

Supporting Information. Part 1

Reactions of 3-acylchromones with dimethyl 1,3-acetonedicarboxylate and 1,3-diphenylacetone: one-pot synthesis of functionalized 2-hydroxybenzophenones, 6H-benzo[*c*]chromenes and benzo[*c*]coumarins

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(A) General Information

NMR spectra were recorded on a Bruker AV 300 instruments. IR spectra were recorded on a Perkin Elmer FT IR 1600 spectrometer (ATR). Mass spectra were obtained on a Hewlett-Packard HPGC/MS 5890/5972 instrument (EI, 70 eV) by GC inlet or on a MX-1321 instrument (EI, 70 eV) by direct inlet. Column chromatography was performed on silica gel (63–200 mesh, Merck), silica gel Merck 60F₂₅₄ plates were used for TLC. All solvents were purified and dried by standard methods. The starting 3-acylchromones **1–3** were prepared according to described procedures.^{6–8}

(B) Typical experimental procedures

General procedure for the synthesis of compounds 4–8

To a stirred reaction mixture of the corresponding chromone (1.0 mmol) and 1,3-C,C-dinucleophile (1.1 mmol) in dioxane (6–7 mL), DBU (0.20 mL, 1.3 mmol) was added slowly via a syringe at room temperature. Stirring at room temperature (for dimethyl acetonedicarboxylate) or at reflux (for 1,3-diphenylacetone) was continued until chromone was consumed completely (followed by TLC, approximately 10–12 h). The reaction mixture was quenched with aqueous solution of 10% NH₄Cl and extracted with chloroform, dried (Na₂SO₄), the solvent was distilled off under reduced pressure, and the resulting residue was subjected to column chromatography on silica gel using heptane–ethylacetate (5:1) as eluent, slowly increasing the polarity up to 3:1 to give the isolated products.

General procedures for the synthesis of compounds 9 and 10

To a stirred reaction mixture of the corresponding compound **4** or **5** (1.0 mmol) in methanol (6–7 mL) potassium hydroxide (8.0 mmol) was added. The reaction mixture was heated under reflux. Stirring and heating were continued until reagent was consumed completely (followed by TLC, approximately 2 days). The solvent was distilled off in vacuum and the resulting residue was quenched with water, then neutralized with aqueous solution of HCl (30%). The resulting residue was filtered and dried.

(C) Synthesis of compounds and their analytical data

3-Methoxalylchromone (Ia). Yield 81%, yellow solid, mp 130–132 °C; ^1H NMR (300 MHz, DMSO- d_6) δ 3.88 (s, 3H, MeO), 7.59 (ddd, $^3J = 8.0$, 7.3 Hz, $^4J = 1.0$ Hz, 1H, H-6), 7.77 (dd, $^3J = 8.5$ Hz, $^4J = 1.0$ Hz, 1H, H-8), 7.90 (ddd, $^3J = 8.5$, 7.3 Hz, $^4J = 1.5$ Hz, 1H, H-7), 8.10 (dd, $^3J = 8.0$ Hz, $^4J = 1.5$ Hz, 1H, H-5), 9.10 (s, 1H, H-2); ^{13}C NMR (62.9 MHz, DMSO- d_6) δ 52.7, 118.5, 118.9, 123.9, 125.2, 127.0, 135.6, 155.6, 164.0, 164.6, 174.1, 184.6; MS (GC, 70 eV) m/z (%) 232 (M^+ , 3), 204 (17), 189 (16), 173 (100), 121 (46), 89 (15), 63 (16), 53 (21); HRMS (ESI): calcd for $\text{C}_{12}\text{H}_9\text{O}_5$ $[\text{M}+\text{H}]^+$ 233.04445, found 233.04445; IR (ATR, cm^{-1}) 3064 (w), 2956 (w), 1721 (m), 1693 (m), 1645 (s), 1612 (s), 1562 (m), 1479 (w), 1458 (s), 1435 (m), 1395 (m), 1327 (s), 1303 (m), 1265 (m), 1232 (m), 1195 (m), 1171 (m), 1143 (w), 1127 (w), 1107 (m), 1034 (m), 1015 (m), 976 (m), 942 (w), 881 (m), 855 (m), 800 (m), 761 (s), 706 (s), 675 (m), 646 (m), 540 (m).

3-Methoxalyl-6-methylchromone (Ib). Yield 93%, yellow solid, mp 134–136 °C; ^1H NMR (300 MHz, DMSO- d_6) δ 2.44 (s, 3H, Me), 3.87 (s, 3H, MeO), 7.66–7.74 (m, 2H, H-7, H-8), 7.89 (s, 1H, H-5), 9.08 (s, 1H, H-2); ^{13}C NMR (62.9 MHz, DMSO- d_6) δ 20.4, 52.7, 118.4, 118.7, 123.6, 124.5, 136.5, 136.9, 153.9, 164.0, 164.4, 174.1, 184.7; MS (GC, 70 eV) m/z (%) 246 (M^+ , 5), 218 (19), 203 (15), 187 (100), 135 (29), 77 (12), 53 (9); HRMS (ED): calcd for $\text{C}_{13}\text{H}_{10}\text{O}_5$ $[\text{M}]^+$ 246.05227, found 246.05262; IR (ATR, cm^{-1}) 3056 (w), 2954 (w), 1749 (s), 1715 (w), 1685 (s), 1658 (s), 1596 (s), 1553 (s), 1475 (s), 1430 (s), 1377 (w), 1338 (m), 1295 (s), 1239 (s), 1204 (s), 1135 (m), 1116 (m), 1029 (s), 998 (m), 976 (m), 960 (m), 914 (m), 872 (m), 830 (s), 816 (m), 795 (s), 762 (m), 746 (s), 712 (s), 658 (m), 550 (m).

7-Methoxy-3-methoxalylchromone (Ic). Yield 83%, yellow solid, mp 153 °C; ^1H NMR (300 MHz, DMSO- d_6) δ 3.87, 3.92 (both s, 3H, MeO), 7.15 (dd, $^3J = 8.9$ Hz, $^4J = 2.3$ Hz, 1H, H-6), 7.28 (d, $^4J = 2.3$ Hz, 1H, H-8), 8.00 (d, 1H, $^3J = 8.9$ Hz, H-5), 9.04 (s, 1H, H-2); ^{13}C NMR (75.5 MHz, DMSO- d_6) δ 52.6, 56.4, 101.6, 115.9, 117.3, 118.5, 126.7, 157.6, 164.1, 164.2, 164.8, 173.3, 184.8; MS (GC, 70 eV) m/z (%) 262 (M^+ , 2), 234 (23), 219 (24), 203 (100), 151 (54), 119 (12), 63 (10), 53 (16); HRMS (ESI): calcd for $\text{C}_{13}\text{H}_{11}\text{O}_6$ $[\text{M}+\text{H}]^+$ 263.05501, found 263.05528; IR (ATR, cm^{-1}) 3043 (w), 2967 (w), 2848 (w), 1743 (m), 1683 (m), 1650 (s), 1614 (s), 1552 (w), 1504 (m), 1464 (w), 1436 (s), 1393 (m), 1350 (w), 1326 (m), 1276 (s), 1226 (s), 1197 (m), 1179 (m), 1143 (m), 1104 (s), 1030 (m), 1012 (s), 971 (m), 943 (m), 921 (w), 879 (m), 849 (s), 818 (s), 785 (s), 748 (s), 721 (s), 677 (m), 633 (w), 599 (m), 578 (m), 543 (m).

6-Chloro-3-methoxalylchromone (Id). Yield 90%, yellow solid, mp 137–139 °C; ^1H NMR (250 MHz, DMSO- d_6) δ 3.88 (s, 3H, MeO), 7.84 (d, $^3J = 9.0$ Hz, 1H, H-8), 7.93 (dd, $^3J = 9.0$ Hz, $^4J = 2.6$ Hz, 1H, H-7), 8.01 (d, $^4J = 2.6$ Hz, 1H, H-5), 9.13 (s, 1H, H-2); ^{13}C NMR (62.9 MHz, DMSO- d_6) δ 52.8, 118.5, 121.4, 124.3, 125.2, 131.5, 135.3, 154.3, 163.8, 164.8, 173.2, 184.2; MS (GC, 70 eV) m/z (%) 266 (M^+ , 4), 238 (12), 223 (10), 207 (100), 155 (34), 123 (13), 63 (12), 53 (30); HRMS (ESI): calcd for $\text{C}_{12}\text{H}_8\text{ClO}_5$ [$\text{M}+\text{H}$] $^+$ 267.00548, found 267.00586; IR (ATR, cm^{-1}) 3068 (w), 2956 (w), 1739 (m), 1688 (m), 1651 (s), 1607 (m), 1553 (s), 1482 (w), 1464 (s), 1439 (s), 1391 (w), 1372 (w), 1327 (s), 1297 (s), 1253 (m), 1219 (m), 1191 (m), 1173 (m), 1139 (w), 1121 (m), 1073 (m), 1023 (s), 955 (s), 899 (m), 868 (m), 840 (s), 816 (s), 795 (s), 761 (s), 744 (m), 715 (s), 685 (m), 665 (s), 633 (s), 590 (w), 543 (s).

6-Chloro-7-methyl-3-methoxalylchromone (Ie). Yield 83%, white solid, mp 184–186 °C; ^1H NMR (300 MHz, CDCl_3) δ 2.52 (s, 3H, Me), 3.98 (s, 3H, MeO), 7.43 (s, 1H, H-8), 8.16 (s, 1H, H-5), 8.60 (s, 1H, H-2); ^{13}C NMR (75.5 MHz, CDCl_3) δ 20.9, 53.0, 119.7, 120.3, 123.6, 125.9, 133.7, 144.7, 154.2, 162.1, 164.0, 173.4, 184.1; MS (GC, 70 eV) m/z (%) 280 (M^+ , 4), 252 (15), 237 (13), 221 (100), 169 (30), 53 (12); HRMS (EI): calcd for $\text{C}_{13}\text{H}_9\text{ClO}_5$ (M^+) 280.01324, found 280.00133; IR (ATR, cm^{-1}) 3067 (w), 2956 (w), 1739 (m), 1683 (m), 1650 (s), 1615 (m), 1588 (m), 1541 (m), 1454 (m), 1436 (m), 1414 (s), 1383 (w), 1367 (w), 1332 (m), 1290 (s), 1247 (m), 1217 (m), 1167 (w), 1128 (m), 1029 (s), 995 (m), 952 (w), 941 (m), 901 (m), 885 (s), 823 (m), 796 (s), 761 (s), 714 (s), 689 (m), 651 (s), 595 (w), 552 (w).

6-Bromo-3-methoxalylchromone (If). Yield 95%, yellow solid, mp 138–140 °C; ^1H NMR (300 MHz, DMSO- d_6) δ 3.88 (s, 3H, MeO), 7.79 (d, $^3J = 8.9$ Hz, 1H, H-8), 8.07 (dd, $^3J = 8.9$ Hz, $^4J = 2.5$ Hz, 1H, H-7), 8.17 (d, $^4J = 2.5$ Hz, 1H, H-5), 9.14 (s, 1H, H-2); ^{13}C NMR (62.9 MHz, DMSO- d_6) δ 52.8, 118.6, 119.5, 121.6, 125.5, 127.4, 138.1, 154.7, 163.8, 164.9, 173.1, 184.2; MS (GC, 70 eV) m/z (%) 312 (M^+ , 6), 282 (13), 269 (12), 253 (100), 199 (26), 88 (9), 53 (18); HRMS (EI): calcd for $\text{C}_{12}\text{H}_7\text{BrO}_5$ [M] $^+$ 311.94509, found 311.94583; IR (ATR, cm^{-1}) 3078 (w), 2961 (w), 1731 (m), 1691 (m), 1651 (s), 1605 (m), 1552 (m), 1504 (w), 1461 (s), 1435 (s), 1380 (w), 1365 (m), 1326 (s), 1295 (s), 1260 (s), 1223 (m), 1179 (m), 1119 (m), 1061 (w), 1021 (s), 949 (m), 886 (m), 862 (m), 829 (s), 812 (s), 795 (s), 770 (s), 744 (m), 705 (s), 674 (m), 655 (m), 604 (s), 536 (s).

3-Methoxalylbenzo[h]chromone (1g). Yield 77%, pale yellow solid, mp 112–114 °C; ^1H NMR (300 MHz, CDCl_3) δ 4.02 (s, 3H, MeO), 7.68–7.82 (m, 3H), 7.92 (d, $^3J = 7.3$ Hz, 1H), 8.08 (d, $^3J = 8.8$ Hz, 1H), 8.42 (d, $^3J = 7.5$ Hz, 1H, H-5), 8.74 (s, 1H, H-2); ^{13}C NMR (75.5 MHz, CDCl_3) δ 53.0, 120.2, 120.9, 121.3, 122.0, 123.4, 126.9, 127.9, 128.2, 130.1, 136.2, 153.6, 161.0, 164.1, 174.3, 184.5; MS (GC, 70 eV) m/z (%) 282 (M^+ , 7), 254 (22), 239 (29), 223 (100), 171 (49), 139 (33), 114 (16), 53 (21); HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{11}\text{O}_5$ [$\text{M}+\text{H}$] $^+$ 283.06010, found 283.06061; IR (ATR, cm^{-1}) 3078 (w), 2961 (w), 1727 (w), 1690 (w), 1641 (s), 1633 (s), 1601 (m), 1590 (m), 1557 (m), 1509 (m), 1462 (m), 1440 (m), 1410 (m), 1402 (m), 1384 (s), 1360 (m), 1338 (m), 1303 (s), 1259 (m), 1236 (m), 1215 (m), 1176 (m), 1153 (w), 1132 (m), 1064 (m), 1039 (m), 1021 (s), 959 (w), 935 (w), 924 (w), 865 (w), 830 (m), 808 (s), 798 (s), 755 (s), 745 (s), 708 (m), 691 (m), 639 (m), 605 (w), 574 (s), 547 (m).

3-Benzoylchromone (3a). Yield 80%, white solid, mp 130 °C; ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 7.50–7.59 (m, 3H), 7.67 (tt, $^3J = 7.4$ Hz, $^4J = 1.3$ Hz, 1H), 7.75 (dd, $^3J = 8.4$ Hz, $^4J = 0.6$ Hz, 1H), 7.86–7.92 (m, 3H), 8.09 (dd, $^3J = 7.9$ Hz, $^4J = 1.5$ Hz, 1H), 8.72 (s, 1H, H-2); ^{13}C NMR (62.9 MHz, $\text{DMSO}-d_6$) δ 118.7, 124.2, 124.5, 125.3, 126.1, 128.5, 128.6, 129.4, 129.5, 133.6, 134.8, 136.9, 155.8, 158.8, 174.3, 191.6; MS (GC, 70 eV) m/z (%) 250 (M^+ , 27), 249 (43), 221 (100), 194 (13), 173 (22), 121 (28), 105 (20), 77 (47), 63 (11), 51 (18); HRMS (EI): calcd for $\text{C}_{16}\text{H}_9\text{O}_3$ [M] $^+$ 249.05462, found 249.05415; IR (ATR, cm^{-1}) 3060 (w), 1946 (w), 1823 (w), 1644 (s), 1610 (s), 1563 (s), 1461 (s), 1383 (m), 1340 (m), 1308 (s), 1251 (m), 1210 (m), 1156 (w), 1135 (s), 1031 (w), 999 (w), 968 (m), 920 (m), 862 (s), 808 (w), 787 (m), 758 (s), 717 (s), 688 (s), 632 (s), 558 (w).

3-(2-Fluorobenzoyl)chromone (3b). Yield 86%, pale yellow solid, mp 143–144 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.04 (td, $^3J = 9.5$ Hz, $^4J = 0.9$ Hz, 1H), 7.19 (td, $^3J = 7.5$ Hz, $^4J = 1.0$ Hz, 1H), 7.37 (td, $^3J = 7.5$ Hz, $^4J = 1.0$ Hz, 1H), 7.42–7.50 (m, 2H), 7.61–7.70 (m, 2H), 8.20 (dd, $^3J = 8.0$ Hz, $^4J = 1.5$ Hz, 1H), 8.42 (s, 1H); ^{19}F NMR (282.4 MHz, CDCl_3) δ -111.4 (s, F); ^{13}C NMR (75.5 MHz, CDCl_3) δ 115.7, 116.0, 118.3, 124.3, 124.4, 126.1, 126.4, 130.4, 130.5, 134.2, 134.3, 134.4, 156.0, 159.5, 162.8, 188.7; MS (GC, 70 eV) m/z (%) 268 (M^+ , 63), 239 (100), 221 (34), 173 (28), 121 (30), 95 (31), 75 (21), 63 (13), 53 (12); HRMS (EI): calcd for $\text{C}_{16}\text{H}_9\text{O}_3\text{F}$ (M^+) 268.05302, found 268.05295; IR (ATR, cm^{-1}) 3081 (w), 1664 (m), 1644 (s), 1609 (s), 1563 (m), 1477 (w), 1460 (s), 1388 (m), 1339 (m), 1314 (m), 1261 (w), 1240 (m), 1207 (m), 1152 (w), 1136 (m), 1099 (m), 1029 (w), 1002 (w), 973 (m), 933 (w), 864 (s), 817 (w), 758 (s), 706 (m), 679 (w), 665 (m), 629 (s), 565 (w), 538 (m).

