Supporting Information

Synthesis of Functionalized Benzo[1,3]dioxin-4-ones from Salicylic Acid and Acetylenic Esters and their Direct Amidation

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1. Experimental section

Unless otherwise stated all reactions were carried out in a Schlenk tube. All the reagents were bought from commercial suppliers and used as such without additional purification. The crude reaction mixture was purified with silica gel (60–120 mesh) column chromatography using a hexane-ethyl acetate solvent mixture as the eluent. The isolated compounds were characterized by $^1$H and $^{13}$C NMR spectroscopy, infrared spectroscopy and high-resolution mass spectrometry (HRMS).

Melting points of the solid samples were determined using the Stuart melting point apparatus. Other characterizations such as $^1$H NMR (400 MHz) and $^{13}$C NMR spectra were recorded in CDCl$_3$/DMSO, on Bruker Ascend™ 400 MHz spectrometer and JEOL JNM-ECZ 400/L1 high resolution multinuclear FT- NMR spectrometer with tetramethyl silane (TMS; $\delta$ H=0 ppm) as an internal standard, and chemical shifts were reported in ppm relative to TMS. The resonance multiplicity is described as s (singlet), d (doublet), t (triplet), m (multiplet), dd (doublet of doublets), and q (quartet). Infrared spectra were recorded on JASCO FTIR-4100 using ATR, and only intense peaks were reported. HRMS were recorded on a Thermo Scientific Exactive mass spectrometer using the ESI method with an orbitrap mass analyzer.

1.1 General procedure for the synthesis of 4H-benzo[d][1,3]dioxin-4-one derivatives

To an oven-dried Schlenk tube equipped with a magnetic stirrer, 2- hydroxybenzoic acid (0.6 mmol, 1.2 equiv.) was added. NaHCO$_3$ (0.6 mmol, 1.2 equiv.) and CuI (0.5 mmol, 1 equiv.) were weighed and added to the Schlenk tube. Alkyne (0.5 mmol, 1 equiv.) was then added, followed by 2 ml acetonitrile solvent. The reaction vessel was then kept for stirring in an oil bath of 80°C temperature. The progress of the reaction was monitored by TLC. After 24 hrs of reaction, the reaction mixture was diluted with ethyl acetate and was subjected to celite filtration. The filtrate was then collected and concentrated, and the residue was purified by silica gel column chromatography using pet ether-ethyl acetate as eluent.
1.2 $^1$H and $^{13}$C NMR spectra of 4H-benzo[d][1,3]dioxin-4-one derivatives

**Methyl 2-(2-methoxy-2-oxoethyl)-4-oxo-4H-benzo[d][1,3]dioxine-2-carboxylate (3aa):** Following the general procedure, the reaction between dimethyl acetylene dicarboxylate (0.5 mmol, 71.0 mg) with 2-hydroxybenzoic acid (0.6 mmol, 82.8 mg) in presence of NaHCO$_3$ (0.6 mmol, 50.4 mg) and additive CuI (0.5 mmol, 95.2 mg) in acetonitrile at 80 °C, yielded the desired product methyl 2-(2-methoxy-2-oxoethyl)-4-oxo-4H-benzo[d][1,3]dioxine-2-carboxylate as a white solid in 88% yield (123 mg). Melting point 99-101°C.

![Chemical Structure](image)

FT-IR (ATR): $\nu_{\text{max}}$ = 2957, 2922, 1757, 1612, 1509, 1467, 1440, 1366, 1302 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.88 (d, $J$ = 7.2 Hz, 1H), 7.52-7.48 (m, 1H), 7.13-7.09 (m, 1H), 6.98 (d, $J$ = 8.0 Hz, 1H), 3.68 (s, 6H), 3.37-3.25 (m, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 165.9, 165.1, 158.0, 154.1, 135.7, 128.8, 122.9, 115.8, 112.8, 99.6, 52.7, 51.4, 41.2 ppm; HRMS (ESI) calcd for C$_{13}$H$_{12}$O$_7$ [M+Na]$^+$ 303.0475 found 303.0478.
Ethyl 2-(2-ethoxy-2-oxoethyl)-4-oxo-4H-benzo[d][1,3]dioxine-2-carboxylate (3ab):

Following the general procedure, the reaction between Diethyl acetylene dicarboxylate (0.5 mmol, 85 mg) with 2-hydroxybenzoic acid (0.6 mmol, 82.8 mg) in presence of NaHCO₃ (0.6 mmol, 50.4 mg) and additive CuI (0.5 mmol, 95.2 mg) in acetonitrile at 80 °C, yielded the desired product Ethyl 2-(2-ethoxy-2-oxoethyl)-4-oxo-4H-benzo[d][1,3]dioxine-2-carboxylate as a viscous oily liquid in 72% yield (110.8 mg).

