Pyrimidinylpalladium(II) Complexes in the Synthesis of Alkenylpyrimidines

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Pyrimidinylpalladium(II) complexes have been prepared by oxidative addition of 4- and 5-halopyrimidines to tetrakis(triphenylphosphine)palladium(0) or tetrakis(triisopropyl phosphite)palladium(0). These complexes are used as catalysts in the synthesis of 4- and 5-alkenylpyrimidines from halopyrimidines and alkenylstannanes.

Heterocycles containing an alkenyl substituent have attracted considerable interest in recent years, e.g. as valuable monomers in polymerization reactions.[1] The purpose of this study was to synthesize alkenylpyrimidines as potential polymerization additives in dental restorative materials. It was envisaged that the alkenyl group would copolymerize with the vinyl monomer[2] in the dental composite and that a leaving group in the 2-position of the pyrimidine ring could be substituted by a nucleophilic center[3] in dentine. This would result in adhesion between dentine and resin; an intricate problem in dentistry.[3] Alkenylpyrimidines with a chloro or sulfonyl substituent in the 2-position were chosen, because these groups are easily substituted by a number of nucleophiles.[4]

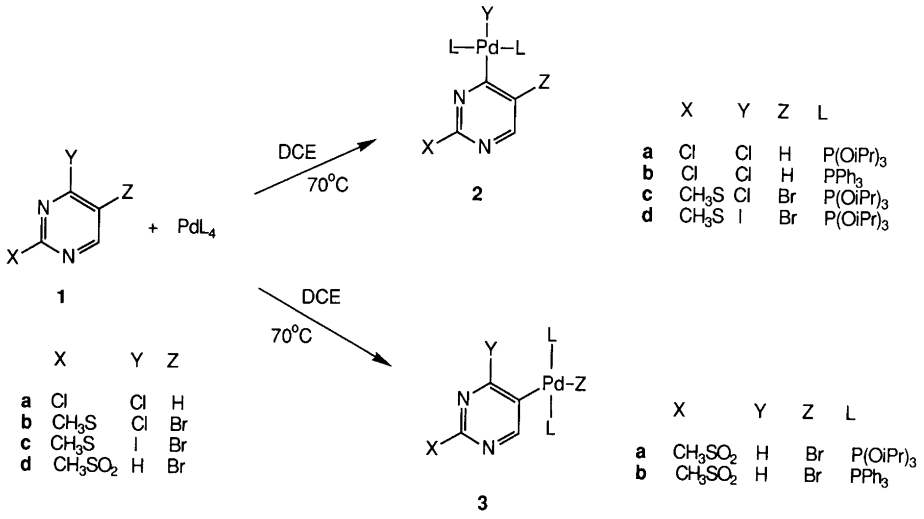
Pyrimidines with an alkenyl group have been made by condensation reactions,[1b] by modification of substituents in the pyrimidine nucleus[4b,5] or more recently by coupling reactions catalyzed by transition metals.[6] In this article 4- and 5-alkenylpyrimidines are synthesized by Pd-catalyzed coupling reactions between halopyrimidines and alkenylstannanes. Preparation of pyrimidinylpalladium(II) complexes and their use as catalysts in coupling reactions is also described. Studies in copolymerization and substitution reactions of the alkenylpyrimidines will be reported elsewhere.

Pd-catalyzed coupling reactions between aryl halides and organostannanes are believed to involve σ-bonded arylpalladium(II) complexes.[7] Such complexes have been prepared and characterized.[8] In the heterocyclic series, however, similar compounds have received much less attention.[9] Arylpalladium(II) complexes are generally prepared by oxidative addition of aryl halides to a Pd(0) compound. Thus the addition of an excess of 2-chloropyrimidine to tetrakis(triphenylphosphine)palladium(0) gives a mixture of a mononuclear and a binuclear complex.[10] We find that the halopyrimidines **1a–d** give only the mononuclear complexes **2** and **3** in good yields (Scheme 1). This difference in reactivity is probably due to the additional electron-withdrawing substituents in **1a–d** compared with 2-chloropyrimidine. The additional electron-withdrawing group reduces the donating ability of the ring nitrogens and hence the tendency to form binuclear complexes.