3-(2-Nitrobenzoyl)chromone (3c). Yield 70%, pale brown solid, mp 155–157 °C; ^1H NMR (300 MHz, DMSO- d_6) δ 7.51–7.57 (m, 2H), 7.74–7.80 (m, 2H), 7.85–7.91 (m, 2H), 7.97 (dd, $^3J = 7.9$ Hz, $^4J = 1.4$ Hz, 1H), 8.26 (d, $^3J = 7.5$ Hz, 1H), 9.17 (s, 1H); ^{13}C NMR (62.9 MHz, DMSO- d_6) δ 118.7, 120.5, 123.7, 124.3, 125.4, 126.7, 127.8, 130.7, 134.8, 135.2, 137.4, 145.9, 155.5, 164.0, 173.7, 189.6; MS (EI, 70 eV) m/z (%) 249 (M-NO $_2$, 100), 173 (6), 121 (10), 57 (5); HRMS (ESI): calcd for C $_{16}$ H $_{10}$ NO $_5$ [M+H] $^+$ 296.05535, found 296.05606; IR (ATR, cm $^{-1}$) 3108 (w), 3078 (w), 2861 (w), 1671 (m), 1652 (m), 1611 (m), 1574 (w), 1552 (m), 1517 (s), 1463 (s), 1404 (w), 1388 (m), 1349 (s), 1307 (s), 1205 (m), 1175 (w), 1156 (m), 1141 (m), 1105 (w), 1084 (w), 1028 (w), 996 (w), 957 (m), 888 (w), 869 (m), 850 (s), 808 (w), 792 (m), 764 (s), 745 (m), 734 (s), 705 (s), 658 (m), 638 (m), 575 (m), 535 (s).

6-Methyl-3-(2-nitrobenzoyl)chromone (3d). Yield 81%, pale brown solid, mp 167–169 °C; ^1H NMR (300 MHz, DMSO- d_6) δ 2.38 (s, 3H, Me), 7.54 (dd, $^3J = 7.5$ Hz, $^4J = 1.4$ Hz, 1H), 7.62–7.69 (m, 2H), 7.74–7.79 (m, 2H), 7.86 (td, $^3J = 7.5$ Hz, $^4J = 1.2$ Hz, 1H), 8.25 (dd, $^3J = 8.1$ Hz, $^4J = 1.1$ Hz, 1H), 9.12 (s, 1H); ^{13}C NMR (62.9 MHz, DMSO- d_6) δ 20.4, 118.5, 120.3, 123.6, 124.0, 124.8, 127.8, 130.7, 134.7, 136.1, 136.5, 137.5, 145.9, 153.8, 163.8, 173.6, 189.7; MS (EI, 70 eV) m/z (%) 263 (M-NO $_2$, 100), 187 (6), 135 (13), 76 (5); HRMS (ESI): calcd for C $_{17}$ H $_{12}$ NO $_5$ [M+H] $^+$ 310.0710, found 310.0714; IR (ATR, cm $^{-1}$) 3061 (w), 2921 (w), 2859 (w), 1668 (m), 1650 (m), 1615 (m), 1574 (m), 1552 (m), 1517 (s), 1478 (s), 1440 (m), 1348 (s), 1306 (s), 1229 (m), 1186 (w), 1163 (m), 1132 (m), 1082 (w), 1041 (w), 1018 (w), 959 (w), 910 (m), 853 (s), 814 (s), 786 (s), 753 (m), 731 (s), 702 (s), 640 (s), 575 (m), 541 (m).

7-Methoxy-3-(2-nitrobenzoyl)chromone (3e). Yield 79%, pale brown solid, mp 146–148 °C; ^1H NMR (300 MHz, DMSO- d_6) δ 3.90 (s, 3H, MeO), 7.08 (dd, $^3J = 8.9$ Hz, $^4J = 2.3$ Hz, 1H), 7.24 (d, $^4J = 2.3$ Hz, 1H), 7.54 (dd, $^3J = 7.5$ Hz, $^4J = 1.4$ Hz, 1H), 7.75 (td, $^3J = 7.5$ Hz, $^4J = 1.4$ Hz, 1H), 7.83–7.89 (m, 2H), 8.24 (dd, $^3J = 8.1$ Hz, $^4J = 1.0$ Hz, 1H), 9.08 (s, 1H); ^{13}C NMR (75.5 MHz, DMSO- d_6) δ 56.3, 101.3, 115.7, 117.8, 120.4, 123.6, 126.9, 127.8, 130.7, 134.7, 137.6, 145.9, 157.3, 163.6, 164.5, 172.9, 189.8; MS (GC, 70 eV) m/z (%) 279 (M-NO $_2$, 100), 236 (23), 151 (12), 76 (6), 63 (5); HRMS (ESI): calcd for C $_{17}$ H $_{12}$ NO $_6$ [M+H] $^+$ 326.06591, found 326.06567; IR (ATR, cm $^{-1}$) 3065 (w), 2952 (w), 2845 (w), 1673 (w), 1621 (s), 1552 (m), 1514 (s), 1435 (s), 1385 (m), 1341 (s), 1302 (s), 1271 (s), 1237 (m), 1207 (m), 1143 (m), 1090 (m), 1035 (w), 1020 (m), 939 (s), 879 (w), 850 (s), 804 (m), 786 (s), 753 (s), 733 (m), 718 (m), 701 (s), 627 (s), 590 (w), 562 (s), 529 (m).

3-(3-Nitrobenzoyl)chromone (3f). Yield 81%, white solid, mp 210 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ 7.58 (td, ³*J* = 7.5 Hz, ⁴*J* = 1.1 Hz, 1H), 7.77–7.84 (m, 2H), 7.91 (td, ³*J* = 7.8 Hz, ⁴*J* = 1.7 Hz, 1H), 8.08 (dd, ³*J* = 7.9 Hz, ⁴*J* = 1.5 Hz, 1H), 8.27 (dt, ³*J* = 7.7 Hz, ⁴*J* = 1.3 Hz, 1H), 8.48 (dq, ³*J* = 8.2 Hz, ⁴*J* = 1.0 Hz, 1H), 8.56 (t, ⁴*J* = 1.8 Hz, 1H), 8.83 (s, 1H, H-2); ¹³C NMR (75.5 MHz, DMSO-*d*₆) δ 118.7, 123.3, 123.4, 124.3, 125.4, 126.4, 127.5, 130.3, 135.0, 135.6, 138.4, 147.9, 155.7, 160.8, 174.2, 190.2; MS (GC, 70 eV) *m/z* (%) 295 (M⁺, 48), 278 (100), 266 (93), 248 (56), 220 (73), 173 (71), 165 (13), 150 (10), 121 (95), 104 (20), 92 (26), 76 (35), 63 (19), 53 (27); HRMS (EI): calcd for C₁₆H₉O₅N [M]⁺ 295.04752, found 295.04744; IR (ATR, cm⁻¹) 3087 (w), 1843 (w), 1668 (m), 1634 (s), 1611 (s), 1559 (w), 1533 (s), 1463 (s), 1384 (m), 1345 (s), 1316 (m), 1292 (m), 1210 (w), 1177 (w), 1141 (m), 1100 (w), 1081 (m), 1030 (w), 992 (m), 966 (w), 924 (m), 897 (m), 854 (m), 823 (w), 802 (w), 757 (s), 739 (m), 715 (s), 661 (m), 630 (m), 556 (w).

3-(4-Nitrobenzoyl)chromone (3g). Yield 83%, white solid, mp 239–240 °C; ¹H NMR (250 MHz, DMSO-*d*₆) δ 7.58 (t, ³*J* = 7.6 Hz, 1H), 7.77 (d, ³*J* = 8.4 Hz, 1H), 7.90 (td, ³*J* = 7.6 Hz, ⁴*J* = 1.4 Hz, 1H), 8.06–8.09 (m, 3H), 8.30–8.33 (m, 2H), 8.83 (s, 1H, H-2); ¹³C NMR (62.9 MHz, DMSO-*d*₆) δ 118.8, 123.5, 123.6, 123.7, 124.3, 125.4, 126.4, 130.5, 130.6, 135.1, 142.1, 149.9, 155.8, 160.7, 174.3, 191.1; MS (GC, 70 eV) *m/z* (%) 295 (M⁺, 29), 278 (64), 266 (100), 248 (29), 220 (50), 173 (40), 165 (12), 121 (65), 104 (18), 92 (25), 76 (25), 63 (15), 53 (21); HRMS (EI): calcd for C₁₆H₉O₅N [M]⁺ 295.04752, found 295.04745; IR (ATR, cm⁻¹) 3107 (w), 2848 (w), 1949 (w), 1661 (w), 1633 (s), 1604 (m), 1563 (w), 1516 (m), 1461 (m), 1406 (w), 1379 (m), 1318 (m), 1287 (m), 1253 (m), 1215 (m), 1150 (w), 1132 (m), 1028 (w), 962 (w), 926 (m), 868 (s), 842 (m), 798 (m), 775 (m), 755 (s), 709 (s), 687 (s), 634 (s), 596 (w), 549 (m), 534 (w).

3-(3,5-Dinitrobenzoyl)chromone (3h). Yield 58%, brown solid, mp 181–183 °C; ¹H NMR (250 MHz, DMSO-*d*₆) δ 7.59 (t, ³*J* = 7.6 Hz, 1H), 7.80 (d, ³*J* = 8.5 Hz, 1H), 7.89–7.95 (m, 1H), 8.08 (d, ³*J* = 7.9 Hz, 1H), 8.91–8.93 (m, 3H), 9.03 (s, 1H, H-2); ¹³C NMR (62.9 MHz, DMSO-*d*₆) δ 118.7, 122.0, 122.5, 124.4, 125.4, 126.5, 128.8, 128.9, 135.1, 140.1, 148.1, 148.2, 155.7, 162.5, 174.3, 188.6; MS (GC, 70 eV) *m/z* (%) 340 (M⁺, 32), 323 (100), 311 (59), 293 (35), 265 (35), 247 (17), 219 (39), 173 (67), 121 (81), 92 (16), 75 (24), 53 (17); HRMS (EI): calcd for C₁₆H₈O₇N₂ [M]⁺ 340.03260, found 340.03257; IR (ATR, cm⁻¹) 3100 (w), 1644 (m), 1611 (m), 1538 (m), 1463 (m), 1384 (w), 1341 (m), 1314 (m), 1290 (m), 1211 (w), 1173 (w), 1105 (m), 1031 (w), 1004 (m), 917 (m), 854 (m), 831 (m), 745 (m), 714 (s), 644 (m), 557 (w).

3-(2-Thenoyl)chromone (3i). Yield 81%, white solid, mp 145–147 °C; ^1H NMR (300 MHz, $\text{DMSO-}d_6$) δ 7.24 (t, $^3J = 4.4$ Hz, 1H), 7.56 (td, $^3J = 7.5$ Hz, $^4J = 1.0$ Hz, 1H), 7.73 (d, $^3J = 7.8$ Hz, 1H), 7.84–7.90 (m, 2H), 8.10–8.15 (m, 2H), 8.76 (s, 1H); ^{13}C NMR (75.5 MHz, $\text{DMSO-}d_6$) δ 118.6, 124.1, 124.2, 125.4, 126.1, 128.9, 134.8, 136.5, 136.6, 143.5, 155.6, 158.1, 173.9, 182.7; MS (GC, 70 eV) m/z (%) 256 (M^+ , 71), 228 (87), 200 (24), 173 (35), 121 (52), 111 (100), 92 (25), 83 (17), 63 (26), 53 (30), 39 (50); HRMS (EI): calcd for $\text{C}_{14}\text{H}_8\text{O}_3\text{S}$ (M^+) 256.01887, found 256.01828; IR (ATR, cm^{-1}) 3097 (w), 1699 (w), 1646 (s), 1606 (s), 1564 (s), 1525 (m), 1460 (s), 1434 (m), 1406 (s), 1381 (s), 1353 (s), 1340 (s), 1308 (s), 1253 (m), 1212 (s), 1168 (m), 1130 (s), 1102 (m), 1084 (m), 1059 (m), 1029 (m), 955 (w), 937 (w), 918 (m), 851 (m), 816 (s), 793 (s), 751 (s), 722 (s), 677 (s), 628 (s), 557 (m), 534 (w).

Trimethyl 3-hydroxy-6-(2-hydroxybenzoyl)benzene-1,2,4-tricarboxylate (4a). Yield 74%, pale yellow solid, mp 138–140 °C; ^1H NMR (300 MHz, CDCl_3) δ 3.63, 3.94, 3.98 (all s, 3H, MeO), 6.85 (ddd, $^3J = 8.0$, 7.3 Hz, $^4J = 1.0$ Hz, 1H, H-5'), 7.06 (dd, $^3J = 8.4$ Hz, $^4J = 1.0$ Hz, 1H, H-3'), 7.29 (dd, $^3J = 8.0$ Hz, $^4J = 1.6$ Hz, 1H, H-6'), 7.51 (ddd, $^3J = 8.4$, 7.3 Hz, $^4J = 1.6$ Hz, 1H, H-4'), 8.04 (s, 1H, H-5), 11.56, 11.63 (both s, 1H, OH); ^{13}C NMR (62.9 MHz, CDCl_3) δ 52.9, 53.0, 53.2, 114.3, 118.4, 119.1, 119.4, 124.0, 129.3, 131.9, 132.4, 136.4, 136.8, 160.2, 162.7, 165.2, 165.3, 168.8, 199.3; MS (GC, 70 eV) m/z (%) 388 (M^+ , 7), 356 (40), 297 (92), 265 (100), 238 (10); HRMS (EI): calcd for $\text{C}_{19}\text{H}_{16}\text{O}_9$ [M] $^+$ 388.07888, found 388.07794; IR (ATR, cm^{-1}) 2951 (w), 1732 (s), 1682 (m), 1631 (m), 1611 (m), 1581 (m), 1514 (w), 1484 (w), 1443 (s), 1415 (w), 1353 (m), 1323 (m), 1295 (s), 1234 (s), 1193 (s), 1140 (s), 1049 (s), 992 (m), 949 (m), 904 (m), 883 (m), 847 (m), 809 (m), 785 (s), 756 (s), 731 (s), 719 (s), 706 (s), 652 (s), 607 (m), 578 (m), 561 (s), 530 (m).

Trimethyl 3-hydroxy-6-(2-hydroxy-5-methylbenzoyl)benzene-1,2,4-tricarboxylate (4b). Yield 87%, white solid, mp 136–138 °C; ^1H NMR (250 MHz, $\text{DMSO-}d_6$) δ 2.22 (s, 3H, Me), 3.59, 3.82, 3.90 (all s, 3H, MeO), 6.88 (d, $^3J = 8.4$ Hz, 1H, H-3'), 7.21 (br s, 1H, H-6'), 7.31 (dd, $^3J = 8.4$ Hz, $^4J = 1.9$ Hz, 1H, H-4'), 7.98 (s, 1H, H-5), 10.40, 11.30 (both s, 1H, OH); ^{13}C NMR (62.9 MHz, $\text{DMSO-}d_6$) δ 19.8, 52.8 (2C), 53.2, 115.5, 117.1, 122.2, 122.8, 128.0, 129.8, 131.1, 133.0, 136.0, 136.3, 156.4, 158.5, 164.8, 165.8, 167.4, 194.9; MS (GC, 70 eV) m/z (%) 402 (M^+ , 10), 370 (31), 311 (71), 279 (100); HRMS (EI): calcd for $\text{C}_{20}\text{H}_{18}\text{O}_9$ [M] $^+$ 402.09453, found 402.09435; IR (ATR, cm^{-1}) 2952 (w), 1733 (s), 1682 (w), 1633 (m), 1606 (w), 1582 (m), 1484 (w), 1441 (m), 1408 (w), 1372 (w), 1352 (m), 1320 (w), 1283 (m), 1232 (s), 1206 (s), 1153 (s), 1137 (s), 1048 (m), 1014 (m), 993 (m), 983 (m), 953 (m), 931 (w), 882 (w), 828 (m), 809 (m), 787 (s), 767 (m), 728 (m), 708 (m), 670 (s), 607 (w), 575 (w), 538 (m).

Trimethyl 3-hydroxy-6-(2-hydroxy-4-methoxybenzoyl)benzene-1,2,4-tricarboxylate (4c). Yield 73%, white solid, mp 137–139 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ 3.61, 3.82, 3.83, 3.91 (all s, 3H, MeO), 6.50–6.54 (m, 2H, H-3', H-5'), 7.36 (d, ³*J* = 8.5 Hz, 1H, H-6'), 7.97 (s, 1H, H-5), 11.24, 11.52 (both s, 1H, OH); ¹³C NMR (62.9 MHz, DMSO-*d*₆) δ 52.8, 53.0, 53.2, 55.8, 101.2, 107.4, 114.3, 115.6, 123.3, 129.6, 132.3, 134.1, 135.7, 158.0, 163.3, 164.8, 165.5, 165.8, 167.4, 195.3; MS (GC, 70 eV) *m/z* (%) 418 (M⁺, 16), 386 (14), 359 (12), 327 (92), 295 (100), 151 (11); HRMS (ESI): calcd for C₂₀H₁₉O₁₀ [M+H]⁺ 419.09727, found 419.09759; IR (ATR, cm⁻¹) 2960 (w), 1738 (s), 1691 (m), 1639 (m), 1601 (m), 1573 (m), 1505 (w), 1429 (m), 1345 (m), 1299 (s), 1248 (s), 1216 (s), 1195 (s), 1165 (s), 1128 (s), 1053 (m), 1002 (m), 973 (m), 950 (m), 922 (m), 870 (m), 817 (m), 780 (s), 712 (s), 624 (m), 558 (m), 531 (m).

