

Scheme A

— the lateral regioselective metallation of polymethylated nitrogenous heterocycles **1a–c**^{4,5}, which leads to the primary lithioenamines **2** after condensation with different nitriles having no α -hydrogen, and

— the regioselective *N*-acylation of the *N*-trimethyl silylenamines **3** with various acid chlorides. This latter method derives from the procedure for *N*-silylenamines **8**⁶. Physical and spectroscopic properties of compounds **3** are summarized in Tables 1 and 3. Acylation of the *N*-silylenamines **3** is a simple and mild procedure giving pure, substituted enamides **4** in moderate to high yields, except with dimethylcarbamyl chloride (see Table 2). Spectral data of products **4** are collected in Table 4.

Pyridines; XV¹. Synthesis of Enamides by Selective *N*-Acylation of Silylated Primary Enamines; Results of the Regioselective Metallation of *s*-Collidine, 2,4-Lutidine and 2,4-Dimethylquinoline

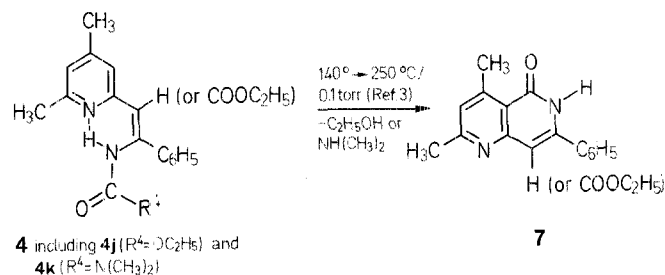
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Nineteen substituted enamides **4** are easily prepared (yields 30–71%) in chloroform by condensation of various acyl chlorides R⁴-COCl with the *N*-trimethylsilylenamines **3**. The compounds **3** are obtained from the regioselective *N*-silylation (yields 60–98%) of the lithioenamines **2**, which result from the condensation of nitriles R³-CN having no α -hydrogen atom with 2-lithiomethyl derivatives of *s*-collidine, 2,4-lutidine and 2,4-dimethylquinoline.

Although enamides are deactivated enamines, numerous reactions, more particularly in the photoexcited state, have been very fruitful². We have just reported³ (Scheme B) that thermocyclization of certain enamides **4** (carbamate or urea derivatives), leads to 2,4-dimethyl-7-phenyl-1,6-naphthyridin-5-(6*H*)-ones **7**.

Several methods for the synthesis of enamides have been recently reviewed², including the use of nitriles. Our method (Scheme A) combines



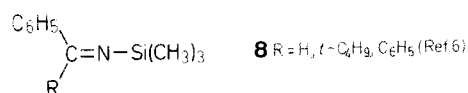
Scheme B

Table 1. *N*-Trimethylsilylenamines **3** Prepared

3	R ¹	R ²	R ³	Yield [%]	b. p. [°C] torr	Molecular Formula ^a
a	CH ₃	H	C ₆ H ₅	98	172/0.6	C ₁₈ H ₂₄ N ₂ Si (296.5)
b	H	H	3-Pyridyl	72	190/0.15	C ₁₆ H ₂₁ N ₃ Si (283.5)
c	-(CH=CH) ₂ -		2-Furyl	79	194/0.5	C ₁₉ H ₂₂ N ₂ OSi (322.5)
d	-(CH=CH) ₂ -		<i>t</i> -C ₄ H ₉	60	122/0.2	C ₁₉ H ₂₈ N ₂ Si (312.6)

^a Very hygroscopic compounds; however microanalyses are relatively satisfactory.

The silylenamines **3** are chosen because lithioenamines have been reported to react with trimethylsilyl chloride to provide mainly the *N*-derivatives⁷. Unfortunately, the direct acylation of the lithioenamine **2** derived from *s*-collidine and benzonitrile leads to mixtures of *C*- and *N*-acylated compounds with numerous by-products³. In this case, *C*-acylation predominates over *N*-acylation with benzoylating agents, contrary to the aliphatic chlorides studied³.



