Electronic supplementary materials *Mendeleev Commun.*, 2022, **32**, 382–383

Novel chromeno[2,3-*c*]pyrroles synthesized *via* intramolecular rhodium(II) carbene trapping

Evgeny Chupakhin, Grigory Kantin, Dmitry Dar'in and Mikhail Krasavin

Contents:

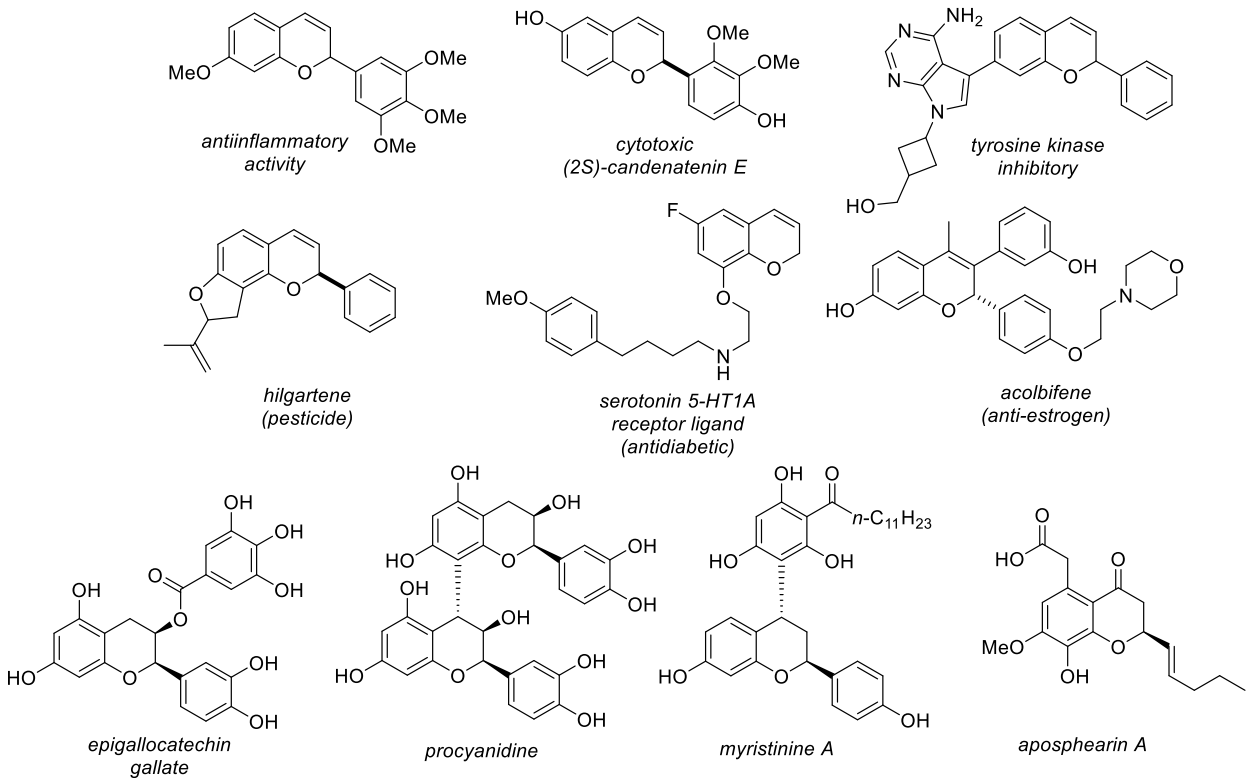


Figure S1. Examples of bioactive compounds based on 2*H*-chromene core and natural products containing a 2*H*-dihydrochromene nucleus.

General considerations

All commercial reagents were used without purification. NMR spectra were recorded using Bruker Avance III spectrometer (^{1}H: 400.13 MHz; ^{13}C: 100.61 MHz; chemical shifts are reported as parts per million (δ, ppm); the residual solvent peaks were used as internal standards: 7.26 and 2.50 ppm for ^{1}H in $CDCl_3$ and DMSO-d_6 respectively, 39.52 and 77.16 ppm for ^{13}C in DMSO-d_6 and $CDCl_3$ respectively; multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet/doublets of doublets, td = triplet of doublets; coupling constants, *J*, are reported in Hz. Mass spectra were recovered using Bruker microTOF spectrometer (ionization by electrospray, positive ions detection). Melting points were determined in open capillary tubes on Stuart SMP50 Automatic Melting Point Apparatus.

General procedure for the preparation of 2-hydroxybenzylidene succinimides 6a-i (GP1). To a solution of maleimide (4.0 mmol) in MeOH (120 ml) was added triphenylphosphine (4.4 mmol), and the mixture was stirred for 30 min followed by addition of the corresponding 2-hydroxybenzaldehyde (4.4 mmol). In several minutes, a precipitate was formed, and the mixture was stirred at ambient temperature for an additional 12 h. Upon cooling in ice bath, the precipitate was filtered off, washed with cold MeOH (40 ml) and dried in air to afford 2-hydroxybenzylidene succinimide **6** which was used in the next step without further purification.

General procedure for the preparation of diazo 2-hydroxybenzylidene succinimides 7a-i (GP2)

The 'SAFE cocktail' was prepared as follows. To a stirred solution of sodium azide (390 mg, 6 mmol) and potassium carbonate (1.24 g, 12 mmol) in water (30 ml), 3-(chlorosulfonyl)benzoic acid (1.32 g, 6 mmol) was added, and the mixture was stirred at ambient temperature for 10 min to give a clear solution which was used for diazo transfer reaction. The 'SAFE cocktail' thus prepared was added to a stirred suspension of the corresponding 2-hydroxybenzylidene succinimide **6** (3 mmol) and potassium carbonate (828 mg, 6 mmol) in MeCN–water (7:1, 75 mL). The mixture was stirred for 20–24 h (TLC control) and extracted with CH_2Cl_2 (2×30 ml). The combined organic extracts were dried over sodium sulfate and evaporated to dryness to give diazo benzylidene succinimide **7** which was purified by column chromatography in CH_2Cl_2.

General procedure for the preparation of chromenes 8a-i (GP3)

Salt $Rh_2(OAc)_4$ (1 mol%) was added to a stirred solution of corresponding diazo benzylidene succinimide **7a-i** (2 mmol) in CH_2Cl_2. The reaction mixture was stirred to complete conversion of diazo compound (control by TLC, 2-4 h) and subjected to column chromatography on silica gel (eluting with *n*-hexane-acetone, 2:1) to afford chromenes **8**.

General procedure for the preparation of dihydrochromenes 9 (GP4) To a solution of the corresponding chromene **8** (1 mmol) in dry THF (10 ml), Pd/C (10% w/w, 1 mol%) was added, and the mixture was stirred in H_2 atmosphere for 12 h. After completion of the reaction (TLC control), the catalyst was removed by centrifugation, the solvent was evaporated under reduced pressure and the crude product was purified by column chromatography on silica gel (eluting with *n*-hexane-acetone, 7:3).

(*E*)-1-Benzyl-3-(2-hydroxybenzylidene)pyrrolidine-2,5-dione 6a.

Following GP1 using *N*-benzylmaleimide (748 mg, 4 mmol) and salicylaldehyde (536 mg, 4.4 mmol) gave **6a** as a white solid; yield: 840 mg (72%); 141.7–143.2 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.22 (s, 1H, OH), 7.86 (s, 1H, CH), 7.51 (d, *J* = 7.5 Hz, 1H, ArH), 7.37 – 7.23 (m, 6H, 6ArH), 6.95 (d, *J* = 8.0 Hz, 1H, ArH), 6.89 (t, *J* = 7.5 Hz, 1H, ArH), 4.69 (s, 2H, CH_2), 3.74 (d, *J* = 2.0 Hz, 2H, CH_2).

^{13}C NMR (101 MHz, DMSO-d_6) δ 174.7, 171.2, 157.6, 136.8, 131.9, 129.6, 128.9, 128.0, 127.8, 123.7, 121.4, 119.8, 116.3, 41.9, 34.2.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{16}NO_3$: 294.1125 found: 294.1118.

(*E*)-1-(3-Fluorophenyl)-3-(2-hydroxybenzylidene)pyrrolidine-2,5-dione 6b.

Following GP1 using *N*-(3-fluorophenyl)maleimide (764 mg, 4 mmol) and salicylaldehyde (536 mg, 4.4 mmol) compound **6b** was obtained as white solid; yield: 984 mg (83%); 117.2–119.2 °C.

^{1}H NMR (500 MHz, DMSO-d_6) δ 10.31 (s, 1H, OH), 7.92 (t, *J* = 2.3 Hz, 1H, CH), 7.60 – 7.54 (m, 2H, 2ArH), 7.33 – 7.24 (m, 4H, ArH), 6.96 (dd, *J* = 8.2, 1.1 Hz, 1H, ArH), 6.92 (t, *J* = 7.5 Hz, 1H, ArH), 3.80 (d, *J* = 2.3 Hz, 2H, CH_2).

^{13}C NMR (126 MHz, DMSO-d_6) δ 173.8, 170.3, 162.21 (d, *J* = 243.9 Hz), 157.6, 134.59 (d, *J* = 10.6 Hz), 132.1, 130.89 (d, *J* = 9.0 Hz), 129.7, 128.3, 123.8, 123.6, 121.4, 120.0, 116.4, 115.6 (d, *J* = 20.7 Hz), 114.9, 114.7, 34.5.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{13}FNO_3$: 298.0874 found: 298.0878.

(*E*)-1-(4-Fluorophenyl)-3-(2-hydroxybenzylidene)pyrrolidine-2,5-dione 6c.

Following GP1 using *N*-(4-fluorophenyl)maleimide (764 mg, 4 mmol) and salicylaldehyde (536 mg, 4.4 mmol) compound **6c** was obtained as white solid; yield: 912 mg (77%); 131.5–133.1 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.25 (s, 1H, OH), 7.92 (s, 1H, CH), 7.56 (dd, *J* = 7.9, 1.6 Hz, 1H, ArH), 7.45 – 7.40 (m, 2H, 2ArH), 7.37 (d, *J* = 8.7 Hz, 2H, 2ArH), 7.33 – 7.26 (m, 1H, ArH), 6.97 (d, *J* = 8.1 Hz, 1H, ArH), 6.92 (t, *J* = 7.5 Hz, 1H, ArH), 3.79 (d, *J* = 2.4 Hz, 2H, CH_2).

^{13}C NMR (101 MHz, DMSO-d_6) δ 174.03, 170.59, 161.85 (d, J = 245.1 Hz), 157.62, 132.01, 129.77 (d, J = 8.9 Hz), 129.66, 129.39 (d, J = 2.9 Hz), 128.09, 123.77, 121.48, 119.96, 116.39, 116.19 (d, J = 22.8 Hz), 34.51.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{13}FNO_3$: 298.0874 found 298.0867.

(*E*)-3-(2-Hydroxybenzylidene)-1-(4-methoxyphenyl)pyrrolidine-2,5-dione 6d.

Following GP1 using *N*-(4-methoxypehyl)maleimide (812 mg, 4 mmol) and salicylaldehyde (536 mg, 4.4 mmol) compound **6d** was obtained as white solid; yield: 976 mg (79%); 151.0–151.8 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.27 (s, 1H, OH), 7.91 (t, J = 2.2 Hz, 1H, CH), 7.55 (dd, J = 7.9, 1.5 Hz, 1H, ArH), 7.33 – 7.21 (m, 3H, 3ArH), 7.06 (d, J = 9.0 Hz, 2H, 2ArH), 6.97 (dd, J = 8.2, 1.1 Hz, 1H, ArH), 6.92 (t, J = 7.6 Hz, 1H, ArH), 3.81 (s, 3H, OCH_3), 3.78 (d, J = 2.3 Hz, 2H, CH_2).

^{13}C NMR (101 MHz, DMSO-d_6) δ 174.2, 170.8, 159.3, 157.6, 131.9, 129.6, 128.8, 127.8, 125.7, 123.9, 121.5, 119.9, 116.4, 114.5, 55.8, 34.4.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{18}H_{15}NNaO_4$: 332.0893; found: 332.0888.

(*E*)-3-(5-Bromo-2-hydroxybenzylidene)-1-(*p*-tolyl)pyrrolidine-2,5-dione 6e.

Following GP1 using *N*-*p*-tolylmaleimide (748 mg, 4 mmol) and 5-bromo-2-hydroxybenzaldehyde (884 mg, 4.4 mmol) compound **6e** was obtained as white solid; yield: 1.25 g (84%); 139.2–140.6 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.59 (s, 1H, OH), 7.78 (t, J = 2.3 Hz, 1H, CH), 7.62 (d, J = 2.4 Hz, 1H, ArH), 7.44 (dd, J = 8.7, 2.4 Hz, 1H, ArH), 7.32 (d, J = 8.2 Hz, 2H, 2ArH), 7.23 (d, J = 8.3 Hz, 2H, 2ArH), 6.93 (d, J = 8.8 Hz, 1H, ArH), 3.83 (d, J = 2.3 Hz, 2H, CH_2), 2.37 (s, 3H, CH_3).

^{13}C NMR (101 MHz, DMSO-d_6) δ 173.9, 170.4, 156.7, 138.2, 134.2, 131.4, 130.4, 129.8, 127.3, 126.4, 125.6, 123.8, 118.5, 111.1, 34.1, 21.2.

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{18}H_{14}BrNNaO_3$: 394.0049 found 494.0054.

(*E*)-1-(4-Acetylphenyl)-3-(2-hydroxybenzylidene)pyrrolidine-2,5-dione 6f.

Following GP1 using *N*-(4-acetylphenyl)maleimide (860 mg, 4 mmol) and salicylaldehyde (536 mg, 4.4 mmol) compound **6f** was obtained as brown solid; yield: 1.17 g (91 %); 176.4–177.8 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.10 (s, 1H, OH), 8.09 (d, J = 7.4 Hz, 2H, 2ArH), 7.97 (s, 1H, ArH), 7.64 – 7.49 (m, 3H, 3ArH), 7.29 (t, J = 7.2 Hz, 1H, CH), 6.99 (d, J = 8.0 Hz, 1H, ArH), 6.93 (t, J = 6.8 Hz, 1H, ArH), 3.82 (s, 2H, CH_2), 2.63 (s, 3H, $COCH_3$).

^{13}C NMR (101 MHz, DMSO-d_6) δ 197.6, 173.6, 170.2, 157.6, 137.2, 136.7, 132.0, 129.7, 129.1, 128.8, 127.4, 123.6, 121.6, 120.0, 119.0, 116.6, 34.6, 27.1.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{16}NO_4$: 322.1074 found 322.1078.

(*E*)-3-(2-Hydroxy-3-methoxybenzylidene)-1-(4-trifluoromethylphenyl)pyrrolidine-2,5-dione 6g.

Following GP1 using *N*-(4-trifluoromethylphenyl)maleimide (964 mg, 4 mmol) and 2-hydroxy-3-methoxybenzaldehyde (668 mg, 4.4 mmol) compound **6g** was obtained as white solid; yield: 1.4 g (93%); 163.2–164.6 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.46 (s, 1H, OH), 7.98 (t, J = 2.1 Hz, 1H, CH), 7.92 (d, J = 8.5 Hz, 2H, 2ArH), 7.65 (d, J = 8.3 Hz, 2H, 2ArH), 7.18 (d, J = 7.9 Hz, 1H, ArH), 7.08 (d, J = 7.3 Hz, 1H, ArH), 6.90 (t, J = 8.0 Hz, 1H, ArH), 3.86 (s, 3H, OCH_3), 3.81 (d, J = 2.2 Hz, 2H, CH_2).

^{13}C NMR (101 MHz, DMSO-d_6) δ 173.73, 170.25, 148.35, 147.02, 136.78, 128.42, 128.27, 126.39, 126.35, 125.82, 123.93, 123.12, 121.72, 121.10, 119.75, 113.92, 56.43, 34.61.

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{19}H_{14}F_3NNaO_4$: 400.0767 found: 400.0762.

(*E*)-3-(2-Hydroxy-4,6-dimethylbenzylidene)-1-phenylpyrrolidine-2,5-dione 6h.

Following GP1 using *N*-phenylmaleimide (692 mg, 4 mmol) and 2-hydroxy-4,6-methylbenzaldehyde (660 mg, 4.4 mmol) compound **6h** was obtained as white solid; yield: 992 mg (81%); 138.1–140.3 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.91 (s, 1H, OH), 7.56 (s, 1H, CH), 7.52 (t, J = 7.6 Hz, 2H, 2ArH), 7.43 (t, J = 7.4 Hz, 1H, ArH), 7.38 (d, J = 7.8 Hz, 2H, 2ArH), 6.63 (s, 1H, ArH), 6.58 (s, 1H, ArH), 3.36 (d, J = 4.2 Hz, 2H, CH_2), 2.23 (s, 3H, CH_3), 2.22 (s, 3H, CH_3).

^{13}C NMR (101 MHz, DMSO-d_6) δ 174.0, 170.0, 155.24, 140.2, 138.7, 133.2, 130.4, 129.3, 128.6, 127.7, 127.4, 122.4, 118.1, 114.7, 35.1, 21.4, 20.4.

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{19}H_{17}NNaO_3$: 330.1101 found: 330.1109.

(*E*)-1-(4-Chlorophenyl)-3-(2-hydroxybenzylidene)pyrrolidine-2,5-dione 6i.

Following GP1 using *N*-(4-chlorophenyl)maleimide (828 mg, 4 mmol) and salicylaldehyde (536 mg, 4.4 mmol) compound **6i** was obtained as white solid; yield: 1.1 g (88 %); 173.4–175.2 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.26 (s, 1H, OH), 7.93 (s, 1H, CH), 7.59 (d, *J* = 8.7 Hz, 2H, 2ArH), 7.56 (d, *J* = 8.1 Hz, 1H, ArH), 7.42 (d, *J* = 8.7 Hz, 2H, 2ArH), 7.29 (t, *J* = 7.7 Hz, 1H, ArH), 6.97 (d, *J* = 8.2 Hz, 1H, ArH), 6.92 (t, *J* = 7.5 Hz, 1H, ArH), 3.80 (d, *J* = 2.2 Hz, 2H, CH_2).

^{13}C NMR (101 MHz, DMSO-d_6) δ 173.9, 170.4, 157.6, 133.1, 132.0, 129.7, 129.3, 128.2, 123.7, 121.4, 121.1, 120.0, 116.4, 34.5.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{13}ClNO_3$: 314.0578 found: 314.0572.

(*E*)-1-Benzyl-3-diazo-4-(2-hydroxybenzylidene)pyrrolidine-2,5-dione 7a.

Following GP2 using **6a** (879 mg, 3 mmol) compound **7a** was obtained as orange solid; yield: 651 mg (68%); 109.6–111.7 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.22 (s, 1H, OH), 7.60 (s, 1H, CH), 7.39 – 7.26 (m, 6H, 6ArH), 7.26 – 7.21 (m, 1H, ArH) 6.93 (d, *J* = 7.9 Hz, 1H, ArH), 6.86 (t, *J* = 7.5 Hz, 1H, ArH), 4.74 (s, 2H, CH_2).

^{13}C NMR (101 MHz, DMSO-d_6) δ 167.3, 164.8, 156.6, 136.7, 131.6, 130.4, 129.0, 128.0, 124.0, 120.7, 119.2, 116.6, 116.2, 60.7, 42.4.

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{18}H_{13}N_3NaO_3$: 342.0849 found: 342.0852.

(*E*)-3-Diazo-1-(3-fluorophenyl)-4-(2-hydroxybenzylidene)pyrrolidine-2,5-dione 7b.

Following GP2 using **6b** (891 mg 3 mmol) compound **7b** was obtained as orange solid; yield: 717 mg (74%); 123.2–124.7 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.29 (s, 1H, OH), 7.68 (s, 1H, CH), 7.62 – 7.55 (m, 1H, ArH), 7.37 – 7.33 (m, 1H, ArH), 7.33 – 7.29 (m, 3H, 3ArH), 7.29 – 7.24 (m, 1H, ArH), 6.96 (d, *J* = 7.8 Hz, 1H, ArH), 6.90 (t, *J* = 7.5 Hz, 1H, ArH).

^{13}C NMR (101 MHz, DMSO-d_6) δ 166.5, 164.0, 162.2 (d, *J* = 244.1 Hz), 156.6, 134.0 (d, *J* = 10.7 Hz), 131.7, 131.0 (d, *J* = 9.0 Hz), 130.3, 124.4, 123.8 (d, *J* = 3.1 Hz), 120.6, 119.3, 116.3 (d, *J* = 9.5 Hz), 115.9, 115.7, 115.0, 114.8, 61.4.

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{17}H_{10}FN_3NaO_3$: 346.0598 found: 346.0590.

(*E*)-3-Diazo-1-(4-fluorophenyl)-4-(2-hydroxybenzylidene)pyrrolidine-2,5-dione 7c.

Following GP2 using **6c** (891 mg 3 mmol) compound **7c** was obtained as orange solid; yield: 705 mg (73%); 141.2–142.7 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.28 (s, 1H, OH), 7.67 (s, 1H, CH), 7.48 (dd, *J* = 9.0, 5.1 Hz, 2H, 2ArH), 7.37 (t, *J* = 8.8 Hz, 2H, 2ArH), 7.31 (dd, *J* = 7.6, 1.2 Hz, 1H, ArH), 7.29 – 7.24 (m, 1H, ArH), 6.96 (d, *J* = 8.0 Hz, 1H, ArH), 6.90 (t, *J* = 7.4 Hz, 1H, ArH).

^{13}C NMR (101 MHz, DMSO-d_6) δ 166.7, 164.3, 161.9 (d, *J* = 245.5 Hz), 156.6, 131.7, 130.3, 129.9 (d, *J* = 8.9 Hz), 128.8 (d, *J* = 2.3 Hz), 124.3, 120.7, 119.3, 116.5, 116.2, 61.2.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{11}FN_3O_3$: 324.0779 found 324.0784.

(*E*)-3-Diazo-4-(2-hydroxybenzylidene)-1-(4-methoxyphenyl)pyrrolidine-2,5-dione 7d.

Following GP2 using **6d** (927 mg 3 mmol) compound **7d** was obtained as orange solid; yield: 774 mg (78 %); 148.3–149.6 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.26 (s, 1H, OH), 7.65 (s, 1H, CH), δ 7.37 – 7.29 (m, 3H, 3ArH), 7.28 – 7.23 (m, 1H, ArH), 7.07 (d, *J* = 8.9 Hz, 2H. 2ArH), 6.95 (d, *J* = 8.1 Hz, 1H, ArH), 6.90 (t, *J* = 7.5 Hz, 1H, ArH), 3.81 (s, 3H, OCH_3).

^{13}C NMR (126 MHz, DMSO-d_6) δ 166.9, 164.5, 159.5, 156.6, 131.6, 130.3, 129.0, 125.1, 124.0, 120.8, 119.3, 117.2, 116.3, 114.7, 71.5, 61.0, 55.9, 31.2.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{14}N_3O_4$: 336.0979 found: 336.0976

(*E*)-3-(5-Bromo-2-hydroxybenzylidene)-4-diazo-1-(*p*-tolyl)pyrrolidine-2,5-dione 7e.

Following GP2 using **6e** (372 mg 3 mmol) compound **7e** was obtained as orange solid; yield: 753 mg (63%); 153.2–155.4 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.59 (s, 1H, OH), 7.56 (s, 1H, CH), 7.47 (d, *J* = 2.4 Hz, 1H, ArH), 7.40 (dd, *J* = 8.7, 2.5 Hz, 1H, ArH), 7.33 (d, *J* = 8.3 Hz, 2H, 2ArH), 7.27 (d, *J* = 8.4 Hz, 2H, 2ArH), 6.91 (d, *J* = 8.7 Hz, 1H, ArH), 2.37 (s, 3H, CH_3).

^{13}C NMR (126 MHz, DMSO- d_6) δ 166.6, 164.3, 155.8, 138.5, 133.9, 129.9, 127.4, 123.0, 122.2, 118.3, 117.9, 110.4, 72.4, 71.6, 66.8, 61.5, 21.2.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{13}BrN_3O_3$: 398.0135 found: 398.0129

(*E*)-1-(4-Acetylphenyl)-3-diazo-4-(2-hydroxybenzylidene)pyrrolidine-2,5-dione 7f.

Following GP2 using **6f** (963 mg 3 mmol) compound **7f** was obtained as yellow solid; yield: 852 mg (82 %); 137.7–139.3 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.33 (s, 1H, OH), 8.10 (d, *J* = 8.5 Hz, 2H, 2ArH), 7.69 (s, 1H, CH), 7.61 (d, *J* = 8.5 Hz, 2H, 2ArH), 7.35 – 7.21 (m, 2H, 2ArH), 6.97 (d, *J* = 8.1 Hz, 1H, ArH), 6.90 (t, *J* = 7.5 Hz, 1H, ArH), 2.63 (s, 3H, $COCH_3$).

^{13}C NMR (126 MHz, DMSO-d_6) δ 197.7, 166.5, 164.0, 156.7, 136.6, 131.8, 130.3, 129.3, 127.4, 124.5, 120.6, 119.3, 116.3, 61.5, 27.3.

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{19}H_{13}N_3NaO_4$: 370.0798 found: 370.0804

(E)-3-diazo-4-(2-hydroxy-3-methoxybenzylidene)-1-(4-trifluoromethylphenyl)pyrrolidine-2,5-dione 7g.

Following GP2 using **6g (**1.14 mg 3 mmol) compound **7g** was obtained as orange solid; yield: 906 mg (75 %); 161.2–163.3 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.52 (s, 1H, OH), 7.92 (d, *J* = 8.5 Hz, 2H, 2ArH), 7.73 – 7.67 (m, 3H, 2ArH, CH), 7.05 (dd, *J* = 7.6, 1.6 Hz, 1H, ArH), 6.94 – 6.85 (m, 2H, 2ArH), 3.85 (s, 3H, OCH_3).

^{13}C NMR (126 MHz, DMSO-d_6) δ 166.4, 163.9, 148.4, 145.8, 136.2, 128.9 (d, *J* = 32.2 Hz), 128.2, 126.6, 126.5 (q, *J* = 3.4 Hz), 126.5, 125.5, 124.3, 123.3, 121.7, 120.9, 119.3, 116.5, 113.7, 61.6, 56.4.

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{19}H_{12}F_3N_3NaO_4$: 426.0672 found: 426.0678

(*E*)-3-Diazo-4-(2-hydroxy-4,6-dimethylbenzylidene)-1-phenylpyrrolidine-2,5-dione 7h.

Following GP2 using **6h (**921 mg 3 mmol) compound **7h** was obtained as orange solid; yield: 738 mg (74%); 141.0–141.7 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.97 (s, 1H, OH), 7.56 – 7.50 (m, 2H, 2ArH), 7.48 (s, 1H, CH), 7.47 – 7.41 (m, 3H, 3ArH), 6.63 (s, 1H, ArH), 6.60 (s, 1H, ArH), 2.24 (s, 3H, CH_3), 2.22 (s, 3H, CH_3).

^{13}C NMR (126 MHz, DMSO-d_6) δ 166.4, 164.2, 155.6, 140.6, 138.9, 132.6, 129.4, 128.8, 127.7, 123.8, 122.5, 118.1, 116.7, 113.9, 79.6, 66.8, 62.4, 21.4, 20.2.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{16}N_3O_3$: 334.3545 found: 334.3538

(E)-1-(4-Chlorophenyl)-3-diazo-4-(2-hydroxybenzylidene)pyrrolidine-2,5-dione 7i.

Following GP2 using **6i (**939 mg 3 mmol) compound **7i** was obtained as orange solid; yield: 792 mg (78%); 171.3–172.6 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.27 (s, 1H, OH), 7.67 (s, 1H, CH), 7.61 (d, *J* = 8.7 Hz, 2H, 2ArH), 7.47 (d, *J* = 8.7 Hz, 2H, 2ArH), 7.31 (d, *J* = 6.6 Hz, 1H, ArH), 7.29 – 7.24 (m, 1H, ArH), 6.96 (d, *J* = 7.8 Hz, 1H, ArH), 6.90 (t, *J* = 7.5 Hz, 1H, ArH).

^{13}C NMR (126 MHz, DMSO-d_6) δ 166.6, 164.1, 133.3, 131.7, 131.4, 130.3, 129.5, 129.4, 124.3, 120.6, 119.3, 116.3, 61.4.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{11}ClN_3O_3$: 340.7425 found: 340.7421

2-Benzylchromeno[2,3-*c*]pyrrole-1,3(2*H*,3a*H*)-dione (8a).

Following GP3 using **7a** (638 mg, 2 mmol) **8a** was obtained as a white solid; yield: 570 mg (89%); mp 131.2–133.1 °C

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.58 (d, *J* = 2.1 Hz, 1H, CH), 7.52 (dd, *J* = 7.8, 1.5 Hz, 1H, ArH), 7.43 – 7.28 (m, 6H, 6ArH), 7.12 (dd, *J* = 7.6, 5.2 Hz, 2H, 2ArH), 5.65 (d, *J* = 2.2 Hz, 1H, CH), 4.72 (s, 2H, CH_2).

^{13}C NMR (126 MHz, DMSO-d_6) δ 170.9, 165.2, 154.4, 136.2, 132.9, 130.8, 129.1, 128.1, 128.1, 127.8, 123.6, 122.2, 122.1, 117.2, 71.3, 41.9.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{14}NO_3$: 292.0968 found 292.0962

2-(3-Fluorophenyl)chromeno[2,3-*c*]pyrrole-1,3(2*H*,3a*H*)-dione (8b).

Following GP3 using **7b** (646 mg, 2 mmol) **8b** was obtained as a white solid; yield: 448 mg (76%); mp 152.2–154.1 °C

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.67 (d, *J* = 2.1 Hz, 1H, CH), 7.64 – 7.58 (m, 1H, ArH), 7.56 (d, *J* = 8.7 Hz, 1H, ArH), 7.43 (td, *J* = 9.1, 8.1, 1.5 Hz, 1H, ArH), 7.37 – 7.28 (m, 3H, ArH), 7.15 (d, *J* = 7.8 Hz, 2H, ArH), 5.72 (d, *J* = 2.2 Hz, 1H, CH).

^{13}C NMR (126 MHz, DMSO-d_6) δ 169.9, 164.3, 163.2, 161.2, 154.5, 133.6, 133.5, 133.1, 131.1 (d, *J* = 9.0 Hz), 130.8, 128.5, 123.8, 123.8, 123.6, 122.2, 121.8, 117.2, 116.2, 116.0, 114.9 (d, *J* = 24.2 Hz), 71.5.

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{17}H_{10}NNaO_3$: 318.0537 found 318.0529

2-(4-Fluorophenyl)chromeno[2,3-*c*]pyrrole-1,3(2*H*,3a*H*)-dione (8c).

Following GP3 using **7c** (646 mg, 2 mmol) **8c** was obtained as a white solid; yield: 476 mg (81 %); mp 163.4–165.1 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.65 (d, *J* = 2.3 Hz, 1H), 7.57 – 7.53 (m, 1H), 7.50 – 7.45 (m, 2H), 7.45 – 7.36 (m, 3H), 7.15 (d, *J* = 7.8 Hz, 2H), 5.70 (d, *J* = 2.2 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 170.2, 164.6, 162.1 (d, J = 245.7 Hz), 154.5, 133.0, 130.8, 129.8 (d, J = 9.0 Hz), 128.3 (d, J = 3.0 Hz), 123.6, 122.2, 121.9, 117.2, 116.4 (d, J = 22.9 Hz), 71.5.

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{17}H_{10}NNaO_3$: 318.0537 found 318.0546

2-(4-Methoxyphenyl)chromeno[2,3-*c*]pyrrole-1,3(2*H*,3a*H*)-dione (8d).