FT-IR (ATR): νₓₓₓ = 2989, 1739, 1610, 1472, 1382, 1300, 1190, 1075, 1013 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 7.87 (d, J= 8 Hz, 1H), 7.52- 7.48 (m, 1H), 7.12- 7.08 (m, 1H), 6.98 (d, J= 8.4 Hz, 1H), 4.17- 4.09 (m, 4H), 3.34 (d, J= 15.6, 1H), 3.24 (d, J= 15.6, 1H), 1.21 (t, 8 Hz, 3H), 1.08 (t, J= 7.2 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ = 165.4, 164.5, 158.2, 154.2, 135.5, 128.7, 122.9, 115.8, 113.1, 99.6, 62.1, 60.5, 41.2, 12.9, 12.7 ppm; HRMS (ESI) calcd for C₁₅H₁₆O₇ [M+Na]⁺ 331.0788 found 331.0800.
methyl 2-(4-oxo-4H-benzo[d][1,3]dioxin-2-yl)acetate (3ac): Following the general procedure, the reaction between methyl propiolate (0.5 mmol, 42 mg) with 2-hydroxybenzoic acid (0.6 mmol, 82.8 mg) in presence of NaHCO₃ (0.6 mmol, 50.4 mg)
and additive CuI (0.5 mmol, 95.2 mg) in acetonitrile at 80 °C, yielded the desired product methyl 2-(4-oxo-4H-benzo[d][1,3]dioxin-2-yl)acetate as a thick viscous liquid in 63% yield (70.1 mg).

FT-IR (ATR): \(\nu_{\text{max}} = 2954, 2922, 1739, 1586, 1472, 1339, 1401, 1390, 1232, 1200, 1129 \text{ cm}^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.92 \text{ (d), } J = 7.6, 1\text{H}), 7.53-7.50 \text{ (m), } 1\text{H}), 7.15-7.11 \text{ (m), } 1\text{H}), 6.99 \text{ (d), } J = 8 \text{ Hz), } 1\text{H}), 5.98 \text{ (t), } J = 5.6 \text{ Hz), } 1\text{H}), 3.71 \text{ (s), } 3\text{H}), 3.11-3.0 \text{ (m), } 2\text{H) ppm}; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 167.0, 160.3, 156.9, 135.4, 129.3, 122.7, 115.7, 113.3, 96.9, 51.3, 38.1 \text{ ppm}; \) HRMS (ESI) calecd for \(C_{11}H_{10}O_5\) [M+Na]\(^+\) 245.0420 found 245.0427.
methyl 2-(2-methoxy-2-oxoethyl)-4-oxo-4H-naphtho[2,3-d][1,3]dioxine-2-carboxylate (3da): Following the general procedure, the reaction between dimethylacetylene dicarboxylate (0.5 mmol, 71 mg) with 2-hydroxynaphthoic acid (0.6 mmol, 112.8 mg) in presence of NaHCO$_3$ (0.6 mmol, 50.4 mg) and additive CuI (0.5 mmol, 95.2 mg) in acetonitrile at 80 °C, yielded the desired product methyl 2-(2-methoxy-2-oxoethyl)-4-oxo-4H-naphtho[2,3-d][1,3]dioxine-2-carboxylate as a pale yellow solid in 60% yield (99 mg). Melting point 171-173°C.

