Notes

Oxidative Pictet−Spengler Cyclizations

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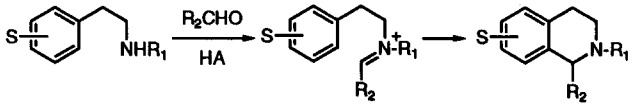
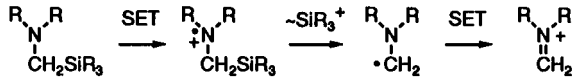
The Pictet−Spengler reaction has stood as one of the most useful synthetic methods to construct D[3,4]-aryl-fused piperidine ring systems. The process is typically promoted by acid-catalyzed condensation of an aryl ethylamine with an aldehyde (Scheme 1). Intramolecular capture of the intermediate iminium cation by the aryl ring leads to generation of the piperidine ring system. Although this process has been used effectively in a large number of alkaloid syntheses[2] and a number of variations have been introduced to produce the iminium cation intermediate,[3] few studies have addressed issues associated with the intervention of *N*-acyliminium cation intermediates and the preparation of ring systems smaller (e.g., five-membered) or larger (e.g., seven- and eight-membered) than piperidines.

Studies in our laboratory of photochemically induced SET-reactions of tertiary α-silylamines and -amides[5] and related metal oxidation reactions[6] have led to the development of a new method to generate both *N*-alkyl- and *N*-acyliminium cations. These efforts have demonstrated that the silicon-substituted amine and amide substrates undergo regioselective oxidative conversion to iminium cations (Scheme 2). The high regiocontrol associated with these processes is due to the more rapid rates of tertiary aminium radical α-desilylation vs competitive α-deprotonation.[7] In a more recent effort, we have shown how this oxidation process can be used effectively to initiate Mannich cyclization reactions of α-silylamines and -amides which possess tethered vinyl- and allylsilane functionality. In this report, we describe the results of a parallel study which has shown how the oxidative protocol can be applied to promote both standard and unique Pictet−Spengler cyclization reactions.

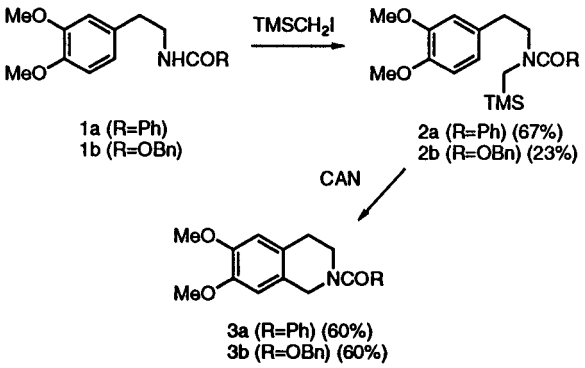
Scheme 1



Scheme 2



Scheme 3



To gain preliminary information about the feasibility of an oxidative Pictet−Spengler cyclization process, the 2-arylethyl α-silylamide **2a** and related carbamate **2b** were prepared by N-silylmethylation and subjected to ceric ammonium nitrate (CAN) oxidation (Scheme 3). The oxidation reactions are conducted by using 2 equiv of CAN in acetonitrile at 25 °C. In each case, workup followed by chromatographic separation leads to isolation of the respective tetrahydroisoquinoline products, **3a** and **3b**.

These results, which suggest that the oxidative protocol is effective in promoting Pictet−Spengler cyclizations, encouraged a further exploratory effort with variously structured arylalkyl α-silyl substrates.[8] Oxidation reactions of the chain-shortened arylmethyl-amide **5a** and -carbamate **5b**, while occurring with lower efficiencies as a result of competitive iminium cation hydrolysis, do lead to production of the corresponding isoindolines **6a** and

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(2) Stevens, R. V. In *The Total Synthesis of Natural Products*; Ap Simon, J., Ed.; J. Wiley and Sons: New York, 1977; Vol. 3, p 439. Zangg, H. E. *Synthesis* **1984**, *2*, 85.

