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Supporting Information for

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Total Syntheses of Vancomycin and Eremomycin Aglycons,
Angew. Chem. **1998**, *19*.

General Information. ^1H and ^{13}C NMR spectra were recorded on Bruker AM-500, AM-400, or DMX-500 spectrometers. Infrared spectra were recorded on a Perkin-Elmer 781 spectrometer. Optical rotations were measured with a Jasco DIP-0181 digital polarimeter. Mass spectra were obtained on a JEOL AX-505 or SX-102 spectrometer. Analytical chromatography was performed on EM Reagents 0.25 mm silica gel 60-F plates. Analytical HPLC was performed on a Hewlett Packard HP1090 and a Zorbax Rx-C8 column (MacMod Analytical) with UV monitoring at 240 nm. The nomenclature for proton resonances in polypeptide derivatives is analogous to that used in the literature for the vancomycin antibiotics (see, for example, *J. Med. Chem.* **1998**, *41*, 2090).

(4S)-3-[[[(4S,5R)-5-(4-fluoro-3-nitrophenyl)-2-thioxo(1,3-oxazolidin-4-yl)]carbonyl]-4-benzyl-1,3-oxazolidin-2-one (5a). TLC R_f = 0.42 (1:1 Hexanes/EtOAc); $[\alpha]^{25}_{\text{NaD}}$ = +94.9 (c = 1.47, EtOAc); IR (film) 3330, 3068, 1779, 1706, 1541, 1481, 1394, 1352, 1256, 1212, 1171 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , rt) δ 8.10 (dd, 1H, J = 6.8, 2.3 Hz, $\text{Ar6}_f\text{H}$), 7.75 (m, 1H, $\text{Ar6}_b\text{H}$), 7.59 (s, 1H, NH), 7.43-7.32 (m, 4H, 3 BnH and $\text{Ar6}_c\text{H}$), 7.20 (m, 2H, 2 BnH), 6.45 (d, 1H, J = 5.1 Hz, z_6H), 4.96 (dd, 1H, J = 5.2, 1.6 Hz, x_6H), 4.81 (m, 1H, NCHBn), 4.46-4.37 (m, 2H, OCHH), 3.24 (dd, 1H, J = 13.6, 3.6 Hz, PhCHH), 2.98 (dd, 1H, J = 13.6, 8.5 Hz, PhCHH); ^{13}C NMR (100 MHz, CDCl_3 , rt) δ 188.1, 165.4, 154.5, 153.8, 133.9, 133.7, 133.0, 132.9, 129.4, 129.3, 128.0, 123.9, 119.7, 119.5, 81.8, 67.9, 65.4, 55.3, 37.6; Exact mass calculated for $\text{M}+\text{Na}^+$, 468.0642, found: 468.0644 (FAB, *m*-nitrobenzyl alcohol and NaI added).

(4S)-3-[[[(4S,5R)-5-(3-chloro-4-fluoro-3-nitrophenyl)-2-thioxo(1,3-oxazolidin-4-yl)]carbonyl]-4-benzyl-1,3-oxazolidin-2-one (5b). TLC R_f = 0.44 (1:1 Hexanes/EtOAc); $[\alpha]^{25}_{\text{D}}$ = +93.1 (c = 1.13, DMSO); IR (KBr) 3312, 3094, 3030, 2972, 1778, 1709, 1618 cm^{-1} ; ^1H NMR (400 MHz, DMSO, rt) δ 10.75 (s, 1H, NH), 8.10 (dd, 1H, J = 6.3, 2.2 Hz, $\text{Ar6}_f\text{H}$), 7.95 (dd, 1H, J = 5.9, 2.2 Hz, $\text{Ar6}_b\text{H}$), 7.33-7.22 (m, 5H, BnH), 6.29 (d, 1H, J = 2.4 Hz, z_6H), 5.57 (d, 1H, J = 2.5 Hz, x_6H), 4.73 (ddt, 1H, J = 7.4, 8.8, 3.1 Hz, NCHBn), 4.44 (t, 1H, J = 8.7 Hz, OCHH), 4.30 (dd, 1H, J = 8.9, 3.2 Hz, OCHH), 3.06 (dd, 1H, J = 13.6, 3.2 Hz, PhCHH), 2.98 (dd, 1H, J = 13.6, 7.5 Hz, PhCHH); ^{13}C NMR (100 MHz, CDCl_3 , rt) δ 188.7, 167.9, 153.6, 152.4, 149.7, 137.9, 137.8, 135.23, 135.17, 133.9, 133.85, 129.6, 128.7, 127.0, 123.0, 122.8, 122.6, 81.6, 67.2, 63.3, 54.7, 36.1; Exact mass calculated for $\text{M}+\text{Na}^+$, 502.0254, found: 502.0252 (FAB, *m*-nitrobenzyl alcohol and NaI added).

***tert*-butyl 4-[[[(4S)-2-oxo-4-benzyl(1,3-oxazolidin-3-yl)]carbonyl](4S,5R)-5-(4-fluoro-3-nitrophenyl)-2-oxo-1,3-oxazolidine-3-carboxylate.** TLC R_f = 0.59 (10% EtOAc/ CH_2Cl_2); $[\alpha]^{25}_{\text{NaD}}$ = +63.8 (c = 1.84, CH_2Cl_2); IR (film) 3063, 2984, 2936, 1825, 1783, 1810, 1543, 1353, 1322, 1154, 1055 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , rt) δ 8.27 (dd, 1H, J = 6.8, 2.3 Hz, $\text{Ar6}_f\text{H}$), 7.84 (m, 1H, $\text{Ar6}_b\text{H}$), 7.40-7.25 (m, 6H, 5 BnH and $\text{Ar6}_c\text{H}$), 5.83 (d, 1H, J = 1.7 Hz, z_6H), 5.43 (d, 1H, J = 0.7 Hz, x_6H),

4.82 (m, 1H, NCHBn), 4.42 (dd, 1H, $J = 8.2, 8.2$ Hz, OCHH), 4.34 (dd, 1H, $J = 9.3, 3.5$ Hz, OCHH), 3.37 (dd, 1H, $J = 13.5, 3.2$ Hz, PhCHH), 2.84 (dd, 1H, $J = 13.4, 9.4$ Hz, PhCHH), 1.54, (s, 9H, Boc-CH₃); ¹³C NMR (100 MHz, CD₃OD, rt) δ 169.0, 158.1, 155.5, 155.4, 152.9, 150.4, 138.5, 136.3, 135.9, 135.8, 134.6, 134.5, 130.7, 130.2, 129.9, 129.88, 129.7, 128.3, 125.7, 120.3, 120.1, 86.2, 75.7, 68.8, 64.2, 61.4, 56.7, 38.0, 28.2, 20.9, 14.4; Exact mass calculated for M+Na⁺, 552.1394, found: 552.1378 (FAB, NaI added).

tert-butyl 4-[(4S)-2-oxo-4-benzyl(1,3-oxazolidin-3-yl)]carbonyl(4S,5R)-5-(3-chloro-4-fluoro-5-nitrophenyl)-2-oxo-1,3-oxazolidine-3-carboxylate. TLC R_f = 0.38 (3% EtOAc/CH₂Cl₂); [α]_D²⁵ = +81.5 (c = 1.54, CH₂Cl₂); IR (KBr) 3426, 3067, 2984, 2933, 1829, 1782, 1711, 1616, 1546 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, rt) δ 8.16 (dd, 1H, $J = 6.0, 2.3$ Hz, Ar6_fH), 7.93 (dd, 1H, $J = 5.8, 2.3$ Hz, Ar6_bH), 7.37-7.25 (m, 5H, BnH), 5.82 (d, 1H, $J = 1.4$ Hz, z₆H), 5.54 (s, 1H, x₆H), 4.87-4.81 (m, 1H, NCHBn), 4.47 (t, 1H, $J = 8.9$ Hz, OCHH), 4.33 (dd, 1H, $J = 9.2, 3.3$ Hz, OCHH), 3.37 (dd, 1H, $J = 13.4, 3.1$ Hz, PhCHH), 2.83 (dd, 1H, $J = 13.4, 9.5$ Hz, PhCHH), 1.51, (s, 9H, Boc-CH₃); ¹³C NMR (100 MHz, CD₃OD, rt) δ 167.1, 153.9, 153.2, 150.6, 150.5, 148.7, 138.4, 138.3, 134.3, 134.0, 133.9, 133.3, 129.4, 129.1, 127.7, 125.0, 124.8, 122.5, 85.6, 73.7, 67.7, 62.9, 55.5, 37.3, 27.8; Exact mass calculated for M+Na⁺, 586.1006, found: 586.1005 (FAB, NaI added).

tert-butyl 4-{N-[(1S)(3,5-dimethoxyphenyl)(N-methylcarbamoyl)methyl]carbamoyl} (4S,5R)-5-(4-fluoro-3-nitrophenyl)-2-oxo-1,3-oxazolidine-3-carboxylate (7a). TLC R_f = 0.33 (4% MeOH/CH₂Cl₂); [α]_D²⁵NaD = +80.5 (c = 1.68, CH₂Cl₂); IR (film) 3281, 3073, 2980, 2840, 1813, 1731, 1647, 1609, 1598, 1542, 1349, 1328, 1156, 1063, 840 cm⁻¹; ¹H NMR (400 MHz, CD₃OD, rt) δ 8.33 (dd, 1H, $J = 6.9, 2.3$ Hz, Ar6_fH), 7.93 (m, 1H, Ar6_bH), 7.54 (dd, 1H, $J = 10.8, 8.7$ Hz, Ar6_cH), 6.61 (d, 2H, $J = 2.3$ Hz, Ar7_bH), 6.41 (t, 1H, $J = 2.3$ Hz, Ar7_dH), 5.56 (d, 1H, $J = 5.4$ Hz, z₆H), 5.42 (s, 1H, x₇H), 4.79 (d, 1H, $J = 5.4$ Hz, x₆H), 3.74 (s, 6H, ArOCH₃), 2.73 (s, 3H, NHCH₃), 1.30 (s, 9H, Boc-CH₃); ¹³C NMR (100 MHz, CD₃OD, rt) δ 172.1, 169.2, 162.6, 158.2, 155.5, 153.1, 149.8, 139.9, 138.9, 138.8, 135.7, 135.7, 134.6, 134.5, 125.3, 120.4, 120.2, 107.1, 101.3, 85.9, 77.0, 64.9, 59.0, 55.8, 27.9, 26.5; Exact mass calculated for M+Na⁺, 599.1765 found: 599.1753 (FAB, *m*-nitrobenzyl alcohol and NaI added).

tert-butyl 4-{N-[(1S)(3,5-dimethoxyphenyl)(N-methylcarbamoyl)methyl]carbamoyl} (4S,5R)-5-(3-chloro-4-fluoro-5-nitrophenyl)-2-oxo-1,3-oxazolidine-3-carboxylate (7b). TLC R_f = 0.51 (10% MeOH/CH₂Cl₂); [α]_D²⁵ = +77.1 (c = 1.09, CH₂Cl₂); IR (film) 3331, 3085, 2980, 2940, 2841, 1817, 1733, 1654, 1598, 1545 cm⁻¹; ¹H NMR (400 MHz, CD₃OD, rt) δ 8.29 (dd, 1H, $J = 6.2, 2.0$ Hz, Ar6_fH), 8.18 (dd, 1H, $J = 5.8, 2.3$ Hz, Ar6_bH), 6.60 (d, 2H, $J = 2.2$ Hz, Ar7_bH), 6.43 (t, 1H, $J = 2.2$ Hz, Ar7_dH), 5.52 (d, 1H, $J = 6.1$ Hz, z₆H), 5.35 (s, 1H, x₇H), 4.68 (d, 1H, $J = 6.0$ Hz, x₆H), 3.75 (s, 6H, ArOCH₃), 2.74 (s, 3H, NHCH₃), 1.32 (s, 9H, Boc-CH₃); ¹³C NMR (100 MHz, CD₃OD, rt) δ 172.2, 172.1, 169.0, 162.6, 154.3, 152.9, 151.7, 149.7, 139.82, 139.77, 139.69, 135.82, 135.77, 134.7, 125.5, 125.3, 123.8, 123.7, 107.0, 101.3, 85.9, 76.5, 64.7, 59.1, 55.8, 27.9, 26.6; Exact mass calculated for M+Na⁺, 633.1377 found: 633.1376 (FAB, *m*-nitrobenzyl alcohol and NaI added).

N-[(1S)(3,5-dimethoxyphenyl)(N-methylcarbamoyl)methyl](2S,3R)-2-[(*tert*-butoxy)carbonylamino]-3-(4-fluoro-3-nitrophenyl)-3-hydroxypropanamide (8a). TLC R_f = 0.20

(4% MeOH/CH₂Cl₂); [α]²⁵_D = +44.0 (c = 0.63, CH₂Cl₂); IR (film) 3323, 2979, 2841, 1645, 1597, 1539, 1350, 1159, 1065, 840 cm⁻¹; ¹H NMR (400 MHz, DMSO, rt) δ 8.55 (d, 1H, *J* = 8.0 Hz, N₇H), 8.27 (d, 1H, *J* = 4.6 Hz, NHMe), 8.14 (d, 1H, *J* = 5.6 Hz, Ar_{6f}H), 7.79 (m, 1H, Ar_{6b}H), 7.52 (dd, 1H, *J* = 11.2(F), 8.8 Hz, Ar_{6c}H), 6.70 (d, 1H, *J* 9.7 Hz, N₆H), 6.61 (d, 2H, *J* = 2.2 Hz, Ar_{7b}H), 6.39 (t, 1H, *J* = 2.2 Hz, Ar_{7d}H), 5.86 (d, 1H, *J* = 5.3 Hz, z₆H), 5.35 (d, 1H, *J* = 8.0 Hz, x₇H), 5.16 (bs, 1H, OH), 4.39 (dd, 1H, *J* = 9.6, 3.0 Hz, x₆H), 3.72 (s, 6H, ArOCH₃), 2.58 (d, 3H, *J* = 4.6 Hz, NHCH₃), 1.18 (s, 9H, Boc-CH₃); ¹³C NMR (100 MHz, DMSO, rt) δ 169.6, 168.6, 160.3, 154.9, 152.4, 141.3, 140.1, 136.1, 105.0, 99.0, 78.3, 71.5, 59.6, 56.2, 55.2, 27.8, 27.4, 25.6; Exact mass calculated for M+Na⁺, 573.1973, found: 573.1956 (FAB, NaI added).

