Electronic Supplementary Information:

Gallium(III) and Iron(III) Complexes of Quinolone Antimicrobials

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S1 Characterization of Quinolone Antimicrobial Agents

S1.1 Ciprofloxacin, Hcipro

Appearance: off-white solid. **Mp**: 253–255°C (brown). **UV-Vis** (CH_3OH with 1.5% DMSO): λ [nm] (ϵ) [$M^{-1}cm^{-1}$] = 289 (19900), 317 (12500), 331 (11800). **IR** (neat): $\tilde{\nu}$ [cm^{-1}] = 3044 (m, br), 2844 (w, br) 1614 (st), 1587 (st), 1540 (md), 1498 (st), 1472 (md), 1448 (sh), 1372 (st, br), 1329 (md), 1310 (w), 1284 (st), 1260 (sh), 1172 (md), 1146 (st), 1130 (sh), 1102 (w), 1076 (w), 1035 (st), 1022 (st), 978 (w), 934 (st), 891 (md), 868 (st), 833 (st), 822 (md), 784 (st), 721 (st), 707 (md), 652 (md), 622 (st), 565 (st), 553 (sh), 543 (st), 494 (st), 479 (sh), 443 (md). **NMR**: $\boldsymbol{\delta_H}$ (600 MHz, 298 K, d_6-DMSO) [ppm] = 14.68 (br s, 1H, COOH); 8.67 (s, 1 H, $C_{ar2}H$); 7.93 (d, $J^3_{H,F}$= 13.0 Hz, 1 H, $C_{ar5}H$); 7.60 (d, $J^4_{H,F}$= 7.4 Hz, 1 H, $C_{ar8}H$); 3.86 (tt, $J^3_{H,H}$= 7.2, 3.7 Hz, 1 H, $C_{prop}H$); 3.54 (t, $J^3_{H,H}$= 5.0 Hz, 4 H, $C_{pip2,6}H_2$); 3.27 (t, $J^3_{H,H}$= 5.0 Hz, 4 H, $C_{pip3,5}H_2$); 1.34–1.31 (m, 2 H, $C_{prop}H_{b,b'}$);[1] 1.20–1.17 (m, 2 H, $C_{prop}H_{a,a'}$). $\boldsymbol{\delta_C}$ (125 MHz, 298 K, d_6-DMSO) [ppm] = 176.4 (s, C_{ar4}); 165.9 (s, COOH); 152.9 (d, $J^1_{C,F}$= 207.9 Hz, C_{ar6}); 148.2 (s, C_{ar2}); 144.3 (d, $J^2_{C,F}$= 7.9 Hz, C_{ar7}); 139.1 (s, $C_{ar8'}$); 119.2 (d, $J^3_{C,F}$= 5.9 Hz, $C_{ar4'}$); 111.2 (d, $J^2_{C,F}$= 19.1 Hz, C_{ar5}); 108 (from HMBC, C_{ar3}); 106.8 (s, C_{ar8}); 46.8 (s, $C_{pip2,6}$); 42.8 (s, $C_{pip3,5}$); 36.0 (s, C_{prop}H); 7.6 (s, $C_{prop}H_2$). $\boldsymbol{\delta_F}$ (282 MHz, 298 K, d_6-DMSO) [ppm] = -121.8 (s, 1 F, $C_{ar6}F$). **MS** (ES+, CH_3OH): m/z (%) = 332 (100) [HL + H^+]. m/z (%)= 685 (100) [$(HL)_2$ + Na^+]. **EA**: Anal. Calcd. (found) [%] for $C_{17}H_{18}FN_3O_3$: C, 61.62 (61.76); H, 5.48 (5.52); N, 12.68 (12.46).

S1.2 Enoxacin, Henox

Appearance: off-white, fine crystalline solid. **Mp**: 226−228°C (yellow). **UV-Vis** (CH_3OH with 1.1% DMSO): λ [nm] (ϵ) [$M^{-1}cm^{-1}$] = 287 (14900), 345 (17800). **IR** (neat): $\tilde{\nu}$ [cm^{-1}] = 3390 (md, br), 2835 (st, br), 2773 (md, br), 2556 (md, br), 1625 (st), 1577 (st), 1468 (sh), 1440 (st), triple crown motiv [1403 (md), 1365 (st), 1340 (st)], 1271 (st, br), 1172 (md), 1144 (md), 1107 (md), 1037 (md, br), 942 (st, br), 918 (sh), 826 (st), 790 (md), 729 (md, br), 681 (md), 639 (w), 622 (st), 546 (w), 561 (w), 524 (w), 474 (md, br). **NMR**: $\boldsymbol{\delta_H}$ (300 MHz, 298 K, d_6-DMSO) [ppm] = 8.93 (s, 1 H, $C_{ar2}H$); 7.98 (d, $J^3_{H,F}$= 13.8 Hz, 1 H, $C_{ar5}H$); 4.45 (q, $J^3_{H,H}$= 7.1 Hz, 2 H, CH_2CH_3); 3.73 (dd, $J^3_{H,H}$= 5.9, 4.1 Hz, 4 H, $C_{pip2,6}H_2$); 2.84 (dd, $J^3_{H,H}$= 5.9, 4.1 Hz, 4 H, $C_{pip3,5}H_2$); 1.37 (t, $J^3_{H,H}$= 7.1 Hz, 3 H, CH_2CH_3). $\boldsymbol{\delta_C}$ (75 MHz, 298 K, d_6-DMSO) [ppm] = 176.2 (d, $J^4_{C,F}$= 2.3 Hz, C_{ar4}); 168.0 (s, $C_{ar8'}$); 165.9 (s, COOH); 149.9 (d, $J^2_{C,F}$= 9.0 Hz, C_{ar7}); 147.5 (s, C_{ar2}); 146.2 (d, $J^1_{C,F}$= 204.2 Hz, C_{ar6}); 119.2 (d, $J^2_{C,F}$= 22.0 Hz, C_{ar5}); 112.2 (d, $J^3_{C,F}$= 3.6 Hz, $C_{ar4'}$); 108.0 (s, C_{ar3}); 48.2 (d, $J^4_{C,F}$= 7.9 Hz, $C_{pip2,6}$); 47.1 (s, CH_2CH_3); 45.6 (s, $C_{pip3,5}$); 14.6 (s, CH_2CH_3). $\boldsymbol{\delta_F}$ (282 MHz, 298 K, d_6-DMSO) [ppm] = -127.3 (s, 1 F, $C_{ar6}F$). **MS** (ES+): *m/z* (%) = 321 (100) [HL + H^+]. *m/z* (%)= 664 (100) [$(HL)_2$ + Na^+]. **EA**: Anal. Calcd. (found) [%] for $C_{15}H_{17}FN_4O_3 \cdot 1.5\ H_2O$: C, 51.87 (51.60); H, 5.80 (5.67); N, 16.13 (15.86).

S1.3 Fleroxacin, Hflex

Appearance: white solid. **Mp**: 260°C (decomposed, pale yellow). **UV-Vis** (CH_3OH with 1.5% DMSO): λ [nm] (ϵ) [$M^{-1}cm^{-1}$] = 294 (27500), 320 (12400), 330 (11500). **IR** (neat): $\tilde{\nu}$ [cm^{-1}] = 3054 (md), 2941 (md), 2796 (md), 1716 (st), 1622 (st), 1556 (md), 1542 (sh), 1513 (md), 1474 (st, br), 1447 (st), 1408 (md), 1390 (w), 1375 (md), 1360 (md), 1327 (md), 1279 (st, br), 1244 (md), 1228 (md), 1214 (md), 1205 (md), 1142 (st), 1122 (sh),

1098 (md), 1061 (st), 1036 (st), 1019 (sh), 1010 (st), 970 (st), 941 (st), 925 (st), 869 (md), 852 (md), 816 (sh), 806 (st), 783 (md), 754 (sh), 741 (st), 672 (w), 656 (md, br), 573 (md), 550 (md), 532 (w), 504 (md), 450 (md, br). **NMR**: $\boldsymbol{\delta_H}$ (600 MHz, 298 K, d_6-DMSO) [ppm] = 14.77 (br s, 1 H, COOH); 8.84 (s, 1 H, C$_{ar2}H$); 7.86 (d, $J^3_{H,F}$= 11.9 Hz, 1 H, C$_{ar5}H$); 4.97−4.84 (m, 4 H, (CH_2)$_2$); 3.34 (br s, 4 H, C$_{pip2,6}H_2$, overlaid with water); 2.45 (br s, 4 H, C$_{pip3,5}H_2$); 2.23 (s, 3 H, CH_3). $\boldsymbol{\delta_C}$ (125 MHz, 298 K, d_6-DMSO) [ppm] = 175.6 (s, C_{ar4}); 165.5 (s, COOH); 154.5 (d, $J^1_{C,F}$= 208.2 Hz, C_{ar6}); 152.1 (s, C_{ar2}); 146.0 (d, $J^1_{C,F}$= 212.2 Hz, C_{ar8}); 133.7 (two overlapping d, $J^2_{C,F}$= 13.9, 11.7 Hz, C_{ar7}); 127.3 (d, $J^2_{C,F}$= 9.1 Hz, $C_{ar8'}$); 120.1 (d, $J^3_{C,F}$= 35.1 Hz, $C_{ar4'}$); 107.0 (d, $J^2_{C,F}$= 19.2 Hz, C_{ar5}); 106 (from HMBC, C_{ar3}); 82.1 (d, $J^1_{C,F}$= 138.2 Hz, CH$_2C$H$_2$F); 57.8 (two overlapping d, $J_{C,F}$= 15.8, 12.2 Hz, CH$_2$CH$_2$F); 55.1 (s, $C_{pip2,6}$); 50.3 (s, $C_{pip3,5}$); 46.0 (s, CH$_3$). $\boldsymbol{\delta_F}$ (282 MHz, 298 K, d_6-DMSO) [ppm] = -119.2 (d, $J^4_{F,F}$= 11.9 Hz, 1 F, C$_{ar6}F$); -127.6 (q, $J_{F,F}$= 5.9 Hz, 1 F, C$_{ar8}F$); -224.1 (d, $J^6_{F,F}$= 5.9 Hz, 1 F, (CH$_2$)$_2F$). **MS** (ES+): m/z (%) = 370 (100) [HL + H$^+$], 762 (80) [(HL)$_2$ + Na$^+$]. **EA**: Anal. Calcd. (found) [%] for C$_{17}$H$_{18}$F$_3$N$_3$O$_3$: C, 55.28 (55.14); H, 4.91 (4.90); N, 11.38 (10.98).