FT-IR (ATR): $\nu_{\text{max}} = 2956, 2922, 1749, 1636, 1607, 1302, 1246, 1193, 1069, 1010$ cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.52$ (s, 1H), 7.84 (d, $J= 8$ Hz, 1H), 7.69 (d, $J= 8$ Hz, 1H), 7.54- 7.50 (m, 1H), 7.42- 7.34 (m, 2H), 3.69 (s, 3H), 3.64 (s, 3H), 3.41 (d, $J= 16$ Hz, 1H), 3.31 (d, $J= 16$ Hz, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 166.1, 165.1, 158.5, 148.9, 136.4, 131.5, 128.9, 128.7, 128.6, 126.2, 124.9, 112.9, 111.7, 52.7, 51.4, 41.2$ ppm; HRMS (ESI) calcd for C$_{17}$H$_{14}$O$_7$ [M+Na]$^+$ 353.0632 found 353.0642.
Ethyl 2-(4-oxo-4H-benzo[d][1,3]dioxin-2-yl)acetate (3ad): Following the general procedure, the reaction between ethyl propiolate (0.5 mmol, 49 mg) with 2-hydroxybenzoic acid (0.6 mmol, 82.8 mg) in presence of NaHCO$_3$ (0.6 mmol, 50.4 mg) and additive CuI
(0.5 mmol, 95.2 mg) in acetonitrile at 80 °C, yielded the desired product ethyl 2-(4-oxo-4H-benzo[d][1,3]dioxin-2-yl)acetate as a thick viscous liquid in 73% yield (85.8 mg).

FT-IR (ATR): $\nu_{\text{max}}$ = 2926, 1738, 1612, 1586, 1472, 1411, 1302, 1234, 1186, 1129, 1023 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.91 (d, $J$ = 7.6 Hz, 1H), 7.53- 7.49 (m, 1H), 7.14- 7.11 (m, 1H), 6.98 (d, $J$ = 8.4 Hz, 1H), 5.98 (t, $J$ = 5.6 Hz, 1H), 4.16 (q, $J$ = 6.8 Hz, 2H), 3.08- 2.98 (m, 2H), 1.23 (t, $J$ = 7.2 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 166.6, 160.4, 156.9, 135.4, 129.3, 122.7, 115.7, 113.3, 97.1, 60.4, 38.4, 13.1 ppm; HRMS (ESI) calcd for C$_{12}$H$_{12}$O$_5$ [M+Na]$^+$ 259.0577 found 259.0587.
methyl 2-(4-oxo-4H-naphtho[2,3-d][1,3]dioxin-2-yl)acetate (3dc): Following the general procedure, the reaction between methyl propiolate (0.5 mmol, 42 mg) with 2-hydroxynaphthoic acid (0.6 mmol, 112.8 mg) in presence of NaHCO$_3$ (0.6 mmol, 50.4 mg) and additive CuI (0.5 mmol, 95.2 mg) in acetonitrile at 80 °C, yielded the desired product methyl 2-(4-oxo-4H-naphtho[2,3-d][1,3]dioxin-2-yl)acetate as a white solid in 46% yield (62.8 mg). Melting point 114-116°C.

FT-IR (ATR): $\nu_{\text{max}}$ = 2956, 2922, 2853, 1742, 1636, 1607, 1577, 1505, 1347, 1247 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.56 (s, 1H), 7.86 (d, J= 8.4 Hz, 1H), 7.77 (d, J= 8 Hz, 1H), 7.56- 7.52 (m, 1H), 7.43- 7.36 (m, 2H), 6.05 (t, J= 5.2 Hz, 1H), 3.73 (s, 3H), 3.14- 3.04 (m, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 168.2, 161.7, 152.8, 137.4, 133.0, 129.9, 129.7, 129.5, 127.2, 125.9, 114.4, 112.5, 98.3, 52.4, 39.4 ppm; HRMS (ESI) calcd for C$_{15}$H$_{12}$O$_5$ [M+Na]$^+$ 295.0577 found 295.0587.
Ethyl 2-(4-oxo-4H-naphtho[2,3-d][1,3]dioxin-2-yl)acetate (3dd): Following the general procedure, the reaction between ethyl propiolate (0.5 mmol, 49 mg) with 2-hydroxynaphthoic acid (0.6 mmol, 112.8 mg) in presence of NaHCO$_3$ (0.6 mmol, 50.4 mg) and additive CuI (0.5 mmol, 95.2 mg) in acetonitrile at 80 °C, yielded the desired
product ethyl 2-(4-oxo-4H-naphtho[2,3-d][1,3]dioxin-2-yl)acetate as a white solid in 65% yield (92.8 mg). Melting point 106-108°C.

