Regiospecific Synthesis of Furan-3,4-diyl Oligomers via Palladium-Catalyzed Self-Coupling of Organoboroxines†

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The palladium-catalyzed reaction of organoboroxines 2 and *o*-bis(bromomethyl)arenes 1 produced regiospecifically the cross-coupled products 3 and the corresponding dimeric bifurans 4. This method has been successfully applied to the synthesis of symmetrical, as well as unsymmetrical furan-3,4-diyl dimers, trimers, and tetramers. A furan-3,4-diyl octamer was also obtained by utilizing this method.

Previous reports[1] from our laboratories have unequivocally demonstrated the usefulness of organoboroxines for the synthesis of 3,4-disubstituted furans. Our strategy begins with the preparation of 3,4-bis(trimethylsilyl)-furan,[1b] which then serves as a versatile building block and can be converted regiospecifically to various boroxines, utilizing an *ipso* substitution[2] of the trimethylsilyl group with boron trichloride and subsequent hydrolysis of the resulting dichloroboranes. A novel Suzuki-type cross-coupling reaction[3] of the boroxines with organohalides furnished 3-(trimethylsilyl)-4-substituted furans in good yields.[1b] A repeat of the pathway on the remaining trimethylsilyl group provided 3,4-disubstituted furans with diverse substituents.

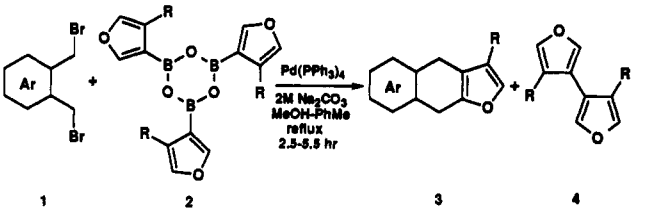
In the course of the above work,[1] the cross-coupling of boroxines with various *o*-bis(bromomethyl)arenes was attempted. In this paper, we wish to disclose the results obtained and the application of this procedure to the efficient and regiospecific synthesis of furan-3,4-diyl oligomers, which are difficult or even impossible to realize otherwise.

Results and Discussion

(a) Palladium-Catalyzed Reaction of Boroxines with *o*-Bis(bromomethyl)arenes. Boroxines are prepared in reasonable yields from the corresponding 3-(trimethylsilyl)-4-substituted furans.[1] Reaction of boroxines 2 with *o*-bis(bromomethyl)arenes 1 using palladium catalyst in the presence of 2 M Na_2CO_3 afforded unexpectedly the cross-coupled products 3 and dimeric furans 4 (Scheme 1). The results are summarized in Table 1.

As can be seen in Table 1, the use of 1,2-bis(bromomethyl)benzene (entry 1), 9,10-bis(bromomethyl)phenanthrene (entry 2), 1,2-bis(bromomethyl)naphthalene (entry 3), and 2,3-bis(bromomethyl)naphthalene (entry 4) favored

Scheme 1



the formation of two products, i.e., the cross-coupled products 3 and the symmetrical bifurans 4, formed presumably through a self-coupling mechanism. In sharp contrast, the use of 1,2,4,5-tetrakis(bromomethyl)benzene (entry 5), 1,4-dimethyl-2,3-bis(bromomethyl)benzene (entry 6), and 2,3-bis(bromomethyl)quinoxaline (entry 7) gave only symmetrical bifurans 4 in good yields. The cross-coupled products 3 were not detected in these experiments.

(b) Reaction Mechanism. The mechanism of the aforementioned palladium-catalyzed cross-coupling reaction can be considered in accordance with the well-established Suzuki reaction.[3a,b] However, to the best of our knowledge, no self-coupling has been observed for the Suzuki reaction thus far. On the basis of the results obtained, a mechanism is proposed, which involves a series of oxidative additions, transmetallations, and reductive eliminations. As depicted in Scheme 2, the mechanism consists of two catalytic cycles A and B,[4] which account for the formation of 3 and 4. Each catalytic cycle begins with the oxidative addition of one of the C–Br bonds of the arenes to the Pd(0) catalyst to give the common Pd(II) complex 5. In the presence of a base (OH^-),[3c] the intermediate 5 goes through a transmetallation process with boroxine 2 to provide the diorganopalladium complex 6, which then undergoes reductive elimination to give 7 in cycle A and regenerates the reactive Pd(0) species. An oxidative addition step of Pd(0) with the C–Br bond of 7 converts it to the organopalladium halide 8, which is able to undergo a Heck-type reaction[5] to form 9. Eventually, a reductive elimination process gives the cross-coupled product 3 and regenerates the Pd(0) catalyst. On the other hand, the bifurans 4 are produced as illustrated in cycle B. In competition with the reductive elimination reaction (i.e., 6 → 7),[6] the Pd(II) complex 6 can also undergo a second oxidative addition with the Pd(0) species to provide

† Dedicated to Professor Emanuel Vogel on the occasion of his 65th birthday.

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(1) 3,4-Disubstituted furans. 6. (a) Part 5: Song, Z. Z.; Wong, H. N. C. *Liebigs Ann. Chem.*, in press. (b) Part 4: Song, Z. Z.; Zhou, Z. Y.; Mak, T. C. W.; Wong, H. N. C. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 432–434.

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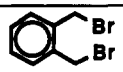
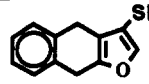
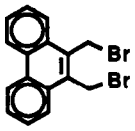
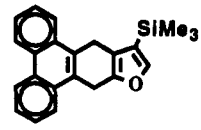
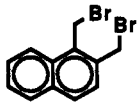
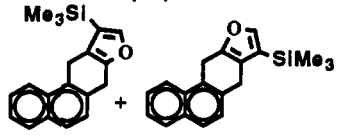
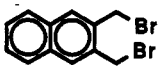
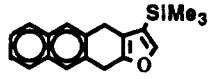
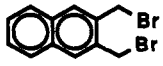
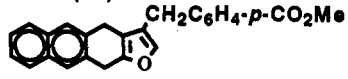
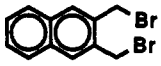
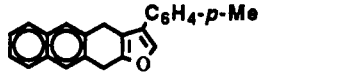
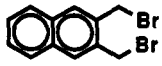
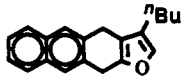
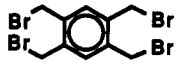
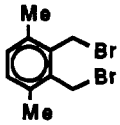
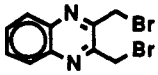
Table 1. Pd(0)-Catalyzed Coupling Reactions of Boroxines 2 with *o*-Bis(bromomethyl)arenes 1[a]

entry	1	2	3 (yield, %)[b]	4 (yield, %)[b]
1		R = $SiMe_3$ **2a**	 **3a (55)**	R = $SiMe_3$ **4a** (40)
2[c]		R = $SiMe_3$ **2a**	 **3b (46)**	R = $SiMe_3$ **4a** (28)
3		R = $SiMe_3$ **2a**	 **3c (28)**	R = $SiMe_3$ **4a** (30)
4		R = $SiMe_3$ **2a**	 **3d (65)**	R = $SiMe_3$ **4a** (30)
4		R = $CH_2C_6H_4$-*p*-CO_2Me **2b**	 **3e (57)**	R = $CH_2C_6H_4$-*p*-CO_2Me **4b** (24)
4		R = C_6H_4-*p*-Me **2c**	 **3f (41)**	R = C_6H_4-*p*-Me **4c** (18)
4		R = *n*-Bu **2d**	 **3g (52)**	R = *n*-Bu **4d** (22)
5		R = $SiMe_3$ **2a**		R = $SiMe_3$ **4a** (89)
6		R = $SiMe_3$ **2a**	(0)	R = $SiMe_3$ **4a** (87)
7		R = $SiMe_3$ **2a**	(0)	R = $SiMe_3$ **4a** (90)

[a] *o*-Bis(bromomethyl)arenes **1** (1.5 mmol), boroxines **2** (1 mmol); $Pd(PPh_3)_4$ (0.1 mmol), 2 M Na_2CO_3 solution (6 mL), MeOH/PhMe (1:1,50 mL), bath temperature 140 °C. [b] Isolated yields. [c] Solvent: MeOH/PhMe (5:1, 50 mL).

10. Subsequent transmetalation with boroxine **2** in the presence of a base[3c] gives the bis(diorganopalladium)-complex **11**, which might go through a disproportionation reaction to give two diorganopalladium complexes **12** and **13**.[7] Complex **12** is able to generate bifuran **4** and the Pd(0) catalyst via a reductive elimination reaction. It is likely that **13**[7] is thermally unstable at room temperature,[8] and the Pd–C bonds would be cleaved in reflux aqueous methanol. One conceivable pathway is the breakdown of **13** to an *o*-xylylene moiety, through which the reactive Pd(0) is simultaneously regenerated. In addition, triphenylphosphine oxide has also been isolated.

Before the results on the successful use of the unexpected self-coupling reaction are presented, it is worthwhile at this point to examine and to verify the proposed mechanism. Interestingly, in the absence of an *o*-bis(bromomethyl)arene, tris[4-[*p*-(methoxycarbonyl)benzyl]furan-3-yl]boroxine (**2b**),[1] tris[4-(*p*-nitrobenzyl)furan-3-yl]boroxine (**2e**),[1] tris[4-(3′,4′,5′-trimethoxybenzyl)furan-3-yl]boroxine (**2f**),[1] and tris[4-[*o*-(*p*-tolyl)phenyl]furan-3-yl]boroxine (**2g**)[1] were consumed completely to give the protonated products **15**, i.e., 3-[*p*-(methoxycarbonyl)benzyl]furan (**15b**), 3-(*p*-nitrobenzyl)furan (**15e**), 3-(3′,4′,5′-trimethoxybenzyl)furan (**15f**), and 3-[*o*-(*p*-tolyl)phenyl]furan (**15g**), respectively (Scheme 3). Thus, the bis(bromomethyl)-arenes are required to achieve furan coupling. Moreover, as shown in Scheme 4, convincing evidence in support of the mechanism has been obtained when a mixture of tris-[4-(trimethylsilyl)furan-3-yl]boroxine (**2a**) and **2b** was allowed to react with Pd(0) in 1 M Na_2CO_3 in the presence of 2,3-bis(bromomethyl)quinoxaline. This afforded a mixture of the self-coupled products 4,4′-bis(trimethylsilyl)-3,3′-bifuran (**4a**) and 4,4′-bis[*p*-(methoxycarbonyl)-

