Samarium Diiodide Induced Reductive Coupling of D-Threose- and D-Erythrose-Derived Nitrones with Methyl Acrylate

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Abstract: An application of the samarium diiodide promoted coupling between nitrones and methyl acrylate using nitrones derived from D-erythrose and D-threose is described. The reaction course of coupling is dependent on the structure of the starting chiral nitrone. The results show that the method has potential use in the preparation γ-*N*-hydroxylamino esters, pyrrolidinones, and pyrrolidines containing carbohydrate residues.

Key words: samarium, *C*-glycosyl nitrones, amino acids, pyrrolidinones, stereoselective synthesis

Over the years, nitrones have become important building blocks in organic synthesis.[1] During the last years we have learned about the preparation of optically active nitrone templates for the asymmetric 1,3-dipolar cycloadditions.[2,3] Py, Vallée, and co-workers[4a,b] have recently described the first samarium diiodide induced umpolung of nitrones, which were able to undergo reductive coupling with α,β-unsaturated esters. D-Glyceraldehyde-derived nitrone **1** reacted with methyl acrylate in the presence of two equivalents SmI_2 in THF at –78 °C with the formation of γ-*N*-hydroxylamino esters **2** in fairly good yields, with a 85:15 diastereomeric ratio (Scheme 1). When chiral nitrones were used as substrates, significant diastereoselectivities were observed in these reactions.[4,5] This methodology provides a general route to γ-*N*-hydroxylamino esters.[4,5] The derivatives of γ-amino buryric acid (GABA) could be potential, selective, and irreversible inhibitors of GABA amino transferase, the enzyme involved in the catabolism of GABA.[6]

As in principle γ-lactams should be easily obtained from the corresponding γ-*N*-hydroxylamino esters we have paid attention to the synthesis of biologically important γ-amino acids from the sugar-derived nitrones previously used by us in the chiral cycloadditions. In our first paper we reported that the reaction course of samarium diiodide induced reductive coupling of chiral nitrones with methyl acrylate is dependent on the structure of the starting chiral nitrone.[7] D-Lyxose-derived nitrone **3** was found effectively to undergo an SmI_2-mediated radical addition to methyl acrylate affording γ-*N*-hydroxylamino ester **4** with high diastereomeric control. On the other hand, D-xylose-derived nitrone **5** in the SmI_2-induced coupling with methyl acrylate afforded the γ-*N*-hydroxylamino ester **6** as the minor product. The major product, nitrone **7**, is formed by unusual reductive deoxygenation of the starting nitrone (Scheme 1).[7] In this communication we wish to describe the SmI_2-induced coupling of readily available chiral sugar D-threose- and D-erythrose-derived nitrones **8**, **9** and **10**, **11** to methyl acrylate with the subsequent conversion of the formed γ-*N*-hydroxylamino esters into γ-lactams.

D-*threo*-Nitrone **8** reacted smoothly with methyl acrylate in THF in the presence of three equivalents of samarium diiodide and eight equivalents of H_2O at –78 °C over two hours to give γ-*N*-hydroxylamino ester **12** in 72% yield along with unreacted **8** (14%, Scheme 2).[8] The addition proceeded with excellent diastereoselectivity (>95:5), with only the *anti* diastereomer **12** being detected. The relative configuration at the new stereogenic center in **12** could not be assigned at this stage; however, it was deduced from the structure of cyclized derivative **13**, prepared by desilylation of pyrrolidinone **16**, whose structure was established by X-ray diffraction studies (Scheme 2).[9,10]

On the other hand, the addition of TBDMS-substituted D-*threo*-nitrone **9** with methyl acrylate under the same conditions proceeded less diastereoselectively and gave two diastereomers **14** and **15** in a 88:12 ratio and 68% yield with *anti*-**14** being predominant (Scheme 3). The ratio of diastereoisomeric esters was determined from quantitative ^{13}C NMR spectra, by interpretation of the peaks from CO_2CH_3 of the esters; purification by flash chromatography provided pure **14**. The relationship between the stereogenic centers was confirmed by conversion of major isomer **14** into pyrrolidinone **16**, whose structure was established unambiguously by X-ray diffraction studies (Figure 1).[9] This allowed us to propose the structures shown in Scheme 3 for diastereomeric esters **14** and **15**. The formation of major *anti* isomers **12** and **15** is consistent with β-chelation transition state suggested by Py and Skrydstrup.[4,5]

