J = 10.0, 3.5 Hz), 5.67 (s, 1 H), 5.55 (b s, 1 H), 5.44 (b s, 1 H), 3.80 (s, 3 H), 3.38 (s, 3 H) ppm.

Attempted Fremy's Salt Oxidation of 10. Treatment of a methylene chloride solution of **10**[17] with Fremy's salt as illustrated in the general procedure yielded recovered starting material. Neither operating at different pH (in the range of 4–10) nor using longer reaction times (up to 48 h) led to any improvement, starting material being recovered unchanged in ca. 70% yield.

Acknowledgment. Financial support by the DGICYT (Project PB87-0019) is gratefully acknowledged. Thanks are also due to the Department of Organic Chemistry of the University of Santiago de Compostela (Dr. D. Dominguez and Dr. G. Tojo) and the Instituto de Productos Naturales Organicos de La Laguna (Prof. J. D. Martin) for their help in obtaining our 250–MHz NMR and HRMS. Prof. S. Kobayashi is thanked for kindly providing us with spectroscopic data of (−)-sanguinine.

Registry No. 1, 13871-59-5; **2**, 123752-57-8; **3**, 14097-39-3; **4**, 123752-58-9; **5**, 123752-59-0; **6**, 60755-80-8; **7**, 123775-12-2; **8**, 123752-60-3; **9**, 123752-61-4; *N*-methyl-4,6-dihydroxy-1,2,3,4-tetrahydroisoquinoline, 23824-24-0; 4,5-dihydroxy-1-methylindole, 123752-62-5; 4,5-diacetoxy-1-methylindole, 123752-63-6; 6-[(dimethylamino)methyl]-3,4-dimethoxyphenol, 115320-11-1; 6-[(dimethylamino)methyl]-2-methoxy-4-methylphenol, 123752-64-7; 4,5-dimethoxy-1,2-benzoquinone, 21086-65-7; 3-methoxy-5-methyl-1,2-benzoquinone, 60824-63-7.

Synthesis and Synthetic Utility of 1-Acyl-5-(trialkylsilyl)-1,2-dihydropyridines. Synthesis of (±)-Elaeokanine A

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The regioselective addition of Grignard reagents to the phenoxycarbonyl salts of 3-(trialkylsilyl)pyridines was studied. Most of the 3-(trialkylsilyl)pyridine salts gave a mixture of dihydropyridines on reaction with aliphatic Grignard reagents. However, all reactions using alkyl or aryl Grignard reagents and the 1-phenoxycarbonyl salt of 3-(triisopropylsilyl)pyridine, or 4-chloro-3-(triisopropylsilyl)pyridine, gave exclusively 1,2-dihydropyridines resulting from attack of the Grignard reagents at the C-6 position of the pyridinium salt. Vilsmeier–Haack formylation of 2-alkyl(aryl)-1-(phenoxycarbonyl)-5-(triisopropylsilyl)-1,2-dihydropyridines **8g,h** and **10h** occurs at C3. Friedel–Crafts acylation of 5-(trialkylsilyl)dihydropyridines **10** gave C-5 acylation via ipso substitution. In contrast, acylation of **10f,h,i** with acyl triflates gives C-3 substitution. The triisopropylsilyl group of the C-3 acylated 1,2-dihydropyridines could be removed on reaction with HBr/HOAc in methylene chloride. The methodology developed for the regiospecific formation and acylation of 5-(triisopropylsilyl)-1,2-dihydropyridines was utilized in the total synthesis of the indolizidine alkaloid, (±)-elaeokanine A. The synthesis was achieved in a regiospecific manner from 3-(triisopropylsilyl)pyridine in six steps.

Over the years there has been considerable interest in 1-acyl-1,2-dihydropyridines as intermediates for the synthesis of substituted pyridines[2,3] and natural products.[2,4] Fowler's discovery that pyridine could be reduced by sodium borohydride in the presence of an alkyl chloroformate provided synthetic chemists with convenient access to 2-unsubstituted 1-(alkoxycarbonyl)-1,2-dihydropyridines.[5] These relatively stable dihydropyridines proved to be interesting dienes for the Diels–Alder reaction and have been utilized by several research groups for the synthesis of alkaloids and novel ring systems. Although Fraenkel and co-workers[6] reported in 1970 that Grignard reagents react with 4-picoline in the presence of ethyl chloroformate to provide 2-substituted 1-(ethoxycarbonyl)-1,2-dihydropyridines, this reaction was not utilized until recently for natural product synthesis. One of the reasons for this slow development is the lack of regioselectivity found with aliphatic Grignard reagents. Although aryl,[7] vinyl,[8] and alkynyl[8,9] Grignard reagents give mainly 1,2-dihydropyridines, most alkyl[7a] Grignard reagents give mixtures of 1,2- and 1,4-dihydropyridines. The synthetic potential of 1-acyl-2-alkyl-1,2-dihydropyridines prompted us to develop a regiospecific synthesis of these heterocycles from alkyl Grignard reagents, a chloroformate, and 4-(trimethylstannyl)pyridine.[4g] The trimethylstannyl substituent acts as a removable blocking group. We also

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(2) For reviews on dihydropyridines, see: Stout, D. M.; Meyers, A. I. *Chem. Rev.* **1982**, *82*, 223–243. Sausins, A.; Duburs, G. *Heterocycles* **1988**, *27*, 291. Also see: Comins, D. L.; O'Connor, S. *Adv. Heterocycl. Chem.* **1988**, *44*, 199.

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(4) For leading and recent references, see: (a) Brown, J. D.; Foley, M. A.; Comins, D. L. *J. Am. Chem. Soc.* **1988**, *110*, 7445. (b) Comins, D. L.; Brown, J. D. *Tetrahedron Lett.* **1986**, *27*, 4549–4552. (c) Comins, D. L.; Brown, J. D. *Ibid.* **1986**, *27*, 2219–2222. (d) Comins, D. L.; Abdullah, A. H. *Ibid.* **1985**, *26*, 43–46. (e) Natsume, M.; Utsunomiya, I.; Yamaguchi, K.; Sakai, S. I. *Tetrahedron* **1985**, *41*, 2115–2123 and references therein. (f) Ogawa, M.; Natsume, M. *Heterocycles* **1985**, *23*, 831–834. (g) Comins, D. L.; Abdullah, A. H.; Mantlo, N. B. *Tetrahedron Lett.* **1984**, *25*, 4867–4870. (h) Nakazono, Y.; Yamaguchi, R.; Kawanisi, M. *Chem. Lett.* **1984**, 1129–1132. (i) Raucher, S.; Lawrence, R. F. *Tetrahedron Lett.* **1983**, *24*, 2927–2930.

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(7) (a) Comins, D. L.; Abdullah, A. H. *J. Org. Chem.* **1982**, *47*, 4315. (b) Comins, D. L.; Mantlo, N. B. *J. Heterocycl. Chem.* **1983**, *20*, 1239. (c) Comins, D. L.; Stroud, E. D.; Herrick, J. J. *Heterocycles* **1984**, *22*, 151.

(8) Natsume, M.; Ogawa, M. *Heterocycles* **1981**, *16*, 973; **1983**, *20*, 601. Yamaguchi, R.; Nakazono, Y.; Kawanisi, M. *Tetrahedron Lett.* **1983**, *24*, 1801.

