Electronic Supplementary Material (ESI) for Green Chemistry

GAP chemistry for pyrrolyl coumarin derivatives: highly efficient one-pot synthesis under catalyst-free conditions

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General Experimental Methods

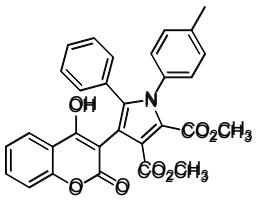
Melting points are uncorrected. IR spectra were recorded on Varian F-1000 spectrometer in KBr with absorptions in cm^{-1}. ^{1}H NMR and ^{13}C NMR were determined on Varian Invoa-400 MHz or Invoa-300 MHz spectrometer in DMSO-d_6 solution. *J* values are in Hz. Chemical shifts are expressed in ppm downfield from internal standard TMS. HRMS analyses were carried out using TOF-MS or GCT-TOF instrument.

General procedure for the synthesis of pyrrolyl coumarin derivatives 5 or **7**

A dry 25 mL flask was charged with 1,3-dicarbonyl compounds **1** or **6** (1 mmol), arylglyoxal monohydrate **2** (1 mmol), dialkyl but-2-ynedioate **3** (1 mmol), amines **4** (1 mmol) and ethanol (5 mL). The mixture was stirred at refluxing temperature for 0.7-4.5 h. After completion of the reaction (confirmed by TLC), the reaction mixture was cooled to room temperature. The crystalline solids were collected and washed with little cold ethanol to give the pure products **5** or **7**.

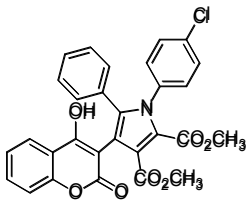
Characterizations for compounds 5 and 7

dimethyl 4-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)-5-phenyl-1-(*p*-tolyl)-1*H*-pyrrole-2,3-dicarboxylate (5a). The reaction of 4-hydroxycoumarin **1** (16.2 mg, 1 mmol), phenylflyoxal monohydrate **2a** (15.2 mg, 1 mmol), dimethyl but-2-ynedioate **3a** (14.2 mg, 1 mmol) and p-toluidine **4a** (10.7 mg, 1 mmol) in ethanol (5 mL), at 80 °C 1 h, afforded 46.3 mg (91 %) of **5a**.



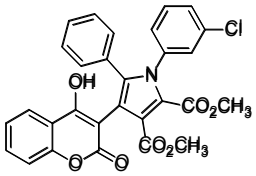
white powder; m.p.: 146-148°C; IR (KBr, *v*, cm^{-1}): 3420, 3061, 3002, 2948, 1717, 1576, 1514, 1488, 1444, 1301, 1269, 1210, 1121, 1078, 1043, 1014, 982, 924, 897, 841, 760, 699, 650; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.3 (s, 1H, OH), 7.74 (d, *J* = 7.6 Hz, 1H, ArH), 7.55 (t, *J* = 7.6 Hz, 1H, ArH), 7.31-7.24 (m, 2H, ArH), 7.11-6.99 (m, 9H, ArH), 3.61 (s, 3H, OCH_3), 3.58 (s, 3H, OCH_3), 2.22 (s, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 164.18, 162.42, 162.13, 162.07, 152.91, 138.50, 137.65, 135.07, 132.82, 130.49, 130.28, 129.82, 128.79, 128.54, 128.34, 127.97, 124.48, 124.09, 118.16, 116.63, 116.30, 113.00, 98.81, 52.90, 52.03, 21.10; HRMS (ESI) calcd for $C_{30}H_{23}NO_7$ $[M]^+$: 509.1475, found: 509.1436.

dimethyl 1-(4-chlorophenyl)-4-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)-5-phenyl-1*H*-pyrrole-2,3-dicarboxylate (5b). The reaction of 4-hydroxycoumarin **1** (16.2 mg, 1 mmol), phenylflyoxal monohydrate **2a** (15.2 mg, 1 mmol), dimethyl but-2-ynedioate **3a** (14.2 mg, 1 mmol) and 4-chloroaniline **4b** (12.7 mg, 1 mmol) in ethanol (5 mL), at 80 °C 1.5 h, afforded 48.7 mg (92 %) of **5b**.



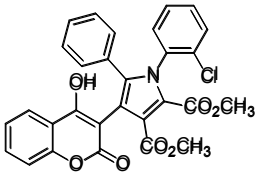
white powder; m.p.: 228-230°C; IR (KBr, *v*, cm^{-1}): 3420, 3062, 2950, 1714, 1675, 1577, 1495, 1417, 1274, 1216, 1151, 1124, 1078, 1016, 986, 924, 899, 857, 759, 700, 649; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.3 (s, 1H, OH), 7.76 (d, *J* = 7.2 Hz, 1H, ArH), 7.54 (t, *J* = 7.2 Hz, 1H, ArH), 7.41-7.04 (m, 11H, ArH), 3.64 (s, 3H, OCH_3), 3.61 (s, 3H, OCH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 164.27, 162.26, 161.64, 152.91, 138.08, 136.61, 133.63, 132.84, 130.30, 130.17, 130.09, 129.37, 129.16, 128.73, 128.45, 127.74, 124.46, 124.09, 119.60, 116.62, 116.22, 113.34, 98.34, 52.90, 52.15; HRMS (ESI) calcd for $C_{29}H_{20}{}^{35}ClNO_7$ $[M]^+$: 529.0928, found: 529.0937.

dimethyl 1-(3-chlorophenyl)-4-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)-5-phenyl-1*H*-pyrrole-2,



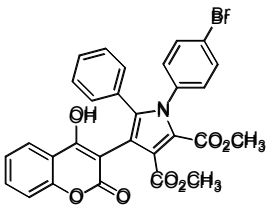
3-dicarboxylate (5c). The reaction of 4-hydroxycoumarin **1** (16.2 mg, 1 mmol), phenylflyoxal monohydrate **2a** (15.2 mg, 1 mmol), dimethyl but-2-ynedioate **3a** (14.2 mg, 1 mmol) and 3-chloroaniline **4c** (12.7 mg, 1 mmol) in ethanol (5 mL), at 80 °C 1.5 h, afforded 46.0 mg (87 %) of **5c**. white powder; m.p.: 242-246°C; IR (KBr, *v*, cm^{-1}): 3423, 3075, 3002, 2951, 2853, 1720, 1683, 1577, 1483, 1444, 1303, 1271, 1213, 1126, 1077, 1043, 1013, 988, 924, 880, 761, 698, 649; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.29 (s, 1H, OH), 7.76 (d, J = 7.6 Hz, 1H, ArH), 7.55 (t, J = 8.0 Hz, 1H, ArH), 7.40-7.18 (m, 6H, ArH), 7.10-7.02 (m, 5H, ArH), 3.63 (s, 3H, OCH_3), 3.60 (s, 3H, OCH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 164.28, 162.30, 162.20, 161.52, 152.91, 139.00, 138.22, 133.24, 132.88, 130.87, 130.27, 129.99, 129.21, 128.80, 128.44, 128.35, 127.59, 127.38, 124.48, 124.09, 119.89, 116.64, 116.16, 113.35, 98.28, 52.89, 52.18; HRMS (ESI) calcd for$C_{29}H_{20}{}^{35}ClNO_7$ $[M]^+$: 529.0928, found: 529.0933.

dimethyl 1-(2-chlorophenyl)-4-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)-5-phenyl-1*H*-pyrrole-2,



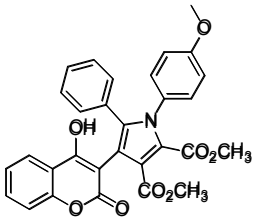
3-dicarboxylate (5d). The reaction of 4-hydroxycoumarin **1a** (16.2 mg, 1 mmol), phenylflyoxal monohydrate **2a** (15.2 mg, 1 mmol), dimethyl but-2-ynedioate **3a** (14.2 mg, 1 mmol) and 2-chloroaniline **4d** (12.7 mg, 1 mmol) in ethanol (5 mL), at 80 °C 4.5 h, afforded 39.7 mg (75 %) of **5d**. red powder; m.p.: 124-125°C; IR (KBr, *v*, cm^{-1}): 3426, 3002, 2981, 1712, 1577, 1486, 1444, 1214, 1127, 1043, 1013, 924, 759, 649; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.33 (s, 1H, OH), 7.95-7.08 (m, 13H, ArH), 3.63 (s, 3H, OCH_3), 3.60 (s, 3H, OCH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 164.66, 162.30, 162.10, 160.76, 152.90, 138.86, 135.66, 132.85, 132.25, 131.39, 131.30, 131.12, 129.96, 128.84, 128.23, 127.98, 125.80, 124.44, 124.07, 121.41, 116.70, 116.62, 116.14, 113.31, 98.17, 52.57, 52.20; HRMS (ESI) calcd for$C_{29}H_{20}{}^{35}ClNO_7$ $[M]^+$: 529.0928, found: 529.0901.

dimethyl 1-(4-bromophenyl)-4-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)-5-phenyl-1*H*-pyrrole-2,

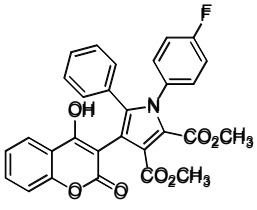


3-dicarboxylate (5e) The reaction of 4-hydroxycoumarin **1a** (16.2 mg, 1 mmol), phenylflyoxal monohydrate **2a** (15.2 mg, 1 mmol), dimethyl but-2-ynedioate **3a** (14.2 mg, 1 mmol) and 4-bromoaniline **4e** (17.1 mg, 1 mmol) in ethanol (5 mL), at 80 °C 1.5 h, afforded 53.4 mg (93 %) of **5e**. white powder; m.p.: 142-144°C; IR (KBr, *v*, cm^{-1}): 3421, 3001, 2950, 1714, 1578, 1521, 1491,

1444, 1271, 1215, 1151, 1122, 1077, 1043, 1013, 982, 924, 897, 847, 758, 711, 698, 649; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.26 (s, 1H, OH), 7.77 (d, J = 7.6 Hz, 1H, ArH), 7.52 (t, J = 7.2 Hz, 3H, ArH), 7.29 (d, J = 8.0 Hz, 1H, ArH), 7.23 (t, J = 7.6 Hz, 1H, ArH), 7.17-7.07 (m, 7H, ArH), 3.64 (s, 3H, OCH_3), 3.61 (s, 3H, OCH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 164.34, 162.36, 161.71, 152.97, 138.11, 137.09, 132.89, 132.37, 130.78, 130.50, 130.37, 130.14, 128.79, 128.51, 127.77, 124.51, 124.14, 122.26, 119.70, 116.66, 116.26, 113.42, 98.42, 52.95, 52.20; HRMS (ESI) calcd for$C_{29}H_{20}{}^{79}BrNO_7$ $[M]^+$: 573.0423, found: 573.0427.



dimethyl 4-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)-1-(4-methoxyphenyl)-5-phenyl-1*H*-pyrrole-2, 3-dicarboxylate (5f). The reaction of 4-hydroxycoumarin **1a** (16.2 mg, 1 mmol), phenylflyoxal monohydrate **2a** (15.2 mg, 1 mmol), dimethyl but-2-ynedioate **3a** (14.2 mg, 1 mmol) and 4-methoxyaniline **4f** (12.3 mg, 1 mmol) in ethanol (5 mL), at 80 °C 1 h, afforded 45.2 mg (86 %) of **5f**. white powder; m.p.: 129-132°C; IR (KBr, v, cm^{-1}): 3425, 3002, 2936, 1715, 1577, 1513, 1444, 1300, 1251, 1212, 1177, 1122, 1079, 1043, 1013, 924, 845, 761, 699, 649; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.28 (s, 1H, OH), 7.76-6.86 (m, 13H, ArH), 3.67-3.60 (m, 9H, 3×OCH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 164.18, 162.37, 162.09, 162.01, 159.33, 152.88, 137.85, 132.76, 130.49, 130.27, 130.01, 129.48, 128.88, 128.48, 128.32, 124.44, 124.07, 118.03, 116.61, 116.27, 114.32, 112.79, 98.80, 55.70, 52.88, 52.01; HRMS (ESI) calcd for$C_{30}H_{23}NO_8$ $[M]^+$: 525.1424, found: 525.1418.



dimethyl 1-(4-fluorophenyl)-4-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)-5-phenyl-1*H*-pyrrole-2, 3-dicarboxylate (5g). The reaction of 4-hydroxycoumarin **1a** (16.2 mg, 1 mmol), phenylflyoxal monohydrate **2a** (15.2 mg, 1 mmol), dimethyl but-2-ynedioate **3a** (14.2 mg, 1 mmol) and 4-fluoroaniline **4g** (11.1 mg, 1 mmol) in ethanol (5 mL), at 80 °C 2 h, afforded 41.1 mg (80 %) of **5g**. white powder; m.p.: 244-245°C; IR (KBr, v, cm^{-1}): 3419, 3121, 3000, 2951, 1715, 1675, 1577, 1511, 1444, 1274, 1216, 1152, 1124, 1078, 1015, 987, 924, 899, 857, 815, 759, 700, 650; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.32 (s, 1H, OH), 7.77 (d, J = 7.2 Hz, 1H, ArH), 7.54 (t, J = 7.2 Hz, 1H,

ArH), 7.31-7.05 (m, 11H, ArH), 3.63 (s, 3H, OCH_3), 3.61 (s, 3H, OCH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 164.35, 163.63, 162.36, 162.24, 161.76, 160.36, 152.96, 138.24, 134.07, 132.82, 130.67, 130.55, 130.36, 130.25, 128.68, 128.41, 128.08, 124.46, 124.11, 119.33, 116.63, 116.35, 116.26, 116.05, 113.18, 98.53, 52.85, 52.12; HRMS (ESI) calcd for$C_{29}H_{20}FNO_7$ $[M]^+$: 513.1224, found: 513.1235.

dimethyl 1-(3,5-dimethylphenyl)-4-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)-5-phenyl-1*H*-pyrrole -2,3-dicarboxylate (5h). The reaction of 4-hydroxycoumarin **1a** (16.2 mg, 1 mmol), phenylflyoxal monohydrate **2a** (15.2 mg, 1 mmol), dimethyl but-2-ynedioate **3a** (14.2 mg, 1 mmol) and 3,4-dimethyl-aniline **4h** (12.1 mg, 1 mmol) in ethanol (5 mL), at 80 °C 1 h, afforded 44.0 mg (84 %) of **5h**. white powder; m.p.: 253-255°C; IR (KBr, *v*, cm^{-1}): 3426, 3072, 3001, 2981, 1715, 1685, 11577, 1490, 1444, 1307, 1210, 1177, 1120, 1084, 1043, 1012, 924, 763, 699, 649; ^1H NMR (DMSO-d_6, 400 MHz): δ 11.29 (s, 1H, OH), 7.77 (d, *J* = 6.4 Hz, 1H, ArH), 7.52 (t, *J* = 6.0 Hz, 1H, ArH), 7.30 (d, *J* = 7.6 Hz, 1H, ArH), 7.25 (t, *J* = 6.4 Hz, 1H, ArH), 7.08-7,06 (m, 5H, ArH), 6.89 (s, 1H, ArH), 6.80 (s, 2H, ArH), 3.63 (s, 3H, OCH_3), 3.59 (s, 3H, OCH_3), 2.12 (s, 6H, 2×CH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 164.21, 162.48, 162.24, 162.08, 152.97, 138.46, 137.52, 132.78, 130.56, 130.50, 130.27, 128.99, 128.92, 128.52, 128.30, 125.75, 124.46, 124.13, 118.06, 116.65, 116.36, 113.05, 98.93, 52.89, 52.02, 21.13; HRMS (ESI) calcd for$C_{31}H_{25}NO_7$ $[M]^+$: 523.1631, found: 523.1643.

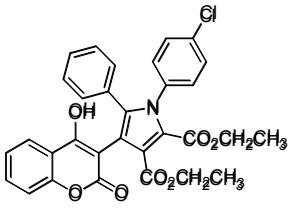
dimethyl 4-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)-1-(4-nitrophenyl)-5-phenyl-1*H*-pyrrole-2, 3-dicarboxylate (5i). The reaction of 4-hydroxycoumarin **1a** (16.2 mg, 1 mmol), phenylflyoxal monohydrate **2a** (15.2 mg, 1 mmol), dimethyl but-2-ynedioate **3a** (14.2 mg, 1 mmol) and 4-nitroaniline **4i** (13.8 mg, 1 mmol) in ethanol (5 mL), at 80 °C 3.5 h, afforded 41.6 mg (77 %) of **5i**. light yellow powder; m.p.: 185-187°C; IR (KBr, *v*, cm^{-1}): 3358, 3070, 3002, 2936, 1697, 1577, 1495, 1447, 1300, 1221, 1169, 1135, 1111, 1042, 1013, 985, 944, 925, 902, 841, 813, 753, 727, 690, 650; ^1H NMR (DMSO-d_6, 400 MHz): δ 11.45 (s, 1H, OH), 8.20 (s, 2H, ArH), 7.78 - 7.04 (m, 11H, ArH), 3.63 (s, 6H, 2×OCH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 164.30, 162.48,

162.21, 161.30, 152.92, 147.34, 143.38, 138.27, 132.95, 130.31, 129.87, 129.74, 128.94, 128.60, 126.97, 124.68, 124.52, 124.16, 120.94, 116.66, 116.19, 113.98, 97.93, 52.98, 52.30; HRMS (ESI) calcd for$C_{29}H_{20}N_2O_9$ $[M]^+$: 540.1169, found: 540.1158.

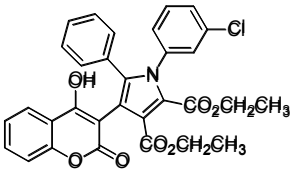
dimethyl 1-butyl-4-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)-5-phenyl-1*H*-pyrrole-2, 3-dicarboxylate (5j). The reaction of 4-hydroxycoumarin **1a** (16.2 mg, 1 mmol), phenylflyoxal monohydrate **2a** (15.2 mg, 1 mmol), dimethyl but-2-ynedioate **3a** (14.2 mg, 1 mmol) and butylamine **4j** (7.3 mg, 1 mmol) in ethanol (5 mL), at 80 °C 0.7 h, afforded 36.1 mg (76 %) of **5j**. white powder; m.p.: 207-208°C; IR (KBr, *v*, cm^{-1}): 3427, 3051, 2966, 2879, 1735, 1704, 1673, 1577, 1484, 1447, 1318, 1295, 1223, 1204, 1116, 1142, 1096, 1014, 956, 924, 884, 841, 803, 765, 728, 703, 649; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.25 (s, 1H, OH), 7.72 (d, J = 7.2 Hz, 1H, ArH), 7.48 (t, J = 7.2 Hz, 1H, ArH), 7.32-7.18 (m, 7H, ArH), 4.05-3.95 (m, 2H, CH_2), 3.82 (s, 3H, OCH_3), 3.58 (s, 3H, OCH_3), 1.50-1.40 (m, 2H, CH_2), 1.14-1.00 (m, 2H, CH_2), 0.61 (t, J = 6.8 Hz, 1H, CH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 164.89, 162.36, 162.26, 162.06, 152.88, 138.38, 132.66, 130.78, 130.44, 129.27, 128.86, 124.45, 124.34, 124.04, 120.69, 116.54, 116.31, 112.95, 98.63, 52.74, 51.98, 45.72, 33.26, 19.56, 13.66; HRMS (ESI) calcd for$C_{27}H_{25}NO_7$ $[M]^+$: 475.1631, found: 475.1639.

diethyl 4-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)-5-phenyl-1-(*p*-tolyl)-1*H*-pyrrole-2, 3-dicarboxylate (5k). The reaction of 4-hydroxycoumarin **1a** (16.2 mg, 1 mmol), phenylflyoxal monohydrate **2a** (15.2 mg, 1 mmol), diethyl but-2-ynedioate **3b** (17.0 mg, 1 mmol) and p-toluidine **4a** (10.7 mg, 1 mmol) in ethanol (5 mL), at 80 °C 1.5 h, afforded 44.1 mg (82 %) of **5k**. white powder; m.p.: 221-223°C; 3425, 3061, 2981, 2935, 1712, 1683, 1575, 1515, 1488, 1420, 1031, 1269, 1201, 1122, 1077, 1044, 1014, 969, 924, 898, 835, 761, 698, 649; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.29 (s, 1H, OH), 7.76 (d, J = 5.6 Hz, 1H, ArH), 7.53 (t, J = 7.2 Hz, 1H, ArH), 7.31-7.23 (m, 2H, ArH), 7.10-7.03 (m, 9H, ArH), 4.04-4.03 (m, 4H, 2×CH_2), 2.20 (s, 3H, CH_3), 1.02-0.98 (m, 6H, 2×CH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 163.52, 162.44, 162.01, 161.61, 152.89, 138.45, 137.31, 135.16, 132.72, 130.57, 130.29, 129.74, 129.28, 128.44, 128.31, 128.02, 124.41, 124.03, 117.91, 116.55, 116.32, 112.88, 99.06, 61.62, 60.21, 21.07, 14.25,

14.05; HRMS (ESI) calcd for$C_{32}H_{26}NO_7$ $[M-H]^+$: 536.1709, found: 536.1694.

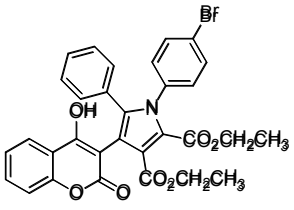


diethyl 1-(4-chlorophenyl)-4-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)-5-phenyl-1*H*-pyrrole-2, 3-dicarboxylate (5l). The reaction of 4-hydroxycoumarin **1a** (16.2 mg, 1 mmol), phenylflyoxal monohydrate **2a** (15.2 mg, 1 mmol), diethyl acetylenedicarboxylate **3b** (17.0 mg, 1 mmol) and 4-chloroaniline **4b** (12.7 mg, 1 mmol) in ethanol (5 mL), at 80 °C 2 h, afforded 47.4 mg (85 %) of **5l**. white powder; m.p.: 227-228°C; IR (KBr, *v*, cm^{-1}): 3412, 3071, 2981, 2902, 1715, 1683, 1522, 1495, 1444, 1420, 1334, 1303, 1265, 1201, 1172, 1123, 1078, 1014, 971, 924, 898, 862, 840, 762, 718, 699, 649; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.31 (s, 1H, OH), 7.77 (d, *J* = 7.6 Hz, 1H, ArH), 7.55 (t, *J* = 7.6 Hz, 1H, ArH), 7.41 (d, *J* = 8.0 Hz, 2H, ArH), 7.32-7.23 (m, 4H, ArH), 7.12-7.05 (m, 5H, ArH), 4.10-4.02 (m, 4H, 2×CH_2), 1.06-0.97 (m, 6H, 2×CH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 163.58, 162.29, 162.19, 161.11, 152.89, 137.75, 136.70, 133.61, 132.80, 130.30, 130.23, 130.16, 129.33, 128.68, 128.43, 128.24, 124.44, 124.04, 119.36, 116.57, 116.22, 113.21, 98.62, 61.64, 60.38, 14.23, 14.05; HRMS (ESI) calcd for$C_{31}H_{24}{}^{35}ClNO_7$ $[M]^+$: 557.1241, found: 557.1209.

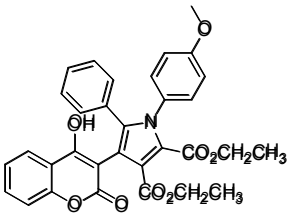


diethyl 1-(3-chlorophenyl)-4-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)-5-phenyl-1*H*-pyrrole-2, 3-dicarboxylate (5m). The reaction of 4-hydroxycoumarin **1a** (16.2 mg, 1 mmol), phenylflyoxal monohydrate **2a** (15.2 mg, 1 mmol), diethyl but-2-ynedioate **3b** (17.0 mg, 1 mmol) and 3-chloroaniline **4c** (12.7 mg, 1 mmol) in ethanol (5 mL), at 80 °C 3 h, afforded 48.0 mg (86 %) of **5m**. white powder; m.p.: 164-165°C; IR (KBr, *v*, cm^{-1}): 3420, 3072, 2979, 2871, 1719, 1682, 1522, 1485, 1421, 1334, 1303, 1264, 1203, 1129, 1078, 1044, 1013, 978, 924, 861, 787, 701, 680, 649; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.27 (s, 1H, OH), 7.78 (d, *J* = 7.6 Hz, 1H, ArH), 7.56 (d, *J* = 7.2 Hz, 1H, ArH), 7.42-7.25 (m, 5H, ArH), 7.20 (d, *J* = 6.8 Hz, 1H, ArH), 7.12-7.05 (m, 5H, ArH), 4.09-4.04 (m, 4H, 2×CH_2), 1.05-0.98 (m, 6H, 2×CH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 163.53, 162.31, 162.23, 161.02, 152.89, 139.06, 137.78, 133.23, 132.85, 130.88, 130.27, 130.04, 129.17, 128.73, 128.44, 128.37, 128.23, 127.40, 124.46, 124.04, 119.49,

116.58, 116.17, 113.22, 98.53, 61.63, 60.40, 14.21, 14.04; HRMS (ESI) calcd for$C_{31}H_{24}{}^{35}ClNO_7$ $[M]^+$: 557.1241, found: 557.1244.

diethyl 1-(4-bromophenyl)-4-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)-5-phenyl-1*H*-pyrrole-2, 3-dicarboxylate (5n). 

The reaction of 4-hydroxycoumarin **1a** (16.2 mg, 1 mmol), phenylflyoxal monohydrate **2a** (15.2 mg, 1 mmol), diethyl but-2-ynedioate **3b** (17.0 mg, 1 mmol) and 4-bromoaniline **4e** (17.1 mg, 1 mmol) in ethanol (5 mL), at 80 °C 3 h, afforded 51.2 mg (85 %) of **5n**. white powder; m.p.: 238-239°C; IR (KBr, *v*, cm^{-1}): 3419, 3065, 2980, 1712, 1577, 1491, 1419, 1341, 1302, 1268, 1203, 1122, 1071, 1012, 967, 924, 898, 840, 760, 699, 649; ^1H NMR (DMSO-d_6, 400 MHz): δ 11.32 (s, 1H, OH), 7.77 (d, J = 7.6 Hz, 1H, ArH), 7.54 (t, J = 7.2 Hz, 3H, ArH), 7.30 (d, J = 8.4 Hz, 1H, ArH), 7.25 (t, J = 7.6 Hz, 1H, ArH), 7.17 (d, J = 8.0 Hz, 2H, ArH), 7.11-7.05 (m, 5H, ArH), 4.11-4.02 (m, 4H, 2×CH_2), 1.06-0.97 (m, 6H, 2×CH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 163.59, 162.30, 162.21, 161.12, 152.90, 137.71, 137.14, 132.81, 132.30, 130.50, 130.31, 130.15, 128.69, 128.45, 128.19, 124.44, 124.05, 122.15, 119.40, 116.57, 116.22, 113.24, 98.61, 61.66, 60.40, 14.24, 14.06; HRMS (ESI) calcd for$C_{31}H_{24}{}^{79}BrNO_7$ $[M]^+$: 601.0736, found: 601.0720.

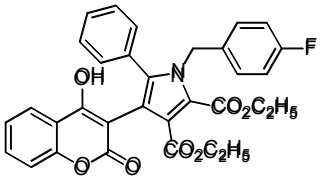
diethyl 4-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)-1-(4-methoxyphenyl)-5-phenyl-1*H*-pyrrole-2, 3-dicarboxylate (5o). 

The reaction of 4-hydroxycoumarin **1a** (16.2 mg, 1 mmol), phenylflyoxal monohydrate **2a** (15.2 mg, 1 mmol), diethyl but-2-ynedioate **3b** (17.0 mg, 1 mmol) and 4-methoxyaniline **4f** (12.3 mg, 1 mmol) in ethanol (5 mL), at 80 °C 1.5 h, afforded 44.3 mg (80 %) of **5o**. white powder; m.p.: 218-220°C; IR (KBr, *v*, cm^{-1}): 3410, 3062, 2980, 2898, 1710, 1681, 1575, 1513, 1488, 1444, 1371, 1302, 1249, 1122, 1106, 1079, 1030, 972, 924, 898, 934, 801, 788, 725, 697, 650; ^1H NMR (DMSO-d_6, 400 MHz): δ 11.30 (s, 1H, OH), 7.78-6.87 (m, 13H, ArH), 4.05-3.65 (m, 7H, 1×CH_3+2×CH_2), 1.01-0.98 (m, 6H, 2×CH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 163.64, 162.55, 162.09, 161.68, 159.44, 152.96, 137.62, 132.76, 130.66, 130.41, 130.38, 129.63, 129.51, 128.49, 128.36, 124.46, 124.09, 117.88, 116.60, 116.37, 114.33, 112.77, 99.17, 61.66, 60.27, 55.74, 14.29, 14.13; HRMS (ESI) calcd

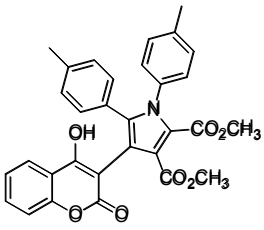
for$C_{32}H_{27}NO_8$ $[M]^+$: 553.1737, found: 553.1745.

diethyl 1-(3-chloro-4-methylphenyl)-4-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)-5-phenyl-1*H*-pyrrole-2,3-dicarboxylate (5p). The reaction of 4-hydroxycoumarin **1a** (16.2 mg, 1 mmol), phenylflyoxal monohydrate **2a** (15.2 mg, 1 mmol), diethyl but-2-ynedioate **3b** (17.0 mg, 1 mmol) and 3-chloro-4-methylaniline **4k** (14.1 mg, 1 mmol) in ethanol (5 mL), at 80 °C 1.5 h, afforded 50.9 mg (89 %) of **5p**. white powder; m.p.: 247-248°C; IR (KBr, *v*, cm^{-1}): 3422, 3082, 2982, 1725, 1681, 1576, 1498, 1424, 1344, 1265, 1201, 1174, 1125, 1086, 1014, 979, 924, 827, 787, 763, 698, 649; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.27 (s, 1H, OH), 7.78 (d, J = 8.0 Hz, 1H, ArH), 7.54 (t, J = 7.6 Hz, 1H, ArH), 7.31-7.24 (m, 4H, ArH), 7.11-7.07 (m, 6H, ArH), 4.12-4.02 (m, 4H, 2×CH_2), 2.23 (s, 3H, CH_3), 1.05 (t, J = 7.2 Hz, 3H, CH_3), 0.99 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 163.52, 162.33, 162.24, 161.19, 152.90, 137.74, 136.62, 136.56, 133.24, 132.79, 131.63, 130.38, 130.29, 130.16, 128.70, 128.52, 128.43, 127.23, 124.43, 124.04, 119.10, 116.56, 116.20, 113.13, 98.65, 61.65, 60.36, 19.66, 14.22, 14.07; HRMS (ESI) calcd for$C_{32}H_{26}{}^{35}ClNO_7$ $[M]^+$: 571.1398, found: 571.1378.

diethyl 1-(3,5-dimethylphenyl)-4-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)-5-phenyl-1*H*-pyrrole-2,3-dicarboxylate (5q). The reaction of 4-hydroxycoumarin **1a** (16.2 mg, 1 mmol), phenylflyoxal monohydrate **2a** (15.2 mg, 1 mmol), diethyl but-2-ynedioate **3b** (17.0 mg, 1 mmol) and 3,4-dimethylaniline **4h** (12.1 mg, 1 mmol) in ethanol (5 mL), at 80 °C 1.5 h, afforded 44.1 mg (80 %) of **5q**. white powder; m.p.: 226-228°C; IR (KBr, *v*, cm^{-1}): 3423, 3077, 2981, 1724, 1683, 1577, 1488, 1445, 1305, 1262, 1203, 1169, 1122, 1090, 1014, 923, 899, 859, 703, 649; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.25 (s, 1H, OH), 7.77 (d, J = 6.8 Hz, 1H, ArH), 7.55 (t, J = 6.8 Hz, 1H, ArH), 7.32-6.80 (m, 10H, ArH), 4.08-4.03 (m, 4H, 2×CH_2), 2.14 (s, 6H, 2×CH_3), 1.04-0.98 (m, 6H, 2×CH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 163.42, 162.43, 161.93, 161.69, 152.88, 138.38, 137.51, 136.94, 132.71, 130.55, 130.36, 130.20, 129.52, 128.41, 128.26, 125.73, 124.40, 124.03, 117.50, 116.56, 116.31, 112.83, 99.13, 61.58, 60.15, 21.10, 14.23, 14.05; HRMS (ESI) calcd for$C_{33}H_{29}NO_7$ $[M]^+$: 551.1944, found: 551.1947.

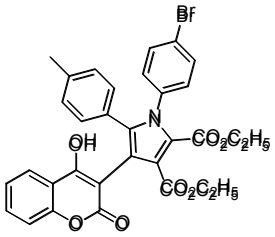
diethyl 1-(4-fluorobenzyl)-4-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)-5-phenyl-1*H*-pyrrole-2,3-dicarboxylate (5r). 

The reaction of 4-hydroxycoumarin **1a** (16.2 mg, 1 mmol), phenylflyoxal monohydrate **2a** (15.2 mg, 1 mmol), diethyl acetylenedicarboxylate **3b** (17.0 mg, 1 mmol) and phenylmethanamine **4l** (10.7 mg, 1 mmol) in ethanol (5 mL), at 80 °C 0.5 h, afforded 48.9 mg (88 %) of **5r**. light red powder; m.p.: 103-105°C; IR (KBr, *v*, cm^{-1}): 3423, 3067, 2975, 2885, 1727, 1614, 1552, 1509, 1416, 1443, 1271, 1158, 1088, 1044, 1013, 897, 836, 755, 649; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.42 (s, 1H, OH), 7.77 (d, *J* = 7.6 Hz, 1H, ArH), 7.50 (t, *J* = 7.6 Hz, 1H, ArH), 7.27-7.20 (m, 7H, ArH), 7.11-7.04 (m, 4H, ArH), 5.28 (q, *J* = 16.3 Hz, 2H, CH_2), 4.11-4.00 (m, 4H, 2×CH_2), 1.08-0.96 (m, 6H, 2×CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 163,96, 163.04, 162.37, 162.07, 161.55, 160.63, 152.85, 138.49, 132.63, 130.40, 130.28, 129.31, 128.84, 128.78, 125.24, 124.30, 123.99, 121.07, 116.47, 116.35, 115.66, 115.45, 113.24, 98.78, 61.36, 60.28, 56.57, 48.63, 18.96, 14.19, 14.05; HRMS (ESI) calcd for$C_{32}H_{26}FNO_7$ $[M]^+$: 555.1693, found: 555.1720.

dimethyl 4-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)-1,5-di-p-tolyl-1*H*-pyrrole-2,3-dicarboxylate (5s). 

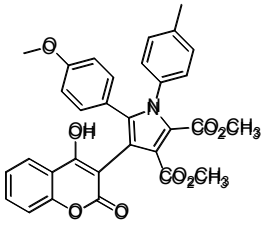
The reaction of 4-hydroxycoumarin **1a** (16.2 mg, 1 mmol), 4-methylphenylflyoxal monohydrate **2b** (16.6 mg, 1 mmol), dimethyl acetylenedicarboxylate **3a** (14.2 mg, 1 mmol) and 4-methylaniline **4a** (10.7 mg, 1 mmol) in ethanol (5 mL), at 80 °C 1.0 h, afforded 47.8 mg (91 %) of **5s**. white powder; m.p.: 242-244°C; IR (KBr, *v*, cm^{-1}): 3428, 3001, 2949, 2936, 1715, 1674, 1577, 1515, 1496, 1441, 1417, 1269, 1077, 1043, 1014, 983, 923, 759, 649; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.23 (s, 1H, OH), 7.76 (d, *J* = 7.6 Hz, 1H, ArH), 7.55 (t, *J* = 7.6 Hz, 1H, ArH), 7.32-7.24 (m, 2H, ArH), 7.13-7.04 (m, 4H, ArH), 6.91-6.86 (m, 4H, ArH), 3.62 (s, 3H, OCH_3), 3.58 (s, 3H, OCH_3), 2.23 (s, 3H, CH_3), 2.05 (s, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 164.14, 162.33, 162.09, 161.93, 152.87, 138.39, 137.81, 137.68, 135.10, 132.72, 130.08, 129.77,

128.97, 128.62, 127.95, 127.49, 124.41, 124.07, 118.08, 116.59, 116.28, 112.76, 99.86, 52.83, 51.97, 21.21, 21.09; HRMS (ESI) calcd for$C_{31}H_{25}NO_7$ $[M]^+$: 523.1631, found: 523.1648.



diethyl 1-(4-bromophenyl)-4-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)-5-(p-tolyl)-1*H*-pyrrole-2,3 –dicarboxylate (5t). The reaction of 4-hydroxycoumarin **1a** (16.2 mg, 1 mmol), 4-methylphenylflyoxal monohydrate **2b** (16.6 mg, 1 mmol), diethyl acetylenedicarboxylate **3b** (17.0 mg, 1 mmol) and 4-bromoaniline **4e** (17.1 mg, 1 mmol) in ethanol (5 mL), at 80 °C 1.5 h, afforded 57.4 mg (93 %) of **5t**. white powder; m.p.: 212-213°C; IR (KBr, *v*, cm^{-1}): 3428, 3032, 2978, 2900, 1733, 1705, 1684, 1609, 1578, 1493, 1423, 1306, 1264, 1197, 1122, 1080, 1044, 1014, 971, 923, 898, 861, 834, 799, 786, 648; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.27 (s, 1H, OH), 7.78 (d, J = 7.6 Hz, 1H, ArH), 7.56 (d, J = 7.2 Hz, 1H, ArH), 7.33-7.26 (m, 2H, ArH), 7.17 (d, J = 8.0 Hz, 2H, ArH), 6.94-6.92 (m, 4H, ArH), 4.11-4.02 (m, 4H, 2×CH_2), 2.09 (s, 3H, CH_3) 1.07-0.99 (m, 6H, 2×CH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 163.57, 162.24, 162.09, 161.08, 152.86, 138.06, 137.77, 137.19, 132.77, 132.26, 130.51, 130.11, 129.08, 128.02, 127.16, 124.42, 124.03, 122.08, 119.37, 116.55, 116.20, 113.04, 98.69, 61.58, 60.33, 21.10, 14.21, 14.03; HRMS (ESI) calcd for$C_{32}H_{26}{}^{79}BrNO_7$ $[M]^+$: 615.0893, found: 615.0900.

dimethyl 4-(4-hydroxy-2-oxo-2H-chromen-3-yl)-5-(4-methoxyphenyl)-1-(p-tolyl)-1H-pyrrole-2,3-dicarboxylate (5u). The reaction of 4-hydroxycoumarin **1a** (16.2 mg, 1 mmol), 4-methoxyphenylflyoxal monohydrate **2c** (18.2 mg, 1 mmol), dimethyl acetylenedicarboxylate **3a** (14.2 mg, 1 mmol) and 4-methylaniline **4a** (10.7 mg, 1 mmol) in ethanol (5 mL), at 80 °C 1.0 h, afforded 45.8 mg (85 %) of **5u**. white powder; m.p.: 257-258°C; IR (KBr, *v*, cm^{-1}): 3428, 3001, 2947, 1710, 1688, 1577, 1516, 1497, 1441, 1352, 1251, 1206, 1176, 1122, 1076, 1043, 923, 764, 648; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.32 (s, 1H, OH), 7.85 (d, J = 7.6 Hz, 1H, ArH), 7.65 (t, J = 7.2 Hz, 1H, ArH), 7.41-7.34 (m, 2H, ArH), 7.23-7.13 (m, 4H, ArH), 7.03 (d, J = 7.6 Hz, 2H, ArH), 7.73 (d, J = 8.0 Hz, 2H, ArH), 3.70-3.63 (m, 9H, 3×OCH_3), 2.32 (s,

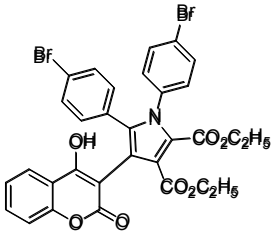


3H, CH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 164.16, 162.31, 162.06, 161.87, 159.18, 152.85, 138.32, 137.63, 132.71, 131.54, 129.73, 128.37, 127.95, 124.40, 122.47, 118.06, 116.57, 116.27, 113.75, 112.61, 99.86, 55.24, 52.79, 51.93, 21.07; HRMS (ESI) calcd for$C_{31}H_{25}NO_8$ $[M]^+$: 539.1580, found: 539.1593.