In contrast, when D-erythrose-derived nitrone **10** was treated with three equivalents of SmI_2 and eight equivalents of H_2O in THF at –78 °C over two hours with methyl acrylate, the expected γ-*N*-hydroxylamino ester **19** was obtained in low 35% yield along with dimethyl adipate

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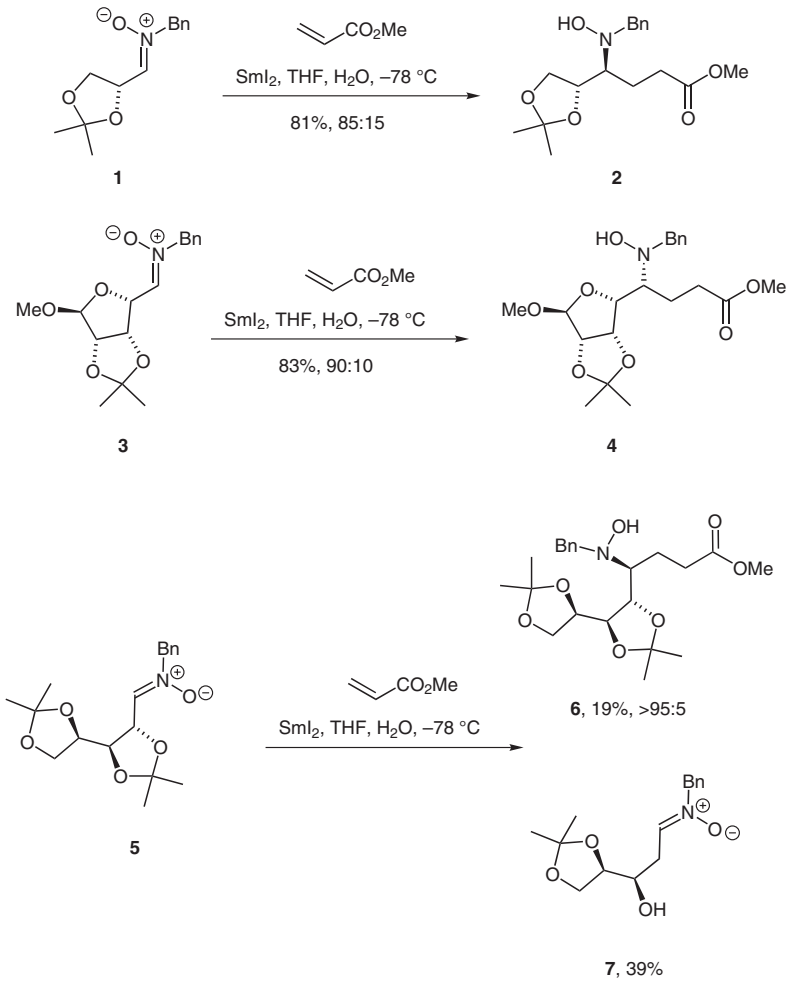
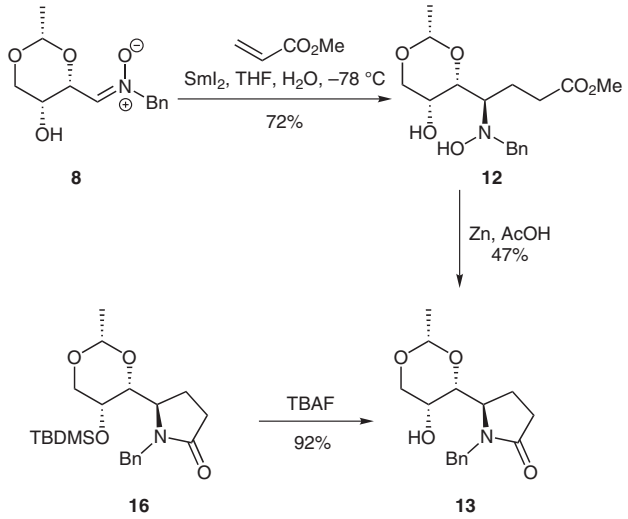


Scheme 1 Samarium diiodide promoted coupling between sugar-derived nitrones and methyl acrylate



Scheme 2 Samarium diiodide promoted coupling between D-*threo*-nitrone **8** and methyl acrylate