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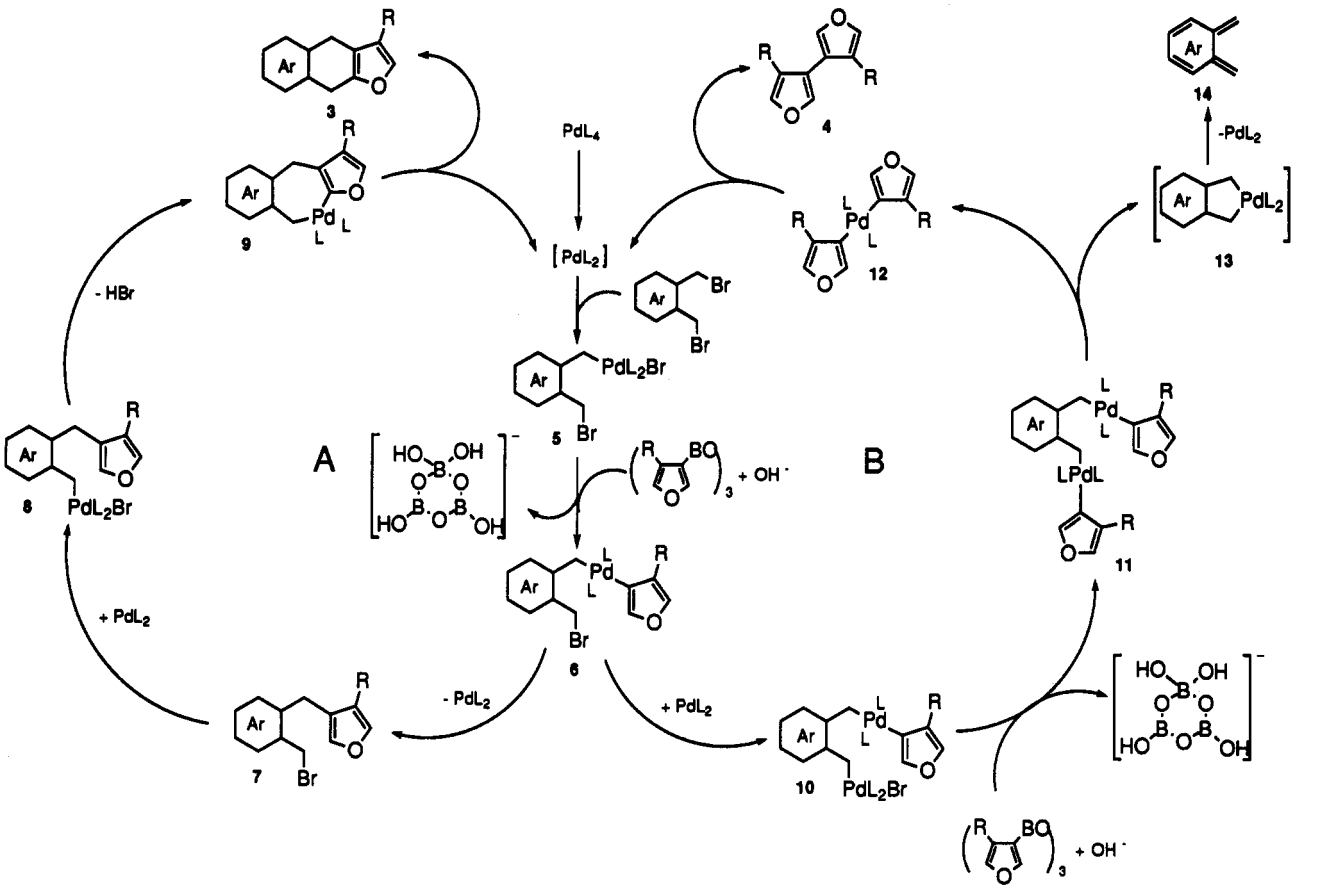
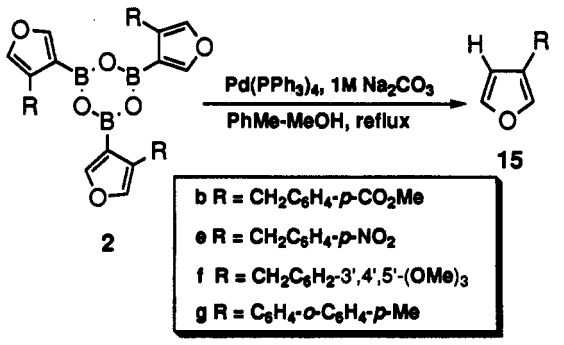
Scheme 2



Scheme 3



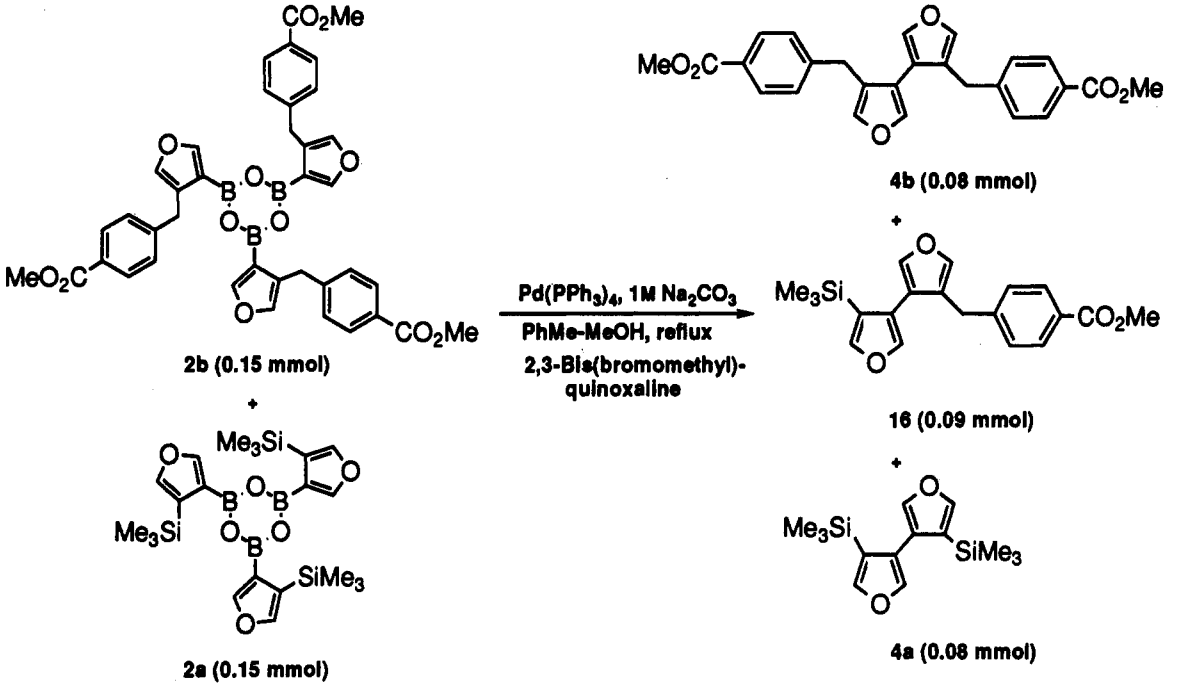
benzyl]-3,3′-bifuran (**4b**) as well as the "cross-coupled" product, namely 4-(trimethylsilyl)-4′-[*p*-(methoxycarbonyl)benzyl]-3,3′-bifuran (**16**). In view of this experimental finding, it is likely that the formation of **4a**, **4b**, and **16** is due to a disproportionation reaction of the three possible intermediate complexes **11**. Nevertheless, the remarkable tendency of 2,3-bis(bromomethyl)quinoxaline (entry 7, Table 1) as well as 1,2,4,5-tetrakis(bromomethyl)benzene (entry 5, Table 1) and 1,4-dimethyl-2,3-bis(bromomethyl)-benzene (entry 6, Table 1) to induce the self-coupling reaction as shown in cycle B (Table 1) is still unclear.

(c) Synthesis of Furan-3,4-diyl Oligomers. Notwithstanding the fact that several reports dealing with five-membered heterocycle-2,5-diyl oligomers have appeared,[9] a direct and regiospecific synthesis of the respective 3,4-diyl counterparts has so far not been recorded. From a synthetic viewpoint, such a lack of activity is particularly true for oligomeric furans and might be attributable to their nontrivial preparation.

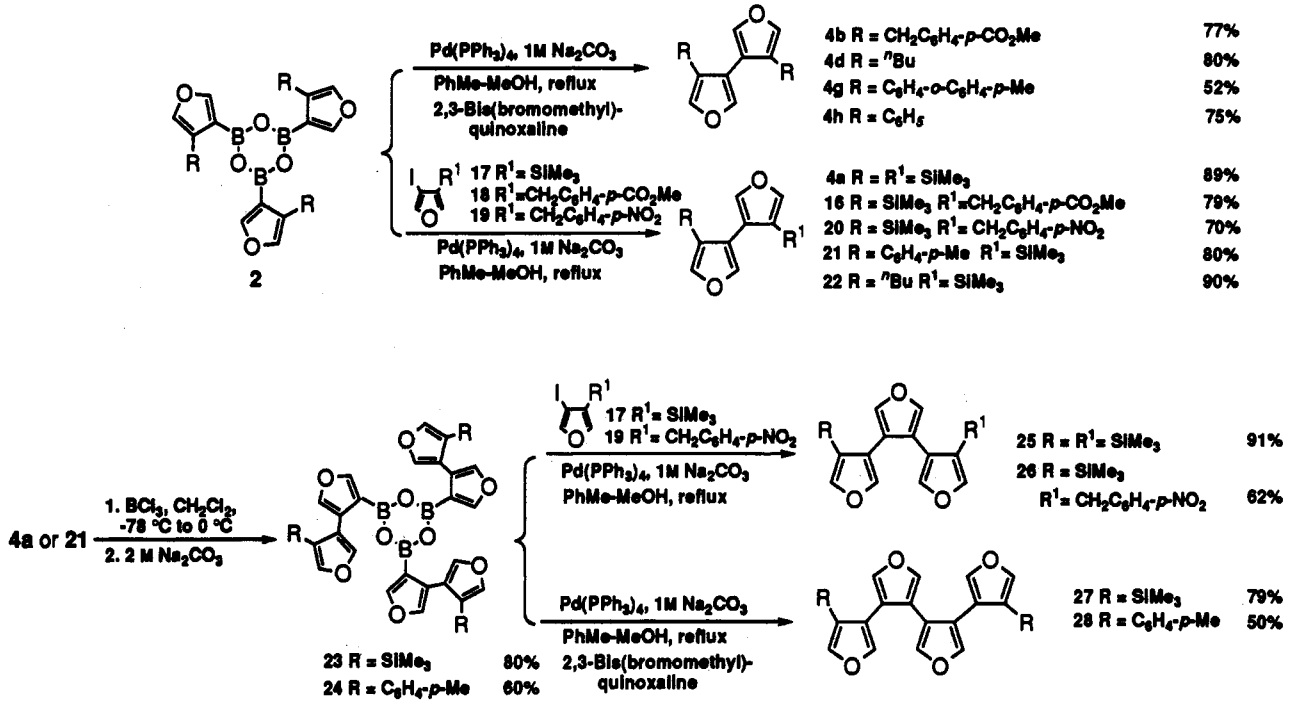
On the basis of the use of palladium-catalyzed reactions, the highly efficient self-coupling procedures which involved the use of boroxines **2** and 2,3-bis(bromomethyl)quinoxaline (entry 7, Table 1), as outlined above, is expected to provide a novel route to symmetrical furan-3,4-diyl oligomers. Furthermore, the palladium-catalyzed cross-coupling reaction that involved boroxines **2** and 3-iodo-4-substituted[1a] furans yielded another pathway to unsymmetrical furan-3,4-diyl oligomers (Scheme 5). In order to test the effectiveness of these reactions, our first endeavor was the synthesis of 3,3′-bifurans (Scheme 5). The Pd(0)-catalyzed coupling of boroxine **2b**, tris[4-(*n*-butyl)furan-3-yl]boroxine (**2d**), boroxine **2g**, and tris(4-phenylfuran-3-yl)boroxine (**2h**) in the presence of 2,3-bis(bromomethyl)quinoxaline gave 4,4′-bis[*p*-(methoxycarbonyl)benzyl]-3,3′-bifuran (**4b**), 4,4′-bis(*n*-butyl)-3,3′-bifuran (**4d**), and 4,4′-bis[*o*-(*p*-tolyl)phenyl]-3,3′-bifuran (**4g**), and 4,4′-diphenyl-3,3′-bifuran (**4h**), respectively. In the synthesis of **4g**, a 21% yield of the protonated product **15g** was also isolated, presumably due to the steric hindrance of the biphenyl group. As can also be seen in Scheme 5, when boroxine **2a** was allowed to undergo a Pd(0)-catalyzed cross-coupling with 3-iodo-4-(trimethylsilyl)furan (**17**)[1a] or 3-iodo-4-[*p*-(methoxycarbonyl)-

