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Supporting Information

Regiospecific construction of diverse and polyfunctionalized γ-pyrone cores by indium (III)-catalyzed annulation of diazodicarbonyls with active methylenes, 4-hydroxycoumarins, or 4-hydroxyquinolinone

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General information

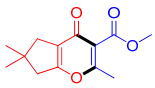
All experiments were carried out under N_2 gas protected reactions. The starting materials, 2-diazocyclohexane-1,3-diones (**1a-1h**) and aliphatic substituted diazo compounds **1i-1m** were all synthesized in the laboratory. Active methylene compounds (**2a-2e**, **4a-4g**, **6a-6c**, **12**, and **14**) were purchased from TCI (Tokyo Chemical Industry), while 4-hydroxy-2*H*-chromen-2-one (**8a-8e**) derivatives, 4-hydroxy-1-methylquinolin-2(1H)-one (**8f**), ethanol (**21a**), and benzyl alcohol (**21b**) were purchased from Sigma-Aldrich. All purchased chemicals were used as received. The catalyst, Indium (III) bromide was purchased from Sigma- Aldrich and was used as received. Merck pre-coated silica gel plates (Art. 5554) with a fluorescent indicator were used for analytical TLC. Flash column chromatography was performed using silica gel 9385 (Merck). Melting points were determined with micro-cover glasses on a Fisher-Johns apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Varian-VNS (600 MHz) or DPX (300 MHz) spectrometer in $CDCl_3$ with 7.24 ppm as the internal standard chemical shift of the solvent. ^{13}C NMR spectra were recorded on a Varian-VNS (150 MHz) or DPX (75 MHz) spectrometer in $CDCl_3$ with 77.0 ppm as the internal standard solvent chemical shift. All chemical shifts (δ) are expressed in units of ppm and J values are given in Hz. Multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or overlap of nonequivalent resonances, and dd = doublet of doublets. Infrared (IR) spectra were recorded on a PerkinElmer Spectrum Two^{TM} IR spectrometer with frequencies expressed in cm^{-1}. With the use of JEOL JMS-700 spectrometer, high resolution mass spectroscopy (HRMS) were obtained at the Korea Basic Science Institute.

General procedure for the synthesis of substituted γ-pyrones 3

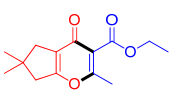
To a magnetically stirred solution of a cyclic diazo compound **1a-1h** (1.2 mmol) or acyclic diazo compound **1i-1j** (1.2 mmol) in toluene (5mL), β-ketoester **2a-2e** (1.0 mmol) was added. It was followed by the addition of $InBr_3$ (10 mol%) in the solution and was thoroughly stirred. The reaction mixture was kept in refluxing toluene condition for 4 hours under N_2 gas protection. It was monitored by TLC (hexane/ethyl acetate = 1:1) until completion of the reaction. Then, the reaction mixture was dried using a rotary evaporator and was subjected for flash column chromatography using hexane/ethyl acetate (20:3) as the solvent system.

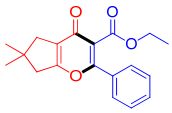
Characterization data of compounds 3

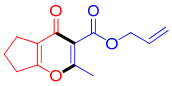
Methyl 2,6,6-trimethyl-4-oxo-4,5,6,7-tetrahydrocyclopenta[*b*]pyran-3-carboxylate (3a). The product **3a** was obtained as a yellow sticky liquid. Yield: 83% (196 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.85 (3H, s), 2.61 (2H, s), 2.49 (2H, s), 2.32 (3H, s), 1.16 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.1, 166.2, 165.8, 165.6, 124.3, 121.5, 52.5, 46.1, 40.7, 36.2, 29.7, 28.0, 18.5; IR (ATR) 2960, 2874, 1729, 1643, 1543, 1456, 1366, 1244, 1208, 1171, 1128, 1049, 978, 805, 558 cm^{-1}; HRMS *m/z* $[M+Na]^+$ calcd for $C_{13}H_{16}NaO_4$: 259.0947, Found: 259.0941.

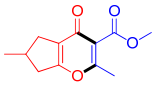


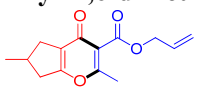
Ethyl 2,6,6-trimethyl-4-oxo-4,5,6,7-tetrahydrocyclopenta[*b*]pyran-3-carboxylate (3b). The product **3b** was obtained as a yellow sticky liquid. Yield: 75% (186 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.32 (2H, q, J = 7.2 Hz), 2.60 (2H, s), 2.48 (2H, s), 2.30 (3H, s), 1.32 (3H, t, J = 7.2 Hz), 1.15 (6H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.1, 166.2, 165.3, 165.0, 124.2, 121.8, 61.6, 46.1, 40.7, 36.2, 29.8, 29.6, 18.3, 14.1; IR (ATR) 2959, 2872, 1730, 1656, 1444, 1255, 1173, 1124, 1047, 803 cm^{-1}; HRMS *m/z* $[M+Na]^+$ calcd for $C_{14}H_{18}NaO_4$: 273.1103, Found: 273.1097.

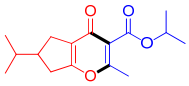


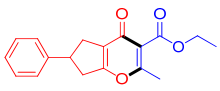
Ethyl 6,6-dimethyl-4-oxo-2-phenyl-4,5,6,7-tetrahydrocyclopenta[*b*]pyran-3-carboxylate (3c). 
The product **3c** was obtained as a pale-yellow solid, mp 100-101 ºC. Yield: 73% (228 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (2H, d, J = 7.8 Hz), 7.48 (1H, t, J = 7.2 Hz), 7.43 (2H, t, J = 7.8 Hz), 4.22 (2H, q, J = 14.4 Hz), 2.72 (2H, s), 2.59 (2H, s), 1.21 (6H,s), 1.12 (3H, t, J = 7.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.5, 167.2, 165.2, 162.8, 131.5, 131.2, 128.7, 127.8, 124.4, 122.0, 61.8, 46.3, 40.8, 36.3, 29.7, 13.8; IR (ATR) 2954, 1726, 1648, 1627, 1423, 1063, 778 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{19}H_{20}O_4$: 312.1362, Found: 312.1360.

Allyl 2-methyl-4-oxo-4,5,6,7-tetrahydrocyclopenta[*b*]pyran-3-carboxylate (3d). 
The product **3d** was obtained as a light-yellow sticky liquid. Yield: 66% (154 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.99-5.93 (1H, m), 5.42 (1H, dd, J = 16.8, 1.2 Hz), 5.25 (1H, dd, J = 11.4, 1.2 Hz), 4.78 (1H, d, J = 5.4 Hz), 2.82 (2H, t, J = 7.8 Hz), 2.71 (2H, t, J = 7.2 Hz), 2.33 (3H, s), 2.06-2.01 (2H, m); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.9, 167.9, 165.4, 165.0, 131.6, 125.2, 121.5, 118.9, 66.1, 31.4, 25.8, 19.4, 18.4; IR (ATR) 2937, 2872, 1728, 1654, 1622, 1428, 1228, 1120, 1040, 965, 935, 791 cm^{-1}; HRMS *m/z* $[M+Na]^+$ calcd for $C_{13}H_{14}NaO_4$: 257.0790, Found: 257.0784.

Methyl 2,6-dimethyl-4-oxo-4,5,6,7-tetrahydrocyclopenta[*b*]pyran-3-carboxylate (3e). 
The product **3e** was obtained as a yellow sticky liquid. Yield: 68% (151 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.85 (3H, s), 2.97 (1H, dd, J = 17.4, 9.0 Hz), 2.87 (1H, dd, J = 15.0, 8.4 Hz), 2.55-2.50 (1H, m), 2.41 (1H, dd, J = 17.4, 5.4 Hz), 2.32 (3H, s), 2.27 (1H, dd, J = 15.6, 5.4 Hz), 1.11 (3H, d, J = 6.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.0, 166.9, 165.8, 165.5, 124.5, 121.4, 52.5, 39.4, 34.0, 28.8, 21.6, 18.5; IR (ATR) 2957, 2872, 1732, 1652, 1444, 1255, 1219, 1122, 1044, 981, 789 cm^{-1}; HRMS *m/z* $[M+Na]^+$ calcd for $C_{12}H_{14}NaO_4$: 245.0790, Found: 245.0784.

Allyl 2,6-dimethyl-4-oxo-4,5,6,7-tetrahydrocyclopenta[*b*]pyran-3-carboxylate (3f). 
The product **3f** was obtained as a light-yellow sticky liquid. Yield: 67% (166 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.00-5.93 (1H, m), 5.42 (1H, dd, J = 17.4, 1.8 Hz), 5.26 (1H, d, J = 10.8 Hz), 4.79 (2H, d, J = 5.4 Hz), 2.99 (1H, dd, J = 16.8, 7.2 Hz), 2.89 (1H, dd, J = 15.6, 7.8 Hz), 2.57-2.51 (1H, m), 2.44 (1H, dd, J = 6.0, 5.4 Hz), 2.41 (1H, dd, J = 6.0, 1.2 Hz), 2.29 (1H, dd, J = 15.6, 4.2 Hz), 1.13 (3H, d, J = 6.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.0, 167.0, 165.4, 165.1, 131.6, 124.6, 121.5, 119.0, 66.2, 39.5, 34.0, 28.9, 21.7, 18.5; IR (ATR) 2959, 2925, 2872, 1730, 1654, 1449, 1253, 1219, 1123, 1042, 981, 933, 794 cm^{-1}; HRMS *m/z* $[M+Na]^+$ calcd for $C_{14}H_{16}NaO_4$: 271.0947, Found: 271.0941.

Isopropyl 6-isopropyl-2-methyl-4-oxo-4,5,6,7-tetrahydrocyclopenta[*b*]pyran-3-carboxylate (3g). 
The product **3g** was obtained as a yellow sticky liquid. Yield: 70% (195 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.23-5.17 (1H, m), 2.83-2.77 (2H, m), 2.55 (1H, dd, J = 18.0, 8.4 Hz), 2.33 (1H, dd, J = 15.6, 7.8 Hz), 2.29 (3H, s), 2.19-2.12 (1H, m), 1.63-1.55 (1H, m), 2.60 (6H, d, J = 6.6 Hz), 0.88 (6H, d, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.9, 167.1, 164.7, 164.4, 162.2, 124.8, 122.0, 69.4, 41.8, 35.6, 30.1, 21.7, 20.4, 20.1, 18.2; IR (ATR) 2960, 2874, 2141, 1727, 1659, 1637, 1430, 1386, 1261, 1219, 1102, 1049, 965, 836, 796 cm^{-1}; HRMS *m/z* $[M+Na]^+$ calcd for $C_{16}H_{22}NaO_4$: 301.1416, Found: 301.1410.

Ethyl 2-methyl-4-oxo-6-phenyl-4,5,6,7-tetrahydrocyclopenta[*b*]pyran-3-carboxylate (3h). 
The product **3h** was obtained as a yellow sticky liquid. Yield: 61% (182 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29-7.25 (4H, m), 7.18 (1H, t, J = 7.2 Hz), 4.32 (2H, q, J = 7.2 Hz), 3.73-3.68 (1H, m), 3.32 (1H, dd, J = 17.4, 9.0 Hz), 3.15 (1H, dd, J = 16.2, 7.8 Hz), 3.03 (1H, dd, J = 18.0, 7.8 Hz), 2.70 (1H, dd, J = 15.6, 7.2 Hz), 2.38 (3H, s), 1.13 (3H, t, J = 7.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.1, 169.9, 167.8, 166.4, 145.7, 129.8, 127.8, 125.0, 122.8, 62.9, 41.12, 41.06, 40.4, 35.4, 14.4; IR (ATR) 2979,

2937, 1728, 1657, 1631, 1431, 1255, 1218, 1055, 1027, 965, 798, 760, 700 cm^{-1}; HRMS *m/z* $[M+Na]^+$ calcd for $C_{18}H_{18}NaO_4$: 321.1103, Found: 321.1097.

Ethyl 4-oxo-2,6-diphenyl-4,5,6,7-tetrahydrocyclopenta[*b*]pyran-3-carboxylate (3i). The product **3i** was obtained as a pale-yellow viscous liquid. Yield: 62% (223 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (2H, d, J = 7.8 Hz), 7.50 (1H, t, J = 7.2 Hz), 7.44 (2H, t, J = 7.8 Hz), 7.32 (2H, t, J = 8.4 Hz), 7.26-7.23 (3H,m), 4.24 (2H, q, J = 14.4 Hz), 3.75-3.70 (1H, m), 3.36 (1H, dd, J = 17.4, 9.6 Hz), 3.30 (1H, dd, J = 16.2, 9.0 Hz), 3.07 (1H, dd, J = 18.0, 7.8 Hz), 2.90 (1H, dd, J = 16.2, 7.2 Hz), 1.15 (3H, t, J = 7.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.0, 166.9, 165.1, 162.8, 144.3, 131.5, 131.2, 128.8, 128.7, 127.8, 126.8, 126.7, 124.5, 122.2, 61.9, 39.9, 39.6, 34.4, 13.8; IR (ATR) 2929, 1730, 1650, 1629, 1444, 1425, 1067, 767, 696 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{23}H_{20}O_4$: 360.1362, Found: 360.1360.

Methyl 6-(benzo[*d*][1,3]dioxol-5-yl)-2-methyl-4-oxo-4,5,6,7-tetrahydrocyclopenta[*b*]pyran-3-carboxylate (3j). The product **3j** was obtained as a brown sticky solid, mp 94-96 °C. Yield: 68% (223 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.72 (1H, d, J = 7.2 Hz), 6.69 (1H, s), 6.65 (1H, d, J = 7.8 Hz), 3.88 (3H, s), 3.60-3.55 (1H, m), 3.23 (1H, dd, J = 17.4, 9.0 Hz), 3.17 (1H, dd, J = 16.2, 9.0 Hz), 2.90 (1H, dd, J = 18.0, 7.8 Hz), 2.74 (1H, dd, J = 15.6, 7.2 Hz), 2.36 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.6, 166.1, 165.8, 165.7, 148.0, 146.3, 138.2, 124.4, 121.7, 119.7, 108.3, 107.0, 101.0, 52.6, 39.9, 39.4, 34.4, 18.6; IR (ATR) 2958, 2891, 1735, 1656, 1619, 1487, 1437, 1387, 1248, 1214, 1118, 1027, 928, 790, 635 cm^{-1}; HRMS *m/z* $[M+Na]^+$ calcd for $C_{18}H_{16}NaO_6$: 351.0845, Found: 351.0839.

Methyl 6-(4-chlorophenyl)-2-methyl-4-oxo-4,5,6,7-tetrahydrocyclopenta[*b*]pyran-3-carboxylate (3k). The product **3k** was obtained as a yellow sticky solid, mp 53-55 °C. Yield: 63% (200 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (2H, d, J = 7.8 Hz), 7.14 (2H, d, J = 9.0 Hz), 3.89 (3H, s), 3.66-3.61 (1H, m), 3.27 (1H, dd, J = 18.0, 9.6 Hz), 3.21 (1H, dd, J = 16.8, 9.6 Hz), 2.92 (1H, dd, J = 17.4, 7.2 Hz), 2.92 (1H, dd, J = 17.4, 7.2 Hz), 2.77 (1H, dd, J = 16.8, 7.2 Hz), 2.37 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.6, 165.9, 165.6, 142.8, 132.5, 128.9, 128.0, 124.3, 121.7, 52.7, 39.7, 38.9, 34.2, 18.6; IR (ATR) 2949, 2851, 2134, 1720, 1657, 1635, 1431, 1261, 1218, 1120, 1060, 1013, 827, 799, 531 cm^{-1} HRMS *m/z* $[M+Na]^+$ calcd for $C_{17}H_{15}ClNaO_4$: 341.0557, Found: 341.0551.

Methyl 6-(furan-2-yl)-2-methyl-4-oxo-4,5,6,7-tetrahydrocyclopenta[*b*]pyran-3-carboxylate (3l). The product **3l** was obtained as a dark brown sticky liquid. Yield: 77% (211 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (1H, s), 6.27 (1H, s), 6.07 (1H, s), 3.88 (3H, s), 3.73-3.68 (1H, m), 3.19 (1H, dd, J = 17.6, 9.0 Hz), 3.12 (1H, dd, J = 16.2, 9.0 Hz), 3.05 (1H, dd, J = 17.4, 5.4 Hz), 2.88 (1H, dd, J = 15.6, 5.4 Hz), 2.35 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.6. 165.9, 165.8, 165.6, 156.4, 141.7, 124.1, 121.6, 110.2, 104.8, 52.6, 37.1, 33.0, 31.6, 18.6; IR (ATR) 3118, 2953, 2925, 2854, 1730, 1656, 1631, 1437, 1340, 1259, 1220, 1122, 1038, 969, 795, 735 cm^{-1}; HRMS *m/z* $[M+Na]^+$ calcd for $C_{15}H_{14}NaO_5$: 297.0739, Found: 297.0733.

Isopropyl 6-(4-(furan-2-yl)phenyl)-2-methyl-4-oxo-4,5,6,7-tetrahydrocyclopenta[*b*]pyran-3-carboxylate (3m). The product **3m** was obtained as a dark brown sticky liquid. Yield: 84% (275 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (1H, s), 6.25 (1H, t, J = 3.0 Hz), 6.04 (1H, d, J = 3.0 Hz), 5.24-5.18 (1H, m), 3.70-3.65 (1H, m), 3.16 (1H, dd, J = 17.4, 9.6 Hz), 3.09 (1H, dd, J = 15.6, 8.4 Hz), 3.01 (1H, dd, J = 17.4, 7.2 Hz), 2.85 (1H, dd, J = 16.2, 6.6 Hz), 2.31 (3H, s), 1.31 (6H, d, J = 6.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.6. 165.9, 164.7, 164.5, 156.4, 141.6, 123.9, 122.1, 110.1, 104.7, 69.4, 36.9, 33.0, 32.9, 31.5, 29.6, 21.6, 18.2; IR (ATR) 3118, 1981, 2931, 2141, 1725, 1659, 1632, 1434, 1260, 1221, 1130, 1101, 1036, 736 cm^{-1}; HRMS *m/z* $[M+Na]^+$ calcd for $C_{17}H_{18}NaO_5$: 325.1052, Found: 325.1046.

Methyl 5,6-diethyl-2-methyl-4-oxo-4*H*-pyran-3-carboxylate (3n). The product **3n** was obtained as a yellow sticky liquid. Yield: 80% (179 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.84 (3H, s), 2.54 (2H, q, J = 15.0 Hz), 2.36 (2H, q, J = 15.0 Hz), 2.29 (3H, s), 1.19 (3H, t, J = 7.8 Hz), 1.01 (3H, t, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.3, 165.8, 165.1, 165.1, 126.0, 119.8, 52.4, 24.2, 18.6, 17.5, 13.3, 11.9; IR (ATR) 2972, 1732, 1656, 1620, 1434, 1412, 1137, 1075, 1034, 941, 785 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{12}H_{16}O_4$: 224.1049, Found: 224.1051.

Ethyl 5,6-diethyl-4-oxo-2-phenyl-4*H*-pyran-3-carboxylate (3o). The product **3o** was obtained as a pale-yellow solid, mp 85-87 °C. Yield: 85% (255 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (2H, d, J = 7.2 Hz), 7.47 (1H, t, J = 7.5 Hz), 7.43 (2H, t, J = 6.6 Hz), 4.23 (2H, q, J = 14.4 Hz), 2.67 (2H, q, J = 15.6 Hz), 2.47 (2H, q, J = 13.8 Hz), 1.28 (3H, t, J = 7.8 Hz), 1.16 (3H, t, J = 6.6 Hz), 1.09 (3H, t, J = 7.8 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.9, 165.6, 165.3, 161.2, 131.7, 131.1, 128.6, 127.6, 126.1, 120.3, 61.7, 24.5, 17.6, 13.8, 13.3, 11.9; IR (ATR) 2971, 1728, 1649, 1613, 1408, 1250, 1102, 776, 704 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{18}H_{20}O_4$: 300.1362, Found: 300.1365.

Methyl 2-methyl-4-oxo-5,6-diphenyl-4*H*-pyran-3-carboxylate (3p). The product **9e** was obtained as a white solid, mp 139-141 °C. Yield: 85% (272 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (1H, t, J = 7.2 Hz), 7.20-7.14 (7H, m), 7.09-7.07 (2H, m), 3.83 (3H, s), 2.41 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.8, 165.6, 165.4, 160.7, 131.9, 131.4, 130.8, 130.1, 129.1, 128.1, 128.1, 127.8, 126.3, 120.9, 52.5, 18.8; IR (ATR) 2926, 2161, 2025, 1976, 1705, 1641, 1399, 1277, 1087, 696 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{20}H_{16}NO_3$: 320.1049, Found: 320.1046.

Ethyl 4-oxo-2,5,6-triphenyl-4*H*-pyran-3-carboxylate (3q). The product **3q** was obtained as a white solid, mp 157-159 °C. Yield: 87% (345 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (2H, d, J = 4.2 Hz), 7.46 (1H, t, J = 7.8 Hz), 7.42 (2H, t, J = 7.2 Hz), 7.25 (3H, d, J = 5.4 Hz), 7.23-7.20 (3H, m), 7.19-7.18 (2H, m), 7.16-7.14 (2H, m), 4.24 (2H, q, J = 13.8 Hz), 1.16 (3H, t, J = 7.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.5, 165.0, 161.5, 161.2, 132.2, 131.5, 131.4, 131.3, 130.8, 130.2, 129.3, 128.8, 128.3, 128.2, 128.0, 127.8, 126.2, 121.4, 62.0, 13.9; IR (ATR) 2926, 2161, 2025, 1976, 1731, 1622, 1397, 1113, 1038, 749, 694 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{26}H_{20}O_4$: 396.1362, Found: 396.1360.

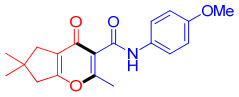
General procedure for the synthesis of substituted γ-pyrones 5

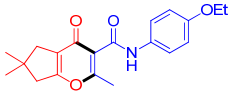
In a magnetically stirred solution of 2-diazo-5,5-dimethylcyclohexane-1,3-dione (**1a**) (1.2 mmol) or acyclic diazo compounds **1i-1j** (1.2 mmol) in toluene (5mL), acetoacetanilide **4a-4g** (1.0 mmol) was added. It was followed by the addition of $InBr_3$ (10 mol%) in the solution and was thoroughly stirred. The reaction mixture was kept in refluxing toluene condition for 4 hours under N_2 gas protection. It was observed by TLC (hexane/ethyl acetate = 1:1) until completion of the reaction. Then, the reaction mixture was dried using a rotary evaporator and was subjected for flash column chromatography using hexane/ethyl acetate (20:3) as the solvent system.

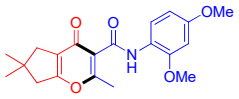
Characterization data of compounds 5

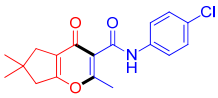
2,6,6-Trimethyl-4-oxo-*N*-phenyl-4,5,6,7-tetrahydrocyclopenta[*b*]pyran-3-carboxamide (5a). The product **5a** was obtained as a white solid, mp 143-145 °C. Yield: 62% (184 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.01 (1H, s), 7.65 (2H, d, J = 7.8 Hz), 7.30 (2H, t, J = 7.2 Hz), 7.07 (1H, t, J = 7.2 Hz), 2.85 (3H, s), 2.70 (2H, s), 2.57 (2H, s), 1.21 (6H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.8, 174.6, 166.6, 162.3, 138.4,

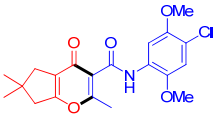
128.8, 124.8, 124.0, 120.6, 117.0, 46.0, 40.7, 36.6, 29.7, 21.7; IR (ATR) 3023, 2934, 2868, 1764, 1686, 1582, 1546, 1440, 1305, 1242, 1173, 1119, 800, 752, 689, 596, 512 cm^{-1}; HRMS *m/z* $[M+Na]^+$ calcd for $C_{18}H_{19}NNaO_3$: 320.1263, Found: 320.1257.

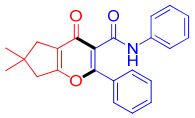
***N*-(4-Methoxyphenyl)-2,6,6-trimethyl-4-oxo-4,5,6,7-tetrahydrocyclopenta[*b*]pyran-3-carboxamide (5b).**  The product **5b** was obtained as a dark brown solid, mp 135-137 °C. Yield: 63% (206 mg); ^1H NMR (600 MHz, $CDCl_3$) δ 11.86 (1H, s), 7.55 (2H, d, J = 9.0 Hz), 6.84 (2H, d, J = 9.0 Hz), 3.76 (3H, s), 2.84 (3H, s), 2.70 (2H, s), 2.56 (2H, s), 1.21 (6H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.8, 174.3, 166.5, 162.0, 156.1, 131.7, 124.7, 122.1, 117.0, 114.0, 55.4, 46.0, 40.7, 36.6, 29.7, 21.6; IR (ATR) 2954, 2925, 1676, 1581, 1542, 1507, 1231, 1172, 1039, 805, 523 cm^{-1}; HRMS *m/z* $[M+Na]^+$ calcd for $C_{19}H_{21}NNaO_4$: 350.1369, Found: 350.1363.

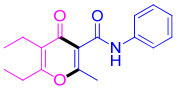
***N*-(4-Ethoxyphenyl)-2,6,6-trimethyl-4-oxo-4,5,6,7-tetrahydrocyclopenta[*b*]pyran-3-carboxamide (5c).**  The product **5c** was obtained as a white solid, mp 170-172 °C. Yield: 70% (239 mg); ^1H NMR (600 MHz, $CDCl_3$) δ 11.85 (1H, s), 7.54 (2H, d, J = 9.0 Hz), 6.84 (2H, d, J = 9.0 Hz), 4.00 (1H, q, J = 7.2 Hz), 2.85 (3H, s), 2.71 (2H, s), 2.57 (2H, s), 1.38 (3H, t, J = 6.6 Hz), 1.21 (6H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.8, 174.4, 166.5, 162.0, 155.5, 131.6, 124.8, 122.1, 114.7, 63.6, 46.1, 40.8, 36.6, 29.8, 21.7, 14.8; IR (ATR) 2958, 2921, 2868, 1678, 1512, 1446, 1374, 1301, 1227, 1171, 1118, 1047, 842, 805, 525 cm^{-1}; HRMS *m/z* $[M+Na]^+$ calcd for $C_{20}H_{23}NNaO_4$: 364.1525, Found: 364.1519.

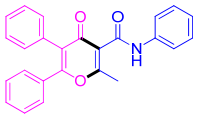
***N*-(2,4-Dimethoxyphenyl)-2,6,6-trimethyl-4-oxo-4,5,6,7-tetrahydrocyclopenta[*b*]pyran-3-carboxamide (5d).**  The product **5d** was obtained as a white solid, mp 151-153 °C. Yield: 68% (243 mg); ^1H NMR (600 MHz, $CDCl_3$) δ 11.93 (1H, s), 8.32 (1H, d, J = 9.0 Hz), 6.47 (1H, s), 6.43 (1H, dd, J = 9.0, 1.8 Hz), 3.89 (3H, s), 3.76 (3H, s), 2.82 (3H, s), 2.67 (2H, s), 2.60 (2H, s), 1.18 (6H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.6, 173.9, 166.2, 161.8, 156.3, 150.5, 124.7, 121.8, 121.4, 117.5, 103.3, 98.5, 55.9, 55.4, 45.9, 40.8, 36.5, 29.7, 21.6; IR (ATR) 2956, 2932, 2868, 1674, 1589. 1541, 1445, 1209, 1158, 1040, 830, 799, 705, 568, 504 cm^{-1}; HRMS *m/z* $[M+Na]^+$ calcd for $C_{20}H_{23}NNaO_5$: 380.1474, Found: 380.1468.

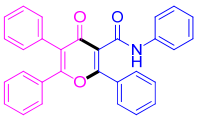
***N*-(4-Chlorophenyl)-2,6,6-trimethyl-4-oxo-4,5,6,7-tetrahydrocyclopenta[*b*]pyran-3-carboxamide (5e).**  The product **5e** was obtained as a white solid, mp 178-180 °C. Yield: 72% (238 mg); ^1H NMR (600 MHz, $CDCl_3$) δ 12.12 (1H, s), 7.57 (2H, d, J = 8.4 Hz), 7.22 (2H, t, J = 7.8 Hz), 2.81 (3H, s), 2.67 (2H, s), 2.53 (2H, s), 1.18 (6H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.7, 174.8, 166.7, 162.3, 137.0, 128.8, 128.7, 124.8, 121.6, 116.6, 46.0, 40.6, 36.6, 29.7, 21.8; IR (ATR) 2954, 2952, 2863, 1684, 1576, 1535, 1489, 1447, 1398, 1305, 1240, 1172, 1091, 829, 804, 511, 441 cm^{-1}; HRMS *m/z* $[M+Na]^+$ calcd for $C_{18}H_{18}ClNNaO_3$: 354.0873, Found: 354.0867.

***N*-(4-Chloro-2,5-dimethoxyphenyl)-2,6,6-trimethyl-4-oxo-4,5,6,7-tetrahydrocyclopenta[*b*]pyran-3-carboxamide (5f).**  The product **5f** was obtained as a white solid, mp 220-222 °C. Yield: 70% (274 mg); ^1H NMR (600 MHz, $CDCl_3$) δ 12.24 (1H, s), 8.36 (1H, s), 6.88 (1H, s), 6.88 (1H, s), 3.89 (6H, s), 2.83 (3H, s), 2.70 (2H, s), 2.58 (2H, s), 1.19 (6H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.6, 174.4, 166.4, 162.3, 148.8, 143.4, 127.9, 124.9, 117.3, 115.6, 112.4, 106.0, 56.80, 56.76, 46.0, 40.8, 36.6, 29.7, 21.7; IR (ATR) 2954, 2859, 1674, 1579, 1515, 1453, 1396, 1211, 1170, 1033, 851, 810, 729 cm^{-1}; HRMS *m/z* $[M+Na]^+$ calcd for $C_{20}H_{22}ClNNaO_5$: 414.1085, Found: 414.1079.

6,6-Dimethyl-4-oxo-*N*,2-diphenyl-4,5,6,7-tetrahydrocyclopenta[*b*]pyran-3-carboxamide (5g). 
The product **5g** was obtained as a white solid, mp 181-183 °C. Yield: 75% (269 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.84 (1H, s), 7.49 (4H, t, J = 9.6 Hz), 7.41-7.39 (1H, m), 7.35 (2H, t, J = 6.6 Hz), 7.17 (2H, t, J = 7.8 Hz), 6.97 (1H, t, J = 7.8 Hz), 2.67 (2H, s), 2.54 (2H, s), 1.16 (6H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.25, 170.2, 167.2, 161.1, 138.2, 133.4, 130.7, 128.7, 128.5, 128.1, 124.8, 124.0, 120.3, 118.8, 46.1, 40.7, 36.5, 29.7; IR (ATR) 3250, 3188, 3036, 2956, 1759, 1596, 1546, 1491, 1441, 1314, 1249, 1170, 1065, 756, 692 cm^{-1}; HRMS *m/z* $[M+Na]^+$ calcd for $C_{23}H_{21}NNaO_3$: 382.1419, Found: 382.1414.

5,6-Diethyl-2-methyl-4-oxo-*N*-phenyl-4*H*-pyran-3-carboxamide (5h). 
The product **5h** was obtained as a brown solid, mp 74-76 °C. Yield: 60% (171 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.14 (1H, s), 7.67 (2H, d, J = 7.8 Hz), 7.30 (2H, t, J = 7.2 Hz), 7.06 (1H, t, J = 7.8 Hz), 2.83 (3H, s), 2.63 (2H, q, J = 15.6 Hz), 2.47 (2H, q, J = 14.4 Hz), 1.26 (3H, t, J = 7.8 Hz), 1.09 (3H, t, J = 7.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 178.9, 173.3, 165.2, 162.4, 138.4, 128.8, 126.2, 123.9, 120.6, 115.6, 24.3, 21.6, 17.7, 13.4, 11.8; IR (ATR) 2975, 2932, 1674, 1651, 1600, 1548, 1410, 1375, 761, 694 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{17}H_{19}NO_3$: 285.1365, Found: 285.1363.

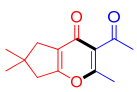
2-Methyl-4-oxo-*N*,5,6-triphenyl-4*H*-pyran-3-carboxamide (5i). 
The product **5i** was obtained as a white solid, mp 226-227 °C. Yield: 43% (164 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.0 (1H, s), 7.67 (2H, d, J = 8.4 Hz), 7.35 (4H, t, J = 7.8 Hz), 7.31-7.30 (4H, m), 7.26 (2H, t, J = 7.2 Hz), 7.19 (2H, d, J = 7.8 Hz), 7.08 (1H, t, J = 5.4 Hz), 3.01 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 178.8, 174.1, 162.0, 160.5, 138.3, 131.6, 131.4, 130.6, 129.2, 128.8, 128.7, 128.4, 128.3, 126.6, 124.1, 120.7, 116.8, 21.9; IR (ATR) 2960, 1730, 1622, 1445, 1397, 1115, 820, 747, 693 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{25}H_{19}NO_3$: 381.1365, Found: 381.1362.

4-Oxo-*N*,2,5,6-tetraphenyl-4*H*-pyran-3-carboxamide (5j). 
The product **5j** was obtained as a white solid, mp 231-232 °C. Yield: 52% (230 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.12 (1H, s), 7.70 (2H, d, J = 7.8 Hz), 7.62 (2H, d, J = 8.4 Hz), 7.54 (1H, t, J = 7.8 Hz), 7.49 (2H, t, J = 6.6 Hz), 7.39-7.35 (3H, m), 7.33 (3H, t, J = 7.8 Hz), 7.28-7.23 (6H, m), 7.06 (1H, t, J = 7.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 178.9, 170.0, 161.0, 160.8, 138.2, 133.3, 131.6, 131.5, 131.2, 130.6, 129.3, 128.9, 128.8, 128.7, 128.4, 128.3, 128.3, 126.7, 124.1, 120.5, 117.8; IR (ATR) 3055, 2924, 2853, 1731, 1622, 1444, 1395, 749, 692 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{30}H_{21}NO_3$: 443.1521, Found: 443.1517.

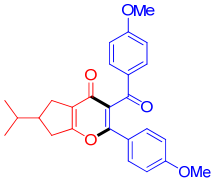
General procedure for the synthesis of substituted γ-pyrones 7

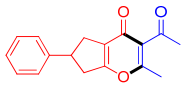
In a magnetically stirred solution of substituted cyclic diazo compounds **1a**, **1d-1h** (1.2 mmol) or acyclic diazo compounds **1i-1j** (1.2 mmol) in toluene (5mL), diketones **6a-6c** (1.0 mmol) was added. It was followed by the addition of $InBr_3$ (10 mol%) in the solution and was thoroughly stirred. The reaction mixture was kept in refluxing toluene condition for 4 hours under N_2 gas protection. It was observed by TLC (hexane/ethyl acetate = 1:1) until completion of the reaction. Then, the reaction mixture was dried using a rotary evaporator and was subjected for flash column chromatography using hexane/ethyl acetate (20:3) as the solvent system.

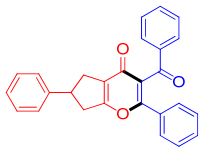
Characterization data of compounds 7

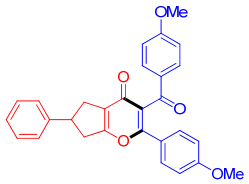
3-Acetyl-2,6,6-trimethyl-6,7-dihydrocyclopenta[*b*]pyran-4(5*H*)-one (7a). 
The product **7a** was obtained as a yellow sticky liquid. Yield: 53% (117 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.63 (2H, s), 2.54 (3H, s), 2.52 (2H, s), 2.32 (3H, s), 1.19 (6H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 201.3, 175.8, 166.7, 166.1, 127.3, 124.8, 46.1, 40.7, 36.3, 32.0, 29.8,

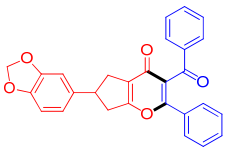
29.7, 18.7; IR (ATR) 2955, 2928, 2864, 1692, 1655, 1624, 1428, 1310, 1239, 1355, 1106, 946, 638 cm^{-1}; HRMS *m/z* $[M+Na]^+$ calcd for $C_{13}H_{16}NaO_3$: 243.0997, Found: 243.0992.

6-Isopropyl-3-(4-methoxybenzoyl)-2-(4-methoxyphenyl)-6,7-dihydrocyclopenta[*b*]pyran-4(5*H*)-one (7b).  The product **7b** was obtained as a light yellow sticky liquid. Yield: 68% (284 mg); ^1H NMR (600 MHz, $CDCl_3$) δ 7.83 (2H, d, J = 8.4 Hz), 7.45 (2H, d, J = 9.0 Hz), 6.83 (2H, d, J = 9.0 Hz), 6.77 (2H, d, J = 9.0 Hz),3.80 (3H, s), 3.74 (3H, s), 2.97 (1H, dd, J = 16.8, 9.0 Hz), 2.90 (1H, dd, J = 15.6, 8.4 Hz), 2.73 (1H, dd, J = 16.8, 7.8 Hz), 2.73 (1H, dd, J = 16.8, 7.8 Hz), 2.44 (1H, dd, J = 16.8, 7.8 Hz), 2.30-2.23 (1H, m), 1.71-1.65 (1H, m), 0.96 (6H, d, J = 6.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.7, 175.9, 167.7, 164.0, 161.5, 161.4, 131.8, 130.2, 129.8, 125.3, 124.7, 123.8, 114.1, 113.9, 55.4, 55.3, 42.1, 36.0, 33.1 30.4, 20.6, 20.2; IR (ATR) 2957, 2842, 1652, 1597, 1506, 1425, 1304, 1252, 1165, 1025, 892, 836, 728 cm^{-1}; HRMS *m/z* $[M+Na]^+$ calcd for $C_{26}H_{26}NaO_5$: 441.1678, Found: 441.1672.

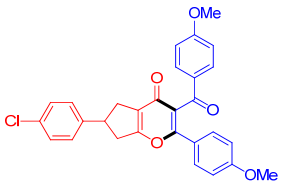
3-Acetyl-2-methyl-6-phenyl-6,7-dihydrocyclopenta[*b*]pyran-4(5*H*)-one (7c).  The product **7c** was obtained as a yellow brown solid, mp 63-65 °C. Yield: 75% (201 mg); ^1H NMR (300 MHz, $CDCl_3$) δ 7.33-7.29 (2H, m), 7.24-7.21 (3H, m), 3.72-3.62 (1H, m), 3.32-3.18 (2H, m), 2.98 (1H, dd, J = 17.4, 7.5 Hz), 2.82 (1H, dd, J = 15.9, 6.9 Hz), 2.56 (3H, s), 2.35 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.1, 175.3, 166.8, 166.1, 144.2, 128.7, 127.3, 126.7, 126.6, 124.9, 39.6, 39.5, 34.2, 32.0, 18.6; IR (ATR) 3059, 2926, 2859, 1661, 1623, 1431, 1355, 1212, 1113, 932, 762, 704, 641, 534 cm^{-1}; HRMS *m/z* $[M+Na]^+$ calcd for $C_{17}H_{16}NaO_3$: 291.0997, Found: 291.0992.

3-Benzoyl-2,6-diphenyl-6,7-dihydrocyclopenta[*b*]pyran-4(5*H*)-one (7d).  The product **7d** was obtained as a yellow sticky liquid. Yield: 73% (286 mg); ^1H NMR (600 MHz, $CDCl_3$) δ 7.81 (2H, d, J = 7.8 Hz), 7.45 (2H, d, J = 7.2 Hz), 7.41 (1H, t, J = 7.8 Hz), 7.30 (2H, t, J = 7.2 Hz), 7.27 (3H, t, J = 7.8 Hz), 7.21 (4H, d, J = 7.2 Hz), 7.20-7.16 (1H, m), 3.72-3.66 (1H, m), 3.34 (1H, dd, J = 18.0 9.6 Hz), 3.23 (1H, dd, J = 15.6, 9.0 Hz), 3.06 (1H, dd, J = 17.4, 7.8 Hz), 2.84 (1H, dd, J = 16.2, 7.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.7, 175.5, 167.2, 162.0, 144.1, 136.7, 133.7, 131.1, 131.0, 129.3, 128.7, 128.6, 128.1, 126.8, 126.7, 126.3, 124.5, 39.9, 39.7, 34.3; IR (ATR) 3060, 2927, 2856, 2245, 1648, 1620, 1442, 1426, 1344, 1224, 1172, 886, 763, 728, 691, 644 cm^{-1}; HRMS *m/z* $[M+Na]^+$ calcd for $C_{27}H_{20}NaO_3$: 415.1310, Found: 415.1305.

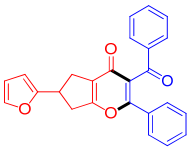
3-(4-Methoxybenzoyl)-2-(4-methoxyphenyl)-6-phenyl-6,7-dihydrocyclopenta[*b*]pyran-4(5*H*)-one (7e).  The product **7e** was obtained as a brown sticky liquid. Yield: 79% (357 mg); ^1H NMR (600 MHz, $CDCl_3$) δ 7.79 (2H, d, J = 9.0 Hz), 7.42 (2H, d, J = 9.0 Hz), 7.25 (2H, t, J = 6.6 Hz), 7.20 (2H, d, J = 7.8 Hz), 7.16 (1H, t, J = 6.6 Hz), 6.76 (2H, d, J = 8.4 Hz), 6.70 (2H, d, J = 9.0 Hz), 3.70 (3H, s), 3.63 (3H, s), 3.32 (1H, dd, J = 17.4, 9.6 Hz), 3.21 (1H, dd, J = 16.2, 9.6 Hz), 3.03 (1H, dd, J = 17.4, 7.2 Hz), 2.81 (1H, dd, J = 15.6, 6.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ192.6. 175.8, 167.0, 164.1, 161.7, 161.6, 144.4, 131.8, 130.1, 129.8, 128.8, 126.84, 126.81, 125.4, 124.2, 123.6, 114.2, 114.0, 55.5, 55.3, 40.0, 39.7, 34.5; IR (ATR) 2934, 2841, 2244, 1650, 1597, 1505, 1426, 1252, 1165, 1025, 892, 836, 728, 701 cm^{-1}; HRMS *m/z* $[M+Na]^+$ calcd for $C_{29}H_{24}NaO_5$: 475.1522, Found: 475.1516.

6-(Benzo[*d*][1,3]dioxol-5-yl)-3-benzoyl-2-phenyl-6,7-dihydrocyclopenta[*b*]pyran-4(5*H*)-one (7f).  The product **7f** was obtained as a light yellow sticky liquid. Yield: 78% (340 mg); ^1H NMR (600 MHz, $CDCl_3$) δ 7.88 (2H, d, J = 7.8 Hz), 7.52-7.48 (3H, m), 7.37 (2H, t, J = 7.8 Hz), 7.34 (1H, d, J = 7.2 Hz), 7.29 (2H, t, J = 7.8 Hz), 6.77-6.72 (3H, m), 3.71-3.66 (1H, m), 3.37 (1H, dd, J = 17.4, 9.6 Hz), 3.27 (1H, dd, J = 15.6, 8.4 Hz), 3.07 (1H, dd, J = 18.0, 7.8 Hz), 2.85 (1H, dd, J = 16.2, 7.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.7, 175.4, 167.1, 162.0, 148.0,

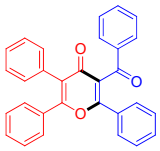
146.3, 138.1, 136.7, 133.7, 131.2, 131.0, 129.3, 128.6, 128.1, 126.4, 124.4, 119.8, 108.3, 107.1, 101.0, 40.1, 39.6, 34.6; IR (ATR) 3060, 2895, 2371, 1671, 1647, 1619, 1491, 1440, 1344, 1234, 1173, 1035, 764, 691 cm^{-1}; HRMS *m/z* $[M+Na]^+$ calcd for $C_{28}H_{20}NaO_5$: 459.1209, Found: 459.1203.

6-(4-Chlorophenyl)-3-(4-methoxybenzoyl)-2-(4-methoxyphenyl)-6,7-dihydrocyclopenta[*b*]pyran-4(5*H*)-one (7g). 

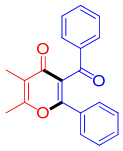
The product **7g** was obtained as a yellow sticky solid, mp 89-91 °C. Yield: 77% (374 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (2H, d, J = 8.4 Hz), 7.48 (2H, d, J = 9.0 Hz), 7.29 (2H, d, J = 8.4 Hz), 7.20 (2H, d, J = 8.4 Hz), 6.84 (2H, d, J = 9.0 Hz), 6.78 (2H, d, J = 8.4 Hz), 3.79 (3H, s), 3.73 (3H, s), 3.71-3.68 (1H, m), 3.40 (1H, dd, J = 18.0, 9.6 Hz), 3.27 (1H, dd, J = 15.6, 8.4 Hz), 3.05 (1H, dd, J = 17.4, 7.8 Hz), 2.84 (1H, dd, J = 15.6, 6.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.4, 175.6, 166.5, 164.0, 161.7, 161.6, 142.8, 132.4, 131.8, 130.0, 129.7, 128.8, 128.1, 1253, 123.9, 123.5, 114.1, 113.9, 55.4, 55.3, 33.9, 39.0, 34.4; IR (ATR) 2936, 2841, 2244, 1649, 1597, 1504, 1426, 1252, 1165, 1023, 832, 727 cm^{-1} HRMS *m/z* $[M+Na]^+$ calcd for $C_{29}H_{23}ClNaO_5$: 509.1132, Found: 509.1126.

3-Benzoyl-6-(4-(furan-2-yl)phenyl)-2-phenyl-6,7-dihydrocyclopenta[*b*]pyran-4(5*H*)-one (7h). 

The product **7h** was obtained as a dark brown sticky liquid. Yield: 76% (290 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (2H, d, J = 7.8 Hz), 7.50-7.47 (3H, m), 7.36 (2H, t, J = 7.8 Hz), 7.33 (2H, d, J = 7.2 Hz), 7.28 (2H, t, J = 7.8 Hz), 6.31 (1H, t, J = 1.8 Hz), 6.13 (1H, d, J = 3.0 Hz), 3.83-3.78 (1H, m), 3.34 (1H, dd, J = 17.4, 8.4 Hz), 3.21 (2H, dd, J = 15.0, 7.8 Hz), 2.99 (1H, dd, J = 16.2, 6.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.6, 175.5, 166.8, 162.0, 156.4, 141.8, 136.7, 133.7, 131.1, 131.0, 129.3, 128.6, 128.1, 126.3, 124.1, 110.2, 104.9, 37.3, 33.0, 31.7; IR (ATR) 3062, 2921, 2246, 2139, 1744, 1649, 1620, 1442, 1344, 1228, 1172, 885, 765, 728, 691 cm^{-1}; HRMS *m/z* $[M+Na]^+$ calcd for $C_{25}H_{18}NaO_4$: 405.1103, Found: 405.1097.

3-Benzoyl-2,5,6-triphenyl-4*H*-pyran-4-one (7i). 

The product **7i** was obtained as a white solid, mp 280-281 °C. Yield: 68% (291 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.0 (2H, d, J = 7.8 Hz), 7.67-7.63 (3H, m), 7.52 (2H, t, J = 7.8 Hz), 7.48-7.40 (5H, m), 7.40 (1H, d, J = 7.2 Hz), 7.35 (2H, t, J = 7.8 Hz), 7.31-7.29 (3H, m), 7.21 (2H, d, J = 7.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.2, 176.2, 161.5, 160.7, 136.3, 134.1, 132.1, 131.8, 131.3, 131.0, 130.8, 130.3, 129.3, 129.1, 129.0, 128.9, 128.3, 128.0, 128.0, 127.7, 125.5, 125.0; IR (ATR) 3061, 1731, 1672, 1620, 1385, 774, 742, 691, 631, 516 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{30}H_{20}O_3$: 428.1412, Found: 428.1408.

3-Benzoyl-5,6-dimethyl-2-phenyl-4*H*-pyran-4-one (7j). 

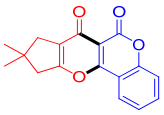
The product **7j** was obtained as a pale yellow solid, mp 153-155 °C. Yield: 75% (226 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (2H, d, J = 7.8 Hz), 7.51-7.47 (3H, m), 7.38-7.33 (3H, m), 7.28 (2H, t, J = 7.2 Hz), 2.41 (3H, s), 1.99 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.9, 177.5, 161.6, 160.8, 136.9, 133.6, 131.4, 130.9, 129.3, 128.6, 128.0, 124.2, 121.3, 17.9, 9.7; IR (ATR) 3069, 2924, 1672, 1650, 1603, 1412, 1374, 885, 760, 695 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{20}H_{16}O_3$: 304.1099, Found: 304.1102.

General procedure for the synthesis of tetrasubstituted γ-pyrones 9

To a solution of 2-diazo-5,5-dimethylcyclohexane-1,3-dione **1a-1e** (1.2 mmol), 4-hydroxy-*2H*-chromen-2-one **8a-8e** (1 mmol) or 4-hydroxy-1-methylquinolin-2(1*H*)-one (**8f**) (1 mmol) was added. It was followed by the addition of $InBr_3$ (10 mol%) in the solution and was thoroughly stirred. The reaction mixture was kept in refluxing toluene condition for 4 hours under N_2 gas protection until completion of the reaction as presented by the TLC. The solvents were evaporated and then the residue was purified by filtration using ethanol (Merck, ≥99.9%) to obtain the product.

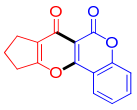
Characterization data of compounds 9

9,9-Dimethyl-9,10-dihydro-6*H*-cyclopenta[5,6]pyrano[3,2-*c*]chromene-6,7(8*H*)-dione (9a). The



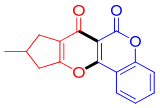
product **9a** was obtained as a white solid, mp 230-232 °C. Yield: 93% (262 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (1H , d, J = 7.8 Hz), 7.60 (1H, t, J = 7.8 Hz), 7.30 (1H, t, J = 7.8 Hz), 7.24 (1H, d, J = 8.4 Hz), 2.79 (2H, s), 2.55 (2H, s), 1.18 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7, 165.2, 164.6, 156.4, 153.1, 134.7, 126.4, 124.6, 123.4, 116.9, 113.0, 107.8, 45.9, 40.8, 36.2, 29.6; IR (ATR) 2933, 2864, 1750, 1657, 1546, 1421, 763 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{17}H_{14}O_4$: 282.0892, Found: 282.0891.

9,10-Dihydro-6*H*-cyclopenta[5,6]pyrano[3,2-*c*]chromene-6,7(8*H*)-dione (9b). The product **9b** was



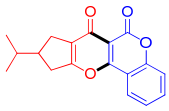
obtained as a light brown solid, mp 243-245 °C. Yield: 90% (228 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (1H , d, J = 8.1 Hz), 7.65 (1H, t, J = 8.1 Hz), 7.38–7.30 (2H, m), 3.03 (2H, t, J = 7.5 Hz), 2.81 (2H, t, J = 7.2 Hz), 2.19–2.09 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.9, 166.7, 165.3, 156.7, 153.3, 134.9, 127.6, 124.8, 123.6, 117.1, 113.1, 107.8, 31.5, 26.1, 19.2; IR (ATR) 3066, 1743, 1606, 1418, 1200, 773 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{15}H_{10}O_4$: 254.0579, Found: : 254.0580.

9-Methyl-9,10-dihydro-6*H*-cyclopenta[5,6]pyrano[3,2-*c*]chromene-6,7(8*H*)-dione (9c). The product **9c**



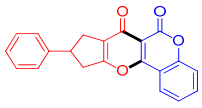
was obtained as an ivory solid, m.p. 241-243 °C. Yield: 78% (206 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (1H , d, J = 7.2 Hz), 7.64 (1H, t, J = 7.5 Hz), 7.36–7.28 (2H, m), 3.17 (1H, dd, J = 18.9, 9.9 Hz), 2.97 (1H, dd, J = 15.9, 8.1 Hz), 2.65–2.57 (2H, m), 2.37 (1H, dd, J = 15.9, 4.8 Hz), 1.17 (3H, d, J = 6.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.8, 165.4, 165.2, 156.5, 153.2, 134.8, 126.9, 124.7, 123.5, 117.0, 113.1, 107.9, 39.4, 34.2, 28.8, 21.6; IR (ATR) 2957, 1740, 1607, 1408, 1201, 763 cm^{-1}; HRMS *m/z* (M^+): calcd for $C_{16}H_{12}O_4$: 268.0736, Found: 268.0734.

9-Isopropyl-9,10-dihydro-6*H*-cyclopenta[5,6]pyrano[3,2-*c*]chromene-6,7(8*H*)-dione (9d). The product



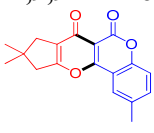
9d was obtained as a light yellow solid, m.p. 207-209 °C. Yield: 88% (255 mg); ^{1}H NMR (600 MHz, Acetone-d_6) δ 8.07 (1H , d, J = 7.8 Hz), 7.79 (1H, t, J = 7.2 Hz), 7.46 (1H, t, J = 8.4 Hz), 7.38 (1H, d, J = 8.4 Hz), 3.12 (1H, dd, J = 18.0, 9.6 Hz), 2.90–2.86 (1H, m), 2.82 (1H, dd, J = 15.0, 7.8 Hz), 2.41–2.30 (2H, m), 1.76–1.70 (1H, m), 0.98 (6H, d, J = 6.0 Hz); ^{13}C NMR (150 MHz, Acetone-d_6) δ 172.6, 166.4, 166.0, 156.3, 154.4, 135.6, 127.4, 125.4, 124.5, 117.5, 114.4, 108.8, 42.7, 36.1, 33.8, 31.1, 20.8, 20.4; IR (ATR) 3063, 2951, 1741, 1432, 1201, 754 cm^{-1}; HRMS *m/z* (M^+): calcd for $C_{18}H_{16}O_4$: 296.1049, Found: 296.1046.

9-Phenyl-9,10-dihydro-6*H*-cyclopenta[5,6]pyrano[3,2-*c*]chromene-6,7(8*H*)-dione (9e).The product **9e**



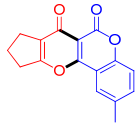
was obtained as a red brown solid, m.p. 213-215 °C. Yield: 76% (246 mg;); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (1H, dd, J = 8.1, 1.2 Hz), 7.66 (1H, t, J = 8.1 Hz), 7.38–7.21 (7H, m), 3.81–3.70 (1H, m), 3.47 (1H, dd, J = 17.4, 9.9 Hz), 3.29 (1H, dd, J = 16.5, 10.2 Hz), 3.16 (1H, dd, J = 17.7, 7.5 Hz), 2.89 (1H, dd, J = 15.9, 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.4, 165.4, 164.7, 156.4, 153.3, 143.7, 134.9, 128.8, 126.9, 126.8, 126.7, 124.7, 123.6, 117.2, 113.1, 108.1, 39.6, 39.5, 34.4; IR (ATR) 3044, 1745, 1644, 1410, 1199, 754, 696 cm^{-1}; HRMS *m/z* (M^+): calcd for $C_{21}H_{14}O_4$: 330.0892, Found: 330.0892.

2,9,9-Trimethyl-9,10-dihydro-6*H*-cyclopenta[5,6]pyrano[3,2-*c*]chromene-6,7(8*H*)-dione (9f). The

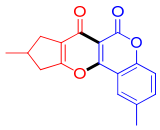


product **9f** was obtained as an ivory solid, m.p. over 300 °C. Yield: 87% (256 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (1H, s), 7.41 (1H, d, J = 8.4 Hz), 7.18 (1H, d, J = 8.4 Hz), 2.78 (2H, s), 2.58 (2H, s), 2.39 (3H, s), 1.19 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.0, 165.4, 164.5, 156.8, 151.5, 135.9, 134.6, 126.6, 123.0, 116.9, 112.9, 108.0, 46.1, 41.0, 36.3, 29.8, 20.9; IR (ATR) 2944, 1750, 1646, 1424, 1215, 804 cm^{-1}; HRMS *m/z* (M^+): calcd for $C_{18}H_{16}O_4$: 296.1049, Found: 296.1050.

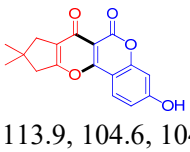
2-Methyl-9,10-dihydro-6*H*-cyclopenta[5,6]pyrano[3,2-*c*]chromene-6,7(8*H*)-dione (9g). The product **9g** was obtained as a red solid, m.p. over 300 °C. Yield: 79% (211 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (1H, s), 7.44 (1H, d, J = 7.2 Hz), 7.20 (1H, d, J = 8.4 Hz), 3.02 (2H, t, J = 7.8 Hz), 2.81 (2H, t, J = 7.2 Hz), 2.43 (3H, s), 2.16–2.11 (2H, m); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.9, 166.4, 165.3, 156.8, 151.6, 135.9, 134.6, 127.5, 123.0, 116.9, 112.8, 107.9, 31.5, 26.1, 20.9, 19.3; IR (ATR) 3066, 1739, 1610, 1419, 1214, 799 cm^{-1}; HRMS *m/z* (M^+): calcd for $C_{16}H_{12}O_4$: 268.0736, Found: 268.0733.



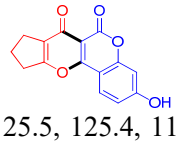
2,9-Dimethyl-9,10-dihydro-6*H*-cyclopenta[5,6]pyrano[3,2-*c*]chromene-6,7(8*H*)-dione (9h). The product **9h** was obtained as a white solid, m.p. 275-277 °C. Yield: 85% (236 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (1H, s), 7.44 (1H, dd, J = 7.8, 1.8 Hz), 7.20 (1H, d, J = 8.4 Hz), 3.20–3.15 (1H, m), 2.97 (1H, dd, J = 16.2, 9.0 Hz), 2.67-2.60 (2H, m), 2.43 (3H, s), 2.39 (1H, dd, J = 19.2, 4.8 Hz), 1.19 (3H, d, J = 7.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.9, 165.3, 156.8, 151.5, 135.9, 134.6, 126.9, 123.0, 116.9, 112.8, 107.9, 39.5, 34.3, 28.8, 21.7, 20.9; IR (ATR) 3056, 2973, 1742, 1414, 1214, 1016, 801 cm^{-1}; HRMS *m/z* (M^+): calcd for $C_{17}H_{14}O_4$: 282.0892, Found: 282.0896.



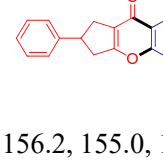
3-Hydroxy-9,9-dimethyl-9,10-dihydro-6*H*-cyclopenta[5,6]pyrano[3,2-*c*]chromene-6,7(8*H*)-dione (9i). The product **9i** was obtained as a light yellow solid, m.p. 289-291°C. Yield: 88% (261 mg); ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.04 (1H, s), 7.74 (1H, d, J = 9.0 Hz), 6.82 (1H, dd, J = 7.8, 1.8 Hz), 6.65 (1H, d, J = 1.8 Hz,), 2.79 (2H, s), 2.40 (2H, s), 1.18 (6H, s); ^{13}C NMR (150 MHz, DMSO-d_6) δ 172.2, 165.4, 164.1, 163.9, 156.1, 154.9, 125.2, 124.5, 113.9, 104.6, 104.5, 102.0, 45.1, 40.6, 35.8, 29.3; IR (ATR) 3076, 2979, 1742, 1646, 1407, 1209, 937 cm^{-1}; HRMS *m/z* (M^+): calcd for $C_{17}H_{14}O_5$: 298.0841, Found: 298.0839.



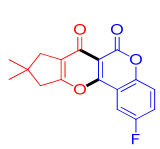
3-Hydroxy-9,10-dihydro-6*H*-cyclopenta[5,6]pyrano[3,2-*c*]chromene-6,7(8*H*)-dione (9j). The product **9j** was obtained as a light browm solid, m.p. over 300 °C. Yield: 83% (221 mg); ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.05 (1H, s), 7.86 (1H, d, J = 8.4 Hz), 6.88 (1H, dd, J = 9.0, 1.8 Hz), 6.73 (1H, d, J = 2.4 Hz,), 2.99 (2H, t, J = 8.4 Hz), 2.62 (2H, t, J = 7.8 Hz), 2.07–2.02 (2H, m); ^{13}C NMR (150 MHz, DMSO-d_6) δ 172.2, 166.1, 165.5, 163.9, 156.2, 154.0, 125.5, 125.4, 113.9, 104.7, 104.6, 102.1, 30.9, 25.8, 18.8; IR (ATR) 3182, 1742, 1558, 1159, 752 cm^{-1}; HRMS *m/z* (M^+): calcd for $C_{15}H_{10}O_5$: 270.0528, Found: 270.0530.

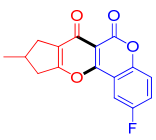


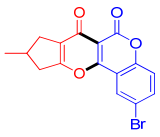
3-Hydroxy-9-phenyl-9,10-dihydro-6*H*-cyclopenta[5,6]pyrano[3,2-*c*]chromene-6,7(8*H*)-dione (9k). The product **9k** was obtained as a light brown solid, m.p. 296-298°C. Yield: 81% (280 mg); ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.10 (1H, s), 7.86 (1H, d, J = 8.4 Hz), 7.37–7.32 (4H, m), 7.24 (1H, t, J = 7.2 Hz,), 6.89 (1H, d, J = 9.0 Hz), 6.74 (1H, s), 3.78–3.73 (1H, m), 3.45 (1H, dd, J = 17.4, 8.4 Hz), 3.16–3.11 (2H, m), 2.63 (1H, dd, J = 15.6, 7.2 Hz); ^{13}C NMR (150 MHz, DMSO-d_6) δ 172.0, 165.6, 164.5, 164.0, 156.2, 155.0, 144.4, 128.6, 126.9, 126.5, 125.4, 124.7, 125.4, 124.7, 114.0, 104.8, 104.6, 102.1, 38.9, 38.8, 34.4; IR (ATR) 3159, 1747, 1557, 1157, 759 cm^{-1}; HRMS *m/z* (M^+): calcd for $C_{21}H_{14}O_5$: 346.0841, Found: 346.0844.

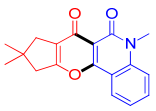


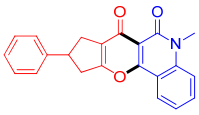
2-Fluoro-9,9-dimethyl-9,10-dihydro-6*H*-cyclopenta[5,6]pyrano[3,2-*c*]chromene-6,7(8*H*)-dione (9l). The product **9l** was obtained as a white solid, m.p. 133-135 °C. Yield: 65% (192 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (1H, dd, J = 7.8, 3.0 Hz), 7.38 (1H, td, J = 9.6, 3.0 Hz), 7.33 (1H, dd, J = 9.6, 4.2 Hz), 2.82 (2H, s), 2.62 (2H, s), 1.23 (6H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.5, 164.6 (d, J = 24.2 Hz), 164.5, 159.6, 158.0, 156.1. 149.5, 127.1, 122.5 (d, J = 24.2 Hz), 119.1 (d, J = 8.0 Hz), 114.1 (d, J = 9.2 Hz), 109.2 (d, J = 25.2 Hz), 108.5, 46.1, 40.9, 36.4, 29.7; IR (ATR) 3031, 2967, 1754, 1650, 1416, 1256, 1160, 981, 822 cm^{-1}; HRMS *m/z* (M^+): calcd for $C_{17}H_{13}FO_4$: 300.0798, Found: 300.0795.



2-Fluoro-9-dimethyl-9,10-dihydro-6*H*-cyclopenta[5,6]pyrano[3,2-*c*]chromene-6,7(8*H*)-dione (9m). 
The product **9m** was obtained as a light yellow solid, m.p. 240-242 °C. Yield: 62% (177 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (1H, dd, J = 7.2, 2.4 Hz), 7.37 (1H, td, J = 9.6, 3.0 Hz), 7.31 (1H, dd, J = 9.0, 4.2 Hz), 3.20–3.15 (1H, m), 2.99 (1H, dd, J = 15.6, 2.4 Hz), 2.67-2.60 (2H, m), 2.39 (1H, dd, J = 15.6, 4.2 Hz), 1.18 (3H, d, J = 7.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.4, 164.9 (d, J = 152.9 Hz), 159.6, 157.9, 156.1, 149.5, 127.3, 122.4 (d, J = 24.2 Hz), 119.1 (d, J = 9.2 Hz), 114.0 (d, J = 9.2 Hz), 109.2 (d, J = 26.4 Hz), 108.4, 39.4, 34.2, 28.8, 21.6; IR (ATR) 3072, 2960, 1745, 1414, 1162, 974, 799 cm^{-1}; HRMS *m/z* (M^+): calcd for $C_{16}H_{11}FO_4$: 286.0641, Found: 286.0643.

2-Bromo-9-methyl-9,10-dihydro-6*H*-cyclopenta[5,6]pyrano[3,2-*c*]chromene-6,7(8*H*)-dione (9n). The 
product **9n** was obtained as a light brown solid, m.p. 254-256 °C. Yield: 55% (188 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (1H, d, J = 1.2 Hz), 7.75 (1H, d, J = 7.8 Hz), 7.25 (1H, s), 3.22–3.18 (1H, m), 3.02 (1H, dd, J = 15.6, 9.0 Hz), 2.68-2.62 (2H, m), 2.42 (1H, dd, J = 16.2, 4.2 Hz), 1.20 (3H, d, J = 5.4 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.4, 165.5, 164.0, 155.9, 152.2, 137.6, 127.4, 126.0, 119.0, 117.5, 114.8, 108.5, 39.5, 34.3, 28.9, 21.7; IR (ATR) 3076, 2979, 1742, 1646, 1407, 1209, 937 cm^{-1}; HRMS *m/z* (M^+): calcd for $C_{16}H_{11}BrO_4$: 345.9841, Found: 345.9843.

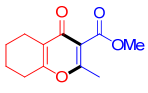
5,9,9-Trimethyl-9,10-dihydrocyclopenta[5,6]pyrano[3,2-*c*]quinoline-6,7(5*H*,8*H*)-dione (9o). The 
product **9o** was obtained as light brown crystals, mp 249-251 ºC. Yield: 93% (275 mg); ^{1}H NMR (600 MHz DMSO-d_6) δ 8.05 (1H , d, J = 8.4 Hz), 7.78 (1H, t, J = 8.4 Hz), 7.55 (1H, d, J = 9.0 Hz), 7.37 (1H, t, J = 7.8 Hz), 3.56 (3H, s), 2.85 (2H, s), 2.44 (2H, s), 1.20 (6H, s); ^{13}C NMR (150 MHz, DMSO-d_6) δ 173.8, 164.9, 162.2, 158.4, 139.6, 134.1, 124.4, 123.4, 122.6, 115.3, 112.4, 110.7, 45.3, 40.8, 40.4, 35.9, 29.3, 29.2; IR (ATR) 2953, 2929, 2852, 1667, 1609, 1552, 1423, 1309, 994, 763, 614 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{18}H_{17}NO_3$: 295.1208, Found: 295.1212.

5-Methyl-9-phenyl-9,10-dihydrocyclopenta[5,6]pyrano[3,2-*c*]quinoline-6,7(5*H*,8*H*)-dione (9p). The 
product **9p** was obtained as a dirty white solid, mp 88-89 ºC. Yield: 76% (261 mg); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.02 (1H , d, J = 7.8 Hz), 7.75 (1H, t, J = 7.8 Hz), 7.50 (1H, d, J = 9.0 Hz), 7.39 (2H, d, J = 7.8 Hz), 7.36-7.32 (3H, m), 7.24 (1H, t, J = 7.8 Hz), 3.79-3.73 (1H, m), 3.53 (3H, s), 3.43 (1H, dd, J = 16.8, 9.0 Hz), 3.16-3.11 (2H, m), 2.64 (1H, dd, J = 15.0, 7.2 Hz); ^{13}C NMR (150 MHz, DMSO-d_6) δ 172.7, 164.4, 162.0, 157.7, 144.4, 139.7, 133.9, 128.6, 126.9, 126.5, 124.6, 123.3, 122.3, 115.0, 112.3, 111.0, 39.9, 38.8, 34.5, 29.0; IR (ATR) 2922, 2852, 1666, 1551, 1425, 1304, 992, 757, 703, 503 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{22}H_{17}NO_3$: 343.1208, Found: 343.1205.

General procedure for the synthesis of tetrasubstituted γ-pyrone 11

In a magnetically stirred solution of 2-diazocycloheptane-1,3-dione (**1m**) (1.2 mmol) in toluene (5mL), methyl 3-oxobutanoate (**2a**) (1.0 mmol) was added. It was followed by the addition of $InBr_3$ (10 mol%) in the solution and was thoroughly stirred. The reaction mixture was kept in refluxing toluene condition for 4 hours under N_2 gas protection. It was observed by TLC (hexane/ethyl acetate = 1:1) until completion of the reaction. Then, the reaction mixture was dried using a rotary evaporator and was subjected for flash column chromatography using hexane/ethyl acetate (20:3) as the solvent system.

Characterization data of compound 11

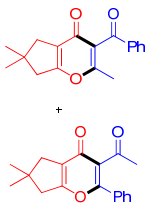
Methyl 2-methyl-4-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carboxylate (11). The product **11** 
was obtained as a yellow solid, mp 55-57 ºC. Yield: 81% (180 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.86 (3H, s), 2.49 (2H, t, J = 6.6 Hz), 2.41 (2H, t, J = 6.6 Hz), 2.32 (3H, s), 1.79-1.75 (2H, m), 1.68-1.64 (2H, m); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.2, 165.7, 165.2, 162.8, 122.5, 119.8, 52.4, 27.2, 21.7, 21.3, 20.6, 18.7; IR (ATR) 2937,

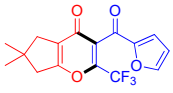
2864, 1711, 1658, 1619, 1415, 1288, 1270, 1160, 1139, 1068, 1001 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{12}H_{14}O_4$: 222.0892, Found: 222.0895.

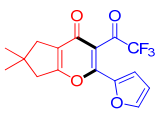
General procedure for the synthesis of tetrasubstituted γ-pyrones 13 and 15

In a magnetically stirred solution of 2-diazo-5,5-dimethylcyclohexane-1,3-dione (**1a**) (1.2 mmol) in toluene (5mL), asymmetric 1,3-diketones such as 1-phenylbutane-1,3-dione (**12**) or 4,4,4-trifluoro-1-(furan-2-yl)butan-1,3-dione (**14**) (1.0 mmol) was added. It was followed by the addition of $InBr_3$ (10 mol%) in the solution and was thoroughly stirred. The reaction mixture was kept in refluxing toluene condition for 4 hours under N_2 gas protection. It was observed by TLC (hexane/ethyl acetate = 1:1) until completion of the reaction. Then, the reaction mixture was dried using a rotary evaporator and was subjected for flash column chromatography using hexane/ethyl acetate (20:3) as the solvent system.

Characterization data of compounds 13 and 15

3-Benzoyl-2,6,6-trimethyl-6,7-dihydrocyclopenta[*b*]pyran-4(5*H*)-one (13a) and 3-Acetyl-6,6-dimethyl-2-phenyl-6,7-dihydrocyclopenta[b]pyran-4(5*H*)-one (13b).  The products **13a** and **13b** were obtained as an inseparable mixture of regioisomers. The isomeric ratio was found to be 1:1 by ^1H NMR. Yellow viscous liquid. Yield: 77% (217 mg); ^1H NMR (600 MHz, $CDCl_3$) δ 7.86 (2H, d, J = 7.8 Hz), 7.54 (1H, t, J = 7.8 Hz), 7.50 (2H, d, J = 7.8 Hz), 7.46 (1H, t, J = 7.2 Hz), 7.41 (4H, q, J = 7.8 Hz), 2.71 (2H, s), 2.68 (2H, s), 2.57 (2H, s), 2.53 (2H, s), 2.34 (3H, s), 2.17 (3H, s), 1.21 (6H, s), 1.20 (6H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 201.0, 194.2, 175.6, 175.4, 167.0, 166.8, 163.7, 161.7, 136.6, 133.7, 131.3, 131.0, 129.3, 128.7, 128.6, 128.5, 128.2, 126.6, 124.5, 124.2, 46.3, 46.2, 40.8, 40.7, 36.2, 36.2, 32.1, 29.7, 29.7, 18.1; IR (ATR) 2956, 2867, 1707, 1650, 1620, 1427, 1339, 1311, 1243, 1166, 919 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{18}H_{18}O_3$: 282.1256, Found: 282.1252.

3-(Furan-2-carbonyl)-6,6-dimethyl-2-(trifluoromethyl)-6,7-dihydrocyclopenta[*b*]pyran-4(5*H*)-one (15a).  The product **15a** was obtained as a yellow solid, mp 164-166 ºC. Yield: 58% (189 mg); ^1H NMR (600 MHz, $CDCl_3$) δ 7.59 (1H, s), 7.23 (1H, d, J = 3.6 Hz), 6.56 (1H, dd, J = 3.6, 1.8 Hz), 2.77 (2H, s), 2.57 (2H, s), 1.23 (6H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.2, 174.0, 167.3, 152.0, 149.0 (d, J = 39.2 Hz), 147.9, 127.3, 126.4, 119.8, 118.5 (d, J = 273.6 Hz), 113.0, 46.0, 40.7, 36.4, 29.7; IR (ATR) 3117, 2963, 1657, 1458, 1371, 1240, 1190, 1144, 1071, 1036, 993 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{16}H_{13}F_3O_4$: 326.0766, Found: 326.0768.

2-(Furan-2-yl)-6,6-dimethyl-3-(2,2,2-trifluoroacetyl)-6,7-dihydrocyclopenta[*b*]pyran-4(5*H*)-one (15b).  The product **15b** was obtained as a brown solid, mp 82-84 ºC. Yield: 16% (52 mg); ^1H NMR (600 MHz, $CDCl_3$) δ 7.54 (1H, s), 7.04 (1H, d, J = 3.6 Hz), 6.57 (1H, t, J = 1.8 Hz), 2.74 (2H, s), 2.57 (2H, s), 1.22 (6H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 184.0 (d, J = 40.2 Hz), 174.4, 166.7, 153.2, 146.5, 144.1, 124.5, 117.8, 115.1 (d, J = 289.7 Hz), 114.9, 112.7, 46.3, 40.7, 36.3, 29.7; IR (ATR) 3103, 2960, 2874, 1763, 1650, 1628, 1427, 1299, 1200, 1145, 1066, 1000 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{16}H_{13}F_3O_4$: 326.0766, Found: 326.0763.

General procedure for the hydrolysis of compound 3a to 20

In a magnetically stirred solution of methyl 2,6,6-trimethyl-4-oxo-4,5,6,7-tetrahydrocyclopenta[*b*]pyran-3-carboxylate (**3a**) (0.2 mmol) in methanol (3 mL), potassium hydroxide (KOH) (3 equiv) was added and thoroughly stirred at room temperature for 6 hours. Until completion, the progress of the reaction was

monitored by TLC (ethyl acetate). Once the reaction completed, it was quenched by the addition of water (15 mL). The aqueous solution was then acidified using 1 N HCl and extracted thrice with ethyl acetate (3 x 15 mL). The organic extracts were dried using anhydrous Na_2SO_4 and filtered. The volatiles were removed *in vacuo* and was subjected for flash column chromatography using ethyl acetate as the solvent system.

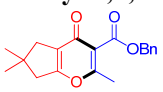
Characterization data of compound 20

2,6,6-trimethyl-4-oxo-4,5,6,7-tetrahydrocyclopenta[*b*]pyran-3-carboxylic acid (20). The product **20** was obtained as clear crystals, mp 144-146 °C. Yield: 43% (19 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 15.01 (1H, s), 2.87 (3H, s), 2.78 (2H, d, J = 1.2 Hz), 2.60 (2H, d, J = 1.8 Hz), 1.23 (6H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 179.4, 176.8, 169.0, 165.1, 124.3, 113.5, 46.2, 40.5, 36.9, 29.7, 21.4; IR (ATR) 3592, 2958, 2870, 1730, 1644, 1543, 1460, 1367, 1310, 1127, 1047, 979 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{12}H_{14}O_4$: 222.0892, Found: 222.0894.

General procedure for the conversion of compound 3a to 3b and 22

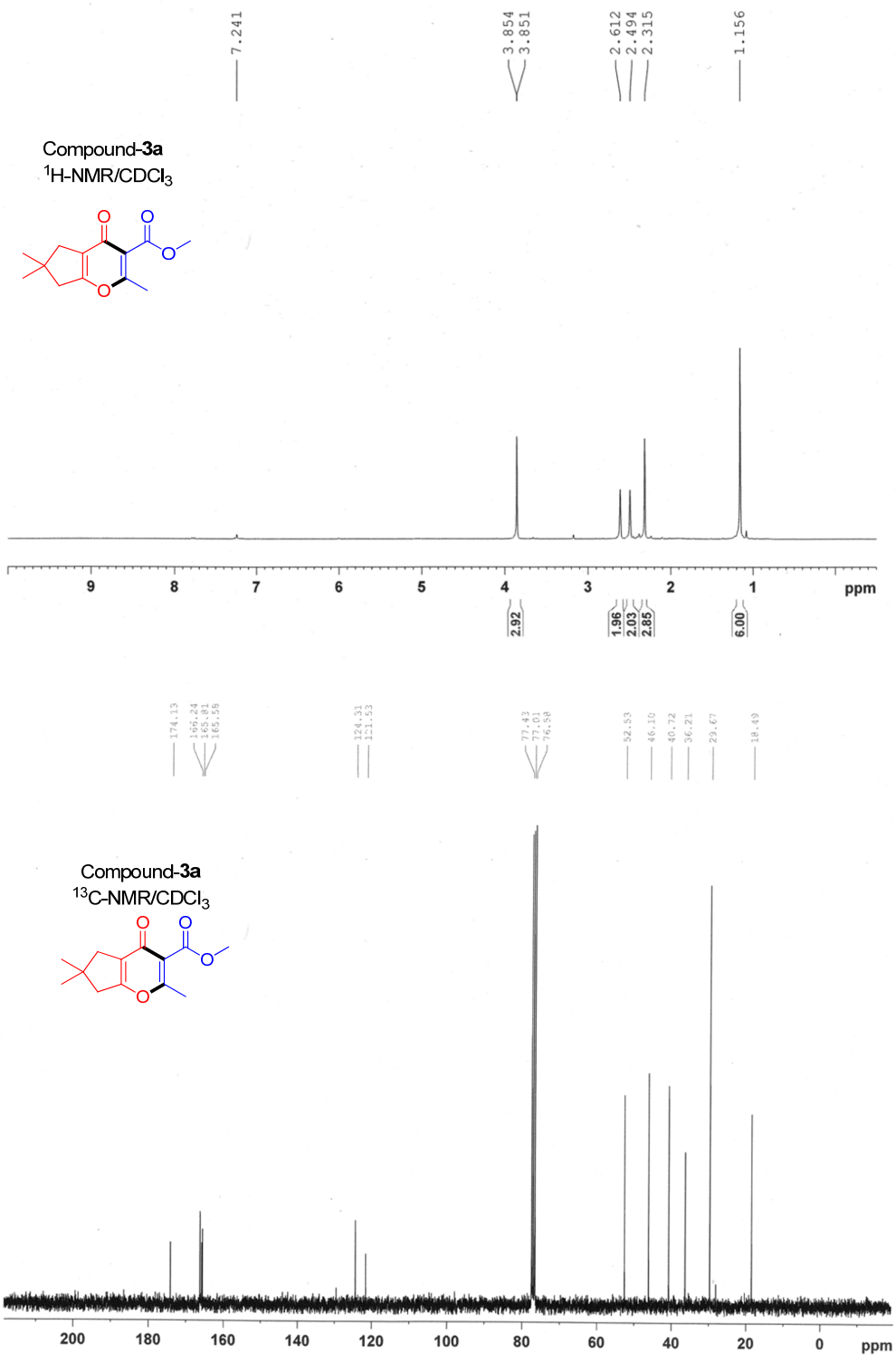
In a magnetically stirred solution of methyl 2,6,6-trimethyl-4-oxo-4,5,6,7-tetrahydrocyclopenta[*b*]pyran-3-carboxylate (**3a**) (0.2 mmol) in toluene (3 mL), ethanol (**21a**) (3 equiv) or benzyl alcohol (**21b**) (3 equiv) was added. It was followed by the addition of $InBr_3$ (10 mol%) and was thoroughly stirred. The reaction mixture was kept in refluxing toluene condition for 4 hours. It was observed by TLC (hexane/ethyl acetate = 20:3) until completion of the reaction. Then, the reaction mixture was dried using a rotary evaporator and was subjected for flash column chromatography using hexane/ethyl acetate (20:1) as the solvent system.

Characterization data of compound 22

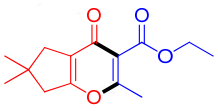


Benzyl 2,6,6-trimethyl-4-oxo-4,5,6,7-tetrahydrocyclopenta[*b*]pyran-3-carboxylate (22). The product **22** was obtained as a colourless viscous liquid. Yield: 89% (278 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (2H, d, J = 7.8 Hz), 7.32 (2H, q, J = 7.8 Hz), 7.29-7.22 (1H, m), 5.31 (2H, s), 2.60 (2H, s), 2.50 (2H, s), 2.26 (3H, s), 1.15 (6H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.0, 166.2, 165.5, 165.1, 135.4, 128.5, 128.2, 128.2, 124.2, 121.4, 67.3, 46.0, 40.6, 36.1, 29.6, 18.4; IR (ATR) 2955, 2867, 1730, 1657, 1629, 1429, 1389, 1338, 1312, 1253, 1214, 1171, 1119, 1045, 976, 909, 738, 697 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{19}H_{20}O_4$: 312.1362, Found: 312.1365.

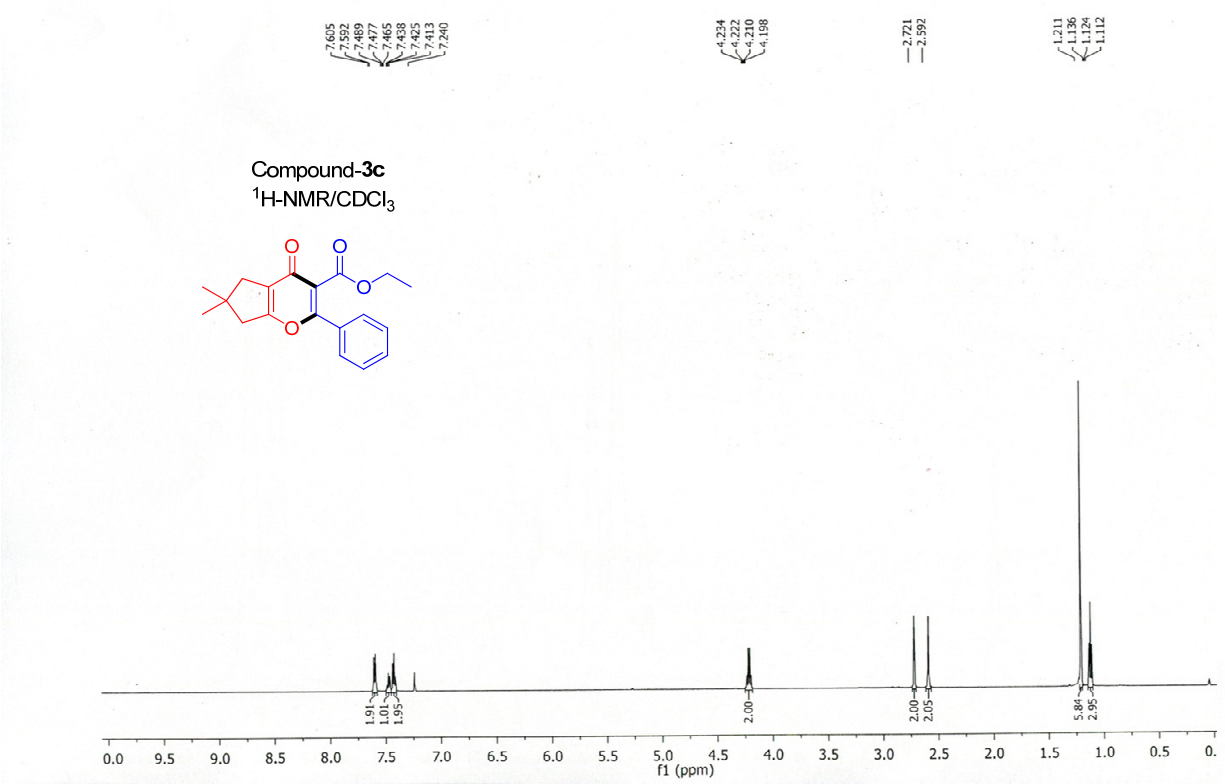
^{1}H NMR and ^{13}C NMR spectra of compounds 3, 5, 7, 9, 11, 13, 15, 20, and 22

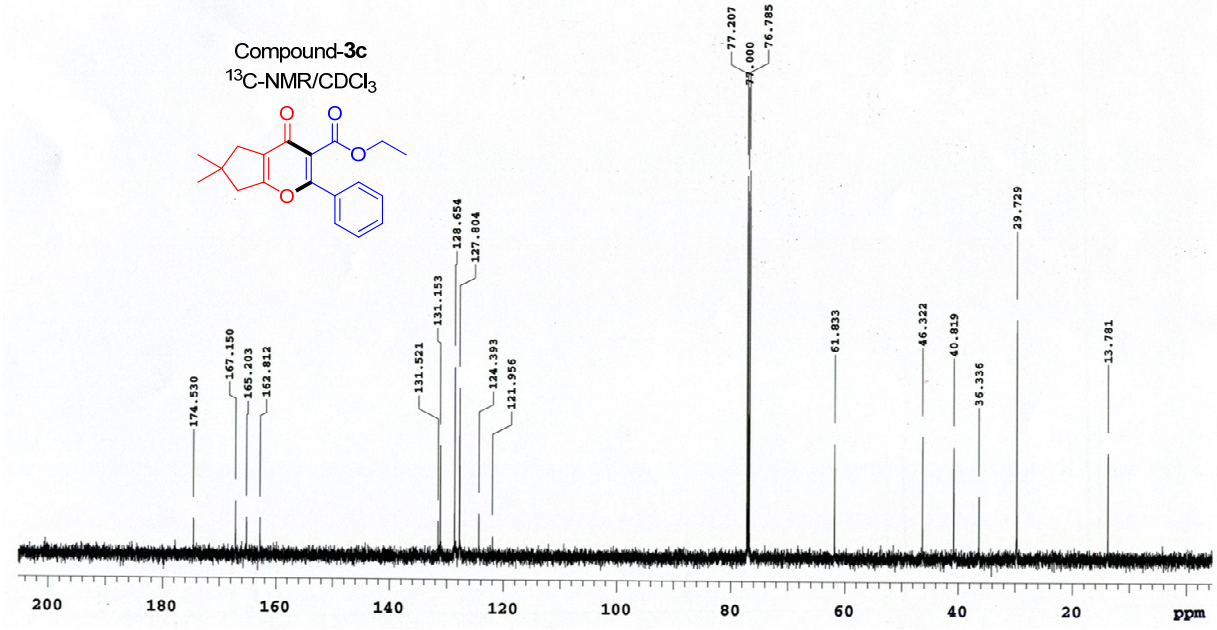


Compound-**3b**
^{1}H-NMR/$CDCl_3$



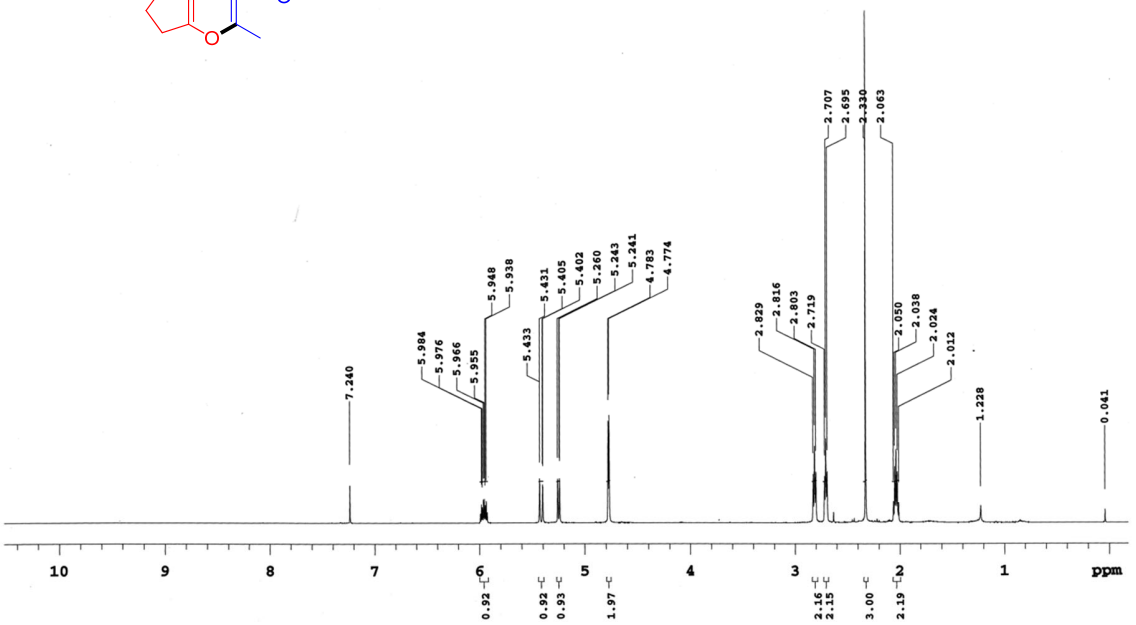
Compound-**3b**
^{13}C-NMR/$CDCl_3$


7.605
7.592
7.489
7.477
7.465
7.438
7.425
7.413
7.240
4.234
4.222
4.210
4.198
2.721
2.392
1.211
1.136
1.124
1.112
Compound-3c
1H-NMR/CDCl3
1.91
1.01
1.95
2.00
2.00
2.05
5.84
2.95
0.0 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.
f1 (ppm)


Compound-3c
13C-NMR/CDCl3
77.207
77.000
76.785
174.530
167.150
165.203
162.812
131.521
131.153
128.654
127.804
124.393
121.956
61.833
46.322
40.819
36.336
29.729
13.781
200 180 160 140 120 100 80 60 40 20 ppm

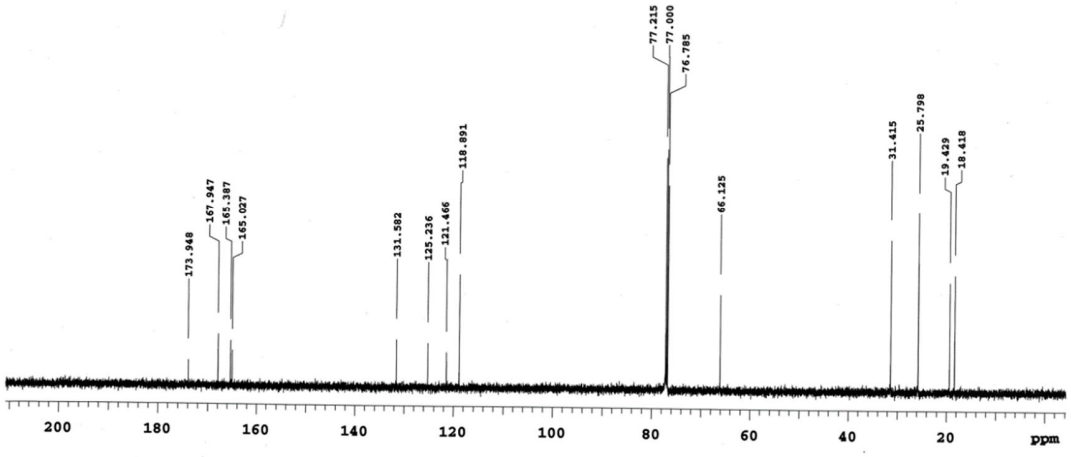
Compound-**3d**

^{1}H-NMR/$CDCl_3$



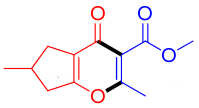
Compound-**3d**

^{13}C-NMR/$CDCl_3$



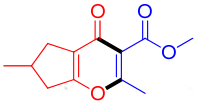
Compound-**3e**

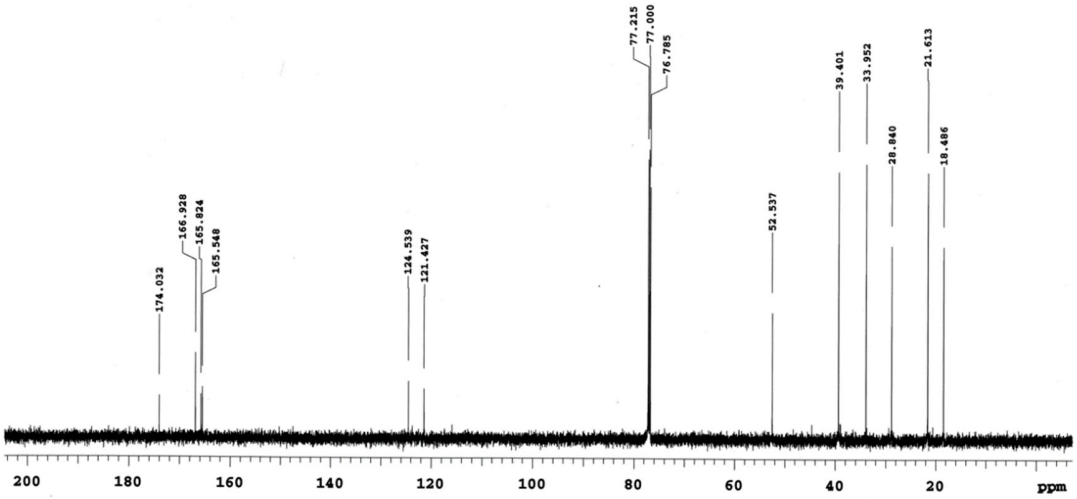
^{1}H-NMR/$CDCl_3$



Compound-**3e**

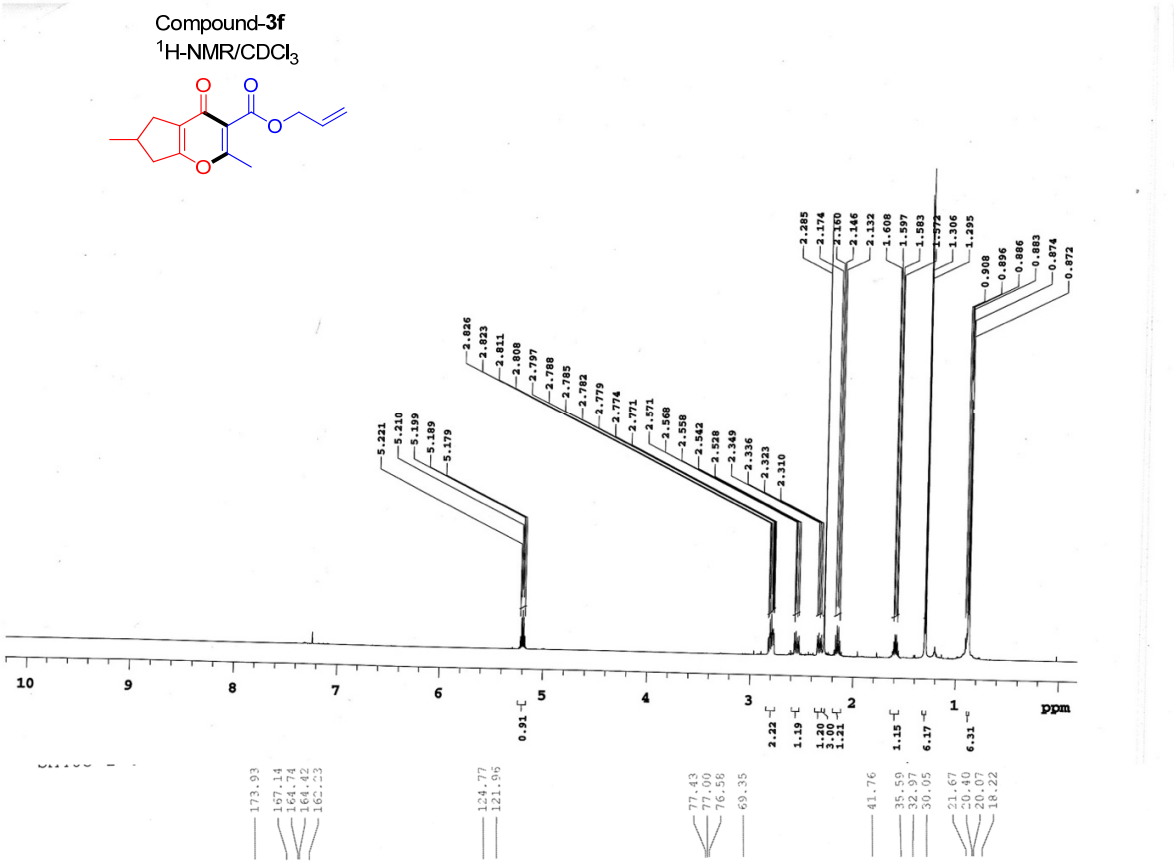
^{13}C-NMR/$CDCl_3$





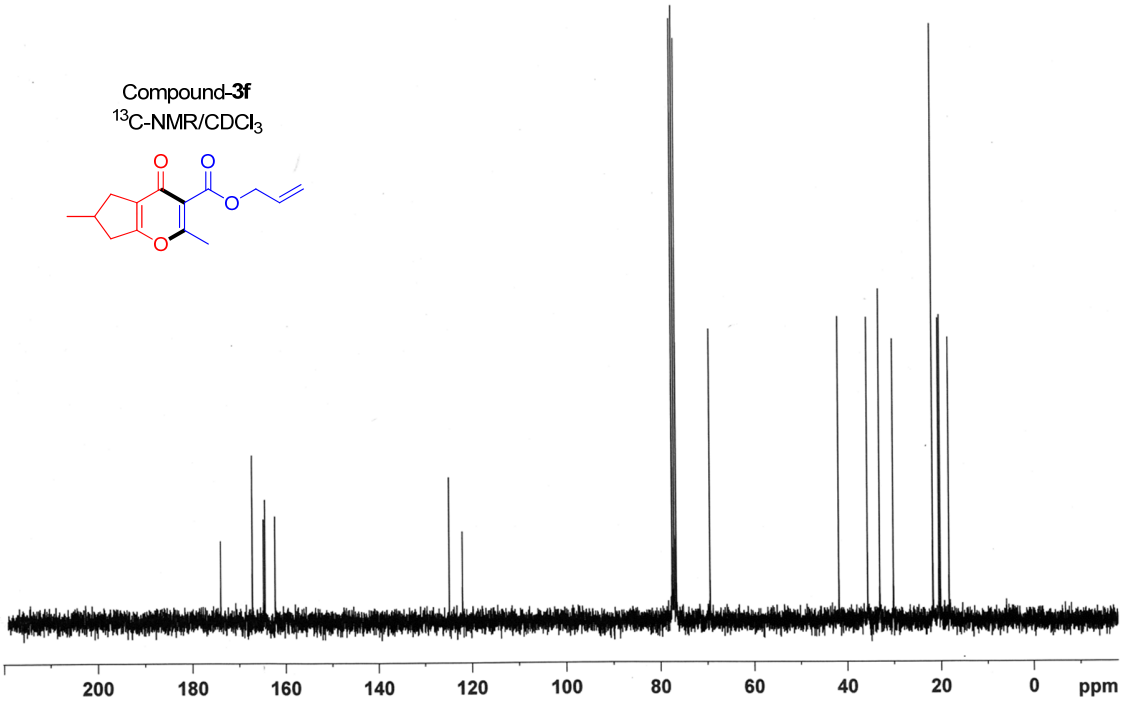
Compound-**3f**

^{1}H-NMR/CDCl$_3$



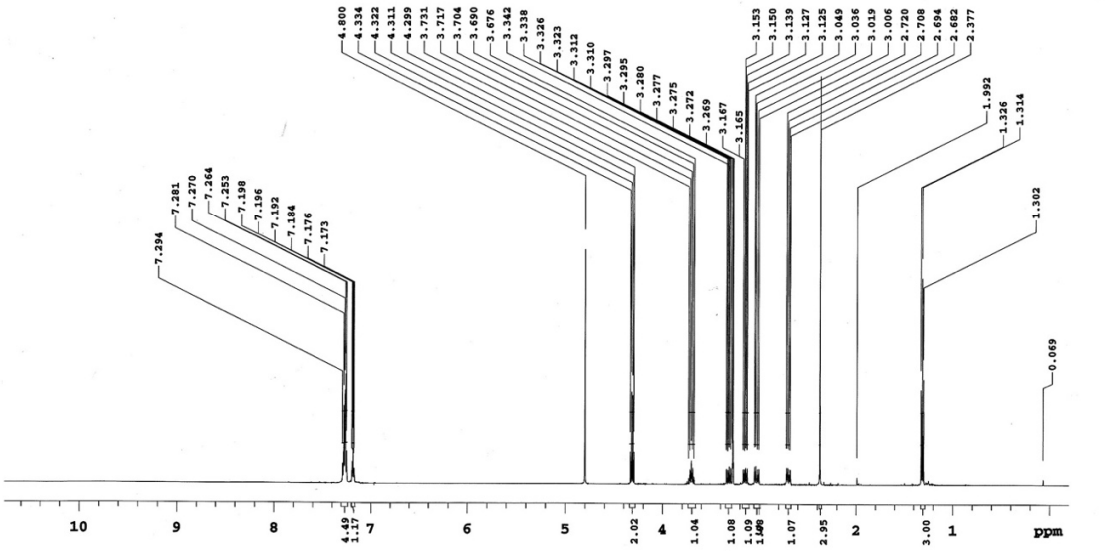
Compound-**3f**

^{13}C-NMR/CDCl$_3$



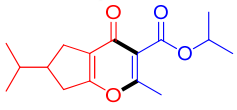
Compound-**3g**

^{1}H-NMR/$CDCl_3$

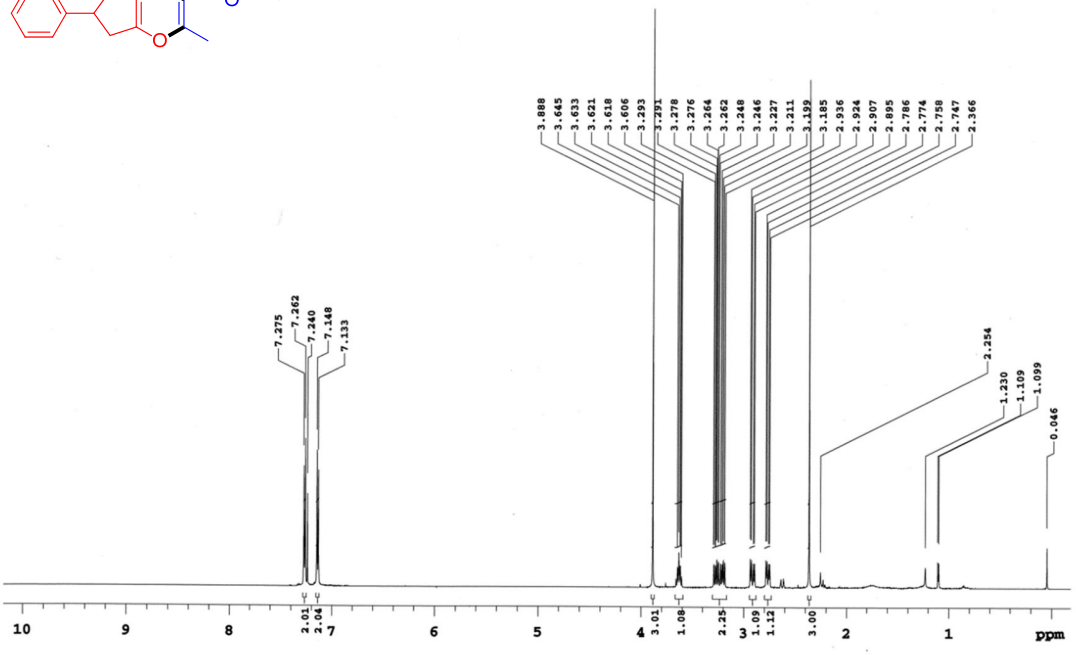


Compound-**3g**

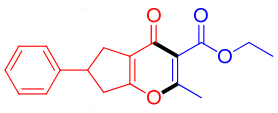
^{13}C-NMR/$CDCl_3$

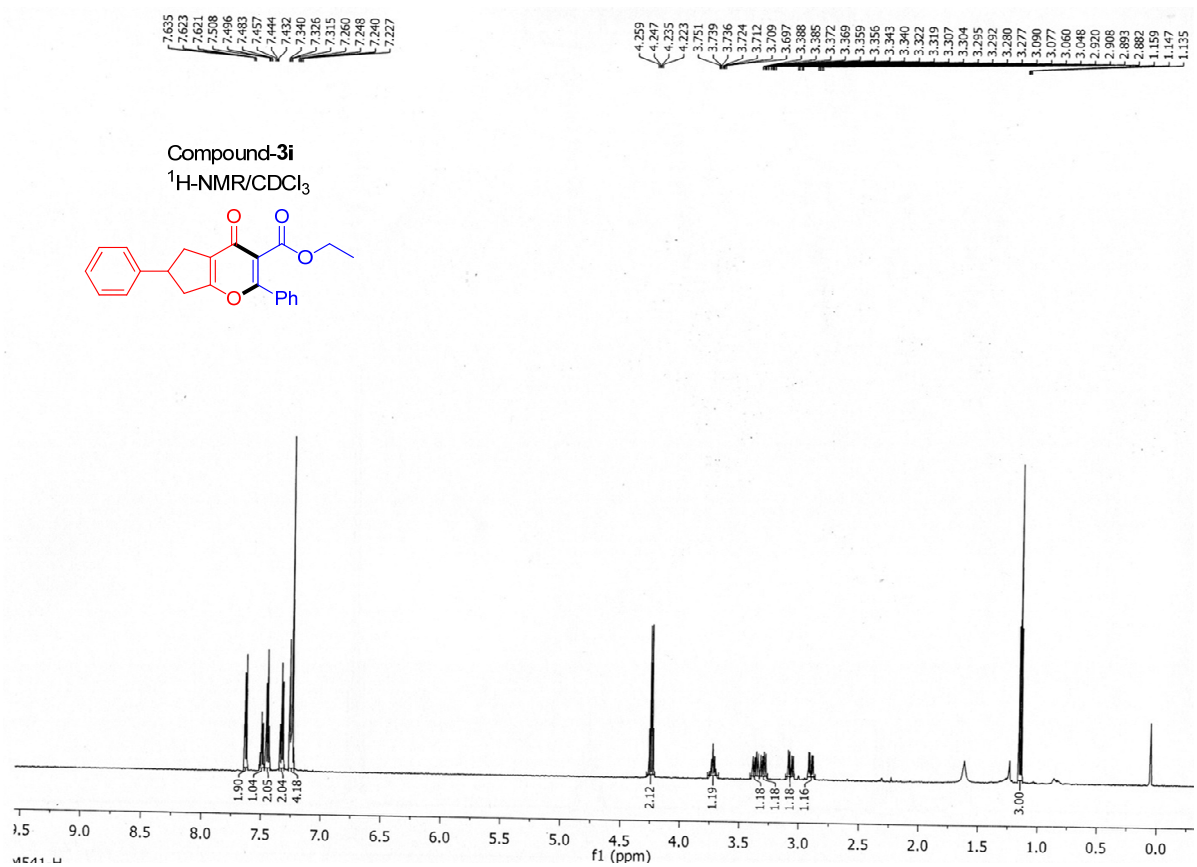


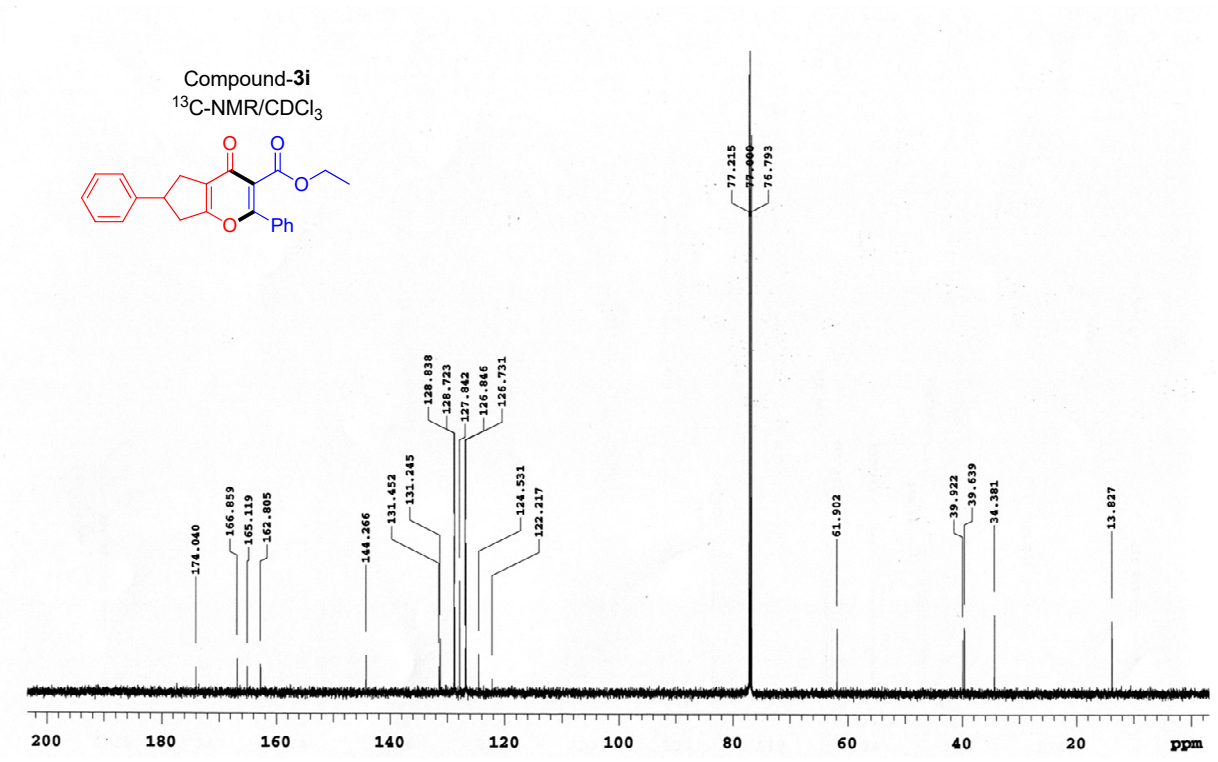
Compound-**3h**
^{1}H-NMR/$CDCl_3$



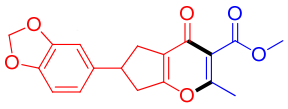
Compound-**3h**
^{13}C-NMR/$CDCl_3$

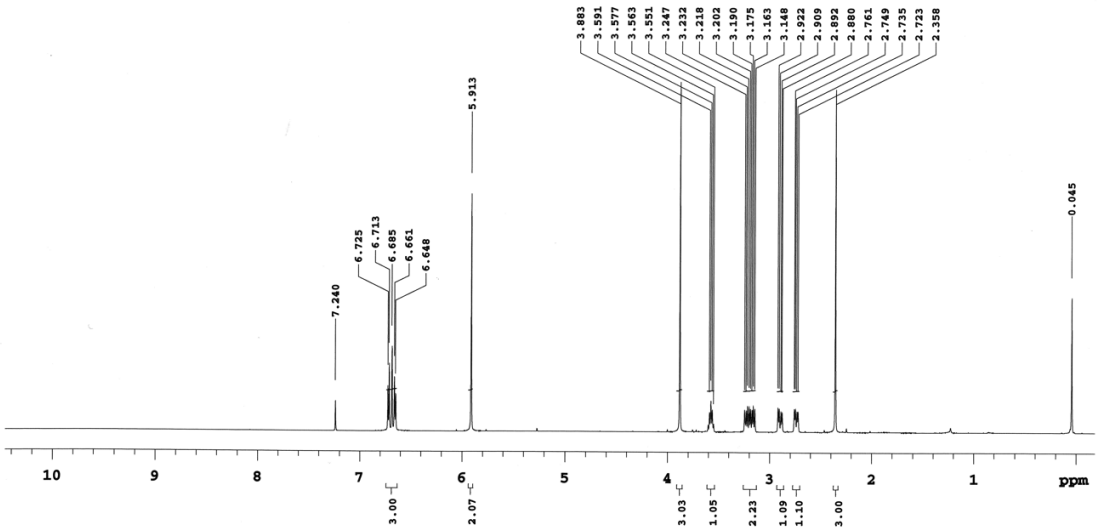



7.635
7.623
7.621
7.508
7.496
7.483
7.457
7.444
7.432
7.340
7.326
7.315
7.260
7.248
7.240
7.227
4.259
4.247
4.235
4.223
3.751
3.739
3.736
3.724
3.712
3.709
3.697
3.388
3.385
3.372
3.369
3.359
3.356
3.343
3.340
3.322
3.319
3.307
3.304
3.295
3.292
3.280
3.277
3.090
3.077
3.060
3.048
2.920
2.908
2.893
2.882
1.159
1.147
1.135
Compound-3i
1H-NMR/CDCl3
O
O
O
O
Ph
1.90
1.04
2.05
2.04
4.18
2.12
1.19
1.18
1.18
1.18
1.16
3.00
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
0.0
f1 (ppm)

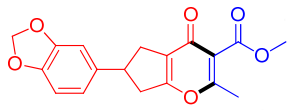

Compound-3i
13C-NMR/CDCl3
O
O
O
O
Ph
174.040
166.859
165.119
162.805
144.266
131.452
131.245
128.838
128.723
127.842
126.846
126.731
124.531
122.217
77.215
76.793
61.902
39.922
39.639
34.381
13.827
200
180
160
140
120
100
80
60
40
20
ppm

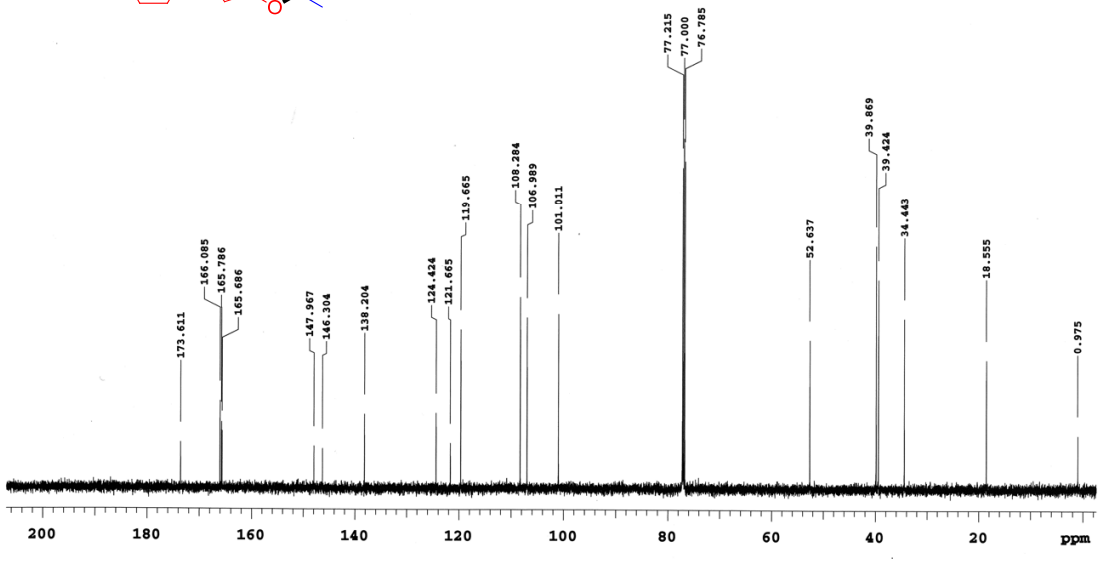
Compound-**3j**
^{1}H-NMR/CDCl$_3$





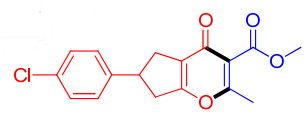
Compound-**3j**
^{13}C-NMR/CDCl$_3$

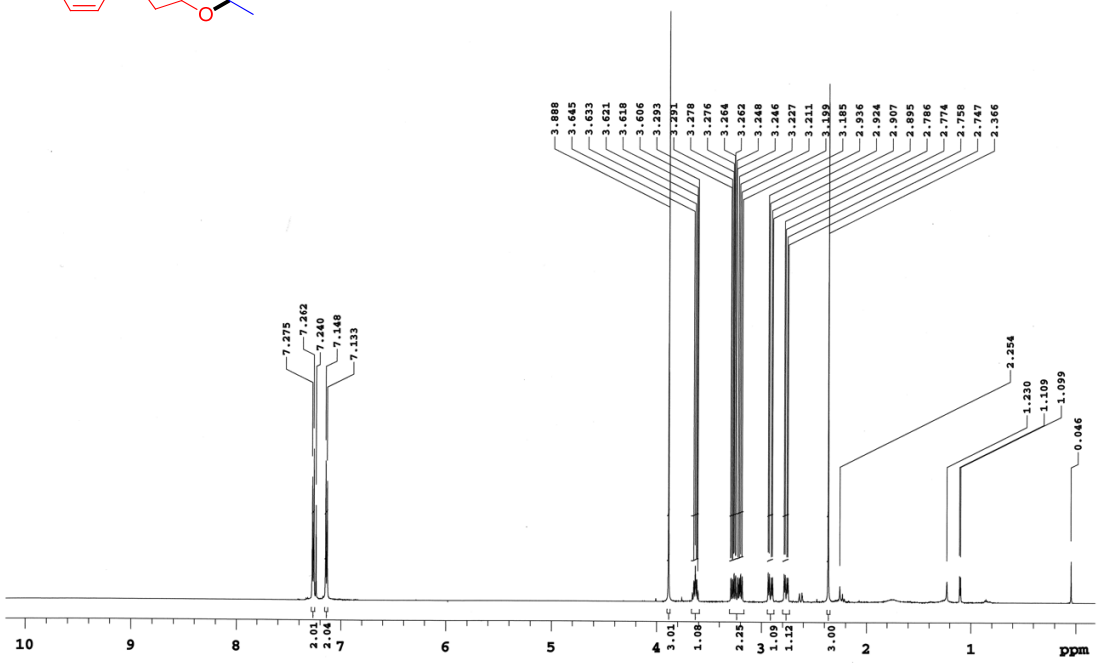




Compound-**3k**

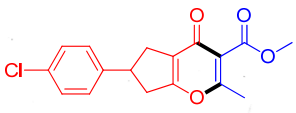
^{1}H-NMR/$CDCl_3$





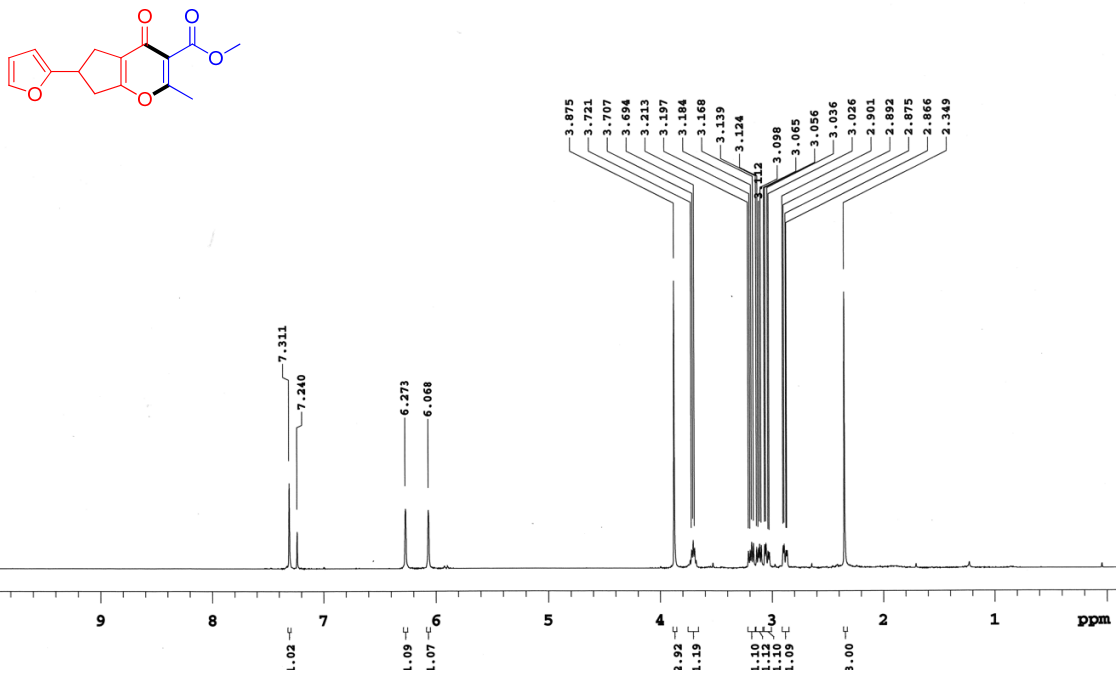
Compound-**3k**

^{13}C-NMR/$CDCl_3$



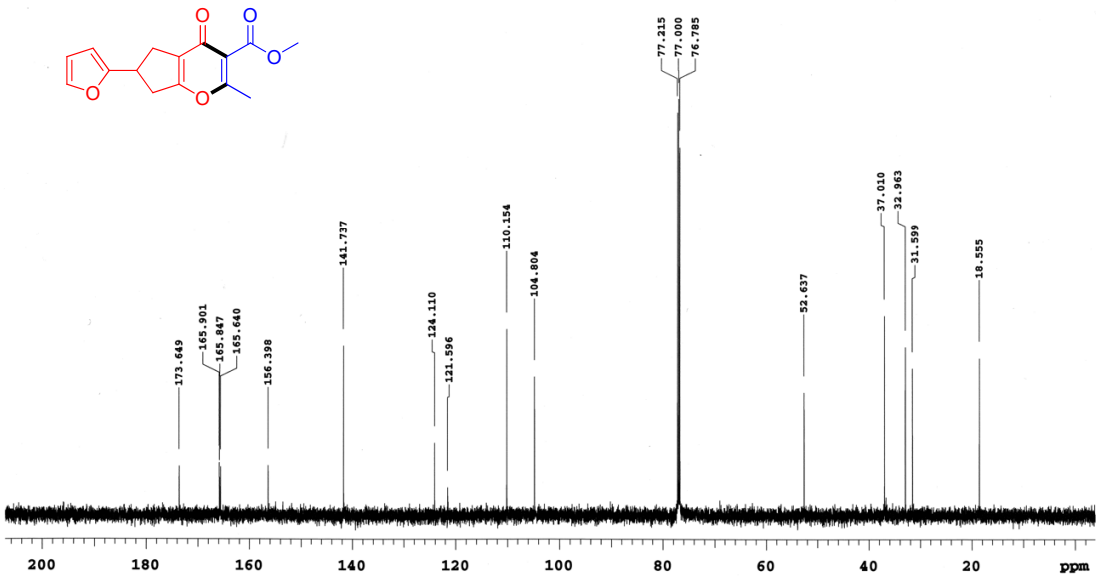
Compound-**3l**

^{1}H-NMR/$CDCl_3$

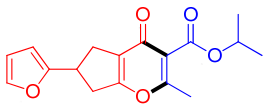


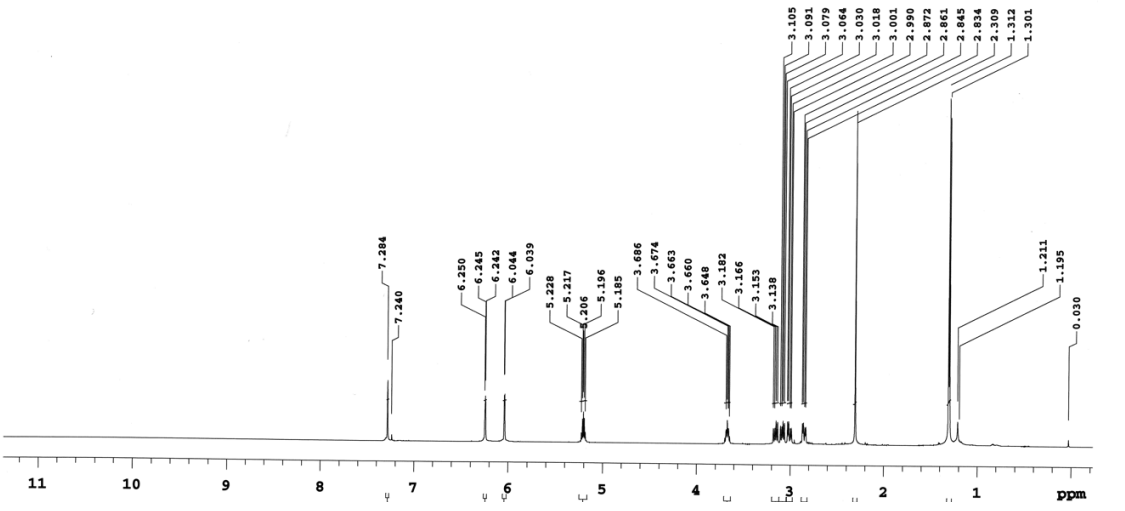
Compound-**3l**

^{13}C-NMR/$CDCl_3$

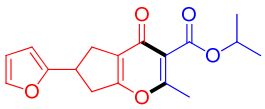


Compound-**3m**
^{1}H-NMR/$CDCl_3$



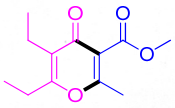


Compound-**3m**
^{13}C-NMR/$CDCl_3$



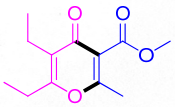
Compound-**3n**

^{1}H-NMR/$CDCl_3$



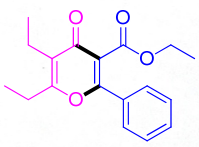
Compound-**3n**

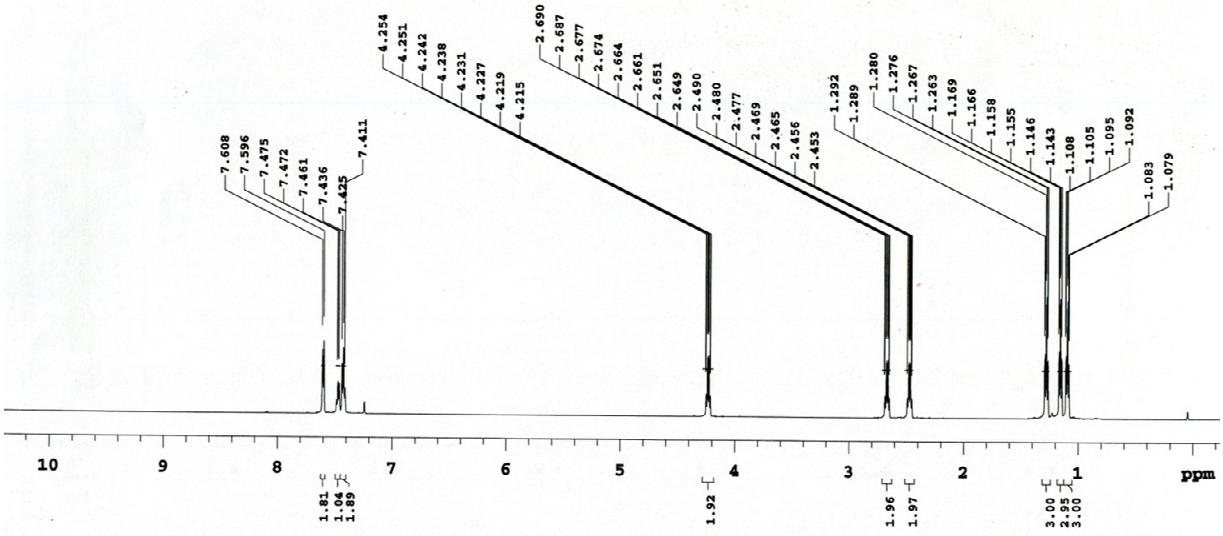
^{13}C-NMR/$CDCl_3$



Compound-**3o**

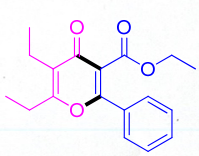
^{1}H-NMR/$CDCl_3$





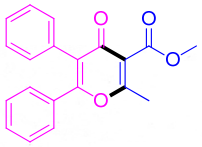
Compound-**3o**

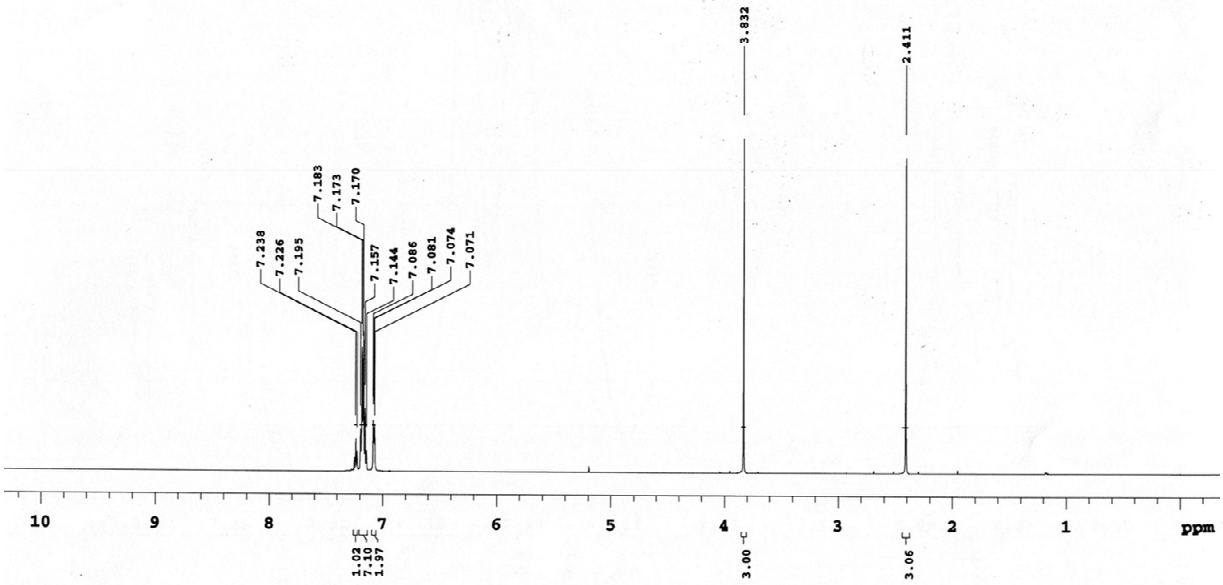
^{13}C-NMR/$CDCl_3$



Compound-**3p**

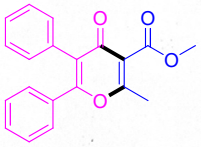
^{1}H-NMR/$CDCl_3$





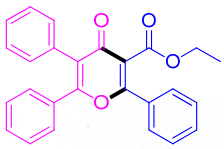
Compound-**3p**

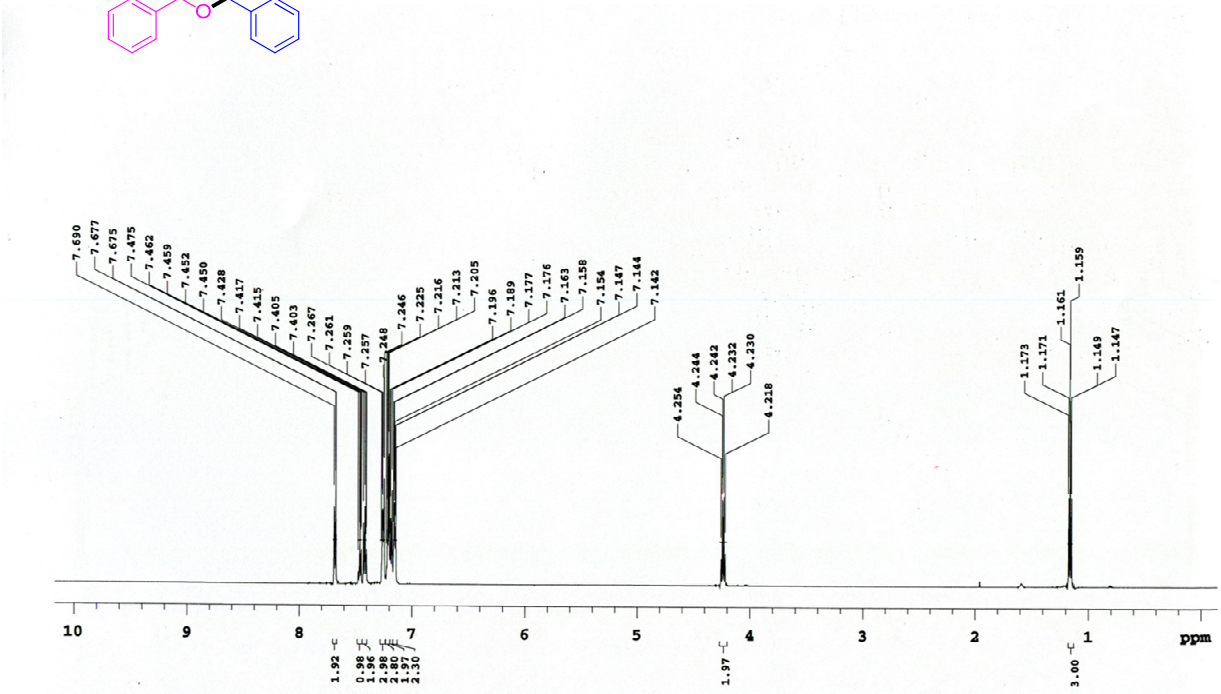
^{13}C-NMR/$CDCl_3$



Compound-**3q**

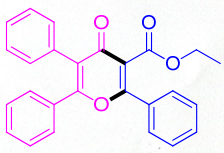
^{1}H-NMR/$CDCl_3$





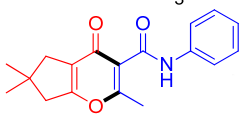
Compound-**3q**

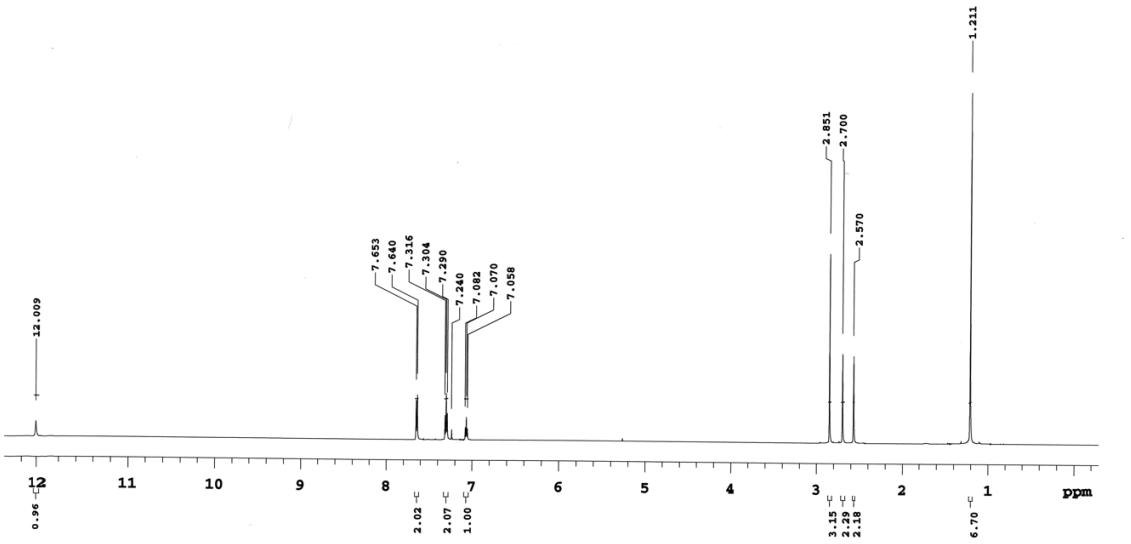
^{13}C-NMR/$CDCl_3$



Compound-**5a**

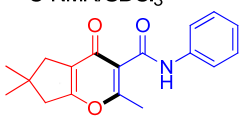
^{1}H-NMR/CDCl$_3$

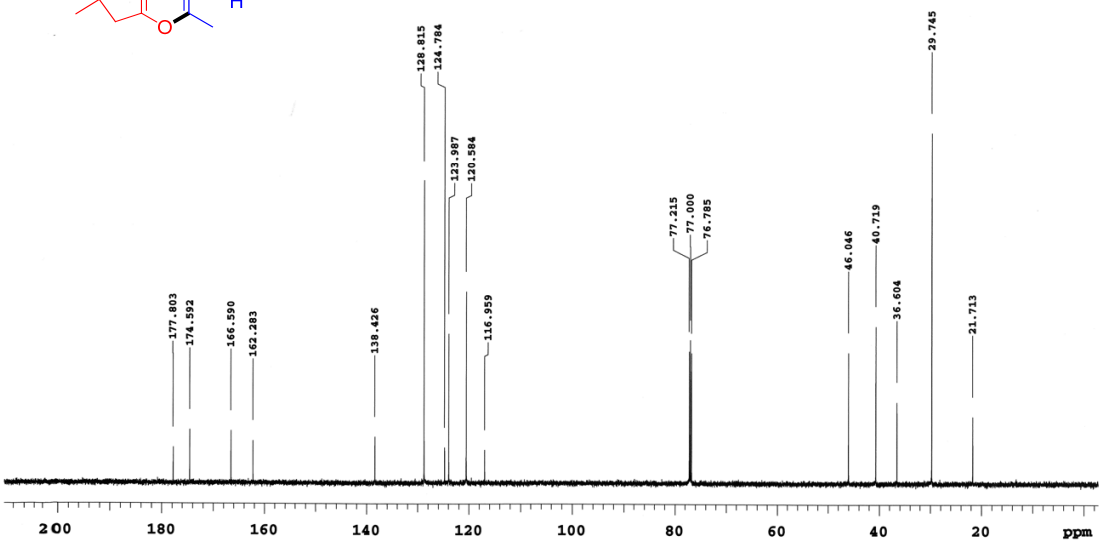




Compound-**5a**

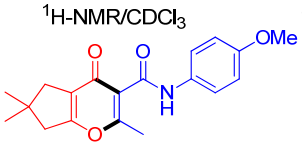
^{13}C-NMR/CDCl$_3$

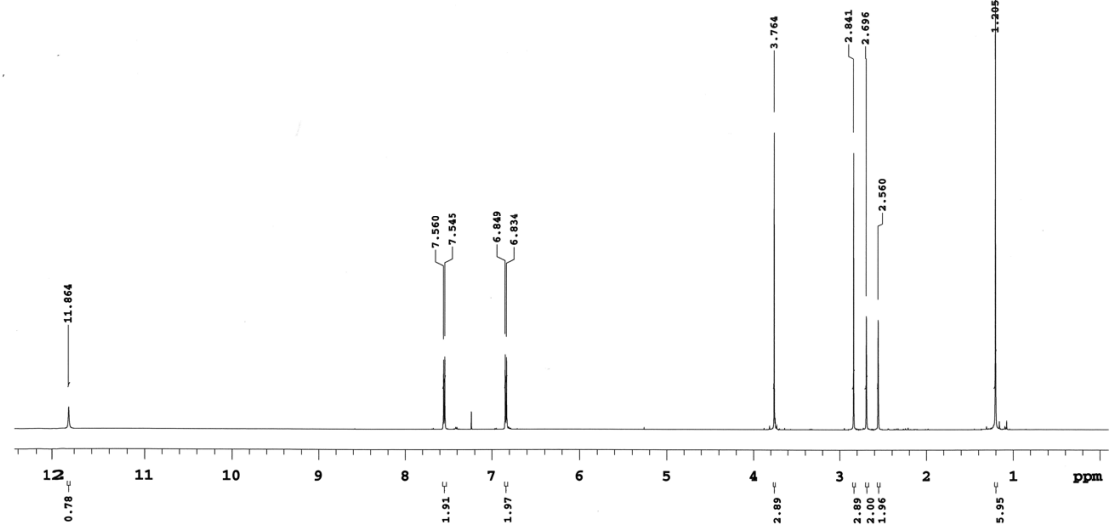




Compound-**5b**

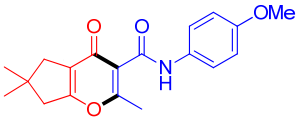
^{1}H-NMR/$CDCl_3$





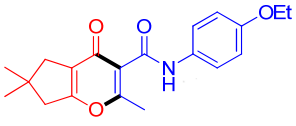
Compound-**5b**

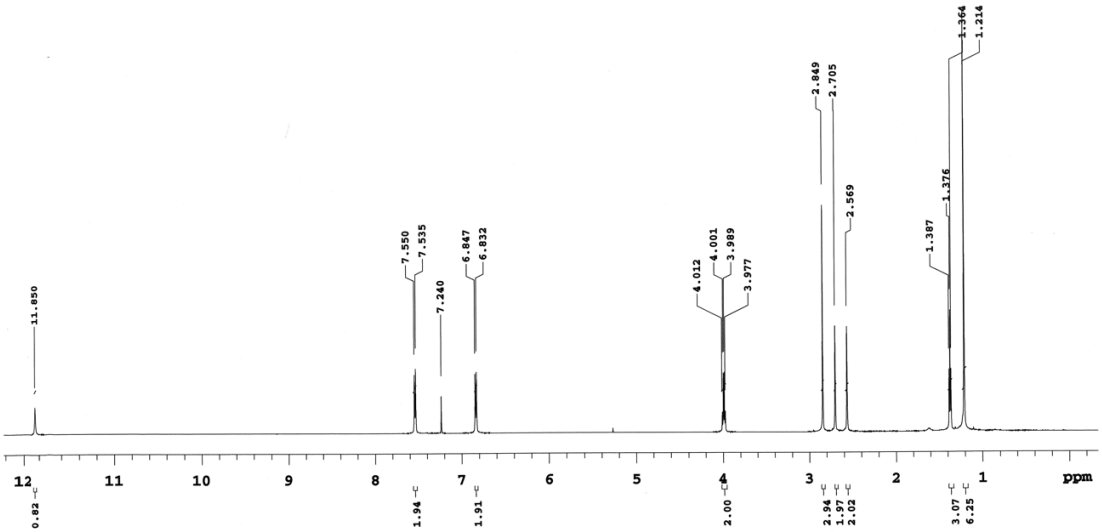
^{13}C-NMR/$CDCl_3$



Compound-**5c**

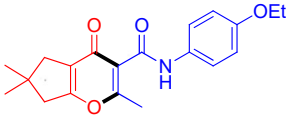
^{1}H-NMR/CDCl$_3$





Compound-**5c**

^{13}C-NMR/CDCl$_3$



Compound-**5d**

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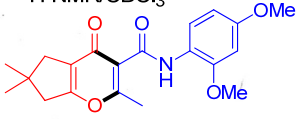
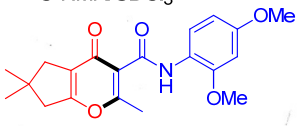


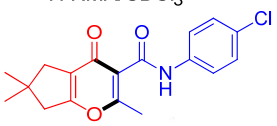
Compound-**5d**

^{13}C-NMR/CDCl$_3$



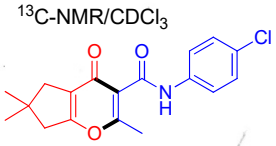
Compound-**5e**

^{1}H-NMR/CDCl$_3$



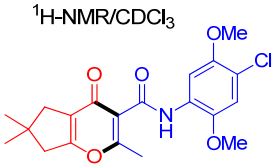
Compound-**5e**

^{13}C-NMR/CDCl$_3$



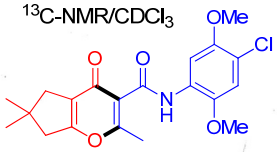
Compound-**5f**

^{1}H-NMR/$CDCl_3$



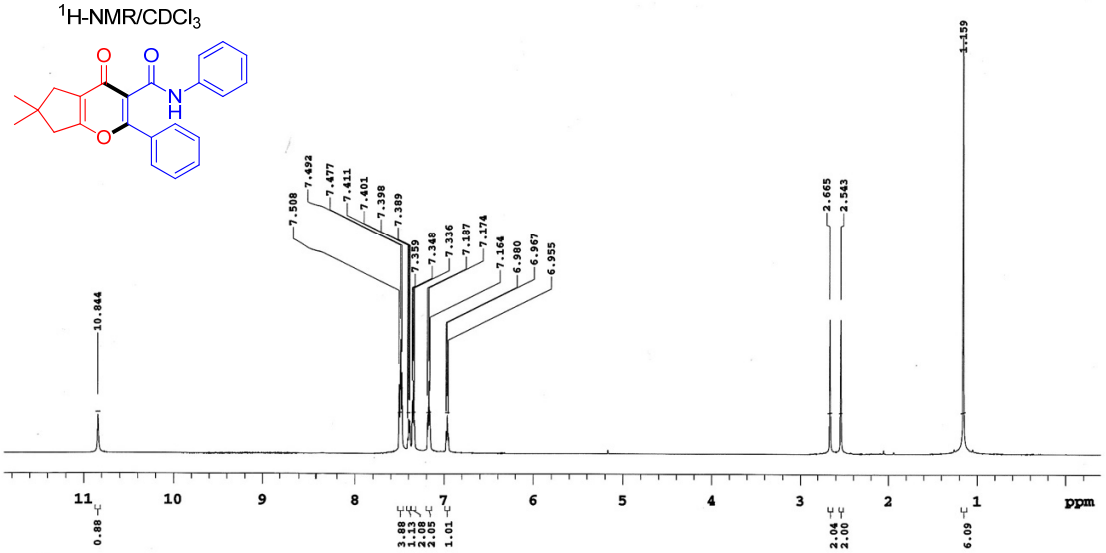
Compound-**5f**

^{13}C-NMR/$CDCl_3$



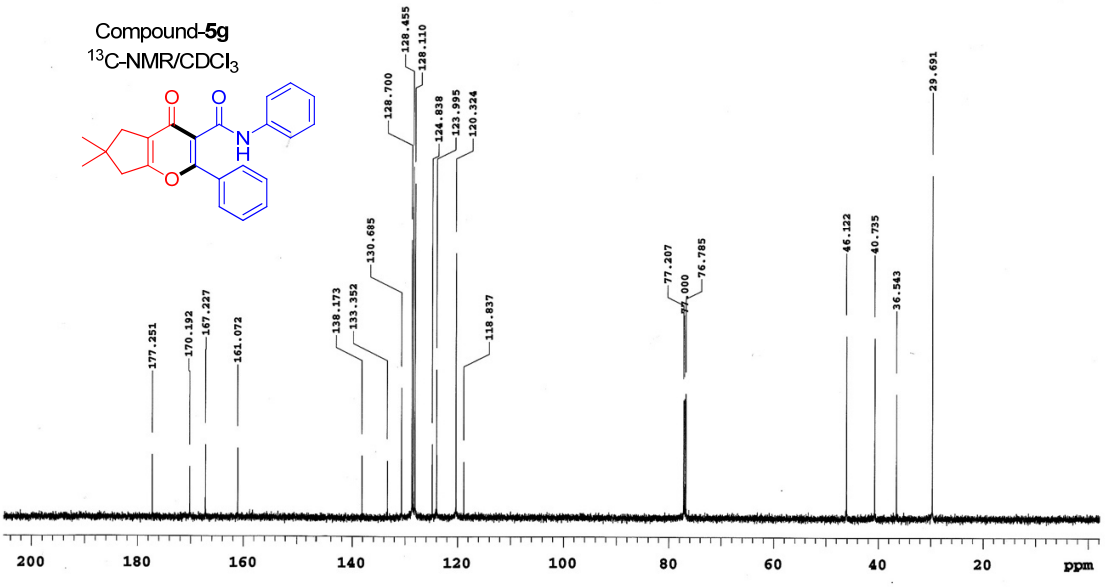
Compound-**5g**

^{1}H-NMR/$CDCl_3$



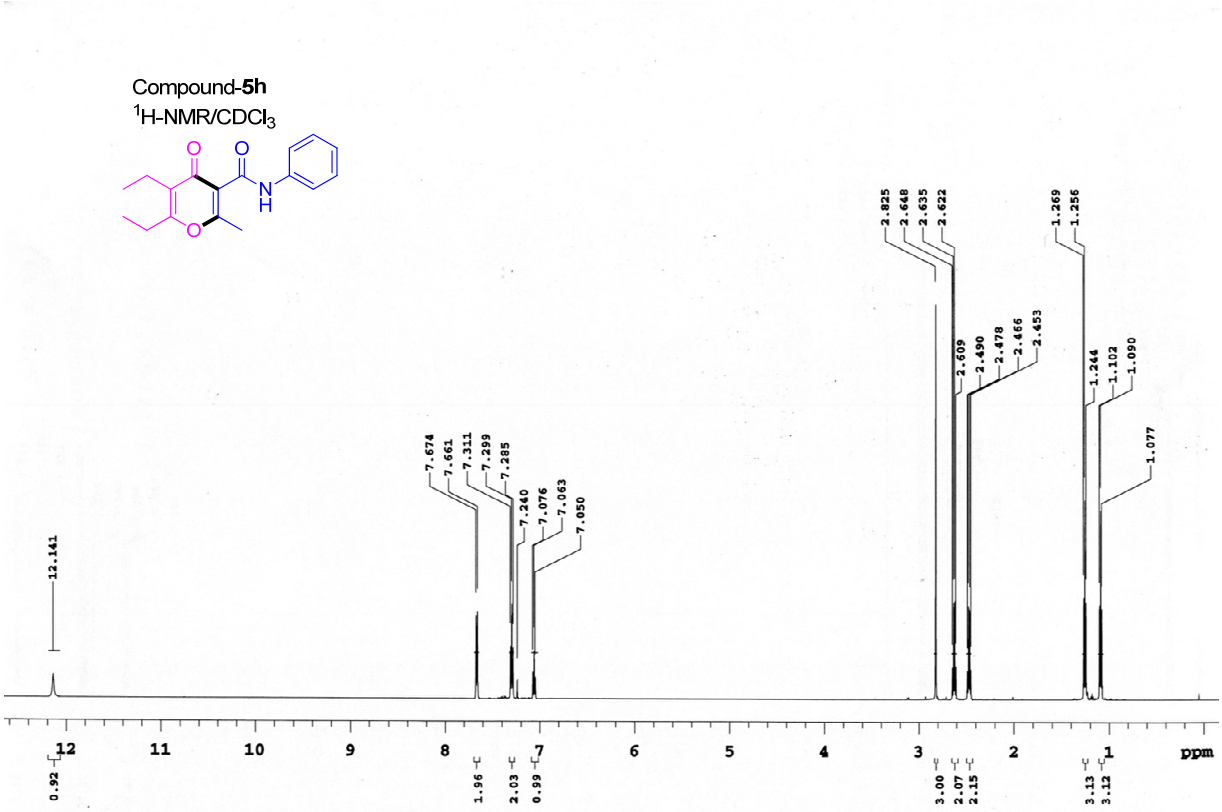
Compound-**5g**

^{13}C-NMR/$CDCl_3$



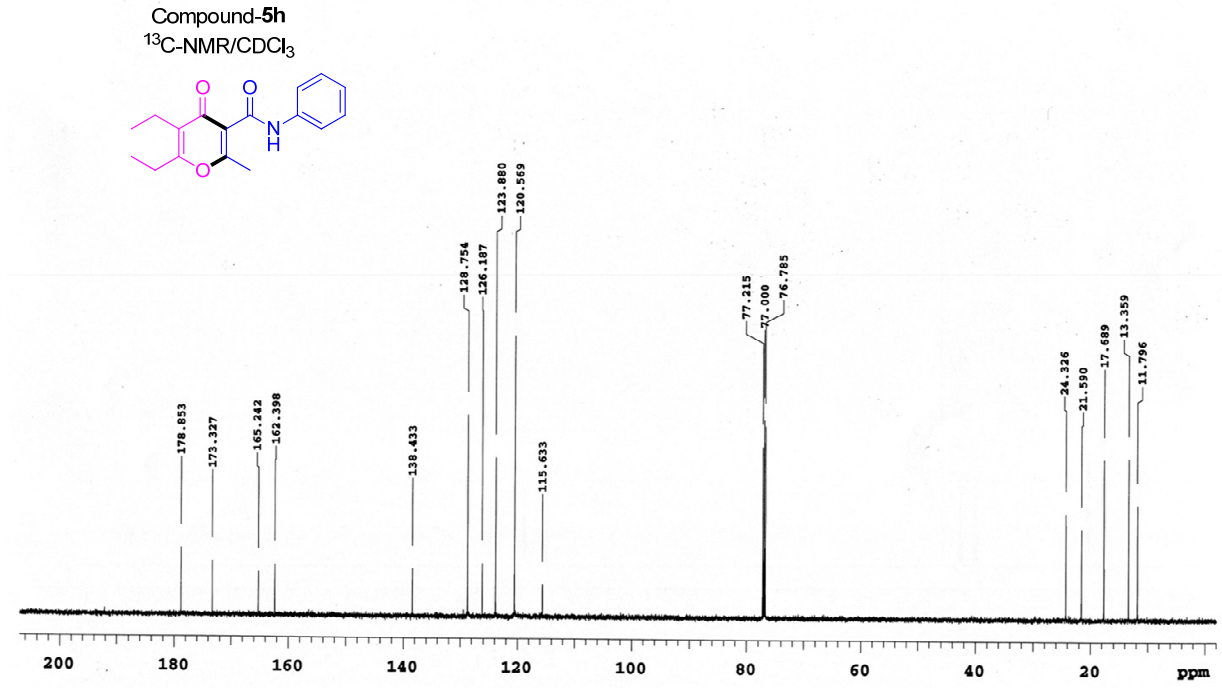
Compound-**5h**

^{1}H-NMR/$CDCl_3$

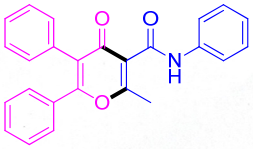


Compound-**5h**

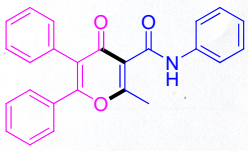
^{13}C-NMR/$CDCl_3$



Compound-**5i**
^{1}H-NMR/$CDCl_3$

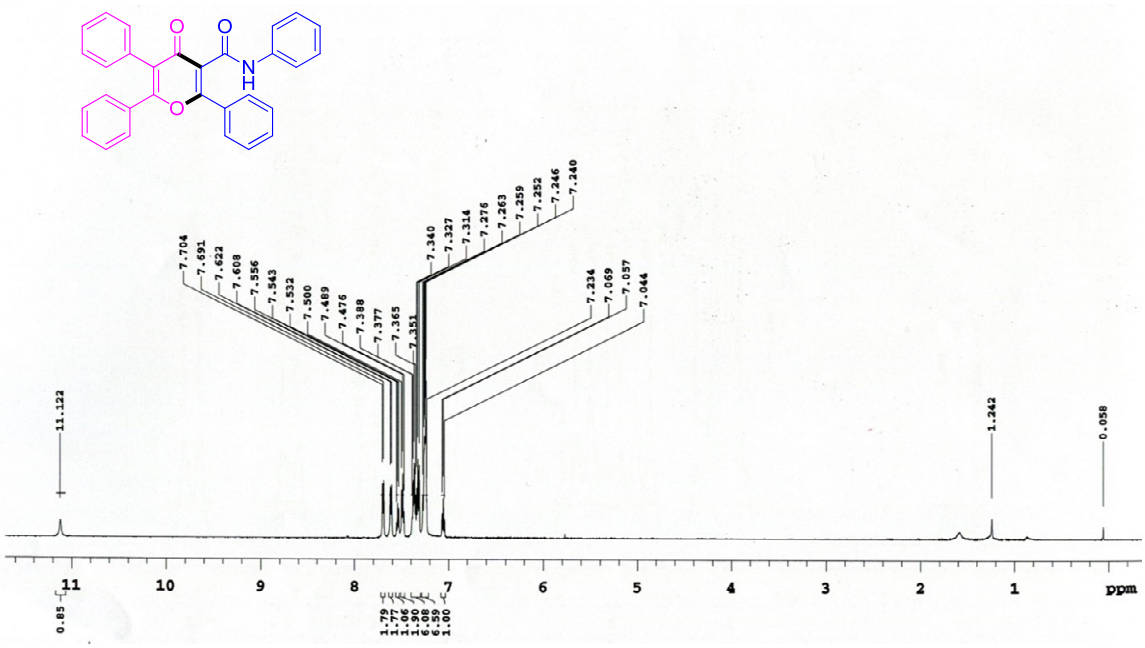


Compound-**5i**
^{13}C-NMR/$CDCl_3$



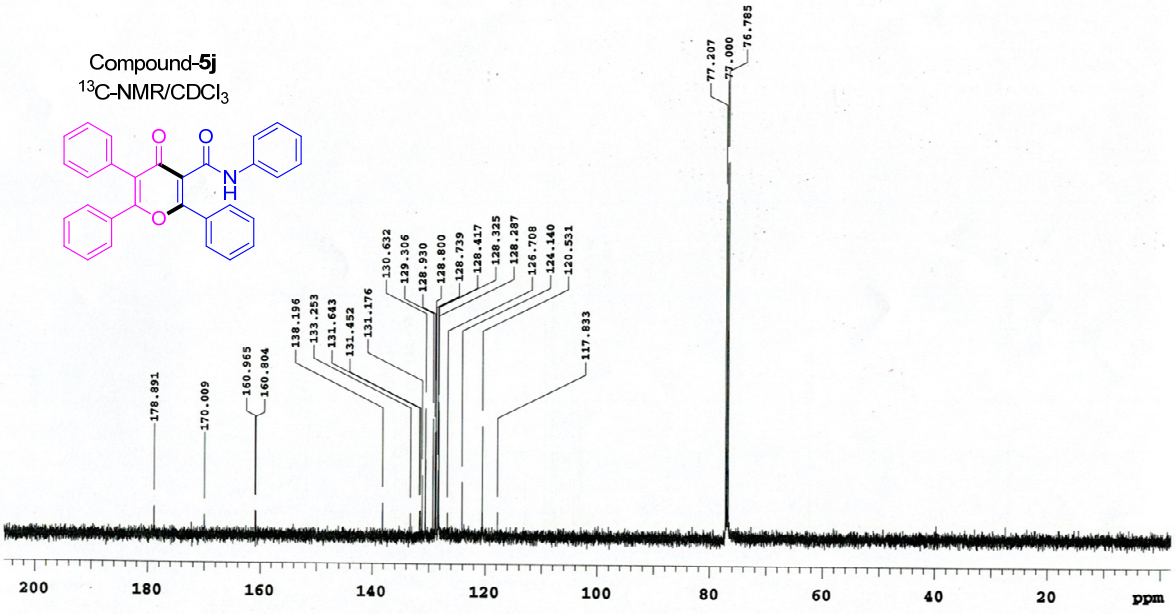
Compound-**5j**

^{1}H-NMR/CDCl$_3$



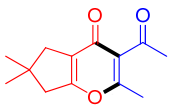
Compound-**5j**

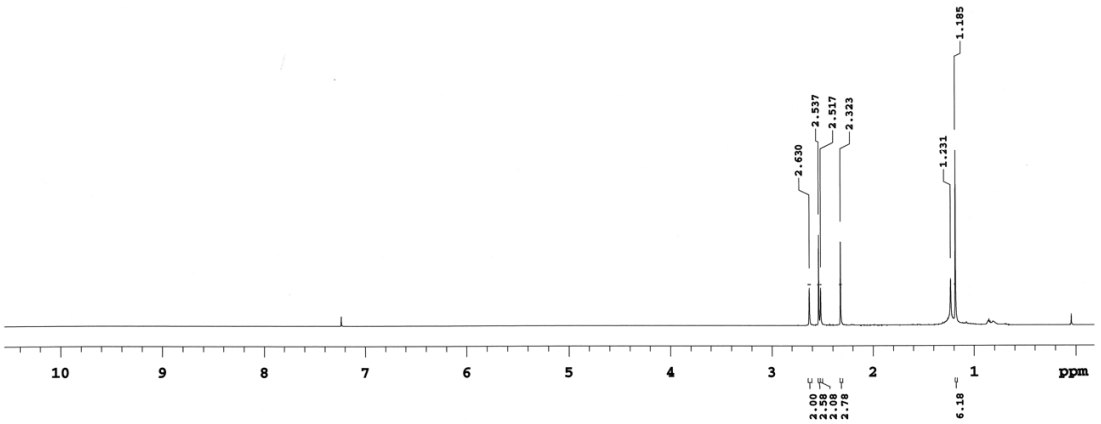
^{13}C-NMR/CDCl$_3$



Compound-**7a**

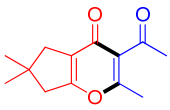
^{1}H-NMR/$CDCl_3$

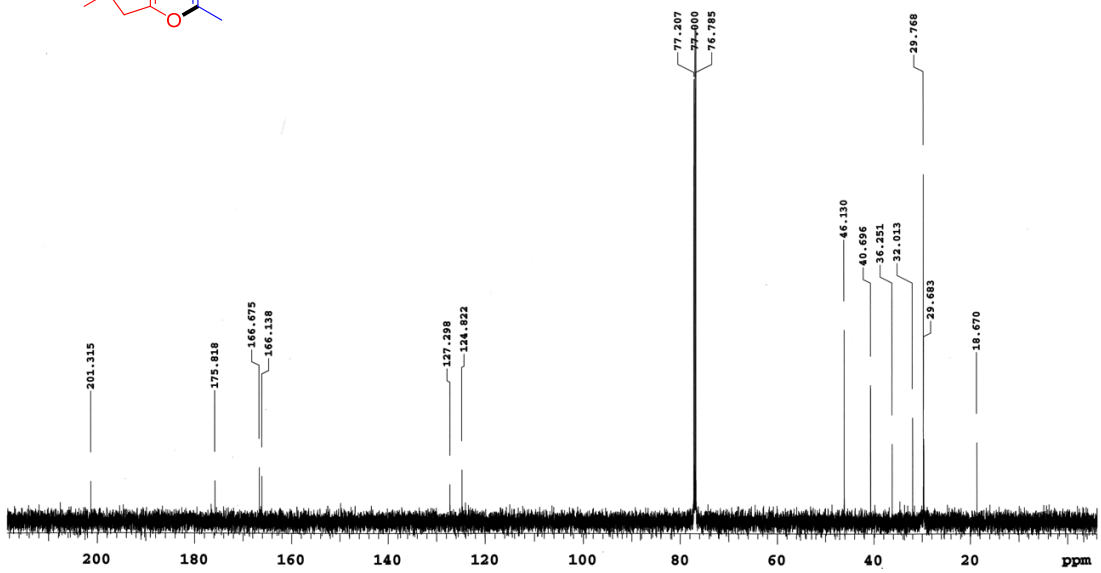




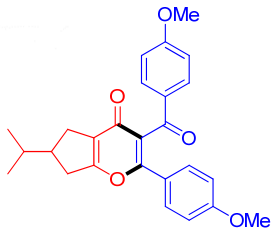
Compound-**7a**

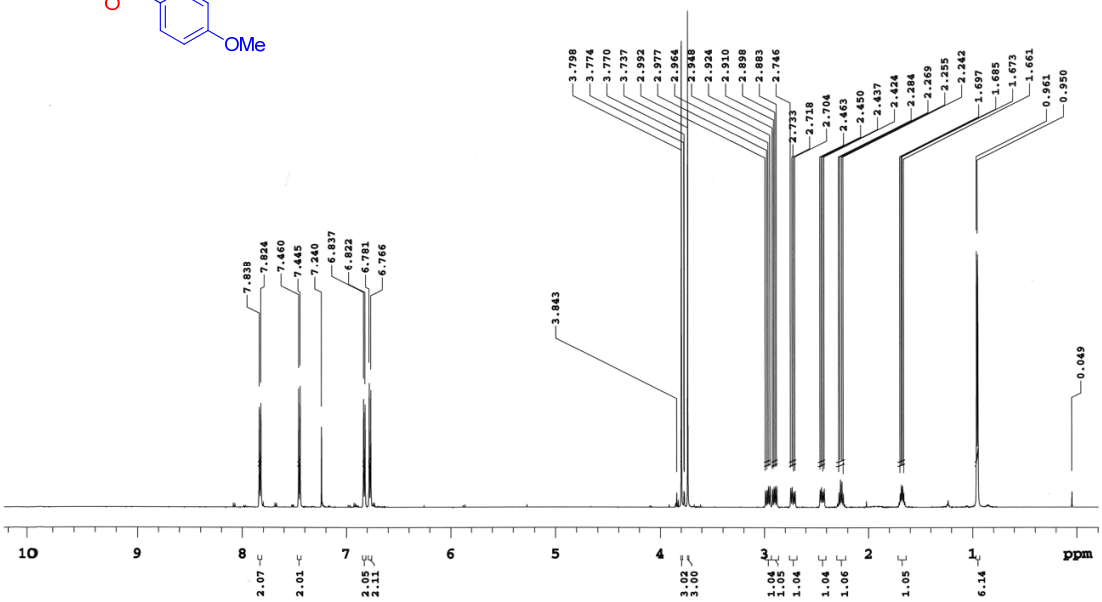
^{13}C-NMR/$CDCl_3$



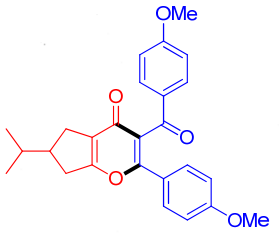


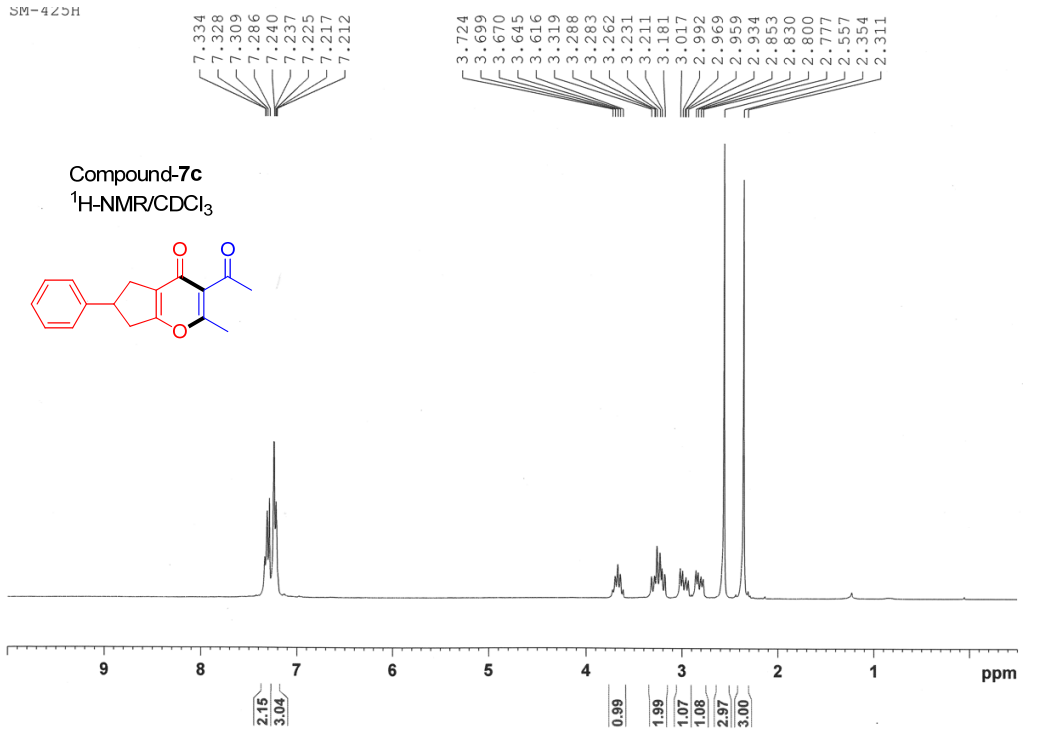
Compound-**7b**
^{1}H-NMR/$CDCl_3$





Compound-**7b**
^{13}C-NMR/$CDCl_3$




SM-425H
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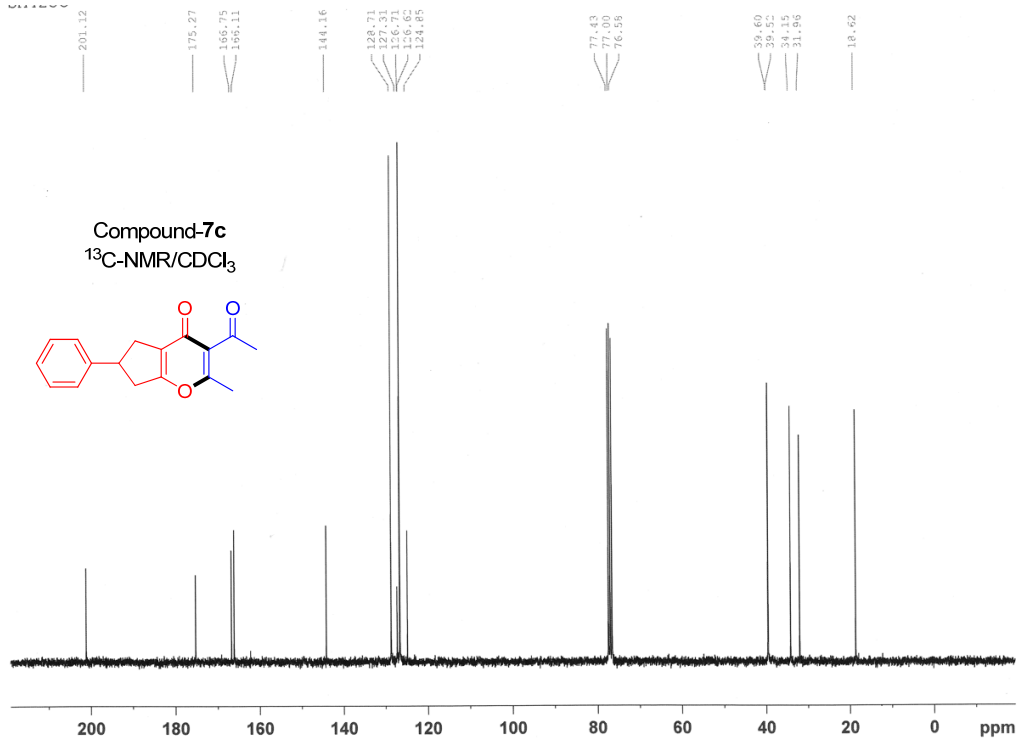
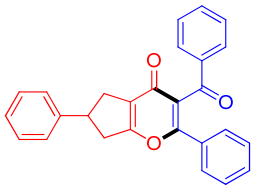
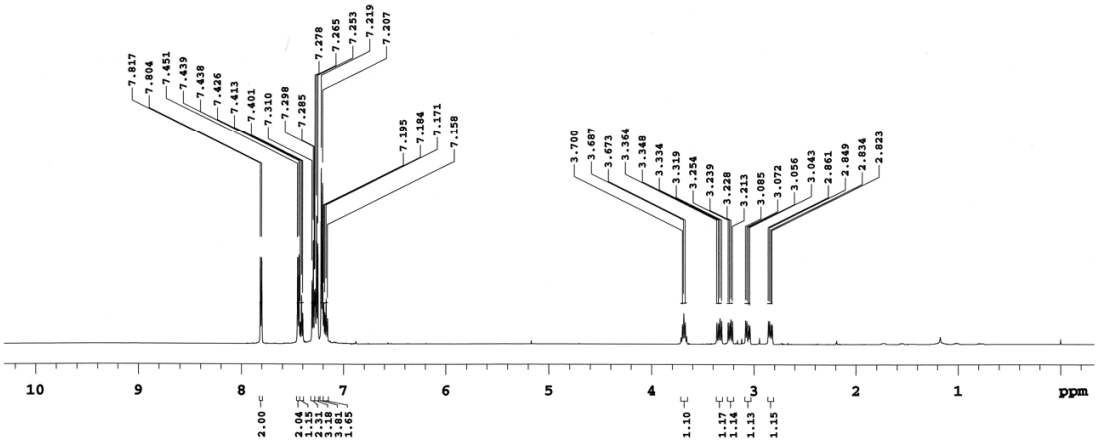
7.328
7.309
7.286
7.240
7.237
7.225
7.217
7.212
3.724
3.699
3.670
3.645
3.616
3.319
3.288
3.283
3.262
3.231
3.211
3.181
3.017
2.992
2.969
2.959
2.934
2.853
2.830
2.800
2.777
2.557
2.354
2.311
Compound-7c
1H-NMR/CDCl3
O
O
O
9
8
7
6
5
4
3
2
1
ppm
2.15
3.04
0.99
1.99
1.07
1.08
2.97
3.00


201.12
175.27
166.75
166.11
144.16
128.71
127.31
156.71
156.62
124.85
77.43
77.00
76.58
39.60
39.52
34.15
31.96
18.62
Compound-7c
13C-NMR/CDCl3
O
O
O
200
180
160
140
120
100
80
60
40
20
0
ppm

Compound-**7d**

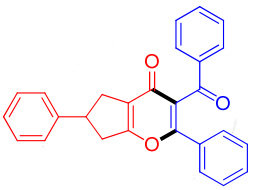
^{1}H-NMR/$CDCl_3$





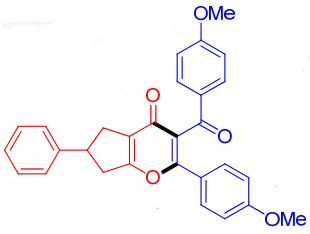
Compound-**7d**

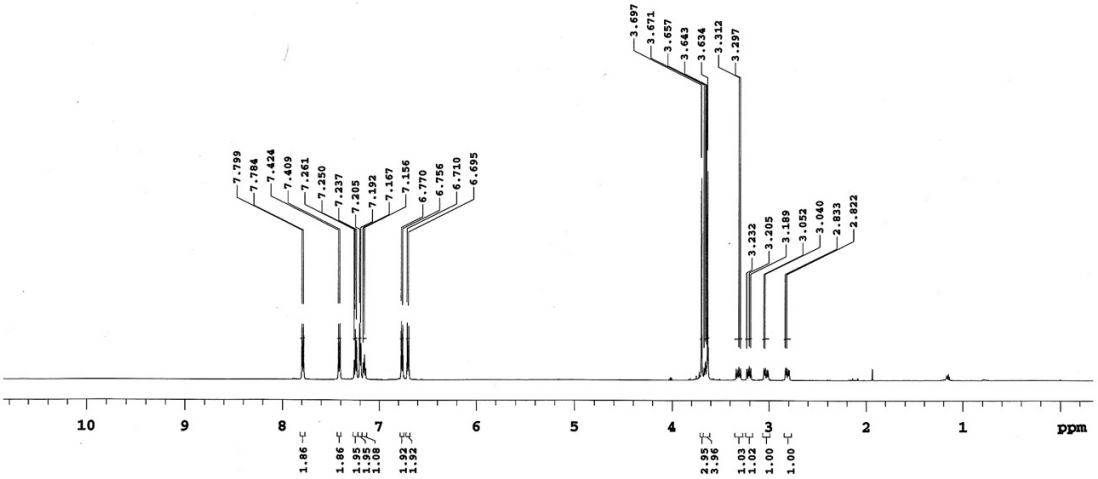
^{13}C-NMR/$CDCl_3$



Compound-**7e**

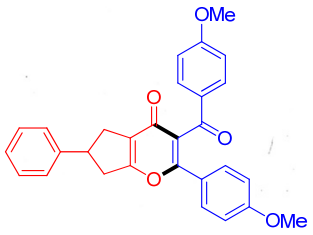
^{1}H-NMR/$CDCl_3$





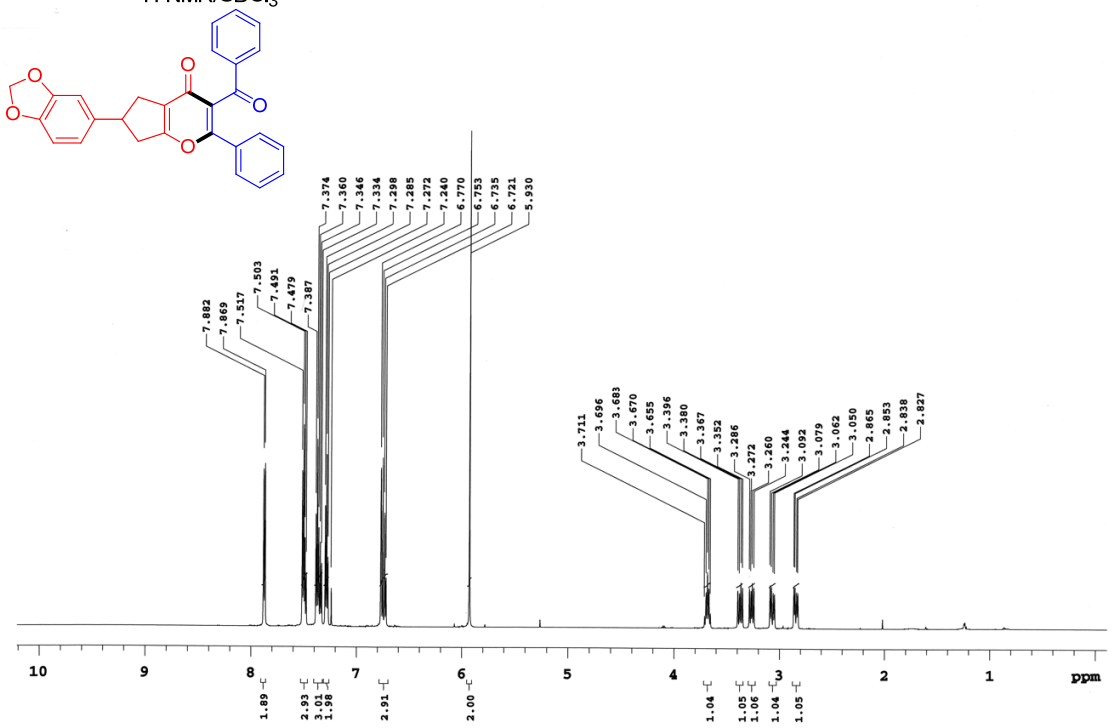
Compound-**7e**

^{13}C-NMR/$CDCl_3$



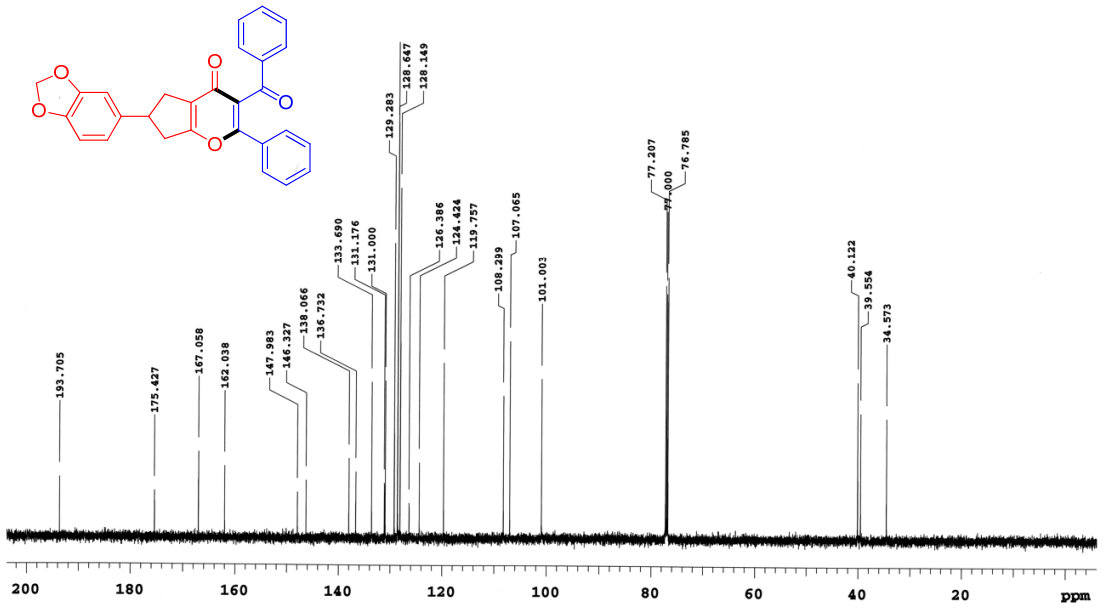
Compound-**7f**

^{1}H-NMR/$CDCl_3$

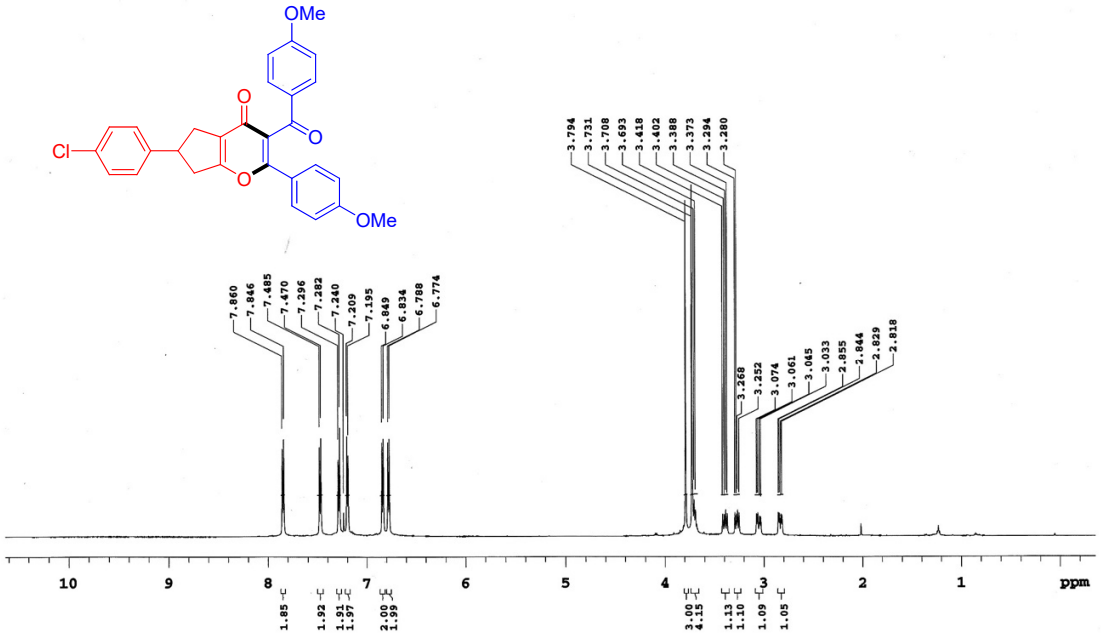


Compound-**7f**

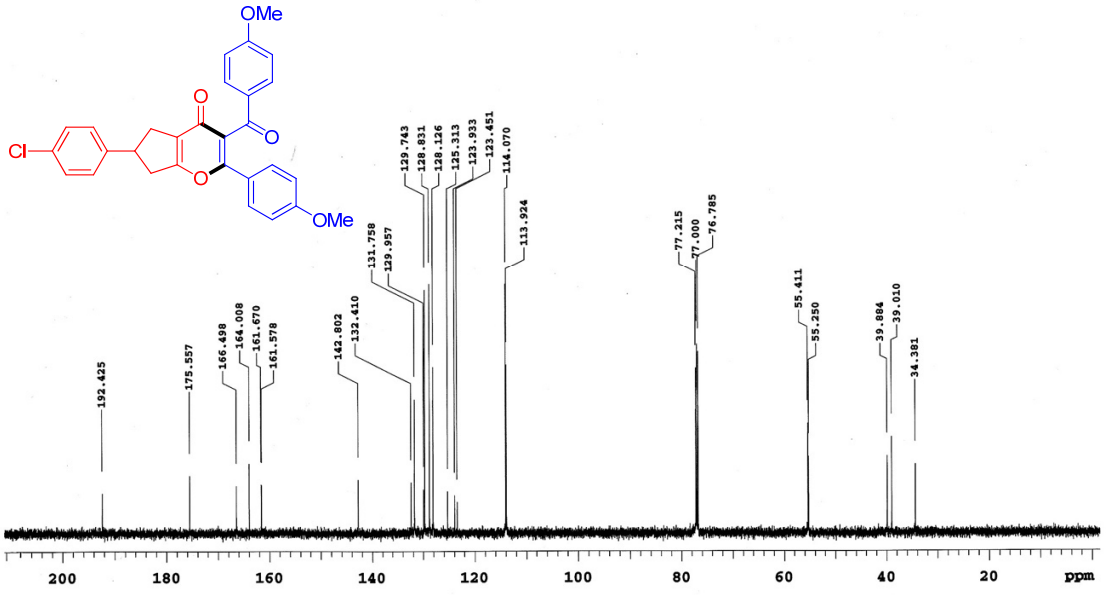
^{13}C-NMR/$CDCl_3$



Compound-**7g**
^{1}H-NMR/$CDCl_3$

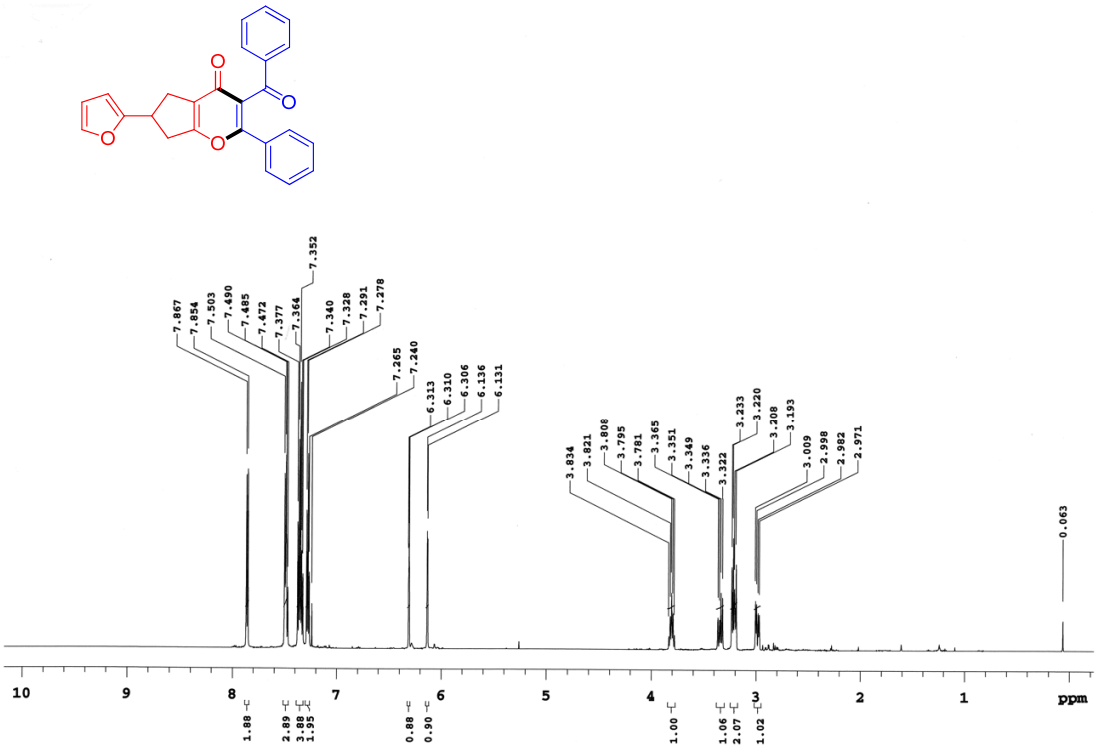


Compound-**7g**
^{13}C-NMR/$CDCl_3$



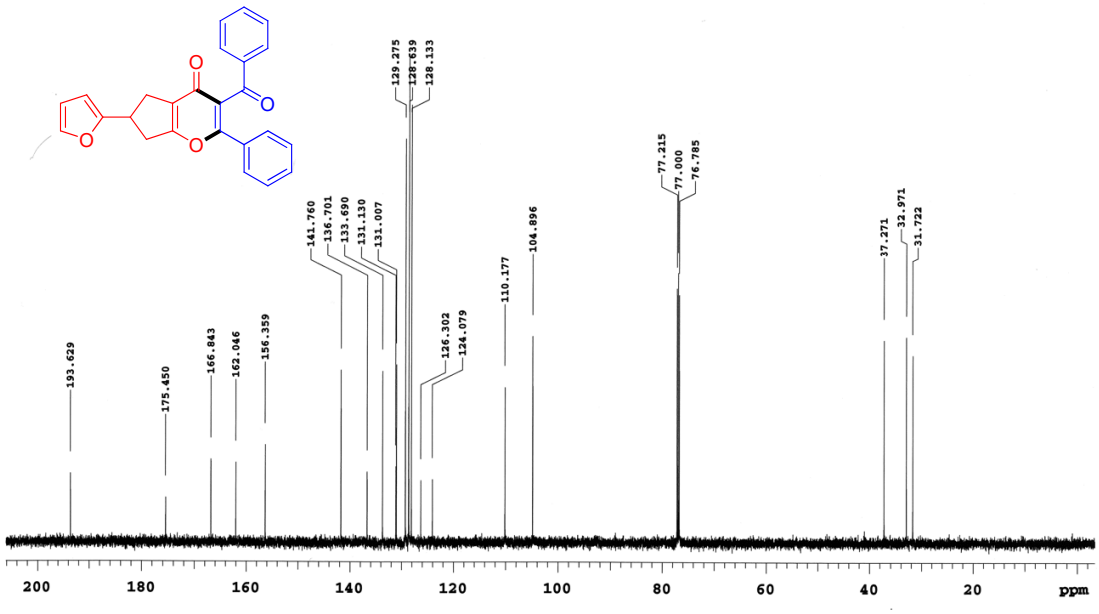
Compound-**7h**

^{1}H-NMR/$CDCl_3$



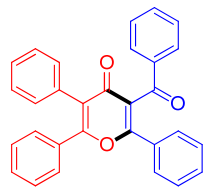
Compound-**7h**

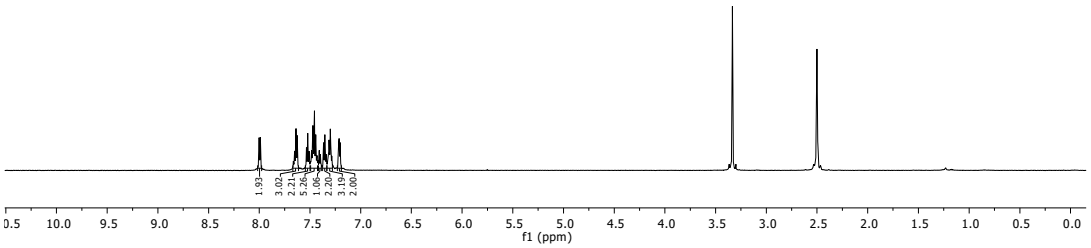
^{13}C-NMR/$CDCl_3$



Compound-**7i**

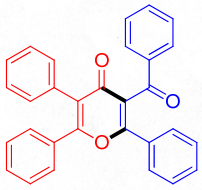
^{1}H-NMR/$CDCl_3$



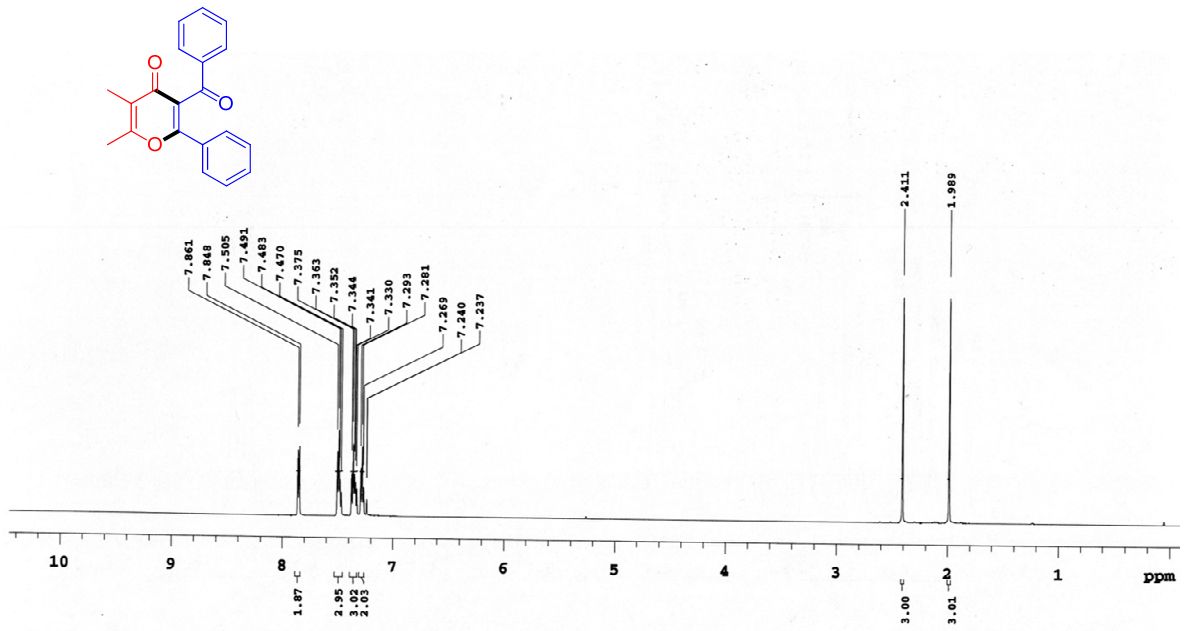


Compound-**7i**

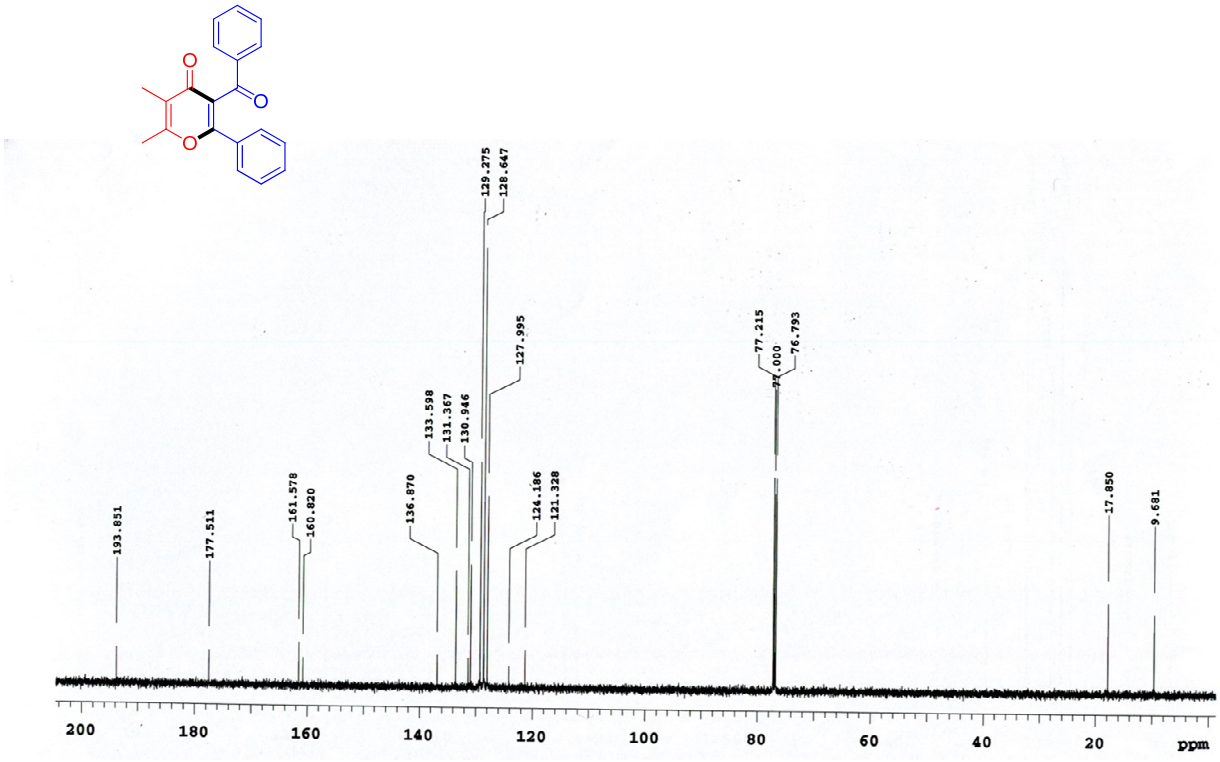
^{13}C-NMR/$CDCl_3$

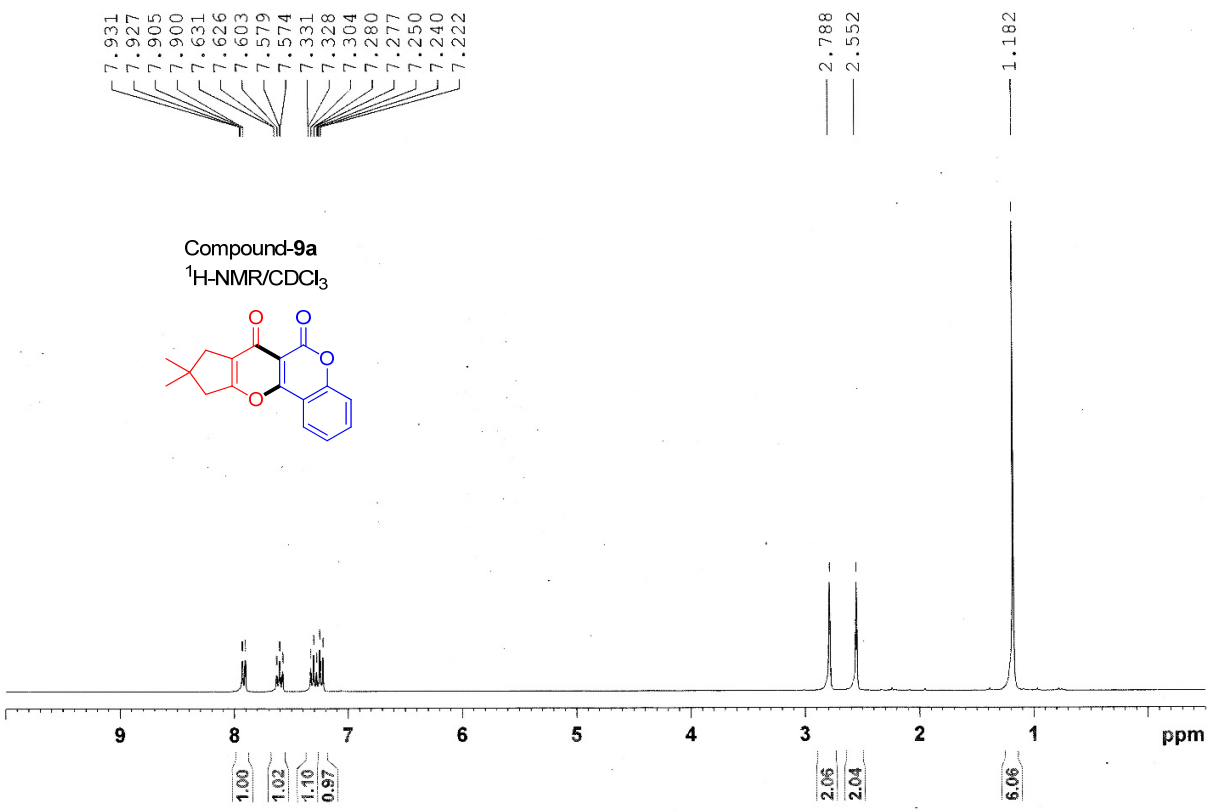


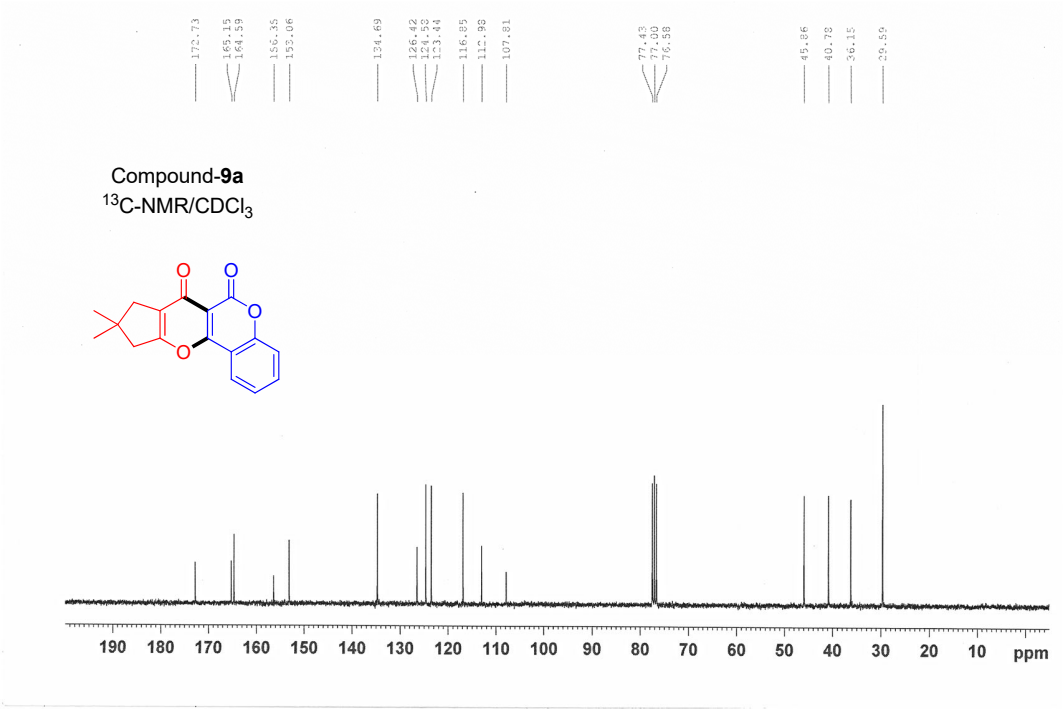
Compound-**7j**
^{1}H-NMR/$CDCl_3$

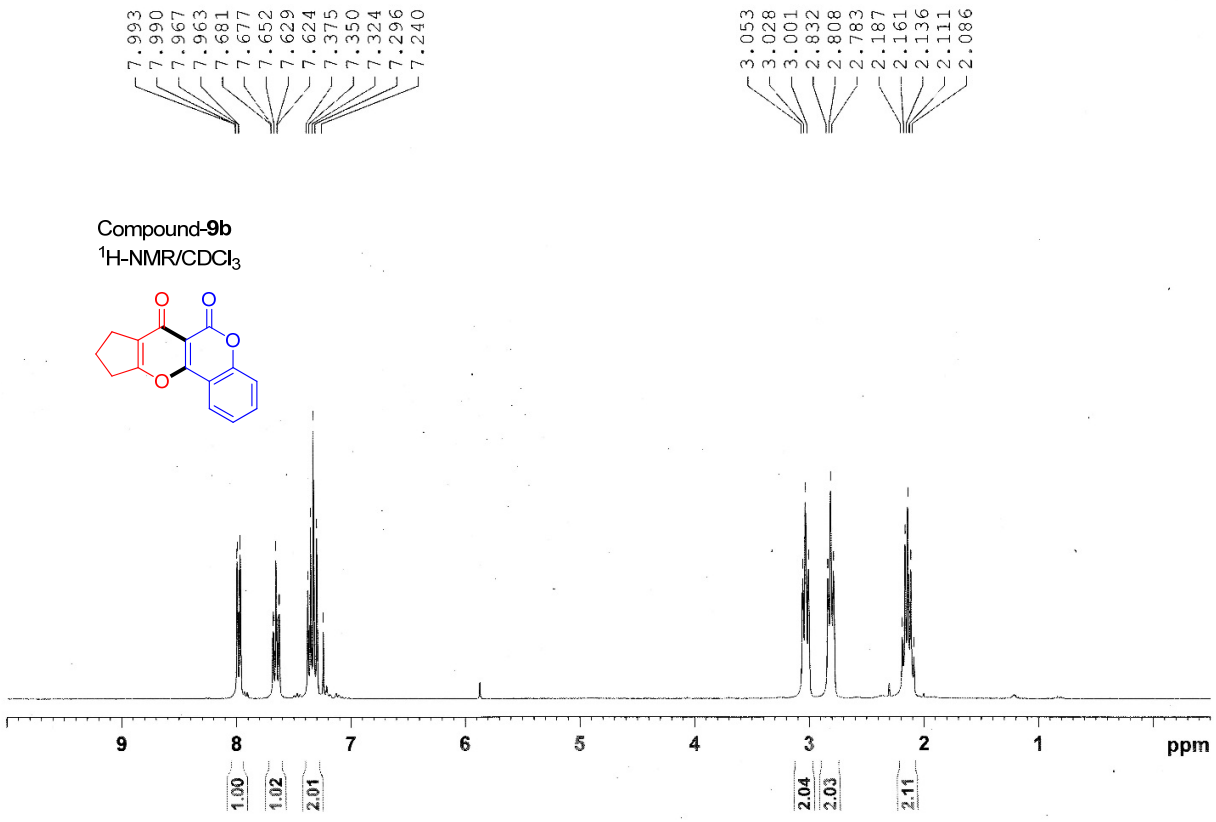


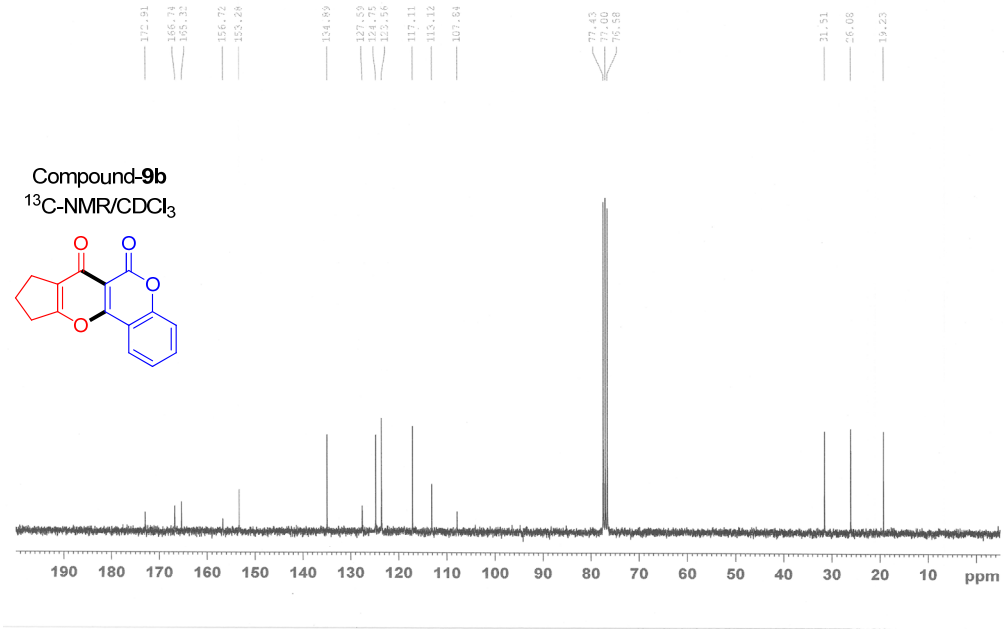
Compound-**7j**
^{13}C-NMR/$CDCl_3$

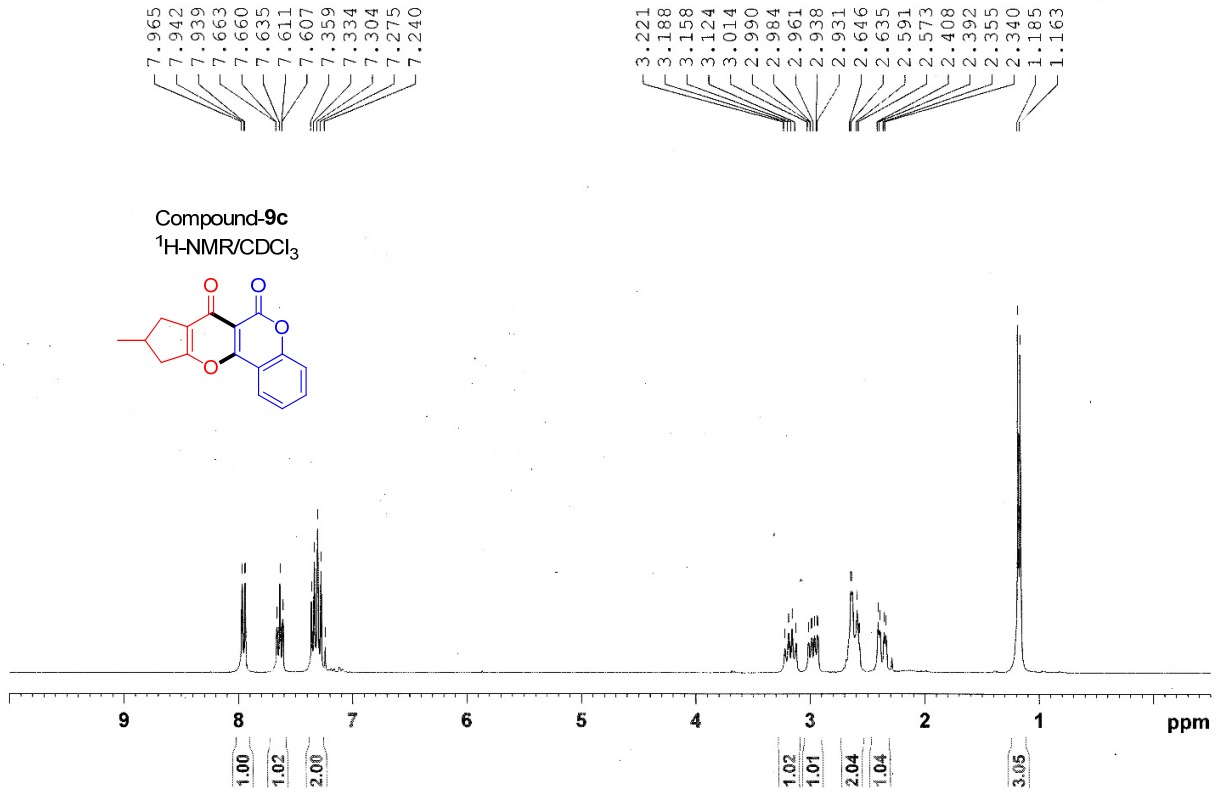


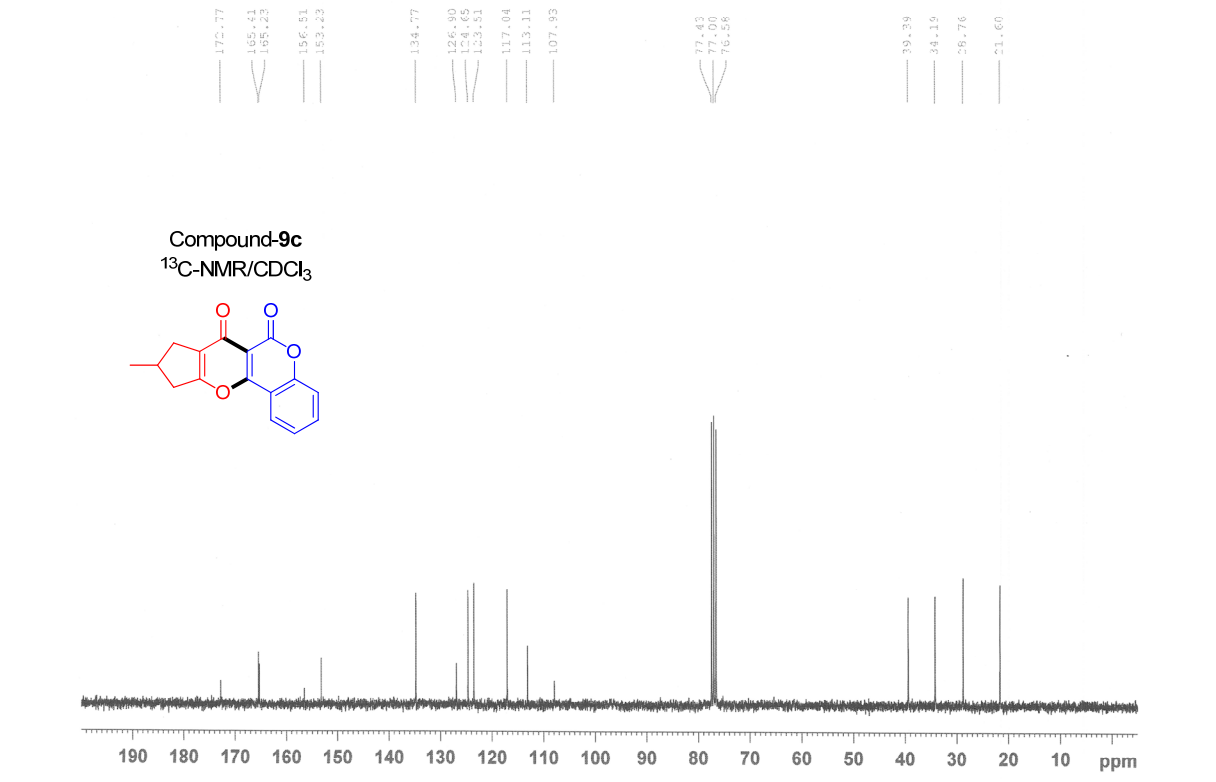

7.931
7.927
7.905
7.900
7.631
7.626
7.603
7.579
7.574
7.331
7.328
7.304
7.280
7.277
7.250
7.240
7.222
2.788
2.552
1.182
Compound-9a
1H-NMR/CDCl3
9
8
7
6
5
4
3
2
1
ppm
1.00
1.02
1.10
0.97
2.05
2.04
6.06

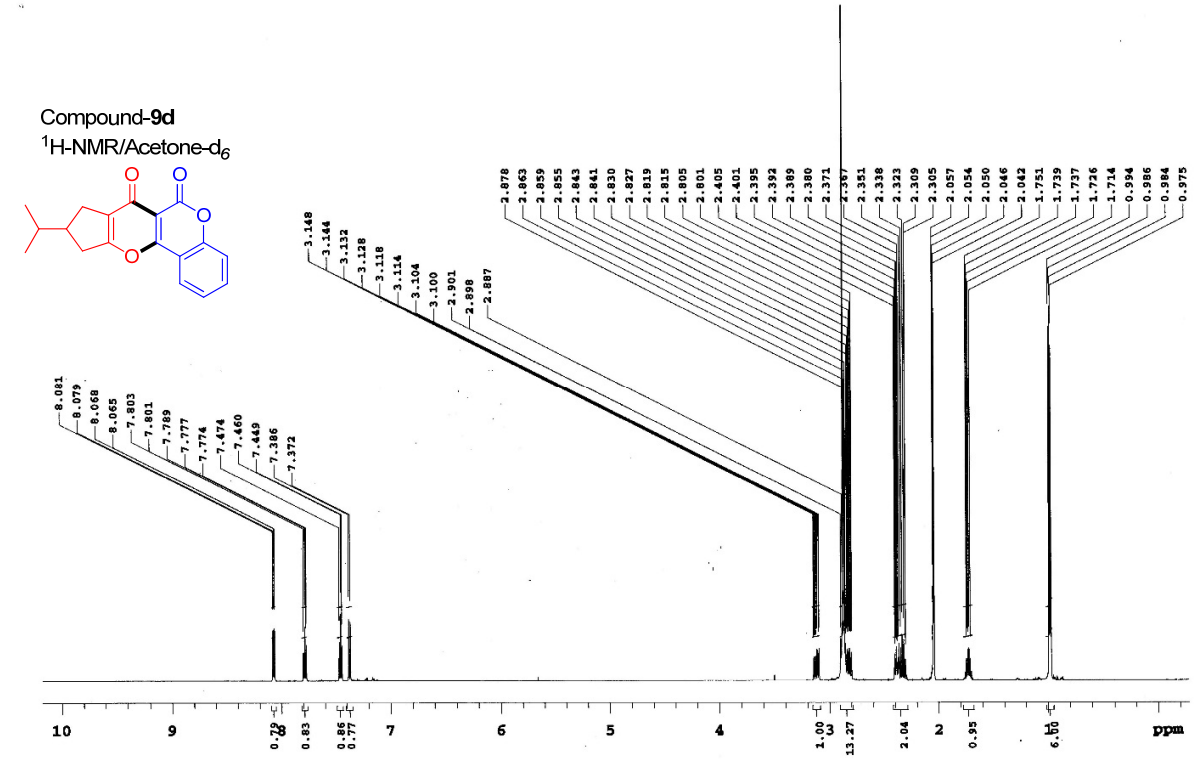

172.73
165.15
164.59
156.35
153.06
134.69
126.42
124.53
123.44
116.85
112.98
107.81
77.43
77.00
76.58
45.86
40.78
36.15
29.59
Compound-9a
13C-NMR/CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

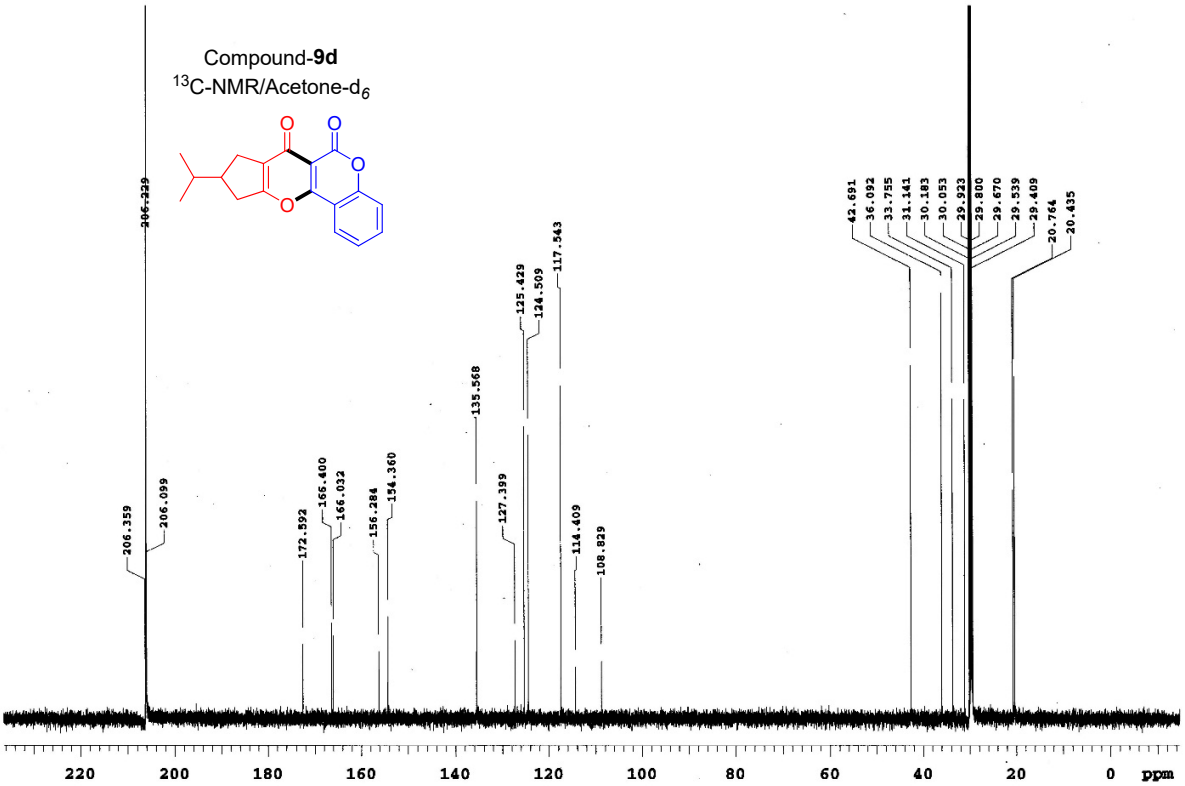

7.993
7.990
7.967
7.963
7.681
7.677
7.652
7.629
7.624
7.375
7.350
7.324
7.296
7.240
3.053
3.028
3.001
2.832
2.808
2.783
2.187
2.161
2.136
2.111
2.086
Compound-9b
1H-NMR/CDCl3
9
8
7
6
5
4
3
2
1
ppm
1.00
1.02
2.01
2.04
2.03
2.11

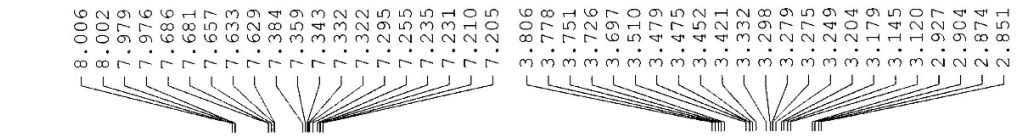

Compound-9b
13C-NMR/CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.965
7.942
7.939
7.663
7.660
7.635
7.611
7.607
7.359
7.334
7.304
7.275
7.240
3.221
3.188
3.158
3.124
3.014
2.990
2.984
2.961
2.938
2.931
2.646
2.635
2.591
2.573
2.408
2.392
2.355
2.340
1.185
1.163
Compound-9c
1H-NMR/CDCl3
9
8
7
6
5
4
3
2
1
ppm
1.00
1.02
2.00
1.02
1.01
2.04
1.04
3.05

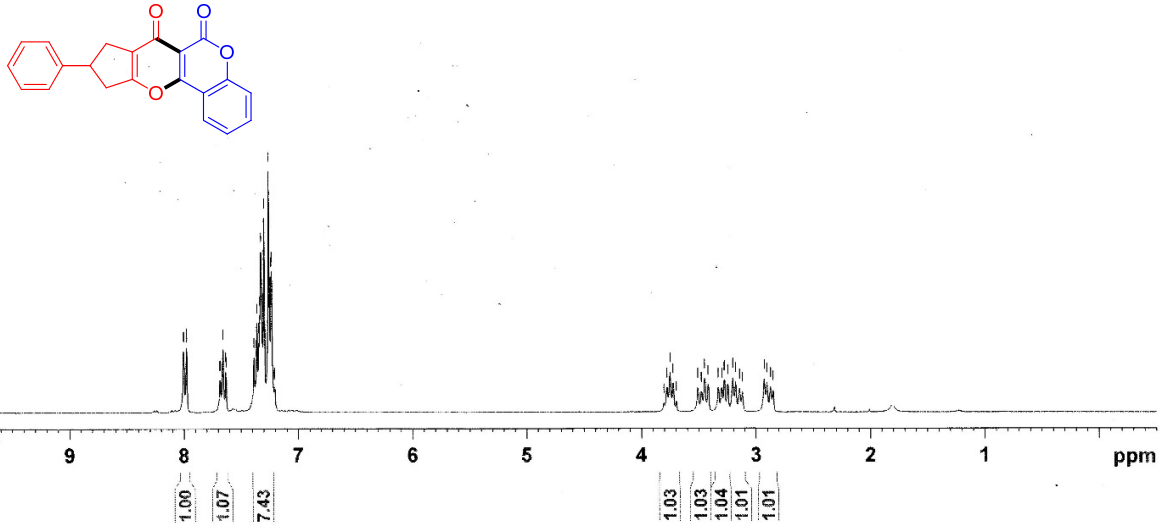

172.77
165.61
165.23
156.51
153.23
134.77
126.90
124.65
123.51
117.04
113.11
107.93
77.43
77.00
76.56
39.39
34.19
26.76
21.60
Compound-9c
13C-NMR/CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Compound-9d
1H-NMR/Acetone-d6
8.081
8.079
8.068
8.065
7.803
7.801
7.789
7.777
7.774
7.474
7.460
7.449
7.386
7.372
3.148
3.144
3.132
3.128
3.118
3.114
3.104
3.100
2.901
2.898
2.887
2.878
2.863
2.859
2.855
2.843
2.841
2.830
2.827
2.819
2.815
2.805
2.801
2.405
2.401
2.395
2.392
2.389
2.380
2.371
2.351
2.338
2.323
2.309
2.305
2.057
2.054
2.050
2.046
2.042
1.751
1.739
1.737
1.726
1.714
0.994
0.986
0.984
0.975
10
9
8
7
6
5
4
3
2
1
ppm

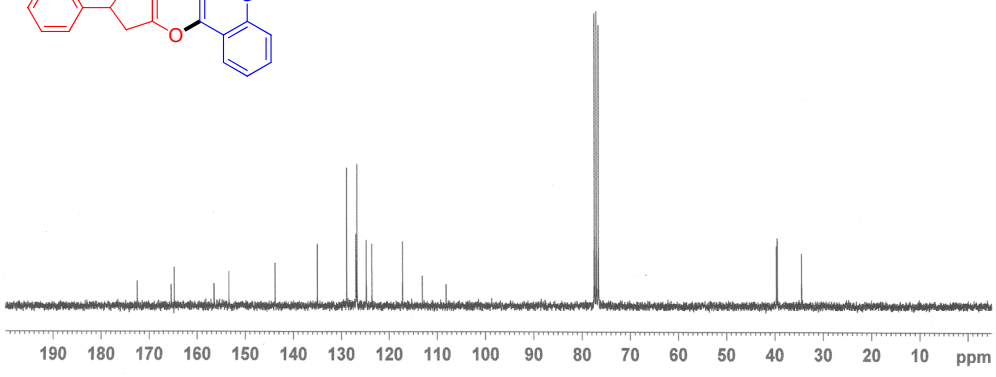

Compound-9d
13C-NMR/Acetone-d6
206.329
206.359
206.099
172.592
166.400
166.032
156.284
154.360
135.568
127.399
125.429
124.509
117.543
114.409
108.829
43.691
36.092
33.755
31.141
30.183
30.053
29.923
29.800
29.670
29.539
29.409
20.764
20.435
220
200
180
160
140
120
100
80
60
40
20
0
ppm

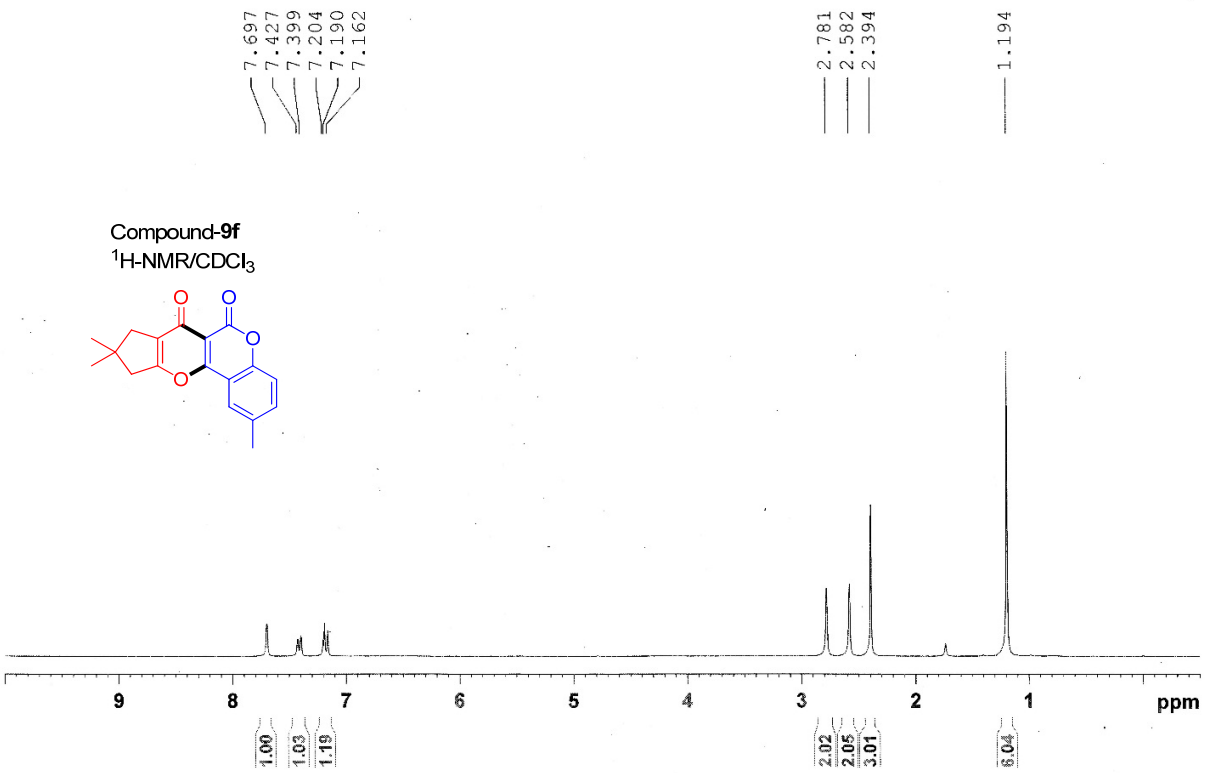


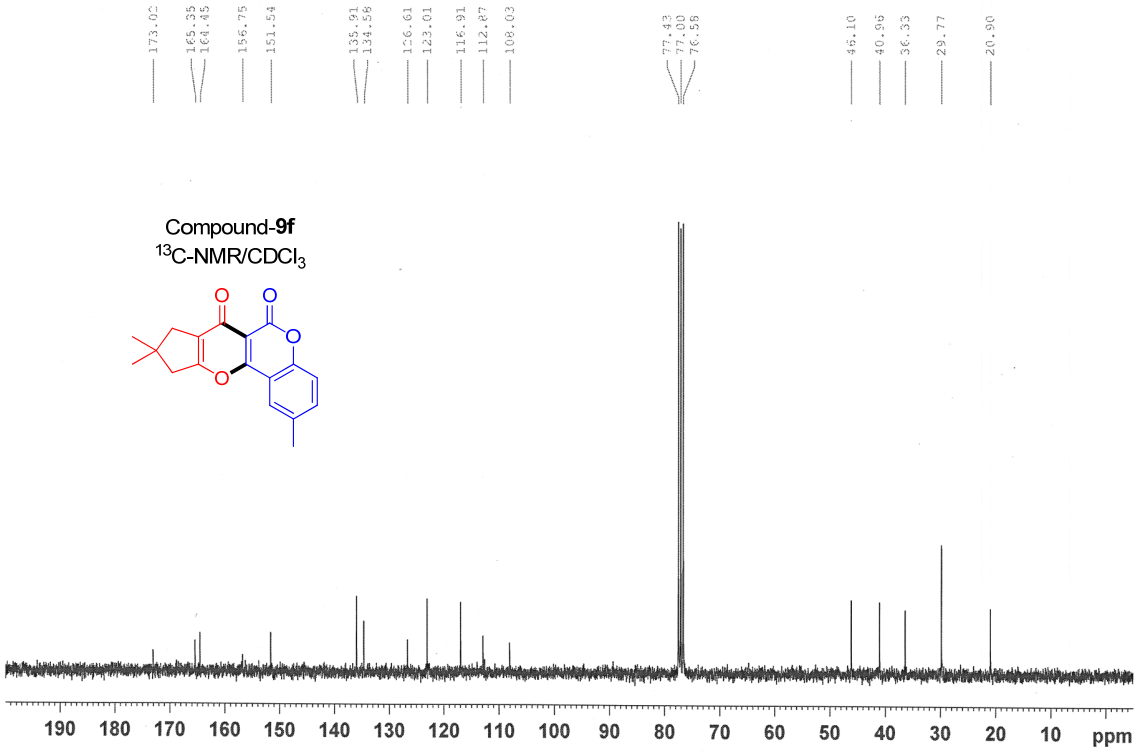
Compound-**9e**
^{1}H-NMR/$CDCl_3$



Compound-**9e**
^{13}C-NMR/$CDCl_3$

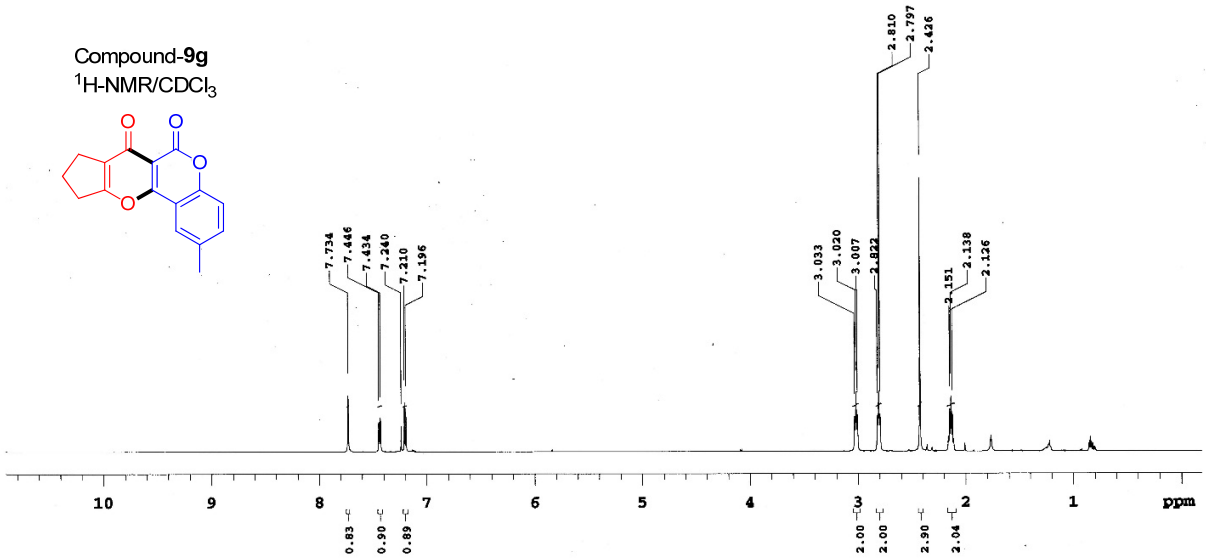



7.697
7.427
7.399
7.204
7.190
7.162
2.781
2.582
2.394
1.194
Compound-9f
1H-NMR/CDCl3
9
8
7
6
5
4
3
2
1
ppm
1.00
1.03
1.19
2.02
2.05
3.01
6.04


173.02
165.35
164.45
156.75
151.54
135.91
134.58
126.61
123.01
116.91
112.87
108.03
77.43
77.00
76.55
46.10
40.96
36.33
29.77
20.90
Compound-9f
13C-NMR/CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

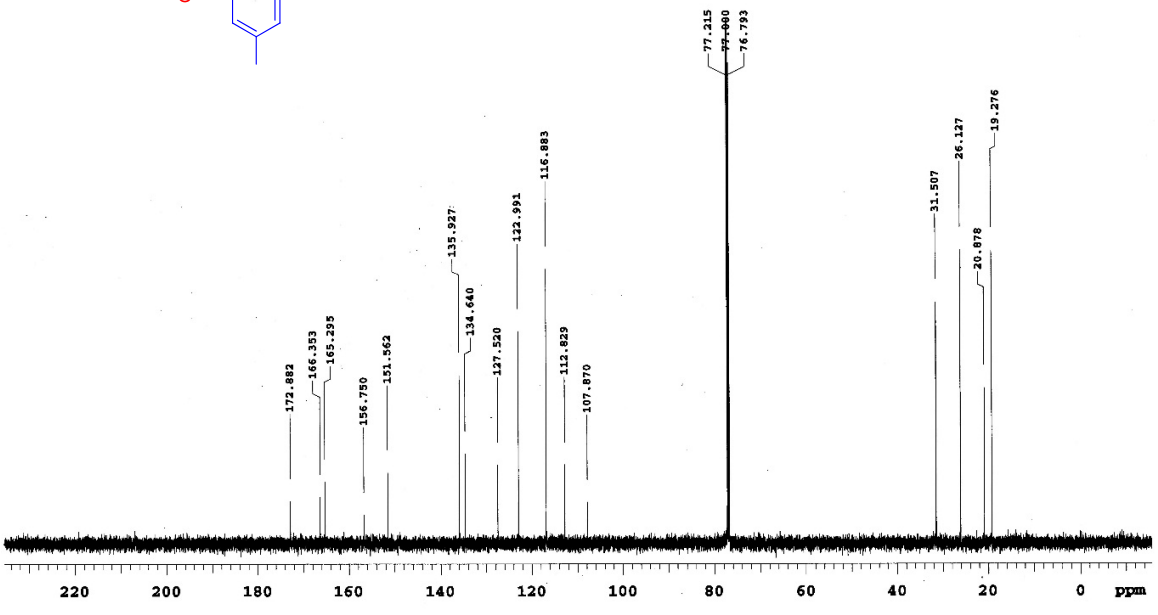
Compound-**9g**

^{1}H-NMR/$CDCl_3$

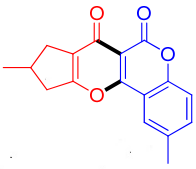


Compound-**9g**

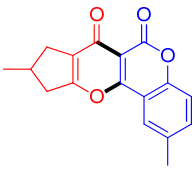
^{13}C-NMR/$CDCl_3$



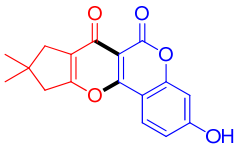
Compound-**9h**
^{1}H-NMR/CDCl$_3$



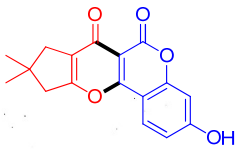
Compound-**9h**
^{13}C-NMR/CDCl$_3$



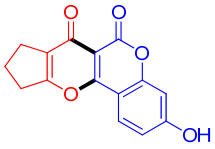
Compound-**9i**
^{1}H-NMR/DMSO-d$_6$



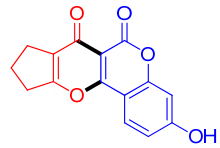
Compound-**9i**
^{13}C-NMR/DMSO-d$_6$



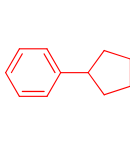
Compound-**9j**
^{1}H-NMR/DMSO-d_6



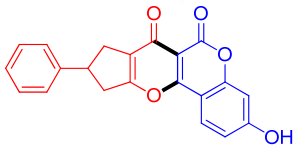
Compound-**9j**
^{13}C-NMR/DMSO-d_6



Compound-**9k**
^{1}H-NMR/DMSO-d$_6$

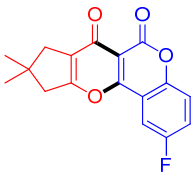


Compound-**9k**
^{13}C-NMR/DMSO-d$_6$



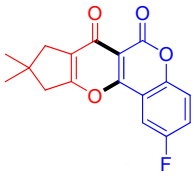
Compound-**9l**

^{1}H-NMR/$CDCl_3$



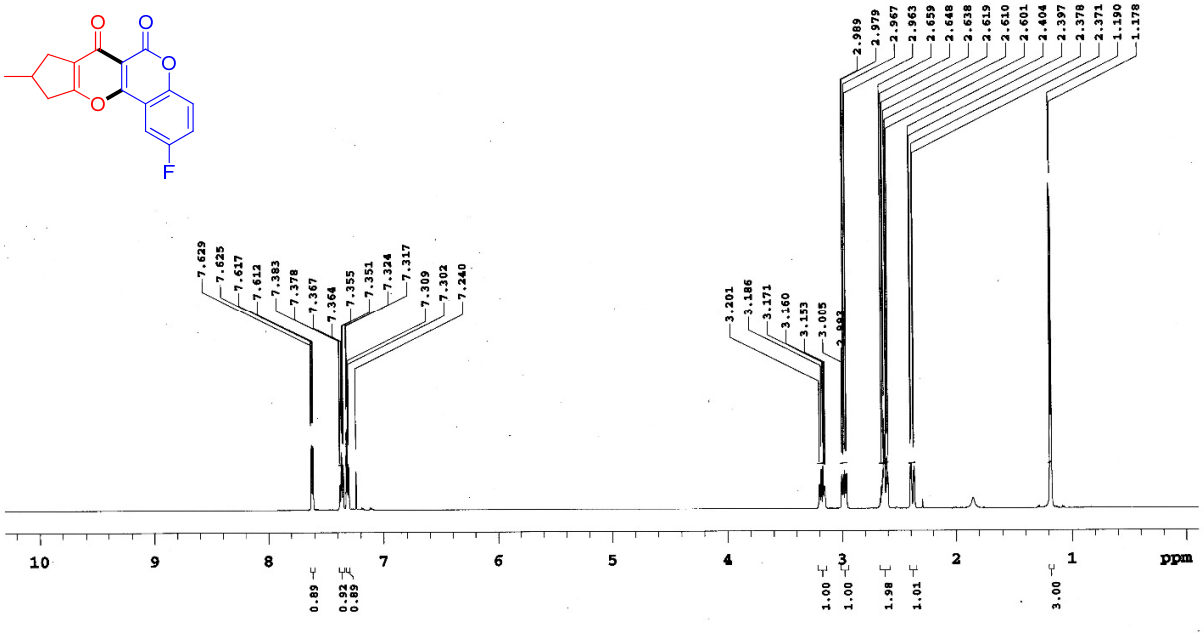
Compound-**9l**

^{13}C-NMR/$CDCl_3$



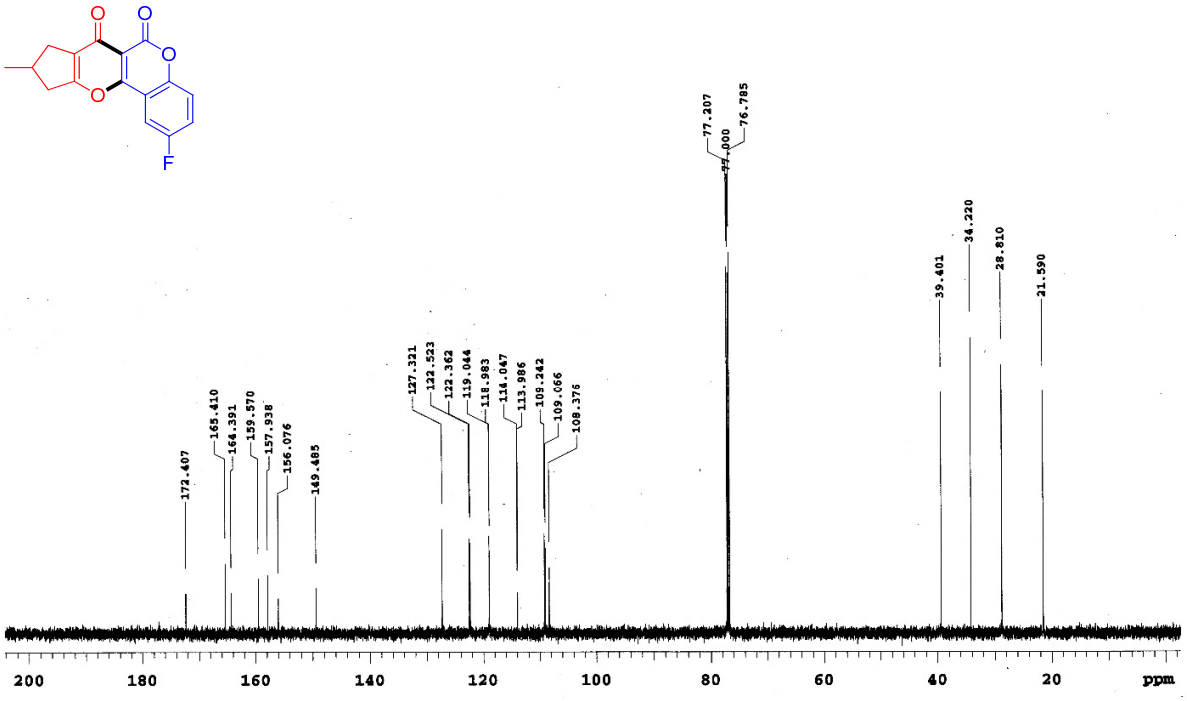
Compound-**9m**

^{1}H-NMR/$CDCl_3$



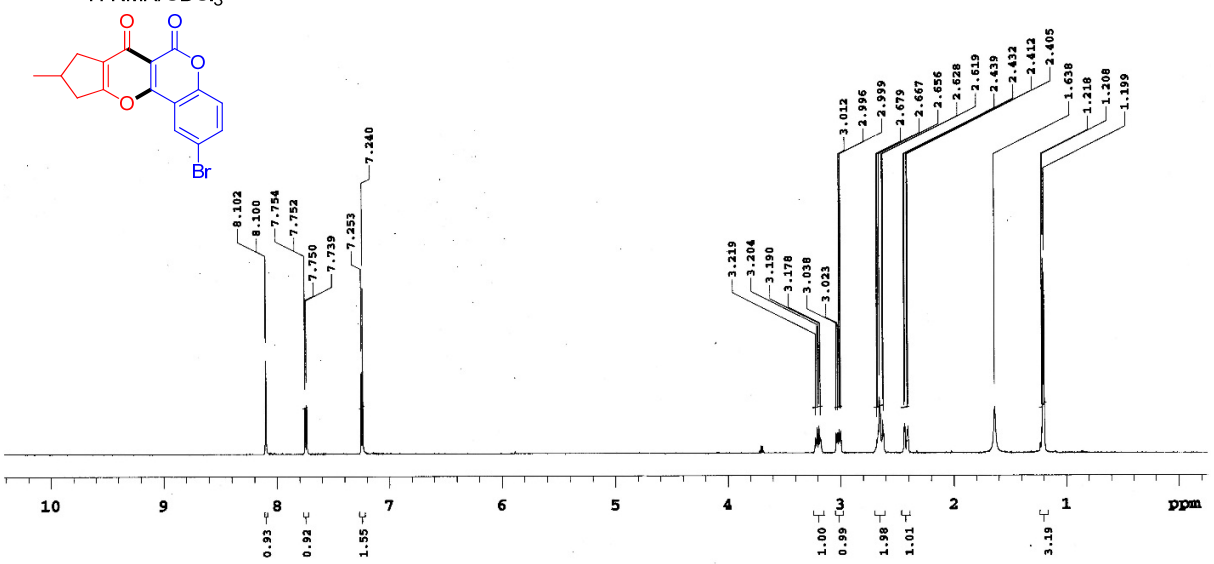
Compound-**9m**

^{13}C-NMR/$CDCl_3$



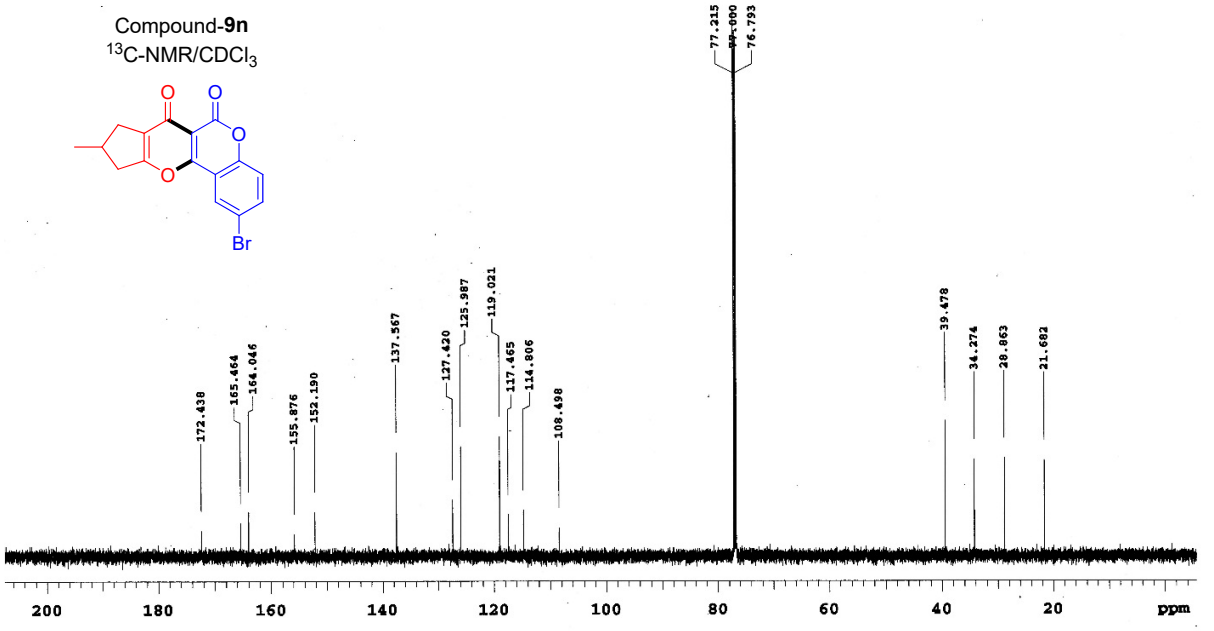
Compound-**9n**

^{1}H-NMR/$CDCl_3$



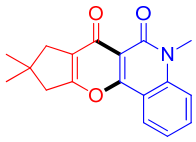
Compound-**9n**

^{13}C-NMR/$CDCl_3$



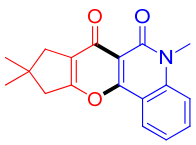
Compound-**9o**

^{1}H-NMR/DMSO-d_6



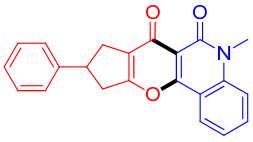
Compound-**9o**

^{13}C-NMR/DMSO-d_6



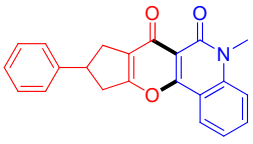
Compound-**9p**

^{1}H-NMR/DMSO-d_6



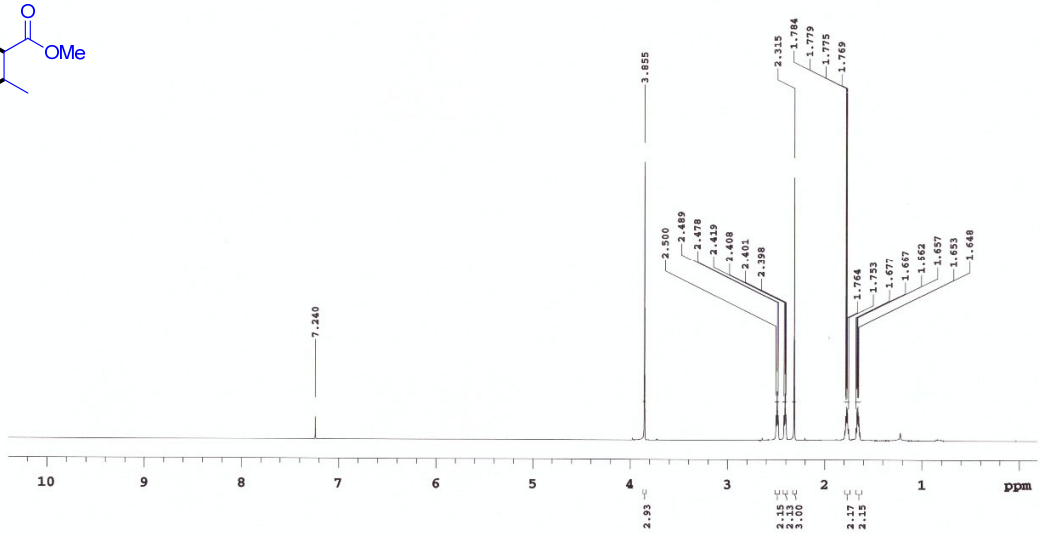
Compound-**9p**

^{13}C-NMR/DMSO-d_6



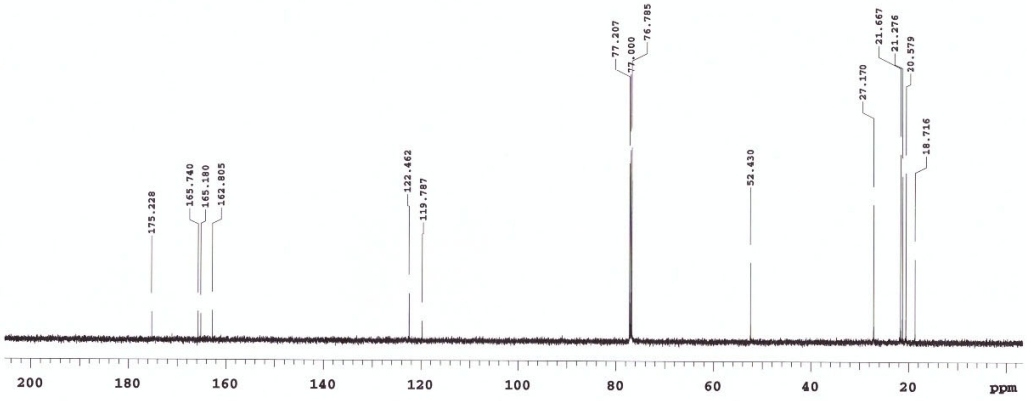
Compound-**11**

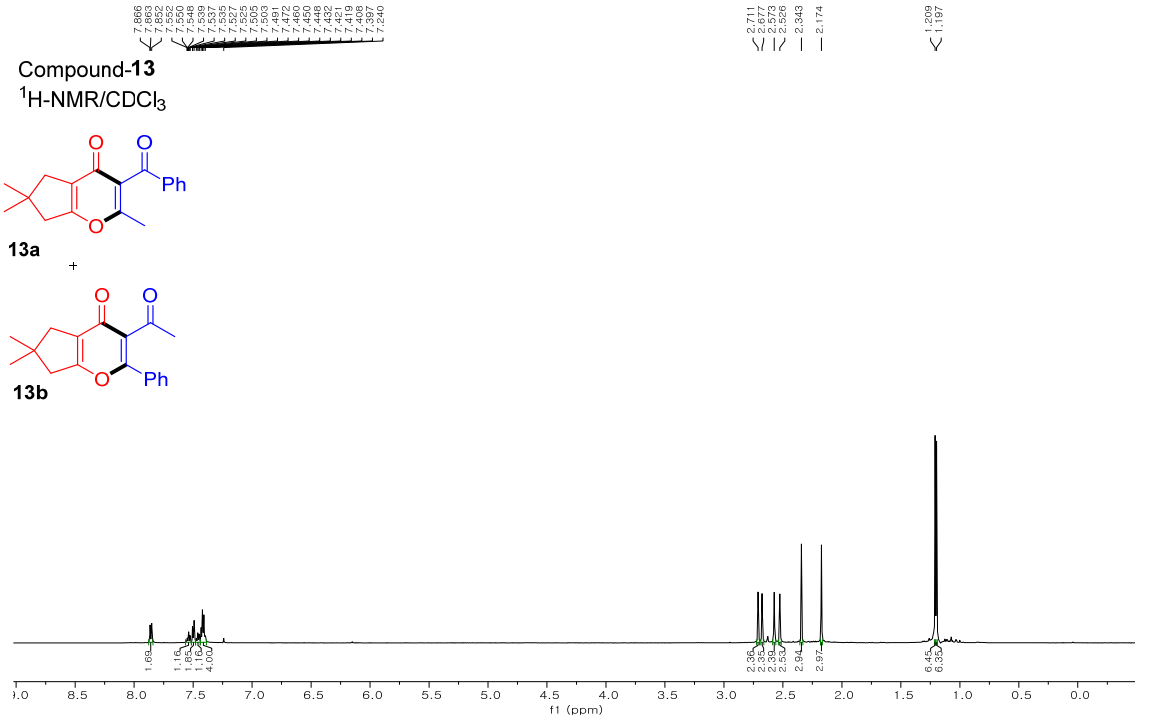
^{1}H-NMR/$CDCl_3$

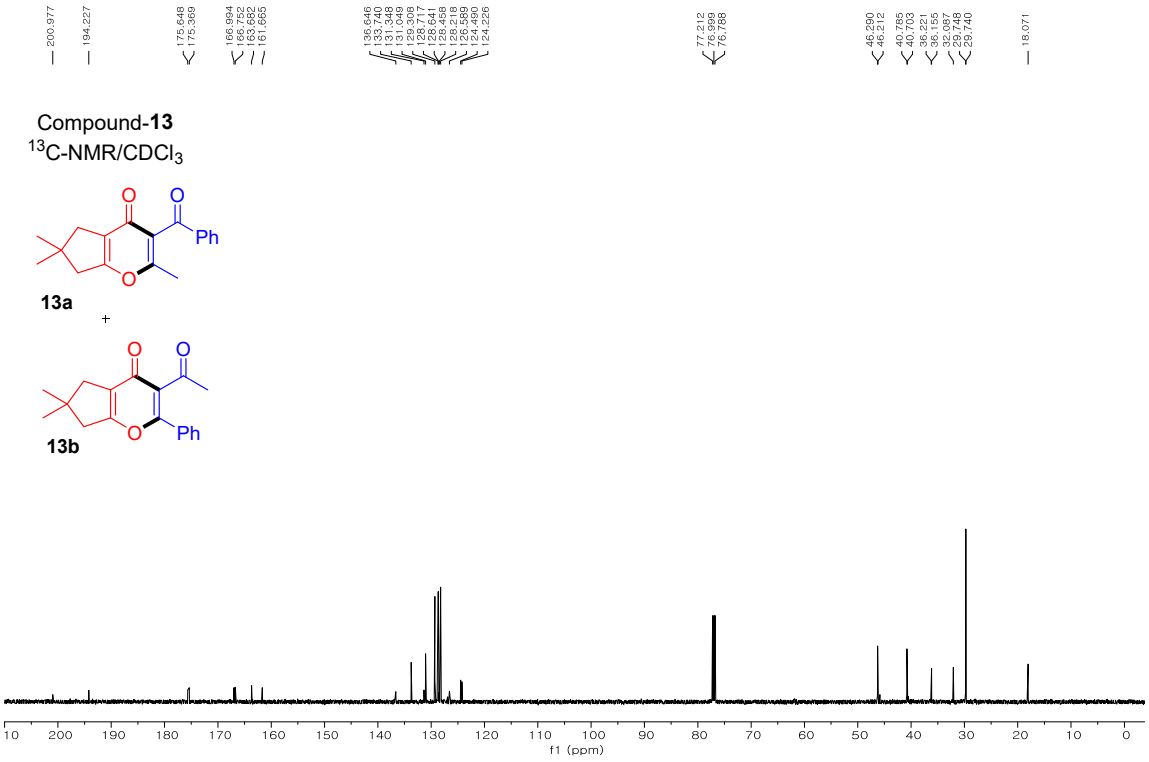


Compound-**11**

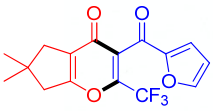
^{13}C-NMR/$CDCl_3$

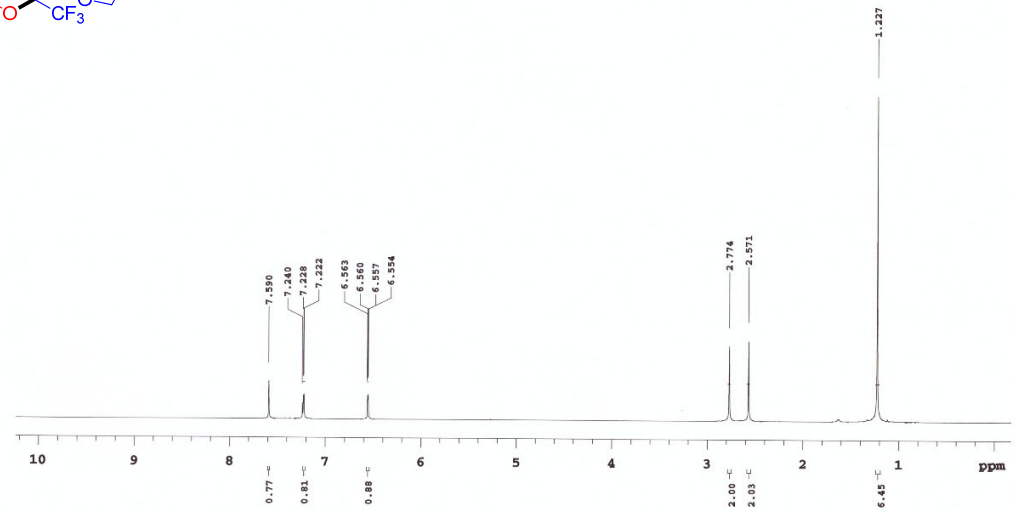



Compound-13
1H-NMR/CDCl3
13a
+
13b
f1 (ppm)

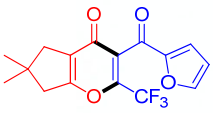

Compound-13
13C-NMR/CDCl3
13a
+
13b
f1 (ppm)

Compound-**15a**
^{1}H-NMR/$CDCl_3$



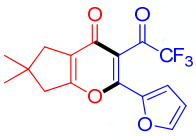


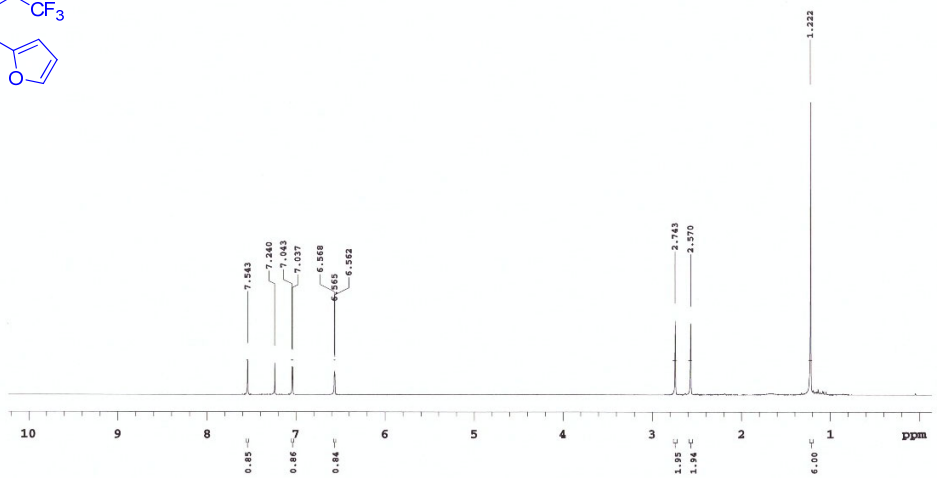
Compound-**15a**
^{13}C-NMR/$CDCl_3$



Compound-**15b**

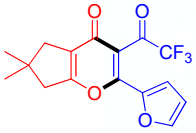
^{1}H-NMR/$CDCl_3$

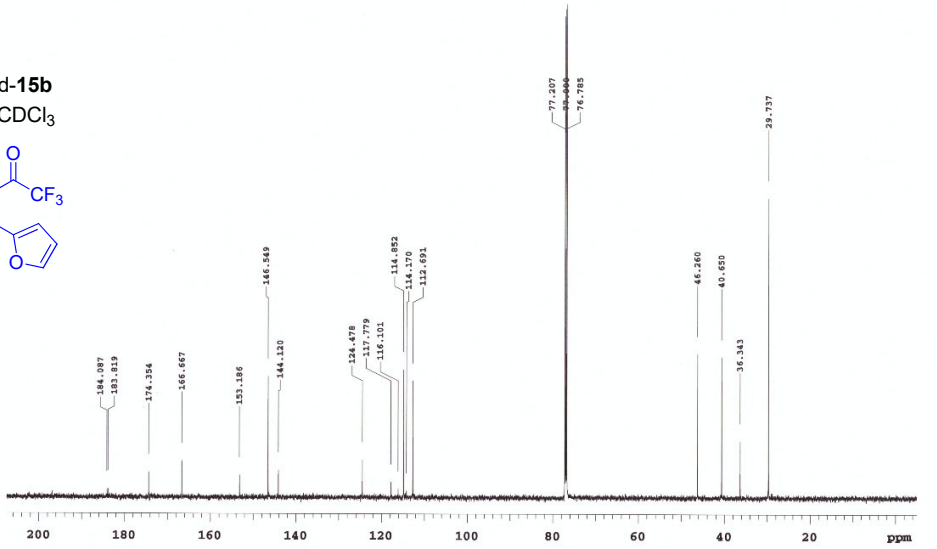




Compound-**15b**

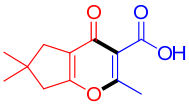
^{13}C-NMR/$CDCl_3$

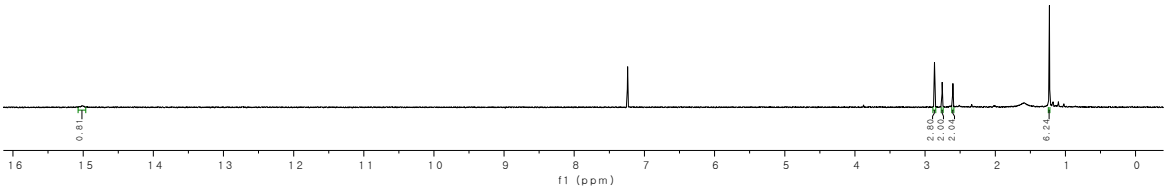




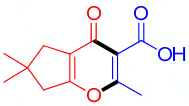
SM-619A-H
STANDARD 1H OBSERVE - profile

Compound-**20**
^{1}H-NMR/CDCl$_3$

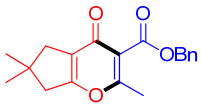




Compound-**20**
^{13}C-NMR/CDCl$_3$



Compound-**22**
^{1}H-NMR/CDCl$_3$



Compound-**22**
^{13}C-NMR/CDCl$_3$