SYNTHESIS OF PYRIMIDINYL TRIFLATES AND PALLADIUM-CATALYZED COUPLING WITH ORGANOTIN AND ORGANOZINC REAGENTS §

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Abstract - Pyrimidinyl triflates have been synthesized from pyrimidinones using triflic anhydride in the presence of triethylamine. The triflates, in the pyrimidine electrophilic positions, are versatile intermediates for substitution reactions. Carbon substituents are readily introduced in any position by Pd-catalyzed coupling reactions between pyrimidinyl triflates and aryl- or alkenyltin or with the corresponding organozinc reagents. Organozinc reagents are generally more reactive in coupling reaction and will effect the introduction of alkyl substituents.

Perfluorosulfonic esters, especially trifluoromethanesulfonates (triflates) are important reagents in organic synthesis,[1] such as the use of aryl triflates in transition metal catalyzed cross-coupling reactions with a variety of organometallic reagents, e.g. organostannanes.[2] The corresponding heteroaryl triflates have hardly been investigated.[3] We have recently reported on the synthesis and use of a heteroaryl ditriflate.[4] Generally, inorganic halides, e.g. LiCl, were needed for the coupling reaction of aryl triflates with organostannanes to proceed.[5] Addition of zinc chloride has also been found to improve reactivity, presumably because of in situ formation of the corresponding organozinc derivative.[6] In fact, organozinc reagents are generated from organolithium or organomagnesium compounds by transmetallation with a zinc salt.[7] These organozinc derivatives have been cross-coupled with aryl halides under the influence of Pd- or Ni-catalysis to form unsymmetrical biaryls and heteroaryl-aryls.[8] Alkyl groups can be readily transferred from alkylzinc reagents.[7] Ni- or Pd-Catalyzed coupling between halopyrimidines and Reformatsky reagents ($ZnBrCH_2CO_2Et$), and with remote Reformatsky reagents [$ZnBr(CH_2)_nCO_2Et$, n = 2-4], have been reported.[9]

Development of convenient methodology for the introduction of carbon substituents into pyrimidines and their fused homologs is of importance because pyrimidine derivatives frequently possess a desired physiological activity. Pd-Catalyzed coupling reactions in pyrimidines have been the subject of recent reviews.[10] We have previously reported the preparation of stannylpyrimidines and their use in Pd-catalyzed coupling reactions with

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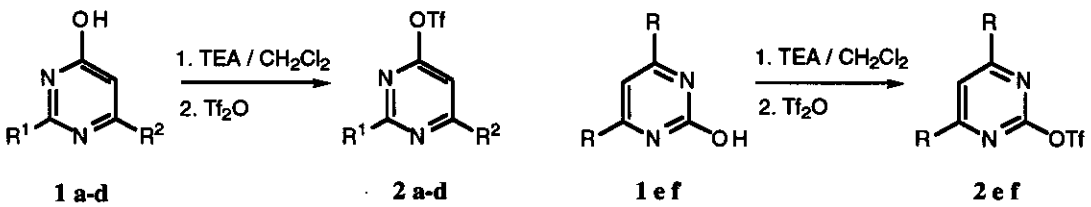
§ Dedicated to Professor Alan R. Katritzky on the occasion of his 65th birthday.

organic halides.[11] The reverse reaction, coupling of halopyrimidines with organostannanes,[10] has also been studied. Instead of halopyrimidines, we herein describe investigations on pyrimidinyl triflates and their coupling reactions with organostannanes and organozinc reagents.

RESULTS AND DISCUSSION

In the synthesis of pyrimidinyl triflates, lithium diisopropylamide (LDA), triethylamine and sodium hydride were all found to be suitable bases. Both N-phenyl-trifluoromethanesulfonimide ($PhNTf_2$) and triflic anhydride (Tf_2O) could be used as triflating agents.[12] With 2-methylthio-4(1H)-pyrimidinone (**1a**) and Tf_2O in the presence of triethylamine (TEA) the triflate (**2a**) was formed (76 %). When $PhNTf_2$ was used compound (**2a**) was isolated in lower yield (44 %) because of the added problems of separation from the co-product N-phenyl-N-trifluoromethanesulphonylamine (PhNHTf). Therefore, the pyrimidinyl triflates (**2a-f**) (Scheme 1) were most conveniently synthesized from the corresponding pyrimidinones using triflic anhydride and triethylamine in dichloromethane at -78 °C to 0 °C; isolated yields 35 - 90 %. The triflates were sufficiently stable for purification by column chromatography on silica gel with dichloromethane as eluent and by bulb-to-bulb distillation.



a R^1 = MeS, R^2 = H

b R^1 = MeS, R^2 = OH, **2 b** R^2 = OTf

c R^1 = MeS, R^2 = Me

d R^1 = Me, R^2 = Me

e R = H

f R = Me

Scheme 1

In the Pd-catalyzed cross-coupling studies, the triflates were reacted with organostannanes (Table 1) and organozinc reagents (Table 2). With alkenyl- and arylstannanes an equimolar amount of triflate and stannane was heated with tetrakis(triphenylphosphine)palladium [$Pd(PPh_3)_4$] (3 mol %) and LiCl (3 equivalents) in dioxane. Reaction of the triflates (**2a, c and e**) with alkenyltri-n-butylstannane gave the alkenylpyrimidines (**3a-e**) (57 - 93 %). trans-Styryltri-n-butylstannane resulted in the corresponding trans-styrylpyrimidine without any isomerized product, in keeping with previous reports.[2a] With 2-thienyltri-n-butylstannane, triflates (**2b, c and e**) furnished the thienyl derivatives (**3f, g and h**) (67 - 88 %).

Organozinc reagents were available from aryl bromides by treatment with n-BuLi at -78 °C for 1 h followed by

the addition of 1 M anhydrous zinc bromide in THF. The reaction of pyrimidinyl triflates (**2a-f**) with arylzinc bromides and Pd(0)-catalysis provided the coupling products (**4a-h**) (55 - 96 %). Work-up and purification of these reaction mixtures were simpler than with organostannanes since the inorganic zinc salts are more readily removed than trialkylstannyl halides. In the absence of the catalyst no product was formed.

Coupling of Pyrimidinyl Triflates with Organostannanes.