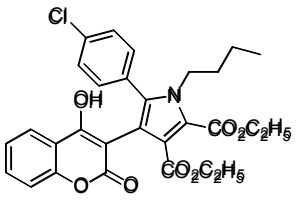
diethyl 1-(4-bromophenyl)-4-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)-5-(4-methoxyphenyl)-1*H*-pyrrole-2,3-dicarboxylate (5v). The reaction of 4-hydroxycoumarin **1a** (16.2 mg, 1 mmol), 4-methoxyphenylflyoxal monohydrate **2c** (18.2 mg, 1 mmol), diethyl acetylenedicarboxylate **3b** (17.0 mg, 1 mmol) and 4-bromoaniline **4e** (17.1 mg, 1 mmol) in ethanol (5 mL), at 80 °C 1.5 h, afforded 57.1 mg (90 %) of **5v**. white powder; m.p.: 155-156°C; IR (KBr, *v*, cm^{-1}): 3429, 3001, 2979, 2935, 1711, 1682, 1577, 1494, 1417, 1338, 1296, 1262, 1202, 1123, 1081, 1013, 923, 861, 835, 802, 763, 648; ^1H NMR (DMSO-d_6, 400 MHz): δ 11.24 (s, 1H, OH), 7.80-7.77 (m, 1H, ArH), 7.58-7.56 (m, 3H, ArH), 7.31-7.28 (m, 2H, ArH), 7.17 (d, J = 6.8 Hz, 2H, ArH), 6.97 (d, J = 6.8 Hz, 2H, ArH), 6.71-6.68 (m, 2H, ArH), 4.09-4.04 (m, 4H, 2×CH_2), 3.58 (s, 3H, OCH_3) 1.05-1.01 (m, 6H, 2×CH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 163.60, 162.24, 162.05, 161.07, 159.33, 152.86, 137.71, 137.23, 132.78, 132.25, 131.59, 130.51, 127.78, 124.44, 124.03, 122.10, 122.03, 119.35, 116.55, 116.20, 113.89, 112.90, 98.70, 61.54, 60.31, 55.27, 14.21, 14.03; HRMS (ESI) calcd for$C_{32}H_{26}{}^{79}BrNO_8$ $[M]^+$: 631.0842, found: 631.0850.

diethyl 1-(4-bromophenyl)-5-(4-chlorophenyl)-4-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)-1*H*-pyrrole-2,3-dicarboxylate (5w). The reaction of 4-hydroxycoumarin **1a** (16.2 mg, 1 mmol), 4-chlorophenylflyoxal monohydrate **2d** (18.6 mg, 1 mmol), diethyl acetylenedicarboxylate **3b** (17.0 mg, 1 mmol) and 4-bromoaniline **4e** (17.1 mg, 1 mmol) in ethanol (5 mL), at 80 °C 2.0 h, afforded 57.5 mg (90 %) of **5w**. white powder; m.p.: 223-224°C; IR (KBr, *v*, cm^{-1}): 3428, 3001, 2981, 2935, 1711, 1689, 1670, 1579, 1491, 1417, 1335, 1307, 1266, 1206, 1172, 1151, 1119, 1043, 1013, 923, 759, 649; ^1H NMR (DMSO-d_6, 400 MHz): δ 11.33 (s, 1H, OH), 7.78 (d, J = 7.6 Hz, 1H, ArH), 7.61-7.58 (m, 3H, ArH), 7.35-7.16 (m, 6H, ArH), 7.02 (d, J = 8.4 Hz, 2H, ArH), 4.11-4.03 (m, 4H, 2×CH_2), 1.07-0.99 (m, 6H, 2×CH_3); ^{13}C

NMR (DMSO-d_6, 75 MHz): δ 163.38, 162.16, 160.97, 152.86, 136.83, 136.22, 132.89, 132.58, 132.42, 131.96, 130.37, 128.97, 128.67, 128.41, 124.48, 124.04, 122.27, 119.29, 116.59, 116.12, 113.54, 98.27, 61.69, 60.39, 14.19, 14.00; HRMS (ESI) calcd for$C_{31}H_{23}{}^{79}Br^{35}ClNO_7$ $[M]^+$: 635.0346, found: 635.0354.

diethyl 1,5-bis(4-bromophenyl)-4-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)-1*H*-pyrrole-2,3-dicarboxylate (5x). 

The reaction of 4-hydroxycoumarin **1a** (16.2 mg, 1 mmol), 4-bromophenylflyoxal monohydrate **2e** (23.1 mg, 1 mmol), diethyl acetylenedicarboxylate **3b** (17.0 mg, 1 mmol) and 4-bromoaniline **4e** (17.1 mg, 1 mmol) in ethanol (5 mL), at 80 °C 2.0 h, afforded 60.4 mg (89 %) of **5x**. white powder; m.p.: 233-234°C; IR (KBr, *v*, cm^{-1}): 3428, 3001, 2981, 2935, 1699, 1579, 1490, 1417, 1335, 1307, 1269, 1204, 1151, 1117, 1043, 1013, 923, 759, 649; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.33 (s, 1H, OH), 7.78 (d, J = 7.6 Hz, 1H, ArH), 7.61-7.58 (m, 3H, ArH), 7.38-7.27 (m, 4H, ArH), 7.17 (d, J = 8.0 Hz, 2H, ArH), 6.96 (d, J = 7.6 Hz, 2H, ArH), 4.10-4.03 (m, 4H, 2×CH_2), 1.07-0.99 (m, 6H, 2×CH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 163.37, 162.16, 160.96, 152.86, 136.81, 136.23, 132.88, 132.73, 132.20, 131.58, 130.36, 129.33, 128.46, 124.47, 124.04, 122.38, 122.28, 119.29, 116.58, 116.12, 113.51, 98.27, 61.69, 60.39, 14.19, 14.00; HRMS (ESI) calcd for$C_{31}H_{23}{}^{79}Br_2NO_7$ $[M]^+$: 678.9841, found: 678.9848.

diethyl 1-butyl-5-(4-chlorophenyl)-4-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)-1*H*-pyrrole-2,3-dicarboxylate (5y). 

The reaction of 4-hydroxycoumarin **1a** (16.2 mg, 1 mmol), 4-chlorophenylflyoxal monohydrate **2d** (18.6 mg, 1 mmol), diethyl acetylenedicarboxylate **3b** (17.0 mg, 1 mmol) and butylamine **4j** (7.3 mg, 1 mmol) in ethanol (5 mL), at 80 °C 1.5 h, afforded 40.0 mg (74 %) of **5y**. white powder; m.p.: 158-159°C; IR (KBr, *v*, cm^{-1}): 3233, 3064, 2961, 2932, 2870, 1737, 1714, 1611, 1565, 1546, 1490, 1456, 1425, 1317, 1270, 1202, 1089, 1032, 1013, 913, 864, 843, 760, 717, 675; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.23 (s, 1H, OH), 7.54 (t, J = 8.0 Hz, 1H, ArH), 7.43 (d, J = 8.4 Hz, 2H, ArH), 7.31-7.23 (m, 4H, ArH), 4.30-4.25 (m, 2H, CH_2), 4.05-3.90 (m, 4H, 2×CH_2), 1.50-1.39 (m, 2H, CH_2), 1.25 (t, J = 7.2 Hz, 3H, CH_3), 1.08-1.03 (m,

2H, CH_2), 0.97 (t, J = 7.2 Hz, 3H, CH_3), 0.66 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 163,88, 162.16, 161.94, 161.64, 152.75, 136.50, 134.06, 132.67, 132.13, 129.57, 128.98, 125.16, 124.32, 123.91, 120.23, 116.46, 116.16, 113.02, 98.47, 61.48, 60.15, 45.61, 33.13, 19.44, 14.24, 14.18, 13.63; HRMS (ESI) calcd for$C_{29}H_{28}{}^{35}ClNO_7$ $[M]^+$: 537.1554, found: 537.1580.

dimethyl 4-(4-hydroxy-6-methyl-2-oxo-2*H*-pyran-3-yl)-5-phenyl-1-(p-tolyl)-1*H*-pyrrole-2,3-dicarboxylate (7a). The reaction of 4-hydroxycoumarin **1b** (12.6 mg, 1 mmol), phenylflyoxal monohydrate **2a** (15.2 mg, 1 mmol), dimethyl acetylenedicarboxylate **3a** (14.2 mg, 1 mmol) and p-toluidine **4a** (10.7 mg, 1 mmol) in ethanol (5 mL), at 80 °C 1 h, afforded 40.2 mg (85 %) of **7a**. white powder; m.p.: 243-245°C; IR (KBr, v, cm^{-1}): 3418, 3001, 2953, 1713, 1641, 1577, 1515, 1443, 1178, 1143, 1093, 1059, 1013, 997, 939, 924, 822, 700, 649; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.01 (s, 1H, OH), 7.12-6.97 (m, 9H, ArH), 5.91 (s, 1H, =CH), 3.60 (s, 6H, 2×OCH_3), 2.23 (s, 3H, CH_3), 2.10 (s, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 167.01, 164.24, 164.17, 161.95, 161.82, 138.32, 136.85, 135.07, 130.91, 130.17, 129.79, 128.55, 128.27, 127.92, 127.83, 118.53, 113.86, 100.47, 95.54, 52.77, 51.94, 21.08, 19.76; HRMS (ESI) calcd for$C_{27}H_{22}NO_7$ $[M-H]^+$: 472.1396, found: 472.1415.

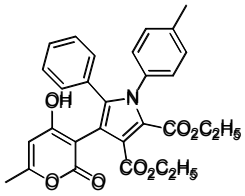
dimethyl 1-(4-chlorophenyl)-4-(4-hydroxy-6-methyl-2-oxo-2*H*-pyran-3-yl)-5-phenyl-1*H*-pyrrole-2,3-dicarboxylate (7b). The reaction of 4-hydroxycoumarin **1b** (12.6 mg, 1 mmol), phenylflyoxal monohydrate **2a** (15.2 mg, 1 mmol), dimethyl but-2-ynedioate **3a** (14.2 mg, 1 mmol) and 4-chloroaniline **4b** (12.7 mg, 1 mmol) in ethanol (5 mL), at 80 °C 3 h, afforded 43.1 mg (87 %) of **7b**. white powder; m.p.: 265-266°C; IR (KBr, v, cm^{-1}): 3421, 3061, 2955, 2853, 1713, 1642, 1577, 1494, 1444, 1272, 1175, 1145, 1090, 1061, 1043, 1017, 998, 971, 924, 856, 773, 754, 733, 698, 649; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.03 (s, 1H, OH), 7.37 (d, J = 8.0 Hz, 2H, ArH), 7.19-7.14 (m, 5H, ArH), 6.99-6.97 (m, 2H, ArH), 5.92 (s, 1H, =CH), 3.63 (s, 3H, OCH_3), 3.61 (s, 3H, OCH_3), 2.10 (s, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 167.11, 164.38, 164.03, 161.95, 161.46, 137.39, 136.66, 133.46, 130.56, 130.23, 130.19, 129.28, 128.47, 128.36, 126.74, 120.08, 114.14, 100.45, 95.17, 52.73, 52.04, 19.74; HRMS (ESI) calcd for$C_{26}H_{19}{}^{35}ClNO_7$ $[M-H]^+$:

492.0850, found: 492.0841.

dimethyl 1-(4-bromophenyl)-4-(4-hydroxy-6-methyl-2-oxo-2*H*-pyran-3-yl)-5-phenyl-1*H*-pyrrole-2,3-dicarboxylate (7c). The reaction of 4-hydroxycoumarin **1b** (12.6 mg, 1 mmol), phenylflyoxal monohydrate **2a** (15.2 mg, 1 mmol), dimethyl but-2-ynedioate **3a** (14.2 mg, 1 mmol) and 4-bromoaniline **4e** (17.1 mg, 1 mmol) in ethanol (5 mL), at 80 °C 2 h, afforded 45.6 mg (85 %) of **7c**. white powder; m.p.: 261-263°C; IR (KBr, *v*, cm^{-1}): 3419, 3092, 3002, 2954, 2714, 2680, 1712, 1640, 1577, 1522, 1443, 1370, 1216, 1174, 1145, 1093, 1043, 1014, 997, 939, 853, 772, 749, 698, 649; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.04 (s, 1H, OH), 7.51 (d, J = 8.0 Hz, 2H, ArH), 7.14-7.10 (m, 5H, ArH), 6.99-6.97 (m, 2H, ArH), 5.92 (s, 1H, =CH), 3.63 (s, 3H, OCH_3), 3.62 (s, 3H, OCH_3), 2.09 (s, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 167.11, 164.36, 164.02, 161.95, 161.46, 137.32, 137.08, 132.23, 130.54, 130.46, 130.23, 128.48, 128.37, 126.70, 121.99, 120.08, 114.16, 100.44, 95.15, 52.74, 52.04, 19.73; HRMS (ESI) calcd for$C_{26}H_{20}{}^{79}BrNO_7$ $[M]^+$: 537.0423, found: 537.0412.

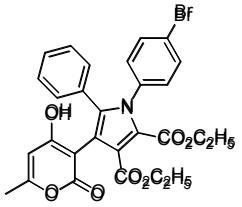
dimethyl 1-(3-chloro-4-methylphenyl)-4-(4-hydroxy-6-methyl-2-oxo-2*H*-pyran-3-yl)-5- phenyl-1*H*-pyrrole-2,3-dicarboxylate (7d). The reaction of 4-hydroxy- coumarin **1b** (12.6 mg, 1 mmol), phenylflyoxal monohydrate **2a** (15.2 mg, 1 mmol), dimethyl but-2-ynedioate **3a** (14.2 mg, 1 mmol) and 3-chloro-4-methylaniline **4k** (14.1 mg, 1 mmol) in ethanol (5 mL), at 80 °C 1.5 h, afforded 44.8 mg (88 %) of **7d**. white powder; m.p.: 249-250°C; IR (KBr, *v*, cm^{-1}): 3426, 3067, 3001, 2949, 1718, 1675, 1576, 1499, 1444, 1272, 1208, 1133, 1094, 1054, 1012, 992, 925, 881, 786, 771, 703, 649; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.02 (s, 1H, OH), 7.26-7.02 (m, 9H, ArH), 5.92 (s, 1H, =CH), 3.62 (s, 6H, 2×OCH_3), 2.24 (s, 3H, CH_3), 2.09 (s, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 167.12, 164.36, 164.01, 161.93, 161.50, 137.45, 136.60, 136.39, 133.25, 131.57, 130.57, 130.24, 128.75, 128.50, 128.35, 127.19, 126.86, 119.96, 114.07, 100.45, 95.18, 52.73, 52.02, 19.72, 19.65; HRMS (ESI) calcd for$C_{27}H_{21}{}^{35}ClNO_7$ $[M-H]^+$: 506.1007, found: 506.1008.

diethyl



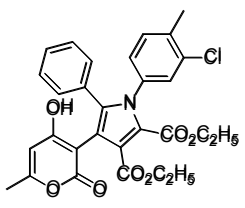
4-(4-hydroxy-6-methyl-2-oxo-2*H*-pyran-3-yl)-5-phenyl-1-(*p*-tolyl)-1*H*-pyrrole-2, 3-dicarboxylate (7e). The reaction of 4-hydroxycoumarin **1b** (12.6 mg, 1 mmol), phenylflyoxal monohydrate **2a** (15.2 mg, 1 mmol), diethyl but-2-ynedioate **3b** (17.0 mg, 1 mmol) and p-toluidine **4a** (10.7 mg, 1 mmol) in ethanol (5 mL), at 80 °C 1 h, afforded 39.1 mg (78 %) of **7e**. white powder; m.p.: 223-224°C; IR (KBr, *v*, cm^{-1}): 3424, 3062, 3002, 2976, 2869, 2716, 2678, 1713, 1578, 1488, 1444, 1399, 1367, 1257, 1173, 1093, 1021, 997, 941, 869, 818, 768, 701, 649; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 10.95 (s, 1H, OH), 7.12-6.97 (m, 9H, ArH), 5.92 (s, 1H, =CH), 4.06-4.01 (m, 4H, 2×CH_2), 2.23 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 1.10-1.00 (m, 6H, 2×CH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 166.94, 164.20, 163.58, 161.66, 161.45, 138.28, 136.50, 135.16, 130.94, 130.17, 129.85, 129.70, 128.40, 128.23, 127.95, 118.25, 113.74, 100.42, 95.85, 61.43, 60.11, 21.03, 19.70, 14.31, 14.03; HRMS (ESI) calcd for$C_{29}H_{26}NO_7$ $[M-H]^+$: 500.1709, found: 500.1702.

diethyl 1-(4-bromophenyl)-4-(4-hydroxy-6-methyl-2-oxo-2*H*-pyran-3-yl)-5-phenyl-1*H*-



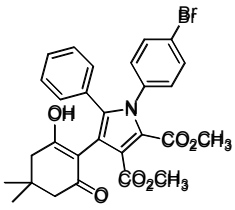
pyrrole-2,3-dicarboxylate (7f). The reaction of 4-hydroxycoumarin **1b** (12.6 mg, 1 mmol), phenylflyoxal monohydrate **2a** (15.2 mg, 1 mmol), diethyl but-2-ynedioate **3b** (17.0 mg, 1 mmol) and 4-bromoaniline **4e** (17.1 mg, 1 mmol) in ethanol (5 mL), at 80 °C 2.5 h, afforded 42.4 mg (75 %) of **7f**. white powder; m.p.: 220-221°C; IR (KBr, *v*, cm^{-1}): 3422, 3088, 2998, 2935, 1704, 1577, 1489, 1443, 1253, 1207, 1172, 1140, 1091, 1044, 1013, 941, 924, 816, 772, 728, 698, 650; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 10.98 (s, 1H, OH), 7.52 (d, *J* = 8.0 Hz, 2H, ArH), 7.14-6.98 (m, 6H, ArH), 5.92 (s, 1H, =CH), 4.09-4.02 (m, 4H, 2×CH_2), 2.10 (s, 3H, CH_3), 1.10 (t, *J* = 7.2 Hz, 3H, CH_3), 1.03 (t, *J* = 6.8 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 167.05, 164.04, 163.66, 161.82, 160.94, 137.16, 136.94, 132.19, 130.55, 130.47, 130.21, 128.41, 128.35, 127.24, 121.93, 119.80, 114.05, 100.39, 95.41, 61.45, 60.29, 19.70, 14.29, 14.03; HRMS (ESI) calcd for$C_{28}H_{23}{}^{79}BrNO_7$ $[M-H]^+$: 564.0658, found: 564.0676.

diethyl 1-(3-chloro-4-methylphenyl)-4-(4-hydroxy-6-methyl-2-oxo-2*H*-pyran-3-yl)-5-phenyl-



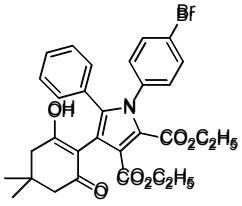
1*H*-pyrrole-2,3-dicarboxylate (7g). The reaction of 4-hydroxycoumarin **1b** (12.6 mg, 1 mmol), phenylflyoxal monohydrate **2a** (15.2 mg, 1 mmol), diethyl but-2-ynedioate **3b** (17.0 mg, 1 mmol) and 3-chloro-4-methylaniline **4k** (14.1 mg, 1 mmol) in ethanol (5 mL), at 80 °C 1.5 h, afforded 45.5 mg (85 %) of **7g**. white powder; m.p.: 238-239°C; IR (KBr, *v*, cm^{-1}): 3420, 3079, 3028, 2981, 1714, 1682, 1577, 1499, 1444, 1341, 1287, 1205, 1137, 1094, 1059, 1014, 989, 943, 854, 769, 699, 649; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 10.97 (s, 1H, OH), 7.28-7.01 (m, 8H, ArH), 5.92 (s, 1H, =CH), 4.08-4.02 (m, 4H, 2×CH_2), 2.25 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 1.09-1.03 (m, 6H, 2×CH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 167.04, 164.04, 163.62, 161.81, 161.02, 136.96, 136.64, 136.35, 133.21, 131.54, 130.57, 130.22, 128.34, 127.51, 127.17, 119.53, 113.94, 100.38, 95.44, 61.45, 60.27, 19.70, 19.64, 14.29, 14.05; HRMS (ESI) calcd for$C_{29}H_{25}{}^{35}ClNO_7$ $[M-H]^+$: 534.1320, found: 534.1338.

dimethyl 1-(4-bromophenyl)-4-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-5-phenyl-



1*H*-pyrrole-2,3-dicarboxylate (7h). The reaction of 5,5-dimethyl-cyclohexane-1,3-dione **1c** (14.0 mg, 1 mmol), phenylflyoxal monohydrate **2a** (15.2 mg, 1 mmol), dimethyl but-2-ynedioate **3a** (14.2 mg, 1 mmol) and 4-bromoaniline **4e** (17.1 mg, 1 mmol) in ethanol (5 mL), at 80 °C 1 h, afforded 50.9 mg (92 %) of **7h**. white powder; m.p.: 234-235°C; IR (KBr, *v*, cm^{-1}): 3419, 3067, 2996, 2950, 2869, 0643, 2617, 1719, 1579, 1491, 1443, 1364, 1276, 1211, 1173, 1086, 1070, 1030, 1013, 971, 923, 842, 798, 767, 697, 680, 649; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 10.13 (s, 1H, OH), 7.50 (s, 2H, ArH), 7.13-7.08 (m, 5H, ArH), 6.93 (s, 2H, ArH), 3.60 (s, 3H, OCH_3), 3.37 (s, 3H, OCH_3), 2.23-1.96 (m, 4H, 2×CH_2), 1.01 (s, 3H, CH_3), 0.81 (s, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 164.55, 161.57, 137.30, 136.98, 132.11, 130.76, 130.40, 130.27, 128.18, 128.11, 126.42, 121.75, 120.55, 115.70, 107.91, 52.60, 51.88, 31.89, 28.53, 27.88; HRMS (ESI) calcd for$C_{28}H_{25}{}^{79}BrNO_6$ $[M-H]^+$: 550.0865, found: 550.0870.

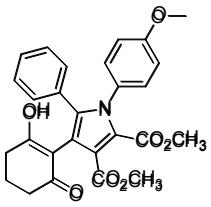
diethyl



1-(4-bromophenyl)-4-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-5-phenyl- 1*H*-pyrrole-2,3-dicarboxylate (7i). The reaction of

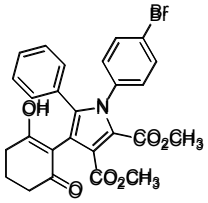
5,5-dimethyl- cyclohexane-1,3-dione **1c** (14.0 mg, 1 mmol), phenylflyoxal monohydrate **2a** (15.2 mg, 1 mmol), diethyl but-2-ynedioate **3b** (17.0 mg, 1 mmol) and 4-bromoaniline **4e** (17.1 mg, 1 mmol) in ethanol (5 mL), at 80 °C 1 h, afforded 50.4 mg (87 %) of **7i**. white powder; m.p.: 217-218°C; IR (KBr, *v*, cm^{-1}): 3423, 3060, 2981, 2889, 1737, 1714, 1576, 1416, 1443, 1271, 1134, 1084, 1044, 1013, 923, 864, 836, 794, 734, 700, 680, 649; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 10.10 (s, 1H, OH), 7.51 (d, J = 7.6 Hz, 2H, ArH), 7.12-7.08 (m, 5H, ArH), 6.93 (s, 2H, ArH), 4.09-4.00 (m, 4H, 2×CH_2), 2.28-1.96 (m, 4H, 2×CH_2), 1.14 (t, J = 6.4 Hz, 3H, CH_3), 1.04-1.00 (m, 6H, 2×CH_3), 0.78 (s, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 164.01, 161.01, 137.43, 136.78, 132.06, 130.79, 130.49, 130.29, 128.14, 128.08, 126.65, 121.69, 120.59, 115.52, 108.02, 61.22, 60.15, 50.66, 31.86, 28.87, 27.58, 14.51, 14.05; HRMS (ESI) calcd for$C_{30}H_{29}{}^{79}BrNO_6$ $[M-H]^+$: 578.1178, found: 578.1183.

dimethyl 4-(2-hydroxy-6-oxocyclohex-1-en-1-yl)-1-(4-methoxyphenyl)-5-phenyl-1*H*-pyrrole-2,



3-dicarboxylate (7j). The reaction of cyclohexane-1,3-dione **1d** (11.2 mg, 1 mmol), phenylflyoxal monohydrate **2a** (15.2 mg, 1 mmol), dimethyl but-2-ynedioate **3a** (14.2 mg, 1 mmol) and 4-methoxyaniline **4f** (12.3 mg, 1 mmol) in ethanol (5 mL), at 80 °C 1 h, afforded 41.8 mg (88 %) of **7j**. white powder; m.p.: 222-223°C; IR (KBr, *v*, cm^{-1}): 3422, 3053, 2978, 2891, 1577, 1514, 1479, 1444, 1358, 1334, 1294, 1250, 1212, 1182, 1130, 1086, 1047, 1025, 984, 923, 841, 798, 763, 700, 649; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 10.12 (s, 1H, OH), 7.12-7.10 (m, 3H, ArH), 7.04 (d, J = 7.6 Hz, 2H, ArH), 6.93-6.90 (m, 2H, ArH), 6.83 (d, J = 8.4 Hz, 2H, ArH), 3.68 (s, 3H, OCH_3), 3.60 (s, 3H, OCH_3), 3.58 (s, 3H, OCH_3), 2.30-2.15 (m, 2H, 2×CH_2), 1.85-1.66 (m, 2H, CH_2); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 164.42, 162.06, 159.07, 136.49, 131.14, 130.57, 130.08, 129.39, 127.99, 127.85, 127.67, 118.93, 115.41, 114.18, 109.52, 55.67, 52.57, 51.66, 20.92; HRMS (ESI) calcd for$C_{27}H_{24}NO_7$ $[M-H]^+$: 474.1553, found: 474.1568.

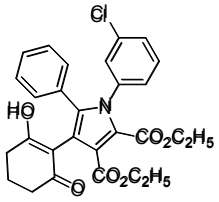
dimethyl 1-(4-bromophenyl)-4-(2-hydroxy-6-oxocyclohex-1-en-1-yl)-5-phenyl-1*H*-pyrrole-2,



3-dicarboxylate (7k). The reaction of cyclohexane-1,3-dione **1d** (11.2 mg, 1 mmol), phenylflyoxal monohydrate **2a** (15.2 mg, 1 mmol), dimethyl

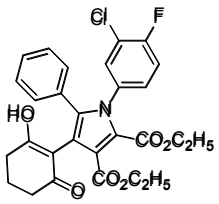
but-2-ynedioate **3a** (14.2 mg, 1 mmol) and 4-bromoaniline **4e** (17.1 mg, 1 mmol) in ethanol (5 mL), at 80 °C 1.5 h, afforded 43.0 mg (82 %) of **7k**. white powder; m.p.: 204-205°C; IR (KBr, *v*, cm^{-1}): 3424, 3001, 2950, 2891, 2661, 2612, 1710, 1577, 1492, 1444, 1372, 1351, 1276, 1253, 1211, 1191, 1137, 1088, 1044, 1014, 987, 924, 848, 799, 767, 738, 698, 649; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 10.17 (s, 1H, OH), 7.50 (d, J = 8.0 Hz, 2H, ArH), 7.13-7.07 (m, 5H, ArH), 6.92 (s, 2H, ArH), 3.61 (s, 3H, OCH_3), 3.60 (s, 3H, OCH_3), 2.36-2.18 (m, 2H, 2×CH_2), 1.82-1.66 (m, 2H, CH_2); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 164.49, 161.62, 137.33, 136.74, 132.14, 130.74, 130.41, 130.20, 130.13, 128.14, 126.49, 121.75, 120.52, 115.91, 109.12, 52.62, 51.82, 20.91; HRMS (ESI) calcd for$C_{26}H_{22}{}^{79}BrNO_6$ $[M]^+$: 523.0631, found: 523.0630.

diethyl 1-(3-chlorophenyl)-4-(2-hydroxy-6-oxocyclohex-1-en-1-yl)-5-phenyl-1*H*-pyrrole-2,



3-dicarboxylate (7l). The reaction of cyclohexane-1,3-dione **1d** (11.2 mg, 1 mmol), phenylflyoxal monohydrate **2a** (15.2 mg, 1 mmol), diethyl but-2-ynedioate **3b** (17.0 mg, 1 mmol) and 3-chloroaniline **4c** (12.7 mg, 1 mmol) in ethanol (5 mL), at 80 °C 2 h, afforded 42.7 mg (84 %) of **7l**. white powder; m.p.: 202-204°C; IR (KBr, *v*, cm^{-1}): 3422, 3057, 2979, 2902, 2659, 2606, 1706, 1577, 1484, 1442, 1376, 1349, 1334, 1276, 1242, 1203, 1096, 1045, 1015, 990, 924, 876, 785, 763, 703, 649; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 10.12 (s, 1H, OH), 7.39-7.25 (m, 3H, ArH), 7.14-7.12 (m, 4H, ArH), 6.94 (s, 2H, ArH), 4.08-4.02 (m, 4H, 2×CH_2), 2.37-2.14 (m, 4H, 2×CH_2), 1.81-1.68 (m, 2H, CH_2), 1.15 (t, J = 6.8 Hz, 3H, CH_3), 1.02 (t, J = 6.8 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 163.94, 161.03, 139.41, 136.58, 133.12, 130.71, 130.13, 128.78, 128.46, 128.35, 128.25, 128.11, 127.37, 126.97, 120.60, 115.84, 109.25, 61.25, 60.13, 20.88, 14.48, 14.03; HRMS (ESI) calcd for$C_{28}H_{25}{}^{35}ClNO_6$ $[M-H]^+$: 506.1370, found: 506.1397.

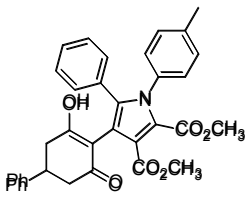
diethyl 1-(3-chloro-4-fluorophenyl)-4-(2-hydroxy-6-oxocyclohex-1-en-1-yl)-5-phenyl-1*H*-



pyrrole-2,3-dicarboxylate (7m). The reaction of cyclohexane-1,3-dione **1d** (11.2 mg, 1 mmol), phenylflyoxal monohydrate **2a** (15.2 mg, 1 mmol), diethyl but-2-ynedioate **3b** (17.0 mg, 1 mmol) and 3-chloro-4-fluoroaniline **4l** (14.5 mg, 1 mmol) in ethanol (5 mL), at 80 °C 2.5 h, afforded 45.8 mg (87 %) of **7m**. white powder; m.p.: 217-218°C; IR (KBr, *v*, cm^{-1}): 3425, 3059, 2979, 2904, 2661,

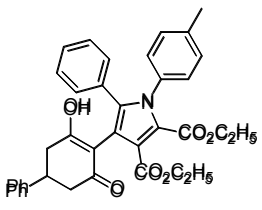
2613, 1703, 1577, 1501, 1418, 1375, 1257, 1226, 1204, 1145, 1090, 1045, 1014, 990, 924, 885, 833, 770, 702, 649; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 10.14 (s, 1H, OH), 7.51-6.98 (m, 8H, ArH), 4.09-4.04 (m, 4H, 2×CH_2), 2.38-2.11 (m, 4H, 2×CH_2), 1.81-1.65 (m, 2H, CH_2), 1.17-1.02 (m, 6H, 2×CH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 164.11, 160.80, 158.84, 155.54, 137.22, 135.33, 130.87, 130.63, 130.26, 129.72, 129.62, 128.18, 126.45, 121.45, 119.84, 119.59, 117.33, 117.04, 115.64, 109.16, 61.22, 60.23, 20.89, 14.48, 14.06; HRMS (ESI) calcd for$C_{28}H_{24}{}^{35}ClFNO_6$ $[M-H]^+$: 524.1276, found: 524.1285.

dimethyl 4-(5-hydroxy-3-oxo-1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)-5-phenyl-1-(p-tolyl)-1*H*-pyrrole-2,3-dicarboxylate (7n).



The reaction of 5-phenyl-cyclohexane-1,3-dione **1e** (18.8 mg, 1 mmol), phenylflyoxal monohydrate **2a** (15.2 mg, 1 mmol), dimethyl but-2-ynedioate **3a** (14.2 mg, 1 mmol) and p-toluidine **4a** (10.7 mg, 1 mmol) in ethanol (5 mL), at 80 °C 1 h, afforded 43.8 mg (82 %) of **7n**. white powder; m.p.: 117-118°C; IR (KBr, *v*, cm^{-1}): 3420, 3056, 3002, 2949, 2630, 1716, 1577, 1515, 1486, 1443, 1330, 1273, 1207, 1132, 1086, 1047, 1018, 979, 983, 923, 833, 800, 765, 699, 649; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 10.33 (s, 1H, OH), 7.27-6.92 (m, 14H, ArH), 3.63-3.56 (m, 6H, 2×OCH_3), 3.42-3.04 (m, 1H, CH), 2.66-2.09 (m, 7H, 1×CH_3+2×CH_2); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 164,46, 162.12, 143.88, 143.74, 138.07, 136.50, 136.22, 135.34, 131.19, 131.10, 130.18, 130.12, 129.70, 129.67, 128.98, 128.93, 128.11, 128.08, 127.95, 127.90, 127.36, 119.10, 118.89, 115.36, 115.32, 109.40, 109.34, 52.63, 51.78, 38.75, 38.53, 21.06; HRMS (ESI) calcd for$C_{33}H_{29}NO_6$ $[M]^+$: 535.1995, found: 535.1990.

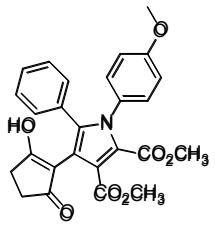
diethyl 4-(5-hydroxy-3-oxo-1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)-5-phenyl-1-(p-tolyl)-1*H*-pyrrole-2,3-dicarboxylate (7o) .



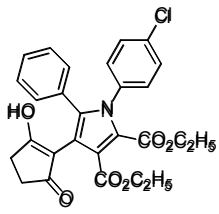
The reaction of 5-phenyl-cyclohexane-1,3-dione **1e** (18.8 mg, 1 mmol), phenylflyoxal monohydrate **2a** (15.2 mg, 1 mmol), diethyl but-2-ynedioate **3b** (17.0 mg, 1 mmol) and p-toluidine **4a** (10.7 mg, 1 mmol) in ethanol (5 mL), at 80 °C 1.5 h, afforded 43.2 mg (77 %) of **7o**. white powder; m.p.: 210-211°C; IR (KBr, *v*, cm^{-1}): 3411, 3060, 2958, 2900, 1711, 1578, 1515, 1423, 1271, 1200, 1133, 1085, 1049, 1018, 946, 923,

835, 803, 763, 649; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 10.32 (s, 1H, OH), 7.27-6.93 (m, 14H, ArH), 4.08-4.00 (m, 4H, 2×CH_2), 3.29-3.03 (m, 1H, CH), 2.69-2.44 (m, 4H, 2×CH_2), 2.21(s, 3H, CH_3), 1.16-0.99 (m, 6H, 2×CH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 163.90, 163.86, 161.63, 143.86, 143.69, 138.05, 136.19, 135.88, 135.43, 131.24, 130.18, 129.62, 128.99, 128.24, 128.08, 127.96, 127.29. 118.82, 115.15, 115.04, 109.53, 61.28, 60.05, 59.97, 38.76, 38.50, 21.04, 14.59, 14.05; HRMS (ESI) calcd for$C_{35}H_{32}NO_6$ $[M-H]^+$: 562.2230, found: 562.2273.

dimethyl 4-(2-hydroxy-5-oxocyclopent-1-en-1-yl)-1-(4-methoxyphenyl)-5-phenyl-1*H*-pyrrole-2,3-dicarboxylate (7p). The reaction of cyclopentane-1,3-dione **1f** (9.8 mg, 1 mmol), phenylflyoxal monohydrate **2a** (15.2 mg, 1 mmol), dimethyl but-2-ynedioate **3a** (14.2 mg, 1 mmol) and 4-methoxyaniline **4f** (12.3 mg, 1 mmol) in ethanol (5 mL), at 80 °C 1 h, afforded 35.0 mg (76 %) of **7p**. white powder; m.p.: 243-246°C; IR (KBr, *v*, cm^{-1}): 3428, 3067, 2957, 2841, 1746, 1708, 1577, 1515, 1444, 1353, 1301, 1275, 1249, 1203, 1172, 1133, 1076, 1043, 1026, 923, 841, 769, 710, 649; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.59 (s, 1H, OH), 7.12-7.00 (m, 7H, ArH), 6.83 (d, J = 7.6 Hz, 2H, ArH), 3.68-3.58 (m, 9H, 3×OCH_3), 2.36-2.28 (m, 4H, 2×CH_2); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 164.49, 161.79, 159.22, 136.78, 130.99, 130.40, 130.31, 129.53, 128.16, 128.09, 127.52, 118.99, 114.26, 113.07, 111.00, 55.71, 52.66, 51.90; HRMS (ESI) calcd for$C_{26}H_{23}NO_7$ $[M]^+$: 461.1475, found: 461.1472.



diethyl 1-(4-chlorophenyl)-4-(2-hydroxy-5-oxocyclopent-1-en-1-yl)-5-phenyl-1*H*-pyrrole-2,3-dicarboxylate (7q). The reaction of cyclopentane-1,3-dione **1f** (9.8 mg, 1 mmol), phenylflyoxal monohydrate **2a** (15.2 mg, 1 mmol), diethyl but-2-ynedioate **3b** (17.0 mg, 1 mmol) and 4-chloroaniline **4b** (12.7 mg, 1 mmol) in ethanol (5 mL), at 80 °C 1.5 h, afforded 41.1 mg (83 %) of **7q**. light red powder; m.p.: 239-241°C; IR (KBr, *v*, cm^{-1}): 3428, 3000, 2979, 2935, 1577, 1496, 1422, 1310, 1248, 1231, 1208, 1132, 1043, 1014, 924, 846, 808, 779, 749, 702, 649; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.63 (s, 1H, OH), 7.37 (d, J = 8.8 Hz, 2H, ArH), 7.17-7.14 (m, 5H, ArH), 6.98 (s, 2H, ArH), 4.10-4.00 (m, 4H, 2×CH_2), 2.36-2.28 (m, 4H, 2×CH_2), 1.14 (t, J = 7.2



Hz, 3H, CH_3), 1.01 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 75MHz): δ 163.91, 160.80, 136.83, 136.66, 133.36, 130.62, 130.32, 129.19, 128.24, 126.80, 120.28, 113.36, 110.80, 61.33, 60.29, 14.37, 14.02; HRMS (ESI) calcd for$C_{27}H_{24}{}^{35}ClNO_6$ $[M]^+$: 493.1292, found: 493.1297.

dimethyl 4-(4-hydroxy-2-oxo-2,5-dihydrofuran-3-yl)-1-(4-methoxyphenyl)-5-phenyl-1*H*-pyrrole-2,3-dicarboxylate (7r). The reaction of tetronic acid **1g** (10.0 mg, 1 mmol), phenylflyoxal monohydrate **2a** (15.2 mg, 1 mmol), dimethyl but-2-ynedioate **3a** (14.2 mg, 1 mmol) and 4-methoxyaniline **4f** (12.3 mg, 1 mmol) in ethanol (5 mL), at 80 °C 1 h, afforded 34.7 mg (75 %) of **7r**. light red powder; m.p.: 143-145°C; IR (KBr, v, cm^{-1}): 3425, 3002, 2936, 2842, 1716, 1577, 1514, 1444, 1250, 1213, 1136, 1088, 1044, 1013, 924, 847, 768, 699, 649; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 12.06 (s, 1H, OH), 7.16-7.02 (m, 7H, ArH), 6.83 (d, J = 8.4 Hz, 2H, ArH), 4.58 (s, 2H, CH_2), 3.69-3.59 (m, 9H, 3×OCH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 175.55, 173.67, 164.15, 161.66, 159.27, 137.40, 130.45, 130.37, 130.05, 129.49, 128.30, 127.91, 118.45, 114.28, 110.77, 94.22, 67.19, 55.72, 52.78, 52.03; HRMS (ESI) calcd for$C_{25}H_{21}NO_8$ $[M]^+$: 463.1267, found: 463.1265.

diethyl 1-(4-bromophenyl)-4-(4-hydroxy-2-oxo-2,5-dihydrofuran-3-yl)-5-phenyl-1*H*-pyrrole-2,3-dicarboxylate (7s). The reaction of tetronic acid **1g** (10.0 mg, 1 mmol), phenylflyoxal monohydrate **2** (15.2 mg, 1 mmol), diethyl but-2-ynedioate **3b** (17.0 mg, 1 mmol) and 4-bromoaniline **4e** (17.1 mg, 1 mmol) in ethanol (5 mL), at 80 °C 1.5 h, afforded 42.1 mg (78 %) of **7s**. white powder; m.p.: 248-249°C; IR (KBr, v, cm^{-1}): 3427, 3061, 2981, 2718, 2660, 1711, 1577, 1492, 1441, 1271, 1207, 1137, 1067, 1043, 1012, 924, 842, 770, 732, 699, 649; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 12.11 (s, 1H, OH), 7.52 (d, J = 5.6 Hz, 2H, ArH), 7.18-7.04 (m, 7H, ArH), 4.58 (s, 2H, CH_2), 4.11-4.03 (m, 4H, 2×CH_2), 1.16-1.02 (m, 6H, 2×CH_3); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 175.69, 173.59, 163.64, 160.70, 137.27, 136.99, 132.21, 130.55, 130.44, 130.14, 128.57, 128.42, 127.10, 122.07, 119.89, 111.21, 94.07, 67.21, 61.50, 60.52, 14.34, 14.01; HRMS (ESI) calcd for$C_{26}H_{22}{}^{79}BrNO_7$ $[M]^+$: 539.0580, found: 539.0588.

Crystal structures of compound

Crystal data for 5p:

$C_{32}H_{26}ClNO_7$; M = 571.99, colorless block crystals, 0.256 × 0.200 × 0.123mm, Monoclinic, space group C2/c, a = 29.861(3) Å, b = 10.2141(11) Å, c = 21.675(2) Å, α = 90 deg., β =117.4550(10) deg., γ = 90 deg., V = 5866.4(11) Å^3, Z = 8, D_c = 1.295 g·cm^{-1}, F(000) = 2384, μ (Mo$K\alpha$) = 0.179 mm^{-1}. Intensity data were collected on a diffractometer with graphite monochromated Mo$K\alpha$ radiation (λ = 0.71073 Å) using ω scan mode with 2.12 º< θ < 28.28 º. 27689 unique reflections were measured and 7239 reflections with $I>2\sigma(I)$ were used in the refinement. The structure was solved by direct methods and expanded using Fourier techniques. The final cycle of full-matrix least squares technique to R = 0.0517 and wR = 0.1258.

