Supporting Information

A remarkable solvent effect on the reaction of 4-hydroxycoumarin with (*E*)-3-aryl-2-nitroprop-2-enol: Facile synthesis of highly substituted furo/pyrano[3,2-*c*]chromenes

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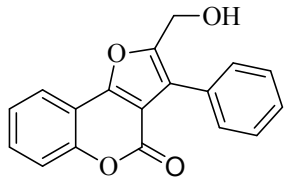
General Information:

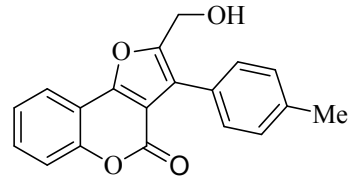
All reactions were carried out either under inert atmosphere or air and monitored by TLC using Merck 60 F_{254} pre coated silica gel plates (0.25 mm thickness) and the products were visualized by UV detection. Flash chromatography was carried out with silica gel (200-300 mesh). FT-IR spectra were recorded on a BrukerTensor-27 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance (III) 400 MHz spectrometer. Data for ^{1}H NMR are reported as a chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet), coupling constant *J* (Hz), integration, and assignment, data for ^{13}C are reported as a chemical shift. High resolutions mass spectral analyses (HRMS) were carried out using ESI-TOF-MS. Single crystal X-ray structural studies were performed on a CCD Agilent Technologies (Oxford Diffraction) SUPER NOVA diffractometer. Data were collected at 293(2) K using graphite-monochromoated Mo Kα radiation (λ_α = 0.71073 Å). The strategy for the Data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by the standard 'phi-omega scan techniques, and were scaled and reduced using CrysAlisPro RED software. The structures were solved by direct methods using SHELXS-97 and refined by full matrix least-squares with SHELXL-97, refining on F^2.[1]

General Procedure for the Synthesis of Furocoumarin Derivatives (3aa-3ec): A heterogenous mixture of substituted 4-hydroxycoumarin (**1a-e**, 0.25 mmol) and (*E*)-3-aryl-2-nitroprop-2-enol (**2a-j**, 0.3 mmol) in water (0.6 mL) was heated at 70 ºC for 5-10h (monitored by TLC). After completion of the reaction, water was decanted or removed by rotary evaporator under reduced pressure to give the gummy residue which was purified by column chromatography over silica gel (eluent: EtOAc/hexane = 1:9 to 1:4) to furnish the pure product **3aa-3ec**. All the products were characterized by their spectroscopic data (IR, ^{1}H and ^{13}C NMR, HRMS).

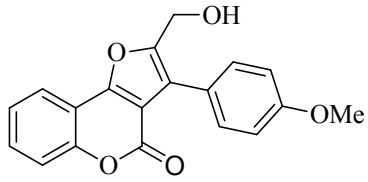
2-(Hydroxymethyl)-3-phenyl-4*H*-furo[3,2-*c*]chromen-4-one (3aa): Yield 83%; IR (KBr) ν 3509, 3048, 2924, 2853, 1743, 1631, 1558, 1502, 1452, 1426, 1373, 1324, 1277 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.97-7.99 (m, 1H), 7.64-7.68 (m, 1H), 7.55-7.60 (m, 3H), 7.47-7.50 (m, 2H), 7.40-7.46 (m, 2H), 5.68 (br s, 1H), 4.53 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 157.4, 152.7, 152.4, 131.0, 129.9, 128.9, 128.4, 128.4, 124.4, 123.9, 121.0, 117.2, 112.6, 109.4, 55.6; HRMS (ESI) m/z calcd. For $C_{18}H_{12}O_4$ $[M+Na]^+$: 315.0628; Found 315.0623.

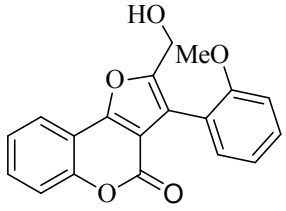


2-(Hydroxymethyl)-3-(4-methylphenyl)-4*H*-furo[3,2-*c*]chromen-4-one (3ab): Yield 84%; IR (KBr) ν 3417, 2924, 2855, 1750, 1630, 1556, 1516, 1497, 1452, 1428, 1372, 1321, 1277, 1217 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.97-7.99 (m, 1H), 7.63-7.67 (m, 1H), 7.54-7.56 (m, 1H), 7.45-7.49 (m, 3H), 7.27-7.29 (m, 2H), 5.65 (t, J_1 = 5.76 Hz, J_2 = 11.04 Hz, 1H), 4.52 (d, J = 5.52 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 157.4, 152.7, 152.2, 138.4, 130.9, 129.8, 129.1, 125.9, 124.4, 123.9, 121.0, 117.2, 112.6, 109.4, 55.7, 21.3; HRMS (ESI) m/z calcd. For $C_{19}H_{14}O_4$ $[M+Na]^+$: 329.0784; Found 329.0785.

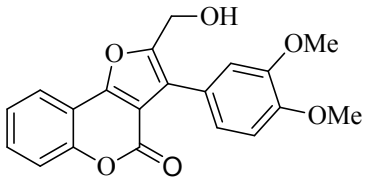


2-(Hydroxymethyl)-3-(4-methoxyphenyl)-4*H*-furo[3,2-*c*]chromen-4-one (3ac): Yield 88%; IR (KBr) ν 3465, 3069, 2935, 2837, 1746, 1649, 1628, 1599, 1570, 1516, 1452, 1429, 1408, 1373, 1349, 1309, 1292, 1276 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.94 (m, 1H), 7.51-7.56 (m, 3H), 7.46-7.46 (m, 1H), 7.35-7.39 (m, 1H), 7.00-7.03 (m, 2H), 4.78 (s, 2H), 3.86 (s, 3H), 2.03 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 157.8, 157.4, 152.8, 152.0, 131.2, 131.0, 124.5, 123.7, 121.2, 121.0, 117.2, 113.9, 112.7, 109.5, 55.7, 55.3; HRMS (ESI) m/z calcd. For $C_{19}H_{14}O_5$$[M+Na]^+$: 345.0733; Found 345.0732.

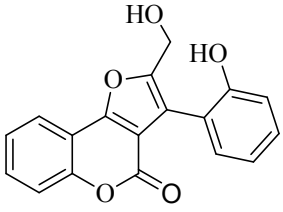


2-(Hydroxymethyl)-3-(2-methoxyphenyl)-4*H*-furo[3,2-*c*]chromen-4-one (3ad): Yield 87%; 

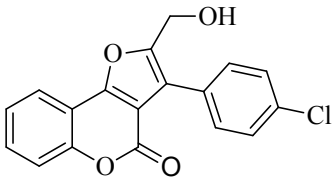
IR (KBr) ν 3432, 2956, 2922, 2852, 1721, 1630, 1597, 1559, 1493, 1463, 1436, 1374, 1320, 1276, 1247, 1214 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.92-7.95 (m, 1H), 7.50-7.54 (m, 1H), 7.41-7.44 (m, 2H), 7.30-7.40 (m, 3H), 7.02-7.10 (m, 2H), 4.63 (s, 2H), 3.83 (s, 3H), 2.16 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 157.3, 156.9, 153.1, 152.7, 132.2, 130.7, 130.2, 124.4, 121.0, 120.9, 118.9, 118.0, 117.2, 112.8, 111.5, 110.4, 56.2, 55.9; HRMS (ESI) m/z calcd. For $C_{19}H_{14}O_5[M+Na]^+$: 345.0733; Found 345.0738.

2-(Hydroxymethyl)-3-(3,4-dimethoxyphenyl)-4*H*-furo[3,2-*c*]chromen-4-one (3ae): Yield 82%; IR (KBr) ν 3493, 2944, 2916, 2834, 1760, 1629, 1587, 1556, 1518, 1470, 1451, 1423, 

1413, 1379, 1359, 1322, 1272 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.93-7.96 (m, 1H), 7.55-7.59 (m, 1H), 7.37-7.49 (m, 2H), 7.26-7.31 (m, 1H), 7.16-7.20 (m, 1H), 6.97-7.00 (m, 1H), 4.82 (s, 2H), 3.96 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 157.3, 152.7, 152.1, 149.2, 148.6, 130.9, 124.4, 123.9, 122.3, 121.4, 121.0, 117.1, 113.5, 112.6, 110.9, 109.3, 55.9, 55.8, 55.7; HRMS (ESI) m/z calcd. For $C_{20}H_{16}O_6[M+Na]^+$ 375.0839; Found 375.0859.

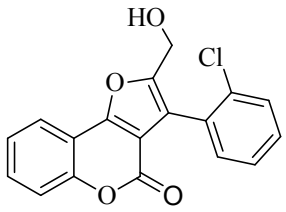
2-(Hydroxymethyl)-3-(2-hydroxyphenyl)-4*H*-furo[3,2-*c*]chromen-4-one (3af): Yield 63%; IR 

(KBr) ν 3423, 2924, 2854, 1720, 1628, 1600, 1560, 1503, 1450, 1424, 1377, 1321, 1288, 1237 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 9.55 (br s, 1H), 7.95-7.97 (m, 1H), 7.61-7.65 (m, 1H), 7.44-7.54 (m, 2H), 7.21-7.26 (m, 2H), 6.85-6.92 (m, 2H), 4.44 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 157.9, 153.6, 153.4, 152.5, 132.2, 131.2, 130.5, 124.8, 121.6, 121.2, 119.1, 118.5, 117.6, 117.3, 112.6, 110.4, 55.8; HRMS (ESI) m/z calcd. For $C_{18}H_{12}O_5[M+Na]^+$: 331.0577; Found 331.0578.

2-(Hydroxymethyl)-3-(4-chlorophenyl)-4*H*-furo[3,2-*c*]chromen-4-one (3ag):Yield 81%; IR 

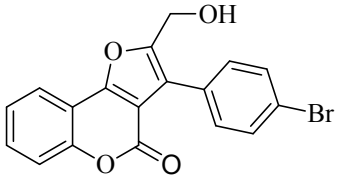
(KBr) ν 3529, 3444, 2956, 2924, 2853, 1883, 1733, 1628, 1556, 1499, 1451, 1423, 1400, 1323, 1275, 1214 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 7.98-7.99 (m, 1H), 7.64-7.69 (m, 1H), 7.60-7.63 (m, 2H), 7.54-7.58 (m, 3H), 7.46-7.50 (m, 1H), 5.71 (t, J = 5.52 Hz, 1H), 4.53 (d, J = 5.52 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 157.5, 152.8, 152.5, 134.7, 131.3, 131.2, 128.6, 127.4, 124.6, 122.9, 121.1, 117.3, 112.5, 109.2, 55.6; HRMS (ESI) m/z calcd. For $C_{18}H_{11}ClO_4$ $[M+Na]^+$: 349.0238; Found 349.0241.

2-(Hydroxymethyl)-3-(2-chlorophenyl)-4*H*-furo[3,2-*c*]chromen-4-one (3ah): Yield 85%; IR



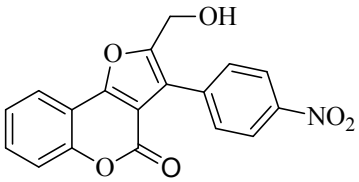
(KBr) ν 3444, 2957, 2924, 2853, 1720, 1630, 1514, 1502, 1452, 1422, 1379, 1320, 1258, 1213 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.95-7.97 (m, 1H), 7.52-7.57 (m, 2H), 7.35-7.46 (m, 5H), 4.59-4.74 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 157.2, 153.2, 152.9, 134.2, 132.2, 131.1, 130.2, 129.8, 128.4, 126.8, 124.5, 121.1, 120.2, 117.3, 112.7, 110.4, 55.8; HRMS (ESI) m/z calcd. For $C_{18}H_{11}ClO_4$ $[M+Na]^+$: 349.0238; Found 349.0239.

2-(Hydroxymethyl)-3-(4-bromophenyl)-4*H*-furo[3,2-*c*]chromen-4-one (3ai): Yield 79%; IR



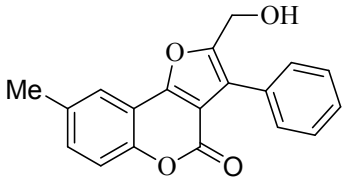
(KBr) ν 3433, 2924, 2854, 1733, 1629, 1597, 1559, 1501, 1450, 1425, 1394, 1366, 1321, 1276, 1261, 1234 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.91-7.93 (m, 1H), 7.58-7.60 (m, 2H), 7.52-7.55 (m, 1H), 7.43-7.48 (m, 3H), 7.34-7.38 (m, 1H), 6.99 (br s, 1H), 4.75 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 152.7, 152.4, 135.9, 131.6, 131.5, 131.2, 127.9, 124.8, 124.6, 122.9, 121.1, 117.3, 112.4, 109.1, 55.5; HRMS (ESI) m/z calcd. For $C_{18}H_{11}BrO_4[M+Na]^+$ 392.9733; Found 392.9732.

2-(Hydroxymethyl)-3-(4-nitrophenyl)-4*H*-furo[3,2-*c*]chromen-4-one (3aj): Yield 83%; IR



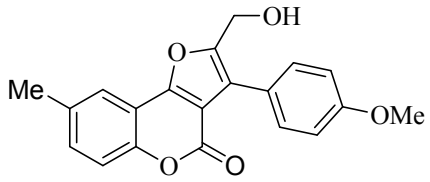
(KBr) ν 3502, 3102, 2917, 1738, 1630, 1596, 1508, 1449, 1425, 1396, 1344, 1214 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.33-8.35 (m, 2H), 7.94-7.96 (m, 1H), 7.80-7.82 (m, 2H), 7.56-7.61 (m, 1H), 7.47-7.49 (m, 1H), 7.38-7.42 (m, 1H), 4.79 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 156.7, 155.3, 153.0, 152.1, 147.0, 136.2, 131.6, 131.2, 125.1, 123.2, 120.9, 119.9, 117.0, 111.8, 108.7, 53.8; HRMS (ESI) m/z calcd. For $C_{18}H_{11}NO_6[M+H]^+$: 338.0659; Found 338.0659.

2-(Hydroxymethyl)-8-methyl-3-phenyl-4*H*-furo[3,2-*c*]chromen-4-one (3ba): Yield 86%; IR



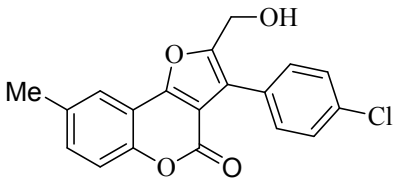
(KBr) ν 3430, 2924, 2854, 2362, 2342, 1719, 1652, 1629, 1570, 1497, 1451, 1433, 1389, 1313, 1277 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.71-7.72 (m, 1H), 7.56-7.58 (m, 2H), 7.45-7.49 (m, 2H), 7.39-7.43 (m, 1H), 7.32-7.33 (m, 2H), 4.76 (s, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 157.5, 152.3, 151.0, 134.3, 132.1, 130.0, 129.1, 128.4 (2C), 123.9, 120.8, 116.9, 112.3, 109.3, 55.7, 21.0; HRMS (ESI) m/z calcd. For $C_{19}H_{14}O_4[M+Na]^+$: 329.0784; Found 329.0780.

2-(Hydroxymethyl)-8-methyl-3-(4-methoxyphenyl)-4*H*-furo[3,2-*c*]chromen-4-one (3bc):



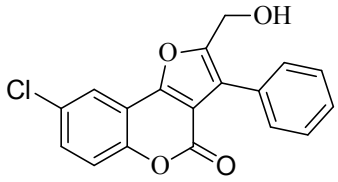
Yield 88%; IR (KBr) ν 3439, 2945, 2918, 2837, 2360, 2339, 1828, 1707, 1656, 1616, 1593, 1566, 1515, 1458, 1435, 1413, 1359, 1316, 1293 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (br s, 1H), 7.50-7.53 (m, 2H), 7.32-7.33 (m, 2H), 6.98-7.01 (m, 2H), 4.76 (s, 2H), 3.85 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 159.7, 157.9, 157.4, 151.8, 150.9, 134.3, 132.0, 131.2, 123.7, 121.2, 120.7, 116.9, 113.9, 112.3, 55.7, 55.3, 20.9; HRMS (ESI) m/z calcd. For $C_{20}H_{16}O_5[M+H]^+$: 337.1071; Found 337.1074.

2-(Hydroxymethyl)-8-methyl-3-(4-chlorophenyl)-4*H*-furo[3,2-*c*]chromen-4-one (3bg): Yield



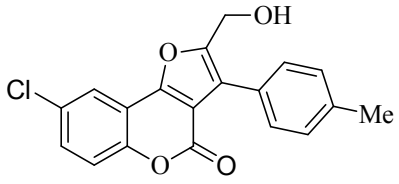
81%; **IR** (KBr) ν 3561, 3428, 2956, 2925, 2854, 2360, 1729, 1632, 1571, 1505, 1493, 1463, 1431, 1407, 1362, 1314, 1276 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (br s, 1H), 7.51-7.54 (m, 2H), 7.42-7.45 (m, 2H), 7.32-7.34 (m, 2H), 4.74 (s, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 157.6, 152.3, 150.9, 134.6, 134.4, 132.3, 131.3, 128.6, 127.5, 122.9, 120.8, 116.9, 112.1, 109.1, 55.6, 20.9; HRMS (ESI) m/z calcd. For $C_{19}H_{13}ClO_4[M+H]^+$: 341.0575; Found 341.0608.

2-(Hydroxymethyl)-8-chloro-3-phenyl-4*H*-furo[3,2-*c*]chromen-4-one (3ca): Yield 79%; IR



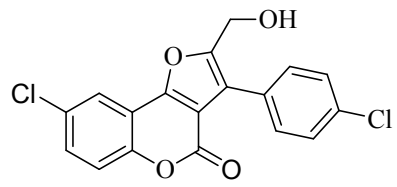
(KBr) ν 3555, 3063, 2925, 2360, 2340, 1747, 1632, 1556, 1502, 1447, 1419, 1362, 1307, 1262, 1241 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.91-7.92 (m, 1H), 7.55-7.57 (m, 2H), 7.42-7.49 (m, 4H), 7.37-7.39 (m, 1H), 4.78 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 156.8, 156.1, 153.0, 149.6, 138.1, 130.9, 130.0, 129.9, 128.6, 128.4, 121.3, 120.6, 118.7, 113.6, 55.6; HRMS (ESI) m/z calcd. For $C_{18}H_{11}ClO_4[M+Na]^+$ 349.0238; Found 349.0234.

2-(Hydroxymethyl)-8-chloro-3-(4-methylphenyl)-4*H*-furo[3,2-*c*]chromen-4-one (3cb): Yield



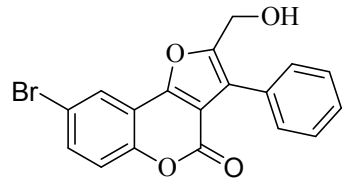
80%; **IR** (KBr) ν 3432, 2922, 2855, 1755, 1630, 1555, 1514, 1492, 1420, 1355, 1309, 1258, 1214 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.89-7.92 (m, 1H), 7.43-7.49 (m, 3H), 7.36-7.39 (m, 1H), 7.26-7.29 (m, 2H), 4.76 (s, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 156.0, 152.8, 150.9, 138.6, 130.9, 130.0, 129.9, 129.8, 129.2, 125.6, 124.0, 120.6, 118.7, 113.7, 55.6, 21.3; HRMS (ESI) m/z calcd. For $C_{19}H_{13}ClO_4[M+Na]^+$: 363.0395; Found 363.0396.

2-(Hydroxymethyl)-8-chloro-3-(4-chlorophenyl)-4*H*-furo[3,2-*c*]chromen-4-one (3cg): Yield

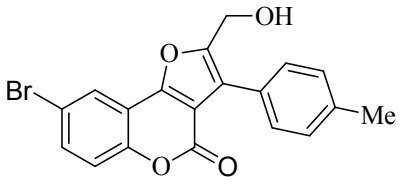


77%; IR (KBr) ν 3429, 2924, 2853, 1750, 1629, 1555, 1494, 1465, 1421, 1355, 1369, 1259 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 7.96-7.97 (m, 1H), 7.66-7.68 (m, 1H), 7.57-7.61 (m, 3H), 7.53-7.56 (m, 2H), 5.70 (t, *J* = 5.52 Hz, 1H), 4.52 (d, *J* = 5.52 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 156.3, 155.0, 150.6, 133.1, 131.7, 130.9, 128.9, 128.2, 128.2, 127.8, 120.7, 120.0, 118.9, 113.3, 109.5, 53.7; HRMS (ESI) m/z calcd. For $C_{18}H_{10}Cl_2O_4[M+Na]^+$: 382.9848; Found 382.9816.

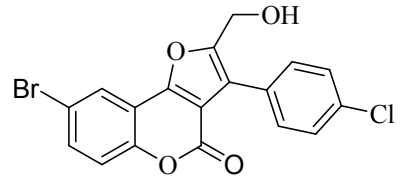
2-(Hydroxymethyl)-8-bromo-3-phenyl-4*H*-furo[3,2-*c*]chromen-4-one (3da): Yield 79%; IR (KBr) ν 3560, 3443, 3062, 2853, 1747, 1630, 1584, 1552, 1499, 1446, 1417, 1359, 1305, 1263 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.05-8.06 (m, 1H), 7.59-7.62 (m, 1H), 7.54-7.57 (m, 2H), 7.39-7.49 (m, 3H), 7.31-7.33 (m, 1H), 4.77 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 155.9, 153.0, 151.5, 133.8, 129.9, 128.6, 128.4, 124.0, 123.6, 123.6, 118.9, 117.3, 114.1, 110.1, 55.6; HRMS (ESI) m/z calcd. For $C_{18}H_{11}BrO_4[M+Na]^+$ 392.9733; Found 392.9704.



2-(Hydroxymethyl)-8-bromo-3-(4-methylphenyl)-4*H*-furo[3,2-*c*]chromen-4-one (3db): Yield 86%; IR (KBr) ν 3431, 2921, 2855, 2360, 2340, 1747, 1626, 1550, 1514, 1491, 1422, 1409, 1355, 1306, 1259 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.05-8.06 (m, 1H), 7.60-7.62 (m, 1H), 7.43-7.45 (m, 2H), 7.30-7.33 (m, 1H), 7.27-7.29 (m, 2H), 4.76 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 155.9, 152.8, 151.5, 138.6, 133.7, 132.9, 129.8, 129.2, 125.6, 124.0, 123.6, 118.9, 117.3, 114.2, 55.6, 21.3; HRMS (ESI) m/z calcd. For $C_{19}H_{13}BrO_4[M+Na]^+$: 406.9889; Found 406.9839.

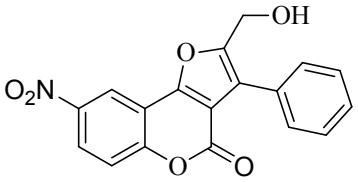


2-(Hydroxymethyl)-8-bromo-3-(4-chlorophenyl)-4*H*-furo[3,2-*c*]chromen-4-one (3dg):Yield

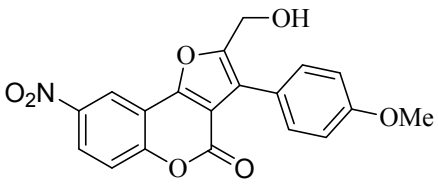


78%; IR (KBr) ν 3439, 2923, 2853, 2360, 2339, 1747, 1627, 1567, 1551, 1492, 1463, 1420, 1353, 1306, 1261 cm^{-1}; ^1H NMR (400 MHz, DMSO-d6) δ 8.08-8.09 (m, 1H), 7.78-7.80 (m, 1H), 7.51-7.61 (m, 5H), 5.70 (br s, 1H), 4.52 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d6) δ 156.3, 155.1, 154.9, 151.0, , 133.8, 133.1, 131.7, 128.2, 127.8, 122.9, 120.7, 119.2, 116.7, 113.8, 109.5, 53.7; HRMS (ESI) m/z calcd. For $C_{18}H_{10}ClO_4Br[M+Na]^+$: 426.9343; Found 426.9319.

2-(Hydroxymethyl)-8-nitro-3-phenyl-4*H*-furo[3,2-*c*]chromen-4-one (3ea): 63%; IR (KBr) ν 3450, 1765, 1745, 1633, 1615, 1524, 1503, 1499, 1422, 1399, 1336, 1254 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.86-8.87 (m, 1H), 8.39-8.42 (m, 1H), 7.56-7.59 (m, 3H), 7.46-7.53 (m, 3H), 4.82 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 155.8, 155.7, 153.9, 144.1, 129.9, 128.9, 128.6, 128.3, 125.7, 124.2, 118.4, 117.4, 113.0, 110.8,55.6; HRMS (ESI) m/z calcd. For $C_{18}H_{11}NO_6[M+Na]^+$: 360.0479; Found 360.0544



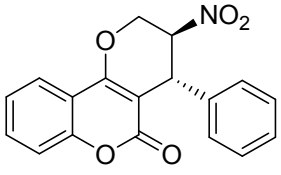
2-(Hydroxymethyl)-8-nitro-3-(4-methoxyphenyl)-4*H*-furo[3,2-*c*]chromen-4-one (3ec): 67%; 3458, 3086, 2360, 1769, 1633, 1614, 1516, 1496, 1351, 1339, 1293, 1254 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.83-8.84 (m, 1H), 8.37-8.40 (m, 1H), 7.55-7.58 (m, 1H), 7.49-7.52 (m, 2H), 7.00-7.03 (m, 2H), 4.80 (br s, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 156.1, 155.7, 155.5, 153.5, 144.1, 131.2, 125.5, 123.9, 120.4, 118.3, 117.3, 114.0, 113.0, 110.7, 55.5, 55.3; HRMS (ESI) m/z calcd. For $C_{19}H_{13}NO_7[M+Na]^+$: 390.0584; Found 390.0588.



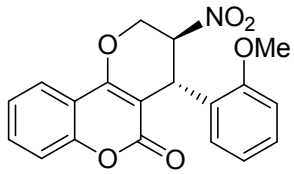
General Procedure for the Synthesis of Dihydropyrano[3,2-*c*]chromene Derivatives (4aa-4ec):

To a stirred solution of 4-hydroxycoumarin (**1a**, 40.5 mg, 0.25 mmol) and (*E*)-3-aryl-2-nitroprop-2-enol (**2a-k**, 0.3 mmol) in DMSO (0.6 mL) was added L-proline (5.75 mg, 0.05 mmol) at 70 ºC for 4-6 h (monitored by TLC). After completion of the reaction, the mixture was extracted with ethyl acetate (3 × 10 mL), washed with water, and dried with Na_2SO_4. The combined organic phase was concentrated under reduced pressure to afford the crude residue which was purified by column chromatography over silica gel (eluent: EtOAc/hexane = 1:19) to give the pure products **4aa-4ec**. The products were characterized by their corresponding spectroscopic data (IR, ^1H and ^{13}C NMR, HRMS). The diastereomeric ratio of the crude product was determined by ^1H NMR spectrum.

***Trans*-3-nitro-4-phenyl-3,4-dihydropyrano[3,2-*c*]chromen-5(2*H*)-one** (**4aa**): Yield 88%; IR (KBr) ν 3441, 2924, 1711, 1631, 1612, 1575, 1554, 1494, 1453, 1404, 1375, 1325, 1271 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82-7.84 (m, 1H), 7.57-7.61 (m, 1H), 7.31-7.39 (m, 5H), 7.27-7.28 (m, 2H), 5.10 (dt, J_1 = 13.04 Hz, J_2 = 2.28 Hz, 1H), 5.01 (br s, 1H), 4.83-4.84 (m, 1H), 4.40 (dd, J_1 = 13.04 Hz, J_2 = 2.24 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 159.7, 152.7, 138.9, 132.5, 129.4, 128.3, 127.9, 124.2, 122.8, 116.9, 114.4, 99.1, 82.2, 62.8, 38.2; HRMS (ESI) m/z calcd. For $C_{18}H_{13}NO_5[M+Na]^+$: 346.0686; Found 346.0687.