(9) Roncali, J. *Chem. Rev.* **1992**, *92*, 711–738. Grigg, R.; Knight, J. A.; Sargent, M. V. *J. Chem. Soc. C* **1966**, 976–981. Cunningham, D. D.; Laguren-Davidson, L.; Mark, H. B., Jr.; Pham, C. V.; Zimmer, H. *J. Chem. Soc., Chem. Commun.* **1987**, 1021–1023. Vogel, E.; Haas, W.; Knipp, B.; Lex, J.; Schmickler, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 406–409; **1988**, *27*, 409–411; **1988**, *27*, 411–414. Gronowitz, S.; Peter, D. *Heterocycles* **1990**, *30*, 645–658. Pomerantz, M.; Chaloner-Gill, B.; Harding, L. O.; Tseng, J. J.; Pomerantz, W. J. *J. Chem. Soc., Chem. Commun.* **1992**, 1672–1673. Delabouglise, D.; Hmyene, M.; Horowitz, G.; Yassar, A.; Garnier, F. *Adv. Mater.* **1992**, *4*, 107–110. Kuroda, M.; Nakayama, J.; Hoshino, M. *Tetrahedron Lett.* **1992**, *33*, 7553–7556. Barbarella, G.; Bongini, A.; Zambianchi, M. *Tetrahedron* **1992**, *48*, 6701–6708. Itahara, T.; Hashimoto, M.; Yumisashi, H. *Synthesis* **1984**, 255–256. Berlin, A.; Paganic, G. A.; Sannicolo, F. *J. Chem. Soc., Chem. Commun.* **1986**, 1663–1664. McCullough, R. D.; Lowe, R. D. *J. Chem. Soc., Chem. Commun.* **1992**, 70–72.

Scheme 4



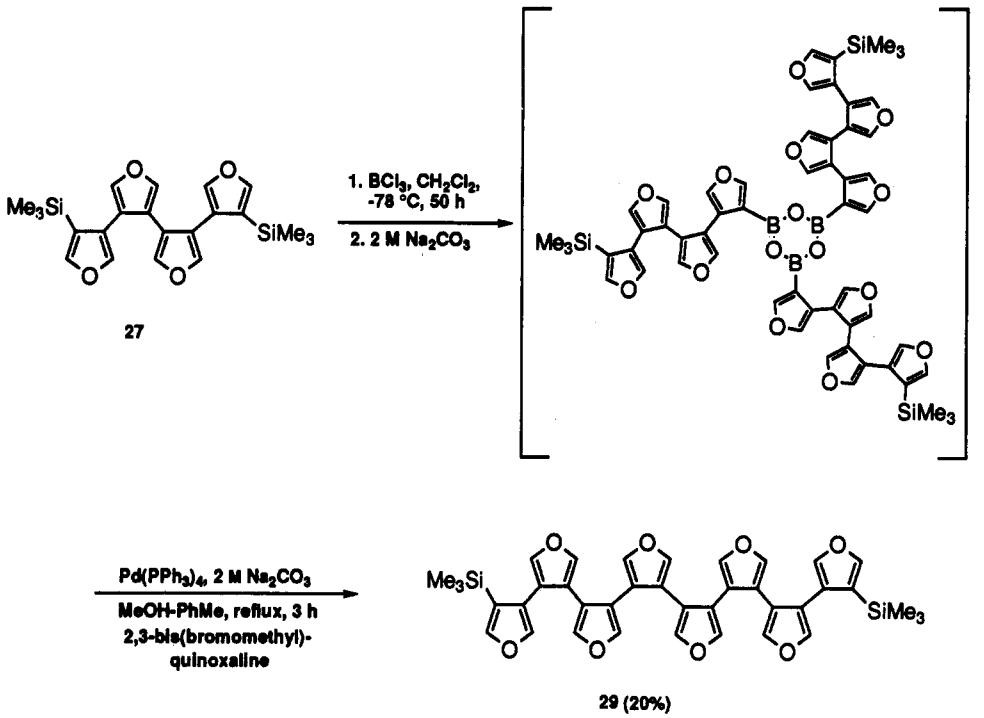
Scheme 5



benzyl]furan (18),[1a] bifurans 4a and 16, respectively, were furnished. Likewise, on reaction with 3-iodo-4-(*p*-nitrobenzyl)furan (19),[1a] boroxines 2a gave 4-(trimethylsilyl)-4′-(*p*-nitrobenzyl)-3,3′-bifuran (20). The reaction between tris[4-(*p*-tolyl)furan-3-yl]boroxine (2c) or tris[4-(*n*-butyl)-furan-3-yl]boroxine (2d) with 3-iodo-4-(trimethylsilyl)-furan (17)[1a] afforded the unsymmetrical 4-(trimethylsilyl)-4′-(*p*-tolyl)-3,3′-bifuran (21) and 4-(trimethylsilyl)-4′-(*n*-butyl)-3,3′-bifuran (22), respectively (Scheme 5).

From the examples mentioned above, it is quite clear that the Pd(0)-catalyzed self- and cross-coupling reactions can be applied also to the synthesis of furan-3,4-diyl trimers and tetramers. In support of this we have found that tris-[4′-(trimethylsilyl)-3,3′-bifuran-4-yl]boroxine (23), which was generated through the usual procedure from 4a, underwent a Pd(0)-catalyzed cross-coupling reaction with 3-iodo-4-(trimethylsilyl)furan (17)[1a] to furnish 4,4″-bis-(trimethylsilyl)-3,3′:4′,3″-terfuran (25). The identity of 25 is unequivocally vindicated by its ^{1}H NMR spectrum, which exhibits a single methyl absorption at δ 0.12 ppm and three 2H olefinic signals at δ 7.22, 7.31, and 7.47 ppm, whose coupling constants, ranging from 0.5 to 1.3 Hz, are in agreement with a 3,3′:4′,3″-terfuran skeleton. The appearance of only seven signals in the ^{13}C NMR spectrum indicates that 25 is a symmetrical terfuran. The structure of 25 is also supported by a correct elemental analysis result. Under similar conditions, the unsymmetrical 4-(trimethylsilyl)-4′-(*p*-nitrobenzyl)-3,3′:4′,3″-terfuran (26) was also prepared from 23 and 3-iodo-4-(*p*-nitrobenzyl)-furan (19).[1a] Of great interest is the Pd(0)-catalyzed self-coupling of 23 in the presence of 2,3-bis(bromomethyl)-quinoxaline, which eventually gave a furan-3,4-diyl

Scheme 6



tetramer, namely 4,4‴-bis(trimethylsilyl)-3,3′:4′,3″:4″,3‴-quaterfuran (**27**). Similar to **4a** and **25**, the structure of quaterfuran **27** is also supported by ^{1}H NMR (a single methyl absorption and four olefinic doublets), ^{13}C NMR (nine absorptions), and a correct elemental analysis result. A further example of this furan-3,4-diyl tetramer synthesis has been given by the conversion of **21** to tris[4′-(*p*-tolyl)-3,3′-bifuran-4-yl]boroxine (**24**), which as expected afforded 4,4‴-bis(*p*-tolyl)-3,3′:4′,3″:4″,3‴-quaterfuran (**28**) under similar coupling conditions. In this reaction, the protonated product 4-(*p*-tolyl)-3,3′-bifuran was also isolated in 15% yield (Scheme 5).

Encouraged by the successful synthesis of furan-3,4-diyl dimers, trimers, and tetramers, the preparation of a furan-3,4-diyl octamer was also sought. Thus, as shown in Scheme 6, the tetramer **27** was converted to its corresponding boroxine, and the subsequent coupling reaction gave the octifuran **29**, albeit in only 20% yield. The structure of **29** has been substantiated by the appearance of the 16 olefinic protons (16 1H doublets at δ 7.07, 7.08, 7.14, 7.17, 7.19, 7.20, 7.21, 7.26, 7.27, 7.28, 7.31, 7.35, 7.36, 7.38, 7.44, and 7.45 ppm) and 18 methyl protons (two 9H singlets at δ 0.03 and 0.08 ppm) in its ^{1}H NMR spectrum, as well as by a correct elemental analysis result. As can be seen in the ^{1}H NMR spectrum of **29**, it is likely that the structure of octamer **29** adopts a helical conformation and is therefore deprived of any molecular symmetry.

