Supporting Information

1,6-Conjugated Addition-Mediated [4+1] Annulation: Approach to 2,3-Dihydrobenzofurans

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1. General Information
Reagents and Solvents: PE refers to petroleum ether b.p. 60-90 °C and EA refers to ethyl acetate. All other starting materials and solvents were commercially available and were used without further purification unless otherwise stated.

Chromatography: Flash column chromatography was carried out using commercially available 200-300 mesh under pressure unless otherwise indicated. Gradient flash chromatography was conducted eluting with PE/EA, they are listed as volume/volume ratios.

Data collection: $^1$H and $^{13}$C NMR spectra were collected on BRUKER AV-300 (300 MHz) spectrometer using CDCl$_3$ as solvent. Chemical shifts of $^1$H NMR were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ = 0.00 ppm) with the solvent resonance as an internal standard (CDCl$_3$: δ = 7.26 ppm). Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, brs = broad singlet, m = multiplet), coupling constant (Hz), and integration. Chemical shifts of $^{13}$C NMR were reported in ppm with the solvent as the internal standard (CDCl$_3$: δ = 77.16 ppm). High Resolution Mass measurement was performed on Agilent Q-TOF 6520 mass spectrometer with electron spray ionization (ESI) as the ion source. Melting point (m.p.) was measured on a microscopic melting point apparatus.

2. Preparation of ortho-Hydroxyphenyl-substituted para-Quinone Methides
ortho-Hydroxyphenyl-substituted para-quinone methides were synthesized from the corresponding aldehydes as shown in Scheme S1.

A solution of phenols (1.1 equiv.) and aldehydes (1.0 equiv.) in toluene (5 mL/mmol substrate) was placed in a Dean-Stark apparatus which was heated to reflux. Piperidine (2.0 equiv.) was added dropwise slowly. Then, the temperature was raised to 140 °C and stirred for 12 h. After that, the reaction mixture was cooled to 120 °C and acetic anhydride (2.0 equiv.) was dropwise added. The stirring was continued for 30 min and the solution was poured on ice-water and extracted with CH$_2$Cl$_2$ (3 × 50 mL). The organic phases were combined, washed with brine and dried over anhydrous Na$_2$SO$_4$. Then the solvent was evaporated under reduced pressure and the corresponding products 1a1–1n1 were obtained after flash column chromatography (PE/EA = 200/1 to 50/1).

To a solution of 1a1–1n1 (1.0 equiv.) in THF (10 mL/mmol substrate) at 0 °C was added tetrabutylammonium fluoride trihydrate (1.1 equiv.). The reaction mixture was stirred for 10 min and a saturated NH$_4$Cl solution was added dropwise to quench the reaction. The resulting solution was extracted with Et$_2$O (3 × 20 mL). Then the combined organic phases were washed with brine and dried over anhydrous Na$_2$SO$_4$. The solvent was removed to give the crude product which was purified by flash column chromatography (PE/EA = 20/1 to 4/1) to afford the desired compounds.
1a–1n. 1o was prepared according to the literature.\textsuperscript{[1]} All structures of ortho-hydroxyphenyl-substituted para-quinone methides were listed in Figure S1.

![Figure S1. Substrates of ortho-hydroxyphenyl-substituted para-quinone methides](image)

3. Preparation of Sulfonium Salts and Ammonium Salts

Sulfonium salts were synthesized from the corresponding aldehydes as shown in Scheme S2.

![Scheme S2. Preparation of sulfonium salts](image)

Dimethyl sulfide (10 mmol) was added to a solution of 2-bromoacetophenone derivatives (10 mmol) in acetone (15 mL). After the mixture had been stirred for 12 h, the residue was filtered and washed with acetone. The solid product (2a–2o) was used as sulfonium bromide without further purification. (Scheme S2) All sulfonium salts were prepared according to the previous reported method.\textsuperscript{[2]} All structures of sulfonium salts were listed in Figure S2.
Figure S2. Substrates of sulfonium salts

Ammonium salts were synthesized from the corresponding aldehydes as shown in Scheme S3.

Scheme S3. Preparation of ammonium salts

To a solution of 2-bromoacetophenone derivatives (1 equiv.) in THF (3.3 mL per mmol starting material) trimethylamine (33% in EtOH - 1 equiv.) was added and the mixture was stirred overnight. The product was filtered off and washed twice with EtOAc and dried under vacuo to get a series of compound 4. All ammonium salts were prepared according to the previous reported method. All structures of ammonium salts were listed in Figure S3.
4. Synthesis of 2,3-Dihydrobenzofurans

\[
\begin{align*}
\text{Scheme S4. Synthesis of compounds 3 from sulfonium salts 2} \\
\text{A sealed tube was charged with ortho-hydroxyphenyl-substituted para-quinone methides (0.2 mmol, 1 equiv.), sulfonium salts (0.24 mmol, 1.2 equiv.), Na}_3\text{PO}_4\cdot12\text{H}_2\text{O (0.30 mmol, 1.5 equiv.). Dichloromethane (1.0 mL) was added in the tube. Then the reaction mixture was stirred at room temperature for 12 h. When the reaction was completed, the solution was concentrated in vacuo and purified by careful chromatography on silica gel (PE/EA = 200/1) to afford the desired product 3.}
\end{align*}
\]

\[
\begin{align*}
\text{Scheme S5. Synthesis of compoud 3 from ammonium salts 4} \\
\text{A sealed tube was charged with ortho-hydroxyphenyl-substituted para-quinone methides (0.2 mmol, 1 equiv.), ammonium salts (0.24 mmol, 1.2 equiv.), Cs}_2\text{CO}_3 (0.30 mmol, 1.5 equiv.). Dichloromethane (1.0 mL) was added in the tube. Then the reaction mixture was stirred at room temperature for 12 h. When the reaction was completed, the solution was concentrated in vacuo and purified by careful chromatography on silica gel (PE/EA = 200/1) to afford the desired product 3. (Scheme S5)
\end{align*}
\]
(3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (3aa)

91% yield (77.9 mg). White solid, m.p. 152 – 154 °C. Rf = 0.5 (PE/EA = 10/1). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.93 (d, $J$ = 7.0 Hz, 2H), 7.58 (t, $J$ = 7.3 Hz, 1H), 7.43 (t, $J$ = 7.6 Hz, 2H), 7.19 (t, $J$ = 7.6 Hz, 1H), 7.04 (d, $J$ = 7.3 Hz, 1H), 6.98 (s, 1H), 6.95 (s, 2H), 6.88 (d, $J$ = 7.2 Hz, 1H), 5.77 (d, $J$ = 6.7 Hz, 1H), 5.17 (s, 1H), 4.85 (d, $J$ = 6.7 Hz, 1H), 1.38 (s, 18H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) δ 194.7, 158.7, 152.5, 135.8, 134.1, 133.2, 132.1, 128.8, 128.2, 128.1, 125.0, 124.3, 121.0, 109.3, 90.3, 50.8, 33.9, 29.8 ppm. IR (KBr): 3609, 3065, 3012, 2964, 2882, 1698, 1597, 1459, 1433, 1261, 1228, 1103, 1051, 1022, 956, 863, 802, 753, 699, 671, 645, 596, 510 cm$^{-1}$. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for C$_{29}$H$_{33}$O$_3$ 429.2424; Found 429.2431.

