Stannylation Reactions and Palladium Catalysis in the Syntheses of Unsymmetrical Biheteroaryls

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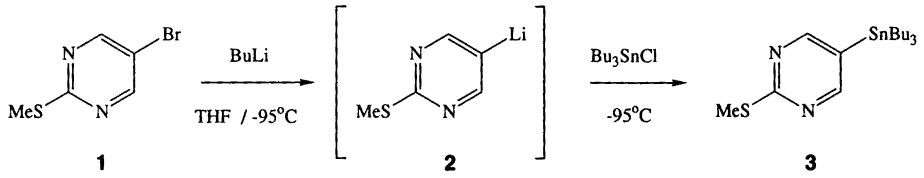
Two syntheses of 5-alkylstannyl-2-methylthiopyrimidines from the corresponding 5-bromopyrimidine are described. These are the palladium-catalysed coupling of the bromide with hexaalkyldistannane in the presence of fluoride ion and substitution reactions using trialkylstannyl anions. The stannylated derivative was subsequently used to obtain the biheteroaryls by palladium-catalysed coupling with heteroaryl bromides.

Palladium-catalysed cross-coupling of organometallic derivatives with aryl halides,[1] is now emerging as an alternative to the more classical approaches in the synthesis of biaryls.[2] In this context, the use of organotin reagents presents itself as an attractive choice, since the isolable and stable organostannanes readily undergo coupling reactions in the presence of palladium catalysts.[3] Cross-coupling between (heteroaryl)trialkylstannanes with aryl halides,[4] and with heteroaryl halides,[5] can be achieved by palladium catalysis. Several methods for the preparation of unsymmetrical tetraorganostannanes are known,[3] but their extension to include heteroaryl derivatives are, however, limited.[4] We have already described an efficient method of synthesizing 5-trialkylstannylpyrimidine (Scheme 1).[6] This involves the cold-temperature lithiation of the bromide **1**, followed by quenching with trialkylstannyl chloride. The same technique has been used in order to synthesis other derivatives of 5-stannylpyrimidines.[7,8]



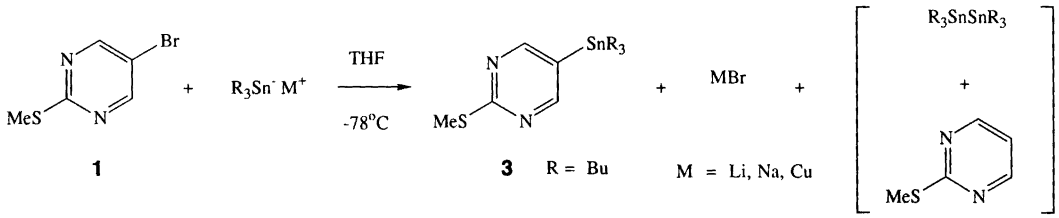
1 **2** **3**

Scheme 1.

In our new approach to the synthesis of 5-trialkylstannylpyrimidines, the polarization of the reactants has been reversed with respect to the above reaction, i.e. reactions between the 5-bromide **1** and the trialkylstannyl anions have been studied. Application of this technique to aryl and heteroaryl halides are few,[9,10] but sodium trimethylstannate(IV) reagent has been reported to furnish good yields of stannylpyridines.[10b]

nyllithium, have been prepared from trialkylstannyl chloride and lithium metal,[11e] from hexaalkyldistannane and butyllithium,[11c] and from tributyltin hydride and lithium diisopropylamide (LDA);[11c] in the form of trialkylstannylsodium, from trimethylstannyl chloride and sodium metal,[10c] and from tributyltin hydride and sodium hydride;[11f] and tributylstannylcopper(I), from tributylstannyllithium and copper(I) iodide.[11g]

The reagents Bu_3SnLi, Bu_3SnNa, Bu_3SnCu and

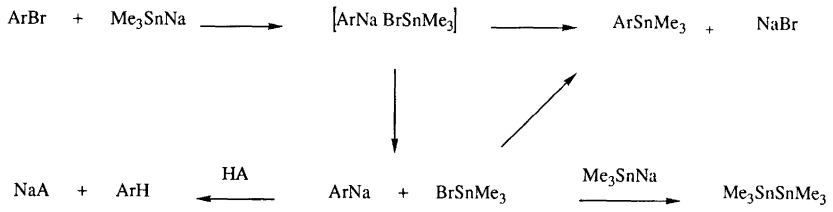


1 **3** R = Bu M = Li, Na, Cu

4 R = Me

Scheme 2.