(3) Various methods have been introduced to promote iminium cation formation in Pictet−Spengler cyclization pathways. Included in this group are the oxidative Polonovsky and $Hg(OAc)_2$ procedures, α-cyano and α-carboxylic acid elimination processes, and enanimine protonations. For a general, recent review of some of these methods, see Overman, L. E.; Ricca, D. J. In *Comprehensive Organic Synthesis*; Heathcock, C. H., Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991, Vol. 2, p 1007.

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(8) As is the case for the classical Pictet−Spengler reactions, lower yields are observed for oxidative cyclizations with less electron rich aryl-substituted systems.

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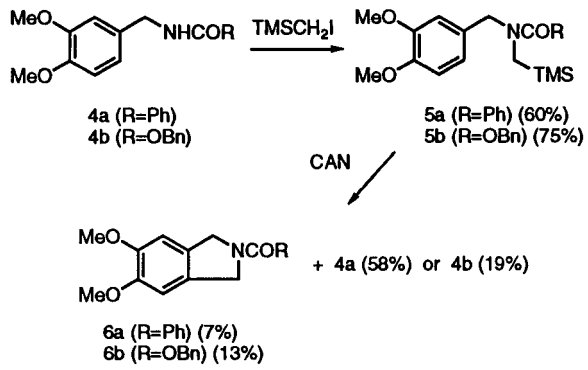
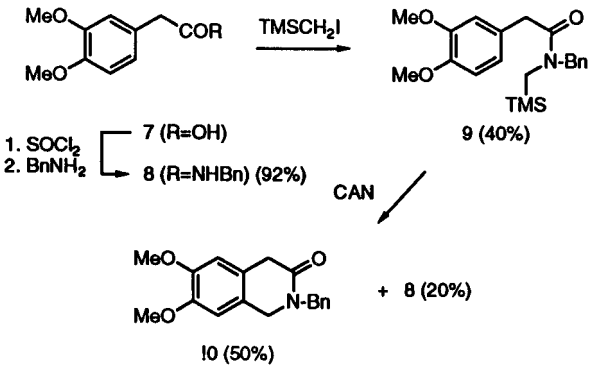
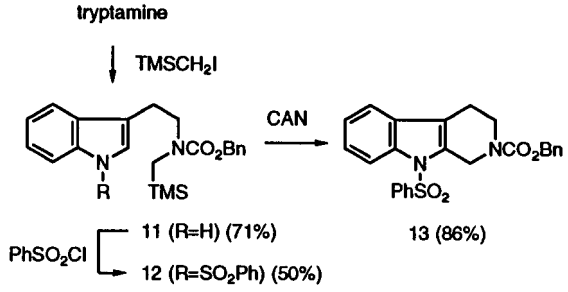
Scheme 4



Scheme 5



Scheme 6



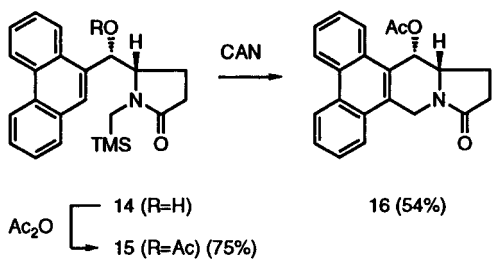
6b (Scheme 4). Likewise, the process is not restricted to systems that have the amide function exocyclic to the forming N-heterocyclic ring. Accordingly, the silylamide **9**, derived from arylacetic acid **7**, cyclizes upon treatment with CAN to form the 3-oxohydroisoquinoline **10** (Scheme 5).

Substances containing the β-carboline and tylophorine types of polycyclic structures also can be prepared by use of this oxidative process. The conversions of N-blocked tryptamine derivative **12** to indolopiperidine **13** and pyroglutamic acid derived[9] pyrrolidinone **15** to phenanthrenoindolizidine **16** (Scheme 7) exemplify the potential (Schemes 6 and 7).