Trimethyl 3-hydroxy-6-(5-chloro-2-hydroxybenzoyl)benzene-1,2,4-tricarboxylate (4d). Yield 72%, yellow solid, mp 172–174 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ 3.61, 3.81, 3.91 (all s, 3H, MeO), 6.97 (d, ³*J* = 8.8 Hz, 1H, H-3'), 7.40 (d, ⁴*J* = 2.7 Hz, 1H, H-6'), 7.50 (dd, ³*J* = 8.8 Hz, ⁴*J* = 2.7 Hz, 1H, H-4'), 7.99 (s, 1H, H-5), 10.65 (s, 1H, OH), 11.33 (br s, 1H, OH); ¹³C NMR (62.9 MHz, DMSO-*d*₆) δ 52.8, 53.2, 115.5, 119.0, 122.7, 122.9, 124.9, 129.4, 129.9, 133.3, 134.1, 136.5, 156.2, 158.8, 164.8, 165.9, 167.3, 192.4; MS (GC, 70 eV) *m/z* (%) 422 (M⁺, 5), 390 (30), 331 (65), 299 (100), 272 (8), 155 (8), 99 (8); HRMS (ESI): calcd for C₁₉H₁₅ClNaO₉ [M+Na]⁺ 445.02968, found 445.03049; IR (ATR, cm⁻¹) 3019 (w), 2957 (w), 1742 (m), 1730 (w), 1693 (m), 1682 (m), 1667 (m), 1622 (m), 1602 (m), 1564 (w), 1525 (w), 1471 (w), 1434 (m), 1402 (w), 1359 (m), 1338 (m), 1317 (m), 1287 (m), 1269 (s), 1229 (s), 1203 (s), 1154 (s), 1104 (m), 1048 (m), 1008 (w), 978 (m), 944 (m), 915 (w), 869 (w), 842 (m), 823 (m), 810 (s), 798 (s), 778 (m), 749 (s), 730 (s), 691 (s), 647 (m), 622 (m), 601 (s), 559 (m), 530 (m).

Trimethyl 6-(5-chloro-2-hydroxy-4-methylbenzoyl)-3-hydroxybenzene-1,2,4-tricarboxylate (4e). Yield 71%, yellow solid, mp 175–177 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ 2.32 (s, 3H, Me), 3.61, 3.82, 3.90 (all s, 3H, MeO), 6.94 (s, 1H, H-3'), 7.41 (s, 1H, H-6'), 7.99 (s, 1H, H-5), 10.65 (s, 1H, OH), 11.30 (br s, 1H, OH); ¹³C NMR (62.9 MHz, DMSO-*d*₆) δ 20.0, 52.8, 52.9, 53.2, 115.5, 119.6, 122.2, 122.8, 123.5, 129.7, 130.5, 133.0, 136.2, 142.9, 156.7, 158.6, 164.8, 165.8, 167.4, 192.7; MS (EI, 70 eV) *m/z* (%) 436 (M⁺, 9), 404 (31), 345 (76), 313 (100); HRMS (ESI): calcd for C₂₀H₁₇ClNaO₉ [M+Na]⁺ 459.04533, found 459.04554; IR (ATR, cm⁻¹) 3060 (w), 2951 (w), 2847 (w), 1731 (s), 1682 (m), 1567 (w), 1482 (w), 1449 (m), 1433 (m),

1360 (w), 1315 (m), 1287 (m), 1252 (s), 1223 (s), 1194 (s), 1179 (s), 1155 (s), 1132 (s), 1058 (m), 1016 (w), 993 (s), 961 (w), 944 (m), 918 (m), 896 (m), 872 (w), 842 (w), 794 (s), 778 (s), 751 (m), 727 (s), 702 (m), 675 (s), 645 (m), 609 (m), 593 (m), 531 (w).

Trimethyl 6-(5-bromo-2-hydroxybenzoyl)-3-hydroxybenzene-1,2,4-tricarboxylate (4f). Yield 81%, white solid, mp 192–194 °C; ¹H NMR (300 MHz, CDCl₃) δ 3.69, 3.95, 4.00 (all s, 3H, MeO), 6.97 (d, ³J = 8.9 Hz, 1H, H-3'), 7.38 (d, ⁴J = 2.4 Hz, 1H, H-6'), 7.58 (dd, ³J = 8.9 Hz, ⁴J = 2.4 Hz, 1H, H-4'), 8.00 (s, 1H, H-5), 11.56, 11.60 (both s, 1H, OH); ¹³C NMR (75.5 MHz, CDCl₃) δ 53.0, 53.1, 53.3, 110.7, 114.5, 120.5, 120.7, 124.3, 128.7, 131.6, 134.3, 136.2, 139.5, 160.5, 161.7, 165.0, 165.1, 168.7, 198.6; MS (EI, 70 eV) *m/z* (%) 468 (M⁺, 8), 436 (46), 377 (89), 345 (100); HRMS (EI): calcd for C₁₉H₁₅BrO₉ [M]⁺ 465.98940, found 465.98946; IR (ATR, cm⁻¹) 2956 (w), 1743 (m), 1730 (m), 1688 (m), 1651 (w), 1623 (m), 1598 (m), 1584 (m), 1531 (w), 1465 (w), 1468 (w), 1440 (m), 1403 (w), 1354 (m), 1318 (m), 1289 (m), 1271 (m), 1257 (m), 1233 (s), 1206 (s), 1164 (s), 1139 (s), 1048 (w), 1006 (w), 984 (m), 943 (m), 904 (w), 878 (w), 838 (m), 812 (m), 789 (m), 761 (m), 728 (m), 686 (s), 632 (w), 616 (m), 562 (m), 546 (w).

Trimethyl 3-hydroxy-6-(1-hydroxy-2-naphthoyl)benzene-1,2,4-tricarboxylate (4g). Yield 46%, yellow solid, mp 187–188 °C; ¹H NMR (300 MHz, CDCl₃) δ 3.64, 3.96, 3.97 (all s, 3H, MeO), 7.19–7.25 (m, 2H), 7.53–7.59 (m, 1H), 7.63–7.68 (m, 1H), 7.74–7.76 (m, 1H), 8.08 (s, 1H, H-5), 8.50 (d, ³J = 8.3 Hz, 1H), 11.56, 13.47 (both s, 1H, OH); ¹³C NMR (75.5 MHz, CDCl₃) δ 53.0 (2C), 53.2, 112.8, 114.3, 118.5, 123.9, 124.4, 125.0, 126.0, 126.2, 127.5, 129.5, 130.6, 131.9, 136.4, 137.4, 160.1, 163.4, 165.3, 168.9, 199.0; MS (EI, 70 eV) *m/z* (%) 438 (M⁺, 10), 406 (23), 347 (64), 315 (100); HRMS (EI): calcd for C₂₃H₁₈O₉ [M]⁺ 438.09453, found 438.09494; IR (ATR, cm⁻¹) 3019 (w), 2960 (w), 1753 (m), 1738 (m), 1690 (m), 1628 (w), 1598 (m), 1568 (m), 1503 (w), 1463 (w), 1439 (m), 1418 (w), 1389 (w), 1334 (m), 1297 (s), 1272 (m), 1245 (s), 1217 (s), 1192 (s), 1167 (s), 1128 (s), 1065 (m), 1024 (w), 1009 (w), 988 (s), 949 (m), 930 (w), 890 (w), 868 (w), 832 (w), 808 (s), 795 (s), 765 (s), 730 (s), 709 (s), 667 (w), 640 (w), 615 (m), 593 (m), 574 (m), 560 (m).

Dimethyl 3'-nitro-3-hydroxy-6-(2-hydroxybenzoyl)[1,1'-biphenyl]-2,4-dicarboxylate (4h). Yield 83%, yellow solid, mp 215 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ 3.54, 3.93 (both s, 3H, MeO), 6.73–6.78 (m, 2H), 7.26–7.33 (m, 2H), 7.57–7.59 (m, 2H), 7.99 (s, 1H), 8.00 (s, 1H, H-5), 8.10–8.14 (m, 1H), 10.48 (s, 1H, OH), 11.17 (br s, 1H, OH); ¹³C NMR (75.5 MHz, DMSO-*d*₆) δ 52.3, 53.1, 113.2, 116.8, 119.1, 123.0, 123.1, 124.0, 124.9, 129.7, 131.1, 131.6, 131.9, 134.7, 135.1, 137.9, 141.8, 147.0, 157.7, 157.8, 165.6, 167.8, 196.9; MS (GC, 70 eV) *m/z* (%) 451 (M⁺, 24), 419 (56), 388 (10),

359 (18), 297 (100), 265 (38), 193 (16), 121 (57), 93 (10), 65 (12); HRMS (EI): calcd for C₂₃H₁₇O₉N [M]⁺ 451.08978, found 451.09001; IR (ATR, cm⁻¹) 3079 (w), 3045 (w), 2965 (w), 2855 (w), 1726 (m), 1678 (m), 1622 (m), 1602 (m), 1573 (w), 1533 (m), 1487 (w), 1441 (m), 1408 (w), 1344 (m), 1296 (m), 1219 (s), 1164 (s), 1132 (m), 1081 (w), 991 (m), 930 (w), 882 (w), 843 (w), 806 (w), 765 (s), 752 (s), 735 (s), 694 (s), 637 (s), 597 (m), 563 (w), 534 (w).

Dimethyl 4'-nitro-3-hydroxy-6-(2-hydroxybenzoyl)[1,1'-biphenyl]-2,4-dicarboxylate (4i). Yield 47%, white solid, mp 186 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ 3.54, 3.92 (both s, 3H, MeO), 6.79–6.83 (m, 2H), 7.31–7.41 (m, 2H), 7.42 (d, ³J = 8.8 Hz, 2H), 7.99 (s, 1H, H-5), 8.15 (d, ³J = 8.8 Hz, 2H), 10.52 (s, 1H, OH), 11.19 (br s, 1H, OH); ¹³C NMR (75.5 MHz, DMSO-*d*₆) δ 52.4, 53.1, 113.1, 117.0, 119.1, 123.0, 123.1, 123.5, 124.8, 129.9, 130.0, 131.4, 131.5, 131.6, 135.1, 142.3, 143.5, 147.0, 157.7, 158.2, 165.5, 167.8, 196.1; MS (EI, 70 eV) *m/z* (%) 451 (M⁺, 25), 419 (77), 388 (10), 359 (21), 297 (100), 265 (25), 241 (9), 121 (52); HRMS (EI): calcd for C₂₃H₁₇O₉N [M]⁺ 451.08978, found 451.09051; IR (ATR, cm⁻¹) 3089 (w), 3004 (w), 2950 (w), 2850 (w), 1745 (m), 1690 (m), 1622 (m), 1604 (m), 1572 (m), 1518 (m), 1482 (m), 1438 (m), 1347 (s), 1296 (m), 1266 (m), 1234 (m), 1208 (s), 1159 (s), 1147 (s), 1119 (m), 1106 (m), 1035 (w), 1001 (m), 949 (m), 931 (w), 917 (w), 877 (w), 864 (m), 854 (m), 845 (m), 799 (m), 767 (s), 740 (m), 713 (s), 698 (s), 664 (m), 642 (m), 623 (m), 599 (m), 562 (m), 534 (m).

Dimethyl 3',5'-dinitro-3-hydroxy-6-(2-hydroxybenzoyl)[1,1'-biphenyl]-2,4-dicarboxylate (4j). Yield 70%, yellow solid, mp 199 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ 3.58, 3.84 (both s, 3H, MeO), 6.69–6.77 (m, 2H), 7.23–7.28 (m, 2H), 8.09 (s, 1H, H-5), 8.38 (d, ⁴J = 2.1 Hz, 2H), 8.72 (t, ⁴J = 2.1 Hz, 1H), 10.35 (s, 1H, OH), 11.27 (br s, 1H, OH); ¹³C NMR (75.5 MHz, DMSO-*d*₆) δ 52.6, 53.1, 114.1, 116.6, 118.3, 119.2, 124.9, 125.0, 128.8, 130.6, 131.6, 132.4, 134.3, 139.5, 140.0, 147.3, 156.8, 158.0, 165.4, 167.6, 194.8; MS (GC, 70 eV) *m/z* (%) 496 (M⁺, 28), 464 (65), 433 (11), 404 (22), 297 (100), 265 (48), 216 (13), 120 (66), 93 (11), 65 (12); HRMS (ESI): calcd for C₂₃H₁₇N₂O₁₁ [M+H]⁺ 497.08270, found 497.08200; IR (ATR, cm⁻¹) 3090 (w), 2958 (w), 1732 (m), 1682 (m), 1651 (w), 1622 (m), 1593 (m), 1568 (m), 1538 (s), 1485 (m), 1442 (s), 1341 (s), 1298 (s), 1256 (m), 1209 (s), 1163 (s), 1116 (m), 1075 (m), 1033 (m), 997 (m), 957 (w), 938 (m), 922 (m), 908 (m), 878 (w), 855 (w), 839 (m), 804 (m), 761 (s), 728 (s), 707 (s), 680 (m), 650 (s), 609 (m), 565 (m), 530 (m).

Dimethyl 3-hydroxy-6-(2-hydroxybenzoyl)[1,1'-biphenyl]-2,4-dicarboxylate (4k). Yield 49%, white solid, mp 178–180 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ 3.52 (s, 3H, MeO), 3.93 (s, 3H, MeO), 6.76–6.82 (m, 2H), 7.12–7.16 (m, 2H), 7.24–7.26 (m, 3H), 7.29 (dd, ³*J* = 7.7 Hz, ⁴*J* = 1.5 Hz, 1H), 7.37 (td, ³*J* = 7.7 Hz, ⁴*J* = 1.5 Hz, 1H), 7.95 (s, 1H), 10.78 (s, 1H, OH), 11.11 (s, 1H, OH); ¹³C NMR (62.9 MHz, DMSO-*d*₆) δ 52.1, 53.0, 112.1, 117.1, 119.0, 122.4, 124.8, 127.9, 128.2, 128.3, 130.7, 131.6, 132.0, 135.5, 136.3, 144.2, 157.5, 159.2, 165.8, 168.1, 197.9; MS (GC, 70 eV) *m/z* (%) 406 (M⁺, 38), 374 (67), 342 (13), 314 (27), 297 (100), 286 (16), 265 (28), 223 (14), 196 (17), 171 (13), 139 (13), 121 (52), 65 (10); HRMS (EI): calcd for C₂₃H₁₈O₇ [M]⁺ 406.10470, found 406.10499; IR (ATR, cm⁻¹) 2953 (w), 2923 (w), 2852 (w), 1733 (m), 1679 (w), 1625 (m), 1607 (w), 1582 (w), 1564 (w), 1486 (w), 1433 (m), 1348 (w), 1324 (w), 1293 (m), 1272 (w), 1260 (w), 1238 (m), 1198 (s), 1160 (s), 1147 (m), 1123 (m), 1111 (m), 1075 (w), 1034 (w), 1010 (w), 987 (m), 945 (w), 926 (w), 907 (w), 876 (w), 817 (w), 802 (w), 788 (w), 764 (s), 738 (m), 724 (m), 704 (s), 677 (m), 644 (s), 619 (m), 603 (w), 584 (m), 565 (w), 536 (m).

Dimethyl 2-hydroxy-5-(2-hydroxybenzoyl)-4-(2-thienyl)isophthalate (4l). Yield 7%, white solid, mp 205–207 °C; ¹H NMR (300 MHz, CDCl₃) δ 3.72 (s, 3H, MeO), 3.96 (s, 3H, MeO), 6.69 (td, ³*J* = 7.6 Hz, ⁴*J* = 1.1 Hz, 1H), 6.84–6.91 (m, 2H), 6.97 (dd, ³*J* = 3.6 Hz, ⁴*J* = 1.2 Hz, 1H), 7.18 (dd, ³*J* = 8.0 Hz, ⁴*J* = 1.6 Hz, 1H), 7.22–7.24 (m, 1H), 7.37 (td, ³*J* = 7.8 Hz, ⁴*J* = 1.6 Hz, 1H), 7.97 (s, 1H), 11.38 (s, 1H, OH), 11.70 (s, 1H, OH); ¹³C NMR (62.9 MHz, CDCl₃) δ 52.7, 53.0, 111.9, 118.1, 118.8, 119.8, 127.4, 128.3, 129.2, 129.4, 130.6, 130.8, 133.0, 136.3, 136.7, 137.7, 159.3, 162.6, 166.2, 169.4, 201.2; MS (GC, 70 eV) *m/z* (%) 412 (M⁺, 100), 380 (37), 362 (14), 348 (63), 330 (12), 320 (68), 292 (54), 260 (48), 229 (19), 202 (29), 174 (26), 145 (15), 121 (48), 93 (17), 65 (23); HRMS (EI): calcd for C₂₁H₁₆O₇S (M⁺) 412.06112, found 412.06127; IR (ATR, cm⁻¹) 3110 (w), 2956 (w), 2923 (w), 2853 (w), 1732 (s), 1682 (m), 1622 (s), 1606 (s), 1568 (m), 1527 (w), 1505 (w), 1486 (w), 1433 (s), 1415 (m), 1353 (m), 1323 (m), 1294 (s), 1269 (m), 1237 (s), 1198 (s), 1159 (s), 1122 (m), 1100 (s), 1081 (m), 1045 (m), 1035 (m), 985 (s), 944 (s), 914 (m), 890 (w), 874 (m), 851 (m), 841 (w), 816 (m), 798 (s), 762 (s), 721 (s), 708 (s), 645 (s), 633 (s), 596 (m), 587 (m), 562 (m), 535 (m).