Me_3SnNa were generated at 0 °C, and then cooled to −78 °C before the addition of the bromide **1**. This was done to avoid 1:1 adduct formation between the reagent and the π-electron deficient pyrimidine. The yields of the products **3** and **4** were 71, 46, 50 and 73 %, respectively. By-products are the corresponding hexaalkyldistannane and the dehalogenated pyrimidine. Product formation can be rationalized by analogy with the explanation given for the course of the reaction between bromobenzene and trimethylstannylsodium (Scheme 3),[12a] although an electron-transfer mechanism should not be disregarded.[12b]

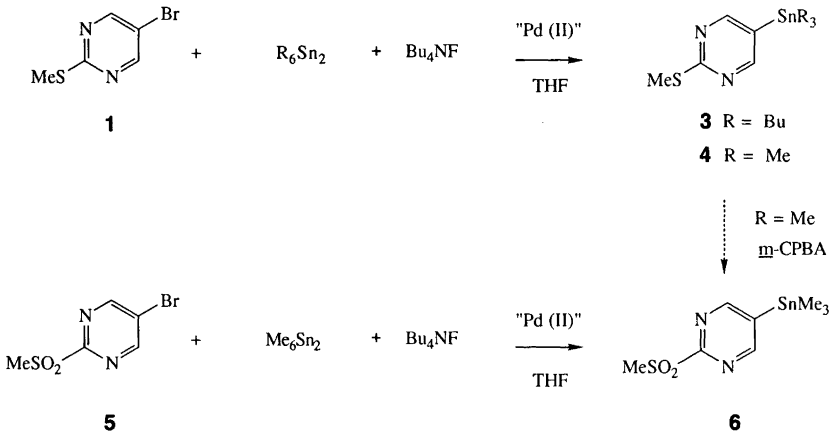


Scheme 3.

A complex is initially formed between bromobenzene and trimethylstannylsodium inside a solvent cage, which may collapse to give the desired stannylated benzene. Alternatively, the complex may dissociate to phenylsodium and trimethylstannyl bromide; the latter could then react with the trialkylstannylsodium to give hexaalkyldistannane, while the former may abstract an 'acidic' proton thus yielding the dehalogenated product.

The methods using a tin halide or a trialkylstannyl anion reagent both suffer from the drawback that the reactions must be carried out at low temperatures. We have therefore developed an alternative reaction that can be run at ambient temperature. This is the palladium-catalysed coupling reaction between our model compound, 5-bromopyrimidine **1**, and hexaalkyldistannane in the presence of fluoride ion. This technique has been used to a limited extent in the synthesis of arylstannanes, especially in the case of aryl substrates containing electron-withdrawing substitutents.[13]

The cross-coupling of the 5-bromopyrimidine with hexaalkyldistannane to form the stannylpyrimidine is dependent on various factors. Among these is the nature of the palladium catalyst. The following catalysts were studied: bis (triphenylphosphine)palladium(II) chloride [$PdCl_2(PPh_3)_2$], bis(acetonitrile)palladium(II) chloride [$PdCl_2(MeCN)_2$], tetrakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$], bis(triphenylphosphine)palladium(II) diacetate [$Pd(OAc)_2(PPh_3)_2$], ammonium palladium(II) tetrachloride [$PdCl_4(NH_4)_2$], bis(benzylideneacetone)palladium [Pd(dba)$_2$] and bis(π-allylpalladium chloride) [(π-C_3H_5-$PdCl)_2$]. The latter was found to be the best catalyst for this reaction, although Pd(dba)$_2$ also gave reasonable yields of the 5-stannylated product albeit more slowly. Both these catalysts have been reported to be active in the stannylation of aryl bromides.[14] $PdCl_2(PPh_3)_2$, the catalyst used exclusively in the biheteroaryl synthesis below, gave little or no product in the stannylation reaction. This catalyst also failed to activate the stannylation of aryl bromides, and the failure has been attributed to unfavourable interference, in the reaction, by the triphenylphosphine ligand.[14] $Pd(PPh_3)_4$, however, has been used successfully in arylstannylation reactions,[13b] but the catalyst was ineffective in our case.