***N*-[(1*S*)(3,5-dimethoxyphenyl)(*N*-methylcarbamoyl)methyl](2*S*,3*R*)-2-[(*tert*-butoxy)carbonylamino]-3-(3-chloro-4-fluoro-5-nitrophenyl)-3-hydroxypropanamide (8b).** TLC R_f = 0.61 (25% acetone/CH₂Cl₂); [α]²⁵_D = +41.6 (c = 0.55, acetone); IR (KBr) 3297, 3088, 2969, 2940, 2840, 1677, 1640, 1597, 1545, 1432, 1368, 1346, 1292, 1272, 1248, 1203, 1160, 1101, 1069, 1023, 947, 825, 888, 854, 791, 748, 694, 620 cm⁻¹; ¹H NMR (400 MHz, DMSO, rt) δ 8.59 (d, 1H, *J* = 8.0 Hz, N₇H), 8.28 (d, 1H, *J* = 4.4 Hz, NHMe), 8.14 (d, 1H, *J* = 5.0 Hz, Ar_{6f}H), 7.98 (d, 1H, *J* = 2.3 Hz, Ar_{6b}H), 6.67 (d, 1H, *J* = 9.6 Hz, N₆H), 6.60 (d, 2H, *J* = 2.1 Hz, Ar_{7b}H), 6.39 (s, 1H, Ar_{7d}H), 5.98 (br s, 1H, OH), 5.35 (d, 1H, *J* = 8.0 Hz, x₇H), 5.17 (br s, 1H, z₆H), 4.42 (dd, 1H, *J* = 9.6, 2.5 Hz, x₆H), 3.72 (s, 6H, ArOCH₃), 2.58 (d, 3H, *J* = 4.5 Hz, NHCH₃), 1.19 (s, 9H, Boc-CH₃); ¹³C NMR (100.6 MHz, DMSO, rt) δ 169.6, 168.2, 160.3, 154.9, 150.9, 148.3, 141.2, 140.4, 137.2, 133.9, 122.7, 121.6, 121.4, 105.0, 99.0, 78.4, 71.4, 59.3, 56.1, 55.2, 27.7, 25.6; Exact mass calculated for M+Na⁺: 607.1583, found: 607.1569 (FAB, *m*-nitrobenzyl alcohol, NaI added).

2-[(2*R*)-2-[(*tert*-butoxy)carbonylamino]-2-[4-methoxy-2-(phenylmethoxy)phenyl]acetylamino]-*N*-[(1*S*)(3,5-dimethoxyphenyl)(*N*-methylcarbamoyl)methyl](2*S*,3*R*)-3-(4-fluoro-3-nitrophenyl)-3-hydroxypropanamide (9a). TLC R_f = 0.17 (5% MeOH/CH₂Cl₂); [α]²⁵_D = -15.8 (c = 0.94, CH₂Cl₂); IR (film) 3323, 2938, 2837, 1653, 1610, 1540, 1506, 1349, 1161, 1065, 835, 736, 698 cm⁻¹; ¹H NMR (400 MHz, CD₃OD, rt) δ 7.97 (d, 1H, *J* = 6.0 Hz, Ar_{6f}H), 7.45 (m, 3H, 2 BnH and Ar_{6b}H), 7.32-7.24 (m, 3H, 3 BnH), 7.05 (dd, 1H, *J* = 10.5(F), 10.5 Hz, Ar_{6c}H), 6.92 (d, 1H, *J* = 8.5 Hz, Ar_{5b}H), 6.59 (d, 2H, *J* = 2.2 Hz, Ar_{7b}H), 6.49 (d, 1H, *J* = 1.6 Hz, Ar_{5e}H), 6.42 (t, 1H, *J* = 2.2 Hz, Ar_{7d}H), 6.36 (bd, 1H, *J* = 8.5 Hz, Ar_{5c}H), 5.46 (s, 1H, x₅H), 5.36 (s, 1H, x₇H), 5.28 (bs, 1H, z₆H), 5.13 (d, 1H, *J* = 12.1 Hz, OCHHPh), 5.03 (d, 1H, *J* = 12.1 Hz, OCHHPh), 4.80 (s, 1H, x₆H), 3.74 (s, 9H, ArOCH₃), 2.73 (s, 3H, NHCH₃), 1.38 (s, 9H, Boc-CH₃); ¹³C NMR (100 MHz, CD₃OD, rt) δ 173.7, 172.6, 170.9, 162.6, 162.3, 157.9, 157.3, 157.0, 154.4, 140.7, 139.7, 138.1, 138.0, 134.3, 134.2, 129.6, 129.0, 128.6, 124.6, 119.5, 119.0, 118.8, 106.8, 106.3, 101.1, 80.8, 71.9, 71.6, 59.6, 59.0, 55.9, 55.7, 54.1, 28.7, 26.6; Exact mass calculated for M+Na⁺, 842.3025, found: 842.3047 (FAB, *m*-nitrobenzyl alcohol and NaI added).

2-((2R)-2-[(*tert*-butoxy)carbonylamino]-2-[4-methoxy-2-(phenylmethoxy)phenyl]acetylamino)-N-[(1S)(3,5-dimethoxyphenyl)(*N*-methylcarbamoyl)methyl](2S,3R)-3-(3-chloro-4-fluoro-5-nitrophenyl)-3-hydroxypropanamide (9b). TLC R_f = 0.50 (10% MeOH/CH₂Cl₂); $[\alpha]^{25}_D$ = -14.2 (c = 1.36, CH₂Cl₂); IR (KBr) 3335, 3087, 2975, 2938, 2839, 1661, 1611 cm⁻¹; ¹H NMR (400 MHz, CD₃OD, 330K) δ 7.84 (dd, 1H, J = 6.2, 1.8 Hz, Ar6_fH), 7.62 (dd, 1H, J = 6.2, 1.8 Hz, Ar6_bH), 7.43-7.41 (m, 2H, BnH), 7.32-7.24 (m, 3H, BnH), 6.96 (d, 1H, J = 8.5 Hz, Ar5_bH), 6.58 (d, 2H, J = 2.2 Hz, Ar7_bH), 6.49 (d, 1H, J = 2.4 Hz, Ar5_eH), 6.43 (t, 1H, J = 2.2 Hz, Ar7_dH), 6.39 (dd, 1H, J = 8.5, 2.4 Hz, Ar5_cH), 5.43 (s, 1H, x₅H), 5.35 (s, 1H, x₇H), 5.23 (d, 1H, J = 2.3 Hz, z₆H), 5.10 (d, 1H, J = 11.9 Hz, OCHHPh), 5.02 (d, 1H, J = 11.9 Hz, OCHHPh), 4.81 (d, 1H, J = 2.9 Hz, x₆H), 3.75 (s, 9H, ArOCH₃), 2.73 (s, 3H, NHCH₃), 1.34 (s, 9H, Boc-CH₃); ¹³C NMR (100 MHz, CD₃OD, 330K) δ 173.3, 172.3, 162.7, 162.3, 157.9, 150.3, 140.9, 140.2, 139.0, 138.1, 134.3, 129.7, 129.6, 129.0, 128.6, 124.2, 124.1, 123.2, 120.0, 107.1, 106.7, 101.4, 80.9, 71.8, 59.2, 58.9, 56.1, 55.8, 54.2, 28.8, 26.6; Exact mass calculated for M+Na⁺, 876.2637, found: 876.2637 (FAB, *m*-nitrobenzyl alcohol and NaI added).

2-((2R)-2-[4-methoxy-2-(phenylmethoxy)phenyl]-2-(2,2,2-trifluoroacetylamino)acetylamino)-N-[(1S)(3,5-dimethoxyphenyl)(*N*-methylcarbamoyl)methyl](2S,3R)-3-(4-fluoro-3-nitrophenyl)-3-hydroxypropanamide (10a). TLC R_f = 0.61 (10% MeOH/CH₂Cl₂); $[\alpha]^{25}_{NaD}$ = +5.2 (c = 1.23, MeOH); IR (film) 3294, 2938, 2836, 1747, 1683, 1652, 1609, 1540, 1506, 1457, 1348, 1293, 1203, 1159, 1065, 836, 727 cm⁻¹; ¹H NMR (400 MHz, CD₃OD, rt) δ 7.96 (m, 1H, Ar6_fH), 7.51-7.43 (m, 3H, 2 BnH and Ar6_bH), 7.35-7.26 (m, 3H, 3 BnH), 7.09 (dd, 1H, J = 11.0(F), 9.0 Hz, Ar6_cH), 6.78 (d, 1H, J = 8.5 Hz, Ar5_bH), 6.63 (d, 2H, J = 2.2 Hz, Ar7_bH), 6.55 (d, 1H, J = 2.4 Hz, Ar5_eH), 6.42 (t, 1H, J = 2.3 Hz, Ar7_dH), 6.32 (dd, 1H, J = 8.6, 2.4 Hz, Ar5_cH), 5.77 (s, 1H, x₅H), 5.38 (s, 1H, x₇H), 5.32 (d, 1H, J = 2.2 Hz, z₆H), 5.14 (d, 1H, J = 11.9 Hz, OCHHPh), 5.07 (d, 1H, J = 11.9 Hz, OCHHPh), 4.78 (d, 1H, J = 2.6 Hz, x₆H), 3.78 (s, 3H, ArOCH₃), 3.74 (s, 6H, ArOCH₃), 2.75 (s, 3H, NHCH₃); ¹³C NMR (100 MHz, CD₃OD, rt) δ 172.6, 171.9, 171.8, 171.1, 162.8, 162.5, 158.6, 158.3, 158.2, 157.0, 154.4, 140.5, 140.4, 140.0, 139.9, 138.0, 137.9, 137.8, 134.2, 134.1, 129.7, 129.6, 129.1, 128.6, 124.6, 124.5, 119.1, 118.8, 118.7, 116.7, 115.8, 106.7, 106.7, 106.1, 101.3, 101.1, 71.7, 71.5, 60.1, 60.0, 59.3, 59.2, 55.8, 55.7, 53.3, 26.7, 26.5; Exact mass calculated for M+Na⁺, 838.2323, found: 838.2314 (FAB, *m*-nitrobenzyl alcohol and NaI added).

2-((2R)-2-[4-methoxy-2-(phenylmethoxy)phenyl]-2-(2,2,2-trifluoroacetylamino)acetylamino)-N-[(1S)(3,5-dimethoxyphenyl)(*N*-methylcarbamoyl)methyl](2S,3R)-3-(3-chloro-4-fluoro-5-nitrophenyl)-3-hydroxypropanamide (10b). TLC R_f = 0.50 (10% MeOH/CH₂Cl₂); $[\alpha]^{25}_D$ = -7.3 (c = 0.85, MeOH); IR (KBr) 3358, 3076, 2943, 2841, 1728, 1664, 1611, 1543, 1502 cm⁻¹; ¹H NMR (400 MHz, 2:1 CD₃OD/(CD₃)₂SO, 330K) δ 8.00 (dd, 1H, J = 1.9, 6.3 Hz, Ar6_fH), 7.83 (dd, 1H, J = 1.9, 6.0 Hz, Ar6_fH), 7.52-7.50 (m, 2H, BnH), 7.42-7.35 (m, 3H, BnH), 6.83 (d, 1H, J = 8.5 Hz, Ar5_bH), 6.70 (d, 2H, J = 2.2 Hz, Ar7_bH), 6.61 (d, 1H, J = 2.4 Hz, Ar5_eH), 6.49 (t, 1H, J = 2.2 Hz, Ar7_dH), 6.35 (dd, 1H, J = 8.5, 2.4 Hz, Ar5_cH), 5.85 (s, 1H, x₅H), 5.41 (s, 1H, x₇H), 5.36 (d, 1H, J = 2.6 Hz, z₆H), 5.19 (d, 1H, J = 12.1 Hz, OCHHPh), 5.14 (d, 1H, J = 12.1 Hz, OCHHPh), 4.97 (d, 1H, J = 2.6 Hz, x₆H), 3.82 (s, 3H, ArOCH₃), 3.80 (s, 6H, ArOCH₃), 2.75 (s, 3H, NHCH₃); ¹³C NMR (100 MHz, 2:1 CD₃OD/(CD₃)₂SO, 330K) δ 172.1, 171.2, 170.4, 162.5, 162.4, 158.3, 158.1, 157.7, 152.8, 150.2, 141.1, 140.8, 140.7, 138.8, 138.7, 138.1, 134.5, 129.8, 129.7, 129.1, 128.6, 124.0, 123.8, 123.3,

118.7, 117.2, 115.8, 106.8, 106.6, 105.9, 101.1, 101.0, 71.8, 71.3, 59.4, 58.9, 56.1, 55.9, 52.9, 26.6; Exact mass calculated for $M+Na^+$, 872.1936, found: 872.1934 (FAB, *m*-nitrobenzyl alcohol and NaI added).

(aR)-N-{11-[(1R)(4-fluoro-3-nitrophenyl)hydroxymethyl](8S,11S,14R)-9,12-diaza-16-hydroxy-3,5,18-trimethoxy-8-(N-methylcarbamoyl)-10,13-dioxotricyclo

[13.3.1.0<2,7>]nonadeca-1(19),2,4,6,15,17-hexaen-14-yl}-2,2,2-trifluoroacetamide (11a). TLC R_f = 0.32 (10% MeOH/CH₂Cl₂); $[\alpha]^{25}_{NaD}$ = +30.4 (c = 1.17, CH₂Cl₂); IR (film) 3404, 3266, 2943, 1718, 1669, 1604, 1540, 1351, 1306, 1206, 1160, 1085, 1036, 838, 732 cm⁻¹; ¹H NMR (400 MHz, CD₃OD, rt) δ 8.05 (d, 1H, J = 5.0 Hz, Ar6_fH), 7.65 (m, 1H, Ar6_bH), 7.34 (m, 2H, Ar6_cH and Ar5_bH), 6.73 (d, 1H, J = 2.3 Hz, Ar7_dH or Ar7_fH), 6.60 (d, 1H, J = 2.2 Hz, Ar7_dH or Ar7_fH), 6.46 (s, 1H, Ar5_eH), 5.53 (s, 2H, x₅H and z₆H), 5.26 (s, 1H, x₇H), 4.64 (s, 1H, x₆H), 3.88 (s, 3H, ArOCH₃), 3.66 (s, 3H, ArOCH₃), 3.64 (s, 3H, ArOCH₃), 2.49 (s, 3H, NHCH₃); ¹³C NMR (100 MHz, CD₃OD, rt) δ 170.6, 169.7, 161.9, 161.8, 161.2, 160.8, 160.4, 158.9, 157.1, 154.5, 140.4, 138.8, 138.5, 138.4, 134.4, 134.3, 130.2, 124.8, 120.7, 119.2, 119.0, 115.7, 110.9, 100.6, 100.3, 99.6, 99.4, 73.1, 70.5, 64.6, 60.3, 59.5, 56.3, 56.2, 56.1, 56.0, 55.9, 52.1, 26.9, 26.8; Exact mass calculated for $M+Na^+$, 746.1697, found: 746.1694 (FAB, *m*-nitrobenzyl alcohol and NaI added).

