

Total Synthesis of Teicoplanin Aglycon

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Supporting Information

(3): IR (thin film) 3238, 3004, 2953, 1716, 1665, 1617, 1536, 1437, 1373, 1350, 1290, 1247, 1211, 1129, 1088, 981, 927, 827 cm^{-1} ; ^1H NMR (3:1 CD_2Cl_2 : CD_3OD , 298 K, 400 MHz) δ 8.20 (dd, 1H, $J = 7.0, 2.2$ Hz), 7.75 (ddd, 1H, $J = 8.4, 4.4, 2.2$ Hz), 7.34-7.29 (m, 2H), 3.79 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (3:1 CD_2Cl_2 : CD_3OD , 298 K, 100 MHz) δ 171.3, 165.9, 155.7 (d, $J = 267.1$ Hz), 137.6, 137.3 (d, $J = 8.8$ Hz), 131.7 (d, $J = 4.4$ Hz), 129.3, 127.4, 127.2 (d, $J = 2.2$ Hz), 119.1 (d, $J = 21.2$ Hz), 53.1, 22.8. Exact mass calculated for $[\text{C}_{12}\text{H}_{11}\text{FN}_2\text{O}_5]^+$: 282.0652; found: 282.0652 (EI+).

(5): IR (thin film) 3280, 3065, 2490, 1745, 1655, 1540, 1440, 1350, 1250, 1215, 1135, 1090, 820 cm^{-1} ; ^1H NMR (CDCl_3 , 298 K, 400 MHz) δ 7.80 (dd, 1H, $J = 7.0, 2.3$ Hz), 7.40 (ddd, 1H, $J = 8.5, 4.1, 2.3$ Hz), 7.21 (dd, 1H, $J = 10.6, 8.5$ Hz), 6.25 (d, 1H, $J = 7.3$ Hz), 4.87 (dt, 1H, $J = 7.4, 5.8$ Hz), 3.75 (s, 3H), 3.24 (dd, 1H, $J = 14, 5.7$ Hz), 3.09 (dd, 1H, $J = 14, 5.9$ Hz), 2.00 (s, 3H); ^{13}C NMR (CDCl_3 , 298 K, 100 MHz) δ 171.5, 169.9, 154.7 (d, $J = 263$ Hz), 137.1 (d, $J = 8$ Hz), 136.4 (d, $J = 8$ Hz), 133.4 (d, $J = 4$ Hz), 126.7 (d, $J = 3$ Hz), 118.6 (d, $J = 21$ Hz), 53.0, 52.7, 36.9, 23.1. Exact mass calculated for $[\text{C}_{12}\text{H}_{13}\text{FN}_2\text{O}_5]^+$: 284.00808; found: 284.0798 (EI+). $[\alpha]^{25}_{\text{D}} = -60.0^\circ$ ($c = 0.69$, CH_2Cl_2).

(6): IR (thin film) 3360, 1744, 1712, 1540, 1351, 1252, 1168 cm^{-1} ; ^1H NMR (CDCl_3 , 298 K, 400 MHz) δ 7.83 (dd, 1H, $J = 7.0, 2.0$ Hz), 7.42 (ddd, 1H, $J = 8.5, 4.2, 2.3$ Hz), 7.22 (dd, 1H, $J = 10.6, 8.6$ Hz), 5.09 (d, 1H, $J = 7.4$ Hz), 4.59 (dd, 1H, $J = 13.1, 6.1$ Hz), 3.76 (s, 3H), 3.25 (dd, 1H, $J = 13.9, 5.4$ Hz), 3.05 (dd, 1H, $J = 13.9, 6.3$ Hz), 1.41 (s, 9H); ^{13}C NMR (CDCl_3 , 298 K, 100 MHz) δ 171.5, 155.0 (d, $J = 265.3$ Hz), 154.9, 137.1, 136.4 (d, $J = 8.3$ Hz), 133.6 (d, $J = 4.5$ Hz), 126.8, 118.5 (d, $J = 21.2$ Hz), 80.4, 54.2, 52.6, 37.4, 28.2, 27.9. Exact mass calculated for $[\text{C}_{15}\text{H}_{19}\text{FN}_2\text{O}_6\text{Na}]^+$: 365.1125; found: 365.1123 (FAB, *m*-nitrobenzyl alcohol, NaI added). $[\alpha]^{25}_{546} = -46.8^\circ$ ($c = 0.85$, CH_2Cl_2).