Triisopropyl phosphite and triphenylphosphine were used as ligands in the Pd(0) complexes. The latter seems to give the more reactive complex. Thus the Pd(II) complex from 2,4-dichloropyrimidine (**2b**) was formed within 2 h using tetrakis(triphenylphosphine)palladium(0), whereas formation of the complex **2a** using tetrakis(triisopropyl phosphite)palladium(0) requires 24 h for completion. The same pattern was observed with 5-bromo-2-methylsulfonylpyrimidine. By analogy with similar complexes the geometry of the phosphine/phosphite ligands is assigned to be *trans*.[10] A *trans* geometry is also indicated by a 1:2:1 triplet pattern of the ^{13}C NMR signal for the Pd carbon.

The mononuclear complexes seem only to be formed cleanly in 1,2-dichloroethane (DCE) at 70 °C from pyrimidines in which at least two electron-withdrawing groups are present. Thus 2,4-dichloropyrimidine (**1a**) forms Pd complexes both with tetrakis(triphenylphosphine)palladium(0) and tetrakis(triisopropyl phosphite)palladium(0), but 4-chloro-2-methylthiopyrimidine (**8a**) gives a mixture with both complexes. Introduction of an electron-withdrawing substituent into the 5-position (**1b**), permits the clean formation of the mononuclear product. Some kind of palladium complex is evidently formed in the case of 4-chloro-2-methylthiopyrimidine (**8a**) since reaction with tributylethenylstannane in the presence of tetrakis(triphenylphosphine)palladium(0) as the catalyst gives the corresponding vinylpyrimidine **7a** in good yield (Scheme 3). Replacement of the methylsulfonyl group in **1d** by a methylthio group also resulted in a reduced tendency to form a mononuclear Pd(II) complex.

In the case of 2,4-dichloropyrimidine (**1a**) complex formation takes place only in the 4-position. This is in accordance with the observations that nucleophilic substitution is easier in the 4-position than in the 2-position in 2,4-dichloropyrimidine.[11] The regiochemistry was proved by reaction of the complex **2b** with 1 equiv. of tributylphenylstannane.

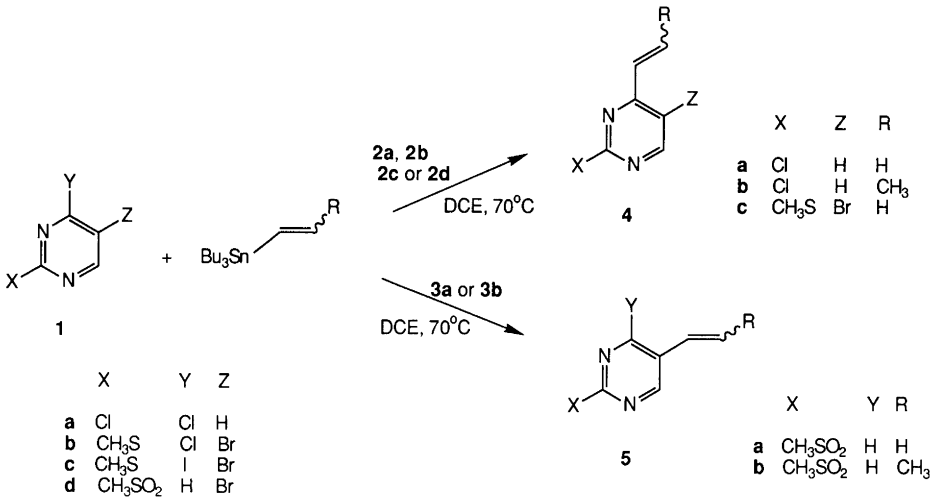


Scheme 1.

