Syntheses of Various 5-(3'-Substituted Phenyl)uracils

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The Suzuki Pd(0)-catalysed coupling between arylboronic acids and aryl bromides or iodides in weakly alkaline medium has been used for the preparation of 5-(3'-chlorophenyl)-, 5-(3'-iodophenyl)-, 5-(3'-aminophenyl)-, 5-(3'-azidophenyl)-, 5-(3'-methylthiophenyl)- and 5-(3'-styryl)-substituted 2,4-di-*t*-butoxypyrimidines. In the coupling between 2,4 di-*t*-butoxy-5-pyrimidineboronic acid and the six different aryl halides that were used as coupling partners, only 1-azido-3-bromobenzene did not give satisfactory yields, 18%. The other five aryl halides gave the desired 5-(3'-substituted phenyl)-2,4-di-*t*-butoxypyrimidines in 41-92% yield. Dealkylation of these five 5-(3'-substituted phenyl)-2,4-di-*t*-butoxypyrimidines in 2.5*M* hydrochloric acid gave the corresponding 5-(bromoaryl)uracils in almost quantitative yields. 5-(3'-Azidophenyl)uracil was prepared in 43% yield directly from 5-(3'-aminophenyl)-2,4-di-*t*-butoxypyrimidine.

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Introduction.

In connection with work on potential antiviral compounds, we have previously prepared various 5-aryl substituted [1] as well as 5-(bromoaryl)-substituted uracils [2,3]. These have been coupled with 2'-deoxyribose in order to investigate the antiviral activity of the corresponding 5-substituted 2'-deoxyuridines [3,4,5] and we have shown that 5-(3"-bromophenyl)-2'-deoxyuridine has a promising activity against human cytomegalovirus infection [6]. These results made it interesting to prepare various 5-(3'-substituted phenyl)uracils with 3'-substituents that are close mimics to bromine. These uracils are easily converted to their corresponding nucleosides [4,7]. When choosing the 3'-substituents, we compared properties such as partition coefficients, molar refractions and Hammett constants [8] and found that chloro, iodo, methylthio, azido and vinyl are the groups that resemble bromo the most (Table 1). We also prepared the amino analogue since 5-(3'-aminophenyl)-2,4-di-*t*-butoxypyrimidine (**11a**) was necessary for the preparation of 5-(3'-azido)uracil (**9b**).

Table 1

Properties of some Functional Groups

Group	π [a]	MR [b]	$\mathcal{F}$ [c]	$\mathcal{R}$ [c]	σ_m	σ_p
-Cl	0.71	6.03	0.41	-0.15	0.37	0.23
-Br	0.86	8.88	0.44	-0.17	0.39	0.23
-I	1.12	13.94	0.40	-0.19	0.35	0.18
-SMe	0.61	13.82	0.20	-0.18	0.15	0.00
$-CH=CH_2$	0.82	10.99	0.07	-0.08	0.05	-0.02
$-N_3$	0.46	10.20	0.30	-0.13	0.27	0.15
$(-NH_2)$	-1.23	5.42	0.02	-0.68	-0.16	-0.66

[a] Partition coefficients from octanol-water system of substituted benzenes. [b] Molar refraction. [c] Calculated from σ_m and σ_p [7].