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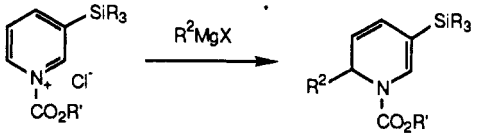
0022-3263/90/1955-0292$02.50/0

have reported a study on the regioselective addition of nucleophiles to 1-(phenoxycarbonyl)-3-(trialkylstannyl)-pyridinium salts.[3b] The 3-trialkylstannyl substituent was found to be effective at blocking the C-2 and C-4 positions against attack by phenylmagnesium chloride, but less effective in reactions with alkyl Grignard reagents.

Since the 3-trialkylstannyl substituent was not as effective a blocking group as desired, we turned our attention to pyridines substituted at C-3 with a trialkylsilyl group. A goal of this project was to find a trialkylsilyl group that would block the C-2 and C-4 positions of 1-acylpyridinium salt 1 and force nucleophilic attack to occur at the less sterically hindered C-6 position to give 1,2-dihydropyridines 2 in a regiospecific manner. It was anticipated

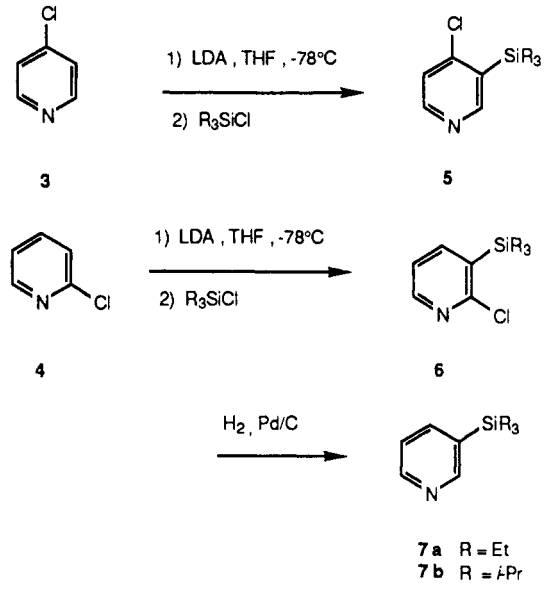


1 2

that the trialkylsilyl group of 2 would allow regioselective substitution to be carried out on the dihydropyridine ring, making these heterocycles even more valuable as synthetic intermediates. To these ends we carried out studies on the synthesis and substitution of 1-acyl-5-(trialkylsilyl)-1,2-dihydropyridines 2.

Results and Discussion

Synthesis of 3-(Trialkylsilyl)pyridines. The desired 3-(trialkylsilyl)pyridines were prepared from 4- or 2-chloropyridine (3 and 4) using directed lithiation methodology. Treatment of the chloropyridine with lithium diisopropylamide (LDA)[10] followed by a chlorotrialkylsilane gave good yields of the 4(or 2)-chloro-3-(trialkylsilyl)pyridines 5 and 6 as is shown in Table I. The chloro substituent can be removed by catalytic hydrogenation. In this manner, 3-(triethylsilyl)pyridine (7a) and 3-(triisopropylsilyl)pyridine (7b) were prepared from 6a and 6b in 91 and 93% yield, respectively.



(10) Halopyridines have been lithiated with LDA, see: Gribble, G. W.; Saulnier, M. G. *Tetrahedron Lett.* **1980**, *21*, 4137. Güngör, T.; Marsais, F.; Quéguiner, G. *J. Organomet. Chem.* **1981**, *215*, 139. Mallet, M.; Quéguiner, G. *Tetrahedron* **1982**, *38*, 3035. Marsais, F.; Lapendrix, B.; Güngor, T.; Mallet, M.; Quéguiner, G. *J. Chem. Res., Miniprint* **1982**, 2863. Marsais, F.; Trécourt, F.; Bréant, P.; Quéguiner, G. *J. Heterocycl. Chem.* **1988**, *25*, 81.

Table I. Synthesis of 4(or 2)-Chloro-3-(trialkylsilyl)pyridines 5 and 6

chloropyridine[a]	R_3SiCl	product	yield,[b] %
3	Me_3SiCl	5a	61
	Et_3SiCl	5b	56
	n-Pr_3SiCl	5c	60
	i-Pr_3SiCl	5d	93
4	Et_3SiCl	6a	63
	i-Pr_3SiCl	6b	47

[a] All reactions were performed using 1.1 equiv of LDA and 1.1 equiv of R_3SiCl at −78 °C in THF. [b] Yield of purified product obtained from radial preparative-layer chromatography.

Table II. Grignard Addition to 4-Chloro-1-(phenoxycarbonyl)-3-(trialkylsilyl)pyridinium Salts

entry	pyridine[a]	R	R'MgCl	yield,[b] %	ratio[c] 8:9
a	5a	Me	Me	92	66:34
b			n-Bu	70	72:28
c	5b	Et	Me	59	88:12
d			n-Bu	62	93:7
e	5c	n-Pr	Me	85	87:13
f			n-Bu	79	93:7
g	5d	i-Pr	Me	66	100:0
h			n-Bu	52	100:0

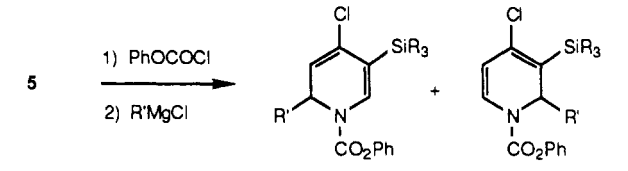
[a] The reactions were generally performed on a 3-mmol scale in THF. [b] Yield of isolated products 8 and 9 obtained from radial preparative-layer chromatography. [c] Ratio determined by 300-MHz ^1H NMR spectroscopy.

Table III. Grignard Addition to 1-(Phenoxycarbonyl)-3-(trialkylsilyl)pyridinium Salts

entry	pyridine[a]	R'MgCl	yield,[b] %	ratio[c] 10:11:12
a	7a	Me	87	74:19:7
b		n-Bu	91	72:14:14
c		c-Hex	79	71:8:21
d		Ph	79	100:0:0
e	7b	Me	96	100:0:0
f		n-Bu	98	100:0:0
g		c-Hex	98	100:0:0
h		Ph	93	100:0:0

[a] The reactions were generally performed on a 3-mmol scale in THF. [b] Yield of isolated products 10, 11, and 12 obtained from radial preparative-layer chromatography. [c] Ratio determined by 300-MHz ^1H NMR spectroscopy.

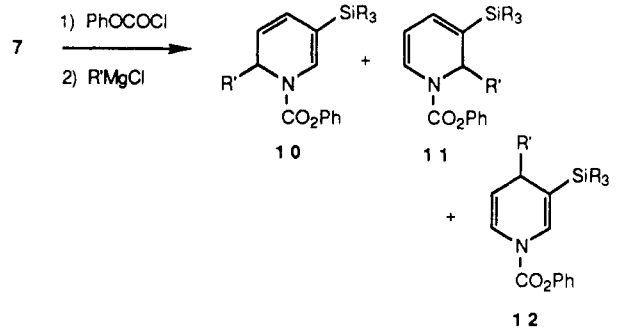
Grignard Addition Studies. Initial studies were performed on the 4-chloro-3-(trialkylsilyl)pyridines 5. Addition of phenyl chloroformate to 5 in THF at −78 °C formed the 1-acylpyridinium salts in situ, which on reaction with Grignard reagents gave 1-acyl-1,2-dihydropyridines. Since the chloro substituent at C-4 blocks that position against nucleophilic addition,[11] only 1,2-dihydropyridines 8 and 9 were formed. In most cases a mixture of 8 and 9 was observed as shown in Table II. However, when 4-chloro-3-(triisopropylsilyl)pyridine was utilized, the reaction was completely regiospecific, providing only 1,2-dihydropyridines 8.