Scheme 4.

Tin–tin bonds are known to be thermally stable,[15] but weakening of the bond can be achieved through the formation of complexes such as [$(Bu_3SnSnBu_3X)^-Bu_4N^+$].[16b] An-

Table 1. Formation of biheteroaryls (**7**) from 5-stannylpyrimidine **3** and heteroaryl bromides by Pd(II) catalysis.

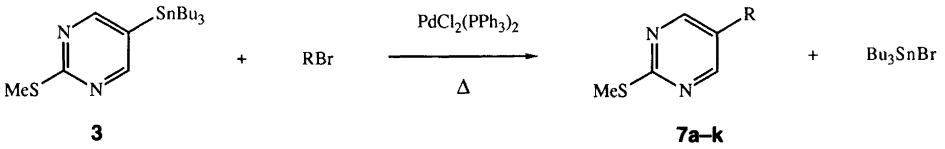
Entry	Heteroaryl bromide (RBr)	Solvent	Time/h	Temp/°C	Yield (%) **7**
a	2-Bromothiophene	THF	10	Δ	71
b	3-Bromothiophene	THF	24	Δ	90
c	2-Bromofuran	DCE[a]	4.5	Δ	89
d	3-Bromofuran	DCE	10	Δ	72
e	2-Bromo-5-formylthiophene	DMF	4.5	80	87
f	5-Bromofurfural	DCE	4.5	Δ	100
g	5-(5-Acetoxymethyl)-2-bromofuran	DCE	4	Δ	82
h	2-Bromopyridine	DMF	24	80	72
i	3-Bromopyridine	THF	24	Δ	65
j	4-Bromopyridine	DMF	10	80	67
k	2-Bromothiazole	DCE	24	Δ	68

[a]DCE = 1,2-dichloroethane.

hydrous fluoride ion (X=F) is better than the chloride ion (X=Cl) for this purpose.[16] In our case, there was no reaction in the absence of halide ion, very slow with chloride ion but coupling occurred readily in the presence of fluoride ion. The course of reaction, however, was dependent on the relative amounts of fluoride ion. Thus with four mole equivalents of fluoride ion the bromide was rapidly consumed (within 5 min) but the stannylated product was not isolated. This has also been observed with aryl bromides.[16b] Mole equivalents of fluoride and bromopyrimidine appeared optimal.

The amount of hexaalkyldistannane in excess of one mole equivalent also affected the yield.[13b] In the present case, two mole equivalents of the ditin reactant maximized stannylation.

The 2-methylthio group in the 5-bromide **1** can be exchanged with the more electron-withdrawing methylsulfonyl group (**5**) without any significant effect on the course of the reaction. The trimethylstannyl derivative **6** has previously been prepared from 2-methylthio-5-trimethylstannylpyrimidine (**4**) by *m*-chloroperbenzoic acid oxidation.[7]



Scheme 5.

Cross-coupling with heteroaryl halides proceeded smoothly and in good yields (Scheme 5, Table 1), except for 2-bromopyridine (entry h) which required either DMF or diglyme as the solvent for any reaction to be observed. These are more polar than either THF or 1,2-dichloroethane, the solvents of choice in most cases. For entries e and j the reactions in THF or 1,2-dichloroethane were slow and the yields low; DMF was decidedly the best solvent. The co-product in these reactions is tributylstannyl bromide, that can be easily removed by treating the reaction mixture with saturated KF, due to the formation of the sparingly soluble stannyl fluoride derivative.[3b]

The presence of electron-withdrawing substitutents on the heteroaryl halide appears to activate the coupling. Similar results have been observed with aryl halides.[17]

In all of these reactions little or no bipyrimidine was formed as a result of homocoupling of the stannylpyrimidine. This is in contrast with the coupling reaction of the stannylpyrimidine with vinyl bromides.[6]

