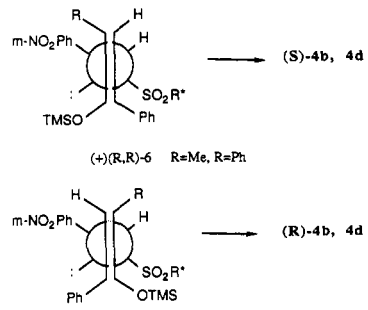
Scheme II



NMR spectra of **2c** are also consistent with the proposed structure.[14] Furthermore, addition of a trace of *p*-toluenesulfonic acid to **2c** resulted in its immediate and quantitative rearrangement to α-siloxy ketone **3c**.[1a] At 60 °C, in the absence of acid, the rearrangement of **2c** to **3c** also appeared to be accelerated. α-Siloxy epoxide **2c** proved to be surprisingly stable when the oxidation was carried out in anhydrous THF (16 h, 25 °C) and was isolated in greater than 90% yield, as an oil, by extraction into *n*-pentane. α-Siloxy epoxides **2b** and **2d** were also observed by NMR, but were much less stable, rearranging within 1–8 h to α-siloxy ketones **3b** and **3d**, respectively (Table II).

Asymmetric oxidation of silyl enol ethers **1b** and **1d** at 60 °C by chiral sulfamyloxaziridine (+)-(*R,R*)-**6**[15] gave, after standard workup, optically active α-hydroxy ketones (−)-(*S*)-**4b** and (+)-(*S*)-**4d**, in 7.5% and 11.0% ee and 31% and 62% isolate yields, respectively.[16] In analogy with the epoxidation of alkenes by chiral 2-sulfonyloxaziridines, an open transition state having planar geometry is predicted for the reaction of silyl enol ethers with (+)-(*R,R*)-**6** (Scheme II).[19] The relatively low enantioselectivities obtained in these asymmetric oxidations are understandable considering that the steric difference for reaction of (+)-(*R,R*)-**6** at the re and si faces of the silyl enol ethers is minimal (Scheme II).

In summary, the first isolation and characterization of the elusive α-siloxy epoxides **2** in the Rubottom reaction (Scheme I) is described. We attributed our ability to isolate these labile species to the use of 2-sulfonyloxaziridine **5**, an aprotic and neutral oxidizing reagent. On hydrolysis α-siloxy epoxides **2** afford good to excellent yields of α-hydroxy ketones **4**. In the synthesis of complex polyfunctionalized molecules that require the Rubottom reaction the use of 2-sulfonyloxaziridine **5** is indicated.

(11) A sample of **7c**[12] was prepared in 87% isolated yeild by heating the alkene at 60 °C with oxaziridine **5** for 18 h as previously reported.[13]

(12) Puterbaugh, W. H.; Hauser, C. R. *J. Am. Chem., Soc.* **1964**, *86*, 1394.

(13) Davis, F. A.; Abdul-Malik, N. F.; Awad, S. B.; Harakal, M. E *Tetrahedron Lett.* **1981**, *22*, 917.

(14) ^{13}C NMR (C_6D_6) **2c**: δ 1.84 (TMS), 20.53 (Me_2), 65.93 (CMe_2), 89.12 (PhC[O]OTMS), 127.53–139.93 (Ph); IR (Nujol) 1250 cm^{-1} (COC). **3c**: δ 2.52 (TMS), 29.66 (Me_2), 81.44 (C(OTMS)Me_2), 123.62–136.29 (Ph), 203.10 (CO). **7c**: δ 26.17 (Me), 32.83 (Me), 68.59 (CMe_2), 72.54 (PhCH[O]), 134.52–145.68 (Ph); IR (neat)[12] 1250 and 910 cm^{-1}.

(15) (+)-(*R,R*)-**6** was prepared as previously described: Davis, F. A.; McCauley, J. P., Jr.; Harakal, M. E. *J. Org. Chem.* **1984**, *49*, 1465. Additional details will be published elsewhere.

(16) The optical purities of (−)-(*S*)-**4b**[17] and (+)-(*S*)-**4d**[18] were determined by comparision of the optical rotations with authentic samples.

(17) Konishi, J.; Ohta, H.; Tsuchihashi, G.-i., *Chem. Lett.* **1985**, 1111 and references cited therein.

