Supporting Information

Di- and Trisubstituted γ -Lactams via Rh(II)-carbenoid Reaction of *N*-C $_{\alpha}$ -Branched, *N*-Bis(trimethylsilyl)methyl α -Diazoamides. Synthesis of ($\pm$)- α -Allokainic acid

Bao Zhang and Andrew G. H. Wee

Department of Chemistry and Biochemistry
University of Regina, Regina, Saskatchewan, Canada S4S 0A2

Contents

	Page
Procedures and Experimental Data	S2 – S19
ORTEP of Compound 30	S20
Tables for Crystallographic Data	S21 – S32
^1H and ^{13}C NMR Spectra	S33 – S95

General. Melting points were determined on a Kofler hot-stage melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 1600 FT spectrophotometer using either neat oil or as a film (CH₂Cl₂). Only the diagnostic signals were reported. NMR spectra were recorded using a Bruker AC200 QNP or Varian Mercury 300 spectrometer. The chemical shifts were recorded in parts per million (δ) relative to the appropriate reference signal. ¹H NMR (200 MHz or 300 MHz) were recorded in deuteriochloroform (CDCl₃) using residual chloroform (δ_H 7.26) as reference; multiplicities of signals were given as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad, and coupling constants are given in Hz. ¹³C were recorded in CDCl₃ using the CDCl₃ triplet centered at δ 77.0 as reference. High-resolution electron-impact (70 ev) or chemical-ionization (NH₃) mass spectra were recorded on a VG-MS-12 spectrometer. Crystallographic data were collected on a Nonius Kappa CCD diffractometer. Reaction progress was monitored by thin-layer chromatography on Merck[®] silica gel 60F₂₅₄ precoated (0.25 mm) on aluminum-backed sheets. Flash chromatography was performed on Silicycle[®] 60Å. Petroleum ether (PE) is the fraction with bp 35–60 °C. Air and moisture sensitive reactions were conducted under a static pressure of Ar. CH₂Cl₂ were dried by distillation from CaH₂. THF and ether were dried by distillation from sodium using sodium benzophenone ketyl as indicators. All organic extracts were dried over anhydrous Na₂SO₄. All crude reaction products were purified by flash column chromatography unless noted otherwise.

General procedure for the Rh(II)-catalyzed reaction. The appropriate rhodium(II) catalyst (2 mol%) was dried under high vacuum at 80 °C for 1 h. A solution of the diazo compound in dry CH₂Cl₂ was transferred via cannula under Ar to a solution of the catalyst in dry CH₂Cl₂ at rt. The reaction was monitored by TLC analysis. After the reaction was complete, the solvent was removed in vacuo, and the crude products were purified. For the acetyl-substituted α -diazoamides **9a**, **9c** and **27**, the reaction was complete after 12 h at rt. For α -unsubstituted α -diazoamides, the reaction was complete within 10 min at rt.

Compound **10a**. Chromatography: 3:1 PE–Et₂O; yield: 65%. Colorless oil; IR (film) 1717, 1674 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 0.09 (s, 9 H, Si(CH₃)₃), δ 0.13 (s, 9 H, Si(CH₃)₃), 0.91 (br t, 3 H, J = 7.0 Hz, CH₃), 1.22–1.59 (m, 4 H, (CH₂)₂), 2.30–2.35 (br s, 1 H, CH(SiMe₃)₂), 2.39 (s, 3 H, C(O)CH₃), 2.50–2.59 (m, 1 H, H -4), 3.18 (d, 1 H, J = 4.1 Hz, H -3), 3.27 (ddd, 1 H, J = 5.3, 3.8, 5.3 Hz, H -5), 3.40 (s, 3 H, OCH₃), 3.55 (dd, 1 H, J = 10.6, 5.3 Hz, OCHH'CH), 3.58 (dd, 1 H, J = 10.6, 5.3 Hz, OCHH'CH),

4.61(d, 1 H, $J = 6.5$ Hz, OCHH'O), 4.64 (d, 1 H, $J = 6.5$ Hz, OCHH'O); ^{13}C NMR (CDCl_3 , 75 MHz) δ 0.4, 0.7, 13.9, 20.3, 29.9, 36.4, 37.5, 38.4, 55.6, 62.2, 65.6, 69.6, 96.8, 168.1, 203.8; HRMS (EI) calcd for $\text{C}_{19}\text{H}_{39}\text{NO}_4\text{Si}_2$ (M^+) 401.2418, found 401.2412.

Compound **10b**. Chromatography: 2:1 PE–Et₂O; yield: 28%. Colorless oil; IR (film) 1676 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 0.11 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 0.13 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 0.92 (br t, 3 H, $J = 7.1$ Hz, CH_3), 1.21–1.55 (m, 4 H, $(\text{CH}_2)_2$), 1.96 (dd, 1 H, $J = 9.9, 5.4$ Hz, $H-3$), 2.01–2.11 (m, 1 H, $H-4$), 2.20–2.26 (br s, 1 H, $\text{CH}(\text{SiMe}_3)_2$), 2.55 (dd, 1 H, $J = 6.6, 8.6$ Hz, $H-3'$), 3.30 (ddd, 1 H, $J = 5.3, 5.3, 3.7$ Hz, $H-5$), 3.38 (s, 3 H, OCH_3), 3.49 (dd, 1 H, $J = 10.5, 5.3$ Hz, OCHH'CH), 3.56 (dd, 1 H, $J = 10.5, 5.3$ Hz, OCHH'CH), 4.62 (s, 2 H, OCH_2O); ^{13}C NMR (CDCl_3 , 75 MHz) δ 0.4, 1.0, 13.9, 20.5, 35.2, 36.1, 37.5, 37.6, 55.6, 66.8, 68.7, 96.8, 173.0; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{37}\text{NO}_3\text{Si}_2$ (M^+) 359.2312, found 359.2312.

Compound **10c**. Chromatography: 2:1 PE–Et₂O; yield: 70%. Obtained as a mixture of two inseparable diastereomers. The relative stereochemistry of the major one was C3, C4-*trans*, C4, C5-*trans*. The relative stereochemistry of the minor diastereomer was not determined. The ratio of the two diastereomers was 15:1, which was determined based on the integration of the double doublet due to one of the pivaloyloxymethylene hydrogens. Colorless oil; IR (film) 1720, 1673 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz, discernible signals for the minor diastereomer in square brackets) δ 0.09 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 0.12 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 0.91 (br t, 3 H, $J = 6.8$ Hz, CH_2CH_3), 1.23 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 1.18–1.58 (m, 4 H, $(\text{CH}_2)_2$), 2.22–2.31 (br s, 1 H, $\text{CH}(\text{SiMe}_3)_2$), 2.39 (s, 3 H, $\text{C}(\text{O})\text{CH}_3$), 2.53–2.62 (m, 1 H, $H-4$), 3.24 (d, 1 H, $J = 4.6$ Hz, $H-3$), 3.29 (ddd, 1 H, $J = 5.9, 3.8, 5.9$ Hz, $H-5$), [4.02 (dd, $J = 12.4, 3.5$ Hz)] and 4.10 (dd, $J = 11.4, 6.0$ Hz) (1 H, OCHH'), 4.17 (dd, $J = 11.4, 6.0$ Hz) and [4.18 (dd, $J = 12.4, 3.5$ Hz)] (1 H, OCHH'); ^{13}C NMR (CDCl_3 , 75 MHz, only the signals for the C3, C4-*trans*, C4, C5-*trans* were detected) δ 0.5, 0.7, 13.9, 20.4, 27.2, 30.2, 36.4, 37.4, 38.5, 38.8, 62.0, 64.8, 65.9, 168.1, 178.1, 203.6; HRMS (EI) calcd for $\text{C}_{22}\text{H}_{43}\text{NO}_4\text{Si}_2$ (M^+) 441.2731, found 441.2721.

Compound **10d**. Trans-diastereomer. Chromatography: 5:1 PE–Et₂O; yield: 61%. White solid, mp 61–63 °C; IR (film) 1734, 1684 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 0.11 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 0.13 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 0.94 (br t, 3 H, $J = 7.2$ Hz,

CH₂CH₃), 1.20–1.55 (m, 4 H, (CH₂)₂), 1.22 (s, 9 H, C(CH₃)₃), 1.95–2.10 (m, 2 H, *H*-3, *H*-4), 2.16 (s, 1 H, CH(SiMe₃)₂), 2.60 (dd, 1 H, *J* = 16.3, 8.7 Hz, *H*-3'), 3.36 (ddd, 1 H, *J* = 4.7, 4.7, 3.1 Hz, *H*-5), 4.04 (dd, 1 H, *J* = 11.7, 4.7 Hz, OCHH'CH), 4.12 (dd, 1 H, *J* = 11.7, 4.7 Hz, OCHH'CH); ¹³C NMR (CDCl₃, 75 MHz) δ 0.5, 0.8, 13.9, 20.4, 27.2, 34.9, 36.2, 37.6, 37.9, 38.7, 64.6, 65.9, 172.9, 178.3; HRMS (EI) calcd for C₂₀H₄₁NO₃Si₂ (M⁺) 399.2625, found 399.2619.

***Cis*-diastereomer.** Chromatography: 5:1 PE–Et₂O; yield: 3%. White solid, mp 80–82 °C; IR (film) 1730, 1673 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 0.11 (s, 9 H, Si(CH₃)₃), 0.13 (s, 9 H, Si(CH₃)₃), 0.93 (br t, 3 H, *J* = 7.3 Hz, CH₂CH₃), 1.22 (s, 9 H, C(CH₃)₃), 1.24–1.53 (m, 4 H, (CH₂)₂), 2.09 (s, 1 H, CH(SiMe₃)₂), 2.24 (dd, 1 H, *J* = 16.3, 12.5 Hz, *H*-3), 2.33 (dd, 1 H, *J* = 16.3, 8.8 Hz, *H*-3'), 2.45–2.60 (m, 1 H, *H*-4), 3.48 (ddd, 1 H, *J* = 7.4, 3.6, 3.6 Hz, *H*-5), 4.04 (dd, 1 H, *J* = 12.7, 3.6 Hz, OCHH'CH), 4.23 (dd, 1 H, *J* = 12.7, 3.6 Hz, OCHH'CH); ¹³C NMR (CDCl₃, 75 MHz) δ 0.1, 0.9, 14.2, 21.4, 27.4, 31.9, 36.3, 37.3, 38.5, 38.6, 62.0, 63.6, 172.9, 178.6; HRMS (EI) calcd for C₂₀H₄₁NO₃Si₂ (M⁺) 399.2625, found 399.2626.

Compound 11b. Chromatography: 2:1 PE–Et₂O; yield: 54%. Obtained as two inseparable *cis*- and *trans*-diastereomers. The ratio of *cis*:*trans* was 1:1, which was determined based on the integration of the H-4 signals. Colorless oil; IR (film) 1682 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz, discernible signals for *cis* in square brackets) δ [0.09 (s, 9 H, Si(CH₃)₃)], [0.12 (s, 9 H, Si(CH₃)₃)] and 0.13 (s, 18 H, 2xSi(CH₃)₃), 0.93 (br t, 3 H, *J* = 6.8 Hz, CH₃), 1.10–1.82 (m, 6 H, (CH₂)₃), 1.90–2.08 (br s, 1 H, CH(SiMe₃)₂), 2.45 (d, 2 H, *J* = 5.6 Hz, *H*-3 and *H*-3') and [2.32 (dd, 1 H, *J* = 17.7, 1.1 Hz, *H*-3)] and [2.61 (dd, 1 H, *J* = 17.7, 6.5 Hz, *H*-3')], [3.36] and 3.37 (s, 3 H, OCH₃), [3.28–3.34] and 3.42–3.50 (m, 1 H, *H*-5), [4.03 (br d, *J* = 6.5 Hz)] and 4.29 (dd, *J* = 11.2, 5.6 Hz) (1 H, *H*-4), 4.60 (d, 1 H, *J* = 6.7 Hz, OCHH'O) and 4.66 (d, 1 H, *J* = 6.7 Hz, OCHH'O) and [4.62 (s, 2 H, OCH₂O)]; ¹³C NMR (CDCl₃, 75 MHz, discernible signals for *cis* in square brackets) δ 0.2 and [0.4], 0.7 and [0.9], 13.9 and [14.0], 22.6 and [23.0], 27.1 and [27.9], 28.2 and [30.3], 36.6 and [37.2], 37.0 and [37.4], 55.5 and [55.8], 65.1 and [68.8], 73.4 and [72.2], 94.5 and [95.7], 170.5 and [171.0]; HRMS (EI) calcd for C₁₇H₃₇NO₃Si₂ (M⁺) 359.2312, found 359.2308.

