2, entry 12). Moreover, a double annulation reaction that allows the facile synthesis of twisted PAHs was performed by using tetrabromoarenes as an electrophile (Table 2, entries 13–15). Thus, 1,2,4,5-tetrabromobenzenes **2i** and **2j** and 2,3,4,5-tetrabromothiophene (**2k**) were coupled with two equivalents of **1** to produce phenanthro[9,10-*b*]triphenylenes **3ai** and **3gj**,<sup>[4e]</sup> and diphenanthro[9,10-*b*:9',10'-*d*]thiophene **3ak**,<sup>[14]</sup> respectively, in good to high yields. The present annulation reaction is, to the best of our knowledge, the first demonstration of **1** to be utilized as 2,2'-dimetalobiaryl equivalents for C–C bond-forming annulation.

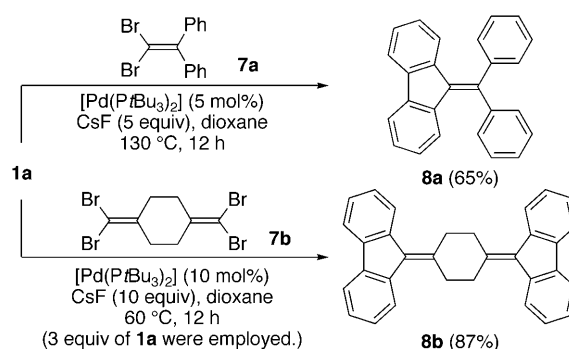
To gain understanding of the characteristic reactivity patterns of **1**, we subjected 2,2'-bis(trimethylstannyl)biphenyl (**4**) and dimethyldiphenylstannane (**5**) to the reaction conditions ( $[\text{Pd}(\text{P}t\text{Bu}_3)_2]$ , THF, 60 °C, 12 h) that were optimized for **1**, in the presence of **2a**. However, no coupling reaction took place and with only quantitative recovery of the stannyl reagents in both cases (Scheme 2).<sup>[15]</sup> These results clearly



**Scheme 2.** Attempts at the coupling reaction of **4** and **5** with **2a**.

indicate that **1** is much more reactive than **4** or **5**. Meanwhile, the  $\text{Pd}^0$  catalyst which is regenerated in the cross-coupling reaction of 1,2-dibromobenzenes and arylboronic acids with the aid of  $[\text{Pd}_2(\text{dba})_3]/\text{P}t\text{Bu}_3$  was reported to undergo oxidative addition exclusively with the remaining C–Br bond of the initial product over the diffusion process.<sup>[16]</sup> Therefore, the success of the present annulation reaction may be ascribed to both the high reactivity of **1**, induced by the cyclic structure, and the unique behavior of **2** with regard to the second oxidative addition process.

Furthermore, 1,1-dibromoalkenes **7a** and **7b** were also found to undergo a double cross-coupling reaction with **1** (Scheme 3). Although the addition of CsF at a higher reaction



**Scheme 3.** Annulation of **1a** with 1,1-dibromoalkenes **7**.

temperature (in the case of **7a**) was necessary to promote the formation of a five-membered ring, the expected products dibenzofulvenes **8a**<sup>[17]</sup> and **8b**<sup>[18]</sup> were isolated in 65 % and 87 % yield, respectively.

In summary, we have developed a palladium-catalyzed double cross-coupling reactions of 9-stannafluorenes and dithienostannole with 1,2-dihaloarenes and 1,1-dibromoalkenes, by which diverse polycyclic aromatic hydrocarbons can be synthesized in good to excellent yields. We have also disclosed that the reactivity of 9,9-dimethyl-9-stannafluorene toward this palladium-catalyzed cross-coupling reaction is much higher than that of 2,2'-bis(trimethylstannyl)biphenyl. Further studies on the elucidation of the mechanism and the development of functional organic materials using the present annulation reaction are in progress.

