Supplementary Information

Stability and Toxicity of Tris-tolyl Bi(V) Dicarboxylates and their Biological Activity against Leishmania major

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1. Experimental details for Compounds 13 – 31

General synthetic procedure (GP): Stoichiometric amounts of BiAr₃ and benzoic acid (1:2) were each dissolved in 5 ml of warm solvent and combined. This was followed by one equivalent of 30% H₂O₂. The mixture was stirred for 10 minutes and filtered. Crystals were subsequently obtained on allowing the filtrate to stand at room temperature overnight.

Grignard reagents were synthesized under Schlenk conditions in Et₂O by the reaction of stoichiometric ratios of Mg turnings with 2-bromotoluene, 3-bromotoluene and 4-bromotoluene respectively. The resulting Grignard reagent was standardized (reference) and reacted with BiCl₃ to obtain the BiAr₃ product.

Compounds 4, 12 and 32 are Bi(o-Tol)₃, Bi(p-Tol)₃, Bi(m-Tol)₃ respectively, these are known compounds and hence will not be discussed in the supplementary.

Synthesis of tris-o-tolylbismuth bis(3,5-dimethylbenzoate), 13

Bi(o-Tol)₃ (0.200 g, 0.41 mmol), 3,5-dimethylbenzoic acid (0.124 g, 0.83 mmol) and 100 µL of 30 % H₂O₂ were reacted in warm diethyl ether according to GP1. Yield: 49.0 % (0.157 g); MP: 120-123 °C; ¹H NMR (400 MHz, (CDCl₃), 25 °C): δ = 7.75 (4H, s, o-CH), 7.57 (3H, dd, J = 7.5 Hz, 1.2 Hz, Tol o-CH), 7.30 (3H, td, J = 7.4 Hz, 1.3 Hz, Tol m-CH), 7.30 (2H, s, p-CH), 7.08 (3H, td, J = 7.3 Hz, 0.76, Tol m-CH), 2.46 (9H, s, Tol CH₃), 2.39 (12H, s, CH₂); ¹³C¹H (150 MHz, CDCl₃, 25 °C): δ = 172.4 (COO), 143.8 (CH₂), 138.8 (CH₃), 138.3(CH₃), 135.5 (CH₃), 130.0 (CH₃), 129.5 (CH₃), 128.8 (CH₃), 128.0 (CH₃), 26.5 (CH₃), 21.3 (CH₃); MS ESI⁺ 209.0 [Bi], 391.0 [Bi(o-Tol)]⁺, 631.1 [Bi(o-Tol)₂]⁺; ESi⁻ 149 [L]; IR 3036 (w), 2914 (w), 1618 (w), 1588 (m), 1527 (m), 1438 (m), 1378 (sh), 1328 (s), 1252 (s), 1204 (sh), 1116 (m), 1037 (m), 986 (sh), 919 (m), 865 (sh), 784 (sh), 747 (s), 676 (sh); Elemental analysis [C₉H₇BiO₄.5C₅H₅CH₃] (1240.58) Calculated C 71.60 H 6.41 Found C 71.21 H 6.60.

Synthesis of tris-o-tolylbismuth bis(3,5-dihydroxybenzoate), 14

Bi(o-Tol)₃ (0.200 g, 0.41 mmol), 3,5-dihydroxybenzoic acid (0.128 g, 0.83 mmol) and 100 µL of 30 % H₂O₂ were reacted in warm diethyl ether and THF according to GP1. Yield: 59.4 % (0.192 g); MP: 120 °C (decomp.); ¹H NMR (400 MHz, (CD₃)₂SO, 25 °C): δ = 9.28 (4H, s, OH), 8.33 (3H, d, J = 7.8 Hz, Tol CH), 7.61 (6H, m, Tol CH), 7.50 (3H, t, J = 7.5, Tol CH), 6.57 (4H, d, J = 2.1, CH), 6.25 (2H, t, J = 2.1, ligand CH), 2.58 (9H, s, Tol CH₃); ¹³C¹H (100 MHz, (CD₃)₂SO, 25 °C): δ = 169.6 (COO), 162.4 (BiC), 158.0 (COH), 141.3 (CCH₂), 134.0 (COCO), 133.4 (CH₂), 131.0 (CH₃), 128.6 (CH₂), 107.4 (CH₃), 105.5 (CH₂), 22.8 (CH₃); MS 209.0 [Bi], 391.0 [Bi(o-Tol)]⁺, 631.1 [Bi(o-Tol)₂]⁺, 725.1[BiL]²⁻; ESi⁻ 153.0 [L], 787.1 [Bi(o-Tol)]₂⁻ – H⁺; IR 3200 (br), 1558 (m), 1448 (m), 1336 (st), 1268 (st), 1203 (sh), 1153 (st), 995 (sh), 950 (m), 847 (m), 769 (sh), 743 (s), 674 (s); Elemental analysis [C₃₃H₃₃BiO₆.2H₂O] (824.64) Calculated C 50.98 H 4.28 Found C 50.81 H 4.58.

Synthesis of tris-o-tolylbismuth bis(2-methoxybenzoate), 15

Bi(o-Tol)₃ (0.200 g, 0.41 mmol), 2-methoxybenzoic acid (0.126 g, 0.83 mmol) and 100 µL 30 % H₂O₂ were reacted in warm diethyl ether according to GP1. Yield: 34.5 % (0.111 g); MP: 136-137 °C; ¹H NMR (400 MHz, (CD₃)₂SO, 25 °C): δ = 8.34 (3H, d, J = 7.9 Hz, Tol CH), 7.59 (6H, m, Tol CH), 7.48 (3H, t, J = 7.5 Hz, Tol CH), 7.29 (2H, m, CH₃), 7.14 (2H, dd, J = 7.7 Hz, 1.7 Hz, CH), 6.94 (2H, d, J = 7.9 Hz, CH), 6.81 (2H, td, J = 7.5 Hz, 0.8 Hz, CH), 3.64 (6H, s, CH₃), 2.60 (9H, s, Tol CH₃); ¹³C¹H (150 MHz, CDCl₃,
25 °C): δ = 171.2 (COO), 163.0 (BiC), 158.1 (COCH₃), 134.9 (CH₃), 133.2 (CH₃), 131.0 (CH₃), 130.8 (CH₃), 130.7 (CH₃), 128.3 (CH₃), 125.6 (CH₃), 120.0 (C(COO), 111.9 (CH₃), 55.8 (OCH₃), 23.8 (CH₃); MS ESI' 209.0 [M], 391.0 [Bi(o-Tol)], 633.1 [Bi(o-Tol)L], 151.1 [L], 692.3 [Bi(m-Tol)L]; IR 2941 (w), 2833 (w), 2113 (w), 1593 (m), 1483 (w), 1458 (m), 1435 (m), 1375 (w), 1327 (s), 1297 (m), 1266 (sh), 1245 (sh), 1206(sh), 1173 (sh), 1161 (sh), 1139 (sh), 1047 (m), 1096 (sh), 1017 (m), 991 (sh), 845 (sh), 784 (sh), 743 (s), 705 (sh); Elemental analysis [C₃H₂BiO₆H₂O] (802.68) Calculated C 55.37, H 4.65; Found 55.26, H 4.48.