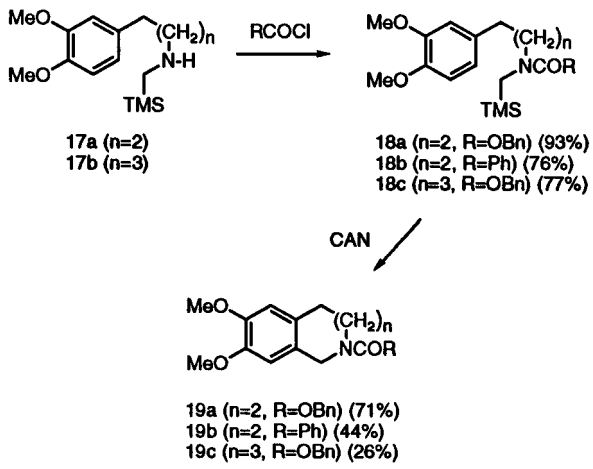
Finally, the reaction sequences depicted in Schemes 8 and 9 indicate that the oxidative Pictet−Spengler reaction can be employed successfully in sequences targeted at both benzo- and indolohydroazepines and -hydroazocines.

The results presented above show that the oxidative protocol can serve as a useful alternative to classical methods for promoting Pictet−Spengler cyclization reac-

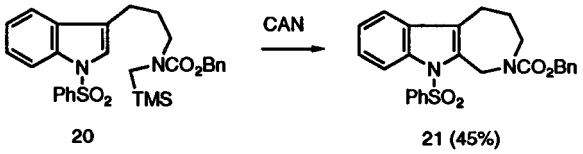
Scheme 7



Scheme 8



Scheme 9



tions. For example, the mild, nonacidic conditions required for the oxidative processes may be advantageous when applied to systems that possess particularly acid sensitive functionality. Of course, one limitation of the oxidative protocol is that it is intolerant of functionality (e.g., aldehydes) which are oxidatively unstable. Another advantage of the CAN-procedure is that it does not require the use of selective imide reduction to access amidol precursors which is used in the more common, acid-catalyzed route[10] to *N*-acyliminium cations. On the other hand, α-silylamides are the requisite starting materials for the oxidative Pictet−Spengler protocol and procedures which are available for their synthesis have limitations. For example, approaches involving amide anion or O-silylimidate N-alkylation depend on the availability of α-halosilanes or related substrates and the facility of their S_N2-reactions. However, with the advent of procedures for the synthesis of structurally complex α-substituted α-silylamines[11] and perhaps alternative starting materials (e.g., α-amino carboxylates, unpublished) the oxidative cyclization method may prove to be generally applicable for the preparation of a wide range of α-substituted aryl-fused piperidines.

Experimental Section

General Procedures. Unless otherwise noted, ^{1}H NMR and ^{13}C NMR spectra were recorded on $CDCl_3$ solutions by using

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200.13, 400.13, or 500.14 MHz operational frequencies for ^{1}H observations and 50.32 and 100.62 MHz for ^{13}C observations. Chemical shifts are reported in parts per million relative to $CDCl_3$ (7.24 ppm for ^{1}H NMR and 77.0 ppm for ^{13}C NMR) as the internal standard. ^{1}H NMR coupling constant determinations (*J*-values reported in Hz) and nuclei assignments were aided by the use of homonuclear decoupling experiments. ^{13}C NMR resonance assignments were aided by use of the DEPT technique to determine numbers of attached hydrogens. Infrared (IR) spectra were obtained on samples which were prepared as neat liquids unless otherwise noted, and band assignments are in units of cm^{-1}. Mass spectrometric data determined by use of either the electron impact (EIMS), chemical ionization (CIMS), or fast atom bombardment (FAB) method are reported as *m*/*z* (relative intensity), and high-resolution mass spectral data (HRMS) are recorded as *m*/*z*. All new compounds were obtained as oils in >90% purity (by ^{1}H and ^{13}C NMR analysis) unless otherwise noted. Column chromatographic separations were performed by using EM Type 60 silica gel (230−400 mesh), Florisil (100−200 mesh), or Type F-20 Alumina (neutral, 80−120 mesh). Preparative TLC was performed on 20 × 20 cm plates coated with EM Type-60 GF-254 silica gel.

