Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

NHC-Catalyzed Enantioselective C2-Functionalization of 3-Hydroxychromenones via α,β-Unsaturated Acylazoliums

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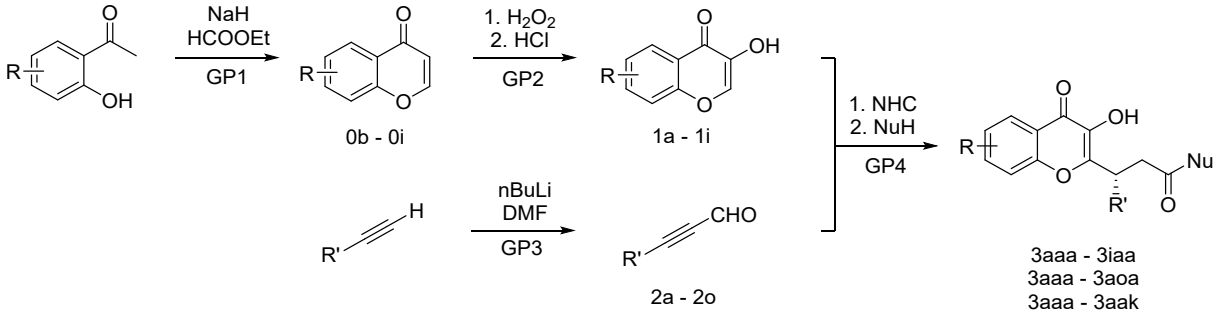
1. General Methods

General information. Presented reactions were carried out in dry glassware under an inert atmosphere of argon. Selected reactions were monitored using thin-layer chromatography (TLC), which was visualized under a UV lamp (254 nm). Anhydrous solvents were prepared using INERT PureSolv Solvent Purification System. Purification of selected products was performed by column chromatography using CombiFlash Rf+ Lumen system with UV-VIS and ELSD detectors. RediSepRf GOLD 4 gram columns were used. NMR spectra were recorded on Bruker AMX 400 [400 MHz (^{1}H)] spectrometer, Bruker AMX 700 [700 MHz (^{1}H)] spectrometer, and Bruker 300 MHz spectrometer using $CDCl_3$ as solvent. Chemical shifts are reported in ppm using the residual solvent peak as reference: δ 7.24 for ^{1}H NMR and relative to the central $CDCl_3$ (δ 77.23) resonance for ^{13}C NMR. Coupling constants (*J*) were provided in Hz. Infrared spectra were measured on Alpha FT-IR spectrometer from Bruker with an ATR module. Mass spectra were recorded on Agilent 6530 Q-TOF LC/MS system coupled with 1290 Infinity II liquid chromatograph. Melting points of obtained products were measured on Stuart SMP50 Melting Point Apparatus and were not corrected. HPLC chromatograms were recorded using Agilent Technologies 1200 Series HPLC with Phenomenex Amylose-1 3 µm column. The diffraction data of the studied compound were collected at room temperature for the single crystal using Oxford Sapphire CCD diffractometer, MoKα radiation λ = 0.71073 Å.

2. Synthetic Procedures

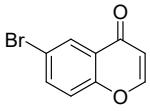


General Procedure 1 (GP1). Sodium hydride (60% dispersion in oil; 4 eq) was washed three times with pentane and dispersed in dry THF. 2-Hydroxyacetophenone derivative (1 eq) was added slowly at room temperature to obtain a 0.5 mol/L solution. Then ethyl formate (3 eq) was added dropwise to the vigorously stirring solution. After the highly exothermic reaction the mixture was stirred for an additional 5 minutes and poured onto the water with ice. The obtained solution was acidified with concentrated hydrochloric acid and extracted with dichloromethane. Combined organic fractions were vigorously stirred with a hydrochloric acid solution (6 mol/L) for an additional hour. The organic fraction was separated, dried over anhydrous magnesium sulfate, and evaporated to obtain pure product.

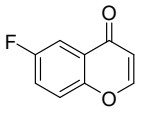
General Procedure 2 (GP2). A 50% hydrogen peroxide solution (2 eq) was added slowly to the 0.75 mol/L DCM solution of chromene derivative (1 eq) at the temperature of 0 °C. Then solid sodium hydroxide (1.5 eq) was added portion-wise, and the mixture was stirred at 0 °C for 3 hours. The reaction was quenched with water, and the product was extracted with dichloromethane. Collected organic fractions were dried over anhydrous magnesium sulfate and evaporated. The obtained crude diol was added to the large excess of concentrated hydrochloric acid and stirred at 70 °C for an hour. The reaction mixture was cooled down to ambient temperature, diluted with water, and extracted with dichloromethane. Collected organic fractions were dried over anhydrous magnesium sulfate and evaporated. Pentane was added to the crude product, and remained solid was filtered off to obtain pure product.

General Procedure 3 (GP3). An acetylene derivative (1 eq) was dissolved in dry THF to obtain a 0.4 mol/L solution. Then the solution of n-butyllithium (2.5 mol/L in hexanes; 1 eq) was added dropwise at the temperature of -40 °C. Dimethylformamide (2 eq) was added quickly, the obtained mixture was warm up to ambient temperature and stirred for additional 30 minutes. The obtained solution was added to the vigorously stirred mixture containing 1 mol/L aqueous solution of KH_2PO_4 (2 eq) and the same volume of methyl-*tert*-butyl ether (MTBE) at 0 °C. The organic fraction was separated, and the aqueous layer was extracted with MTBE. Combined organic fractions were washed with water, dried over anhydrous magnesium sulfate, and evaporated. The obtained crude product was purified using flash column chromatography.

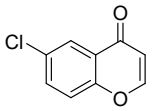
General procedure 4 (GP4). Precatalyst (0.025 mmol) and 1,8-bis(dimethylamino)naphthalene (0.025 mmol) were dissolved in dry dichloromethane (2.5 mL) and stirred at ambient temperature for 15 minutes. Then ynal (0.38 mmol) and 3-hydroxy-4*H*-chromen-4-one derivative (0.25 mmol) were added. The reaction mixture was stirred for 5 hours and the nucleophilic agent (alcohol or amine; 2.5 mL) was added. The obtained solution was stirred for an additional time defined as an opening time. Then the solution was evaporated and purified by flash column chromatography.



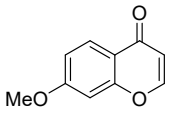
6-Bromo-4*H*-chromen-4-one (**0b**). GP1. A scale of 25.0 mmol, solid, 5.123 g (22.8 mmol), isolated yield of 91%; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.33 (dd, J = 0.4, 2.6 Hz, 1H), 7.85 (d, J = 6.0 Hz, 1H), 7.75 (dd, J = 2.5, 8.9 Hz, 1H), 7.36 (dd, J = 0.4, 8.8 Hz, 1H), 6.35 (d, J = 6.0 Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 176.2, 155.5, 155.2, 136.7, 128.4, 126.1, 120.2, 118.7, 113.0; IR ν_{max}: 3070, 1635, 1605, 1558, 1461, 1437, 1187, 1136, 817 cm^{-1}; HRMS (ESI-TOF) m/z: (M + H)$^{+}$ calcd for $C_9H_6{}^{79}BrO_2$ 224.9551; found: 224.9554; mp 134.8−138.2 °C. The above analysis results correspond to the literature data.[1]



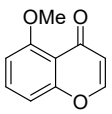
6-Fluoro-4*H*-chromen-4-one (**0c**). GP1. A scale of 25.0 mmol, solid, 3.796 g (23.1 mmol), isolated yield of 92%; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.89 (d, J = 5.9 Hz, 1H), 7.87 (ddd, J = 0.4, 3.1, 8.1 Hz, 1H), 7.50 (ddd, J = 0.4, 4.2, 9.2 Hz, 1H), 7.42 (ddd, J = 3.2, 7.5, 9.1 Hz, 1H), 6.36 (dd, J = 0.4, 5.9 Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 176.8 (d, J=2.1 Hz), 159.5 (d, J=247.1 Hz), 155.5, 152.7 (d, J=2.1 Hz), 126.0 (d, J=6.9 Hz), 122.0 (d, J=25.6 Hz), 120.3 (d, J=8.3 Hz), 112.2, 110.6 (d, J=23.5 Hz); IR ν_{max}: 3083, 1642, 1615, 1573, 1478, 1456, 1133, 1064, 1025, 826 cm^{-1}; HRMS (ESI-TOF) m/z: (M + H)$^{+}$ calcd for $C_9H_6FO_2$ 165.0352; found: 165.0353; mp 157.8−163.2 °C. The above analysis results correspond to the literature data.[1]



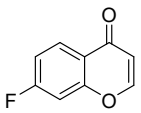
6-Chloro-4*H*-chromen-4-one (**0d**). GP1. A scale of 25.0 mmol, solid, 4.180 g (23.1 mmol), isolated yield of 93%; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.18-8.17 (m, 1H), 7.85 (d, J = 6.0 Hz, 1H), 7.61 (dd, J = 2.7, 8.9 Hz, 1H), 7.42 (dd, J = 0.4, 8.8 Hz, 1H), 6.35 (d, J = 6.0 Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 176.3, 155.5, 154.8, 134.0, 131.2, 125.7, 125.2, 119.9, 112.9; IR ν_{max}: 3068, 1634, 1610, 1562, 1464, 1439, 1137, 841, 817 cm^{-1}; HRMS (ESI-TOF) m/z: (M + H)$^{+}$ calcd for $C_9H_6{}^{35}ClO_2$ 181.0056; found: 181.0054; mp 135.2−139.8 °C. The above analysis results correspond to the literature data.[2]



7-Methoxy-4*H*-chromen-4-one (**0e**). GP1. A scale of 25.0 mmol, solid, 0.967 g (5.5 mmol), isolated yield of 22%; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.12-8.10 (m, 1H), 7.77 (d, J = 6.0 Hz, 1H), 6.97 (dd, J = 2.5, 8.9 Hz, 1H), 6.83 (d, J = 2.4 Hz, 1H), 6.27 (d, J = 6.0 Hz, 1H), 3.90 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 177.0, 164.1, 158.2, 154.8, 127.2, 118.7, 114.5, 112.9, 100.3, 55.8; IR ν_{max}: 3064, 3021, 1619, 1589, 1498, 1435, 1268, 1223, 823 cm^{-1}; HRMS (ESI-TOF) m/z: (M + H)$^{+}$ calcd for $C_{10}H_9O_3$ 177.0552; found: 177.0552; mp 106.1−107.9 °C. The above analysis results correspond to the literature data.[3]

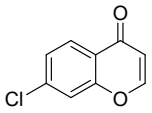


5-Methoxy-4*H*-chromen-4-one (**0f**). GP1. A scale of 25.0 mmol, solid, 3.347 g (19.0 mmol), isolated yield of 76%; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.67 (dd, J = 0.5, 5.9 Hz, 1H), 7.53 (dt, J = 1.0, 8.3 Hz, 1H), 7.02-6.97 (m, 1H), 6.80 (d, J = 8.4 Hz, 1H), 6.23 (dd, J = 1.1, 6.0 Hz, 1H), 3.96 (d, J = 1.1 Hz, 3 H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 177.4, 159.8, 158.5, 153.1, 133.7, 115.6, 114.6, 110.2, 106.4, 56.4; IR ν_{max}: 3083, 1638, 1600, 1569, 1471, 1451, 1263, 1084, 1065, 835 cm^{-1}; HRMS (ESI-TOF) m/z: (M + H)$^{+}$ calcd for $C_{10}H_9O_3$ 177.0552; found: 177.0551; mp 78.2−81.1 °C. The above analysis results correspond to the literature data.[4]

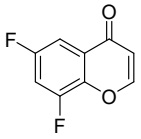


7-Fluoro-4*H*-chromen-4-one (**0g**). GP1. A scale of 25.0 mmol, solid, 3.833 g (23.4 mmol), isolated yield of 93%; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.22 (dd, J = 6.1, 9.6 Hz, 1H), 7.83 (d, J = 6.0 Hz, 1H), 7.15-7.12 (m, 2H), 6.33 (d, J = 6.0 Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

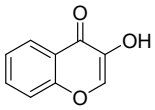
δ 176.6, 165.6 (d, J=255.3 Hz), 157.4 (d, J=13.1 Hz), 155.4, 128.4 (d, J=10.4 Hz), 121.7 (d, J=2.8 Hz), 114.1 (d, J=22.8 Hz), 113.1, 104.8 (d, J=24.9 Hz); IR ν_{max}: 3092, 1648, 1613, 1496, 1437, 1212, 1126, 1021, 844, 814 cm^{-1}; HRMS (ESI-TOF) m/z: (M + H)$^{+}$ calcd for $C_9H_6FO_2$ 165.0352; found: 165.0349; mp 110.1−112.1 °C. The above analysis results correspond to the literature data.[5]



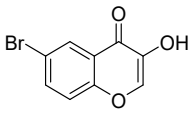
7-Chloro-4*H*-chromen-4-one (**0h**). GP1. A scale of 12.5 mmol, solid, 2.038 g (11.3 mmol), isolated yield of 90%; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.15-8.13 (m, 1H), 7.82 (d, J = 6.0 Hz, 1H), 7.48 (d, J = 1.9 Hz, 1H), 7.37 (dd, J = 1.9, 8.6 Hz, 1H), 6.33 (d, J = 6.0 Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 176.7, 156.5, 155.3, 139.8, 127.2, 126.1, 123.4, 118.2, 113.3; IR ν_{max}: 3080, 1645, 1598, 1557, 1424, 1177, 1019, 809 cm^{-1}; HRMS (ESI-TOF) m/z: (M + H)$^{+}$ calcd for $C_9H_6{}^{35}ClO_2$ 181.0056; found: 181.0055; mp 93.1−97.4 °C. The above analysis results correspond to the literature data.[6]



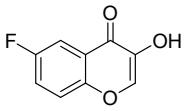
6,8-Difluoro-4*H*-chromen-4-one (**0i**). GP1. A scale of 12.5 mmol, solid, 2.275 g (12.5 mmol), isolated yield of 99%; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.89 (d, J = 6.0 Hz, 1H), 7.64 (ddd, J = 1.8, 3.0, 8.1 Hz, 1H), 7.24 (ddd, J = 3.0, 8.0, 10.1 Hz, 1H), 6.37 (d, J = 6.0 Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 175.5 (dd, J=2.8, 2.1 Hz), 158.3 (dd, J=249.8, 9.7 Hz), 155.0, 151.5 (dd, J=258.1, 11.1 Hz), 142.1 (dd, J=11.1, 2.8 Hz), 127.0 (d, J=8.3 Hz), 112.7, 109.2 (dd, J=28.4, 20.1 Hz), 106.0 (dd, J=23.5, 4.2 Hz); IR ν_{max}: 3093, 3034, 1646, 1633, 1613, 1575, 1479, 1452, 1112, 1004 cm^{-1}; HRMS (ESI-TOF) m/z: (M + H)$^{+}$ calcd for $C_9H_5F_2O_2$ 183.0258; found: 183.0262; mp 149.8−153.6 °C.



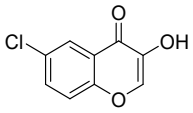
3-Hydroxy-4*H*-chromen-4-one (**1a**). GP2. A scale of 15.0 mmol, solid, 0.780 g (4.8 mmol), isolated yield of 32%; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.29 (ddd, J = 0.4, 1.8, 8.1 Hz, 1H), 8.04 (s, 1H), 7.75-7.68 (m, 1H), 7.52 (d, J = 8.6 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H), 6.29 (s, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 173.4, 156.3, 141.8, 138.5, 133.5, 125.5, 124.6, 121.9, 118.5; IR ν_{max}: 3269, 3096, 1636, 1599, 1562, 1489, 1466, 1421, 1272, 756 cm^{-1}; HRMS (ESI-TOF) m/z: (M + H)$^{+}$ calcd for $C_9H_7O_3$ 163.0395; found: 163.0398; mp 175.1−179.5 °C. The above analysis results correspond to the literature data.[7]



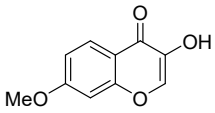
6-Bromo-3-hydroxy-4*H*-chromen-4-one (**1b**). GP2. A scale of 21.4 mmol, solid, 0.405 g (1.7 mmol), isolated yield of 8%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 2.4 Hz, 1H), 8.02 (s, 1H), 7.78 (dd, J = 2.4, 8.8 Hz, 1H), 7.42 (d, J = 9.0 Hz, 1H), 6.07 (s, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 172.1, 155.0, 141.9, 138.6, 136.6, 128.0, 123.1, 120.4, 118.0; IR ν_{max}: 3101, 1620, 1599, 1556, 1469, 1405, 1269, 814 cm^{-1}; HRMS (ESI-TOF) m/z: (M + H)$^{+}$ calcd for $C_9H_6{}^{79}BrO_3$ 240.9500; found: 240.9504; mp 199.9−204.3 °C.



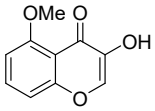
6-Fluoro-3-hydroxy-4*H*-chromen-4-one (**1c**). GP2. A scale of 21.3 mmol, solid, 1.223 g (6.8 mmol), isolated yield of 32%; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.90 (ddd, J = 0.4, 3.1, 8.1 Hz, 1H), 7.56-7.51 (m, J = 0.4, 4.2 Hz, 1H), 7.44 (ddd, J = 3.1, 7.5, 9.2 Hz, 1H), 6.10 (s, 1H); ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 172.7, 159.1 (d, J=246.9 Hz), 152.7, 141.4, 138.6, 122.9 (d, J=8.2 Hz), 122.2 (d, J=26.2 Hz), 120.7 (d, J=8.2 Hz), 110.0 (d, J=22.9 Hz); IR ν_{max}: 3331, 1638, 1609, 1575, 1479, 1467, 1405, 1261, 790, 784 cm^{-1}; HRMS (ESI-TOF) m/z: (M + H)$^{+}$ calcd for $C_9H_6FO_3$ 181.0301; found: 181.0303; mp 219.5−225.2 °C.



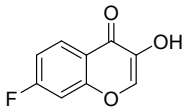
6-Chloro-3-hydroxy-4*H*-chromen-4-one (**1d**). GP2. A scale of 21.0 mmol, solid, 0.606 g (3.2 mmol), isolated yield of 15%; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.22 (dd, J = 0.4, 2.6 Hz, 1H), 8.00 (s, 1H), 7.62 (dd, J = 2.6, 9.0 Hz, 1H), 7.46 (d, J = 9.0 Hz, 1H), 6.04 (s, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 172.3, 154.6, 141.8, 138.6, 133.9, 130.7, 124.8, 122.7, 120.2; IR ν_{max}: 3290, 3085, 1629, 1605, 1564, 1470, 1455, 1395, 1248, 824, 769 cm^{-1}; HRMS (ESI-TOF) m/z: (M + H)$^{+}$ calcd for $C_9H_6{}^{35}ClO_3$ 197.0005; found: 197.0002; mp 162.3−168.4 °C. The above analysis results correspond to the literature data.[7]



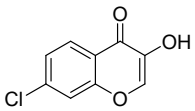
3-Hydroxy-7-methoxy-4*H*-chromen-4-one (**1e**). GP2. A scale of 4.9 mmol, solid, 0.286 g (1.5 mmol), isolated yield of 30%; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.14 (d, J = 8.8 Hz, 1H), 7.91 (s, 1H), 6.98 (dd, J = 2.4, 9.0 Hz, 1H), 6.84 (d, J = 2.4 Hz, 1H), 6.25 (s, 1 H), 3.90 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 172.8, 164.1, 158.2, 141.5, 137.8, 126.8, 115.8, 114.9, 100.0, 55.8; IR ν_{max}: 3284, 3086, 1600, 1566, 1508, 1454, 1433, 1411, 1248, 818, 779 cm^{-1}; HRMS (ESI-TOF) m/z: (M + H)$^+$ calcd for $C_{10}H_9O_4$ 193.0501; found: 193.0502; mp 171.1−174.5 °C. The above analysis results correspond to the literature data.[8]



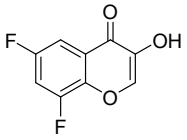
3-Hydroxy-5-methoxy-4*H*-chromen-4-one (**1f**). GP2. A scale of 16.5 mmol, solid, 1.321 g (6.9 mmol), isolated yield of 42%; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.55 (t, J = 8.4 Hz, 1H), 7.04 (dd, J = 1.0, 8.5 Hz, 1H), 6.78 (dd, J = 0.4, 8.2 Hz, 1H), 6.41 (s, 1 H), 4.01 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 172.8, 159.8, 158.3, 142.0, 135.7, 133.8, 112.6, 110.5, 105.0, 56.4; IR ν_{max}: 3279, 3089, 1624, 1604, 1571, 1475, 1443, 1417, 1267, 803, 700 cm^{-1}; HRMS (ESI-TOF) m/z: (M + H)$^+$ calcd for $C_{10}H_9O_4$ 193.0501; found: 193.0503; mp 148.2−153.0 °C.



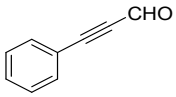
7-Fluoro-3-hydroxy-4*H*-chromen-4-one (**1g**). GP2. A scale of 23.2 mmol, solid, 1.547 g (8.6 mmol), isolated yield of 37%; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.27 (ddd, J = 0.4, 6.2, 8.8 Hz, 1H), 7.98 (s, 1H), 7.19-7.13 (m, 2H), 6.13 (s, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 172.6, 165.6 (d, J=255.3 Hz), 157.3 (d, J=13.8 Hz), 141.7, 138.4 (d, J=1.4 Hz), 128.1 (d, J=11.1 Hz), 118.7 (d, J=2.1 Hz), 114.0 (d, J=23.5 Hz), 104.9 (d, J=25.6 Hz); IR ν_{max}: 3286, 3098, 1635, 1602, 1493, 1454, 1406, 1268, 852, 812, 774 cm^{-1}; HRMS (ESI-TOF) m/z: (M + H)$^+$ calcd for $C_9H_6FO_3$ 181.0301; found: 181.0302; mp 213.3−219.9 °C.



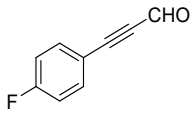
7-Chloro-3-hydroxy-4*H*-chromen-4-one (**1h**). GP2. A scale of 11.1 mmol, solid, 0.306 g (1.6 mmol), isolated yield of 14%; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.18 (dd, J = 0.4, 8.6 Hz, 1H), 7.97 (s, 1H), 7.52 (d, J = 1.9 Hz, 1H), 7.37 (dd, J = 1.9, 8.6 Hz, 1H), 6.21 (s, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 172.7, 156.3, 141.9, 139.9, 138.4, 126.9, 125.7, 120.4, 118.4; IR ν_{max}: 3307, 3110, 1624, 1608, 1561, 1481, 1449, 1400, 1270, 891, 863, 778 cm^{-1}; HRMS (ESI-TOF) m/z: (M + H)$^+$ calcd for $C_9H_6{}^{35}ClO_3$ 197.0005; found: 197.0006; mp 177.8−185.3 °C.



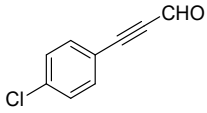
6,8-Difluoro-3-hydroxy-4*H*-chromen-4-one (**1i**). GP2. A scale of 9.7 mmol, solid, 0.860 g (4.4 mmol), isolated yield of 45%; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.71 (ddd, J = 2.0, 3.0, 8.0 Hz, 1H), 7.31-7.27 (m, 1H), 6.12 (s, 1H); ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 171.9 (t, J=3.3 Hz), 158.0 (dd, J=248.5, 9.8 Hz), 151.8 (dd, J=258.3, 11.4 Hz), 142.2 (d, J=9.8 Hz), 141.8, 138.5, 123.9 (d, J=8.2 Hz), 109.0 (dd, J=29.4, 19.6 Hz), 105.4 (dd, J=22.9, 4.9 Hz); IR ν_{max}: 3321, 3099, 1641, 1619, 1583, 1499, 1451, 1433, 1297, 864, 768 cm^{-1}; HRMS (ESI-TOF) m/z: (M + H)$^+$ calcd for $C_9H_5F_2O_3$ 199.0207; found: 199.0203; mp 197.4−204.8 °C.



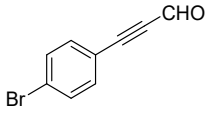
3-Phenylpropiolaldehyde (**2a**). GP3. A scale of 25.0 mmol, liquid, 2.459 g (19.0 mmol), isolated yield of 76%; ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.43 (s, 1H), 7.63-7.58 (m, 2H), 7.50 (tdd, J = 1.2, 7.0, 8.0 Hz, 1H), 7.43-7.39 (m, 2H); ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 176.4, 132.9, 130.9, 128.4, 119.0, 94.7, 88.1; IR ν_{max}: 2854, 2184, 1653, 1595, 1489 cm^{-1}; HRMS (ESI-TOF) m/z: (M + H)$^+$ calcd for C_9H_7O 131.0497; found: 131.0499. The above analysis results correspond to the literature data.[9]



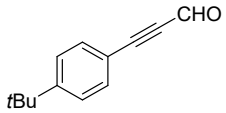
3-(4-Fluorophenyl)propiolaldehyde (**2b**). GP3. A scale of 15.0 mmol, solid, 0.632 g (4.2 mmol), isolated yield of 28%; ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.43 (s, 1H), 7.67-7.61 (m, 2H), 7.16-7.10 (m, 2H); $^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$) δ 176.4, 164.3 (d, J=255.0 Hz), 135.6 (d, J=9.8 Hz), 116.3 (d, J=21.3 Hz), 115.6 (d, J=3.3 Hz), 93.8, 88.4; IR ν_{max}: 2889, 2187, 1649, 1595, 1503 cm^{-1}; HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for C_9H_6FO 149.0403; found: 149.0405; mp 44.6−48.2 °C. The above analysis results correspond to the literature data.[10]



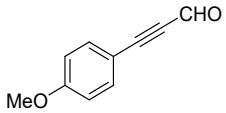
3-(4-Chlorophenyl)propiolaldehyde (**2c**). GP3. A scale of 15.0 mmol, solid, 1.469 g (9.0 mmol), isolated yield of 60%; ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.41 (s, 1H), 7.55-7.52 (m, 2H), 7.41-7.37 (m, 2H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 176.4, 137.8, 134.4, 129.2, 117.9, 93.5, 89.0; IR ν_{max}: 2187, 1649, 1587, 1476 cm^{-1}; HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_9H_6{}^{35}ClO$ 165.0107; found: 165.0108; mp 92.3−95.9 °C. The above analysis results correspond to the literature data.[9]



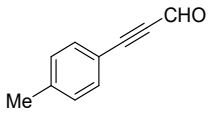
3-(4-Bromophenyl)propiolaldehyde (**2d**). GP3. A scale of 15.0 mmol, solid, 1.050 g (5.0 mmol), isolated yield of 33%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (s, 1H), 7.59-7.54 (m, 2H), 7.50-7.44 (m, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 176.4, 134.5, 132.2, 126.2, 118.4, 93.5, 89.1; IR ν_{max}: 2972, 2890, 2188, 1649, 1581, 1474 cm^{-1}; HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_9H_6{}^{79}BrO$ 208.9602; found: 208.9607; mp 95.5−98.0 °C. The above analysis results correspond to the literature data.[10]



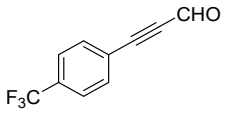
3-(4-(*tert*-Butyl)phenyl)propiolaldehyde (**2e**). GP3. A scale of 15.0 mmol, solid, 1.110 g (6.0 mmol), isolated yield of 40%; ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.44 (s, 1H), 7.58-7.56 (m, 2H), 7.46-7.44 (m, 2H), 1.35 (s, 9H); $^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$) δ 176.8, 155.2, 133.3, 125.9, 116.4, 95.9, 88.5, 35.2, 31.0; IR ν_{max}: 3042, 2955, 2906, 2868, 2185, 1651, 1598, 1502, 1477 cm^{-1}; HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{13}H_{15}O$ 187.1123; found: 187.1122; mp 40.5−43.1 °C. The above analysis results correspond to the literature data.[10]



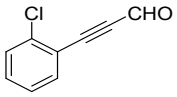
3-(4-Methoxyphenyl)propiolaldehyde (**2f**). GP3. A scale of 15.0 mmol, solid, 2.214 g (13.8 mmol), isolated yield of 92%; ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.39 (s, 1H), 7.57-7.55 (m, 2H), 6.93-6.90 (m, 2H), 3.85 (s, 3H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 176.7, 162.1, 135.4, 114.5, 111.1, 96.5, 88.7, 55.4; IR ν_{max}: 2176, 1642, 1597, 1566, 1507 cm^{-1}; HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{10}H_9O_2$ 161.0603; found: 161.0602; mp 45.5−48.0 °C. The above analysis results correspond to the literature data.[10]



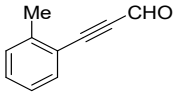
3-(*p*-Tolyl)propiolaldehyde (**2g**). GP3. A scale of 15.0 mmol, liquid, 1.311 g (9.2 mmol), isolated yield of 61%; ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.43 (s, 1H), 7.53-7.51 (m, 2H), 7.25-7.22 (m, 2H), 2.42 (s, 3H); $^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$) δ 176.9, 142.2, 133.4, 129.6, 116.3, 96.0, 88.5, 21.8; IR ν_{max}: 2921, 2854, 2737, 2180, 1651, 1604, 1507 cm^{-1}; HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{10}H_9O$ 145.0653; found: 145.0655. The above analysis results correspond to the literature data.[10]



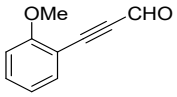
3-(4-(Trifluoromethyl)phenyl)propiolaldehyde (**2h**). GP3. A scale of 15.0 mmol, solid, 0.629 g (3.2 mmol), isolated yield of 21%; ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.47 (s, 1H), 7.74 (d, J = 8.1 Hz, 2H), 7.70 (d, J = 8.1 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$) δ 176.2, 133.3, 132.7 (q, J=32.7 Hz), 125.7 (q, J=3.3 Hz), 123.3, 123.5 (q, J=273.0 Hz), 92.1, 89.2; IR ν_{max}: 2891, 2191, 1653, 1613, 1258 cm^{-1}; HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{10}H_6F_3O$ 199.0371; found: 199.0371; mp 36.3−38.7 °C. The above analysis results correspond to the literature data.[10]



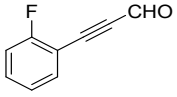
3-(2-Chlorophenyl)propiolaldehyde (**2i**). GP3. A scale of 15.0 mmol, liquid, 1.700 g (10.3 mmol), isolated yield of 69%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (s, 1H), 7.63 (ddd, J = 0.5, 1.7, 7.6 Hz, 1H), 7.51-7.40 (m, 2H), 7.35-7.29 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 176.4, 137.6, 135.0, 132.2, 129.8, 126.8, 119.8, 92.1, 90.9; IR ν_{max}: 2859, 2189, 1654, 1587, 1471 cm^{-1}; HRMS (ESI-TOF) m/z: (M + H)$^+$ calcd for $C_9H_6{}^{35}ClO$ 165.0107; found: 165.0105. The above analysis results correspond to the literature data.[11]



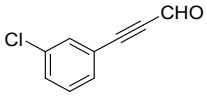
3-(*o*-Tolyl)propiolaldehyde (**2j**). GP3. A scale of 7.5 mmol, liquid, 0.695 g (4.8 mmol), isolated yield of 64%; ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.46 (s, 1H), 7.56 (ddd, J = 0.4, 0.9, 7.7 Hz, 1H), 7.39-7.36 (m, 1H), 7.27 (tdd, J = 0.6, 1.3, 7.7 Hz, 1H), 7.23-7.20 (m, 1H), 2.50 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 176.8, 142.6, 133.8, 131.3, 129.9, 126.0, 119.2, 94.4, 92.2, 20.5; IR ν_{max}: 2863, 2181, 1653, 1598, 1483 cm^{-1}; HRMS (ESI-TOF) m/z: (M + H)$^+$ calcd for $C_{10}H_9O$ 145.0653; found: 145.0656. The above analysis results correspond to the literature data.[9]



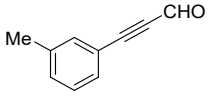
3-(2-Methoxyphenyl)propiolaldehyde (**2k**). GP3. A scale of 15.0 mmol, liquid, 1.540 g (9.6 mmol), isolated yield of 64%; ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.47 (s, 1H), 7.55 (ddd, J = 0.4, 1.8, 7.7 Hz, 1H), 7.47 (ddd, J = 1.8, 7.5, 8.4 Hz, 1H), 6.98 (dt, J = 1.0, 7.5 Hz, 1H), 6.94 (d, J = 8.6 Hz, 1H), 3.93 (s, 3H); ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 176.8, 161.7, 135.1, 133.3, 120.7, 111.0, 108.4, 92.7, 92.5, 55.8; IR ν_{max}: 2946, 2840, 2739, 2177, 1648, 1594, 1573, 1489 cm^{-1}; HRMS (ESI-TOF) m/z: (M + H)$^+$ calcd for $C_{10}H_9O_2$ 161.0603; found: 161.0601. The above analysis results correspond to the literature data.[10]



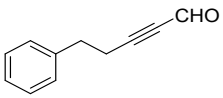
3-(2-Fluorophenyl)propiolaldehyde (**2l**). GP3. A scale of 15.0 mmol, liquid, 0.920 g (6.2 mmol), isolated yield of 41%; ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.47 (s, 1H), 7.60 (ddd, J = 1.8, 6.6, 7.9 Hz, 1H), 7.53-7.49 (m, 1H), 7.21 (dt, J = 0.9, 7.6 Hz, 1H), 7.19-7.15 (m, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 176.3, 163.7 (d, J=256.7 Hz), 134.8, 133.3 (d, J=8.2 Hz), 124.4 (d, J=3.3 Hz), 116.0 (d, J=19.6 Hz), 108.4 (d, J=14.7 Hz), 92.5 (d, J=3.3 Hz), 88.1; IR ν_{max}: 2862, 2742, 2191, 1656, 1609, 1574, 1489 cm^{-1}; HRMS (ESI-TOF) m/z: (M + H)$^+$ calcd for C_9H_6FO 149.0403; found: 149.0401. The above analysis results correspond to the literature data.[12]



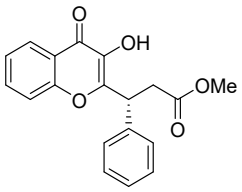
3-(3-Chlorophenyl)propiolaldehyde (**2m**). GP3. A scale of 15.0 mmol, liquid, 1.441 g (8.7 mmol), isolated yield of 58%; ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.41 (s, 1H), 7.60-7.56 (m, 1H), 7.50-7.43 (m, 2H), 7.37-7.31 (m, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 176.4, 134.7, 132.8, 131.5, 131.2, 130.0, 121.1, 92.7, 88.6; IR ν_{max}: 2190, 1657, 1589, 1560, 1473 cm^{-1}; HRMS (ESI-TOF) m/z: (M + H)$^+$ calcd for $C_9H_6{}^{35}ClO$ 165.0107; found: 165.0110. The above analysis results correspond to the literature data.[11]



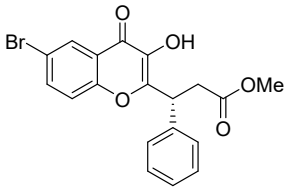
3-(*m*-Tolyl)propiolaldehyde (**2n**). GP3. A scale of 15.0 mmol, liquid, 1.010 g (7.0 mmol), isolated yield of 47%; ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.44 (s, 1H), 7.46-7.42 (m, 2H), 7.34-7.30 (m, 2H), 2.39 (s, 3H); ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 176.8, 138.6, 133.7, 132.3, 130.4, 128.7, 119.2, 95.6, 88.3, 21.1; IR ν_{max}: 2922, 2855, 2737, 2183, 1655, 1578, 1481 cm^{-1}; HRMS (ESI-TOF) m/z: (M + H)$^+$ calcd for $C_{10}H_9O$ 145.0653; found: 145.0654. The above analysis results correspond to the literature data.[9]



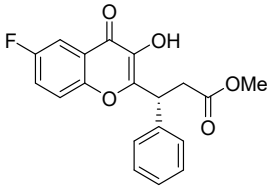
5-Phenylpent-2-ynal (**2o**). GP3. A scale of 15.0 mmol, liquid, 1.038 g (6.6 mmol), isolated yield of 44%; ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.18 (t, J = 0.9 Hz, 1H), 7.37-7.33 (m, 2H), 7.29-7.23 (m, 3H), 2.94 (t, J = 7.5 Hz, 2H), 2.74 (dt, J = 0.7, 7.5 Hz, 2H); ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 176.9, 139.5, 128.6, 128.4, 126.8, 97.9, 82.2, 33.8, 21.2; IR ν_{max}: 3029, 2929, 2860, 2742, 2197, 1659, 1602, 1495 cm^{-1}; HRMS (ESI-TOF) m/z: (M + H)$^+$ calcd for $C_{11}H_{11}O$ 159.0810; found: 159.0806. The above analysis results correspond to the literature data.[13]



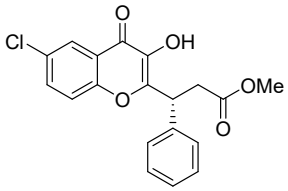
Methyl (*R*)-3-(3-hydroxy-4-oxo-4*H*-chromen-2-yl)-3-phenylpropanoate (**3aaa**). GP4. A scale of 0.25 mmol, opening time was equal to 24 h, solid, 61.95 mg (0.19 mmol), isolated yield of 77%, 95% *ee*; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.22 (ddd, *J* = 0.4, 1.8, 7.9 Hz, 1H), 7.67 (ddd, *J* = 1.5, 7.0, 8.6 Hz, 1H), 7.53-7.50 (m, 1H), 7.49-7.45 (m, 2H), 7.39 (ddd, *J* = 1.0, 7.0, 8.0 Hz, 1H), 7.37-7.33 (m, 2H), 7.30-7.27 (m, 1H), 6.36 (s, 1H), 5.01 (dd, *J* = 7.0, 9.0 Hz, 1H), 3.66 (s, 3H), 3.39 (dd, *J* = 9.0, 16.5 Hz, 1H), 3.16 (dd, *J* = 6.9, 16.4 Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 172.8, 171.4, 155.5, 150.5, 139.2, 137.8, 133.2, 128.8, 127.8, 127.6, 125.5, 124.5, 121.3, 118.2, 51.9, 41.0, 36.6; IR ν_{max}: 3255, 1733, 1609, 1569, 1484, 1468, 1434, 1284, 1258, 754, 700, cm^{-1}; HRMS (ESI-TOF) m/z: (M + H)$^{+}$ calcd for $C_{19}H_{17}O_5$ 325.1076; found: 325.1079; mp 108.4−117.4 °C.



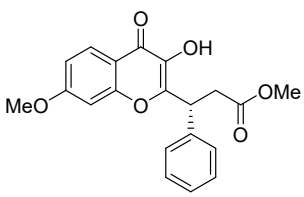
Methyl (*R*)-3-(6-bromo-3-hydroxy-4-oxo-4*H*-chromen-2-yl)-3-phenylpropanoate (**3baa**). GP4. A scale of 0.25 mmol, opening time was equal to 24 h, solid, 95.54 mg (0.24 mmol), isolated yield of 95%, 83% *ee*; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.30 (d, *J* = 2.4 Hz, 1H), 7.70 (dd, *J* = 2.6, 9.0 Hz, 1H), 7.43-7.40 (m, 2H), 7.38 (d, *J* = 9.0 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.27-7.24 (m, 1H), 6.32 (s, 1H), 4.95 (dd, *J* = 7.0, 8.9 Hz, 1H), 3.62 (s, 3H), 3.35 (dd, *J* = 9.1, 16.5 Hz, 1H), 3.10 (dd, *J* = 6.8, 16.5 Hz, 1H); ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 171.6, 171.3, 154.2, 151.0, 139.0, 138.0, 136.2, 128.9, 128.0, 127.7, 127.7, 122.7, 120.1, 117.9, 51.9, 41.1, 36.5; IR ν_{max}: 1736, 1621, 1601, 1584, 1566, 1530, 1495, 1467, 1455, 1436, 1266, 1201, 699 cm^{-1}; HRMS (ESI-TOF) m/z: (M + H)$^{+}$ calcd for $C_{19}H_{16}{}^{79}BrO_5$ 403.0181; found: 403.0184; mp 132.7−143.2 °C.



Methyl (*R*)-3-(6-fluoro-3-hydroxy-4-oxo-4*H*-chromen-2-yl)-3-phenylpropanoate (**3caa**). GP4. A scale of 0.25 mmol, opening time was equal to 24 h, solid, 59.05 mg (0.17 mmol), isolated yield of 69%, 88% *ee*; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 3.0, 8.0 Hz, 1H), 7.49 (dd, *J* = 4.1, 9.2 Hz, 1H), 7.42 (dd, *J* = 1.0, 8.1 Hz, 2H), 7.37 (ddd, *J* = 3.0, 7.5, 9.3 Hz, 1H), 7.34-7.30 (m, 2H), 7.28-7.24 (m, 1H), 6.31 (s, 1H), 4.97 (dd, *J* = 6.9, 9.0 Hz, 1H), 3.63 (s, 3H), 3.36 (dd, *J* = 9.1, 16.5 Hz, 1H), 3.11 (dd, *J* = 6.9, 16.6 Hz, 1H); ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 172.1 (d, *J*=3.3 Hz), 171.3, 158.4 (d, *J*=246.9 Hz), 151.8, 151.0, 139.1, 137.5, 128.9, 127.7, 127.7, 122.3 (d, *J*=8.2 Hz), 121.7 (d, *J*=26.2 Hz), 120.3 (d, *J*=8.2 Hz), 110.0 (d, *J*=22.9 Hz), 51.9, 41.2, 36.6; IR ν_{max}: 1737, 1731, 1609, 1575, 1483, 1408, 1259, 1218, 762, 707 cm^{-1}; HRMS (ESI-TOF) m/z: (M + H)$^{+}$ calcd for $C_{19}H_{16}FO_5$ 343.0982; found: 343.0981; mp 140.8−147.9 °C.

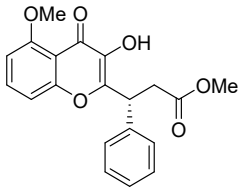


Methyl (*R*)-3-(6-chloro-3-hydroxy-4-oxo-4*H*-chromen-2-yl)-3-phenylpropanoate (**3daa**). GP4. A scale of 0.25 mmol, opening time was equal to 24 h, solid, 76.25 mg (0.21 mmol), isolated yield of 85%, 91% *ee*; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.14 (d, *J* = 2.6 Hz, 1H), 7.57 (dd, *J* = 2.6, 9.0 Hz, 1H), 7.44 (dd, *J* = 0.4, 9.0 Hz, 1H), 7.43-7.40 (m, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.28-7.25 (m, 1H), 6.23 (s, 1H), 4.95 (dd, *J* = 6.7, 9.2 Hz, 1H), 3.63 (s, 3H), 3.35 (dd, *J* = 9.1, 16.5 Hz, 1H), 3.11 (dd, *J* = 6.8, 16.5 Hz, 1H); ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 171.7, 171.3, 153.8, 151.0, 139.0, 137.9, 133.5, 130.6, 128.9, 127.7, 127.7, 124.7, 122.2, 119.9, 51.9, 41.1, 36.5; IR ν_{max}: 3286, 1733, 1621, 1604, 1566, 1469, 1453, 1263, 1227, 698 cm^{-1}; HRMS (ESI-TOF) m/z: (M + H)$^{+}$ calcd for $C_{19}H_{16}{}^{35}ClO_5$ 359.0686; found: 359.0688; mp 125.8−135.2 °C.

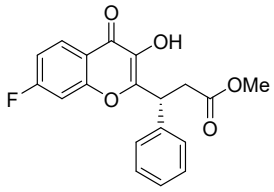


Methyl (*R*)-3-(3-hydroxy-7-methoxy-4-oxo-4*H*-chromen-2-yl)-3-phenylpropanoate (**3eaa**). GP4. A scale of 0.25 mmol, opening time was equal to 24 h, solid, 58.13 mg (0.16 mmol), isolated yield of 66%, 98% *ee*; ^{1}H NMR

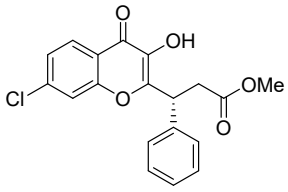
(700 MHz, $CDCl_3$) δ 8.06 (d, J = 8.8 Hz, 1H), 7.44-7.41 (m, 2H), 7.32 (t, J = 7.7 Hz, 2H), 7.25-7.23 (m, 1H), 6.94 (dd, J = 2.4, 8.8 Hz, 1H), 6.84 (d, J = 2.4 Hz, 1H), 6.26 (s, 1H), 4.92 (dd, J = 7.1, 9.0 Hz, 1H), 3.90 (s, 3H), 3.62 (s, 3H), 3.34 (dd, J = 9.0, 16.3 Hz, 1H), 3.11 (dd, J = 6.9, 16.3 Hz, 1H); $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$) δ 172.3, 171.4, 164.0, 157.4, 149.5, 139.5, 137.5, 128.8, 127.7, 127.5, 126.8, 115.2, 114.7, 100.0, 55.8, 51.8, 41.1, 36.7; IR ν_{max}: 3275, 1723, 1632, 1601, 1505, 1447, 1436, 1423, 1270, 1218, 706, 697 cm^{-1}; HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{20}H_{19}O_6$ 355.1182; found: 355.1184; mp 136.9−145.0 °C.



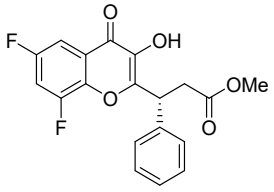
Methyl (*R*)-3-(3-hydroxy-5-methoxy-4-oxo-4*H*-c.hromen-2-yl)-3-phenyl-propanoate (**3faa**). GP4. A scale of 0.25 mmol, opening time was equal to 24 h, solid, 86.27 mg (0.24 mmol), isolated yield of 97%, 99% *ee*; ^1H NMR (700 MHz, $CDCl_3$) δ 7.51 (t, J = 8.4 Hz, 1H), 7.43-7.40 (m, 2H), 7.33-7.29 (m, 2H), 7.25-7.23 (m, 1H), 7.03 (dd, J = 1.0, 8.6 Hz, 1H), 6.73 (d, J = 7.6 Hz, 1H), 6.58 (s, 1H), 4.88 (dd, J = 7.2, 8.8 Hz, 1H), 3.97 (s, 3H), 3.61 (s, 3H), 3.31 (dd, J = 8.8, 16.3 Hz, 1H), 3.10 (dd, J = 7.2, 16.3 Hz, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 172.4, 171.4, 159.7, 157.5, 147.6, 139.3, 138.0, 133.5, 128.8, 127.7, 127.5, 111.9, 110.3, 105.1, 56.4, 51.9, 41.0, 36.6; IR ν_{max}: 1733, 1606, 1480, 1438, 1258, 1228, 699 cm^{-1}; HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{20}H_{19}O_6$ 355.1182; found: 355.1181; mp 74.4−87.7 °C.



Methyl (*R*)-3-(7-fluoro-3-hydroxy-4-oxo-4*H*-chromen-2-yl)-3-phenyl-propanoate (**3gaa**). GP4. A scale of 0.25 mmol, opening time was equal to 24 h, solid, 84.35 mg (0.25 mmol), isolated yield of 99%, 93% *ee*; ^1H NMR (700 MHz, $CDCl_3$) δ 8.22 (dd, J = 6.2, 9.0 Hz, 1H), 7.46-7.43 (m, 2H), 7.35 (t, J = 7.7 Hz, 2H), 7.31-7.29 (m, 1H), 7.20 (dd, J = 2.3, 9.1 Hz, 1H), 7.14 (ddd, J = 2.4, 8.1, 8.8 Hz, 1H), 6.28 (s, 1H), 4.97 (dd, J = 6.7, 9.1 Hz, 1H), 3.66 (s, 3H), 3.37 (dd, J = 9.1, 16.4 Hz, 1H), 3.13 (dd, J = 6.8, 16.5 Hz, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 172.1, 171.4, 165.4 (d, J=255.3 Hz), 156.4 (d, J=13.1 Hz), 150.7 (d, J=2.1 Hz), 139.0, 137.7, 128.9, 128.0 (d, J=10.4 Hz), 127.7, 127.6, 118.1 (d, J=2.1 Hz), 113.8 (d, J=23.5 Hz), 104.7 (d, J=25.6 Hz), 51.9, 41.0, 36.4; IR ν_{max}: 3287, 1732, 1639, 1607, 1496, 1452, 1423, 1253, 1237, 704 cm^{-1}; HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{19}H_{16}FO_5$ 343.0982; found: 343.0984; mp 141.6−149.5 °C.

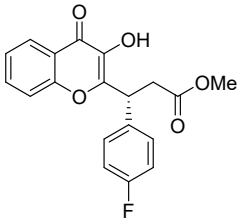


Methyl (*R*)-3-(7-chloro-3-hydroxy-4-oxo-4*H*-chromen-2-yl)-3-phenyl-propanoate (**3haa**). GP4. A scale of 0.25 mmol, opening time was equal to 24 h, solid, 75.06 mg (0.21 mmol), isolated yield of 84%, 93% *ee*; ^1H NMR (700 MHz, $CDCl_3$) δ 8.11 (d, J = 8.6 Hz, 1H), 7.52 (d, J = 1.9 Hz, 1H), 7.43-7.40 (m, 2H), 7.35-7.31 (m, 3H), 7.28-7.26 (m, 1H), 6.22 (s, 1H), 4.94 (dd, J = 6.8, 9.1 Hz, 1H), 3.63 (s, 3H), 3.34 (dd, J = 9.3, 16.3 Hz, 1H), 3.10 (dd, J = 6.8, 16.5 Hz, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 172.1, 171.3, 155.5, 150.7, 139.5, 138.9, 137.9, 128.9, 127.7, 127.7, 126.8, 125.5, 119.8, 118.2, 51.9, 41.0, 36.4; IR ν_{max}: 3286, 1722, 1629, 1602, 1560, 1442, 1264, 1221, 705, 697 cm^{-1}; HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{19}H_{16}{}^{35}ClO_5$ 359.0686; found: 359.0689; mp 143.4−150.2 °C.

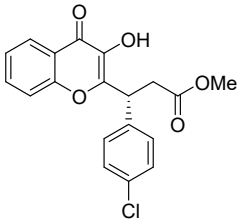


Methyl (*R*)-3-(6,8-difluoro-3-hydroxy-4-oxo-4*H*-chromen-2-yl)-3-phenyl-propanoate (**3iaa**). GP4. A scale of 0.25 mmol, opening time was equal to 24 h, solid, 66.74 mg (0.19 mmol), isolated yield of 74%, 56% *ee*; ^1H NMR (700 MHz, $CDCl_3$) δ 7.64 (ddd, J = 2.0, 2.9, 7.9 Hz, 1H), 7.50-7.46 (m, 2H), 7.38-7.35 (m, 2H), 7.32-7.29 (m, 1H), 7.24 (ddd, J = 3.0, 7.7, 10.2 Hz, 1H), 6.30 (s, 1H), 5.00 (dd, J = 6.7, 9.4 Hz, 1H), 3.67 (s, 3H), 3.41 (dd, J = 9.2, 16.7 Hz, 1H), 3.15 (dd, J = 6.8, 16.5 Hz, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 171.4, 157.8 (dd, J=249.1, 9.7 Hz), 151.4, 151.5 (dd, J=258.1,

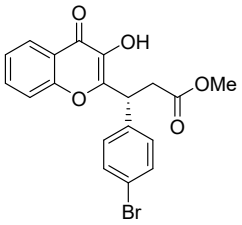
11.8 Hz), 141.2 (dd, *J*=12.5, 2.1 Hz), 138.7, 137.8, 129.0, 127.9, 127.8, 123.4 (d, *J*=9.0 Hz), 108.7 (dd, *J*=29.1, 20.1 Hz), 105.4 (dd, *J*=23.5, 4.8 Hz), 52.0, 40.9, 36.4; IR ν_{max}: 3285, 1731, 1619, 1587, 1494, 1422, 1247, 1225, 701 cm^{-1}; HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{19}H_{15}F_2O_5$ 361.0888; found: 361.0887; mp 116.1−124.2 °C.



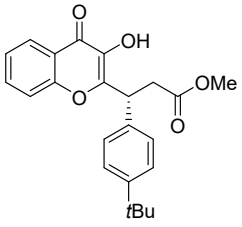
Methyl (*R*)-3-(4-fluorophenyl)-3-(3-hydroxy-4-oxo-4*H*-chromen-2-yl)-propanoate (**3aba**). GP4. A scale of 0.25 mmol, opening time was equal to 24 h, solid, 69.92 mg (0.20 mmol), isolated yield of 82%, 80% *ee*; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 0.4, 7.9 Hz, 1H), 7.68 (ddd, *J* = 1.8, 7.0, 8.6 Hz, 1H), 7.51 (dd, *J* = 0.4, 8.6 Hz, 1H), 7.46-7.42 (m, 2H), 7.40 (ddd, *J* = 1.0, 7.0, 8.0 Hz, 1H), 7.08-6.99 (m, 2H), 6.40 (s, 1H), 4.99 (t, *J* = 7.9 Hz, 1H), 3.66 (s, 3H), 3.34 (dd, *J* = 8.5, 16.4 Hz, 1H), 3.14 (dd, *J* = 7.4, 16.4 Hz, 1H); ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 172.8, 171.2, 162.2 (d, *J*=245.2 Hz), 155.5, 150.2, 137.7, 135.0 (d, *J*=3.3 Hz), 133.3, 129.4 (d, *J*=8.2 Hz), 125.6, 124.6, 121.3, 118.1, 115.7 (d, *J*=21.3 Hz), 51.9, 40.4, 36.7; IR ν_{max}: 3256, 1738, 1622, 1608, 1569, 1509, 1469, 1437, 1288, 1217, 755 cm^{-1}; HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{19}H_{16}FO_5$ 343.0982; found: 343.0980; mp 120.5−122.8 °C.



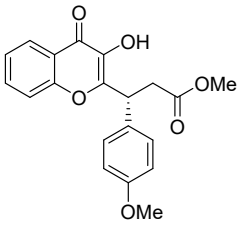
Methyl (*R*)-3-(4-chlorophenyl)-3-(3-hydroxy-4-oxo-4*H*-chromen-2-yl)-propanoate (**3aca**). GP4. A scale of 0.25 mmol, opening time was equal to 24 h, solid, 59.20 mg (0.17 mmol), isolated yield of 66%, 93% *ee*; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.23-8.20 (m, 1H), 7.68 (ddd, *J* = 1.8, 7.0, 8.6 Hz, 1H), 7.52-7.49 (m, 1H), 7.43-7.39 (m, 3H), 7.34-7.30 (m, 2H), 4.97 (t, *J* = 7.9 Hz, 1H), 3.66 (s, 3H), 3.34 (dd, *J* = 8.5, 16.4 Hz, 1H), 3.14 (dd, *J* = 7.5, 16.5 Hz, 1H); ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 172.8, 171.1, 155.5, 149.8, 137.7, 133.5, 133.3, 129.1, 129.0, 125.6, 124.6, 121.3, 118.1, 51.9, 40.5, 36.5; IR ν_{max}: 3266, 2955, 1731, 1612, 1574, 1493, 1481, 1470, 1440, 1426, 1291, 1256, 1223, 758, 703 cm^{-1}; HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{19}H_{16}{}^{35}ClO_5$ 359.0686; found: 359.0687; mp 153.5−155.2 °C.



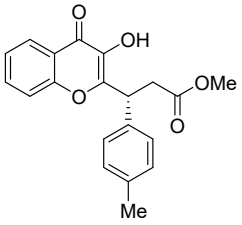
Methyl (*R*)-3-(4-bromophenyl)-3-(3-hydroxy-4-oxo-4*H*-chromen-2-yl)-propanoate (**3ada**). GP4. A scale of 0.25 mmol, opening time was equal to 24 h, solid, 87.57 mg (0.22 mmol), isolated yield of 87%, 83% *ee*; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.22 (ddd, *J* = 0.4, 1.8, 7.9 Hz, 1H), 7.68 (ddd, *J* = 1.8, 6.8, 8.6 Hz, 1H), 7.52-7.49 (m, 1H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.42-7.39 (m, 1H), 7.35 (s, 2H), 6.41 (s, 1H), 4.97 (t, *J* = 7.9 Hz, 1H), 3.66 (s, 3H), 3.34 (dd, *J* = 8.5, 16.4 Hz, 1H), 3.15 (dd, *J* = 7.6, 16.4 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.9, 171.1, 155.5, 149.8, 138.3, 137.8, 133.4, 132.0, 129.5, 127.8, 125.6, 124.6, 121.6, 118.1, 52.0, 40.5, 36.4; IR ν_{max}: 3270, 2950, 1732, 1610, 1570, 1484, 1469, 1434, 757, 702 cm^{-1}; HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{19}H_{16}{}^{79}BrO_5$ 403.0181; found: 403.0185; mp 123.6−128.9 °C.



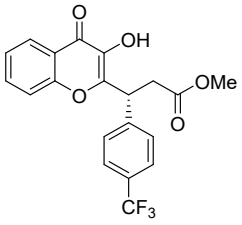
Methyl (*R*)-3-(4-(*tert*-butyl)phenyl)-3-(3-hydroxy-4-oxo-4*H*-chromen-2-yl)-propanoate (**3aea**). GP4. A scale of 0.25 mmol, opening time was equal to 24 h, solid, 48.90 mg (0.13 mmol), isolated yield of 51%, 92% *ee*; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 1.5, 7.9 Hz, 1H), 7.67 (ddd, *J* = 1.8, 7.3, 8.4 Hz, 1H), 7.52 (dd, *J* = 0.4, 8.6 Hz, 1H), 7.41-7.38 (m, 3H), 7.37-7.34 (m, 2H), 6.28 (s, 1H), 4.97 (dd, *J* = 6.6, 9.2 Hz, 1H), 3.65 (s, 3H), 3.40 (dd, *J* = 9.2, 16.5 Hz, 1H), 3.12 (dd, *J* = 6.6, 16.5 Hz, 1H), 1.30 (s, 9H); ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 172.8, 171.5, 155.6, 150.7, 150.5, 137.8, 136.2, 133.1, 127.4, 125.8, 125.5, 124.4, 121.4, 118.2, 51.8, 40.6, 36.7, 34.4, 31.3; IR ν_{max}: 3282, 2956, 1732, 1624, 1612, 1573, 1516, 1469, 1429, 1290, 1226, 763, 753 cm^{-1}; HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{23}H_{25}O_5$ 381.1702; found: 381.1705; mp 153.3−162.5 °C.



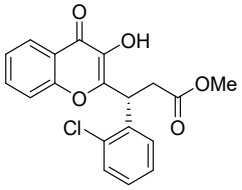
Methyl (*R*)-3-(3-hydroxy-4-oxo-4*H*-chromen-2-yl)-3-(4-methoxyphenyl)-propanoate (**3afa**). GP4. A scale of 0.25 mmol, opening time was equal to 24 h, solid, 59.36 mg (0.17 mmol), isolated yield of 67%, 94% *ee*; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.66 (ddd, *J* = 1.5, 7.1, 8.5 Hz, 1H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.42-7.37 (m, 3H), 6.90-6.86 (m, 2H), 6.39 (s, 1H), 4.96 (t, *J* = 7.9 Hz, 1H), 3.79 (s, 3H), 3.65 (s, 3H), 3.35 (dd, *J* = 8.8, 16.3 Hz, 1H), 3.13 (dd, *J* = 7.3, 16.3 Hz, 1H); ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 172.8, 171.4, 159.1, 155.5, 150.8, 137.6, 133.1, 131.3, 128.8, 125.5, 124.5, 121.3, 118.1, 114.3, 55.2, 51.8, 40.4, 36.8; IR ν_{max}: 3277, 2998, 1733, 1611, 1574, 1513, 1466, 1436, 1418, 1289, 1263, 1223, 758, 702 cm^{-1}; HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{20}H_{19}O_6$ 355.1182; found: 355.1180; mp 150.3−152.6 °C.



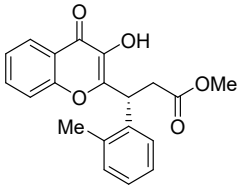
Methyl (*R*)-3-(3-hydroxy-4-oxo-4*H*-chromen-2-yl)-3-(*p*-tolyl)propanoate (**3aga**). GP4. A scale of 0.25 mmol, opening time was equal to 24 h, solid, 80.33 mg (0.24 mmol), isolated yield of 95%, 93% *ee*; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 1.3, 8.1 Hz, 1H), 7.66 (ddd, *J* = 1.8, 7.0, 8.6 Hz, 1H), 7.51 (dd, *J* = 0.6, 8.5 Hz, 1H), 7.39 (ddd, *J* = 1.0, 7.0, 8.0 Hz, 1H), 7.37-7.34 (m, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 6.39 (s, 1H), 4.97 (dd, *J* = 7.0, 9.0 Hz, 1H), 3.65 (s, 3H), 3.37 (dd, *J* = 8.9, 16.4 Hz, 1H), 3.14 (dd, *J* = 6.9, 16.4 Hz, 1H), 2.33 (s, 3H); ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 172.9, 171.5, 155.5, 151.0, 137.8, 137.3, 136.3, 133.1, 129.5, 127.7, 125.5, 124.5, 121.4, 118.1, 51.8, 40.7, 36.7, 21.0; IR ν_{max}: 3297, 1730, 1621, 1613, 1574, 1471, 1432, 1418, 1287, 1256, 1218, 757, 703 cm^{-1}; HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{20}H_{19}O_5$ 339.1232; found: 339.1233; mp 129.3−135.8 °C.



