Supporting Information

for

A Practical Synthesis of Kifunensine and Analogues as Inhibitors of Endoplasmic Reticulum α-Mannosidase I

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**General Experimental Methods.** All reactions were performed under an atmosphere of dry nitrogen or argon in flame-dried glassware equipped with tightly fitting rubber septa. All syringes and needles were oven-dried and cooled in a dessicator prior to use. Reactions at 0 °C were carried out in an ice/water bath. Reactions between 0 °C and –78 °C were carried out in a dry ice/acetone bath (with varied amounts of dry ice to maintain the desired temperature). All reagents were obtained from commercial suppliers and were used without further purification unless otherwise noted. Solvents were freshly prepared before use. Benzene, toluene, methylene chloride (CH$_2$Cl$_2$), pyridine and triethylamine were distilled from calcium hydride. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium/benzophenone ketyl. Dimethylformamide (DMF) was distilled from barium oxide under reduced pressure.

![Chemical Structure](image)

**12**

(2R,3R,4R,5R)-2-Azido-4,5-isopropylidenedioxy-1,3,6-hexanetriol (12). Tetra-$n$-butylammonium fluoride (3.22 mL, 1.0 M solution in THF, 3.22 mmol) was added to a solution of TBS-ether 18 (776 mg, 2.15 mmol) in THF (14 mL) at 0 °C and stirred for 10 minutes. The reaction was then poured into brine, extracted with EtOAc, dried (MgSO$_4$) and concentrated to yield a clear oil. Chromatography (80% EtOAc / hexanes) afforded 474 mg (89%) of the title compound as a clear oil. Data for 12: $R_f = 0.07$ (50% EtOAc / hexanes); $[\alpha]^{23}_D = -55.5^o$ (c = 1.31, CH$_2$Cl$_2$); $^1$H NMR (benzene-d$_6$, 400 MHz) $\delta$4.14 (dd, $J = 0.8, 7.2$ Hz, 1H), 4.03 (br s, 1H), 3.88-3.78 (m, 3H), 3.64-3.60 (m, 2H), 3.50-3.41 (m, 2H), 2.87 (br s, 1H), 2.60 (br s, 1H), 1.45 (s, 3H), 1.21 (s, 3H); $^{13}$C NMR (benzene-d$_6$,
100 MHz) δ 108.4, 77.0, 76.3, 69.2, 64.6, 63.0, 60.3, 26.6, 24.8; IR (neat) 3391 (br s), 2102 (s) cm⁻¹; MS (CI w/ NH₃) m/z (rel int) 265 (M + NH₄, 24), 248 (M+H, 28), 220 (100), 202 (69), 190 (74), 172 (51), 160 (84); HRMS (CI w/ NH₃) calcd for C₉H₁₈N₃O₅ (M + H) 248.1246, found 248.1254.

(2R,3R,4R,5R)-2-Azido-1-tert-butyldimethylsilyloxy-4,5-O-isopropylidene-dioxy-6-pivaloyl-3-hexanol (19). Pyridine (4.62 mL, 4.52 g, 57.1 mmol) and trimethylacetyl chloride (3.37 mL, 3.30 g, 27.4 mmol) were added to a solution of diol 18 (8.25 g, 22.8 mmol) in CH₂Cl₂ (60 mL) at room temperature and stirred for 20 hours. The reaction was then diluted with CH₂Cl₂ (120 mL), washed with water, dried (MgSO₄) and concentrated to yield an oily white solid. Chromatography (5% EtOAc / hexanes) afforded 8.04 g (79%) of the title compound as a clear oil. Data for 19: Rᵢ = 0.80 (30% EtOAc / hexanes); [α]D²¹ = -29.8° (c = 1.05, CH₂Cl₂); ¹H NMR (CDCl₃, 400 MHz) δ 4.45-4.28 (m, 4H), 4.07 (dd, J = 3.2, 10.6 Hz, 1H), 3.86 (dd, J = 6.3, 10.6 Hz, 1H), 3.59 (br d, J = 5.9 Hz, 1H), 3.39 (ddd, J = 3.2, 6.3, 9.4 Hz, 1H), 2.38 (br s, 1H), 1.50 (s, 3H), 1.39 (s, 3H), 1.20 (s, 9H), 0.91 (s, 9H), 0.09 (app d, J = 2.6 Hz, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 178.0, 108.7, 75.1, 74.8, 68.00, 64.1, 64.0, 63.1, 38.7, 27.1, 26.8, 25.8, 24.5, 18.2, -5.6; IR (neat) 3512 (br m), 2099 (s), 1733 (s) cm⁻¹; MS (EI) m/z (rel int) 430 (M - CH₃, 2), 330 (26), 157 (31), 116 (26), 84 (97), 49 (100); HRMS (Electrospray) calcd for C₂₀H₃₉N₃NaO₆Si (M + Na) 468.2506, found 468.2498.
(2R,3R,4R,5R)-2-Azido-1,3:4,5-diisopropylidenedioxy-6-pivaloylhexane (20).

Tetra-n-butylammonium fluoride (21.7 mL, 1.0 M solution in THF, 21.7 mmol) was added to a solution of TBS-ether 19 (8.04 g, 18.0 mmol) in THF (120 mL) at -20 °C and stirred for 1 hour. The reaction was then warmed to room temperature, poured into brine, extracted with EtOAc, dried (MgSO₄) and concentrated to yield a pale yellow oil. Chromatography (40% EtOAc / hexanes) afforded 5.82 g (97%) of the intermediate diol as a clear oil. Data for the intermediate diol: R_f = 0.19 (30% EtOAc / hexanes); [α]D²³ = -31.4° (c = 0.49, CH₂Cl₂); ¹H NMR (CDCl₃, 400 MHz) δ 4.47-4.30 (m, 4H), 4.03 (ddd, J = 4.1, 5.5, 11.8 Hz, 1H), 3.90 (ddd, J = 5.2, 6.8, 12.0 Hz, 1H), 3.70 (t, J = 9.0 Hz, 1H), 3.50 (ddd, J = 4.0, 5.1, 9.0 Hz, 1H), 2.57-2.40 (m, 2H), 1.52 (s, 3H), 1.41 (s, 3H), 1.22 (s, 9H); ¹³C NMR (CDCl₃, 100 MHz) δ 178.2, 108.9, 75.0, 74.9, 68.6, 64.4, 63.2, 62.7, 38.7, 27.1, 26.1, 24.4; IR (neat) 3477 (br m), 2102 (s), 1726 (s) cm⁻¹; MS (EI) m/z (rel int) 316 (M - CH₃, 5), 157 (44), 57 (100); HRMS (ES) calcd for C₁₄H₂₅N₃NaO₆ (M + Na) 354.1641, found 354.1635.

The title compound was then prepared by the method of Wolfrom for the formation of acetonides. 2-Methoxypropene (3.37 mL, 2.53 g, 35.1 mmol) and para-toluenesulfonic acid (563 mg, 2.96 mmol) were added to a solution of intermediate diol (5.82 g, 17.6 mmol) in CH₂Cl₂ (60 mL) at room temperature and stirred 15 minutes. The reaction was quenched with water and extracted with CH₂Cl₂. The combined organic
phases were washed with brine, dried (MgSO₄) and concentrated to yield 6.34 g (97%) of
the title compound as a yellow oil. The crude material was sufficiently pure for
characterization. Data for 20: Rₒ = 0.81 (30% EtOAc / hexanes); [α]²³D = -72.7° (c =
1.16, CH₂Cl₂); ¹H NMR (benzene-d₆, 400 MHz) δ4.46 (dd, J = 6.6, 10.6 Hz, 1H), 4.32
(td, J = 4.8, 6.6 Hz, 1H), 4.27 (dd, J = 4.8, 10.6 Hz, 1H), 4.18, (dd, J = 1.1, 6.6 Hz, 1H),
3.66 (td, J = 5.5, 9.5 Hz, 1H), 3.59 (dd, J = 5.5, 11.2 Hz, 1H), 3.38 (dd, J = 1.1, 9.5 Hz,
1H), 3.35 (dd, J = 9.5, 11.2, Hz, 1H), 1.54 (s, 3H), 1.25 (s, 3H), 1.24 (s, 3H), 1.16 (s, 9H),
1.12 (s, 3H); ¹³C NMR (benzene-d₆, 100 MHz) δ177.6, 109.8, 98.9, 75.2, 75.0, 71.5, 63.6,
62.2, 54.9, 38.7, 28.4, 27.2, 26.7, 25.7, 18.8; IR (neat) 2110 (s), 1733 (s) cm⁻¹; MS (EI)
ₘ/z (rel int) 356 (M - CH₃, 22), 157 (49), 57 (100); HRMS (ES) calcd for C₁₇H₂₀N₃NaO₆
(M + Na) 394.1954, found 394.1955.

