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INTRAMOLECULAR DIELS-ALDER REACTIONS OF PYRIMIDINES: SYNTHESIS OF TRICYCLIC ANNELATED PYRIDINES.

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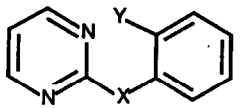
Abstract: 2-(2-Trimethylsilylethynylphenyl-X)-pyrimidines (**2**, X= O, S, NAc, CH_2, C=O) easily undergo intramolecular Diels-Alder reaction with inverse electron demand, to give tricyclic annelated pyridines in excellent yields. The synthesis of **2** and the cycloaddition reaction to give the tricyclic annelated pyridines is described.

INTRODUCTION

Inverse electron-demand Diels-Alder reactions of heterocyclic azadienes with electron-rich dienophiles have received considerable attention in the last two decades[1,2]. In our laboratory attention is focussed on reactions of pyrimidines, pyrazines and pyridines as electron deficient azadienes[3]. The entropic advantage inherent to intramolecular Diels-Alder reactions has allowed us to explore cycloadditions with less reactive dienophiles such as alkynes under relatively mild conditions. In previous papers we described the cycloaddition reactions of pyrimidines and pyrazines containing an -X-CH_2-CH_2-C≡CH (X = O, NAc, S, SO, SO_2 or $C(CN)_2$) side chain which gave bicyclic annelated pyridine derivatives[3d-g]. In this paper the cycloaddition reaction of several pyrimidines containing an -X-(2-phenylene)-C≡C-$Si(CH_3)_3$ (X = O, S, NH, NAc, CH_2, C=O) group at position 2 to give tricyclic annelated pyridines is described. For these compounds a higher reactivity for cycloaddition is expected than for the corresponding pyrimidines containing an -X-CH_2-CH_2-C≡CH side chain due to the limited conformational freedom inherent to the *o*-phenylene group[4].

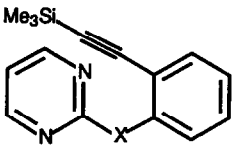
RESULTS AND DISCUSSION

For the synthesis of the 2-(2-trimethylsilylethynylphenyl-X)-pyrimidines **2a-f** we used 2-chloropyrimidine as a starting material. This was reacted with 2-bromophenol, 2-iodoaniline, 2-bromoaniline or 2-aminothiophenol respectively to give the corresponding 2-substituted pyrimidines (**1a-c, f**). The N-acetylated derivatives **1d** and **1e** were obtained by reacting **1b** and **1c** respectively, with acetic anhydride in dry pyridine with a catalytic amount of dimethylaminopy-



1

a: X = O, Y = Br
b: X = NH, Y = I
c: X = NH, Y = Br
d: X = NAc, Y = I
e: X = NAc, Y = Br
f: X = S, Y = NH_2
g: X = S, Y = I
h: X = CH_2, Y = Br
i: X = C=O, Y = Br



2

a: X = O
b: X = NH
c: X = NAc
d: X = S
e: X = CH_2
f: X = C=O

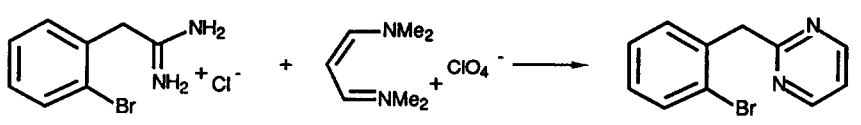
Table I: Trimethylsilylacetylene compounds **2** from **1**.

Starting Compounds	Reaction Products	Reaction Conditions Temp.(°C)	Time (h)	Yield (%)
1a	**2a**	90	2	90
1b	**2b**	40	4	76
1c	**2b**	90	4	60
1d	**2c**	40	1	81
1e	**2c**	60	4	74
1g	**2d**	40	3	91
1h	**2e**	80	6	72
1i	**2f**	80	3	61

ridine. 2-(2-Iodophenylthio)-pyrimidine (**1g**) was prepared in good yield by diazotation of **1f** and subsequent reaction with sodium iodide[5].

