Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

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

Yih Ching Ong, Victoria L. Blair, Lukasz Kedzierski, Kellie L. Tuck and Philip C. Andrews

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1. Experimental details for Compounds 13 – 31

General synthetic procedure (GP): Stiochiometric amounts of $BiAr_3$ and benzoic acid (1:2) were each dissolved in 5 ml of warm solvent and combined. This was followed by one equivalent of 30% H_2O_2. 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 Et_2O 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 $BiCl_3$ to obtain the $BiAr_3$ 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 % H_2O_2 were reacted in warm diethyl ether according to GP1. Yield: 49.0 % (0.157 g); MP: 120-123 °C; ^{1}H NMR (400 MHz, ($CDCl_3$, 25 °C): δ = 7.75 (4H, s, *o*-CH), 7.57 (3H, dd, *J* = 7.5 Hz, 1.2 Hz, Tol *o*-C*H*), 7.30 (3H, td, *J* = 7.4 Hz, 1.3 Hz, Tol *m*-C*H*), 7.30 (2H, s, *p*-C*H*), 7.08 (3H, td, *J* = 7.3 Hz, 0.76, Tol *m*-C*H*), 2.46 (9H, s, Tol CH_3), 2.39 (12H, s, CH_3); ^{13}C{^{1}H} (150 MHz, $CDCl_3$, 25 °C): δ = 172.4 (*C*OO), 143.8 (*C*H$_{ar}$), 138.8 (*C*H$_{ar}$), 138.3(*C*H$_{ar}$), 135.5 (*C*H$_{ar}$), 130.0 (*C*H$_{ar}$), 129.5 (*C*H$_{ar}$), 128.8 (*C*H$_{ar}$), 128.4 (*C*H$_{ar}$), 128.0 (*C*H$_{ar}$), 26.5 (*C*H$_3$) , 21.3 (*C*H$_3$); MS ESI$^+$ 209.0 [Bi], 391.0 [Bi(*o*-Tol)]$^+$, 631.1 [Bi(*o*-Tol)$_3$L]$^+$; 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 [$C_{39}H_{39}BiO_4.5C_6H_5CH_3$] (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 30 % H_2O_2 were reacted in warm diethyl ether and THF according to GP1. Yield: 59.4 % (0.192 g); MP: 120 °C (decomp.); ^{1}H NMR (400 MHz, $(CD_3)_2SO$, 25 °C): δ = 9.28 (4H, s, O*H*), 8.33 (3H, d, J = 7.8 Hz, Tol C*H*), 7.61 (6H, m, Tol C*H*), 7.50 (3H, t, J = 7.5, Tol C*H*), 6.57 (4H, d, *J* = 2.1, C*H*), 6.25 (2H, t, *J* = 2.1, ligand C*H*), 2.58 (9H, s, Tol CH_3); ^{13}C{^{1}H} (100 MHz, $(CD_3)_2SO$, 25 °C): δ = 169.6 (*C*OO), 162.4 (Bi*C*), 158.0 (*C*OH), 141.3 (*C*CH$_3$), 134.0 (*C*COO), 133.4 (*C*H$_{ar}$), 131.0 (*C*H$_{ar}$), 128.6 (*C*H$_{ar}$), 107.4 (*C*H$_{ar}$), 105.5 (*C*H$_{ar}$), 22.8 (*C*H$_3$); MS 209.0 [Bi], 391.0 [Bi(*o*-Tol)$_2$]$^+$, 635.1 [Bi(*o*-Tol)$_3$L]$^+$, 725.1[BiL]$^{2+}$; ESI$^-$ 153.0 [L]$^-$, 787.1 [Bi(*o*-Tol)$_3$L$_2$ – 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 [$C_{35}H_{31}BiO_8.2H_2O$] (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 % H_2O_2 were reacted in warm diethyl ether according to GP1. Yield: 34.5 % (0.111 g); MP: 136-137 °C; ^{1}H NMR (400 MHz, $(CD_3)_2SO$, 25 °C): δ = 8.34 (3H, d, *J* = 7.9 Hz, Tol C*H*),7.59 (6H, m, Tol C*H*), 7.48 (3H, t, *J* = 7.5 Hz, Tol C*H*), 7.29 (2H, m, C*H*), 7.14 (2H, dd, *J* = 7.7 Hz, 1.7 Hz, C*H*), 6.94 (2H, d, J = 7.9 Hz, C*H*), 6.81 (2H, td, J = 7.5 Hz, 0.8 Hz, C*H*), 3.64 (6H, s, CH_3), 2.60 (9H, s, Tol CH_3); ^{13}C{^{1}H} (150 MHz, $CDCl_3$,

25 °C): δ = 171.2 (COO), 163.0 (BiC), 158.1 ($COCH_3$), 134.9 (CH_{ar}), 133.2 (CH_{ar}), 131.0 (CH_{ar}), 130.8 (CH_{ar}), 130.7 (CH_{ar}), 128.3 (CH_{ar}), 125.6 (CH_{ar}), 120.0 (CCOO), 111.9 (CH_{ar}), 55.8 (OCH_3), 23.8 (CH_3); MS ESI^+ 209.0 [Bi], 391.0 [Bi(*o*-Tol)$_2$], 633.1 [Bi(*o*-Tol)$_3$L]$^+$; ESI^- 151.1 [L]$^-$, 693.2 [Bi(*m*-Tol)$_2$L$_2$]$^-$; 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 [$C_{37}H_{35}BiO_6.H_2O$] (802.68) Calculated C 55.37, H 4.65; Found 55.26, H 4.48.

Synthesis of *tris*-*o*-tolylbismuth bis(5-chlorosalicyate), **16**

Bi(*o*-Tol)$_3$ (0.200 g, 0.41 mmol), 5-chlorosalicylic acid (0.143 g, 0.83 mmol) and 100 μL 30 % H_2O_2 were reacted in warm diethyl ether according to GP. Yield: 28.6 % (0.097 g); MP: 152-153 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 11.69 (2H, s, O*H*), 8.37 (3H, dd, *J* = 7.9 Hz, 1.2 Hz, Tol C*H*), 7.56 (8H, m, Tol C*H* + ligand C*H*), 7.48 (3H, td, *J* = 7.4 Hz, 1.2 Hz, Tol C*H*), 7.21 (2H, dd, *J* = 8.7 Hz, 2.7 Hz, C*H*), 6.76 (2H, d, *J* = 8.8, C*H*), 2.66 (9H, s, Tol CH_3); ^{13}C{^{1}H} (100 MHz, $(CD_3)_2SO$, 25 °C): δ = 172.6 (*C*OO), 161.9 (*C*OH), 160.2 (Bi*C*), 142.2 (Bi*C*), 142.2 (*C*CH_3), 134.7 (CH_{ar}), 134.0 (CH_{ar}), 131.8 (CH_{ar}), 130.1 (CH_{ar}), 129.1 (CH_{ar}), 123.0 (i-Car), 118.5 (CH_{ar}), 117.0 (CH_{ar}), 23.8 (CH_3); MS ESI^+ 209.0 [Bi], 391.0 [Bi(*o*-Tol)$_2$]$^+$, 653.1 [Bi(*o*-Tol)$_3$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 [$C_{35}H_{29}BiCl_2O_6$] (825.49) Calculated C 50.93 H 3.54 Found C 50.72 H 3.59.

Synthesis of *tris*-*m*-tolylbismuth bis(5-bromosalicyate), **17**

Bi(*o*-Tol)$_3$ (0.200 g, 0.41 mmol), 5-bromosalicylic acid (0.180 g, 0.83 mmol) and 100 μL 30 % H_2O_2 were reacted in warm diethyl ether according to GP. Yield: 20.0 % (0.075 g); MP: 152-154 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 11.7 (2H, s, OH), 8.36 (3H, dd, *J* = 8.0 Hz, 1.0 Hz, *o*-CH_{ar}), 7.70 (2H, d, *J* = 2.4 Hz, (O_2C)CC*H*C(Br)), 7.59 (3H, d, *J* = 7.6 Hz, *m*- CH_{ar}), 7.59 (3H, d, *J* = 7.6 Hz, *m*-CH_{ar}), 7.55 (3H, t, *J* = 7.6 Hz, *p*-CH_{ar}), 7.48 (3H, t, *J* = 7.4 Hz, 1.1 Hz, *m*-CH_{ar}), 7.34 (2H, dd, *J* = 8.9 Hz, 2.5 Hz, *p*-CH_{ar}), 6.71 (2H, d, *J* = 8.7 Hz, *m*-CH_{ar}), 2.66 (9H, s, CH_3);^{13}C{^{1}H} (100 MHz, $CDCl_3$, 25 °C): δ = 172.4 (*C*OO), 161.8 (*C*OH), 160.6 (Bi*C*), 142.1 (*C*CH_3), 136.8 (CH_{ar}), 134.7 (CH_{ar}), 134.0 (CH_{ar}), 131.8 (CH_{ar}), 129.1 (CH_{ar}), 118.9 (CH_{ar}), 117.5 (*i*-C_{ar}), 110.0 (CH_{ar}), 23.9 (CH_3); MS 208.9 [Bi]; 391.0 [Bi(*m*-Tol)$_2$]$^+$; 697 [Bi(*m*-Tol)$_3$LH + 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 [$C_{35}H_{29}BiBr_2O_6$] (914.40) Calculated C 45.97 H 3.20 Found C 45.81 H 3.34.

Synthesis of *tris*-*o*-tolylbismuth 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 % H_2O_2 were reacted in warm diethyl ether according to GP. Yield: 14.3 % (0.064 g); MP: 134-136 °C; ^{1}H NMR (400 MHz, $(CD_3)_2SO$, 25 °C): δ = 9.47 (2H, s, N*H*), 8.41 (3H, d, *J* = 8.2 Hz, CH_{ar}), 7.70 (2H, dd, *J* = 8.0 Hz, 1.6 Hz, CH_{ar}), 7.59 (6H, m, CH_{ar}), 7.46 (5H, m, CH_{ar}), 7.31 (2H, t, *J* = 7.6 Hz, CH_{ar}), 7.25 (4H, t, *J* = 7.8 Hz, CH_{ar}), 7.17 (4H, m, CH_{ar}), 6.78 (2H, t, *J* = 7.5 Hz, CH_{ar}), 2.56 (9H, s, CH_3); ^{13}C{^{1}H} (100 MHz, $(CD_3)_2SO$, 25 °C): δ = 171.3 (*C*OO), 162.2 (Bi*C*), 144.6 (*C*(NH)), 144.1 (*C*(NH)), 142.3 (*C*F_3), 141.4 (*C*(CH_3)), 138.8 (CH_{ar}), 134.2 (CH_{ar}), 133.7 (CH_{ar}), 132.8 (CH_{ar}), 132.1 (CH_{ar}), 131.3 (CH_{ar}), 130.5 (CH_{ar}), 130.0 (*C*CF_3), 128.9 (CH_{ar}), 122.7 (CH_{ar}), 119.0 (CH_{ar}), 117.9 (*C*COO), 115.2 (CH_{ar}), 22.9 (CH_3); MS ESI^+ 209.0 [Bi], 391.0 [Bi(*o*-Tol)$_2$]$^+$, 762.1 [Bi(*o*-Tol)$_3$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 [$C_{49}H_{39}BiF_6N_2O_4$] (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*-tolylbismuth bis(5-chlorosalicyate), **19**

Bi(*m*-Tol)$_3$ (0.200 g, 0.41 mmol), 5-chlorosalicylic acid (0.143 g, 0.83 mmol) and 100 μL 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): δ = 8.00 (3H, s, Tol *o*-C*H*), 7.98 (3H, d, 3J = 8.2 Hz, Tol *o*-C*H*), 7.75 (2H, d, *J* = 2.6 Hz, *o*-C*H*), 7.56 (3H, t, *J* = 7.8 Hz, Tol *m*-C*H*), 7.33 (3H, d, *J* = 7.6 Hz, Tol *p*-C*H*), 7.26 (2H, dd, *J* = 8.7 Hz, 2.7 Hz, *p*-C*H*), 6.81 (2H, d, *J* = 8.8 Hz, *m*-C*H*), 2.43 (9H, s, Tol CH_3); ^{13}C{^{1}H} (150 MHz, $(CD_3)_2SO$, 25 °C): δ = 173.8 (*C*OO), 160.1 (Bi*C*), 158.5 (*C*OH), 142.3 (*C*Cl), 134.4 (*C*H$_{ar}$), 132.6 (*C*H$_{ar}$), 131.2 (*C*H$_{ar}$), 130.5 (*C*H$_{ar}$), 123.2 (*C*CH$_3$), 22.2 (*C*H$_3$); MS ESI+ 209.0 [Bi], 391.2 [Bi(*m*-Tol)$_2$]$^+$, 653.2 [Bi(*m*-Tol)$_3$L]$^+$; 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), 900 (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*-tolylbismuth bis(5-bromosalicyate), **20**

Bi(*m*-Tol)$_3$ (0.200 g, 0.41 mmol), 5-bromosalicylic acid (0.180 g, 0.83 mmol) and 100 μL 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): δ = 8.00 (3H, s, Tol *o*-C*H*), 7.98 (3H, d, ^{3}*J* = 8.2 Hz, Tol *o*-C*H*), 7.90 (2H, d, *J* = 2.4 Hz, *o*-C*H*), 7.56 (3H, t, *J* = 7.7 Hz, *o*-C*H*), 7.39 (2H, dd, *J* = 8.6 Hz, 2.4 Hz, Tol *m*-C*H*), 7.33 (3H, d, ^{3}*J* = 7.5 Hz, Tol *p*-C*H*), 6.76 (2H, d, *J* = 8.8 Hz, *m*-C*H*), 2.43 (9H, s, Tol CH_3); ^{13}C{^{1}H} (150 MHz, $CDCl_3$, 25 °C): δ = 173.7 (*C*OO), 160.6 (*C*OH), 158.4 (Bi*C*), 142.3 (*C*CH$_3$), 137.2 (*C*H$_{ar}$), 134.3 (*C*H$_{ar}$), 133.5 (*C*H$_{ar}$), 132.5 (*C*H$_{ar}$), 131.5 (*C*H$_{ar}$), 131.1 (*C*H$_{ar}$), 119.0 (*C*H$_{ar}$), 117.1 (*C*Br), 110.2 (*C*COO), 22.2 (*C*H$_3$); MS ESI$^+$ 209.0 [Bi], 391.2 [Bi(*m*-Tol)$_2$]$^+$, 699.1 [Bi(*m*-Tol)$_3$L]$^+$; 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 [$C_{35}H_{29}BiBr_2O_6$.$(C_2H_5)_2O$] (988.52) Calculated C 47.39 H 3.98 Found C 46.96 H 3.74.

Synthesis of *tris*-*m*-tolylbismuth bis(2', 4'-difluoro-4-hydroxybiphenyl-3-carboxylate), **21**

Bi(*m*-Tol)$_3$ (0.2 g, 0.41 mmol), Diflunisal (0.21 g, 0.83 mmol) and 100 μL 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, $(CD_3)_2SO$, 25 °C): δ = 8.05 (3H, s, Tol *o*-C*H*), 7.98 (3H, d, *J* = 7.7 Hz, Tol *o*-C*H*), 7.90 (2H, s, *o*-C*H*), 7.86 (3H, t, *J* = 7.7 Hz, Tol *m*-C*H*), 7.54 (4H, m, C*H*), 7.44 (3H, d, *J* = 7.7 Hz, Tol *p*-C*H*), 7.33 (2H, td, *J* = 10.3 Hz, 2.7 Hz, C*H*), 7.16 (2H, td, *J* = 8.4 Hz, 2.5 Hz, C*H*), 6.94 (2H, d, *J* = 8.6 Hz, C*H*), 2.37 (9H, s, CH_3); ^{13}C{^{1}H} (100 MHz, $(CD_3)_2SO$, 25 °C): δ = 161.2 (BiC), 158.7 (CF), 142.1 (CF), 134.5 (CHar), 132.4 (*C*H$_{ar}$), 131.4 (*C*H$_{ar}$), 117.3 (*C*H$_{ar}$), 111.7 (*C*H$_{ar}$), 111.5 (*C*H$_{ar}$), 115.2 (COH), 104.4 (*C*H$_{ar}$), 22.1 (CH$_3$); MS ESI$^+$ 209.0 [Bi], 391.2 [Bi(*m*-Tol)$_2$]$^+$, 731.2 [Bi(*m*-Tol)$_3$L]$^+$; 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 (w), 998 (w), 965 (sh), 892 (sh), 869 (sh), 843 (sh), 814 (sh), 765 (sh), 735 (m), 718 (sh), 670 (sh); Elemental Analysis [$C_{47}H_{35}BiF_4O_6$] (980.77) Calculated C 57.56 H 3.60 Found C 57.58 H 3.77.

Synthesis of *tris*-*m*-tolylbismuth bis(2-[(3-chloro-2-methylphenyl)amino]benzoate), **22**

Bi(*m*-Tol)$_3$ (0.400 g, 0.82 mmol), tolfenamic acid (0.434 g, 1.64 mmol) and 100 μL 30 % H_2O_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, N*H*), 8.00 (3H, s, Tol *o*-C*H*), 7.95 (3H, d, ^3J = 8.0 Hz, Tol *o*-C*H*), 7.89 (2H, dd, *J* = 8.0 Hz, 1.6 Hz, *o*-C*H*), 7.37 (3H, t, *J* = 7.7 Hz, Tol *m*-C*H*), 7.16 (3H, d, *J* = 7.4 Hz, Tol *p*-C*H*), 7.07 (6H, m, C*H*), 6.97 (2H, t, *J* = 7.9 Hz, C*H*), 6.73 (2H, dd, *J* = 8.6 Hz, 0.7 Hz, C*H*), 6.58 (2H, td, *J* = 7.5 Hz, 1.0 Hz, C*H*), 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 (*C*OO), 160.7 (Bi*C*), 147.6 (*i*-*C*$_{ar}$), 141.5 (*i*-*C*$_{ar}$), 135.5 (*i*-*C*$_{ar}$), 134.4 (*C*H$_{ar}$), 133.0 (*C*H$_{ar}$), 132.9 (*C*H$_{ar}$), 131.8 (*C*H$_{ar}$), 131.0 (*C*H$_{ar}$), 130.9 (*i*-*C*$_{ar}$), 126.8 (*C*H$_{ar}$), 124.7 (*C*H$_{ar}$), 121.9 (*C*H$_{ar}$), 116.9 (*C*H$_{ar}$), 115.6 (*C*COO), 113.6 (*C*H$_{ar}$), 22.0 (*C*H$_3$), 15.0 (*C*H$_3$); MS ESI$^+$ 209.0 [Bi], 391.2 [Bi(*m*-Tol)$_2$]$^+$, 742.2 [Bi(*m*-Tol)$_3$L]$^+$; 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 [$C_{49}H_{45}BiCl_2N_2O_4$.$(C_2H_5)_2O$] (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*-*p*-tolylbismuth bis(3,5-dimethylbenzoate), **23**

Bi(*p*-Tol)$_3$ (0.200 g, 0.41 mmol), 3,5-dimethylbenzoic acid (0.125 g, 0.83 mmol) and 100 μL 30 % H_2O_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, $(CD_3)_2SO$, 25 °C): δ = 8.05 (6H, d, *J* = 8.2 Hz, Tol o-C*H*), 7.51 (6H, d, *J* = 8.1 Hz, Tol m-C*H*),7.46 (4H, s, *o*-C*H*), 7.12 (2H, s, *p*-C*H*), 2.32 (9H, s, Tol CH_3), 2.26 (12H, s, CH_3); ^{13}C{^{1}H} (100 MHz, $(CD_3)_2SO$, 25 °C): δ =171.8 (*C*OO), 157.5 (Bi*C*), 141.0 (*C*CH$_3$), 137.4 (*C*CH$_3$), 133.4 (*C*COO), 133.2 (BiC*C*H), 132.3 (Bi(OOC)C*C*H), 132.0 ((OOC)CCHC(CH$_3$)), 127.4 (C(CH$_3$)*C*HC(CH$_3$)), 20.8 (*C*H$_3$), 20.7 (*C*H$_3$); MS ESI$^+$ 208.8 [Bi], 527.1 [Bi(*p*-Tol)L + DMSO]$^+$, 631.1 [Bi(*p*-Tol)$_3$L]$^+$; ESI- 149.1 [L]$^-$, 391.1 [Bi(*p*-Tol)$_2$]; IR 3054 (w), 2916 (w), 2863 (w), 1577 (sh), 1560 (m), 1482 (m), 1482 (m), 1444 (m), 1381 (sh), 1344 (s), 1309 (sh), 1206 (sh), 1185 (sh), 1115 (w), 1039 (w), 999 (sh), 944 (w), 921 (w), 868 (sh), 783 (sh), 768 (sh), 677 (sh); Elemental analysis [$C_{39}H_{39}BiO_4$.H_2O] (798.73) Calculated C 58.62 H 5.17 Found C 58.28, H 5.08.