Conclusion

We have described in this paper an unusual palladium(0)-catalyzed coupling reaction of organoboroxines **2** with *o*-bis(bromomethyl)arenes **1**, which provided a convenient method to convert **2** into mixtures of dihydro[2,3-*b*]furans **3** and furan-3,4-diyl dimers **4**. In the presence of 2,3-bis(bromomethyl)quinoxaline, similar coupling reactions of **2** gave exclusively the corresponding symmetrical self-coupled product **4**. However, the question is still open on the possible role played by 2,3-bis(bromomethyl)quinoxaline, as well as by some other *o*-bis(bromomethyl)arenes (*vide supra*) in the exclusive self-coupling reactions. Furthermore, cross-coupling reactions of **2** with 3-iodo-4-substituted furans provided an alternate entry to furan-3,4-diyl oligomers. By virtue of the incorporation of trimethylsilyl groups in the oligomers, a variety of substituents can be introduced by utilizing the standard procedures developed in our laboratories.[1] It is also likely that a combination of these approaches will allow the synthesis of symmetrical and unsymmetrical quinquefurans and sexifurans as well as septifurans. To our best knowledge, the realization of these furan-3,4-diyl oligomers from organoboroxines is unprecedented. We believe that the oligomeric furans can serve as prototypic structures for the study of novel furan-3,4-diyl polymers[10] and nonlinear optical materials.[11]

Experimental Section

General. Melting points were measured on a Reichert Microscope apparatus and were uncorrected. NMR spectra were recorded on a Bruker-Cryospec WM 250 spectrometer. ^{1}H NMR (250.132 MHz) chemical shifts are reported relative to $CDCl_3$ at δ 7.24 ppm and tetramethylsilane at δ 0.00 ppm. Coupling constants are reported in Hz. ^{13}C NMR (62.896 MHz) chemical shifts are expressed relative to $CDCl_3$ at δ 77.00 ppm and tetramethylsilane at δ 0.00 ppm. NMR spectroscopic terms were reported by using the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet. Mass spectra (EIMS, CIMS and HRMS) were obtained with a VG Micromass 7070F spectrometer and determined at an ionizing voltage of 70 eV; relevant data were tabulated as *m/e*. Elemental analyses were performed at Shanghai Institute of Organic Chemistry, The Chinese Academy of Sciences, China.

Unless otherwise stated, all reactions were carried out in oven-dried glassware. THF was distilled from sodium benzophenone ketyl. Methylene chloride was distilled from CaH_2. Reagents were from commercial suppliers and used without further purification. All solutions were evaporated under reduced

(10) Scherf, U.; Müllen, K. *Synthesis* **1992**, 23–38. Qian, R.-Y. *Makromol. Chem. Macromol. Symp.* **1990**, *33*, 327–339 and references cited therein.

(11) Kaino, T.; Tomaru, S. *Adv. Mater.* **1993**, *5*, 172–178. Buckley, A. *Adv. Mater.* **1992**, *4*, 153–158. Eaton, D. F.; Meredith, G. R.; Miller, J. S. *Adv. Mater.* **1992**, *4*, 45–48.

pressure with a rotary evaporator, and the residue was chromatographed on a silica gel column using hexanes–diethyl ether as the eluent unless specified otherwise. Flash chromatography was performed using E. Merck silica gel 60 (230–400 mesh). The plates used for thin-layer chromatography (TLC) were E. Merck silica gel 60 F_{254} (0.25-mm thickness) precoated on aluminum plate, and they were visualized under both long (365-nm) and short (254-nm) UV light.

Materials. 1,2-bis(bromomethyl)benzene, 2,3-bis(bromomethyl)naphthalene, 1,2-bis(bromomethyl)naphthalene, 1,2,4,5-tetrakis(bromomethyl)benzene, 3,6-dimethyl-1,2-bis(bromomethyl)benzene, and 9,10-bis(bromomethyl)phenanthrene were prepared by bromination of the corresponding methyl-substituted arenes.[12] Tetrakis(triphenylphosphine)palladium(0) and 2,3-bis(bromomethyl)quinoxaline were purchased from Aldrich Chemical Co. and were used as received.

General Procedure for Preparation of Boroxines. (a) Tris[4′-(trimethylsilyl)-3,3′-bifuran-4-yl]boroxine (23).[1b] To a solution of **4a** (834 mg, 3 mmol) in CH_2Cl_2 (100 mL) was added a solution of BCl_3 (1.0 M) in CH_2Cl_2 (6 mL) under a nitrogen atmosphere at −78 °C. After 6 h, the reaction was quenched with 2 M Na_2CO_3 solution (5 mL) and the mixture was extracted with ether (3 × 50 mL). The organic layer was dried ($MgSO_4$), and the solvent was evaporated. The crude product was chromatographed on silica gel (200 g, hexanes–ether (1:1)) to give **23** (556 mg, 80%) as a semisolid: ^{1}H NMR ($CDCl_3$) δ 0.06 (s, 18H, 2 × $SiMe_3$), 0.07 (s, 9H, $SiMe_3$), 7.38 (d, 2H, J = 1.5 Hz), 7.41 (d, 2H, J = 1.6 Hz), 7.42 (d, 2H, J = 1.6 Hz), 7.43 (d, 2H, J = 1.6 Hz), 7.49 (d, 1H, J = 1.5 Hz), 7.52 (d, 2H, J = 1.5 Hz), 7.80 (d, 1H, J = 1.5 Hz); ^{13}C NMR ($CDCl_3$) δ −0.32, 120.51, 120.72, 121.37, 141.62, 141.75, 141.96, 147.69, 149.34, 151.36, 154.89; MS m/e 696 (M^+, 11). Anal. Calcd for $C_{33}H_{39}O_9B_3Si_3$: C, 56.92; H, 5.65. Found: C, 57.09; H, 5.86.

(b) Tris[4′-(*p*-tolyl)-3,3′-bifuran-4-yl]boroxine (24) was prepared from **21** (266, 0.9 mmol) and a solution of BCl_3 (1.0 M) in CH_2Cl_2 (2 mL) to give **24** (131 mg, 60%) as a semisolid: ^{1}H NMR ($CDCl_3$) δ 2.15 (s, 9H, 3 × CH_3), 6.91 (d, 6H, J = 7.8 Hz), 6.99 (d, 6H, J = 8.3 Hz), 7.23 (d, 3H, J = 1.5 Hz), 7.44 (d, 3H, J = 1.7 Hz), 7.48 (d, 3H, J = 1.8 Hz), 7.56 (d, 3H, J = 1.6 Hz); ^{13}C NMR ($CDCl_3$) δ 20.96, 116.49, 119.43, 126.68, 127.64, 128.18, 129.10, 129.42, 129.61, 136.72, 139.68, 141.49, 141.70, 154.42. Anal. Calcd for $C_{45}H_{33}O_6B_3$: C, 74.18; H, 4.56. Found: C, 74.34; H, 4.42.

(c) Tris[4-(trimethylsilyl)furan-3-yl]boroxine (2a) was prepared from 3,4-bis(trimethylsilyl)furan[1b] (636 mg, 3 mmol) and a solution of BCl_3 (1.0 M) in CH_2Cl_2 (5 mL) to give **2a** (498 mg, 100%) as colorless needles: mp 167–168 °C; ^{1}H NMR ($CDCl_3$) δ 0.38 (s, 27H, 3 × $SiMe_3$), 7.43 (d, 3H, J = 1 Hz), 8.17 (d, 3H, J = 1 Hz); ^{13}C NMR ($CDCl_3$) δ −0.48, 117.03, 122.10, 148.97, 156.54; MS m/e 498 (M^+, 13). Anal. Calcd for $C_{21}H_{33}O_6B_3Si_3$: C, 50.63; H, 6.68. Found: C, 50.41; H, 6.61.

(d) Tris[4-[*p*-(methoxycarbonyl)benzyl]furan-3-yl]boroxine (2b) was prepared from 4-[*p*-(methoxycarbonyl)benzyl]-3-(trimethylsilyl)furan[1a] (864 mg, 3 mmol) and a solution of BCl_3 (1.0 M) in CH_2Cl_2 (5 mL) to give **2b** (515 mg, 71%) as white microcrystalline solids: mp 101–102 °C; ^{1}H NMR ($CDCl_3$) δ 3.90 (s, 9H, 3 × CH_3), 4.04 (s, 6H, 3 × CH_2), 7.10 (d, 3H, J = 1.2 Hz), 7.24 (d, 6H, J = 8.3 Hz), 7.81 (d, 3H, J = 1.5 Hz), 7.93 (d, 6H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ 31.04, 51.86, 126.98, 128.43, 128.60, 129.79, 141.84, 145.88, 155.13, 166.97; MS m/e 695 (M^+ − OMe, 10). Anal. Calcd for $C_{39}H_{33}O_{12}B_3$: C, 64.51; H, 4.58. Found: C, 63.91; H, 4.60.

(e) Tris[4-(*p*-tolyl)furan-3-yl]boroxine (2c) was prepared from 4-(*p*-tolyl)-3-(trimethylsilyl)furan[1b] (690 mg, 3 mmol) and a solution of BCl_3 (1.0 M) in CH_2Cl_2 (5 mL) to give **2c** (369 mg, 67%) as pale yellow microcrystalline solids: mp 158–159 °C; ^{1}H NMR ($CDCl_3$) δ 2.61 (s, 9H, 3 × CH_3), 7.39 (d, 6H, J = 7.8 Hz), 7.61 (d, 6H, J = 8.1 Hz), 7.69 (d, 3H, J = 1.6 Hz), 7.72 (d, 3H, J = 1.5 Hz); ^{13}C NMR ($CDCl_3$) δ 21.12, 113.20, 128.28, 128.67, 128.90, 129.90, 130.18, 130.40, 136.90, 140.52, 156.31; MS m/e 552 (M^+, 100). Anal. Calcd for $C_{33}H_{27}O_6B_3$: C, 71.71; H, 4.93. Found: C, 71.46; H, 4.91.

(f) Tris[4-(*n*-butyl)furan-3-yl]boroxine (2d) was prepared from 4-(*n*-butyl)-3-(trimethylsilyl)furan[1a] (672 mg, 3 mmol) and a solution of BCl_3 (1.0 M) in CH_2Cl_2 (5 mL) to give **2d** (333 mg, 74%) as a semisolid: ^{1}H NMR ($CDCl_3$) δ 0.95 (t, 9H, J = 7.3 Hz, 3 × CH_3), 1.41 (m, 6H, 3 × CH_2), 1.63 (m, 6H, 3 × CH_2), 2.71 (t, 6H, J = 7.3 Hz, 3 × CH_2), 7.29 (d, 3H, J = 1.5 Hz), 7.92 (d, 3H, J = 1.5 Hz); ^{13}C NMR ($CDCl_3$) δ 13.94, 22.50, 24.78, 32.27, 114.36, 129.28, 140.36, 154.82; MS m/e 450 (M^+, 10). Anal. Calcd for $C_{24}H_{33}O_6B_3$: C, 64.07; H, 7.39. Found: C, 64.13; H, 7.19.

(g) Tris[4-(*p*-nitrobenzyl)furan-3-yl]boroxine (2e) was prepared from 4-(*p*-nitrobenzyl)-3-(trimethylsilyl)furan[1b] (825 mg, 3 mmol) and a solution of BCl_3 (1.0 M) in CH_2Cl_2 (5 mL) to give **2e** (522 mg, 76%) as a pale yellow microcrystalline solid: mp 135–136 °C; ^{1}H NMR ($CDCl_3$) δ 4.11 (s, 6H, 3 × CH_2), 7.16 (s, 3H), 7.34 (d, 6H, J = 8.6 Hz), 7.83 (s, 3H), 8.08 (d, 6H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ 30.80, 113.85, 123.45, 123.61, 126.11, 129.11, 129.33, 141.98, 146.80, 148.17, 155.19; MS m/e 687 (M^+, 19). Anal. Calcd for $C_{33}H_{24}O_{12}B_3N_3$: C, 57.63; H, 3.52; N, 6.12. Found: C, 57.31; H, 3.20; N, 6.05.