Synthesis of tris-o-tolylibismuth bis(5-chlorosalicylate), 16

Bi(o-Tol)₃ (0.200 g, 0.41 mmol), 5-chlorosalicylic acid (0.143 g, 0.83 mmol) and 100 µL 30 % H₂O₂ were reacted in warm diethyl ether according to GP. Yield: 28.6 % (0.097 g); MP: 152-153 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 11.69 (2H, s, OH), 8.37 (3H, dd, J = 7.9 Hz, 1.2 Hz, Tol CH), 7.56 (8H, m, Tol CH + ligand CH), 7.48 (3H, td, J = 7.4 Hz, 1.2 Hz, Tol CH), 7.21 (2H, dd, J = 8.7 Hz, 2.7 Hz, CH), 6.76 (2H, d, J = 8.8, CH), 2.66 (9H, s, Tol CH₃); ¹³C (¹H) (100 MHz, (CD₃)₂SO, 25 °C): δ = 172.6 (COO), 161.9 (COH), 160.2 (BiC), 142.2 (BiC), 142.2 (C(CH₃)), 134.7 (CH₃), 134.0 (CH₃), 131.8 (CH₃), 130.1 (CH₃), 129.1 (CH₃), 123.0 (i-Car), 118.5 (CH₃), 117.0 (CH₃), 23.8 (CH₃); MS ESI' 209.0 [Bi], 391.0 [Bi(o-Tol)], 653.1 [Bi(o-Tol)L]”; ESI’ 171.0 [L]; IR 2967 (br), 1629 (sh), 1579 (sh), 1465 (sh), 1407 (sh), 1365 (sh), 1342 (sh), 1287 (sh), 1232 (sh), 1205 (sh), 1104 (sh), 995 (sh), 896 (w), 809 (sh), 744 (sh), 713 (sh); Elemental analysis [C₃H₂BiCl₂O₆] (825.49) Calculated C 50.93 H 3.54 Found C 50.72 H 3.59.

Synthesis of tris-m-tolylibismuth bis(5-bromosalicylate), 17

Bi(o-Tol)₃ (0.200 g, 0.41 mmol), 5-bromosalicylic acid (0.180 g, 0.83 mmol) and 100 µL 30 % H₂O₂ were reacted in warm diethyl ether according to GP. Yield: 20.0 % (0.075 g); MP: 152-154 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 11.7 (2H, s, OH), 8.36 (3H, dd, J = 8.0 Hz, 1.0 Hz, o-CH₃), 7.70 (2H, d, J = 2.4 Hz, (O₂C)CCH(Br)), 7.59 (3H, d, J = 7.6 Hz, m-CH₃), 7.59 (3H, d, J = 7.6 Hz, m-CH₃), 7.55 (3H, t, J = 7.6 Hz, p-CH₃), 7.48 (3H, t, J = 7.4 Hz, 1.1 Hz, m-CH₃), 7.34 (2H, dd, J = 8.9 Hz, 2.5 Hz, p-CH₃), 6.71 (2H, d, J = 8.7 Hz, m-CH₂), 2.66 (9H, s, CH₃); ¹³C (¹H) (100 MHz, CDCl₃, 25 °C): δ = 172.4 (COO), 161.8 (COH), 160.6 (BiC), 142.1 (C(CH₃)), 136.8 (CH₃), 134.7 (CH₃), 134.0 (CH₃), 131.8 (CH₃), 129.1 (CH₃), 118.9 (CH₃), 117.5 (i-Car), 110.0 (CH₃), 23.9 (CH₃); MS 208.9 [Bi]; 391.0 [Bi(m-Tol)]; 697 [Bi(m-Tol)L][H + H]”; ESI’ 216.9 [L]; IR 3047 (w), 2973 (w), 2863 (w), 1626 (sh), 1583 (sh), 1561 (sh), 1464 (sh), 1335 (sh), 1287 (sh), 1236 (sh), 1098 (sh), 1035 (w), 1001 (sh), 898 (w), 879 (w), 806 (sh), 742 (sh), 695 (sh); Elemental analysis [C₃H₂BiBr₂O₆] (914.40) Calculated C 45.97 H 3.20 Found C 45.81 H 3.34.

Synthesis of tris-o-tolylibismuth bis(2-[(3-[(Trifluoromethyl)phenyl]amino)benzoate], 18

Bi(o-Tol)₃ (0.200 g, 0.41 mmol), flufenamic acid (0.233 g, 0.83 mmol) and 100 µL 30 % H₂O₂ were reacted in warm diethyl ether according to GP. Yield: 14.3 % (0.064 g); MP: 134-136 °C; ¹H NMR (400 MHz, (CD₃)₂SO, 25 °C): δ = 9.47 (2H, s, NH), 8.41 (3H, d, J = 8.2 Hz, CH₃), 7.70 (2H, dd, J = 8.0 Hz, 1.6 Hz, CH₃), 7.59 (6H, m, CH₃), 7.46 (5H, m, CH₃), 7.31 (2H, t, J = 7.6 Hz, CH₃), 7.25 (4H, t, J = 7.8 Hz, CH₃), 7.17 (4H, m, CH₃), 6.78 (2H, t, J = 7.5 Hz, CH₃), 2.56 (9H, s, CH₃); ¹³C (¹H) (100 MHz, (CD₃)₂SO, 25 °C): δ = 171.3 (COO), 162.2 (BiC), 144.6 (C(NH)), 144.1 (C(NH)), 142.3 (CF₃), 141.4 (C(CH₃)), 138.8 (CH₃), 134.2 (CH₃), 133.7 (CH₃), 132.8 (CH₃), 132.1 (CH₃), 131.3 (CH₃), 130.5 (CH₃), 130.0 (CCF₃), 128.9 (CH₃), 122.7 (CH₃), 119.0 (CH₃), 117.9 (CCO), 115.2 (CH₃), 22.9 (CH₃); MS ESI’ 209.0 [Bi]; 391.0 [Bi(o-Tol)], 762.1 [Bi(o-Tol)L]”; ESI’ 280.1 [L]; IR 3258 (w), 1607 (m), 1579 (sh), 1502 (sh),
1460 (m), 1442 (m), 1414 (w), 1332 (sh), 1265 (sh), 1262 (sh), 1235 (m), 1208 (w), 1235 (sh), 1165 (sh), 1118 (sh), 1092 (m), 1069 (sh), 1044 (w), 995 (m), 928 (w), 898 (w), 855 (w), 796 (sh), 743 (sh), 697 (sh), 665 (sh); Elemental analysis [C_{69}H_{79}BiF_{6}N_{2}O_{4}] (1042.83) Calculated C 56.44 H 3.77 N 2.69

Found C 56.48 H 3.73 N 2.62.