Following GP3 using **7d** (670 mg, 2 mmol) **8d** was obtained as a white solid; yield: 436 mg (71 %); mp 146.4–148.2 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.62 (d, J = 2.1 Hz, 1H, CH), 7.55 (dd, J = 7.9, 1.4 Hz, 1H, ArH), 7.42 (td, J = 8.0, 1.5 Hz, 1H, ArH), 7.32 (d, J = 8.9 Hz, 2H, 2ArH), 7.14 (d, J = 7.8 Hz, 2H, 2ArH), 7.08 (d, J = 8.9 Hz, 2H, 2ArH), 5.69 (d, J = 2.2 Hz, 1H, CH), 3.82 (s, 3H, OCH_3).

^{13}C NMR (126 MHz, DMSO-d_6) δ 170.5, 164.9, 159.6, 154.5, 132.9, 130.8, 128.8, 127.9, 124.6, 123.6, 122.2, 117.2, 114.6, 71.5, 55.9.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{14}NO_4$: 308.0917 found 308.0923

7-Bromo-2-(*p*-tolyl)chromeno[2,3-*c*]pyrrole-1,3(2*H*,3a*H*)-dione (8e).

Following GP3 using **7e** (796 mg, 2 mmol) **8e** was obtained as a white solid; yield: 620 mg (84 %); mp 132.4–133.6 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.95 (d, J = 8.5 Hz, 2H, 2ArH), 7.69 (d, J = 8.3 Hz, 2H, 2ArH), 7.67 (d, J = 2.3 Hz, 1H, CH), 7.17 (td, J = 8.1, 1.4 Hz, 1H, ArH), 7.13 (d, J = 1.3 Hz, 1H, ArH), 7.09 (d, J = 7.8 Hz, 1H, ArH), 5.67 (d, J = 2.2 Hz, 1H, CH), 3.85 (s, 3H, CH_3).

^{13}C NMR (126 MHz, DMSO-d_6) δ 169.9, 164.2, 148.6, 143.5, 135.7, 129.4, 128.8, 128.3, 126.5, 126.5, 125.5, 123.3, 122.8, 122.2, 121.7, 116.3, 71.5, 56.3.

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{18}H_{12}BrNNaO_3$: 391.9893 found 391.9896

2-(4-Acetylphenyl)chromeno[2,3-*c*]pyrrole-1,3(2*H*,3a*H*)-dione (8f).

Following GP3 using **7f** (694 mg, 2 mmol) **8f** was obtained as a white solid; yield: 548 mg (86 %); mp 163.5–165.8 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.12 (d, J = 8.5 Hz, 2H, 2ArH), 7.68 (d, J = 2.1 Hz, 1H, CH), 7.60 (d, J = 8.5 Hz, 2H, 2ArH), 7.56 (d, J = 7.7 Hz, 1H, ArH), 7.43 (td, J = 7.8, 1.4 Hz, 1H, ArH), 7.16 (d, J = 7.8 Hz, 2H, 2ArH), 5.74 (d, J = 2.2 Hz, 1H, CH), 2.64 (s, 3H, $COCH_3$).

^{13}C NMR (126 MHz, DMSO-d_6) δ 197.6, 169.9, 164.2, 154.6, 137.2, 136.1, 133.1, 130.8, 129.2, 128.6, 127.4, 123.6, 122.2, 121.8, 117.2, 71.6, 31.0, 27.2.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{14}NO_4$: 320.0917 found 320.0923

5-Methoxy-2-(4-(trifluoromethyl)phenyl)chromeno[2,3-*c*]pyrrole-1,3(2*H*,3a*H*)-dione (8g).

Following GP3 using **7g** (806 mg, 2 mmol) **8g** was obtained as a white sold; yield: 510 mg (68 %); mp 177.4–178.7 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.95 (d, J = 8.5 Hz, 2H, 2ArH), 7.70 (s, 1H, CH), 7.69 – 7.66 (m, 2H, 2ArH), 7.17 (td, J = 8.1, 1.5 Hz, 1H, ArH), 7.13 (d, J = 1.4 Hz, 1H, ArH), 7.09 (d, J = 7.8 Hz, 1H, ArH), 5.67 (d, J = 2.3 Hz, 1H, CH), 3.85 (s, 3H, OCH_3).

^{13}C NMR (126 MHz, DMSO-d_6) δ 169.9, 164.3, 148.7, 143.5, 135.8, 129.3 (d, J = 32.1 Hz), 128.9, 128.3, 126.6 (q, J = 3.6 Hz), 123.3, 122.9, 122.3, 121.7, 116.4, 71.5, 56.4.

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{19}H_{12}F_3NNaO_4$: 398.0611 found 398.0624

6,8-Dimethyl-2-phenylchromeno[2,3-*c*]pyrrole-1,3(2*H*,3a*H*)-dione (8h).

Following GP2 using **7h** (666 mg, 2 mmol) **8h** was obtained as a white solid; yield: 444 mg (73 %); mp 181.2–182.7 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.67 (d, J = 2.1 Hz, 1H, CH), 7.58 – 7.51 (m, 2H, 2ArH), 7.50 – 7.44 (m, 1H, ArH), 7.43 – 7.39 (m, 2H, 2ArH), 6.82 (s, 2H, 2ArH), 5.58 (d, J = 2.2 Hz, 1H, CH), 2.40 (s, 3H, CH_3), 2.29 (s, 3H, CH_3).

^{13}C NMR (126 MHz, DMSO-d_6) δ 170.4, 164.8, 154.9, 143.1, 138.7, 132.2, 129.4, 129.1, 127.5, 126.1, 125.8, 120.7, 118.8, 115.3, 71.1, 21.7, 18.9.

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{19}H_{15}NNaO_3$: 328.0944 found 328.0956

2-(4-Chlorophenyl)chromeno[2,3-*c*]pyrrole-1,3(2*H*,3a*H*)-dione (8i).

Following GP3 using **7i** (668 mg, 2 mmol) **8i** was obtained as a white solid; yield: 528 mg (85 %); mp 164.5–165.4 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.66 (s, 1H, CH), 7.62 (d, J = 8.5 Hz, 2H, 2ArH), 7.55 (d, J = 7.2 Hz, 1H, ArH), 7.46 (d, J = 8.5 Hz, 2H, 2ArH), 7.41 (d, J = 7.6 Hz, 1H, ArH), 7.15 (d, J = 7.7 Hz, 2H, 2ArH) 5.70 (d, J = 2.1 Hz, 1H, CH).

^{13}C NMR (126 MHz, DMSO-d_6) δ 170.1, 164.4, 154.5, 133.6, 133.1, 130.9, 130.8, 129.5, 129.3, 128.4, 123.6, 122.2, 121.9, 117.2, 71.5.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{11}ClNO_3$: 312.0422 found 312.0426

(3a*R,9a*S**)-2-(4-Acetylphenyl)-9,9a-dihydrochromeno[2,3-*c*]pyrrole-1,3(2*H*,3a*H*)-dione (9a)**.

Following GP4 using **8f** (319 mg, 1 mmol), **9a** was obtained as a white solid; yield 285 mg (89%); mp 131.2–133.1 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.03 (d, *J* = 8.6 Hz, 1H, ArH), 7.28 – 7.18 (m, 3H, 3ArH), 7.03 (td, *J* = 7.5, 1.2 Hz, 1H, ArH), 6.98 (dd, J = 8.0, 1.2 Hz, 1H, ArH), 5.31 (d, *J* = 8.7 Hz, 1H, CH), 3.80 (ddd, *J* = 8.6, 7.1, 5.0 Hz, 1H), 3.15 – 3.00 (m, 2H, CH_2), 2.59 (s, 3H, $COCH_3$).

^{13}C NMR (126 MHz, DMSO-d_6) δ 197.7, 176.7, 173.4, 153.8, 136.9, 136.0, 129.4, 129.1, 128.7, 127.1, 125.7, 123.6, 118.1, 74.4, 41.8, 27.3, 24.7.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{16}NO_4$: 322.1074 found 322.1068

(3a*R,9a*S**)-2-(4-Chlorophenyl)-9,9a-dihydrochromeno[2,3-*c*]pyrrole-1,3(2*H*,3a*H*)-dione (9b)**.

Following GP4 using **8i** (311 mg, 1 mmol), **9b** was obtained as a white solid; yield: 288 mg (92 %); 135.7–137.2 °C.

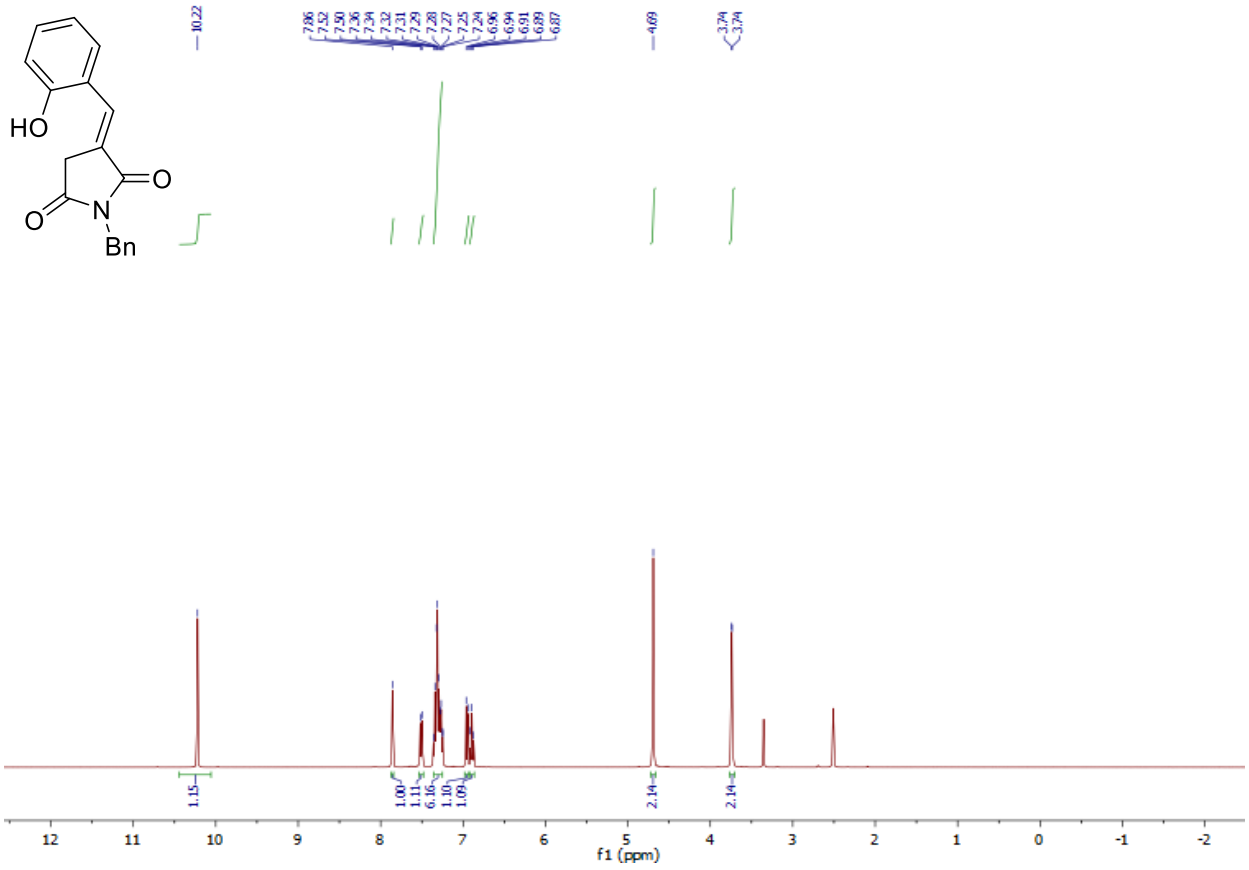
^{1}H NMR (400 MHz, DMSO-d_6) δ 7.54 (d, *J* = 8.7 Hz, 2H, 2ArH), 7.26 – 7.19 (m, 2H, 2ArH), 7.08 (d, *J* = 8.7 Hz, 2H, 2ArH), 7.05 – 7.00 (m, 1H, ArH), 6.98 (d, *J* = 7.9 Hz, 1H, ArH), 5.29 (d, *J* = 8.6 Hz, 1H, CH), 3.77 (ddd, *J* = 8.5, 7.1, 5.0 Hz, 1H, CH), 3.06 (td, *J* = 15.2, 8.6 Hz, 2H, CH_2).

^{13}C NMR (126 MHz, DMSO-d_6) δ 176.8, 173.5, 153.8, 133.6, 130.9, 129.1, 128.8, 128.7, 125.7, 123.6, 118.1, 74.3, 41.7, 24.7.

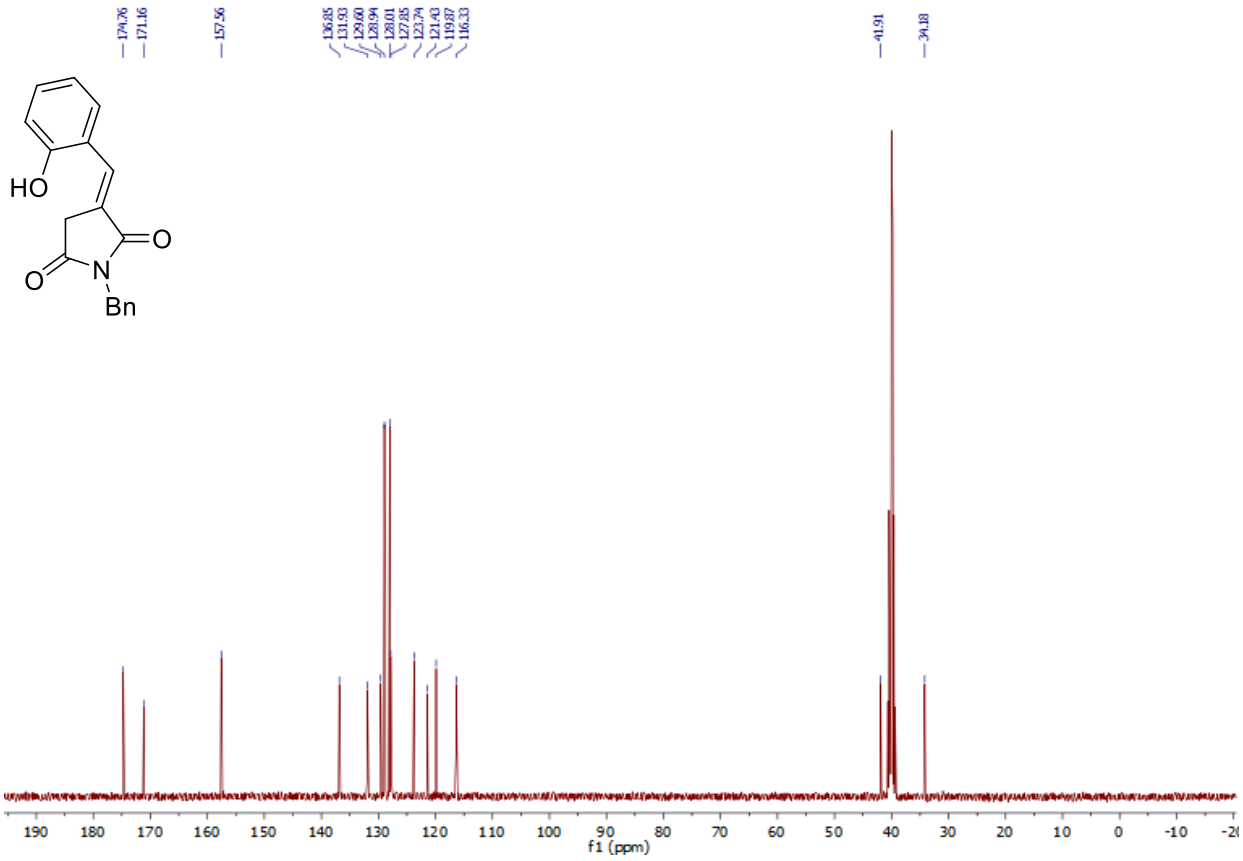
HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{13}ClNO_3$: 314.0578 found 314.0584.