Compounds 11d and 12d. Chromatography: 5:1 PE–Et₂O; yield: 14%. Two compounds were obtained as an inseparable mixture and the ratio was determined as 1: 1 based on the integration of

the doublet due to one of the oxymethylene hydrogens in the β -lactam and the H-4 multiplet in the γ -lactam. IR (film) 1740, 1713 cm^{-1} ; γ -lactam **11d**: ^1H NMR (CDCl_3 , 300 MHz) δ 0.16 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 0.18 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 0.93 (t, 3 H, $J = 7.0$ Hz, CH_3), 1.26 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 1.15–1.48 (m, 4 H, extensive overlap of signals for $(\text{CH}_2)_2$), 1.93–2.08 (m, 2 H, CH_2), 2.28 (s, 1 H, $\text{CH}(\text{SiMe}_3)_2$), 2.30 (dd, 1 H, $J = 17.6$, 2.0 Hz, H -3), 2.65 (dd, 1 H, $J = 17.6$, 6.1 Hz, H -3'), 3.63 (ddd, 1 H, $J = 9.8$, 5.2, 5.2 Hz, H -5), 5.28–5.36 (m, 1 H, H -4). β -lactam **12d**: ^1H NMR (CDCl_3 , 300 MHz) δ 0.12 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 0.15 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 0.92 (t, 3 H, $J = 7.0$ Hz, CH_3), 1.20 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 1.15–1.48 (m, 5 H, extensive overlap of signals for $(\text{CH}_2)_2$, $\text{CH}(\text{SiMe}_3)_2$), 1.55–1.75 (m, 2 H, CH_2), 2.54 (d, 1 H, $J = 14.4$ Hz, H -3), 2.61 (d, 1 H, $J = 14.4$ Hz, H -3'), 4.05 (d, 1 H, $J = 12.3$ Hz, OCHH'), 4.35 (d, 1 H, $J = 12.5$ Hz, OCHH').

Compound **12a**. Chromatography: 3:1 PE–Et₂O; yield: 8%. Obtained as two inseparable *cis*- and *trans*-diastereomers. The ratio of *cis:trans* was 1:4, which was determined based on the integration of the methyl singlet due to the acetyl group. Colorless oil; IR (film) 1740, 1712 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz,

discernible signals for *cis* in square brackets) δ [0.175] and 0.185 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 0.19 and [0.20] (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 0.86–0.98 (m, 3 H, CH_3), 1.28–1.46, 1.78–1.86, 1.94–2.04 (m, 6 H, $(\text{CH}_2)_3$), 2.28 (s, 1 H, $\text{CH}(\text{SiMe}_3)_2$), [2.30] and 2.33 (s, 3 H, $\text{C}(\text{O})\text{CH}_3$), 3.36 and [3.40] (s, 3 H, OCH_3), 3.49 and [3.70] (s, 1 H, H -3), [3.61 (d, $J = 10.3$ Hz)] and 3.65 (d, $J = 10.9$ Hz) (1 H, $\text{OCHH}'\text{C}$), [3.75 (d, 1 H, $J = 10.3$ Hz)] and 3.80 (d, $J = 10.9$ Hz) (1 H, $\text{OCHH}'\text{C}$), 4.50 (d, 1 H, $J = 6.7$ Hz, $\text{OCHH}'\text{O}$) and 4.54 (d, 1 H, $J = 6.7$ Hz, $\text{OCHH}'\text{O}$) and [4.63 (s, 2 H, OCH_2O)]; ^{13}C NMR (CDCl_3 , 75 MHz, only the signals for the *trans* were detected) δ 0.4, 0.7, 13.9, 23.1, 27.5, 30.5, 34.9, 36.5, 56.3, 65.6, 66.1, 67.9, 97.2, 163.4, 202.1; HRMS (EI) calcd for $\text{C}_{19}\text{H}_{39}\text{NO}_4\text{Si}_2$ (M^+) 401.2418, found 401.2430.

Compound **12c**. Chromatography: 1:1 PE–Et₂O; yield: 18%. Obtained as inseparable *cis*- and *trans*-diastereomers. The ratio of *cis:trans* was 1:2, which was determined based on the integration of the doublet due to one of the oxymethylene hydrogens. Colorless oil; IR (film) 1740, 1713 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz,

discernible signals for *cis* in square bracket) δ 0.16 and [0.17] (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 0.18 and [0.21] (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 0.85–0.95 (m, 3 H, extensive overlap of signals for CH_3), 1.25–1.45, 1.81–1.89, 2.00–2.11 (m, 6 H, extensive overlap of signals for $(\text{CH}_2)_3$), [2.28] and 2.30 (s, 1 H, $\text{CH}(\text{SiMe}_3)_2$), 2.33 and [2.36] (s, 3 H, $\text{C}(\text{O})\text{CH}_3$), 3.69 and [3.69] (s, 1 H, H -3), [4.04 (d, $J = 12.5$ Hz)] and 4.15 (d, $J =$

12.5 Hz) (1 H, OCHH'), [4.40 (d, $J = 12.5$ Hz)] and 4.65 (d, $J = 12.5$ Hz) (1 H, OCHH'); ^{13}C NMR (CDCl_3 , 75 MHz, discernible signals for *cis* in square bracket) δ 0.3 and [0.4], [0.6] and 0.7, [13.7] and 13.8, 22.9 and [23.1], [26.7] and 27.2, [27.25] and 27.3, [30.2] and 30.5, [32.1] and 35.1, 37.4 and [37.5], 38.8 and [38.9], [63.9] and 64.5, [64.1] and 65.6, 67.0 and [67.4], [162.4] and 162.5, [177.2] and 177.25, 200.8 and [201.1]; HRMS (EI) calcd for $\text{C}_{22}\text{H}_{43}\text{NO}_4\text{Si}_2$ (M^+) 441.2731, found 441.2741.

Compound **13d**. Chromatography: 5:1 PE–Et₂O; yield: 5%. Colorless oil; IR (film) 1728, 1627 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 0.09 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 0.11 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 0.91 (br t, 3 H, $J = 7.5$ Hz, CH_2CH_3), 1.22 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 1.25–1.35 (m, 4 H, CH_2 , CH_2), 1.81–1.98 (m, 3 H, $\text{CH}(\text{SiMe}_3)_2$, CH_2), 2.43–2.56 (m, 1 H, $H-4$), 3.38–3.49 (m, 1 H, $H-6$), 3.99 (dd, 1H, $J = 11.5$, 9.8 Hz, OCHH'),

4.24 (dd, 1 H, $J = 11.5$, 3.8 Hz, OCHH'); HRMS (EI) calcd for $\text{C}_{20}\text{H}_{41}\text{NO}_3\text{Si}_2$ 399.2625 (M^+), found 399.2611.

Compound **15a**. Chromatography: 5:1 PE–Et₂O. Colorless oil; IR (film) 1729, 1679 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 0.00 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 0.11 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 1.16 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 2.14 (s, 1 H, $\text{CH}(\text{SiMe}_3)_2$), 2.52 (dd, 1 H, $J = 17.1$, 5.6 Hz, $H-3$), 2.80 (dd, 1 H, $J = 17.1$, 9.2 Hz, $H-3'$), 3.22 (ddd, 1 H, $J = 9.6$, 5.2, 4.4 Hz, $H-4$), 3.56 (br q, 1 H, $J = 4.7$ Hz, $H-5$), 4.06 (dd, 1 H, $J = 11.8$, 4.9 Hz, OCHH'), 4.16

(dd, 1 H, $J = 11.8$, 4.8 Hz, OCHH'), 7.13–7.33 (m, 5 H, PhH); ^{13}C NMR (CDCl_3 , 75 MHz) δ 0.4, 0.9, 27.2, 37.0, 37.9, 38.8, 41.0, 64.3, 68.2, 127.0, 127.3, 128.9, 142.4, 172.5, 178.2; HRMS (EI) calcd for $\text{C}_{23}\text{H}_{39}\text{NO}_3\text{Si}_2$ (M^+) 433.2469, found 433.2478.

γ -Lactam **15b** and *cis*- γ -lactam **16b** were obtained as an inseparable mixture. However, a small amount of pure **15b** was successfully separated by flash chromatography for the purpose of spectral analysis. The yield of **15b** was calculated from the weight ratio of **15b** to *cis*-**16b**, which was determined based on the integration of the H-5 multiplet in **15b** and the H-5 quartet in *cis*-**16b** (see ^1H NMR spectral result of *cis*-**16b**). Chromatography: 5:1 PE–Et₂O. Colorless oil; IR

(film) 1731, 1682 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 0.04 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 0.16 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 1.22 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 2.12–2.22 (br s, 1 H, $\text{CH}(\text{SiMe}_3)_2$), 2.55 (dd, 1 H, $J = 17.2$, 5.1 Hz, $H-3$), 2.94 (dd, 1 H, $J = 17.2$, 9.8 Hz, $H-3'$), 3.42 (ddd, 1 H, $J = 9.8$, 5.1, 4.7 Hz, $H-4$), 3.58 (ddd, 1 H, $J = 4.7$, 4.7,

4.7 Hz, *H*-5), 4.13 (dd, 1 H, *J* = 11.9, 4.7 Hz, OCHH'), 4.28 (dd, 1 H, *J* = 11.9, 4.7 Hz, OCHH'), 7.37–7.43 (m, 2 H, ArH), 8.19–8.25 (m, 2 H, ArH); ¹³C NMR (CDCl₃, 75 MHz) δ 0.1, 0.8, 27.2, 36.5, 38.2, 39.0, 40.9, 64.0, 67.8, 124.3, 127.9, 147.2, 150.0, 171.8, 178.1; HRMS (EI) calcd for C₂₃H₃₈N₂O₅Si₂ (M⁺) 478.2319, found 478.2312.

Compound **16a**. Chromatography: 3:1 PE–Et₂O. Obtained as inseparable *cis*- and *trans*-diastereomers. The ratio of *cis:trans* was calculated based on the integration of the H-4 multiplet. Colorless oil; IR (film) 1726, 1684 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz, discernible signals for *cis*-diastereomer in square brackets) δ [0.07 (s, 9

H, Si(CH₃)₃)] and 0.16 (s, 18 H, 2xSi(CH₃)₃) and [0.18 (s, 9 H, Si(CH₃)₃)], 1.10 and [1.20] (s, 9 H, C(CH₃)₃), 2.00–2.08 (br s, 1 H, CH(SiMe₃)₂), 2.25 (dd, *J* = 18.0, 1.0 Hz) and [2.30 (dd, *J* = 17.3, 2.5 Hz)] (1 H, *H*-3), 2.56 (dd, *J* = 14.0, 9.9 Hz) and [2.95 (dd, *J* = 13.9, 8.4 Hz)] (1 H, PhCHH'), [2.61 (dd, *J* = 17.3, 6.0 Hz)] and 2.84 (dd, *J* = 18.0, 6.2 Hz) (1 H, *H*-3'), [3.04 (dd, *J* = 13.9, 6.1 Hz)] and 3.05 (dd, *J* = 14.0, 5.0 Hz) (1 H, PhCHH'), 3.78 (dd, *J* = 9.9, 5.0 Hz) and [4.08 (ddd, *J* = 8.4, 6.1, 5.0 Hz)] (1 H, *H*-5), 4.98 (br d, *J* = 6.2 Hz) and [5.14–5.22 (m)] (1 H, *H*-4), 7.15–7.38 (m, extensive overlap of aromatic hydrogens, PhH); HRMS (EI) calcd for C₂₃H₃₉NO₃Si₂ (M⁺) 433.2469, found 433.2461.