(4a R, 6S, 7S, 8R, 8aS)-8-Benzyl-8-methoxy-6-phénylhexahydropyrano-
[3,2-δ][1,3]-dioxin-7-ylamine  (Methyl 2-amino-3-benzyl-4,6-benzylidenedioxy-
2-deoxy-α-D-mannopyranoside) (32). Lithium aluminum hydride (69 mg, 1.8 mmol)
was added to a solution of known methyl 2-azido-3-O-benzyl-4,6-O-benzylidene-2-
deoxy-α-D-mannopyranoside 36² (362 mg, 0.910 mmol) in ether (18 mL) at 0 °C and
stirred for 3 hours. The reaction was quenched with successive addition of water (69 µL),
10% NaOH (69 µL) and water (138 µL), the ether poured off, and the solid extracted
with EtOAc. The combined organic phases were dried (Na₂SO₄) and concentrated to

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yield 327 mg (97%) of the title compound as a clear oil. The crude material was sufficiently pure for characterization. Data for 32: R\_f = 0.20 (100% EtOAc); [\alpha]^{23D} = 35.0° (c = 0.98, CH\_2Cl\_2); \textsuperscript{1}H NMR (CDCl\_3, 400 MHz) \(\delta\) 7.52-7.46 (m, 2H), 7.40-7.23 (m, 8H), 5.60 (s, 1H), 4.74 (ABq, J = 12.1, \Delta\nu = 49.7 Hz, 2H), 4.65 (d, J = 1.1 Hz, 1H), 4.30-4.22 (m, 1H), 4.06-4.00 (m, 1H), 3.91 (dd, J = 4.4, 9.9 Hz, 1H), 3.87-3.79 (m, 2H), 3.39 (dd, J = 1.1, 4.4 Hz, 1H), 3.35 (s, 3H), 1.54 (br s, 2H); \textsuperscript{13}C NMR (CDCl\_3, 100 MHz) \(\delta\) 138.4, 137.5, 128.8, 128.3, 128.1, 127.6, 126.0, 102.8, 101.5, 78.7, 75.5, 72.6, 68.9, 63.4, 54.8, 53.5; IR (neat) 3385 (w), 1095 (vs) cm\(^{-1}\); MS (EI) m/z (rel int) 340 (M - OMe, 3), 248 (3), 149 (30), 120 (39), 91 (100); HRMS (ES) calcd for C\textsubscript{21}H\textsubscript{25}N\textsubscript{3}NaO\textsubscript{5} (M + Na) 394.1630, found 394.1624.

(4a \textit{R}, 6\textit{S}, 7\textit{S}, 8\textit{R}, 8\textit{aS})-N-(8-Benzylxoy-6-methoxy-2-phenylhexahydro-pyrano-[3,2-\textit{d}] [1,3]-dioxin-7-yl)-2'-azidoacetamide [Methyl 2-(2'-azidoacetamido)-3-benzylxoy-4,6-benzylidenedioxy-2-deoxy-\textalpha-D-mannopyranoside] (40). 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (94 mg, 0.49 mmol) was added to a solution of 2-azidoacetic acid\textsuperscript{1} (42 mg, 0.42 mmol) and amine 32 (130 mg, 0.350 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (1.8 mL) at room temperature and stirred for 30 minutes. The reaction was then diluted with CH\textsubscript{2}Cl\textsubscript{2}, washed with saturated aqueous ammonium chloride, water, 0.3M NaOH and brine, dried (MgSO\textsubscript{4}) and concentrated to yield 143 mg
(90%) of the title compound as a clear, foamy oil. The crude material was sufficiently pure for characterization. Data for 40: $R_f = 0.47$ (50% EtOAc / hexanes); $[\alpha]^{23}_D = -29.4^\circ$ ($c = 0.91$, CH$_2$Cl$_2$); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta 7.52$-$7.48$ (m, 2H), $7.42$-$7.24$ (m, 8H), 6.61 (br d, $J = 7.7$ Hz, 1H), 5.63 (s, 1H), 4.82 (d, $J = 1.5$ Hz, 1H), 4.66 (ABq, $J = 12.1$, $\Delta\nu = 23.9$ Hz, 2H), 4.57-4.34 (m, 1H), 4.31-4.26 (m, 3H), 4.02 (ABq, $J = 16.7$, $\Delta\nu = 10.4$ Hz, 2H), 4.90-3.72 (m, 3H), 3.36 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta 167.0$, 137.7, 137.2, 129.0, 128.3, 128.2, 127.7, 127.6, 126.0, 101.7, 100.2, 78.6, 72.9, 71.7, 68.7, 62.9, 55.1, 52.5, 50.9; IR (neat) 3401 (w), 3314 (m), 2108 (s), 1686 (m), 1662 (m), 1525 (s), 1101 (s) cm$^{-1}$; MS (El) m/z (rel int) 426 (M - N$_2$, 7), 149 (22), 91 (100); HRMS (ES) calcd for C$_{23}$H$_{26}$N$_4$NaO$_6$ (M + Na) 477.1750, found 477.1750.

![Structure of 41](image)

(41). 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (93 mg, 0.49 mmol) was added to a solution of 3-azidopropionic acid$^4$ (48 mg, 0.42 mmol) and amine 32 (130 mg, 0.349 mmol) in CH$_2$Cl$_2$ (1.8 mL) at room temperature and stirred for 30 minutes. The reaction was then diluted with CH$_2$Cl$_2$, washed with saturated aqueous
ammonium chloride, water, 0.3M NaOH and brine, dried (MgSO₄) and concentrated to yield 150 mg (92%) of the title compound as a clear, foamy oil. The crude material was sufficiently pure for characterization. Data for 41: R_f = 0.34 (50% EtOAc / hexanes); [α]_{D}^{23} = -14.5° (c = 0.83, CH₂Cl₂); ¹H NMR (CDCl₃, 400 MHz) δ7.52-7.48 (m, 2H), 7.42-7.24 (m, 8H), 6.05 (br d, J = 7.3 Hz, 1H), 5.60 (s, 1H), 4.82 (d, J = 1.1 Hz, 1H), 4.65 (ABq, J = 12.0, Δν = 30.5 Hz, 2H), 4.64-4.59 (m, 1H), 4.27 (dd, J = 4.1, 9.5 Hz, 1H), 4.09 (dd, J = 5.2, 9.9 Hz, 1H), 3.89-3.72 (m, 3H), 3.67-3.54 (m, 2H), 3.34 (s, 3H), 2.47 (t, J = 6.5 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ170.4, 137.7, 137.2, 128.9, 128.3, 128.1, 127.7, 127.6, 126.0, 101.7, 100.5, 78.6, 72.8, 71.5, 68.7, 62.8, 55.0, 50.9, 47.2, 35.7; IR (neat) 3311 (m), 2101 (s), 1648 (s), 1540 (s), 1101 (s) cm⁻¹; MS (EI) m/z (rel int) 437 (M - OMe, <1), 141 (35), 91 (100); HRMS (ES) calcd for C₂₄H₂₈N₄NaO₆ (M + Na) 491.1907, found 491.1912.

![Chemical structure](image)

(4a R, 6S, 7S, 8R, 8aS)-N-(8-Benzylloxy-6-methoxy-2-phenylhexahydropyrano-[3,2-d]-[1,3]-dioxin-7-yl)-4’-azidobutyramide [Methyl 2-(4’-azidobutyramido)-3-benzyloxy-4,6-benzylidenedioxy-2-deoxy-α-D-mannopyranoside] (42). 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (94 mg, 0.49 mmol) was added to a solution of 4-azidobutyric acid⁵ (54 mg, 0.42 mmol) and amine 32 (130 mg, 0.350 mmol) in CH₂Cl₂ (1.8 mL) at room temperature and stirred for 30 minutes. The
reaction was then diluted with CH$_2$Cl$_2$, washed with saturated aqueous ammonium chloride, water, 0.3M NaOH and brine, dried (MgSO$_4$) and concentrated to yield 157 mg (93%) of the title compound as a clear, foamy oil. The crude material was sufficiently pure for characterization. Data for 42: R$_f$ = 0.37 (50% EtOAc / hexanes); [$\alpha$]$^{23}_D$ = -18.2° (c = 0.86, CH$_2$Cl$_2$); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$7.52-7.48 (m, 2H), 7.42-7.24 (m, 8H), 5.87 (br d, J = 7.7 Hz, 1H), 5.61 (s, 1H), 4.80 (d, J = 0.6 Hz, 1H), 4.65 (ABq, J = 12.0, $\Delta$\nu = 25.4 Hz, 2H), 4.62-4.60 (m, 1H), 4.27 (dd, J = 4.0, 9.5 Hz, 1H), 4.08 (dd, J = 4.8, 9.9 Hz, 1H), 3.89-3.70 (m, 3H), 3.40-3.28 (m, 2H), 3.35 (s, 3H), 2.32 (t, J = 7.3 Hz, 2H), 1.95-1.83 (m, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$172.2, 137.7, 137.2, 128.9, 128.3, 128.1, 127.7, 127.7, 126.0, 101.7, 101.7, 100.7, 78.7, 73.0, 71.6, 68.8, 62.8, 55.0, 50.7, 50.4, 33.1, 24.7; IR (neat) 3307 (m), 2098 (s), 1647 (s), 1539 (s), 1102 (s) cm$^{-1}$; MS (EI) m/z (rel int) 454 (M - N$_2$, 2), 149 (24), 91 (100); HRMS (ES) calcd for C$_{25}$H$_{30}$N$_4$NaO$_6$ (M + Na) 505.2063, found 505.2065.