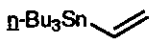
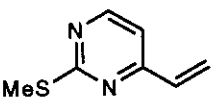
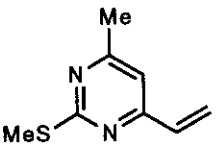
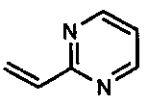
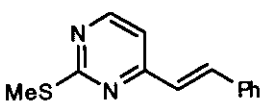
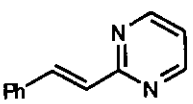
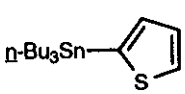
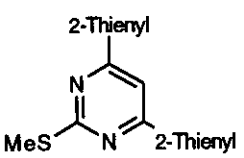
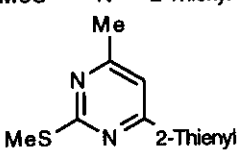
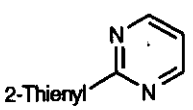
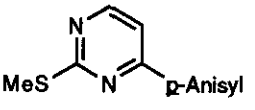
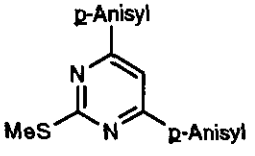
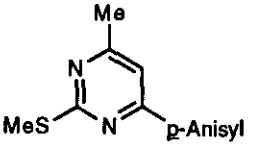
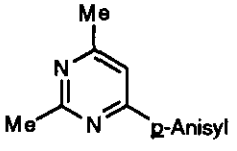
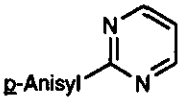
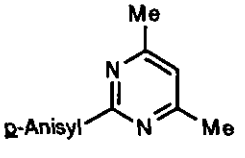
Triflate	Stannane	Time(h)	Product	Yield(%)
2 a		2	**3 a** 	93
2 c	"	1	**3 b** 	60
2 e	"	10	**3 c** 	68
2 a		2	**3 d** 	68
2 e	"	3	**3 e** 	57
2 b		10	**3 f** 	73
2 c	"	1	**3 g** 	88
2 e	"	10	**3 h** 	67

Table 1

Pyrimidinyl triflates have comparable reactivity as chloropyrimidines in the Pd-catalyzed coupling reactions. With p-anisylzinc bromide, the coupling product (**4a**) was formed in 78 % yield from 4-chloro-2-methylthiopyrimidine, while it was formed in 87 % from the triflate (**2a**) under the same conditions. The coupling product (**4e**) was obtained in 85 % yield when 2-chloropyrimidine was reacted with p-anisylzinc bromide, and in 86 % yield from 2-pyrimidinyl triflate (**2e**).

Vinylzinc bromide, generated from vinylmagnesium bromide and zinc bromide, was reacted with triflates (**2c**) and (**2e**) to give the coupling products (**3b** and **3c**) in 45 and 93 % yield respectively. The yield of 2-vinylpyrimidine (**3c**) using the zinc reagent is higher (93 %) than from vinyltri-n-butylstannane (68 %). Similarly, 6-methyl-2-methylthio-4-(2-thienyl)pyrimidine (**3g**) was formed in 88 % yield from the stannyl reagent and in 94 % using 2-thienylzinc bromide.

Coupling of Pyrimidinyl Triflates with Organozinc Reagents.

Triflate	RZnBr	Time(h)	Product		Yield (%)
2 a	p-Anisyl	1.5	**4 a**		87
2 b	"	1.5	**4 b**		89
2 c	"	1.5	**4 c**		76
2 d	"	1.0	**4 d**		55
2 e	"	1.0	**4 e**		86
2 f	"	1.0	**4 f**		96

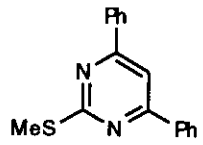
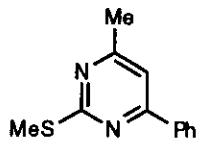
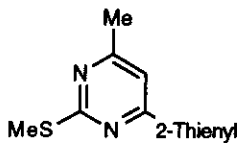
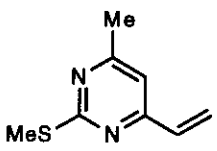
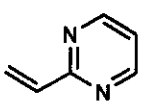
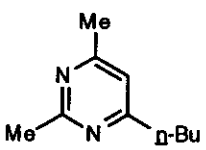
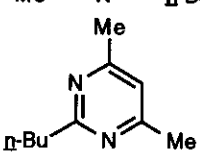
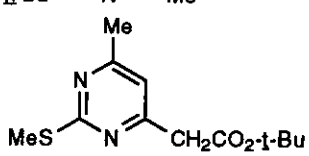
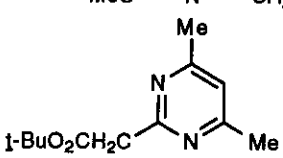
2 b	Phenyl	2.0	**4 g**		82
2 c	"	1.5	**4 h**		73
2 c	2-Thienyl	1.0	**3 g**		94
2 c	Vinyl	1.0	**3 b**		45
2 e	"	1.0	**3 c**		93
2 d	n-Bu	2.0	**4 i**		21
2 f	"	2.0	**4 j**		71
2 c	CH_2CO_2-t-Bu	2.0	**4 k**		31
2 f	"	2.0	**4 l**		37

Table 2

Next, n-butylzinc bromide, formed from n-BuLi and $ZnBr_2$, was coupled with pyrimidinyl triflates (**2d, f**). While the yield of the 4-n-butylpyrimidine (**4i**) was low (21 %), 2-n-butylpyrimidine (**4j**) was formed in 71 % yield. The coupling products (**4k, l**) (yields 31 and 37 % respectively) were obtained when the Reformatsky reagent, $ZnBrCH_2CO_2$-t-Bu, was reacted with the pyrimidinyl triflates (**2c, f**). Although the yields of alkyl-substituted pyrimidines were modest, these reactions demonstrate that it is possible to introduce alkyl substituents into the 2- and 4/6-positions of pyrimidine using pyrimidinyl triflates and organozinc reagents.

In conclusion, we have shown that pyrimidinyl triflates (**2a-f**) are readily formed from pyrimidinones using triflic anhydride in the presence of triethylamine. The triflates are suitable substrates for the Pd-catalyzed coupling with selected organostannanes and organozinc reagents. The latter react under milder conditions than the former to provide 2- and 4/6-substituted pyrimidines. Since the reaction using organozinc derivatives occurs at lower temperatures than that for the stannanes, possible decomposition of starting triflate is reduced. Work-up and purification are simpler with organozinc reagents. Their use also avoids the presence of toxic stannyl by-products making these reagents more attractive for synthesizing 2- and 4/6-substituted pyrimidines.