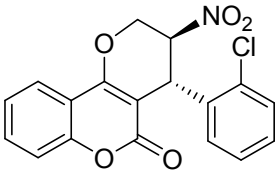


***Trans*-3-nitro-4-(2-methoxyphenyl)-3,4-dihydropyrano[3,2-*c*]chromen-5(2*H*)-one**



(**4ad**):Yield 90%; IR (KBr) ν 3446, 2923, 2852, 1710, 1628, 1577, 1550, 1491, 1460, 1437, 1407, 1377, 1357, 1315, 1286, 1271 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.79-7.82 (m, 1H), 7.56-7.60 (m, 1H), 7.34-7.37 (m, 1H), 7.27-7.32 (m, 2H), 6.86-6.96 (m, 3H), 5.28 (br s, 1H), 5.05 (dd, J_1 = 12.56 Hz, J_2 = 2.28 Hz, 1H), 4.96 (m, 1H), 4.28-4.31 (m, 1H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 160.2, 156.4, 152.7, 132.4, 129.5, 128.6, 126.3, 124.1, 122.7, 120.9, 116.8, 110.8, 99.2, 79.9, 63.6, 55.6, 32.9; HRMS (ESI) m/z calcd. For $C_{19}H_{15}NO_6[M+H]^+$: 354.0972; Found 354.0975

***Trans*-3-nitro-4-(2-chlorophenyl)-3,4-dihydropyrano[3,2-*c*]chromen-5(2*H*)-one** (**4ah**): Yield



85%; IR (KBr) ν 3434, 2924, 2853, 1710, 1627, 1611, 1573, 1552, 1493, 1456, 1439, 1405, 1373, 1358, 1314, 1275 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82-7.84 (m, 1H), 7.59-7.63 (m, 1H), 7.49-7.51 (m, 1H), 7.28-7.39 (m, 3H), 7.22-7.26 (m, 1H), 7.05-7.07 (m, 1H), 5.37 (br s, 1H), 5.12 (dd, J_1 = 12.8 Hz, J_2 = 2.28 Hz, 1H), 4.95 (m, 1H), 4.29-4.33 (m, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 160.4, 152.8, 135.8, 133.9, 132.7, 130.7, 129.7, 129.3, 127.6, 124.3, 122.8, 116.9, 114.3, 98.7, 79.8, 63.2, 35.8; HRMS (ESI) m/z calcd. For $C_{18}H_{12}ClNO_5[M+Na]^+$: 380.0296; Found 380.0296.

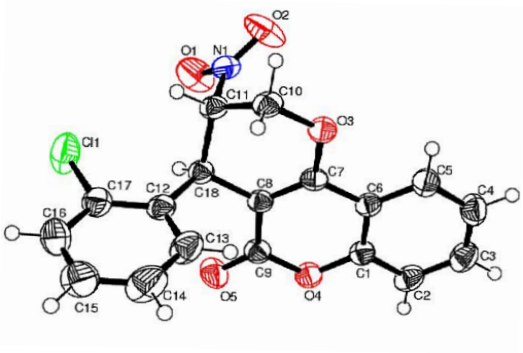


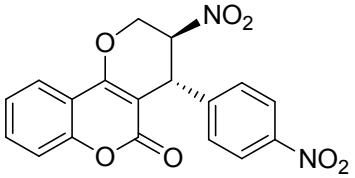
Figure 1. ORTEP diagram of 4ah.

Table 1. Crystal data for compound 4ah.

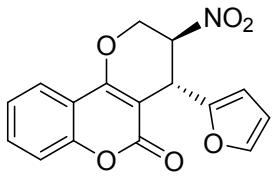
Compound	Compound **4ah**
Empirical formula	C18 H12 Cl N O5
Molecular weight	357.74
Temperature	150(2) K
Wavelength (Å)	0.7107A
Crystal system, space group	monoclinic, P 21/c

a (Å) *b* (Å) *c* (Å) α (°) β (°) γ (°)	a = 14.7809(9) A b = 8.0602(3) A c = 14.9746(8) A alpha = 90 deg. beta =116.158(7) deg. gamma = 90 deg
Volume (Å^3)	1601.31(14) A^3
Z, Calculated density (mg/m^3)	4, 1.484 Mg/m^3
Absorption coefficient (mm^{-1})	0.268 mm^-1
F(000)	736
Crystal size (mm)	0.15 x 0.11 x 0.05 mm
θ range (deg)	2.95 to 25.00 deg.
Limiting indices	-17<=h<=17, -9<=k<=9, -17<=l<=16
Reflections collected / unique	12705 / 2809 [R(int) = 0.0511]
Completeness to θ = 25	99.9 %
Max. and min. transmission	0.9867 and 0.9608
Data / restraints / parameters	2809 / 0 / 226
Goodness-of-fit on F^2	1.072
Final R indices [I>2sigma(I)]	R1 = 0.0579, wR2 = 0.1461
R indices (all data)	R1 = 0.0664, wR2 = 0.1517
Largest diff. peak and hole (e.A^{-3})	0.281 and -0.313 e.A^-3
CCDC	**1011395**

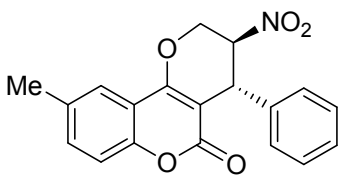
***Trans*-3-nitro-4-(2-methoxyphenyl)-3,4-dihydropyrano[3,2-*c*]chromen-5(2*H*)-one** (**4aj**):Yield 87%; IR (KBr) ν 3439, 2925, 2853, 2360, 1710, 1629, 1576, 1553, 1518, 1494, 1454, 1411, 1376, 1350, 1321, 1273 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23-8.27 (m, 2H), 7.84-7.87 (m, 1H), 7.61-7.66 (m, 1H), 7.49-7.52 (m, 2H), 7.35-7.39 (m, 2H), 5.12-5.20 (m, 2H), 4.85-4.87 (m, 1H), 4.36-4.40 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 160.4, 152.8, 147.8, 146.0, 133.1, 129.0, 124.6, 124.5, 123.0, 117.0, 114.1, 98.3, 81.6, 62.8, 38.3; HRMS (ESI) m/z calcd. For $C_{18}H_{12}N2O_7[M+H]^+$: 369.0717; Found 369.0726.



***Trans*-3-nitro-4-(2-furyl)-3,4-dihydropyrano[3,2-*c*]chromen-5(2*H*)-one** (**4ak**):Yield 85%; IR (KBr) ν 3433, 2924, 2853, 1718, 1631, 1556, 1495, 1456, 1410, 1377, 1359, 1321, 1274 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.81 (m, 1H), 7.55-7.60 (m, 1H), 7.29-7.38 (m, 3H), 6.26-6.35 (m, 2H), 5.20 (dd, J_1 = 12.8 Hz, J_2 = 3.2 Hz, 1H), 5.06-5.07 (m, 2H), 4.58-4.62 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 159.5, 152.6, 150.5, 143.0, 132.7, 124.2, 122.9, 116.8, 114.5, 111.0, 109.4, 97.9, 79.0, 64.1, 32.3; HRMS (ESI) m/z calcd. For $C_{16}H_{11}NO_6[M+H]^+$: 314.0659; Found 314.0603.

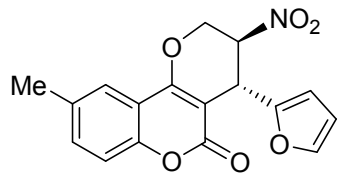


***Trans*-3-nitro-4-phenyl-9-methyl-3,4-dihydropyrano[3,2-*c*]chromen-5(2*H*)-one** (**4ba**): Yield



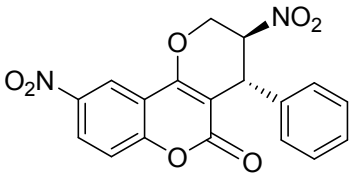
93%; IR (KBr) ν 3441, 2924, 2853, 2360, 1710, 1634, 1586, 1552, 1494, 1454, 1425, 1397, 1373, 1355, 1306, 1270 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.62-7.63 (m, 1H), 7.35-7.40 (m, 3H), 7.30-7.33 (m, 1H), 7.23-7.29 (m, 3H), 5.09 (dd, J_1 = 12.8 Hz, J_2 = 2.28 Hz, 1H), 5.00 (br s, 1H), 4.83 (br s, 1H)), 4.38 (dd, J_1 = 12.8 Hz, J_2 = 2.0 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 159.7, 150.9, 138.9, 134.0, 133.5, 129.4, 128.2, 127.9, 122.5, 116.6, 114.0, 98.9, 82.2, 62.7, 38.3, 20.9; HRMS (ESI) m/z calcd. For $C_{19}H_{15}NO_5[M+Na]^+$: 360.0842; Found 360.0843.

***Trans*-3-nitro-4-(2-furyl)-9-methyl-3,4-dihydropyrano[3,2-*c*]chromen-5(2*H*)-one** (**4bk**):



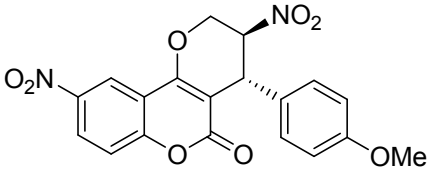
Yield 90%; **IR** (KBr) ν 3434, 2924, 2853, 1714, 1635, 1586, 1554, 1498, 1455, 1427, 1401, 1374, 1357, 1307, 1277 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59-7.60 (m, 1H), 7.36-7.39 (m, 2H), 7.22-7.25 (m, 1H), 6.25-6.35 (m, 2H), 5.19 (dd, J_1 = 12.8 Hz, J_2 = 2.28 Hz, 1H), 5.05-5.06 (m, 2H), 4.56 (dd, J_1 = 12.8 Hz, J_2= 3.2 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 159.5, 150.8, 150.6, 142.9, 134.1, 133.7, 122.6, 116.6, 114.1, 111.0, 109.3, 97.7, 79.0, 64.0, 32.4, 20.9; HRMS (ESI) m/z calcd. For $C_{17}H_{13}NO_6[M+Na]^+$: 350.0635; Found 350.0642.

***Trans*-3,9-dinitro-4-phenyl-3,4-dihydropyrano[3,2-*c*]chromen-5(2*H*)-one** (**4ea**): Yield 92%



IR (KBr) ν 3464, 1742, 1556, 1527, 1488, 1455, 1401, 1343, 1308, 1258, 1212 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.76-8.77 (m, 1H), 8.44-8.47 (m, 1H), 7.48-7.51 (m, 1H), 7.34-7.43 (m, 4H), 7.27-7.28 (m, 1H), 5.20 (dd, J_1 = 12.8 Hz, J_2 = 3.6 Hz, 1H), 5.00-5.01 (m, 1H), 4.89-4.90 (m, 1H), 4.46-4.50 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 158.4, 156.1, 144.1, 138.1, 129.7, 128.7, 127.8, 127.3, 119.5, 118.2, 114.9, 101.0, 81.9, 63.3, 38.3; HRMS (ESI) m/z calcd. For $C_{18}H_{12}N_2O_7[M+Na]^+$: 391.0537; Found 391.0545.

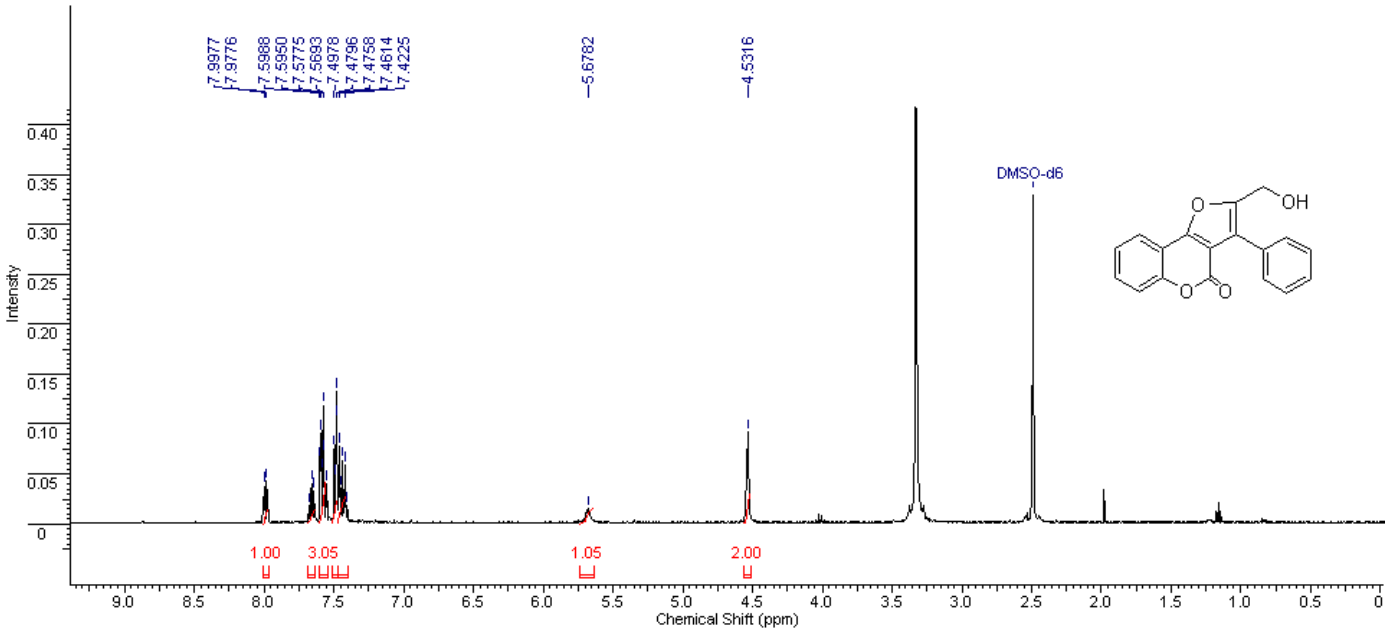
***Trans*-3,9-dinitro-4-phenyl-3,4-dihydropyrano[3,2-*c*]chromen-5(2*H*)-one** (**4ec**): Yield 89%

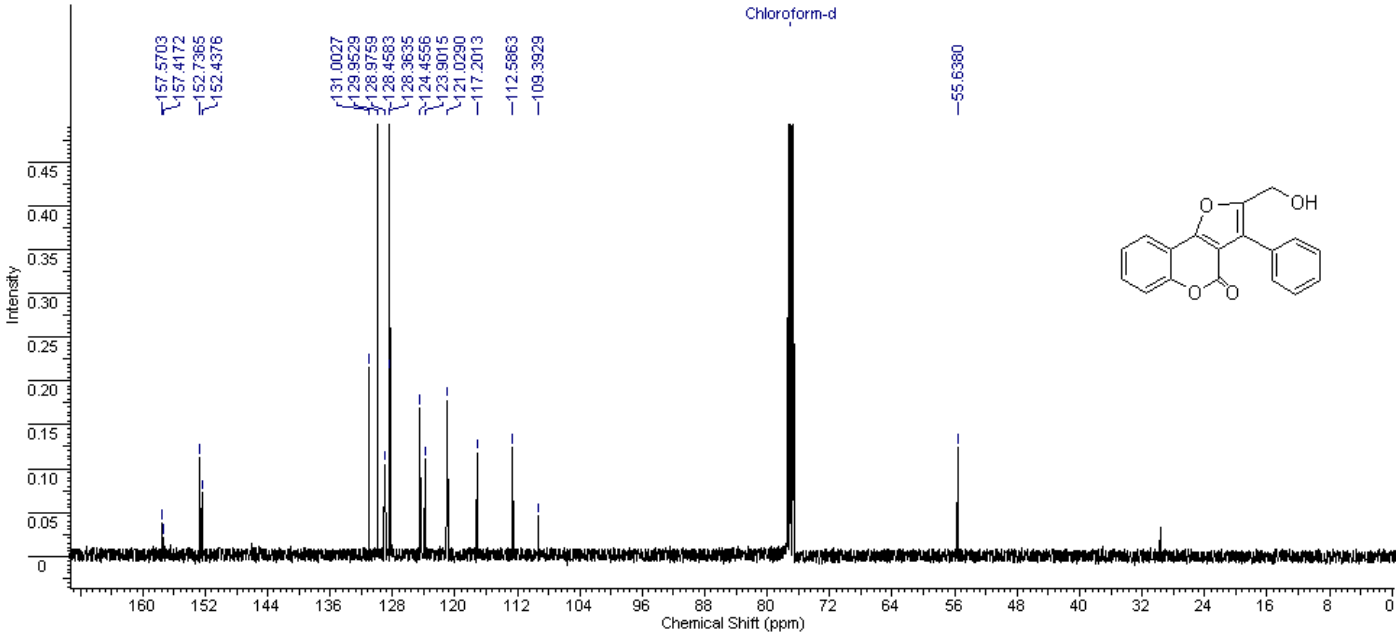


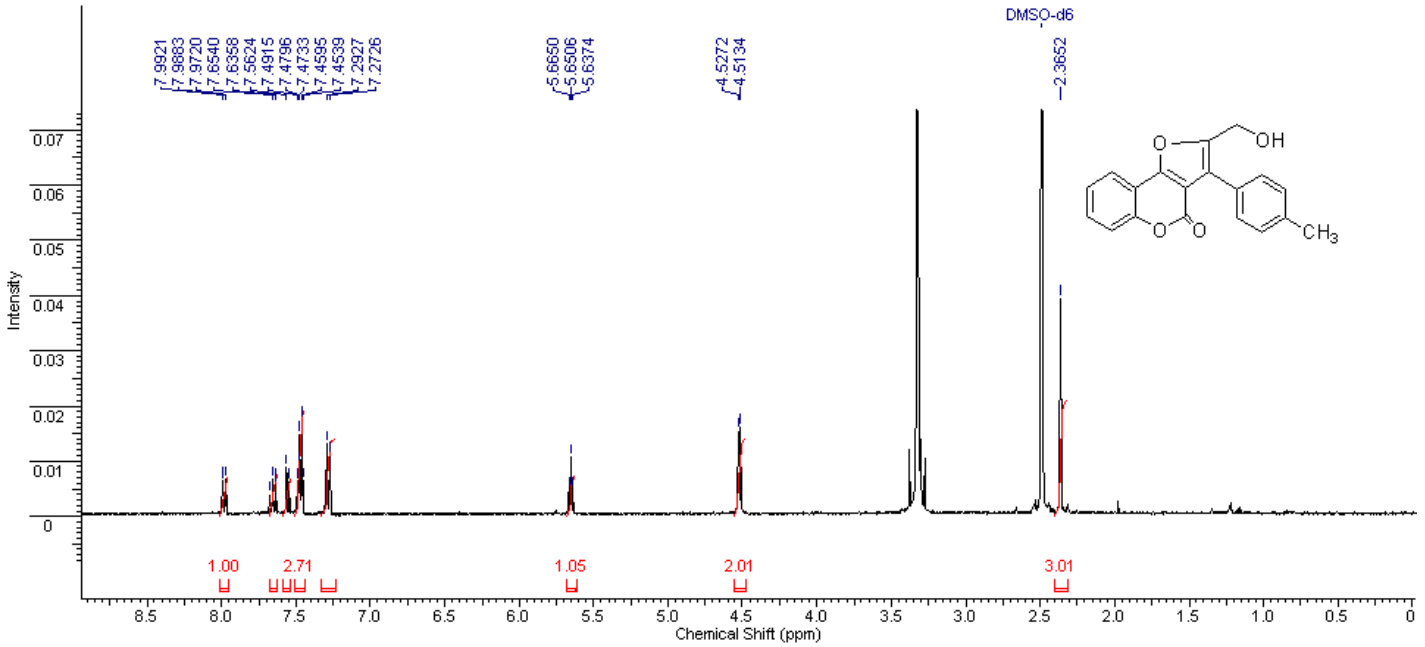
IR (KBr) ν 3456, 2360, 1737, 1643, 1625, 1610, 1557, 1527, 1513, 1487, 1455, 1400, 1341, 1257 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.75-8.76 (m, 1H), 8.43-8.46 (m, 1H), 7.48-7.50 (m, 1H), 7.16-7.19 (m, 2H), 6.90-6.93 (m, 2H), 5.17 (dd, J_1 = 12.8 Hz, J_2 = 2.0 Hz, 1H), 4.85-4.94 (m, 2H), 4.46-4.50 (m, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 159.6, 158.2, 156.0, 144.1, 129.9, 128.9, 127.2, 119.5, 118.1, 115.0, 114.9, 101.3, 82.0, 63.3, 55.4, 37.6; HRMS (ESI) m/z calcd. For $C_{19}H_{14}N_2O_8[M+Na]^+$: 421.0642; Found 421.0650.

References:

1. G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *A64,* 112-122. *Program for Crystal Structure Solution and Refinement;* University of Goettingen: Goettingen, Germany, 1997.


7.9977
7.9776
7.5988
7.5950
7.5775
7.5693
7.4978
7.4796
7.4758
7.4614
7.4225
5.6782
4.5316
DMSO-d6
OH
O
O
O
Intensity
1.00
3.05
1.05
2.00
Chemical Shift (ppm)


Chloroform-d
157.5703
157.4172
152.7365
152.4376
131.0027
129.9529
128.9759
128.4583
128.3635
124.4556
123.9015
121.0290
117.2013
112.5863
109.3929
55.6380
OH
O
O
O
Intensity
Chemical Shift (ppm)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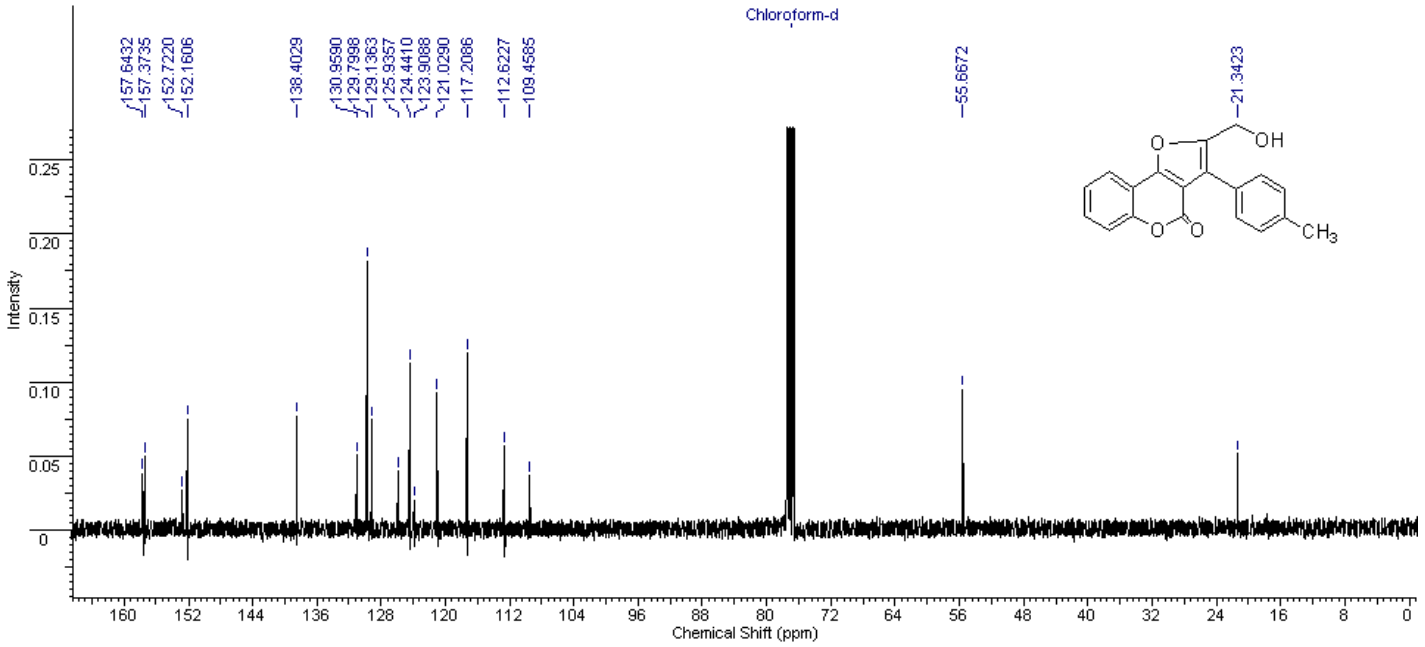
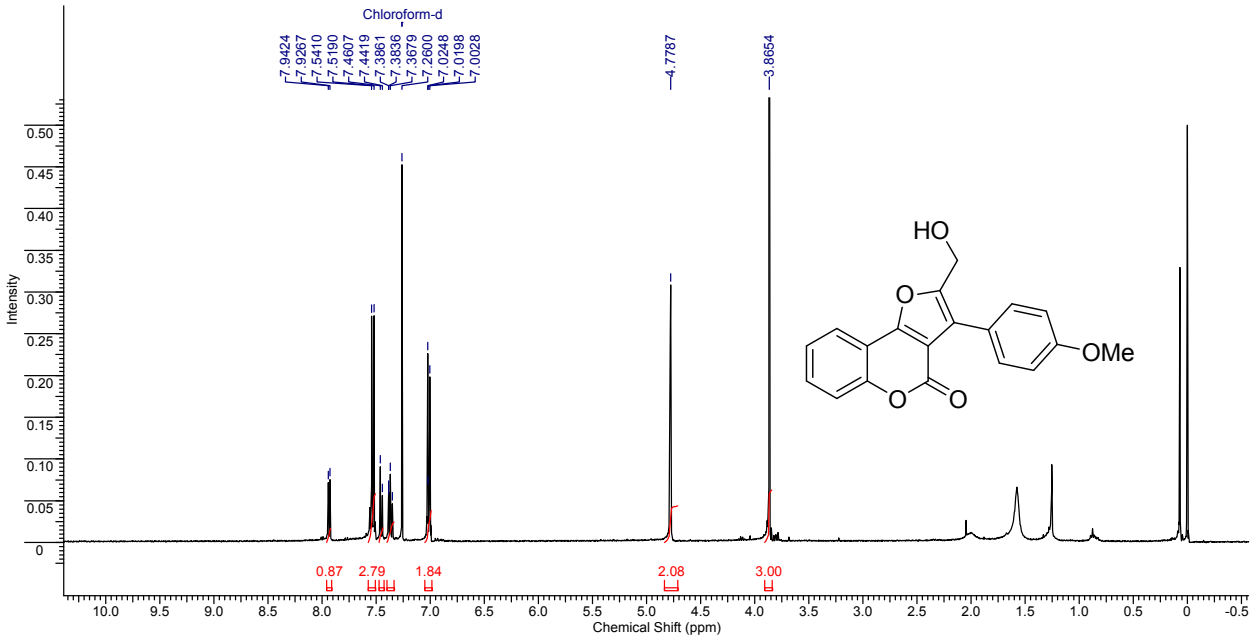
7.9883
7.9720
7.6540
7.6358
7.5624
7.4915
7.4796
7.4733
7.4595
7.4539
7.2927
7.2726
5.6650
5.6506
5.6374
4.5272
4.5134
2.3652
OH
O
O
O
CH3
Intensity
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
1.00
2.71
1.05
2.01
3.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


Chloroform-d
157.6432
157.3735
152.7220
152.1606
138.4029
130.9590
129.7998
129.1363
125.9357
124.4410
123.9088
121.0290
117.2086
112.6227
109.4585
55.6672
21.3423
OH
O
O
O
CH3
Intensity
0.25
0.20
0.15
0.10
0.05
0
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