S1.4 Levofloxacin, Hlevox

Appearance: pale yellow solid. **Mp**: 224−226°C (dark brown). **UV-Vis** (CH$_3$OH with 1.5% DMSO): λ [nm] (ϵ) [M^{-1}cm^{-1}] = 299 (25100), 318 (10200). **IR** (neat): $\tilde{\nu}$ [cm^{-1}] = 3247 (md, br), 2935 (md), 2884 (md), 2848 (md), 2802 (md), 1720 (st), 1619 (st), 1538 (md), 1518 (md), 1492 (md), 1468 (sh), 1439 (st, br), 1414 (sh), 1394 (st), 1359 (md), 1340 (st), 1315 (sh), 1289 (st), 1240 (st), 1207 (sh), 1195 (md), 1163 (md), 1136 (st), 1116 (md), 1086 (st, br), 1066 (sh), 1048 (md), 1004 (st), 963 (sh), 951 (md, br), 903 (sh), 873 (st), 839 (md), 800 (st), 778 (md), 755 (md), 741 (st), 727 (md), 695 (w), 666 (w), 650 (st), 578

(w), 559 (st), 490 (md), 459 (md). **NMR**: $\boldsymbol{\delta_H}$ (600 MHz, 298 K, d_6-DMSO) [ppm] = 15.20 (br s, 1 H, COOH); 8.96 (s, 1 H, C$_{ar2}H$); 7.56 (d, $J^3_{H,F}$= 12.4 Hz, 1 H, C$_{ar5}H$); 4.91 (d, $J_{H,H}$= 6.8 Hz, 1 H, CH); 4.58 (dd, $J_{H,H}$= 11.5, 1.7 Hz, 1 H) and 4.36 (dd, $J_{H,H}$= 11.5, 2.3 Hz, 1 H) (OCH_2CH); 3.33–3.25 (m, 4 H, C$_{pip2,6}H_2$); 2.43 (br s, 4 H, C$_{pip3,5}H_2$); 2.23 (s, 3 H, NCH_3); 1.44 (d, $J^3_{H,H}$= 3.3 Hz, 3 H, CHCH_3). $\boldsymbol{\delta_C}$ (125 MHz, 298 K, d_6-DMSO) [ppm] = 176.4 (s, C_{ar4}); 166.1 (s, COOH); 155.5 (d, $J^1_{C,F}$= 206.3 Hz, C_{ar6}); 146.2 (s, C_{ar2}); 140.1 (d, $J^3_{C,F}$= 5.7 Hz, C_{ar8}); 132.1 (d, $J^2_{C,F}$= 11.9 Hz, C_{ar7}); 124.8 (s, $C_{ar8'}$); 119.6 (d, $J^3_{C,F}$= 7.7 Hz, $C_{ar4'}$); 106.6 (s, C_{ar3}); 103.3 (d, $J^2_{C,F}$= 20.4 Hz, C_{ar5}); 68.0 (s, OCH$_2$CH); 55.3 (s, $C_{pip2,6}$); 54.8 (s, CH); 50.1 (s, $C_{pip3,5}$); 46.1 (s, NCH$_3$); 17.9 (s, CH(CH$_3$)). $\boldsymbol{\delta_F}$ (282 MHz, 298 K, d_6-DMSO) [ppm] = -120.2 (s, 1 F, C$_{ar6}F$). **MS** (ES+): m/z (%) = 362 (100) [HL + H$^+$]. m/z (%)= 541 (100), 745 (60) [(HL)$_2$ + Na$^+$], 1173 (30). **EA**: Anal. Calcd. (found) [%] for $C_{18}H_{20}FN_3O_4$: C, 59.83 (59.44); H, 5.58 (5.66); N, 11.63 (11.43).

S1.5 Lomefloxacin, Hlomx

Appearance: white solid. **Mp**: >260°C. **UV-Vis** (CH_3OH with 1.1% DMSO): λ [nm] (ϵ) [M^{-1}cm^{-1}] = 291 (34500), 320 (15800), 332 (13100). **IR** (neat): $\tilde{\nu}$ [cm^{-1}] = 3055 (w), 2936 (md), 2842 (w), 2756 (sh), 2698 (st, br), 2456 (md), 1721 (st), 1611 (st), 1543 (sh), 1524 (md), 1491 (st), 1471 (sh), 1448 (st, br), 1411 (w), 1392 (st), 1328 (st), 1299 (md), 1281 (md), 1253 (st), 1205 (st), 1182 (w), 1166 (w), 1141 (md), 1114 (md), 1093 (st), 1065 (w), 1041 (st), 1021 (md), 1006 (st), 979 (md), 928 (st), 892 (st), 844 (md), 821 (md), 807 (st), 791 (sh), 756 (sh), 738 (st), 653 (md), 578 (w), 555 (md), 545 (md), 534 (md), 513 (st), 488 (md), 476 (md), 452 (md). **NMR**: $\boldsymbol{\delta_H}$ (600 MHz, 298 K, D_2O) [ppm] = 8.55 (s, 1 H, C$_{ar2}H$); 7.46 (d, $J^3_{H,F}$= 11.4 Hz, 1 H, C$_{ar5}H$); 4.48 (d, $J^3_{H,H}$= 6.0 Hz, 2H, CH_2CH$_3$); 3.70–3.53 (m, 5 H, C$_{pip2,6}H_2$ and C$_{pip3}H$); 3.42–3.38 (m, 2 H, C$_{pip4}H_2$); 1.49

(t, $J^3_{H,H}$= 7.1 Hz, 3 H, CH_2CH_3); 1.40 (d, $J^3_{H,H}$= 6.6 Hz, 3 H, CH_3). $\boldsymbol{\delta_C}$ (125 MHz, 298 K, d_6-DMSO) [ppm] = 175.3 (s, C_{ar4}); 168.3 (COOH); 154.9 (d, $J^1_{C,F}$= 208.6 Hz, C_{ar6}); 150.6 (s, C_{ar2}); 146.1 (d, $J^1_{C,F}$= 210.3 Hz, C_{ar8}); 133.0 (two overlapping d, $J^2_{C,F}$= 11.6, 11.6 Hz, C_{ar7}); 127.0 (d, $J^2_{C,F}$= 5.6 Hz, $C_{ar8'}$); 120.8 (d, $J^3_{C,F}$= 7.3 Hz, $C_{ar4'}$); 106.8 (d, $J^2_{C,F}$= 19.1 Hz, C_{ar5}); 106.1 (s, C_{ar3}); 55.0 (d, $J^4_{C,F}$= 13.5 Hz, C_{pip2}); 53.4 (s, CH_2CH_3); 51.7 (s, C_{pip6}); 46.7 (s, C_{pip3}); 43.5 (s, C_{pip5}); 15.3 (s, CH_2CH_3); 14.9 (s, CH_3). $\boldsymbol{\delta_F}$ (282 MHz, 298 K, d_6-DMSO) [ppm] = -118.6 (d, $J^4_{F,F}$= 10.7 Hz, 1 F, $C_{ar6}F$); -128.6 (d, $J^4_{F,F}$= 11.3 Hz, 1 F, $C_{ar8}F$). **MS** (ES+): *m/z* (%) = 352 (100) [HL + H^+]. *m/z* (%)= 769 (100), 725 (60) [$(HL)_2$ + Na^+], 1143 (30). **EA**: Anal. Calcd. (found) [%] for $C_{17}H_{20}F_2N_3O_3$·1 HCl: C, 52.65 (52.79); H, 5.20 (5.17); N, 10.84 (10.56).

S1.6 Nalidixic acid, Hnxa

Appearance: white solid. **Mp**: 228–230°C (soft pink). **UV-Vis** (CH_3OH with 1.1% DMSO): λ [nm] (ϵ) [$M^{-1}cm^{-1}$] = 320 (13500), 328 (13700). **IR** (neat): $\tilde{\nu}$ [cm^{-1}] = 3044 (md, br), 2987 (w, br), 2948 (w), 1707 (st, br), 1614 (st, br), 1562 (w), 1538 (w), 1518 (md), 1465 (sh), 1440 (st, br), 1384 (w), 1370 (md), 1353 (md), 1327 (w), 1294 (md), 1270 (sh), 1252 (st), 1227 (st), 1129 (st), 1102 (w), 1051 (w), 1034 (w), 971 (st, br), 875 (md), 803 (st), 777 (sh), 706 (md), 656 (md), 634 (md), 563 (w), 539 (md), 505 (w), 485 (st), 454 (md). **NMR**: $\boldsymbol{\delta_H}$ (300 MHz, 298 K, d_6-DMSO) [ppm] = 9.18 (s, 1 H, $C_{ar2}H$); 8.60 (d, $J^3_{H,H}$= 8.2 Hz, 1 H, $C_{ar5}H$); 7.59 (d, $J^3_{H,H}$= 8.2 Hz, 1 H, $C_{ar6}H$); 4.64 (q, $J^3_{H,H}$= 7.1 Hz, 2 H, CH_2CH_3); 2.71 (s, 3 H, CH_3); 1.42 (t, $J^3_{H,H}$= 7.1 Hz, 3 H, CH_2CH_3). $\boldsymbol{\delta_C}$ (75 MHz, 298 K, d_6-DMSO) [ppm] = 178.2 (s, C_{ar4}); 165.6 (s, $C_{ar8'}$); 164.7 (s, COOH); 149.7 (s, C_{ar2}); 148.3 (s, C_{ar7}); 135.6 (s, C_{ar5}); 122.6 (s, C_{ar6}); 118.3 (s, $C_{ar4'}$); 108.6 (s, C_{ar3}); 46.8 (s, CH_2CH_3); 25.1 (s, CH_3); 15.0 (s, CH_2CH_3). **MS** (ES+): *m/z* (%) = 255 (100)

[HL + Na^+], 233 (60) [HL + H^+]. *m/z* (%)= 786 (100) [$(HL)_3$ + Na^+], 1040 (30) [$(HL)_4$ + Na^+], 1294 (10) [$(HL)_5$ + Na^+]. **EA**: Anal. Calcd. (found) [%] for $C_{12}H_{12}N_2O_3$: C, 62.06 (62.32); H, 5.21 (5.18); N, 12.06 (11.94).

S1.7 Norfloxacin, Hnofx

Appearance: pale yellow solid. **Mp**: 221−223°C (yellow). **UV-Vis** (CH_3OH with 1.5% DMSO): λ [nm] (ϵ) [$M^{-1}cm^{-1}$] = 290 (21900), 317 (9900), 330 (8700). **IR** (neat): $\tilde{\nu}$ [cm^{-1}] = 3046 (w, br), 2944 (md), 2827 (md, br), 1722 (st), 1614 (st), 1519 (md), 1471 (st), 1439 (st), 1401 (w), 1373 (md), 1350 (md), 1323 (w), 1300 (md), 1272 (w), 1248 (st), 1210 (md), 1198 (st), 1148 (md), 1127 (md), 1102 (st), 1090 (sh), 1050 (w), 1025 (md), 978 (w), 945 (st, br), 885 (st), 838 (st), 826 (sh), 804 (st), 783 (md), 748 (st), 712 (w), 698 (st), 664 (md), 638 (md), 620 (md), 557 (md), 514 (md), 498 (md), 485 (w), 450 (md). **NMR**: $\boldsymbol{\delta_H}$ (300 MHz, 298 K, d_6-DMSO) [ppm] = 8.92 (s, 1 H, $C_{ar2}H$); 7.85 (d, $J^3_{H,F}$= 13.5 Hz, 1 H, $C_{ar5}H$); 7.12 (d, $J^4_{H,F}$= 7.3 Hz, 1 H, C_{ar8}H); 4.57 (q, $J^3_{H,H}$= 7.1 Hz, 2 H, CH_2CH_3); 3.22 (dd, $J^3_{H,H}$= 5.9, 3.8 Hz, 4 H, $C_{pip2,6}H_2$); 2.89 (dd, $J^3_{H,H}$= 5.9, 3.8 Hz, 4 H, $C_{pip3,5}H_2$); 1.41 (t, $J^3_{H,H}$= 7.1 Hz, 3 H, CH_2CH_3). $\boldsymbol{\delta_C}$ (75 MHz, 298 K, d_6-DMSO) [ppm] = 176.1 (d, $J^4_{C,F}$= 2.7 Hz, C_{ar4}); 166.1 (s, COOH); 152.5 (d, $J^1_{C,F}$= 207.5 Hz, C_{ar6}); 148.3 (s, C_{ar2}); 145.9 (d, $J^2_{C,F}$= 9.7 Hz, C_{ar7}); 137.2 (s, $C_{ar8'}$); 118.9 (d, $J^3_{C,F}$= 7.7 Hz, $C_{ar4'}$); 111.0 (d, $J^2_{C,F}$= 23.1 Hz, C_{ar5}); 107.0 (s, C_{ar3}); 105.4 (d, $J^3_{C,F}$= 3.7 Hz, C_{ar8}); 50.8 (d, $J^4_{C,F}$= 4.8 Hz, $C_{pip2,6}$); 49.0 (s, CH_2CH_3); 45.4 (s, $C_{pip3,5}$); 14.3 (s, CH_2CH_3). $\boldsymbol{\delta_F}$ (282 MHz, 298 K, d_6-DMSO) [ppm] = -121.3 (s, 1 F, $C_{ar6}F$). **MS** (ES+): *m/z* (%) = 320 (100) [HL + H^+]. *m/z* (%)= 662 (70) [2 HL + Na^+]. **EA**: Anal. Calcd. (found) [%] for $C_{16}H_{18}FN_3O_3$: C, 60.18 (60.02); H, 5.68 (5.75); N, 13.16 (12.92).

S1.8 Oxolinic acid, Hoxa

Appearance: white solid. **Mp**: >260°C. **UV-Vis** (CH_3OH with 2.2% DMSO): λ [nm] (ϵ) [$M^{-1}cm^{-1}$] = 322 (7600), 336 (7700). **IR** (neat): $\tilde{\nu}$ [cm^{-1}] = 3061 (md), 2984 (md), 2930 (md, br), 1698 (st), 1632 (st), 1573 (st), 1504 (md), 1440 (st, br), 1384 (md), 1350 (sh), 1301 (md) 1259 (st), 1222 (w), 1204 (w), 1186 (md), 1127 (md), 1094 (w), 1075 (md), 1036 (st), 936 (st, br), 876 (st), 856 (st), 807 (st), 773 (md), 754 (md), 690 (md), 645 (st), 605 (md), 556 (md), 498 (md), 447 (md). **NMR**: $\boldsymbol{\delta_H}$ (300 MHz, 298 K, d_6-DMSO) [ppm] = 8.89 (s, 1 H, $C_{ar2}H$); 7.63 (s, 1 H, $C_{ar8}H$); 7.61 (s, 1 H, $C_{ar5}H$); 6.29 (s, 2 H, OCH_2O); 4.53 (q, $J^3_{H,H}$= 7.1 Hz, 2 H, CH_2CH_3); 1.38 (t, $J^3_{H,H}$= 7.1 Hz, 3 H, CH_2CH_3). $\boldsymbol{\delta_C}$ (75 MHz, 298 K, d_6-DMSO) [ppm] = 176.0 (s, C_{ar4}); 166.3 (s, COOH); 153.7 (s, C_{ar7}); 147.10 (s, C_{ar6}); 147.0 (s, C_{ar2}); 136.9 (s, $C_{ar8'}$); 121.3 (s, $C_{ar4'}$); 107.3 (s, C_{ar3}); 103.3 (s, OCH_2O); 101.8 (s, C_{ar5}); 97.2 (s, C_{ar8}); 49.6 (s, CH_2CH_3); 14.6 (s, CH_2CH_3). **MS** (ES+): *m/z* (%) = 284 (100) [HL + Na^+], 262 (10) [HL + H^+]. *m/z* (%)= 589 (90) [$(HL)_2$ + Na^+], 873 (100) [$(HL)_3$ + Na^+], 1156 (30) [$(HL)_4$ + Na^+]. **EA**: Anal. Calcd. (found) [%] for $C_{13}H_{11}NO_5$: C, 59.77 (59.83); H, 4.24 (4.24); N, 5.36 (5.37).

S1.9 Pipemidic acid, Hpia

Appearance: white, fine powdered solid. **Mp**: 258–260°C (orange-brown). **UV-Vis** (CH_3OH with 2.2% DMSO): λ [nm] (ϵ) [$M^{-1}cm^{-1}$] = 288 (13500), 325 (7300), 342 (5400). **IR** (neat): $\tilde{\nu}$ [cm^{-1}] = 3365 (md, br), 3028 (w), 2979 (w), 1615 (st), 1577 (st), 1532 (md), 1510 (md), 1471 (st), 1429 (st), 1378 (sh), 1357 (st, br), 1309 (md), 1279 (md), 1238 (st, br), 1259 (w), 1159 (w), 1147 (w), 1127 (st), 1092 (md), 1078 (md), 1044 (md) 1022 (st), 975 (md), 940 (md), 914 (st), 903 (md), 867 (md), 832 (st), 802 (md), 783 (md), 743 (st), 715 (md), 655 (w), 608 (w), 540 (st), 489 (md), 453 (md). **NMR**: $\boldsymbol{\delta_H}$ (300 MHz, 298 K,

d_6-DMSO) [ppm] = 9.15 (s, 1 H, $C_{ar5}H$); 8.93 (s, 1 H, $C_{ar2}H$); 4.36 (q, $J^3_{H,H}$= 7.1 Hz, 2 H, CH_2CH_3); 3.84 (d, $J^3_{H,H}$= 17.1 Hz, 4 H, $C_{pip2,6}H_2$); 2.78 (br s, 4 H, $C_{pip3,5}H_2$); 1.35 (t, $J^3_{H,H}$= 7.1 Hz, 3 H, CH_2CH_3). $\boldsymbol{\delta_C}$ (75 MHz, 298 K, d_6-DMSO) [ppm] = 177.1 (s, C_{ar4}); 165.3 (s, *C*OOH); 160.5 (C_{ar7}); 160.1 (s, C_{ar5}); 155.1 (s, $C_{ar8'}$); 150.6 (s, C_{ar2}); 109.5 (s, $C_{ar4'}$); 108.3 (s, C_{ar3}); 45.8 (s, CH_2CH_3); 45.3 (br s, $C_{pip2,3,5,6}$); 14.4 (s, CH_2CH_3). **MS** (ES+): *m/z* (%) = 304 (50) [HL + H^+], 326 (70) [HL + Na^+], 348 (100) [HL + CO_2 + H^+]. *m/z* (%)= 673 (40) [$(NaL)_2$ + Na^+], 999 (95) [$(NaL)_3$ + Na^+]. **EA**: Anal. Calcd. (found) [%] for $C_{14}H_{17}N_5O_3$: C, 55.44 (55.10); H, 5.65 (5.63); N, 23.09 (22.96).

S2 Synthesis & Characterization of Tris(quinolono)metal(III) Complexes

The tris(quinolino)metal(III) complexes were synthesized according to the following three general synthetic methods:

Method (a): To a solution of metal(III)nitrate nonahydrate (0.1 mmol) in water (2 mL), an acidified aqueous solution (8 mL) of the quinolone (0.3 mmol) was added dropwise. During the addition the pH was carefully monitored and kept below pH 5; finally, raising the pH to pH 7.5 with aqueous sodium hydroxide (1.0 M and 0.1 M) resulted in a characteristically colored solution (yellow for Ga^{3+}, red-brown for Fe^{3+}) that was stirred vigorously at room temperature for 20 min, before the vial was closed tightly and placed in the fridge at 4°C. After 3–5 days the desired product had precipitated. The solid was separated by filtration (glass frit size F), thoroughly washed with water (2 mL) and methanol (2 mL), and dried *in vacuo*.

Method (b) is a modification of the reported synthesis of tris(nalidixido)iron(III):[2] The

quinolone (0.3 mmol) was heated with sodium bicarbonate or sodium hydroxide (0.3 mmol) in water (10 mL) until the initially white suspension had turned into a clear solution, which was then added onto the solid metal(III) nitrate nonahydrate (0.1 mmol). Upon addition the pH was kept at pH$\leq$5, the desired product started forming immediately and precipitated as solid (final pH$\sim$7). The suspension was stirred vigorously until it had cooled to room temperature (for a minimum of 30 min, often overnight). The desired product, which precipitated often at room temperature or otherwise after placing the reaction vial in the fridge (4°C) was separated by filtration (glass grit, size F) as a solid, washed with water (2 mL) and methanol (2 mL), and dried *in vacuo*.

Method (c) is a modification of the reported synthesis of tris(ciprofloxacino)iron(III):[3] A suspension of quinolone (0.31 mmol) with sodium hydroxide or potassium hydroxide (0.33 mmol) in methanol (15 mL) was refluxed until it turned into a clear, colorless solution. The hot methanolic solution was added onto the solid metal(III)nitrate nonahydrate (0.1 mmol), and the resulting colored solution was refluxed further for thirty minutes. The reaction solution was left to cool in air. Evaporation of the solvent in air, or a reduction of the solvent by at least 50% volume, led to precipitation of a colored solid, which was separated by filtration (glass frit, size F), thoroughly washed with water (2 mL) and methanol (2 mL), and dried *in vacuo*.

The method that gave the highest product purity, as determined by EA and HR-ESI mass spectrometry, at a 0.1 mmol scale is reported.