![Structure](image)

(4a $R$, 6$S$, 7$S$, 8$R$, 8a$S$)-2'-Amino-N-(8-benzyloxy-6-methoxy-2-phenylhexahydro-pyrano-[3,2-$d$]-[1,3]-dioxin-7-yl)-acetamide [Methyl 2-(2'-aminoacetamido)-3-benzyloxy-4,6-benzylidenedioxy-2-deoxy-$\alpha$-D-mannopyranoside] (33). 10% Palladium on carbon (15 mg) was added to a solution of the azide 40 (146 mg, 0.322 mmol) in EtOAc (8.0 mL) and stirred under a balloon of hydrogen at room temperature
for 20 hours. The reaction was then filtered through Celite and concentrated to yield 134 mg (97%) of the title compound as a clear oil. The crude material was sufficiently pure for characterization. Data for 33: \( R_f = 0.20 \) (10% MeOH / CH\(_2\)Cl\(_2\)); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \( \delta 7.76 \) (br d, \( J = 6.4 \) Hz, 1H), 7.52-7.48 (m, 2H), 7.41-7.22 (m, 8H), 5.62 (s, 1H), 4.79 (d, \( J = 0.7 \) Hz, 1H), 4.66 (ABq, \( J = 12.1 \), \( \Delta \nu = 39.3 \) Hz, 2H), 4.68-4.59 (m, 1H), 4.27 (dd, \( J = 3.7 \), 9.1 Hz, 1H), 4.10 (dd, \( J = 4.9 \), 9.7 Hz, 1H), 3.91-3.75 (m, 1H), 3.37 (s, 2H), 3.36 (s, 3H), 1.44 (s, 2H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \( \delta 173.2 \), 137.9, 137.3, 128.9, 128.3, 128.1, 127.7, 127.6, 126.0, 101.7, 100.9, 78.8, 73.2, 71.3, 68.8, 63.0, 55.0, 50.1, 44.7; IR (neat) 3328 (m), 1676 (s), 1515 (s), 1102 (s) cm\(^{-1}\); MS (EI) \( m/z \) (rel int) 428 (M\(^+\), 3), 397 (3), 290 (11), 248 (15), 149 (20), 91 (100); HRMS (ES) calcd for C\(_{23}\)H\(_{28}\)N\(_2\)NaO\(_6\) (M + Na) 451.1845, found 451.1848.

(4a \( R \), 6\( S \), 7\( S \), 8\( R \), 8a\( S \))-3’-Amino-N-(8-benzyloxy-6-methoxy-2-phenylhexahydro-pyano-[3,2-\( d \)]-[1,3]-dioxin-7-yl)-propionamide  [Methyl 2-(3’-amino-propionamido)-3-benzyloxy-4,6-benzylidenedioxy-2-deoxy-\( \alpha \)-D-mannopyranoside]

(34). 10% Palladium on carbon (20 mg) was added to a solution of the azide 41 (162 mg, 0.346 mmol) in EtOAc (8.0 mL) and stirred under a balloon of hydrogen at room temperature for 20 hours. The reaction was then filtered through Celite and concentrated to yield 151 mg (99%) of the title compound as a clear oil. The crude material was
sufficiently pure for characterization. Data for 34: R_f = 0.09 (10% MeOH / CH_2Cl_2); ^1H NMR (CDCl_3, 400 MHz) δ 7.90 (br d, J = 8.5 Hz, 1H), 7.52-7.48 (m, 2H), 7.41-7.22 (m, 8H), 5.60 (s, 1H), 4.76 (d, J = 0.7 Hz, 1H), 4.73-4.67 (m, 1H), 4.65 (ABq, J = 11.8, Δν = 39.0 Hz, 2H), 4.25 (dd, J = 4.2, 9.7 Hz, 1H), 4.06 (dd, J = 5.0, 9.8 Hz, 1H), 3.89-3.74 (m, 3H), 3.35 (s, 3H), 2.99 (t, J = 5.9 Hz, 2H), 2.36 (t, J = 5.9 Hz, 2H), 1.57 (br s, 2H); ^13C NMR (CDCl_3, 100 MHz) δ 173.1, 138.0, 137.3, 128.9, 128.3, 128.1, 127.7, 127.6, 126.1, 101.7, 101.2, 78.9, 73.2, 71.3, 68.9, 63.0, 55.0, 50.1, 38.3, 38.1; IR (neat) 3299 (w), 1652 (s), 1542 (s), 1101 (vs) cm^-1; MS (EI) m/z (rel int) 442 (M^+, 2), 411 (2), 351 (3), 248 (12), 91 (100); HRMS (ES) calcd for C_{24}H_{30}N_2NaO_6 (M + Na) 465.2002, found 465.2002.

![Chemical structure of compound 35](image)

(4a R , 6S , 7S , 8R , 8aS )-4’-Amino-N-(8-benzyloxy-6-methoxy-2-phenylhexahydro-pyrano-[3,2-d]-[1,3]-dioxin-7-yl)-butyramide  [Methyl 2-(4’-aminobutyramido)-3-benzyloxy-4,6-benzylidenedioxy-2-deoxy-α-D-mannopyranoside] (35). 10% Palladium on carbon (20 mg) was added to a solution of the azide 42 (164 mg, 0.340 mmol) in EtOAc (8.0 mL) and stirred under a balloon of hydrogen at room temperature for 20 hours. The reaction was then filtered through Celite and concentrated to yield 144 mg (93%) of the title compound as a clear oil. The crude material was sufficiently pure for characterization. Data for 35: R_f = 0.08 (10% MeOH / CH_2Cl_2); ^1H NMR (CDCl_3, 400 MHz) δ 7.52-7.48 (m, 2H), 7.41-7.22 (m, 8H), 6.63 (br d,
\[ J = 7.7 \text{ Hz, 1H}, \ 5.60 \ (s, \ 1H), \ 4.78 \ (d, \ J = 0.7 \text{ Hz}, \ 1H), \ 4.65-4.60 \ (m, \ 1H), \ 4.64 \ (\text{ABq, } J = 11.8, \ \Delta v = 32.0 \text{ Hz}, \ 2H), \ 4.26 \ (dd, \ J = 3.8, 9.7 \text{ Hz}, \ 1H), \ 4.09 \ (dd, \ J = 4.9, 9.7 \text{ Hz}, \ 1H), \ 3.89-3.74 \ (m, \ 3H), \ 3.35 \ (s, \ 3H), \ 2.76-2.62 \ (m, \ 2H), \ 1.82-1.67 \ (m, \ 2H), \ 1.33 \ (br s, \ 2H); \ \delta^{13}C \text{ NMR (CDCl}_3, \ 100 \text{ MHz}) \delta 173.4, \ 137.8, \ 137.3, \ 128.9, \ 128.3, \ 128.2, \ 127.7, \ 127.7, \ 126.0, \ 101.7, \ 101.7, \ 101.0, \ 78.7, \ 73.1, \ 71.5, \ 68.9, \ 62.9, \ 55.0, \ 50.5, \ 41.1, \ 34.1, \ 28.5; \ \text{IR (neat)} \ 3298 \ (w), \ 1651 \ (s), \ 1542 \ (s), \ 1101 \ (vs) \ \text{cm}^{-1}; \ \text{MS (EI) m/z (rel int)} \ 425 \ (M - \text{OMe, 2}), \ 413 \ (27), \ 381 \ (12), \ 149 \ (26), \ 91 \ (100); \ \text{HRMS (ES) calcd for } C_{25}H_{33}N_2O_6 (M+H) 457.2338, \ \text{found 457.2338.}