Compound *trans*-**16b**. Chromatography: 3:1 PE–Et₂O. Colorless oil; IR (film) 1726, 1684 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 0.16 (s, 9 H, Si(CH₃)₃), 0.17 (s, 9 H, Si(CH₃)₃), 1.10 (s, 9 H, C(CH₃)₃), 1.92–2.01 (br s, 1 H, CH(SiMe₃)₂), 2.28 (dd, 1 H, *J* = 18.3, 1.1 Hz, *H*-3), 2.65 (dd, 1 H, *J* = 14.2, 10.1 Hz, ArCHH'), 2.83 (dd, 1 H, *J* = 18.3, 6.3 Hz, *H*-3'), 3.16 (dd, 1

H, *J* = 14.2, 4.4 Hz, ArCHH'), 3.76 (dd, 1 H, *J* = 10.1, 4.4 Hz, *H*-5), 4.93 (d, 1 H, *J* = 6.3 Hz, *H*-4), 7.37 (ddd, 2 H, *J* = 8.7, 1.6, 1.6 Hz, ArH), 8.22 (ddd, 2 H, *J* = 8.7, 1.6, 1.6 Hz, ArH); ¹³C NMR (CDCl₃, 75 MHz) δ 0.3, 1.0, 26.9, 36.3, 37.4, 38.4, 38.6, 68.6, 71.0, 124.2, 129.3, 144.3, 147.2, 170.2, 177.6; HRMS (EI) calcd for C₂₃H₃₈N₂O₅Si₂ (M⁺) 478.2319, found 478.2311.

Compound *cis*-**16b**. The yield of *cis*-**16b** was calculated from the weight ratio of γ-lactam **15b** to *cis*-**16b**, which was determined based on the integration of the H-5 multiplet in **15b** (see ¹H NMR spectral result of **15b**) and the H-5 quartet in *cis*-**16b**. IR (film) 1730, 1684 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 0.10 (s, 9 H, Si(CH₃)₃), 0.18 (s, 9 H, Si(CH₃)₃), 1.18 (s, 9 H, C(CH₃)₃),

1.92–2.19 (br s, 1 H, $\text{CH}(\text{SiMe}_3)_2$), 2.31 (dd, 1 H, $J = 17.2, 3.0$ Hz, $H\text{-}3$), 2.63 (dd, 1 H, $J = 17.2, 6.0$ Hz, $H\text{-}3'$), 3.03 (dd, 1 H, $J = 14.2, 8.9$ Hz, ArCHH'), 3.14 (dd, 1 H, $J = 14.2, 5.6$ Hz, ArCHH'), 4.06–4.16 (m, 1 H, $H\text{-}5$), 5.16 (ddd, 1 H, $J = 6.0, 5.1, 3.0$ Hz, $H\text{-}4$), 7.31–7.36 (m, 2 H, ArH), 8.16–8.23 (m, 2 H, ArH).

17a

Compound **17a**. Chromatography: 3:1 PE–Et₂O. Colorless oil; IR (film) 1734 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 0.17 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 0.24 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 1.29 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 2.44 (s, 1 H, $\text{CH}(\text{SiMe}_3)_2$), 2.49 (d, 1 H, $J = 14.4$ Hz, $H\text{-}3$), 2.81 (d, 1 H, $J = 14.4$ Hz, PhCHH'), 2.93 (d, 1 H, $J = 14.4$ Hz, $H\text{-}3'$), 3.31 (d, 1 H, $J = 13.2$ Hz, PhCHH'), 3.99 (d, 1 H, $J = 12.2$ Hz, OCHH'), 4.08 (d, 1 H, $J = 12.2$ Hz, OCHH'), 7.09–7.18 (m, 2 H, PhH), 7.21–7.35 (m, 3 H, PhH); ¹³C NMR (CDCl₃, 75 MHz) δ 0.5, 0.8, 27.4, 37.5, 38.9, 40.6, 43.2, 60.3, 66.8, 127.3, 128.9, 129.5, 135.8, 164.9, 177.5; HRMS (EI) calcd for C₂₃H₃₉NO₃Si₂ (M⁺) 433.2469, found 433.2463.

17b

Compound **17b**. Chromatography: 2:1 PE–Et₂O. White solid, mp 148–150 °C; IR (film) 1736 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 0.18 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 0.25 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 1.29 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 2.42 (s, 1 H, $\text{CH}(\text{SiMe}_3)_2$), 2.54 (d, 1 H, $J = 14.0$ Hz, ArCHH'), 2.92 (d, 1 H, $J = 13.5$ Hz, $H\text{-}3$), 2.94 (d, 1 H, $J = 14.0$ Hz, ArCHH'), 3.45 (d, 1 H, $J = 13.5$ Hz, $H\text{-}3'$), 3.98 (d, 1 H, $J = 12.4$ Hz, OCHH'), 4.04 (d, 1 H, $J = 12.4$ Hz, OCHH'), 7.29–7.36 (m, 2 H, ArH), 8.15–8.23 (m, 2 H, ArH); ¹³C NMR (CDCl₃, 75 MHz) δ 0.4, 0.8, 27.4, 37.7, 38.8, 40.5, 43.2, 60.0, 66.4, 124.0, 130.3, 143.4, 147.2, 164.3, 177.3; HRMS (EI) calcd for C₂₃H₃₈N₂O₅Si₂ (M⁺) 478.2319, found 478.2303.

18a

Compound **18a**. Chromatography: 7:1 PE–Et₂O. Colorless oil; IR (film) 1729, 1640, 1627 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 0.11 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 0.15 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 1.21 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 1.99 (s, 1 H, $\text{CH}(\text{SiMe}_3)_2$), 2.52 (br d, 1 H, $J = 5.0$ Hz, $H\text{-}9a$), 2.62 (dd, 1 H, $J = 15.3, 2.5$ Hz, $H\text{-}4$), 2.80–2.92 (m, 1 H, $H\text{-}4'$), 3.50–3.58 (m, 1 H, $H\text{-}3$), 3.91 (dd, 1 H, $J = 11.3, 8.5$ Hz, OCHH'), 4.29 (dd, 1 H, $J = 11.3, 3.8$ Hz, OCHH'), 5.48 (dd, 1 H, $J = 9.9, 5.0$ Hz, $H\text{-}9$), 6.01 (br d, 1 H, $J = 5.0$ Hz, $H\text{-}5$), 6.23 (dd, 1 H, $J = 9.9, 5.0$ Hz, $H\text{-}8$), 6.52 (dd, 1 H, $J = 11.2, 5.0$ Hz, $H\text{-}6$), 6.59 (dd, 1 H, $J = 11.2, 5.0$ Hz, $H\text{-}7$); ¹³C NMR (CDCl₃, 75 MHz) δ 0.1, 1.1, 27.2, 32.8, 38.8, 45.1, 47.5, 58.9, 62.9, 122.0, 123.0, 125.7, 129.6, 129.8, 130.4, 168.5, 178.2; HRMS (EI) calcd for C₂₃H₃₉NO₃Si₂ (M⁺) 433.2469, found 433.2453.

Compound **18b**. Chromatography: 7:1 PE–Et₂O. Compound **18b** was not stable, and decomposed after its ¹H NMR spectrum was recorded. Yellow oil; IR (film) 1730, 1643 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 0.12 (s, 9 H, Si(CH₃)₃), 0.16 (s, 9 H, Si(CH₃)₃), 1.20 (s, 9 H, C(CH₃)₃), 2.00 (s, 1 H, CH(SiMe₃)₂), 2.62 (d, 1 H, *J* = 6.7 Hz, *H*-9a), 2.80 (dd, 1 H, *J* = 16.7, 2.7 Hz, *H*-4), 2.82–2.95 (m, 1 H, *H*-4'), 3.55–3.68 (m, 1 H, *H*-3), 3.92 (dd, 1 H, *J* = 7.0, 11.7 Hz, OCHH'), 4.30 (dd, 1 H, *J* = 3.7, 11.7 Hz, OCHH'), 5.71 (dd, 1 H, *J* = 6.7, 10.0 Hz, *H*-9), 6.28 (d, 1 H, *J* = 7.0 Hz, *H*-5), 7.02 (d, 1 H, *J* = 10.0 Hz, *H*-8), 6.28 (d, 2 H, *J* = 7.0 Hz, *H*-6).

Compound *trans*-**20a**. Chromatography: 5:1 PE–Et₂O. White solid, mp 130–132 °C; IR (film) 1726, 1675 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 0.13 (s, 9 H, Si(CH₃)₃), 0.16 (s, 9 H, Si(CH₃)₃), 2.14 (s, 9 H, C(CH₃)₃), 2.10 (dd, 1 H, *J* = 16.8, 3.0 Hz, *H*-3), 2.38–2.50 (m, 1 H, *H*-4), 2.55 (dd, 1 H, *J* = 16.8, 8.9 Hz, *H*-3'), 2.71 (dd, 1 H, *J* = 13.9, 8.0 Hz, PhCHH'), 2.85 (dd, 1 H, *J* = 13.9, 7.4 Hz, PhCHH'), 3.43 (ddd, 1 H, *J* = 4.9, 4.9, 3.4 Hz, *H*-5), 3.99 (dd, 1 H, *J* = 11.9, 4.9 Hz, OCHH'), 4.06 (dd, 1 H, *J* = 11.9, 4.8 Hz, OCHH'), 7.13–7.34 (m, 5 H, PhH); ¹³C NMR (CDCl₃, 75 MHz) δ 0.6, 1.0, 27.2, 35.6, 36.4, 37.9, 38.8, 41.2, 64.3, 65.5, 126.7, 128.7, 128.9, 138.7, 172.6, 178.3; HRMS (EI) calcd for C₂₄H₄₁NO₃Si₂ (M⁺) 447.2625, found 447.2630.

Compound *cis*-**20a**. Chromatography: 5:1 PE–Et₂O. White solid, mp 121–123 °C; IR (film) 1728, 1676 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 0.11 (s, 9 H, Si(CH₃)₃), 0.13 (s, 9 H, Si(CH₃)₃), 1.26 (s, 9 H, C(CH₃)₃), 2.05 (s, 1 H, CH(SiMe₃)₂), 2.18 (dd, 1 H, *J* = 15.9, 7.9 Hz, *H*-3), 2.36 (dd, 1 H, *J* = 15.9, 11.4 Hz, *H*-3'), 2.71 (dd, 1 H, *J* = 15.3, 11.6 Hz, PhCHH'), 2.80–2.95 (m, 2 H, PhCHH', *H*-4), 3.55 (ddd, 1 H, *J* = 7.5, 3.9, 3.9 Hz, *H*-5), 4.12 (dd, 1 H, *J* = 12.8, 3.9 Hz, OCHH'), 4.26 (dd, 1 H, *J* = 12.8, 3.9 Hz, OCHH'), 7.10–7.35 (m, 5 H, PhH); ¹³C NMR (CDCl₃, 75 MHz) δ 0.1, 0.9, 27.5, 35.8, 36.2, 38.5, 38.6, 38.7, 61.9, 63.4, 126.5, 128.4, 128.7, 139.3, 172.6, 178.4; HRMS (EI) calcd for C₂₄H₄₁NO₃Si₂ (M⁺) 447.2625, found: 447.2634.