Representative Procedures. Preparation and CAN-Promoted Cyclization of Benzyl *N*-[2-(3,4-Dimethoxyphenyl)eth-1-yl]-*N*-[(trimethylsilyl)methyl]carbamate (2b). A mixture of benzyl *N*-[2-(3,4-dimethoxyphenyl)eth-1-yl]carbamate (**1b**)[12] (5.00 g, 15.8 mmol) and sodium hydride (0.69 g, 15.8 mmol) in 25 mL of THF was stirred at 0 °C for 1 h. (Trimethylsilyl-)methyl iodide (4.00 g, 19.0 mmol) was added, and the mixture was stirred at reflux for 19 h and concentrated in vacuo, giving a residue which was triturated with CH_2Cl_2. The triturate was dried and concentrated in vacuo to give a residue which was subjected to column chromatography (silica gel, 1:3 ethyl acetate: hexane) to yield 1.48 g (23%) of **2b**: (rotamer A:B = 1.3:1) ^{1}H NMR 0.01 (A) and 0.08 (B) (s, 9H, TMS), 2.80 (A and B) (m, 4H, CH_2TMS and ArCH_2), 3.43 (A and B) (m, 2H, CH_2N), 3.78 (A) and 3.85 (B) (s, 6H, CH_3O), 5.09 (A) and 5.11 (B) (s, 2H, CH_2-Ph), 6.70 (A and B) and 7.35 (A and B) (m, 8H, Ar and Ph); ^{13}C NMR −1.06 (B) and −1.02 (A) (TMS), 34.5 (B) and 34.6 (A) (Ar*C*H$_2$), 39.5 (B) and 39.6 (A) (TMS), 51.6 (A) and 52.1 (B) (*C*H$_2$N), 56.3 and 56.4 (A and B) (*C*H$_3$O), 67.5 (A and B) (*C*H$_2$-Ar), 111.9, 112.6, 121.2, 128.4, 128.5, 128.6, 128.7, 128.8, 132.1, 137.5 and 137.6, 148.1, 149.5, 156.4 (Ar and Ph), 156.4 (C═O); IR 3032, 2953, 1703, 1516; EIMS 401 (M, 5), 386 (34), 310 (72), 294 (36), 206 (71), 151 (42), 91 (100); HRMS 401.2009, $C_{22}H_{31}NO_4Si$ requires 401.2022.

A solution of **2b** (0.100 g, 0.258 mmol) and CAN (0.283 g, 0.515 mmol) in 10 mL of anhydrous acetonitrile was stirred at 25 °C for 18 h, diluted with CH_2Cl_2, and filtered. The filtrate was washed with brine, dried, and concentrated in vacuo, giving a residue which was subjected to column chromatography (silica gel, 1:2 ethyl acetate−hexane) to give 47 mg (60%) of tetrahydroisoquinoline **3b**. ^{1}H NMR 2.78 (t, *J* = 5.5, 2H, (ArCH_2), 3.72 (t, *J* = 5.5, 2H, (CH_2N), 3.86 (s, 6H, (CH_3O), 4.58 (s, 2H, (ArCH_2N), 5.18 (s, 2H, OCH_2Ar), 6.63(m, 2H, Ar), 7.36 (m, 5H, Ar); ^{13}C NMR 28.8 (Ar*C*H$_2$), 42.0 (*C*H$_2$N), 45.9 (Ar*C*H$_2$N), 56.3 (*C*H$_3$O), 67.5 (O*C*H$_2$Ar), 109.7, 112.1, 125.2, 125.4, 126.7, 128.9, 128.4, 137.3, 148.1, 148.2 (Ar), 155.8 (C═O); IR 3080, 2935, 1632, 1518; EIMS 327 (M, 2), 236 (100), 91 (38); HRMS 327.1466, $C_{19}H_{21}NO_4$ requires 327.1471.