EXPERIMENTAL

^1H Nmr spectra were recorded at 200 or 300 MHz , ^{13}C nmr spectra at 50 or 75 MHz. Mass spectra were recorded at 70 eV ionizing voltage. Ammonia was used for chemical ionization (CI). Ms spectra are presented as *m/z* (*% rel. int.*). *THF used in the reactions was* dried by distillation over metallic sodium/benzophenone, dichloromethane distilled over calcium hydride and DMF was first shaken with NaOH pellets, then distilled over BaO. $MgSO_4$ was the drying agent used. Tri-n-butylvinylstannane, 2-mercapto-4(1H)-pyrimidinone, 2(1H)-pyrimidinone, 2-mercapto-6-methyl-4(1H)-pyrimidinone, 6-hydroxy-2-methylthio-4(1H)-pyrimidinone, 2,6-dimethyl-4(1H)-pyrimidinone and 4,6-dimethyl-2(1H)-pyrimidinone are commercially available.

Starting materials prepared by literature methods 2-Methylthio-4(1H)-pyrimidinone,[13] 6-methyl-2-methylthio-4(1H)-pyrimidinone,[13] β-styryltri-n-butylstannane,[14] and 2-thienyltri-n-butylstannane.[15]

General method for triflating pyrimidinones Pyrimidinone (10 mmol) and triethylamine (1.01 g, 10 mmol) were dissolved in CH_2Cl_2 (50 ml) and stirred for 1-8 h at - 78 °C / 0 °C before the triflating agent (Tf_2O) (2.82 g, 10 mmol) was added. The reaction mixture was stirred for a further 2-24 h and allowed to come to ambient temperature, washed (H_2O), dried ($MgSO_4$) and purified by chromatography on a silica gel column with CH_2Cl_2 or $CHCl_3$ as eluent followed by distillation of the product.

2-Methylthio-4-pyrimidinyl triflate (**2a**) A mixture of 2-methylthio-4(1H)-pyrimidinone (1.42 g, 10 mmol) and LDA (10 mmol in THF) was stirred together at -78 °C for 2 h before $PhNTf_2$ (3.58 g, 10 mmol) was introduced, and the mixture was stirred at 0 °C overnight. Ether was added, the mixture was washed (H_2O) and dried. Purification was by chromatography using Et_2O/light petroleum (1:1) to give a mixture of compound (**2a**) (1.2 g, 44 %) and PhNHTf (44 %) as identified by GCms and nmr. When the same reaction was repeated with Tf_2O (2.82g, 10 mmol) as triflating agent, the yield of **2a** was 2.08 g (76 %) after silica gel chromatography with

CH_2Cl_2 as eluent and Kugelrohr distillation, bp 100 °C / 0.005 mmHg. ^1H Nmr ($CDCl_3$, 300 MHz): δ 8.64 (d, 1H, $J_{6,5}$ 5.4 Hz), 6.81 (d, 1H, H-5, $J_{5,6}$ 5.4 Hz), 2.57 (s, 3H, SMe). ^{13}C Nmr ($CDCl_3$, 75 MHz): δ 174.68 (C-2), 162.26 (C-4), 161.02 (C-6), 118.29 (q, CF_3, $J_{C,F}$ 320.5 Hz), 105.34 (C-5), 14.02 (SMe). Ms (EI): 274 (22, M$^+$), 141 (100), 95 (74), 92 (16), 82 (28), 69 (87). Anal. Calcd for $C_6H_5N_2O_3F_3S_2$: C 26.28, H 1.84. Found: C 26.47, H 1.98.

2-Methylthio-4,6-pyrimidinyl ditriflate (**2b**) 6-Hydroxy-2-methylthio-4(1H)-pyrimidinone (1.52 g, 10 mmol), triethylamine (2.02 g, 20 mmol) and CH_2Cl_2 (100 ml) were stirred together for 1 h at 0 °C, then Tf_2O (5.64 g, 20 mmol) was added and stirring continued for a further 1 h. Work up and purification with CH_2Cl_2 as eluent for chromatography resulted in 3.08 g (73 %) of product (**2b**); bp 150 °C / 0.004 mmHg. ^1H Nmr ($CDCl_3$, 300 MHz): δ 6.56 (s, 1H, H-5), 2.57 (s, 3H, SMe). ^{13}C Nmr ($CDCl_3$, 75 MHz): δ 175.97 (C-2), 164.13 (C-4,6), 118.48 (q, CF_3, $J_{C,F}$ 322 Hz), 95.11 (C-5), 14.53 (SMe). Ms (EI): 422 (22, M$^+$), 289 (33), 243 (21), 179 (11), 156 (26), 113 (13), 69 (100). Anal. Calcd for $C_7H_4N_2O_6F_6S_3$: C 19.91, H 0.95. Found: C 20.12, H 1.23.

6-Methyl-2-methylthio-4-pyrimidinyl triflate (**2c**) 6-Methyl-2-methylthio-4(1H)-pyrimidinone (1.56 g, 10 mmol), triethylamine (1.01 g, 10 mmol), CH_2Cl_2 (50 ml) and Tf_2O (2.82 g, 10 mmol) were reacted together as described above. CH_2Cl_2 was eluent for chromatography; yield 2.59 g (90 %); bp 60 °C / 0.001 mmHg. ^1H Nmr ($CDCl_3$, 300 MHz): δ 6.57 (s, 1H, H-5), 2.47 (s, 3H, Me), 2.46 (s, 3H, Me). ^{13}C Nmr ($CDCl_3$, 75 MHz): δ 173.96 (C-2), 172.43 (C-4), 162.72 (C-6), 118.43 (q, CF_3, $J_{C,F}$ 320.6 Hz), 104.75 (C-5), 24.73 (CMe), 14.09 (SMe). Ms (EI): 288 (23, M$^+$), 163 (8), 156 (100), 109 (74), 96 (18), 93 (10), 83 (11), 69 (52). Anal. Calcd for $C_7H_7N_2O_3F_3S_2$: C 29.17, H 2.45. Found: C 29.34, H 2.63.

2,6-Dimethyl-4-pyrimidinyl triflate (**2d**) 2,6-Dimethyl-4(1H)-pyrimidinone (1.24 g, 10 mmol), CH_2Cl_2 (50 ml), triethylamine (1.01 g, 10 mmol) and Tf_2O (2.82 g, 10 mmol) were reacted together as described above. CH_2Cl_2 was eluent for chromatography; yield 1.64 g (65 %); bp 50 °C / 0.001 mmHg. ^1H Nmr ($CDCl_3$, 300 MHz): δ 6.82 (s, 1H, H-5), 2.68 (s, 3H, CMe), 2.56 (s, 3H, CMe). ^{13}C Nmr ($CDCl_3$, 75 Hz): δ 171.81 (C-2), 168.73 (C-4), 163.19 (C-6), 119.07 (q, CF_3, $J_{C,F}$ 319 Hz), 107.02 (C-5), 25.72 (Me), 24.50 (Me). Ms (EI): 256 (100, M$^+$), 228 (62), 192 (13), 146 (20), 124 (12), 110 (24), 107 (40), 95 (26), 69 (66). Anal. Calcd for $C_7H_7N_2O_3F_3S$: C 32.82, H 2.75. Found: C 33.02, H 2.99.