Table 1. Bond lengths (Å) for **4{*1,1,1*}**

Bond	Bond Lengths	Bond	Bond Lengths	Bond	Bond Lengths
N(1)-C(1)	1.373(2)	C(8)-C(33)	1.522(3)	C(21)-C(22)	1.377(4)
N(1)-C(4)	1.384(2)	C(9)-C(10)	1.387(3)	C(22)-C(23)	1.372(3)
N(1)-C(5)	1.442(2)	C(9)-Cl(1')	1.771(3)	C(23)-C(24)	1.385(3)
C(1)-C(2)	1.374(2)	C(11)-C(12)	1.380(3)	C(24)-O(7)	1.373(2)
C(1)-C(29)	1.480(2)	C(11)-C(16)	1.381(3)	C(25)-O(5)	1.212(2)
C(2)-C(3)	1.422(2)	C(12)-C(13)	1.377(3)	C(25)-O(7)	1.377(2)
C(2)-C(26)	1.470(3)	C(13)-C(14)	1.362(4)	C(26)-O(1)	1.196(2)
C(3)-C(4)	1.373(2)	C(14)-C(15)	1.359(4)	C(26)-O(2)	1.337(2)
C(3)-C(17)	1.477(2)	C(15)-C(16)	1.385(3)	C(27)-O(2)	1.449(3)
C(4)-C(11)	1.471(3)	C(17)-C(18)	1.353(2)	C(27)-C(28)	1.464(4)
C(5)-C(6)	1.362(3)	C(17)-C(25)	1.437(2)	C(29)-O(3)	1.193(2)
C(5)-C(10)	1.363(3)	C(18)-O(6)	1.331(2)	C(29)-O(4)	1.320(2)
C(6)-C(7)	1.382(3)	C(18)-C(19)	1.447(2)	C(30)-O(4)	1.447(3)
C(7)-C(8)	1.355(4)	C(19)-C(24)	1.379(3)	C(30)-C(31)	1.480(4)
C(7)-Cl(1)	1.741(4)	C(19)-C(20)	1.392(3)	O(6)-H(6)	0.868(10)
C(8)-C(9)	1.376(4)	C(20)-C(21)	1.376(3)		

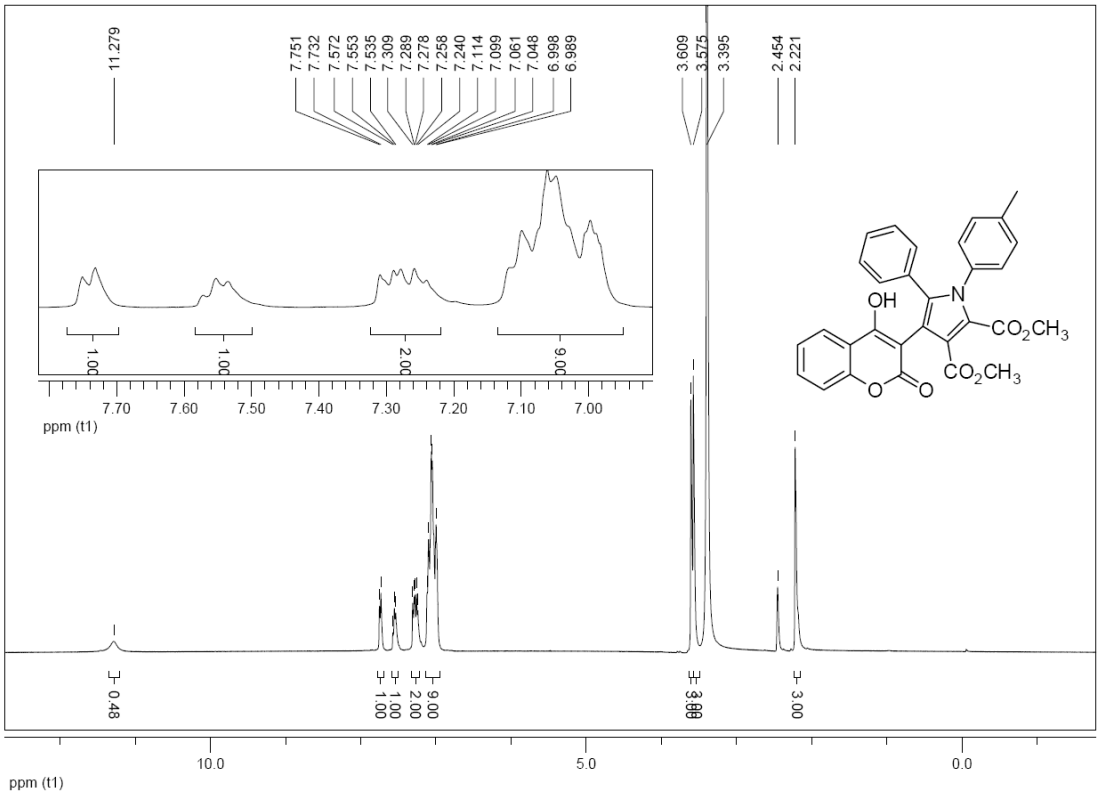
Table 2. Bond angles (°) for **4{*1,1,1*}**

Angles	(°)	Angles	(°)
C(1)-N(1)-C(4)	109.04(14)	C(15)-C(14)-C(13)	119.6(2)
C(1)-N(1)-C(5)	124.63(14)	C(14)-C(15)-C(16)	120.3(2)
C(4)-N(1)-C(5)	126.21(15)	C(11)-C(16)-C(15)	120.8(2)
N(1)-C(1)-C(2)	108.37(15)	C(18)-C(17)-C(25)	120.33(15)

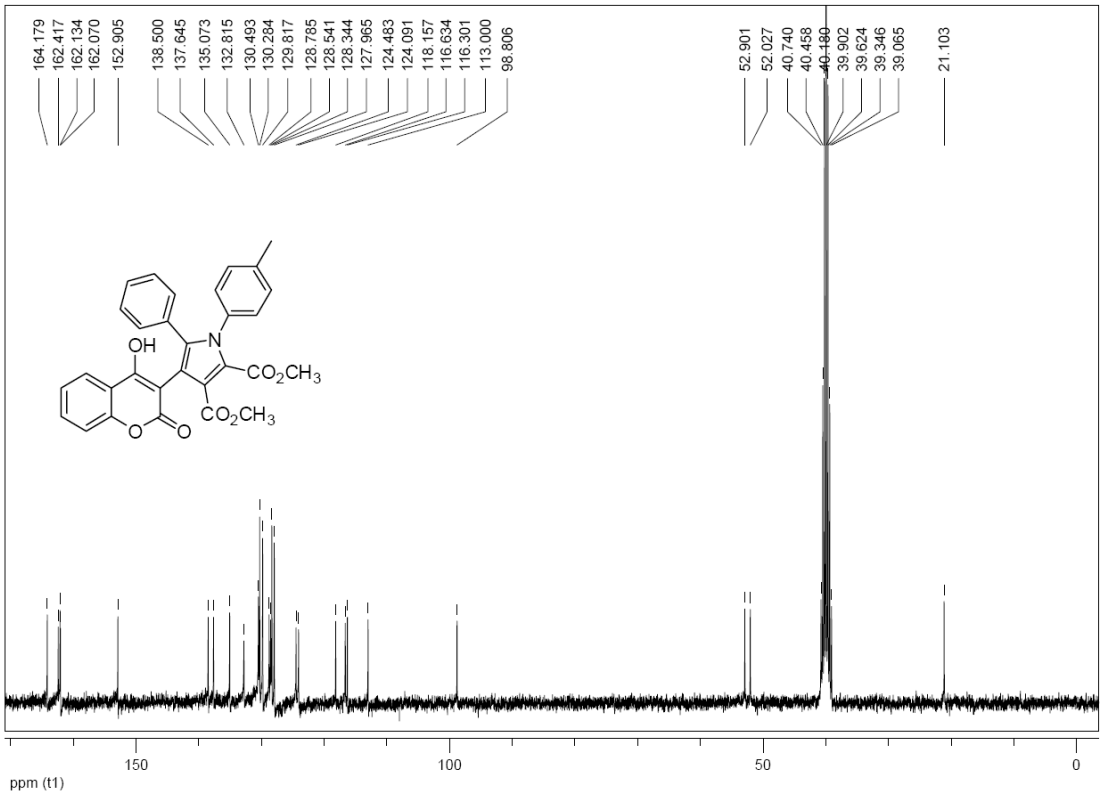
N(1)-C(1)-C(29)	122.07(15)	C(18)-C(17)-C(3)	121.68(15)
C(2)-C(1)-C(29)	129.52(17)	C(25)-C(17)-C(3)	117.86(15)
C(1)-C(2)-C(3)	107.11(15)	O(6)-C(18)-C(17)	125.14(16)
C(1)-C(2)-C(26)	124.10(17)	O(6)-C(18)-C(19)	114.29(16)
C(3)-C(2)-C(26)	128.31(16)	C(17)-C(18)-C(19)	120.55(16)
C(4)-C(3)-C(2)	107.77(14)	C(24)-C(19)-C(20)	118.52(17)
C(4)-C(3)-C(17)	124.81(16)	C(24)-C(19)-C(18)	117.78(17)
C(2)-C(3)-C(17)	127.22(15)	C(20)-C(19)-C(18)	123.65(18)
C(3)-C(4)-N(1)	107.68(15)	C(21)-C(20)-C(19)	120.0(2)
C(3)-C(4)-C(11)	128.56(15)	C(20)-C(21)-C(22)	120.1(2)
N(1)-C(4)-C(11)	123.65(15)	C(23)-C(22)-C(21)	121.2(2)
C(6)-C(5)-C(10)	120.37(19)	C(22)-C(23)-C(24)	118.2(2)
C(6)-C(5)-N(1)	119.98(18)	O(7)-C(24)-C(19)	121.38(15)
C(10)-C(5)-N(1)	119.60(18)	O(7)-C(24)-C(23)	116.64(18)
C(5)-C(6)-C(7)	118.8(2)	C(19)-C(24)-C(23)	121.97(19)
C(8)-C(7)-C(6)	123.4(3)	O(5)-C(25)-O(7)	115.02(16)
C(8)-C(7)-Cl(1)	120.2(2)	O(5)-C(25)-C(17)	126.80(16)
C(6)-C(7)-Cl(1)	116.0(3)	O(7)-C(25)-C(17)	118.18(16)
C(7)-C(8)-C(9)	116.1(2)	O(1)-C(26)-O(2)	123.70(19)
C(7)-C(8)-C(33)	122.9(3)	O(1)-C(26)-C(2)	125.28(18)
C(9)-C(8)-C(33)	121.0(3)	O(2)-C(26)-C(2)	111.00(17)
C(8)-C(9)-C(10)	122.5(2)	O(2)-C(27)-C(28)	106.6(2)
C(8)-C(9)-Cl(1')	120.2(2)	O(3)-C(29)-O(4)	124.00(18)
C(10)-C(9)-Cl(1')	117.2(3)	O(3)-C(29)-C(1)	125.48(19)
C(5)-C(10)-C(9)	118.8(2)	O(4)-C(29)-C(1)	110.48(17)
C(12)-C(11)-C(16)	117.85(19)	O(4)-C(30)-C(31)	107.8(2)
C(12)-C(11)-C(4)	122.30(17)	C(26)-O(2)-C(27)	117.07(17)
C(16)-C(11)-C(4)	119.70(17)	C(29)-O(4)-C(30)	116.82(17)
C(13)-C(12)-C(11)	120.8(2)	C(18)-O(6)-H(6)	114.0(16)
C(14)-C(13)-C(12)	120.7(2)	C(24)-O(7)-C(25)	121.73(15)