(aR)-N-{11-[(1R)(3-chloro-4-fluoro-5-nitrophenyl)hydroxymethyl](8S,11S,14R)-9,12-diaza-16-hydroxy-3,5,18-trimethoxy-8-(N-methylcarbamoyl)-10,13-dioxotricyclo

[13.3.1.0<2,7>]nonadeca-1(19),2,4,6,15,17-hexaen-14-yl}-2,2,2-trifluoroacetamide (11b). TLC R_f = 0.45 (10% MeOH/CH₂Cl₂); $[\alpha]^{25}_D$ = +57.0 (c = 0.58, MeOH); IR (KBr) 3405, 2943, 2843, 1673, 1606, 1578, 1543, 1467, 1414, 1351, 1307, 1272, 1210, 1161, 1084, 1035, 942, 839, 750 cm⁻¹; ¹H NMR (400 MHz, CD₃OD, 330 K) δ 8.05 (dd, 1H, J = 6.3, 1.6 Hz, Ar6_fH), 7.79 (dd, 1H, J = 6.0, 1.6 Hz, Ar6_bH), 7.09 (s, 1H, Ar5_eH), 6.73 (d, 1H, J = 2.2 Hz, Ar7_dH or Ar7_fH), 6.61 (d, 1H, J = 2.2 Hz, Ar7_dH or Ar7_fH), 6.49 (s, 1H, Ar5_bH), 5.60 (s, 1H, x₅H), 5.53 (d, 1H, J = 2.7 Hz, z₆H), 5.26 (s, 1H, x₇H), 4.53 (br s, 1H, x₆H), 3.87 (s, 3H, ArOCH₃), 3.67 (s, 3H, ArOCH₃), 3.65 (s, 3H, ArOCH₃), 2.51 (s, 3H, NHCH₃); ¹³C NMR (100.6 MHz, CD₃OD, 330 K) δ 173.8, 170.6, 169.3, 161.9, 161.2, 161.0, 157.9, 153.1, 150.4, 140.8, 139.5, 138.9, 134.9, 134.3, 124.6, 124.4, 123.3, 121.0, 116.9, 111.8, 111.4, 100.9, 100.1, 70.3, 61.2, 59.7, 56.5, 56.2, 56.1, 54.0, 26.7; Exact mass calculated for $M+Na^+$: 780.1308; found: 780.1315 (FAB, *m*-nitrobenzyl alcohol, NaI added).

(aR,2R)-N-{11-[(1R)(4-fluoro-3-nitrophenyl)hydroxymethyl](8S,11S,14R)-9,12-diaza-16-hydroxy-3,5,18-trimethoxy-8-(N-methylcarbamoyl)-10,13-dioxotricyclo

[13.3.1.0<2,7>]nonadeca-1(19),2(7),3,5,15,17-hexaen-14-yl}-2-[(*tert*-butoxy)carbonylamino]-2-[5-(methylsulfonyl)-4-prop-2-enyloxy-3-(*tert*-butyldimethylsilyloxy)phenyl]acetamide (13a). TLC R_f = 0.45 (10% MeOH/CH₂Cl₂); $[\alpha]^{25}_{NaD}$ = +4.1 (c = 0.83, CH₂Cl₂); IR (cell-CH₂Cl₂) 3414, 3263, 2961, 2956, 2859, 1666, 1603, 1578, 1540, 1490, 1369, 1160, 1059, 970, 842 cm⁻¹; ¹H NMR (400 MHz, CD₃OD, rt) δ 8.29 (bs, 1H, Ar6_fH), 7.51 (bs, 1H, Ar6_bH), 7.32 (m, 1H, Ar6_cH), 7.15 (d, 1H, J = 1.8 Hz, Ar5_bH), 7.08 (m, 2H, Ar4_bH and Ar4_fH), 6.70 (d, 1H, J = 2.3 Hz, Ar7_dH or Ar7_fH), 6.62 (d, 1H, J = 2.2 Hz, Ar7_dH or Ar7_fH), 6.46 (s, 1H, Ar5_eH), 6.04 (m, 1H, OCH₂CH=CH₂), 5.40 (m, 2H, z₆H and x₄H), 5.32 (m, 1H, OCH₂CH=CH₂), 5.19 (m, 2H, x₅H and OCH₂CH=CH₂), 5.00 (bs, 1H, x₇H), 4.50 (m, 3H, x₆H and allyl-CH₂), 3.99 (s, 3H, ArOCH₃), 3.69 (s, 3H, ArOCH₃), 3.63 (s, 3H, ArOCH₃), 3.18

(s, 3H, SO₂CH₃), 2.44 (s, 3H, NHCH₃), 1.35 (s, 9H, Boc-CH₃), 1.00 (s, 9H, TBS-*t*-Bu), 0.21 (s, 3H, TBS-CH₃), 0.19 (s, 3H, TBS-CH₃); ¹³C NMR (100 MHz, CD₃OD, 330K) δ 174.7, 172.9, 170.5, 170.5, 170.1, 161.9, 161.8, 160.9, 460.6, 157.7, 157.4, 157.1, 154.5, 151.8, 145.0, 143.8, 140.2, 139.0, 138.6, 138.5, 135.0, 134.5, 134.4, 133.4, 130.2, 125.3, 120.6, 120.3, 119.2, 119.0, 118.8, 118.4, 117.1, 116.5, 113.4, 112.8, 111.4, 111.2, 101.0, 100.9, 100.0, 99.9, 81.7, 75.3, 72.6, 70.6, 70.2, 59.9, 59.7, 56.5, 56.4, 56.1, 55.0, 54.1, 38.7, 29.1, 28.7, 283.6, 26.7, 26.2, 19.2, 19.1, -4.15, -4.22; Exact mass calculated for M+Na⁺, 1163, found: 1163 (FAB, *m*-nitrobenzyl alcohol and NaI added).

(aR,2R)-N-{11-[(1R)(3-chloro-4-fluoro-5-nitrophenyl)hydroxymethyl](8S,11S,14R)-9,12-diaza-16-hydroxy-3,5,18-trimethoxy-8-(*N*-methylcarbamoyl)-10,13-dioxotricyclo[13.3.1.0<2,7>]nonadeca-1(19),2(7),3,5,15,17-hexaen-14-yl}-2-[(*tert*-butoxy)carbonylamino]-2-[5-(methylsulfonyl)-4-prop-2-enyloxy-3-(*tert*-butyldimethylsilyloxy)phenyl]acetamide (13b). TLC R_f = 0.27 (7.5% MeOH/CH₂Cl₂); [α]²⁵_D = -27.5 (c = 2.0, CH₂Cl₂); IR (KBr) 3408, 3086, 2937, 2859, 1680, 1606, 1578, 1543, 1493, 1437 cm⁻¹; ¹H NMR (400 MHz, CD₃OD, 330K) δ 8.08 (bs, 1H, Ar6_fH), 7.80 (bs, 1H, Ar6_bH), 7.09 (d, 1H, *J* = 2.0 Hz, Ar4_bH or Ar4_fH), 7.02 (d, 1H, *J* = 2.1 Hz, Ar4_bH or Ar4_fH), 7.01 (s, 1H, Ar5_bH or Ar5_eH), 6.69 (d, 1H, *J* = 2.3 Hz, Ar7_dH or Ar7_fH), 6.61 (d, 1H, *J* = 2.3 Hz, Ar7_dH or Ar7_fH), 6.48 (s, 1H, Ar5_bH or Ar5_eH), 6.05 (dddd, 1H, *J* = 16.3, 10.5, 5.8, 5.8 Hz, OCH₂CH=CH₂), 5.43 (m, 2H, z₆H and x₄H), 5.31 (ddd, 1H, *J* = 17.3, 3.1, 1.5 Hz, OCH₂CH=CHH), 5.21 (s, 2H, x₅H), 5.18 (ddd, 1H, *J* = 10.5, 2.7, 1.5 Hz, OCH₂CH=CHH), 5.06 (s, 1H, x₇H), 4.52 (m, 3H, x₆H and OCH₂CH=CHH), 3.87 (s, 3H, ArOCH₃), 3.69 (s, 3H, ArOCH₃), 3.64 (s, 3H, ArOCH₃), 3.15 (s, 3H, SO₂CH₃), 2.47 (s, 3H, NHCH₃), 1.34 (s, 9H, Boc-CH₃), 0.98 (s, 9H, TBS-*t*-Bu), 0.20 (s, 3H, TBS-CH₃), 0.19 (s, 3H, TBS-CH₃); ¹³C NMR (100 MHz, CD₃OD, 330K) δ 174.7, 172.9, 170.6, 170.0, 162.0, 161.0, 157.7, 153.1, 151.8, 150.5, 145.0, 143.9, 140.7, 139.7, 139.6, 139.0, 135.0, 134.7, 133.4, 124.3, 124.1, 132.9, 120.7, 120.5, 118.4, 117.2, 116.6, 113.5, 111.4, 101.2, 100.0, 81.8, 75.3, 70.5, 59.8, 56.5, 56.2, 54.3, 38.8, 28.7, 28.6, 26.2, 19.1, -4.1, -4.2; Mass calculated for M+Na⁺, 1197, found: 1197 (FAB, *m*-nitrobenzyl alcohol and NaI added).

(aR,2R)-N-{11-[(1R)(4-fluoro-3-nitrophenyl)hydroxymethyl](8S,11S,14R)-9,12-diaza-16-hydroxy-3,5,18-trimethoxy-8-(*N*-methylcarbamoyl)-10,13-dioxotricyclo

[13.3.1.0<2,7>]nonadeca-1(19),2(7),3,5,15,17-hexaen-14-yl}-2-[(*tert*-butoxy)carbonylamino]-2-(5-(methylsulfonyloxy)-3-hydroxy-4-prop-2-enyloxyphenyl)acetamide (14a). TLC R_f = 0.39 (10% MeOH/CH₂Cl₂); [α]²⁵_{Hg435} = +29.4 (c = 1.13, CH₂Cl₂); IR (cell-CH₂Cl₂) 3411, 3275, 2941, 1665, 1602, 1578, 1540, 1498, 1370, 1308, 1161, 1036, 970, 841, 807 cm⁻¹; ¹H NMR (400 MHz, CD₃OD, 330K) δ 8.13 (bs, 1H, Ar6_fH), 7.52 (bs, 1H, Ar6_bH), 7.30 (m, 1H, Ar6_cH), 7.07 (s, 1H, Ar5_bH), 7.00 (d, 1H, *J* = 2.0 Hz, Ar4_bH or Ar4_fH), 6.98 (d, 1H, *J* = 2.0 Hz, Ar4_bH or Ar4_fH), 6.69 (d, 1H, *J* = 2.4 Hz, Ar7_dH or Ar7_fH), 6.62 (d, 1H, *J* = 2.4 Hz, Ar7_dH or Ar7_fH), 6.47 (s, 1H, Ar5_eH), 6.06 (m, 1H, OCH₂CH=CH₂), 5.46 (s, 1H, z₆H), 5.41 (s, 1H, x₄H), 5.30 (m, 1H, OCH₂CH=CHH), 5.19-5.15 (m, 2H, x₅H and OCH₂CH=CHH), 5.08 (s, 1H, x₇H), 4.54 (m, 2H, allyl-CH₂), 4.48 (s, 1H, x₆H), 3.88 (s, 3H, ArOCH₃), 3.70 (s, 3H, ArOCH₃), 3.63 (s, 3H, ArOCH₃), 3.11 (s, 3H, SO₂CH₃), 2.46 (s, 3H, NHCH₃), 1.36 (s, 9H, Boc-CH₃); ¹³C NMR (100 MHz, CD₃OD, rt) δ 175.0, 173.4, 170.5, 161.8, 160.8, 160.7, 159.9, 157.6, 157.1, 154.5, 153.3, 144.6, 140.2, 138.9, 138.5, 138.4, 135.1, 134.5, 133.9, 133.0, 125.6, 120.2, 119.0, 118.8, 117.0, 115.4, 114.9, 113.1, 112.5, 110.9, 100.5, 99.5, 81.6, 75.4, 70.5, 68.5, 62.8, 60.6, 60.2, 59.7, 56.3, 56.2, 56.0, 55.9, 54.8, 54.4, 38.4, 28.5, 27.0, 26.7, 20.9; Exact

mass calculated for $M+Na^+$, 1049, found: 1049 (FAB, *m*-nitrobenzyl alcohol and NaI added).

