

# A Sequential Suzuki Coupling Approach to Unsymmetrical Aryl s-Triazines from Cyanuric Chloride

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**Abstract:** A practical approach has been developed for efficient synthesis of unsymmetrical aryl *s*triazines via highly selective sequential Suzuki coupling of cyanuric chloride (2,4,6-trichlorotriazine) with aryl or vinyl boronic or diarylborinic acids catalysed by 0.1–0.5 mol% Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> under mild conditions. The second and third Suzuki couplings for unsymmetrically trisubstituted aryl *s*triazines could be more practically conducted in one-pot procedure. An electron-withdrawing conjugate group at phenyl ring of arylboronic acids was unexpectedly found to completely block the coupling while steric hindrance from an ortho electrondonating substituent could be overcome.

**Keywords:** Boron; Cross-coupling; Heterocycles; Palladium; Triazines

Aryl s-triazine moieties have been increasingly found in advanced materials,<sup>[1]</sup> in particular thermally activated delayed fluorescence emitters,<sup>[2]</sup> broad-band UV absorbers,<sup>[3]</sup> biologically active reagents<sup>[4]</sup> and framedirecting ligands in coordination chemistry.<sup>[5]</sup> Friedel-Crafts type arylation and nucleophilic substitution of aryl organometallics on cyanuric chloride (2,4,6trichlorotriazine) represent the most practical and straightforward way to aryl s-triazines. Unfortunately, the Friedel-Crafts type approach has intrinsic problems in over-arylation, regioselectivity, substrate scope and pollution associated with disposal of AlCl<sub>3</sub> while the organometallic substitution is hampered by poor functional group compatibility, low efficiency in triarylation and moisture-free conditions. Suzuki coupling, which has advantages of good functional group

compatibility, operational simplicity and environmental protection, has promised an effective alternative to the traditional approaches but has shown low efficiency in coupling of cyanuric chloride<sup>[6]</sup> because of its AcCl-like property and subsequent over-arylation via the preferred intramolecular activation.<sup>[7]</sup>

In the last decade, Suzuki coupling of conventionally difficult substrates, e.g. site-selective coupling of polyhaloheteroaromatics<sup>[8]</sup> and acylative coupling of low-compatibility acid chlorides,<sup>[9]</sup> has advanced greatly. In particular, Houk et al. has elegantly elucidated the origin of the site-selectivity.<sup>[10]</sup> Handy and Dodd et al. have developed one-pot procedures based on predicting the reactivity of C-X bonds of polyhaloheteroaromatics in coupling reaction.<sup>[11]</sup> Langer et al. has effected highly site-selective Suzuki coupling of various sorts of polyhalogenated heteroarenes through carefully optimizing reaction parameters, i.e. catalyst, base, solvent, and substrate ratio.<sup>[8f,12]</sup> Given these achievements and the fact that reactivity of C-Cl bonds subsequently decreases from cyanuric chloride (the parent trichloro-s-triazine) to monochlorotriazines, we anticipate a general and effective synthesis of unsymmetrical aryl s-triazines from cyanuric chloride via Suzuki coupling should be possible provided a proper procedure could be developed. Herein, we report a highly selective sequential Suzuki coupling of cyanuric chloride with aryl or vinyl boronic or diarylborinic acids for efficient synthesis of unsymmetrical aryl s-triazines under mild conditions.

Considering the AcCl-like reactivity of cyanuric chloride, an anhydrous condition similar to acylative Suzuki coupling,  $Pd(PPh_3)_2Cl_2$  as catalyst in the presence of  $K_2CO_3$  in toluene at 60°C, was adopted at first for its coupling with *p*-tolylboronic acid (**1a**) or bis(*p*-tolyl)acid (**2a**) which, we have recently shown,<sup>[13]</sup>

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could be used as a cost-effective aryl source in Suzuki coupling since both of aryl groups could be effectively used (Table 1). However, the desired monoaryl dichloro *s*-triazine **3a** was obtained in just 19% yield using equivalent **1a** due to di/tricoupling. The yields of **3a** could be increased to 49–52% when excess (1.5–2.0 equiv.) cyanuric chloride was used. Although solvent and catalyst screening failed to improve the reaction, good yields could be obtained by increasing catalyst (0.5–1 mol%) (Table 1, entries 13–15) and base loadings (4-6 equiv.  $K_2CO_3$ ). Bis(*p*-tolyl)acid (**2a**) was found to react similarly under the identical conditions, although these kinds of compounds usually need different conditions in cross-coupling reactions (Table 1, entry 16).