Whereas the *N*-silylimines **8** are known to be stable⁶, the isolated primary enamine **5a** and silylenamines **3** are extremely moisture sensitive. Compounds **3** and **5** are very

Table 2. 2-Pyridyl- and 2-Quinolylenamides **4** Prepared

4	R ¹	R ²	R ³	R ⁴	Yield [%]	m.p. [°C] (solvent)	Molecular Formula ^a
a^b	CH ₃	H	C ₆ H ₅	C ₆ H ₅	71 ^c	103° (hexane/ diisopropyl ether)	C ₂₂ H ₂₀ N ₂ O (328.4)
b	CH ₃	H	C ₆ H ₅	2-FC ₆ H ₄	31	100° (isopropyl alcohol)	C ₂₂ H ₁₉ N ₂ OF (346.4)
c	CH ₃	H	C ₆ H ₅	4-CH ₃ OC ₆ H ₄	53	106° (diisopropyl ether)	C ₂₃ H ₂₂ N ₂ O ₂ (358.4)
d^d	CH ₃	H	C ₆ H ₅	CH ₃	46	90° (ethyl acetate/ diisopropyl ether)	C ₁₇ H ₁₈ N ₂ O (266.3)
e	CH ₃	H	C ₆ H ₅	CH ₃ (CH ₂) ₁₄	49	60° (diisopropyl ether/ pentane)	C ₃₁ H ₄₆ N ₂ O (462.7)
f	CH ₃	H	C ₆ H ₅	CH ₃ OOC(CH ₂) ₂	48	71° (diisopropyl ether)	C ₂₀ H ₂₂ N ₂ O ₃ (338.4)
g	CH ₃	H	C ₆ H ₅	C(CH ₂) ₃	50	70° (pentane/ ethyl acetate)	C ₁₉ H ₂₁ N ₂ OCl (328.8)
h	CH ₃	H	C ₆ H ₅	C ₆ H ₅ CH ₂	69	81° (diisopropyl ether/ pentane)	C ₂₃ H ₂₂ N ₂ O (342.4)
i	CH ₃	H	C ₆ H ₅	C ₂ H ₅ OOC	60	liquid ^e	C ₁₉ H ₂₀ N ₂ O ₃ (324.4)
j	CH ₃	H	C ₆ H ₅	C ₂ H ₅ O	60	liquid ^e	C ₁₈ H ₂₀ N ₂ O ₂ (296.4)
k^b	CH ₃	H	C ₆ H ₅	(CH ₃) ₂ N	5 ^f	144° (ethanol 95°/ hexane)	C ₁₈ H ₂₁ N ₃ O (295.4)
l	H	H	3-Pyridyl	CH ₃ OOC(CH ₂) ₂	60	liquid ^e	C ₁₈ H ₁₉ N ₃ O ₃ (325.4)
m	H	H	3-Pyridyl	C ₆ H ₅ CH ₂	73	127° (diisopropyl ether/ ethyl acetate)	C ₂₁ H ₁₉ N ₃ O (329.4)
n	—(CH=CH) ₂ —	2-Furyl	<i>t</i> -C ₄ H ₉		66	144° (hexane/ diisopropyl ether)	C ₂₁ H ₂₂ N ₂ O ₂ (334.4)
o	—(CH=CH) ₂ —	2-Furyl	CH ₂ =C(CH ₃)		40	94° (hexane/ diisopropyl ether)	C ₂₀ H ₁₈ N ₂ O ₂ ^g (318.4)
p	—(CH=CH) ₂ —	2-Furyl	C ₂ H ₅ O		36	114° (hexane)	C ₁₉ H ₁₈ N ₂ O ₃ (322.4)
q	—(CH=CH) ₂ —	<i>t</i> -C ₄ H ₉	C ₆ H ₅		42	153° (cyclohexane)	C ₂₃ H ₂₄ N ₂ O (344.5)
r	—(CH=CH) ₂ —	<i>t</i> -C ₄ H ₉	2-Furyl		30	119° (diisopropyl ether)	C ₂₁ H ₂₂ N ₂ O ₂ (334.4)
s	—(CH=CH) ₂ —	<i>t</i> -C ₄ H ₉	C ₂ H ₅ OOC		34	130° (diisopropyl ether)	C ₂₀ H ₂₄ N ₂ O ₃ (340.4)

^a Satisfactory microanalyses obtained: C ± 0.23, H ± 0.35, N ± 0.30, Cl ± 0.09, O ± 0.50.