2- Pyrimidinyl triflate (**2e**) 2(1H)-Pyrimidinone (0.96 g, 10 mmol), CH_2Cl_2 (50 ml), and triethylamine (1.01 g, 10 mmol) were stirred together at 0 °C overnight, Tf_2O (2.82 g, 10 mmol) was added and the stirring was continued for another 10 h. Work-up and purification as described in general procedure. $CHCl_3$ was used as eluent for chromatography to give 0.82 g (36 %) of compound (**2e**); bp 150 °C / 0.002 mmHg. ^1H Nmr ($CDCl_3$, 300 MHz): δ 8.80 (d, 2H, $J_{4/6,5}$ 4.8 Hz), 7.47 (t, 1H, H-5, $J_{5,4/6}$ 4.8 Hz). ^{13}C Nmr ($CDCl_3$, 75 MHz): δ 160.92 (C-4,6), 158.73 (C-2), 121.38 (C-5), 118.59 (q, CF_3, $J_{C,F}$ 320 Hz). Ms (EI): 228 (31, M$^+$), 159 (23), 136 (28), 133 (16), 117 (11), 109 (6), 80 (17), 79 (13), 70 (19), 69 (100). Anal. Calcd for $C_5H_3N_2O_3F_3S$: C 26.32, H 1.33. Found: C 26.51, H 1.38.

4,6-Dimethyl-2-pyrimidinyl triflate (**2f**) 4,6-Dimethyl-2(1H)-pyrimidinone (1.24 g, 10 mmol), CH_2Cl_2 (50 ml), triethylamine (1.01 g, 10 mmol) and Tf_2O (2.82 g, 10 mmol) were reacted together as described above. CH_2Cl_2 was the eluent for chromatography; yield 2.1 g (82 %); bp 75 °C /0.001 mmHg. ^{1}H Nmr ($CDCl_3$, 300 MHz): δ 7.09 (s, 1H, H-5), 2.47 (s, 6H, 2 Me). ^{13}C Nmr ($CDCl_3$, 75 MHz): δ 170.88 (C-4,6), 157.60 (C-2), 119.89 (C-5), 118.21 (q, CF_3, $J_{C,F}$ 317.8 Hz), 23.89 (C-Me). Ms (EI): 256 (76, M^+), 228 (23), 187 (5), 123 (39), 107 (31), 106 (73), 105 (24), 95 (37), 69 (100). Anal. Calcd for $C_7H_7N_2O_3F_3S$: C 32.82, H 2.75. Found: C 33.06, H 3.02.

General method for palladium-catalysed coupling reactions of triflates with stannanes The triflate (2 mmol), the tri-n-butylstannane (2 mmol), LiCl (0.25 g, 6 mmol), and $Pd(PPh_3)_4$ (0.07 g, 3 mol %) were heated at 80 °C in dioxane (7 ml) till there was no more starting triflate as shown by tlc. The reaction mixture was diluted with light petroleum, treated with saturated aqueous KF solution and the precipitated tri-n-butylstannyl fluoride was removed by filtration through a plug of celite. The reaction mixture was washed with water, dried ($MgSO_4$) and was purified on a silica gel column before recrystallization or distillation using a Kugelrohr oven.

2-Methylthio-4-vinylpyrimidine (**3a**) 2-Methylthio-4-pyrimidinyl triflate (0.55 g, 2 mmol) and tri-n-butylvinylstannane (0.65 g, 2 mmol) were heated for 2 h. The eluent for chromatography was light petroleum / EtOAc (1:1); yield 0.28 g (93 %); bp 60 °C / 0.002 mmHg. ^{1}H Nmr ($CDCl_3$, 300 MHz): δ 8.40(d, H-6, $J_{6,5}$ 5.1 Hz), 6.77 (d, 1H, H-5, $J_{5,6}$ 5.1 Hz), 6.51 (dd, 1H, J_{trans} 17.3 Hz, J_{cis} 10.1 Hz), 6.33 (dd, 1H, J_{gem}1.8 Hz, J_{trans}17.3 Hz), 5.52 (dd, 1H, J_{gem}1.8 Hz, J_{cis}10.1 Hz), 2.43 (s, 3H, SMe). ^{13}C Nmr ($CDCl_3$, 75 Hz): δ 172.41 (C-2), 162.13 (C-4), 157.48 (C-6), 134.74 (CH), 123.00 (CH_2), 113.00 (C-5), 14.0 (SMe). Ms (EI): 152 (100, M^+), 151 (56), 107 (11), 106 (60), 105 (15), 79 (67), 73 (11). Anal. Calcd for $C_7H_8N_2S$: C 55.24, H 5.30. Found: C 55.44, H 5.60.
This compound was made in 92 % yield from the 4-chloro compound.[16]

6-Methyl-2-methylthio-4-vinylpyrimidine (**3b**) 6-Methyl-2-methylthio-4-pyrimidinyl triflate (0.58 g, 2 mmol), tri-n-butylvinylstannane (0.63 g, 2 mmol) were reacted together as described above for 1 h. The eluent used for chromatography was light petroleum/EtOAc (4:1); yield 0.20 g (60 %); an oil. ^{1}H Nmr ($CDCl_3$, 200 MHz): δ 6.74 (s, 1H, H-5), 6.61 (dd, 1 H, J_{trans} 17.3 Hz, J_{cis} 9.93 Hz), 6.45 (dd, 1 H, J_{trans} 17.3 Hz, J_{gem} 2.08 Hz), 5.71 (dd, 1 H, J_{cis} 9.93 Hz, J_{gem} 2.08 Hz), 2.56 (s, 3H, CMe), 2.42 (s, 3 H, SMe). ^{13}C Nmr ($CDCl_3$, 50 MHz): δ 171.02 (C-2), 166.87 (C-6), 161.11 (C-4), 134.53 (CH), 122.02 (CH_2), 112.57 (C-5), 24.45 (CMe), 14.56 (SMe). Ms (EI): 166 (100, M^+), 165 (54), 121 (14), 120 (82), 119 (71), 78 (12), 74 (15), 67 (29). Anal. Calcd for $C_8H_{10}N_2S$: C 57.81, H 6.06. Found: C 57.92, H 6.17.