Copies of ^{1}H NMR and ^{13}C NMR of compounds 5 amd 7

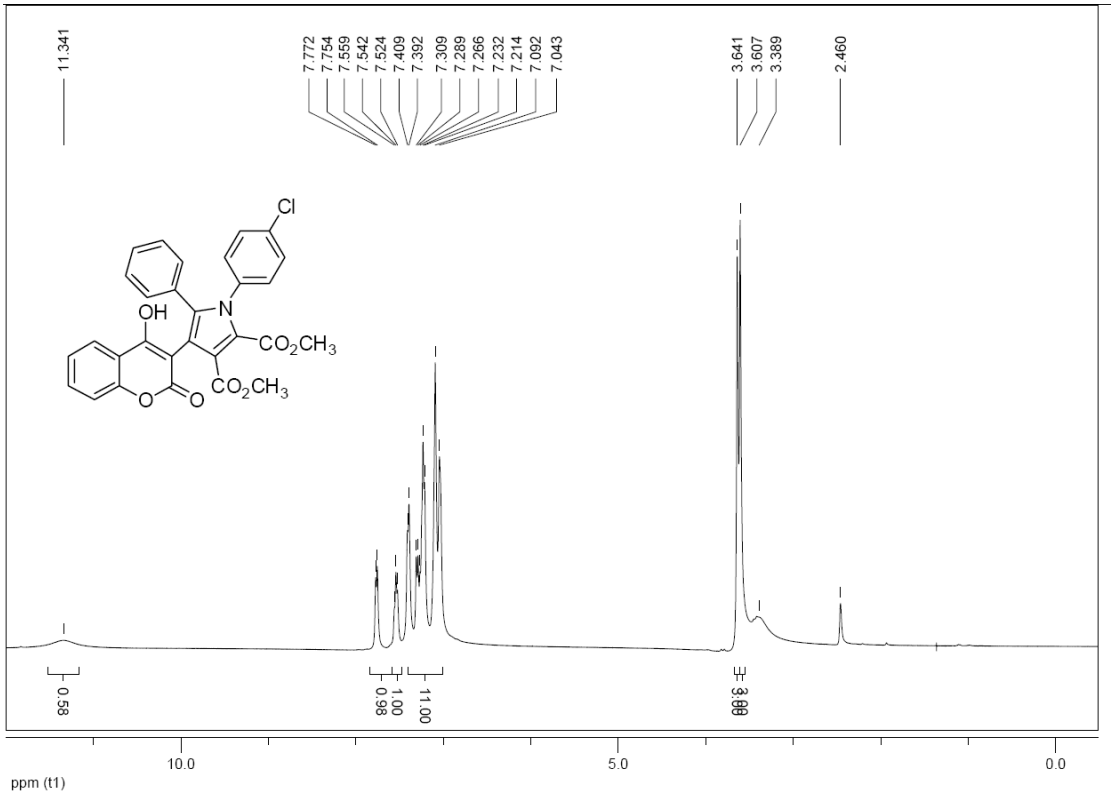
^{1}H NMR spectrum of compound **5a**



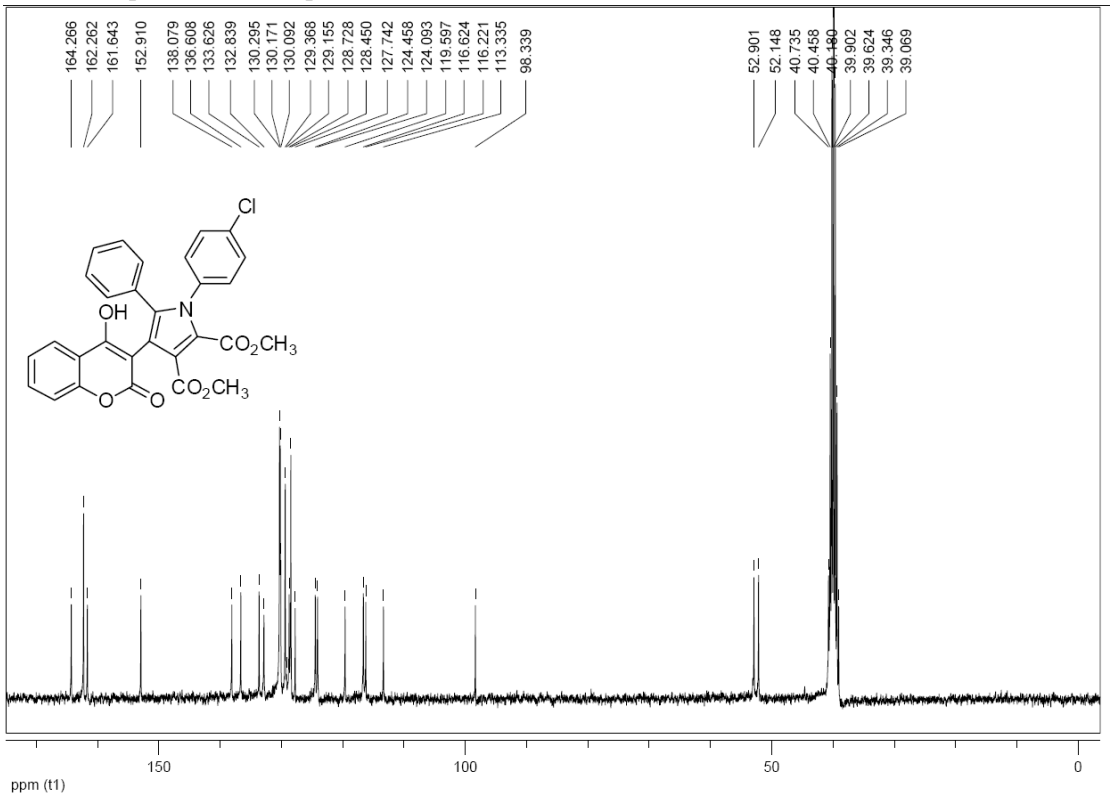
^{13}C NMR spectrum of compound **5a**



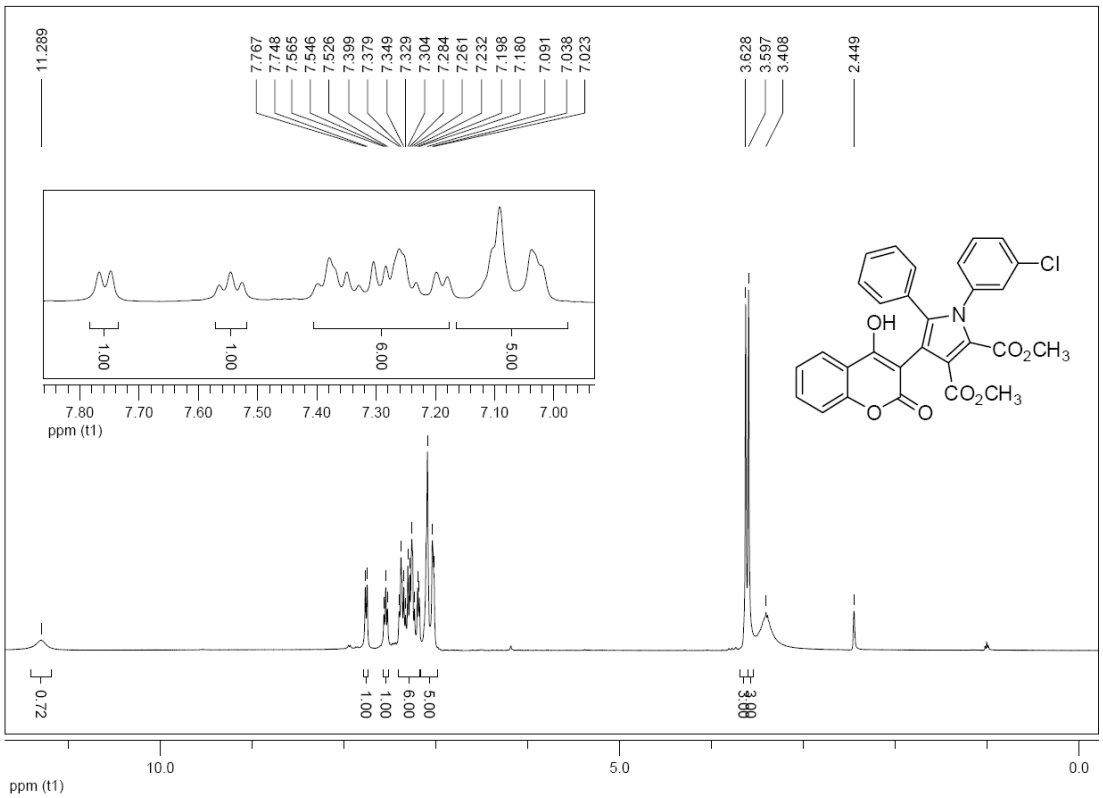
^{1}H NMR spectrum of compound **5b**



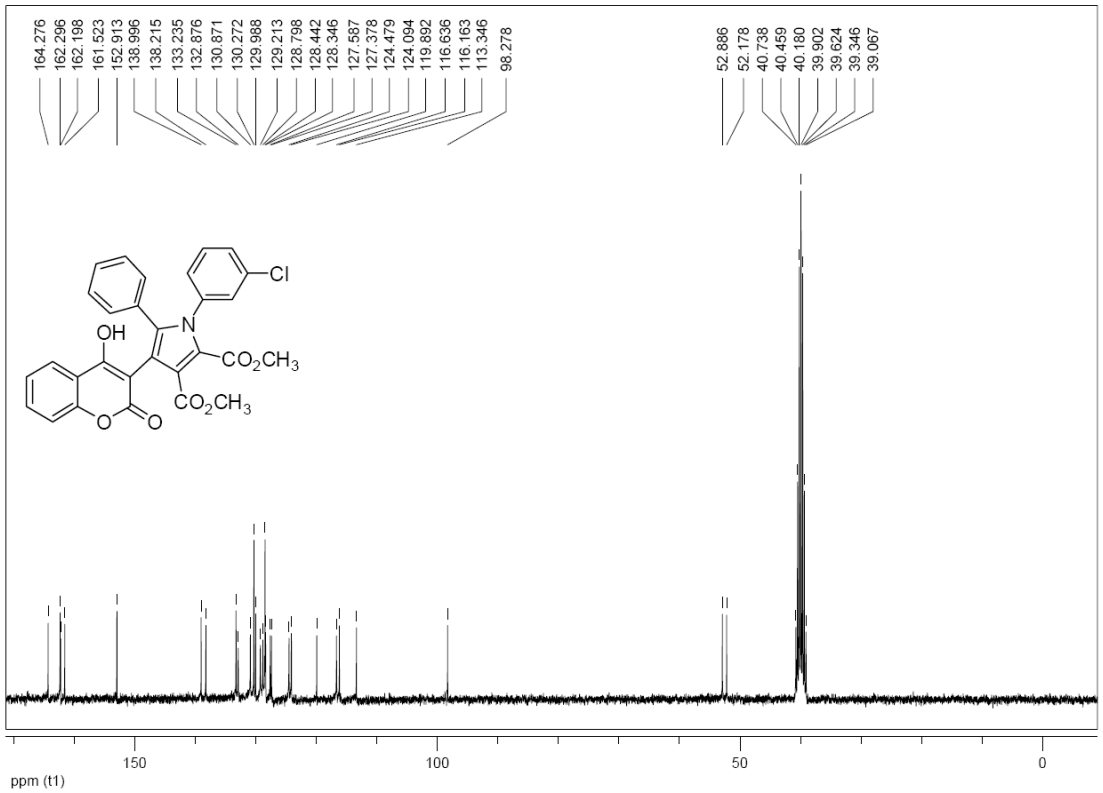
^{13}C NMR spectrum of compound **5b**



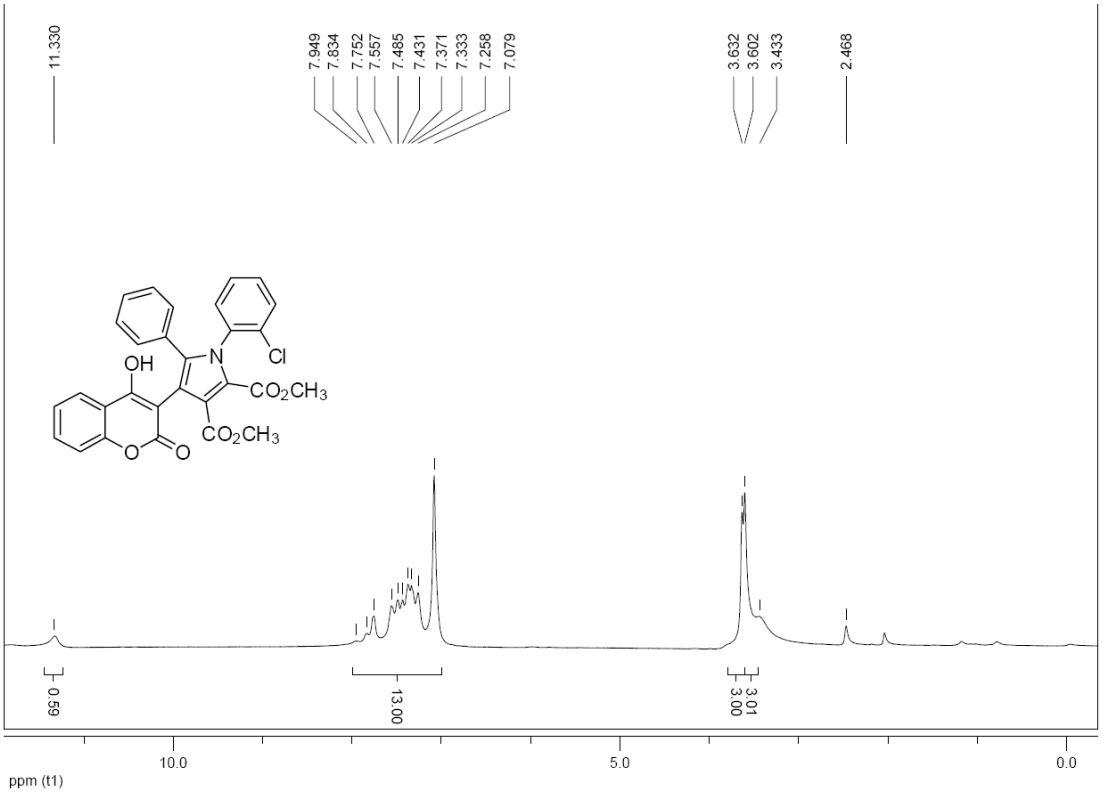
^{1}H NMR spectrum of compound **5c**



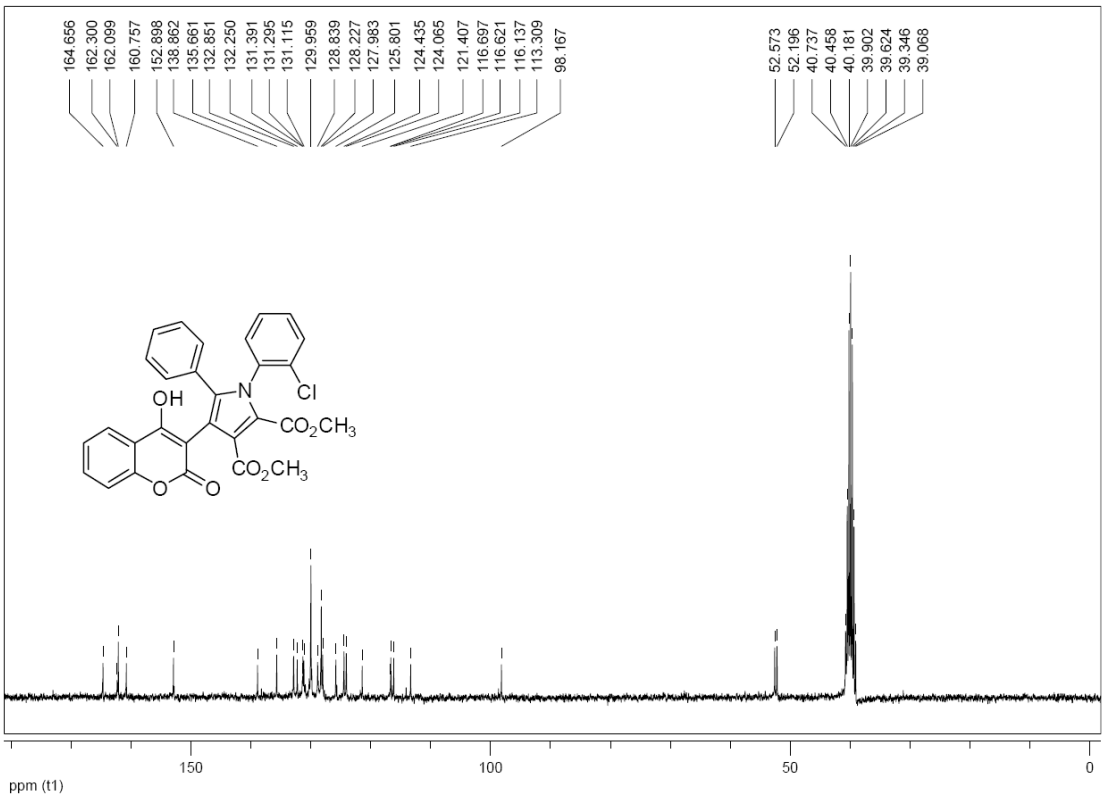
^{13}C NMR spectrum of compound **5c**



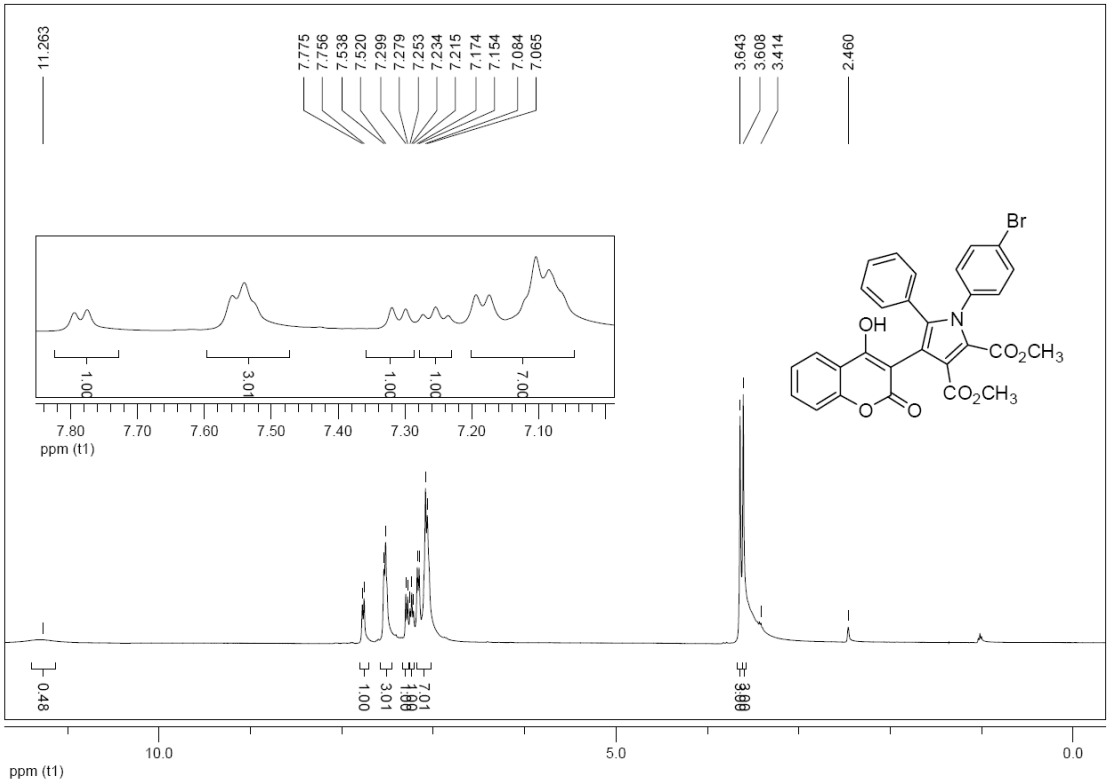
^{1}H NMR spectrum of compound **5d**



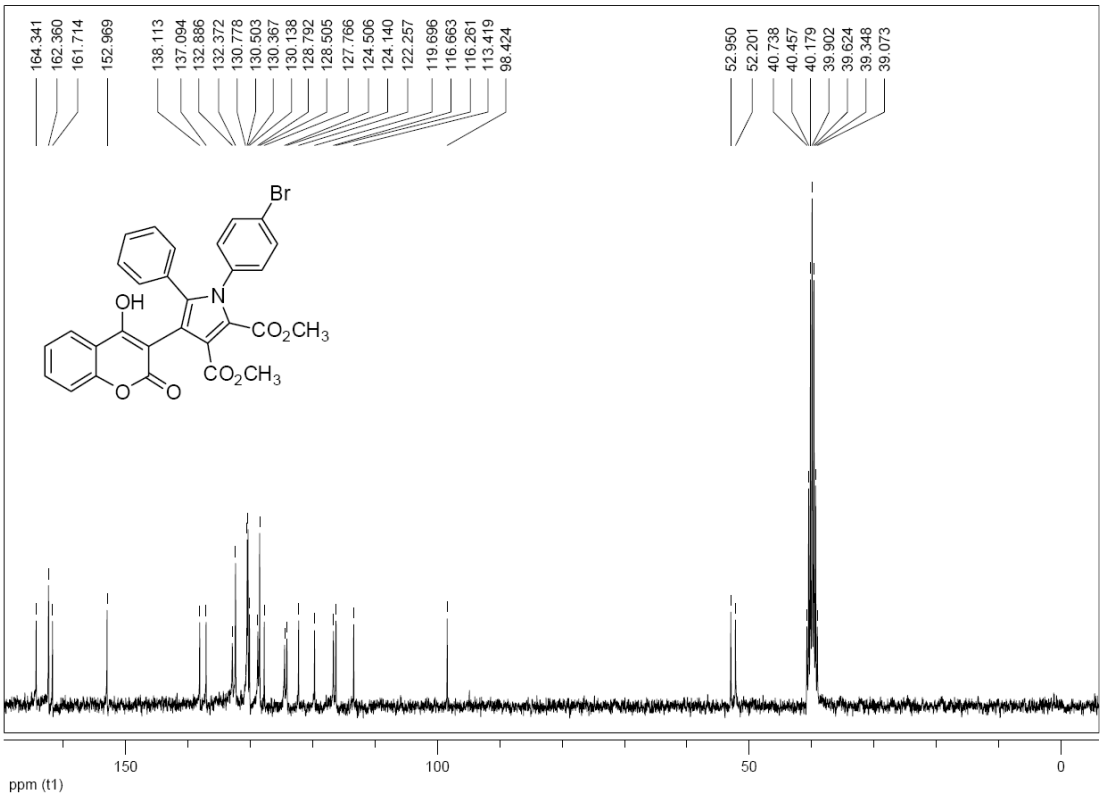
^{13}C NMR spectrum of compound **5d**



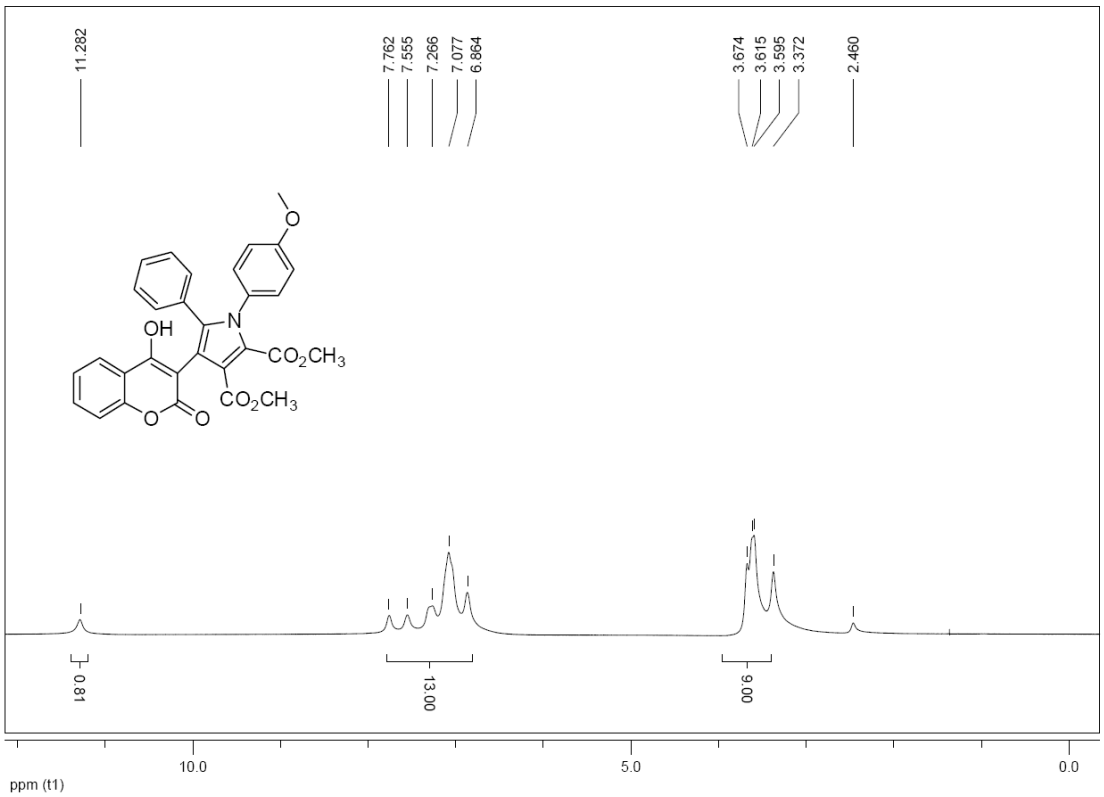
^{1}H NMR spectrum of compound **5e**



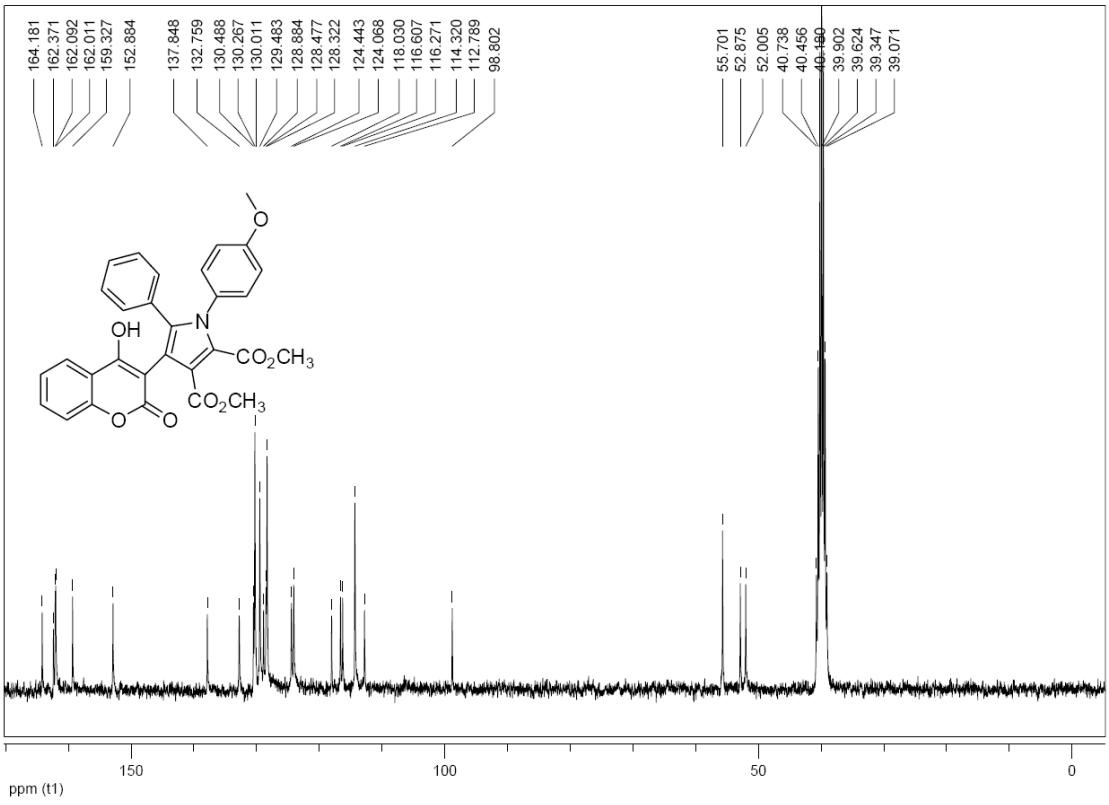
^{13}C NMR spectrum of compound **5e**



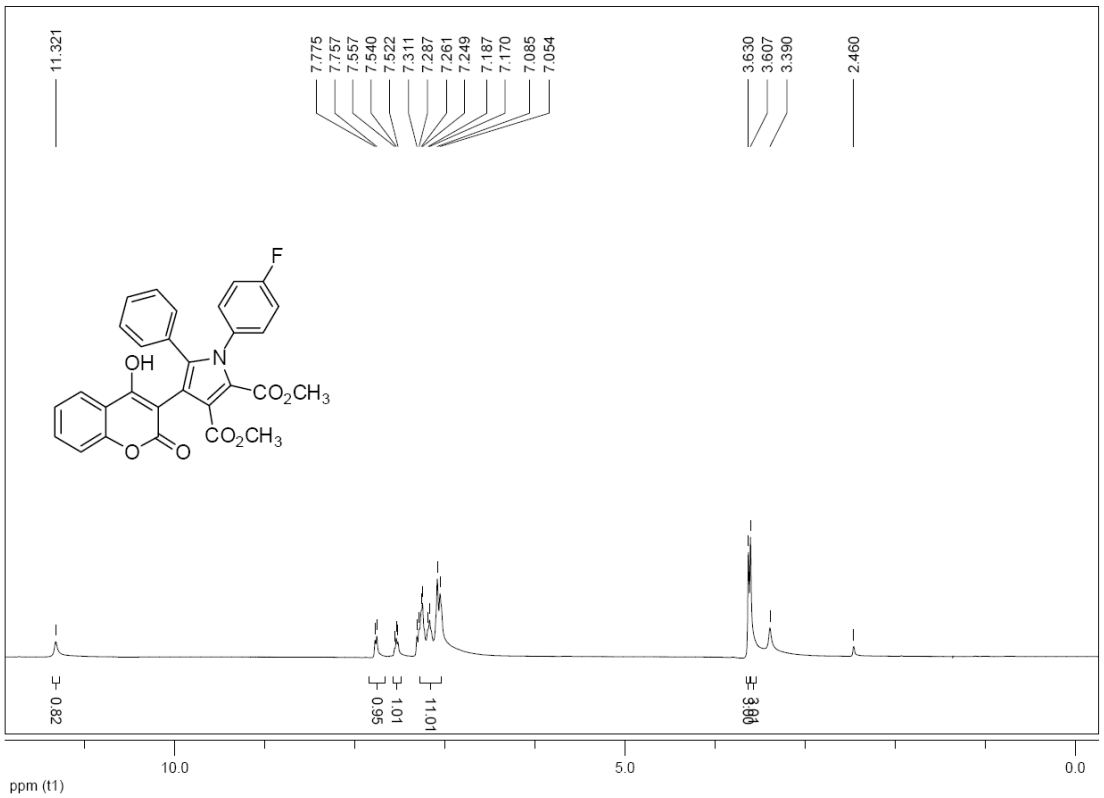
^{1}H NMR spectrum of compound **5f**



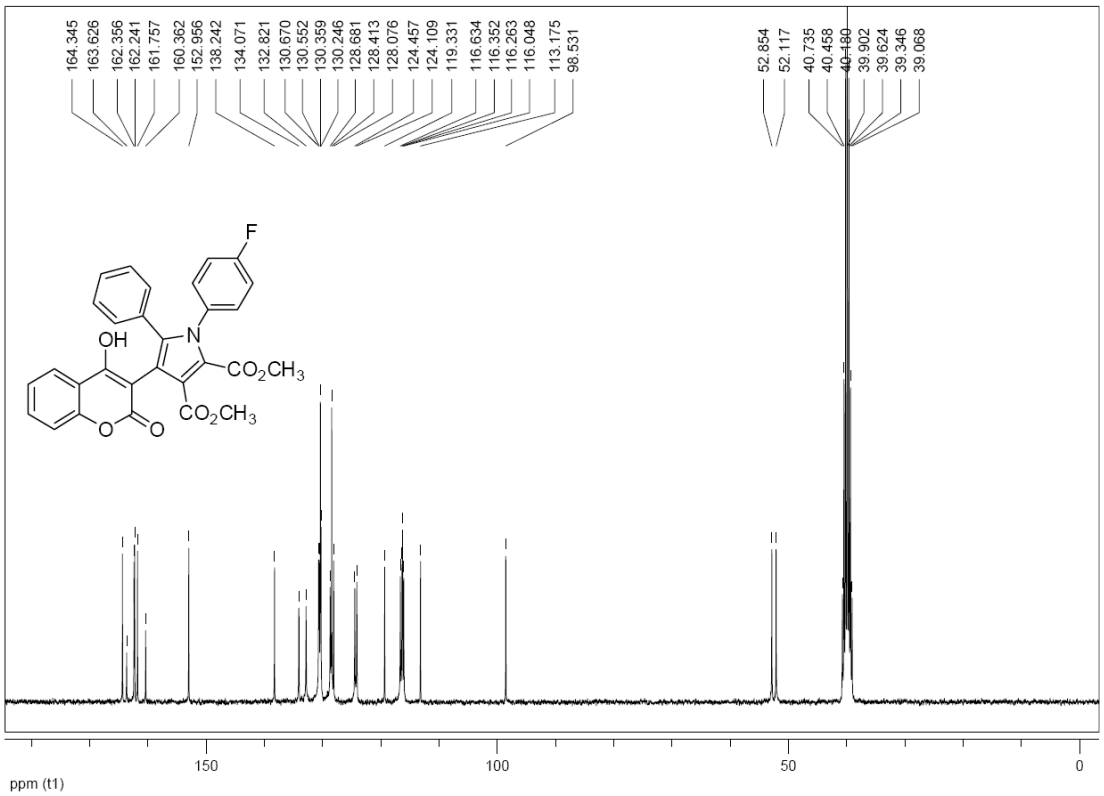
^{13}C NMR spectrum of compound **5f**



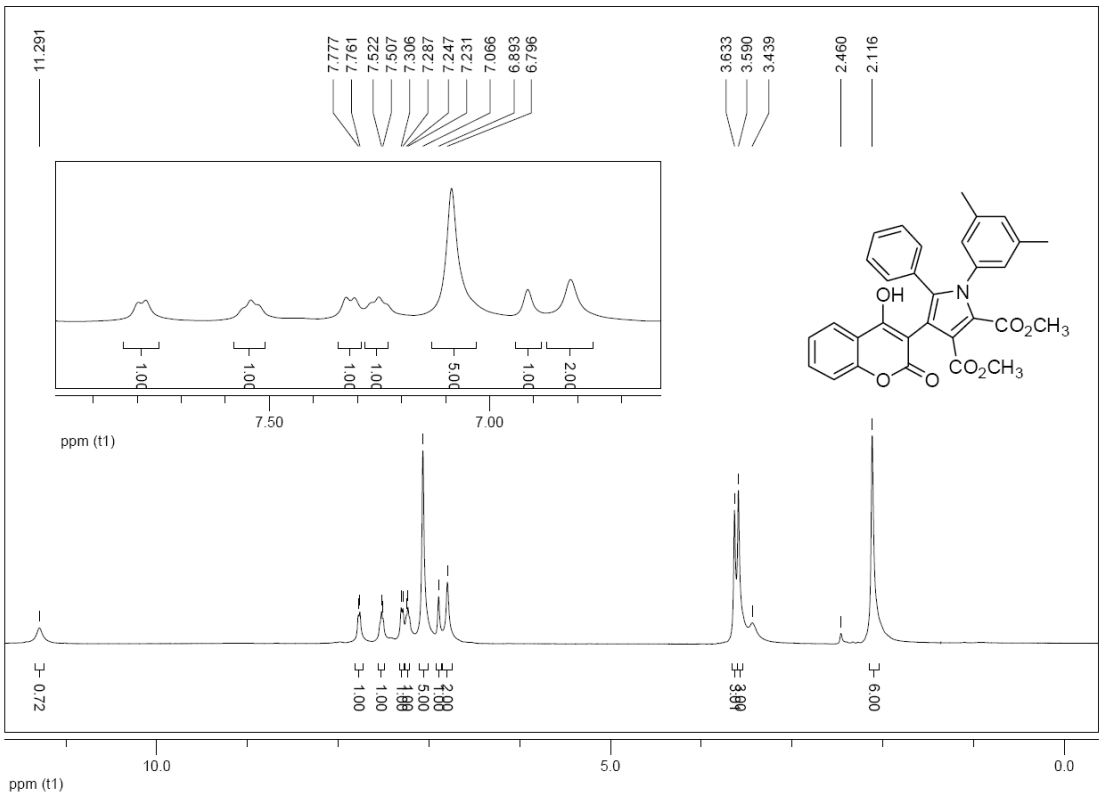
^{1}H NMR spectrum of compound **5g**



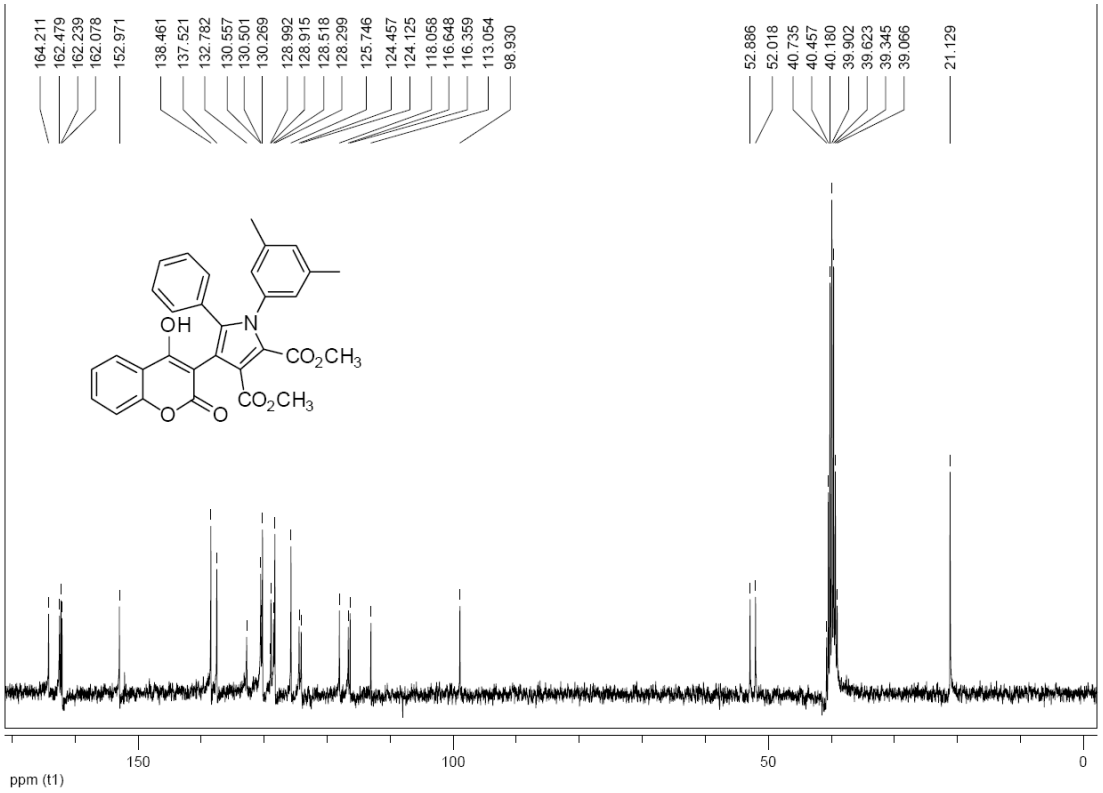
^{13}C NMR spectrum of compound **5g**



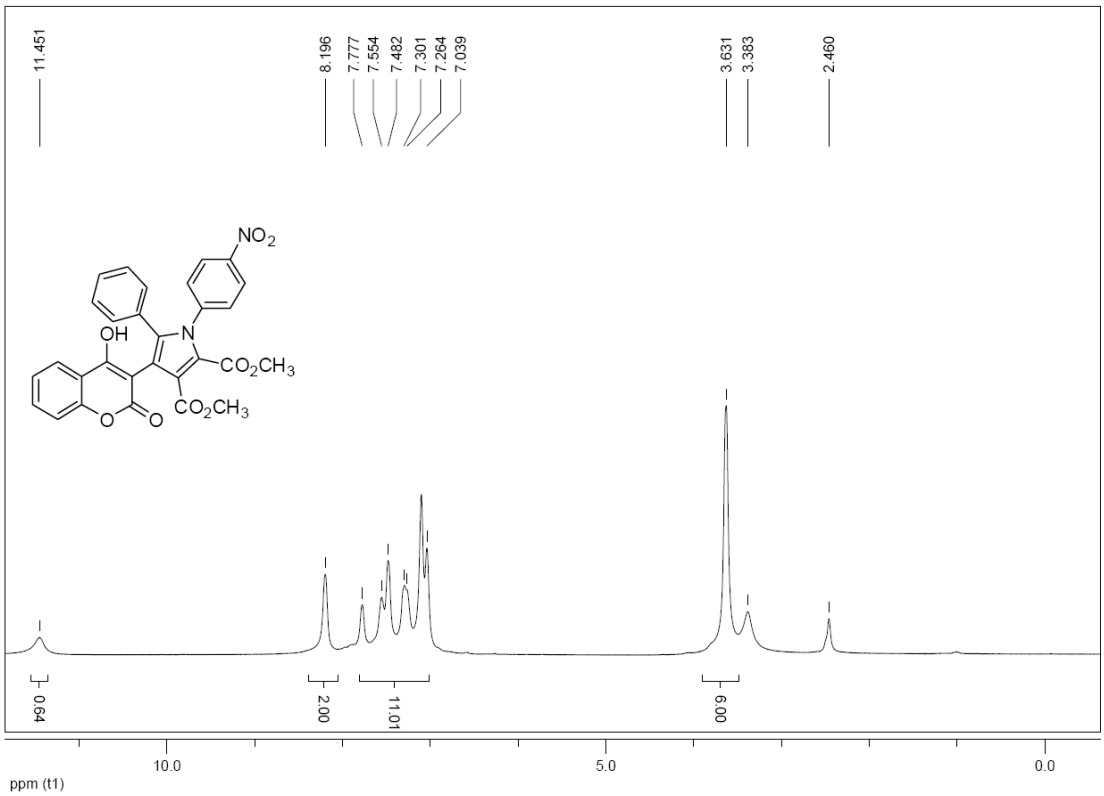
^{1}H NMR spectrum of compound **5h**



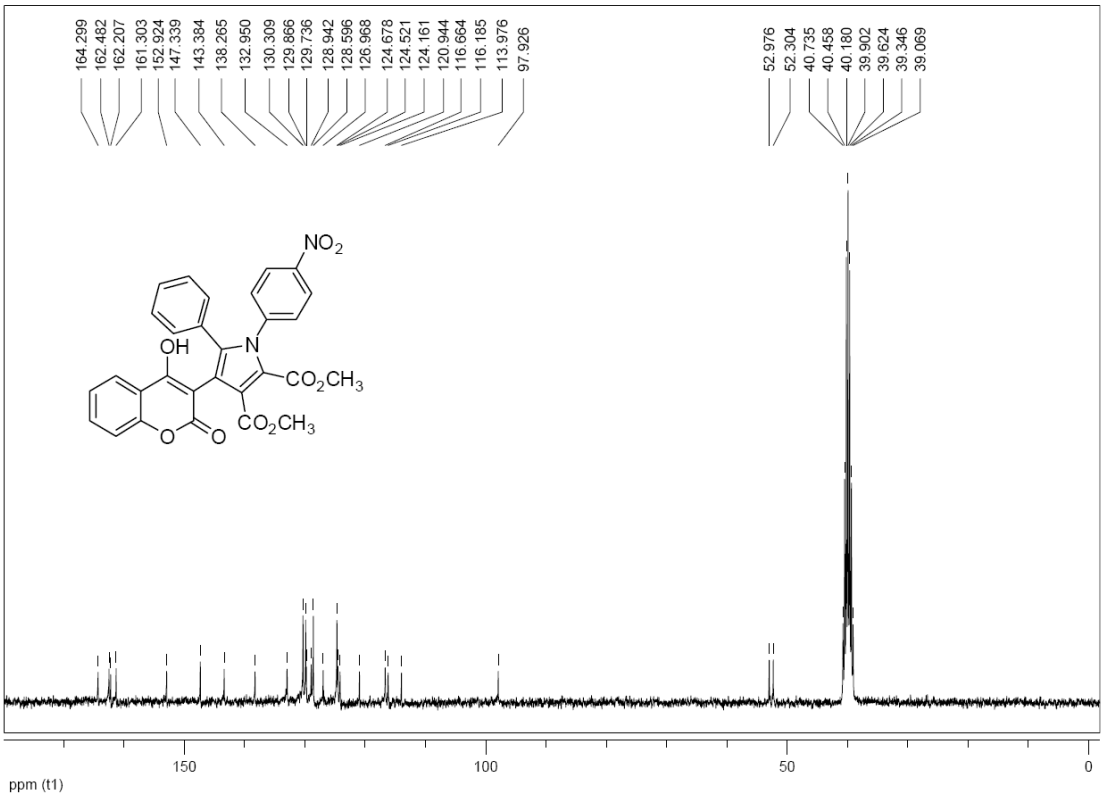
^{13}C NMR spectrum of compound **5h**



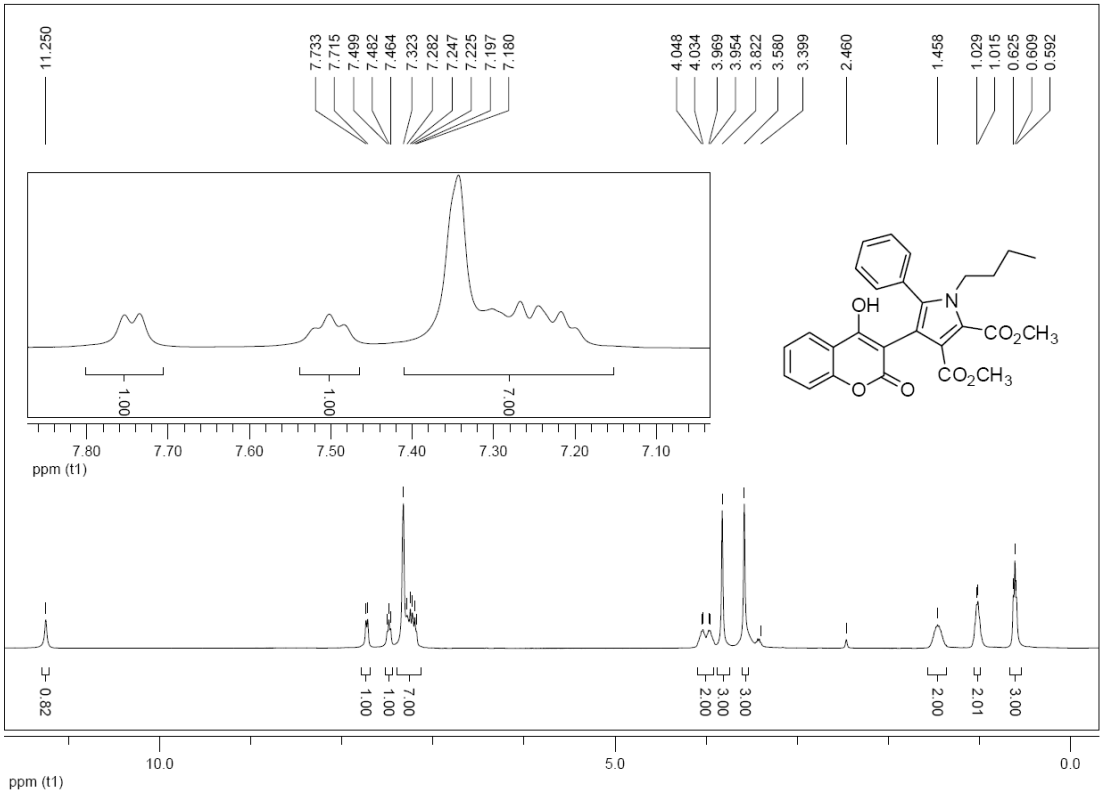