\begin{center}
\includegraphics[width=0.2\textwidth]{28b.png}
\end{center}

\textbf{28b}

(3aS, 3bS, 6bR, 10aR, 10bS)-2,2,9,9-Tetramethyl-1,3,8,10-tetraoxacyclohexa[e]-cyclopenta[g]-6-one-4-methylazaindolizidine (28b). Dimethyl sulfoxide (17 \mu L, 19 mg, 0.24 mmol) was added with stirring to a solution of oxalyl chloride (60 \mu L, 2.0 M solution in CH\textsubscript{2}Cl\textsubscript{2}, 0.12 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (1.4 mL) at -78 °C. After 30 minutes, a solution of alcohol 29 (37 mg, 0.11 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (0.8 mL) was added drop-wise and the reaction stirred at -78 °C for an additional 30 minutes. Triethylamine (75 \mu L, 55 mg, 0.54 mmol) was then added at -78 °C, the reaction stirred for a further 20 minutes, warmed to room temperature and concentrated to yield an oily, pale yellow solid. The residue was treated with 2.0 N MeNH\textsubscript{2}-MeOH (5.40 mL, 10.8 mmol MeNH\textsubscript{2}) and stirred for 14 hours at room temperature. The reaction was concentrated to yield an oily, yellow solid. Chromatography (2% MeOH / CH\textsubscript{2}Cl\textsubscript{2}) afforded 23 mg (68%) of the title
compound as a clear oil. Data for 28b: \( R_f = 0.52 \) (10% MeOH / CH\(_2\)Cl\(_2\)); \([\alpha]^{23}_D = -77.6^o \) (c = 1.02, CH\(_2\)Cl\(_2\)); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \( \delta \)4.81 (dd, \( J = 4.8, 11.0 \) Hz, 1H), 4.27 (t, \( J = 8.3 \) Hz, 1H), 4.10 (t, \( J = 8.3 \) Hz, 1H), 4.01 (d, \( J = 8.0 \) Hz, 1H), 4.02 (dd, \( J = 8.4, 11.4 \) Hz, 1H), 3.72 (t, \( J = 10.6 \) Hz, 1H), 3.51 (dd, \( J = 1.5, 14.6 \) Hz, 1H), 3.40 (td, \( J = 4.8, 10.8 \) Hz, 1H), 3.11 (d, \( J = 14.6 \) Hz, 1H), 2.55 (s, 3H), 1.53 (app d, \( J = 1.1 \) Hz, 6H), 1.46 (s, 3H), 1.36 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \( \delta \)172.2, 110.9, 99.6, 79.4, 78.6, 76.2, 71.2, 61.9, 57.6, 47.7, 41.3, 29.1, 26.7, 24.2, 19.0; IR (neat) 1713 (s) cm\(^{-1}\); MS (EI) \( m/z \) (rel int) 312 (M\(^+\), 12), 297 (19), 254 (33), 239 (25), 125 (100), 99 (72); HRMS (ES) calcd for C\(_{15}\)H\(_{25}\)N\(_2\)O\(_5\) (M+H) 313.1763, found 313.1761. Stereochemical assignment for 28b was determined based on COSY analysis and comparison of the observed \( J \)-coupling between \( H_8 \) (4.27 ppm, t, 8.3 Hz) and \( H_{8a} \) (4.01 ppm, d, 8.0 Hz) of approximately 8.2 Hz to those reported in the literature for the closely related structures kifunensine diacetonide (\( J \)-coupling between \( H_8 \) and \( H_{8a} \) of 8.0 Hz) and 8a-epi kifunensine diacetonide (\( J \)-coupling between \( H_8 \) and \( H_{8a} \) of 3.0 Hz).\(^6,7\)

![28c](image)

**(3aS, 3bS, 6bR, 10aR, 10bS)-2,2,9,9-Tetramethyl-1,3,8,10-tetraoxacyclohexa-[e]cyclopenta[g]-6-one-4-cyclohexylazaindolizidine** (28c). A solution of alcohol 29 (22 mg, 0.064 mmol) in CH\(_2\)Cl\(_2\) (0.3 mL) was added to a dry round bottom flask containing activated powdered 4Å molecular sieves (32 mg) followed by successive addition of \( N-\)
methylmorpholine-N-oxide (11 mg, 0.096 mmol) and tetra-n-propylammonium perruthenate (1 mg, 0.003 mmol). After stirring at room temperature for 30 minutes, the reaction was filtered through a short plug of silica with EtOAc, and the filtrate concentrated to give a white foamy oil. The residue was dissolved in MeOH (0.3 mL), 4Å molecular sieves, sodium methoxide (7 mg, 0.1 mmole) and cyclohexylamine (33 µL, 28 mg, 0.28 mmol) were added and the mixture heated to reflux with stirring for 20 hours. The reaction was then cooled to room temperature and concentrated to yield an oily, yellow solid. Chromatography (50% EtOAc / hexanes) afforded 6 mg (24%) of the title compound as a clear oil. Data for 28c: Rf = 0.76 (100% EtOAc); [α]$_{D}^{23}$ = -65.6° (c = 0.60, CH$_2$Cl$_2$); $^1$H NMR (CDCl$_3$, 400 MHz) δ4.60 (dd, J = 5.0, 10.9 Hz, 1H), 4.40 (d, J = 8.1 Hz, 1H), 4.23 (t, J = 8.1 Hz, 1H), 4.04 (dd, J = 8.1, 12.1 Hz, 1H), 3.67 (t, J = 10.6 Hz, 1H), 3.42 (ABq, J = 15.6, Δν = 24.2 Hz, 2H), 3.41-3.35 (m, 1H), 2.78-2.68 (m, 1H), 1.90-1.62 (m, 5H), 1.54 (s, 3H), 1.52 (s, 3H), 1.47 (s, 3H), 1.35 (s, 3H), 1.33-1.04 (m, 5H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ173.9, 110.6, 99.7, 79.1, 76.2, 73.8, 71.1, 62.3, 59.7, 49.8, 47.9, 31.4, 29.2, 26.9, 26.7, 25.9, 25.8, 25.4, 24.1, 19.1; IR (neat) 1710 (s) cm$^{-1}$; MS (EI) m/z (rel int) 380 (M$^+$, 5), 365 (11), 322 (20), 307 (35), 193 (100), 167 (67); HRMS (EI) calcd for C$_{20}$H$_{32}$N$_2$O$_5$ (M$^+$) 380.2311, found 380.2300. Stereochemical assignment for 28c was determined based on COSY analysis and comparison of the observed J-coupling between H$_8$ (4.03 ppm, t, 8.1 Hz) and H$_{8a}$ (4.40 ppm, d, 8.1 Hz) to those reported in the literature for the closely related structures kifunensine diacetonide (J-coupling between H$_8$ and H$_{8a}$ of 8.0 Hz) and 8a-epi kifunensine diacetonide (J-coupling between H$_8$ and H$_{8a}$ of 3.0 Hz).$^{6,7}$
(3aS, 3bS, 6bR, 10aR, 10bS)-2,2,9,9-Tetramethyl-1,3,8,10-tetraoxacyclohexa-
[e]cyclopenta[g]-5,6-dione-4-methylazaindolizidine (30a). By an alternate method of
preparation for this known compound,\textsuperscript{7} Dess-Martin periodinane (94 mg, 0.22 mmol) was
added to a solution of alcohol 21 (49 mg, 0.15 mmol) in \( \text{CH}_2\text{Cl}_2 \) (3.0 mL) at room
temperature and stirred for 2 hours. The reaction was then diluted with ether (12 mL),
filtered through Celite and concentrated to yield a clear oil. The residue was dissolved in
2.0 N \( \text{MeNH}_2\text{-MeOH} \) (7.40 mL, 14.8 mmol \( \text{MeNH}_2 \)) and stirred at room temperature for
18 hours. The reaction was then concentrated to yield a yellow oil. Chromatography
(70\% EtOAc / hexanes) afforded 35 mg (72\%) of the title compound as a white solid. \(^1\text{H}
NMR and \(^{13}\text{C} \) NMR spectral data for 30a matched published reports.\textsuperscript{7}
oil. The residue was dissolved in CH$_2$Cl$_2$ (1.0 mL) with 4Å molecular sieves in a sealed tube. N,N-Diisopropylethylamine (21 µL, 15 mg, 0.12 mmol) and cyclohexylamine (14 µL, 12 mg, 0.12 mmol) were added and the reaction was heated to 60 °C with stirring for 17 hours. The reaction was then cooled to room temperature, filtered and concentrated to yield a brown oil. Chromatography (40% EtOAc / hexanes) afforded 13 mg (54%) of the title compound as a viscous, white oil. Data for 30b: $R_f = 0.69$ (100% EtOAc); $[\alpha]^{23}_D = -74.4^\circ$ (c = 0.59, CH$_2$Cl$_2$); $^1$H NMR (CDCl$_3$, 400 MHz) δ 4.81 (d, $J = 8.4$ Hz, 1H), 4.66 (dd, $J = 4.8, 11.0$ Hz, 1H), 4.35 (t, $J = 8.4$ Hz, 1H), 4.17 (dd, $J = 8.4, 11.0$ Hz, 1H), 3.98 (t, $J = 8.4$ Hz, 1H), 3.84 (tt, $J = 12.3$ Hz, 1H), 3.75 (t, $J = 10.7$ Hz, 1H), 3.59 (td, $J = 4.8, 10.8$ Hz, 1H), 2.16-1.96 (m, 2H), 1.89-1.65 (m, 5H), 1.60 (s, 3H), 1.56 (s, 3H), 1.49 (s, 3H), 1.39 (s, 3H), 1.38-1.13 (m, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 159.8, 157.1, 111.6, 100.1, 78.6, 75.8, 70.3, 67.3, 61.5, 55.1, 47.8, 29.8, 29.3, 29.0, 26.5, 25.8, 25.6, 25.0, 24.0, 19.0; IR (neat) 1719 (m), 1752 (s) cm$^{-1}$; MS (EI) $m/z$ (rel int) 394 (M$^+$, 3), 379 (19), 336 (16), 302 (22), 287 (36), 156 (100); HRMS (ES) calcd for C$_{20}$H$_{30}$N$_2$NaO$_6$ (M + Na) 417.2002, found 417.2004. Stereochemical assignment for 30b was determined based on COSY analysis and comparison of the observed $J$-coupling between H$_8$ (3.98 ppm, t, 8.4 Hz) and H$_{8a}$ (4.81 ppm, d, 8.4 Hz) to those reported in the literature for the closely related structures kifunensine diacetonide ($J$-coupling between H$_8$ and H$_{8a}$ of 8.0 Hz) and 8a-epi kifunensine diacetonide ($J$-coupling between H$_8$ and H$_{8a}$ of 3.0 Hz).
30c