(3-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-fluoro-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (3ba)

95% yield (84.4 mg). White solid, m.p. 146 – 148 °C. Rf = 0.5 (PE/EA = 10/1). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.93 – 7.90 (m, 2H), 7.58 (t, $J$ = 7.4 Hz, 1H), 7.43 (t, $J$ = 7.7 Hz, 2H), 6.95 (s, 2H), 6.88 (d, $J$ = 4.8 Hz, 2H), 6.74 (d, $J$ = 6.5 Hz, 1H), 5.80 (d, $J$ = 6.6 Hz, 1H), 5.20 (s, 1H), 4.84 (d, $J$ = 6.6 Hz, 1H), 1.39 (s, 18H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) δ 194.3, 157.6 (d, $J$ = 238.0 Hz), 153.7 (d, $J$ = 142.2 Hz), 136.0, 134.0, 133.3, 131.4, 130.5 (d, $J$ = 8.4 Hz), 128.8, 128.1, 124.2, 114.6 (d, $J$ = 24.4 Hz), 112.0, 111.7, 109.6 (d, $J$ = 8.4 Hz), 90.8, 50.9 (d, $J$ = 1.8 Hz), 33.9, 29.8 ppm. $^{19}$F NMR (282 MHz, CDCl$_3$) δ -121.97, -121.99 ppm. IR (KBr): 3624, 3602, 3065, 2872, 1687, 1597, 1571, 1481, 1434, 1231, 1212, 1120, 960, 900, 781, 762, 688, 644 cm$^{-1}$. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for C$_{29}$H$_{32}$FO$_3$ 447.2330; Found 447.2335.
(5-chloro-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (3ca)

61% yield (56.5 mg). White solid, m.p. 138 – 140 °C. Rf = 0.5 (PE/EA = 10/1). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.92 – 7.89 (m, 2H), 7.59 (t, \(J = 7.4\) Hz, 1H), 7.44 (t, \(J = 7.6\) Hz, 2H), 7.15 (dd, \(J = 8.5, 2.3\) Hz, 1H), 7.00 (s, 1H), 6.94 (s, 2H), 6.89 (d, \(J = 8.6\) Hz, 1H), 5.81 (d, \(J = 6.5\) Hz, 1H), 5.20 (s, 1H), 4.81 (d, \(J = 6.5\) Hz, 1H), 1.39 (s, 18H) ppm. \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 194.6, 157.8, 153.3, 136.5, 134.4, 133.8, 131.9, 131.5, 129.3, 128.6, 126.2, 125.5, 124.6, 110.8, 91.3, 51.2, 34.4, 30.3 ppm. IR (KBr): 3583, 3134, 3061, 3004, 2965, 2918, 2872, 1695, 1592, 1474, 1435, 1401, 1298, 1227, 1165, 1118, 1081, 1058, 961, 869, 816, 771, 730, 695, 678, 465 cm\(^{-1}\). HRMS (ESI-TOF) m/z: [M + H]\(^+\) Calcd for C\(_{29}\)H\(_{32}\)ClO\(_3\) 463.2035; Found 463.2037.

(5-bromo-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (3da)

84% yield (85.0 mg). White solid, m.p. 156 – 158 °C. Rf = 0.5 (PE/EA = 10/1). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.90 (d, \(J = 7.5\) Hz, 2H), 7.59 (t, \(J = 7.2\) Hz, 1H), 7.43 (t, \(J = 7.5\) Hz, 2H), 7.31 – 7.27 (m, 1H), 7.14 (s, 1H), 6.93 (s, 2H), 6.85 (d, \(J = 8.5\) Hz, 1H), 5.81 (d, \(J = 6.5\) Hz, 1H), 5.21 (s, 1H), 4.81 (d, \(J = 6.4\) Hz, 1H), 1.39 (s, 18H) ppm. \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 194.5, 158.3, 153.3, 136.5, 134.3, 133.8, 132.0, 131.9, 131.6, 129.3, 128.7, 128.4, 124.7, 113.3, 111.5, 91.2, 51.1, 34.4, 30.3 ppm. IR (KBr): 3589, 3065, 2956, 2924, 2871, 1698, 1471, 1434, 1364, 1230, 1155, 1112, 1053, 871, 862, 773, 696, 668 cm\(^{-1}\). HRMS (ESI-TOF) m/z: [M + H]\(^+\) Calcd for C\(_{29}\)H\(_{32}\)BrO\(_3\) 507.1530; Found 507.1531.
(3-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-nitro-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (3ea)

62% yield (58.8 mg). White solid, m.p. 126 – 127 °C. Rf = 0.3 (PE/EA = 10/1). $^1$H NMR (300 MHz, CDCl$_3$) δ 8.19 (dd, $J = 8.9$, 2.5 Hz, 1H), 7.95 – 7.90 (m, 3H), 7.63 (t, $J = 7.3$ Hz, 1H), 7.47 (t, $J = 7.6$ Hz, 2H), 7.05 (d, $J = 8.9$ Hz, 1H), 6.92 (s, 2H), 5.98 (d, $J = 6.3$ Hz, 1H), 5.25 (s, 1H), 4.85 (d, $J = 6.3$ Hz, 1H), 1.39 (s, 18H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) δ 193.0, 163.7, 153.1, 142.4, 136.3, 133.7, 133.3, 131.0, 130.6, 128.8, 128.3, 125.7, 124.1, 121.5, 109.4, 91.8, 50.0, 33.9, 29.7 ppm. IR (KBr): 3576, 3964, 2922, 2865, 1692, 1597, 1478, 1435, 1338, 1235, 1115, 1071, 1042, 967, 900, 829, 776, 750, 694, 670 cm$^{-1}$. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for C$_{29}$H$_{32}$NO$_5$ 474.2275; Found 474.2284.

(3-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-methyl-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (3fa)

68% yield (60.2 mg). White solid, m.p. 149 – 150 °C. Rf = 0.5 (PE/EA = 10/1). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.91 (d, $J = 7.1$ Hz, 2H), 7.56 (t, $J = 7.3$ Hz, 1H), 7.41 (t, $J = 7.7$ Hz, 2H), 6.99 – 6.96 (m, 3H), 6.86 – 6.84 (m, 2H), 5.75 (d, $J = 6.5$ Hz, 1H), 5.17 (s, 1H), 4.80 (d, $J = 6.5$ Hz, 1H), 2.23 (s, 3H), 1.39 (s, 18H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) δ 195.3, 157.2, 153.0, 136.3, 134.7, 133.6, 132.8, 130.7, 129.3, 129.1, 128.6, 125.9, 124.8, 109.3, 91.0, 51.4, 34.4, 30.3, 20.8 ppm. IR (KBr): 3629, 3607, 3066, 3013, 2966, 2869, 1690, 1488, 1434, 1236, 1199, 1152, 1114, 1057, 963, 886, 869, 803, 774, 759, 703, 694 cm$^{-1}$. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for C$_{30}$H$_{35}$O$_3$ 443.2581; Found 443.2589.
(3-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-methoxy-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (3ga)

![Chemical structure of 3ga]