^{1}H NMR spectrum of compound **5i**



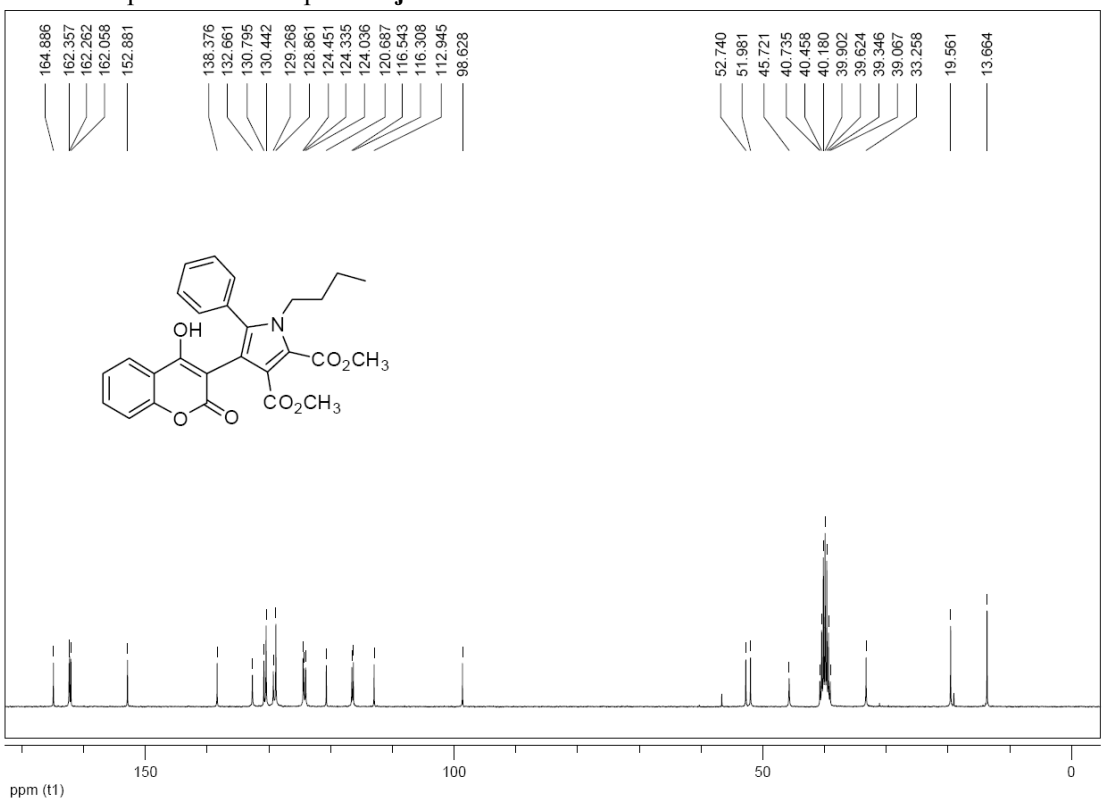
^{13}C NMR spectrum of compound **5i**



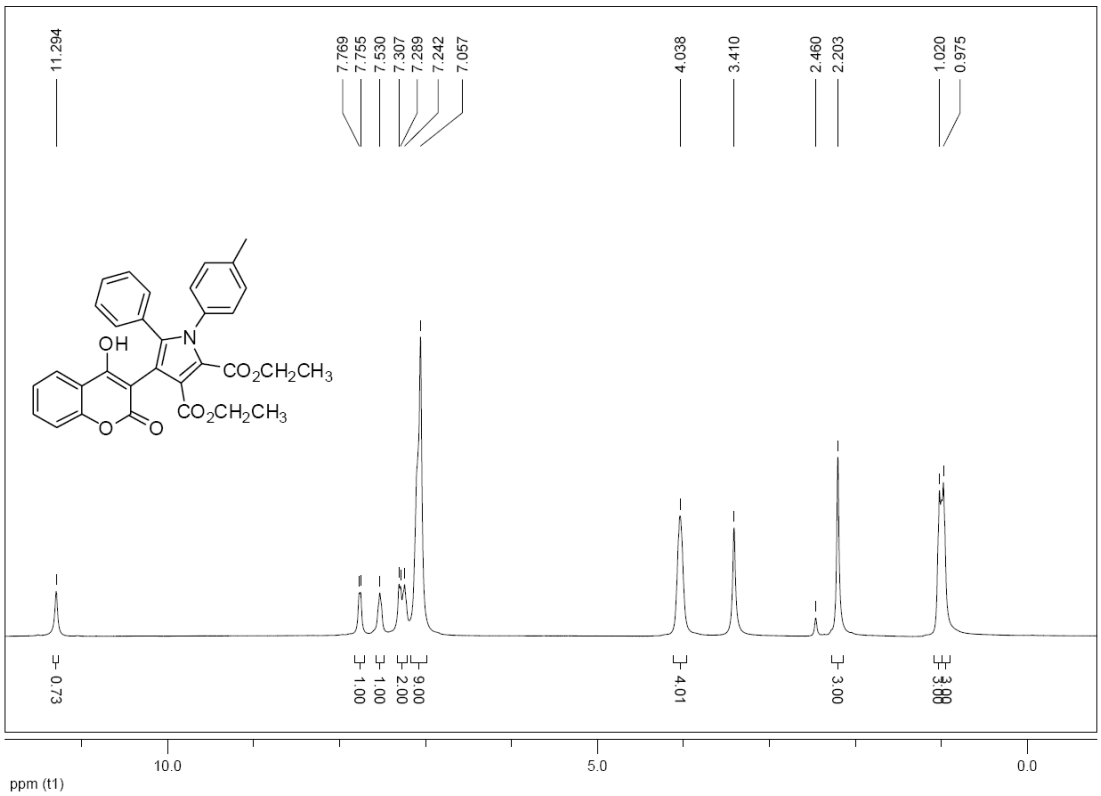
^{1}H NMR spectrum of compound **5j**



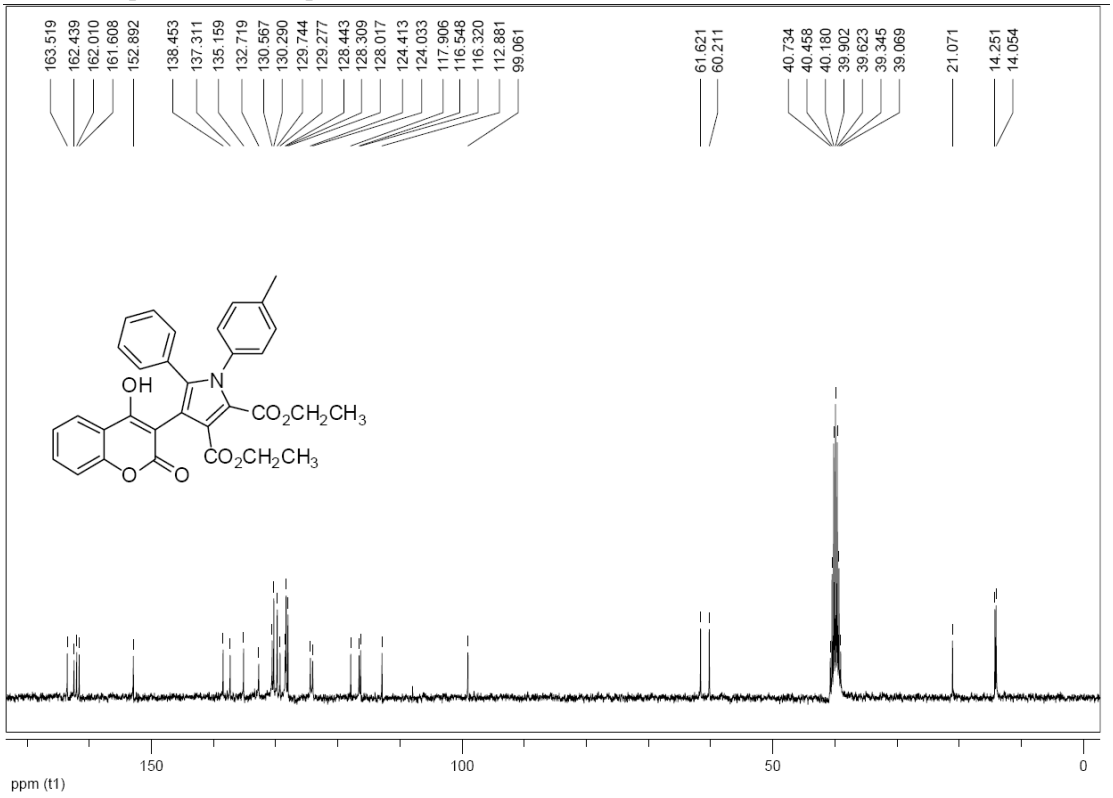
^{13}C NMR spectrum of compound **5j**



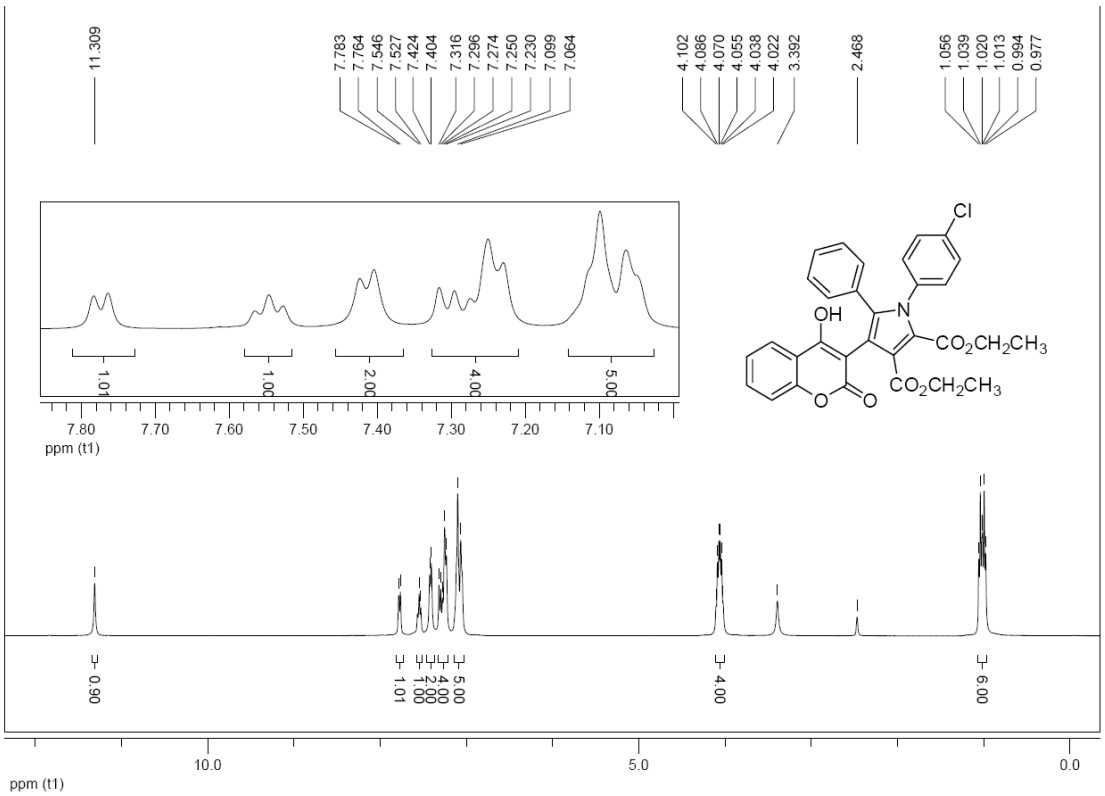
^{1}H NMR spectrum of compound **5k**



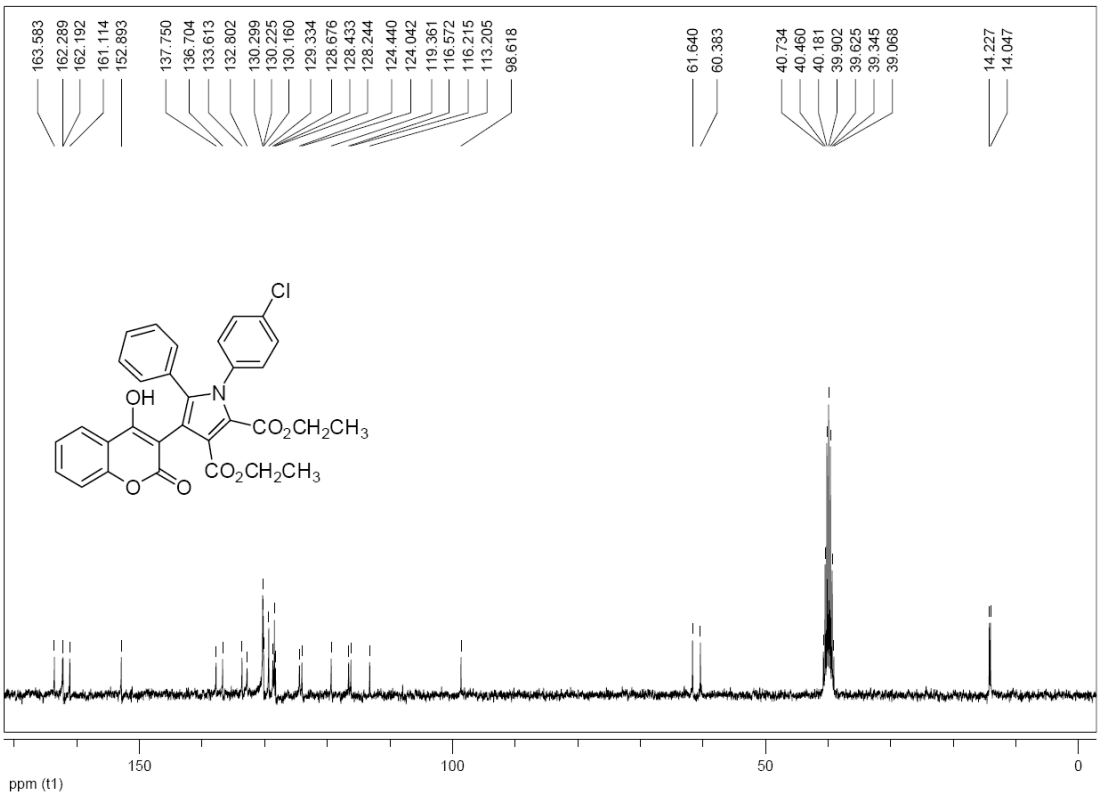
^{13}C NMR spectrum of compound **5k**



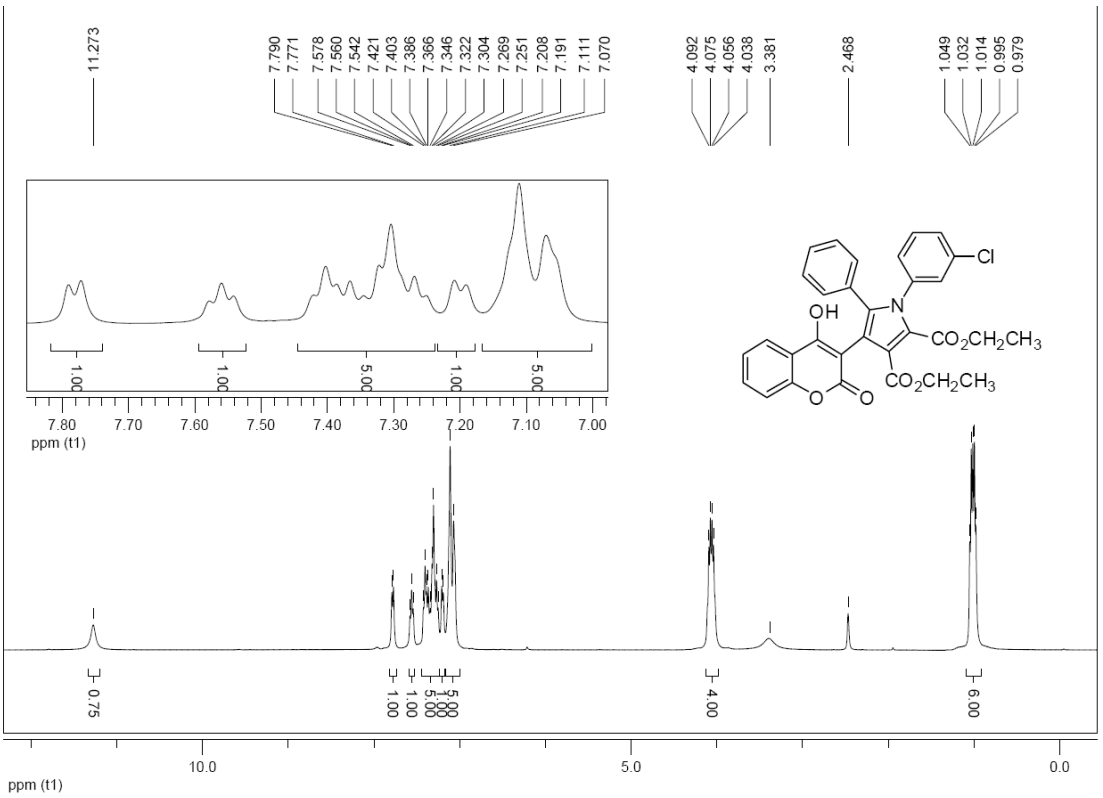
^{1}H NMR spectrum of compound **5l**



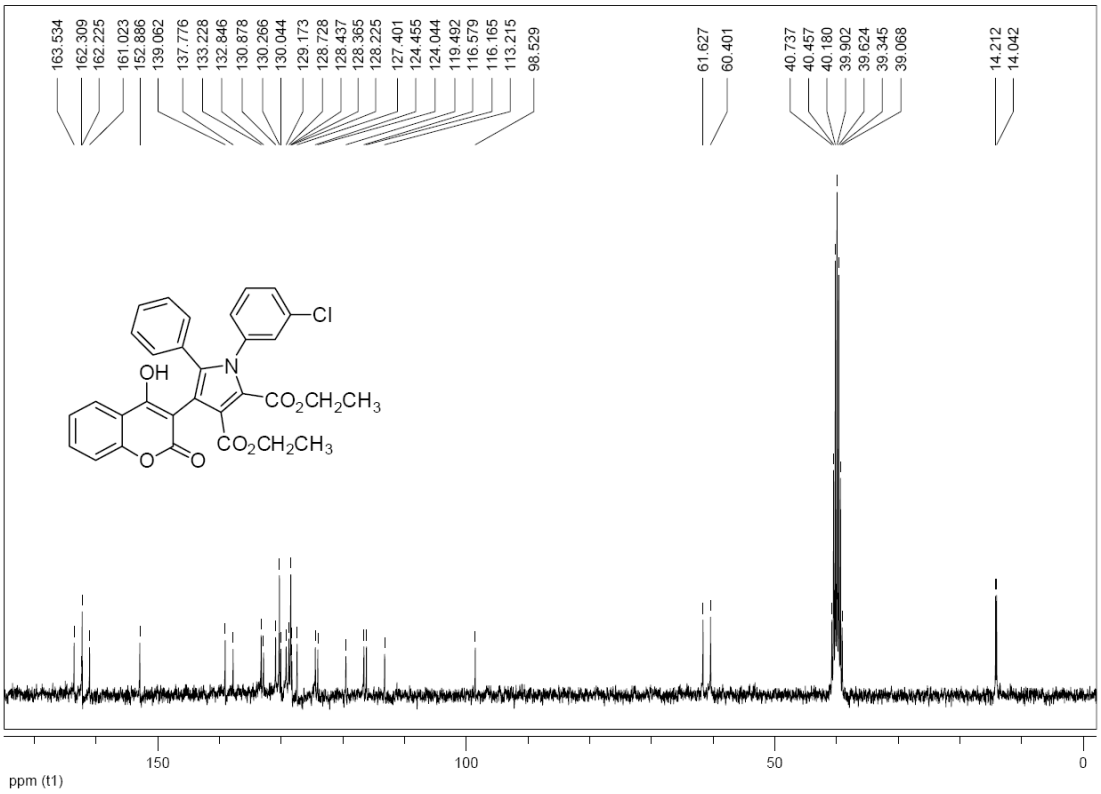
^{13}C NMR spectrum of compound **5l**



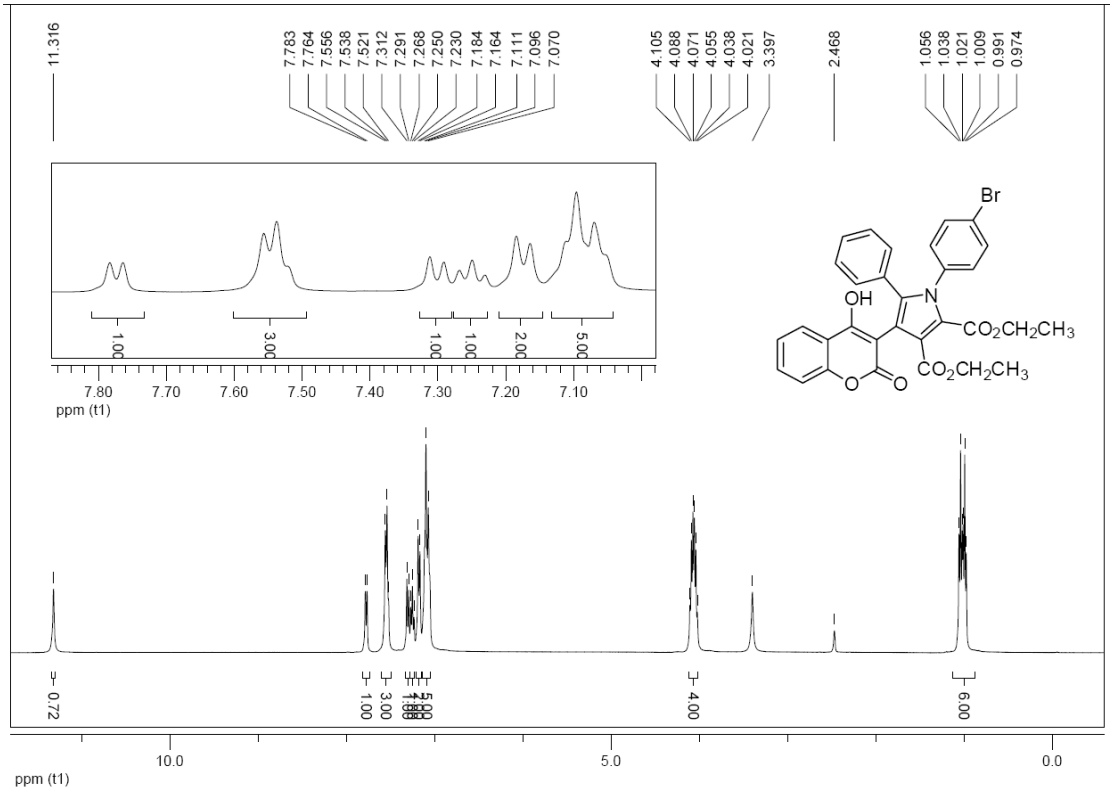
^{1}H NMR spectrum of compound **5m**



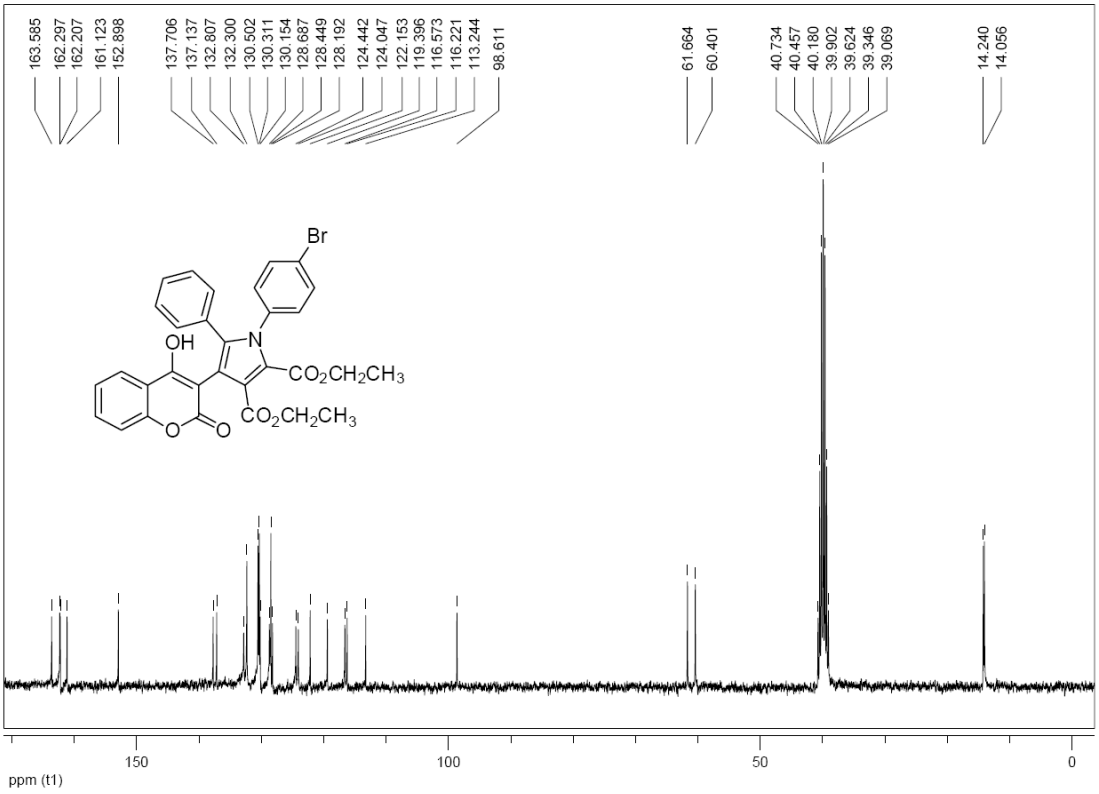
^{13}C NMR spectrum of compound **5m**



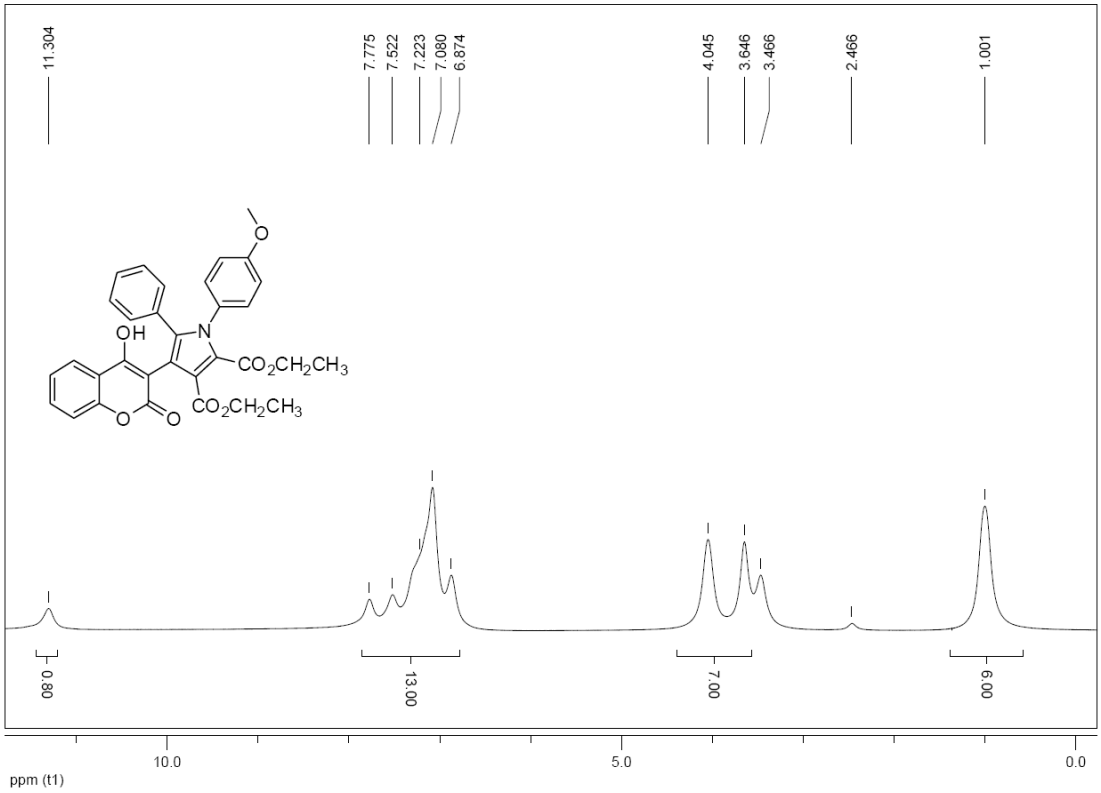
^{1}H NMR spectrum of compound **5n**



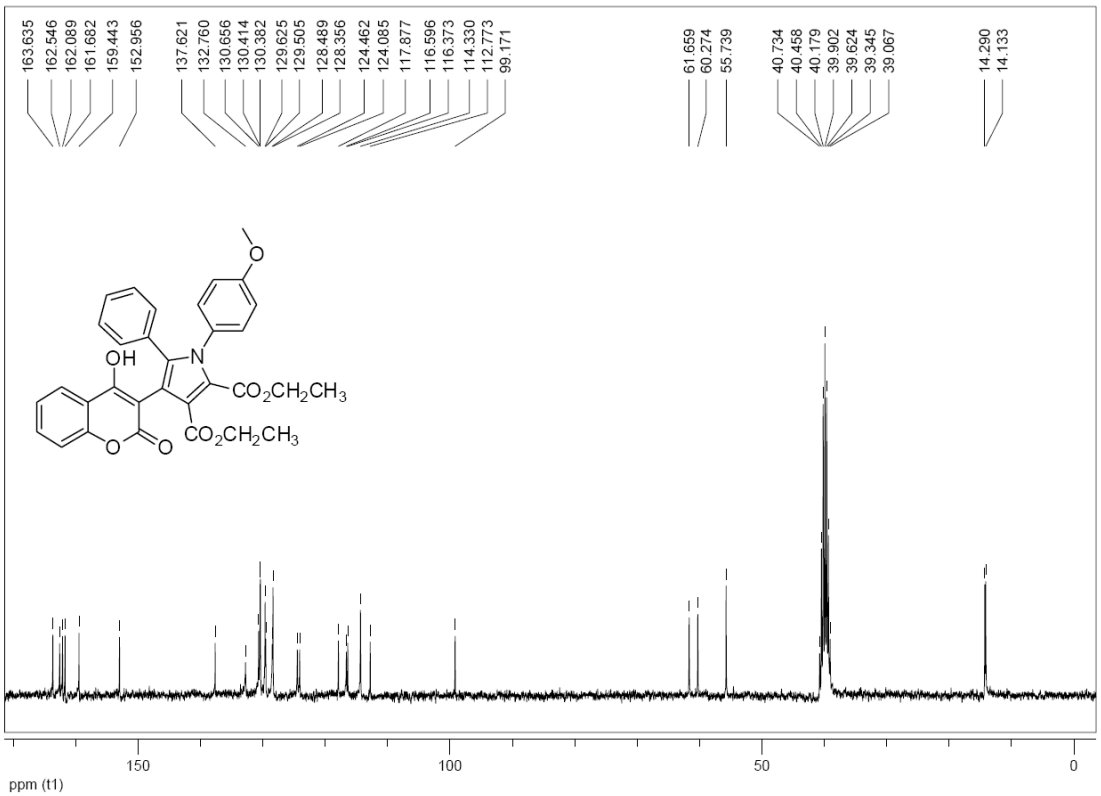
^{13}C NMR spectrum of compound **5n**



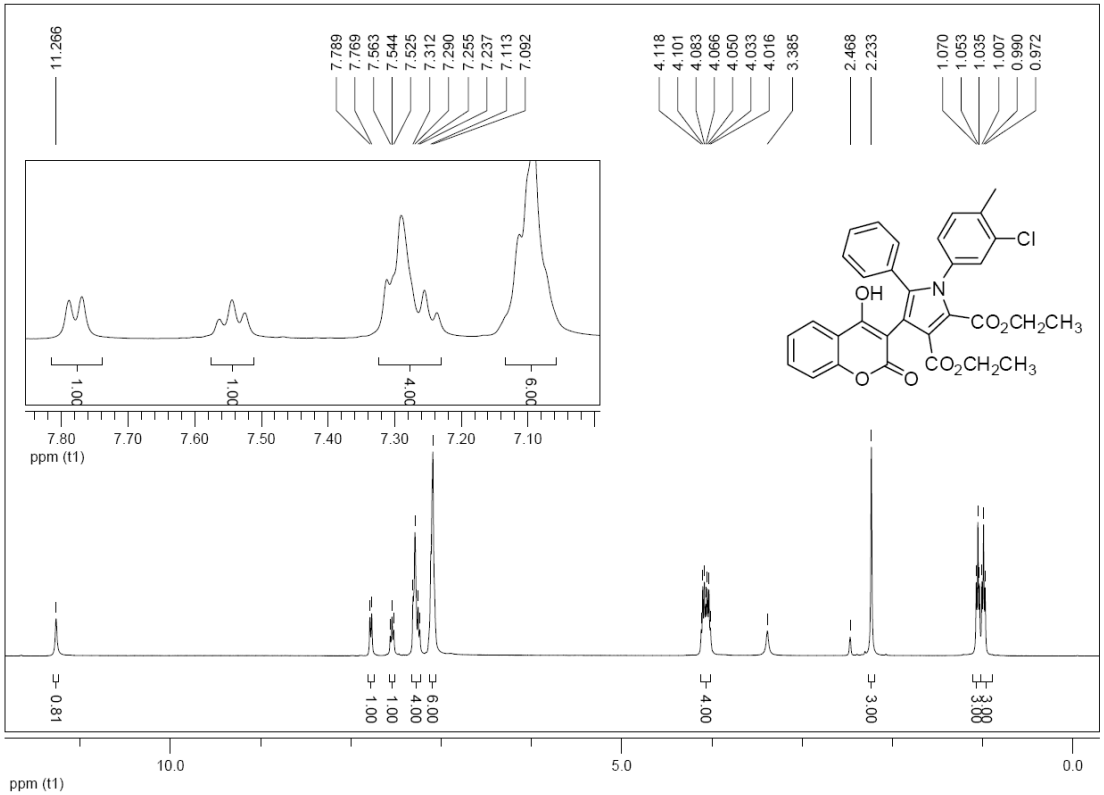
NMR spectrum of compound **5o**



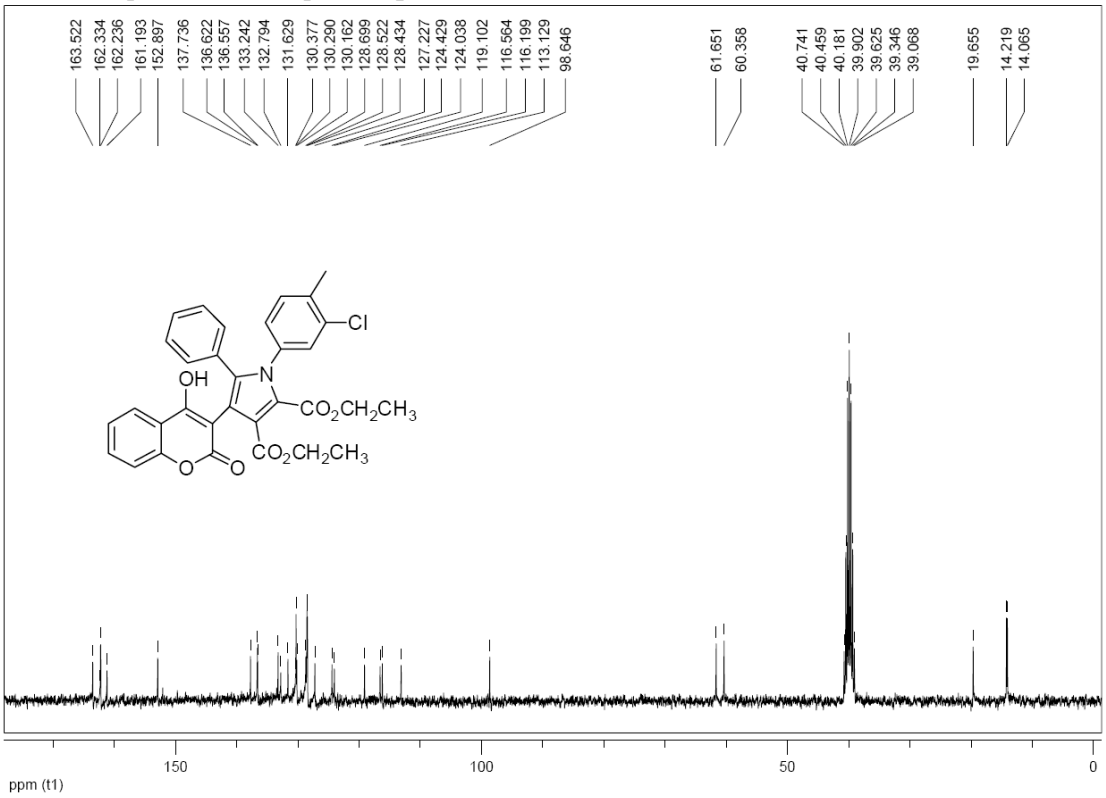
^{13}C NMR spectrum of compound **5o**



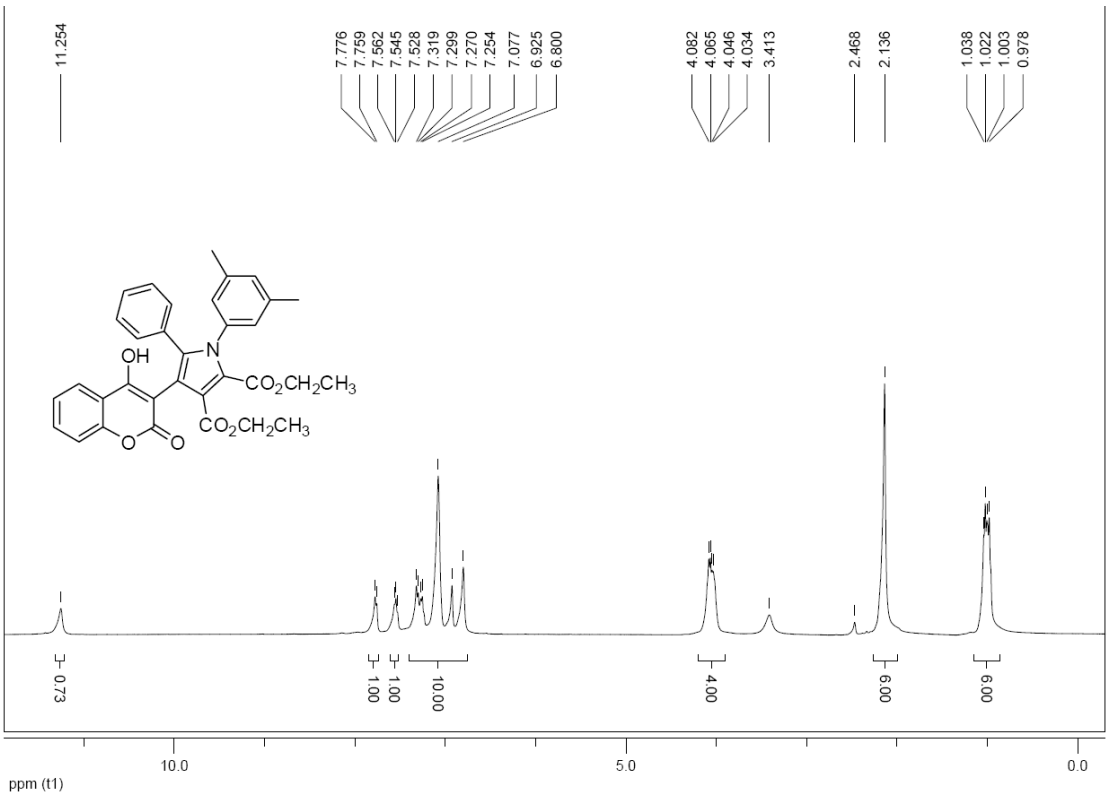
^{1}H NMR spectrum of compound **5p**



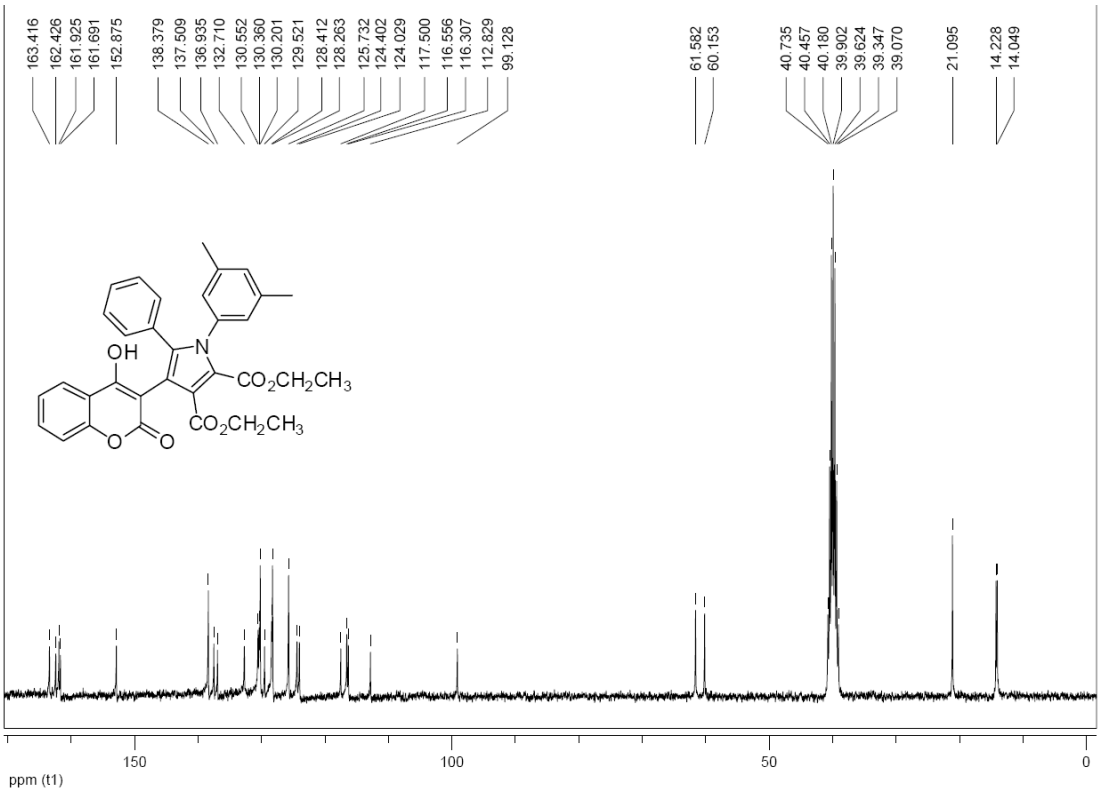
^{13}C NMR spectrum of compound **5p**



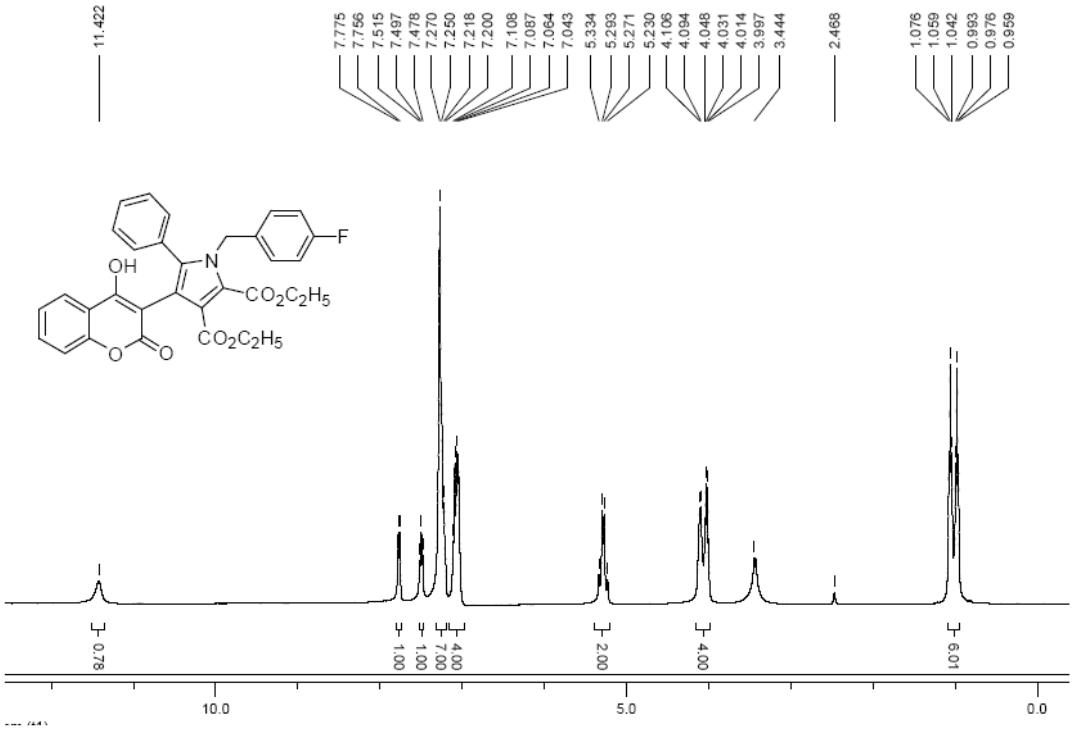
^{1}H NMR spectrum of compound **5q**



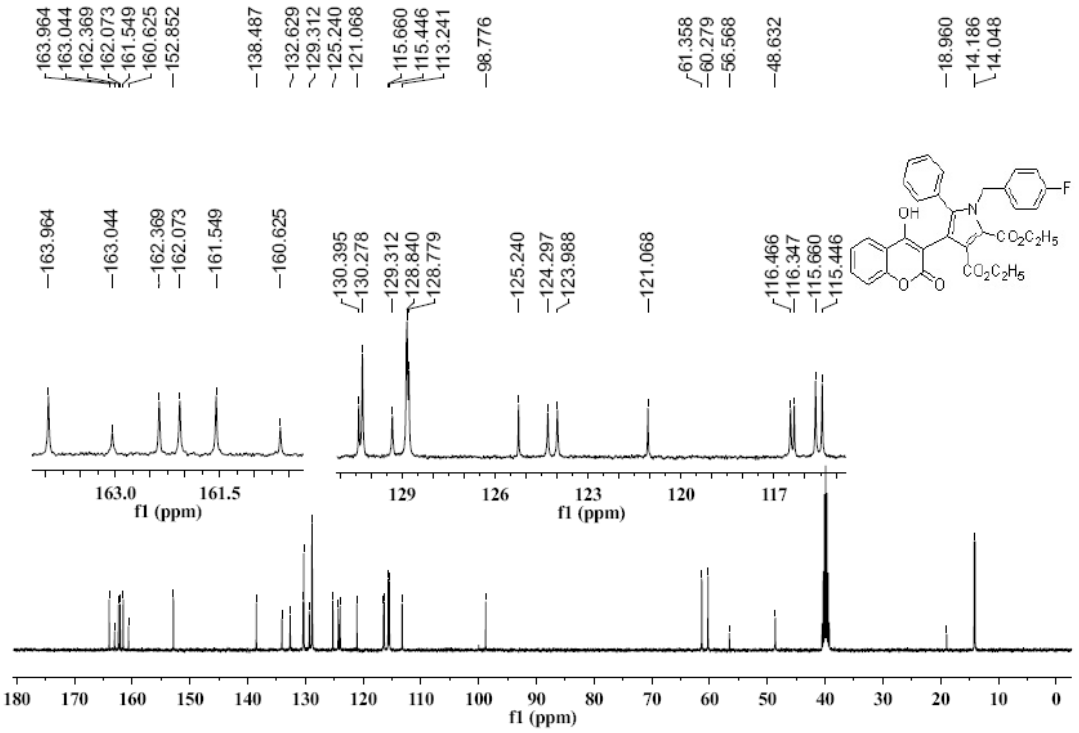
^{13}C NMR spectrum of compound **5q**