(3aS, 3bS, 6bR, 10aR, 10bS)-N-(2,2,9,9-Tetramethyl-1,3,8,10-tetraoxacyclohexa-\[e\]cyclopenta[g]-5,6-dione-(2’,2’-Dimethyl[1’,3’]dioxan-5’-yl))-4-azaindolizidine (30c). Dess-Martin periodinane (69 mg, 0.16 mmol) was added to a solution of alcohol 21 (36 mg, 0.11 mmol) in CH₂Cl₂ (2.2 mL) at room temperature and stirred for 2 hours. The reaction was then diluted with ether (9 mL), filtered through Celite and concentrated to yield a clear oil. The residue was dissolved in CH₂Cl₂ (2.2 mL) and added to a sealed tube containing 2,2-dimethyl-[1,3]-dioxan-5-ylamine 31 (28 mg, 0.22 mmol). Triethylamine (45 µL, 33 mg, 0.32 mmol) and 4Å molecular sieves were added and the reaction heated to 60 °C with stirring for 16 hours. The reaction was then cooled to room temperature, filtered and concentrated to yield a brown oil. Chromatography (20% EtOAc / hexanes to 50% EtOAc / hexanes gradient) afforded 10 mg (22%) of the title compound as a white oil. Data for 30c: R_f = 0.68 (100% EtOAc); [α]_D^23 = -50.8° (c = 0.62, CH₂Cl₂); \(^1\)H NMR (CDCl₃, 400 MHz) δ4.71 (d, J = 8.3 Hz, 1H), 4.69-4.58 (m, 3H), 4.36 (t, J = 8.3 Hz, 1H), 4.16 (dd, J = 8.3, 11.4 Hz, 1H), 3.95 (t, J = 8.3 Hz, 1H), 3.86-3.81 (m, 1H), 3.79-3.71 (m, 2H), 3.59 (td, J = 4.7, 11.0 Hz, 1H), 1.63 (s, 3H), 1.61 (s, 3H), 1.56 (s, 3H), 1.49 (s, 3H), 1.44 (s, 3H), 1.39 (s, 3H); \(^13\)C NMR (CDCl₃, 100 MHz) δ158.9, 157.5, 112.3, 100.2, 98.4, 78.7, 75.8, 70.4, 68.1, 61.5, 59.3, 58.6, 49.2, 48.0, 29.0, 28.4, 26.6, 24.0, 19.0, 18.9; IR (neat) 1750 (s) cm⁻¹; MS (EI) m/z (rel int) 411 (M - CH₃, 71), 353 (43), 313 (91),156 (100); HRMS (ES) calcd for C_{20}H_{35}N₂NaO₈ (M + Na) 449.1900, found 449.1910. Stereochemical assignment for 30c was determined based on COSY analysis and comparison of the observed J-coupling between H₈ (3.95 ppm, t, 8.3 Hz) and H₈₉ (4.71 ppm, d, 8.3 Hz) to those reported in the
literature for the closely related structures kifunensine diacetonide (J-coupling between H₈ and H₈a of 8.0 Hz) and 8a-epi kifunensine diacetonide (J-coupling between H₈ and H₈a of 3.0 Hz).⁶ ⁷

![Chemical Structure](image)

30e

(3aS, 3bS, 6bR, 10aR, 10bS)-N-((2,2,9,9-Tetramethyl-1,3,8,10-tetraoxa-cyclohexa-[e]cyclopenta[g]-5,6-dione-[[4'a R, 6'S, 7'S, 8'R, 8'aS]-8'-benzyloxy-6'-methoxy-2'-phenylhexahydro-pyran-3',2'-[d]-[1',3']-dioxin-7'-ylacetamide-2''-yl])-4-azaindolizidine (30e). Dess-Martin periodinane (252 mg, 0.594 mmol) was added to a solution of alcohol 21 (152 mg, 0.457 mmol) in CH₂Cl₂ (9.0 mL) at room temperature and stirred for 1 hour. The reaction was then diluted with ether (36 mL), filtered through Celite and concentrated to yield a clear oil. The residue was dissolved in MeOH (6.0 mL) and added to a flask fitted with a condensor containing amine 32 (391 mg, 0.913 mmol). Triethylamine (191 µL, 55.4 mg, 0.547 mmol) and 4 Å molecular sieves were added and the reaction was heated to reflux with stirring for 22 hours. The reaction was then cooled to room temperature, filtered through Celite, and concentrated to yield a foamy, yellow oil. Chromatography (80% EtOAc / hexanes) gave 178 mg of a yellow oil that was determined to be impure product by ¹H NMR. This was further purified by normal phase HPLC (80% EtOAc / hexanes, 10 mL/min, tᵣ = 20.8 min) to afford 111 mg (34%) of the title compound as a white oil. Data for 30e: Rᵣ = 0.42 (90% EtOAc /
hexanes); $[\alpha]_D^{23} = -30.1^\circ \ (c = 0.86, \text{CH}_2\text{Cl}_2)$; $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.52-7.48 (m, 2H), 7.42-7.26 (m, 8H), 6.39 (d, $J = 7.3$ Hz, 1H), 5.66 (s, 1H), 5.06 (d, $J = 8.8$ Hz, 1H), 4.81 (d, $J = 1.2$ Hz, 1H), 4.72 (dd, $J = 5.1$, 11.2 Hz, 1H), 4.67 (s, 2H), 4.52-4.47 (m, 1H), 4.39 (ABq, $J = 16.2$, $\Delta \nu = 100.0$ Hz, 2H), 4.26-4.13 (m, 3H), 4.08 (dd, $J = 4.9$, 9.3 Hz, 1H), 3.95 (t, $J = 8.2$ Hz, 1H), 3.87-3.80 (m, 3H), 3.77 (t, $J = 10.8$ Hz, 1H), 3.52 (td, $J = 4.7$, 10.4 Hz, 1H), 3.35 (s, 3H), 1.53 (s, 3H), 1.48 (s, 3H), 1.44 (s, 3H), 1.28 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 167.0, 158.6, 158.3, 137.9, 137.3, 129.0, 128.4, 128.2, 127.8, 127.5, 126.1, 112.2, 101.6, 100.1, 78.8, 77.9, 77.2, 75.9, 73.0, 72.0, 70.6, 68.7, 68.2, 62.9, 61.5, 55.1, 51.7, 47.9, 44.8, 29.0, 26.5, 24.3, 18.9; IR (neat) 3341 (br w), 1754 (s), 1689 (m), 1092 (s) cm$^{-1}$; MS (EI) $m/z$ (rel int) 723 (M$^+$, 6), 708 (7), 665 (25), 353 (9), 91 (100); HRMS (ES) calcd for C$_{37}$H$_{45}$N$_3$NaO$_{12}$ (M + Na) 746.2901, found 746.2913.

Stereochemical assignment for 30e was determined based on COSY analysis and comparison of the observed $J$-coupling between H$_8$ (3.95 ppm, t, 8.2 Hz) and H$_{8a}$ (5.06 ppm, d, 8.8 Hz) of approximately 8.5 Hz to those reported in the literature for the closely related structures kifunensine diacetonide ($J$-coupling between H$_8$ and H$_{8a}$ of 8.0 Hz) and 8a-epi kifunensine diacetonide ($J$-coupling between H$_8$ and H$_{8a}$ of 3.0 Hz).$^6,7$

![Structure 30f]

(3aS, 3bS, 6bR, 10aR, 10bS)-N-(2,2,9,9-Tetramethyl-1,3,8,10-tetraoxa-cyclohexa-[e]cyclopenta[g]-5,6-dione-[[4'a R, 6'S, 7'S, 8'R, 8'aS]-8'-benzyloxy-6'-}
methoxy-2'-phenylhexahydro-pyrano-[3',2'-d]-[1',3']-dioxin-7'-ylpropionamide-3”-yl])-4-azaindolizidine (30f). Dess-Martin periodinane (111 mg, 0.261 mmol) was added to a solution of alcohol 21 (67 mg, 0.20 mmol) in CH₂Cl₂ (4.0 mL) at room temperature and stirred for 1.5 hours. The reaction was then diluted with ether (16 mL), filtered through Celite and concentrated to yield a clear oil. The residue was dissolved in MeOH (2.0 mL) and added to a flask fitted with a condensor containing amine 33 (172 mg, 0.390 mmole). Triethylamine (84 µL, 61 mg, 0.60 mmol) and 4 Å molecular sieves were added and the reaction was heated to reflux with stirring for 17 hours. The reaction was then cooled to room temperature, filtered through Celite, and concentrated to yield a brown oil. Chromatography (80% EtOAc / hexanes) gave 77 mg of a yellow oil that was determined to be impure product by ¹H NMR. This was further purified by normal phase HPLC (85% EtOAc / hexanes, 10 mL/min, tᵣ = 25.2 min) to afford 50 mg (34%) of the title compound as a white oil. Data for 30f: Rₛ = 0.37 (90% EtOAc / hexanes); [α]ᵣ²³ = -21.8° (c = 0.41, CH₂Cl₂); ¹H NMR (CDCl₃, 500 MHz) δ 7.52-7.48 (m, 2H), 7.41-7.26 (m, 8H), 6.39 (br s, 1H), 5.64 (s, 1H), 4.86 (d, J = 8.6 Hz, 1H), 4.76 (d, J = 1.0 Hz, 1H), 4.70-4.62 (m, 1H), 4.66 (ABq, J = 12.3, Δν = 20.0 Hz, 2H), 4.53-4.50 (m, 1H), 4.27-4.21 (m, 2H), 4.16 (dd, J = 8.3, 11.2 Hz, 1H), 4.07 (dd, J = 5.0, 9.7 Hz, 1H), 3.98-3.79 (m, 6H), 3.76 (t, J = 10.6 Hz, 1H), 3.52 (td, J = 4.7, 10.6 Hz, 1H), 3.35 (s, 3H), 2.91 (ddd, 6.4, 8.3, 14.9 Hz, 1H), 2.66-2.59 (m, 1H), 1.60 (s, 3H), 1.54 (s, 3H), 1.48 (s, 3H), 1.34 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 170.6, 159.1, 158.2, 138.0, 137.4, 128.9, 128.4, 128.2, 127.7, 127.5, 126.1, 112.1, 101.5, 100.4, 100.1, 78.3, 78.3, 77.2, 75.8, 73.1, 71.8, 70.6, 68.6, 68.2, 63.2, 61.6, 55.0, 51.3, 47.9, 39.3, 34.0, 29.0, 26.6, 24.2, 19.1; IR (neat) 3351 (br w), 1749 (s), 1677 (m), 1090 (s) cm⁻¹; MS (EI) m/z (rel int) 737 (M⁺, 5), 722 (8), 542 (11),
367 (52), 149 (38), 91 (100); HRMS (ES) calcd for C_{38}H_{47}N_{3}NaO_{12} (M + Na) 760.3057, found 760.3056. Stereochemical assignment for 30f was determined based on COSY analysis and comparison of the observed J-coupling between H\textsubscript{8} (3.98-3.79 ppm, m) and H\textsubscript{8a} (4.86 ppm, d, 8.6 Hz) of approximately 8.6 Hz to those reported in the literature for the closely related structures kifunensine diacetonide (J-coupling between H\textsubscript{8} and H\textsubscript{8a} of 8.0 Hz) and 8a-epi kifunensine diacetonide (J-coupling between H\textsubscript{8} and H\textsubscript{8a} of 3.0 Hz).\textsuperscript{6,7}

