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Addition of Indolyl and Pyrrolyl Grignard Reagents to 1-Acylpyridinium Salts

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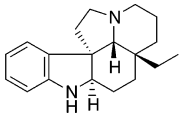
Abstract: Certain indolyl and pyrrolyl Grignard reagents add to 1-acyl salts of 4-methoxy-3-(triisopropylsilyl)pyridine to give the corresponding 1-acyl-2-heteroaryl-2,3-dihydro-4-pyridones in good to high yield. When the 1-acyl group contained a chiral auxiliary, (±)-*trans*-2-(α-cumyl)cyclohexyloxy, addition of the indolyl Grignards resulted in a separable mixture of diastereomeric 2,3-dihydro-4-pyridones.

The indole nucleus in an important feature in a wide variety of structurally diverse and biologically active natural products.[1] Indoles bearing a highly functionalized piperidine ring in either the 2- or 3-position encompass several structural classes of natural products including Aspidosperma, Strychnos, Eburnan, Corynanthean, and Rauwolfia families of alkaloids.[2] In addition, pyrrolidinyl alkaloids such as the biogenetically intriguing smipine also possess a substituted piperidine ring in the 2-position.[3] Methods for the construction of the polycyclic framework found in many of these alkaloids rely on the preparation of synthetic intermediates in enantiomerically pure form.



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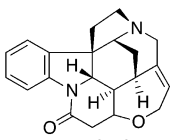

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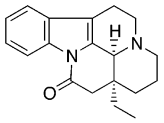
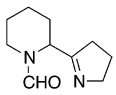


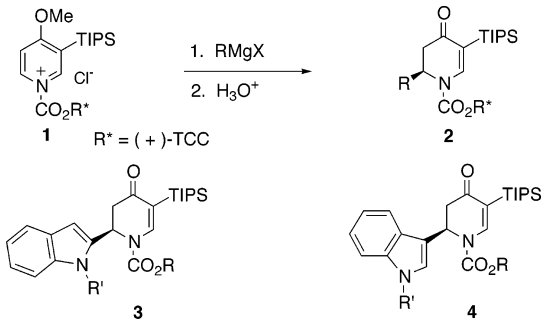
eburnamonine



smipine

The addition of Grignard reagents[4] or certain other organometallics[5] to chiral 1-acylpyridinium salts **1** is a useful synthetic method for the synthesis of 2-substituted 1-acyl-2,3-dihydro-4-pyridones of type **2** (Scheme 1). These compounds have proven to be valuable building blocks for alkaloid synthesis because of their ease of preparation in either enantiomerically pure form, as well as the facility with which ring substituents can be introduced in a regio- and stereocontrolled manner.[6] The potential of heterocycles **3** and **4**, and the corresponding

SCHEME 1



pyrrole derivatives, to serve as intermediates for alkaloid synthesis prompted us to investigate the addition of Grignard reagents derived from substituted indoles and pyrrole to 1-acylpyridinium salt **1**.

Grignard reagents obtained from commercial or readily available alkyl and aryl halides add to **1** in high yield and high diastereoselectivity.[4−6] While oxidative addition of metallic magnesium to alkyl or aryl halides has been widely employed for the preparation of Grignard reagents, the reaction of metallic magnesium with haloindoles and pyrroles fails to bring about Grignard formation.[7] The metalation of *N*-substituted indoles and pyrroles most often involves direct lithiation or lithium−halogen exchange reactions which are typically conducted at low temperature (−78 °C).[8] Few reports on the preparation of Grignard reagents derived from *N*-substituted indoles and pyrroles have appeared in the literature.[7,9]

To verify whether indolyl and pyrrolyl Grignard reagents would add to **1**, we examined the addition of the simple Grignard reagents **6**[10] and **9** (Scheme 2).[11] For example, slow addition of **6** to pyridinium salt **5** at −40 °C, prepared from 4-methoxy-3-(triisopropylsilyl)pyridine and benzyl chloroformate, followed by acid hydrolysis

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(5) Comins, D. L.; Kuethe, J. T.; Hong, H.; Lakner, F. J. *J. Am. Chem. Soc.* **1999**, *121*, 2651 and references therein.