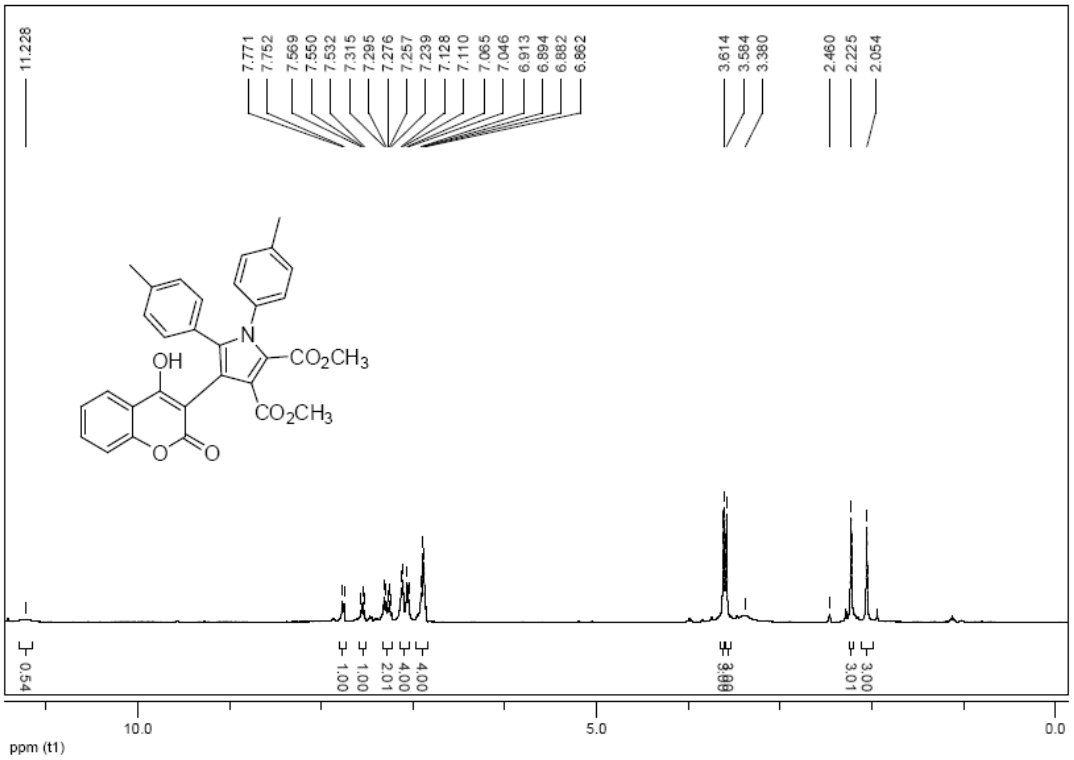
^{1}H NMR spectrum of compound **5r**



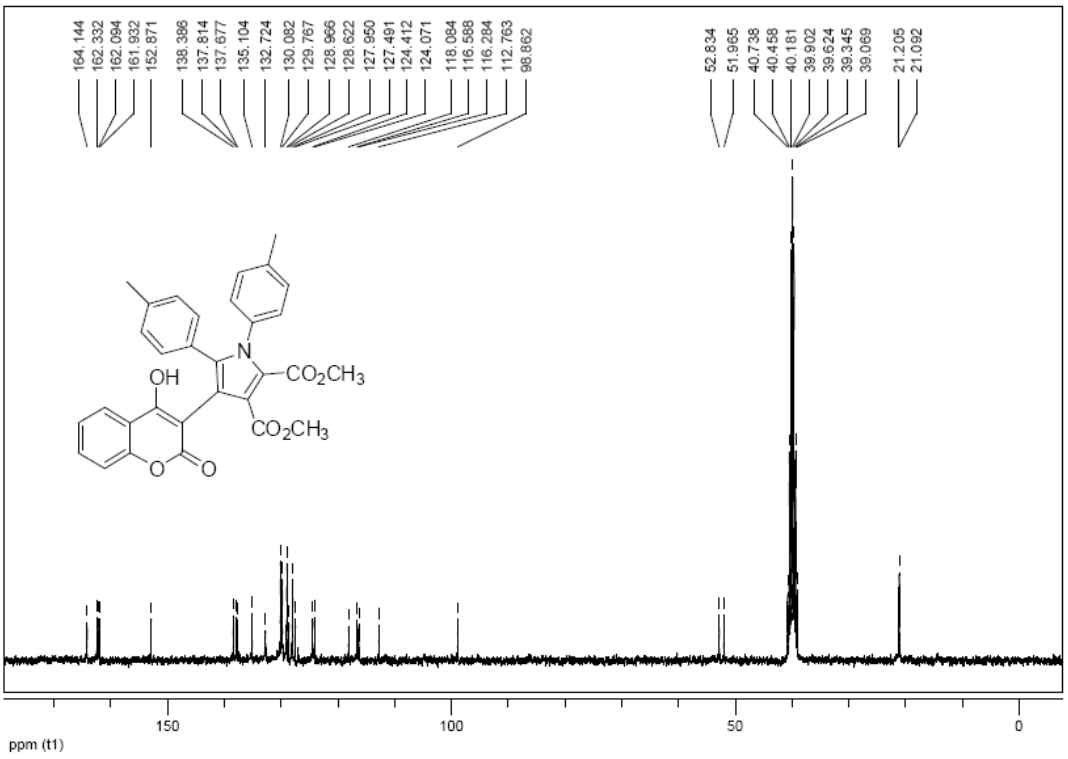
^{13}C NMR spectrum of compound **5r**



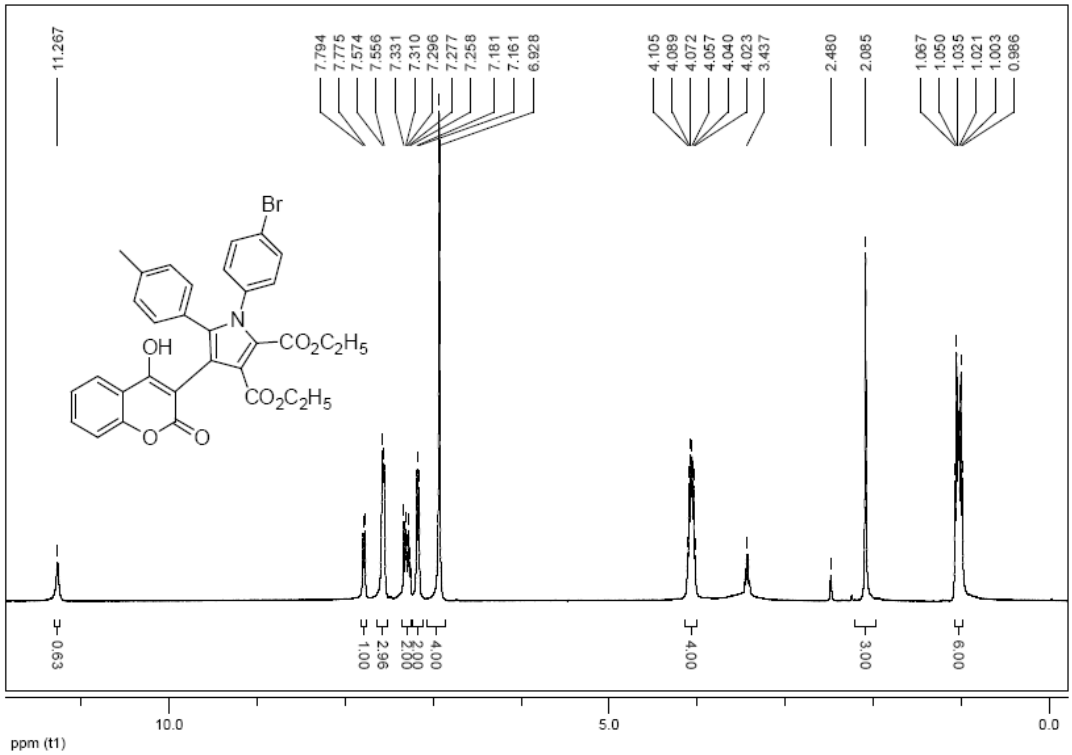
^{1}H NMR spectrum of compound **5s**



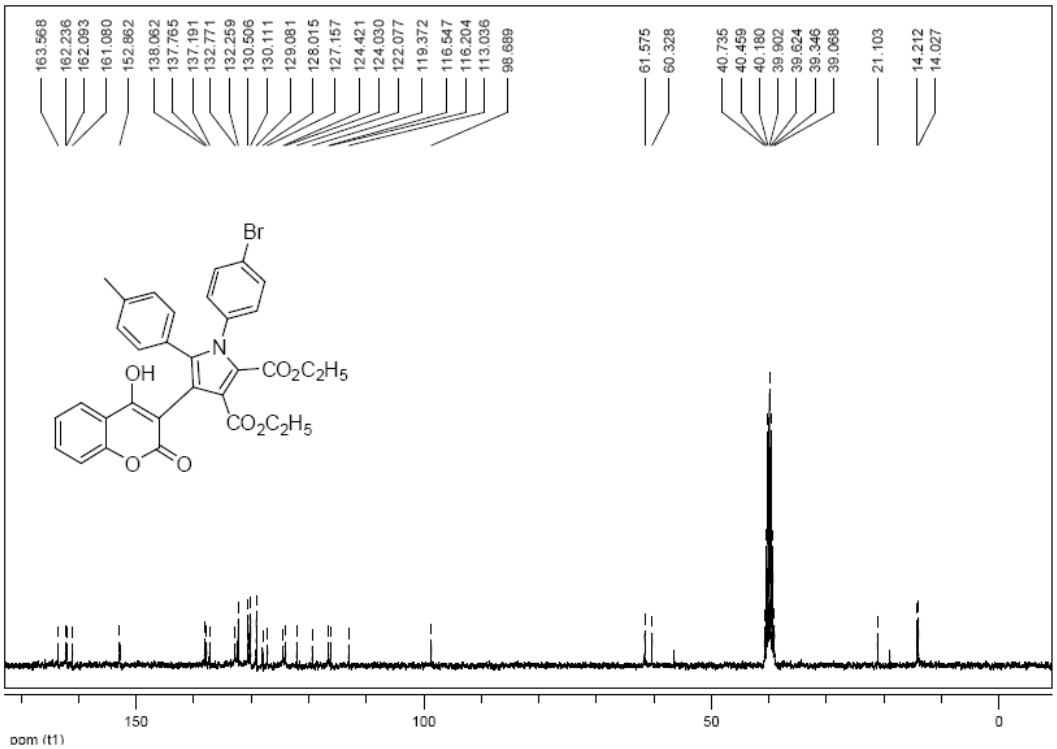
^{13}C NMR spectrum of compound **5s**



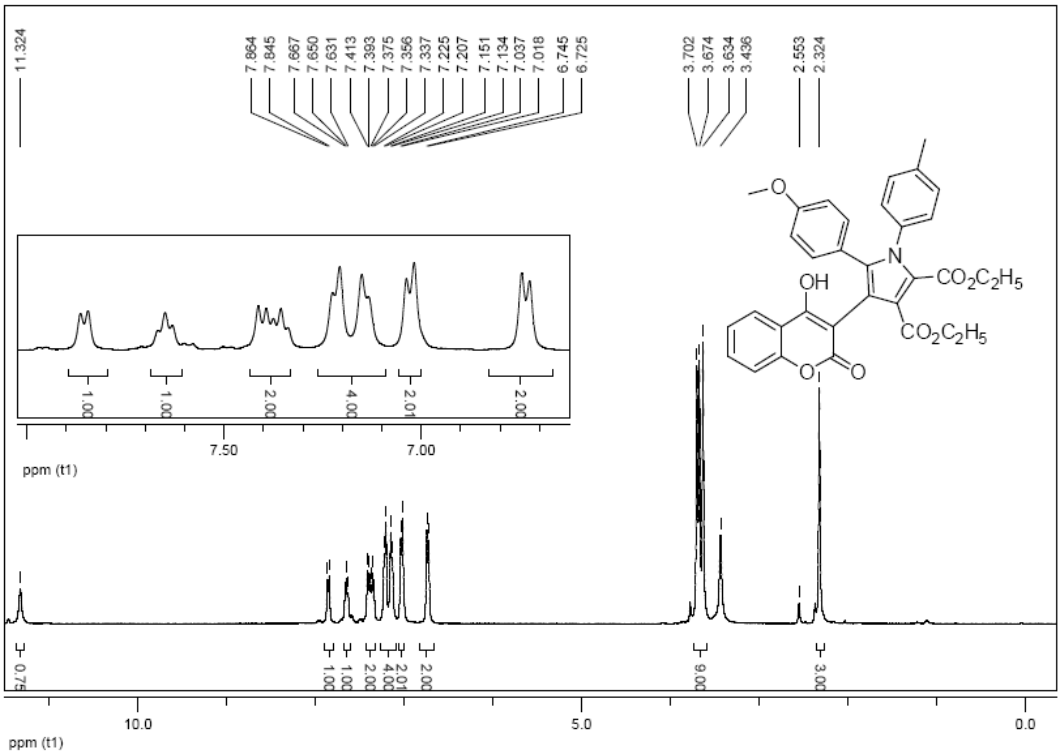
^{1}H NMR spectrum of compound **5t**



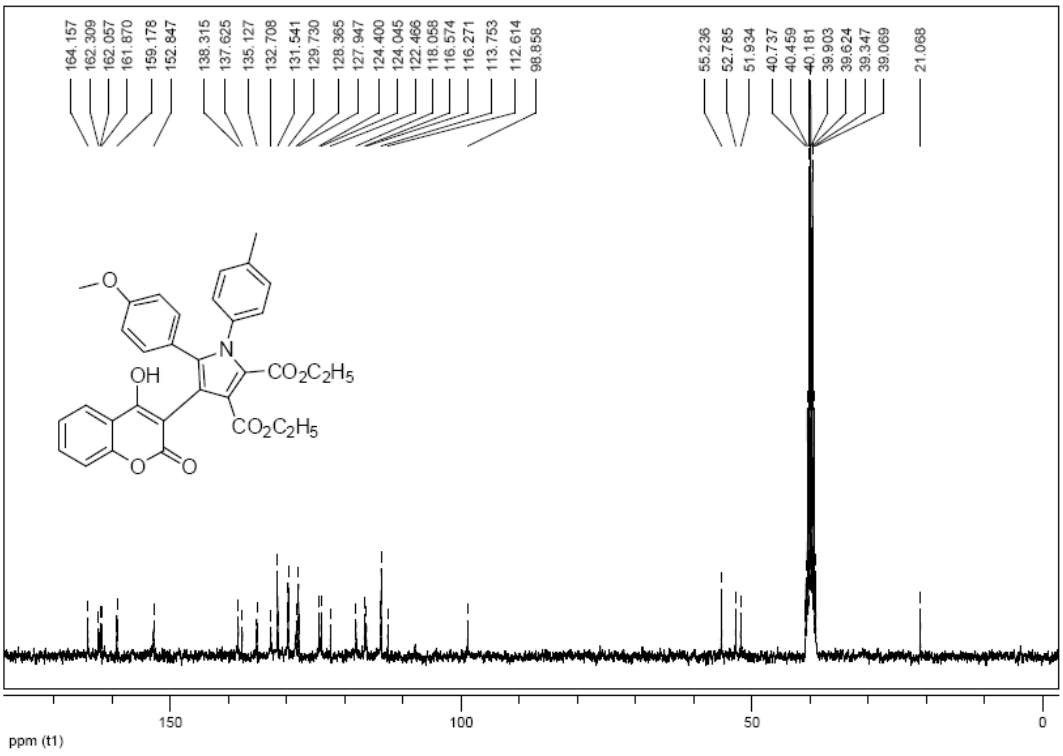
^{13}C NMR spectrum of compound **5t**



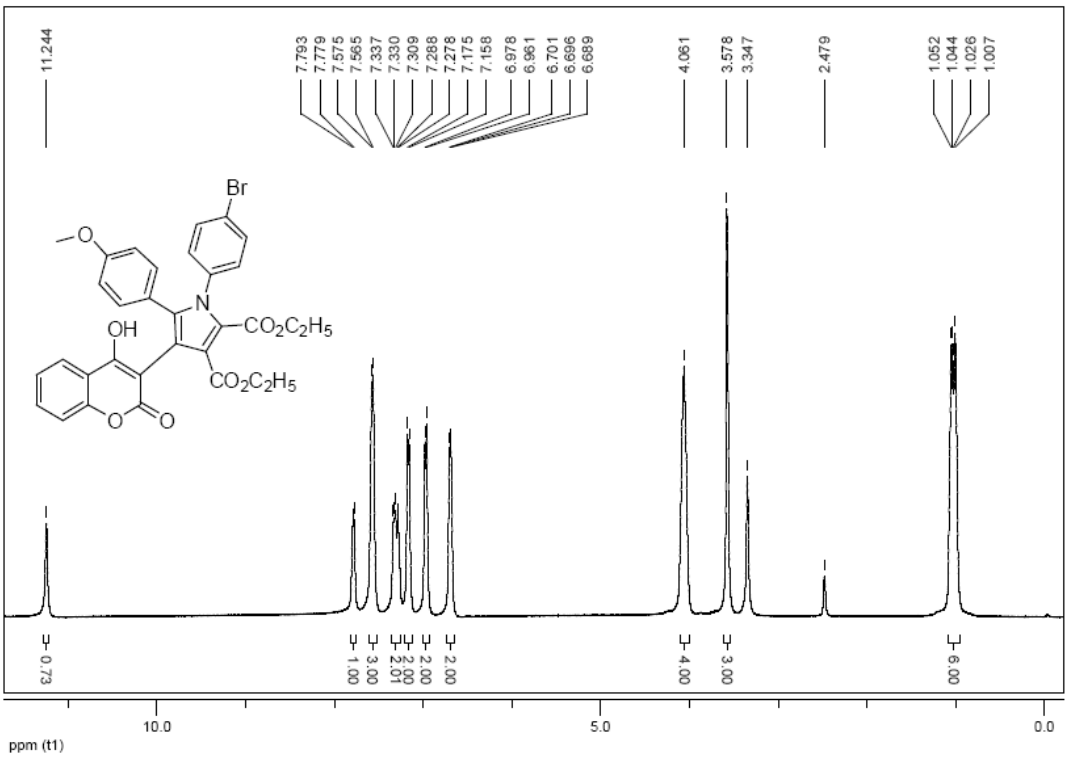
^{1}H NMR spectrum of compound **5u**



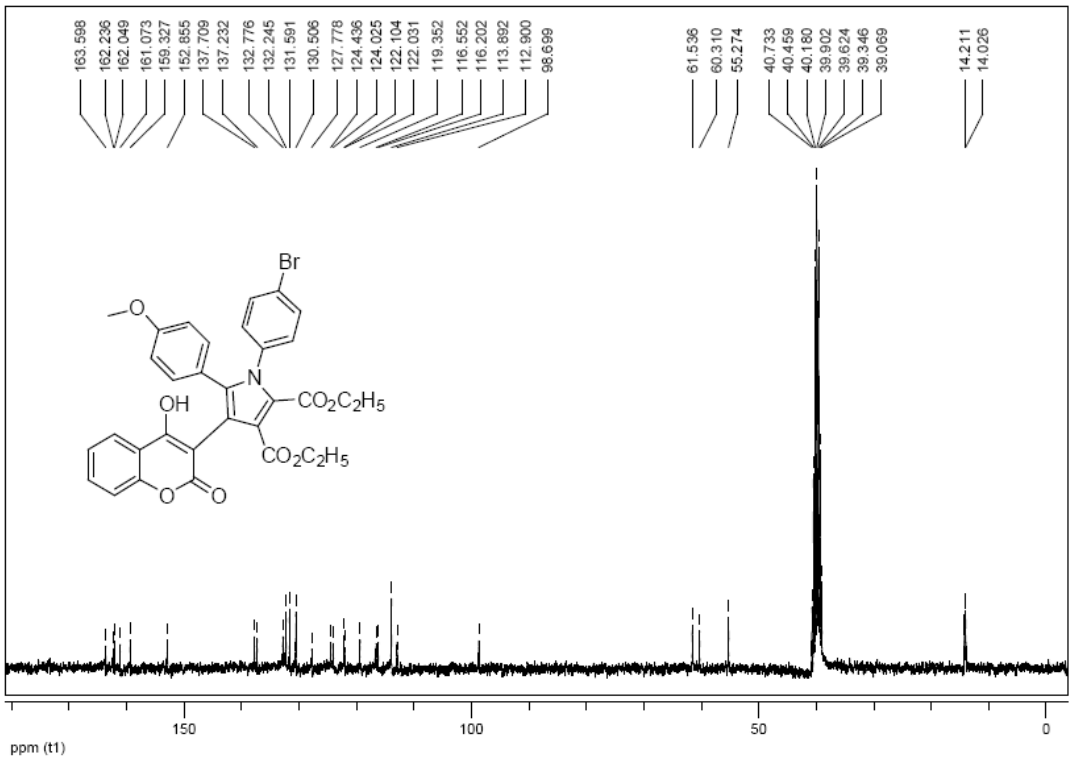
^{13}C NMR spectrum of compound **5u**



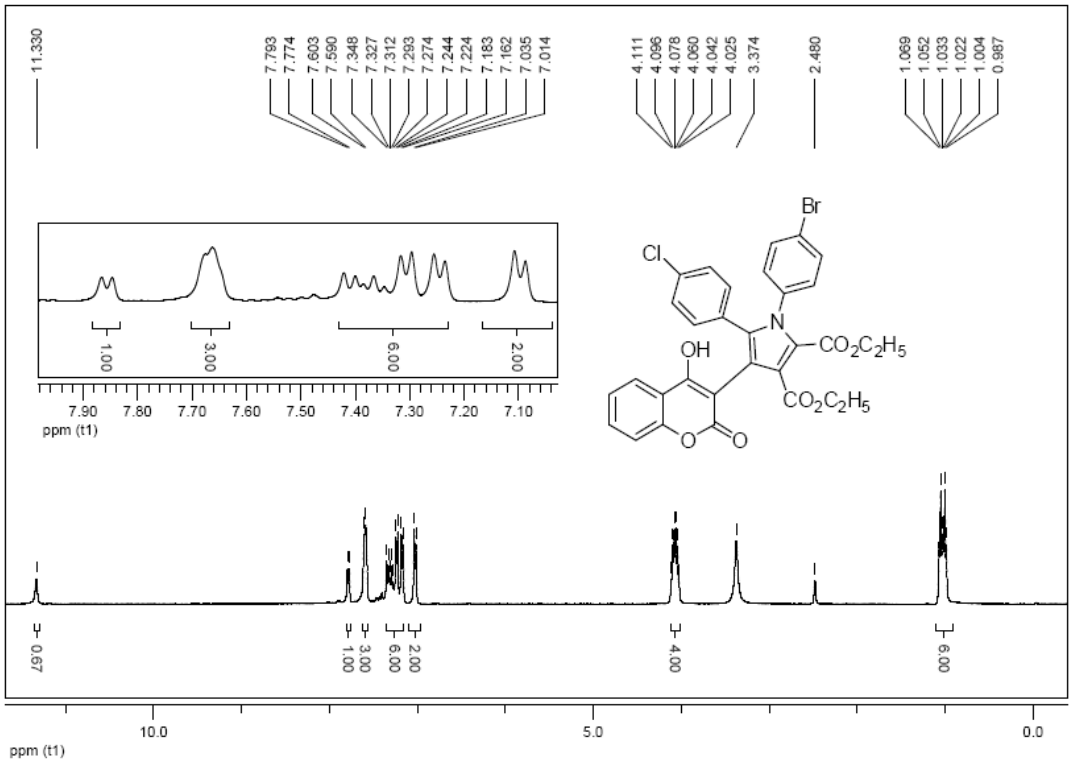
^{1}H NMR spectrum of compound **5v**



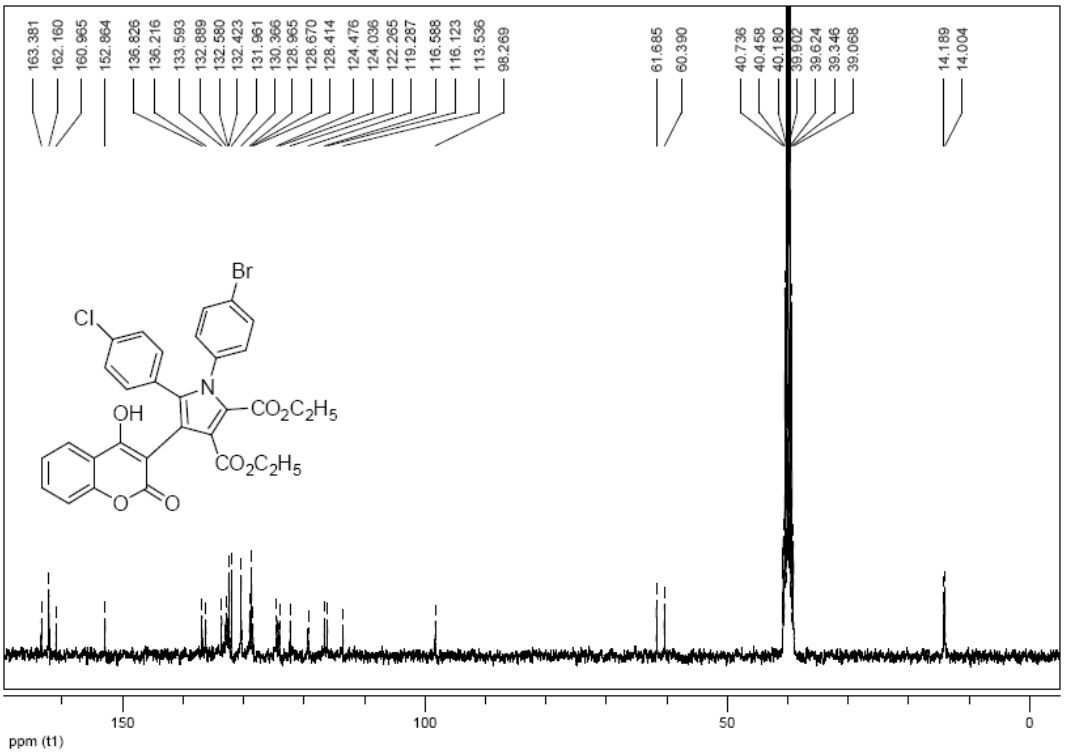
^{13}C NMR spectrum of compound **5v**



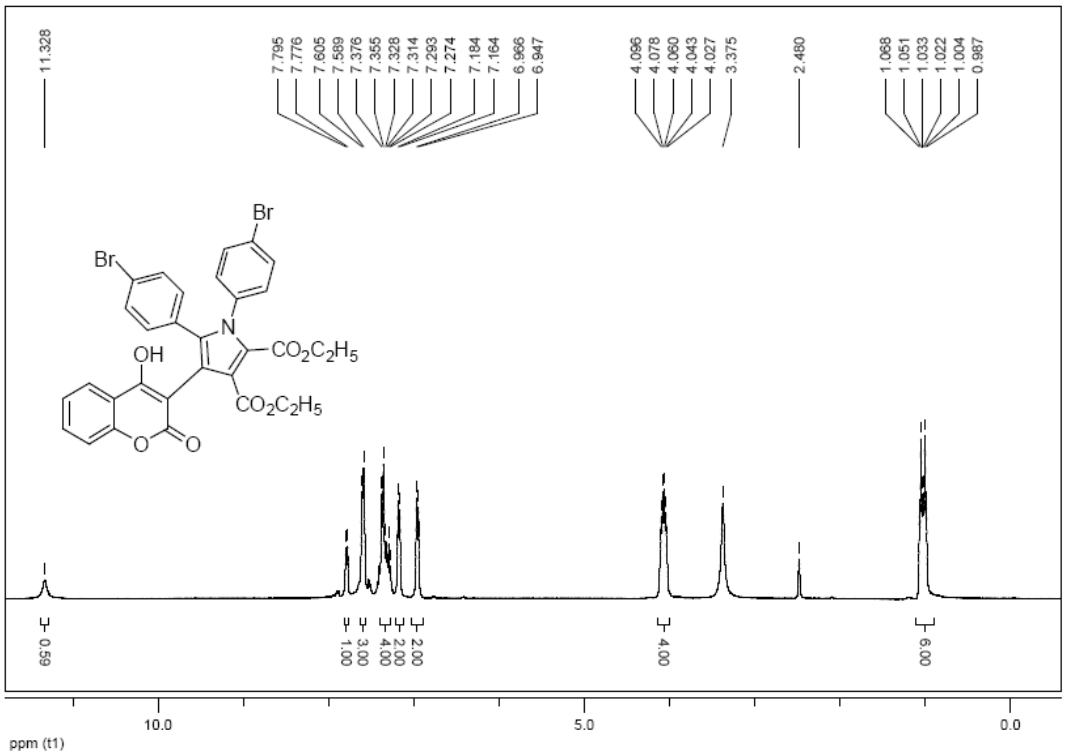
^{1}H NMR spectrum of compound **5w**



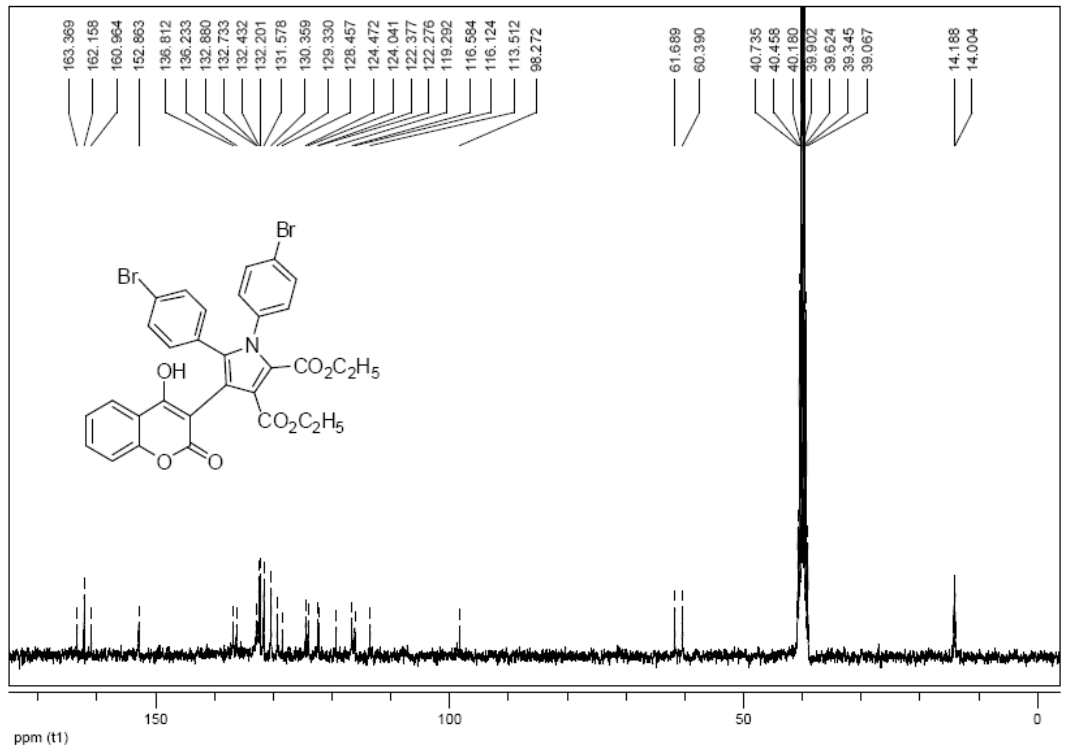
^{13}C NMR spectrum of compound **5w**



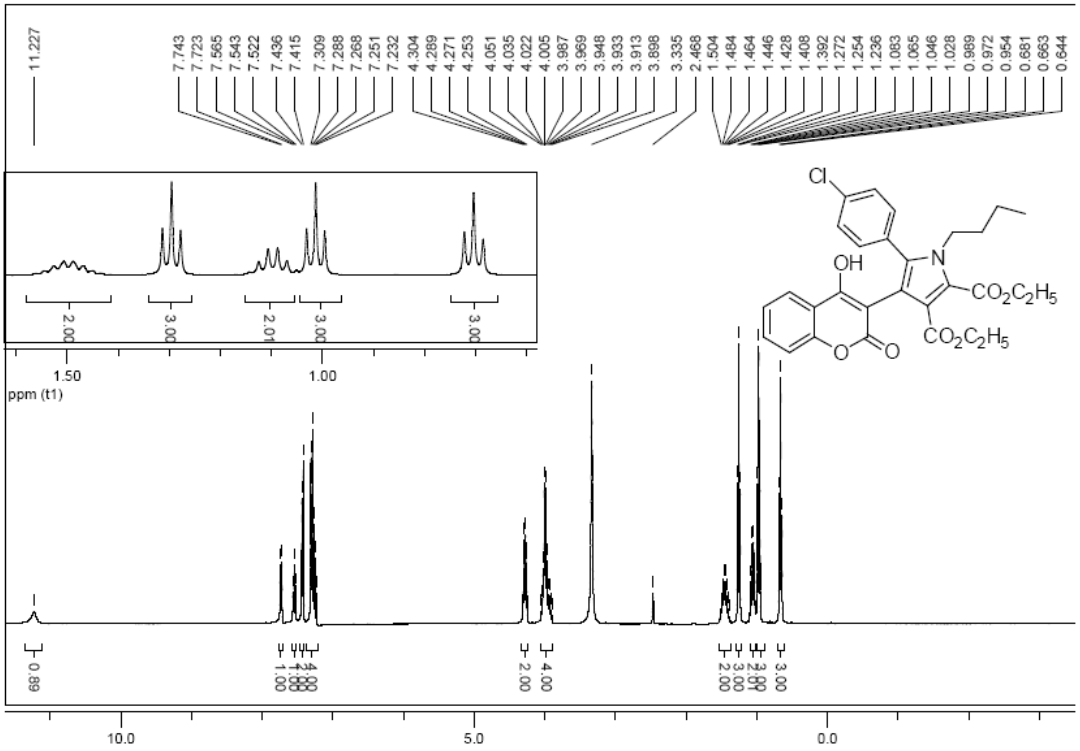
^{1}H NMR spectrum of compound **5x**



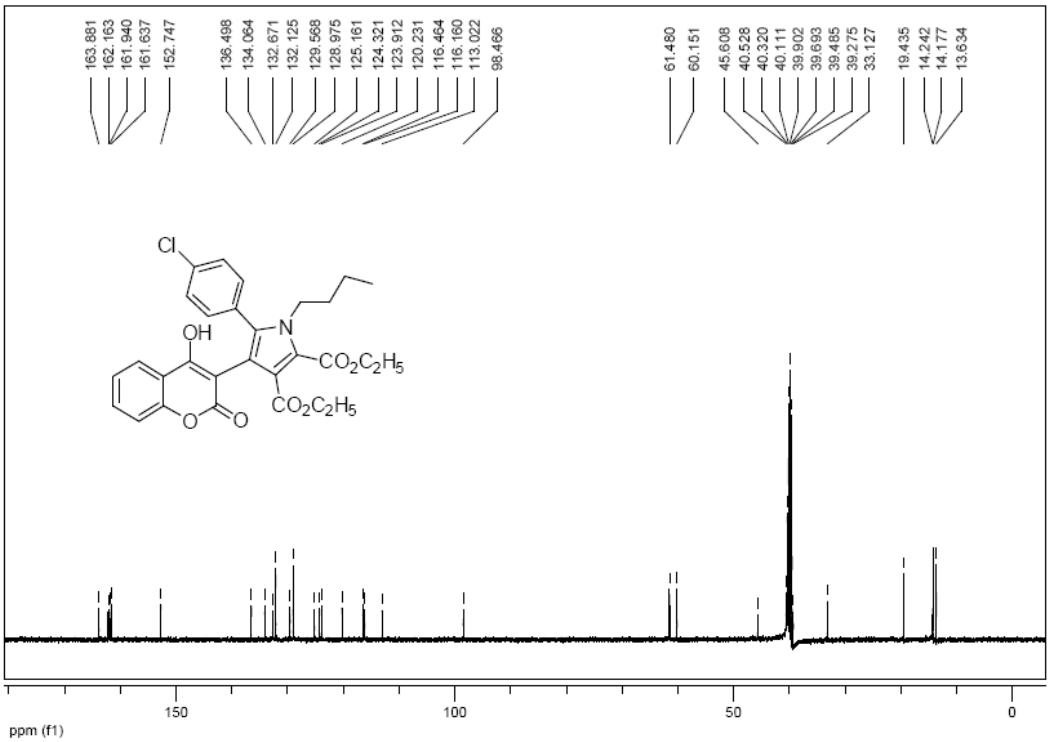
^{13}C NMR spectrum of compound **5x**



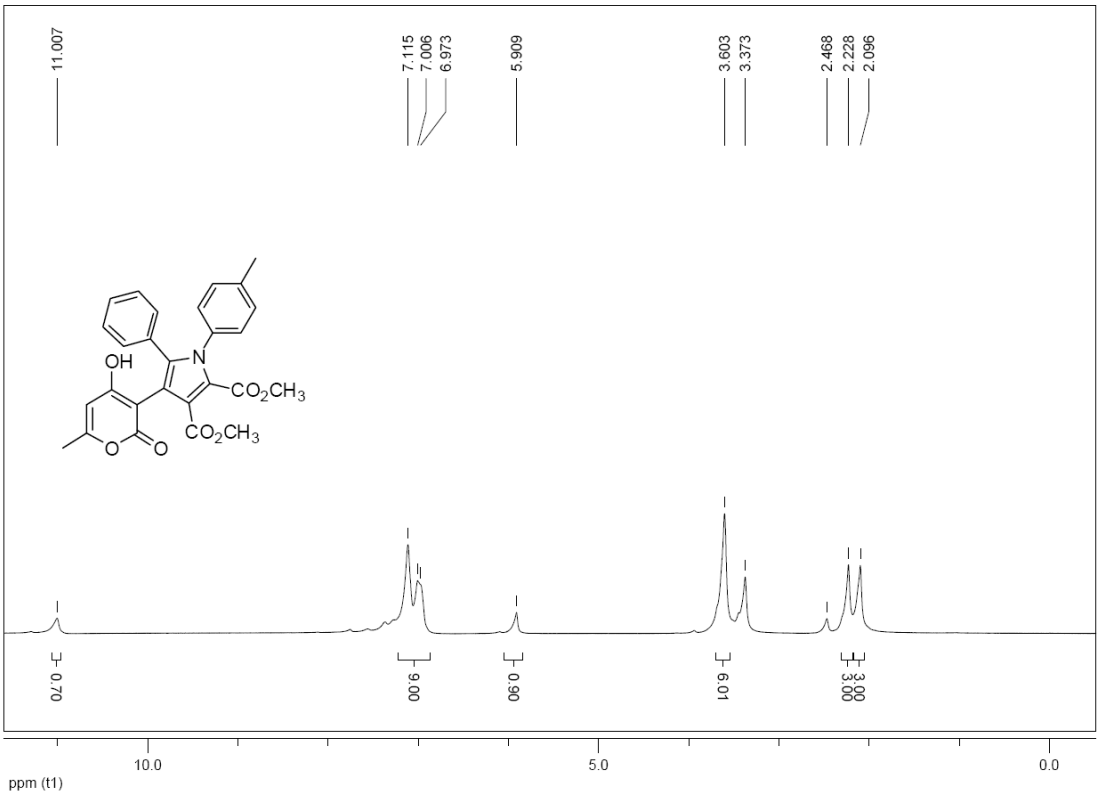
^{1}H NMR spectrum of compound **5y**



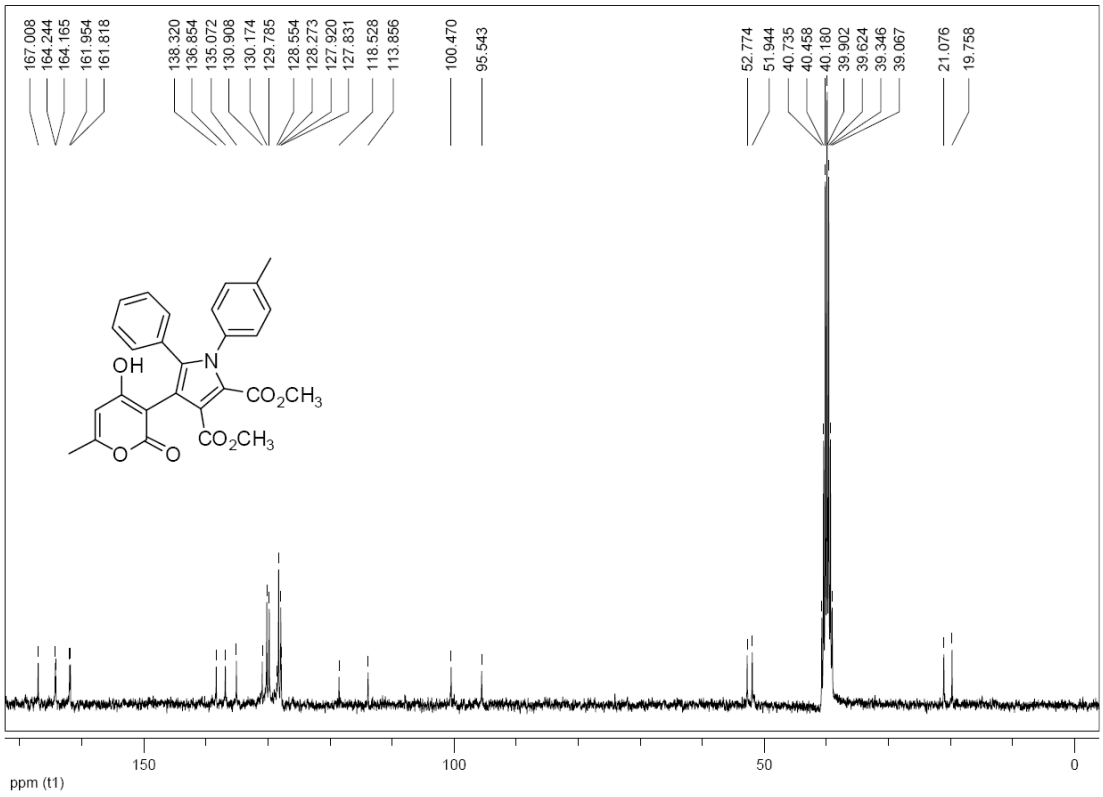
^{13}C NMR spectrum of compound **5y**



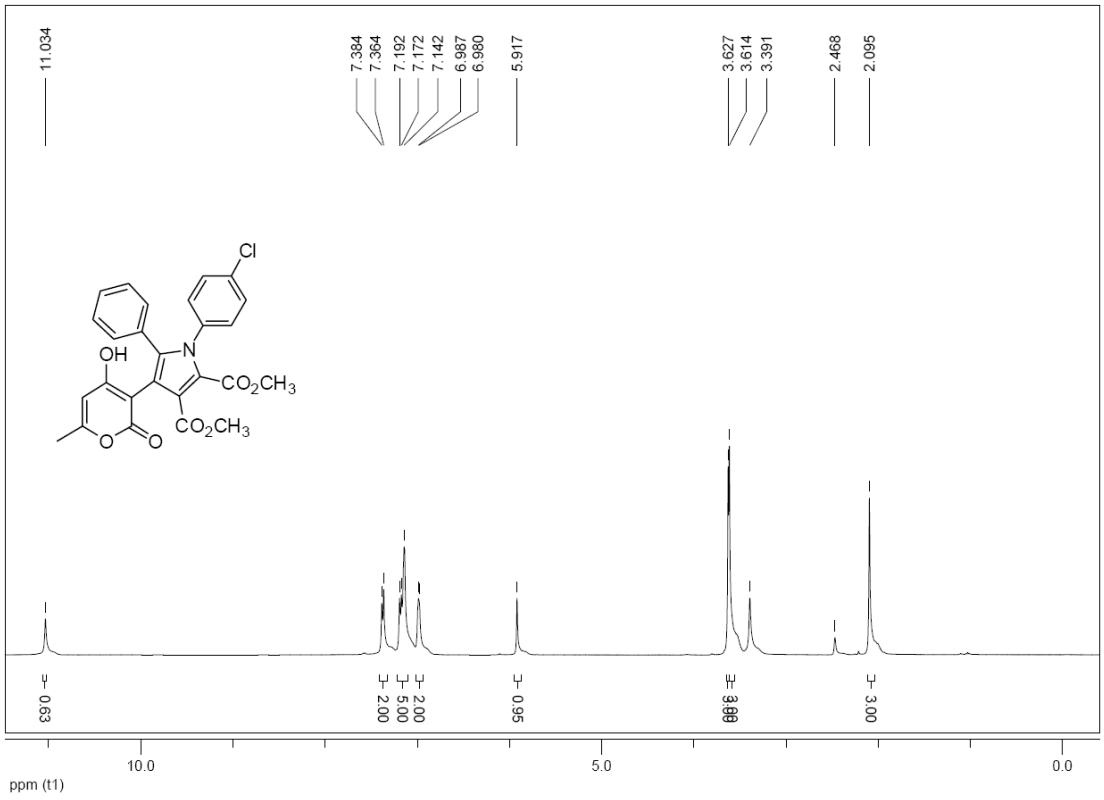
^{1}H NMR spectrum of compound **7a**



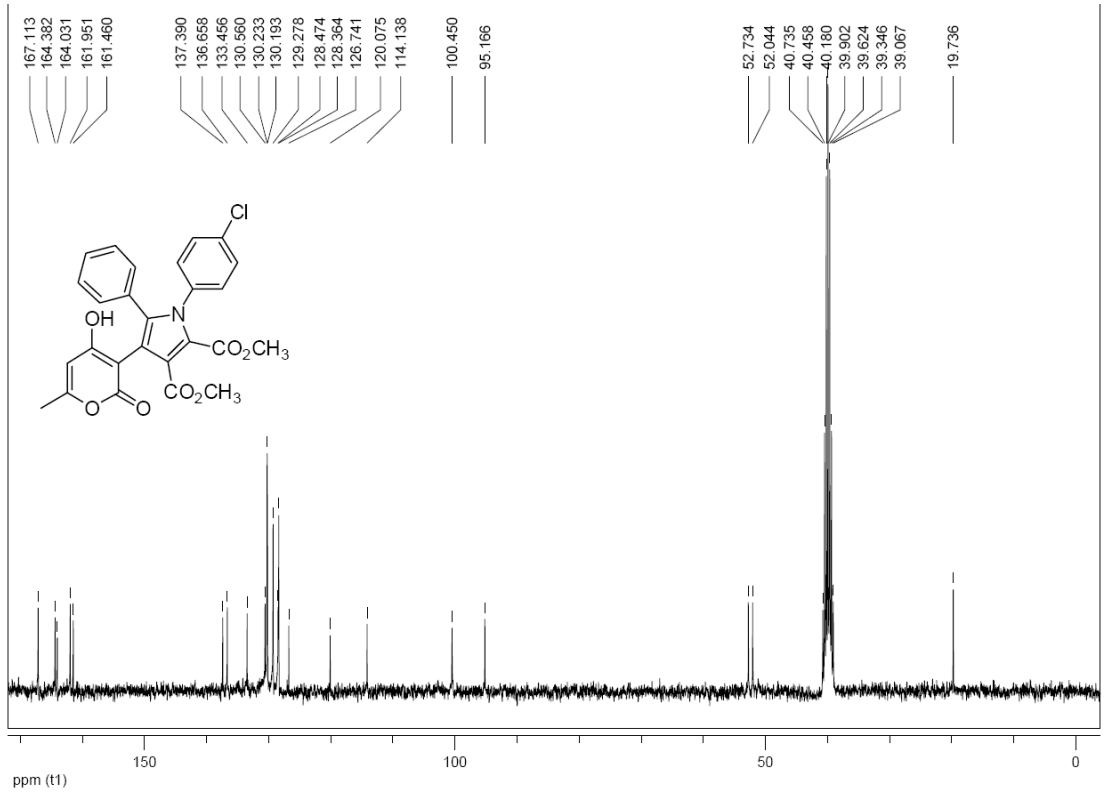
