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Short Communication

Silyl Ethers of Stannylated Hydroxymethylfurans and Bromopyrimidinones in Palladium-mediated Coupling Reactions

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Appropriately activated pyrimidin-2(1*H*)-ones possess the ability reversibly to arrest the mitosis of cells in metaphase; particularly 5-halo derivatives have been investigated.[1] 5-Substituents with moderately electron-withdrawing or polarizable properties may replace the halogen to furnish reversible metaphase arrestors.[2] We herein report synthesis of a group of 5-hydroxymethylfuran derivatives (**5**). Since most of the *N*-alkylated and 5-substituted pyrimidin-2(1*H*)-ones show low water solubility,[1] a 5-hydroxymethylfuran substituent was introduced into the pyrimidine 5-position to confer water solubility to the resultant pyrimidinone.

The key step in the reaction sequence, which was designed to yield the protected 5-furylpyrimidine **4**, was a Pd-catalysed coupling reaction between 2-stannylfuran **2** and the *N*-1 substituted 5-bromopyrimidinone **3**. The coupling reaction is analogous to methodology we have described recently.[3] The reaction was run in 1,2-dichloroethane (DCE) with bis(triphenylphosphine)palladium(II) chloride as the catalyst. The trimethylstannyl derivative **2b** was more reactive than its tributyl homologue **2a** in the coupling reaction.

The stannyl derivatives **2** were prepared from the corresponding silyl ethers **1** which were lithiated in the 5-position with BuLi in THF in the temperature interval −78°C to 20°C.[4] Subsequently, the lithiated species were quenched at −78°C by the addition of the stannyl chloride. The silyl ethers **1** were available by the reaction between the alcohol and the respective silyl chloride in the presence of triethylamine (TEA), as a base, and 4-dimethylaminopyridine (DMAP), as a catalyst, run initially at −78°C.

The *tert*-butyldimethylsilyl (TBDMS) protecting group in **4** was removed with tetrabutylammonium fluoride (Bu_4NF) in dry THF to furnish the target molecule **5**.

In a versatile route designed to yield variously *N*-1-substituted pyrimidinones (e.g., **5**) the silyl-protected hydroxymethyl derivative **8** was prepared. Selective *N*-alkylation of **8** in contrast with *O*-alkylation, can be achieved with alkylating agents and methodologies we have previously discussed in closely related systems.[5]

In the preparation of **8**, the furan and the pyrimidine rings were joined by a Pd-mediated coupling reaction. Before this reaction the 5-bromopyrimidin-2(1*H*)-one was *O*-protected as the TBDMS ether **6**. In this approach, the silyl group on the phenolic oxygen of pyrimidine was to be removed selectively in the presence of the silyl group on the alcoholic oxygen in the hydroxymethyl substituent of furan. The latter was protected as a dimethylthexylsilyl (TDS) ether since TDS ethers are more stable than TBDMS ethers to cleavage.[6] The coupling between the stannane **2c** and the bromopyrimidinyl TBDMS ether **6** was complete after reflux in DCE for 90 min, yield 89%. Selective cleavage of the phenolic TBDMS function proceeded quickly and cleanly by acetic acid in chloroform without heating to yield the target molecule **8b**. Subsequently it was found that when the TBDMS reactants **2a** and **6** were heated together in DCE under coupling conditions overnight, the product was the pyrimidin-2(1*H*)-one **8a**. In this case the intermediate bis(TBDMS) ether coupling product suffered selective cleavage of the phenolic TBDMS ether function. The cleavage is presumably caused by the tributylstannyl bromide which was generated in the coupling reaction, and is another example from our work of the ease of cleavage of TBDMS 2-pyrimidinyl ethers by stannyl halides.[7]

In summary, we have shown that 1-alkyl-5-(5-hydroxymethyl-2-furyl)pyrimidin-2(1*H*)-ones are available from the appropriately substituted and protected furans and pyrimidines by Pd-mediated catalysis, and that silyl

ethers derived from hydroxypyrimidines can be selectively cleaved in the presence of alkyl silyl ethers.

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. 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, dichloromethane was distilled over calcium hydride and 1,2-dichloroethane over phosphorus pentaoxide. DMF was first shaken with NaOH pellets, then distilled over Ba_2O.