2-Vinylpyrimidine (**3c**) 2-Pyrimidinyl triflate (0.456 g, 2 mmol) and tri-n-butylvinylstannane (0.76 g, 2.4 mmol) were heated overnight. Ether was the eluent for chromatography; yield 0.18 g (68 %); an oil. ^{1}H Nmr ($CDCl_3$, 300 MHz): δ 8.56 (d, 2H, H-4,6, $J_{4,5}$ 4.86 Hz), 6.99 (t, 1H, H-5, $J_{5,4}$ 4.86 Hz), 6.75 (dd, 1H, J_{cis} 10.42 Hz, J_{trans} 17.33 Hz), 6.49 (dd, 1H, J_{gem} 1.95 Hz, J_{trans} 17.33 Hz), 5.59 (dd, 1H, J_{gem} 1.95 Hz, J_{cis} 10.42 Hz). ^{13}C Nmr ($CDCl_3$, 75 MHz): δ 164.34 (C-2), 157.00 (C-4,6), 136.41 (CH), 124.28 (CH_2),

119.57 (C-5). Ms (EI): 106 (100, M$^+$), 105 (28), 80 (70), 79 (38), 78 (12), 53 (51), 52 (85). Anal. Calcd for $C_6H_6N_2$: C 67.91, H 5.70. Found: C 68.06, H 5.81.

2-Methylthio-4-β-styrylpyrimidine (**3d**) 2-Methylthio-4-pyrimidinyl triflate (0.55 g, 2 mmol) and β-styryltri-n-butylstannane (0.87 g, 2 mmol) were reacted together as above for 2 h. The eluent for chromatography was light petroleum/EtOAc (4:1) to give 0.31 g (68 %) of **3d** ; bp 159 °C / 0.02 mmHg: This was identical to an authentic sample; bp 160 °C / 0.02 mmHg.[17]

2-β-Styrylpyrimidine (**3e**) 2-Pyrimidinyl triflate (0.46 g, 2 mmol) and β-styryltri-n-butylstannane (0.87 g, 2 mmol) were reacted together as above for 3 h The eluent for chromatography was light petroleum/EtOAc (9:1) to yield 0.21 g (57 %) of compound (**3e**); mp 72 °C; which was identical to an authentic sample; mp 71.5 -72.5 °C.[18]

4,6-Di-(2-thienyl)-2-methylthiopyrimidine (**3f**) 2-Methylthio-4,6-pyrimidinyl ditriflate (0.84 g, 2 mmol), 2-thienyltri-n-butylstannane (1.49 g, 4 mmol), LiCl (0.5 g, 6 mmol) and $Pd(PPh_3)_4$ (0.14 g, 3 mol %) were heated together in DMF (10 ml) at 80 °C overnight. Eluent for chromatography was EtOAc/light petroleum (1:1); yield 0.42 g (73 %); mp 97-98 °C. ^{1}H Nmr ($CDCl_3$, 200 MHz): δ 7.81 (d, 2 H, H-3′, J 2.85 Hz), 7.52 (d, 2H, H-5′, J 4.92 Hz), 7.45 (s, 1H, H-5), 7.16 (t, 2H, H-4′, J 4.6 Hz), 2.65 (s, 3H, SMe). ^{13}C Nmr ($CDCl_3$, 50 MHz): δ 159.57 (C-4/6), 159.50 (C-2), 142.76 (C2′), 130.51 (C-5′), 128.73 C-4′), 127.93 (C-3′), 104 79 (C-5), 14.90 (SMe). Ms (EI): 290 (100, M$^+$), 289 (32), 244 (47), 243 (40), 203 (7), 135 (27), 134 (21), 109 (23), 108 (38), 83 (11), 82 (11). Anal. Calcd for $C_{13}H_{10}N_2S_3$: C 53.77, H 3.47. Found 53.94, H 3.61.

6-Methyl-2-methylthio-4-(2-thienyl)pyrimidine (**3g**) 6-Methyl-2-methylthio-4-pyrimidinyl triflate (0.58 g, 2 mmol) and 2-thienyltri-n-butylstannane (0.75 g, 2 mmol) in DMF (10 ml) were heated (80 °C) together for 1 h as described above. Eluent for chromatography was hexane/EtOAc (4:1); yield 0.39 g (88 %); mp 50 °C. ^{1}H Nmr ($CDCl_3$, 300 MHz): δ 7.72 (dd, 1H, H-3′, $J_{3',5'}$ 1.1 Hz, $J_{3',4'}$ 3.7 Hz), 7.48 (dd, 1H, H-5′, $J_{5',3'}$ 1.1 Hz, $J_{5',4'}$ 5.0 Hz), 7.12 (dd, 1H, H-4′, $J_{4',3'}$ 3.7 Hz, $J_{4',5'}$ 5.0 Hz), 7.06 (s, 1H, H-5), 2.61 (s, 3H, CMe) 2.46 (s, 3H, SMe). ^{13}C Nmr ($CDCl_3$, 75 MHz): δ 172.14 (C-2), 167.52 (C-6), 158.55 (C-4), 142.40 (C-2′), 129.84 (C-5′), 128.21 (C-4′), 127.22 (C-3′), 109.64 (C-5), 24.12 (CMe), 14.10 (SMe). Ms (EI): 222 (100, M$^+$), 221 (42), 276 (61), 175 (79), 150 (6), 149 (8), 143 (12), 134 (15), 108 (14), 67 (19). Anal. Calcd for $C_{10}H_{10}N_2S_2$: C 54.03, H 4.53. Found: C 54.23, H 4.72.

2-(2-Thienyl)pyrimidine (**3h**) 2-Pyrimidinyl triflate (0.46 g, 2 mmol), and 2-thienyltri-n-butylstannane (0.75 g, 2 mmol) were reacted together as above overnight. Hexane/EtOAc (4:1) was eluent for chromatography; yield 0.22 g (67 %); mp 89-90 °C. This was identical (lit., mp 92-93 °C) to the known compound.[19]

General Procedure for Reaction with Zinc Reagents n-BuLi (5 mmol) was added to a solution of aryl bromide (5 mmol) in THF (20 ml) at -78 °C under N_2. After 1 h, an anhydrous zinc bromide solution in dry THF (5 ml, 1

M, 5 mmol) was added dropwise and the stirring continued for a further 1 h at -78 °C at which time the cold bath was removed and the reaction mixture was allowed to reach ambient temperature. The pyrimidinyl triflate (3 mmol) and $Pd(PPh_3)_4$ (0.1 g, 3 mol %), both dissolved in dry THF (5 ml each), were added via a syringe, and the resulting solution was heated at 50 °C. The reaction mixture was cooled, 10 % solution of NH_4Cl (20 ml) was added and the aqueous phase extracted with EtOAc (3 x 50 ml), washed with H_2O (2x 50 ml), dried ($MgSO_4$) and evaporated. The product was purified by chromatography on a silica gel column.