73% yield (67.3mg). White solid, m.p. 137 – 138 °C. Rf = 0.4 (PE/EA = 10/1). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.92 (d, J = 7.1 Hz, 2H), 7.58 (t, J = 7.5 Hz, 1H), 7.43 (t, J = 7.7 Hz, 2H), 6.97 (s, 2H), 6.87 (d, J = 8.7 Hz, 1H), 6.75 (dd, J = 8.7, 2.7 Hz, 1H), 6.61 (d, J = 2.2 Hz, 1H), 5.74 (d, J = 6.7 Hz, 1H), 5.18 (s, 1H), 4.84 (d, J = 6.7 Hz, 1H), 3.70 (s, 3H), 1.38 (s, 18H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) δ 195.3, 154.9, 153.4, 153.1, 136.3, 134.7, 133.6, 132.3, 130.2, 129.3, 128.6, 124.8, 114.3, 111.1, 109.9, 91.1, 56.1, 51.6, 34.4, 30.3 ppm. IR (KBr): 3636, 3065, 2952, 2925, 2865, 1696, 1596, 1484, 1433, 1362, 1203, 1179, 1116, 1082, 1005, 967, 802, 866, 763, 748, 702 cm$^{-1}$. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for C$_{30}$H$_{35}$O$_4$ 459.2530; Found 459.2539.

(6-bromo-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (3ha)

![Chemical structure of 3ha]

93% yield (94.4 mg). White solid, m.p. 167 – 170 °C. Rf = 0.6 (PE/EA = 10/1). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.91 (d, J = 7.3 Hz, 2H), 7.59 (t, J = 7.3 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 7.13 (s, 1H), 7.02 (d, J = 8.6 Hz, 1H), 6.92 (s, 2H), 6.89 (d, J = 8.0 Hz, 1H), 5.80 (d, J = 6.6 Hz, 1H), 5.19 (s, 1H), 4.78 (d, J = 6.5 Hz, 1H), 1.38 (s, 18H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) δ 194.4, 159.9, 153.0, 136.3, 134.2, 133.6, 131.8, 129.1, 128.7, 128.5, 126.3, 124.5, 124.4, 121.5, 113.3, 91.2, 50.6, 34.2, 30.1 ppm. IR (KBr): 3581, 3072, 2953, 2924, 2871, 1701, 1593, 1474, 1435, 1414, 1297, 1224, 1116, 1051, 959, 874, 841, 788, 769, 692 cm$^{-1}$. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for C$_{29}$H$_{32}$BrO$_3$ 507.1530; Found 507.1531.
(3-(3,5-di-tert-butyl-4-hydroxyphenyl)-6-methoxy-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (3ia)

85% yield (78.2 mg). White solid, m.p. 152 – 154 °C. Rf = 0.4 (PE/EA = 10/1). 1H NMR (300 MHz, CDCl3) δ 7.91 (d, J = 6.9 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.7 Hz, 2H), 6.94 (s, 2H), 6.91 (d, J = 8.5 Hz, 1H), 6.57 (d, J = 2.3 Hz, 1H), 6.45 (dd, J = 8.3, 2.3 Hz, 1H), 5.78 (d, J = 6.4 Hz, 1H), 5.17 (s, 1H), 4.75 (d, J = 6.4 Hz, 1H), 3.78 (s, 3H), 1.38 (s, 18H) ppm. 13C NMR (75 MHz, CDCl3) δ 195.2, 160.8, 160.6, 153.0, 136.3, 134.6, 133.6, 132.9, 132.9, 128.6, 125.6, 124.7, 121.3, 107.6, 96.1, 91.7, 55.5, 50.9, 34.4, 30.3 ppm. IR (KBr): 3580, 3065, 2955, 2925, 2961, 2833, 1701, 1624, 1597, 1498, 1446, 1436, 1282, 1234, 1173, 1147, 1109, 967, 833, 771, 637 cm⁻¹. HRMS (ESI-TOF) m/z: [M + H]+ Calcd for C30H35O4 459.2530; Found 459.2536.

(7-bromo-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (3ja)

99% yield (101.2 mg). White solid, m.p. 169 – 170 °C. Rf = 0.5 (PE/EA = 10/1). 1H NMR (300 MHz, CDCl3) δ 7.96 (d, J = 7.4 Hz, 2H), 7.59 (t, J = 7.2 Hz, 1H), 7.45 (d, J = 7.5 Hz, 2H), 7.35 (d, J = 7.8 Hz, 1H), 6.99 (s, 1H), 6.95 (s, 2H), 6.78 (t, J = 7.6 Hz, 1H), 5.83 (d, J = 7.0 Hz, 1H), 5.21 (s, 1H), 4.96 (d, J = 6.9 Hz, 1H), 1.38 (s, 18H) ppm. 13C NMR (75 MHz, CDCl3) δ 194.4, 156.5, 153.2, 136.4, 134.5, 133.8, 131.8, 130.9, 129.4, 128.6, 124.7, 124.5, 122.8, 102.8, 90.9, 52.1, 34.4, 30.3 ppm. IR (KBr): 3569, 3069, 2962, 2923, 2873, 2853, 1698, 1595, 1580, 1453, 1435, 1220, 1116, 1056, 964, 918, 882, 863, 748, 695 cm⁻¹. HRMS (ESI-TOF) m/z: [M + H]+ Calcd for C29H32BrO3 507.1530; Found 507.1534.
(3-(3,5-di-tert-butyl-4-hydroxyphenyl)-7-methoxy-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (3ka)

93% yield (85.1 mg). White solid, m.p. 148 – 149 °C. Rf = 0.4 (PE/EA = 10/1). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.94 (d, $J = 7.4$ Hz, 2H), 7.56 (t, $J = 7.3$ Hz, 1H), 7.42 (t, $J = 7.6$ Hz, 2H), 6.95 (s, 2H), 6.84 (d, $J = 6.8$ Hz, 2H), 6.66 (d, $J = 7.1$ Hz, 1H), 5.81 (d, $J = 6.8$ Hz, 1H), 5.16 (s, 1H), 4.88 (d, $J = 6.8$ Hz, 1H), 3.91 (s, 3H), 1.37 (s, 18H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 194.8, 153.1, 147.8, 144.6, 136.3, 134.7, 133.6, 132.4, 130.6, 129.3, 128.6, 124.8, 122.1, 117.6, 112.0, 91.2, 56.2, 51.9, 34.4, 30.3 ppm. IR (KBr): 3598, 3053, 3004, 2954, 2924, 2853, 1684, 1492, 1621, 1595, 1435, 1279, 1178, 1118, 1086, 926, 886, 653, 734, 684 cm$^{-1}$. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for C$_{30}$H$_{35}$O$_4$ 459.2530; Found 459.2533.