*2-*tert*-Butyldimethylsilyloxymethylfuran (***1a***).* Furfuryl alcohol (9.8 g, 0.10 mol), *tert*-butyldimethylsilyl chloride (16.6 g, 0.11 mol), DMAP (0.5 g, 4 mol %) and triethylamine (12 g, 0.12 mol) were dissolved in CH_2Cl_2 (100 ml) at −78 °C. The cold bath was removed after 1 h and the reaction was allowed to reach ambient temperature and then left overnight. The reaction mixture was washed with water, then with sat. NH_4Cl solution, the organic layer was dried ($MgSO_4$), the solvent was evaporated and the crude product was purified by distillation; b.p. 50 °C/0.03 mmHg to give compound **1a** (21.0 g, 100%). Anal. $C_{11}H_{20}O_2Si$: C, H. ^{1}H NMR ($CDCl_3$): δ 0.76 (s, 6 H, $SiMe_2$), 0.91 (s, 9 H, $SiCMe_3$), 4.63 (s, 2 H, OCH_2), 6.20 (br d, 1 H, H-5, $J_{5,4}$ 3.14 Hz), 6.28 (dd, 1 H, H-4, $J_{4,5}$ 3.14 Hz, $J_{4,3}$ 1.6 Hz), 7.33 (dd, 1 H, H-3, $J_{3,4}$ 1.6, $J_{3,5}$ 0.7 Hz). ^{13}C NMR ($CDCl_3$): δ −5.42 ($SiMe_2$), 18.3 ($SiCMe_3$), 25.74 ($SiCMe_3$), 58.01 (OCH_2), 107.2 (C-4/3), 110.1 (C-3/4), 141.82 (C-5), 154.20 (C-2). MS(CI): 213 (3, $M^+ + 1$), 173 (9), 155 (24), 123 (49), 98 (51), 92 (51), 91 (60), 81 (100), 75 (36).

*2-Dimethylthexylsilyloxymethylfuran (***1b***).* Compound **1b** was obtained as above in 96% yield (23.0 g) from furfuryl alcohol (9.8 g, 0.10 mol) and dimethylthexylsilyl chloride (18.0 g, 0.11 mol), b.p. 60 °C/0.02 mmHg. Anal. $C_{13}H_{24}O_2Si$: C, H. ^{1}H NMR ($CDCl_3$): δ 0.14 (s, 6 H, $SiMe_2$), 0.88 (s, 6 H, $SiCMe_2$), 0.90 (d, 6 H, Si–C–CMe_2, $J_{Me,H}$ 6.87 Hz), 1.65 (m, 1 H, Si–C–CH), 4.63 (s, 2 H, OCH_2), 6.26 (dd, 1 H, H-5, $J_{5,4}$ 3.2 Hz, $J_{5,3}$ 0.75 Hz), 6.35 (dd, 1 H, H-4, $J_{4,5}$ 3.2 Hz, $J_{4,3}$ 1.76 Hz), 7.40 (dd, 1 H, H-3, $J_{3,4}$ 1.76 Hz, $J_{3,5}$ 0.75 Hz). ^{13}C NMR ($CDCl_3$): δ −3.52 ($SiMe_2$), 18.31 ($SiCMe_2$), 20.11 (Si–C–CMe_2), 25.06 (Si–C), 34.0 (Si–C–*C*), 57.76 (OCH_2), 107.25 (C-4), 109.95 (C-3), 141.69 (C-5), 154.27 (C-2).

