Supporting Information

Total Synthesis of the Vancomycin Aglycon

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(1*S*)-*N*-(Benzyloxycarbonyl)-1-(2-bromo-3,5-dimethoxyphenyl)-2-hydroxyethylamine (4). A solution of **3** (3.35 g, 10.1 mmol) in CH_3CN (80 mL) was treated portionwise with NBS (1.76 g, 9.9 mmol) at 0 °C over 5 min, and the mixture was stirred at 0 °C for 30 min. The reaction mixture was concentrated *in vacuo*. Chromatography (SiO_2, 5 × 20 cm, 33% EtOAc–$CHCl_3$) afforded **4** (3.92 g, 4.15 g theoretical, 95%) as a white film: $[\alpha]^{25}_{D}$ +8 (*c* 0.24, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.34 (br s, 5H), 6.47 (d, *J* = 2.7 Hz, 1H), 6.42 (d, *J* = 2.7 Hz, 1H), 5.66 (br s, 1H), 5.26 (dd, *J* = 2.4, 2.0 Hz, 1H), 5.08 (s, 2H), 3.89 (d, *J* = 2.4 Hz, 2H), 3.86 (s, 3H), 3.75 (s, 3H); IR (film) ν_{max} 3334, 2938, 1694, 1589, 1538, 1454, 1322, 1261, 1204, 1053, 834, 696 cm^{-1}; FABHRMS (NBA–NaI) *m/z* 410.0613 (M^+ + H, $C_{18}H_{20}BrNO_5$ requires 410.0603).

(1*S*)-*N*-(Benzyloxycarbonyl)-1-(2-bromo-3,5-dimethoxyphenyl)-2-(2-methoxyethoxymethoxy)ethylamine (5). A solution of **4** (1.90 g, 4.64 mmol) in CH_2Cl_2–THF (2:1, 30 mL) was treated sequentially with diisopropylethylamine (3.24 mL, 18.6 mmol), and MEMCl (1.59 mL, 13.9 mmol) at 0 °C. The reaction mixture was slowly warmed to 25 °C and was stirred for 22 h. The reaction mixture was cooled to 0 °C, quenched by the addition of 1 N aqueous HCl (10 mL). The two layers were separated and the aqueous phase was extracted with EtOAc (2 × 60 mL). The combined organic layers were washed with saturated aqueous NaCl (20 mL), dried (Na_2SO_4), and concentrated *in vacuo*. Chromatography (SiO_2, 5 × 15 cm, 20% EtOAc–$CHCl_3$) afforded **5** (2.21 g, 2.31 g theoretical, 96%) as a white film: $[\alpha]^{25}_{D}$ +14 (*c* 0.30, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.33 (br s, 5H), 6.50 (d, *J* = 2.7 Hz, 1H), 6.39 (d, *J* = 2.7 Hz, 1H), 6.00 (br s, 1H), 5.31 (td, *J* = 6.5, 3.8 Hz, 1H), 5.07 (br s, 2H), 4.66 (d, *J* = 6.8 Hz, 1H), 4.61 (d, *J* = 6.8 Hz, 1H), 3.85 (s, 3H), 3.73 (s, 3H), 3.61 (br s, 2H), 3.46 (br s, 2H), 3.33 (s, 3H); IR (film) ν_{max} 3328, 2938, 2887, 1722, 1588, 1527, 1455, 1324, 1202, 1162, 1050, 842, 740 cm^{-1}; FABHRMS (NBA–NaI) *m/z* 498.1115 (M^+ + H, $C_{22}H_{28}BrNO_7$ requires 498.1127).

6: A solution of **5** (499 mg, 1.00 mmol) in THF (15 mL) was treated with isopropylmagnesium chloride (2.0 M solution in THF, 0.75 mL, 1.50 mmol) at 0 °C. After 30 min, the reaction mixture was cooled to –78 °C and *t*-BuLi (1.6 M solution in pentane, 1.5 mL, 2.40 mmol) was added dropwise over 5 min. After 5 min, $(MeO)_3B$ (0.897 mL, 8.01 mmol) was added and the resulting mixture was warmed to 0 °C, stirred for 30 min, and quenched by the addition of 1 N aqueous HCl until pH = 3. The aqueous phase was extracted with EtOAc (2 × 50 mL). The combined organic layers were washed with saturated aqueous NaCl (15 mL), dried (Na_2SO_4), and concentrated *in vacuo*. Flash chromatography (SiO_2, 2.5 × 10 cm, 50% EtOAc–hexane then 10% CH_3OH–EtOAc) afforded **6** as a colorless oil (276 mg, 464 mg theoretical, 59%) and **7** as a white powder (147 mg, 420 mg theoretical, 35%).

For **6**: $[\alpha]_D^{25}$ +22 (*c* 0.17, $CHCl_3$); ^1H NMR (CD_3CN, 400 MHz) δ 7.39–7.33 (m, 5H), 6.61 (d, *J* = 1.6 Hz, 1H), 6.38 (d, *J* = 1.6 Hz, 1H), 5.29 (d, *J* = 12.4 Hz, 1H), 5.22 (d, *J* = 12.4 Hz, 1H), 4.77 (t, *J* = 3.0 Hz, 1H), 4.60 (s, 1H), 4.45 (d, *J* = 6.8 Hz, 1H), 4.43 (d, *J* = 6.8 Hz, 1H), 3.97 (d, *J* = 3.0 Hz, 2H), 3.81 (s, 3H), 3.80 (s, 3H), 3.32–3.25 (m, 4H), 3.22 (s, 3H); IR (film) ν_{max} 3317, 2959, 2930, 2859, 1727, 1601, 1582, 1503, 1462, 1273, 1123, 1072, 1039, 938, 836, 778, 743 cm^{-1}.

For **7:** $[\alpha]_D^{25}$ +29 (*c* 0.42, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.33 (br s, 5H), 6.45 (br s, 2H), 6.39 (t, *J* = 2.0 Hz, 1H), 5.74 (br s, 1H), 5.10 (d, *J* = 12.2 Hz, 1H), 5.04 (d, *J* = 12.2 Hz, 1H), 4.83 (br s, 1H), 4.66 (d, *J* = 7.0 Hz, 1H), 4.63 (d, *J* = 7.0 Hz, 1H), 3.74 (s, 6H), 3.64–3.56 (m, 2H), 3.52–3.42 (m, 2H), 3.33 (s, 3H); IR (film) ν_{max} 3327, 2939, 2888, 1722, 1598, 1531, 1327, 1243, 1205, 1156, 1048 cm^{-1}; MALDIFTMS (DHB) *m/z* 442.1856 (M^+ + Na, $C_{22}H_{29}NO_7$ requires 442.1842).

L-Alanyl-D-(*N-tert*-butyloxycarbonyl)-2-(3-bromo-4-methoxyphenyl)glycine Methyl Ester (9). A solution of L-alanine methyl ester hydrochloride (0.99 g, 6.47 mmol, 1.1 equiv) in anhydrous DMF (50.0 mL) was treated sequentially with $NaHCO_3$ (0.54 g, 6.47 mmol, 1.1 equiv), HOBt (2.0 g, 14.7 mmol, 2.5 equiv), **8**[16] (2.12 g, 5.88 mmol, 1.0 equiv), and EDCI (2.2 g, 12.9 mmol, 2.2 equiv) at 0 °C under Ar, and stirred for 12 h. After removal of the solvent *in vacuo*, H_2O (25 mL) and EtOAc (55 mL) were added to the residue. The aqueous phase was extracted with EtOAc (3 x 80 mL). The combined organic layers were washed with H_2O (30 mL) and saturated aqueous NaCl (30 mL), dried (Na_2SO_4), and concentrated *in vacuo*. Chromatography (SiO_2, 5% CH_3OH–$CHCl_3$) afforded **9**[25] (2.0 g, 81%) as a white film: $[\alpha]_D^{25}$ –30 (*c* 0.15, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.54 (d, *J* = 2.2 Hz, 1H), 7.28 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 6.45 (br d, *J* = 6.5 Hz, 1H), 5.71 (br s, 1H), 5.11 (br s, 1H), 4.55 (quintuplet, *J* = 7.2 Hz, 1H), 3.87 (s, 3H), 3.74 (s, 3H), 1.40 (s, 9H), 1.31 (d, *J* = 7.2 Hz, 3H); ^1H NMR (CD_3CN, 600 MHz) δ 7.57 (d, *J* = 2.1 Hz, 1H), 7.34 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.11 (d, *J* = 7.0 Hz, 1H), 7.00 (d, *J* = 8.5 Hz, 1H), 6.05 (s, 1H), 5.06 (s, 1H), 4.33 (m, 1H), 3.86 (s, 3H), 3.67 (s, 3H), 1.39 (s, 9H), 1.28 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 173.0, 169.4, 155.8, 154.9, 132.0, 131.7, 127.6, 112.0, 80.3, 60.4, 57.3, 56.2, 52.6, 48.2, 28.2, 18.0; IR (neat) ν_{max} 3358, 2926, 1684, 1496, 1457, 1367, 1258, 1164, 1056 cm¥1; FABHRMS (NBA–NaI) *m/z* 455.0964 (M^+ + H, $C_{18}H_{25}BrN_2O_6$ requires 445.0974).

10: A mixture of **9** (16.6 mg, 0.037 mmol, 1.0 equiv), **6** (34.5 mg, 0.075 mmol, 2.0 equiv), $Pd_2(dba)_3$ (10.2 mg, 0.011 mmol, 0.3 equiv), (*o*-tolyl)$_3$P (17.0 mg, 0.056 mmol, 1.5 equiv) and aqueous Na_2CO_3 (0.074 mL, 1 M, 2.0 equiv) in toluene (0.70 mL) and CH_3OH (0.20 mL) was degassed and stirred at 80 °C for 15 min. The resulting mixture was cooled to 25 °C and quenched with the addition of 15% aqueous citric acid (1 mL). The aqueous phase was extracted with EtOAc (3 x 5 mL). The combined organic layers were washed with H_2O (3 mL) and saturated aqueous NaCl (3 mL), dried (Na_2SO_4), and concentrated *in vacuo*. PTLC (SiO_2, 50% EtOAc–hexane) afforded **10** (26.3 mg, 90%, *S*:*R* = 2:1).

S-**10**: white film; $[\alpha]_D^{25}$ –48 (*c* 0.10, $CHCl_3$); ^1H NMR (CD_3OD, 600 MHz) δ 7.34–7.32 (m, 5H), 7.27 (m, 2H), 7.01 (d, *J* = 8.5 Hz, 1H), 6.62 (s, 1H), 6.49 (s, 1H), 5.14–5.08 (m, 3H), 4.68 (m, 1H), 4.42 (d, *J* = 6.7 Hz, 1H), 4.37 (m, 2H), 3.81 (s, 3H), 3.71 (s, 3H), 3.63 (s, 3H), 3.56 (s, 3H), 3.45 (m, 2H), 3.39 (m, 5H), 3.31 (s, 3H), 1.41 (s, 9H), 1.2 (d, 3H, *J* = 7.0 Hz); IR (neat) ν_{max} 3356, 2916, 2037, 1701, 1673, 1606, 1506, 1456, 1366, 1321, 1256, 1158, 1034 cm^{-1}; FABHRMS (NBA–CsI) *m/z* 916.2612 (M^+ + Cs, $C_{40}H_{53}N_3O_{13}$ requires 916.2633).

R-**10**: white film; $[\alpha]_D^{25}$ –17 (*c* 0.13, $CHCl_3$); ^1H NMR (CD_3OD, 600 MHz) δ 7.38 (d, *J* =

7.5 Hz, 1H), 7.32 (s, 3H), 7.26 (m, 2H), 7.06 (s, 1H), 6.97 (m, 1H), 6.67 (s, 1H), 6.51 (s, 1H), 5.14 (s, 1H), 4.98 (m, 2H), 4.93 (m, 1H), 4.61 (m, 1H), 4.46 (s, 2H), 4.34 (q, *J* = 7.2 Hz, 1H), 3.81 (s, 3H), 3.66 (s, 3H), 3.62 (s, 5H), 3.49 (br s, 5H), 3.42 (m, 2H), 3.31 (s, 3H), 1.43 (s, 9H), 1.33 (d, 3H, *J* = 7.0 Hz); IR (neat) ν_{max} 3356, 2936, 2038, 1706, 1675, 1605, 1506, 1456, 1419, 1319, 1201, 1158, 1035 cm^{-1}; FABHRMS (NBA–CsI) *m/z* 916.2614 (M^+ + Cs, $C_{40}H_{53}N_3O_{13}$ requires 916.2633).

11: A solution of **10** (30.1 mg, 0.038 mmol, 1.0 equiv) in THF (0.88 mL) was treated with aqueous LiOH (0.2 M, 0.29 mL, 0.058 mmol, 1.5 equiv) at 0 °C under Ar for 1.5 h. The reaction mixture was quenched with the addition of 15% aqueous citric acid (1 mL) at 0 °C, and the volatiles were removed *in vacuo*. The aqueous phase was extracted with EtOAc (3 × 10 mL). The combined organic phases were washed with H_2O (10 mL) and saturated aqueous NaCl (10 mL), dried (Na_2SO_4), and concentrated *in vacuo*. PTLC (SiO_2, 15% CH_3OH–$CHCl_3$) afforded **11** (28.1 mg, 96%, *S*:*R* = 2:1).

S-**11** (less polar isomer): white film; $[\alpha]^{25}_{D}$ –51 (*c* 1.3, CH_3OH); ^1H NMR (CD_3OD, 600 MHz) δ 7.59 (m, 1H), 7.35 (m, 3H), 7.31 (m, 2H), 7.26 (m, 2H), 7.00 (d, *J* = 8.5 Hz, 1H), 6.61 (s, 1H), 6.48 (s, 1H), 5.14 (m, 1H), 5.10 (m, 2H), 4.68 (m, 1H), 4.42 (d, *J* = 6.7 Hz, 1H), 4.37–4.31 (m, 2H), 3.80 (s, 3H), 3.71 (s, 3H), 3.62 (s, 3H), 3.45 (m, 2H), 3.39 (m, 4H), 3.31 (s, 3H), 1.40 (s, 9H), 1.22 (d, *J* = 7.2 Hz, 3H); IR (neat) ν_{max} 3324, 2937, 1704, 1606, 1506, 1456, 1367, 1321, 1256, 1160, 1035 cm^{-1}; FABHRMS (NBA–CsI) *m/z* 902.2468 (M^+ + Cs, $C_{39}H_{51}N_3O_{13}$ requires 902.2476).

R-**11** (more polar isomer): white film; $[\alpha]^{25}_{D}$ –19 (*c* 0.30, $CHCl_3$); ^1H NMR (CD_3OD, 600 MHz) δ 7.37 (d, *J* = 8.2 Hz, 1H), 7.32 (s, 3H), 7.26 (m, 2H), 7.06 (s, 1H), 6.96 (d, *J* = 7.0 Hz, 1H), 6.66 (s, 1H), 6.50 (s, 1H), 5.14 (s, 1H), 4.98 (m, 3H), 4.63 (m, 1H), 4.46 (s, 2H), 4.34 (q, *J* = 7.1 Hz, 1H), 3.81 (s, 3H), 3.62 (m, 5H), 3.49 (m, 5H), 3.42 (m, 2H), 3.31 (s, 3H), 1.43 (s, 9H), 1.33 (d, *J* = 7.0 Hz, 3H); IR (neat) ν_{max} 3319, 2936, 1710, 1606, 1504, 1455, 1367, 1320, 1248, 1160, 1037 cm^{-1}; FABHRMS (NBA–CsI) *m/z* 902.2469 (M^+ + Cs, $C_{39}H_{51}N_3O_{13}$ requires 902.2476).

12: A solution of **11** (15.8 mg, 0.021 mmol) dissolved in CH_3OH (0.69 mL) at 25 °C was treated with 10% Pd/C (3.2 mg, 0.2 wt equiv) and was stirred under one atmosphere of H_2 for 2.5 h. The reaction mixture was filtered through a pad of Celite (15% CH_3OH–$CHCl_3$, 3 x 15 mL) and the solvent was removed *in vacuo*. PTLC (SiO_2, 20% CH_3OH–$CHCl_3$) afforded **6** (12.9 mg, 99%).

S-**12** (less polar isomer): white film; $[\alpha]^{25}_{D}$ –24 (*c* 0.90, CH_3OH); ^1H NMR (CD_3OD, 600 MHz) δ 7.42 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.10 (d, *J* = 2.3 Hz, 1H), 7.08 (d, *J* = 8.7 Hz, 1H), 6.72 (d, *J* = 2.3 Hz, 1H), 6.64 (d, *J* = 2.3 Hz, 1H), 5.14 (s, 1H), 4.60 (q, *J* = 6.9 Hz, 2H), 4.21–4.18 (m, 2H), 3.87 (s, 3H), 3.73 (s, 3H), 3.69 (m, 2H), 3.65 (s, 3H), 3.57 (m, 1H), 3.54 (m, 1H), 3.46 (t, *J* = 4.7 Hz, 2H), 3.31 (s, 3H), 1.46 (s, 9H), 1.30 (d, *J* = 7.1 Hz, 3H); IR (neat) ν_{max} 3246, 2937, 1711, 1672, 1610, 1510, 1461, 1392, 1366, 1250, 1205, 1162, 1048 cm^{-1}; FABHRMS (NBA–CsI) *m/z* 768.2130 (M^+ + Cs, $C_{31}H_{45}N_3O_{11}$ requires 768.2108).