The 2-(2-bromobenzyl)pyrimidine (**1h**) was produced from 2-bromophenylacetamidine (**3**)[6] and (3-dimethylamino-1-propenyl)dimethylimmonium perchlorate (**4**)[7] according to Scheme I. Oxidation of **1h** with potassium permanganate under phase transfer conditions (water/chloroform)[8] gave the benzoyl derivative **1i**.

Scheme I



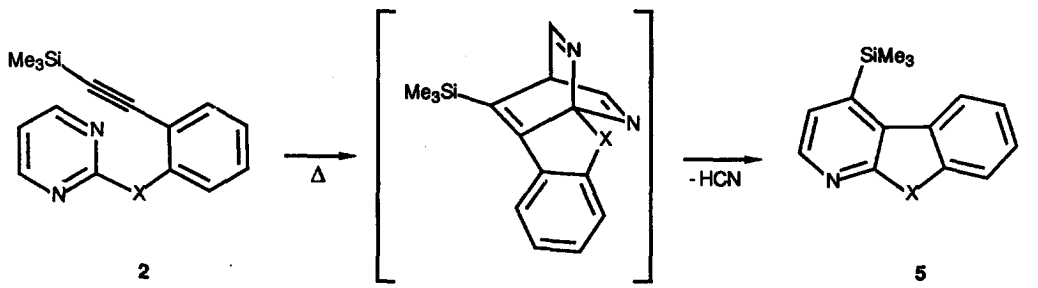
3 4 1h

The 2-(2-trimethylsilylethynylphenyl-X)-pyrimidines (**2a-f**) were prepared from their halogeno precursors **1**. The halogen (I or Br) on position 2 of the phenyl ring of compounds **1a-e** and **1g-i** was replaced by a trimethylsilylethynyl group by means of a Pd° catalyzed substitution reaction. Under the conditions used by Takahashi[9] only iodide is reactive enough to be substituted in deactivated aryl systems. However, if the reaction is carried out in a sealed tube at 60-90 °C even bromide is substituted in high yields (Table I).

The cycloaddition of the 2-(2-trimethylsilylethynylphenyl-X)-pyrimidines (**2a,c-f**) and the subsequent retro Diels-Alder reaction (to give the annelated pyridines **5a,c-f**) was performed in nitrobenzene at 160 °C (Scheme II). At this temperature the reaction was complete within one (X = C=O) to eighteen (X = S) hours. By this method we succeeded in synthesizing 4-trimethylsilylbenzofuro[2,3-b]pyridine (**5a**), 9-acetyl-4-trimethylsilylpyrido[2,3-b]indole (**5c**), 4-trimethylsilylbenzothieno[2,3-b]pyridine (**5d**), 4-trimethylsilylindeno[2,1-b]pyridine (**5e**) and 4-trimethylsilylindeno[2,1-b]pyridin-9-one (**5f**).

We were unable to accomplish cycloaddition with **2b** (X = NH), even when the reaction was performed in refluxing nitrobenzene for 24 hours. The yields and reactivities ($t_{1/2}$) for the other compounds are given in Table II.

Scheme II



2

a: X = O **d**: X = S
b: X = NH **e**: X = CH_2
c: X = NAc **f**: X = C=O

5

a: X = O **e**: X = CH_2
c: X = NAc **f**: X = C=O
d: X = S

It is clear that the intramolecular cycloaddition of the 2-(2-trimethylsilylethynylphenyl-X)-pyrimidines **1** and the subsequent retro Diels-Alder reaction occurs very easily under the experimental conditions and in very good yields. Surprisingly, **2f** (X = C=O) was found to react very rapidly at 160 °C. Even at 120 °C this compound was completely converted into **5f** within 2 h. The reluctance of **2b** (X = NH) to give cycloaddition is not without precedent and has also been observed for other pyrimidines[3e,g], for pyrazines[3c] and triazines[10] containing an NH as link between the heterocycle and the dienophilic side chain.

Table II: Products, reaction rates at 160 °C and yields for the intramolecular cycloaddition reaction of compounds 2.