**Table 1.** Optimization on Suzuki coupling of cyanuric chloride with 1a/2a for aryl dichloro *s*-triazine 3a.<sup>[a]</sup>

	<sup>N</sup> + ( <i>p</i> -Tolyl) <sub>n</sub> B(OH) <sub>3</sub> . n = 1, <b>1a</b> Cl n = 2, <b>2a</b>	n N <sub>2,</sub>	at. "Pd" Base N 60ºC, 6h CI	N N Tol-p <b>3a</b>
Entry	Cat.(mol%)	Sol.	Base(equiv.)	Yield <sup>[b]</sup>
1 <sup>[c]</sup>	$Pd(PPh_3)_2Cl_2(0.3)$	Tol	$K_2CO_3(2)$	19
2	$Pd(PPh_3)_2Cl_2(0.3)$	Tol	$K_2CO_3(2)$	52
3 <sup>[d]</sup>	$Pd(PPh_3)_2Cl_2(0.3)$	Tol	$K_2CO_3(2)$	49
4	$Pd(PPh_3)_2Cl_2(0.3)$	Tol	$K_3PO_4(2)$	45
5	$Pd(PPh_3)_2Cl_2(0.3)$	EA	$K_2CO_3(2)$	19
6	$Pd(PPh_3)_2Cl_2(0.3)$	THF	$K_2CO_3(2)$	16
7	$Pd(dppm)_2(0.3)$	Tol	$K_2CO_3(2)$	22
8	$Pd(dppp)_2(0.3)$	Tol	$K_2CO_3(2)$	33
9	$Pd(dppf)_2(0.3)$	Tol	$K_2CO_3(2)$	39
10	$Pd(Cy)_2Cl_2(0.3)$	Tol	$K_2CO_3(2)$	7
11	$Pd(PPh_3)_2Cl_2(0.3)$	Tol	$K_2CO_3(4)$	69
12	$Pd(PPh_3)_2Cl_2(0.3)$	Tol	$K_2CO_3(6)$	67
13	$Pd(PPh_3)_2Cl_2(0.5)$	Tol	$K_2CO_3(4)$	84
14	$Pd(PPh_3)_2Cl_2(0.5)$	Tol	$K_2CO_3(4)$	81 <sup>[e]</sup>
15	$Pd(PPh_3)_2Cl_2(1)$	Tol	$K_2CO_3(4)$	85
16 <sup>[f]</sup>	$Pd(PPh_3)_2Cl_2(0.5)$	Tol	$K_2CO_3(4)$	80

<sup>[a]</sup> Reaction run at 1mmole scale (1a) with 1.5 equiv. cyanuric chloride at  $60 \degree C$  under N<sub>2</sub> for 12 h.

<sup>[b]</sup> Isolated yield (%).

<sup>[c]</sup> 1.0 equiv. cyanuric chloride used.

<sup>[d]</sup> 2.0 equiv. cyanuric chloride.

<sup>[e]</sup> At 100 °C.

<sup>[f]</sup> 0.5 mmole **2a** used.

Dichloro s-triazines are versatile intermediates for a variety of aryl s-triazine derivatives. Therefore, the scope and limitation of palladium-catalysed monocoupling of cyanuric chloride with aryl, vinyl and heterocyclic boronic acids, in particular diarylborinic acids, were explored (Scheme 1). Influence of an electrondonating (*m*-Me, **1b/2b**; *m*-MeO, **1i/2i**; *p*-MeO, **1j/2j**) or neutral group (H, **1e/2e**), or halo group (*p*-Cl, **1f/2f**)