Received: July 10, 2009

Published online: September 8, 2009

**Keywords:** arenes · cross-coupling · palladium · stannanes · synthetic methods

- [1] a) *Chem. Rev.* **2007**, *107*, 923–1386 (Special issue on Organic Electronics and Optoelectronics edited by S. R. Forrest and M. E. Thompson); b) J. Wu, W. Pisula, K. Müllen, *Chem. Rev.* **2007**, *107*, 718–747; c) S. Laschat, A. Baro, N. Steinke, F. Giesselmann, C. Hägele, G. Scalia, R. Judele, E. Kapatsina, S. Sauer, A. Schreivogel, M. Tosoni, *Angew. Chem.* **2007**, *119*, 4916–4973; *Angew. Chem. Int. Ed.* **2007**, *46*, 4832–4887; d) J. E. Anthony, *Chem. Rev.* **2006**, *106*, 5028–5048; e) M. D. Watson, A. Fechtenkötter, K. Müllen, *Chem. Rev.* **2001**, *101*, 1267–1300; f) A. J. Berresheim, M. Müller, K. Müllen, *Chem. Rev.* **1999**, *99*, 1747–1786.
- [2] a) R. G. Harvey, *Polycyclic Aromatic Hydrocarbons*, Wiley, New York, **1997**; b) M. M. Boorum, L. T. Scott in *Modern Arene Chemistry* (Ed.: D. Astruc), Wiley-VCH, Weinheim, **2002**, pp. 20–31; c) R. G. Harvey, *Curr. Org. Chem.* **2004**, *8*, 303–323; d) L. T. Scott, *Angew. Chem.* **2004**, *116*, 5102–5116; *Angew. Chem. Int. Ed.* **2004**, *43*, 4994–5007; e) D. Perez, E. Guitian, *Chem. Soc. Rev.* **2004**, *33*, 274–283.
- [3] a) *Metal-Catalyzed Cross-Coupling Reactions* (Eds.: F. Diederich, P. J. Stang), Wiley-VCH, Weinheim, **1998**; b) *Top. Curr. Chem.*, Vol. 219 (Ed.: N. Miyaura), Springer, Berlin, **2002**; c) *Metal-Catalyzed Cross-Coupling Reactions* (Eds.: A. de Meijere, F. Diederich), Wiley-VCH, Weinheim, **2004**.
- [4] Palladium-catalyzed annulation of 2,2'-diborylbiphenyls: a) J. W. Goodby, M. Hird, K. J. Toyne, T. Watson, *J. Chem. Soc. Chem.*