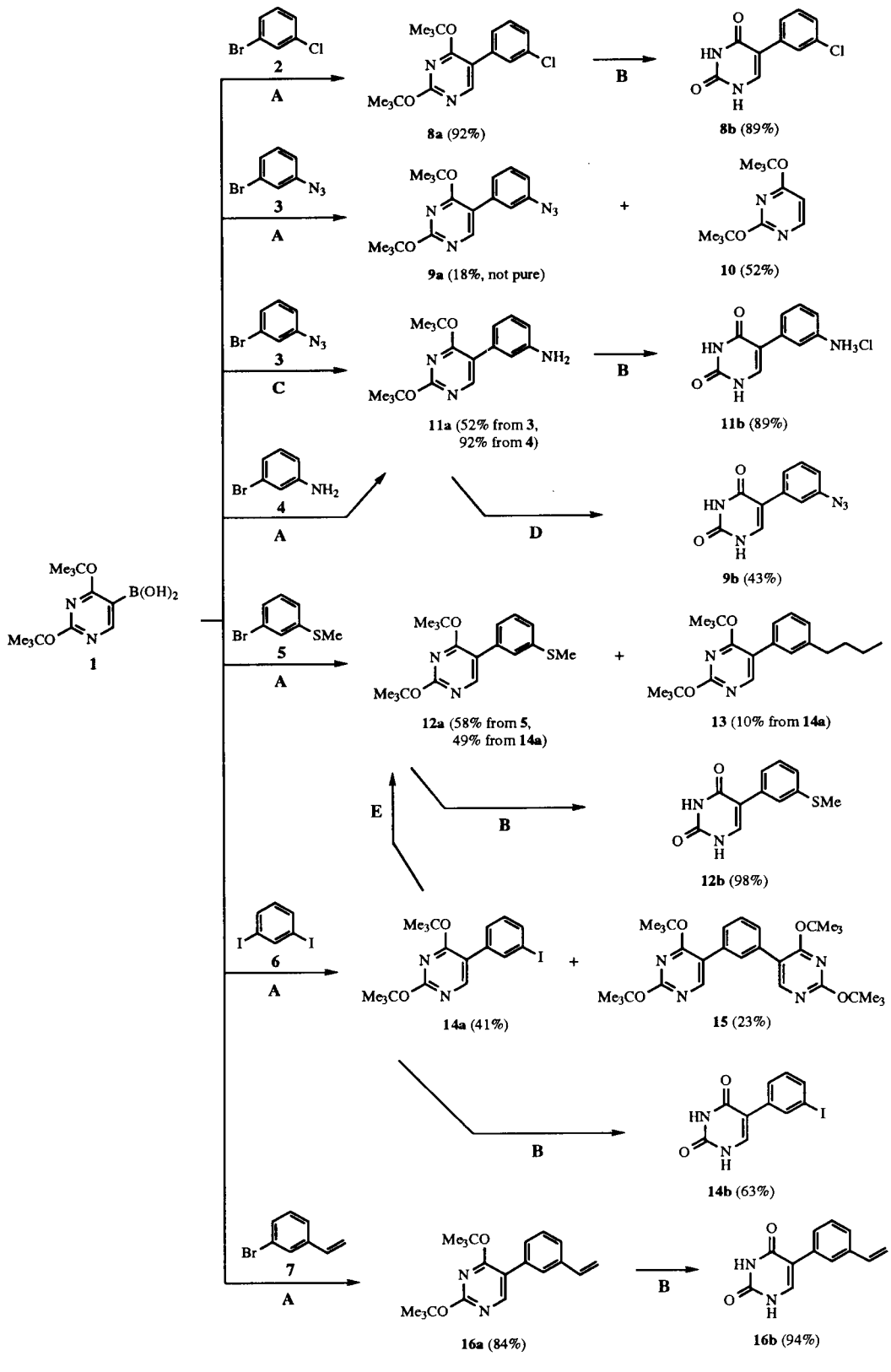
We have previously used the Suzuki Pd(0)-catalysed coupling between 2,4-di-*t*-butoxy-5-pyrimidineboronic acid and aryl bromides [1] and aryl dibromides in weakly alkaline medium [2,3] with satisfying results and we decided to use it also for the preparation of the new series of 5-aryl-substituted uracils. The method is widely used for the preparation of unsymmetrical biaryls [9-14], and modifications of the procedure involve the use of fluoride-mediation [15], palladium(II) acetate catalysis in aqueous ethanol [16] and palladium(II) acetate catalysis in water [17].