S2.1 Tris(ciprofloxacino)gallium(III), [Ga(cipro)$_3$]

Method (c) gave a pale yellow solid (99 mg, 0.094 mmol, 94%). **Mp**: $\geq$220°C, decomposition to brown solid. **IR** (neat): $\tilde{\nu}$ [cm^{-1}] = 3418 (md, br, water), 2846 (w, br) 1620 (st),

1545 (w), 1516 (sh), 1472 (st), 1451 (sh), 1373 (st, br), 1287 (sh), 1252 (st), 1182 (md) 1146 (md), 1106 (sh), 1025 (st), 949 (st), 893 (md), 810 (md), 787 (md), 765 (sh), 740 (st, br), 704 (md), 627 (st), 540 (md), 505 (st). **NMR**: $\boldsymbol{\delta_H}$ (600 MHz, 298 K, d_6-DMSO) [ppm] = 8.93 (s), 8.84 (s), 8.80 (s), (3 H, $C_{ar2}H$); 7.65 (d, $J^3_{H,F}$= 13.8 Hz), 7.57−7.53 (m), 7.41 (d, $J^4_{H,F}$= 7.2 Hz), (6 H, $C_{ar5}H$ and $C_{ar8}H$); 3.95−3.81 (m, 3 H, $C_{prop}H$); 3.29−3.20 (m, 12 H overlaid with water, $C_{pip2,6}H_2$); 2.96−2.91 (m, 12 H, $C_{pip3,5}H_2$); 1.36−1.32 (m, 6 H, $C_{prop}H_{b,b'}$); 1.23−0.82 (m, 6 H, $C_{prop}H_{a,a'}$). $\boldsymbol{\delta_C}$ (125 MHz, 298 K, d_6-DMSO) [ppm] = 173.7 (s), 173.6 (s), 173.2 (s), (C_{ar4}); 165.6 (s), 165.5 (s), 165.3 (s), (COOH); 153.1 (d, $J^1_{C,F}$= 206.1 Hz), 153.0 (d, $J^1_{C,F}$= 207.1 Hz), 152.9 (d, $J^1_{C,F}$= 207.3 Hz), (C_{ar6}); 149.8 (s), 149.6 (s), 149.3 (s), 149.2 (s), (C_{ar2}); 145.4 (d, $J^2_{C,F}$= 21.0 Hz), 145.3 (d, $J^2_{C,F}$= 21.8 Hz), 145.2 (d, $J^2_{C,F}$= 19.5 Hz), (C_{ar7}); 139.0 (s), 138.8 (s), 138.7 (s), ($C_{ar8'}$); 118.7 (d, $J^3_{C,F}$= 6.9 Hz), 118.6 (d, $J^3_{C,F}$= 7.0 Hz), 118.4 (d, $J^3_{C,F}$= 7.8 Hz), ($C_{ar4'}$); 111.8 (s), 111.7 (s), 111.5 (s), (C_{ar5}); 110.5 (s), 110.3 (s), 110.2 (s), (C_{ar3}); 106.3 (s), 105.7 (s), 105.3 (s), (C_{ar8}); 50.1 (s), 50.0 (s), 49.9 (s), ($C_{pip2,6}$); 45.0 (s), 44.9 (s), 44.8 (s), ($C_{pip3,5}$); 36.2 (s), 36.0 (s), 35.9 (s), 35.8 (s), (C_{prop}H); 7.7 (s), 7.6 (s), 7.5 (s), ($C_{prop}H_2$). $\boldsymbol{\delta_F}$ (282 MHz, 298 K, d_6-DMSO) [ppm] = -121.1 (s), -121.15 (s), -121.21 (s), (3 F, $C_{ar6}F$). **MS** (ES+, CH_3OH): *m/z* (%) = 1083 (40) [ML_3 + Na^+], 730 (100) $[ML_2]^+$. **HR-ESI-MS**: *m/z* for $C_{51}H_{51}F_3$ $^{69}GaN_9O_9$ + H^+ calcd. (found): 1060.3096 (1060.3073); for $C_{34}H_{34}F_2$ $^{69}GaN_6O_6{}^+$ calcd. (found): 729.1764 (729.1785). **EA**: Anal. Calcd. (found) [%] for $C_{51}H_{51}F_3GaN_9O_9{\cdot}8$ H_2O: C, 50.84 (50.61); H, 5.60 (4.80); N, 10.46 (10.79).

S2.2 Tris(enoxacino)gallium(III), [Ga(enox)$_3$]

Method (b) gave a pale yellow solid (85 mg, 0.082 mmol, 82%). **Mp**: ≥200°C, decomposition to light brown solid. **IR** (neat): $\tilde{\nu}$ [cm^{-1}] = 3404 (md, br, water), 3045 (w, br), 2977

(w, br), 1625 (st), 1562 (md), 1519 (md), 1469 (sh), 1434 (st, br), 1369 (md), 1346 (st), 1323 (md), 1276 (st), 1253 (st, br), 1185 (md), 1153 (w), 1119 (md), 1092 (md), 1039 (md, br), 972 (md), 941 (md, br), 908 (sh), 812 (st), 789 (md), 766 (md), 746 (md), 677 (w), 651 (md), 626 (st), 563 (md), 516 (st), 453 (w). **NMR**: $\boldsymbol{\delta_H}$ (300 MHz, 298 K, d_6-DMSO) [ppm] = 9.18 (s), 9.13 (s), 9.08 (s), 9.04 (s), 8.99 (s) (3 H, $C_{ar2}H$); 8.12 (d, $J^3_{H,F}$= 13.2 Hz), 7.75 (d, $J^3_{H,F}$= 13.2 Hz), 7.72 (d, $J^3_{H,F}$= 14.0 Hz), 7.69 (d, $J^3_{H,F}$= 13.8 Hz), (3 H, $C_{ar5}H$); 4.59−4.43 (m, 6 H, CH_2CH_3); 3.92−3.85 (m, 12 H, $C_{pip2,6}H_2$); 3.12−3.02 (m, 12 H, $C_{pip3,5}H_2$); 1.43−1.23 (m, 9 H, CH_2CH_3). $\boldsymbol{\delta_C}$ (75 MHz, 298 K, d_6-DMSO) [ppm] = 173.9 (s), 173.5 (s), 173.4 (s), (C_{ar4}); 168.9 (s), 168.8 (s), 168.7 (s), ($C_{ar8'}$); 165.8 (s), 165.6 (s), 165.5 (s), 165.3 (s), (COOH); 149.6 (d, $J^2_{H,F}$= 90.3 Hz), 149.4 (d, $J^2_{H,F}$= 85.1 Hz), 149.0 (d, $J^2_{H,F}$= 89.4 Hz), (C_{ar7}); 147.2 (d, $J^1_{H,F}$= 207.0 Hz), 147.1 (d, $J^1_{H,F}$= 202.8 Hz), 147.0 (d, $J^2_{H,F}$= 214.6 Hz), 146.9 (d, $J^1_{H,F}$= 215.4 Hz), (C_{ar6}); 144.7 (s), 144.3 (s), 144.1 (s), (C_{ar2}); 119.6 (d, $J^2_{C,F}$= 18.1 Hz), 119.0 (d, $J^2_{C,F}$= 17.5 Hz), 118.70 (d, $J^2_{C,F}$= 19.6 Hz), (C_{ar5}); 113.2−112.6 (m, $C_{ar4'}$); 108.1 (s), 108.0 (s), 109.9 (s), (C_{ar3}); 47.5 (s), 47.3 (s), 47.2 (s), ($C_{pip2,6}$); 46.2 (s), 45.9 (s), 45.6 (s), (CH$_2$CH$_3$); 44.2 (s), 44.0 (s), 43. 7 (s), ($C_{pip3,5}$); 14.9 (s), 14.8 (s), 14.7 (s), (CH$_2C$H$_3$). $\boldsymbol{\delta_F}$ (282 MHz, 298 K, d_6-DMSO) [ppm] = -126.4, -126.5, -126.6, -126.8 (3 F, $C_{ar6}F$). **MS** (ES+, CH_3OH): *m/z* (%) = 1050 (20) [ML_3 + Na^+], 708 (100) $[ML_2]^+$. **HR-ESI-MS**: *m/z* for $C_{45}H_{48}F_3\ ^{69}GaN_{12}O_9$ + Na^+ calcd. (found): 1049.2773 (1049.2797).

S2.3 Tris(fleroxacino)gallium(III), [Ga(flex)$_3$]

Method (b) gave a pale yellow solid (85 mg, 0.082 mmol, 82%). **Mp**: ≥230°C, decomposition to orange-brown solid. **IR** (neat): $\tilde{\nu}$ [cm^{-1}] = 3392 (w, br, water), 3054 (md), 2943 (md), 2848 (w), 2796 (md), 1622 (st), 1556 (md), 1514 (md), 1475 (st, br), 1449 (sh), 1409

(w), 1391 (w), 1376 (md), 1360 (md), 1328 (md), 1280 (st), 1245 (md), 1230 (w), 1214 (w), 1206 (w), 1143 (st), 1123 (md), 1099 (w), 1077 (w), 1062 (md), 1037 (md), 1020 (st), 1010 (st), 970 (md), 942 (md), 926 (md), 869 (md), 853 (md), 807 (st), 783 (md), 754 (sh), 741 (st), 672 (w), 656 (st), 573 (st), 550 (md), 532 (w), 505 (w, br), 450 (md, br). **NMR**: $\boldsymbol{\delta_H}$ (600 MHz, 298 K, d_6-DMSO) [ppm] = 8.86 (s, 3 H, $C_{ar2}H$); 7.87 (d, $J^3_{H,F}$= 11.4 Hz, 3 H, $C_{ar5}H$); 4.98−4.96 (m), 4.93−4.90 (m), 4.86−4.84 (m) (12 H, $(CH_2)_2$); 3.36 (br s, 12 H overlaid with water, $C_{pip2,6}H_2$); 2.44 (s, 12 H, $C_{pip3,5}H_2$); 2.23 (s, 9 H, CH_3). $\boldsymbol{\delta_C}$ (125 MHz, 298 K, d_6-DMSO) [ppm] = 175.8 (s, C_{ar4}); 165.5 (s, COOH); 154.6 (d, $J^1_{C,F}$= 205.9 Hz), 154.5 (d, $J^1_{C,F}$= 206.5 Hz), (C_{ar6}); 152.1 (s, C_{ar2}); 146.1 (d, $J^1_{C,F}$= 205.9 Hz, C_{ar8}), 146.0 (d, $J^1_{C,F}$= 205.9 Hz, (C_{ar8}); 133.9 (two overlapping d, $J^2_{C,F}$= 11.3, 11.5 Hz, C_{ar7}); 127.4 (d, $J^2_{C,F}$= 9.1 Hz, $C_{ar8'}$); 120.1 (d, $J^3_{C,F}$= 6.8 Hz, $C_{ar4'}$); 107.1 (d, $J^2_{C,F}$= 18.9 Hz, C_{ar5}); 106.6 (s, C_{ar3}); 82.0 (d, $J^1_{C,F}$= 137.0 Hz, CH_2CH_2F); 58.0 (d, $J_{C,F}$= 11.9 Hz), 57.8 (d, $J_{C,F}$= 16.4 Hz), (CH_2CH_2F); 55.1 (s, $C_{pip2,6}$); 50.3 (s, $C_{pip3,5}$); 46.0 (s, CH_3). $\boldsymbol{\delta_F}$ (282 MHz, 298 K, d_6-DMSO) [ppm] = -119.2 (d, $J^4_{F,F}$= 11.0 Hz, 3 F, $C_{ar6}F$); -127.6 (q, $J_{F,F}$= 5.6 Hz, 3 F, $C_{ar8}F$); -224.2 (d, $J^6_{C,F}$= 6.0 Hz, 3 F, $(CH_2)_2F$). **MS** (ES+, CH_3OH): *m/z* (%) = 1197 (80) [ML_3 + Na^+], 806 (100) $[ML_2]^+$. **HR-ESI-MS**: *m/z* for $C_{51}H_{51}F_9$ $^{69}GaN_9O_9$ + Na^+ calcd. (found): 1196.2820 (1196.2838); for $C_{34}H_{34}F_6$ $^{69}GaN_6O_6{}^+$ calcd. (found): 805.1700 (805.1719).