Synthesis of *tris*-*p*-tolylbismuth bis(3,5-dihydroxybenzoate), **24**

Bi(*p*-Tol)$_3$ (0.200 g, 0.41 mmol), 3,5-dihydroxybenzoic acid (0.128 g, 0.83 mmol) and 100 μL 30 % H_2O_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, $(CD_3)_2SO$, 25 °C): δ = 9.39 (4H, s, OH), 8.00 (6H, d, *J* = 8.3 Hz, Tol *o*-C*H*), 7.51 (6H, d, *J* = 8.7 Hz, Tol *m*-C*H*), 6.71 (4H, d, *J* = 2.2, *o*-C*H*), 6.30 (2H, t, *J* = 2.3, *p*-C*H*), 2.34 (9H, s, Tol CH_3); ^{13}C{^{1}H} (100 MHz, $(CD_3)_2SO$, 25 °C): δ = 171.7 (*C*OO), 158.1 (Bi*C*), 157.4 (*i*-C$_{ar}$), 141.1 (*i*-C$_{ar}$), 134.3 (*C*H$_{ar}$), 133.1 (*C*H$_{ar}$), 131.9 (*C*H$_{ar}$), 107.7 (*C*H$_{ar}$), 106.1 (*C*H$_{ar}$), 20.9 (*C*H$_{ar}$); MS ESI$^+$ 208.9 [Bi], 391.0 [Bi(*p*-Tol)$_2$]$^+$, [Bi(*p*-Tol)$_3$L]$^+$, 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 [$C_{35}H_{31}BiO_8$] (788.61) Calculated C 53.31 H 3.96 Found C 53.66 H 4.24.

Synthesis of *tris*-*p*-tolylbismuth bis(2-methoxybenzoate), **25**

Bi(*p*-Tol)$_3$ (0.200 g, 0.41 mmol), 2-methoxybenzoic acid (0.126 g, 0.83 mmol) and 100 μL 30 % H_2O_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, $(CD_3)_2SO$, 25 °C): δ = 8.09 (6H, dt, *J* = 8.2 Hz, 2.3 Hz, Tol *o*-C*H*), 7.52 (6H, dd, *J* = 8.5 Hz, 0.6

Hz, Tol *m*-C*H*), 7.39 (4H, m, C*H*), 7.02 (2H, d, *J* = 8.2 Hz, C*H*), 6.09 (2H, t, *J* = 7.35 Hz, C*H*), 3.77 (6H, s, OCH_3), 2.35 (9H, s, Tol CH_3); $^{13}C\{^1H\}$ (100 MHz, $(CD_3)_2SO$, 25 °C): δ = 171.9 (*C*OO), 157.8 (Bi*C*), 156.8 (*C*OCH_3), 141.1 (*C*H_{ar}), 133.4 (*C*H_{ar}), 132.0 (*C*H_{ar}), 130.3 (*C*H_{ar}), 123.7 (*C*H_{ar}), 119.9 (*C*COO), 112.5 (*C*H_{ar}), 55.8 (O*C*H_3), 20.8 (*C*H_3); MS ESI$^+$ 209.0 [Bi], 391.0 [Bi(p-Tol)$_2$]$^+$, 633.1 [Bi(p-Tol)$_3$L]$^+$; 151.1 [L]$^-$; 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), 1097 (m), 1048 (sh), 1017 (sh), 999 (sh), 956 (w), 852 (w), 789 (w), 755 (sh), 660 (sh); Elemental analysis [$C_{37}H_{35}BiO_6.H_2O$] (802.23) Calculated C 55.37 H4.65 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 % H_2O_2 were reacted in warm diethyl ether according to GP. Yield: 42.9 % (0.143 g); MP: 163-165 °C; ^{1}H NMR (400 MHz, $(CD_3)_2SO$, 25 °C): δ = 8.13 (6H, d, *J* = 8.1 Hz, Tol *o*-C*H*), 7.50 (6H, d, *J* = 8.0 Hz, Tol *m*-C*H*), 7.36 (4H, m, C*H*), 7.00 (2H, d, *J* = 8.0 Hz, C*H*), 6.88 (2H, t, *J* = 8.0 Hz, C*H*), 4.00 (4H, q, *J* = 6.7 Hz, OCH_2CH$_3$), 2.35 (9H, s, Tol CH_3), 1.31 (6H, t, *J* = 7.0 Hz, OCH$_2$CH_3); $^{13}C\{^1H\}$ (100 MHz, $(CD_3)_2SO$, 25 °C): δ = 172.3 (COO), 157.3 (BiC), 157.0 (i-Car), 140.9 (CCH3), 133.3 (*C*H_{ar}), 131.8 (*C*H_{ar}), 130.3 (*C*H_{ar}), 123.9 (*C*H_{ar}), 119.9 (*C*H_{ar}), 113.4 (*C*H_{ar}), 64.9 (O*C*H$_2$CH$_3$), 20.8 (*C*H_3), 15.2 (OCH$_2$*C*H$_3$); MS ESI+ 208.9 [Bi], 647.1 [Bi(*p*-Tol)3L]+, [Bi(*p*-Tol)$_3$L$_2$ + Na]$^+$; ESI- [L]$^-$, [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 [$C_{39}H_{39}BiO_6.H_2O$] (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 % H_2O_2 were reacted in warm diethyl ether according to GP. Yield: 43.8 %, (0.146 g); MP: 94-98 °C; ^{1}H NMR (600 MHz, $(CD_3)_2SO$, 25 °C): δ = 8.22 (4H, d, *J* = 8.8 Hz, *o*-C*H*), 8.07 (10H, m, *m*-C*H* + Tol *o*-C*H*), 7.55 (6H, dd, *J* = 8.8 Hz, 0.5 Hz, Tol *m*-C*H*), 2.34 (9H, s, CH_3); $^{13}C\{^1H\}$ (150 MHz, $(CD_3)_2SO$, 25 °C): δ = 169.4 (*C*OO), 155.6 (Bi*C*), 149.5 (*C*NO_2), 141.6 (*C*CH$_3$), 138.2 (*C*H_{ar}), 133.4 (*C*H_{ar}), 132.3 (*C*H_{ar}), 130.8 (*C*H_{ar}), 123.5 (*C*COO), 20.9 (*C*H_3); MS ESI$^+$ 208.9 [Bi], 648.1 [Bi(*p*-Tol)$_3$L]$^+$, ESI$^-$ 166.0 [L]$^-$; IR 3052 (w), 1624 (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 [$C_{35}H_{29}BiN_2O_8$] (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-chlorosalicyate), **28**

Bi(*p*-Tol)$_3$ (0.200 g, 0.41 mmol), 5-chlorosalicylic acid (0.143 g, 0.83 mmol) and 100 μL 30 % H_2O_2 were reacted in warm diethyl ether according to GP. Yield: 80.4 % (0.272 g); MP: 201-203 °C; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 11.59 (2H, s, OH), 8.07 (6H, d, *J* = 8.4 Hz, *o*-CH_{ar}), 7.73 (2H, d, *J* = 2.3 Hz, *o*-CH_{ar}), 7.45 (6H, d, *J* = 8.2 Hz, *m*-CH_{ar}), 7.25 (2H, dd, CH_{ar}, *J* = 8.8 Hz, 2.4 Hz, CH_{ar}), 6.80 (2H, d, CH_{ar}, *J* = 8.7 Hz, 2.41, CH_{ar}), 2.41 (9H, s, CH_3); $^{13}C\{^1H\}$ (150 MHz, $(CD_3)_2SO$, 25 °C): δ = 173.9 (*C*OO), 160.1 (*C*OH), 155.7 (Bi*C*), 142.2 (*C*CH$_3$), 134.4 (*C*H_{ar}), 134.0 (*C*H_{ar}), 132.5 (*C*H_{ar}), 130.5 (*C*H_{ar}), 123.1 (*C*COO), 118.5 (*C*Cl), 116.4 (*C*H_{ar}), 21.6 (*C*H_3); MS ESI$^+$ 209.0 [Bi], 653.0 [Bi(p-Tol)$_3$L]$^+$, ESI$^-$ 171.0 (L]$^-$; IR 3059 (w), 2919 (w), 2861 (w), 1629 (sh), 1586 (sh), 1586 (sh), 1558 (sh), 1467 (sh); Elemental analysis [$C_{35}H_{29}BiCl_2O_6$] (825.49) Calculated C 50.93 H 3.54 Found C 50.83 H 3.65.

Synthesis of *tris*-*p*-tolylbismuth bis(5-bromosalicyate), **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_2O_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*-C*H*$_{ar}$), 7.87 (2H, d, *J* = 2.1 Hz, C*H*$_{ar}$), 7.45 (6H, d, *J* = 8.0 Hz, *m*-C*H*$_{ar}$), 7.38 (2H, dd, *J* = 8.9 Hz, 2.1 Hz, C*H*$_{ar}$), 6.75 (2H, d, *J* = 8.7 Hz, C*H*$_{ar}$), 2.41 (9H, s, C*H*$_3$); ^{13}C{^{1}H} (100 MHz, $CDCl_3$, 25 °C): δ = 173.8 (*C*OO), 160.5 (*C*OH), 155.7 (Bi*C*), 142.2 (*C*CH$_3$), 137.2 (*C*H$_{ar}$), 134.0 (*C*H$_{ar}$), 133.4 (*C*H$_{ar}$), 132.5 (*C*H$_{ar}$), 119.0 (*C*H$_{ar}$), 117.0 (*C*Br), 110.2 (*C*COO), 21.6 (*C*H$_3$); MS ESI$^+$ 209.0 [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 [$C_{35}H_{29}BiBr_2O_6$] (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), Diflunisal (0.210 g, 0.83 mmol) and 100 μL 30 % H_2O_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*-C*H*$_{ar}$), 7.82 (2H, s, C*H*$_{ar}$), 7.34 (8H, m, *m*-C*H*$_{ar}$ + C*H*$_{ar}$), 7.22 (2H, m, C*H*$_{ar}$), 6.80 (6H, m, C*H*$_{ar}$), 2.29 (9H, s, C*H*$_3$); ^{13}C{^{1}H} (100 MHz, $CDCl_3$, 25 °C): δ = 174.6 (*C*OO), 161.2 (Bi*C*). 158.5 (*C*F), 156.1 (*C*F), 142.0 (*C*CH$_3$), 135.0 (*C*COO), 134.0 (*o*-*C*H$_{ar}$), 132.4 (*m*-*C*H$_{ar}$), 131.5 (*C*H$_{ar}$), 131.2 (*C*H$_{ar}$), 125.4 (*i*-C$_{ar}$), 117.3 (*C*H$_{ar}$), 115.5 (*C*OH), 111.7 (*C*H$_{ar}$), 111.5 (*C*H$_{ar}$), 104.5 (*C*H$_{ar}$), 21.6 (*C*H$_3$); 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 [$C_{47}H_{35}BiF_4O_6$] (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_2O_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, N*H*), 8.15 (6H, d, *o*-C*H*$_{ar}$), 7.98 (2H, d, *J* = 7.9 Hz, C*H*$_{ar}$), 7.37 (6H, d, *J* = 7.9 Hz, *m*-C*H*$_{ar}$), 7.21 (2H, d, *J* = 7.8 Hz, C*H*$_{ar}$), 7.18 (2H, t, *J* = 7.7 Hz, C*H*$_{ar}$), 7.14 (2H, d, *J* = 7.8 Hz, C*H*$_{ar}$), 7.08 (2H, t, *J* = 7.8 Hz, C*H*$_{ar}$), 6.84 (2H, d, *J* = 8.1 Hz, C*H*$_{ar}$), 6.67 (2H, t, *J* = 7.4 Hz, C*H*$_{ar}$), 2.37 (9H, s, CH$_3$), 2.23 (6H, s, C*H*$_3$); ^{13}C{^{1}H} (100 MHz, $CDCl_3$, 25 °C): δ = 174.3 (*C*OO), 157.7 (Bi*C*), 147.6 (*i*-*C*$_{ar}$), 147.6 (*i*-*C*$_{ar}$), 141.6 (*i*-*C*$_{ar}$), 141.3 (*i*-*C*$_{ar}$), 135.5 (*i*-*C*$_{ar}$), 133.9 (*C*H$_{ar}$), 133.8 (*C*H$_{ar}$), 133.0 (*C*H$_{ar}$), 132.3 (*C*H$_{ar}$), 131.9 (*C*H$_{ar}$), 130.7 (*i*-C$_{ar}$), 126.7 (*C*H$_{ar}$), 124.6 (*C*H$_{ar}$), 121.8 (*C*H$_{ar}$), 116.9 (*C*H$_{ar}$), 115.6 (CCOO), 113.5 (*C*H$_{ar}$), 21.5 (*C*H$_3$), 15.0 (*C*H$_3$); 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 [$C_{49}H_{45}BiCl_2N_2O_4$.$(C_2H_5)_2O$] (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

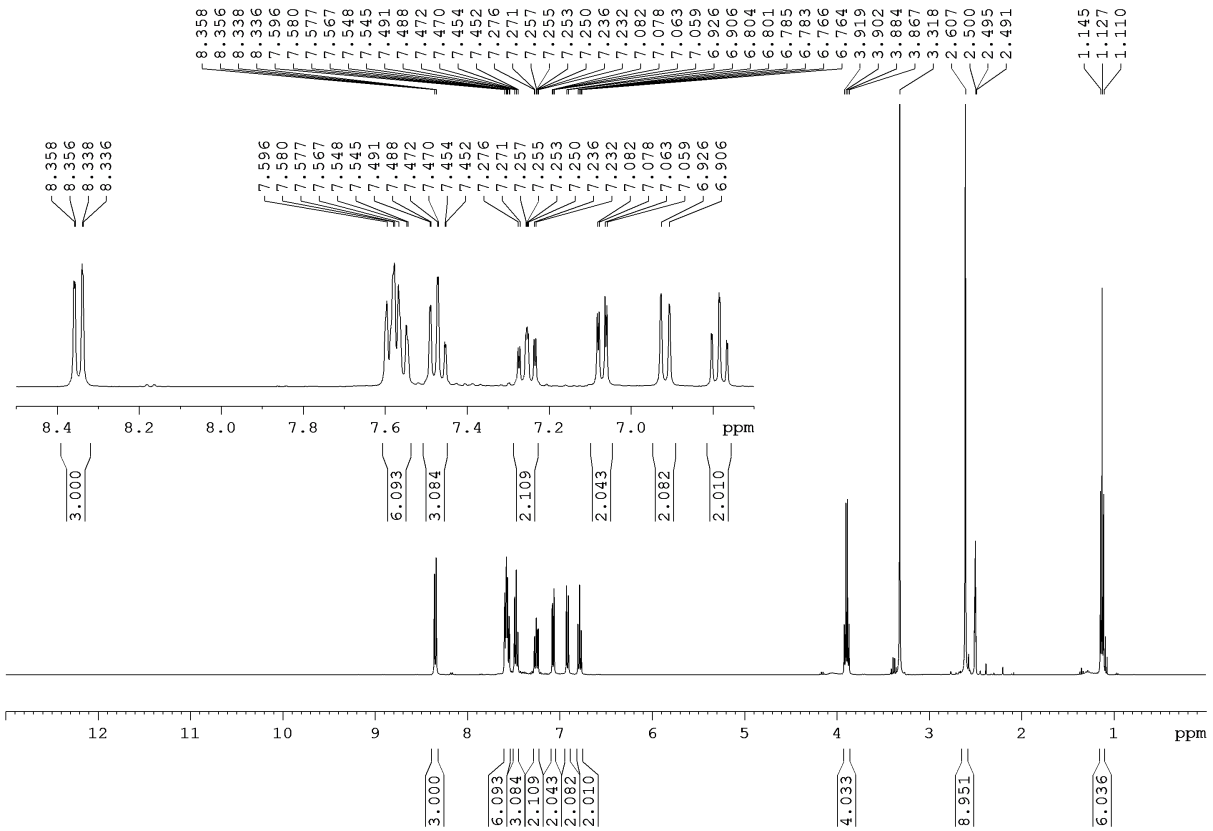

Figure S1 ^{1}H NMR of tri-*o*-tolylbismuth bis(2-ethoxybenzoate), **1** in $(CD_3)_2SO$ at 25 °C, 400 MHz

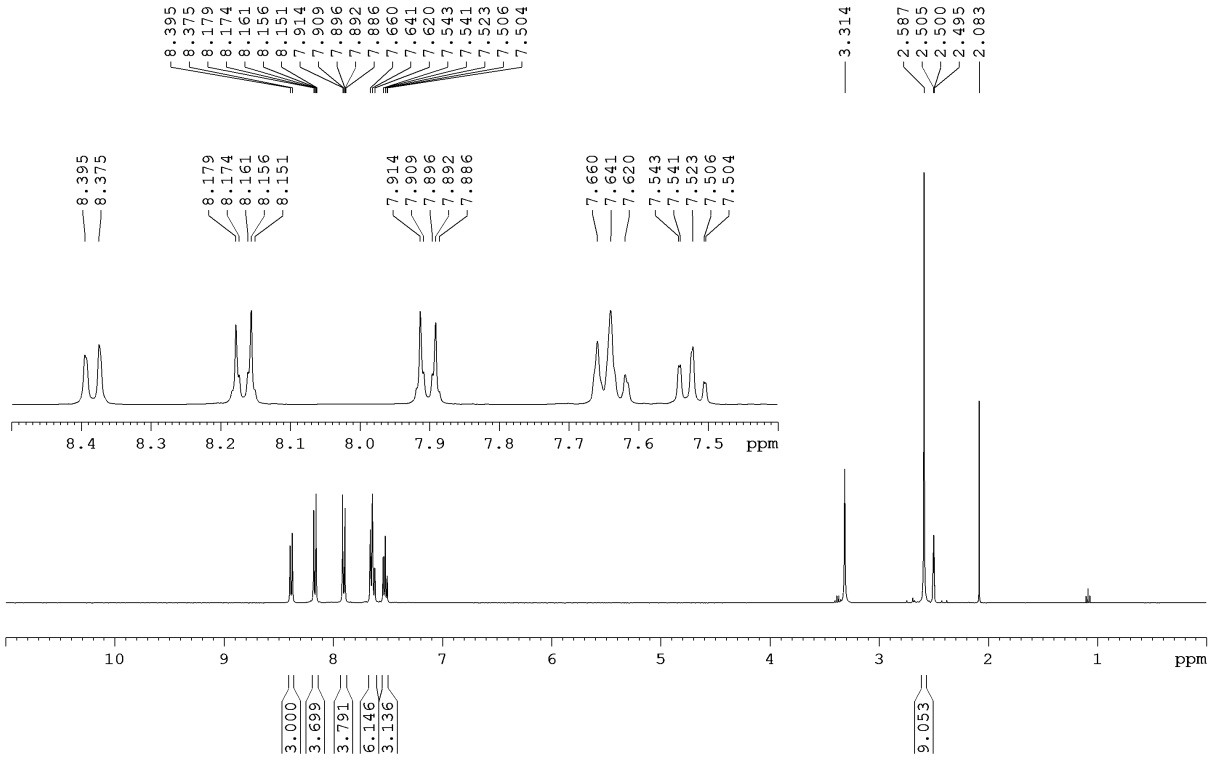

Figure S2 ^{1}H NMR of tri-*o*-tolylbismuth bis(4-nitrobenzoate), **2** in $(CD_3)_2SO$ at 25 °C, 400 MHz.

