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Supplementary Material

Thermal Atropisomerism of Aglucovancomycin Derivatives: Preparation of (*M,M,M*)- and (*P,M,M*)-Aglucovancomycin

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(*M,M,M*)-2: natural atropisomer configuration; $[\alpha]_D^{25} +61$ (*c* 0.20, CH₃OH); ¹H NMR (CD₃OD, 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, C₆⁷-H), 6.40 (d, *J* = 2.2 Hz, 1H, C_{4b}⁷-H), 6.03 (br s, 1H, C₂⁴-H), 5.95 (br s, 1H, C_{4b}⁴-H), 5.34 (s, 1H, C₂⁶-H), 5.33 (d, *J* = 1.6 Hz, 1H, C_{4a}⁴-H), 5.24 (d, *J* = 2.8 Hz, 1H, C₃²-H), 4.79–4.82 (d, 1H, C₂²-H obscured by H₂O), 4.74 (s, 1H, C₂⁵-H), 4.68 (s, 1H, C₂⁷-H), 4.25 (br dd, *J* = 8.4 Hz, 1H, C₂³-H), 4.16 (s, 1H, C₂⁶-H), 3.98 (m, 1H, C₂¹-H), 2.96 (br dd, *J* = 15.5 Hz, 1H, C₃³-H), 2.76 (s, 3H, NCH₃), 2.04–1.93 (br m, 1H, C₃³-H), 1.88–1.80 (br m, 1H, C₃¹-H₂), 1.69–1.56 (br m, 2H, C₄¹-H and C₃¹-H₂), 0.97–0.81 (br m, 6H, C_{5a}¹-H₃ and C_{5b}¹-H₃); ¹³C NMR (CD₃OD, 297 K, 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, C₅₃H₅₂N₈O₁₇Cl₂ requires 1143.2906).

nOe enhancements (¹H–¹H ROESY NMR, CD₃OD, 313 K, 600 MHz) diagnostic: C_{5a}⁶-H (7.63)/C₃⁶-H (5.34) (s), C_{5a}⁶-H (7.63)/C₂⁶-H (4.16) (s), C_{6b}⁶-H (7.77)/C_{4a}⁴-H (5.33) (s), C₂⁶-H (4.16)/C₂⁵-H (4.74) (s), C₂⁶-H (4.16)/C_{4a}⁵-H (7.06) (s), C₂⁴-H (6.03)/C_{4a}⁴-H (5.33) (w), C₃²-H (5.24)/C_{5a}²-H (7.71) (s), C₃²-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), C₃⁶-H (5.34)/C₂⁶-H (4.16) (s), C_{4b}⁷-H (6.40)/C₂⁷-H (4.68) (w), C_{4a}⁵-H (7.06)/C₂⁵-H (4.74) (s), C_{4b}⁵-H (6.65)/C₂⁵-H (4.74) (w), C₃³-H (2.96)/C₃³-H (2.04–1.93) (m), C₃¹-H (1.88–1.80)/C₃¹-H (1.69–1.56) (m), C₂¹-H (3.98)/NCH₃ (2.76) (m), C_{5b}²-H (7.54)/C_{6b}²-H (7.15) (s).

(*P,M,M*)-2: unnatural atropisomer configuration; $[\alpha]_D^{25} +24$ (*c* 0.05, CH₃OH); ¹H NMR (CD₃OD, 313 K, 600 MHz) δ 7.76 (br d, *J* = 8.3 Hz, 1H, C_{6b}⁶-H), 7.67 (d, *J* = 1.3 Hz, 1H, C_{5a}⁶-H), 7.65 (d, *J* = 1.3 Hz, 1H, C_{5a}²-H), 7.44 (m, *J* = 7.9 Hz, 1H, C_{5b}²-H), 7.37 (br d, *J* = 8.3 Hz, 1H, C_{5b}⁶-H), 7.06 (d, *J* = 0.9 Hz, 1H, C_{4a}⁵-H), 6.90–6.80 (br m, 1H, C_{6b}²-H), 6.76–6.72 (br dm, 1H, C_{4b}⁵-H), 6.69 (d, *J* = 8.3 Hz, 1H, C_{5b}⁵-H), 6.43 (d, *J* = 2.1 Hz, 1H, C₆⁷-H), 6.40 (d, *J* = 2.1 Hz, 1H, C_{4b}⁷-H), 6.03 (br s, 1H, C₂⁴-H), 5.89 (s, 1H, C_{4b}⁴-H), 5.41 (s, 2H, C_{4a}⁴-H and C₃⁶-H), 5.31 (d, *J* = 3.0 Hz, 1H, C₃²-H), 4.97–4.82 (d, *J* = 3.0 Hz, 1H, C₂²-H obscured by H₂O), 4.82 (s, 1H, C₂⁵-H), 4.72 (s, 1H, C₂⁷-H), 4.23 (br d, *J* = 9.4 Hz, 1H, C₂³-H), 4.19 (s, 1H, C₂⁶-H), 3.95 (br m, 1H, C₂¹-H), 2.90 (d, *J* = 16.0 Hz, 1H, C₃³-H), 2.74 (s, 3H, NCH₃), 2.05–1.98 (m, 1H, C₃³-H), 1.88–1.78 (m, 1H, C₃¹-H₂), 1.70–1.55 (m, 2H, C₄¹-H and C₃¹-H₂), 0.91 (d, *J* = 6.0 Hz, 3H, C_{5a}¹-H), 0.84 (d, *J* = 6.0 Hz, 3H, C_{5b}¹-H₃); IR (film) ν_{\max} 3292, 1667, 1513, 1482, 1426, 1200, 1133 cm⁻¹; FABHRMS (NBA–CsI) *m/z* 1143.2924 (M⁺ + H, C₅₃H₅₂N₈O₁₇Cl₂ requires 1143.2906).

nOe enhancements (¹H–¹H ROESY NMR, CD₃OD, 313 K, 600 MHz) diagnostic: C_{5a}⁶-H (7.67)/C₃⁶-H (5.41) (s), C_{5a}⁶-H (7.67)/C₂⁶-H (4.19) (s), C₂⁶-H (4.19)/C₂⁵-H (4.82) (s), C₂⁶-H (4.19)/C_{4a}⁵-H (7.06) (s), C₃²-H (5.31)/C_{5b}²-H

(7.44) (s); additional: C_{5b}⁶-H (7.37)/C_{6b}⁶-H (7.76) (s), C₃⁶-H (5.41)/C₂⁶-H (4.19) (s), C_{4a}⁵-H (7.06)/C₂⁵-H (4.82) (s).