^b See Ref. 3.

^c Isolated as monohydrochloride; yield: 75%.

^d See Ref. 8, m.p. 88°C.

^e Isolated after column chromatography on silica gel, eluent hexane/diisopropyl ether (1 : 1) for **4i** and **4j**; acetonitrile/dichloromethane (1 : 3) for **4l**.

^f Calculated from the ¹H-NMR spectrum of the crude extract.

^g No microanalyses performed; MS (70 eV) *m/e* (relative intensity, %): 318 (M⁺, 51), 290 ([M—CO]⁺, 25), 289 (31), 277 ([M—C₃H₅]⁺, 100), 233 (32), 232 ([277-HCONH₂]⁺, 49), 218 (32), 69 (C₃H₅CO⁺, 30), 41 (C₃H₅⁺, 65).

rapidly hydrolyzed to enolized ketones **6**. In contrast, the enamides **4** are usually easily crystallized and are stable. In general, enamides show varying sensitivity to aqueous acids, the hydration of the double bond leading to ketones and amides². In our case, the moderate to high yields observed show that the enamides **4** offer a relative high resistance to hydrolysis by diluted aqueous acid or base (see experimental).

Compounds **3**, **4**, **5** and **6** exist predominantly in the chelated form (see Tables 3 and 4).

The IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer. The ¹H-NMR spectra were recorded on a Perkin-Elmer R24 spectrometer. Mass spectra were recorded on an AEI MS902 spectrometer (direct introduction, 70 eV). All reactions were carried out under an argon or nitrogen atmosphere.

4,6-Dimethyl-2-(2'-trimethylsilylamino-2'-phenyl-vinyl)pyridine (**3a**); Typical Procedure:

To a solution of phenyllithium [from lithium (2.10 g, 0.30 mol) and bromobenzene (23.56 g, 0.15 mol)] in anhydrous ether (200 ml) at room temperature, is added dropwise with stirring, a solution of *s*-collidine (15.15 g, 0.125 mol) in ether (20 ml). After 1 h, benzonitrile (7.73 g, 0.075 mol) in ether (10 ml) is added dropwise followed by stirring for 1.5 h. The solution is cooled to 0°C, and chlorotrimethylsilane (19.04 ml, 0.15 mol) in ether (20 ml) is added in a similar manner. The mixture is allowed to stand overnight. The precipitated salts are filtered (with the aid of white quartz) under an inert atmosphere. The volatile components are removed *in vacuo* at 50°C. The oily residue is fractionally distilled using a Vigreux column; yield: 21.79 g (98%); b.p. 172°C/0.6 torr; very hygroscopic.

C₁₈H₂₄N₂Si calc. C 72.92 H 8.16 N 9.45 Si 9.47
(296.5) found 72.60 8.35 8.82 8.70

2-Pyridyl and 2-Quinolyl Enamides **4**; General Procedure:

The *N*-silylenamine **3** (0.015 mol; weighed under an argon atmosphere) is dissolved in anhydrous chloroform (30 ml; dried with 3 Å

Molecular Sieves) at room temperature. A solution of the acyl chloride (0.015 mol) in anhydrous chloroform (30 ml) is added dropwise over 15 min with stirring. After complete addition, the mixture is refluxed with stirring until the acyl chloride IR frequency disappears. After completion of the reaction, the solvent is evaporated *in vacuo* at 50°C. The residue is treated with water (50 ml), then with 2 normal sulfuric acid (pH 1) and extracted with ether (3 × 50 ml). The aqueous layer is alkalized with dry sodium hydrogen carbonate (pH 8–9) and extracted with ether (5 × 50 ml). The ether layer is washed with water (2 × 50 ml) until neutral. This latter generally contains the enamide **4**; except in the case of **4b**, **4c** and **4j**, where the largest quantity is recovered from the first ether extract. On the other hand, the crude enamide hydrochloride, **4a** · HCl, precipitates from the reaction mixture. The precipitate is collected by filtration. The ether extracts are dried with anhydrous sodium sulfate and concentrated to dryness. The crude product is purified by column chromatography and/or recrystallization.