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and p-F, 1g/2g) at meta- or para- positions of benzene ring in arylboronic or diarylborinic acids appeared to be negligible while an ortho-substituent (o-Me, 1c/2c; o-Et, 1d/2d; or o-MeO, 1h/2h) slightly decreased the yields of aryl dichloro-s-triazines 3. When arylboronic acids bearing an electron-withdrawing conjugate group, e.g. acetyl (-Ac), nitrile (-CN) or methoxycarbonyl (–CO<sub>2</sub>Me) regardless of positions were used no desired cross-coupling was observed. Instead, arylboronic acids were recovered, implying that transmetalation of aryl group from boron to palladium(II) would be the rate-determining step in the catalytic cycle (vide infra). Three representative vinyl boronic acids, e.g. 1-pentenylboronic acid (1k), 1-cyclohexenylboronic acid (11) and trans-(2-phenylethenyl)acid (1m), reacted similarly to electron-rich aryl boronic acids while heterocyclic boronic acids (2- or 3-furanylboronic acids (1n, 1o) and 3-pyridylboronic acid (1p)) completely failed (10, 1p) or reacted sluggishly (1n).



**Scheme 1.** Scope of the Pd-catalysed monocoupling of cyanuric chloride with aryl, vinyl and heterocyclic boronic or diarylborinic acids.

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2,4-Dichloro s-triazines are moisture-stable and more suitable in Suzuki coupling than cyanuric chloride. However, the C-Cl reactivity gap from dichloro to monochloro s-triazines, thus the selectivity for unsymmetrical diaryl chloro-s-triazines, strongly depend on nucleophiles and the electronic effects of substituent on the core ring. Control of step-wise substitution on chloro-s-triazines has proven easy for N or O-centered nucleophiles.<sup>[14]</sup> However, little is known about the controllability of Suzuki coupling except for two recent reports on 6-alkylamino substituted dichloro s-triazines.<sup>[15]</sup> In fact, only a modest vield (54%) was obtained for intermediate product, 2chloro-4-phenyl-6-(p-tolyl)-1,3,5-triazine (4ea) from reaction of **3e** with **2a** under the anhydrous conditions for monocoupling of cyanuric chloride (Table 2, entry 1).

**Table 2.** Optimization on cross-coupling of aryl dichloro *s*-triazine with 1a/2a.<sup>[a]</sup>

Ph N N CI N 3e	l <sub>+</sub> ( <i>p</i> -Tolyl) <sub>n</sub> B( ` n = 1, 1a `Cl n = 2, 2a	Pd OH) <sub>3-n</sub>	I(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> (mol%) O <sub>3</sub> (2M. aq.,2equiv) I <sub>2,</sub> Tol. 60°C, 6h <i>p</i> -Tol	Ph N N yl N X X = Cl, <b>4ea</b> X = <i>p</i> -Tolyl, <b>5ea</b>
Entry	Pd mol%	T(°C)	<b>1 a/2 a</b> (equiv)	Yield <sup>[b]</sup>
1 <sup>[c]</sup>	1	60	<b>1</b> a (1.1)	54 ( <b>4ea</b> )
2	1	60	<b>1</b> a (1.1)	95 ( <b>4ea</b> )
3	0.3	60	<b>1</b> a (1.1)	94 ( <b>4ea</b> )
4	0.1	60	<b>1</b> a (1.1)	94 ( <b>4ea</b> )
5 <sup>[d]</sup>	0.1	rt	<b>1</b> a (1.1)	68 ( <b>4ea</b> )
6	0.1	60	2a(0.55)	94 ( <b>4ea</b> )
7	0.1	60	<b>1a</b> (2.2)	80 ( <b>5 ea</b> )
8	0.1	100	<b>1a</b> (2.2)	99 ( <b>4ea</b> )
9	0.1	100	<b>2</b> a (1.1)	98 ( <b>5 ea</b> )

<sup>[a]</sup> Reaction run at 1mmole scale (3e) with 1.1 equiv. arylboronic acid (1a) or 0.55 equiv. diarylborinic acid (2a).
<sup>[b]</sup> Isolated yield (%).

<sup>[c]</sup> Anhydrous  $K_2CO_3$  used.