Compound *trans*-**20b**. Chromatography: 5:1 PE–Et₂O. White powder, mp 83–85 °C; IR (film) 1728, 1676 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 0.13 (s, 9 H, Si(CH₃)₃), 0.15 (s, 9 H, Si(CH₃)₃), 1.18 (s, 9 H, C(CH₃)₃), 2.08 (dd, 1 H, *J* = 17.1, 3.1 Hz, *H*-3), 2.13 (s, 1 H, CH(SiMe₃)₂), 2.32–2.45 (m, 1 H, *H*-4), 2.52 (dd, 1 H, *J* = 17.1, 9.3 Hz, *H*-3'), 2.65 (dd, 1 H, *J* = 14.0, 8.1 Hz, ArCHH'), 2.76 (dd, 1 H, *J* = 14.0, 7.8 Hz, ArCHH'), 3.41 (ddd, 1 H, *J* = 4.4, 4.4, 3.1 Hz, *H*-5), 3.78 (s, 3 H, OCH₃), 3.99 (dd, 1 H, *J* = 12.2, 4.4 Hz, OCHH'), 4.05 (dd, 1 H, *J* = 12.2, 4.4 Hz, OCHH'), 6.80–6.89 (m, 2 H, ArH), 7.03–7.10 (m, 2 H, ArH); ¹³C NMR (CDCl₃, 75 MHz) δ 0.6, 0.95, 27.2, 35.5, 36.5, 37.8, 38.7, 40.4, 55.2, 64.2, 65.4, 114.0, 129.8, 130.7, 158.3, 172.5, 178.3; HRMS (EI) calcd for C₂₅H₄₃NO₄Si₂ (M⁺) 477.2731, found 477.2734.

Compound *cis*-**20b**. Chromatography: 5:1 PE–Et₂O. White powder, mp 121–122 °C; IR (film) 1727, 1676 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 0.11 (s, 9 H, Si(CH₃)₃), 0.13 (s, 9 H, Si(CH₃)₃), 1.26 (s, 9 H, C(CH₃)₃), 2.05 (s, 1 H, CH(SiMe₃)₂), 2.20 (dd, 1 H, *J* = 15.8, 7.9 Hz, *H*-3), 2.35 (dd, 1 H, *J* = 15.8, 10.9 Hz, *H*-3'), 2.65 (dd, 1 H, *J* = 15.5, 11.9 Hz, ArCHH'), 2.76–2.86 (m, 2 H, ArCHH', *H*-4), 3.53 (ddd, 1 H, *J* = 7.1, 3.4, 3.4 Hz, *H*-5), 3.79 (s, 3 H, OCH₃), 4.10 (dd, 1 H, *J* = 12.4, 3.4 Hz, OCHH'), 4.25 (dd, 1 H, *J* = 12.4, 3.7 Hz, OCHH'), 6.80–6.88 (m, 2 H, ArH), 7.03–7.10 (m, 2 H, ArH); ¹³C NMR (CDCl₃, 75 MHz) δ 0.2, 1.0, 27.4, 34.9, 36.2, 38.5, 38.7, 38.8, 55.3, 61.9, 63.3, 114.2, 129.3, 131.2, 158.7, 172.6, 178.4; HRMS (EI) calcd for C₂₅H₄₃NO₄Si₂ (M⁺) 477.2731, found 477.2733.

Compound *trans*-**20c**. Chromatography: 5:1 PE–EtOAc. White powder, mp 116.5–118.5 °C; IR (film) 1729, 1679 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 0.14 (s, 9 H, Si(CH₃)₃), 0.16 (s, 9 H, Si(CH₃)₃), 1.19 (s, 9 H, C(CH₃)₃), 2.05 (dd, 1 H, *J* = 16.3, 3.2 Hz, *H*-3), 2.15 (s, 1 H, CH(SiMe₃)₂), 2.41–2.52 (m, 1 H, *H*-4), 2.56 (dd, 1 H, *J* = 16.3, 9.4 Hz, *H*-3'), 2.81 (dd, 1 H, *J* = 14.4, 8.8 Hz, ArCHH'), 2.98 (dd, 1 H, *J* = 14.4, 6.5 Hz, ArCHH'), 3.41 (ddd, 1 H, *J* = 4.6, 4.6, 3.0 Hz, *H*-5), 4.02 (dd, 1 H, *J* = 11.8, 4.6 Hz, OCHH'), 4.12 (dd, 1 H, *J* = 11.8, 4.6 Hz, OCHH'), 7.31–7.39 (m, 2 H, ArH), 8.13–8.20 (m, 2 H, ArH); ¹³C NMR (CDCl₃, 75 MHz) δ 0.6, 1.0, 27.2, 35.4, 36.2, 38.0, 38.8, 40.9, 64.0, 65.5, 124.0, 129.7, 146.4, 146.9, 171.9, 178.2; HRMS (EI) calcd for C₂₄H₄₀N₂O₅Si₂ (M⁺) 492.2476, found 492.2483.

Compound **cis-20c**. Chromatography: 5:1 PE–EtOAc. Colorless oil; IR (film) 1728, 1677 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 0.11 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 0.14 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 1.27 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 2.06 (s, 1 H, $\text{CH}(\text{SiMe}_3)_2$), 2.16 (dd, 1 H, $J = 15.7, 7.9$ Hz, $H-3$), 2.34 (dd, 1 H, $J = 15.7, 10.8$ Hz, $H-3'$), 2.76–2.93 (m, 2 H, ArCHH' , $H-4$), 3.01 (dd, 1 H, $J = 11.8, 3.9$ Hz, ArCHH'), 3.58 (ddd, 1 H, $J = 7.0, 3.9, 3.9$ Hz, $H-5$), 4.13 (dd, 1 H, $J = 12.7, 3.9$ Hz, OCHH'), 4.26 (dd, 1 H, $J = 12.7, 3.9$ Hz, OCHH'), 7.30–7.36 (m, 2 H, ArH), 8.15–8.22 (m, 2 H, ArH); ^{13}C NMR (CDCl_3 , 75 MHz) δ 0.02, 1.0, 27.5, 35.8, 35.9, 38.2, 38.7, 38.8, 61.6, 63.2, 124.0, 129.2, 146.9, 171.8, 178.2; HRMS (EI) calcd for $\text{C}_{24}\text{H}_{40}\text{N}_2\text{O}_5\text{Si}_2$ (M^+) 492.2476, found 492.2466.

Compound **21a**. Chromatography: 5:1 PE–Et₂O. Compound **21a** was obtained as inseparable *cis*- and *trans*-diastereomers. Colorless oil; IR (film) 1725, 1677 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz, discernible signals for *cis-21a* in square brackets) δ 0.04 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 0.13 and [0.15] (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 1.20 and [1.24] (s, 9 H, $\text{C}(\text{CH}_3)_3$), 1.60–1.69 (m, extensive overlap of signals for $\text{PhCH}_2\text{CHH}'$ and $\text{CH}(\text{SiMe}_3)_2$ in *cis-21a*), 1.90–2.06 (m, extensive overlap of signals for $\text{PhCH}_2\text{CHH}'$), 1.85 (s, 1 H, $\text{CH}(\text{SiMe}_3)_2$), 2.29 (d, 1 H, $J = 18.5$ Hz, $H-3$), 2.60–2.96 (m, extensive overlap of signals for PhCH_2 , $H-3$ and $H-3'$ in *cis-21a*), 2.78 (dd, 1 H, $J = 18.5, 6.6$ Hz, $H-3'$), 3.32 (dd, $J = 10.7, 3.4$ Hz) and [3.61–3.69 (m)] [1 H, $H-5$], 5.11 (d, $J = 6.6$ Hz) and [5.38–5.43 (m)] (1 H, $H-4$), 7.12–7.38 (m, extensive overlap of aromatic hydrogens, PhH); HRMS (EI) calcd for $\text{C}_{24}\text{H}_{41}\text{NO}_3\text{Si}_2$ (M^+) 447.2625, found 447.2627.

Compound **21b**. Chromatography: 5:1 PE–Et₂O. Compound **21b** was obtained as inseparable *cis*- and *trans*-diastereomers. Colorless oil; IR (film) 1725, 1676 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz, discernible signals for *cis-21b* in square brackets) δ [0.05 (s, 18 H, $2\times\text{Si}(\text{CH}_3)_3$)] and 0.13 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 0.14 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 1.20 and [1.23] (s, 9, $\text{C}(\text{CH}_3)_3$), 1.50–1.65 (m, 2 H, ArCH_2CH_2), 1.80–2.00 (m, 2 H, ArCH_2CH_2), [1.44] and 1.85 (s, 1 H, $\text{CH}(\text{SiMe}_3)_2$), 2.25–2.48, 2.55–2.86 (m, extensive overlap of signals for ArCH_2CH_2 and $H-3$), 3.35 (dd, $J = 10.7, 2.9$ Hz) and [3.65 (ddd, $J = 9.7, 5.1, 5.1$ Hz)] (1 H, $H-5$), 3.79 (s, extensive overlap of signals for OCH_3), 5.10 (d, $J = 6.0$ Hz) and [5.35–5.44 (m)] (1 H, $H-4$), 6.80–6.89 (m, extensive overlap of aromatic hydrogens ArH), 7.02–7.15 (m, extensive overlap of aromatic hydrogens ArH); ^{13}C NMR (CDCl_3 , 75 MHz,

discernible signals for *cis*-**21b** in square brackets) δ 0.0, 0.4 and [0.8] and [1.0], 27.0 and [28.9], [29.7] and 30.3, 30.5 and [30.7], [32.0] and 36.5, 37.3 and [37.8], 38.6 and [39.0], [55.29] and 55.3, 63.0, [67.3] and 71.5, 114.0 and [114.05], [129.1] and 129.22, 132.50 and [132.55], 158.10 and [158.11], 169.9 and [171.08], [177.82] and 178.09; HRMS (EI) calcd for $C_{25}H_{43}NO_4Si_2$ (M^+) 477.2731, found: 477.2729.

Compound **21c**. Chromatography: 5:1 PE–EtOAc. Compound **21c** was obtained as inseparable *cis*- and *trans*-diastereomers. Colorless oil; IR (film) 1725, 1676 cm^{-1} ; 1H NMR ($CDCl_3$, 300 MHz, discernible signals for *cis*-**21c** in square brackets) δ 0.06 and [0.07] (s, 9 H, $Si(CH_3)_3$), 0.13

and [0.15] (s, 9 H, $Si(CH_3)_3$), 1.21 and [1.23] (s, 9, $C(CH_3)_3$), 1.50–1.71, 1.90–2.06, 2.28–2.38, 2.55–2.73 (m, extensive overlap of signals for $ArCH_2CH_2$), [1.49] and 1.85 (s, 1 H, $CH(SiMe_3)_2$), 2.73–2.92, 2.95–3.09 (m, extensive overlap of signals for *H*-3 and *H*-3'), 3.33 (dd, $J = 11.3$, 2.8 Hz) and [3.63–3.72 (m)] (1 H, *H*-5), 5.11 (d, $J = 6.0$ Hz) and [5.41–5.48 (m)] (1 H, *H*-4), 7.30–7.40, 8.15–8.23 (m, extensive overlap of aromatic hydrogens *ArH*); HRMS (EI) calcd for $C_{24}H_{40}N_2O_5Si_2$ (M^+) 492.2476, found 492.2487.

Compound **22a**. Chromatography: 3:1 PE–Et₂O. White solid, mp 77–79 °C; IR (film) 1733 cm^{-1} ; 1H NMR ($CDCl_3$, 300 MHz) δ 0.15 (s, 9 H, $Si(CH_3)_3$), 0.17 (s, 9 H, $Si(CH_3)_3$), 1.26 (s, 9 H, $C(CH_3)_3$), 1.80 (ddd, 1 H, $J = 13.5$, 13.0, 5.5 Hz, $PhCH_2CHH'$), 2.29 (s, 1 H, $CH(SiMe_3)_2$), 2.28–2.39 (m, 1 H, $PhCH_2CHH'$), 2.49–2.72 (m, 4 H, $PhCH_2$, *H*-3, *H*-3'), 4.12 (d, 1 H, $OCHH'$), 4.49 (d, 1 H, $OCHH'$), 7.09–7.35 (m, 5 H, *PhH*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 0.4, 0.7, 27.3,

31.4, 35.9, 37.3, 38.9, 43.3, 59.8, 66.7, 126.3, 128.0, 128.7, 140.6, 165.1, 177.7; HRMS (EI) calcd for $C_{24}H_{41}NO_3Si_2$ (M^+) 447.2625, found 447.2613.