Synthesis of tris-\(m\)-tolyblismut bis(5-chlorosalicylate), 19

Bi(m-Tol)_3 (0.200 g, 0.41 mmol), 5-chlorosalicylic acid (0.143 g, 0.83 mmol) and 100 \(\mu\)L 30 \% \(H_2O_2\) were reacted in warm diethyl ether according to GP. Yield: 26.6 \% (0.090 g); MP: 182-185 °C; \(^1\)H NMR (600 MHz, CDCl_3, 25 °C): \(\delta = 8.00\) (3H, s, Tol -o-CH), 7.98 (3H, d, \(J = 8.2\) Hz, Tol -o-CH), 7.75 (2H, d, \(J = 2.6\) Hz, o-CH), 7.56 (3H, t, \(J = 7.8\) Hz, Tol m-CH), 7.33 (3H, d, \(J = 7.6\) Hz, Tol p-CH), 7.26 (2H, dd, \(J = 8.7\) Hz, 2.7 Hz, p-CH), 6.81 (2H, d, \(J = 8.8\) Hz, m-CH), 2.43 (9H, s, Tol CH_3); 13\(^C\) (1H) (150 MHz, CDCl_3, 25 °C): \(\delta = 173.8\) (COO), 160.1 (BiC), 158.5 (COH), 142.3 (CCH_3), 134.4 (CH_3ar), 132.6 (CH_3r), 131.2 (CH_3ar), 130.5 (CH=), 123.2 (CCH_3), 22.2 (CH_3); MS ESI+: 209.0 [Bi], 391.2 [Bi(m-Tol)_3]^+, 653.2 [Bi(m-Tol)_3L]^+; ESI- 127.0 [L-COO], 170.9 [L]; IR 2853 (br), 1626 (sh), 1582 (sh), 1561 (sh), 1465 (sh), 1405 (sh), 1379 (sh), 1352 (sh), 1288 (sh), 1232 (sh), 1210 (sh), 1066 (m), 980 (sh), 990 (m), 867 (w), 814 (sh), 772 (sh), 713 (sh), 674 (sh); Elemental analysis [C_{35}H_{29}BiCl_2O_6] (825.49) Calculated C 50.93 H 3.54 Found C 51.40 H 3.96.

Synthesis of tris-\(m\)-tolyblismut bis(5-bromosalicylate), 20

Bi(m-Tol)_3 (0.200 g, 0.41 mmol), 5-bromosalicylic acid (0.180 g, 0.83 mmol) and 100 \(\mu\)L 30 \% \(H_2O_2\) were reacted in warm diethyl ether according to GP. Yield: 48.0 \% (0.180 g); MP: 190-192 °C; \(^1\)H NMR (600 MHz, CDCl_3, 25 °C): \(\delta = 8.00\) (3H, s, Tol -o-CH), 7.98 (3H, d, \(J = 8.2\) Hz, Tol -o-CH), 7.90 (2H, d, \(J = 2.4\) Hz, o-CH), 7.56 (3H, t, \(J = 7.7\) Hz, o-CH), 7.39 (2H, dd, \(J = 8.6\) Hz, 2.4 Hz, Tol m-CH), 7.33 (3H, d, \(J = 7.5\) Hz, Tol p-CH), 6.76 (2H, d, \(J = 8.8\) Hz, m-CH), 2.43 (9H, s, Tol CH_3); 13\(^C\) (1H) (150 MHz, CDCl_3, 25 °C): \(\delta = 173.7\) (COO), 160.5 (COH), 158.4 (BiC), 142.3 (CCH_3), 137.2 (CH_3ar), 134.3 (CH_3r), 133.5 (CH_3r), 132.5 (CH=), 131.5 (CH_3r), 119.0 (CH_3ar), 117.1 (CBr), 110.2 (CCOO), 22.2 (CH_3); MS ESI+: 209.0 [Bi], 391.2 [Bi(m-Tol)_3]^+, 699.1 [Bi(m-Tol)_3L]^+; ESI- 170.9 [L-COO], 214.9 [L]; IR 2856 (br), 1624 (sh), 1584 (sh), 1560 (m), 1466 (sh), 1399 (sh), 1377 (sh), 1346 (sh), 1290 (sh), 1244 (sh), 1209 (m), 1099 (w), 1065 (w), 999 (w), 980 (sh), 900 (w), 812 (sh), 768 (sh), 698 (sh), 673 (sh); Elemental analysis [C_{35}H_{29}BiBr_2O_6(C_6H_5)_2O] (988.52) Calculated C 47.39 H 3.98 Found C 46.96 H 3.74.

Synthesis of tris-\(m\)-tolyblismut bis(2', 4'-difluoro-4-hydroxybenzylphenyl-3-carboxylate), 21

Bi(m-Tol)_3 (0.2 g, 0.41 mmol), Diflunisal (0.21 g, 0.83 mmol) and 100 \(\mu\)L 30 \% \(H_2O_2\) were reacted in warm diethyl ether according to GP. Yield: 56.2 \% (0.226 g); MP: 190 °C (decomp); \(^1\)H NMR (400 MHz, CDCl_3SO, 25 °C): \(\delta = 8.05\) (3H, s, Tol -o-CH), 7.98 (3H, d, \(J = 7.7\) Hz, Tol -o-CH), 7.90 (2H, d, o-CH), 7.86 (3H, t, \(J = 7.7\) Hz, Tol m-CH), 7.54 (4H, m, CH), 7.44 (3H, d, \(J = 7.7\) Hz, Tol p-CH), 7.33 (2H, td, \(J = 10.3\) Hz, 2.7 Hz, CH), 7.16 (2H, td, \(J = 8.4\) Hz, 2.5 Hz, CH), 6.94 (2H, d, \(J = 8.6\) Hz, CH), 2.37 (9H, s, CH_3); 13\(^C\) (1H) (100 MHz, CDCl_3SO, 25 °C): \(\delta = 161.2\) (BiC), 158.7 (CF), 142.1 (CF), 134.5 (Char), 132.4 (CH_3r), 131.4 (CH_3r), 117.3 (CH_3r), 111.7 (CH_3r), 111.5 (COH), 104.4 (CH_3ar), 22.1 (CH_3); MS ESI+: 209.0 [Bi], 391.2 [Bi(m-Tol)_3]^+, 731.2 [Bi(m-Tol)_3L]^+; ESI- 205.0 [L-COO], 249.0 [L]; IR 3019 (br), 1630 (m), 1591 (m), 1561 (sh), 1508 (sh), 1475 (sh), 1427 (m), 1409 (m), 1475 (sh), 1381 (s), 1359 (sh), 1246 (s), 1220 (sh), 1136 (sh), 1094 (sh), 1034 (d), 998 (w), 965 (sh), 892 (sh), 869 (sh), 843 (sh), 814 (sh), 765 (sh), 735 (m), 718 (sh), 670 (sh); Elemental Analysis [C_{69}H_{79}BiF_4O_4] (980.77) Calculated C 57.56 H 3.60 Found C 57.58 H 3.77.
Synthesis of tris-\textit{m}-tolylbismuth bis(2-[[3-chloro-2-methylphenyl]amino]benzoate), 22