S2.4 Tris(levofloxacino)gallium(III), [Ga(levox)$_3$]

Method (a) gave a yellow solid (47 mg, 0.041 mmol, 41%). **Mp**: ≥190°C, decomposition to orange-brown solid. **IR** (neat): $\tilde{\nu}$ [cm^{-1}] = 3426 (md, br, water), 3033 (w, br), 2931 (w), 2848 (w), 2794 (w), 1616 (st), 1519 (st), 1447 (st), 1385 (md, sh), 1331 (st, br), 1261 (st), 1150 (sh), 1129 (md), 1093 (md), 1047 (st), 1003 (md), 978 (st), 898 (md), 866 (md),

844 (w), 810 (st), 763 (md), 744 (st), 696 (md), 638 (w), 554 (md), 510 (st), 463 (md, br). **NMR**: $\boldsymbol{\delta_H}$ (600 MHz, 298 K, d_6-DMSO) [ppm] = 9.25 (s), 9.19 (s), 9.13 (s), 9.01 (s), 9.98 (s), 9.93 (s), 8.98 (s), (3 H, C$_{ar2}H$); 7.60 (d, $J^3_{H,F}$= 12.0 Hz), 7.48−7.45 (m), 7.42 (d, $J^3_{H,F}$= 12.0 Hz), 7.29 (d, $J^3_{H,F}$= 12.0 Hz), 7.24−7.211, 7.14 (d, $J^3_{H,F}$= 12.6 Hz), (3 H, C$_{ar5}H$); 5.08−4.88 (m, 3 H, CH); 4.64−4.27 (m, 6 H, OCH_2CH); 3.50−3.26 (m, 12 H overlaid with water, C$_{pip2,6}H_2$); 2.76−2.61 (m, 12 H, C$_{pip3,5}H_2$); 2.46−2.38 (m, 9 H, NCH_3); 1.52−1.42 (m), 1.23 (br s), 1.14−1.08 (m), (9 H, CHCH_3). $\boldsymbol{\delta_C}$ (125 MHz, 298 K, d_6-DMSO) [ppm] = 176.4 (s), 173.6 (s), 173.4 (s), 173.2 (s), (C_{ar4}); 166.0 (s), 165.8 (s), 165.6 (s), 165.4 (s), (COOH); 155.5 (d, $J^1_{C,F}$= 204.8 Hz), 155.4 (d, $J^1_{C,F}$= 203.3 Hz), 155.2 (d, $J^1_{C,F}$= 200.0 Hz), (C_{ar6}); 148.2 (s), 147.9 (s), 147.7 (s), 147.5 (s), 146.3 (s), (C_{ar2}); 140.4 (d, $J^3_{C,F}$= 5.8 Hz), 139.8 (d, $J^3_{C,F}$= 8.9 Hz), 139.2 (d, $J^3_{C,F}$= 10.4 Hz), (C_{ar8}); 131.1−130.8 (m, C_{ar7}); 124.9 (s), 124.6 (s), 124.5 (s), 124.2 (s), ($C_{ar8'}$); 120.0 (s), 119.8 (s), 119.5 (s), 119.4 (s) ($C_{ar4'}$); 112.6 (s), 112.5 (s), 111.8 (s), 111.6 (s), 106.7 (s), (C_{ar3}); 103.3 (d, $J^2_{C,F}$= 20.4 Hz), 102.9 (d, $J^2_{C,F}$= 24.5 Hz), 102.3 (d, $J^2_{C,F}$= 22.8 Hz), (C_{ar5}); 68.2 (s), 68.0 (s), 67.9 (s), (OCH$_2$CH); 55.2 (s), 55.0 (s), 54.8 (s), ($C_{pip2,6}$); 54.7 (s), 54.6 (s), 54.5 (s), (CH); 49.4−48.8 (m, $C_{pip3,5}$); 45.2−44.4 (m, NCH$_3$); 18.2−17.7 (m, CH(CH$_3$)). $\boldsymbol{\delta_F}$ (282 MHz, 298 K, d_6-DMSO) [ppm] = -119.4 (s), -119.5 (s), -119.7 (s), -119.8 (s), -119.86 (s), -119.93 (s), (3 F, C$_{ar6}F$). **MS** (ES+, CH$_3$OH): *m/z* (%) = 1173 (40) [ML$_3$ + Na$^+$], 790 (100) [ML$_2$]$^+$. **HR-ESI-MS**: *m/z* for C$_{54}$H$_{57}$F$_3$ ^{69}GaN$_9$O$_{12}$ + Na$^+$ calcd. (found): 1172.3232 (1172.3248); for C$_{36}$H$_{38}$F$_2$ ^{69}GaN$_6$O$_8^+$ calcd. (found): 789.1975 (789.1989).

S2.5 Tris(lomefloxacino)gallium(III), [Ga(lomx)$_3$]

Method (a) gave a pale yellow solid (40 mg, 0.035 mmol, 35%). **Mp**: ≥200°C, decomposition to brown solid. **IR** (neat): $\tilde{\nu}$ [cm^{-1}] = 3419 (md, br, water), 2980 (w, br), 2848

(w, br), 2478 (w, br), 1619 (st), 1556 (w), 1523 (st), 1452 (st), 1354 (md, sh), 1323 (st, br), 1277 (md), 1247 (st), 1123 (md), 1090 (md), 1050 (st), 1001 (st), 932 (st), 886 (md), 811 (st), 776 (w), 742 (md), 651 (md), 542 (sh), 505 (md, br). **NMR**: $\boldsymbol{\delta_H}$ (600 MHz, 298 K, D_2O) [ppm] = 9.18 (s), 9.15 (s), 9.01 (s), 9.05 (s), 8.94 (s), (3 H, $C_{ar2}H$); 7.87 (d, $J^3_{H,F}$= 11.4 Hz), 7.66 (d, $J^3_{H,F}$= 11.4 Hz), 7.61 (d, $J^3_{H,F}$= 10.8 Hz), 7.51 (d, $J^3_{H,F}$= 10.2 Hz), (3 H, $C_{ar5}H$); 4.68−4.58 (m, 6 H, CH_2CH_3); 3.43−3.28 (m, 12 H, $C_{pip2,6}H_2$, and 3 H, $C_{pip3}H$); 3.10−2.91 (m, 12 H, $C_{pip4}H_2$); 1.48−1.34 (m, 9 H, CH_2CH_3); 1.10−1.07 (m, 9 H, CH_3). $\boldsymbol{\delta_C}$ (125 MHz, 298 K, d_6-DMSO) [ppm] = 175.7 (s), 173.1 (s), 172.8 (s), (C_{ar4}); 165.7 (s), 165.3 (s), 165.0 (s), 164.1 (s), (COOH); 154.8 (d, $J^1_{C,F}$= 207.1 Hz), 154.6 (d, $J^1_{C,F}$= 205.8 Hz), 154.6 (d, $J^1_{C,F}$= 207.8 Hz), (C_{ar6}); 153.4 (s), 153.1 (s), 152.8 (s), 151.4 (s), (C_{ar2}); 146.2 (d, $J^1_{C,F}$= 207.0 Hz); 146.1 (d, $J^1_{C,F}$= 207.4 Hz); 145.5 (d, $J^1_{C,F}$= 212.2 Hz), (C_{ar8}); 133.7 (s), 133.6 (s), 133.5 (s), 133.4 (s), (C_{ar7}); 127.4 (d, $J^2_{C,F}$= 5.5 Hz), 127.2 (d, $J^2_{C,F}$= 5.0 Hz), ($C_{ar8'}$); 120.8 (d, $J^3_{C,F}$= 6.3 Hz), 120.4 (d, $J^3_{C,F}$= 6.0 Hz), ($C_{ar4'}$); 112.3 (s), 112.2 (s), 112.1 (s), (C_{ar5}); 107.2 (s), 107.1 (s), 106.6 (s), (C_{ar3}); 56.5 (s), 56.4 (s), 56.3 (s), (C_{pip2}); 54.2 (s), 54.1 (s), 53.9 (s), 53.8 (s), (CH_2CH_3); 51.0 (s), 50.9 (s), 49.5 (s), (C_{pip6}); 49.5 (br s, C_{pip3}); 44.9 (br, s, C_{pip5}); 17.9 (s), 17.7 (br s) (CH_2CH_3); 16.3 (s), 16.2 (s), 16.1 (s), (CH_3). $\boldsymbol{\delta_F}$ (282 MHz, 298 K, d_6-DMSO) [ppm] = (-118.8)−(-118.9) (m), -119.4 (d, $J^4_{F,F}$= 10.7 Hz), (3 F, $C_{ar6}F$); -129.4 (d, $J^4_{F,F}$= 10.4 Hz), (-129.9)−(-130.4) (m), (3 F, $C_{ar8}F$). **MS** (ES+, CH_3OH): *m/z* (%) = 1143 (30) [ML_3 + Na^+], 770 (100) $[ML_2]^+$. **HR-ESI-MS**: *m/z* for $C_{51}H_{54}F_6$ $^{69}GaN_9O_9$ + Na^+ calcd. (found): 1142.3102 (1142.3093).

S2.6 Tris(nalidixo)gallium(III), [Ga(nxa)$_3$]