Copies of ^{1}H and ^{13}C NMR spectra

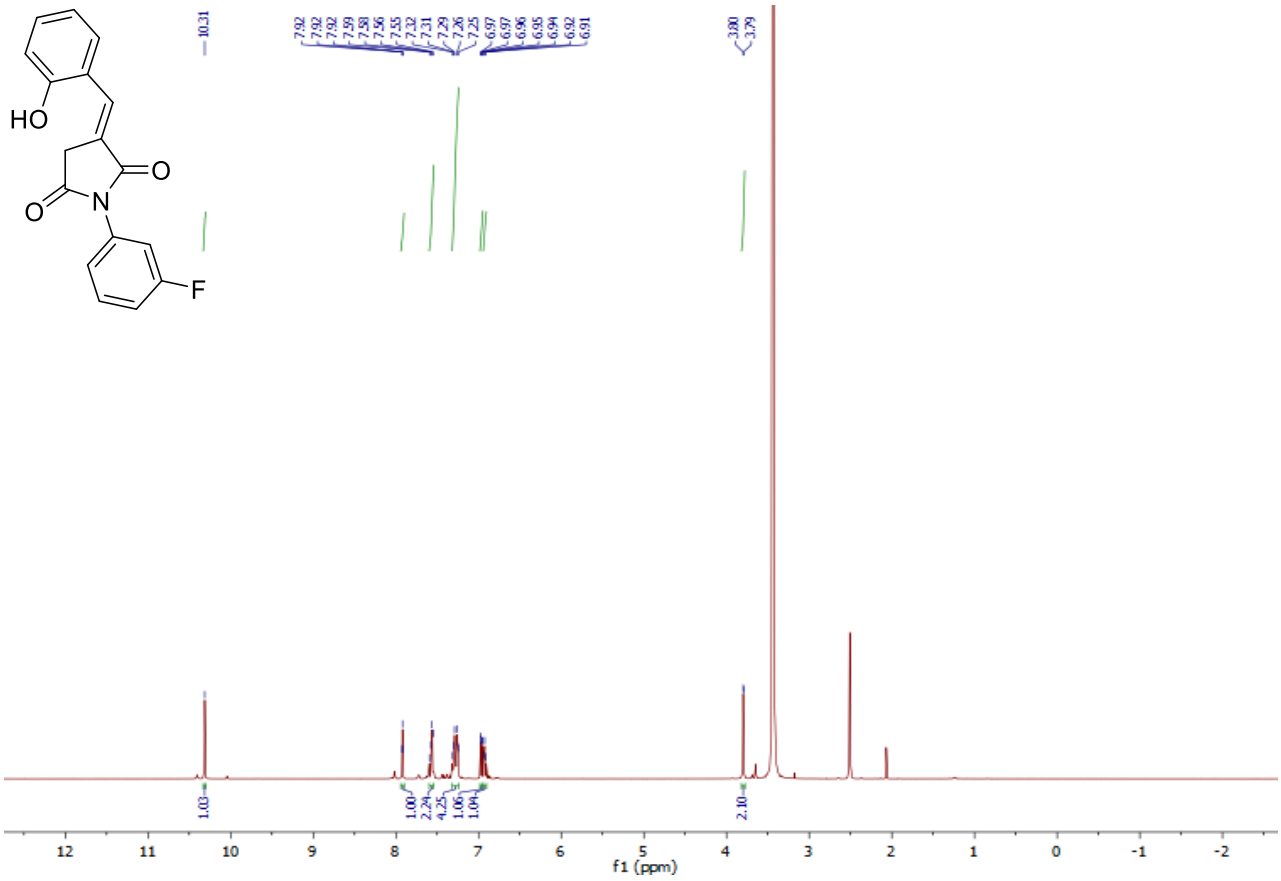
^{1}H NMR spectrum of compound **6a**



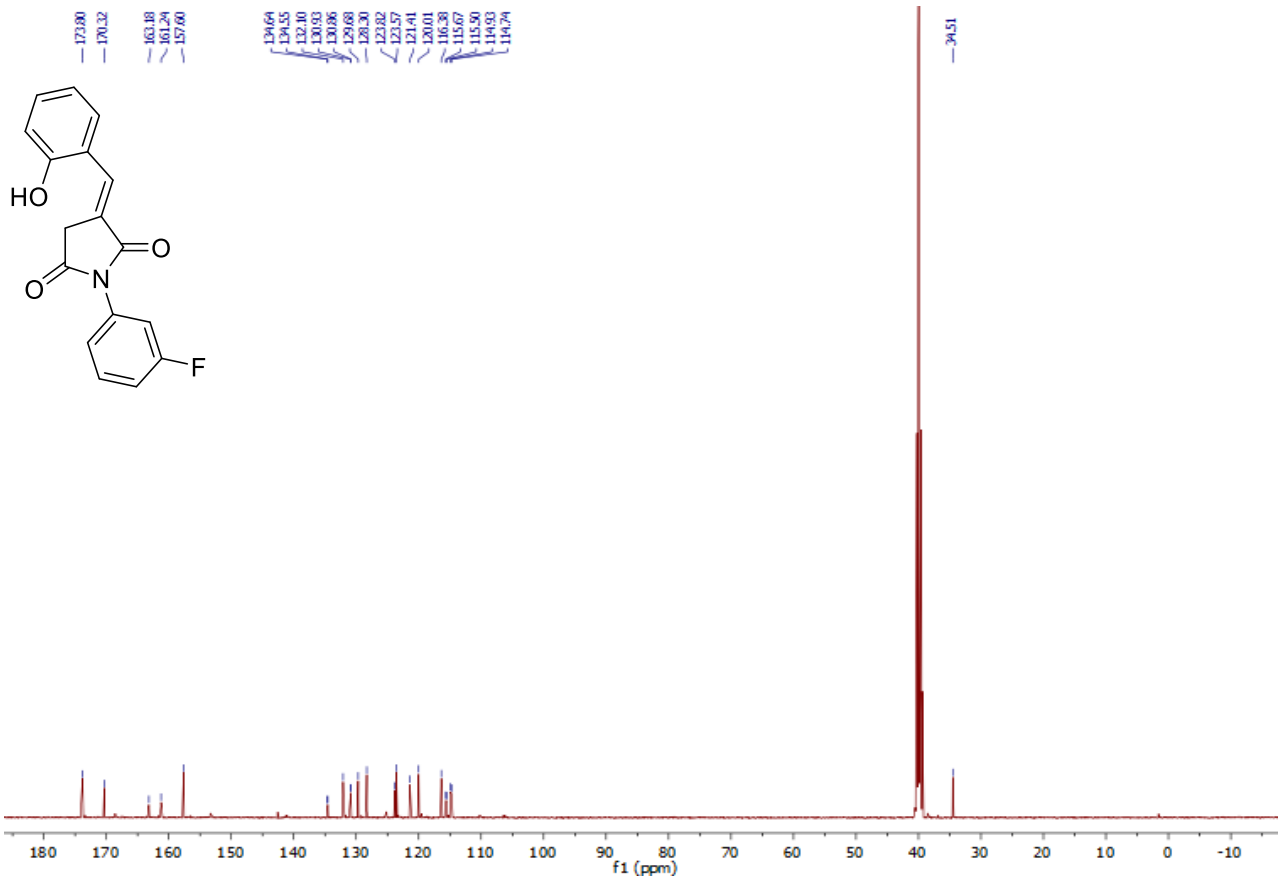
^{13}C NMR spectrum of compound **6a**



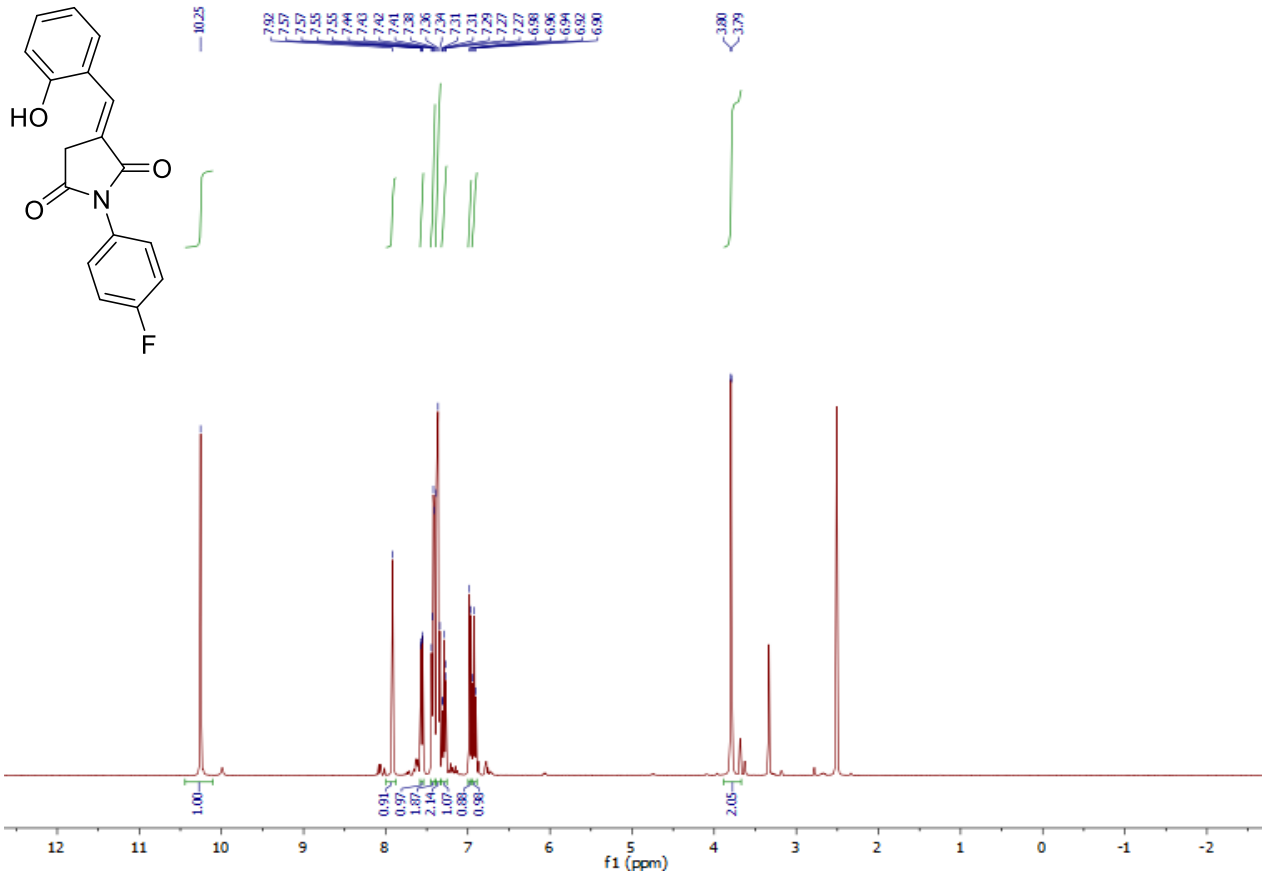
^{1}H NMR spectrum of compound **6b**



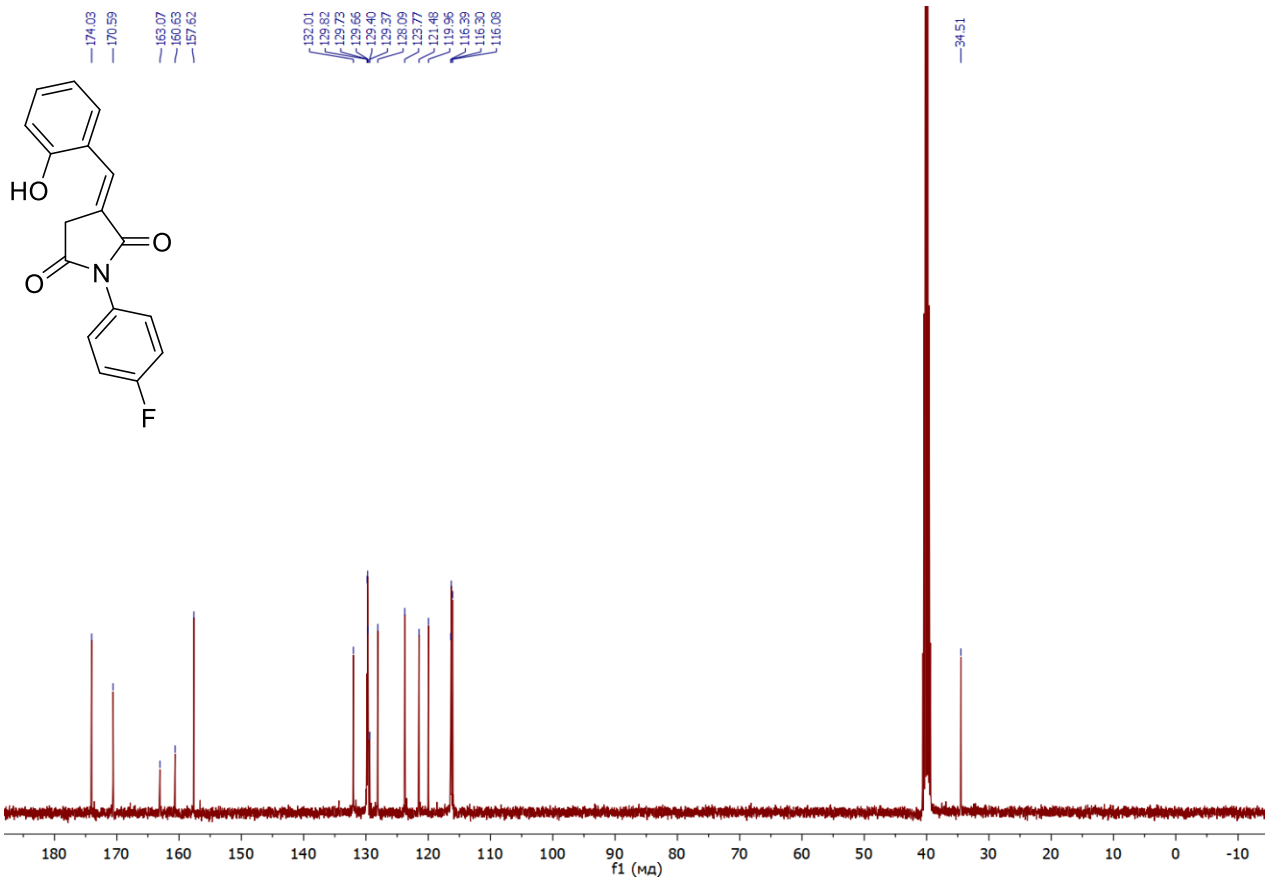
^{13}C NMR spectrum of compound **6b**



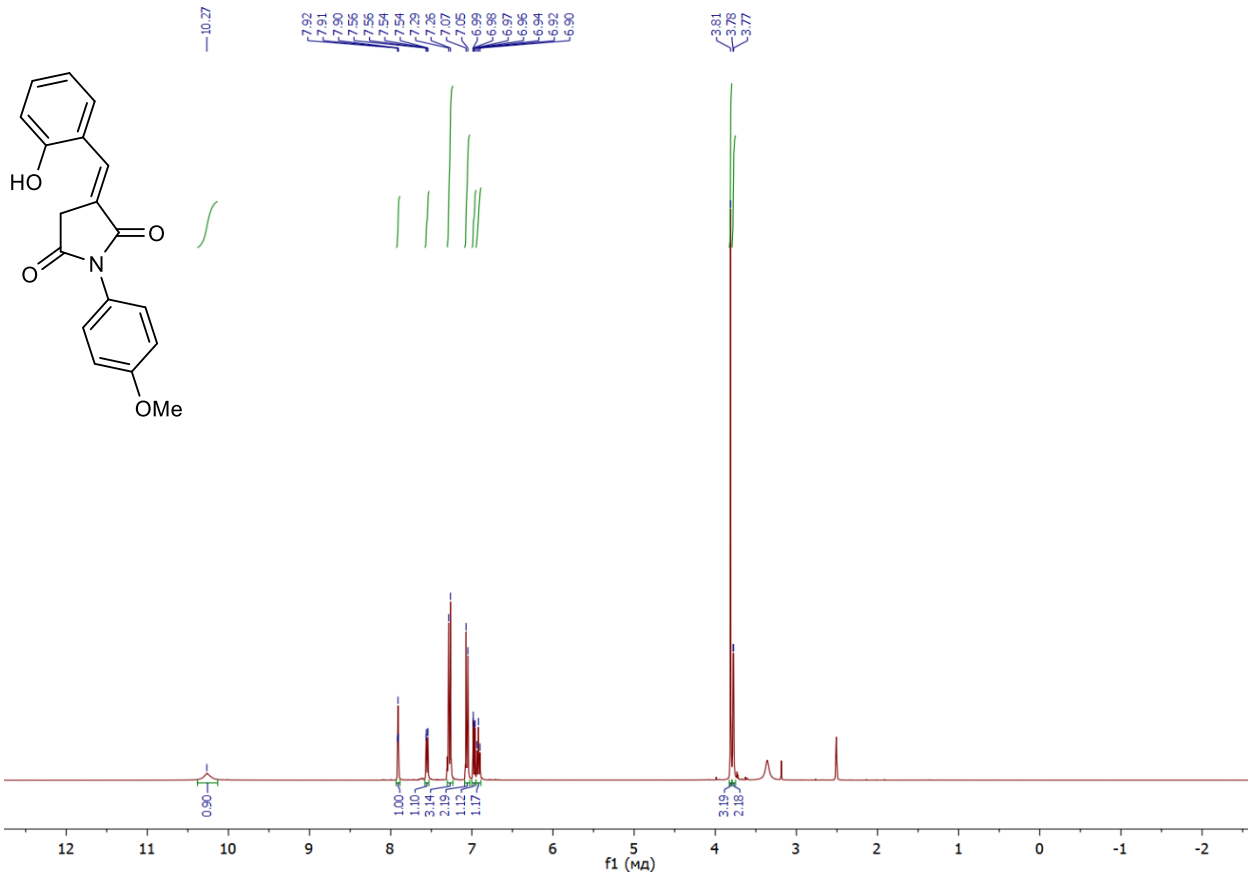
^{1}H NMR spectrum of compound **6c**



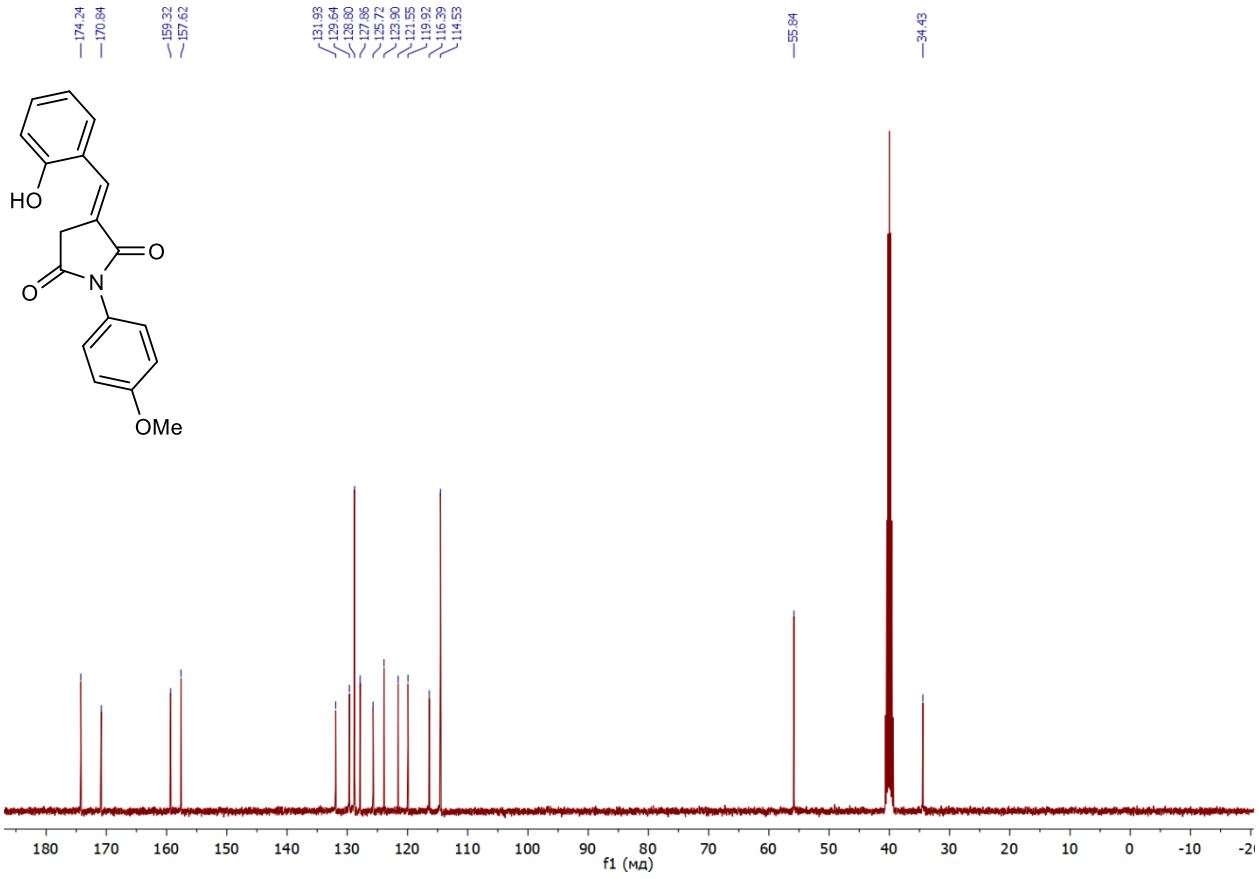
^{13}C NMR spectrum of compound **6c**



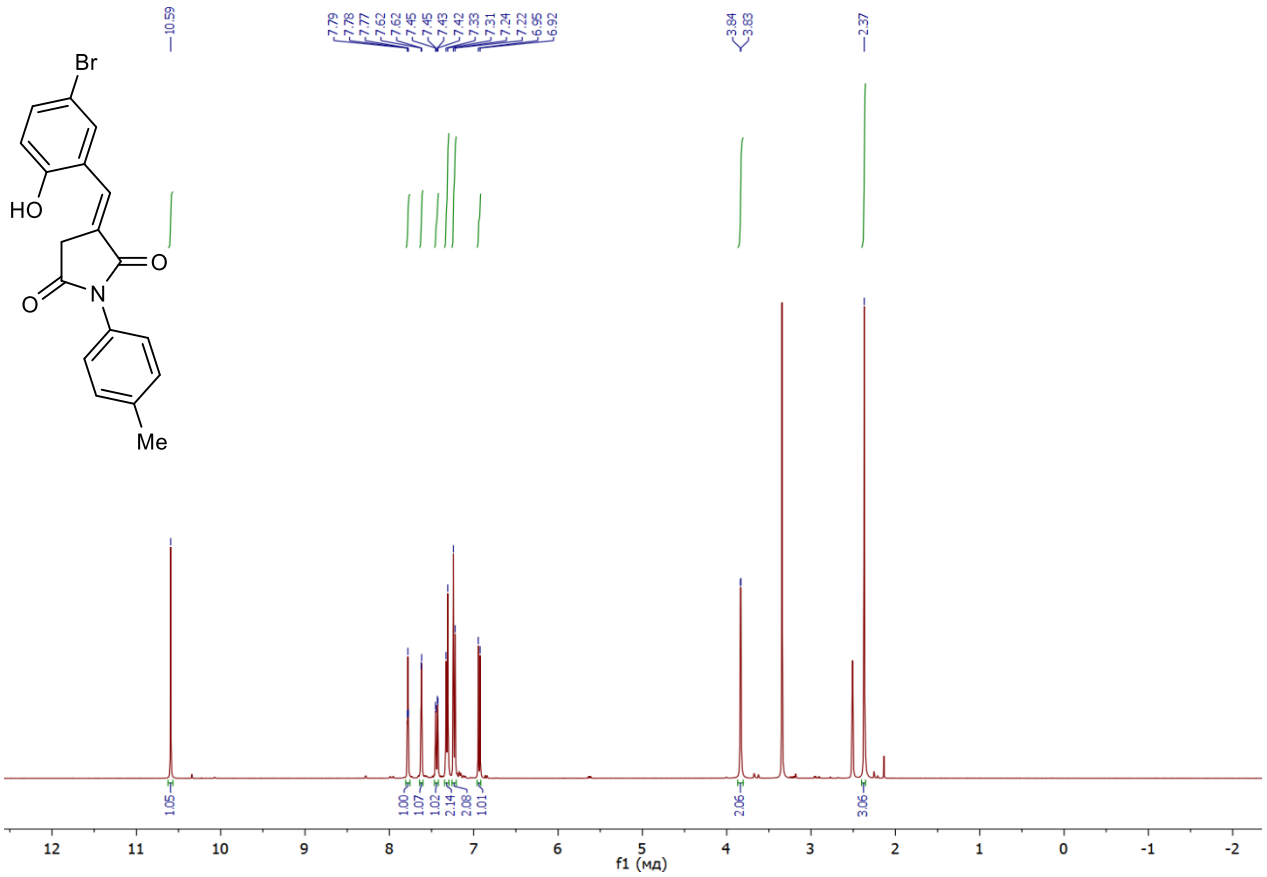
^{1}H NMR spectrum of compound **6d**



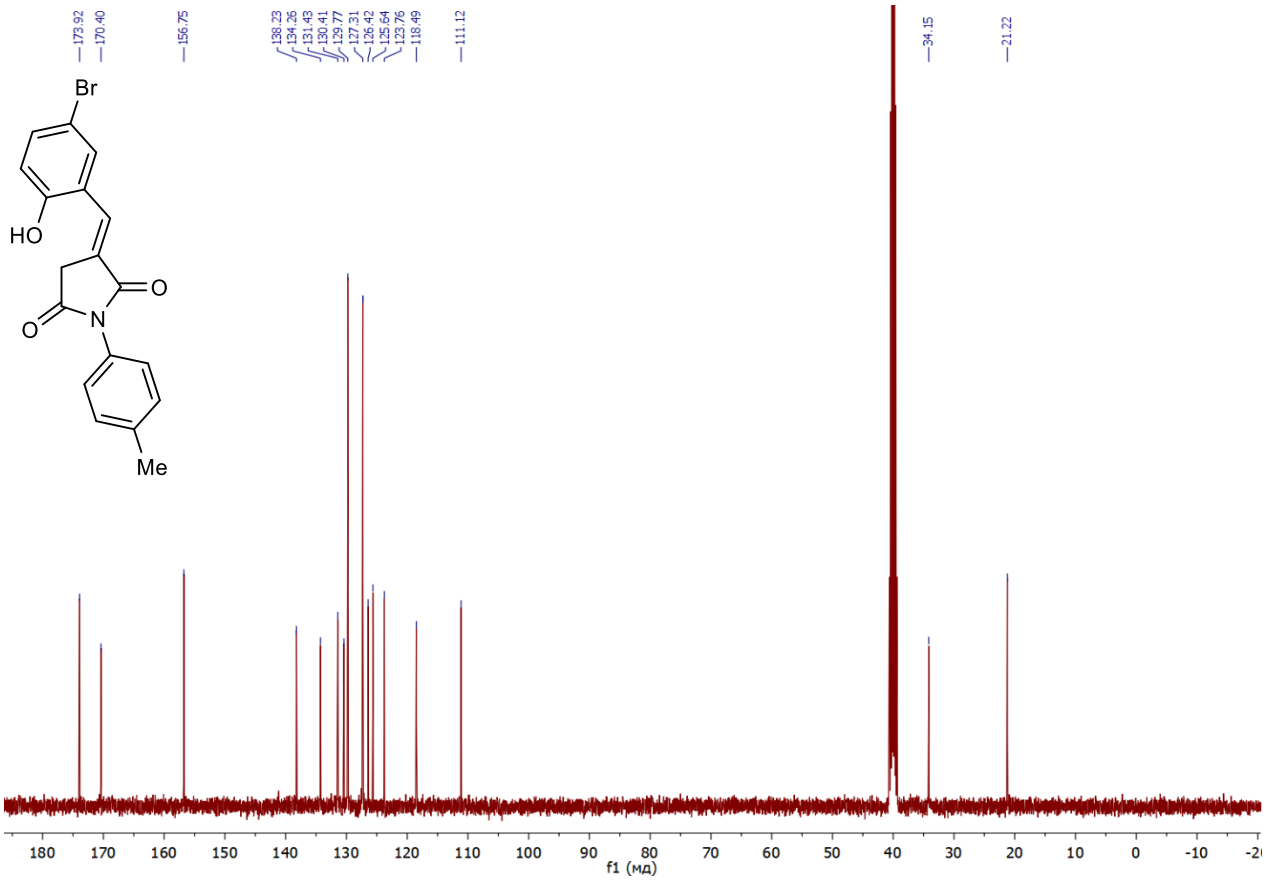
^{13}C NMR spectrum of compound **6d**



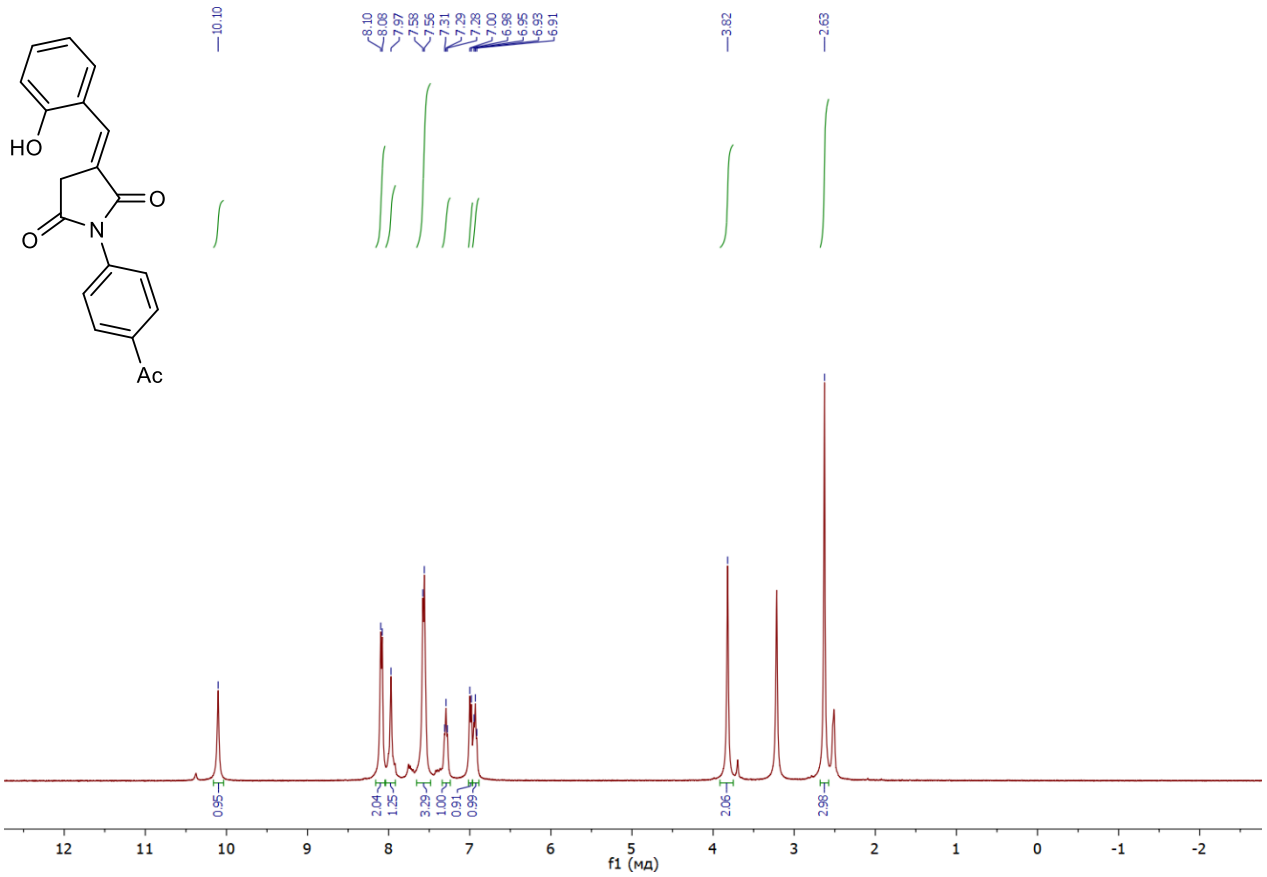
^{1}H NMR spectrum of compound **6e**



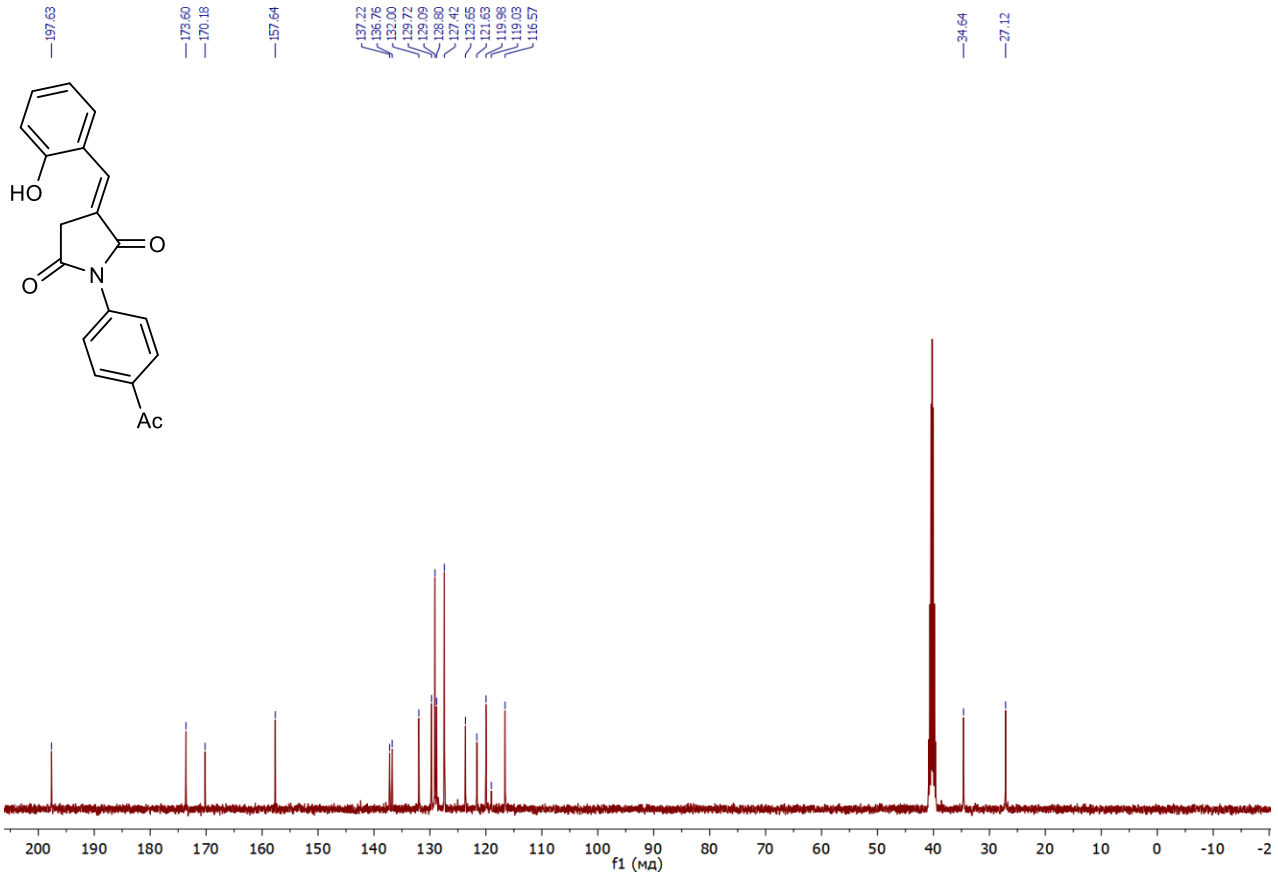