*2 - tert - Butyldimethylsilyloxymethyl - 5 - tributylstannylfuran (***2a***).* 2-*tert*-Butyldimethylsilyloxymethylfuran (1.07 g, 5 mmol) was dissolved in THF (50 ml), the solution was cooled to −78 °C, and BuLi (3.3 ml of 1.5 M soln., 5 mmol) was added dropwise with stirring under N_2 and the stirring continued at ambient temperature for a further 2 h to ensure complete lithiation. The mixture was then cooled to −78 °C and tributylstannyl chloride (1.63 g, 5 mmol), dissolved in THF (15 ml), was introduced gradually. The reaction mixture was stirred overnight, quenched with sat. NH_4Cl solution, extracted (EtOAc), washed (H_2O), dried ($MgSO_4$), and purified by distillation, b.p. 140 °C/0.001 mmHg to yield 62% (1.56 g) of compound **2**. Anal. $C_{23}H_{47}O_2SiSn$: C, H. ^{1}H NMR ($CDCl_3$): δ 0.07 (s, 6 H, $SiMe_2$), 0.89 (s, 9 H, $SiCMe_3$), 0.9 (m, 9 H, 3 × Me), 1.0 (m, 6 H, 3 × CH_2), 1.33 (m, 6 H, 3 × CH_2), 1.5 (m, 6 H, 3 × CH_2), 4.67 (s, 2 H, OCH_2), 6.22 (d, 1 H, H-3/4, $J_{3,4}$ 2.95 Hz), 6.46 (d, 1 H, H-4/3, $J_{4,3}$ 2.95 Hz). ^{13}C NMR ($CDCl_3$): δ −5.3 ($SiMe_2$), 9.97 (3 × CH_2), 13.53 (3 × Me), 18.31 ($SiCMe_3$), 25.81 ($SiCMe_3$), 27.08 (3 × CH_2), 28.85 (3 × CH_2), 58.25 (OCH_2), 107.05 (C-3), 121.94 (C-4), 158.76 (C-2), 160.22 (C-5). MS(CI): 503 (2, $M^+ + 1$), 502 (1), 462 (34), 460 (27), 412 (46), 410 (32), 395 (12), 371 (66), 369 (44), 308 (100), 266 (24).

*2-*tert*-Butyldimethylsilyloxymethyl-5-trimethylstannylfuran (***2b***).* Compound **2a** was obtained in 82% yield when the lithiated 2-*tert*-butyldimethylsilyloxymethylfuran was quenched with trimethylstannyl chloride as above, b.p. 90 °C/0.01 mmHg. Anal. $C_{14}H_{28}O_2SiSn$: C, H. ^{1}H NMR ($CDCl_3$): δ 0.15 (s, 6 H, $SiMe_2$), 0.38 (s, 9 H, $SnMe_3$), 0.97 (s, 9 H, $SiCMe_3$), 4.75 (s, 2 H, OCH_2), 6.30 (d, 2 H, H-3/4, $J_{3,4}$ 3.12 Hz), 6.56 (d, 2 H, H-4/3, $J_{4,3}$ 3.12 Hz). ^{13}C NMR ($CDCl_3$): δ −9.40 ($SnMe_3$), −5.35 ($SiMe_2$), 18.28 ($SiCMe_3$), 25.76 ($SiCMe_3$), 58.17 (OCH_2), 107.07 (C-3), 121.41 (C-4), 158.73 (C-2), 159.98 (C-5). MS(CI): 375 (2, $M^+ + 1$), 309 (11), 245 (12), 228 (8), 211 (7), 196 (14), 195 (100), 182 (52), 180 (36), 178 (22).