(7): IR (thin film) 3301, 3101, 2976, 1682, 1661, 1571, 1524, 1367, 1268, 1163, 1053 cm^{-1} ; ^1H NMR (CD_3OD , 298 K, 400 MHz) δ 7.12 (d, 1H, $J = 1.5$ Hz), 7.03 (s, 1H), 6.93 (t, 1H, $J = 1.8$ Hz), 5.04 (s, 1H), 3.79 (s, 3H), 2.72 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (CD_3OD , 298 K, 100 MHz) δ 172.7, 162.0, 157.2, 142.8, 123.7, 123.5, 117.8, 113.2, 81.0, 59.3, 56.1, 28.6, 26.5. Exact mass calculated for $[\text{C}_{15}\text{H}_{24}\text{BrN}_2\text{O}_4\text{Na}]^+$: 395.0582; found: 395.0565 (FAB, *m*-nitrobenzyl alcohol, NaI added). $[\alpha]^{25}_{\text{D}} = +113.6^\circ$ ($c = 1.0$, CH_2Cl_2).

(8): IR (thin film) 3333, 2974, 2933, 1667, 1590, 1451, 1426, 1369, 1251, 1164, 1062 cm^{-1} ; ^1H NMR (CD_3OD , 298 K, 500 MHz) δ 7.18 (s, 1H), 7.07 (s, 1H), 6.98 (s, 1H), 5.07 (s, 1H), 3.79 (s, 3H), 2.72 (s, 3H), 1.43 (s, 9H); Exact mass calculated for $[\text{C}_{15}\text{H}_{24}\text{BN}_2\text{O}_6]^+$: 339.1727; found: 339.1727 (TOF ES+). $[\alpha]^{25}_{\text{D}} = +95^\circ$ ($c = 0.3$, MeOH).

(9): IR (thin film) 3344, 2974, 2933, 1697, 1513, 1369, 1272, 1164, 1051, 1026 cm^{-1} ; ^1H NMR (CD_3OD , 298 K, 500 MHz) δ 6.88-6.83 (m, 3H), 4.98 (s, 1H), 3.83 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (CD_3OD , 298 K, 125 MHz) δ 174.6, 157.5, 149.1, 147.7, 131.1, 120.0, 115.5, 112.7, 80.8, 68.9, 58.8, 56.4, 28.7. Exact mass calculated for $[\text{C}_{14}\text{H}_{17}\text{NO}_6]^-$: 296.1134; found: 296.1123 (TOF ES-). $[\alpha]^{25}_{\text{D}} = -122.2^\circ$ ($c = 1.0$, CH_2Cl_2).

(10): IR (thin film) 3374, 2974, 1744, 1662, 1539, 1513, 1441, 1354, 1272, 1251, 1164 cm^{-1} ; ^1H NMR (CD_3OD , 298 K, 500 MHz) δ 7.93 (d, 1H, $J = 6.3$ Hz), 7.49 (m, 1H), 7.23 (dd, 1H, $J = 6.3, 2.4$ Hz), 6.81 (d, 1H, $J = 8.3$ Hz), 6.75 (s, 1H), 6.70 (d, 1H, $J = 7.8$ Hz), 4.95 (s, 1H), 4.72 (dd, 1H, $J = 9.8, 5.4$ Hz), 3.84 (s, 3H), 3.68 (s, 3H), 3.31-3.26 (m, 1H + CHD_2OD), 3.07 (dd, 1H, $J = 14.3, 9.9$ Hz), 1.42 (s, 9H); ^{13}C NMR (CD_3OD , 298 K, 100 MHz) δ 173.0, 172.1, 156.9, 155.3 (d, $J = 260.9$ Hz), 148.7, 147.3, 138.0 (d, $J = 7.6$ Hz), 137.7 (d, $J = 8.4$ Hz), 135.5, 130.9, 127.5, 119.1, 119.0 (d, $J = 20.6$ Hz), 115.2, 112.2, 80.7, 59.4, 56.2, 54.4, 52.9, 36.9, 28.7.

Exact mass calculated for $[C_{24}H_{29}FN_3O_9]^+$: 522.1888; found: 522.1909 (TOF ES+). $[\alpha]^{25}_D = -23.4^\circ$ ($c = 1.0$, CH_3OH).