(18) (−)-(*S*)-2-Hydroxy-1-phenylpropanone (**4b**) was prepared optically pure by reaction of the 1,3-dioxlanone of (−)-(*S*)-lactic acid with phenyllithium at −78 °C: $[\alpha]_D$ −86.7 (*c* 2, $CHCl_3$).[4d]

(19) Davis, F. A.; Harakal, M. E.; Awad, S. B. *J. Am. Chem. Soc.* **1983**, *105*, 3123. Davis, F. A.; Chattopadhyay, S. *Tetrahedron Lett.* **1986**, *27*, 5079.

(20) Harada, K.; Shiono, S. *Bull. Chem. Soc. Jpn.* **1984**, *51*, 1040.

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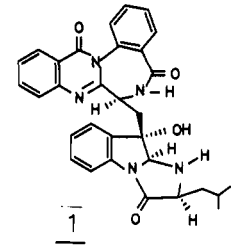
Crystallization-Induced Asymmetric Transformation: Stereospecific Synthesis of a Potent Peripheral CCK Antagonist

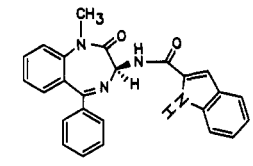
Summary: An efficient, catalytic method for the total conversion of a racemate into a single enantiomer is reported. The combined, in situ resolution–racemization was applied to 3(*RS*)-amino-1,3-dihydro-1-methyl-5-phenyl-2*H*-1,4-benzodiazepin-2-one to produce the optically pure *S* enantiomer in 91% yield. Acylation with indole-2-carboxylic acid produced L-364,718, an extremely potent nonpeptidal peripheral CCK antagonist.

Sir: The recent isolation of asperlicin (**1**)[1] and its identification as a selective antagonist of the gastrointestinal hormone cholecystokinin (CCK) has spawned great activity in this area.[2] Asperlicin's lack of oral bioavailability, modest potency, and poor water solubility make it unattractive as a potential therapeutic agent. Thus, a search for a better antagonist, either semisynthetic or synthetic, was undertaken.[3] The result was an extremely potent nonpeptidal CCK antagonist with high selectivity for peripheral tissue: L-364,718 (**2**).[3,4]



1

ASPERLICIN



2

L-364,718

The differences in potency[3] of (*S*)-**2** vs. racemic **2** made it desirable to use the optically pure antagonist as the drug candidate. Thus, a practical asymmetric synthesis was required to permit clinical trials. This paper describes the synthesis of 3(*S*)-amino-1,3-dihydro-1-methyl-5-phenyl-2*H*-1,4-benzodiazepin-2-one [(*S*)-**3**], the key intermediate for the preparation of L-364,718 (**2**), via an efficient, catalytic, one-pot resolution–racemization sequence which renders alternate methods of asymmetric synthesis moot (Scheme I).

(1) (a) Goetz, M. A.; Lopez, M.; Monaghan, R. L.; Chang, R. S. L.; Lotti, V. J.; Chen, T. B. *J. Antibiot.* **1985**, *38*, 1633. (b) Liesch, J. M.; Hensens, O. D.; Springer, J. P.; Chang, R. S. L.; Lotti, V. J. *J. Antibiot.* **1985**, *38*, 1638. (c) Chang, R. S. L.; Lotti, V. J.; Monaghan, R. L.; Birnbaum, J.; Stapley, E. O.; Goetz, M. A.; Albers-Schonberg, G.; Patchett, A. A.; Liesch, J. M.; Hensens, O. D.; Springer, J. P. *Science (Washington, D. C.)* **1985**, *230*, 177.

(2) Albers-Schonberg, G.; Chang, R. S. L.; Lotti, V. J.; Chen, T. B.; Monaghan, R. L.; Birnbaum, J.; Stapley, E. O.; Goetz, M. A.; Lopez, M.; Patchett, A. A.; Liesch, J. M.; Hensens, O. D.; Springer, J. P. In *Proceedings of the Ninth American Peptide Symposium* Deber, C. M., Hruby, V. J., Kopple, K. D., Eds.; Pierce Chemical Co.: Rockford, IL, 1985; pp 565–574.