\begin{center}
30g
\end{center}

\((3aS, 3bS, 6bR, 10aR, 10bS)-N-(2,2,9,9-Tetramethyl-1,3,8,10-tetraoxa-cyclohexa-[e]cyclopenta[g]-5,6-dione-\{[4′a R, 6′S, 7′S, 8′R, 8′aS]-8′-benzyloxy-6′-methoxy-2′-phenylhexahydro-pyra-no-[3′,2′-d]-1′,3′-dioxin-7′-ylbutyramide-4′-yl\})-4-azaindolizidine (30g). Dess-Martin periodinane (51 mg, 0.12 mmol) was added to a solution of alcohol 21 (31 mg, 0.092 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (1.8 mL) at room temperature and stirred for 2.0 hours. The reaction was then diluted with ether, filtered through Celite and concentrated to yield a clear oil. The residue was dissolved in CH\textsubscript{2}Cl\textsubscript{2} (1.5 mL) and added to a sealed tube containing amine 34 (84 mg, 0.18 mmole). Triethylamine (39 µL, 28 mg, 0.28 mmol) and 4 Å molecular sieves were added and the reaction was stirred at 60 °C for 16 hours. The reaction was then cooled to room temperature, filtered through Celite, and concentrated to yield a brown oil. Chromatography (90% EtOAc / hexanes)
gave 38 mg of a milky oil that was determined to be impure product by $^1$H NMR. This was further purified by normal phase HPLC (95% EtOAc / hexanes, 10 mL/min, $t_R = 23.7$ min) to afford 23 mg (33%) of the title compound as a white oil. Data for 30g: $R_f = 0.36$ (100% EtOAc); $\left[\alpha\right]^{23}_D = -54.8^\circ$ (c = 0.63, CH$_2$Cl$_2$); $^1$H NMR (CDCl$_3$, 500 MHz) δ7.52-7.48 (m, 2H), 7.41-7.26 (m, 8H), 6.66 (d, $J = 8.5$ Hz, 1H), 5.63 (s, 1H), 4.82 (d, $J = 8.6$ Hz, 1H), 4.74 (d, $J = 1.0$ Hz, 1H), 4.70-4.65 (m, 1H), 4.66 (ABq, $J = 11.8$, $\Delta\nu = 28.4$ Hz, 2H), 4.64-4.61 (m, 1H), 4.30 (t, $J = 8.2$ Hz, 1H), 4.24 (dd, $J = 4.4$, 9.8 Hz, 1H), 4.19 (dd, $J = 8.3$, 11.2 Hz, 1H), 4.06 (dd, $J = 4.6$, 10.0 Hz, 1H), 3.97-3.84 (m, 4H), 3.83 (dd, $J = 4.2$, 9.4 Hz, 1H), 3.78 (t, $J = 10.7$ Hz, 1H), 3.35 (s, 3H), 2.28 (t, 6.7 Hz, 2H), 2.08-1.98 (m, 1H), 1.97-1.88 (m, 1H), 1.58 (s, 3H), 1.56 (s, 3H), 1.49 (s, 3H), 1.34 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ172.3, 159.1, 158.4, 138.2, 137.5, 128.9, 128.2, 128.1, 127.6, 127.5, 126.1, 112.0, 101.6, 100.9, 100.2, 78.5, 78.0, 75.8, 73.3, 71.5, 70.6, 68.8, 67.1, 63.2, 61.5, 54.9, 50.6, 47.9, 41.3, 33.7, 29.0, 26.5, 24.1, 23.9, 19.0; IR (neat) 3346 (br w), 1748 (s), 1675 (m), 1090 (s) cm$^{-1}$; MS (EI) m/z (rel int) 751 (M$,^+$, 5), 736 (12), 542 (11), 381 (35), 149 (28), 91 (100); HRMS (ES) calcd for C$_{39}$H$_{49}$N$_3$NaO$_{12}$ (M + Na) 774.3214, found 774.3228.

Stereochemical assignment for 30g was determined based on COSY analysis and comparison of the observed $J$-coupling between H$_8$ (3.97-3.84 ppm, m) and H$_{8a}$ (4.82 ppm, d, 8.6 Hz) of approximately 8.6 Hz to those reported in the literature for the closely related structures kifunensine diacetonide ($J$-coupling between H$_8$ and H$_{8a}$ of 8.0 Hz) and 8a-epi kifunensine diacetonide ($J$-coupling between H$_8$ and H$_{8a}$ of 3.0 Hz).$^{6,7}$
**(5R, 6R, 7S, 8S, 8aS)-6,7,8-trihydroxy-5-hydroxymethyl-1-methylhexahydroimidazo[1,2-a]pyridine-2,3-dione (4).** By an alternate method of preparation for this known compound a solution of 30a (10 mg, 0.030 mmol) in THF (0.3 mL) was treated with 1N HCl (0.3 mL) and stirred at room temperature for 3 hours. The reaction was then concentrated to yield 7 mg (97%) of the title compound as a white solid. The crude material was sufficiently pure for characterization and $^1$H NMR and $^{13}$C NMR spectral data for 4 matched published reports.

**(5R, 6R, 7S, 8S, 8aS)-1-Cyclohexyl-6,7,8-trihydroxy-5-hydroxymethylhexahydroimidazo[1,2-a]pyridine-2,3-dione (5).** A solution of 30b (40 mg, 0.10 mmol) in THF (1.0 mL) was treated with 1N HCl (1.0 mL) and stirred at room temperature for 3 hours. The reaction was then concentrated to give an oily white solid. Reverse phase HPLC (55% CH$_3$CN / H$_2$O, 1.5 mL/min, $t_r = 24$ min) afforded 24 mg (77%) of the title compound as an amorphous white solid. Data for 5: R$_f$ = 0.29 (10% MeOH / CH$_2$Cl$_2$); [$\alpha$]$_D^{23}$ = 22.3° (c = 0.81, MeOH); $^1$H NMR (CD$_3$OD, 400 MHz) $\delta$4.97 (d, $J = 8.8$ Hz, 1H), 4.40 (dd, $J = 4.8$, 8.8 Hz, 1H), 4.02-3.85 (m, 4H), 3.73 (dd, $J = 4.8$, 12.1 Hz, 1H), 3.63 (dd, $J = 2.9$, 8.8 Hz, 1H), 2.35-2.17 (m, 2H), 1.95-1.76 (m, 4H), 1.67
(br d, $J = 11.4$ Hz, 1H), 1.38-1.18 (m, 3H); $^{13}$C NMR (CD$_3$OD, 100 MHz) $\delta$161.1, 160.3, 74.3, 74.0, 70.7, 68.2, 61.8, 60.3, 58.3, 30.7, 29.9, 27.3, 27.1, 26.5; IR (MeOH) 1726 (s) cm$^{-1}$; MS (EI) $m/z$ (rel int) 314 (M$^+$, 29), 296 (31), 278 (26), 255 (84), 55 (100); HRMS (ES) calcd for C$_{14}$H$_{22}$N$_2$O$_6$ (M$^+$) 314.1478, found 314.1481.