Method (b) gave an off-white solid (37 mg, 0.046 mmol, 46%). **Mp**: ≥190°C, decomposition to beige-brown solid. **IR** (neat): $\tilde{\nu}$ [cm^{-1}] = 3443 (md, br, water), 3025 (md, br), 2985 (w), 1676 (sh), 1608 (st, br), 1557 (st), 1518 (sh), 1490 (st), 1440 (st), 1380 (w), 1365 (md), 1348 (md), 1320 (md), 1293 (st), 1256 (st), 1227 (sh), 1168 (w), 1130 (st), 1109 (w), 1089 (md), 991 (w, br), 944 (w), 898 (md), 843 (w), 807 (st), 776 (st), 702 (w), 663 (md), 639 (md), 561 (sh), 543 (md), 506 (st), 452 (st). **NMR**: $\boldsymbol{\delta_H}$ (600 MHz, 298 K, d_6-DMSO) [ppm] = 9.45 (s), 9.35 (s), 9.27 (s), 9.19 (s), (3 H, C$_{ar2}H$); 8.62 (d, $J^3_{H,H}$= 8.2 Hz), 8.43−8.31 (m) (3 H, C$_{ar5}H$); 7.61 (d, $J^3_{H,H}$= 8.2 Hz), 7.56 (d, $J^3_{H,H}$= 8.4 Hz), 7.51 (d, $J^3_{H,H}$= 7.8 Hz), (3 H, C$_{ar6}H$); 4.76−4.57 (m, 6 H, CH_2CH$_3$); 2.69 (d, $J^4_{H,H}$= 30.0 Hz, 9 H, C$_{ar7}$CH_3); 1.45 (t, $J^3_{H,H}$= 6.9 Hz), 1.42 (t, $J^3_{H,H}$= 7.1 Hz), 1.31 (t, $J^3_{H,H}$= 7.1 Hz), (9 H, CH$_2$CH_3). $\boldsymbol{\delta_C}$ (125 MHz, 298 K, d_6-DMSO) [ppm] = 178.1 (s), 175.6 (s), 175.4 (s), 175.2 (s), (C_{ar4}); 165.6 (s), 165.3 (s), 165.1 (s), 165.0 (s), ($C_{ar8'}$) 164.9 (s), 164.8 (s), 164.7 (s), (COOH) 151.7 (s), 151.4 (s), 151.3 (s), 151.1 (s), (C_{ar2}); 149.7 (s), 148.4 (s), 147.7 (s), 147.4 (s), (C_{ar7}); 135.9 (s), 135.7 (s), 135.4 (s), 135.3 (s), (C_{ar5}); 123.0 (s), 122.9 (s), 122.6 (s), (C_{ar6}); 118.4 (s), 118.2 (s), 118.1 (s), 118.0 (s), ($C_{ar4'}$); 113.7 (s), 113.6 (s), 113.3 (s), (C_{ar3}); 47.1 (s), 47.0 (s), 46.9 (s), 46.8 (s), (CH$_2$CH$_3$); 25.1 (br s) (CH$_3$); 15.2 (s), 15.1 (s), 15.0 (s), (CH$_2C$H$_3$). **MS** (ES+, CH$_3$OH): *m/z* (%) = 1296 (10) [M$_2$L$_5$]$^+$, 785 (100) [ML$_3$ + Na$^+$], 531 (20) [ML$_2$]$^+$. **HR-ESI-MS**: *m/z* for C$_{36}$H$_{33}$ ^{69}GaN$_6$O$_9$ + Na$^+$ calcd. (found): 785.1463 (785.1479). **EA**: Anal. Calcd. (found) [%] for C$_{36}$H$_{33}$GaN$_6$O$_9$·1.5 H$_2$O: C, 54.70 (54.59); H, 4.59 (4.42); N, 10.63 (10.24).

S2.7 Tris(norfloxacino)gallium(III), [Ga(nofx)$_3$]

Method (a) gave a pale yellow solid (38 mg, 0.036 mmol, 36%). **Mp**: ≥200°C, decomposition to orange-brown solid. **IR** (neat): $\tilde{\nu}$ [cm^{-1}] = 3391 (md, br, water), 2839 (w, br), 1615 (st, br), 1551 (w), 1519 (md), 1471 (st, br), 1377 (md), 1320 (md), 1255 (st, br), 1188 (md), 1129 (md), 1089 (w), 1037 (md), 971 (w), 930 (st), 889 (sh), 812 (st), 788 (md), 769 (md), 747 (st), 697 (w), 628 (st), 561 (md), 513 (st). **NMR**: $\boldsymbol{\delta_H}$ (600 MHz, 298 K, d_6-DMSO) [ppm] = 9.19 (s), 9.09 (s), 9.05 (s), 8.97 (s), (3 H, C$_{ar2}H$); 7.94 (d, $J^3_{H,F}$= 13.2 Hz), 7.75 (d, $J^3_{H,F}$= 13.2 Hz), 7.57 (d, $J^3_{H,F}$= 13.8 Hz), 7.53 (d, $J^3_{H,F}$= 13.2 Hz), (3 H, C$_{ar5}H$); 7.26 (d, $J^4_{H,F}$= 6.6 Hz), 7.21 (d, $J^4_{H,F}$= 7.8 Hz), 7.19 (d, $J^4_{H,F}$= 7.2 Hz), 7.13 (d, $J^4_{H,F}$= 7.2 Hz), (3 H, C$_{ar8}H$); 4.70−4.48 (m, 6 H, CH_2CH$_3$); 3.44−3.31 (m, 12 H overlaid with water, C$_{pip2,6}H_2$); 3.09−3.02 (m, 12 H, C$_{pip3,5}H_2$); 1.46−1.40 (m), 1.30 (t, $J^3_{H,H}$= 7.2 Hz), (9 H, CH$_2$CH_3). $\boldsymbol{\delta_C}$ (125 MHz, 298 K, d_6-DMSO) [ppm] = 173.5 (s), 172.9 (s), 172.8 (s), (C_{ar4}); 165.7 (s), 165.6 (s), 165.4 (s), (COOH); 152.9 (d, $J^1_{C,F}$= 208.4 Hz), 152.7 (d, $J^1_{C,F}$= 206.9 Hz), (C_{ar6}); 150.5 (s), 150.0 (s), 149.9 (s), (C_{ar2}); 145.5−145.0 (m, C_{ar7}); 136.9, 136.8, 136.6 ($C_{ar8'}$); 119.3 (d, $J^3_{C,F}$= 7.8 Hz), 119.2 (d, $J^3_{C,F}$= 8.2 Hz), 119.0 (d, $J^3_{C,F}$= 7.4 Hz), ($C_{ar4'}$); 112.0−110.4 (m, C_{ar5} and C_{ar3}); 105.5 (s), 105.3 (s), 105.0 (s), (C_{ar8}); 49.4−48.5 (m, $C_{pip2,6}$ and CH$_2$CH$_3$); 44.4 (s), 44.2 (s), 44.1 (s), 44.0 (s), ($C_{pip3,5}$); 14.62 (s), 14.60 (s), 14.5 (s), 14.4 (s), (CH$_2C$H$_3$). $\boldsymbol{\delta_F}$ (282 MHz, 298 K, d_6-DMSO) [ppm] = -120.9 (s), -121.0 (s), -121.1 (s), -121.2 (s), (3 F, C$_{ar6}F$). **MS** (ES+, CH$_3$OH): *m/z* (%) = 1047 (10) [ML$_3$ + Na$^+$], 706 (100) [ML$_2$]$^+$. **HR-ESI-MS**: *m/z* for C$_{48}$H$_{51}$F$_3$ ^{69}GaN$_9$O$_9$ + Na$^+$ calcd. (found): 1046.2915 (1046.2925).

S2.8 Tris(oxalino)gallium(III), [Ga(oxa)$_3$]

Method (b) gave an off-white solid (69 mg, 0.082 mmol, 82%). **Mp**: ≥240°C, decomposition to beige-brown solid. **IR** (neat): $\tilde{\nu}$ [cm^{-1}] = 3402 (md, br), 3060 (w, br), 2979 (w, br), 2918 (w,br), 1637 (st), 1599 (st), 1567 (md), 1539 (st), 1463 (st, br), 1412 (sh), 1387 (md), 1329 (md), 1258 (st, br), 1193 (md), 1158 (w), 1126 (w), 1087 (w), 1029 (st, br), 933 (md), 904 (md), 846 (w), 812 (st), 777 (st, br), 656 (md), 618 (md), 563 (w). **NMR**: $\boldsymbol{\delta_H}$ (600 MHz, 298 K, d_6-DMSO) [ppm] = 8.90 (s, 3 H, C$_{ar2}H$); 7.64 (s, 3 H, C$_{ar8}H$); 7.63 (s, 3 H, C$_{ar5}H$); 6.30 (s, 6 H, OCH_2O); 4.53 (q, $J^3_{H,H}$= 7.1 Hz, 6 H, CH_2CH$_3$); 1.37 (t, $J^3_{H,H}$= 7.1 Hz, 9 H, CH$_2$CH_3). $\boldsymbol{\delta_C}$ (125 MHz, 298 K, d_6-DMSO) [ppm] = 176.0 (s, C_{ar4}); 166.3 (s, COOH); 153.7 (s, C_{ar7}); 147.1 (s, C_{ar6}); 147.0 (s, C_{ar2}); 136.9 (s, $C_{ar8'}$); 121.3 (s, $C_{ar4'}$); 107.4 (s, C_{ar3}); 103.3 (s, OCH$_2$O); 101.9 (s, C_{ar5}); 97.3 (s, C_{ar8}); 49.6 (s, CH$_2$CH$_3$); 14.6 (s, CH$_2$$CH_3$). **MS** (ES+, CH$_3$OH): *m/z* (%) = 873 (100) [ML$_3$ + Na$^+$], 589 (80) [ML$_2$]$^+$. **HR-ESI-MS**: *m/z* for C$_{39}$H$_{30}$ ^{69}GaN$_3$O$_{15}$ + Na$^+$ calcd. (found): 872.0830 (872.0822). **EA**: Anal. Calcd. (found) [%] for C$_{39}$H$_{30}$GaN$_3$O$_{15}$·3.5 H$_2$O: C, 51.28 (51.37); H, 4.08 (3.97); N, 4.60 (4.70).

S2.9 Tris(pipemido)gallium(III), [Ga(pia)$_3$]

Method (b) gave an off-white solid (64 mg, 0.066 mmol, 66%). **Mp**: ≥190°C, decomposition to beige-brown solid. **IR** (neat): $\tilde{\nu}$ [cm^{-1}] = 3373 (st, br, water), 3029 (w), 2980 (w), 1616 (st), 1578 (st), 1536 (md), 1510 (md), 1471 (st), 1430 (st), 1378 (sh), 1358 (st, br), 1310 (md), 1280 (md), 1249 (st, br), 1159 (w), 1148 (w), 1128 (st), 1092 (md), 1079 (md), 1045 (md), 1024 (st), 976 (md), 940 (md), 915 (st), 903 (md) 868 (md), 832 (st), 802 (md), 744 (st), 715 (md), 703 (md), 657 (w), 609 (w), 541 (md), 489 (md), 463 (st). **NMR**: $\boldsymbol{\delta_H}$ (600 MHz, 298 K, d_6-DMSO) [ppm] = 9.17 (s, 3 H, C$_{ar5}H$); 8.94 (s, 3 H, C$_{ar2}H$); 4.37 (q,

$J^3_{H,H}$= 7.1 Hz, 6 H, CH_2CH$_3$); 3.85 (d, $J_{H,H}$= 40.1 Hz, 12 H, C$_{pip2,6}H_2$); 2.78 (d, $J_{H,H}$= 16.2 Hz, 12 H, C$_{pip3,5}H_2$); 1.35 (t, $J^3_{H,H}$= 6.9 Hz, 9 H, CH$_2$CH_3). $\boldsymbol{\delta_C}$ (125 MHz, 298 K, d_6-DMSO) [ppm] = 177.1 (s, C_{ar4}); 165.4 (s, COOH); 160.6 (s, C_{ar7}); 160.1 (s, C_{ar5}); 155.1 (s, $C_{ar8'}$); 150.6 (s, C_{ar2}); 109.7 (s, $C_{ar4'}$); 108.3 (s, C_{ar3}); 45.9 (s, CH$_2$CH$_3$); 45.6 (s), 45.3 (s), ($C_{pip2,3,5,6}$); 14.4 (s, CH$_2$$CH_3$). **MS** (ES+, CH$_3$OH): *m/z* (%) = 999 (100) [ML$_3$ + Na$^+$], 673 (80) [ML$_2$]$^+$. **HR-ESI-MS**: *m/z* for C$_{42}$H$_{48}$ ^{69}GaN$_{15}$O$_9$ + Na$^+$ calcd. (found): 998.2913 (998.2939); for C$_{28}$H$_{32}$ ^{69}GaN$_{10}$O$_6^+$ calcd. (found): 673.1762 (673.1776). **EA**: Anal. Calcd. (found) [%] for C$_{42}$H$_{48}$GaN$_{15}$O$_9$·12.5 H$_2$O: C, 41.97 (41.70); H, 6.12 (5.85); N, 17.48 (17.26).