(11): IR (thin film) 3292, 3077, 2954, 1729, 1668, 1538, 1513, 1441, 1352, 1272, 1215, 1180 cm^{-1} ; 1H NMR (CD_3OD , 298 K, 400 MHz) δ 7.93 (dd, 1H, $J = 7.0, 2.2$ Hz), 7.53 (ddd, 1H, $J = 8.4, 4.4, 2.2$ Hz), 7.26 (dd, 1H, $J = 11.3, 8.5$ Hz), 6.87 (d, 1H, $J = 8.4$ Hz), 6.84 (d, 1H, $J = 2.2$ Hz), 6.80 (dd, 1H, $J = 8.4, 2.3$ Hz), 5.32 (s, 1H), 4.71 (dd, 1H, $J = 9.2, 5.1$ Hz), 3.84 (s, 3H), 3.67 (s, 3H), 3.31-3.25 (m, 1H + CHD_2OD), 3.07 (dd, 1H, $J = 14.3, 9.2$ Hz); ^{13}C NMR (CD_3OD , 298 K, 100 MHz) δ 172.3, 171.2, 158.4 (q, $J = 37.4$ Hz), 155.6 (d, $J = 261.7$ Hz), 149.5, 147.8, 138.4 (d, $J = 7.6$ Hz), 137.9 (d, $J = 8.4$ Hz), 135.7 (d, $J = 3.8$ Hz), 129.1, 127.7 (d, $J = 2.3$ Hz), 120.6, 119.2 (d, $J = 20.6$ Hz), 117.3 (q, $J = 286.1$ Hz), 116.0, 112.5, 58.3, 56.3, 54.8, 52.9, 36.8. Exact mass calculated for $[C_{21}H_{19}F_4N_3O_8Na]^+$: 540.1006; found: 540.0982 (TOF ES+). $[\alpha]^{25}_{546} = -52.0^\circ$ ($c = 1.0$, MeOH).

(12): IR (thin film) 3282, 3067, 2933, 1718, 1662, 1600, 1539, 1513, 1436, 1354, 1210, 1159 cm^{-1} ; 1H NMR (CD_3OD , 298 K, 400 MHz) δ 7.94 (dd, 1H, $J = 7.0, 2.2$ Hz), 7.56 (ddd, 1H, $J = 8.4, 4.4, 2.2$ Hz), 7.27 (dd, 1H, $J = 11.4, 8.8$ Hz), 7.22 (dd, 1H, $J = 8.8, 2.6$ Hz), 7.11 (d, 1H, $J = 2.2$ Hz), 7.09 (d, 1H, $J = 8.8$ Hz), 6.64 (t, 1H, $J = 1.8$ Hz), 6.51 (t, 1H, $J = 1.8$ Hz), 6.32 (s, 1H), 5.40 (s, 1H), 4.99 (s, 1H), 4.73 (dd, 1H, $J = 8.8, 5.1$ Hz), 3.77 (s, 3H), 3.72 (s, 3H), 3.63 (s, 3H), 3.31-3.25 (m, 1H + CHD_2OD), 3.07 (dd, 1H, $J = 14.3, 9.2$ Hz), 2.70 (s, 3H), 1.42 (bs, 9H); ^{13}C NMR (CD_3OD , 298 K, 100 MHz) δ 173.2, 172.3, 170.9, 162.5, 160.7, 158.4 (q, $J = 37.4$ Hz), 157.3, 155.6 (d, $J = 261.7$ Hz), 153.5, 145.2, 141.8, 138.4 (d, $J = 8.4$ Hz), 137.9 (d, $J = 8.4$ Hz), 135.6 (d, $J = 4.6$ Hz), 129.5, 127.8 (d, $J = 2.3$ Hz), 126.4, 122.9, 119.3 (d, $J = 21.4$ Hz), 117.3 (q, $J = 286.9$ Hz), 114.3, 108.8, 107.8, 103.2, 80.9, 59.8, 57.9, 56.4, 55.9, 54.7, 52.9, 36.8, 28.7, 26.5. Exact mass calculated for $[C_{36}H_{39}F_4N_5O_{12}Na]^+$: 832.2429; found: 832.2396 (TOF ES+). $[\alpha]^{25}_D = +9.3^\circ$ ($c = 0.57$, 10:1 CH_2Cl_2 :MeOH).