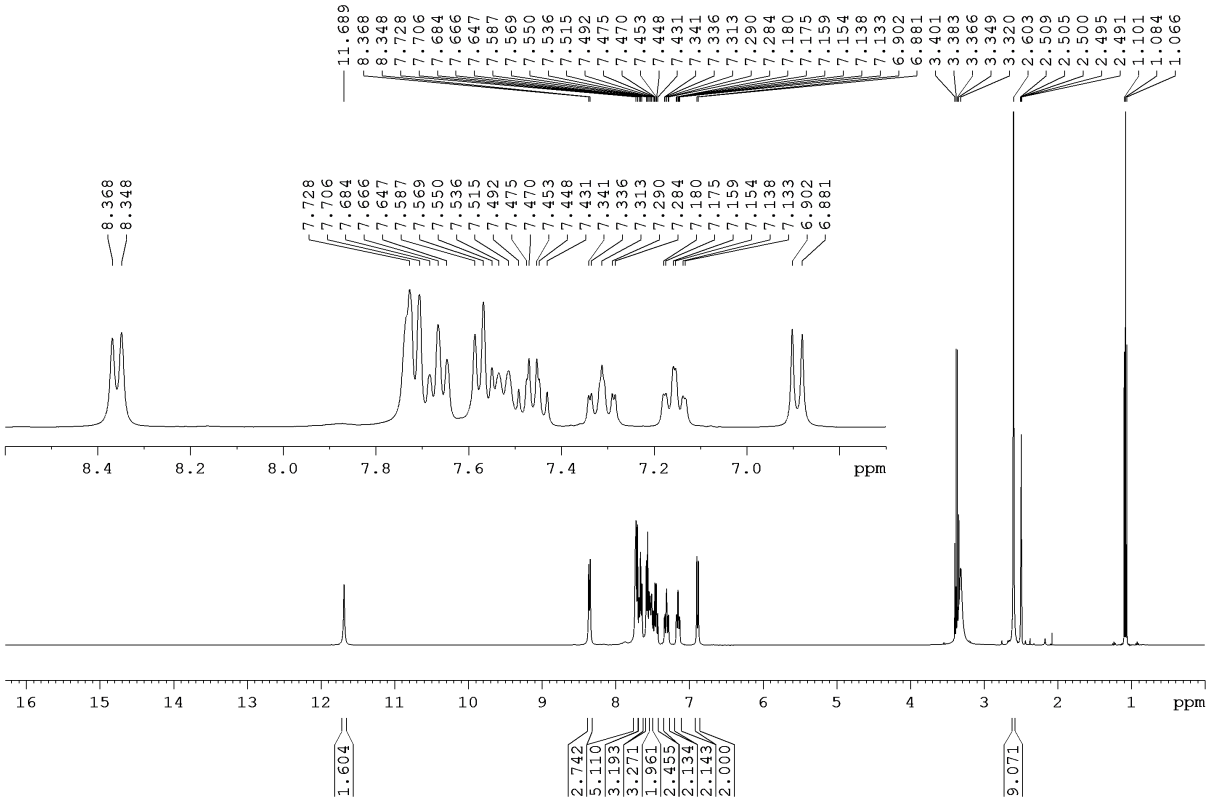

Figure S3 ^{1}H NMR of tri-*o*-tolylbismuth bis(2',4'-difluoro-4-hydroxybiphenyl-3-carboxylate), **3** in $(CD_3)_2SO$ at 25 °C, 400 MHz.

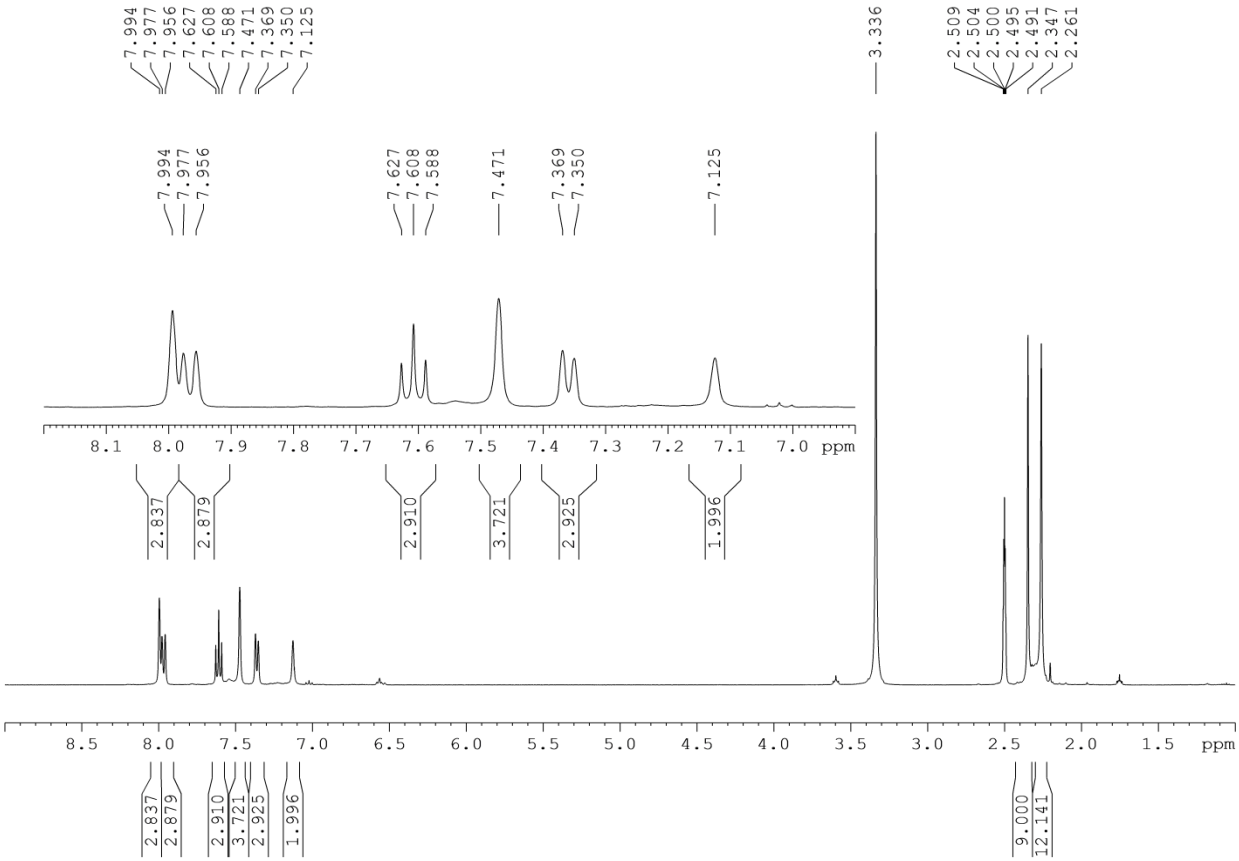

Figure S4 ^{1}H NMR of tri-*m*-tolylbismuth bis(3,5-dimethylbenzoate), **5** in $(CD_3)_2SO$ at 25 °C, 400 MHz.

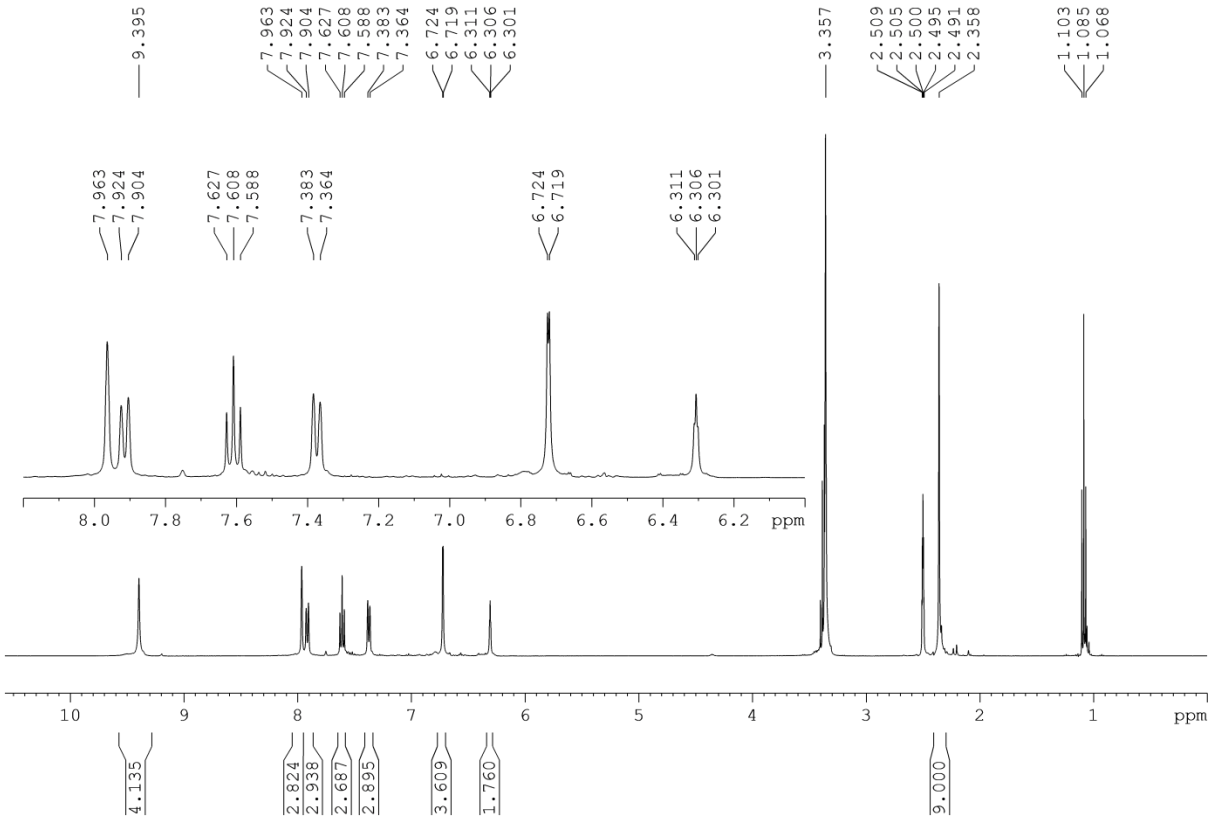

Figure S5 ^{1}H NMR of tri-*m*-tolylbismuth bis(3,5-dihydroxybenzoate), **6** in $(CD_3)_2SO$ at 25 °C, 400 MHz.

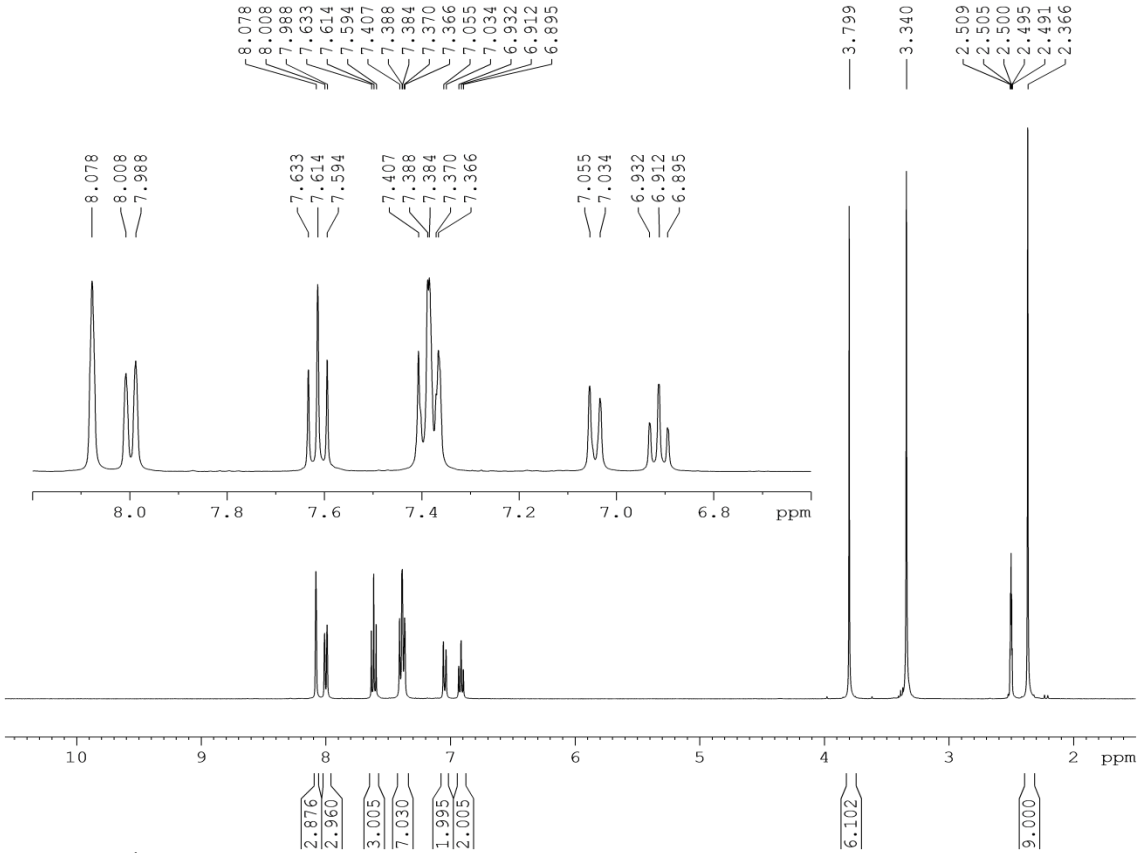

Figure S6 ^{1}H NMR of tri-*m*-tolylbismuth bis(2-methoxybenzoate), **7** in $(CD_3)_2SO$ at 25 ˚C, 400 MHz.

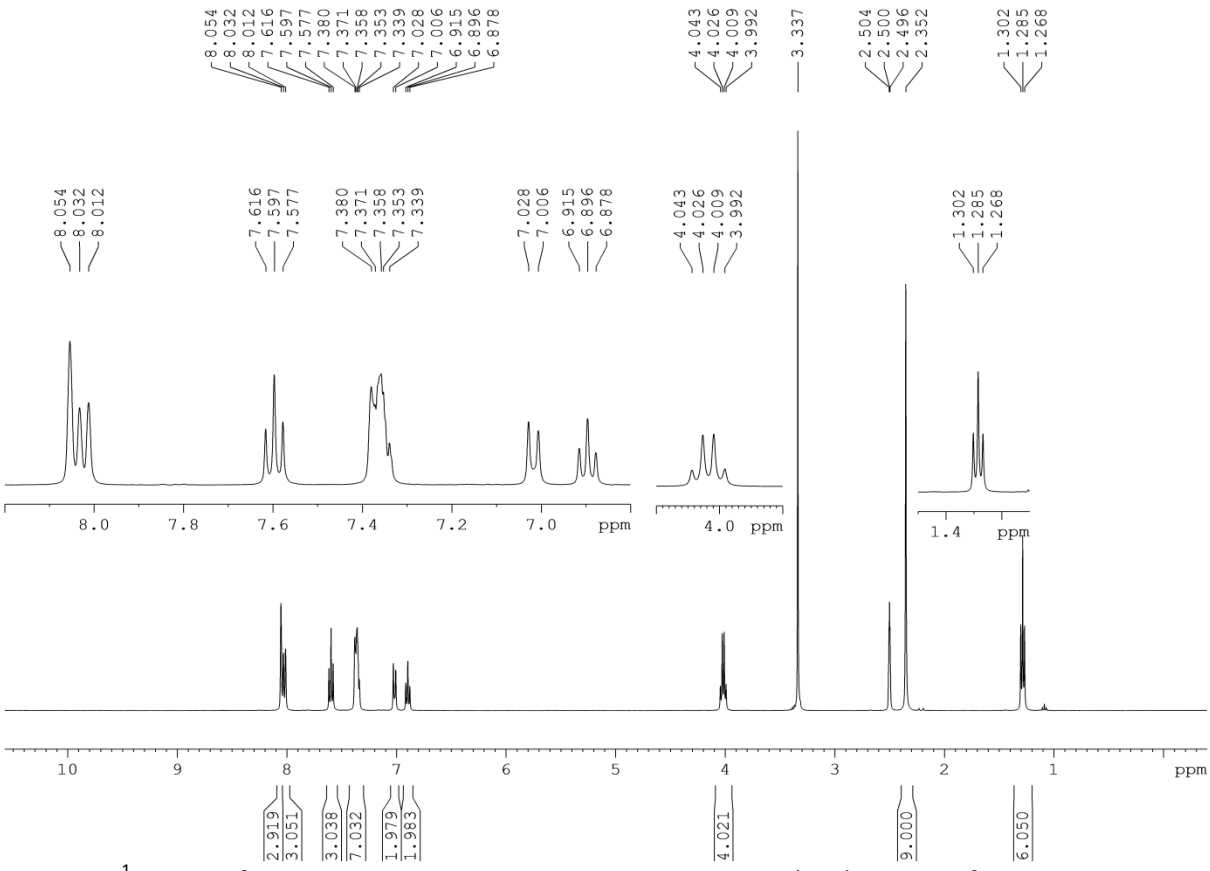

Figure S7 ^{1}H NMR of tri-*m*-tolylbismuth bis(2-ethoxybenzoate), **8** in $(CD_3)_2SO$ at 25 °C, 400 MHz.