Chloroform-d
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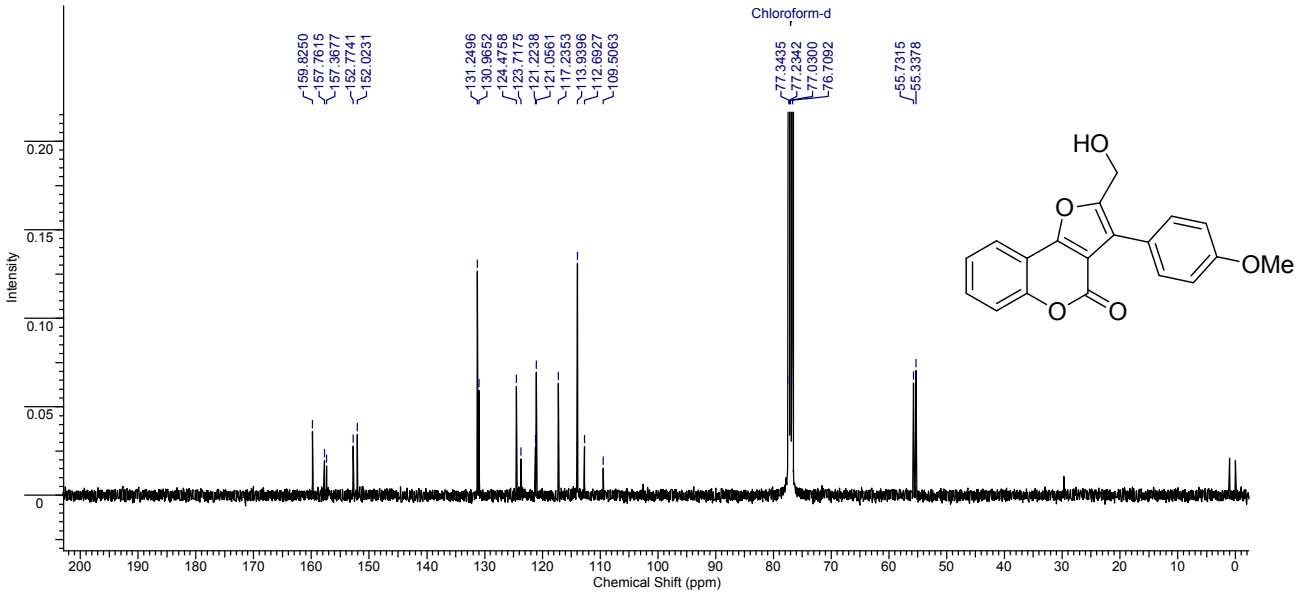
7.9267
7.5410
7.5190
7.4607
7.4419
7.3861
7.3836
7.3679
7.2600
7.0248
7.0198
7.0028
4.7787
3.8654
HO
O
OMe
O
O
Intensity
0.87
2.79
1.84
2.08
3.00
Chemical Shift (ppm)


Chloroform-d
159.8250
157.7615
157.3677
152.7741
152.0231
131.2496
130.9652
124.4758
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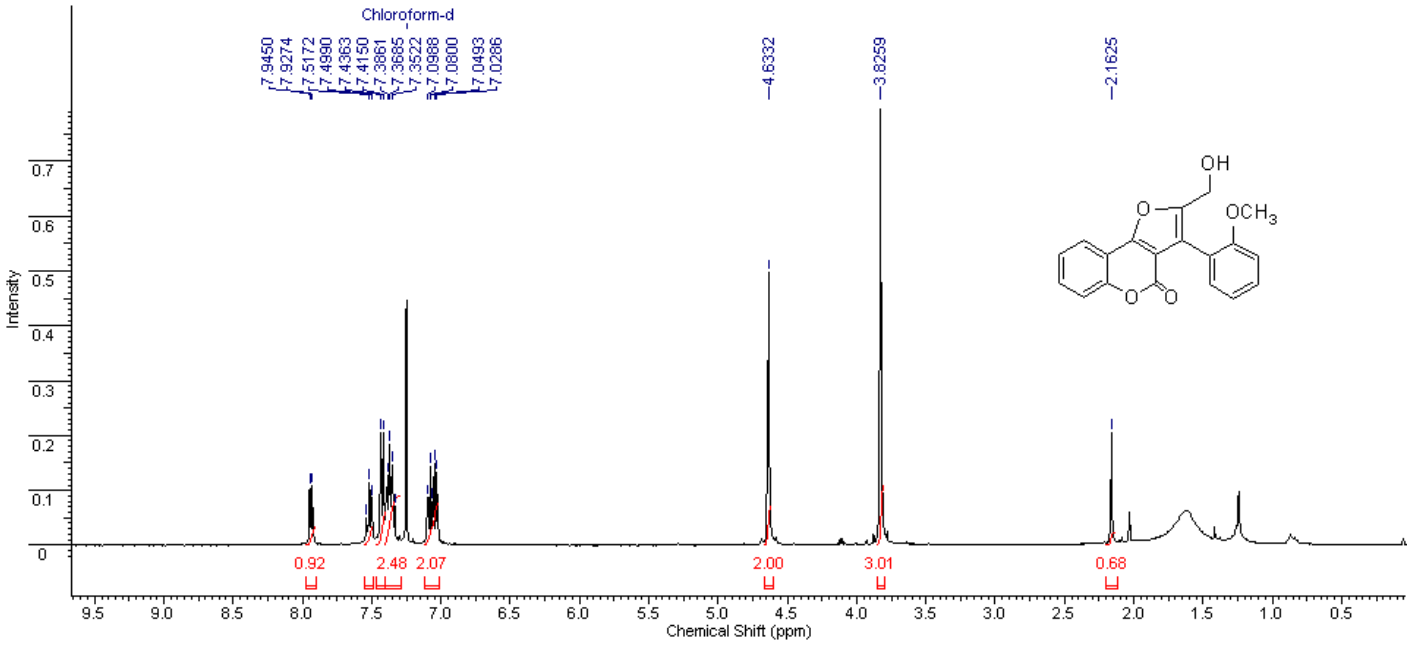
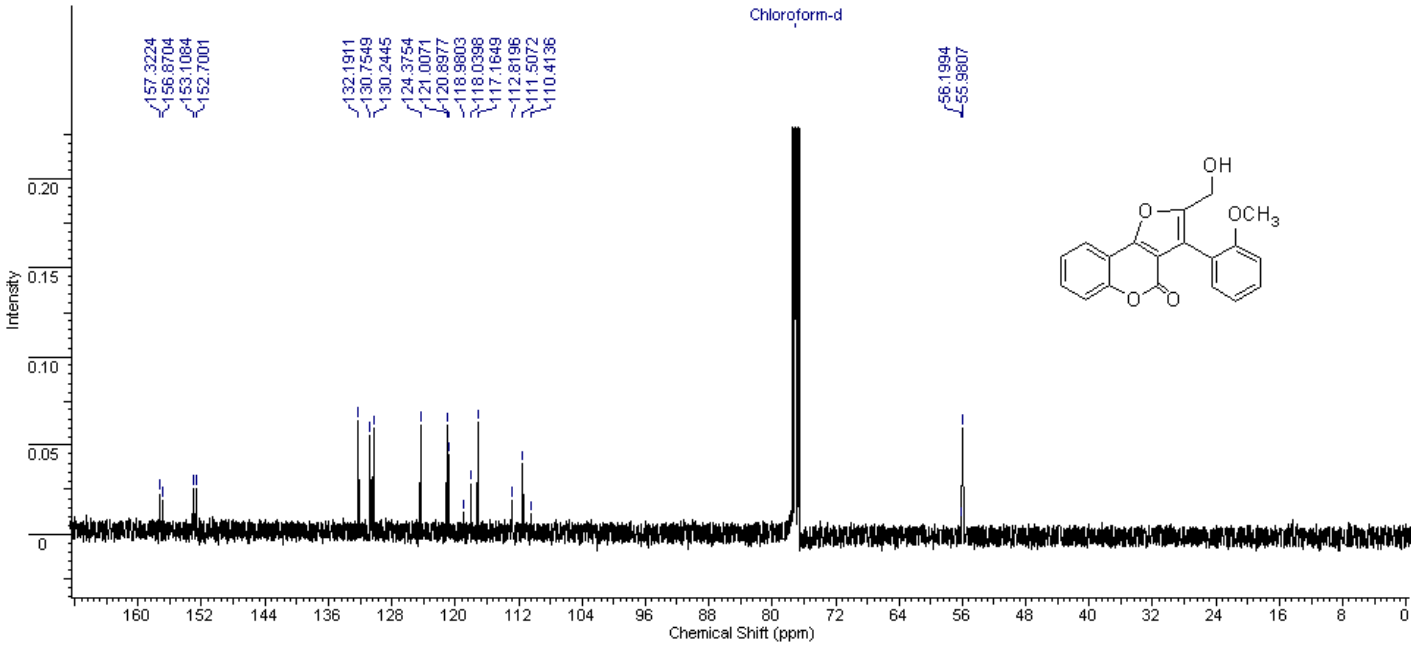
121.2238
121.0561
117.2353
113.9396
112.6927
109.5063
77.3435
77.2342
77.0300
76.7092
55.7315
55.3378
HO
O
OMe
O
O
Intensity
Chemical Shift (ppm)


Chloroform-d
7.9450
7.9274
7.5172
7.4990
7.4363
7.4150
7.3861
7.3685
7.3522
7.0988
7.0800
7.0493
7.0286
4.6332
3.8259
2.1625
OH
O
OCH3
O
O
Intensity
0.92
2.48
2.07
2.00
3.01
0.68
Chemical Shift (ppm)


Chloroform-d
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153.1084
152.7001
132.1911
130.7549
130.2445
124.3754
121.0071
120.8977
118.9803
118.0398
117.1649
112.8196
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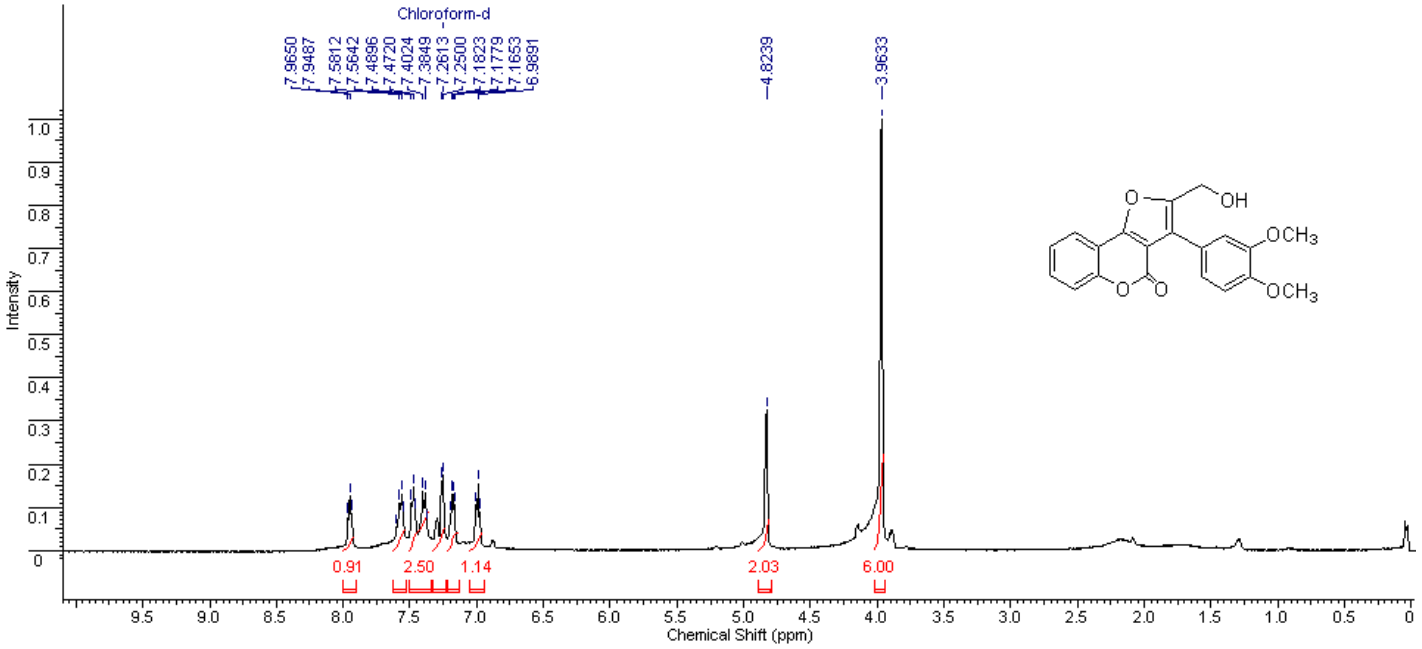
110.4136
56.1994
55.9807
OH
O
OCH3
O
O
Intensity
Chemical Shift (ppm)


Chloroform-d
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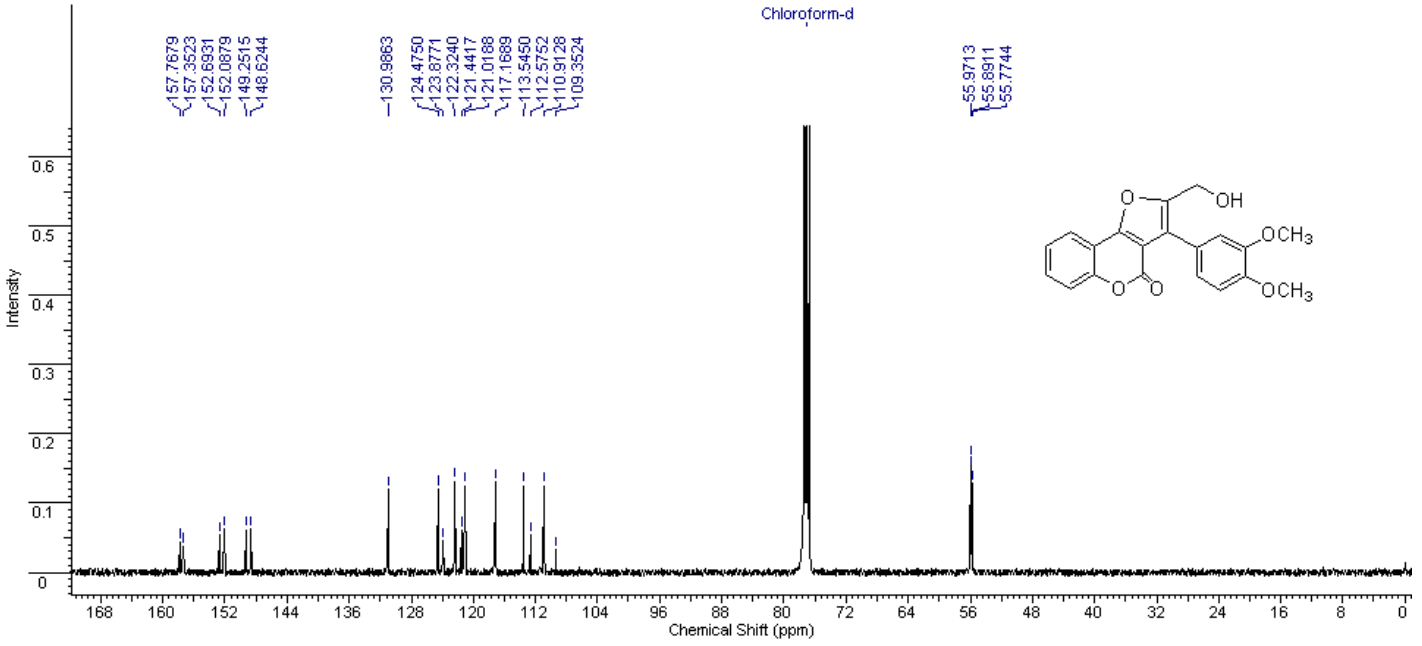
7.5812
7.5642
7.4896
7.4720
7.4024
7.3849
7.2613
7.2500
7.1823
7.1779
7.1653
6.9891
4.8239
3.9633
0.91
2.50
1.14
2.03
6.00
Intensity
Chemical Shift (ppm)
OH
OCH3
OCH3


Chloroform-d
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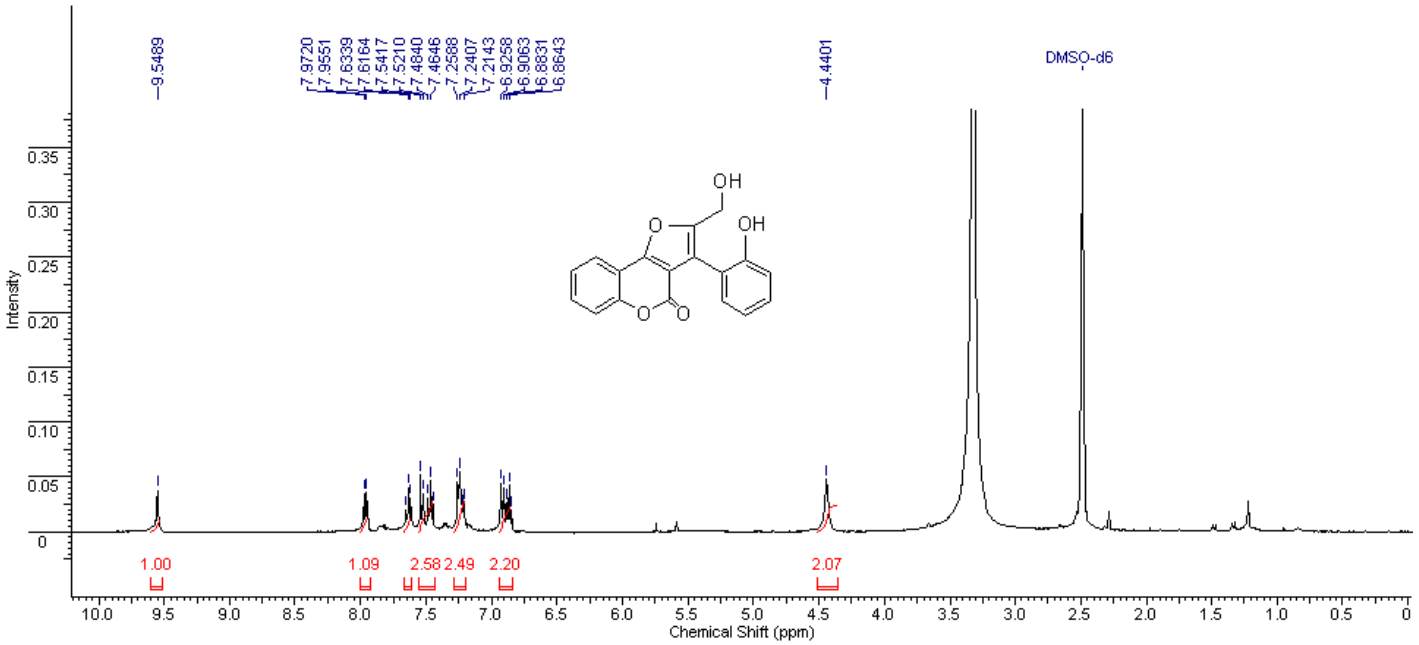
157.3523
152.6931
152.0879
149.2515
148.6244
130.9863
124.4750
123.8771
122.3240
121.4417
121.0188
117.1689
113.5450
112.5752
110.9128
109.3524
55.9713
55.8911
55.7744
Intensity
Chemical Shift (ppm)
OH
OCH3
OCH3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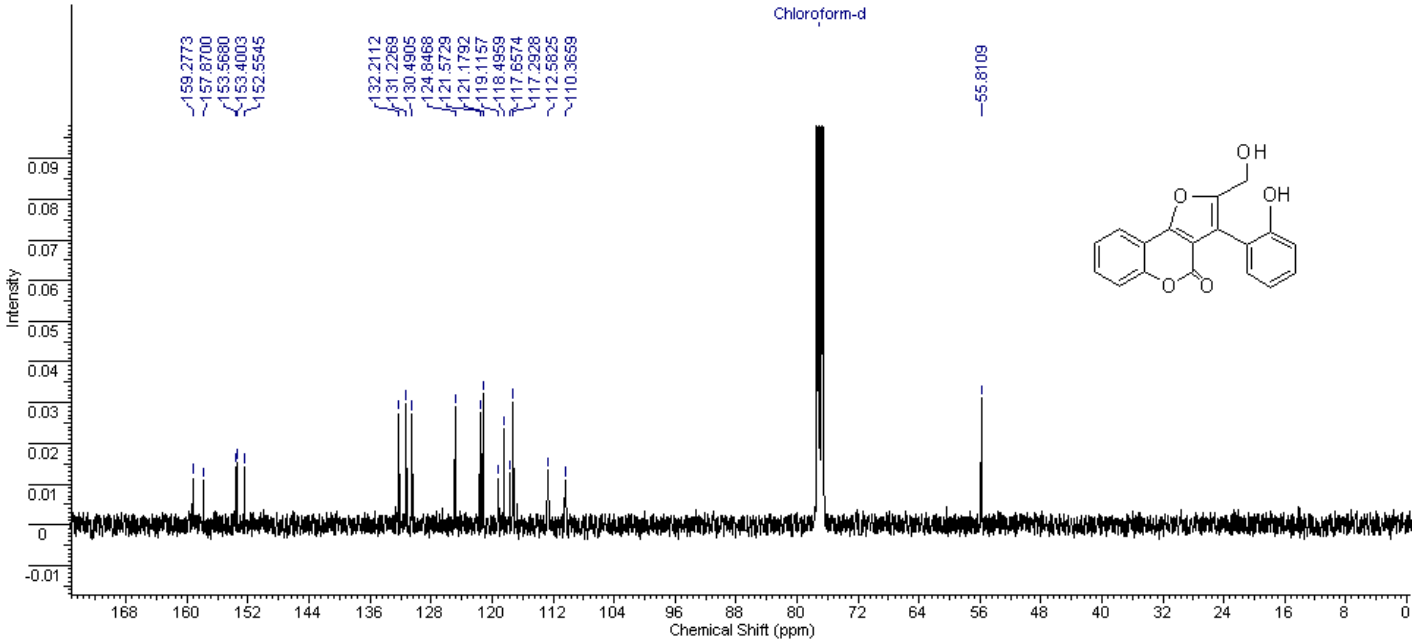
7.2407
7.2143
6.9258
6.9063
6.8831
6.8643
4.4401
DMSO-d6
OH
OH
O
O
O
Intensity
1.00
1.09
2.58
2.49
2.20
2.07
Chemical Shift (ppm)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153.5680
153.4003
152.5545
132.2112
131.2269
130.4905
124.8468
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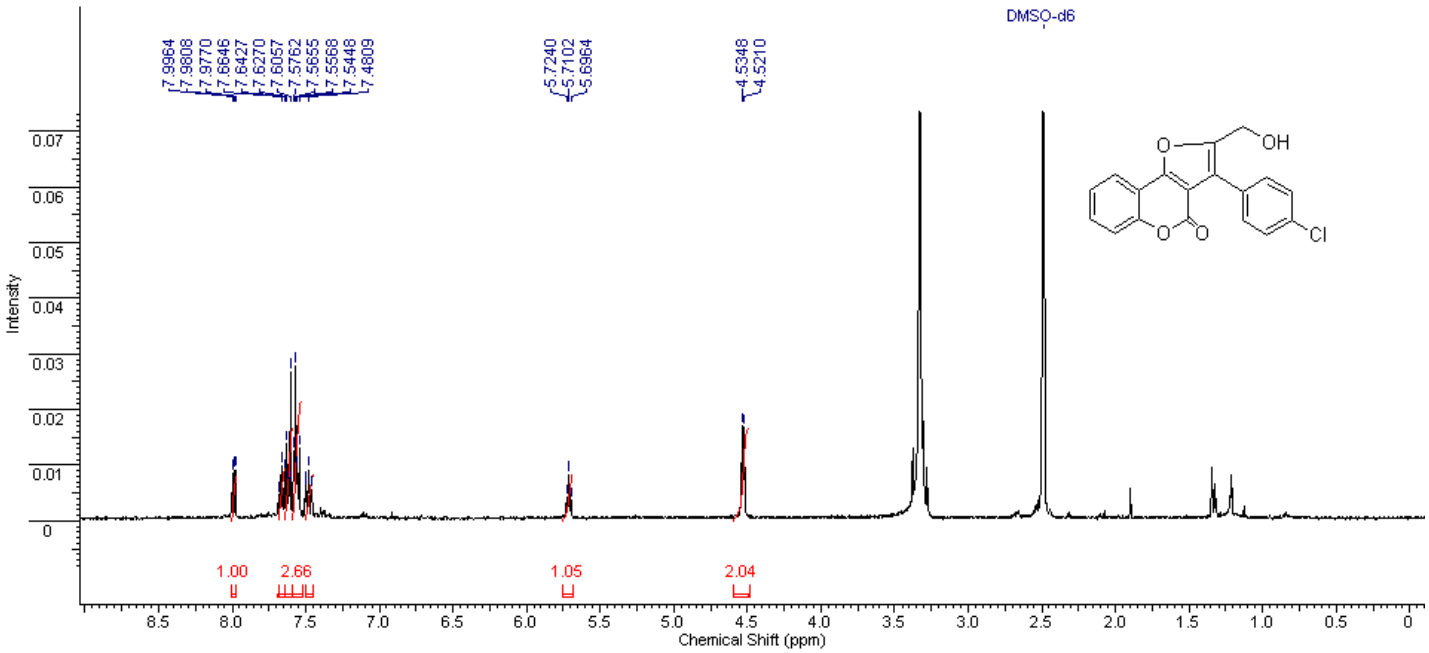
121.1792
119.1157
118.4959
117.6574
117.2928
112.5825
110.3659
55.8109
OH
OH
O
O
O
Intensity
Chemical Shift (ppm)


DMSO-d6
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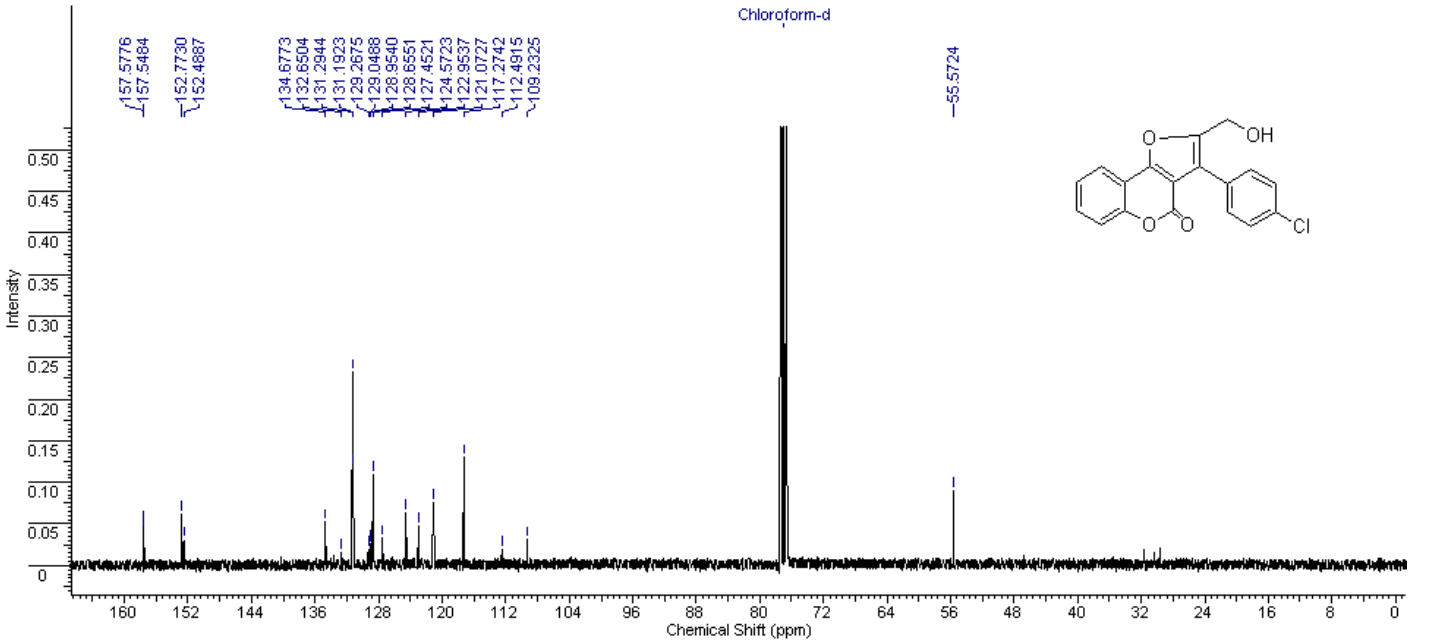
7.9808
7.9770
7.6646
7.6427
7.6270
7.6057
7.5762
7.5655
7.5568
7.5448
7.4809
5.7240
5.7102
5.6964
4.5348
4.5210
OH
O
O
O
Cl
Intensity
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
1.00
2.66
1.05
2.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