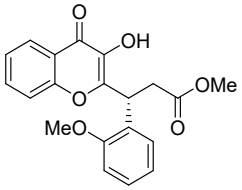
Methyl (*R*)-3-(3-hydroxy-4-oxo-4*H*-chromen-2-yl)-3-(4-(trifluoromethyl)-phenyl)propanoate (**3aha**). GP4. A scale of 0.25 mmol, opening time was equal to 24 h, solid, 64.60 mg (0.16 mmol), isolated yield of 66%, 63% *ee*; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 1.3, 7.9 Hz, 1H), 7.69 (ddd, *J* = 1.7, 7.1, 8.6 Hz, 1H), 7.63-7.58 (m, 4H), 7.52 (d, *J* = 8.6 Hz, 1H), 7.41 (ddd, *J* = 1.0, 7.1, 8.0 Hz, 1H), 6.50 (s, 1H), 5.08 (t, *J* = 7.8 Hz, 1H), 3.67 (s, 3H), 3.38 (dd, *J* = 8.4, 16.5 Hz, 1H), 3.20 (dd, *J* = 7.5, 16.5 Hz, 1H); ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 172.8, 171.0, 155.6, 149.4, 143.2, 137.9, 133.4, 130.0 (q, *J*=32.7 Hz), 128.2, 125.8 (q, *J*=3.3 Hz), 125.6, 124.7, 122.4 (q, *J*=271.4 Hz), 121.3, 118.1, 52.0, 40.9, 36.3; IR ν_{max}: 3292, 2955, 1737, 1611, 1572, 1469, 1420, 1291, 1231, 757, 705 cm^{-1}; HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{20}H_{16}F_3O_5$ 393.0950; found: 393.0952; mp 121.5−124.2 °C.



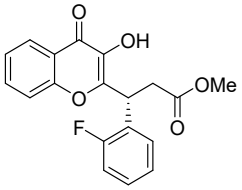
Methyl (*R*)-3-(2-chlorophenyl)-3-(3-hydroxy-4-oxo-4*H*-chromen-2-yl)-propanoate (**3aia**). GP4. A scale of 0.25 mmol, opening time was equal to 24 h, solid, 86.74 mg (0.24 mmol), isolated yield of 97%, 92% *ee*; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 1.4, 8.0 Hz, 1H), 7.65 (ddd, *J* = 1.7, 7.0, 8.6 Hz, 1H), 7.47 (dd, *J* = 0.6, 8.6 Hz, 1H), 7.42-7.37 (m, 3H), 7.24-7.19 (m, 2H), 6.26 (s, 1H), 5.42 (dd, *J* = 6.2, 9.5 Hz, 1H), 3.64 (s, 3H), 3.33 (dd, *J* = 9.6, 16.5 Hz, 1H), 3.08 (dd, *J* = 6.2, 16.6 Hz, 1H); ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 172.8, 171.1, 155.6, 149.2, 138.5, 136.9, 133.9, 133.3, 130.0, 128.8, 128.7, 127.2, 125.6, 124.6, 121.3, 118.2, 51.9, 38.6, 36.3; IR ν_{max}: 3062, 1732, 1620, 1610, 1567, 1471, 1434, 1292, 1225, 755, 695 cm^{-1}; HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{19}H_{16}{}^{35}ClO_5$ 359.0686; found: 359.0689; mp 133.8−136.4 °C.



Methyl (*R*)-3-(3-hydroxy-4-oxo-4*H*-chromen-2-yl)-3-(*o*-tolyl)propanoate (**3aja**). GP4. A scale of 0.25 mmol, opening time was equal to 24 h, oil, 56.65 mg (0.17 mmol), isolated yield of 67%, 89% *ee*; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 1.4, 8.0 Hz, 1H), 7.67 (ddd, *J* = 1.8, 7.0, 8.6 Hz, 1H), 7.51 (d, *J* = 8.6 Hz, 1H), 7.49-7.45 (m, 1H), 7.40 (ddd, *J* = 1.0, 7.1, 8.0 Hz, 1H), 7.23-7.15 (m, 3H), 6.33 (s, 1H), 5.24 (dd, *J* = 6.9, 8.7 Hz, 1H), 3.65 (s, 3H), 3.34 (dd, *J* = 8.8, 16.3 Hz, 1H), 3.11 (dd, *J* = 6.9, 16.4 Hz, 1H), 2.56 (s, 3H); ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 172.8, 171.5, 155.6, 150.5, 137.8, 137.6, 136.5, 133.2, 130.8, 127.4, 127.1, 126.4, 125.5, 124.5, 121.3, 118.1, 51.8, 37.0, 36.9, 19.7; IR ν_{max}: 3272, 3066, 1734, 1610, 1567, 1483, 1468, 1435, 1422, 1290, 1231, 756 cm^{-1}; HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{20}H_{19}O_5$ 339.1232; found: 339.1232.

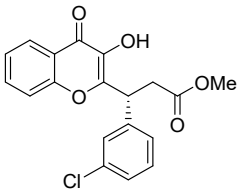


Methyl (*R*)-3-(3-hydroxy-4-oxo-4*H*-chromen-2-yl)-3-(2-methoxyphenyl)-propanoate (**3aka**). GP4. A scale of 0.25 mmol, opening time was equal to 24 h, solid, 24.54 mg (0.07 mmol), isolated yield of 28%, 91% *ee*; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.25-8.22 (m, 1H), 7.66 (ddd, *J* = 1.8, 7.0, 8.6 Hz, 1H), 7.50 (dd, *J* = 0.4, 8.6 Hz, 1H), 7.40 (ddd, *J* = 1.0, 7.0, 8.0 Hz, 1H), 7.30 (dd, *J* = 1.7, 7.6 Hz, 1H), 7.27 (ddd, *J* = 1.5, 7.5, 8.1 Hz, 1H), 6.92 (dq, *J* = 1.0, 7.7 Hz, 2H), 6.31 (s, 1H), 5.36 (dd, *J* = 5.7, 10.1 Hz, 1H), 3.87 (s, 3H), 3.65 (s, 3H), 3.35 (dd, *J* = 10.1, 16.5 Hz, 1H), 3.07 (dd, *J* = 5.7, 16.5 Hz, 1H); ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 172.8, 171.8, 156.9, 155.6, 150.8, 138.4, 133.0, 128.6, 128.3, 127.7, 125.5, 124.4, 121.4, 120.8, 118.2, 111.1, 55.7, 51.7, 36.0, 35.5; IR ν_{max}: 3164, 2995, 1735, 1621, 1611, 1586, 1567, 1491, 1470, 1433, 1291, 1228, 754 cm^{-1}; HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{20}H_{19}O_6$ 355.1182; found: 355.1183; mp 114.2−122.5 °C.

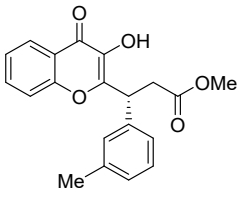


Methyl (*R*)-3-(2-fluorophenyl)-3-(3-hydroxy-4-oxo-4*H*-chromen-2-yl)-propanoate (**3ala**). GP4. A scale of 0.25 mmol, opening time was equal to 24 h, solid, 72.94 mg (0.21 mmol), isolated yield of 85%, 87% *ee*; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 1.4, 8.0 Hz, 1H), 7.67 (ddd, *J* = 1.5, 7.0, 8.6 Hz, 1H), 7.51 (dd, *J* = 0.4, 8.6 Hz, 1H), 7.45 (dt, *J* = 1.7, 7.6 Hz, 1H), 7.40 (ddd, *J* = 1.0, 7.1, 8.0 Hz, 1H), 7.28-7.25 (m, 1H), 7.13 (dt, *J* = 1.1, 7.6 Hz, 1H), 7.08 (ddd, *J* = 1.1, 8.4, 10.3 Hz, 1H), 6.46 (s, 1H), 5.28 (dd, *J* = 6.7, 9.1 Hz, 1 H), 3.66 (s, 3H), 3.41 (dd, *J* = 9.1, 16.6 Hz, 1H), 3.14 (dd, *J* = 6.8, 16.5 Hz, 1H);

^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 172.9, 171.2, 160.6 (d, *J*=248.5 Hz), 155.6, 149.4, 138.2, 133.3, 129.4 (d, *J*=3.3 Hz), 129.2 (d, *J*=8.2 Hz), 126.1 (d, *J*=14.7 Hz), 125.5, 124.5 (d, *J*=24.5 Hz), 121.3, 118.2, 115.9 (d, *J*=22.9 Hz), 51.9, 35.9, 35.2; IR ν_{max}: 3135, 2949, 1733, 1622, 1611, 1566, 1490, 1471, 1434, 1291, 1219, 757 cm^{-1}; HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{19}H_{16}FO_5$ 343.0982; found: 343.0983; mp 117.8−126.2 °C.

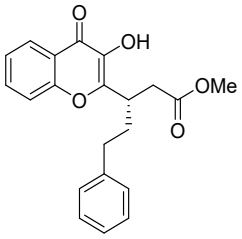


Methyl (*R*)-3-(3-chlorophenyl)-3-(3-hydroxy-4-oxo-4*H*-chromen-2-yl)-propanoate (**3ama**). GP4. A scale of 0.25 mmol, opening time was equal to 24 h, solid, 77.73 mg (0.22 mmol), isolated yield of 87%, 82% *ee*; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 1.8, 7.9 Hz, 1H), 7.69 (ddd, *J* = 1.5, 7.0, 8.6 Hz, 1H), 7.52 (dd, *J* = 0.4, 8.6 Hz, 1H), 7.45 (t, *J* = 1.9 Hz, 1H), 7.41 (ddd, *J* = 1.1, 7.2, 8.0 Hz, 1H), 7.36 (td, *J* = 1.6, 7.2 Hz, 1H), 7.28-7.25 (m, 2H), 6.38 (s, 1H), 4.97 (dd, *J* = 7.2, 8.7 Hz, 1H), 3.67 (s, 3H), 3.36 (dd, *J* = 8.6, 16.5 Hz, 1H), 3.14 (dd, *J* = 7.3, 16.5 Hz, 1H); ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 172.9, 171.1, 155.5, 149.8, 141.2, 137.9, 134.7, 133.4, 130.1, 128.0, 127.8, 126.1, 125.6, 124.6, 121.4, 118.2, 52.0, 40.7, 36.4; IR ν_{max}:

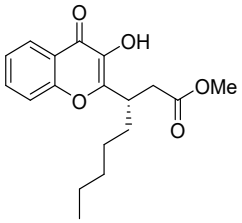


3264, 2951, 1734, 1609, 1570, 1469, 1422, 1290, 756, 698 cm^{-1}; HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{19}H_{16}{}^{35}ClO_5$ 359.0686; found: 359.0687; mp 109.5−113.1 °C.

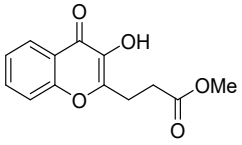
Methyl (*R*)-3-(3-hydroxy-4-oxo-4*H*-chromen-2-yl)-3-(*m*-tolyl)propanoate (**3ana**). GP4. A scale of 0.25 mmol, opening time was equal to 24 h, solid, 82.08 mg (0.24 mmol), isolated yield of 97%, 89% *ee*; ^1H NMR (700 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 1.3, 8.1 Hz, 1H), 7.67 (ddd, *J* = 1.5, 7.0, 8.6 Hz, 1H), 7.52 (dd, *J* = 0.4, 8.6 Hz, 1H), 7.40 (ddd, *J* = 1.0, 7.0, 8.0 Hz, 1H), 7.28-7.21 (m, 3H), 7.09 (d, *J* = 7.0 Hz, 1H), 6.31 (s, 1H), 4.96 (dd, *J* = 6.8, 9.0 Hz, 1H), 3.66 (s, 3H), 3.38 (dd, *J* = 9.1, 16.4 Hz, 1H), 3.13 (dd, *J* = 6.8, 16.5 Hz, 1H), 2.35 (s, 3H); $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$) δ 172.8, 171.5, 155.6, 150.5, 139.2, 138.5, 137.8, 133.2, 128.7, 128.6, 128.3, 125.5, 124.7, 124.5, 121.3, 118.2, 51.8, 41.1, 36.6, 21.4; IR ν_{max}: 3277, 2948, 1732, 1624, 1612, 1575, 1469, 1439, 1426, 1290, 1250, 1229, 717 cm^{-1}; HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{20}H_{19}O_5$ 339.1232; found: 339.1233; mp 97.6−104.8 °C.



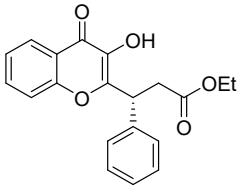
Methyl (*S*)-3-(3-hydroxy-4-oxo-4*H*-chromen-2-yl)-5-phenylpentanoate (**3aoa**). GP4. A scale of 0.25 mmol, opening time was equal to 24 h, oil, 80.76 mg (0.23 mmol), isolated yield of 92%, 95% *ee*; ^1H NMR (700 MHz, $CDCl_3$) δ 8.24 (ddd, *J* = 0.4, 1.8, 7.9 Hz, 1H), 7.69 (ddd, *J* = 1.8, 7.0, 8.6 Hz, 1H), 7.49 (ddd, *J* = 0.4, 1.1, 8.6 Hz, 1H), 7.42 (ddd, *J* = 1.0, 7.0, 8.0 Hz, 1H), 7.24-7.21 (m, 2H), 7.17-7.11 (m, 3H), 6.29 (s, 1H), 3.79-3.74 (m, 1H), 3.65 (s, 3H), 2.91 (dd, *J* = 8.1, 15.8 Hz, 1H), 2.76 (dd, *J* = 6.7, 16.0 Hz, 1H), 2.69 (ddd, *J* = 6.4, 9.6, 13.9 Hz, 1H), 2.62 (ddd, *J* = 5.7, 9.7, 14.1 Hz, 1H), 2.23 (dtd, *J* = 5.9, 9.8, 13.6 Hz, 1H), 2.06 (dddd, *J* = 5.1, 6.6, 9.9, 13.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$) δ 172.6, 171.8, 155.6, 151.7, 141.1, 138.6, 133.2, 128.3, 128.3, 126.0, 125.5, 124.5, 121.4, 118.1, 51.8, 36.9, 35.9, 33.8, 33.6; IR ν_{max}: 3267, 2949, 1736, 1610, 1571, 1469, 1433, 1286, 1214, 751, 702 cm^{-1}; HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{21}H_{21}O_5$ 353.1389; found: 353.1388.



Methyl (*S*)-3-(3-hydroxy-4-oxo-4*H*-chromen-2-yl)octanoate (**3apa**). GP4. A scale of 0.25 mmol, opening time was equal to 24 h, oil, 18.60 mg (0.06 mmol), isolated yield of 23%, 96% *ee*; ^1H NMR (700 MHz, $CDCl_3$) δ 8.24 (ddd, *J* = 0.4, 1.8, 7.9 Hz, 1H), 7.68 (ddd, *J* = 1.7, 7.0, 8.5 Hz, 1H), 7.50 (dd, *J* = 0.4, 8.6 Hz, 1H), 7.41 (ddd, *J* = 1.0, 7.0, 8.0 Hz, 1H), 6.21 (s, 1H), 3.71 (dddd, *J* = 5.5, 6.4, 8.5, 9.5 Hz, 1H), 3.66 (s, 3H), 2.88 (dd, *J* = 8.5, 16.0 Hz, 1H), 2.73 (dd, *J* = 6.4, 15.8 Hz, 1H), 1.88-1.81 (m, 1H), 1.74-1.68 (m, 1H), 1.36-1.26 (m, 6H), 0.86 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$) δ 172.6, 172.0, 155.6, 152.1, 138.5, 133.1, 125.5, 124.4, 121.3, 118.1, 51.7, 36.8, 35.9, 32.3, 31.5, 26.7, 22.4, 13.9; IR ν_{max}: 3297, 2949, 1737, 1624, 1612, 1574, 1469, 1427, 1296, 1226, 751, 703 cm^{-1}; HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{18}H_{23}O_5$ 319.1545; found: 319.1545.

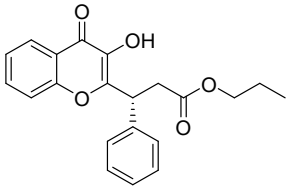


Methyl 3-(3-hydroxy-4-oxo-4*H*-chromen-2-yl)propanoate (**3aqa**). GP4. A scale of 0.25 mmol, opening time was equal to 24 h, solid, 37.24 mg (0.15 mmol), isolated yield of 60%; ^1H NMR (700 MHz, $CDCl_3$) δ 8.24 (ddd, *J* = 0.4, 1.8, 7.9 Hz, 1H), 7.68 (ddd, *J* = 1.8, 7.0, 8.6 Hz, 1H), 7.48 (ddd, *J* = 0.4, 1.1, 8.6 Hz, 1H), 7.41 (ddd, *J* = 1.0, 7.0, 8.0 Hz, 1H), 6.26 (s, 1H), 3.74 (s, 3H), 3.22 (t, *J* = 7.5 Hz, 2H), 2.84 (t, *J* = 7.7 Hz, 2H); $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$) δ 172.5, 172.4, 155.6, 149.7, 138.4, 133.1, 125.5, 124.4, 121.5, 118.1, 51.8, 30.6, 24.5; IR ν_{max}: 3278, 2951, 1731, 1603, 1563, 1484, 1467, 1422, 1287, 753, 695 cm^{-1}; HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{13}H_{13}O_5$ 249.0763; found: 249.0760; mp 98.6−106.7 °C.

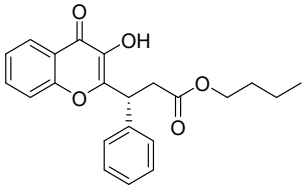


Ethyl (*R*)-3-(3-hydroxy-4-oxo-4*H*-chromen-2-yl)-3-phenylpropanoate (**3aab**). GP4. A scale of 0.25 mmol, opening time was equal to 72 h, oil, 74.24 mg

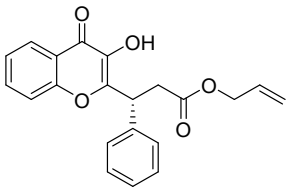
(0.22 mmol), isolated yield of 88%, 83% *ee*; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.21 (ddd, J = 0.4, 1.8, 8.1 Hz, 1H), 7.67 (ddd, J = 1.8, 7.0, 8.6 Hz, 1H), 7.52 (ddd, J = 0.4, 1.1, 8.6 Hz, 1H), 7.49-7.46 (m, 2H), 7.41-7.38 (m, 1H), 7.37-7.33 (m, 2H), 7.28-7.26 (m, 1H), 6.33 (s, 1H), 5.00 (dd, J = 7.0, 9.0 Hz, 1H), 4.10 (q, J = 7.2 Hz, 2H), 3.37 (dd, J = 9.1, 16.2 Hz, 1H), 3.14 (dd, J = 6.9, 16.2 Hz, 1H), 1.16 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 172.8, 170.9, 155.5, 150.6, 139.3, 137.8, 133.2, 128.8, 127.8, 127.5, 125.5, 124.5, 121.3, 118.1, 60.7, 41.1, 36.9, 14.0; IR ν_{max}: 3278, 2981, 1731, 1610, 1569, 1468, 1422, 1290, 1230, 755, 698 cm^{-1}; HRMS (ESI-TOF) m/z: (M + H)$^+$ calcd for $C_{20}H_{19}O_5$ 339.1232; found: 339.1234.



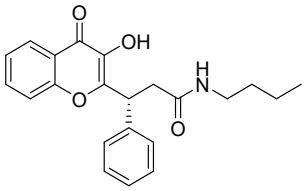
Propyl (*R*)-3-(3-hydroxy-4-oxo-4*H*-chromen-2-yl)-3-phenylpropanoate (**3aac**). GP4. A scale of 0.25 mmol, opening time was equal to 72 h, oil, 59.95 mg (0.17 mmol), isolated yield of 68%, 82% *ee*; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.21 (dd, J = 1.3, 7.9 Hz, 1H), 7.67 (ddd, J = 1.8, 7.0, 8.6 Hz, 1H), 7.52 (d, J = 8.1 Hz, 1H), 7.48 (dd, J = 1.1, 8.1 Hz, 2H), 7.40 (ddd, J = 1.0, 7.0, 8.0 Hz, 1H), 7.37-7.33 (m, 2H), 7.28-7.26 (m, 1H), 6.33 (s, 1H), 5.00 (dd, J = 6.9, 9.1 Hz, 1H), 4.00 (t, J = 6.6 Hz, 2H), 3.39 (dd, J = 9.2, 16.3 Hz, 1H), 3.16 (dd, J = 6.9, 16.2 Hz, 1H), 1.56 (sxt, J = 7.1 Hz, 2H), 0.85 (t, J = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 172.9, 171.1, 155.4, 150.8, 139.3, 137.8, 133.2, 128.8, 127.8, 127.5, 125.5, 124.5, 121.3, 118.1, 66.4, 41.0, 36.9, 21.8, 10.2; IR ν_{max}: 3289, 2966, 1731, 1610, 1569, 1468, 1422, 1289, 1229, 756, 698 cm^{-1}; HRMS (ESI-TOF) m/z: (M + H)$^+$ calcd for $C_{21}H_{21}O_5$ 353.1389; found: 353.1389.



Butyl (*R*)-3-(3-hydroxy-4-oxo-4*H*-chromen-2-yl)-3-phenylpropanoate (**3aad**). GP4. A scale of 0.25 mmol, opening time was equal to 72 h, oil, 79.32 mg (0.22 mmol), isolated yield of 87%, 84% *ee*; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.22 (ddd, J = 0.4, 1.8, 7.9 Hz, 1H), 7.67 (ddd, J = 1.8, 7.0, 8.6 Hz, 1H), 7.52 (dd, J = 0.4, 8.6 Hz, 1H), 7.48 (dd, J = 0.9, 8.1 Hz, 2H), 7.40 (ddd, J = 1.0, 7.0, 8.0 Hz, 1H), 7.36-7.33 (m, 2H), 7.28-7.26 (m, 1H), 6.43 (s, 1H), 5.01 (dd, J = 7.0, 9.0 Hz, 1H), 4.05 (t, J = 6.6 Hz, 2H), 3.38 (dd, J = 9.2, 16.3 Hz, 1H), 3.15 (dd, J = 7.0, 16.3 Hz, 1H), 1.53-1.47 (m, 2H), 1.26 (qd, J = 7.4, 15.1 Hz, 2H), 0.84 (t, J = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 172.8, 171.0, 155.5, 150.8, 139.2, 137.8, 133.2, 128.8, 127.8, 127.5, 125.5, 124.5, 121.3, 118.1, 64.7, 41.0, 36.9, 30.5, 19.0, 13.6; IR ν_{max}: 3285, 2959, 1731, 1611, 1568, 1469, 1422, 1290, 1230, 756, 698 cm^{-1}; HRMS (ESI-TOF) m/z: (M + H)$^+$ calcd for $C_{22}H_{23}O_5$ 367.1545; found: 367.1547.

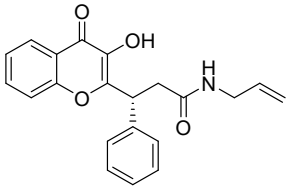


Allyl (*R*)-3-(3-hydroxy-4-oxo-4*H*-chromen-2-yl)-3-phenylpropanoate (**3aae**). GP4. A scale of 0.25 mmol, opening time was equal to 72 h, oil, 51.96 mg (0.15 mmol), isolated yield of 59%, 90% *ee*; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.18 (dd, J = 1.7, 8.0 Hz, 1H), 7.64 (ddd, J = 1.7, 7.0, 8.7 Hz, 1H), 7.51-7.47 (m, 1H), 7.46-7.43 (m, 2H), 7.37 (ddd, J = 1.1, 7.0, 8.0 Hz, 1H), 7.34-7.30 (m, 2H), 7.25-7.23 (m, 1H), 6.29 (s, 1H), 5.78 (tdd, J = 5.8, 10.4, 17.2 Hz, 1H), 5.20 (qd, J = 1.5, 17.2 Hz, 1H), 5.14 (qd, J = 1.3, 10.4 Hz, 1H), 4.98 (dd, J = 7.0, 9.1 Hz, 1H), 4.52 (td, J = 1.4, 5.8 Hz, 2H), 3.39 (dd, J = 9.2, 16.3 Hz, 1H), 3.15 (dd, J = 6.9, 16.3 Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 172.8, 170.6, 155.5, 150.4, 139.1, 137.7, 133.2, 131.7, 128.8, 127.8, 127.6, 125.5, 124.5, 121.2, 118.4, 118.2, 65.4, 41.0, 36.8; IR ν_{max}: 3282, 3064, 1733, 1610, 1569, 1482, 1469, 1422, 1290, 1229, 757, 698 cm^{-1}; HRMS (ESI-TOF) m/z: (M + H)$^+$ calcd for $C_{21}H_{19}O_5$ 351.1232; found: 351.1231.

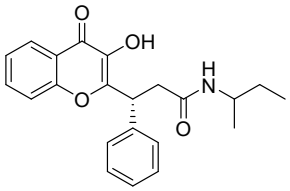


(*R*)-*N*-Butyl-3-(3-hydroxy-4-oxo-4*H*-chromen-2-yl)-3-phenylpropanamide (**3aaf**). GP4. A scale of 0.25 mmol, opening time was equal to 24 h, solid,

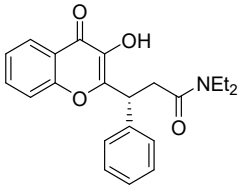
63.46 mg (0.17 mmol), isolated yield of 69%, 87% *ee*; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 1.3, 8.0 Hz, 1H), 7.63 (ddd, *J* = 1.7, 7.0, 8.5 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.45-7.43 (m, 2H), 7.35 (ddd, *J* = 1.0, 7.1, 8.1 Hz, 1H), 7.33-7.29 (m, 2H), 7.25-7.22 (m, 1H), 5.62 (s, 1H), 4.94 (dd, *J* = 7.0, 9.1 Hz, 1H), 3.23 (dd, *J* = 9.1, 14.7 Hz, 1H), 3.18-3.11 (m, 2H), 2.95 (dd, *J* = 7.0, 14.7 Hz, 1H), 1.32-1.26 (m, 2H), 1.14 (qd, *J* = 7.4, 15.0 Hz, 2H), 0.77 (t, *J* = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 172.9, 170.0, 155.6, 151.2, 139.7, 137.9, 133.2, 128.8, 127.9, 127.5, 125.5, 124.5, 121.3, 118.1, 42.3, 39.4, 39.3, 31.5, 19.8, 13.5; IR ν_{max}: 3301, 2960, 2927, 1622, 1610, 1545, 1469, 1423, 1291, 1277, 1236, 752, 696 cm^{-1}; HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{22}H_{24}NO_4$ 366.1705; found: 366.1705; mp 154.1−163.4 °C.



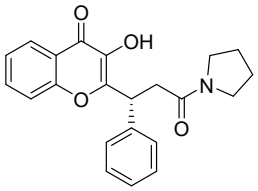
(*R*)-*N*-Allyl-3-(3-hydroxy-4-oxo-4*H*-chromen-2-yl)-3-phenylpropanamide (**3aag**). GP4. A scale of 0.25 mmol, opening time was equal to 24 h, solid, 86.56 mg (0.25 mmol), isolated yield of 99%, 91% *ee*; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 1.5, 7.9 Hz, 1H), 7.67 (ddd, *J* = 1.7, 7.1, 8.6 Hz, 1H), 7.50 (d, *J* = 8.6 Hz, 1H), 7.48 (dd, *J* = 1.0, 8.3 Hz, 2H), 7.40 (ddd, *J* = 1.0, 7.1, 8.0 Hz, 1H), 7.37-7.33 (m, 2H), 7.28-7.27 (m, 1H), 6.38 (s, 1H), 5.69 (tdd, *J* = 5.7, 10.3, 17.1 Hz, 1H), 5.62 (s, 1H), 5.04-5.01 (m, 1H), 5.00-4.97 (m, 1H), 3.82 (tt, *J* = 1.5, 5.7 Hz, 2H), 3.30 (dd, *J* = 9.0, 15.0 Hz, 1H), 3.00 (dd, *J* = 6.9, 14.9 Hz, 1H); ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 172.9, 169.9, 155.5, 150.9, 139.6, 137.8, 133.8, 133.2, 128.9, 127.8, 127.5, 125.5, 124.5, 121.2, 118.2, 116.3, 42.2, 41.9, 39.2; IR ν_{max}: 3280, 3065, 2919, 1632, 1609, 1538, 1469, 1421, 1293, 1235, 1221, 750, 697 cm^{-1}; HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{21}H_{20}NO_4$ 350.1392; found: 350.1393; mp 170.1−177.6 °C.



(3*R*)-*N*-(*sec*-Butyl)-3-(3-hydroxy-4-oxo-4*H*-chromen-2-yl)-3-phenylpropanamide (**3aah**). GP4. A scale of 0.25 mmol, opening time was equal to 24 h, solid, 83.99 mg (0.23 mmol), isolated yield of 92%, 92% *ee*, *dr* 1:1; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.19-8.15 (m, 1H), 7.63 (qt, *J* = 0.9, 7.8 Hz, 1H), 7.49-7.43 (m, 3H), 7.36 (tdd, *J* = 0.9, 7.1, 8.0 Hz, 1H), 7.33-7.28 (m, 2H), 7.25-7.22 (m, 1H), 6.40 (s, 1H), 5.33 (s, 1H), 4.93 (ddd, *J* = 2.8, 7.4, 8.8 Hz, 1H), 3.83-3.78 (m, 1H), 3.20 (td, *J* = 8.8, 14.5 Hz, 1H), 2.93 (ddd, *J* = 5.5, 7.2, 14.6 Hz, 1H), 1.32-1.24 (m, 2H), 0.94 (dd, *J* = 6.6, 10.3 Hz, 3H), 0.70 (td, *J* = 7.5, 9.2 Hz, 3H); ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 172.9, 169.3, 169.3, 155.6, 150.9, 150.9, 139.7, 139.6, 137.9, 133.2, 128.9, 127.9, 127.5, 125.5, 124.5, 121.2, 118.1, 46.6, 42.5, 42.5, 39.7, 39.7, 29.5, 29.5, 20.2, 20.2, 10.0; IR ν_{max}: 3301, 2963, 2929, 1633, 1621, 1612, 1568, 1548, 1470, 1425, 1275, 1238, 751, 696 cm^{-1}; HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{22}H_{24}NO_4$ 366.1705; found: 366.1704; mp 183.8−191.3 °C.

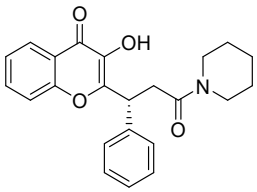


(*R*)-*N*,*N*-Diethyl-3-(3-hydroxy-4-oxo-4*H*-chromen-2-yl)-3-phenylpropanamide (**3aai**). GP4. A scale of 0.25 mmol, opening time was equal to 72 h, oil, 44.89 mg (0.12 mmol), isolated yield of 49%, 66% *ee*; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 1.5, 7.9 Hz, 1H), 7.64 (ddd, *J* = 1.8, 7.0, 8.6 Hz, 1H), 7.51-7.45 (m, 3H), 7.39-7.32 (m, 3H), 7.28-7.25 (m, 1H), 6.47 (s, 1H), 5.06 (dd, *J* = 5.4, 10.0 Hz, 1H), 3.51 (dd, *J* = 10.1, 16.1 Hz, 1H), 3.42-3.34 (m, 3H), 3.30 (qd, *J* = 7.0, 13.8 Hz, 1H), 3.00 (dd, *J* = 5.5, 16.1 Hz, 1H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.04 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 172.8, 169.2, 155.4, 151.9, 140.3, 137.9, 132.9, 128.8, 127.9, 127.3, 125.5, 124.4, 121.4, 118.1, 42.2, 41.9, 40.3, 36.1, 14.3, 12.9; IR ν_{max}: 3281, 2974, 2931, 1609, 1568, 1481, 1467, 1426, 1289, 1265, 755, 699 cm^{-1}; HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{22}H_{24}NO_4$ 366.1705; found: 366.1705.



(*R*)-3-Hydroxy-2-(3-oxo-1-phenyl-3-(pyrrolidin-1-yl)propyl)-4*H*-chromen-4-one (**3aaj**). GP4. A scale of 0.25 mmol, opening time was equal to 72 h, oil, 60.75 mg (0.17 mmol), isolated yield of 67%, 72% *ee*; ^{1}H NMR (700 MHz, $CDCl_3$)

δ 8.18 (ddd, *J* = 0.4, 1.7, 8.2 Hz, 1H), 7.61 (ddd, *J* = 1.7, 7.0, 8.5 Hz, 1H), 7.49-7.43 (m, 3H), 7.36-7.28 (m, 3H), 7.25-7.22 (m, 1H), 6.42 (s, 1H), 5.03 (dd, *J* = 5.7, 9.6 Hz, 1H), 3.50 (s, 1H), 3.45-3.37 (m, 4H), 2.97 (dd, *J* = 5.7, 16.0 Hz, 1H), 1.92 (s, 2H), 1.81 (s, 2H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) *δ* 172.9, 168.7, 155.5, 151.7, 140.3, 137.9, 132.9, 128.8, 127.9, 127.3, 125.5, 124.3, 121.4, 118.1, 46.6, 45.7, 41.8, 37.5, 26.0, 24.3; IR ν_{max}: 3260, 2927, 2872, 1608, 1567, 1467, 1423, 1288, 757, 698 cm^{-1}; HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{22}H_{22}NO_4$ 364.1549; found: 364.1550.



(*R*)-3-Hydroxy-2-(3-oxo-1-phenyl-3-(piperidin-1-yl)propyl)-4*H*-chromen-4-one (**3aak**). GP4. A scale of 0.25 mmol, opening time was equal to 72 h, oil, 46.88 mg (0.12 mmol), isolated yield of 50%, 91% *ee*; ^{1}H NMR (700 MHz, $CDCl_3$) *δ* 8.18 (ddd, *J* = 0.4, 1.7, 8.0 Hz, 1H), 7.62 (ddd, *J* = 1.6, 7.0, 8.6 Hz, 1H), 7.49-7.43 (m, 3H), 7.35 (ddd, *J* = 1.1, 7.0, 8.0 Hz, 1H), 7.33-7.29 (m, 2H), 7.25-7.22 (m, 1H), 5.00 (dd, *J* = 5.5, 9.8 Hz, 1H), 3.52-3.42 (m, 5H), 3.01 (dd, *J* = 5.6, 16.1 Hz, 1H), 1.71-1.58 (m, 6H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) *δ* 172.9, 168.4, 155.5, 151.8, 140.3, 137.8, 132.9, 128.8, 127.9, 127.3, 125.5, 124.3, 121.4, 118.1, 46.6, 42.9, 42.1, 36.0, 26.4, 25.5, 24.5; IR ν_{max}: 3271, 2930, 2854, 1608, 1567, 1468, 1441, 1288, 1231, 757, 698 cm^{-1}; HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{23}H_{24}NO_4$ 378.1705; found: 378.1705.

3. X-Ray Crystallography Data

The diffraction data of the studied compounds were collected at room temperature for the single crystal using Oxford Sapphire CCD diffractometer, MoKα radiation λ = 0.71073 Å. The numerical absorption correction was applied.[14] The structure was solved by the direct methods and refined with full-matrix least-squares procedure on F2 (SHELX-97[15]). All heavy atoms were refined with anisotropic displacement parameters. Positions of hydrogen atoms attached to carbon atoms were assigned at calculated positions with thermal displacement parameters fixed to a value of 20% or 50% higher than those of the corresponding carbon atoms, whereas positions of hydrogen atoms from hydroxyl groups were found from difference electron density synthesis. To maintain reasonable geometry and to keep stable refinement process atoms from positionally disordered O44 ester group were refined with constraints (DFIX and EADP). All figures were prepared in DIAMOND[16] and ORTEP-3.[17] The results of

the data collections and refinement have been summarized in Table 1. CCDC 2088560 contain the supplementary crystallographic data for **3daa**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk.data_request/cif.

Table 1. Crystal data and structure refinement

Identification code	**3daa**
Empirical formula	$C_{19}H_{15}O_5Br$
Formula weight	403.22
Temperature [K]	293(2)
Wavelength [Å]	0.71073
Crystal system, space group	monoclinic, $P2_1$
Unit cell dimensions [Å] and [°]	a = 17.401(8) $\alpha = 90$ b = 5.9984(13) $\beta = 115.06(5)$ c = 18.889(6) $\gamma = 90$
Volume [Å^3]	1786.1(13)
Z, Calculated density [Mg·m^{-3}]	4, 1.500
Absorption coefficient [mm^{-1}]	2.327
F(000)	816
Crystal size [mm]	0.550 x 0.120 x 0.050
Theta range for data collection [°]	2.095 to 26.372
Limiting indices	-21<=h<=16 -7<=k<=7 -22<=l<=23
Reflections collected/unique	11460 / 6739 [R(int) = 0.0431]
Completeness [%] to theta [°]	25.242° 99.9 %
Absorption correction	Analytical
Max. and min. transmission	0.869 and 0.320
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6739 / 17 / 466
Goodness-of-fit on F^2	1.004
Final R Indices [I>2sigma(I)]	$R1^a = 0.0551$, $wR2^b = 0.1122$
R indices (all data)	$R1^a = 0.1233$, $wR2^b = 0.1451$
Absolute structure parameter	-0.014(13)

Largest diff. peak and hole [eÅ^{-3}]	0.247 and -0.254

[a] $R1 = \Sigma || F_o| - |F_c|| / \Sigma |F_o|$ [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma (w(F_o^2)^2)]^{1/2}$

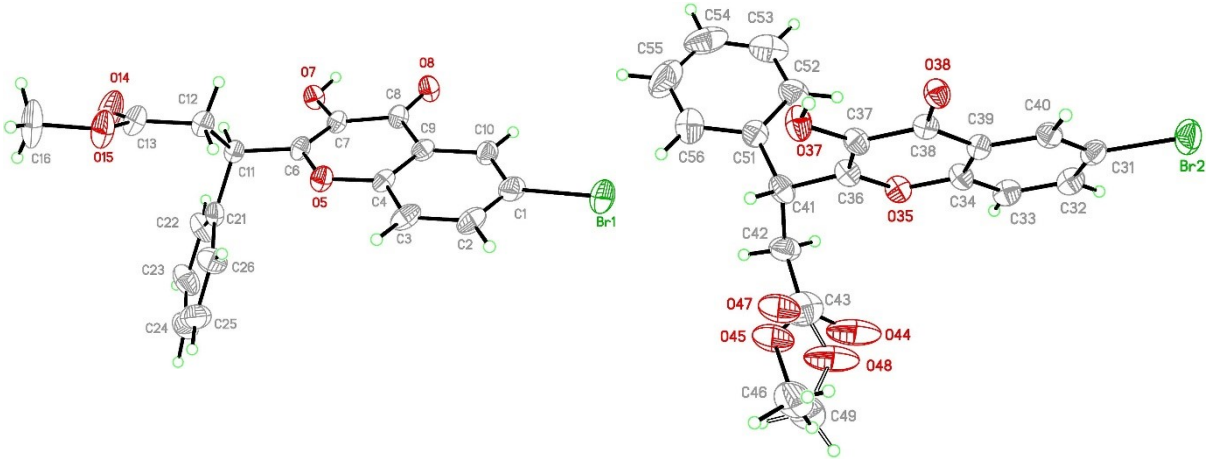


Figure S1**.** Structure of $C_{19}H_{15}O_5Br$ **3daa** with thermal ellipsoids at 20% of probability. There are two crystallographically (both occurring in *R* configuration) independent molecules in the asymmetric unit. O5 molecule is presented to the left and O35 one to the right.

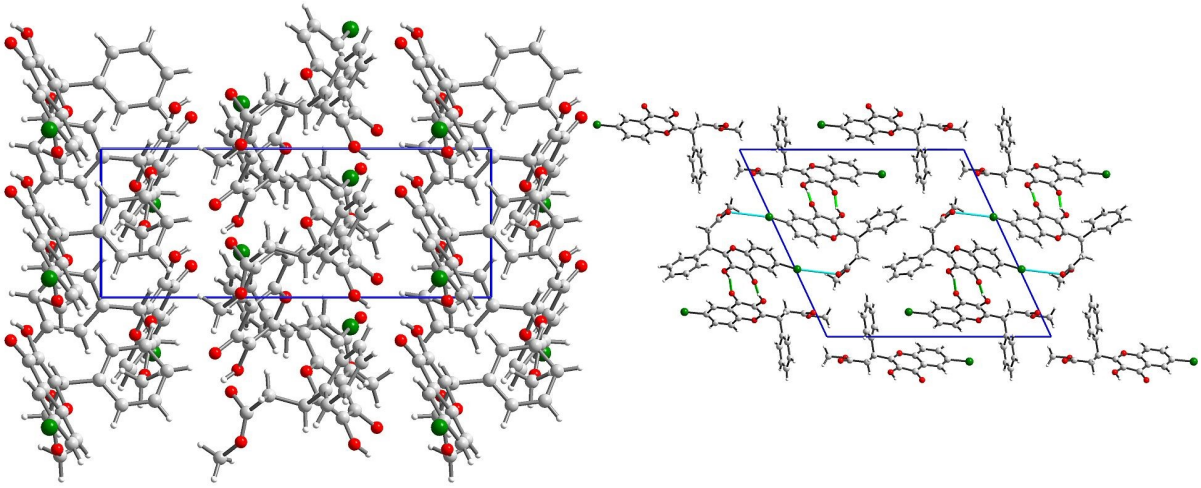


Figure S2**.** Packing of **3daa** along c axis shows *bc* double layers (left) composed solely of O5 or O35 molecules. View along *b* axis show interlayer interactions assured by hydrogen bonds (green, right). However, intralayer interactions differ significantly and weak halogen bond (cyan) occurs only between O35 molecules due to subtle conformational changes in torsion angles around C6-C11 (C36-C41) bonds.