(13): IR (thin film) 3277, 3063, 2940, 1720, 1663, 1601, 1540, 1511, 1351, 1269, 1212, 1159 cm^{-1} ; 1H NMR (CD_3OD , 298 K, 400 MHz) δ 7.96 (dd, 1H, $J = 6.9, 1.8$ Hz), 7.59 (m, 1H), 7.26 (dd, 1H, $J = 11.0, 8.8$ Hz), 7.22 (dd, 1H, $J = 8.4, 2.2$ Hz), 7.12 (d, 1H, $J = 2.2$ Hz), 7.07 (d, 1H, $J = 8.4$ Hz), 6.63 (s, 1H), 6.47 (t, 1H, $J = 1.8$ Hz), 6.35 (s, 1H), 5.41 (s, 1H), 4.99 (s, 1H), 4.66 (dd, 1H, $J = 8.1, 5.1$ Hz), 3.76 (s, 3H), 3.72 (s, 3H), 3.32-3.27 (m, 1H + CHD_2OD), 3.08 (dd, 1H, $J = 14.3, 8.4$ Hz), 2.70 (s, 3H), 1.42 (bs, 9H); ^{13}C NMR (CD_3OD , 298 K, 100 MHz) δ 174.1, 173.2, 170.7, 162.4, 160.6, 158.4 (q, $J = 37.4$ Hz), 157.3, 155.6 (d, $J = 261.7$ Hz), 153.3, 145.2, 141.7, 138.3 (d, $J = 7.6$ Hz), 138.0 (d, $J = 8.4$ Hz), 136.0, 129.6, 127.8 (d, $J = 2.3$ Hz), 126.2, 122.7, 119.1 (d, $J = 20.6$ Hz), 117.3 (q, $J = 286.1$ Hz), 114.3, 108.8, 108.0, 103.3, 81.0, 59.8, 58.0, 56.4, 55.9, 55.0, 37.2, 28.7, 26.5. Exact mass calculated for $[C_{35}H_{37}F_4N_5O_{12}Na]^+$: 818.2272; found: 818.2280 (FAB, *m*-nitrobenzyl alcohol, NaI added). $[\alpha]^{25}_D = -33.1^\circ$ ($c = 1.0$, CH_2Cl_2).

(14): 1H NMR ($DMSO-d_6$, 298 K, 500 MHz) δ 9.84 (d, 1H, $J = 8.4$ Hz), 8.53 (d, 1H, $J = 8.8$ Hz), 8.39 (d, 1H, $J = 4.9$ Hz), 7.99 (d, 1H, $J = 9.8$ Hz), 7.94 (dd, 1H, $J = 8.8, 1.9$ Hz), 7.64 (m, 1H), 7.50 (dd, 1H, $J = 11.2, 8.8$ Hz), 7.31-7.25 (m, 2H), 6.96 (d, 1H, $J = 1.8$ Hz), 6.78 (s, 1H), 6.80 (t, 1H, $J = 2.2$ Hz), 6.44 (s, 1H), 5.29 (d, 1H, $J = 8.1$ Hz), 5.28 (d, 1H, $J = 8.4$ Hz), 4.53 (ddd, 1H, $J = 10.0, 9.9, 6.8$ Hz), 3.84 (s, 3H), 3.75 (s, 3H), 3.11-2.98 (m, 2H), 2.57 (d, 3H, $J = 4.4$ Hz); ^{13}C NMR ($DMSO-d_6$, 298 K, 100 MHz) δ 169.0, 168.8, 167.3, 160.5, 159.3, 155.6 (q, $J = 37.3$ Hz), 153.5 (d, $J = 260.9$ Hz), 151.3, 143.7, 142.5, 137.1 (d, $J = 8.4$ Hz), 136.3 (d, $J = 7.6$ Hz), 134.8 (d, $J = 3.8$ Hz), 127.8, 127.4, 126.5 (d, $J = 2.3$ Hz), 122.4, 118.4 (d, $J = 20.6$ Hz), 115.8 (q, $J = 288.4$ Hz), 113.4, 108.0, 104.4, 102.1, 56.2, 56.0, 55.8, 55.5, 55.3, 35.2, 25.7. Exact mass calculated for $[C_{30}H_{27}F_4N_5O_9Na]^+$: 700.1643; found: 700.1664 (TOF ES+). $[\alpha]^{25}_D = -12.0^\circ$ ($c = 0.25$, DMF).