R-**12** (more polar isomer): white film; $[\alpha]^{25}_{D}$ –9.5 (*c* 0.12, $CHCl_3$); ^1H NMR (CD_3OD, 600 MHz) δ 7.41 (d, *J* = 8.1 Hz, 1H), 7.09 (m, 1H), 7.06 (d, *J* = 8.6 Hz, 1H), 6.68 (d, *J* = 2.2 Hz, 1H), 6.62 (d, *J* = 2.2 Hz, 1H), 5.14 (s, 1H), 4.61 (d, *J* = 6.8 Hz, 1H), 4.55 (d, *J* = 6.8 Hz, 1H), 4.19 (q, *J* = 6.9 Hz, 1H), 4.03 (m, 1H), 3.86 (s, 3H), 3.74 (s, 3H), 3.65 (m, 4H), 3.58 (m, 3H), 3.47 (m, 2H), 3.32 (s, 3H), 1.43 (s, 9H), 1.29 (d, *J* = 7.0 Hz, 3H); IR (neat) ν_{max} 3307, 2934, 1704, 1666, 1606, 1486, 1462, 1402, 1366, 1250, 1204, 1163, 1048 cm^{-1}; FABHRMS (NBA–CsI) *m/z* 768.2131 (M^+ + Cs, $C_{31}H_{45}N_3O_{11}$ requires 768.2108).

S-**13**: A solution of PyBOP (18.8 mg, 0.036 mmol, 2.0 equiv) and DMAP (6.62 mg, 0.054

mmol, 3.0 equiv) in anhydrous DMF (10.0 mL) was treated dropwise (30 min) with *S*-**12** (11.5 mg, 0.018 mmol, 1.0 equiv) in anhydrous DMF (8.0 mL) at 25 °C under Ar. The reaction mixture was quenched with the addition of 15% aqueous citric acid (5 mL), and the solvents were removed *in vacuo*. H_2O (10 mL) and EtOAc (15 mL) were added to the residue, and the aqueous phase was extracted with EtOAc (3 × 10 mL). The combined organic phases were washed with H_2O (5 mL) and saturated aqueous NaCl (5 mL), dried (Na_2SO_4), and concentrated *in vacuo*. PTLC (SiO_2, 5% CH_3OH–$CHCl_3$) afforded *S*-**13** (10.1 mg, 91%) as a white film: $[\alpha]_D^{25}$ +9 (*c* 0.3, $CHCl_3$); ^1H NMR (CD_3OD, 600 MHz) mixture of two conformers (*cis*:*trans* = 5:1) δ for the *cis* conformer 7.18 (m, 1H), 7.03 (d, *J* = 2.3 Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 1H), 6.82 (d, *J* = 2.2 Hz, 1H), 6.61 (d, *J* = 2.2 Hz, 1H), 5.15 (s, 1H), 4.68 (m, 2H), 4.36 (m, 1H), 4.26 (m, 1H), 3.86 (m, 4H), 3.72 (m, 4H), 3.68 (s, 3H), 3.65 (m, 2H), 3.52 (t, *J* = 4.8 Hz, 2H), 3.33 (s, 3H), 1.43 (s, 9H), 1.25 (d, *J* = 7.1 Hz, 3H); ^1H NMR (DMSO-d_6, 600 MHz) mixture of two conformers (*cis* : *trans* = 4:1) δ for the *cis* conformer 7.81 (d, *J* = 6.8 Hz, 1H), 7.44 (d, *J* = 9.8 Hz, 1H), 7.12 (m, 2H), 7.07 (m, 1H), 6.93 (d, *J* = 8.7 Hz, 1H), 6.72 (m, 1H), 6.63 (m, 1H), 4.98 (d, *J* = 7.5 Hz, 1H), 4.62 (m, 2H), 4.25 (m, 1H), 4.12 (m, 1H), 3.82 (s, 3H), 3.75 (t, *J* = 9.5 Hz, 1H), 3.65 (m, 3H), 3.62 (s, 3H), 3.60–3.53 (m, 2H), 3.48 (m, 1H), 3.47 (t, *J* = 4.7 Hz, 2H), 3.23 (s, 3H), 1.37 (s, 9H), 1.11 (d, *J* = 6.6 Hz, 3H); ^1H NMR (CD_3CN, 600 MHz) mixture of two conformers (*cis* : *trans* = 8:1) δ for the *cis* conformer 7.08 (d, *J* = 8.9 Hz, 1H), 6.99 (m, 2H), 6.74 (m, 1H), 6.61 (s, 1H), 6.33 (m, 1H), 6.28 (m, 1H), 6.04 (d, *J* = 9.7 Hz, 1H), 5.08 (s, 1H), 4.63 (m, 2H), 4.22 (m, 1H), 4.17 (m, 1H), 3.84 (s, 3H), 3.81 (m, 1H), 3.70 (s, 3H), 3.67 (s, 3H), 3.64–3.56 (m, 3H), 3.47 (t, *J* = 4.8 Hz, 2H), 3.28 (s, 3H), 1.38 (s, 9H), 1.17 (d, *J* = 7.0 Hz, 3H); IR (neat) ν_{max} 3312, 2934, 1700, 1653, 1604, 1506, 1457, 1395, 1321, 1266, 1201, 1159, 1052 cm^{-1}; FABHRMS (NBA–CsI) *m/z* 750.2021 (M^+ + Cs, $C_{31}H_{43}N_3O_{10}$ requires 750.2003).

The 2D ^1H–^1H ROESY NMR spectrum (CD_3CN, 600 MHz) displayed the following diagnostic NOE crosspeaks: $C_{4a}{}^1$-H/$C_2{}^1$-H (δ 7.00/5.08, s), $C_{4a}{}^1$-H/$C_2{}^2$-H (δ 7.00/4.18, m), $C_2{}^1$-H/$C_2{}^2$-H (δ 5.08/4.18, s). The latter is diagnostic of a cis amide bond. Additional NOE's: $C_{4a}{}^1$-H/$C_{5b}{}^3$-OCH_3 (δ 7.00/3.70, s), $C_1{}^3$-H/$C_{4a}{}^3$-H (δ 4.63/6.74, m), $C_1{}^3$-H/$C_{5a}{}^3$-OCH_3 (δ 4.63/3.84, m), $C_{4a}{}^3$-H/$C_{5a}{}^3$-OCH_3 (δ 6.74/3.84, m), $C_6{}^3$-H/$C_{5a}{}^3$-OCH_3 (δ 6.60/3.84, m), $C_6{}^3$-H/$C_{5b}{}^3$-OCH_3 (δ 6.60/3.70, m).

$C_2{}^2$ Epimer of *S*-13: white film; $[\alpha]_D^{25}$+69 (*c* 0.09, $CHCl_3$); ^1H NMR (CD_3OD, 600 MHz) δ 7.27 (d, *J* = 7.3 Hz, 1H), 7.10 (s, 1H), 6.96 (d, *J* = 8.7 Hz, 1H), 6.90 (m, 1H), 6.61 (m, 1H), 5.09 (s, 1H), 4.66 (m, 2H), 4.33 (q, *J* = 7.3 Hz, 1H), 4.12 (m, 1H), 3.96 (m, 1H), 3.86 (s, 3H), 3.70 (s, 3H), 3.67 (s, 3H), 3.65–3.60 (m, 3H), 3.51 (t, *J* = 4.8 Hz, 2H), 3.33 (s, 3H), 1.47 (s, 9H), 1.28 (d, *J* = 7.2 Hz, 3H); ^1H NMR (DMSO-d_6, 600 MHz) δ 7.33 (m, 2H), 7.27 (d, *J* = 8.6 Hz, 1H), 7.15 (m, 2H), 6.90 (d, *J* = 8.6 Hz, 1H), 6.80 (m, 1H), 6.64 (m, 1H), 4.95 (d, *J* = 7.7 Hz, 1H), 4.55 (s, 2H), 4.10 (m, 1H), 3.82 (s, 3H), 3.77 (m, 1H), 3.65 (s, 3H), 3.63 (s, 3H), 3.54–3.50 (m, 2H), 3.42 (t, *J* = 4.8 Hz, 2H), 3.22 (s, 3H), 1.40 (s, 9H), 1.19 (d, *J* = 7.4 Hz, 3H); IR (neat) ν_{max} 3355, 2931, 2036, 1713, 1668, 1634, 1505, 1456, 1403, 1367, 1319, 1260, 1201, 1159, 1059 cm^{-1}; FABHRMS (NBA–CsI) *m/z* 750.2021 (M^+ + Cs, $C_{31}H_{43}N_3O_{10}$ requires 750.2003).

The 2D ^1H–^1H ROESY NMR spectrum displayed the following diagnostic NOE crosspeaks: (DMSO-d_6, 600 MHz) $C_{4b}{}^1$-H/$C_2{}^1$-H (δ 7.28/4.95, s), N^2-H/$C_2{}^1$-H (δ 7.34/4.95, s), N^2-H/$C_2{}^2$-H (δ 7.34/4.10, s), N^2-H/$C_3{}^2$-H (δ 7.34/1.19, s), N^3-H/$C_2{}^1$-H (δ 7.16/4.95, s), N^3-H/$C_2{}^2$-H (δ 7.16/4.10, w), N^3-H/$C_3{}^2$-H (δ 7.16/1.19, s); (CD_3OD, 600 MHz) $C_{4b}{}^1$-H/$C_2{}^1$-H (δ 7.10/5.09, s) with additional NOE's of $C_2{}^3$-H/$C_{5a}{}^3$-OCH_3 (δ 4.12/3.85, s), $C_{4a}{}^3$-H/$C_{5a}{}^3$-OCH_3 (δ 6.90/3.85, s), $C_6{}^3$-H/$C_{5a}{}^3$-OCH_3 (δ 6.61/3.85, s), $C_{5b}{}^1$-H/$C_{5b}{}^3$-OCH_3 (δ 6.96/3.67, s), $C_6{}^3$-H/$C_{5b}{}^3$-OCH_3 (δ 6.61/3.67, s).

R-**13**: A solution of HATU (11.0 mg, 0.029 mmol, 3.0 equiv) and DMAP (4.7 mg, 0.038 mmol, 4.0 equiv) in anhydrous DMF (5.0 mL) was treated dropwise with *R*-**12** (6.1 mg, 0.0096 mmol, 1.0 equiv) in anhydrous DMF (4.6 mL) at 25 °C under Ar over 0.5 h. The reaction mixture was stirred at 25 °C for 24 h and quenched with the addition of 15% aqueous citric acid (2 mL), and the solvents were removed *in vacuo*. H_2O (3 mL) and EtOAc (10 mL) were added to the residue, and the aqueous phase was extracted with EtOAc (3 × 10 mL). The combined organic phases were washed with H_2O (5 mL) and saturated aqueous NaCl (5 mL), dried (Na_2SO_4), and concentrated *in vacuo*. PTLC (SiO_2, 5% CH_3OH–$CHCl_3$) afforded *R*-**13** (4.8 mg, 81%) as a white solid; $[\alpha]_D^{25}$–66 (*c* 0.16, $CHCl_3$); ^{1}H NMR (CD_3OD, 600 MHz) δ 7.44 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.41 (br s, 1H), 7.06 (d, *J* = 8.5 Hz, 1H), 6.55 (dd, *J* = 7.6, 2.1 Hz, 2H), 4.95 (s, 1H), 4.81 (d, *J* = 8.5 Hz, 2H), 4.45 (d, *J* = 6.7 Hz, 1H), 4.42 (br s, 1H), 4.37 (d, *J* = 6.7 Hz, 1H), 3.83 (s, 3H), 3.76 (s, 3H), 3.66 (s, 3H), 3.46–3.39 (m, 5H), 3.32 (s, 3H), 1.44 (s, 9H), 1.35 (d, *J* = 7.1 Hz, 3H); IR (neat) ν_{max} 3424, 3312, 2925, 1712, 1678, 1604, 1504, 1463, 1367, 1323, 1265, 1161, 1035 cm^{-1}; FABHRMS (NBA–NaI) *m/z* 618.3018 (M^+ + H, $C_{31}H_{44}N_3O_{10}$ requires 618.3027).

The 2D ^{1}H–^{1}H ROESY NMR spectrum (DMSO-d_6, 600 MHz) displayed the following diagnostic NOE crosspeaks: $C_{4b}{}^1$-H/$C_2{}^1$-H (δ 7.36/4.79, m), with additional NOE's of $C_{5a}{}^1$-H/$C_6{}^1$-OCH_3 (δ 7.00/3.68, s), $C_{4a}{}^3$-H/$C_{5a}{}^3$-OCH_3 (δ 6.58/3.79, s), $C_6{}^3$-H/$C_{5a}{}^3$-OCH_3 (δ 6.53/3.79, s), $C_6{}^3$-H/$C_{5b}{}^3$-OCH_3 (δ 6.53/3.61, s); (CD_3OD, 600 MHz) $C_{4b}{}^1$-/$C_2{}^1$-H (δ 7.43/4.81, s), $C_{5b}{}^1$-H/$C_6{}^1$-OCH_3 (δ 7.05/3.76, s), $C_{4a}{}^3$-H/$C_{5a}{}^3$-OCH_3 (δ 6.56/3.83, s), $C_6{}^3$-H/$C_{5a}{}^3$-OCH_3 (δ 6.55/3.83, s), $C_6{}^3$-H/$C_{5b}{}^3$-OCH_3 (δ 6.55/3.66, s).

14: A solution of **11** (21 mg, 0.027 mmol) in DMF (0.3 mL) was treated with $NaHCO_3$ (46 mg, 0.54 mmol) and benzyl bromide (0.05 mL, 0.40 mmol) at 25 °C. The resulting mixture was stirred for 9 h at 25 °C and poured into ice cold water. The organic phase was extracted with EtOAc (3 × 10 mL) and the combined organic solution was washed with H_2O (5 mL) and saturated aqueous NaCl, dried (Na_2SO_4), and concentrated *in vacuo*. PTLC (SiO_2, 5% CH_3OH–CH_2Cl_2) afforded **14** (23.5 mg, 100%) as a white film; $[\alpha]_D^{25}$ –37 (*c* 0.17, CH_2Cl_2); ^{1}H NMR (CD_3OD, 400 MHz) δ 7.69 (br d, *J* = 8.3 Hz, 1H, NH), 7.37–7.28 (m, 12H), 6.99 (d, *J* = 8.6 Hz, 1H), 6.63 (d, *J* = 2.1 Hz, 1H), 6.45 (s, 1H), 5.13 (br s, 1H), 5.10 (d, *J* = 12.6 Hz, 1H), 5.06 (d, *J* = 12.6 Hz, 1H), 5.02 (s, 1H), 4.70 (br s, 1H), 4.42 (d, *J* = 6.7 Hz, 1H), 4.37 (d, *J* = 6.7 Hz, 1H), 3.79 (s, 3H), 3.72 (s, 3H), 3.59 (s, 3H), 3.47–3.38 (m, 6H), 1.42 (s, 9H), 1.24 (d, *J* = 7.0 Hz, 3H); IR (film) ν_{max} 3314, 2933, 1704, 1682, 1605, 1538, 1505, 1488, 1455, 1365, 1321, 1255, 1200, 1158, 1033, 844, 739, 697 cm^{-1}; MALDFTMS (DHB) *m/z* 882.3781 (M^+ + Na, $C_{46}H_{57}N_3O_{13}$ requires 882.3789).

15: A solution of **14** (19 mg, 0.022 mmol) in 3.4 M HCl in EtOAc (1.3 mL) was stirred for 1 h at 0 °C and poured into a cold aqueous NH_4OH solution. The aqueous phase was extracted with EtOAc (3 × 10 mL) and the combined organic solution was washed with saturated aqueous NaCl, dried (Na_2SO_4), and concentrated *in vacuo*. The resulting crude product was dissolved in THF (0.6 mL) and H_2O (0.6 mL) and treated with $NaHCO_3$ (12 mg, 0.13 mmol) and BOC_2O (7.3 mg, 0.033 mmol) at 0 °C. The reaction mixture was stirred for 9 h at 25 °C before being worked up and extracted with EtOAc (3 × 10 mL). The combined organic solution was washed with saturated aqueous NaCl, dried (Na_2SO_4), and concentrated *in vacuo*. PTLC (SiO_2, 5% CH_3OH–CH_2Cl_2) afforded **15** (11 mg, 17.7 mg theoretical, 62%) as a white film: $[\alpha]_D^{25}$ –63 (*c* 0.13, CH_2Cl_2); ^{1}H NMR (CD_3OD, 400 MHz) δ 7.52 (br d, *J* = 8.6 Hz, 1H, NH), 7.34–7.26 (m, 12H), 6.98 (d, *J* = 8.6 Hz, 1H), 6.63 (d, *J* = 2.1 Hz, 1H), 6.43 (s, 1H), 5.13 (br s, 1H), 5.09 (s, 2H), 5.01 (s, 2H), 4.59 (br s, 1H), 4.43

(d, $J = 7.2$ Hz, 1H), 3.79 (s, 3H), 3.71 (s, 3H), 3.58 (s, 3H), 3.40 (d, $J = 5.9$ Hz, 2H), 1.42 (s, 9H), 1.26 (d, $J = 6.5$ Hz, 3H); IR (film) ν_{max} 3329, 2959, 2930, 2859, 1732, 1716, 1682, 1580, 1531, 1486, 1455, 1381, 1273, 1123, 1071, 959, 743, 701 cm^{-1}; MALDIFTMS (DHB) *m/z* 794.3298 (M^+ + Na, $C_{42}H_{49}N_3O_{11}$ requires 794.3265).