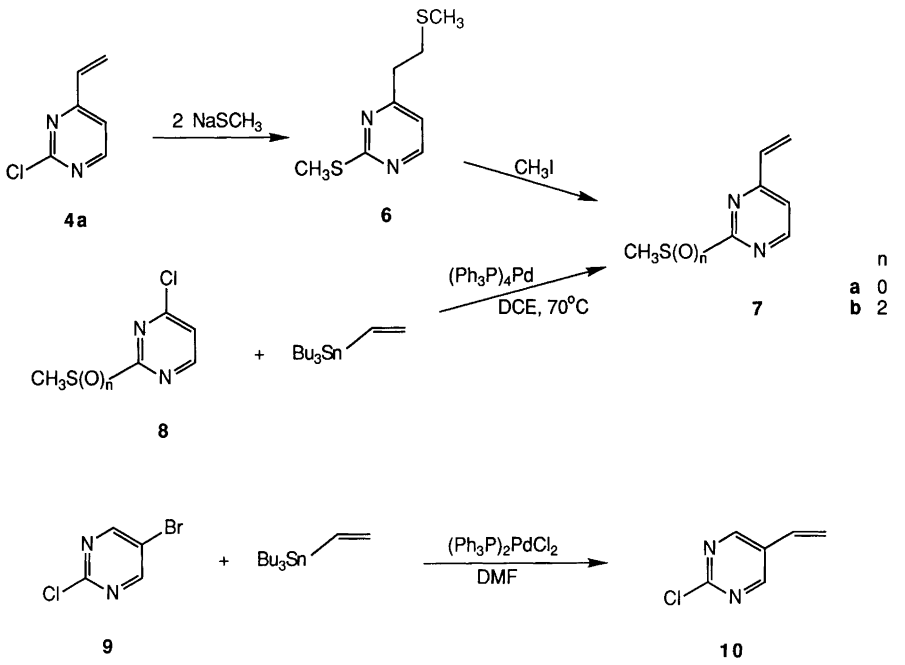
The only isomer found was 2-chloro-4-phenylpyrimidine[12] (82 % yield). The high reactivity of a 4-halo substituent is also demonstrated in the reaction of **1b** and **1c** with palladium(0). The 4-iodo substituent in **1c** reacts, as expected, more rapidly than the 5-bromo substituent, but the 4-chloro substituent in **1b** is also more reactive than the 5-bromo substituent in this reaction.

The pyrimidinylpalladium(II) complexes **2** or **3** were used as catalysts in the coupling reactions of the halopyrimidines **1** with alkenylstannanes. The reactions were run in DCE at 70 °C with 5 mol % of the catalyst (Scheme 2).

The regiochemistry in the coupling reactions of the dihalopyrimidines **1a–1c** with alkenylstannanes, was exclusive coupling in the 4-position. This is also as expected.[4c] In the case of **1a** the regiochemistry was established by transformation of 2-chloro-4-vinylpyrimidine (**4a**) into 2-methylthio-4-vinylpyrimidine (**7a**) (Scheme 3). Two equivalents of sodium methanethiolate had to be used in order to effect substitution in the 2-position, because the methanethiolate also added to the vinyl group. In fact, it could be shown that addition to the vinyl group was faster than substitution of the 2-chloro group. The identity of 2-methylthio-4-vinylpyrimidine (**7a**) was proved by a separate synthesis from 4-chloro-2-methylthiopyrimidine (**8a**) (Scheme 3). The formation of dicoupled products from the dihalocompounds **1a–1c** was no problem using 1.2 equiv. of the alkenylstannane. Even 2.7 equiv. tributylethenylstannane and **1a** gave, after reflux in DCE for 24 h, only a small amount of 2,4-divinylpyrimidine. Change of solvent to toluene and heating at 120 °C for 24 h resulted in formation of polymeric material, and the 2,4-divinylpyrimidine was isolated in low yield (20 %). A high degree of selectivity has also been observed in the coupling of 1,4-dibromobenzene with tributylethenylstannane.[13] The coupling reaction of 2,4-dichloropyrimidine (**1a**) and tributylethenylstannane using the pyrimidinylpalladium(II) complex (**2b**) as catalyst, was complete in 2 h at 70 °C in DCE. The same reaction using tetrakis(triphenylphosphine)palladium(0) as the catalyst was only 33 % complete (GLC) after 5 h under the same conditions. In the reaction of 5-bromo-2-methylsulfonyl-



Scheme 2.



Scheme 3.

pyrimidine (**1d**), however, there was no significant difference in reaction rate using the pyrimidinylpalladium(II) complex **3b** or tetrakis(triphenylphosphine)palladium(0). This indicates that reduction of the phosphine ligand may be beneficial in some of these reactions, but unimportant in others.