(6) Comins, D. L.; Joseph, S. P. In *Advances in Nitrogen Heterocycles*; Moody, C. J., Ed.; JAI Press: Greenwich, Vol. 2, p 251 and references therein.

(7) Kondo, Y.; Yoshida, A.; Sato, S.; Sakamoto, T. *Heterocycles* **1996**, *42*, 105.

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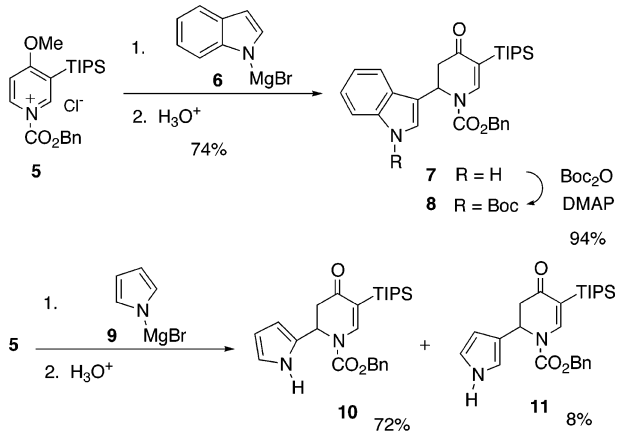
SCHEME 2

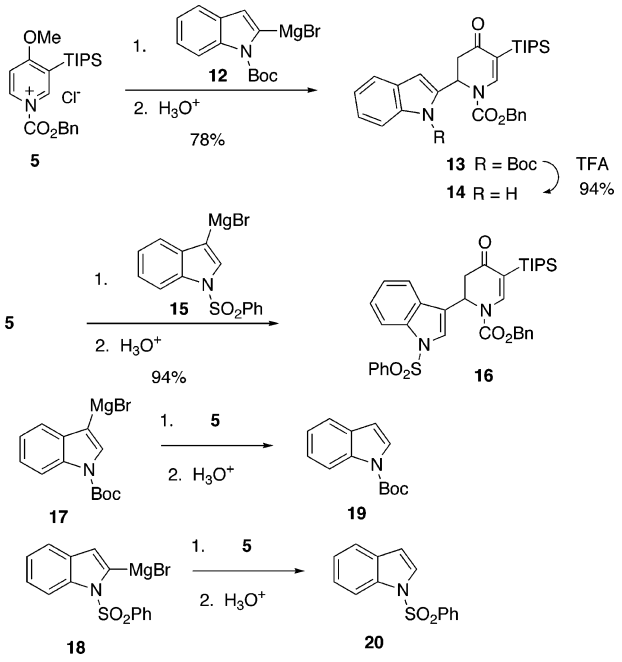


provided dihydropyridone **7** in 74% isolated yield. The use of the preformed Grignard reagent was crucial for the success of the reaction. When indole was added directly to pyridinium salt **5**, no reaction occurred. The indole nitrogen of dihydropyridone **7** was easily protected by reaction with $(Boc)_2O$ and catalytic DMAP to afford **8** in 94% yield. Reaction of **5** with Grignard reagent **9** also proceeded smoothly; however, a mixture of dihydropyridones **10** and **11** was obtained in 72% and 8% yield, respectively. These isomers were easily separated by chromatography on silica gel.

Our attention next turned to the preparation and addition of *N*-substituted indolyl Grignard reagents to **5** (Scheme 3). Reaction of **5** with Grignard reagent **12**, prepared from 1-*tert*-butoxycarbonyl-2-iodoindole[12] by treatment with EtMgBr at rt in THF, gave dihydropyridone **13** in 78% yield after acid hydrolysis. The protecting group could easily be removed by reaction with TFA at rt to afford indole **14** in 94% yield. When pyridinium salt **5** was allowed to react with Grignard reagent **15**,[7] dihydropyridone **16** was obtained in 94% yield. There was no apparent isomerization of the Grignard reagent to the 2-position prior to reaction with **5**.[7,13] Interestingly, the corresponding isomeric Grignard reagents **17** and **18** failed to add to pyridinium salt **5**. The only observed products were the dehalogenated indoles **19** and **20**, respectively, and other unidentified decomposition products.