^{13}C NMR spectrum of compound **7a**



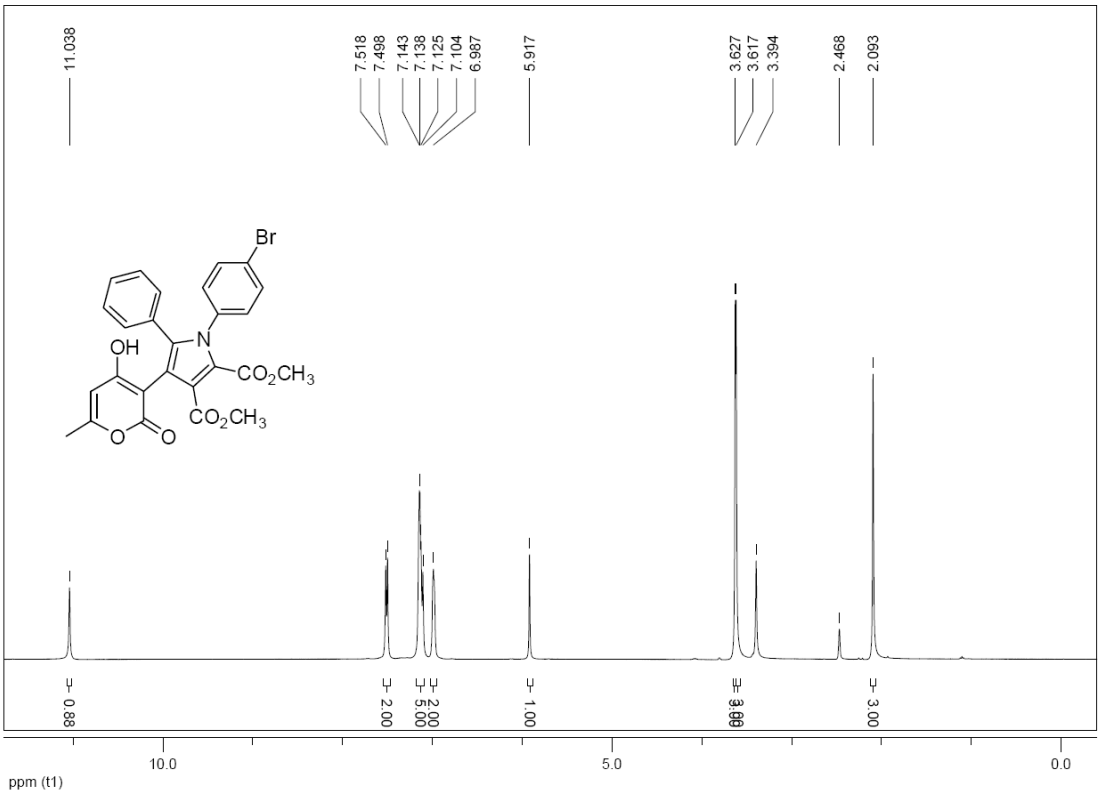
^{1}H NMR spectrum of compound **7b**



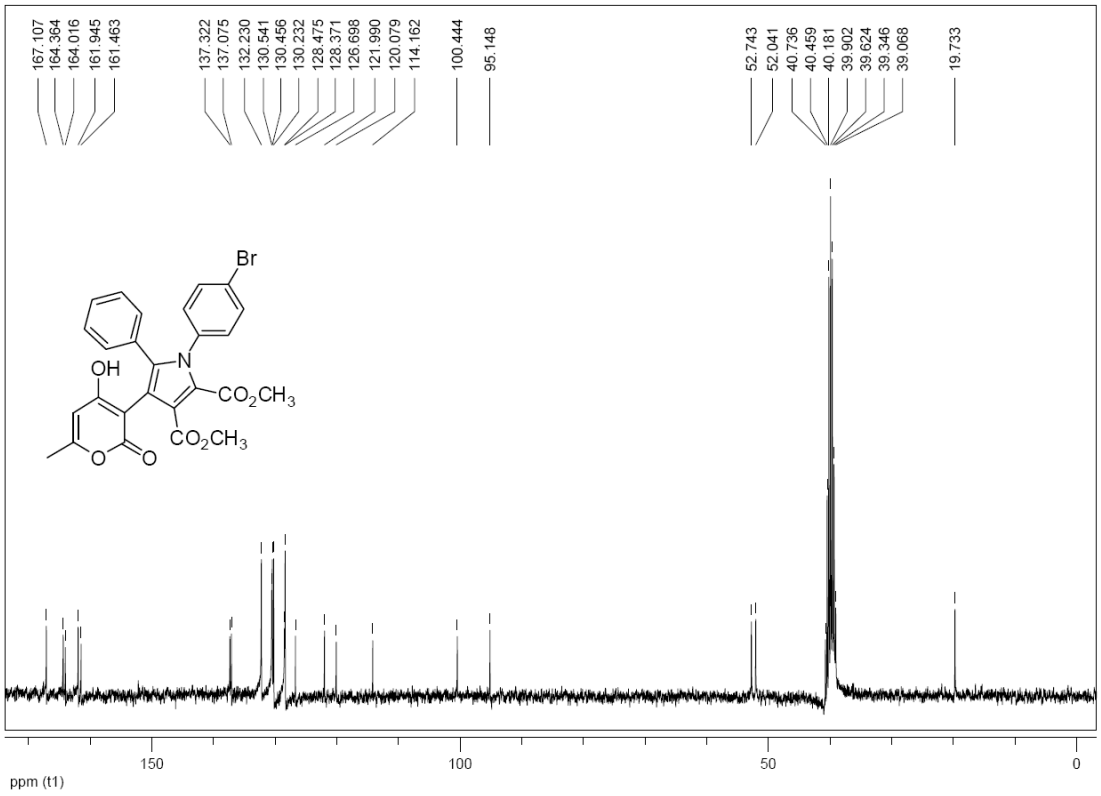
^{13}C NMR spectrum of compound **7b**



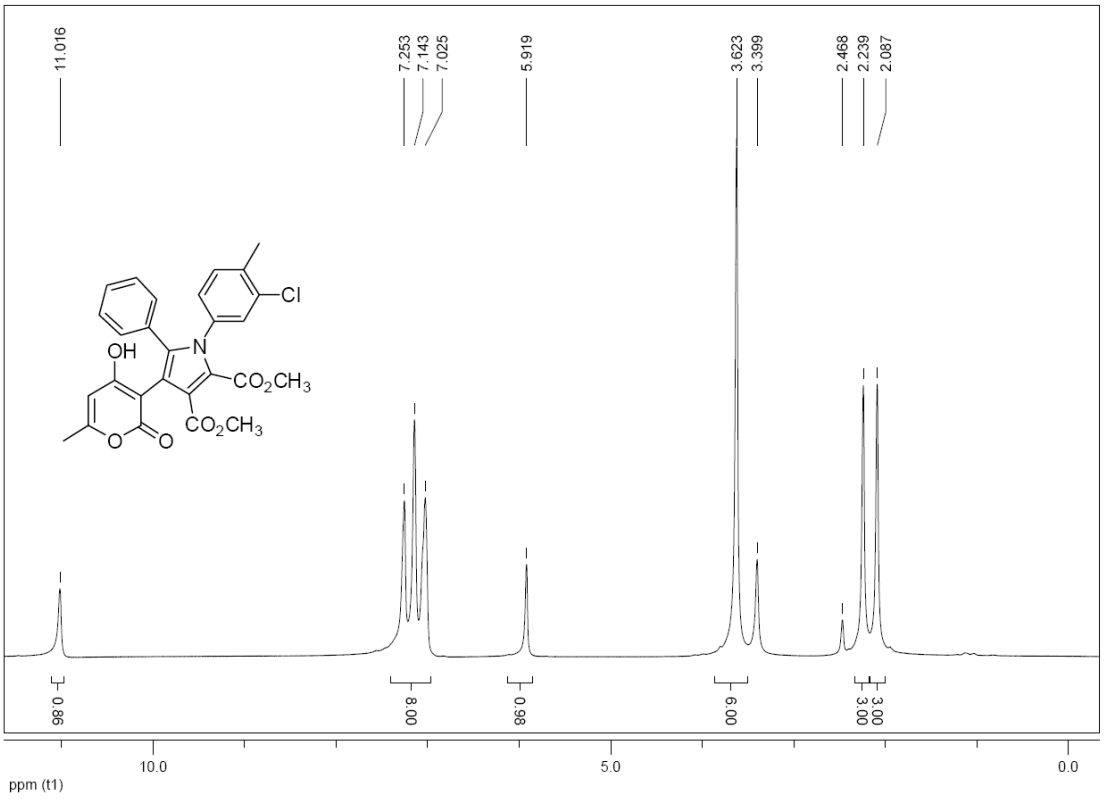
^{1}H NMR spectrum of compound **7c**



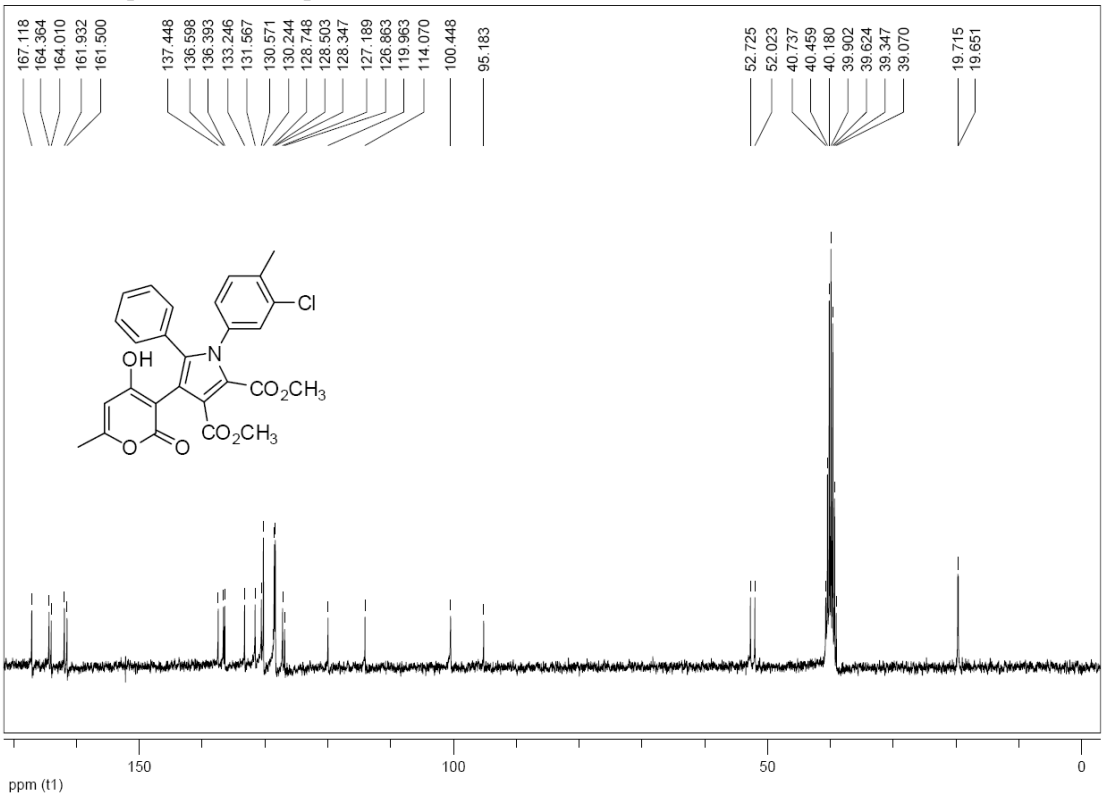
^{13}C NMR spectrum of compound **7c**



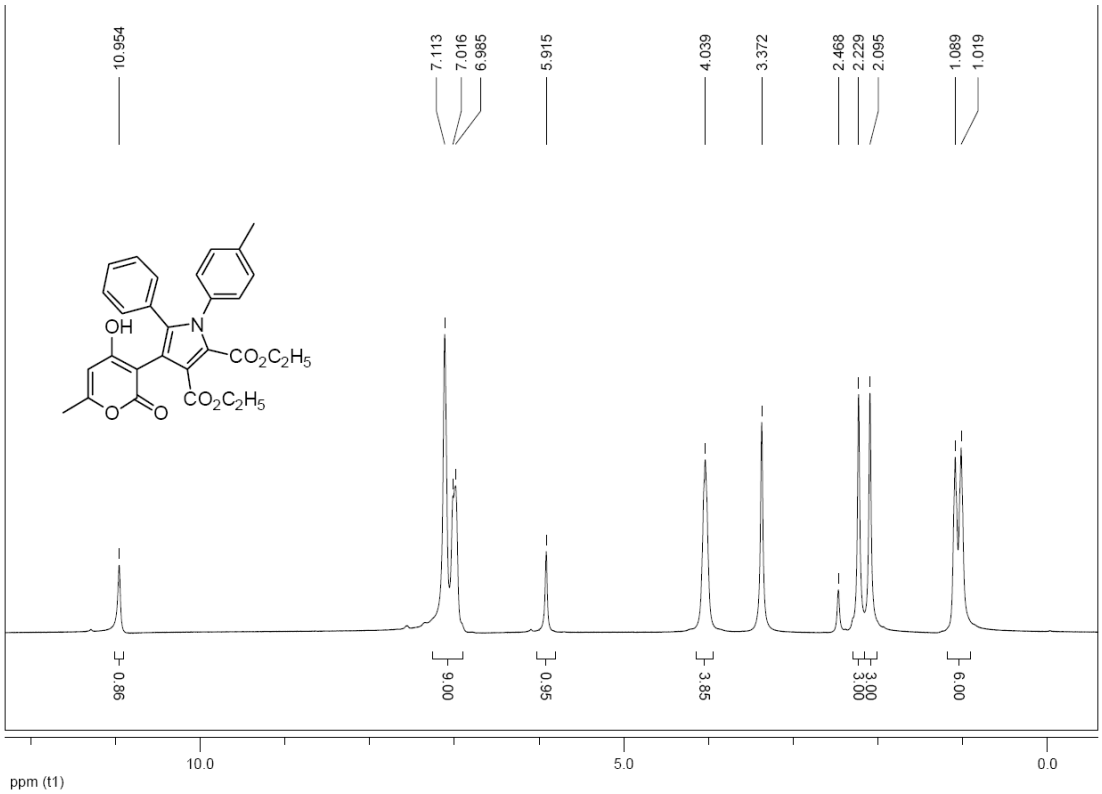
^{1}H NMR spectrum of compound **7d**



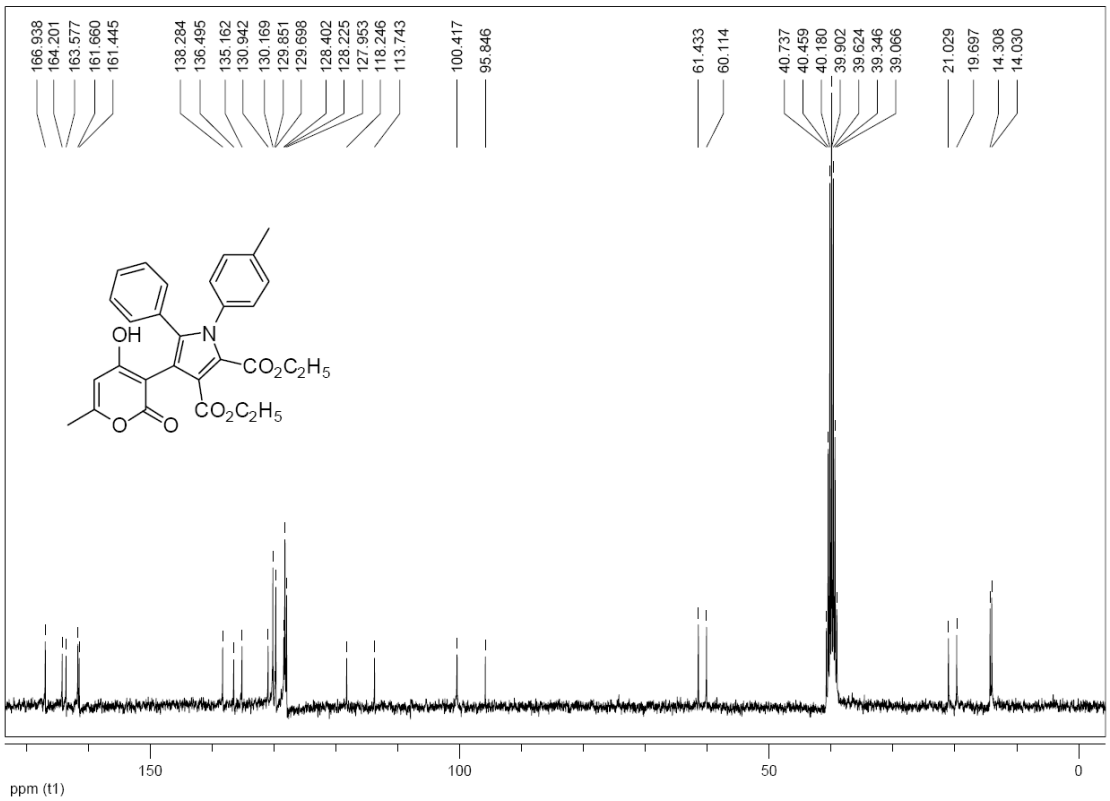
^{13}C NMR spectrum of compound **7d**



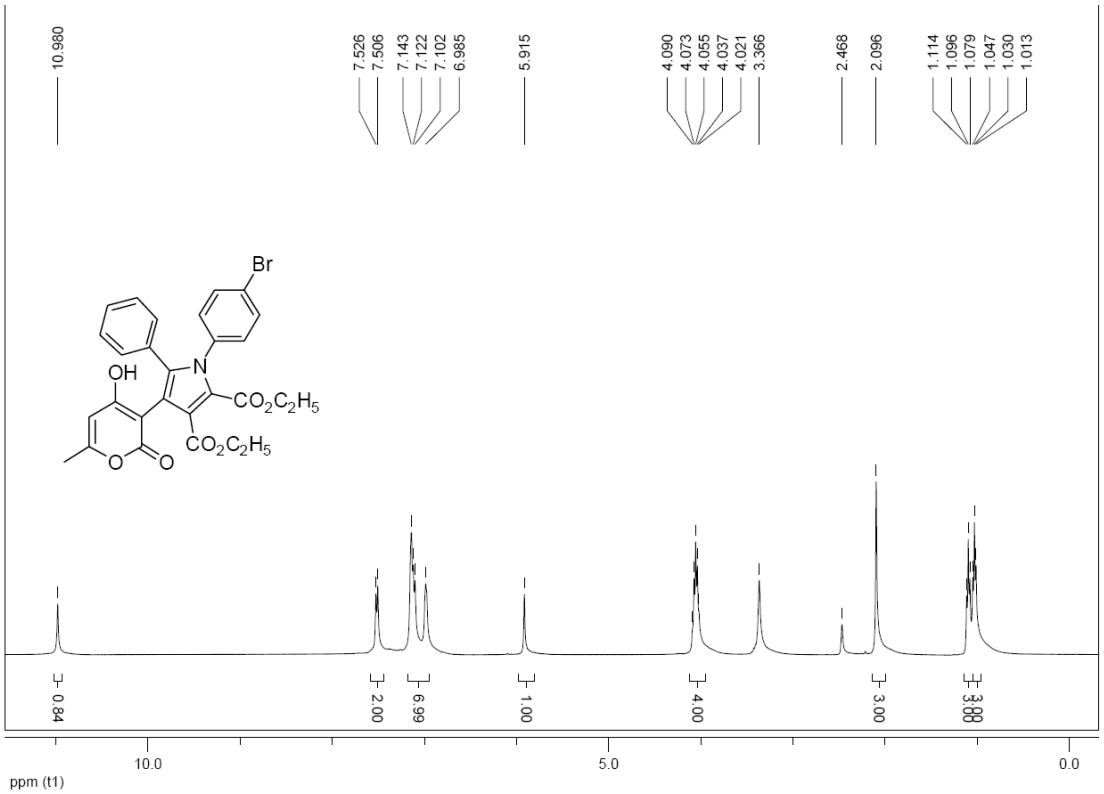
^{1}H NMR spectrum of compound **7e**



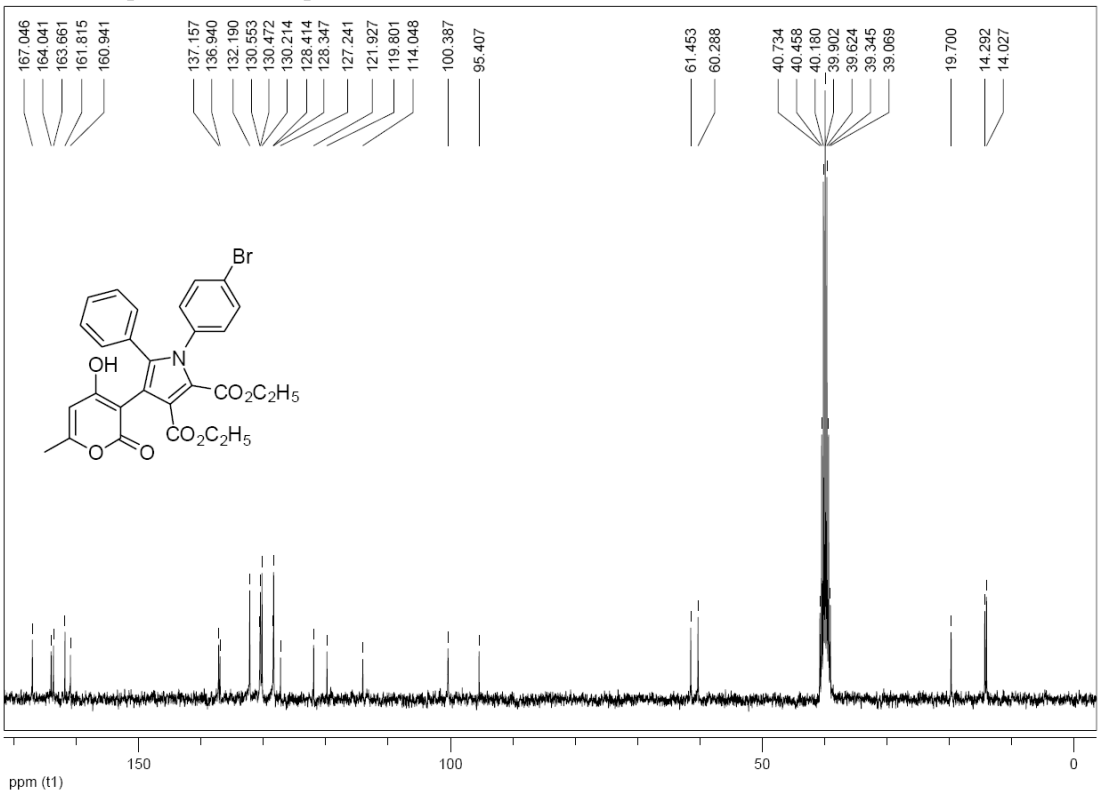
^{13}C NMR spectrum of compound **7e**



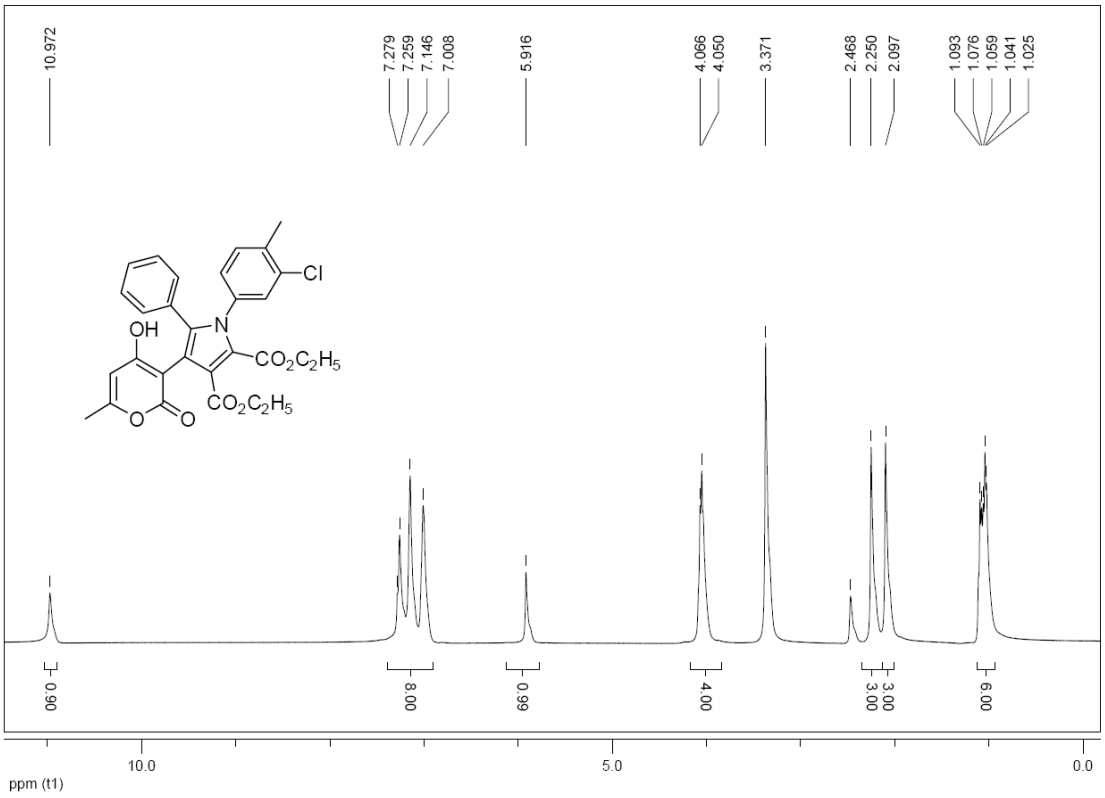
^{1}H NMR spectrum of compound **7f**



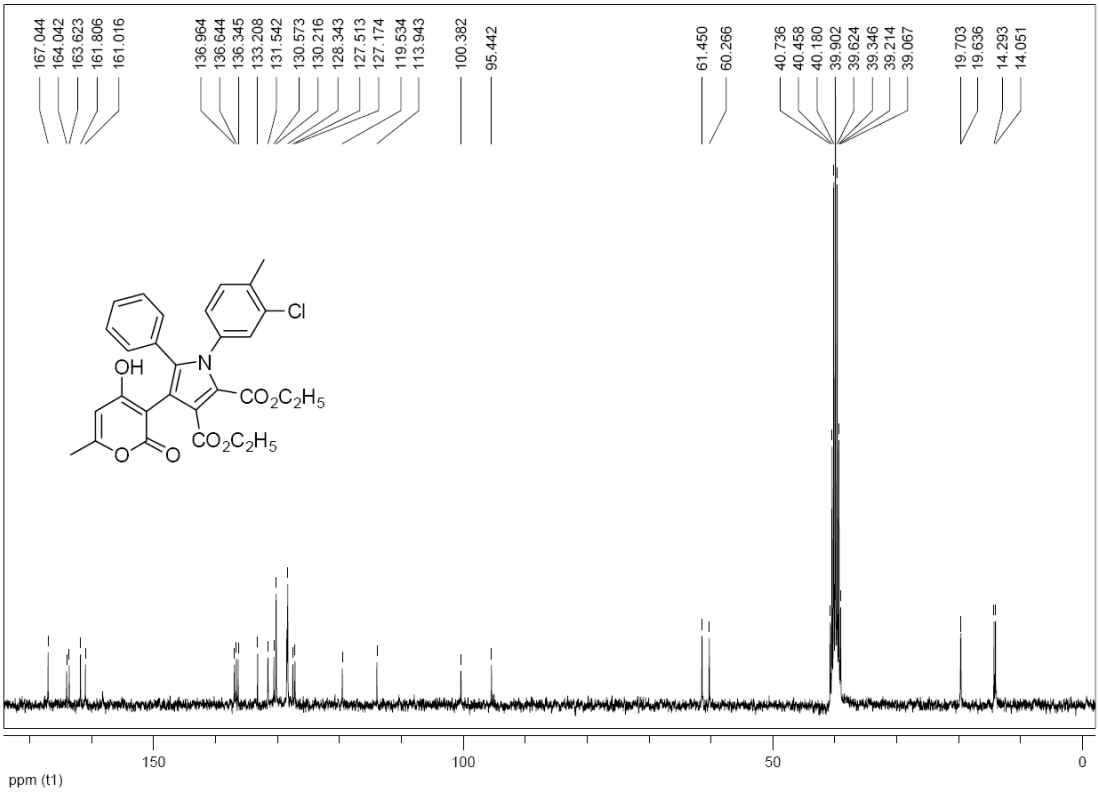
^{13}C NMR spectrum of compound **7f**



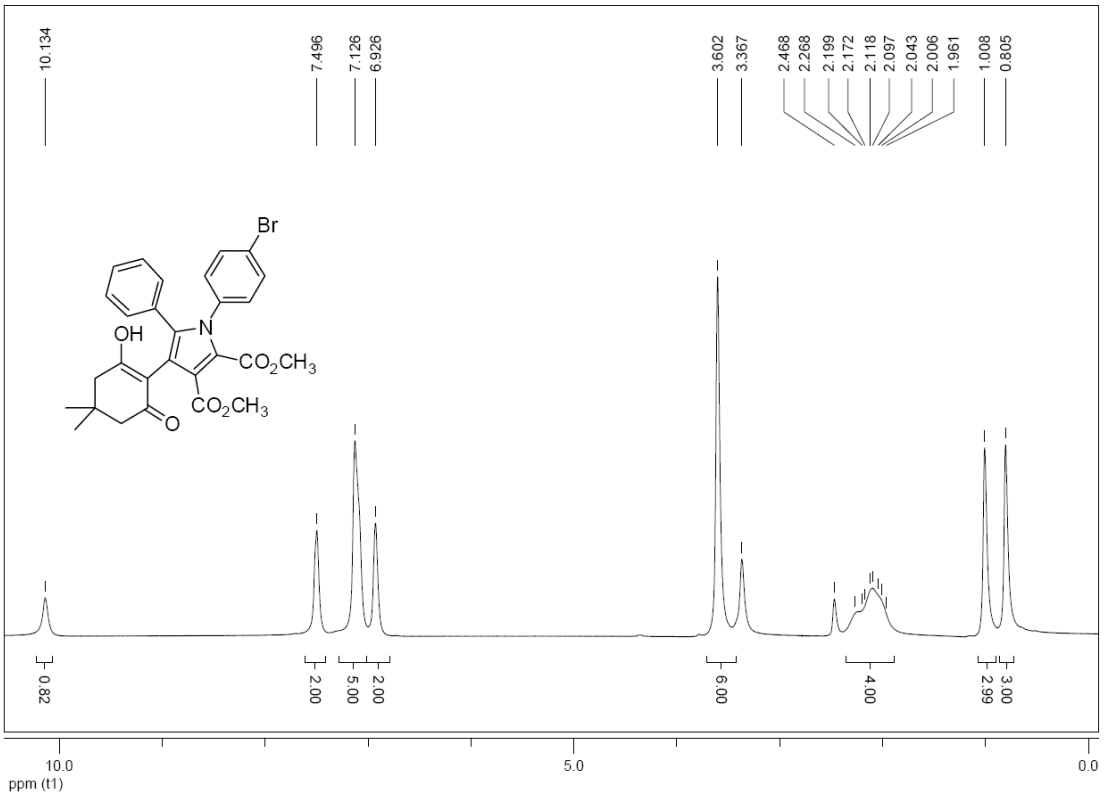
^{1}H NMR spectrum of compound **7g**



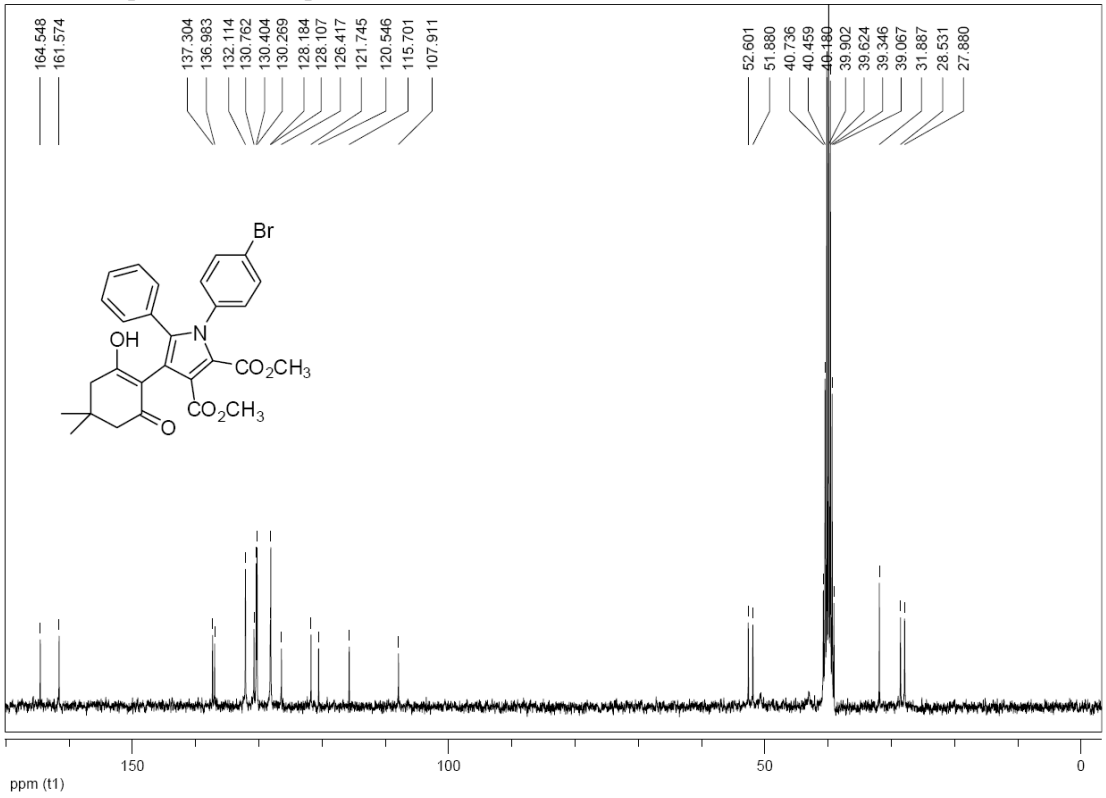
^{13}C NMR spectrum of compound **7g**



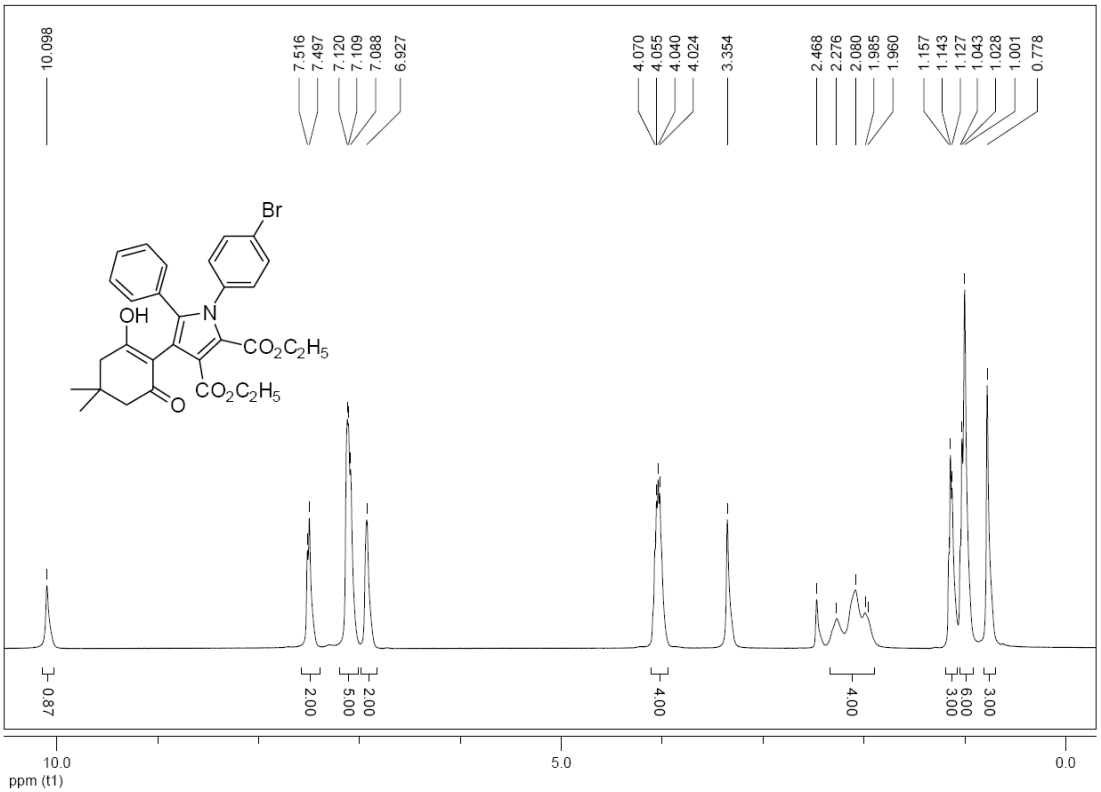
^{1}H NMR spectrum of compound **7h**



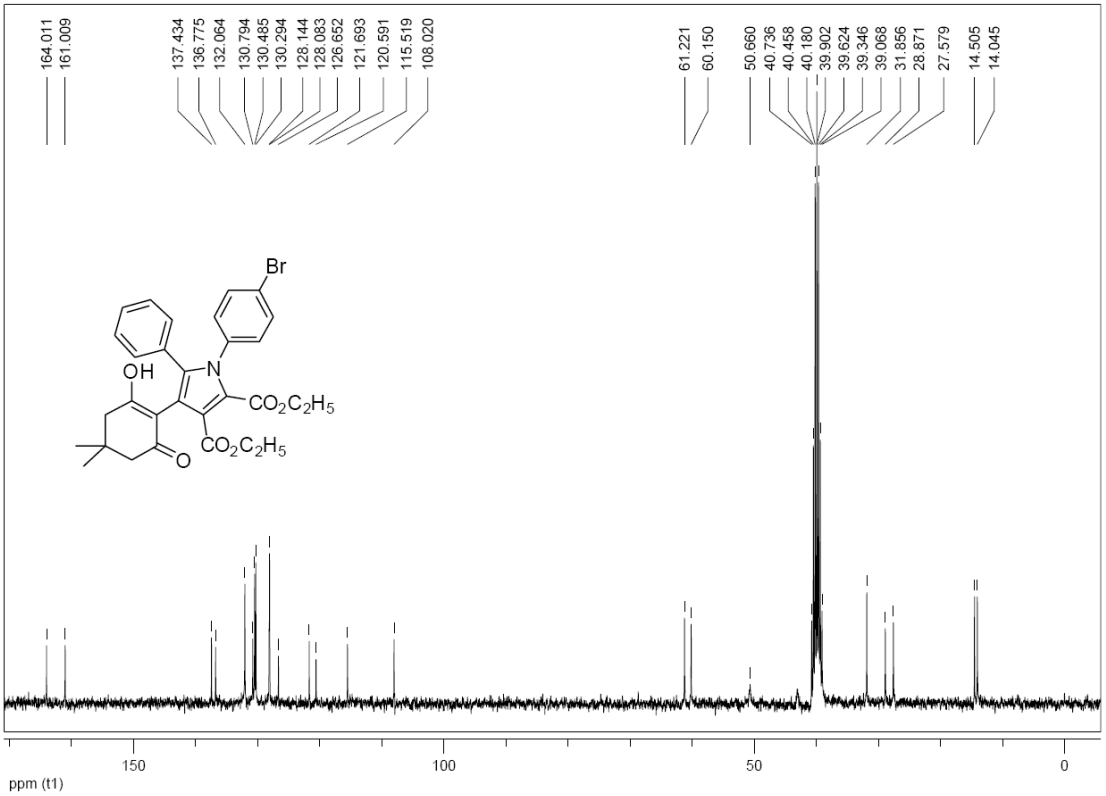
^{13}C NMR spectrum of compound **7h**



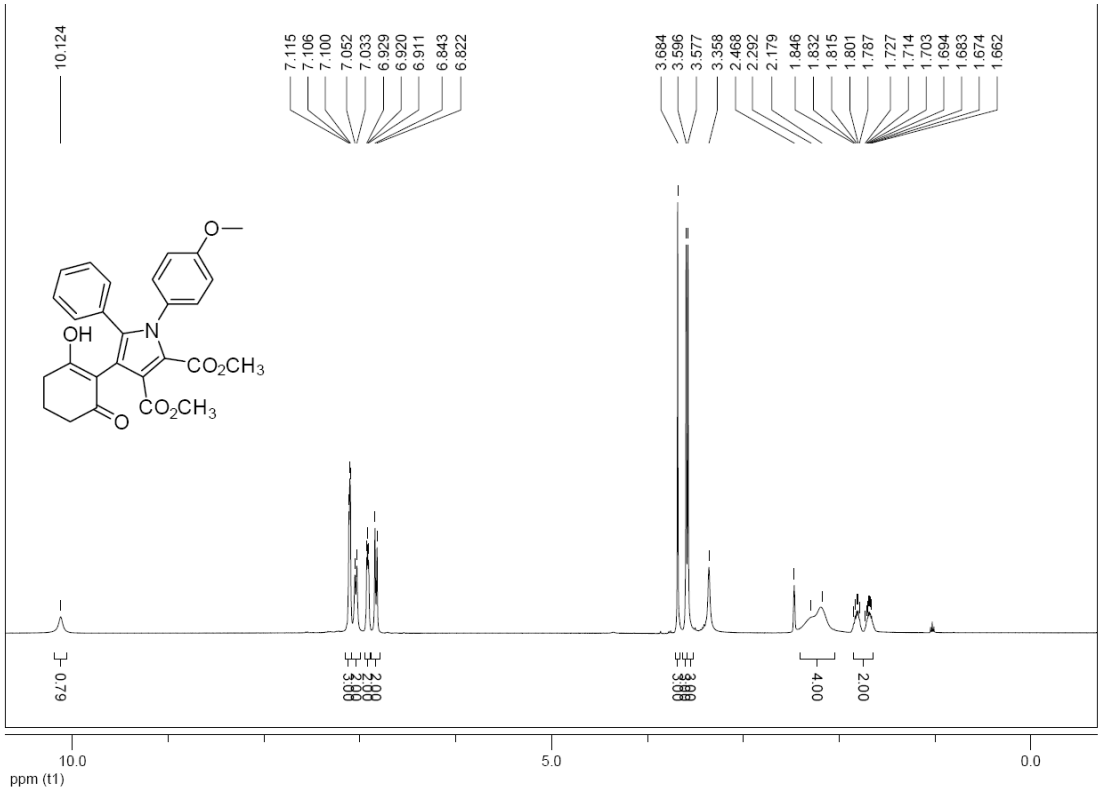
^{1}H NMR spectrum of compound **7i**



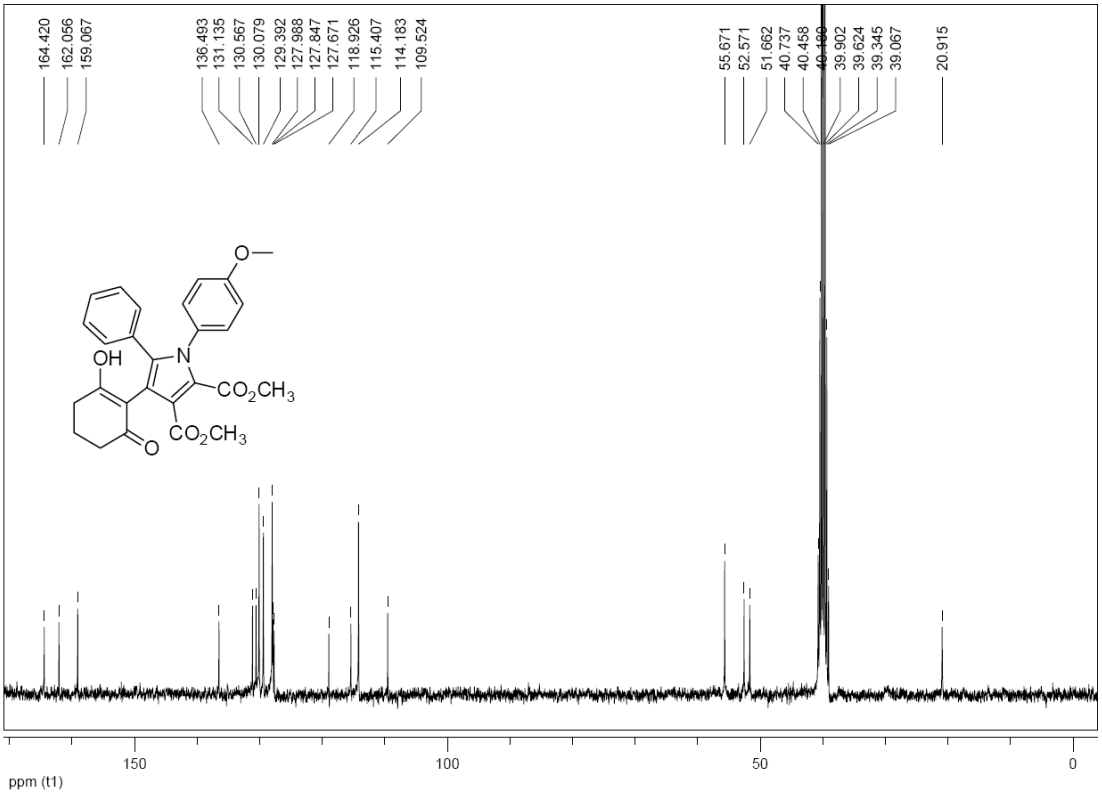
^{13}C NMR spectrum of compound **7i**



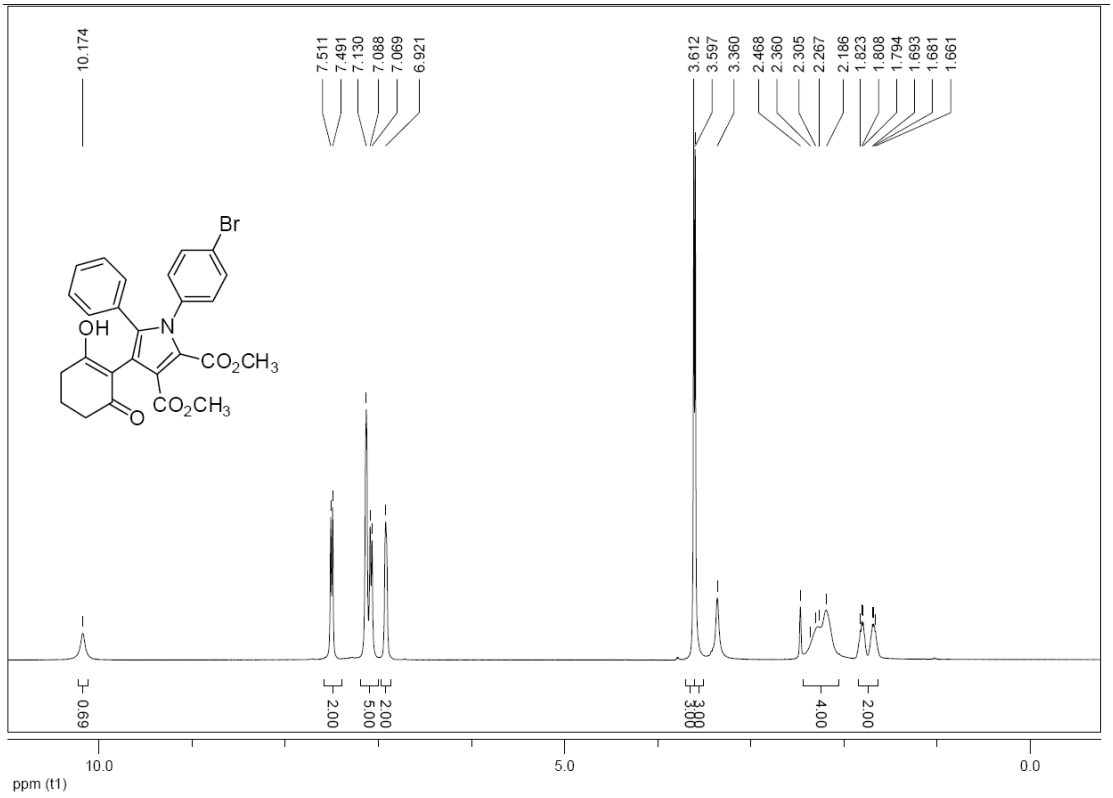
^{1}H NMR spectrum of compound **7j**