<Chemical Structure Image>

(5R, 6R, 7S, 8S, 8aS)-6,7,8-Trihydroxy-1-(2'-hydroxy-1'-hydroxymethyl-ethyl)-5-hydroxymethylhexahydroimidazo[1,2-a]pyridine-2,3-dione (6). A solution of 30c (16 mg, 0.038 mmol) in THF (0.4 mL) was treated with 1N HCl (0.4 mL) and stirred at room temperature for 2.5 hours. The reaction was then concentrated to give a clear, foamy oil. Reverse phase HPLC (37% CH$_3$CN / H$_2$O, 1.5 mL/min, $t_R = 15.5$ min) afforded 9 mg (100%) of the title compound as a clear, foamy oil. Data for 6: R$_f$ = 0.32 (10% MeOH / CH$_2$Cl$_2$); $[\alpha]_D^{23}$ = 32.5° ($c = 0.35$, MeOH); $^1$H NMR (CD$_3$OD, 500 MHz) $\delta$5.01 (d, $J = 8.8$ Hz, 1H), 4.41 (dd, $J = 5.1, 9.1$ Hz, 1H), 4.24-4.18 (m, 1H), 4.15-4.08 (m, 2H), 4.00 (dd, $J = 1.0, 3.6$ Hz, 1H), 3.97 (dd, $J = 9.1, 12.0$ Hz, 1H), 3.93 (t, $J = 3.2$ Hz, 1H), 3.89 (dd, $J = 5.2, 11.0$ Hz, 1H), 3.80 (dd, $J = 4.9, 11.3$ Hz, 1H), 3.73 (dd $J = 5.1, 12.0$ Hz, 1H), 3.70 (dd, $J = 2.9, 8.8$ Hz, 1H); $^{13}$C NMR (CD$_3$OD, 100 MHz) $\delta$161.1, 160.6, 74.3, 73.9, 70.6, 69.8, 63.1, 61.7, 60.5, 60.4, 60.1; IR (MeOH) 1731 (s) cm$^{-1}$; MS (EI) $m/z$ (rel int) 288 (M - H$_2$O, 27), 270 (100), 197 (95); HRMS (ES) calcd for C$_{11}$H$_{18}$N$_2$NaO$_6$ (M + Na) 329.0961, found 329.0957.
(5R, 6R, 7S, 8S, 8aS)-6,7,8-Trihydroxy-5-hydroxymethylhexahydroimidazo-[1,2-a]pyridine-3-one (2). A solution of 28a (16.9 mg, 0.0566 mmol) in THF (0.6 mL) was treated with 1N HCl (0.6 mL) and stirred at room temperature for 3 hours. The reaction was then concentrated to give a foamy, off-white oil. The residue was redissolved in MeOH (0.5 mL), passed through a short column of Dowex 1x8-200 mesh anion exchange resin (OH- form) (1.0 g) with MeOH, and concentrated to give 11 mg (91%) of the title compound as a clear oil. Data for 2: Rf = 0.10 (10% MeOH / CH2Cl2); [α]23D = 25.5° (c = 0.13, H2O); 1H NMR (CD3OD, 400 MHz) δ 4.69 (d, J = 9.3 Hz, 1H), 4.15 (m, 1H), 3.97 (d, J = 1.1, 3.6 Hz, 1H), 3.94-3.91 (m, 1H), 3.85 (dd, J = 7.6, 11.6 Hz, 1H), 3.73 (dd, J = 5.7, 11.6 Hz, 1H), 3.60 (dd, J = 3.2, 9.3 Hz, 1H), 3.54 (d, J = 15.9 Hz, 1H), 3.41 (dd, J = 1.4, 15.9 Hz, 1H); 13C NMR (D2O, 100 MHz) δ 167.9, 71.1, 69.4, 68.2, 66.7, 59.2, 58.6, 45.2; IR (MeOH) 1708 (s) cm⁻¹; MS (El) m/z (rel int) 201 (M - OH, 7), 85 (100); HRMS (ES) calcd for C8H14N2NaO5 (M + Na) 241.0800, found 241.0806.

(5R, 6R, 7S, 8S, 8aS)-6,7,8-Trihydroxy-5-hydroxymethyl-1-methylhexahydroimidazo[1,2-a]pyridine-3-one (3). A solution of 28b (22 mg, 0.072 mmol) in THF (0.7 mL) was treated with 1N HCl (0.7 mL) and stirred at room temperature for 3 hours.
reaction was then concentrated to give a foamy brown oil. The residue was redissolved in MeOH (0.5 mL), passed through a short column of Dowex 1x8-200 mesh anion exchange resin (OH- form) (1.0 g) with MeOH, and concentrated to yield 16 mg (96%) of the title compound as a clear oil. Data for 3: R$_f$ = 0.30 (10% MeOH / CH$_2$Cl$_2$); [$\alpha$]$^{23}_D$ = 22.7° (c = 0.73, MeOH); $^1$H NMR (CD$_3$OD, 400 MHz) $\delta$4.90-4.12 (m, 2H), 3.97 (dd, J = 1.1, 3.6 Hz, 1H), 3.87 (t, J = 3.6 Hz, 1H), 3.82 (dd, J = 7.2,11.7 Hz, 1H), 3.73 (dd, J = 5.9, 11.7 Hz, 1H), 3.69 (dd, J = 2.9, 8.4 Hz, 1H), 3.56 (dd, J = 1.8, 15.0 Hz, 1H), 3.17 (dd, J = 1.5, 15.0 Hz, 1H), 2.62 (s, 3H); $^{13}$C NMR (CD$_3$OD, 100 MHz) $\delta$173.5, 79.0, 73.7, 72.9, 70.7, 62.1, 59.2, 59.0, 43.4; IR (MeOH) 1680 (s) cm$^{-1}$; MS (EI) m/z (rel int) 232 (M$^+$, 7), 215 (25), 99 (100), 71 (23); HRMS (ES) calcd for C$_9$H$_{16}$N$_2$NaO$_5$ (M + Na) 255.0597, found 255.0597.

Sodium methoxide powder (10.7 mg, 0.243 mmol) was added to a solution of compound 44 (19 mg, 0.024 mmol) in MeOH (0.5 mL) and stirred at room temperature for 30 minutes. The reaction was then passed over a short column of Dowex 50Wx8-100 resin (pyridinium form), the product eluted with MeOH and concentrated to yield 12 mg (99%)
of the title compound as a clear oil. Data for 7: \( R_f = 0.01 \) (30% MeOH / CH₂Cl₂); \( [\alpha]^{23}_D = 42.7^\circ \) (c = 0.54, MeOH); \(^1\)H NMR (CD₃OD, 500 MHz) \( \delta \) 8.03 (d, \( J = 9.2 \) Hz, 1H), 5.05 (d, \( J = 9.2 \) Hz, 1H), 4.60 (d, \( J = 1.0 \) Hz, 1H), 4.39 (dd, \( J = 4.6, 8.8 \) Hz, 1H), 4.31-4.26 (m, 1H), 4.20-4.12 (m, 1H), 4.06-3.96 (m, 3H), 3.91 (br t, \( J = 3.3 \) Hz, 1H), 3.88 (dd, \( J = 4.9, 9.6 \) Hz, 1H), 3.83-3.78 (m, 2H), 3.73 (dd, \( J = 4.8, 12.1 \) Hz, 1H), 3.67 (dd, \( J = 3.0, 9.1 \) Hz, 1H), 3.56 (t, \( J = 9.8 \) Hz, 1H), 3.48 (dt, \( J = 3.2, 9.8 \) Hz, 1H) 3.35 (s, 3H), 2.80-2.64 (m, 2H); \(^{13}\)C NMR (CD₃OD, 100 MHz) \( \delta \) 172.9, 159.5, 159.0, 100.3, 72.7, 72.4, 72.4, 69.5, 69.2, 67.0, 66.4, 61.0, 60.5, 58.9, 54.0, 53.0, 39.7, 33.9; IR (MeOH) 1734 (s), 1652 (m), 1061 (m) cm⁻¹; MS (ES) m/z (rel int) 502 (M + Na 100); HRMS (ES) calcd for C₁₈H₂₉N₃NaO₁₂ (M + Na) 402.1649, found 502.1652.

\[ \text{(5R, 6R, 7S, 8S, 8aS)-N-(6,7,8-Trihydroxy-5-hydroxymethyl-1-\{[1'S, 2'S, 3'R, 4'S, 5'R\}-3',4'-dihydroxy-5'-hydroxymethyl-1'-methoxytetrahydropyran-2'-ylbutyr-amide-4''-yl\})-hexahydroimidazo[1,2-\alpha]pyridine-2,3-dione (9).} \]