We next looked at some analogous reactions starting with 3-(trialkylsilyl)pyridines 7. Since these pyridines

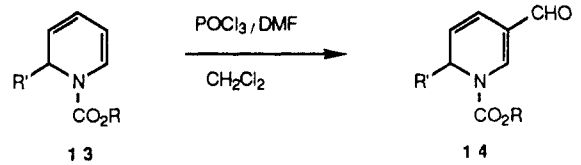
(11) Comins, D. L.; Mantlo, N. B. *J. Org. Chem.* **1985**, *50*, 4410.

contained no blocking group at C-4, addition of the Grignard reagent could occur at that position. With 3-(triethylsilyl)pyridine (**7a**), a mixture of three dihydropyridines (**10–12**) was obtained on reaction with aliphatic Grignard reagents as shown in Table III. The reaction using phenylmagnesium chloride gave only 1,2-dihydropyridine **10d**. All reactions using alkyl or aryl Grignard

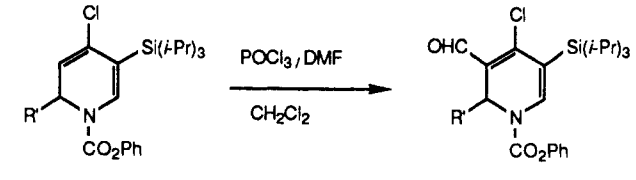


reagents and 3-(triisopropylsilyl)pyridine (**7b**) gave exclusively 1,2-dihydropyridines **10**, as determined by 300-MHz ^1H NMR spectroscopy. Success in the development of this regiospecific synthesis prompted us to examine substitution reactions of dihydropyridines **10**.

Formylation and Acylation of Dihydropyridines 10. We recently reported the β-formylation of 1-(phenoxycarbonyl)-1,2-dihydropyridines by the Vilsmeier–Haack reaction.[12] With a C-5 unsubstituted 1-acyldihydropyridine (i.e., **13**), formylation was regiospecific, giving carboxaldehyde **14**. The analogous reaction with a C-5

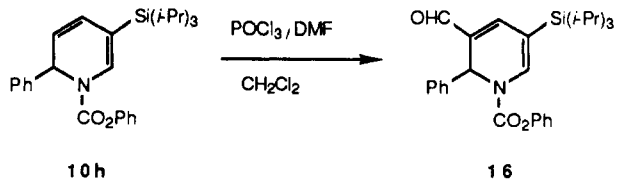


silylated derivative could proceed in a similar manner via ipso substitution, or attack at C-3 may be preferred for steric reasons. The 1,2-dihydropyridines **8g**, **8h**, and **10h** were subjected to the Vilsmeier–Haack reaction. In all cases clean substitution occurred at C-3 to provide formylated dihydropyridines **15a**, **15b**, and **16** in 50, 88, and 97% yield, respectively. Dihydropyridines **15a,b** were converted to highly substituted pyridines **18a,b** through



8g R' = Me
8h R' = *n*-Bu

15a R' = Me
15b R' = *n*-Bu



10h **16**

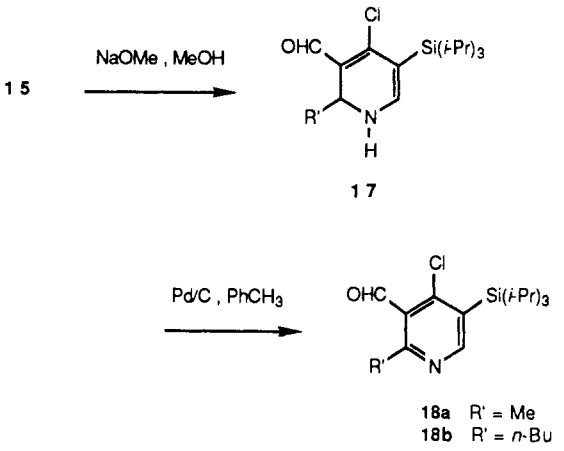
(12) Comins, D. L.; Mantlo, N. B. *J. Org. Chem.* **1986**, *51*, 5456, ref 3a. *N*-(Methoxycarbonyl)-1,2- and -1,4-dihydroquinolines have been formylated using the Vilsmeier–Haack reagent, see: Natsume, M.; Kumadaki, S.; Kanda, Y.; Kiuchi, K. *Tetrahedron Lett.* **1973**, 2335.

Table IV. Regiospecific Acylation of Dihydropyridines 10 with Trifluoromethanesulfonic–Carboxylic Anhydrides

dihydropyridine[a]	R'	conditions	product	yield,[b] %
10f	*n*-Bu	1.0 *n*-$PrCO_2Tf$, −78 °C, 30 min; RT,[c] 30 min	**20a**	37
	n-Bu	1.1 *n*-$PrCO_2Tf$, −78 °C, 30 min; 0 °C, 30 min	**20a**	45
10h	Ph	1.0 *n*-$PrCO_2Tf$, −78 °C, 30 min; RT, 30 min	**20b**	50
10i	C_3H_6Cl	1.0 *n*-$PrCO_2Tf$, −78 °C, 1 h		no reaction
	C_3H_6Cl	1.4 *n*-$PrCO_2Tf$, −78 °C, 30 min; 0 °C, 30 min	**20c**	60

[a] The reactions were generally performed on a 2-mmol scale in CH_2Cl_2. [b] Yield of isolated products **20** obtained from radial preparative-layer chromatography. [c] Room temperature.

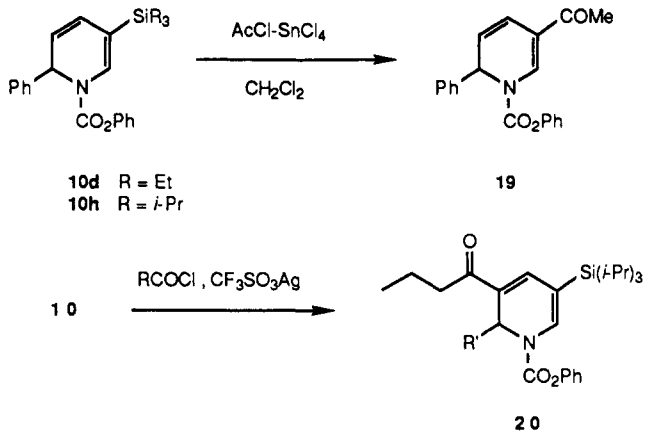
a two-step procedure. The *N*-acyl group was first removed with sodium methoxide in methanol. The resulting dihydropyridines **17** were aromatized using palladium on charcoal in toluene to give pyridines **18** in 29 and 56% yield, respectively.