Although the pyrimidinylpalladium(II) complexes **2** and **3** seem to be efficient catalysts in coupling reactions of halopyrimidines with alkenylstannanes, vinylpyrimidines can also be made using tetrakis(triphenylphosphine)palladium(0) or bis(triphenylphosphine)palladium(II) dichloride as catalysts (Scheme 3).

Experimental

The ^1H and the ^{13}C NMR spectra were recorded in $CDCl_3$ at 300 and 75 MHz, respectively, unless otherwise specified. The mass spectra under electron impact conditions were recorded at 70 eV ionizing voltage. Ammonia was used for chemical ionization (CI) mass spectra.

Starting material available by literature methods. 5-Bromo-4-chloro-2-methylthiopyrimidine,[14] 5-bromo-2-chloropyrimidine,[15] 5-bromo-4-iodo-2-methylthiopyrimidine,[16] 2,4-dichloropyrimidine,[17] 4-chloro-2-methylsulfonylpyrimidine,[18] 4-chloro-2-methylthiopyrimidine,[19] tributyl(1-propenyl)stannane,[20] tris(triisopropyl phosphite)palladium.[21]

General procedure for the synthesis of the pyrimidinylpalladium(II) complexes **2** *an* **3**. The halopyrimidine **1** (0.5 mmol) and the Pd(0) catalyst (0.5 mmol) were dissolved in 1,2-dichloroethane (DCE, 3 ml). The mixture was heated at 70 °C under N_2 until all starting material was consumed according to TLC (**2a** 6 h, **2b** 3 h, **2c** 36 h, **2d** 18 h, **3a** 6 h, **3b** 5 h). The solvent was evaporated and the complexes were purified by chromatography on silica or by recrystallization.

2-Chloro-4-[chlorobis(triisopropyl phosphite)palladio]pyrimidine (**2a**). Hexane/EtOAc 10:1 was used for flash chromatography. The product was heated in a 'cold finger' at 50 °C/10 mmHg for 2–3 h to remove traces of unchanged 2,4-dichloropyrimidine. Yield: 53%, m.p. 72 °C. Anal. $C_{22}H_{44}Cl_2N_2O_6P_2Pd$: C, H. ^1H NMR: δ 1.24 (36 H, d, *J* 6.3 Hz), 4.9–5.1 (6 H, m), 7.20 (1 H, d, *J* 5.1 Hz), 7.75 (1 H, ddd, *J* 2.1, 2.1 and 5.1 Hz). ^{13}C NMR: δ 23.8, 70.6, 130.7 (t, *J* 8.3 Hz), 151.0, 157.0, 196.6. MS (CI): 677 (M^++6, 2.6), 676 (M^++5, 1.9), 675 (M^++4, 7.8), 674 (M^++3, 3.7), 673 (M^++2, 11.4), 671 (M^+, 9.6), 670 (M^+−1, 5.8), 669 (M^+−2, 2.6), 561 (2), 559 (3), 558 (2), 557 (3), 556 (2), 555 (1), 391 (4), 357 (10), 210 (27), 209 (100).

2-Chloro-4-[chlorobis(triphenylphosphine)palladio]pyrimidine (**2b**). The crude product was purified by being washed with diethyl ether. Yield: 67%, m.p. 230–240 °C (decomp.). Anal. $C_{40}H_{32}Cl_2N_2P_2Pd$: C, H. ^1H NMR: δ 6.68 (1 H, d, *J* 5.1 Hz), 6.85 (1 H, d, *J* 5.1 Hz), 7.2–7.4 (18 H, m), 7.6–7.7 (12 H, m). ^{13}C NMR: δ 128.1, 129.7, 130.0, 130.3, 130.8 (t, *J* 8 Hz), 134.3, 134.4, 134.5, 151.0, 156.7, 203.4. MS: 263 (Ph_3P +1, 100), 262 (31), 261 (40), 183 (14), 108 (6), 107 (6), 78 (10), 77 (5).