Chloroform-d
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152.4887
134.6773
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129.0488
128.9540
128.6551
127.4521
124.5723
122.9537
121.0727
117.2742
112.4915
109.2325
55.5724
OH
O
O
O
Cl
Intensity
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
160
152
144
136
128
120
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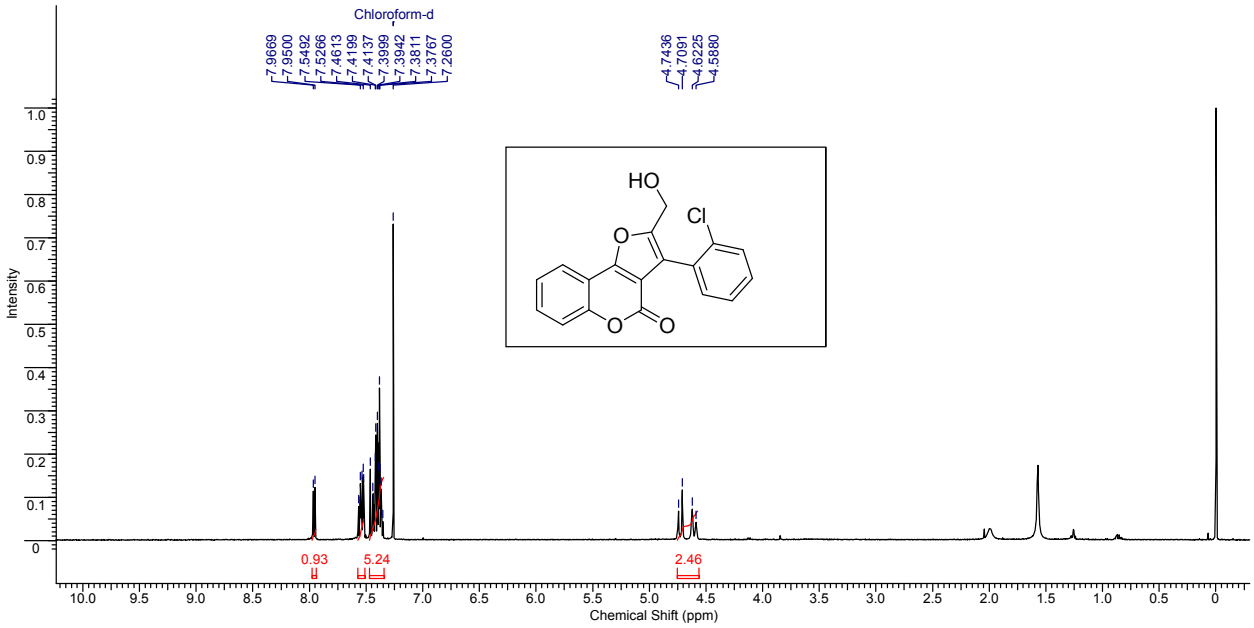
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


Chloroform-d
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7.5492
7.5266
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7.4137
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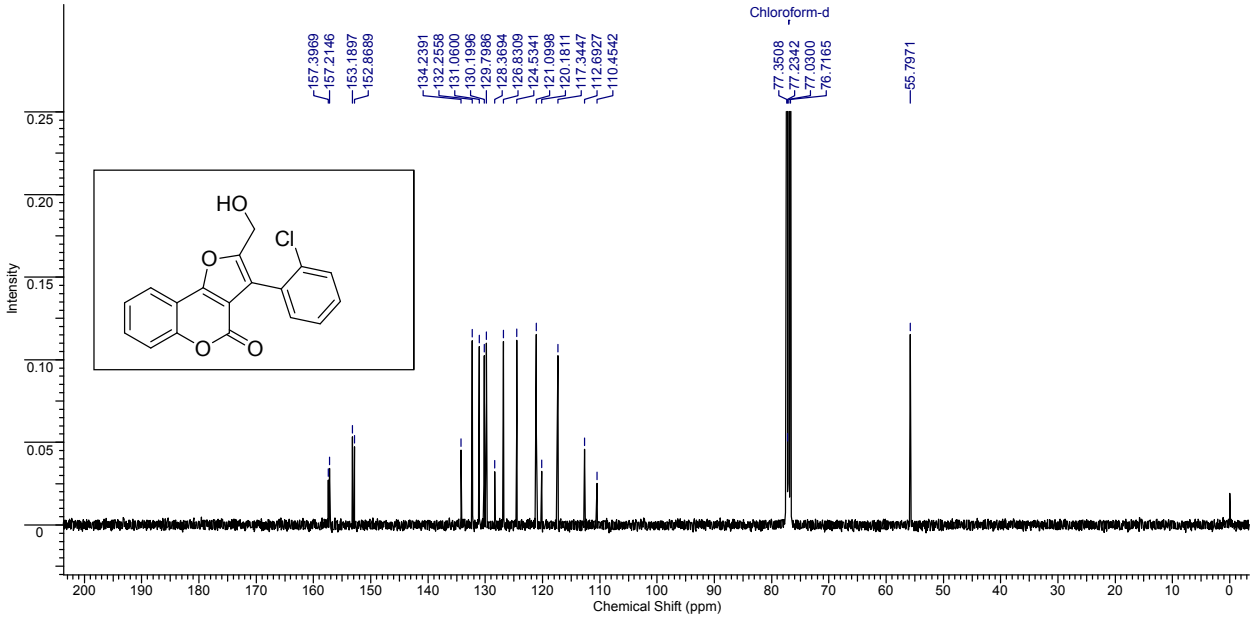
7.3811
7.3767
7.2600
4.7436
4.7091
4.6225
4.5880
HO
Cl
O
O
O
Intensity
0.93
5.24
2.46
Chemical Shift (ppm)


Chloroform-d
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126.8309
124.5341
121.0998
120.1811
117.3447
112.6927
110.4542
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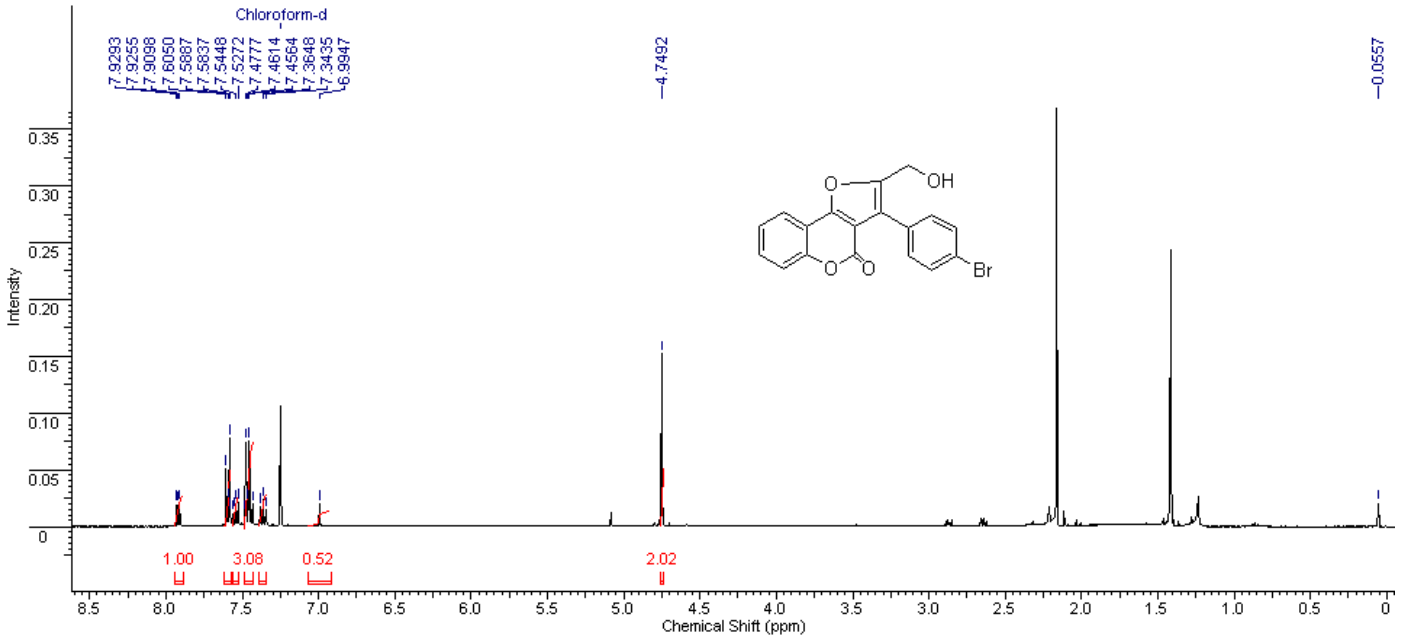
77.0300
76.7165
55.7971
HO
Cl
O
O
O
Intensity
Chemical Shift (ppm)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7.6050
7.5887
7.5837
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7.5272
7.4777
7.4614
7.4564
7.3648
7.3435
6.9947
4.7492
0.0557
OH
O
O
O
Br
Intensity
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
1.00
3.08
0.52
2.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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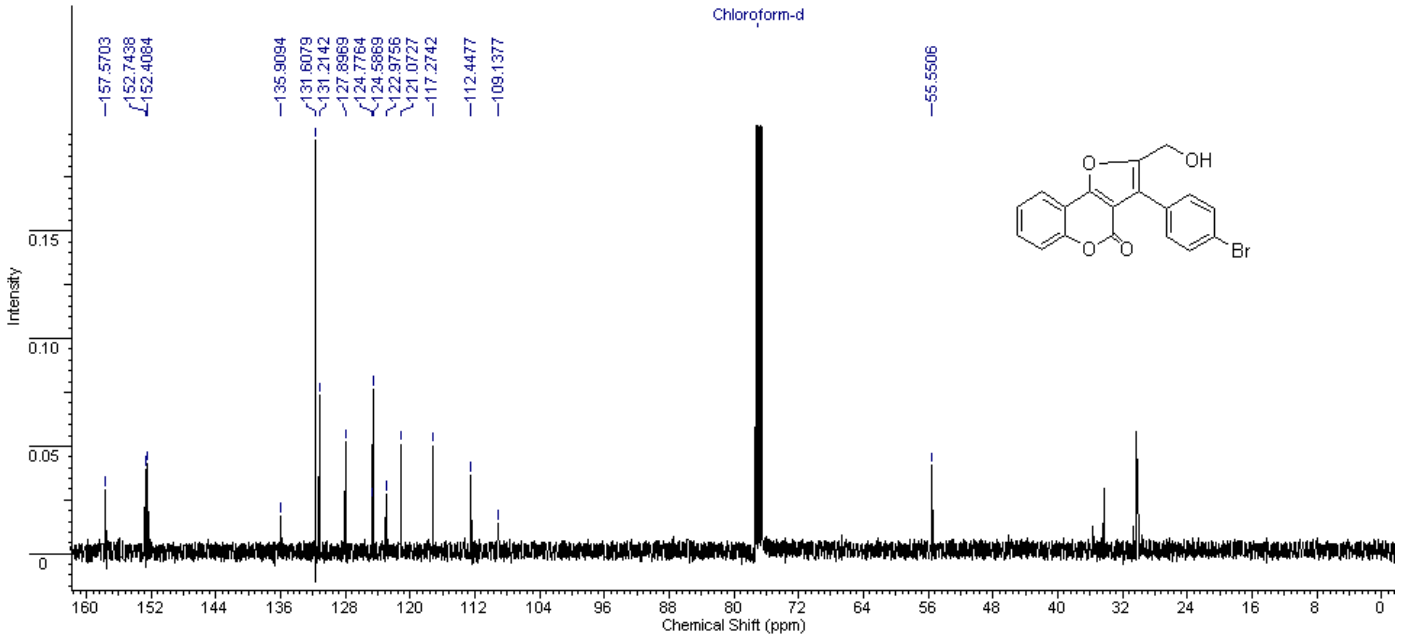
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


Chloroform-d
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131.2142
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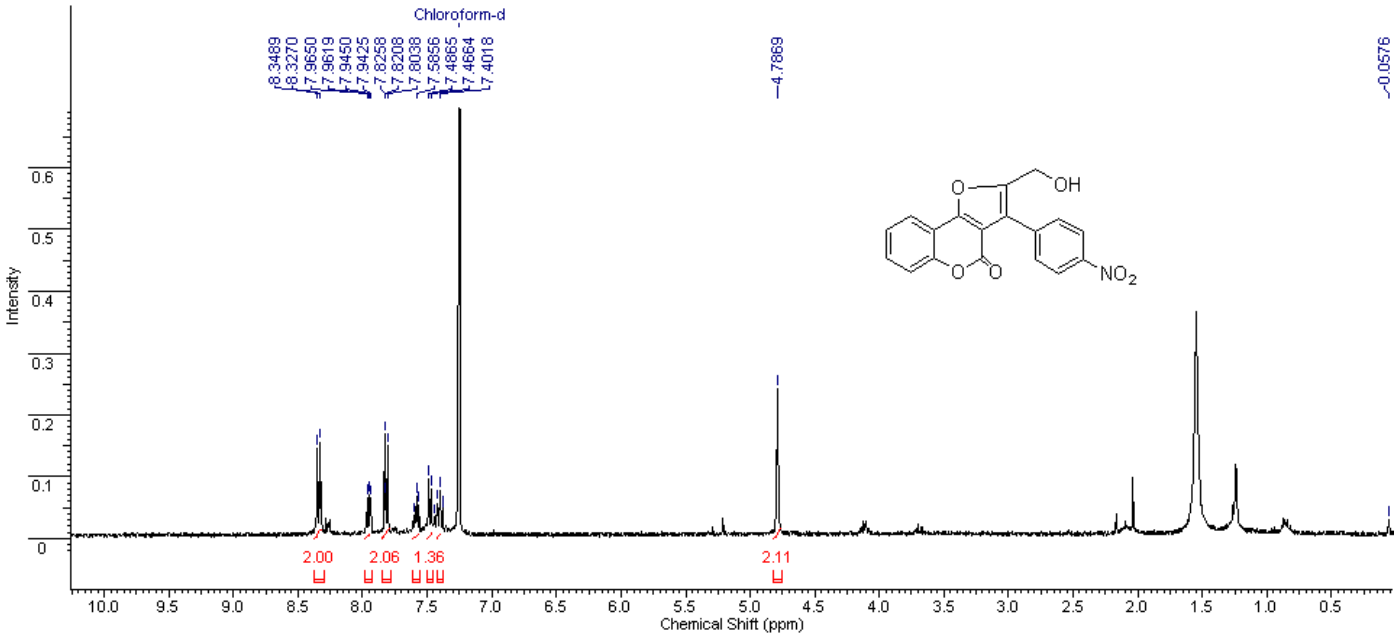
124.7764
124.5869
122.9756
121.0727
117.2742
112.4477
109.1377
55.5506
OH
O
O
O
Br
Intensity
0.15
0.10
0.05
0
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


Chloroform-d
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7.9650
7.9619
7.9450
7.9425
7.8258
7.8208
7.8038
7.5856
7.4885
7.4664
7.4018
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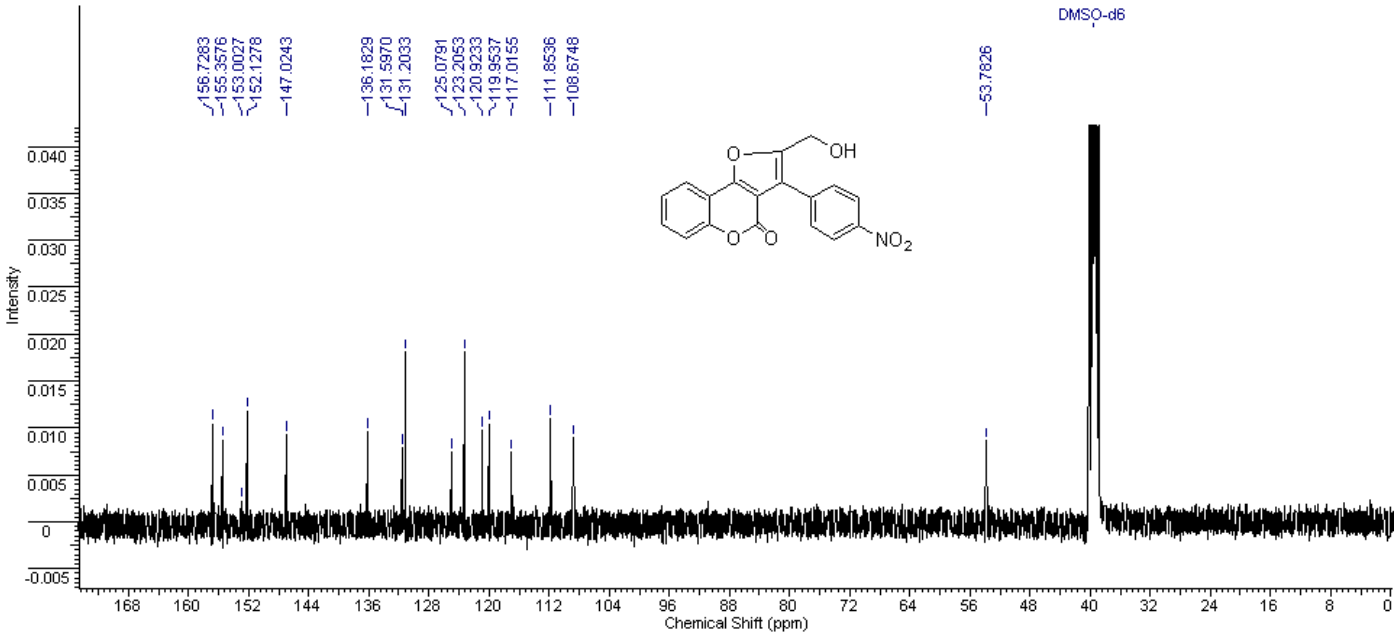
OH
O
O
O
NO2
Intensity
2.00
2.06
1.36
2.11
Chemical Shift (ppm)


DMSO-d6
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155.3576
153.0027
152.1278
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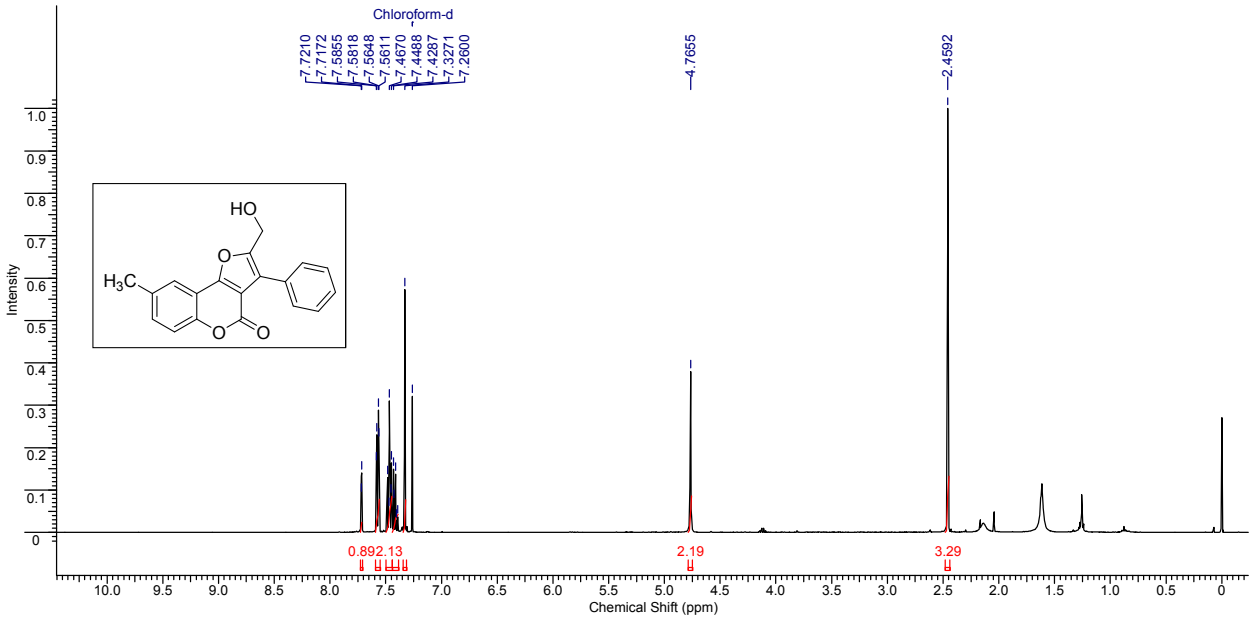
136.1829
131.5970
131.2033
125.0791
123.2053
120.9233
119.9537
117.0155
111.8536
108.6748
53.7826
OH
O
O
O
NO2
Intensity
Chemical Shift (ppm)


Chloroform-d
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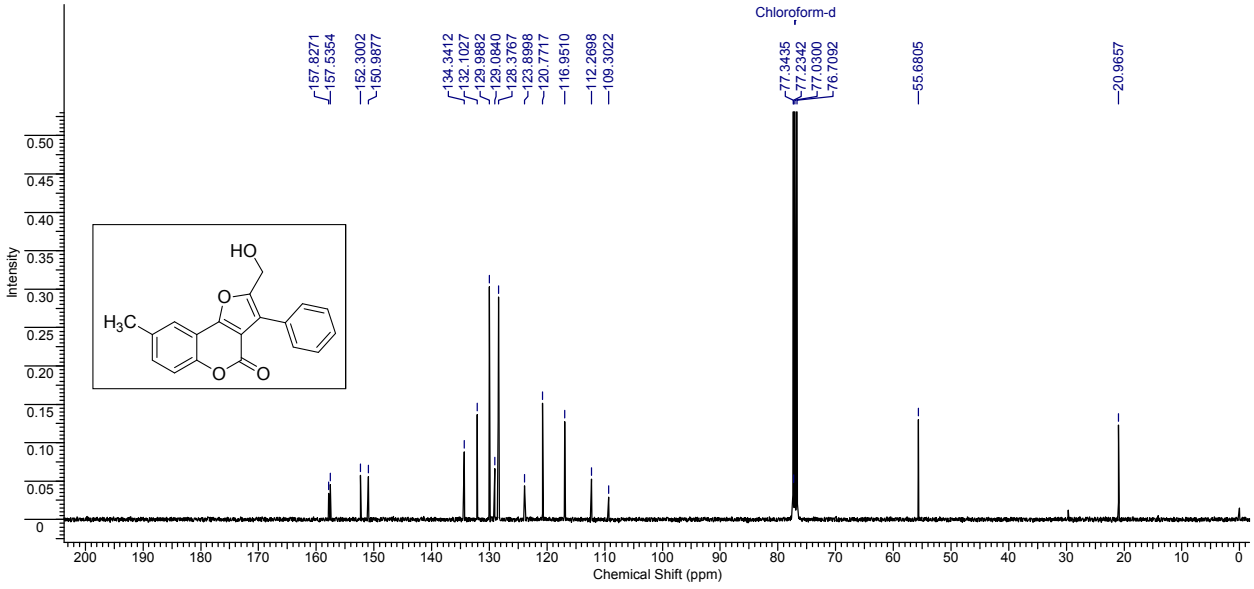
7.5855
7.5818
7.5648
7.5611
7.4670
7.4488
7.4287
7.3271
7.2600
4.7655
2.4592
HO
O
H_3C
O
O
Intensity
0.89
2.13
2.19
3.29
Chemical Shift (ppm)


Chloroform-d
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120.7717
116.9510
112.2698
109.3022
77.3435
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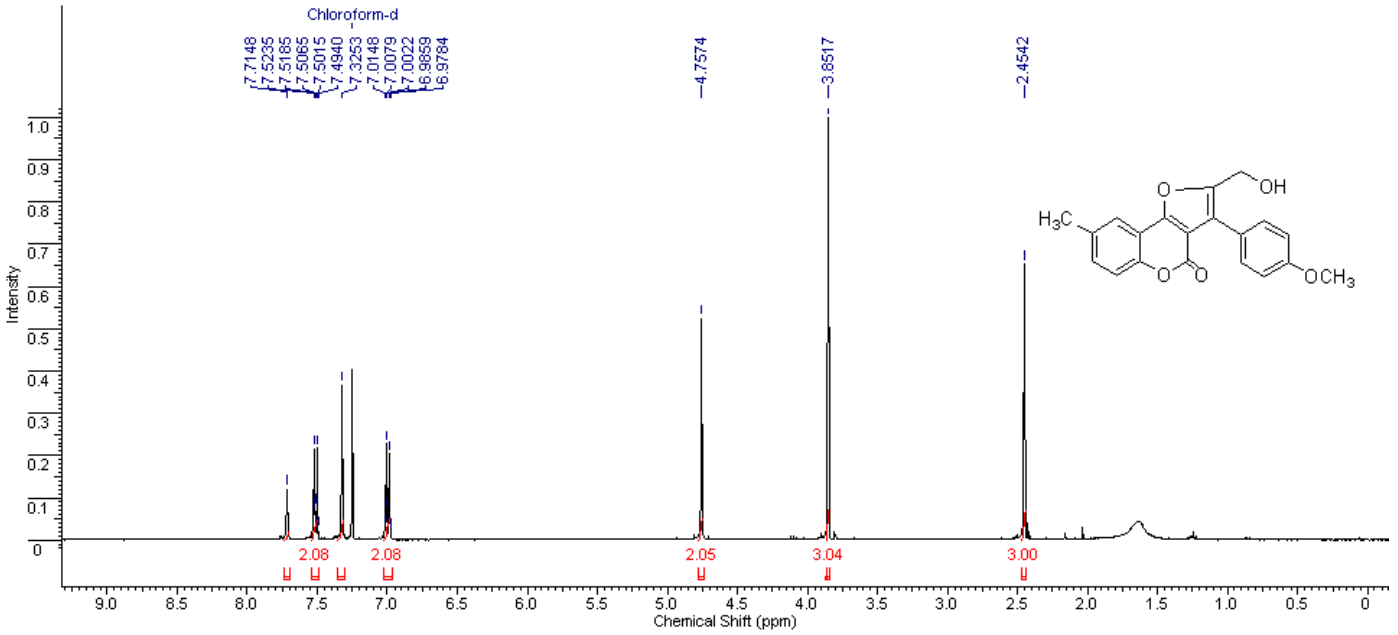
HO
O
H_3C
O
O
Intensity
Chemical Shift (ppm)


Chloroform-d
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7.5235
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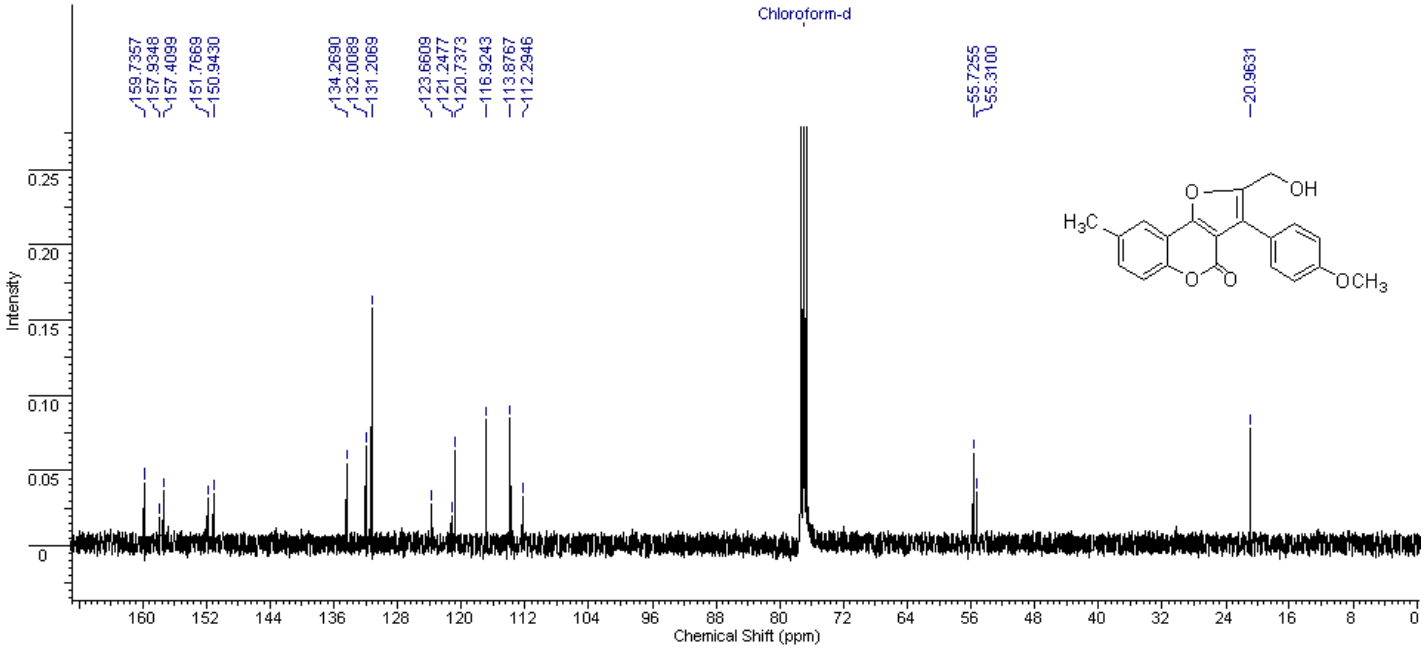
7.4940
7.3253
7.0148
7.0079
7.0022
6.9859
6.9784
4.7574
3.8517
2.4542
Intensity
2.08
2.08
2.05
3.04
3.00
Chemical Shift (ppm)
OH
O
H3C
O
O
OCH3