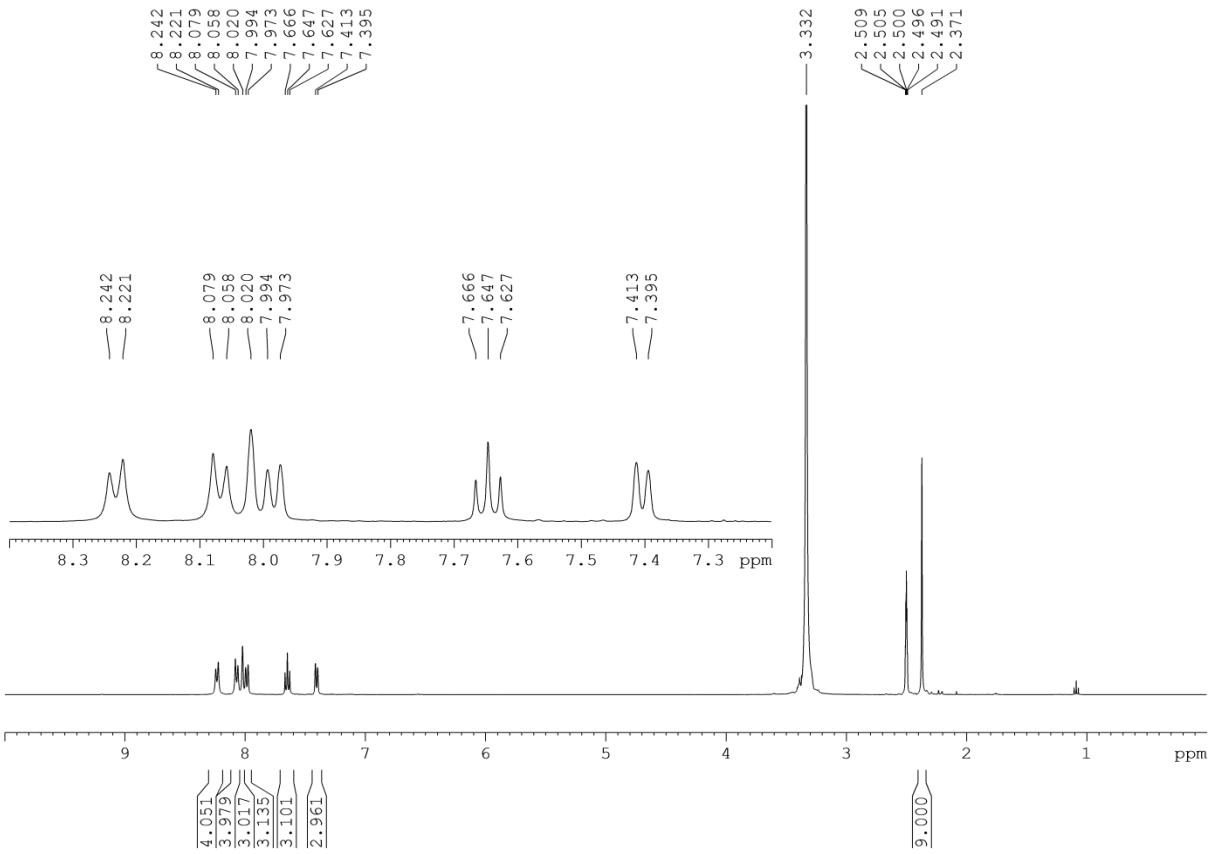

Figure S8 ^{1}H NMR of tri-*m*-tolyl-bismuth bis(4-nitrobenzoate), **9** in $(CD_3)_2SO$ at 25 °C, 400 MHz.

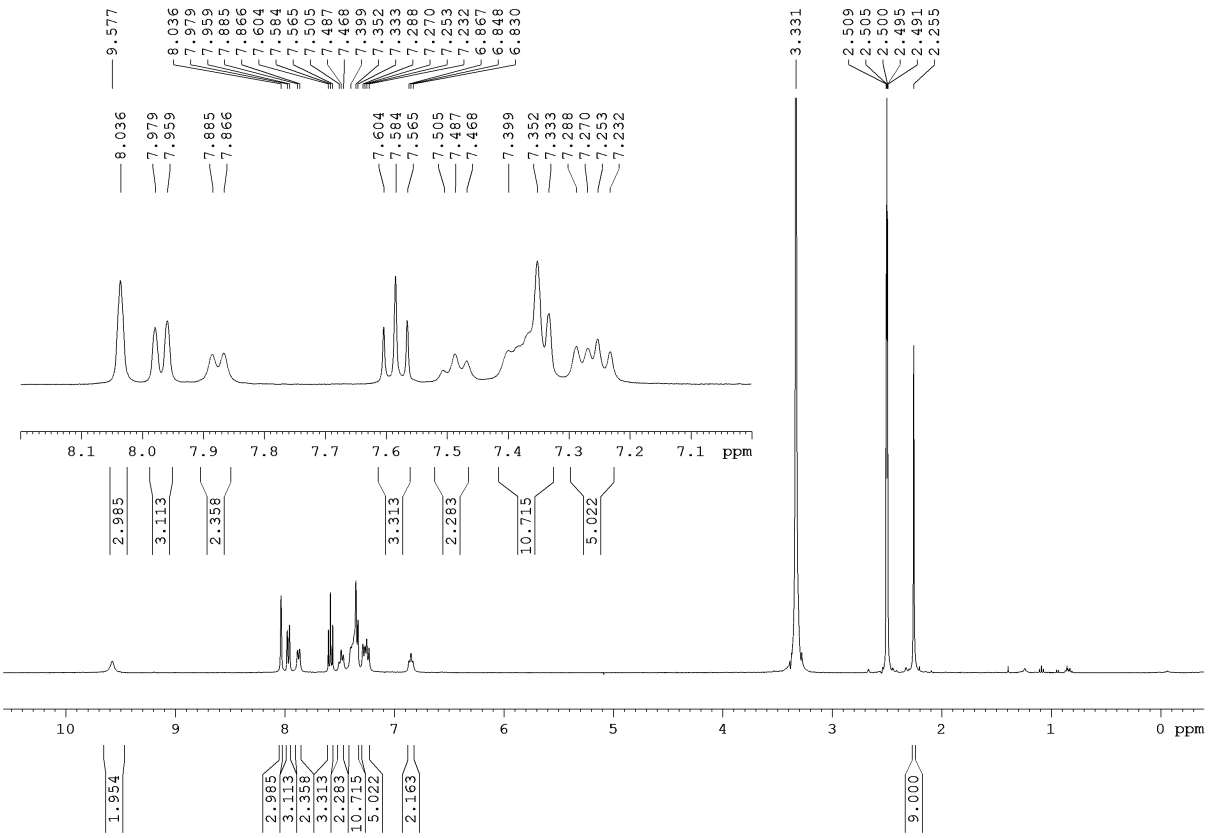

Figure S9 ^{1}H NMR of tri-*m*-tolylbismuth bis(2-{[3-trifluoromethyl)phenyl]amino}benzoate), **10** in $(CD_3)_2SO$ at 25 °C, 400 MHz.

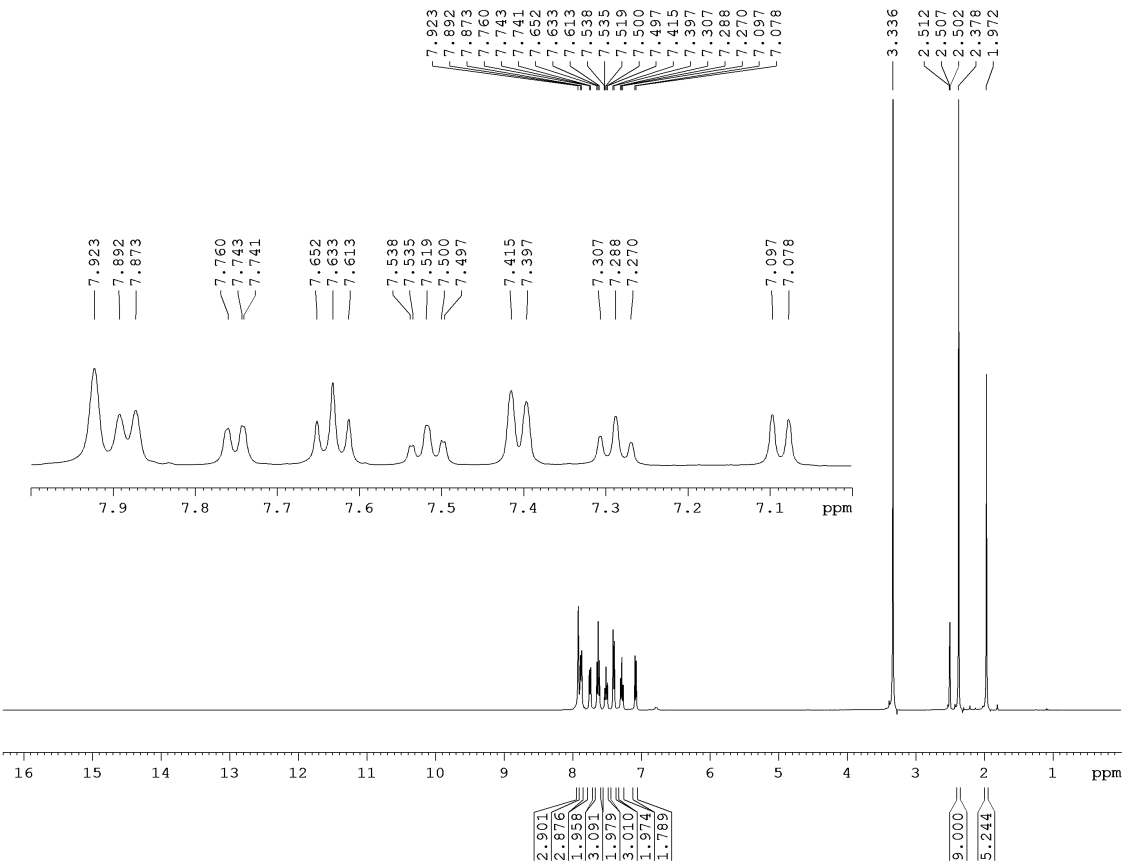

Figure S10 ^{1}H NMR of tri-*m*-tolylbismuth bis(2-(acetoxy)benzoate), **11** in $(CD_3)_2SO$ at 25 °C, 400 MHz

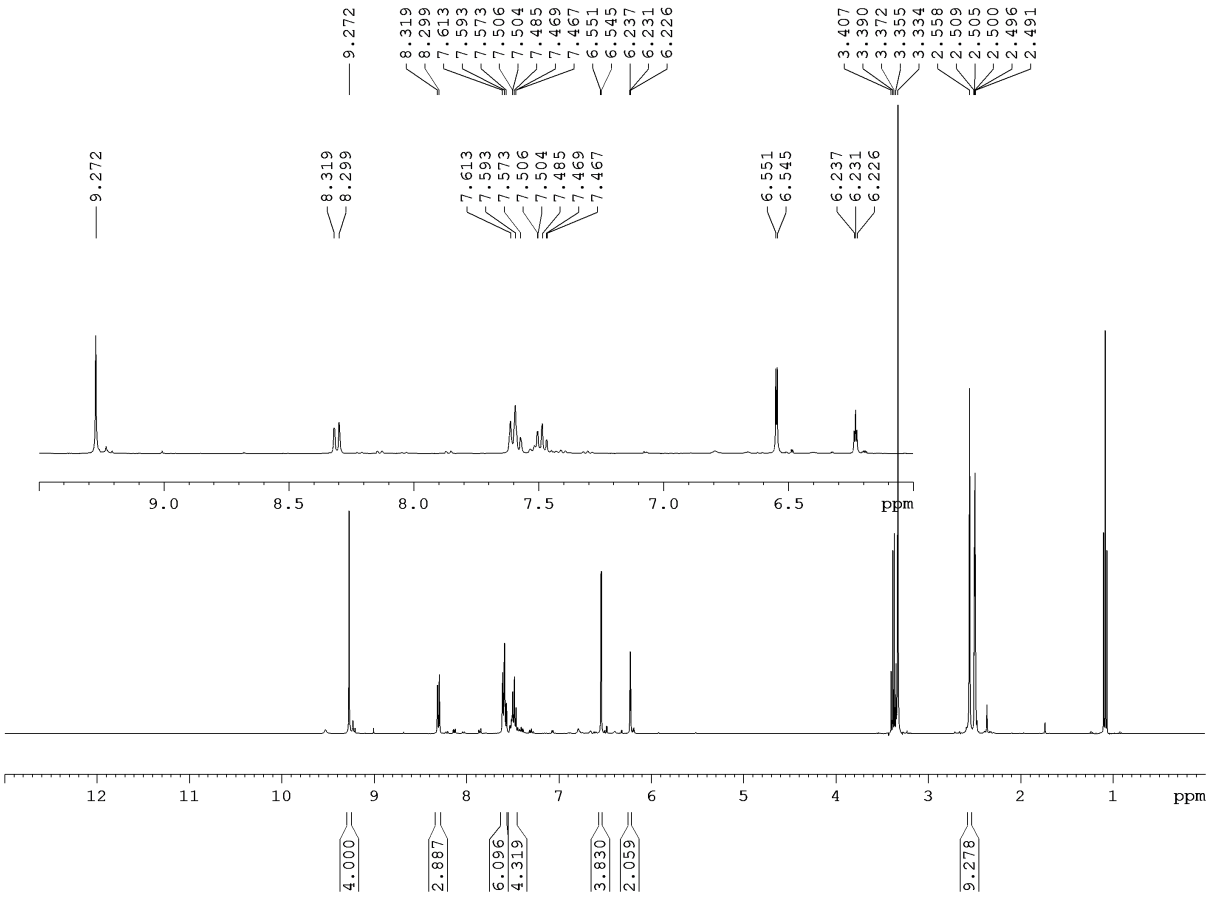

Figure S11 ^{1}H NMR of tri-*o*-tolylbismuth bis(3,5-dimethylbenzoate), **13** in $CDCl_3$ at 25 °C, 400 MHz

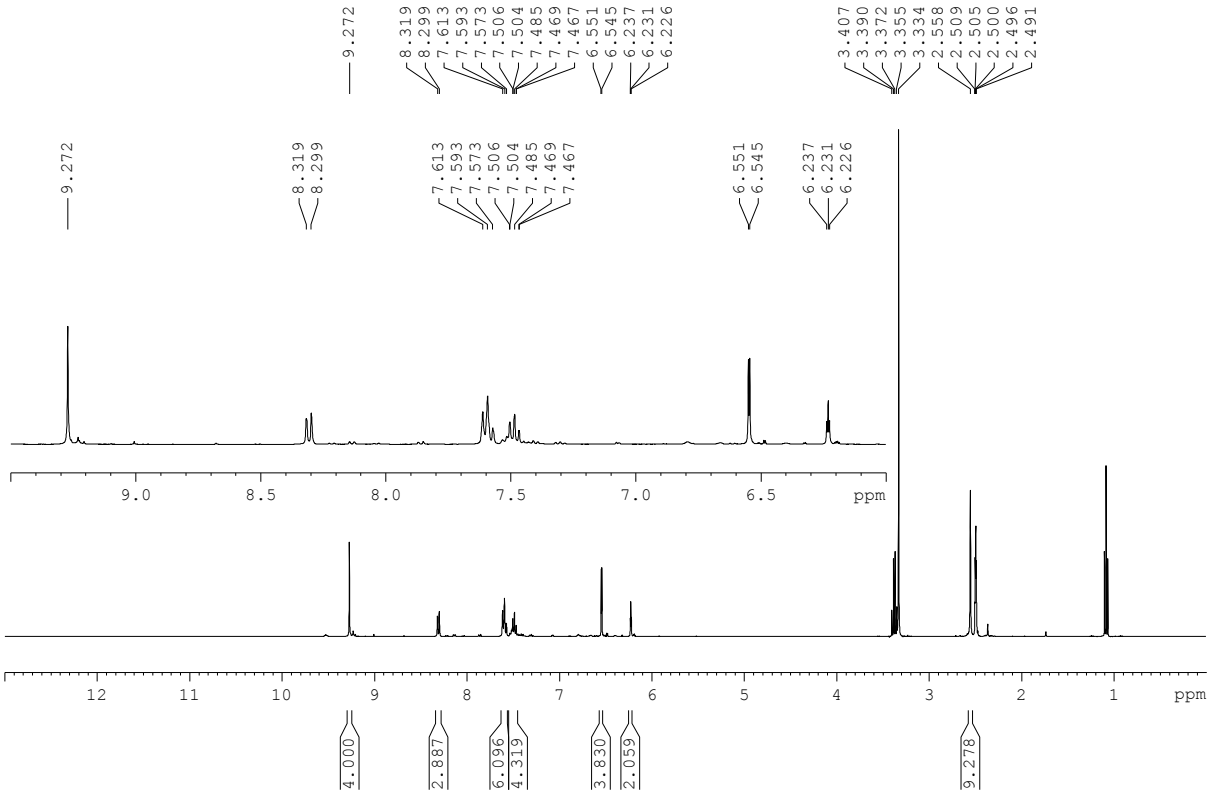

Figure S12 ^{1}H NMR of tri-*o*-tolylbismuth bis(3,5-dihydroxybenzoate), **14** in $CDCl_3$ at 25 °C, 400 MHz