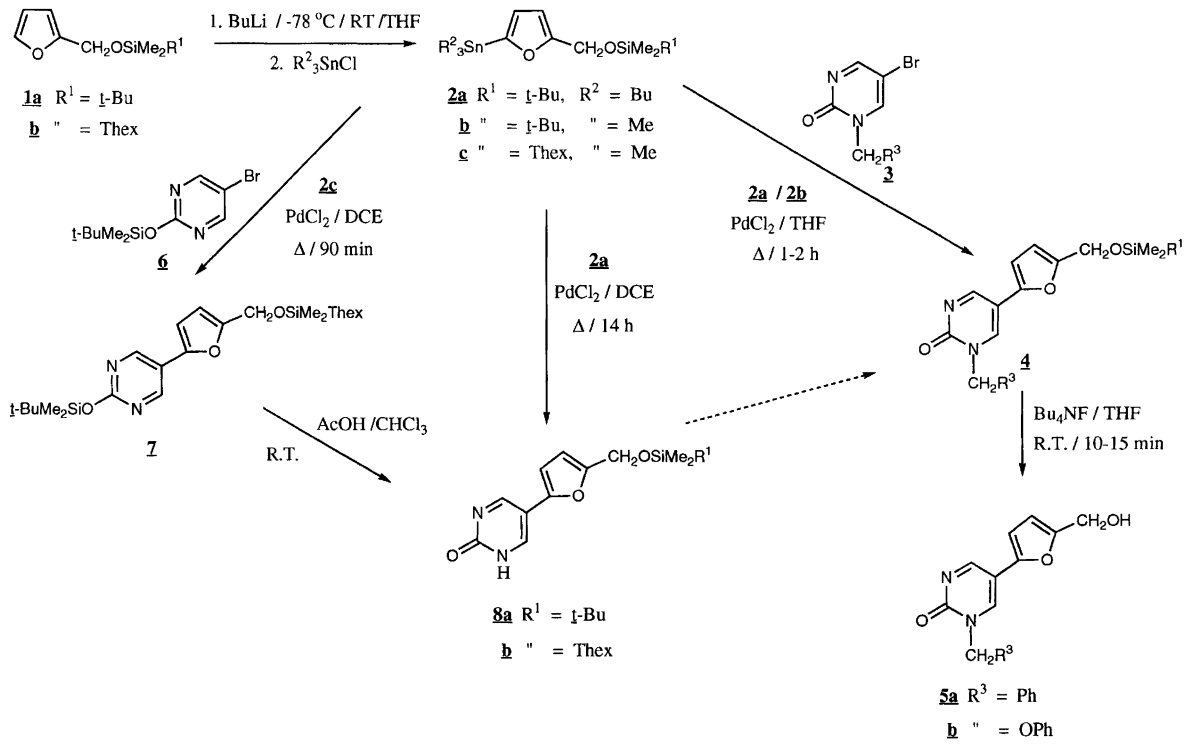
*2 - Dimethylthexylsilyloxymethyl - 5 - trimethylstannylfuran (***2c***).* Compound **2c** was obtained as above by lithiation of 2-dimethylthexylsilyloxymethylfuran followed by quenching with trimethylstannyl chloride; b.p. 140 °C/0.03 mmHg; yield 77%. Anal. $C_{16}H_{32}O_2SiSn$: C, H. ^{1}H NMR ($CDCl_3$): δ 0.14 (s, 6 H, $SiMe_2$), 0.34 (s, 9 H, $SnMe_2$, $J_{Sn,H}$ 29.12, 27.85 Hz), 0.89 (s, 6 H, $SiCMe_2$), 0.92 (d, 6 H, Si–C–CMe_2, $J_{Me,H}$ 6.84 Hz), 1.6 (m, 1 H, Si–C–CH), 4.70 (s, 2 H, OCH_2), 6.25 (d, 1 H, H-3, $J_{3,4}$ 2.99 Hz), 6.52 (d, 1 H, H-4, $J_{4,3}$ 2.99 Hz). ^{13}C NMR ($CDCl_3$): δ −9.40 ($SnMe_3$), −3.39 ($SiMe_2$), 18.39 (CMe_2), 20.19 (Si–C–CMe_2), 25.11 ($SiCMe_2$), 34.07 (Si–C–*C*H), 58.00 (OCH_2), 106.86 (C-3), 121.39 (C-4), 154.91 (C-2), 159.80 (C-5). MS(CI): 404 (3, $M^+ + 1$), 393 (9), 326 (100), 245 (16), 243 (13), 165 (19), 163 (13), 161 (13), 95 (25), 81 (47), 75 (44).

General method for palladium-catalysed coupling reaction. The stannylfuran (1 equiv.), bromopyrimidine (1.1–1.3 equiv.), and the catalyst bis(triphenylphosphine)palladium(II) chloride (3–4 mol%) were refluxed in a suitable solvent until TLC monitoring showed no remaining starting furan. The reaction mixture was diluted with light petroleum, sat. KF soln. was added and the precipitated stannyl fluoride was filtered off and the filtrate extracted with EtOAc, washed and purified on a silica gel column.