Bi(\textit{m}-Tol)$_3$ (0.400 g, 0.82 mmol), tolfenamic acid (0.434 g, 1.64 mmol) and 100 \textmu L 30 % H$_2$O$_2$ were reacted in warm diethyl ether according to GP. Yield: 59.6 % (0.491 g); MP: 130-134 °C; $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 9.49 (2H, s, NH), 8.00 (3H, s, Tol-\textit{o}-CH), 7.95 (3H, d, $^3$J = 8.0 Hz, Tol-\textit{o}-CH), 7.89 (2H, dd, J = 8.0 Hz, 1.6 Hz, \textit{o}-CH), 7.37 (3H, t, J = 7.7 Hz, Tol-\textit{m}-CH), 7.16 (3H, d, J = 7.4 Hz, Tol-\textit{p}-CH), 7.07 (6H, m, CH), 6.97 (2H, t, J = 7.9 Hz, CH), 6.73 (2H, dd, J = 8.6 Hz, 0.7 Hz, CH), 6.58 (2H, td, J = 7.5 Hz, 1.0 Hz, CH), 2.24 (9H, s, Tol-CH$_3$), 2.13 (6H, s, CH$_3$); $^{13}$C($^1$H) (150 MHz, CDCl$_3$, 25 °C): δ = 174.3 (COO), 160.7 (BiC), 147.6 (i-C$_{3}$-CH$_3$), 141.5 (i-C$_{4}$-CH$_3$), 135.5 (i-C$_{5}$-CH$_3$), 134.4 (CH$_2$), 133.0 (CH$_3$), 132.9 (CH$_3$), 131.8 (CH$_3$), 131.0 (i-C$_{5}$-CH$_3$), 126.8 (CH$_{2}$), 124.7 (CH$_3$), 121.9 (CH$_3$), 116.9 (CH$_3$), 115.6 (CCOO), 113.6 (CH$_2$), 22.0 (CH$_3$), 15.0 (CH$_3$); MS ESI$^+$ 209.0 [Bi], 391.2 [Bi(\textit{m}-Tol)$_3$]$^+$, 742.2 [Bi(\textit{m}-Tol)$_3$]$_2^+$; ESI- 216.0 [L - COO], 260.0 [L]; IR 3241 (br), 3051 (w), 1654 (w), 1612 (sh), 1581 (sh), 1499 (sh), 1458 (m), 1438 (m), 1359 (s), 1159 (m), 1042 (w), 1012 (m), 979 (sh), 908 (m), 849 (sh), 810 (sh), 774 (sh), 747 (sh), 702 (m), 670 (sh); Elemental analysis [C$_{49}$H$_{45}$BiCl$_2$N$_2$O$_4$C$_2$(CH$_3$)$_2$O] (1077.90) Calculated C 59.06 H 4.96 N 2.60 Found C 59.66 H 4.50 N 3.17

Synthesis of tris-\textit{p}-tolylbismuth bis(3,5-dimethylbenzoate), 23

Bi(\textit{p}-Tol)$_3$ (0.200 g, 0.41 mmol), 3,5-dimethylbenzoic acid (0.125 g, 0.83 mmol) and 100 \textmu L 30 % H$_2$O$_2$ were reacted in warm diethyl ether according to GP. Yield: 33.4 % (0.107 g); MP: 166 °C (decomp.); $^1$H NMR (400 MHz, (CD$_3$)$_2$SO, 25 °C): δ = 8.05 (6H, d, J = 8.2 Hz, Tol-\textit{o}-CH), 7.51 (6H, d, J = 8.1 Hz, Tol-\textit{m}-CH), 7.46 (4H, s, \textit{o}-CH), 7.12 (2H, s, p-CH), 2.32 (9H, s, Tol-CH$_3$), 2.26 (12H, s, CH$_3$); $^{13}$C($^1$H) (100 MHz, (CD$_3$)$_2$SO, 25 °C): δ = 171.8 (COO), 157.5 (BiC), 141.0 (CCCH), 137.4 (CCH$_3$), 133.4 (CCOO), 133.2 (BiCCH), 132.3 (Bi(OOC)CCH), 132.0 ((OOC)CCHCH$_3$), 127.4 (C(CH$_3$)CHCH$_3$), 20.8 (CH$_3$), 20.7 (CH$_3$); MS ESI$^+$ 208.8 [Bi], 527.1 [Bi(\textit{p}-Tol)$_3$]+ + DMSO$^-$, 631.1 [Bi(\textit{p}-Tol)$_3$]$_2^-$; ESI- 149.1 [L$^-$], 391.1 [Bi(\textit{p}-Tol)$_3$]$^-$; IR 3054 (w), 2916 (w), 2863 (w), 1577 (sh), 1560 (m), 1482 (m), 1444 (m), 1381 (sh), 1344 (s), 1309 (sh), 1260 (sh), 1185 (sh), 1115 (w), 1039 (w), 999 (sh), 944 (w), 921 (w), 868 (sh), 783 (sh), 768 (sh), 677 (sh); Elemental analysis [C$_{49}$H$_{45}$BiCl$_2$N$_2$O$_4$(C$_2$(CH$_3$)$_2$O) (798.73) Calculated C 58.62 H 5.17 Found C 58.28, H 5.08.

Synthesis of tris-\textit{p}-tolylbismuth bis(3,5-dihydroxybenzoate), 24

Bi(\textit{p}-Tol)$_3$ (0.200 g, 0.41 mmol), 3,5-dihydroxybenzoic acid (0.128 g, 0.83 mmol) and 100 \textmu L 30 % H$_2$O$_2$ were reacted in warm diethyl ether according to GP. Yield: 0.196 g (0.196 g); MP: 155 °C (decomp.); $^1$H NMR (400 MHz, (CD$_3$)$_2$SO, 25 °C): δ = 9.39 (4H, s, OH), 8.00 (6H, d, J = 8.3 Hz, Tol-\textit{o}-CH), 7.51 (6H, d, J = 8.7 Hz, Tol-\textit{m}-CH), 6.71 (4H, d, J = 2.2, \textit{o}-CH), 6.30 (2H, t, J = 2.3, p-CH), 2.34 (9H, s, Tol-CH$_3$); $^{13}$C($^1$H) (100 MHz, (CD$_3$)$_2$SO, 25 °C): δ = 171.8 (COO), 158.1 (BiC), 157.4 (i-C$_{3}$-CH$_3$), 141.1 (i-C$_{4}$-CH$_3$), 134.3 (CH$_2$), 133.1 (CH$_3$), 131.9 (CH$_3$), 107.7 (CH$_2$), 106.1 (CH$_2$), 20.9 (CH$_3$); MS ESI$^+$ 208.9 [Bi], 390.1 [Bi(\textit{p}-Tol)$_3$]$^+$, [Bi(\textit{p}-Tol)$_3$]$_2^+$; ESI- 153.0 [L$^-$]; IR 3237 (br), 1543 (s), 1482 (m), 1446 (w), 1343 (s), 1294 (m), 1204 (w), 1184 (sh), 1151 (s), 1099 (w), 995 (sh), 953 (m), 858 (m), 776 (s), 677 (m); Elemental analysis [C$_{35}$H$_{33}$BiO$_4$] (788.61) Calculated C 53.31 H 3.96 Found C 53.66 H 4.24.