Preparation and CAN-Promoted Cyclization of Benzyl *N*-[(*N*-Benzenesulfonyl)-*β*-trytophyl]-*N*-[(trimethylsilyl)-methyl]carbamate (12). A solution of tryptamine (1.50 g, 9.35 mmol), triethylamine (0.95 g, 9.35 mmol), and (trimethylsilyl-)methyl iodide (2.67 g, 9.35 mmol) in 50 mL of CH_2Cl_2 was stirred at reflux for 6 h, cooled, washed with H_2O, dried, and concentrated in vacuo. To a solution of the residue and triethylamine (0.95 g, 9.35 mmol) in 50 mL of CH_2Cl_2 was added benzyl chloroformate (2.13 g, 9.35 mmol) in 20 mL of CH_2Cl_2, and the mixture was stirred for 2 h at 25 °C, washed with H_2O, dried, and concentrated in vacuo to give a residue which was subjected to column chromatography (silica gel, 1:3 ethyl acetate−hexane) to yield 2.52 g (71%) of **11**: rotamers A and B, 1.8:1) ^{1}H NMR −0.01 (B) and 0.09 (A) (s, 9H, TMS), 2.81(B) and 2.86 (A) (s, 2H, CH_2TMS), 3.01 (A and B) (m, 2H, ArCH_2), 3.55 (A and B) (m, 2H, CH_2N), 5.10 (A) and 5.15 (B) (OCH_2Ar), 7.18 (A and B) (m, 8H, Ar), 7.68 (A and B) (m, 1H, Ar), 8.01 (s, 1H, N*H*); ^{13}C NMR −1.06 (B) and −0.94 (A) (TMS) 23.9 (A) and 24.6 (A) (*C*H$_2$-TMS), 39.1 (B) and 39.7 (A) (Ar*C*H$_2$), 50.6 (A) and 51.1 (B) (*C*H$_2$N), 67.6 (B) and 67.7 (A) (O*C*H$_2$Ar), 113.4, 128.0, 111.7, 119.2, 119.7, 119.8, 122.3, 122.5, 122.7, 128.2, 128.3, 128.4, 128.6, 129.0, 129.3, 136.8, 137.4 (Ar) 156.7 (C═O); IR 3416, 3319, 3090, 2908, 1699, 1448; EIMS 380 (M, 4), 289 (24), 234 (20), 206 (28), 130 (30); HRMS 380.1917, $C_{22}H_{28}N_2O_2Si$ requires 380.1920.

A solution of **11** (2.50 g, 6.60 mmol) and sodium hydride (0.29 g, 6.60 mmol) in 30 mL of THF was stirred at reflux for 1.5 h before adding benzene sulfonyl chloride (1.17 g, 6.60 mmol), stirring at reflux for 1.5 h, cooling to 25 °C, and concentrating in vacuo. The residue was triturated with CH_2Cl_2, and the triturate was dried and concentrated in vacuo to give a residue which was subjected to column chromatography (silica gel, 1:3 ethyl acetate−hexane) to yield 1.72 g (50%) of **12** (rotamer A:B = 1.2:1) ^{1}H NMR −0.01 (B) and 0.09 (A) (s, 3H, TMS), 2.68 (B) and 2.78 (A) (s, 2H, CH_2TMS), 2.93 (A and B) (m, 2H, ArCH_2), 3.51 (A and B) (m, 2H, CH_2N), 5.04 (A) and 5.16 (B) (s, 2H, OCH_2-Ar), 7.14 (A and B) (m, 1H, Ar), 7.40 (A and B) (m, 11H, Ar), 7.85 (A and B) (m, 2H, Ar), 8.02 (A and B) (m, 1H, Ar); ^{13}C NMR −1.16 (B) and −0.99 (A) (TMS), 23.7 (B) and 24.4 (A) (Ar*C*H$_2$), 39.4 (B) and 39.7 (A) (*C*H$_2$TMS), 49.5 (A) and 50.1 (B) (*C*H$_2$N), 67.7 (A and B) (O*C*H$_2$Ar), 119.9 and 120.3, 114.2, 123.8, 125.3, 127.2, 128.6, 128.7, 129.0, 129.3, 129.4, 129.7, 129.9, 131.2 and 131.4, 135.8 and 137.3 and 138.7 (Ar), 156.3 (A) and 156.5 (B) (C═O); IR 3090, 2953, 1693, 1464; EIMS 506 (M, 9), 429 (77), 270 (45), 233 (33), 206 (100); HRMS 506.1704, $C_{27}H_{30}N_2O_4SiS$ requires 506.1696.