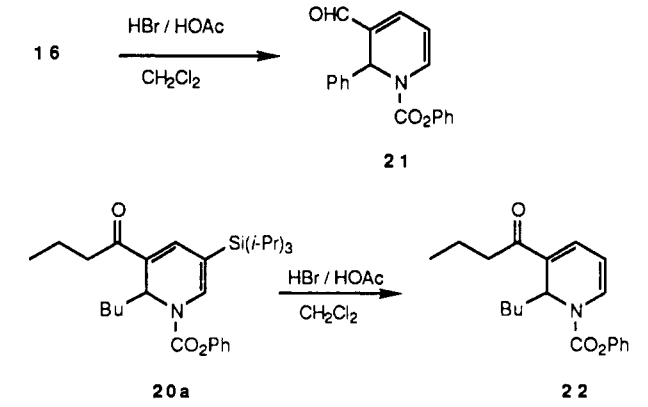
We have described the Friedel–Crafts acylation of several 1-acyl-1,4-dihydropyridines and one example using a 1-acyl-5-(trimethylsilyl)-1,2-dihydropyridine. In the latter case, ipso substitution occurred to give the C-5 acylated 1,2-dihydropyridine in 35% yield.[13] Friedel–Crafts acylation of (trialkylsilyl)dihydropyridines **10d,h** gave similar results, providing 5-acetyl-1,2-dihydropyridines **19** in 25–35% yield. Considerable decomposition results during these reactions, presumably due to polymerization caused by the instability of 1,2-dihydropyridines in the presence of a Lewis acid. Several attempts to acylate dihydropyridines **10** with *N,N*-dimethylacetamide or *N*-acetylmorpholide using Vilsmeier–Haack procedures were unsuccessful.

Trifluoromethanesulfonic–carboxylic anhydrides have been shown to be powerful acylating agents.[14] We prepared the mixed anhydrides in situ by treating acid chlorides with silver triflate. Addition of dihydropyridines **10** to these active acylating agents gave C-3 acylated products **20** as shown in Table IV. Although some decomposition occurs, the reaction appears to be regiospecific for no products of ipso substitution were isolated.

(13) Comins, D. L.; Mantlo, N. B. *Tetrahedron Lett.* **1983**, *24*, 3683.
(14) Effenberger, F.; Epple, G. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 299.



Protodesilylation of (Trialkylsilyl)dihydropyridines. The triisopropylsilyl group at the C-3 position of a pyridine proved to be effective at blocking the C-2 and C-4 positions against nucleophilic attack. This group was also effective at blocking the C-5 position of 1,2-dihydropyridines **8** and **10** against formylation and certain acylations. The synthetic potential of this methodology would be enhanced if a simple procedure were available for the removal of the triisopropylsilyl group once it has served its purpose. To this end we investigated the protodesilylation of formylated dihydropyridine **16** and acylated dihydropyridine **20a** and found HBr in acetic acid to effect the desired transformation to give **21** and **22** in 44 and 91% yield, respectively.



Synthesis of (±)-Elaeokanine A. Our success in preparing C-3 acylated 1,2-dihydropyridines in a regiospecific manner prompted us to investigate the synthesis of the *Elaeocarpus* alkaloid, (±)-elaeokanine A (**23**).[15] Our synthetic plan followed the retrosynthetic analysis shown in Figure 1.

We decided to introduce the required halopropyl side chain of **26** in two steps from 3-(triisopropylsilyl)pyridine (**7b**). Reaction of the 1-methoxycarbonyl salt of **7b** with Grignard reagent **24**[16] in THF gave, on workup with 10% HCl, the alcohol **25** in 80% yield. The alcohol **25** was converted to chloride **26** in 70% yield by treatment with triphenylphosphine and *N*-chlorosuccinimide.[17] Acylation of **26** at C-3 was effected using the triflate mixed anhydride **27** in 66% yield. The trialkylsilyl group was removed on treatment with HBr/AcOH in methylene chloride to provide 1,2-dihydropyridine **29**.

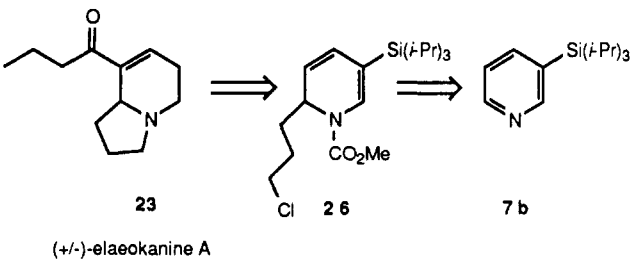


Figure 1.

Dihydropyridine **29** is a viable intermediate for the synthesis of elaeokanine A only if selective reduction of the 5,6-double bond is feasible. Fowler[18] has reported that sodium borohydride and trifluoroacetic acid (TFA) in benzene reduce the 5,6-double bond of 3-ethyl-*N*-(methoxycarbonyl)-1,2-dihydropyridine, and we[3c] found triethylsilane and TFA in methylene chloride were also effective in a similar reduction. Since dihydropyridine **29** contains a reducible ketone function, the triethylsilane reduction was utilized. In this manner **29** was reduced to give tetrahydropyridine **30** in 85% yield. Completion of this synthesis required the removal of the *N*-acyl group and subsequent cyclization. This was achieved in one step by treatment of **30** with sodium iodide and chlorotrimethylsilane in refluxing acetonitrile to give a 55% yield of (±)-elaeokanine A (**23**),[19] which showed spectral properties identical with those of natural material.[15,20]

Experimental Section

Reactions involving organometallic reagents were performed in oven-dried glassware under a N_2 or Ar atmosphere. Tetrahydrofuran (THF) was dried by distillation from sodium benzophenone ketyl prior to use. Other solvents and reagents from commercial sources were generally used without further purification.

Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Varian XL-300 spectrometer. Chemical shifts for ^1H NMR (300 MHz) spectra are reported in ppm relative to Me_4Si (δ 0), and coupling constants are in hertz. ^{13}C NMR (75 MHz) spectra are reported in ppm relative to the $CDCl_3$ adsorption (77.0 ppm). Radial preparative-layer chromatography (radial PLC) was carried out by using a Chromatotron (Harrison Associates, Palo Alto, CA). Elemental analyses were carried out by M-H-W Laboratories, Phoenix, AZ. Due to their instability, some of the dihydropyridines were not submitted for elemental analysis.

4-Chloro-3-(triisopropylsilyl)pyridine (5d). General Procedure for the Preparation of Pyridines 5 and 6. To a solution of LDA at −78 °C, prepared from 7.7 mL (55 mmol) of diisopropylamine and *n*-butyllithium (55 mmol) in 60 mL of THF, was added dropwise 4.73 mL (50 mmol) of 4-chloropyridine. After stirring for 20 min at −78 °C, 11.8 mL (55 mmol) of chlorotriisopropylsilane was added slowly. The mixture was stirred at −78 °C for 1 h and at room temperature for 1 h. The solution was

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(16) Ponaras, A. A. *Tetrahedron Lett.* **1976**, 3105. Becker, D.; Harel, Z.; Nagler, M.; Gillon, A. *J. Org. Chem.* **1982**, *47*, 3297.
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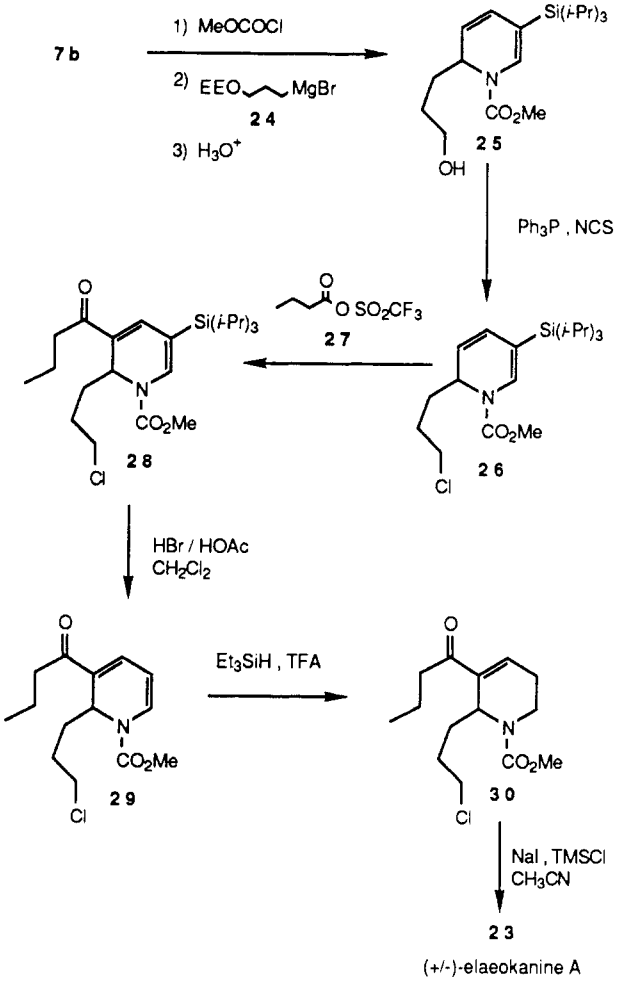