Compound **22b**. Chromatography: 3:1 PE–Et₂O. Colorless oil; IR (film) 1732 cm^{-1} ; 1H NMR ($CDCl_3$, 300 MHz) δ 0.15 (s, 9 H, $Si(CH_3)_3$), 0.17 (s, 9 H, $Si(CH_3)_3$), 1.26 (s, 9 H, $C(CH_3)_3$), 1.68 (ddd, 1 H, $J = 7.7$, 7.4, 5.2 Hz, $ArCH_2CHH'$), 2.30 (s, 1 H, $CH(SiMe_3)_2$), 2.22–2.35 (m, 1 H, $ArCH_2CHH'$), 2.42–2.65 (m, 4 H, $ArCH_2$, *H*-3, *H*-3'), 3.80 (s, 3 H, OCH_3), 4.11 (d, 1 H, $J = 12.3$ Hz, $OCHH'$), 4.49 (d, 1 H, $J =$

12.3 Hz, OCHH'), 6.81–6.89 (m, 2 H, ArH), 7.02–7.11 (m, 2 H, ArH); ^{13}C NMR (CDCl_3 , 75 MHz) δ 0.4, 0.8, 27.3, 30.5, 36.2, 37.3, 38.9, 43.3, 55.3, 59.9, 66.7, 114.1, 128.9, 132.6, 158.1, 165.2, 177.7; HRMS (EI) calcd for $\text{C}_{25}\text{H}_{43}\text{NO}_4\text{Si}_2$ (M^+) 477.2731, found 477.2728.

Compound **22c**. Chromatography: 5:1 PE–EtOAc. Colorless oil; IR (film) 1735 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 0.14 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 0.18 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 1.27 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 1.78 (ddd, 1 H, $J = 12.7, 12.7, 5.2$ Hz, $\text{ArCH}_2\text{CHH}'$), 2.30 (s, 1 H, $\text{CH}(\text{SiMe}_3)_2$), 2.29 (ddd, 1 H, $J = 11.2, 11.2, 5.2$ Hz, $\text{ArCH}_2\text{CHH}'$), 2.60–2.84 (m, 4 H, ArCH_2 , H -3, H -3'), 4.13 (d, 1 H, OCHH'), 4.56 (d, 1 H, OCHH'), 7.30–7.36 (m, 2 H, ArH), 8.15–8.22 (m, 2 H, ArH); ^{13}C NMR (CDCl_3 , 75 MHz) δ 0.4, 0.7, 27.3, 31.3, 35.7, 37.5, 38.9, 43.3, 59.6, 66.5, 124.1, 128.8, 146.8, 148.3, 164.7, 177.7; HRMS (EI) calcd for $\text{C}_{24}\text{H}_{40}\text{N}_2\text{O}_5\text{Si}_2$ (M^+) 492.2476, found 492.2458.

Compound **23a**. Chromatography: 7:1 PE–Et₂O. Compound **23a** was obtained as two inseparable diastereomers. Colorless oil; IR (film) 1720, 1630 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz, discernible signals for the minor diastereomer in square brackets) δ 0.13 and [0.14] (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 0.15 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 1.23 (s, extensive overlap of signals for $\text{C}(\text{CH}_3)_3$), [1.98] and 2.09 (s, 1 H, $\text{CH}(\text{SiMe}_3)_2$), [1.82 (ddd, $J = 13.9, 12.5, 8.9$ Hz)] and 1.99–2.09 (m) (1 H, H -5), [2.22–2.39 (m, 1 H, H -5')] and 2.40–2.56 (m, 2 H, H -5', H -3), 2.60–2.78 (m, 1 H, H -3'), 3.20–3.33 (m, 1 H, PhCH), 3.43–3.59 (m) and [3.61–3.71 (m)] (1 H, H -6), [4.01 (dd, $J = 11.4, 3.6$ Hz)] and 4.12 (dd, $J = 10.7, 8.9$ Hz) (1 H, OCHH'), [4.20 (dd, $J = 11.4, 3.6$ Hz)] and 4.31 (dd, $J = 10.7, 7.1$ Hz) (1 H, OCHH'), 7.18–7.39 (m, extensive overlap of aromatic hydrogens, PhH); HRMS (EI) calcd for $\text{C}_{23}\text{H}_{38}\text{NO}_3\text{Si}_2$ ($\text{M}-15$) 432.2390, found 432.2387.

Compound **23b**. Chromatography: 7:1 PE–Et₂O. Colorless oil; IR (film) 1732, 1634 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 0.12 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 0.14 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 1.21 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 1.90–2.03 (m, 2 H, H -5, $\text{CH}(\text{SiMe}_3)_2$), 2.05–2.14 (m, 1 H, H -5'), 2.41 (dd, 1 H, $J = 17.6, 12.6$ Hz, H -3), 2.65 (dd, 1 H, $J = 17.6, 1.9$ Hz, H -3'), 3.15–3.30 (m, 1 H, H -4), 3.45–3.55 (m, 1 H, H -6), 3.80 (s, 3 H, OCH₃), 4.14 (dd, 1 H, $J = 11.0, 8.8$ Hz, OCHH'), 4.32 (dd, 1 H, $J = 11.0, 4.1$ Hz, OCHH'), 6.82–6.95 (m, 2 H, ArH), 7.10–7.18 (m, 2 H, ArH); ^{13}C NMR (CDCl_3 , 75 MHz) δ 0.4,

1.1, 27.3, 32.4, 33.4, 38.8, 39.3, 55.4, 58.6, 62.6, 114.2, 127.5, 135.5, 158.5, 167.8, 178.1; HRMS (EI) calcd for C₂₅H₄₃NO₄Si₂ (M⁺) 477.2731, found 477.2738.

Compound **23c**. Chromatography: 7:1 PE–EtOAc. Colorless oil; IR (film) 1726, 1630 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 0.12 (s, 9 H, Si(CH₃)₃), 0.18 (s, 9 H, Si(CH₃)₃), 1.24 (s, 9 H, C(CH₃)₃), 2.05–2.21 (m, 1 H, *H*-5), 2.24–2.42 (m, 1 H, *H*-5'), 2.76 (s, 1 H, CH(SiMe₃)₂), 2.79–3.03 (m, 3 H, *H*-3, *H*-3', *H*-4), 3.23–3.28 (m, 1 H, *H*-6), 4.45 (dd, 1 H, *J* = 11.6, 7.3 Hz, OCHH'), 4.50 (dd, 1 H, *J* = 11.6, 4.2 Hz, OCHH'), 7.31–7.36 (m, 2 H, Ar*H*), 8.12–8.19 (m, 2 H, Ar*H*); ¹³C NMR (CDCl₃, 75 MHz) δ -1.6, -1.4, 27.2, 32.2, 32.6, 38.9, 40.3, 43.7, 55.9, 62.8, 123.9, 129.2, 145.6, 149.2, 167.1, 178.3; HRMS (EI) calcd for C₂₄H₄₀N₂O₅Si₂ (M⁺) 492.2476, found 492.2476.

Compound **27**. Chromatography: 7:1 PE–EtOAc; yield: 73%. Yellow oil; IR (film) 2098, 1660, 1615 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 0.12 (s, 9 H, Si(CH₃)₃), 0.13 (s, 9 H, Si(CH₃)₃), 1.25 (s, 9 H, C(CH₃)₃), 1.85–2.01 (m, 2 H, ArCH₂CH₂), 2.12 (s, 3 H, C(O)CH₃), 2.32 (s, 1 H, CH(SiMe₃)₂), 2.52 (ddd, 1 H, *J* = 14.1, 7.7, 7.7 Hz, ArCHH'CH₂), 2.65 (ddd, 1 H, *J* = 14.1, 8.4, 5.6 Hz, ArCHH'CH₂), 3.65–3.76 (m, 1 H, OCH₂CH), 3.78 (s, 3 H, OCH₃), 4.23 (dd, 1 H, *J* = 12.9, 2.3 Hz, OCHH'CH), 4.35 (dd, 1 H, *J* = 12.9, 5.8 Hz, OCHH'CH), 6.80–6.87 (m, 2 H, Ar*H*), 7.03–7.12 (m, 2 H, Ar*H*); ¹³C NMR (CDCl₃, 75 MHz) δ 1.4, 1.8, 26.4, 27.3, 31.6, 32.5, 38.8, 40.2, 55.3, 58.5, 64.2, 114.0, 129.2, 132.5, 158.1, 158.7, 178.0; HRMS (EI) calcd for C₂₇H₄₅N₃O₅Si₂ (M⁺) 547.2898, found 547.2909.

Compounds **26a** and **26b**. Chromatography: 7:1 PE–EtOAc. Compounds **26a** and **26b** were obtained as inseparable *trans,trans*-(**26a**) and *trans,cis*-(**26b**) diastereomers. The ratio of **26a**:**26b** was calculated based on the integration of *tert*-butyl singlet. Colorless oil; IR (film) 1729, 1677 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz, discernible signals for **26b** in square brackets) δ [0.07] and 0.09 (s, 9 H, Si(CH₃)₃), [0.12] and 0.15 (s, 9 H, Si(CH₃)₃), 1.21 and [1.29] (s, 9 H, C(CH₃)₃), [2.11] and 2.17 (s, 3 H, C(O)CH₃), 2.21–2.31 (br s, 1 H, CH(SiMe₃)₂), [2.73 (dd, 1 H, *J* = 14.4, 7.2 Hz, ArCHH')], 2.46–2.65 (m, 2 H, extensive overlap of signals for the *H*-4 of **26a** and ArCHH' of **26b**), 2.80–2.96 (m, 3 H, extensive overlap of signals for ArCH₂ of **26a** and the *H*-4 of **26b**), 3.29 (d, 1 H, *J*

= 4.3 Hz, *H*-3), 3.38 (ddd, 1 H, *J* = 5.8, 3.8, 5.8 Hz, *H*-5) and [3.42–3.58 (m, 2H, *H*-3, *H*-5)], 3.76 (s, 3 H, OCH₃), [4.02–4.11 (m)] and 4.06 (dd, *J* = 11.5, 5.8 Hz) (1 H, OCHH'), 4.15 (dd, *J* = 11.5, 5.8 Hz) and [4.23 (dd, *J* = 12.8, 3.0 Hz)] (1 H, OCHH'), 6.78–6.85 (m, extensive overlap of aromatic hydrogens, Ar*H*), 7.01–7.10 (m, extensive overlap of aromatic hydrogens, Ar*H*); ¹³C NMR (CDCl₃, 75 MHz, only the signals for **26a** were detected) δ 0.5, 0.7, 27.1, 30.1, 38.4, 38.55, 38.7, 39.6, 55.2, 60.5, 64.3, 65.5, 114.1, 129.8, 158.45, 167.9, 177.95, 203.45; HRMS (EI) calcd for C₂₇H₄₅NO₅Si₂ (M⁺) 519.2836, found 519.2836.

Compound **28**. Chromatography: 3:1 PE–EtOAc. Compound **28** was obtained as inseparable *cis*- and *trans*-diastereomers. The ratio of *cis:trans* was calculated based on the integration of the doublet due to one of the pivaloyloxymethylene hydrogens. Colorless oil; IR (film) 1737, 1713 cm⁻¹;

¹H NMR (CDCl₃, 300 MHz, discernible signals for *cis*-**28** in square brackets) δ 0.16 and [0.17] (s, 9 H, Si(CH₃)₃), 0.17 and [0.18] (s, 9 H, Si(CH₃)₃), 1.25 and [1.28] (s, 9 H, C(CH₃)₃), 1.65 (ddd, 1 H, *J* = 12.9, 11.0, 5.9 Hz, ArCH₂CHH'), [2.05–2.25 (m, 2 H, ArCH₂CH₂)] and 2.30–2.45 (m, 1 H, ArCH₂CHH'), 2.23 and [2.38] (s, 3 H, C(O)CH₃), [2.32] and 2.34 (s, 1 H, CH(SiMe₃)₂), 2.46–2.63 (m, 1 H, ArCHH'CH₂), 2.71 (ddd, 1 H, *J* = 14.7, 11.0, 5.5 Hz, ArCHH'CH₂), 3.65 and [3.75] (s, 1 H, *H*-3), [4.11 (d, *J* = 12.0 Hz)] and 4.27 (d, *J* = 12.9 Hz) (1 H, OCHH'), [4.51 (d, *J* = 12.0 Hz)] and 4.83 (d, *J* = 12.9 Hz) (1 H, OCHH'), 6.79–6.86 (m, extensive overlap of aromatic hydrogens, Ar*H*), 7.05–7.10 (m, extensive overlap of aromatic hydrogens, Ar*H*); ¹³C NMR (CDCl₃, 75 MHz, discernible signals for *cis*-**28** in square brackets) δ 0.35 and [0.4], [0.6] and 0.7, [27.3] and 27.35, [30.2] and 30.5, 32.0 and [32.8], 37.05, [37.5] and 37.52, 38.84 and [38.86], [55.22] and 55.28, 63.95 and [63.96], 64.25 and [65.58], [67.1] and 67.42, [114.02] and 114.1, [128.99] and 129.02, 132.3 and [132.88], 158.18, [162.22] and 162.28, 177.23, 200.6 and [201.0]; HRMS (EI) calcd for C₂₇H₄₅NO₅Si₂ 519.2836 (M⁺), found 519.2824.