(h) Tris[4-(3′,4′,5′-trimethoxybenzyl)furan-3-yl]boroxine (2f) was prepared from 4-(3′,4′,5′-trimethoxybenzyl)-3-(trimethylsilyl)furan[1b] (960 mg, 3 mmol) and a solution of BCl_3 (1.0 M) in CH_2Cl_2 (5 mL) to give **2f** (255 mg, 31%) as a semisolid: ^{1}H NMR ($CDCl_3$) δ 3.74 (s, 6H, 3 × CH_2), 3.81 (s, 27H, 9 × OCH_3), 6.45 (s, 6H), 7.17 (d, 3H, J = 1.2 Hz), 7.13 (d, 3H, J = 1.4 Hz); ^{13}C NMR ($CDCl_3$) δ 31.43, 56.08, 60.73, 106.02, 127.96, 136.03, 141.72, 153.27, 155.04. Anal. Calcd for $C_{42}H_{45}O_{15}B_3$: C, 61.29; H, 5.52. Found: C, 61.40; H, 5.14.

(i) Tris[4-[*o*-(*p*-tolyl)phenyl]furan-3-yl]boroxine (2g) was prepared from 4-[*o*-(*p*-tolyl)phenyl]-3-(trimethylsilyl)furan[1b] (918 mg, 3 mmol) and a solution of BCl_3 (1.0 M) in CH_2Cl_2 (5 mL) to give **2g** (452 mg, 58%) as a semisolid: ^{1}H NMR ($CDCl_3$) δ 2.25 (s, 9H, 3 × CH_3), 6.95–7.06 (m, 15H), 7.10 (d, 3H, J = 1.5 Hz), 7.31–7.39 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 20.99, 126.47, 127.41, 128.35, 128.67, 129.59, 129.81, 130.82, 131.25, 131.72, 136.09, 138.73, 141.11, 141.36, 141.72, 154.01; MS m/e 780 (M^+, 5). Anal. Calcd for $C_{51}H_{39}O_6B_3$: C, 78.50; H, 5.04. Found: C, 79.18; H, 5.38.

(j) Tris(4-phenylfuran-3-yl)boroxine (2h) was prepared from 4-phenyl-3-(trimethylsilyl)furan[1b] (648 mg, 3 mmol) and a solution of BCl_3 (1.0 M) in CH_2Cl_2 (5 mL) to give **2h** (367 mg, 72%) as a pale yellow microcrystalline solid: mp 134–135 °C; ^{1}H NMR ($CDCl_3$) δ 7.40–7.42 (m, 12H), 7.50–7.54 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 127.85, 127.99, 128.37, 128.77, 129.08, 129.19, 133.19, 140.73, 156.27; MS m/e 510 (M^+, 100). Anal. Calcd for $C_{30}H_{21}O_6B_3$: C, 70.57; H, 4.15. Found: C, 70.29; H, 3.85.

General Procedure for Iodination of Boroxines. (a) 3-Iodo-4-(trimethylsilyl)furan (17).[1a,13] Tris[4-(trimethylsilyl)furan-3-yl]boroxine (**2a**) (249 mg, 0.5 mmol) was dissolved in dry THF (30 mL) under nitrogen and was cooled in a dry ice–acetone bath to −78 °C. Silver tetrafluoroborate (330 mg, 1.7 mmol) was added, and the mixture was stirred for 5 min to ensure complete dissolution. Then iodine (431 mg, 1.7 mmol) in dry THF (10 mL) was added dropwise, and the reaction mixture was stirred at −78 °C for 4 h. The product **17** was obtained by dilution with ether (20 mL) and filtration through Celite. The filtering cake was washed with ether. The filtrates were washed with 50% sodium thiosulfate (2 × 20 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (hexanes) to give **17** (287 mg, 72%) as an oil: ^{1}H NMR ($CDCl_3$) δ 0.30 (s, 9H, $SiMe_3$), 7.22 (d, 1H, J = 1.5 Hz), 7.49 (d, 1H, J = 1.5 Hz); MS m/e 266 (M^+, 32). Accurate mass calcd for $C_7H_{11}OISi$ 265.9626, found 265.9621.

(b) 3-Iodo-4-[*p*-(methoxycarbonyl)benzyl]furan (18) was prepared from tris[4-[*p*-(methoxycarbonyl)benzyl]furan-3-yl]-boroxine (**2b**) (145 mg, 0.2 mmol), iodine (152 mg, 0.6 mmol), and silver tetrafluoroborate (116 mg, 0.6 mmol) to give **18** (154 mg, 75%) as white needles: mp 80–81 °C; ^{1}H NMR ($CDCl_3$) δ 3.65 (s, 2H, CH_2), 3.80 (s, 3H, CH_3), 7.01 (d, 1H, J = 1.1 Hz), 7.19 (d, 2H, J = 8.2 Hz), 7.34 (d, 1H, J = 1.6 Hz), 7.88 (d, 2H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ 31.87, 51.86, 69.88, 126.14, 128.56, 128.77, 129.79, 140.54, 144.22, 146.11, 166.85; MS m/e 342 (M^+, 53). Anal. Calcd for $C_{13}H_{11}O_3I$: C, 45.64; H, 3.24. Found: C, 45.85; H, 3.00.

(c) 3-Iodo-4-(*p*-nitrobenzyl)furan (19) was prepared from tris[4-(nitrobenzyl)furan-3-yl[boroxine (**2e**) (137 mg, 0.2 mmol), iodine (152 mg, 0.6 mmol), and silver tetrafluoroborate (116 mg,

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(13) Wilson, S. R.; Jacob, L. A. *J. Org. Chem.* **1986**, *51*, 4833–4836. Jacob, L. A.; Chen, B.-L.; Stec, D. *Synthesis* **1993**, 611–614.

0.6 mmol) to give **19** (138 mg, 70%) as pale yellow needles: mp 72–73 °C; ^{1}H NMR ($CDCl_3$) δ 3.80 (s, 2H, CH_2), 7.17 (s, 1H), 7.36 (d, 2H, J = 8.6 Hz), 7.44 (d, 1H, J = 1.5 Hz), 8.14 (d, 2H, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$) δ 31.72, 123.76, 125.46, 129.59, 140.71, 146.49; MS m/e 329 (M^+, 100). Anal. Calcd for $C_{11}H_8O_3NI$: C, 40.14; H, 2.45; N, 4.25. Found: C, 40.38; H, 2.26; N, 4.17.

General Procedure for the Pd-Catalyzed Reaction of Boroxines with *o*-Bis(bromomethyl)arenes. (a) 3-(Trimethylsilyl)-4,9-dihydronaphto[2,3-*b*]furan (3a) and 4,4′-Bis(trimethylsilyl)-3,3′-bifuran (4a). To a stirred solution containing 1,2-bis(bromomethyl)benzene (117 mg, 0.45 mmol), tris[4-(trimethylsilyl)furan-3-yl]boroxine (**2a**) (150 mg, 0.3 mmol), and tetrakis(triphenylphosphine)palladium(0) (35 mg, 0.03 mmol) in methanol–toluene (1:1, 30 mL) was added a 2 M Na_2CO_3 solution (4 mL). The reaction mixture was heated at reflux for 3–4 h and was then poured into ice–water (50 mL). The resulting mixture was extracted with ether (3 × 50 mL). The combined ether extracts were dried over $MgSO_4$, and the solvent was removed. The residue was purified by chromatography on silica gel (40 g, hexanes) to give **3a** (60 mg, 55%) and **4a** (50 mg, 40%). **3a**: oil; ^{1}H NMR ($CDCl_3$) δ 0.36 (s, 9H, $SiMe_3$), 4.01 (d, 2H, J = 4.6 Hz, CH_2), 4.08 (d, 2H, J = 4.6 Hz, CH_2), 7.30–7.38 (m, 5H); ^{13}C NMR ($CDCl_3$) δ –0.60, 27.94, 29.08, 118.11, 126.24, 129.44, 129.62, 130.17, 132.65, 134.15, 141.22, 146.19, 148.46; MS m/e 242 (M^+, 68). Anal. Calcd for $C_{15}H_{18}OSi$: C, 74.35; H, 7.49. Found: C, 74.25; H, 7.52. **4a**: oil; ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 18H, 2 × $SiMe_3$), 7.33 (d, 2H, J = 1.2 Hz), 7.41 (d, 2H, J = 1.5 Hz); ^{13}C NMR ($CDCl_3$) δ –0.22, 120.65, 121.53, 141.79, 147.87; MS m/e 278 (M^+, 25). Anal. Calcd for $C_{14}H_{22}O_2Si_2$: C, 60.38; H, 7.96. Found: C, 60.50; H, 7.56.

(b) 3-(Trimethylsilyl)-4,13-dihydrotriphenyleno[2,3-*b*]furan (3b) was prepared from 9,10-bis(bromomethyl)phenanthrene (273 mg, 0.75 mmol) and tris[4-(trimethylsilyl)furan-3-yl]boroxine (**2a**) (250 mg, 0.5 mmol) to afford **3b** (118 mg, 46%) and **4a** (58 mg, 28%). **3b**: a pale yellow microcrystalline solid; mp 110–112 °C; ^{1}H NMR ($CDCl_3$) δ 0.37 (s, 9H, $SiMe_3$), 4.24–4.31 (m, 4H, 2 × CH_2), 7.37 (s, 1H), 7.62–7.69 (m, 4H), 8.02–8.14 (m, 2H), 8.70–8.73 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –0.40, 26.22, 27.54, 117.18, 118.02, 121.85, 123.63, 123.77, 126.09, 126.58, 127.62, 129.87, 131.40, 146.43, 148.55; MS m/e 342 (M^+, 100). Anal. Calcd for $C_{23}H_{22}OSi$: C, 80.67; H, 6.48. Found: C, 80.27; H, 6.40.

(c) 3-(Trimethylsilyl)-4,11-dihydrophenanthro[2,3-*b*]furan (3c) was prepared from 1,2-bis(bromomethyl)naphthalene (235 mg, 0.75 mmol) and tris[4-(trimethylsilyl)furan-3-yl]boroxine (**2a**) (250 mg, 0.5 mmol) to afford **3c** (61 mg, 28%) and **4a** (62 mg, 30%). **3c**: pale yellow wax; ^{1}H NMR ($CDCl_3$) δ 0.35 (s, 9H, $SiMe_3$), 4.06–4.10 (m, 2H), 4.31–4.35 (m, 2H), 7.31–7.41 (m, 2H), 7.51–7.59 (m, 2H), 7.75 (d, 1H, J = 8.5 Hz), 7.87 (d, 1H, J = 7.6 Hz), 7.99 (d, 1H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ –0.54, 25.47, 30.09, 117.55, 122.97, 125.21, 126.25, 12.6.81, 127.51, 127.84, 128.40, 129.11, 131.49, 132.34, 132.49, 141.29, 146.34, 148.95; MS m/e 292 (M^+, 51). Anal. Calcd for $C_{19}H_{20}OSi$: C, 78.05; H, 6.90. Found: C, 77.66; H, 7.12.