4. NMR Spectra

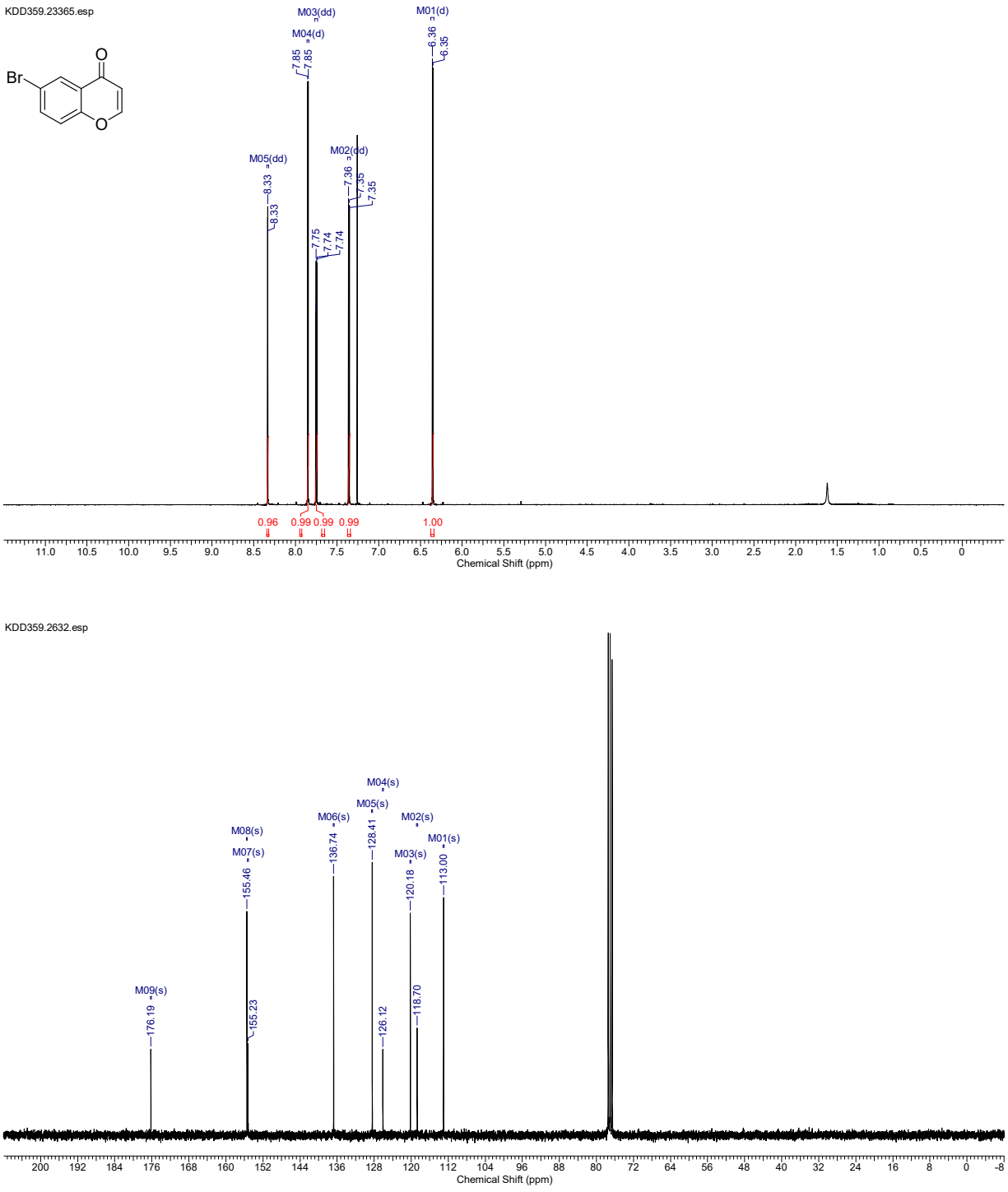


Figure S3. ^{1}H and ^{13}C NMR spectra of **0b**

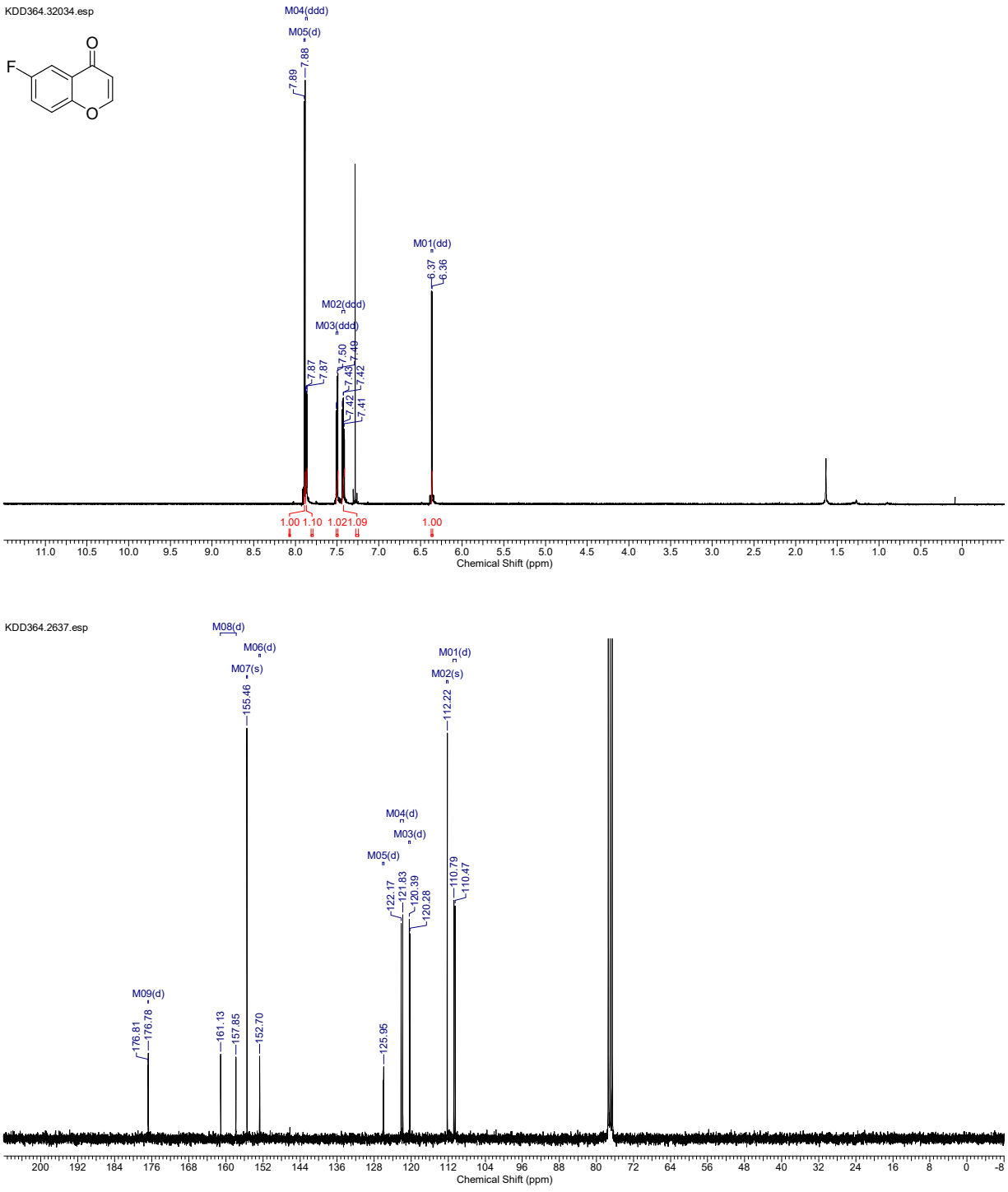


Figure S4. ^{1}H and ^{13}C NMR spectra of **0c**

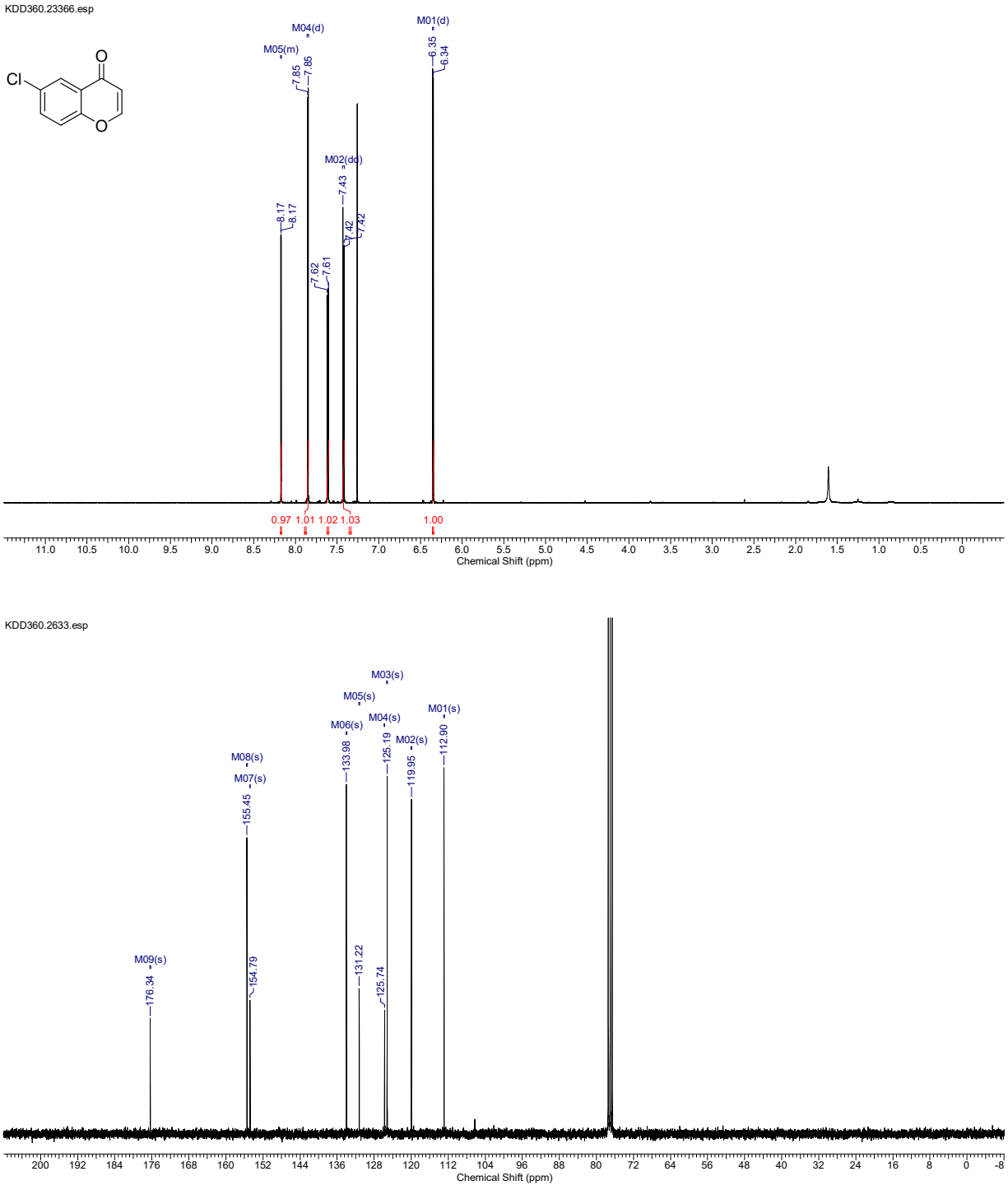


Figure S5. ^{1}H and ^{13}C NMR spectra of **0d**

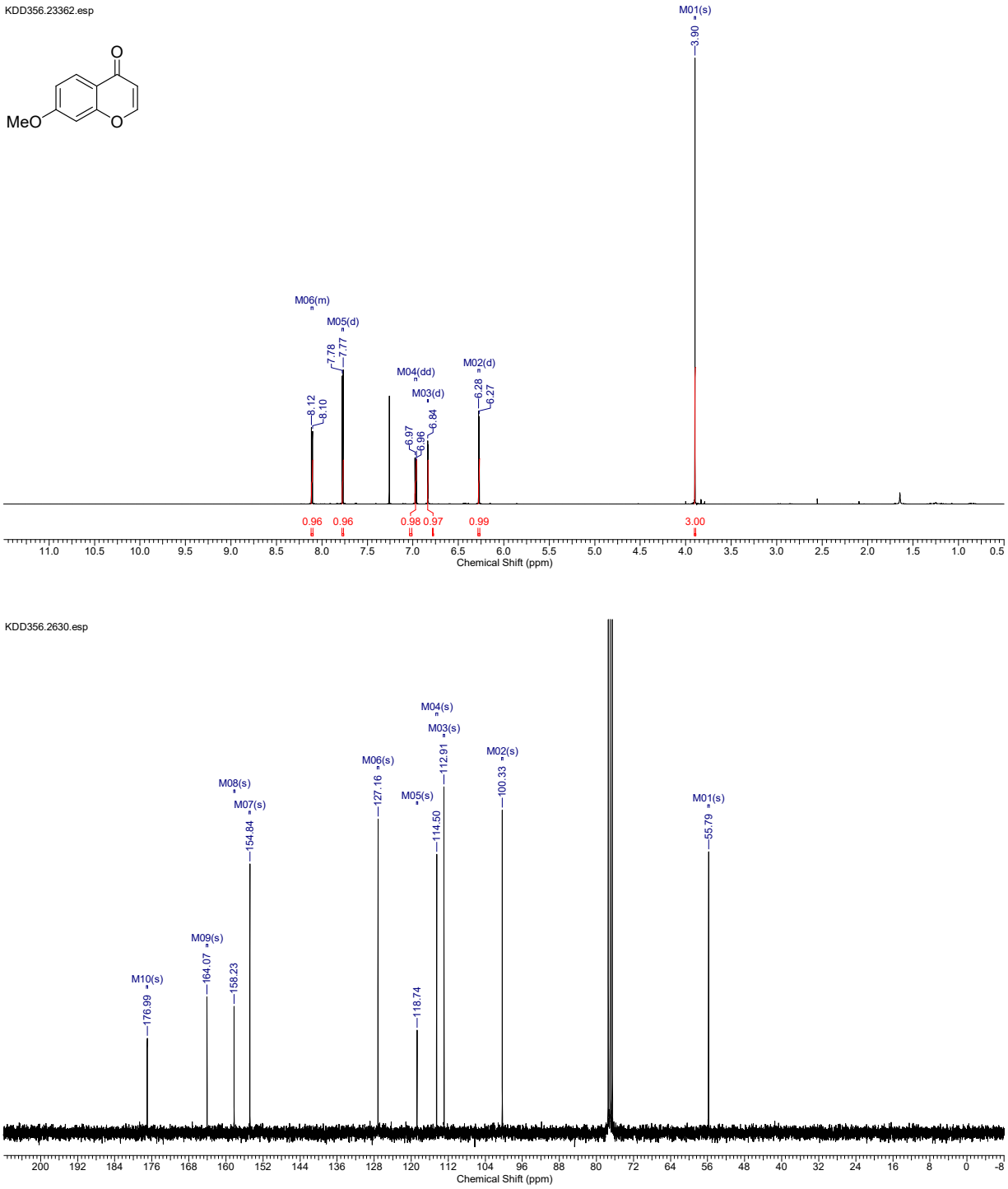


Figure S6. ^{1}H and ^{13}C NMR spectra of **0e**

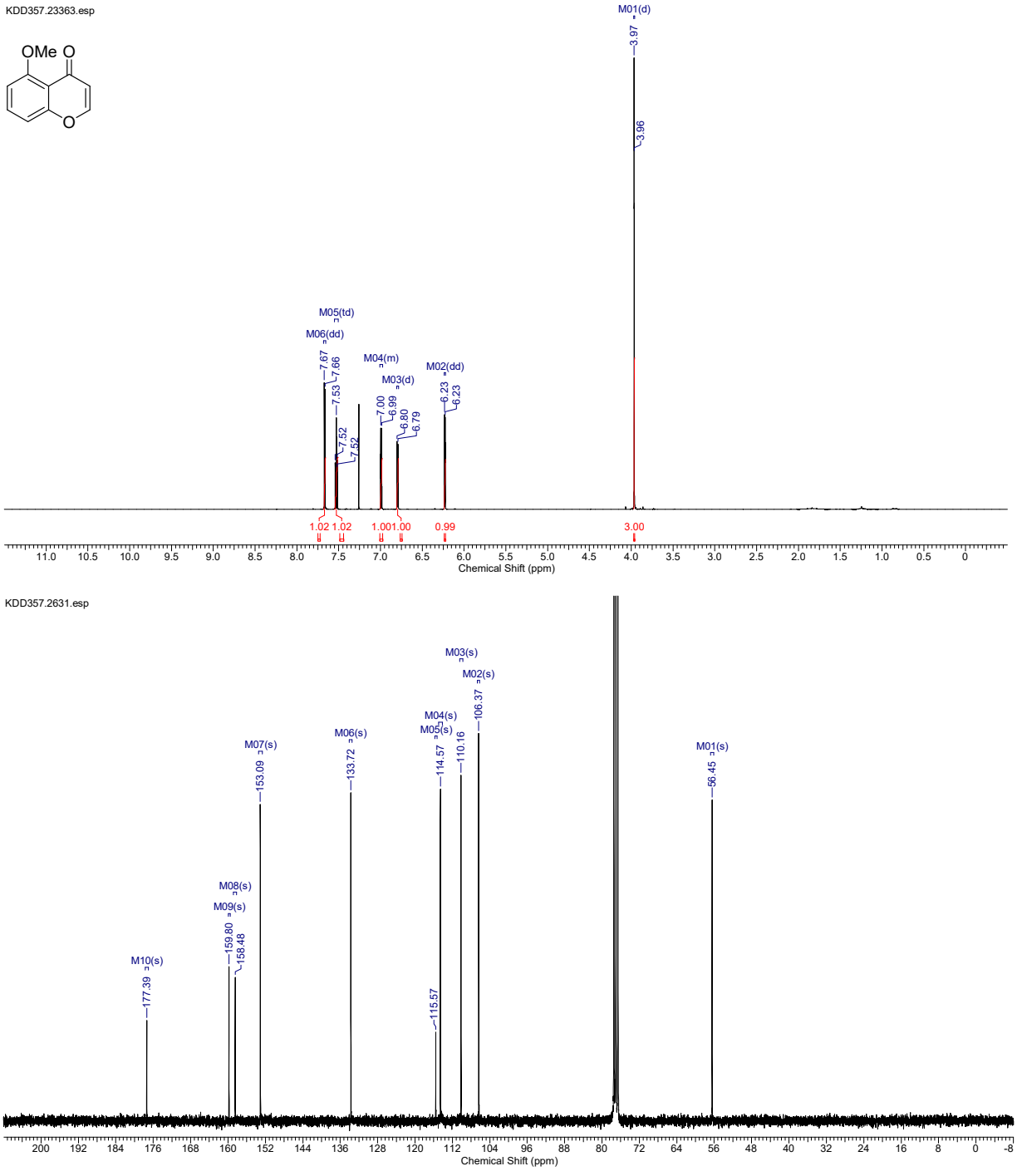


Figure S7. ^{1}H and ^{13}C NMR spectra of **0f**

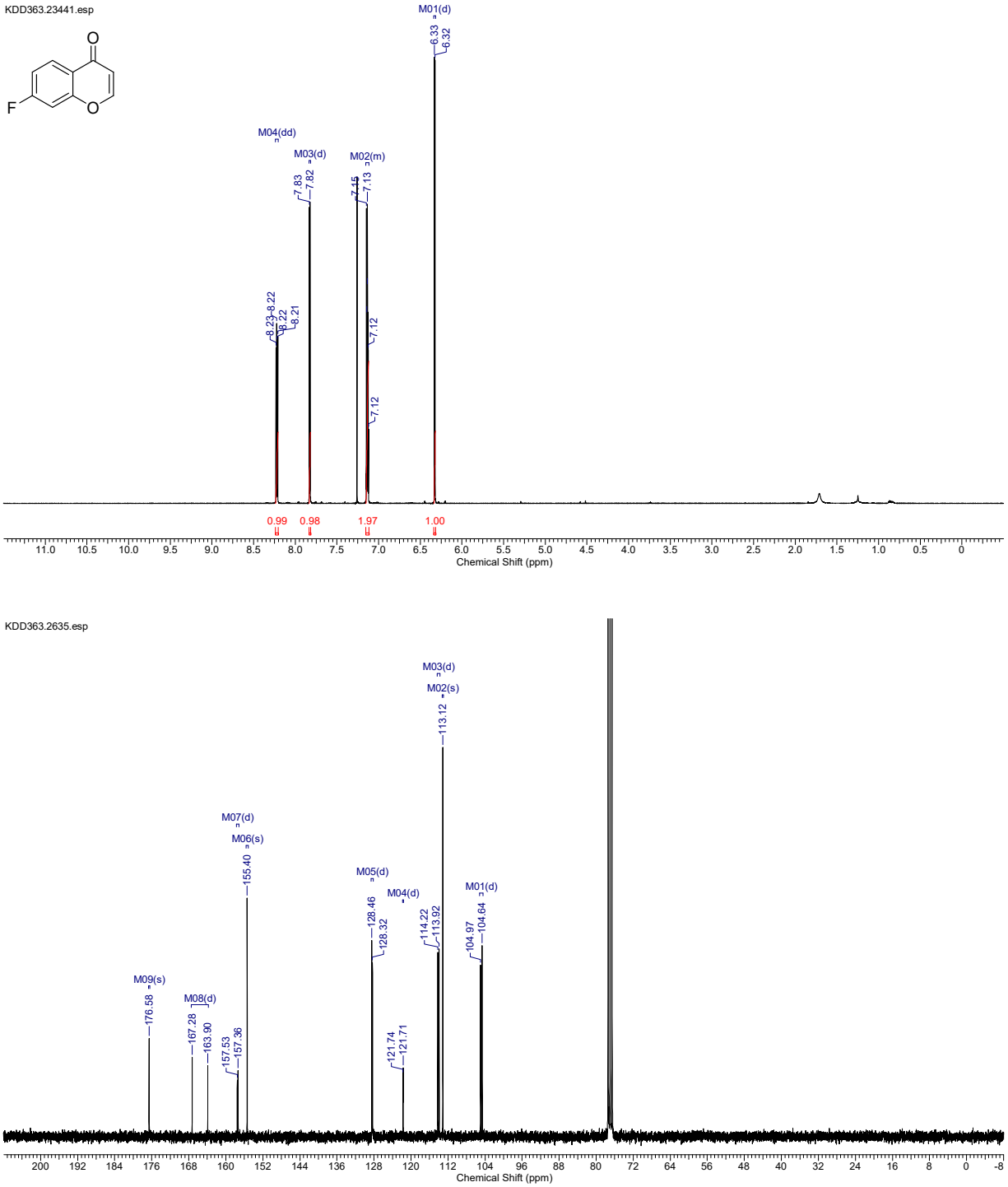


Figure S8. ^{1}H and ^{13}C NMR spectra of **0g**

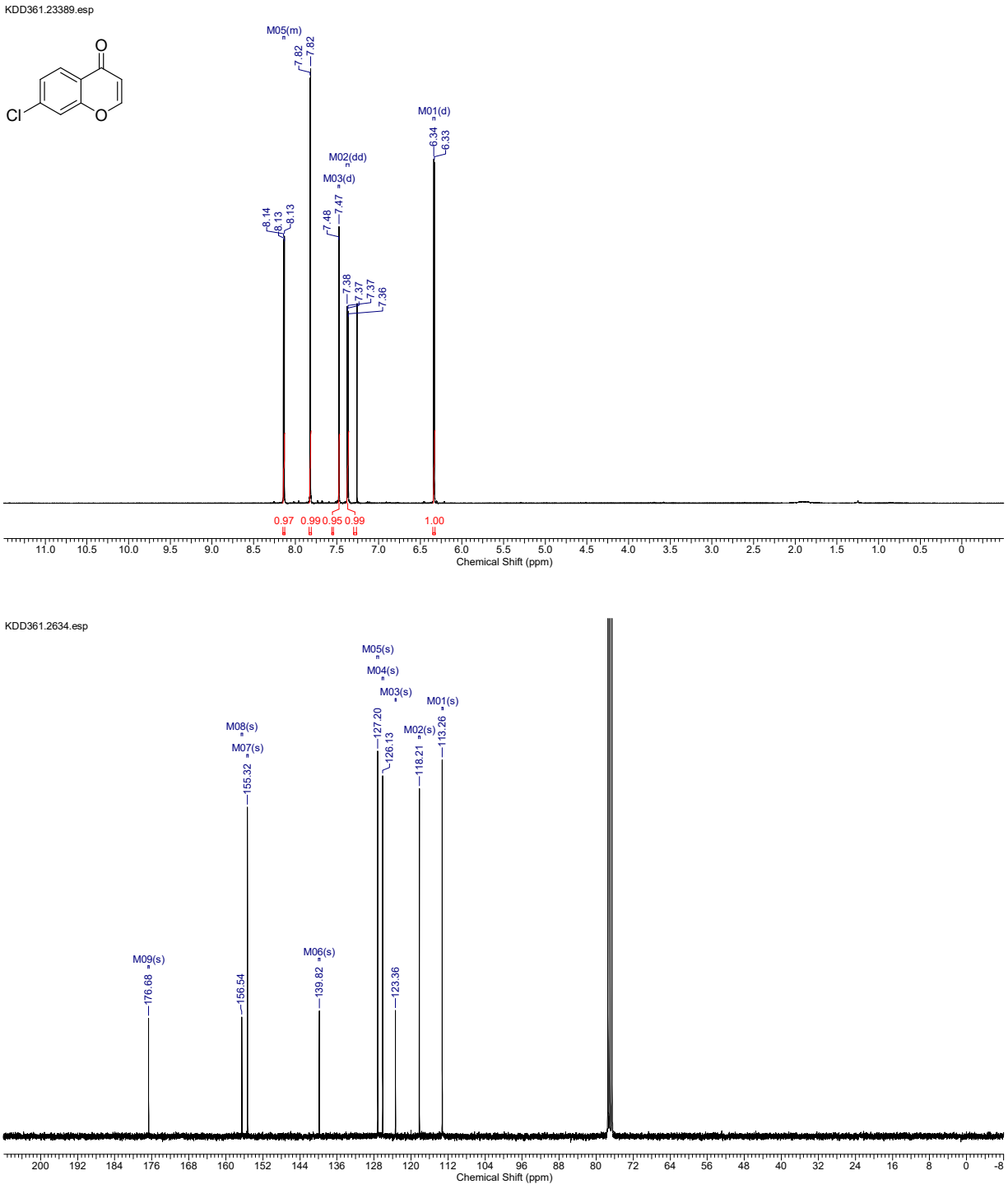


Figure S9. ^{1}H and ^{13}C NMR spectra of **0h**

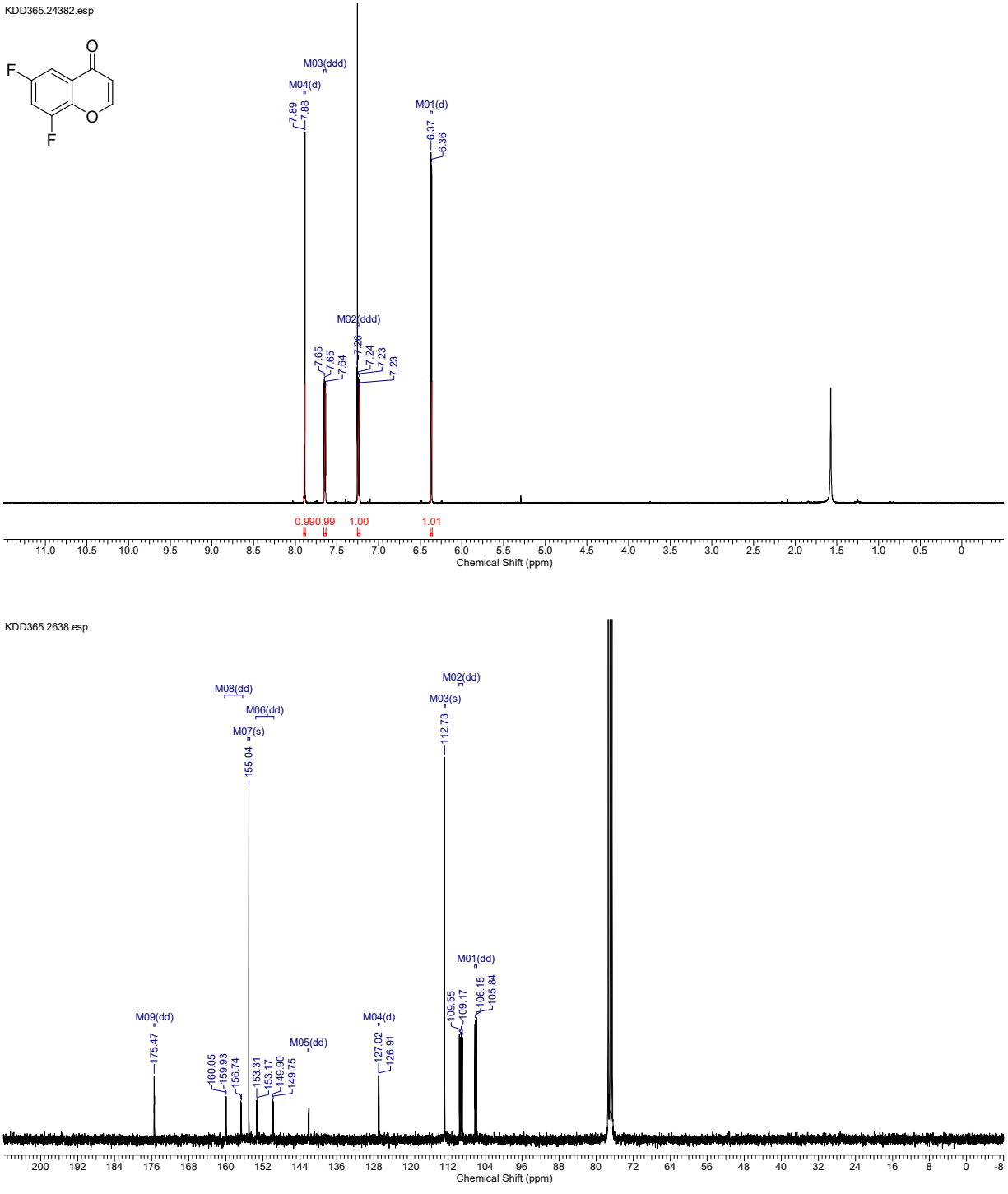


Figure S10. ^{1}H and ^{13}C NMR spectra of **0i**

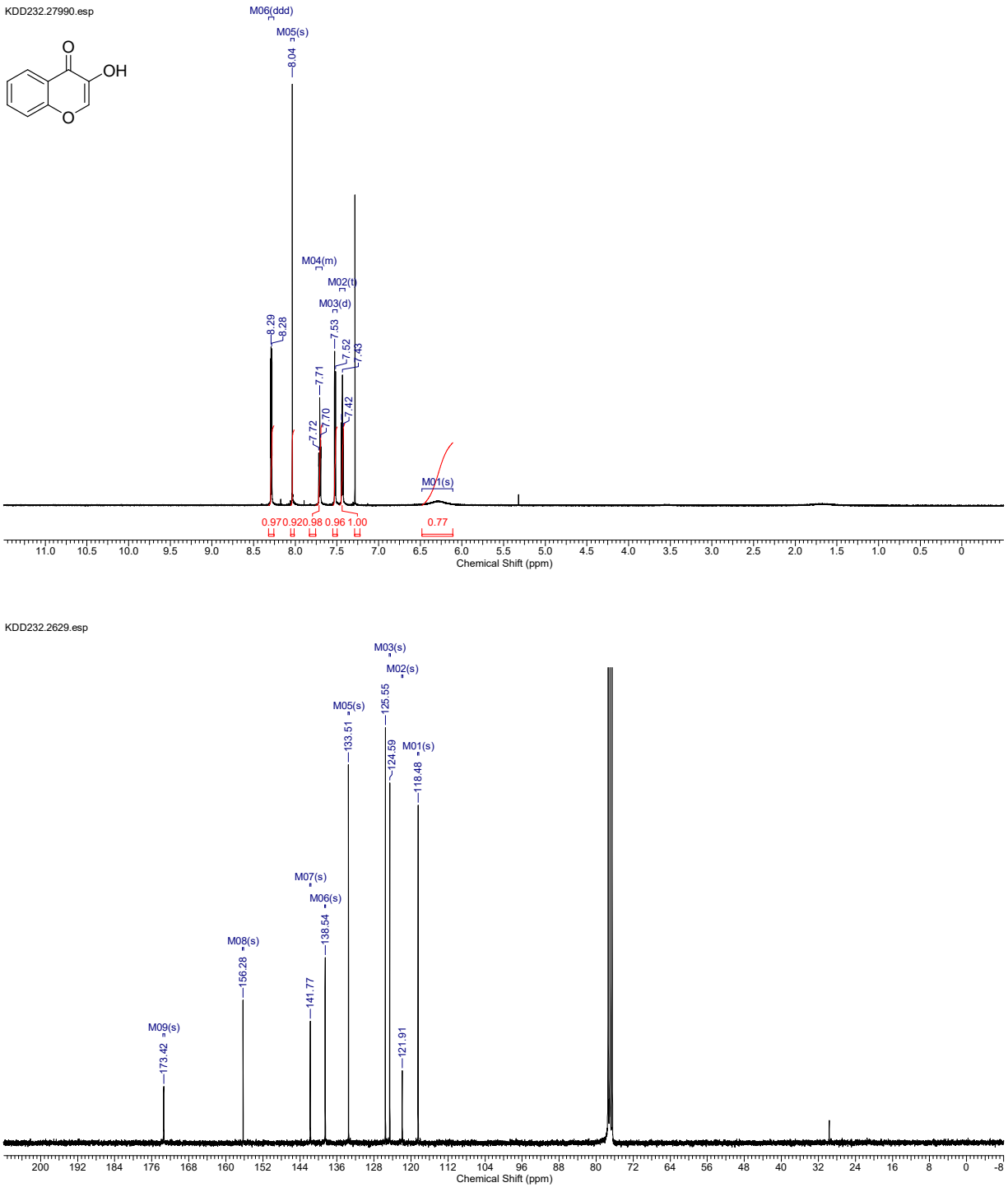


Figure S11. ^{1}H and ^{13}C NMR spectra of **1a**

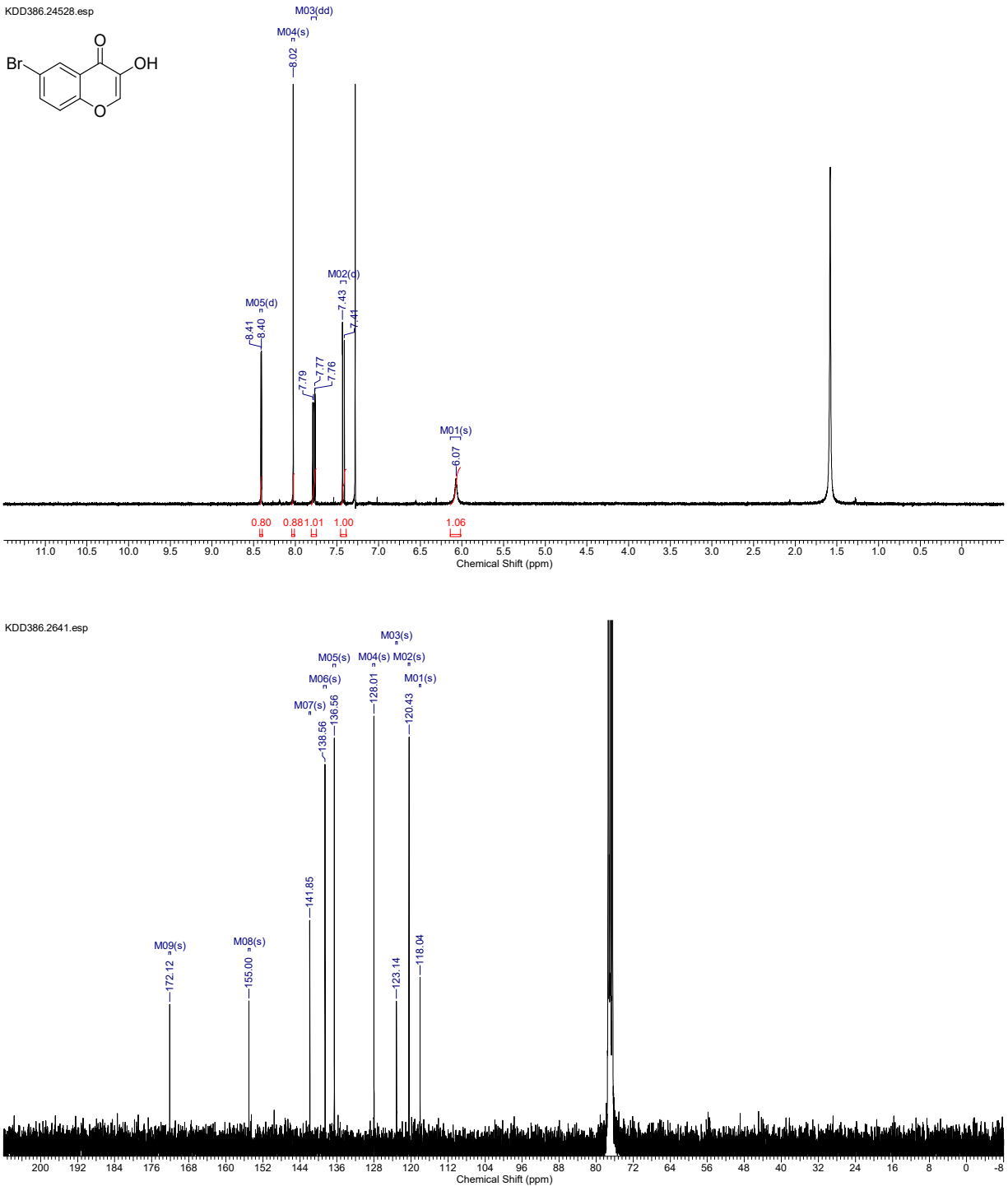


Figure S12. ^{1}H and ^{13}C NMR spectra of **1b**

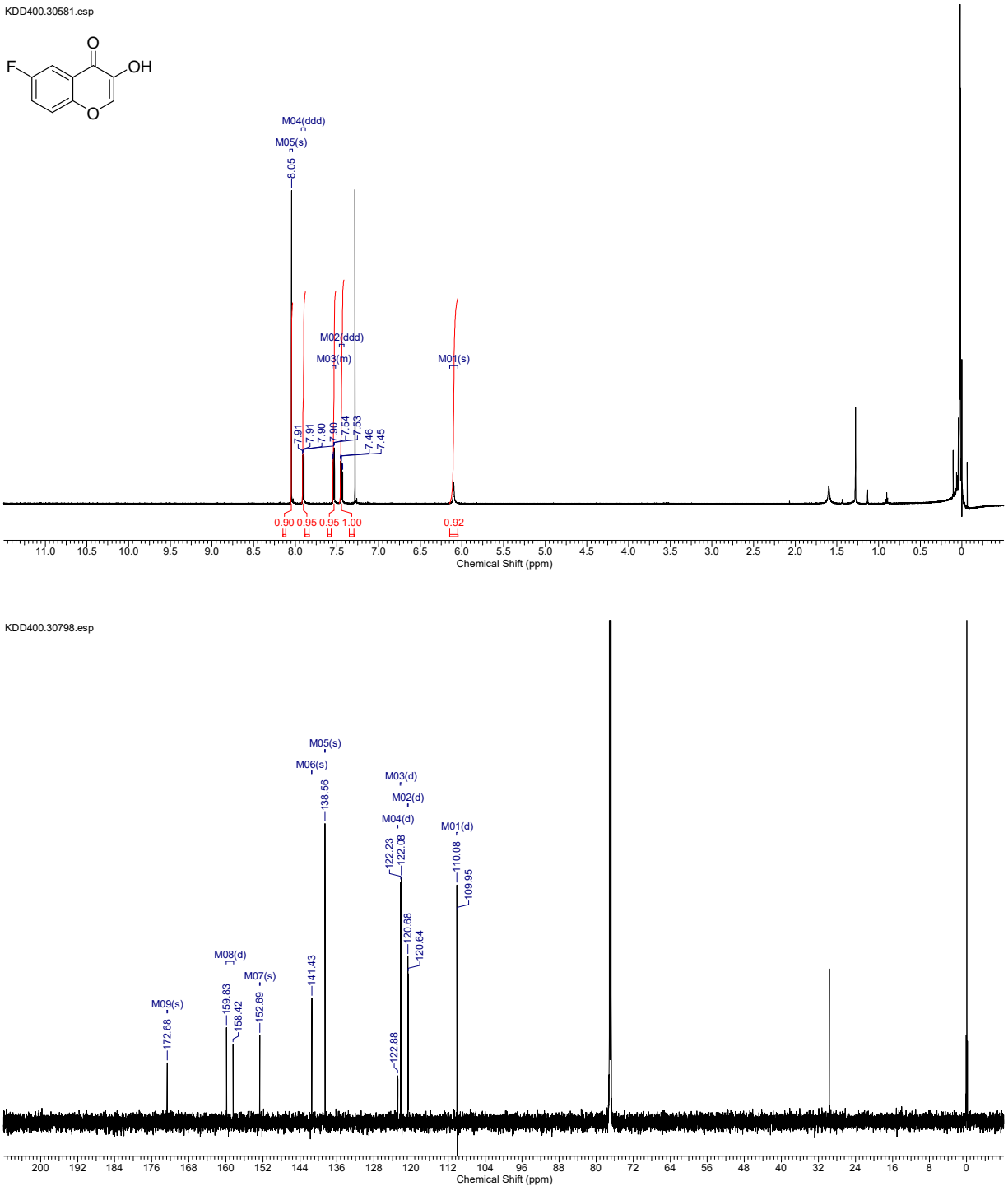


Figure S13. ^{1}H and ^{13}C NMR spectra of **1c**

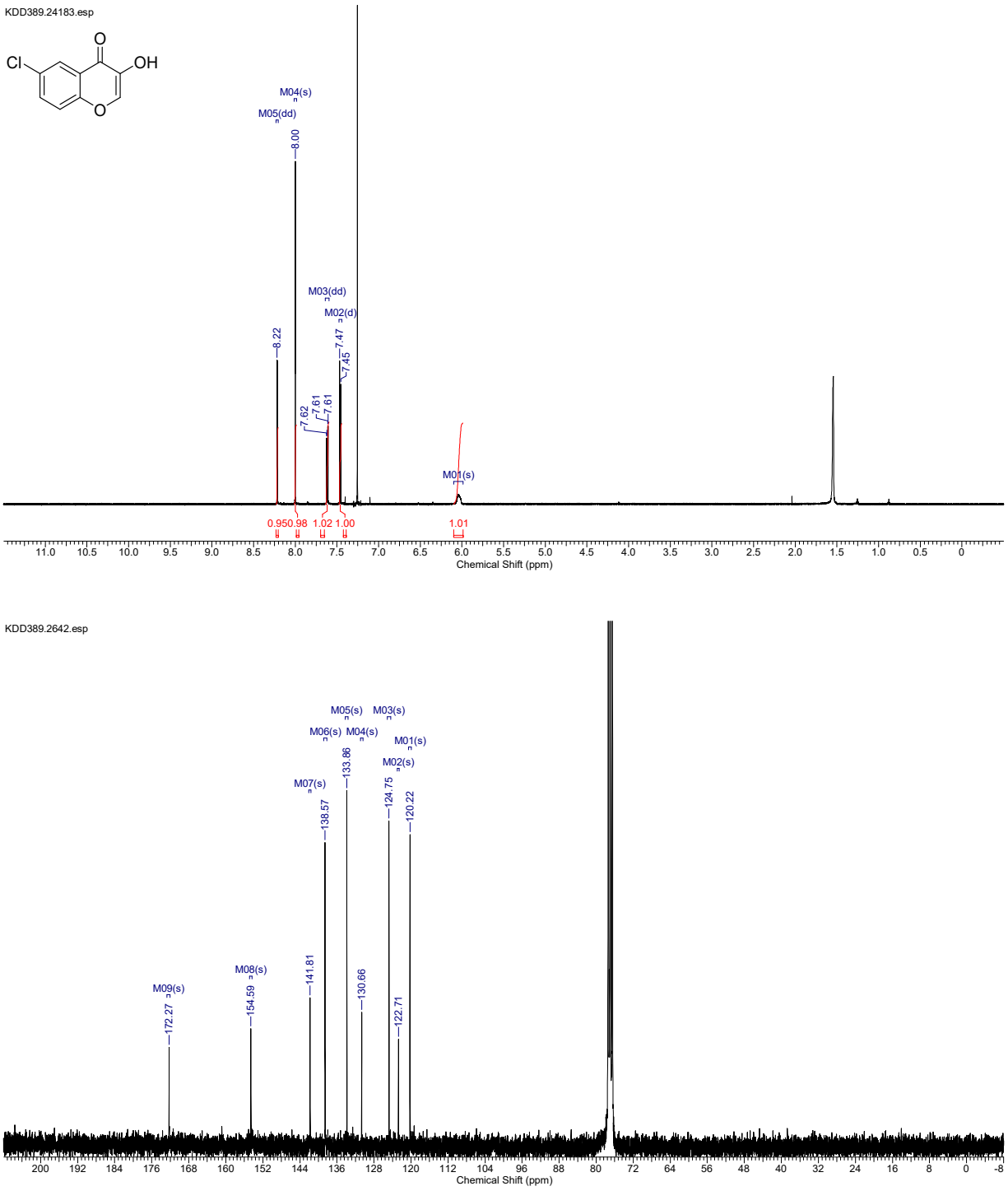


Figure S14. ^{1}H and ^{13}C NMR spectra of **1d**

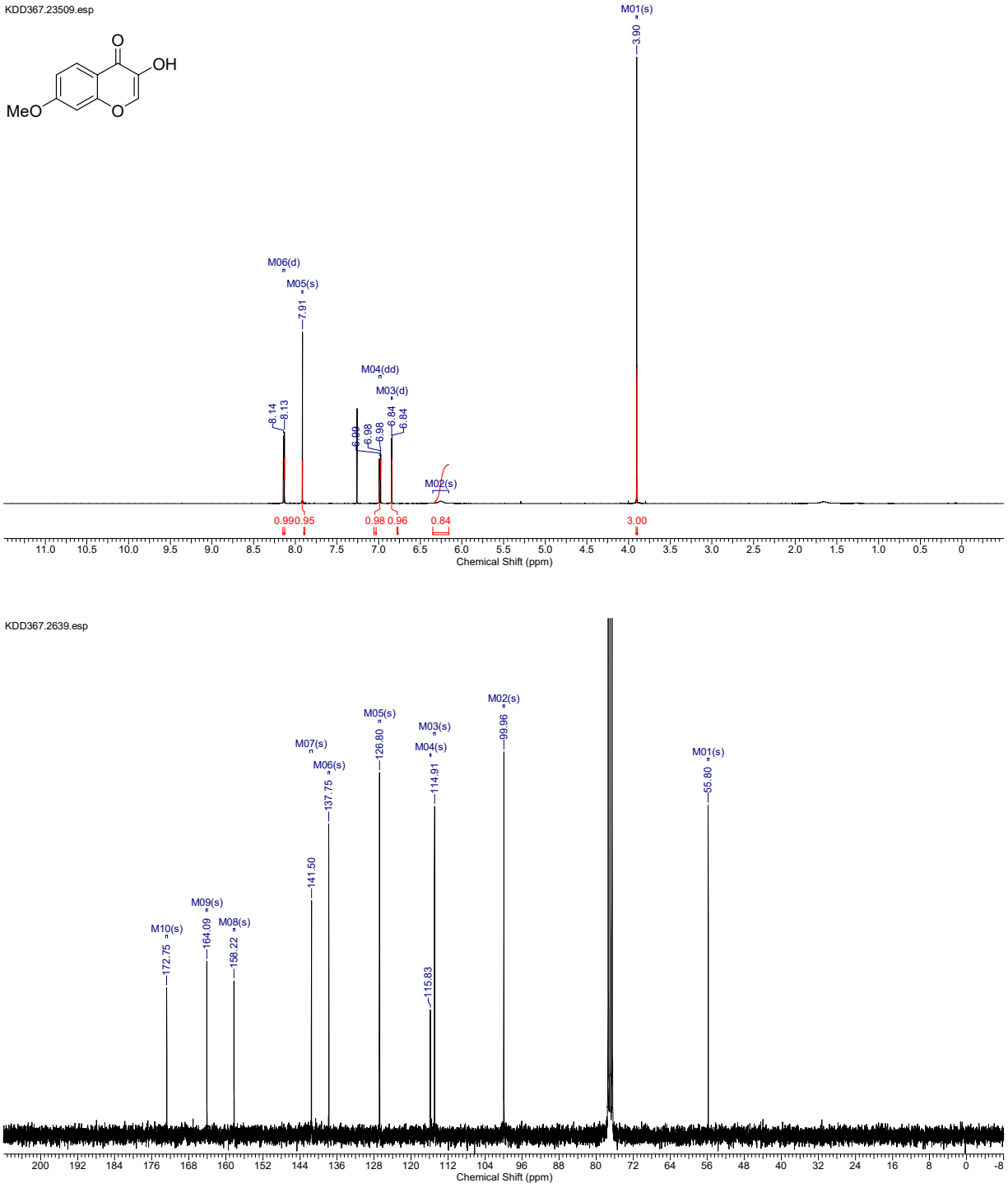


Figure S15. ^{1}H and ^{13}C NMR spectra of **1e**

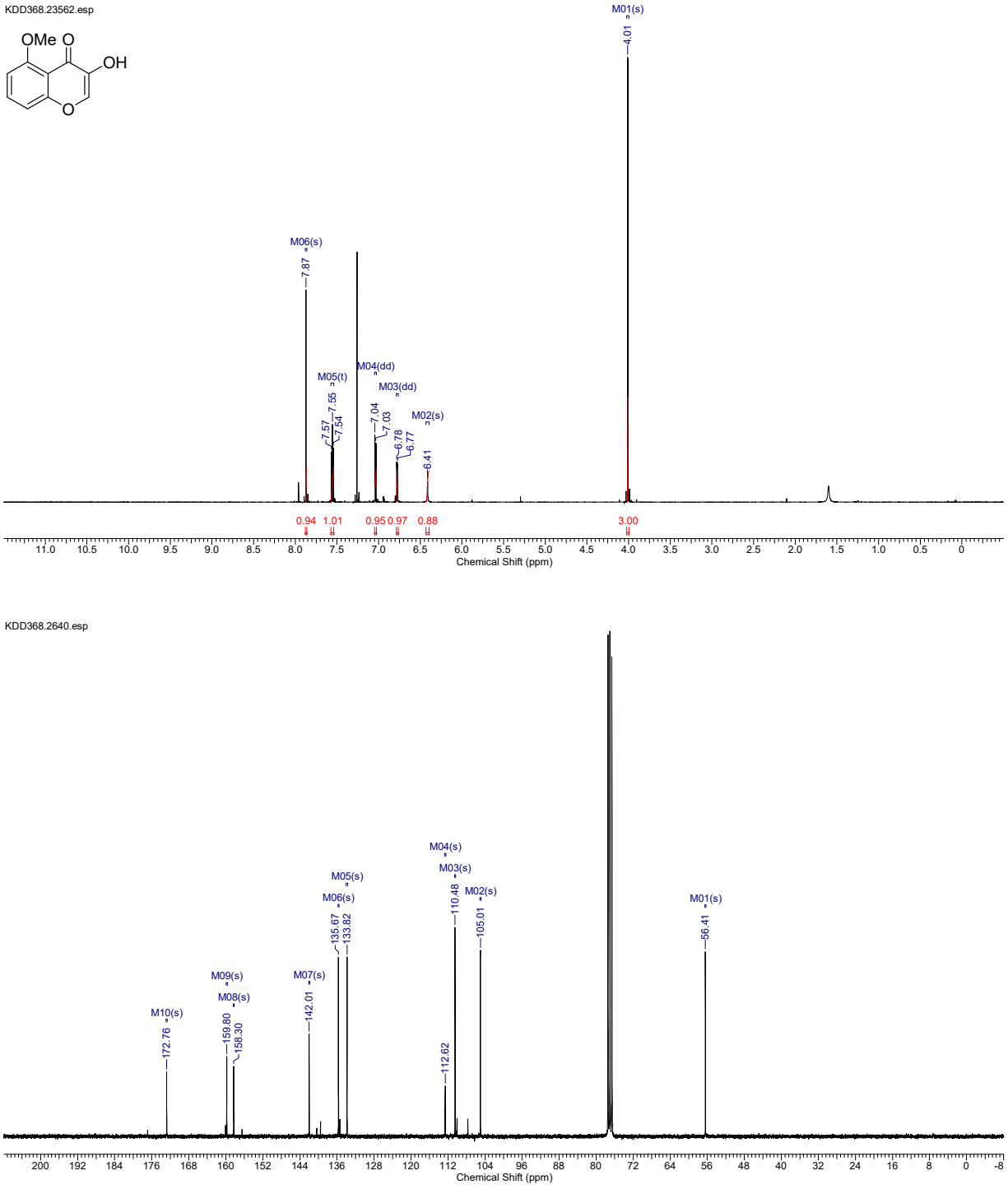


Figure S16. ^{1}H and ^{13}C NMR spectra of **1f**

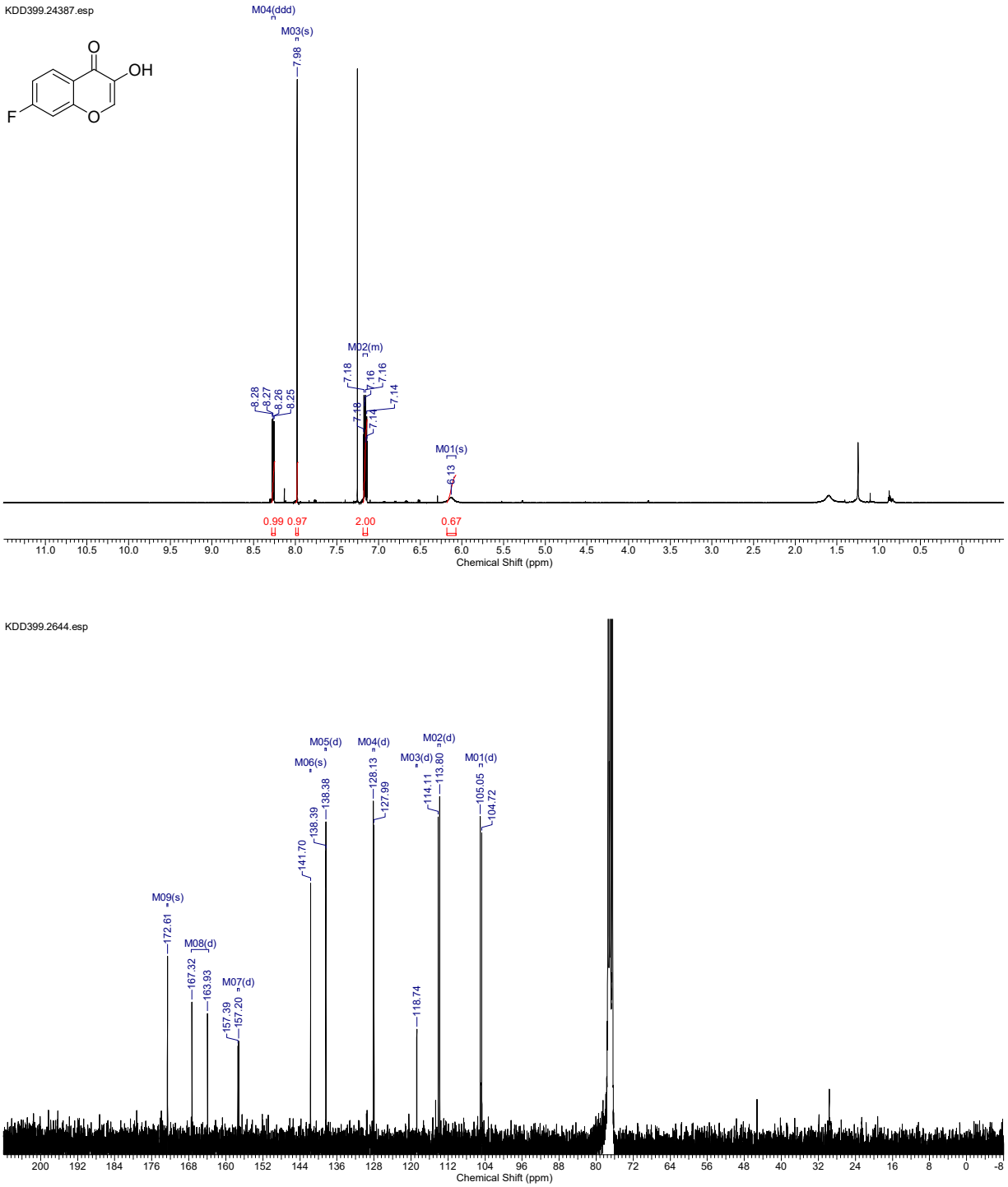
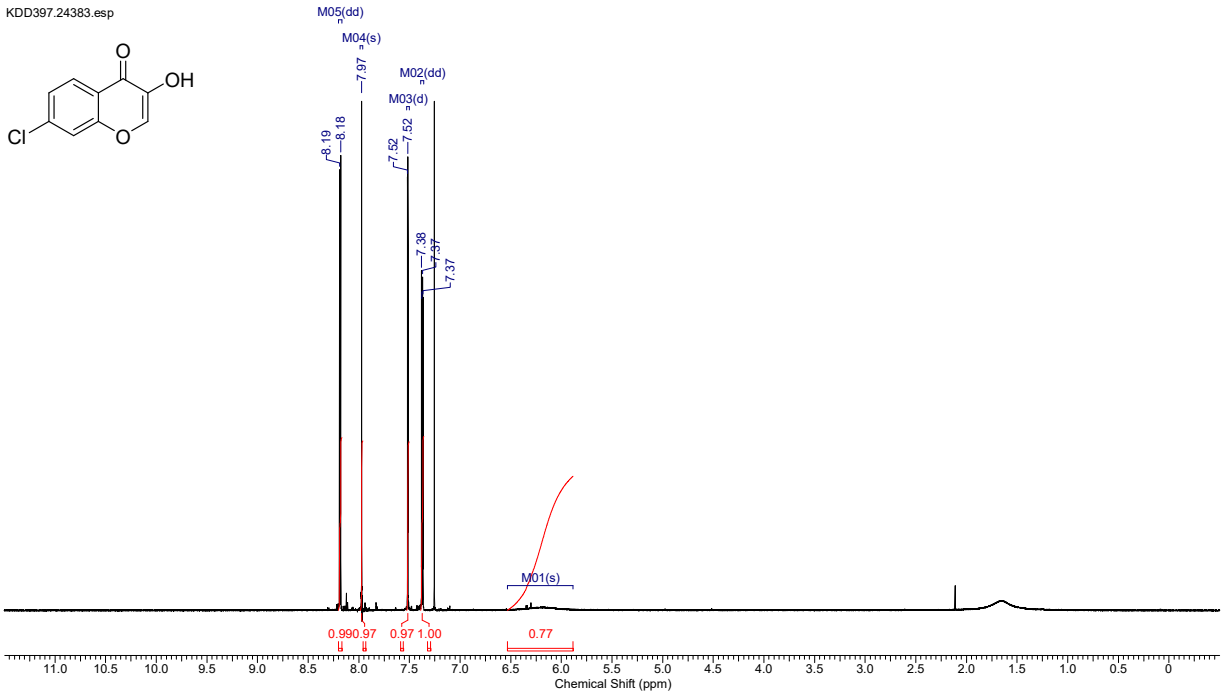


Figure S17. ^{1}H and ^{13}C NMR spectra of **1g**


KDD397.24383.esp
O
OH
Cl
O
M05(dd)
M04(s)
M02(dd)
M03(d)
8.19
8.18
7.97
7.52
7.52
7.38
7.37
7.37
M01(s)
0.99
0.97
0.97
1.00
0.77
11.0
10.5
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)

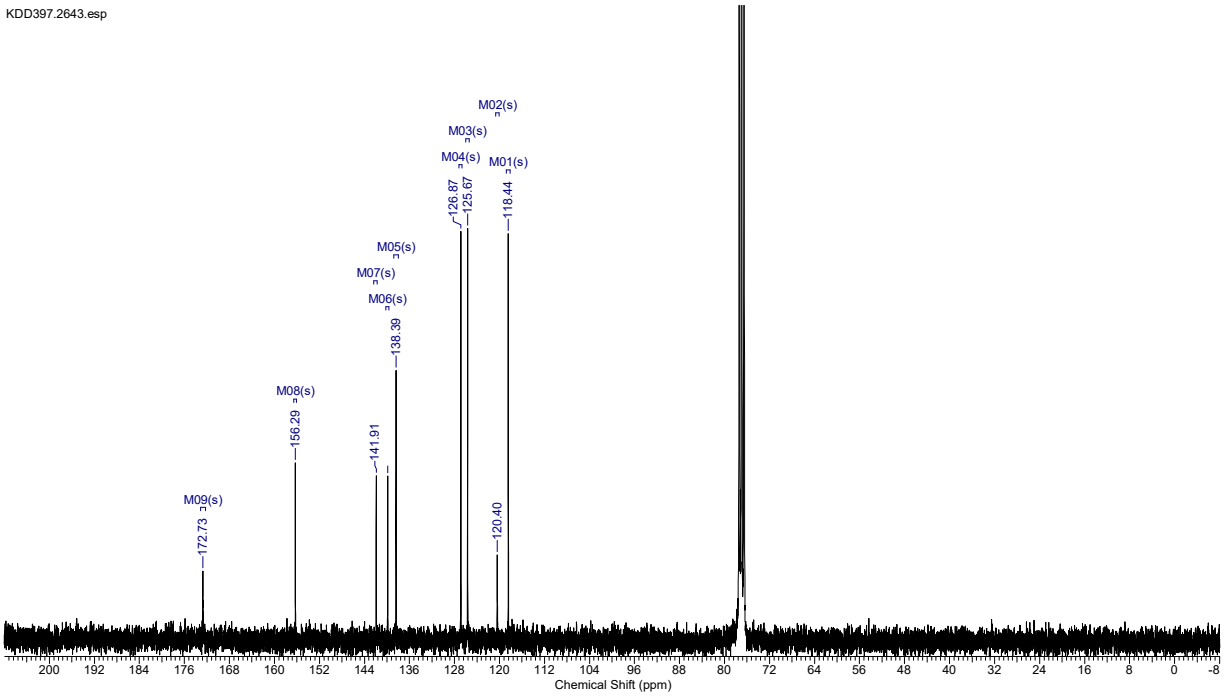


Figure S18. ^{1}H and ^{13}C NMR spectra of **1h**

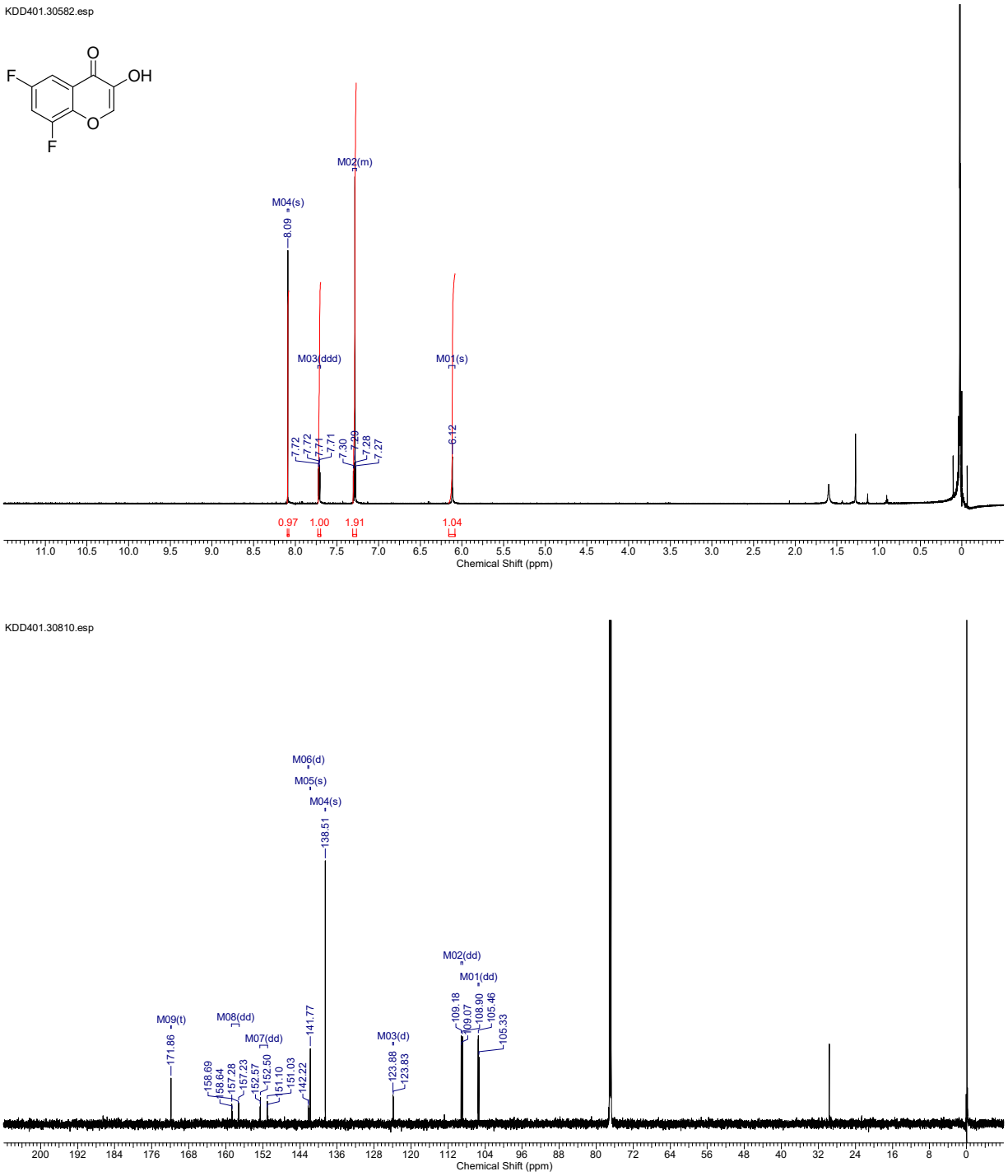


Figure S19. ^{1}H and ^{13}C NMR spectra of **1i**

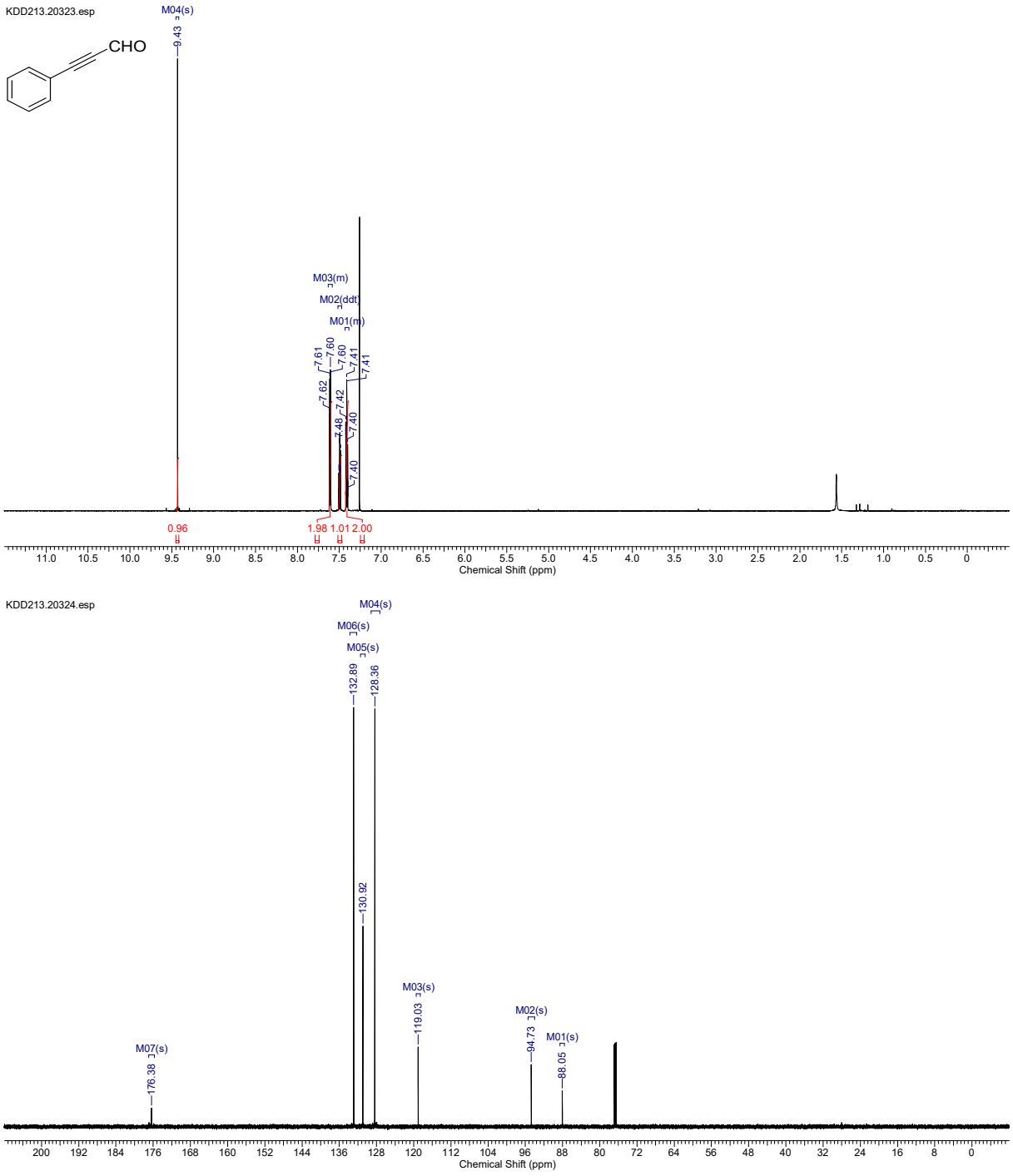


Figure S20. ^{1}H and ^{13}C NMR spectra of **2a**

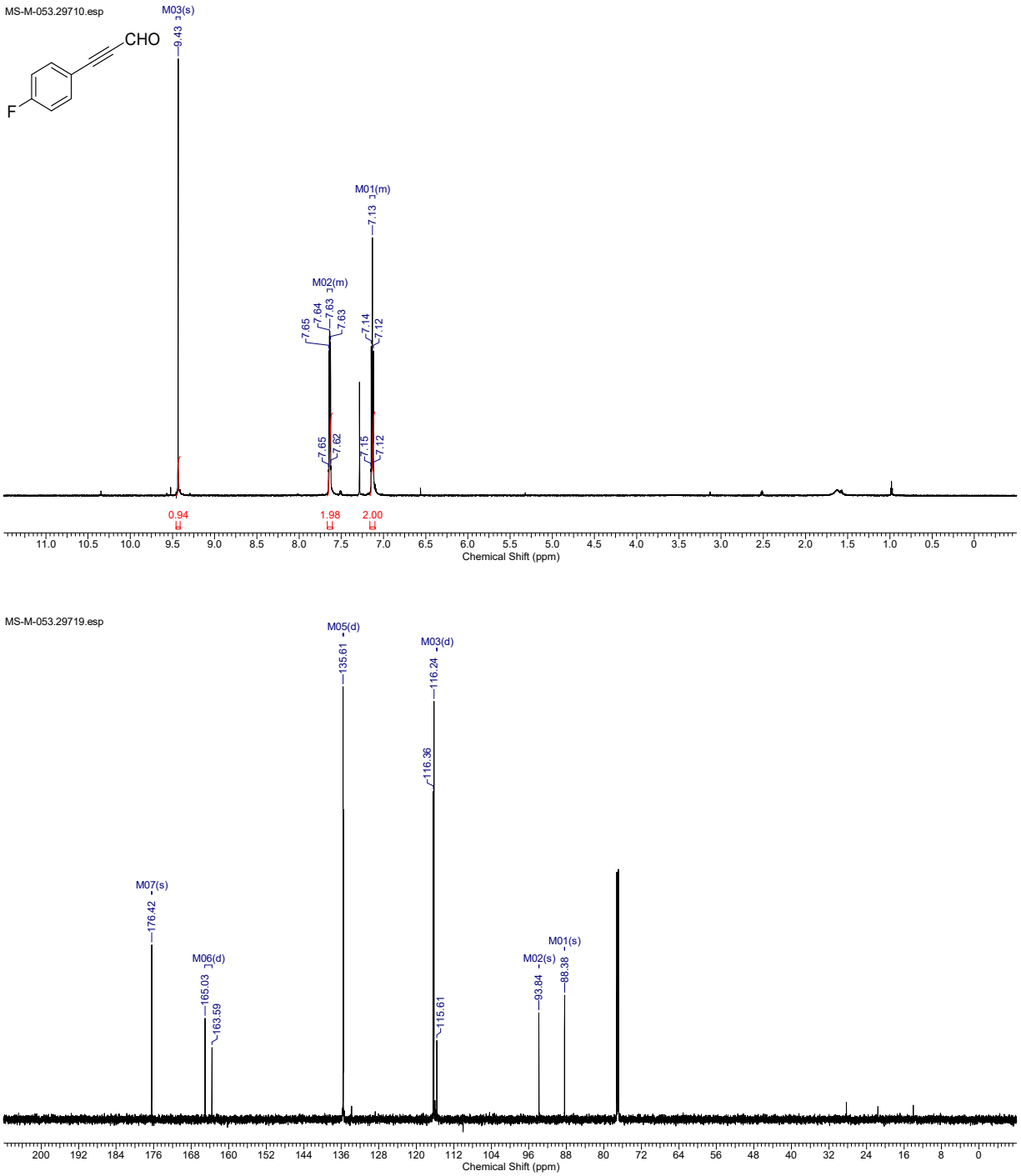


Figure S21. ^{1}H and ^{13}C NMR spectra of **2b**

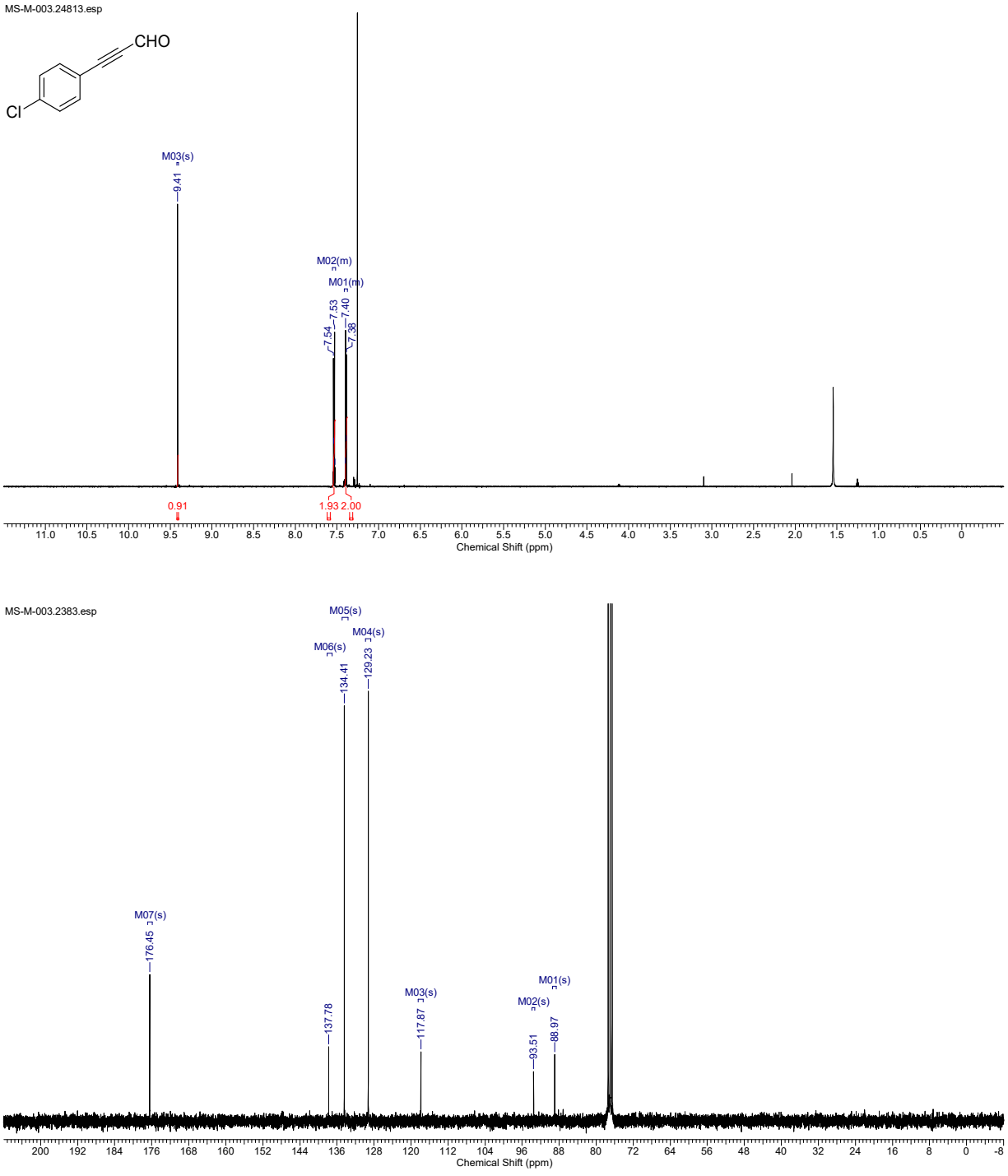


Figure S22. ^{1}H and ^{13}C NMR spectra of **2c**

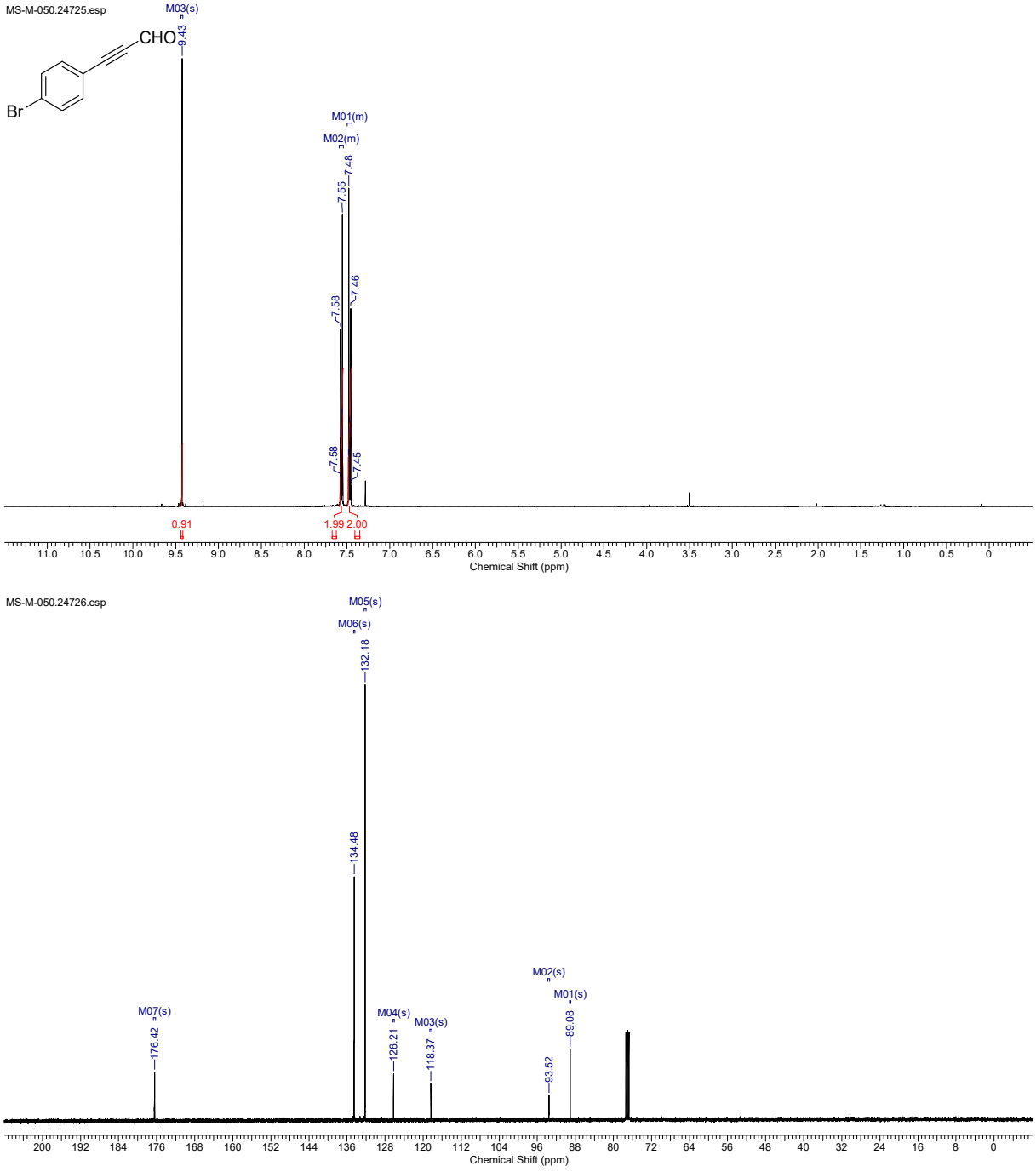


Figure S23. ^{1}H and ^{13}C NMR spectra of **2d**

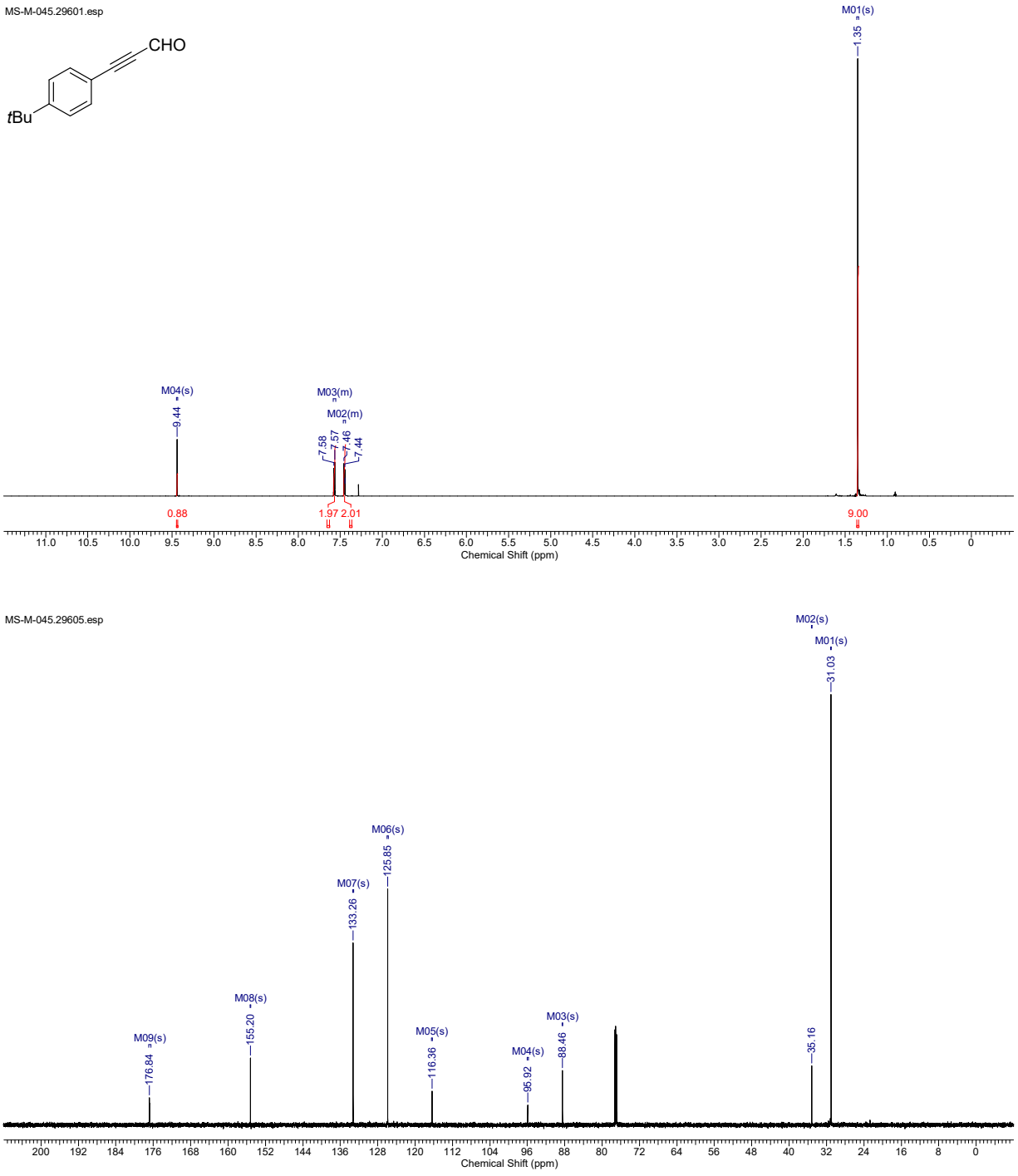
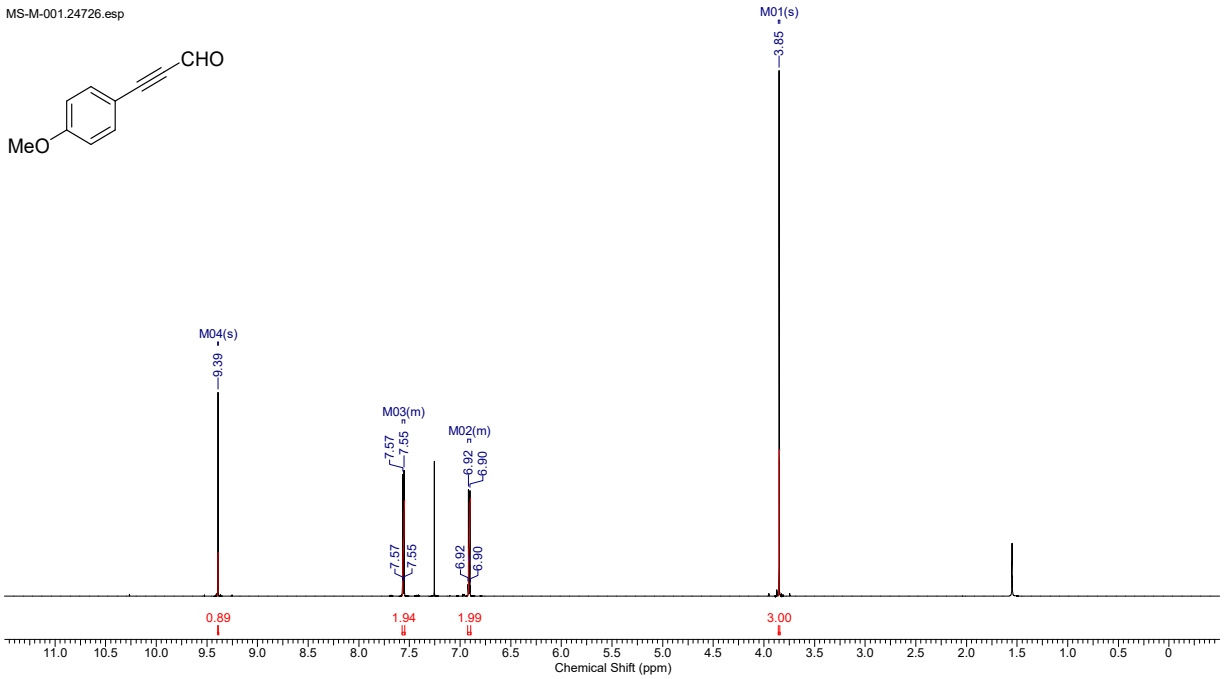