5-Bromo-4-[chlorobis(triisopropyl phosphite)palladio]-2-methylthiopyrimidine (**2c**). Hexane/EtOAc 14:1 was used for flash chromatography. Yield: 57%, m.p. 117–118 °C (light

petroleum). Anal. $C_{23}H_{46}BrClN_2O_6P_2PdS$: C, H. ^1H NMR: 1.21 (18 H, d, *J* 6.3 Hz), 1.27 (18 H, d, *J* 6.0 Hz), 2.48 (3 H, s), 5.0–5.1 (6 H, m), 7.93 (1 H, t, *J* 2.3 Hz). ^{13}C NMR: δ 24.0, 70.6, 127.6 (t, *J* 6.7 Hz), 150.8, 165.0, 194.7 (t, *J* 13.0 Hz). MS(CI): 767 (M^++7, 1.6), 766 (M^++6, 1.0), 765 (M^++5, 3.4), 764 (M^++4, 1.7), 763 (M^++3, 3.4), 762 (M^++2, 2.5), 761 (M^++1, 2.8), 760 (M^+, 1.3), 725 (M^+−Cl, 1), 357 (10), 210 (40), 209 (100), 156 (40), 140 (11).

5-Bromo-4-[iodobis(triisopropyl phosphite)palladio]-2-methylthiopyrimidine (**2d**). Hexane/EtOAc 14:1 was used for flash chromatography. Yield: 70 %, m.p. 84 °C. Anal. $C_{23}H_{46}BrIN_2O_6P_2PdS$: H. Calc C 32.35. Found 33.02. ^1H NMR: δ 1.21 (18 H, d, *J* 6.1 Hz), 1.27 (18 H, d, *J* 6.1 Hz), 2.48 (3 H, s), 4.9–5.1 (6 H, m), 7.95 (1 H, t, *J* 2.4 Hz). ^{13}C NMR: δ 23.8, 71.0, 127.6 (t, *J* 6.6 Hz), 151.0, 165.1, 198.5 (t, *J* 16.5 Hz). MS(CI): 357 (3), 331 (1), 291 (14), 251 (2), 209 (100), 167 (17), 127 (6).

5-[Bromobis(triisopropyl phosphite)palladio]-2-methylsulfonylpyrimidine (**3a**). Hexane/EtOAc 20:7 was used for flash chromatography. Yield: 44 %, m.p. 150 °C (decomp.). Anal. $C_{23}H_{47}BrN_2O_8P_2PdS$: H. Calc C 36.34. Found C 37.24. ^1H NMR: δ 1.02 (36 H, d, *J* 9.0 Hz), 3.04 (3 H, s), 4.7–4.8 (6 H, m), 8.42 (2 H, s). ^{13}C NMR: δ 23.8, 39.7, 71.2, 153.9, 161.2, 162.4 (t, *J* 4.8 Hz).

5-[Bromobis(triphenylphosphine)palladio]-2-methylsulfonylpyrimidine (**3b**). The crude product was purified by being washed with diethyl ether. Yield: 99 %, m.p. 220–240 °C (decomp.). Anal. $C_{41}H_{35}BrN_2O_2P_2PdS$: C, H. ^1H NMR: δ 2.97 (3 H, s), 7.2–7.7 (36 H, m), 7.94 (2 H, d, *J* 2.1 Hz). ^{13}C NMR: δ 39.6, 128.28, 128.35, 128.42, 128.50, 130.6, 134.20, 134.28, 134.37, 134.46, 161.7 (t, *J* 4.0 Hz), 162.0 (t, *J* 4.1 Hz). MS(CI): 280 (Ph_3P+18, 25), 263 (Ph_3P+1, 100), 262 (24), 261 (4), 183 (15), 154 (4), 108 (8), 107 (9), 78 (29), 77 (15).

General procedure for the synthesis of the vinylpyrimidines **4** *and* **5**. The alkenylstannane (1.1 mmol) was added to a mixture of the halopyrimidine **1** (1.0 mmol) and the corresponding pyrimidinylpalladium(II) complex (**2** or **3**, 0.05 mmol) in DCE (2 ml). The mixture was heated at 70 °C under N_2 until the reaction was complete according to TLC. (**4a** 24 h with **2a**, **4a** 2 h with **2b**, **4b** 24 h, **4c** 24 h, **5a** 9 h with **3a**, **5a** 2 h with **3b**, **5b** 24 h). The solvent was evaporated, the residue washed with light petroleum and purified by recrystallization or chromatography on silica.