*1-Benzyl-5-(5-*tert*-butyldimethylsilyloxymethyl-2-furyl)pyrimidin-2(1*H*)-one* (**4a**). 2-*tert*-Butyldimethylsilyloxymethyl-5-tributylstannylfuran (1.0 g, 2.0 mmol), 1-benzyl-5-bromopyrimidin-2(1*H*)-one, (0.53 g, 2 mmol) and bis-(triphenylphosphine)palladium(II) chloride (0.42 g, 3 mol%) in THF (20 ml) were heated together under reflux for 1 h. The reaction mixture was diluted with light petroleum, sat. KF soln. was added and the precipitated stannyl fluoride was filtered off and the filtrate extracted with EtOAc, washed and purified on a silica column using hexane–EtOAc (2:1); yield 72%; m.p. 105°C. Compound **4a** was also obtained from the trimethylstannyl derivative **2b** in the same manner in 98% yield. ^{1}H NMR ($CDCl_3$): δ 0.06 (s, 6 H, $SiMe_2$), 0.88 (s, 9 H, $SiCMe_3$), 4.60 (s, 2 H, OCH_2), 5.13 (s, 2 H, $PhCH_2$), 6.25 (d, 1 H, H-4', $J_{4',3'}$ 3.35 Hz), 6.39 (d, 1 H, H-3', $J_{3',4'}$ 3.35 Hz), 7.32–7.38 (m, 5 H, Ph), 7.86 (d, 1 H, H-6, $J_{6,4}$ 3.3 Hz), 8.83 (d, 1 H, H-4, $J_{4,6}$ 3.3 Hz). ^{13}C NMR ($CDCl_3$): δ −5.30 ($SiMe_2$), 18.26 ($SiCMe_3$), 25.71 ($SiCMe_3$), 54.08 ($PhCH_2$), 57.85 (OCH_2), 105.24 (H-3'), 109.18 (H-4'), 110.24 (C-5), 128.51/128.61/128.87/134.03 (Ph), 141.10 (C-6), 154.23 (C-5'), 155.33 (C-2'), 162.51 (C-4). MS (CI): 397 (100, $M^+ + 1$), 396 (19), 339 (12), 265 (41), 91 (18).

*1-(Phenoxymethyl)-5-(5-*tert*-butyldimethylsilyloxy-2-furyl)-pyrimidin-2(1*H*)-one* (**4b**). 2-*tert*-Butyldimethylsilyloxymethyl-5-tributylstannylfuran (0.75 g, 2 mmol), 5-bromo-1-phenoxymethylpyrimidin-2(1*H*)-one (0.56 g, 2 mmol) and bis(triphenylphosphine)palladium(II) chloride (0.042 g, 3 mol %), in THF (10 ml) were refluxed for 2 h and purified as above; yield 85%, m.p. 92°C. Anal. $C_{22}H_{28}N_2O_4Si$: C, H. ^{1}H NMR ($CDCl_3$): δ 0.002 (s, 6 H, $SiMe_2$), 0.82 (s, 9 H, $SiCMe_3$), 4.55 (s, 2 H, OCH_2), 5.83 (s, 2 H, NCH_2O), 6.19 (d, 1 H, H-4', $J_{4',3'}$ 3.0 Hz), 6.36 (d, 1 H, H-3', $J_{3',4'}$ 3.0 Hz), 6.91–7.20 (m, 5 H, Ph), 8.01 (d, 1 H, H-6, $J_{6,4}$ 3.18 Hz), 8.79 (d, 1 H, H-4, $J_{4,6}$ 3.18 Hz). ^{13}C NMR ($CDCl_3$): δ −5.39 ($SiMe_2$), 18.17 ($SiCMe_3$), 25.63 ($SiCMe_3$), 57.79 (OCH_2), 75.51 (NCH_2), 105.64 (C-4'), 109.12 (C-3'), 110.56 (C-5), 115.41/122.95/129.76/146.12 (Ph), 138.69 (C-4), 154.30 (C-5'), 154.42 (C-2'), 155.32 (C-2), 163.49 (C-6). MS(CI): 413 (100, $M^+ + 1$), 412 (26), 355 (21), 303 (3), 281 (26), 187 (4), 159 (5), 146 (3), 107 (2), 105 (2).

*1-Benzyl-5-(5-hydroxymethyl-2-furyl)pyrimidin-2(1*H*)-one* (**5a**). 1-Benzyl-5-(5-*tert*-butyldimethylsilyloxymethyl-2-furyl)pyrimidin-2(1*H*)-one (0.4 g, 1 mmol) and tetrabutylammonium fluoride in THF (4 ml) were stirred together for 10 min at ambient temperature, water was added and the solution acidified with 1 M HCl, extracted with EtOAc, washed, dried ($MgSO_4$) and purified on silica gel with EtOAc as the eluent; yield 95%, m.p. 110°C. Anal. $C_{16}H_{14}N_2O_3$: C, H. ^{1}H NMR ($CDCl_3$): δ 3.01 (br s, 1 H, OH–removed on shaking with D_2O), 4.57 (s, 2 H, CH_2Ph), 5.15 (s, 2 H, OCH_2), 6.31 (d, 1 H, H-3'/4', $J_{3',4'}$ 3.5 Hz), 6.43 (d, 1 H, H-4'/3', $J_{4',3'}$ 3.5 Hz), 7.33–7.38 (m, 5 H, Ph), 8.08 (d, 1 H, H-4, $J_{4,6}$ 3.15 Hz), 8.40 (d, 1 H, H-6, $J_{6,4}$ 3.15 Hz). ^{13}C NMR ($CDCl_3$): δ 53.5 ($PhCH_2$), 57.1 (OCH_2), 104.7 (H-3'), 108.6 (H-4'), 109.7



Scheme 1.