(3) Evans, B. E.; Bock, M. G.; Rittle, K. E.; DiPardo, R. M.; Whitter, W. L.; Veber, D. F.; Anderson, P. S.; Freidinger, R. M. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 4918.

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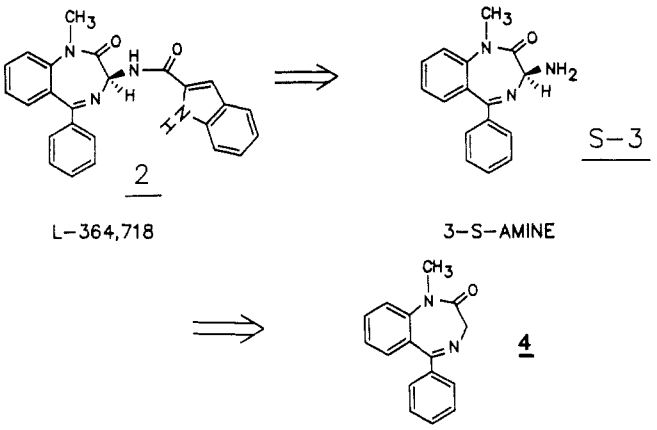
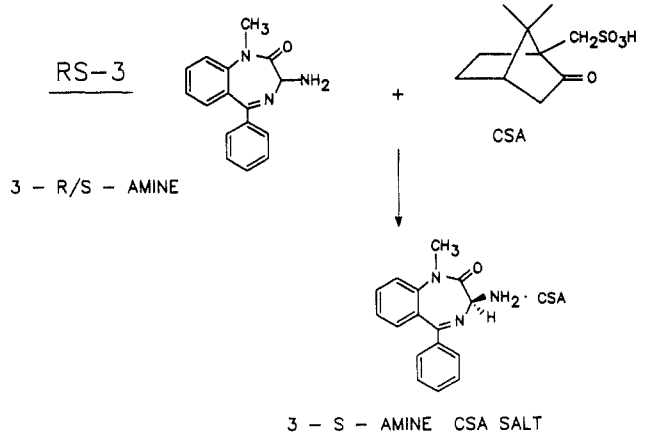
Scheme I

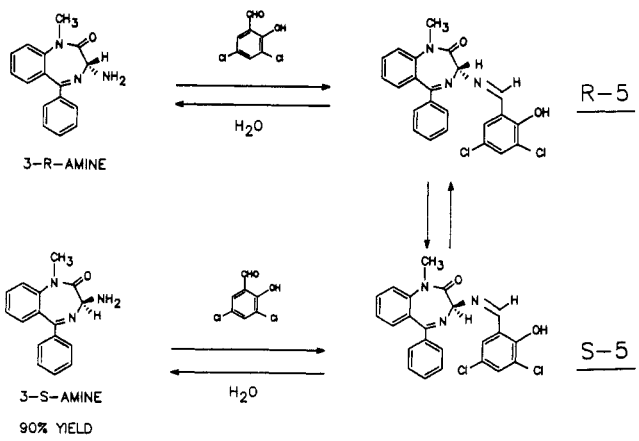


Scheme II. Resolution



Racemic 3-aminobenzodiazepinones can be prepared from the 3-hydroxy compounds[5] or from the readily available[6] *N*-methylbenzodiazepinone **4**.[7] The problem of establishing the "correct" stereochemistry of amine **3** was solved by a classical resolution. The racemic amine [(*RS*)-**3**] was resolved by selectively crystallizing the 3-(*S*)-amine as its (1*S*)-(+)-10-camphorsulfonic acid (CSA) salt. Thus, treatment of a solution of (*RS*)-**3** with 0.5 equiv of CSA and seeding[8] effected resolution in ethyl acetate, isopropyl acetate, or acetonitrile; providing the 3(*S*)-amine–CSA salt with greater than 99.5% enantiomeric purity.[9] Isolated yields were generally 40–42% (80–84% of theory) with the mother liquors containing ca. 90:10 ratio of 3(*R*)/3(*S*)-amine (Scheme II). While resolution via the diastereomeric camphorsulfonate salt provided a route to chiral L-364,718 (**2**), the inherent loss of material was a significant drawback.