2-Chloro-4-vinylpyrimidine (**4a**). Hexane/EtOAc 5:1 was used for flash chromatography. Yield: 85 % with **2a**, 94 % with **2b**. Oily substance. Mol wt. Found 152.0148. Calc. for $C_7H_5ClN_2$: 152.0140. ^1H NMR: δ 5.80 (1 H, dd, *J* 0.9, *J* 10.5 Hz), 6.54 (1 H, dd, *J* 0.9, 17.4 Hz), 6.71 (1 H, dd, *J* 10.5, 17.4 Hz), 7.23 (1 H, d, *J* 5.1 Hz), 8.57 (1 H, d, *J* 5.1 Hz). ^{13}C NMR: δ 116.4, 125.3, 133.8, 159.9, 161.6, 165.5. MS: 142 (M^++2, 15), 140 (M^+, 52) 139 (18), 116 (7), 114 (26), 105 (98), 103 (7), 88 (20), 87 (4), 79 (100).

2-Chloro-4-(1-propenyl)pyrimidine (**4b**). Hexane/EtOAc 5:1 was used for flash chromatography. Yield: 83 %. Oily substance. ^1H NMR: δ 1.98 (3 H, dd, *J* 1.8, 6.9 Hz), 6.40 (1 H, dq, *J* 1.8, 15.3 Hz), 7.09 (1 H, d, *J* 5.1 Hz), 7.15 (1 H, dq, *J* 6.9, 15.3 Hz), 8.48 (1 H, d, *J* 5.1 Hz). ^{13}C NMR: δ 18.5, 115.8, 128.2, 130.0, 159.2, 161.3, 165.7. MS(CI): 172 (M^++18,1), 158 (4), 157 (M^++3, 39), 157 (M^++2, 13), 155 (M^++1, 100), 154 (10), 153 (6), 121 (6), 119 (2).

5-Bromo-2-methylthio-4-vinylpyrimidine (**4c**). Hexane/EtOAc 20:1 was used for flash chromatography. Yield: 55 % with **2c**, 64 % with **2d**. Oily substance. ^1H NMR: δ 2.57 (3 H, s), 5.78 (1 H, dd, *J* 2.0, 10.2 Hz), 6.75 (1 H, dd, *J* 2.0, 16.8 Hz), 7.08 (1 H, dd, *J* 10.2, 16.8 Hz), 8.42 (1 H, s). ^{13}C NMR: δ 29.6, 125.9, 131.5, 158.9, 159.4, 170.5. MS (CI): 233 (M^++3, 99), 231 (M^++1, 100), 230 (M^+, 7), 154 (6), 153 (51), 151 (5).

2-Methylsulfonyl-5-vinylpyrimidine (**5a**). Hexane/EtOAc 1:1 was used for flash chromatography. Yield: 48 % with **3a**, 90 % with **3b**, m.p. 88 °C. Anal. $C_7H_8N_2O_2S$: C, H. ^1H NMR: δ 3.45 (3 H, s), 5.70 (1 H, d, *J* 11 Hz), 6.07 (1 H, d, *J* 17 Hz), 6.82 (1 H, dd, *J* 11, 17 Hz).

2-Methylsulfonyl-5-(1-propenyl)pyrimidine (**5b**). The crude product was purified by being washed with diethyl ether. Yield: 86 %, m.p. 94–96 °C. Mol wt. Found 198.0468. Calc. for $C_8H_{10}N_2O_2S$: 198.0463. ^1H NMR: δ 1.01 (2 H, d, *J* 6.6 Hz), 3.35 (3 H, s), 6.42 (1 H, d, *J* 16.1 Hz). 6.61 (1 H, dd, *J* 6.6, 16.1 Hz), 8.83 (2 H, s). ^{13}C NMR: δ 18.9, 39.4, 122.8, 133.5, 134.8, 154.8, 157.6. MS: 198 (M^+, 27), 136 (20), 135 (100), 121 (14), 119 (36), 108 (12), 94 (11), 92 (51).