FT-IR (ATR): $\nu_{\text{max}} = 2923, 2860, 2853, 1735, 1635, 1575, 1505, 1475, 1346, 1188 \text{ cm}^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.56$ (s, 1H), 7.86 (d, $J = 8.4$ Hz, 1H), 7.71 (d, $J = 8.4$ Hz, 1H), 7.55-7.51 (m, 1H), 7.42-7.36 (m, 2H), 6.05 (t, $J = 5.2$ Hz, 1H), 4.19 (dd, $J = 6.8$ Hz, 2H), 3.12-3.02 (m, 2H), 1.25 (t, $J = 7.6$ Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 166.7, 160.7, 151.8, 136.4, 131.9, 128.9, 128.7, 128.5, 126.1, 124.8, 113.4, 111.4, 97.4, 60.4, 38.6, 13.1$ ppm; HRMS (ESI) calcd for C$_{16}$H$_{14}$O$_5$ [M+Na]$^+$ 309.0733 found 309.0741.
Ethyl 2-(7-methoxy-4-oxo-4H-benzo[d][1,3]dioxin-2-yl)acetate (3bd): Following the general procedure, the reaction between ethyl propiolate (0.5 mmol, 49 mg) with 2-hydroxy-4-methoxybenzoic acid (0.6 mmol, 100 mg) in presence of NaHCO$_3$ (0.6 mmol, 50.4 mg) and additive CuI (0.5 mmol, 95.2 mg) in acetonitrile at 80 °C, yielded the desired product ethyl 2-(7-methoxy-4-oxo-4H-benzo[d][1,3]dioxin-2-yl)acetate as an oily liquid in 36% yield (48 mg).

FT-IR (ATR): $v_{\text{max}}$ = 2924, 2853, 1736, 1615, 1498, 1454, 1380, 12254, 1158, 1119 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.80 (d, J= 8.8 Hz, 1H), 6.66- 6.63 (m, 1H), 6.43 (s, 1H), 5.96 (t, 5.6 Hz, 1H), 4.16 (dd, J= 7.2 Hz, 2H), 3.78 (s, 3H), 3.05- 2.96 (m, 2H), 1.23 (t, J= 7.2 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 166.7, 165.2, 160.4, 158.9, 130.8, 110.6, 105.8, 99.4, 97.0, 60.3, 54.8, 38.4, 13.1 ppm; HRMS (ESI) calcd for C$_{13}$H$_{14}$O$_6$ [M+Na]$^+$ 289.0683 found 289.0693.
Methyl 2-(2-methoxy-2-oxoethyl)-4-oxo-4H-benzo[d][1,3]oxathiine-2-carboxylate (3ea): Following the general procedure, the reaction between dimethyl acetylene dicarboxylate (0.5 mmol, 71 mg) with 2-mercaptobenzoic acid (0.6 mmol, 92.5 mg) in presence of NaHCO$_3$ (0.6 mmol, 50.4 mg) and additive CuI (0.5 mmol, 95.2 mg) in acetonitrile at 80 °C, yielded the desired product methyl 2-(2-methoxy-2-oxoethyl)-4-oxo-4H-benzo[d][1,3]oxathiine-2-carboxylate as a white solid in 53% yield (78.4 mg). Melting point 120-122°C.