(*M,M,M*)-3: more polar isomer, $R_f = 0.20$ (SiO₂, 5% CH₃OH-CHCl₃), natural atropisomer configuration; $[\alpha]_D^{25} +44$ (c 0.16, CH₃OH); ¹H NMR (CD₃OD, 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, C₆⁷-H), 6.33 (d, $J = 2.2$ Hz, 1H, C_{4a}⁷-H), 5.88 (br s, 1H, C₂⁴-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, C₃²-H), 5.29 (s, 1H, C₃⁶-H), 4.96–4.88 (br m, 1H, C₂²-H), 4.89–4.83 (br m, 1H, C₂¹-H), 4.84–4.77 (br m, 1H, C₂³-H), 4.75 (s, 1H, C₂⁷-H), 4.60 (s, 1H, C₂⁵-H), 4.14 (s, 3H, C₆⁴-OCH₃), 4.11 (d, $J = 1.8$ Hz, 1H, C₂⁶-H), 3.84 (s, 3H, C_{5b}⁷-OCH₃), 3.80 (s, 3H, CO₂CH₃), 3.70 (s, 3H, C₆⁵-OCH₃), 3.66 (s, 3H, C_{5a}⁷-OCH₃), 2.81 (br s, 3H, NCH₃), 2.70–2.59 (br m, 1H, C₃³-H), 2.40–2.36 (br m, 1H, C₃³-H), 1.81–1.72 (br m, 1H, C₃¹-H₂), 1.56–1.45 (m, 2H, C₄¹-H, and C₃¹-H₂ obscured by BOC), 1.50 (s, 9H, BOC), 0.99–0.92 (br m, 3H, C_{5a}¹-H₃), 0.93–0.85 (br m, 3H, C_{5b}¹-H₃); ¹³C NMR (acetone-*d*₆, 297 K, 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, C₆₃H₇₀N₈O₁₉Cl₂ requires 1445.3189).

nOe enhancements (¹H-¹H ROESY NMR, CD₃OD, 313 K, 600 MHz) diagnostic: C_{5a}⁶-H (7.59)/C₃⁶-H (5.29) (s), C_{5a}⁶-H (7.59)/C₂⁶-H (4.11) (s), C_{5a}⁶-H (7.59)/C₂⁵-H (4.60) (w), C₂⁵-H (4.60)/C_{4a}⁴-H (5.44–5.36) (m), C₂⁶-H (4.11)/C₂⁵-H (4.60) (s), C₂⁶-H (4.11)/C_{4a}⁵-H (7.01) (s), C₂⁷-H (4.75)/C_{4a}⁵-H (7.01) (m), C₂²-H (4.96–4.88)/C_{5a}²-H (7.48–7.39) (m), C₃²-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: C₃⁶-H (5.29)/C₂⁶-H (4.11) (s), C_{4b}⁷-H (6.33)/CO₂CH₃ (3.80) (w), C_{4b}⁷-H (6.33)/C₂⁷-H (4.75) (m), C_{4b}⁷-H (6.33)/C_{5b}⁷-OCH₃ (3.84) (s), C_{5b}⁷-OCH₃ (3.84)/C₆⁷-H (6.67) (s), C₆⁷-H (6.67)/C_{5a}⁷-OCH₃ (3.66) (s), C₆⁵-OCH₃ (3.70)/C_{5b}⁵-H (6.96) (s), C_{4a}⁵-H (7.01)/C₂⁵-H (4.60) (s), C₃³-H (2.70–2.59)/C₃³-H (2.40–2.36) (m), C_{5b}²-H (7.74–7.65)/C_{6b}²-H (7.25) (s), C_{5a}¹-H₃ (0.99–0.92)/C₄¹-H (1.56–1.45) (m), C_{5b}¹-H₃ (0.93–0.85)/C₄¹-H (1.56–1.45) (m), C_{5a}¹-H₃ (0.99–0.92)/C₃¹-H₂ (1.81–1.72) (m), C_{5b}¹-H₃ (0.93–0.85)/C₃¹-H₂ (1.81–1.72) (m), C_{5a}¹-H₃ (0.99–0.92)/C₂¹-H (4.89–4.83) (w), C_{5b}¹-H₃ (0.93–0.85)/C₂¹-H (4.89–4.83) (w), C₃¹-H₂ (1.56–1.45)/C₂¹-H (4.89–4.83) (w), C₃¹-H₂ (1.81–1.72)/C₂¹-H (4.89–4.83) (w), C₃¹-H₂ (1.56–1.45)/NCH₃ (2.81) (m), C₃¹-H₂ (1.81–1.72)/NCH₃ (2.81) (m).

(*P,M,M*)-3: less polar isomer, $R_f = 0.24$ (SiO₂, 5% CH₃OH-CHCl₃), unnatural atropisomer configuration; $[\alpha]_D^{25} +14$ (c 0.31, CH₃OH); ¹H NMR (CD₃OD, 313 K, 600 MHz) δ 7.90–7.80 (br m, 1H, C_{5a}²-H), 7.63 (br s, 1H, C_{5a}⁶-H), 7.56 (br dd, $J \approx 6.0$ Hz, 1H, C_{5b}⁶-H), 7.35–7.27 (br m, 1H, C_{5b}²-H or C_{6b}²-H or C_{6b}⁶-H), 7.25–7.15 (br m, 1H, C_{5b}²-H or C_{6b}²-H or C_{6b}⁶-H), 7.15–7.06 (br m, 1H, C_{5b}²-H or C_{6b}²-H or C_{6b}⁶-H), 7.10 (dd, $J = 8.7, 2.4$ Hz, 1H, C_{4b}⁵-H), 7.01 (d, $J = 2.3$ Hz, 1H, C_{4a}⁵-H), 6.95 (d, $J = 8.8$ Hz, 1H, C_{5b}⁵-H), 6.67 (d, $J = 2.2$ Hz, 1H, C₆⁷-H), 6.33 (d, $J = 2.2$ Hz, 1H, C_{4a}⁷-H), 5.90–5.79 (br s, 1H, C₂⁴-H), 5.72 (br s, 1H, C_{4b}⁴-H), 5.40–5.25 (two br m, 2H, C_{4a}⁴-H and C₃²-H, obscured by C₃⁶-H), 5.31 (s, 1H, C₃⁶-H), 4.98–4.83 (br m, 1H, C₂²-H), 4.86–4.80 (br m, 1H, C₂¹-H), 4.81–4.76 (br m, 1H, C₂³-H), 4.74 (s, 1H, C₂⁷-H), 4.62 (s, 1H, C₂⁵-H), 4.16 (s, 3H, C₆⁴-OCH₃), 4.12 (d, $J = 1.2$ Hz, 1H, C₂⁶-H), 3.84 (s, 3H, C_{5b}⁷-OCH₃), 3.80 (s, 3H, CO₂CH₃), 3.69 (s, 3H, C₆⁵-OCH₃), 3.66 (s, 3H, C_{5a}⁷-OCH₃), 2.83 (br s, 3H, NCH₃), 2.76–2.65 (br m, 1H, C₃³-H), 2.35–2.22 (br m, 1H, C₃³-H), 1.79–1.72 (m, 1H, C₃¹-H₂), 1.55–1.45 (m, 2H, C₄¹-H and C₃¹-H₂, obscured by BOC), 1.52 (s, 9H, BOC), 0.96 (d, $J = 6.4$ Hz, 3H, C_{5a}¹-H₃), 0.96–0.87 (br m, 3H, C_{5b}¹-H₃); IR (film) ν_{\max} 3327, 2926, 2854, 1683, 1652, 1506, 1489, 1418, 1255, 1231, 1158, 1108, 1056, 1020 cm⁻¹; FABHRMS (NBA-CsI) m/z 1445.3285 (M⁺ + Cs, C₆₃H₇₀N₈O₁₉Cl₂ requires 1445.3189).