Figure S24. ^{1}H and ^{13}C NMR spectra of **2e**



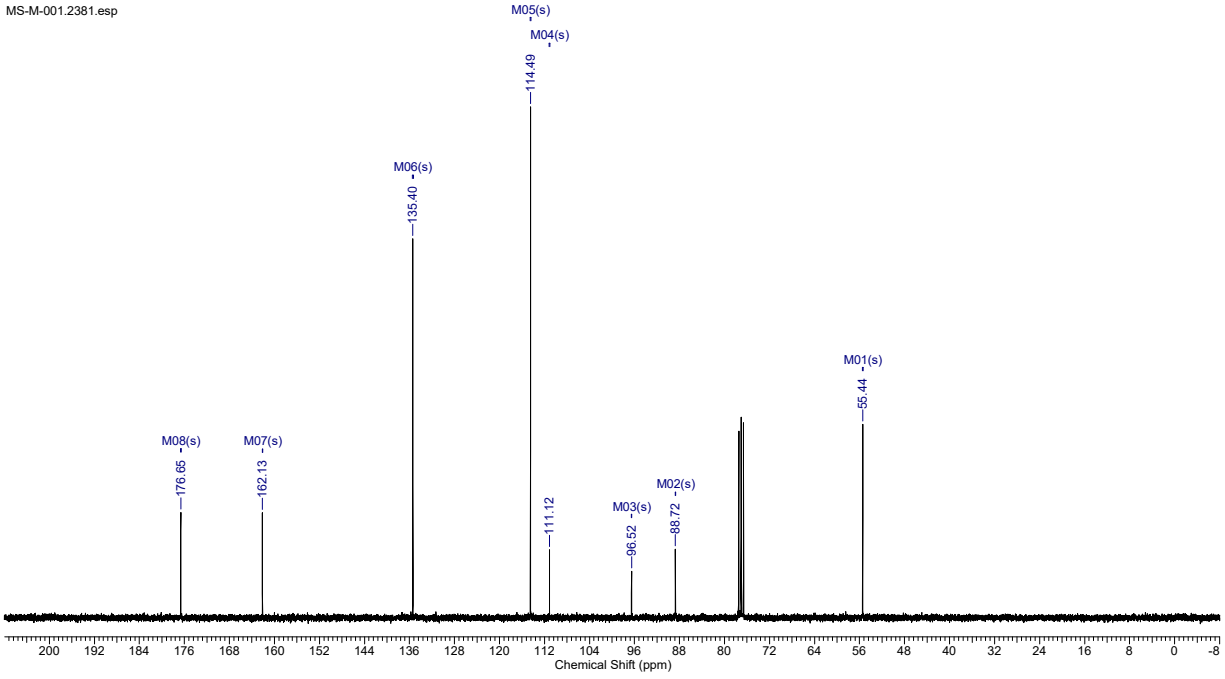
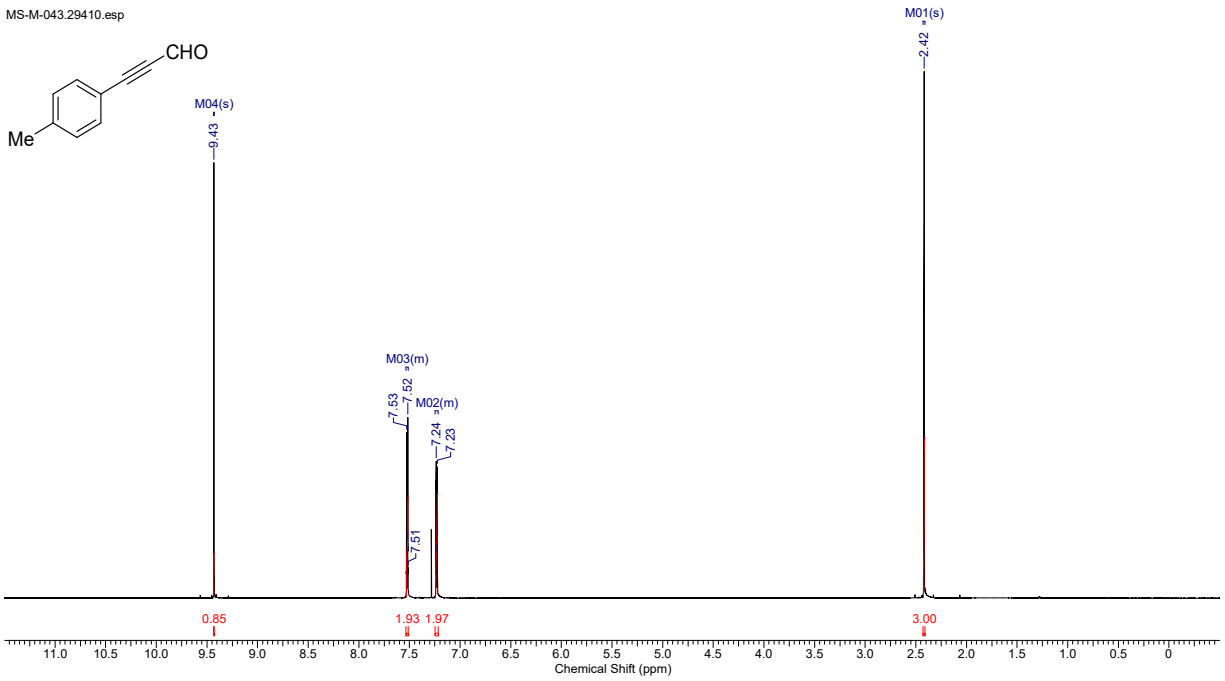


Figure S25. ^{1}H and ^{13}C NMR spectra of **2f**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CHO
Me
M04(s)
9.43
M01(s)
2.42
M03(m)
7.53
7.52
M02(m)
7.24
7.23
7.51
0.85
1.93
1.97
3.00
Chemical Shift (ppm)

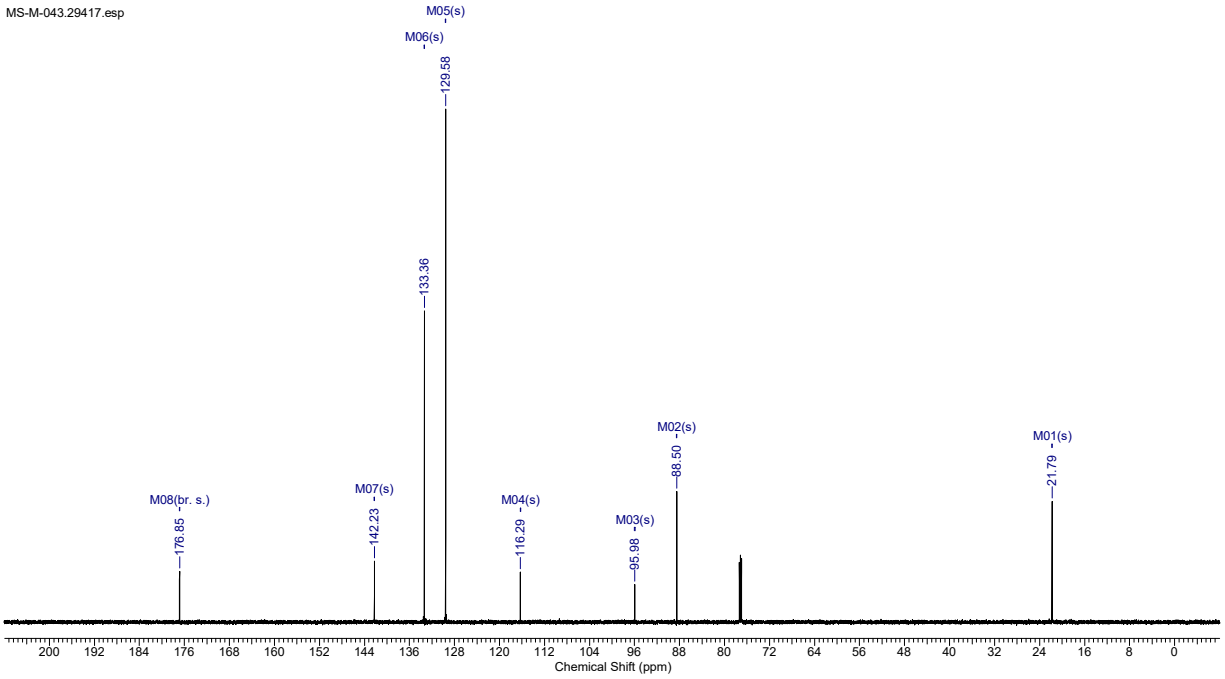
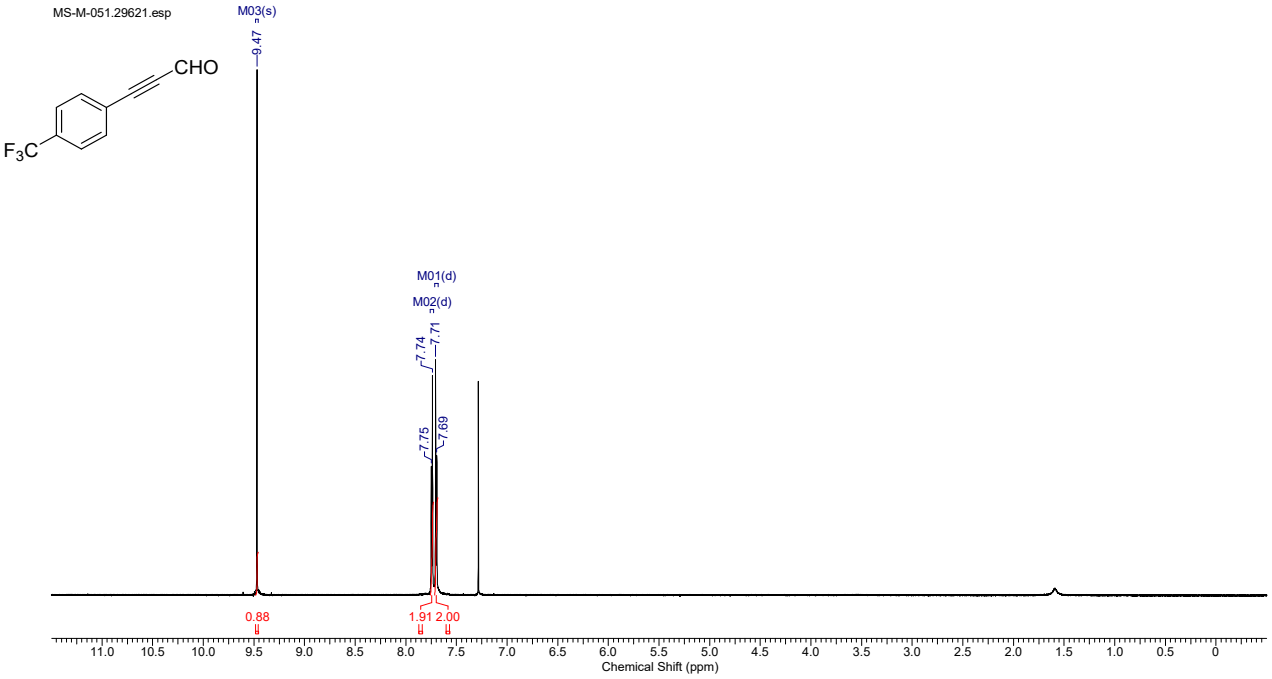


Figure S26. ^{1}H and ^{13}C NMR spectra of **2g**



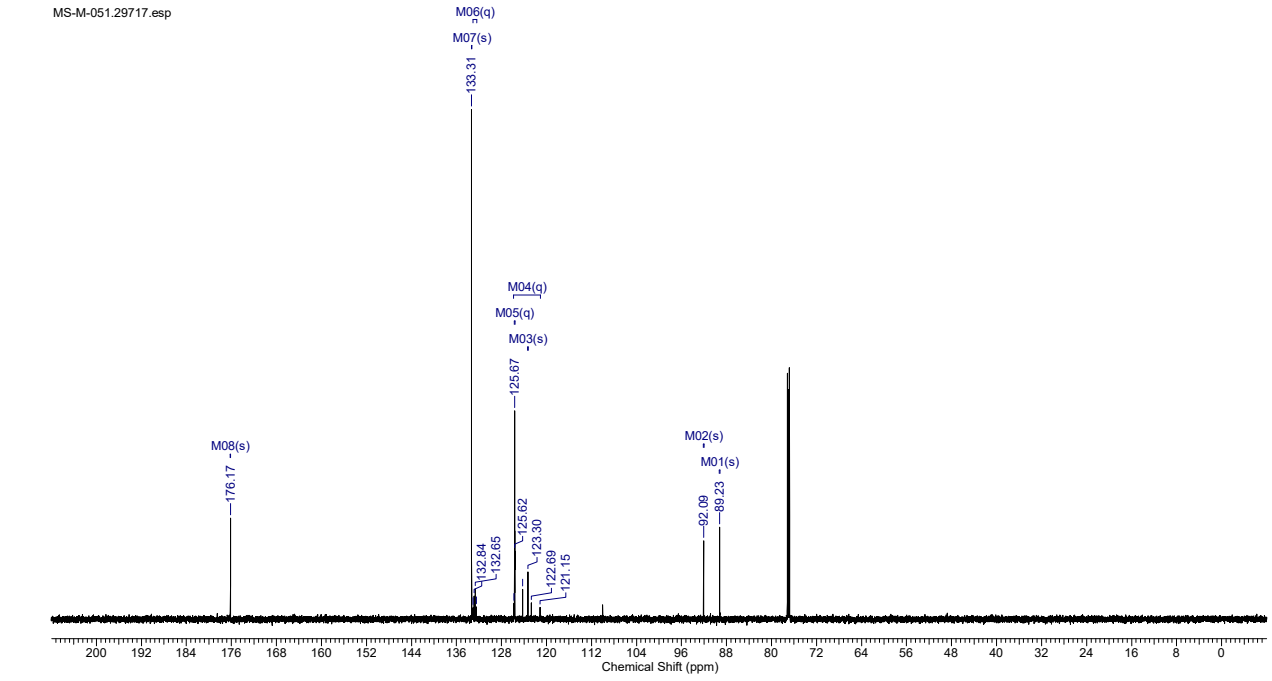


Figure S27. ^{1}H and ^{13}C NMR spectra of **2h**

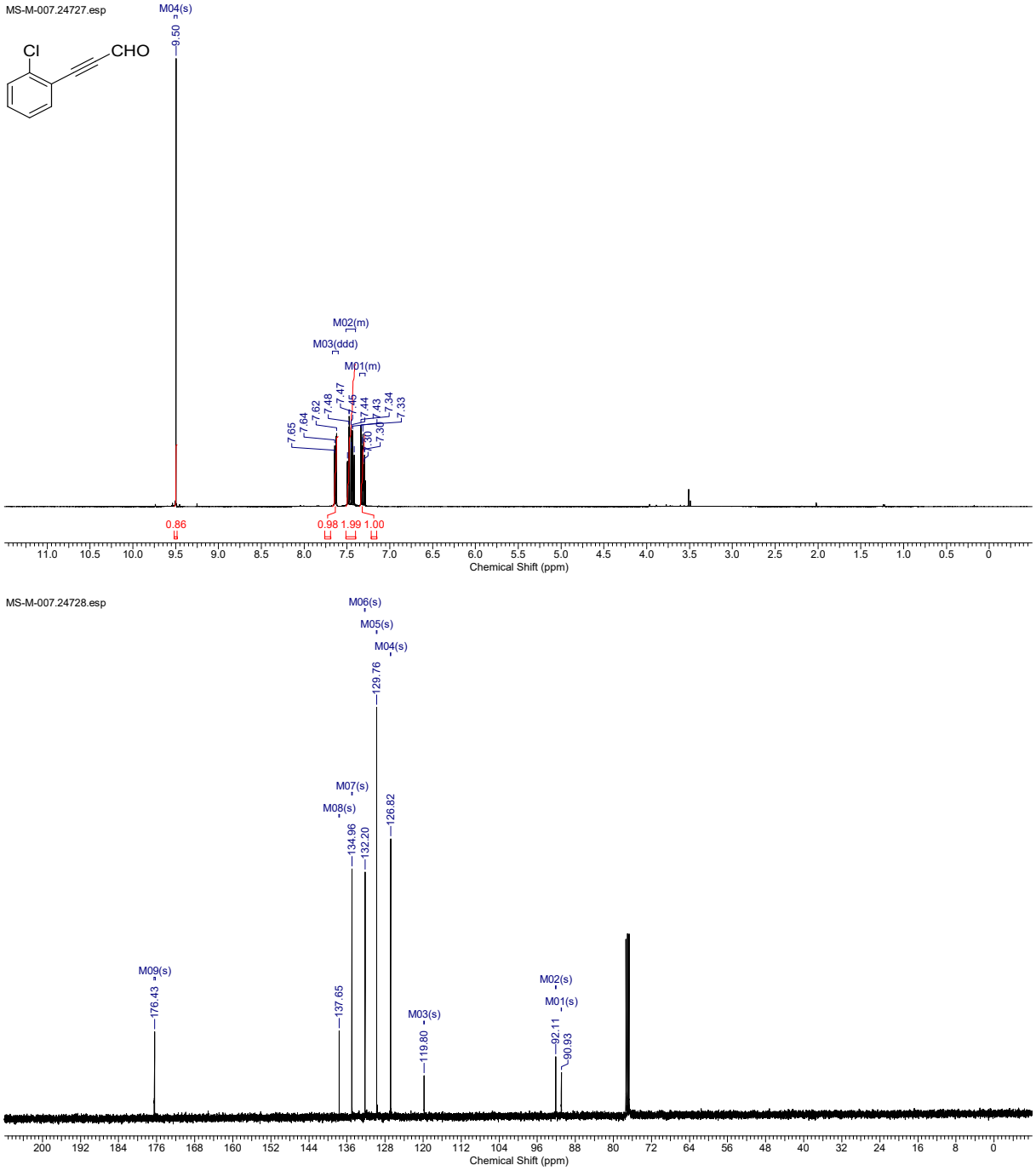


Figure S28. ^{1}H and ^{13}C NMR spectra of **2i**

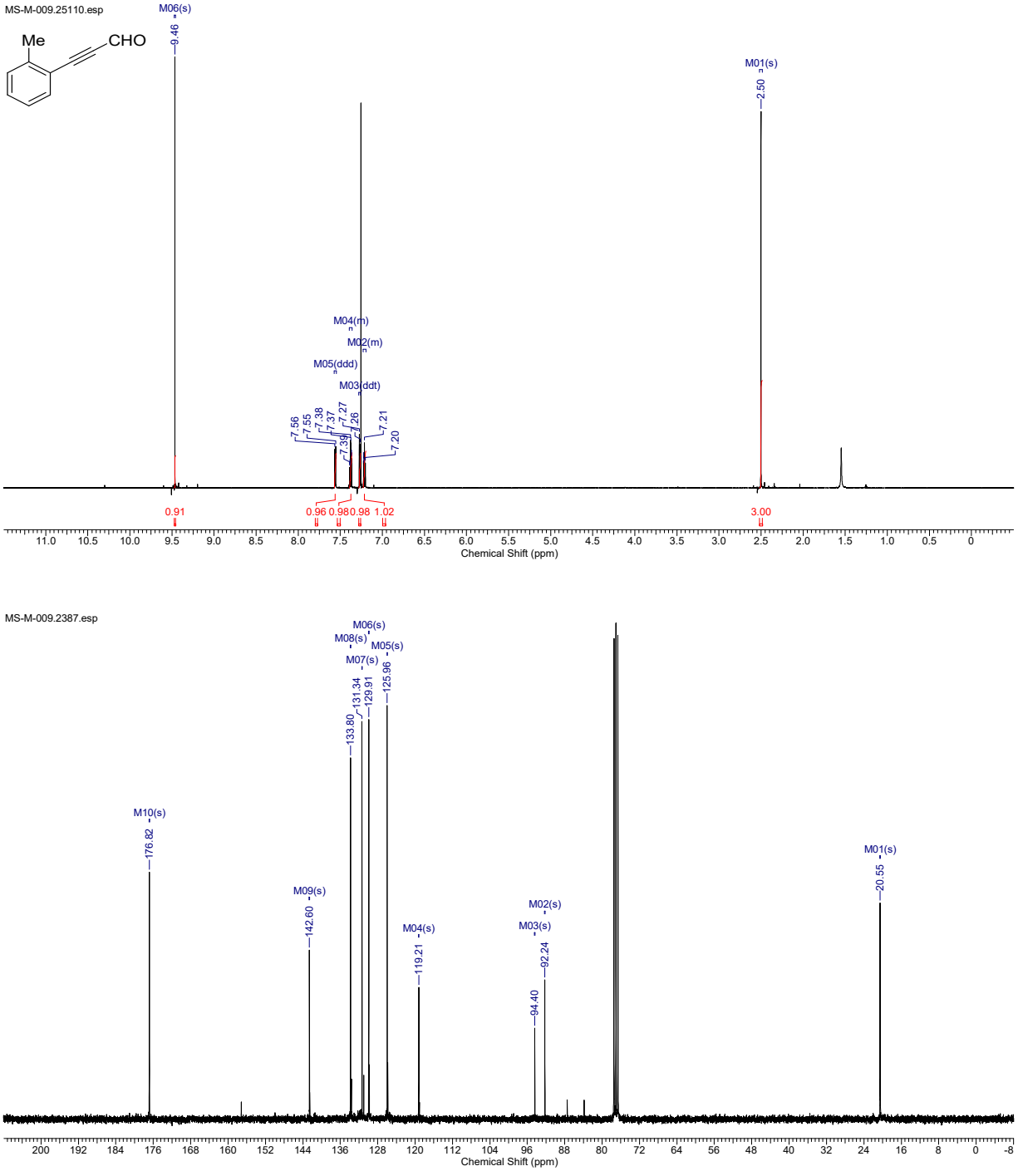


Figure S29. ^{1}H and ^{13}C NMR spectra of **2j**

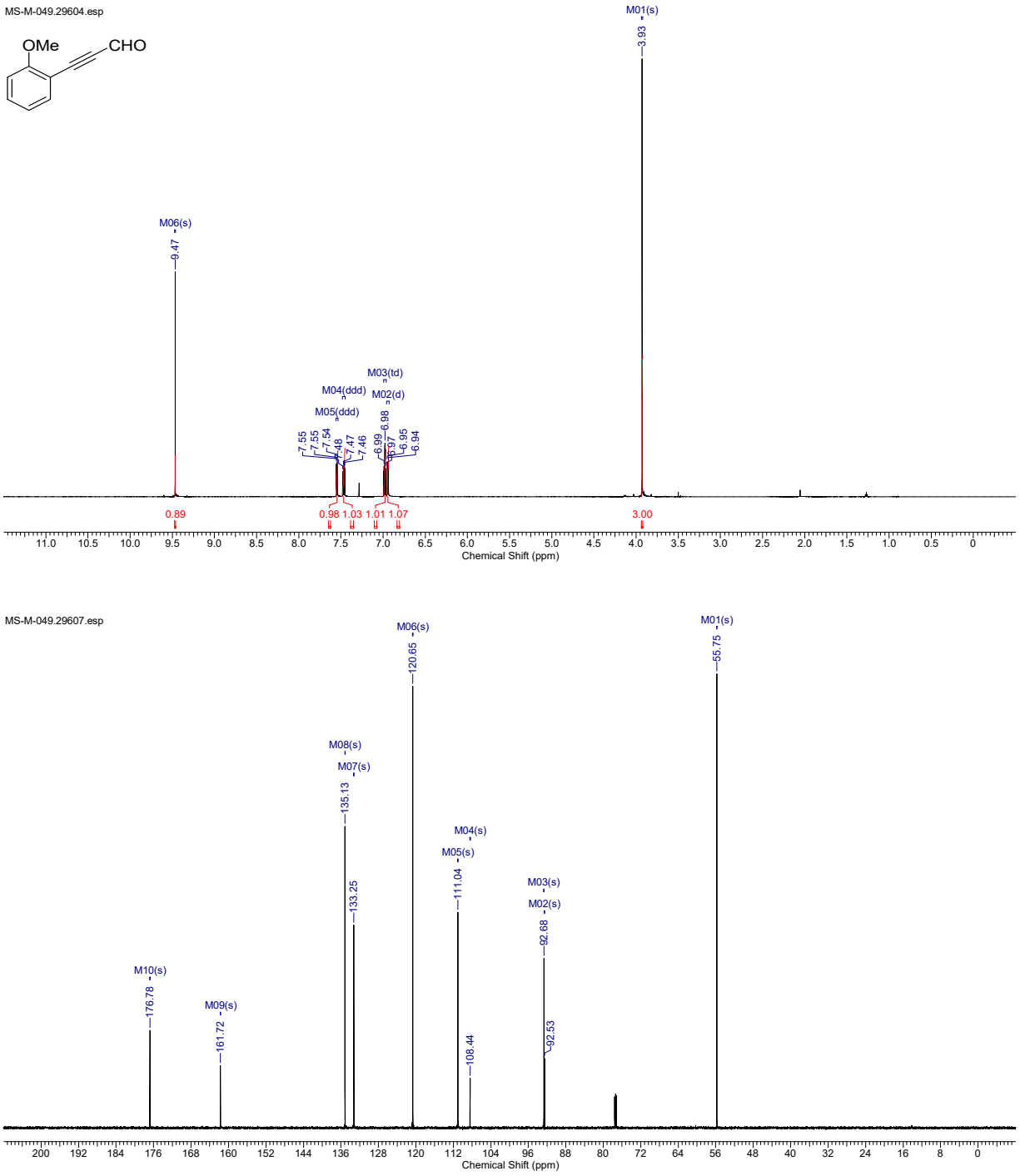


Figure S30. ^{1}H and ^{13}C NMR spectra of **2k**

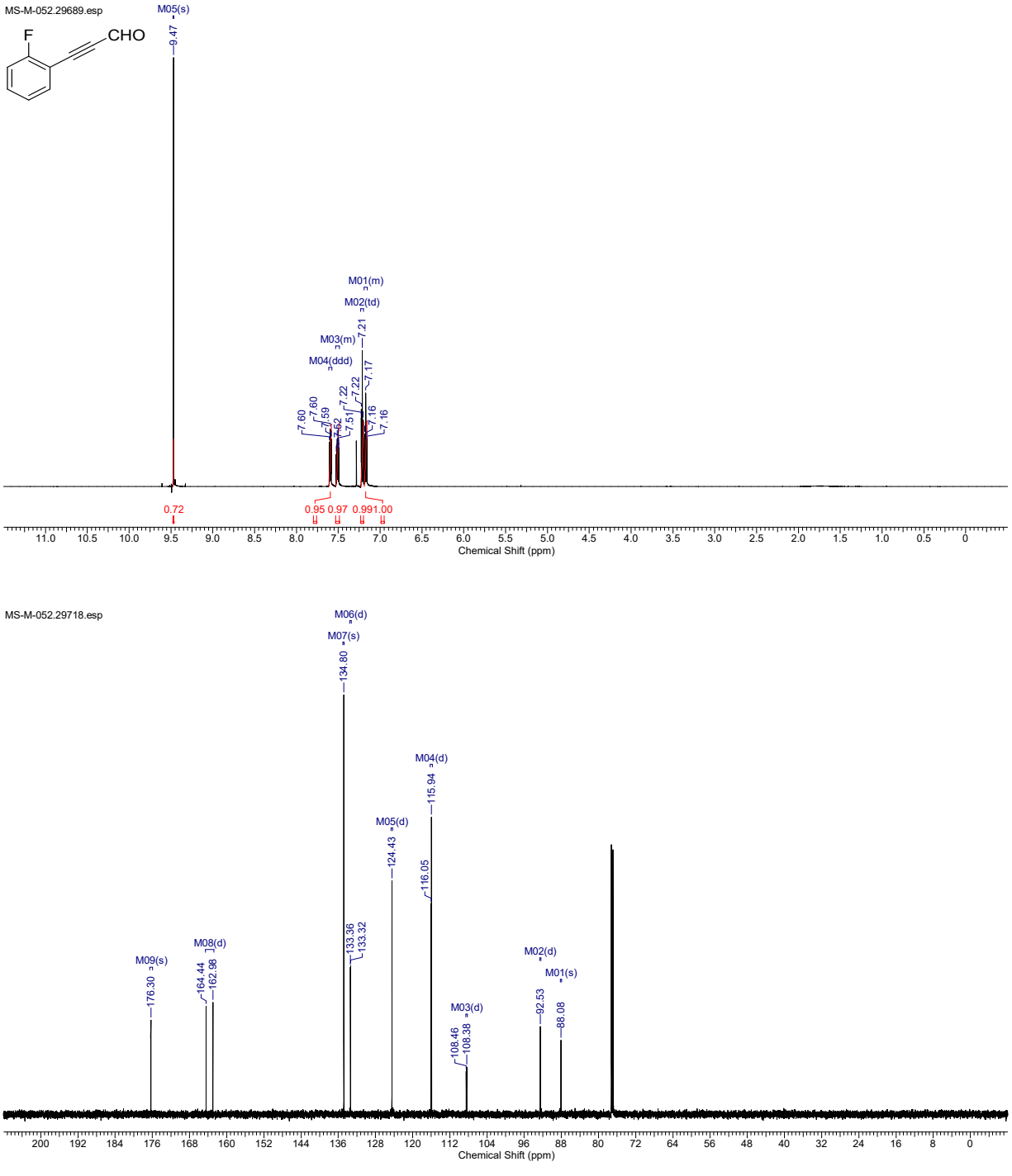


Figure S31. ^{1}H and ^{13}C NMR spectra of **2l**

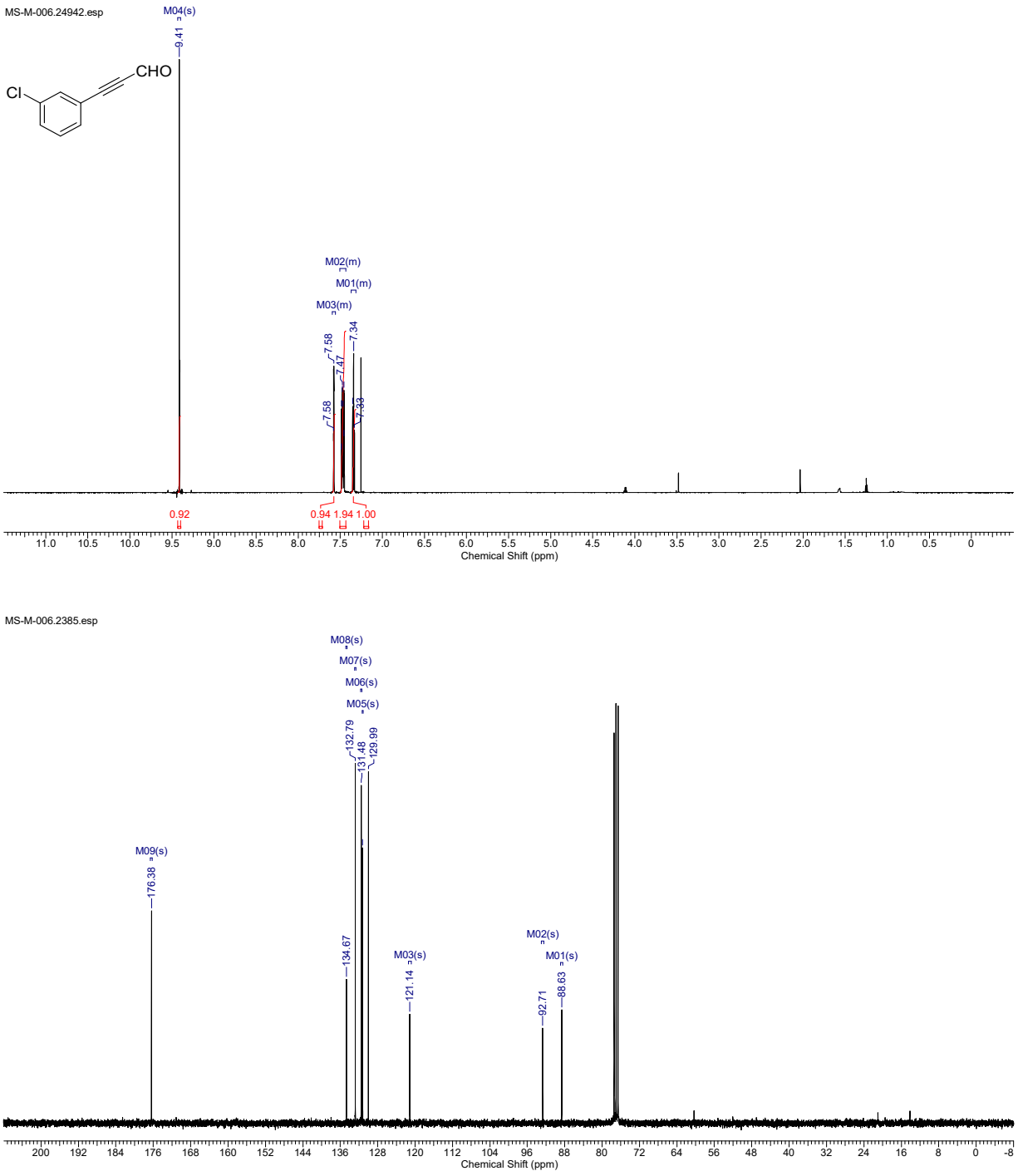


Figure S32. ^{1}H and ^{13}C NMR spectra of **2m**

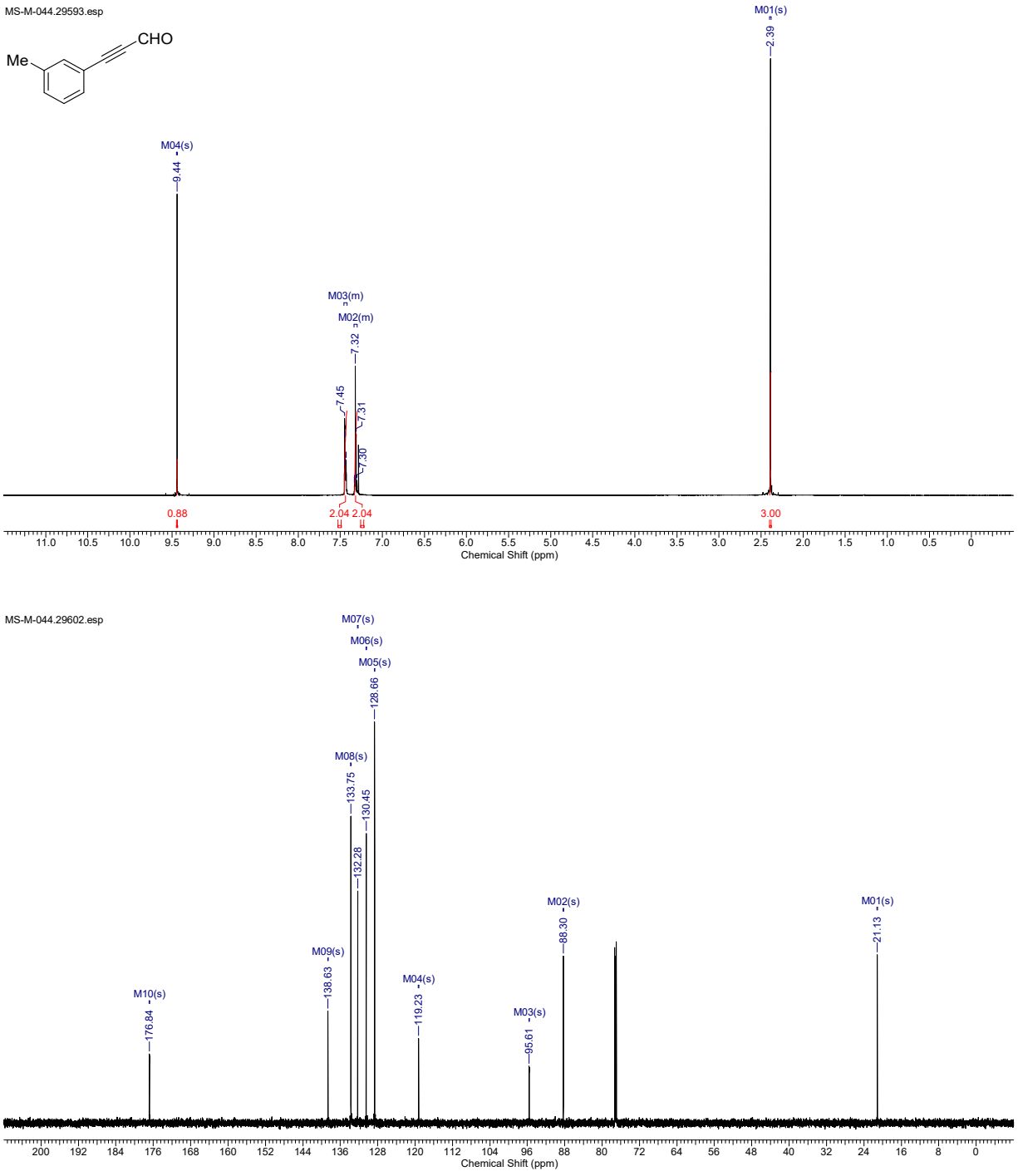


Figure S33. ^{1}H and ^{13}C NMR spectra of **2n**

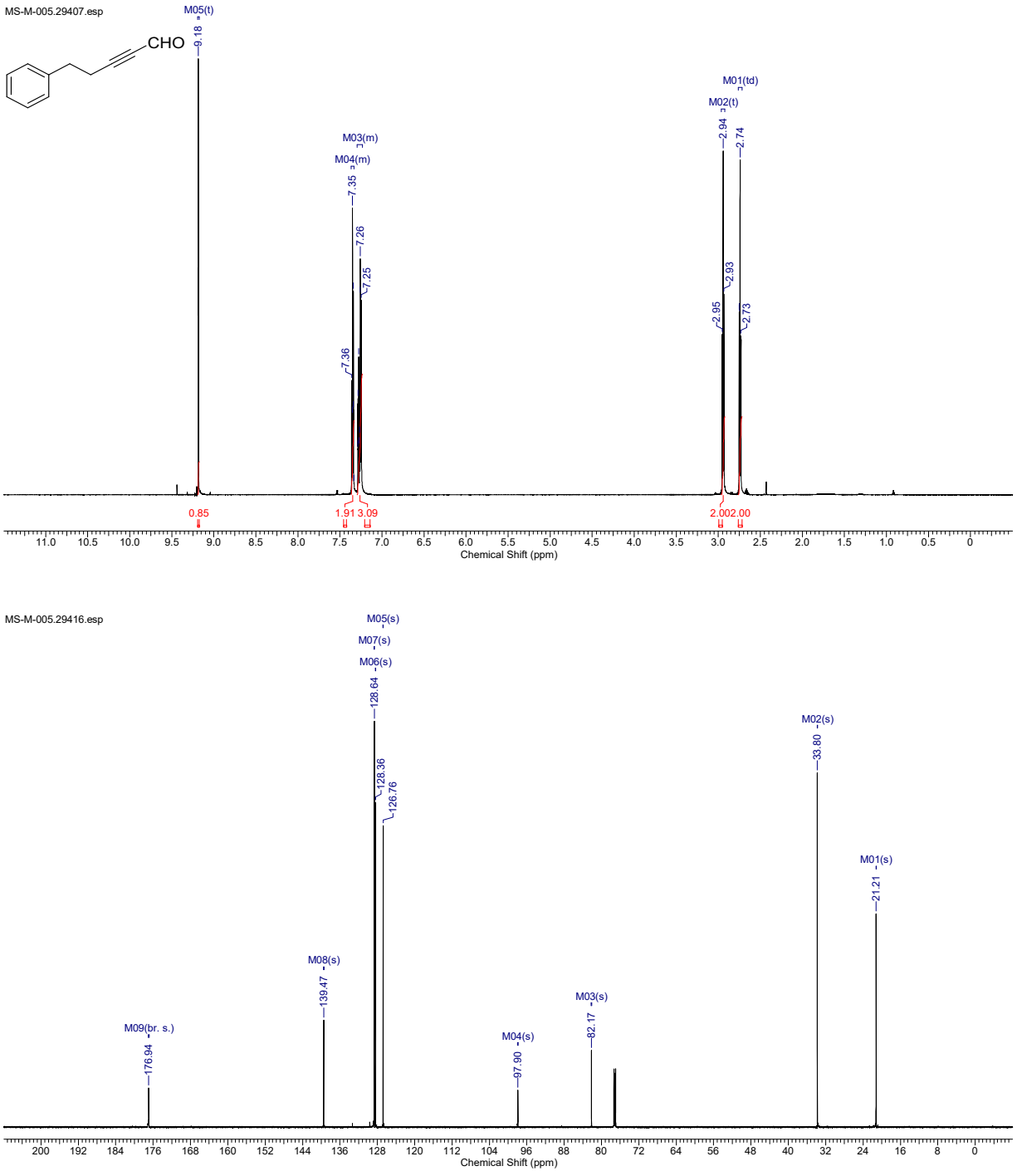
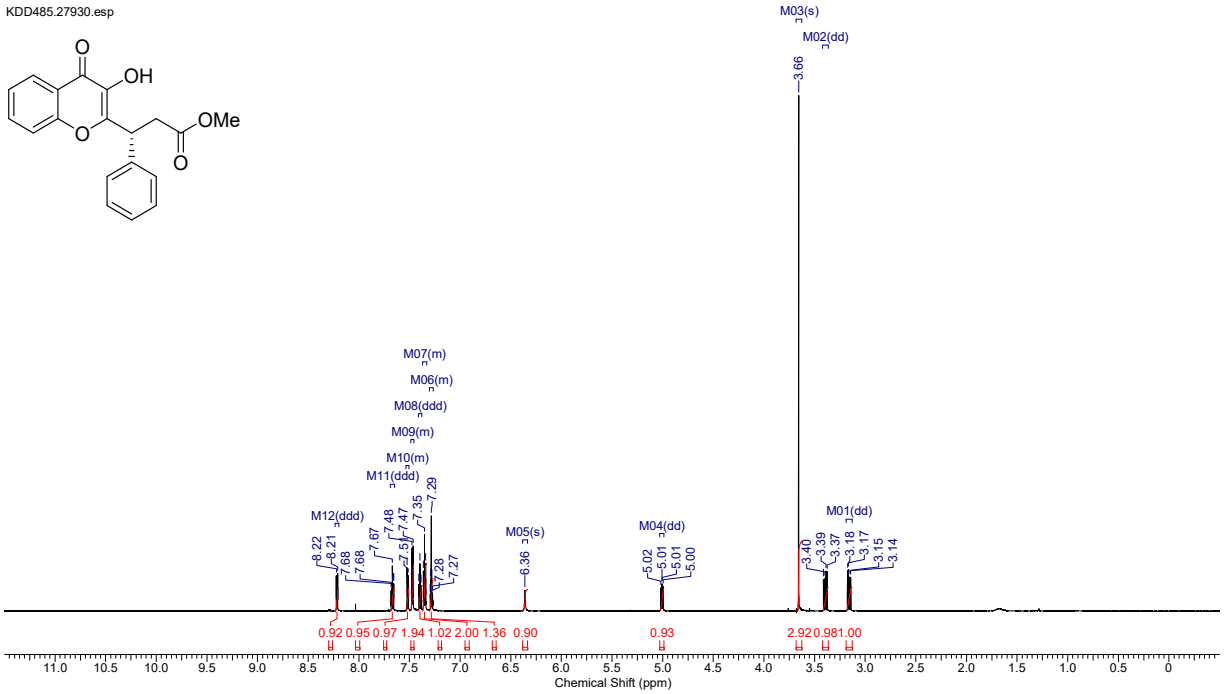


Figure S34. ^{1}H and ^{13}C NMR spectra of **2o**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O
OH
O
OMe
O
M03(s)
M02(dd)
3.66
M07(m)
M06(m)
M08(ddd)
M09(m)
M10(m)
M11(ddd)
7.29
M12(ddd)
8.22
8.21
7.68
7.68
7.67
7.48
7.47
7.35
7.28
7.27
M05(s)
6.36
M04(dd)
5.02
5.01
5.01
5.00
M01(dd)
3.40
3.39
3.37
3.18
3.17
3.15
3.14
0.92 0.95 0.97 1.94 1.02 2.00 1.36 0.90
0.93
2.92 0.98 1.00
11.0 10.5 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)