17: A solution of **15** (3.3 mg, 0.0043 mmol) in phosphate buffer solution (pH 7, 70 μL) and CH_3CN (0.1 mL) was treated with TEMPO (4.3 μL, 0.1 M solution in CH_3CN, 4.3 μmol), $NaClO_2$ (34 μL, 1 M solution in H_2O, 34 μmol), and NaOCl (50 μL, 0.007 M solution in H_2O, 0.35 μmol). The resulting mixture was stirred for 10 h at 35 °C, and quenched by addition of cold saturated aqueous Na_2SO_3. The mixture was acidified with the addition of 5% aqueous citric acid and extracted with EtOAc (3 × 5 mL). The combined organic solution was washed with saturated aqueous NaCl, dried (Na_2SO_4), and concentrated *in vacuo*.

The crude acid **16** was dissolved in benzene (0.2 mL) and CH_3OH (0.05 mL) and treated with excess $TMSCHN_2$ (0.1 mL, 2 M solution in hexane). The resulting solution was stirred for 5 min and was concentrated *in vacuo*. PTLC (SiO_2, 10% CH_3OH–CH_2Cl_2) afforded **17** (3.1 mg, 3.4 mg theoretical, 90%) as a white film: $[\alpha]^{25}_{D}$ –11 (*c* 0.15, CH_2Cl_2); ^{1}H NMR (CD_3OD, 400 MHz) δ 7.36–7.22 (m, 12H), 6.99 (d, $J = 8.3$ Hz, 1H), 6.59 (d, $J = 2.1$ Hz, 1H), 6.52 (d, $J = 2.1$ Hz, 1H), 5.15 (s, 1H), 5.13–5.08 (m, 5H), 4.43 (q, $J = 7.2$ Hz, 1H), 3.80 (s, 3H), 3.72 (s, 3H), 3.62 (s, 3H), 3.57 (s, 3H), 1.41 (s, 9H), 1.25 (d, $J = 7.0$ Hz, 3H); IR (film) ν_{max} 3343, 2958, 2928, 2858, 1737, 1731, 1715, 1606, 1531, 1504, 1462, 1337, 1274, 1203, 1160, 1072, 958, 742, 697 cm^{-1}; MALDIFTMS (DHB) *m/z* 822.3213 (M^+ + Na, $C_{43}H_{49}N_3O_{12}$ requires 822.3214).

S-**19**: A solution of **17** (3.5 mg, 0.043 mmol) in EtOH (0.5 mL) was treated with 10% Pd/C (0.5 mg) at 25 °C and was stirred under 1 atm of H_2 for 2 h. The reaction mixture was diluted with EtOAc (3 mL) and filtered through a pad of Celite and the solvent was removed *in vacuo*. The crude product **18** was used for the next reaction without further purification.

A solution of *O*-(7-azabenzotriazol-1-yl)-*N,N,N',N'*-tetramethyluronium hexafluorophosphate (HATU, 3 mg, 0.008 mmol) and DMAP (1.3 mg, 0.01 mmol) in CH_2Cl_2–DMF (3:1, 2.5 mL) was treated dropwise (30 min) with **18** (1.5 mg, 0.0026 mmol) in CH_2Cl_2–DMF (3:1, 0.1 mL) at 25 °C. The reaction mixture was stirred for 2 h at 25 °C and poured into cold water. The organic phase was extracted with CH_2Cl_2 and the combined organic solution was washed with H_2O and saturated aqueous NaCl, dried (Na_2SO_4), and concentrated *in vacuo*. PTLC (SiO_2, 5% CH_3OH–CH_2Cl_2) afforded *S*-**19** (1.0 mg, 1.5 mg theoretical, 63%) as a white film: $[\alpha]^{25}_{D}$ –15 (*c* 0.09, $CHCl_3$); ^{1}H NMR (CD_3OD, 310 K, 400 MHz) mixture of two conformers, δ for the major conformer 7.21 (dd, $J = 7.6$, 2.1 Hz, 1H), 7.04–7.01 (m, 2H), 6.67 (d, $J = 2.1$ Hz, 1H), 6.29 (d, $J = 2.1$ Hz, 1H), 5.15 (br s, 1H), 4.84 (s, 1H), 4.32 (q, $J = 7.0$ Hz, 1H), 3.83 (s, 3H), 3.76 (s, 3H), 3.75 (s, 3H), 3.72 (s, 3H), 1.49 (s, 9H), 1.31 (d, $J = 7.2$ Hz, 3H); IR (film) ν_{max} 3300, 2958, 2929, 2859, 1727, 1693, 1666, 1600, 1580, 1454, 1381, 1273, 1122, 1072, 1039, 959, 772, 742, 705, 651 cm^{-1}; MALDIFTMS (DHB) *m/z* 580.2288 (M^+ + Na, $C_{28}H_{35}N_3O_9$ requires 580.2271).

S-**19** (from *S*-**13**): A solution of *S*-**13** (4.5 mg, 0.0072 mmol) in 3.4 M HCl in EtOAc (1.0 mL) was stirred for 1.5 h at 0 °C and poured into a cold aqueous NH_4OH solution. The mixture was extracted with EtOAc (3 × 5 mL) and the combined organic solution was washed with saturated aqueous NaCl, dried (Na_2SO_4), and concentrated *in vacuo*. The resulting crude product was dissolved in THF (0.2 mL) and H_2O (0.2 mL) and treated with $NaHCO_3$ (6 mg, 0.071 mmol) and BOC_2O (3 mg, 0.014 mmol) at 0 °C. The reaction mixture was stirred for 9 h at 25 °C and the mixture was extracted with EtOAc (3 × 5 mL). The combined organic solution was washed with saturated aqueous NaCl, dried (Na_2SO_4), and concentrated *in vacuo*. PTLC (SiO_2, 7% CH_3OH–CH_2Cl_2) afforded the corresponding primary alcohol (1.7 mg, 3.8 mg theoretical, 45%) as a white film: ^{1}H NMR (CD_3OD, 600 MHz) δ 7.20 (d, J = 5.8 Hz, 1H), 7.05 (br s, 1H), 7.00 (d, J = 5.8 Hz, 1H), 6.84 (d, J = 1.5 Hz, 1H), 6.61 (d, J = 1.5 Hz, 1H), 5.16 (br s, 1H), 4.29 (m, 1H), 4.21 (m, 1H), 3.86 (s, 3H), 3.71 (s, 3H), 3.69 (s, 3H), 1.44 (s, 9H), 1.28 (d, J = 6.4 Hz, 3H); MALDIFTMS (DHB) *m/z* 552.2347 (M^+ + Na, $C_{27}H_{35}N_3O_8$ requires 552.2321).

A solution of the alcohol (1.7 mg, 0.0032 mmol) in CH_2Cl_2 (0.5 mL) at 0 °C was treated with Dess–Martin periodinane (4.6 mg, 0.01 mmol), and the resulting heterogeneous mixture was gradually warmed to 25 °C. After 1 h stirring, the suspension was diluted with Et_2O (2 mL), poured into a mixture of saturated aqueous $NaHCO_3$ (1 mL) and saturated aqueous Na_2SO_3 (1 mL), stirred until two distinct layers were observed, and the organic phase was extracted with Et_2O (3 × 10 mL). The combined organic solution was washed with saturated aqueous $NaHCO_3$ and saturated aqueous NaCl, dried (Na_2SO_4), and concentrated *in vacuo* to afford the crude aldehyde which was sufficiently pure to use in the subsequent step.

A buffered solution of $NaClO_2$ (3.0 mg, 0.034 mmol) and aqueous NaH_2PO_4 (3.5 mg, 0.026 mmol) in H_2O (35 μL) was added dropwise to a solution of the crude aldehyde (1.7 mg, 0.0032 mmol) in 2-methyl-2-butene (0.05 mL) and *t*-BuOH (0.2 mL) at 25 °C. After stirring the reaction mixture for 1 h at 25 °C, the volatiles were removed *in vacuo*, and the residue was diluted with H_2O (1.0 mL) and extracted with EtOAc (3 × 5 mL). The combined organic layer was dried (Na_2SO_4) and concentrated *in vacuo* to afford the crude carboxylic acid.

The crude acid was dissolved in benzene (0.2 mL) and CH_3OH (0.05 mL) and treated with excess $TMSCHN_2$ (0.05 mL, 2 M solution in hexane). The resulting solution was stirred for 30 min at 25 °C and concentrated *in vacuo*. PTLC (SiO_2, 5% CH_3OH–CH_2Cl_2) afforded *S*-**19** (0.7 mg, 1.4 mg theoretical, 50%) as a white film.

S-**23**: white film; $[\alpha]_D^{25}$ –60 (*c* 0.08, $CHCl_3$); ^{1}H NMR (CD_3CN, 400 MHz) δ 7.51 (d, J = 1.9 Hz, 1H), 7.39 (d, J = 6.2 Hz, 2H), 7.31 (br s, 2H), 7.29 (s, 1H), 7.17 (d, J = 5.7 Hz, 1H), 7.11 (d, J = 8.4 Hz, 2H), 6.99 (d, J = 8.4 Hz, 2H), 6.58–6.47 (m, 5H), 6.15 (br d, J = 7.8 Hz, 1H), 5.85 (br d, J = 9.5 Hz, 1H), 5.48 (d, J = 7.8 Hz, 1H), 5.39 (br s, 1H), 5.23 (br d, J = 8.1 Hz, 1H), 4.69 (td, J = 8.6 and 4.1 Hz, 1H), 4.54 (br s, 1H), 4.52 (s, 1H), 4.43 (br s, 1H), 4.40 (d, J = 6.8 Hz, 1H), 4.31 (d, J = 6.8 Hz, 1H), 3.82 (s, 3H), 3.77 (s, 3H), 3.75 (s, 3H), 3.71 (s, 3H), 3.69 (s, 3H), 3.39–3.24 (m, 6H), 3.22 (s, 3H), 1.41 (s, 9H), 0.73 (s, 9H), –0.07 and –0.20 (two s, 3H each); IR (film) ν_{max} 3325, 2929, 1694, 1605, 1504, 1328, 1251, 1199, 1159, 1061, 834 cm^{-1}; FABHRMS (NBA–CsI) *m/z* 1349.3736 (M^+ + Cs, $C_{61}H_{77}ClN_4O_{18}Si$ requires 1349.3245).

R-**23**: pale yellow film; $[\alpha]_D^{25}$ +5 (*c* 0.20, $CHCl_3$); ^{1}H NMR (CD_3CN, 400 MHz) δ 7.54 (d, J = 1.9 Hz, 1H), 7.36 (dd, J = 8.4, 1.6 Hz, 1H), 7.32 (br s, 4H), 7.25 (d, J = 8.6 Hz, 1H), 7.12 (d, J = 9.2 Hz, 1H), 7.08 (d, J = 2.4 Hz, 1H), 6.65 (d, J = 7.0 Hz, 1H), 6.63 (d, J = 1.6 Hz, 1H), 6.56 and 6.53 (two d, J = 2.4 Hz, 1H each), 6.44 (d, J = 1.9 Hz, 1H), 5.86 (d, J = 8.6 Hz, 1H), 5.43 (d, J = 1.6 Hz, 1H), 5.27 (d, J = 7.0 Hz, 1H), 5.14 (br d, J = 8.1 Hz, 1H), 4.97 (s, 2H), 4.60 (dd, J = 8.7, 1.9 Hz, 1H), 4.50 (m, 1H), 4.38 (s, 2H), 3.98 (s, 3H), 3.82 (s, 3H), 3.70 (s, 3H), 3.68 (s, 3H), 3.63 (br s, 3H), 3.46–3.38 (m, 2H), 3.34 (d, J = 4.3 Hz, 1H), 3.33 (d, J = 3.5 Hz, 1H), 3.22–3.20 (m, 2H), 3.13 (s, 3H), 1.38 (s, 9H), 0.81 (s, 9H), –0.02 and –0.12 (two s, 3H each); IR (film) ν_{max} 3317, 2959, 2930, 2859, 1727, 1601, 1562, 1503, 1462, 1273, 1123, 1072, 1040, 938, 836, 779, 743, 705 cm^{-1}; FABHRMS (NBA–CsI) *m/z* 1349.3829 (M^+ + Cs, $C_{61}H_{77}ClN_4O_{18}Si$ requires 1349.3245).

24: white film; $[\alpha]_D^{25}$ –86 (*c* 0.21, $CHCl_3$); ^{1}H NMR (CD_3OD, 400 MHz) δ 7.64 (d, J = 8.3

Hz, 1H), 7.45 (s, 1H), 7.42 (s, 1H), 7.36 (s, 1H), 7.27–7.18 (m, 5H), 7.11 (d, J = 8.3 Hz, 1H), 6.91 (d, J = 7.8 Hz, 1H), 6.85 (d, J = 9.5 Hz, 1H), 6.64 (br s, 1H), 6.52 (d, J = 2.0 Hz, 1H), 6.51 (br s, 1H), 6.30 (br s, 1H), 5.48 (s, 1H), 5.40 (br s, 1H), 5.32 (br s, 2H), 4.64–4.58 (m, 3H), 4.46 (d, J = 6.8 Hz, 1H), 4.41 (d, J = 6.8 Hz, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 3.73 (s, 3H), 3.68 (s, 3H), 3.50–3.34 (m, 7H), 3.28 (s, 3H), 1.44 (s, 9H); IR (film) ν_{max} 3331, 2934, 1694, 1605, 1580, 1504, 1455, 1325, 1240, 1200, 1159, 1062, 1039, 843, 736, 697 cm^{-1}; FABHRMS (NBA–CsI) m/z 1235.2830 (M^+ + Cs, $C_{55}H_{63}ClN_4O_{18}$ requires 1235.2880).

25: white film; $[\alpha]_D^{25}$ –53 (c 0.15, CH_3OH); ^1H NMR (CD_3OD, 400 MHz) δ 7.62 (d, J = 8.9 Hz, 1H), 7.46 (br s, 2H), 7.37 (s, 1H), 7.25 (d, J = 7.3 Hz, 1H), 7.22 (d, J = 7.0 Hz, 1H), 7.16 (br s, 4H), 7.08 (d, J = 8.4 Hz, 1H), 6.87 (d, J = 9.5 Hz, 1H), 6.83 (d, J = 8.4 Hz, 1H), 6.63 (d, J = 1.6 Hz, 1H), 6.53 (d, J = 1.9 Hz, 1H), 6.49 (s, 1H), 6.41 (d, J = 8.4 Hz, 1H), 5.47 (s, 1H), 5.44 (s, 1H), 5.33 (d, J = 1.6 Hz, 1H), 4.61–4.55 (m, 1H), 4.48 (d, J = 12.4 Hz, 1H), 4.47 (d, J = 6.8 Hz, 1H), 4.43 (d, J = 6.8 Hz, 1H), 4.30 (d, J = 1.6 Hz, 1H), 4.24 (d, J = 12.4 Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 3.77 (s, 3H), 3.72 (s, 3H), 3.52–3.38 (m, 6H), 3.27 (s, 3H), 1.44 (s, 9H); IR (film) ν_{max} 3345, 2935, 1694, 1605, 1505, 1392, 1326, 1238, 1159, 1039, 847, 695 cm^{-1}; MALDIFTMS (DHB) m/z 1111.3591 (M^+ + Na, $C_{54}H_{61}ClN_4O_{18}$ requires 1111.3567).

26: white film; $[\alpha]_D^{25}$ +11 (c 0.10, CH_3OH); ^1H NMR (CD_3OD, 400 MHz) δ 7.44 (d, J = 1.9 Hz, 1H), 7.42 (br s, 1H), 7.41 (br s, 1H), 7.14 (br s, 1H), 7.12 (d, J = 1.6 Hz, 1H), 7.10 (d, J = 2.1 Hz, 1H), 6.76 (d, J = 2.4 Hz, 1H), 6.63 (br s, 2H), 6.09 (br s, 1H), 5.55 (s, 1H), 5.37 (d, J = 3.2 Hz, 1H), 5.33 (br s, 1H), 4.65 (d, J = 7.0 Hz, 1H), 4.61 (d, J = 7.0 Hz, 1H), 4.31 (d, J = 3.2 Hz, 1H), 4.22 (dd, J = 7.8 and 4.1 Hz, 1H), 3.98 (s, 3H), 3.87 (s, 3H), 3.75 (s, 3H), 3.74–3.70 (m, 2H), 3.65 (s, 3H), 3.62–3.56 (m, 2H), 3.51–3.47 (m, 2H), 3.33 (s, 3H), 1.46 (s, 9H); IR (film) ν_{max} 3339, 2935, 1692, 1643, 1586, 1493, 1367, 1237, 1161, 1039, 734, 695 cm^{-1}; FABHRMS (NBA–CsI) m/z 1087.2311 (M^+ + Cs, $C_{46}H_{55}ClN_4O_{16}$ requires 1087.2356).