(C-5), 127.6/127.7/128.0/133.8 (Ph), 140.5 (C-6), 153.7 (C-5′), 154.8 (C-2′), 161.9 (C-4). MS (CI): 283 (100, $M^+ + 1$), 282 (23), 281 (10), 269 (62), 268 (31), 267 (80), 266 (17), 205 (6), 177 (5), 135 (7), 91 (41).

*1-Phenoxymethyl-5-(5-hydroxymethyl-2-furyl)pyrimidin-2(1H)-one (**5b**).* Compound **5b** was obtained as above from 5-(5-*tert*-butyldimethylsilyloxymethyl-2-furyl)pyrimidin-2(1*H*)-one (0.62 g, 1.5 mmol), and was purified by chromatography on silica gel using EtOAc as the eluent; yield 87%, m.p. 72°C. Anal. $C_{16}H_{14}N_2O_4$: C, H. ^{1}H NMR ($CDCl_3$): δ 4.91 (s, 2 H, OCH_2), 6.32 (s, 2 H, NCH_2O), 6.54 (d, 1 H, H-4′, $J_{4',3'}$ 3.2 Hz), 6.87 (d, 1 H, H-3′, $J_{3',4'}$ 3.2 Hz), 6.91–7.73 (m, 5 H, Ph), 8.41 (d, 1 H, H-6, $J_{6,4}$ 3.18 Hz), 8.98 (d, 1 H, H-4, $J_{4,6}$ 3.18 Hz). ^{13}C NMR ($CDCl_3$): δ 58.91 (OCH_2), 77.97 (NCH_2), 106.23 (C-4′), 110.32 (C-3′), 111-34 (C-5), 115.86/123.35/130.24/146.67 (Ph), 139.32 (C-4), 154.92 (C-5′), 155.20 (C-2′), 155.87 (C-2), 164.12 (C-6). MS(CI): 299 (7, $M^+ + 1$), 298 (1.3), 283 (100), 281 (91), 210 (7), 203 (21), 195 (60), 193 (65), 189 (25), 177 (27), 152 (96), 150 (93), 94 (31).

*2-tert-Butyldimethylsilyloxy-5-(5-dimethylthexylsilyloxymethyl-2-furyl)pyrimidine (**7**).* A solution of 2-*tert*-butyldimethylsilyloxy-5-bromopyrimidine (2.02 g, 5 mmol), 2-dimethylthexylsilyloxymethyl-5-trimethylstannylfuran (1.5g, 5.2 mmol) and bis(triphenylphosphine)palladium(II) chloride (0.1 g, 3 mol %) in 1,2-dichloroethane (5 ml) was heated under reflux for 1.5 h. The cold reaction mixture was treated with sat. KF soln., filtered, washed thoroughly with 10% NaCl solution and then with water, the dried solution was evaporated and the residue was chromatographed on silica using light petroleum–EtOAc (9:1). The eluent was evaporated off and the product was distilled in a Kugelrohr apparatus, oven temp. 250°C/0.01 mmHg; yield 89%. Anal. $C_{23}H_{40}N_2O_3Si_2$: C, H. ^{1}H NMR ($CDCl_3$): δ 0.10 (s, 6 H, Si*Me*$_2$thexyl), 0.33 (s, 6 H, Si*Me*$_2$CMe_3), 0.82 (s, 6 H, Si–CMe_2–C), 0.84 (d, 6 H, Si–C–C*Me*$_2$H, 0.98 (s, 9 H, SiCMe_3), 1.6 (m, 1 H, Si–C–CH), 4.62 (OCH_2), 6.25 (d, 1 H, H-3′ $J_{3',4'}$ 3.3 Hz), 6.50 (d, 1 H, H-4′, $J_{4',3'}$ 3.3 Hz), 8.67 (s, 2 H, H-4,6). ^{13}C NMR ($CDCl_3$): δ −4.76 (Si*Me*$_2$–thexyl), −3.49 (Si*Me*$_2$–CMe_3), 17.71 (Si–*C*Me_2–C), 18.24 (Si–C*Me*$_2$–C), 20.04 (Si–C–C*Me*$_2$), 25.00 (Si–*C*Me_3), 25.53 (Si–C*Me*$_3$), 33.90 (Si–C–*C*H), 57.66 (OCH_2), 105.80 (C-4′), 108.88 (C-3′), 119.31 (C-5), 147.73 (C-2′), 154.32 (C-4,6), 154.70 (C-5′), 162.52 (C-2). MS(CI): 449 (4, $M^+ + 1$), 391 (2), 335 (20), 279 (11), 249 (13), 234 (10), 206 (12), 175 (14), 164 (16), 147 (11), 103 (23), 92 (37), 84 (63), 75 (100).