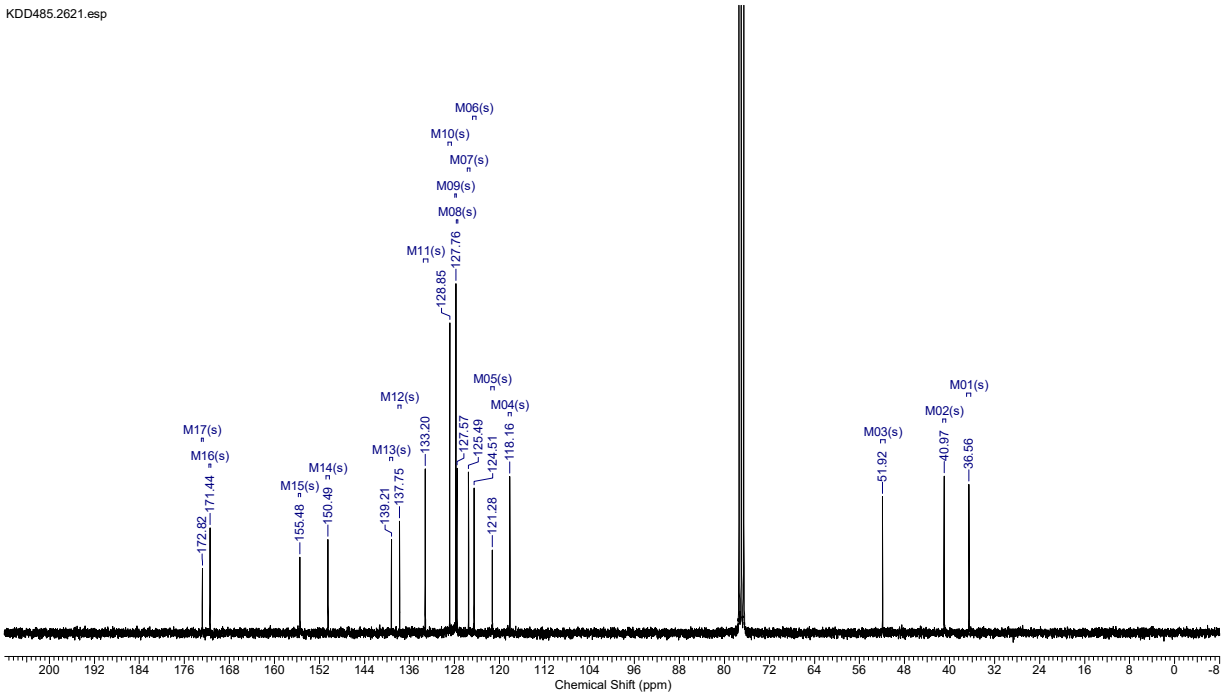


Figure S35. ^{1}H and ^{13}C NMR spectra of **3aaa**

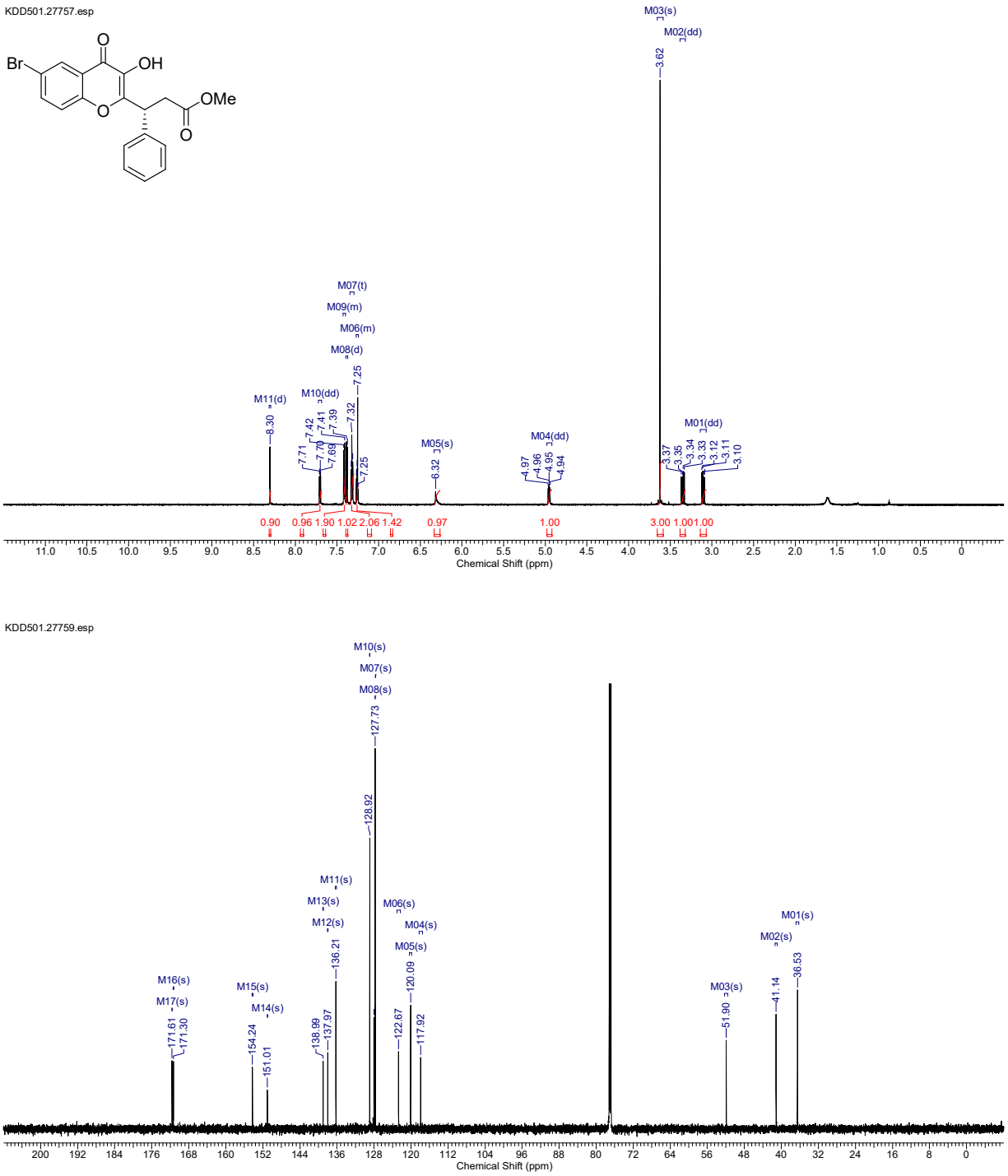


Figure S36. ^{1}H and ^{13}C NMR spectra of **3baa**

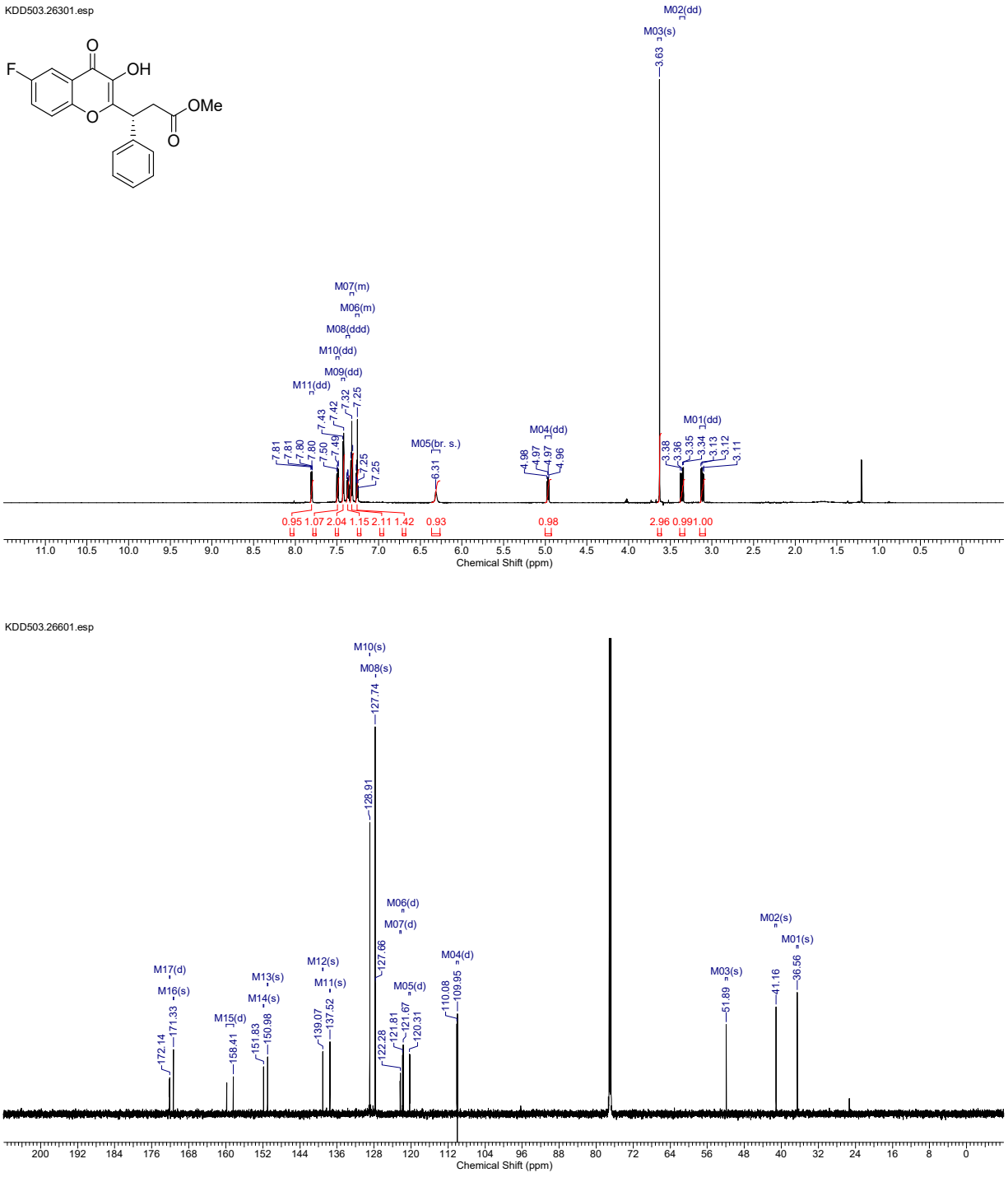


Figure S37. ^{1}H and ^{13}C NMR spectra of **3caa**

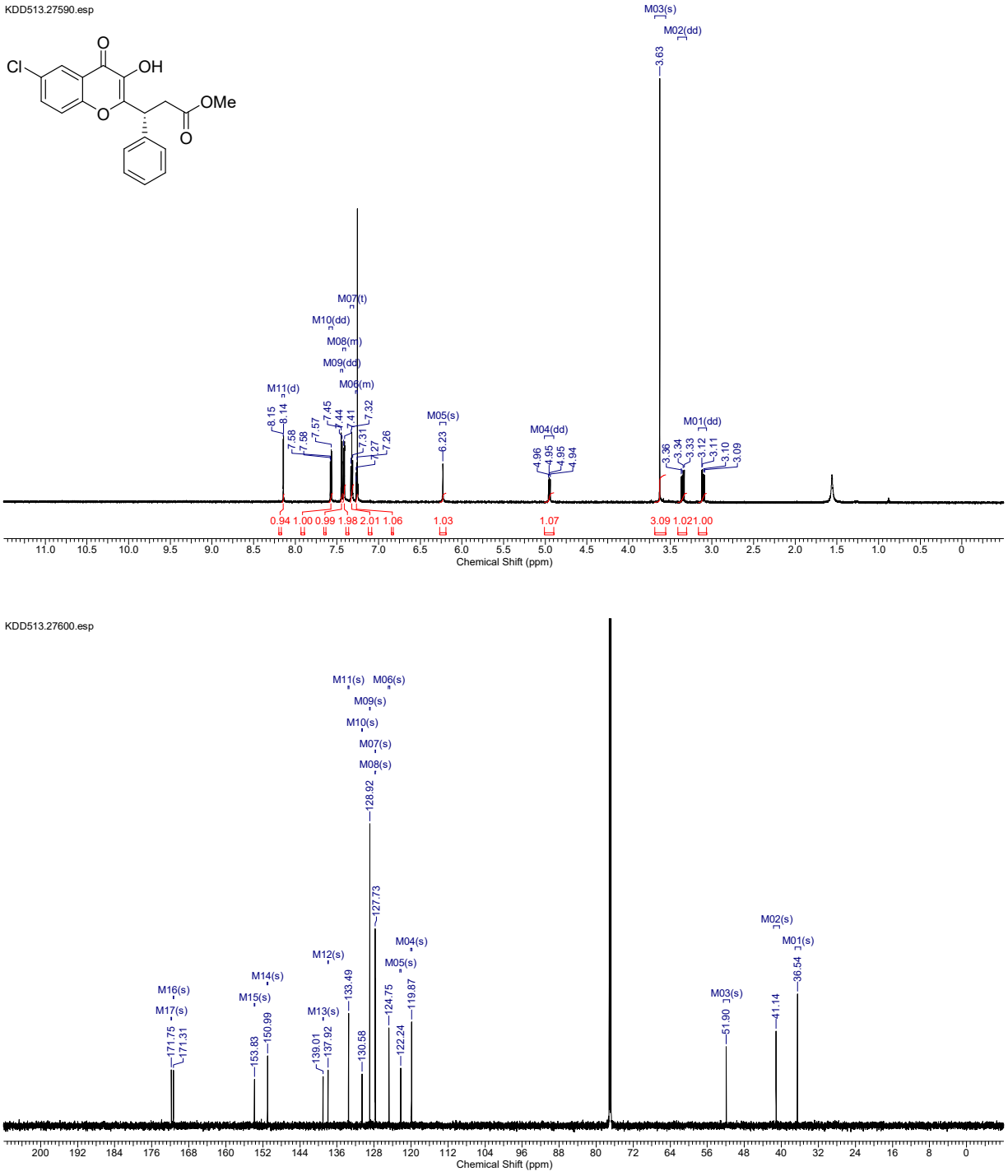
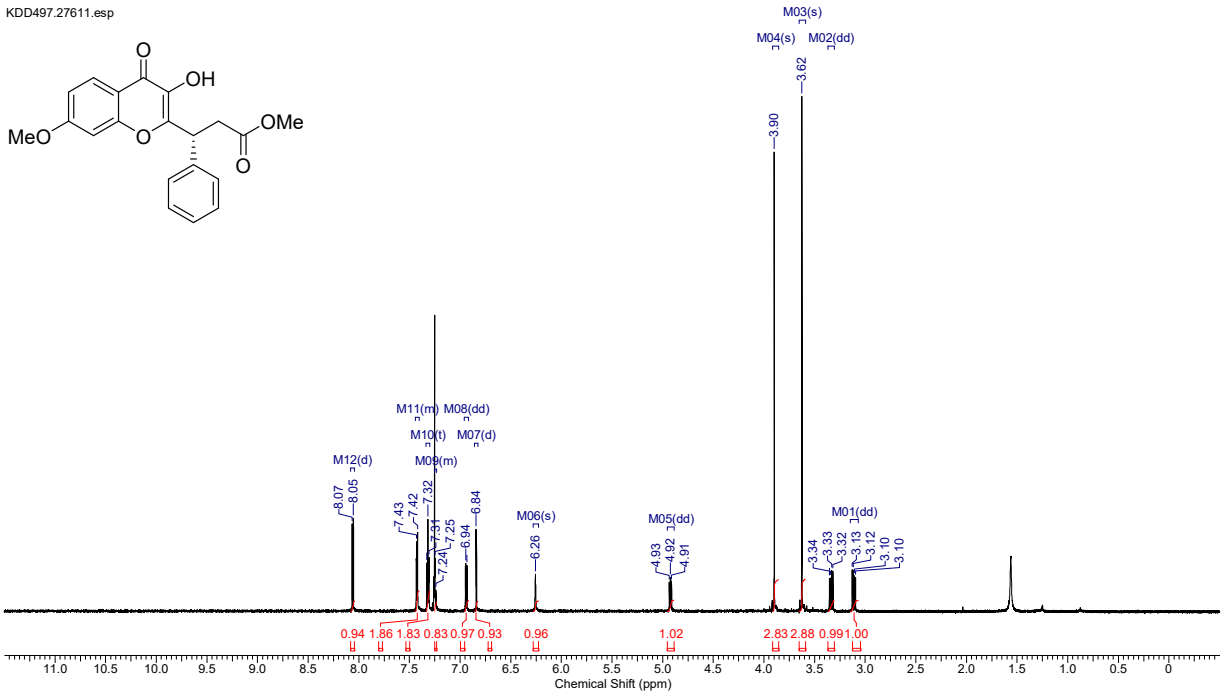


Figure S38. ^{1}H and ^{13}C NMR spectra of **3daa**


KDD497.27611.esp
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MeO
O
OMe
O
M03(s)
M04(s)
M02(dd)
3.62
3.90
M11(m)
M08(dd)
M10(t)
M07(d)
M12(d)
M09(m)
8.07
8.05
7.43
7.42
7.32
7.31
7.25
7.24
6.94
6.84
M06(s)
6.26
M05(dd)
4.93
4.92
4.91
M01(dd)
3.34
3.33
3.32
3.13
3.12
3.10
3.10
0.94 1.86 1.83 0.83 0.97 0.93 0.96 1.02 2.83 2.88 0.99 1.00
11.0 10.5 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)

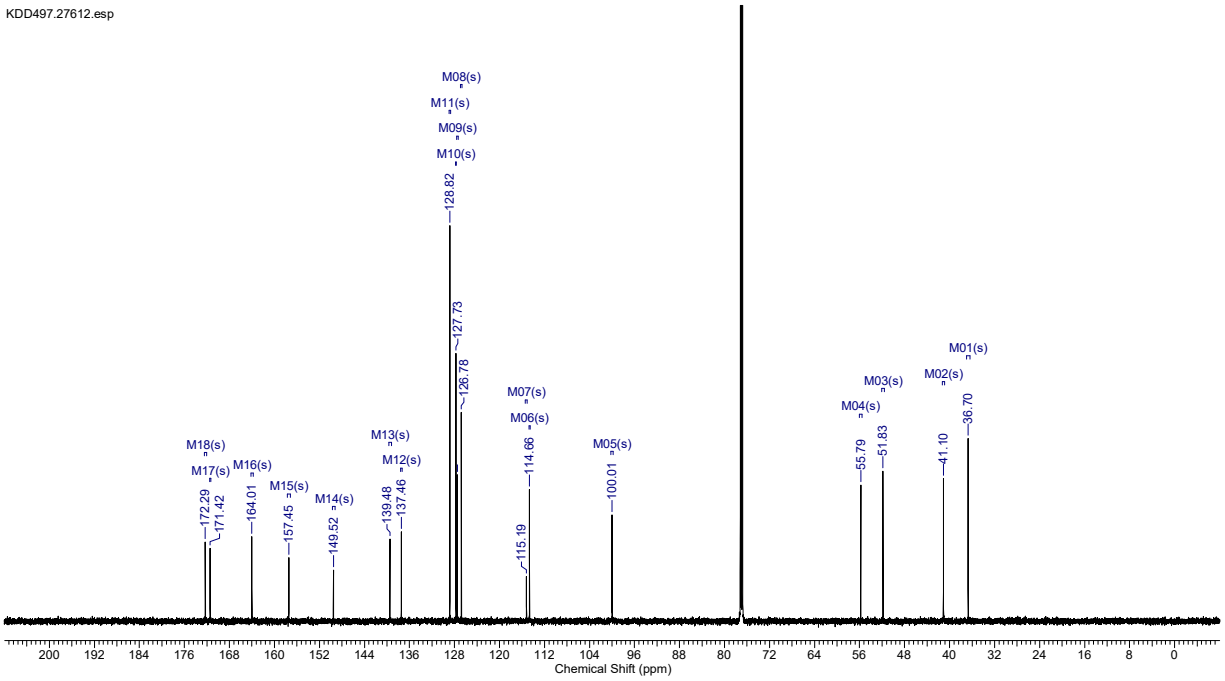


Figure S39. ^{1}H and ^{13}C NMR spectra of **3eaa**

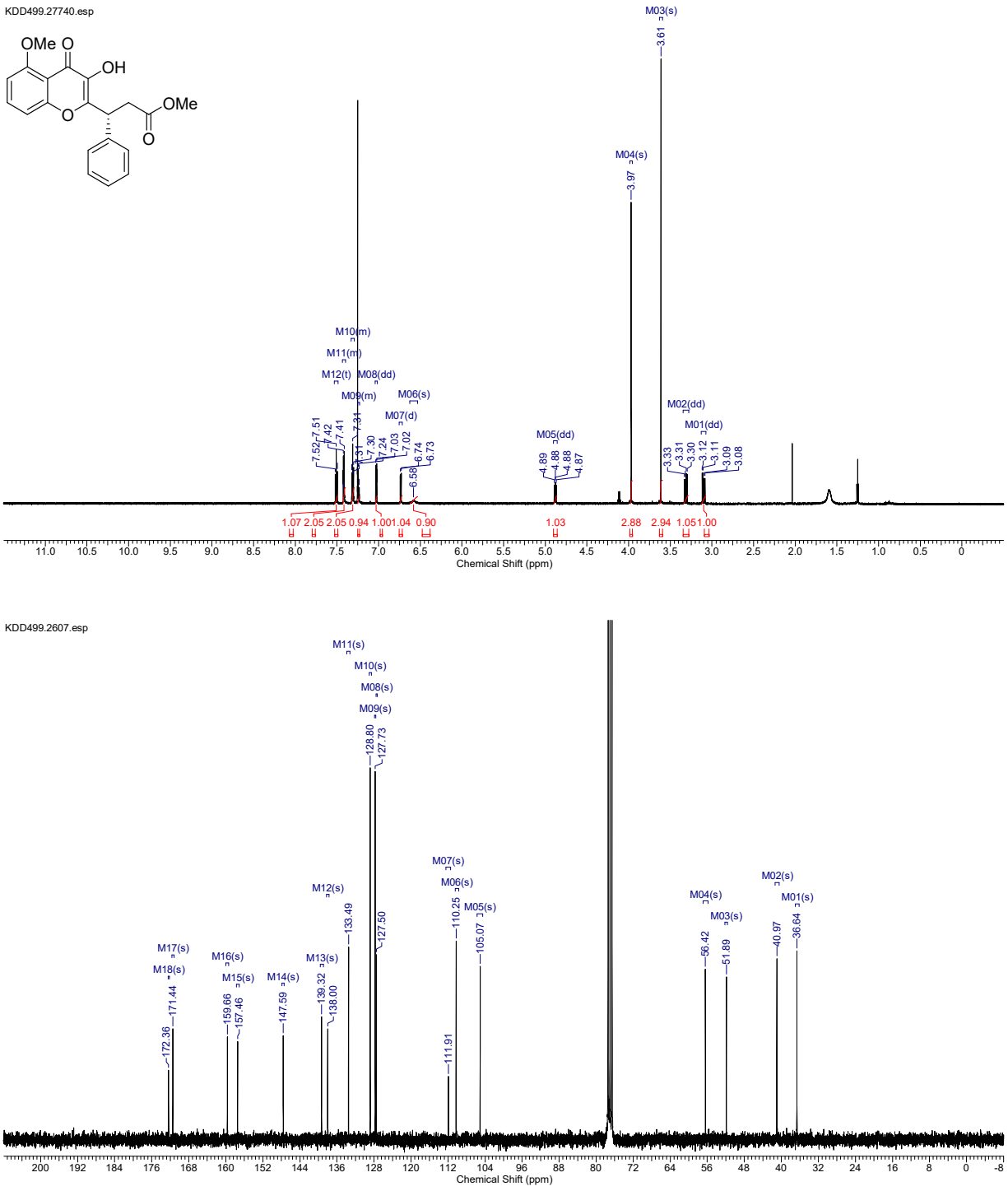


Figure S40. ^{1}H and ^{13}C NMR spectra of **3faa**

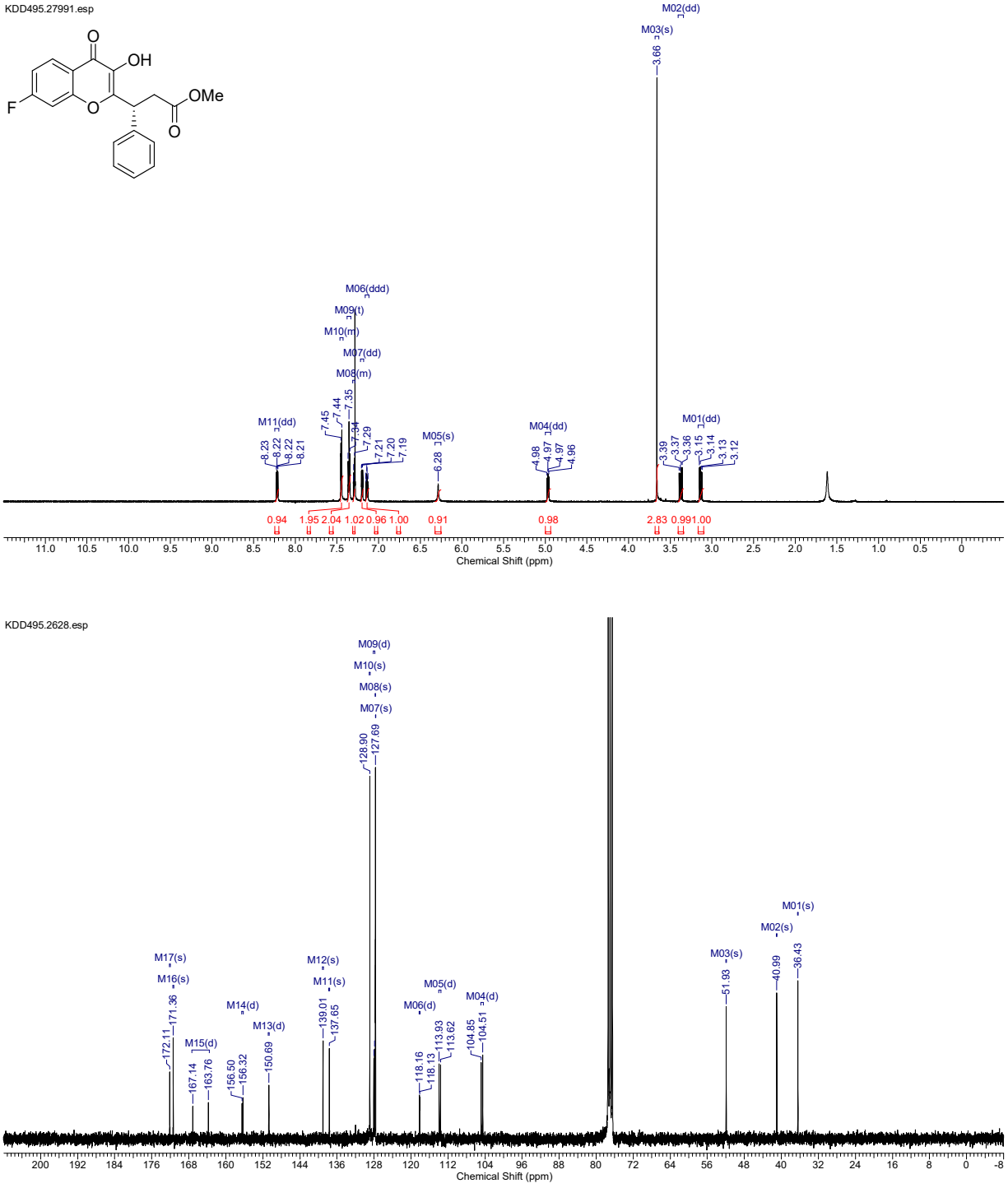


Figure S41. ^{1}H and ^{13}C NMR spectra of **3gaa**

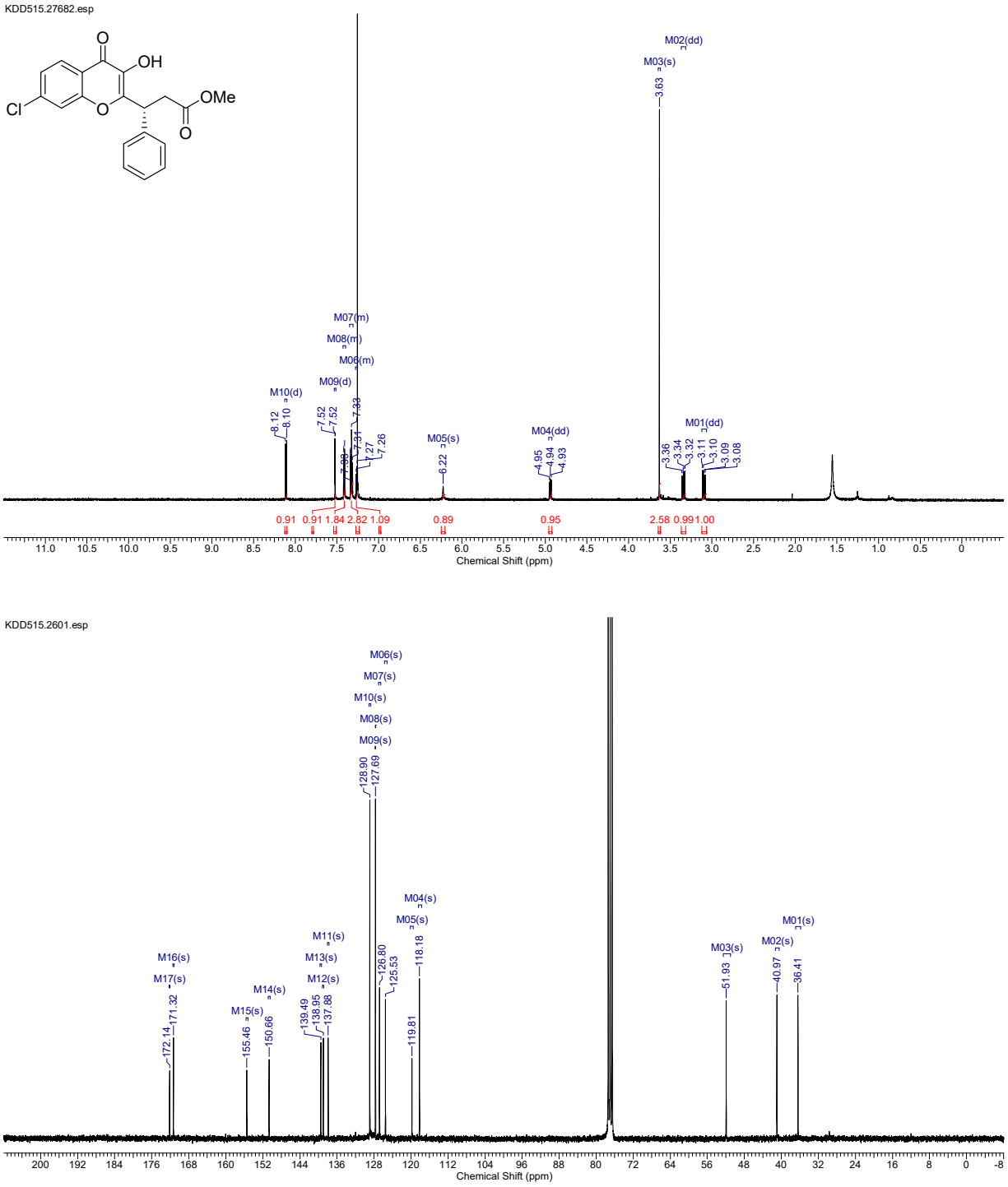


Figure S42. ^{1}H and ^{13}C NMR spectra of **3haa**

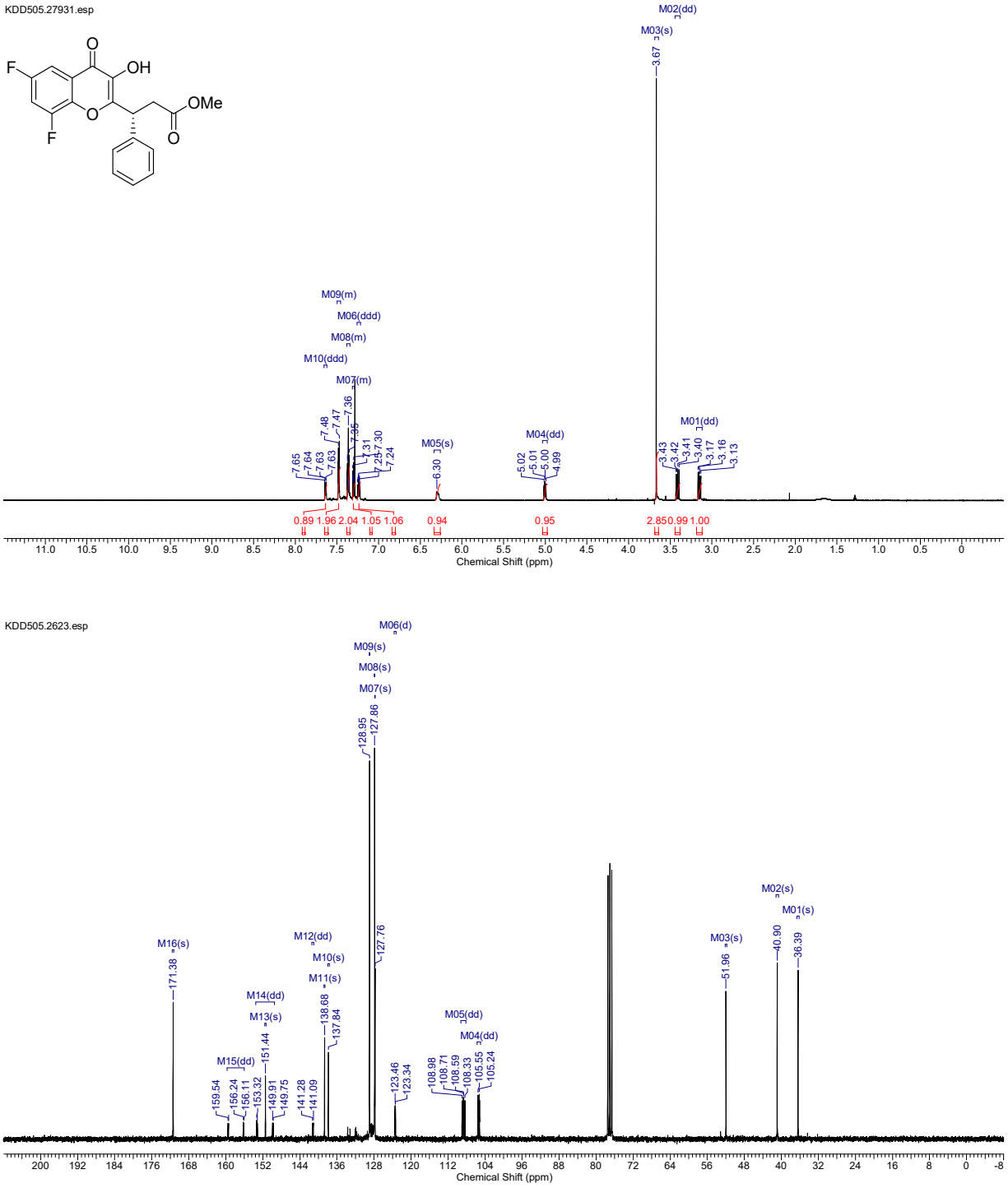


Figure S43. ^{1}H and ^{13}C NMR spectra of **3iaa**

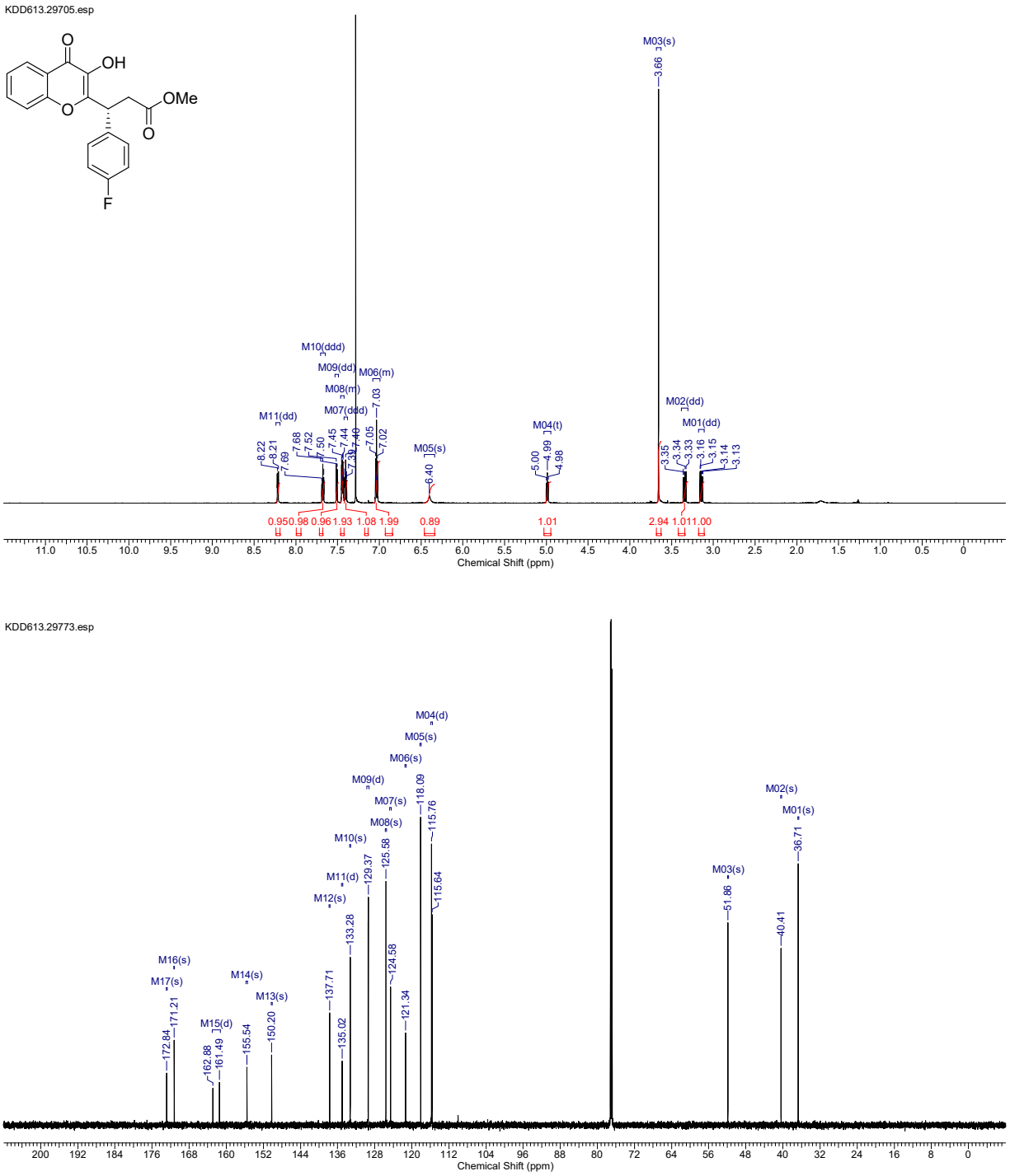


Figure S44. ^{1}H and ^{13}C NMR spectra of **3aba**

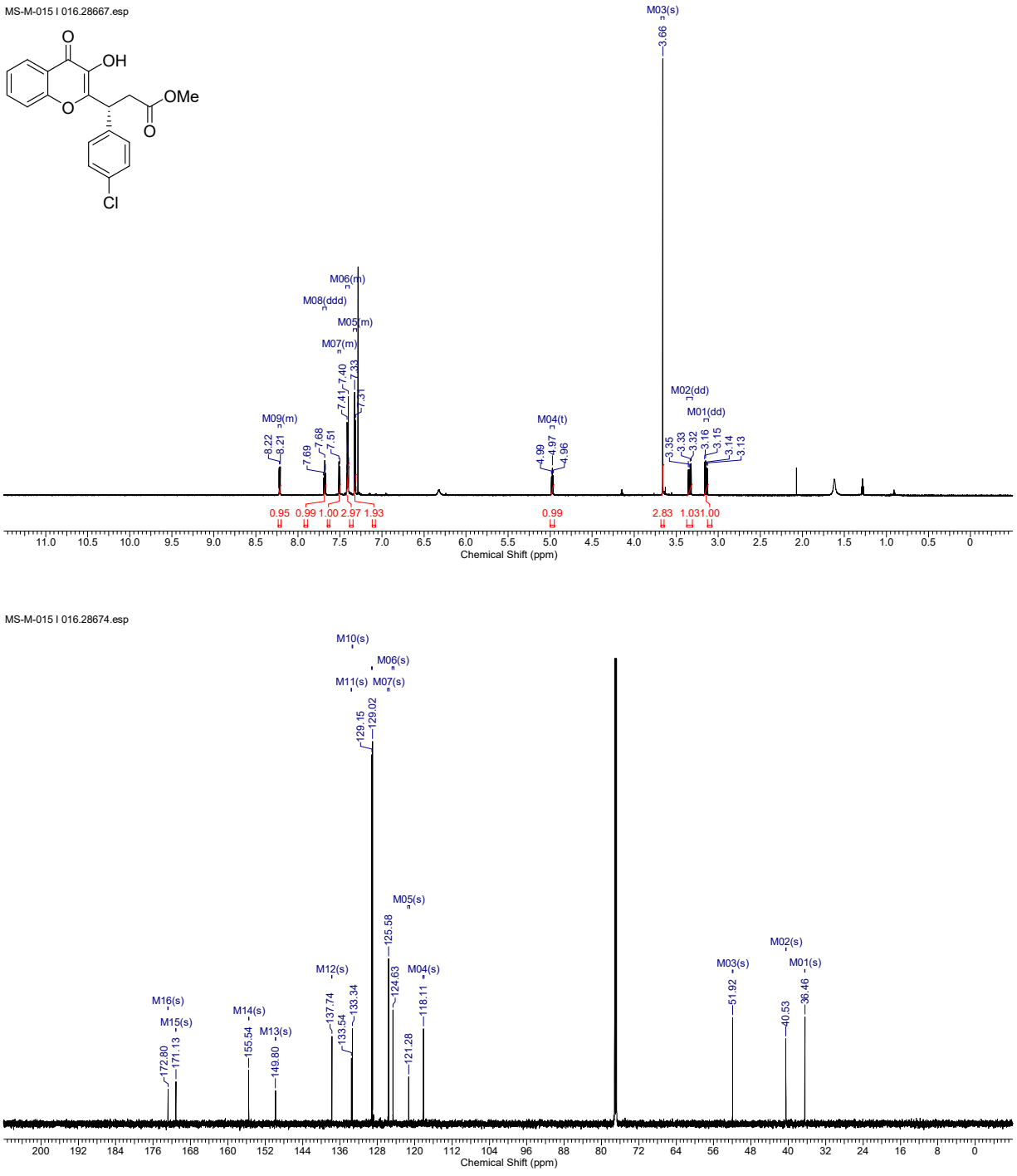
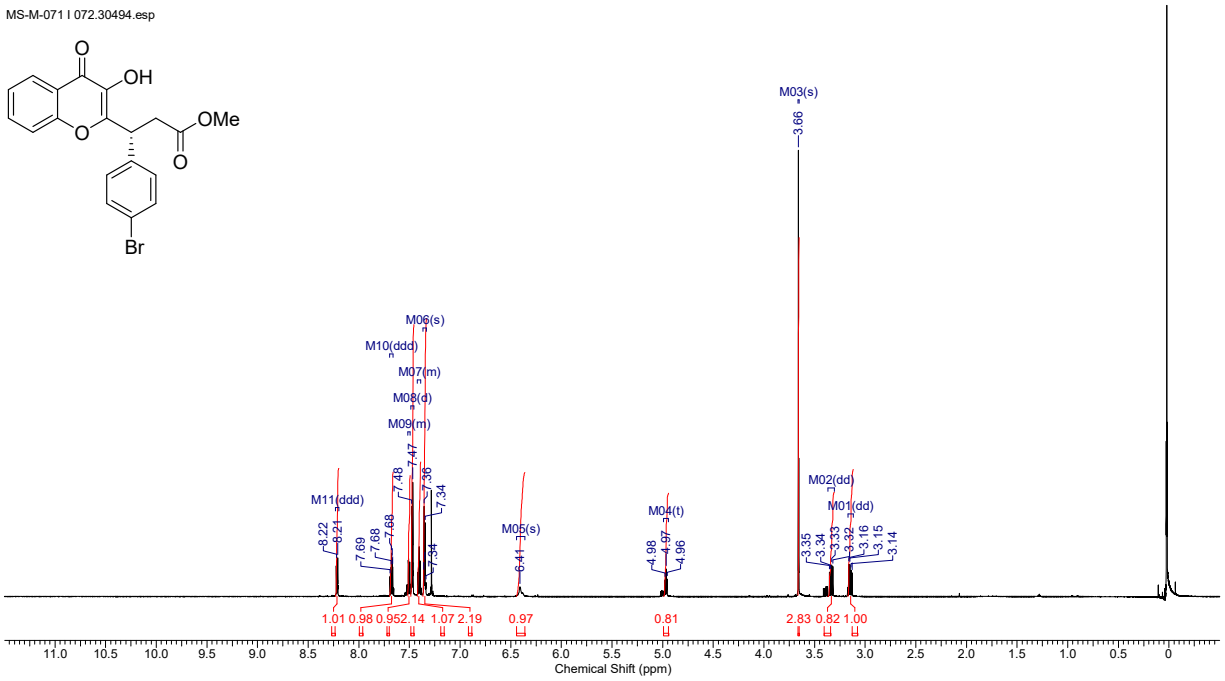


Figure S45. ^{1}H and ^{13}C NMR spectra of **3aca**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O
OH
O
OMe
O
Br
M03(s)
3.66
M06(s)
M10(ddd)
M07(m)
M08(d)
M09(m)
M11(ddd)
M05(s)
M04(t)
M02(dd)
M01(dd)
8.22
8.21
7.69
7.68
7.68
7.48
7.47
7.36
7.34
7.34
6.41
4.98
4.97
4.96
3.35
3.34
3.33
3.32
3.16
3.15
3.14
1.01 0.98 0.95 2.14 1.07 2.19
0.97
0.81
2.83 0.82 1.00
11.0 10.5 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)