A solution of **12** (0.23 g, 0.44 mmol) and CAN (0.49 g, 0.88 mmol) in 25 mL of anhydrous acetonitrile was stirred at 24 °C for 6 h, diluted with CH_2Cl_2, and filtered. The filtrate was washed with brine, dried, and concentrated in vacuo, giving a residue which was subjected to column chromatography (silica gel, 1:2 ethyl acetate−hexane) to give 168 mg (86%) of carbazole **13**: (rotamer A:B = 1:1) ^{1}H NMR 2.72 (m, 2H, ArCH_2), 3.79 (m, 2H, CH_2N), 5.02 (s, 2H, ArCH_2Ar), 5.22 (s, 2H, ArCH_2N), 7.32 (m, 11H, Ar), 7.77 (m, 1H, Ar), 7.89 (m, 1H, Ar), 8.17 (m, 1H, Ar). ^{13}C NMR 21.6 and 22.1 (Ar*C*H$_2$), 41.0 (Ar*C*H$_2$N), 43.9 (*C*H$_2$N) 68.0 (O*C*H$_2$Ar),117.0 117.6 (ArCH$_2$CH$_2$N ArC$_7$ quaternary), 114.1, 118.3, 123.5, 124.6, 126.2, 127.8, 128.0, 128.4, 129.2, 129.3, 133.7, 130.7, 131.2, 135.9, 136.4, 138.1 (Ar), 155.3 (C═O); IR 3067, 2920, 1703, 1427; EIMS 446 (M, 1), 355 (100), 214 (34); HRMS 446.1294, $C_{25}H_{22}N_2O_4S$ requires 446.1256.

Preparation and CAN-Promoted Cyclization of [1-[(Trimethylsilyl)methyl]-2-oxopyrrolidin-5-yl][9-Phenanthrenyl]methyl Acetate (15). A solution of phenanthrenyl alcohol **14**[8] (112 mg, 0.20 mmol), DMAP (11 mg, 0.09 mmol), and acetic anhydride (0.20 mL, 0.22 g, 2.1 mmol) in pyridine (3 mL) was stirred at 25 °C for 17 h, diluted with H_2O, and extracted with CH_2Cl_2. The extracts were washed with 5% HCl, satd $NaHCO_3$, and H_2O, dried, and concentrated in vacuo to provide a residue which was subjected to column chromatography (Florisil, Et_2O), yielding 83 mg (75%) of the acetate **15**: ^{1}H NMR 0.01 (s, 9 H, Si(CH_3)$_3$), 1.75 (m, 1 H, CH_2), 1.92 (m, 1 H, CH_2), 2.18 (m, 1 H, CH_2), 2.16 (s, 3 H, CH_3), 2.34 (m, 1 H, CH_2), 2.41 and 3.35 (ABq, *J* = 15.2, 2 H, SiCH_2N), 4.23 (ddd, *J* = 8.6, 6.6, and 2.4, 1 H, C*H*), 6.49 (d, *J* = 6.6, 1 H, C*H*OAc), 7.65 (m, 4 H, Ar), 7.79 (s, 1 H, Ar H-10), 7.88 (dd, *J* = 7.9 and 1.1, 1 H, Ar), 8.20 (d, *J* = 9.5, 1 H, Ar), 8.65 (d, *J* = 8.2, 1 H, Ar H-4 or H-5), 8.75 (dd, *J* = 7.7 and 2.0, 1 H, Ar H-4 or H-5); ^{13}C NMR −1.3 (TMS), 21.3 (*C*H$_3$CO), 22.9 (*C*H$_2$), 29.4 (*C*H$_2$), 34.6 (Si*C*H$_2$N), 62.8(*C*H), 122.5, 123.6, 123.7, 126.6, 126.8, 126.99, 127.05, 127.4, 128.8, 129.4, 130.3, 130.7, 130.8, 132.0 (Ar), 169.6 (OCO), 174.5 (NCO); IR 3050, 2954, 1747, 1682; CIMS 421 (M+1, 1), 170 (100), 74 (30); HRMS 420.19875, $C_{25}H_{30}O_3NSi$ requires 420.19949.