Starting Compounds	Reaction Products	$t_{1/2}$ (h)	Yield (%)
2a	**5a**	0.47	>95
2b	--	--	--
2c	**5c**	0.30	>95
2d	**5d**	1.74	>95
2e	**5e**	0.82	>95
2f	**5f**	<0.05[a]	>95

[a] The $t_{1/2}$ of this compound was 0.27 h at 120 °C

The higher reactivity of the compounds investigated in this study as compared to the 2-(butynyl-X)-pyrimidines[3e,g] may be due to a limited conformational freedom in the side chain by the presence of the *o*-phenylene group and thus an enhanced entropic advantage. Furthermore, molecular mechanics calculations (MNDO) indicate that a planar conformation of the two aromatic rings appears to have a higher energy than a twisted conformation, from which a conformation for cycloaddition is more easily attainable. When the observed order of reactivity (NH << S < CH_2 < O < NAc < C=O) is compared with the order of reactivity observed for ω-butynyl-X-triazines[10], -pyrimidines[3g,11] and -pyrazines[3c] (NH << O < S < CH_2 < NAc) there are some significant changes. In our opinion the order of reactivity can hardly be explained by differences in electron donating properties of the X group[12]. More important factors seem to be the preferred conformation of the starting material and the energy required to reach a reactive conformation from which reaction can occur between the π-electron systems of the diene and the dienophile. Presently, molecular mechanics calculations are performed to gain more insight into the observed differences in reactivity.

EXPERIMENTAL SECTION

Melting points are uncorrected. ^{1}H-NMR spectra were recorded on a Varian EM 390 spectrometer. Chemical shifts are determined in ppm downfield from tetramethylsilane. Mass spectral data were obtained on a AEI MS 902 spectrometer equipped with a VG ZAB console. Column chromatography was performed on Merck silica gel 60 (70-230 mesh ASTM).

2-Bromophenylacetamidine hydrochloride (3).
One equivalent of hydrochloric acid was passed into a solution of *o*-bromophenylacetonitrile (50 mmol)[13] in absolute ethanol. The mixture was allowed to stand for two days at room temperature to give the imidate, which was isolated by filtration as the hydrochloride in 80% yield. The amidine salt (3) was obtained by stirring the imidate salt for two days at 40 °C in a solution of ammonia in ethanol. The mixture was concentrated under reduced pressure and the residue was recrystallized from ethanol. Yield 87 %: mp 100-102 °C (ethanol).
^{1}H-NMR ($CDCl_3$) δ 8.00 (bs, NH_2), 7.65-7.00 (Ar, 4H), 3.12 (s, CH_2).
Anal. calcd. for $C_8H_{10}BrClN_2$: C, 38.5; H, 4.0; N, 11.2. Found: C, 38.0; H, 4.1; N, 11.6.

2-(2-Bromophenyloxy)pyrimidine (1a).
A solution of commercially available 2-chloropyrimidine (1.14 g; 10 mmol) and 2-bromophenol (3.50 g; 21 mmol) in diphenyl ether (15 ml) was heated overnight at 160 °C. The product was isolated by column chromatography using n-hexane as eluent to remove the diphenyl ether, followed by chloroform to give **1a**. Yield 91%: mp 89-90 °C (n-hexane / ether 1:2).
^{1}H-NMR ($CDCl_3$) δ 8.58 (d, J=4.5 Hz, 2H), 7.68 (d, J=9.0 Hz, 1H), 7.50-6.99 (Ar, 4H).
HRMS calcd. for $C_{10}H_7BrN_2O$: 249.9742. Found: 249.9741.
Anal. calcd.: C, 47.8; H, 2.8; N, 11.2. Found: C, 48.1; H, 2.8; N, 11.2.

2-(2-Iodophenylamino)pyrimidine (1b).
This compound was prepared from 2-chloropyrimidine (10 mmol) and 2-iodoaniline (4.4 g; 20 mmol) by the method described for the synthesis of **1a**. Yield 24%: mp 65-66 °C (n-hexane / ether 1:2).
^{1}H-NMR ($CDCl_3$) δ 8.42 (d, J=4.5 Hz, 2H), 8.30 (dd, J_1=9.0 Hz, J_2=2.5 Hz, 1H), 7.80 (dd, J_1=9.0 Hz, J_2=2.5 Hz, 1H), 7.45 (bs, NH), 7.31 (dt, J_1=9.0 Hz, J_2=3.0 Hz, 2H), 6.72 (t, J=4.5 Hz, 1H).
HRMS calcd. for $C_{10}H_8IN_3$: 296.9765. Found: 296.9761.
Anal. calcd.: C, 40.4; H, 2.7; N, 14.1. Found: C, 40.3; H, 2.7; N, 13.8.