FT-IR (ATR): $v_{\text{max}}$ = 2955, 1735, 1438, 1283, 1204, 1139, 1061 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.13 (d, J= 7.6 Hz, 1H), 7.42- 7.38 (m, 1H), 7.28- 7.24 (m, 1H), 7.14 (d, J= 7.6 Hz, 1H), 3.69 (s, 3H), 3.65 (s, 3H), 3.32- 3.23 (m, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 168.0, 167.3, 161.8, 133.9, 132.3, 131.8, 127.4, 127.0, 123.6, 82.9, 53.8, 52.6, 42.6 ppm; HRMS (ESI) calcd for C$_{13}$H$_{12}$O$_6$S [M+Na]$^+$ 319.0247 found 319.0261.
2-(4-oxo-2-phenyl-4H-benzo[d][1,3]dioxin-2-yl)acetonitrile (3ae): Following the general procedure, the reaction between 3-phenylpropionitrile (0.5 mmol, 63.5 mg) with 2-hydroxy benzoic acid (0.6 mmol, 82.8 mg) in presence of NaHCO$_3$ (0.6 mmol, 50.4 mg) and additive CuI (0.5 mmol, 95.2 mg) in acetonitrile at 80 °C, yielded the desired product 2-(4-oxo-2-phenyl-4H-benzo[d][1,3]dioxin-2-yl)acetonitrile as a white solid in 55% yield (73 mg). Melting point 148-150°C.

FT-IR (ATR): $\nu_{\text{max}}$ = 2954, 2923, 2255, 1749, 1612, 1590, 1479, 1466, 1450, 1302, 1089, 1028 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.74 (d, J= 7.6 Hz, 1H), 7.51- 7.47 (m, 3H), 7.32- 7.27 (m, 3H), 7.07 (d, J= 8 Hz, 1H), 6.99 (t, J= 7.6 Hz, 1H), 3.26- 3.14 (m, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 159.4, 155.5, 136.9, 136.4, 130.4, 130.0, 129.2 (2C), 126.4 (2C), 123.7, 117.3, 114.3, 113.9, 103.5, 32.8 ppm; HRMS (ESI) calcd for C$_{16}$H$_{11}$NO$_3$ [M+Na]$^+$ 288.0631 found 288.0642.
methyl 7-bromo-2-(2-methoxy-2-oxoethyl)-4-oxo-4H-benzo[d][1,3]dioxine-2-carboxylate (3ca): Following the general procedure, the reaction between dimethyl acetylene dicarboxylate (0.5 mmol, 71 mg) with 4-bromo-2-hydroxybenzoic acid (0.6 mmol, 130 mg) in presence of NaHCO₃ (0.6 mmol, 50.4 mg) and additive CuI (0.5 mmol,
95.2 mg) in acetonitrile at 80 °C, yielded the desired product methyl methyl 7-bromo-2-(2-methoxy-2-oxoethyl)-4-oxo-4H-benzo[d][1,3]dioxine-2-carboxylate as a white solid in 69% yield (80 mg). Melting point 115-117°C.

FT-IR (ATR): $\nu_{\text{max}} =$ 2956, 2921, 1757, 1602, 1578, 1423, 1367, 1307, 1273, 1169 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta =$ 7.73 (d, J= 8.4 Hz, 1H), 7.26- 7.19 (m, 2H), 3.71 (s, 3H), 3.69 (s, 3H), 3.36- 3.24 (m, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta =$ 165.8, 164.6, 157.3, 154.4, 130.1, 129.8, 126.6, 119.2, 111.6, 99.8, 52.9, 51.5, 41.0 ppm; HRMS (ESI) calcd for C$_{13}$H$_{11}$BrO$_7$: [(M+2)+Na]$^+$ 382.9580 found 382.9573.
2-cyano-1-phenylvinyl (2-(2-cyano-1,2-diphenylvinyl)thio)benzoate (4ee): Following the general procedure, the reaction between 3-phenylpropiolonitrile (0.5 mmol, 63.5 mg) with 2-mercaptobenzoic acid (0.6 mmol, 92.5 mg) in presence of NaHCO$_3$ (0.6 mmol, 50.4 mg) and additive CuI (0.5 mmol, 95.2 mg) in acetonitrile at 80°C, yielded the product 2-cyano-1-phenylvinyl (2-(2-cyano-1,2-diphenylvinyl)thio)benzoate as a white solid in 36% yield (60 mg). Melting point 152-154°C.

