Supporting Information

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1. General information

- Chemicals were purchased from Acros or Aldrich and used without further purification unless otherwise noted. Solvents were predistilled according to standard laboratory methods.
- Chromatographic purification of the products was performed on Merck silica gel 60, particle size 0.040-0.063 mm (230-240 mesh, flash).
- Analytical TLC: SIL G-25 UV254 from MACHEREY&NAGEL. Visualization of the developed TLC plates was performed with ultraviolet irradiation (254 nm) or by staining with basic potassium permanganate solution.
- Melting points were determined using a Büchi 510 apparatus and are uncorrected.
- Mass spectra were acquired on a Finnigan SSQ7000 (EI/Cl) spectrometer and high resolution mass spectra on a Finnigan MAT 95 (EI/Cl) or on a ThermoFisher Scientific LTQOrbitrap XL (ESI). All signals over 10% relative intensity are listed.
- IR spectra were taken on a Perkin-Elmer FT-IR Spectrum 100 using a Diamant/KRS5 ATR. Evaluation was done using the supplementary software. The absorption bands are given in wave numbers (cm⁻¹).
- ¹H- and ¹³C- NMR spectra were recorded at ambient temperature on Varian Mercury 300, VNMRS 600 and Inova 400 instruments. The chemical shifts are reported in ppm downfield of tetramethylsilane (TMS) and referenced to residual solvent peaks resonance as internal standard. The order of citation in parentheses is a) multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd= doublet of doublet, ddd= doublet of doublet of doublet, td = triplet of doublet, m = multiplet), b) coupling constants, c) number of protons. Coupling constants (J) are reported in Hertz (Hz).
2. Experimental Procedures and Characterization Data for 3a-3s:

A 10 mL glass tube equipped with a stirring bar was charged with p-QMs 1 (0.40 mmol, 1.0 equiv), sulfonium bromides 2 (0.48 mmol, 1.2 equiv), Cs$_2$CO$_3$ (0.48 mmol, 120 mol %) and CH$_3$CN (4.0 mL). The resulting solution was stirred at room temperature for the indicated time. Then the solvent was evaporated under reduced pressure to give a residue, which was directly purified by flash column chromatography (pentane/Et$_2$O from 30/1 to 10/1) to provide the desired product 3a-3s.

Ethyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-carboxylate (3a)

According to the general procedure, 3a was obtained as a colorless solid (0.151 g, 95% yield) in 0.5 h.

Melting Point: 112-114 °C.

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.22 – 7.19 (m, 1H), 7.07 (d, $J = 7.2$ Hz, 1H), 7.00 (s, 2H), 6.98 (d, $J = 7.8$ Hz, 1H), 6.93 – 6.90 (m, 1H), 5.18 (s, 1H), 5.00 (d, $J = 6.6$ Hz, 1H), 4.75 (d, $J = 6.6$ Hz, 1H), 4.36 – 4.24 (m, 2H), 1.41 (s, 18H), 1.33 (t, $J = 7.2$ Hz, 3H) ppm.

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 170.9, 159.2, 153.0, 136.1, 132.5, 128.7, 128.6, 125.4, 124.4 (2C), 121.4, 109.9, 87.4, 61.6, 52.6 (2C), 34.4 (2C), 30.2 (6C), 14.3 ppm.

IR (ATR): 3771, 3634, 3460, 2967, 2645, 2334, 2084, 1900, 1740, 1594, 1437, 1366, 1217, 1103, 1042, 898, 672 cm$^{-1}$.

MS (ESI): $m/z$ = 419.2 [M+Na]$^+$. 

HRMS (ESI): $m/z$ [M+Na]$^+$ calcd for C$_{25}$H$_{32}$O$_4$Na$: 419.2193$; found 419.2194.

The gram scale reaction for the synthesis of 3a was carried out in a similar manner. A round-bottom flask equipped with a stirring bar was charged with p-QMs 1a (0.931 g, 3.0 mmol, 1.0 equiv), sulfonium bromide 2a (0.825 g, 3.6 mmol, 1.2 equiv), Cs$_2$CO$_3$ (1.173 g, 3.6 mmol, 120 mol %) and CH$_3$CN (30 mL). The resulting solution was stirred at room temperature for 1.5 h and then the solvent was evaporated under reduced pressure to give a residue which was directly purified by flash column chromatography (pentane/Et$_2$O from 30/1 to 10/1) to provide the desired product 3a (1.106 g, 93%). The analytical data of the gram scale reaction of 3a are consistent with those of the 0.4 mmol scale experiment.
Methyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-carboxylate (3b)

According to the general procedure, 3b was obtained as a colorless solid (0.120 g, 79% yield) in 1 h.