2-(2-Bromophenylamino)pyrimidine (1c).
This compound was prepared from 2-chloropyrimidine (10 mmol) and 2-bromoaniline (3.45 g; 20 mmol) by the method described for the synthesis of **2a**. Yield 92%: mp 78-79 °C (n-hexane / ether 1:2).
^{1}H-NMR ($CDCl_3$) δ 8.45 (d, J=4.5 Hz, 2H), 7.62 (bs, NH), 7.58 (dd, J_1=9.0 Hz, J_2=2.5 Hz, 1H), 7.30 (dt, J_1=9.0 Hz, J_2=3.0 Hz, 2H), 6.92 (dd, J_1=9.0 Hz, J_2=2.5 Hz, 1H), 6.72 (t, J=4.5 Hz, 1H).
HRMS calcd. for $C_{10}H_8BrN_3$: 248.9901. Found: 248.9901.
Anal. calcd.: C, 48.0; H, 3.2; N, 16.8. Found: C, 48.00; H, 3.2; N, 16.9.

2-(N-acetyl-2-iodophenylamino)pyrimidine (1d).
A solution of **1b** (3.0 g; 10 mmol) in dry pyridine (25 ml) was treated with acetic anhydride (5 ml) and a catalytic amount of 4-dimethylaminopyridine. The solution was heated at 70 °C for 24 h. After removing the pyridine and acetic acid under reduced pressure, column chromatography using diethyl ether as eluent gave the pure **1d**. Yield 73 %: oil.
^{1}H-NMR ($CDCl_3$) δ 8.61 (d, J=4.5 Hz, 2H), 7.93 (d, J=6.2 Hz, 1H), 7.52-7.08 (Ar, 3H), 7.00 (t, J=4.5 Hz, 1H), 2.58 (s, 3H).
HRMS calcd. for $C_{12}H_{10}IN_3O$: 338.9871. Found: 338.9866.

2-(N-acetyl-2-bromophenylamino)pyrimidine (1e).
This compound was prepared from **1c** (10 mmol) by the method described for the synthesis of **1d**. Yield 68 %: mp 105-106 °C (n-hexane / ether 2:1).
^{1}H-NMR ($CDCl_3$) δ 8.59 (d, J=4.5 Hz, 2H), 7.66 (d, J=6.2 Hz, 2H), 7.50-7.10 (Ar, 3H), 7.00 (t, J=4.5 Hz, 1H), 2.48 (s, 3H).
HRMS calcd. for $C_{12}H_{10}BrN_3O$: 291.0008. Found: 291.0012.
Anal. calcd.: C, 49.3; H, 3.5; N, 14.4. Found: C, 49.1; H, 3.4; N, 14.3.

2-(2-Aminophenylthio)pyrimidine (1f).
This compound was prepared from 2-chloropyrimidine (10 mmol) and 2-aminothiophenol (2.00 g; 20 mmol) by the method described for **1a**. Yield 84%: mp 127-129 °C (n-hexane / ether 1:2).

^{1}H-NMR ($CDCl_3$) δ 8.50 (d, J=4.5 Hz, 2H), 7.48 (dd, J_1=9.0 Hz, J_2=2.5 Hz, 1H), 7.23 (dt , J_1=8.7 Hz, J_2=3.0 Hz, 1H), 7.94 (t, J=4.5 Hz, 1H), 7.87 (m, 2H), 4.25 (bs, NH_2).
HRMS calcd. for $C_{10}H_9N_3S$: 203.0517. Found: 203.0517.
Anal. calcd.: C, 59.2; H, 4.5; N, 20.7. Found: C, 59.5; H, 4.5; N, 21.0.