For **27**: white film; $[\alpha]_D^{25}$ –22 (c 0.26, $CHCl_3$); ^1H NMR (CD_3OD, 400 MHz) δ 7.64 (br s, 4H), 6.92 (d, J = 2.2 Hz, 1H), 6.72 (br d, J = 8.6 Hz, 1H), 6.64 (d, J = 2.4 Hz, 1H), 6.60 (br s, 1H), 5.48 (br d, J = 2.9 Hz, 1H), 5.19 (br s, 2H), 4.76 (s, 2H), 4.68 (br s, 1H), 4.36 (dd, J = 7.8 and 4.6 Hz, 1H), 4.07 (s, 1H), 4.05 (dd, J = 10.0 and 8.1 Hz, 1H), 3.94 (s, 3H), 3.88 (s, 3H), 3.77–3.70 (m, 3H), 3.69 (s, 3H), 3.65 (s, 3H), 3.58 and 3.57 (two d, J = 4.4 Hz, 1H each), 3.36 (s, 3H), 1.43 (s, 9H); IR (film) ν_{max} 3323, 2930, 1658, 1605, 1581, 1503, 1462, 1323, 1236, 1159, 1036 cm^{-1}; MALDIFTMS (DHB) m/z 959.3112 (M^+ + Na, $C_{46}H_{53}ClN_4O_{15}$ requires 959.3094).

The 2D ^1H–^1H ROESY NMR spectrum (CD_3OD, 600 MHz) displayed the following diagnostic NOE crosspeaks: C_{4a}^2-H/C_2^2-H (s, δ 7.05/4.68), C_{4a}^2-H/C_2^3-H (s, δ 7.05/4.07), C_2^2-H/C_2^3-H (s, δ 4.68/4.07), C_{5a}^3-H / C_3^3-H (m, δ 7.64/5.19), C_{5a}^3-H/C_2^3–H (m, δ 7.64/4.07). NOE not observed: C_{4b}^2-H/C_2^2-H (δ 7.14/4.68).

C_2^3 Epimer of 27: white film; $[\alpha]_D^{25}$ +22 (c 0.18, $CHCl_3$); ^1H NMR (CD_3OD, 325 K, 400 MHz) δ 7.55 (br s, 1H), 7.27 (dd, J = 8.6 and 2.4 Hz, 1H), 7.22 (d, J = 1.9 Hz, 1H), 7.15 (br s, 1H), 7.06 (d, J = 8.4 Hz, 1H), 6.97 (d, J = 8.6 Hz, 1H), 6.75 (d, J = 2.4 Hz, 1H), 6.66 (dd, J = 2.1 and 1.1 Hz, 1H), 6.59 (d, J = 2.1 Hz, 1H), 5.65 (br s, 1H), 5.53 (s, 1H), 5.47 (s, 1H), 4.85 (br s, 1H), 4.60 (br s, 2H), 3.97 (s, 3H), 3.87 (s, 3H), 3.71 (s, 3H), 3.70 (s, 3H), 3.60–3.55 (m, 3H), 3.49–3.47 (m, 3H), 1.48 (s, 9H); IR (film) ν_{max} 3306, 2958, 2931, 2874, 2479, 1732, 1694, 1651, 1644, 1605, 1504, 1462, 1434, 1274, 1164, 1124, 1064, 1039, 850, 744, cm^{-1}; FABHRMS (NBA–CsI) m/z 1069.2294 (M^+ + Cs, $C_{46}H_{53}ClN_4O_{15}$ requires 1069.2250).

The 2D ^1H–^1H ROESY NMR spectrum (CD_3OD, 325 K, 600 MHz) displayed the following diagnostic NOE crosspeaks: C_3^3-H / C_2^2-H (s, δ 5.45/4.90), C_3^3-H / C_{5a}^3-H (m, δ 5.45/7.22), C_2^2-H / C_{5a}^3-H (m, δ 4.90/7.22), C_2^1-H / C_{4b}^2-H (w, δ 5.50/7.27).

Methyl ester precursor to 29: white foam; $[\alpha]_D^{25}$ +60 (*c* 0.32, $CHCl_3$); ^{1}H NMR (acetone-d_6, 400 MHz) δ 8.22–8.17 (m, 1H), 8.17 (dd, *J* = 2.0, 7.3 Hz, 1H), 7.83–7.80 (m, 1H), 7.44 (dd, *J* = 8.6, 11.1 Hz, 1H), 7.30–7.10 (m, 1H), 5.43 (d, *J* = 4.6 Hz, 1H), 5.13 (dd, *J* = 5.1, 6.7 Hz, 1H), 4.87–4.78 (m, 2H), 4.67–4.53 (m, 1H), 3.74 (s, 3H), 3.10–2.99 (m, 2H), 2.54 (s, 3H), 1.56–1.50 (m, 2H), 1.42 (s, 9H), 1.42–1.36 (m, 1H), 0.88 (d, *J* = 6.6 Hz, 3H), 0.85 (d, *J* = 5.8 Hz, 3H); ^{13}C NMR (acetone-d_6, 100 MHz) δ 172.0, 170.5, 170.0, 155.5 (d, *J* = 260 Hz), 139.6, 137.8, 135.4 (d, *J* = 9 Hz), 125.4 (2C), 118.8 (d, *J* = 21 Hz), 117.6, 80.4, 73.4, 58.6, 57.7, 56.8, 53.2, 50.0, 37.5, 28.4 (3C), 25.4, 23.5, 21.7, 20.8; IR (film) ν_{max} 3306, 2959, 1750, 1683, 1652, 1539, 1506, 1350, 1249, 1155 cm^{-1}; FABHRMS (NBA–NaI) *m/z* 604.2416 (M^+ + Na, $C_{26}H_{36}FN_5O_9$ requires 604.2395).

29: white foam; $[\alpha]_D^{25}$ +51 (*c* 0.42, CH_3OH); ^{1}H NMR (CD_3OD, 400 MHz) δ 8.13 (dd, *J* = 2.1, 7.2 Hz, 1H), 7.77–7.73 (m, 1H), 7.39–7.32 (m, 1H), 4.97 (d, *J* = 6.4 Hz, 1H), 4.74–4.69 (m, 2H), 4.61–4.49 (m, 1H), 3.05 (dd, *J* = 5.5, 17.0 Hz, 1H), 2.98 (dd, *J* = 6.6, 17.0 Hz, 1H), 2.56 (s, 3H), 1.59–1.52 (m, 1H), 1.51–1.39 (m, 2H, partially obscured), 1.44 (s, 9H), 0.91 (d, *J* = 6.4 Hz, 3H), 0.88 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (CD_3OD, 100 MHz) δ 173.3, 173.2, 171.6, 171.5, 156.1 (d, *J* = 260 Hz), 140.1, 135.6 (d, *J* = 9 Hz), 125.8 (2C), 119.2 (d, *J* = 22 Hz), 118.1, 73.4, 59.0, 58.9, 57.3, 50.4, 38.2, 28.6 (3C), 25.9, 23.5, 21.9, 21.1 (2C); IR (film) ν_{max} 3332, 2960, 1731, 1651, 1540, 1350, 1155 cm^{-1}; FABHRMS (NBA–CsI) *m/z* 700.1418 (M^+ + Cs, $C_{25}H_{34}FN_5O_9$ requires 700.1395).

30: white film; $[\alpha]_D^{25}$ +22 (*c* 0.06, CH_3OH); ^{1}H NMR (CD_3OD, 400 MHz) δ 8.09 (d, *J* = 7.0 Hz, 1H), 7.75–7.60 (m, 1H), 7.64 (s, 1H), 7.49 (dd, *J* = 1.9, 8.4 Hz, 1H), 7.40–7.15 (m, 1H), 7.18–7.03 (m, 1H), 6.96 (d, *J* = 8.6 Hz, 1H), 6.91 (d, *J* = 2.2 Hz, 1H), 6.63 (d, *J* = 2.2 Hz, 1H), 6.54 (s, 1H), 5.80 (s, 1H), 5.25 (s, 1H), 5.19 (s, 1H), 4.93–4.68 (m, 3H), 4.76 (s, 2H), 4.66–4.50 (m, 1H), 4.35 (m, 1H), 4.08 (s, 3H), 4.09–4.02 (m, 1H), 3.98–3.90 (m, 1H), 3.94 (s, 3H), 3.89 (s, 3H), 3.78–3.68 (m, 2H), 3.68 (s, 3H), 3.64 (s, 3H), 3.57 (t, *J* = 4.6 Hz, 2H), 3.37 (s, 3H), 3.02–2.82 (m, 2H), 2.52 (s, 3H), 1.65–1.45 (m, 3H), 1.42 (s, 9H), 0.95–0.80 (m, 6H); IR (film) ν_{max} 3303, 2933, 1646, 1538, 1503, 1426, 1349, 1323, 1241, 1154, 1062, 1036 cm^{-1}; FABHRMS (NBA–CsI) *m/z* 1519.7374 (M^+ + Cs, $C_{66}H_{77}ClFN_9O_{21}$ requires 1519.7459).

***P*-31**: Natural DE atropisomer configuration, white film; $[\alpha]_D^{25}$ +38 (*c* 0.05, CH_3OH); ^{1}H NMR (CD_3OD, 400 MHz) δ 8.10 (d, *J* = 8.6 Hz, 1H), 7.88 (s, 1H), 7.61 (s, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 8.6 Hz, 1H), 7.16–7.05 (m, 1H), 7.08 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.01 (d, *J* = 2.4 Hz, 1H), 6.95 (d, *J* = 8.6 Hz, 1H), 6.90 (d, *J* = 2.2 Hz, 1H), 6.62 (d, *J* = 2.2 Hz, 1H), 5.84 (s, 1H), 5.66 (s, 1H), 5.50–5.43 (m, 2H), 5.21 (s, 1H), 4.90–4.74 (m, 2H), 4.75 (s, 2H), 4.61 (br s, 2H), 4.33 (dd, *J* = 7.8, 4.0 Hz, 1H), 4.14 (s, 3H), 4.07 (s, 1H), 4.05 (dd, *J* = 10.2, 7.8 Hz, 1H), 3.92 (dd, *J* = 10.1, 4.0 Hz, 1H), 3.87 (s, 3H), 3.76–3.68 (m, 2H), 3.67 (s, 3H), 3.62 (s, 3H), 3.57 (t, *J* = 4.6 Hz, 2H), 3.36 (s, 3H), 2.88–2.78 (m, 1H), 2.78 (s, 3H), 2.64 (dd, *J* = 17.2, 8.0 Hz, 1H), 1.90–1.80 (m, 1H), 1.65–1.45 (m, 2H), 1.54 (s, 9H), 0.95 (d, *J* = 5.9 Hz, 3H), 0.88 (d, *J* = 7.3 Hz, 3H); IR (film) ν_{max} 3296, 2924, 1651, 1533, 1503, 1482, 1323, 1234, 1158, 1082, 1058, 1021 cm^{-1}; FABHRMS (NBA–CsI) *m/z* 1499.7314 (M^+ + Cs, $C_{66}H_{76}ClN_9O_{21}$ requires 1499.7395).

The 2D ^{1}H–^{1}H ROESY NMR spectrum (CD_3OD, 600 MHz) displayed the following diagnostic NOE crosspeaks: C_{4a}^5-H/C_2^5-H (δ 7.01/4.61, s), C_{4a}^5-H/C_2^6-H (δ 7.01/4.07, s), C_2^5-H/C_2^6-H (δ 4.61/4.07, s), C_{5a}^6-H/C_3^6-H (δ 7.62/5.21, s), C_{5a}^6-H/C_2^6-H (δ 7.62/4.07, m), C_{5a}^2-H/C_3^2-H (δ 7.87/5.47, s).

M-**31**: unnatural DE atropisomer configuration, white film; $[\alpha]_D^{25}$ +42 (*c* 0.11, CH_3OH); ^1H NMR (CD_3OD, 400 MHz) δ 8.39 (s, 1H), 7.61 (s, 1H), 7.56 (d, *J* = 6.7 Hz, 1H), 7.43 (d, *J* = 5.2 Hz, 1H), 7.20 (d, *J* = 5.2 Hz, 1H), 7.13–7.04 (m, 2H), 7.01 (d, *J* = 1.4 Hz, 1H), 6.93 (d, *J* = 5.9 Hz, 1H), 6.90 (d, *J* = 1.2 Hz, 1H), 6.62 (d, *J* = 1.2 Hz, 1H), 5.86 (s, 1H), 5.78 (s, 1H), 5.54 (s, 1H), 5.49 (d, *J* = 2.9 Hz, 1H), 5.22 (s, 1H), 4.95–4.73 (m, 4H), 4.60 (s, 1H), 4.58 (s, 1H), 4.32 (m, 1H), 4.10 (s, 3H), 4.09–4.03 (m, 2H), 3.95–3.90 (m, 1H), 3.87 (s, 3H), 3.75–3.68 (m, 2H), 3.66 (s, 1H), 3.62 (s, 1H), 3.60–3.55 (m, 2H), 3.36 (s, 3H), 2.85–2.68 (m, 1H), 2.77 (s, 3H), 2.70–2.60 (m, 1H), 1.85–1.35 (m, 3H), 1.49 (s, 9H), 0.99–0.89 (m, 6H); IR (film) ν_{max} 3301, 2930, 1658, 1644, 1537, 1503, 1485, 1322, 1158, 1021 cm^{-1}; FABHRMS (NBA–CsI) *m/z* 1499.7476 (M^+ + Cs, $C_{66}H_{76}ClN_9O_{21}$ requires 1499.7395).

The 2D ^1H–^1H ROESY NMR spectrum (CD_3OD, 600 MHz) displayed the following diagnostic NOE crosspeaks: C_3^6-H / C_{5a}^6-H (s, δ 5.20/7.61), C_2^6-H / C_{5a}^6-H (s, δ 4.07/7.61), C_2^6-H / C_{4a}^5-H (s, δ 4.07/7.05), C_2^6-H / C_2^5-H (s, δ 4.07/4.59), C_{4a}^5-H / C_2^5-H (s, δ 7.05/4.59), C_{4b}^5-H / C_{5b}^5-H (s, δ 7.09/6.95). NOE not observed : C_{5a}^2-H / C_3^2-H.