(*M,M,M*)-4: natural atropisomer configuration; $[\alpha]_D^{25} -82$ (c 0.06, CH₃OH); ¹H NMR (CD₃OD, 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, C₆⁷-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, C₂⁴-H), 5.76 (s, 1H, C_{4b}⁴-H), 5.55 (d, *J* = 4.4 Hz, 1H, C₃²-H), 5.45 (s, 1H, C_{4a}⁴-H), 5.36 (s, 1H, C₃⁶-H), 5.02 (br m, 1H, C₂²-H), 4.97–4.90 (br m, 2H, C₂³-H and C₂¹-H), 4.82 (s, 1H, C₂⁷-H), 4.59 (s, 1H, C₂⁵-H), 4.22 (s, 3H, C₆⁴-OCH₃), 4.07 (m, 1H, C₂⁶-H), 3.84 (s, 3H, C_{5b}⁷-OCH₃), 3.79 (s, 3H, CO₂CH₃), 3.71 (s, 3H, C₆⁵-OCH₃), 3.66 (s, 3H, C_{5a}⁷-OCH₃), 2.84 (s, 3H, NCH₃), 2.62 (br dd, 1H, C₃³-H), 2.41 (br dd, *J* = 12.6 Hz, 1H, C₃³-H), 1.82 (br m, 1H, C₃¹-H₂), 1.51 (s, 9H, BOC), 1.50–1.40 (br m, 2H, C₄¹-H and C₃¹-H₂), 0.96 (s, 9H, SiC(CH₃)₃), 0.95 (d, 3H, C_{5a}¹-H₃, partially obscured by BOC), 0.93 (d, *J* = 6.0 Hz, 3H, C_{5b}¹-H₃), 0.89 (s, 9H, SiC(CH₃)₃), 0.13 (s, 3H, SiCH₃), 0.12 (s, 6H, SiCH₃), 0.11 (s, 3H, SiCH₃), 0.09 (s, 3H, SiCH₃); ¹³C NMR (acetone-*d*₆, 297 K, 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, C₇₅H₉₈N₈O₁₉Cl₂Si₂ requires 1673.4918).

nOe enhancements (¹H-¹H ROESY NMR, CD₃OD, 313 K, 600 MHz) diagnostic: C_{5a}⁶-H (7.46)/C₃⁶-H (5.36) (s), C_{5a}⁶-H (7.46)/C₂⁶-H (4.07) (s), C_{5a}⁶-H (7.46)/C₂⁵-H (4.59) (w), C_{6b}⁶-H (6.32)/C_{4a}⁴-H (5.45) (w), C₃⁶-H (5.36)/C₂⁵-H (4.59) (w), C₂⁶-H (4.07)/C₂⁵-H (4.59) (s), C₂⁶-H (4.07)/C_{4a}⁵-H (7.03–6.99) (s), C₂⁵-H (4.59)/C_{4a}⁴-H (5.45) (m), C₃²-H (5.55)/C_{5a}²-H (7.33–7.29) (s), C₃²-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: C₃⁶-H (5.36)/C₂⁶-H (4.07) (s), C_{4b}⁷-H (6.37)/CO₂CH₃ (3.79) (m), CO₂CH₃ (3.79)/C₂⁷-H (4.82) (w), C_{4b}⁷-H (6.37)/C_{5b}⁷-OCH₃ (3.84) (m), C_{5b}⁷-OCH₃ (3.84)/C₆⁷-H (6.68) (m), C₆⁷-H (6.68)/C_{5a}⁷-OCH₃ (3.66) (s), C₆⁵-OCH₃ (3.71)/C_{5b}⁵-H (7.03–6.99) (s), C_{4a}⁵-H (7.03–6.99)/C₂⁵-H (4.59) (s), C₃³-H (2.62)/C₃³-H (2.41) (s), C₃³-H (2.62)/C₂³-H (4.97–4.90) (m), C₃³-H (2.41)/C₂³-H (4.97–4.90) (m), C₂²-H (5.02)/C₃²-H (5.55) (s), C_{5b}²-H (7.71)/C_{6b}²-H (7.33–7.27) (s), C_{5a}¹-H₃ (0.95)/C₄¹-H (1.50–1.40) (m), C_{5b}¹-H₃ (0.93)/C₄¹-H (1.50–1.40) (m), C₄¹-H (1.50–1.40)/C₃¹-H₂ (1.82) (m), C₃¹-H₂ (1.50–1.40)/C₂¹-H (4.97–4.90) (w), C₃¹-H₂ (1.50–1.40)/NCH₃ (2.84) (m), C₃¹-H₂ (1.82)/NCH₃ (2.84) (m).

(*P,M,M*)-4: unnatural atropisomer configuration; [α]_D²⁵ -16 (c 0.14, CH₃OH), ¹H NMR (CD₃OD, 313 K, 600 MHz) δ 7.87 (br m, 1H, C_{5a}²-H), 7.53 (m, 1H, C_{5a}⁶-H), 7.44 (dm, *J* = 9.1 Hz, 1H, C_{5b}⁶-H), 7.23–7.17 (br m, 2H, C_{5b}²-H and C_{6b}²-H), 7.10 (dd, *J* = 9.0, 2.4 Hz, 1H, C_{4b}⁵-H), 7.04–6.96 (m, 2H, C_{4a}⁵-H and C_{5b}⁵-H), 6.68 (m, 1H, C₆⁷-H), 6.36 (d, *J* = 2.1 Hz, 1H, C_{4b}⁷-H), 6.29 (br m, 1H, C_{6b}⁶-H), 6.16 (br s, 1H, C₂⁴-H), 5.83 (m, 1H, C_{4b}⁴-H), 5.56 (d, *J* = 4.9 Hz, 1H, C₃²-H), 5.43 (s, 1H, C_{4a}⁴-H), 5.36 (d, *J* = 5.8 Hz, 1H, C₃⁶-H), 5.00–4.95 (br m, 1H, C₂²-H), 4.96–4.86 (br m, 2H, C₂³-H and C₂¹-H), 4.80 (s, 1H, C₂⁷-H), 4.60 (s, 1H, C₂⁵-H), 4.23 (s, 3H, C₆⁴-OCH₃), 4.09 (m, 1H, C₂⁶-H), 3.86 (s, 3H, C_{5b}⁷-OCH₃), 3.79 (s, 3H, CO₂CH₃), 3.71 (s, 3H, C₆⁵-OCH₃), 3.67 (s, 3H, C_{5a}⁷-OCH₃), 2.82 (br s, 3H, NCH₃), 2.66–2.54 (br m, 1H, C₃³-H), 2.40 (dd, *J* = 15.6, 5.4 Hz, 1H, C₃³-H), 1.86–1.75 (m, 1H, C₃¹-H₂), 1.54 (s, 9H, BOC), 1.48–1.40 (br m, 2H, C₄¹-H and C₃¹-H₂), 0.95 (s, 9H, SiC(CH₃)₃), 0.94–0.91 (br m, 3H, C_{5a}¹-H₃), 0.89 (s, 9H, SiC(CH₃)₃), 0.91–0.87 (m, 3H, C_{5b}¹-H₃, obscured by SiC(CH₃)₃), 0.13 (s, 3H, SiCH₃), 0.12 (s, 3H, SiCH₃), 0.11 (s, 3H, SiCH₃), 0.10 (s, 3H, SiCH₃); IR (film) ν_{max} 3300, 2963, 2927, 1651, 1505, 1489, 1418, 1395, 1323, 1231, 1156, 1059, 1023 cm⁻¹; FABHRMS (NBA–CsI) *m/z* 1673.4820 (M⁺ + Cs, C₇₅H₉₈N₈O₁₉Cl₂Si₂ requires 1673.4918).