(15): 1H NMR ($DMSO-d_6$, 298 K, 500 MHz) δ 9.83 (d, 1H, $J = 8.3$ Hz), 8.70 (d, 1H, $J = 7.8$ Hz), 8.08 (d, 1H, $J = 9.8$ Hz), 7.98 (dd, 1H, $J = 7.4, 1.9$ Hz), 7.66 (ddd, 1H, $J = 8.3, 4.4, 1.9$ Hz), 7.50 (dd, 1H, $J = 11.2, 8.8$ Hz), 7.28-7.23 (m, 2H), 6.96 (d, 1H, $J = 1.9$ Hz), 6.70 (t, 1H, $J = 2.2$ Hz), 6.68 (s, 1H), 6.46 (s, 1H), 5.34 (d, 1H, $J = 8.3$ Hz), 5.14 (d, 1H, $J = 8.3$ Hz), 4.55 (dd, 1H, $J = 9.3, 7.3$ Hz), 3.83 (s, 3H), 3.76 (s, 3H), 3.11-2.99 (m, 2H); ^{13}C NMR ($DMSO-d_6$, 298 K, 100 MHz) δ 170.8, 169.0, 167.5, 160.5, 159.0, 155.6 (q, $J = 36.6$ Hz), 153.5 (d, $J = 261$ Hz), 151.0, 143.7, 141.5, 137.1 (d, $J = 9.1$ Hz), 136.4, 134.7, 127.8, 127.0, 126.6, 121.6, 118.3 (d, $J = 20.6$ Hz), 115.8 (q, $J = 288$ Hz), 113.4, 109.2, 104.9, 102.6, 55.9 (2 C), 55.8, 55.6, 55.5; 35.4. Exact mass calculated for $[C_{29}H_{24}F_4N_4O_{10}Na]^+$: 687.1326; found: 687.1318 (TOF ES+). $[\alpha]^{25}_D = -7.5^\circ$ ($c = 0.20$, DMF).

(*N*-Boc **16**): IR (thin film) 3305, 2934, 1669, 1651, 1504, 1325, 1236, 1158, 1062, 1038 cm^{-1} ; ^1H NMR (CD_3OD , 298 K, 500 MHz) δ 7.65 (d, 1H, $J = 2.0$ Hz), 7.49 (dd, 1H, $J = 8.3, 1.9$ Hz), 7.16 (dd, 1H, $J = 2.0$ Hz), 7.08 (d, 1H, $J = 2.4$ Hz), 7.05 (d, 1H, $J = 8.3$ Hz), 7.00 (d, 1H, $J = 8.8$ Hz), 6.66 (d, 1H, $J = 2.4$ Hz), 6.62 (s, 1H), 6.52 (d, 1H, $J = 2.0$ Hz), 5.45 (s, 1H), 5.33 (s, 1H), 5.23 (d, 1H, $J = 2.0$ Hz), 4.69 (s, 1H), 4.66 (s, 1H), 4.16 (s, 1H), 3.96 (s, 3H), 3.84 (s, 3H), 3.73 (s, 3H), 3.66 (s, 3H), 2.85 (s, 3H), 1.41 (s, 9H). Exact mass calculated for $[\text{C}_{43}\text{H}_{47}\text{ClN}_5\text{O}_{13}]^+$: 876.2859; found: 876.2887 (TOF ES+). $[\alpha]^{25}_{\text{D}} = +32.8^\circ$ ($c = 0.47$, MeOH).

(**17**): IR (thin film) 3272, 2933, 2841, 1661, 1626, 1605, 1585, 1538, 1513, 1426, 1349, 1328, 1267, 1231, 1144, 1062 cm^{-1} ; ^1H NMR (2:1 $\text{CD}_3\text{OD}:\text{CDCl}_3$, 298 K, 500 MHz) δ 7.93 (dd, 1H, $J = 1.9$ Hz), 7.63 (d, 1H, $J = 1.5$ Hz), 7.47-7.45 (m, 2H), 7.22 (dd, 1H, $J = 8.3, 2.4$ Hz), 7.16-7.03 (m, 5H), 6.99 (d, 1H, $J = 2.4$ Hz), 6.93 (d, 1H, $J = 8.8$ Hz), 6.67 (s, 1H), 6.65 (t, 1H, $J = 2.2$ Hz), 6.58 (d, 1H, $J = 2.4$ Hz), 6.49 (d, 1H, $J = 2.4$ Hz), 6.41 (s, 1H), 6.29 (d, 1H, $J = 1.5$ Hz), 5.62 (s, 1H), 5.41 (s, 1H), 5.31 (s, 1H), 5.17 (d, 1H, $J = 1.9$ Hz), 5.15 (s, 1H), 4.66-4.62 (m, 3H), 4.14 (s, 1H), 3.94 (s, 3H), 3.85 (s, 3H), 3.83 (s, 3H), 3.71 (s, 3H), 3.70 (s, 3H), 3.58 (s, 3H), 3.10 (dd, 1H, $J = 14.7, 6.8$ Hz), 2.98-2.94 (m, 1H), 2.83 (s, 3H). Mass calculated for $[\text{C}_{69}\text{H}_{52}\text{ClF}_4\text{N}_8\text{O}_{20}\text{Na}]^+$: 1444; found: 1444 (TOF ES+). $[\alpha]^{25}_{\text{D}} = -30.0^\circ$ ($c = 0.15$, 10% MeOH in CH_2Cl_2).