Experimental

^{1}H NMR spectra were recorded at 300 MHz, ^{13}C NMR spectra at 75 MHz. Mass spectra were recorded at 70 eV ionizing voltage. Isobutane or ammonia was used for chemical ionization (CI). Mass spectra are presented as *m/z* (% rel. int.). THF used in the reactions was dried by distillation over metallic sodium/benzophenone, and 1,2-dichloroethane was distilled over phosphorous pentoxide. DMF was first shaken with NaOH pellets, then distilled over Ba_2O. Tetrabutylammonium fluoride (TBAF) was dehydrated by azeotropic distillation with anhydrous benzene (3×50 ml), then dried under high vacuum for 2 days at 35 °C. Maintaining a N_2 atmosphere, it was then dissolved in enough freshly distilled THF to give a 0.5 M solution. Commercial hexabutyldistannane, tributyltin hydride and hexamethyldistannane were used without purification. All other reagents were either recrystallized or distilled before use.

Starting materials prepared by literature methods. 5-Bromo-2-methylthiopyrimidine,[18] 5-bromo-2-methylsulfonylpyrimidine,[19] 5-bromo-2-furfural,[20] 5-bromo-2-acetoxymethylfuran.[21]

Stannylation by trialkylstannyl anions

2-Methylthio-5-tributylstannylpyrimidine (**3**). A solution of 5-bromo-2-methylthiopyrimidine (1.05 g, 5 mmol) in THF (10 ml) was added dropwise to a stirred solution of tributylstannyllithium (5 mmol) in THF (10 ml) maintained at −78 °C under N_2. The tributylstannyllithium reagent was generated from tributyltin hydride and LDA.[11c] TLC and GLC (2.5 m column packed with 3 % SP2100) were used to monitor the reaction. After 10 h, the reaction was quenched with saturated aqueous NH_4Cl solution, extracted with EtOAc, washed, dried ($MgSO_4$) and purified by flash chromatography on silica using hexane/EtOAc (1:1) as the eluent and finally by distillation; b.p. 130 °C/0.002 mmHg, yield 1.47 g (71 %).[6]

The reaction with tributylstannylsodium[11f] and tributylstannylcopper(I)[11g] were run under the same conditions for 24 and 10 h, respectively; yields 46 and 50 %.

2-Methylthio-5-trimethylstannylpyrimidine (**4**). Compound **4** was obtained as above from trimethylstannylsodium which was generated from trimethylstannyl chloride and sodium metal.[11e] The reaction was run for 10 h, and 73 % of **4** was isolated and characterized by comparison with the known compound.[7]

Stannylation by palladium catalysis

2-Methylthio-5-tributylstannylpyrimidine (**3**). To a mixture of hexabutyldistannane (2.32 g, 4 mmol), 5-bromo-2-methylthiopyrimidine (0.41 g, 2 mmol) and bis(π-allylpalladium chloride) (0.022 g, 3 mol %) was added a THF solution of tetrabutylammonium fluoride (4 ml of 0.5 M soln., 2 mmol) under a N_2 stream, and stirred at ambient temperature for 4 h. GLC monitoring showed that the reaction had gone 95 % towards completion at this time. EtOAc (30 ml) was added and the mixture was washed with water and worked up as above; yield 72 %.[6]

2-Methylthio-5-trimethylstannylpyrimidine (**4**). Compound **4** was obtained from hexamethyldistannane (1.31 g, 4 mmol) by the same method in 74 % yield.[7]

2-Methylsulfonyl-5-trimethylstannylpyrimidine (**6**). Compound **6** was prepared similarly from 5-bromo-2-methylsulfonylpyrimidine (0.474 g, 2 mmol) and hexamethyldistannane (1.31 g, 4 mmol); yield 72 %.[7]