2-(2-Iodophenylthio)pyrimidine (**1g**).
A solution of sodium nitrite (11 mmol) in water (5 ml) was added dropwise in 0.5 h to a stirred solution of **1f** (2.03 g; 10 mmol) in a mixture of concentrated hydrochloric acid (3 ml) and water (5 ml) at 0 °C. After 2 h a solution of potassium iodide (22 mmol) in water (10 ml) was added to the reaction mixture. The mixture was extracted with chloroform (3 x 20 ml) and the organic layer was dried ($MgSO_4$) and evaporated. Column chromatography using ether as eluent gave the pure **1g**. Yield 68 %: mp 93-94 °C (n-hexane / ether 2:1).
^{1}H-NMR ($CDCl_3$) δ 8.48 (d, J=4.5 Hz, 2H), 8.00 (dd, J_1=9.0 Hz, J_2=3.0 Hz, 1H), 7.73 (dd , J_1=9.0 Hz, J_2=3.0 Hz, 1H), 7.38 (dt, J_1=9.0, J_2=3.0 Hz, 1H), 7.09 (dt, J_1=9.0, J_2=3.0 Hz, 1H), 6.94 (t, J=4.5 Hz, 1H).
HRMS calcd. for $C_{10}H_7IN_2S$: 313.9377. Found: 313.9373.
Anal. calcd. C, 38.3; H, 2.3; N, 8.9. Found: C, 38.3; H, 2.2; N, 9.0.

2-(2-Bromobenzyl)pyrimidine (**1h**).
A solution of sodium ethanolate (15 mmol) in ethanol (20 ml) is added to a solution of **3** (2.5 g; 10 mmol) and **4** (2.1 g; 10 mmol) in ethanol (20 ml). After 0.5 h again 15 mmol of sodium ethanolate was added and the mixture was refluxed for 2.5 h. The ethanol was removed under reduced pressure. Water (20 ml) was added to the residue and the aqueous layer was extracted with ether (3 x 40 ml). The organic layer was dried ($MgSO_4$) and evaporated to give the crude **1h**. Column chromatography using methylene chloride as eluent gave the pure **1h**. Yield 70 %: oil.
^{1}H-NMR ($CDCl_3$) δ 8.64 (d, J=4.5 Hz, 2H), 7.52 (d, J=9.0 Hz, 1H), 7.30-7.00 (Ar, 4H), 4.45 (s, CH_2).
HRMS calcd. for $C_{11}H_9BrN_2$: 246.9871. Found: 246.9878.

2-(2-Bromobenzoyl)pyrimidine (**1i**).
To a solution of **1h** (2.5 g; 10 mmol) in chloroform (30 ml), was added a solution of potassium permanganate (30 mmol), potassium hydroxide (10 mmol) and tetraethylammonium hydrogen sulphate (2 mmol) in water. The two phase reaction mixture was violently stirred for several days at 70 °C until the violet color had disappeared. The mixture was acidified with acetic acid (10 ml) and small portions of sodium bisulfite were added until the brown colour had disappeared. The organic layer was separated, washed with water, dried over $MgSO_4$ and evaporated to give the crude product. Recrystallization in ether gave the pure **1i**. Yield 56 %: mp 135-137 °C (ether); IR (KBr): 1685 cm^{-1} (ϑ C=O).
^{1}H-NMR ($CDCl_3$) δ 8.92 (d, J= 4.5 Hz, 2H), 7.72-7.30 (m, 5H).
Anal. calcd. for $C_{11}H_7BrN_2O$: C, 50.2; H, 2.7; N, 10.7 Found: C, 50.4; H, 2.7; N, 10.7.