4-(p-Anisyl)-2-methylthiopyrimidine (**4a**) p-Bromoanisole (0.935 g, 5 mmol) and 2-methylthio-4-pyrimidinyl triflate (0.822 g, 3 mmol) were reacted together as described above for 1.5 h. Eluent for chromatography was hexane/EtOAc (4:1); yield 0.61 g (87 %); mp 80 °C. ^{1}H Nmr ($CDCl_3$, 200 MHz): δ 8.47 (d, 1H, H-6, $J_{6,5}$ 5.37 Hz), 8.06 (d, 2H, H-2′,6′, $J_{2',3'}$ 8.9 Hz), 7.29 (d, 1H, H-5, $J_{5,6}$ 5.37 Hz), 7.00 (d, 2H, H.3′,5′, $J_{3',2'}$ 8.9 Hz), 3.87 (s, 3H,OMe), 2.63 (s, 3H,SMe). ^{13}C Nmr ($CDCl_3$, 50 MHz): δ 172.57 (C-2), 163.43 (C-4), 162.33 (C-1′), 157.44 (C-6), 129.10 (3′,5′), 128.64 (C-4′), 114.73 (C-2′,6′), 111.45 (C-5), 56.30 (OMe), 15.34 (SMe). *Ms (EI): 232 (100, M$^+$): 231 (25), 186 (33), 185 (27), 171 (27), 155 (8), 143 (5),* 134 (5), 116 (7), 89 (12). Anal. Calcd for $C_{12}H_{12}N_2OS$: C 62.05, H 5.21. Found: C 62.25, H 5.33.
When 4-chloro-2-methylthiopyrimidine (0.48 g, 3 mmol) was used instead of the triflate, 0.54 g (78 %) of compound (**4a**) was obtained.

4,6-(Di-p-anisyl)-2-methylthiopyrimidine (**4b**) p-Bromoanisole (0.935 g, 5 mmol) 2-methylthio-4,6-pyrimidinyl ditriflate (0.547 g, 1.3 mmol), $Pd(PPh_3)_4$ (0.09 g, 3 mol %) were reacted as above for 1.5 h; Hexane/EtOAc (4:1) was the eluent for chromatography; yield 0.39 g (89 %); mp 135 °C. ^{1}H Nmr ($CDCl_3$, 200 MHz): δ 8.14 (d, 2H, H-2′,6′, $J_{2',3'}$ 8.92 Hz), 7.65 (s, 1H, H-5), 7.02 (d, 1H, H′-3′5′, $J_{3',2'}$ 8.92 Hz), 3.89 (s, 3H, OMe), 2.71 (s, 3H, SMe). ^{13}C Nmr ($CDCl_3$, 50 MHz): δ 172.34 (C-2), 163.93 (C-4,6), 162.09 (C-1′), 129.88 (C-4′), 129.10 (C-3′,5′), 114.65 (C-2′,6′), 106.64 (C-5), 56.32 (OMe), 14.56 (SMe). Ms (EI): 338 (100, M$^+$), 337 (19), 29 (20), 277 (25), 261 (6), 248 (6), 149 (15), 135 (14). Anal. Calcd for $C_{19}H_{18}N_2O_2S$: C 67.43, H 5.36. Found: C 67.72, H 5.53.

4-(p-Anisyl)-6-methyl-2-methylthiopyrimidine (**4c**) p-Bromanisole (0.56 g, 3 mmol), and 6-methyl-2-methylthio-4-pyrimidinyl triflate (0.86 g, 3 mmol) were reacted together as above for 1.5 h; eluent for chromatography was hexane/EtOAc (4:1); Kugelrohr distillation bp 175 °C / 0.002 mmHg; yield 0.56 g (76 %). ^{1}H Nmr ($CDCl_3$, 300 MHz): δ 8.07 (d, 2H, J 8.8 Hz), 7.16 (s, 1H, H-5), 6.99 (d, 2H, J 8.8 Hz), 3.87 (s, 3H, OMe), 2.65 (SMe), 2.48 (CMe). ^{13}C Nmr ($CDCl_3$, 75 MHz): δ 171.92 (C-2), 167.43 (C-6), 163.09 (C-4), 162.01 (C-1′), 129.04 (C-4′), 128.70 (C-3′,5′), 114.18 (C-2′,6′), 110.56 (C-5), 55.40 (OMe), 24.18 (CMe), 14.16 (SMe). Ms (EI): 246 (100, M$^+$), 245 (44), 200 (52), 199 (43), 185 (37), 169 (15), 159 (11), 158 (9). Anal. Calcd for $C_{13}H_{14}N_2OS$: C 63.39, H 5.73. Found 63.61, H 5.79.

2,6-Dimethyl-4-(p-anisyl)pyrimidine (**4d**) p-Bromoanisole (0.935 g, 5 mmol) and 2,6-dimethyl-4-pyrimidinyl triflate (0.77 g, 3 mmol) were reacted as described above for 1 h; eluent for chromatography was CH_2Cl_2; thick oil; yield 0.35 g (55 %). ^{1}H Nmr ($CDCl_3$, 200 MHz): δ 7.92 (d, 2H, H-2′,6′, $J_{2',3'}$ 8.87 Hz), 7.17 (s, 1H,

H-5), 6.87 (d, 2H, H-3′5′, $J_{3',2'}$ 8.87 Hz), 3.73 (s, 3H, OMe), 2.63 (s, 3H, C2-Me), 2,40 (s, 3H, C6-Me). ^{13}C Nmr ($CDCl_3$, 50 MHz): δ 167.56 (C-2), 166.72 (C-4), 163.24 (C-6), 161.61 (C-1′), 129.38 (C-4′), 128.49 (C-2′,3′), 114.64 (C-2′6′), 112.24 (C-5), 55.18 (OMe), 26.03 (CMe), 24.10 (CMe). Ms (EI): 214 (100, M+), 199 (12), 173 (15), 158 (6), 132 (23), 117 (6), 89 (7). Anal. Calcd for $C_{13}H_{14}N_2O$: C 72.87, H 6.59. Found: 72.91, H 6.65.