- Commun.* **1994**, 1701–1702; copper-mediated annulation of zirconacyclopentadienes: b) T. Takahashi, R. Hara, Y. Nishihara, M. Kitora, *J. Am. Chem. Soc.* **1996**, *118*, 5154–5155; c) T. Takahashi, Y. Li, P. Stepnicka, M. Kitamura, Y. Liu, K. Nakajima, M. Kitora, *J. Am. Chem. Soc.* **2002**, *124*, 576–582; d) T. Seri, H. Qu, L. Zhou, K. I. Kanno, T. Takahashi, *Chem. Asian J.* **2008**, *3*, 388–392; uncatalyzed annulation of [Zr(2,2'-biphenyldiyl)<sub>3</sub>][Li·(THF)<sub>4</sub>]<sub>2</sub>: e) C. L. Hilton, C. R. Jamison, B. T. King, *J. Am. Chem. Soc.* **2006**, *128*, 14824; f) C. L. Hilton, J. M. Crowfoot, P. Rempala, B. T. King, *J. Am. Chem. Soc.* **2008**, *130*, 13392–13399; g) C. L. Hilton, C. R. Jamison, H. K. Zane, B. T. King, *J. Org. Chem.* **2009**, *74*, 405–407; palladium-catalyzed annulation of 2,2'-bis(trimethylstannyl)binaphthyl with 1,2-diiodobenzene: h) X. Xue, L. T. Scott, *Org. Lett.* **2007**, *9*, 3937–3940; palladium-catalyzed annulation of *vic*-diborylalkenes and -phenanthrenes: i) M. Shimizu, I. Nagao, Y. Tomioka, T. Hiyama, *Angew. Chem.* **2008**, *120*, 8216–8219; *Angew. Chem. Int. Ed.* **2008**, *47*, 8096–8099; copper-mediated annulation of 1,4-dilithiobutadienes: j) L. Zhou, K. Nakajima, K.-i. Kanno, T. Takahashi, *Tetrahedron Lett.* **2009**, *50*, 2722–2726.
- [5] Review on twisted acenes: R. A. Pascal, Jr., *Chem. Rev.* **2006**, *106*, 4809–4819.
- [6] For example: P. A. Chase, W. E. Piers, B. O. Patrick, *J. Am. Chem. Soc.* **2000**, *122*, 12911–12912.
- [7] Reviews on cross-coupling reactions of organostannanes: a) J. K. Stille, *Angew. Chem.* **1986**, *98*, 504–519; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 508–524; b) T. N. Mitchell, *Synthesis* **1992**, 803–815; c) V. Farina, V. Krishnamurthy, W. K. Scott in *Organic Reactions*, Vol. 50, Wiley, New York, **1997**, pp. 1–652; d) T. N. Mitchell in *Metal-Catalyzed Cross-Coupling Reactions* (Eds.: F. Diederich, P. J. Stang), Wiley-VCH, Weinheim, **1998**, pp. 167–202; e) M. A. J. Duncun, G. Pattenden, *J. Chem. Soc. Perkin Trans. 1* **1999**, 1235–1246; f) K. Fugami, M. Kosugi in *Cross-Coupling Reactions A Practical Guide*, Vol. 219 (Ed.: N. Miyauro), Springer, Berlin, **2002**, pp. 87–130; g) T. N. Mitchell in *Metal-Catalyzed Cross-Coupling Reactions*, Vol. 1, 2nd ed. (Eds.: A. de Meijere, F. Diederich), Wiley-VCH, Weinheim, **2004**, pp. 125–161.
- [8] The X-ray analysis of 9,9-dimethyl-9-stannafluorene (**1a**) has been reported: G. P. M. van Klink, H. J. R. de Boer, G. Schat, O. S. Akkerman, F. Bickelhaupt, A. L. Spek, *Organometallics* **2002**, *21*, 2119–2135.
- [9] For details see the Supporting Information.
- [10] A. F. Littke, L. Schwarz, G. C. Fu, *J. Am. Chem. Soc.* **2002**, *124*, 6343–6348.
- [11] S. P. H. Mee, V. Lee, J. E. Baldwin, *Chem. Eur. J.* **2005**, *11*, 3294–3308.
- [12] a) P. Espinet, A. M. Echavarren, *Angew. Chem.* **2004**, *116*, 4808–4839; *Angew. Chem. Int. Ed.* **2004**, *43*, 4704–4734; b) Ref. [10].
- [13] Ir complexes bearing **3ah** as ligands were used as light emitters in OLED devices. H. F. Boerner, H. Hummel, WO049762A1, **2005**.
- [14] An organic transistor device consisting of **3ak** has been reported to exhibit high mobility, on/off ratio, and stability. M. Nakatsuka (Jpn. Kokai Tokkyo Koho), JP20099965, **2004**.
- [15] The annulation of 2,2'-bis(trimethylstannyl)binaphthyl with 1,2-diiodobenzene was reported to proceed in the presence of [Pd(PtBu<sub>3</sub>)<sub>2</sub>] and CsF in dioxane at 130 °C upon microwave irradiation to give the corresponding benzo[5]helicene in 82 % yield, see Ref. [4h].
- [16] C.-G. Dong, Q.-S. Hu, *J. Am. Chem. Soc.* **2005**, *127*, 10006–10007.
- [17] H. Tong, Y. Dong, M. Häussler, Z. Li, B. Mi, H. S. Kwok, B. Z. Tang, *Mol. Cryst. Liq. Cryst.* **2006**, *446*, 183–191.
- [18] B. J. Dahl, N. S. Mills, *J. Am. Chem. Soc.* **2008**, *130*, 10179–10186.