nOe enhancements (¹H-¹H ROESY NMR, CD₃OD, 313 K, 600 MHz) diagnostic: C_{5a}⁶-H (7.53)/C₃⁶-H (5.36) (s), C_{5a}⁶-H (7.53)/C₃⁶-H (4.09) (s), C₂⁶-H (4.09)/C₂⁵-H (4.60) (s), C₂⁶-H (4.09)/C_{4a}⁵-H (7.04–6.96) (s), C₂⁵-H (4.60)/C_{4a}⁴-H (5.43) (s), C₃²-H (5.56)/C_{5b}³-H (7.23–7.17) (s), C₃²-H (5.56)/C_{5a}³-H (7.87) (w), C_{6b}²-H (7.23–7.17)/C_{4b}⁴-H (5.83) (m); additional: C₃⁶-H (5.36)/C₂⁶-H (4.09) (s), C₂⁵-H (4.60)/C_{4a}⁵-H (7.04–6.96) (s), C₂⁵-H (4.60)/C_{4a}⁴-H (7.10) (w), C_{4b}⁷-H (6.36)/CO₂CH₃ (3.79) (m), CO₂CH₃ (3.79)/C₂⁷-H (4.80) (w), C₂⁷-H (4.80)/C_{4a}⁵-H (7.04–6.96) (w), C_{4b}⁷-H (6.36)/C_{5b}⁷-OCH₃ (3.86) (s), C_{5b}⁷-OCH₃ (3.86)/C₆⁷-H (6.68) (s), C₆⁷-H (6.68)/C_{5a}⁷-OCH₃ (3.67) (s), C₆⁵-

OCH₃ (3.71)/C_{5b}⁵-H (7.04–6.96) (s), C₆⁵-OCH₃ (3.71)/C_{4b}⁵-H (7.10) (m), C₃³-H (2.40)/C₃³-H (2.66–2.54) (s), C₃³-H (2.66–2.54)/C₂³-H (4.96–4.86) (w), C₃³-H (2.40)/C₂³-H (4.96–4.86) (w), C₂²-H (5.00–4.95)/C₃²-H (5.56) (s), C_{5a}¹-H₃ (0.94–0.91)/C₄¹-H (1.48–1.40) (m), C_{5b}¹-H₃ (0.91–0.87)/C₄¹-H (1.48–1.40) (m), C_{5b}¹-H₃ (0.91–0.87)/C₃¹-H₂ (1.86–1.75) (m), C_{5b}¹-H₃ (0.91–0.87)/C₂¹-H (4.96–4.86) (m), C₄¹-H (1.48–1.40)/C₃¹-H₂ (1.86–1.75) (s), C₃¹-H₂ (1.86–1.75)/NCH₃ (2.82) (m), C₃¹-H₂ (1.86–1.75)/C₂¹-H (4.96–4.86) (w), C₂¹-H (4.96–4.86)/NCH₃ (2.82) (w).

(*M,M,M*)-5: white solid; [α]_D²⁵ –15 (c 0.70, CH₃OH); ¹H NMR (CD₃OD, 313 K, 600 MHz) δ 7.77 (br m, 1H, C_{5b}²-H), 7.53–7.47 (m, 2H, C_{5a}⁶-H and C_{5b}⁶-H), 7.36 (br m, 1H, C_{5a}²-H), 7.29 (d, *J* = 8.2 Hz, 1H, C_{6b}²-H), 7.09 (d, *J* = 8.6 Hz, 1H, C_{4b}⁵-H), 7.02–6.97 (m, 2H, C_{5b}⁵-H and C_{4a}⁵-H), 6.68 (d, *J* = 2.1 Hz, 1H, C₆⁷-H), 6.36 (d, *J* = 2.1 Hz, 1H, C_{4b}⁷-H), 6.26 (br m, 2H, C_{6b}⁶ and C₂⁴-H), 5.76 (s, 1H, C_{4b}⁴-H), 5.43 (br s, 1H, C_{4a}⁴-H), 5.41–5.35 (m, 2H, C₃²-H and C₃⁶-H), 4.95–4.80 (br m, 3H, C₂¹-H, C₂²-H and C₂³-H), 4.82 (s, 1H, C₂⁷-H), 4.59 (s, 1H, C₂⁵-H), 4.20 (s, 3H, C₆⁴-OCH₃), 4.08 (m, 1H, C₂⁶-H), 3.85 (s, 3H, C_{5b}⁷-OCH₃), 3.79 (s, 3H, CO₂CH₃), 3.72 (s, 3H, C₆⁵-OCH₃), 3.67 (s, 3H, C_{5a}⁷-OCH₃), 2.81 (br s, 3H, NCH₃), 2.64 (br dd, 1H, C₃³-H), 2.43 (dd, *J* = 16.2, 6.0 Hz, 1H, C₃³-H), 1.76 (br m, 1H, C₃¹-H₂), 1.52 (s, 9H, BOC), 1.60–1.40 (m, 2H, C₄¹-H and C₃¹-H₂, obscured by BOC), 0.95 (s, 9H, SiC(CH₃)₃), 0.97–0.82 (m, 6H, C_{5a}¹-H₃, and C_{5b}¹-H₃, obscured by , SiC(CH₃)₃), 0.112 (s, 3H, SiCH₃), 0.109 (s, 3H, SiCH₃); IR (film) ν_{\max} 3292, 2960, 2941, 2860, 1690, 1650, 1512, 1490, 1223, 1160, 1110 cm⁻¹; FABHRMS (NBA–CsI) *m/z* 1559.4169 (M⁺ + Cs, C₆₉H₈₄N₈O₁₉Cl₂Si requires 1559.4053).

nOe enhancements (¹H-¹H ROESY NMR, CD₃OD, 313 K, 600 MHz) diagnostic: C_{5a}⁶-H (7.53–7.47)/C₃⁶-H (5.41–5.35) (s), C_{5a}⁶-H (7.53–7.47)/C₂⁶-H (4.08) (m), C₂⁶-H (4.08)/C₂⁵-H (4.59) (s), C₂⁶-H (4.08)/C_{4a}⁵-H (7.02–6.97) (s), C₂⁵-H (4.59)/C_{4a}⁴-H (5.43) (s), C₂⁷-H (4.82)/C_{4a}⁵-H (7.02–6.97) (w), C₃²-H (5.41–5.35)/C_{5a}²-H (7.36) (s), C₂²-H (4.95–4.80)/C_{5a}²-H (7.36) (w), C_{6b}²-H (7.29)/C_{4b}⁴-H (5.76) (w); additional: C₃⁶-H (5.41–5.35)/C₂⁶-H (4.08) (s), SiCH₃ (0.11)/SiC(CH₃)₃ (0.95) (m), SiCH₃ (0.11)/CO₂CH₃ (3.79) (w), SiCH₃ (0.11)/C₃⁶-H (5.41–5.35) (m), C_{4b}⁷-H (6.36)/CO₂CH₃ (3.79) (s), C_{4b}⁷-H (6.36)/C₂⁷-H (4.82) (w), C_{4b}⁷-H (6.36)/C_{5b}⁷-OCH₃ (3.85) (s), C_{5b}⁷-OCH₃ (3.85)/C₆⁷-H (6.68) (s), C₆⁷-H (6.68)/C_{5a}⁷-OCH₃ (3.67) (s), C₆⁵-OCH₃ (3.72)/C_{5b}⁵-H (7.02–6.97) (s), C_{4a}⁵-H (7.02–6.97)/C₂⁵-H (4.59) (s), C_{4b}⁵-H (7.09)/C₂⁵-H (4.59) (w), C₃³-H (2.63)/C₃³-H (2.43) (m), C₃³-H (2.43)/C₂³-H (4.95–4.80) (w), C_{5b}²-H (7.77)/C_{6b}²-H (7.29) (s), C₅¹-H₃ (0.97–0.82)/C₄¹-H (1.49) (m), C₅¹-H₃ (0.97–0.82)/C₃¹-H₂ (1.76) (m), C₅¹-H₃ (0.97–0.82)/C₂¹-H (4.95–4.80) (m), C₃¹-H₂ (1.49)/C₂¹-H (4.95–4.80) (w), C₃¹-H₂ (1.50–1.40)/NCH₃ (2.81) (w), C₃¹-H₂ (1.76)/NCH₃ (2.81) (w), C₃¹-H₂ (1.76)/C₂¹-H (4.95–4.80) (w), C₂¹-H (4.95–4.80)/NCH₃ (2.81) (w).