**Melting Point:** 126-128 °C.

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.22 – 7.19 (m, 1H), 7.07 (d, $J = 7.8$ Hz, 1H), 6.98 (s, 2H), 6.97 (d, $J = 7.2$ Hz, 1H), 6.93 – 6.90 (m, 1H), 5.17 (s, 1H), 5.03 (d, $J = 6.6$ Hz, 1H), 4.75 (d, $J = 6.6$ Hz, 1H), 3.83 (s, 3H), 1.40 (s, 18H) ppm.

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 171.4, 159.0, 153.0, 136.1, 132.4, 128.7, 128.6, 125.4, 124.3 (2C), 121.5, 109.9, 87.3, 52.5, 52.4, 34.4 (2C), 30.2 (6C) ppm.

IR (ATR): 3398, 2954, 2150, 1745, 1615, 1435, 1186, 1046, 746 cm$^{-1}$.

MS (ESI): $m/z$ = 405.2 [M+Na]$^+$.  


*Methyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-carboxylate (3c)*

According to the general procedure, 3c was obtained as a colorless solid (0.139 g, 82% yield) in 0.5 h.

**Melting Point:** 146-148 °C.

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.22 – 7.18 (m, 1H), 7.07 (d, $J = 7.8$ Hz, 1H), 6.99 – 6.96 (m, 3H), 6.92 – 6.89 (m, 1H), 5.17 (s, 1H), 4.89 (d, $J = 6.6$ Hz, 1H), 4.67 (d, $J = 6.6$ Hz, 1H), 1.53 (s, 9H), 1.41 (s, 18H) ppm.

$^{13}$C NMR (150 MHz, CDCl$_3$) δ 170.0, 159.5, 152.9, 136.1, 132.8, 128.7, 125.4, 124.3 (2C), 121.2, 109.9, 87.7, 82.2, 52.8 (2C), 34.4 (3C), 30.2 (6C), 28.1 (3C) ppm.

IR (ATR): 3602, 3463, 2962, 2322, 2099, 2990, 2905, 1742, 1598, 1475, 1436, 1366, 1313, 1227, 1152, 1036, 937, 823, 753 cm$^{-1}$.

MS (ESI): $m/z$ = 447.2 [M+Na]$^+$.  

HRMS (ESI): $m/z$ [M+Na]$^+$ calcd for C$_{27}$H$_{36}$O$_4$Na$: 447.2506$; found 447.2493.
(3-(3,5-di-tert-Butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (3d)

According to the general procedure, 3d was obtained as a colorless solid (0.144 g, 84% yield) in 12 h.

**Melting Point:** 145-147 °C.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.93 – 7.90 (m, 2H), 7.58 (t, $J = 7.6$ Hz, 1H), 7.45 – 7.41 (m, 2H), 7.22 – 7.16 (m, 1H), 7.03 (d, $J = 7.6$ Hz, 1H), 6.96 (d, $J = 8.0$ Hz, 1H), 6.93 (s, 2H), 6.90 – 6.86 (m, 1H), 5.76 (d, $J = 6.8$ Hz, 1H), 5.16 (s, 1H), 4.84 (d, $J = 6.8$ Hz, 1H), 1.37 (s, 18H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 195.2, 159.2, 153.0, 136.2 (2C), 134.6, 133.6, 132.5, 129.3 (2C), 128.6, 128.5 (2C), 125.4, 124.7 (2C), 121.4, 109.8, 90.8, 51.2 (2C), 34.3 (2C), 30.2 (6C) ppm.


[1,1'-Biphenyl]-4-yl(3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl)methanone (3e)

According to the general procedure, 3e was obtained as a colorless solid (0.200 g, 99% yield) in 0.5 h.