32: white solid; R_f = 0.59 (SiO_2, 10% CH_3OH–$CHCl_3$); $[\alpha]_D^{25}$ +20 (*c* 0.01, $CHCl_3$); ^1H NMR (CD_3OD, 600 MHz) δ 9.32–9.16 (br s, 1H, CONH), 8.32–8.16 (br m, 1H, CONH), 7.74 (br dd, *J* = 8.8 Hz, 1H, C_{5b}^6-H), 7.67–7.58 (br m, 1H, C_{6b}^6-H), 7.56 (br s, 1H, C_{5a}^6-H), 7.51 (br dd, *J* = 8.3 Hz, 1H, C_{5b}^6-H), 7.31 (s, 1H, C_{5a}^2-H), 7.25 (d, *J* = 8.4 Hz, 1H, C_{6b}^2-H), 7.08 (dd, *J* = 8.7, 2.2 Hz, 1H, C_{4b}^5-H), 7.02 (d, *J* = 2.0 Hz, 1H, C_{4a}^5-H), 6.97 (d, *J* = 8.8 Hz, 1H, C_{5b}^5-H), 6.89–6.84 (br m, 1H, CONH), 6.90 (d, *J* = 2.0 Hz, 1H, C_{4a}^7-H), 6.61 (d, *J* = 2.0 Hz, 1H, C_6^7-H), 6.08–5.94 (br s, 1H, C_2^4-H), 5.69 (s, 1H, C_{4b}^4-H), 5.46 (s, 1H, C_{4a}^4-H), 5.37 (d, *J* = 4.7 Hz, 1H, C_3^2-H), 5.20 (s, 1H, C_3^6-H), 5.05–4.96 (br m, 1H, C_2^2-H or C_2^3-H), 4.95–4.75 (2 m, 2H, obscured by H_2O, C_2^5-H and C_2^1-H or C_2^3-H), 4.75 (s, 2H, OCH_2O), 4.61 (br d, *J* = 5.4 Hz, C_2^2-H), 4.39–4.30 (br m, C_2^7-H), 4.16 (s, 3H, C_6^4-OCH_3), 4.09–4.02 (m, 2H, C_2^6-H and C_1^7-H_2), 3.92 (dd, *J* = 10.3, 4.1 Hz, 1H, C_1^7-H_2), 3.87 (s, 3H, C_{5b}^7-OCH_3), 3.77–3.67 (m, 2H, MEM-CH_2CH_2), 3.67 (s, 3H, C_6^5-OCH_3), 3.61 (s, 3H, C_{5a}^7-OCH_3), 3.57 (t, *J* = 4.7 Hz, 2H, MEM-CH_2CH_2), 3.37 (s, 3H, MEM-OCH_3), 2.81 (br dd, *J* = 16.6, 5.8 Hz, 1H, C_3^3-H_2), 2.77 (s, 3H, NCH_3), 2.61 (br dd, *J* = 16.6, 7.5 Hz, 1H, C_3^3-H_2), 1.87–1.79 (br m, 1H, C_3^1-H_2), 1.54 (s, 9H, BOC), 1.52–1.28 (br m, 2H, C_3^1-H_2 and C_4^1-H), 0.94 (br d, *J* = 6.4 Hz, 3H, C_{5a}^1-H_3), 0.92–0.83 (br m, 3H, C_{5b}^1-H_3); ^1H NMR (CD_3OD, 323 K, 600 MHz) δ 7.75–7.64 (br m, 1H, C_{5b}^2-H), 7.60 (d, *J* = 1.9 Hz, 1H, C_{5a}^6-H), 7.54 (dd, *J* = 8.3, 1.6 Hz, C_{5b}^6-H), 7.38–7.30 (br m, C_{5a}^2-H), 7.20 (d, *J* = 8.4 Hz, 1H, C_{6b}^2-H), 7.12 (dd, *J* = 8.4, 1.9 Hz, 1H, C_{6b}^6-H), 7.10 (dd, *J* = 8.7, 2.5 Hz, 1H, C_{4b}^5-H), 7.01 (d, *J* = 2.4 Hz, 1H, C_{4a}^5-H), 6.95 (d, *J* = 8.7 Hz, 1H, C_{5b}^5-H), 6.91 (d, *J* = 2.2 Hz, 1H, C_{4a}^7-H), 6.61 (d, *J* = 2.3 Hz, 1H, C_6^7-H), 5.80 (s, 1H, C_2^4-H), 5.69 (s, 1H, C_{4b}^4-H), 5.45 (s, 1H, C_{4a}^4-H), 5.36 (d, *J* = 4.8 Hz, 1H, C_3^2-H), 5.23 (s, 1H, C_3^6-H), 4.95–4.85 (br m, 1H, C_2^1-H), 4.81 (d, *J* = 4.9 Hz, 1H, C_2^2-H), 4.78 (d, *J* = 6.6 Hz, 1H, OCH_2O), 4.75 (d, *J* = 6.6 Hz, 1H, OCH_2O), 4.62 (s, 1H, C_2^5-H), 4.32 (dd, *J* = 7.7, 4.4 Hz, 1H, C_2^7-H), 4.14 (s, 3H, C_6^4-OCH_3), 4.06 (d, *J* = 1.6 Hz, 1H, C_2^6-H), 4.05 (dd, *J* = 10.7, 7.7 Hz, 1H, C_1^7-H_2), 3.95 (dd, *J* = 10.3, 4.4 Hz, 1H, C_1^7-H_2), 3.87 (s, 3H, C_{5b}^7-OCH_3), 3.75–3.67 (m, 2H, MEM-CH_2CH_2), 3.67 (s, 3H, C_6^5-OCH_3), 3.61 (s, 3H, C_{5a}^7-OCH_3), 3.56 (t, *J* = 4.8 Hz, 2H, MEM-CH_2CH_2), 3.36 (s, 3H, MEM-OCH_3), 2.84–2.74 (m, 1H, obscured by NCH_3, C_3^3-H_2), 2.79 (s, 3H, NCH_3), 2.70–2.68 (br m, 1H, C_3^3-H_2), 1.85–1.75 (m, 1H, C_3^1-H_2), 1.52 (s, 9H, BOC), 1.55–1.40 (m, 2H, C_3^1-H_2 and C_4^1-H), 0.94 (d, *J* = 5.8 Hz, 3H, C_{5a}^1-H_3), 0.87–0.82 (m, 3H, C_{5b}^1-H_3); ^{13}C NMR (CD_3CN, 150 MHz) δ 173.2, 173.1, 171.4, 170.3, 170.1, 169.2, 169.0, 167.9, 161.1, 159.4, 158.3, 157.8, 154.5, 153.5, 151.8, 150.7, 142.1, 139.8, 139.2, 139.1, 138.2, 135.7, 134.9, 130.3, 129.4, 128.8, 128.7, 128.2, 127.6, 127.4, 126.8, 125.3, 125.2, 124.3, 121.8, 113.7, 107.0, 106.3, 105.7, 98.6, 96.3, 81.0, 72.5, 72.4, 71.7, 68.1, 67.9, 67.6, 61.9, 59.0, 58.8, 56.9, 56.5, 56.1, 53.0, 52.8, 51.4, 36.6, 30.6, 30.3, 28.7 (3C), 25.4, 23.6, 22.9, 22.1; IR (film) ν_{max} 3417, 2933, 1682, 1667, 1651, 1417, 1235, 1061 cm^{-1}; FABHRMS (NBA–CsI) *m/z* 1487.3737 (M$^+$ + Cs, $C_{66}H_{75}N_8O_{19}Cl_2$ requires 1487.3658).

P-**33**: white solid; R_f = 0.29 (SiO_2, 5% CH_3OH–$CHCl_3$); $[\alpha]_D^{25}$ –23 (*c* 0.32, $CHCl_3$); ^{1}H NMR (CD_3OD, 323 K, 600 MHz) δ 7.71–7.60 (br m, 1H, $C_{5b}{}^2$-H), 7.47 (dd, *J* = 8.4, 1.8 Hz, 1H, $C_{5b}{}^6$-H), 7.45 (s, 1H, $C_{5a}{}^6$-H), 7.31 (d, *J* = 8.4 Hz, 1H, $C_{6b}{}^2$-H), 7.29–7.26 (br s, 1H, $C_{5a}{}^2$-H), 7.08 (dd, *J* = 8.7, 2.1 Hz, 1H, $C_{4b}{}^5$-H), 7.01 (d, *J* = 8.8 Hz, 1H, $C_{5b}{}^5$-H), 7.00 (d, *J* = 1.7 Hz, 1H, $C_{4a}{}^5$-H), 6.92 (d, *J* = 1.7 Hz, 1H, $C_{4b}{}^7$-H), 6.62 (d, *J* = 2.2 Hz, 1H, $C_6{}^7$-H), 6.49–6.31 (br m, 1H, $C_{5b}{}^6$-H), 6.17–5.92 (br s, 1H, $C_2{}^4$-H), 5.72 (dd, *J* = 1.9, 1.0 Hz, 1H, $C_{4b}{}^4$-H), 5.56 (d, *J* = 4.7 Hz, 1H, $C_3{}^2$-H), 5.49 (dd, *J* = 1.9, 1.0 Hz, 1H, $C_{4a}{}^4$-H), 5.31 (s, 1H, $C_3{}^6$-H), 5.22–5.14 (br m, 1H, $C_2{}^3$-H), 5.07–5.01 (br m, 1H, $C_2{}^2$-H), 4.91–4.85 (br m, 1H, $C_2{}^1$-H), 4.74 (d, *J* = 6.5 Hz, 1H, OCH_2O), 4.70 (d, *J* = 6.5 Hz, 1H, OCH_2O), 4.65–4.60 (br m, 1H, $C_2{}^5$-H), 4.41–4.33 (br m, 1H, $C_2{}^7$-H), 4.22 (s, 3H, $C_6{}^4$-OCH_3), 4.04 (s, 1H, $C_2{}^6$-H), 4.01–3.94 (br m, 1H, $C_1{}^7$-H_2), 3.91 (dd, *J* = 10.2, 9.2 Hz, 1H, $C_1{}^7$-H_2), 3.88 (s, 3H, $C_{5b}{}^7$-OCH_3), 3.73–3.70 (m, 2H, MEM-CH_2CH_2), 3.69 (s, 3H, $C_6{}^5$-OCH_3), 3.62 (s, 3H, $C_{5a}{}^7$-OCH_3), 3.57–3.54 (m, 2H, MEM-CH_2CH_2), 3.36 (s, 3H, MEM-OCH_3), 2.94 (dd, *J* = 17.3, 4.7 Hz, 1H, $C_3{}^3$-H_2), 2.84 (s, 3H, NCH_3), 2.64 (dd, *J* = 17.3, 9.3 Hz, 1H, $C_3{}^3$-H_2), 1.90–1.82 (br m, 1H, $C_3{}^1$-H_2), 1.52 (s, 9H, BOC), 1.50–1.43 (br m, 2H, $C_3{}^1$-H_2 and $C_4{}^1$-H), 1.01 (s, 9H, $C_3{}^6$-$OSiC(CH_3)_3$), 0.95 (d, *J* = 6.4 Hz, 1H, $C_{5a}{}^1$-H_3), 0.90 (s, 9H, $C_3{}^2$ -$OSiC(CH_3)_3$), 0.89 (d, *J* = 6.3 Hz, 3H, $C_{5b}{}^1$-H_3), 0.13 (s, 3H, $SiCH_3$), 0.12 (s, 3H, $SiCH_3$), 0.11 (s, 3H, $SiCH_3$), 0.09 (s, 3H, $SiCH_3$); ^{13}C NMR (CD_3CN, 150 MHz) δ 173.5 (br), 172.4, 170.6 (br), 170.1, 168.8, 167.8 (br), 161.2, 159.4, 158.3, 157.5, 155.0, 153.2, 151.8, 151.5, 141.7, 139.8, 139.1, 138.7, 135.9 (br), 135.1 (br) 130.0, 129.7, 128.7, 128.6 (br), 128.3, 127.6, 127.5 (br), 126.2, 125.3, 125.1, 124.3, 122.0, 117.4, 114.0, 106.2, 106.0, 98.7, 96.1, 80.8, 74.2, 73.5, 72.4, 68.1, 67.6, 67.5, 62.0, 59.9, 58.8, 56.5, 56.4, 56.2, 56.1, 55.1, 52.7, 50.8, 36.6, 30.0, 28.9, 28.7 (3C), 26.3 (3C), 26.2 (3C), 26.1, 25.4, 23.7, 23.4 (br), 22.0, 19.1, 19.0, –4.5, –4.6, –4.8, –4.9; IR (film) ν_{max} 3311, 2932, 1652, 1487, 1234, 1109, 1060, 1023 cm^{-1}; FABHRMS (NBA–CsI) *m/z* 1717.5517 (M$^+$ + Cs, $C_{78}H_{104}Cl_2N_8O_{19}Si_2$ requires 1717.5396).

NOE enhancements (^{1}H–^{1}H ROESY NMR, CD_3OD, 323 K) diagnostic: $C_{5a}{}^6$-H (7.45)/$C_3{}^6$-H (5.31) (s), $C_{5a}{}^6$-H (7.45)/$C_2{}^6$-H (4.09) (s), $C_2{}^6$-H (4.04)/$C_2{}^5$-H (4.65–4.60) (s), $C_2{}^6$-H (4.04)/$C_{4a}{}^5$-H (7.00) (s), $C_2{}^5$-H (4.65–4.60)/$C_{4a}{}^5$-H (7.00) (s), $C_3{}^7$-H_2 (4.01–3.94)/$C_{4b}{}^7$-H (6.92) (w), $C_3{}^7$-H_2 (3.91)/$C_{4b}{}^7$-H (6.92) (w), MEM-CH_2CH_2 (3.73–3.79)/$C_{4b}{}^7$-H (6.92) (m), $C_3{}^2$-H (5.56)/$C_{5a}{}^2$-H (7.71–7.60) (s), $C_3{}^2$-H (5.56)/$C_{5b}{}^2$-H (7.29–7.26) (w), $C_{6b}{}^2$-H (7.30)/$C_{4b}{}^4$ (5.72) (m); additional: $C_2{}^7$-H (4.41–4.33)/$C_{5a}{}^7$-H (6.92) (w), MEM-CH_2CH_2 (3.73–3.70)/OCH_2O (4.74) (m), MEM-CH_2CH_2 (3.73–3.70)/OCH_2O (4.70) (m), $C_1{}^7$-H_2 (4.01–3.94)/$C_{5b}{}^7$-H (6.92) (w), $C_1{}^7$-H_2 (3.91)/$C_{5b}{}^7$-H (6.92) (w), $C_{4b}{}^7$-H (6.92)/$C_{5b}{}^2$-OCH_3 (3.88) (s), $C_{5b}{}^2$-OCH_3 (3.88)/$C_6{}^7$-H (6.62) (s), $C_6{}^7$-H (6.62)/$C_{5a}{}^7$-OCH_3 (3.61) (s), $C_6{}^5$-OCH_3 (3.70)/$C_{5b}{}^5$-H (7.00) (s), $C_6{}^5$-OCH_3 (3.70)/$C_{4b}{}^5$-H (7.08) (m), $C_3{}^3$-H_2 (2.93)/$C_2{}^3$-H (5.22–5.14) (w), $C_3{}^3$-H_2 (2.93)/$C_2{}^3$-H (5.22–5.14) (w), $C_2{}^2$-H (5.08–5.03)/$C_3{}^2$-H (5.56) (s), $C_3{}^1$-H_2 (1.50–1.42)/$C_3{}^1$-H_2 (1.90–1.82) (s), $C_3{}^1$-H_2 (1.90–1.82)/$C_2{}^1$-H (4.92–4.88) (s), $C_3{}^1$-H_2 (1.50–1.42)/$C_2{}^1$-H (4.92–4.88) (m), $C_3{}^1$-H_2 (1.90–1.82)/NCH_3 (2.83) (m), $C_3{}^1$-H_2 (1.50–1.42)/NCH_3 (2.83) (m).

M-**33**: $[\alpha]_D^{25}$ – 46 (*c* 0.10, $CHCl_3$); ^{1}H NMR (CD_3OD, 400 MHz) δ 7.89 (s, 1H), 7.52–7.49 (m, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 8.1 Hz, 1H), 7.07–7.02 (m, 2H), 7.01–6.96 (m, 2H), 6.90 (s, 1H), 6.61 (d, *J* = 1.9 Hz, 1H), 5.75 (s, 1H), 5.54 (d, *J* = 4.9 Hz, 1H), 5.46–5.41 (m, 1H), 5.28 (s, 1H), 5.11–5.05 (m, 1H), 4.98–4.91 (m, 1H, partially obscured), 4.74–4.68 (m, 3H), 4.59 (s, 1H), 4.39–4.32 (m, 1H), 4.22 (s, 3H), 4.05 (s, 1H), 3.98–3.91 (m, 2H), 3.90–

3.86 (m, 1H, partially obscured), 3.86 (s, 3H), 3.71 (t, $J = 4.7$ Hz, 1H), 3.66 (s, 3H), 3.61 (s, 3H), 3.58–3.53 (m, 2H), 3.35 (s, 3H), 2.89–2.82 (m, 1H), 2.79 (s, 3H), 2.56 (dd, $J = 9.2$, 17.3 Hz, 1H), 1.90–1.81 (m, 1H), 1.55 (s, 9H), 1.48–1.38 (m, 2H), 0.97 (s, 9H), 0.93 (d, $J = 6.5$ Hz, 3H), 0.91–0.89 (m, 3H), 0.88 (s, 9H), 0.14 (s, 3H), 0.13 (s, 3H), 0.10 (s, 3H), 0.08 (s, 3H); IR (film) ν_{max} 1683, 1652, 1558, 1506, 1489, 1456, 1258, 1232, 1158, 1106 cm^{-1}; FABHRMS (NBA–CsI) *m/z* 1715.5311 (M$^+$ + Cs, $C_{78}H_{104}Cl_2N_8O_{19}Si_2$ requires 1715.5388).

34: white solid; $[\alpha]_D^{25}$ –20 (*c* 0.09, CH_3OH); ^{1}H NMR (CD_3OD, 323 K, 600 MHz) δ 7.66–7.62 (br m, 1H, $C_{5b}{}^2$-H), 7.53–7.51 (br m, 1H, $C_{5a}{}^6$-H), 7.48 (dd, $J = 8.4$, 1.9 Hz, 1H, $C_{5b}{}^6$-H), 7.33–7.28 (br m, 1H, $C_{5a}{}^2$-H), 7.28 (d, $J = 8.4$ Hz, 1H, $C_{6b}{}^2$-H), 7.09 (dd, $J = 8.7$, 2.4 Hz, 1H, $C_{4b}{}^5$-H), 7.01 (d, $J = 2.4$ Hz, 1H, $C_{4a}{}^5$-H), 6.99 (d, $J = 8.8$ Hz, 1H, $C_{5b}{}^5$-H), 6.92 (d, $J = 2.3$ Hz, 1H, $C_{4b}{}^7$-H), 6.62 (d, $J = 2.3$ Hz, 1H, $C_6{}^7$-H), 6.18–6.08 (br s, 1H, $C_2{}^4$-H), 5.71 (dd, $J = 1.9$, 0.9 Hz, 1H, $C_{4b}{}^4$-H), 5.55 (d, $J = 4.7$ Hz, 1H, $C_3{}^2$-H), 5.47 (dd, $J = 1.9$, 0.9 Hz, 1H, $C_{4a}{}^4$-H), 5.30 (d, $J = 1.7$ Hz, 1H, $C_3{}^6$-H), 5.13–5.05 (br m, 1H, $C_2{}^3$-H), 5.04–4.98 (br m, 1H, $C_2{}^2$-H), 4.89–4.93 (br m, 1H, $C_2{}^1$-H), 4.62 (s, 1H, $C_2{}^5$-H), 4.23 (dd, $J = 8.5$, 4.6 Hz, 1H, $C_2{}^7$-H), 4.19 (s, 3H, $C_6{}^4$-OCH_3), 4.07 (d, $J = 1.2$ Hz, 1H, $C_2{}^6$-H), 3.99 (dd, $J = 11.0$, 8.5 Hz, 1H, $C_1{}^7$-H_2), 3.92 (dd, $J = 11.0$, 4.6 Hz, 1H, $C_1{}^7$-H_2), 3.88 (s, 3H, $C_{4b}{}^7$-H), 3.68 (s, 3H, $C_6{}^5$-OCH_3), 3.61 (s, 3H, $C_{5a}{}^7$-OCH_3), 2.90 (dd, $J = 17.1$, 5.0 Hz, 1H, $C_3{}^3$-H_2), 2.83 (s, 3H, NCH_3), 2.63 (dd, $J = 17.1$, 9.1 Hz, 1H, $C_3{}^3$-H_2), 1.89–1.82 (br m, 1H, $C_3{}^1$-H_2), 1.52 (s, 9H, BOC), 1.50–1.43 (br m, 2H, $C_3{}^1$-H_2 and $C_4{}^1$-H), 0.97 (s, 9H, $C_3{}^6$-$OSiC(CH_3)_3$), 0.94 (d, $J = 6.5$ Hz, 3H, $C_{5a}{}^1$-H_3), 0.90 (s, 9H, $C_3{}^2$-$OSiC(CH_3)_3$), 0.90–0.85 (br m, 3H, $C_{5b}{}^1$-H_3), 0.13 (s, 3H, $SiCH_3$), 0.11 (s, 3H, $SiCH_3$), 0.10 (s, 3H, $SiCH_3$), 0.08 (s, 3H, $SiCH_3$); ^{13}C NMR (CD_3CN, 150 MHz) δ 173.4, 173.3, 172.4, 171.0, 170.8, 168.8, 168.6, 167.8, 161.0, 159.5, 158.0, 157.5, 155.1, 153.7, 151.8, 151.5, 140.5, 139.6, 139.0, 138.6, 135.7, 135.0, 129.8, 129.7, 128.8, 128.7, 128.2, 127.6, 127.4, 126.8, 125.3, 125.0, 124.3, 121.7, 117.4, 113.7, 107.0, 106.3, 105.7, 98.5, 80.5, 74.5, 73.6, 67.6, 62.0, 59.9, 56.5, 56.4, 56.3, 55.9, 55.1, 52.7, 50.8, 36.7, 29.9, 28.2, 28.7 (3C), 26.3 (3C), 26.2 (3C), 25.4, 23.7, 23.2, 22.0, 19.0, 18.9, –4.5, –4.6, –4.8, –4.9; IR (film) ν_{max} 3310, 2929, 1651, 1486, 1236, 1107, 1020 cm^{-1}; FABHRMS (NBA–CsI) *m/z* 1627.4770 (M$^+$ + Cs, $C_{74}H_{96}Cl_2N_8O_{17}Si_2$ requires 1627.4863).