Having established that certain indolyl Grignard reagents readily add to 1-acylpyridinium salt **5**, the addition of these reagents to pyridinium salt **21** (R* = (±)-*trans*-2-(α-cumyl)cyclohexyl, (±)-TCC)[14] was examined in order to gauge the diastereoselectivity of the process (Scheme 4). Slow addition of **6** to pyridinium salt **21**

SCHEME 3



afforded dihydropyridones **22a** and **22b** in 82% combined yield. Analysis of the crude reaction mixture revealed that the diastereomeric excess (de) was 35%. The individual diastereomers were easily separated by chromatography. Reaction of **21** with Grignard **15** provided a separable mixture of **23a** and **23b** in 62% combined yield (de = 48% by HPLC). The reaction of **21** with **12** furnished **24** in 70% overall yield (de = 50% by HPLC). The diastereomeric mixture **24** proved difficult to separate by chromatography. Treatment of the mixture with TFA in refluxing chloroform removed both the Boc protecting group and the triisopropylsilyl group and gave **25a** and **25b** as a separable mixture of diastereomers in 81% yield. The relative stereochemistry of dihydropyridones **22**−**25** was determined by H^1 NMR.[4a]

In conclusion, we have demonstrated that certain indolyl and pyrrolyl Grignard reagents add to 1-acylpyridinium salts in good to excellent yield. While this work used racemic staring materials, the diastereoselectivity of the reaction lends itself to the preparation of enantiopure intermediates using (+)- or (−)-TCC chloroformate.[14] This approach should be amenable to the synthesis of more complex indole alkaloids possessing a piperidine moiety in either the 2- or 3-position of the indole ring.

Experimental Section

1-[(Benzyloxy)carbonyl]-2-(3-indolyl)-5-(triisopropylsilyl)-2,3-dihydro-4-pyridone (7). To a solution of 86 mg (0.734 mmol) of indole in 10 mL of THF was added dropwise 0.25 mL of a 3 M solution of MeMgBr. The resulting mixture was heated to reflux for 1 h and cooled to rt. The mixture was cannulated into a solution (−40 °C) of pyridinium salt **5** which was formed from 150 mg (0.565 mmol) of 4-methoxy-3-(triisopropylsilyl)-pyridine and 96.4 mg (0.565 mmol) of benzyl chloroformate in toluene at −23 °C for 40 min. After 2 h, 15 mL of aqueous 10% HCl was added, and the mixture was allowed to warm to rt. The mixture was extracted with ethyl acetate. The organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by radial PLC (silica gel,

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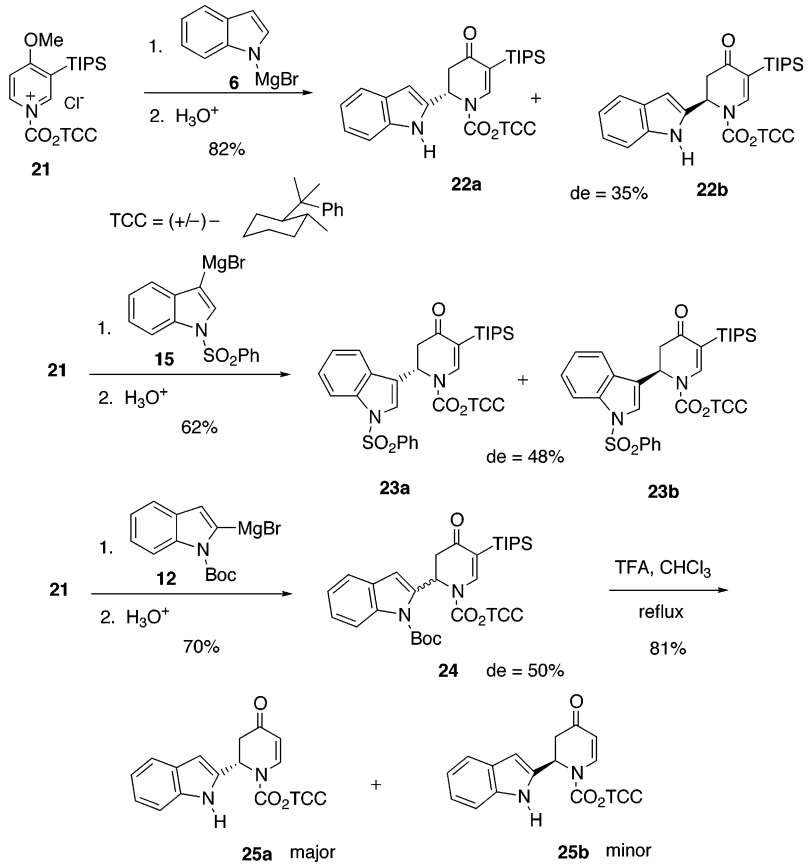
SCHEME 4