(*M,M,M*)-6: less polar isomer, *R*_f = 0.34 (SiO₂, 3% CH₃OH–CHCl₃), natural atropisomer configuration; [α]_D²⁵ –12 (c 0.18, CH₃OH); ¹H NMR (CD₃OD, 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, C₆⁷-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, C₂⁴-H), 5.72 (dd, *J* = 2.4, 1.2 Hz, 1H, C_{4b}⁴-H), 5.57 (d, *J* = 4.6 Hz, 1H, C₃²-H), 5.47 (dd, *J* = 1.8, 0.6 Hz, 1H, C_{4a}⁴-H), 5.36 (d, *J* = 1.2 Hz, 1H, C₃⁶-H), 5.23–5.16 (br m, 1H, C₂³-H), 5.07–5.02 (br m, 1H, C₂²-H), 4.91–4.85 (br m, 1H, C₂¹-H), 4.81 (s, 1H, C₂⁷-H), 4.61 (s, 1H, C₂⁵-H), 4.22 (s, 3H, C₆⁴-OCH₃), 4.07 (m, 1H, C₂⁶-H), 3.84 (s, 3H, C_{5b}⁷-OCH₃), 3.79 (s, 3H, CO₂CH₃), 3.72 (s, 3H, C₆⁵-OCH₃), 3.64 (s, 3H, C_{5a}⁷-OCH₃), 2.93 (dd, *J* = 17.5, 4.6 Hz, 1H, C₃³-H), 2.83 (s, 3H, NCH₃), 2.61 (dd, *J* = 17.5, 8.4 Hz, 1H, C₃³-H), 1.92–1.84 (br m, 1H, C₃¹-H₂), 1.53 (s, 9H, BOC), 1.50–1.39 (br m, 2H, C₄¹-H and C₃¹-H₂), 0.99 (s, 9H, C₃⁶-OSiC(CH₃)₃), 0.94 (d, *J* = 6.4 Hz, 3H, C_{5a}¹-H₃), 0.90 (s, 9H, C₃²-OSiC(CH₃)₃), 0.88 (br d, *J* = 6.6 Hz, 3H, C_{5b}¹-H₃), 0.134 (s, 3H, C₃²-OSiCH₃), 0.125 (s, 6H, C₃²-OSiCH₃ and C₃⁶-OSiCH₃), 0.10 (s, 3H, C₃⁶-OSiCH₃); ¹³C NMR (CD₃OD, 296 K, 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, $\text{C}_{75}\text{H}_{96}\text{N}_8\text{O}_{18}\text{Cl}_2\text{Si}_2$ requires 1655.4813).

nOe enhancements (^1H - ^1H ROESY NMR, CD_3OD , 313 K, 600 MHz) diagnostic: $\text{C}_{5a}^6\text{-H}$ (7.47)/ $\text{C}_3^6\text{-H}$ (5.36) (s), $\text{C}_{5a}^6\text{-H}$ (7.47)/ $\text{C}_2^6\text{-H}$ (4.07) (m), $\text{C}_2^6\text{-H}$ (4.07)/ $\text{C}_2^5\text{-H}$ (4.61) (s), $\text{C}_2^6\text{-H}$ (4.07)/ $\text{C}_{4a}^5\text{-H}$ (7.00) (s), $\text{C}_2^5\text{-H}$ (4.61)/ $\text{C}_{4a}^5\text{-H}$ (5.47) (m), $\text{C}_3^2\text{-H}$ (5.57)/ $\text{C}_{5a}^2\text{-H}$ (7.29-7.25) (m), $\text{C}_3^2\text{-H}$ (5.57)/ $\text{C}_{5b}^2\text{-H}$ (7.71-7.65) (w), $\text{C}_2^2\text{-H}$ (5.07-5.02)/ $\text{C}_{5a}^2\text{-H}$ (7.29-7.25) (w), $\text{C}_{6b}^2\text{-H}$ (7.31)/ $\text{C}_{4b}^4\text{-H}$ (5.71) (w), BOC (1.65)/ $\text{C}_{5b}^2\text{-H}$ (7.71-7.65) (w), BOC (1.65)/ $\text{C}_{6b}^2\text{-H}$ (7.31) (w), additional: $\text{C}_3^6\text{-H}$ (5.36)/ $\text{C}_2^6\text{-H}$ (4.07) (s), $\text{C}_3^6\text{-OSiCH}_3$ (0.10)/ $\text{C}_3^6\text{-H}$ (5.36) (w), $\text{C}_3^6\text{-OSiC}(\text{CH}_3)_3$ (0.99)/ $\text{C}_3^6\text{-OSiCH}_3$ (0.10) (m), $\text{C}_3^6\text{-OSiC}(\text{CH}_3)_3$ (0.99)/ $\text{C}_3^6\text{-OSiCH}_3$ (0.125) (m), $\text{C}_{4b}^7\text{-H}$ (6.36)/ $\text{C}_2^7\text{-H}$ (4.81) (w), $\text{C}_{4b}^7\text{-H}$ (6.36)/ $\text{C}_{5b}^7\text{-OCH}_3$ (3.84) (m), $\text{C}_{5b}^7\text{-OCH}_3$ (3.84)/ $\text{C}_6^7\text{-H}$ (6.67) (m), $\text{C}_6^7\text{-H}$ (6.67)/ $\text{C}_{5a}^7\text{-OCH}_3$ (3.64) (s), $\text{C}_6^5\text{-OCH}_3$ (3.72)/ $\text{C}_{5b}^5\text{-H}$ (7.03) (m), $\text{C}_{4a}^5\text{-H}$ (7.00)/ $\text{C}_2^5\text{-H}$ (4.61) (s), $\text{C}_3^3\text{-H}$ (2.93)/ $\text{C}_3^3\text{-H}$ (2.61) (s), $\text{C}_3^3\text{-H}$ (2.93)/ $\text{C}_2^3\text{-H}$ (5.23-5.16) (w), $\text{C}_3^3\text{-H}$ (2.61)/ $\text{C}_2^3\text{-H}$ (5.23-5.16) (w), $\text{C}_2^2\text{-H}$ (5.07-5.02)/ $\text{C}_3^2\text{-H}$ (5.57) (m), $\text{C}_{5b}^2\text{-H}$ (7.71-7.65)/ $\text{C}_{6b}^2\text{-H}$ (7.31) (s), $\text{C}_3^2\text{-OSiC}(\text{CH}_3)_3$ (0.91)/ $\text{C}_3^2\text{-OSiCH}_3$ (0.134) (m), $\text{C}_3^2\text{-OSiC}(\text{CH}_3)_3$ (0.91)/ $\text{C}_3^2\text{-OSiCH}_3$ (0.125) (m), $\text{C}_3^2\text{-H}$ (5.57)/ $\text{C}_3^2\text{-OSiCH}_3$ (0.125) (w), $\text{C}_{5b}^1\text{-H}_3$ (0.88)/ $\text{C}_2^1\text{-H}$ (4.91-4.85) (m), $\text{C}_4^1\text{-H}$ (1.50-1.39)/ $\text{C}_3^1\text{-H}_2$ (1.92-1.84) (s), $\text{C}_4^1\text{-H}$ (1.50-1.39)/ $\text{C}_2^1\text{-H}$ (4.91-4.85) (m), $\text{C}_3^1\text{-H}_2$ (1.50-1.39)/ NCH_3 (2.83) (m), $\text{C}_3^1\text{-H}_2$ (1.92-1.84)/ $\text{C}_2^1\text{-H}$ (4.91-4.85) (w), $\text{C}_3^1\text{-H}_2$ (1.92-1.84)/ NCH_3 (2.83) (s), $\text{C}_2^1\text{-H}$ (4.91-4.85)/ NCH_3 (2.83) (w), NCH_3 (2.83)/BOC (1.53) (m), NCH_3 (2.83)/ $\text{C}_3^2\text{-OSiCH}_3$ (0.125) (m), BOC (1.53)/ $\text{C}_3^2\text{-OSiCH}_3$ (0.125) (m).