poured into 20 mL of water and extracted with ether. The combined ether extracts were washed with water and brine, dried over K_2CO_3, filtered, and concentrated to yield 13.9 g of crude product as a yellow oil. This material was purified by radial PLC (silica gel, 10% EtOAc/hexane) to give 12.55 g (93%) of **5d** as a clear oil: ^{1}H NMR ($CDCl_3$) δ 8.62 (s, 1 H), 8.45 (d, 1 H, J = 5.0 Hz), 7.30 (d, 1 H, J = 5.0 Hz), 2.60 (m, 3 H), 1.05 (d, 18 H, J = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 156.9, 151.37, 150.35, 125.21, 18.71, 12.36; IR (neat) 2947, 2868, 1558, 1540, 1466, 1389 cm^{-1}. Anal. Calcd for $C_{14}H_{24}ClNSi$: C, 62.30; H, 8.96; N, 5.19. Found: C, 62.29; H, 8.91; N, 5.09.

2-Chloro-3-(triisopropylsilyl)pyridine (6b). This compound was prepared from 2-chloropyridine in 47% yield as described above for the synthesis of **5d**. The product was isolated as a clear oil: bp 104–108 °C (0.5 mmHg); ^{1}H NMR ($CDCl_3$) δ 8.36 (dd, 1 H, J = 5 and 2 Hz), 7.84–7.82 (dd, 1 H, J = 7 and 2 Hz), 7.22–7.18 (dd, 1 H, J = 7 and 5 Hz), 1.7–1.6 (m, 3 H), 1.13 (d, 18 H, J = 7 Hz); IR (neat) 2950, 2870, 1555, 1460, 1365, 1120, 1058, 880 cm^{-1}. Anal. Calcd for $C_{14}H_{24}ClNSi$: C, 62.30; H, 8.96; N, 5.19. Found: C, 62.49; H, 8.95; N, 5.11.

3-(Triisopropylsilyl)pyridine (7b). To a solution of 2-chloro-3-(triisopropylsilyl)pyridine (**6b**) (0.688 g, 2.55 mmol) in 30 mL of absolute ethanol under nitrogen was added 0.20 g (5.1 mmol) of solid sodium hydroxide and 0.30 g of 5% Pd/C. The reaction mixture was stirred under 1 atm of hydrogen overnight. The solution was filtered through Celite and concentrated. The residue was dissolved in 50 mL of ether, washed with brine, dried (K_2CO_3), and concentrated. Purification of the crude product by radial PLC (silica gel, 10% EtOAc/hexane) provided 0.66 g (91%) of pure **7b** as a clear oil: bp 103–105 °C (0.5 mmHg); ^{1}H NMR ($CDCl_3$) δ 8.67 (s, 1 H), 8.57 (d, 1 H, J = 6 Hz), 7.77 (d, 1 H, J = 7.5 Hz), 7.27 (m, 1 H), 2.4 (m, 3 H), 1.10 (d, 18 H, J = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 155.27, 149.54, 142.72, 129.71, 122.92, 18.26, 10.43; IR (neat) 2944, 2890, 2867, 1572, 1557, 1462, 1388, 1334, 1120 cm^{-1}. Anal. Calcd for $C_{14}H_{25}NSi$: C, 71.42; H, 10.70; N, 5.95. Found: C, 71.39; H, 10.84; N, 6.08.

4-Chloro-2-methyl-1-(phenoxycarbonyl)-5-(triisopropylsilyl)-1,2-dihydropyridine (8g). General Procedure for the Preparation of Dihydropyridines 8 and 9. To a solution of 4-chloro-3-(triisopropylsilyl)pyridine (**5d**) (1.0 g, 3.71 mmol) in 10 mL of THF (−78 °C) was added phenyl chloroformate (0.47 mL, 3.71 mmol) dropwise. Methylmagnesium chloride (4.08 mmol) in 1.36 mL of THF was added dropwise, and the mixture was stirred at −78 °C for 20 min. After warming to room temperature, 10 mL of aqueous 20% NH_4Cl solution was added. The mixture was extracted with ether. The combined organic layers were washed with 15-mL portions of water and brine. After drying (K_2CO_3), the solution was concentrated to give the crude product. Purification by radial PLC (silica gel, 10% EtOAc/hexane) gave 0.99 g (66%) of **8g** as an oil: ^{1}H NMR ($CDCl_3$) δ 7.5–7.2 (m, 5 H), 6.99–6.96 (d, 1 H), 5.72–5.70 (d, 1 H, J = 7 Hz), 5.2–4.8 (m, 1 H), 1.4–1.0 (m, 24 H); ^{13}C NMR ($CDCl_3$) δ 152.00, 134.29, 133.23, 129.44, 126.00, 121.46, 120.73, 120.24, 49.72, 18.97, 12.59; IR (Nujol) 2929, 2855, 1739, 1722, 1461, 1378, 1327, 1197 cm^{-1}. Anal. Calcd for $C_{22}H_{32}ClNO_2Si$: C, 65.08; H, 7.94; N, 3.45. Found: C, 64.86; H, 7.95; N, 3.44.

2-*n*-Butyl-4-chloro-1-(phenoxycarbonyl)-5-(triisopropylsilyl)-1,2-dihydropyridine (8h). This compound was prepared in 52% yield as described above for the synthesis of **8d**: ^{1}H NMR ($CDCl_3$) δ 7.4–7.1 (m, 5 H), 7.03 and 7.00 (pair of s due to rotamers, 1 H), 5.75 (d, 1 H, J = 6 Hz) 4.9–4.8 (m, 1 H), 1.8–0.85 (m, 30 H); ^{13}C NMR ($CDCl_3$) δ 135.10, 133.99, 129.35, 125.95, 121.54, 119.73, 119.25, 53.53, 33.93, 33.07, 26.52, 22.62, 18.94, 13.93, 12.21; IR (neat) 2940, 2865, 1730, 1490, 1320, 1270, 1195, 1000 cm^{-1}; HRMS calcd for $C_{25}H_{38}ClNO_2Si$ 447.2360, found 447.2360.