^{13}C NMR spectrum of compound **6e**



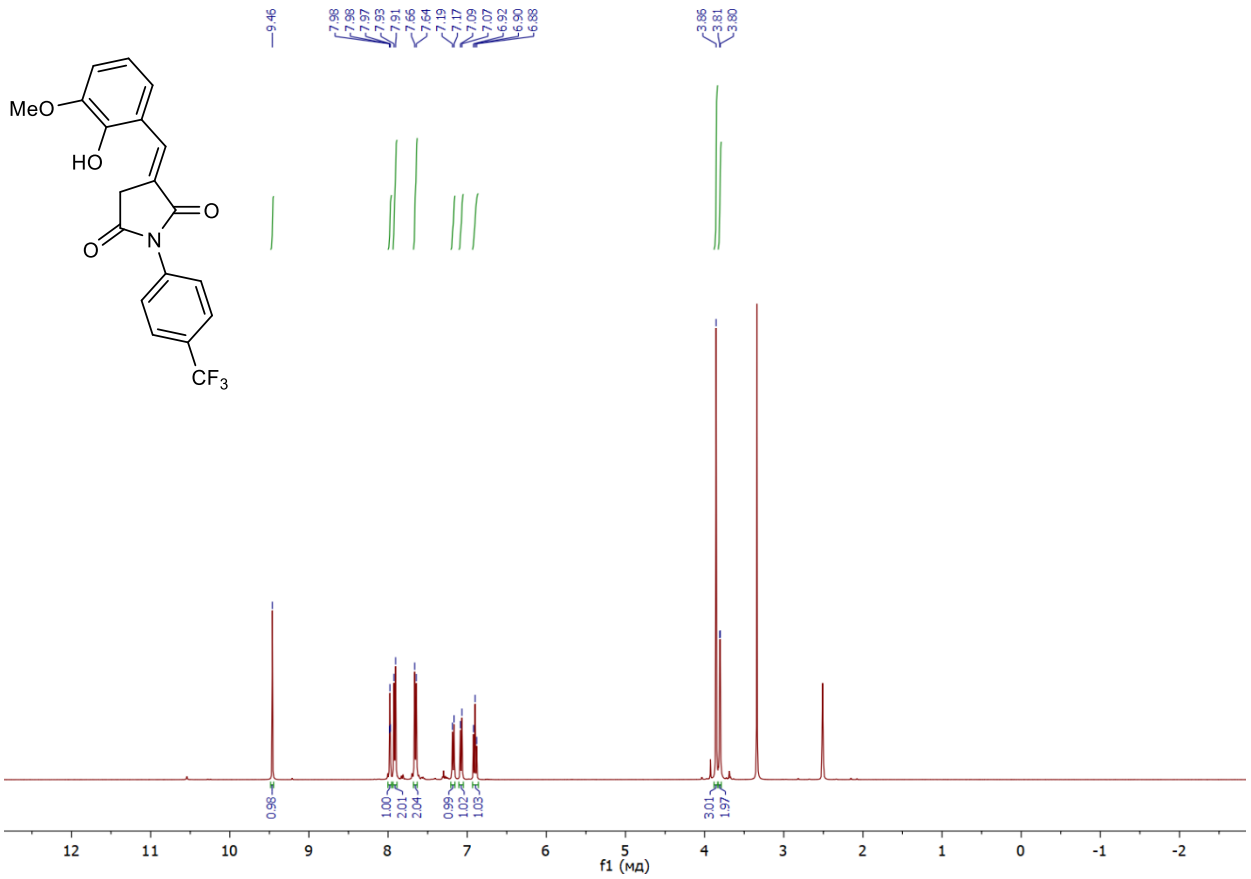
^{1}H NMR spectrum of compound **6f**



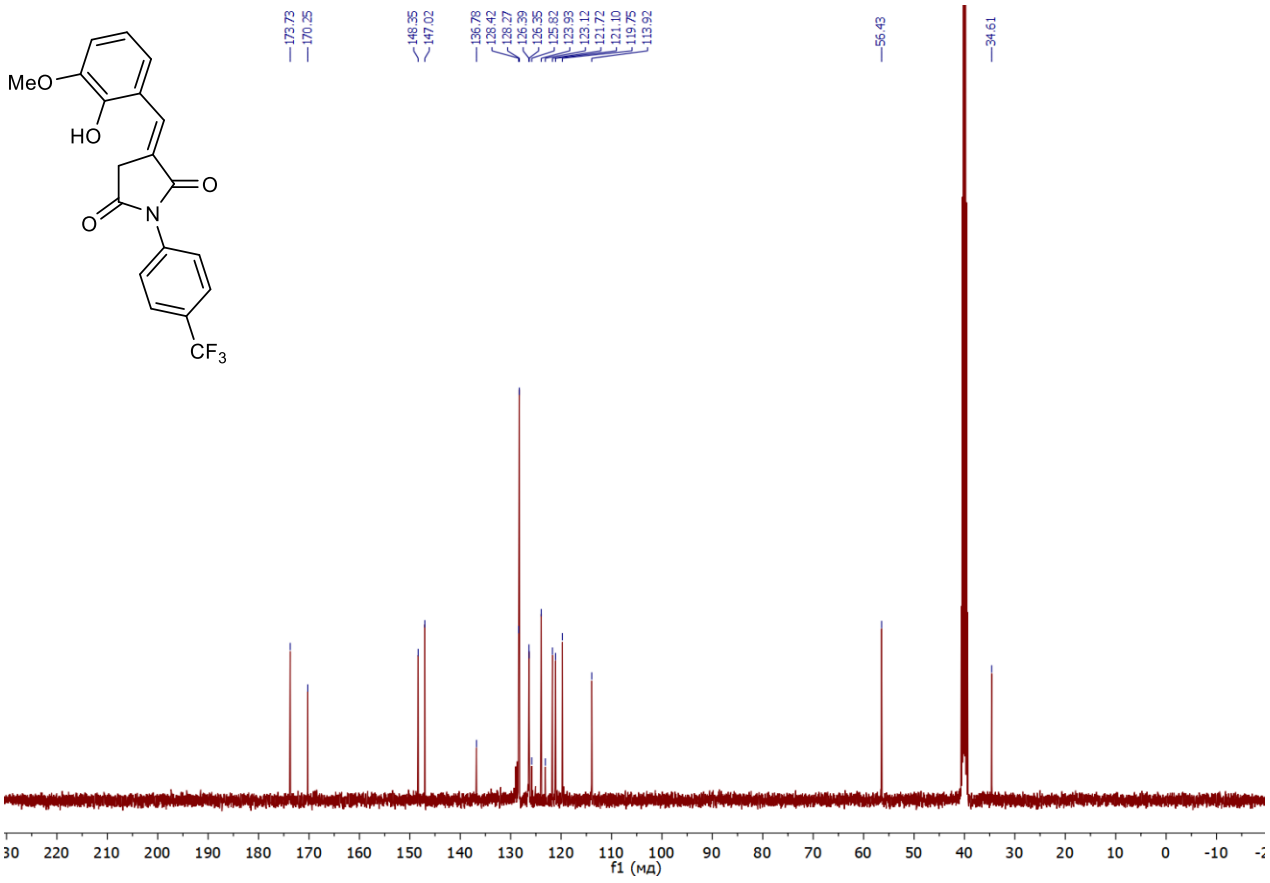
^{13}C NMR spectrum of compound **6f**



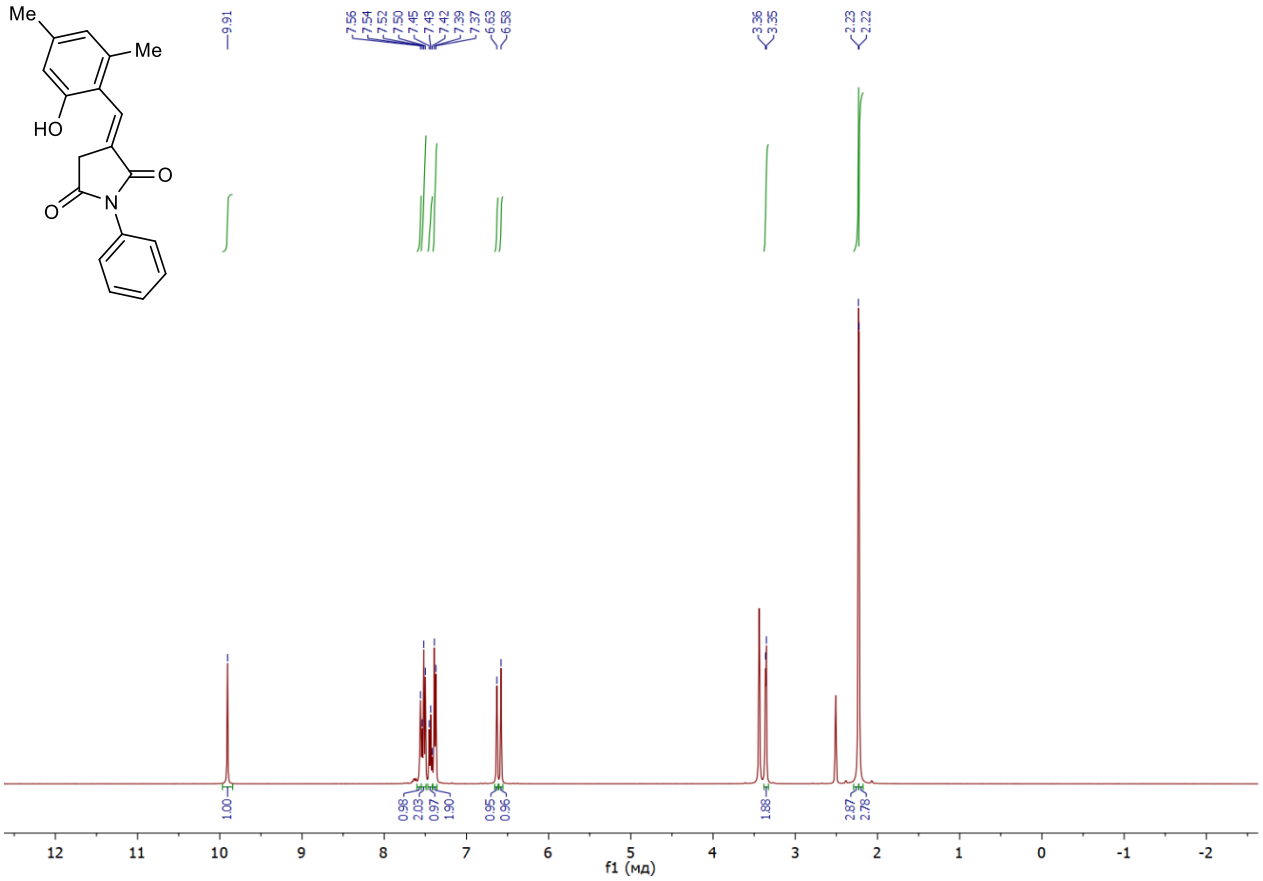
^{1}H NMR spectrum of compound **6g**



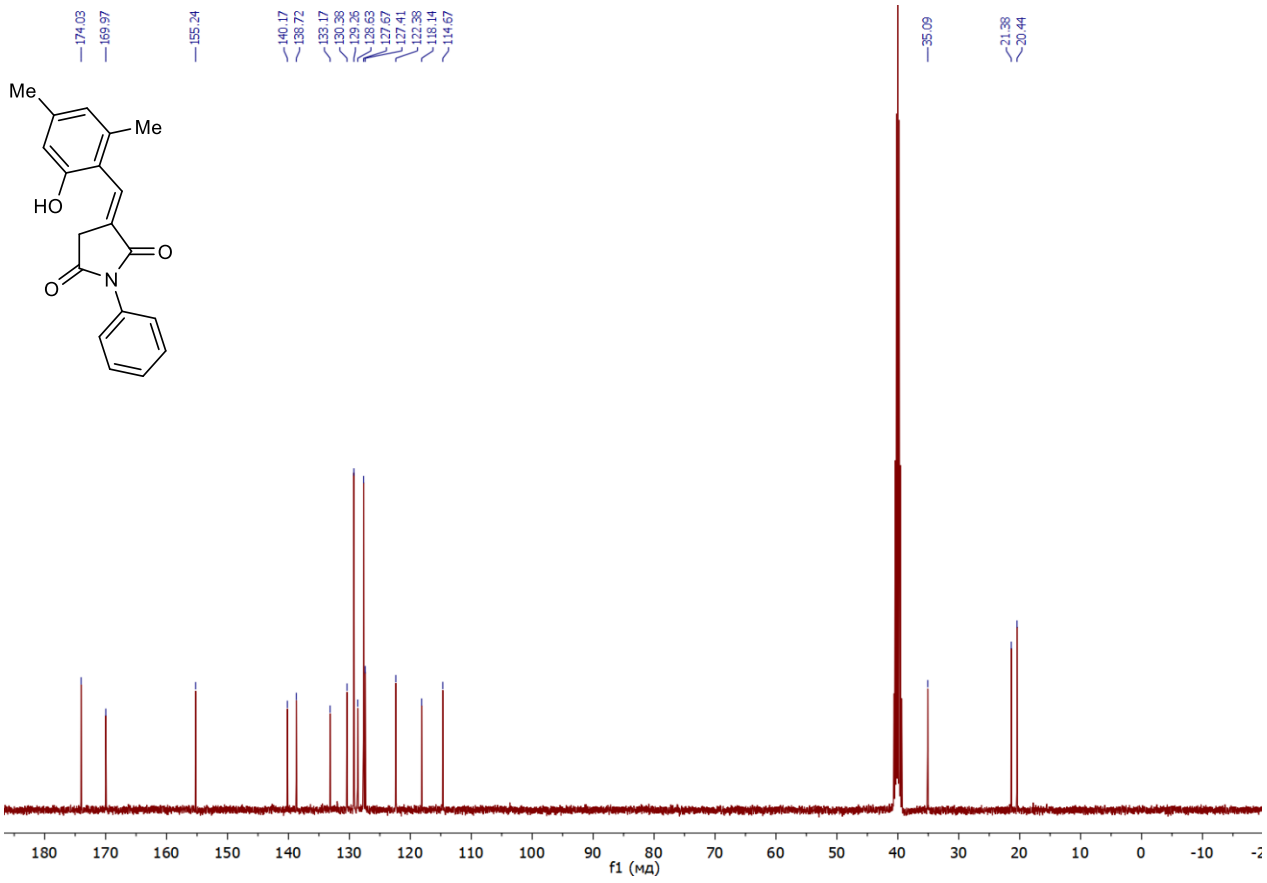
^{13}C NMR spectrum of compound **6g**



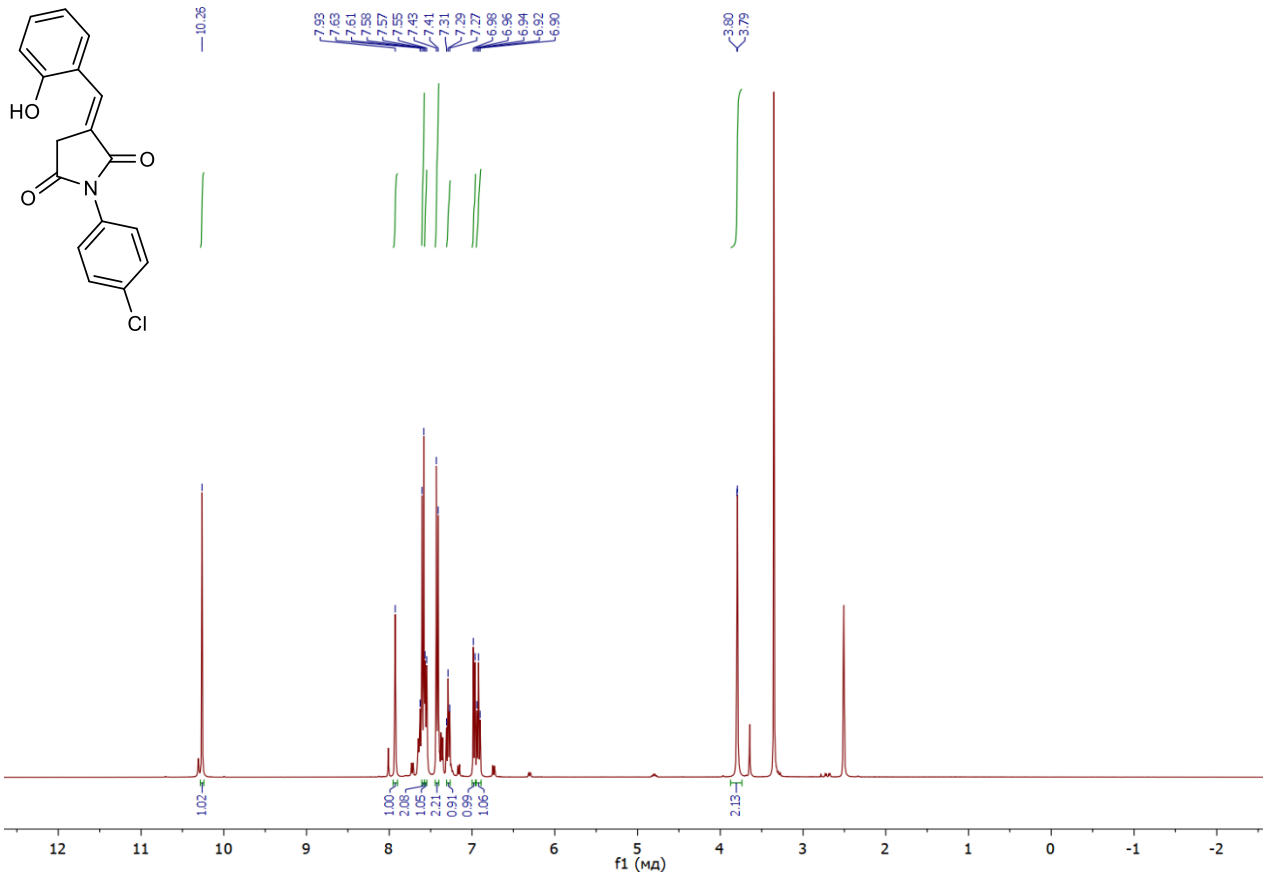
^{1}H NMR spectrum of compound **6h**



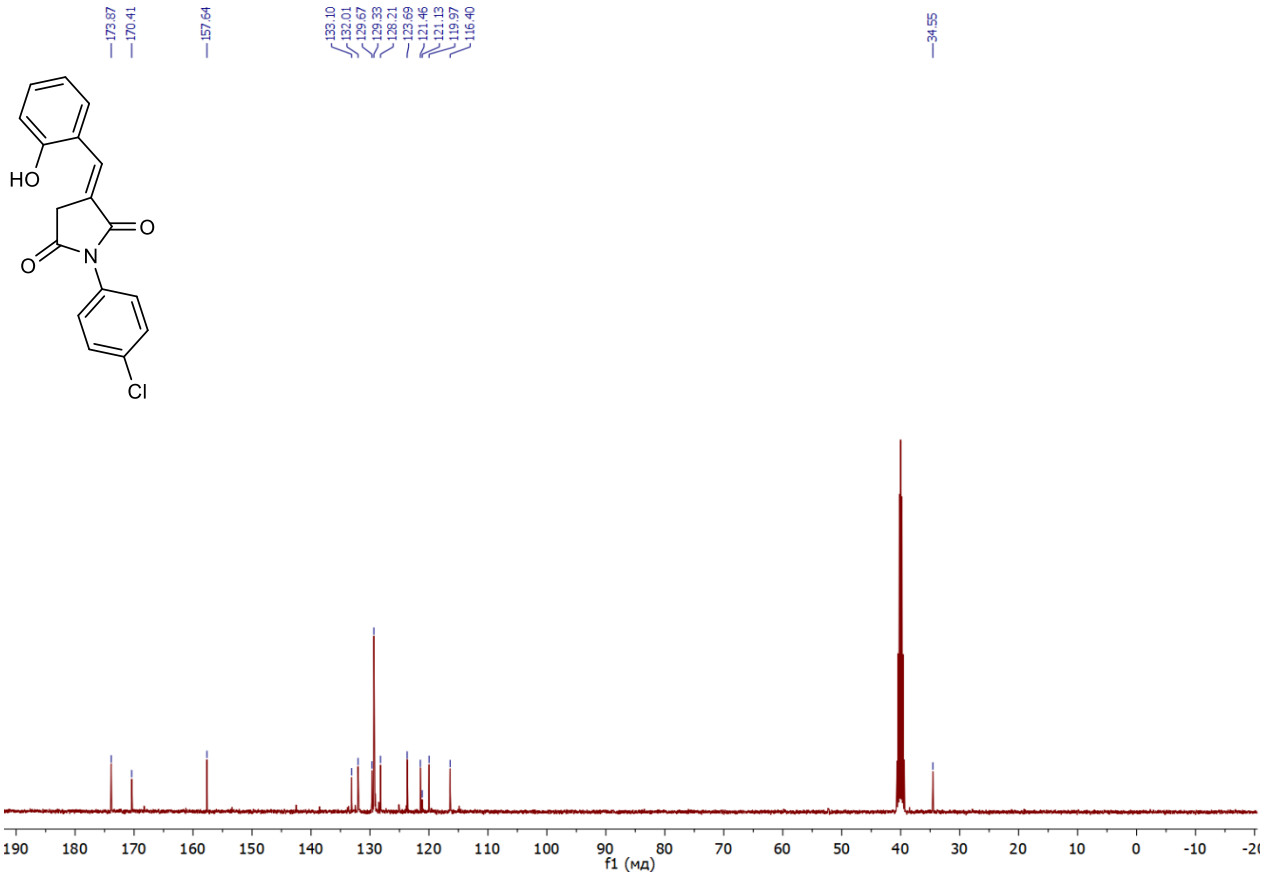
^{13}C NMR spectrum of compound **6h**



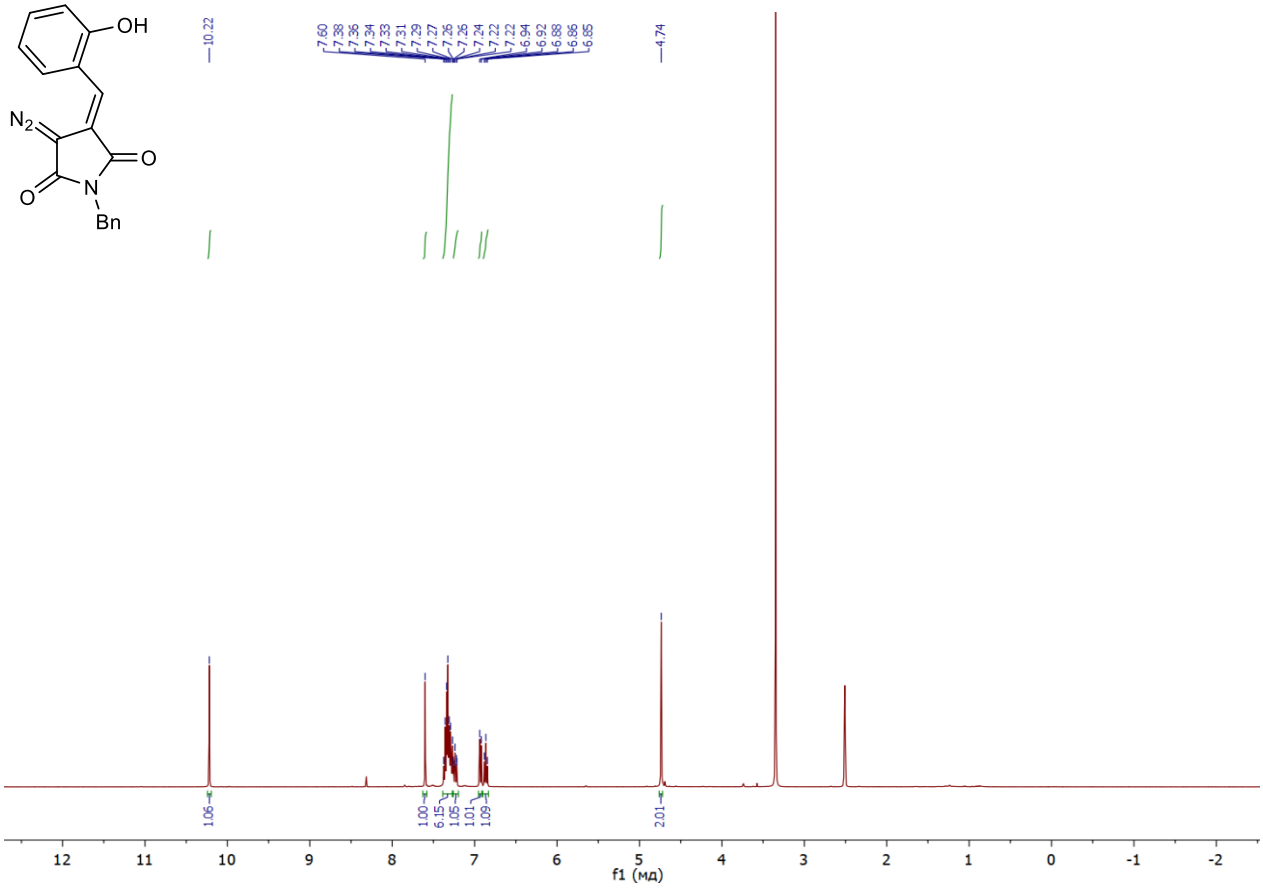
^{1}H NMR spectrum of compound **6i**



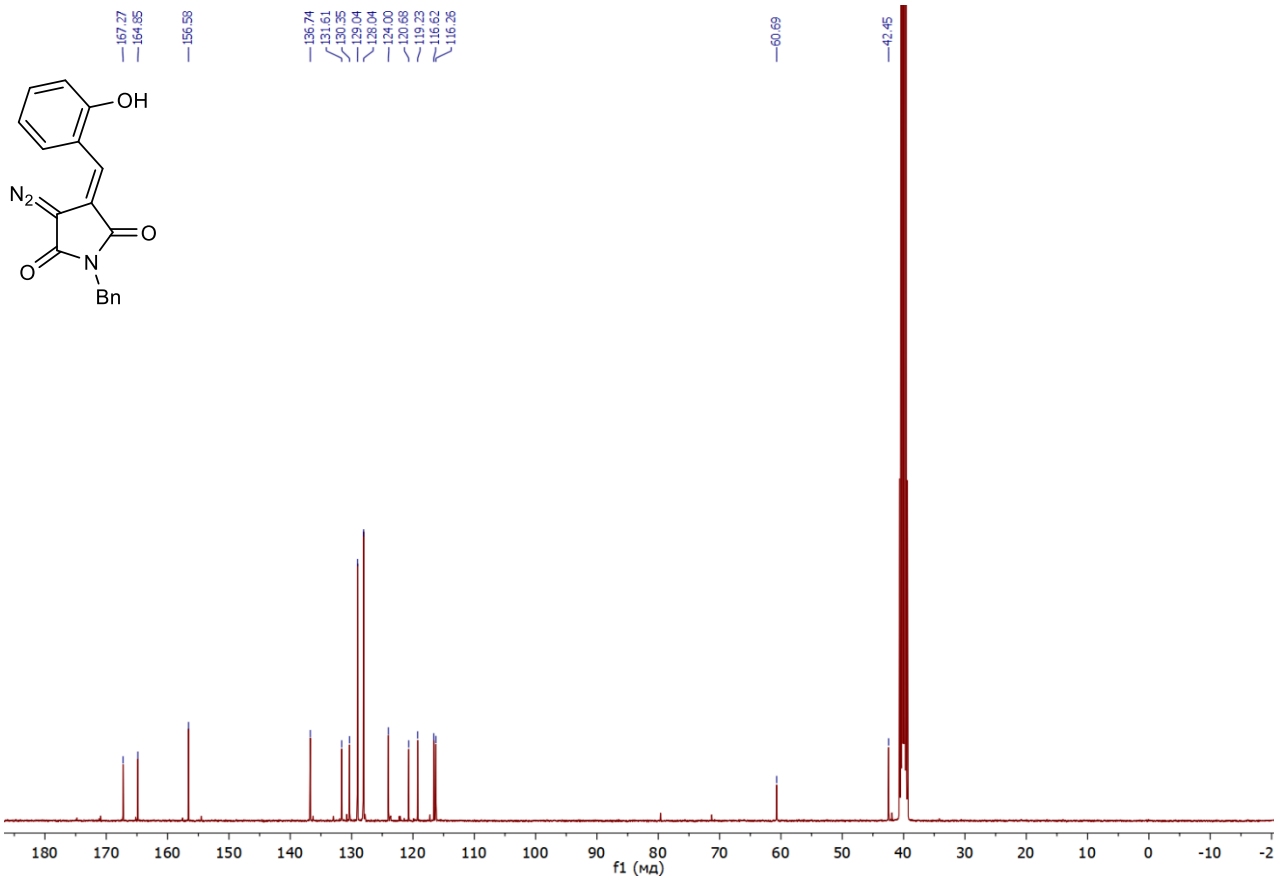
^{13}C NMR spectrum of compound **6i**



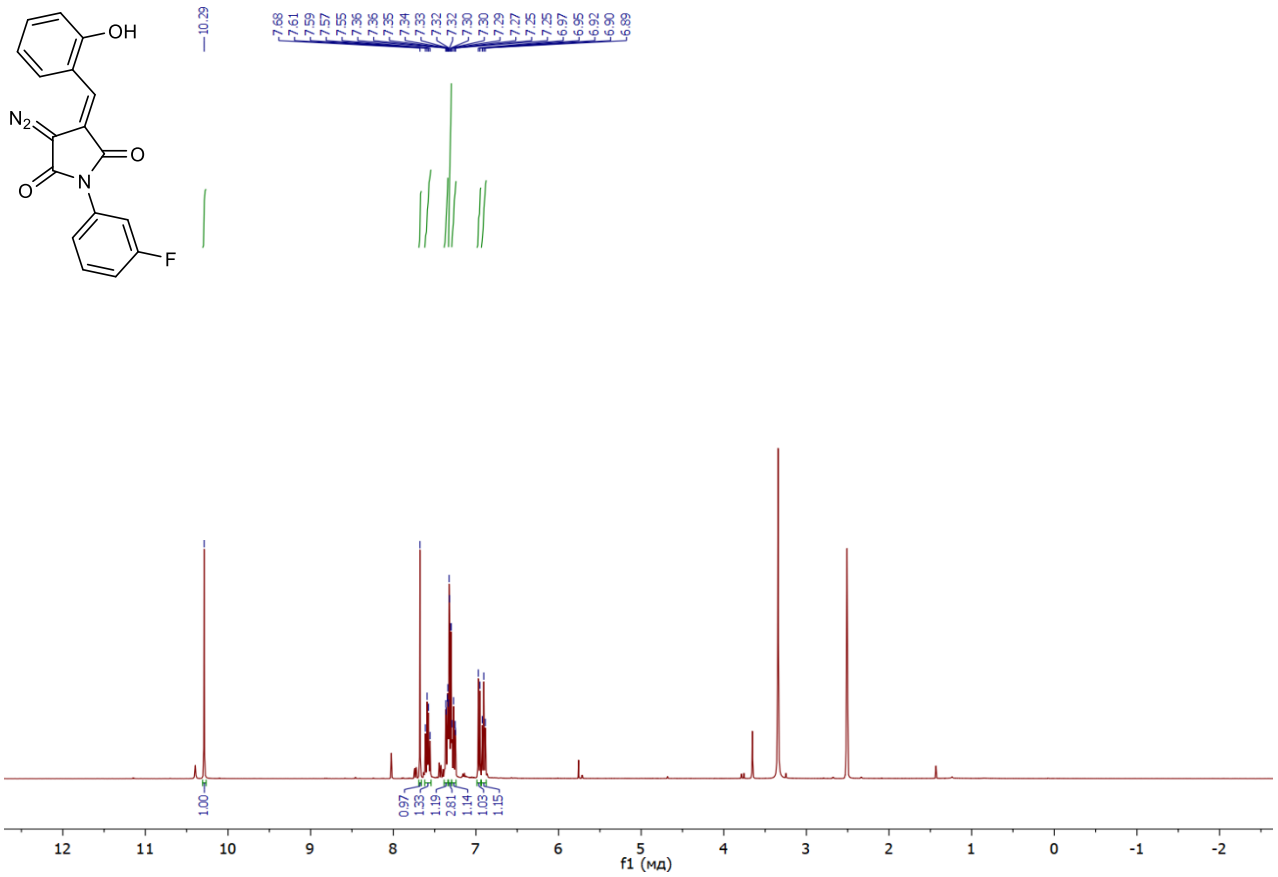
^{1}H NMR spectrum of compound **7a**