(d) 3-(Trimethylsilyl)-4,11-dihydroanthro[2,3-*b*]furan (3d) was prepared from 2,3-bis(bromomethyl)naphthalene (141 mg, 0.45 mmol) and tris[4-(trimethylsilyl)furan-3-yl]boroxine (**2a**) (150 mg, 0.3 mmol) to afford **3d** (60 mg, 46%) and **4a** (37 mg, 30%). **3d**: pale yellow microcrystalline solid; mp 102–103 °C; ^{1}H NMR ($CDCl_3$) δ 0.32 (s, 9H, $SiMe_3$), 4.13 (d, 2H, J = 3.8 Hz), 4.19 (d, 2H, J = 3.8 Hz), 7.31 (s, 1H), 7.40–7.52 (m, 2H), 7.76–7.80 (m, 4H); ^{13}C NMR ($CDCl_3$) δ –0.56, 28.03, 29.00, 118.31, 125.44, 127.10, 127.67, 127.89, 131.69, 132.20, 132.38, 132.76, 141.38, 146.26, 148.66; MS m/e 292 (M^+, 36). Anal. Calcd for $C_{19}H_{20}OSi$: C, 78.05; H, 6.90. Found: C, 78.29; H, 7.18.

(e) 3-[*p*-(Methoxycarbonyl)benzyl]-4,11-dihydroanthro[2,3-*b*]furan (3e) and 4,4′-Bis[*p*-(methoxycarbonyl)benzyl]-3,3′-bifuran (4b) were prepared from 2,3-bis(bromomethyl)naphthalene (88 mg, 0.28 mmol) and tris[4-[*p*-(methoxycarbonyl)phenyl]furan-3-yl]boroxine (**2b**) (130 mg, 0.18 mmol) to afford **3e** (58 mg, 57%) and **4b** (28 mg, 24%). **3e**: pale yellow powder; mp 147–148 °C; ^{1}H NMR ($CDCl_3$) δ 3.63–3.66 (m, 2H, CH_2), 3.75 (s, 2H, CH_2), 3.79 (s, 3H, OCH_3), 4.02–4.05 (m, 2H, CH_2), 7.10 (s, 1H, J = 0.6 Hz), 7.23 (d, 2H, J = 8 Hz), 7.27–7.31 (m, 2H), 7.54 (s, 1H), 7.60–7.64 (m, 3H), 7.89 (d, 2H, J = 8 Hz); ^{13}C NMR ($CDCl_3$) δ 26.83, 28.21, 30.32, 51.87, 115.11, 122.29, 125.49, 127.07, 127.69, 127.89, 128.61, 129.85, 131.43, 132.02, 132.12, 132.29, 138.58, 145.28, 148.89, 166.96; MS m/e 368 (M^+, 10). Anal. Calcd for $C_{25}H_{20}O_3$: C, 81.49; H, 5.48. Found: C, 81.06; H, 5.29. **4b**: colorless needles; mp 132–132.5 °C; ^{1}H NMR ($CDCl_3$) δ 3.61 (s, 4H, 2 × CH_2), 3.81 (s, 6H, 2 × OCH_3), 6.81–7.11 (m, 8H), 7.84 (d, 4H, J = 6.3 Hz); ^{13}C NMR ($CDCl_3$) δ 30.12, 51.83, 116.43, 123.28, 128.47, 129.73, 140.94, 145.14, 166.84; MS m/e 430 (M^+, 44). Anal. Calcd for $C_{26}H_{22}O_6$: C, 72.53; H, 5.15. Found: C, 72.55; H, 4.86.

(f) 3-(*p*-Methylphenyl)-4,11-dihydroanthro[2,3-*b*]furan (3f) and 4,4′-Bis(*p*-methylphenyl)-3,3′-bifuran (4c) were prepared from 2,3-bis(bromomethyl)naphthalene (47 mg, 0.15 mmol) and tris[4-(*p*-methylphenyl)furan-3-yl]boroxine (**2c**) (55 mg, 0.1 mmol) to afford **3f** (19 mg, 41%) and **4c** (9 mg, 18%). **3f**: pale yellow microcrystalline solid; mp 178–180 °C; ^{1}H NMR ($CDCl_3$) δ 2.33 (s, 3H, CH_3), 4.16 (s, 4H), 7.16–7.19 (m, 2H), 7.32–7.36 (m, 4H), 7.50 (s, 1H), 9.70–9.77 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 21.13, 28.36, 29.71, 114.14, 125.57, 127.11, 127.19, 127.75, 127.88, 127.99, 128.94, 129.52, 131.47, 132.54, 136.67, 137.64, 139.87, 141.55, 149.25; MS m/e 310 (M^+, 100); accurate mass calcd for $C_{23}H_{18}O$ 310.1357, found 310.1377. **4c**: colorless needles; mp 104–105 °C; ^{1}H NMR ($CDCl_3$) δ 2.29 (s, 6H, 2 × CH_3), 7.00 (dd, 4H, J = 6.4, 6.6 Hz), 7.06 (dd, 4H, J = 6.0, 6.4 Hz), 7.25 (d, 2H, J = 1.8 Hz), 7.50 (d, 2H, J = 1.6 Hz); ^{13}C NMR ($CDCl_3$) δ 21.05, 115.91, 126.84, 127.96, 128.93, 129.21, 136.58, 139.84, 141.52; MS m/e 314 (M^+, 100). Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 84.58; H, 6.07.

(g) 3-(*n*-Butyl)-4,11-dihydroanthro[2,3-*b*]furan (3g) and 4,4′-Bis(*n*-butyl)-3,3′-bifuran (4d) were prepared from 2,3-bis(bromomethyl)naphthalene (47 mg, 0.15 mmol) and tris[4-(*n*-butyl)furan-3-yl]boroxine (**2d**) (45 mg, 0.1 mmol) to afford **3g** (22 mg, 52%) and **4d** (10 mg, 22%). **3g**: pale yellow solid; mp 67–68 °C; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3H, J = 7.3 Hz, CH_3), 1.30–1.56 (m, 4H), 2.34–2.40 (m, 2H), 3.91 (t, 2H, J = 3.8 Hz), 4.07 (t, 2H, J = 3.8 Hz), 7.09 (s, 1H), 7.30–7.34 (m, 2H), 7.66–7.69 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.85, 22.54, 23.34, 27.15, 28.06, 31.72, 115.23, 124.45, 125.47, 126.87, 127.13, 127.71, 127.94, 131.96, 132.25, 132.43, 132.61, 137.50, 148.12; MS m/e 276 (M^+, 17). Anal. Calcd for $C_{20}H_{20}O$: C, 86.91; H, 7.30. Found: C, 86.83; H, 7.48. **4d**: colorless needles; mp 132–132.5 °C; ^{1}H NMR ($CDCl_3$) δ 0.82 (t, 6H, J = 7.2 Hz, 2 × CH_3), 1.18–1.34 (m, 4H, 2 × CH_2), 1.37–1.46 (m, 4H, 2 × CH_2), 2.30 (t, 4H, J = 7.5 Hz, 2 × CH_2), 7.18 (dd, 2H, J = 1.1, 1.1 Hz), 7.32 (d, 2H, J = 1.7 Hz); ^{13}C NMR ($CDCl_3$) δ 13.76, 22.46, 23.83, 31.50, 117.11, 125.31, 139.52, 140.17; MS m/e 246 (M^+, 84). Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.00; H, 9.01. Found: C, 78.10; H, 8.97.

(h) Bifuran **4a** (186 mg, 89%) was prepared from the coupling reaction of 1,2,4,5-tetrakis(bromomethyl)benzene (450 mg, 1 mmol) with **2a** (250 mg, 0.5 mmol).

(i) Bifuran **4a** (108 mg, 87%) was prepared from the coupling reaction of 1,4-dimethyl-2,3-bis(bromomethyl)benzene (130 mg, 0.45 mmol) with **2a** (150 mg, 0.3 mmol).

(j) Bifuran **4a** (188 mg, 90%) was prepared from the coupling reaction of 2,3-bis(bromomethyl)quinoxaline (111 mg, 0.7 mmol) with **2a** (250 mg, 0.5 mmol).

General Procedure for Pd-Catalyzed Reduction of Boroxines. (a) 3-[*p*-(Methoxycarbonyl)benzyl]furan (15b). A mixture of tris[4-[*p*-(methoxycarbonyl)benzyl]furan-3-yl]boroxine (**2b**) (363 mg, 0.5 mmol) and $Pd(PPh_3)_4$ (46 mg, 0.04 mmol) in methanol–toluene (1:1, 20 mL) was stirred for 5 min, after which time 1 M Na_2CO_3 solution (4 mL) was added. The reaction mixture was further stirred and refluxed for 4 h. After addition of water (50 mL) and cooling to room temperature, the mixture was extracted with ether (3 × 30 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated. Purification by chromatography on silica gel (hexanes–ethyl (5:1)) yielded 3-[*p*-(methoxycarbonyl)benzyl]furan (**15b**) (252 mg, 78%) as an oil: ^{1}H NMR ($CDCl_3$) δ 3.79 (s, 2H, CH_2), 3.87 (s, 3H, CH_3), 6.19 (d, 1H, J = 0.7 Hz), 7.19 (s, 1H), 7.25 (d, 2H, J = 8.6 Hz), 7.34 (s, 1H), 7.94 (d, 2H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$) δ 31.27, 51.86, 111.11, 123.40, 128.59, 129.85, 139.78, 143.26, 145.75, 166.98; MS m/e 216 (M^+, 50); accurate mass calcd for $C_{13}H_{12}O_3$ 216.0786, found 216.0812.

(b) 3-Nitrobenzylfuran (15e) as a pale yellow oil (200 mg, 66%) was prepared from **2e** (344 mg, 0.5 mmol): ^{1}H NMR ($CDCl_3$) δ 3.86 (s, 2H, CH_2), 6.21 (d, 1H, J = 1 Hz), 7.24 (s, 1H), 7.35 (d, 2H, J = 8.9 Hz), 7.36 (s, 1H), 8.11 (d, 2H, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$) δ 30.96, 110.87, 122.50, 123.58, 129.23, 139.82, 143.43,

146.68, 148.01; MS *m/e* 203 (M^+, 100); accurate mass calcd for $C_{11}H_9O_3N$ 203.0579, found 203.0549.