General procedure for coupling reactions between 2-methylthio-5-tributylstannylpyrimidine and heteroaryl bromides (Table 1). Freshly distilled solvent (5 ml) was added to a mixture of the heteroaryl bromide (5.1–5.5 mmol), 5-stannylpyrimidine **1** (2.075 g, 5 mmol) and $PdCl_2(PPh_3)_2$ (0.105 g, 0.015 mmol, 3 mol %) under N_2 and the reaction was refluxed until TLC showed that all the stannylpyrimidine had reacted. The reaction mixture was cooled, diluted with light petroleum (10 ml), and treated with a saturated aqueous solution of KF. The precipitated Bu_3SnF was filtered off, washed with diethyl ether/light petroleum. The filtrate was concentrated, and the residue was purified by flash chromatography on a silica column, where necessary, followed by recrystallization from a mixture of light petroleum/ethyl acetate (unless stated otherwise).

2-Methylthio-5-(2-thienyl)pyrimidine (**7a**). EtOAc was the eluent for chromatography. M.p. 90 °C. Anal. $C_9H_8N_2S_2$: C,H. ^{1}H NMR ($CDCl_3$): δ 2.60 (SMe), 7.14 (H-4′, dd, $J_{4'5'}$ 5 Hz), 7.32 (H-3′, dd, $J_{3'4'}$ 3.7 Hz), 7.39 (H-5′, dd, $J_{3'5'}$ 1 Hz), 8.74 (s, 2 H, H-4,6). ^{13}C NMR ($CDCl_3$): δ 14.21 (SMe), 123.81 (C-5), 124.30/126.26/128.44 (C-3′,4′,5′), 136.61 (C-2′), 153.85 (C-4,6), 171.24 (C-2). MS(EI): 208 (100, M^+), 207 (16), 175 (22), 163 (14), 162 (15), 136 (21), 108 (40), 69 (16), 63 (15).

2-Methylthio-5-(3-thienyl)pyrimidine (**7b**). The eluent for chromatography was EtOAc. M.p. 135 °C. Anal. $C_9H_8N_2S_2$: C,H. ^{1}H NMR ($CDCl_3$): δ 2.60 (SMe), 7.34 (dd, H-4′, $J_{4'5'}$ 4.9 Hz), 7.47 (dd, H-5′, $J_{5'2'}$ 2.9 Hz), 7.51 (dd, H-2′, $J_{2'4'}$ 1.4 Hz), 8.74 (s, 2 H, H-4,6). ^{13}C NMR ($CDCl_3$): δ 14.03 (SMe), 121.21/124.54/125.10/127.40 (C-2′,4′,5′,5), 135.02 (C-3′), 154.35 (C-4,6), 170.81 (C-2). MS(EI): 208 (100, M^+), 207 (20), 175 (14), 162 (19), 136 (44), 122 (10), 108 (51), 82 (12), 69 (18), 63 (24).

5-(2-Furyl)-2-methylthiopyrimidine (**7c**). 1,2-Dichloroethane was used as the eluent for chromatography. M.p. 89 °C. Anal. $C_9H_8N_2OS$: C,H. ^{1}H NMR ($CDCl_3$): δ 2.59 (SMe), 6.51 (dd, H-4′, $J_{4'5'}$ 1.8 Hz), 6.71 (dd, H-3′, $J_{3'4'}$ 3.4 Hz), 7.52 (dd, H-5′, $J_{5'3'}$ 0.82 Hz), 8.78 (s, 2 H, H-4,6). ^{13}C NMR ($CDCl_3$): δ 14.00 (SMe), 106.31/111.72 (C-3′,4′), 120.19 (C-5), 143.08 (C-5′), 148.12 (C-2′), 152.03 (C-4,6), 170.69 (C-2). MS(CI−NH_3): 193 (100, M^++1), 192 (33, M^+), 159 (1.7), 147 (2.2), 146 (2.6), 118 (2.1), 92 (3.6).