4,6-Dimethyl-2-(2'-phenylacetyl-amino-2'-phenylvinyl)pyridine **4h**:

The general procedure is followed using phenylacetyl chloride and enamine **3a** (4.45 g, 0.015 mol). The crude product (4.0 g) is purified by column chromatography (Merck silica gel 60 using diisopropyl ether/hexane, 1:9 increasing to 3:2, as eluent) to provide enamide **4h** as a viscous oil which solidifies. The product recrystallizes from diisopropyl ether/pentane as a flaky, white solid; yield: 3.56 g (69%); m.p. 81°C.

C₂₃H₂₂N₂O calc. C 80.67 H 6.48 N 8.18 O 4.67
(342.4) found 80.80 6.30 7.91 4.87

IR (KBr): ν = 3435 (br w), 3160 (NH), 1680 (s, C=O), 1630 (s, C=C), 1600 (m), 1555 (m), 1490 (s), 1450 (m), 1412, 1365, 1322 (m), 1270, 1255, 1195, 1145, 1080, 1030, 990, 890, 870, 765 (s), 730 (m), 700 cm⁻¹ (s).

¹H-NMR (CDCl₃/TMS_{int}): δ = 2.32 (s, 3 H, CH₃-4); 2.54 (s, 3 H, CH₃-6); 3.80 (s, 2 H, COCH₂); 5.75 (s, 1 H_{olefin}); 6.82 (s, 2 H_{pyridine}); 7.10–7.65 (m, 10 H_{arom}); 12.95 ppm (br s, 1 H, exchangeable with D₂O, NH).

Table 3. Spectral Data for 2-Pyridyl- and 2-Quinolyl-Silylenamines **3** and for Enamine **5a** and Enol **6a**

Prod- uct	IR (KBr) ν [cm ⁻¹]	¹ H-NMR (CDCl ₃ /TMS _{int} ^a ; 27°C) δ [ppm]						
		CH ₃ -6 (s, 3 H)	CH ₃ -4 (s, 3 H)	H _{olefin} (s, 1 H)	Pyridine or Quinoline β -H	NH(OH) ^b (br. s)	H _{arom}	Miscellaneous
3a	3450 (br. w, NH); 1615 (s, C=C); 1600 (s)	2.47	2.26	5.20	6.55 (~s, 2 H)	10.0	7.1–7.7 (m, 5H)	0.00 (s, 9H, Si(CH ₃) ₃)
3b	1612 (s, C=C); 1600 (s)		2.20	5.17	6.72 (m, 2H); 7.1–7.4 (m, 1H)	9.75	7.6–7.9 (m, 1H) 8.2–8.9 (m, 3H)	0.00 (s, 9H, Si(CH ₃) ₃)
3c	—		2.25	5.40	6.60 (s, 1H)	10.5	6.9–7.9 (m, 5H, including α -furyl H)	0.00 (s, 9H, Si(CH ₃) ₃); 6.15 (dd, 1H, <i>J</i> = 4 Hz, 2 Hz, β' - furyl H); 6.35 (d, 1H, <i>J</i> = 4 Hz, β -furyl H)
3d	3460 (br. w, NH); 1625 (m, C=C); 1590 (s)		2.40	5.35	6.75 (s, 1H)	11.0	7.0–8.0 (m, 4H)	0.00 (s, 9H, Si(CH ₃) ₃); 1.20 (s, 9H, C(CH ₃) ₃)
5a ^c	3450 (s), 3250, 3210, 3170 (w, NH); 1610 (s, C=C); 1600 (s)	2.47	2.25	5.42	6.60 (~s, 1H); 6.70 (~s, 1H)	6.80	7.1–7.7 (m, 5H)	
6a ^d	~2600 (br. w, enol); 1680 (w, C=O); 1632 (s, C=C); 1610 (s)	2.48	2.25	5.95	6.50 (~s, 1H); 6.60 (~s, 1H)	(15.5)	7.2–7.6 (m, 3H); 7.7–8.2 (m, 2H)	4.40 (s, CH ₂ , keto form)

^a ¹H-NMR spectra were recorded without TMS for **3**.