4-Chloro-3-formyl-2-methyl-1-(phenoxycarbonyl)-5-(triisopropylsilyl)-1,2-dihydropyridine (15a). Phosphorous oxychloride (0.39 mL, 4.14 mmol) was added slowly to a stirred solution of 1.39 mL (17.9 mmol) of DMF in 3 mL of CH_2Cl_2 at 0 °C. The solution was stirred at room temperature for 25 min and then transferred via a double-tipped needle into a solution of 1.12 g (2.76 mmol) of 1,2-dihydropyridine **8g** in 5 mL of dry CH_2Cl_2 at 0 °C. The reaction mixture was refluxed for 16 h under a nitrogen atmosphere. After cooling to 0 °C, an aqueous solution of KOAc (1.47 g) in H_2O (10 mL) was added slowly. The mixture was refluxed for 20 min, cooled, and extracted with CH_2Cl_2 (20 mL). The organic phase was washed with 40-mL portions of water, saturated $NaHCO_3$, water, and brine and dried over $MgSO_4$. The solution was filtered and concentrated to yield 1.3 g of crude product. This material was purified by radial PLC (silica gel, hexane/CH_2Cl_2, 50:50) to yield 0.602 g (50%) of **15a** as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 10.1 (s, 1 H), 7.5–7.2 (m, 6 H), 5.6 (m, 1 H), 1.5–1.0 (m, 24 H); ^{13}C NMR ($CDCl_3$) δ 187.78, 150.40, 140.94, 129.50, 126.23, 121.23, 47.9, 18.87, 17.95, 12.19; IR (Nujol) 2925, 2856, 1744, 1658, 1591, 1520, 1461, 1377, 1316, 1178, 1027 cm^{-1}. Anal. Calcd for $C_{23}H_{32}ClNO_3Si$: C, 63.65; H, 7.43; N, 3.23. Found: C, 63.41; H, 7.45; N, 3.25.

2-*n*-Butyl-4-chloro-3-formyl-5-(triisopropylsilyl)-1,2-dihydropyridine (15b). This compound was prepared from **8h** in 88% yield as described above for the synthesis of **15a**: ^{1}H NMR ($CDCl_3$) δ 10.1 (s, 1 H), 7.5–7.1 (m, 6 H), 5.6 (m, 1 H), 1.8–0.95 (m, 30 H); ^{13}C NMR ($CDCl_3$) δ 187.96, 141.80, 129.47, 121.89, 52.00, 33.90, 31.53, 26.91, 22.60, 22.52, 18.86, 13.81, 12.33; IR (neat) 2954, 2867, 1743, 1660, 1590, 1524, 1377, 1313, 1183 cm^{-1}; HRMS calcd for $C_{26}H_{38}ClNO_3Si$ 475.23096, found 475.23081.

3-Formyl-1-(phenoxycarbonyl)-2-phenyl-5-(triisopropylsilyl)-1,2-dihydropyridine (16). Phosphorous oxychloride (2.4 mL, 26.1 mmol) was added slowly to a stirred solution of 8.7 mL (113 mmol) of DMF in 5 mL of CH_2Cl_2 at 0 °C. The solution was stirred at room temperature for 25 min and then transferred via a double-tipped needle into a solution of 7.12 g (16.4 mmol) of dihydropyridine **10h** in 10 mL of CH_2Cl_2 at 0 °C. The reaction mixture was refluxed for 14 h under a nitrogen atmosphere. After cooling to 0 °C, an aqueous solution of KOAc (2.56 g) in 60 mL of water was added slowly. This mixture was refluxed for 1 h, cooled, and extracted with CH_2Cl_2. The organic phase was washed with 40-mL portions of water, saturated $NaHCO_3$, water, and brine and dried over $MgSO_4$. Purification by radial PLC (silica gel, 5% EtOAc/hexane) gave 7.32 g (97%) of **16** as an oil: ^{1}H NMR ($CDCl_3$) δ 9.5 (s, 1 H), 7.5–7.1 (m, 10 H), 7.0 (d, 2 H), 6.45 (br s, 1 H), 1.4–1.0 (m, 21 H); ^{13}C NMR ($CDCl_3$) δ 189.79, 144.00, 140.00, 129.39, 128.50, 128.33, 126.64, 126.08, 121.29, 108.00, 54.16, 53.38,

18.40, 10.66; IR (Nujol) 2942, 2865, 1743, 1678, 1623, 1538, 1459, 1310, 1202, 1180 cm^{-1}. Anal. Calcd for $C_{28}H_{35}NO_3Si$: C, 72.84; H, 7.64; N, 3.03. Found: C, 72.76; H, 7.49; N, 3.00.

4-Chloro-3-formyl-2-methyl-5-(triisopropylsilyl)pyridine (18a). In a 50-mL round-bottomed flask was placed 0.49 g (1.1 mmol) of dihydropyridine **15a**, 7 mL of dry methanol, and 0.7 mL (3.3 mmol) of sodium methoxide in methanol. The mixture was stirred for 1 h at room temperature. Acetic acid (0.19 mL) was added, and stirring was continued at room temperature for 20 min, during which time the reaction turned dark yellow. After concentration, 1 g of 5% Pd/C and 8 mL of toluene were added. The mixture was refluxed for 4 h and filtered through Celite. The solution was evaporated to yield 0.36 g of crude product. Purification by radial PLC (5% EtOAc/hexane) gave 0.10 g (29%) of **18a** as a yellow-orange oil: ^1H NMR ($CDCl_3$) δ 10.71 (s, 1 H), 8.60 (s, 1 H), 2.77 (s, 3 H), 1.61 (m, 3 H), 1.13 (d, 18 H, J = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 192.11, 161.30, 158.98, 154.93, 129.47, 127.37, 24.15, 19.00, 12.04. Anal. Calcd for $C_{16}H_{26}ClNOSi$: C, 61.61; H, 8.40; N, 4.49. Found: C, 61.30; H, 8.23; N, 4.44.

2-*n*-Butyl-4-chloro-3-formyl-5-(triisopropylsilyl)pyridine (18b). This compound was prepared from **15b** in 56% yield as described above for the synthesis of **18a**: ^1H NMR ($CDCl_3$) δ 10.67 (s, 1 H), 8.63 (s, 1 H), 3.05 (m, 2 H), 1.8–0.8 (m, 28 H); ^{13}C NMR ($CDCl_3$) δ 192.06, 164.97, 158.90, 154.31, 129.13, 127.64, 35.79, 31.71, 22.83, 18.81, 13.89, 12.05; IR (neat) 2945, 2860, 1695, 1545, 1508, 1455, 1015, 875 cm^{-1}; HRMS calcd for $C_{19}H_{32}ClNOSi$ 353.1942, found 353.1941.

5-Acetyl-1-(phenoxycarbonyl)-2-phenyl-1,2-dihydropyridine (19). Tin tetrachloride (0.47 mL, 4.02 mmol) was added slowly to a stirred solution of 0.29 mL (4.20 mmol) of acetyl chloride in 2 mL of CH_2Cl_2. The solution was cooled to −78 °C for 15 min and transferred via a double-tipped needle into a solution of 0.583 g (1.34 mmol) of 1,2-dihydropyridine **10h** in 2 mL of dry CH_2Cl_2 at −78 °C. This reaction mixture was stirred at −78 °C for 30 min, warmed to room temperature, and stirred for 1 h. After extracting with CH_2Cl_2, the organic phase was washed with water and brine and dried over $MgSO_4$. The solution was concentrated, and the residue was purified by radial PLC (silica gel, 10% EtOAc/hexane) to afford 0.105 g (25%) of **19** as an oil: ^1H NMR ($CDCl_3$) δ 8.04 (s, 1 H), 7.40–7.27 (m, 10 H), 6.70 (m, 1 H), 5.95 (d, 1 H, J = 5 Hz), 5.8 and 5.7 (dd, 1 H, J = 5 and 10 Hz), 2.37 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 193.70, 150.08, 135.25, 134.41, 129.31, 128.60, 128.31, 126.08, 122.56, 121.04, 117.87, 58.25, 57.15, 24.63; IR (neat) 3070, 3040, 2930, 1738, 1650, 1590, 1490, 1388, 1085, 745 cm^{-1}; HRMS calcd for $C_{20}H_{17}NO_3$ 319.1208, found 319.1208.