**Melting Point:** 157-159 °C.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.02 (d, $J = 8.0$ Hz, 2H), 7.67 (d, $J = 8.0$ Hz, 2H), 7.65 – 7.60 (m, 2H), 7.49 – 7.43 (m, 2H), 7.42 – 7.38 (m, 1H), 7.22 (t, $J = 8.0$ Hz, 1H), 7.08 (d, $J = 7.2$ Hz, 1H), 7.02 – 6.97 (m, 3H), 6.92 (t, $J = 7.2$ Hz, 1H), 5.81 (d, $J = 6.4$ Hz, 1H), 5.19 (s, 1H), 4.93 (d, $J = 6.4$ Hz, 1H), 1.40 (s, 18H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 194.8, 159.2, 153.0, 146.3, 139.8, 136.3, 133.3, 132.6, 129.9 (2C), 129.4, 129.0 (2C), 128.7, 128.4, 127.3 (2C), 127.2 (2C), 125.5, 124.8 (2C), 121.5, 109.8, 90.8, 51.2 (2C), 34.4 (2C), 30.3 (6C) ppm.

IR (ATR): 3930, 3782, 3581, 2953, 2316, 2081, 1911, 1739, 1684, 1597, 1446, 1366, 1223, 1299,
1223, 1113, 997, 953, 860, 744, 685 cm\(^{-1}\).

**MS (ESI):** \(m/z = 505.1\) [M+H]*.

**HRMS (ESI):** \(m/z\) [M+Na]* calcd for C\(_{35}\)H\(_{36}\)O\(_3\)Na*: 527.2557; found 527.2540.

![Chemical structure](image)

(3-(3,5-di-tert-Butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl)(p-tolyl)methanone (3f)

According to the general procedure, 3f was obtained as a colorless solid (0.160 g, 90% yield) in 0.5 h.

**Melting Point:** 159-161 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.82 (d, \(J = 8.8\) Hz, 2H), 7.23 (d, \(J = 8.8\) Hz, 2H), 7.22 - 7.17 (m, 1H), 7.04 (d, \(J = 7.6\) Hz, 1H), 6.97 (d, \(J = 8.0\) Hz, 1H), 6.94 (s, 2H), 6.92 - 6.85 (m, 1H), 5.75 (d, \(J = 6.8\) Hz, 1H), 5.17 (s, 1H), 4.84 (d, \(J = 6.8\) Hz, 1H), 2.41 (s, 3H), 1.38 (s, 18H) ppm.

\(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 194.8, 159.2, 153.0, 140.7, 136.2, 132.6, 132.1, 129.4 (2C), 129.3, 129.2 (2C), 128.6, 125.4, 124.8 (2C), 121.4, 109.8, 90.7, 51.3 (2C), 34.3 (2C), 30.2 (6C), 21.7 ppm.

**IR (ATR):** 3924, 3784, 3710, 3596, 2959, 2324, 2108, 1920, 1744, 1677, 1599, 1442, 1368, 1306, 1229, 1114, 956, 863, 821, 750, 664 cm\(^{-1}\).

**MS (EI):** \(m/z\) (%): 442.3 (72) [M]*, 425.3 (75) [M - OH]*, 119.1 (100) [M - C\(_{22}\)H\(_{27}\)O\(_2\)]*.

**HRMS (ESI):** \(m/z\) [M+Na]* calcd for C\(_{35}\)H\(_{36}\)O\(_3\)Na*: 465.2400; found 465.2394.

![Chemical structure](image)

(4-Bromophenyl)(3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl)metha-
none (3g)

According to the general procedure, 3g was obtained as an off-white solid (0.145 g, 72% yield) in 0.5 h.

**Melting Point:** 175-177 °C.
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.78 (d, \(J = 8.8\) Hz, 2H), 7.56 (d, \(J = 8.8\) Hz, 2H), 7.21 – 7.17 (m, 1H), 7.04 (d, \(J = 7.6\) Hz, 1H), 6.94 (s, 2H), 6.93 (d, \(J = 7.6\) Hz, 1H), 6.91 – 6.88 (m, 1H), 5.68 (d, \(J = 7.2\) Hz, 1H), 5.17 (s, 1H), 4.87 (d, \(J = 7.2\) Hz, 1H), 1.37 (s, 1H) ppm.

\(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 194.3, 158.9, 153.1, 136.3, 133.4, 132.3, 131.9 (2C), 130.8 (2C), 129.2, 128.9, 128.7, 125.4, 124.7 (2C), 121.6, 109.8, 90.8, 51.0 (2C), 34.3 (2C), 30.2 (6C) ppm.

IR (ATR): 3784, 3605, 2958, 2324, 2106, 1919, 1739, 1689, 1583, 1469, 1394, 1304, 1224, 1147, 1068, 1000, 960, 863, 820, 748 cm\(^{-1}\).