Synthesis of tris-\textit{p}-tolylbismuth bis(2-methoxybenzoate), 25

Bi(\textit{p}-Tol)$_3$ (0.200 g, 0.41 mmol), 2-methoxybenzoic acid (0.126 g, 0.83 mmol) and 100 \textmu L 30 % H$_2$O$_2$ were reacted in warm diethyl ether according to GP. Yield: 68.7 % (0.221 g); MP: 153-156 °C; $^1$H NMR (400 MHz, (CD$_3$)$_2$SO, 25 °C): δ = 8.09 (6H, dt, J = 8.2 Hz, 2.3 Hz, Tol-\textit{o}-CH), 7.52 (6H, dd, J = 8.5 Hz, 0.6
Hz, Tol m-CH), 7.39 (4H, m, CH), 7.02 (2H, d, J = 8.2 Hz, CH), 6.09 (2H, t, J = 7.35 Hz, CH), 3.77 (6H, s, OCH₃), 2.35 (9H, s, Tol CH₃); ¹³C(¹H) (100 MHz, (CD₃)₂SO, 25 °C): δ = 171.9 (COO), 157.8 (BIC), 156.8 (COCH₃), 141.1 (CH₃), 133.4 (CH₃), 132.0 (CH₃), 130.3 (CH₃), 123.7 (CH₃), 119.9 (CCOO), 112.5 (CH₂), 55.8 (OCH₃), 20.8 (CH₃); MS ESI⁺ 209.0 [Bi], 391.0 [Bi(p-Tol)₂]⁺, 633.1 [Bi(p-Tol)₃]⁺; 151.1 [Li]; IR 2953 (br), 2832(w), 1686 (w), 1586 (sh), 1560 (sh), 1482 (sh), 1463 (sh), 1389 (sh), 1343 (sh), 1288 (m), 1245 (m), 1143 (sh), 1048 (sh), 1017 (sh), 999 (sh), 956 (w), 852 (w), 789 (w), 755 (sh), 660 (sh); Elemental analysis [C₃₉H₃₅BiO₆·H₂O] (802.23) Calculated C 55.37 H 4.65 Found C 55.77 H 4.51.

Synthesis of tris-p-tolylbismuth bis(2-ethoxybenzoate), 26

Bi(p-Tol)₃ (0.200 g, 0.41 mmol), 2-ethoxybenzoic acid (0.125 g, 0.83 mmol) and 100 µL 30 % H₂O₂ were reacted in warm diethyl ether according to GP. Yield: 42.9 % (0.143 g); MP: 163-165 °C; ¹H NMR (400 MHz, (CD₃)₂SO, 25 °C): δ = 8.13 (6H, d, J = 8.1 Hz, Tol o-CH), 7.50 (6H, d, J = 8.0 Hz, Tol m-CH), 7.36 (4H, m, CH), 7.00 (2H, d, J = 8.0 Hz, CH), 6.88 (2H, t, J = 6.7 Hz, OCH₂CH₃), 2.35 (9H, s, Tol CH₃), 1.31 (6H, t, J = 7.0 Hz, OCH₂CH₃); ¹³C(¹H) (100 MHz, (CD₃)₂SO, 25 °C): δ = 172.3 (COO), 157.3 (BIC), 157.0 (i-Car), 140.9 (CCH₃), 133.3 (CH₃), 131.8 (CH₃), 130.3 (CH₃), 123.9 (CH₃), 119.9 (CH₃), 113.4 (CH₃), 64.9 (OCH₂CH₃), 20.8 (CH₃), 15.2 (OCH₂CH₃); MS ESI⁺ 208.9 [Bi], 647.1 [Bi(p-Tol)₃]⁺, [Bi(p-Tol)₂ + Na]⁺; ESI⁻ [Li]⁻, [Bi(p-Tol)₂]; IR 3055 (w), 2982 (w), 2918 (w), 2872 (w), 1583 (sh), 1546 (m), 1484 (sh), 1385 (m), 1352 (s), 1292 (m), 1268 (sh), 1235 (m), 1163 (sh), 1146 (sh), 1110 (m), 999 (sh), 955 (w), 922 (m), 851 (sh), 809 (sh), 790 (sh), 754 (sh), 703 (sh), 667 (sh); Elemental analysis [C₃₉H₃₅BiO₆·H₂O] (830.27) Calculated C 56.39 H 4.97 Found C 56.89 H 4.87.

Synthesis of tris-p-tolylbismuth bis(4-nitrobenzoate), 27

Bi(p-Tol)₃ (0.200 g, 0.41 mmol), 4-nitrobenzoic acid (0.138 g, 0.83 mmol) and 100 µL 30 % H₂O₂ were reacted in warm diethyl ether according to GP. Yield: 43.8 % (0.146 g); MP: 94-98 °C; ¹H NMR (600 MHz, (CD₃)₂SO, 25 °C): δ = 8.22 (4H, d, J = 8.8 Hz, o-CH), 8.07 (10H, m, m-CH + Tol o-CH), 7.55 (6H, dd, J = 8.8 Hz, 0.5 Hz, Tol m-CH), 2.34 (9H, s, CH₃); ¹³C(¹H) (150 MHz, (CD₃)₂SO, 25 °C): δ = 169.4 (COO), 155.6 (BiC), 149.5 (CNO₂), 141.6 (CCH₃), 138.2 (CH₂), 133.4 (CH₃), 132.3 (CH₃), 130.8 (CH₂), 123.5 (CCOO), 20.9 (CH₃); MS ESI⁺ 208.9 [Bi], 648.1 [Bi(p-Tol)₂]⁺; ESI⁻ [Li]⁻, [Bi(p-Tol)₂]; IR 3052 (w), 2982 (w), 2918 (w), 1583 (m), 1520 (sh), 1484 (w), 1406 (w), 1388 (w), 1331 (st), 1309 (st), 1205 (w), 1184 (sh), 1164 (sh), 1129 (sh), 1102 (sh), 1040 (w), 1012 (sh), 996 (sh), 876 (sh), 831 (sh), 792 (sh), 722 (sh); Elemental analysis [C₃₉H₃₅BiO₆·H₂O] (814.60) Calculated C 51.61 H 3.59 N 3.44 Found C 51.28 H 3.59 N 3.36.