The fact that 3-bromostyrene (**7**) coupled to 2,4-di-*t*-butoxy-5-pyrimidineboronic acid (**1**) in 84% yield without traces of polymerised byproducts as a result of self-coupling *via* the Heck reaction was rather surprising. Substrates containing both vinylic and boronic functions have been found to react according to the Suzuki reaction path selectively with sodium methoxide as base in tetrahydrofurane (THF) [18]. No reaction conditions have been found for selective Heck coupling [18,19]. We therefore decided to examine what conditions favour the Suzuki reaction over the Heck reaction. It has been shown that the Heck reaction can be performed in water with the addition of tri-*n*-butylamine or tetra-*n*-butylammonium bromide [20]. This prompted us to try the reaction without **1** in dimethoxyethane (DME) and aqueous 1*M* sodium hydrogen carbonate with and without these additives. The reaction was also performed in DME and in acetonitrile without aqueous sodium hydrogen carbonate but with 1.1 equivalent of tri-*n*-butylamine as base in order to see of and how fast the Heck reaction would occur.

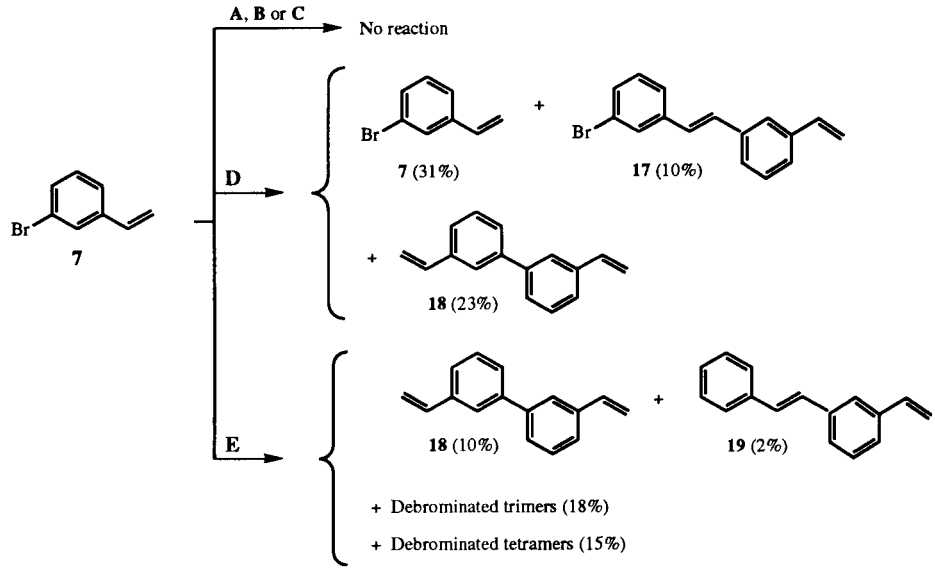
Results.

The palladium(0) catalysed couplings between 2,4-di-*t*-butoxy-5-pyrimidineboronic acid (**1**) and 1-bromo-3-chlorobenzene (**2**), 3-bromoaniline (**4**), 3-bromothioanisole (**5**) and 3-bromostyrene (**7**) gave acceptable to excellent yields of the desired products after 1 hour of reaction time (Scheme 1). When 1-azido-3-bromobenzene was tried as the coupling partner, only 18% of impure 5-(3'-azidophenyl)-2,4-di-*t*-butoxypyrimidine (**9a**) was obtained together with 52% of deboronated starting material **10** after 24 hours of reaction time. The reason was thought to be reduction of the azido group to the amine, resulting in destruction of the Pd(0) catalyst. This was confirmed by performing the reaction with

Scheme 1


Me3CO
B(OH)2
Me3CO
1
Br
Cl
2
A
8a (92%)
B
8b (89%)
Br
N3
3
A
9a (18%, not pure)
+
10 (52%)
Br
N3
3
C
11a (52% from 3, 92% from 4)
B
11b (89%)
Br
NH2
4
A
D
9b (43%)
Br
SMe
5
A
12a (58% from 5, 49% from 14a)
+
13 (10% from 14a)
E
B
12b (98%)
I
I
6
A
14a (41%)
+
15 (23%)
B
14b (63%)
Br
7
A
16a (84%)
B
16b (94%)

Scheme 2



Reaction conditions: **A**: 0.03 eq $Pd(PPh_3)_4$, DME, 1*M* $NaHCO_3$ (aq). **B**: As for **A** but with addition of 0.10 eq Bu_3N. **C**: As for **A** but with addition of 0.05 eq Bu_3NBr. **D**: 0.03 eq $Pd(PPh_3)_4$, DME, 1.1 eq Bu_3N. **E**: As for **D** but in MeCN instead of DME.