^b Exchangeable H with D₂O.

^c Unstable yellow viscous oil; b.p. 210°C/15 torr; yield 71% after hydrolysis of **2a** with water only; satisfactory microanalyses; C₁₅H₁₆N₂ (224.3).

^d Yellow oil; cf. Ref. 4; b.p. 165°C/1.3 torr; yield 98% after hydrolysis of **2a** with 6 normal aqueous hydrochloric acid.

Table 4. Spectral Data of 2-Pyridyl- and 2-Quinolylenamides **4** Prepared

Prod- uct 4	IR (KBr) ν [cm ⁻¹]	¹ H-NMR (CDCl ₃ /TMS _{int} ; 27°C) δ [ppm]						Miscellaneous
		CH ₃ -6 (s, 3H)	CH ₃ -4 (s, 3H)	H _{olefin} (s, 1H)	Pyridine or Quinoline β -H	NH (br. s)	H _{arom}	
a^a	3460 (br. w, NH); 1675 (s, N-C=O); 1625 (s, C=C); 1600 (m)	2.45	2.25	5.75	6.75 (s, 2H)	13.7	6.9-7.7 (m, 8H); 8.0-8.3 (m, 2H, α -benzoyl)	
b	3460 (v w, br, NH); 1665 (s, N-C=O); 1630 (s, C=C); 1610 (s)	2.40	2.25	5.73	6.72 (s, 1H); 6.77 (s, 1H)	13.4	7.0-8.2 (m, 9H)	
c	3450 (br. w, NH); 1685 (m, N-C=O); 1630 (s, C=C); 1605 (s)	2.48	2.27	5.75	6.72 (s, 1H); 6.77 (s, 1H)	13.6	7.2-7.6 (m, 5H); 6.92 (d, 2H, J = 10 Hz); 8.05 (d, 2H, J = 10 Hz)	3.82 (s, 3H, OCH ₃)
d^b	3380 (br. w, NH); 1695 (s, N-C=O); 1625 (s, C=C); 1600 (m)	2.50	2.20	5.63	6.70 (s, 2H)	12.5 (v br.)	7.1-7.6 (m, 5H)	2.12 (s, 3H, COCH ₃)
e	3400 (v w, NH); 1690 (s, N-C=O); 1628 (s, C=C); 1602 (m)	2.52	2.28	5.65	6.78 (s, 2H)	12.8 (v br.)	7.35 (~s, 5H)	0.90 (m, 3H, H ₃ C(CH ₂) ₄ CO); 1.25 (s, 26H, H ₃ C(CH ₂) ₁₃ CH ₂ CO); 2.42 (m, 2H, H ₃ C(CH ₂) ₁₃ CH ₂ CO); 2.72 (s, 4H, OC(CH ₂) ₂ CO); 3.65 (s, 3H, OCH ₃)
f	3400 (v w, NH); 1728 (s, O-C=O); 1695 (s, N-C=O); 1630 (s, C=C); 1600 (m)	2.55	2.30	5.70	6.80 (s, 2H)	13.0	7.38 (~s, 5H)	
g	3400 (v w, NH); 1700 (m, N-C=O); 1625 (s, C=C); 1600 (w)	2.52	2.25	5.67	6.75 (s, 2H)	13.0	7.32 (~s, 5H)	2.60 (t, 2H, J = 6 Hz, COCH ₂); 2.12 (m, 2H, J = 6 Hz, CH ₂); 3.60 (t, 2H, J = 6 Hz, CH ₂ Cl)
h	3435 (br. w, NH); 3160 (w); 1680 (s, N-C=O); 1630 (s, C=C); 1600 (m)	2.54	2.32	5.75	6.82 (s, 2H)	12.9	7.10-7.65 (m, centered on 7.30, 10H)	3.80 (s, 2H, COCH ₂)
i	3180 (br. w, NH); 1710 (s, N-C=O); 1625 (s, C=C); 1605 (w)	2.60	2.20	5.77	6.75 (s, 2H)	12.5 (v br.)	7.30 (~s, 5H)	4.31 (q, 2H, J = 7 Hz, OCH ₂ CH ₃); 1.32 (t, 3H, J = 7 Hz, OCH ₂ CH ₃)
j	3450 (v w, NH); 1732 (s, N-C=O); 1630 (s, C=C); 1600 (s)	2.52	2.25	5.60	6.70 (s, 2H)	12.5	7.2-7.6 (m, 5H)	4.05 (q, 2H, J = 7 Hz, OCH ₂ CH ₃); 2.18 (t, 3H, J = 7 Hz, OCH ₂ CH ₃)
k^a	3440 (br. w, NH); 1675 (s, N-C(=O)-N); 1628 (s, C=C); 1602 (m)	2.40	2.17	5.55	6.62 (m, 2H) (d, J = 2 Hz)	12.2	6.95-7.55 (m, 5H)	2.98 (s, 3H, N(CH ₃)); 3.03 (s, 3H, N(CH ₃))
l	3560 (w, NH); 1730 (s, O-C=O); 1695 (s, N-C=O); 1628 (s, C=C); 1600 (m)		2.32	5.74	6.95 (d, 1H, J = 7 Hz); 6.97 (s, 1H); 7.2 (dd, 1H, J = 5 Hz, 7 Hz)	12.8	7.7 (m, 1H, J = 7 Hz); 8.4-8.8 (m, 3H)	2.84 (m, 4H, CH ₂ -CH ₂); 3.65 (s, 3H, OCH ₃)
m	3440 (br. w, NH); 1680 (s, N-C=O); 1630 (m, C=C); 1600 (m)		2.28	5.68	6.87 (d, 1H, J = 7 Hz); 6.90 (s, 1H)	12.5	7.1-7.9 (m, 7H, including 1 β -pyridyl H); 8.05 (d, 1H, J = 7 Hz); 8.50 (d, 1H, J = 7 Hz); 8.65 (d, 1H, J = 2 Hz)	3.70 (s, 2H, CH ₂ -CO)
n	3450 (v w, NH); 1690 (s, N-C=O); 1630 (s, C=C); 1595 (s)		2.52	6.12	6.95 (s, 1H)	12.4	7.3-8.1 (m, 5H, including 1 α -furyl H)	1.42 (s, 9H, C(CH ₃) ₃); 6.4 (dd, 1H, J = 4 Hz, 2 Hz, β -furyl H); 6.5 (d, 1H, J = 4 Hz, β -furyl H)