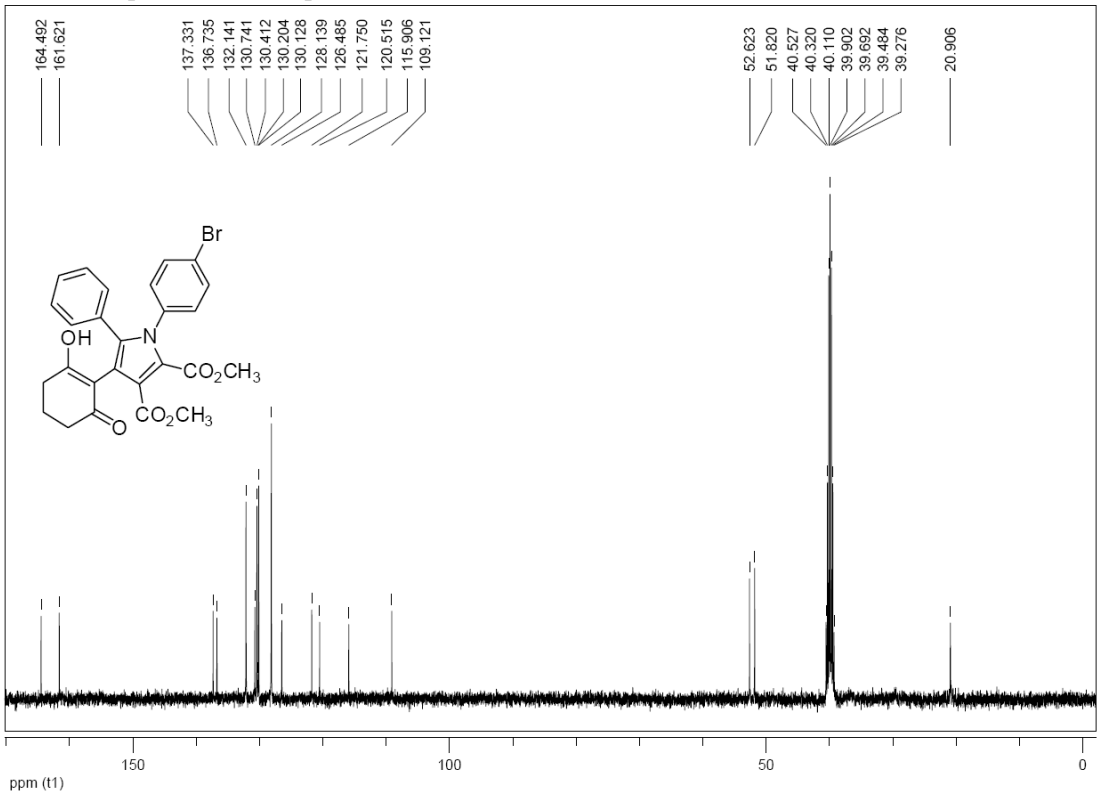
^{13}C NMR spectrum of compound **7j**



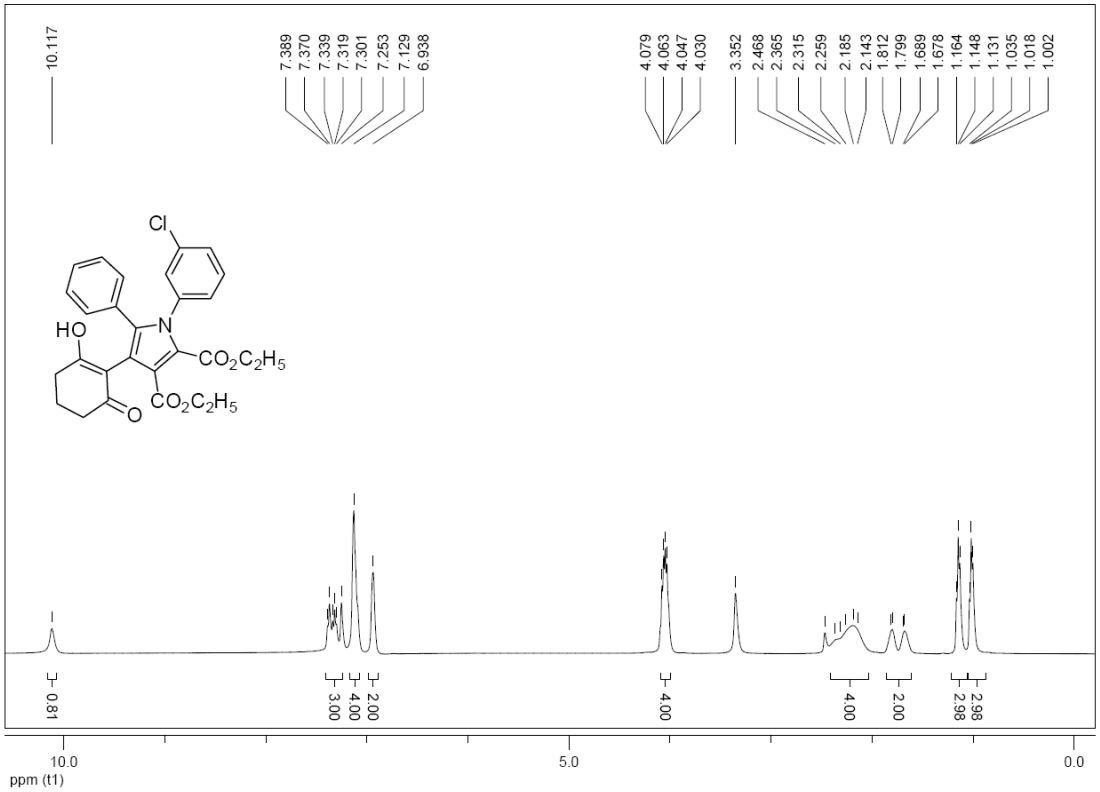
^{1}H NMR spectrum of compound **7k**



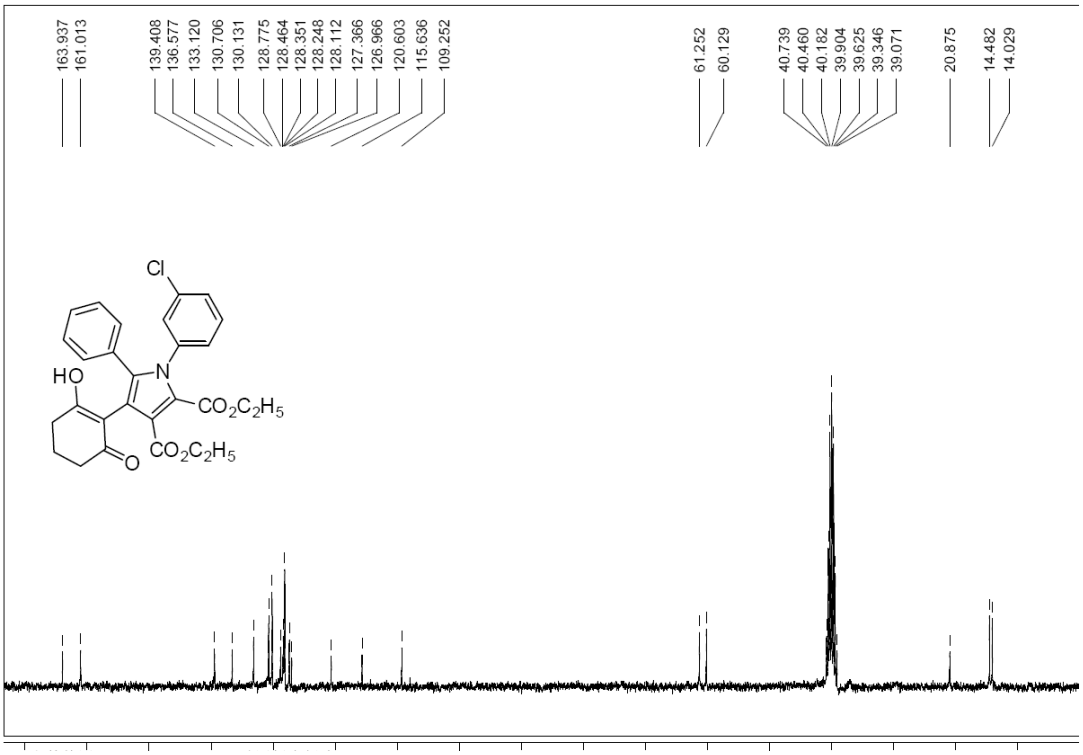
^{13}C NMR spectrum of compound **7k**



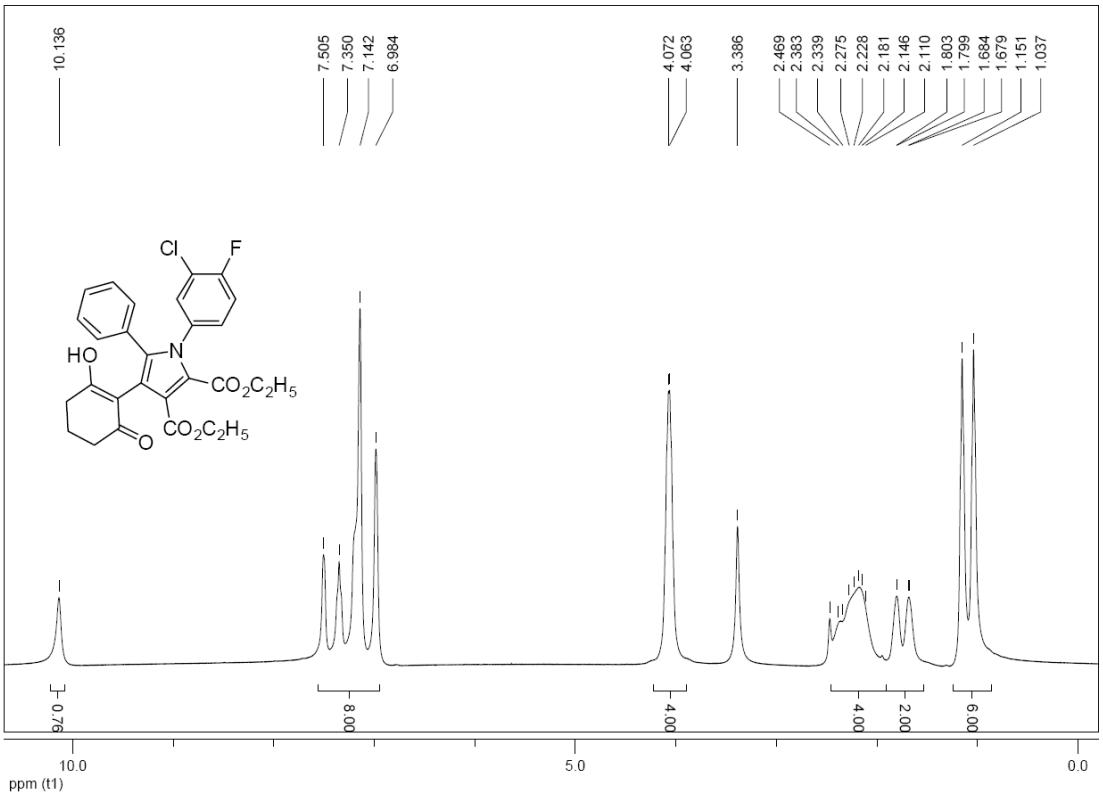
^{1}H NMR spectrum of compound **7l**



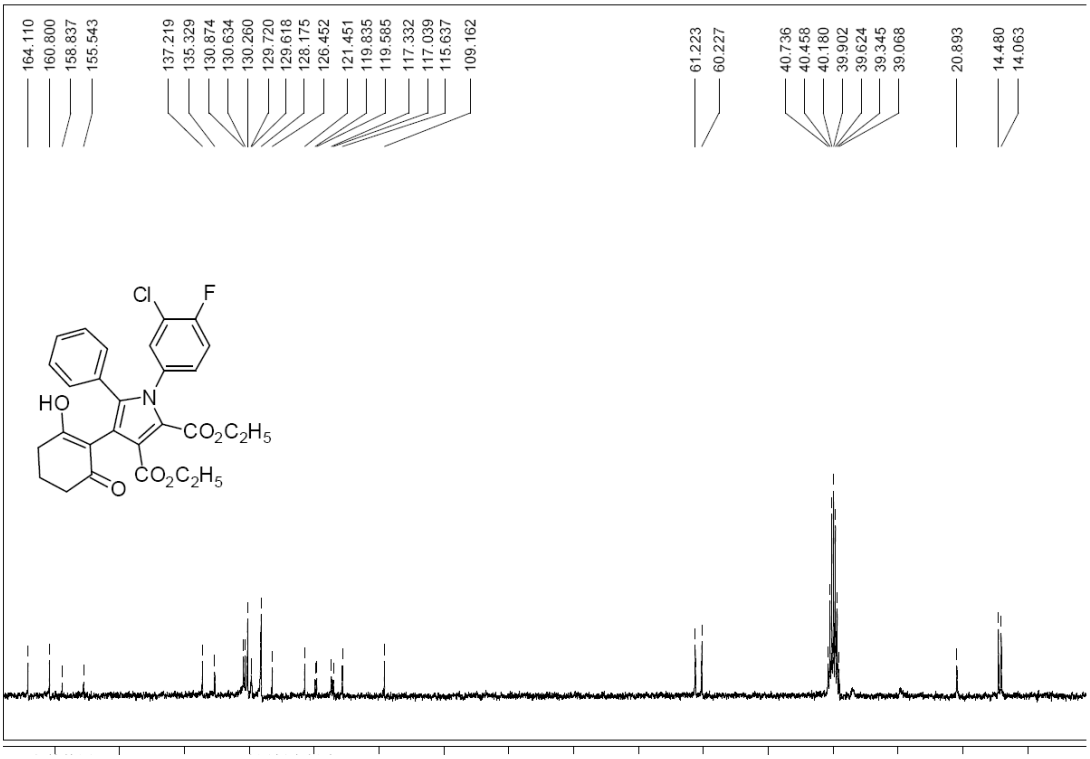
^{13}C NMR spectrum of compound **7l**



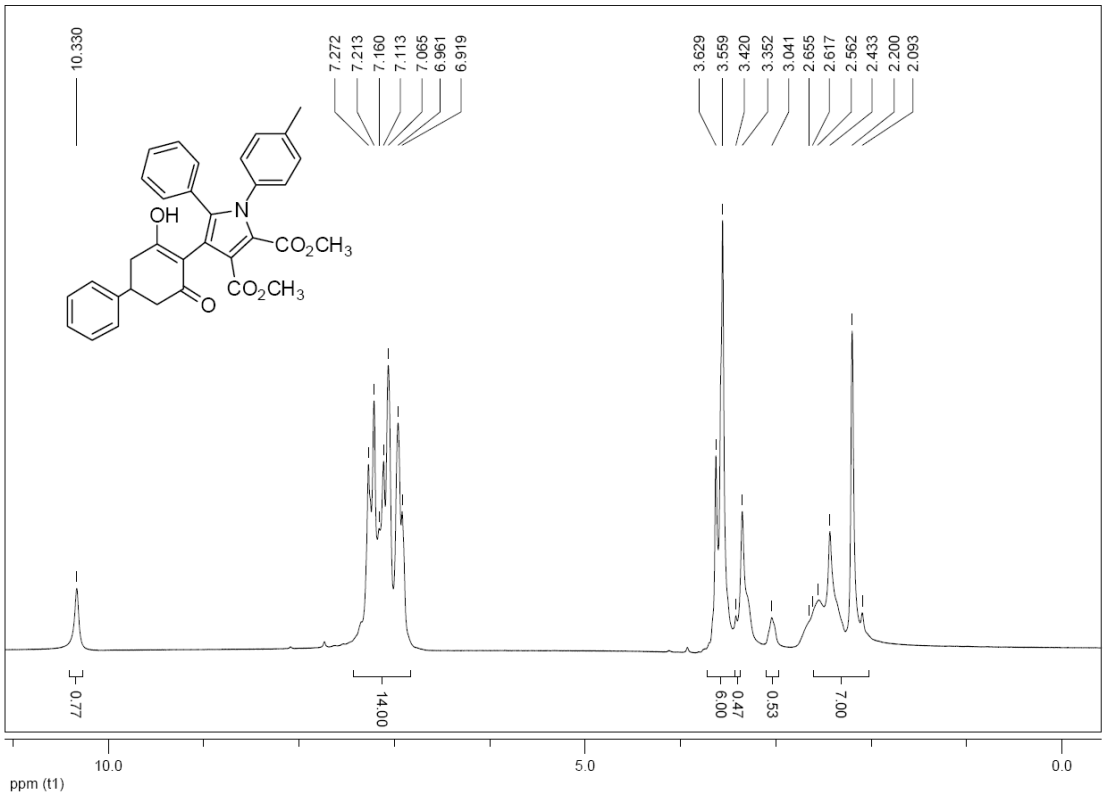
^{1}H NMR spectrum of compound **7m**



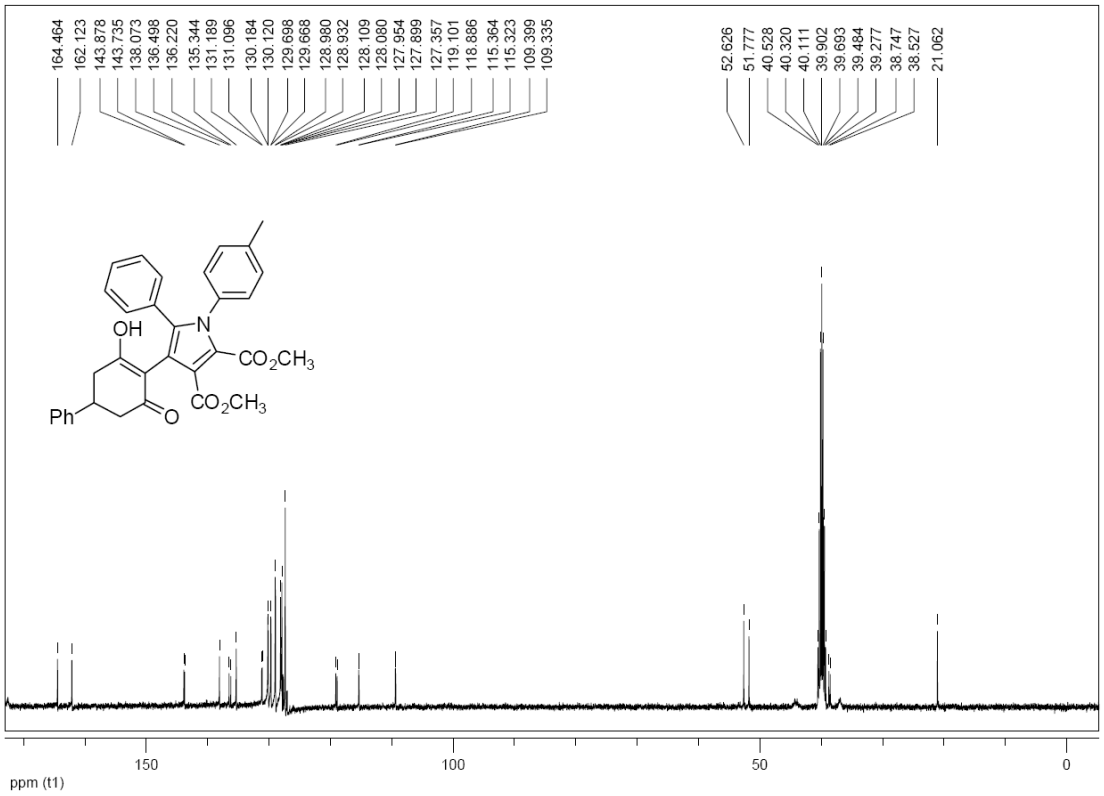
^{13}C NMR spectrum of compound **7m**



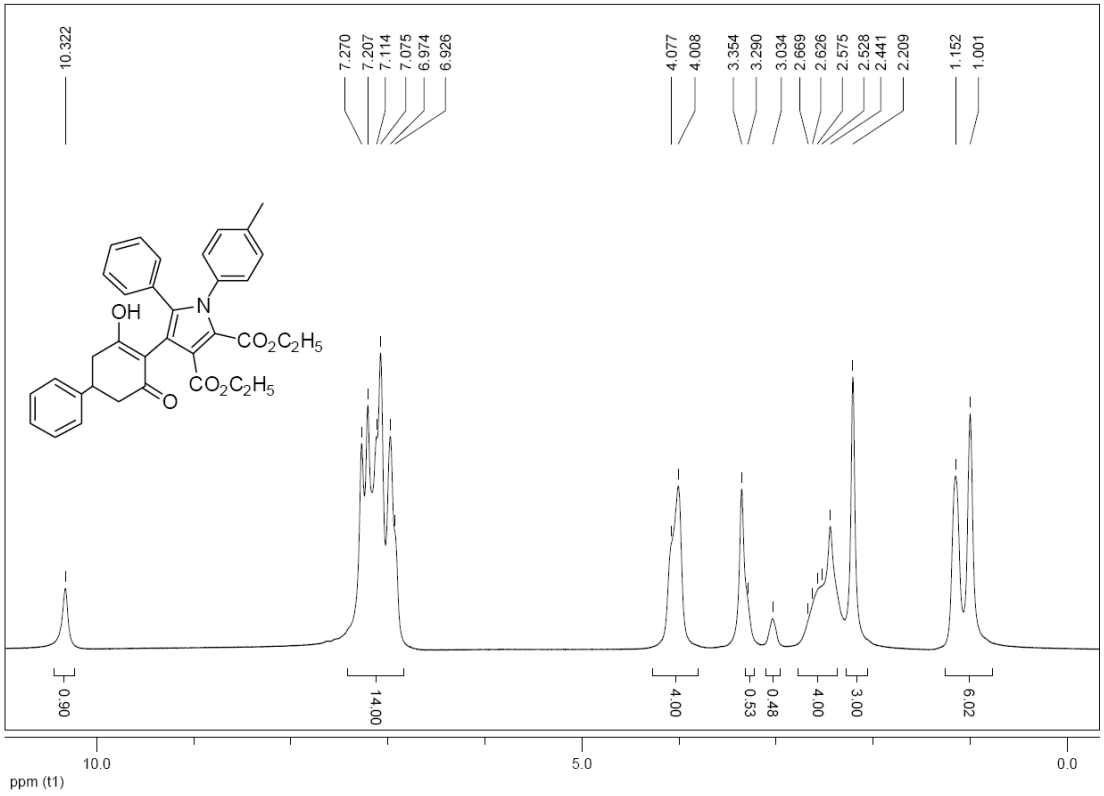
^{1}H NMR spectrum of compound **7n**



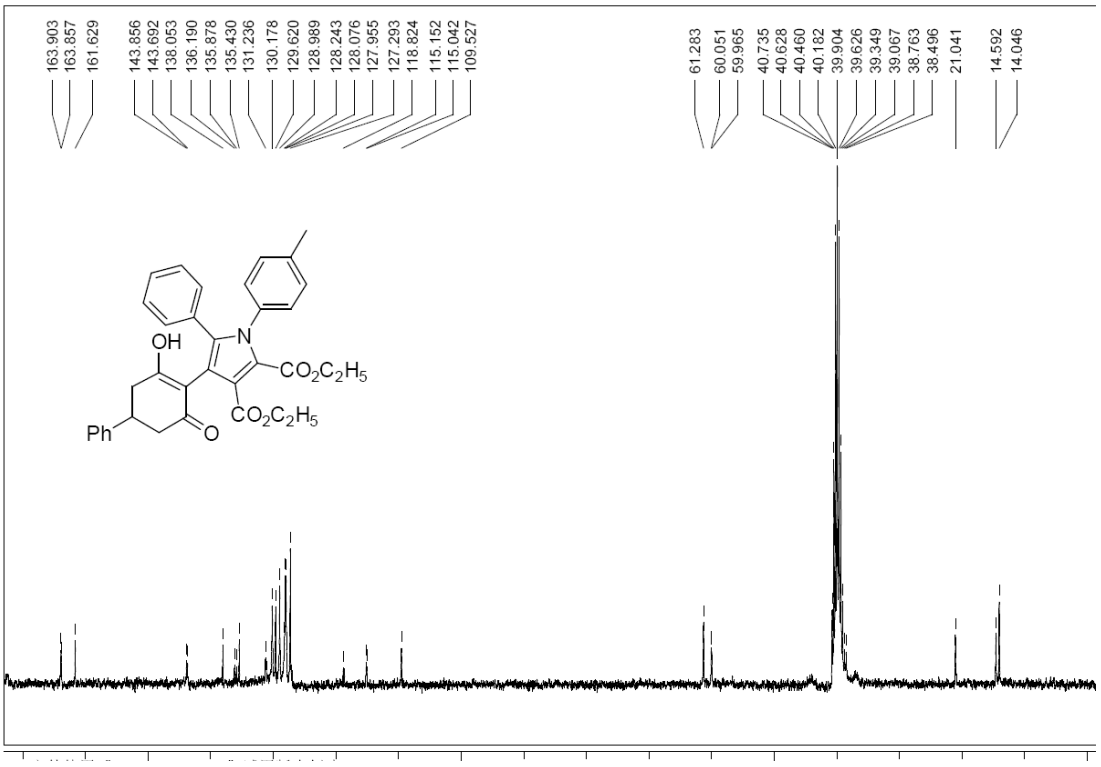
^{13}C NMR spectrum of compound **7n**



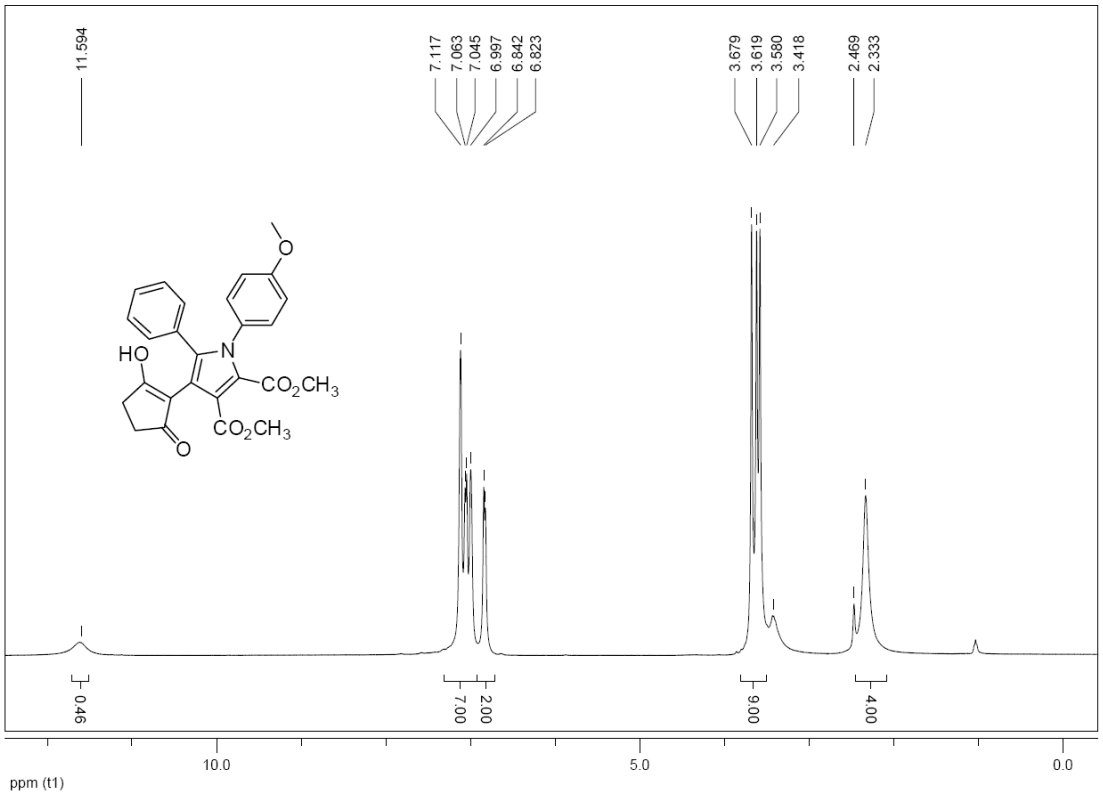
^{1}H NMR spectrum of compound **7o**



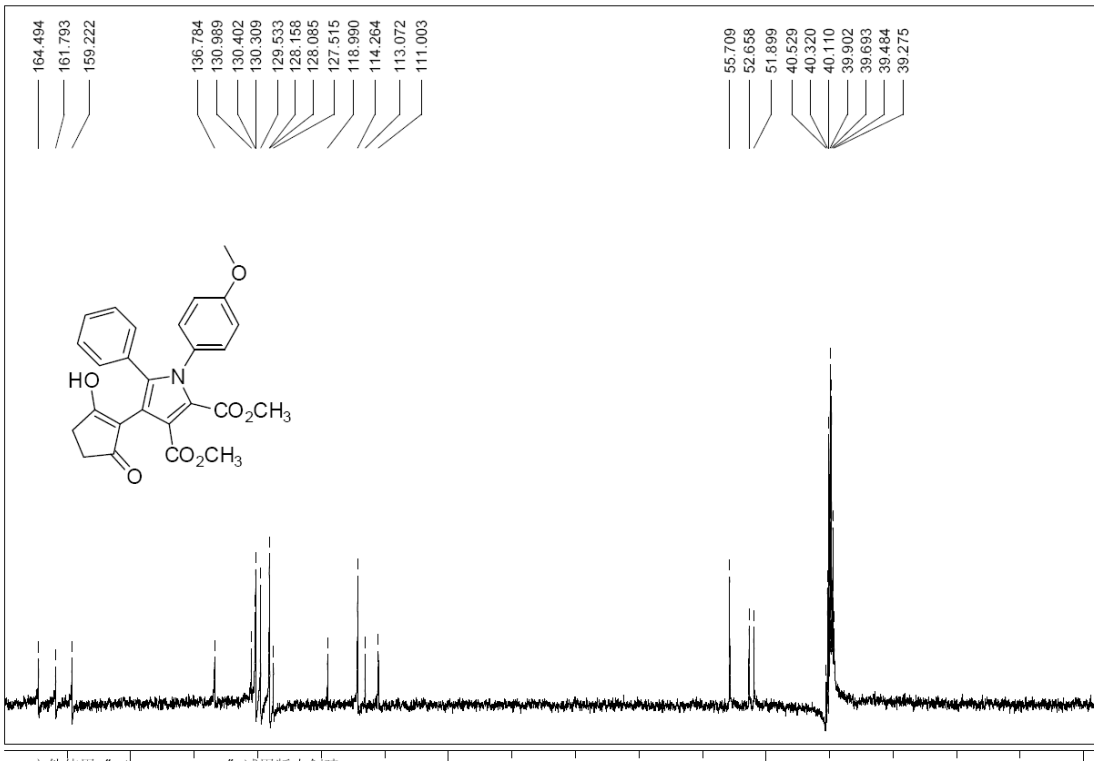
^{13}C NMR spectrum of compound **7o**



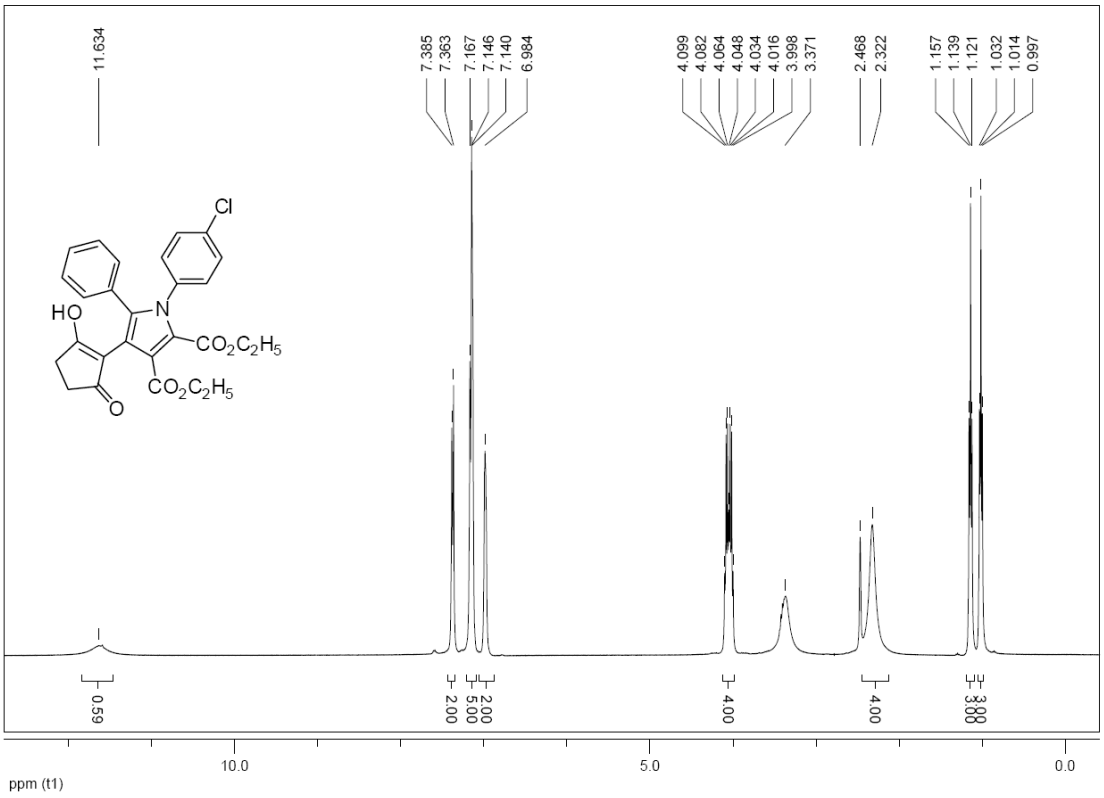
^{1}H NMR spectrum of compound **7p**



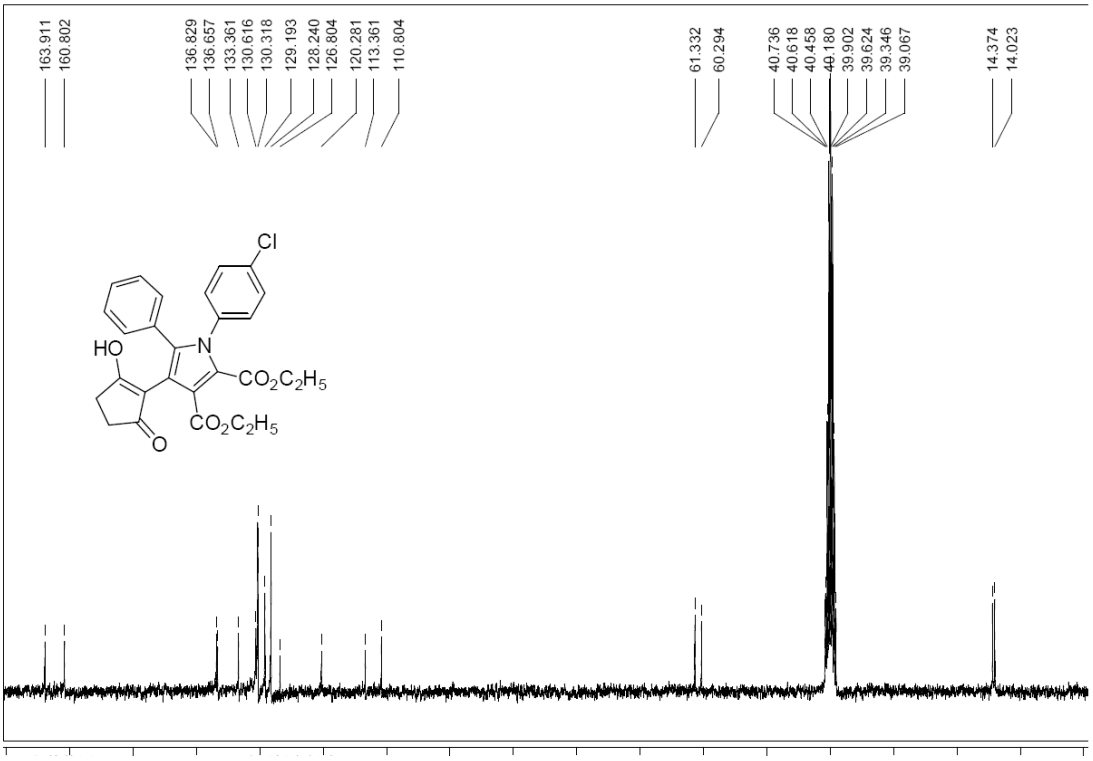
^{13}C NMR spectrum of compound **7p**



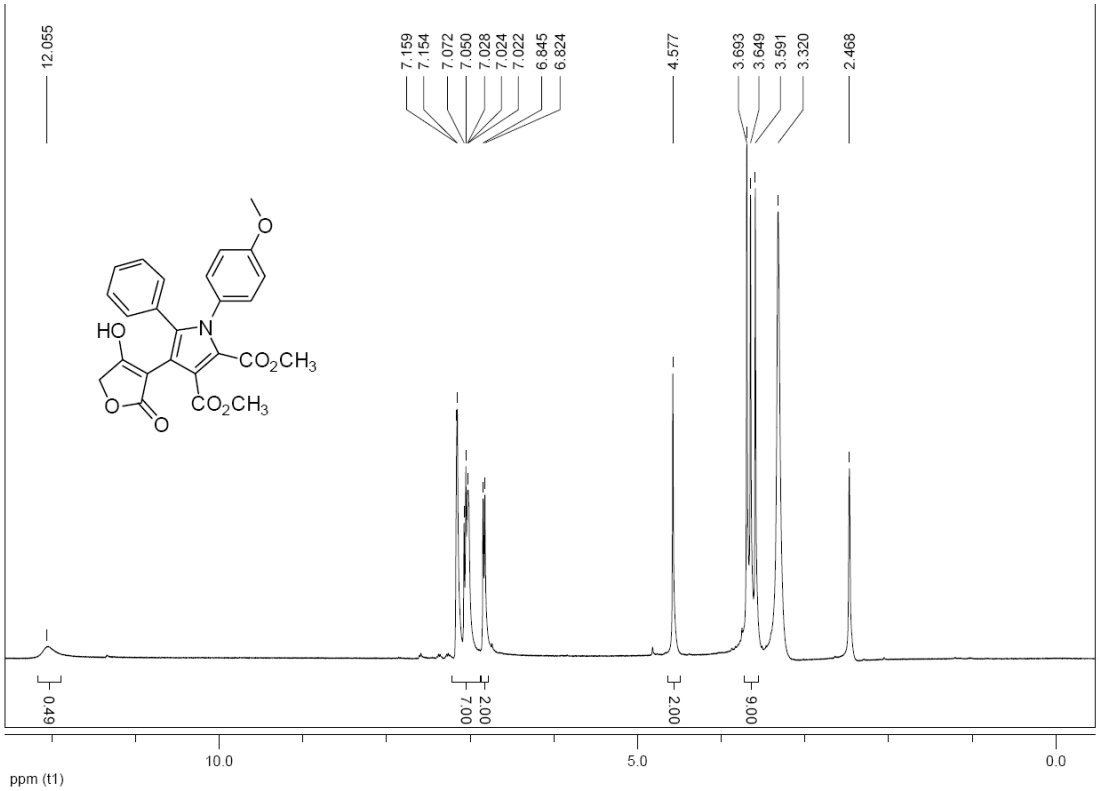
^{1}H NMR spectrum of compound **7q**



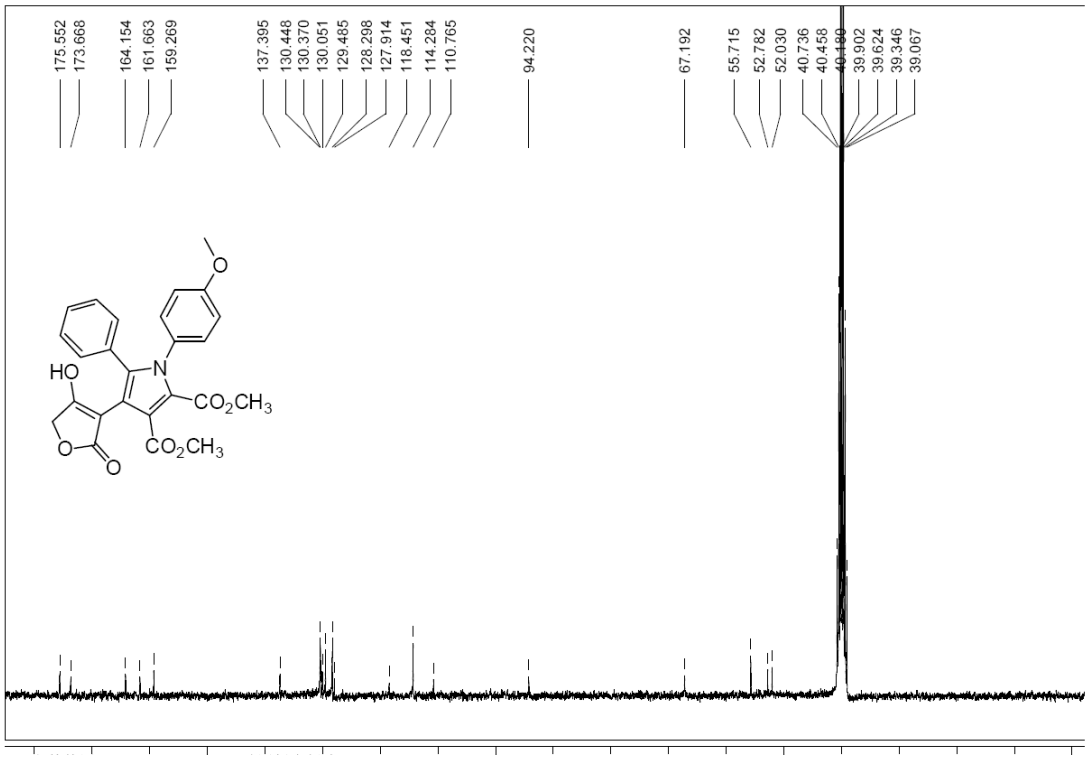
^{13}C NMR spectrum of compound **7q**



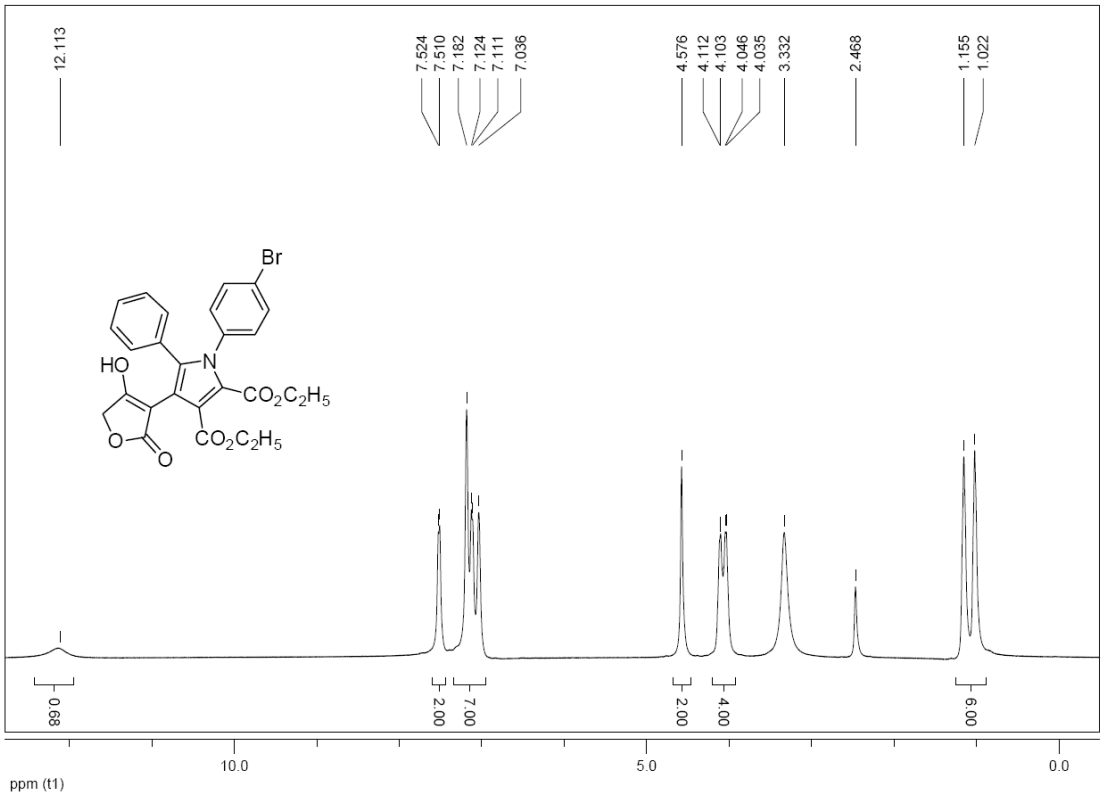
^{1}H NMR spectrum of compound **7r**



^{13}C NMR spectrum of compound **7r**



^{1}H NMR spectrum of compound **7s**



^{13}C NMR spectrum of compound **7s**