Compounds **29a** and **29b**. The γ-lactam **26a** (173 mg, 0.33 mmol), which was obtained from the Rh₂(OAc)₄-catalyzed reaction of α-diazoamide **27** in a ratio of *trans,trans:trans,cis*, 21:1, was dissolved in benzene (30 mL). Then ethylene glycol (740 μL, 13.2 mmol) and PTSA (7.0 mg, 0.033 mmol) was added. The solution was refluxed overnight under azeotropic

removal of water using a Dean-Stark trap. The solution was cooled to rt, and Et₂O (40 mL) was added.

The mixture was washed with saturated aq NaHCO₃ (5 mL) and brine (5 mL). The organic layer was dried, filtered and evaporated in vacuo. The crude ketal was purified (PE–EtOAc 7:1) to afford compounds **29a** and **29b**. Compound **29a**: Colorless oil (153 mg, 82%). IR (film) 1725, 1673 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 0.13 (s, 18 H, 2xSi(CH₃)₃), 1.14 (s, 9 H, C(CH₃)₃), 1.39 (s, 3 H, CH₃), 2.15–2.31 (m, 2 H, CH(SiMe₃)₂, *H*-4), 2.50 (d, 1 H, *J* = 4.5 Hz, *H*-3), 2.69 (dd, 1 H, *J* = 13.7, 8.1 Hz, ArCHH'), 2.80 (dd, 1 H, *J* = 13.7, 6.8 Hz, ArCHH'), 3.35 (ddd, 1 H, *J* = 5.7, 5.7, 3.5 Hz, *H*-5), 3.77 (s, 3 H, OCH₃), 3.88–4.00 (m, 6 H, OCH₂CH₂O, OCH₂), 6.78–6.84 (m, 2 H, ArH), 7.04–7.11 (m, 2 H, ArH); ¹³C NMR (CDCl₃, 75 MHz) δ 0.8, 1.0, 22.5, 27.0, 38.5, 38.6, 39.1, 41.4, 54.6, 55.2, 63.4, 64.6, 64.7, 66.5, 109.6, 114.0, 130.3, 130.6, 158.4, 170.8, 178.0; HRMS (EI) calcd for C₂₉H₄₉NO₆Si₂ (M⁺) 563.3098, found 563.3098. Compound **29b**: White solid (7.0 mg, 4%), mp 136–138 °C. IR (film) 1727, 1676 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 0.10 (s, 9 H, Si(CH₃)₃), 0.12 (s, 9 H, Si(CH₃)₃), 1.25 (s, 9 H, C(CH₃)₃), 1.90–2.05 (br s, 1 H, CH(SiMe₃)₂), 2.62 (dd, 1 H, *J* = 15.0, 10.7 Hz, ArCHH'), 2.74 (d, 1 H, *J* = 8.6 Hz, *H*-3), 2.85–3.00 (m, 1 H, *H*-4), 3.21 (dd, 1 H, *J* = 15.0, 6.0 Hz, ArCHH'), 3.46 (br ddd, 1 H, *J* = 7.3, 3.0, 3.0 Hz, *H*-5), 3.78 (s, 3 H, OCH₃), 3.91–4.08 (m, 4 H, OCH₂CH₂O), 4.04 (dd, 1 H, *J* = 12.7, 3.5 Hz, OCHH'), 4.15 (dd, 1 H, *J* = 12.7, 2.7 Hz, OCHH'), 6.80–6.86 (m, 2 H, ArH), 7.02–7.10 (m, 2 H, ArH); ¹³C NMR (CDCl₃, 75 MHz) δ 0.0, 1.0, 22.8, 27.2, 34.1, 38.2, 38.7, 38.8, 53.6, 55.2, 60.4, 62.4, 64.6, 64.7, 110.5, 114.1, 129.1, 131.5, 158.2, 170.9, 178.4; HRMS (EI) calcd for C₂₉H₄₉NO₆Si₂ (M⁺) 563.3098, found 563.3088.

Compound **30**. To a solution of **29a** (65mg, 0.115mmol) in CH₃CN (3mL) was transferred a solution of CAN in water (1mL) at rt. The mixture was stirred at rt for 20min. Sodium bisulfite (3mL, 40%) was added. The resulting mixture was stirred at rt for 10 min, then was extracted with EtOAc (3x5mL). The combined organic layers were dried over Na₂SO₄. After

filtration, the organic solvent was removed in vacuo and the resulting product was filtered through a short pad of silica gel using PE–EtOAc (1:1) as solvent. The crude product was used for next step without further purification.

The crude product obtained above was dissolved in MeOH (3mL). Na₂CO₃ (18mg, 0.17mmol) was added at rt. After stirring at rt for 30min, MeOH was removed in vacuo. The residue was taken up into CH₂Cl₂ (5mL). The mixture was washed with sat. NaCl (3mL). The organic layer was dried over Na₂SO₄. After filtration, the organic solvent was removed under reduced pressure and the crude

product was purified by flash chromatography with PE-EtOAc (1:1) to give 41.9 mg of colorless crystalline compound **30** in 90% yield, mp 138–140 °C. IR (film) 3202, 1725, 1697 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 1.15 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 1.49 (s, 3 H, CH_3), 2.28–2.39 (m, 1 H, $H-4$), 2.55 (d, 1 H, $J = 6.5$ Hz, $H-3$), 2.65 (dd, 1 H, $J = 13.2, 10.1$ Hz, ArCHH'), 2.99 (dd, 1 H, $J = 13.2, 5.2$ Hz, ArCHH'), 3.51 (br ddd, 1 H, $J = 8.0, 4.8, 4.8$ Hz, $H-5$), 3.61 (dd, 1 H, $J = 10.6, 8.0$ Hz, OCHH'), 3.71–3.81 (m, 4 H, OCH_3 , OCHH'), 3.93–4.08 (m, 4 H, OCH_2 , CH_2O), 6.28 (s, 1 H, NH), 6.83 (ddd, 2 H, $J = 10.2, 2.6, 2.6$ Hz, ArH), 7.08 (ddd, 2 H, $J = 10.2, 2.6, 2.6$ Hz, ArH); ^{13}C NMR (CDCl_3 , 75 MHz) δ 22.5, 27.1, 38.7, 40.2, 40.4, 54.4, 55.2, 55.6, 64.6, 64.8, 66.9, 109.5, 114.0, 130.1, 130.5, 158.4, 174.7, 178.0; HRMS (EI) calcd for $\text{C}_{22}\text{H}_{31}\text{NO}_6$ (M^+) 405.2151, found 405.2146.

Compound **25**. To a refluxing suspension of LAH (95%, 304 mg, 7.6 mmol) in THF (10 mL) was added a solution of compound **30** (77 mg, 0.19 mmol) in THF (2 mL). The resulting mixture was refluxed for 50 h, cooled to rt, and then cooled to 0 °C. Water (1 mL) was slowly added followed by 2 M aq NaOH (8 mL). The mixture was stirred for 20 min at 0 °C. A solution of $(\text{Boc})_2\text{O}$ (104 mg, 0.475 mmol) in THF (2 mL) was added and the mixture was stirred at rt for 4 h. The product was extracted with EtOAc (3x5 mL), the combined organic layers were dried, filtered, evaporated and the crude product was purified (PE–EtOAc 2:1) to give a colorless oil (56.5 mg, 73%). IR (film) 3398, 1664, 1612 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 1.28 (s, 3 H, CH_3), 1.42 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 2.01–2.12 (m, 1 H, $H-3$), 2.28 (dd, 1 H, $J = 17.0, 9.7$ Hz, $H-4$), 2.65 (dd, 1 H, $J = 13.7, 9.7$ Hz, ArCHH'), 2.98 (dd, 1 H, $J = 13.7, 3.7$ Hz, ArCHH'), 3.19 (dd, 1 H, $J = 10.7, 10.0$ Hz, OCHH'), 3.31–3.48 (m, 3 H, $H-2$, NCHH' , OH), 3.64–3.81 (m, 5 H, OCH_3 , OCHH' , NCHH'), 3.92–4.08 (m, 4 H, $\text{OCH}_2\text{CH}_2\text{O}$), 6.79–6.86 (m, 2 H, ArH), 7.08–7.16 (m, 2 H, ArH); ^{13}C NMR (CDCl_3 , 75 MHz) δ 22.5, 28.5, 38.9, 43.6, 48.2, 49.3, 55.2, 64.5, 64.8, 65.0, 66.5, 80.2, 110.0, 113.8, 130.5, 131.2, 158.2; HRMS (EI) calcd for $\text{C}_{22}\text{H}_{33}\text{NO}_6$ (M^+) 407.2308, found 407.2307.

Compound **31**. To a solution of compound **25** (51 mg, 0.125 mmol) in acetone (5 mL) was added PTSA·(24 mg, 0.125 mmol). The reaction mixture was stirred at rt overnight and then concentrated in vacuo. The resulting residue was taken up into Et_2O and filtered through a short pad of silica gel (60Å) using Et_2O as the eluent. The solvent was removed in vacuo. The crude product was used for the next step without further purification.

NaIO₄ (802 mg, 3.75 mmol) was added to the mixture of EtOAc (2 mL), CH₃CN (2 mL) and water (4 mL). Then this solution was transferred to a flask containing the crude product obtained above and RuCl₃ (1 mg, 0.005 mmol). The flask was stoppered and heated at 30 °C with stirring for 30 h. The solution was diluted with EtOAc (2 mL) and water (2 mL), filtered through a pad of Celite[®], and then the precipitate was washed with EtOAc (2 mL) and water (2 mL). The filtrate was charged with brine, and the resulting mixture was extracted with EtOAc (2x3 mL). The combined organic layers were dried, filtered and the organic solvent was evaporated in vacuo. The crude product was taken up in Et₂O and the mixture was cooled to 0 °C. Ethereal diazomethane was added dropwise until a yellow color remained. The solution was stirred at 0 °C for an additional 10 min. The solvent was removed in vacuo and the residue was purified (PE–EtOAc 3:1) to give a colorless oil (26.2 mg, 61%). IR (film) 1740, 1700 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz, mixture of two rotamers; discernible signals for other rotamer in brackets) δ 1.39 (s) and (1.45 (s)) (9 H, C(CH₃)₃), 2.19 (s, 3 H, C(O)CH₃), 2.44–2.70 (m, 2 H, C(O)CHH', *H*-3), 2.96–3.14 (m, 2 H, C(O)CHH', *H*-4), 3.40–3.56 (m, 1 H, NCHH'), 3.66 (s, 3 H), 3.73 (s, 3 H), (3.80–3.92 (m)) and 3.93–4.12 (m, 2 H, NCHH', *H*-2); ¹³C NMR (CDCl₃, 75 MHz, discernible signals for other rotamer in brackets) δ 28.2 and (28.3), 29.1 and (29.3), 36.1 and (36.6), (40.9) and 41.6, 48.1, 51.8 and (51.9), 52.2 and (52.4), 54.1 and (55.1), (63.4) and 63.7, (80.6) and 80.7, 153.3 and (153.7), 171.4 and (171.5), 171.8 and (172.1), (205.3) and 205.4; HRMS (EI) calcd for C₁₂H₁₇NO₇ (M-56) 287.1005, found 287.1009.