Synthesis of tris-p-tolylbismuth bis(5-chlorosalicylate), 28

Bi(p-Tol)₃ (0.200 g, 0.41 mmol), 5-chlorosalicylic acid (0.143 g, 0.83 mmol) and 100 µL 30 % H₂O₂ were reacted in warm diethyl ether according to GP. Yield: 80.4 % (0.272 g); MP: 201-203 °C; ¹H NMR (600 MHz, CDCl₃, 25 °C): δ = 11.59 (2H, s, OH), 8.07 (6H, d, J = 8.4 Hz, o-CH₃), 7.73 (2H, d, J = 2.3 Hz, o-CH₃), 7.45 (6H, d, J = 8.2 Hz, m-CH₃), 7.25 (2H, dd, CH₃), 8.8 (2H, d, CH₃), J = 8.7 Hz, 2.41, CH₃), 2.41 (9H, s, CH₃); ¹³C(¹H) (150 MHz, (CD₃)₂SO, 25 °C): δ = 173.9 (COO), 160.1 (COH), 155.7 (BiC), 142.2 (CCH₃), 134.4 (CH₃), 134.0 (CH₃), 132.5 (CH₃), 130.5 (CH₃), 123.1 (CCOO), 118.5 (CCl), 116.4 (CH₃), 21.6 (CH₃); MS ESI⁺ 209.0 [Bi], 653.0 [Bi(p-Tol)₃]⁺, ESI⁻ 171.0 [Li]; IR 3059 (w), 2919 (w), 2861 (w), 1629 (sh), 1586 (sh), 1586 (sh), 1558 (sh), 1467 (sh); Elemental analysis [C₃₉H₂₉BiCl₃O₆] (825.49) Calculated C 50.93 H 3.54 Found C 50.83 H 3.65.
Synthesis of tris-p-tolylbismuth bis(5-bromosalicylate), 29

Bi(p-Tol)$_3$ (0.200 g, 0.41 mmol), 5-bromosalicylic acid (0.180 g, 0.83 mmol) and 100 μL 30 % H$_2$O$_2$ were reacted in warm diethyl ether according to GP. Yield: 93.3 % (0.350 g); MP: 201-203 °C; $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 11.61 (2H, s, OH), 8.07 (6H, d, J = 8.2 Hz, o-CH$_2$), 7.87 (2H, d, J = 2.1 Hz, CH$_s$), 7.45 (6H, d, J = 8.0 Hz, m-CH$_2$), 7.38 (2H, dd, J = 8.9 Hz, 2.1 Hz, CH$_d$), 6.75 (2H, d, J = 8.7 Hz, CH$_d$). 2.41 (9H, s, CH$_3$); $^{13}$C$^1$(H) (100 MHz, CDCl$_3$, 25 °C): δ = 173.8 (COO), 160.5 (COH), 155.7 (BiC), 142.2 (C(CH$_3$)$_2$), 137.2 (CH$_d$), 134.0 (CH$_s$), 133.4 (CH$_s$), 132.5 (CH$_d$), 119.0 (CH$_d$), 117.0 (CBr), 110.2 (CCOO), 21.6 (CH$_3$); MS ESI$^+$ 209.9 [Bi], 698.9 [Bi(p-Tol)$_3$]L$^-$; ESI$^-$ 216.9 (L$^-$); IR 3057 (w), 1625 (sh), 1586 (sh), 1554 (sh), 1554 (sh), 1465 (sh), 1465 (sh), 1399 (sh), 1399 (s), 1376 (s), 1345 (s), 1240 (sh), 1186 (sh), 1099 (m), 1052 (w), 997 (sh), 814 (sh), 793 (sh), 738 (w), 698 (sh); Elemental analysis [C$_{35}$H$_{29}$BiBr$_3$O$_4$] (912.01) Calculated C 45.97 H 3.20 Found C 46.05 H 3.31.

Synthesis of tris-p-tolylbismuth bis(2', 4'-difluoro-4-hydroxybiphenyl-3-carboxylate), 30

Bi(p-Tol)$_3$ (0.200 g, 0.41 mmol), Difunisol (0.210 g, 0.83 mmol) and 100 μL 30 % H$_2$O$_2$ were reacted in warm diethyl ether according to GP. Yield: 49.7 % (0.200 g); MP: 211 °C (decomp); $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 11.60 (2H, s, OH), 8.00 (6H, d, J = 8.3 Hz, o-CH$_2$), 7.82 (2H, s, CH$_d$), 7.34 (8H, m, m-CH$_2$ + CH$_s$), 7.22 (2H, m, CH$_s$), 6.80 (6H, m, CH$_d$), 2.29 (9H, s, CH$_3$); $^{13}$C$^1$(H) (100 MHz, CDCl$_3$, 25 °C): δ = 174.6 (COO), 161.2 (BiC), 158.5 (CF), 156.1 (CF), 142.0 (CH$_2$), 135.0 (CCOO), 134.0 (o-CH$_2$), 132.4 (m-CH$_2$), 131.5 (CH$_d$), 131.2 (CH$_s$), 125.4 (i-C$_3$H$_7$), 117.3 (CH$_d$), 115.5 (COH), 111.7 (CH$_d$), 111.5 (CH$_3$), 104.5 (CH$_2$), 21.6 (CH$_3$); MS ESI$^+$ 208.9 [Bi], 731.0 [Bi(p-Tol)$_3$]L$^-$; ESI$^-$ 249.0 (L$^-$); IR 2868 (w), 1629 (sh), 1529 (w), 1561 (sh), 1508 (w), 1478 (sh), 1431 (sh), 1380 (s), 1366 (s), 1296 (sh), 1244 (s), 1202 (sh), 1186 (sh), 1138 (sh), 1104 (sh), 1033 (w), 996 (sh), 966 (sh), 891 (sh), 853 (sh), 812 (w), 792 (sh), 731 (sh), 714 (sh), 663 (sh); Elemental Analysis [C$_{45}$H$_{35}$BiF$_3$O$_4$] (980.77) Calculated C 57.56 H 3.60 Found C 57.61 H 3.68.