MS (EI): \(m/z\) 529.3 [M+Na]*

HRMS (ESI): \(m/z\) [M+Na] calcd for C\(_{29}\)H\(_{31}\)O\(_3\)BrNa*: 529.1349; found 529.1346.

(4-Chlorophenyl)(3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl)methane (3h)

According to the general procedure, 3h was obtained as an off-white solid (0.167 g, 90% yield) in 0.5 h.

Melting Point: 172-174\(^\circ\)C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.86 (d, \(J = 8.8\) Hz, 2H), 7.39 (d, \(J = 8.8\) Hz, 2H), 7.21 – 7.17 (m, 1H), 7.03 (d, \(J = 7.2\) Hz, 1H), 6.94 (d, \(J = 7.2\) Hz, 1H), 6.93 (s, 2H), 6.91 – 6.87 (m, 1H), 5.68 (d, \(J = 6.8\) Hz, 1H), 5.17 (s, 1H), 4.86 (d, \(J = 6.8\) Hz, 1H), 1.37 (s, 1H) ppm.

\(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 194.1, 158.9, 153.1, 140.1, 136.3, 133.0, 132.3, 130.7 (2C), 129.2, 128.9 (2C), 128.7, 125.4, 124.7 (2C), 121.6, 109.8, 90.8, 51.0 (2C), 34.3 (2C), 30.2 (6C) ppm.

IR (ATR): 3785, 3613, 2955, 2325, 2104, 1912, 1745, 1682, 1583, 1467, 1303, 1224, 1089, 958, 862, 824, 749 cm\(^{-1}\).

MS (EI): \(m/z\) (%): 462.2 (73) [M]* = [C\(_{29}\)H\(_{31}\)O\(_2\)Cl]*, 445.2 (77) [M - OH]* = [C\(_{29}\)H\(_{30}\)O\(_2\)Cl]*, 139.0 (100) [M - C\(_2\)H\(_2\)O\(_2\)]* = [C\(_3\)H\(_4\)OCl]*.

HRMS (ESI): \(m/z\) [M+Na]* calcd for C\(_{29}\)H\(_{31}\)O\(_3\)ClNa*: 485.1854; found 485.1843.
(3-(3,5-di-tert-Butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl)(3,4-difluorophenyl) methanone (3i)

According to the general procedure, 3i was obtained as a colorless solid (0.183 g, 98% yield) in 0.5 h.

**Melting Point:** 164-166 °C.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.82 – 7.72 (m, 2H), 7.26 – 7.17 (m, 2H), 7.05 (d, J = 7.2 Hz, 1H), 6.96 (s, 2H), 6.93 – 6.89 (m, 2H), 5.64 (d, J = 7.2 Hz, 1H), 5.19 (s, 1H), 4.90 (d, J = 7.2 Hz, 1H), 1.38 (s, 18H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 192.8, 158.8, 154.0 (dd, J = 256.6, 12.9 Hz), 153.1, 150.3 (dd, J = 249.6, 13.0 Hz), 136.4, 132.2, 131.7, 129.2, 128.7, 126.5 (dd, J = 7.4, 3.6 Hz), 125.5, 124.7 (2C), 121.7, 118.7 (d, J = 20.0 Hz), 117.4 (d, J = 17.7 Hz), 109.8, 90.8, 50.9 (2C), 34.3 (2C), 30.2 (6C) ppm.

IR (ATR): 3929, 3786, 3613, 3362, 2958, 2670, 2326, 2024, 1914, 1691, 1600, 1435, 1361, 1280, 1231, 1119, 972, 874, 825, 755, 663 cm$^{-1}$.

**MS (EI):** m/z (%): 464.2 (100) [M]$^+ = [C_{29}H_{30}O_3F_2]^+$, 447.2 (92) [M - OH]$^+ = [C_{29}H_{29}O_2F_2]^+$, 141.1 (100) [M - C$_{22}$H$_{22}$O$_2$]$^+ = [C$_7$H$_3$OF$_2]^+$.

**HRMS (ESI):** m/z [M+Na]$^+$ calcd for C$_{29}$H$_{30}$O$_3$F$_2$Na$^+: 487.2056$; found 487.2049.

![3j](image)

**Ethyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-methyl-2,3-dihydrobenzofuran-2-carboxylate (3j)**

According to the general procedure, 3j was obtained as a colorless solid (0.113 g, 68% yield) in 0.5 h.