1.1 equivalents of catalyst, yielding 52% of **11a**. With 1,3-diiodobenzene (1.5 equivalents) as the coupling partner, 43% of the desired monocoupled product **14a** was obtained together with 23% of the dicoupled (**15**). The high yield of dicoupled product compared to the case when 1,3-dibromobenzene is used as coupling partner [2] is attributed to the higher reactivity of the iodo group in this kind of Pd(0) catalysed reactions. The mono- and dicoupled products were easily separated by column chromatography using silica gel 60 and heptane:ethyl acetate as eluent. Compound **14a** could be converted to (3'-methylthiophenyl)-2,4-di-*t*-butoxypyrimidine (**12a**) in 49% yield by the action of *n*-butyllitium followed by dimethyl disulphide at -78° as an alternative approach to direct coupling between **1** and **5**. The disadvantage of this procedure is the formation of 10% of (3'-*n*-butylphenyl)-2,4-di-*t*-butoxypyrimidine (**13**).

Attempts to self-couple **7** in DME/1*M* sodium hydrogen carbonate (aqueous) with or without tri-*n*-butyl amine (0.10 equivalent) or tetra-*n*-butylammonium bromide (0.05 equivalent) failed. Only starting materials could be detected after 24 hours of reaction time (Scheme 2). Using pure DME or acetonitrile, afforded traces of product after 4 hours, and after 120 hours, 31% of the starting material **7**, 11% of dicoupled Heck product **17** and 23% of homo coupled **18** could be isolated when DME was used as solvent. With acetonitrile, higher polymers were obtained and debromination was more profound. The debrominated dimers **18** and **19** were isolated in 10% and 2%, respectively, together with 18% of debrominated trimers and 15% of debrominated tetramers. These results indicate that 3-bromostyrene is a poor substrate for self-coupling *via* the Heck mechanism and that selective Suzuki Pd(0) catalysed coupling can be achieved using this starting material.

Table 2

Elemental Analyses for some 5-Substituted Pyrimidines

Compound		Calcd.			Found		
		%C	%H	%N	%C	%H	%N
8a	$C_{18}H_{23}ClN_2O_2$	64.56	6.92	8.37	64.48	7.08	8.31
9a	$C_{18}H_{23}N_5O_2$				[a]		
11a	$C_{18}H_{25}N_3O_2$	68.54	7.99	13.33	68.59	8.06	13.26
12a	$C_{19}H_{26}N_2O_2S$	65.86	7.56	8.09	65.89	7.64	8.01
14a	$C_{18}H_{23}IN_2O_2$	50.71	5.44	6.57	50.62	5.43	6.53
16a	$C_{20}H_{26}N_2O_2$	73.58	8.03	8.58	73.34	8.06	8.49

[a] Could not be obtained pure enough for EA.

Table 3

Yields, Melting Points and Molecular Weight Data for some 5-Substituted Pyrimidines

Compound	Yield (%)	mp (°C)	Calcd. MW	Found MW
8a	92	78-80	334.1/336.1	334/336
9a	18	[a]	341.2	341
11a	92	126-127	315.2	315
12a	58	105-107	346.2	346
14a	41	104-106	426.1	426
16a	84	102-103	326.2	326

[a] Was obtained as a slightly impure syrup.

Table 4

^{1}H NMR Chemical Shifts (ppm) for some 5-Substituted Pyrimidines in Deuteriochloroform

Compound	H-6	H-2'	H-4'	H-5'	H-6'	Other
8a	8.20	7.50	[	7.26-7.35	]	
9a	8.22	[7.22-7.26]		7.36	6.96	
11a	8.20	6.81	6.88	7.16	6.63	3.67 (NH_2)
12a	8.20	7.39	7.24	7.30	7.19	2.49 (SMe)
14a	8.18	7.87	7.62	7.10	7.42	
16a	8.24	7.56	[	7.34-7.56	]	[a]

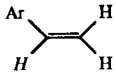
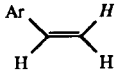
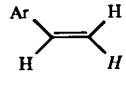
[a]  : 6.75;  : 5.77;  : 5.27.