FT-IR (ATR): $\nu_{\text{max}}$ = 2924, 2854, 2216, 1739, 1627, 1561, 1490, 1457, 1264, 1187, 1137 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.17 (d, J= 6.8 Hz, 1H), 7.54- 7.37 (m, 7H), 7.28- 7.22 (m, 5H), 7.063 (d, J= 7.2 Hz, 1H), 5.83 (s, 1H), 5.78 (s, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 164.3, 162.1, 159.1, 137.4, 135.9, 133.5, 132.4, 132.1 (2C), 131.4, 131.0, 129.3 (2C), 129.0 (2C), 128.2 (2C), 127.4, 127.2, 125.8 (2C), 116.2, 114.6, 101.3, 87.7 ppm; HRMS (ESI) calcd for C$_{25}$H$_{16}$N$_2$O$_2$S [M+Na]$^+$ 431.0825 found 431.0839.
1.3 General procedure for the synthesis of salicylamide derivatives from 4H-benzo[d][1,3]dioxin-4-ones

To a 25 ml round bottom flask 0.2 mmol of 4H-benzo[d][1,3]dioxin-4-one derivative was added along with 10 mol% DMAP and 1 equiv. DBU in 4 ml acetonitrile. The mixture was kept for stirring at room temperature and to the stirring solution, 1.1 equiv. amine was added drop-wise. The progress of the reaction was monitored using TLC. After the completion of the reaction, acetonitrile was evaporated off under reduced pressure. The reaction mixture was subjected to column chromatography using 100-200 mesh-sized silica as the stationary phase and petether-ethyl acetate mixture as the eluent.

1.4 $^1$H and $^{13}$C NMR spectral data and images of salicylamide derivatives

Synthesis of 3-hydroxy-N-propyl-2-naphthamide (6a): To a 25 ml round bottom flask methyl 2-(2-methoxy-2-oxoethyl)-4-oxo-4H-naphtho[2,3-d][1,3]dioxine-2-carboxylate (0.2 mmol, 66 mg) was added along with DMAP (10 mol%, 2 mg) and DBU (0.2 mmol, 30 mg) in 4 ml acetonitrile. The mixture was kept for stirring at room temperature, and to the stirring solution, n-propylamine (0.22 mmol, 13 mg) was added drop-wise. The progress of the reaction was monitored using TLC. After 8 hrs of reaction, acetonitrile was evaporated off under reduced pressure. The reaction mixture was subjected to column chromatography using 100-200 mesh-sized silica as the stationary phase and petether-ethyl acetate mixture as the eluent. The product 3-hydroxy-N-propyl-2-naphthamide was obtained as a pale-yellow solid in 80% (37 mg).

FT-IR (ATR): $v_{\text{max}} = 3380, 2922, 2858, 1727, 1653, 1586, 1541, 1452$ cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 11.73$ (s, 1H), 7.86 (s, 1H), 7.68 (d, $J = 8.4$ Hz, 1H), 7.61 (d, $J = 8.4$ Hz, 1H), 7.40 (t, $J = 7.2$ Hz, 1H), 7.26- 7.22 (m, 2H), 6.50 (s, 1H), 3.42 (q, $J = 7.2$ Hz, 2H), 1.69- 1.60 (m, 2H), 0.97 (t, $J = 7.2$ Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 169.7, 156.5, 137.0, 128.4$ (2C), 126.8, 126.6, 126.3, 123.9, 117.2, 112.3,
Synthesis of 2-hydroxy-N-isopropylbenzamide (6b): To a 25 ml round bottom flask methyl 2-(2-methoxy-2-oxoethyl)-4-oxo-4H-benzo[d][1,3]dioxine-2-carboxylate (0.2
mmol, 56 mg) was added along with DMAP (10 mol%, 2 mg) and DBU (0.2 mmol, 30 mg) in 4 ml acetonitrile. The mixture was kept for stirring at room temperature, and to the stirring solution, Isopropylamine (0.22 mmol, 13 mg) was added drop-wise. The progress of the reaction was monitored using TLC. After 8 hrs of reaction, acetonitrile was evaporated off under reduced pressure. The reaction mixture was subjected to column chromatography using 100-200 mesh-sized silica as the stationary phase and petether-ethyl acetate mixture as the eluent. The product 2-hydroxy-N-isopropylbenzamide was obtained as a colourless oily liquid in 56% (21 mg).

FT-IR (ATR): $\nu_{\text{max}} = 3370, 2974, 2927, 2861, 1636, 1591, 1539, 1496, 1455, 1366, 1299 \text{ cm}^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta =$ 12.46 (s, 1H), 7.38- 7.32 (m, 2H), 6.97- 6.94 (m, 1H), 6.83- 6.79 (m, 1H), 6.19 (s, 1H), 4.31- 4.22 (m, 1H), 1.26 (d, $J = 6.4 \text{ Hz}$, 6H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta =$ 169.3, 161.6, 134.1, 125.3, 118.6 (2C), 114.5, 41.9, 22.7 (2C) ppm.
Synthesis of N-benzyl-2-hydroxybenzamide (6c): To a 25 ml round bottom flask methyl 2-(2-methoxy-2-oxoethyl)-4-oxo-4H-benzo[d][1,3]dioxine-2-carboxylate (0.2 mmol, 56 mg) was added along with DMAP (10 mol%, 2 mg) and DBU (0.2 mmol, 30 mg) in 4 ml acetonitrile. The mixture was kept for stirring at room temperature, and to the stirring solution, Benzylamine (0.22 mmol, 23.5 mg) was added drop-wise. The progress of the reaction was monitored using TLC. After 8 hrs of reaction, acetonitrile was evaporated off under reduced pressure. The reaction mixture was subjected to column chromatography using 100-200 mesh-sized silica as the stationary phase and petether-ethyl acetate mixture as the eluent. The product N-benzyl-2-hydroxybenzamide was obtained as a white solid in 69% (31 mg).

FT-IR (ATR): ν_{max} = 3370, 3034, 2922, 2854, 1729, 1637, 1594, 1539, 1237 cm^{-1}; \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ = 12.32 (s, 1H), 7.41- 7.29 (m, 6H), 7.25 (m, 1H), 6.99 (d, J= 8.4 Hz, 1H), 6.84-6.80 (m, 1H), 6.61 (s, 1H), 4.63 (d, J= 6 Hz, 2H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ = 169.9, 161.7, 137.5, 134.5,129.0 (2C), 128.0 (3C), 125.4, 118.8 (2C), 114.2, 43.8 ppm.
Synthesis of N-cyclohexyl-3-hydroxy-2-naphthamide (6d): To a 25 ml round bottom flask methyl 2-(2-methoxy-2-oxoethyl)-4-oxo-4H-naphtho[2,3-d][1,3]dioxine-2-carboxylate (0.25 mmol, 82.6 mg) was added along with DMAP (10 mol%, 3 mg) and DBU (0.25 mmol, 38 mg) in 4 ml acetonitrile. The mixture was kept for stirring at room temperature, and to the stirring solution, Cyclohexylamine (0.275 mmol, 27.3 mg) was added drop-wise. The progress of the reaction was monitored using TLC. After 10 hrs of reaction, acetonitrile was evaporated off under reduced pressure. The reaction mixture was subjected to column chromatography using 100-200 mesh-sized silica as the stationary phase and petether-ethyl acetate mixture as the eluent. The product N-cyclohexyl-3-hydroxy-2-naphthamide was obtained as a pale-yellow solid in 51% (34 mg).

\[
\text{FT-IR (ATR): } \nu_{\text{max}} = 3351, 3056, 2928, 2855, 1710, 1580, 1533, 1453, 1305, 1226 \text{ cm}^{-1}; \ \text{^1H NMR (400 MHz, CDCl}_3) \ \delta = 11.89 (s, 1H), 7.91 (s, 1H), 7.72 (d, J= 8.4 Hz, 1H), 7.65 (d, J= 8.4 Hz, 1H), 7.47-7.43 (m, 1H), 7.30-7.26 (m, 2H), 6.44 (s, 1H), 4.05-3.96 (m, 1H), 2.09-2.04 (m 2H), 1.82-1.65 (m, 4H), 1.49-1.19 (m, 4H) ppm; \ \text{^13C NMR (100 MHz, CDCl}_3) \ \delta = 169.0, 156.9, 137.0, 128.5, 128.48, 126.8, 126.6, 126.3, 123.9, 117.4, 112.4, 49.1, 33.1 (2C), 25.5, 24.9 (2C) ppm.\]
1.5 $^1$H and $^{13}$C NMR spectral data of isolated intermediate dimethyl 2-((2 hydroxybenzoyl)oxy)maleate

Following the general procedure, the reaction between dimethyl acetylene dicarboxylate (0.5 mmol, 71.0 mg) with 2-hydroxybenzoic acid (0.6 mmol, 82.8 mg) in presence of NaHCO$_3$ (0.6 mmol, 50.4 mg) and additive CuI (0.5 mmol, 95.2 mg) in acetonitrile at room temperature for 24 h afforded only the 1:1 linear adduct dimethyl 2-((2 hydroxybenzoyl)oxy)maleate 7aa as a viscous oil (25 mg, 18%). The cyclized 1,3-benzoxazinone 6aa was not at all observed at room temperature. However, under the standard condition – in acetonitrile at 80 °C – 6aa formation gradually increases with time.

$^1$H NMR (400 MHz, CDCl$_3$) δ = 9.97 (s, 1H), 7.99- 7.97 (m, 1H), 7.55- 7.51 (m, 1H), 7.03- 7.00 (m, 1H), 6.97- 6.93 (m, 1H), 6.80 (s, 1H), 3.86 (s, 3H), 3.72 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ = 167.3, 163.1, 162.1, 161.4, 146.2, 137.1, 130.9, 119.9, 117.9, 117.86, 111.0, 53.5, 52.4 ppm.
The NMR data of the intermediate obtained is in good agreement with the NMR data reported by Ming-Jin Fan et al. given below.² *(Tetrahedron, 2006, 62, 6782–6791).*

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta = 9.99\) (s, 1H), 6.94–8.01 (m, 4H), 6.82 (s, 1H), 3.88 (s, 3H), 3.74 (s, 3H). \(^1\)C NMR (75 MHz, CDCl\(_3\)) \(\delta = 167.1, 162.9, 162.0, 161.3, 146.0, 136.9, 130.8, 119.7, 117.8, 110.9, 53.4, 52.3.\)
1.6 Single Crystal X-ray Data of the Compound 3da

\[
\text{Compound 3da}
\]

CCDC No: 2084126
Crystal data and structure refinement for Compound 3da – CCDC No: 2084126

Identification code: shelx
Empirical formula: C_{17} H_{14} O_{7}
Formula weight: 330.28
Temperature: 296(2) K
Wavelength: 0.71073 Å
Crystal system, space group: Monoclinic, P 21/c
Unit cell dimensions:
\[ a = 6.2678(7) \ \text{Å} \quad \alpha = 90 \ \text{deg.} \]
\[ b = 13.2735(14) \ \text{Å} \quad \beta = 90.548(4) \ \text{deg.} \]
\[ c = 18.564(2) \text{ Å} \quad \text{gamma} = 90 \text{ deg.} \]

Volume \[ 1544.4(3) \text{ Å}^3 \]

\[ Z, \text{ Calculated density} \quad 4, \quad 1.420 \text{ mg/m}^3 \]

Absorption coefficient \[ 0.112 \text{ mm}^{-1} \]

\[ F(000) \quad 688 \]

Crystal size \[ 0.350 \times 0.350 \times 0.300 \text{ mm} \]

Theta range for data collection \[ 2.194 \text{ to } 28.463 \text{ deg.} \]

Limiting indices \[ -7 \leq h \leq 8, -15 \leq k \leq 17, -23 \leq l \leq 24 \]

Reflections collected / unique \[ 12619 / 3793 \quad [R(\text{int}) = 0.0272] \]

Completeness to theta = 25.242 \[ 99.7 \% \]

Absorption correction \quad Semi-empirical from equivalents

Max. and min. transmission \[ 0.967 \text{ and } 0.962 \]

Refinement method \quad Full-matrix least-squares on \( F^2 \)

Data / restraints / parameters \[ 3793 / 0 / 219 \]

Goodness-of-fit on \( F^2 \) \[ 0.974 \]

Final R indices \( [I>2\sigma(I)] \) \[ R1 = 0.0463, \quad wR2 = 0.1311 \]

R indices (all data) \[ R1 = 0.0658, \quad wR2 = 0.1492 \]

Extinction coefficient \quad n/a

Largest diff. peak and hole \[ 0.223 \text{ and } -0.253 \text{ e.A}^{-3} \]

References


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