2-(2-Trimethylsilylethynylphenyloxy)pyrimidine (**2a**).
To a solution of **1a** (2.50 g; 10 mmol) and trimethylsilylacetylene (2.0 g; 20 mmol) in 15-20 ml of triethylamine were added $PdCl_2(PPh_3)_2$ (150 mg) and CuI (0.05 mg) and the solution was heated in a sealed tube for 2 h at 90 °C (see Table I). After evaporation of the triethylamine the residue was purified with column chromatography using ether/n-hexane (2:1) as eluent to give **2a**. Yield 80 %: mp 116-117 °C (n-hexane).
^{1}H-NMR ($CDCl_3$) δ 8.55 (d, J=4.5 Hz, 2H), 7.62-7.10 (Ar, 4H), 7.00 (t, J=4.5 Hz, 1H), 0.10 (s, 9H).
HRMS calcd. for $C_{15}H_{16}N_2OSi$: 268.1032. Found: 268.1036.
Anal. calcd. C, 67.1; H, 6.1; N, 10.4 .Found: C, 67.1; H, 6.1; N, 10.3.

2-(2-Trimethylsilylethynylphenylamino)pyrimidine (**2b**).
A solution of **1b** (3.0 g; 10 mmol) or **1c** (2.5 g; 10 mmol) was treated with 2.0 g of trimethylsilylacetylene in the same way as for the synthesis of **2a**. The period of heating was 4 h for **1b** at 40 °C and 4 h for **1c**, both at 90 °C. Yield 76 % from **1b** and 60 % from **1c**: oil.
^{1}H-NMR ($CDCl_3$) δ 8.53 (d, J=6.3 Hz, 1H), 8.48 (d, J=4.5 Hz, 2H), 7.80 (br s, 1H), 7.60-7.20 (Ar, 2H), 6.92 (t, J=4.5 Hz, 1H), 6.76 (t, J=6 Hz, 1H), 0.30 (s, 9H).
HRMS calcd. for $C_{13}H_{17}N_3Si$: 267.1191. Found: 267.1199.

2-(N-acetyl-2-trimethylsilylethynylphenylamino)pyrimidine (2c).
A solution of **1d** (3.4 g; 10 mol) or **1e** (2.9 g; 10 mmol) was treated with 2.0 g of trimethylsilylacetylene in the same way as for the synthesis of **2a**. The period of heating was 4 h at 40 °C for **1d** and 4 h for **1e**, both at 60 °C. Yield 81 % from **1c** and 74 % from **1e**: oil.
^{1}H-NMR ($CDCl_3$) δ 8.88 (d, J=4.5 Hz, 2H), 7.90-7.38 (Ar, 4H), 7.24 (t, J=4.5 Hz, 1H), 2.72 (s, 3H), 0.35 (s, 9H).
HRMS calcd. for $C_{15}H_{19}N_3OSi$: 309.1297 Found: 309.1290.

2-(Trimethylsilylethynylphenylthio)pyrimidine (2d).
A solution of **1g** (3.2 g; 10 mmol) was treated with 2.0 g of trimethylsilylacetylene in the same way as for the synthesis of **2a**. The periode of heating was 4 h at 80 °C. Yield 91 %: mp 76-77 °C (n-hexane).
^{1}H-NMR ($CDCl_3$) δ 8.45 (d, J=4.5 Hz, 2H), 7.70-7.12 (Ar, 4H), 6.92 (t, J=4.5 Hz, 1H), 0.05 (s, 9H).
HRMS calcd. for $C_{15}H_{16}N_2SSi$: 284.0803. Found: 284.0803.
Anal. calcd.: C, 63.4; H, 5.7; N, 9.9. Found: C, 63.3; H, 5.7; N, 9.9.

2-(2-Trimethylsilylethynylbenzyl)pyrimidine (2e).
A solution of **1h** (2.5 g; 10 mmol) was treated with 2.0 g of trimethylsilylacetylene in the same way as for the synthesis of **2a**. The period of heating was 6 h at 80 °C. Yield 72 %: oil.
^{1}H-NMR ($CDCl_3$) δ 8.68 (d, J=4.5 Hz, 2H), 7.59-7.03 (Ar, 5H), 4.50 (s, CH_2), 0.15 (s, 9H).
HRMS calcd. for $C_{16}H_{18}N_2Si$: 265.1161. Found: 265.1170.