S2.10 Tris(ciprofloxacino)iron(III), [Fe(cipro)$_3$]

Method (c) gave a red-brown solid (51 mg, 0.049 mmol, 49%). **Mp**: ≥220°C, decomposition to black-brown solid. **IR** (neat): $\tilde{\nu}$ [cm^{-1}] = 3411 (w, br, water), 2846 (w, br), 1610 (st), 1543 (w), 1513 (sh), 1450 (st, br), 1371 (md, br), 1285 (sh), 1252 (st), 1182 (md), 1129 (md), 1108 (sh), 1026 (st), 949 (st), 890 (md), 809 (md), 788 (md), 761 (sh), 738 (st), 702 (md), 627 (st), 577 (md), 556 (w), 538 (w), 506 (st). **MS** (ES+, CH$_3$OH): *m/z* (%) = 1763 (≤10) [M$_2$L$_5$]$^+$, 716 (100) [ML$_2$]$^+$. **HR-ESI-MS**: *m/z* for C$_{51}$H$_{51}$F$_3$ ^{56}FeN$_9$O$_9$ + Na$^+$ calcd. (found): 1069.3009 (1069.3007). **EA**: Anal. Calcd. (found) [%] for C$_{51}$H$_{51}$F$_3$FeN$_9$O$_9$·2.5 H$_2$O: C, 56.10 (56.04); H, 5.17 (4.80); N, 11.55 (11.27).

S2.11 Tris(enoxacino)iron(III), [Fe(enox)$_3$]

Method (b) gave a red-orange solid (59 mg, 0.058 mmol, 58%) **Mp**: ≥200°C, decomposition to black brown solid. **IR** (neat): $\tilde{\nu}$ [cm^{-1}] = 3403 (md, br, water), 3039 (w, br), 2976 (w, br), 1626 (st), 1565 (md), 1516 (md), 1441 (st, br), 1368 (md), 1347 (md), 1323 (md), 1275

(st), 1251 (st, br), 1184 (md), 1153 (w), 1119 (md), 1093 (md), 1039 (md, br), 971 (md), 943 (md, br), 907 (sh), 812 (st), 788 (md), 763 (md), 744 (md), 677 (w), 650 (md), 625 (st), 562 (md), 518 (st). **MS** (ES+, CH_3NO_2): *m/z* (%) = 694 (100) $[ML_2]^+$ **HR-ESI-MS**: *m/z* for $C_{45}H_{48}F_3\ ^{56}FeN_{12}O_9$ + Na^+ calcd. (found): 1036.2866 (1036.2866). **EA**: Anal. Calcd. (found) [%] for $C_{45}H_{48}F_3FeN_{12}O_9{\cdot}3\ H_2O$: C, 50.62 (50.48); H, 5.10 (4.82); N, 15.74 (16.07).

S2.12 Tris(fleroxacino)iron(III), [Fe(flex)$_3$]

Method (b) gave a red-brown solid (91 mg, 0.078 mmol, 78%). **Mp**: ≥230°C, decomposition to brown solid. **IR** (neat): $\tilde{\nu}$ [cm^{-1}] = 3054 (w), 2930 (md), 2848 (md), 2792 (md), 1625 (st), 1548 (w), 1526 (md), 1471 (sh), 1447 (st, br), 1413 (md), 1389 (w), 1377 (md), 1358 (md), 1325 (md), 1295 (st), 1245 (md), 1236 (sh), 1203 (md), 1160 (md), 1144 (st), 1121 (md), 1097 (w), 1075 (w), 1045 (md), 1026 (st), 1002 (st), 963 (md), 949 (md, br), 896 (md), 861 (md), 803 (st), 779 (md), 752 (md), 736 (md), 714 (md), 648 (st), 599 (md), 568 (st), 536 (w, br), 517 (w), 491 (w), 474 (w). **MS** (ES+, CH_3OH): *m/z* (%) = 1184 (20) [ML_3 + Na^+], 793 (100) $[ML_2]^+$. **HR-ESI-MS**: *m/z* for $C_{51}H_{51}F_9\ ^{56}FeN_9O_9$ + Na^+ calcd. (found): 1183.2913 (1183.2938); for $C_{34}H_{34}F_6\ ^{56}FeN_6O_6^+$: 792.1793 (792.1785). **EA**: Anal. Calcd. (found) [%] for $C_{51}H_{51}F_9FeN_9O_9$: C, 52.77 (52.78); H, 4.43 (4.53); N, 10.86 (10.49).

S2.13 Tris(levofloxacino)iron(III), [Fe(levox)$_3$]

Method (a) gave a red-brown solid (102 mg, 0.090 mmol, 90%). **Mp**: ≥190°C, decomposition to black-brown solid. **IR** (neat): $\tilde{\nu}$ [cm^{-1}] = 3427 (water), 3041 (w, br), 2935 (w), 2846 (w), 2797 (w), 1615 (st), 1518 (st), 1443 (st), 1382 (md, br), 1330 (st, br), 1291 (w),

1256 (st, br), 1150 (sh), 1129 (md), 1094 (md), 1048 (st), 1003 (md), 978 (st), 896 (md), 864 (w), 843 (w), 826 (sh), 810 (st), 759 (md), 742 (md), 693 (md), 637 (w), 553 (md, br), 508 (st), 443 (st, br). **MS** (ES+, CH_3OH): *m/z* (%) = 1160 (40) [ML_3 + Na^+], 777 (100) [ML_2]$^+$. **HR-ESI-MS**: *m/z* for $C_{54}H_{57}F_3$ $^{56}FeN_9O_{12}$ + Na^+ calcd. (found): 1159.3326 (1159.3328); for $C_{36}H_{38}F_2$ $^{56}FeN_6O_8$ calcd. (found): 776.2069 (776.2065).

S2.14 Tris(lomefloxacino)iron(III), [Fe(lomx)$_3$]

Method (b) gave a red-brown solid (80 mg, 0.072 mmol, 72%). **Mp**: ≥210°C, decomposition to black-brown solid. **IR** (neat): $\tilde{\nu}$ [cm^{-1}] = 3423 (w, br), 2979 (w, br), 2844 (w, br), 2725 (w, br), 2467 (w, br), 1616 (st), 1552 (w), 1520 (st), 1446 (st), 1358 (md, sh), 1321 (st, br), 1275 (w), 1244 (st), 1122 (md), 1089 (md), 1049 (st), 1002 (st), 932 (st), 880 (md), 810 (st), 760 (md, br), 738 (md), 654 (md), 541 (sh), 502 (md), 449 (md). **MS** (ES+, CH_3OH): *m/z* (%) = 1130 (10) [ML_3 + Na^+], 756 (100) [ML_2]$^+$. **HR-ESI-MS**: *m/z* for $C_{51}H_{54}F_6$ $^{56}FeN_9O_9$ + Na^+ calcd. (found): 1129.3196 (1129.3193).

S2.15 Tris(nalidixo)iron(III), [Fe(nxa)$_3$]

Method (b) gave a red-brown solid (66 mg, 0.089 mmol, 89%). **Mp**: ≥180°C, decomposition to black-brown solid. **IR** (neat): $\tilde{\nu}$ [cm^{-1}] = 3436 (water), 3023 (md, br), 2983 (w), 1668 (sh), 1606 (st, br), 1556 (st), 1515 (sh), 1486 (st), 1440 (st), 1366 (md), 1347 (md), 1313 (md), 1289 (st), 1255 (st), 1226 (sh), 1168 (w), 1129 (st), 1089 (md), 990 (w, br), 942 (w), 895 (md), 842 (w), 806 (st), 769 (st), 702 (w), 663 (md), 639 (md), 559 (w), 545 (md), 503 (st), 442 (st). **MS** (ES+, CH_3OH): *m/z* (%) = 1268 (≤10) [M_2L_5]$^+$, 772 (100) [ML_3 + Na^+], 518 (40) [ML_2]$^+$. **HR-ESI-MS**: *m/z* for $C_{36}H_{33}$ $^{56}FeN_6O_9$ + Na^+ calcd. (found): 772.1556 (772.1562). **EA**: Anal. Calcd. (found) [%] for $C_{36}H_{33}FeN_6O_9 \cdot 1\ H_2O$:

C, 56.33 (56.62); 4.60 (4.80); N, 10.95 (11.05).

S2.16 Tris(norfloxacino)iron(III), [Fe(nofx)$_3$]

Method (b) gave a red-brown solid (68 mg, 0.067 mmol, 67%). **Mp**: ≥190°C, decomposition to black-brown solid. **IR** (neat): $\tilde{\nu}$ [cm^{-1}] = 3371 (md, br, water), 2838 (w, br), 1610 (st, br), 1547 (w), 1516 (md), 1453 (st, br), 1380 (st), 1324 (md), 1282 (sh), 1252 (st, br), 1186 (st), 1124 (md, br), 1024 (md), 923 (st, br), 891 (sh), 875 (w), 810 (md), 786 (md), 760 (md), 738 (st), 694 (w), 624 (md), 558 (md), 512 (md), 443 (md, br). **MS** (ES+, CH_3OH): *m/z* (%) = 692 (100) $[ML_2]^+$, 1033 (20) $[ML_3 + Na^+]$. **HR-ESI-MS**: *m/z* for $C_{48}H_{51}F_3$ $^{56}FeN_9O_9 + Na^+$ calcd. (found): 1033.3009 (1033.3002). **EA**: Anal. Calcd. (found) [%] for $C_{48}H_{51}F_3FeN_9O_9 \cdot 6\ H_2O$: C, 51.52 (51.42); H, 5.67 (5.72); N, 11.27 (10.89).

S2.17 Tris(oxalino)iron(III), [Fe(oxa)$_3$]

Method (b) gave a golden-brown solid solid (70 mg, 0.084 mmol, 84%). **Mp**: ≥240°C, decmposition to brown solid. **IR** (neat): $\tilde{\nu}$ [cm^{-1}] = 3030 (w, br), 2979 (w, br), 2913 (w, br), 1633 (st), 1604 (st), 1563 (md), 1536 (md), 1493 (sh), 1460 (st, br), 1410 (sh), 1385 (md), 1319 (md), 1288 (md), 1259 (st, br), 1198 (st), 1155 (w), 1130 (w), 1079 (w), 1041 (st, br), 978 (w), 934 (md), 899 (w), 886 (w), 875 (w), 849 (w), 813 (st), 775 (st), 759 (sh), 714 (w), 656 (md), 621 (md), 570 (md), 524 (st), 504 (sh), 455 (st). **MS** (ES+, CH_3OH): *m/z* (%) = 860 (≤10) $[ML_3 + Na^+]$, 576 (100) $[ML_2]^+$. **HR-ESI-MS**: *m/z* for $C_{39}H_{30}$ $^{56}FeN_3O_{15} + Na^+$ calcd. (found): 859.0924 (859.0914). **EA**: Anal. Calcd. (found) [%] for $C_{39}H_{30}FeN_3O_{15} \cdot 1.5\ H_2O$: C, 54.24 (54.24); H, 3.85 (3.72); N, 4.87 (4.74).