Chloroform-d
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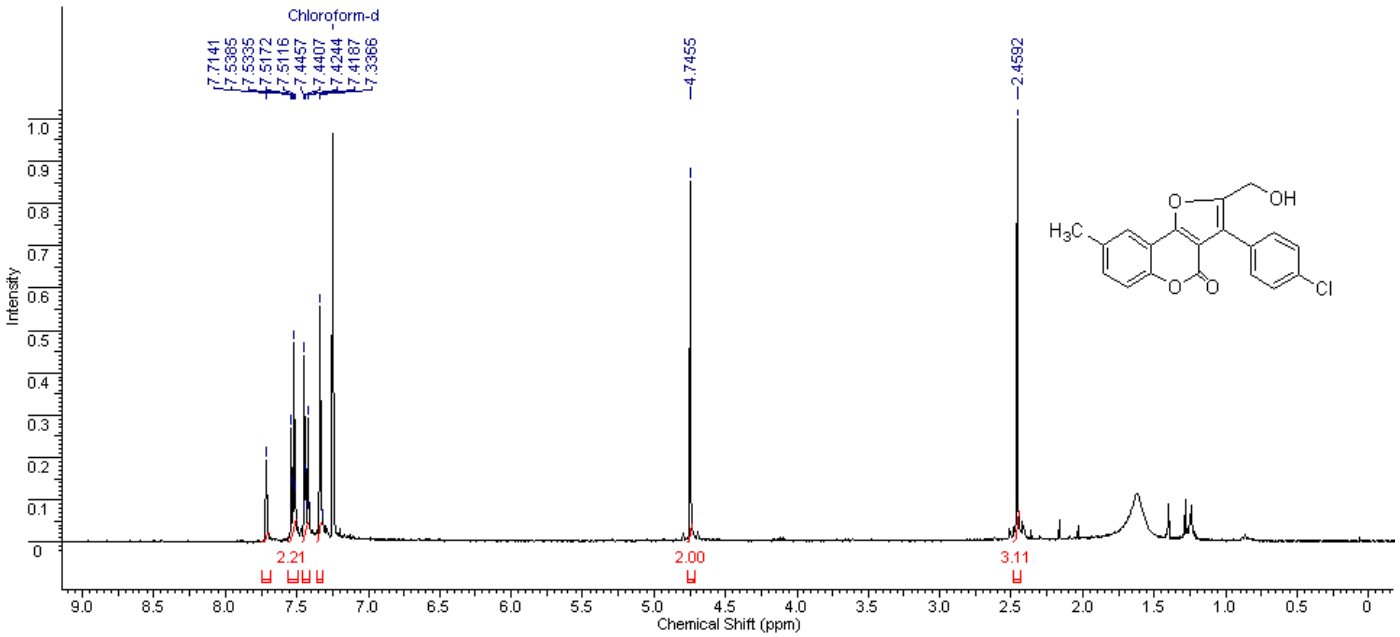
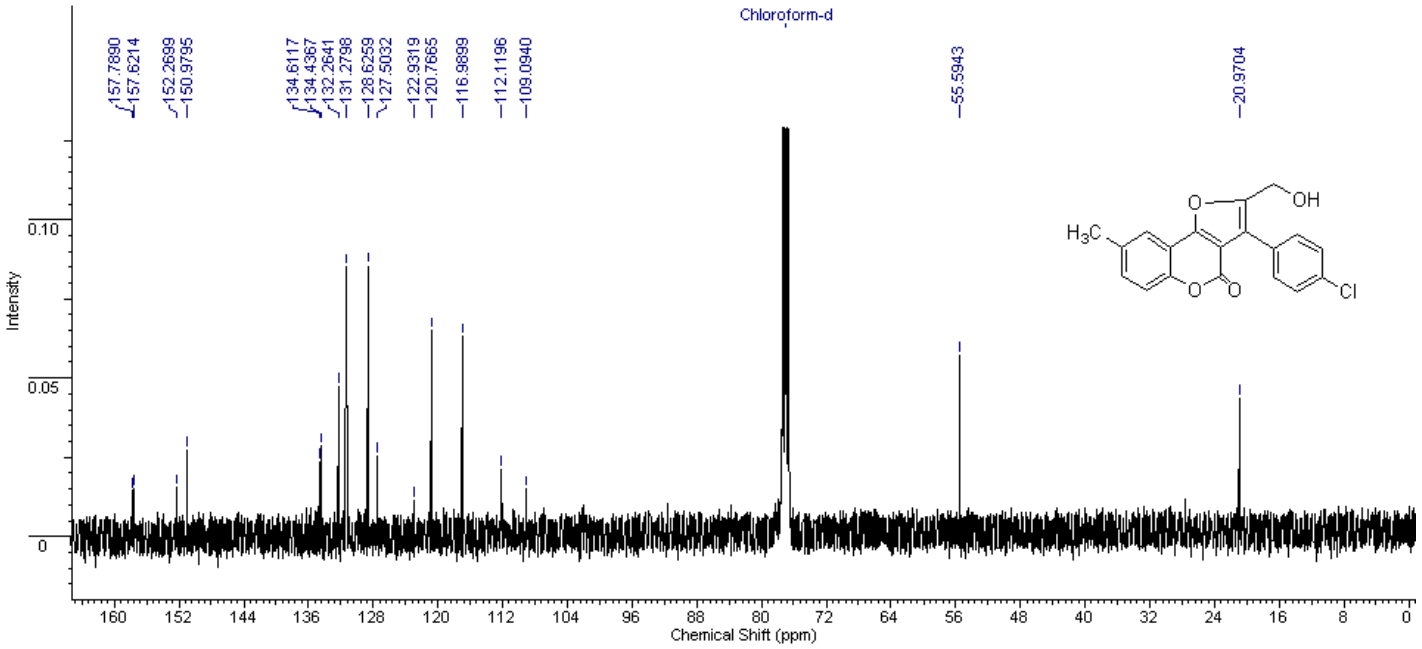
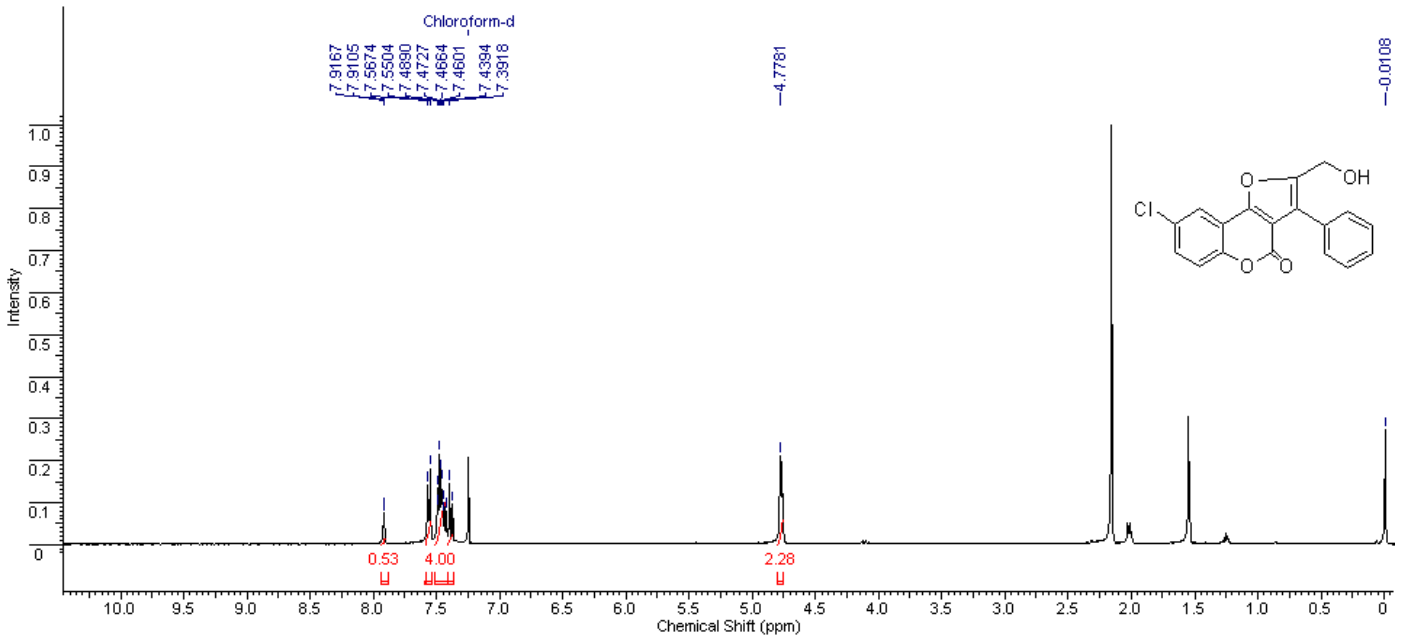
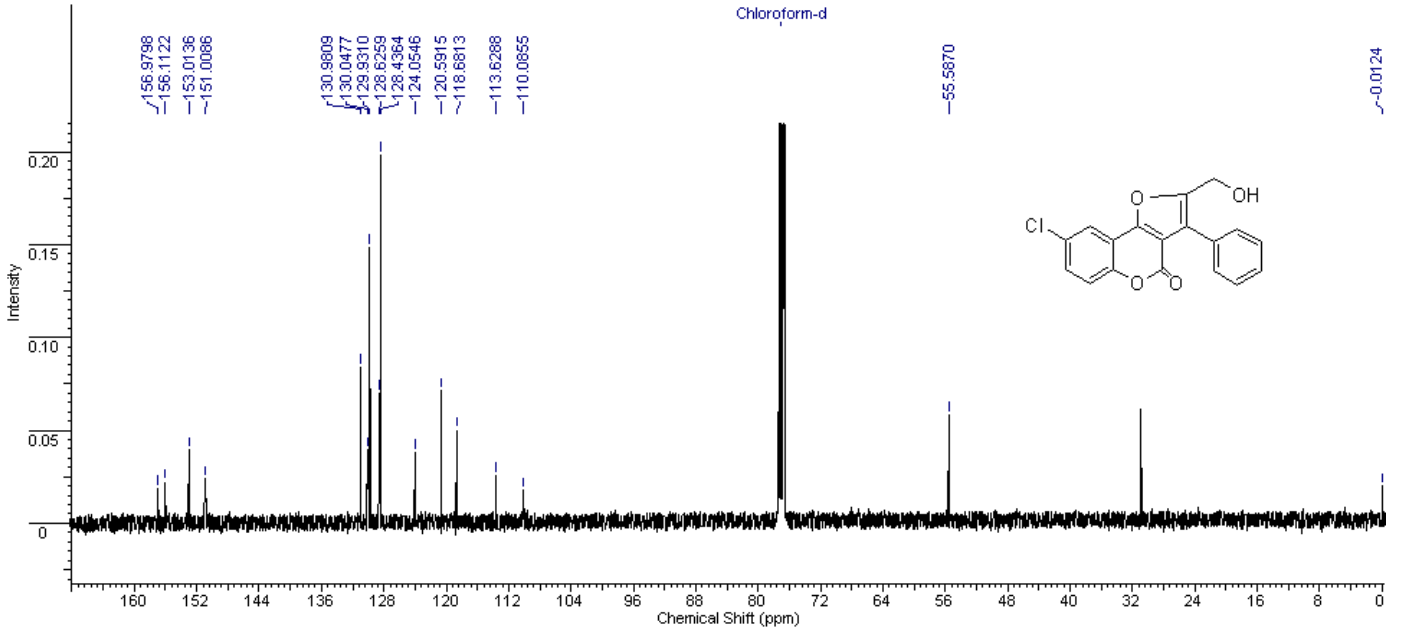
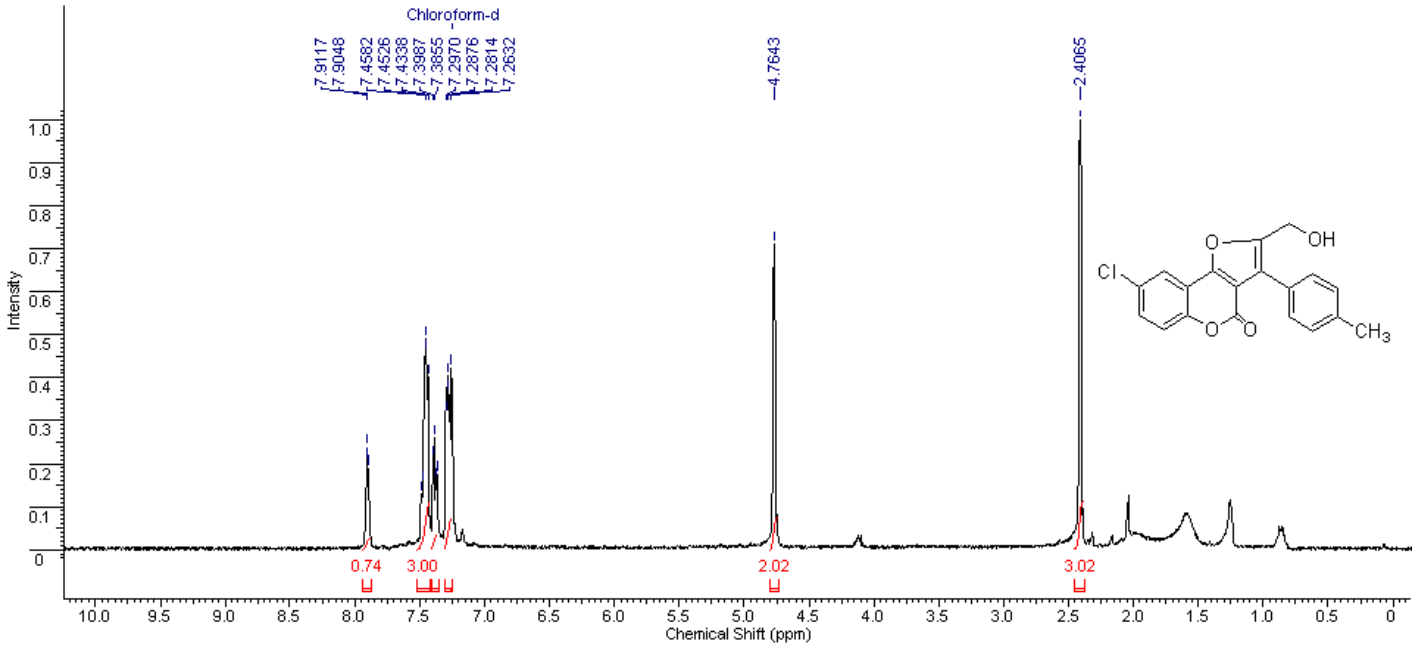
123.6609
121.2477
120.7373
116.9243
113.8767
112.2946
55.7255
55.3100
20.9631
Intensity
Chemical Shift (ppm)
OH
O
H3C
O
O
OCH3

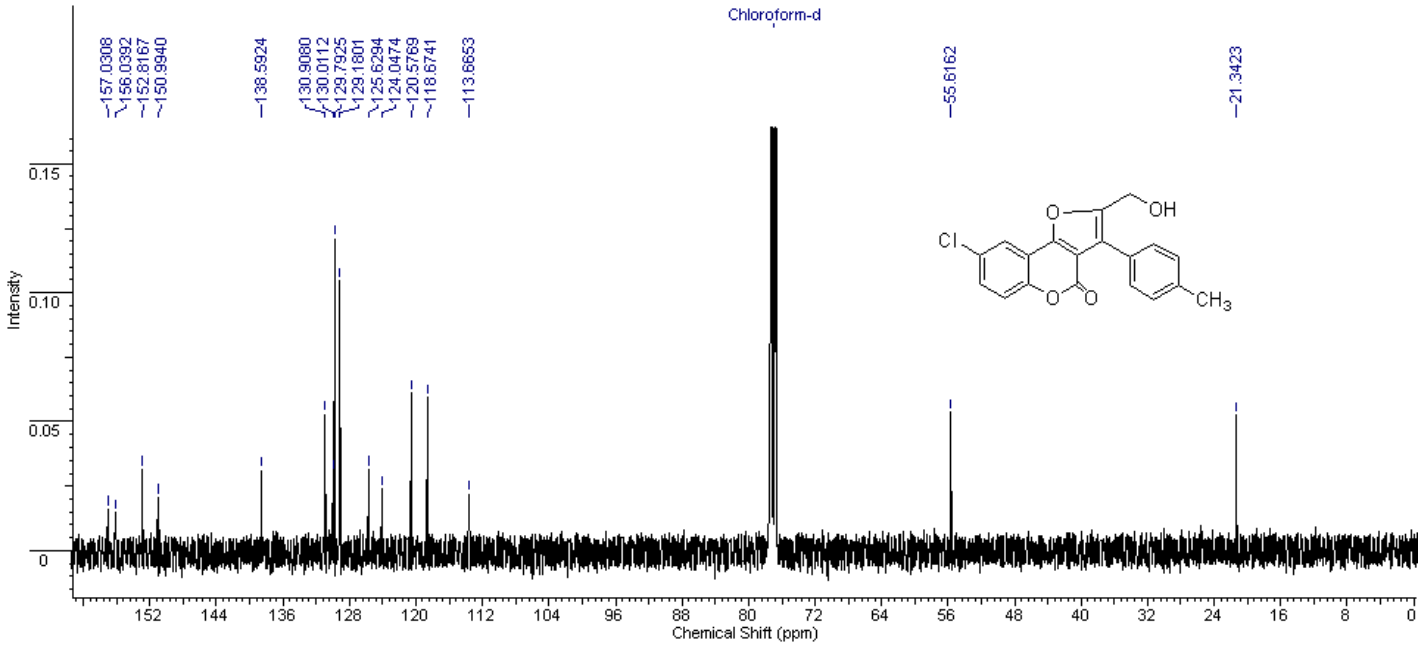

Chloroform-d
7.7141
7.5385
7.5335
7.5172
7.5116
7.4457
7.4407
7.4244
7.4187
7.3366
4.7455
2.4592
Intensity
2.21
2.00
3.11
Chemical Shift (ppm)
OH
H3C
O
O
O
Cl

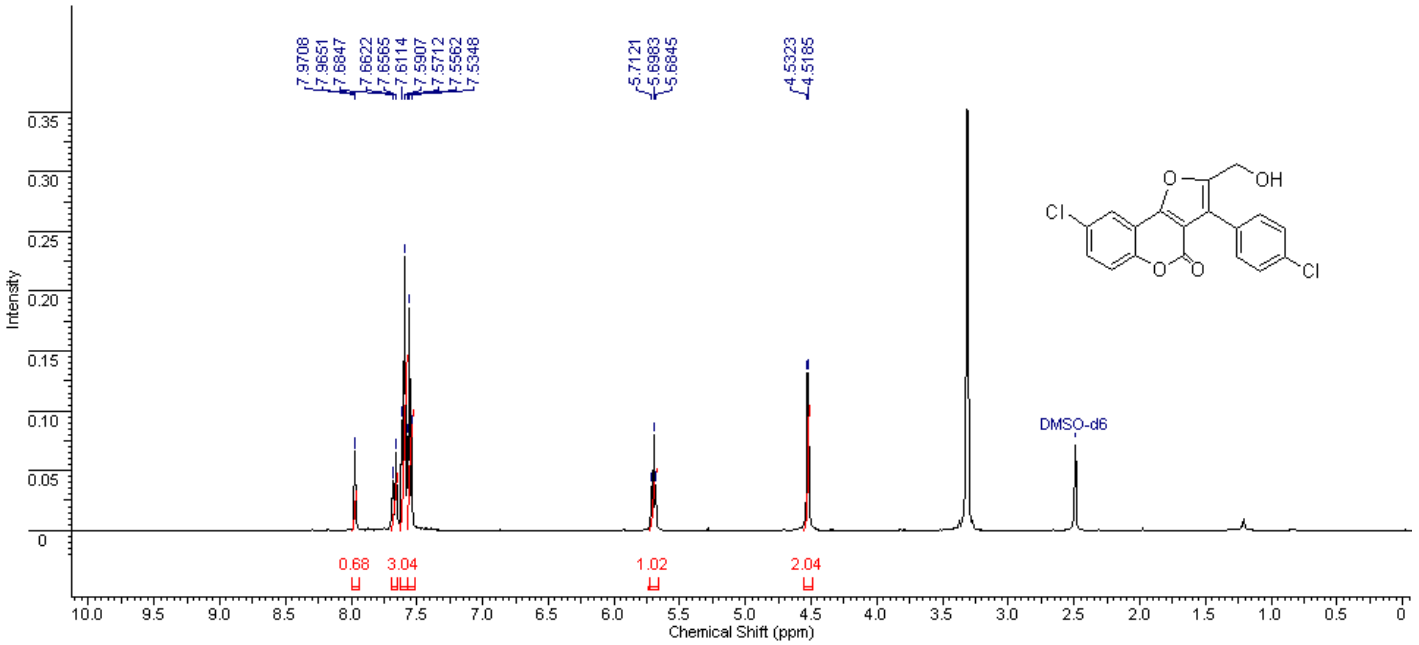

Chloroform-d
157.7890
157.6214
152.2699
150.9795
134.6117
134.4367
132.2641
131.2798
128.6259
127.5032
122.9319
120.7665
116.9899
112.1196
109.0940
55.5943
20.9704
Intensity
Chemical Shift (ppm)
OH
H3C
O
O
O
Cl

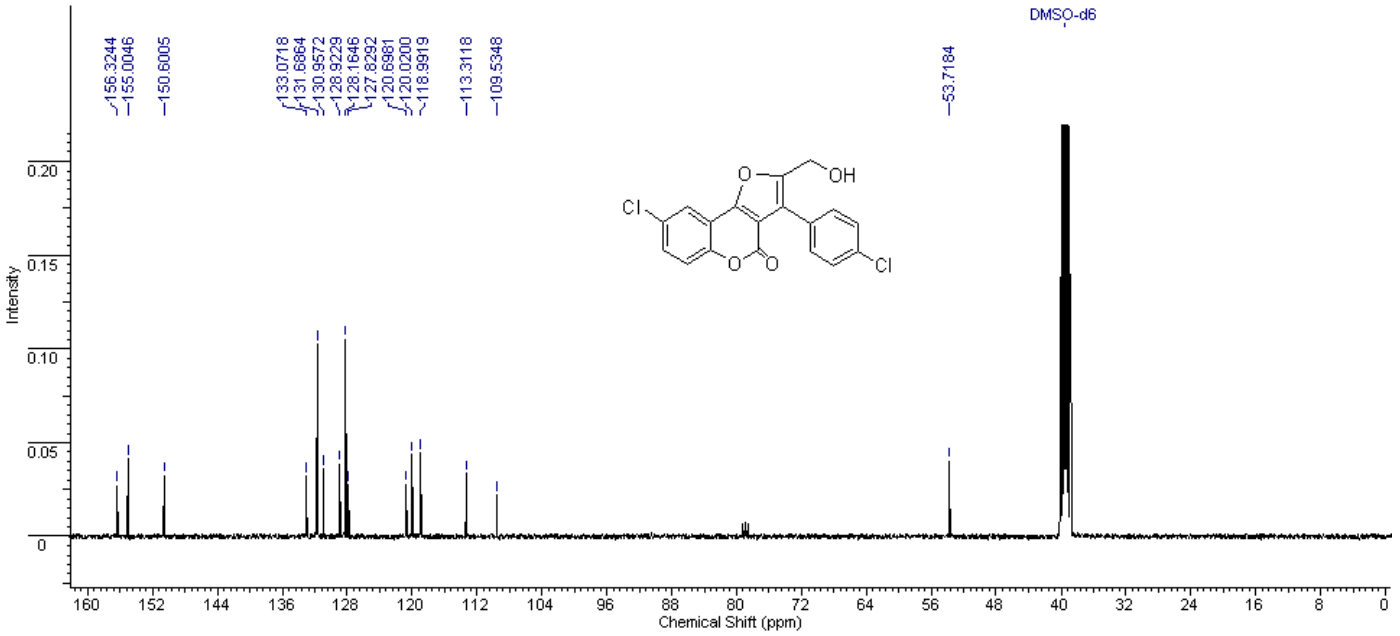

Chloroform-d
7.9167
7.9105
7.5674
7.5504
7.4890
7.4727
7.4664
7.4601
7.4394
7.3918
4.7781
0.0108
Intensity
0.53
4.00
2.28
Chemical Shift (ppm)
Cl
OH
O
O
O

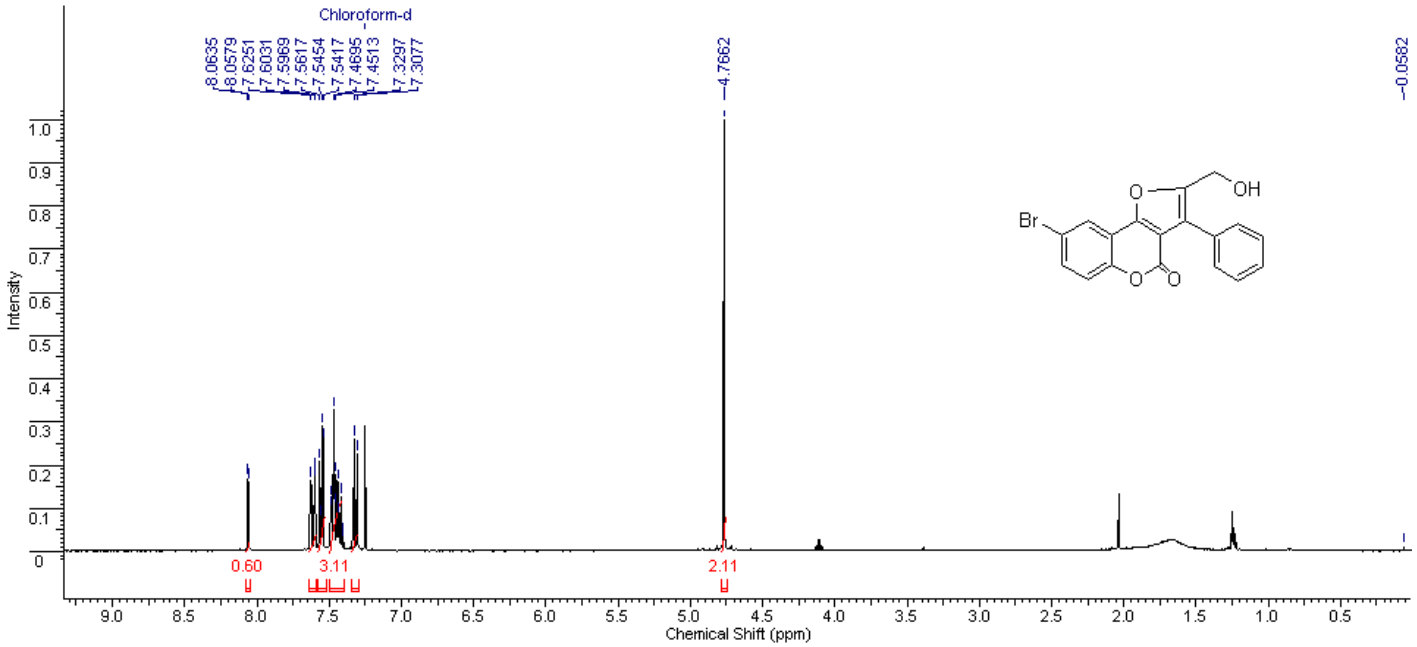

Chloroform-d
156.9798
156.1122
153.0136
151.0086
130.9809
130.0477
129.9310
128.6259
128.4364
124.0546
120.5915
118.6813
113.6288
110.0855
55.5870
0.0124
Intensity
Chemical Shift (ppm)
Cl
OH
O
O
O