2-Methylthio-4-vinylpyrimidine (**7a**) *from* **4a**. Sodium methanethiolate (82 mg, 1.20 mmol) in ethanol (1 ml) was added to a solution of 2-chloro-4-vinylpyrimidine (74 mg, 0.53 mmol) in ethanol (1 ml) at 0 °C. The mixture was stirred at ambient temperature for 4 h, before water was added. The product was extracted into diethyl ether, dried ($MgSO_4$) and evaporated to give 2-methylthio-4-(2-methylthioethyl)pyrimidine (**6**) [^1H NMR (60 MHz): δ 2.17 (3 H, s), 2.59 (3 H, s), 2.94 (4 H, br s), 6.90 (1 H, d, *J* 5 Hz), 8.47 (1 H, d, *J* 5 Hz)]. To the crude product in toluene was added diisopropylethylamine (129 mg, 1.0 mmol) and methyl iodide (0.5 ml, 8 mmol). The mixture was heated at 50 °C for 4 h, the solvent evaporated and the title compound isolated by chromatography on silica (Hexane/EtOAc 15:2. Yield: 10 mg (13 %). Oily substance. ^1H NMR: δ 2.59 (3 H, s), 5.68 (1 H, dd, *J* 1.5, 10.5 Hz), 6.48 (1 H, dd, *J* 1.5, 17.4 Hz), 6.67 (1 H, dd, *J* 10.5, 17.4 Hz), 6.91 (1 H, d, *J* 5.1 Hz), 8.46 (1 H, d, *J* 5.1 Hz). ^{13}C NMR: δ 13.9, 113.1, 123.2, 134.8, 157.4, 162.2. MS: 152 (M^+, 100), 151 (25), 106 (49), 79 (40), 52 (29), 51 (25), 44 (43).

2-Methylthio-4-vinylpyrimidine (**7a**) *from* **8a**. A mixture of 4-chloro-2-methylthiopyrimidine (161 mg, 1.0 mmol), tributylethenylstannane (380 mg, 1.2 mmol) and tetrakis(triphenylphosphine)palladium(0) (58 mg, 0.05 mmol) was heated at 70 °C under N_2 in DCE (2.5 ml) for 48 h. The solvent was evaporated off and the residue triturated with light petroleum. The crude compound was purified by chromatography on silica (hexane/EtOAc 10:1). Yield: 140 mg (92 %).

2-Methylsulsulfonyl-4-vinylpyrimidine (**7b**) was prepared as **7a** above from 4-chloro-2-methylsulfonylpyrimidine. Hexane/EtOAc 1:1 was used for flash chromatography. Oily substance. Yield: 49 %. ^{1}H NMR: δ 3.39 (3 H, s), 5.89 (1 H, d, *J* 10.5 Hz), 6.65 (1 H, d, *J* 17.4 Hz), 6.86 (1 H, dd, *J* 10.5, 17.4 Hz), 7.49 (1 H, d, *J* 5.1 Hz), 8.85 (1 H, d, *J* 5.1 Hz). ^{13}C NMR: δ 39.1, 120.3, 127.5, 133.5, 159.0, 164.4.

2-Chloro-4-vinylpyrimidine (**10**). A mixture of 5-bromo-2-chloropyrimidine (386 mg, 2.0 mmol), tributylethenylstannane (696 mg, 2.2 mmol) and bis(triphenylphosphine)palladium(II) chloride was stirred together in DCE (5 ml) at 80 °C for 6 h. Diethyl ether was added and the tributylstannyl chloride converted into the fluoride with aqueous KF. The crude product was purified by chromatography on silica (hexane/EtOAc 10:3). Yield: 171 mg (61 %), m.p. 38–40 °C. Anal. $C_6H_5ClN_2$: C, H. ^{1}H NMR: δ 5.56 (1 H, d, *J* 11.1 Hz), 5.94 (1 H, d, *J* 17.7 Hz), 6.65 (1 H, dd, *J* 11.1, 17.7 Hz), 8.65 (1 H, s). ^{13}C NMR: δ 119.1, 128.6, 129.4, 156.6, 159.8. MS: 142 (M^++2, 21) 140 (M^+, 45), 115 (4), 113 (13), 105 (13), 104 (11), 95 (17), 69 (100).

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