**Melting Point:** 127-129 °C.

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.01 – 6.98 (m, 3H), 6.87 – 6.84 (m, 2H), 5.17 (s, 1H), 4.98 (d, J = 6.6 Hz, 1H), 4.69 (d, J = 6.6 Hz, 1H), 4.34 – 4.21 (m, 2H), 2.25 (s, 3H), 1.41 (s, 18H), 1.32 (t, J = 7.2 Hz, 3H) ppm.

$^{13}$C NMR (150 MHz, CDCl$_3$) δ 171.0, 157.1, 153.0, 136.1, 132.7, 130.7, 129.1, 128.7, 125.7, 124.4 (2C), 109.4, 87.5, 61.5, 52.7 (2C), 34.4 (2C), 30.2 (6C), 20.8, 14.2 ppm.

**IR (ATR):** 3593, 2951, 2305, 2076, 1750, 1619, 1454, 1194, 1044, 810 cm$^{-1}$.

**MS (ESI):** m/z = 433.2 [M+Na]$^+$.

**HRMS (ESI):** m/z [M+Na]$^+$ calcd for C$_{26}$H$_{34}$O$_4$Na$^+: 433.2349$; found 433.2329.
Ethyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)-6-methoxy-2,3-dihydrobenzofuran-2-carboxylate (3k)

According to the general procedure, 3k was obtained as a colorless solid (0.152 g, 89% yield) in 0.5 h.

Melting Point: 140-142 °C.

$^1$H NMR (600 MHz, CDCl$_3$) δ 6.99 (s, 2H), 6.94 (d, $J = 8.4$ Hz, 1H), 6.57 (d, $J = 2.4$ Hz, 1H), 6.47 (dd, $J = 8.4$, 2.4 Hz, 1H), 5.16 (s, 1H), 4.99 (d, $J = 6.0$ Hz, 1H), 4.67 (d, $J = 6.0$ Hz, 1H), 4.37 - 4.23 (m, 2H), 3.80 (s, 3H), 1.40 (s, 18H), 1.33 (t, $J = 7.2$ Hz, 3H) ppm.

$^{13}$C NMR (150 MHz, CDCl$_3$) δ 170.9, 160.7, 160.5, 153.0, 136.2, 132.6, 125.4, 124.3 (2C), 120.5, 107.5, 96.2, 88.2, 61.5, 55.5, 55.4, 52.1, 34.4 (2C), 30.2 (6C), 14.3 ppm.

IR (ATR): 3779, 3550, 2949, 2174, 2092, 1986, 1904, 1739, 1619, 1487, 1442, 1365, 1329, 1269, 1154, 1052, 925, 834, 775 cm$^{-1}$.

MS (ESI): $m/z = 449.2$ [M+Na]$^+$.  
HRMS (ESI): $m/z$ [M+Na]$^+$ calcd for C$_{26}$H$_{34}$O$_5$Na$: 449.2299$; found 449.2292.

(3-(3,5-di-tert-Butyl-4-hydroxyphenyl)-6-methoxy-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (3l)

According to the general procedure, 3l was obtained as a colorless solid (0.178 g, 97% yield) in 12 h.

Melting Point: 153-155 °C.

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.92 (d, $J = 8.4$ Hz, 2H), 7.59 (t, $J = 7.2$ Hz, 1H), 7.44 (t, $J = 7.8$ Hz, 2H), 6.94 (s, 2H), 6.92 (d, $J = 7.8$ Hz, 1H), 6.59 (d, $J = 2.4$ Hz, 1H), 6.46 (dd, $J = 7.8$, 2.4 Hz, 1H), 5.79 (d, $J = 6.6$ Hz, 1H), 5.18 (s, 1H), 4.75 (d, $J = 6.6$ Hz, 1H), 3.80 (s, 3H), 1.39 (s, 18H) ppm.

$^{13}$C NMR (150 MHz, CDCl$_3$) δ 195.2, 160.7, 160.5, 153.0, 136.2, 134.5, 133.6, 132.9, 129.3 (2C), 128.6 (2C), 125.6, 124.6 (2C), 121.2, 107.5, 96.0, 91.7, 55.5, 55.4, 50.9, 34.4 (2C), 30.3 (6C) ppm.

IR (ATR): 3753, 3572, 2959, 2640, 2288, 2096, 1952, 1737, 1610, 1493, 1441, 1362, 1285, 1225, 1106, 1045, 966, 882, 833, 770, 685 cm$^{-1}$.

MS (ESI): $m/z = 481.2$ [M+Na]$^+$.  

**Ethyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)-7-methoxy-2,3-dihydrobenzofuran-2-carboxylate (3m)**

According to the general procedure, 3m was obtained as a colorless solid (0.156 g, 92% yield) in 0.5 h.

**Melting Point:** 139-141 °C.

**H NMR (600 MHz, CDCl₃)** δ 6.99 (s, 2H), 6.88 – 6.85 (m, 1H), 6.81 (d, J = 7.8 Hz, 1H), 6.68 (d, J = 7.2 Hz, 1H), 5.17 (s, 1H), 5.04 (d, J = 6.6 Hz, 1H), 4.77 (d, J = 6.6 Hz, 1H), 4.35 – 4.23 (m, 2H), 3.93 (s, 3H), 1.40 (s, 18H), 1.32 (t, J = 7.2 Hz, 3H) ppm.

**C NMR (150 MHz, CDCl₃)** δ 170.6, 153.0, 147.7, 144.5, 136.1, 132.2, 129.9, 124.4 (2C), 122.0, 117.4, 111.7, 87.9, 61.5, 56.2, 53.2 (2C), 34.5 (2C), 30.2 (6C), 14.2 ppm.

**IR (ATR):** 3598, 2956, 2629, 2302, 2166, 2065, 1925, 1742, 1613, 1441, 1362, 1281, 1192, 1089, 1035, 947, 882, 816, 742 cm⁻¹.

**MS (ESI):** m/z = 449.2 [M+Na⁺].

**HRMS (ESI):** m/z [M+Na]⁺ calcd for C₃₀H₃₄O₄Na⁺: 481.2349; found 481.2338.

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**(5-Chloro-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (3n)**

According to the general procedure, 3n was obtained as an off-white solid (0.175 g, 95% yield) in 12 h.

**Melting Point:** 139-141 °C.

**H NMR (600 MHz, CDCl₃)** δ 7.94 – 7.90 (m, 2H), 7.60 (d, J = 7.2 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.16 (dd, J = 8.4, 2.4 Hz, 1H), 7.01 (d, J = 2.4 Hz, 1H), 6.94 (s, 2H), 6.91 (d, J = 8.4 Hz, 1H), 5.83 (d, J = 6.6 Hz, 1H), 5.22 (s, 1H), 4.82 (d, J = 6.6 Hz, 1H), 1.40 (s, 1H) ppm.

**C NMR (150 MHz, CDCl₃)** δ 194.6, 157.8, 153.3, 136.4, 134.3, 133.8, 131.9, 131.5, 129.3 (2C), 128.7, 128.6 (2C), 126.2, 125.5, 124.7 (2C), 110.8, 91.2, 91.2, 51.1, 51.1, 34.4 (2C), 30.2 (6C) ppm.

**IR (ATR):** 3812, 3590, 3463, 2956, 2642, 2293, 2072, 1953, 1738, 1590, 1461, 1364, 1223, 1113,
1054, 963, 875, 812, 685 cm$^{-1}$.

**MS (ESI):** $m/z = 485.2$ [M+Na]$^+$.  
**HRMS (ESI):** $m/z$ [M+Na]$^+$ calcd for C$_{29}$H$_{31}$O$_3$ClNa$^+$: 485.1854; found 485.1838.

![Chemical Structure](image)

**Ethyl-5-chloro-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-carboxylate (3o)**  
According to the general procedure, 3o was obtained as a colorless solid (0.155 g, 90% yield) in 0.5 h.

**Melting Point:** 145-147 °C.  
**$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.16 (dd, $J = 9.0, 2.4$ Hz, 1H), 7.02 (d, $J = 2.4$ Hz, 1H), 6.97 (s, 2H), 6.90 (d, $J = 9.0$ Hz, 1H), 5.21 (s, 1H), 5.04 (d, $J = 6.0$ Hz, 1H), 4.70 (d, $J = 6.0$ Hz, 1H), 4.35 – 4.24 (m, 2H), 1.41 (s, 18H), 1.33 (t, $J = 7.2$ Hz, 3H) ppm.  
**$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 170.4, 157.8, 153.2, 136.3, 131.8, 131.0, 128.7, 126.2, 125.4, 124.2 (2C), 110.9, 87.9, 61.7, 52.5 (2C), 34.4 (2C), 30.2 (6C), 14.2 ppm.  
**IR (ATR):** 3784, 3541, 2953, 2326, 2113, 1741, 1591, 1466, 1368, 1213, 1157, 1115, 1044, 875, 811, 766, 685 cm$^{-1}$.  
**MS (EI):** $m/z$ (%): 430.0 (2) [M]$^+$ = [C$_{25}$H$_{31}$O$_4$Cl]$^+$, 57.2 (100) [M - C$_{21}$H$_{22}$O$_4$Cl]$^+$ = [C$_{4}$H$_{9}$]$^+$.