(**18**): IR (thin film) 3282, 2923, 2841, 1656, 1610, 1579, 1508, 1420, 1323, 1267, 1231, 1159, 1144, 1087, 1061, 1027 cm^{-1} ; ^1H NMR (CD_3OD , 298 K, 500 MHz) δ 7.93 (s, 1H), 7.67 (dd, 1H, $J = 8.8, 1.9$ Hz), 7.63 (d, 1H, $J = 1.9$ Hz), 7.55 (d, 1H, $J = 8.3$ Hz), 7.23-7.02 (m, 7H), 6.98 (d, 1H, $J = 8.8$ Hz), 6.69 (d, 1H, $J = 2.4$ Hz), 6.51-6.48 (m, 2H), 6.28 (s, 1H), 6.15 (s, 1H), 5.81 (s, 1H), 5.66 (s, 1H), 5.50 (s, 1H), 5.46 (s, 1H), 5.34 (s, 1H), 5.00 (s, 1H), 4.65-4.62 (m, 2H), 4.55 (s, 1H), 4.14 (s, 3H), 3.85 (s, 3H), 3.78 (s, 3H), 3.74 (s, 3H), 3.73 (s, 3H), 3.37 (dd, 1H, $J = 14.2, 6.3$ Hz), 3.01-2.97 (m, 4H), 2.85 (s, 3H). Mass calculated for $[\text{C}_{69}\text{H}_{51}\text{ClF}_3\text{N}_9\text{O}_{19}\text{Na}]^+$: 1424; found: 1424 (TOF ES+). $[\alpha]^{25}_{\text{D}} = +67^\circ$ ($c = 0.10$, 10% MeOH in CH_2Cl_2).

(**19**): IR (thin film) 3292, 2933, 1661, 1605, 1585, 1513, 1487, 1426, 1231, 1200, 1144, 1062, 1026 cm^{-1} ; ^1H NMR (CD_3OD , 298 K, 600 MHz) δ 7.63 (s, 1H), 7.56 (dd, 1H, $J = 8.3, 1.5$ Hz), 7.42 (d, 1H, $J = 8.3$ Hz), 7.38 (s, 1H), 7.27 (d, 1H, $J = 8.3$ Hz), 7.24 (dd, 1H, $J = 8.8, 1.9$ Hz), 7.18 (d, 1H, $J = 1.9$ Hz), 7.13-7.11 (m, 2H), 7.03 (d, 1H, $J = 8.3$ Hz), 7.02 (d, 1H, $J = 1.9$ Hz), 6.99 (d, 1H, $J = 8.8$ Hz), 6.68 (d, 1H, $J = 1.9$ Hz), 6.51 (t, 1H, $J = 1.9$ Hz), 6.49 (d, 1H, $J = 1.9$ Hz), 6.25 (s, 1H), 6.23 (s, 1H), 5.78 (s, 1H), 5.61 (s, 1H), 5.48 (s, 1H), 5.39 (s, 1H), 5.34 (s, 1H), 5.17 (s, 1H), 4.65 (d, 1H, $J = 5.9$ Hz), 4.55 (s, 1H), 4.11 (s, 3H), 4.12 (s, 3H), 3.85 (s, 3H), 3.78 (s, 3H), 3.74 (s, 3H), 3.73 (s, 3H), 3.09 (s, 3H), 2.99 (dd, 1H, $J = 14.2, 6.3$ Hz), 2.85 (s, 3H). Mass calculated for $[\text{C}_{69}\text{H}_{51}\text{Cl}_2\text{F}_3\text{N}_8\text{O}_{17}]^-$: 1390; found: 1390 (APCI-). $[\alpha]^{25}_{\text{D}} = +158^\circ$ ($c = 0.10$, MeOH).