Table 5

^{1}H NMR Coupling Constants (Hz) for some 5-Substituted Pyrimidines

Compound	2'-4'	2'-6'	4'-5'	4'-6'	5'-6'	*cis*	*trans*	*gem*
8a	1.3	1.5	[a]	[a]	[a]			
9a	2.2	2.2	8.0	1.2	7.9			
11a	1.5	2.3	8.0	1.0	7.7			
12a	[a]	[a]	7.1	2.0	7.1			
14a	1.6	1.6	7.8	1.0	7.8			
16a	[a]	[a]	[a]	[a]	[a]	10.9	17.6	[b]

[a] Could not be determined. [b] Was not observed.

Table 6

Elemental Analyses for some 5-Substituted Uracils

Compound		Found %C	%H	%N	Calcd. %C	%H	%N
8b	$C_{10}H_7ClN_2O_2$	53.79	3.21	12.44	53.95	3.17	12.59
9b	$C_{10}H_7N_5O_2$	52.28	3.47	30.28	52.40	3.08	30.56
11b	$C_{10}H_{10}ClN_3O_2$	49.73	4.49	17.45	50.11	4.21	17.54
12b	$C_{11}H_{10}N_2O_2S$	56.32	4.35	11.93	56.39	4.30	11.96
14b	$C_{10}H_7IN_2O_2$	38.09	2.21	8.84	38.24	2.25	8.92
16b	$C_{12}H_{10}N_2O_2$	67.18	4.78	13.15	67.28	4.71	13.08

EXPERIMENTAL

Melting points were recorded on a Lietz Wetzlar Microscope Heating Stage 350 Melting Point Apparatus and are uncorrected. The ^{1}H nmr spectra were recorded on a Varian XL-200 or XL-300 spectrometer. The mass spectra were recorded on a JEOL-SX 102 spectrometer.

1-Azido-3-bromobenzene (**3**).

The procedure of Spauschus *et al.* [21] was followed, but instead of destillation, the crude product was purified by column chromatography using silica gel 60 and heptane as eluent.

3-Bromothioanisole (**5**).

To 25 g (88 mmoles) of 1-bromo-3-iodobenzene dissolved in 190 ml of dry THF cooled to -78° was added 43.5 ml of 2.03*M* *n*-butyllithium at such a rate that the temperature never exceeded -75°. The reaction mixture was stirred at -78° for 2 hours, then 19.8 g (97 mmoles) of dimethyl disulphide was added at such rate that the temperature never exceeded -75°. The reaction mixture was allowed to reach room temperature and was then poured into 300 ml of water. The organic phase was separated and the aqueous phase was extracted three times with ether. The combined organic phases were dried over magnesium sulphate, filtered and the ether was removed by evaporation *in vacuo*. The crude product was distilled at reduced pressure yielding 17.1 g (95%) of 3-bromothioanisole, bp 115-118°/11 mm Hg (lit 110-116°/12 mm Hg [22]).

1,3-Diiodobenzene (**6**).

To 25 g (72 mmoles) of 2,4-di-iodoaniline [23] dissolved in 700 ml of 80% acetic acid (aqueous) cooled to -5° was added 5.5 g (80 mmoles) of sodium nitrite at such a rate that the temperature never exceeded 0°. After stirring for an additional 2 hours, the solution was rapidly poured into 75 ml of ice cold 30% hypophosphorous acid (aqueous). The reaction mixture was stirred at 0° for 12 hours and then at room temperature for

Table 7

Yields, Melting Points and Molecular Weight Data for some 5-Substituted Uracils

Compound	Yield(%)	mp(°C)	Calcd. MW	Found MW
8b	89	326-329	222.0/224.0	222/224
9b	43	>350 [a]	229.1	229
11b	89	308-311[b]	203.1	203
12b	98	294-298	234.1	234
14b	63	305-308	314.0	314
16b	94	>350[c]	214.1	214

[a] Starts to decompose at ~220°C. [b] With decomposition. [c] Starts to decompose at ~260°C.