Sodium methoxide powder (5.6 mg, 0.128 mmol) was added to a solution of compound 45 (10 mg, 0.013 mmol) in MeOH (0.3 mL) and stirred at room temperature for 30 minutes. The reaction was then passed over a short column of Dowex 50Wx8-100 resin (pyridinium form), the product eluted with MeOH and concentrated to yield 6 mg (95%) of the title compound as a clear oil. Data for 9: \( R_f = 0.01 \) (30% MeOH / CH₂Cl₂); \( [\alpha]^{23}_D = 42.7^\circ \) (c = 0.54, MeOH); \(^1\)H NMR (CD₃OD, 500 MHz) \( \delta \) 8.03 (d, \( J = 9.2 \) Hz, 1H), 5.05 (d, \( J = 9.2 \) Hz, 1H), 4.60 (d, \( J = 1.0 \) Hz, 1H), 4.39 (dd, \( J = 4.6, 8.8 \) Hz, 1H), 4.31-4.26 (m, 1H), 4.20-4.12 (m, 1H), 4.06-3.96 (m, 3H), 3.91 (br t, \( J = 3.3 \) Hz, 1H), 3.88 (dd, \( J = 4.9, 9.6 \) Hz, 1H), 3.83-3.78 (m, 2H), 3.73 (dd, \( J = 4.8, 12.1 \) Hz, 1H), 3.67 (dd, \( J = 3.0, 9.1 \) Hz, 1H), 3.56 (t, \( J = 9.8 \) Hz, 1H), 3.48 (dt, \( J = 3.2, 9.8 \) Hz, 1H) 3.35 (s, 3H), 2.80-2.64 (m, 2H); \(^{13}\)C NMR (CD₃OD, 100 MHz) \( \delta \) 172.9, 159.5, 159.0, 100.3, 72.7, 72.4, 72.4, 69.5, 69.2, 67.0, 66.4, 61.0, 60.5, 58.9, 54.0, 53.0, 39.7, 33.9; IR (MeOH) 1734 (s), 1652 (m), 1061 (m) cm⁻¹; MS (ES) m/z (rel int) 502 (M + Na 100); HRMS (ES) calcd for C₁₈H₂₉N₃NaO₁₂ (M + Na) 402.1649, found 502.1652.
= 33.4° (c = 0.32, MeOH); \(^1\)H NMR (CD\(_3\)OD, 500 MHz) \(\delta\) 7.87 (d, \(J = 9.0\) Hz, 1H) 5.02 (d, \(J = 9.0\) Hz, 1H), 4.58 (d, \(J = 1.2\) Hz, 1H), 4.40 (dd, \(J = 5.1, 8.8\) Hz, 1H), 4.27 (ddd, \(J = 1.5, 4.7, 9.2\) Hz, 1H), 4.03-3.96 (m, 2H), 3.91 (t, \(J = 3.2\) Hz, 1H), 3.89-3.78 (m, 5H), 3.75 (dd, \(J = 5.0, 11.8\) Hz, 1H), 3.67 (dd, \(J = 3.2, 9.0\) Hz, 1H), 3.57 (t, \(J = 9.8\) Hz, 1H), 3.48 (dt, \(J = 3.6, 9.8\) Hz, 1H), 3.36 (s, 3H) 2.37-2.30 (m, 2H), 2.10-2.02 (m, 2H); \(^{13}\)C NMR (CD\(_3\)OD, 100 MHz) \(\delta\) 175.8, 161.0, 160.3, 101.8, 74.2, 73.8, 73.6, 71.1, 70.4, 68.4, 67.6, 62.4, 61.8, 60.1, 55.4, 54.4, 43.7, 34.1, 24.9; IR (MeOH) 1733 (s), 1651 (w), 1062 (m) cm\(^{-1}\); MS (El) \(m/z\) (rel int) 457 (M - 2 H\(_2\)O, <1), 355 (11), 151 (46), 135 (78), 121 (100); HRMS (ES) calcd for C\(_{19}\)H\(_{31}\)N\(_3\)NaO\(_{12}\) (M + Na) 516.1805, found 516.1810.

\[\text{(3aS, 3bS, 6bR, 10aR, 10bS)-N-(2,2,9,9-Tetramethyl-1,3,8,10-tetraoxacyclohexa-[e]cyclopenta[g]-5,6-dione-{6'-tert-butoxycarbonylamino}hexyl-1'-yl})-4-azaindolizidine (46).}\] Dess-Martin periodinane (98 mg, 0.23 mmol) was added to a solution of alcohol 21 (51 mg, 0.15 mmol) in CH\(_2\)Cl\(_2\) (3.0 mL) at room temperature and stirred for 5.5 hours. The reaction was then diluted with ether (12 mL), filtered through Celite and concentrated to yield a clear oil. The residue was dissolved in CH\(_2\)Cl\(_2\) (3.0 mL) and added to a sealed tube with 4Å molecular sieves. Triethylamine (64 \(\mu\)L, 46 mg, 0.46 mmol) and \(\text{tert-butyl N-(6-aminohexyl)carbamate hydrochloride (77 mg, 0.31 mmol)}\) were added and the reaction heated to 60 °C with stirring for 16 hours. The reaction was then cooled to room temperature, filtered and concentrated to yield a brown
oil. Chromatography (50% EtOAc / Hexanes) afforded 52 mg (66%) of the title compound as a clear oil. Data for 46: \( R_f = 0.66 \) (100% EtOAc); \( [\alpha]^23_D = -38.4^\circ \) (c = 0.94, \( \text{CH}_2\text{Cl}_2 \)); \(^1\)H NMR (\( \text{CDCl}_3 \), 500 MHz) \( \delta \) 4.78 (d, \( J = 8.6 \) Hz, 1H), 4.71 (dd, \( J = 5.1 \), 11.0 Hz, 1H), 4.61 (br s, 1H), 4.37 (t, \( J = 8.2 \) Hz, 1H), 4.21 (dd, \( J = 4.9 \), 10.7 Hz, 1H), 3.82-3.74 (m, 2H), 3.59 (td, \( J = 4.9 \), 10.7 Hz, 1H), 3.46 (ddd, \( J = 5.4 \), 8.7, 13.8 Hz, 1H), 3.13-3.06 (m, 2H), 1.74-1.30 (m, 8H), 1.57 (s, 6H), 1.49 (s, 3H), 1.44 (s, 9H), 1.38 (s, 3H); \(^{13}\)C NMR (\( \text{CDCl}_3 \), 100 MHz) \( \delta \) 159.5, 157.3, 156.0, 111.8, 100.0, 79.0, 78.1, 75.8, 70.5, 67.4, 61.5, 47.7, 42.0, 40.2, 29.8, 29.0, 28.3, 27.3, 26.5, 26.1, 26.1, 24.0, 19.0; IR (neat) 3369 (w), 1749 (s), 1717 (m), 1696 (m) cm\(^{-1}\); MS (EI) \( m/z \) (rel int) 496 (M - CH\(_3\), 2), 438 (12), 411 (24), 396 (17), 382 (17), 156 (100); HRMS (ES) calcd for C\(_{25}\)H\(_{41}\)N\(_3\)NaO\(_8\) (M + Na) 534.2791, found 534.2799. Stereochemical assignment for 46 was determined based on COSY analysis and comparison of the observed \( J \)-coupling between \( H_8 \) (4.04 ppm, t, 8.3 Hz) and \( H_{8a} \) (4.78 ppm, d, 8.6 Hz) of approximately 8.5 Hz to those reported in the literature for the closely related structures kifunensine diacetonide (\( J \)-coupling between \( H_8 \) and \( H_{8a} \) of 8.0 Hz) and 8a-epi kifunensine diacetonide (\( J \)-coupling between \( H_8 \) and \( H_{8a} \) of 3.0 Hz).\(^6,7\)

![Structure of 48](image)

\( (5R, 6R, 7S, 8S, 8aS)-6,7,8-\text{Triacetoxy}-5-\text{acetoxymethyl-1-(6'-acetylamino-hexyl)-hexahydroimidazo[1,2-\alpha]pyridine-2,3-dione (48).} \) Acetic anhydride (67 µL, 667 mg, 0.66 mmol) and triethylamine (91 µL, 66 mg, 0.66 mmol) were added to a solution of 47 (24 mg, 0.066 mmol) in DMF (0.6 mL) and stirred at room temperature for
20 hours. The reaction was then concentrated to yield a brown oil. Chromatography (2% MeOH / CH₂Cl₂ to 4% MeOH / CH₂Cl₂ gradient) afforded 25 mg (69%) of the title compound as a clear oil. Data for 48: Rf = 0.46 (10% MeOH / CH₂Cl₂); ¹H NMR (CDCl₃, 400 MHz) δ5.66 (br s, 1H), 5.42 (t, J = 3.5 Hz, 2H), 5.13 (d, J = 9.5 Hz, 1H), 5.00 (d, J = 3.6 Hz, 1H), 4.86 (dd, J = 3.1, 9.4 Hz, 1H), 4.75-4.66 (m, 2H), 4.09 (dd, J = 10.7, 17.3 Hz, 1H), 3.79-3.70 (m, 1H), 3.28-3.12 (m, 3H), 2.16 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 1.98 (s, 3H), 1.92 (s, 3H), 1.73-1.61 (m, 1H), 1.57-1.40 (m, 3H), 1.38-1.21 (m, 4H); ¹³C NMR (CDCl₃, 100 MHz) δ170.9, 170.1, 168.9, 168.7, 168.6, 157.6, 157.5, 72.5, 67.1, 67.0, 62.9, 60.1, 52.4, 42.8, 39.0, 29.3, 27.4, 26.0, 25.9, 23.3, 20.7, 20.6, 20.6, 20.6; IR (neat) 3353 (br w), 1749 (s), 1663 (m), 1221 (s) cm⁻¹; MS (ES) m/z (rel int) 564 (M + Na, 100); HRMS (ES) calcd for C₂₄H₃₅N₃NaO₁₁ (M + Na) 564.2169, found 564.2171.

REFERENCES