5-(3-Furyl)-2-methylthiopyrimidine (**7d**). 1,2-Dichloroethane was the eluent for chromatography. M.p. 140.5 °C. Anal. $C_9H_8N_2OS$: C,H. ^{1}H NMR ($CDCl_3$): δ 2.59 (SMe), 6.67 (dd, H-4′, $J_{4'5'}$ 1.9 Hz), 7.54 (dd, H-5′, $J_{5'2'}$ 1.5 Hz), 7.77 (dd, H-2′, $J_{2'4'}$ 0.95 Hz), 8.63 (s, 2 H, H-4,6). ^{13}C NMR ($CDCl_3$): δ 13.96 (SMe), 107.87/119.76 (C-3′,4′), 121.40 (C-5), 138.58 (C-5′), 144.29 (C-2′), 153.92 (C-4,6), 170.75 (C-2). MS(EI): 192 (100, M^+), 191 (35), 159 (12), 146 (14), 120 (16), 118 (34), 92 (36), 91 (18).

5-(5-Formyl-2-thienyl)-2-methylthiopyrimidine (**7e**). On completion of the reaction, the mixture was cooled, diluted with light petroleum and the precipitated product was washed with diethyl ether and recrystallized from methanol/hexane (1:1). M.p. 158 °C. Anal. $C_{10}H_8N_2OS_2$: C,H. ^{1}H NMR ($CDCl_3$): δ 2.61 (SMe), 7.44 (d, H-3′, $J_{3'4'}$ 3.9 Hz), 7.80 (d, H-4′), 8.79 (s, 2 H, H-4,6), 9.93 (CHO). ^{13}C NMR ($CDCl_3$): δ 14.09 (SMe), 122.31 (C-5), 124.79 (C-3′), 136.96 (C-4′), 143.47/145.95 (C-2′,5′), 153.86 (C-4,6), 173.29 (C-2), 182.26 (CHO). MS(CI−NH_3): 237 (100,

M^++1), 236 (48, M^+), 220 (1), 191 (0.6), 163 (1.3), 161 (1.4), 136 (2), 135 (3.4).

5-(5-Formyl-2-furyl)-2-methylthiopyrimidine (**7f**). The product precipitated out when the reaction mixture was diluted with light petroleum and it was recrystallized from MeOH. M.p. 164 °C. Anal. $C_{10}H_8N_2O_2S$: C,H. ^{1}H NMR (CD_3CN): δ 2.58 (SMe), 7.09 (d, H-3′, $J_{3'4'}$ 3.8 Hz), 7.45 (d, H-4′), 8.94 (s, 2 H, H-4,6), 9.63 (CHO). ^{13}C NMR (CD_3CN): δ 14.50 (SMe), 110.45 (C-3′), 120.29 (C-5), 124.89 (C-4′), 154.64 (C-4,6), 153.95/154.79 (C-2′,5′), 173.96 (C-2), 178.63 (CHO). MS(CI−Isobutane): 221 (100, M^++1), 220 (24, M^+), 207 (1.1), 175 (1.1), 120 (1.2), 97 (1), 85 (3.8), 83 (2.4), 81 (2.8).

5-(5-Acetoxymethyl-2-furyl)-2-methylthiopyrimidine (**7g**). The product precipitated out when light petroleum was added to the cold reaction mixture and was further purified on a silica column with EtOAc/$CHCl_3$ (1:1) as the eluent. M.p. 124 °C. Anal. $C_{12}H_{12}N_2O_3S$: C,H. ^{1}H NMR ($CDCl_3$): δ 2.12 (s, 3 H, COMe), 2.6 (s, 3 H, SMe), 5.11 (s, 2 H, CH_2), 6.53/6.69 (2 d, H-3′,4′, $J_{3'4'}$ 3.4 Hz), 8.79 (s, 2 H, H-4,6). ^{13}C NMR ($CDCl_3$): δ 14.20 (SMe), 20.89 (COMe), 57.90 (CH_2), 107.34/112.85 (C-3′,4′), 120.04 (C-5), 148.91/150.41 (C-2′,5′), 152.32 (C-4,6), 170.54/171.26 (C-2,CO). MS(CI−NH_3): 165 (200, M^++1), 264 (24, M^+), 251 (3.6), 207 (8), 205 (23), 172 (1), 163 (0.6), 105 (2.2).