Table 8

^{1}H NMR Chemical shifts (ppm) for some 5-Substituted Uracils in DMSO-d_6

Compound	N1-H	N3-H	H-6	H-2'	H-4'	H-5'	H-6'	Other
8b	[11.30	]	7.75	7.66	7.53	7.38	7.32	
9b	[11.27	]	7.73	7.40	7.36	7.37	7.02	
11b	11.29	11.32	7.67	7.64	7.52	7.45	7.27	10.20 (NH_3)
12b	[11.22	]	7.67	7.43	[7.28-7.32]		7.18	2.48 (SMe)
14b	[11.26	]	7.70	7.95	7.63	7.17	7.56	
16b	[11.21	]	7.66	7.61	7.46	7.32	7.39	[a]

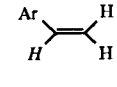
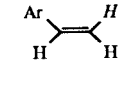
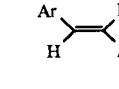
[a]  : 6.74;  : 5.84;  : 5.27.

Table 9

^{1}H NMR Coupling Constants (Hz) for some 5-Substituted Uracils

Compound	1-6	2'-4'	2'-6'	4'-5'	4'-6'	5'-6'	*cis*	*trans*	*gem*
8a	[a]	~1.9	~1.9	7.8	~1.9	7.9			
9a	[a]	~1.3	~1.3	[b]	2.2	[b]			
11a	6.0	1.6	1.6	7.7	1.6	7.7			
12a	[a]	[b]	[b]	[b]	[b]	[b]			
14a	[a]	1.7	1.6	7.8	1.0	7.8			
16a	[a]	1.7	1.7	7.2	1.8	7.5	10.9	17.6	1.0

[a] Was not observed. [b] Could not be determined.

an additional 12 hours. The volatiles were evaporated *in vacuo* and the residue was distributed between water and ether. The organic phase was separated and the aqueous phase was extracted two times with ether. The combined organic phases were dried over magnesium sulphate, filtered and the ether was removed by evaporation *in vacuo*. The crude product was distilled at reduced pressure yielding 13.6 g (58%) of 1,3-diiodobenzene, bp 97-110°/1 mm Hg, mp 37-39° (lit mp 36.5° [24]).

General Procedure for the Palladium(0)-catalysed Coupling Reaction Between 2,4-Di-*t*-butoxy-5-pyrimidineboronic Acid and Aryl Halides.

The procedure follows the one presented by Peters *et al.* [1] with the boronic acid in excess (1.1 equivalents) except for the reaction with 1,3-diiodobenzene (1.5 equivalents of 1,3-diiodobenzene). A 250 ml three-necked flask equipped with condenser, magnetic stirrer and nitrogen inlet was charged with 22.0 (**2-5, 7**) or 36.6 (**6**) mmoles of the aryl halide, 0.75 mmole of tetrakis-(triphenylphosphine)palladium(0) [25] and 80 ml of DME. After stirring for 10 minutes 24.2 mmoles of **1** was added, immediately followed by 60 ml of 1*M* sodium bicarbonate solution. The reaction mixture was refluxed for 1 hour (compounds **8a, 11a, 12a, 14a, 16a**) or 24 hours (compound **9a**) with vigorous stirring. After cooling to room temperature, the organic phase was separated. The aqueous phase was extracted with three 50 ml portions of ether and the combined organic phases were washed with water and saturated aqueous sodium chloride solution. After drying over magnesium sulphate the organic solvents were evaporated *in vacuo*. The residue was flash chromatographed using silica gel 60 and heptane:ethyl acetate 19:1 (compounds **8a, 9a, 14a, 16a**), 37:3 (compound **12a**) or 7:3 (compounds **11a**) as eluent.

Compound **11a** was also obtained from coupling between **1** and **3** as described above but with 1.1 equivalents of tetrakis-(triphenylphosphine)palladium(0).