(c) 3-(3′,4′,5′-Trimethoxybenzyl)furan (15f) as an oil (111 mg, 75%) was prepared from **2f** (164 mg, 0.2 mmol): ^1H NMR ($CDCl_3$) δ 3.82 (s, 9H, 3 × OCH_3), 3.77 (s, 2H, CH_2), 6.25 (m, 1H), 6.43 (s, 2H), 7.23 (s, 1H), 7.36 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 31.42, 56.15, 60.71, 106.09, 111.17, 124.07, 135.90, 139.61, 143.02, 153.31; MS *m/e* 248 (M^+, 100). Anal. Calcd for $C_{14}H_{16}O_4$, C, 67.73; H, 6.49. Found C, 67.88; H, 6.54.

(d) 3-[*o*-(*p*-Tolyl)phenyl]furan (15g) as colorless needles (94 mg, 70%), mp 54–55 °C, was prepared from **2g** (156 mg, 0.2 mmol): ^1H NMR ($CDCl_3$) δ 2.38 (s, 3H, CH_3), 6.10 (m, 1H), 7.10–7.17 (m, 5H), 7.22–7.25 (m, 1H), 7.30–7.35 (m, 3H), 7.42–7.45 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 21.10, 111.34, 125.78, 127.08, 127.33, 128.79, 129.23, 129.38, 130.68, 131.27, 136.61, 139.08, 140.23, 140.83, 142.15; MS *m/e* 224 (M^+, 100). Anal. Calcd for $C_{17}H_{14}O$: C, 87.14; H, 6.03. Found: C, 87.15; H, 6.01.

General Procedure for Pd-Catalyzed Self-Coupling Reactions of Boroxines. (a) 4,4′-Bis[*p*-(methoxycarbonyl)benzyl]-3,3′-bifuran (4b). A mixture of tris[4-[*p*-(methoxycarbonyl)benzyl]furan-3-yl]boroxine (**2b**) (363 mg, 0.5 mmol), 2,3-bis(bromomethyl)quinoxaline (126 mg, 0.4 mmol), and $Pd(PPh_3)_4$ (46 mg, 0.04 mmol) in methanol–toluene (1:1, 20 mL) was stirred for 5 min. After that 1 M Na_2CO_3 solution (4 mL) was added, the reaction mixture was further stirred and refluxed for 4 h. After addition of water (50 mL) and cooling to room temperature, the mixture was extracted with ether (3 × 30 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated. Purification by silica gel chromatography (40 g, hexanes–ether (5:1)) yielded **4b** (248 mg, 77%), whose physical and spectroscopic data are identical with an authentic sample prepared previously.

(b) 4,4′-Bis(*n*-butyl)-3,3′-bifuran (4d) was prepared from tris[4-(*n*-butyl)furan-3-yl]boroxine (**2d**) (225 mg, 0.5 mmol) and 2,3-bis(bromomethyl)quinoxaline (126 mg, 0.4 mmol) to afford **4d** (147 mg, 80%), whose physical and spectroscopic data are identical with an authentic sample prepared previously.

(c) 4,4′-Bis[*o*-(*p*-tolyl)phenyl]-3,3′-bifuran (4g) was prepared from tris[4-[*o*-(*p*-tolyl)phenyl]furan-3-yl]boroxine (**2g**) (78 mg, 0.1 mmol) and 2,3-bis(bromomethyl)quinoxaline (32 mg, 0.1 mmol) to afford **4g** (36 mg, 52%) and 3-[*o*-(*p*-tolyl)phenyl]furan (15 mg, 21%). **4g**: colorless needles; mp 152–153 °C; ^1H NMR ($CDCl_3$) δ 2.30 (s, 6H, 2 × CH_3), 6.53 (d, 2H, *J* = 1.7 Hz), 6.76 (dd, 2H, *J* = 1.6, 1.7 Hz), 6.85 (dd, 4H, *J* = 2.0, 6.5 Hz), 6.96 (d, 4H, *J* = 7.9 Hz), 7.01 (d, 2H, *J* = 1.6 Hz), 7.11 (m, 2H), 7.25–7.28 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 21.02, 117.05, 125.44, 126.81, 127.60, 128.32, 129.17, 129.99, 130.46, 131.14, 136.02, 138.70, 139.66, 140.46, 141.66; MS *m/e* 466 (M^+, 100). Anal. Calcd for $C_{34}H_{26}O_2$: C, 87.52; H, 5.61. Found: C, 87.51; H, 5.47.

(d) 4,4′-Diphenyl-3,3′-bifuran (4h) was prepared from tris(4-phenylfuran-3-yl)boroxine (**2h**) (255 mg, 0.5 mmol) and 2,3-bis(bromomethyl)quinoxaline (126 mg, 0.4 mmol) to afford **4h** (161 mg, 75%) as colorless prisms: mp 126–127 °C; ^1H NMR ($CDCl_3$) δ 7.03–7.07 (m, 10H), 7.25 (d, 2H, *J* = 1.6 Hz), 7.44 (d, 2H, *J* = 1.8 Hz); ^{13}C NMR ($CDCl_3$) δ 115.82, 126.84, 127.96, 128.17, 132.10, 140.13, 141.49; MS *m/e* 286 (M^+, 100). Anal. Calcd for $C_{20}H_{14}O_2$: C, 83.89; H, 4.93. Found: C, 83.70; H, 5.01.

(e) 4,4‴-Bis(trimethylsilyl)-3,3′:4′,3″:4″,3‴-quaterfuran (27) was prepared from **23** (139 mg, 0.2 mmol) and 2,3-bis(bromomethyl)quinoxaline (47 mg, 0.15 mmol) as a colorless microcrystalline solid (97 mg, 79%), mp 60–61 °C: ^1H NMR ($CDCl_3$) δ 0.03 (s, 18H, 2 × $SiMe_3$), 7.02 (d, 2H, *J* = 1.6 Hz), 7.29 (dd, 4H, *J* = 1.3, 1.6 Hz), 7.36 (d, 2H, *J* = 1.3 Hz); ^{13}C NMR ($CDCl_3$) δ −0.51, 117.34, 117.77, 119.75, 120.46, 139.92, 141.33, 141.79, 148.43; MS *m/e* 410 (M^+, 18). Anal. Calcd for $C_{22}H_{26}O_4Si_2$: C, 64.36; H, 6.38. Found: C, 64.59; H, 6.29.

(f) 4,4‴-Bis(*p*-tolyl)-3,3′:4′,3″:4″,3‴-quaterfuran (28) and 4-(*p*-tolyl)-3,3′-bifuran were prepared from **24** (145 mg, 0.2 mmol) and 2,3-bis(bromomethyl)quinoxaline (47 mg, 0.15 mmol) to afford **28** (67 mg, 50%) and 4-(*p*-tolyl)-3,3′-bifuran (34 mg, 25%). **28**: colorless needles; mp 134–135 °C; ^1H NMR ($CDCl_3$) δ 2.33 (s, 6H, 2 × CH_3), 7.05–7.06 (m, 10H), 7.15–7.16 (m, 4H), 7.47–7.48 (d, 2H, *J* = 1.4 Hz); MS *m/e* 446 (M^+, 41). Anal. Calcd for $C_{30}H_{22}O_4$: C, 80.70; H, 4.97. Found: C, 80.72; H, 4.95. 4-(*p*-Tolyl)-3,3′-bifuran: oil; ^1H NMR ($CDCl_3$) δ 2.37 (s, 3H, CH_3), 6.34 (m, 1H), 7.14 (dd, 3H, *J* = 8.0, 0.6 Hz), 7.24 (d, 2H, *J* = 8.0 Hz), 7.37 (d, 1H, *J* = 1.8 Hz), 7.47 (d, 1H, *J* = 1.6 Hz), 7.54 (d, 1H, *J* = 1.6 Hz); MS *m/e* 224 (M^+, 100). Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39. Found: C, 80.64; H, 5.45.

Pd-Catalyzed Self- and Cross-Coupling Reaction of Boroxines 2a and 2b. A mixture of **2a** (75 mg, 0.15 mmol), **2b** (109 mg, 0.15 mmol), 2,3-bis(bromomethyl)quinoxaline (95 mg, 0.3 mmol), and $Pd(PPh_3)_4$ (35 mg, 0.03 mmol) in methanol–toluene (1:1, 50 mL) was stirred for 5 min. After that 1 M Na_2CO_3 solution (3 mL) was added, and the reaction mixture was further stirred and refluxed for 4 h. After addition of water (50 mL) and cooling to room temperature, the mixture was extracted with ether (3 × 30 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated. Purification by silica gel chromatography (50 g, hexanes–ether (7:1)) yielded **4a** (22 mg, 0.08 mol), **4b** (34 mg, 0.08 mmol), and **16** (32 mg, 0.09 mmol).

General Procedure for Pd-Catalyzed Cross-Coupling Reaction. (a) 4,4′-Bis(trimethylsilyl)-3,3′-bifuran (4a). A mixture of tris[4-(trimethylsilyl)furan-3-yl]boroxine (**2a**) (249 mg, 0.5 mmol), 3-iodo-4-(trimethylsilyl)furan (**17**) (400 mg, 1.5 mmol), and $Pd(PPh_3)_4$ (86 mg, 0.075 mmol) in methanol–toluene (1:1, 20 mL) was stirred for 5 min, after which time 1 M Na_2CO_3 solution (4 mL) was added. The reaction mixture was further stirred and refluxed for 4 h. After addition of water (50 mL) and cooling to room temperature, the mixture was extracted with ether (3 × 30 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated. Purification by chromatography on silica gel (40 g, hexanes) yielded **4a** (371 mg, 89%), whose physical and spectroscopic data are identical with an authentic sample prepared previously.

(b) 4-(Trimethylsilyl)-4′-[*p*-(methoxycarbonyl)benzyl]-3,3′-bifuran (16) was prepared from tris[4-(trimethylsilyl)furan-3-yl]boroxine (**2a**) (100 mg, 0.2 mmol) and 3-iodo-4-[*p*-(methoxycarbonyl)benzyl]furan (**18**) (205 mg, 0.6 mmol) to afford **16** (168 mg, 79%) as an oil: ^1H NMR ($CDCl_3$) δ 0.17 (s, 9H, $SiMe_3$), 3.76 (s, 2H, CH_2), 3.94 (s, 3H, CH_3), 7.21–7.24 (m, 4H), 7.37 (d, 1H, *J* = 1.3 Hz), 7.45 (d, 1H, *J* = 1.4 Hz), 7.98 (d, 2H, *J* = 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ −0.49, 30.07, 51.75, 111.03, 118.63, 118.97, 120.07, 123.96, 128.28, 128.53, 129.64, 140.43, 141.43, 141.51, 145.42, 148.26, 166.84; MS *m/e* 354 (M^+, 65). Anal. Calcd for $C_{20}H_{22}O_4Si$: C, 67.77; H, 6.26. Found: C, 67.72; H, 6.62.