(*P,M,M*)-6: more polar isomer, $R_f = 0.29$ (SiO_2 , 3% CH_3OH - CHCl_3), unnatural atropisomer configuration; $[\alpha]_D^{25} -33$ (c 0.16, CH_3OH); ^1H NMR (CD_3OD , 313 K, 600 MHz) δ 7.91-7.83 (br m, 1H, $\text{C}_{5a}^2\text{-H}$), 7.55 (d, 1H, $J = 2.0$ Hz, $\text{C}_{5a}^6\text{-H}$), 7.45 (dd, $J = 8.4, 1.9$ Hz, 1H, $\text{C}_{5b}^6\text{-H}$), 7.23 (d, 1H, $J = 8.2$ Hz, $\text{C}_{6b}^2\text{-H}$), 7.14 (br d, $J = 8.2$ Hz, 1H, $\text{C}_{5b}^2\text{-H}$), 7.10 (dd, $J = 8.7, 2.4$ Hz, 1H, $\text{C}_{4b}^5\text{-H}$), 7.03-6.98 (m, 2H, $\text{C}_{4a}^5\text{-H}$ and $\text{C}_{5b}^5\text{-H}$), 6.67 (d, $J = 2.3$ Hz, 1H, $\text{C}_6^7\text{-H}$), 6.36 (d, $J = 2.3$ Hz, 1H, $\text{C}_{4b}^7\text{-H}$), 6.35-6.30 (br m, 1H, $\text{C}_{5b}^6\text{-H}$), 6.23-6.16 (br s, 1H, $\text{C}_2^4\text{-H}$), 5.77 (dd, $J = 1.8, 0.6$ Hz, 1H, $\text{C}_{4b}^4\text{-H}$), 5.56 (d, $J = 5.0$ Hz, 1H, $\text{C}_3^2\text{-H}$), 5.44 (dd, $J = 2.4, 1.2$ Hz, 1H, $\text{C}_{4a}^4\text{-H}$), 5.37 (s, 1H, $\text{C}_3^6\text{-H}$), 5.07 (br dd, $J = 8.9, 5.4$ Hz, 1H, $\text{C}_2^3\text{-H}$), 4.96 (br s, 1H, $\text{C}_2^2\text{-H}$), 4.91-4.85 (br m, 1H, $\text{C}_2^1\text{-H}$), 4.79 (s, 1H, $\text{C}_2^7\text{-H}$), 4.60 (s, 1H, $\text{C}_2^5\text{-H}$), 4.23 (s, 3H, $\text{C}_6^4\text{-OCH}_3$), 4.10 (d, 1H, $J = 1.9$ Hz, $\text{C}_2^6\text{-H}$), 3.84 (s, 3H, $\text{C}_{5b}^7\text{-OCH}_3$), 3.79 (s, 3H, CO_2CH_3), 3.71 (s, 3H, $\text{C}_6^5\text{-OCH}_3$), 3.65 (s, 3H, $\text{C}_{5a}^7\text{-OCH}_3$), 2.84 (br dd, $J = 17.5, 5.4$ Hz, 1H, $\text{C}_3^3\text{-H}$), 2.80 (br s, 3H, NCH_3), 2.59 (dd, $J = 17.5, 8.9$ Hz, 1H, $\text{C}_3^3\text{-H}$), 1.87-1.79 (m, 1H, $\text{C}_3^1\text{-H}_2$), 1.55 (s, 9H, BOC), 1.45-1.40 (br m, 2H, $\text{C}_4^1\text{-H}$ and $\text{C}_3^1\text{-H}_2$), 0.94 (s, 9H, $\text{C}_3^6\text{-OSiC}(\text{CH}_3)_3$), 0.94 (d, $J = 6.0$ Hz, 3H, $\text{C}_{5a}^1\text{-H}_3$), 0.90 (s, 9H, $\text{C}_3^2\text{-OSiC}(\text{CH}_3)_3$), 0.89-0.86 (br d, 3H, $\text{C}_{5b}^1\text{-H}_3$), 0.13 (s, 6H, two SiCH_3), 0.12 (s, 3H, SiCH_3), 0.10 (s, 3H, SiCH_3); ^{13}C NMR (CD_3OD , 297 K, 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, $\text{C}_{75}\text{H}_{96}\text{N}_8\text{O}_{18}\text{Cl}_2\text{Si}_2$ requires 1655.4813).