(3-(3,5-di-tert-butyl-4-hydroxyphenyl)-4,6-dimethoxy-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (3la)

67% yield (65.7 mg). White solid, m.p. 126 – 128 °C. Rf = 0.4 (PE/EA = 10/1). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.94 (d, $J = 7.0$ Hz, 2H), 7.59 (t, $J = 7.4$ Hz, 1H), 7.46 (t, $J = 7.6$ Hz, 2H), 6.95 (s, 2H), 6.27 (d, $J = 2.0$ Hz, 1H), 6.01 (d, $J = 2.0$ Hz, 1H), 5.80 (d, $J = 4.0$ Hz, 1H), 5.11 (s, 1H), 4.68 (d, $J = 4.0$ Hz, 1H), 3.80 (s, 3H), 3.59 (s, 3H), 1.39 (s, 18H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 195.3, 162.2, 161.5, 156.9, 152.7, 135.9, 134.2, 133.5, 132.5, 129.1, 128.6, 123.9, 128.1, 92.4, 89.1, 88.4, 55.5, 55.3, 49.0, 34.3, 30.3 ppm. IR (KBr): 3605, 2958, 2927, 1679, 1628, 1598, 1502, 1433, 1233, 1216, 1202, 1143, 1097, 1046, 955, 882, 813, 767, 739, 678 cm$^{-1}$. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for C$_{31}$H$_{37}$O$_5$ 489.2636; Found 489.2639.
(1-(3,5-di-tert-butyl-4-hydroxyphenyl)-1,2-dihyronaphtho[2,1-b]furan-2-yl)(phenyl)methanone (3ma)

89% yield (85.3 mg). White solid, m.p. 165 – 166 °C. Rf = 0.4 (PE/EA = 10/1). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.99 – 7.96 (m, 2H), 7.77 (dd, \(J = 8.5, 4.7\) Hz, 2H), 7.60 (t, \(J = 7.4\) Hz, 1H), 7.46 (t, \(J = 7.5\) Hz, 2H), 7.29 (d, \(J = 8.9\) Hz, 2H), 7.25 – 7.21 (m, 2H), 6.99 (s, 2H), 5.92 (d, \(J = 5.3\) Hz, 1H), 5.16 (d, \(J = 5.4\) Hz, 1H), 5.13 (s, 1H), 1.34 (s, 18H) ppm. \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 195.1, 157.1, 153.0, 136.4, 134.5, 133.7, 132.8, 130.6, 130.3, 130.1, 129.4, 128.7, 128.6, 126.5, 124.5, 123.1, 123.0, 120.1, 112.1, 91.8, 51.1, 34.4, 30.3 ppm. IR (KBr): 3607, 3061, 2954, 2870, 1698, 1692, 1632, 1600, 1522, 1433, 1238, 1140, 979, 857, 751, 704, 692 cm\(^{-1}\). HRMS (ESI-TOF) m/z: [M + H]\(^+\) Calcd for C\(_{33}\)H\(_{35}\)O\(_3\) 479.2581; Found 479.2581.

(3-(3,5-di-tert-butyl-4-hydroxyphenyl)-7,7-dimethyl-3,5,6,7-tetrahydro-2H-furo[3,2-g]chromen-2-yl)(phenyl)methanone (3na)

62% yield (63.1 mg). White solid, m.p. 144 – 146 °C. Rf = 0.6 (PE/EA = 10/1). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.89 (d, \(J = 7.0\) Hz, 2H), 7.57 (t, \(J = 7.4\) Hz, 1H), 7.42 (t, \(J = 7.7\) Hz, 2H), 6.95 (s, 2H), 6.70 (s, 1H), 6.42 (s, 1H), 5.71 (d, \(J = 6.3\) Hz, 1H), 5.16 (s, 1H), 4.69 (d, \(J = 6.2\) Hz, 1H), 2.64 (t, \(J = 6.7\) Hz, 2H), 1.75 (t, \(J = 6.8\) Hz, 2H), 1.39 (s, 18H), 1.33 (s, 3H), 1.30 (s, 3H) ppm. \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 195.5, 158.7, 154.5, 152.9, 136.2, 134.7, 133.5, 133.2, 129.3, 128.5, 125.3, 124.7, 120.9, 113.8, 98.7, 91.4, 74.2, 51.1, 34.4, 32.9, 30.3, 27.2, 26.5, 22.2 ppm. IR (KBr): 3587, 3135, 2959, 2922, 2878, 1692, 1627, 1599, 1478, 1435, 1399, 1237, 1151, 1121, 1097, 965, 906, 873, 842, 690, 663 cm\(^{-1}\). HRMS (ESI-TOF) m/z: [M + Na]\(^+\) Calcd for C\(_{34}\)H\(_{40}\)O\(_4\)Na 535.2819; Found 535.2820.
(3-(4-hydroxy-3,5-diisopropylphenyl)-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (3oa)

78% yield (62.8 mg). White solid, m.p. 130 – 132 °C. Rf = 0.4 (PE/EA = 10/1). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.93 (d, $J = 7.9$ Hz, 2H), 7.58 (t, $J = 7.4$ Hz, 1H), 7.43 (t, $J = 7.7$ Hz, 2H), 7.20 (t, $J = 8.0$ Hz, 1H), 7.02 – 6.97 (m, 2H), 6.91 – 6.85 (m, 3H), 5.78 (d, $J = 6.7$ Hz, 1H), 4.85 (d, $J = 6.7$ Hz, 1H), 4.78 (s, 1H), 3.19 – 3.05 (m, 2H), 1.23 (d, $J = 6.9$ Hz, 6H), 1.18 (d, $J = 6.8$ Hz, 6H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) δ 195.1, 159.1, 149.3, 134.5, 134.1, 133.9, 133.6, 129.4, 129.3, 128.6, 128.5, 125.3, 123.3, 121.4, 109.8, 90.8, 51.2, 27.3, 22.6, 22.6 ppm. IR (KBr): 3435, 3422, 2962, 2928, 2864, 1692, 1595, 1447, 1260, 1211, 1196, 1184, 1152, 1184, 1123, 962, 773, 745, 691 cm$^{-1}$. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for C$_{27}$H$_{29}$O$_3$ 401.2111; Found 401.2107.

(3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl)(4-fluorophenyl)methanone (3ab)

90% yield (80.3 mg). White solid, m.p. 166 – 168 °C. Rf = 0.5 (PE/EA = 10/1). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.97 (s, 2H), 7.19 – 6.89 (m, 8H), 5.70 (d, $J = 6.9$ Hz, 1H), 5.17 (s, 1H), 4.90 (d, $J = 6.9$ Hz, 1H), 1.38 (s, 18H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) δ 193.7, 167.7, 164.3, 157.6 (d, $J = 238.0$ Hz), 136.4, 132.4, 132.1 (d, $J = 9.3$ Hz), 131.2, 129.4, 128.7, 125.5, 124.8, 121.5, 115.7 (d, $J = 21.8$ Hz), 109.8, 90.9, 51.1, 34.4, 30.3 ppm. $^{19}$F NMR (282 MHz, CDCl$_3$) δ -102.75 ppm. IR (KBr): 3613, 2958, 2924, 2969, 1686, 1596, 1505, 1435, 1228, 1156, 1119, 962, 865, 754, 653 cm$^{-1}$. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for C$_{29}$H$_{32}$FO$_3$ 447.2330; Found 447.2322.
(4-chlorophenyl)(3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl)methanone (3ac)

87% yield (80.7 mg). White solid, m.p. 179 – 180 °C. Rf = 0.5 (PE/EA = 10/1). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.87 (d, $J = 8.2$ Hz, 2H), 7.39 (d, $J = 8.2$ Hz, 2H), 7.19 (t, $J = 7.5$ Hz, 1H), 7.04 (d, $J = 7.4$ Hz, 1H), 6.96 – 6.87 (m, 4H), 5.69 (d, $J = 6.9$ Hz, 1H), 5.17 (s, 1H), 4.89 (d, $J = 6.9$ Hz, 1H), 1.38 (s, 18H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) δ 194.1, 159.0, 153.1, 140.2, 136.4, 133.1, 132.4, 130.9, 128.9, 128.7, 125.5, 124.8, 121.6, 109.8, 90.9, 51.1, 34.4, 30.3 ppm. IR (KBr): 3615, 2963, 2926, 2865, 1687, 1588, 1478, 1460, 1345, 1301, 1223, 1120, 1090, 1012, 963, 864, 820, 654 cm$^{-1}$. HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{29}$H$_{31}$ClO$_3$Na 485.1854; Found 485.1855.