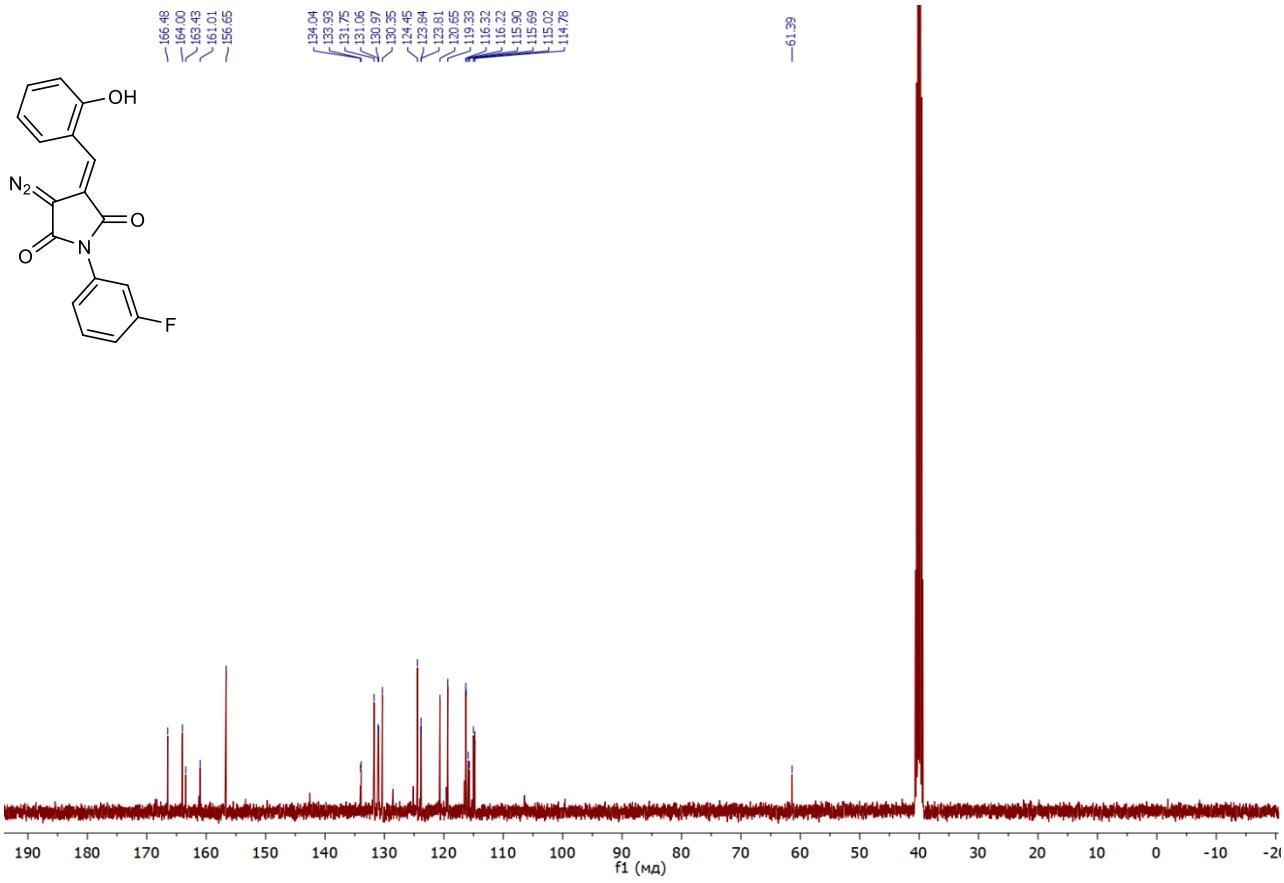
^{13}C NMR spectrum of compound **7a**



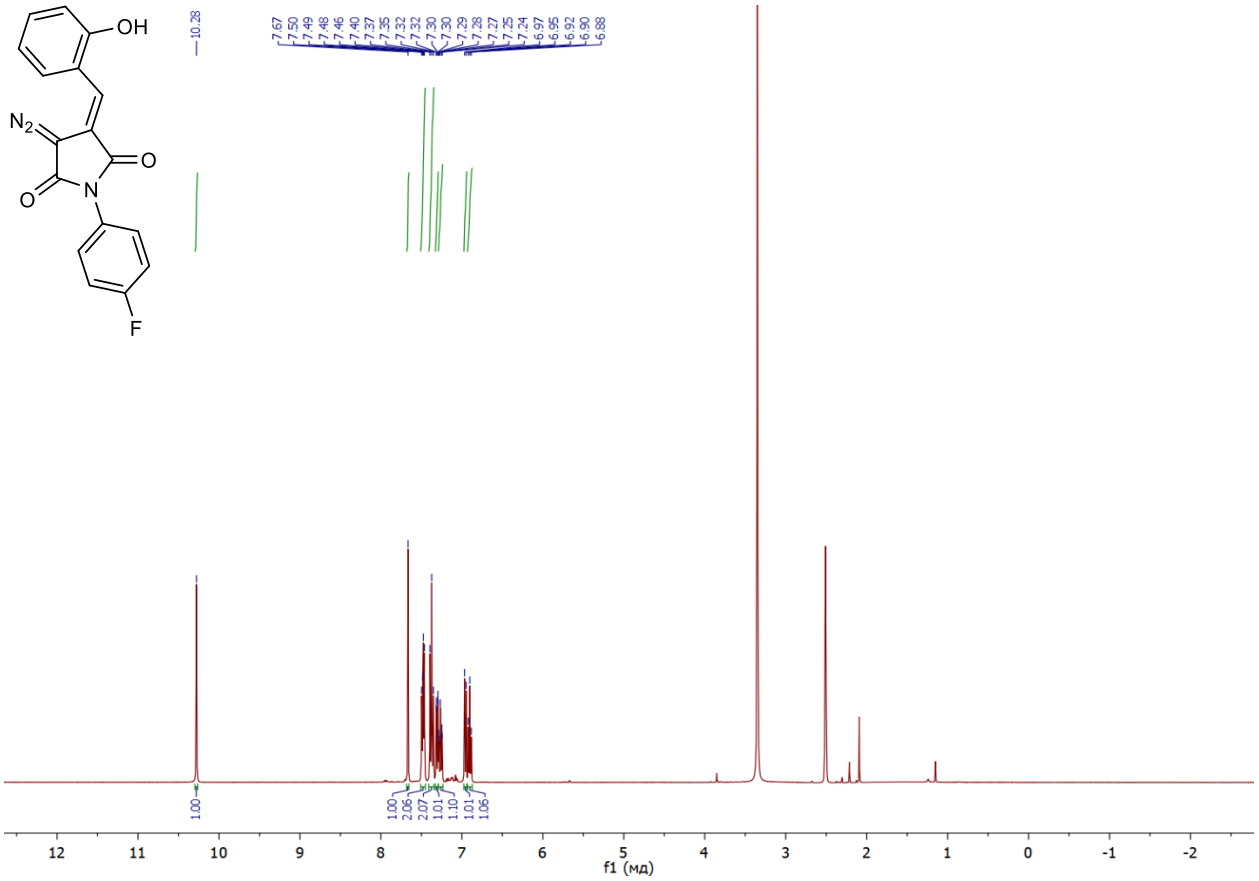
^{1}H NMR spectrum of compound **7b**



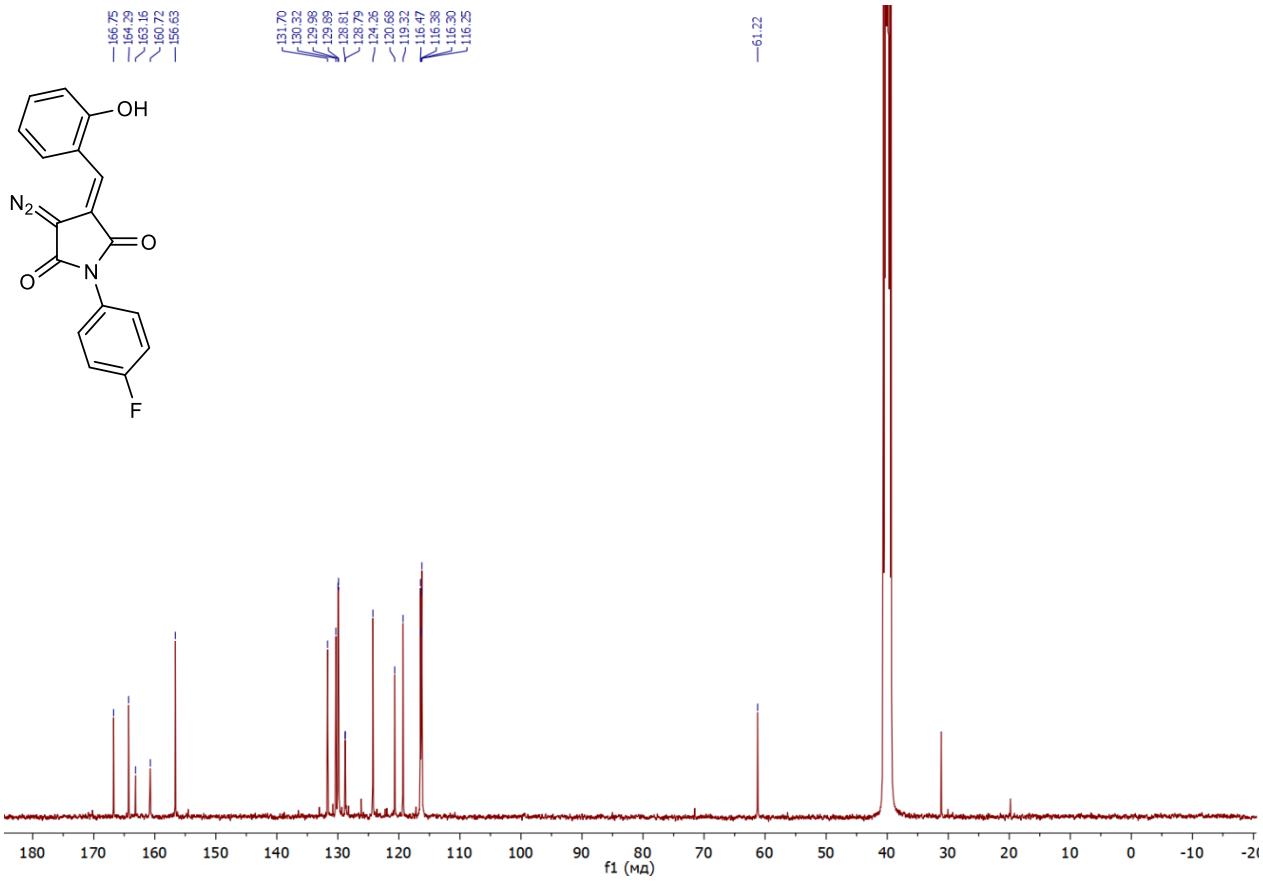
^{13}C NMR spectrum of compound **7b**



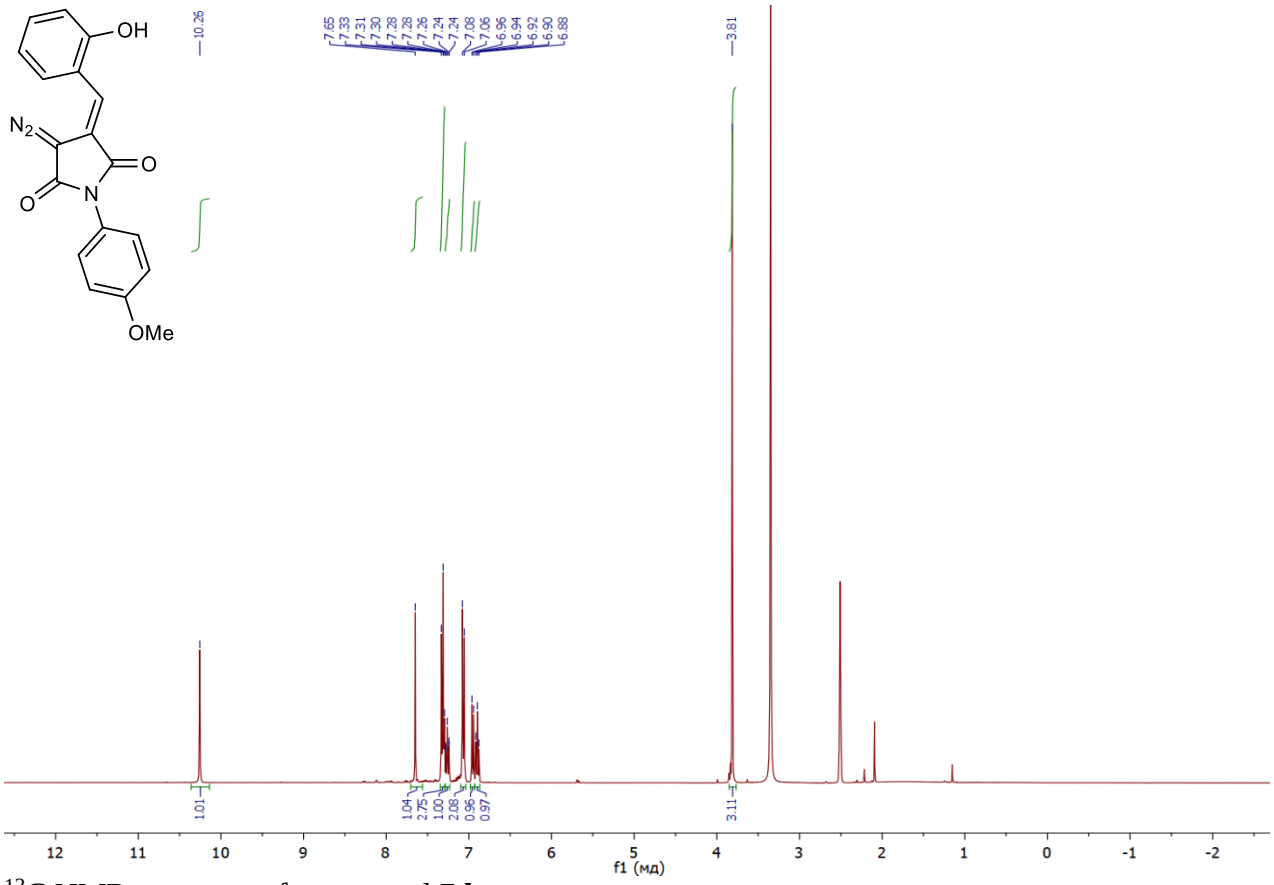
^{1}H NMR spectrum of compound **7c**



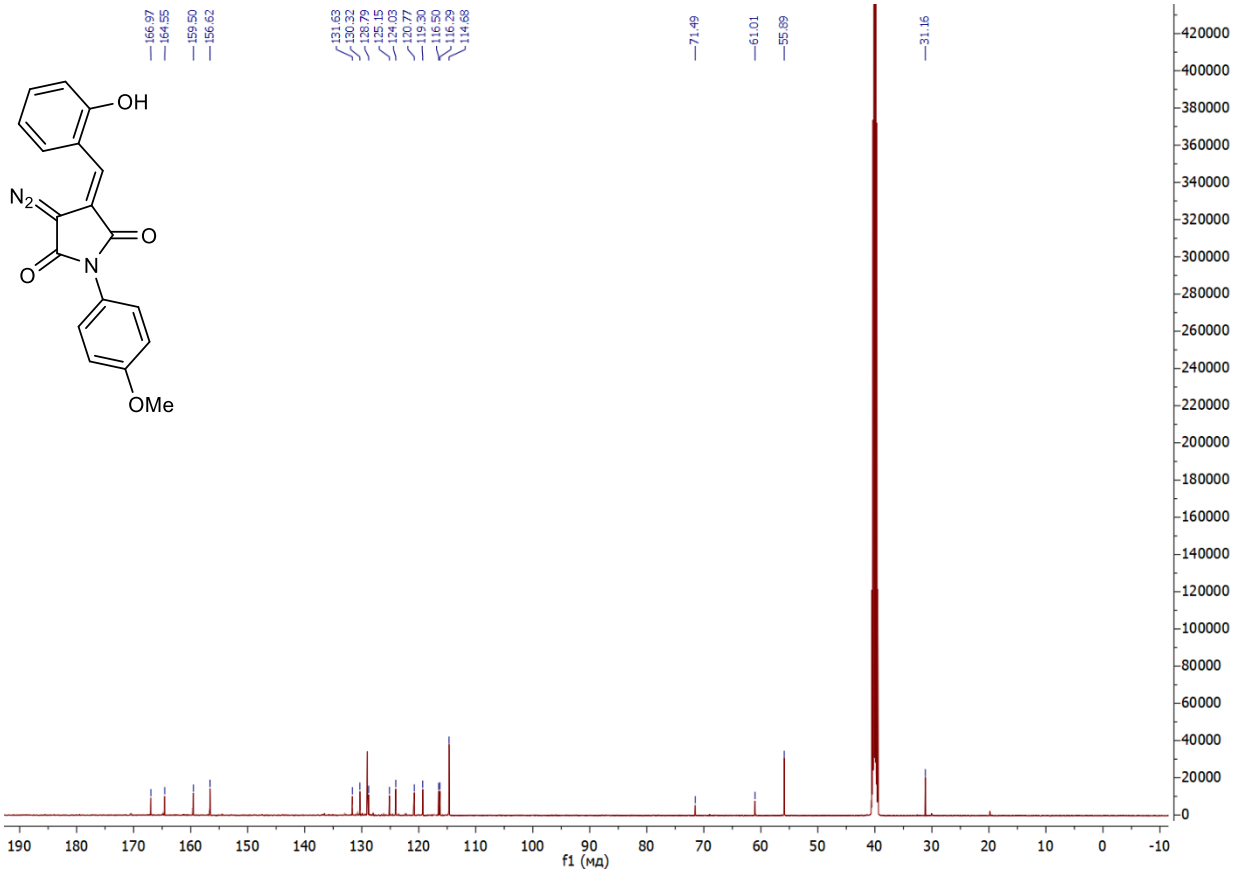
^{13}C NMR spectrum of compound **7c**



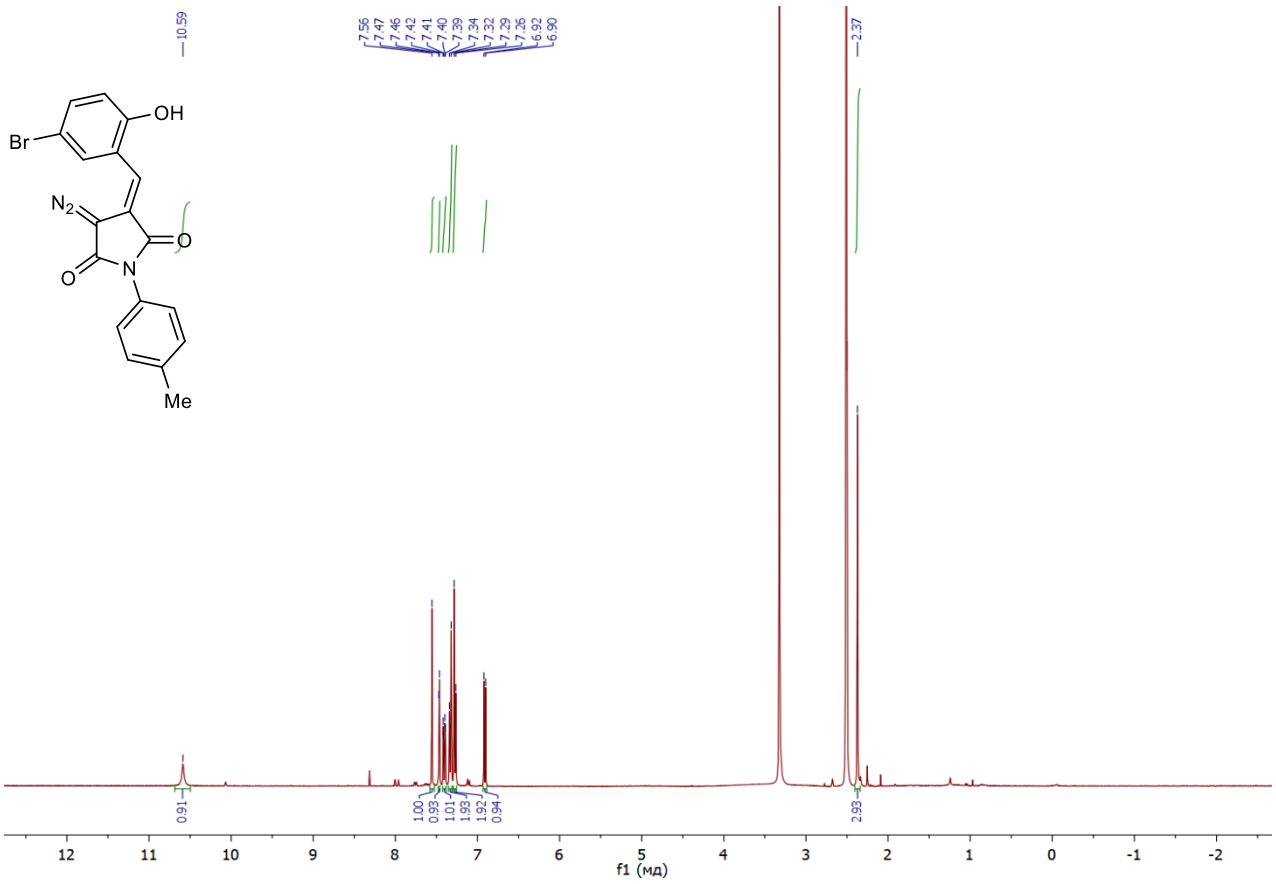
^{1}H NMR spectrum of compound **7d**



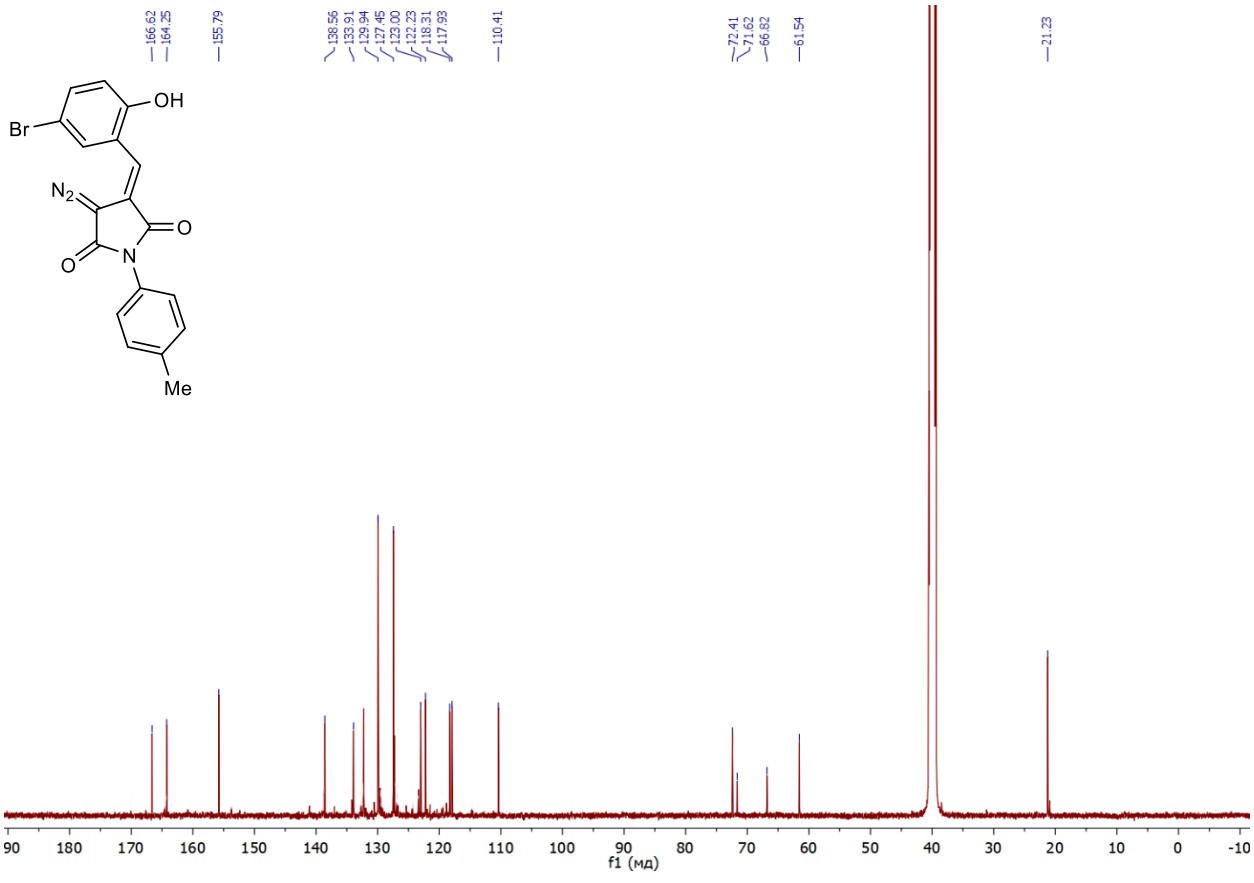
^{13}C NMR spectrum of compound **7d**



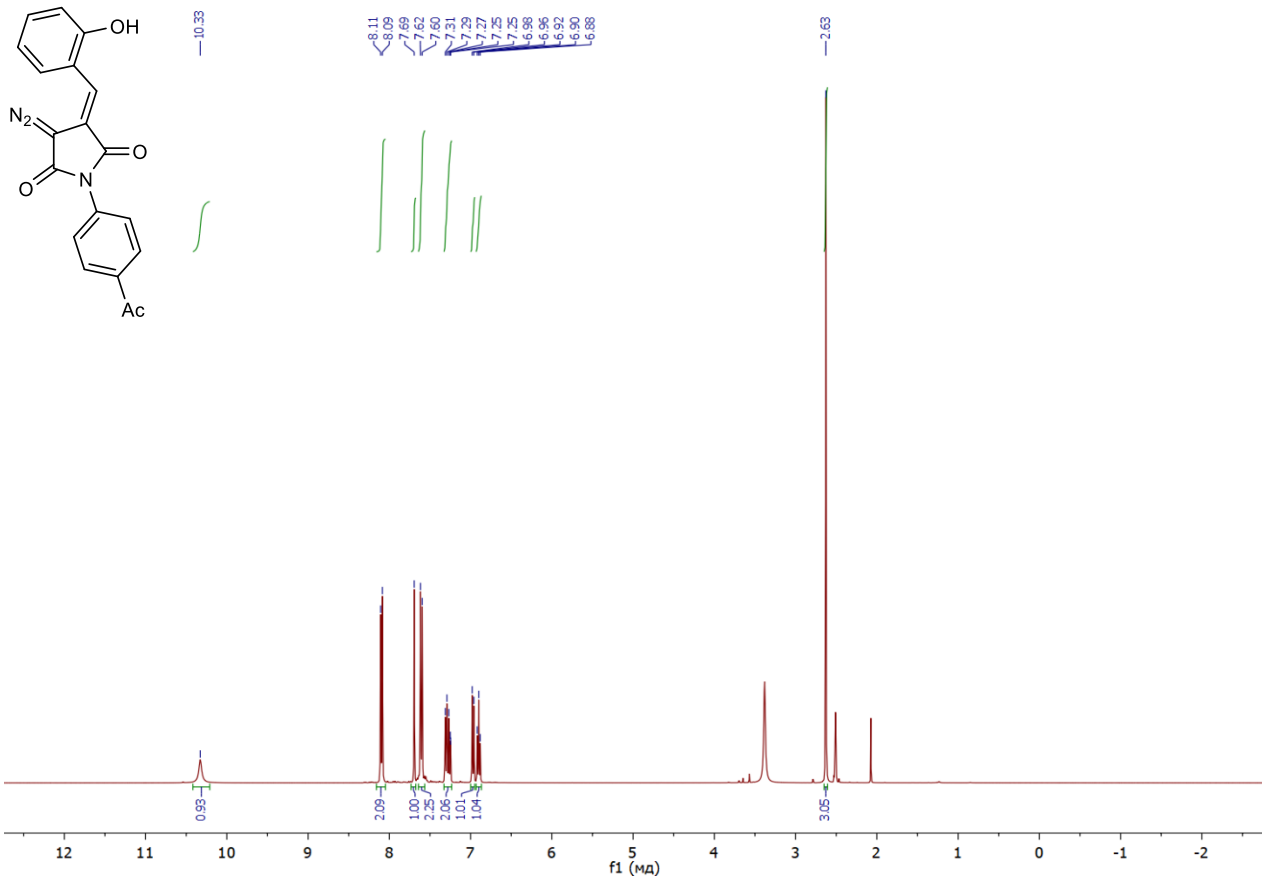
^{1}H NMR spectrum of compound **7e**



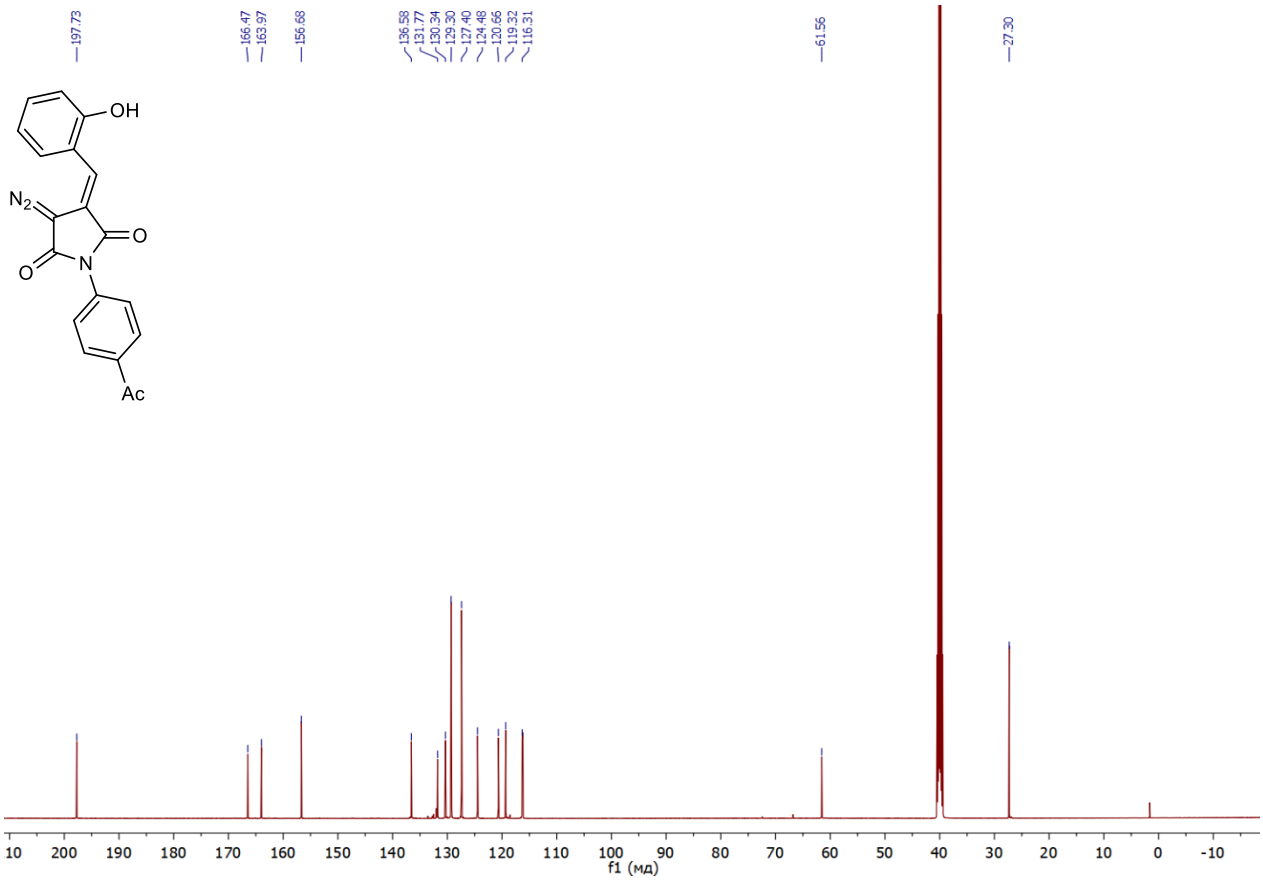
^{13}C NMR spectrum of compound **7e**



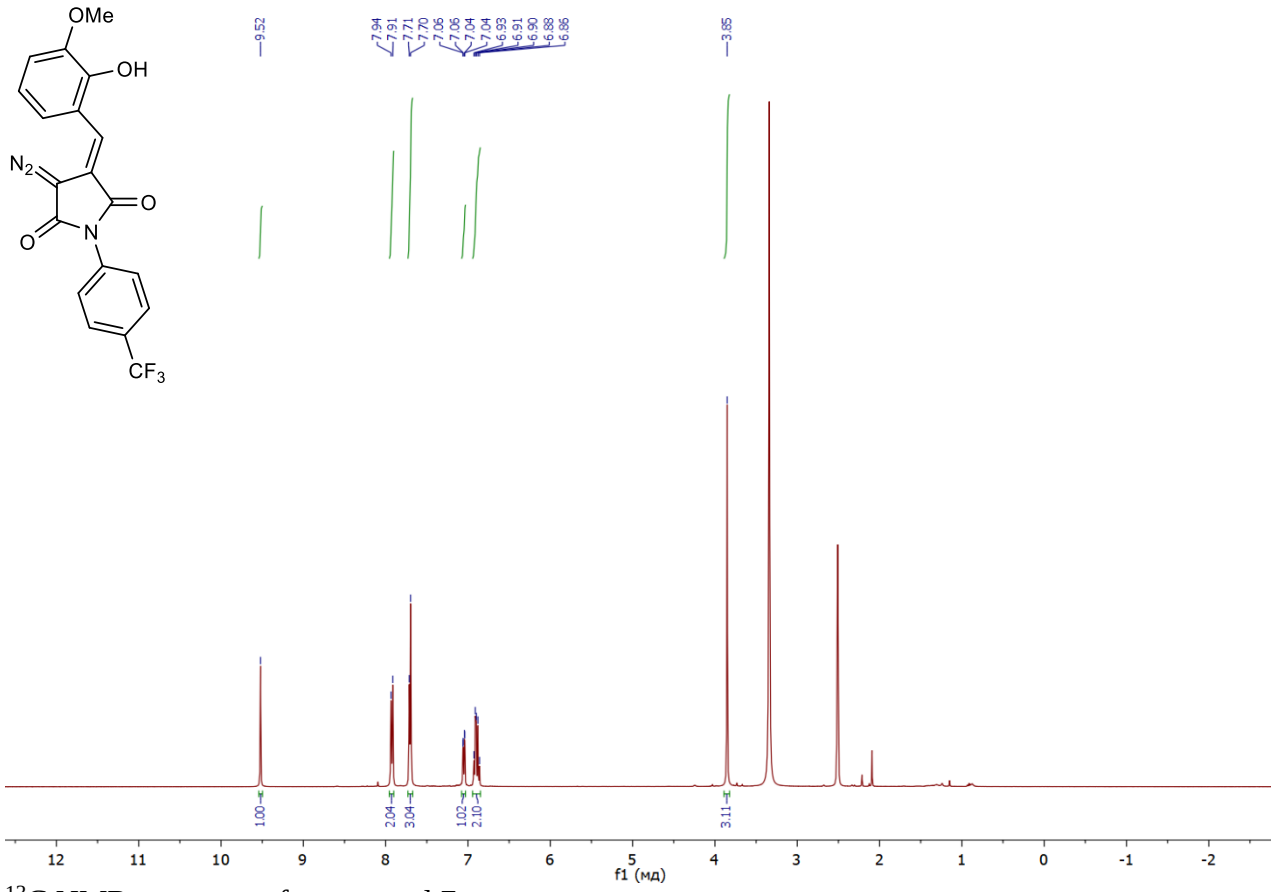
^{1}H NMR spectrum of compound **7f**