2,4-Di-*t*-butoxy-5-(3'-methylthiophenyl)pyrimidine (**12a**) from 2,4-Di-*t*-butoxy-5-(3'-iodophenyl)pyrimidine (**14a**).

To 1.0 g (2.4 mmoles) of **14a** dissolved in 5 ml of dry THF cooled to -78° 1.4 ml of 2.03*M* *n*-butyllithium was added at such a rate that the temperature never exceeded -75°. The reaction mixture was stirred at -78° for 2 hours, then 0.26 g (2.8 mmoles) of dimethyl disulphide was added at such a rate that the temperature never exceeded -75°. The reaction mixture was allowed to reach room temperature and was then poured into 20 ml of water. The organic phase was separated and the aqueous phase was extracted three times with ether. The combined organic phases were dried over magnesium sulphate, filtered and the ether was removed by evaporation *in vacuo*. Workup as described for the General Procedure above yielded 0.40 g (49%) of **12a**.

Elemental analyses for compounds **8a, 9a, 11a, 12a, 14a** and **16a** are given in Table 2, yields, melting point and molecular weight data in Table 3 and ^{1}H-nmr data in Tables 4 and 5.

The dealkylation of compounds **8a, 11a, 12a, 14a** and **16a** was performed as described by Peters *et al.* [1].

5-(3'-Azidophenyl)Uracil (9b) from 2,4-Di-*t*-butoxy-5-(3'-amino-phenyl)pyrimidine (**11a**).

To 4.0 g (12.7 mmoles) of **11a** dissolved in 125 ml of 80% aqueous acetic acid cooled to -5°, 0.97 g (14.0 mmoles) of sodium nitrite was added at such a rate that the temperature never exceeded 0°. After stirring for an additional 15 minutes, a solution of 0.91 g (14.0 mmoles) of sodium azide in water, pre-cooled to -5°, was added dropwise. The reaction mixture was stirred at -5° for 2.5 hours and then allowed to reach room temperature. The volatiles were evaporated *in vacuo* and the residue was carefully washed with three small portions of ice cold water and then with three portions of ice cold ether.

Elemental analyses for compounds **8a, 9a, 11a, 12a, 14a** and **16a** are given in Table 6, melting point and molecular weight data in Table 7 and ^{1}H-nmr data in Tables 8 and 9.

Attempts Toward Self-coupling of 3-Bromostyrene (**7**) (Scheme 2).

I. Aqueous Systems **A**, **B** and **C**.

A: To 0.50 g (2.73 mmoles) of **7** dissolved in 8 ml of DME were added 0.09 g (0.08 mmole) of tetrakis(triphenylphosphine)-palladium(0) and 6 ml of 1*M* sodium hydrogen carbonate (aqueous). The reaction mixture was heated to reflux for 24 hours, after which only starting material **7** could be detected.

B: The process was carried out as described for **A** but with the addition of 0.042 g (0.14 mmoles) of tri-*n*-butylamine.

C: The process was carried out as described for **A** but with the addition of 0.042 g (0.14 mmole) of tetra-*n*-butylammonium bromide.

II. Non-aqueous Systems (**D** and **E**).

D: To 0.50 g (2.73 mmoles) of **7** dissolved in 10 ml of DME were added 0.09 g (0.08 mmole) of tetrakis(triphenyl-phosphine)palladium(0) and 0.56 g (3.0 mmoles) of tri-*n*-butylamine. The reaction mixture was heated to reflux for 120 hours and was then allowed to reach room temperature. The solvent was evaporated *in vacuo* and the residue was applied to a column of silica gel 60. Elution with heptane afforded 31% of starting material **7**, 11% of the Heck-coupled dimer **17** and 23% of the homo-coupled dimer **18**.

E: The process was carried out as described for **D** but with 10 ml of acetonitrile instead of DME as the solvent. Column chromatography using heptane as the eluent afforded 10% of the homo-coupled dimer **18**, 2% of the debrominated Heck-coupled dimer **19** as well as debrominated trimers and tetramers in 18% and 15% yield, respectively.

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