NOE enhancements (^{1}H–^{1}H ROESY NMR, CD_3OD, 323 K, 600 MHz) diagnostic: $C_{4a}{}^6$-H (7.53–7.51)/$C_3{}^6$-H (5.30) (s), $C_{4a}{}^6$-H (7.53–7.57)/$C_2{}^6$-H (4.07) (s), $C_2{}^6$-H (4.07)/$C_2{}^5$-H (4.62) (s), $C_2{}^6$-H (4.07)/$C_{4a}{}^5$-H (7.01) (s), $C_2{}^5$-H (4.62)/$C_{4a}{}^5$-H (7.01) (s), $C_2{}^5$-H (4.62)/$C_{4a}{}^4$-H (5.47) (m), $C_2{}^2$-H (5.04–4.98)/$C_{5a}{}^2$-H (7.33–7.28) (w), $C_3{}^2$-H (5.55)/$C_{5a}{}^2$-H (7.33–7.28) (s), $C_3{}^2$-H (5.55)/$C_{5b}{}^2$-H (7.88–7.62) (w), $C_{6b}{}^2$-H (7.28)/$C_{4b}{}^4$-H (5.71) (w); additional: $C_3{}^6$-H (5.30)/$C_2{}^6$-H (4.07) (s), $C_1{}^7$-H_2 (3.92)/$C_{4b}{}^7$-H (6.92) (s), $C_1{}^7$-H_2 (3.99)/$C_{4b}{}^7$-H (6.92) (s), $C_{4b}{}^7$-H (6.92)/$C_{5b}{}^7$-OCH_3 (3.89) (s), $C_{5b}{}^7$-OCH_3 (3.88)/$C_6{}^7$-H (6.62) (s), $C_6{}^7$-H (6.62)/$C_{5a}{}^7$-OCH_3 (3.61) (s), $C_6{}^5$-OCH_3 (3.68)/$C_{5b}{}^5$-H (6.99) (s), $C_6{}^5$-OCH_3 (3.68)/$C_{4b}{}^5$-H (7.09) (m), $C_3{}^3$-H_2 (2.90)/$C_2{}^3$-H (5.13–5.05) (w), $C_3{}^3$-H_2 (2.63)/$C_2{}^3$-H (5.13–5.05) (w), $C_3{}^3$-H_2 (2.90)/$C_3{}^3$-H_2 (2.63) (s), $C_2{}^2$-H (5.04–4.98)/$C_3{}^2$-H (5.55) (s), $C_{5b}{}^2$-H (7.88–7.62)/$C_{6b}{}^2$-H (7.28) (s), $C_3{}^1$-H_2 (1.89–1.82)/$C_3{}^1$-H_2 (1.50–1.43) (s), $C_3{}^1$-H_2 (1.89–1.82)/$C_2{}^1$-H (4.89–4.83) (s), $C_3{}^1$-H_2 (1.50–1.82)/$C_2{}^1$-H (4.89–4.83) (m), $C_3{}^1$-H_2 (1.89–1.82)/BOC (1.52) (w), $C_3{}^1$-H_2 (1.50–1.43)/BOC (1.52) (m), $C_2{}^1$-H (4.89–4.83)/NCH_3 (2.83) (m).

P-**35**: white film; R_f = 0.34 (SiO_2, 3% CH_3OH–$CHCl_3$); $[\alpha]_D^{25}$ –12 (*c* 0.18, CH_3OH); ^{1}H NMR (CD_3OD, 313 K, 600 MHz) δ 7.71–7.65 (br m, 1H, $C_{5b}{}^2$-H), 7.50–7.45 (dd, 1H, $C_{5b}{}^6$-H, partially obscured by $C_{5a}{}^6$-H), 7.47 (s, 1H, $C_{5a}{}^6$-H), 7.31 (d, 1H, $J = 8.4$ Hz, $C_{6b}{}^2$-H), 7.29–7.25 (br m, 1H, $C_{5a}{}^2$-H), 7.09 (dd, $J = 8.7$, 2.2 Hz, 1H, $C_{4b}{}^5$-H), 7.04 (d, $J = 8.8$ Hz, 1H, $C_{5b}{}^5$-H), 7.00 (d, J = 2.2 Hz, 1H, $C_{4a}{}^5$-H), 6.67 (d, $J = 2.3$ Hz, 1H, $C_6{}^7$-H), 6.44–6.31 (br m, 1H, $C_{5b}{}^6$-H), 6.36 (d, J = 2.3

Hz, 1H, C_{4b}^{7}-H), 6.07–5.86 (br s, 1H, C_{2}^{4}-H), 5.72 (dd, J = 2.4, 1.2 Hz, 1H, C_{4b}^{4}-H), 5.57 (d, J = 4.6 Hz, 1H, C_{3}^{2}-H), 5.47 (dd, J = 1.8, 0.6 Hz, 1H, C_{4a}^{4}-H), 5.36 (d, J = 1.2 Hz, 1H, C_{3}^{6}-H), 5.23–5.16 (br m, 1H, C_{2}^{3}-H), 5.07–5.02 (br m, 1H, C_{2}^{2}-H), 4.91–4.85 (br m, 1H, C_{2}^{1}-H), 4.81 (s, 1H, C_{2}^{7}-H), 4.61 (s, 1H, C_{2}^{5}-H), 4.22 (s, 3H, C_{6}^{4}-OCH_3), 4.07 (m, 1H, C_{2}^{6}-H), 3.84 (s, 3H, C_{5b}^{7}-OCH_3), 3.79 (s, 3H, CO_2CH_3), 3.72 (s, 3H, C_{6}^{5}-OCH_3), 3.64 (s, 3H, C_{5a}^{7}-OCH_3), 2.93 (dd, J = 17.5, 4.6 Hz, 1H, C_{3}^{3}-H), 2.83 (s, 3H, NCH_3), 2.61 (dd, J = 17.5, 8.4 Hz, 1H, C_{3}^{3}-H), 1.92–1.84 (br m, 1H, C_{3}^{1}-H_2), 1.53 (s, 9H, BOC), 1.50–1.39 (br m, 2H, C_{4}^{1}-H and C_{3}^{1}-H_2), 0.99 (s, 9H, C_{3}^{6}-$OSiC(CH_3)_3$), 0.94 (d, J = 6.4 Hz, 3H, C_{5a}^{1}-H_3), 0.90 (s, 9H, C_{3}^{2}-$OSiC(CH_3)_3$), 0.88 (br d, J = 6.6 Hz, 3H, C_{5b}^{1}-H_3), 0.134 (s, 3H, C_{3}^{2}-$OSiCH_3$), 0.125 (s, 6H, C_{3}^{2}-$OSiCH_3$ and C_{3}^{6}-$OSiCH_3$), 0.10 (s, 3H, C_{3}^{6}-$OSiCH_3$); ^{13}C NMR (CD_3OD, 100 MHz) δ 174.0, 172.5, 171.8, 171.7, 171.0, 169.4, 169.2, 161.9, 160.3, 158.9, 158.4, 155.3, 153.6, 152.6, 152.1, 141.9, 139.8, 139.1, 136.9, 136.8, 135.2, 130.7, 130.0, 129.5, 128.3, 128.1, 128.0, 127.9, 127.1, 125.7, 125.0, 124.8, 122.2, 117.5, 113.9, 106.5, 106.2, 106.0, 99.2, 82.1, 74.7, 74.1, 65.0, 62.3, 60.8, 57.9, 56.7, 56.3, 56.2, 56.0, 55.8, 55.4, 52. 8, 51.8, 36.6, 30.8, 30.1, 28.8 (3C), 26.5 (3C), 26.4 (3C), 25.7, 24.0, 22.8, 21.6, 19.4, –4.4, –4.7, –4.9; IR (film) ν_{max} 3281, 2960, 2992, 2356, 1646, 1505, 1485, 1256, 1233, 1103 cm^{-1}; FABHRMS (NBA–CsI) m/z 1655.4909 (M^+ + Cs, $C_{75}H_{96}Cl_2N_8O_{18}Si_2$ requires 1655.4813).

NOE enhancements (^{1}H–^{1}H ROESY NMR, CD_3OD, 313 K, 600 MHz) diagnostic: C_{5a}^{6}-H (7.47)/C_{3}^{6}-H (5.36) (s), C_{5a}^{6}-H (7.47)/C_{2}^{6}-H (4.07) (m), C_{2}^{6}-H (4.07)/C_{2}^{5}-H (4.61) (s), C_{2}^{6}-H (4.07)/C_{4a}^{5}-H (7.00) (s), C_{2}^{5}-H (4.61)/C_{4a}^{4}-H (5.47) (m), C_{3}^{2}-H (5.57)/C_{5a}^{2}-H (7.29–7.25) (m), C_{3}^{2}-H (5.57)/C_{5b}^{2}-H (7.71–7.65) (w), C_{2}^{2}-H (5.07–5.02)/C_{5a}^{2}-H (7.29–7.25) (w), C_{6b}^{2}-H (7.31)/C_{4b}^{4}-H (5.71) (w), BOC (1.65)/C_{5b}^{2}-H (7.71–7.65) (w), BOC (1.65)/C_{6b}^{2}-H (7.31) (w), additional: C_{3}^{6}-H (5.36)/C_{2}^{6}-H (4.07) (s), C_{3}^{6}-$OSiCH_3$ (0.10)/C_{3}^{6}-H (5.36) (w), C_{3}^{6}-$OSiC(CH_3)_3$ (0.99)/C_{3}^{6}-$OSiCH_3$ (0.10) (m), C_{3}^{6}-$OSiC(CH_3)_3$ (0.99)/C_{3}^{6}-$OSiCH_3$ (0.125) (m), C_{4b}^{7}-H (6.36)/C_{2}^{7}-H (4.81) (w), C_{4b}^{7}-H (6.36)/C_{5b}^{7}-OCH_3 (3.84) (m), C_{5b}^{7}-OCH_3 (3.84)/C_{6}^{7}-H (6.67) (m), C_{6}^{7}-H (6.67)/C_{5a}^{7}-OCH_3 (3.64) (s), C_{6}^{5}-OCH_3 (3.72)/C_{5b}^{5}-H (7.03) (m), C_{4a}^{5}-H (7.00)/C_{2}^{5}-H (4.61) (s), C_{3}^{3}-H (2.93)/C_{3}^{3}-H (2.61) (s), C_{3}^{3}-H (2.93)/C_{2}^{3}-H (5.23–5.16) (w), C_{3}^{3}-H (2.61)/C_{2}^{3}-H (5.23–5.16) (w), C_{2}^{2}-H (5.07–5.02)/C_{3}^{2}-H (5.57) (m), C_{5b}^{2}-H (7.71–7.65)/C_{6b}^{2}-H (7.31) (s), C_{3}^{2}-$OSiC(CH_3)_3$ (0.91)/C_{3}^{2}-$OSiCH_3$ (0.134) (m), C_{3}^{2}-$OSiC(CH_3)_3$ (0.91)/C_{3}^{2}-$OSiCH_3$ (0.125) (m), C_{3}^{2}-H (5.57)/C_{3}^{2}-$OSiCH_3$ (0.125) (w), C_{5b}^{1}-H_3 (0.88)/C_{2}^{1}-H (4.91–4.85) (m), C_{4}^{1}-H (1.50–1.39)/C_{3}^{1}-H_2 (1.92–1.84) (s), C_{4}^{1}-H (1.50–1.39)/C_{2}^{1}-H (4.91–4.85) (m), C_{3}^{1}-H_2 (1.50–1.39)/NCH_3 (2.83) (m), C_{3}^{1}-H_2 (1.92–1.84)/C_{2}^{1}-H (4.91–4.85) (w), C_{3}^{1}-H_2 (1.92–1.84)/NCH_3 (2.83) (s), C_{2}^{1}-H (4.91–4.85)/NCH_3 (2.83) (w), NCH_3 (2.83)/BOC (1.53) (m), NCH_3 (2.83)/C_{3}^{2}-$OSiCH_3$ (0.125) (m), BOC (1.53)/C_{3}^{2}-$OSiCH_3$ (0.125) (m).

M-**35**: more polar isomer, R_f = 0.29 (SiO_2, 3% CH_3OH–$CHCl_3$), unnatural DE atropisomer configuration; $[\alpha]_D^{25}$ –33 (c 0.16, CH_3OH); ^{1}H NMR (CD_3OD, 313 K, 600 MHz) δ 7.91–7.83 (br m, 1H, C_{5a}^{2}-H), 7.55 (d, 1H, J = 2.0 Hz, C_{5a}^{6}-H), 7.45 (dd, J = 8.4, 1.9 Hz, 1H, C_{5b}^{6}-H), 7.23 (d, 1H, J = 8.2 Hz, C_{6b}^{2}-H), 7.14 (br d, J = 8.2 Hz, 1H, C_{5b}^{2}-H), 7.10 (dd, J = 8.7, 2.4 Hz, 1H, C_{4b}^{5}-H), 7.03–6.98 (m, 2H, C_{4a}^{5}-H and C_{5b}^{5}-H), 6.67 (d, J = 2.3 Hz, 1H, C_{6}^{7}-H), 6.36 (d, J = 2.3 Hz, 1H, C_{4b}^{7}-H), 6.35–6.30 (br m, 1H, C_{5b}^{6}-H), 6.23–6.16 (br s, 1H, C_{2}^{4}-H), 5.77 (dd, J = 1.8, 0.6 Hz, 1H, C_{4b}^{4}-H), 5.56 (d, J = 5.0 Hz, 1H, C_{3}^{2}-H), 5.44 (dd, J = 2.4, 1.2 Hz, 1H, C_{4a}^{4}-H), 5.37 (s, 1H, C_{3}^{6}-H), 5.07 (br dd, J = 8.9, 5.4 Hz, 1H, C_{2}^{3}-H), 4.96 (br s, 1H, C_{2}^{2}-H), 4.91–4.85 (br m, 1H, C_{2}^{1}-H), 4.79 (s, 1H, C_{2}^{7}-H), 4.60 (s, 1H, C_{2}^{5}-H), 4.23 (s, 3H, C_{6}^{4}-OCH_3), 4.10 (d, 1H, J = 1.9 Hz, C_{2}^{6}-H), 3.84 (s, 3H, C_{5b}^{7}-OCH_3), 3.79 (s, 3H, CO_2CH_3), 3.71 (s, 3H, C_{6}^{5}-OCH_3), 3.65 (s, 3H, C_{5a}^{7}-OCH_3), 2.84 (br dd, J = 17.5, 5.4 Hz, 1H, C_{3}^{3}-H), 2.80 (br s, 3H, NCH_3), 2.59 (dd, J = 17.5, 8.9 Hz, 1H, C_{3}^{3}-H), 1.87–1.79 (m, 1H, C_{3}^{1}-H_2), 1.55 (s, 9H, BOC), 1.45–1.40 (br m, 2H, C_{4}^{1}-H and C_{3}^{1}-H_2), 0.94 (s, 9H, C_{3}^{6}-

$OSiC(CH_3)_3$), 0.94 (d, J = 6.0 Hz, 3H, $C_{5a}{}^1$-H_3), 0.90 (s, 9H, $C_3{}^2$-$OSiC(CH_3)_3$), 0.89–0.86 (br d, 3H, $C_{5b}{}^1$-H_3), 0.13 (s, 6H, two $SiCH_3$), 0.12 (s, 3H, $SiCH_3$), 0.10 (s, 3H, $SiCH_3$); ^{13}C NMR (CD_3OD, 100 MHz) δ 174.6, 172.7, 171.9, 171.6, 171.1, 169.5, 162.1, 160.5, 159.1, 158.6, 155.2, 154.6, 152.8, 151.8, 142.4, 140.0, 139.2, 137.0, 135.2, 130.0, 129.9, 129.2, 128.7, 128.5, 128.3, 128.1, 127.9, 127.2, 125.1, 124.6, 122.3, 117.5, 114.0, 106.5, 106.4, 106.1, 99.2, 82.2, 75.0, 74.1, 65.0, 62.1, 61.2, 58.2, 56.8, 56.5, 56.4, 56.3, 56.1, 55.9, 55.7, 53.0, 52.1, 36.7, 30.3, 29.1 (3C), 28.9, 26.6 (3C), 26.4 (3C), 25.9, 24.1, 19.6, –4.3, –4.4, –4.6, –4.7; IR (film) ν_{max} 3293, 2954, 2931, 2853, 1651, 1582, 1505, 1485, 1254, 1231, 1154, 1108, 1015 cm^{-1}; FABHRMS (NBA–CsI) *m/z* 1655.4697 (M^+ + Cs, $C_{75}H_{96}N_8O_{18}Cl_2Si_2$ requires 1655.4813).