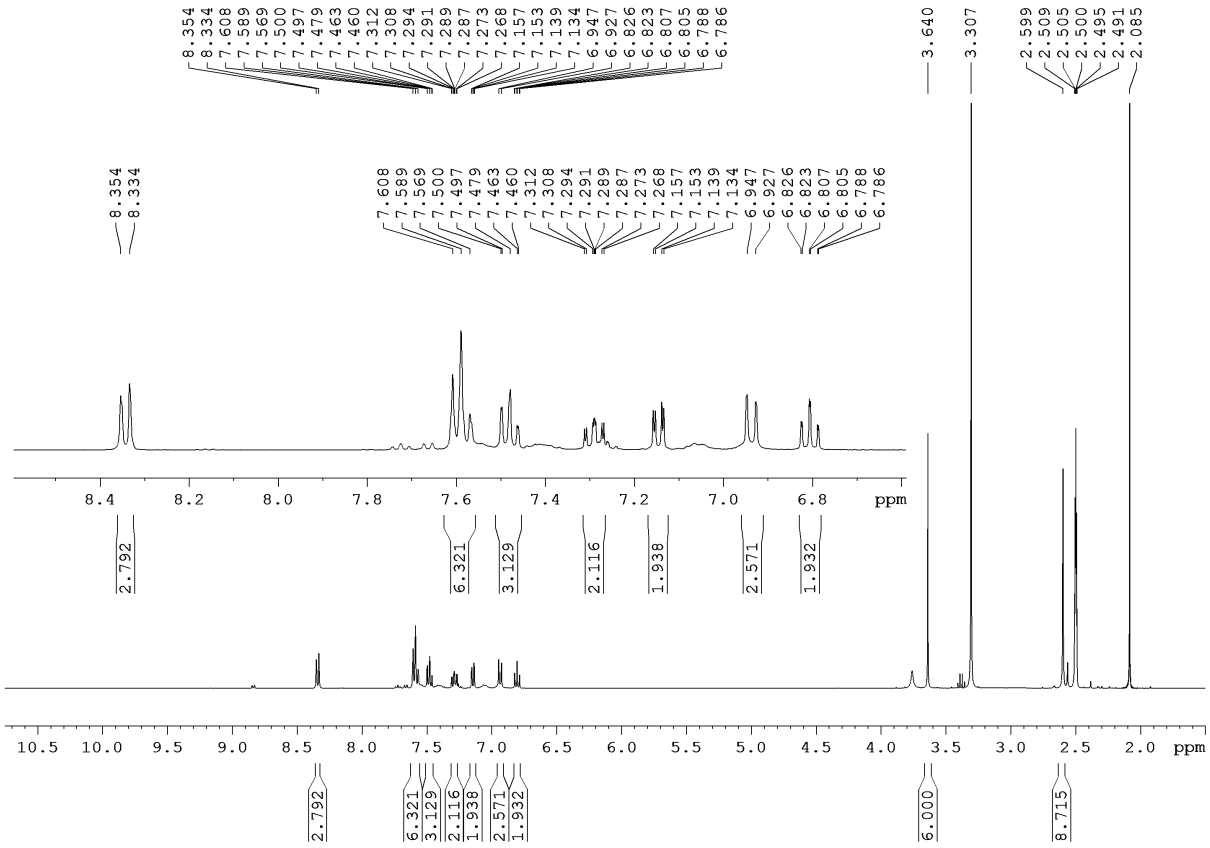

Figure S13 ^{1}H NMR of tri-*o*-tolylbismuth bis(2-methoxybenzoate), **15** in $(CD_3)_2SO$ at 25 °C, 400 MHz

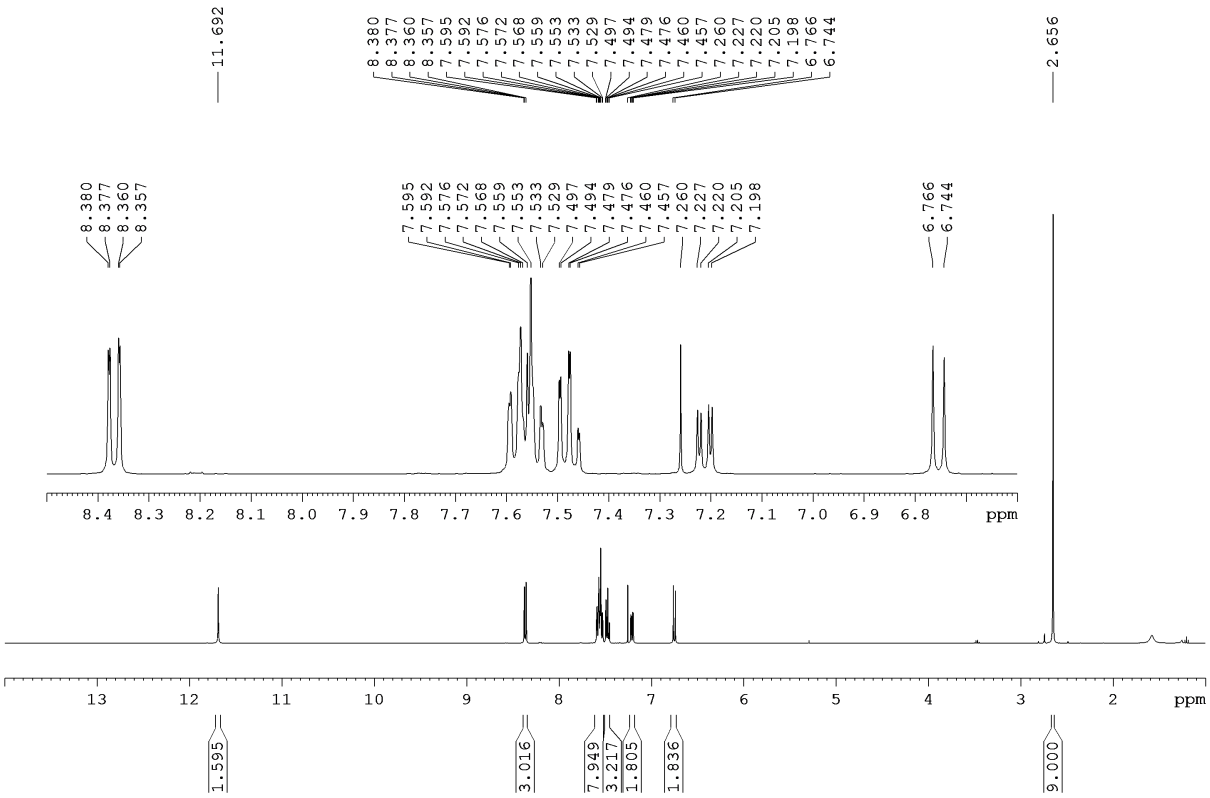

Figure S14 ^{1}H NMR of tri-*o*-tolylbismuth bis(5-chlorosalicyate), **16** in CDCl3 at 25 °C, 400 MHz

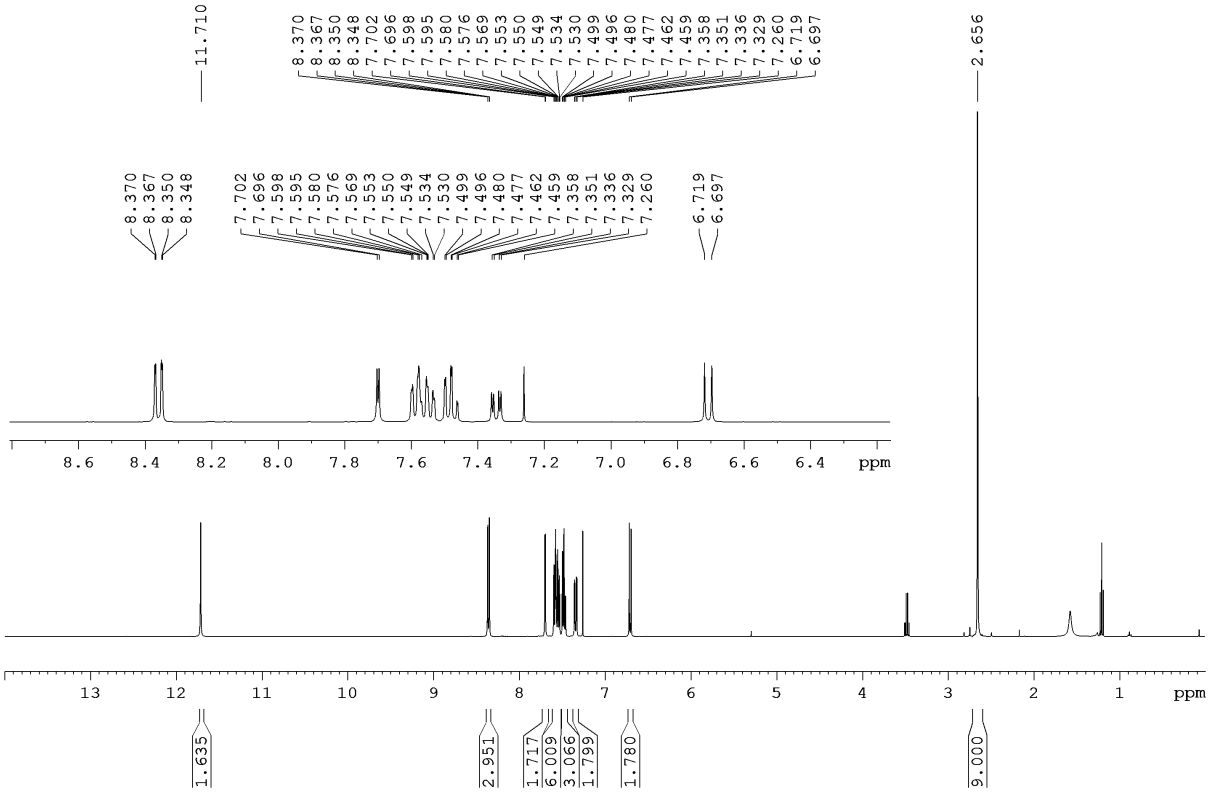

Figure S15 ^{1}H NMR of tri-*m*-tolylbismuth bis(5-bromosalicyate), **17** in $CDCl_3$ at 25 °C, 400 MHz

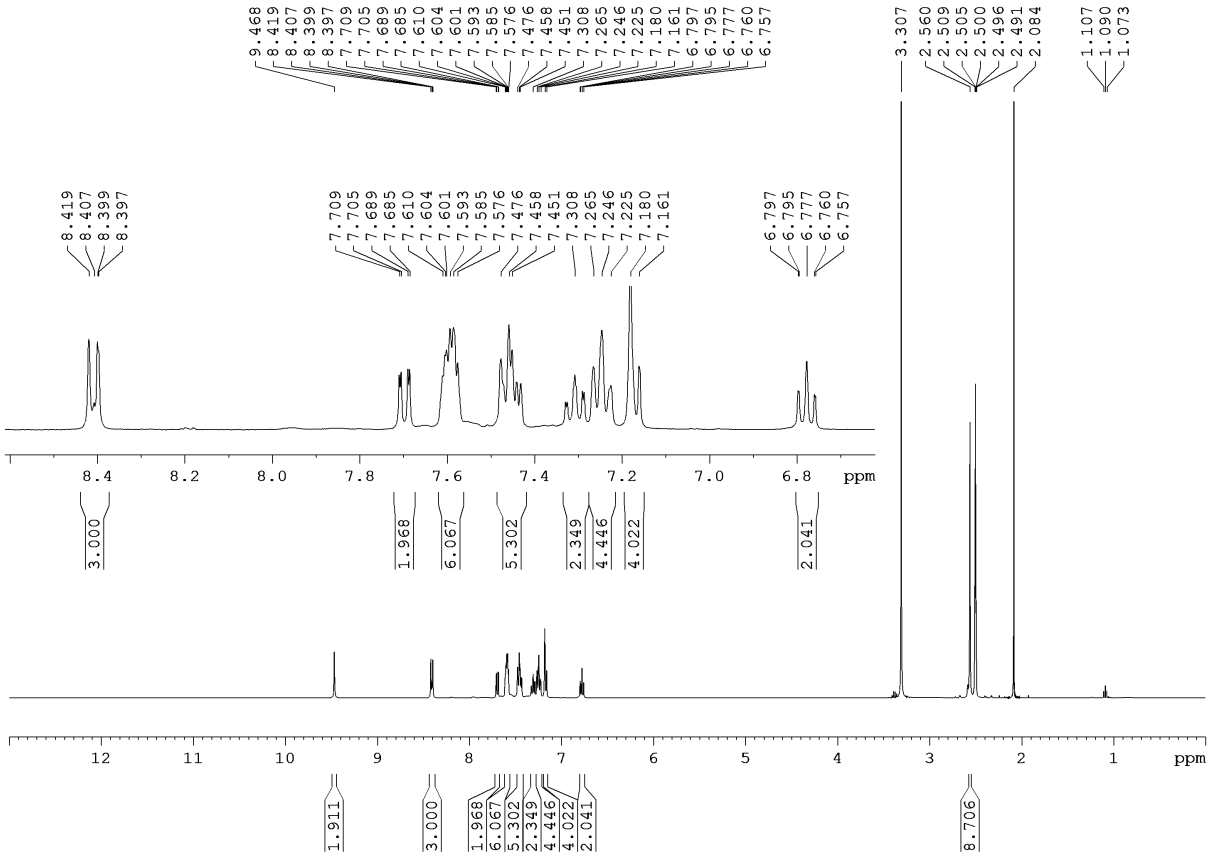

Figure S16 ^{1}H NMR of tri-*o*-tolylbismuth bis(2-{[3-(Trifluoromethyl)phenyl]amino}benzoate), **18** in $(CD_3)_2SO$ at 25 °C, 400 MHz

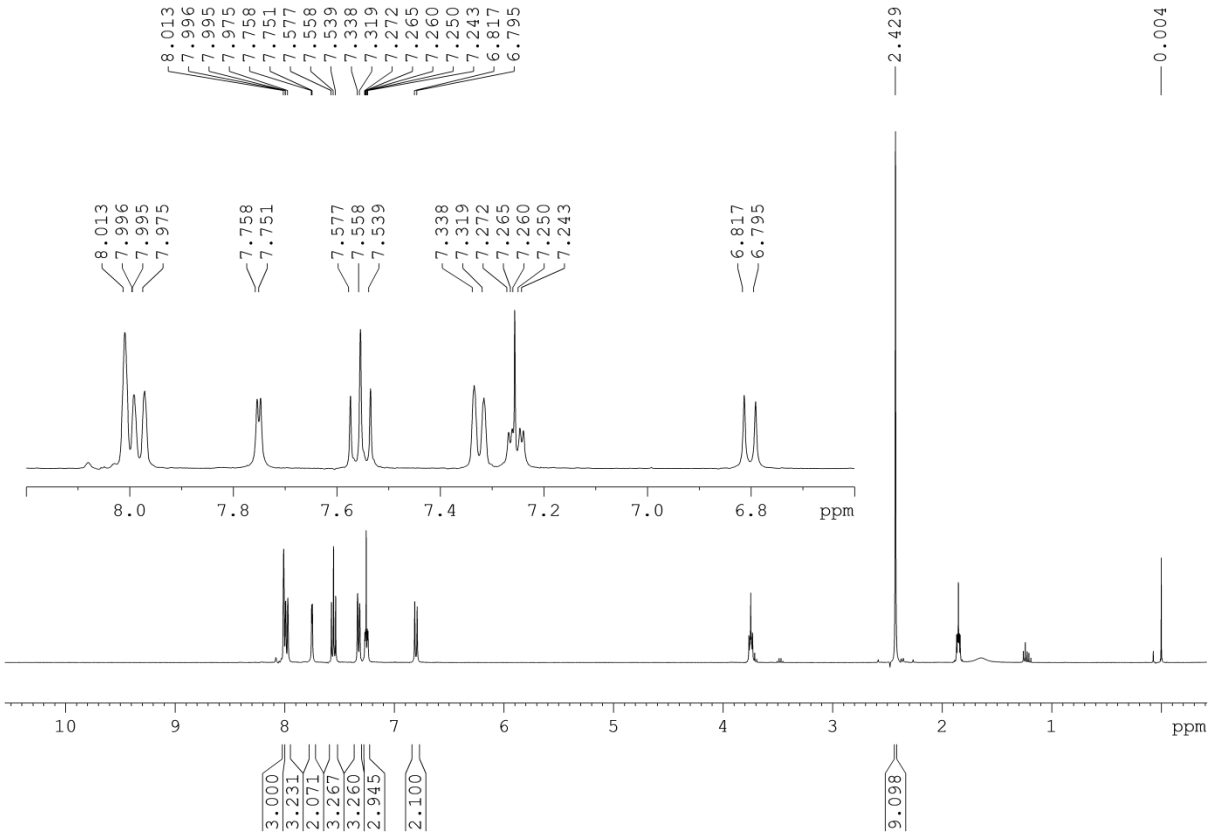

Figure S17 ^{1}H NMR of tri-*m*-tolylbismuth bis(5-chlorosalicyate), **19** in $CDCl_3$ at 25 °C, 400 MHz.

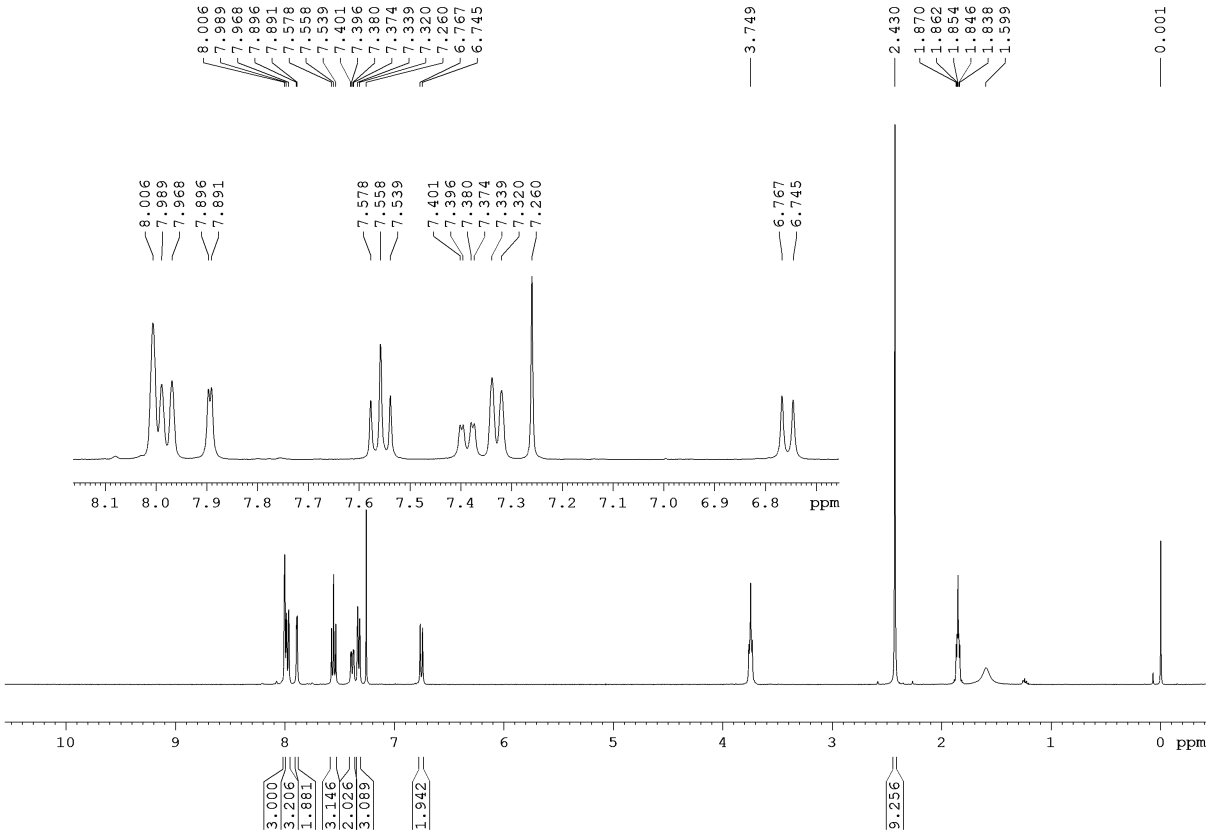

Figure S18 ^{1}H NMR of tri-*m*-tolylbismuth bis(5-bromosalicyate), **20** in $CDCl_3$ at 25 °C, 400 MHz.

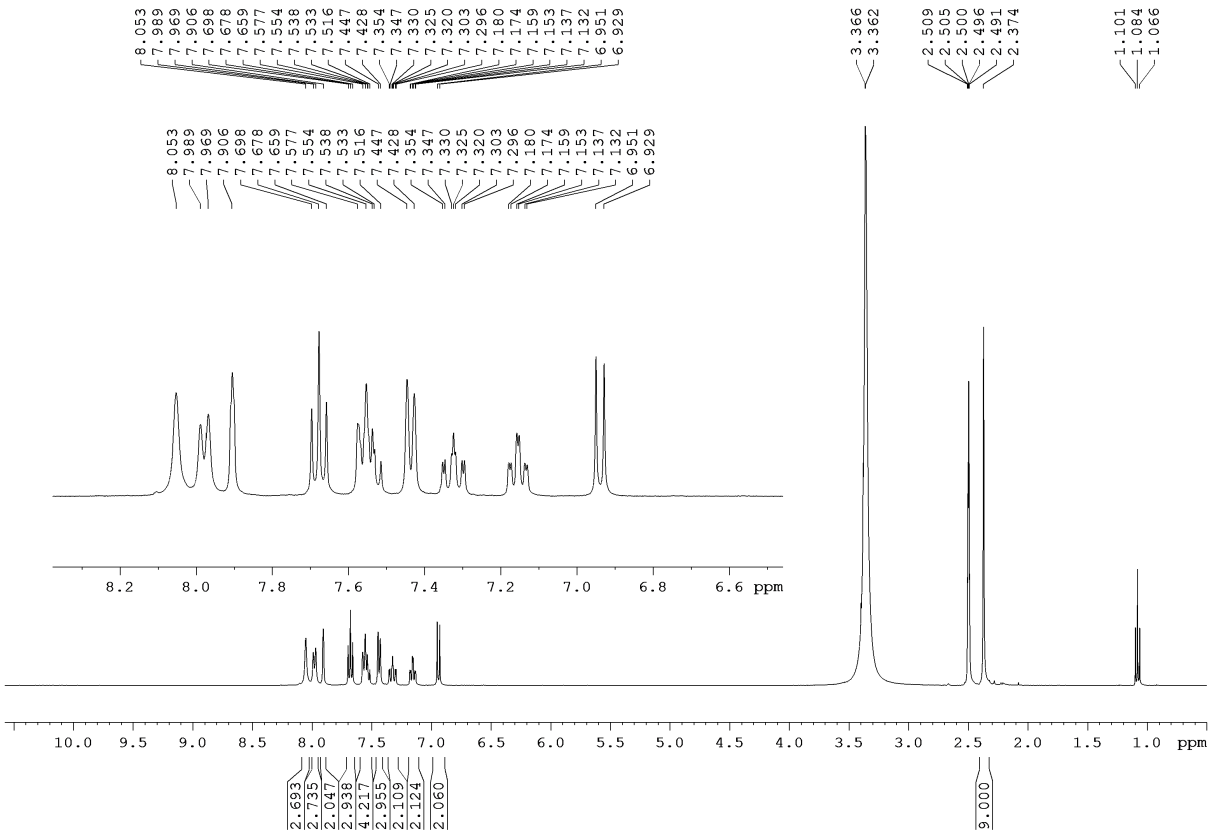

Figure S19 ^{1}H NMR of tri-*m*-tolylbismuth bis(2', 4'-difluoro-4-hydroxybiphenyl-3-carboxylate), **21** in $(CD_3)_2SO$ at 25 °C, 400 MHz.

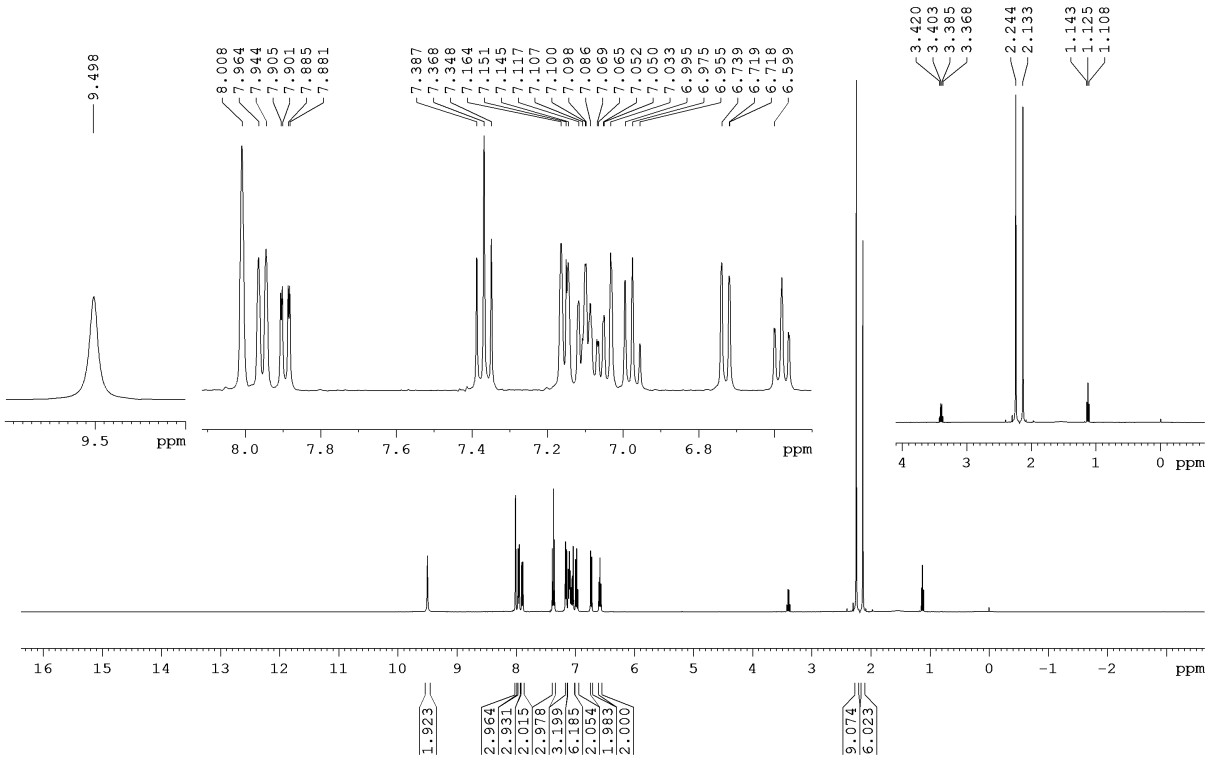

Figure S20 ^{1}H NMR of tri-*m*-tolylbismuth bis(2-[(3-chloro-2-methylphenyl)amino]benzoate), **22** in $CDCl_3$ at 25 °C, 400 MHz

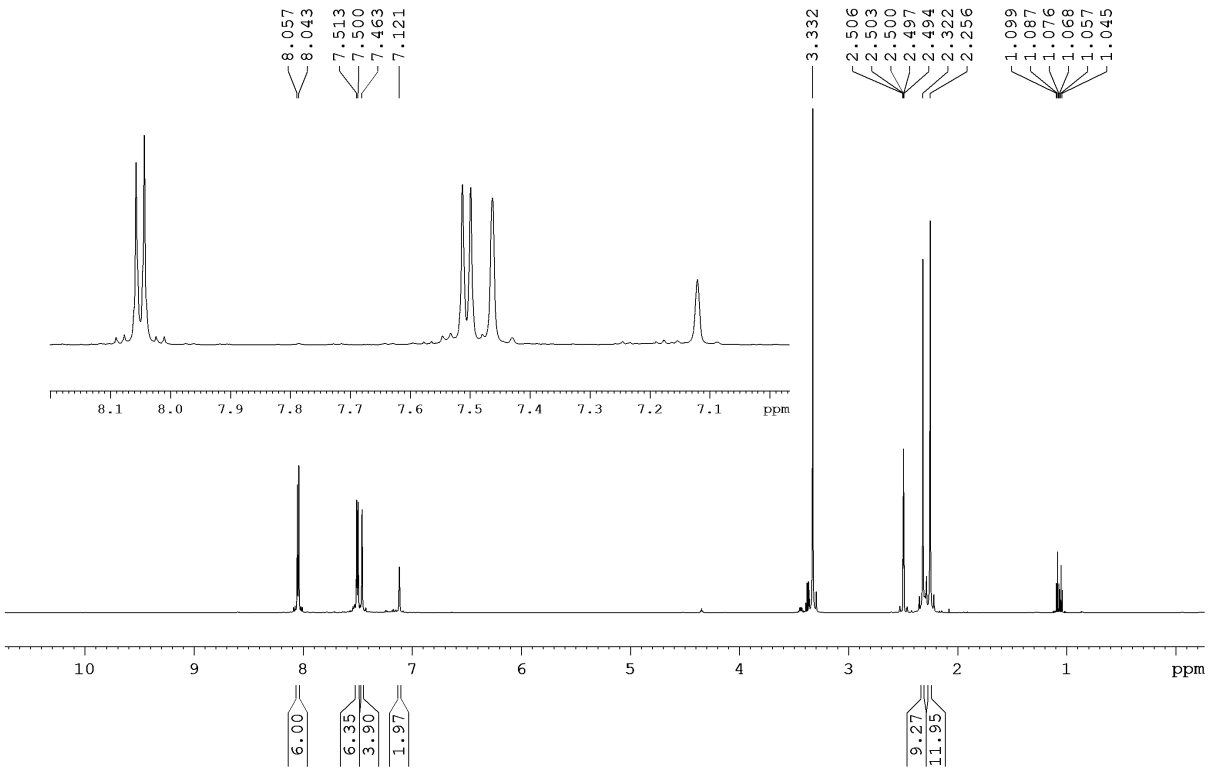

Figure S21 ^{1}H NMR of tri-*p*-tolylbismuth bis(3,5-dimethylbenzoate), **23** in $(CD_3)_2SO$ at 25 °C, 400 MHz.

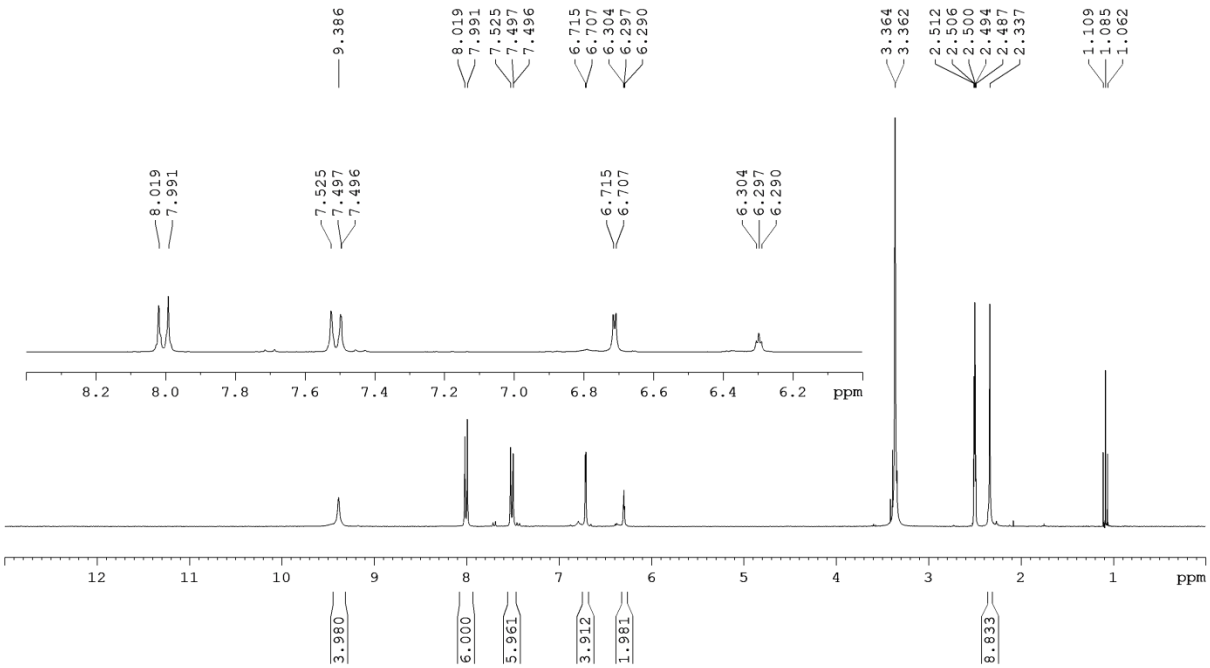

Figure S22 ^{1}H NMR of tri-*p*-tolylbismuth bis(3,5-dihydroxybenzoate), **24** in $(CD_3)_2SO$ at 25 °C, 400 MHz.

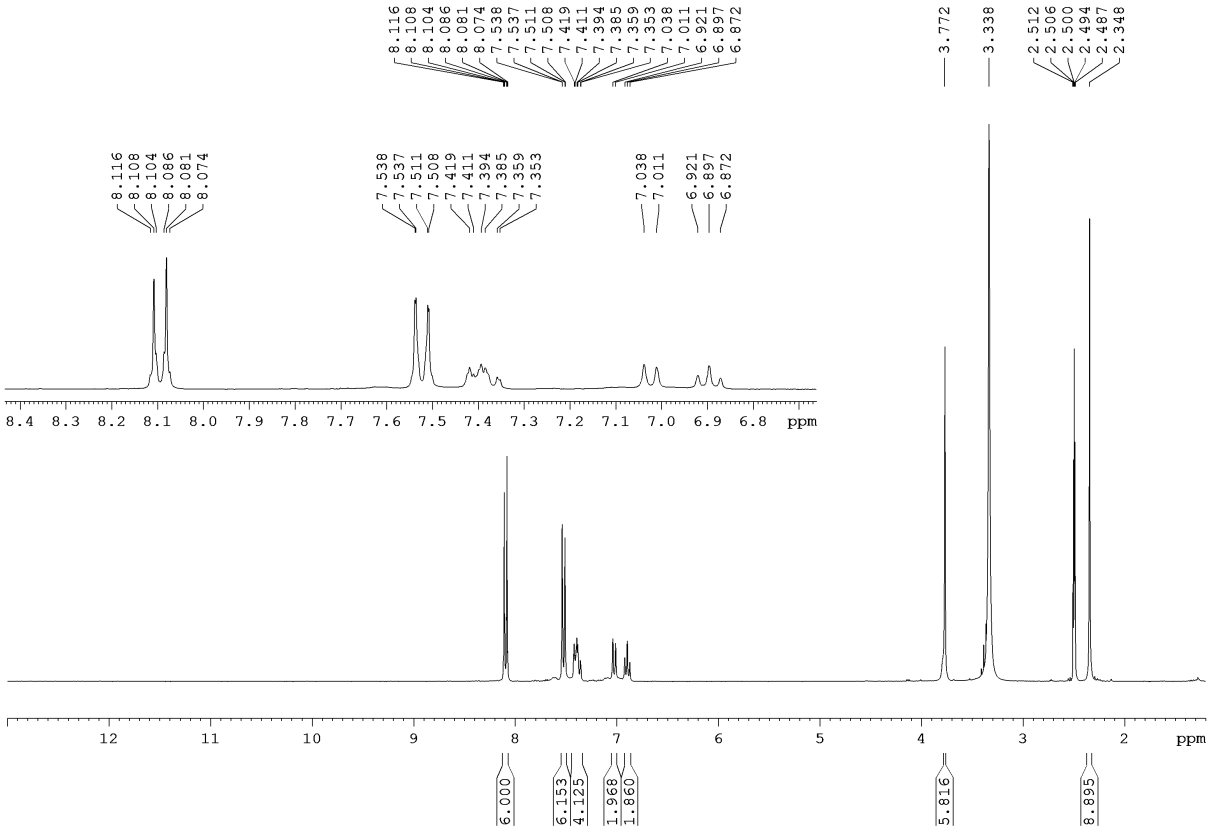

Figure S23 ^{1}H NMR of tri-*p*-tolylbismuth bis(2-methoxybenzoate), **25** in $(CD_3)_2SO$ at 25 °C, 400 MHz.

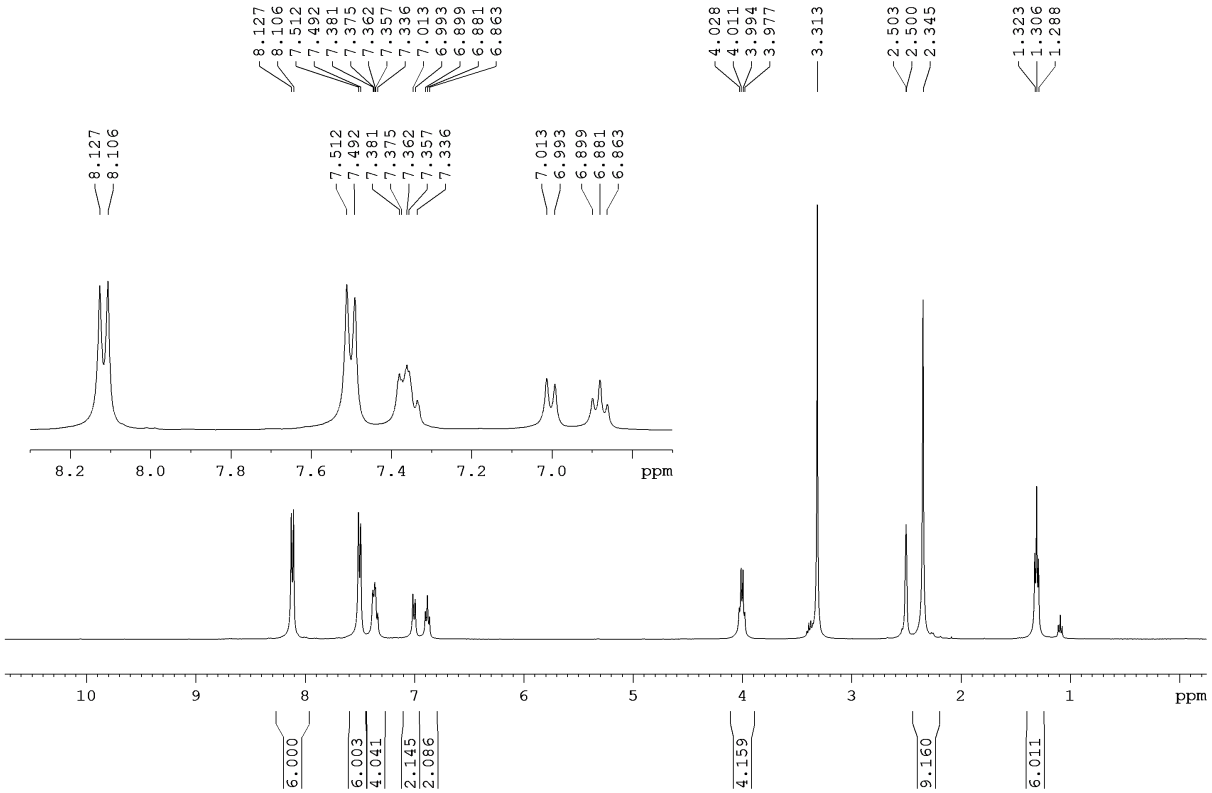

Figure S24 ^{1}H NMR of tri-*p*-tolylbismuth bis(2-ethoxybenzoate), **26** in $(CD_3)_2SO$ at 25 °C, 400 MHz

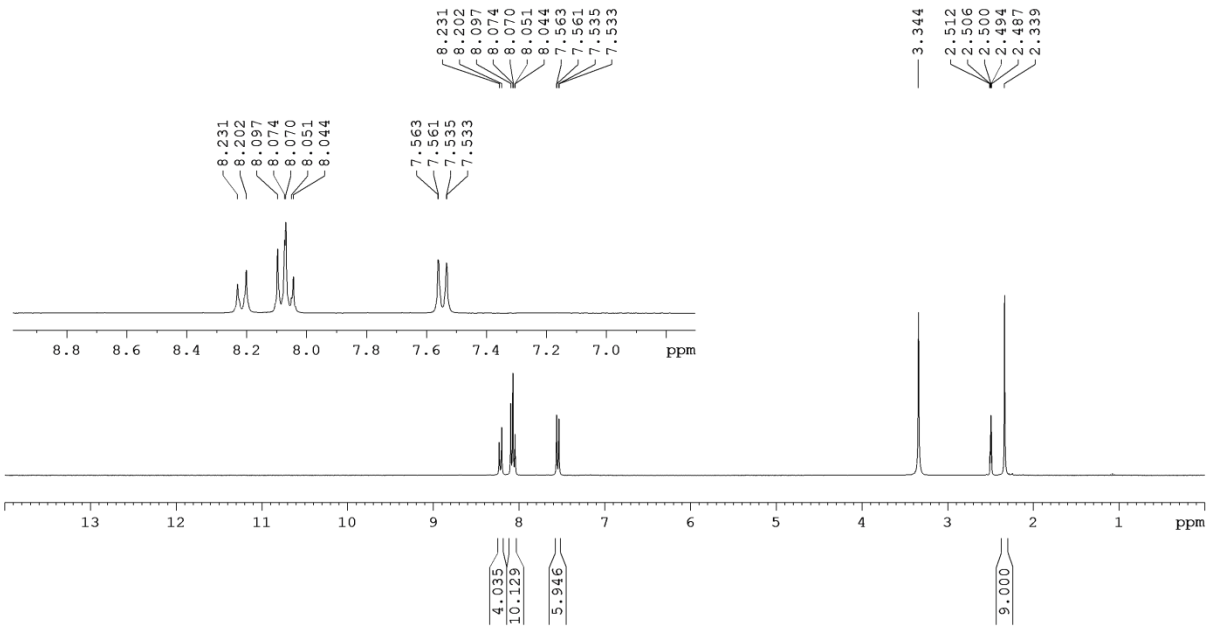

Figure S25 ^{1}H NMR of tri-*p*-tolylbismuth bis(4-nitrobenzoate), **27** in $(CD_3)_2SO$ at 25 °C, 400 MHz

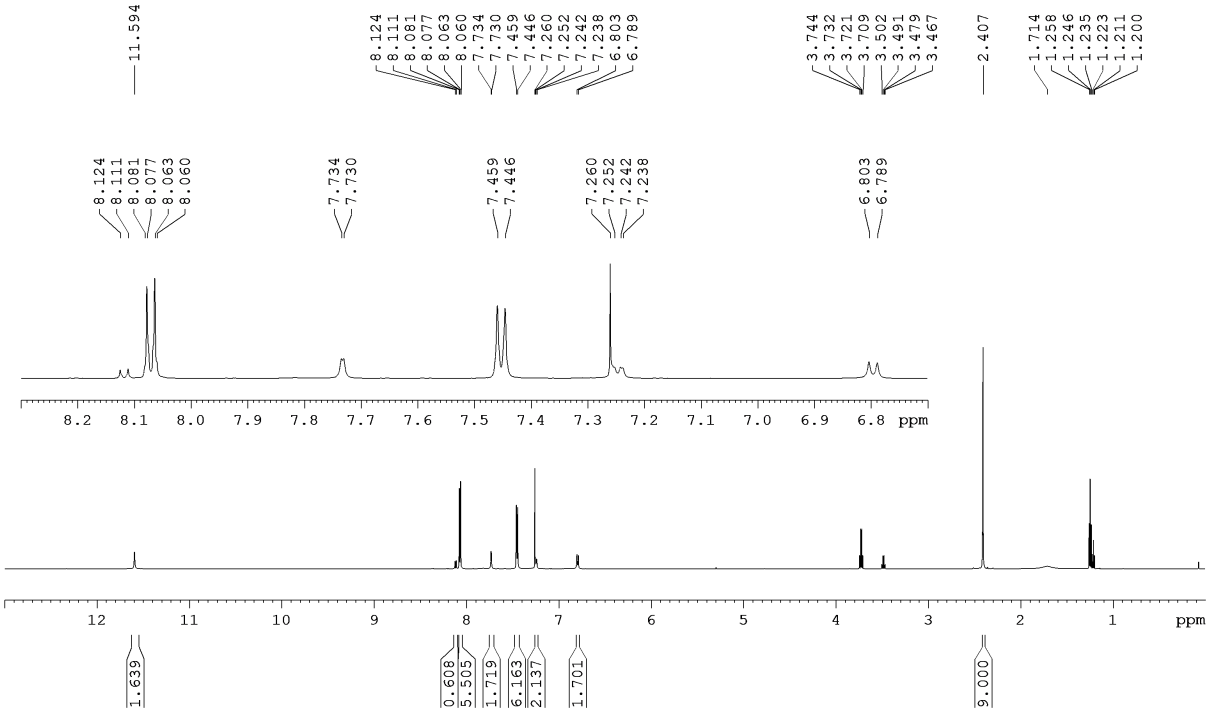

Figure S26 ^{1}H NMR of tri-*p*-tolylbismuth bis(5-chlorosalicyate), **28** in $CDCl_3$ at 25 °C, 400 MHz

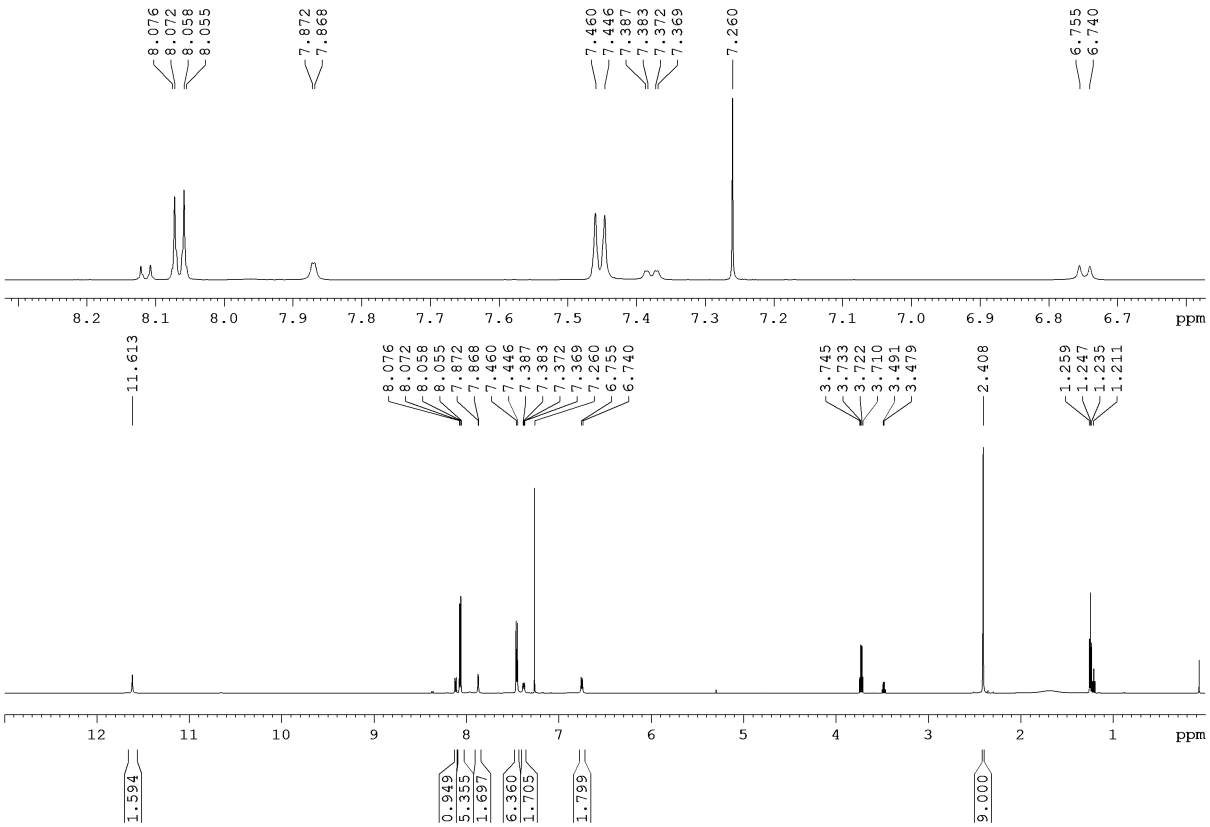

Figure S27 ^{1}H NMR of tri-*p*-tolylbismuth bis(5-bromosalicyate), **29** in $CDCl_3$ at 25 °C, 400 MHz

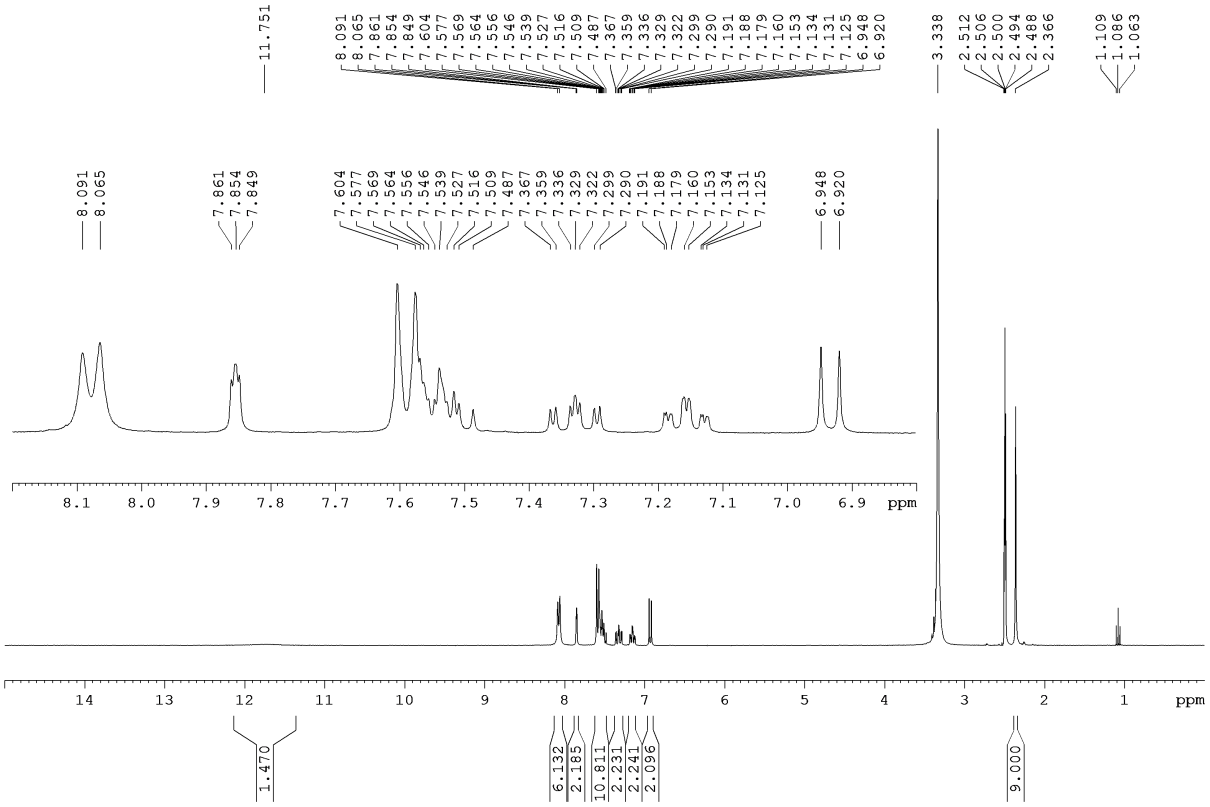

Figure S28 ^{1}H NMR of tri-*p*-tolylbismuth bis(2', 4'-difluoro-4-hydroxybiphenyl-3-carboxylate), **30** in $CDCl_3$ at 25 °C, 400 MHz

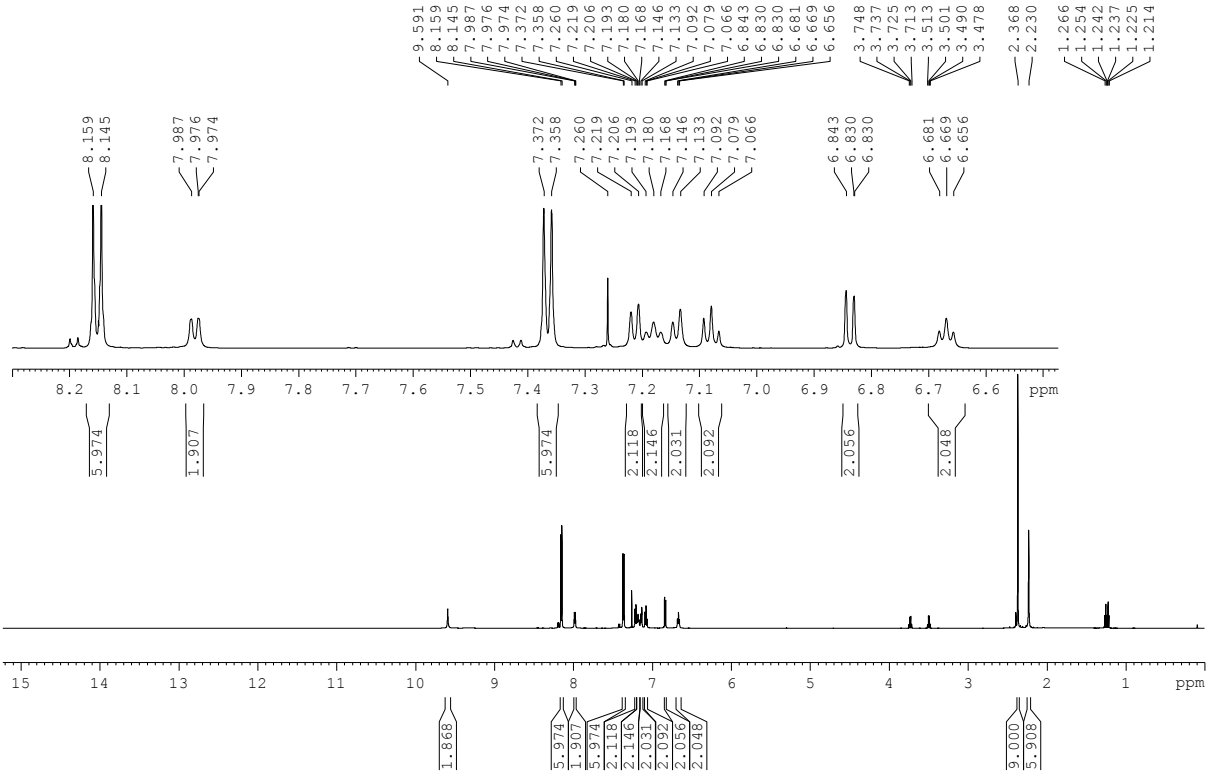

Figure S29 ^{1}H NMR of tri-*p*-tolylbismuth bis(2-[(3-chloro-2-methylphenyl)amino]benzoate), **31** in $CDCl_3$ at 25 °C, 400 MHz

3. Biological graphs for Compounds **25 – 29** and **32**

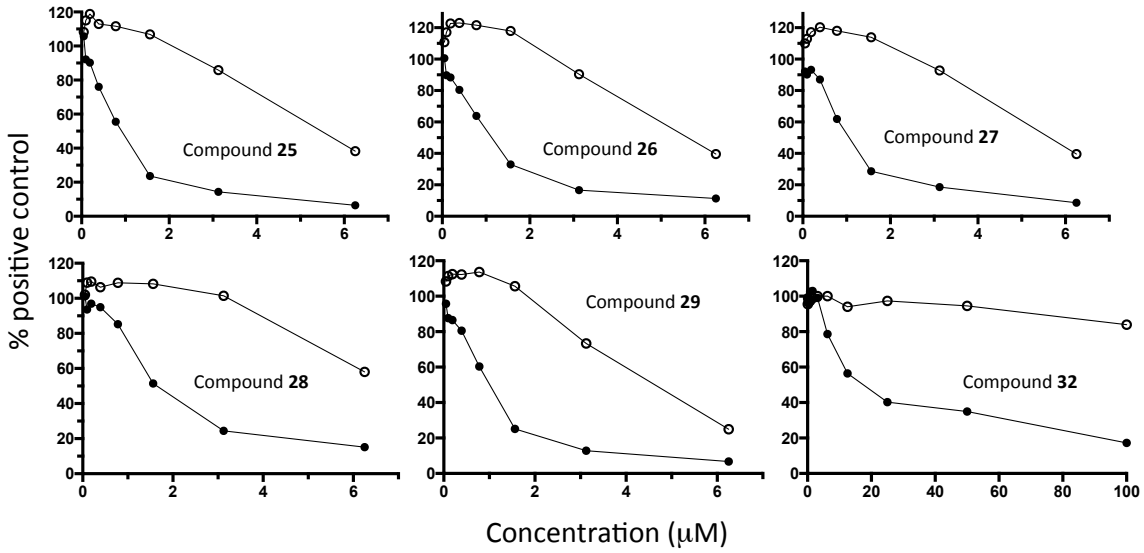

Figure S30 Activity of 25-29 and 32 on *L. major* promastigotes (●) and human fibroblasts (○) after 48 hours

4. Solid state structures for Compounds 6, 8, 9, 19, 22, 25 – 28 and 31

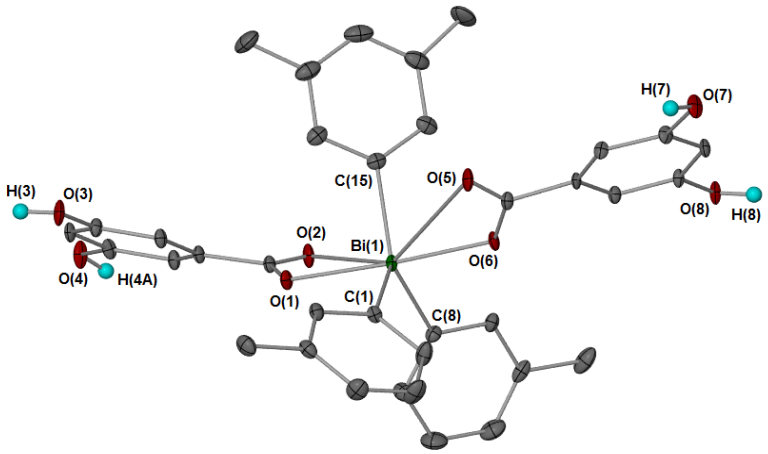

Figure S31 Molecular structure of [Bi(*m*-Tol)$_3$($O_2CC_6H_3$(2,5-OH))$_2$] **6** showing thermal ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Bi(1)-C(1) 2.186(3); Bi(1)-C(8) 2.191(3); Bi(1)-C(15) 2.202(4); Bi(1)-O(6) 2.247(2); Bi(1)-O(1) 2.267(2); Bi(1)-O(2) 3.071(3); Bi(1)-O(5) 3.262(3).

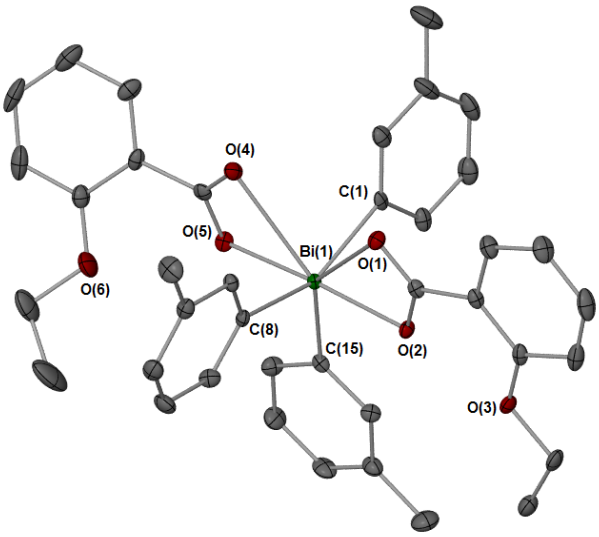

Figure S32 Molecular structure of [Bi(*m*-Tol)$_3$($O_2CC_6H_4$(2-EtO))$_2$] **8** showing thermal ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Bi(1)-C(1) 2.195(4); Bi(1)-C(8) 2.203(4); Bi(1)-C(15) 2.216(4); Bi(1)-O(5) 2.305(3); Bi(1)-O(2) 2.309(3); Bi(1)-O(1) 2.686(3); Bi(1)-O(4) 2.743(3).

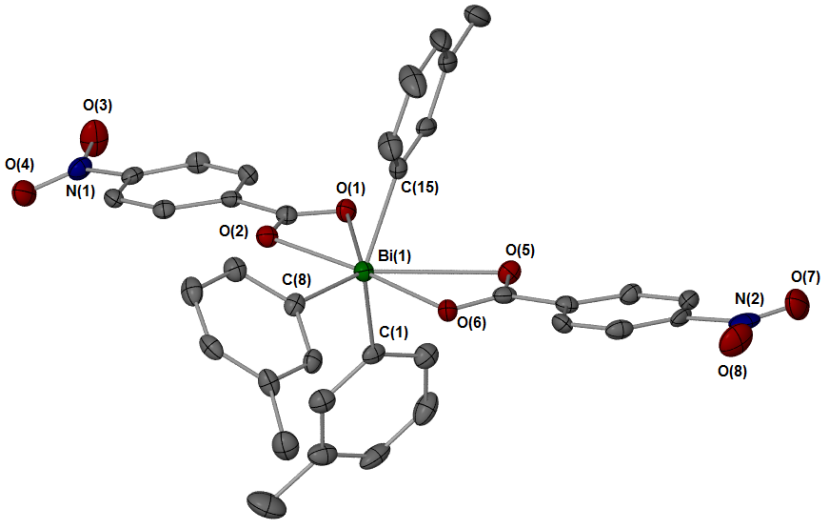

Figure S33 Molecular structure of [Bi(*m*-Tol)$_3$(O$_2$CC$_6$H$_4$(4-NO$_2$))$_2$] **9** showing thermal ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Bi(1)-C(15) 2.182(4); Bi(1)-C(1) 2.195(4); Bi(1)-C(8) 2.205(7); Bi(1)-O(6) 2.274(4); Bi(1)-O(2) 2.287(3);Bi(1)-O(1) 2.841(2); Bi(1)-O(5) 2.899(3).

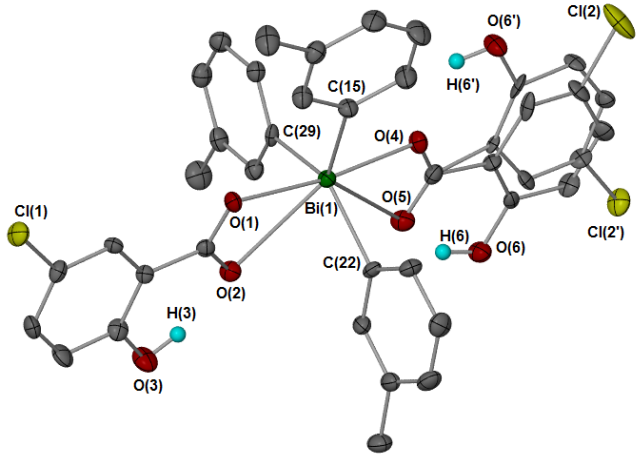

Figure S34 Molecular structure of [Bi(*m*-Tol)$_3$(O$_2$CC$_6$H$_3$(2-OH,5-Cl))$_2$] **19** showing thermal ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Bi(1)-C(29) 2.176(4); Bi(1)-C(22) 2.189(4); Bi(1)-C(15) 2.224(5); Bi(1)-O(4) 2.280(3); Bi(1)-O(1) 2.318(3); Bi(1)-O(2) 2.849(3); Bi(1)-O(5) 3.047(3).

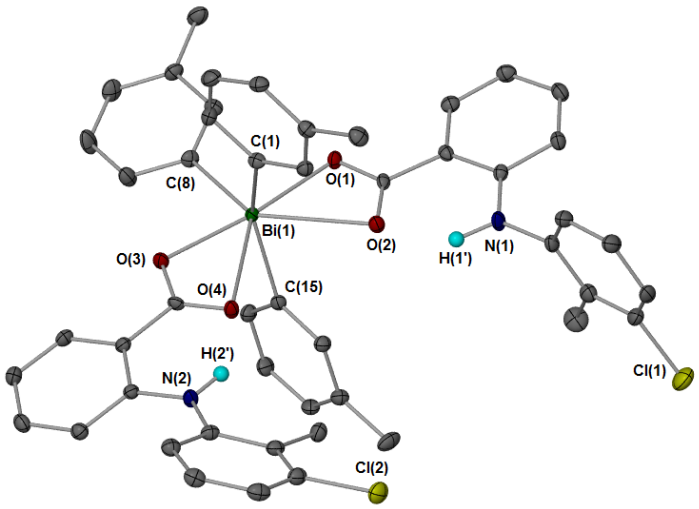

Figure S35 Molecular structure of [Bi(*m*-Tol)$_3$(O$_2$CC$_6$H$_4$(2-NHC$_6$H$_3$(2-Me,3-Cl))$_2$] **22** showing thermal ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Bi(1)-C(15) 2.200(4); Bi(1)-C(1) 2.201(4); Bi(1)-C(8) 2.238(5); Bi(1)-O(3)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

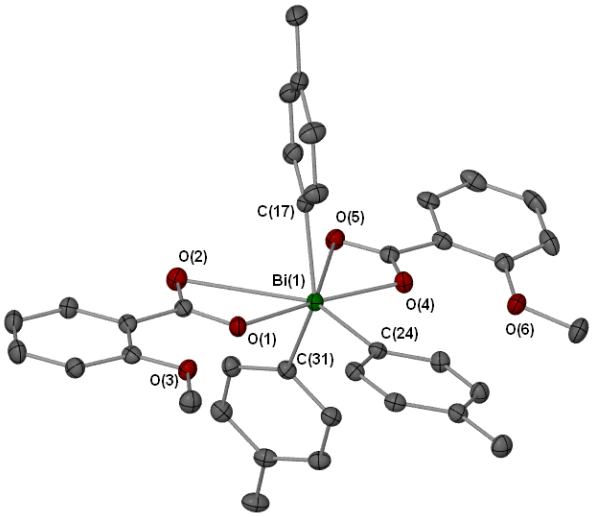

Figure S36 Molecular structure of [Bi(*p*-Tol)$_3$(O$_2$CC$_6$H$_4$(2-OMe))$_2$] **25** showing thermal ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Bi(1)-C(31) 2.186(4); Bi(1)-C(17) 2.195(3); Bi(1)-C(24) 2.205(3); Bi(1)-O(1) 2.249(2); Bi(1)-O(4) 2.257(2); Bi(1)-O(5) 2.905(3); Bi(1)-O(2) 2.983(3).

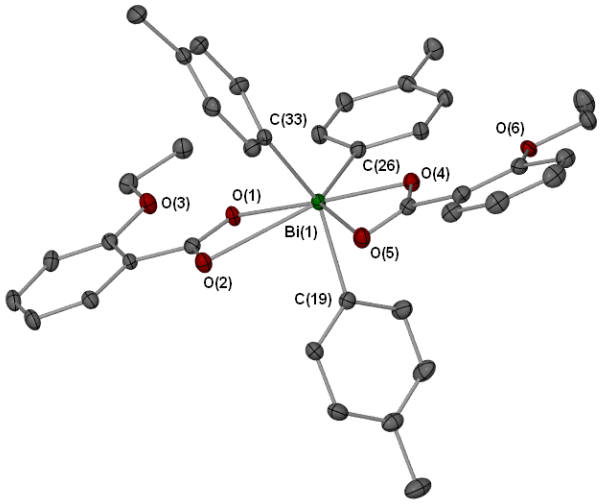

Figure S37 Molecular structure of [Bi(*p*-Tol)$_3$(O$_2$CC$_6$H$_4$(2-OEt))$_2$] **26** showing thermal ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Bi(1)-C(33) 2.193(3); Bi(1)-C(19) 2.195(3); Bi(1)-C(26) 2.207(3); Bi(1)-O(4) 2.276(2); Bi(1)-O(1) 2.278(2); Bi(1)-O(2) 2.820(2); Bi(1)-O(5) 2.857(2).

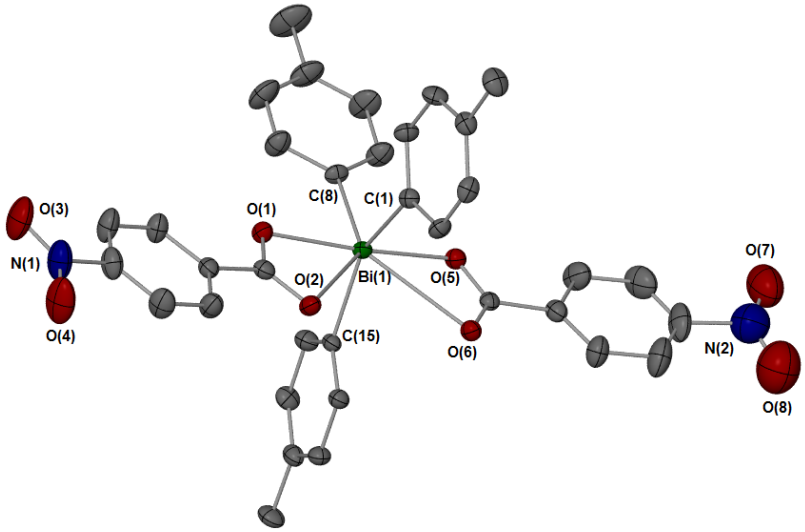

Figure S38 Molecular structure of [Bi(*p*-Tol)$_3$(O$_2$CC$_6$H$_4$(4-NO$_2$))$_2$] **27** showing thermal ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Bi(1)-C(15) 2.186(5); Bi(1)-C(1) 2.190(5); Bi(1)-C(8) 2.212(5); Bi(1)-O(5) 2.256(3); Bi(1)-O(1) 2.338(3); Bi(1)-O(2) 2.727(4); Bi(1)-O(6) 2.869(4).

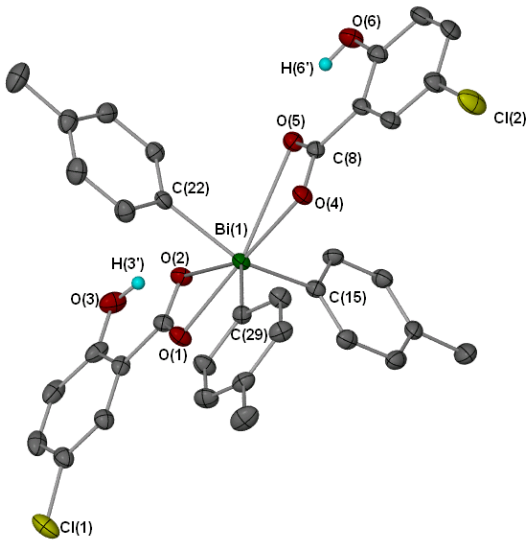

Figure S39 Molecular structure of [Bi(*p*-Tol)$_3$(O$_2$CC$_6$H$_3$(2-OH,5-Cl))$_2$] **28** showing thermal ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Bi(1)-C(15) 2.174(4); Bi(1)-C(22) 2.192(4); Bi(1)-C(29) 2.204(4); Bi(1)-O(4) 2.265(3); Bi(1)-O(1) 2.289(3); Bi(1)-O(2) 2.951(4); Bi(1)-O(5), 3.001(3).

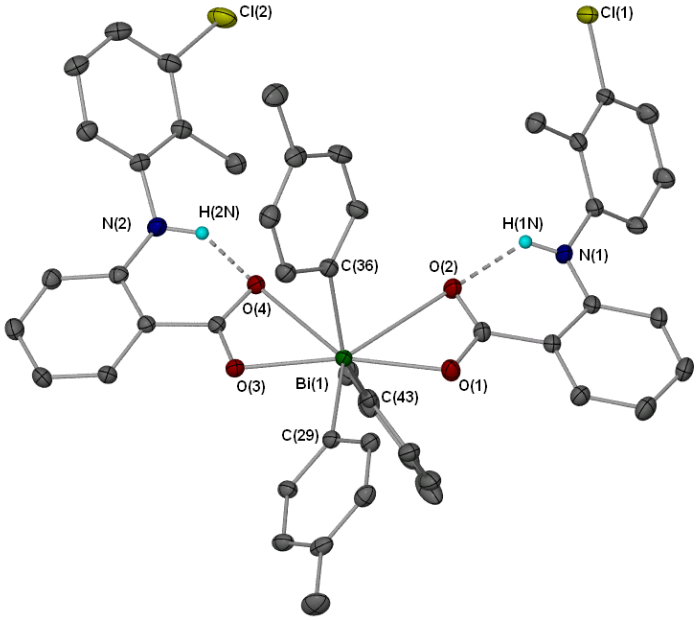

Figure S40 Molecular structure of [Bi(*p*-Tol)$_3$(O$_2$CC$_6$H$_4$(2-NHC$_6$H$_3$(2-Me,3-Cl))$_2$] **31** showing thermal ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Bi(1)-C(29) 2.192(3); Bi(1)-C(36) 2.193(3); Bi(1)-C(43) 2.198(3); Bi(1)-O(1) 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 – 28** and **31**

Table S1 Summary of crystallographic data for Compound 6, 8, 9, 19, 22, 25 – 28, 31 ([a] $I > 2\sigma(I)$); [b] all data).

Compound	**6**	**8**	**9**	**19**	**22**	**25**	**26**	**27**	**28**	**31**
Chemical formula	$C_{39}H_{45}BiO_{11}$	$C_{39}H_{39}BiO_6$	$C_{35}H_{29}BiN_2O_8$	$C_{35}H_{29}BiCl_2O_6$	$C_{49}H_{43}BiCl_2N_2O_4$	$C_{37}H_{35}BiO_6$	$C_{39}H_{39}BiO_6$	$C_{39}H_{37}BiN_2O_9$	$C_{35}H_{29}BiCl_2O_6$	$C_{49}H_{43}BiCl_2N_2O_4$
Formula Mass	898.73	812.68	814.58	825.46	35459	784.63	812.68	886.69	825.46	1003.73
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Orthorhombic
a/Å	15.636(3)	9.1878(4)	17.8158(13)	9.0562(4)	9.0480(18)	10.960(2)	10.949(2)	10.5176(3)	9.1030(18)	20.797(4)
b/Å	15.607(3)	18.7150(10)	14.7358(6)	11.5012(5)	11.217(2)	15.975(3)	15.980(3)	27.1933(8)	10.781(2)	15.314(3)
c/Å	30.709(6)	19.9856(10)	15.0730(10)	16.2432(7)	20.912(4)	17.886(4)	18.978(4)	14.2016(5)	18.399(4)	26.182(5)
α/°	90	90	90	107.263(4)	101.82(3)	90	90	90	98.62(3)	90
β/°	90	90	125.227(10)	90.519(4)	90.76(3)	91.79(3)	93.65(3)	102.235(2)	96.46(3)	90
γ/°	90	90	90	99.342(4)	90.17(3)	90	90	90	113.48(3)	90
V/Å^3	7494(3)	3436.5(3)	3232.5(3)	1591.26(12)	2077.2(7)	3130.1(11)	3313.7(12)	3969.5(2)	1607.7(6)	8339(3)
Space group	*Pbca*	$P2_12_12_1$	*C2*	*P-1*	*P-1*	*P21/c*	*P-1*	$P2_1/c$	P-1	Pbca
Z	8	4	4	2	2	4	4	4	2	8
Reflections collected	123455	20817	15330	24451	35459	58996	61780	27244	30394	184688
Ind. reflns	8933	10969	7286	7585	9060	7976	9449	9783	7821	14783
R_{int}	0.0617	0.0421	0.0342	0.0637	0.0411	0.0476	0.0451	0.0411	0.0405	0.0917
Final R_1 values[a]	0.0331	0.0373	0.0281	0.0400	0.0398	0.0353	0.0316	0.0418	0.0350	0.0402
Final $wR(F^2)$ values[a]	0.0846	0.0639	0.0417	0.0672	0.1003	0.0891	0.0853	0.0961	0.0905	0.1085
Final R_1 values[b]	0.0353	0.0482	0.0356	0.0625	0.0443	0.0433	0.0348	0.0606	0.0367	0.0470
Final $wR(F^2)$ values[b]	0.0858	0.0685	0.0444	0.0769	0.1027	0.0943	0.0876	0.1029	0.0920	0.1131
GoF	1.150	1.023	0.910	1.037	1.091	1.038	0.966	1.061	1.082	1.041
Temperature (K)	173(2)	123(2)	123(2)	123(2)	173(2)	173(2)	173(2)	123(2)	173(2)	100(2)