(4-bromophenyl)(3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl)methanone (3ad)

82% yield (83.5 mg). White solid, m.p. 172 – 174 °C. Rf = 0.5 (PE/EA = 10/1). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.78 (d, $J = 8.3$ Hz, 2H), 7.56 (d, $J = 8.2$ Hz, 2H), 7.18 (t, $J = 7.4$ Hz, 1H), 7.04 (d, $J = 7.1$ Hz, 1H), 6.95 – 6.86 (m, 4H), 5.68 (d, $J = 7.0$ Hz, 1H), 5.17 (s, 1H), 4.88 (d, $J = 7.0$ Hz, 1H), 1.37 (s, 18H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) δ 194.4, 159.0, 153.1, 136.4, 133.5, 132.3, 131.9, 130.9, 129.3, 128.9, 128.7, 125.5, 124.8, 121.6, 109.8, 90.9, 51.1, 34.4, 30.3 ppm. IR (KBr): 3602, 3432, 3188, 2963, 2922, 2865, 1386, 1584, 1478, 1459, 1434, 1399, 1371, 1225, 1161, 1099, 1070, 1009, 863, 812, 784, 753, 649 cm$^{-1}$. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for C$_{29}$H$_{32}$BrO$_3$ 507.1530; Found 507.1523.
(3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl)(4-(trifluoromethyl)phenyl) methanone (3ae)

88% yield (87.3 mg). White solid, m.p. 141 – 142 °C. Rf = 0.6 (PE/EA = 10/1). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.05 (d, $J = 8.1$ Hz, 2H), 7.70 (d, $J = 8.2$ Hz, 2H), 7.20 (t, $J = 7.7$ Hz, 1H), 7.06 (d, $J = 7.4$ Hz, 1H), 6.96 – 6.89 (m, 4H), 5.73 (d, $J = 6.9$ Hz, 1H), 5.18 (s, 1H), 4.92 (d, $J = 6.9$ Hz, 1H), 1.38 (s, 18H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 194.6, 158.8, 153.2, 137.6, 136.5, 134.8 (d, $J = 32.8$ Hz), 132.2, 129.7, 129.2, 128.8, 125.6 (d, $J = 3.7$ Hz), 152.5, 124.7, 121.7, 109.9, 91.1, 50.9, 34.4, 30.2 ppm. $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -62.12 ppm. IR (KBr): 3608, 2958, 2927, 2873, 1698, 1596, 1478, 1409, 1237, 1226, 1172, 1134, 1068, 1015, 955, 867, 845, 753, 657 cm$^{-1}$. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for C$_{30}$H$_{32}$F$_3$O$_3$ 497.2298; Found 497.2294.

4-(3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-carbonyl)benzonitrile (3af)

85% yield (77.1 mg). White solid, m.p. 208 – 210 °C. Rf = 0.4 (PE/EA = 10/1). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.05 (d, $J = 8.0$ Hz, 2H), 7.74 (d, $J = 8.0$ Hz, 2H), 7.20 (t, $J = 7.6$ Hz, 1H), 7.07 (d, $J = 7.3$ Hz, 1H), 6.97 (s, 2H), 6.95 – 6.90 (m, 2H), 5.70 (d, $J = 6.9$ Hz, 1H), 5.21 (s, 1H), 4.94 (d, $J = 6.9$ Hz, 1H), 1.39 (s, 18H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 194.3, 158.7, 153.2, 137.9, 136.5, 132.3, 132.1, 129.8, 129.1, 128.8, 125.6, 124.7, 121.8, 117.8, 116.8, 109.9, 91.1, 50.7, 34.4, 30.3 ppm. IR (KBr): 3606, 3004, 2954, 2922, 2872, 1696, 1597, 1480, 1460, 1435, 1409, 1290, 1229, 1218, 1122, 977, 961, 965, 847, 754, 682, 653 cm$^{-1}$. HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for C$_{30}$H$_{30}$NO$_3$ 452.2231; Found 452.2230.
(3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl)(4-nitrophenyl)methanone (3ag)

82% yield (77.7 mg). Yellow solid, m.p. 190 – 192 °C. Rf = 0.4 (PE/EA = 10/1). 1H NMR (300 MHz, CDCl3) δ 8.29 (d, J = 8.8 Hz, 2H), 8.13 (d, J = 8.9 Hz, 2H), 7.23 – 7.18 (m, 1H), 7.08 (d, J = 7.9 Hz, 1H), 6.99 (s, 2H), 6.95 – 6.90 (m, 2H), 5.72 (d, J = 6.9 Hz, 1H), 5.21 (s, 1H), 4.97 (d, J = 6.9 Hz, 1H), 1.39 (s, 18H) ppm. 13C NMR (75 MHz, CDCl3) δ 194.2, 158.6, 153.2, 150.5, 139.4, 136.5, 132.1, 129.1, 128.8, 125.6, 124.7, 123.7, 121.9, 109.9, 91.2, 50.6, 34.4, 30.3 ppm. IR (KBr): 3596, 3111, 3080, 2957, 2921, 2870, 1705, 1605, 1594, 1491, 1436, 1344, 1225, 1154, 1053, 984, 958, 857, 845, 753, 700, 645 cm⁻¹. HRMS (ESI-TOF) m/z: [M + Na]⁺ Calcd for C29H31NO5Na 496.2094; Found 496.2095.

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

92% yield (81.8 mg). White solid, m.p. 166 – 168 °C. Rf = 0.5 (PE/EA = 10/1). 1H NMR (300 MHz, CDCl3) δ 7.82 (d, J = 7.9 Hz, 2H), 7.23 – 7.16 (m, 3H), 7.03 (d, J = 7.3 Hz, 1H), 6.97 – 6.95 (m, 3H), 6.88 (t, J = 7.4 Hz, 1H), 5.75 (d, J = 6.8 Hz, 1H), 5.16 (s, 1H), 4.85 (d, J = 6.7 Hz, 1H), 2.40 (s, 3H), 1.38 (s, 18H) ppm. 13C NMR (75 MHz, CDCl3) δ 194.8, 159.3, 153.0, 144.6, 136.3, 132.6, 132.2, 129.5, 129.4, 129.3, 128.6, 125.5, 124.8, 121.4, 109.8, 90.8, 51.4, 34.4, 30.3, 21.7 ppm. IR (KBr): 3597, 2962, 2922, 2861, 1678, 1606, 1477, 1460, 1434, 1303, 1233, 1185, 1116, 1012, 963, 950, 863, 773, 753, 739, 655 cm⁻¹. HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C30H35O3 443.2581; Found 443.2582.
(3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl)(4-methoxyphenyl)methanone (3ai)