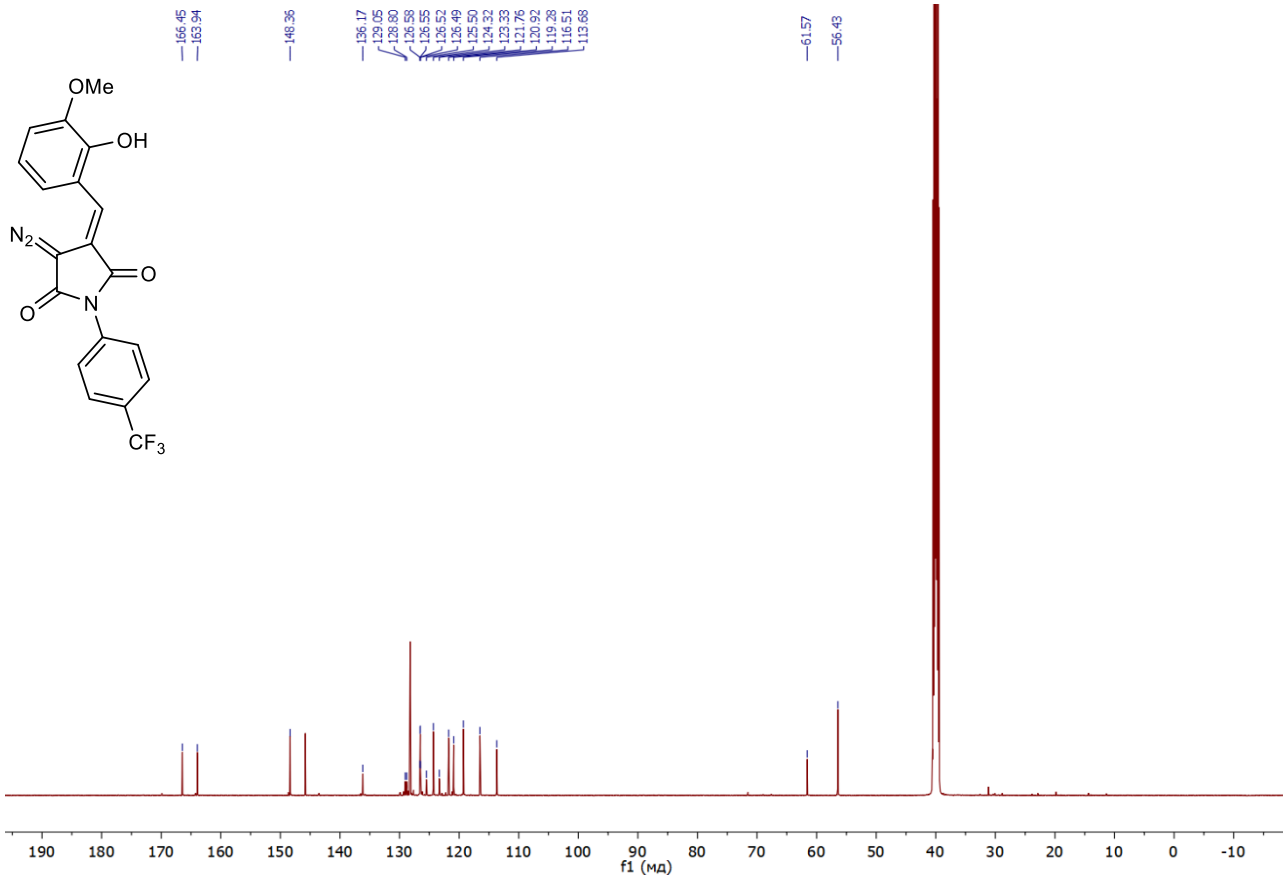
^{13}C NMR spectrum of compound **7f**



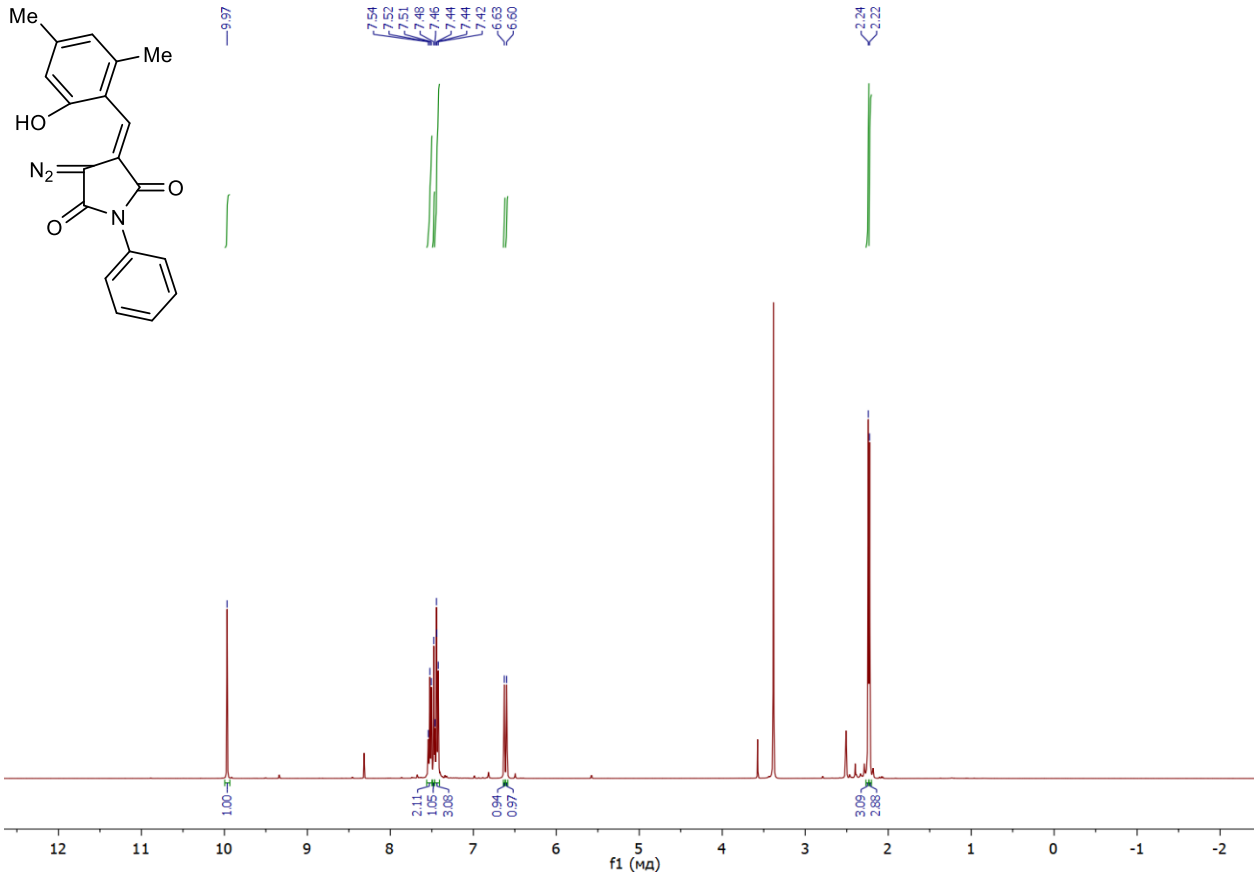
^{1}H NMR spectrum of compound **7g**



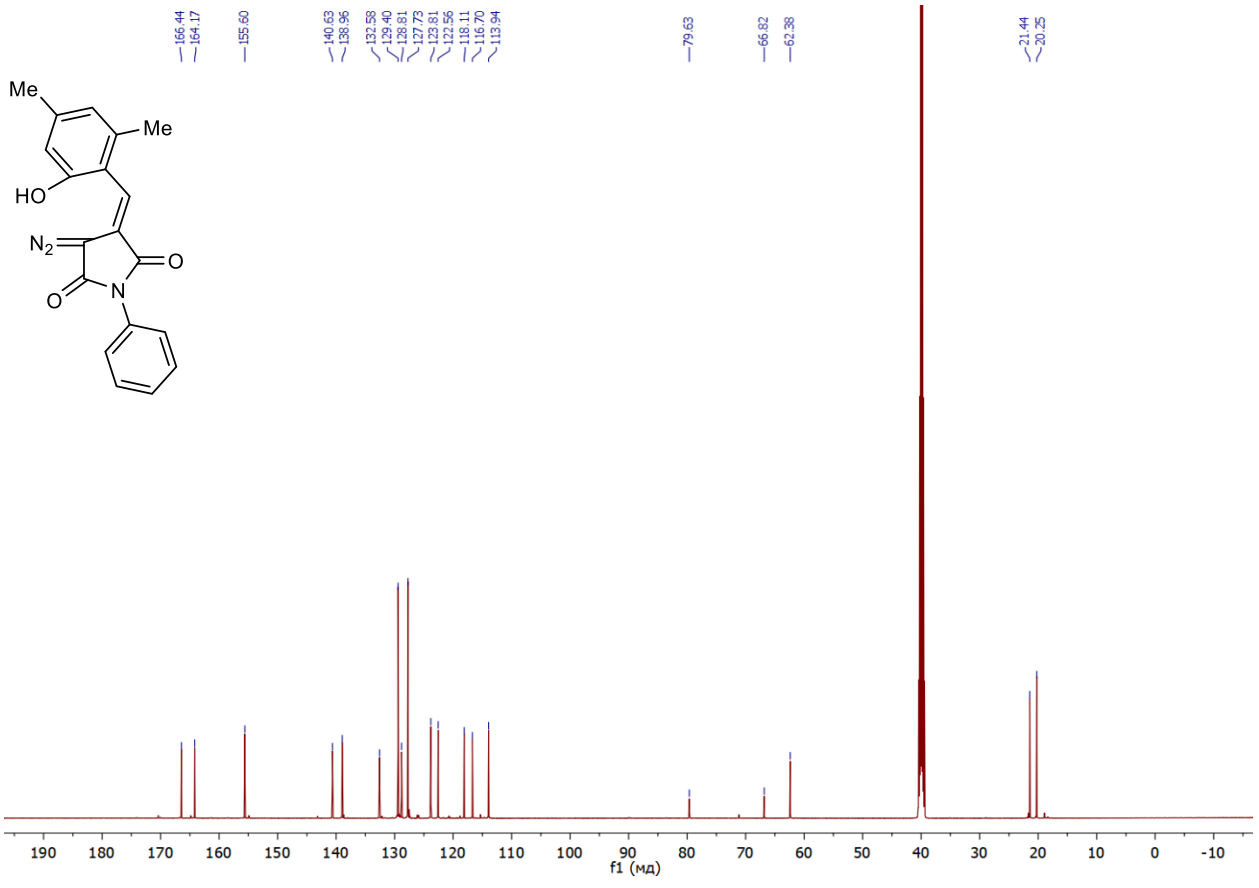
^{13}C NMR spectrum of compound **7g**



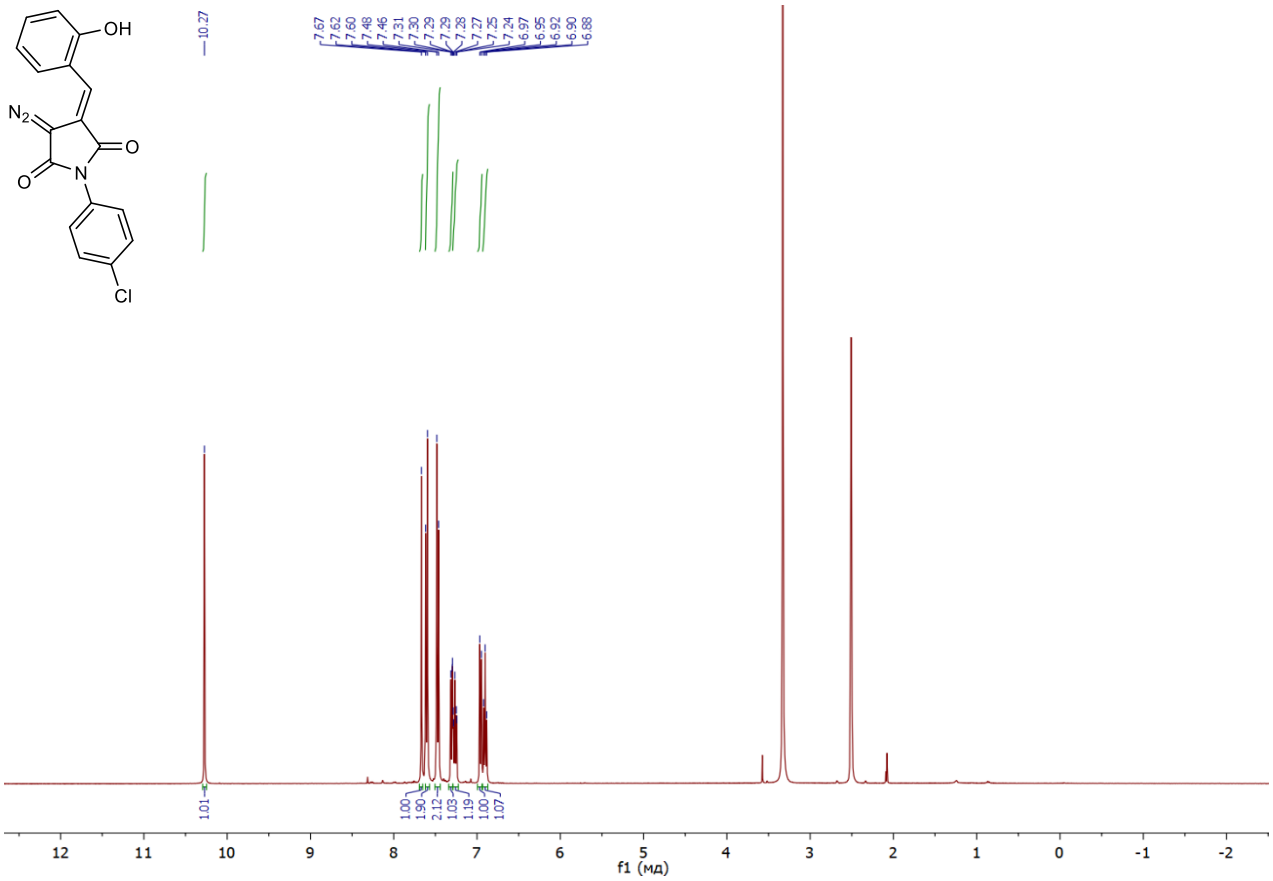
^{1}H NMR spectrum of compound **7h**



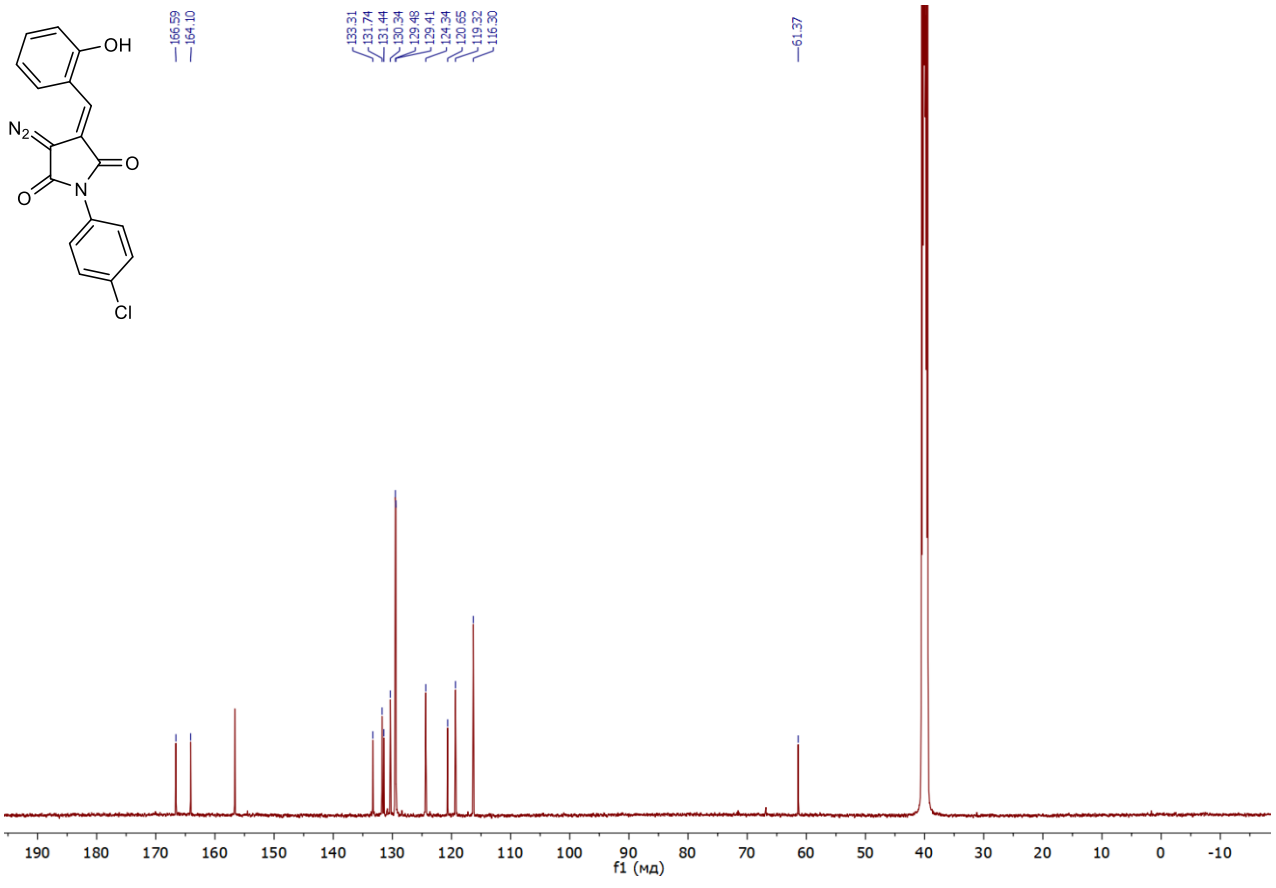
^{13}C NMR spectrum of compound **7h**



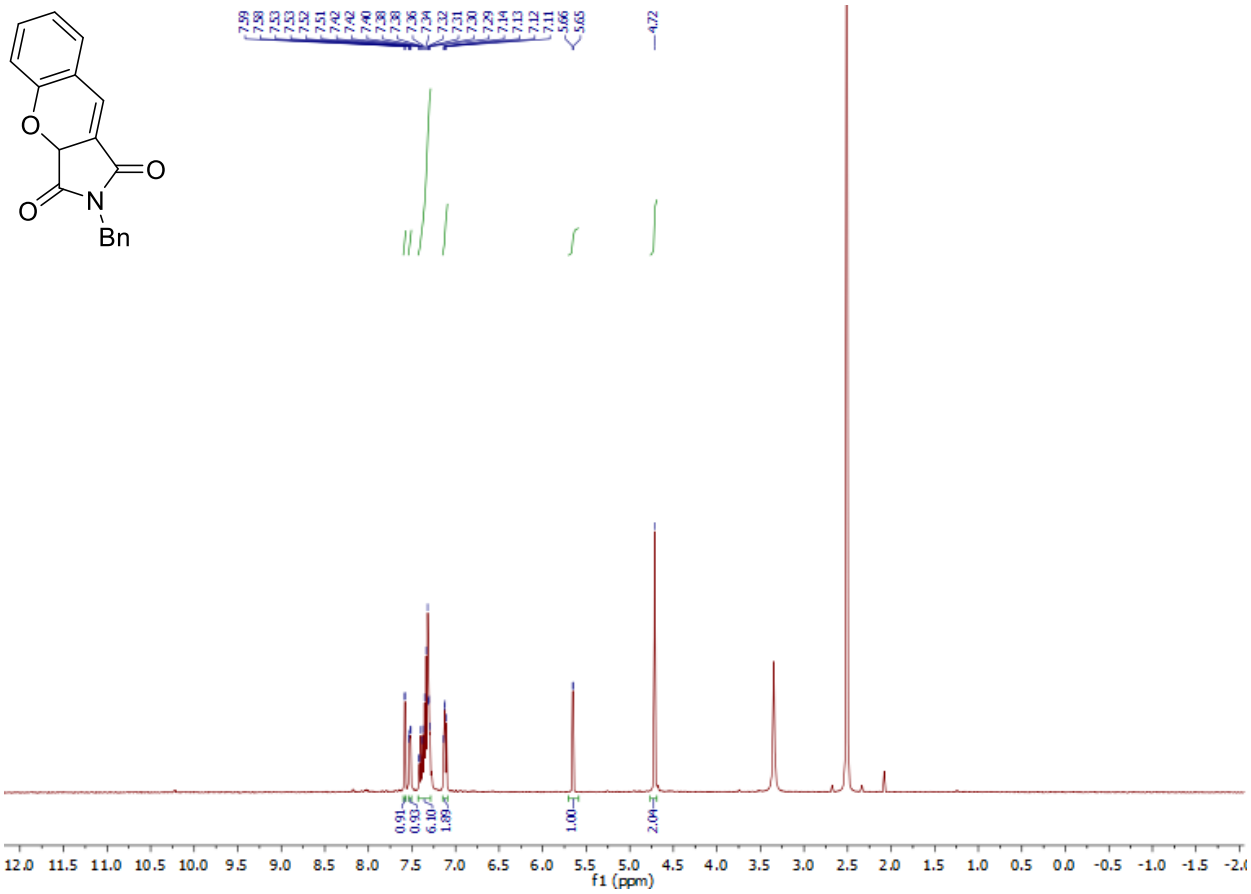
^{1}H NMR spectrum of compound **7i**



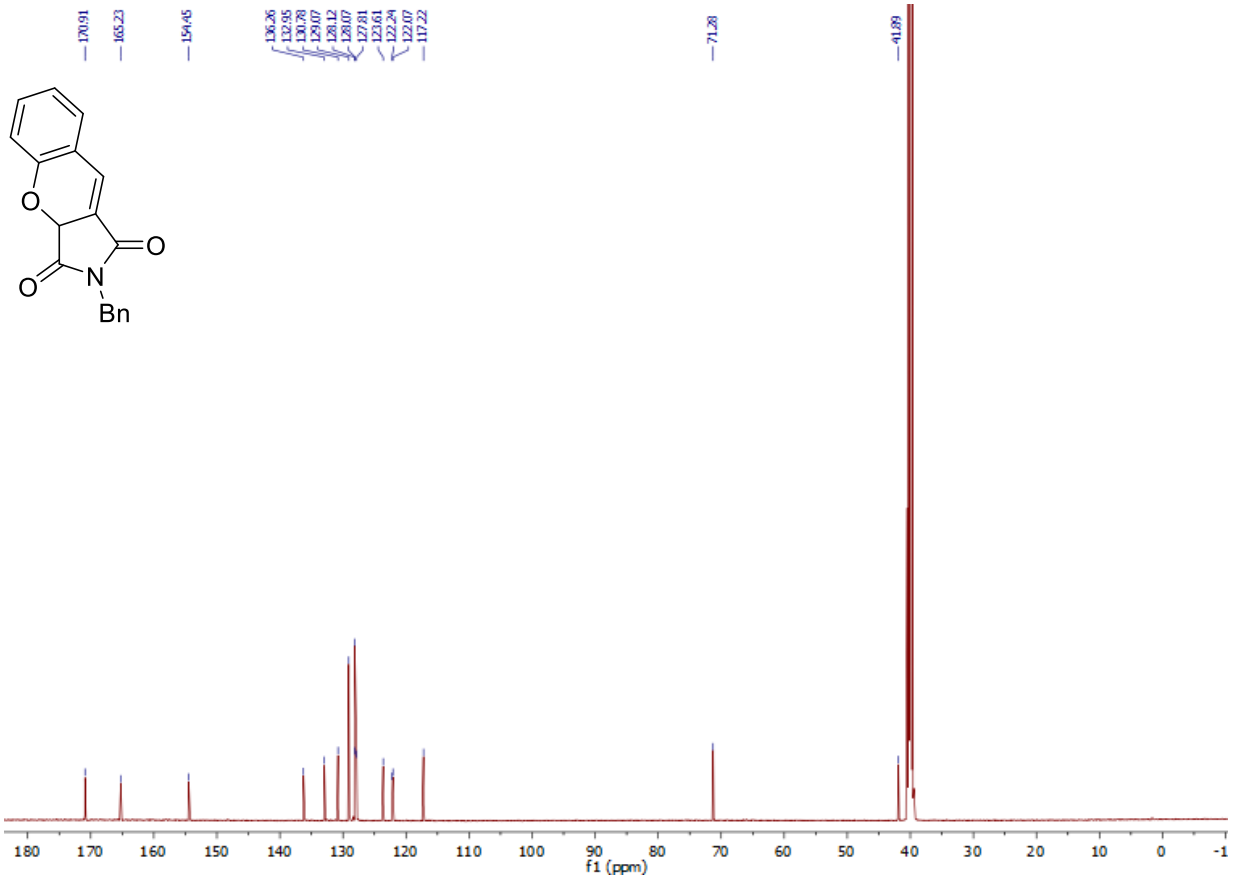
^{13}C NMR spectrum of compound **7i**



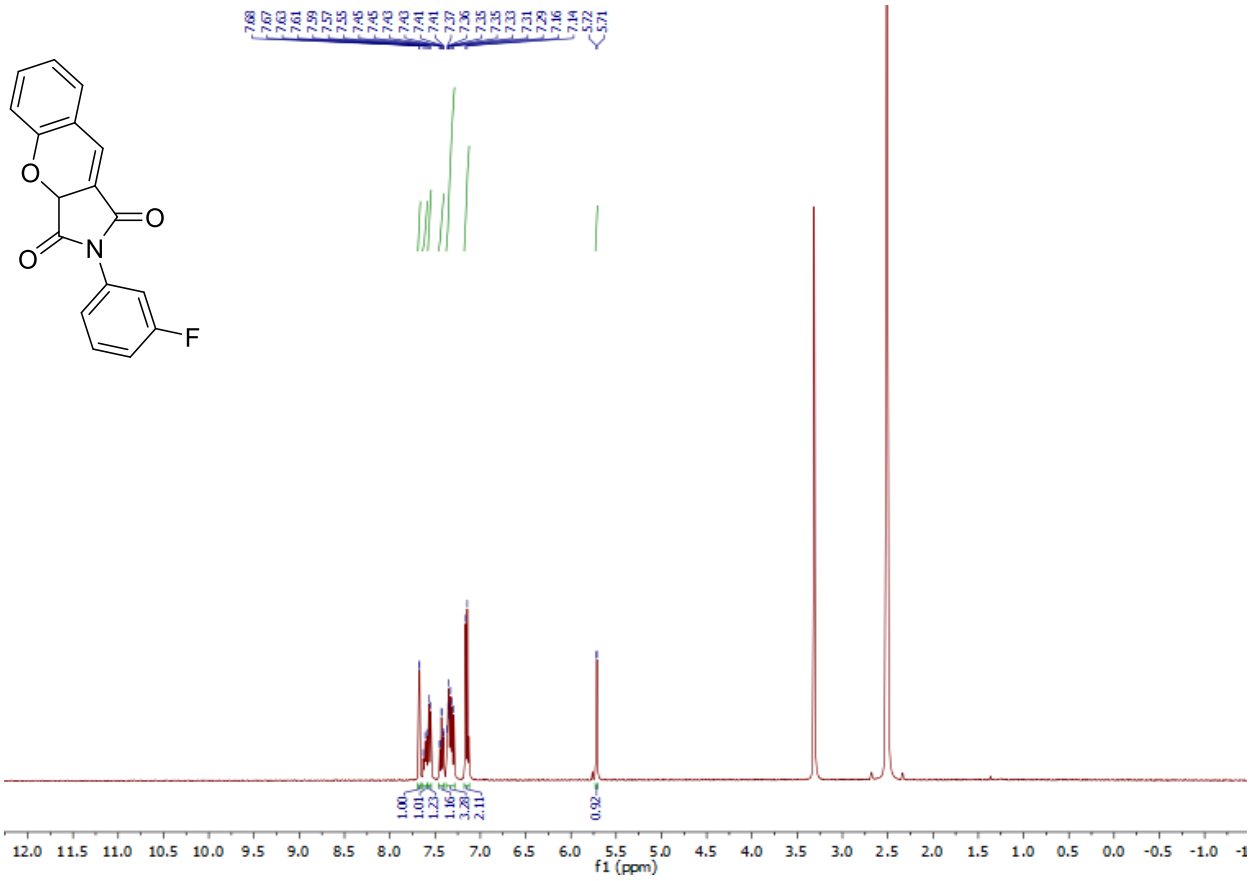
^{1}H NMR spectrum of compound **8a**



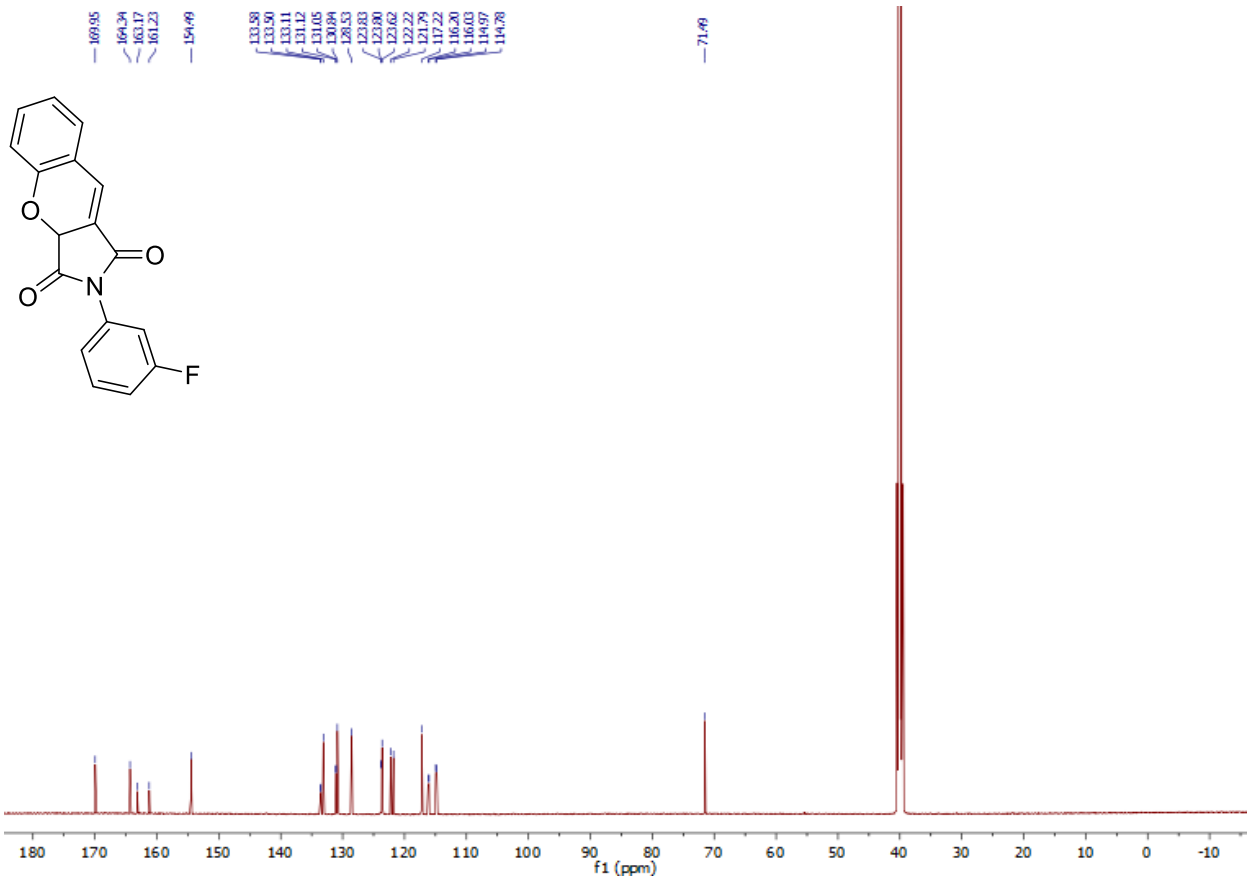
^{13}C NMR spectrum of compound **8a**



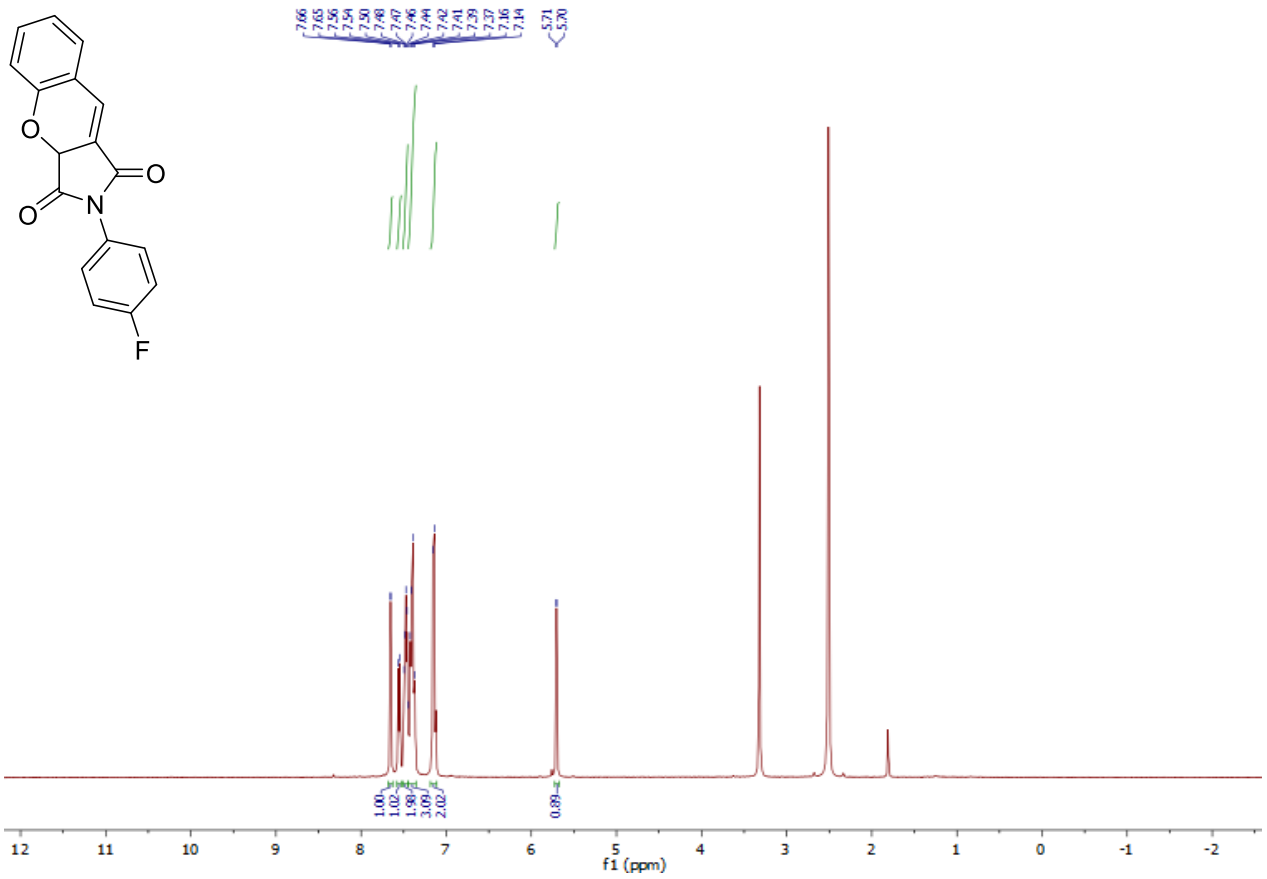
^{1}H NMR spectrum of compound **8b**