Table 4. (Continued)

Prod- uct	IR (KBr) ν [cm ⁻¹]	¹ H-NMR (CDCl ₃ /TMS _{int} ; 27°C) δ [ppm]						Miscellaneous
		CH ₃ -6 (s, 3H)	CH ₃ -4 (s, 3H)	H _{olefin} (s, 1H)	Pyridine or Quinoline β -H (br. s)	H _{arom}		
o	3420 (br. w, NH); 1690 (m, N—C=O); 1630 (m, C=C); 1590 (s)		2.62	5.70	7.15 (s, 1H)	13.1	7.3–8.0 (m, 4H, including 1 α -furyl H); 8.4 (dd, 1H, J = 7 Hz, 2 Hz)	2.15 (s, 3H, allylic H); 6.1–6.7 (m, 4H, vinylic and β -furyl H)
p	3450 (w, NH); 1730 (s, N—C(=O)—O); 1625 (s, C=C); 1590 (s)		2.55	6.10	6.98 (s, 1H)	12.6	7.1–8.1 (m, 5H, including 1 α -furyl H)	1.30 (t, 3H, J = 7 Hz, CH ₂ —CH ₃); 4.20 (q, 2H, J = 7 Hz, CH ₂ —CH ₃); 6.45 (dd, 1H, J = 2 Hz, 4 Hz, β -furyl H); 6.68 (d, 1H, J = 4 Hz, β -furyl H)
q	1675 (s, N—C=O); 1625 (s, C=C); 1595 (s)		2.50	6.00	7.00 (s, 1H)	13.7	7.2–7.8 (m, 7H); 7.9–8.3 (m, 2H, α -benzoyl)	1.50 (~s, 9H, C(CH ₃) ₃)
r	3420 (br. w, NH); 1675 (1685 sh, s, N—C=O); 1630 (s, C=C); 1598 (s)		2.62	6.08	7.10 (s, 1H)	13.6	7.3–8.1 (m, 4H)	1.60 (s, 9H, C(CH ₃) ₃); 6.63 (m, 1H, β -furyl H); 7.20 (d, 1H, J = 4 Hz, β -furyl H); 7.65 (d, 1H, J = 2 Hz, α -furyl H)
s	3400 (w, NH); 1705 (1725 sh, s, N—C=O, O—C=O); 1625 (s, C=C); 1590 (s)		2.60	6.02	7.02 (s, 1H)	14.5	7.4–8.0 (m, 3H); 8.32 (dd, 1H, J = 7 Hz, 3 Hz)	1.42 (t, 3H, J = 7 Hz, CH ₂ —CH ₃); 1.45 (s, 9H, C(CH ₃) ₃); 4.42 (q, 2H, J = 7 Hz, OCH ₂ —CH ₃)