78% yield (71.5 mg). White solid, m.p. 152 – 154 °C. Rf = 0.4 (PE/EA = 10/1). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.82 (d, $J = 8.0$ Hz, 2H), 7.23 – 7.16 (m, 3H), 7.03 (d, $J = 7.3$ Hz, 1H), 6.97 – 6.95 (m, 3H), 6.88 (t, $J = 7.4$ Hz, 1H), 5.75 (d, $J = 6.8$ Hz, 1H), 5.16 (s, 1H), 4.85 (d, $J = 6.7$ Hz, 1H), 2.40 (s, 3H), 1.38 (s, 18H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) δ 193.6, 163.9, 159.3, 153.0, 136.3, 132.7, 129.5, 128.6, 127.7, 125.4, 124.8, 121.4, 113.8, 109.8, 90.7, 55.5, 51.4, 34.4, 30.3 ppm. IR (KBr): 3597, 2959, 2925, 2869, 1675, 1594, 1510, 1479, 1435, 1306, 1234, 1172, 1113, 1024, 863, 835, 755 cm$^{-1}$. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for C$_{30}$H$_{35}$O$_4$ 459.2530; Found 459.2534.

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

82% yield (83.1 mg). White solid, m.p. 155 – 156 °C. Rf = 0.6 (PE/EA = 10/1). $^1$H NMR (300 MHz, CDCl$_3$) δ 8.01 (d, $J = 8.1$ Hz, 2H), 7.67 – 7.60 (m, 4H), 7.49 – 7.37 (m, 3H), 7.20 (t, $J = 7.5$ Hz,1H), 7.07 – 6.98 (m, 4H), 6.90 (t, $J = 7.3$ Hz, 1H), 5.80 (d, $J = 6.7$ Hz, 1H), 5.17 (s, 1H), 4.91 (d, $J = 6.7$ Hz, 1H), 1.38 (s, 18H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) δ 194.8, 159.2, 153.1, 146.4, 139.8, 136.3, 133.4, 132.6, 130.0, 129.4, 129.0, 128.7, 128.4, 127.3, 127.2, 125.5, 124.8, 121.5, 109.9, 90.9, 51.3, 34.4, 30.3 ppm. IR (KBr): 3587, 3012, 2951, 2923, 2873, 1683, 1603, 1477, 1457, 1435, 1232, 1162, 1119, 950, 867, 837, 820, 747, 690 cm$^{-1}$. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for C$_{35}$H$_{37}$O$_3$ 505.2737; Found 505.2748.
(3-bromophenyl)(3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl)methanone (3ak)

78% yield (79.0 mg). White solid, m.p. 152 – 154 °C. Rf = 0.6 (PE/EA = 10/1). $^1$H NMR (300 MHz, CDCl$_3$) δ 8.00 (s, 1H), 7.86 (d, $J = 7.8$ Hz, 1H), 7.68 (d, $J = 1.9$ Hz, 1H), 7.31 (t, $J = 7.9$ Hz, 1H), 7.20 (t, $J = 7.6$ Hz, 1H), 7.04 (d, $J = 7.3$ Hz, 1H), 6.95 – 6.98 (m, 3H), 6.90 (t, $J = 7.4$ Hz, 1H), 5.70 (d, $J = 7.0$ Hz, 1H), 5.18 (s, 1H), 4.84 (d, $J = 6.9$ Hz, 1H), 1.38 (s, 18H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) δ 194.0, 158.9, 153.1, 136.4, 132.2, 132.2, 130.1, 129.2, 128.7, 127.8, 125.4, 124.7, 122.8, 121.6, 109.8, 90.8, 51.2, 34.3, 30.2 ppm. IR (KBr): 3635, 3128, 3072, 3003, 2961, 2907, 2873, 1696, 1597, 1567, 1478, 1461, 1433, 1400, 1222, 1209, 1144, 1105, 1016, 967, 863, 787, 751, 732, 693, 637 cm$^{-1}$. HRMS (ESI-TOF) m/z: [M + NH$_4$]$^+$ Calcd for C$_{29}$H$_{35}$NBrO$_3$ 524.1795; Found 524.1798.

(2-bromophenyl)(3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl)methanone (3al)

55% yield (55.8mg). White solid, m.p. 136 – 138 °C. Rf = 0.5 (PE/EA = 10/1). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.60 (d, $J = 4.4$ Hz, 1H), 7.31 – 7.27 (m, 3H), 7.17 (t, $J = 7.7$ Hz, 1H), 7.05 (d, $J = 7.4$ Hz, 1H), 6.90 (dd, $J = 7.2$, 4.2 Hz, 2H), 6.85 (s, 2H), 5.67 (d, $J = 6.5$ Hz, 1H), 5.11 (s, 1H), 4.85 (d, $J = 6.6$ Hz, 1H), 1.34 (s, 18H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) δ 200.4, 159.0, 152.9, 139.1, 136.1, 133.6, 132.3, 131.9, 129.2, 128.8, 128.7, 127.0, 125.5, 124.4, 121.5, 119.6, 109.9, 92.5, 51.3, 34.3, 30.2 ppm. IR (KBr): 3614, 3007, 2956, 2906, 2865, 1705, 1595, 1480, 1462, 1434, 1306, 1234, 1211, 1120, 1020, 971, 837, 752, 732, 690, 639 cm$^{-1}$. HRMS (ESI-TOF) m/z: [M + NH$_4$]$^+$ Calcd for C$_{29}$H$_{35}$NBrO$_3$ 524.1795; Found 524.1798.
(3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl)(naphthalen-2-yl)methanone (3am)

88% yield (83.3 mg). White solid, m.p. 156 − 158 °C. Rf = 0.4 (PE/EA = 10/1). 1H NMR (300 MHz, CDCl₃) δ 8.24 (d, J = 1.7 Hz, 1H), 8.05 (d, J = 1.4 Hz, 1H), 7.88 − 7.83 (m, 2H), 7.75 (d, J = 8.0 Hz, 1H), 7.57 (t, J = 6.8 Hz, 1H), 7.49 (t, J = 7.1 Hz, 1H), 7.19 (d, J = 7.5 Hz, 1H), 7.06 − 6.97 (m, 4H), 6.90 (t, J = 7.3 Hz, 1H), 5.96 (d, J = 7.1 Hz, 1H), 5.18 (s, 1H), 4.88 (d, J = 7.1 Hz, 1H), 1.34 (s, 18H) ppm. 13C NMR (75 MHz, CDCl₃) δ 195.1, 159.3, 153.1, 136.4, 135.8, 132.5, 132.3, 132.0, 131.5, 129.8, 129.5, 128.7, 128.4, 127.8, 126.8, 125.5, 124.9, 124.5, 121.5, 109.9, 91.1, 51.9, 34.4, 30.3 ppm. IR (KBr): 3579, 3053, 2965, 2912, 2871, 1684, 1628, 1598, 1477, 1434, 1400, 1302, 1236, 1224, 1197, 1124, 1058, 970, 897, 864, 825, 776, 755, 641 cm⁻¹. HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₃₃H₃₅O₄ 479.2581; Found 479.2586.