2-Methylthio-5-(2-pyridinyl)pyrimidine (**7h**). EtOAc/pentane (2:3) was the eluent used for chromatography. M.p. 122 °C (2-PrOH/pentane). Anal. $C_{10}H_9N_3S$: C,H. ^{1}H NMR ($CDCl_3$): δ 2.63 (SMe), 7.30 (m, H-5′, $J_{5'3'}$ 1.0 Hz, $J_{5'6'}$ 4.9 Hz, $J_{5'4'}$ 7.5 Hz), 7.68 (m, H-3′, $J_{3'4'}$ 7.8 Hz, $J_{3'6'}$ ≈ 1 Hz), 7.79 (m, H-4′, $J_{4'6'}$ 1.8 Hz), 8.70 (m, H-6′), 9.12 (s, 2 H, H-4,6). ^{13}C NMR ($CDCl_3$): δ 14.01 (SMe), 119.57/122.85 (C-3′,5′), 127.30 (C-5), 136.90 (C-4′), 150.05 (C-6′), 152.06 (C-2′), 155.10 (C-4,6), 172.83 (C-2). MS (CI−NH_3): 204 (100, M^++1), 203 (25, M^+), 188 (4), 170 (1.5), 157 (0.7), 130 (2), 129 (1), 104 (1.6), 95 (1).

2-Methylthio-5-(3-pyridinyl)pyrimidine (**7i**). When the reaction mixture was cooled and diluted with light petroleum, the product precipitated out and was purified on a silica column with EtOAc as the eluent. M.p. 132 °C. Anal. $C_{10}H_9N_3S$: C,H. ^{1}H NMR ($CDCl_3$): δ 2.62 (SMe), 7.45 (m, H-5′, $J_{5'6'}$ 4.6 Hz, $J_{5'2'}$ ≈ 1 Hz), 7.86 (m, H-4′, $J_{4'5'}$ 7.8 Hz, $J_{4'6'}$ 1.8 Hz), 8.7 (m, H-2′, $J_{2'6'}$ = 1 Hz), 8.75 (s, 2 H, H-4,6), 8.83 (m, H-2′). ^{13}C NMR ($CDCl_3$): δ 14.09 (SMe), 123.95 (C-5′), 126.14 (C-5,3′), 133.784 (C-4′), 147.44/149.59 (C-2′,6′), 154.96 (C-4,6), 172.57 (C-2). MS(EI): 204 (12.8, M^++1), 203 (100, M^+), 202 (80), 156 (24), 145 (4), 131 (21), 129 (5), 104 (9), 103 (30), 76 (36).

2-Methylthio-5-(4-pyridinyl)pyrimidine (**7j**). EtOAc/hexane (9:1) was the eluent used in chromatography. M.p. 141 °C. Anal. $C_{10}H_9N_3S$: C,H. ^{1}H NMR ($CDCl_3$): δ 2.62 (SMe), 7.49 (br d, H-3′,5′, $J_{3'2'}$ 5.90 Hz), 8.77 (m, H-2′,6′), 8.80 (s, 2 H, H-4,6). ^{13}C NMR ($CDCl_3$): δ 14.00 (SMe), 120.49 (C-3′,5′), 126 (C-5), 141.64 (C-4′), 150.54 (C-2′,6′), 154.81 (C-4,6), 173.42 (C-2). MS(EI): 204 (14, M^++1), 203 (100, M^+), 202 (18), 158 (10), 157 (26), 131 (8), 130 (8), 103 (15), 76 (17).

2-Methylthio-5-(2-thiazolyl)pyrimidine (**7k**). The eluent used was EtOAc/hexane (3:1). M.p. 111 °C. Anal. $C_8H_7N_3S_2$: C,H. ^{1}H NMR ($CDCl_3$): δ 2.62 (SMe), 7.42 (d, H-5′, $J_{4'5'}$ 3.3 Hz), 7.92 (d, H-4′), 9.04 (s, 2 H, H-4,6). ^{13}C NMR ($CDCl_3$): δ 14.12 (SMe), 119.30 (C-5′), 122.93 (C-5), 144.13 (C-4′), 154.35 (C-4,6), 161.68 (C-2′), 173.85 (C-2). MS(EI): 210 (8, M^++1), 209 (100, M^+), 208 (10), 194 (10), 176 (5), 164 (5), 163 (6), 136 (25), 109 (17), 105 (5).

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