2-*n*-Butyl-3-butyryl-1-(phenoxycarbonyl)-5-(triisopropylsilyl)-1,2-dihydropyridine (20a). This compound was prepared from **10h** in 45% yield as described below for the synthesis of **28**: ^1H NMR ($CDCl_3$) δ 7.4–7.2 (m, 6 H), 7.0 (m, 1 H), 5.6 (br m, 1 H), 2.65 (t, 2 H), 1.8–0.8 (m, 35 H); ^{13}C NMR ($CDCl_3$) δ 198.32, 152.96, 137.52, 136.29, 135.77, 134.64, 131.86, 131.70, 129.41, 125.92, 121.43, 109.70, 50.12, 49.67, 38.97, 32.54, 32.28, 32.19, 27.21, 22.62, 18.75, 18.65, 18.42, 18.30, 13.97, 10.67; IR (neat) 2950, 2865, 1732, 1725, 1650, 1530, 1490, 1460, 1180, 880 cm^{-1}; HRMS calcd for $C_{29}H_{45}NO_3Si$ 483.3169, found 483.3168.

3-Formyl-1-(phenoxycarbonyl)-2-phenyl-1,2-dihydropyridine (21). To a stirred solution of aldehyde **16** (6.52 g, 14.1 mmol) in CH_2Cl_2 (80 mL) was added dropwise 31.9 mL (141 mmol) of 30% HBr/AcOH under an atmosphere of nitrogen. The mixture was stirred at room temperature for 10 h, and then the orange solution was poured into water. The mixture was extracted with CH_2Cl_2, washed with water and brine, and dried over K_2CO_3. The solution was filtered through Celite and silica gel. After the solvent was removed, the crude product was purified by radial PLC (silica gel, 10% EtOAc/hexane) to yield 1.90 g (44%) of **21** as a yellow oil: ^1H NMR ($CDCl_3$) δ 9.5 (s, 1 H), 7.6–7.2 (m, 10 H), 7.0 (m, 2 H), 6.5 (m, 1 H), 5.7 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 189.43, 139.83, 138.80, 133.92, 132.72, 129.40, 128.52, 128.38, 127.23, 126.62, 126.09, 121.24, 104.58, 54.16, 53.38; IR (Nujol) 2925, 2853, 1731, 1667, 1553, 1457, 1377, 1312, 1263, 1201, 1169 cm^{-1}. Anal. Calcd for $C_{19}H_{15}NO_3$: C, 74.74; H, 4.95; N, 4.59. Found: C, 74.56; H, 4.85; N, 4.57.

2-*n*-Butyl-3-butyryl-1-(phenoxycarbonyl)-1,2-dihydropyridine (22). This compound was prepared from **20a** in 91% yield as described above for the synthesis of **21**: ^1H NMR ($CDCl_3$) δ 7.5–7.1 (m, 6 H), 7.02 and 6.97 (pair of d due to rotamers, 1 H, J = 6 Hz), 5.7–5.5 (m, 2 H), 2.65 (t, 2 H), 1.8–0.9 (m, 14 H); ^{13}C NMR ($CDCl_3$) δ 198.09, 152.73, 150.70, 150.50, 132.18, 131.21, 130.25, 129.37, 125.88, 121.33, 106.47, 106.01, 53.38, 50.64, 50.15, 38.84, 32.38, 32.12, 27.05, 22.53, 18.39, 13.83; IR (neat) 2960, 2940, 2875, 1730, 1650, 1550, 1489, 1330, 1185, 745 cm^{-1}; HRMS calcd for $C_{20}H_{25}NO_3$ 327.18346, found 327.18344.

2-(3-Hydroxypropyl)-1-(methoxycarbonyl)-5-(triisopropylsilyl)-1,2-dihydropyridine (25). To a suspension of magnesium (0.42 g, 17.3 mmol) in 15 mL of THF was added dibromoethane (0.1 mL). When all the dibromoethane had reacted, the gray solution was removed by syringe. After rinsing the magnesium with THF (10 mL), 10 mL of THF was added. To the suspension was added ethyl 3-bromopropyl acetaldehyde acetal (1.13 mL, 6.92 mmol). The mixture was stirred for 3 h at 20–25 °C and treated for 1 h with an ultrasound bath at 5–10 °C. The solution, containing Grignard reagent **24**, was transferred via a double-tipped needle into the 1-methoxycarbonyl salt of 3-(triisopropylsilyl)pyridine in 8 mL of dry THF, prepared by the addition of methyl chloroformate (0.29 mL, 3.81 mmol) to **7b** (0.815 g, 3.46 mmol) at −23 °C. The mixture was stirred for 30 min at −23 °C and at room temperature for 15 min. After hydrolysis with aqueous 10% HCl (20 mL) for 20 min, the mixture was extracted with ether. The combined organic layers were washed with water and brine and dried (K_2CO_3). The solvent was removed, and the residue was purified by radial PLC (10% EtOAc/hexane) to give 0.979 g (80%) of **25** as a clear oil: ^1H NMR ($CDCl_3$) δ 6.85 and 6.69 (pair of s due to rotamers, 1 H), 5.92 (d, 1 H, J = 9 Hz), 5.61 (m, 1 H), 4.8 and 4.7 (pair of m due to rotamers, 1 H), 3.8 (s, 3 H), 3.62 (m, 2 H), 1.7–1.5 (m, 4 H), 1.3–1.0 (m, 21 H); ^{13}C NMR ($CDCl_3$) δ 154.00, 132.42, 131.24, 125.19, 121.58, 120.82, 108.76, 62.89, 53.24, 51.09, 27.41, 18.51, 10.57; IR (neat) 3449, 2943, 2891, 2866, 1717, 1443, 1384, 1348, 1315, 1248, 1127, 1071 cm^{-1}. Anal. Calcd for $C_{19}H_{35}NO_3Si$: C, 64.55; H, 9.98; N, 3.96. Found: C, 64.49; H, 9.97; N, 3.89.

2-(3-Chloropropyl)-1-(methoxycarbonyl)-5-(triisopropylsilyl)-1,2-dihydropyridine (26). The alcohol **25** (1.27 g, 3.58 mmol) was dissolved in 12 mL of DMF under nitrogen. To this solution was added 0.96 g (7.16 mmol) of *N*-chlorosuccinimide, and the solution was cooled to 0 °C. Triphenylphosphine (1.88 g, 7.16 mmol) was added slowly, and after all the triphenylphosphine had been added, the solution was warmed to 50 °C and held there for 4 h. To this solution was added 1 mL of methanol to consume the excess reagents. The reaction mixture was poured into water and extracted with ether. The combined ether extracts were washed twice with water and once with brine and dried over $MgSO_4$. Concentration of the organic phase gave the crude product, which was purified by radial PLC (silica gel, 5% EtOAc/hexane) to give 0.938 g (70%) of **26** as a clear oil: ^1H NMR ($CDCl_3$) δ 6.9 and 6.7 (pair of s due to rotamers, 1 H), 5.95 (d, 1 H, J = 9 Hz), 5.61 (m, 1 H), 4.8 and 4.7 (pair of m due to rotamers, 1 H), 3.82 (s, 3 H), 3.52 (t, 3 H), 1.9–1.5 (m, 4 H), 1.3–1.0 (m, 21 H); ^{13}C NMR ($CDCl_3$) δ 154.00, 131.38, 126.05, 121.09, 108.78, 53.15, 51.09, 44.94, 30.99, 27.61, 18.70, 10.59; IR (neat) 2944, 2865, 1718, 1561, 1462, 1441, 1315 cm^{-1}. Anal. Calcd for $C_{19}H_{34}ClNO_2Si$: C, 61.34; H, 9.21; N, 3.76. Found: C, 61.13; H, 9.10; N, 3.76.