(3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl)(thiophen-2-yl)methanone (3an)

92% yield (79.6 mg). White solid, m.p. 157 − 158 °C. Rf = 0.5 (PE/EA = 10/1). 1H NMR (300 MHz, CDCl₃) δ 7.70 (d, J = 3.8 Hz, 1H), 7.66 (d, J = 5.0 Hz, 1H), 7.18 (t, J = 8.2 Hz, 1H), 7.07 − 7.03 (m, 2H), 6.97 − 6.95 (m, 3H), 6.89 (t, J = 7.4 Hz, 1H), 5.48 (d, J = 6.8 Hz, 1H), 5.15 (s, 1H), 4.88 (d, J = 6.8 Hz, 1H), 1.36 (s, 18H) ppm. 13C NMR (75 MHz, CDCl₃) δ 189.4, 159.1, 153.1, 141.1, 136.3, 135.0, 134.2, 132.4, 129.2, 128.7, 128.2, 125.6, 124.8, 121.6, 109.9, 92.0, 52.1, 34.4, 30.3 ppm. IR (KBr): 3604, 3126, 3086, 3068, 3010, 2951, 2923, 2873, 2849, 1675, 1596, 1515, 1479, 1460, 1433, 1411, 1361, 1303, 1234, 1160, 1118, 1032, 984, 932, 832, 755, 734, 694, 649 cm⁻¹. HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₂₇H₃₂O₅S 435.1989; Found 435.1996.
ethyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-carboxylate (3ao)

37% yield (29mg). White solid, m.p. 107 – 108 °C. Rf = 0.5 (PE/EA = 10/1). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.20 (t, $J = 7.8$ Hz, 1H), 7.06 (d, $J = 7.3$ Hz, 1H), 6.98 – 6.96 (m, 3H), 6.91 (td, $J = 7.4$, 1.0 Hz, 1H), 5.16 (s, 1H), 4.99 (d, $J = 6.6$ Hz, 1H), 4.74 (d, $J = 6.6$ Hz, 1H), 4.35 – 4.24 (m, 2H), 1.40 (s, 18H), 1.33 (t, $J = 7.1$ Hz, 3H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) δ 188.6, 170.9, 159.2, 153.0, 136.1, 132.5, 128.7, 125.4, 124.4, 121.4, 109.9, 87.4, 61.6, 52.6, 34.4, 30.2, 14.3 ppm. IR (KBr): 3589, 2957, 2924, 2871, 1751, 1613, 1597, 1480, 1460, 1435, 1375, 1260, 1238, 1209, 1118, 1042, 886, 821, 751 cm$^{-1}$. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for C$_{25}$H$_{33}$O$_4$ 397.2374; Found 397.2372.
5. Further Transformations of 3aa

![Scheme S6. Synthesis of 5aa](image)

The compound 3aa (85.6 mg, 0.2 mmol) was dissolved in 3 mL dry toluene. Then AlCl$_3$ (133.3 mg, 5.0 equiv.) was added. The reaction was stirred for 2 h at 60 °C and 5 mL H$_2$O was added. The layers were separated and the aqueous layer was extracted with ethyl acetate (3 × 10 mL). The combined extracts were washed with 20 mL brine and dried over anhydrous Na$_2$SO$_4$. The solvent was concentrated under reduced pressure. The residue obtained was purified by flash column chromatography on silica gel (PE/EA = 10/1) to afford the desired product 5aa.

(3-(4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl)(phenyl)methane (5aa)

69% yield (43.9 mg). White solid, m.p. 188 – 190 °C. Rf = 0.5 (PE/EA = 10/1). $^1$H NMR (300 MHz, DMSO-$_d$6) $\delta$ 9.38 (s, 1H), 7.88 (d, $J = 7.3$ Hz, 2H), 7.68 (t, $J = 7.3$ Hz, 1H), 7.53 (t, $J = 7.6$ Hz, 2H), 7.18 (t, $J = 7.6$ Hz, 1H), 7.02 – 6.95 (m, 4H), 6.85 (t, $J = 7.4$ Hz, 1H), 6.73 (d, $J = 8.3$ Hz, 2H), 6.12 (d, $J = 5.6$ Hz, 1H), 4.70 (d, $J = 5.6$ Hz, 1H). $^{13}$C NMR (75 MHz, DMSO-$_d$6) $\delta$ 195.1, 158.5, 156.5, 134.0, 133.8, 132.3, 130.0, 128.8, 128.7, 128.6, 125.1, 121.1, 115.5, 109.4, 89.2, 49.6 ppm. IR (KBr): 3385, 3180, 2960, 2924, 2851, 1679, 1613, 1513, 1400, 1234, 1105, 1049, 982, 838, 818, 773, 753, 693, 645 cm$^{-1}$. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for C$_{21}$H$_{17}$O$_3$ 317.1172; Found 317.1174.

Scheme S7. Synthesis of 6aa

To a sealing tube were added 3aa (85.6 mg, 0.2 mmol), 3.0 equiv. K$_2$CO$_3$ (82.8 mg) and anhydrous DMF (1 mL). Then the oxidation reaction was conducted at 80 °C for 2 hours. After the
reaction was completed, the solvent was removed to give a residue which was purified by flash column chromatography (PE/EA = 100/1) to give the desired product 6aa. (Scheme S7)

(3-(3,5-di-tert-butyl-4-hydroxyphenyl)benzofuran-2-yl)(phenyl)methanone (6aa)

68% yield (58.0 mg). White solid, m.p. 150 – 152 °C. Rf = 0.3 (PE/EA = 4/1). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.75 (d, \(J = 7.6\) Hz, 1H), 7.70 – 7.65 (m, 3H), 7.53 (td, \(J = 8.4, 7.7, 1.3\) Hz, 1H), 7.39 – 7.33 (m, 2H), 7.21 – 7.17 (m, 4H), 5.25 (s, 1H), 1.35 (s, 18H) ppm.

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 186.0, 154.4, 153.5, 146.2, 136.9, 135.5, 131.8, 130.1, 129.3, 127.7, 127.7, 127.2, 126.6, 123.2, 122.2, 121.3, 112.0, 33.7, 29.7 ppm. IR (KBr): 3540, 3132, 2956, 2924, 2872, 1731, 1635, 1552, 1447, 1379, 1294, 1258, 1161, 1122, 966, 882, 752, 730, 696, 657 cm\(^{-1}\). HRMS (ESI-TOF) m/z: [M + H]\(^+\) Calcd for C\(_{29}\)H\(_{31}\)O\(_3\) 427.2268; Found 427.2271.
6. Screening Asymmetric Reaction Conditions

Table 1. Attempt to synthesize enantiopure 3aa\textsuperscript{[a],[b]}

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<th>Entry</th>
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<th>Yield (%)</th>
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<th>ee\textsuperscript{[c]}</th>
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<td>3</td>
<td>7c</td>
<td>Na$_3$PO$_4$·12H$_2$O</td>
<td>80</td>
<td>&gt; 20:1</td>
<td>61</td>
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</table>

[a] Reaction Conditions: 1a (0.20 mmol), 7 (0.24 mmol), and base (0.50 mmol) in CH$_2$Cl$_2$ (1.0 mL) at room temperature for 12 h. [b] All yields refer to the isolated yields. [c] Determined by HPLC analysis using a chiral stationary phase.
HPLC acquisition parameters:
Chiral column: CHIRALCEL® OD-H, Wave length: 254 nm,
Mobile phase: iPrOH:Hex=20:80, Flow rate: 0.5mL/min, Temperature: 28 °C.