EtOAc/hexanes) to give 216 mg (74%) of **7** as a white foam: IR (thin film) 3368, 2939, 2851, 1727, 1650, 1567, 1457, 1391, 1287, 1246, 1116 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.01 (m, 18H), 1.31 (m, 3H), 2.81 (d, 1H, J = 15.7 Hz), 3.14 (dd, 1H, J = 15.7, 7.0 Hz), 5.24 (s, 2H), 6.09 (d, 1H, J = 6.4 Hz), 6.99 (s, 1H), 7.07 (t, 1H, J = 7.4 Hz), 7.18 (t, 1H, J = 7.7 Hz), 7.29 (m, 6H), 7.65 (d, 1H, J = 6.1 Hz), 7.94 (s, 1H), 8.21 (br s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 11.4, 19.0, 42.7, 49.8, 69.1, 111.4, 111.6, 114.3, 119.4, 120.1, 122.2, 122.7, 125.8, 128.3, 128.7, 128.8, 135.3, 136.3, 147.6, 153.0, 197.0. Anal. Calcd for $C_{30}H_{38}N_2O_3Si$: C, 71.67; H, 7.62; N, 5.57. Found: C, 71.71; H, 7.69; N, 5.50.

1-[(Benzyloxy)carbonyl]-2-[(1-tert-butoxycarbonyl)-3-indolyl]-5-(triisopropylsilyl)-2,3-dihydro-4-pyridone (8). To a stirred solution of 65 mg (0.129 mmol) of **7** in 4 mL of CH_2Cl_2 at rt was added 34 mg (0.156 mmol) of di-*tert*-butyl dicarbonate, 29 mg (0.29 mmol) of triethylamine, and 2 mg of DMAP. After being stirred for 1 h, the reaction mixture was diluted with water and extracted with CH_2Cl_2, and the organic extracts were dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue purified by radial PLC (silica gel, EtOAc/hexanes) to give 73 mg (94%) of **8** as a white foam: IR (thin film) 2942, 2867, 1734, 1664, 1588, 1453, 1371, 1251, 1154, 1081 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.04 (m, 18H), 1.32 (m, 3H), 1.60 (s, 9H), 2.79 (d, 1H, J = 15.6 Hz), 3.13 (dd, 1H, J = 15.6, 7.1 Hz), 5.24 (s, 2H), 6.01 (d, 1H, J = 6.3 Hz), 7.29 (m, 8H), 7.54 (m, 1H), 8.02 (s, 1H), 8.17 (d, 1H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 11.4, 19.1, 28.3, 41.9, 49.7, 69.2, 84.1, 112.0, 115.7, 118.2, 119.0, 122.9, 123.0, 125.1, 128.2, 128.7, 128.8, 135.2, 136.0, 142.3, 147.4, 149.4, 152.8, 195.7; HRMS calcd for $C_{35}H_{46}N_2O_5Si$ 603.3254 $[M + H]^+$, found 603.3277 $[M + H]^+$.

1-[(Benzyloxy)carbonyl]-2-(2-pyrrolyl)-5-(triisopropylsilyl)-2,3-dihydro-4-pyridone (10) and 1-[(Benzyloxy)carbonyl]-2-(3-pyrrolyl)-5-(triisopropylsilyl)-2,3-dihydro-4-pyridone (11). To a solution of 63.1 mg (0.94 mmol) of pyrrole in 10 mL of THF was added dropwise 0.28 mL of a 3 M solution of MeMgBr. The resulting mixture was heated to reflux for 1 h and then cooled to rt. The resulting solution was cannulated into a solution (−40 °C) of pyridinium salt **5** which was formed from 123 mg (0.462 mmol) of 4-methoxy-3-(triisopropylsilyl)pyridine and 79.0 mg (0.462 mmol) of benzyl chloroformate in toluene at −23 °C for 40 min. After 2 h, 15 mL of aqueous 10% HCl was added, and the mixture was allowed to warm to rt. The mixture was extracted with ethyl acetate. The organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure, and the residue was purified by radial PLC (silica gel, EtOAc/hexanes). The first product to elute (151 mg, 72%) was identified as **10**: white solid; mp 132−133 °C; IR (thin film) 3437, 2943, 1713, 1655, 1566, 1326, 1255 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.98 (d, 9H, J = 7.4 Hz), 1.04 (d, 9H, J = 7.4 Hz), 1.27 (m, 3H), 2.86 (d, 1H, J = 15.9 Hz), 3.02 (dd, 1H, J = 15.9, 7.2 Hz), 5.27 (d, 1H, J = 12.1 Hz), 5.40 (d, 1H, J = 12.1 Hz), 5.70 (d, 1H, J = 6.9 Hz), 6.07 (m, 2H), 6.67 (m, 1H), 7.41 (m, 5H), 7.66 (s, 1H), 8.76 (br s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 11.3, 18.9, 40.2, 50.1, 69.4, 108.2, 111.6, 118.4, 128.3, 128.5, 128.6, 128.7, 129.0, 135.0, 145.4, 156.9, 196.2. Anal. Calcd for $C_{26}H_{36}N_2O_3Si$: C, 68.99; H, 8.02; N, 6.19. Found: C, 68.81; H, 8.13; N, 6.10.

The second product to elute (17 mg, 8%) was identified as **11**: clear oil; IR (neat) 3307, 2942, 1707, 1660, 1522, 1302 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.96 (d, 9H, J = 7.2 Hz), 1.01 (d, 9H, J = 7.2 Hz), 1.26 (m, 3H), 2.82 (d, 1H, J = 16.0 Hz), 3.04 (dd, 1H, J = 16.0, 7.3 Hz), 5.28 (m, 3H), 5.68 (d, 1H, J = 6.4 Hz), 6.09 (s, 1H), 6.79 (s, 1H), 7.37 (m, 5H), 7.67 (s, 1H), 9.40 (br s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 11.3, 18.9, 39.9, 49.9, 69.8, 109.9, 115.5, 123.2, 128.4, 128.5, 128.7, 129.0, 134.2, 134.8, 136.3, 160.8, 195.6. HRMS calcd for $C_{26}H_{36}N_2O_3Si$ 453.2573 $[M + H]^+$, found 453.2568 $[M + H]^+$.

1-[(Benzyloxy)carbonyl]-2-[(1-*tert*-butoxycarbonyl)-2-indolyl]-5-(triisopropylsilyl)-2,3-dihydro-4-pyridone (13). To a solution of 250 mg (0.729 mmol) of 1-*tert*-butoxycarbonyl-2-iodoindole[12] in 15 mL of THF was added dropwise 0.25 mL of a 3 M solution of MeMgBr. The resulting mixture was stirred for 1 h at rt. The mixture was cannulated into a solution (−40 °C)

of pyridinium salt **5** which was formed from 150 mg (0.565 mmol) of 4-methoxy-3-(triisopropylsilyl)pyridine and 96.4 mg (0.565 mmol) of benzyl chloroformate in toluene at −23 °C for 40 min. After 2 h, 15 mL of aqueous 10% HCl was added, and the mixture was allowed to warm to rt. The mixture was extracted with ethyl acetate. The organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by radial PLC (silica gel, EtOAc/hexanes) to give 266 mg (78%) of **13** as a colorless solid: mp 116−117 °C; IR (thin film) 2936, 1728, 1661, 1578, 1453, 1327, 1298, 1240 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.05 (m, 18H), 1.31 (m, 3H), 1.64 (s, 9H), 2.87 (d, 1H, J = 16.0 Hz), 3.13 (dd, 1H, J = 16.0, 7.7 Hz), 5.21 (m, 2H), 6.36 (s, 1H), 6.54 (d, 1H, J = 7.2 Hz), 7.25 (m, 8H), 8.04 (d, 1H, J = 8.2 Hz), 8.17 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 11.4, 18.9, 19.1, 28.3, 41.8, 52.0, 69.2, 85.0, 107.7, 112.2, 116.1, 120.6, 123.3, 124.5, 127.9, 128.7, 128.8, 135.2, 137.1, 138.0, 148.1, 150.3, 195.7. Anal. Calcd for $C_{35}H_{46}N_2O_5Si$: C, 69.73; H, 7.69; N, 4.65. Found: C, 69.85; H, 7.75; N, 4.56.

1-[(Benzyloxy)carbonyl]-2-(3-indolyl)-5-(triisopropylsilyl)-2,3-dihydro-4-pyridone (14). To a stirred solution of 40 mg (0.066 mmol) of **13** in 15 mL of CH_2Cl_2 was added 61 mg (0.531 mmol) of TFA. The resulting mixture was stirred for 3 h at rt, quenched with saturated $NaHCO_3$, and extracted with CH_2Cl_2. The combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by radial PLC (silica gel, EtOAc/hexanes) to afford 31 mg (94%) of **14** as a white foam: IR (neat) 3392, 2940, 2868, 1720, 1664, 1571, 1453, 1387, 1335, 1305, 1253 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.97 (d, 9H, J = 7.5 Hz), 1.03 (d, 9H, J = 7.5 Hz), 1.27 (m, 3H), 2.90 (d, 1H, J = 16.1 Hz), 3.11 (dd, 1H, J = 16.1, 7.2 Hz), 5.29 (d, 1H, J = 11.7 Hz), 5.46 (d, 1H, J = 11.7 Hz), 6.39 (s, 2H), 7.07 (t, 1H, J = 7.7 Hz), 7.17 (t, 1H, J = 7.5 Hz), 7.42 (m, 6H), 7.52 (d, 1H, J = 7.7 Hz), 7.70 (s, 1H), 8.67 (br s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 11.3, 18.9, 40.1, 50.4, 69.7, 102.7, 111.0, 112.1, 120.2, 121.1, 122.9, 127.6, 128.4, 128.8, 129.1, 135.0, 135.3, 136.1, 145.6, 154.0, 196.0; HRMS calcd for $C_{30}H_{38}N_2O_3Si$ 503.2730 $[M + H]^+$, found 503.2730 $[M + H]^+$.

1-[(Benzyloxy)carbonyl]-2-[1-(phenylsulfonyl)-3-indolyl]-5-(triisopropylsilyl)-2,3-dihydro-4-pyridone (16). To a solution of 390 mg (0.734 mmol) of 3-iodo-1-phenylsulfonylindole[7] in 20 mL of THF was added dropwise 1.00 mL of a 1 M solution of EtMgBr. The resulting mixture was stirred for 1 h at rt. The mixture was cannulated into a solution (−40 °C) of pyridinium salt **5**, which was formed from 135 mg (0.509 mmol) of 4-methoxy-3-(triisopropylsilyl)pyridine and 87.0 mg (0.509 mmol) of benzyl chloroformate in toluene at −23 °C for 40 min. After 2 h, 20 mL of aqueous 10% HCl was added, and the mixture was allowed to warm to rt. The mixture was extracted with ethyl acetate. The organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by radial PLC (silica gel, EtOAc/hexanes) to give 309 mg (94%) of **16** as a white solid: mp 136−137 °C; IR (thin film) 2944, 2860, 1725, 1664, 1572, 1447, 1378, 1280, 1241, 1175, 1119, 1019 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.06 (m, 18H), 1.32 (m, 3H), 2.72 (d, 1H, J = 15.4 Hz), 3.14 (dd, 1H, J = 15.4, 7.2 Hz), 5.22 (s, 2H), 5.96 (d, 1H, J = 5.9 Hz), 7.19−7.51 (m, 12H), 7.79 (d, 2H, J = 7.7 Hz), 7.92 (d, 1H, J = 8.2 Hz), 8.04 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 11.3, 19.0, 41.7, 49.5, 69.3, 111.9, 113.9, 119.7, 120.5, 123.1, 123.6, 125.4, 126.9, 128.2, 128.6, 128.8, 129.5, 134.1, 135.0, 135.2, 138.3, 147.5, 152.6, 195.3. Anal. Calcd for $C_{36}H_{42}N_2O_5SSi$: C, 67.26; H, 6.59; N, 4.36. Found: C, 67.37; H, 6.68; N, 4.33.

(2*S- and 2*R**)-2-(3-Indolyl)-1-[((1*R**,2*S**)-2-(1-methyl-1-phenylethyl)cyclohexyloxy)carbonyl]-5-(triisopropylsilyl)-2,3-dihydro-4-pyridones (22).** To a solution of 200 mg (1.71 mmol) of indole in 25 mL of THF was added dropwise 0.57 mL of a 3 M solution of MeMgBr. The resulting mixture was heated to reflux for 1 h and cooled to rt. The resulting mixture was cannulated into a solution (−78 °C) of pyridinium salt **21** which was formed from 150 mg (0.565 mmol) of 4-methoxy-3-(triisopropylsilyl)pyridine and 0.57 mL of a 1 M solution of (1*R**,2*S**)-2-(α-cumyl)cyclohexyl chloroformate in toluene at −23 °C for 40 min. After 2 h, 35 mL of aqueous 10% HCl was added, and the mixture was allowed to warm to rt. The mixture was extracted with ethyl acetate. The organic extracts were dried over $MgSO_4$, concentrated under reduced pressure, and the residue was purified by radial PLC (silica gel, EtOAc/hexanes). The first product to elute (173 mg, 50%) was identified as the major diastereomer **22a**: white solid; mp 162−163 °C; IR (thin film) 3359, 2931, 1712, 1648, 1568, 1322, 1290, 1242 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.80−1.61 (m, 34H), 1.97 (m, 2H), 2.42 (m, 1H), 2.72 (m, 1H), 4.19 (m, 1H), 4.78 (m, 1H), 6.71 (s, 1H), 7.18 (m, 4H), 7.39 (m, 5H), 7.96 (s, 1H), 8.06 (br s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 11.4, 19.1, 21.5, 24.7, 25.9, 26.9, 31.1, 32.7, 39.7, 42.7, 48.9, 51.1, 78.3, 110.4, 111.4, 114.7, 119.2, 119.7, 120.8, 122.4, 125.3, 125.5, 128.4, 136.3, 148.3, 153.0, 153.1, 196.8. Anal. Calcd for $C_{38}H_{52}N_2O_3Si$: C, 74.47; H, 8.55; N, 4.57. Found: C, 74.41; H, 8.60; N, 4.62.

The second product to elute (112 mg, 32%) was identified as the minor diastereomer **22b**: white solid; mp 173−174 °C; IR (thin film) 3359, 2942, 1717, 1653, 1568, 1322, 1285, 1253 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.46 (m, 37H), 2.78 (d, 1H, J = 15.6 Hz), 3.07 (dd, 1H, J = 15.6, 6.7 Hz), 4.94 (m, 1H), 5.96 (d, 1H, J = 6.4 Hz), 6.91 (s, 1H), 7.20 (m, 7H), 7.60 (m, 1H), 7.74 (d, 1H, J = 7.5 Hz), 8.07 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 11.5, 19.2, 24.7, 25.7, 26.9, 27.3, 34.1, 40.3, 42.7, 49.7, 51.6, 78.3, 110.6, 111.4, 114.4, 119.5, 120.1, 122.1, 122.6, 125.5, 125.7, 125.9, 128.2, 136.4, 147.6, 150.7, 151.9, 197.0. Anal. Calcd for $C_{38}H_{52}N_2O_3Si$: C, 74.47; H, 8.55; N, 4.57. Found: C, 74.30; H, 8.59; N, 4.48.

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Supporting Information Available: Experimental procedure for compounds **23**−**25** and copies of ^1H and ^{13}C NMR spectra for **8**, **11**, **14**, and **23b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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