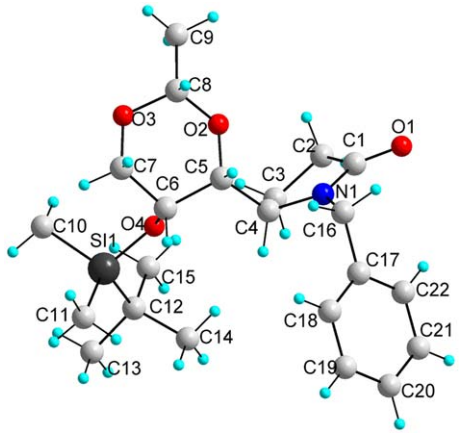
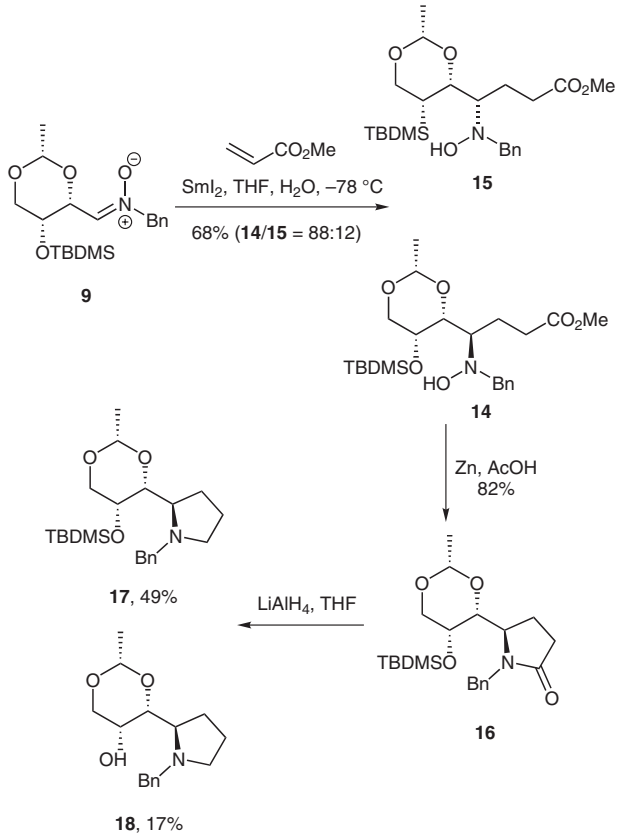


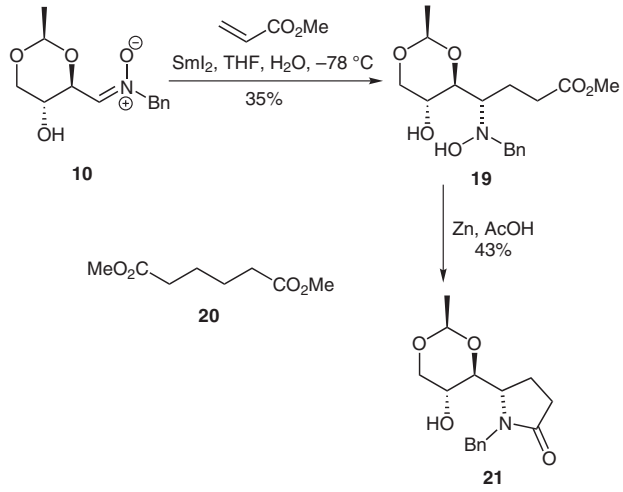
Figure 1 The molecular structure of **16**, with the numbering scheme[11] of the asymmetric unit; displacement ellipsoids are drawn at the 30% probability level

(25%) and substantial amounts of unreacted **10** (34%, Scheme 4). On the other hand, the reaction is completely diastereoselective (>95:5) within the limits of NMR analysis of the crude product.

The TBDMS-substituted D-*erythro*-nitrone **11** showed by samarium diiodide reductive coupling with methyl acrylate different behavior (Scheme 5). Treatment of nitrone **11** with three equivalents of SmI_2 and eight equivalents of H_2O in THF at –78 °C over two hours with methyl acrylate led to the expected γ-*N*-hydroxylamino ester **22** as the