2-p-Anisylpyrimidine (**4e**) p-Bromoanisole (0.935 g, 5 mmol) and 2-pyrimidinyl triflate (0.684 g, 3 mmol) were reacted together as above. Eluent for chromatography was hexane/EtOAc (4:1). Kugelrohr distillation, bp 125 °C / 0.001 mmHg; yield 0.48 g (86 %). ^1H Nmr ($CDCl_3$, 200 MHz): δ 8.71 (d, 2 H, H-4,6, $J_{4,5}$ 4.82 Hz), 8.40 (d, 2H, H-2′,6′, $J_{2',3'}$ 8.9 Hz), 7.06 (t, 1 H, H-5, $J_{5,4}$ 4.82 Hz), 7.00 (d, 2H, H-3′,5′, $J_{3',2'}$ 8.9 Hz), 3.63 (s, 3H, OMe). ^{13}C Nmr ($CDCl_3$, 50 MHz): δ 163.55 (C-2), 160.96 (C-1′), 156.11 (C4,6), 129.66 (C-4′), 129.15 (C-2′,6′), 117.74 (C-5), 113.44 (C-3′,5′), 55.44 (OMe). Ms (EI): 186 (100, M+), 185 (7), 171 (17), 155 (15), 143 (18), 133 (25), 103 (7), 90 (10). Anal. Calcd for $C_{11}H_{10}N_2O$: C 70.95, H 5.41. Found: C 70.87, H 5.58.
Similar yield (0.47 g, 85 %) of **4e** was obtained when 2-chloropyrimidine (0.34 g, 3 mmol) was used instead of the 2-triflate.

4,6-Dimethyl-2-(p-anisyl)pyrimidine (**4f**) p-Bromoanisole (0.935 g, 5 mmol) and 4,6-dimethyl-2-pyrimidinyl triflate (0.77 g, 3 mmol) were reacted together as above for 1 h; eluent for chromatography was CH_2Cl_2; yield 0.62 g (96 %); mp 88 °C. ^1H Nmr ($CDCl_3$, 200 MHz): δ 8.40 (d, 2H, H-2′, 6′, $J_{2',3'}$ 9.0 Hz), 6.98 (d, 2H, H-3′,5′, $J_{3',2'}$ 9.0 Hz), 6.85 (s, 1H, H-5), 3.86 (OMe), 2.50 (CMe). ^{13}C Nmr ($CDCl_3$, 50 MHz): δ 166.41 (C4, 6), 163.80 (C-2), 161.51 (C-1′), 131.16 (C-4′), 130.10 (3′, 5′), 117.59 (C-5), 114.21 (C-2′, 6′), 56.41 (OMe), 25.56 (CMe). Ms (EI): 214 (100, M+), 199 (35), 171 (9), 133 (12), 107 (5), 90 (6). Anal. Calcd for $C_{13}H_{14}N_2O$: C 72.87, H 6.59. Found: 73.03, H 6.78.

4,6-Diphenyl-2-methylthiopyrimidine (**4g**) Bromobenzene (0.942 g, 6 mmol), n-BuLi (4 ml, 1.5 M, 6 mmol), $ZnBr_2$ (6 ml, 1M, 6 mmol), 2-methylthio-4,6-pyrimidinyl ditriflate (1.055 g, 2.5 mmol) and $Pd(PPh_3)_4$ (0.11 g, 2 mol %) were reacted as above for 2 h; eluent for chromatography was hexane/EtOAc (9:1); yield 0.57 g (85 %); mp 156-158 °C. ^1H Nmr ($CDCl_3$, 300 MHz): δ 8.16 (m, 4H, H-2′, 6′), 7.78 (s, 1H, H-5), 7.53 (m, 6H, H-3′, 4′, 5′), 2.73 (s, 3H, SMe). ^{13}C Nmr ($CDCl_3$, 75 MHz): δ 172.78 (C-2), 164.66 (C-4, 6), 136.93 (C-1′), 130.92 (C-4′), 128.87 (C-3′, 5′), 127.26 (C-2′, 6′), 107.87 (C-5), 14.37 (SMe). Ms (EI): 278 (100, M+), 277 (48), 232 (62), 231 (32), 204 (13), 191 (19), 129 (34), 128 (16). Anal. Calcd for $C_{17}H_{14}N_2S$: C 73.35, H 5.07. Found: C 73.64, H 5.3.

4-Methyl-2-methylthio-6-phenylpyrimidine (**4h**) Bromobenzene (0.78 g , 5 mmol) and 6-methyl-2-methylthio-4-pyrimidinyl triflate (0.86 g, 3 mmol) were reacted together as above for 1.5 h; eluent for chromatography was hexane/EtOAc (4:1); Kugelrohr distillation bp 155 °C / 0.002 mmHg; yield 0.47 g (73 %). ^1H Nmr ($CDCl_3$, 300 MHz). δ 8.08 (m, 2H, H-2′, 6′), 7.47 (m, 3H, H-3′, 4′, 5′), 7.21 (s, 1H, H-5), 2.64 (s, 3H, CMe), 2.50 (s, 3H, SMe). ^{13}C Nmr ($CDCl_3$, 75 MHz): δ 172.19 (C-2), 167.79 (C-4), 163.55 (C-6), 136.66 (C-

1′), 130.84 (C-4′), 128.80 (C-3′, 5′), 127.13 (C-2′, 6′), 111.46 (C-5′), 24.23 (CMe), 14.17 (SMe). Ms (EI): 216 (100, M$^+$), 215 (40), 171 (11), 170 (56), 169 (76), 155 (10), 143 (7), 129 (17). Anal. Calcd for $C_{12}H_{12}N_2S$: C 66.64, H 5.59. Found: C 66.72, H 5.63.

6-Methyl-2-methylthio-4-(2-thienyl)pyrimidine (**3g**) 2-Bromothiophene (0.815 g, 5 mmol) and 6-methyl-2-methylthio-4-pyrimidinyl triflate (0.86 g, 2.7 mmol), were reacted together as above for 1h; eluent for chromatography was hexane/EtOAc (9:1); yield 0.626 g (94 %); mp 50 °C. Data see above.

6-Methyl-2-methylthio-4-vinylpyrimidine (**3b**) Vinylmagnesium bromide (5 ml, 1 M, 5 mmol), $ZnBr_2$ (5 ml, 1 M, 5 mmol), 6-methyl-2-methylthio-4-pyrimidinyl triflate (0.86 g, 3 mmol), and $Pd(PPh_3)_4$ (0.104 g, 3 mol %) were reacted together as above for 2 h; eluent for chromatography was CH_2Cl_2; yield 0.22 g (45 %). Data see above.