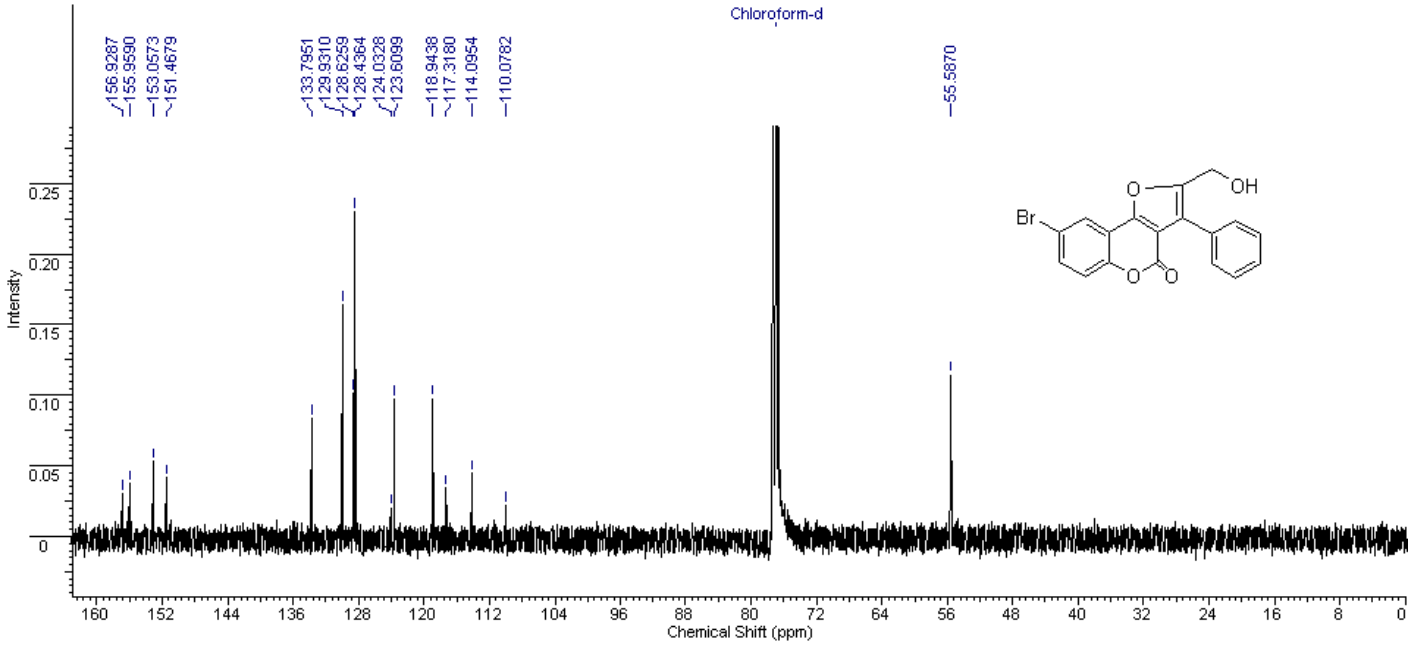

Chloroform-d
7.9117
7.9048
7.4582
7.4526
7.4338
7.3987
7.3855
7.2970
7.2876
7.2814
7.2632
4.7643
2.4065
Intensity
0.74
3.00
2.02
3.02
Chemical Shift (ppm)
Cl
OH
O
O
O
CH3

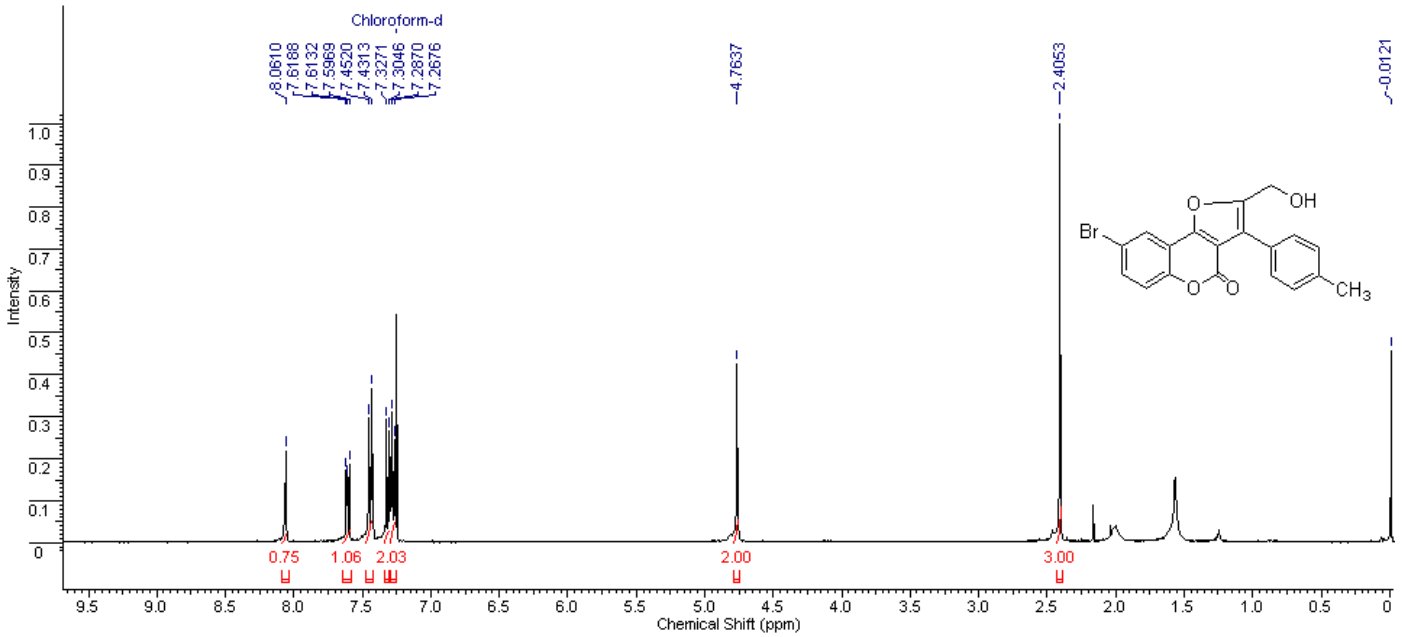

Chloroform-d
157.0308
156.0392
152.8167
150.9940
138.5924
130.9080
130.0112
129.7925
129.1801
125.6294
124.0474
120.5769
118.6741
113.6653
55.6162
21.3423
Intensity
Chemical Shift (ppm)
Cl
OH
O
O
O
CH3

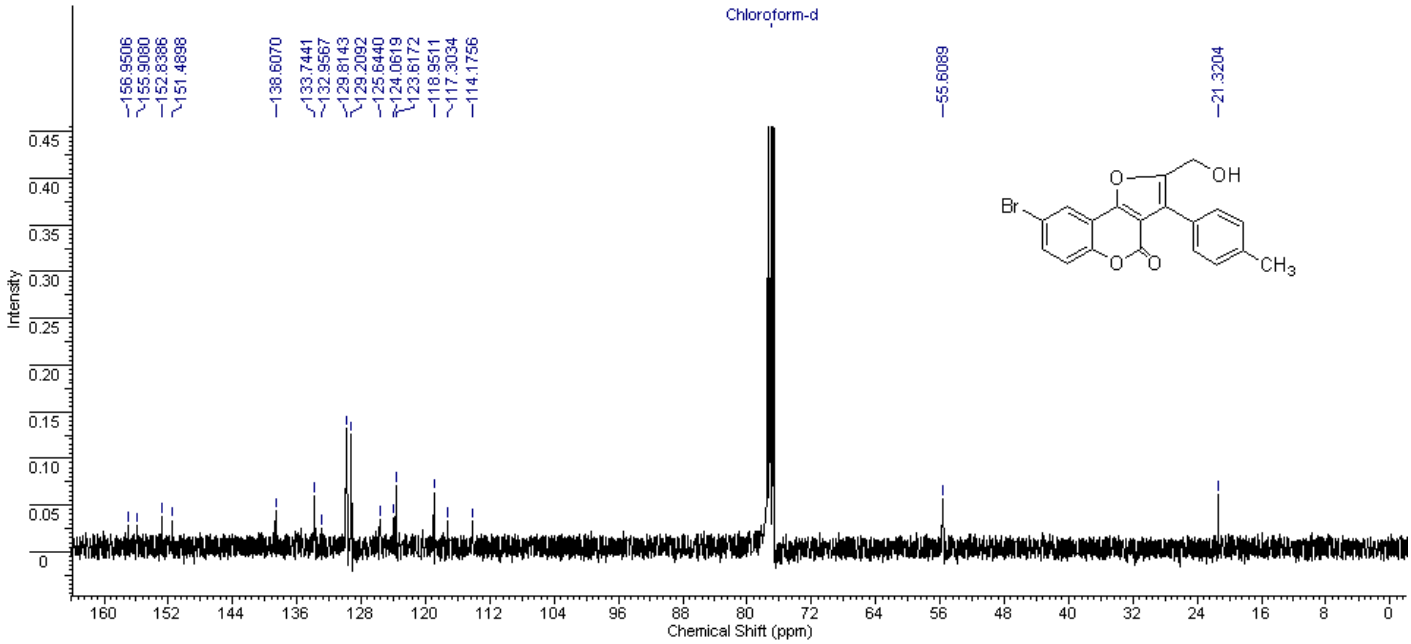

7.9708
7.9651
7.6847
7.6622
7.6565
7.6114
7.5907
7.5712
7.5562
7.5348
5.7121
5.6983
5.6845
4.5323
4.5185
DMSO-d6
0.68
3.04
1.02
2.04
Intensity
Chemical Shift (ppm)
Cl
O
OH
O
O
Cl

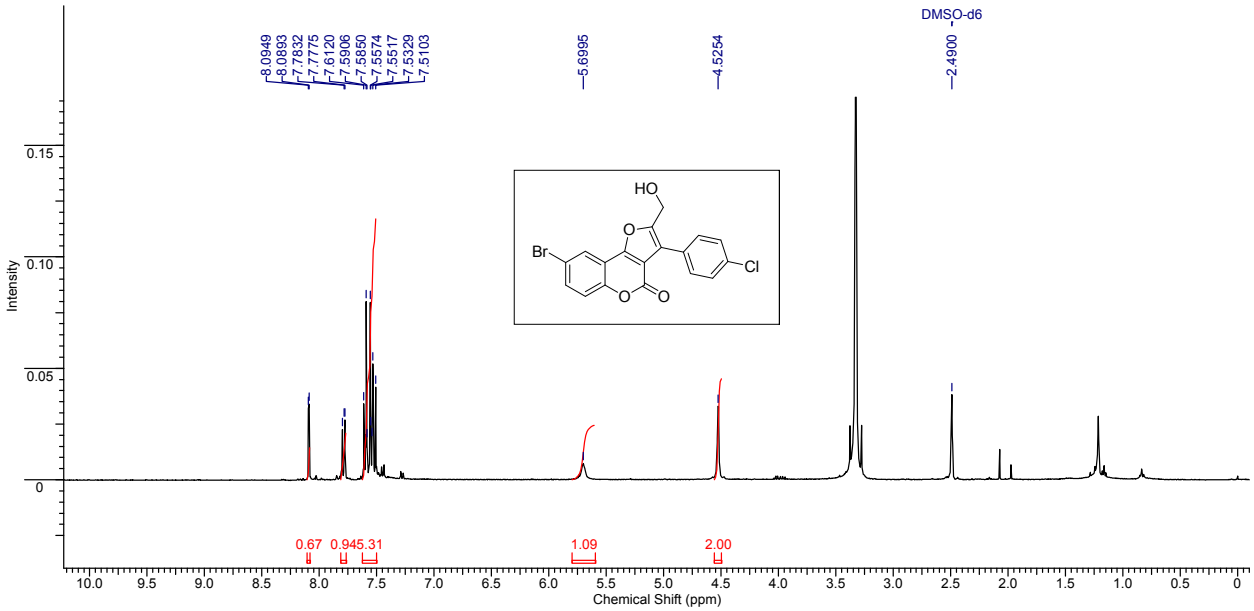

156.3244
155.0046
150.6005
133.0718
131.6864
130.9572
128.9229
128.1646
127.8292
120.6981
120.0200
118.9919
113.3118
109.5348
53.7184
DMSO-d6
Intensity
Chemical Shift (ppm)
Cl
O
OH
O
O
Cl

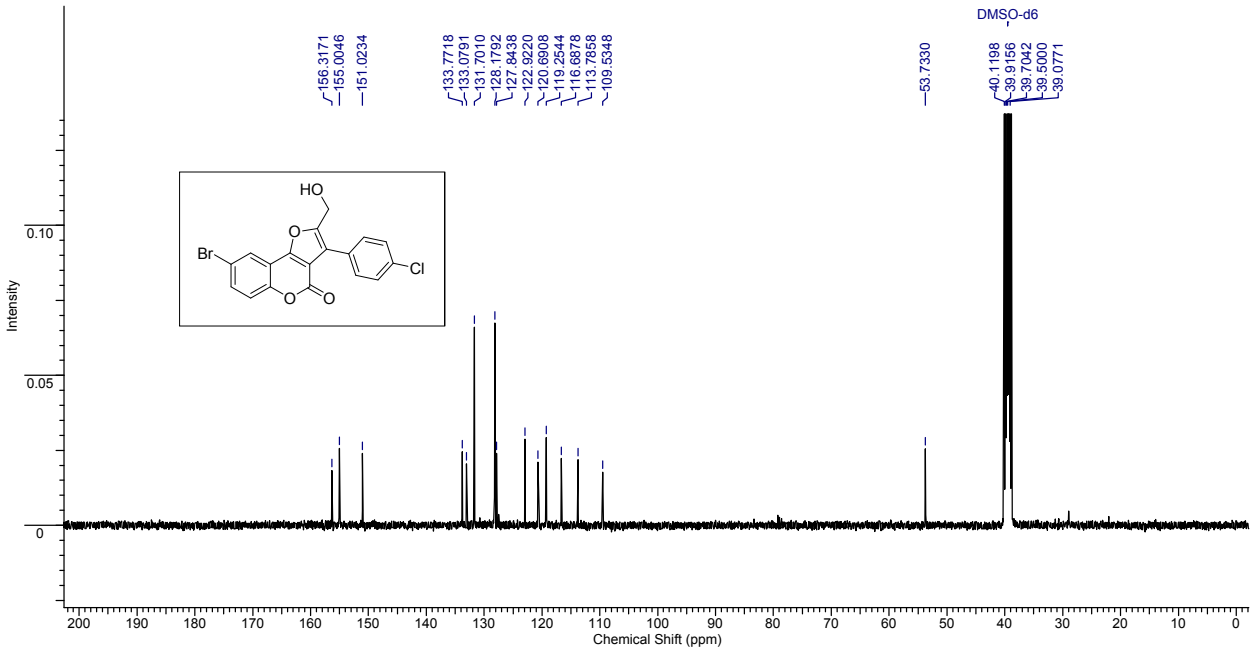

Chloroform-d
8.0635
8.0579
7.6251
7.6031
7.5969
7.5617
7.5454
7.5417
7.4695
7.4513
7.3297
7.3077
4.7662
0.0582
0.60
3.11
2.11
Intensity
Chemical Shift (ppm)
Br
OH
O
O
O

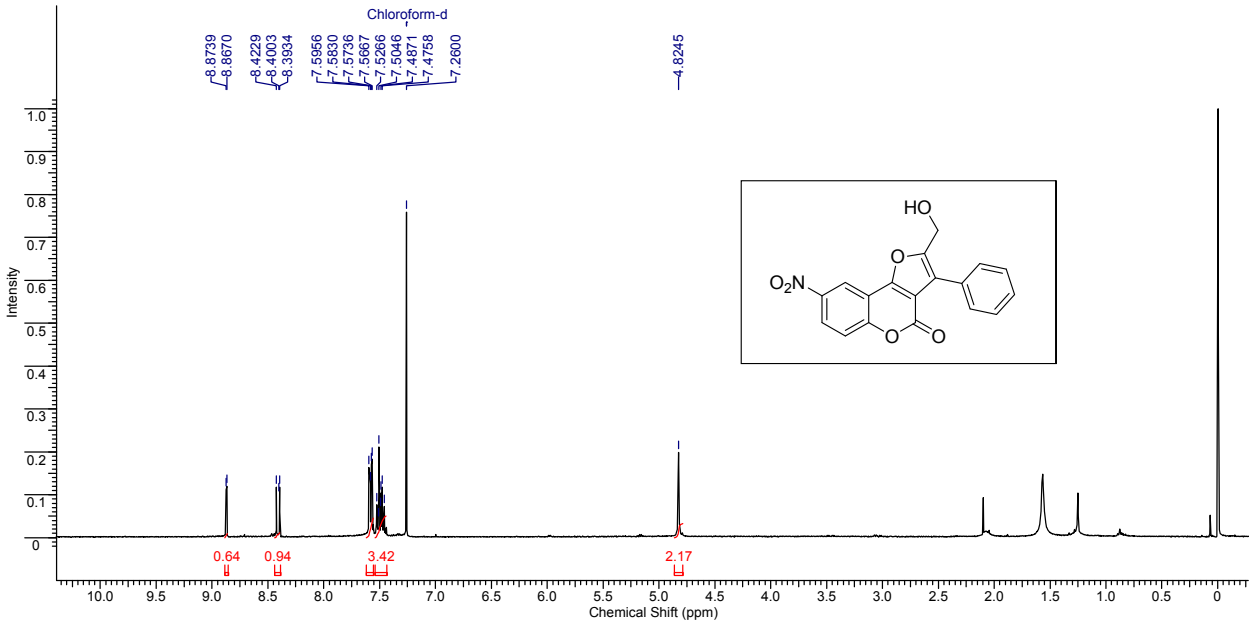

Chloroform-d
156.9287
155.9590
153.0573
151.4679
133.7951
129.9310
128.6259
128.4364
124.0328
123.6099
118.9438
117.3180
114.0954
110.0782
55.5870
Intensity
Chemical Shift (ppm)
Br
OH
O
O
O

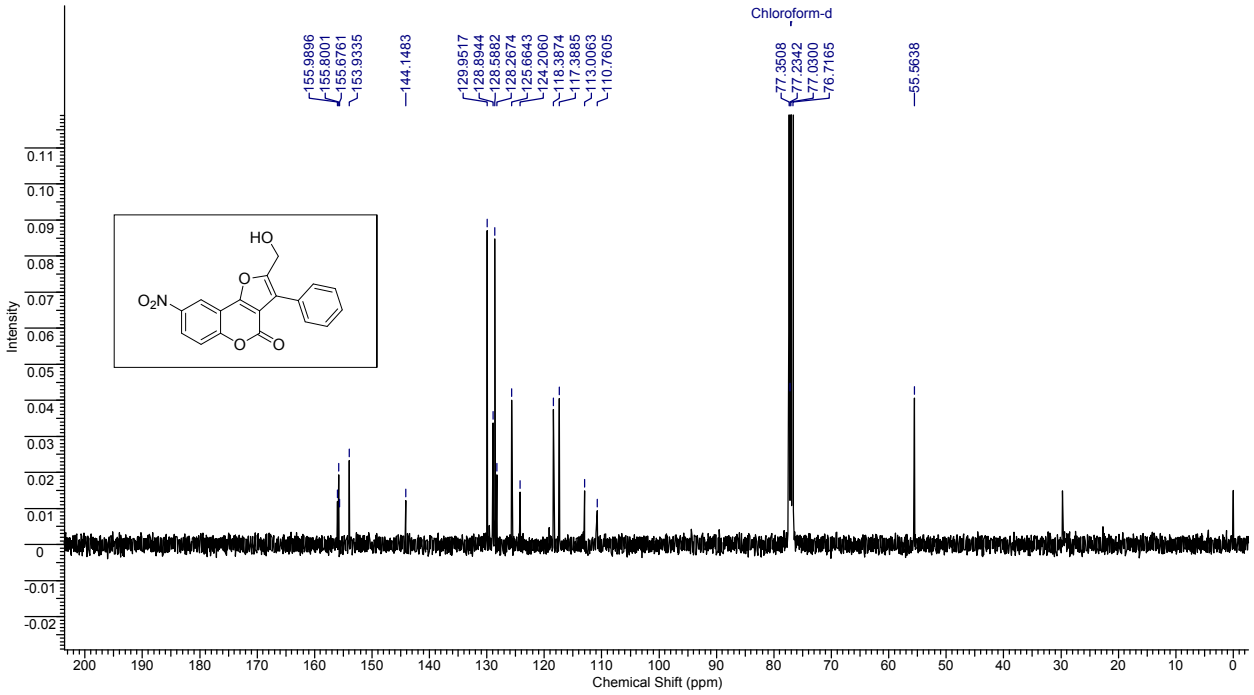

Chloroform-d
8.0610
7.6188
7.6132
7.5969
7.4520
7.4313
7.3271
7.3046
7.2870
7.2676
4.7637
2.4053
0.0121
0.75
1.06
2.03
2.00
3.00
Intensity
Chemical Shift (ppm)
OH
Br
O
O
O
CH3

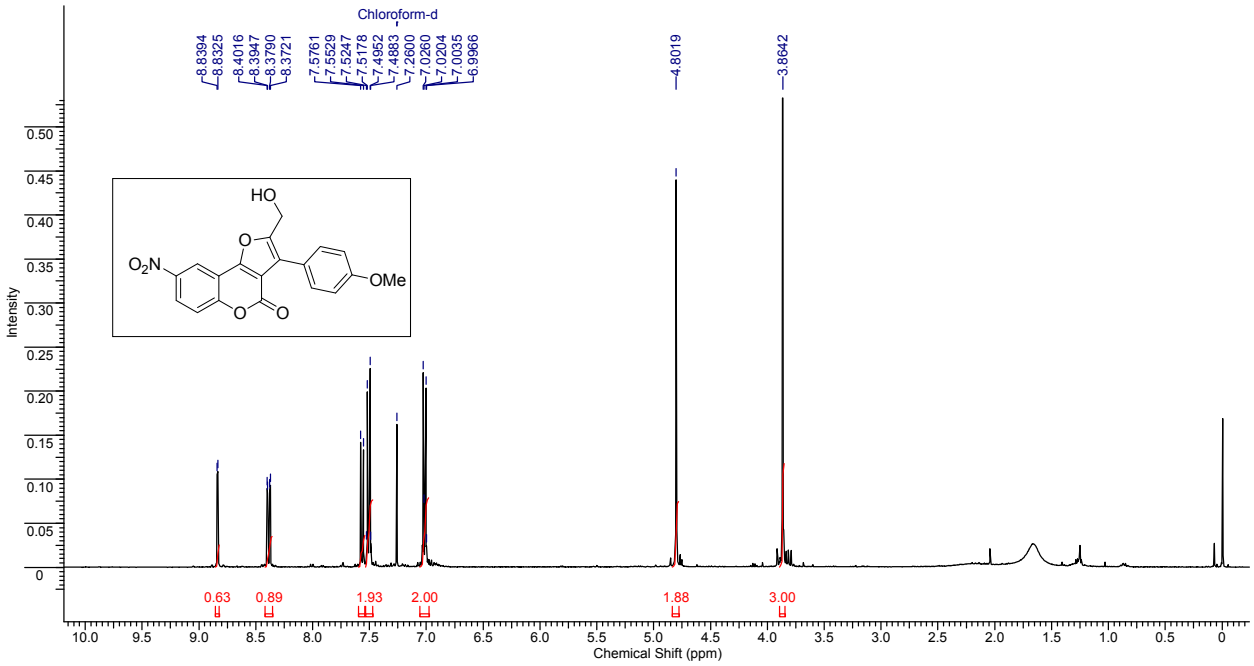

Chloroform-d
156.9506
155.9080
152.8386
151.4898
138.6070
133.7441
132.9567
129.8143
129.2092
125.6440
124.0619
123.6172
118.9511
117.3034
114.1756
55.6089
21.3204
Intensity
Chemical Shift (ppm)
OH
Br
O
O
O
CH3

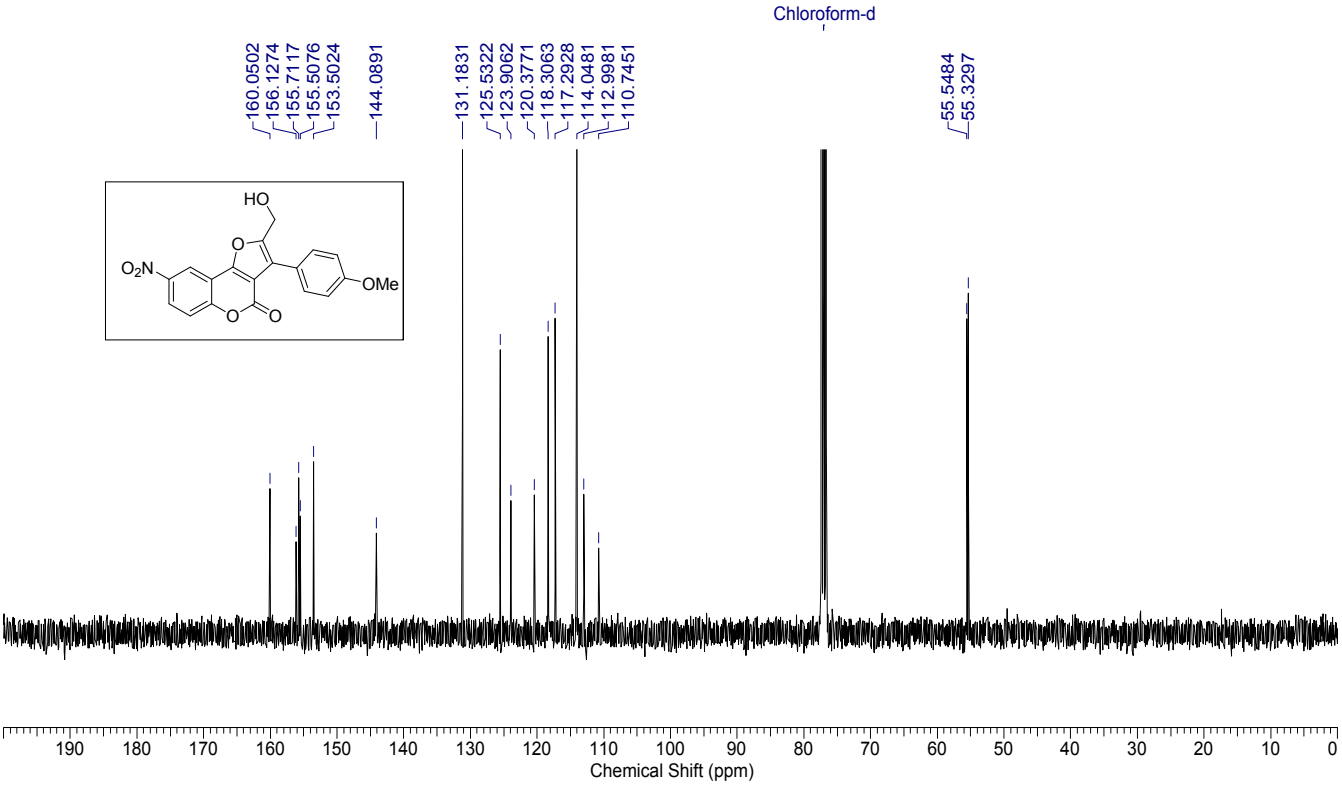

DMSO-d6
8.0949
8.0893
7.7832
7.7775
7.6120
7.5906
7.5850
7.5574
7.5517
7.5329
7.5103
5.6995
4.5254
2.4900
HO
O
Br
Cl
O
O
Intensity
0.15
0.10
0.05
0
0.67
0.94
5.31
1.09
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