A solution of **15** (38 mg, 0.091 mmol) and CAN (218 mg, 0.4 mmol) in 1.5 mL of anhydrous acetonitrile was stirred at 25 °C for 18 h, diluted with satd $NaHCO_3$, and extracted with CH_2Cl_2. The extracts were washed with brine, dried, and concentrated in vacuo to give a residue which was subjected to HPLC (reverse phase C-18, Et_2O to 4:1 Et_2O−acetone) to provide 17 mg (54%) of indolizidine **16**: ^{1}H NMR 2.09 (m, 1 H, CH_2), 2.05 (s, 3 H, CH_3CO), 2.37 (m, 1 H, CH_2), 2.52 (m, 2 H, CH_2), 4.12

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(ddd, J = 8.6, 3.8, 2.1, 1 H, C*H*) 4.66 and 5.57 (ABq, J = 18.0, 2 H, NCH_2), 6.83 (d, J = 2.1, 1 H, C*H*OAc), 7.67 (m, 4 H, Ar), 8.00 (d, J = 8.0, 1 H, Ar), 8.08 (m, 1 H, Ar), 8.70 (d, J = 8.6, 1 H, H-4, H-5 Ar); ^{13}C NMR 20.0 (*C*H_2), 21.0 (*C*H_3CO), 30.3 (*C*H_2), 40.9 (N*C*H_2), 56.9 (*C*H), 66.0 (*C*HOAc), 123.1, 123.2, 123.3, 125,7, 126.8, 127.4, 127.8, 125.7, 128.5, 128.9. 129.7, 130.3, 130.5 (Ar), 171.1 (CON), 174.5 (OCO). IR 3030, 2974, 1732, 1686; EIMS 345 (M, 4), 285 (22), 284 (100), 229 (27); HRMS 345.13633, $C_{22}H_{19}O_3N$ requires 345.13651.

Preparation and CAN-Promoted Cyclization of Benzyl *N*-[3-(3,4-Dimethoxyphenyl)prop-1-yl]-*N*-[(trimethylsilyl)-methyl]carbamate (18a). A solution of 3-(3,4-dimethoxyphenyl)prop-1-ylamine[13] (1.85 g, 9.48 mmol) and iodo(methyltrimethyl)silane (2.11 g, 9.85 mmol) in 15 mL of acetonitrile was stirred at reflux for 12 h and concentrated in vacuo, and the residue was dissolved in CH_2Cl_2, washed with water, dried, and concentrated in vacuo to give 2.60 g (95%) of the secondary amine **17a** which was used without further purification: ^{1}H NMR 0.03 (s, 9H, TMS), 1.05 (s, 1H, NH), 1.79 (quin, J = 7.5, 2H, CH_2), 2.05 (s, 2H, CH_2), 2.62 (m, 4H, $(CH_2)_2$), 3.84 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 6.761 (m, 3H, Ar); ^{13}C NMR −2.6 (TMS), 31.2, 33.0, 40.0, 53.8, 55.6 (OCH_3), 55.7 (OCH_3), 111.0, 111.5, 119.9, 134.7, 146.9, 148.6; EIMS 281 (M, 1.8), 44 (100); HRMS 281.1811, $C_{15}H_{27}NO_2Si$ requires 281.1811.

