Organic &
Biomolecular
Chemistry

Cite this: *Org. Biomol. Chem.*, 2011, **9**, 370

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Site-selective Suzuki–Miyaura cross-coupling reactions of 2,3,4,5-tetrabromofuran†

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Received 8th September 2010, Accepted 22nd October 2010
DOI: 10.1039/c0ob00695e

Suzuki–Miyaura reactions of 2,3,4,5-tetrabromofuran allow a convenient and site-selective synthesis of mono-, di- and tetraarylfurans which are not readily available by other methods.

Substituted furans correspond to one of the most important classes of five-membered heterocycles and have great significance in medicinal, agricultural and material chemistry. In addition, they are widely found in natural products which include, for example, the cembranolides lophotoxin, kallolides, pukalide, the cytotoxic glanvillic acids A and B, the Plakorsins A–C, rosefuran and several other prominent molecules.[1–3] Substituted furans constitute an omnipresent molecular entity of several classes of biologically active compounds and are present in commercially important pharmaceuticals, flavor and fragrance additives (insect and fish antifeedants).[1c,4] In addition, furans are key synthetic intermediates which have been widely used in the synthesis of various cyclic and acyclic target molecules.[4] The development of new synthetic approaches to polysubstituted furans thus represents an important area of research in organic chemistry.[5–8]

Two main strategies for the synthesis of substituted furans can be distinguished: a) the functionalization of existing furan derivatives and b) the assembly of the furan system by means of cyclization reactions of acyclic precursors.[9] Classic examples of the first strategy mainly rely on electrophilic substitution reactions. A variety of classic furan syntheses are based on cyclocondensation reactions (*e.g.*, the Feist–Benary reaction or other methods). An attractive approach to mono- and disubstituted furans relies on transition metal-catalyzed cycloisomerization reactions of unsaturated acyclic precursors, such as allenyl ketones, alkynyl ketones, or epoxides.[5] In this context, the work of Marshall and coworkers and of Hashmi and coworkers have demonstrated great utility. Recently, tetra-substituted furans have been prepared from alkynes by a tandem process of palladium-catalyzed oxidation and Lewis acid-catalyzed cyclization.[4,10] Nakano and co-workers have reported the synthesis of tetra-substituted furans by palladium-catalyzed reactions of 3-furancarboxylic acids.[10a] Müller and coworkers reported a versatile approach to highly functionalized furans by domino Sonogashira coupling/cyclocondensation reactions and related transformations.[11] The tendency of furans to readily undergo lithiation and electrophilic reactions at positions C-2 or C-5 and to undergo acid-mediated decomposition makes the selective synthesis of highly substituted furans a rather demanding task. Although many strategies are known, they are often not applicable to the selective synthesis of highly substituted furans.

The low stability of furans, in particular under aerobic and acidic conditions, makes their cross-coupling reactions more fragile and the product isolation more difficult than in the thiophene series. Palladium(0)-catalysed cross-coupling reactions of 2,3-dibromofuran and substituted derivatives have been previously studied. In this context, Negishi, Stille, Suzuki and Sonogashira coupling reactions and nucleophilic aromatic substitution reactions have been reported.[12] These reactions proceed with excellent site-selectivity in favour of carbon atoms C-2 and C-5. Bellina, Sulikowski and Rossi and their coworkers reported site-selective transition metal-catalyzed reactions of several dibromofuranones.[13]

2,3,4,5-Tetrabromofuran represents an interesting substrate for transition metal-catalyzed cross-coupling reactions as all four carbon atoms are halogenated. To the best of our knowledge, palladium(0)-catalysed cross-coupling reactions of 2,3,4,5-tetrabromofuran have not been reported to date. Recently, we have reported Suzuki-Miyaura reactions of tetrabromothiophene and -selenophene.[14] Herein, we report our preliminary results related to Suzuki–Miyaura reactions of 2,3,4,5-tetrabromofuran. These reactions provide a convenient and site-selective approach to a variety of aryl-substituted furans which are not readily available by other methods. Due to the unstable nature of furans compared to thiophenes, the reactions of 2,3,4,5-tetrabromofuran reported herein are much more prone to side-reactions and need much more optimization than the corresponding reactions of 2,3,4,5-tetrabromothiophene.