(aR,2R)-N-{11-[(1R)(3-chloro-4-fluoro-5-nitrophenyl)hydroxymethyl](8S,11S,14R)-9,12-diaza-16-hydroxy-3,5,18-trimethoxy-8-(*N*-methylcarbamoyl)-10,13-dioxotricyclo[13.3.1.0<2,7>]nonadeca-1(19),2(7),3,5,15,17-hexaen-14-yl}-2-[(*tert*-butoxy)carbonylamino]-2-(5-(methylsulfonyloxy)-3-hydroxy-4-prop-2-enyloxyphenyl)acetamide (14b). TLC R_f = 0.31 (10% MeOH/CH₂Cl₂); $[\alpha]^{25}_D$ = -23.0 (c = 1.47, CH₂Cl₂); IR (KBr) 3396, 2979, 2938, 2533, 1664, 1604, 1542 cm⁻¹; ¹H NMR (400 MHz, CD₃OD, rt) δ 8.21 (bs, 1H, Ar6_fH), 7.91 (bs, 1H, Ar6_bH), 7.09 (bs, 1H, Ar5_bH), 6.98 (m, 2H, J = 2.0 Hz, Ar4_bH and Ar4_fH), 6.68 (d, 1H, J = 2.3 Hz, Ar7_dH or Ar7_fH), 6.61 (d, 1H, J = 2.2 Hz, Ar7_dH or Ar7_fH), 6.45 (s, 1H, Ar5_eH), 6.08 (dddd, 1H, J = 16.5, 10.5, 6.0, 6.0 Hz, OCH₂CH=CH₂), 5.40-5.30 (m, 3H, z₆H, x₄H and OCH₂CH=CHH), 5.19-5.17 (m, 2H, x₅H and OCH₂CH=CHH), 4.98 (s, 1H, x₇H), 4.55 (m, 3H, x₆H and allyl-CH₂), 3.88 (s, 3H, ArOCH₃), 3.69 (s, 3H, ArOCH₃), 3.62 (s, 3H, ArOCH₃), 3.13 (s, 3H, SO₂CH₃), 2.43 (s, 3H, NHCH₃), 1.33 (s, 9H, Boc-CH₃); ¹³C NMR (100 MHz, CD₃OD, 330K) δ 179.1, 175.0, 170.5, 161.9, 160.9, 160.8, 157.8, 157.7, 153.3, 153.2, 150.5, 144.7, 144.5, 140.7, 140.3, 139.6, 139.5, 138.9, 135.1, 134.6, 133.9, 133.0, 124.2, 124.0, 120.2, 118.9, 117.1, 115.7, 114.9, 113.1, 110.9, 100.5, 99.6, 81.7, 75.4, 70.3, 61.5, 60.6, 59.7, 56.2, 56.0, 54.8, 54.4, 38.4, 28.5, 26.7, 20.8, 14.4; Mass calculated for $M+Na^+$, 1083, found: 1083 (FAB, *m*-nitrobenzyl alcohol and NaI added).

(21a-22a R,5 aS,1S,28S,2R,13R,16R)-5-amino-15,29,31-triaza-13-[(*tert*-butoxy)carbonylamino]-2-hydroxy-20,23,25-trimethoxy-28-(*N*-methylcarbamoyl)-10-(methylsulfonyloxy)-7-oxa-14,30,32-trioxo-9-prop-2-enyloxyhexacyclo[14.14.2.2<3,6>.1<8,12>.1<17,21>.0<22,27>]hexatriaconta-3,5,8(35),9,11,17,19,21(36),22(27),23,25,33-dodecaen-18-yl (trifluoromethyl)sulfonate (16). TLC R_f = 0.48 (10% MeOH/CH₂Cl₂); $[\alpha]^{25}_{Hg435}$ = -155.5 (c = 1.04, CH₂Cl₂); IR (cell-CH₂Cl₂) 3684, 3391, 2941, 2842, 1688, 1664, 1607, 1508, 1370, 1217, 1182, 1159, 1139, 1019, 970, 828 cm⁻¹; ¹H NMR (400 MHz, CD₃OD, 330K) δ 7.65 (bs, 1H, Ar5_bH), 7.28 (dd, 1H, J = 2.0, 1.0 Hz, Ar6_fH), 6.91 (m, 3H, Ar4_bH, Ar5_eH, Ar6_cH), 6.73 (d, 1H, J = 2.3 Hz, Ar7_dH or Ar7_fH), 6.66 (d, 1H, J = 2.3 Hz, Ar7_dH or Ar7_fH), 6.57 (dd, 1H, J = 8.9, 2.0 Hz, Ar6_bH), 6.19 (m, 1H, OCH₂CH=CH₂), 5.68 (bs, 2H, Ar4_fH and x₄H), 5.49 (d, 1H, J = 3.8 Hz, z₆H), 5.43 (m, 1H, OCH₂CH=CHH), 5.27 (m, 1H, OCH₂CH=CHH), 5.22 (s, 1H, x₅H), 5.11 (s, 1H, x₇H), 4.79 (m, 2H, allyl-CH₂), 4.74 (m, 1H, x₆H), 3.89 (s, 3H, ArOCH₃), 3.71 (s, 3H, ArOCH₃), 3.70 (s, 3H, ArOCH₃), 3.29 (s, 3H, SO₂CH₃), 2.34 (s, 3H, NHCH₃), 1.42 (s, 9H, Boc-CH₃); Exact mass calculated for $M+Na^+$, 1131, found: 1131 (FAB, *m*-nitrobenzyl alcohol and NaI added).

(34aR,21a-22aR,1S,28S,2R,13R,16R)-15,29,31-triaza-13-[(tert-butoxy)carbonylamino]-34-chloro-2-hydroxy-20,23,25-trimethoxy-28-(N-methylcarbamoyl)-10-(methanesulfonyloxy)-5-nitro-7-oxa-14,30,32-trioxo-9-prop-2-enyloxyhexacyclo[14.14.2.2<3,6>.1<8,12>.1<17,21>.0<22,27>]hexatriaconta-3,5,8(35),9,11,17,19,21(36),22(27),23,25,33-dodecaen-18-yl (trifluoromethyl)sulfonate (17). 5:1 mixture of atropdiastereomers. HPLC *rt* = 16.4 min (55/45 CH₃CN/water(0.1%TFA), Rx-C8, 1 mL/min); IR (KBr) 3422, 2940, 1686, 1608, 1578, 1540, 1508, 1423, 1368, 1215, 1181, 1019, 973, 831 cm⁻¹; ¹H NMR (400 MHz, CD₃OD, 330K) δ 8.43 (dd, 1H, *J* = 2.0, 0.8 Hz, major Ar6fH), 8.28 (dd, 1H', *J* = 2.0, 0.8 Hz, minor Ar6fH), 7.91 (d, 1H', *J* = 1.5 Hz, minor Ar6bH), 7.56 (br s, 1H, major Ar6bH), 7.43-7.38 (m, 1H, 1H', Ar5bH), 7.05 (m, 1H, 1H', Ar4bH), 6.93 (s, 1H, 1H' Ar5eH), 6.76 (d, 1H, 1H', *J* = 2.2 Hz, Ar7dH or Ar7fH), 6.64 (d, 1H, 1H', *J* = 2.3 Hz, Ar7dH or Ar7fH), 6.21-6.11 (m, 1H, 1H', OCH₂CH=CH₂), 5.72 (s, 2H, 2H', Ar4fH, z₆H), 5.45-5.39 (m, 2H, 2H', x₄H, OCH₂CH=CHH), 5.27-5.23 (m, 3H, 3H', OCH₂CH=CHH, x₅H, x₇H), 4.81-4.72 (m, 3H, 3H', x₆H, OCH₂-CH=CHH), 3.891 (s, 3H', minor Ar7eOCH₃), 3.888 (s, 3H, major Ar7eOCH₃), 3.73 (s, 3H', minor Ar5OCH₃), 3.72 (s, 3H, major Ar5OCH₃), 3.69 (s, 3H', minor Ar7cOCH₃), 3.68 (s, 3H, major Ar7cOCH₃), 3.28 (s, 3H, 3H', SO₂CH₃), 2.48 (s, 3H, major NHCH₃), 2.46 (s, 3H', minor NHCH₃), 1.43 (s, 9H, 9H', Boc-CH₃); ¹³C NMR (100.6 MHz, CD₃OD, 330 K) δ 170.3, 170.1, 162.7, 161.6, 160.7, 153.0, 148.8, 146.0, 144.9, 144.2, 142.7, 140.8, 138.6, 135.5, 134.9, 133.6, 134.4, 119.0, 118.6, 116.8, 112.4, 111.4, 106.3, 99.9, 81.6, 76.2, 61.3, 59.6, 57.6, 56.9, 56.6, 56.2, 38.8, 28.7, 26.6; Mass calculated for M+Na⁺, 1195, found: 1195 (FAB, *m*-nitrobenzyl alcohol, NaI added).

(21a-22a R,5a R,1S,28S,2R,13R,16R)-15,29,31-triaza-13-[(tert-butoxy)carbonylamino]-5-chloro-2-hydroxy-20,23,25-trimethoxy-28-(N-methylcarbamoyl)-10-(methanesulfonyloxy)-7-oxa-14,30,32-trioxo-9-prop-2-enyloxyhexacyclo[14.14.2.2<3,6>.1<8,12>.1<17,21>.0<22,27>]hexatriaconta-3(33),4,6(34),8(35),9,11,17,19,21(36),22(27),23,25-dodecaen-18-yl (trifluoromethyl)sulfonate. HPLC *rt* = 13.9 min (55/45 CH₃CN/water(0.1%TFA), Rx-C8, 1 mL/min); [α]_D²⁴ = -2.1 (c = 0.34, MeOH); IR (KBr) 3419, 2940, 1684, 1608, 1577, 1507, 1369, 1280, 1216, 1190, 1160, 1057, 1021, 975, 847; ¹H NMR (400 MHz, CD₃OD, 330K) δ 7.80 (ddd, 1H, *J* = 8.5, 2.1, 0.9 Hz, Ar6fH), 7.56 (s, 1H, Ar5bH), 7.41 (d, 1H, *J* = 1.5 Hz, Ar6bH), 7.25 (d, 1H, *J* = 8.5 Hz, Ar6eH), 6.97 (m, 1H, Ar4bH), 6.92 (s, 1H, Ar5eH), 6.75 (d, 1H, *J* = 2.3 Hz, Ar7dH or Ar7fH), 6.65 (d, 1H, *J* = 2.3 Hz, Ar7dH or Ar7fH), 6.19 (dddd, 1H, *J* = 16.4, 10.4, 6.0, 6.0, OCH₂CH=CH₂), 5.75 (s, 1H, Ar4fH), 5.54 (d, 1H, *J* = 4.5 Hz, z₆H), 5.49 (s, 1H, x₄H), 5.42 (ddd, 1H, *J* = 17.2, 3.1, 1.5 Hz, OCH₂CH=CHH), 5.26 (ddd, 1H, *J* = 10.4, 2.5, 1.0 Hz, OCH₂CH=CHH), 5.20 (s, 1H, x₅H), 5.18 (s, 1H, x₇H), 4.86 (ddt, 1H, *J* = 12.2, 5.9, 1.3, OCH₂CH=CHH), 4.81 (d, 1H, *J* = 4.5 Hz, x₆H), 4.76 (ddt, 1H, *J* = 12.2, 6.1, 1.2, OCH₂CH=CHH), 3.89 (s, 3H, Ar7eOCH₃), 3.71 (s, 3H, Ar5OCH₃), 3.70 (s, 3H, Ar7cOCH₃), 3.28 (s, 3H, SO₂CH₃), 2.40 (s, 3H, NHCH₃), 1.42 (s, 9H, Boc-CH₃); ¹³C NMR (100.6 MHz, CD₃OD, 330 K) δ 170.6, 170.2, 162.7, 161.6, 160.8, 154.8, 151.4, 148.8, 144.78, 139.0, 135.1, 118.9, 118.7, 115.8, 113.3, 111.8, 106.2, 100.0, 81.7, 76.1, 62.8, 60.1, 56.9, 56.6, 56.2, 38.9, 28.7, 26.5; Mass calculated for M+Na⁺, 1150, found: 1150 (FAB, *m*-nitrobenzyl alcohol, NaI added).

(21a-22aR,5aR,1S,28S,2R,13R,16R)-15,29,31-triaza-13-[(tert-butoxy)carbonylamino]-5-chloro-2,9-dihydroxy-20,23,25-trimethoxy-28-(N-methylcarbamoyl)-7-oxa-14,30,32-trioxohexacyclo[14.14.2.2<3,6>.1<8,12>.1<17,21>.0<22,27>]hexatriaconta-

3(33),4,6(34),8(35),9,11,17,19,21(36),22(27),23,25-dodecaen-10-yl methylsulfonate (18). HPLC *rt* = 4.3 min (55/45 CH₃CN/water(0.1%TFA), Rx-C8, 1 mL/min); [α]²⁴_D = -14.4 (*c* = 1.12, MeOH); IR (KBr) 3410, 2939, 1670, 1606, 1576, 1508, 1367, 1266, 1176, 1058, 1009, 971, 812, 717 cm⁻¹; ¹H NMR (400 MHz, CD₃OD, 330 K) δ 7.78 (ddd, 1H, *J* = 8.5, 2.0, 0.9 Hz, Ar6_fH), 7.37 (dd, 1H, *J* = 8.3, 2.5 Hz, Ar5_fH), 7.36 (s, 1H, Ar6_bH), 7.30 (s, 1H, Ar5_bH), 7.24 (d, 1H, *J* = 8.5 Hz, Ar6_eH), 6.95 (d, 1H, *J* = 8.3 Hz, Ar5_eH), 6.94 (s, 1H, Ar4_bH), 6.71 (d, 1H, *J* = 2.3 Hz, Ar7_dH or Ar7_fH), 6.64 (d, 1H, *J* = 2.3 Hz, Ar7_dH or Ar7_fH), 5.62 (s, 1H, Ar4_fH), 5.57 (d, 1H, *J* = 4.7 Hz, z₆H), 5.45 (s, 1H, x₄H), 5.21 (s, 1H, x₇H), 5.13 (s, 1H, x₅H), 4.79 (bs, 1H, x₆H), 3.89 (s, 3H, Ar7_eOCH₃), 3.69 (s, 3H, Ar5_eOCH₃), 3.67 (s, 3H, Ar7_cOCH₃), 3.29 (s, 3H, SO₂CH₃), 2.40 (s, 3H, NHCH₃), 1.40 (s, 9H, Boc-CH₃); Exact mass calculated for M+Na⁺, 962.2297, found: 962.2285 (FAB, *m*-nitrobenzyl alcohol, NaI added).