<sup>[d]</sup> 12 h.

However, the catalytic efficiency and selectivity increased dramatically under aqueous conditions. A highly selective and efficient reaction was observed to give diaryl product **4ea** in 95% yield with only 4% triaryl side-product (**5ea**) by using 2 M K<sub>2</sub>CO<sub>3</sub>(aq.) as base in toluene. In fact, complete reaction could even be achieved by using as low as 0.1 mol% catalyst loading at 60 °C for 6 h although the reaction failed to complete at room temperature after 12 h (Table 2, entries 4 and 5). The unexpected increase in catalytic efficiency under aqueous conditions is consistent with the proposal that transmetalation from boron to palladium hydroxide species (Pd<sup>II</sup>-OH) should be the rate-determining step in the catalytic cycle.<sup>[16]</sup> It is noteworthy that the high selectivity for diaryl chloro *s*-triazines could be readily switched to favour triaryl products by simply increasing the stoichiometry of arylboronic or diarylborinic acids (2.2 equiv. with respect to aryl group) (Table 2, entry 7). Triaryl *s*-triazine **5ea** could be obtained even in 99% yield by further increasing reaction temperature to  $100^{\circ}$ C, indicating the third arylation proceeded quantitatively. Again, diarylborinic acid **2a** performed as well as boronic acid **1a**.

Scope and limitation of the palladium catalysed highly selective and efficient Suzuki coupling of dichloro s-triazines with aryl, vinyl and heterocyclic boronic and diarylborinic acids were further explored (Scheme 2). Similar to the coupling with cvanuric chloride, arylboronic acids bearing an electron-withdrawing conjugate group (Ac, CN or CO<sub>2</sub>Me) on phenyl ring gave trace coupling products while an electron-neutral, -donating or halogen (Cl and F) group, even at ortho position, showed negligible influence. For example, reaction of ortho-substituted arylboronic or diarylborinic acids 1c/2c (o-Me), 1d/2d (o-Et) and 1h/2h (o-OMe) with 3e gave 4ec, 4ed and 4eh in 97%/93%, 94%/92% and 95%/95% yields, respectively.<sup>[17]</sup> Vinyl boronic acids, e.g. 1-pentenylboronic acid (1k), 1-cyclohexenylboronic acid (1l) and trans-(2-phenylethenyl)acid (1m), reacted with aryl dichloro s-triazines (3j or 3e) efficiently, giving the corresponding monochloro s-triazines 4jk, 4jl, 4jm and 4ek in 90-93% yields. No reaction was observed for **3j** and 2- or 3-furanylboronic acids (**1n**, **1o**) or 3pyridylboronic acid (1p).

Given that the high selectivity in step-wise arylation of dichloro s-triazines with aryl and vinyl borons could be achieved by using proper stoichiometry and temperature, we anticipated that a one-pot procedure for synthesis of unsymmetrically trisubstituted aryl striazines (5) could be effected through sequential Suzuki coupling, in which, after completion of the second Suzuki coupling, the third boron reagents were directly added to the reaction mixture and then heated at 100 °C for another 6 h. A couple of unsymmetrically trisubstituted aryl s-triazines were obtained by the one-pot sequential procedure in 80–93% yields (Scheme 3).

Diarylborinic acids also reacted efficiently to give the desired unsymmetrical triaryl *s*-triazines in comparable yields to their arylboronic acid analogues. The order of introduction of the second and third aryl groups showed little influence on the overall yields of unsymmetrical triaryl *s*-triazines (**5**).

In summary, a highly selective and efficient Suzuki coupling approach has been developed for synthesis of unsymmetrical di/triaryl *s*-triazines from cyanuric chloride and aryl or vinyl boronic acids or diary-lborinic acids by using a practical catalyst system, 0.1-0.5 mol% Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> in the presence of 2–4 equiv.

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Scheme 2. Suzuki coupling of aryl dichloro s-triazines with aryl and vinyl boronic and diarylborinic acids.