*5-(5-tert-Butyldimethylsilyloxy-2-furyl)pyrimidin-2(1H)-one (**8a**).* A mixture of 2-*tert*-butyldimethylsilyloxy-5-bromopyrimidine (2.02 g, 5 mmol), 2-*tert*-butyldimethylsilyloxymethyl-5-tributylstannylfuran (2.6 g, 5.2 mmol) and bis(triphenylphosphine)palladium(II) chloride (0.05 g, 3 mol%) was heated under reflux in DCE (5 ml) overnight. The mixture was treated with sat. KF solution, filtered, and washed, the organic solution was dried ($MgSO_4$), and evaporated and the residue chromatographed on silica using EtOAc–light petroleum (1:1); yield 85%, m.p. 161°C. Anal. $C_{15}H_{22}N_2O_3Si$: C, H. ^{1}H NMR ($CDCl_3$): δ 0.087 (s, 6 H, $SiMe_2$), 0.89 (s, 9 H, SiC*Me*$_3$), 4.64 (s, 2 H, OCH_2), 6.28 (d, 1 H, H-4′, $J_{4,3}$ 3.3 Hz), 6.48 (d, 1 H, H-3′, $J_{3',4}$ 3.3 Hz), 8.57 (s, 2 H, H-4,6). ^{13}C NMR ($CDCl_3$): δ −5.3 ($SiMe_2$), 18.27 (*C*Me_3), 25.73 (C*Me*$_3$), 57.93 (OCH_2), 105.67 (C-4′), 109.19 (C-3′), 111.19 (C-5), 146.36 (C-4/6), 152.0 (C-5′), 152.67 (C-2′), 154.63 (C-6/4), 157.92 (C-2).

*5-(5-Dimethylthexylsilyloxymethyl-2-furyl)pyrimidin-2(1H)-one (**8b**).* 2-*tert*-Butyldimethylsilyloxy-5-(5-dimethylthexylsilyloxymethyl-2-furyl)pyrimidine (1.5 g, 3.35 mmol) was dissolved in $CHCl_3$ and acidified with AcOH. TLC after 30 min showed the reaction to be complete. The precipitate formed was filtered off, washed with light petroleum and recrystallized with i-PrOH–pentane (1:1); yield 86%. Anal. $C_{17}H_{26}N_2O_3Si$: C, H. ^{1}H NMR ($CDCl_3$): δ 1.13 (s, 6 H, $SiMe_2$), 1.84 (s, 6 H, Si-C*Me*$_2$–C), 1.87 (d, 6 H, Si–C–C*Me*$_2$, $J_{Me,H}$ 7.04 Hz), 2.62 (m, 1 H, Si–C–CH), 3.56 (s, 1 H, NH), 5.62 (s, 1 H, OCH_2), 7.33 (d, 1 H, H-3′/4′, $J_{3',4'}$ 2.1 Hz), 7.66 (d, 1 H, H-4′/3′, $J_{4',3'}$ 2.1 Hz), 9.37 (br s, 1 H, H-4), 9.52 (s, 1 H, H-6). ^{13}C NMR ($CDCl_3$): δ −3.43 ($SiMe_2$), 18.26 (Si*C*Me_2), 20.06 (Si–C–C*Me*$_2$), 24.75 (Si–*C*Me_2), 33.69 (Si–C–*C*H), 57.26 (OCH_2), 104.92 (C-4′/3′), 109.19 (C-3′/4′), 109.32 (C-2), 147.02 (C-5′/2′)′, 153.39 (C-4,6), 156.01 (C-2′/5′). MS(CI): 335 (100, $M^+ + 1$), 266 (5), 249 (13), 192 (4), 177 (142), 175 (13).

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