(**20**): IR (thin film) 3292, 2923, 2851, 1661, 1610, 1585, 1503, 1487, 1420, 1267, 1231, 1144, 1062, 1021 cm^{-1} ; ^1H NMR (CD_3OD , 298 K, 500 MHz) δ 7.63 (d, 1H, $J = 1.5$ Hz), 7.54 (dd, 1H, $J = 8.3, 1.9$ Hz), 7.44 (d, 1H, $J = 8.3$ Hz), 7.36 (d, 1H, $J = 1.5$ Hz), 7.26-7.22 (m, 2H), 7.16 (d, 1H, $J = 2.4$ Hz), 7.11-7.01 (m, 4H), 6.94 (d, 1H, $J = 8.8$ Hz), 6.75 (s, 1H), 6.63 (d, 1H, $J = 1.9$ Hz), 6.51 (t, 1H, $J = 2.2$ Hz), 6.27 (s, 1H), 6.24 (s, 1H), 5.78 (s, 1H), 5.62 (s, 1H), 5.52 (s, 1H), 5.40 (s, 1H), 5.33, 3.71 (s, 3H), 3.69 (s, 3H), 3.30 (m, 1H + CHD_2OD), 3.14 (s, 3H), 2.99 (dd, $J = 14.1, 5.4$ Hz). Mass calculated for $[\text{C}_{68}\text{H}_{48}\text{Cl}_2\text{F}_3\text{N}_7\text{O}_{10}]^+$: 1377; found: (APCI+) 1377. $[\alpha]^{25}_{\text{D}} = +18.2^\circ$ ($c = 0.17$, 1:1 CH_2Cl_2 :MeOH).

(**2**): IR (thin film) 3293, 1672, 1652, 1520, 1490, 1439, 1297, 1231, 1205, 1139, 1063, 1017 cm^{-1} ; ^1H NMR ($\text{DMF}-d_7$, 298 K, 500 MHz) 9.96 (s, 1H), 9.95 (s, 1H), 9.67 (s, 1H), 9.64 (s, 1H), 9.34 (s, 1H), 8.89 (s, 1H), 8.86 (s, 3H), 8.50 (d, 1H, $J = 5.4$ Hz), 8.40 (d, 1H, $J = 5.9$ Hz), 8.27 (d, 1H, $J = 8.8$ Hz), 8.12 (d, 1H, $J = 10.3$ Hz), 7.91 (d, 1H, $J = 1.9$ Hz), 7.79 (d, 1H, $J = 8.3$ Hz), 7.61 (d, 1H, $J = 8.3$ Hz), 7.36 (d, 1H, $J = 8.3$ Hz), 7.31 (d, 1H, $J = 1.9$ Hz), 7.24 (d, 1H, $J = 8.3$ Hz), 7.12 (d, 1H, $J = 8.3$ Hz), 7.06-7.05 (m, 2H), 7.01 (d, 1H, $J = 8.3$ Hz), 6.90 (d, 1H, $J = 1.9$ Hz), 6.79 (dd, $J = 8.3, 2.4$ Hz), 6.74 (d, 1H, $J = 8.8$ Hz), 6.64-6.61 (m, 3H), 6.45-6.43 (m, 2H), 6.36 (s, 1H), 5.77 (d, 1H, $J = 8.3$ Hz), 5.73 (s, 1H), 5.66 (s, 1H), 5.55 (d, 1H, $J = 10.2$ Hz), 5.40 (d, 1H, $J = 5.9$ Hz), 5.24 (s, 1H), 5.04 (m, 1H), 4.69 (d, 1H, $J = 5.9$ Hz), 4.48 (d, 1H, $J = 4.9$ Hz), 4.36 (d, 1H, $J = 12.7$ Hz), 3.51 (m, solvent + 1H), 2.98 (m, solvent + 1H). Mass calculated for $[\text{C}_{60}\text{H}_{38}\text{Cl}_2\text{N}_7\text{O}_{17}]^+$: 1198; found: 1198 (TOF ES+). $[\alpha]^{25}_{\text{D}} = -36.2^\circ$ ($c = 0.13$, MeOH).