 $K_2CO_3$  in toluene or aqueous toluene at 60–100 °C. Scope exploration on the boron counterparts indicated that heterocyclic boronic acids or electron-deficient arylboronic acids bearing an electron-withdrawing conjugate group at phenyl ring could completely block the coupling while a small steric hindrance from an electron-donating o-substituent of aryl groups could be overcome. The remarkable structural effects of boronic acids on the cross-coupling was tentatively attributed to the rate-determining role played by transmetalation of organic group from boron to palladium (II) species in the catalytic cycle. The second and third Suzuki coupling to unsymmetrically trisubstituted aryltriazines could be conducted in one-



Scheme 3. One-pot synthesis of unsymmetrically trisubstituted aryl s-triazines via sequential Suzuki coupling.<sup>[a]</sup> Introduction of  $R^2$  prior to  $R^1$ .

pot procedure. The sequential Suzuki coupling approach, in particular using cost-effective diarylborinic acids, promises a practical access to unsymmetrical aryl s-triazine derivatives.

## **Experimental Section**

General information: All reactions were carried out under nitrogen by using standard Schlenk techniques unless otherwise stated. Commercially available chemicals were used as received. Diarylborinic acids were prepared according to our

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previously reported procedures.<sup>[13]</sup> Column chromatograph was performed on 200–300 mesh silica gal. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> at ambient temperature. Chemical shifts in NMR are reported in ppm ( $\delta$ ), relative to the internal standard of tetramethylsilane (TMS). All new compounds were further characterized by HRMS (see supporting information for details).

# General Procedure for Suzuki Monocoupling of Cyanuric Chloride

Under a N<sub>2</sub> atmosphere, to a 10 mL Schlenk flask were added cyanuric chloride (277.0 mg, 1.5 mmol), aryl, vinyl or heterocyclic boronic acid **1** (1.0 mmol) or diarylboronic acid **2** (0.5 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (3.5 mg, 0.5 mmol%), K<sub>2</sub>CO<sub>3</sub> (552.8 mg, 4.0 mmol), and toluene (5 mL). The mixture was stirred at 60 °C for 12 h. The reaction progress was monitored by TLC. The reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (15 mL), followed by washing with H<sub>2</sub>O (2×10 mL). The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated under reduced pressure to give crude product, which was purified by through flash column chromatography over silica gel using ethyl acetate/petroleum ether (60–90 °C) gradient to afford 2,4-dichloro-6-aryl/vinyl-s-triazine **3**.

#### General Procedure for the Second Suzuki Coupling

Under a N<sub>2</sub> atmosphere, to a 10 mL Schlenk flask were added dichloro-s-triazine **3** (1.0 mmol), aryl or vinyl boronic acid **1** (1.1 mmol) or diarylboronic acid **2** (0.55 mmol), Pd (PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.7 mg, 0.1 mmol%), K<sub>2</sub>CO<sub>3</sub>(aq.) (1 mL, 2 M/L), and toluene (5 mL). The mixture was stirred at 60 °C for 6 h or monitored by TLC until the starting material was completely consumed. The work-up procedure for **3** was adopted to offer the analytically pure product, 2-chloro-4,6-diaryl/arylvinyl s-triazine **4**.

#### General Procedure for One-Pot Sequential Suzuki Coupling

To a 10 mL Schlenk flask were added dichloro-s-triazine **3** (1.0 mmol), aryl boronic acid **1** (1.1 mmol) or diarylboronic acid **2** (0.55 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.7 mg, 0.1 mmol%), K<sub>2</sub> CO<sub>3</sub>(aq.) (1 mL, 2 M/L), and toluene (5 mL). The mixture was stirred at 60 °C under nitrogen with the progress monitored by TLC. When dichloro-s-triazine completely consumed, the second aryl or vinyl boronic acid **1** (1.1 mmol) or diarylboronic acid **2** (0.55 mmol) was added. The reaction mixture was further stirred for another 6 h at 100 °C and monitored by TLC. The work-up procedure for **3** was adopted to offer the analytically pure product, trisubstituted aryl s-triazine **5**.

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# UPDATES

A Sequential Suzuki Coupling Approach to Unsymmetrical Aryl *s*-Triazines from Cyanuric Chloride

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