2-(2-Trimethylsilylethynylbenzoyl)pyrimidine (2f).
A solution of **1i** (0.53 g; 2.0 mmol) was treated with 1.0 g of trimethylsilylacetylene in the same way as for the synthesis of **2a**. The period of heating was 3 h at 80 °C. Yield 61%: mp 105-106 °C (n-hexane).
^{1}H-NMR ($CDCl_3$) δ 8.80 (d, J=4.5 Hz, 2H), 7.64 (t, J=4.5 Hz, 1H), 7.46-7.23 (Ar, 4H), 0.00 (s, 9H).
Anal. calcd. for $C_{16}H_7N_2OSi$: C, 68.5; H, 5.8; N, 10.0. Found: C, 68.4; H, 5.7; N, 9.9.

4-Trimethylsilylbenzofuro[2,3-b]pyridine (5a).
A solution of **2a** (0.27 g; 1 mmol) in 1 ml of nitrobenzene was heated at 160 °C for 12 h. After cooling the reaction mixture was chromatographed. The column was first eluted with hexane to remove the nitrobenzene and then with chloroform to give the pure **5a**. Yield >95 %: mp 86-87 °C (n-hexane).
^{1}H-NMR ($CDCl_3$) δ 8.30 (br s, 1H), 8.15 (m, 1H), 7.78 (m, 1H), 7.44-7.12 (Ar, 3H), 0.35 (s, 9H).
HRMS calcd. for $C_{14}H_{15}NOSi$: 241.0923. Found: 241.0931.
Anal. calcd.: C, 69.7; H, 6.3; N, 5.8. Found: C, 69.7; H, 6.3; N, 5.8.

9-Acetyl-4-trimethylsilylpyrido[2,3-b]indole (5c).
This compound was prepared from **2c** (0.25 g; 1 mmol) by the same method described for the synthesis of **5a**, except that heating at 160 °C was performed for 6 h. Yield >95 %: oil.
^{1}H-NMR ($CDCl_3$) δ 8.82 (d, J=4.5 Hz, 1H), 8.42 (d, J=2.25 Hz, 1H), 8.09 (d, J=2.5 Hz, 1H), 7.60-7.28 (Ar, 3H), 3.10 (s, 3H), 0.50 (s, 9H).
HRMS calcd. for $C_{16}H_{18}N_2OSi$: 282.1188. Found: 282.1185.

4-Trimethylsilylbenzothieno[2,3-b]pyridine (5d).
This compound was prepared from **2d** (0.28 g; 1 mmol) by the same method described for the synthesis of **5a**, except that heating at 160 °C was performed for 18 h. Yield >95 %: oil.
^{1}H-NMR ($CDCl_3$) δ 8.30 (br s, 1H), 8.15 (m, 1H), 7.80 (m, 1H), 7.44-7.10 (Ar, 3H), 0.30 (s, 9H).
HRMS calcd. for $C_{14}H_{15}NSSi$: 257.0694. Found: 257.0694.

4-Trimethylsilylindeno[2,1-b]pyridine (5e).
This compound was prepared from **2e** (0.27 g; 1 mmol) by the same method described for the synthesis of **5a**, except that heating at 160 °C was performed for 12 h. Yield >95 %: mp 77-79 °C (n-hexane).
^{1}H-NMR ($CDCl_3$) δ 8.55 (d, J=4.5 Hz, 1H), 8.15-7.30 (m, 5H), 0.50 (s, 9H).
HRMS calcd. for $C_{15}H_{17}NSi$: 239.1130. Found: 239.1127.
Anal. calcd.: C, 75.3; H, 7.2; N, 5.9. Found: C, 75.2; H, 7.4; N, 5.6.

4-Trimethylsilylindeno[2,1-b]pyridin-9-one (5f).
This compound was prepared from **2f** (0.28 g; 1 mmol) by the same method described for the synthesis of **5a**, except that heating was performed at 120 °C for 2 h. Yield >95%: mp 180-181 °C (n-hexane).
^{1}H-NMR ($CDCl_3$) δ 8.56 (d, J=4.5 Hz, 2H), 7.90-7.28 (Ar, 4H), 0.50 (s, 9H).
Anal. calcd. for $C_{15}H_{15}NOSi$: C, 71.2; H, 6.0; N, 5.5 Found: C, 71.0; H, 6.0; N, 5.5.

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