NOE enhancements (^{1}H–^{1}H ROESY NMR, CD_3OD, 313 K, 600 MHz) diagnostic: $C_{5b}{}^6$-H (7.55)/$C_3{}^6$-H (5.37) (w), $C_{5a}{}^6$-H (7.55)/$C_3{}^6$-H (5.37) (s), $C_{5a}{}^6$-H (7.55)/$C_2{}^6$-H (4.10) (m), $C_2{}^6$-H (4.10)/$C_2{}^5$-H (4.60) (s), $C_2{}^6$-H (4.10)/$C_{4a}{}^5$-H (7.03–6.98) (s), $C_2{}^5$-H (4.60)/$C_{4a}{}^4$-H (5.44) (m), $C_3{}^2$-H (5.56)/$C_{5b}{}^3$-H (7.14) (s), $C_{6b}{}^2$-H (7.23)/$C_{4b}{}^4$-H (5.77) (m); additional: $C_3{}^6$-H (5.37)/$C_2{}^6$-H (4.10) (s), $C_2{}^5$-H (4.60)/$C_{4a}{}^5$-H (7.03–6.98) (s), $C_{4b}{}^7$-H (6.36)/$C_2{}^7$-H (4.79) (w), $C_{4b}{}^7$-H (6.36)/$C_{5b}{}^7$-OCH_3 (3.84) (m), $C_{4b}{}^7$-H (6.36)/CO_2CH_3 (3.79) (m), $C_{5b}{}^7$-OCH_3 (3.84)/$C_6{}^7$-H (6.67) (s), $C_6{}^7$-H (6.67)/$C_{5a}{}^7$-OCH_3 (3.65) (m), $C_6{}^5$-OCH_3 (3.71)/$C_{5b}{}^5$-H (7.03–6.98) (m), $C_3{}^3$-H (2.84)/$C_3{}^3$-H (2.80) (s), $C_3{}^3$-H (2.84)/$C_2{}^3$-H (5.07) (m), $C_3{}^3$-H (2.80)/$C_2{}^3$-H (5.07) (w), $C_2{}^2$-H (4.96)/$C_3{}^2$-H (5.56) (s), $C_{5a}{}^1$-H_3 (0.94)/$C_4{}^1$-H (1.45–1.40) (m), $C_{5b}{}^1$-H_3 (0.89–0.86)/$C_4{}^1$-H (1.45–1.40) (m), $C_{5b}{}^1$-H_3 (0.89–0.86)/$C_2{}^1$-H (4.91–4.85) (m), $C_4{}^1$-H (1.45–1.40)/$C_3{}^1$-H_2 (1.87–1.79) (s), $C_3{}^1$-H_2 (1.87–1.79)/$C_2{}^1$-H (4.91–4.85) (w), $C_3{}^1$-H_2 (1.87–1.79)/NCH_3 (2.80) (m), $C_2{}^1$-H (4.91–4.85)/NCH_3 (2.80) (w).

36: white film; $[\alpha]_D^{25}$ –82 (*c* 0.06, CH_3OH); ^{1}H NMR (CD_3OD, 313 K, 600 MHz) δ 7.71 (br m, 1H, $C_{5b}{}^2$-H), 7.46 (s, 1H, $C_{5a}{}^6$-H), 7.42 (dm, J = 8.4 Hz, 1H, $C_{5b}{}^6$-H), 7.33–7.29 (m, 2H, $C_{5a}{}^2$-H and $C_{6b}{}^2$-H), 7.11 (dd, J = 8.7, 2.3 Hz, 1H, $C_{4b}{}^5$-H), 7.03–6.99 (m, 2H, $C_{5b}{}^5$-H and $C_{4a}{}^5$-H), 6.68 (d, J = 1.9 Hz, 1H, $C_6{}^7$-H), 6.37 (d, J = 1.9 Hz, 1H, $C_{4b}{}^7$-H), 6.32 (br m, 1H, $C_{6b}{}^6$-H), 6.07 (br s, 1H, $C_2{}^4$-H), 5.76 (s, 1H, $C_{4b}{}^4$-H), 5.55 (d, J = 4.4 Hz, 1H, $C_3{}^2$-H), 5.45 (s, 1H, $C_{4a}{}^4$-H), 5.36 (s, 1H, $C_3{}^6$-H), 5.02 (br m, 1H, $C_2{}^2$-H), 4.97–4.90 (br m, 2H, $C_2{}^3$-H and $C_2{}^1$-H), 4.82 (s, 1H, $C_2{}^7$-H), 4.59 (s, 1H, $C_2{}^5$-H), 4.22 (s, 3H, $C_6{}^4$-OCH_3), 4.07 (m, 1H, $C_2{}^6$-H), 3.84 (s, 3H, $C_{5b}{}^7$-OCH_3), 3.79 (s, 3H, CO_2CH_3), 3.71 (s, 3H, $C_6{}^5$-OCH_3), 3.66 (s, 3H, $C_{5a}{}^7$-OCH_3), 2.84 (s, 3H, NCH_3), 2.62 (br dd, 1H, $C_3{}^3$-H), 2.41 (br dd, J = 12.6 Hz, 1H, $C_3{}^3$-H), 1.82 (br m, 1H, $C_3{}^1$-H_2), 1.51 (s, 9H, BOC), 1.50–1.40 (br m, 2H, $C_4{}^1$-H and $C_3{}^1$-H_2), 0.96 (s, 9H, $SiC(CH_3)_3$), 0.95 (d, 3H, $C_{5a}{}^1$-H_3, partially obscured by BOC), 0.93 (d, J = 6.0 Hz, 3H, $C_{5b}{}^1$-H_3), 0.89 (s, 9H, $SiC(CH_3)_3$), 0.13 (s, 3H, $SiCH_3$), 0.12 (s, 6H, $SiCH_3$) 0.11 (s, 3H, $SiCH_3$), 0.09 (s, 3H, $SiCH_3$); ^{13}C NMR (acetone-d_6, 100 MHz) δ 172.4, 172.0, 171.8, 171.4, 171.1, 171.0, 169.1, 168.0, 161.3, 160.0, 158.2, 157.0, 154.6, 153.1, 151.6, 141.7, 140.1, 138.5, 137.2, 136.3, 135.8, 130.1, 129.4, 128.4, 128.0, 127.7, 126.4, 125.5, 124.8, 124.2, 122.1, 113.8, 106.6, 106.2, 106.1, 99.2, 80.5, 79.1, 74.7, 74.1, 71.5, 69.8, 64.4, 61.7, 60.1, 57.6, 56.5, 56.3, 56.2, 55.9, 55.5, 55.4, 52.5, 52.1, 38.3, 37.3, 32.1, 28.8 (3C), 26.5 (3C), 26.4 (3C), 25.8, 23.8, 22.8, 19.2, –4.4, –4.5, –4.7, –4.8; IR (film) ν_{max} 3299, 2954, 2931, 2857, 1683, 1657, 1505, 1486, 1236, 1158, 1109, 1061, 1022 cm^{-1}; FABHRMS (NBA–CsI) *m/z* 1673.5036 (M^+ + Cs, $C_{75}H_{98}Cl_2N_8O_{19}Si_2$ requires 1673.4918).

NOE enhancements (^{1}H–^{1}H ROESY NMR, CD_3OD, 313 K, 600 MHz) diagnostic: $C_{5a}{}^6$-H (7.46)/$C_3{}^6$-H (5.36) (s), $C_{5a}{}^6$-H (7.46)/$C_2{}^6$-H (4.07) (s), $C_{5a}{}^6$-H (7.46)/$C_2{}^5$-H (4.59) (w), $C_{6b}{}^6$-H (6.32)/$C_{4a}{}^4$-H (5.45) (w), $C_3{}^6$-H (5.36)/$C_2{}^5$-H (4.59) (w), $C_2{}^6$-H (4.07)/$C_2{}^5$-H (4.59) (s), $C_2{}^6$-H (4.07)/$C_{4a}{}^5$-H (7.03–6.99) (s), $C_2{}^5$-H (4.59)/$C_{4a}{}^4$-H (5.45) (m), $C_3{}^2$-H (5.55)/$C_{5a}{}^2$-H (7.33–7.29) (s), $C_3{}^2$-H (5.55)/$C_{5b}{}^2$-H (7.71) (w), $C_{6b}{}^2$-H (7.33–7.27)/$C_{4b}{}^4$-H (5.76) (w); additional: $C_3{}^6$-H (5.36)/$C_2{}^6$-H

(4.07) (s), C_{4b}^7-H (6.37)/CO_2CH_3 (3.79) (m), CO_2CH_3 (3.79)/ C_2^7-H (4.82) (w), C_{4b}^7-H (6.37)/C_{5b}^7-OCH_3 (3.84) (m), C_{5b}^7-OCH_3 (3.84)/C_6^7-H (6.68) (m), C_6^7-H (6.68)/C_{5a}^7-OCH_3 (3.66) (s), C_6^5-OCH_3 (3.71)/C_{5b}^5-H (7.03–6.99) (s), C_{4a}^5-H (7.03–6.99)/C_2^5-H (4.59) (s), C_3^3-H (2.62)/C_3^3-H (2.41) (s), C_3^3-H (2.62)/C_2^3-H (4.97–4.90) (m), C_3^3-H (2.41)/C_2^3-H (4.97–4.90) (m), C_2^2-H (5.02)/C_3^2-H (5.55) (s), C_{5b}^2-H (7.71)/C_{6b}^2-H (7.33–7.27) (s), C_{5a}^1-H_3 (0.95)/C_4^1-H (1.50–1.40) (m), C_{5b}^1-H_3 (0.93)/C_4^1-H (1.50–1.40) (m), C_4^1-H (1.50–1.40)/C_3^1-H_2 (1.82) (m), C_3^1-H_2 (1.50–1.40)/C_2^1-H (4.97–4.90) (w), C_3^1-H_2 (1.50–1.40)/NCH_3 (2.84) (m), C_3^1-H_2 (1.82)/NCH_3 (2.84) (m).

37: white film; R_f = 0.20 (SiO_2, 5% CH_3OH–$CHCl_3$); $[\alpha]_D^{25}$ +44 (*c* 0.16, CH_3OH); ^1H NMR (CD_3OD, 313 K, 600 MHz) δ 7.74–7.65 (br m, 1H, C_{5b}^2-H), 7.59 (s, 1H, C_{5a}^6-H), 7.56 (br dd, *J* = 7.5 Hz, 1H, C_{5b}^6-H), 7.48–7.39 (br m, 1H, C_{5a}^2-H), 7.25 (d, *J* = 8.3 Hz, 1H, C_{6b}^2-H), 7.12–7.03 (br m, 1H, C_{4b}^5-H), 7.01 (d, *J* = 2.3 Hz, 1H, C_{4a}^5-H), 7.00–6.94 (m, 1H, C_{6b}^6-H), 6.96 (d, *J* = 8.8 Hz, 1H, C_{5b}^5-H), 6.67 (d, *J* = 2.2 Hz, 1H, C_6^7-H), 6.33 (d, *J* = 2.2 Hz, 1H, C_{4a}^7-H), 5.88 (br s, 1H, C_2^4-H), 5.72 (br s, 1H, C_{4b}^4-H), 5.44–5.36 (br m, 1H, C_{4a}^4-H), 5.36–5.30 (br m, 1H, C_3^2-H), 5.29 (s, 1H, C_3^6-H), 4.96–4.88 (br m, 1H, C_2^2-H), 4.89–4.83 (br m, 1H, C_2^1-H), 4.84–4.77 (br m, 1H, C_2^3-H), 4.75 (s, 1H, C_2^7-H), 4.60 (s, 1H, C_2^5-H), 4.14 (s, 3H, C_6^4-OCH_3), 4.11 (d, *J* = 1.8 Hz, 1H, C_2^6-H), 3.84 (s, 3H, C_{5b}^7-OCH_3), 3.80 (s, 3H, CO_2CH_3), 3.70 (s, 3H, C_6^5-OCH_3), 3.66 (s, 3H, C_{5a}^7-OCH_3), 2.81 (br s, 3H, NCH_3), 2.70–2.59 (br m, 1H, C_3^3-H), 2.40–2.36 (br m, 1H, C_3^3-H), 1.81–1.72 (br m, 1H, C_3^1-H_2), 1.56–1.45 (m, 2H, C_4^1-H, and C_3^1-H_2 obscured by BOC), 1.50 (s, 9H, BOC), 0.99–0.92 (br m, 3H, C_{5a}^1-H_3), 0.93–0.85 (br m, 3H, C_{5b}^1-H_3); ^{13}C NMR (acetone-d_6, 100 MHz) δ 172.4, 172.3, 172.2, 172.1, 171.3, 170.0, 168.7, 161.3, 160.1, 160.0, 158.3, 157.3, 153.9, 153.7, 153.6, 153.5, 151.3, 151.1, 150.6, 142.4, 140.9, 137.8, 137.5, 136.8, 135.9, 129.8, 129.2, 129.1, 128.5, 128.1, 127.3, 125.5, 124.8, 124.1, 122.2, 113.7, 105.7, 99.1, 80.8, 80.5, 73.3., 73.2, 72.4, 63.8, 61.5, 59.9, 57.8, 57.0, 56.3, 56.2, 55.9, 55.2, 55.1, 52.6, 52.4, 37.2, 28.7 (3C), 25.6, 23.8, 22.3; IR (film) ν_{max} 3292, 2944, 1656, 1508, 1490, 1321, 1233, 1154, 1059, 1023 cm^{-1}; FABHRMS (NBA–CsI) *m/z* 1445.3274 (M^+ + Cs, $C_{63}H_{70}Cl_2N_8O_{19}$ requires 1445.3189).

NOE enhancements (^1H–^1H ROESY NMR, CD_3OD, 313 K, 600 MHz) diagnostic: C_{5a}^6-H (7.59)/C_3^6-H (5.29) (s), C_{5a}^6-H (7.59)/C_2^6-H (4.11) (s), C_{5a}^6-H (7.59)/C_2^5-H (4.60) (w), C_2^5-H (4.60)/C_{4a}^4-H (5.44–5.36) (m), C_2^6-H (4.11)/C_2^5-H (4.60) (s), C_2^6-H (4.11)/C_{4a}^5-H (7.01) (s), C_2^7-H (4.75)/C_{4a}^5-H (7.01) (m), C_2^2-H (4.96–4.88)/C_{5a}^2-H (7.48–7.39) (m), C_3^2-H (5.36–5.30)/C_{5a}^2-H (7.48–7.39) (s), C_{6b}^2-H (7.25)/C_{4b}^4-H (5.72) (w); additional: C_3^6-H (5.29)/C_2^6-H (4.11) (s), C_{4b}^7-H (6.33)/CO_2CH_3 (3.80) (w), C_{4b}^7-H (6.33)/ C_2^7-H (4.75) (m), C_{4b}^7-H (6.33)/C_{5b}^7-OCH_3 (3.84) (s), C_{5b}^7-OCH_3 (3.84)/C_6^7-H (6.67) (s), C_6^7-H (6.67)/C_{5a}^7-OCH_3 (3.66) (s), C_6^5-OCH_3 (3.70)/C_{5b}^5-H (6.96) (s), C_{4a}^5-H (7.01)/C_2^5-H (4.60) (s), C_3^3-H (2.70–2.59)/C_3^3-H (2.40–2.36) (m), C_{5b}^2-H (7.74–7.65)/C_{6b}^2-H (7.25) (s), C_{5a}^1-H_3 (0.99–0.92)/C_4^1-H (1.56–1.45) (m), C_{5b}^1-H_3 (0.93–0.85)/C_4^1-H (1.56–1.45) (m), C_{5a}^1-H_3 (0.99–0.92)/C_3^1-H_2 (1.81–1.72) (m), C_{5b}^1-H_3 (0.93–0.85)/C_3^1-H_2 (1.81–1.72) (m), C_{5a}^1-H_3 (0.99–0.92)/C_2^1-H (4.89–4.83) (w), C_{5b}^1-H_3 (0.93–0.85)/C_2^1-H (4.89–4.83) (w), C_3^1-H_2 (1.56–1.45)/C_2^1-H (4.89–4.83) (w), C_3^1-H_2 (1.81–1.72)/C_2^1-H (4.89–4.83) (w), C_3^1-H_2 (1.56–1.45)/NCH_3 (2.81) (m), C_3^1-H_2 (1.81–1.72)/NCH_3 (2.81) (m).

1: white film; $[\alpha]_D^{25}$ +61 (*c* 0.20, CH_3OH); ^1H NMR (CD_3OD, 313 K, 600 MHz) δ 7.77 (br d, *J* = 7.5 Hz, 1H, C_{6b}^6-H), 7.71 (s, 1H, C_{5a}^2-H), 7.63 (d, *J* = 1.8 Hz, 1H, C_{5a}^6-H), 7.54 (br d, *J* = 7.4 Hz, 1H, C_{5b}^2-H), 7.53 (br d, *J* = 7.4 Hz, 1H, C_{5b}^6-H), 7.15 (d, *J* = 8.4 Hz, 1H, C_{6b}^2-H), 7.06 (s, 1H, C_{4a}^5-H), 6.65 (s, 2H, C_{4b}^5-H and C_{5b}^5-H), 6.43 (d, *J* = 2.2 Hz, 1H, C_6^7-H), 6.40 (d, *J* = 2.2 Hz, 1H, C_{4b}^7-H), 6.03 (br s, 1H, C_2^4-H), 5.95 (br s, 1H, C_{4b}^4-H), 5.34 (s, 1H, C_2^6-H), 5.33 (d, *J* = 1.6 Hz, 1H, C_{4a}^4-H), 5.24 (d, *J* = 2.8 Hz, 1H, C_3^2-H), 4.79–4.82 (d, 1H, C_2^2-H obscured by H_2O), 4.74 (s, 1H, C_2^5-

H), 4.68 (s, 1H, C_2^7-H), 4.25 (br dd, J = 8.4 Hz, 1H, C_2^3-H), 4.16 (s, 1H, C_2^6-H), 3.98 (m, 1H, C_2^1-H), 2.96 (br dd, J = 15.5 Hz, 1H, C_3^3-H), 2.76 (s, 3H, NCH_3), 2.04–1.93 (br m, 1H, C_3^3-H), 1.88–1.80 (br m, 1H, C_3^1-H_2), 1.69–1.56 (br m, 2H, C_4^1-H and C_3^1-H_2), 0.97–0.81 (br m, 6H, C_{5a}^1-H_3 and C_{5b}^1-H_3); ^{13}C NMR (CD_3OD, 100 MHz) δ 175.9, 175.1, 172.7, 172.0, 170.4, 170.2, 169.5, 169.1, 159.4, 158.3, 156.7, 153.5, 151.7, 150.1, 148.3, 142.7, 141.3, 137.7, 137.4, ,137.3, 136.1, 132.3, 130.5, 129.4, 129.3, 129.1, 128.5, 128.1, 127.4, 127.2, 125.6, 122.5, 119.0, 118.5, 110.5, 107.9, 106.9, 104.1, 74.6, 73.6, 72.4, 64.0, 62.2, 59.5, 58.8, 56.7, 55.4, 52.7, 40.4, 36.8, 33.2, 25.6, 23.2, 23.0; IR (film) ν_{max} 3316, 1667, 1644, 1520, 1488, 1428, 1337, 1228, 1204, 1141, 1061, 1014 cm^{-1}; FABHRMS (NBA–CsI) *m/z* 1143.2968 (M^+ + H, $C_{53}H_{52}Cl_2N_8O_{17}$ requires 1143.2906).

NOE enhancements (^1H–^1H ROESY NMR, CD_3OD, 313 K, 600 MHz) diagnostic: C_{5a}^6-H (7.63)/C_3^6-H (5.34 (s), C_{5a}^6-H (7.63)/C_2^6-H (4.16) (s), C_{6b}^6-H (7.77)/C_{4a}^4-H (5.33) (s), C_2^6-H (4.16)/C_2^5-H (4.74) (s), C_2^6-H (4.16)/C_{4a}^5-H (7.06) (s), C_2^4-H (6.30)/C_{4a}^4-H (5.33) (w), C_3^2-H (5.24)/C_{5a}^2-H (7.71) (s), C_3^2-H (5.24)/C_{5b}^2-H (7.54) (w), C_{6b}^2-H (7.15)/C_{4b}^4-H (5.95) (w); additional: C_{5b}^6-H (7.53)/C_{6b}^6-H (7.77) (s), C_3^6-H (5.34)/C_2^6-H (4.16) (s), C_{4b}^7-H (6.40)/C_2^7-H (4.68) (w), C_{4a}^5-H (7.06)/C_2^5-H (4.74) (s), C_{4b}^5-H (6.65)/C_2^5-H (4.74) (w), C_3^3-H (2.96)/C_3^3-H (2.04–1.93) (m), C_3^1-H (1.88–1.80)/C_3^1-H (1.69–1.56) (m), C_2^1-H (3.98)/NCH_3 (2.76) (m), C_{5b}^2-H (7.54)/C_{6b}^2-H (7.15) (s).

38: A solution of **32** (1.7 mg, 0.0013 mmol) in CH_2Cl_2 at 0 °C under Ar was treated with *B*-catecholborane (0.2 M solution in CH_2Cl_2, 75 μL, 12 equiv) and stirrred at 0 °C for 2 h. The reaction was quenched with saturated aqueous $NaHCO_3$ (0.5 mL), and the mixture was extracted with EtOAc (3 × 1 mL). The combined organic layers were washed with saturated aqueous NaCl (1 mL), dried (Na_2SO_4), and concentrated *in vacuo*. PTLC (SiO_2, 10% CH_3OH–$CHCl_3$) afforded **39** (0.7 mg, 1.5 mg theoretical, 48%) as a white film: $[\alpha]^{25}_D$ +27 (*c* 0.030, CH_3OH); ^1H NMR (CD_3OD, 400 MHz) δ 7.65–7.61 (m, 1H), 7.63 (s, 1H), 7.57 (d, J = 9.7 Hz, 1H), 7.48 (s, 1H), 7.26 (d, J = 8.2 Hz, 1H), 7.22 (d, J = 7.4 Hz, 1H), 7.09 (dd, J = 2.8, 8.3 Hz, 1H), 7.03 (s, 1H), 6.95 (d, J = 8.8 Hz, 1H), 6.87 (s, 1H), 6.61 (s, 1H), 5.81 (s, 1H), 5.72 (s, 1H), 5.40 (s, 1H), 5.34 (d, J = 3.8 Hz, 1H), 5.24 (s, 1H), 5.03–5.00 (m, 1H), 4.94 (s, 1H), 4.71–4.68 (m, 1H), 4.64 (s, 1H), 4.24–4.19 (m, 1H), 4.13 (s, 3H), 4.09 (s, 1H), 4.03 (dd, J = 7.0, 10.3 Hz, 1H), 3.97 (dd, J = 5.0, 11.2 Hz, 1H), 3.88 (s, 3H), 3.67 (s, 3H), 3.60 (s, 3H), 2.91–2.88 (m, 1H), 2.86–2.81 (m, 1H), 2.47 (s, 3H), 1.81–1.77 (m, 1H), 1.64–1.56 (m, 2H), 0.98 (d, J = 6.5 Hz, 3H), 0.95 (d, J = 6.7 Hz, 3H); IR (film) ν_{max} 2924, 1683, 1652, 1538, 1505 cm^{-1}; MALDIFTMS (DHB) *m/z* 1189.3428 (M^+ + Na, $C_{57}H_{60}Cl_2N_8O_{15}$ requires 1189.3453).

39: A vial charged with **35** (7.5 mg, 0.0049 mmol) was treated with Bu_4NF–HOAc (1:1, 0.95 M solution in THF, 156 μL, 0.15 mmol, 30 equiv) and stirred at 25 °C under Ar for 23.5 h. The mixture was diluted with EtOAc (3 mL) and washed with H_2O (3 mL) and saturated aqueous Nacl (3 mL). The combined aqueous layers were extracted with EtOAc (2 × 6 mL), and the combined organic layers were dried (Na_2SO_4), and concentrated *in vacuo*. The resulting crude residue was cooled to 0 °C, treated with HCl (4.0 M solution in dioxane, 0.5 mL, 2.0 mmol), and stirred at 25 °C for 1 h. The mixture was concentrated *in vacuo* at 0 °C, and the residue was treated with saturated aqueous $NaHCO_3$ (0.5 mL), extracted with EtOAc (4 × 1.5 mL), washed with saturated aqueous NaCl (1.5 mL), dried (Na_2SO_4), and concentrated *in vacuo*. PTLC (SiO_2, 10% CH_3OH–$CHCl_3$) afforded **39** (2.0 mg, 5.9 mg theoretical, 34%) as a white film: $[\alpha]^{25}_D$ +29 (*c* 0.035, CH_3OH); ^1H NMR (CD_3OD, 500 MHz) δ 7.65–7.62 (m, 1H), 7.62 (s, 1H), 7.57 (dd, J = 1.4, 8.4 Hz, 1H), 7.47 (d, J = 1.4 Hz, 1H), 7.26 (d, J = 8.4 Hz, 1H), 7.14 (d, J = 8.4 Hz, 1H), 7.10 (dd, J = 2.2, 8.8 Hz, 1H), 7.02 (d, J = 2.6 Hz, 1H), 6.97 (d, J = 8.8 Hz, 1H), 6.66 (d, J = 2.2 Hz, 1H), 6.32 (d, J

= 2.2 Hz, 1H), 5.86 (s, 1H), 5.73 (s, 1H), 5.40 (s, 1H), 5.34 (d, J = 4.0 Hz, 1H), 5.29 (s, 1H), 5.04–5.01 (m, 1H), 4.74 (s, 1H), 4.73–4.69 (m, 1H), 4.63 (s, 1H), 4.15 (s, 1H), 4.14 (s, 3H), 4.13 (s, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 3.71 (s, 3H), 3.63 (s,3H), 2.92 (dd, J = 6.6, 17.2 Hz, 1H), 2.85 (dd, J = 7.0, 16.9 Hz, 1H), 2.41 (s, 3H), 1.83–1.77 (m, 1H), 1.64–1.54 (m, 2H), 0.97 (d, J = 6.6 Hz, 3H), 0.95 (d, J = 6.6 Hz, 3H); IR (film) ν_{max} 2961, 1650, 1504, 1487, 1231, 1061 cm^{-1}; MALDIFTMS (DHB) *m/z* 1195.3628 (M^+ + H, $C_{58}H_{60}Cl_2N_8O_{16}$ requires 1195.3577).

40: A solution of **37** (30.3 mg, 23.1 μmol) in anhydrous dioxane (1 mL) was treated with 4 N HCl–EtOAc (2 mL) under Ar, and the resulting mixture was stirred at 25 °C for 0.5 h. The reaction mixture was concentrated *in vacuo*, and the residue was triturated with EtOAc (5 mL) to give **40** (24.9 mg, 28.8 mg theoretical, 86%) as a white solid: $[\alpha]_D^{25}$ +46 (*c* 0.11, CH_3OH); ^{1}H NMR (CD_3OD, 297 K, 400 MHz) δ 9.01 (d, J = 6.2 Hz, 1H), 7.77 (d, J = 7.0 Hz, 1H), 7.72 (s, 1H), 7.67–7.50 (m, 3H), 7.23 (d, J = 8.6 Hz, 1H), 7.05 (s, 1H), 6.92–6.83 (br s, 2H), 6.64 (d, J = 2.2 Hz, 1H), 6.31 (d, J = 2.2 Hz, 1H), 5.97 (s, 1H), 5.82 (s, 1H), 5.37 (d, J = 1.9 Hz, 1H), 5.34 (s, 1H), 5.26 (d, J = 3.5 Hz, 1H), 4.77–4.72 (m, 1H), 4.67 (s, 1H), 4.27 (d, J = 10.5 Hz, 1H), 4.16 (s, 1H), 4.17–4.05 (m, 1H), 4.10 (s, 3H), 4.06–3.96 (m, 1H), 3.84 (s, 3H), 3.79 (s, 3H), 3.66 (s, 3H), 3.64 (s, 3H), 3.00 (d, J = 14.8 Hz, 1H), 2.76 (s, 3H), 2.15–2.04 (m, 1H), 1.94–1.82 (m, 1H), 1.69–1.58 (m, 2H), 0.91 (d, J = 6.0 Hz, 3H), 0.87 (d, J = 6.0 Hz, 3H): IR (film) ν_{max} 3308, 1736, 1644, 1607, 1582, 1505, 1418, 1325, 1233, 1059, 1028 cm^{-1}; FABHRMS (NBA–CsI) *m/z* 1345.2609 (M^+ + Cs, $C_{58}H_{62}N_8O_{17}Cl_2$ requires 1345.2664).

AB precursor

Compd	Conditions	t (h)	(*R*)/(*S*)
10	*o*-$C_6H_4Cl_2$, 120 °C	0.0	76 : 24
		0.3	74 : 26
		1.0	73 : 27
		2.0	66 : 34
		3.0	59 : 41
		4.7	53 : 47
10	*o*-$C_6H_4Cl_2$, 140 °C	0.0	76 : 24
		0.7	57 : 43
		1.0	53 : 47
		1.4	44 : 56
		1.7	43 : 57
		2.0	34 : 66
		6.0	25 : 75
23	*o*-$C_6H_4Cl_2$, 120 °C	0.0	100 : 0
		2.5	71 : 29
		4.5	56 : 44
		6.5	43 : 57
		9.5	34 : 66
		14	27 : 73
		18	25 : 75
23	*o*-$C_6H_4Cl_2$, 135 °C	0.0	100 : 0
		0.5	75 : 26
		1.0	60 : 40
		1.7	45 : 55
		2.0	41 : 59
		2.5	37 : 63

for **10** (*o*-$Cl_2C_6H_4$): E_a = 25.2 kcal/mol, $\Delta H^‡$ = 24.2 kcal/mol, $\Delta S^‡$ = –2.5 eu, $\Delta G^‡$(120 °C) = 25.2 kcal/mol

for **23** (*o*-$Cl_2C_6H_4$): E_a = 25.1 kcal/mol, $\Delta H^‡$ = 24.2 kcal/mol, $\Delta S^‡$ = –1.6 eu, $\Delta G^‡$(120 °C) = 24.8 kcal/mol

Compd	Conditions	k (h^{-1})	$t_{1/2}$ (h)
10	*o*-$Cl_2C_6H_4$, 120 °C	0.08	6.12
10	*o*-$Cl_2C_6H_4$, 140 °C	0.37	1.28
23	*o*-$Cl_2C_6H_4$, 120 °C	0.13	3.88
23	*o*-$Cl_2C_6H_4$, 135 °C	0.41	1.02

DE ring system

Compd	Conditions	t (h)	(*P*)/(*M*)
33	*o*-$Cl_2C_6H_4$, 120 °C	0.0	100 : 0
		0.5	94 : 6
		1.0	91 : 9
		2.0	81 : 19
		4.5	76 : 24
33	*o*-$Cl_2C_6H_4$, 140 °C	0.0	100 : 0
		0.17	93 : 7
		0.42	88 : 12
		1.2	72 : 28
		1.5	68 : 32
		1.8	64 : 36

for **33** (*o*-$Cl_2C_6H_4$): E_a = 24.8 kcal/mol, $\Delta H^‡$ = 24.7 kcal/mol, $\Delta S^‡$ = -2.3 eu, $\Delta G^‡$(120 °C) = 25.6 kcal/mol

Compd	Conditions	k (h^{-1})	$t_{1/2}$ (h)
33	*o*-$Cl_2C_6H_4$, 120 °C	0.052	5.0
33	*o*-$Cl_2C_6H_4$, 140 °C	0.24	1.1

AB ring system

Compd	Conditions	t (h)	(*S*)/(*R*)
13	*o*-$Cl_2C_6H_4$, 140 °C	0.0	100 : 0
		1.5	92 : 8
		11.5	69 : 31
		16.7	60 : 40
		20.0	56 : 44
		24.8	46 : 54
13	*o*-$Cl_2C_6H_4$, 150 °C	0.0	100 : 0
		1.5	82 : 18
		2.3	68 : 32
		3.2	64 : 36
		4.2	62 : 38
		5.2	57 : 43

for **13** (*o*-$Cl_2C_6H_4$): E_a = 37.8 kcal/mol, $\Delta H^‡$ = 35.2 kcal/mol, $\Delta S^‡$ = –19.1 eu, $\Delta G^‡$(130 °C) = 42.9 kcal/mol

Compd	Conditions	k (h^{-1})	$t_{1/2}$ (h)
13	*o*-$Cl_2C_6H_4$, 140 °C	0.029	10.9
13	*o*-$Cl_2C_6H_4$, 150 °C	0.087	3.66

The data and thermodynamic parameters for **21**,[16] **22**,[16] and **35**[21] have been disclosed in prior efforts.