Scheme III. Resolution-Racemization



Having observed that the undesired 3(*R*)-amine could be racemized thermally (90 °C) in the presence of camphorsulfonic acid (albeit with concommitant decomposition),[10] we devised a system wherein the acidity of the α proton of **3** would be so enhanced that spontaneous racemization would occur under mild conditions. The result was a catalytic, one-pot process that generated optically pure 3(*S*)-amine (*S*)-**3** in greater than 90% yield.

This "crystallization-induced asymmetric transformation"[11] was achieved by the addition of a catalytic amount (3 mol %) of an aromatic aldehyde (e.g., 3,5-dichlorosalicylaldehyde, salicylaldehyde, benzaldehyde, *p*-nitrobenzaldehyde). As shown in Scheme III an equilibrium concentration of imine **5** is established. The resulting increase in the acidity of the α proton allows the chiral center to racemize at ambient temperature and basicity.[12] In the presence of CSA the crystalline 3(*S*)-amine–CSA salt is essentially removed from the system by virtue of its insolubility, driving the equilibrium. Thus, the 3(*R*)-amine is continuously shunted through the imines (*R*)-**5** to (*S*)-**5** to the desired 3(*S*)-amine.

A typical resolution–racemization is shown in the following experiment: A solution of the racemic amine (*RS*)-**3** (6102 g, 23 mol) in isopropyl acetate (188 L) was treated with 92 mol % of (1*S*)-(+)-10-camphorsulfonic acid (4915 g, 21.16 mol) in acetonitrile (47 liters) while maintaining the temperature at 20–25 °C. The mixture was seeded with 10 g of crystalline 3(*S*)-amine–CSA salt and mixed for 4 h. The resulting white slurry was treated with 3,5-dichlorosalicylaldehyde (132 g, 0.69 mol) and mixed for an additional 12 h. The product was filtered, washed with isopropyl acetate, and vacuum-dried to produce the optically pure 3(*S*)-amine–CSA salt (10 423 g, 91%).

Chiral amine (*S*)-**3** was converted to L-364,718 (**2**) (79% yield, 99.8% optical purity)[13,14] via the acylimidazolide of indole-2-carboxylic acid.[7]

Although the concept of a combined resolution–racemization as a method for the total conversion of a racemate

(4) Chang, R. S. L.; Lotti, V. J. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 4923.

(5) Bell, S. C.; McCaully, R. J.; Childress, S. J. *J. Org. Chem.* **1968**, *33*, 216; *Tetrahedron Lett.* **1965**, 2889; *J. Heterocycl. Chem.* **1967**, *4*, 647; *J. Org. Chem.* **1962**, *27*, 1691.

(6) Sternbach, L. H.; Fryer, R. I.; Metlesics, W.; Reeder, E.; Sach, G.; Saucy, G.; Stempl, A. *J. Org. Chem.* **1962**, *278* 3788. (a) Alternatively, catalytic dechlorination (H_2, Pd/C) of Diazepam cleanly provides **4** in 93% yield.

(7) Methods for introduction of the C-3 amino group are beyond the scope of this paper and will be reported in a full paper along with details of the subsequent acylation.

(8) The original seeds of the 3(*S*)-amine–CSA salt were made from the 3(*S*)-amine. This material was prepared by chromatographic separation of covalent (phenylalanyl) diastereomers. Cf.: Rittle, K. E.; Evans, B. E.; Bock, M. G.; DiPardo, R. M.; Whitter, W. L.; Homnick, C. F.; Veber, D. F.; Freidinger, R. M. Presented at the Amer. Chem. Soc. 20th Middle Atlantic Regional Meeting of the American Chemical Society, Baltimore, MD, Sept. 1986.

(9) Optical purity was determined by chiral HPLC analysis of the corresponding acetamides made by treatment with excess acetic anhydride (25 °C): Pirkle Type IA column (Regis Chemical Co., Morton Grove, IL); eluant, hexane/chloroform/isopropyl alcohol = 70/28/2; flow = 3 mL/min; UV detector, 254 nm; (3*S*)-*N*-acetyl, t_r = 9.1 min; (3*R*)-*N*-acetyl, t_r = 10.9 min.

(10) The ratio of 3*R*/3*S* amines remaining in the resolution mother liquors was readily determined by chiral HPLC as in ref 9.

(11) Jacques, J.; Collet, A.; Wilen, S. H. *Enantiomers, Racemates, and Resolutions*; Wiley: New York, 1981; pp 369–377.