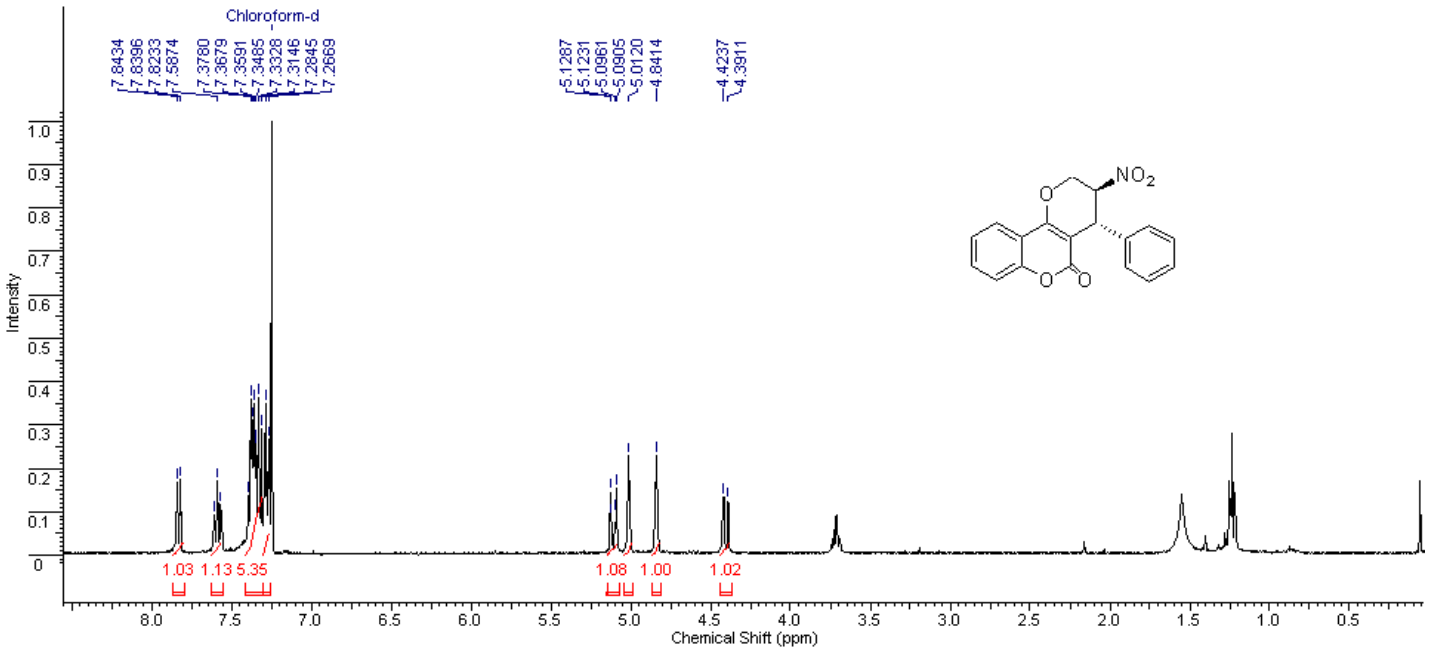

DMSO-d6
156.3171
155.0046
151.0234
133.7718
133.0791
131.7010
128.1792
127.8438
122.9220
120.6908
119.2544
116.6878
113.7858
109.5348
53.7330
40.1198
39.9156
39.7042
39.5000
39.0771
HO
O
Br
Cl
O
O
Intensity
0.10
0.05
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

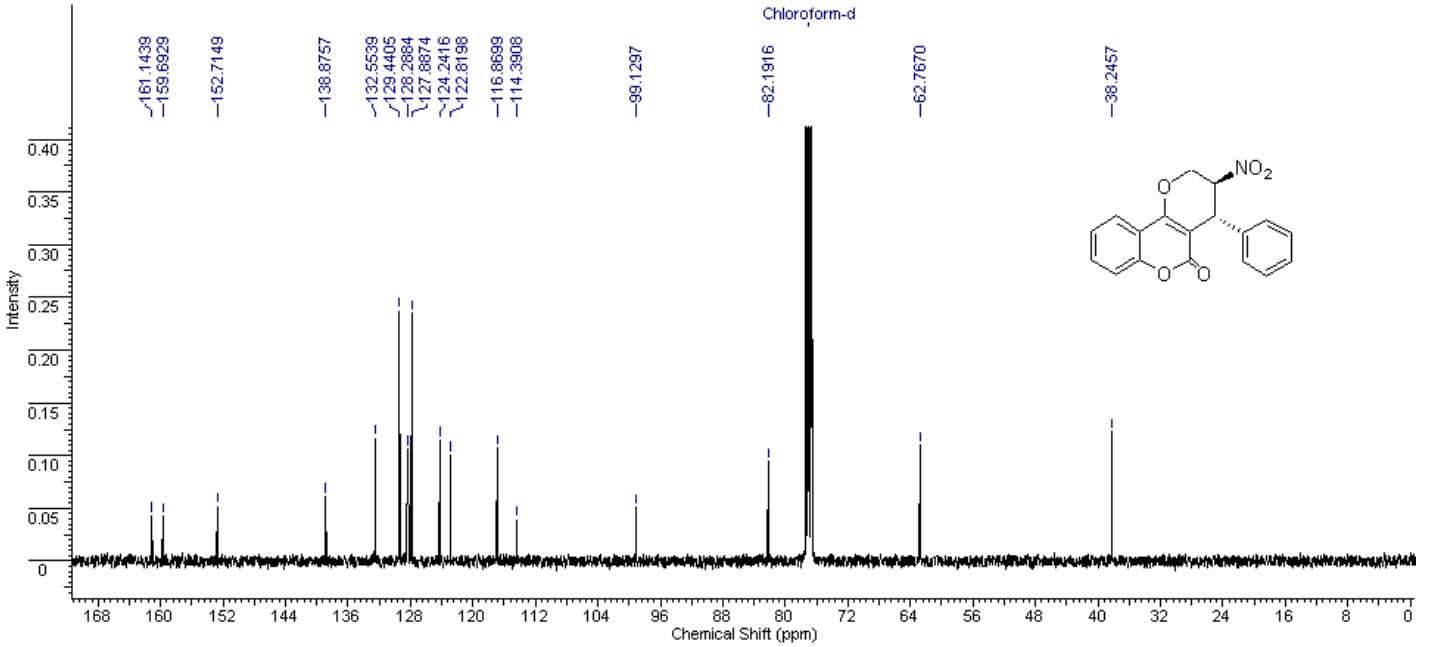

Chloroform-d
8.8739
8.8670
8.4229
8.4003
8.3934
7.5956
7.5830
7.5736
7.5667
7.5266
7.5046
7.4871
7.4758
7.2600
4.8245
HO
O
O_2N
O
O
Intensity
0.64
0.94
3.42
2.17
Chemical Shift (ppm)

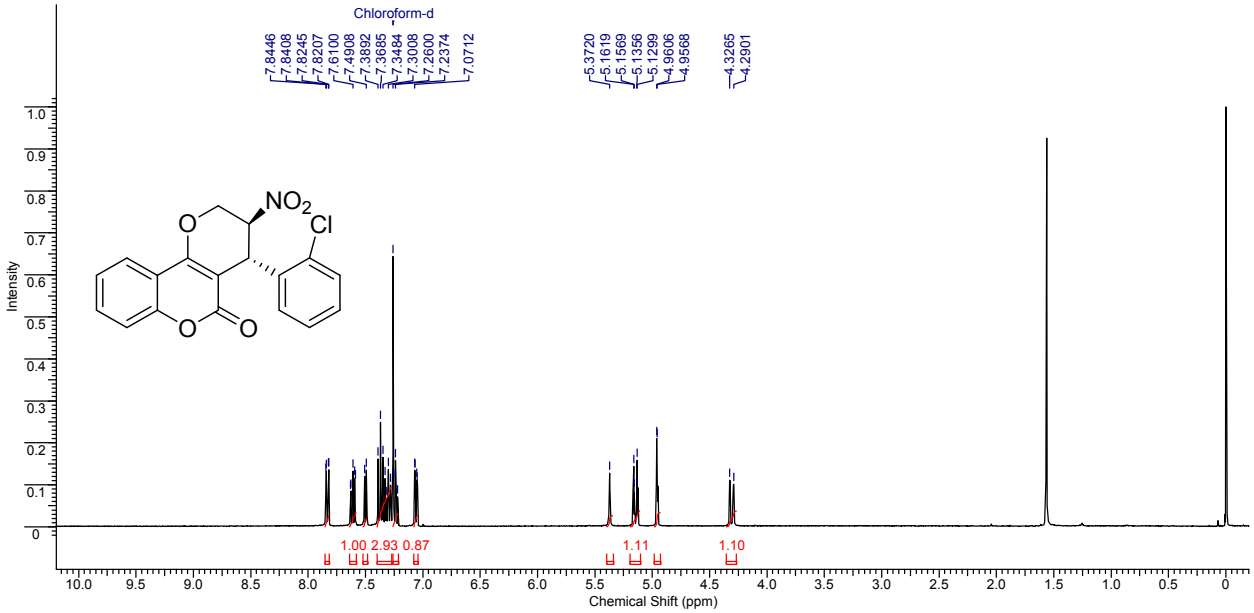

Chloroform-d
155.9896
155.8001
155.6761
153.9335
144.1483
129.9517
128.8944
128.5882
128.2674
125.6643
124.2060
118.3874
117.3885
113.0063
110.7605
77.3508
77.2342
77.0300
76.7165
55.5638
HO
O
O_2N
O
O
Intensity
Chemical Shift (ppm)

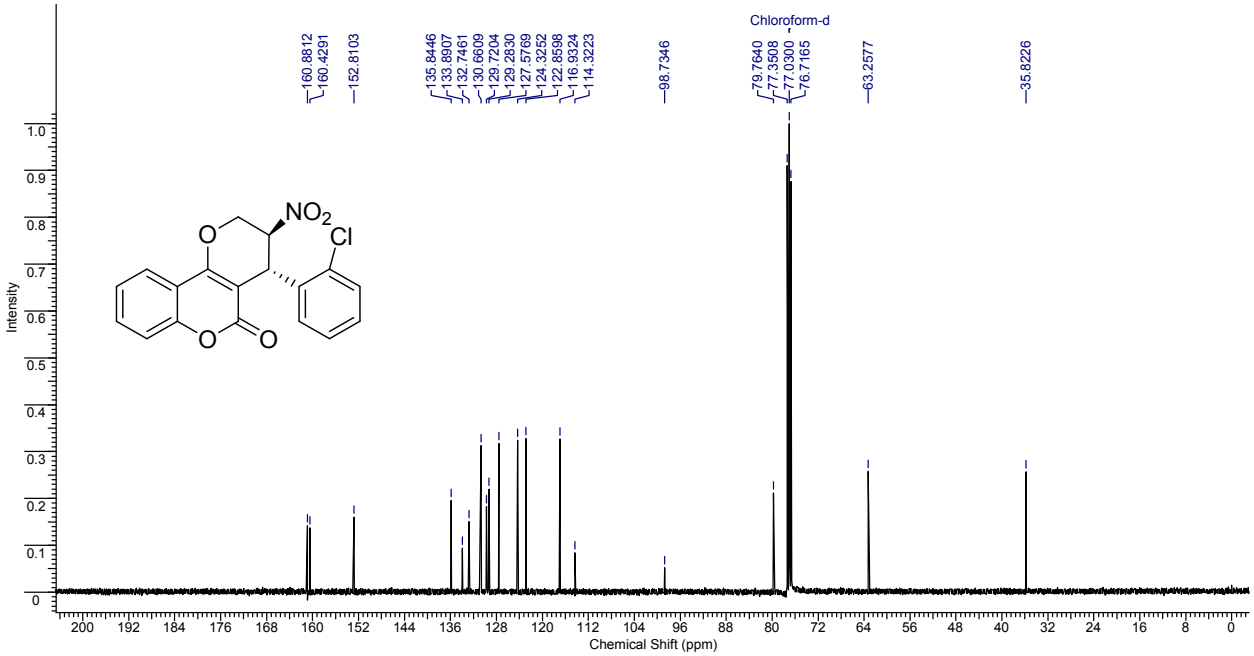

Chloroform-d
8.8394
8.8325
8.4016
8.3947
8.3790
8.3721
7.5761
7.5529
7.5247
7.5178
7.4952
7.4883
7.2600
7.0260
7.0204
7.0035
6.9966
4.8019
3.8642
HO
O
O2N
OMe
O
Intensity
0.63
0.89
1.93
2.00
1.88
3.00
Chemical Shift (ppm)

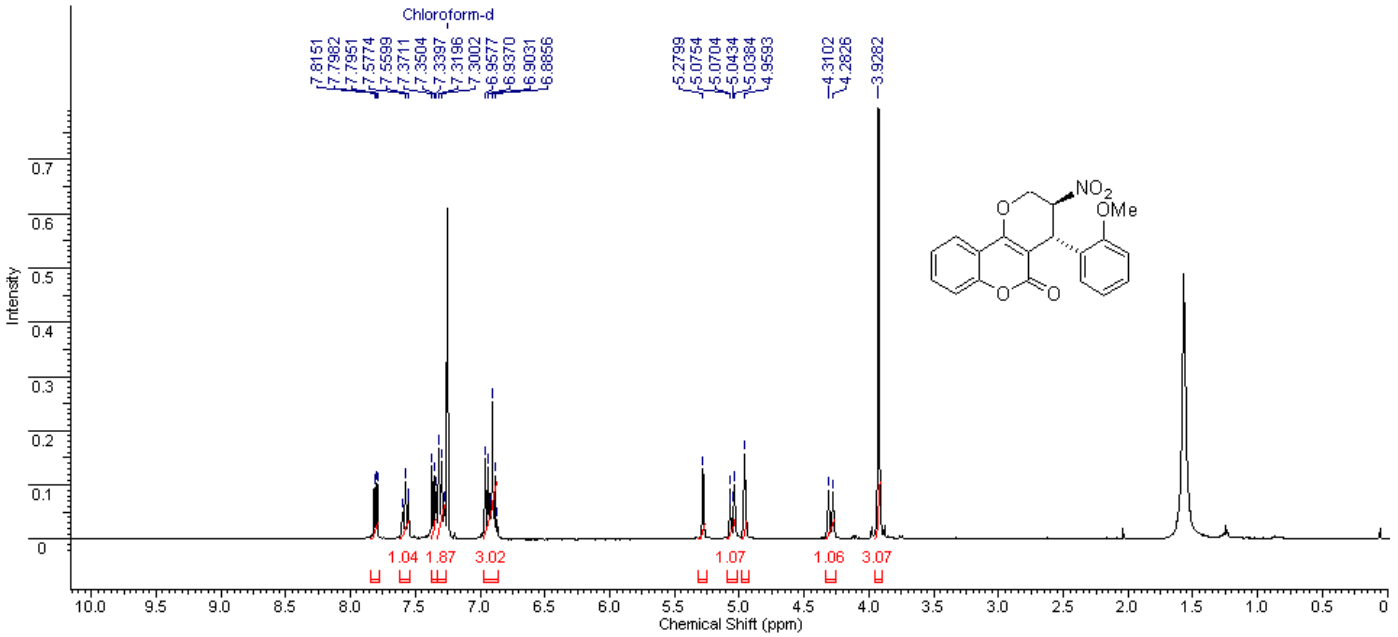

Chloroform-d
160.0502
156.1274
155.7117
155.5076
153.5024
144.0891
131.1831
125.5322
123.9062
120.3771
118.3063
117.2928
114.0481
112.9981
110.7451
55.5484
55.3297
HO
O
O2N
OMe
O
Chemical Shift (ppm)

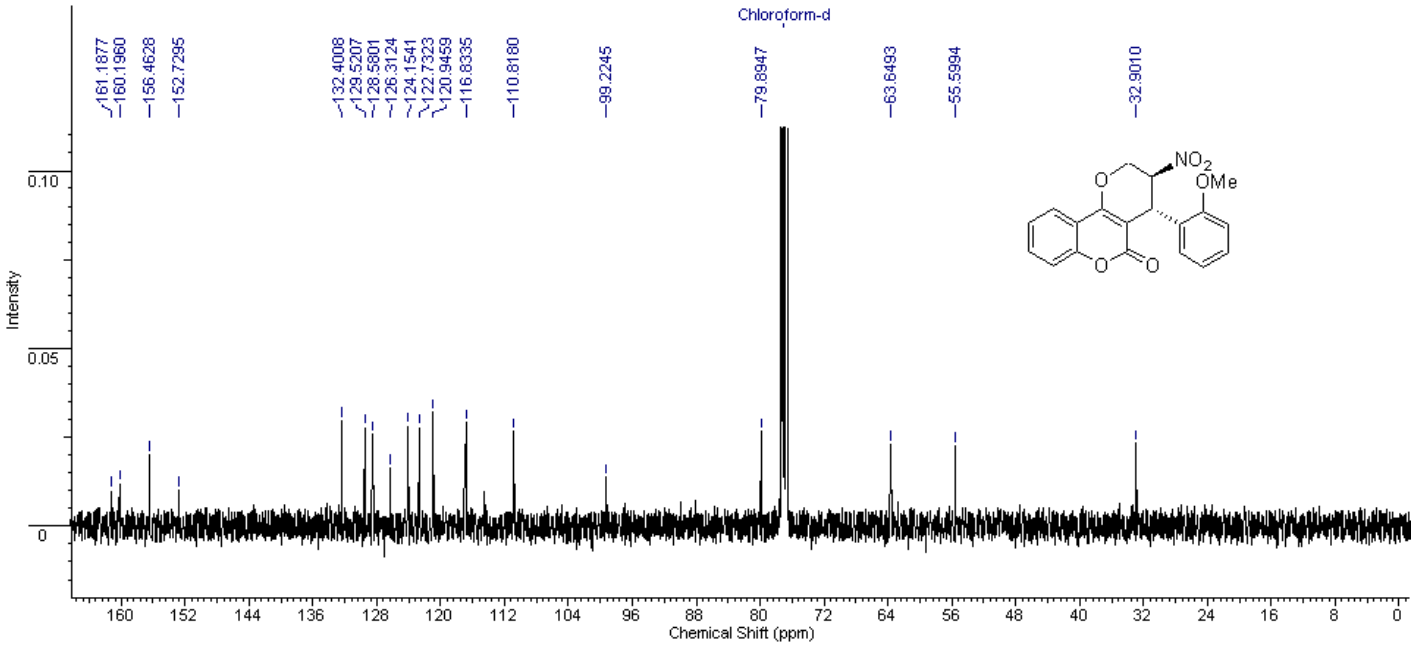

Chloroform-d
7.8434
7.8396
7.8233
7.5874
7.3780
7.3679
7.3591
7.3485
7.3328
7.3146
7.2845
7.2669
5.1287
5.1231
5.0961
5.0905
5.0120
4.8414
4.4237
4.3911
1.03
1.13
5.35
1.08
1.00
1.02
Intensity
Chemical Shift (ppm)
NO2

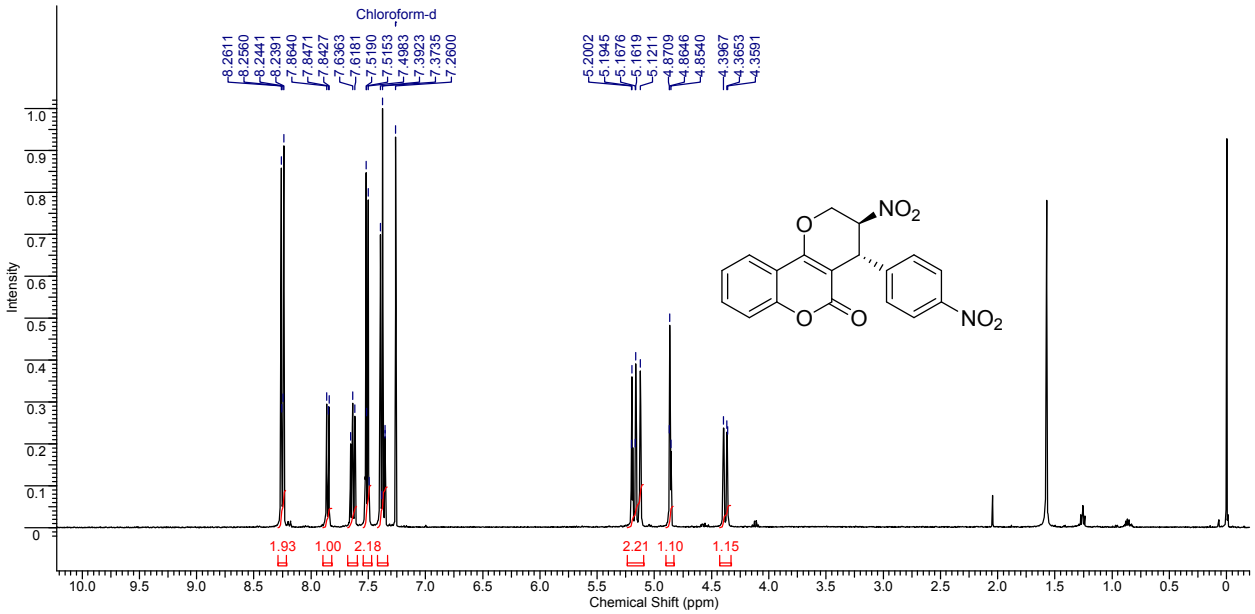

Chloroform-d
161.1439
159.6929
152.7149
138.8757
132.5539
129.4405
128.2884
127.8874
124.2416
122.8198
116.8699
114.3908
99.1297
82.1916
62.7670
38.2457
Intensity
Chemical Shift (ppm)
NO2

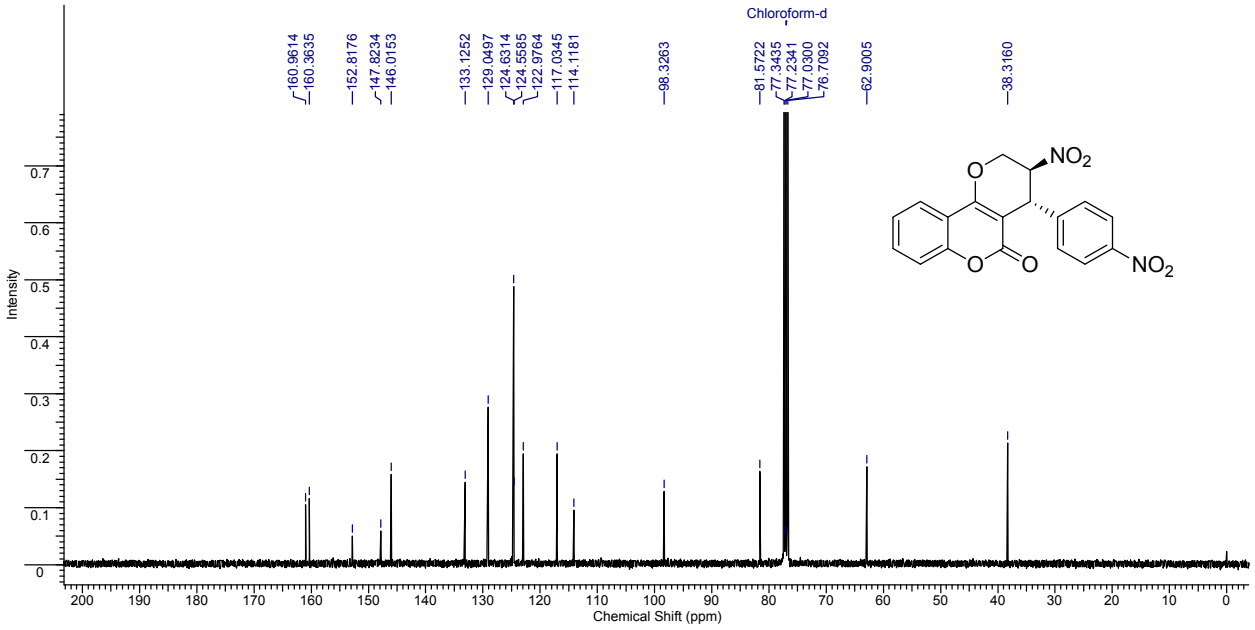

Chloroform-d
7.8446
7.8408
7.8245
7.8207
7.6100
7.4908
7.3892
7.3685
7.3484
7.3008
7.2600
7.2374
7.0712
5.3720
5.1619
5.1569
5.1356
5.1299
4.9606
4.9568
4.3265
4.2901
NO2
Cl
O
O
O
1.00 2.93 0.87
1.11
1.10
Intensity
Chemical Shift (ppm)

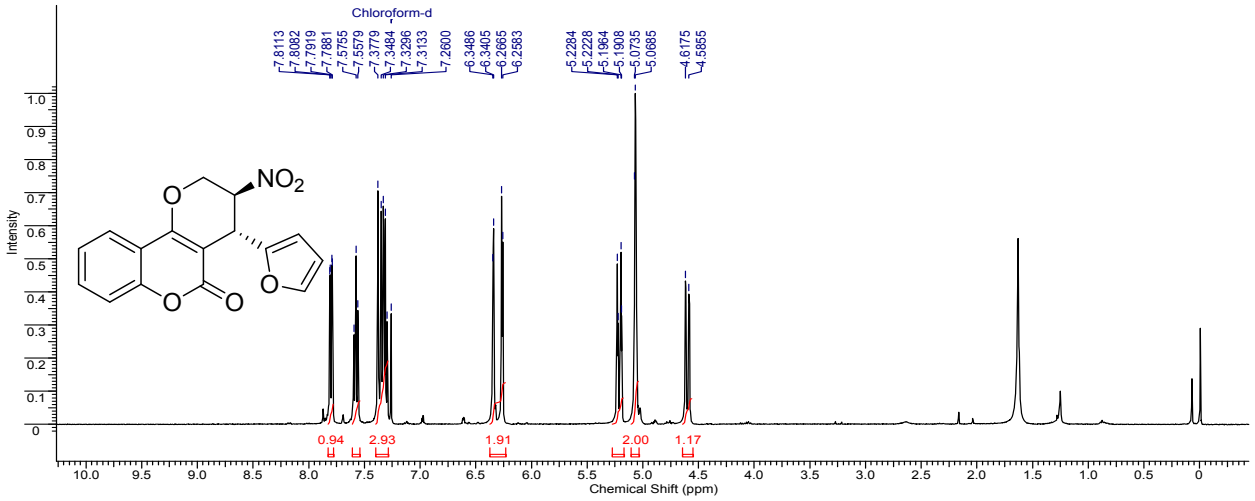

Chloroform-d
160.8812
160.4291
152.8103
135.8446
133.8907
132.7461
130.6609
129.7204
129.2830
127.5769
124.3252
122.8598
116.9324
114.3223
98.7346
79.7640
77.3508
77.0300
76.7165
63.2577
35.8226
NO2
Cl
O
O
O
Intensity
Chemical Shift (ppm)