(±)-α-Allokainic acid (**24**). To a suspension of Ph₃PMeBr (61 mg, 0.172 mmol) in dry THF (3 mL) at –78 °C was added BuLi (2.5 M, 65 μL, 0.163 mmol) dropwise. After stirring for 30 min at –78 °C and 20 min at rt, the mixture was recooled to –78 °C. A solution of ketone **31** (29.6 mg, 0.086 mmol) in THF (2 mL) was added at –78

°C, the reaction mixture was stirred at –78 °C for 1 h, and then warmed slowly to rt over a period of 1 h. The reaction mixture was then quenched with saturated aq NH₄Cl and extracted with EtOAc (3x3 mL). The combined organic layers were dried, filtered, evaporated and the crude product was purified (PE–EtOAc 5:1) to give the C4-isopropenyl compound as a colorless oil in 83% yield.

To a solution of the above colorless oil (22 mg, 0.064 mmol) in MeOH (1 mL) was added 3% aq KOH (3 mL) at rt, and the resulting mixture was stirred overnight. MeOH was then removed in vacuo, the aqueous solution was acidified by 5% aq HCl and extracted with EtOAc (5x2 mL). The combined organic layers were dried, filtered and evaporated to provide the crude diacid, which used in the next step without further purification.

The crude diacid obtained above was dissolved in CH₂Cl₂ (2 mL) and trifluoroacetic acid (70 μL, 0.83 mmol) was added and the mixture was stirred at rt for 3 h. The solvent was then removed in vacuo and the crude product was passed through a column containing Dowex-50 (H⁺) ion exchange resin. Elution with 3% aq NH₄OH and evaporation of the collected fractions in vacuo gave a white solid (11 mg). Further recrystallization of the crude product in 95% aq MeOH afforded (±)-**24** as needle-like crystals (8.5 mg, 62%). mp 229–238 °C (dec.) [For (±)-**24**: Lit.¹ mp 245–250 °C (dec.); For (+)-**24**: Lit.¹ mp 238–242 °C (dec.); Lit.² mp 230–237 °C (dec.)]; IR (nujol) br 3095–3500, 1725, 1629 cm⁻¹; ¹H NMR (D₂O, 300 MHz) δ 1.78 (s, 3 H, CH₃), 2.62–2.98 (m, 4 H), 3.37 (t, 1 H, *J* = 11.2 Hz, NCHH'), 3.58 (dd, 1 H, *J* = 11.7, 8.0 Hz, NCHCH'), 3.98 (d, 1 H, *J* = 8.9 Hz, NCH), 5.04 (br s, 2 H, CCH₂); ¹³C NMR (D₂O, 75 MHz) δ 17.6, 35.9, 41.8, 48.1, 51.5, 64.7, 115.7, 140.2, 173.2, 176.0; HRMS (EI) calcd for C₁₀H₁₄NO₄ (M–1) 212.0923, found 212.0921.

1. Oppolzer, W.; Andres, H. *Tetrahedron Lett.* **1978**, *19*, 3397.
2. Anada, M.; Sugimoto, T.; Watanabe, N.; Nakajima, M.; Hashimoto, S. *Heterocycles* **1999**, *50*, 969.

X-ray crystallographic data of compound **30**.

ORTEP drawing of compound **30**

Table 1. Crystal data and structure refinement for **30**.

Identification code	30	
Empirical formula	$C_{22}H_{31}NO_6$	
Formula weight	405.48	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	I2/a	
Unit cell dimensions	a = 21.7453(16) Å	$\alpha = 90^\circ$.
	b = 18.8909(14) Å	$\beta = 100.6320(10)^\circ$.
	c = 21.9832(16) Å	$\gamma = 90^\circ$.
Volume	8875.4(11) Å ³	
Z	16	
Density (calculated)	1.214 Mg/m ³	
Absorption coefficient	0.088 mm ⁻¹	
F(000)	3488	
Crystal size	0.47 x 0.45 x 0.35 mm ³	
Theta range for data collection	1.43 to 26.34°.	
Index ranges	-27<= <i>h</i> <=27, -23<= <i>k</i> <=23, -27<= <i>l</i> <=27	
Reflections collected	34666	
Independent reflections	9033 [R(int) = 0.0157]	
Completeness to theta = 26.34°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9703 and 0.9597	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9033 / 0 / 531	
Goodness-of-fit on F ²	1.030	
Final R indices [I>2sigma(I)]	R1 = 0.0473, wR2 = 0.1277	
R indices (all data)	R1 = 0.0557, wR2 = 0.1358	
Largest diff. peak and hole	0.498 and -0.395 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **30**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
C(1)	415(1)	9977(1)	4245(1)	36(1)
C(2)	764(1)	9838(1)	3714(1)	34(1)
C(3)	1113(1)	9133(1)	3878(1)	34(1)
C(4)	958(1)	8908(1)	4513(1)	33(1)
C(5)	1187(1)	10459(1)	3612(1)	38(1)
C(6)	834(1)	11130(1)	3392(1)	51(1)
C(7)	2195(1)	10803(1)	4004(1)	62(1)
C(8)	2135(1)	10616(1)	3328(1)	61(1)
C(9)	917(1)	8575(1)	3371(1)	44(1)
C(10)	1180(1)	7841(1)	3522(1)	41(1)
C(11)	793(1)	7249(1)	3418(1)	49(1)
C(12)	1024(1)	6573(1)	3544(1)	54(1)
C(13)	1805(1)	7722(1)	3755(1)	47(1)
C(14)	2048(1)	7047(1)	3888(1)	50(1)
C(15)	1648(1)	6470(1)	3786(1)	51(1)
C(16)	2481(1)	5643(1)	4062(2)	101(1)
C(17)	1533(1)	8882(1)	5010(1)	41(1)
C(18)	1717(1)	8845(1)	6106(1)	43(1)
C(19)	1468(1)	8653(1)	6689(1)	50(1)
C(20)	1286(1)	9345(1)	6960(1)	77(1)
C(21)	874(1)	8190(1)	6557(1)	70(1)
C(22)	1981(2)	8266(3)	7120(1)	142(2)
C(51)	3317(1)	2468(1)	3075(1)	35(1)
C(52)	3908(1)	2580(1)	3553(1)	34(1)
C(53)	3840(1)	3334(1)	3801(1)	33(1)
C(54)	3150(1)	3544(1)	3555(1)	33(1)
C(55)	4011(1)	2009(1)	4053(1)	38(1)
C(56)	4076(1)	1264(1)	3812(1)	51(1)
C(57)	3803(2)	1871(1)	5012(1)	80(1)
C(58)	4461(1)	2095(1)	5082(1)	73(1)
C(59)	4298(1)	3850(1)	3583(1)	42(1)
C(60)	4218(1)	4608(1)	3770(1)	38(1)

C(61)	4303(1)	4800(1)	4388(1)	41(1)
C(62)	4210(1)	5487(1)	4571(1)	42(1)
C(63)	4041(1)	5133(1)	3332(1)	45(1)
C(64)	3951(1)	5822(1)	3507(1)	49(1)
C(65)	4032(1)	6002(1)	4128(1)	42(1)
C(66)	4029(2)	6903(1)	4880(1)	76(1)
C(67)	2755(1)	3545(1)	4054(1)	40(1)
C(68)	1658(1)	3362(1)	3718(1)	43(1)
C(69)	1033(1)	3743(1)	3506(1)	41(1)
C(70)	854(1)	4082(1)	4080(1)	62(1)
C(71)	1086(1)	4311(1)	3022(1)	47(1)
C(72)	553(1)	3186(1)	3240(1)	56(1)
N(1)	534(1)	9450(1)	4651(1)	36(1)
N(51)	2938(1)	3018(1)	3082(1)	34(1)
O(1)	68(1)	10482(1)	4286(1)	48(1)
O(2)	1620(1)	10570(1)	4170(1)	45(1)
O(3)	1557(1)	10236(1)	3177(1)	46(1)
O(5)	1827(1)	5784(1)	3914(1)	73(1)
O(6)	1326(1)	8695(1)	5582(1)	44(1)
O(7)	2221(1)	9108(1)	6105(1)	64(1)
O(51)	3213(1)	1951(1)	2726(1)	49(1)
O(52)	3519(1)	2051(1)	4387(1)	51(1)
O(53)	4569(1)	2195(1)	4474(1)	52(1)
O(55)	3918(1)	6691(1)	4253(1)	61(1)
O(56)	2139(1)	3814(1)	3804(1)	45(1)
O(57)	1723(1)	2735(1)	3804(1)	71(1)

Table 3. Bond lengths [Å] and angles [°] for **30**.

C(1)-O(1)	1.231(2)
C(1)-N(1)	1.330(2)
C(1)-C(2)	1.527(2)
C(2)-C(5)	1.532(2)
C(2)-C(3)	1.542(2)
C(3)-C(9)	1.536(2)
C(3)-C(4)	1.5546(19)
C(4)-N(1)	1.448(2)
C(4)-C(17)	1.503(2)
C(5)-O(2)	1.418(2)
C(5)-O(3)	1.4221(19)
C(5)-C(6)	1.515(2)
C(7)-O(2)	1.434(2)
C(7)-C(8)	1.511(3)
C(8)-O(3)	1.431(2)
C(9)-C(10)	1.514(2)
C(10)-C(13)	1.380(3)
C(10)-C(11)	1.392(2)
C(11)-C(12)	1.382(3)
C(12)-C(15)	1.376(3)
C(13)-C(14)	1.390(3)
C(14)-C(15)	1.387(3)
C(15)-O(5)	1.368(2)
C(16)-O(5)	1.424(3)
C(17)-O(6)	1.4541(18)
C(18)-O(7)	1.203(2)
C(18)-O(6)	1.330(2)
C(18)-C(19)	1.524(2)
C(19)-C(22)	1.512(3)
C(19)-C(20)	1.519(3)
C(19)-C(21)	1.542(3)
C(51)-O(51)	1.2368(19)
C(51)-N(51)	1.328(2)
C(51)-C(52)	1.519(2)
C(52)-C(55)	1.528(2)

C(52)-C(53)	1.542(2)
C(53)-C(59)	1.533(2)
C(53)-C(54)	1.550(2)
C(54)-N(51)	1.4498(19)
C(54)-C(67)	1.513(2)
C(55)-O(52)	1.407(2)
C(55)-O(53)	1.4288(19)
C(55)-C(56)	1.519(2)
C(57)-O(52)	1.439(3)
C(57)-C(58)	1.472(4)
C(58)-O(53)	1.411(3)
C(59)-C(60)	1.509(2)
C(60)-C(61)	1.384(2)
C(60)-C(63)	1.387(2)
C(61)-C(62)	1.384(2)
C(62)-C(65)	1.379(2)
C(63)-C(64)	1.382(3)
C(64)-C(65)	1.387(2)
C(65)-O(55)	1.363(2)
C(66)-O(55)	1.413(3)
C(67)-O(56)	1.4436(19)
C(68)-O(57)	1.204(2)
C(68)-O(56)	1.336(2)
C(68)-C(69)	1.531(2)
C(69)-C(72)	1.522(3)
C(69)-C(70)	1.529(2)
C(69)-C(71)	1.530(2)
O(1)-C(1)-N(1)	125.17(14)
O(1)-C(1)-C(2)	125.95(14)
N(1)-C(1)-C(2)	108.86(13)
C(1)-C(2)-C(5)	112.20(13)
C(1)-C(2)-C(3)	105.19(12)
C(5)-C(2)-C(3)	114.36(13)
C(9)-C(3)-C(2)	111.43(13)
C(9)-C(3)-C(4)	112.66(13)
C(2)-C(3)-C(4)	105.52(12)