(12) Racemization is presumably effected by the unprotonated primary amine **3**. When 100 mol % of CSA was added, the racemization did not occur at an appreciable rate, the concentration of free amine being too low. Subsequent addition of 5 mol % of free amine **3** reestablished the equilibrium and complete racemization was achieved.

(13) The absolute configuration of L-364,718 (**2**) was confirmed by solution of the single-crystal X-ray diffraction pattern of the 0.5 mol of isopropyl acetate solvate. We are deeply indebted to Jordon Hirshfield and Dr. J. P. Springer for their efforts.

into a single enantiomer has been reported,[11] the practical application to an important and chemically complex intermediate (*RS*)-**3** has rarely been achieved. The simplicity and efficiency of this asymmetric transformation make it the clear method of choice in this case. Although such methods are not currently in vogue, their utility should not be overlooked.

Acknowledgment. We are deeply indebted to T. Truppi, Dr. A. O. King, and Dr. J. M. McNamara for their support. We are also grateful to Drs. Roger Freidinger and Mark G. Bock for many helpful discussions and procedures.

(14) **Physical Data. 2** (L-364,718): $[\alpha]^{25}_D$ -113.7° (*c* 1, CH_3CN); IR (KBr) 3400, 3280, 1695, 1647, 1540, 1510, 1491 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 3.53 (s, 3 H, CH_3N), 5.76 (d, 1 H, *J* = 8 Hz, CHN), 7.1-7.7 (m, 14 H, Ar), 8.07 (d, 1 H, *J* = 8 Hz, NH), 9.4 (s, 1 H, indole NH). Anal. Calcd for $C_{25}H_{20}N_4O_2$: C, 73.51; H, 4.94; N, 13.72. Found: C, 73.22; H, 5.01; N, 13.52. (*RS*)-**3** (free base): mp 110-112 °C; IR (KBr) 3378, 3310, 1675, 1605 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.4 (br, 2 H, NH_2), 3.47 (s, 3 H, CH_3N), 4.47 (s, 1 H, $CHNH_2$), 7.18-7.64 (m, 9 H, Ar). (*RS*)-**3** (benzenesulfonic acid salt): mp 224-227 °C. Anal. Calcd for $C_{22}H_{21}N_3O_4S$: C, 62.40; H, 5.00; N, 9.92; S, 7.57. Found: C, 62.09; H, 4.88; N, 10.07; S, 7.67. (*S*)-**3** (free base): mp 148-149 °C; $[\alpha]^{25}_D$ -269° (*c* 1, CH_3CN). (*S*)-**3** (CSA salt): mp 135-138 °C; $[\alpha]^{25}_D$ -27.8° (*c* 1, H_2O); NMR (CD_3CN, 300 MHz) δ 3.52 (s, 3 H, CH_3N), 5.24 (s, 1 H, $CHNH_3^+$). Anal. Calcd for $C_{26}H_{31}N_3O_5S \cdot 0.75H_2O$: C, 61.09; H, 6.41; N, 8.22; S, 6.27. Found: C, 60.96; H, 6.25; N, 8.59; S, 6.18. (*RS*)-**5**: mp 178-180 °C; NMR ($CDCl_3$, 300 MHz) δ 1.6 (s, 1 H, ArOH), 3.48 (s, 3 H, CH_3N), 5.5 (s, 1 H, CHN=C), 7.23-7.75 (m, 11 H, Ar), 9.24 (s, 1 H, N=CH). Anal. Calcd for $C_{23}H_{17}Cl_2N_3O_2$: C, 63.02; H, 3.91; N, 9.59; Cl, 16.18. Found: C, 63.02; H, 4.19; N, 9.66; Cl, 15.95.

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Metalated Allylaminosilane: A New, Practical Reagent for the Stereoselective α-Hydroxyallylation of Aldehydes to Erythro-1,2-diol Skeletons[1]

Summary: A zinc reagent derived from allyl(diisopropylamino)dimethylsilane reacts with aldehydes regio- and stereoselectively to form *erythro*-3-silyl-1-alken-4-ols, which are further transformed into *erythro*-1-alkene-3,4-diols by hydrogen peroxide oxidation of the carbon-silicon bonds.