Dimethyl 2'-fluoro-3-hydroxy-6-(2-hydroxybenzoyl)[1,1'-biphenyl]-2,4-dicarboxylate (4m). Yield 23%, white solid, mp 170–173 °C; ¹H NMR (300 MHz, CDCl₃) δ 3.59 (s, 3H, MeO), 3.96 (s, 3H, MeO), 6.76 (t, ³*J* = 7.6 Hz, 1H), 6.89–6.96 (m, 2H), 7.06 (t, ³*J* = 7.5 Hz, 1H), 7.18–7.28 (m, 2H), 7.34–7.43 (m, 2H), 8.02 (s, 1H), 11.50 (s, 2H, 2OH); ¹³C NMR (75.5 MHz, CDCl₃) δ 52.4, 53.0, 111.8, 115.3, 115.6, 118.1, 118.8, 119.4, 123.8, 123.9, 130.3, 130.6, 130.7, 130.8, 131.4, 133.1, 136.6, 140.0, 159.9, 162.8, 165.8, 169.4, 200.1; ¹⁹F NMR (282.4 MHz, CDCl₃) δ -113.4 (s, 1F); MS (EI, 70

eV) m/z (%) 424 (M^+ , 1), 392 (100), 359 (50), 332 (16), 297 (19), 265 (37), 237 (18), 180 (12), 123 (53), 95 (13); HRMS (EI): calcd for $C_{23}H_{17}O_7F$ (M^+) 424.09528, found 424.095487; IR (ATR, cm^{-1}) 3000 (w), 2946 (w), 2839 (w), 1711 (m), 1678 (s), 1602 (s), 1503 (w), 1480 (w), 1444 (s), 1351 (w), 1302 (m), 1274 (m), 1238 (s), 1198 (s), 1168 (s), 1115 (m), 1036 (w), 1005 (m), 968 (m), 942 (w), 913 (m), 884 (w), 858 (w), 814 (m), 793 (m), 765 (s), 742 (s), 686 (w), 665 (s), 641 (s), 568 (m).

Dimethyl 2-chloro-6,9-dihydroxy-6-(trifluoromethyl)-6H-benzo[c]chromene-8,10-dicarboxylate (5a). Yield 64%, yellow solid, mp 213 °C; 1H NMR (300 MHz, $DMSO-d_6$) δ 3.92, 3.97 (both s, 3H, MeO), 7.26 (d, $^3J = 8.7$ Hz, 1H, H-4), 7.42 (d, $^4J = 2.4$ Hz, 1H, H-1), 7.54 (dd, $^3J = 8.7$, $^4J = 2.4$ Hz, 1H, H-3), 8.13 (s, 1H, H-7), 9.49, 11.09 (both s, 1H, OH); ^{19}F NMR (282.4 MHz, $DMSO-d_6$) δ -82.3 (s, CF_3); ^{13}C NMR (75.5 MHz, $DMSO-d_6$) δ 53.0, 53.2, 95.3 (q, $^2J_{C,F} = 32.6$ Hz), 113.8, 119.3, 119.4, 119.9, 120.8, 122.4 (q, $^2J_{C,F} = 290.6$ Hz), 124.3, 126.8, 129.7, 131.1, 131.9, 150.5, 158.4, 167.1, 167.6; MS (GC, 70 eV) m/z (%) 400 (M-H-MeO, 45), 369 (22), 331 (91), 299 (100), 264 (10), 231 (13); HRMS (ESI): calcd for $C_{18}H_{13}ClF_3O_7$ $[M+H]^+$ 433.02964, found 433.03073; IR (ATR, cm^{-1}) 3425 (w), 2951 (w), 1705 (m), 1687 (m), 1615 (w), 1594 (w), 1563 (w), 1482 (w), 1461 (w), 1445 (m), 1432 (m), 1408 (w), 1340 (m), 1310 (m), 1272 (w), 1246 (m), 1227 (s), 1191 (s), 1176 (s), 1144 (s), 1056 (m), 996 (s), 947 (m), 937 (m), 924 (m), 887 (w), 858 (m), 825 (m), 806 (s), 778 (m), 759 (m), 746 (m), 721 (m), 703 (s), 665 (s), 619 (w), 591 (m), 568 (w), 545 (m).

Dimethyl 2-bromo-6,9-dihydroxy-6-(trifluoromethyl)-6H-benzo[c]chromene-8,10-dicarboxylate (5b). Yield 59%, white solid, mp 205 °C; 1H NMR (300 MHz, $DMSO-d_6$) δ 3.92, 3.97 (both s, 3H, MeO), 7.19 (d, $^3J = 8.7$ Hz, 1H, H-4), 7.56 (d, $^4J = 2.3$ Hz, 1H, H-1), 7.65 (dd, $^3J = 8.7$ Hz, $^4J = 2.3$ Hz, 1H, H-3), 8.12 (s, 1H, H-7), 9.50, 11.09 (both s, 1H, OH); ^{19}F NMR (282.4 MHz, $DMSO-d_6$) δ -82.3 (s, CF_3); ^{13}C NMR (62.9 MHz, $DMSO-d_6$) δ 53.0, 53.2, 95.3 (q, $^2J_{C,F} = 32.5$ Hz), 113.8, 114.4, 119.3, 119.8, 120.2, 120.7, 122.4 (q, $^2J_{C,F} = 291.3$ Hz), 127.3, 129.7, 131.0, 134.7, 150.9, 158.3, 167.1, 167.6; MS (GC, 70 eV) m/z (%) 476 (M^+ , 23), 445 (15), 377 (74), 345 (100), 198 (39), 173 (23); HRMS (ESI): calcd for $C_{18}H_{12}BrF_3O_7$ $[M+H]^+$ 476.97913, found 476.97958; IR (ATR, cm^{-1}) 3434 (w), 3076 (w), 2953 (w), 1922 (w), 1717 (s), 1677 (m), 1614 (w), 1593 (w), 1557 (w), 1462 (w), 1446 (m), 1403 (w), 1346 (w), 1312 (m), 1229 (s), 1197 (s), 1174 (s), 1143 (s), 1082 (w), 1051 (m), 995 (s), 933 (w), 921 (w), 878 (w), 853 (w), 835 (m), 806 (s), 788 (w), 750 (m), 699 (m), 662 (m), 587 (m), 569 (w), 536 (w).

Dimethyl 6,9-dihydroxy-6-(pentafluoroethyl)-6H-benzo[c]chromene-8,10-dicarboxylate (5c). Yield 65%, white solid, mp 221–223 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ 3.92, 3.98 (both s, 3H, MeO), 7.10–7.20 (m, 2H, H-2, H-4), 7.43–7.50 (m, 2H, H-1, H-3), 8.13 (d, ⁵J_{H,F} = 1.6 Hz, 1H, H-7), 9.46 (d, ⁴J_{H,F} = 3.9 Hz, 1H, OH), 11.08 (s, 1H, OH); ¹⁹F NMR (282.4 MHz, DMSO-*d*₆) δ -77.9 (s, 3F, CF₃), -121.8 (d, ²J = 279.5 Hz, 1F, CFF), -124.0 (d, ²J = 279.5 Hz, 1F, CFF); ¹³C NMR (62.9 MHz, DMSO-*d*₆) δ 53.0, 53.1, 96.7 (t, ²J_{C,F} = 28.2 Hz), 112.8, 117.7, 117.9, 119.0, 120.9, 123.3, 124.9, 130.6, 132.4, 133.2, 151.8, 158.6, 167.3, 167.9; MS (EI, 70 eV) *m/z* (%) 448 (M⁺, 3), 417 (10), 385 (18), 329 (86), 297 (100), 265 (70), 210 (12), 133 (9); HRMS (ESI): calcd for C₁₉H₁₄F₅O₇ [M+H]⁺ 449.06542, found 449.06548; IR (ATR, cm⁻¹) 3420 (w), 2959 (w), 1712 (m), 1676 (m), 1608 (w), 1596 (w), 1568 (w), 1494 (w), 1464 (w), 1433 (m), 1393 (w), 1337 (m), 1319 (m), 1298 (w), 1273 (w), 1251 (m), 1222 (s), 1175 (s), 1143 (s), 1072 (s), 1052 (m), 1042 (m), 998 (s), 970 (m), 946 (w), 933 (m), 908 (m), 877 (w), 863 (w), 842 (m), 806 (m), 778 (s), 759 (s), 736 (s), 709 (m), 687 (m), 662 (m), 645 (w), 614 (m), 579 (w), 533 (m).

Dimethyl 6,9-dihydroxy-3-methoxy-6-(pentafluoroethyl)-6H-benzo[c]chromene-8,10-dicarboxylate (5d). Yield 65%, pale yellow solid, mp 217–219 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ 3.81, 3.91, 3.97 (all s, 3H, MeO), 6.65 (d, ⁴J = 2.5 Hz, 1H, H-4), 6.79 (dd, ³J = 9.0 Hz, ⁴J = 2.6 Hz, 1H, H-2), 7.38 (d, ³J = 9.0 Hz, 1H, H-1), 8.08 (d, ⁵J_{H,F} = 1.4 Hz, 1H, H-7), 9.43 (d, 1H, ⁴J_{H,F} = 3.8 Hz, OH), 11.07 (s, 1H, OH); ¹⁹F NMR (282.4 MHz, DMSO-*d*₆) δ -77.8 (s, 3F, CF₃), -122.0 (d, ²J = 279.5 Hz, 1F, CFF), -124.4 (d, ²J = 279.5 Hz, 1F, CFF); ¹³C NMR (62.9 MHz, DMSO-*d*₆) δ 52.9, 53.0, 55.7, 97.0 (t, ²J_{C,F} = 28.1 Hz), 102.5, 109.9, 110.5, 111.5, 117.9, 119.7, 126.3, 130.6, 133.5, 153.5, 158.8, 162.4, 167.4, 168.1; MS (EI, 70 eV) *m/z* (%) 478 (M⁺, 9), 446 (16), 415 (12), 359 (42), 327 (100), 295 (61), 240 (7), 148 (7); HRMS (ESI): calcd for C₂₀H₁₆F₅O₈ [M+H]⁺ 449.07598, found 449.07621; IR (ATR, cm⁻¹) 3287 (w), 2960 (w), 2847 (w), 1716 (m), 1668 (w), 1606 (m), 1567 (w), 1512 (w), 1442 (m), 1392 (w), 1361 (w), 1315 (m), 1283 (w), 1236 (s), 1218 (s), 1192 (s), 1168 (s), 1146 (s), 1111 (s), 1070 (s), 1028 (m), 997 (s), 973 (m), 940 (w), 929 (m), 890 (m), 843 (m), 811 (w), 797 (s), 767 (w), 744 (m), 727 (m), 709 (m), 650 (m), 619 (m), 608 (m), 596 (m), 536 (w).

Dimethyl 2-chloro-6,9-dihydroxy-3-methyl-6-(pentafluoroethyl)-6H-benzo[c]chromene-8,10-dicarboxylate (5e). Yield 57%, white solid, mp 224 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ 2.35 (s, 3H, Me), 3.92, 3.97 (both s, 3H, MeO), 7.18 (s, 1H, H-4), 7.41 (s, 1H, H-1), 8.11 (d, ⁵J_{H,F} = 1.4 Hz, 1H, H-7), 9.59 (d, ⁴J_{H,F} = 3.9 Hz, 1H, OH), 11.09 (s, 1H, OH); ¹⁹F NMR (282.4 MHz, DMSO-*d*₆) δ -77.9 (s, 3F, CF₃), -122.8 (d, ²J = 279.5 Hz, 1F, CFF), -124.1 (d, ²J = 279.5 Hz, 1F, CFF); ¹³C NMR (75.5 MHz, DMSO-*d*₆) δ 19.6, 53.0, 53.1, 97.1 (t, ²J_{C,F} = 28.8 Hz), 113.3, 117.0, 118.8, 120.0, 120.4,

124.5, 127.2, 130.8, 131.7, 140.5, 150.5, 158.5, 167.2, 167.7; MS (EI, 70 eV) m/z (%) 496 (M^+ , 7), 464 (18), 433 (18), 377 (88), 345 (100), 313 (74), 258 (11), 157 (11); HRMS (ESI): calcd for $C_{20}H_{15}ClF_5O_7$ $[M+H]^+$ 497.04210, found 497.04264; IR (ATR, cm^{-1}) 3434 (w), 3006 (w), 2953 (w), 1713 (s), 1687 (m), 1613 (m), 1592 (w), 1552 (w), 1497 (w), 1443 (m), 1385 (w), 1336 (s), 1306 (m), 1289 (w), 1261 (m), 1228 (s), 1188 (s), 1171 (s), 1155 (s), 1140 (s), 1080 (s), 1053 (s), 1016 (m), 998 (s), 974 (m), 935 (m), 926 (m), 898 (m), 887 (m), 868 (m), 818 (m), 808 (s), 783 (m), 767 (m), 744 (m), 731 (m), 710 (s), 665 (m), 641 (w), 631 (s), 615 (w), 603 (m), 583 (w), 550 (m), 535 (w).

Dimethyl 2-bromo-6,9-dihydroxy-6-(pentafluoroethyl)-6H-benzo[c]chromene-8,10-dicarboxylate (5f). Yield 68%, white solid, mp 225–227 °C; 1H NMR (300 MHz, $DMSO-d_6$) δ 3.93, 3.98 (both s, 3H, MeO), 7.13 (d, $^3J = 8.7$ Hz, 1H, H-4), 7.55 (d, $^4J = 2.2$ Hz, 1H, H-1), 7.65 (dd, $^3J = 8.7$ Hz, $^4J = 2.2$ Hz, 1H, H-3), 8.12 (d, $^5J_{H,F} = 1.3$ Hz, 1H, H-7), 9.65 (d, $^4J_{H,F} = 3.6$ Hz, 1H, OH), 11.10 (s, 1H, OH); ^{19}F NMR (282.4 MHz, $DMSO-d_6$) δ -78.0 (s, 3F, CF_3), -121.8 (d, $^2J = 279.7$ Hz, 1F, CFF), -124.0 (d, $^2J = 279.7$ Hz, 1F, CFF); ^{13}C NMR (75.5 MHz, $DMSO-d_6$) δ 53.0, 53.2, 97.1 (t, $^2J_{C,F} = 28.8$ Hz), 113.8, 114.4, 119.2, 119.9, 120.1, 120.7, 127.2, 130.8, 131.4, 134.8, 151.0, 158.5, 167.2, 167.6; MS (EI, 70 eV) m/z (%) 528 (M^+ , 4), 496 (14), 463 (12), 409 (57), 377 (100), 343 (34), 288 (8), 264 (62), 236 (13), 173 (10), 44 (11); HRMS (ESI): calcd for $C_{19}H_{13}BrF_5O_7$ $[M+H]^+$ 526.97593, found 526.97523; IR (ATR, cm^{-1}) 3427 (w), 2957 (w), 1722 (s), 1674 (m), 1650 (w), 1613 (w), 1592 (w), 1556 (w), 1480 (w), 1442 (m), 1341 (m), 1308 (m), 1253 (m), 1217 (s), 1177 (s), 1143 (s), 1071 (s), 1043 (m), 997 (s), 937 (m), 908 (m), 877 (m), 843 (m), 819 (s), 775 (m), 748 (s), 708 (s), 664 (m), 628 (s), 561 (w), 542 (m).

Dimethyl 6,9-dihydroxy-6-(pentafluoroethyl)-6H-dibenzo[c,h]chromene-8,10-dicarboxylate (5g). Yield 78%, pale yellow solid, mp 234 °C; 1H NMR (300 MHz, $DMSO-d_6$) δ 3.94, 3.99 (both s, 3H, MeO), 7.53 (d, $^3J = 8.9$ Hz, 1H), 7.64–7.72 (m, 3H), 7.93–7.97 (m, 1H), 8.17–8.23 (m, 2H), 9.74 (d, $^4J_{H,F} = 3.8$ Hz, 1H, OH), 11.14 (s, 1H, OH); ^{19}F NMR (282.4 MHz, $DMSO-d_6$) δ -77.5 (s, 3F, CF_3), -121.8 (d, $^2J = 277.9$ Hz, 1F, CFF), -124.6 (d, $^2J = 277.9$ Hz, 1F, CFF); ^{13}C NMR (75.5 MHz, $DMSO-d_6$) δ 53.0, 53.1, 97.6 (t, $^2J_{C,F} = 28.6$ Hz), 112.4, 118.9, 120.1, 120.7, 120.9, 121.8, 122.5, 123.8, 127.0, 127.7, 128.6, 130.5, 133.6, 134.6, 147.9, 158.8, 167.3, 167.9; MS (EI, 70 eV) m/z (%) 498 (M^+ , 11), 466 (64), 435 (10), 379 (20), 347 (100), 315 (91), 287 (13), 259 (9), 231 (10), 157 (15), 97 (10), 57 (15); HRMS (ESI): calcd for $C_{23}H_{16}F_5O_7$ $[M+H]^+$ 449.08107, found 449.08116; IR (ATR, cm^{-1}) 3282 (w), 3107 (w), 2953 (w), 1708 (m), 1679 (m), 1633 (w), 1615 (m), 1603 (w), 1589 (w), 1565 (w), 1479 (w), 1443 (m), 1433 (m), 1403 (w),

1383 (w), 1327 (m), 1306 (w), 1251 (m), 1205 (s), 1174 (s), 1156 (s), 1140 (s), 1087 (s), 1049 (m), 1031 (m), 1016 (m), 984 (m), 964 (m), 949 (w), 926 (m), 907 (m), 876 (m), 827 (w), 812 (m), 794 (s), 780 (m), 761 (w), 751 (m), 712 (s), 660 (m), 627 (w), 608 (m), 687 (w), 572 (m), 555 (w).

Dimethyl 6-(heptafluoropropyl)-6,9-dihydroxy-6H-benzo[c]chromene-8,10-dicarboxylate (5h). Yield 69%, white solid, mp 211–212 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ 3.92, 3.98 (s, 3H, MeO), 7.09–7.20 (m, 2H, H-2, H-4), 7.43–7.50 (m, 2H, H-1, H-3), 8.13 (s, 1H, H-7), 9.51 (d, ⁴*J*_{H,F} = 4.1 Hz, 1H, OH), 11.08 (s, 1H, OH); ¹⁹F NMR (282.4 MHz, DMSO-*d*₆) δ –80.0 (s, 3F, CF₃), –118.3 (dq, ²*J* = 284.6 Hz, ⁴*J* = 8.5 Hz, 1F, CFF), –120.7 (dq, ²*J* = 284.6 Hz, ⁴*J* = 8.5 Hz, 1F, CFF), –123.8 (s, 1F, CFF), –123.9 (s, 1F, CFF); ¹³C NMR (62.9 MHz, DMSO-*d*₆) δ 52.3, 53.1, 97.4 (t, ²*J*_{C,F} = 29.1 Hz), 112.8, 117.7, 119.0, 121.0, 123.2, 124.9, 130.7, 132.3, 133.1, 151.7, 158.6, 167.3, 167.9; MS (EI, 70 eV) *m/z* (%) 498 (M⁺, 2), 466 (12), 435 (18), 329 (62), 297 (100), 265 (85), 238 (10), 210 (11), 133 (10); HRMS (ESI): calcd for C₂₀H₁₄F₇O₇ [M+H]⁺ 499.06223, found 499.06318; IR (ATR, cm⁻¹) 3417 (w), 2960 (w), 1716 (m), 1675 (m), 1607 (w), 1567 (w), 1494 (w), 1454 (w), 1440 (m), 1392 (w), 1336 (m), 1319 (m), 1297 (w), 1213 (s), 1143 (s), 1115 (s), 1058 (m), 997 (s), 927 (m), 903 (w), 882 (m), 837(w), 810 (m), 774 (m), 759 (s) 735 (s), 712 (s), 694 (w), 678 (m), 646 (w), 618 (m), 582 (w), 532 (m).

Dimethyl 6-(heptafluoropropyl)-6,9-dihydroxy-2-methyl-6H-benzo[c]chromene-8,10-dicarboxylate (5i). Yield 64% white solid, mp 322–324 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ 2.29 (s, 3H, Me), 3.91, 3.97 (both s, 3H, MeO), 7.00 (d, ⁴*J* = 8.2 Hz, 1H, H-4), 7.24–7.28 (m, 2H, H-1, H-3), 8.11 (d, ⁵*J*_{H,F} = 1.6 Hz, 1H, H-7), 9.44 (d, ⁴*J*_{H,F} = 4.3 Hz, 1H, OH), 11.07 (s, 1H, OH); ¹⁹F NMR (282.4 MHz, DMSO-*d*₆) δ –80.0 (t, ³*J* = 8.7 Hz, 3F, CF₃), –118.3 (dq, *J* = 284.9 Hz, *J* = 9.1 Hz, 1F, CFF), –120.7 (dq, ²*J* = 284.9 Hz, ³*J* = 8.4 Hz, 1F, CFF), –123.8 (s, 1F, CFF), –123.9 (s, 1F, CFF); ¹³C NMR (62.9 MHz, CDCl₃) δ 19.0, 50.8, 51.1, 95.4 (t, ²*J*_{C,F} = 27.1 Hz), 109.7, 115.7, 116.4, 118.6, 123.6, 128.5, 130.2, 130.7, 132.3, 147.5, 158.2, 166.4, 167.4; MS (EI, 70 eV) *m/z* (%) 512 (M⁺, 4), 480 (20), 449 (16), 343 (53), 311 (100), 279 (80), 251 (8), 224 (15), 139 (13); HRMS (ESI): calcd for C₂₁H₁₆F₇O₇ [M+H]⁺ 513.07788, found 513.07787; IR (ATR, cm⁻¹) 3234 (w), 2958 (w), 2925 (w), 2853 (w), 1709 (m), 1682 (m), 1616 (w), 1596 (w), 1573 (w), 1491 (w), 1439 (m), 1405 (w), 1337 (m), 1317 (w), 1291 (m), 1275 (m), 1223 (s), 1186 (s), 1147 (s), 1116 (s), 1072 (m), 1017 (m), 995 (s), 949 (m), 928 (w), 890 (m), 841 (w), 822 (m), 803 (s), 781 (w), 741 (m), 728 (m), 679 (m), 642 (m), 599 (w), 564 (m), 533 (w).

Dimethyl 6-(heptafluoropropyl)-6,9-dihydroxy-3-methoxy-6H-benzo[c]chromene-8,10-dicarboxylate (5j). Yield 67% white solid, mp 193–195 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ 3.81, 3.91, 3.97 (all s, 3H, MeO), 6.62 (d, ⁴*J* = 2.1 Hz, 1H, H-4), 6.79 (dd, ³*J* = 8.9 Hz, ⁴*J* = 2.1 Hz, 1H, H-2), 7.38 (d, ³*J* = 8.9 Hz, 1H, H-1), 8.09 (s, 1H, H-7), 9.49, 11.08 (both s, 1H, OH); ¹⁹F NMR (282.4 MHz, DMSO-*d*₆) δ –80.0 (t, ³*J* = 8.7 Hz, 3F, CF₃), –118.5 (dq, ²*J* = 284.2 Hz, ³*J* = 8.5 Hz, 1F, CFF), –121.2 (dq, ²*J* = 284.2, ⁴*J* = 8.7 Hz, 1F, CFF), –123.7 (s, 1F, CFF), –123.8 (s, 1F, CFF); ¹³C NMR (62.9 MHz, DMSO-*d*₆) δ 52.9, 53.1, 55.7, 97.7 (t, ²*J*_{C,F} = 29.0 Hz), 102.5, 109.9, 110.4, 111.5, 117.9, 119.7, 126.2, 130.7, 133.5, 153.4, 158.8, 162.4, 167.4, 168.1; MS (EI, 70 eV) *m/z* (%) 528 (M⁺, 7), 496 (19), 465 (13), 359 (43), 327 (100), 295 (70), 240 (7), 148 (8), 97 (9), 57 (15); HRMS (ESI): calcd for C₂₁H₁₆F₇O₈ [M+H]⁺ 529.07279, found 529.07372; IR (ATR, cm⁻¹) 3271 (w), 2960 (w), 1714 (m), 1673 (m), 1651 (w), 1607 (m), 1537 (w), 1512 (w), 1444 (m), 1352 (m), 1331 (m), 1314 (m), 1291 (w), 1212 (s), 1189 (s), 1141 (s), 1110 (s), 1058 (m), 1028 (m), 994 (s), 958 (m), 920 (s), 882 (m), 861 (m), 836 (m), 816 (w), 797 (s), 764 (m), 739 (m), 713 (m), 672 (m), 618 (s), 579 (m), 548 (m), 535 (m).

Dimethyl 2-chloro-6-(heptafluoropropyl)-6,9-dihydroxy-6H-benzo[c]chromene-8,10-dicarboxylate (5k). Yield 77%, pale yellow solid, mp 200–201 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ 3.92, 3.98 (both s, 3H, MeO), 7.17 (d, ³*J* = 8.7 Hz, 1H, H-4), 7.42 (d, ⁴*J* = 2.4 Hz, 1H, H-1), 7.53 (dd, ³*J* = 8.7, ⁴*J* = 2.4 Hz, 1H, H-3), 8.13 (d, ⁵*J*_{H,F} = 1.7 Hz, 1H, H-7), 9.69 (d, ⁴*J*_{H,F} = 3.8 Hz, 1H, OH), 11.10 (s, 1H, OH); ¹⁹F NMR (282.4 MHz, DMSO-*d*₆) δ –80.1 (t, ³*J* = 8.9 Hz, 3F, CF₃), –118.3 (dq, 1F, *J* = 285.2 Hz, *J* = 9.2 Hz, CFF), –120.7 (dq, ²*J* = 285.2 Hz, ⁴*J* = 8.6 Hz, 1F, CFF), –123.8 (s, 1F, CFF), –124.0 (s, 1F, CFF); ¹³C NMR (62.9 MHz, DMSO-*d*₆) δ 53.1, 53.2, 97.8 (t, ²*J*_{C,F} = 26.2 Hz), 113.8, 119.2, 119.3, 119.7, 120.8, 124.3, 126.8, 130.9, 131.5, 131.9, 150.5, 158.5, 167.2, 167.6; MS (EI, 70 eV) *m/z* (%) 532 (M⁺, 3), 501 (10), 469 (14), 363 (78), 331 (100), 299 (54), 244 (11), 150 (10); HRMS (ESI): calcd for C₂₀H₁₃ClF₇O₇ [M+H]⁺ 533.02325, found 533.02296; IR (ATR, cm⁻¹) 3426 (w), 2956 (w), 2850 (w), 1721 (s), 1675 (m), 1643 (w), 1616 (w), 1563 (w), 1484 (w), 1462 (w), 1443 (m), 1407 (w), 1385 (w), 1347 (m), 1310 (m), 1253 (m), 1212 (s), 1193 (s), 1174 (s), 1142 (s), 1120 (s), 1098 (m), 1054 (m), 996 (s), 962 (m), 939 (m), 905 (m), 885 (m), 824 (m), 809 (m), 773 (m), 756 (s), 738 (m), 726 (m), 715 (m), 684 (w), 664 (w), 632 (m), 597 (w), 552 (w), 533 (w).

Dimethyl 2-chloro-6-(heptafluoropropyl)-6,9-dihydroxy-3-methyl-6H-benzo[c]chromene-8,10-dicarboxylate (5l). Yield 71%, pale yellow solid, mp 207–208 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ 2.35 (s, 3H, Me), 3.92, 3.97 (both s, 3H, MeO), 7.17 (s, 1H, H-4), 7.41 (s, 1H, H-1), 8.12 (s, 1H, H-7), 9.64 (d, ⁴*J*_{H,F} = 4.2 Hz, 1H, OH), 11.09 (s, 1H, OH); ¹⁹F NMR (282.4 MHz, DMSO-*d*₆) δ –80.0 (t, ³*J* = 8.3 Hz, 3F, CF₃), –118.4 (dq, ²*J* = 284.8 Hz, ⁴*J*

= 9.0 Hz, 1F, CFF), -120.8 (dq, $^2J = 284.8$, $^4J = 8.5$ Hz, 1F, CFF), -123.7 (s, 1F, CFF), -123.9 (s, 1F, CFF); ^{13}C NMR (62.9 MHz, DMSO- d_6) δ 19.6, 53.0, 53.2, 97.8 (t, $^2J_{\text{C,F}} = 29.4$ Hz), 113.3, 116.9, 118.8, 120.0, 120.4, 124.5, 127.2, 130.9, 131.7, 140.5, 150.4, 158.5, 167.2, 167.7; MS (GC, 70 eV) m/z (%) 514 (M-H-MeO, 21), 483 (14), 345 (100), 313 (81), 278 (16), 245 (9), 139 (10); HRMS (ESI): calcd for $\text{C}_{21}\text{H}_{15}\text{ClF}_7\text{O}_7$ [M+H] $^+$ 547.0389, found 547.03908; IR (ATR, cm^{-1}) 3272 (w), 2956 (w), 2853 (w), 1707 (m), 1687 (m), 1652 (w), 1613 (m), 1589 (w), 1549 (w), 1496 (w), 1436 (m), 1395 (w), 1352 (m), 1336 (m), 1295 (m), 1259 (m), 1207 (s), 1169 (s), 1144 (s), 1120 (s), 1075 (m), 1018 (m), 988 (m), 949 (w), 920 (m), 885 (m), 856 (m), 825 (m), 801 (m), 777 (w), 769 (w), 744 (m), 720 (m), 704 (s), 692 (m), 665 (m), 645 (m), 595 (m), 561 (m), 554 (m), 535 (w).

Dimethyl 2-bromo-6-(heptafluoropropyl)-6,9-dihydroxy-6H-benzo[c]chromene-8,10-dicarboxylate (5m). Yield 56%, white solid, mp 205–207 °C; ^1H NMR (300 MHz, DMSO- d_6) δ 3.93, 3.97 (both s, 3H, MeO), 7.11 (d, $^3J = 8.7$ Hz, 1H, H-4), 7.55 (d, $^4J = 2.3$ Hz, 1H, H-1), 7.65 (dd, $^3J = 8.7$, $^4J = 2.3$ Hz, 1H, H-3), 8.12 (d, $^5J_{\text{H,F}} = 1.4$ Hz, 1H, H-7), 9.69 (d, $^4J_{\text{H,F}} = 4.3$ Hz, 1H, OH), 11.10 (s, 1H, OH); ^{19}F NMR (282.4 MHz, DMSO- d_6) δ -80.0 (t, $^3J = 8.7$ Hz, 3F, CF_3), -118.3 (dq, $^2J = 285.4$ Hz, $^3J = 8.7$ Hz, 1F, CFF), -120.7 (dq, $^2J = 285.5$, $^3J = 8.7$ Hz, 1F, CFF), -123.8 (s, 1F, CFF), -123.9 (s, 1F, CFF); ^{13}C NMR (75.5 MHz, DMSO- d_6) δ 53.0, 53.2, 97.6 (t, $^2J_{\text{C,F}} = 29.6$ Hz), 113.8, 114.4, 119.1, 119.8, 120.0, 120.7, 127.2, 130.9, 131.4, 134.8, 150.9, 158.5, 167.1, 167.5; MS (EI, 70 eV) m/z (%) 578 ($\text{M}^+ + 2$, 2), 546 (15), 513 (10), 407 (42), 377 (100), 345 (28), 264 (61), 236 (9); HRMS (EI): calcd for $\text{C}_{20}\text{H}_{12}\text{BrF}_7\text{O}_7$ [M] $^+$ 575.96491, found 575.96594; IR (ATR, cm^{-1}) 3341 (w), 2962 (w), 1715 (w), 1688 (w), 1617 (w), 1595 (w), 1562 (w), 1462 (w), 1440 (w), 1403 (w), 1333 (w), 1290 (w), 1258 (m), 1213 (m), 1191 (m), 1143 (m), 1118 (s), 1089 (s), 1055 (s), 994 (s), 397 (m), 878 (m), 839 (m), 800 (s), 731 (s), 709 (s), 657 (m), 628 (m), 599 (m), 534 (m).

Dimethyl 6-(heptafluoropropyl)-6,9-dihydroxy-6H-dibenzo[c,h]chromene-8,10-dicarboxylate (5n). Yield 71%, pale yellow solid, mp 209–210 °C; ^1H NMR (300 MHz, DMSO- d_6) δ 3.94, 3.99 (both s, 3H, MeO), 7.53 (d, $^3J = 8.9$ Hz, 1H), 7.64–7.72 (m, 3H), 7.93–7.96 (m, 1H), 8.19–8.22 (m, 2H), 9.81, 11.14 (both s, 1H, OH); ^{19}F NMR (282.4 MHz, DMSO- d_6) δ -80.2 (t, $^3J = 9.2$ Hz, 3F, CF_3), -118.0 (dq, $^2J = 283.1$ Hz, $^3J = 8.8$ Hz, 1F, CFF), -121.5 (dq, $^2J = 288.1$, $^3J = 8.7$ Hz, 1F, CFF), -123.1 (s, 1F, CFF), -123.7 (s, 1F, CFF); ^{13}C NMR (62.9 MHz, DMSO- d_6) δ 52.9, 53.1, 98.3 (t, $^2J_{\text{C,F}} = 29.2$ Hz), 112.3, 112.4, 118.9, 120.2, 120.9, 121.8, 122.5, 123.8, 127.0, 127.7, 128.5, 130.5, 133.6, 134.6, 147.9, 158.9, 167.3, 168.0; MS (EI, 70 eV) m/z (%) 548 (M^+ , 6), 516 (26), 378 (100), 347 (80), 315 (99), 288 (32), 260 (10), 231 (13), 175 (13), 88 (6); HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{16}\text{F}_7\text{O}_7$ [M+H] $^+$ 549.07788, found 549.07701; IR (ATR, cm^{-1}) 3271 (w), 2953 (w), 1738 (w), 1704 (m), 1683 (m), 1634 (w), 1616 (w), 1591 (w), 1565 (w),

1539 (w), 1476 (w), 1444 (m), 1351 (m), 1333 (m), 1315 (w), 1252 (m), 1220 (s), 1152 (m), 1138 (m), 1119 (s), 1059 (w), 1040 (m), 1020 (w), 910 (m), 971 (m), 961 (w), 923 (w), 888 (m), 875 (m), 796 (s), 780 (w), 769 (w), 759 (w), 738 (s), 714 (m), 685 (m), 663 (w), 648 (w), 608 (m), 572 (m), 530 (m).

Methyl 7-hydroxy-10-(2-nitrobenzoyl)-6-oxo-6H-benzo[c]chromene-8-carboxylate (6a). Yield 72%, white solid, mp 330–332 °C; ¹H NMR (300 MHz, CDCl₃) δ 3.91 (s, 3H, MeO), 7.23–7.28 (m, 1H), 7.41 (d, ³J = 8.4 Hz, 1H), 7.53–7.58 (m, 2H), 7.66–7.76 (m, 2H), 8.01 (dd, ³J = 7.8 Hz, ⁴J = 1.4 Hz, 1H), 8.20 (s, 1H, H-9), 8.28 (dd, ³J = 8.3 Hz, ⁴J = 1.2 Hz, 1H), 13.31 (s, 1H, OH); ¹³C NMR (75.5 MHz, CDCl₃) δ 52.7, 116.1, 116.2, 117.6, 124.8, 125.5, 129.5, 131.2, 132.9, 133.0, 133.3, 133.4, 134.9, 140.5, 141.1, 148.8, 151.2, 164.7, 164.9, 165.1, 165.6, 191.9; MS (EI, 70 eV) *m/z* (%) 419 (M⁺, 8), 388 (8), 285 (100), 265 (10), 253 (70), 225 (11), 134 (29), 104 (17); IR (ATR, cm⁻¹) 3032 (w), 2949 (w), 2824 (w), 1711 (s), 1678 (s), 1594 (m), 1541 (s), 1434 (m), 1366 (m), 1352 (w), 1307 (m), 1274 (m), 1245 (s), 1198 (s), 1167 (s), 1107 (m), 1006 (w), 973 (m), 950 (w), 914 (w), 852 (w), 815 (s), 775 (s), 743 (s), 711 (m), 669 (m), 638 (m), 584 (w), 569 (w).

Methyl 7-hydroxy-2-methyl-10-(2-nitrobenzoyl)-6-oxo-6H-benzo[c]chromene-8-carboxylate (6b). Yield 84%, yellow solid, mp 326–328 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ 2.18 (s, 3H, Me), 3.85 (s, 3H, MeO), 7.38 (s, 2H), 7.48–7.57 (m, 2H), 7.63 (s, 1H), 7.77 (td, ³J = 7.5 Hz, ⁴J = 1.6 Hz, 1H), 8.01 (d, ³J = 8.0 Hz, 1H), 8.24 (s, 1H, H-9), 13.00 (br s, 1H, OH); ¹³C NMR (62.9 MHz, DMSO-*d*₆) δ 19.9, 52.5, 109.0, 115.6, 116.8, 117.2, 124.0, 124.5, 128.4, 130.5, 131.6, 132.7, 133.6, 134.1, 134.4, 138.9, 140.5, 148.8, 149.0, 163.7, 164.2, 164.4, 191.8; MS (EI, 70 eV) *m/z* (%) 433 (M⁺, 17), 402 (11), 299 (100), 267 (87), 239 (15), 134 (29), 104 (15), 44 (11); HRMS (ESI): calcd for C₂₃H₁₆NO₈ [M+H]⁺ 434.08704, found 434.08618; IR (ATR, cm⁻¹) 3030 (w), 2951 (w), 1707 (m), 1672 (s), 1590 (m), 1550 (s), 1430 (m), 1403 (w), 1368 (m), 1350 (w), 1299 (m), 1273 (w), 1245 (s), 1183 (s), 1137 (m), 1111 (m), 1024 (w), 977 (w), 921 (m), 816 (s), 779 (s), 760 (s), 711 (m), 679 (m), 657 (m), 637 (s), 615 (m), 589 (m), 532 (m).

Methyl 7-hydroxy-3-methoxy-10-(2-nitrobenzoyl)-6-oxo-6H-benzo[c]chromene-8-carboxylate (6c). Yield 73%, yellow solid, mp 370–372 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ 3.81, 3.83 (both s, 3H, MeO), 6.80 (dd, ³J = 9.1 Hz, ⁴J = 2.6 Hz, 1H), 7.07 (d, ⁴J = 2.5 Hz, 1H), 7.62–7.72 (m, 2H), 7.81–7.86 (m, 2H), 8.06–8.11 (m, 2H), 12.95 (br s, 1H, OH); ¹³C NMR (75.5 MHz, DMSO-*d*₆) δ 52.3, 56.1, 101.3, 108.8, 112.3, 115.1, 123.2, 124.7, 130.0, 131.3, 131.8, 132.0, 133.3, 134.0, 139.9, 140.2, 148.7, 152.6, 162.6, 164.1, 164.3, 164.6, 192.0; MS (EI, 70 eV) *m/z* (%) 449 (M⁺, 31), 419 (24), 386

(18), 343 (10), 315 (100), 300 (19), 283 (94), 255 (33), 227 (10), 207 (12), 134 (30), 104 (20), 77 (11), 44 (65); HRMS (ESI): calcd for C₂₃H₁₆NO₉ [M+H]⁺ 450.08196, found 450.08216; IR (ATR, cm⁻¹) 3035 (w), 2944 (w), 1716 (m), 1670 (m), 1593 (m), 1537 (s), 1433 (m), 1362 (m), 1321 (w), 1288 (m), 1241 (s), 1201 (s), 1162 (m), 1111 (m), 1027 (m), 989 (w), 948 (w), 918 (w), 841 (m), 804 (s), 742 (m), 710 (w), 692 (m), 650 (w), 618 (m), 580 (w), 546 (w).

Methyl 10-benzoyl-7-hydroxy-6-oxo-6H-benzo[c]chromene-8-carboxylate (6d). Yield 27%, yellow solid, mp 144–146 °C; ¹H NMR (250 MHz, DMSO-*d*₆) δ 3.84 (s, 3H, MeO), 7.12–7.18 (m, 1H), 7.50–7.59 (m, 5H), 7.64–7.70 (m, 1H), 7.85 (d, ³J = 7.8 Hz, 2H), 8.08 (s, 1H, H-9), 12.80 (s, 1H, OH); ¹³C NMR (62.9 MHz, DMSO-*d*₆) δ 52.4, 108.6, 116.1, 116.7, 117.8, 124.9, 126.4, 127.3, 129.1, 129.2, 129.9, 130.0, 132.3, 134.5, 135.9, 137.0, 137.8, 150.7, 162.4, 164.3, 164.4, 196.4; MS (EI, 70 eV) *m/z* (%) 374 (M⁺, 100), 343 (23), 297 (22), 265 (28), 183 (20), 105 (43), 77 (24); HRMS (EI): calcd for C₂₂H₁₄O₆ [M]⁺ 374.07849, found 374.07772; IR (ATR, cm⁻¹) 3063 (w), 2952 (w), 1693 (s), 1651 (m), 1639 (m), 1607 (w), 1593 (m), 1576 (w), 1556 (m), 1538 (w), 1519 (m), 1488 (w), 1441 (s), 1408 (w), 1352 (w), 1311 (m), 1279 (w), 1228 (s), 1178 (s), 1163 (s), 1144 (s), 1082 (m), 1008 (w), 978 (w), 939 (w), 923 (w), 849 (w), 823 (m), 783 (w), 758 (m), 734 (s), 720 (w), 698 (m), 673 (s), 647 (m), 633 (s), 567 (w), 551 (w).

Methyl 7-hydroxy-10-(2-thenoyl)-6-oxo-6H-benzo[c]chromene-8-carboxylate (6e). Yield 63%, yellow solid, mp 175–178 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ 3.85 (s, 3H, MeO), 7.14–7.26 (m, 2H), 7.50–7.67 (m, 4H), 8.16–8.19 (m, 2H), 12.81 (s, OH); ¹³C NMR (75.5 MHz, DMSO-*d*₆) δ 52.4, 108.7, 116.1, 116.6, 117.8, 125.0, 126.1, 127.0, 129.3, 132.3, 136.7, 137.3, 137.8, 138.0, 143.1, 150.7, 162.4, 164.2, 164.4, 188.6; MS (EI, 70 eV) *m/z* (%) 380 (M⁺, 50), 347 (49), 315 (50), 292 (19), 265 (12), 237 (11), 181 (17), 131 (13), 111 (100), 83 (14), 69 (43), 57 (10), 44 (33); HRMS (EI): calcd for C₂₀H₁₂O₆S (M⁺) 380.03491, found 380.03487; IR (ATR, cm⁻¹) 3107 (w), 2945 (w), 1712 (m), 1681 (m), 1651 (m), 1595 (m), 1516 (w), 1431 (m), 1409 (m), 1351 (w), 1308 (m), 1275 (m), 1250 (s), 1185 (s), 1132 (m), 1100 (m), 1056 (m), 991 (w), 971 (w), 944 (w), 920 (w), 889 (w), 852 (m), 815 (m), 794 (w), 761 (s), 738 (s), 671 (m), 649 (s), 627 (s), 564 (m).

Methyl 7-hydroxy-10-(2-fluorobenzoyl)-6-oxo-6H-benzo[c]chromene-8-carboxylate (6f). Yield 46%, white solid, mp 158–160 °C; ¹H NMR (300 MHz, CDCl₃) δ 3.92 (s, 3H, MeO), 7.03–7.13 (m, 2H), 7.24–7.28 (m, 1H), 7.36 (dd, ³J = 8.3 Hz, ⁴J = 1.2 Hz, 1H), 7.46 (td, ³J = 7.3 Hz, ⁴J = 1.3 Hz, 1H), 7.52–7.60 (m, 1H), 7.67 (dd, ³J = 8.2 Hz, ⁴J = 1.2 Hz, 1H), 7.84 (td, ³J = 7.6 Hz, ⁴J = 1.8 Hz, 1H), 8.23 (s, 1H), 13.05 (s, 1H, OH); ¹³C NMR (62.9

MHz, CDCl₃) δ 52.6, 108.2, 116.2, 116.4, 116.9, 117.3, 117.8, 124.7, 124.8, 128.0, 128.8, 131.8, 132.2, 135.9, 136.1, 138.7, 151.0, 159.8, 164.0, 164.5, 164.9, 193.0; ¹⁹F NMR (282.4 MHz, CDCl₃) δ -109.0 (s, 1F); MS (GC, 70 eV) *m/z* (%) 392 (M⁺, 100), 359 (40), 332 (13), 297 (15), 265 (36), 237 (22), 181 (13), 123 (68), 95 (35), 75 (18); HRMS (ESI): calcd for C₂₂H₁₄FO₆ [M+H]⁺ 393.07689, found 393.07703, calcd for C₂₂H₁₃FNaO₆ [M+Na]⁺ 416.06222, found 416.06204; IR (ATR, cm⁻¹) $\tilde{\nu}$ 3108 (w), 2923 (w), 2851 (w), 1712 (m), 1679 (s), 1602 (s), 1574 (m), 1504 (w), 1480 (w), 1444 (m), 1350 (w), 1302 (m), 1274 (m), 1259 (m), 1238 (s), 1221 (s), 1198 (s), 1185 (s), 1168 (s), 1152 (s), 1134 (m), 1101 (m), 1006 (s), 968 (m), 941 (w), 913 (m), 858 (m), 814 (s), 793 (s), 763 (s), 742 (s), 701 (m), 686 (m), 665 (s), 641 (m), 625 (m), 567 (m), 550 (m).

Methyl 3-hydroxy-6-(2-hydroxybenzoyl)-2,4-diphenylbenzoate (7a). Yield 49%, white solid, mp 181 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ 3.34 (s, 3H, MeO), 6.91–7.00 (m, 2H), 7.29–7.53 (m, 13H), 9.22, 11.64 (both s, 1H, OH); ¹³C NMR (62.9 MHz, DMSO-*d*₆) δ 51.6, 117.0, 119.1, 123.4, 127.6, 127.7, 128.0, 128.4, 129.2, 129.6, 130.0, 131.2, 132.8, 132.9, 134.1, 134.2, 134.6, 134.8, 137.1, 154.6, 157.9, 167.9, 196.3; MS (GC, 70 eV) *m/z* (%) 424 (M⁺, 10), 392 (100), 375 (18), 363 (36), 347 (13), 315 (54), 274 (7), 215 (19), 121 (11), 65 (7); HRMS (ESI): calcd for C₂₇H₂₁O₅ [M+H]⁺ 425.13835, found 425.13906; IR (ATR, cm⁻¹) 3432 (w), 2952 (w), 1731 (s), 1628 (m), 1599 (w), 1579 (w), 1568 (w), 1487 (m), 1443 (w), 1430 (w), 1406 (m), 1353 (w), 1332 (w), 1312 (w), 1284 (m), 1268 (s), 1244 (s), 1217 (m), 1193 (m), 1172 (w), 1152 (m), 1132 (s), 1120 (m), 1082 (m), 1030 (m), 998 (m), 967 (m), 921 (w), 899 (w), 868 (w), 840 (m), 821 (w), 801 (w), 790 (w), 774 (m), 763 (s), 745 (s), 708 (m), 696 (s), 672 (m), 663 (m), 638 (w), 608 (m), 596 (m), 567 (m), 545 (m).

Methyl 3-hydroxy-6-(5-bromo-2-hydroxybenzoyl)-2,4-diphenylbenzoate (7b). Yield 54%, yellow solid, mp 256–258 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ 3.37 (s, 3H, MeO), 6.93 (d, ³*J* = 8.8 Hz, 1H, H-3'), 7.28–7.31 (m, 2H), 7.36–7.57 (m, 11H), 9.30, 10.52 (both s, 1H, OH); ¹³C NMR (75.5 MHz, DMSO-*d*₆) δ 51.6, 110.1, 119.0, 126.7, 127.1, 127.7, 127.8, 128.0, 128.5, 129.1, 129.4, 129.9, 130.0, 132.3, 133.6, 134.6, 134.8, 135.5, 137.1, 155.2, 155.6, 167.9, 193.2; MS (EI, 70 eV) *m/z* (%) 504 (M⁺, 8), 472 (100), 443 (25), 393 (19), 215 (24), 69 (17), 41 (10); HRMS (ESI): calcd for C₂₇H₂₀BrO₅ [M+H]⁺ 503.04886, found 503.04855; IR (ATR, cm⁻¹) 3397 (w), 3025 (w), 2945 (w), 1743 (s), 1629 (m), 1600 (w), 1580 (w), 1568 (w), 1492 (w), 1464 (m), 1446 (w), 1431 (m), 1409 (m), 1352 (m), 1321 (w), 1288 (m), 1271 (m), 1251 (s), 1201 (s), 1173 (m), 1122 (s), 1089 (m), 1080 (m), 1028 (m), 1010 (m), 972 (m), 959 (w), 909 (m), 889 (w), 847 (w), 829 (m), 821 (m), 800 (m), 779 (m), 755 (m), 740 (m), 699 (s), 657 (m), 646 (w), 609 (s), 594 (m), 552 (m).

4-(2-Hydroxybenzoyl)-2,6-diphenyl-3-(3-nitrophenyl)phenol (7c). Yield 42%, white solid, mp 211–213 °C; ^1H NMR (250 MHz, DMSO- d_6) δ 6.78–6.83 (m, 2H), 7.14–7.28 (m, 5H), 7.31–7.50 (m, 8H), 7.60–7.63 (m, 2H), 7.73 (s, 1H), 7.82–7.86 (m, 1H), 8.81, 10.92 (both s, 1H, OH); ^{13}C NMR (62.9 MHz, DMSO- d_6) δ 117.0, 118.9, 121.2, 121.3, 122.7, 124.7, 127.0, 127.4, 127.7, 127.8, 128.3, 128.4, 128.6, 129.1, 129.2, 129.3, 130.3, 131.1, 131.2, 131.4, 132.3, 135.2, 135.3, 136.7, 137.4, 138.0, 140.5, 146.4, 153.2, 159.3, 199.9; MS (EI, 70 eV) m/z (%) 487 (M^+ , 90), 367 (100), 289 (10), 121 (50); HRMS (EI): calcd for $\text{C}_{31}\text{H}_{21}\text{O}_5\text{N}$ [M] $^+$ 487.14142, found 487.14136; IR (ATR, cm^{-1}) 3533 (w), 3502 (w), 1599 (w), 1529 (m), 1483 (m), 1443 (w), 1402 (w), 1348 (m), 1304 (w), 1278 (m), 1239 (m), 1214 (m), 1158 (m), 1129 (m), 1030 (w), 971 (w), 933 (w), 903 (w), 860 (w), 822 (w), 789 (w), 761 (m), 731 (m), 698 (s), 666 (m), 619 (m), 594 (w), 547 (w), 531 (w).

4-(2-Hydroxybenzoyl)-2,6-diphenyl-3-(4-nitrophenyl)phenol (7d). Yield 69%, yellow solid, mp 231–235 °C; ^1H NMR (300 MHz, DMSO- d_6) δ 6.83–6.87 (m, 2H), 7.11–7.16 (m, 2H), 7.18–7.25 (m, 5H), 7.35–7.40 (m, 3H), 7.44–7.51 (m, 3H), 7.60–7.62 (m, 2H), 7.85 (s, 1H), 7.88 (s, 1H), 8.82, 11.01 (both s, 1H, OH); ^{13}C NMR (75.5 MHz, DMSO- d_6) δ 117.2, 119.0, 122.0, 122.1, 122.4, 127.0, 127.4, 127.7, 127.8, 128.2, 128.4, 128.5, 129.0, 129.2, 129.3, 130.4, 131.0, 131.1, 131.2, 131.3, 131.4, 132.5, 135.3, 135.4, 137.4, 138.5, 145.7, 146.4, 153.2, 159.7, 199.9; MS (GC, 70 eV) m/z (%) 487 (M^+ , 63), 367 (100), 289 (16), 121 (51); HRMS (EI): calcd for $\text{C}_{31}\text{H}_{21}\text{O}_5\text{N}$ [M] $^+$ 487.14142, found 487.14134; IR (ATR, cm^{-1}) 3453 (w), 3077 (w), 2925 (w), 2849 (w), 1623 (w), 1597 (m), 1578 (w), 1515 (s), 1481 (w), 1446 (w), 1394 (w), 1339 (s), 1285 (m), 1240 (m), 1209 (s), 1156 (m), 1128 (m), 1106 (m), 1031 (m), 967 (m), 901 (w), 852 (m), 749 (s), 700 (s), 638 (w), 617 (m), 571 (w), 545 (w).

4-(2-Hydroxybenzoyl)-2,6-diphenyl-3-(3,5-dinitrophenyl)phenol (7e). Yield 74%, yellow solid, mp 100–102 °C; ^1H NMR (300 MHz, DMSO- d_6) δ 6.74–6.81 (m, 2H), 7.13–7.31 (m, 6H), 7.36–7.41 (m, 2H), 7.45–7.50 (m, 3H), 7.55–7.61 (m, 2H), 8.14 (d, $^4J = 2.1$ Hz, 2H), 8.48 (t, $^4J = 2.1$ Hz, 1H), 9.04, 10.53 (both s, 1H, OH); ^{13}C NMR (75.5 MHz, DMSO- d_6) δ 116.4, 116.8, 116.9, 119.0, 119.1, 124.5, 127.3, 127.6, 128.0, 128.1, 128.4, 128.5, 129.2, 129.3, 129.7, 130.3, 130.4, 131.1, 131.2, 131.3, 131.4, 134.3, 134.8, 136.6, 137.3, 142.6, 146.6, 146.7, 153.8, 157.8, 197.9; MS (EI, 70 eV) m/z (%) 532 (M^+ , 62), 438 (10), 412 (81), 365 (84), 289 (19), 121 (100), 93 (11), 65 (11); HRMS (EI): calcd for $\text{C}_{31}\text{H}_{20}\text{O}_7\text{N}_2$ [M] $^+$ 532.12650, found 532.12681; IR (ATR, cm^{-1}) 3507 (w), 3086 (w), 2921 (w), 1622 (m), 1605 (w), 1579 (w), 1538 (s), 1481 (w), 1446 (w), 1401 (w), 1342 (s), 1313 (m),

1286 (m), 1212 (m), 1170 (m), 1154 (m), 1127 (m), 1075 (w), 1031 (w), 1001 (w), 979 (w), 952 (w), 908 (w), 867 (w), 848 (w), 832 (w), 758 (m), 725 (s), 699 (s), 670 (m), 618 (m), 595 (w), 567 (w), 530 (w).

4-(2-Hydroxybenzoyl)-2,3,6-triphenylphenol (7f). Yield 32%, yellow solid, mp 209–212 °C; ¹H NMR (250 MHz, DMSO-*d*₆) δ 6.79–6.98 (m, 7H), 7.09–7.23 (m, 5H), 7.33–7.48 (m, 6H), 7.60–7.63 (m, 2H), 8.56, 11.44 (both s, 1H, OH); ¹³C NMR (75.5 MHz, DMSO-*d*₆) δ 117.2, 118.9, 121.2, 126.4, 126.6, 127.0, 127.3, 127.5, 128.2, 128.3, 129.1, 129.2, 129.3, 130.0, 131.1, 131.2, 131.3, 133.2, 135.8, 135.9, 137.6, 138.4, 140.0, 152.6, 160.7, 201.9; MS (GC, 70 eV) *m/z* (%) 442 (M⁺, 63), 365 (50), 322 (100), 302 (14), 215 (12), 121 (19); HRMS (EI): calcd for C₃₁H₂₂O₃ [M]⁺ 442.15635, found 442.15625; IR (ATR, cm⁻¹) 3467 (w), 3429 (w), 3053 (w), 3025 (w), 2918 (w), 2851 (w), 1714 (w), 1622 (m), 1601 (m), 1575 (w), 1557 (w), 1539 (w), 1532 (w), 1520 (w), 1514 (w), 1504 (w), 1495 (w), 1485 (w), 1471 (w), 1456 (w), 1446 (w), 1403 (w), 1342 (m), 1310 (w), 1274 (m), 1234 (m), 1211 (s), 1186 (m), 1155 (s), 1130 (m), 1107 (m), 1075 (m), 1064 (m), 1028 (m), 1001 (m), 966 (m), 924 (w), 897 (m), 866 (w), 852 (w), 835 (m), 820 (m), 801 (m), 783 (w), 748 (s), 697 (s), 669 (m), 638 (m), 630 (m), 618 (m), 594 (m), 568 (m), 541 (m).

4-(2-Hydroxybenzoyl)-2,6-diphenyl-3-(2-thienyl)phenol (7g). Yield 29%, yellow solid, mp 207–210 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ 6.56 (dd, ³*J* = 3.5 Hz, ⁴*J* = 1.2 Hz, 1H), 6.63–6.66 (m, 1H), 6.78–6.87 (m, 2H), 7.16–7.21 (m, 3H), 7.22–7.30 (m, 3H), 7.34 (s, 1H), 7.37–7.48 (m, 5H), 7.60–7.63 (m, 2H), 8.61 (s, 1H), 11.50 (s, 1H); ¹³C NMR (75.5 MHz, DMSO-*d*₆) δ 117.2, 118.9, 120.9, 126.1, 127.1, 127.3, 127.4, 127.7, 128.3, 128.9, 129.0, 129.2, 129.3, 130.9, 131.7, 132.1, 132.2, 133.0, 135.8, 136.0, 137.4, 138.9, 152.6, 160.7, 201.9; MS (GC, 70 eV) *m/z* (%) 448 (M⁺, 100), 413 (14), 353 (16), 328 (96), 295 (15), 121 (18); HRMS (EI): calcd for C₂₉H₂₀O₃S [M]⁺ 448.11277, found 448.11285; IR (ATR, cm⁻¹) 3422 (w), 3055 (w), 3029 (w), 2961 (w), 2924 (w), 2853 (w), 1622 (m), 1579 (w), 1531 (w), 1483 (w), 1458 (w), 1445 (w), 1425 (w), 1398 (w), 1343 (m), 1308 (w), 1277 (m), 1266 (m), 1239 (w), 1219 (m), 1210 (m), 1192 (m), 1147 (m), 1101 (w), 1072 (w), 1039 (m), 1028 (w), 976 (w), 962 (w), 921 (w), 903 (w), 878 (w), 868 (w), 849 (w), 839 (w), 819 (w), 793 (w), 778 (w), 755 (s), 726 (m), 709 (m), 698 (s), 666 (m), 635 (w), 621 (m), 608 (w), 596 (m), 573 (w), 531 (w).

2,6-Diphenyl-3-(2-hydroxyphenyl)-4-(2-nitrobenzoyl)phenol (8a). Yield 59%, yellow solid, mp 119–121 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ 6.28–6.32 (m, 2H), 6.57 (dd, ³*J* = 7.8 Hz, ⁴*J* = 1.5 Hz, 1H), 6.67 (td, ³*J* = 7.7 Hz, ⁴*J* = 1.6 Hz, 1H), 7.02–7.18 (m, 5H), 7.34–7.51 (m, 4H), 7.53–7.62 (m, 5H), 7.89 (dd, ³*J* = 7.8 Hz, ⁴*J* = 1.3 Hz, 1H), 8.72, 9.15 (both s, 1H, OH); ¹³C NMR (75.5 MHz, DMSO-*d*₆) δ 114.2, 117.7, 123.7, 123.8, 125.5, 126.6,

127.3, 127.4, 128.0, 128.2, 128.5, 129.1, 129.2, 129.3, 130.6, 130.7, 130.7, 130.8, 131.9, 132.4, 133.2, 133.3, 136.0, 136.4, 137.6, 139.9, 146.3, 154.1, 155.0, 170.4, 193.1; MS (EI, 70 eV) m/z (%) 487 (M^+ , 100), 470 (37), 455 (16), 438 (72), 365 (84), 337 (40), 319 (11), 289 (14), 44 (13); HRMS (ESI): calcd for $C_{31}H_{22}NO_5$ $[M+H]^+$ 488.14925, found 488.15003; IR (ATR, cm^{-1}) 3494 (w), 3058 (w), 1651 (w), 1606 (w), 1575 (w), 1553 (w), 1524 (m), 1445 (w), 1403 (w), 1344 (m), 1281 (m), 1217 (m), 1151 (m), 1123 (w), 1103 (w), 1028 (w), 966 (w), 902 (w), 855 (w), 825 (w), 788 (w), 748 (m), 699 (s), 609 (m), 547 (w).

2,6-Diphenyl-3-(2-hydroxy-5-methylphenyl)-4-(2-nitrobenzoyl)phenol (8b). Yield 73%, yellow solid, mp 211–213 °C; 1H NMR (300 MHz, $DMSO-d_6$) δ 1.86 (s, 3H, Me), 6.15 (d, $^3J = 7.5$ Hz, 1H), 6.33 (s, 1H), 6.44 (d, $^3J = 7.5$ Hz, 1H), 6.91–7.10 (m, 5H), 7.36–7.39 (m, 2H), 7.45–7.59 (m, 6H), 7.65 (s, 1H), 7.86 (d, $^3J = 7.6$ Hz, 1H), 8.71, 8.90 (both s, 1H, OH); ^{13}C NMR (62.9 MHz, $DMSO-d_6$) δ 19.8, 114.0, 123.5, 125.0, 125.6, 126.6, 127.2, 127.3, 128.2, 128.5, 128.6, 129.1, 129.2, 130.3, 131.4, 131.7, 132.3, 133.2, 136.0, 136.5, 137.7, 140.0, 146.0, 151.9, 154.9, 193.3; MS (EI, 70 eV) m/z (%) 501 (M^+ , 49), 484 (12), 452 (33), 379 (20), 351 (21), 287 (72), 273 (100), 215 (33), 197 (96), 183 (68), 165 (12), 135 (72), 121 (55), 73 (56); HRMS (ESI): calcd for $C_{32}H_{24}NO_5$ $[M+H]^+$ 502.1649, found 502.16558; IR (ATR, cm^{-1}) 3509 (w), 3350 (w), 2920 (w), 1732 (w), 1651 (m), 1591 (w), 1556 (w), 1529 (s), 1443 (w), 1402 (w), 1341 (m), 1312 (m), 1257 (m), 1223 (s), 1149 (m), 1130 (m), 1061 (w), 1030 (m), 1001 (w), 968 (w), 911 (m), 887 (w), 857 (m), 819 (m), 774 (s), 742 (s), 697 (s), 667 (m), 610 (s), 591 (m), 566 (m).

2,6-Diphenyl-3-(2-hydroxy-4-methoxyphenyl)-4-(2-nitrobenzoyl)phenol (8c). Yield 61%, yellow solid, mp 198–200 °C; 1H NMR (300 MHz, $DMSO-d_6$) δ 3.50 (s, 3H, MeO), 5.82 (d, $^4J = 2.4$ Hz, 1H), 5.89 (dd, $^3J = 8.4$ Hz, $^4J = 2.4$ Hz, 1H), 6.44 (d, $^3J = 8.4$ Hz, 1H), 6.99–7.28 (m, 5H), 7.34–7.40 (m, 2H), 7.45–7.52 (m, 3H), 7.54–7.59 (m, 3H), 7.62 (s, 1H), 7.88 (dd, $^3J = 7.9$ Hz, $^4J = 1.3$ Hz, 1H), 8.68, 9.19 (both s, 1H, OH); ^{13}C NMR (75.5 MHz, $DMSO-d_6$) δ 54.6, 100.1, 103.5, 118.2, 123.6, 126.5, 127.3, 127.4, 128.2, 128.4, 128.5, 129.1, 129.2, 129.6, 130.2, 130.3, 131.2, 131.3, 132.1, 132.3, 132.4, 133.2, 133.3, 136.2, 136.6, 137.7, 139.7, 146.0, 154.9, 155.0, 159.1, 193.4; MS (EI, 70 eV) m/z (%) 517 (M^+ , 100), 500 (25), 485 (10), 468 (40), 395 (74), 367 (25), 351 (10), 276 (8), 151 (8); HRMS (ESI): calcd for $C_{32}H_{24}NO_6$ $[M+H]^+$ 518.15981, found 518.16061; IR (ATR, cm^{-1}) 3480 (w), 2917 (w), 2849 (w), 1711 (w), 1674 (w), 1640 (m), 1615 (m), 1552 (w), 1525 (s), 1464 (w), 1440 (m), 1346 (m), 1292 (m), 1244 (s), 1197 (m), 1149 (s), 1099 (s), 1025 (m), 966 (m), 915 (m), 853 (m), 822 (m), 791 (m), 764 (m), 744 (m), 724 (m), 701 (s), 609 (s), 559 (m), 531 (m).

4-Benzoyl-2,6-diphenyl-3-(2-hydroxyphenyl)phenol (8d). Yield 25%, yellow solid, mp 145–148 °C; ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 6.35–6.45 (m, 2H), 6.67 (d, $^3J = 7.5$ Hz, 1H), 6.75 (td, $^3J = 7.2$ Hz, $^4J = 1.5$ Hz, 1H), 7.07–7.15 (m, 4H), 7.26 (s, 1H), 7.34–7.50 (m, 7H), 7.60 (d, $^3J = 7.2$ Hz, 2H), 7.70 (d, $^3J = 7.1$ Hz, 2H), 8.39, 9.07 (both s, 1H, OH); ^{13}C NMR (62.9 MHz, $\text{DMSO}-d_6$) δ 114.4, 117.6, 125.7, 126.4, 127.0, 127.1, 127.2, 127.6, 127.7, 127.8, 128.0, 128.3, 128.9, 129.0, 129.3, 129.6, 129.8, 130.6, 130.6, 130.7, 131.7, 131.9, 132.2, 132.3, 136.5, 137.8, 138.0, 138.1, 152.7, 154.2, 196.2; IR (ATR, cm^{-1}) $\tilde{\nu}$ 3518 (w), 3508 (w), 3360 (w), 3057 (w), 3029 (w), 2920 (w), 2851 (w), 1732 (w), 1653 (m), 1634 (w), 1598 (w), 1575 (w), 1557 (w), 1539 (w), 1486 (w), 1462 (w), 1442 (m), 1397 (w), 1343 (w), 1319 (w), 1300 (w), 1286 (w), 1258 (m), 1220 (m), 1153 (m), 1108 (w), 1075 (w), 1049 (w), 1022 (w), 993 (m), 967 (m), 939 (w), 918 (w), 899 (m), 861 (w), 822 (w), 822 (w), 767 (m), 749 (s), 734 (s), 721 (m), 692 (s), 667 (m), 639 (m), 614 (m), 604 (m), 590 (m), 562 (w), 539 (w).

2,6-Diphenyl-3-(2-hydroxyphenyl)-4-(2-thenoyl)phenol (8e). Yield 18%, yellow solid, mp 175–177 °C; ^1H NMR (250 MHz, $\text{DMSO}-d_6$) δ 6.39–6.50 (m, 2H), 6.70 (d, $^3J = 7.4$ Hz, 1H), 6.80 (t, $^3J = 7.6$ Hz, 1H), 7.12–7.14 (m, 6H), 7.33–7.49 (m, 4H), 7.60–7.65 (m, 3H), 7.90 (dd, $^3J = 4.9$ Hz, $^4J = 1.0$ Hz, 1H), 8.40, 9.08 (both s, 1H, OH); ^{13}C NMR (62.9 MHz, $\text{DMSO}-d_6$) δ 114.4, 117.6, 125.6, 126.4, 127.1, 127.2, 127.7, 127.8, 128.2, 128.3, 129.3, 129.5, 130.5, 130.6, 131.6, 131.9, 132.0, 134.5, 135.1, 136.4, 137.7, 137.9, 144.4, 152.7, 154.2, 188.0; MS (GC, 70 eV) m/z (%) 448 (M^+ , 31), 111 (100), 39 (6); HRMS (ESI): calcd for $\text{C}_{29}\text{H}_{21}\text{SO}_3$ [$\text{M}+\text{H}$] $^+$ 449.12059, found 449.12008; IR (ATR, cm^{-1}) 3508 (w), 3390 (w), 3055 (w), 2922 (w), 2852 (w), 1622 (m), 1603 (w), 1580 (w), 1557 (w), 1539 (w), 1505 (w), 1495 (w), 1446 (w), 1435 (w), 1408 (m), 1353 (m), 1343 (m), 1318 (w), 1284 (m), 1259 (m), 1228 (m), 1150 (m), 1120 (w), 1099 (w), 1075 (w), 1063 (w), 1046 (w), 1028 (w), 1001 (w), 958 (w), 940 (w), 903 (w), 889 (w), 854 (w), 821 (w), 796 (w), 749 (s), 721 (s), 698 (s), 674 (m), 637 (w), 618 (m), 610 (m), 593 (s), 549 (w).

3-Hydroxy-6-(2-hydroxybenzoyl)-1,2,4-benzenetricarboxylic acid (9a). Yield 80%, white solid, mp 279–281 °C; ^1H NMR (300 MHz, CDCl_3) δ 6.87–6.95 (m, 2H, H-3', H-5'), 7.30 (d, $^3J = 7.5$ Hz, 1H, H-6'), 7.42 (t, $^3J = 7.5$ Hz, 1H, H-4'), 7.85 (s, 1H, H-5); ^{13}C NMR (62.9 MHz, CDCl_3) δ 116.0, 116.4, 117.2, 118.8, 122.3, 124.5, 130.9, 133.7, 136.3, 144.5, 158.1, 167.0, 167.7, 169.6, 170.8, 196.8; HRMS (ESI): calcd for $\text{C}_{16}\text{H}_9\text{O}_9$ [$\text{M}-\text{H}$] $^+$ 345.02521, found 345.02546; IR (ATR, cm^{-1}) 3401 (w), 1660 (w), 1643 (w), 1623 (m), 1588 (s), 1537 (w), 1485 (w), 1462 (w), 1446 (m), 1332 (m), 1291 (m), 1224 (s), 1157 (w), 1039 (w), 968 (w), 944 (w), 888 (w), 844 (w), 827 (m), 806 (w), 787 (w), 757 (s), 699 (m), 639 (s), 589 (m), 553 (m), 530 (w).

3-Hydroxy-6-(2-hydroxy-5-methylbenzoyl)-1,2,4-benzenetricarboxylic acid (9b). Yield 84%, white solid, mp 298–300 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ 2.21 (s, 3H, Me), 6.88 (d, ³*J* = 8.4 Hz, 1H, H-3'), 7.11 (s, 1H, H-6'), 7.28 (dd, ³*J* = 8.4 Hz, ⁴*J* = 2.0 Hz, 1H, H-4'), 7.93 (s, 1H, H-5), 10.47 (br s, 1H, OH); ¹³C NMR (62.9 MHz, DMSO-*d*₆) δ 19.9, 115.4, 117.0, 119.1, 123.0, 124.4, 127.8, 131.0, 135.1, 135.6, 140.7, 156.2, 166.1, 167.1, 167.9, 168.5, 196.1; HRMS (ESI): calcd for C₁₇H₁₁O₉ [M–H]⁺ 359.04086, found 359.0412; IR (ATR, cm⁻¹) 2858 (w), 1704 (w), 1681 (w), 1651 (w), 1644 (m), 1582 (m), 1519 (w), 1504 (w), 1434 (m), 1384 (w), 1334 (s), 1292 (s), 1222 (s), 1169 (m), 1037 (w), 974 (w), 880 (w), 822 (m), 793 (m), 745 (m), 700 (m), 672 (m), 640 (m), 582 (m), 534 (m).

3-Hydroxy-6-(5-chloro-2-hydroxy-4-methylbenzoyl)-1,2,4-benzenetricarboxylic acid (9e). Yield 92%, white solid, mp 362–364 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ 2.32 (s, 3H, Me), 6.96 (s, 1H, H-3'), 7.33 (s, 1H, H-6'), 7.91 (s, 1H, H-5), 10.71 (br s, 1H, OH); ¹³C NMR (62.9 MHz, DMSO-*d*₆) δ 20.0, 114.7, 119.6, 122.3, 122.5, 123.3, 127.0, 130.7, 133.4, 138.6, 142.7, 157.1, 162.6, 166.1, 167.3, 169.8, 194.2; MS (EI, 70 eV) *m/z* (%) 376 (M–H₂O, 76), 331 (15), 313 (100), 286 (23), 258 (11), 168 (17), 139 (11), 77 (19); HRMS (ESI): calcd for C₁₇H₁₀ClO₉ [M–H]⁺ 393.00188, found 393.00275; IR (ATR, cm⁻¹) 3490 (w), 2848 (w), 2521 (w), 1704 (m), 1688 (m), 1622 (m), 1599 (m), 1574 (m), 1476 (w), 1434 (w), 1392 (w), 1374 (w), 1334 (m), 1239 (s), 1212 (s), 1179 (s), 1160 (s), 1052 (m), 1009 (w), 952 (w), 884 (m), 826 (m), 816 (w), 803 (m), 792 (m), 747 (s), 722 (m), 709 (m), 686 (s), 635 (m), 619 (m), 596 (s).

3-Hydroxy-6-(1-hydroxy-2-naphthoyl)benzene-1,2,4-tricarboxylic acid (9g). Yield 89%, yellow solid, mp 304–306 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ 7.32–7.42 (m, 2H), 7.63 (t, ³*J* = 7.2 Hz, 1H), 7.74 (t, ³*J* = 7.1 Hz, 1H), 7.93 (d, ³*J* = 8.0 Hz, 1H), 7.98 (s, 1H), 8.38 (d, ³*J* = 8.2 Hz, 1H), 13.37 (s, 1H, OH); ¹³C NMR (62.9 MHz, DMSO-*d*₆) δ 113.5, 116.4, 117.4, 118.3, 122.1, 123.6, 124.4, 126.4, 127.0, 127.8, 130.4, 135.2, 136.8, 141.7, 161.4, 166.2, 167.6, 168.1, 169.7, 199.3; MS (EI, 70 eV) *m/z* (%) 378 (M–H₂O, 58), 360 (10), 315 (45), 288 (20), 260 (13), 217 (11), 170 (32), 144 (29), 115 (25), 97 (30), 78 (76), 69 (56), 63 (100), 43 (86); HRMS (ESI): calcd for C₂₀H₁₁O₉ [M–H]⁺ 395.04086, found 395.04184; IR (ATR, cm⁻¹) 3391 (w), 2916 (w), 2590 (w), 1714 (w), 1651 (w), 1627 (w), 1584 (m), 1514 (m), 1504 (m), 1485 (w), 1455 (s), 1413 (m), 1384 (m), 1329 (m), 1271 (s), 1250 (s), 1210 (s), 1151 (m), 1108 (w), 1054 (w), 1023 (w), 991 (w), 946 (w), 876 (w), 829 (w), 778 (s), 742 (m), 717 (m), 685 (w), 660 (w), 640 (w), 612 (m), 601 (m), 575 (w), 557 (m).

9-Hydroxy-6-oxo-6H-benzo[c]chromene-8,10-dicarboxylic acid (10c). Yield 70%, white solid, mp 360–362 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.37–7.44 (m, 2H, H-2, H-4), 7.61 (t, $^3J = 7.7$ Hz, 1H, H-3), 8.13 (d, $^3J = 7.8$ Hz, 1H, H-1), 8.68 (s, 1H, H-7); ^{13}C NMR (62.9 MHz, CDCl_3) δ 109.9, 116.3, 116.9, 117.9, 120.5, 124.4, 125.1, 133.6, 131.7, 133.6, 151.4, 159.6, 166.1, 169.2, 169.6; HRMS (ESI): calcd for $\text{C}_{15}\text{H}_7\text{O}_7$ $[\text{M}-\text{H}]^+$ 299.01973, found 299.02026; IR (ATR, cm^{-1}) 2849 (w), 1704 (m), 1682 (m), 1651 (m), 1594 (s), 1557 (m), 1495 (w), 1446 (w), 1417 (w), 1318 (m), 1286 (m), 1200 (s), 1148 (s), 1113 (s), 932 (m), 893 (m), 855 (m), 809 (m), 744 (s), 727 (s), 713 (s), 686 (s), 640 (s).

9-Hydroxy-6-oxo-6H-dibenzo[c,h]chromene-8,10-dicarboxylic acid (10n). Yield 92%, pale yellow solid, mp 310–312 °C; ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 7.70–7.73 (m, 2H), 7.87 (d, $^3J = 9.2$ Hz, 1H), 7.99–8.02 (m, 1H), 8.12 (d, $^3J = 9.1$ Hz, 1H), 8.39–8.42 (m, 1H), 8.76 (s, H-7, 1H); ^{13}C NMR (75.5 MHz, $\text{DMSO}-d_6$) δ 111.2, 112.1, 115.0, 120.5, 120.7, 122.0, 123.0, 124.0, 127.6, 127.7, 129.0, 133.8, 134.1, 135.2, 147.9, 159.2, 163.3, 168.6, 170.3; MS (EI, 70 eV) m/z (%) 306 (M–CO₂, 87), 288 (100), 260 (33), 232 (11), 204 (14), 176 (30), 144 (8), 116 (11), 88 (21), 63 (10), 44 (39); HRMS (ESI): calcd for $\text{C}_{19}\text{H}_9\text{O}_7$ $[\text{M}-\text{H}]^+$ 349.03538, found 349.03602; IR (ATR, cm^{-1}) 3418 (w), 2872 (w), 2538 (w), 1713 (s), 1699 (s), 1682 (s), 1668 (s), 1633 (m), 1587 (s), 1557 (m), 1505 (w), 1495 (w), 1477 (w), 1446 (s), 1424 (m), 1353 (m), 1336 (m), 1302 (m), 1257 (s), 1216 (s), 1195 (s), 1164 (s), 1145 (s), 1122 (s), 1034 (m), 1013 (m), 964 (m), 939 (m), 895 (m), 870 (w), 800 (s), 773 (s), 736 (s), 680 (s), 666 (s), 634 (s), 622 (s), 609 (s), 563 (s), 537 (m).

(D) X-Ray structures

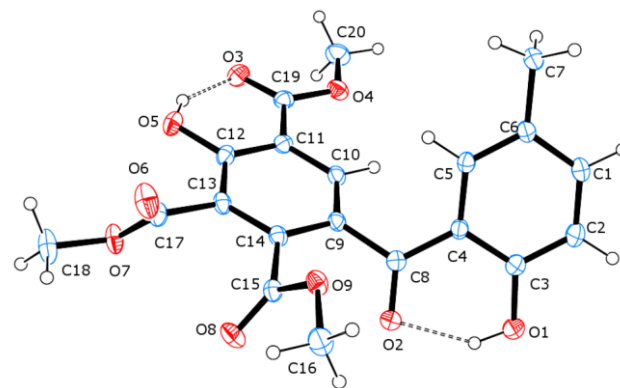


Figure 1. Molecular structure of compound **4b**.

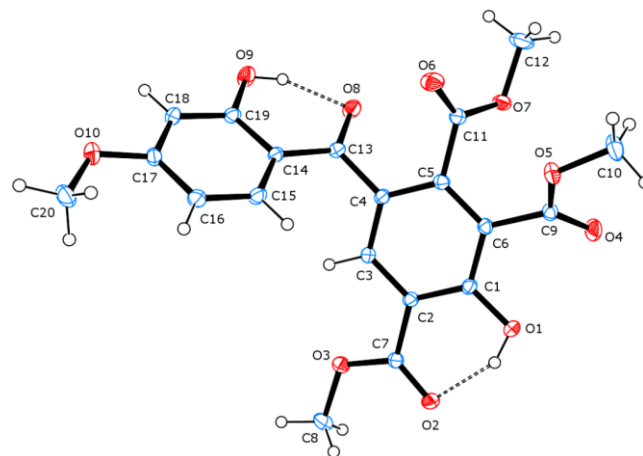


Figure 2. Molecular structure of compound **4c**.

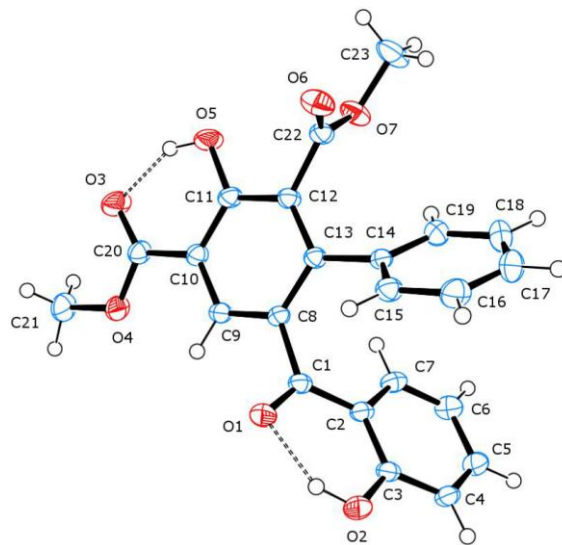


Figure 3. Molecular structure of compound **4k**

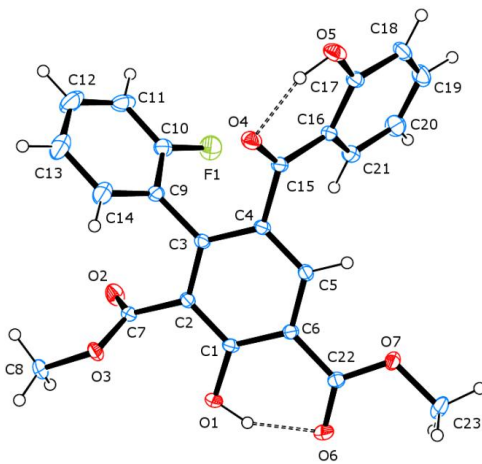


Figure 4. Molecular structure of compound **4m**.

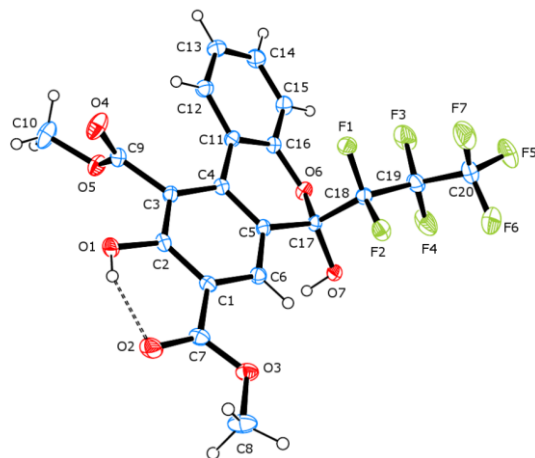


Figure 5. Molecular structure of compound **5h**.

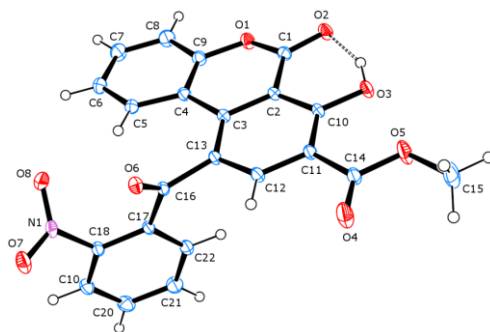


Figure 6. Molecular structure of compound **6a**.

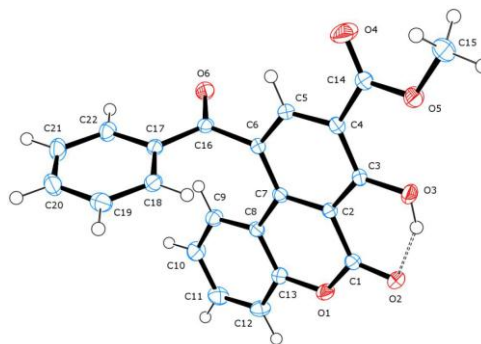


Figure 7. Molecular structure of compound **6d**.

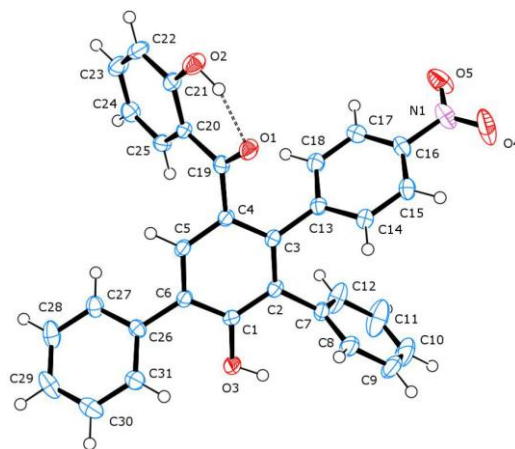


Figure 8. Molecular structure of compound **7f**.

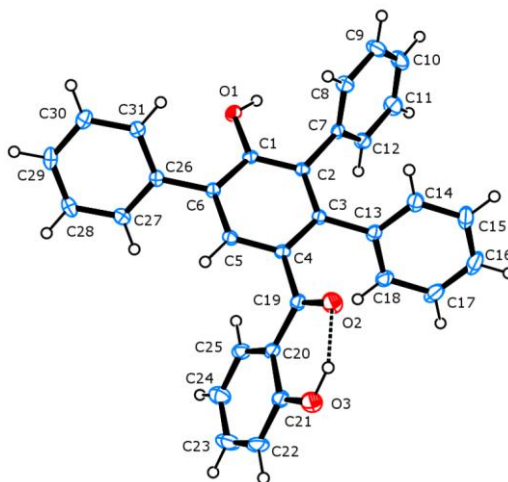


Figure 9. Molecular structure of compound **7f**.

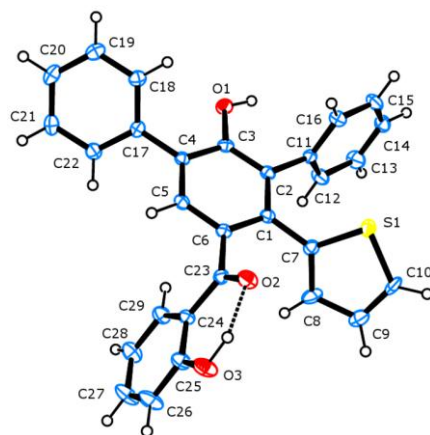


Figure 10. Molecular structure of compound **7g**.

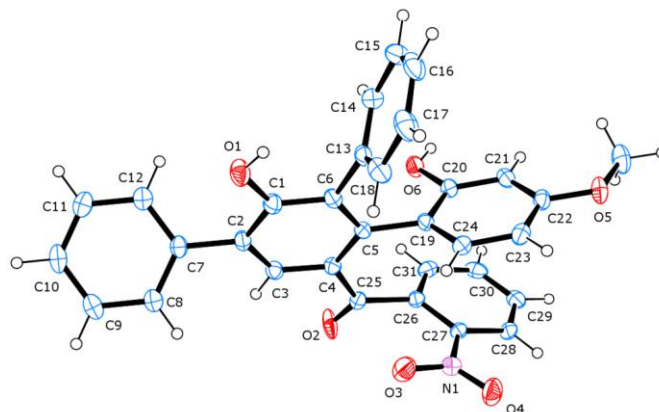


Figure 11. Molecular structure of compound **8c**.

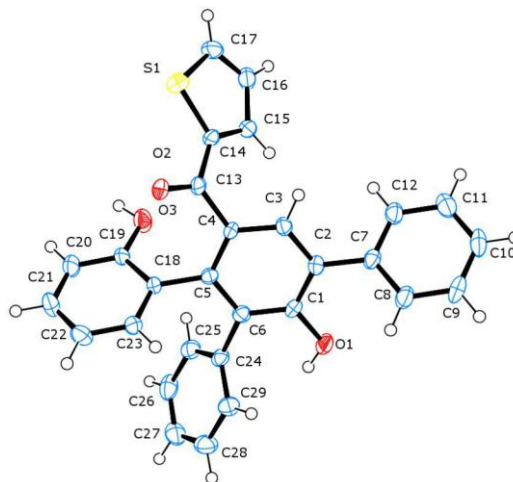


Figure 12. Molecular structure of compound **8e**.