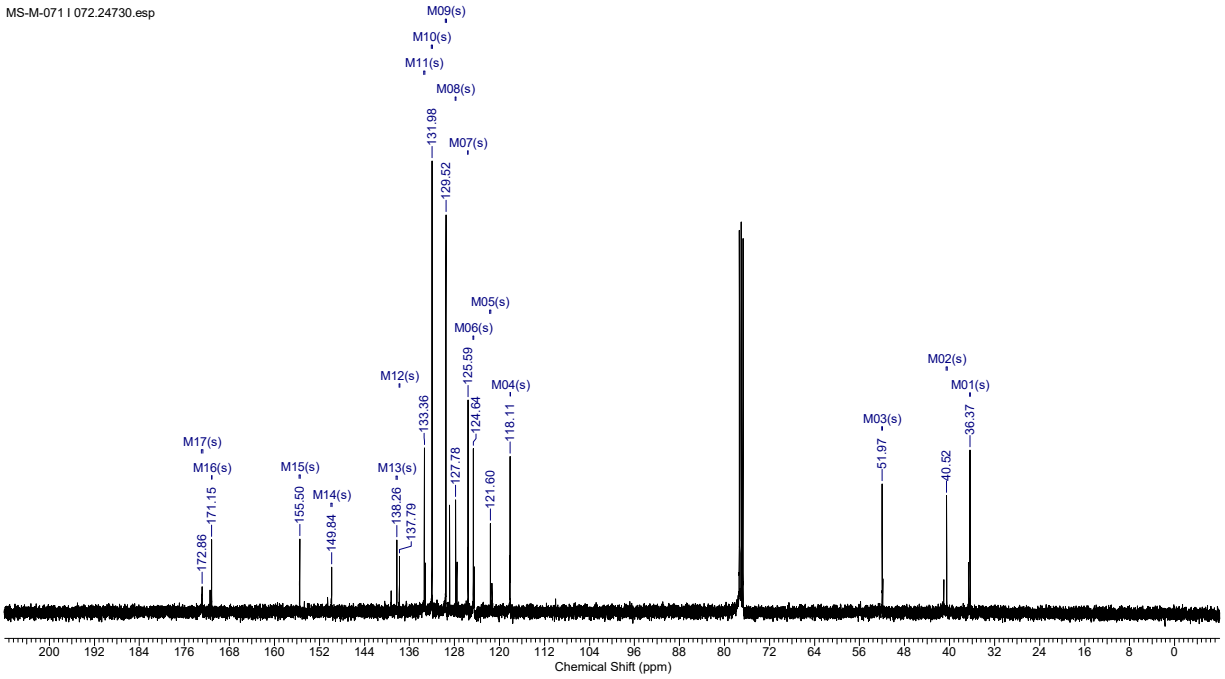


Figure S46. ^{1}H and ^{13}C NMR spectra of **3ada**

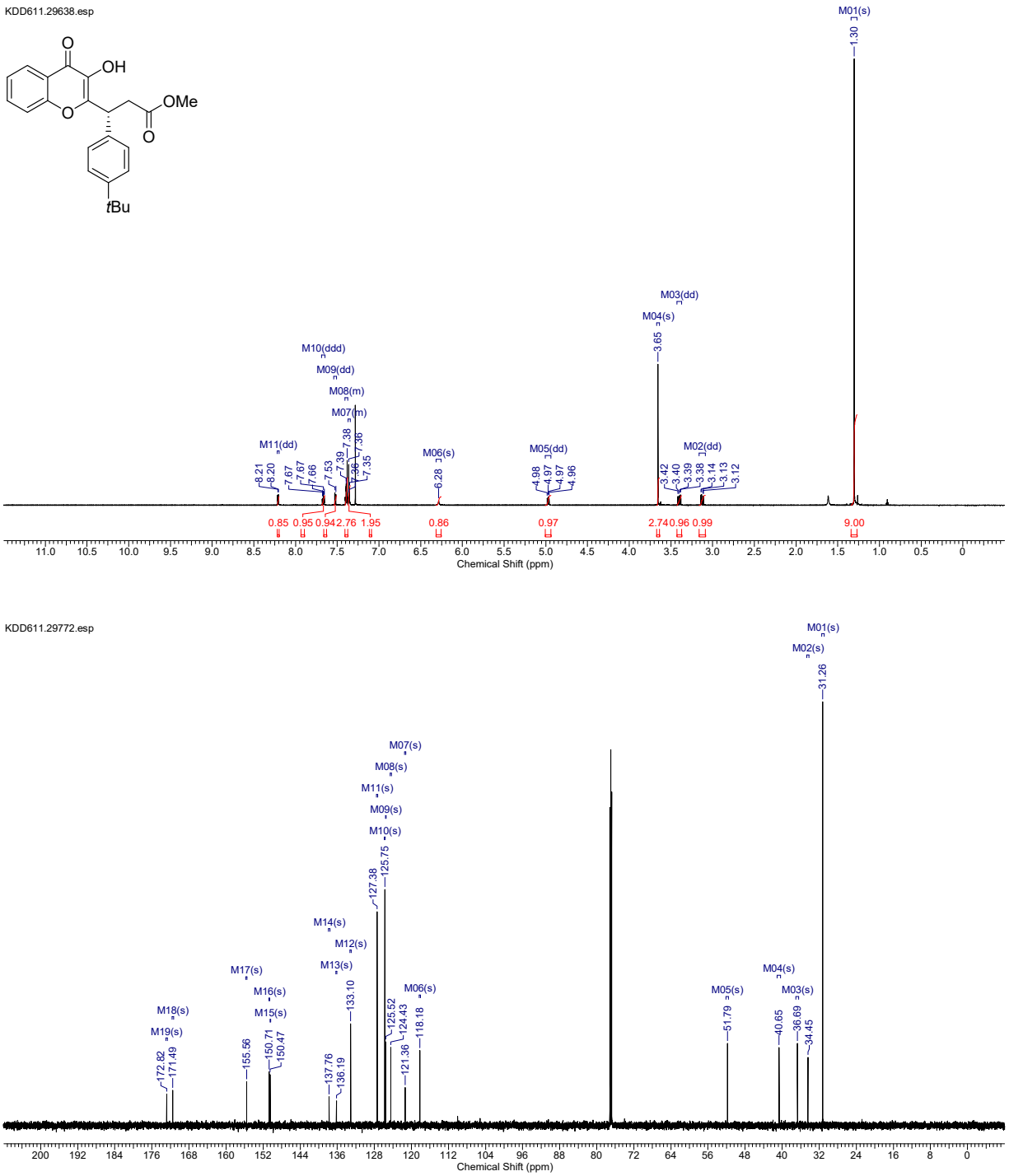


Figure S47. ^{1}H and ^{13}C NMR spectra of **3aea**

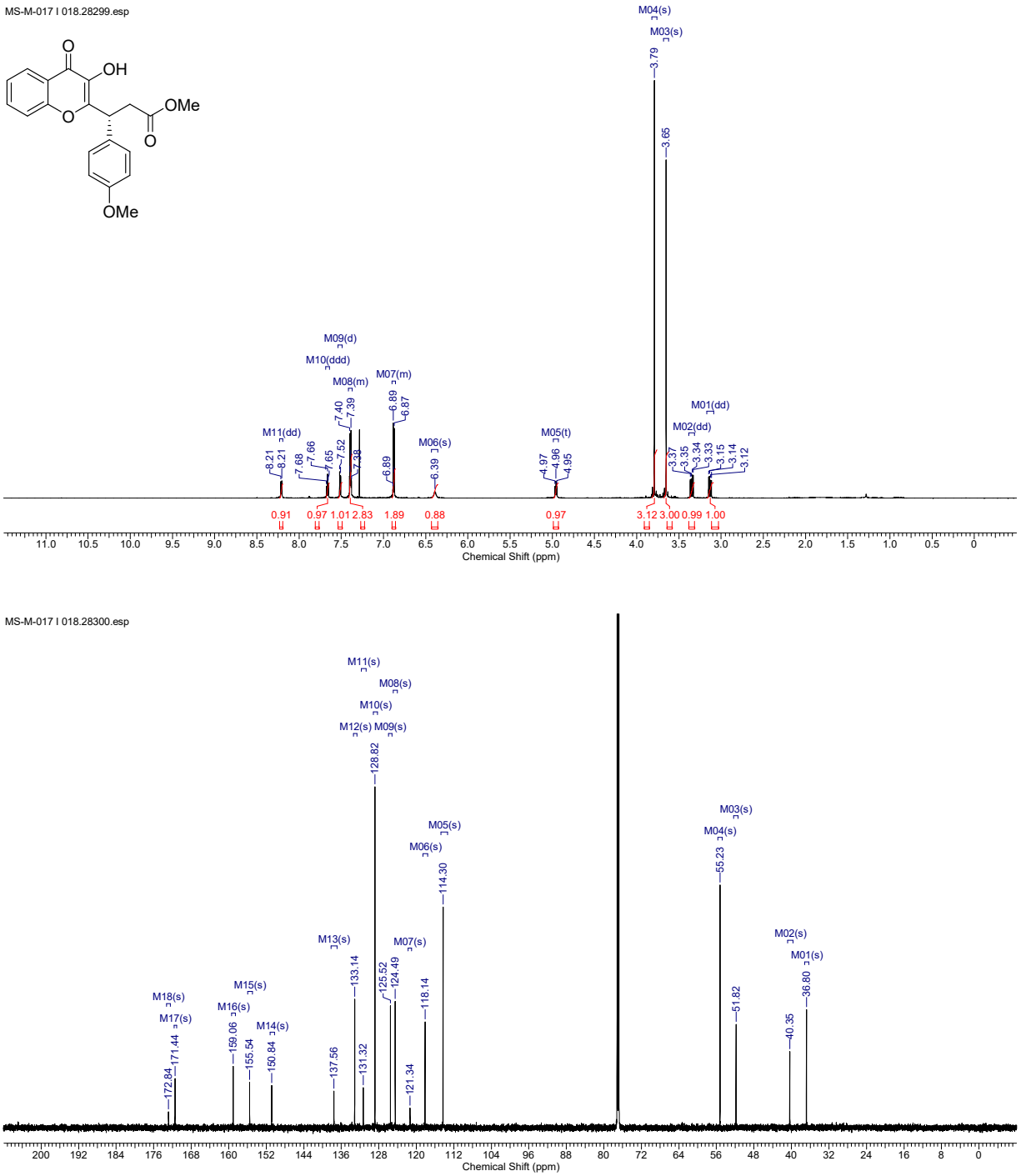


Figure S48. ^{1}H and ^{13}C NMR spectra of **3afa**

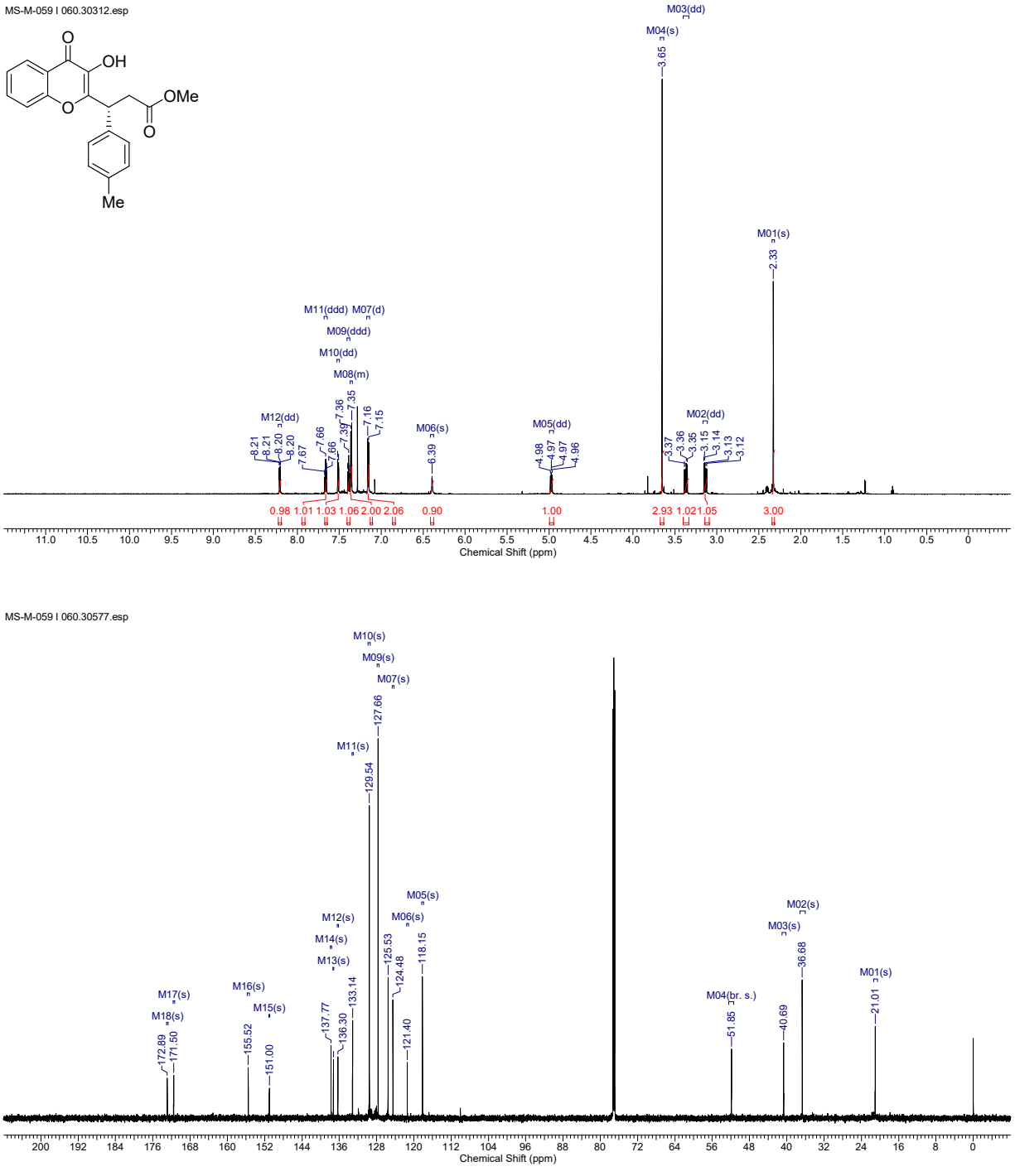


Figure S49. ^{1}H and ^{13}C NMR spectra of **3aga**

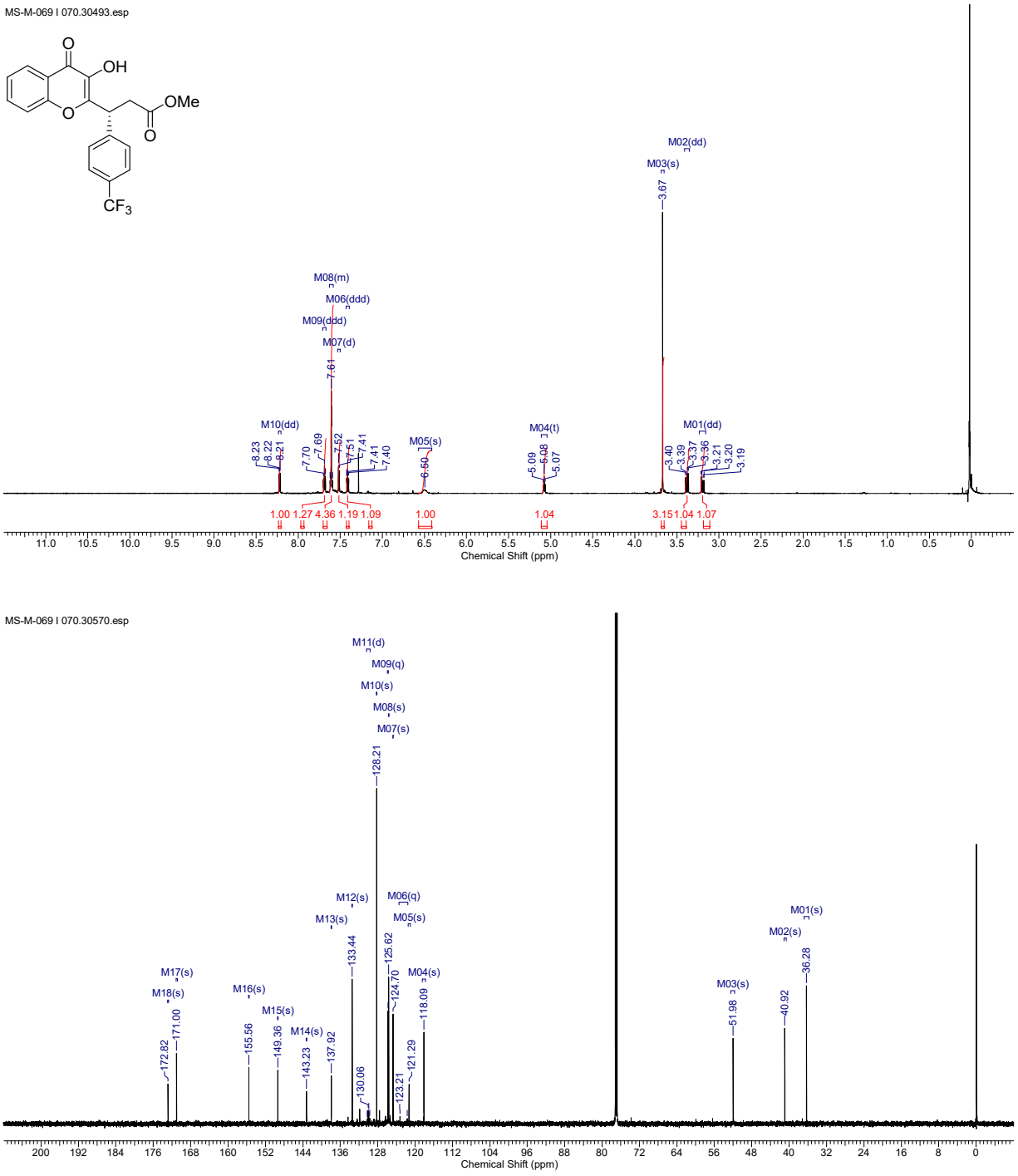


Figure S50. ^{1}H and ^{13}C NMR spectra of **3aha**

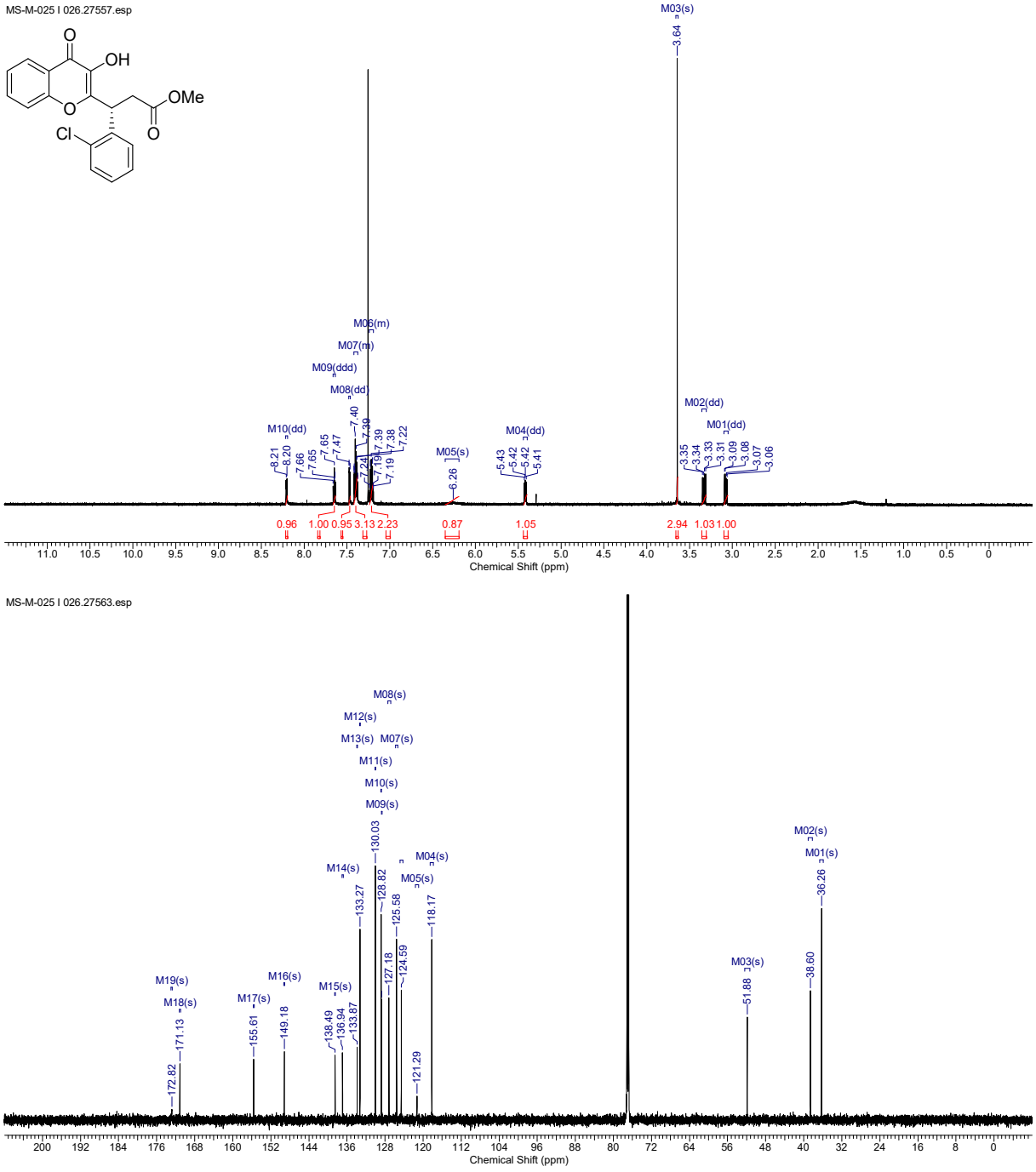


Figure S51. ^{1}H and ^{13}C NMR spectra of **3aia**

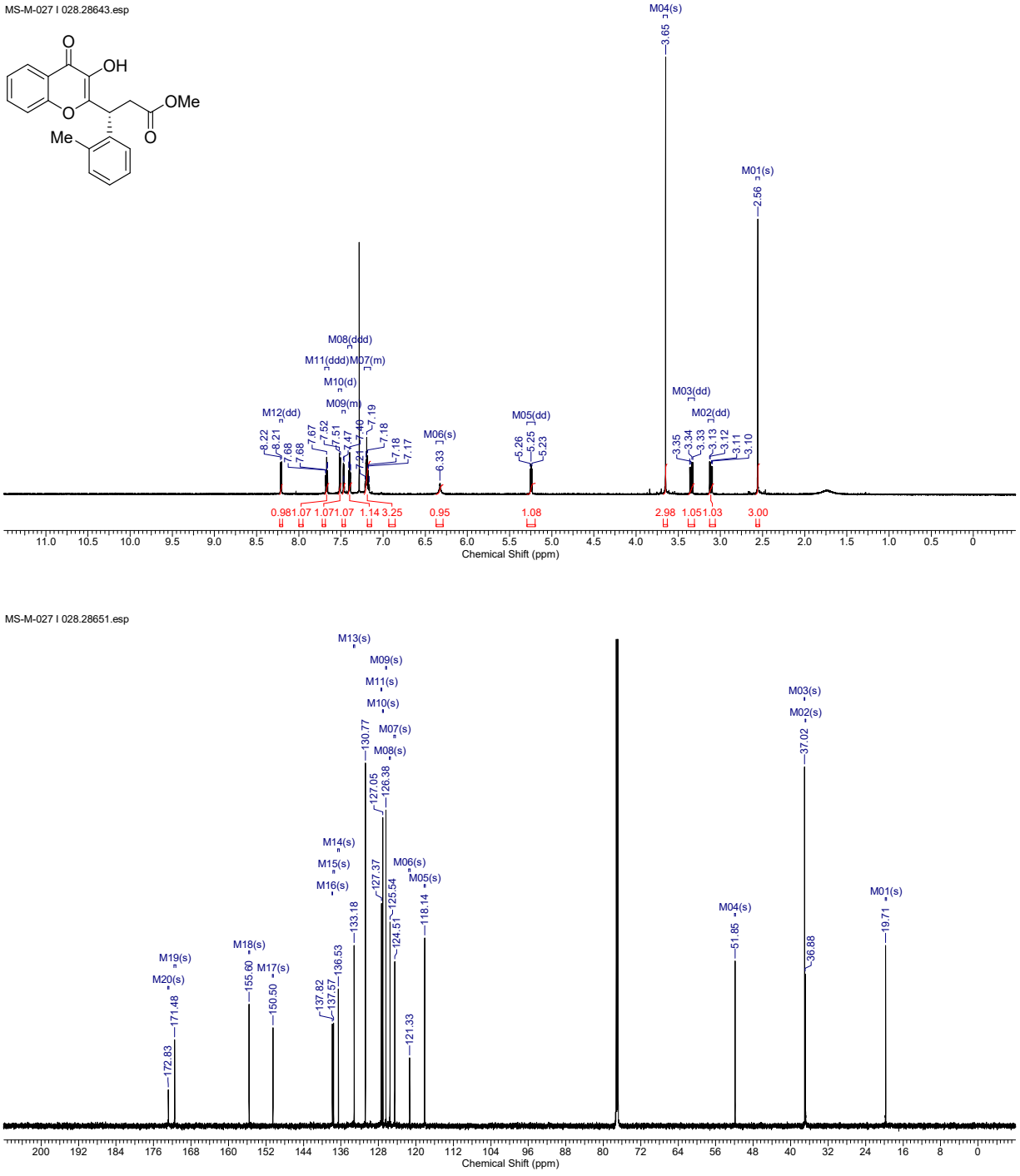


Figure S52. ^{1}H and ^{13}C NMR spectra of **3aja**

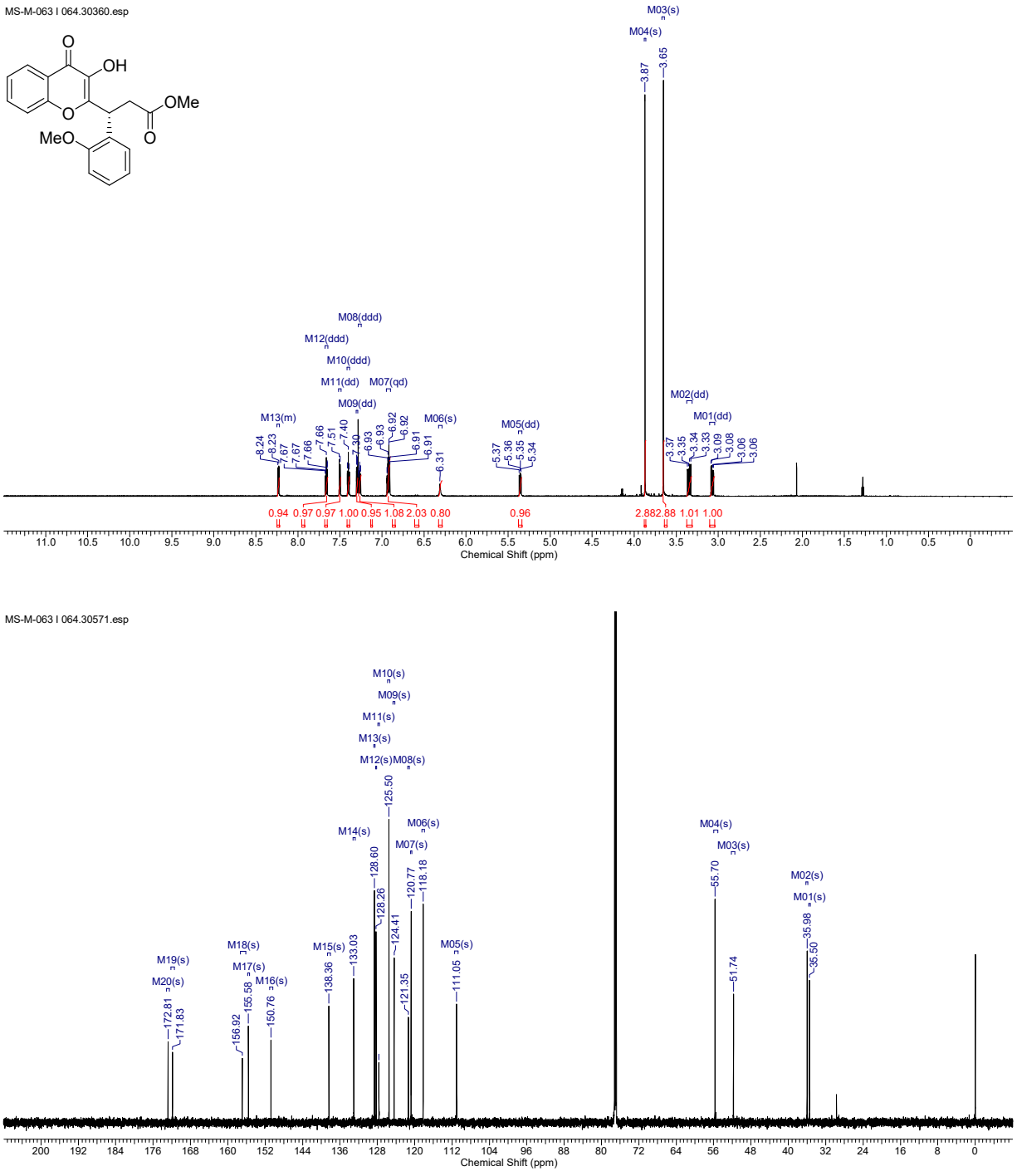
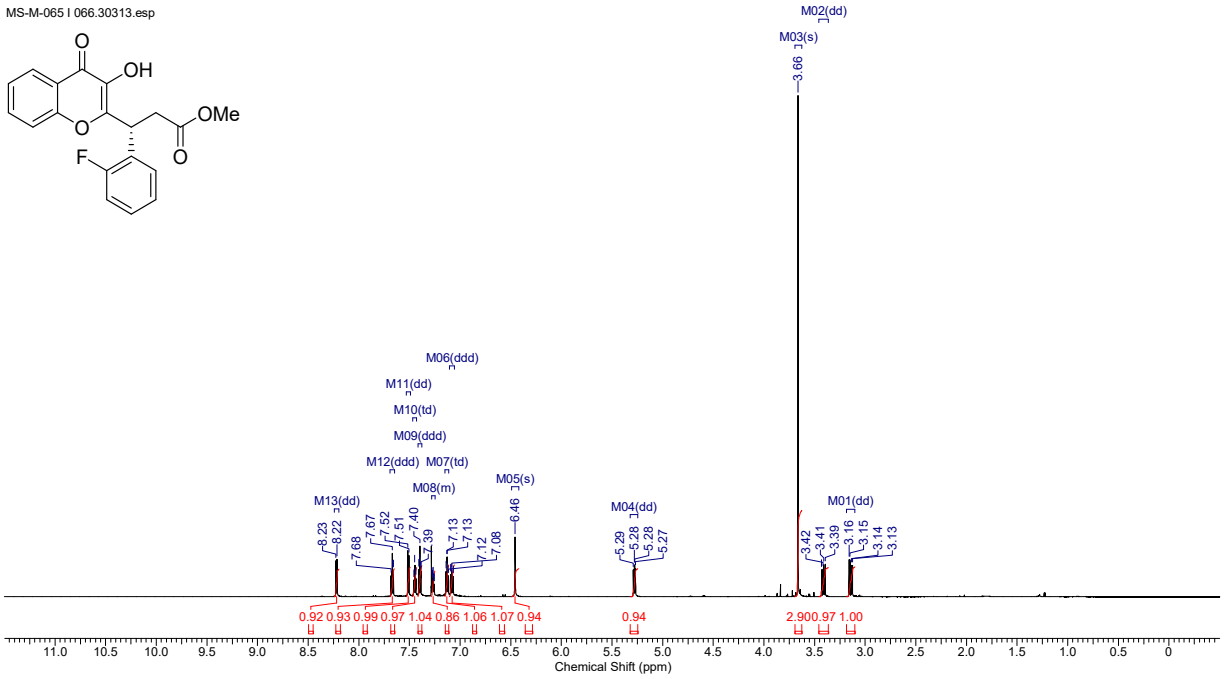


Figure S53. ^{1}H and ^{13}C NMR spectra of **3aka**


MS-M-065 I 066.30313.esp
O
OH
O
OMe
O
F
M02(dd)
M03(s)
3.66
M06(ddd)
M11(dd)
M10(td)
M09(ddd)
M12(ddd)
M07(td)
M08(m)
M05(s)
M13(dd)
M04(dd)
M01(dd)
8.23
8.22
7.68
7.67
7.52
7.51
7.40
7.39
7.13
7.13
7.12
7.08
6.46
5.29
5.28
5.28
5.27
3.42
3.41
3.39
3.16
3.15
3.14
3.13
0.92 0.93 0.99 0.97 1.04 0.86 1.06 1.07 0.94
0.94
2.90 0.97 1.00
11.0 10.5 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)