nOe enhancements (^1H - ^1H ROESY NMR, CD_3OD , 313 K, 600 MHz) diagnostic: $\text{C}_{5b}^6\text{-H}$ (7.55)/ $\text{C}_3^6\text{-H}$ (5.37) (w), $\text{C}_{5a}^6\text{-H}$ (7.55)/ $\text{C}_3^6\text{-H}$ (5.37) (s), $\text{C}_{5a}^6\text{-H}$ (7.55)/ $\text{C}_2^6\text{-H}$ (4.10) (m), $\text{C}_2^6\text{-H}$ (4.10)/ $\text{C}_2^5\text{-H}$ (4.60) (s), $\text{C}_2^6\text{-H}$ (4.10)/ $\text{C}_{4a}^5\text{-H}$ (7.03-6.98) (s), $\text{C}_2^5\text{-H}$ (4.60)/ $\text{C}_{4a}^5\text{-H}$ (5.44) (m), $\text{C}_3^2\text{-H}$ (5.56)/ $\text{C}_{5b}^3\text{-H}$ (7.14) (s), $\text{C}_{6b}^2\text{-H}$ (7.23)/ $\text{C}_{4b}^4\text{-H}$ (5.77) (m); additional: $\text{C}_3^6\text{-H}$ (5.37)/ $\text{C}_2^6\text{-H}$ (4.10) (s), $\text{C}_2^5\text{-H}$ (4.60)/ $\text{C}_{4a}^5\text{-H}$ (7.03-6.98) (s), $\text{C}_{4b}^7\text{-H}$ (6.36)/ $\text{C}_2^7\text{-H}$ (4.79) (w), $\text{C}_{4b}^7\text{-H}$ (6.36)/ $\text{C}_{5b}^7\text{-OCH}_3$ (3.84) (m), $\text{C}_{4b}^7\text{-H}$ (6.36)/ CO_2CH_3 (3.79) (m), $\text{C}_{5b}^7\text{-OCH}_3$ (3.84)/ $\text{C}_6^7\text{-H}$ (6.67) (s), $\text{C}_6^7\text{-H}$ (6.67)/ $\text{C}_{5a}^7\text{-OCH}_3$ (3.65) (m), $\text{C}_6^5\text{-OCH}_3$ (3.71)/ $\text{C}_{5b}^5\text{-H}$ (7.03-6.98) (m), $\text{C}_3^3\text{-H}$ (2.84)/ $\text{C}_3^3\text{-H}$ (2.80) (s), $\text{C}_3^3\text{-H}$ (2.84)/ $\text{C}_2^3\text{-H}$ (5.07) (m), $\text{C}_3^3\text{-H}$ (2.80)/ $\text{C}_2^3\text{-H}$ (5.07) (w), $\text{C}_2^2\text{-H}$ (4.96)/ $\text{C}_3^2\text{-H}$ (5.56) (s), $\text{C}_{5a}^1\text{-H}_3$ (0.94)/ $\text{C}_4^1\text{-H}$ (1.45-1.40) (m), $\text{C}_{5b}^1\text{-H}_3$ (0.89-0.86)/ $\text{C}_4^1\text{-H}$ (1.45-1.40) (m), $\text{C}_{5b}^1\text{-H}_3$ (0.89-0.86)/ $\text{C}_2^1\text{-H}$ (4.91-4.85) (m), $\text{C}_4^1\text{-H}$

(1.45–1.40)/C₃¹-H₂ (1.87–1.79) (s), C₃¹-H₂ (1.87–1.79)/C₂¹-H (4.91–4.85) (w), C₃¹-H₂ (1.87–1.79)/NCH₃ (2.80) (m), C₂¹-H (4.91–4.85)/NCH₃ (2.80) (w).

(*M,M,M*)-7: less polar isomer, $R_f = 0.60$ (SiO₂, 4% CH₃OH–CHCl₃), natural atropisomer configuration, white solid; $[\alpha]_D^{25} +48$ (c 0.50, CH₃OH); ¹H NMR (CD₃OD, 313 K, 600 MHz) δ 7.68 (d, $J = 2.0$ Hz, 1H), 7.53 (dd, $J = 8.4, 1.8$ Hz, 1H), 7.49 (d, $J = 1.6$ Hz, 1H), 7.42 (dd, $J = 8.0, 2.0$ Hz, 1H), 7.32 (d, $J = 8.3$ Hz, 1H), 7.20 (d, $J = 8.4$ Hz, 1H), 7.00–7.08 (br m, 1H), 6.99 (d, $J = 2.4$ Hz, 1H), 6.94 (d, $J = 8.8$ Hz, 1H), 6.66 (d, $J = 2.2$ Hz, 1H), 6.34 (d, $J = 2.2$ Hz, 1H), 6.03 (s, 1H), 5.38 (s, 1H), 5.38–5.36 (m, 3H), 5.24 (d, $J = 3.5$ Hz, 1H), 4.79 (s, 1H), 4.76 (d, $J = 3.6$ Hz, 1H), 4.56 (s, 1H), 4.33 (dd, $J = 8.1, 2.7$ Hz, 1H), 4.11 (s, 3H), 4.09 (m, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 3.70 (s, 3H), 3.61 (s, 3H), 3.01 (dd, $J = 18.7, 8.2$ Hz, 1H), 2.84 (s, 3H, NCH₃), 2.12 (dd, $J = 18.6, 2.5$ Hz, 1H), 1.80–1.74 (m, 2H), 1.67–1.57 (br m, 1H), 1.48 (s, 9H, BOC), 0.98–0.85 (br m, 6H, obscured by SiC(CH₃)₃), 0.99 (s, 9H, SiC(CH₃)₃), 0.89 (s, 9H, SiC(CH₃)₃), 0.15 (s, 3H, SiCH₃), 0.08 (s, 3H, SiCH₃), 0.06 (s, 3H, SiCH₃), –0.10 (s, 3H, SiCH₃); IR (film) ν_{\max} 3400, 2930, 2855, 1716, 1794, 1683, 1645, 1575, 1489, 1361, 1234, 1153, 1111, 1061, 1027, 898, 834, 779, 715 cm⁻¹; FABHRMS (NBA–CsI) m/z 1656.4786 (M⁺ + Cs, C₇₅H₉₅Cl₂N₇O₁₉Si₂ requires 1656.4653).

(*P,M,M*)-7: more polar isomer, $R_f = 0.58$ (SiO₂, 4% CH₃OH–CHCl₃), unnatural atropisomer configuration, white solid; $[\alpha]_D^{25} +51$ (c 0.30, CH₃OH); ¹H NMR (CD₃OD, 313 K, 600 MHz) δ 7.68 (d, $J = 2.0$ Hz, 1H), 7.61 (d, $J = 1.8$ Hz, 1H), 7.54 (dd, $J = 8.3, 1.8$ Hz, 1H), 7.33 (dd, $J = 8.5, 1.7$ Hz, 1H), 7.22 (d, $J = 8.4$ Hz, 1H), 7.05–7.00 (m, 1H), 6.99 (d, $J = 2.2$ Hz, 1H), 6.94 (d, $J = 8.7$ Hz, 1H), 6.92 (d, $J = 8.5$ Hz, 1H), 6.66 (d, $J = 2.2$ Hz, 1H), 6.34 (d, $J = 2.3$ Hz, 1H), 6.07 (s, 1H), 5.47 (m, 1H), 5.37 (m, 2H), 5.36 (dd, $J = 2.2, 0.9$ Hz, 1H), 5.19 (d, $J = 2.7$ Hz, 1H), 4.79 (s, 1H), 4.80–4.60 (m, 1H, obscured by water), 4.57 (s, 1H), 4.31 (dd, $J = 7.8, 1.9$ Hz, 1H), 4.11 (s, 3H), 4.07 (m, 1H), 3.84 (s, 3H), 3.79 (s, 3H), 3.70 (s, 3H), 3.61 (s, 3H), 2.98 (dd, $J = 18.7, 7.8$ Hz, 1H), 2.84 (s, 3H, NCH₃), 2.26 (dd, $J = 18.3, 2.0$ Hz, 1H), 1.80–1.73 (m, 2H), 1.67–1.58 (br m, 1H), 1.48 (s, 9H, BOC), 1.00–0.94 (br m, 6H, obscured by SiC(CH₃)₃), 0.98 (s, 9H, SiC(CH₃)₃), 0.89 (s, 9H, SiC(CH₃)₃), 0.14 (s, 3H, SiCH₃), 0.08 (s, 3H, SiCH₃), 0.06 (s, 3H, SiCH₃), –0.12 (s, 3H, SiCH₃); IR (film) ν_{\max} 3404, 2926, 2855, 1843, 1716, 1698, 1682, 1652, 1584, 1456, 1386, 1259, 1109, 1027, 838, 780, 723 cm⁻¹; FABHRMS (NBA–CsI) m/z 1656.4783 (M⁺ + Cs, C₇₅H₉₅Cl₂N₇O₁₉Si₂ requires 1656.4653).