Synthesis of tris-p-tolylbismuth bis(2-[(3-chloro-2-methylphenyl)amino]benzoate), 31

Bi(p-Tol)$_3$ (0.200 g, 0.41 mmol), Tolfenamic acid (0.217 g, 0.83 mmol) and 100 μL 30 % H$_2$O$_2$ were reacted in warm diethyl ether according to GP. Yield: 55.4 % (0.228 g); MP: 175-177 °C; $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 9.59 (2H, s, NH), 8.15 (6H, d, o-CH$_2$), 7.98 (2H, d, J = 7.9 Hz, CH$_d$), 7.37 (6H, d, J = 7.9 Hz, m-CH$_2$), 7.21 (2H, d, J = 7.8 Hz, CH$_s$), 7.18 (2H, t, J = 7.7 Hz, CH$_s$), 7.14 (2H, d, J = 7.8 Hz, CH$_d$), 7.08 (2H, t, J = 7.8 Hz, CH$_d$), 6.84 (2H, d, J = 8.1 Hz, CH$_d$), 6.67 (2H, t, J = 7.4 Hz, CH$_s$), 2.37 (9H, s, CH$_3$), 2.23 (6H, s, CH$_3$); $^{13}$C$^1$(H) (100 MHz, CDCl$_3$, 25 °C): δ = 174.3 (COO), 157.7 (BiC), 147.6 (i-C$_3$H$_7$), 147.6 (i-C$_3$H$_7$), 141.6 (i-C$_3$H$_7$), 141.3 (i-C$_3$H$_7$), 135.5 (i-C$_3$H$_7$), 133.9 (CH$_d$), 133.8 (CH$_d$), 133.0 (CH$_s$), 132.3 (CH$_d$), 131.9 (CH$_s$), 130.7 (i-C$_3$H$_7$), 126.7 (CH$_d$), 124.6 (CH$_s$), 121.8 (CH$_d$), 116.9 (CH$_d$), 115.6 (CCOO), 113.5 (CH$_d$), 21.5 (CH$_3$), 15.0 (CH$_3$); MS 209.0 [Bi], 742.2 [Bi(p-Tol)$_3$]L$^-$; ESI$^-$ 260.1 (L$^-$); IR 3234 (w), 1614 (sh), 1582 (sh), 1555 (sh), 1509 (m), 1458 (m), 1419 (w), 1359 (s), 1318 (w), 1267 (s), 1205 (s), 1183 (w), 1150 (m), 1041 (s), 1011 (sh), 997 (sh), 909 (sh), 848 (sh), 793 (sh), 768 (sh), 744 (sh), 698 (sh), 669 (sh); Elemental analysis [C$_{45}$H$_{35}$BiCl$_3$N$_2$O$_4$.(C$_3$H$_7$)$_2$O] (1077.90) Calculated C 59.06 H 4.96 N 2.60 Found C 58.76 H 4.47 N 2.67.

2. $^1$H NMR Spectra of Complexes 1 - 3, 5 - 11, 13 - 29.
Figure S1 $^1$H NMR of tri-o-tolylbismuth bis(2-ethoxybenzoate), 1 in (CD$_3$)$_2$SO at 25 °C, 400 MHz

Figure S2 $^1$H NMR of tri-o-tolylbismuth bis(4-nitrobenzoate), 2 in (CD$_3$)$_2$SO at 25 °C, 400 MHz.
Figure S3 $^1$H NMR of tri-\(\alpha\)-tolylbismuth bis(2',4'-difluoro-4-hydroxybiphenyl-3-carboxylate), 3 in (CD$_3$)$_2$SO at 25 °C, 400 MHz.

Figure S4 $^1$H NMR of tri-\(m\)-tolylbismuth bis(3,5-dimethylbenzoate), 5 in (CD$_3$)$_2$SO at 25 °C, 400 MHz.
Figure S5 $^1$H NMR of tri-$m$-tolylbismuth bis(3,5-dihydroxybenzoate), 6 in (CD$_3$)$_2$SO at 25 °C, 400 MHz.

Figure S6 $^1$H NMR of tri-$m$-tolylbismuth bis(2-methoxybenzoate), 7 in (CD$_3$)$_2$SO at 25 °C, 400 MHz.
Figure S7 $^1$H NMR of tri-$m$-tolylbismuth bis(2-ethoxybenzoate), 8 in (CD$_3$)$_2$SO at 25 °C, 400 MHz.

Figure S8 $^1$H NMR of tri-$m$-tolyl-bismuth bis(4-nitrobenzoate), 9 in (CD$_3$)$_2$SO at 25 °C, 400 MHz.
Figure S9 $^1$H NMR of tri-$m$-tolylbismuth bis(2-[(3-trifluoromethyl)phenyl]amino)benzoate), 10 in (CD$_3$)$_2$SO at 25 °C, 400 MHz.
Figure S10 $^1$H NMR of tri-$m$-tolylbismuth bis(2-(acetoxy)benzoate), 11 in (CD$_3$)$_2$SO at 25 °C, 400 MHz

Figure S11 $^1$H NMR of tri-$o$-tolylbismuth bis(3,5-dimethylbenzoate), 13 in CDCl$_3$ at 25 °C, 400 MHz
Figure S12 $^1$H NMR of tri-o-tolylbismuth bis(3,5-dihydroxybenzoate), 14 in CDCl$_3$ at 25 °C, 400 MHz

Figure S13 $^1$H NMR of tri-o-tolylbismuth bis(2-methoxybenzoate), 15 in (CD$_3$)$_2$SO at 25 °C, 400 MHz

Figure S14 $^1$H NMR of tri-o-tolylbismuth bis(5-chlorosalicylate), 16 in CDCl$_3$ at 25 °C, 400 MHz
Figure S15 $^1$H NMR of tri-$m$-tolylbismuth bis(5-bromosalicylate), 17 in CDCl$_3$ at 25 °C, 400 MHz

Figure S16 $^1$H NMR of tri-$o$-tolylbismuth bis(2-[[3-(Trifluoromethyl)phenyl]amino]benzoate), 18 in (CD$_3$)$_2$SO at 25 °C, 400 MHz
Figure S17 $^1$H NMR of tri-$m$-tolylbismuth bis(5-chlorosalicylate), 19 in CDCl$_3$ at 25 °C, 400 MHz.

Figure S18 $^1$H NMR of tri-$m$-tolylbismuth bis(5-bromosalicylate), 20 in CDCl$_3$ at 25 °C, 400 MHz.
Figure S19 $^1$H NMR of tri-$m$-tolylbismuth bis(2', 4'-difluoro-4-hydroxybiphenyl-3-carboxylate), 21 in (CD$_3$)$_2$SO at 25 °C, 400 MHz.

Figure S20 $^1$H NMR of tri-$m$-tolylbismuth bis(2-[(3-chloro-2-methylphenyl)amino]benzoate), 22 in CDCl$_3$ at 25 °C, 400 MHz.
Figure S21 $^1$H NMR of tri-p-tolylbismuth bis(3,5-dimethylbenzoate), 23 in (CD$_3$)$_2$SO at 25 °C, 400 MHz.

Figure S22 $^1$H NMR of tri-p-tolylbismuth bis(3,5-dihydroxybenzoate), 24 in (CD$_3$)$_2$SO at 25 °C, 400 MHz.
Figure S23 $^1$H NMR of tri-$p$-tolylbismuth bis(2-methoxybenzoate), 25 in (CD$_3$)$_2$SO at 25 °C, 400 MHz.