**HRMS (ESI):** $m/z$ [M+Na]$^+$ calcd for C$_{25}$H$_{31}$O$_4$ClNa$^+$: 453.1803; found 453.1797.

![Chemical Structure](image)

**Ethyl-5-bromo-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-carboxylate (3p)**  
According to the general procedure, 3p was obtained as a colorless solid (0.168 g, 89% yield) in 0.5 h.

**Melting Point:** 150-152 °C.  
**$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.30 (dd, $J = 8.4, 1.8$ Hz, 1H), 7.15 (d, $J = 1.8$ Hz, 1H), 6.96 (s, 2H), 6.87 (d, $J = 8.4$ Hz, 1H), 5.21 (s, 1H), 5.03 (d, $J = 6.0$ Hz, 1H), 4.70 (d, $J = 6.0$ Hz, 1H), 4.35 – 4.23 (m, 2H), 1.41 (s, 18H), 1.32 (t, $J = 7.2$ Hz, 3H) ppm.  
**$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 170.4, 158.3, 153.2, 136.3, 131.8, 131.6, 131.5, 128.3, 124.3 (2C), 113.3, 111.5, 87.9, 61.7, 52.5 (2C), 34.4 (2C), 30.2 (6C), 14.2 ppm.
IR (ATR): 3852, 3637, 3074, 2958, 2324, 2174, 2063, 1986, 1934, 1749, 1587, 1470, 1435, 1369, 1300, 1199, 1153, 1112, 1047, 879, 807, 761, 726, 671 cm\(^{-1}\).

MS (ESI): \(m/z = 499.1\) [M+Na]\(^+\).

HRMS (ESI): \(m/z\) [M+Na]\(^+\) calcd for C\(_{25}\)H\(_{31}\)O\(_4\)BrNa\(^+\): 497.1298; found 497.1294.

Ethyl-1-(3,5-di-tert-butyl-4-hydroxyphenyl)-1,2-dihydronaphtho[2,1-b]furan-2-carboxylate (3q)

According to the general procedure, 3q was obtained as a colorless solid (0.151 g, 85% yield) in 1 h.

Melting Point: 143-145 °C.

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.81 (d, \(J = 7.8\) Hz, 1H), 7.79 (d, \(J = 8.4\) Hz, 1H), 7.36 (d, \(J = 7.8\) Hz, 1H), 7.33 – 7.25 (m, 3H), 7.02 (s, 2H), 5.16 (d, \(J = 5.4\) Hz, 1H), 5.14 (s, 1H), 5.10 (d, \(J = 5.4\) Hz, 1H), 4.38 – 4.24 (m, 2H), 1.36 – 1.33 (m, 21H) ppm.

\(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 171.1, 157.1, 152.9, 136.1, 132.6, 130.5, 130.3, 130.0, 128.7, 126.5, 124.2 (2C), 123.2, 123.1, 119.5, 112.2, 88.2, 61.6, 52.3 (2C), 34.3 (2C), 30.2 (6C), 14.3 ppm.

IR (ATR): 3586, 2939, 2326, 2078, 1913, 1747, 1615, 1427, 1195, 1047, 752 cm\(^{-1}\).

MS (ESI): \(m/z = 469.2\) [M+Na]\(^+\).

HRMS (ESI): \(m/z\) [M+Na]\(^+\) calcd for C\(_{29}\)H\(_{34}\)O\(_4\)Na\(^+\): 469.2349; found 469.2332.

(1-(3,5-di-tert-Butyl-4-hydroxyphenyl)-1,2-dihydronaphtho[2,1-b]furan-2-yl)(phenyl)methanone (3r)

According to the general procedure, 3r was obtained as a colorless solid (0.120 g, 63% yield) in 12 h.

Melting Point: 160-162 °C.