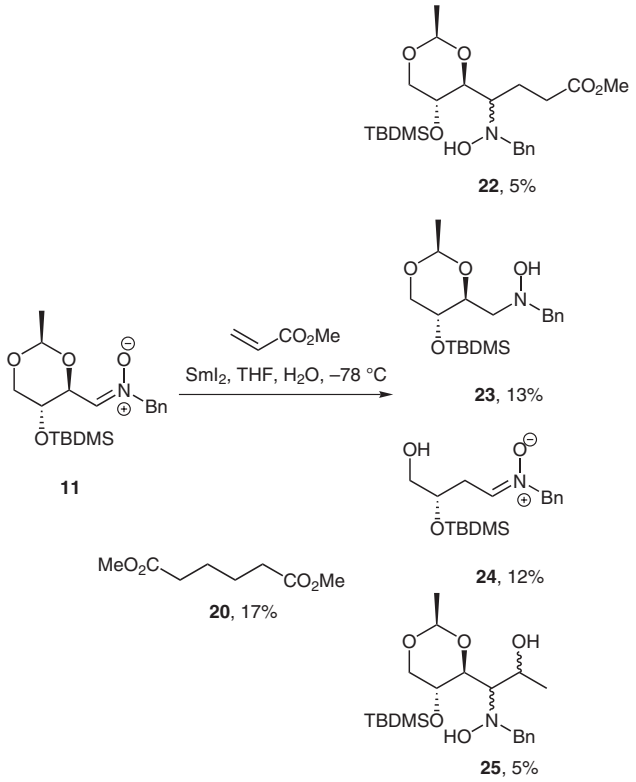
Scheme 3 Samarium diiodide promoted coupling betweenTBDMS-substituted D-*threo*-nitrone **9** and methyl acrylate



Scheme 4 Samarium diiodide promoted coupling between D-*erythro*-nitrone **10** and methyl acrylate

minor product in very low yield (5%) along with two *N*-hydroxylamino derivatives **23** (13%) and **25** (5%), nitrone **24** (12%), and dimethyl adipate (17%, Scheme 5). Purification by flash chromatography allowed the isolation of all reaction products; their structure is supported by NMR analysis. The compounds **23** and **24** are the products of the overreduction of the starting nitrone **11** that undergoes deoxygenation and reduction, respectively, instead of coupling. This was proved by the reaction of the nitrone **11** under the same conditions in the absence of methyl acrylate where **23** and **24** were formed in 8% and 49% yield, respectively.

This kind of reductive cleavage of the starting α-alkoxy-substituted nitrone **11**, producing nitrone **24** by SmI_2-induced reduction, was previously observed in the formation of nitrone **7** from nitrone **5** (Scheme 1).[7] The origin of the further unexpected β-*N*-hydroxylamino alcohol **25** can be explained by the coupling of the starting nitrone **11** with in situ formed acetaldehyde by aforementioned deoxygenation of nitrone **11**. The formation of dimer **20** suggests that the C–C bond-forming reaction between D-*erythro*-nitrone **11** and methyl acrylate is comparable with the radical dimerization–addition step involving the acrylate. The formation of the corresponding dimers in 70% yield has been described by Skrydstrup by the treatment of alkyl acrylates with SmI_2 (3 equiv) and H_2O (8 equiv) in THF at –78 °C in the absence of the alkylating reagent.[11] However, in the presence of the alkylating reagent only traces of the dimers of alkyl acrylates were obtained.



Scheme 5 Samarium diiodide promoted coupling between TBDMS-substituted D-*erythro*-nitrone **11** and methyl acrylate

As has been mentioned in our previous communication, we have found that the reaction course of samarium diiodide induced reductive coupling of chiral nitrones with methyl acrylate is dependent on the structure of the starting chiral nitrone.[7] The results obtained using diastereomeric D-*threo*-nitrones **8**, **9** and D-*erythro*-nitrones **10**, **11** support this observation. In both cases the coupling of the nitrones **5**, **10**, and **11** possessing a C2/C3 *erythro* config-

uration with methyl acrylate proceeded slower and therefore the products resulting from overreduction, deoxygenation, and radical dimerization–addition step involving the acrylate are formed.

Considering the well-known propensity of *N*-hydroxylamines to be reduced to amines, we have prepared pyrrolidinones **13**, **16**, and **21** in a single step from the γ-*N*-hydroxylamino esters involving N–O cleavage with Zn/AcOH and subsequent spontaneous cyclization from moderate to good yields. The newly created stereogenic center in **16** was assigned the *R*-configuration on the basis of a single-crystal X-ray structure of the pyrrolidinone **16** (Figure 1). Finally, the pyrrolidinone **16** was reduced with $LiAlH_4$ in THF to afford the pyrrolidines **17** and **18** in moderate yield (Scheme 3).

In conclusion, an application of the samarium diiodide promoted coupling between nitrones and methyl acrylate using nitrones derived from D-erythrose and D-threose is described. The reaction course of coupling is dependent on the structure of the starting chiral nitrone. The results show that the method has potential use in the preparation γ-*N*-hydroxylamino esters, pyrrolidinones, and pyrrolidines containing carbohydrate residues.

Acknowledgment

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(8) **Typical Experimental Procedure for Samarium Diiodide Mediated Coupling**
A stirred and carefully deoxygenated solution of the corresponding nitrone (0.5 mmol) in dry THF (5 mL) was cooled to –78 °C under argon. Methyl acrylate and H_2O were degassed by boiling under a stream of argon for 20 min. Methyl acrylate (0.7 mmol), H_2O (4 mmol), and a solution of SmI_2 (15 mL of 0.1 M in THF, 1.5 mmol) were then added. The temperature was kept at –78 °C until the reaction was judged to be complete by TLC (2 h), whereupon a sat. aq solution of $Na_2S_2O_3$ (40 mL) was added. The mixture was extracted with EtOAc (4 × 30 mL) and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated in a rotatory evaporator. The residue was purified by silica gel column chromatography using EtOAc–hexanes (1:2).

(9) **Crystal Data**
$C_{22}H_{35}NO_4Si$, M = 405.60, orthorhombic, $P2_12_12_1$, a = 7.800(2) Å, 13.749(3) Å, 22.468(5) Å, V = 2409.5(9) Å^3, Z = 4, D_x = 1.118 Mg m^{-3}, μ (Mo-Kα) = 0.1220 mm^{-1}, F(000) = 880, colorless block, 0.305 × 0.492 × 0.739 mm^{-3}, 42540 diffractions measured (R_{int} = 0.021), 4901 unique, $wR2$ = 0.0951, conventional R = 0.044 on I values of 4507 diffractions with $I > 2.0\ \sigma(I)$, $(\Delta/\sigma)_{max}$ = 0.001, S = 1.160 for all data and 254 parameters. Unit cell determination and intensity data collection (θ_{max} = 26.40°) were performed on a Gemini R diffractometer[12] at 100 (1) K. Structure solution was direct methods[13] and refinements were achieved by full-matrix least-squares method[13] on F**2. Further details of the crystal structure investigation can be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (CCDC deposition 677669).
Representative Data for Products
Compound **12**: $[\alpha]_D^{25}$ –19.3 (*c* 0.28, $CHCl_3$); mp 59–61 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.46 (d, 3 H, J = 5.0 Hz, $CHCH_3$), 2.01–2.3 (m, 2 H, H-3), 2.51–2.71 (m, 2 H, H-2), 3.17 (dt, J = 6.1, 7.9 Hz, 1 H, H-4), 3.71 (s, 3 H, CO_2CH_3), 3.76 (s, 1 H, H-5′), 4.03 (d, J = 7.9 Hz, 1 H, H-4′), 4.07 (d, J = 13.1 Hz, 1 H, H-6′A), 4.14 (d, J = 13.1 Hz, 1 H, H-6′B), 3.80–4.20 (br s, 2 H, NOH, OH), 3.96–4.20 (dd, J = 12.2 Hz,

2 H, NCH_2Ph), 4.85 (q, *J* = 5.0 Hz, 1 H, H-2′), 7.36–7.51 (m, 5 H, NCH$_2$*Ph*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.9 (q, CH*C*H$_3$), 22.0 (t, C-3), 32.2 (t, C-2), 51.6 (q, CO_2CH_3), 61.3 (t, C-6′), 64.1 (d, C-5′), 64.5 (d, C-4), 71.8 (t, N*C*H$_2$Ph), 79.8 (d, C-4′), 99.7 (d, C-2′), 127.2, 128.3, 129.0, 138.3 (3 d, s, NCH$_2$*Ph*), 175.1 (s, C-1) ppm. IR (KBr): ν = 3502, 3471, 3032, 3000, 2965, 2923, 2868, 2845, 1710 cm^{-1}. Anal. Calcd for $C_{17}H_{25}NO_6$ (339.3): C, 60.16; H, 7.42; N, 4.13. Found: C, 59.87; H, 7.41; N, 3.92.

Compound **13**: $[\alpha]_D^{25}$ –19.8 (*c* 0.40, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.29 (d, *J* = 5.2 Hz, 3 H, CHCH_3), 1.96–2.38 (m, 2 H, H-4), 2.24–2.63 (m, 2 H, H-3), 3.15–3.20 (br s, 1 H, OH), 3.42 (s, 1 H, H-5′), 3.59–3.67 (m, 2 H, H-5, H-4′), 3.74 (d, *J* = 12.0 Hz, 1 H, H-6′A), 3.98 (d, *J* = 12.0 Hz, 1 H, H-6′B), 4.49 (q, *J* = 5.2 Hz, 1 H, H-2′), 4.24–4.85 (d, d, *J* = 14.0 Hz, 2 H, NCH_2Ph), 7.23–7.32 (m, 5 H, NCH$_2$*Ph*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7 (q, CH*C*H$_3$), 21.2 (t, C-4), 29.9 (t, C-3), 45.1 (t, N*C*H$_2$Ph), 58.7 (d, C-5), 64.4 (d, C-5′), 72.1 (t, C-6′), 77.4 (d, C-4′), 99.5 (d, C-2′) 127.3, 127.8, 128.3, 136.9 (3 d, s, CH$_2$*Ph*), 176.2 (s, C-2) ppm. IR (KBr): 3430, 3030, 2991, 2967, 2939, 2864, 1675 cm^{-1}. Anal. Calcd for $C_{16}H_{21}NO_4$ (291.3): C, 65.96; H, 7.27; N, 4.81. Found: C, 65.63; H, 7.22; N, 4.79.

Compound **16**: $[\alpha]_D^{25}$ +9.4 (*c* 0.5, $CHCl_3$); mp 93–95 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = –0.03, 0.03 [2 s, 6 H, Si(CH_3)$_2$C(CH$_3$)$_3$], 0.88 [s, 9 H, Si(CH$_3$)$_2$C(CH_3)$_3$], 1.28 (d, *J* = 5.0 Hz, 3 H, CHCH_3), 1.87–2.05 (m, 1 H, H-4A), 2.25–2.38 (m, 1 H, H-3A), 2.53–2.74 (m, 2 H, H-3B, H-4B), 3.36 (d, *J* = 1.9 Hz, 1 H, H-5′), 3.49 (d, *J* = 8.9 Hz, 1 H, H-5), 3.61–3.66 (m, 1 H, H-6′A), 3.65 (s, 1 H, H-4′), 3.91–3.85 (dd, *J* = 1.0, 12.1 Hz, 1 H, H-6′B), 4.35 (q, *J* = 5.0 Hz, 1 H, H-2′), 4.34–4.71 (d, d, *J* = 15.3 Hz, 2 H, NCH_2Ph), 7.19–7.35 (m, 5 H, NCH$_2$*Ph*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –4.7, –4.6 [2 q, Si(*C*H$_3$)$_2$C(CH$_3$)$_3$], 17.9 [s, Si(CH$_3$)$_2$*C*(CH$_3$)$_3$], 20.4 (t, C-4), 20.8 (q, CH*C*H$_3$), 25.7 [q, Si(CH$_3$)$_2$C(*C*H$_3$)$_3$], 30.9 (t, C-3), 44.9 (t, N*C*H$_2$Ph), 61.3 (d, C-5), 66.4 (d, C-5′), 72.1 (t, C-6′), 76.6 (d, C-4′), 98.8 (d, C-2′), 127.3, 127.4, 128.5, 136.8 (3 d, s, NCH$_2$*Ph*), 176.5 (s, C-2) ppm. IR (KBr): 3031, 2952, 2930, 2887, 2857, 1683 cm^{-1}. Anal. Calcd for $C_{22}H_{35}NO_4Si$ (437.6): C, 65.15; H, 8.70; N, 3.45. Found: C, 65.34; H, 8.78; N, 3.25.

Compound **17**: $[\alpha]_D^{25}$ +31.7 (*c* 0.45, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.04, 0.12 [2 s, 6 H, Si(CH_3)$_2$C(CH$_3$)$_3$], 0.92 [s, 9 H, Si(CH$_3$)$_2$C(CH_3)$_3$], 1.35 (d, *J* = 5.0 Hz, 3 H, CHCH_3), 1.64–1.75 (m, 2 H, H-3), 1.79–1.90 (1 H, m, H-4A), 2.00–2.10 (m, 1 H, H-4B), 2.23–2.33 (m, 1 H, H-2A), 2.84–2.92 (1 H, m, H-2B), 2.96–3.04 (1 H, m, H-5), 3.28 (d, *J* = 7.3 Hz, 1 H, H-4′), 3.54 (d, *J* = 13.1 Hz, 1 H, NCH_2PhA), 3.72 (d, *J* = 11.9 Hz, 1 H, H-6′A), 3.79 (1 H, s, H-5′), 4.04 (d, *J* = 11.9 Hz, 1 H, H-6′B), 4.13 (d, *J* = 13.1 Hz, 1 H, NCH_2PhB), 4.72 (q, *J* = 5.0 Hz, 1 H, H-2′), 7.20–7.33 (m, 5 H, NCH$_2$*Ph*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –3.9, –3.7 [2 q, Si(*C*H$_3$)$_2$C(CH$_3$)$_3$], 18.4 [s, Si(CH$_3$)$_2$*C*(CH$_3$)$_3$], 21.1 (q, CH*C*H$_3$), 24.3 (t, C-3), 26.0 [q, Si(CH$_3$)$_2$C(*C*H$_3$)$_3$], 27.0 (t, C-4), 54.6 (t, C-2), 60.8 (t, N*C*H$_2$Ph), 63.3 (d, C-5), 65.4 (d, C-5′), 71.7 (t, C-6′), 82.2 (d, C-4′), 99.2 (d, C-2′), 126.8, 128.2, 128.6, 140.2 (3 d, s, NCH$_2$*Ph*) ppm. IR (KBr): 2956, 2885, 2856, 2790, 1685, 1604 cm^{-1}. Anal. Calcd for $C_{22}H_{37}NO_3Si$ (391.6): C, 67.47; H, 9.52; N, 3.58. Found: C, 67.47; H, 9.57; N, 3.36.

Compound **19**: $[\alpha]_D^{25}$ +25.0 (*c* 0.2, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.27 (d, *J* = 4.9 Hz, 3 H, CHCH_3), 1.93–2.31 (m, 2 H, H-3), 2.45–2.69 (m, 2 H, H-2), 2.96–3.04 (m, 1 H, H-4), 3.16–3.23 (m, 1 H, H-5′), 3.44–3.56 (m, 2 H, H-4′, H-6′A), 3.68 (s, 3 H, CO_2CH_3), 3.91–3.96 (m, 1 H, H-6′B), 3.91–4.09 (2 d, *J* = 12.5 Hz, 2 H, NCH_2Ph), 4.58 (q, *J* = 4.9 Hz, 1 H, H-2′), 7.26–7.47 (m, 5 H, NCH$_2$*Ph*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.4 (q, CH*C*H$_3$), 20.8 (t, C-3), 32.3 (t, C-2), 51.5 (q, CO_2CH_3), 61.0 (t, C-6′), 67.4 (d, C-5′), 68.5 (d, C-4), 69.8 (t, N*C*H$_2$Ph), 79.9 (d, C-4′), 99.1 (d, C-2′), 127.8, 128.6, 129.5, 136.6 (3 d, s, NCH$_2$*Ph*), 174.4 (s, C-1) ppm. IR (KBr): ν = 3362, 3063, 2994, 2967, 2950, 2881, 1728 cm^{-1}. Anal. Calcd for $C_{17}H_{25}NO_6$ (339.3): C, 60.16; H, 7.42; N, 4.13. Found: C, 60.09; H, 7.16; N, 3.79.

Compound **21**: $[\alpha]_D^{25}$ –19.8 (*c* 0.05, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.22 (d, *J* = 5.0 Hz, 3 H, CHCH_3), 1.89–2.15 (m, 2 H, H-4), 2.16–2.59 (m, 2 H, H-3), 3.24 (dd, *J* = 9.8, 11.2 Hz, 1 H, H-6′A), 3.46 (d, *J* = 9.6 Hz, 1 H, H-4′), 3.53 (dd, *J* = 5.1, 9.6 Hz, 1 H, H-5′), 3.59–3.79 (br s, 1 H, OH), 3.91–3.97 (m, 1 H, H-5), 4.03 (dd, *J* = 5.1, 11.2 Hz, 1 H, H-6′B), 4.25 (q, *J* = 5.0 Hz, 1 H, H-2′), 4.32–4.64 (dd, *J* = 15.3 Hz, 2 H, NCH_2Ph), 7.22–7.33 (m, 5 H, NCH$_2$*Ph*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.8 (t, C-4), 20.3 (q, CH*C*H$_3$), 30.5 (t, C-3), 44.8 (t, N*C*H$_2$Ph), 58.1 (d, C-5), 61.5 (d, C-5′), 70.8 (t, C-6′), 79.2 (d, C-4′), 98.6 (d, C-2′), 127.3, 127.8, 128.3, 136.8 (3 d, s, NCH$_2$*Ph*), 176.5 (s, C-2) ppm. IR (KBr): 3388, 3029, 2991, 2964, 2935, 2861, 1662 cm^{-1}. Anal. Calcd for $C_{16}H_{21}NO_4$ (291.3): C, 65.96; H, 7.27; N, 4.81. Found: C, 65.78; H, 7.38; N, 4.86.