(21a-22aR, 5aR, 1S, 28S, 2R, 13R, 16R)-15, 29, 31-triaza-13-[(tert-butoxy)carbonylamino]-5-chloro-2-hydroxy-20,23,25-trimethoxy-28-(N-methylcarbamoyl)-10-(methylsulfonyloxy)-7-oxa-14,30,32-trioxohexacyclo[14.14.2.2<3,6>.1<8,12>.1<17,21>.0<22,27>]hexatriaconta-3(33),4,6(34),8(35),9,11,17,19,21(36),22(27),23,25-dodecaen-9-yl 2,2-dimethylpropanoate. TLC *R_f* = 0.38 (10% MeOH/CH₂Cl₂); [α]²⁴_D = -9.7 (*c* = 0.45, MeOH); IR (KBr) 3414, 2977, 2939, 1759, 1675, 1606, 1577, 1506, 1422, 1370, 1269, 1183, 1093, 1026, 969, 802 cm⁻¹; ¹H NMR (400 MHz, CD₃OD, 330 K) δ 7.78 (ddd, 1H, *J* = 8.5, 2.2, 0.8 Hz, Ar6_fH), 7.39-7.36 (m, 1H, Ar5_fH), 7.36 (s, 1H, Ar6_bH), 7.30 (s, 1H, Ar5_bH), 7.22 (d, 1H, *J* = 8.5 Hz, Ar6_eH), 7.15 (dd, 1H, *J* = 1.9, 1.1 Hz, Ar4_bH), 6.96 (d, 1H, *J* = 8.5 Hz, Ar5_eH), 6.71 (d, 1H, *J* = 2.3 Hz, Ar7_dH or Ar7_fH), 6.64 (d, 1H, *J* = 2.3 Hz, Ar7_dH or Ar7_fH), 5.73 (s, 1H, Ar4_fH), 5.56 (d, 1H, *J* = 4.8 Hz, z₆H), 5.45 (s, 1H, x₄H), 5.23 (s, 1H, x₅H), 5.22 (s, 1H, x₇H), 4.78 (s, 1H, x₆H), 3.88 (s, 3H, Ar7_eOCH₃), 3.69 (s, 3H, Ar5_eOCH₃), 3.68 (s, 3H, Ar7_cOCH₃), 3.25 (s, 3H, SO₂CH₃), 2.40 (s, 3H, NHCH₃), 1.42 (s, 9H, Piv-CH₃), 1.41 (s, 9H, Boc-CH₃); Mass calculated for M+Na⁺: 1046; found: 1046 (FAB, *m*-nitrobenzyl alcohol, NaI added).

(21a-22aR, 5aR, 1S, 28S, 2R, 13R, 16R)-15, 29, 31-triaza-5-chloro-2-hydroxy-20,23,25-trimethoxy-28-(N-methylcarbamoyl)-10-(methylsulfonyloxy)-7-oxa-14,30,32-trioxo-13-(2,2,2-trifluoroacetyl amino)hexacyclo[14.14.2.2<3,6>.1<8,12>.1<17,21>.0<22,27>]hexatriaconta-3,5,8(35),9,11,17,19,21(36),22(27),23,25,33-dodecaen-9-yl 2,2-dimethylpropanoate (19). TLC *R_f* = 0.41 (10% MeOH/CH₂Cl₂); [α]²⁴_D = +12.1 (*c* = 0.45, MeOH); IR (KBr) 3412, 2975, 2940, 2841, 1672, 1606, 1508, 1372, 1270, 1214, 1182, 1094, 1027, 969, 802 cm⁻¹; ¹H NMR (400 MHz, CD₃OD, 330 K) δ 7.78 (ddd, 1H, *J* = 8.5, 2.1, 1.0 Hz, Ar6_fH), 7.39- (dd, 1H, *J* = 8.4, 2.5 Hz, Ar5_fH), 7.36 (d, 1H, *J* = 1.6 Hz, Ar6_bH), 7.26 (s, 1H, Ar5_bH), 7.19 (d, 1H, *J* = 8.6 Hz, Ar6_eH), 7.04 (dd, 1H, *J* = 2.0, 1.0 Hz, Ar4_bH), 6.96 (d, 1H, *J* = 8.5 Hz, Ar5_eH), 6.72 (d, 1H, *J* = 2.3 Hz, Ar7_dH or Ar7_fH), 6.64 (d, 1H, *J* = 2.3 Hz, Ar7_dH or Ar7_fH), 5.85 (s, 1H, Ar4_fH), 5.66 (s, 1H, x₄H), 5.53 (d, 1H, *J* = 4.9 Hz, z₆H), 5.48 (s, 1H, x₅H), 5.24 (s, 1H, x₇H), 4.74 (s, 1H, x₆H), 3.88 (s, 3H, Ar7_eOCH₃), 3.681 (s, 3H, Ar5_eOCH₃), 3.678 (s, 3H, Ar7_cOCH₃), 3.25 (s, 3H, SO₂CH₃), 2.42 (s, 3H, NHCH₃), 1.42 (s, 9H, Piv-CH₃); Exact mass calculated for M+Na⁺: 1042; found: 1042 (FAB, *m*-nitrobenzyl alcohol, NaI added).

(21a-22aS, 5aR, 1S, 28S, 2R, 13R, 16R)-15, 29, 31-triaza-5-chloro-2,20,23,25-tetrahydroxy-28-(N-methylcarbamoyl)-10-(methylsulfonyloxy)-7-oxa-14,30,32-trioxo-13-(2,2,2-trifluoroacetyl amino)hexacyclo

[14.14.2.2<3,6>.1<8,12>.1<17,21>.0<22,27>]hexatriaconta-

3(33),4,6(34),8(35),9,11,17,19,21(36),22(27),23,25-dodecaen-9-yl 2,2-dimethylpropanoate (20).

TLC R_f = 0.14 (10% MeOH/CH₂Cl₂); $[\alpha]^{24}_D$ = +43.8 (c = 0.58, MeOH); IR (KBr) 3375, 2982, 2940, 1753, 1719, 1661, 1503, 1429, 1369, 1230, 1179, 1100, 1030, 971, 805, 713 cm⁻¹; ¹H NMR (400 MHz, CD₃OD, 330K) δ 7.72 (d, 1H, J = 2.0 Hz, Ar6_bH), 7.51 (dd, 1H, J = 8.2, 2.0 Hz, Ar6_fH), 7.16 (dd, 1H, J = 2.0, 0.8 Hz, Ar4_bH), 7.10 (d, 1H, J = 8.6 Hz, Ar6_eH), 7.09 (d, 1H, J = 2.6 Hz, Ar5_bH), 7.05 (dd, 1H, J = 8.5, 2.4 Hz, Ar5_fH), 6.86 (d, 1H, J = 8.5 Hz, Ar5_eH), 6.46 (d, 1H, J = 2.3 Hz, Ar7_dH), 6.40 (d, 1H, J = 2.3 Hz, Ar7_fH), 5.90 (d, 1H, J = 2.0 Hz, Ar4_fH), 5.88 (s, 1H, x₄H), 5.34 (s, 1H, z₆H), 4.72 (s, 1H, x₅H), 4.66 (s, 1H, x₇H), 4.17 (d, 1H, J = 1.4 Hz, x₆H), 3.27 (s, 3H, SO₂CH₃), 2.84 (s, 3H, NHCH₃), 1.41 (s, 9H, Piv-CH₃); Exact mass calculated for M+Na⁺, 1000.1702, found: 1000.1702 (FAB, *m*-nitrobenzyl alcohol, NaI added).

(21a-22aS,5aR,1S,28S,2R,13R,16R)-15,29,31-triaza-5-chloro-2-hydroxy-28-(*N*-methylcarbamoyl)-10-(methylsulfonyloxy)-7-oxa-14,30,32-trioxo-13-(2,2,2-trifluoroacetylamino)-20,23,25-tris(phenylmethoxy)hexacyclo

[14.14.2.2<3,6>.1<8,12>.1<17,21>.0<22,27>]hexatriaconta-

3(33),4,6(34),8(35),9,11,17,19,21(36),22,24,26-dodecaen-9-yl 2,2-dimethylpropanoate. TLC R_f = 0.56 (10% MeOH/CH₂Cl₂); $[\alpha]^{24}_D$ = +24.8 (c = 0.83, MeOH); IR (KBr) 3388, 2932, 2877, 1758, 1664, 1606, 1505, 1373, 1324, 1215, 1179, 1093, 1060, 1028, 968 cm⁻¹; ¹H NMR (400 MHz, CD₃OD, 330 K) δ 7.53 (d, 1H, J = 2.0 Hz, Ar6_bH), 7.52 (dd, 1H, J = 8.3, 2.0 Hz, Ar6_fH), 7.43-7.30 (m, 4H, benzyl ArH), 7.19-7.04 (m, 15H, 11 benzyl ArH, Ar4_bH, Ar6_eH, Ar5_bH, Ar5_fH), 7.00 (d, 1H, J = 8.6 Hz, Ar5_eH), 6.80 (d, 1H, J = 2.3 Hz, Ar7_dH), 6.64 (d, 1H, J = 2.2 Hz, Ar7_fH), 5.91 (m, 2H, Ar4_fH, x₄H), 5.33 (s, 1H, z₆H), 5.13 (s, 2H, OCH₂Ph), 5.10 (d, 1H, J = 12.4 Hz, OCH₂Ph), 4.98-4.96 (m, 3H, OCH₂Ph), 4.77 (s, 1H, x₅H), 4.75 (s, 1H, x₇H), 4.18 (s, 1H, x₆H), 3.27 (s, 3H, SO₂CH₃), 2.78 (s, 3H, NHCH₃), 1.41 (s, 9H, Piv-CH₃); Mass calculated for M+Na⁺: 1270; found: 1270 (FAB, *m*-nitrobenzyl alcohol, NaI added).

(21a-22aS,5aR,1S,28S,2R,13R,16R)-15,29,31-triaza-5-chloro-2,9-dihydroxy-28-(*N*-methylcarbamoyl)-7-oxa-14,30,32-trioxo-13-(2,2,2-trifluoroacetylamino)-20,23,25-tris(phenylmethoxy)hexacyclo

3(33),4,6(34),8(35),9,11,17,19,21(36),22,24,26-dodecaen-10-yl methylsulfonate. TLC R_f = 0.45

(10% MeOH/CH₂Cl₂); $[\alpha]^{24}_D$ = +28.7 (c = 1.00, MeOH); IR (CH₃CN) 3629, 3544, 3342, 1725, 1700, 1676, 1606, 1507, 1310, 1214, 1178, 1009, 813, 701 cm⁻¹; ¹H NMR (400 MHz, CD₃OD, 330 K) δ 7.69 (d, 1H, J = 1.9 Hz, Ar6_bH), 7.52 (dd, 1H, J = 8.4, 1.8 Hz, Ar6_fH), 7.43-7.30 (m, 4H, benzyl ArH), 7.19-7.04 (m, 14H, 11 benzyl ArH, Ar6_eH, Ar5_bH, Ar5_fH), 7.00 (d, 1H, J = 8.7 Hz, Ar5_eH), 6.96 (d, 1H, J = 1.5 Hz, Ar4_bH), 6.80 (d, 1H, J = 2.3 Hz, Ar7_dH), 6.64 (d, 1H, J = 2.2 Hz, Ar7_fH), 5.83 (d, 1H, J = 2.2 Hz, Ar4_fH), 5.81 (s, 1H, x₄H), 5.34 (s, 1H, z₆H), 5.13 (s, 2H, OCH₂Ph), 5.05 (d, 1H, J = 12.4 Hz, OCH₂Ph), 4.99-4.95 (m, 3H, OCH₂Ph), 4.76 (s, 2H, x₅H, x₇H), 4.18 (s, 1H, x₆H), 3.30 (s, 3H, SO₂CH₃), 2.78 (s, 3H, NHCH₃); Mass calculated for M+Na⁺: 1186; found: 1186 (FAB, *m*-nitrobenzyl alcohol, NaI added).

(21a-22aS,5aR,1S,28S,2R,13R,16R)-15,29,31-triaza-5-chloro-2-hydroxy-28-(*N*-methylcarbamoyl)-7-oxa-14,30,32-trioxo-9-prop-2-enyloxy-13-(2,2,2-trifluoroacetylamino)-20,23,25-

tris(phenylmethoxy)hexacyclo

[14.14.2.2<3,6>.1<8,12>.1<17,21>.0<22,27>]hexatriaconta-

3(33),4,6(34),8(35),9,11,17,19,21(36),22,24,26-dodecaen-10-yl methylsulfonate. TLC R_f = 0.56 (10% MeOH/CH₂Cl₂); $[\alpha]^{24}_D$ = +16.2 (c = 1.00, MeOH); IR (CH₃CN) 3632, 3543, 2939, 1726, 1676, 1632, 1501, 1311, 1216, 1180, 1060, 1023, 972, 803 cm⁻¹; ¹H NMR (400 MHz, CD₃OD, 330K) δ 7.71 (d, 1H, J = 2.0 Hz, Ar6_bH), 7.55 (dd, 1H, J = 8.4, 2.0 Hz, Ar6_fH), 7.43-7.29 (m, 4H, benzyl ArH), 7.20-7.03 (m, 14H, 11 benzyl ArH, Ar6_eH, Ar5_bH, Ar5_fH), 7.00 (d, 1H, J = 8.6 Hz, Ar5_eH), 7.00 (dd, 1H, J = 2.1, 0.8 Hz, Ar4_bH), 6.80 (d, 1H, J = 2.3 Hz, Ar7_dH), 6.64 (d, 1H, J = 2.2 Hz, Ar7_fH), 6.17 (dddd, 1H, J = 16.4, 10.4, 6.0, 6.0 Hz, OCH₂CH=CH₂), 5.88 (s, 1H, x₄H), 5.83 (d, 1H, J = 2.2 Hz, Ar4_fH), 5.41 (ddd, 1H, J = 17.2, 3.0, 1.5 Hz, OCH₂CH=CHH), 5.35 (br s, 1H, z₆H), 5.25 (ddd, 1H, J = 10.4, 2.6, 1.1 Hz, OCH₂CH=CHH), 5.13 (s, 2H, OCH₂Ph), 5.04 (d, 1H, J = 12.3 Hz, OCH₂Ph), 4.98-4.92 (m, 3H, OCH₂Ph), 4.85-4.76 (m, 2H, OCH₂CH=CHH), 4.79 (s, 1H, x₅H), 4.76 (s, 1H, x₇H), 4.20 (s, 1H, x₆H), 3.30 (s, 3H, SO₂CH₃), 2.78 (s, 3H, NHCH₃); Mass calculated for M+Na⁺: 1226; found: 1226 (FAB, *m*-nitrobenzyl alcohol, NaI added).