2-Vinylpyrimidine (**3c**) 2-Pyrimidinyl triflate (0.684 g, 3 mmol), vinylmagnesium bromide (5 ml, 1M, 5 mmol), $ZnBr_2$ (5 ml, 1M, 5 mmol) and $Pd(PPh_3)_4$ (0.104 g, 3 mol %) were reacted together as above for 1 h; eluent for chromatography was hexane/EtOAc (4:1); yield 0.30 g (93 %); data see above.

2,6-Dimethyl-4-n-butylpyrimidine (**4i**) n-BuLi (3.3 ml, 1.5 M, 5 mmol), $ZnBr_2$ (5 ml, 1M, 5 mmol), 2,6-dimethyl-4-pyrimidinyl triflate (0.768 g, 3 mmol) and $Pd(PPh_3)_4$ (0.1 g, 3 mol %) were reacted together as above for 2 h; eluent for chromatography was light petroleum/EtOAc (1:1); yield 0.103 g (21 %); bp 95 °C / 10 mmHg. ^{1}H Nmr ($CDCl_3$, 200 MHz): δ 6.82 (s, 1H, H-5), 2.65 (s, 3H, C2-Me), 2.64 (br. t, 2H, CH_2), 2.43 (s, 3H, C6-Me), 1.65 (m, 2H, CH_2), 1.34 (m, 2H, CH_2), 0.91 (br. t, 3H, CH_3). ^{13}C Nmr ($CDCl_3$, 50 MHz): δ 170.63 (C-2), 167.24 (C-4), 166.47 (C-6), 116.40 (C-5), 37.51 (CH_2), 31.18 (CH_2), 25.92 (C2-Me), 23.94 (C6-Me), 22.49 (CH_2), 13.84 (CH_3). Ms (EI): 164 (10, M$^+$), 163 (2), 149 (9), 135 (18), 122 (100), 107 (2), 95 (2). Anal. Calcd for $C_{10}H_{16}N_2$: C 73.13, H 9.82. Found: C 73.25, H 10.0. When the triflate was reacted directly with n-BuLi polymerization occurred.

4,6-Dimethyl-2-n-butylpyrimidine (**4j**) n-BuLi (3.3 ml, 1.5 M, 5 mmol), $ZnBr_2$ (5 ml, 1 M, 5 mmol), 4,6-dimethyl-2-pyrimidinyl triflate (0.768 g, 3 mmol) and $Pd(PPh_3)_4$ (0.1 g, 3 mol %) were reacted together for 2 h; eluent for chromatography was light petroleum/EtOAc (1:1); yield 0.35 g (71 %), bp 78 °C / 10 mmHg. ^{1}H Nmr ($CDCl_3$, 200 MHz): δ 6.75 (H-5), 2.78 (br. t, 2H, CH_2, J 8 Hz), 2.36 (s, 6H, 2xMe), 1.69 (m, 2H, CH_2), 1.31 (m, 2H, CH_2), 1.10 (m, 2H, CH_2), 0.85 (br. t, 3H, CH_3, J 7.2 Hz). ^{13}C Nmr (50 MHz, $CDCl_3$): δ 170.49 (C-2), 166.00 (C-4, 6), 116.75 (C-5), 39.10 (CH_2), 30.94 (CH_2), 23.55 (2xMe), 22.35 (CH_2), 13.56 (CH_3). Ms (EI): 164 (3.0, M$^+$), 163 (3), 149 (12), 135 (29), 122 (100), 108 (3), 107 (4). Anal. Calcd for $C_{10}H_{16}N_2$: C 73.13, H 9.82. Found: C 73.42, H 10.11.

t-Butyl (6-methyl-2-methylthio-4-pyrimidinyl)acetate (**4k**) LDA (5 mmol) was generated from diisopropylamine (0.8 ml, 5 mmol) and n-BuLi (3.3 ml, 1.5 M, 5 mmol) and to this t-butyl acetate (0.58 g, 5 mmol) and $ZnBr_2$ (5 ml, 1 M, 5 mmol) were added followed by 6-methyl-2-methylthio-4-pyrimidinyl triflate (0.86 g, 3

mmol) and $Pd(PPh_3)_4$ (0.104 g, 3 mol %) and heated for 2 h; $CHCl_3$ was eluent for chromatography; yield 0.24 g (31 %); bp 150 °C / 10 mmHg. ^1H Nmr ($CDCl_3$, 200 MHz): δ 6.79 (s,1H, H-5), 3.57 (s, 2H, CH_2), 2.51 (s, 3H, CMe), 2.40 (s, 3H, SMe), 1.42 (s, 9H, t-Bu). ^{13}C Nmr ($CDCl_3$, 50 MHz): δ 172.14 (C-2), 168.77 (CO), 167.54 (C-6), 163.32 (C-4), 82.16 ($Me_3\underline{C}$), 45.14 (CH_2), 28.84 (t-Bu), 24.79 (CMe), 14.87 (SMe). Ms (EI): 254 (17, $\underline{M}^+$), 214 (21), 198 (78), 181 (30), 152 (41), 152 (41), 149 (28). Anal. Calcd for $C_{12}H_{18}N_2O_2S$: C 56.67, H 7.13. Found: C 56.82, H 7.31.

t-Butyl (4,6-dimethyl-2-pyrimidinyl)acetate (**4l**) LDA (5 mmol) was generated from diisopropylamine (0.8 ml, 5 mmol) and n-BuLi (3.3 ml, 1.5 M, 5 mmol) and to this t-butyl acetate (0.58 g, 5 mmol) and $ZnBr_2$ (5 ml, 1 M, 5mmol) were added followed by 4,6-dimethyl-2-pyrimidinyl triflate (0.768 g, 3 mmol) and $Pd(PPh_3)_4$ (0.1 g, 3 mol %) and heated for 2 h; light petroleum/EtOAc (1:1) was the eluent for chromatography; yield 0.25 g (37 %); mp 76-78 °C. ^1H Nmr ($CDCl_3$, 200 MHz): δ 6.85 (s, 1H, H-5), 3.79 (s, 2H, CH_2), 2.39 (s, 6H, 2xMe), 1.39 (s, 9H, t-Bu). ^{13}C Nmr ($CDCl_3$, 50 MHz): δ 169.13 (C-2), 166.67 (C-4, 6), 164.00 (CO), 117.83 (C-5), 81.01 ($Me_3\underline{C}$), 46.30 ($O\underline{C}H_2$), 27.98 (t-Bu), 23.73 (2xMe). Ms (CI): 223 (100, $\underline{M}^+$+1), 207 (3), 195 (15), 168 (16), 167 (100), 149 (33), 123 (14), 122 (21), 57 (84). Anal. Calcd for $C_{12}H_{18}N_2O_2$: C 64.84, H 8.16. Found: C 65.07, H 8.34.

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