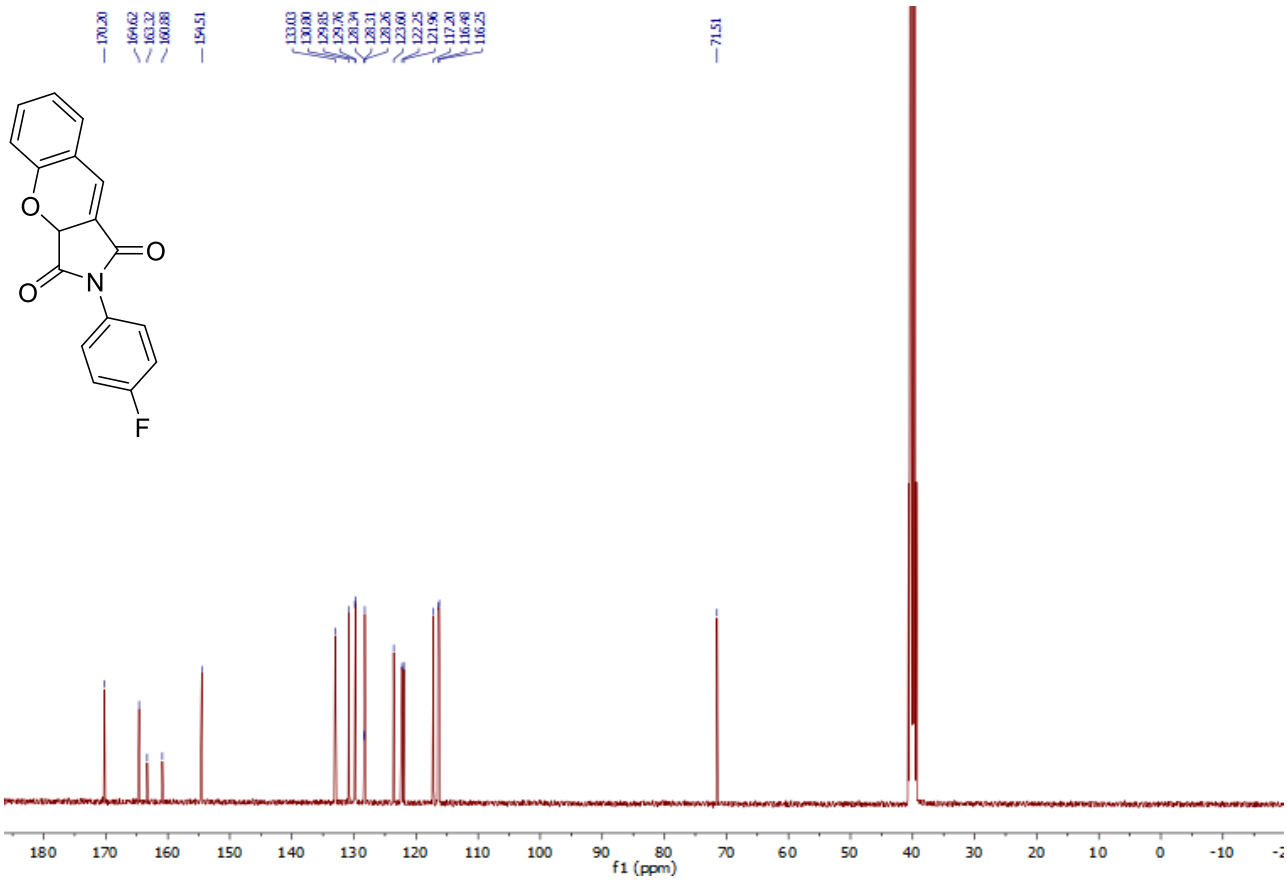
^{13}C NMR spectrum of compound **8b**



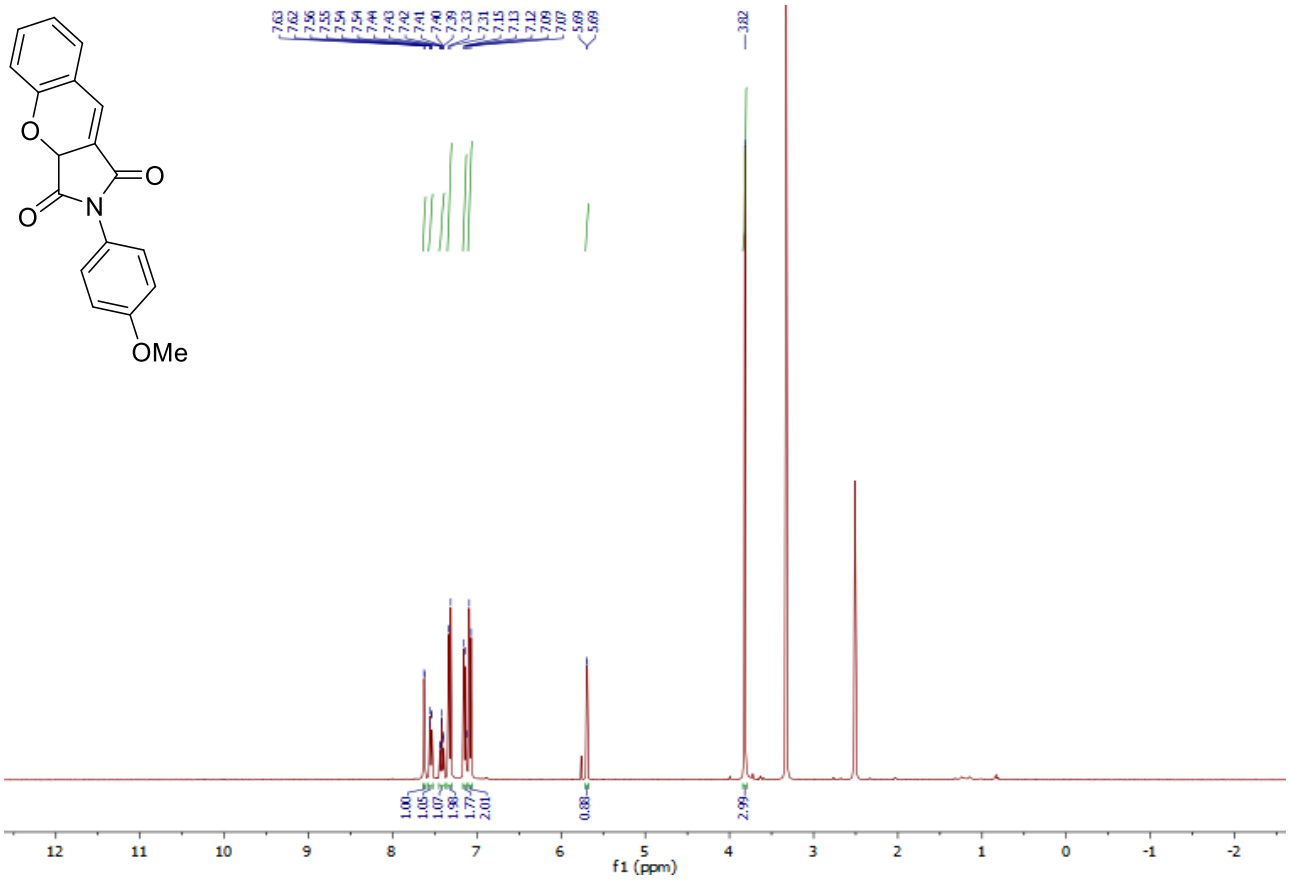
^{1}H NMR spectrum of compound **8c**



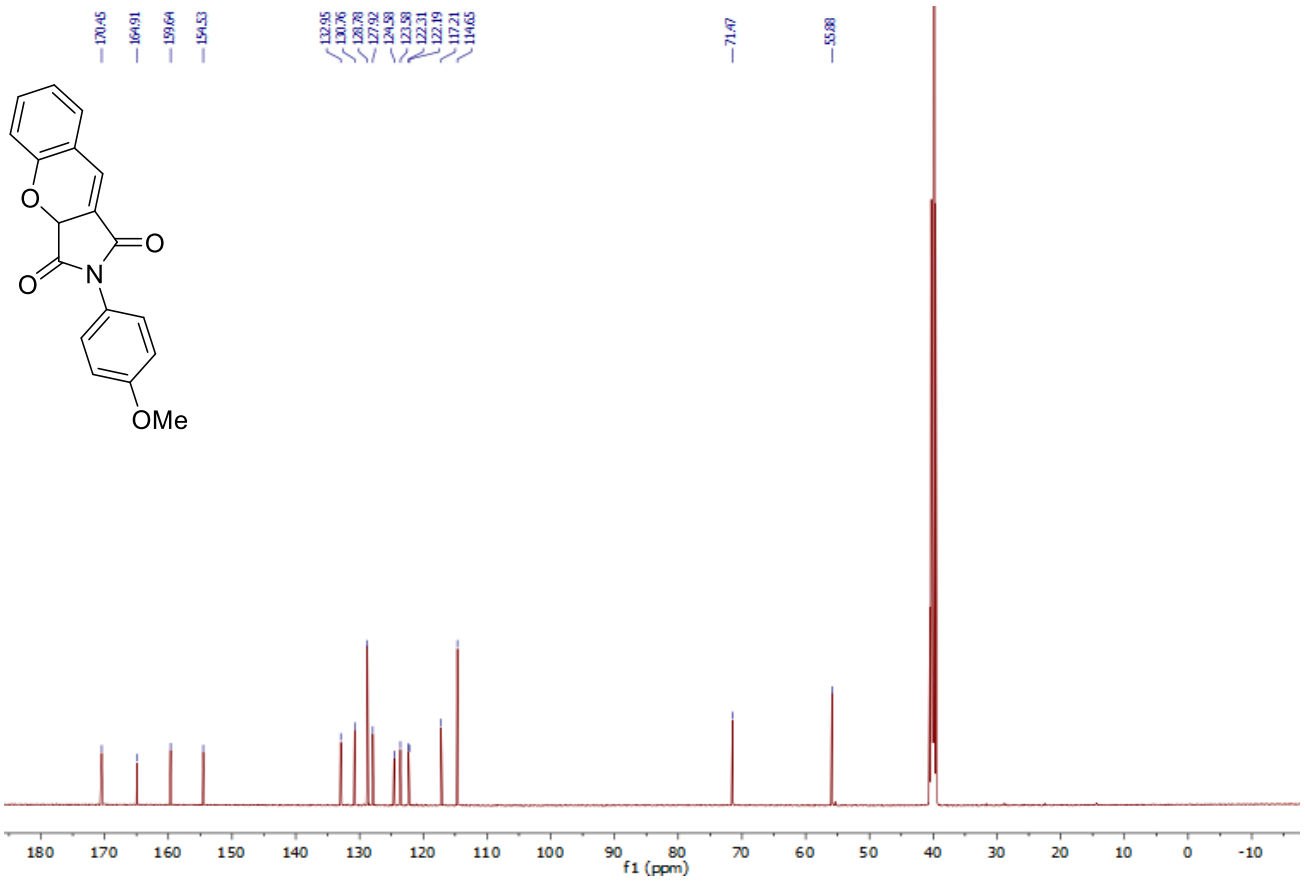
^{13}C NMR spectrum of compound **8c**



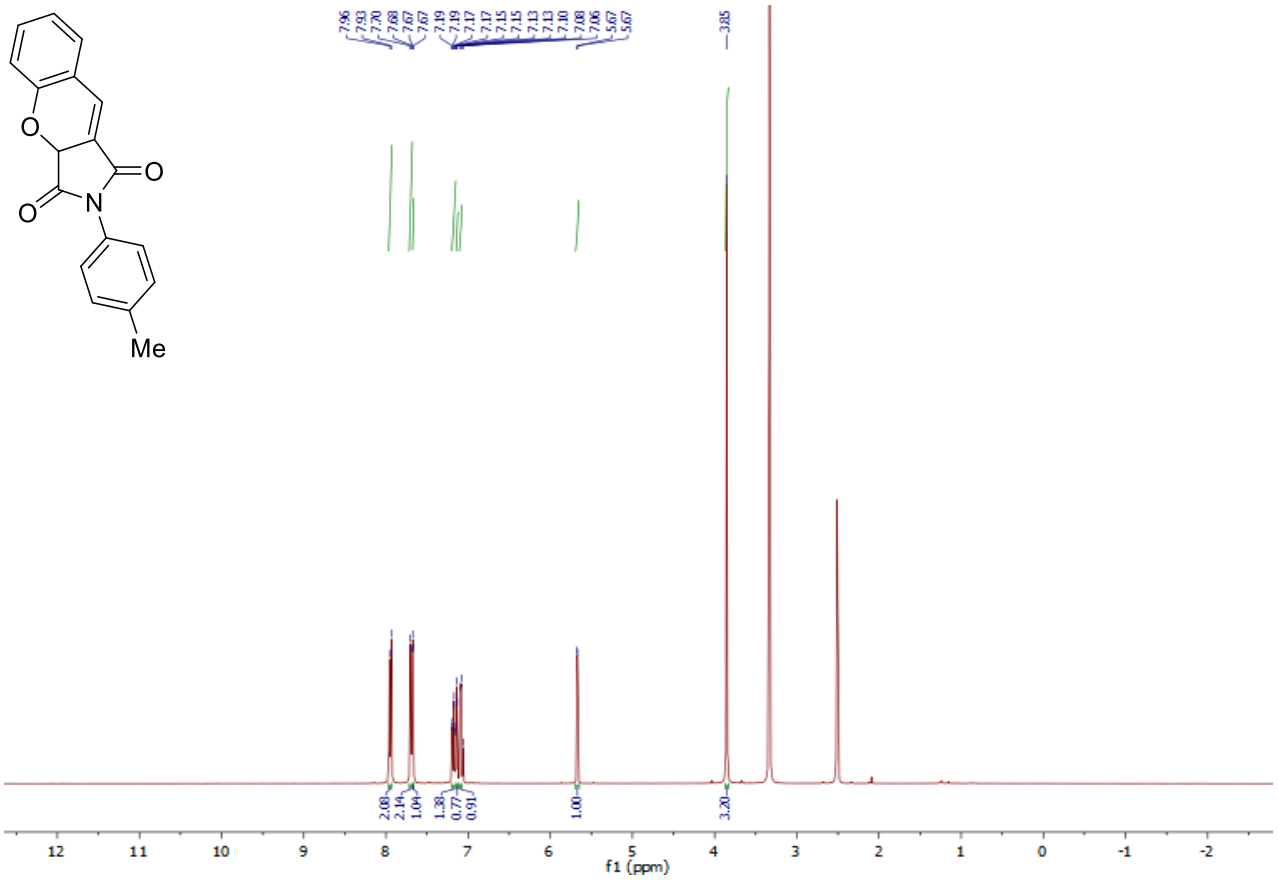
^{1}H NMR spectrum of compound **8d**



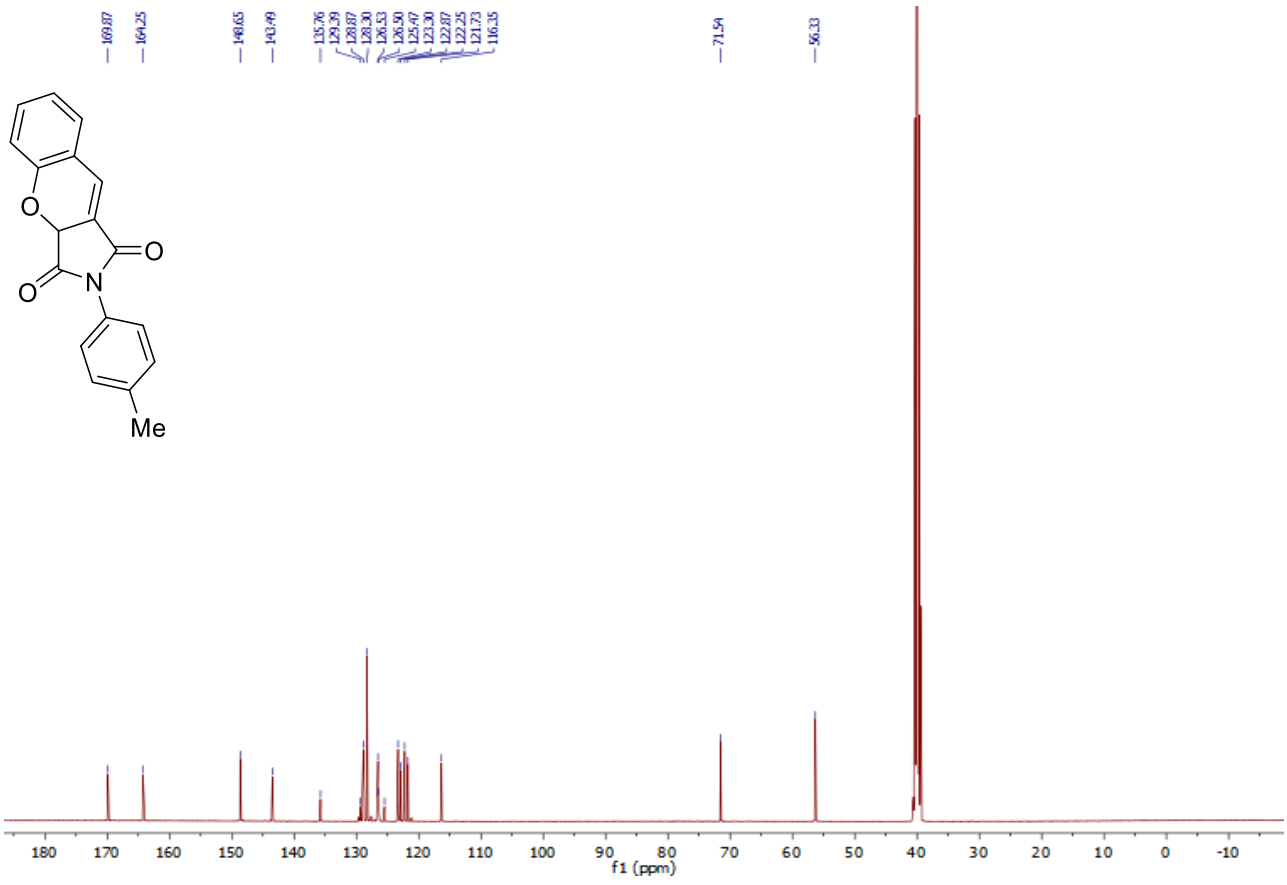
^{13}C NMR spectrum of compound **8d**



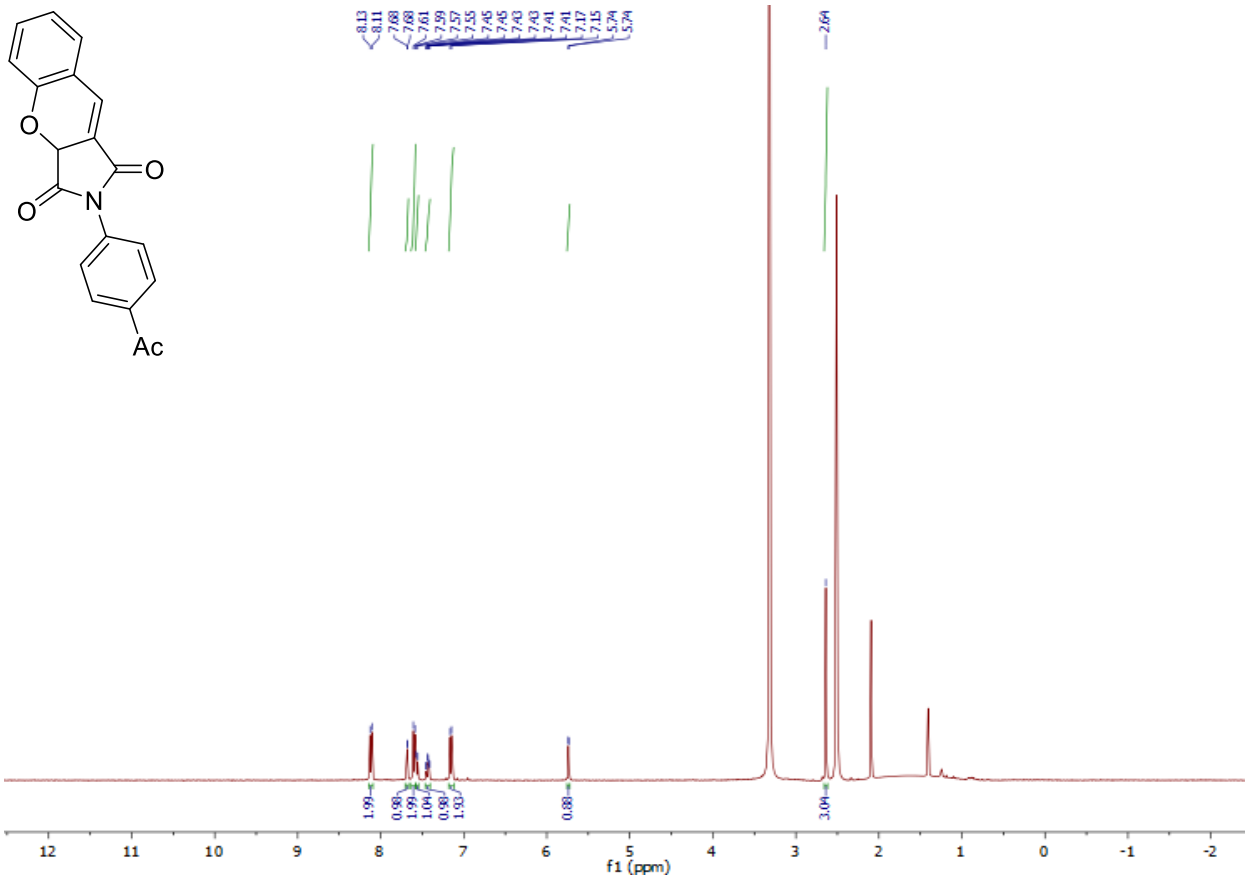
^{1}H NMR spectrum of compound **8e**



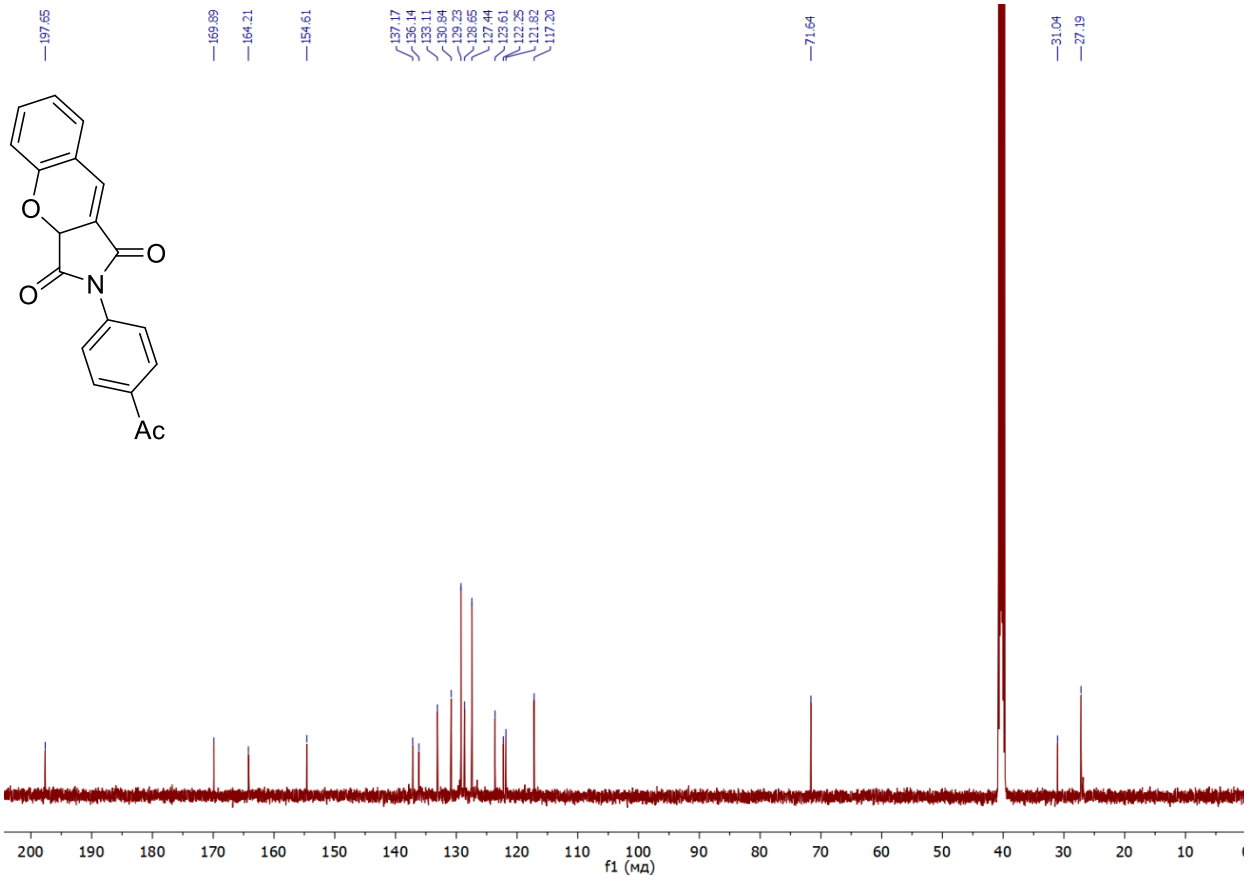
^{13}C NMR spectrum of compound **8e**



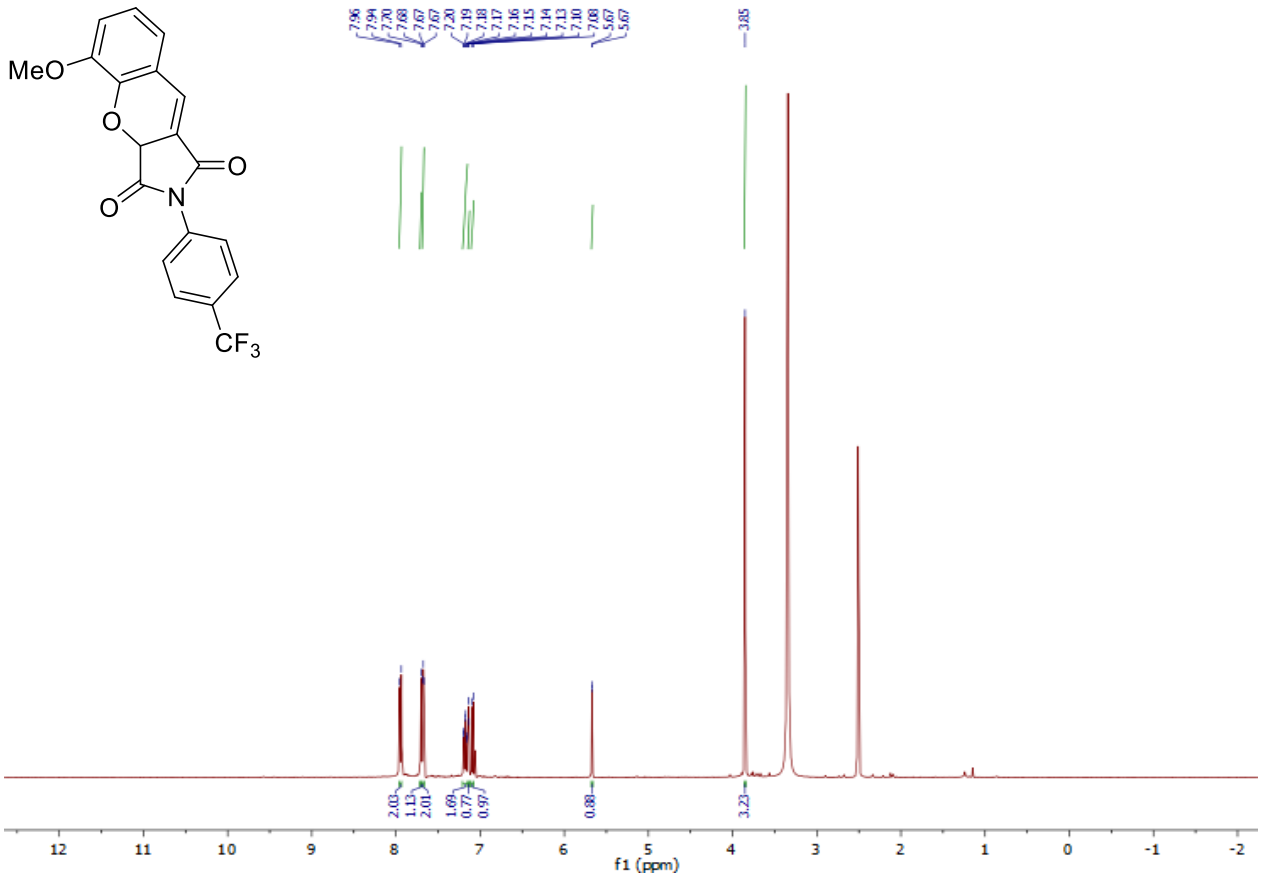
^{1}H NMR spectrum of compound **8f**



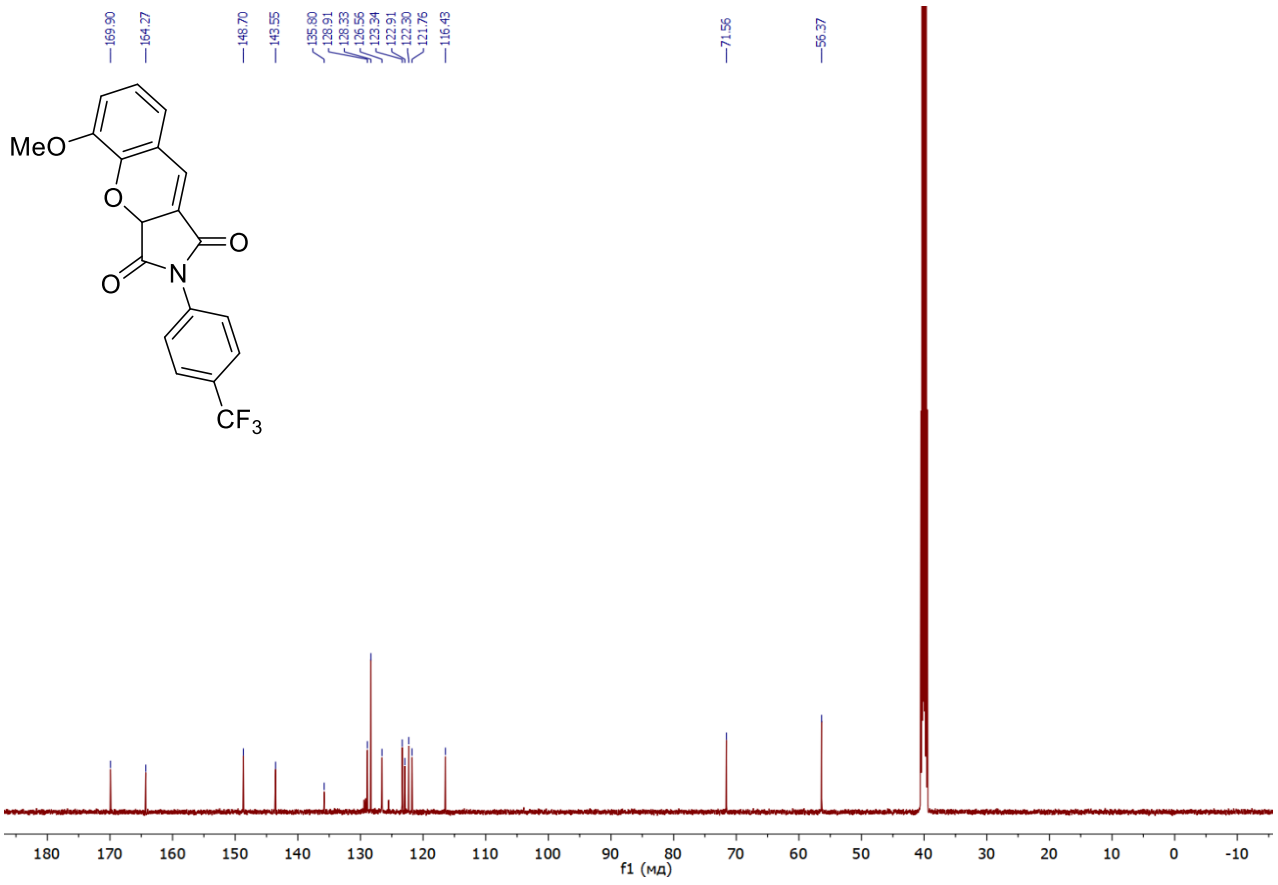
^{13}C NMR spectrum of compound **8f**



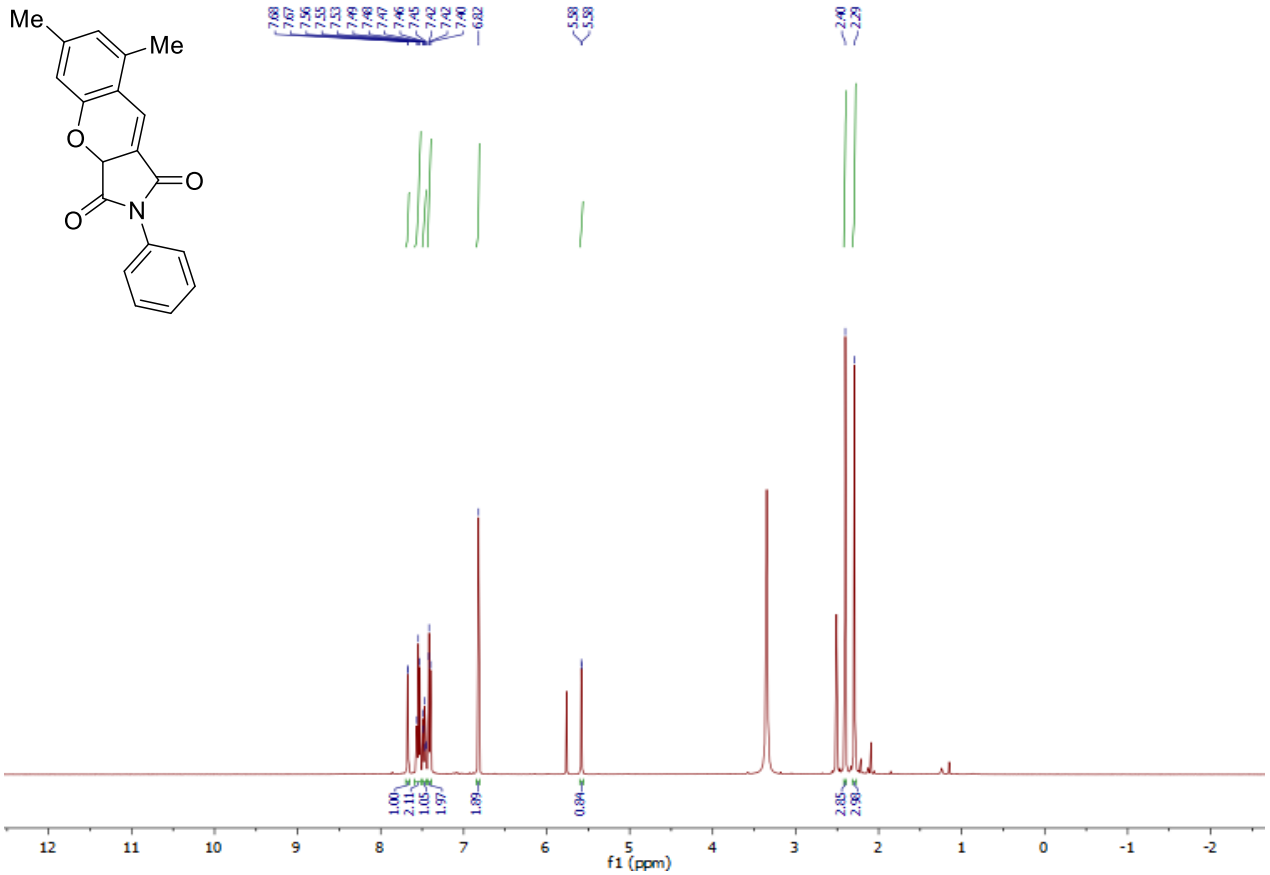