To a solution of **17a** (0.27 g, 0.96 mmol) and benzyl chloroformate (0.20 g, 1.17 mmol) in 20 mL of CH_2Cl_2 was added Et_3N (0.2 mL, 1.4 mmol), and the mixture was stirred for 1 h at 25 °C, washed with satd $NaHCO_3$ and brine, dried, and concentrated in vacuo to give a residue which was subjected to column chromatography (silica gel, 1:2 EtOAc−hexane) to give carbamate **18a** (0.37 g, 93%): (rotamer A:B = 1:1) ^{1}H NMR −0.01 and 0.06 (s, 9H, TMS), 1.87 (m, 2H, CH_2), 2.55 (m, 2H, CH_2), 2.79 (s, 2H, CH_2TMS), 3.27 (m, 2H, CH_2), 3.87 (s, 6H, OCH_3), 5.13 (s, 2H, OCH_2), 6.72 (m, 3H, Ar), 7.34 (s, 5H, Ar); ^{13}C NMR −1.8 and −1.5, 29.0 and 29.5, 32.6 and 32.6, 37.9 and 38.8, 48.6 and 49.1, 55.7, 55.8, 66.8, 111.1, 111.5, 111.6, 119.9, 127.6, 127.7, 127.9, 128.1, 128.3, 128.3, 134.0, 134.3, 136.8, 137.1, 147.1, 148.7, 155.9 and 156.1 (C═O); EIMS 415 (M, 2.3), 400 (33), 308 (30), 165 (85), 73 (100); HRMS 415.2176, $C_{23}H_{33}NO_4Si$ requires 415.2179.

To a solution of **18a** (0.369 g, 0.884 mmol) in 40 mL of anhydrous acetonitrile was added CAN (0.980 g, 1.79 mmol), and the mixture was stirred at 25 °C for 0.5 h, diluted with CH_2Cl_2, washed with satd $NaHCO_3$ and water, dried, and concentrated in vacuo, giving a residue which was subjected to column chromatography (silica gel, 1:2 EtOAc−hexane) to give tetrahydrobenzazepine **19a** (0.214 g, 71%); mp 103−105 °C; (rotamer A:B = 2:1); ^{1}H NMR 1.77 (m, 2H, CH_2), 2.87 (m, 2H, CH_2), 3.57, 3.83 (A) and 3.86 (B) (s, 6H, OCH_3), 3.73 (m, 2H, CH_2), 4.35 (A) and 4.40 (B) (s, 2H, CH_2), 5.02 (A) and 5.04 (B) (s, 2H, CH_2), 6.54, 6.65 and 6.86 (A and B) (s, 2H, Ar), 7.29 (s, 5H, Ar); ^{13}C NMR (A) 28.1, 34.8, 50.9, 51.6, 55.6, 55.8, 67.1, 113.0, 113.2, 127.8, 127.9, 128.3, 130.6, 134.0, 136.6, 146.2, 147.4, 155.4 (C═O); (B) 28.7, 34.8, 50.3, 52.1, 55.7, 55.9, 66.8, 113.0, 113.2, 127.7, 127.9, 128.3, 130.4, 133.6, 136.7, 146.5, 147.5, 155.2 (C═O); EIMS 341 (M, 7), 250 (100), 206 (20), 91 (60); HRMS 341.1599, $C_{20}H_{23}NO_4$ requires 341.1623.

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Supporting Information Available: Experimental details and ^{1}H NMR spectroscopic data for the new substances described in this publication (48 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from ACS; see any current masthead page for ordering information.

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