(21a-22aS, 5aR)-[(1S,28S,2R,13R,16R)-13-amino-15,29,31-triaza-5-chloro-2,10-dihydroxy-7-oxa-14,30,32-trioxo-9-prop-2-enyloxy-20,23,25-

tris(phenylmethoxy)hexacyclo[14.14.2.2<3,6>.1<8,12>.1<17,21>.0<22,27>]hexatriaconta-

3(33),4,6(34),8(35),9,11,17,19,21(36),22,24,26-dodecaen-28-yl]-N-methylcarboxamide (21). HPLC r_t = 4.3 min (60/40 CH₃CN/water(0.1%TFA), Rx-C8, 1 mL/min); $[\alpha]^{24}_D$ = -23.6 (c = 0.86, MeOH); IR (CH₃CN) 3634, 3542, 3378, 2938, 1672, 1632, 1611, 1581, 1502, 1323, 1240, 1161, 742, 701 cm⁻¹; ¹H NMR (400 MHz, CD₃OD, 330 K) δ 7.65 (d, 1H, J = 2.0 Hz, Ar6_bH), 7.48 (dd, 1H, J = 8.5, 2.0 Hz, Ar6_fH), 7.42-7.24 (m, 4H, benzyl ArH), 7.19-7.08 (m, 14H, 11 benzyl ArH, Ar6_eH, Ar5_bH, Ar5_fH), 6.99 (d, 1H, J = 8.6 Hz, Ar5_eH), 6.80 (dd, 1H, J = 2.2, 0.9 Hz, Ar4_bH), 6.78 (d, 1H, J = 2.3 Hz, Ar7_dH), 6.63 (d, 1H, J = 2.2 Hz, Ar7_fH), 6.17 (dddd, 1H, J = 16.5, 10.3, 6.1, 6.1 Hz, OCH₂CH=CH₂), 5.38-5.33 (m, 1H, OCH₂CH=CHH), 5.33 (s, 1H, Ar4_fH), 5.25 (d, 1H, J = 2.1 Hz, z₆H), 5.20-5.16 (m, 1H, OCH₂CH=CHH), 5.12 (s, 2H, OCH₂Ph), 5.05 (d, 1H, J = 12.3 Hz, OCH₂Ph), 4.97 (d, 1H, J = 11.3 Hz, OCH₂Ph), 4.95 (s, 2H, OCH₂Ph), 4.75 (s, 1H, x₅H or x₇H), 4.73 (s, 1H, x₅H or x₇H), 4.71-4.68 (m, 2H, OCH₂CH=CHH), 4.48 (s, 1H, x₄H), 4.18 (s, 1H, x₆H), 2.78 (s, 3H, NHCH₃); Mass calculated for M+Na⁺: 1052; found: 1052 (FAB, *m*-nitrobenzyl alcohol, NaI added).

(21a-22aS,5aR)-2-((2R,3R)-2-((2S)-2-[(*tert*-butoxy)-N-methylcarbonylamino]-4-methylpentanoylamino)-3-(4-fluoro-3-nitrophenyl)-3-hydroxypropanoylamino)(2S)-N-[(1S,28S,2R,13R,16R)-15,29,31-triaza-5-chloro-2,10-dihydroxy-20,23,25-tris(phenylmethoxy)-28-(N-methylcarbonyl)-7-oxa-14,30,32-trioxo-9-prop-2-enyloxyhexacyclo[14.14.2.2<3,6>.1<8,12>.1<17,21>.0<22,27>]hexatriaconta-

3(33),4,6(34),8(35),9,11,17,19,21(36),22,24,26-dodecaen-13-yl]-N'-[bis(4-methoxyphenyl)methyl]butane-1,4-diamide (23). TLC R_f = 0.48 (10% MeOH/CH₂Cl₂); $[\alpha]^{24}_D$ = +5.2 (c = 0.57, MeOH); IR (CH₃CN) 3635, 3542, 2936, 1644, 1512, 1323, 1249, 1179, 1064, 741 cm⁻¹; ¹H NMR (400 MHz, CD₃OD, 330 K) δ 7.95 (dd, 1H, J = 7.1, 2.2 Hz, Ar2_bH), 7.63 (d, 1H, J = 2.0 Hz, Ar6_bH), 7.51-7.48 (m, 1H, Ar2_fH), 7.50 (dd, 1H, J = 8.5, 2.0 Hz, Ar6_fH), 7.39-7.28 (m, 4H, benzyl ArH), 7.23-7.06 (m, 19H, 11 benzyl ArH, 4 Ddm ArH, Ar6_eH, Ar2_eH, Ar5_bH, Ar5_fH), 6.97 (d, 1H, J =

8.7 Hz, Ar5_eH), 6.81 (d, 4H, *J* = 8.8 Hz, Ddm ArH), 6.71 (d, 1H, *J* = 2.3 Hz, Ar7_dH), 6.61 (d, 1H, *J* = 2.2 Hz, Ar7_fH), 6.54 (dd, 1H, *J* = 2.1, 0.9 Hz, Ar4_bH), 6.16 (dddd, 1H, *J* = 16.5, 10.4, 6.1, 6.1 Hz, OCH₂CH=CH₂), 5.99 (s, 1H, Ddm Ar₂CH), 5.76 (s, 1H, Ar4_fH), 5.35 (ddd, 1H, *J* = 17.3, 3.1, 1.5 Hz, OCH₂CH=CHH), 5.32 (s, 1H, x₄H), 5.28 (dd, 1H, *J* = 2.2, 0.7 Hz, z₆H), 5.18 (ddd, 1H, *J* = 10.3, 2.7, 1.1 Hz, OCH₂CH=CHH), 5.08 (s, 2H, OCH₂Ph), 5.05 (d, 1H, *J* = 12.4 Hz, OCH₂Ph), 4.98-4.92 (m, 3H, OCH₂Ph), 4.83-4.79 (m, 2H, x₃H and z₂H), 4.73 (s, 2H, x₅H and x₇H), 4.71-4.68 (m, 2H, OCH₂CH=CHH), 4.55 (d, 1H, *J* = 7.0 Hz, x₂H), 4.45 (dd, 1H, *J* = 9.8, 5.4 Hz, x₁H), 4.17 (d, 1H, *J* = 1.4 Hz, x₆H), 3.727 (s, 3H, ArOCH₃), 3.725 (s, 3H, ArOCH₃), 2.79-2.76 (m, 2H, 3_aCH₂), 2.78 (s, 3H, (CO)NHCH₃), 2.51 (s, 3H, N(Boc)CH₃), 1.52-1.39 (m, 3H, 1_aCHH, 1_aCHH, 1_bCH), 1.37 (s, 9H, Boc-CH₃), 0.83 (d, 3H, *J* = 6.5 Hz, 1_cCH₃), 0.80 (d, 3H, *J* = 6.4 Hz, 1_cCH₃); Mass calculated for M+Na⁺: 1846, found: 1846 (FAB, *m*-nitrobenzyl alcohol, NaI added).

(33a-34a *S*,5a*R*,15a*R*)-[19-{(2*R*)-2-[(*tert*-butoxy)-*N*-methylcarbonylamino]-4-methylpentanoylamino}(1*S*,22*S*,40*S*,2*R*,18*R*,19*R*,25*R*,28*R*)-15-amino-21,24,27,41,43-pentaaza-22-({*N*-[bis(4-methoxyphenyl)methyl]carbamoyl)methyl)-5-chloro-2,18-dihydroxy-7,13-dioxo-20,23,26,42,44-pentaoxo-49-prop-2-enyloxy-32,35,37-tris(phenylmethoxy)octacyclo[26.14.2.2<3,6>.2<14,17>.1<8,12>.1<29,33>.0<10,25>.0<34,39>]pentaconta-3(45),4,6(46),8,10,12(49),14,16,29,31,33(50),34,36,38,47-pentadecaen-40-yl]-*N*-methylcarboxamide. HPLC *rt* = 11.6 min (70/30 CH₃CN / water (0.1%TFA), Rx-C8, 1 mL/min); [α]²⁴_D = +51.9 (*c* = 0.85, MeOH); IR (CH₃CN) 3630, 3546, 2936, 1677, 1633, 1510, 1379, 1249, 1178, 1158, 835 cm⁻¹; ¹H NMR (400 MHz, CD₃OD, 330 K) δ 7.65 (d, 1H, *J* = 1.9 Hz, Ar6_bH), 7.55 (dd, 1H, *J* = 8.5, 1.9 Hz, Ar6_fH), 7.40-7.27 (m, 4H, benzyl ArH), 7.21 (d, 1H, *J* = 8.5 Hz, Ar6_eH), 7.19-6.69 (m, 25H, 11 benzyl ArH, 8 Ddm ArH, Ar2_bH, Ar2_eH, Ar2_fH, Ar5_bH, Ar5_eH, Ar5_fH), 6.67 (d, 1H, *J* = 2.2 Hz, Ar7_dH), 6.60 (d, 1H, *J* = 2.1 Hz, Ar7_fH), 6.27 (dddd, 1H, *J* = 16.4, 10.4, 6.0, 6.0 Hz, OCH₂CH=CH₂), 5.98 (s, 1H, Ar4_bH), 5.85 (s, 1H, Ddm Ar₂CH), 5.69 (s, 1H, x₄H), 5.45 (ddd, 1H, *J* = 17.2, 3.1, 1.5 Hz, OCH₂CH=CHH), 5.37 (s, 1H, Ar4_fH), 5.34 (s, 1H, z₆H), 5.27-5.24 (m, 1H, OCH₂CH=CHH), 5.22 (d, 1H, *J* = 4.0 Hz, z₂H), 5.07 (s, 2H, OCH₂Ph), 5.07-5.03 (m, 1H, OCH₂Ph), 4.98 (d, 1H, *J* = 12.4 Hz, OCH₂Ph), 4.86-4.84 (m, 3H, x₃H, OCH₂CH=CHH), 4.84-4.78 (m, 2H, OCH₂Ph), 4.73 (s, 1H, x₅H), 4.70-4.69 (m, 3H, x₇H, x₂H, x₁H), 4.17 (s, 1H, x₆H), 3.73 (s, 3H, ArOCH₃), 3.67 (s, 3H, ArOCH₃), 2.79 (s, 3H, (CO)NHCH₃), 2.77 (s, 3H, N(Boc)CH₃), 2.63-2.59 (m, 1H, 3_aCHH), 2.46 (dd, 1H, *J* = 15.6, 7.2 Hz, 3_aCHH), 1.69-1.62 (m, 1H, 1_aCHH), 1.54-1.46 (m, 2H, 1_aCHH, 1_bCH), 1.46 (s, 9H, Boc-CH₃), 0.88 (d, 3H, *J* = 6.6 Hz, 1_cCH₃), 0.81 (d, 3H, *J* = 6.4 Hz, 1_cCH₃); Mass calculated for M+Na⁺, 1796, found: 1796 (FAB, *m*-nitrobenzyl alcohol, NaI added).

(33a-34a *S*,5a *R*15a *R*)-[19-{(2*R*)-2-[(*tert*-butoxy)-*N*-methylcarbonylamino]-4-methylpentanoylamino}(1*S*,22*S*,40*S*,2*R*,18*R*,19*R*,25*R*,28*R*)-21,24,27,41,43-pentaaza-22-({*N*-[bis(4-methoxyphenyl)methyl]carbamoyl)methyl)-5,15-dichloro-2,18-dihydroxy-7,13-dioxo-20,23,26,42,44-pentaoxo-49-prop-2-enyloxy-32,35,37-tris(phenylmethoxy)octacyclo[26.14.2.2<3,6>.2<14,17>.1<8,12>.1<29,33>.0<10,25>.0<34,39>]pentaconta-3(45),4,6(46),8,10,12(49),14,16,29,31,33(50),34,36,38,47-pentadecaen-40-yl]-*N*-methylcarboxamide (25). HPLC *rt* = 9.9 min (75 / 25 CH₃CN / water (0.1%TFA), Rx-C8, 1 mL/min); [α]²⁴_D = +22.5 (*c* = 0.62, MeOH); IR (CH₃CN) 3633, 3545, 2962, 1677, 1635, 1511, 1321, 1235,

1178, 1158, 925, 834, 700 cm⁻¹; ¹H NMR (400 MHz, CD₃OD, 330K) δ 7.64 (d, 1H, *J* = 1.9 Hz, Ar6_bH), 7.58-7.55 (m, 1H, Ar2_bH), 7.57 (dd, 1H, *J* = 8.3, 1.8 Hz, Ar6_fH), 7.48 (br s, 1H, Ar2_fH), 7.40-7.27 (m, 4H, benzyl ArH), 7.23 (d, 1H, *J* = 8.4 Hz, Ar6_eH), 7.20-6.90 (m, 19H, 11 benzyl ArH, 4 Ddm ArH, Ar2_eH, Ar5_bH, Ar5_fH, Ar5_eH), 6.77 (d, 2H, *J* = 8.8 Hz, 2 Ddm ArH), 6.69 (d, 2H, *J* = 8.7 Hz, 2 Ddm ArH), 6.67 (d, 1H, *J* = 2.3 Hz, Ar7_dH), 6.60 (d, 1H, *J* = 2.2 Hz, Ar7_fH), 6.26 (dddd, 1H, *J* = 16.4, 10.4, 6.0, 6.0 Hz, OCH₂CH=CH₂), 5.84 (s, 1H, Ddm Ar₂CH), 5.74 (s, 1H, Ar4_bH), 5.72 (s, 1H, x₄H), 5.48-5.42 (m, 1H, OCH₂CH=CHH), 5.41 (s, 1H, Ar4_fH), 5.34 (s, 1H, z₆H), 5.29 (d, 1H, *J* = 3.9 Hz, z₂H), 5.27-5.24 (m, 1H, OCH₂CH=CHH), 5.07 (s, 2H, OCH₂Ph), 5.07-5.03 (m, 1H, OCH₂Ph), 4.98 (d, 1H, *J* = 12.3 Hz, OCH₂Ph), 4.90-4.84 (m, 2H, OCH₂CH=CHH), 4.83 (br d, 1H, *J* = 4.0 Hz, x₃H), 4.77 (d, 1H, *J* = 4.0 Hz, x₂H), 4.72 (s, 1H, x₅H), 4.72-4.68 (m, 1H, x₁H), 4.68 (s, 1H, x₇H), 4.16 (s, 1H, x₆H), 3.73 (s, 3H, ArOCH₃), 3.67 (s, 3H, ArOCH₃), 2.79 (s, 3H, (CO)NHCH₃), 2.77 (s, 3H, N(Boc)CH₃), 2.71-2.63 (m, 1H, 3_aCHH), 2.42 (dd, 1H, *J* = 15.3, 7.4 Hz, 3_aCHH), 1.72-1.65 (m, 1H, 1_aCHH), 1.57-1.48 (m, 2H, 1_aCHH, 1_bCH), 1.48 (s, 9H, Boc-CH₃), 0.88 (d, 3H, *J* = 6.5 Hz, 1_cCH₃), 0.83 (d, 3H, *J* = 6.4 Hz, 1_cCH₃); Mass calculated for M+Na⁺: 1816; found: 1816 (FAB, *m*-nitrobenzyl alcohol, NaI added).