Compound **23**: $[\alpha]_D^{25}$ –23.8 (*c* = 0.34, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.01, 0.03 [2 s, 6 H, Si(CH_3)$_2$C(CH$_3$)$_3$], 0.81 [s, 9 H, Si(CH$_3$)$_2$C(CH_3)$_3$], 1.31 (d, *J* = 5.1 Hz, 3 H, CHCH_3), 2.79 (dd, *J* = 8.1, 13.2 Hz, 1 H, CH_2NCH$_2$PhA), 3.07 (dd, *J* = 2.1, 13.2 Hz, 1 H, CH_2NCH$_2$PhB), 3.35 (t, *J* = 10.2 Hz, 1 H, H-6A), 3.53 (dt, *J* = 4.9, 9.3 Hz, 1 H, H-5), 3.71 (dt, *J* = 2.1, 9.3 Hz, 1 H, H-4), 3.80–3.92 (d, d, *J* = 13.2 Hz, 2 H, NCH_2Ph), 3.99 (dd, *J* = 4.9, 10.2 Hz, 1 H, H-6B), 4.67 (q, *J* = 5.1 Hz, 1 H, H-2), 6.12–6.31 (br s, OH), 7.22–7.38 (m, 5 H, NCH$_2$*Ph*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –4.9, –4.2 [2 q, Si(*C*H$_3$)$_2$C(CH$_3$)$_3$], 17.8 [s, Si(CH$_3$)$_2$*C*(CH$_3$)$_3$], 20.5 (q, CH*C*H$_3$), 25.6 [q, Si(CH$_3$)$_2$C(*C*H$_3$)$_3$], 59.9 (t, *C*H$_2$NCH$_2$Ph), 64.2 (d, C-5), 64.5 (t, N*C*H$_2$Ph), 71.2 (t, C-6), 80.5 (d, C-4), 98.8 (d, C-2), 128.3, 128.9, 129.6, 136.8 (3 d, s, NCH$_2$*Ph*) ppm. IR (KBr): 3423, 3298, 3063, 3030, 2956, 2930, 2886, 2857, 1583, 1472, 1411 cm^{-1}. Anal. Calcd for $C_{19}H_{33}NO_4Si$ (367.5): C, 62.09; H, 9.05; N, 3.81. Found: C, 62.16; H, 8.99; N, 3.52.

Compound **24**: $[\alpha]_D^{25}$ +1.36 (*c* 0.22, MeOH). ^{1}H NMR (300 MHz, CD_3OD): δ = 1.01, 1.04 [2 s, 6 H, Si(CH_3)$_2$C(CH$_3$)$_3$], 1.83 [s, 9 H, Si(CH$_3$)$_2$C(CH_3)$_3$], 3.65 (t, *J* = 5.1 Hz, 2 H, H-2), 4.25–4.28 (br s, 1 H, OH), 4.34 (dd, *J* = 6.0, 11.2 Hz, 1 H, H-4B), 4.45 (dd, *J* = 5.1, 11.2 Hz, 1 H, H-4A), 4.96–5.01 (m, 1 H, H-3), 5.92 (s, 2 H, NCH_2Ph), 8.27 (t, 1 H, *J* = 5.1 Hz, H-1), 8.34–8.41 (m, 5 H, NCH$_2$*Ph*) ppm. ^{13}C NMR (75 MHz, CD_3OD): δ = –4.7, –4.3 [2 q, Si(*C*H$_3$)$_2$C(CH$_3$)$_3$], 18.9 [s, Si(CH$_3$)$_2$*C*(CH$_3$)$_3$], 26.3 [q, Si(CH$_3$)$_2$C(*C*H$_3$)$_3$], 33.3 (t, C-2), 66.9 (t, C-4), 69.5 (t, N*C*H$_2$Ph), 71.3 (d, C-3), 129.9, 130.1, 130.5, 134.4 (3 d, s, NCH$_2$*Ph*), 143.2 (C-1) ppm. IR (KBr): 3355, 2957, 2926, 2873, 1728, 1708, 1662 cm^{-1}. Anal. Calcd for $C_{17}H_{29}NO_3Si$ (323.5): C, 63.12; H, 9.04; N, 4.33. Found: C, 62.94; H, 8.91; N, 4.01.

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