HPLC Spectra of racemic 3aa

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HPLC Spectra of enantiomeric 3aa

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7. Synthesis of Spiro[2.5]octa-4,7-dien-6-ones

A sealed tube was charged with para-quinone methide 1a1 (0.3 mmol, 1 equiv), sulfur ylide 2a'(0.3 mmol, 1 equiv), and dichloromethane (1.0 mL). The reaction mixture was stirred at room temperature for 12 h. Then the reaction mixture was concentrated in vacuo and purified by careful chromatography on silica gel to afford the desired product 8.

1-benzoyl-5,7-di-tert-butyl-2-(2-((tert-butyldimethylsilyl)oxy)phenyl)spiro[2.5]octa-4,7-dien-6-one (8)

37% yield (61.0 mg). White solid, m.p. 121 – 122 °C. Rf = 0.6 (PE/EA = 10/1). ¹H NMR (300 MHz, CDCl₃) δ 7.89 (d, J = 7.0 Hz, 2H), 7.63 (t, J = 7.2 Hz, 1H), 7.52 (t, J = 7.4 Hz, 2H), 7.26 (t, J = 6.9 Hz, 2H), 7.01 (t, J = 7.3 Hz, 1H), 6.90 (d, J = 7.8 Hz, 1H), 6.66 (d, J = 2.8 Hz, 1H), 6.11 (d, J = 2.7 Hz, 1H), 4.13 (d, J = 7.7 Hz, 1H), 3.98 (d, J = 7.7 Hz, 1H), 1.19 (d, J = 2.8 Hz, 18H), 0.98 (s, 9H), 0.28 (s, 3H), 0.20 (s, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 197.4, 188.1, 158.0, 152.6, 152.3, 141.1, 140.9, 140.2, 135.9, 131.9, 131.4, 131.3, 130.7, 128.5, 123.3, 121.2, 43.0, 43.0, 39.2, 37.7, 37.7, 31.8, 28.5, 20.8 ppm. IR (KBr): 3474, 2957, 2928, 2858, 1670, 1645, 1618, 1354, 1319, 1265, 1215, 1175, 1109, 916, 783, 754 cm⁻¹. HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₃₅H₆₀O₃Si 543.3298; Found 543.3280.
8. Characterization of 9a and 10aa

tert-butyl (2-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)phenyl)carbamate (9a)

Yellow solid, m.p. 144 – 146 °C. Rf = 0.5 (PE/EA = 10/1). $^1$H NMR (300 MHz, CDCl$_3$) δ 8.00 (d, $J$ = 8.3 Hz, 1H), 7.39 (t, $J$ = 7.6 Hz, 1H), 7.32 – 7.22 (m, 2H), 7.16 (d, $J$ = 7.4 Hz, 1H), 7.11 (s, 1H), 7.08 (d, $J$ = 2.4 Hz, 1H), 6.47 (s, 1H), 1.52 (s, 9H), 1.35 (s, 9H), 1.26 (s, 9H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) δ 186.5, 152.6, 149.6, 148.2, 137.1, 137.0, 134.3, 133.7, 131.3, 130.1, 128.0, 123.4, 121.1, 81.1, 35.4, 35.1, 29.5, 29.5, 28.3 ppm. IR (KBr): 3413, 3127, 1635, 1614, 1508, 1400, 1252, 1151, 1077, 945, 854, 547 cm$^{-1}$. HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{26}$H$_{35}$NNaO$_3$ 432.2509; Found 432.2517.

tert-butyl (2-((1R,2R)-2-benzoyl-5,7-di-tert-butyl-6-oxospiro[2.5]octa-4,7-dien-1-yl)phenyl)carbamate (10aa)

26% yield (26.9 mg). White solid, m.p. 130 – 132 °C. Rf = 0.5 (PE/EA = 10/1). $^1$H NMR (300 MHz, CDCl$_3$) δ 8.08 (d, $J$ = 7.8 Hz, 1H), 7.91 (d, $J$ = 7.7 Hz, 2H), 7.63 (t, $J$ = 7.2 Hz, 1H), 7.51 (t, $J$ = 7.5 Hz, 2H), 7.32 (t, $J$ = 7.7 Hz, 1H), 7.20 (d, $J$ = 7.6 Hz, 1H), 7.03 (t, $J$ = 7.2 Hz, 1H), 6.67 (s, 1H), 6.12 (s, 1H), 5.89 (s, 1H), 3.93 (d, $J$ = 7.2 Hz, 1H), 3.80 (d, $J$ = 7.2 Hz, 1H), 1.41 (s, 9H), 1.19 (s, 9H), 1.12 (s, 9H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) δ 194.3, 185.1, 152.3, 151.2, 151.1, 138.2, 137.5, 137.2, 136.0, 133.8, 129.3, 129.1, 128.9, 128.3, 123.5, 122.8, 119.5, 80.8, 41.2, 39.5, 36.3, 35.3, 35.2, 29.4, 29.1, 28.2 ppm. IR (KBr): 3421, 3126, 3003, 1732, 1641, 1520, 1446, 1400, 1366, 1234, 1155, 907, 742 cm$^{-1}$. HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for C$_{34}$H$_{41}$NNaO$_4$ 550.2928; Found 550.2930.
9. Characterization of 11a

2,6-di-tert-butyl-4-(2-methoxybenzylidene)cyclohexa-2,5-dienone (11a)

\[ \text{O} \]

\[ \text{tBu} \]

\[ \text{tBu} \]

52% yield (33.7.0 mg). Yellow solid, m.p. 137 – 138 °C. Rf = 0.7 (PE/EA = 10/1). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.47 (d, \(J = 2.4\) Hz, 1H), 7.45 – 7.34 (m, 3H), 7.08 (d, \(J = 2.4\) Hz, 1H), 7.03 (t, \(J = 7.5\) Hz, 1H), 6.95 (d, \(J = 8.7\) Hz, 1H), 3.89 (s, 3H), 1.34 (s, 9H), 1.29 (s, 9H) ppm. \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 186.7, 158.3, 148.9, 147.3, 138.9, 135.3, 131.8, 131.5, 130.9, 128.4, 124.9, 120.5, 110.8, 55.6, 35.4, 35.0, 29.6, 29.5 ppm. IR (KBr): 3128, 2957, 1615, 1587, 1476, 1461, 1400, 1358, 1252, 1160, 1110, 1048, 1028, 951, 892, 751 cm\(^{-1}\). HRMS (ESI-TOF) m/z: [M + H]\(^+\) Calcd for C\(_{22}\)H\(_{29}\)O\(_2\) 325.2162; Found 325.2175.
10. Crystal Structure of 3aa

![Crystal Structure Diagram](image)

**Figure S4. ORTEP plot of the crystal structure of 3aa.**

X-ray crystallographic data of 3aa

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11. References

12. NMR Spectra

$^1$H NMR (CDCl$_3$, 300 MHz)

$^{13}$C NMR (CDCl$_3$, 75 MHz)
$^1$H NMR (CDCl$_3$, 300 MHz)

$^{13}$C NMR (CDCl$_3$, 75 MHz)