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.99 – 7.97 (m, 2H), 7.80 – 7.77 (m, 2H), 7.63 (t, \(J = 7.2\) Hz, 1H), 7.50 – 7.47 (m, 2H), 7.33 – 7.30 (m, 2H), 7.29 – 7.22 (m, 2H), 7.00 (s, 2H), 5.94 (d, \(J = 5.4\) Hz, 1H), 5.15 (s, 1H), 5.14 (d, \(J = 5.4\) Hz, 1H), 1.35 (s, 18H) ppm.
**13C NMR (150 MHz, CDCl₃)** δ 195.1, 157.1, 153.0, 136.3, 134.3, 133.7, 132.7, 130.5, 130.2, 130.0, 129.4 (2C), 128.7, 128.6 (2C), 126.5, 124.4 (2C), 123.1, 123.0, 120.1, 112.1, 91.8, 51.1 (2C), 34.3 (2C), 30.3 (6C) ppm.

**IR (ATR):** 3817, 3607, 3449, 2953, 2642, 2333, 2086, 1904, 1739, 1583, 1520, 1441, 1366, 1225, 1126, 1051, 965, 862, 811, 754, 690 cm⁻¹.

**MS (ESI):** *m/z* = 501.2 [M+Na]⁺.

**HRMS (ESI):** *m/z* [M+Na]⁺ calcd for C₃₃H₃₄O₃Na⁺: 501.2400; found 501.2389.

![3s](image)

3-(3,5-di-tert-Butyl-4-hydroxyphenyl)-N-methyl-2,3-dihydrobenzofuran-2-carboxamide (3s)

According to the general procedure, 3s was obtained as a wax (0.099 g, 65% yield) in 1 h.

**1H NMR (400 MHz, CDCl₃)** δ 7.23 – 7.17 (m, 1H), 7.13 – 7.11 (m, 1H), 7.01 (s, 2H), 6.97 – 6.91 (m, 2H), 6.66 – 6.58 (m, 1H), 5.13 (s, 1H), 4.95 (d, *J* = 5.2 Hz, 1H), 4.80 (d, *J* = 5.2 Hz, 1H), 2.85 (d, *J* = 4.9 Hz, 3H), 1.38 (s, 18H) ppm.

**13C NMR (100 MHz, CDCl₃)** δ 172.0, 158.4, 152.9, 136.2, 133.7, 129.2, 128.7, 126.3, 124.3 (2C), 122.0, 109.8, 88.7, 52.2 (2C), 34.5 (2C), 30.3 (6C), 25.9 ppm.

**IR (ATR):** 3634, 3440, 3334, 2955, 2913, 1664, 1597, 1537, 1476, 1460, 1434, 1318, 1265, 1229, 1154, 1119, 908. 861, 821, 732, 649 cm⁻¹.

**MS (ESI):** *m/z* = 382.0 [M+H]⁺.

**HRMS (ESI):** *m/z* [M+Na]⁺ calcd for C₂₄H₂₃NO₃Na⁺: 404.2197; found 404.2191.
3. NMR Spectra:

$^1$H NMR of 3a:

$tBu\quad OH\quad tBu$

$\text{3a}$

$^1$H NMR of 3a:

$tBu\quad OH\quad tBu$

$\text{3a}$

$^13$C NMR of 3a:

$tBu\quad OH\quad tBu$

$\text{3a}$
$^1$H NMR of 3b:

$^{13}$C NMR of 3b:
$^1$H NMR of 3c:

$^{13}$C NMR of 3c:
$^1$H NMR of 3d:

![H NMR spectrum of 3d](image)

$^{13}$C NMR of 3d:

![C NMR spectrum of 3d](image)
$^1$H NMR of 3e:

$^{13}$C NMR of 3e:
$^1$H NMR of 3f:

$^{13}$C NMR of 3f:
$^1$H NMR of 3g:

$^{13}$C NMR of 3g:
$^1$H NMR of 3h:

$^{13}$C NMR of 3h:
$^1$H NMR of 3i:

$^{13}$C NMR of 3i:
$^1$H NMR of 3j:

$^{13}$C NMR of 3j:
$^1$H NMR of 3k:

$^{13}$C NMR of 3k:
$^1$H NMR of 3l:

$^{13}$C NMR of 3l:
$^1$H NMR of 3m:

$^{13}$C NMR of 3m:
$^1$H NMR of 3n:

$^{13}$C NMR of 3n:
$^1$H NMR of 3o:

$^{13}$C NMR of 3o:
$^1$H NMR of 3p:

$^{13}$C NMR of 3p:
$^1$H NMR of 3q:

$^{13}$C NMR of 3q:
$^1$H NMR of 3r:

$^{13}$C NMR of 3r:
$^1$H NMR of 3s:

$^{13}$C NMR of 3s: