Supporting Information

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

Rasmi P. Bhaskaran, Kalinga H Nayak and Beneesh P. Babu*[a]

[a] Department of Chemistry, National Institute of Technology Karnataka (NITK), Surathkal 575025, Mangalore, INDIA. E-mail: pbbeneesh@nitk.edu.in

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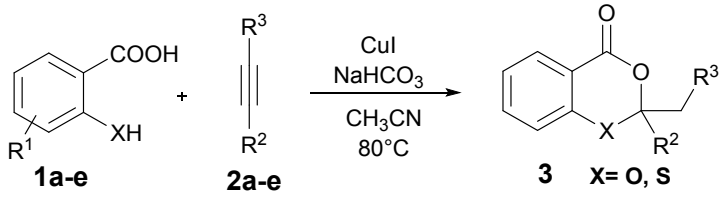
1. Experimental section

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^{TM} 400 MHz spectrometer and JEOL JNM-ECZ 400/L1 high resolution multinuclear FT- NMR spectrometer with tetramethyl silane (TMS; δ 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.

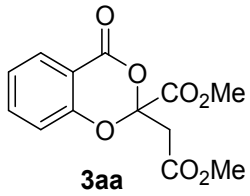
1.1 General procedure for the synthesis of 4H-benzo[d][1,3]dioxin-4-one derivatives



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.

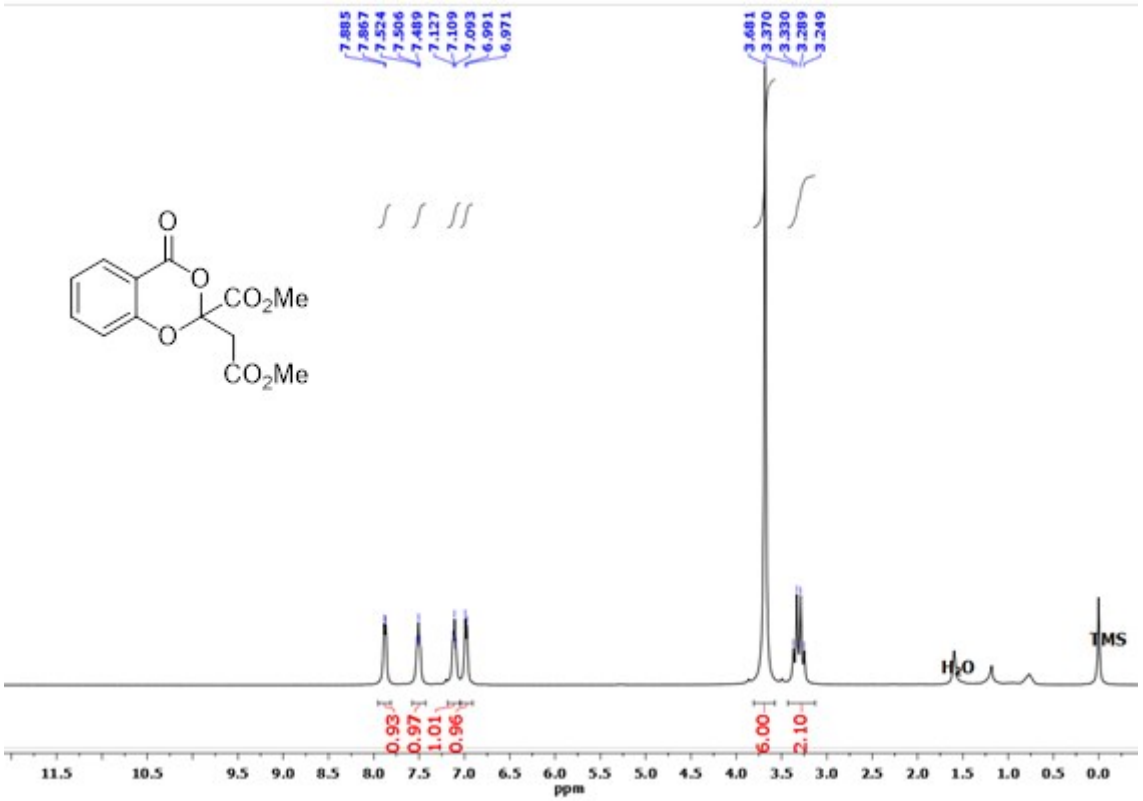
1.2 ^{1}H and ^{13}C NMR spectra of 4H-benzo[d][1,3]dioxin-4-one derivatives

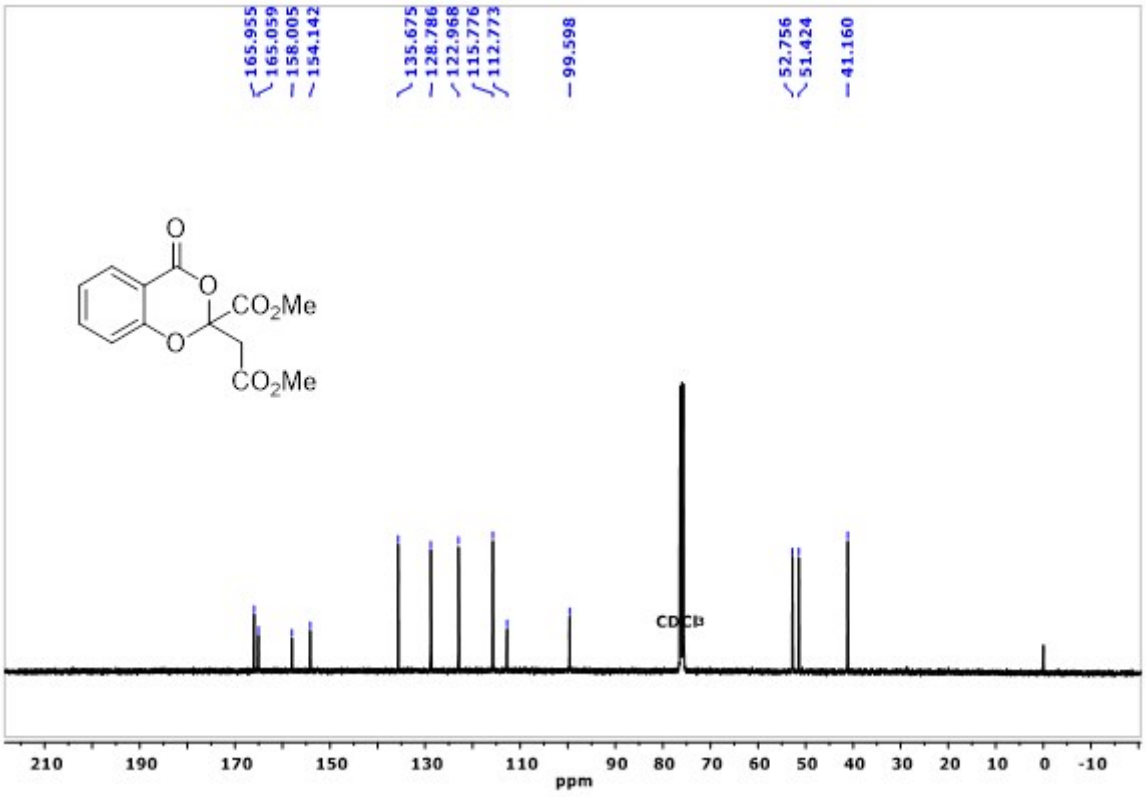
Methyl 2-(2-methoxy-2-oxoethyl)-4-oxo-4H-benzo[d][1,3]dioxine-2-carboxylate (3aa) : Following the general procedure, the reaction between dimethyl acetylene dicarboxylate (0.5 mmol, 71.0 mg) with 2-hydroxybenzoic acid (0.6 mmol, 82.8 mg) in presence of $NaHCO_3$ (0.6 mmol, 50.4 mg) and additive CuI (0.5 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.



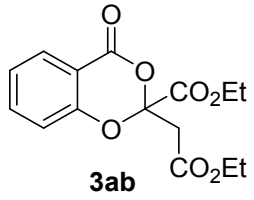
3aa

FT-IR (ATR): ν_{max}= 2957, 2922, 1757, 1612, 1509, 1467, 1440, 1366, 1302 cm^{-1} ; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 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, $CDCl_3$) δ = 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.



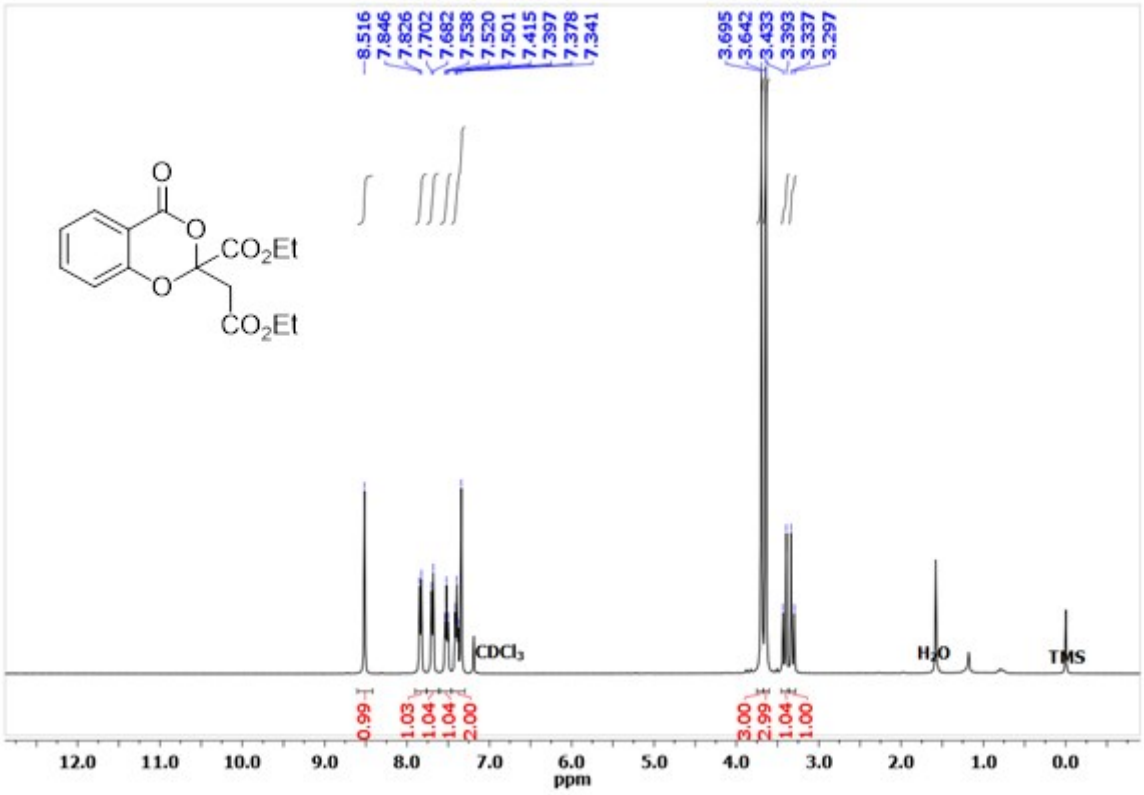


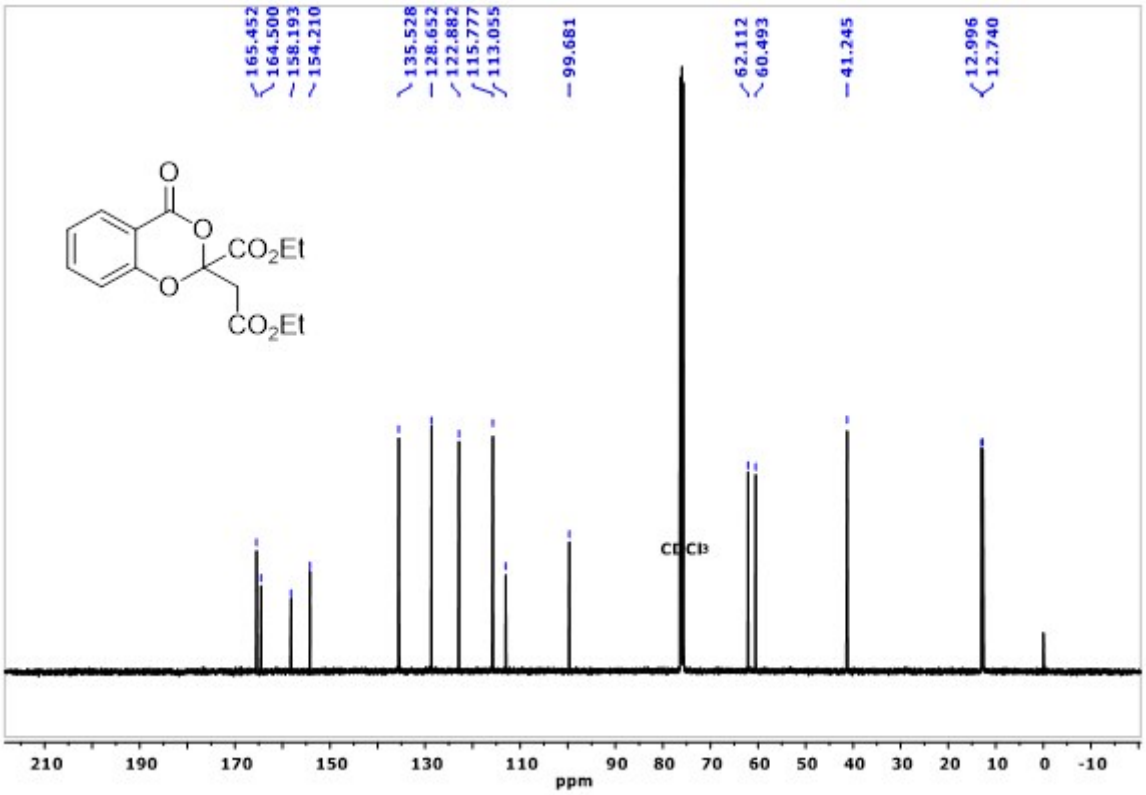
Ethyl 2-(2-ethoxy-2-oxoethyl)-4-oxo-4H-benzo[d][1,3]dioxine-2-carboxylate (3ab): Following the general procedure, the reaction between Diethyl acetylene dicarboxylate (0.5 mmol, 85 mg) with 2-hydroxybenzoic acid (0.6 mmol, 82.8 mg) in presence of $NaHCO_3$ (0.6 mmol, 50.4 mg) and additive CuI (0.5 mmol, 95.2 mg) in acetonitrile at 80 °C, yielded the desired product Ethyl 2-(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).



3ab

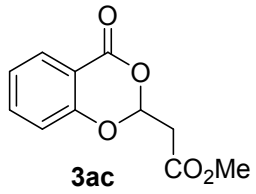
FT-IR (ATR): ν_{max}= 2989, 1739, 1610, 1472, 1382, 1300, 1190, 1075, 1013 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.87 (d, *J*= 8 Hz, 1H), 7.52- 7.48 (m, 1H), 7.12- 7.08 (m, 1H), 6.98 (d, *J*= 8.4 Hz, 1H), 4.17- 4.09 (m, 4H), 3.34 (d, *J*= 15.6, 1H), 3.24 (d, *J*= 15.6, 1H), 1.21 (t, 8 Hz, 3H), 1.08 (t, *J*= 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{15}H_{16}O_7$ $[M+Na]^+$ 331.0788 found 331.0800.





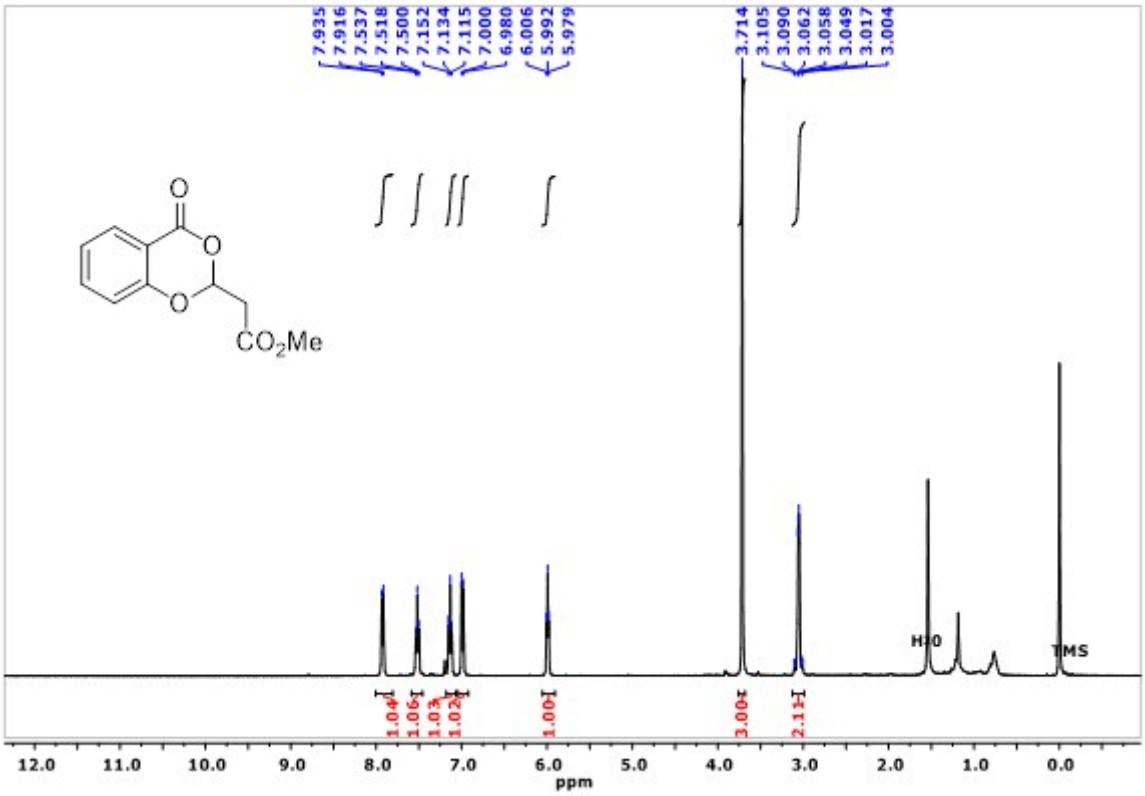
methyl 2-(4-oxo-4H-benzo[d][1,3]dioxin-2-yl)acetate (3ac): Following the general procedure, the reaction between methyl propiolate (0.5 mmol, 42 mg) with 2-hydroxybenzoic acid (0.6 mmol, 82.8 mg) in presence of $NaHCO_3$ (0.6 mmol, 50.4 mg)

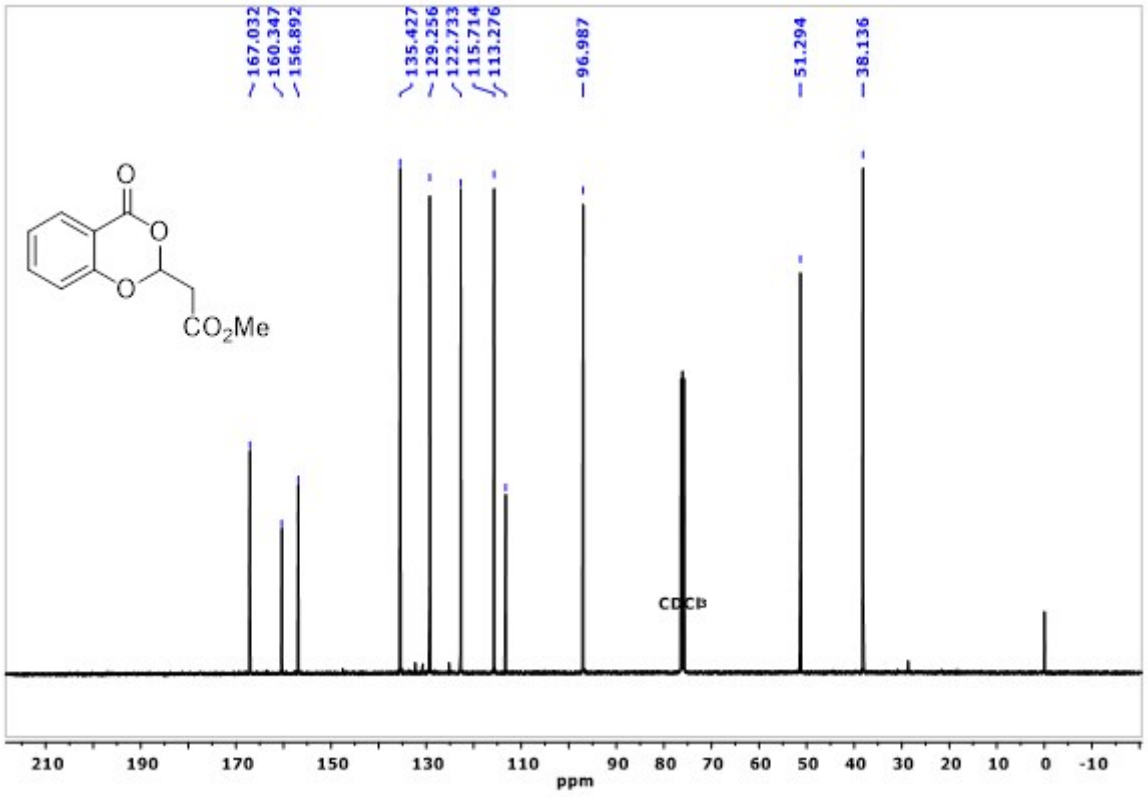
and additive CuI (0.5 mmol, 95.2 mg) in acetonitrile at 80 °C, yielded the desired product methyl 2-(4-oxo-4H-benzo[d][1,3]dioxin-2-yl)acetate as a thick viscous liquid in 63% yield (70.1 mg).



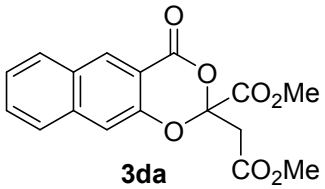
3ac

FT-IR (ATR): ν_{max}= 2954, 2922, 1739, 1612, 1586, 1472, 1339, 1401, 1302, 1232, 1200, 1129 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92 (d, *J*= 7.6, 1H), 7.53- 7.50 (m, 1H), 7.15- 7.11 (m, 1H), 6.99 (d, *J*= 8 Hz, 1H), 5.98 (t, *J*= 5.6 Hz, 1 H), 3.71 (s, 3H), 3.11-3.0 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.0, 160.3, 156.9, 135.4, 129.3, 122.7, 115.7, 113.3, 96.9, 51.3, 38.1 ppm; HRMS (ESI) calcd for $C_{11}H_{10}O_5$ $[M+Na]^+$ 245.0420 found 245.0427.



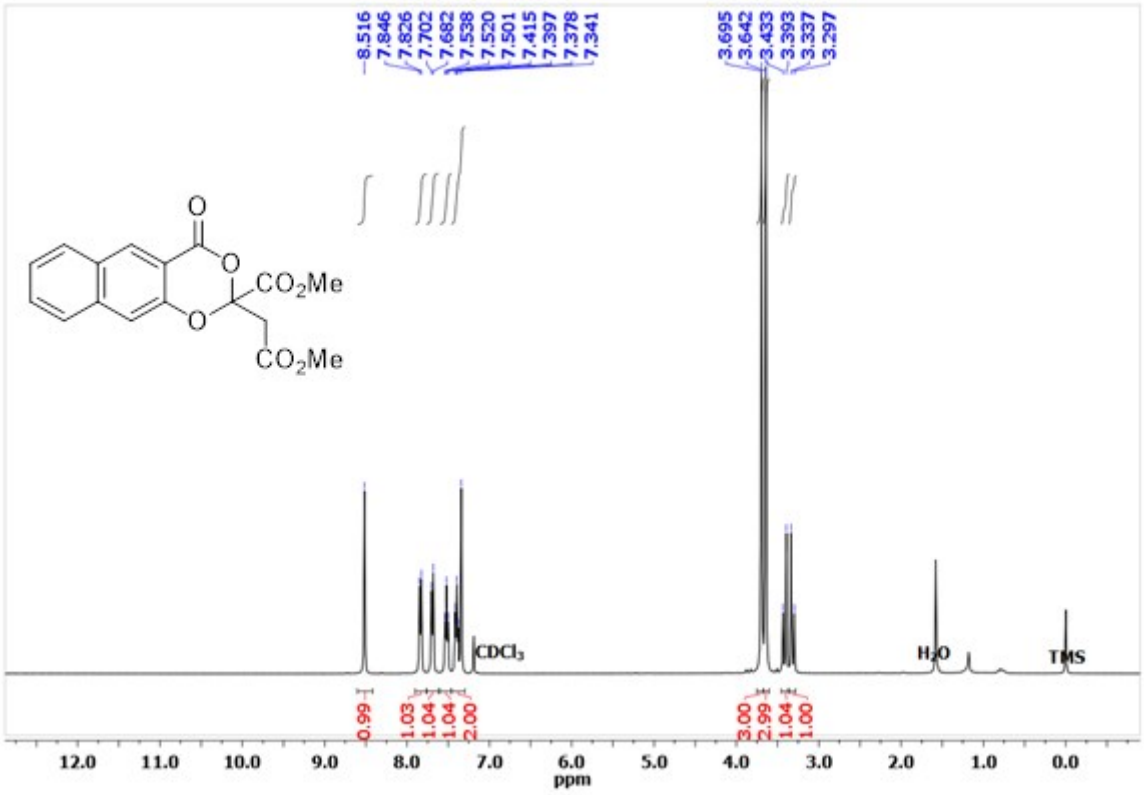


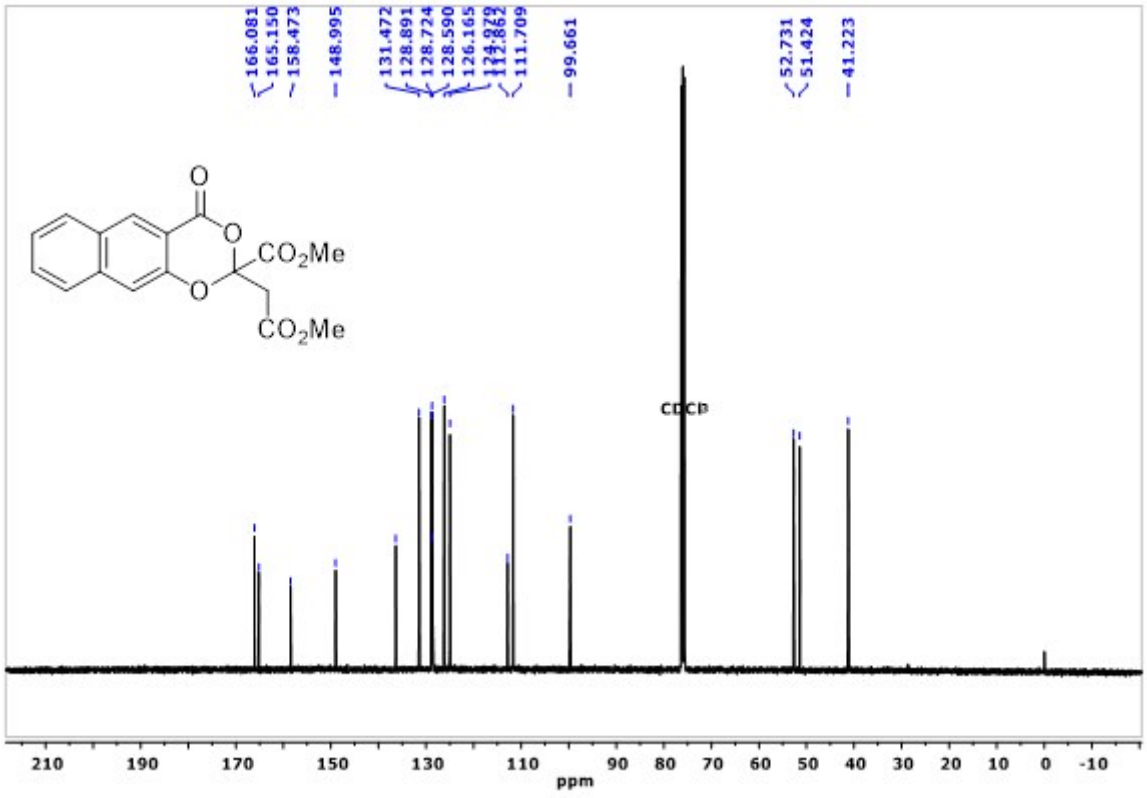
methyl 2-(2-methoxy-2-oxoethyl)-4-oxo-4H-naphtho[2,3-d][1,3]dioxine-2-carboxylate (3da): Following the general procedure, the reaction between dimethylacetylene dicarboxylate (0.5 mmol, 71 mg) with 2-hydroxynaphthoic acid (0.6 mmol, 112.8 mg) in presence of $NaHCO_3$ (0.6 mmol, 50.4 mg) and additive 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.



3da

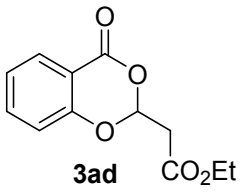
FT-IR (ATR): ν_{max}= 2956, 2922, 1749, 1636, 1607, 1302, 1246, 1193, 1069, 1010 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.52 (s, 1H), 7.84 (d, *J*= 8 Hz, 1H), 7.69 (d, *J*= 8 Hz, 1H), 7.54- 7.50 (m, 1H), 7.42- 7.34 (m, 2H), 3.69 (s, 3H), 3.64 (s, 3H), 3.41 (d, *J*= 16 Hz, 1H), 3.31 (d, *J*= 16 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 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.





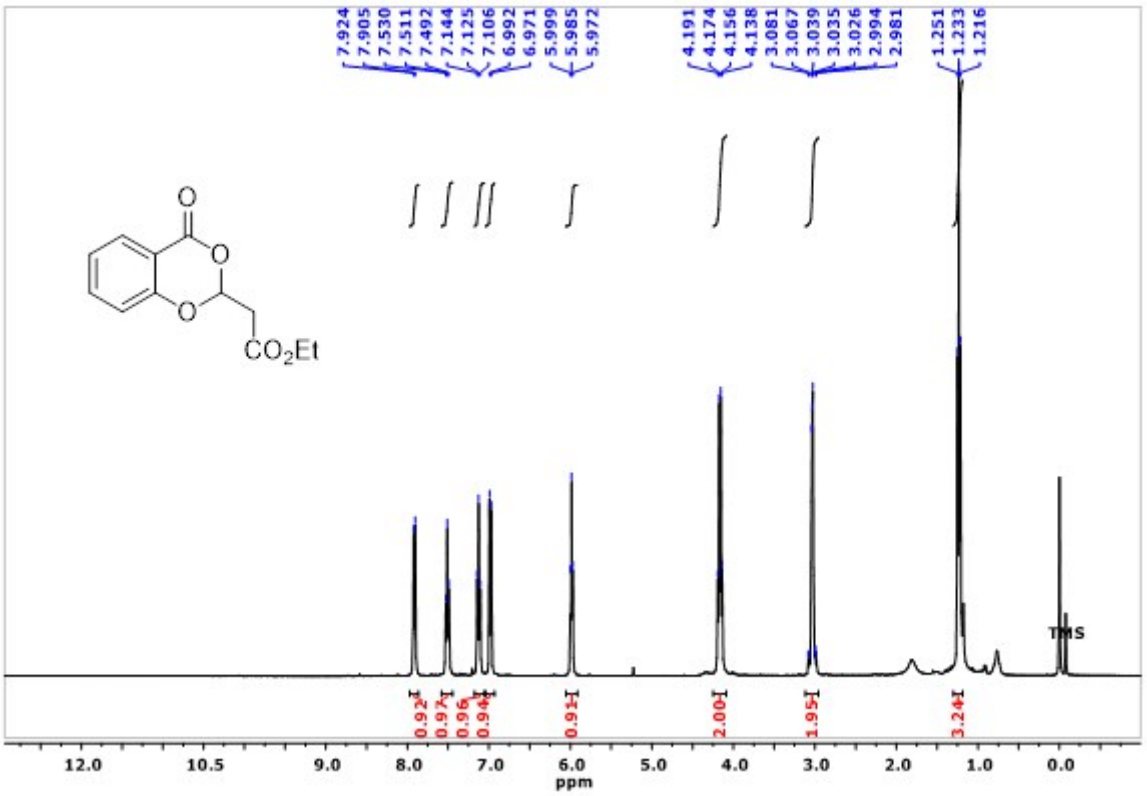
Ethyl 2-(4-oxo-4H-benzo[d][1,3]dioxin-2-yl)acetate (3ad): Following the general procedure, the reaction between ethyl propiolate (0.5 mmol, 49 mg) with 2-hydroxybenzoic acid (0.6 mmol, 82.8 mg) in presence of $NaHCO_3$ (0.6 mmol, 50.4 mg) and additive CuI

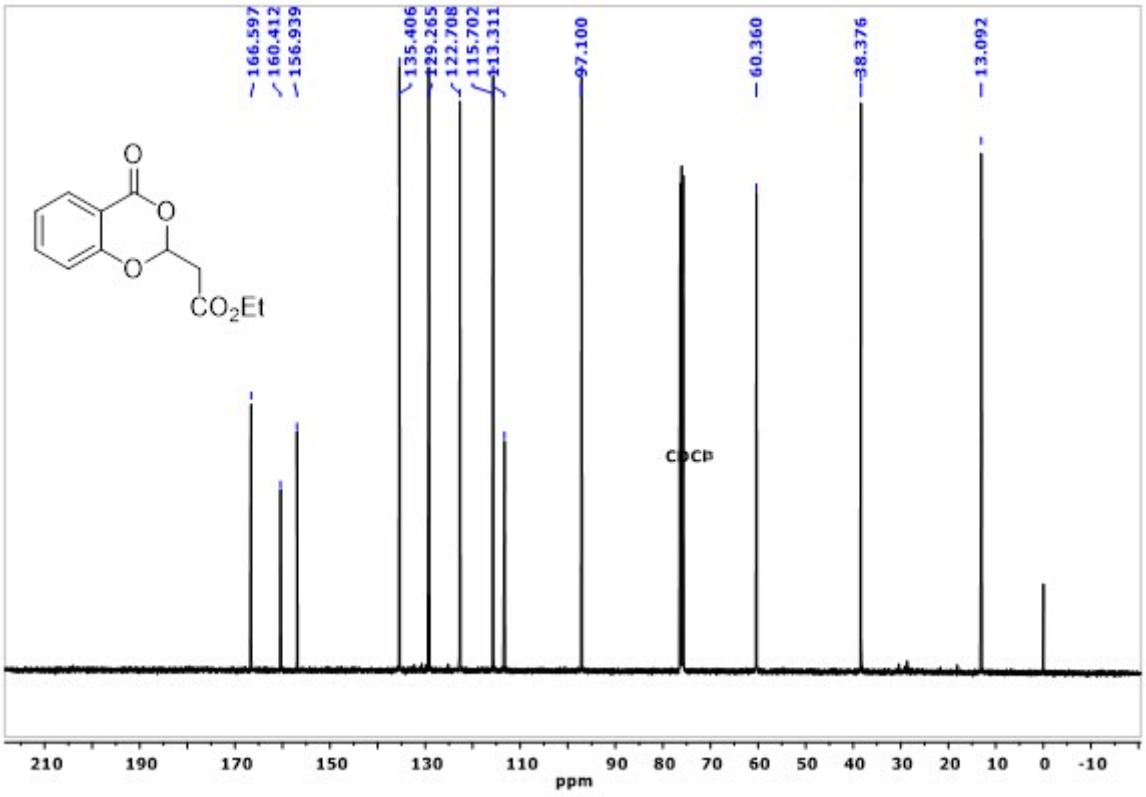
(0.5 mmol, 95.2 mg) in acetonitrile at 80 °C, yielded the desired product ethyl 2-(4-oxo-4H-benzo[d][1,3]dioxin-2-yl)acetate as a thick viscous liquid in 73% yield (85.8 mg).



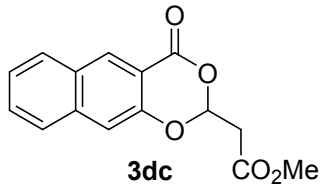
3ad

FT-IR (ATR): ν_{max}= 2926, 1738, 1612, 1586, 1472, 1411, 1302, 1234, 1186, 1129, 1023 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 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, $CDCl_3$) δ = 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.

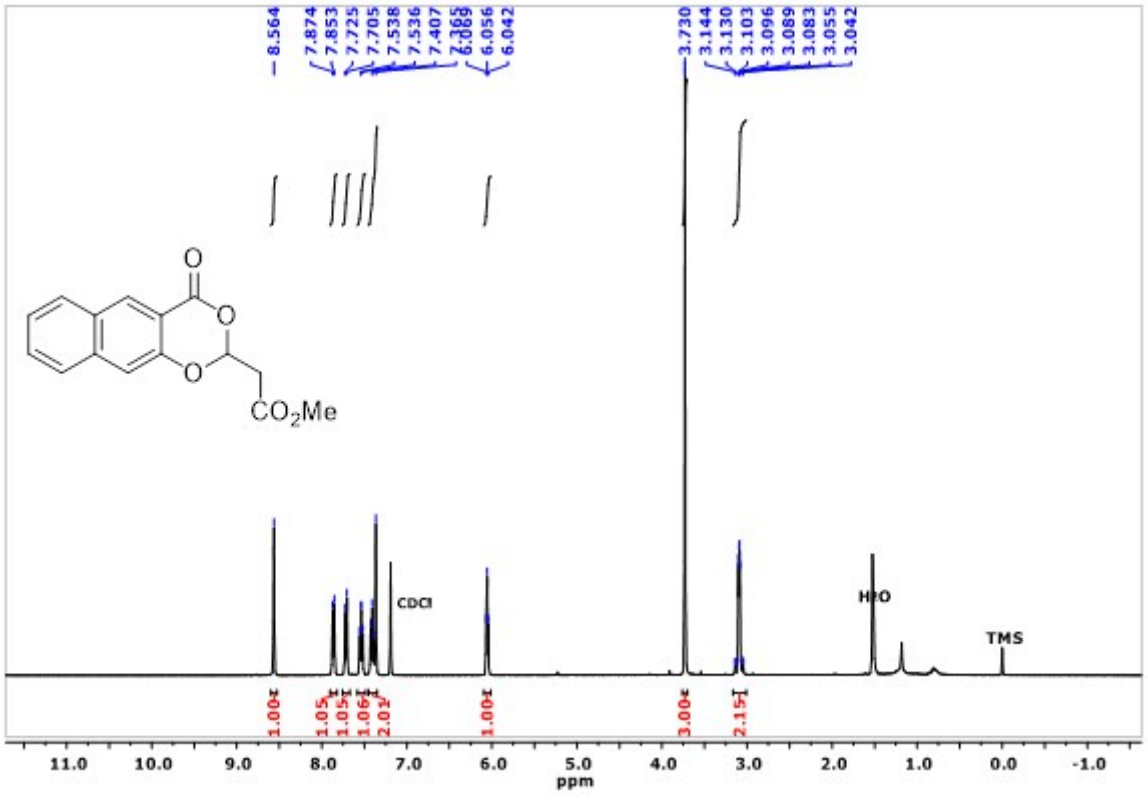


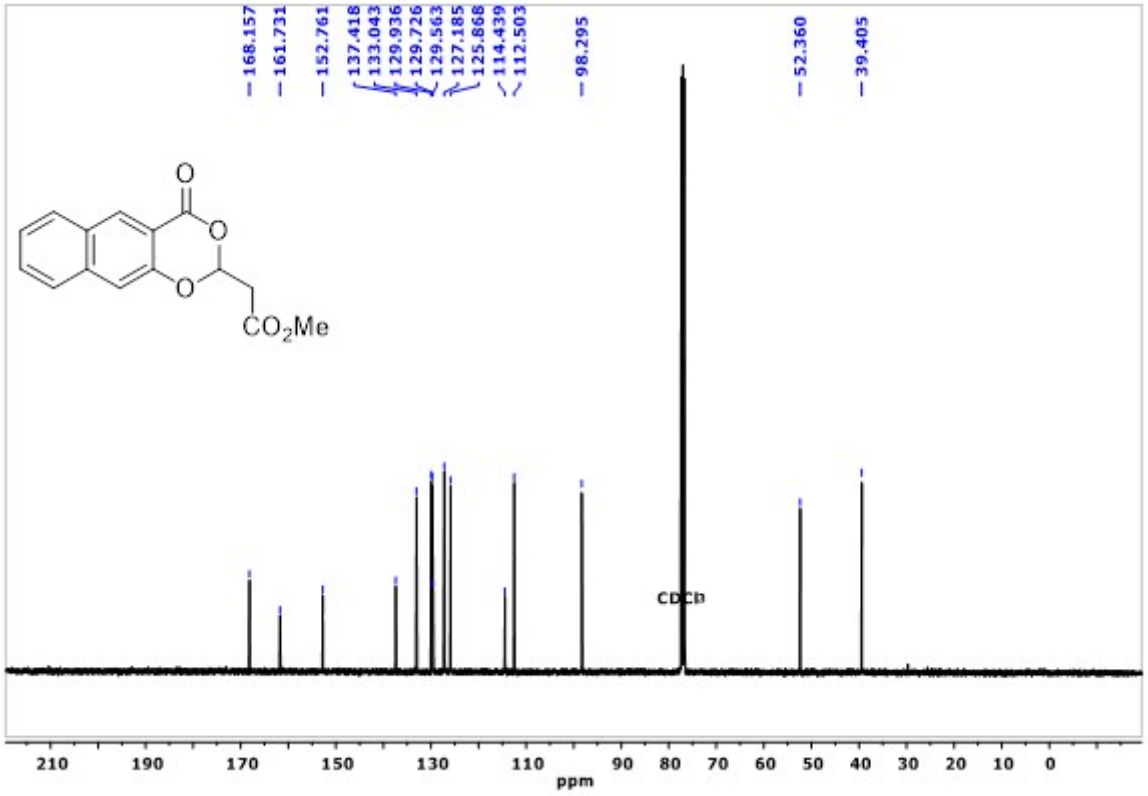


methyl 2-(4-oxo-4H-naphtho[2,3-d][1,3]dioxin-2-yl)acetate (3dc): Following the general procedure, the reaction between methyl propiolate (0.5 mmol, 42 mg) with 2-hydroxynaphthoic acid (0.6 mmol, 112.8 mg)) in presence of $NaHCO_3$ (0.6 mmol, 50.4 mg) and additive CuI (0.5 mmol, 95.2 mg) in acetonitrile 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.



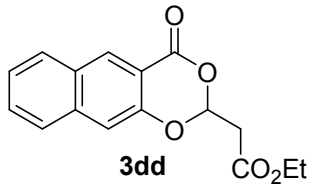
FT-IR (ATR): ν_{max}= 2956, 2922, 2853, 1742, 1636, 1607, 1577, 1505, 1347, 1247 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.56 (s, 1H), 7.86 (d, J= 8.4 Hz, 1H), 7.77 (d, J= 8 Hz, 1H), 7.56- 7.52 (m, 1H), 7.43- 7.36 (m, 2H), 6.05 (t, J= 5.2 Hz, 1H), 3.73 (s, 3H), 3.14- 3.04 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 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.





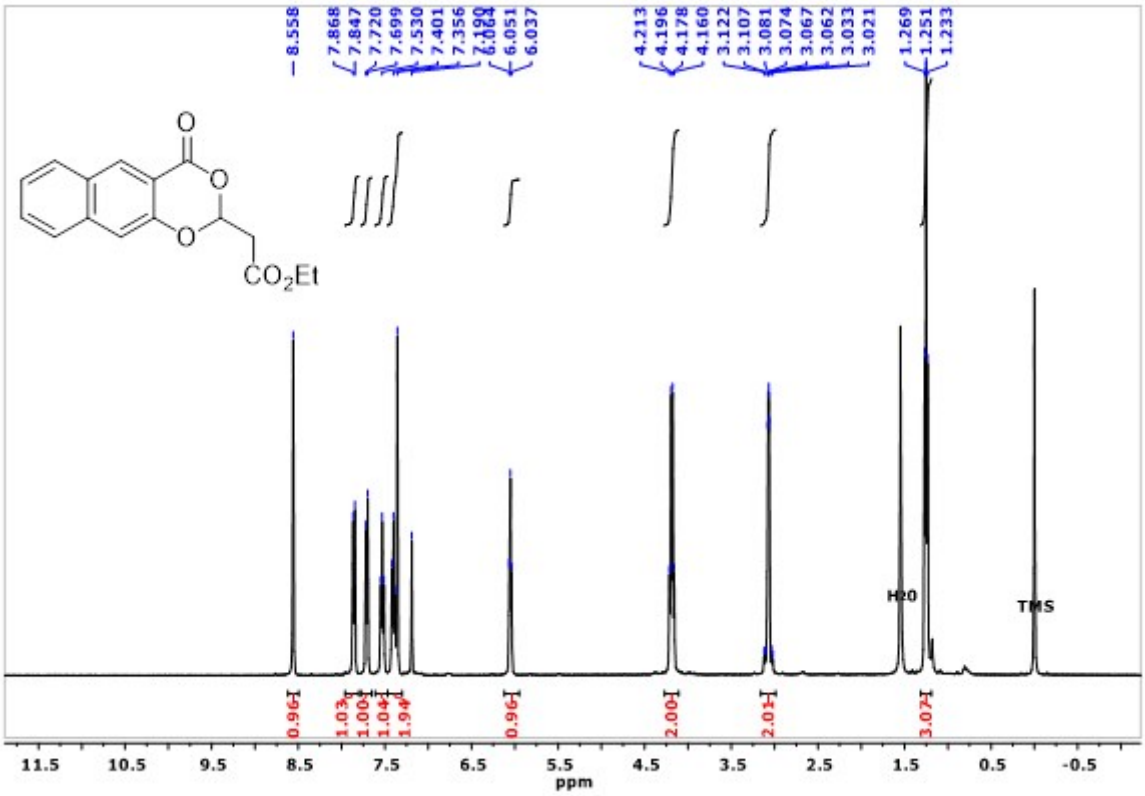
Ethyl 2-(4-oxo-4H-naphtho[2,3-d][1,3]dioxin-2-yl)acetate (3dd): Following the general procedure, the reaction between ethyl propiolate (0.5 mmol, 49 mg) with 2-hydroxynaphthoic acid (0.6 mmol, 112.8 mg)) in presence of $NaHCO_3$ (0.6 mmol, 50.4 mg) and additive CuI (0.5 mmol, 95.2 mg) in acetonitrile at 80 °C, yielded the desired

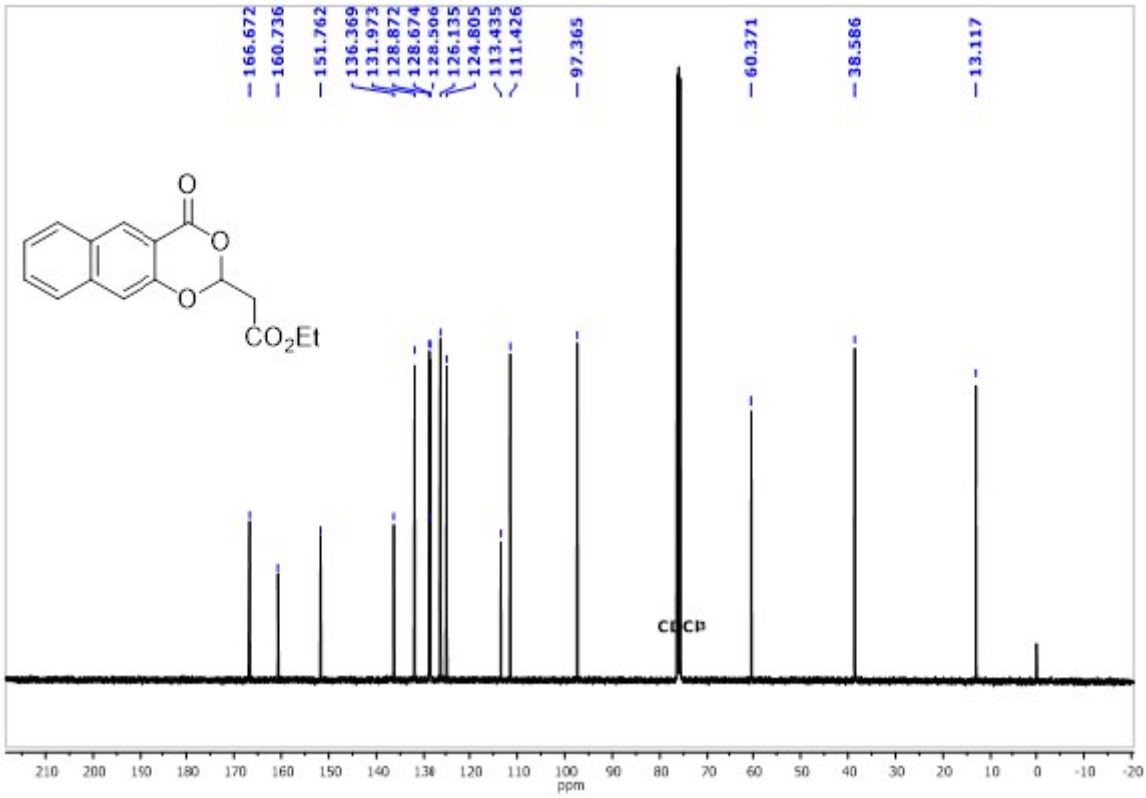
product ethyl 2-(4-oxo-4H-naphtho[2,3-d][1,3]dioxin-2-yl)acetate as a white solid in 65% yield (92.8 mg). Melting point 106-108°C.



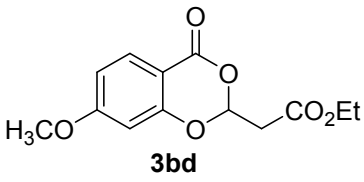
3dd

FT-IR (ATR): ν_{max}= 2923, 2860, 2853, 1735, 1635, 1575, 1505, 1475, 1346, 1188 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 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, $CDCl_3$) δ = 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.



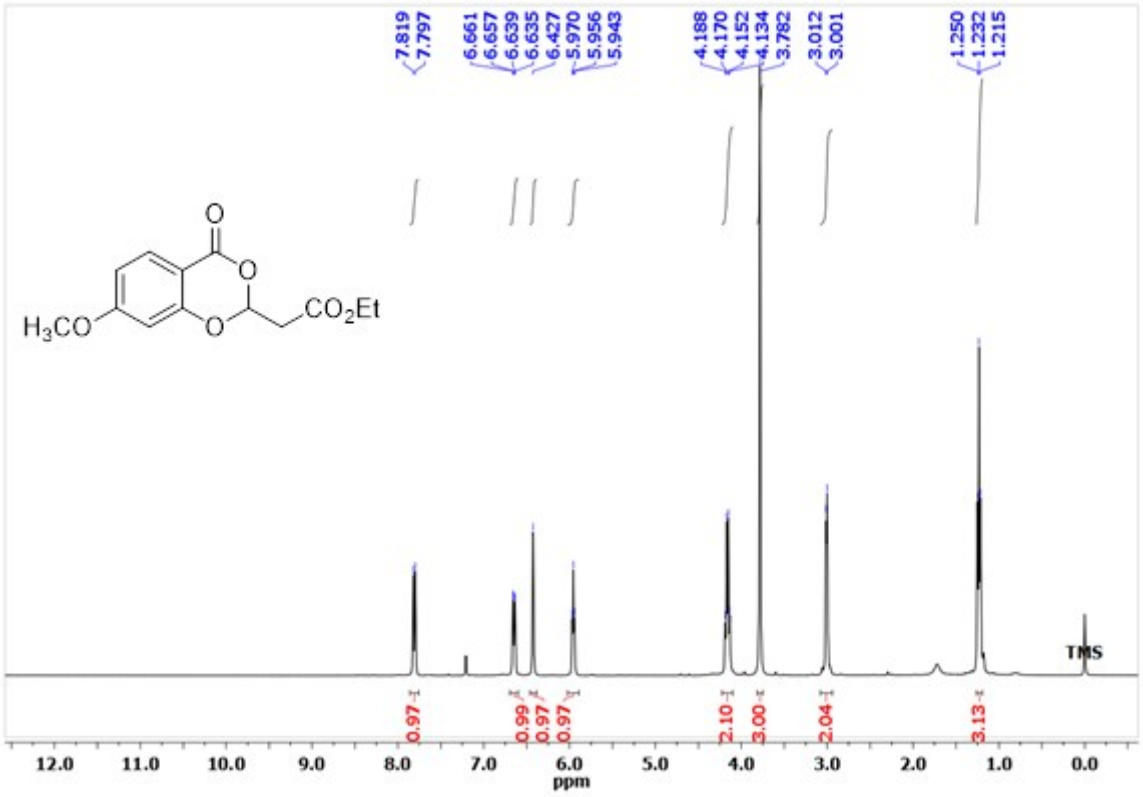


Ethyl 2-(7-methoxy-4-oxo-4H-benzo[d][1,3]dioxin-2-yl)acetate (3bd): Following the general procedure, the reaction between ethyl propiolate (0.5 mmol, 49 mg) with 2-hydroxy-4-methoxybenzoic acid (0.6 mmol, 100 mg)) in presence of $NaHCO_3$ (0.6 mmol, 50.4 mg) and additive CuI (0.5 mmol, 95.2 mg) in acetonitrile 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).



3bd

FT-IR (ATR): ν_{max}= 2924, 2853, 1736, 1615, 1498, 1454, 1380, 12254, 1158, 1119 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 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, $CDCl_3$) δ = 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.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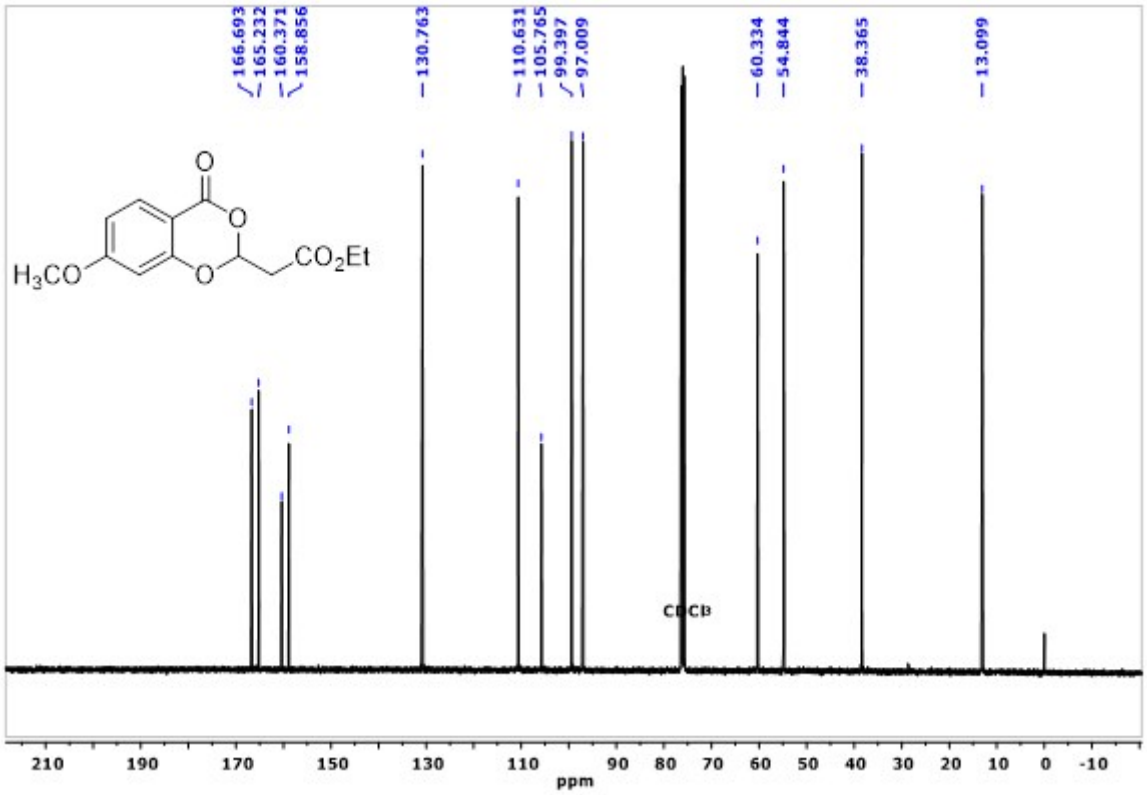
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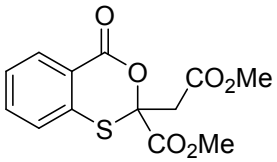
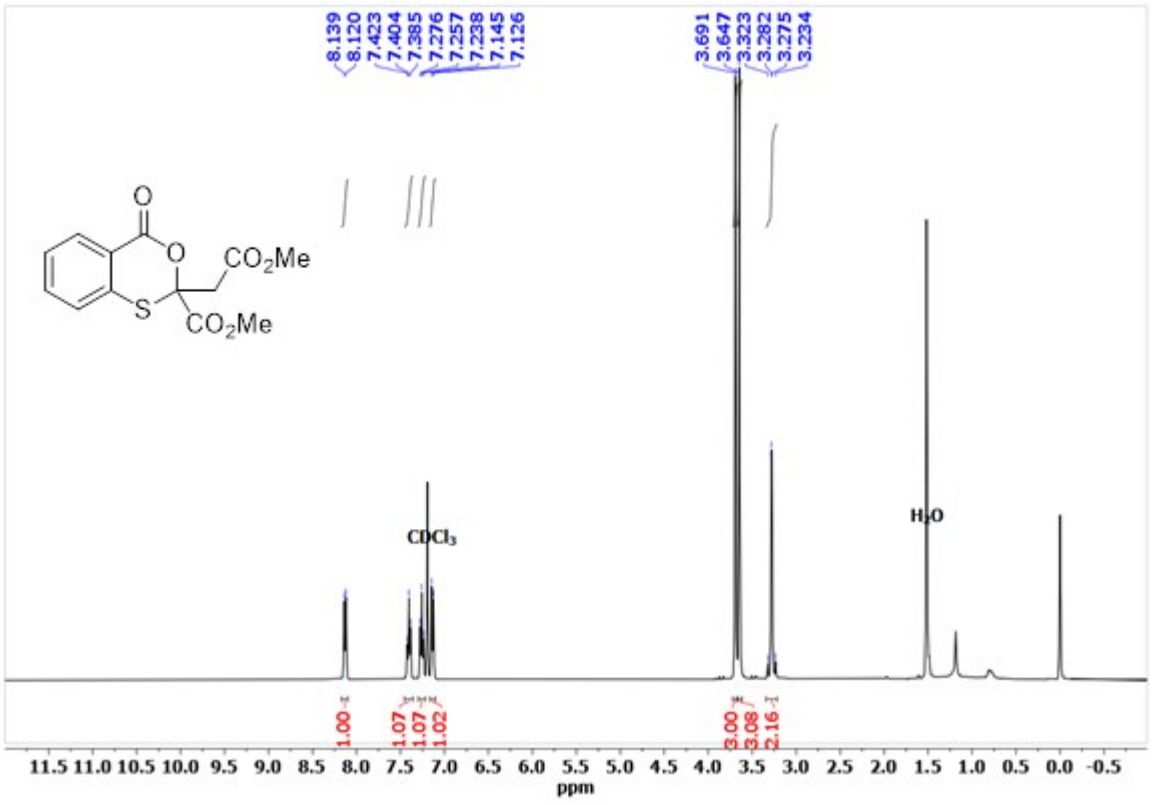
CDCl3
ppm

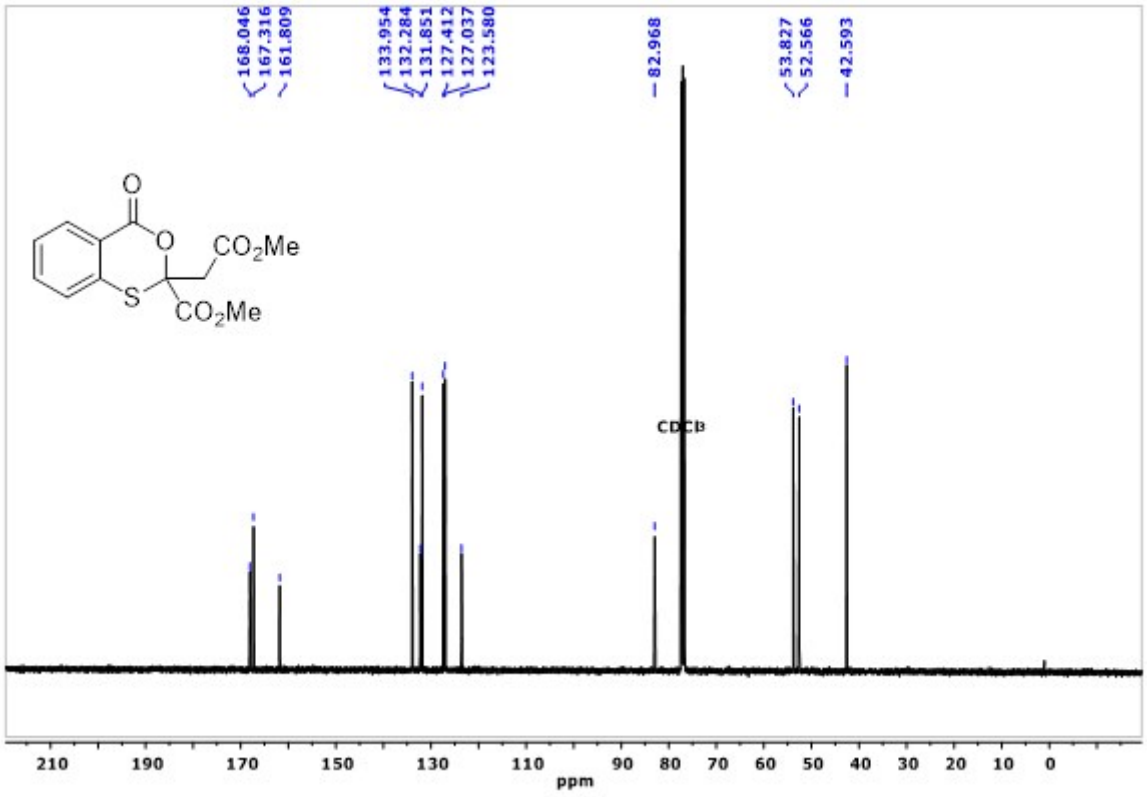
Methyl 2-(2-methoxy-2-oxoethyl)-4-oxo-4H-benzo[d][1,3]oxathiine-2-carboxylate (3ea): Following the general procedure, the reaction between dimethyl acetylene dicarboxylate (0.5 mmol, 71 mg) with 2-mercaptobenzoic acid (0.6 mmol, 92.5 mg)) in presence of $NaHCO_3$ (0.6 mmol, 50.4 mg) and additive CuI (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.



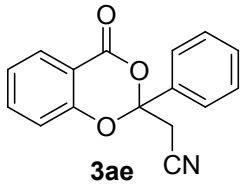
3ea

FT-IR (ATR): ν_{max}= 2955, 1735, 1438, 1403, 1283, 1204, 1139, 1061 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 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, $CDCl_3$) δ = 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 $C_{13}H_{12}O_6S$ $[M+Na]^+$ 319.0247 found 319.0261.



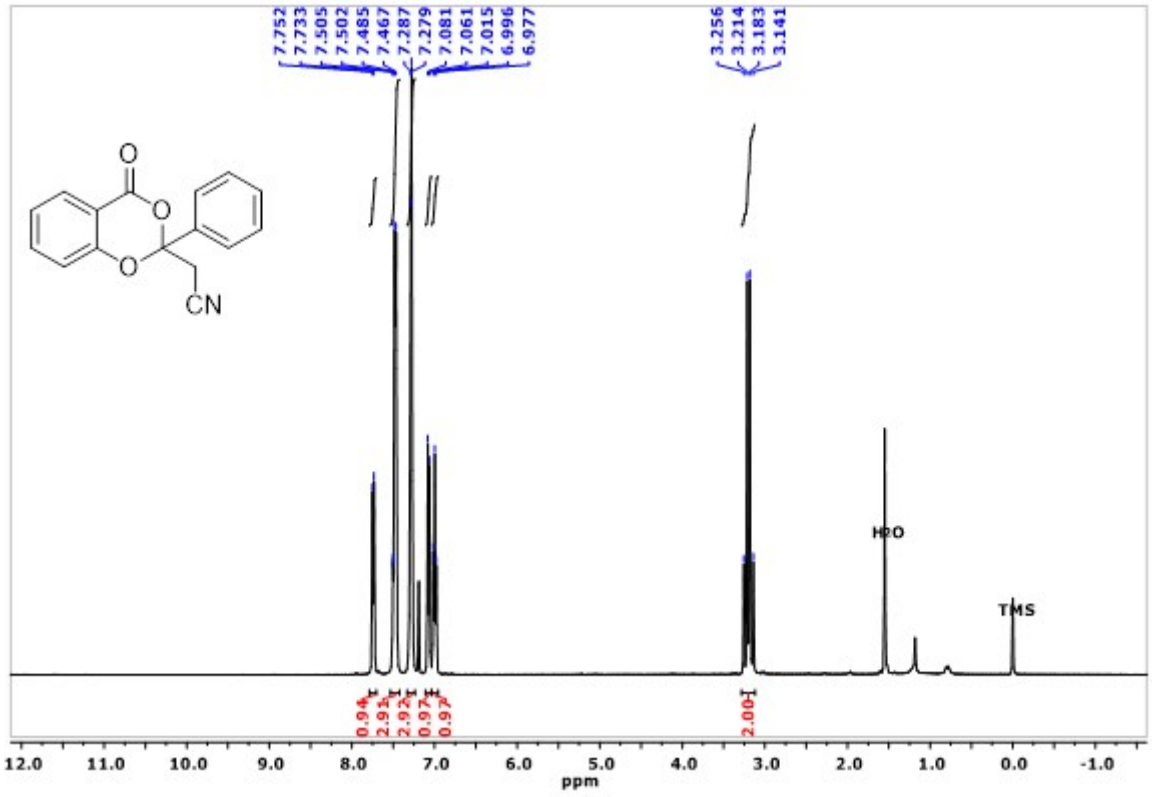


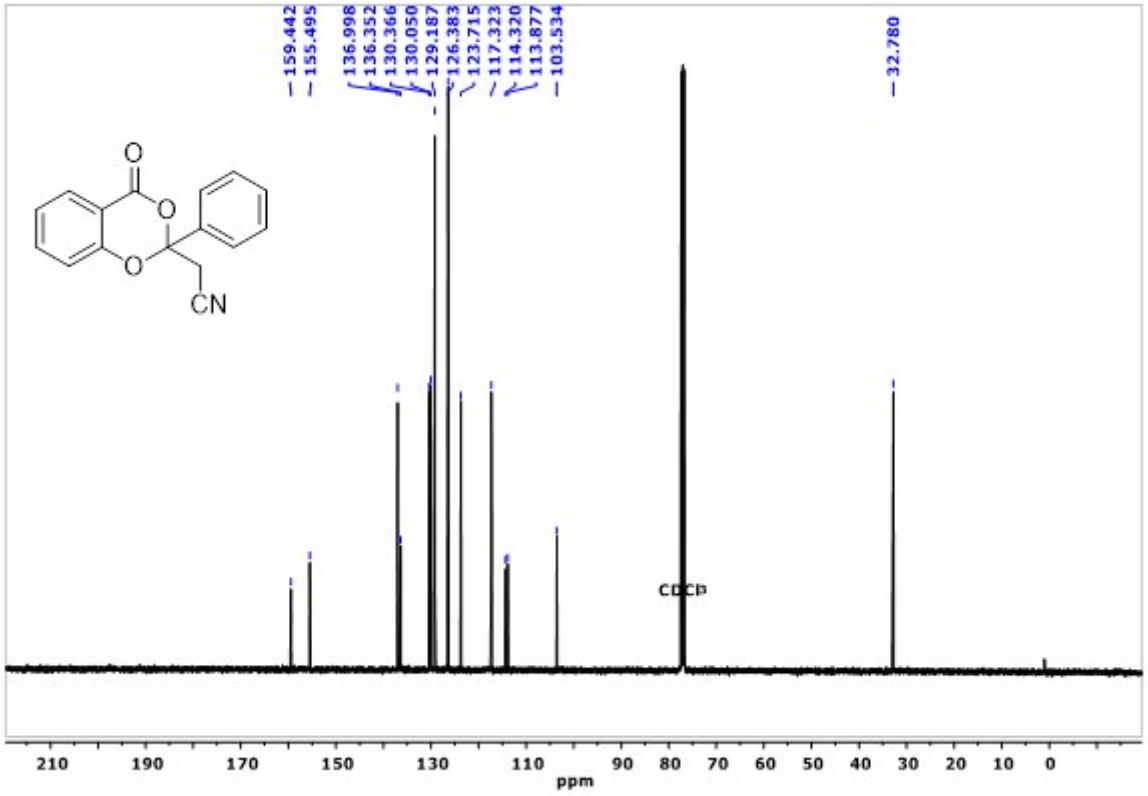
2-(4-oxo-2-phenyl-4H-benzo[d][1,3]dioxin-2-yl)acetonitrile (3ae): Following the general procedure, the reaction between 3-phenylpropiolonitrile (0.5 mmol, 63.5 mg) with 2-hydroxy benzoic acid (0.6 mmol, 82.8 mg)) in presence of $NaHCO_3$ (0.6 mmol, 50.4 mg) and additive CuI (0.5 mmol, 95.2 mg) in acetonitrile 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.



3ae

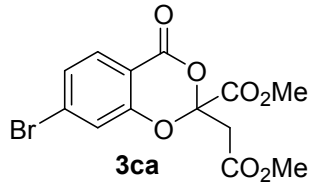
FT-IR (ATR): ν_{max}= 2954, 2923, 2255, 1749, 1612, 1590, 1479, 1466, 1450, 1302, 1089, 1028cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.74 (d, J= 7.6 Hz, 1H), 7.51- 7.47 (m, 3H), 7.32- 7.27 (m, 3H), 7.07 (d, J= 8 Hz, 1H), 6.99 (t, J= 7.6 Hz, 1H), 3.26- 3.14 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 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.





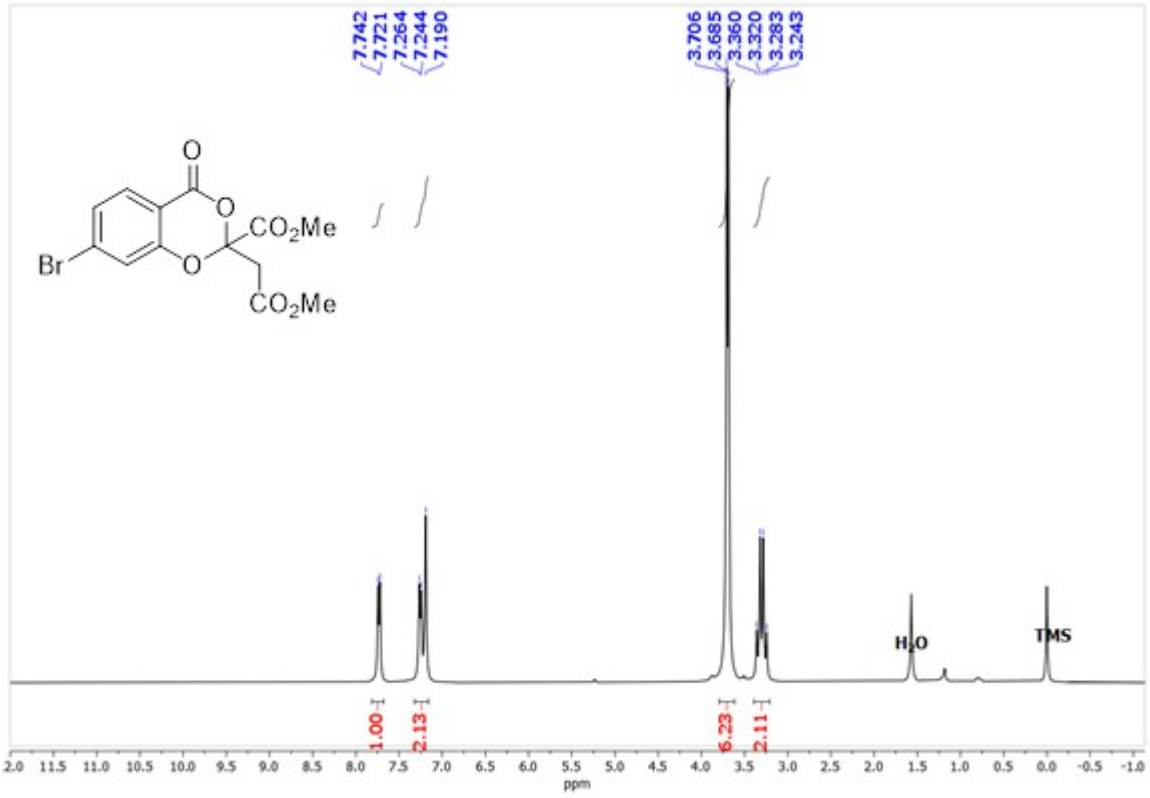
methyl 7-bromo-2-(2-methoxy-2-oxoethyl)-4-oxo-4H-benzo[d][1,3]dioxine-2-carboxylate (3ca): Following the general procedure, the reaction between dimethyl acetylene dicarboxylate (0.5 mmol, 71mg) with 4-bromo-2-hydroxybenzoic acid (0.6 mmol, 130 mg)) in presence of $NaHCO_3$ (0.6 mmol, 50.4 mg) and additive CuI (0.5 mmol,

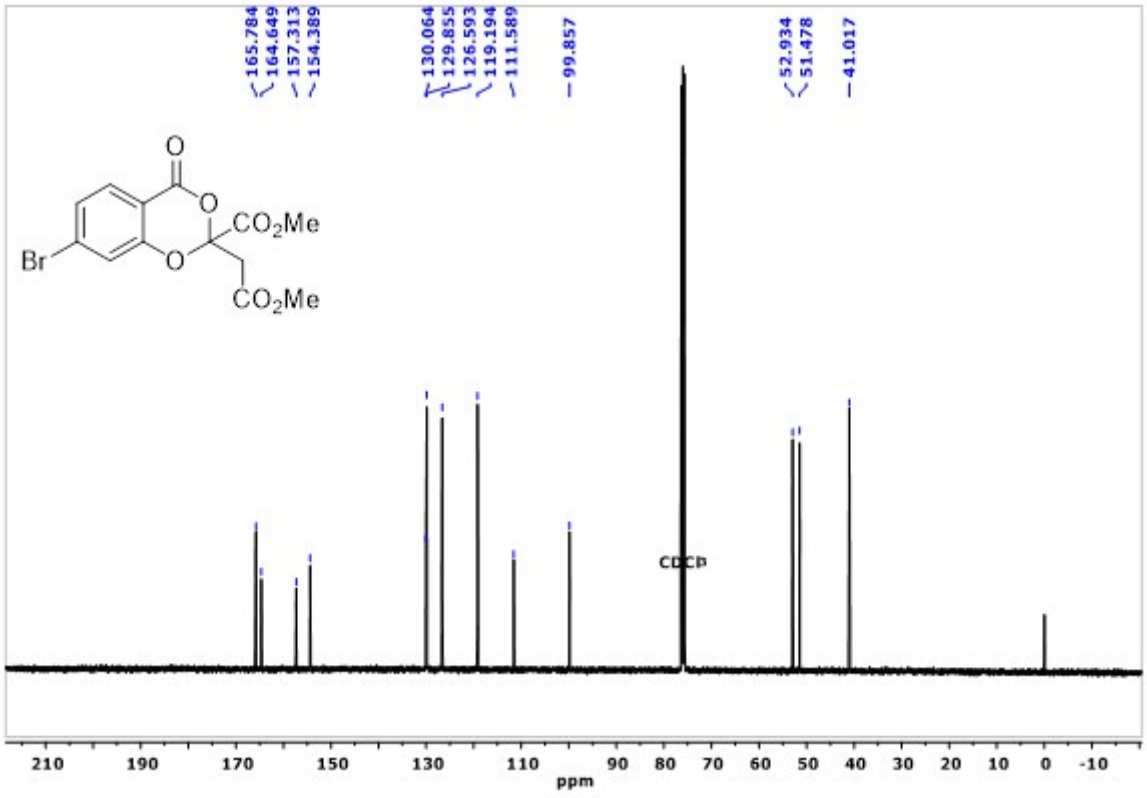
95.2 mg) in acetonitrile at 80 °C, yielded the desired product methyl methyl 7-bromo-2-(2-methoxy-2-oxoethyl)-4-oxo-4H-benzo[d][1,3]dioxine-2-carboxylate as a white solid in 69% yield (80 mg). Melting point 115-117°C.



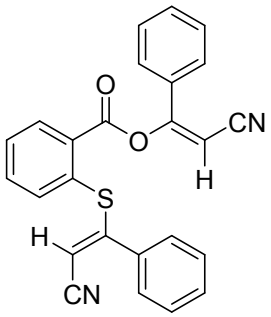
3ca

FT-IR (ATR): ν_{max}= 2956, 2921, 1757, 1602, 1578, 1423, 1367, 1307, 1273, 1169 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 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, $CDCl_3$) δ = 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 $C_{13}H_{11}Br^{81}O_7$ $[(M+2)+Na]^+$ 382.9580 found 382.9573.



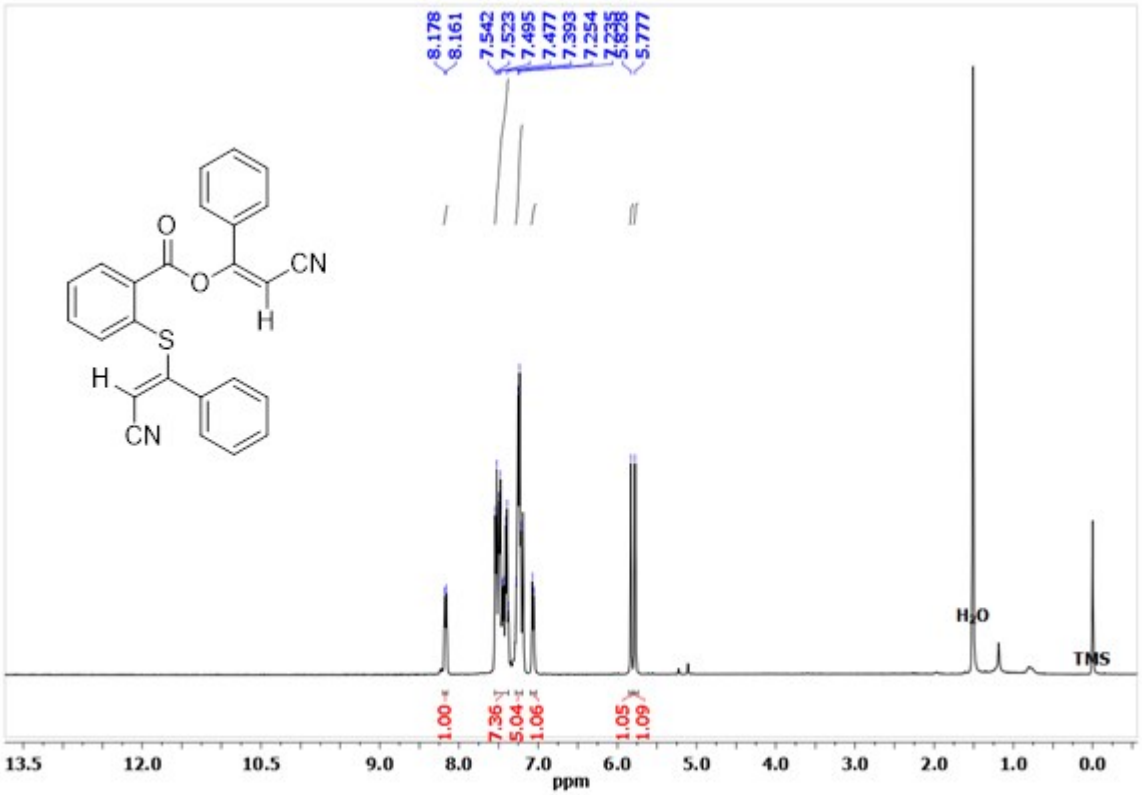


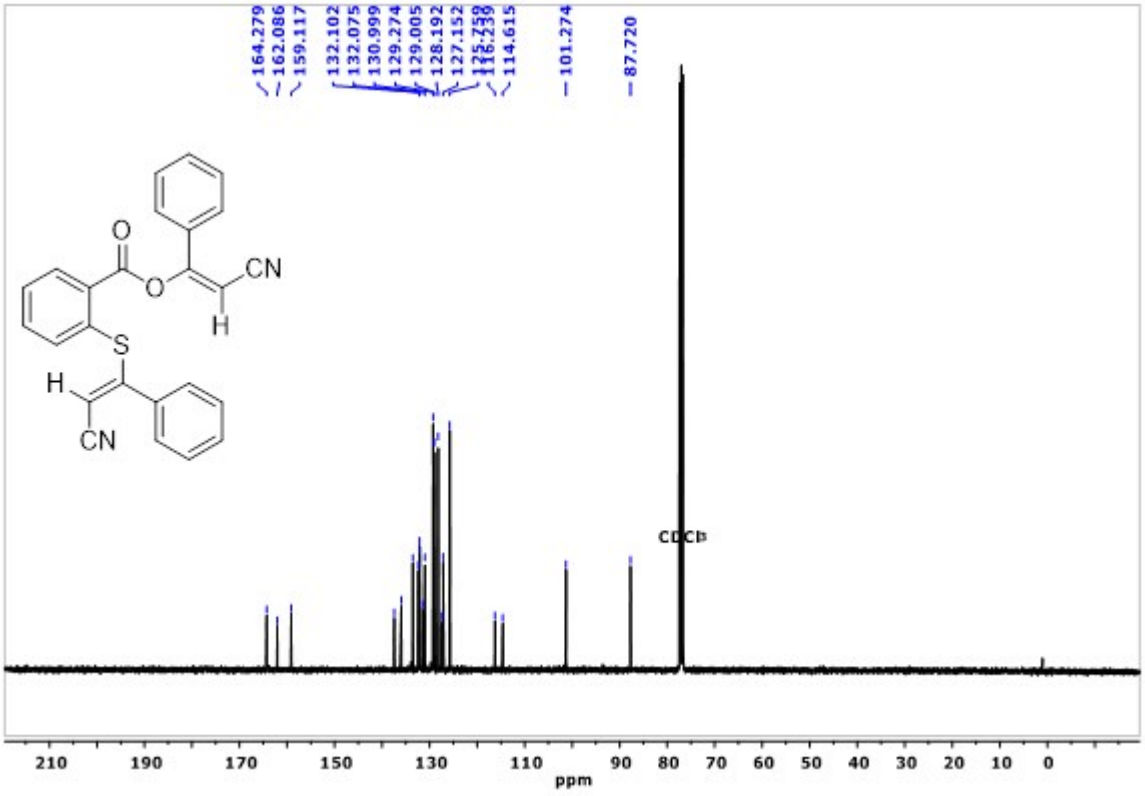
2-cyano-1-phenylvinyl (2-(2-cyano-1,2-diphenylvinyl)thio)benzoate (4ee): Following the general procedure, the reaction between 3-phenylpropiolonitrile (0.5 mmol, 63.5 mg) with 2-mercaptobenzoic acid (0.6 mmol, 92.5 mg)) in presence of $NaHCO_3$ (0.6 mmol, 50.4 mg) and additive CuI (0.5 mmol, 95.2 mg) 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.



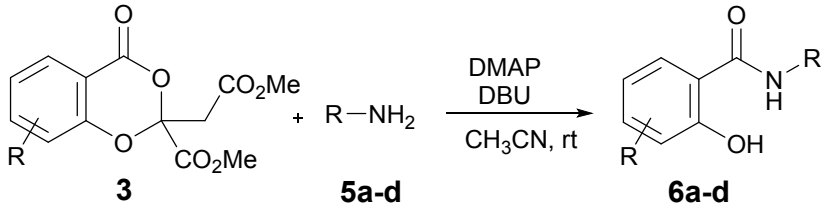
4ee

FT-IR (ATR): ν_{max}= 2924, 2854, 2216, 1739, 1627, 1561, 1490, 1457, 1264, 1228, 1187, 1137 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 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, $CDCl_3$) δ = 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 $C_{25}H_{16}N_2O_2S$ $[M+Na]^+$ 431.0825 found 431.0839.


8.178
8.161
7.542
7.523
7.495
7.477
7.393
7.254
7.235
5.828
5.777
O
O
CN
H
S
H
CN
H2O
TMS
1.00
7.36
5.04
1.06
1.05
1.09
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm


164.279
162.086
159.117
132.102
132.075
130.999
129.274
129.005
128.192
127.152
116.239
114.615
101.274
87.720
O
O
CN
H
S
H
CN
CDCl3
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
ppm

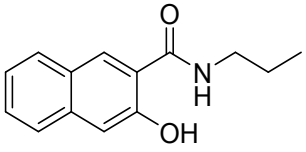
1.3 General procedure for the synthesis of salicylamide derivatives from 4H-benzo[d][1,3]dioxin-4-ones



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

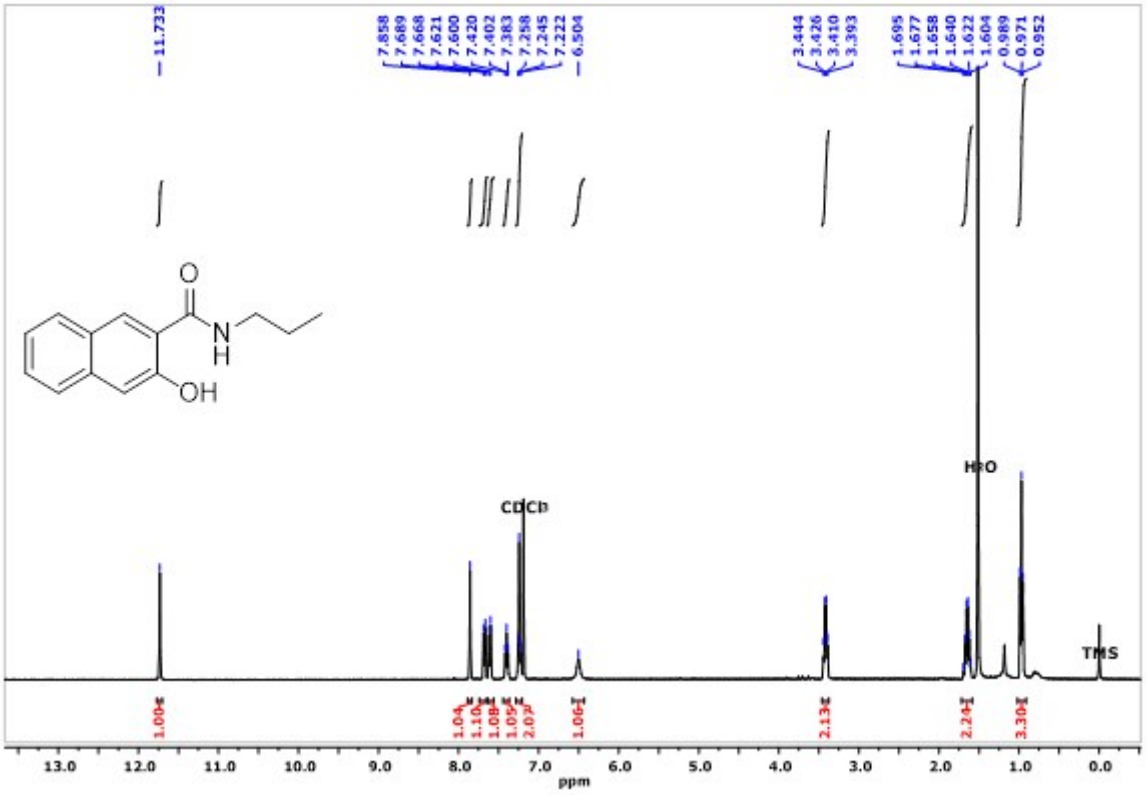
Synthesis of 3-hydroxy-N-propyl-2-naphthamide (6a): To a 25 ml round bottom flask methyl 2-(2-methoxy-2-oxoethyl)-4-oxo-4H-naphtho[2,3-d][1,3]dioxine-2-carboxylate (0.2 mmol, 66 mg) was added along with DMAP (10 mol%, 2 mg) and DBU (0.2 mmol, 30 mg) in 4 ml acetonitrile. The mixture was kept for stirring 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).

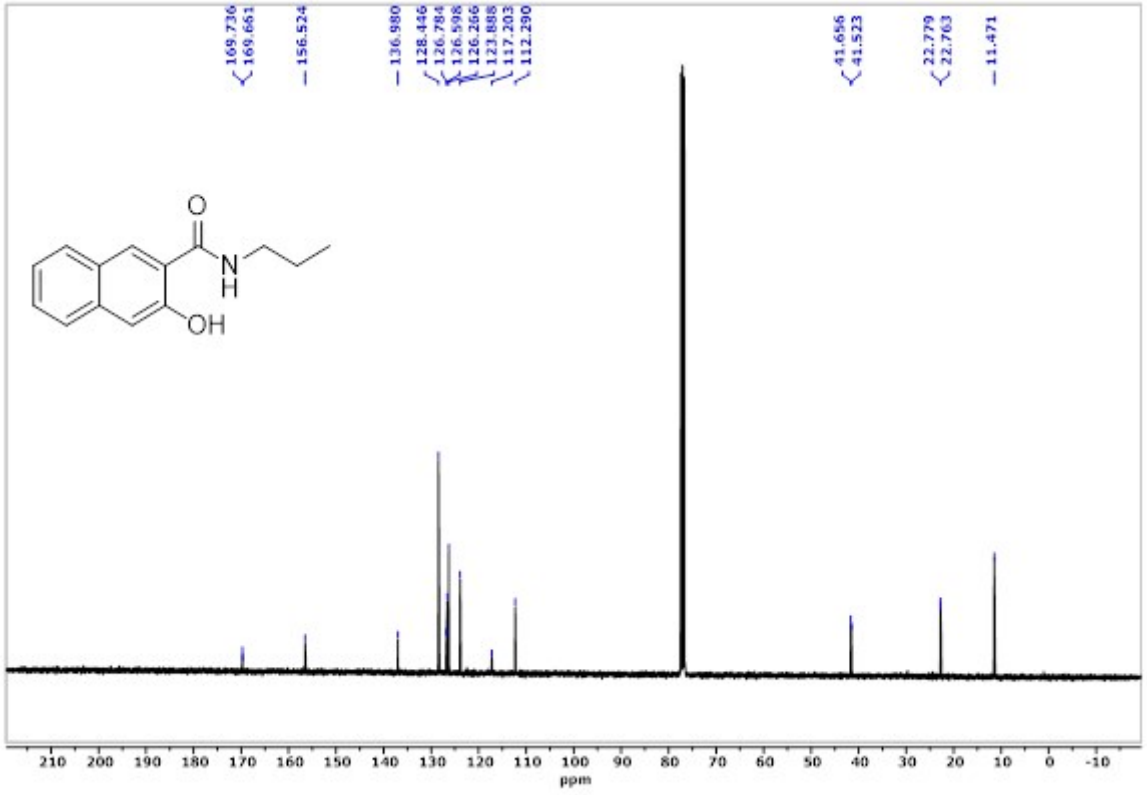


6a

FT-IR (ATR): ν_{max}= 3380, 2922, 2858, 1727, 1653, 1586, 1541, 1452 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 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, $CDCl_3$) δ = 169.7, 156.5, 137.0, 128.4 (2C), 126.8, 126.6, 126.3, 123.9, 117.2, 112.3,

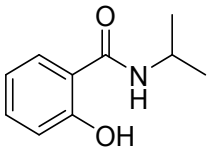
41.6, 22.8, 11.5 ppm.





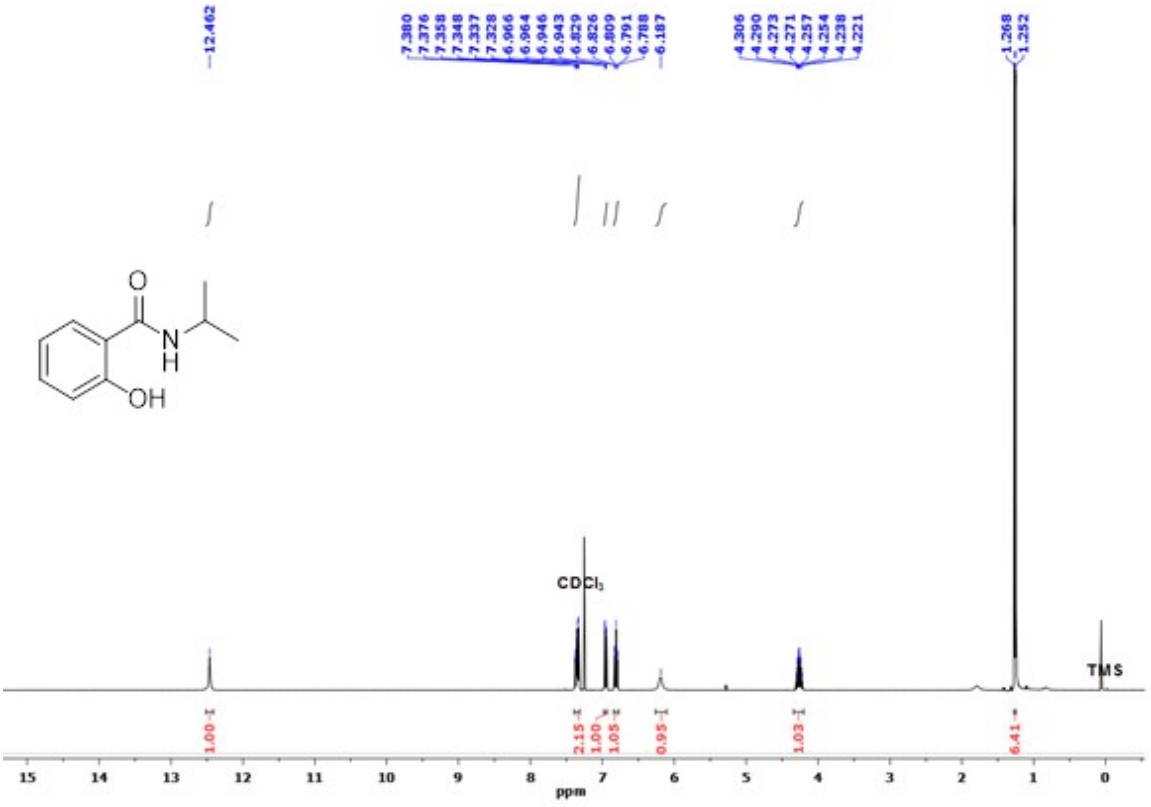
Synthesis of 2-hydroxy-N-isopropylbenzamide (6b): To a 25 ml round bottom flask methyl 2-(2-methoxy-2-oxoethyl)-4-oxo-4H-benzo[d][1,3]dioxine-2-carboxylate (0.2

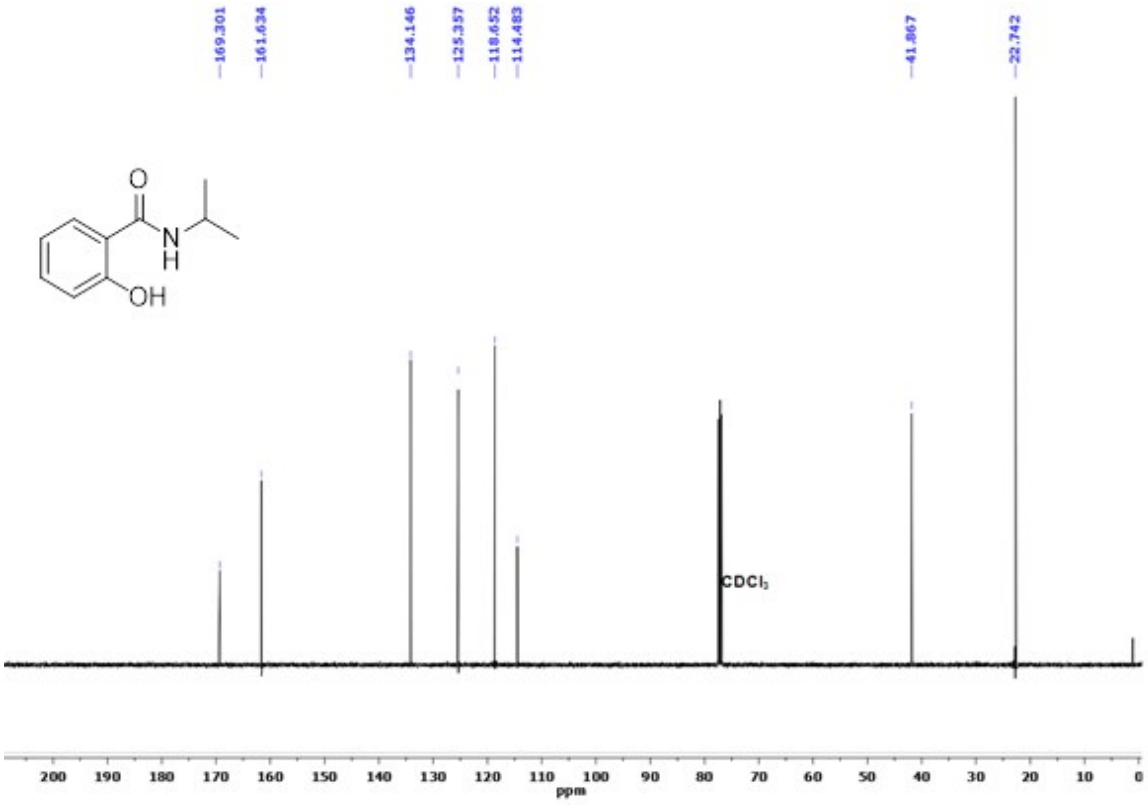
mmol, 56 mg) was added along with DMAP (10 mol%, 2 mg) and DBU (0.2 mmol, 30 mg) in 4 ml acetonitrile. The mixture was kept for stirring at room temperature, and to the stirring solution, Isopropylamine (0.22 mmol, 13 mg) was added drop-wise. The progress of the reaction was monitored using TLC. After 8 hrs of reaction, acetonitrile was evaporated off under reduced pressure. The reaction mixture was subjected to coloumn 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).



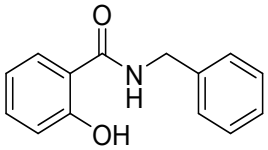
6b

FT-IR (ATR): ν_{max}= 3370, 2974, 2927, 2861, 1636, 1591, 1539, 1496, 1455, 1366, 1299 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 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 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 169.3, 161.6, 134.1, 125.3, 118.6 (2C), 114.5, 41.9, 22.7 (2C) ppm.



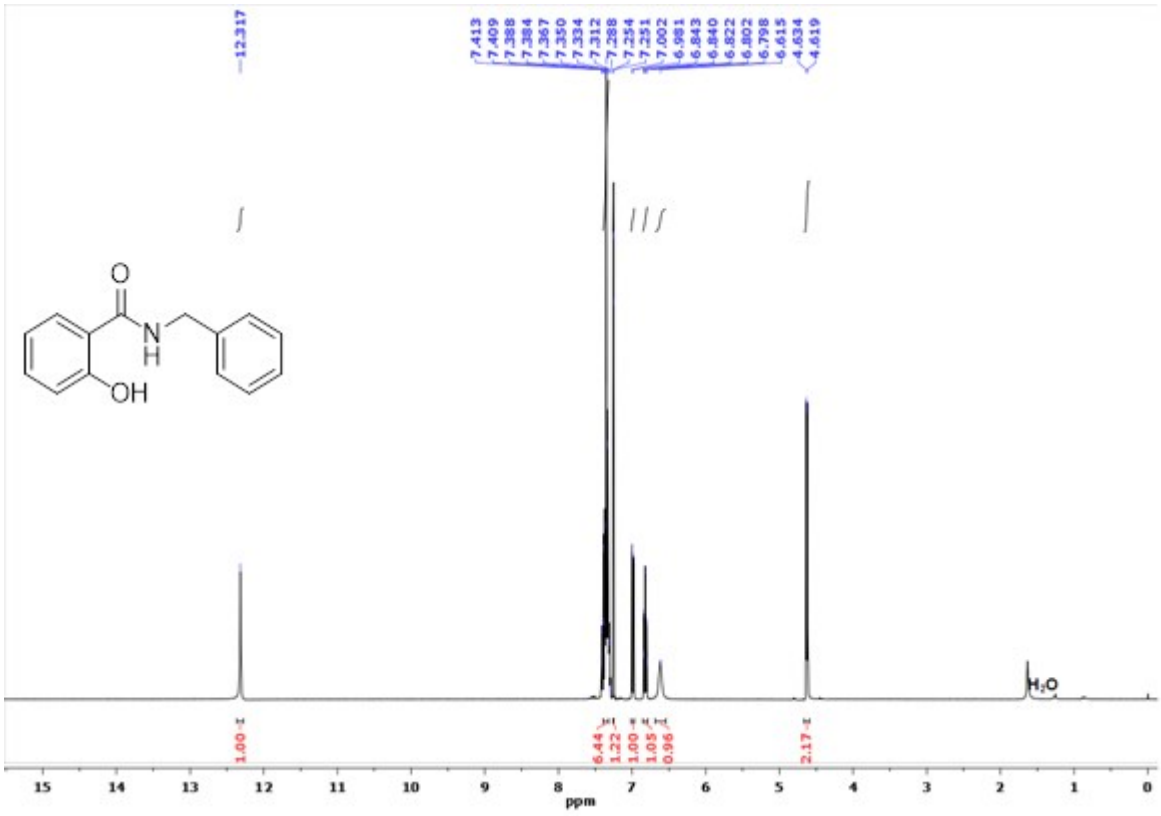


Synthesis of N-benzyl-2-hydroxybenzamide (6c): To a 25 ml round bottom flask methyl 2-(2-methoxy-2-oxoethyl)-4-oxo-4H-benzo[d][1,3]dioxine-2-carboxylate (0.2 mmol, 56 mg) was added along with DMAP (10 mol%, 2 mg) and DBU (0.2 mmol, 30 mg) in 4 ml acetonitrile. The mixture was kept for stirring at room 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).



6c

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.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7.409
7.388
7.384
7.367
7.350
7.334
7.312
7.288
7.254
7.251
7.002
6.981
6.843
6.840
6.822
6.802
6.798
6.615
4.634
4.619
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H
OH
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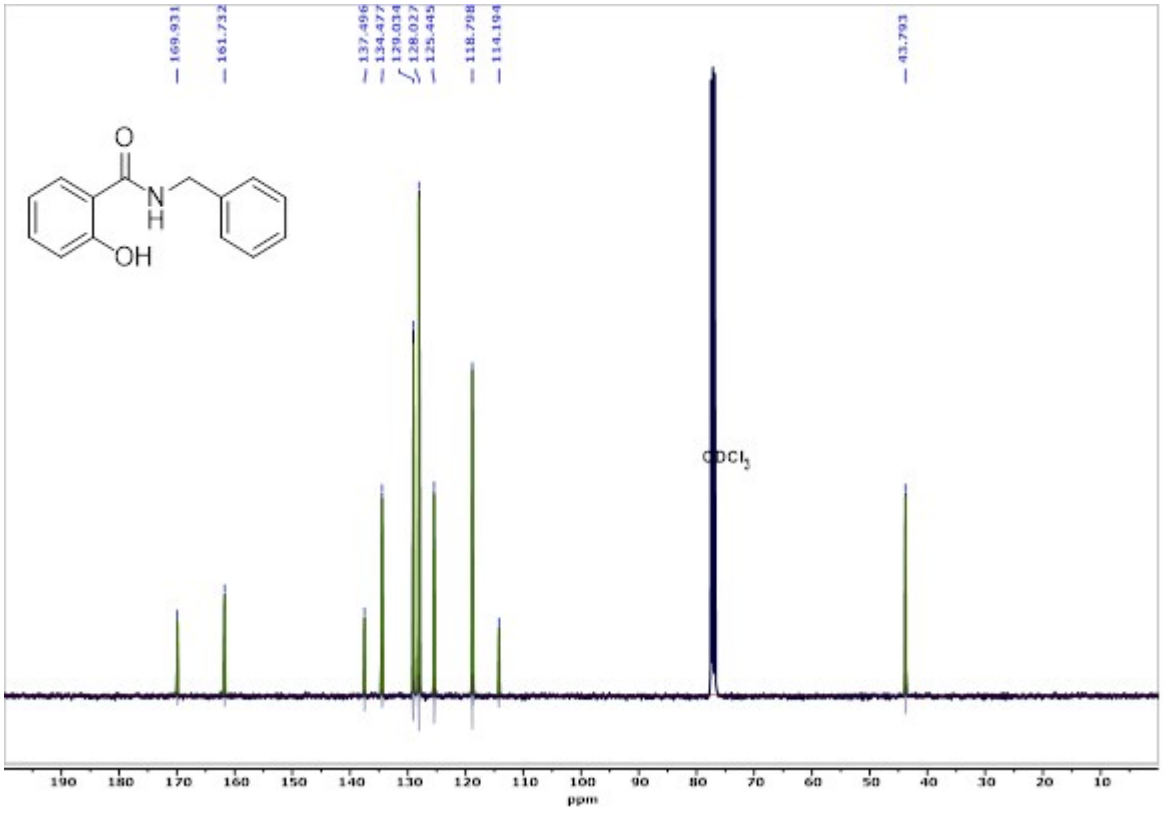
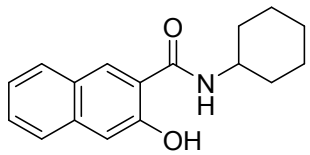
1.22
1.00
1.05
0.96
2.17
ppm

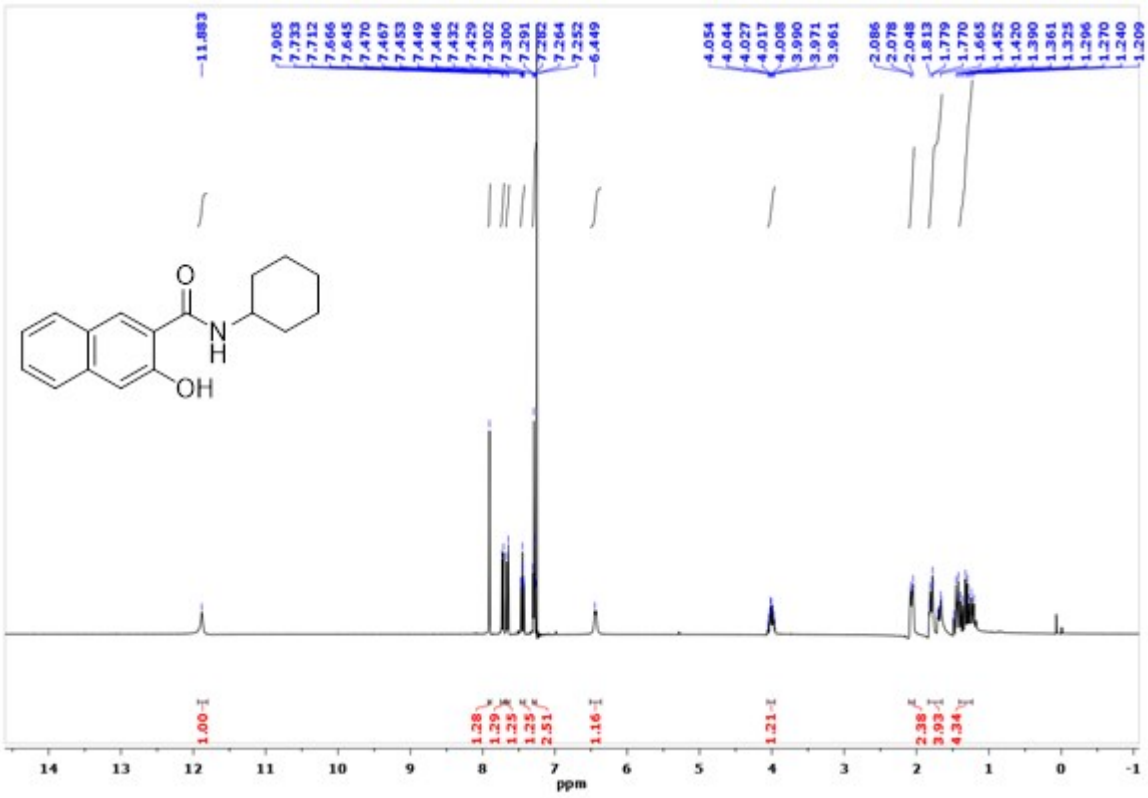

169.931
161.732
137.496
134.477
129.034
128.027
125.445
118.798
114.194
43.793
O
N
H
OH
CDCl3
ppm

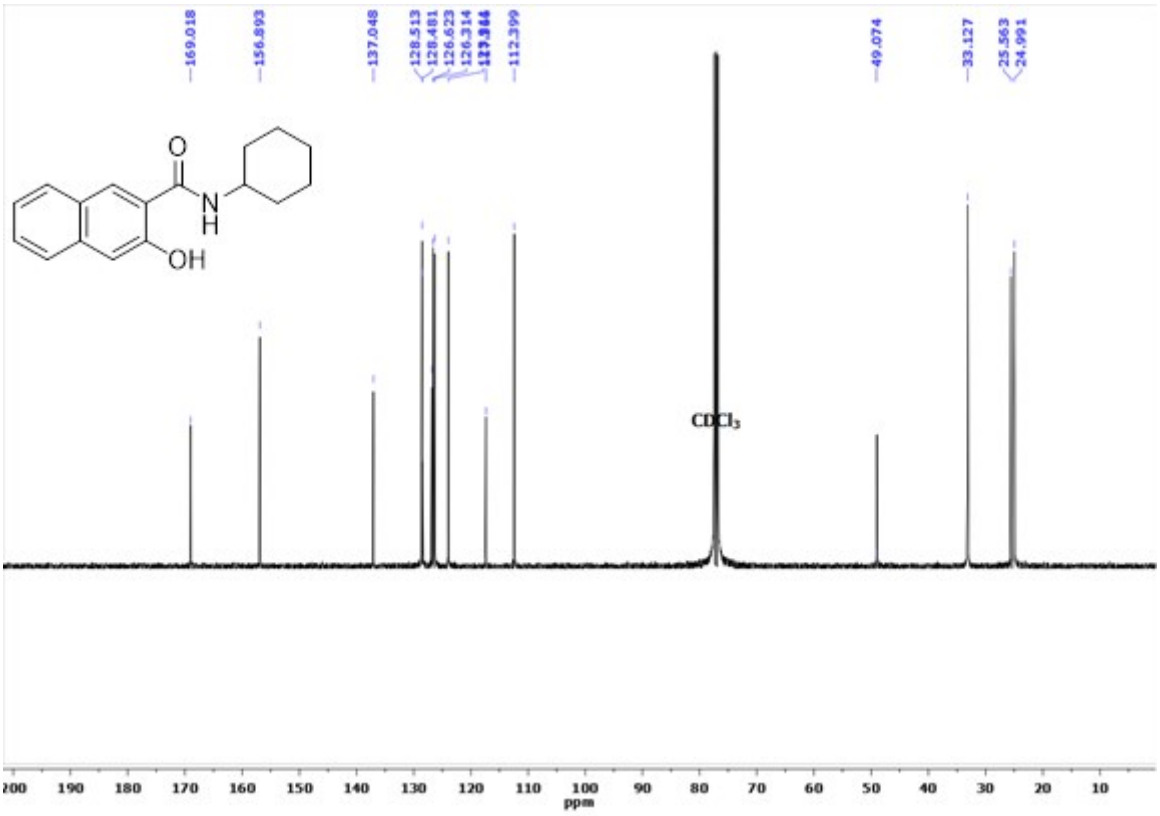
Synthesis of N-cyclohexyl-3-hydroxy-2-naphthamide (6d): To a 25 ml round bottom flask methyl 2-(2-methoxy-2-oxoethyl)-4-oxo-4H-naphtho[2,3-d][1,3]dioxine-2-carboxylate (0.25 mmol, 82.6 mg) was added along with DMAP (10 mol%, 3 mg) and DBU (0.25 mmol, 38 mg) in 4 ml acetonitrile. The mixture was kept 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).



6d

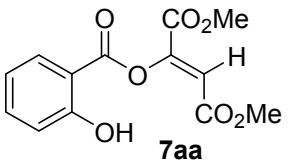
FT-IR (ATR): ν_{max}= 3351, 3056, 2928, 2855, 1710, 1580, 1533, 1453, 1305, 1226 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 11.89 (s, 1H), 7.91 (s, 1H), 7.72 (d, *J*= 8.4 Hz, 1H), 7.65 (d, *J*= 8.4 Hz, 1H), 7.47- 7.43 (m, 1H), 7.30- 7.26 (m, 2H), 6.44 (s, 1H), 4.05- 3.96 (m, 1H), 2.09- 2.04 (m 2H), 1.82- 1.65 (m, 4H), 1.49- 1.19 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 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-benzodioxinone **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.

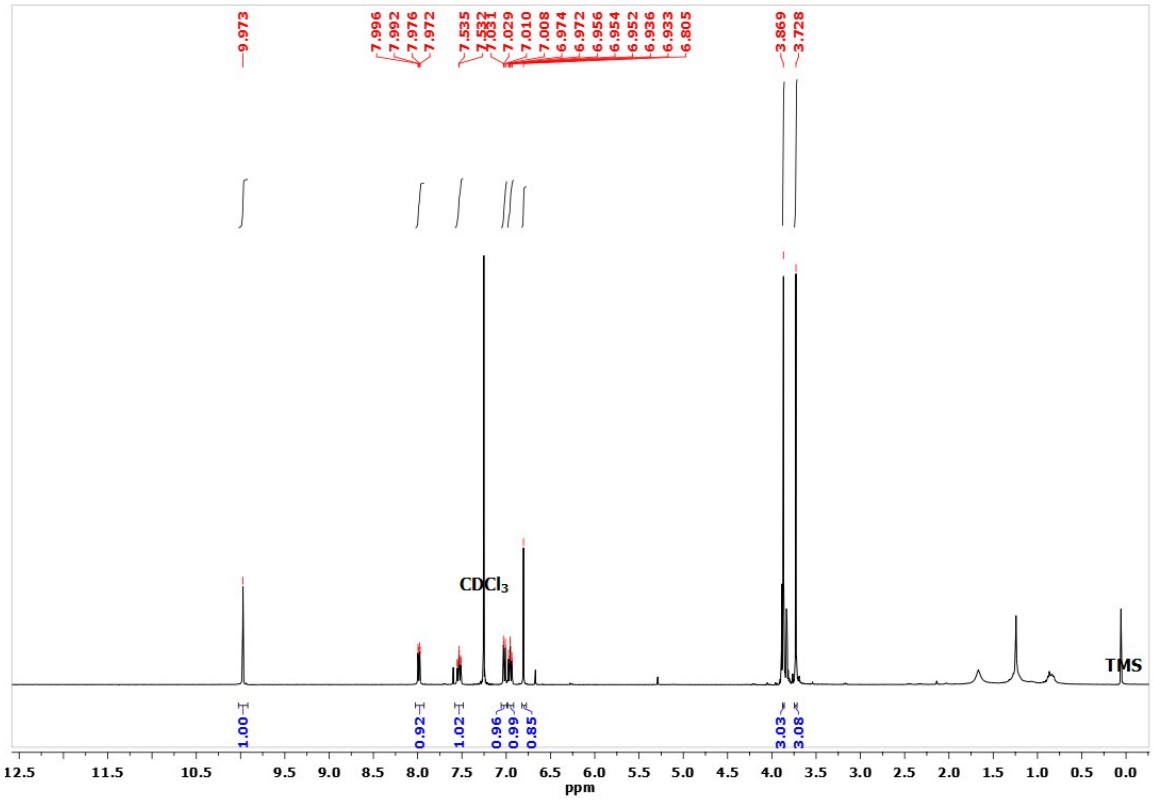


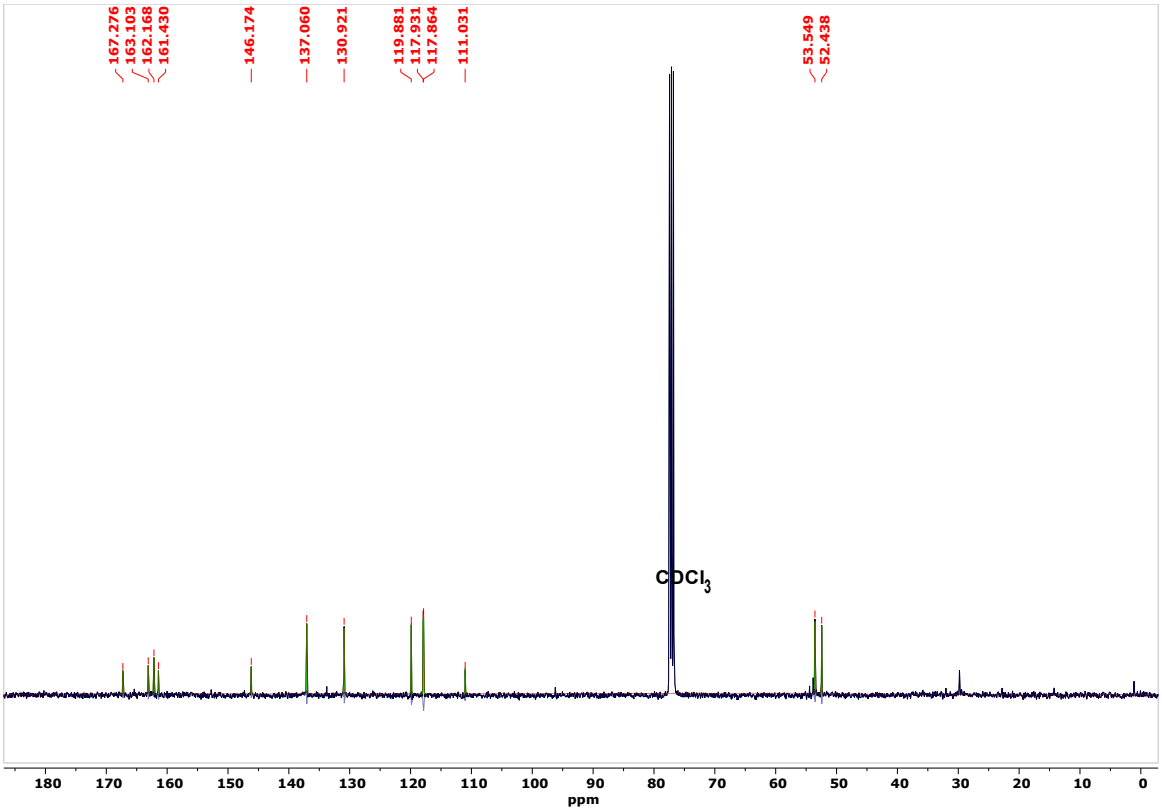
7aa

^{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 repprted by Ming-Jin Fan et al. given below.[2] (*Tetrahedron*, 2006, **62**, 6782–6791).

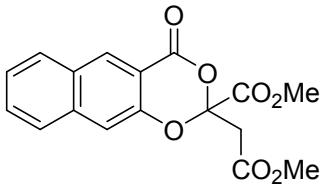
^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.99 (s, 1H), 6.94– 8.01 (m, 4H), 6.82 (s, 1H), 3.88 (s, 3H), 3.74 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ =167.1, 162.9, 162.0, 161.3, 146.0, 136.9, 130.8, 119.7, 117.8, 110.9, 53.4, 52.3.



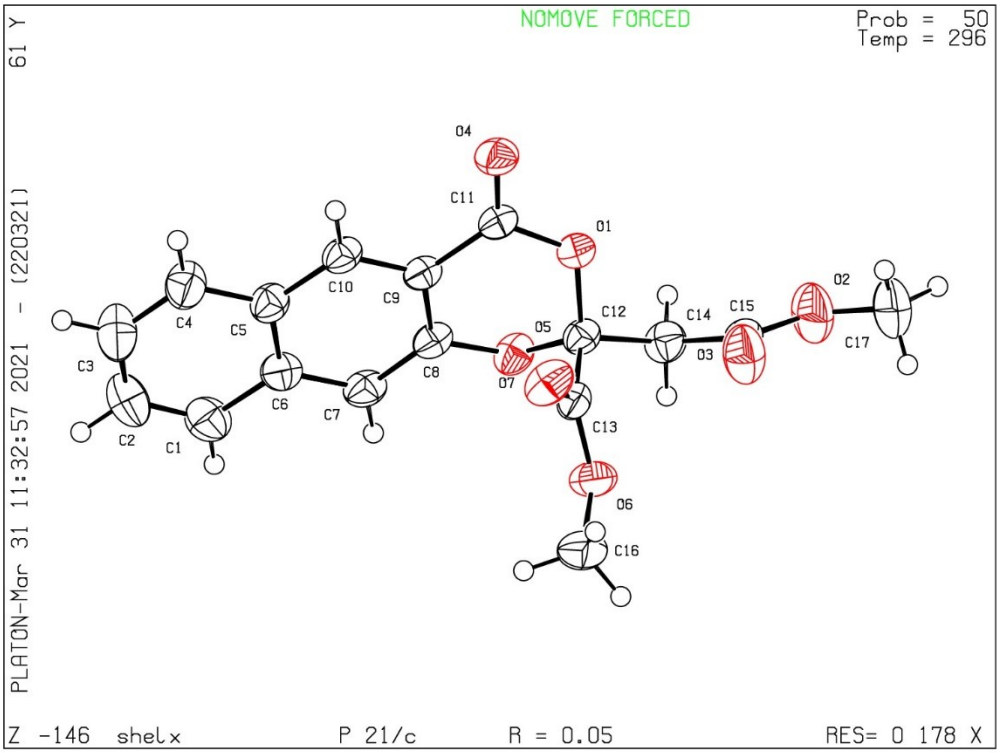


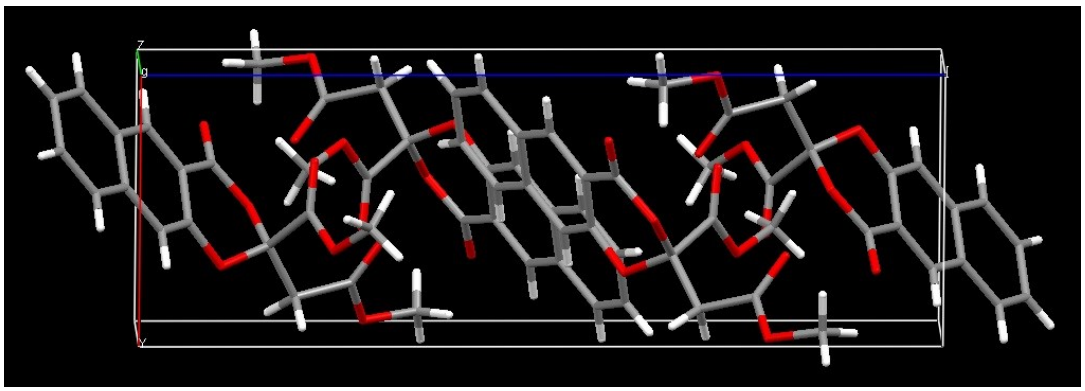
1.6 Single Crystal X-ray Data of the Compound *3da*

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) Å alpha = 90 deg.
	b = 13.2735(14) Å beta = 90.548(4) deg.

	c = 18.564(2) Å gamma = 90 deg.
Volume	1544.4(3) $Å^3$
Z, Calculated density	4, 1.420 mg/m^3
Absorption coefficient	0.112 mm^{-1}
F(000)	688
Crystal size	0.350 x 0.350 x 0.300 mm
Theta range for data collection	2.194 to 28.463 deg.
Limiting indices	-7<=h<=8, -15<=k<=17, -23<=l<=24
Reflections collected / unique	12619 / 3793 [R(int) = 0.0272]
Completeness to theta = 25.242	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.967 and 0.962
Refinement method	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>2sigma(I)]	R1 = 0.0463, wR2 = 0.1311
R indices (all data)	R1 = 0.0658, wR2 = 0.1492
Extinction coefficient	n/a
Largest diff. peak and hole	0.223 and -0.253 e.A^-3

References

1. X. Yang and V. B. Birman, *Org. Lett.,* 2009, **11**, 1499-1502.
2. M. J. Fan, G. Q. Li and Y. M. Liang, *Tetrahedron*, 2006, **62**, 6782–6791.

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