(*M,M,M*)-8: less polar isomer, $R_f = 0.27$ (SiO₂, 3% CH₃OH–CHCl₃), natural atropisomer configuration, white solid; ¹H NMR (CD₃OD, 313 K, 600 MHz) δ 7.68 (d, $J = 2.0$ Hz, 1H), 7.59 (d, $J = 1.8$ Hz, 1H), 7.52 (dd, $J = 8.5, 1.8$ Hz, 1H), 7.38 (dd, $J = 8.4, 1.9$ Hz, 1H), 7.31 (d, $J = 8.5$ Hz, 1H), 7.21 (d, $J = 8.5$ Hz, 1H), 7.07 (dd, $J = 8.8, 2.0$ Hz, 1H), 6.99 (d, $J = 2.3$ Hz, 1H), 6.94 (d, $J = 8.8$ Hz, 1H), 6.66 (d, $J = 2.2$ Hz, 1H), 6.34 (d, $J = 2.2$ Hz, 1H), 5.98 (s, 1H), 5.40 (m, 1H), 5.37 (m, 2H), 5.36 (dd, $J = 1.8, 1.2$ Hz, 1H), 5.09 (d, $J = 3.6$ Hz, 1H), 5.05–4.65 (two m, 2H, obscured by water), 4.57 (s, 1H), 4.29 (dd, $J = 8.1, 2.1$ Hz, 1H), 4.11 (s, 3H), 4.09 (m, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 3.69 (s, 3H), 3.61 (s, 3H), 2.97 (dd, $J = 18.7, 8.2$ Hz, 1H), 2.84 (s, 3H, NCH₃), 2.13 (dd, $J = 18.7, 3.0$ Hz, 1H), 1.78–1.71 (m, 1H), 1.71–1.65 (m, 1H), 1.63–1.55 (m, 1H), 1.50 (s, 9H, BOC), 0.98 (d, $J = 6.7$ Hz, 3H), 0.96 (d, $J = 6.5$ Hz, 3H), 0.89 (s, 9H, SiC(CH₃)₃), 0.07 (s, 3H, SiCH₃), 0.06 (s, 3H, SiCH₃); FABHRMS (NBA–CsI) m/z 1542.3695 (M⁺ + Cs, C₆₆H₈₄N₇O₁₉Cl₂Si requires 1542.3788).

(*P,M,M*)-8: more polar isomer, $R_f = 0.26$ (SiO₂, 3% CH₃OH–CHCl₃), unnatural atropisomer configuration, white solid; ¹H NMR (CD₃OD, 313 K, 600 MHz) δ 7.68 (d, $J = 2.0$ Hz, 1H), 7.56 (d, $J = 1.9$ Hz, 1H), 7.53 (dd, $J = 8.4, 1.9$ Hz, 1H), 7.45 (dd, $J = 8.5, 1.7$ Hz, 1H), 7.23 (d, $J = 8.4$ Hz, 1H), 7.07 (dd, $J = 8.8, 2.3$ Hz, 1H), 6.98 (d, $J = 2.4$ Hz, 1H), 6.95 (d, $J = 8.5$ Hz, 1H), 6.94 (d, $J = 8.7$ Hz, 1H), 6.66 (d, $J = 2.2$ Hz, 1H), 6.34 (d, $J = 2.2$ Hz, 1H), 6.02 (s, 1H), 5.43 (m, 1H), 5.37 (m, 2H), 5.35 (dd, $J = 2.1, 0.8$ Hz, 1H), 5.05 (d, $J = 3.4$ Hz, 1H), 4.62–4.60 (m, 1H), 4.58 (s, 1H), 4.27 (dd, $J = 7.8, 1.8$ Hz, 1H), 4.05–4.10 (m, 1H, obscured by water), 4.10 (s, 3H), 4.10–4.09 (m, 1H), 3.84 (s, 3H), 3.79 (s, 3H), 3.69 (s, 3H), 3.61 (s, 3H), 2.95 (dd, $J = 18.7, 8.0$ Hz, 1H), 2.84 (s, 3H, NCH₃), 2.27 (br

dd, $J = 18.0$ Hz, 1H), 1.80–1.71 (m, 1H), 1.71–1.64 (m, 1H), 1.64–1.56 (m, 1H), 1.50 (s, 9H, BOC), 0.98 (d, $J = 6.6$ Hz, 3H), 0.96 (d, $J = 6.5$ Hz, 3H), 0.89 (s, 9H, SiC(CH₃)₃), 0.07 (s, 3H, SiCH₃), 0.06 (s, 3H, SiCH₃); FABHRMS (NBA–CsI) m/z 1542.3678 ($M^+ + \text{Cs}$, C₆₆H₈₄N₇O₁₉Cl₂Si requires 1542.3788).

(*M,M,M*)-**9**: $[\alpha]_D^{25} +46$ (c 0.11, CH₃OH); ¹H NMR (CD₃OD, 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 ($M^+ + \text{Cs}$, C₅₈H₆₂N₈O₁₇Cl₂ requires 1345.2664).

Retro aldol CD ring cleaved **3**: $R_f = 0.18$ (SiO₂, 5% CH₃OH–CHCl₃); $[\alpha]_D^{25} +32$ (c 0.60, CH₃OH); ¹H NMR (CD₃OD, 313 K, 600 MHz) δ 9.87 (s, 1H), 8.03 (d, $J = 1.9$ Hz, 1H), 7.79 (dd, $J = 8.5, 2.0$ Hz, 1H), 7.69 (d, $J = 2.1$ Hz, 1H), 7.56 (dd, $J = 8.6, 2.1$ Hz, 1H), 7.19 (d, $J = 8.4$ Hz, 1H), 7.16 (dd, $J = 8.8, 2.0$ Hz, 1H), 7.06 (d, $J = 2.2$ Hz, 1H), 6.98 (d, $J = 8.8$ Hz, 1H), 6.95 (d, $J = 8.4$ Hz, 1H), 6.85 (m, 1H), 6.70 (d, $J = 2.3$ Hz, 1H), 6.35 (d, $J = 2.2$ Hz, 1H), 5.79 (s, 1H), 5.67 (d, $J = 1.9$ Hz, 1H), 5.37–5.31 (m, 1H), 5.30 (s, 1H), 4.77 (s, 1H), 4.75 (s, 1H), 4.55–4.45 (m, 1H, obscured by water), 4.39 (s, 1H), 4.15 (m, 1H), 3.90 (s, 3H), 3.86 (s, 3H), 3.81 (s, 3H), 3.72 (s, 3H), 3.69 (s, 3H), 2.74 (s, 3H, NCH₃), 2.59 (dd, $J = 15.5, 6.6$ Hz, 1H), 2.30–2.20 (m, 1H), 1.70–1.55 (br m, 2H), 1.55–1.45 (br m, 1H), 1.43 (s, 9H, BOC), 0.93 (d, $J = 6.6$ Hz, 3H), 0.93–0.85 (br d, 3H); IR (film) ν_{max} 3290, 2954, 1720, 1659, 1518, 1495, 1341, 1224, 1142, 1059, 1031 cm⁻¹; FABHRMS (NBA–CsI) m/z 1445.3322 ($M^+ + \text{Cs}$, C₆₃H₇₀N₈O₁₉Cl₂ requires 1445.3189).