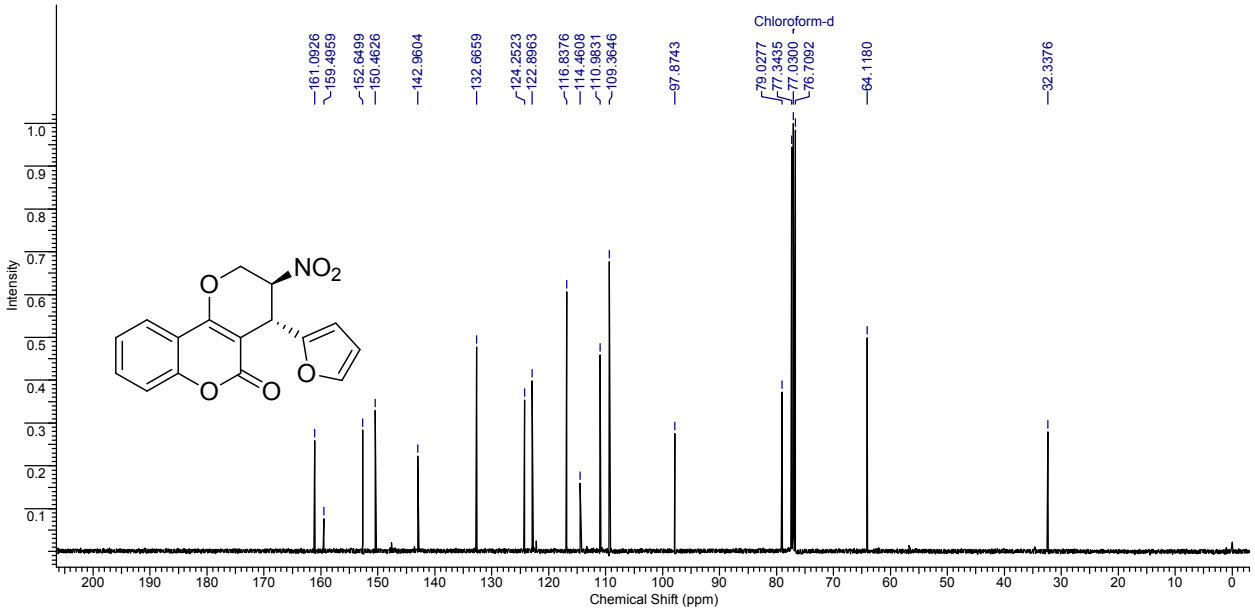

Chloroform-d
7.8151
7.7982
7.7951
7.5774
7.5599
7.3711
7.3504
7.3397
7.3196
7.3002
6.9577
6.9370
6.9031
6.8856
5.2799
5.0754
5.0704
5.0434
5.0384
4.9593
4.3102
4.2826
3.9282
1.04
1.87
3.02
1.07
1.06
3.07
Intensity
Chemical Shift (ppm)
NO2
OMe
O
O
O

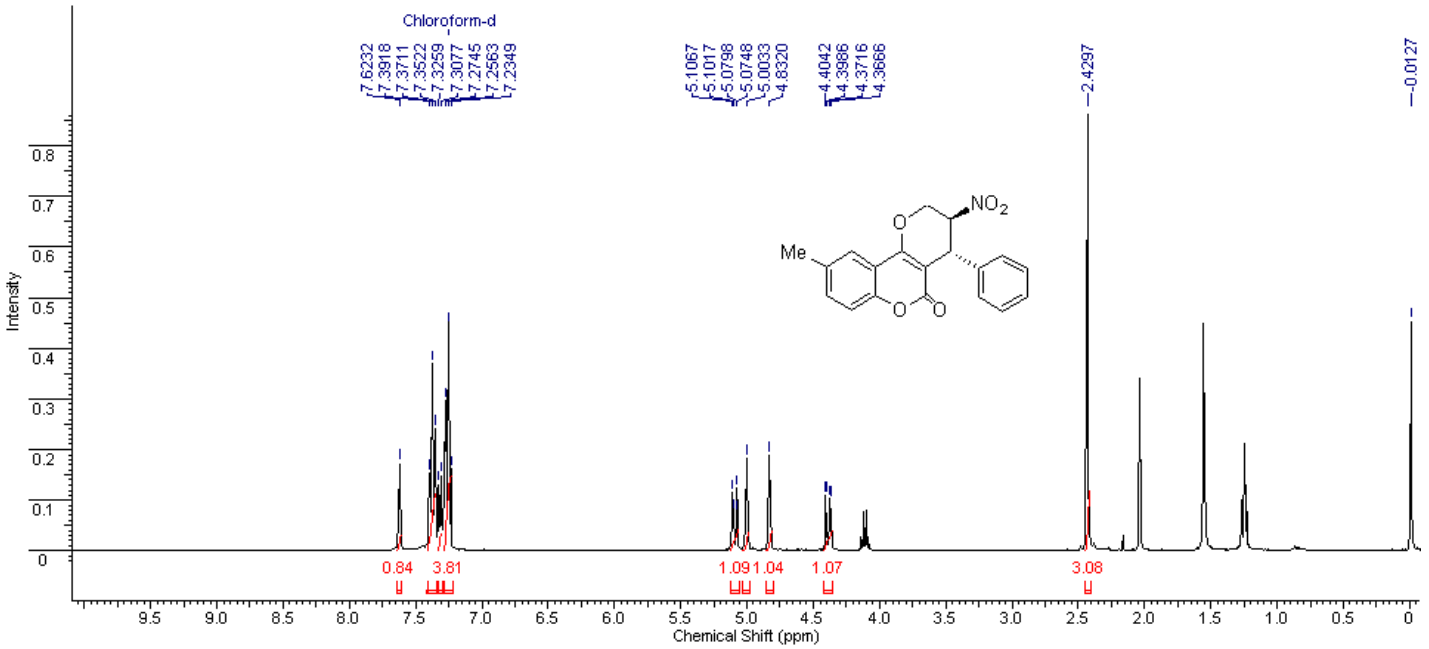

Chloroform-d
161.1877
160.1960
156.4628
152.7295
132.4008
129.5207
128.5801
126.3124
124.1541
122.7323
120.9459
116.8335
110.8180
99.2245
79.8947
63.6493
55.5994
32.9010
Intensity
Chemical Shift (ppm)
NO2
OMe
O
O
O

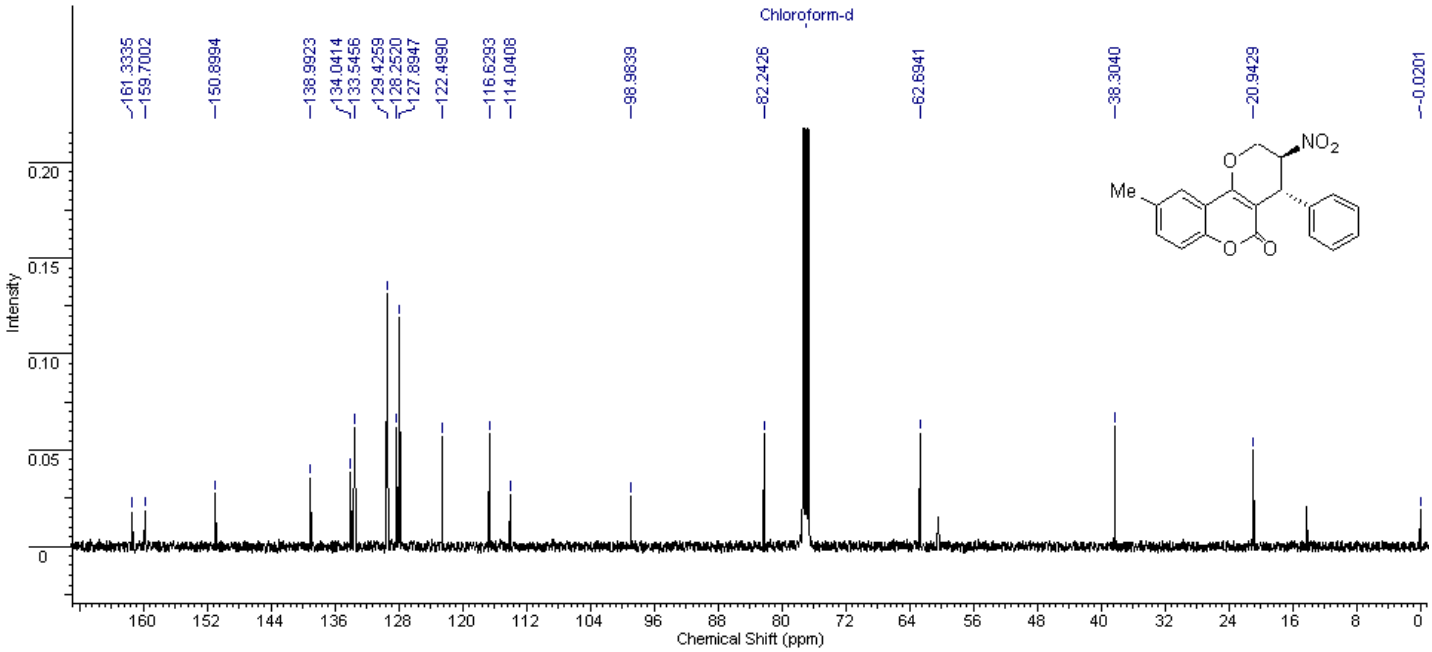

Chloroform-d
8.2611
8.2560
8.2441
8.2391
7.8640
7.8471
7.8427
7.6363
7.6181
7.5190
7.5153
7.4983
7.3923
7.3735
7.2600
5.2002
5.1945
5.1676
5.1619
5.1211
4.8709
4.8646
4.8540
4.3967
4.3653
4.3591
1.93
1.00
2.18
2.21
1.10
1.15
Intensity
Chemical Shift (ppm)
NO2
NO2
O
O
O

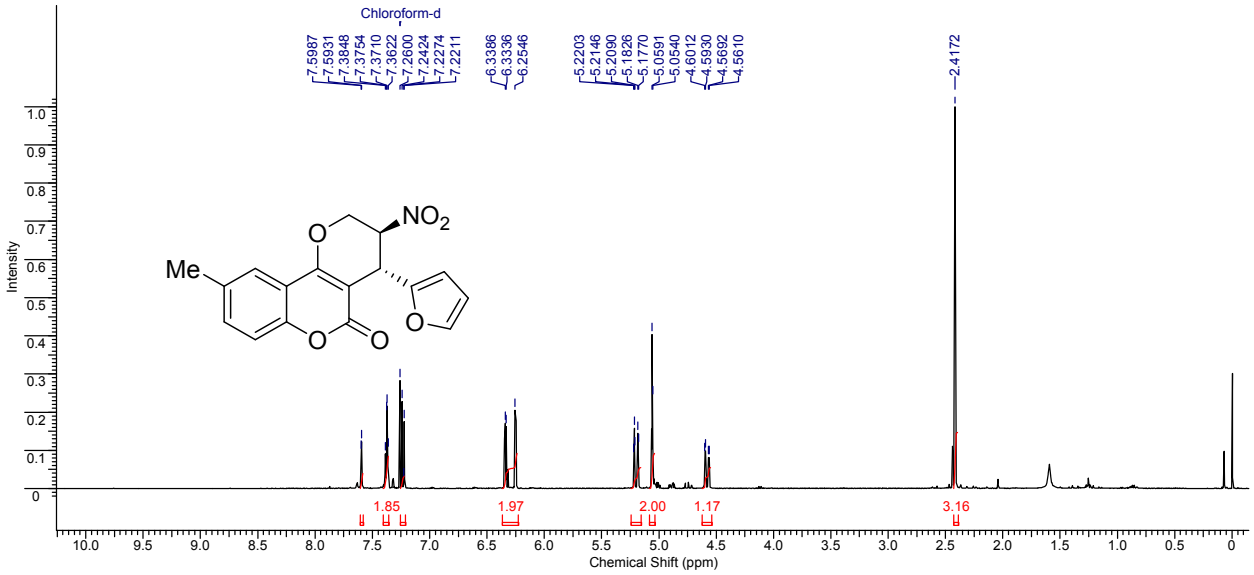

Chloroform-d
160.9614
160.3635
152.8176
147.8234
146.0153
133.1252
129.0497
124.6314
124.5585
122.9764
117.0345
114.1181
98.3263
81.5722
77.3435
77.2341
77.0300
76.7092
62.9005
38.3160
Intensity
Chemical Shift (ppm)
NO2
NO2
O
O
O

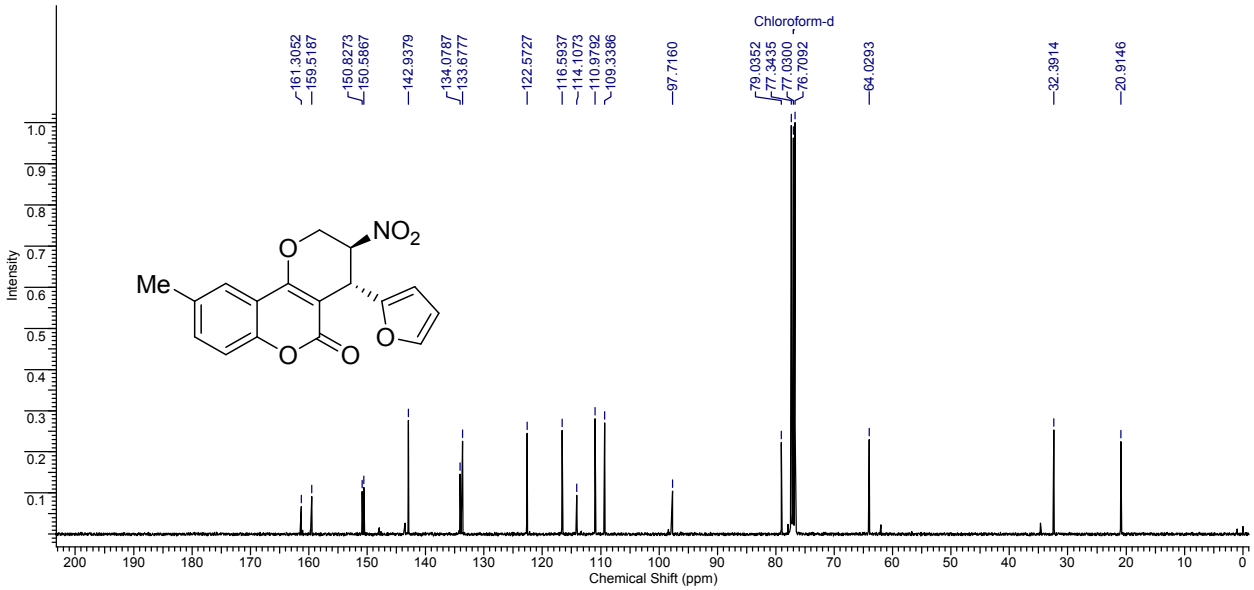

Chloroform-d
7.8113
7.8082
7.7919
7.7881
7.5755
7.5579
7.3779
7.3484
7.3296
7.3133
7.2600
6.3486
6.3405
6.2665
6.2583
5.2284
5.2228
5.1964
5.1908
5.0735
5.0685
4.6175
4.5855
NO2
O
O
O
O
0.94
2.93
1.91
2.00
1.17
Intensity
Chemical Shift (ppm)

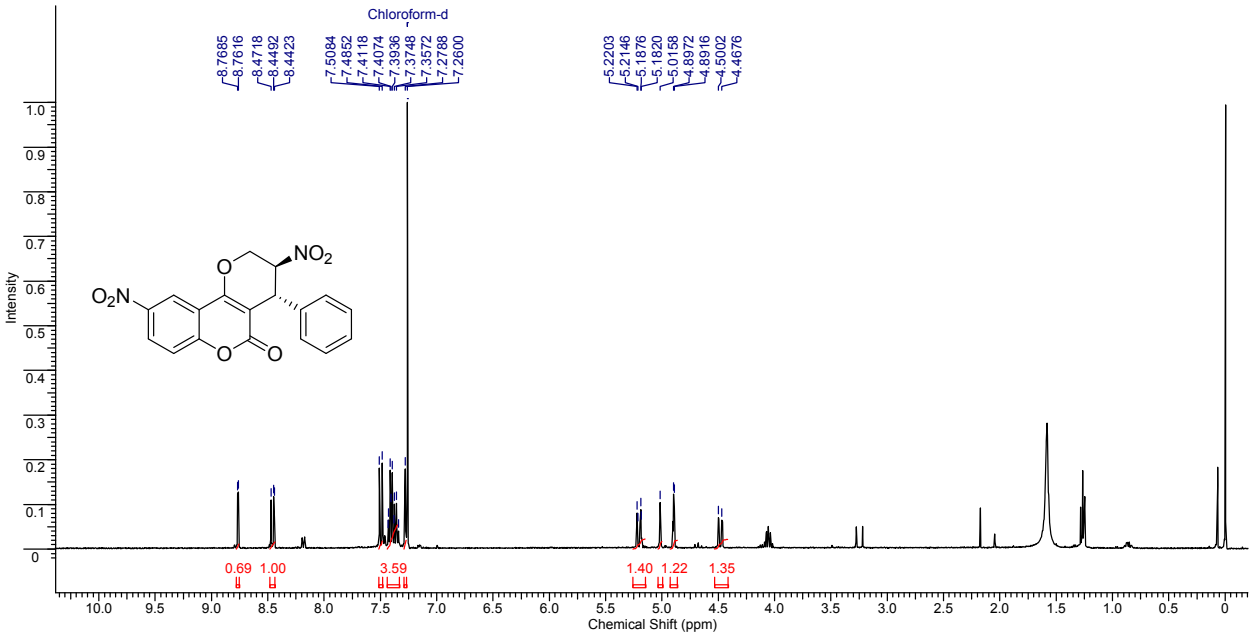

Chloroform-d
161.0926
159.4959
152.6499
150.4626
142.9604
132.6659
124.2523
122.8963
116.8376
114.4608
110.9831
109.3646
97.8743
79.0277
77.3435
77.0300
76.7092
64.1180
32.3376
NO2
O
O
O
O
Intensity
Chemical Shift (ppm)

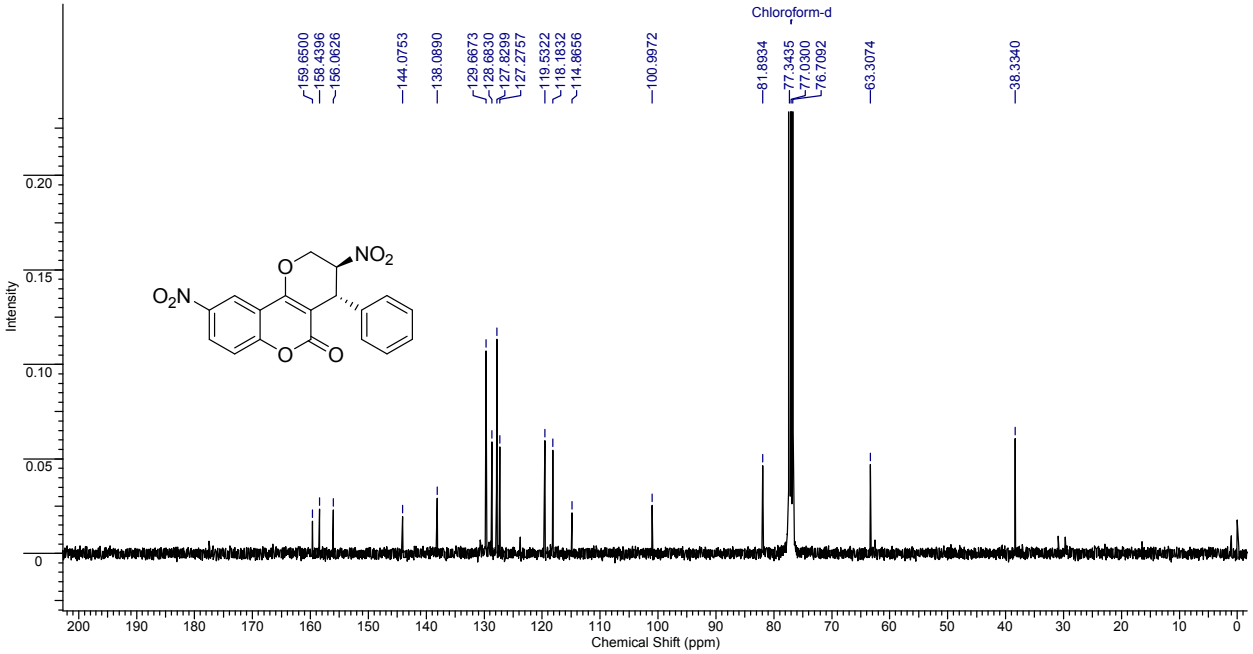

Chloroform-d
7.6232
7.3918
7.3711
7.3522
7.3259
7.3077
7.2745
7.2563
7.2349
5.1067
5.1017
5.0798
5.0748
5.0033
4.8320
4.4042
4.3986
4.3716
4.3666
2.4297
-0.0127
Intensity
0.84
3.81
1.09
1.04
1.07
3.08
Chemical Shift (ppm)
NO2
Me
O
O
O

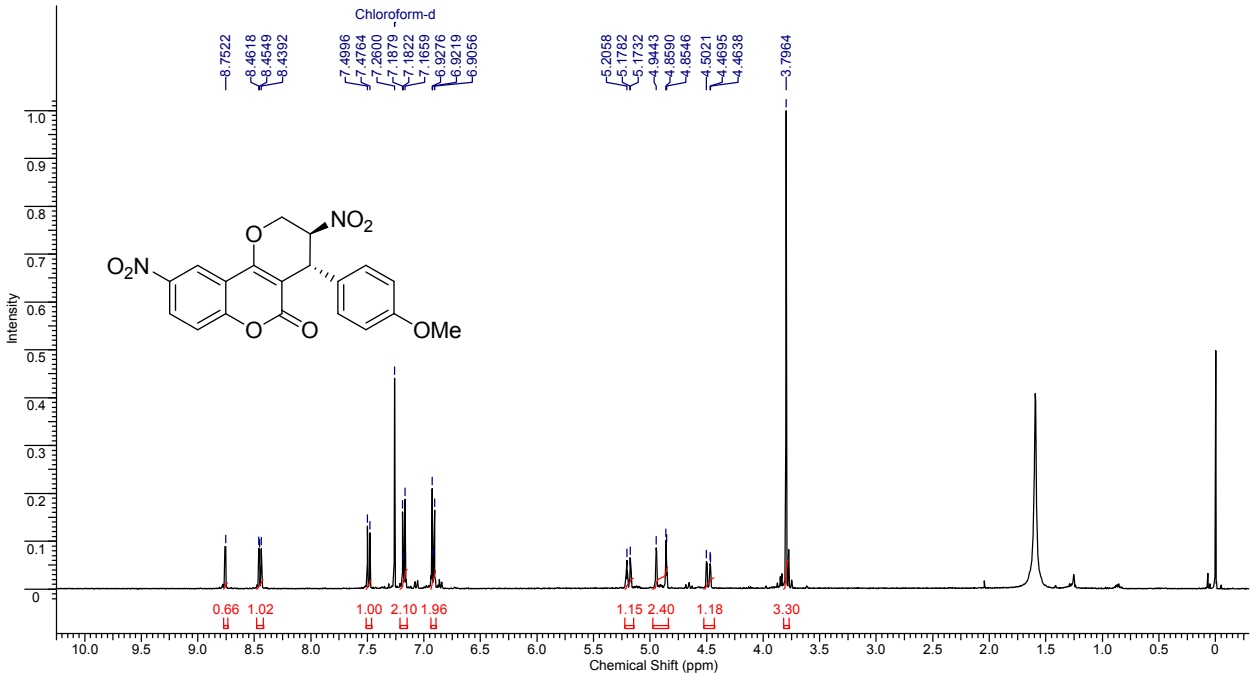

Chloroform-d
161.3335
159.7002
150.8994
138.9923
134.0414
133.5456
129.4259
128.2520
127.8947
122.4990
116.6293
114.0408
98.9839
82.2426
62.6941
38.3040
20.9429
-0.0201
Intensity
Chemical Shift (ppm)
NO2
Me
O
O
O

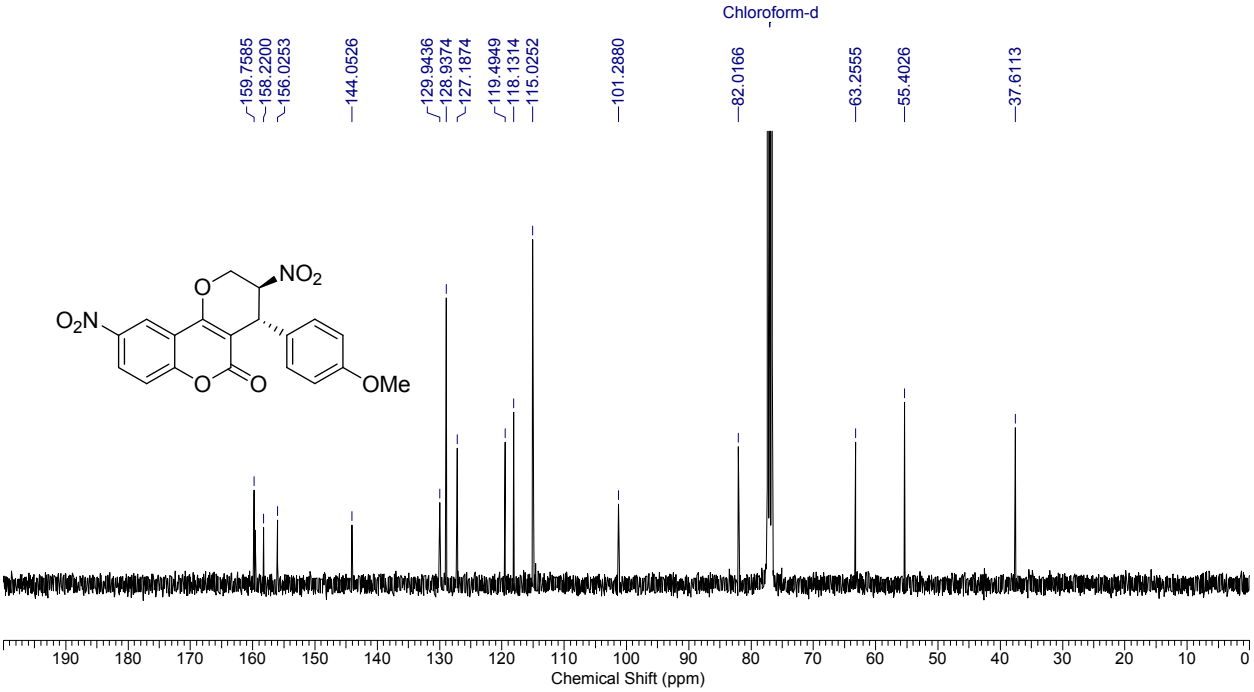

Chloroform-d
7.5987
7.5931
7.3848
7.3754
7.3710
7.3622
7.2600
7.2424
7.2274
7.2211
6.3386
6.3336
6.2546
5.2203
5.2146
5.2090
5.1826
5.1770
5.0591
5.0540
4.6012
4.5930
4.5692
4.5610
2.4172
NO2
Me
O
O
O
O
Intensity
1.85
1.97
2.00
1.17
3.16
Chemical Shift (ppm)


Chloroform-d
161.3052
159.5187
150.8273
150.5867
142.9379
134.0787
133.6777
122.5727
116.5937
114.1073
110.9792
109.3386
97.7160
79.0352
77.3435
77.0300
76.7092
64.0293
32.3914
20.9146
NO2
Me
O
O
O
O
Intensity
Chemical Shift (ppm)


Chloroform-d
8.7685
8.7616
8.4718
8.4492
8.4423
7.5084
7.4852
7.4118
7.4074
7.3936
7.3748
7.3572
7.2788
7.2600
5.2203
5.2146
5.1876
5.1820
5.0158
4.8972
4.8916
4.5002
4.4676
Intensity
0.69
1.00
3.59
1.40
1.22
1.35
Chemical Shift (ppm)


Chloroform-d
159.6500
158.4396
156.0626
144.0753
138.0890
129.6673
128.6830
127.8299
127.2757
119.5322
118.1832
114.8656
100.9972
81.8934
77.3435
77.0300
76.7092
63.3074
38.3340
Intensity
Chemical Shift (ppm)


Chloroform-d
8.7522
8.4618
8.4549
8.4392
7.4996
7.4764
7.2600
7.1879
7.1822
7.1659
6.9276
6.9219
6.9056
5.2058
5.1782
5.1732
4.9443
4.8590
4.8546
4.5021
4.4695
4.4638
3.7964
Intensity
0.66 1.02 1.00 2.10 1.96 1.15 2.40 1.18 3.30
Chemical Shift (ppm)


Chloroform-d
159.7585
158.2200
156.0253
144.0526
129.9436
128.9374
127.1874
119.4949
118.1314
115.0252
101.2880
82.0166
63.2555
55.4026
37.6113
Chemical Shift (ppm)