^{1}H NMR spectrum of compound **8g**



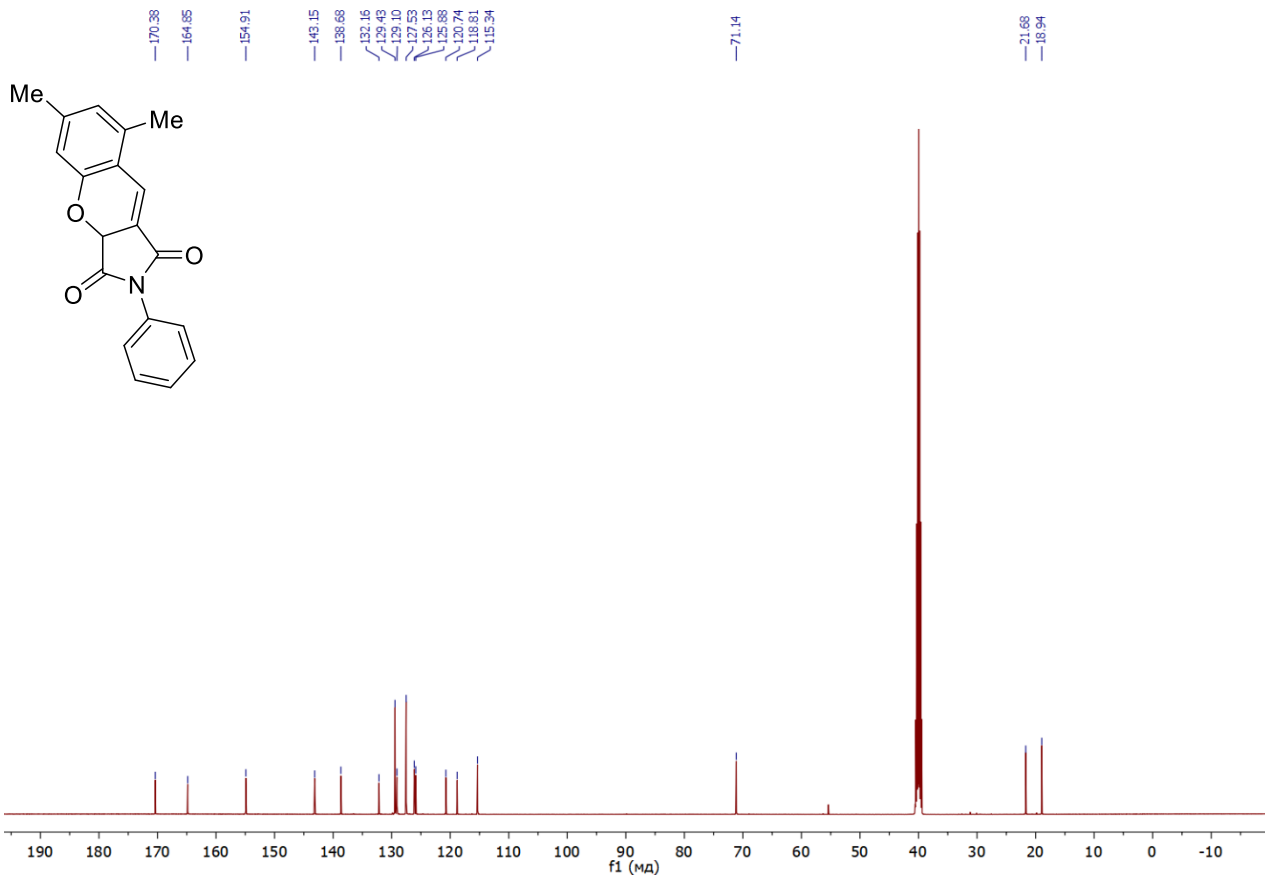
^{13}C NMR spectrum of compound **8g**



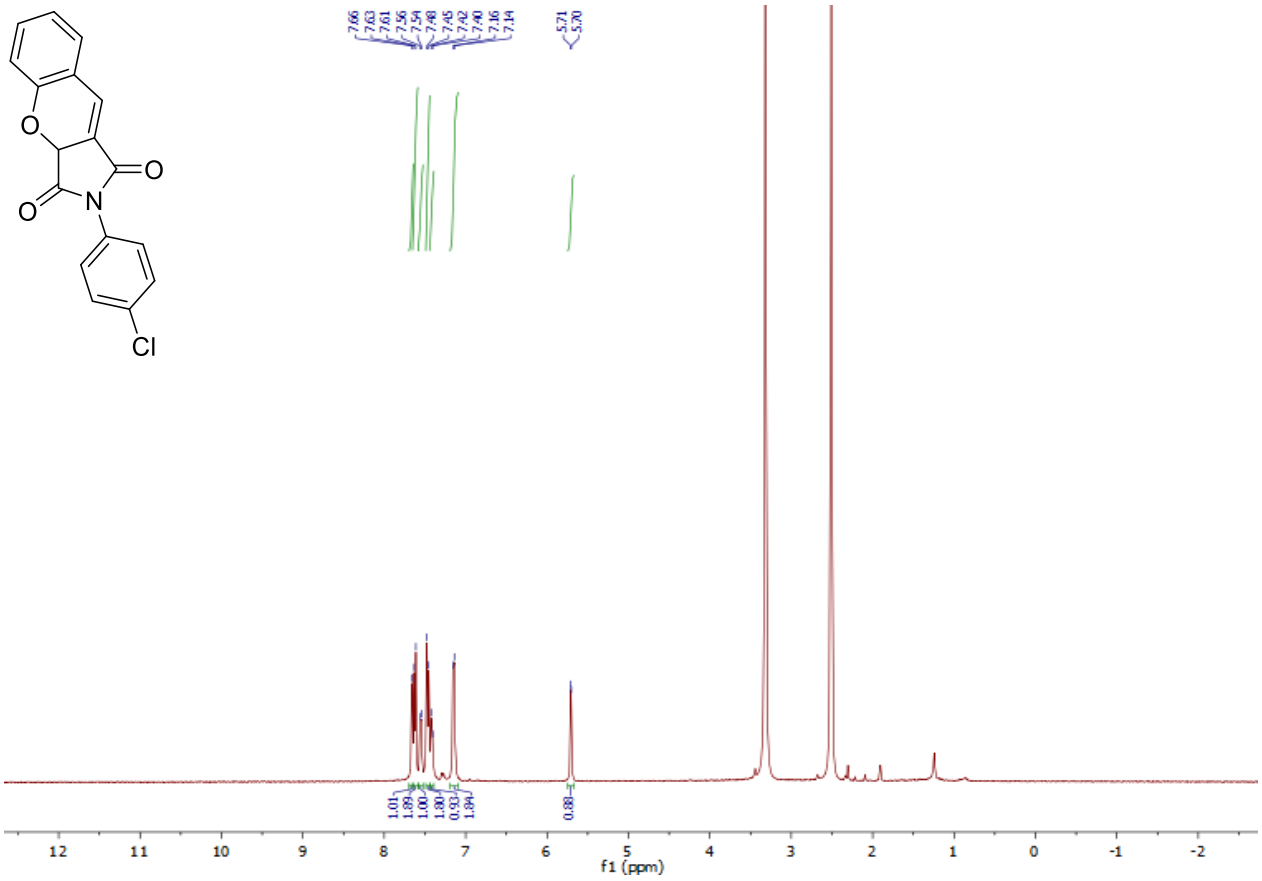
^{1}H NMR spectrum of compound **8h**



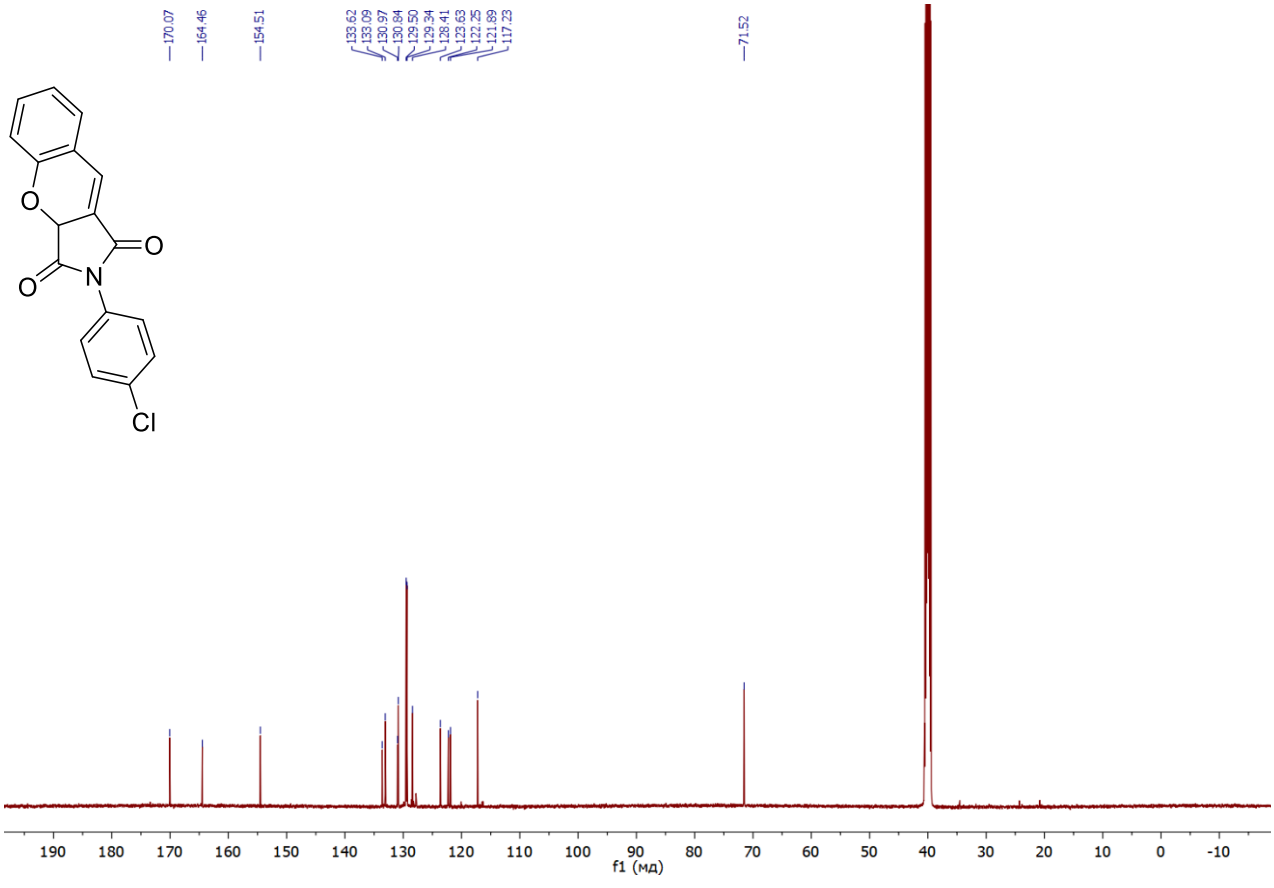
^{13}C NMR spectrum of compound **8h**



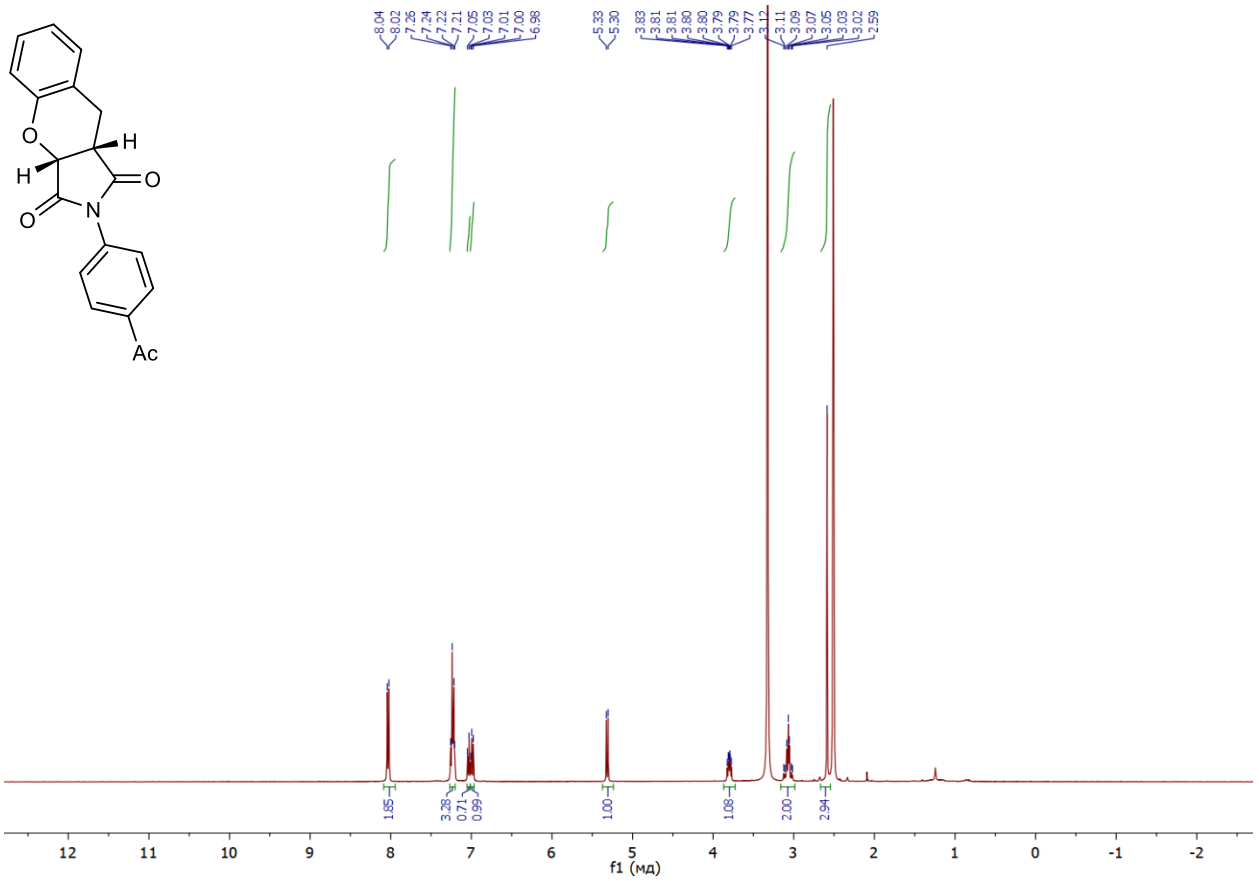
^{1}H NMR spectrum of compound **8i**



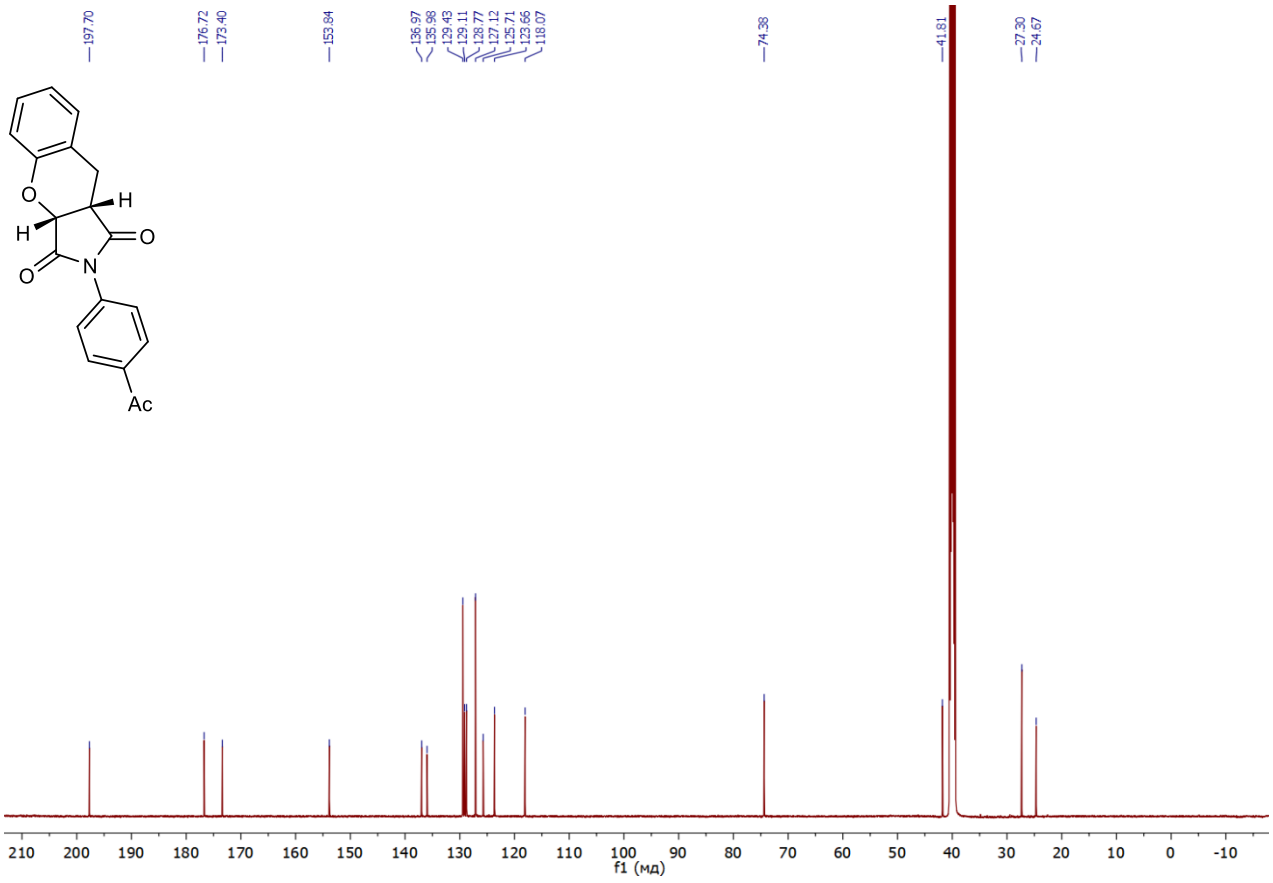
^{13}C NMR spectrum of compound **8i**



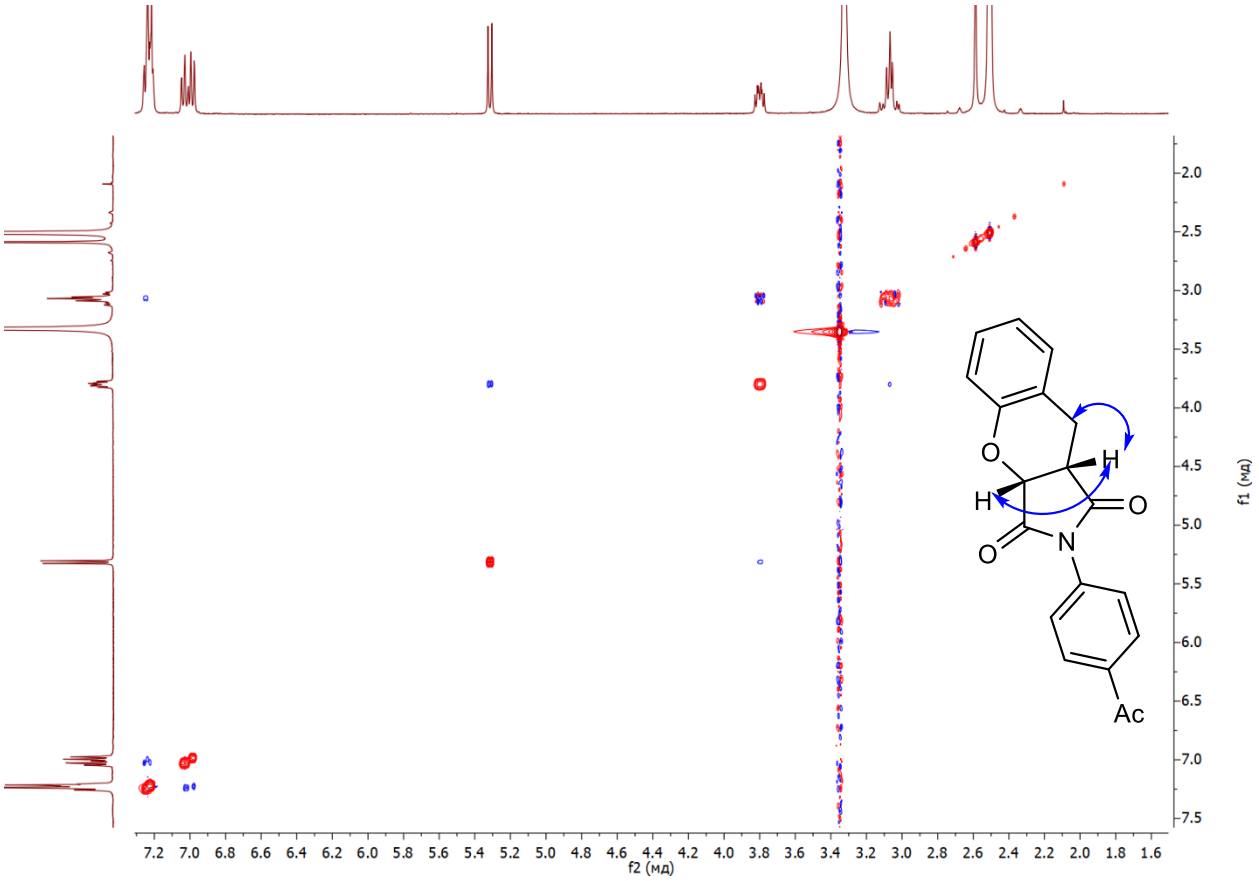
^{1}H NMR spectrum of compound **9a**



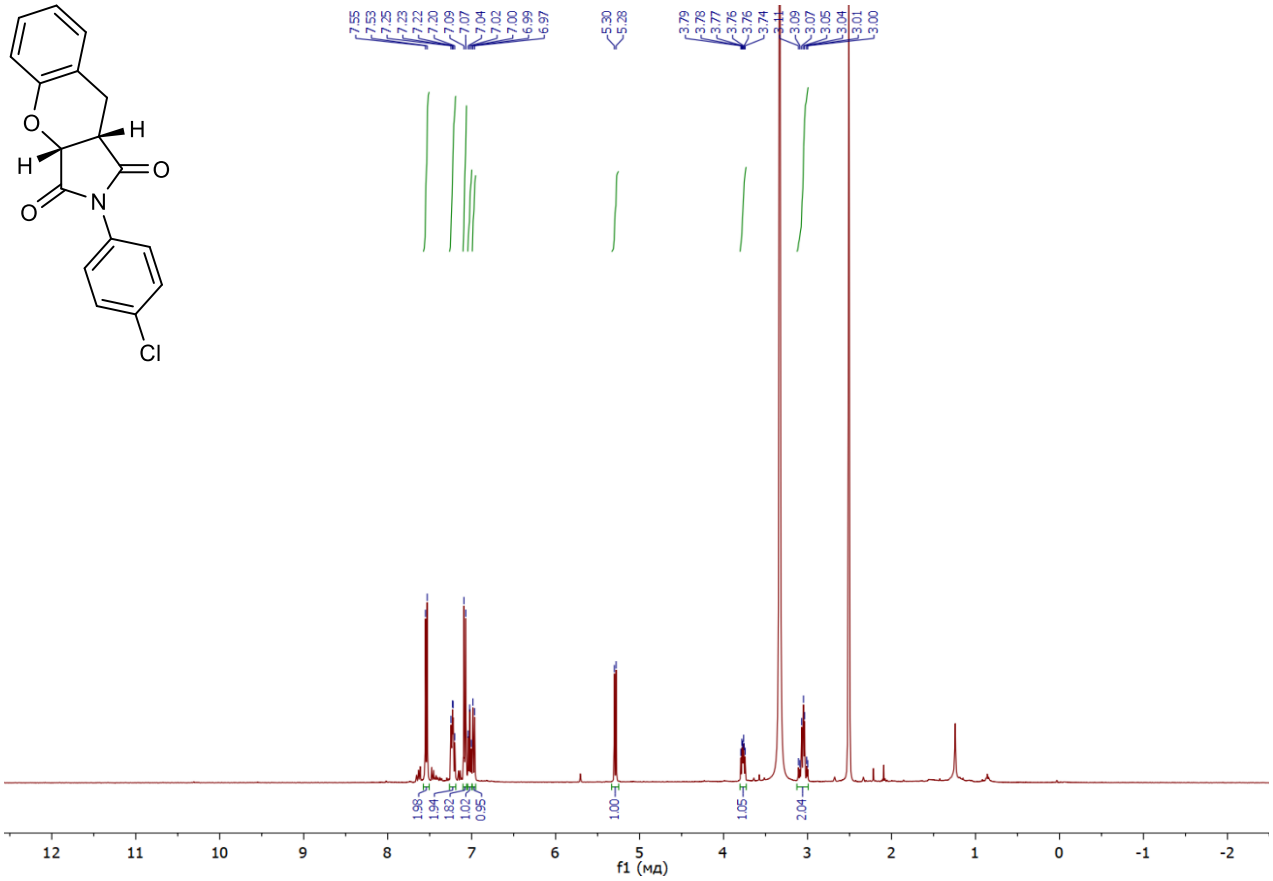
^{13}C NMR spectrum of compound **9a**



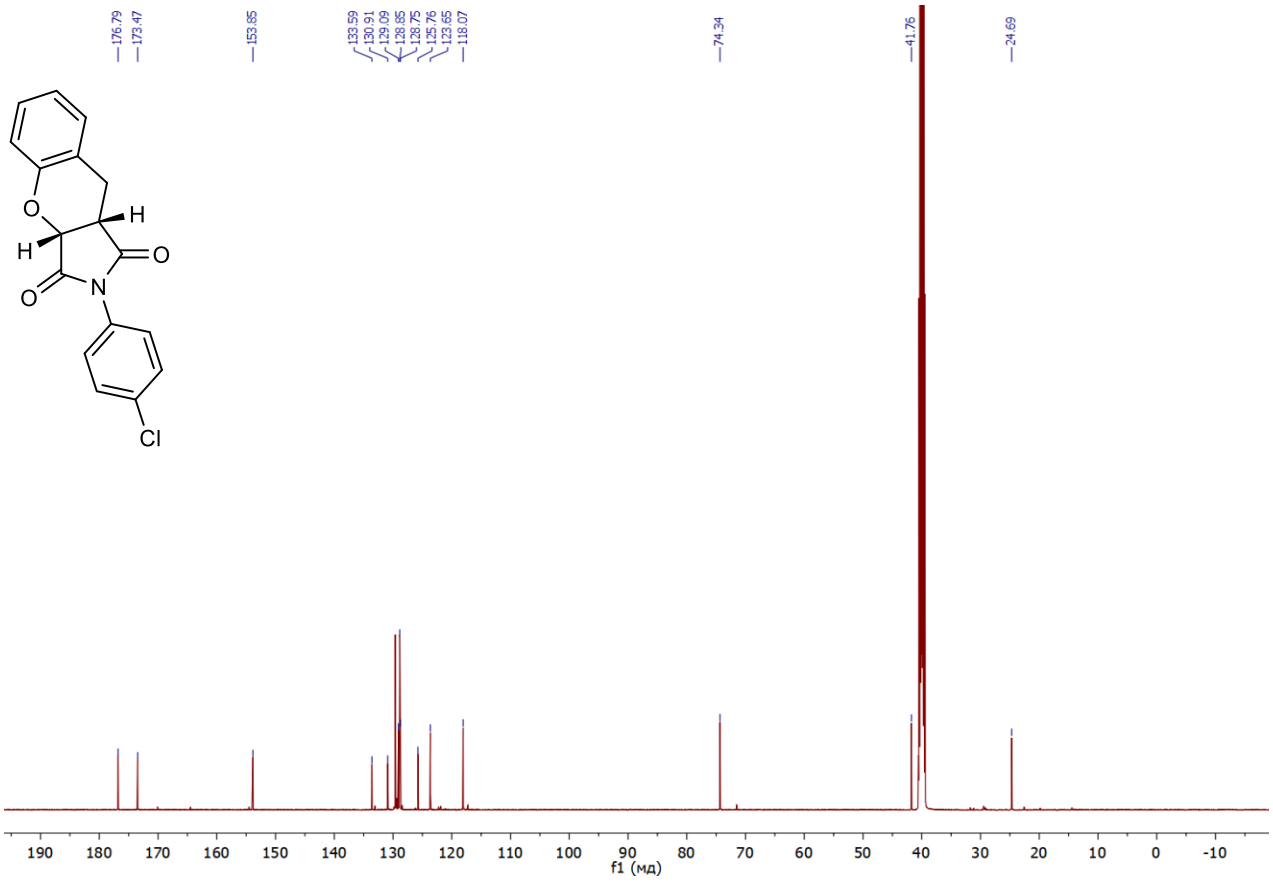
NOESY NMR spectrum of compound **9a**



^{1}H NMR spectrum of compound **9b**



^{13}C NMR spectrum of compound **9b**



NOESY NMR spectrum of compound **9b**