(33a-34a *S*,5a *R*,15a *R*)-19-[(2*R*)-2-[(*tert*-butoxy)-*N*-methylcarbonylamino]-4-methylpentanoylamino](1*S*,22*S*,40*S*,2*R*,18*R*,19*R*,25*R*,28*R*)-21,24,27,41,43-pentaaza-22-({*N*-[bis(4-methoxyphenyl)methyl]carbamoyl)methyl)-5,15-dichloro-2,18-dihydroxy-7,13-dioxo-20,23,26,42,44-penta-49-prop-2-enyloxy-32,35,37-tris(phenylmethoxy)octacyclo[26.14.2.2<3,6>.2<14,17>.1<8,12>.1<29,33>.0<10,25>.0<34,39>]pentaconta-3(45),4,6(46),8,10,12(49),14,16,29,31,33(50),34,36,38,47-pentadecaene-40-carboxylic acid (26). HPLC rt = 9.5 min (75 / 25 CH₃CN / water (0.1%TFA), Rx-C8, 1 mL/min); [α]_D²⁴ = +33.1 (c = 0.28, MeOH); IR (CH₃CN) 3628, 3543, 2934, 1676, 1635, 1511, 1323, 1235, 1178, 1160, 819 cm⁻¹; ¹H NMR (400 MHz, CD₃OD, 330 K) δ 7.63 (d, 1H, *J* = 1.7 Hz, Ar6_bH), 7.57 (dd, 1H, *J* = 8.3, 1.8 Hz, Ar6_fH), 7.55 (m, 1H, Ar2_bH), 7.48 (br s, 1H, Ar2_fH), 7.41-7.27 (m, 4H, benzyl ArH), 7.21-7.13 (m, 7H, Ar6_eH, Ar2_eH, 5 benzyl ArH), 7.07-6.89 (m, 14H, 6 benzyl ArH, 4 Ddm ArH, Ar5_bH, Ar5_fH, Ar5_eH, Ar7_dH or Ar7_fH), 6.77 (d, 2H, *J* = 8.8 Hz, 2 Ddm ArH), 6.69 (d, 2H, *J* = 8.2 Hz, 2 Ddm ArH), 6.65 (s, 1H, Ar7_dH or Ar7_fH), 6.26 (dddd, 1H, *J* = 16.4, 10.4, 6.0, 6.0 Hz, OCH₂CH=CH₂), 5.84 (s, 1H, Ddm Ar₂CH), 5.74 (s, 2H, Ar4_bH, x₄H), 5.47-5.42 (m, 1H, OCH₂CH=CHH), 5.41 (s, 1H, Ar4_fH), 5.32 (s, 1H, z₆H), 5.29 (d, 1H, *J* = 4.1 Hz, z₂H), 5.27-5.24 (m, 1H, OCH₂CH=CHH), 5.06 (s, 2H, OCH₂Ph), 5.01 (d, 2H, *J* = 3.0 Hz, OCH₂Ph), 4.87-4.84 (m, 2H, OCH₂CH=CHH), 4.81-4.77 (m, 2H, x₃H, x₂H), 4.72-4.70 (m, 1H, x₁H), 4.68 (s, 1H, x₅H), 4.56 (br s, 1H, x₇H), 4.13 (s, 1H, x₆H), 3.73 (s, 3H, ArOCH₃), 3.67 (s, 3H, ArOCH₃), 2.79 (s, 3H, N(Boc)CH₃), 2.72-2.68 (m, 1H, 3_aCHH), 2.42 (dd, 1H, *J* = 15.5, 7.4 Hz, 3_aCHH), 1.72-1.65 (m, 1H, 1_aCHH), 1.53-1.42 (m, 2H, 1_aCHH, 1_bCH), 1.49 (s, 9H, Boc-CH₃), 0.88 (d, 3H, *J* = 6.5 Hz, 1_cCH₃), 0.82 (d, 3H, *J* = 6.4 Hz, 1_cCH₃); Mass calculated for M+Na⁺: 1803; found: 1803 (FAB, *m*-nitrobenzyl alcohol, NaI added).

(33a-34a *S*,5a *R*,15a *R*)-19-[(2*R*)-2-[(*tert*-butoxy)-*N*-methylcarbonylamino]-4-methylpentanoylamino](1*S*,22*S*,40*S*,2*R*,18*R*,19*R*,25*R*,28*R*)-21,24,27,41,43-pentaaza-22-({*N*-[bis(4-methoxyphenyl)methyl]carbamoyl)methyl)-5,15-dichloro-2,18,49-trihydroxy-7,13-dioxo-20,23,26,42,44-penta-49-tris(phenylmethoxy)octacyclo[26.14.2.2<3,6>.2<14,17>.1<8,12>.1<29,33>.0<10,25>.0<34,39>]penta

conta-3(45),4,6(46),8,10,12(49),14,16,29,31,33(50),34,36,38,47-pentadecaene-40-carboxylic acid. HPLC rt = 6.4 min (75 / 25 CH₃CN / water (0.1%TFA), Rx-C8, 1 mL/min); [α]²⁴_D = +36.0 (c = 0.26, MeOH); IR (CH₃CN) 3629, 3542, 2966, 2938, 1757, 1675, 1636, 1513, 1490, 1322, 1248, 1178, 1160, 833, 760, 702 cm⁻¹; ¹H NMR (400 MHz, CD₃OD, 330 K) δ 7.62 (d, 1H, *J* = 1.8 Hz, Ar6_bH), 7.56 (dd, 1H, *J* = 8.3, 1.8 Hz, Ar6_fH), 7.54 (m, 1H, Ar2_bH), 7.45 (br s, 1H, Ar2_fH), 7.39-7.27 (m, 4H, benzyl ArH), 7.25 (d, 1H, *J* = 8.4 Hz, Ar6_eH), 7.21-7.12 (m, 6H, Ar2_eH, 5 benzyl ArH), 7.08-6.98 (m, 14H, 6 benzyl ArH, 4 Ddm ArH, Ar5_bH, Ar5_fH, Ar5_eH, Ar7_dH or Ar7_fH), 6.77 (d, 2H, *J* = 8.7 Hz, 2 Ddm ArH), 6.69 (d, 2H, *J* = 8.6 Hz, 2 Ddm ArH), 6.65 (s, 1H, Ar7_dH or Ar7_fH), 5.85 (s, 1H, Ddm Ar₂CH), 5.74 (s, 1H, x₄H), 5.69 (s, 1H, Ar4_bH), 5.40 (d, 1H, *J* = 1.1 Hz, z₆H), 5.31 (s, 1H, Ar4_fH), 5.31-5.29 (m, 1H, z₂H), 5.09-5.06 (m, 1H, OCH₂Ph), 5.06 (s, 2H, OCH₂Ph), 5.01 (d, 2H, *J* = 3.1 Hz, OCH₂Ph), 4.92 (d, 1H, *J* = 5.8 Hz, OCH₂Ph), 4.81 (d, 1H, *J* = 4.5 Hz, x₃H), 4.77 (d, 1H, *J* = 4.3 Hz, x₂H), 4.73-4.69 (m, 1H, x₁H), 4.67 (s, 1H, x₅H), 4.61 (br s, 1H, x₇H), 4.12 (s, 1H, x₆H), 3.73 (s, 3H, ArOCH₃), 3.67 (s, 3H, ArOCH₃), 2.78 (s, 3H, N(Boc)CH₃), 2.71-2.63 (m, 1H, 3_aCHH), 2.43 (dd, 1H, *J* = 15.5, 7.1 Hz, 3_aCHH), 1.71-1.63 (m, 1H, 1_aCHH), 1.50-1.48 (m, 2H, 1_aCHH, 1_bCH), 1.48 (s, 9H, Boc-CH₃), 0.87 (d, 3H, *J* = 6.4 Hz, 1_cCH₃), 0.81 (d, 3H, *J* = 6.2 Hz, 1_cCH₃); Mass calculated for M+Na⁺: 1763; found: 1763 (FAB, *m*-nitrobenzyl alcohol, NaI added).

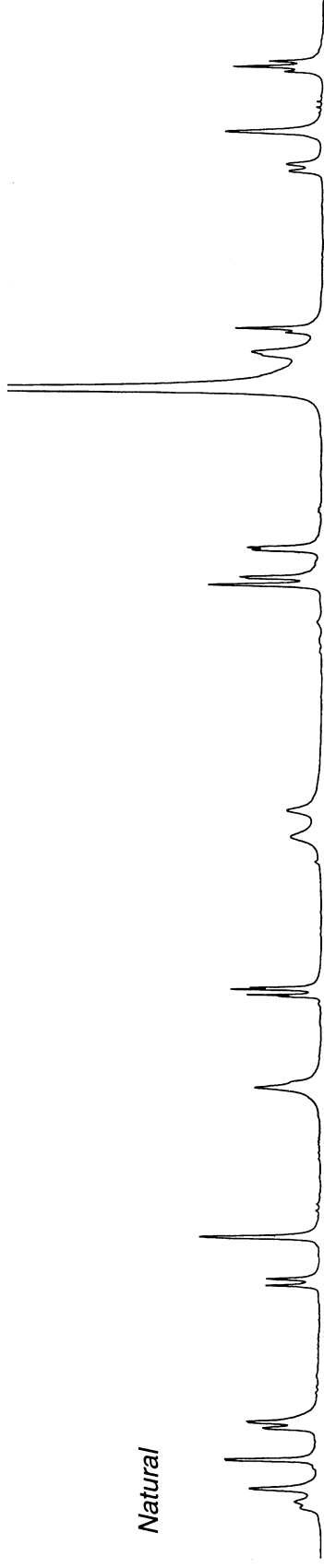
(33a-34a S,5a R,15a R)-19-[(2R)-2-[(*tert*-butoxy)-*N*-methylcarbonylamino]-4-methylpentanoylamino](1S,22S,40S,2R,18R,19R,25R,28R)-21,24,27,41,43-pentaaza-22-({*N*-[bis(4-methoxyphenyl)methyl]carbamoyl)methyl)-5,15-dichloro-2,18,32,35,37,49-hexahydroxy-7,13-dioxa-20,23,26,42,44-pentaooxocyclo[26.14.2.2<3,6>.2<14,17>.1<8,12>.1<29,33>.0<10,25>.0<34,39>]pentaconta-3(45),4,6(46),8,10,12(49),14,16,29,31,33(50),34,36,38,47-pentadecaene-40-carboxylic acid. HPLC rt = 8.8 min (50 / 50 CH₃CN / water (0.1%TFA), Rx-C8, 1 mL/min); [α]²⁴_D = +19.2 (c = 0.16, MeOH); ¹H NMR (400 MHz, CD₃OD, 330 K) δ 7.62 (s, 1H, Ar6_bH), 7.58 (m, 1H, Ar2_bH), 7.54 (d, 1H, *J* = 8.6 Hz, Ar6_fH), 7.44 (s, 1H, Ar2_fH), 7.26 (d, 1H, *J* = 8.3 Hz, Ar6_eH), 7.19 (d, 1H, *J* = 8.4 Hz, Ar2_eH), 7.04 (d, 2H, *J* = 8.5 Hz, 2 Ddm ArH), 7.05-7.03 (m, 2H, Ar5_bH, Ar5_fH), 6.99 (d, 2H, *J* = 8.5 Hz, 2 Ddm ArH), 6.94 (d, 1H, *J* = 8.1 Hz, Ar5_eH), 6.83 (d, 2H, *J* = 8.7 Hz, 2 Ddm ArH), 6.79 (s, 1H, Ar7_dH or Ar7_fH), 6.78 (d, 2H, *J* = 8.6 Hz, 2 Ddm ArH), 6.42 (s, 1H, Ar7_dH or Ar7_fH), 5.91 (s, 1H, Ddm Ar₂CH), 5.74 (s, 1H, x₄H), 5.62 (s, 1H, Ar4_bH), 5.39 (s, 1H, Ar4_fH), 5.34 (s, 1H, z₆H), 5.30 (d, 1H, *J* = 4.4 Hz, z₂H), 4.77 (d, 1H, *J* = 4.3 Hz, x₂H), 4.77 (m, 2H, x₃H, x₁H), 4.61 (s, 2H, x₅H, x₇H), 4.11 (s, 1H, x₆H), 3.76 (s, 3H, ArOCH₃), 3.74 (s, 3H, ArOCH₃), 2.79 (s, 3H, N(Boc)CH₃), 2.70-2.66 (m, 1H, 3_aCHH), 2.45 (dd, 1H, *J* = 15.6, 7.4 Hz, 3_aCHH), 1.71-1.65 (m, 1H, 1_aCHH), 1.48 (m, 2H, 1_aCHH, 1_bCH), 1.48 (s, 9H, Boc-CH₃), 0.90 (d, 3H, *J* = 6.4 Hz, 1_cCH₃), 0.86 (d, 3H, *J* = 6.2 Hz, 1_cCH₃); Mass calculated for M+Na⁺: 1492; found: 1492 (FAB, *m*-nitrobenzyl alcohol, NaI added).