3-Butyryl-2-(3-chloropropyl)-1-(methoxycarbonyl)-5-(triisopropylsilyl)-1,2-dihydropyridine (28). To a mixture of 0.72 g (2.8 mmol) of silver tetrafluoromethanesulfonate in 4 mL of CH_2Cl_2 at −78 °C was added 0.31 mL (3.0 mmol) of butyryl chloride. After 1 h at −78 °C, 0.74 g (1.99 mmol) of dihydropyridine **26** in CH_2Cl_2 (3 mL) was added. After 30 min of stirring at −78 °C, the solution was warmed to 0 °C and quenched with water. The mixture was extracted with methylene chloride, and the combined extracts were washed with water and brine. After drying (K_2CO_3), the solvent was evaporated, and the residue was purified by radial PLC (silica gel, 5% EtOAc/hexane) to give 0.58 g (66%) of **28** as a yellow oil: ^1H NMR ($CDCl_3$) δ 7.2 (br s, 1 H), 7.0 (s, 1 H), 5.5 (m, 1 H), 3.85 (s, 3 H), 3.5 (m, 2 H), 2.6 (t, 2 H), 1.8–1.4 (m, 6 H), 1.3–0.9 (m, 24 H); ^{13}C NMR ($CDCl_3$) δ 199.00, 154.00, 137.86, 136.74, 130.00, 108.35, 53.66, 48.61, 44.70, 38.81, 29.85, 28.02, 18.41, 17.46, 14.90, 12.24, 10.66; IR (neat) 2944, 2866,

1729, 1654, 1533, 1463, 1442, 1310, 1191 cm^{-1}. Anal. Calcd for $C_{23}H_{40}ClNO_3Si$: C, 62.48; H, 9.12; N, 3.17. Found: C, 62.59; H, 9.17; N, 2.93.

3-Butyryl-2-(3-chloropropyl)-1-(methoxycarbonyl)-1,2-dihydropyridine (29). To a stirred solution of dihydropyridine **28** (0.584 g, 1.32 mmol) in 12 mL of CH_2Cl_2 was added 2.82 mL (13.2 mmol) of 30% HBr/AcOH under a nitrogen atmosphere. The mixture was stirred at room temperature for 24 h, and the orange solution was poured into water. The mixture was extracted with CH_2Cl_2, washed with water and brine, and dried over K_2CO_3. The solution was filtered and concentrated to yield the crude product. The residue was purified by radial PLC (silica gel, 10% EtOAc/hexane) to afford 0.28 g (74%) of **29** as a yellow oil: ^1H NMR ($CDCl_3$) δ 7.2–7.0 (br m, 2 H), 5.5 (br m, 2 H), 3.82 (s, 3 H), 3.5 (m, 2 H), 2.6 (t, 2 H), 1.8–1.4 (m, 6 H), 0.95 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 199.00, 153.00, 152.00, 131.59, 130.20, 105.18, 53.47, 49.01, 44.52, 38.65, 29.77, 27.79, 18.29, 13.71; IR (neat) 2960, 1724, 1653, 1551, 1442, 1337, 1263, 1241, 1192 cm^{-1}. Anal. Calcd for $C_{14}H_{20}ClNO_3$: C, 58.84; H, 7.05; N, 4.90. Found: C, 58.64; H, 7.20; N, 4.91.

3-Butyryl-2-(3-chloropropyl)-1-(methoxycarbonyl)-1,2,5,6-tetrahydropyridine (30). Dihydropyridine **29** (0.218 g, 0.76 mmol) was dissolved in 5 mL of CH_2Cl_2 and cooled to 0 °C. The solution was treated with triethylsilane (0.13 mL, 0.84 mmol), followed by the addition of trifluoroacetic acid (0.59 mL, 7.6 mmol) at 0 °C. The reaction mixture was stirred for 6 h at room temperature and then refluxed for 6 h. Water was added to the reaction mixture, which was then extracted with CH_2Cl_2. The combined organic extracts were washed with aqueous $NaHCO_3$, water, and brine. The organic layer was dried over K_2CO_3 and concentrated to give the crude product. Purification by radial PLC (silica gel, 0.5% CH_3OH/CH_2Cl_2) afforded 0.123 g (56%) of **30** as a clear oil: ^1H NMR ($CDCl_3$) δ 7.0–6.9 (br d, 1 H), 5.1–4.9 (dd, 1 H), 4.3–4.0 (dm, 1 H), 3.7 (s, 3 H), 3.7–3.5 (m, 2 H), 3.0 (m, 1 H), 2.6 (t, 2 H), 2.6–2.5 (m, 1 H), 2.25 (m, 1 H), 2.0–1.5 (m, 6 H), 0.95 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 199.23, 155.95, 141.00, 138.07, 137.26, 52.58, 49.64, 44.51, 39.00, 35.37, 29.94, 25.13, 17.92, 13.73; IR (neat) 2960, 2875, 1669, 1640, 1451, 1411, 1344, 1301, 1284, 1202 cm^{-1}. Anal. Calcd for $C_{14}H_{22}ClNO_3$: C, 58.43; H, 7.71; N, 4.87. Found: C, 58.22; H, 7.81; N, 4.84.

Preparation of (±)-Elaeokanine A (23). To a solution of tetrahydropyridine **30** (0.108 g, 0.375 mmol) in dry acetonitrile (3 mL) was added dry sodium iodide (0.225 g, 1.5 mmol) at 0 °C. After stirring for 10 min, chlorotrimethylsilane (0.19 mL, 1.5 mmol) was added dropwise at 0 °C. The heterogeneous mixture was refluxed overnight. The solution was poured into 20 mL of saturated sodium bicarbonate. Water (5 mL) was added, and the mixture was stirred at room temperature for 1 h. The mixture was extracted three times with ether (10 mL), and the combined organic layers were dried over K_2CO_3. Concentration gave the crude product, which was purified by radial PLC (silica gel, 1% CH_3OH/1% TEA/98% CH_2Cl_2) to give 0.040 g (55%) of **23** as a yellow oil: ^1H NMR ($CDCl_3$) δ 6.88 (t, 1 H), 3.46 (t, 1 H), 2.96–2.80 (m, 2 H), 2.78–2.68 (m, 1 H), 2.62–2.50 (m, 3 H), 2.48–2.26 (m, 3 H), 1.90–1.72 (m, 2 H), 1.70–1.58 (m, 2 H), 1.42–1.28 (m, 1 H), 0.93 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 200.70, 141.96, 136.84, 58.70, 52.64, 45.09, 39.18, 29.38, 25.51, 22.34, 18.10, 13.78; IR (neat) 3315, 2960, 2875, 2793, 1667, 1460, 1419, 1395, 1276 cm^{-1}. Anal. Calcd for $C_{12}H_{19}NO$: C, 74.57; H, 9.91; N, 7.25. Found: C, 74.46; H, 9.96; N, 7.13. These data are in agreement with published spectra.[15,20]

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