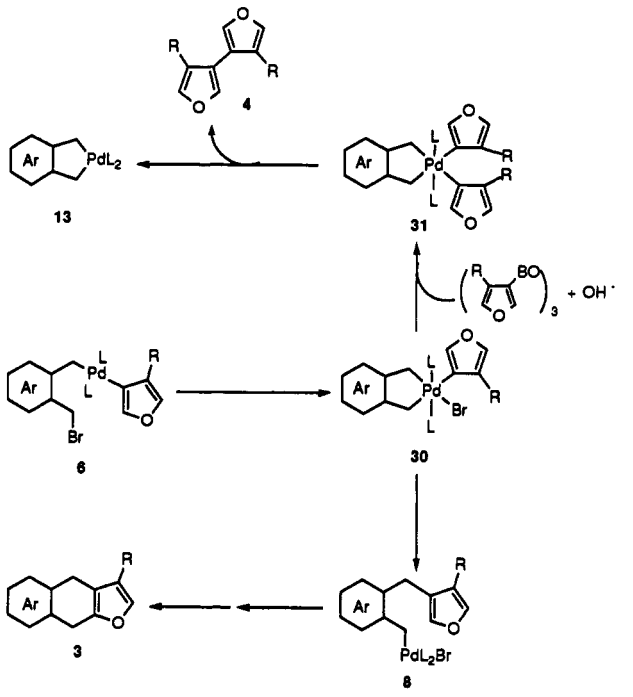
(c) 4-(Trimethylsilyl)-4′-(*p*-nitrobenzyl)-3,3′-bifuran (20) was prepared from tris[4-(trimethylsilyl)furan-3-yl]boroxine (**2a**) (100 mg, 0.2 mmol) and 3-iodo-4-(*p*-nitrobenzyl)furan (**17**) (197 mg, 0.6 mmol) to afford **20** (143 mg, 70%) as a pale yellow wax: ^1H NMR ($CDCl_3$) δ 0.11 (s, 9H, $SiMe_3$), 3.77 (s, 2H, CH_2), 7.19 (d, 1H, *J* = 1.5 Hz), 7.23–7.26 (m, 3H), 7.32 (d, 1H, *J* = 1.5 Hz), 7.40 (d, 1H, *J* = 1.6 Hz), 8.10 (d, 2H, *J* = 8.8 Hz); ^{13}C NMR ($CDCl_3$) δ −0.46, 29.98, 109.72, 118.55, 118.87, 120.13, 123.31, 123.58, 129.34, 140.37, 140.50, 141.46, 141.74, 147.75, 148.46; MS *m/e* 341 (M^+, 100); accurate mass calcd for $C_{18}H_{19}O_4NSi$ 341.1083, found 341.1075.

(d) 4-(Trimethylsilyl)-4′-(*p*-tolyl)-3,3′-bifuran (21) was prepared from tris[4-(*p*-tolyl)furan-3-yl]boroxine (**2c**) (234 mg, 0.3 mmol) and 4-iodo-3-(trimethylsilyl)furan (**17**) (240 mg, 0.9 mmol) to afford **21** (213 mg, 80%) as an oil: ^1H NMR ($CDCl_3$) δ 0.24 (s, 9H, $SiMe_3$), 2.55 (s, 3H, CH_3), 7.31 (d, 2H, *J* = 8.1 Hz), 7.39 (d, 2H, *J* = 8.3 Hz), 7.58 (d, 1H, *J* = 1.5 Hz), 7.59 (d, 1H, *J* = 1.5 Hz), 7.64 (d, 1H, *J* = 1.8 Hz), 7.84 (d, 1H, *J* = 1.7 Hz); ^{13}C NMR ($CDCl_3$) δ −0.59, 21.02, 117.45, 119.75, 120.34, 126.94, 127.63, 129.11, 129.31, 136.58, 139.53, 141.80, 141.91, 148.43; MS *m/e* 296 (M^+, 75). Anal. Calcd for $C_{18}H_{20}O_2Si$: C, 72.93; H, 6.80. Found: C, 73.44; H, 6.67.

(e) 4-(Trimethylsilyl)-4′-(*n*-butyl)-3,3′-bifuran (22) was prepared from tris[4-(*n*-butyl)furan-3-yl]boroxine (**2d**) (135 mg, 0.3 mmol) and 4-iodo-3-(trimethylsilyl)furan (**17**) (160 mg, 0.6 mmol) to afford **22** (141 mg, 90%) as an oil: ^1H NMR ($CDCl_3$) δ 0.11 (s, 9H, $SiMe_3$), 0.85 (t, 3H, *J* = 7.2 Hz), 1.29 (m, 2H), 1.41 (m, 2H), 2.28 (t, 2H, *J* = 7.2 Hz), 7.21 (d, 1H, *J* = 1.3 Hz), 7.31 (d, 1H, *J* = 1.6 Hz), 7.33 (d, 1H, *J* = 1.5 Hz), 7.41 (d, 1H, *J* = 1.4 Hz); ^{13}C NMR ($CDCl_3$) δ −0.40, 13.76, 22.42, 23.48, 31.62, 118.67, 119.73, 120.26, 125.79, 139.17, 140.94, 141.31, 148.22; MS *m/e* 262 (M^+, 66). Anal. Calcd for $C_{15}H_{22}O_2Si$: C, 68.65; H, 8.45. Found: C, 69.00; H, 8.35.

(f) 4,4″-Bis(trimethylsilyl)-3,3′:4′,3″-terfuran (25) was prepared from **23** (160 mg, 0.2 mmol) and 4-iodo-3-(trimethylsilyl)furan (**17**) (140 mg, 0.6 mmol) to afford **25** (188 mg, 91%) as colorless microcrystalline solids, mp 68–68.5 °C: ^1H NMR ($CDCl_3$) δ 0.12 (s, 18H, 2 × $SiMe_3$), 7.22 (d, 2H, *J* = 1.3 Hz), 7.31

Scheme 7



(d, 2H, J = 1.2 Hz), 7.47 (d, 2H, J = 0.5 Hz); ^{13}C NMR ($CDCl_3$) δ −0.40, 118.76, 119.34, 119.72, 140.85, 141.61, 148.52; MS m/e 344 (M^+, 26). Anal. Calcd for $C_{18}H_{24}O_3Si_2$: C, 62.75; H, 7.02. Found: C, 62.86; H, 7.10.

(g) 4-(Trimethylsilyl)-4″-(*p*-nitrobenzyl)-3,3′:4′,3″-terfuran (26) was prepared from **23** (140 mg, 0.2 mmol) and 3-iodo-4-(*p*-nitrobenzyl)furan (**19**) (197 mg, 0.6 mmol) to afford **26** (151 mg, 62%) as a pale yellow wax: ^{1}H NMR ($CDCl_3$) δ 0.03 (s, 9H, $SiMe_3$), 3.77 (s, 2H), 7.08 (d, 1H, J = 1.0 Hz), 7.15 (d, 1H, J = 1.5 Hz), 7.23–7.28 (m, 3H), 7.33 (d, 1H, J = 1.5 Hz), 7.36 (d, 1H, J = 0.4 Hz), 7.39 (d, 1H, J = 1.3 Hz), 8.09 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ −0.57, 30.28, 110.91, 116.68, 117.96, 119.49, 122.13, 123.65, 129.23, 139.82, 141.11, 141.28, 141.44, 141.58, 143.51, 147.31, 148.64; MS m/e 407 (M^+, 53). Anal. Calcd for $C_{22}H_{21}O_5NSi$: C, 64.85; H, 5.19; N, 3.44. Found: C, 64.90; H, 5.04; N, 3.68.

4,4‴″″-Bis(Trimethylsilyl)-3,3′:4′,3″:4″,3‴:4‴,3⁗:4⁗,3⁗′:4⁗′,3⁗″:4⁗″,3⁗‴:4⁗‴,3⁗⁗′-octifuran (29). To a solution of **27** (82 mg, 0.2 mmol) in CH_2Cl_2 (20 mL) was added a solution of BCl_3 (1.0 M) in CH_2Cl_2 (0.3 mL) under a nitrogen atmosphere at −78 °C. After 50 h, the reaction was quenched with 2 M Na_2CO_3 solution (3 mL), and the mixture was extracted with ether (3 × 30 mL). The organic layer was dried ($MgSO_4$), and the solvent was evaporated. The crude product was chromatographed on silica gel (30 g, hexanes–ether (1:1)) to give the corresponding boroxine intermediate, which was reacted under self-coupling condition as stated above to afford **29** (13 mg, 20%) as a wax: ^{1}H NMR ($CDCl_3$) δ 0.03 (s, 9H, $SiMe_3$), 0.08 (s, 9H, $SiMe_3$), 7.07 (d, 1H, J = 1.8 Hz), 7.08 (d, 1H, J = 1.8 Hz), 7.14 (d, 1H, J = 1.7 Hz), 7.17 (d, 1H, J = 1.7 Hz), 7.19 (d, 1H, J = 1.9 Hz), 7.20 (d, 1H, J = 1.5 Hz), 7.21 (d, 1H, J = 1.5 Hz), 7.26 (d, 1H, J = 1.5 Hz), 7.27 (d, 1H, J = 1.5 Hz), 7.28 (d, 1H, J = 1.3 Hz), 7.31 (d, 1H, J = 1.7 Hz), 7.35 (d, 1H, J = 1.5 Hz), 7.36 (d, 1H, J = 1.7 Hz), 7.38 (d, 1H, J = 1.8 Hz), 7.44 (d, 1H, J = 1.5 Hz), 7.45 (d, 1H, J = 1.7 Hz); ^{13}C NMR ($CDCl_3$) δ −0.54, −0.46, 110.48, 115.76, 116.00, 117.02, 117.36, 117.52, 119.60, 120.21, 139.42, 139.91, 140.54, 140.82, 141.19, 141.37, 141.64, 141.73, 142.98, 148.51; MS (CI) m/e 675 (M^+ + 1, 2). Anal. Calcd for $C_{38}H_{34}O_8Si_2$: C, 67.64; H, 5.08. Found: C, 67.75; H, 4.68.

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Note Added in Proof. Since Pd(0) was only used in a catalytic amount, it is therefore highly likely that the complex **6** would only undergo an intramolecular oxidative addition to provide a Pd(IV) species **30**[14] as shown in Scheme 7. It is possible that the quinoxaline molecules also function as ligands. The Pd(IV) complex **30** might then either go through a reductive elimination step to proceed eventually to the dihydrobenzo[*b*]furan **3** or go through, to the best of our knowledge, an unprecedented transmetalation step to complex **31**. Reductive elimination of **31** would therefore afford the bifuran **4** and the palladacyclopentene **13**, which would regenerate the Pd(0) species. We wish to thank Dr. Gerald Dyker, Institut für Organische Chemie, Universität Braunschweig, Germany, for helpful suggestions.

Supplementary Material Available: ^{1}H and ^{13}C NMR spectra (40 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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