^a See Ref. 3, including MS data for **4k**.

^b See Ref. 8, including MS data.

4,6-Dimethyl-2-(2'-benzoylamino-2'-phenylvinyl)pyridine **4a**:

The general procedure is followed using benzoyl chloride and enamine **3a** (4.45 g, 0.015 mol). The crude precipitate of hydrochloride is recrystallized from methanol as a pale yellow crystalline powder; yield: 4.10 g (75%); m.p. 200°C.

C₂₂H₂₁N₂OCl calc. C 72.42 H 5.80 N 7.68 Cl 9.72 O 4.38
(364.9) found 72.32 5.81 7.60 9.64 4.40

IR (KBr): ν = 3420, 3150, 2640 (br, m to s, NH⁺); 1665 (s, C=O); 1630 (s, C=C); 1610 cm⁻¹ (s).

The base **4a** is released from its hydrochloride with triethylamine, giving an oil which solidifies. The product is recrystallized from hexane/diisopropyl ether; yield: 3.50 g (71%); m.p. 103°C.

C₂₂H₂₀N₂O calc. C 80.46 H 6.14 N 8.53 O 4.87
(328.4) found 80.39 6.08 8.61 4.87

IR (KBr): ν = 3460 (br, w, NH); 1675 (s, C=O); 1625 (s, C=C); 1600 cm⁻¹ (m).

¹H-NMR (CDCl₃/TMS_{int}): δ = 2.25 (s, 3H, CH₃-4); 2.45 (s, 3H, CH₃-6); 5.75 (s, 1H_{olefin}); 6.75 (s, 2H_{pyridine}); 6.9–7.7 (m, 8H); 8.0–8.3 (m, 2H, α -benzoyl); 13.7 ppm (br s, 1H, exchangeable with D₂O, NH).

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¹ For Part XIV see: Compagnon, P.-L., Gasquez, F., Kimny, T. *Bull. Soc. Chim. Belg.* **1986**, 95, 57.

² Review: Lenz, G.R. *Synthesis* **1978**, 489.

³ Compagnon, P.-L., Gasquez, F., Kimny, T. *Bull. Soc. Chim. Belg.* **1986**, 95, 49.

⁴ Compagnon, O., Compagnon, P.-L. *Bull. Soc. Chim. Fr.* **1973**, 3381, 3385 and references therein.

⁵ Review: Kaiser, E.M. *Tetrahedron* **1983**, 39, 2055.

⁶ Kupfer, R., Meier, S., Würthwein, E.-U. *Synthesis* **1984**, 688.

⁷ Ahlbrecht, H., Liesching, D. *Synthesis* **1976**, 746.

⁸ Compagnon, P.-L., Gasquez, F., Compagnon, O., Kimny, T. *Bull. Soc. Chim. Belg.* **1982**, 91, 931.