2,3,4,5-Tetrabromofuran (**1**) was prepared following a literature procedure.[15] It must be prepared in highly pure, crystalline form and should be stored at –20 °C since slightly impure or oily material is considerably less stable. The reaction of **1** with arylboronic acids **2a–j** (4.4 equiv.) afforded the stable 2,3,4,5-tetraarylfurans **3a–j** (Scheme 1, Table 1). The products were isolated in good to excellent yields for both electron-rich and electron-poor arylboronic acids. The reaction conditions were systematically optimized for derivatives **3c**, **3f**, and **3i** which are

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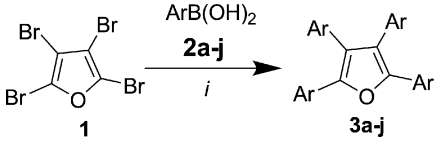
† Electronic supplementary information (ESI) available: Supplementary information. See DOI: 10.1039/c0ob00695e

Table 1 Synthesis of tetraarylfurans **3a–j**

2,3	Ar	% (**3**)[a]
a	C_6H_5	92
b	4-MeC_6H_4	90
c	4-EtC_6H_4	92
d	4-*t*BuC_6H_4	92
e	3-ClC_6H_4	80
f	4-FC_6H_4	85
g	4-$(CF_3)C_6H_4$	89
h	3-$(CF_3)C_6H_4$	82
i	4-$(MeO)C_6H_4$	98
j	3,5-$Me_2C_6H_3$	76

[a] Yields of isolated products.



Scheme 1 Synthesis of **3a–j**. *Conditions*: *i*, **2a–j** (4.4 equiv.), $Pd(PPh_3)_4$ (3 mol-%), aq. K_2CO_3 (2 M), dioxane, 80 °C, 5 h.

derived from arylboronic acids containing electron-donating and electron-withdrawing substituents (Table 2).

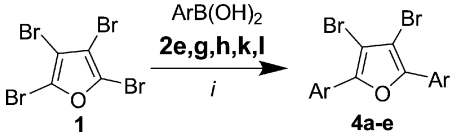
The best yields were obtained when $Pd(PPh_3)_4$ or $Pd(PPh_3)_2Cl_2$ (3 mol-%) were used as the catalyst (dioxane, 80 °C, 5 h) (entries 1–4, Table 2). Excellent yields were obtained when an aqueous solution of K_2CO_3 (2 M) or when K_3PO_4 were employed as the base. The yields dropped when $Pd(OAc)_2$ (3 mol-%) in the presence of XPhos or $(Cy)_3P$ were employed (entries 5–7, Table 2). In conclusion, the application of the reaction conditions given in entry 3 of Table 2 allowed to prepare the products in excellent yields. It was also noted that electron-poor arylboronic acids provided slightly lower yields than electron-rich arylboronic acids. This can be explained by the lower nucleophilicity of electron-poor boronic acids.

The Suzuki–Miyaura reaction of **1** with arylboronic acids **2e, g, h, k–m** (2.0 equiv.), in the presence of $Pd(PPh_3)_4$, gave the 2,5-diaryl-3,4-dibromofurans **4a–e** (Scheme 2, Table 3). During the synthesis of inhibitors of B-Raf kinase, Andrew and co-workers studied site-selective Suzuki–Miyaura reactions of 2,3-dibromofuran. These reactions, which were carried out in a $DME/H_2O/K_2CO_3$ system, proceeded in rather low yields.[10a] The application of these conditions to Suzuki reactions of **1** proved to be unsuccessful. Therefore we decided to optimize the reaction conditions methodically for different solvent systems,

Table 3 Synthesis of 2,5-diaryl-4,5-dibromofurans **4a–e**

2	4	Ar	% (**4**)[a]
e	**a**	3-ClC_6H_4	87
g	**b**	4-$(CF_3)C_6H_4$	91
h	**c**	3-$(CF_3)C_6H_4$	85
k	**d**	4-$(MeO)C_6H_4$	89
l	**e**	4-ClC_6H_4	88
m	**f**	2-Naphthyl	0[b]

[a] Yields of isolated products. [b] Decomposition.



Scheme 2 Synthesis of **4a–e**. *Conditions*: *i*, **2e, g, h, k, l** (2.0 equiv.), $Pd(PPh_3)_4$ (2 mol%), aq. K_2CO_3 (2 M), toluene/dioxane (4 : 1), 80 °C, 3 h.

reaction times and catalyst systems. Arylboronic acids **2e, g, h, k, m** were selected for the optimization studies based on their electron-withdrawing and -donating nature and steric effects. During the optimization, we have found that the temperature did not have an important influence on the yield of **4** and on the regioselectivity provided that exactly 2.0 equiv. of the boronic acids were used. Using dioxane as the solvent, $Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$ and $Pd(OAc)_2$, in the presence of Cy_3P or XPhos, were studied as the catalysts in the reactions of **1** with boronic acids **2e, g, h, k**. All these reactions resulted in the formation of complex mixtures of mono-, di-, tri- and tetraarylfurans. In case of **2m**, a reduced product formed by loss of a bromine atom was formed. The use of different bases (2 M aqueous solution of K_2CO_3 or the use of K_3PO_4 or Cs_2CO_3 in organic solvents) and a decrease of the reaction temperature did not allow to solve the problems related to the site-selectivity. The reaction suffered from low conversions when the solvents toluene and DME were used. The employment of THF as the solvent, using $Pd(PPh_3)_4$ and 2 M K_2CO_3, resulted in the formation of complex mixtures for different reaction times (3–8 h) and temperatures (60–80 °C).