N(1)-C(4)-C(17)	110.25(12)
N(1)-C(4)-C(3)	104.30(12)
C(17)-C(4)-C(3)	111.94(12)
O(2)-C(5)-O(3)	104.93(13)
O(2)-C(5)-C(6)	111.67(14)
O(3)-C(5)-C(6)	110.44(13)
O(2)-C(5)-C(2)	107.84(12)
O(3)-C(5)-C(2)	107.60(13)
C(6)-C(5)-C(2)	113.89(14)
O(2)-C(7)-C(8)	104.90(16)
O(3)-C(8)-C(7)	104.97(14)
C(10)-C(9)-C(3)	115.29(14)
C(13)-C(10)-C(11)	117.07(17)
C(13)-C(10)-C(9)	122.45(16)
C(11)-C(10)-C(9)	120.46(16)
C(12)-C(11)-C(10)	121.51(18)
C(15)-C(12)-C(11)	120.32(17)
C(10)-C(13)-C(14)	122.42(16)
C(15)-C(14)-C(13)	119.02(18)
O(5)-C(15)-C(12)	115.92(17)
O(5)-C(15)-C(14)	124.43(18)
C(12)-C(15)-C(14)	119.65(18)
O(6)-C(17)-C(4)	106.74(13)
O(7)-C(18)-O(6)	121.54(16)
O(7)-C(18)-C(19)	124.36(16)
O(6)-C(18)-C(19)	114.09(16)
C(22)-C(19)-C(20)	112.7(2)
C(22)-C(19)-C(18)	107.92(17)
C(20)-C(19)-C(18)	106.43(17)
C(22)-C(19)-C(21)	109.8(2)
C(20)-C(19)-C(21)	106.98(18)
C(18)-C(19)-C(21)	113.07(15)
O(51)-C(51)-N(51)	125.69(14)
O(51)-C(51)-C(52)	124.97(13)
N(51)-C(51)-C(52)	109.32(13)
C(51)-C(52)-C(55)	113.11(13)
C(51)-C(52)-C(53)	104.39(12)

C(55)-C(52)-C(53)	114.11(12)
C(59)-C(53)-C(52)	111.46(12)
C(59)-C(53)-C(54)	111.83(13)
C(52)-C(53)-C(54)	105.28(12)
N(51)-C(54)-C(67)	111.95(13)
N(51)-C(54)-C(53)	103.54(11)
C(67)-C(54)-C(53)	112.94(12)
O(52)-C(55)-O(53)	106.56(13)
O(52)-C(55)-C(56)	111.26(15)
O(53)-C(55)-C(56)	109.37(13)
O(52)-C(55)-C(52)	108.16(12)
O(53)-C(55)-C(52)	106.68(13)
C(56)-C(55)-C(52)	114.42(14)
O(52)-C(57)-C(58)	105.65(18)
O(53)-C(58)-C(57)	105.58(18)
C(60)-C(59)-C(53)	113.85(13)
C(61)-C(60)-C(63)	117.65(15)
C(61)-C(60)-C(59)	121.01(15)
C(63)-C(60)-C(59)	121.32(15)
C(60)-C(61)-C(62)	122.03(15)
C(65)-C(62)-C(61)	119.57(15)
C(64)-C(63)-C(60)	120.99(16)
C(63)-C(64)-C(65)	120.46(16)
O(55)-C(65)-C(62)	124.79(16)
O(55)-C(65)-C(64)	115.90(15)
C(62)-C(65)-C(64)	119.30(16)
O(56)-C(67)-C(54)	109.52(13)
O(57)-C(68)-O(56)	122.74(16)
O(57)-C(68)-C(69)	125.51(17)
O(56)-C(68)-C(69)	111.74(14)
C(72)-C(69)-C(70)	110.24(16)
C(72)-C(69)-C(71)	110.62(16)
C(70)-C(69)-C(71)	110.06(16)
C(72)-C(69)-C(68)	107.46(15)
C(70)-C(69)-C(68)	107.01(15)
C(71)-C(69)-C(68)	111.36(13)
C(1)-N(1)-C(4)	116.06(13)

C(51)-N(51)-C(54)	115.39(13)
C(5)-O(2)-C(7)	107.19(14)
C(5)-O(3)-C(8)	106.12(14)
C(15)-O(5)-C(16)	117.33(18)
C(18)-O(6)-C(17)	116.49(14)
C(55)-O(52)-C(57)	104.53(16)
C(58)-O(53)-C(55)	108.07(17)
C(65)-O(55)-C(66)	117.48(15)
C(68)-O(56)-C(67)	118.44(13)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **30**. The anisotropic displacement factor exponent takes the form: $-2 \text{ }^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
C(1)	35(1)	39(1)	35(1)	4(1)	10(1)	-3(1)
C(2)	39(1)	38(1)	27(1)	2(1)	9(1)	-2(1)
C(3)	39(1)	35(1)	29(1)	-1(1)	11(1)	-4(1)
C(4)	39(1)	31(1)	30(1)	-1(1)	10(1)	-4(1)
C(5)	47(1)	39(1)	32(1)	2(1)	17(1)	-2(1)
C(6)	62(1)	42(1)	54(1)	13(1)	25(1)	3(1)
C(7)	48(1)	59(1)	82(2)	-5(1)	20(1)	-14(1)
C(8)	56(1)	61(1)	74(1)	13(1)	33(1)	-7(1)
C(9)	55(1)	46(1)	32(1)	-7(1)	13(1)	-3(1)
C(10)	50(1)	43(1)	36(1)	-10(1)	20(1)	-4(1)
C(11)	43(1)	51(1)	57(1)	-16(1)	20(1)	-6(1)
C(12)	49(1)	44(1)	77(1)	-20(1)	29(1)	-11(1)
C(13)	48(1)	43(1)	52(1)	-11(1)	19(1)	-10(1)
C(14)	44(1)	48(1)	61(1)	-13(1)	18(1)	-3(1)
C(15)	52(1)	40(1)	67(1)	-14(1)	29(1)	-2(1)
C(16)	68(2)	53(1)	178(3)	-18(2)	14(2)	15(1)
C(17)	43(1)	50(1)	30(1)	1(1)	11(1)	2(1)
C(18)	45(1)	47(1)	34(1)	2(1)	3(1)	18(1)
C(19)	62(1)	61(1)	29(1)	3(1)	9(1)	24(1)
C(20)	97(2)	65(1)	81(2)	-27(1)	48(1)	-14(1)
C(21)	112(2)	57(1)	46(1)	3(1)	29(1)	-11(1)
C(22)	109(2)	269(5)	54(2)	76(2)	33(2)	109(3)
C(51)	35(1)	38(1)	31(1)	-4(1)	4(1)	7(1)
C(52)	30(1)	35(1)	35(1)	-4(1)	5(1)	4(1)
C(53)	32(1)	32(1)	34(1)	-2(1)	5(1)	2(1)
C(54)	34(1)	27(1)	37(1)	-2(1)	5(1)	2(1)
C(55)	36(1)	36(1)	40(1)	-2(1)	0(1)	6(1)
C(56)	55(1)	36(1)	56(1)	-3(1)	-4(1)	11(1)
C(57)	121(2)	73(2)	51(1)	21(1)	30(1)	15(2)
C(58)	107(2)	65(1)	40(1)	-3(1)	-4(1)	20(1)
C(59)	38(1)	42(1)	47(1)	-6(1)	14(1)	-5(1)
C(60)	35(1)	38(1)	40(1)	-2(1)	9(1)	-8(1)

C(61)	45(1)	39(1)	37(1)	4(1)	2(1)	-6(1)
C(62)	50(1)	42(1)	31(1)	-2(1)	4(1)	-10(1)
C(63)	58(1)	47(1)	31(1)	-1(1)	10(1)	-10(1)
C(64)	68(1)	41(1)	36(1)	7(1)	7(1)	-7(1)
C(65)	52(1)	34(1)	41(1)	0(1)	8(1)	-9(1)
C(66)	122(2)	46(1)	59(1)	-16(1)	13(1)	0(1)
C(67)	37(1)	41(1)	42(1)	-8(1)	9(1)	6(1)
C(68)	44(1)	41(1)	48(1)	9(1)	17(1)	2(1)
C(69)	38(1)	43(1)	45(1)	2(1)	16(1)	5(1)
C(70)	61(1)	71(1)	61(1)	-7(1)	30(1)	6(1)
C(71)	50(1)	42(1)	51(1)	6(1)	13(1)	12(1)
C(72)	49(1)	52(1)	69(1)	-1(1)	13(1)	0(1)
N(1)	40(1)	38(1)	32(1)	3(1)	16(1)	0(1)
N(51)	32(1)	36(1)	33(1)	-4(1)	1(1)	7(1)
O(1)	53(1)	48(1)	50(1)	16(1)	26(1)	13(1)
O(2)	47(1)	47(1)	43(1)	-5(1)	12(1)	-12(1)
O(3)	54(1)	51(1)	40(1)	4(1)	25(1)	-1(1)
O(5)	62(1)	38(1)	123(1)	-13(1)	29(1)	1(1)
O(6)	51(1)	54(1)	28(1)	1(1)	10(1)	0(1)
O(7)	52(1)	94(1)	43(1)	2(1)	-3(1)	4(1)
O(51)	46(1)	48(1)	45(1)	-19(1)	-7(1)	17(1)
O(52)	61(1)	44(1)	53(1)	14(1)	20(1)	12(1)
O(53)	53(1)	52(1)	43(1)	-2(1)	-13(1)	6(1)
O(55)	95(1)	35(1)	50(1)	-2(1)	10(1)	-3(1)
O(56)	35(1)	34(1)	66(1)	-2(1)	13(1)	6(1)
O(57)	57(1)	44(1)	111(1)	24(1)	11(1)	1(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **30**.

	x	y	z	U(eq)
H(2)	448	9767	3327	41
H(3)	1573	9218	3926	41
H(4)	745	8436	4475	39
H(6A)	539	11034	3007	77
H(6B)	1131	11496	3317	77
H(6C)	604	11295	3709	77
H(7A)	2557	10558	4255	75
H(7B)	2249	11320	4067	75
H(8A)	2124	11048	3072	73
H(8B)	2490	10316	3260	73
H(9A)	454	8544	3285	53
H(9B)	1049	8739	2988	53
H(11)	360	7312	3255	59
H(12)	751	6178	3465	65
H(13)	2080	8117	3826	56
H(14)	2481	6983	4048	60
H(16A)	2548	5136	4142	151
H(16B)	2666	5911	4432	151
H(16C)	2678	5784	3714	151
H(17A)	1831	8524	4909	49
H(17B)	1744	9349	5052	49
H(20A)	1123	9248	7338	116
H(20B)	963	9581	6658	116
H(20C)	1654	9652	7057	116
H(21A)	973	7736	6383	105
H(21B)	551	8433	6261	105
H(21C)	721	8108	6943	105
H(22A)	2080	7824	6925	213
H(22B)	1839	8157	7508	213
H(22C)	2355	8565	7207	213
H(52)	4274	2576	3335	40

H(53)	3918	3323	4263	39
H(54)	3136	4023	3360	39
H(56A)	4425	1249	3587	76
H(56B)	3688	1131	3532	76
H(56C)	4155	933	4160	76
H(57A)	3776	1355	5081	96
H(57B)	3593	2123	5311	96
H(58A)	4531	2541	5321	88
H(58B)	4743	1727	5299	88
H(59A)	4731	3697	3754	50
H(59B)	4242	3826	3126	50
H(61)	4428	4449	4695	49
H(62)	4269	5603	4998	50
H(63)	3980	5017	2904	54
H(64)	3832	6175	3200	58
H(66A)	3929	7407	4907	114
H(66B)	4470	6824	5062	114
H(66C)	3764	6625	5107	114
H(67A)	2722	3058	4211	48
H(67B)	2955	3846	4404	48
H(70A)	1168	4437	4249	93
H(70B)	836	3717	4393	93
H(70C)	444	4310	3967	93
H(71A)	1205	4089	2658	71
H(71B)	1406	4657	3198	71
H(71C)	683	4550	2901	71
H(72A)	672	2974	2871	84
H(72B)	140	3408	3126	84
H(72C)	537	2817	3550	84
H(1)	386(9)	9450(10)	4975(9)	43(5)
H(51)	2587(9)	3036(10)	2851(9)	41(5)

180

160

140

120

100

80

9

40

20

C

26a and 26b

1.647
1.613

3.224
4.209
2.643
1.135
0.999
0.948
0.957
1.076

7.218
2.991