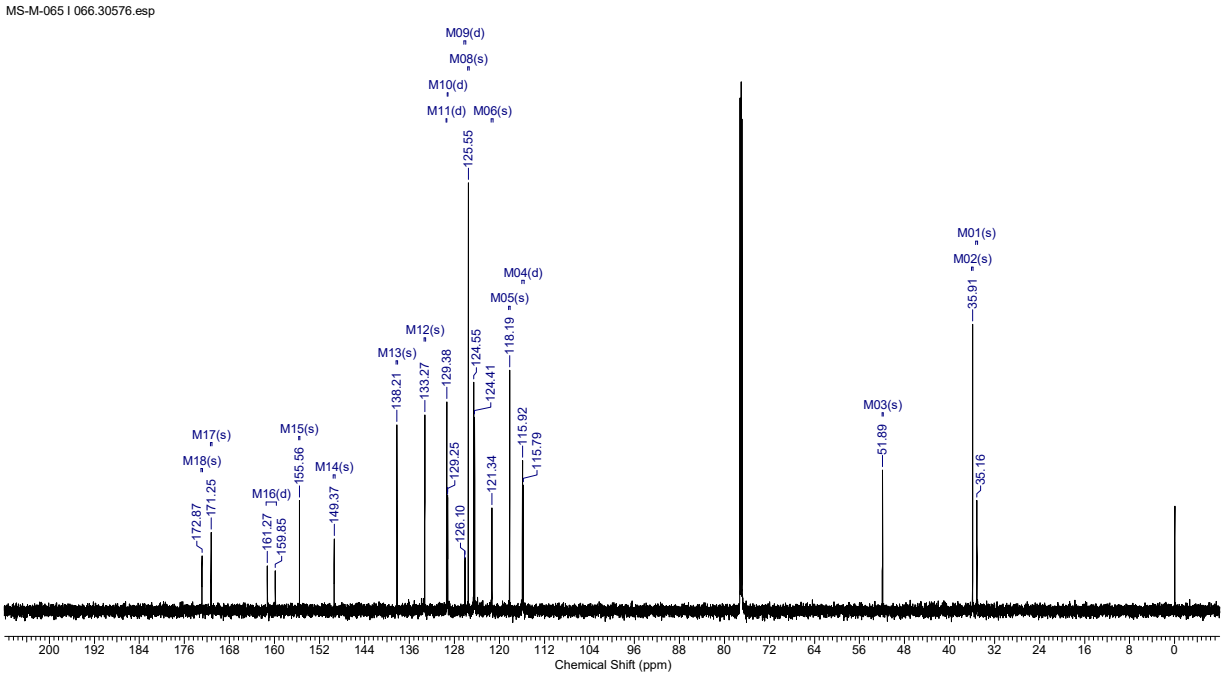


Figure S54. ^{1}H and ^{13}C NMR spectra of **3ala**

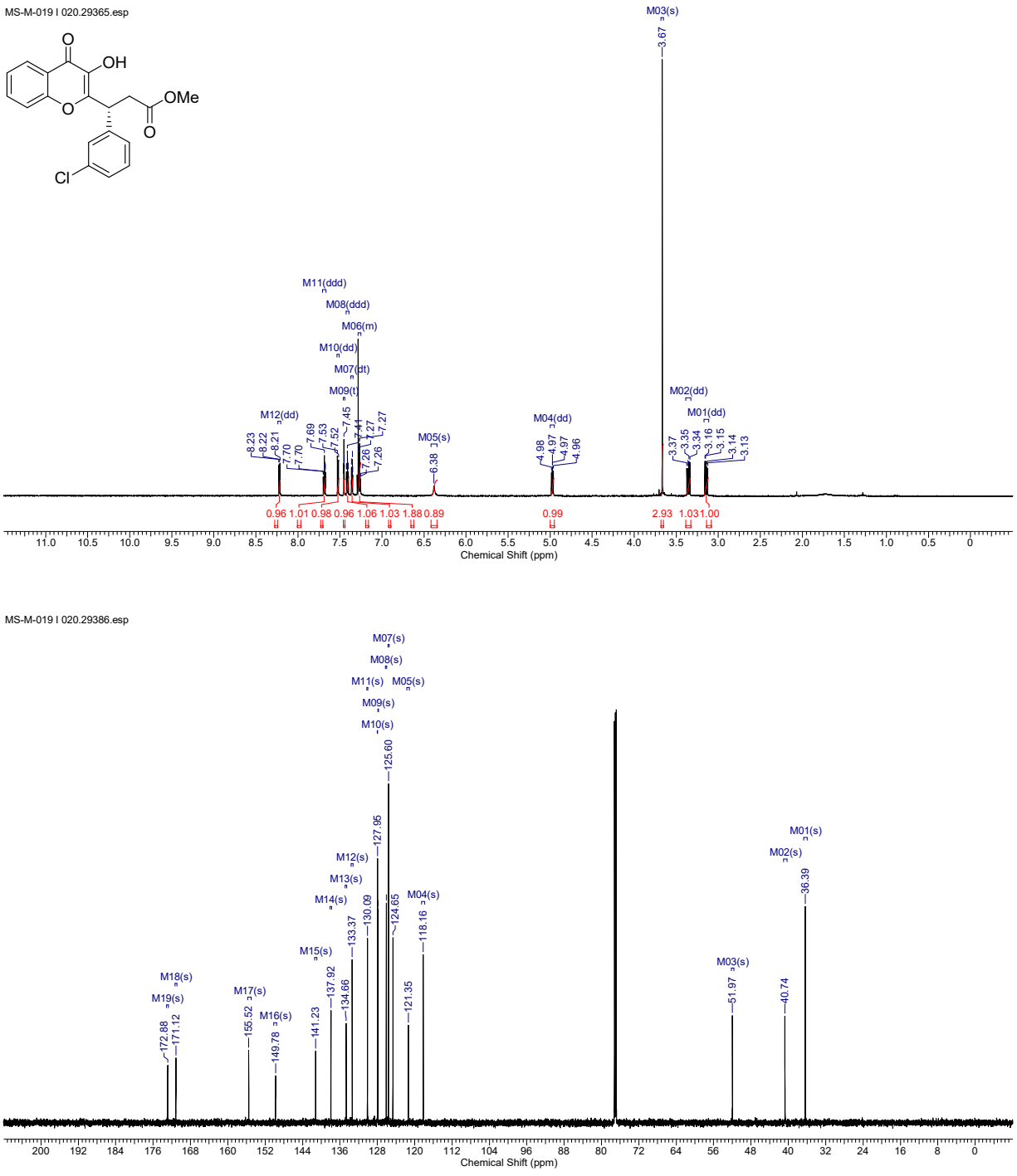


Figure S55. ^{1}H and ^{13}C NMR spectra of **3ama**

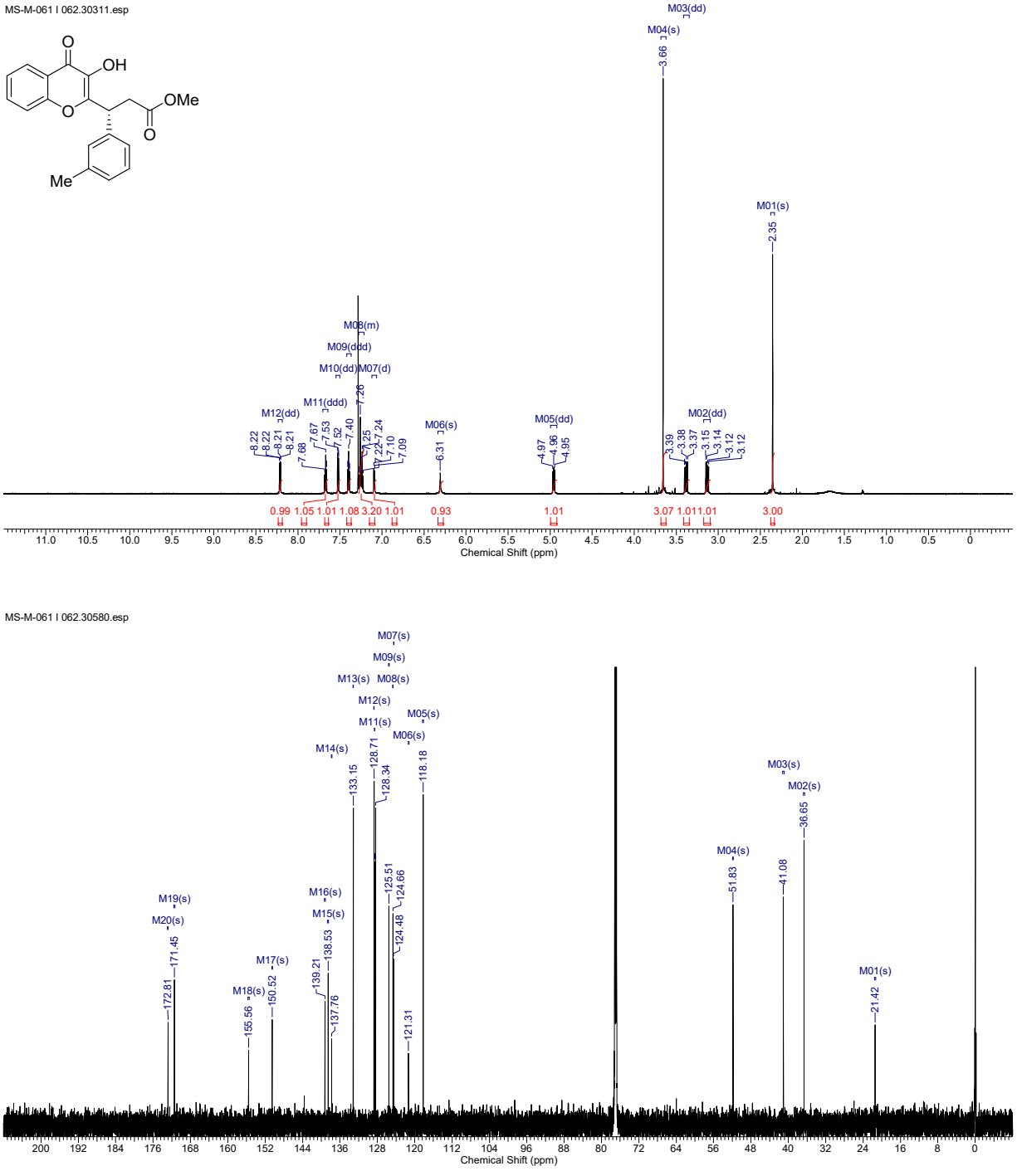


Figure S56. ^{1}H and ^{13}C NMR spectra of **3ana**

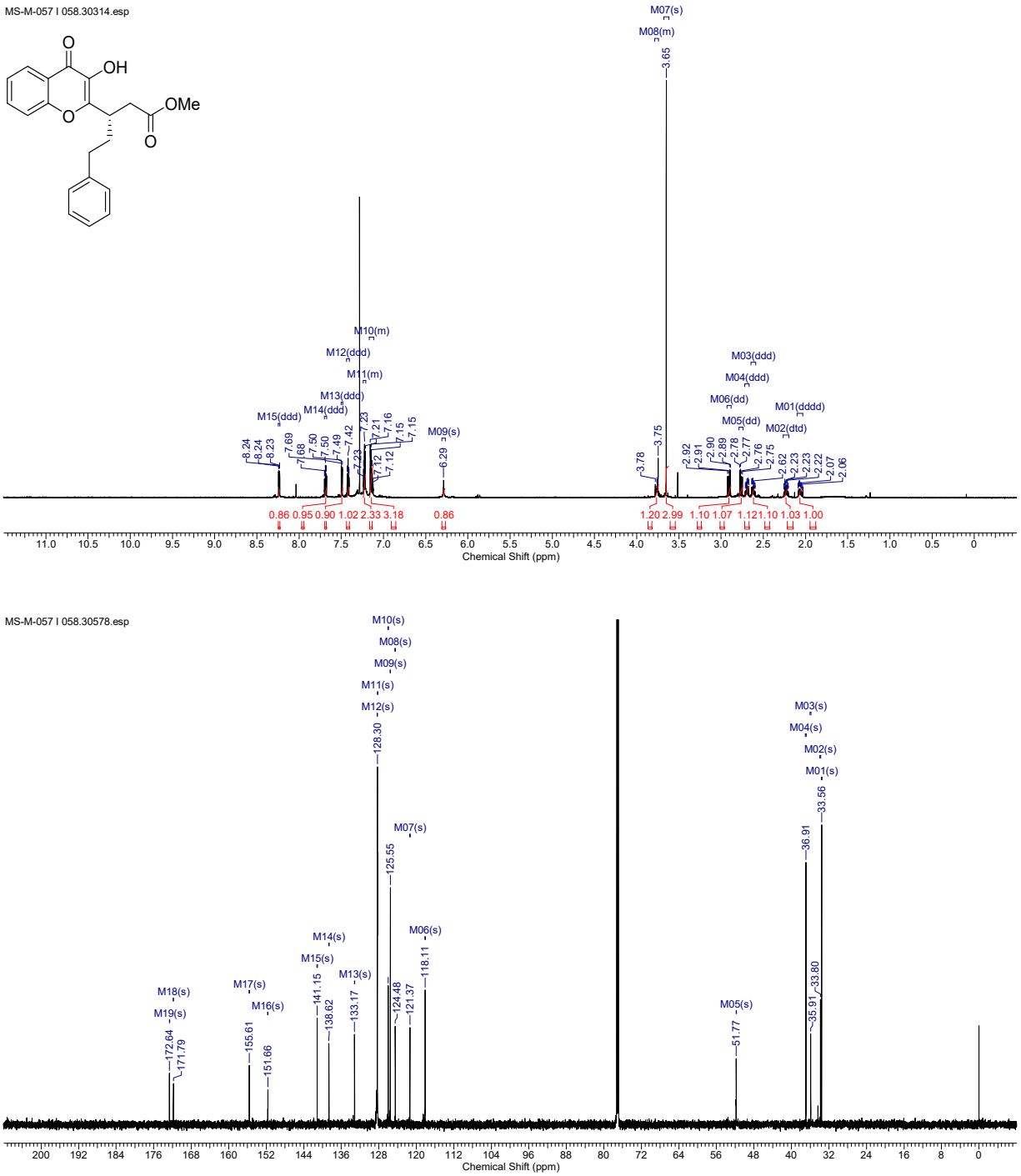


Figure S57. ^{1}H and ^{13}C NMR spectra of **3aoa**

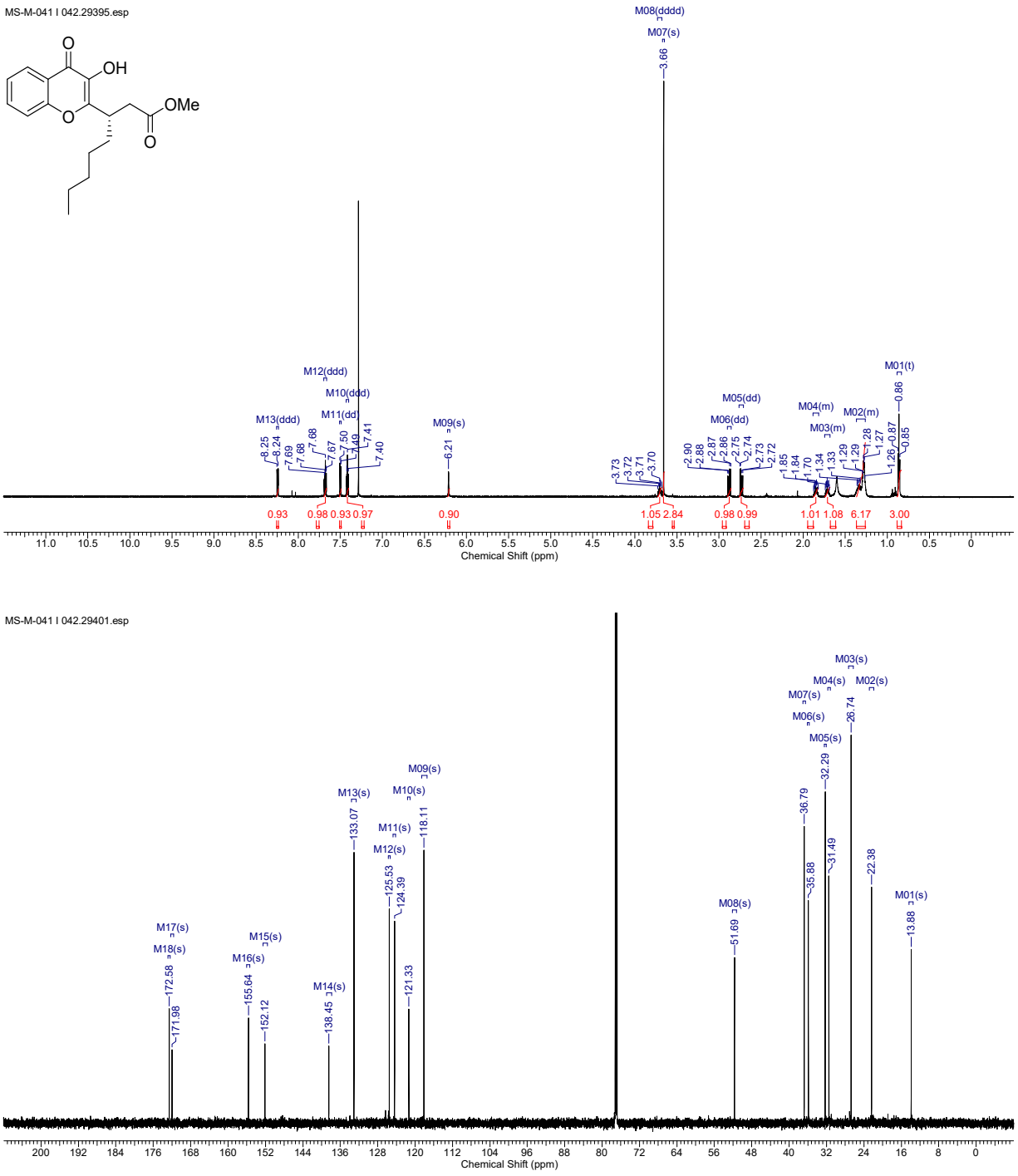


Figure S58. ^{1}H and ^{13}C NMR spectra of **3apa**

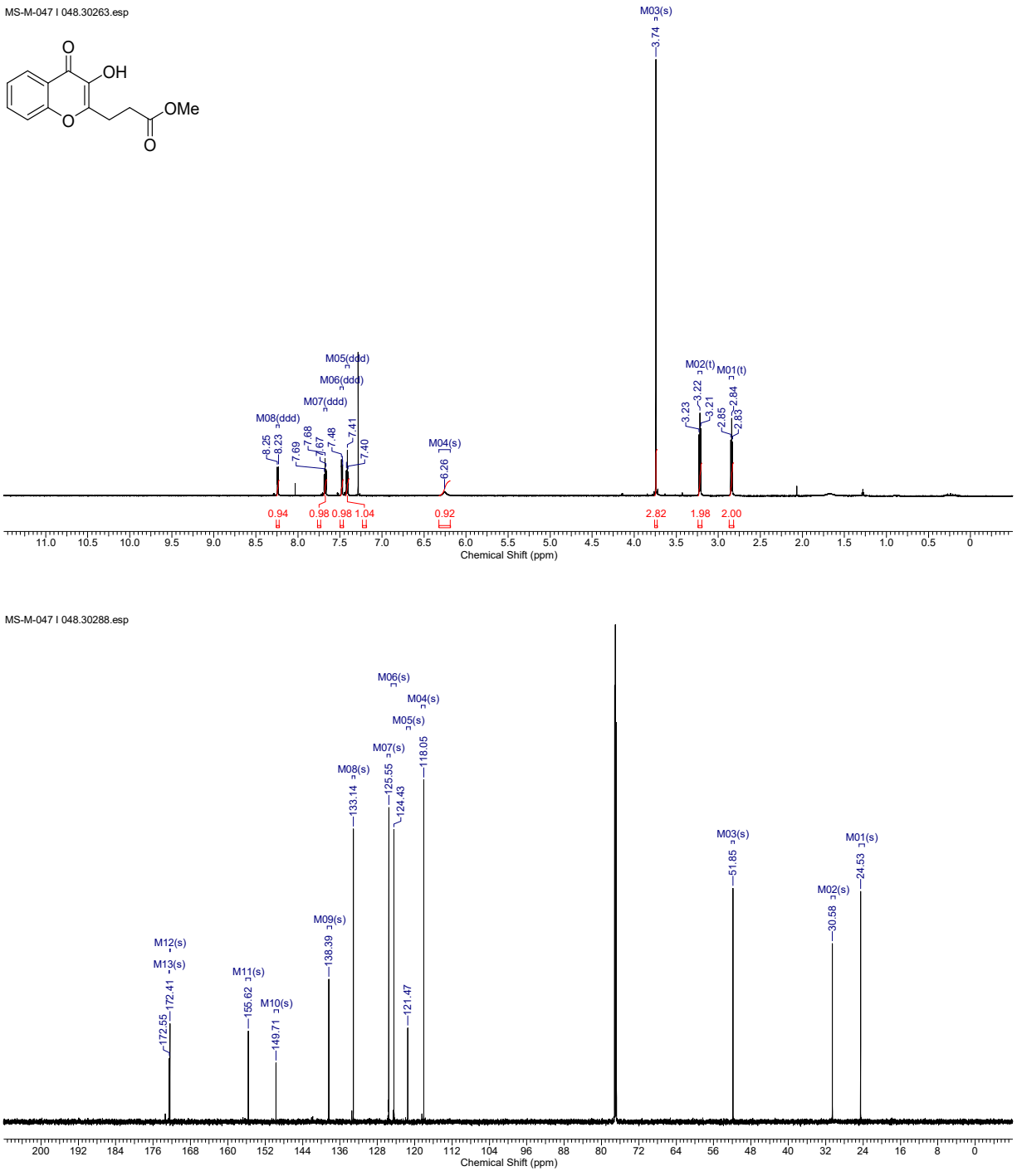


Figure S59. ^{1}H and ^{13}C NMR spectra of **3aqa**

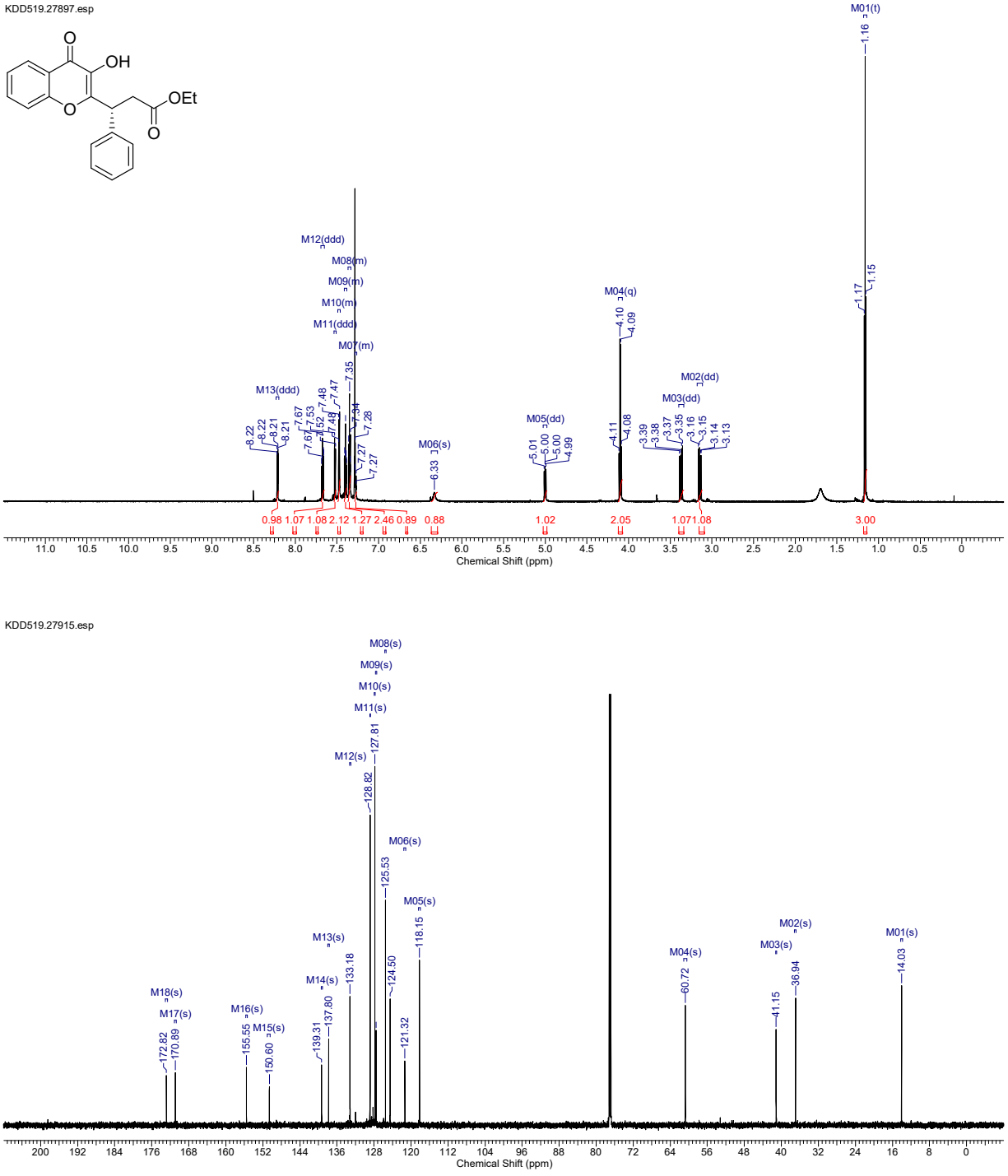


Figure S60. ^{1}H and ^{13}C NMR spectra of **3aab**

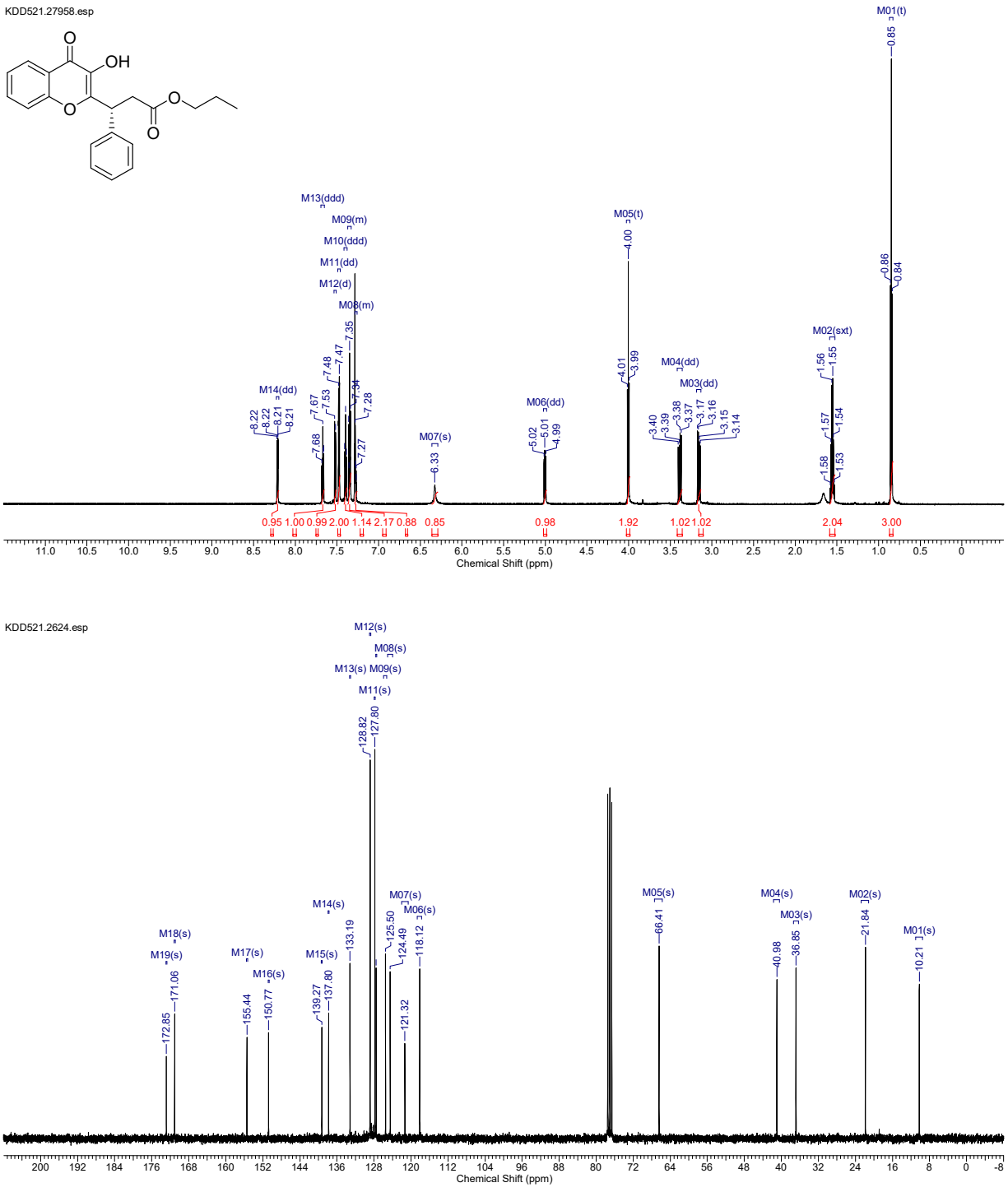


Figure S61. ^{1}H and ^{13}C NMR spectra of **3aac**

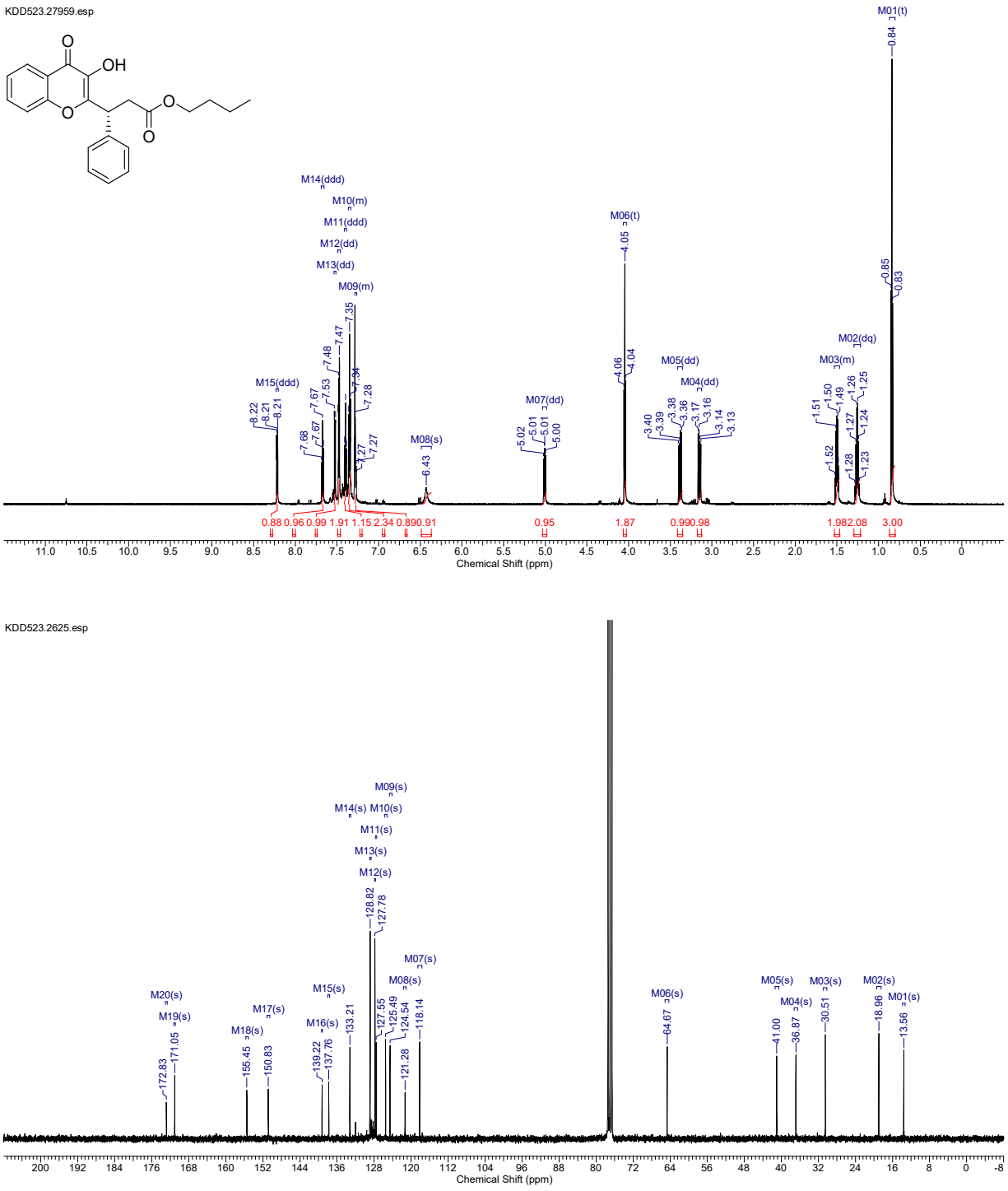


Figure S62. ^{1}H and ^{13}C NMR spectra of **3aad**

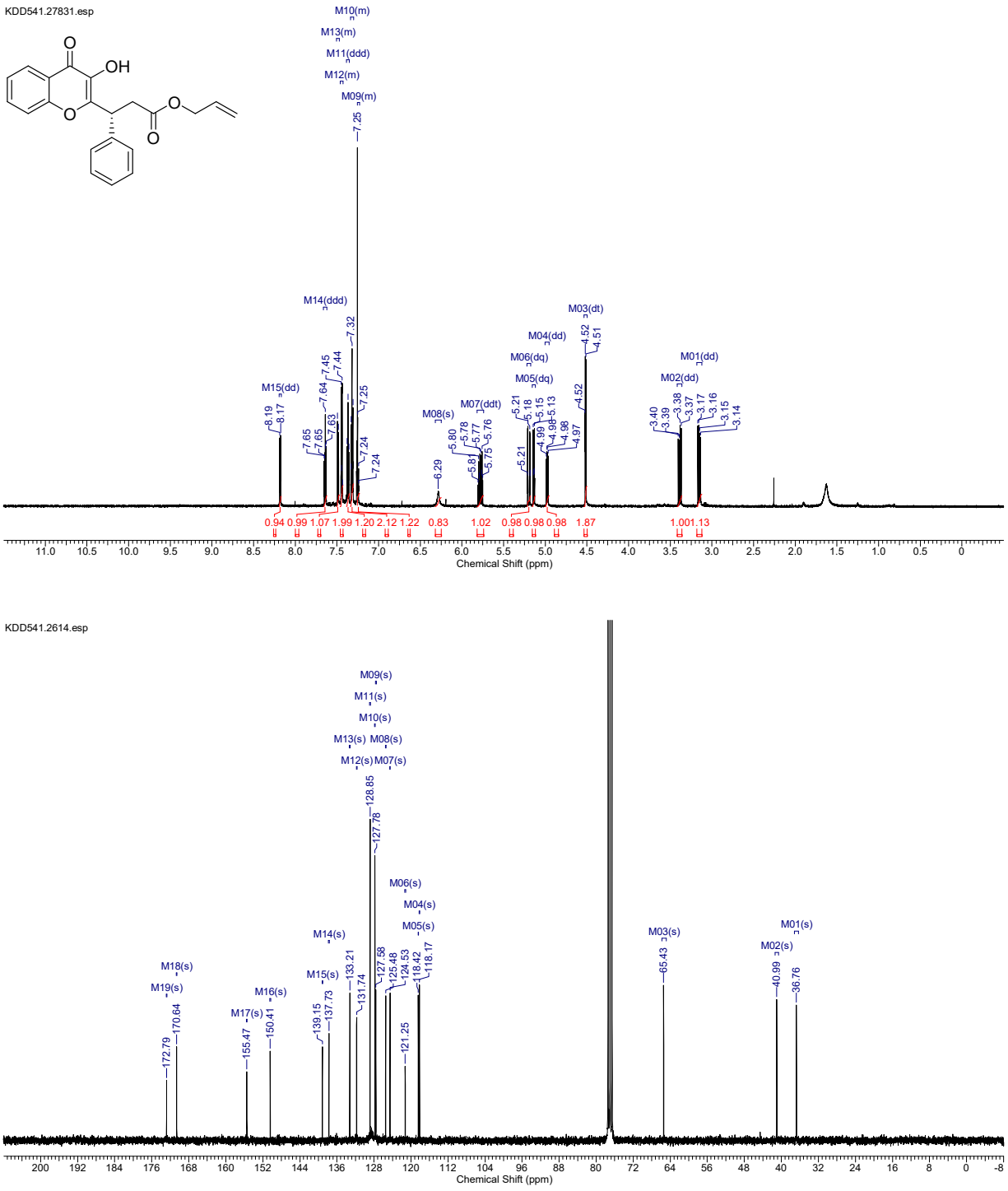


Figure S63. ^{1}H and ^{13}C NMR spectra of **3aae**

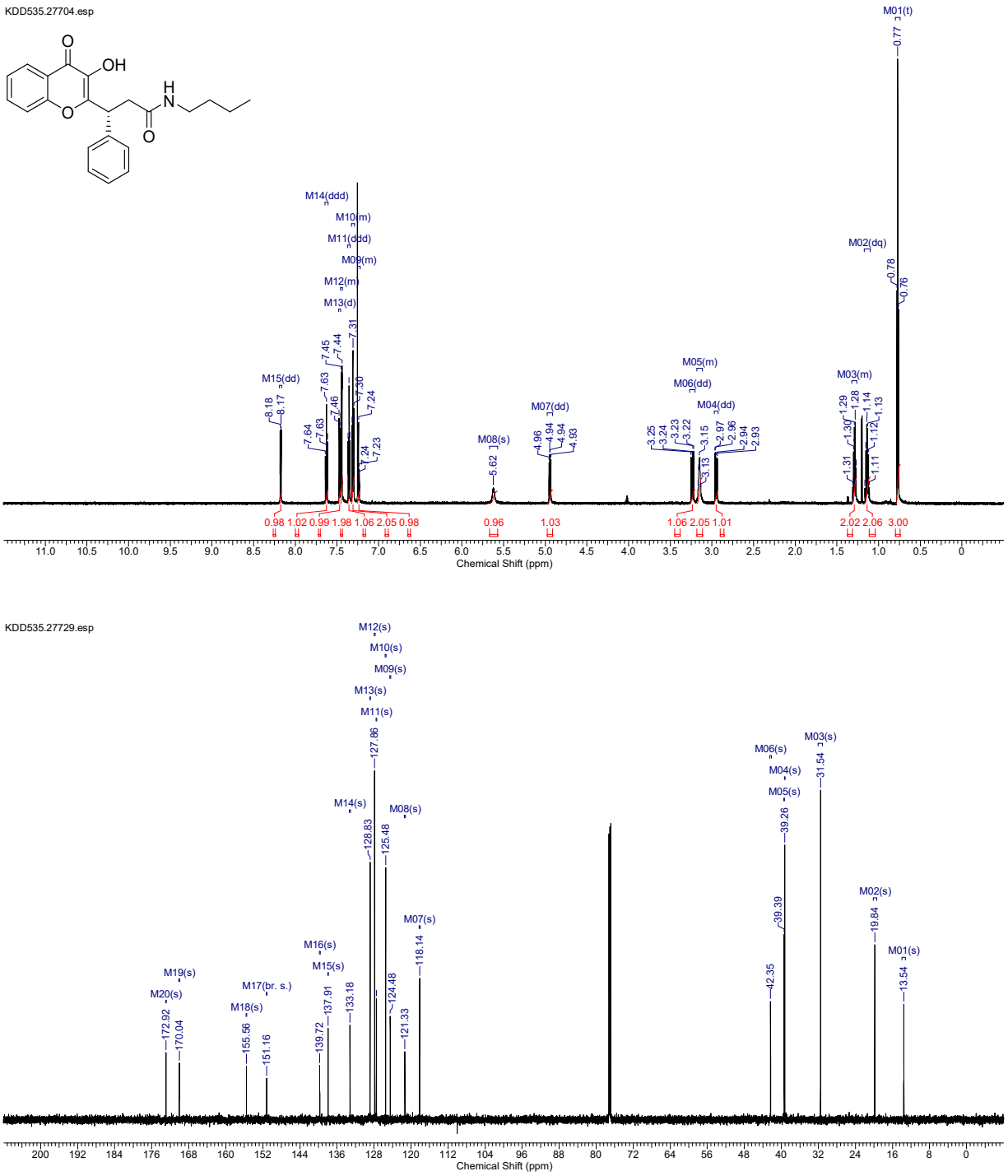


Figure S64. ^{1}H and ^{13}C NMR spectra of **3aaf**

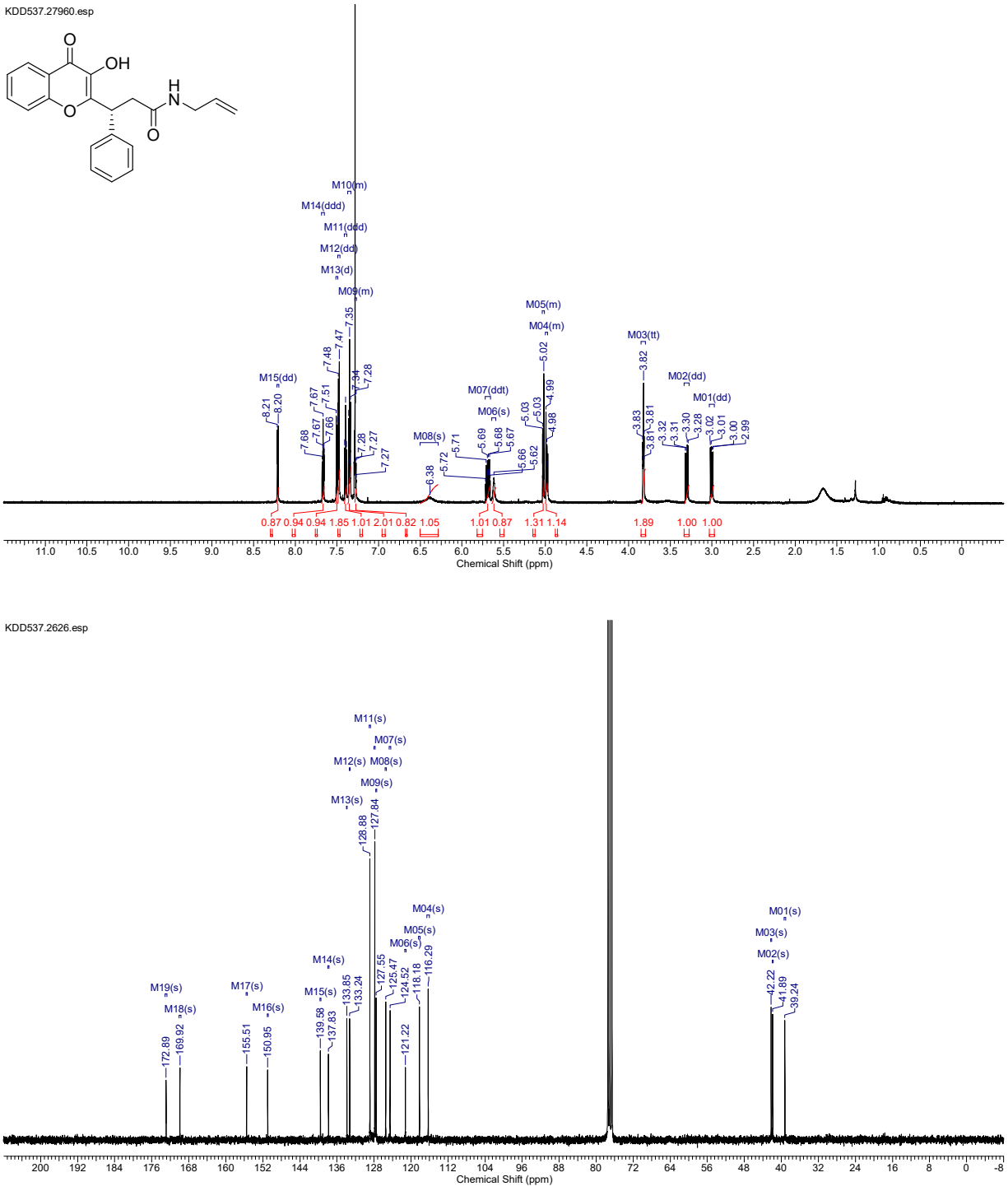


Figure S65. ^{1}H and ^{13}C NMR spectra of **3aag**

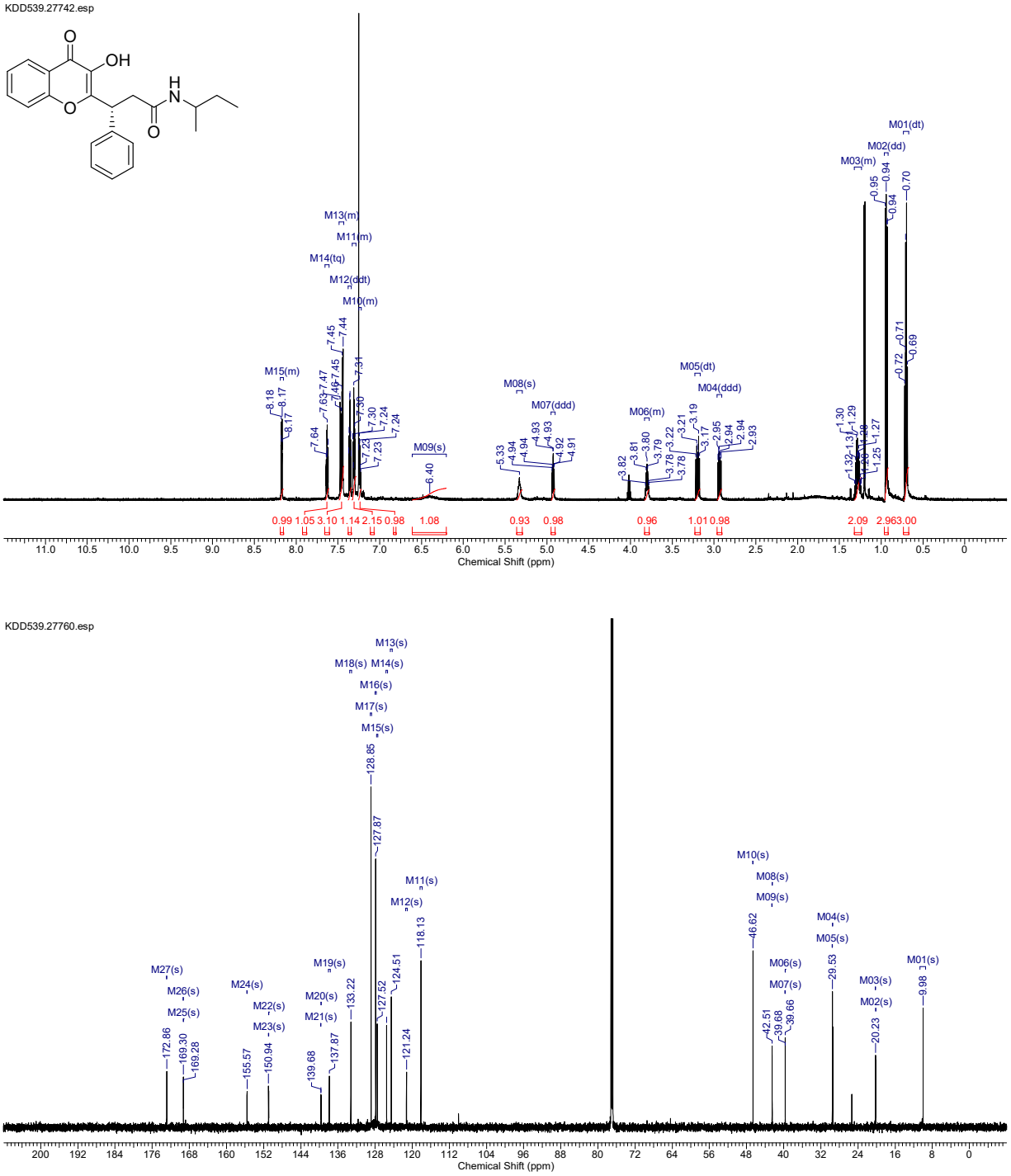


Figure S66. ^{1}H and ^{13}C NMR spectra of **3aah**

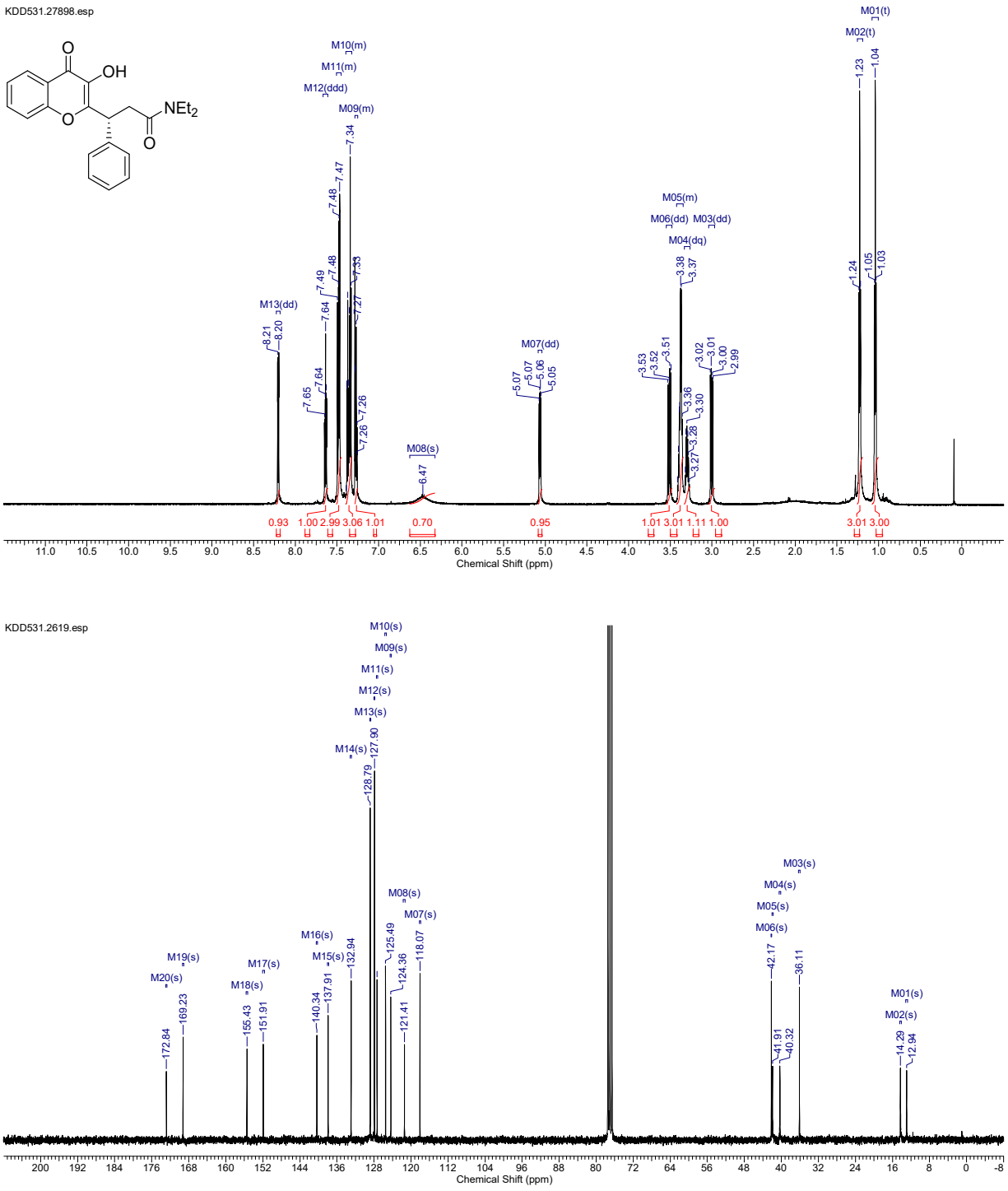


Figure S67. ^{1}H and ^{13}C NMR spectra of **3aai**

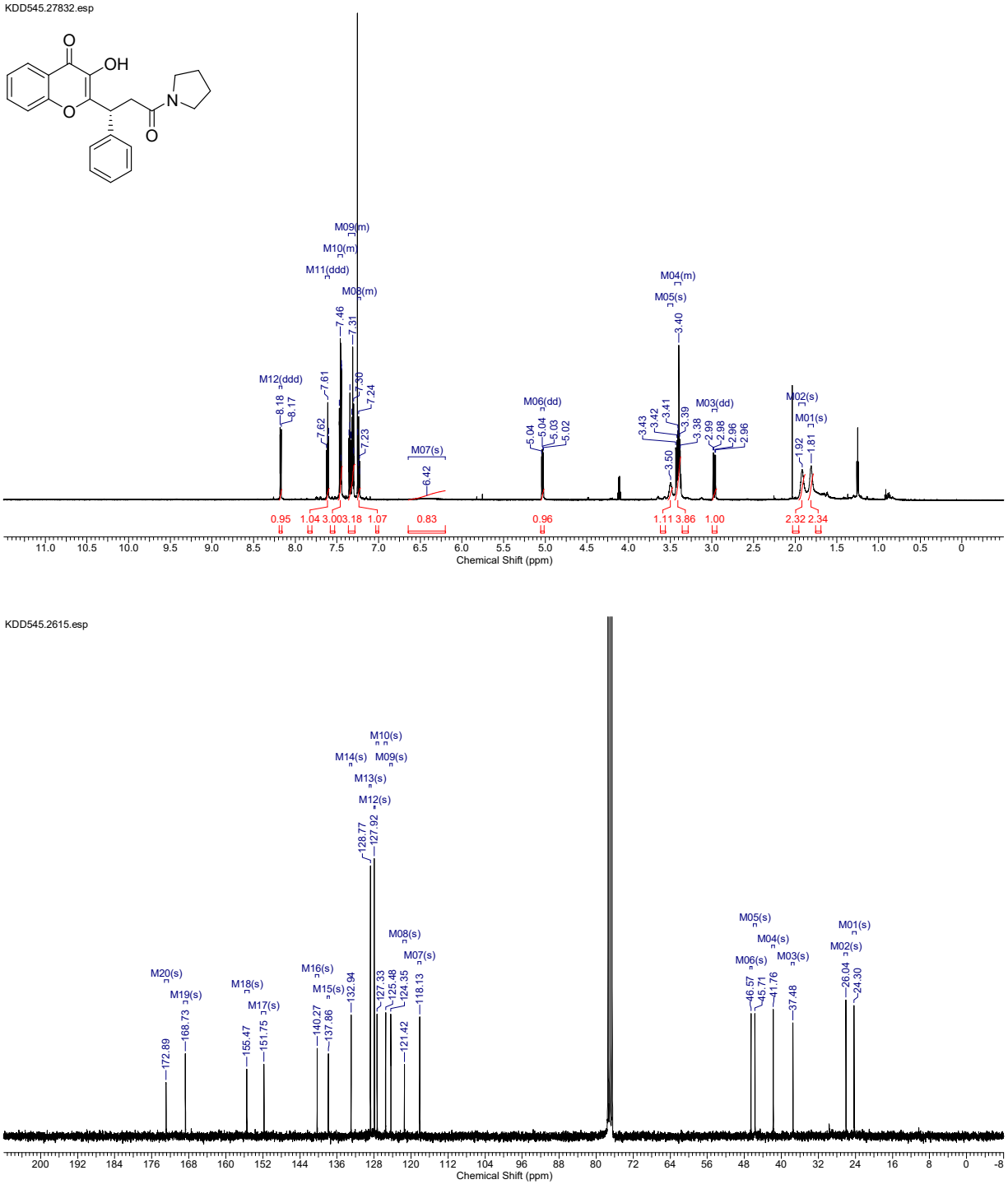


Figure S68. ^{1}H and ^{13}C NMR spectra of **3aaj**

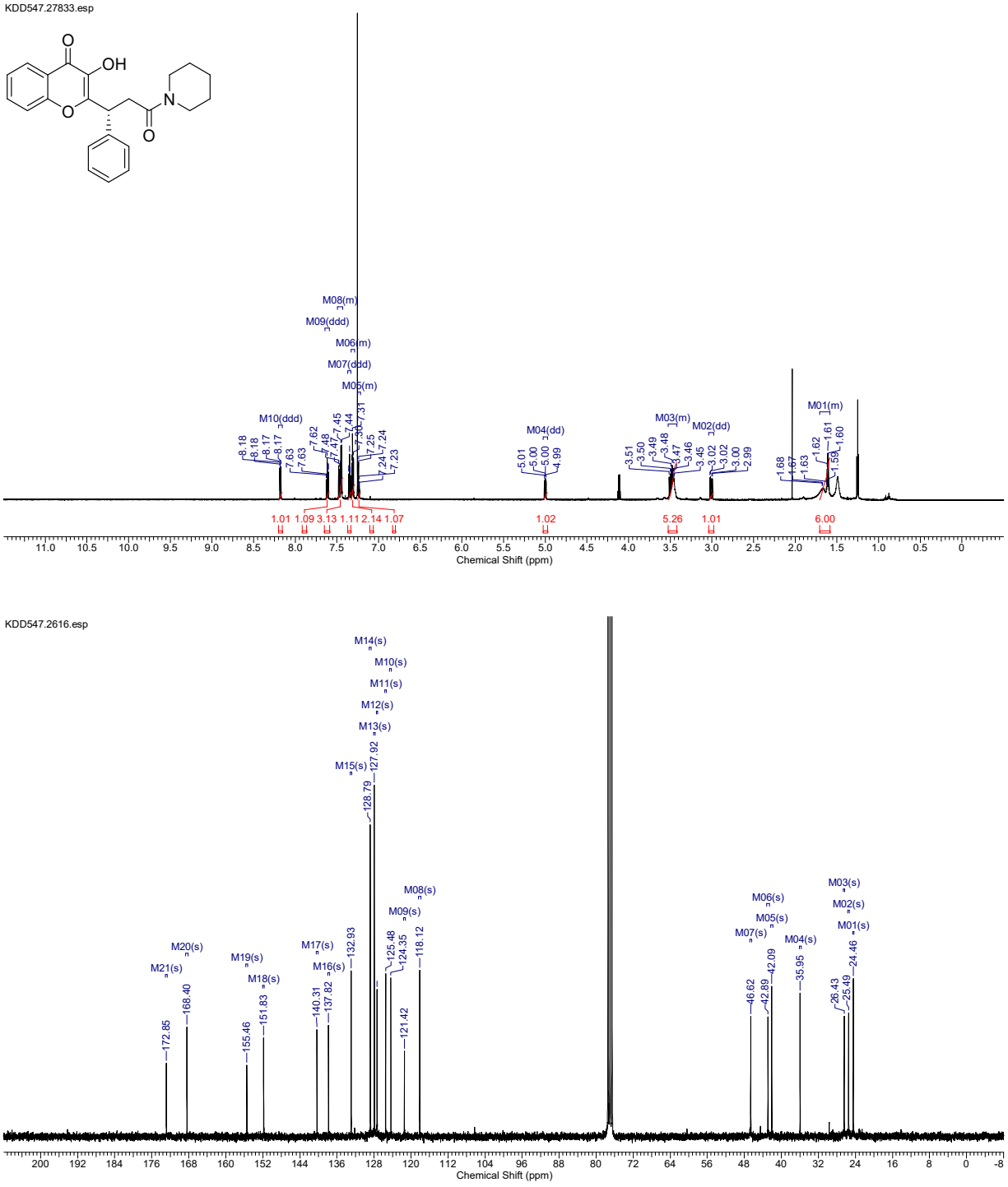
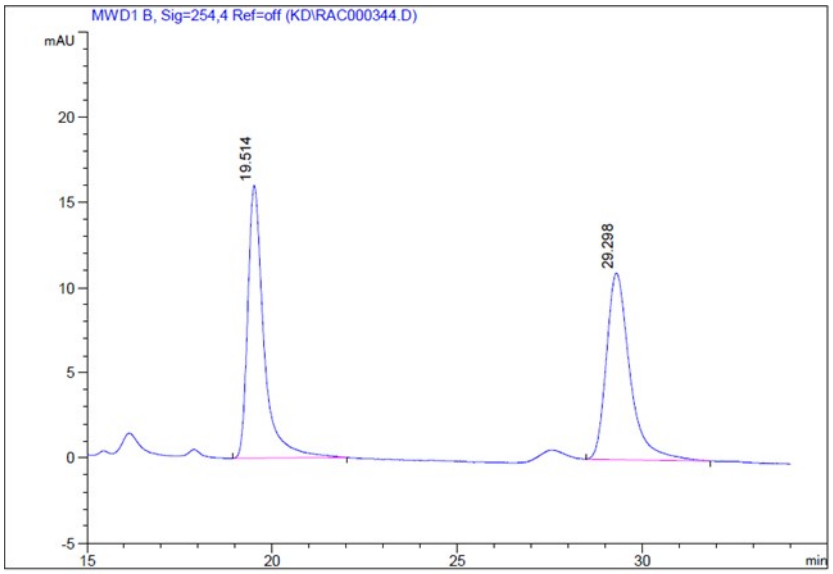
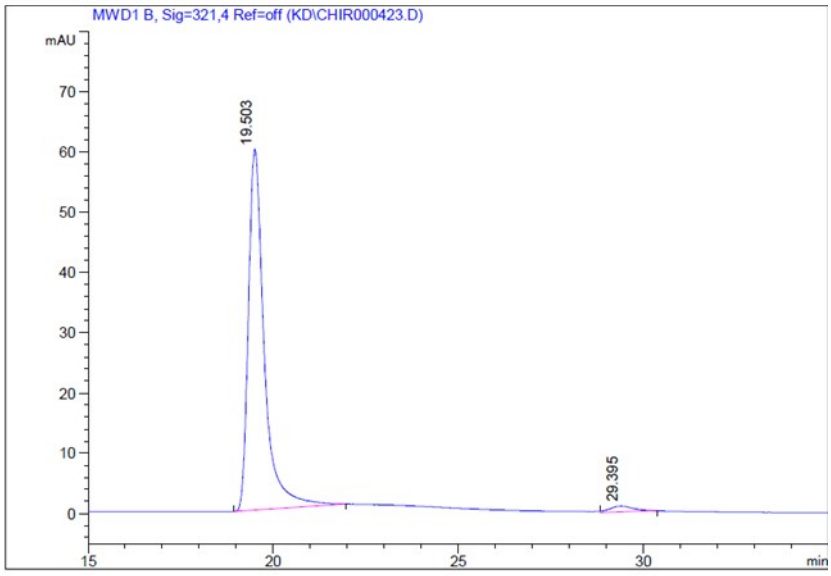