While the use of a single solvent was unsuccessful for the regioselective synthesis of 2,5-diaryl-3,4-dibromofurans **4a–e**, the use of solvent mixtures allowed to address the problem. We selected dioxane/toluene as a solvent system to control the solubility of the boronic acids. $Pd(PPh_3)_4$ and 2 M K_2CO_3 were again used as the catalyst and base, respectively. While the use of a 4 : 1 dioxane/toluene mixture again provided mixtures of products, the use of a 3 : 2 and 1 : 1 dioxane/toluene mixture

Table 2 Optimization of the synthesis of tetraarylfurans

Entry	Conditions	% (**3c**)[a]	% (**3f**)[a]	% (**3i**)[a]
1	$Pd(PPh_3)_2Cl_2$ (3 mol-%), aq. K_2CO_3 (2 M)	90	82	96
2	$Pd(PPh_3)_2Cl_2$ (3 mol-%), K_3PO_4	85	75	88
3	**$Pd(PPh_3)_4$ (3 mol-%), aq. K_2CO_3 (2 M)**	**92**	**85**	**98**
4	$Pd(PPh_3)_4$ (3 mol-%), K_3PO_4	88	78	92
5	$Pd(OAc)_2$ (3 mol-%), XPhos (6 mol-%), aq. K_2CO_3 (2 M)	10	5	15
6	$Pd(OAc)_2$ (3 mol-%), $(Cy)_3P$ (6 mol-%), aq. K_2CO_3 (2 M)	65	45	69
7	$Pd(OAc)_2$ (3 mol-%), $(Cy)_3P$ (6 mol-%), K_3PO_4	50	43	55

[a] Yields of isolated products; all reactions were carried out in dioxane (80 °C, 5 h).

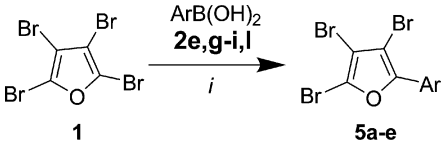
Table 4 Synthesis of 2-aryl-3,4,5-tribromofurans **5a–e**

2	**5**	Ar	% (**5**)[a]
e	**a**	3-ClC_6H_4	87
g	**b**	4-$(CF_3)C_6H_4$	91
h	**c**	3-$(CF_3)C_6H_4$	85
i	**d**	4-$(MeO)C_6H_4$	89
l	**e**	4-ClC_6H_4	88

[a] Yields of isolated products.

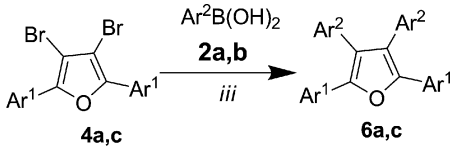
showed better results for boronic acids **2g, h, k**. In fact, the desired products **4** were formed as the major products among a complex mixture of other products. Gratifyingly, the employment of a 1 : 4 dioxane/toluene mixture afforded exclusively 2,5-biaryl-3,4-dibromofurans **4a–d** which could be isolated in excellent yields (85–91%). It is worth to note that the use of a 1 : 4 dioxane/toluene mixture of solvents allowed excellent site-selectivities to be obtained even when the reactions were carried out at reflux (110 °C).

The Suzuki–Miyaura reaction of **1** with arylboronic acids **2e, g–i, l** (1.0 equiv.) afforded the 2-aryl-3,4,5-tribromofurans **5a–e** (Scheme 3, Table 4). The stoichiometry (employment of exactly 1.0 equiv. of the arylboronic acid) played an important role. The best yields (85–91%) were obtained when the conditions developed for the synthesis of products **4a–e** were employed (*vide supra*), *i.e.* the use of $Pd(PPh_3)_4$ (2 mol%) as the catalyst, the use of an aqueous solution of K_2CO_3 (2 M) as the base, and the use of a 4 : 1 mixture of toluene and dioxane.



Scheme 3 Synthesis of **5a–e**. *Conditions*: *i*, **2e, g–i, l** (1.0 equiv.), $Pd(PPh_3)_4$ (2 mol%), aq. K_2CO_3 (2 M), toluene/dioxane (4 : 1), 80 °C, 3 h.