Sir: Much effort has been devoted to the stereocontrolled synthesis of erythro and threo[2] 1,2-diols in connection with the total synthesis of a variety of polyoxy natural products. The existing methodologies include (1) dihydroxylation[3] or epoxidation[4] of stereodefined olefins, (2) reduction[5] or alkylation[6] of α-hydroxy carbonyl compounds, and (3) reaction of the carbonyl group with α-hydroxy carbanions or their equivalents.[7] The last method is quite unique and attractive, since the carbon-carbon bond formation and the stereocontrolled generation of two chiral centers on both sides of the substrate and the reagent may be achieved simultaneously. Several types of metalated allyl ethers have been successfully used.[7] Since intramolecular chelation between oxygen and metal in such reagents fixes the *Z* configuration,[7,8] threo isomers are created rather readily with boron or aluminum reagents through six-membered transition states, as exemplified by A.[7a-c] On the other hand, erythro isomers are relatively inaccessible[7c,j] owing to the lack of availability of *E* isomers. A facile route to erythro 1,2-diols would complement existing methodology.

We have recently devised a novel, practical route to erythro isomers. Our method uses the zinc reagent **2** derived from an allylaminosilane **1** as an α-hydroxyallyl anion equivalent, as shown in Scheme I. The absence of intramolecular chelation by nitrogen on silicon has been suggested by formation of (*E*)-$(R_2N)Me_2SiCH{=}CHCH_2SiMe_3$ exclusively upon quenching the metalated species with Me_3SiCl. Thus, our predicted stereochemical outcome through the most favorable cyclic transition state (B)[9] should be erythro. In addition to the complete stereocontrol, the exclusive α-regioselectivity observed with aldehydes is noted, since the zinc reagent **2** reacted with ketones exclusively γ to silicon.[10] The presence of the bulky (*i*-$Pr_2N)Me_2Si$ group in the zinc reagent was essential for our new process: otherwise formation of 1,3-dienes arising from the Peterson olefination predominated under the alkylation conditions.

In a general procedure, allyl(diisopropylamino)dimethylsilane (**1**)[11] was lithiated with *n*-BuLi (a hexane solution, 1 equiv) in the presence of TMEDA (1 equiv) in Et_2O at 0 °C for 4 h. The resulting solution was added to dried $ZnCl_2$ (1 equiv) at 0 °C. After being stirred at 0 °C for 1 h, the white suspension was cooled to -78 °C followed by the dropwise addition of aldehyde (0.7 equiv). The mixture was allowed to warm to 0 °C cover 2 h and stirred for another 2 h.[12] After evaporation of the volatile materials in vacuo, the remaining solids were subjected to oxidative cleavage of the carbon-silicon bond [30% H_2O_2 (20 molar equiv)/KF (2 equiv)/$KHCO_3$ (2 equiv)/MeOH/THF/room temperature/5-15 h][13] and the usual

(1) Silafunctional Compounds in Organic Synthesis. 33. Part 32: Tamao, K.; Akita, M.; Maeda, K.; Kumada, M. *J. Org. Chem.*, in press. Part 31: Tamao, K.; Nakajima, T.; Sumiya, R.; Arai, H.; Higuchi, N.; Ito, Y. *J. Am. Chem. Soc.* **1986**, *108*, 6090.

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(9) Cf.: Reetz, M. T.; Steinbach, R.; Westermann, J.; Peter, R.; Wendroth, B. *Chem. Ber.* **1985**, *118*, 1441.

(10) Trimethylsilyl counterparts: Lau, P. W. K.; Chan, T. H. *Tetrahedron Lett.* **1978**, 2383. Ehlinger, E.; Magnus, P. *J. Am. Chem. Soc.* **1980**, *102*, 5004.

(11) Prepared in two steps from Me_2SiCl_2 by (1) monoamination [*i*-Pr_2NH, 3 equiv, 80 °C; 81% yield; bp 94-96 °C (48 mmHg)] and (2) allylation [$CH_2{=}CHCH_2MgCl$, Et_2O; 85% yield; bp 86-88 °C (18 mmHg)].

(12) It was also possible to isolate the intermediate adduct at this stage as an O-silylated form **3** by treatment with Me_3SiCl (2 equiv) at 0 °C to room temperature overnight. Yields are listed in Table I.

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