Figure S69. ^{1}H and ^{13}C NMR spectra of **3aak**

5. HPLC Chromatograms

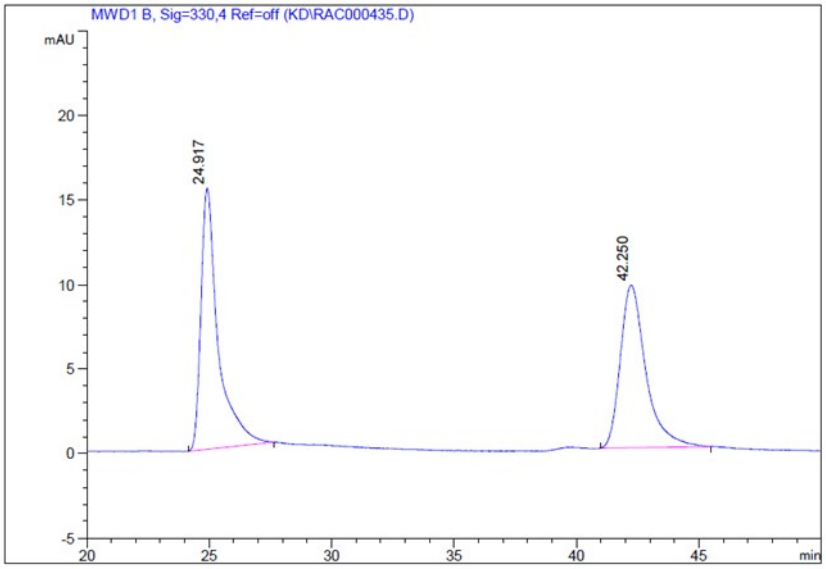


#	Meas. R	Area	Area %
1	19.514	487.202	50.126
2	29.298	484.743	49.874

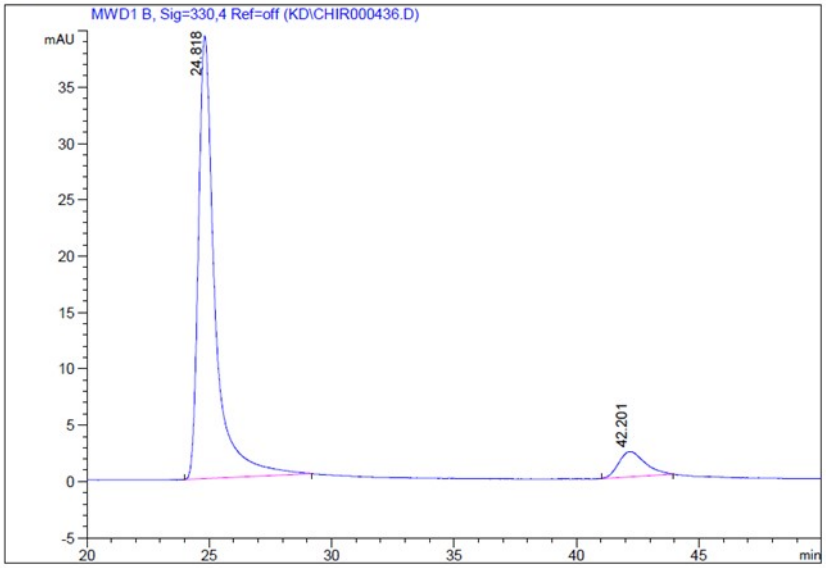


#	Meas. R	Area	Area %
1	19.503	1.786e3	97.724
2	29.395	41.590	2.276

Figure S70. HPLC chromatograms of **3aaa**

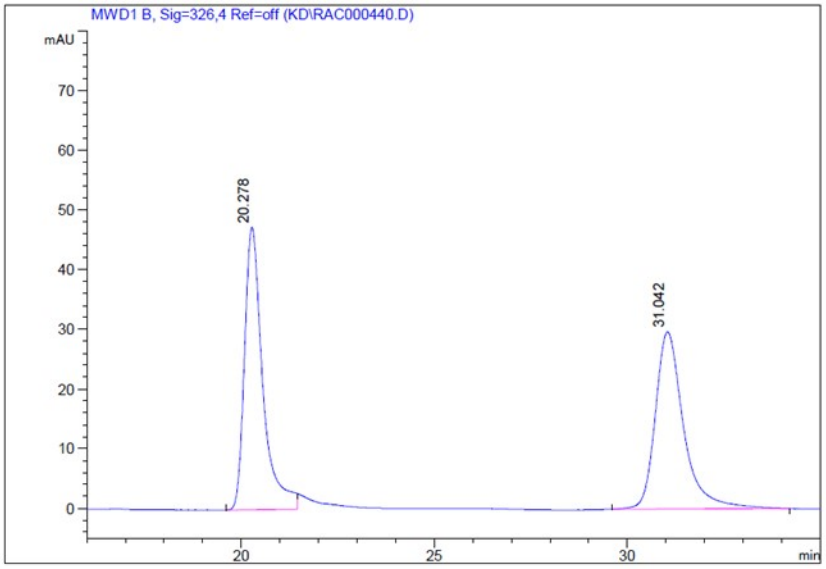


#	Meas. R	Area	Area %
1	24.917	751.141	51.847
2	42.250	697.619	48.153

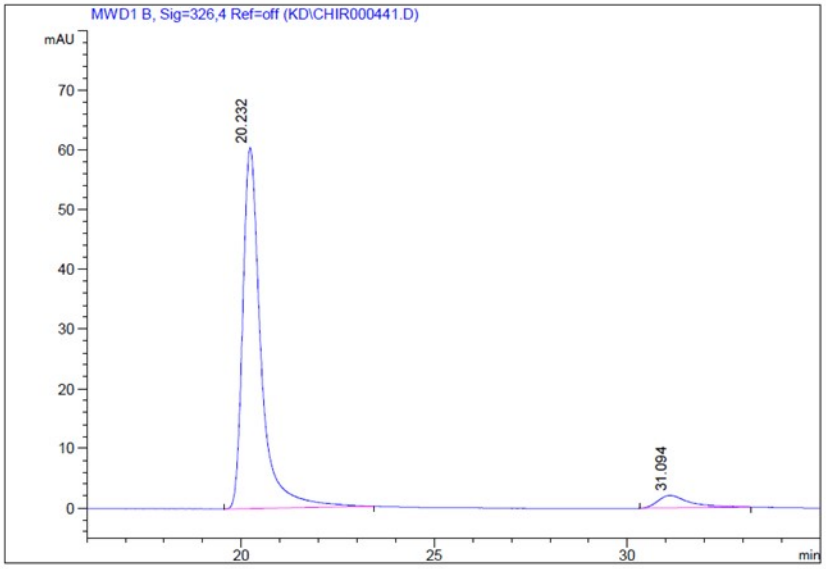


#	Meas. R	Area	Area %
1	24.818	1.852e3	91.718
2	42.201	167.205	8.282

Figure S71. HPLC chromatograms of **3baa**

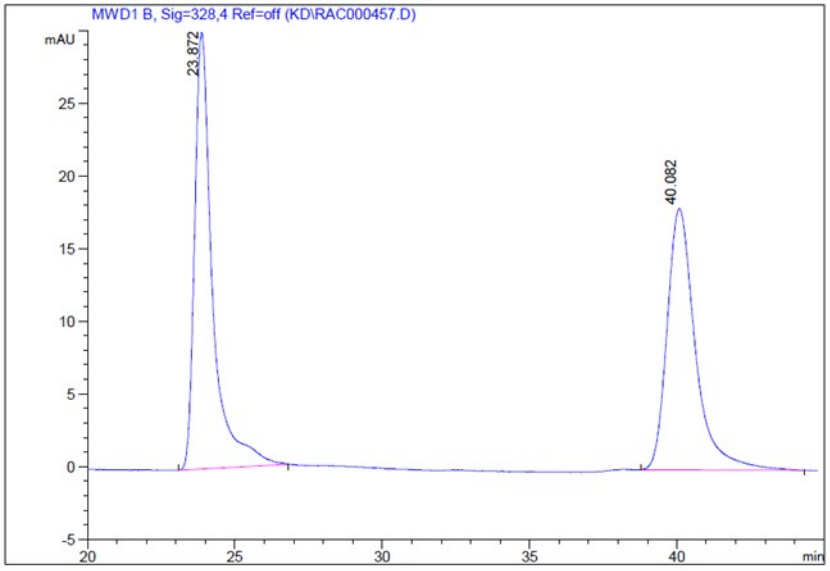


#	Meas. R	Area	Area %
1	20.278	1.558e3	50.758
2	31.042	1.512e3	49.242

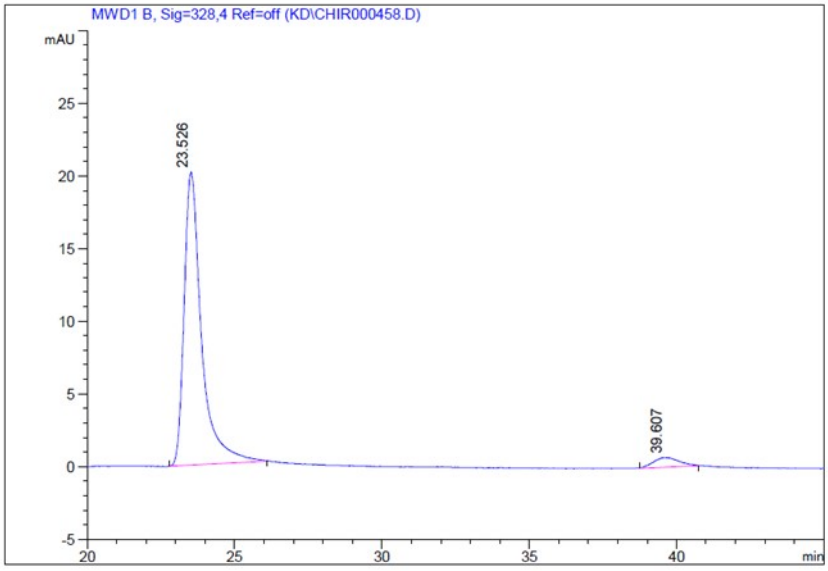


#	Meas. R	Area	Area %
1	20.232	1.981e3	94.217
2	31.094	121.595	5.783

Figure S72. HPLC chromatograms of **3caa**

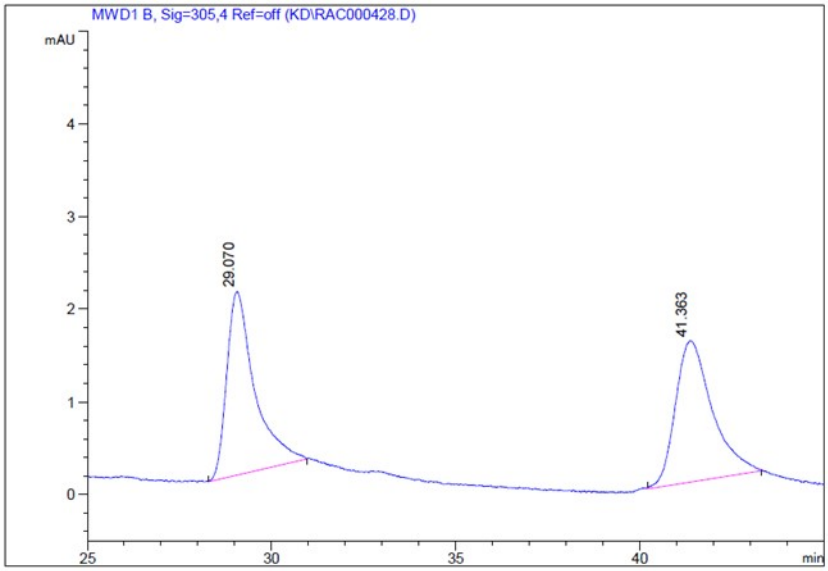


#	Meas. R	Area	Area %
1	23.872	1.270e3	51.356
2	40.082	1.203e3	48.644

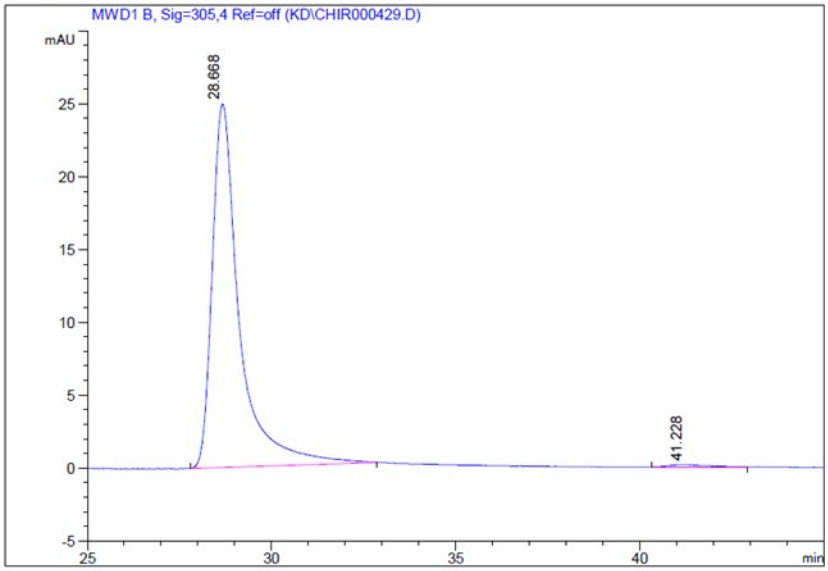


#	Meas. R	Area	Area %
1	23.526	827.818	95.468
2	39.607	39.296	4.532

Figure S73. HPLC chromatograms of **3daa**

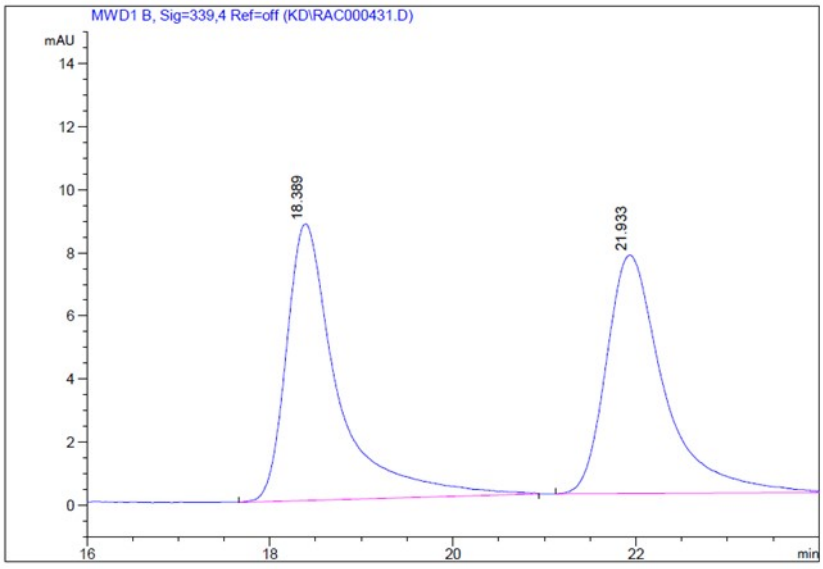


#	Meas. R	Area	Area %
1	29.070	104.144	49.549
2	41.363	106.041	50.451

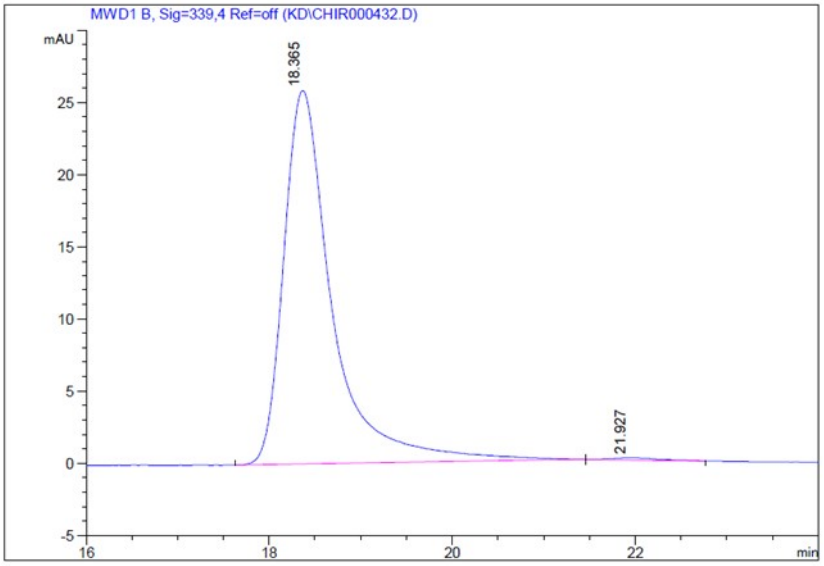


#	Meas. R	Area	Area %
1	28.668	1.279e3	99.177
2	41.228	10.608	0.823

Figure S74. HPLC chromatograms of **3eaa**

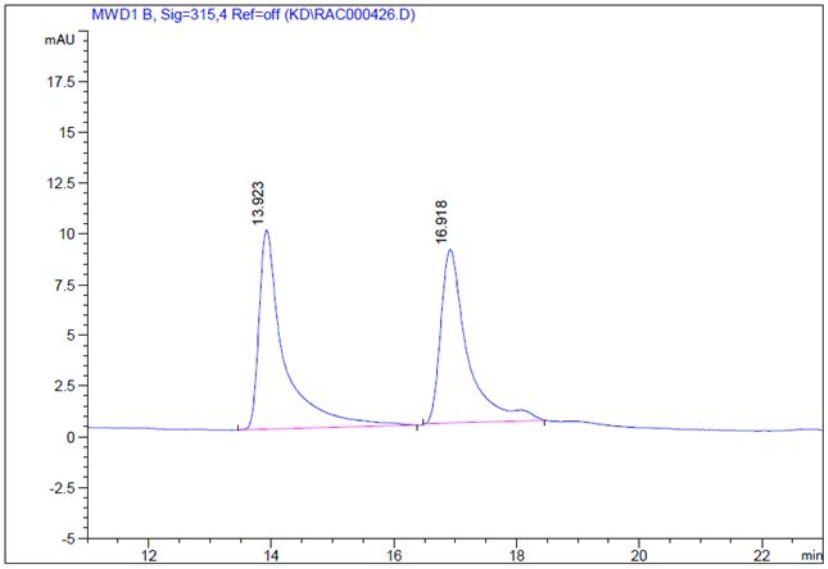


#	Meas. R	Area	Area %
1	18.389	342.711	50.891
2	21.933	330.709	49.109

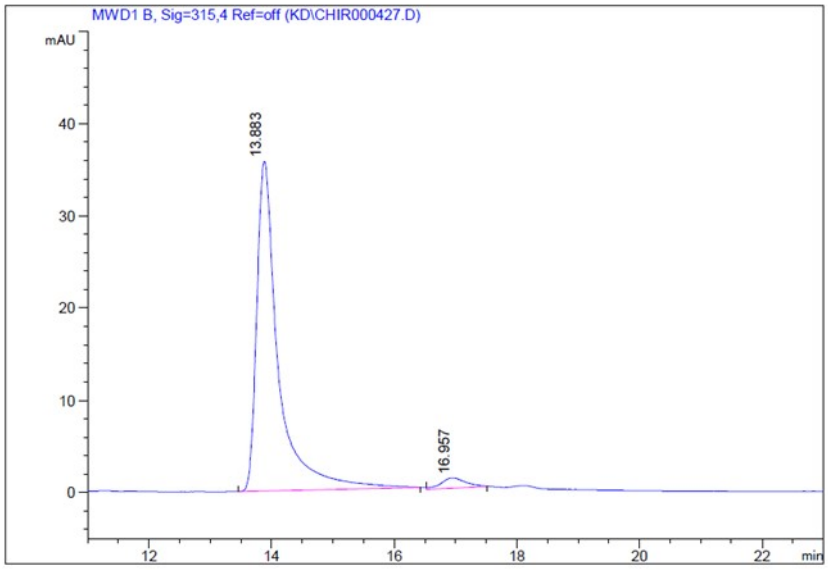


#	Meas. R	Area	Area %
1	18.365	959.351	99.343
2	21.927	6.341	0.657

Figure S75. HPLC chromatograms of **3faa**

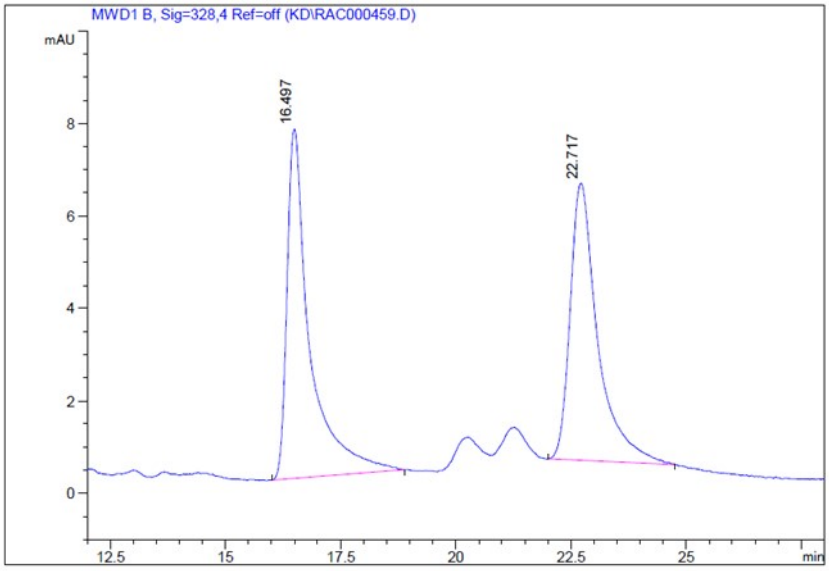


#	Meas. R	Area	Area %
1	13.923	280.371	52.113
2	16.918	257.635	47.887

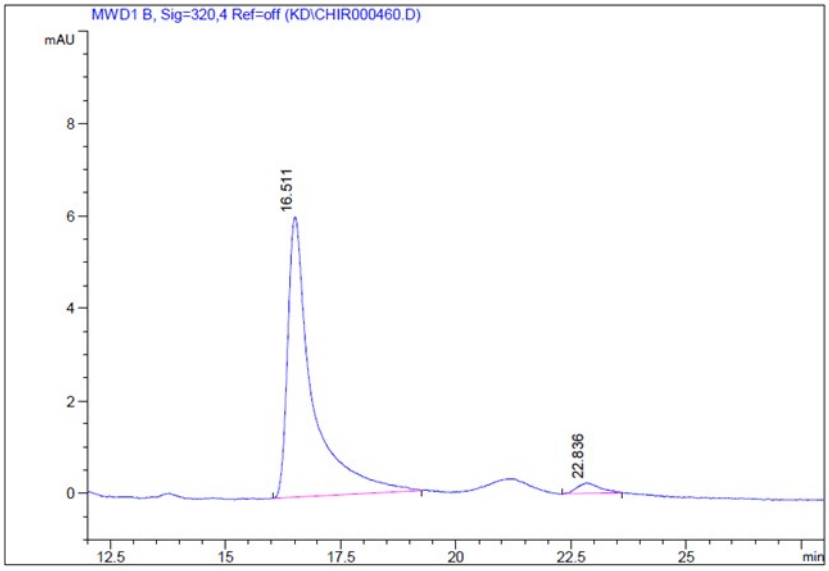


#	Meas. R	Area	Area %
1	13.883	878.630	96.538
2	16.957	31.511	3.462

Figure S76. HPLC chromatograms of **3gaa**

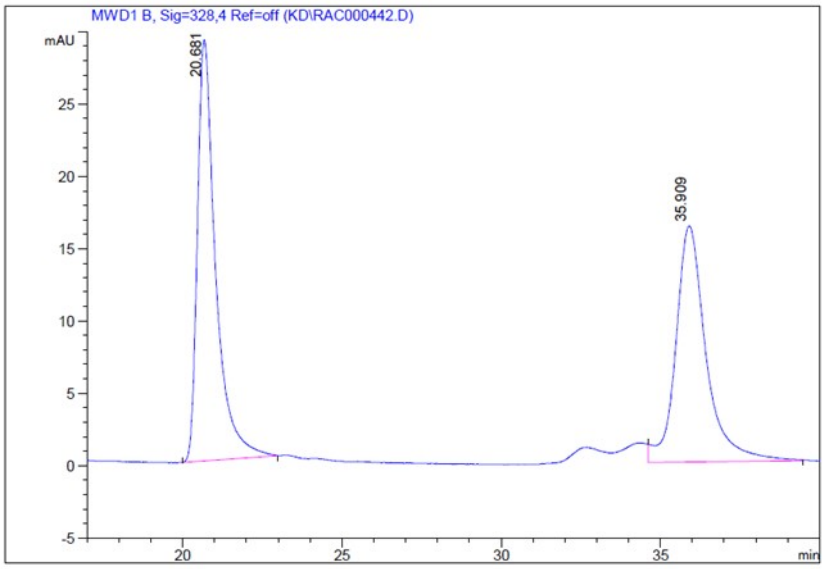


#	Meas. R	Area	Area %
1	16.497	259.582	51.032
2	22.717	249.084	48.968

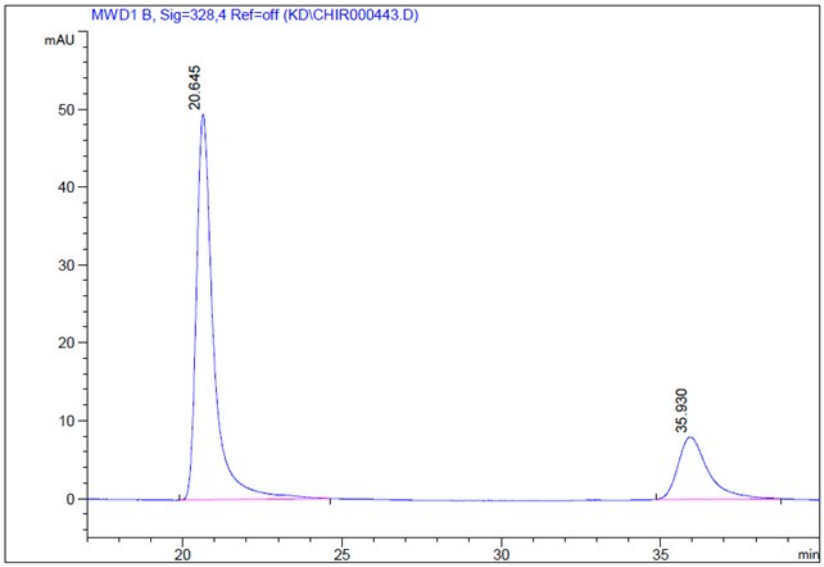


#	Meas. R	Area	Area %
1	16.511	224.861	96.738
2	22.836	7.582	3.262

Figure S77. HPLC chromatograms of **3haa**

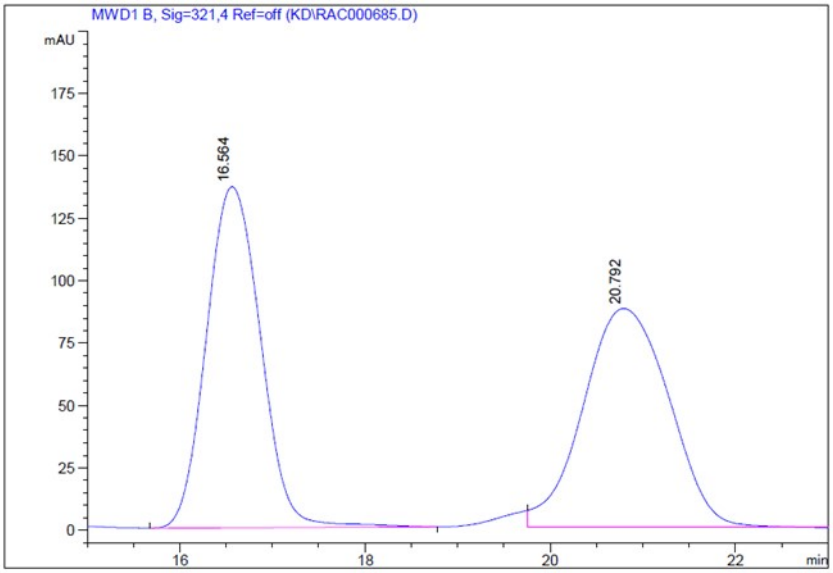


#	Meas. R	Area	Area %
1	20.681	1.156e3	51.659
2	35.909	1.081e3	48.341

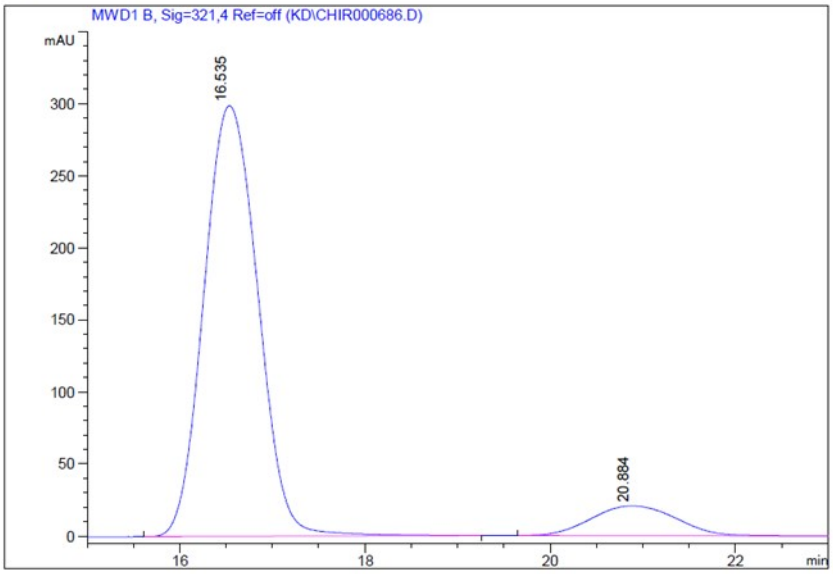


#	Meas. R	Area	Area %
1	20.645	1.842e3	77.908
2	35.930	522.449	22.092

Figure S78. HPLC chromatograms of **3iaa**

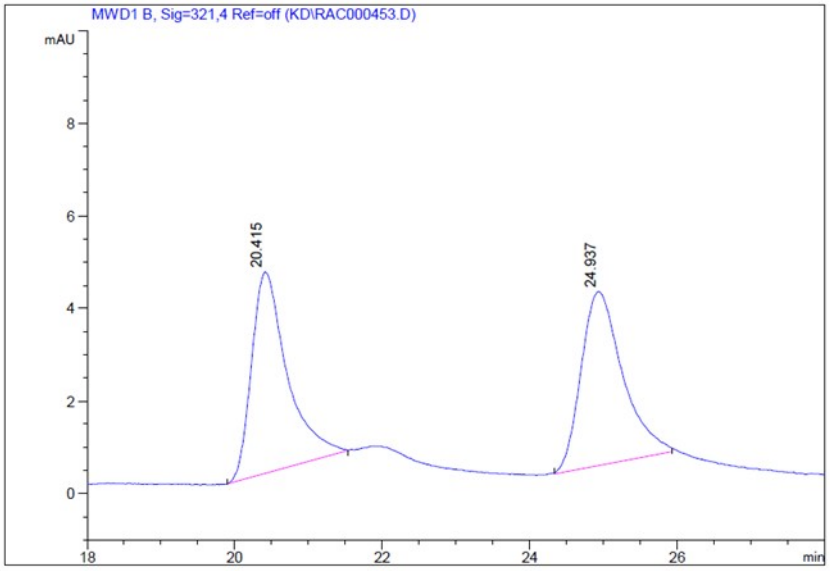


#	Meas. R	Area	Area %
1	16.564	5.551e3	49.462
2	20.792	5.672e3	50.538

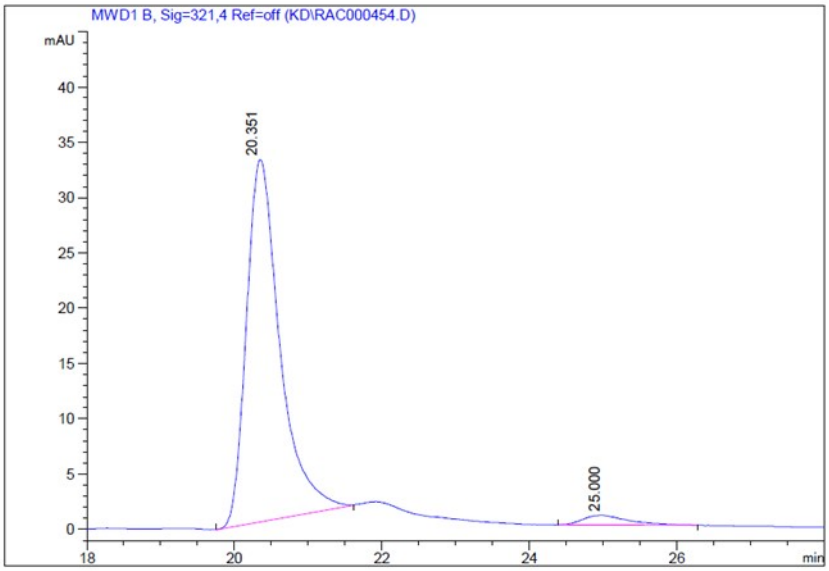


#	Meas. R	Area	Area %
1	16.535	1.209e4	90.071
2	20.884	1.333e3	9.929

Figure S79. HPLC chromatograms of **3aba**

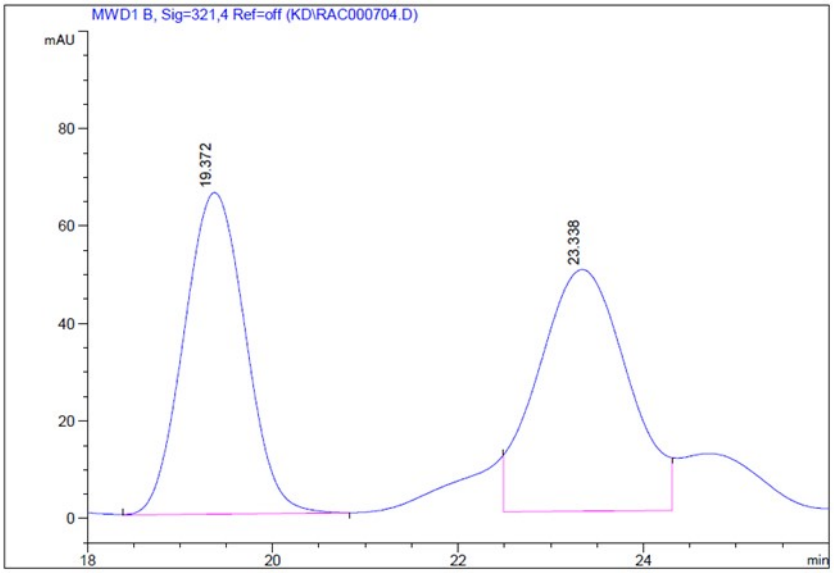


#	Meas. R	Area	Area %
1	20.415	145.844	49.722
2	24.937	147.476	50.278

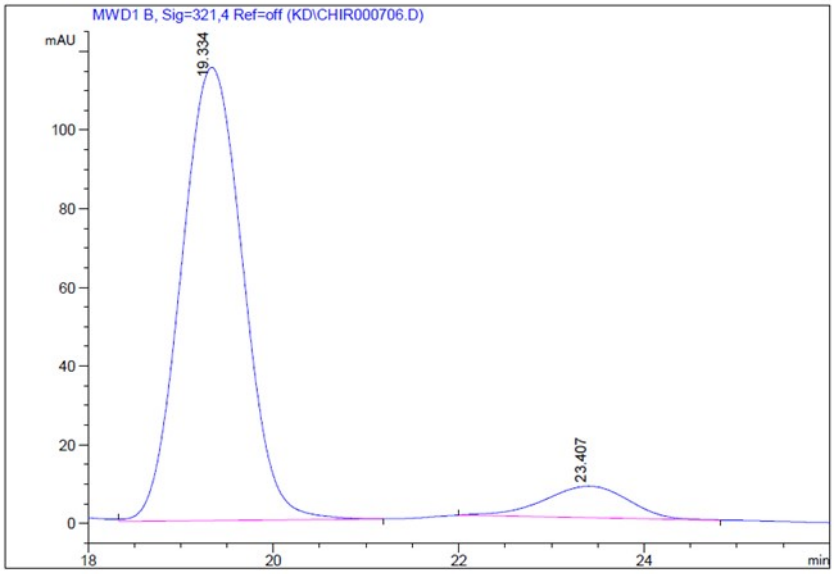


#	Meas. R	Area	Area %
1	20.351	1.033e3	96.492
2	25.000	37.570	3.508

Figure S80. HPLC chromatograms of **3aca**

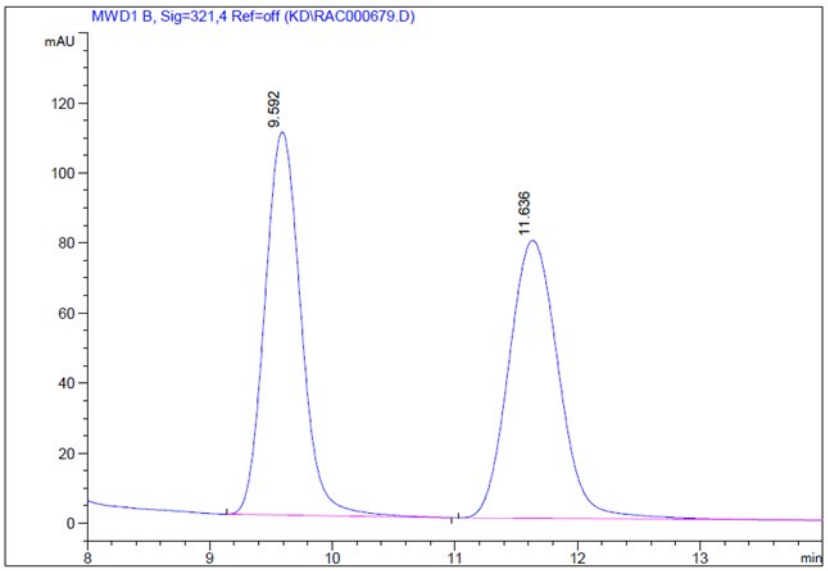


#	Meas. R	Area	Area %
1	19.372	3.029e3	47.708
2	23.338	3.320e3	52.292

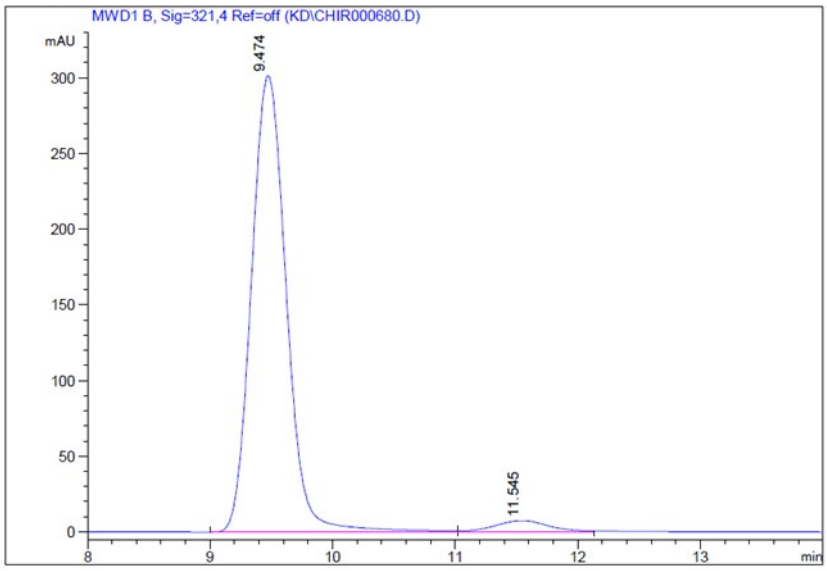


#	Meas. R	Area	Area %
1	19.334	5.320e3	91.390
2	23.407	501.165	8.610

Figure S81. HPLC chromatograms of **3ada**

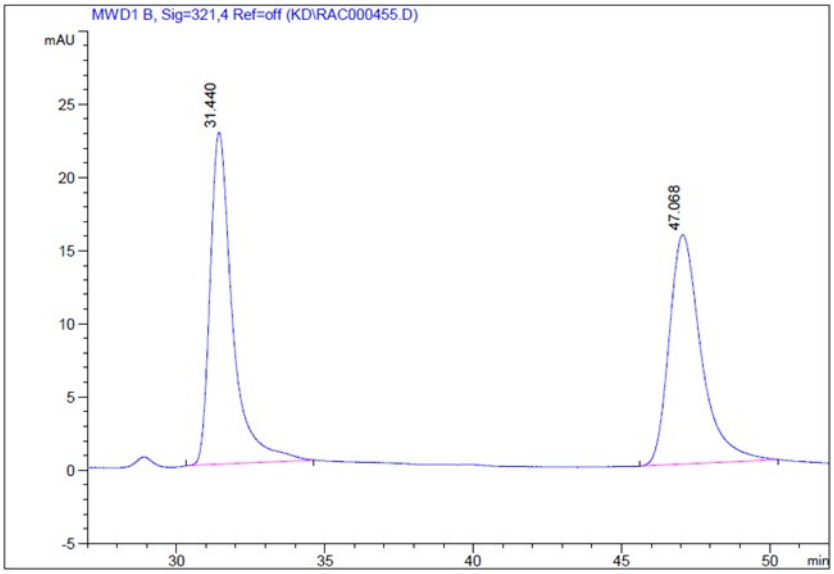


#	Meas. R	Area	Area %
1	9.592	2.234e3	49.897
2	11.636	2.243e3	50.103

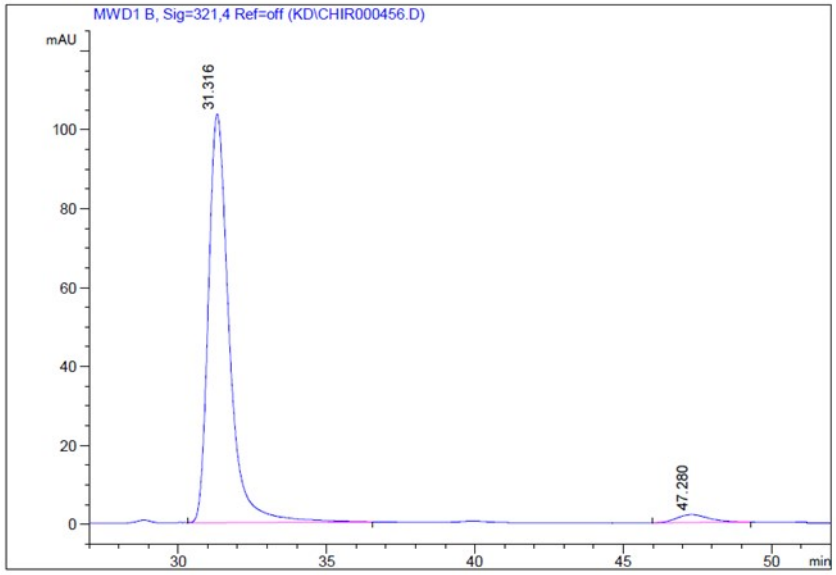


#	Meas. R	Area	Area %
1	9.474	5.970e3	96.078
2	11.545	243.701	3.922

Figure S82. HPLC chromatograms of **3aea**

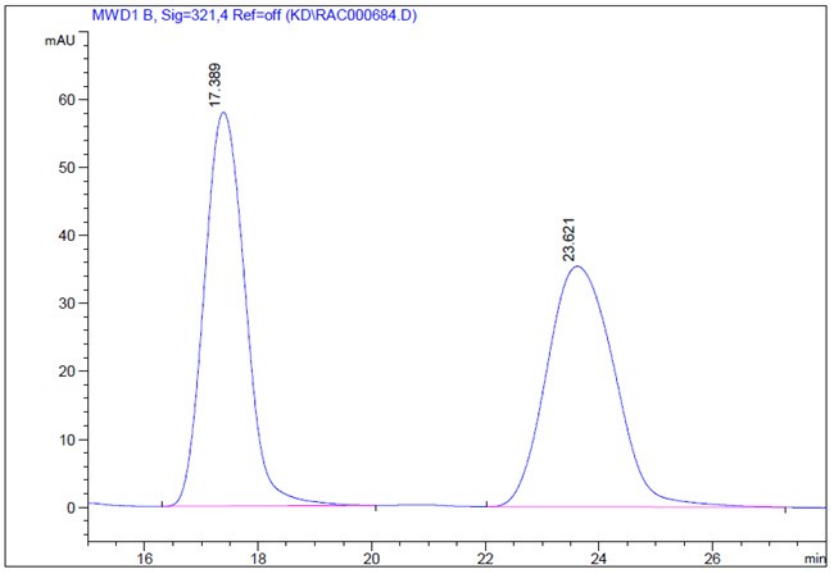


#	Meas. R	Area	Area %
1	31.440	1.191e3	50.209
2	47.068	1.181e3	49.791

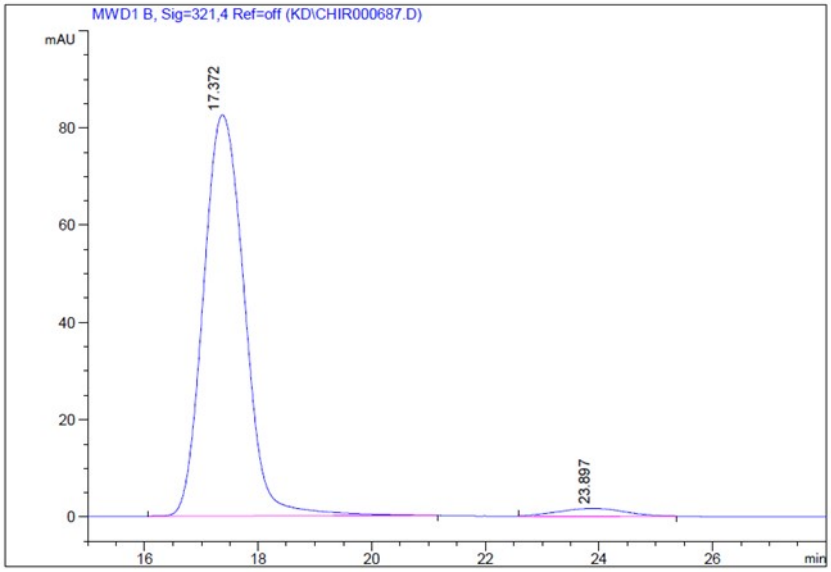


#	Meas. R	Area	Area %
1	31.316	5.029e3	97.024
2	47.280	154.279	2.976

Figure S83. HPLC chromatograms of **3afa**

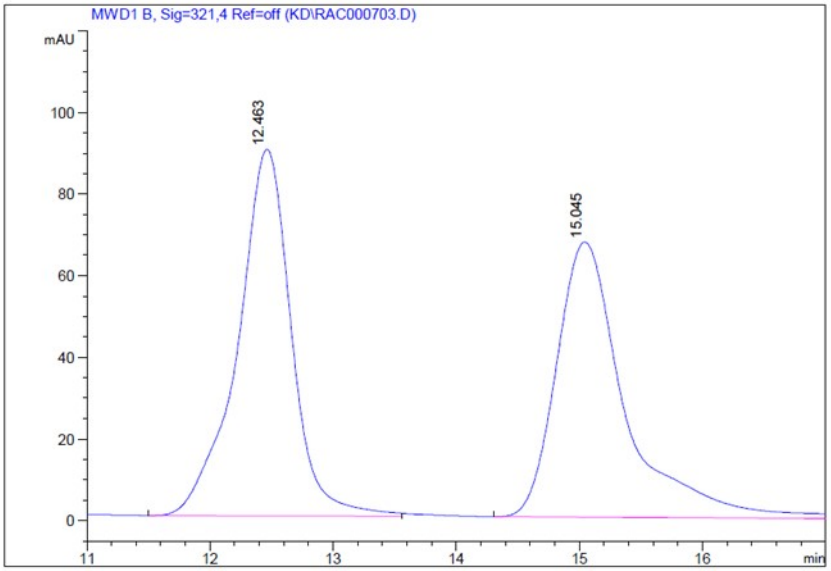


#	Meas. R	Area	Area %
1	17.389	2.892e3	49.699
2	23.621	2.927e3	50.301

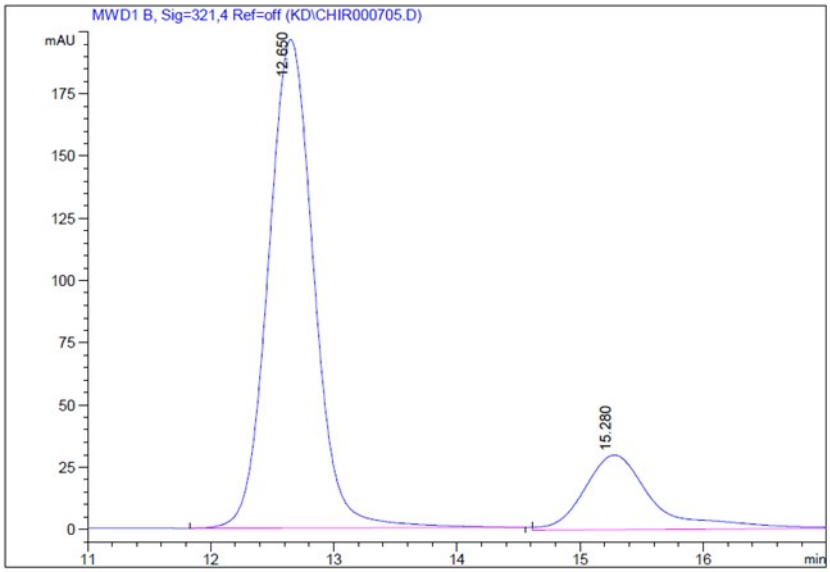


#	Meas. R	Area	Area %
1	17.372	4.129e3	96.727
2	23.897	139.735	3.273

Figure S84. HPLC chromatograms of **3aga**

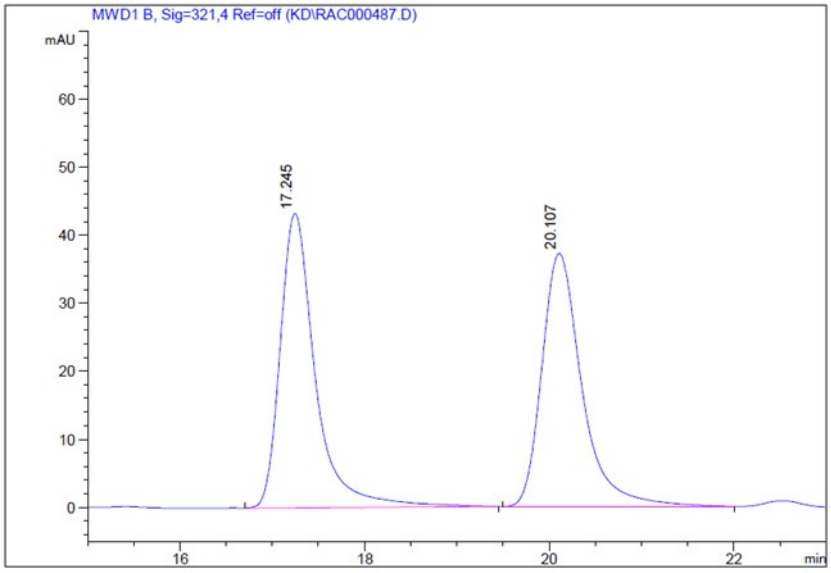


#	Meas. R	Area	Area %
1	12.463	2.723e3	50.868
2	15.045	2.630e3	49.132

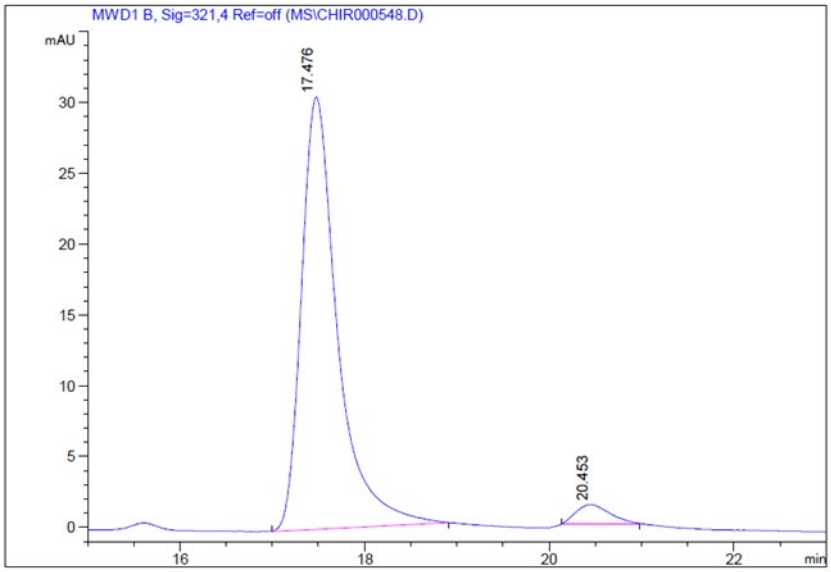


#	Meas. R	Area	Area %
1	12.650	5.038e3	81.259
2	15.280	1.162e3	18.741

Figure S85. HPLC chromatograms of **3aha**

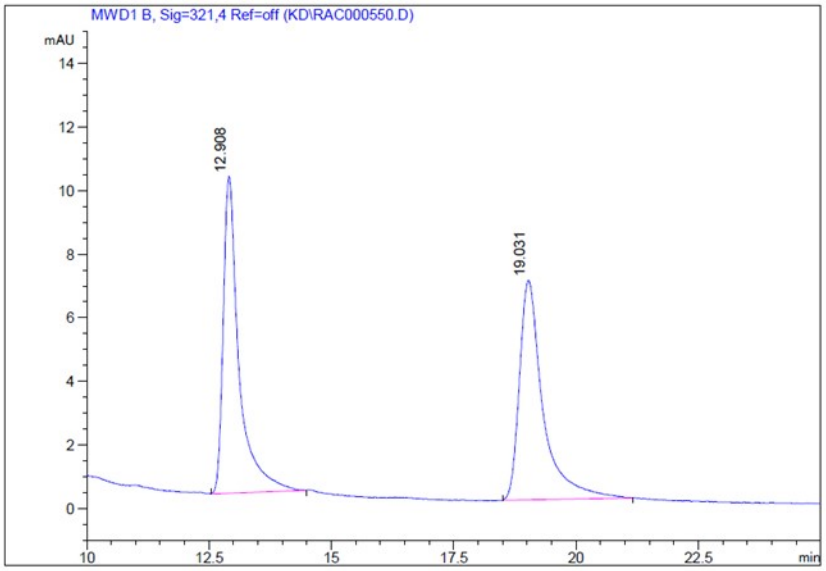


#	Meas. R	Area	Area %
1	17.245	1.145e3	50.498
2	20.107	1.122e3	49.502

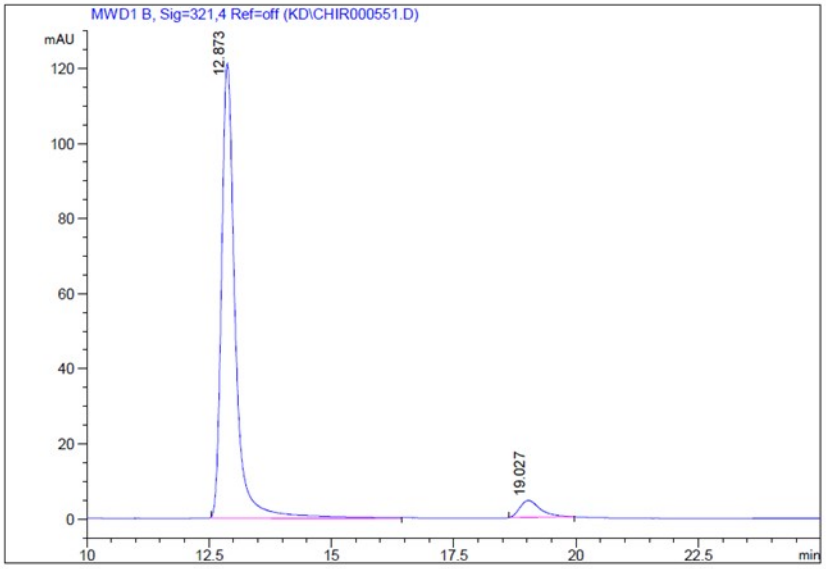


#	Meas. R	Area	Area %
1	17.476	827.696	95.806
2	20.453	36.236	4.194

Figure S86. HPLC chromatograms of **3aia**

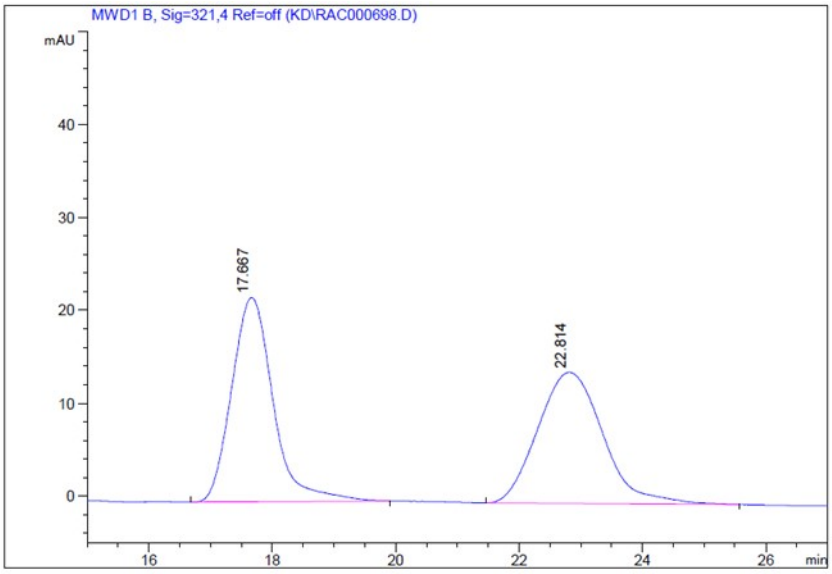


#	Meas. R	Area	Area %
1	12.908	222.606	49.117
2	19.031	230.612	50.883

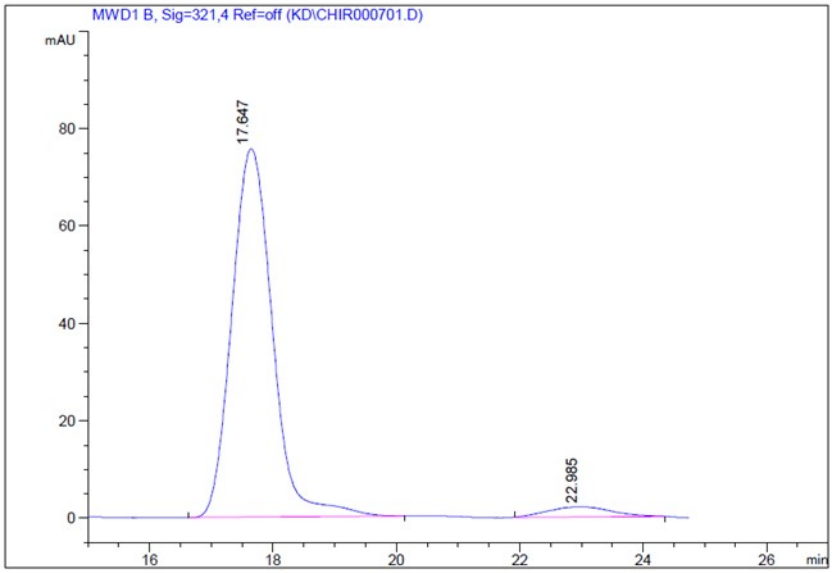


#	Meas. R	Area	Area %
1	12.873	2.363e3	94.718
2	19.027	131.750	5.282

Figure S87. HPLC chromatograms of **3aja**

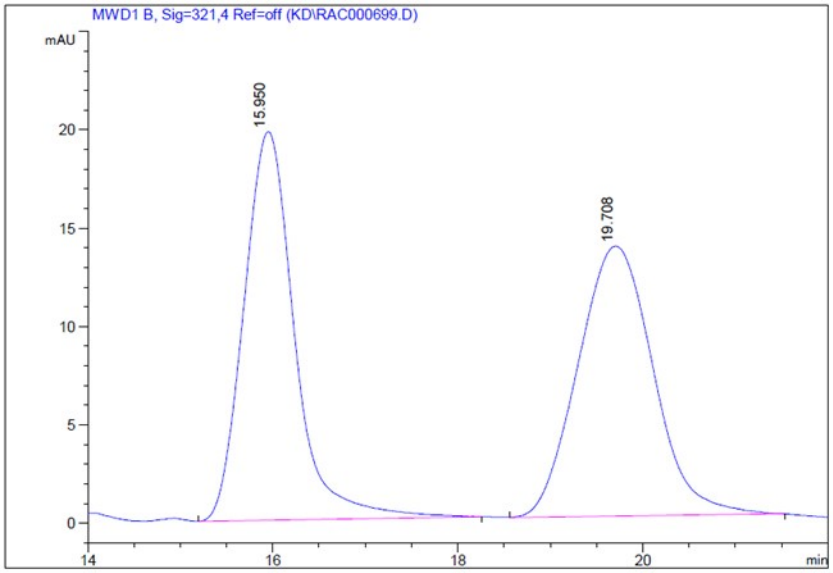


#	Meas. R	Area	Area %
1	17.667	1.028e3	49.804
2	22.814	1.036e3	50.196

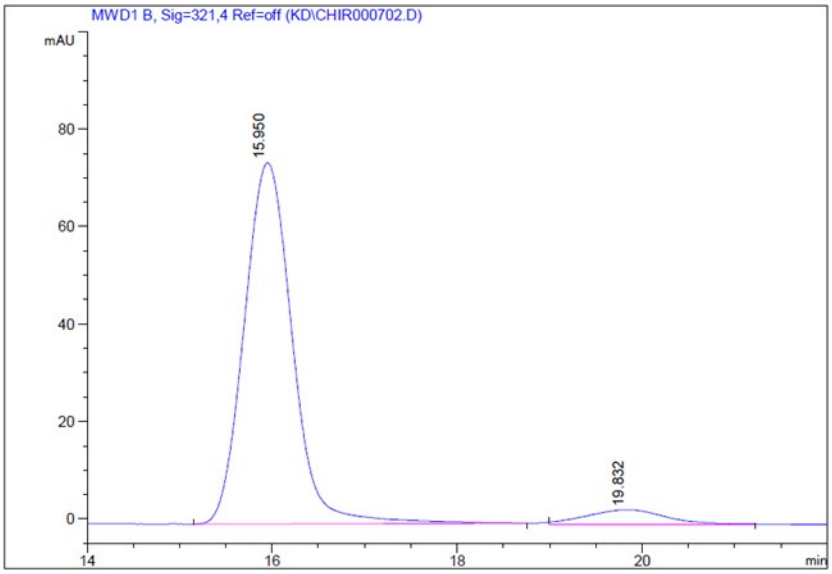


#	Meas. R	Area	Area %
1	17.647	3.458e3	95.745
2	22.985	153.688	4.255

Figure S88. HPLC chromatograms of **3aka**

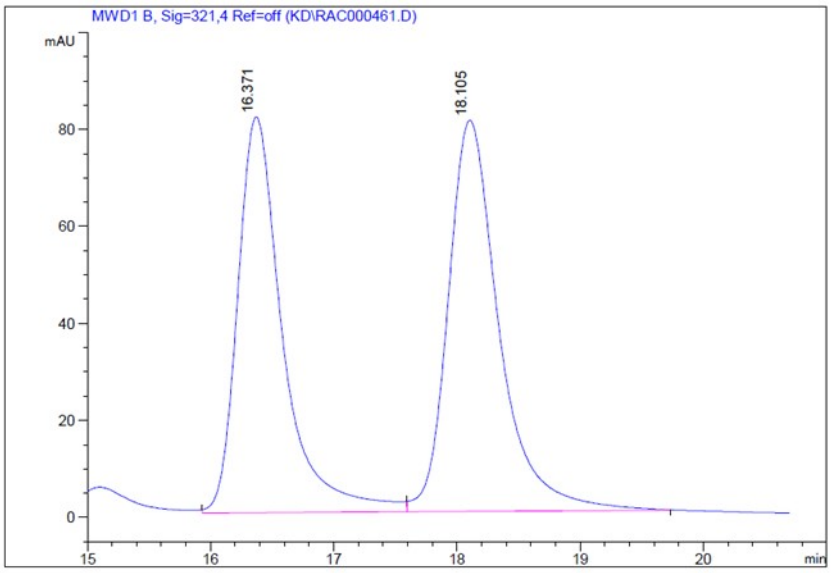


#	Meas. R	Area	Area %
1	15.950	753.543	49.327
2	19.708	774.097	50.673

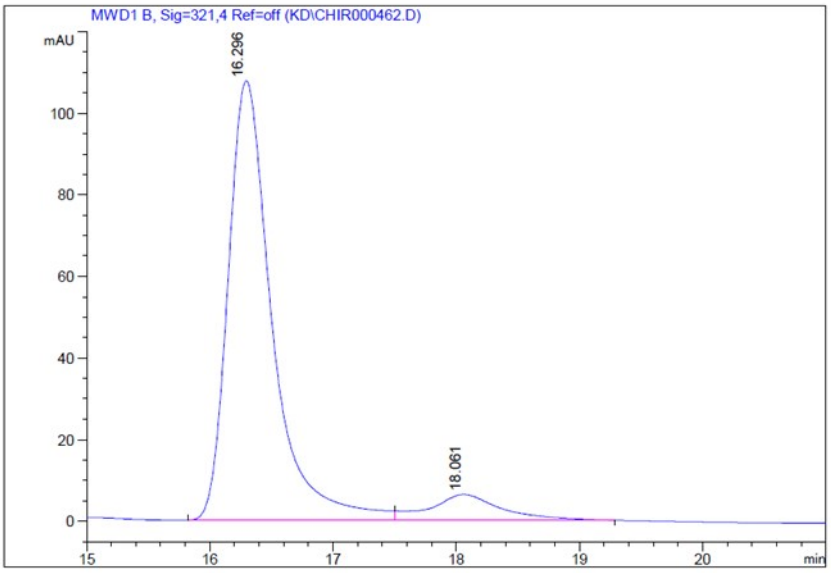


#	Meas. R	Area	Area %
1	15.950	2.673e3	93.445
2	19.832	187.483	6.555

Figure S89. HPLC chromatograms of **3ala**

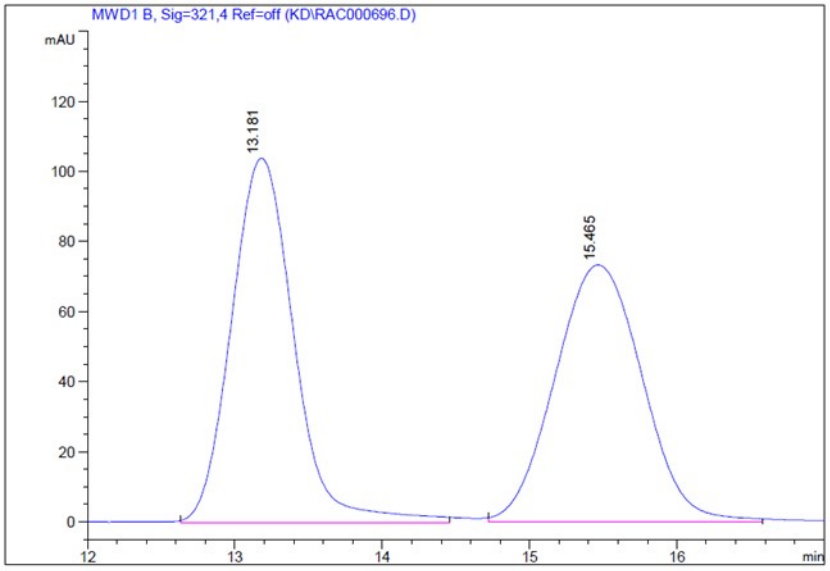


#	Meas. R	Area	Area %
1	16.371	2.080e3	47.305
2	18.105	2.317e3	52.695

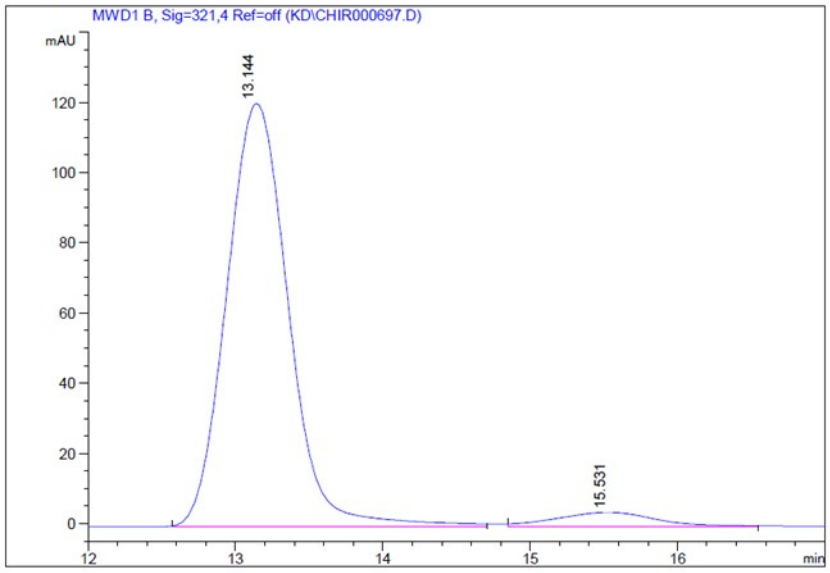


#	Meas. R	Area	Area %
1	16.296	2.671e3	91.244
2	18.061	256.346	8.756

Figure S90. HPLC chromatograms of **3ama**

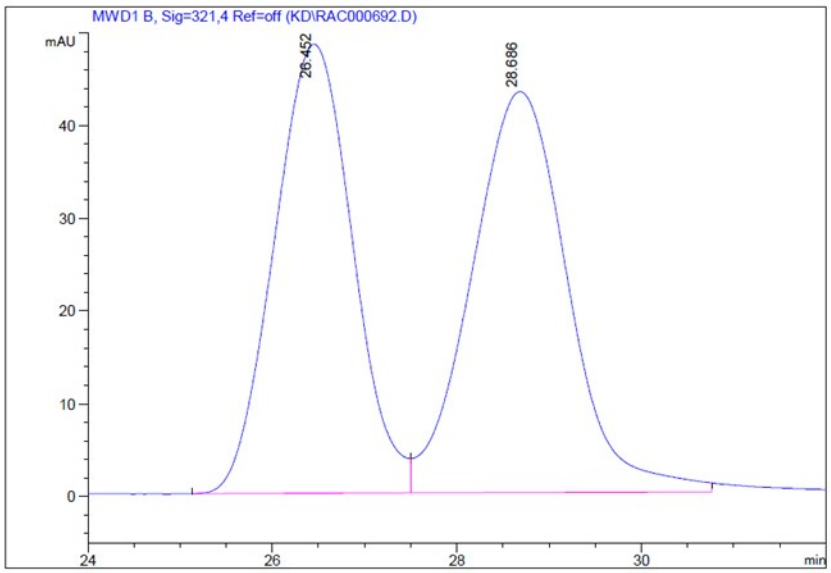


#	Meas. R	Area	Area %
1	13.181	3.087e3	50.676
2	15.465	3.004e3	49.324

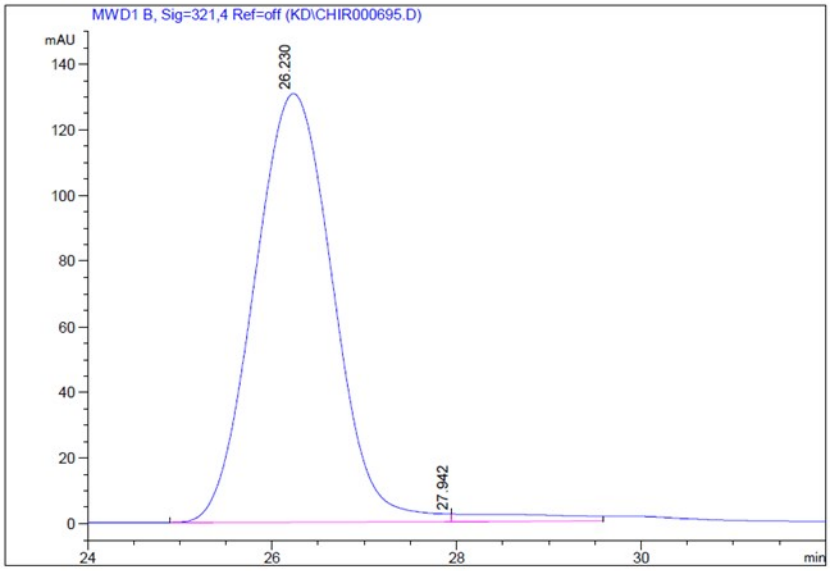


#	Meas. R	Area	Area %
1	13.144	3.511e3	94.706
2	15.531	196.255	5.294

Figure S91. HPLC chromatogram of **3ana**

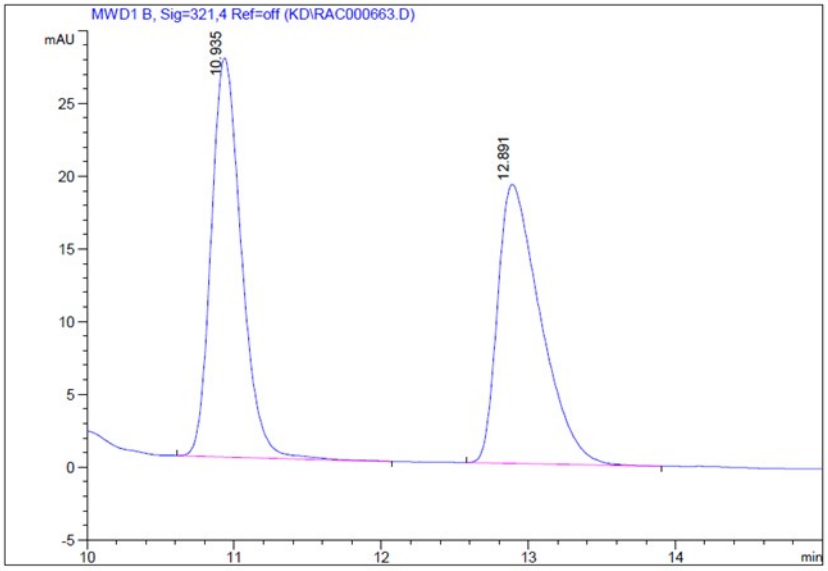


#	Meas. R	Area	Area %
1	26.452	2.853e3	47.740
2	28.686	3.123e3	52.260

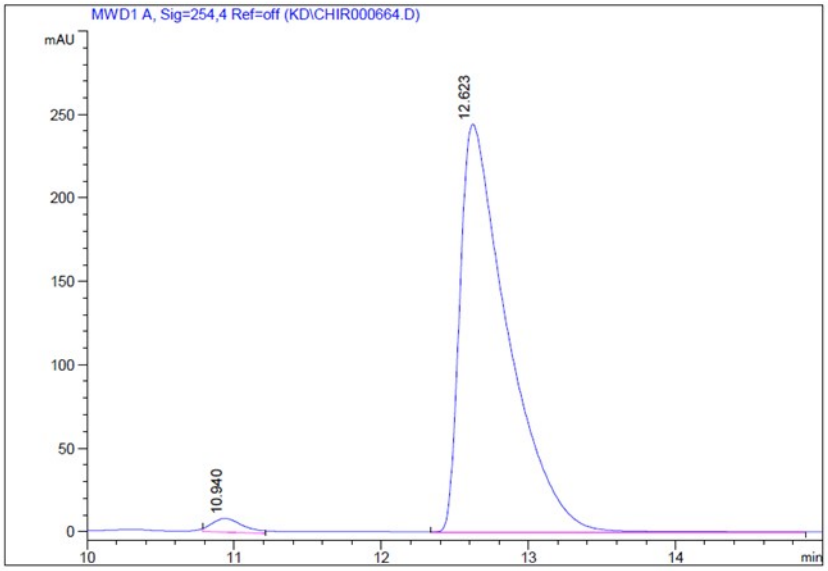


#	Meas. R	Area	Area %
1	26.230	7.708e3	97.612
2	27.942	188.588	2.388

Figure S92. HPLC chromatograms of **3aoa**

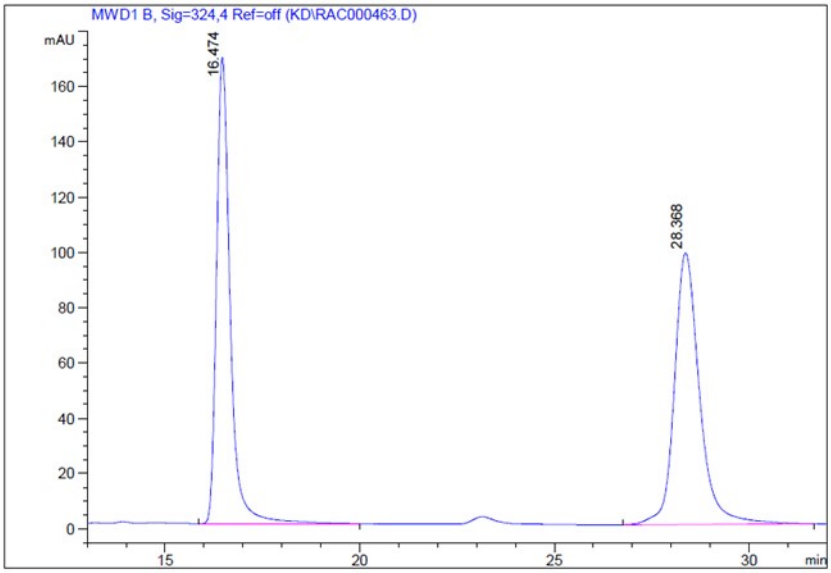


#	Meas. R	Area	Area %
1	10.935	390.622	50.087
2	12.891	389.265	49.913

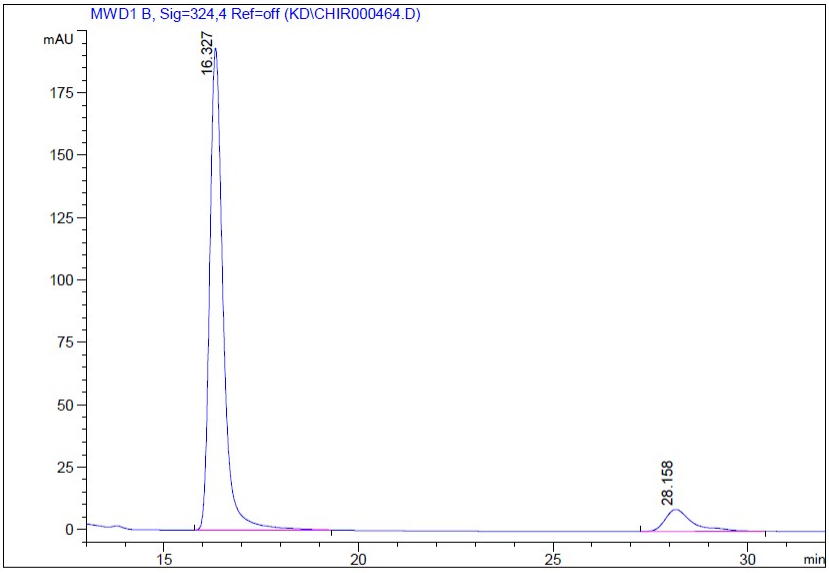


#	Meas. R	Area	Area %
1	10.940	118.741	2.117
2	12.623	5.491e3	97.883

Figure S93. HPLC chromatograms of **3apa**

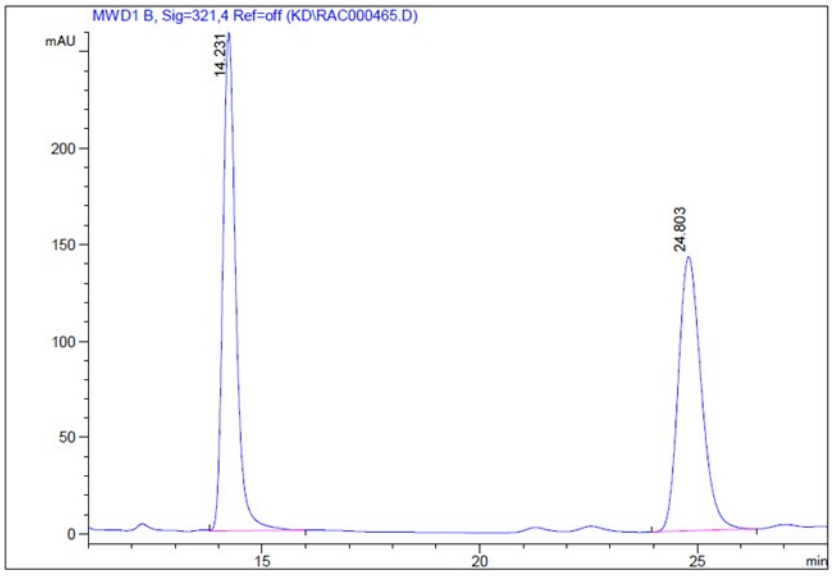


#	Meas. R	Area	Area %
1	16.474	4.097e3	48.130
2	28.368	4.416e3	51.870

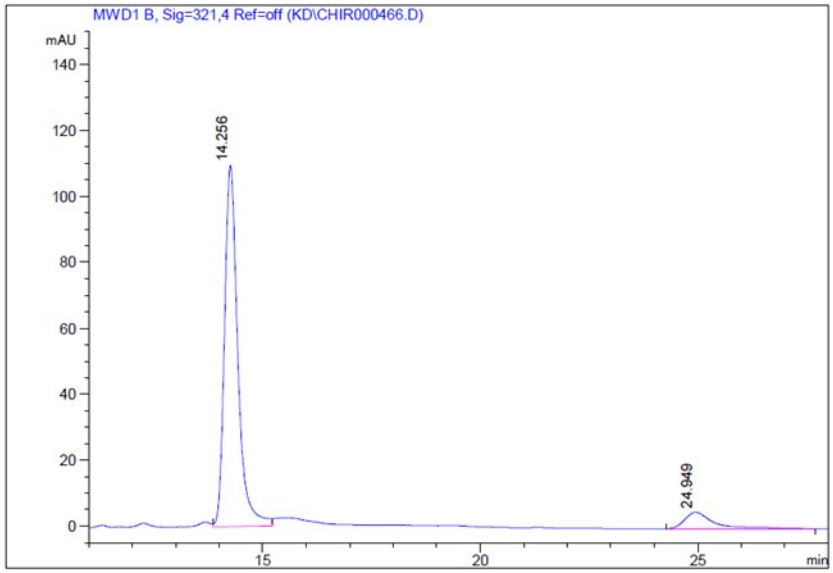


#	Meas. R	Area	Area %
1	16.327	4.618e3	91.405
2	28.158	434.194	8.595

Figure S94. HPLC chromatograms of **3aab**

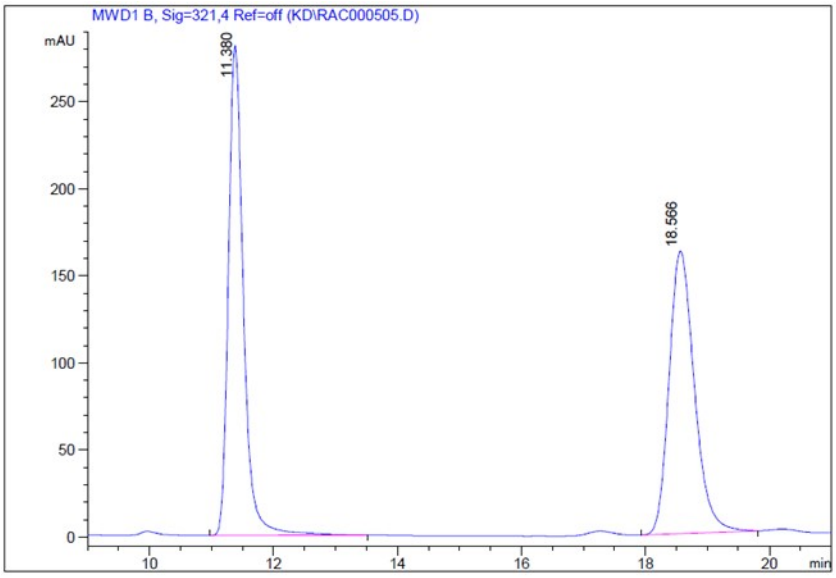


#	Meas. R	Area	Area %
1	14.231	5.345e3	50.570
2	24.803	5.224e3	49.430

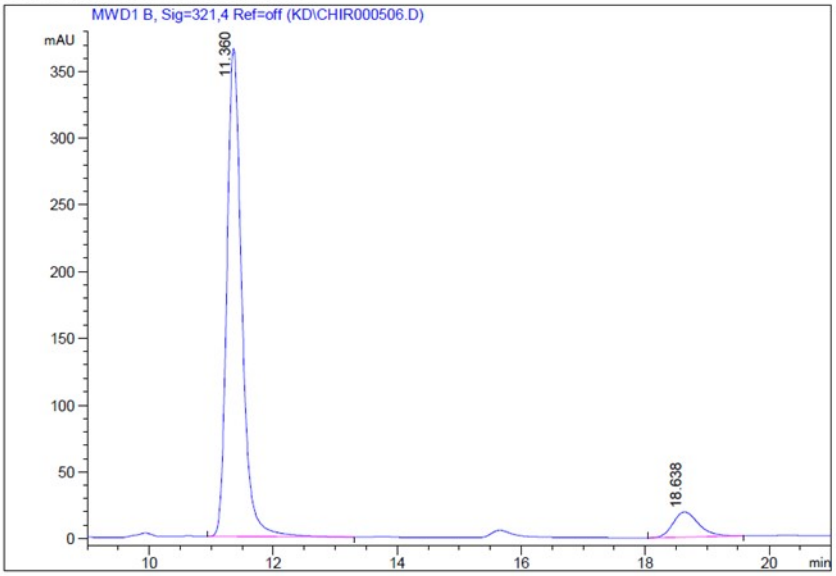


#	Meas. R	Area	Area %
1	14.256	2.327e3	90.965
2	24.949	231.141	9.035

Figure S95. HPLC chromatograms of **3aac**

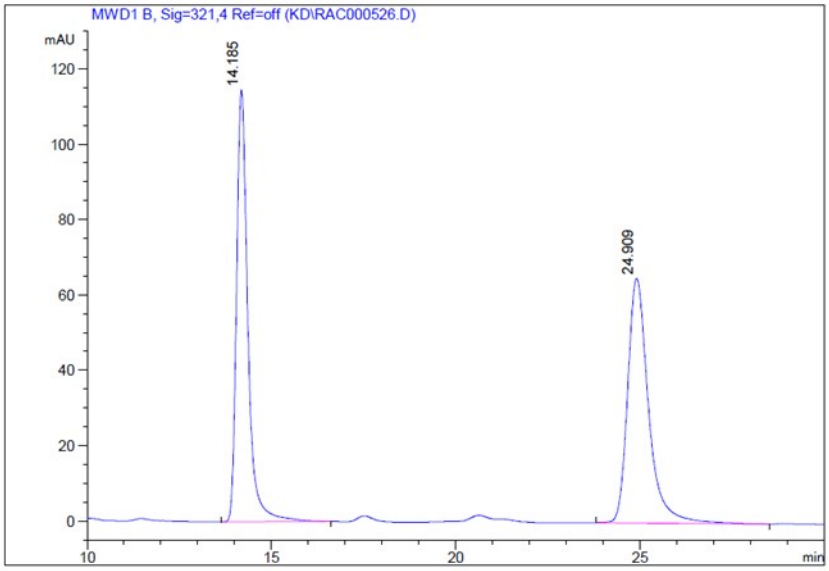


#	Meas. R	Area	Area %
1	11.380	4.743e3	50.775
2	18.566	4.598e3	49.225

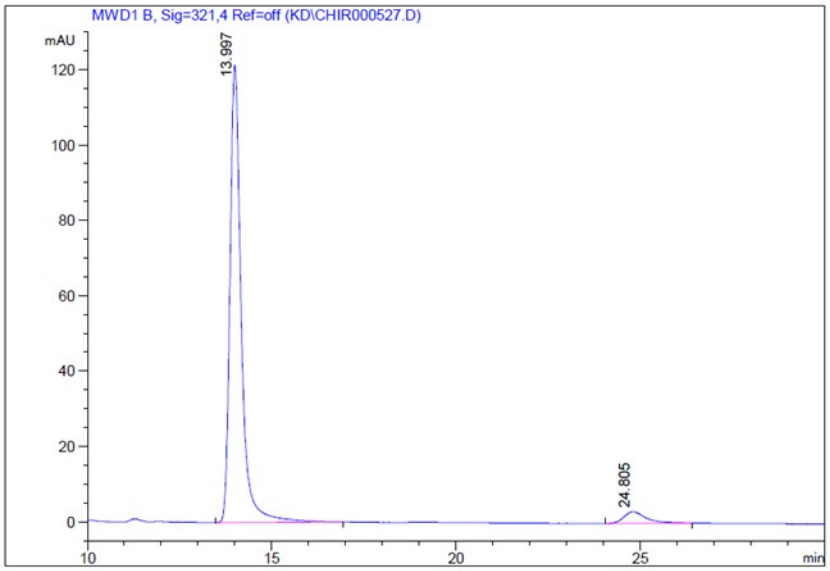


#	Meas. R	Area	Area %
1	11.360	6.100e3	91.803
2	18.638	544.644	8.197

Figure S96. HPLC chromatograms of **3aad**

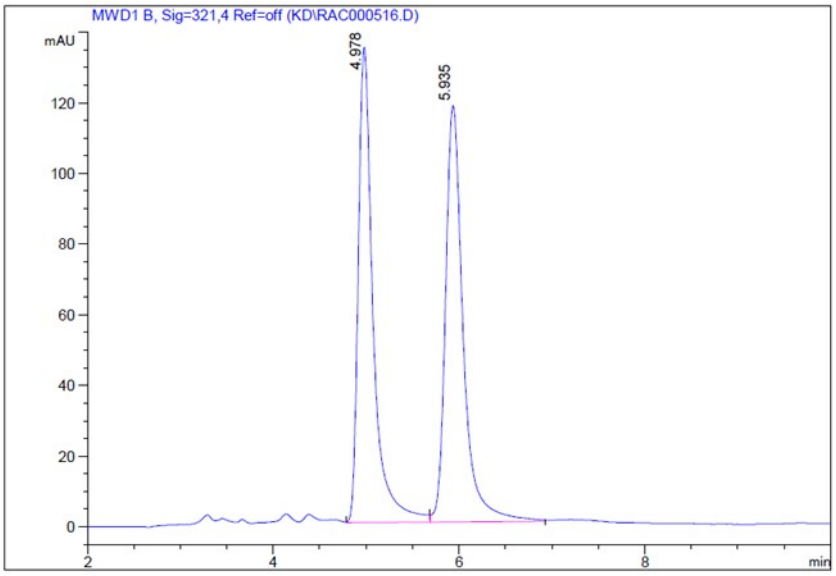


#	Meas. R	Area	Area %
1	14.185	2.439e3	48.850
2	24.909	2.553e3	51.150

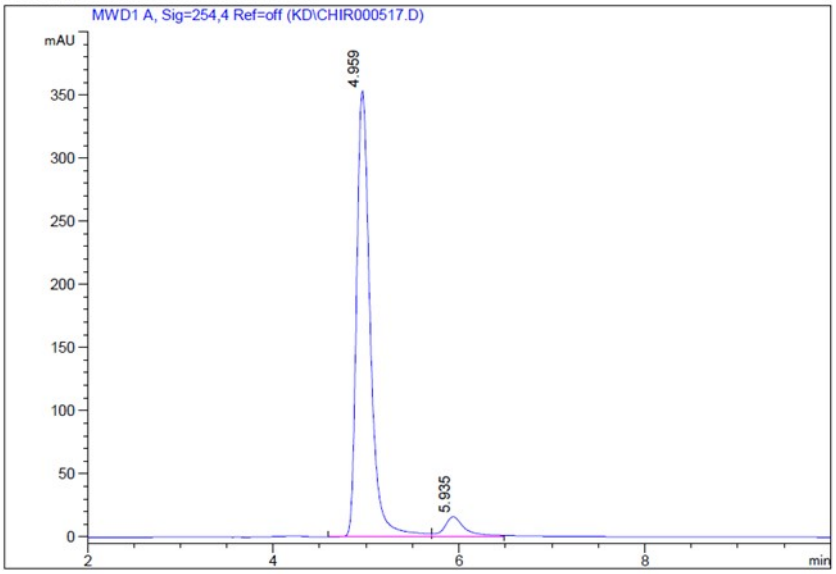


#	Meas. R	Area	Area %
1	13.997	2.572e3	95.164
2	24.805	130.694	4.836

Figure S97. HPLC chromatograms of **3aae**

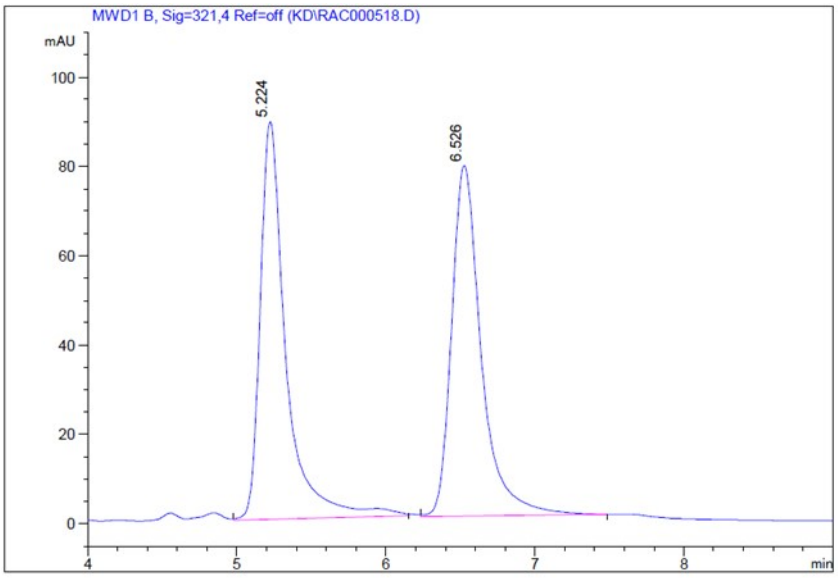


#	Meas. R	Area	Area %
1	4.978	1.494e3	48.993
2	5.935	1.555e3	51.007

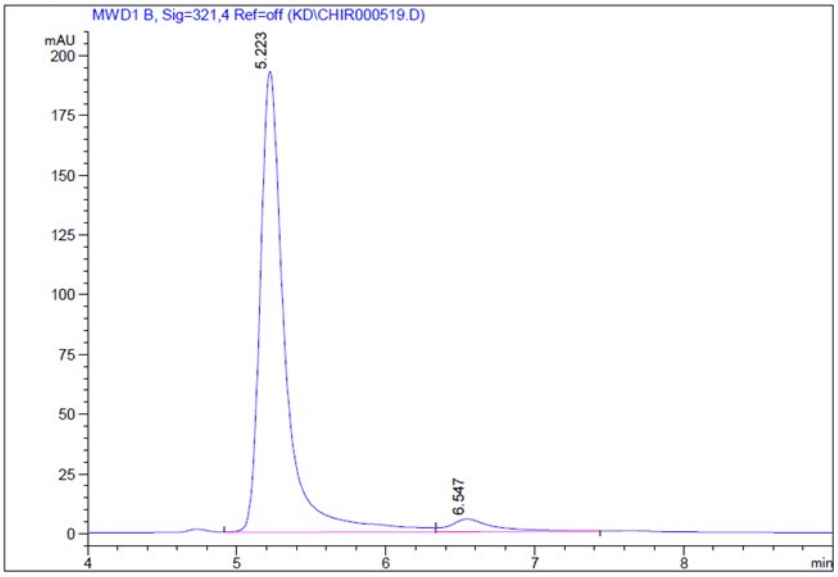


#	Meas. R	Area	Area %
1	4.959	3.603e3	93.256
2	5.935	260.544	6.744

Figure S98. HPLC chromatograms of **3aaf**

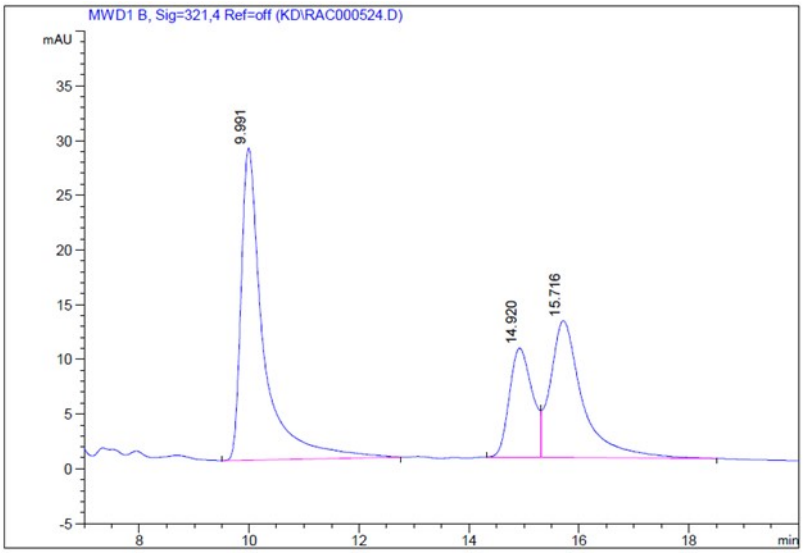


#	Meas. R	Area	Area %
1	5.224	1.068e3	49.576
2	6.526	1.086e3	50.424

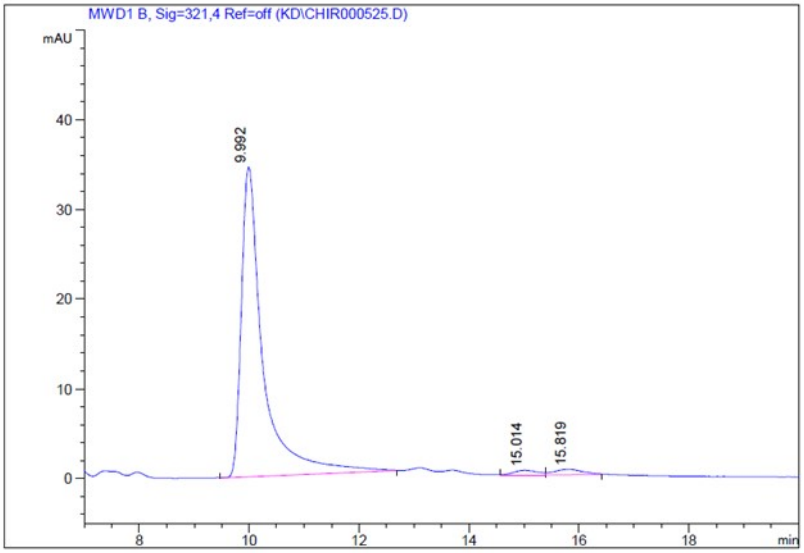


#	Meas. R	Area	Area %
1	5.223	2.222e3	95.464
2	6.547	105.553	4.536

Figure S99. HPLC chromatograms of **3aag**

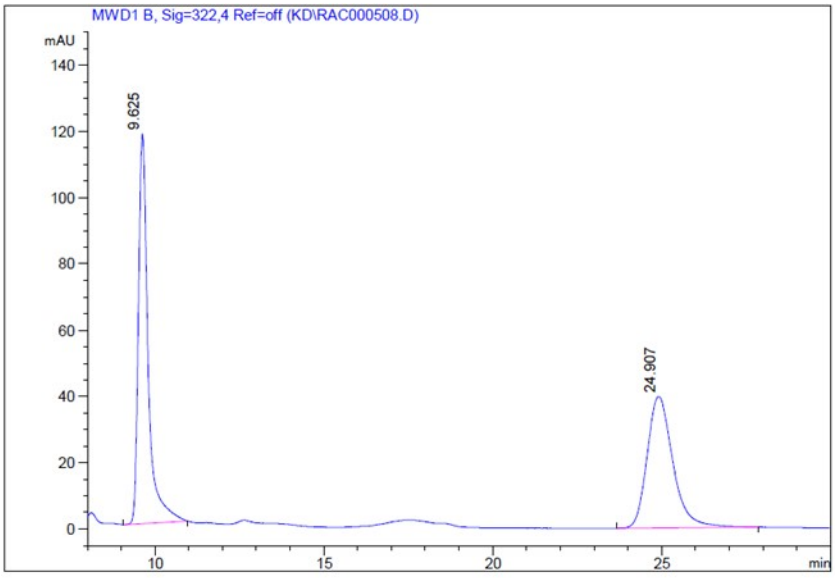


#	Meas. R	Area	Area %
1	9.991	804.179	50.076
2	14.920	289.344	18.017
3	15.716	512.402	31.907

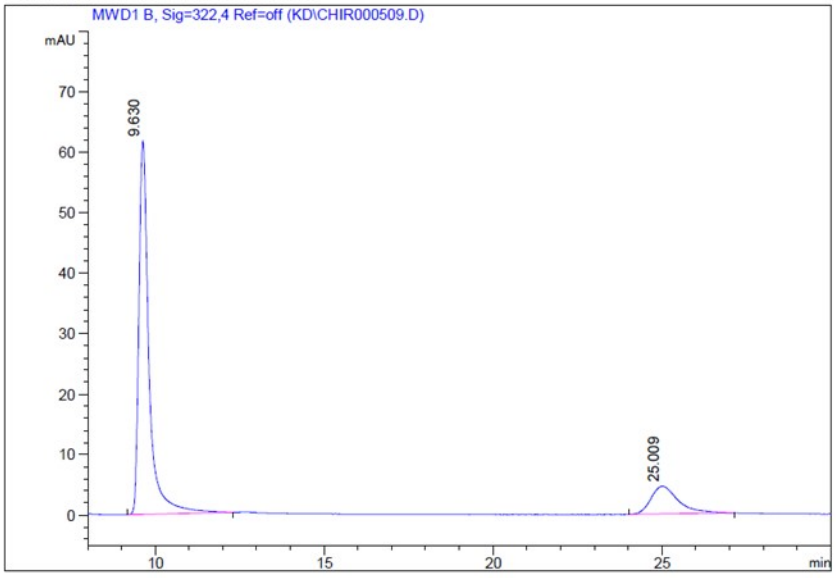


#	Meas. R	Area	Area %
1	9.992	944.618	96.236
2	15.014	15.001	1.528
3	15.819	21.945	2.236

Figure S100. HPLC chromatograms of **3aah**

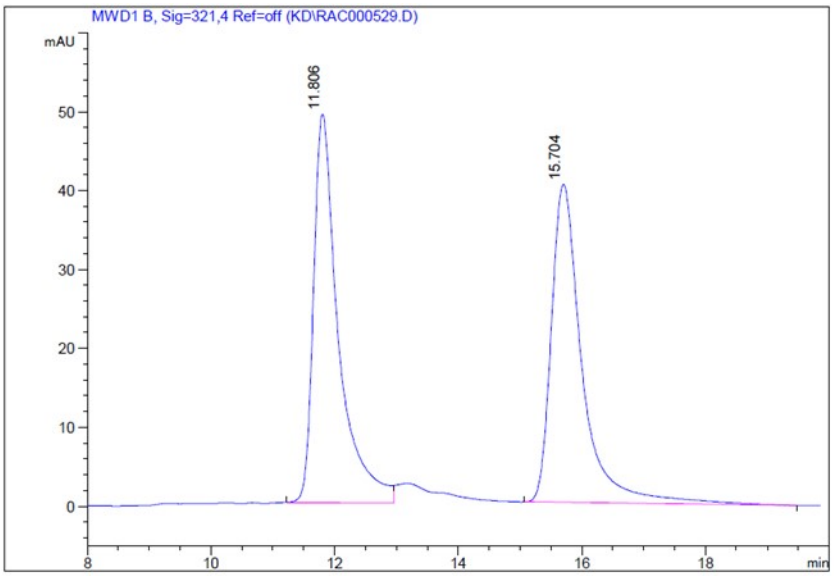


#	Meas. R	Area	Area %
1	9.625	2.338e3	52.593
2	24.907	2.107e3	47.407

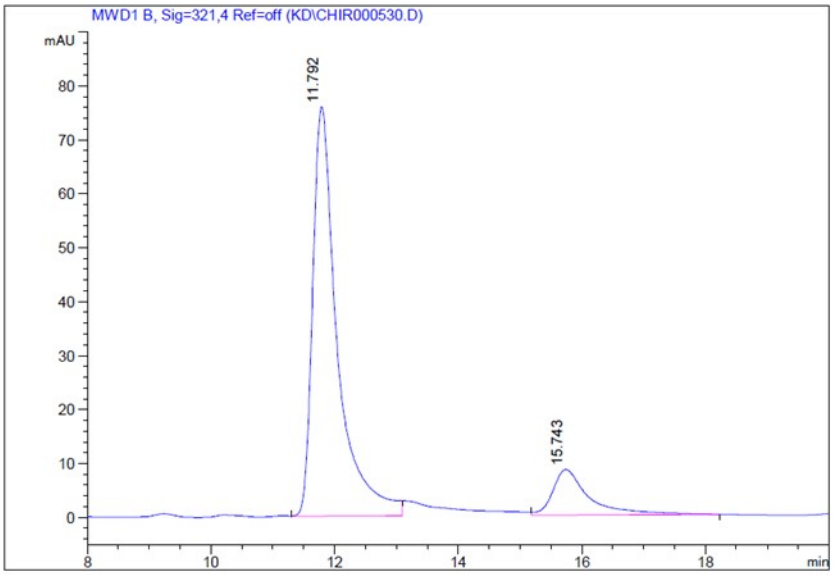


#	Meas. R	Area	Area %
1	9.630	1.279e3	82.994
2	25.009	262.027	17.006

Figure S101. HPLC chromatograms of **3aai**

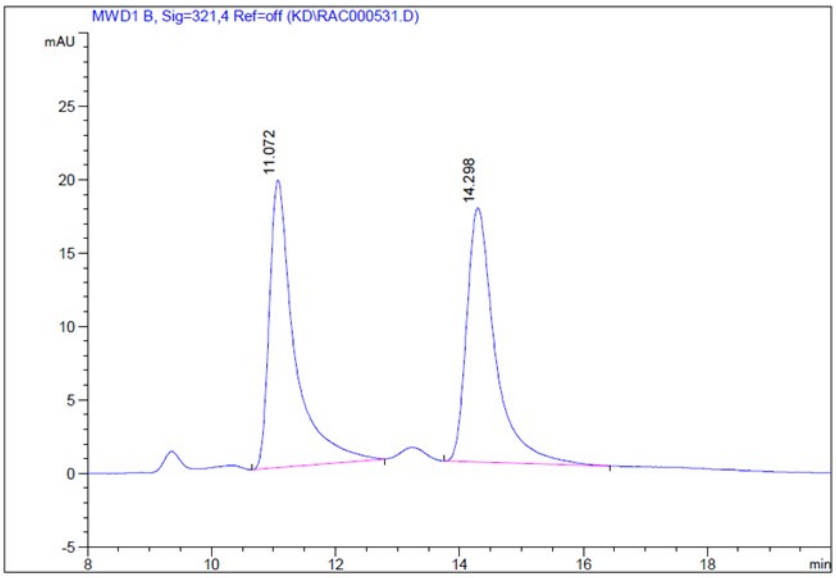


#	Meas. R	Area	Area %
1	11.806	1.381e3	49.717
2	15.704	1.396e3	50.283

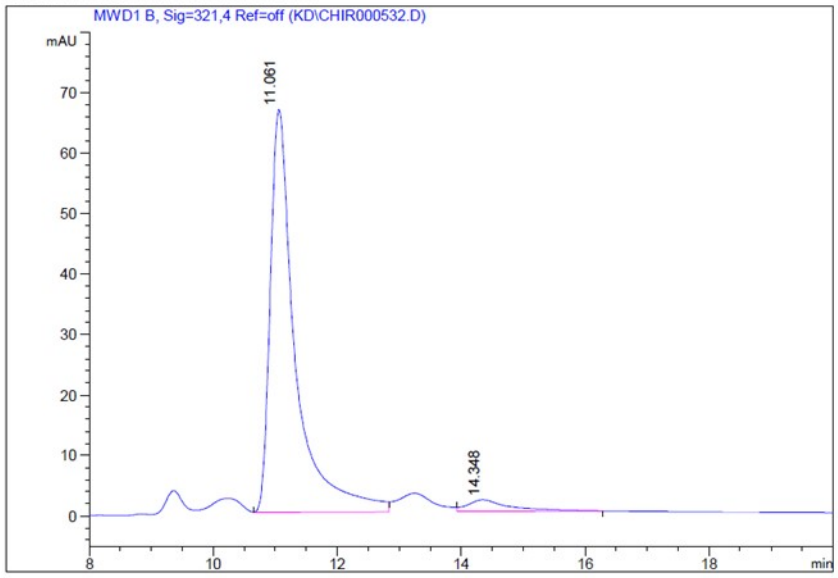


#	Meas. R	Area	Area %
1	11.792	2.097e3	85.835
2	15.743	345.990	14.165

Figure S102. HPLC chromatograms of **3aaj**



#	Meas. R	Area	Area %
1	11.072	552.841	50.043
2	14.298	551.898	49.957



#	Meas. R	Area	Area %
1	11.061	1.870e3	95.358
2	14.348	91.012	4.642

Figure S103. HPLC chromatograms of **3aak**

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