Vancomycin aglycon. (33a-34a S,5a R, 15a R)-19-[(2R)-4-methyl-2-(methylamino)pentanoylamino](1S,22S,40S,2R,18R,19R,25R,28R)-21,24,27,41,43-pentaaza-22-(carbamoylmethyl)-5,15-dichloro-2,18,32,35,37,49-hexahydroxy-7,13-dioxa-20,23,26,42,44-pentaooxocyclo[26.14.2.2<3,6>.2<14,17>.1<8,12>.1<29,33>.0<10,25>.0<34,39>]pentaconta-3(45),4,6(46),8,10,12(49),14,16,29,31,33(50),34,36,38,47-pentadecaene-40-carboxylic acid (1). *Synthetic sample:* HPLC rt = 9.98 min (gradient: 0-9 min, 15/85 MeCN/water (0.1%TFA) to 30/70; 9-12 min, hold at 30/70; Rx-C8, 1 mL/min); [α]²⁴_D = +23.5 (c = 0.13, MeOH); ¹H NMR (500 MHz, CD₃OD,

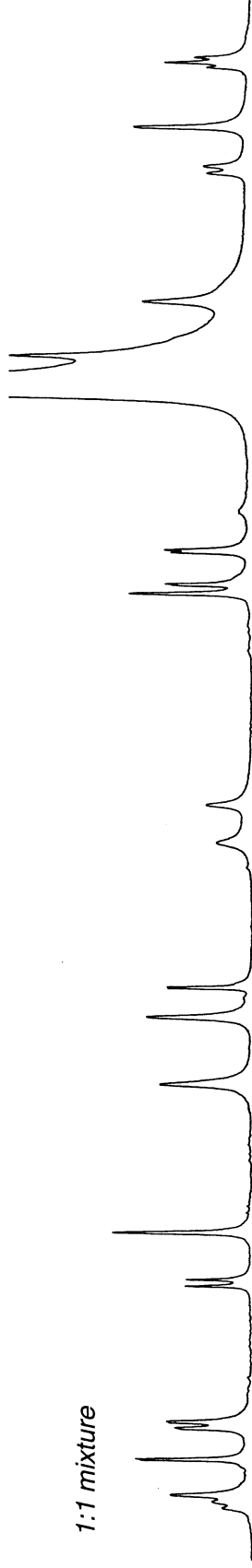
300K) δ 8.94 (d, 1H, J = 6.2 Hz, w_5H , slowly exchanged out), 8.70 (d, 1H, J = 5.6 Hz, w_7H , slowly exchanged out), 7.97 (s, exchangeable), 7.76 (m, 1H, $Ar6_fH$), 7.71 (s, 1H, $Ar2_bH$), 7.64 (d, 1H, J = 1.9 Hz, $Ar6_bH$), 7.55 (d, 1H, J = 8.6 Hz, $Ar6_eH$), 7.53 (m, 1H, $Ar2_fH$), 7.17 (d, 1H, J = 8.4 Hz, $Ar2_eH$), 7.06 (s, 1H, $Ar5_bH$), 6.67 (m, 2H, $Ar5_fH$, $Ar5_eH$), 6.43 (d, 1H, J = 2.3 Hz, $Ar7_dH$ or $Ar7_fH$), 6.39 (d, 1H, J = 2.3 Hz, $Ar7_dH$ or $Ar7_fH$), 5.99 (br s, 1H, x_4H), 5.94 (br s, 1H, $Ar4_bH$), 5.34 (s, 1H, z_6H), 5.33 (d, 1H, J = 1.9 Hz, $Ar4_fH$), 5.25 (d, 1H, J = 3.1 Hz, z_2H), 4.74 (d, 1H, J = 6.0 Hz, x_5H , collapses to singlet as w_5H exchanges), 4.70 (d, 1H, J = 5.7 Hz, x_7H , collapses to singlet as w_7H exchanges), 4.25 (d, 1H, J = 5.3 Hz, x_3H), 4.16 (s, 1H, x_6H), 4.00 (t, 1H, J = 7.0 Hz, x_1H), 2.98 (s, exchangeable), 2.94 (d, 1H, J = 15.2 Hz, 3_aCHH), 2.76 (s, 3H, NCH_3), 2.85 (s, exchangeable), 2.02-1.97 (m, 1H, 3_aCHH), 1.89-1.84 (m, 1H, 1_aCHH), 1.67-1.59 (m, 2H, 1_aCHH and 1_bCH), 0.92 (d, 3H, J = 6.1 Hz, 1_cCH_3), 0.90 (d, 3H, J = 6.2 Hz, 1_cCH_3); Mass calculated for $M+H^+$: 1143; found: 1143 (electrospray). *Natural sample*: HPLC rt = 9.98 min (gradient: 0-9 min, 15/85 MeCN/water (0.1%TFA) to 30/70; 9-12 min, hold at 30/70; Rx-C8, 1 mL/min); $[\alpha]^{24}_D$ = +46.3 (c = 0.13, MeOH); 1H NMR (500 MHz, CD_3OD , 300K) δ 8.95 (d, 1H, J = 6.0 Hz, w_5H , slowly exchanged out), 8.70 (d, 1H, J = 5.3 Hz, w_7H , slowly exchanged out), 7.76 (m, 1H, $Ar6_fH$), 7.72 (s, 1H, $Ar2_bH$), 7.64 (d, 1H, J = 1.6 Hz, $Ar6_bH$), 7.55 (d, 1H, J = 8.4 Hz, $Ar6_eH$), 7.55 (m, 1H, $Ar2_fH$), 7.17 (d, 1H, J = 8.4 Hz, $Ar2_eH$), 7.06 (s, 1H, $Ar5_bH$), 6.66 (m, 2H, $Ar5_fH$, $Ar5_eH$), 6.42 (d, 1H, J = 2.2 Hz, $Ar7_dH$ or $Ar7_fH$), 6.40 (d, 1H, J = 2.2 Hz, $Ar7_dH$ or $Ar7_fH$), 6.01 (br s, 1H, x_4H), 5.94 (br s, 1H, $Ar4_bH$), 5.35 (s, 1H, z_6H), 5.33 (d, 1H, J = 1.6 Hz, $Ar4_fH$), 5.25 (d, 1H, J = 3.1 Hz, z_2H), 4.74 (d, 1H, J = 4.1 Hz, x_5H , collapses to singlet as w_5H exchanges), 4.68 (d, 1H, J = 5.4 Hz, x_7H , collapses to singlet as w_7H exchanges), 4.26 (d, 1H, J = 9.4 Hz, x_3H), 4.16 (s, 1H, x_6H), 3.99 (t, 1H, J = 7.0 Hz, x_1H), 2.95 (d, 1H, J = 15.2 Hz, 3_aCHH), 2.77 (s, 3H, NCH_3), 2.02-1.98 (m, 1H, 3_aCHH), 1.87-1.82 (m, 1H, 1_aCHH), 1.68-1.59 (m, 2H, 1_aCHH and 1_bCH), 0.91 (d, 3H, J = 6.7 Hz, 1_cCH_3), 0.90 (d, 3H, J = 6.6 Hz, 1_cCH_3); Mass calculated for $M+H^+$: 1143; found: 1143 (electrospray).

The identity of the natural and synthetic compounds was further verified by HPLC co-injection: rt = 9.98 min (gradient: 0-9 min, 15/85 MeCN/water (0.1%TFA) to 30/70; 9-12 min, hold at 30/70; Rx-C8, 1 mL/min); overlay of 1H COSY spectra; and 1H NMR (see below) of a 1:1 mixture of natural and synthetic material, which showed a single entity with no doubling of peaks.

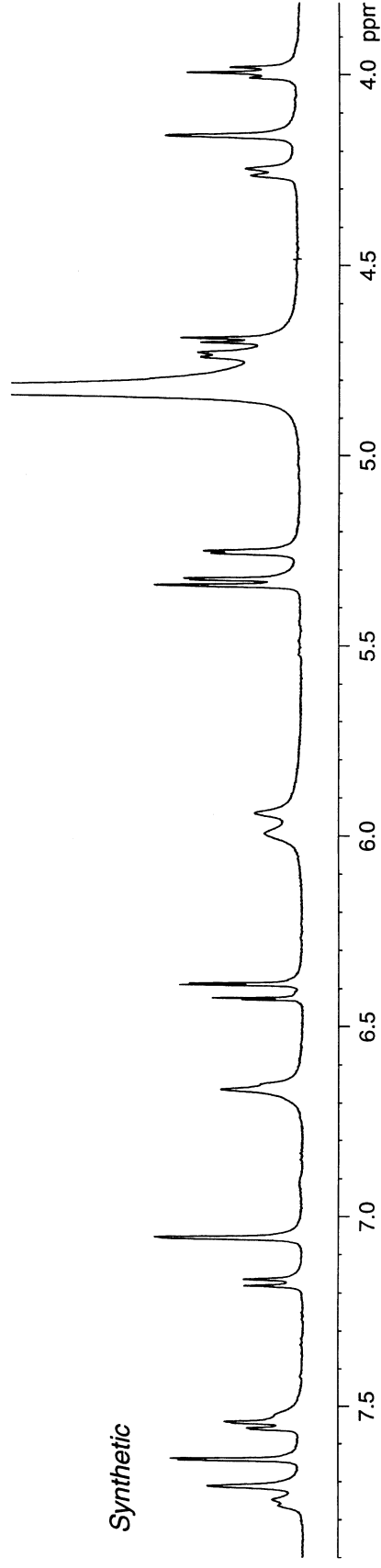
Natural

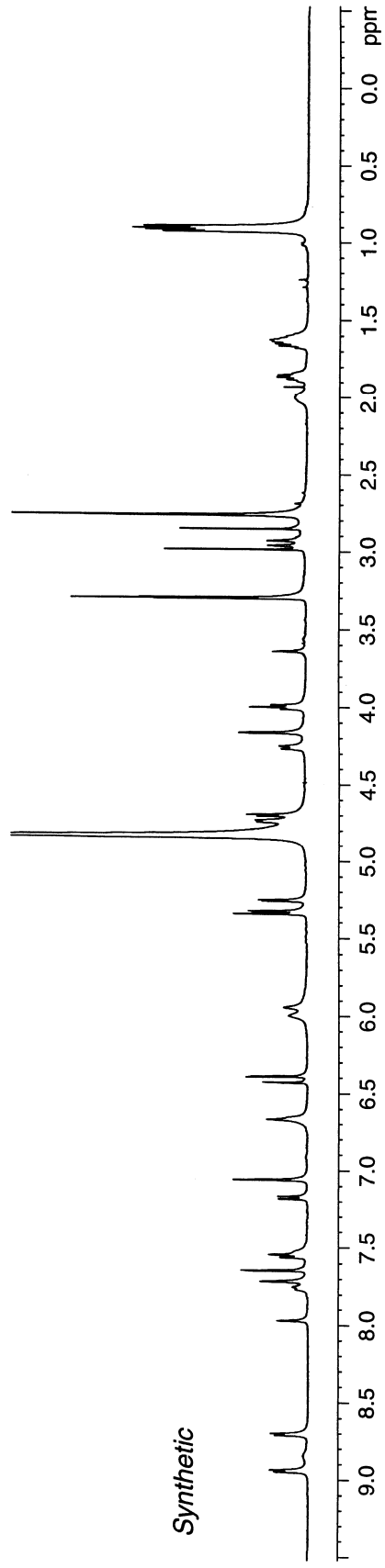
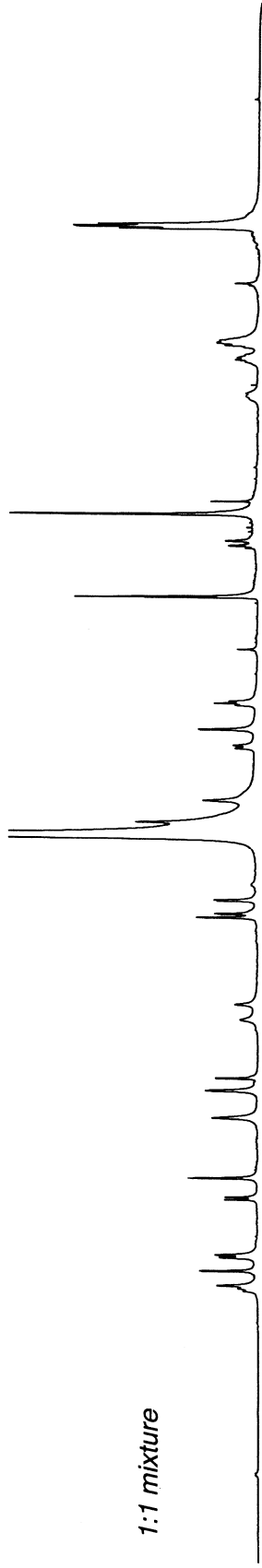
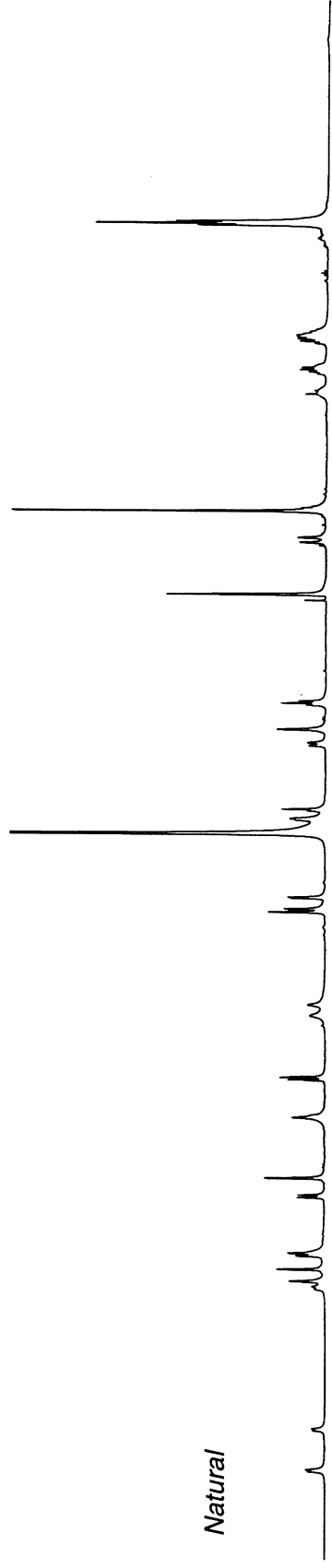


1:1 mixture



Synthetic





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