The unsymmetrical tetraarylfurans **6a, c** were synthesized by Suzuki reactions of 2,5-diaryl-3,4-dibromofurans **4a, c** with **2a, b** (Scheme 4, Table 5). During the synthesis of **6a, c**, no issue of site-selectivity had to be addressed. Hence, the reactions could be successfully carried out in dioxane and the use of a toluene/dioxane mixture was not necessary.



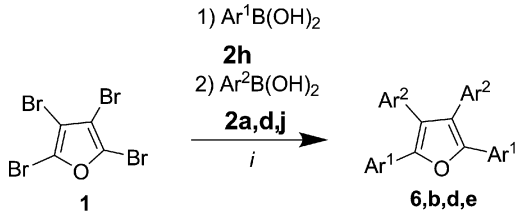
Scheme 4 Synthesis of **6a, c**. *Conditions*: *i*, **2a, b** (2.0 equiv.), $Pd(PPh_3)_4$ (2 mol%), aq. K_2CO_3 (2 M), dioxane (4 : 1), 80 °C, 3 h.

A one-pot strategy to accomplish the synthesis of the unsymmetrical tetraarylfurans **6b, d, e** was also studied. The Suzuki–Miyaura reaction of **1** with arylboronic acid **2h** (2.0 equiv.) in toluene/dioxane (4 : 1), separation of the solution in three equal portions and subsequent addition of arylboronic acids **2a**, **2d** or **2j** afforded products **6b**, **6d** and **6e** in high yields, respectively (Scheme 5, Table 5).

Table 5 Synthesis of unsymmetrical tetraaryfurans **6a–e**

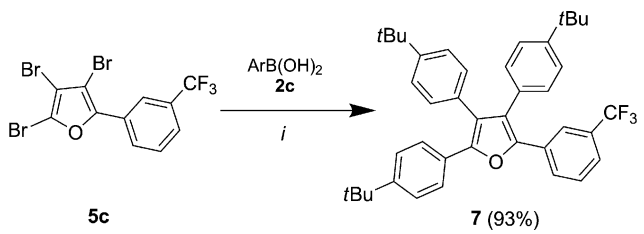
6	Ar^1	Ar^2	% (**6**)[a]
a	3-ClC_6H_4	C_6H_5	88
b	3-$(CF_3)C_6H_4$	C_6H_5	86[b]
c	3-$(CF_3)C_6H_4$	4-MeC_6H_4	93
d	3-$(CF_3)C_6H_4$	4-*t*BuC_6H_4	93[b]
e	3-$(CF_3)C_6H_4$	3,5-$Me_2C_6H_3$	88[b]

[a] Yields of isolated products. [b] Prepared by a one-pot procedure from **1**.



Scheme 5 Synthesis of **6b, d–e**. *Conditions*: *i*, boronic acid **2h** (2.0 equiv.), $Pd(PPh_3)_4$ (3 mol%), aq. K_2CO_3 (2 M), toluene/dioxane (4 : 1), 80 °C, 3 h, *ii*, boronic acid **2a, d, j** (2.2 equiv.), 80 °C, 3 h.

The unsymmetrical tetraarylfuran **7** was prepared by Suzuki–Miyaura reaction of 2-aryl-3,4,5-tribromofuran **5c** with 4-*tert*-butylarylboronic acid (**2d**) in dioxane at 80 °C for 5 h (Scheme 6).



Scheme 6 Synthesis of **7**. *Conditions*: *i*, **2c** (3.3 equiv.), $Pd(PPh_3)_4$ (2 mol%), aq. K_2CO_3 (2 M), dioxane 80 °C, 5 h.

The structures of all products of this report were established by 2D NMR techniques (NOESY, HMBC) or by X-ray crystal structure analyses.

In conclusion, we have studied the synthesis of mono-, di- and tetraarylfurans by the first Suzuki–Miyaura reactions of 2,3,4,5-tetrabromofuran. The use of a binary solvent system toluene-dioxane played an important role during the optimization of the site-selectivity of the reactions. The products reported are not readily accessible by other methods. All reactions proceed with excellent site-selectivity in favour of position 2 and 5 which are more electron-deficient than positions 3 and 4 and, thus, more rapidly undergo an oxidative addition with the palladium(0) catalyst.

Acknowledgements

Financial support by the State of Vietnam (MOET scholarship for N. T. H.), by the DAAD (scholarship for R. A. K.), by the State of Mecklenburg–Vorpommern (scholarship for M. H.) and by the Higher Education Commission of Pakistan (scholarship for M. H.) is gratefully acknowledged.

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