S2.18 Tris(pipemido)iron(III), [Fe(pia)$_3$]

Method (b) gave a brown solid (78 mg, 0.081 mmol, 81%). **Mp**: ≥200°C, decomposition to brown solid. **IR** (neat): $\tilde{\nu}$ [cm^{-1}] = 3406 (md, br), 3028 (w), 2979 (w), 1615 (st), 1578 (st) 1534 (md), 1510 (md), 1471 (st), 1429 (st), 1377 (sh), 1357 (st, br), 1310 (md), 1280 (md), 1248 (st, br), 1158 (w), 1147 (w), 1128 (st), 1092 (md), 1078 (md), 1045 (md), 1023 (st), 975 (md), 940 (md), 914 (st), 903 (md), 867 (w), 832 (st), 802 (md), 784 (md), 744 (st), 715 (md), 704 (sh), 656 (w), 609 (w), 540 (md), 489 (md), 454 (st). **MS** (ES+, CH_3OH): *m/z* (%) = 986 (20) [ML_3 + Na^+], 715 (100) [$ML_2{\cdot}3H_2O]^+$, 661 [$ML_2]^+$ (10). **HR-ESI-MS**: *m/z* for $C_{42}H_{48}$ $^{56}FeN_{15}O_9$ (M + Na^+) calcd. (found): 985.3007 (985.3017). **EA**: Anal. Calcd. (found) [%] for $C_{42}H_{48}FeN_{15}O_9{\cdot}4$ H_2O: C, 48.75 (48.94); H, 5.45 (6.23); N, 20.30 (20.33).

S3 Synthesis & Characterization of Tris(maltolato)metal(III) Complexes

S3.1 Tris(maltolato)gallium(III), [Ga(ma)$_3$]

The synthesis followed the literature procedure.[4] Scale: 3-hydroxy-2-methyl-4*H*-pyran-4-one (2.60 g, 20.55 mmol), gallium(III) nitrate nonahydrate (2.86 g, 6.85 mmol), water (40 mL). Yield: off-white solid (1.957 g, 4.40 mmol, 64%). **IR** (neat): $\tilde{\nu}$ [cm^{-1}] = 3027 (w), 1611 (sh), 1568 (st), 1514 (st), 1456 (st), 1295 (sh), 1277 (st), 1241 (md), 1192 (st), 1087 (w), 1043 (md), 921 (md), 850 (st), 830 (st), 745 (st), 720 (st), 664 (md), 617 (md), 557 (sh), 528 (sh), 511 (w), 493 (md). **MS** (ES+, CH_3OH): *m/z* (%) = 765 (100) $[M_2L_5]^+$, 445 (10) [ML_3H^+], 319 (40) [$ML_2]^+$. **HR-ESI-MS**: *m/z* for $C_{18}H_{15}$ $^{69}GaO_9$ (M + Na^+) calcd. (found): 466.9870 (466.9866). **EA**: Anal. Calcd. (found) [%] for $C_{18}H_{15}GaO_9{\cdot}1$ H_2O: C,

46.69 (46.77); H, 3.70 (3.34).

S3.2 Tris(maltolato)iron(III), [Fe(ma)$_3$]

The synthesis followed the literature procedure.[5] Scale: 3-hydroxy-2-methyl-4*H*-pyran-4-one (3.792 g, 3.0 mmol), iron(III) nonahydrate (4.037 g, 1.0 mmol), water and ethanol (100 mL each). Yield: ruby-red solid (0.354 g, 0.82 mmol, 82%). **IR** (neat): $\tilde{\nu}$ [cm^{-1}] = 3024 (w), 1605 (sh), 1564 (st), 1505 (st), 1455 (st), 1293 (sh), 1272 (st), 1238 (md), 1190 (st), 1084 (w), 1038 (md), 920 (md), 849 (st), 829 (st), 745 (st), 719 (st), 664 (md), 607 (md), 536 (st), 470 (st). **MS** (ES+, CH_3OH): *m/z* (%) = 737 (20) $[M_2L_5]^+$, 454 (70) $[ML_3Na^+]$, 306 (100) $[ML_2]^+$. **HR-ESI-MS**: *m/z* for $C_{18}H_{15}$ $^{56}FeO_9$ (M + Na^+) calcd. (found): 453.9963 (453.9963). **EA**: Anal. Calcd. (found) [%] for $C_{18}H_{15}FeO_9 \cdot 2\ H_2O$: C, 46.28 (46.19); H, 4.10 (3.86).

S4 Antimicrobial Susceptibility Single-Disk Test Procedure

This procedure describes the antimicrobial susceptibility testing by single-disk method following a modified version of the original procedure by Kirby and Bauer[6,7] taking into account recommendations from the CLSI[8,9] and EUCAST[10] test procedures. One major deviation from the CLSI and EUCAST test procedures is the use of Iso-Sensitest medium instead of Mueller-Hinton medium. It should be clarified that both biological growth media, Iso-Sensitest[11] and Mueller-Hinton,[12] contain relatively large amounts of metal salts compared to the concentrations of test compounds (0.1 mM), after all these are nutrient rich media to grow biological cultures. The fact, however, that Mueller-Hinton medium is less defined than the purely synthetic Iso-Sensitest medium and that the composition of Mueller-Hinton, especially in regard to cations, such as Ca^{2+} and Mg^{2+}, has been

known to vary widely across manufacturers and even across different batches from the same manufacturer,[13] made Iso-Sensitest medium occur as the better choice of the necessary evil, as at least the ingredients of Iso-Sensitest medium are clearly defined. Furthermore, test results of several potential metalloantimicrobials in Iso-Sensitest medium have been reported in the literature without any comments regarding cross-metalation, including coordination complexes of gallium(III)[14,15] and iron(III).[16]

The antimicrobial tests were performed in UBC's Biological Services Laboratory, a class II facility, following respective operating and safety procedures. Disposable petri dishes (150 mm diameter) were marked with placement positions for not more than fourteen disks per plate and with a distance between each disk (center to center) of at least 24 mm.

The dehydrated Iso-Sensitest media (agar, broth) were prepared according to the manufacturer's specifications; the agar was poured evenly into the dishes to a depth of about 4 mm on a level surface. Bacteria were grown in Iso-Sensitest broth 37 °C on a shaker to an $OD_{600} \geq 1$.

All compound test solutions were prepared fresh on the day of the experiment in methanol and DMSO. The latter was needed to dissolve the test compounds. DMSO was filtered (Millex-FG 0.20 μm) before use, and its concentration was kept below 2% in the test solution. Solutions of pure methanol, 2%-DMSO-methanol, gallium(III) nitrate and iron(III) nitrate were included on each test plate as controls.

The following steps were done in triplicate. The paper filter disks were loaded with 20 μL of the respective test or control solution and left for the solvent to evaporate (about 5 min). During this drying time, the agar plates were inoculated with the respective bacteria growth solution (inoculation volume 0.5 mL). Then, the loaded filter disks were placed on the agar plate in the previously marked positions and carefully pressed onto the agar. The

lid of the test dish was put back. Tightly sealed with parafilm, the test plates were placed upside-down in an incubator at 37 °C for 20 h. On the following day, the test plates were removed from the incubator and inspected for bacterial growth. To do so, each test plate was placed on a non-reflecting black surface so that the zone of no growth around each disk could be determined with the naked eye and measured with a ruler. Following the convention, inhibition zone sizes were recorded as diameters rounded to the nearest millimeter, wherein the diameter of each paper filter disk (0.6 mm) was included in the measurement. If growth was observed up to the edge of a disk, this was recorded as 0 mm inhibition. Taking into account the measured inhibition zone sizes from all three test plates, the average inhibition zone size, including the standard deviation, was calculated for each test compound against each bacterium tested.

S5 MIC and IC_{50} Studies

Minimum inhibitory concentration (MIC) and half-maximal inhibitory concentration (IC_{50}) studies were performed against *P. aeruginosa* strain K767 PAO1 wild type in cation-adjusted Mueller-Hinton broth at the Centre for Drug Research and Development (CDRD).[17] One colony of the bacterium was picked up and inoculated into 5 mL Mueller-Hinton broth at 37°C overnight. On the next day, the growth solution was diluted to an OD_{625} of 0.112 as the equivalent of 0.5 McFarland standard or ∼1-2$x10^8$ CFU/mL; a volume of 0.5 mL of the dilution was further diluted with cation-adjusted Mueller-Hinton broth to a total volume of 50 mL.

On the test day, an acidic (HCl_{aq}) stock solution of ciprofloxacin (0.1 mM) was prepared in deionized water, which had been purified through a ELGA MAXIMA ultra pure water system with a resistivity of 18 MΩ·cm at 25°C, together with aqueous stock solutions

of gallium(III) nitrate nonahydrate (10 mM) and citric acid (10 mM). From these stock solutions, test solution were prepared at stoichiometric ratios of Ga:Hcipro of 0:1, 1:1, 1:2, 1:3, and 1:4.

A 96-well plate was prepared to test the antimicrobial efficacy of the Ga:Hcipro test solutions against *P. aeruginosa* including as a negative control test solutions without the bacterium and as a positive growth control *P. aeruginosa* only. Using a multichannel pipettor, the test solutions were diluted across the 96-well test plate with Mueller-Hinton broth. A volume of 100 μL of the diluted *P. aeruginosa* solution was added to the respective wells. Three plates were prepared in parallel, incubated at 37°C overnight, and read for absorbance at OD_{600} the next day. The obtained MIC and IC_{50} values are summarized in Table S1.

No differences in MIC values were observed for any of the stoichiometric ratios of Ga:Hcipro test solutions in the *P. aeruginosa* growth assay. The obtained MIC value for

Table S1: MIC and IC_{50} values for aqueous solutions of gallium(III) nitrate and ciprofloxacin at different ratios tested against *P. aeruginosa* in Mueller-Hinton broth.

Ratio Ga:Hcipro	pH	MIC [μg/mL]	IC_{50} [μg/mL]
0:1	2.57	0.129	0.059
1:1	2.43	0.129	0.061
1:2	2.12	0.129	0.038
1:3	1.97	0.194	0.050
1:4	2.97	0.129	0.032
1:0[(a)]	1.87	–	–

[(a)] Aqueous solution of gallium(III) nitrate mixed with an aqueous solution of citrate.

the ciprofloxacin control compared well with the 0.1 mg/L reported for *P. aeruginosa* strain K767 PAO1 wild type by Liz *et al.*.[18] Slight, almost insignificant, differences in IC_{50} values were found for Ga:Hcipro ratios of $\leq$1:2. In conclusion, no synergistic or combinational effects were observed for the interaction of Ga^{3+} and ciprofloxacin in the solution-based MIC and IC_{50} studies against *P. aeruginosa*.

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