Figure S24 $^1$H NMR of tri-$p$-tolylbismuth bis(2-ethoxybenzoate), 26 in (CD$_3$)$_2$SO at 25 °C, 400 MHz.
Figure S25 $^1$H NMR of tri-$p$-tolylobismuth bis(4-nitrobenzoate), 27 in $(CD_3)_2SO$ at 25 °C, 400 MHz

Figure S26 $^1$H NMR of tri-$p$-tolylobismuth bis(5-chlorosalicylate), 28 in CDCl$_3$ at 25 °C, 400 MHz
Figure S27 $^1$H NMR of tri-p-tolylbismuth bis(5-bromosalicylate), 29 in CDCl$_3$ at 25 °C, 400 MHz

Figure S28 $^1$H NMR of tri-p-tolylbismuth bis(2', 4'-difluoro-4-hydroxybiphenyl-3-carboxylate), 30 in CDCl$_3$ at 25 °C, 400 MHz
Figure S29 ¹H NMR of tri-p-tolylbismuth bis[2-[3-chloro-2-methylphenyl]amino]benzoate, 31 in CDCl₃ at 25 °C, 400 MHz

3. Biological graphs for Compounds 25 – 29 and 32

Figure S30 Activity of 25-29 and 32 on L. major promastigotes (●) and human fibroblasts (○) after 48 hours
4. Solid state structures for Compounds 6, 8, 9, 19, 22, 25 – 28 and 31

**Figure S31** Molecular structure of [Bi(m-Tol)₃(O₂CC₆H₄(2,5-OH))₂] 6 showing thermal ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Bi(1)-C(1) 2.186(3); Bi(1)-C(8) 2.191(3); Bi(1)-C(15) 2.202(4); Bi(1)-O(6) 2.247(2); Bi(1)-O(1) 2.267(2); Bi(1)-O(2) 3.071(3); Bi(1)-O(5) 3.262(3).

**Figure S32** Molecular structure of [Bi(m-Tol)₃(O₂CC₆H₄(2-EtO))₂] 8 showing thermal ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Bi(1)-C(1) 2.195(4); Bi(1)-C(8) 2.203(4); Bi(1)-C(15) 2.216(4); Bi(1)-O(5) 2.305(3); Bi(1)-O(2) 2.309(3); Bi(1)-O(1) 2.686(3); Bi(1)-O(4) 2.743(3).
Figure S33 Molecular structure of [Bi(m-Tol)$_3$(O$_2$CC$_6$H$_3$(4-NO$_2$))]$_2$ 9 showing thermal ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Bi(1)-C(15) 2.182(4); Bi(1)-C(1) 2.195(4); Bi(1)-C(8) 2.205(7); Bi(1)-O(6) 2.274(4); Bi(1)-O(2) 2.287(3); Bi(1)-O(1) 2.841(2); Bi(1)-O(5) 2.899(3).

Figure S34 Molecular structure of [Bi(m-Tol)$_3$(O$_2$CC$_6$H$_3$(2-OH,5-Cl))]$_2$ 19 showing thermal ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Bi(1)-C(29) 2.176(4); Bi(1)-C(22) 2.189(4); Bi(1)-C(15) 2.224(5); Bi(1)-O(4) 2.280(3); Bi(1)-O(1) 2.318(3); Bi(1)-O(2) 2.849(3); Bi(1)-O(5) 3.047(3).
**Figure S35** Molecular structure of $[\text{Bi}(m\text{-Tol})_3\{\text{O}_2\text{C}_6\text{H}_4(2\text{-NHC}_6\text{H}_3(2\text{-Me},3\text{-Cl}))\}_2]$ showing thermal ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Bi(1)-C(15) 2.200(4); Bi(1)-C(1) 2.201(4); Bi(1)-C(8) 2.238(5); Bi(1)-O(3) 2.270(3); Bi(1)-O(1) 2.313(3); Bi(1)-O(2) 2.706(3); Bi(1)-O(4) 2.835(3).

**Figure S36** Molecular structure of $[\text{Bi}(\rho\text{-Tol})_3\{\text{O}_2\text{C}_6\text{H}_4(2\text{-OMe})\}_2]$ showing thermal ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Bi(1)-C(31) 2.186(4); Bi(1)-C(17) 2.195(3); Bi(1)-C(24) 2.205(3); Bi(1)-O(1) 2.249(2); Bi(1)-O(4) 2.257(2); Bi(1)-O(5) 2.905(3); Bi(1)-O(2) 2.983(3).
**Figure S37** Molecular structure of $[\text{Bi}(p\text{-Tol})_3\text{O}_2\text{C}_6\text{H}_4(2\text{-OEt})_2]_2$ 26 showing thermal ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Bi(1)-C(33) 2.193(3); Bi(1)-C(19) 2.195(3); Bi(1)-C(26) 2.207(3); Bi(1)-O(4) 2.276(2); Bi(1)-O(1) 2.278(2); Bi(1)-O(2) 2.820(2); Bi(1)-O(5) 2.857(2).

**Figure S38** Molecular structure of $[\text{Bi}(p\text{-Tol})_3\text{O}_2\text{C}_6\text{H}_4(4\text{-NO}_2)_2]_2$ 27 showing thermal ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Bi(1)-C(15) 2.186(5); Bi(1)-C(1) 2.190(5); Bi(1)-C(8) 2.212(5); Bi(1)-O(5) 2.256(3); Bi(1)-O(1) 2.338(3); Bi(1)-O(2) 2.727(4); Bi(1)-O(6) 2.869(4).
Figure S39 Molecular structure of [Bi(\textit{p}-Tol)_3(O_2C,C_6H_3(2-OH,5-Cl))_2] 28 showing thermal ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Bi(1)-C(15) 2.174(4); Bi(1)-C(22) 2.192(4); Bi(1)-C(29) 2.204(4); Bi(1)-O(4) 2.265(3); Bi(1)-O(1) 2.289(3); Bi(1)-O(2) 2.951(4); Bi(1)-O(5), 3.001(3).

Figure S40 Molecular structure of [Bi(\textit{p}-Tol)_3(O_2C,C_6H_4(2-NHC,H_3(2-Me,3-Cl))_2] 31 showing thermal ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Bi(1)-C(29) 2.192(3); Bi(1)-C(36) 2.193(3); Bi(1)-C(43) 2.198(3); Bi(1)-O(1) 2.281(2); Bi(1)-O(3) 2.282(2); Bi(1)-O(2) 2.816(2); Bi(1)-O(4) 2.905(2).
5. Crystallographic summary of 6, 8, 9, 19, 22, 25 – 31

Table S1 Summary of crystallographic data for Compound 6, 8, 9, 19, 22, 25 – 31 (\(I > 2\sigma(I)\)); \(^b^\) all data.

<table>
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<th>Compound</th>
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<th>8</th>
<th>9</th>
<th>19</th>
<th>22</th>
<th>25</th>
<th>26</th>
<th>27</th>
<th>28</th>
<th>31</th>
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<td>C(<em>{38})H(</em>{38})BiCl(<em>{2})O(</em>{6})</td>
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