

Supporting Information

Regioselective Construction of Coumarin-1,2,4-Triazines via a Cs₂CO₃-Catalyzed [3 + 3] Cycloaddition Reaction

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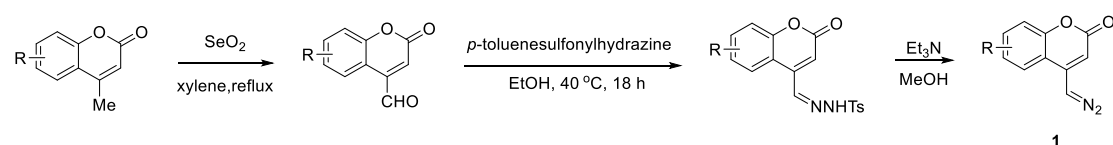
General Information

Nuclear magnetic resonance (NMR) spectroscopies were recorded at 400 or 600 MHz for ^1H NMR spectroscopy, 101 or 151 MHz for ^{13}C NMR spectroscopy (decoupled), and 376 or 565 MHz for ^{19}F NMR spectroscopy (decoupled), respectively. Chemical shifts were reported in ppm down field from internal Me_4Si and external CHCl_3 , respectively. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), and br (broad signal). Coupling constants were reported in Hertz (Hz). High resolution mass spectrometry (HRMS) spectra were obtained on a Bruker miorOTOF-QII instrument. Melting points were measured on a SGW X-4A digital melting point apparatus and are uncorrected. X-ray structural analysis was conducted on a Bruker APEX-II CCD instrument.

Materials: All purchased reagents were used without further purification. Thin-layer chromatography (TLC) was performed on precoated GF254 silica gel plates (Qingdao Marine Chemical Inc.) and compounds were visualized with a UV light at 254 nm. Flash chromatography separations were carried out using silica gel (200–300 mesh, Qingdao Marine Chemical Inc.). Glycine imino esters **2** were prepared according to reported procedures.¹⁻²

General Procedure

General procedure 1 for the synthesis of 4-diazomethylcoumarins.³⁻⁵

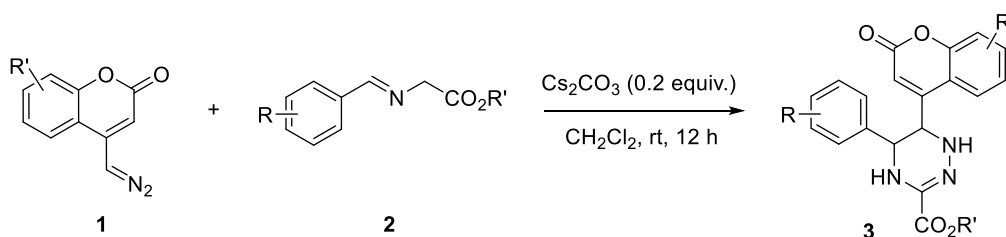


Powdered SeO_2 (4.4 g, 40 mmol, 2 equiv.) was added to a solution of 4-methylcoumarin (20 mmol, 1 equiv.) dissolved in a suitable amount of hot dry xylene and the whole was refluxed for 16 h with vigorous stirring. The reaction mixture was filtered hot to remove black Se, and the deep orange filtrate was cooled to room temperature and add 80 mL of petroleum ether to stand overnight. Separated from the solution led to the almost pure crystals of coumarin-4-carbaldehydes which were used directly for the next step without any further purification.

A mixture of coumarin-4-carbaldehydes (10 mmol, 1 equiv.) and *p*-toluenesulfonylhydrazine (11 mmol, 1.1 equiv.) was suspended in EtOH (20 mL) and vigorously stirred at 40 °C. After 18 h, the precipitates were collected, washed with EtOH, and recrystallized to give the corresponding coumarin-4-carbaldehyde tosylhydrazones.

Triethylamine (2 mmol, 1 equiv.) was added dropwise to a stirred suspension of coumarin-4-carbaldehyde tosylhydrazones (2 mmol, 1 equiv.) in MeOH (8 mL) at room temperature, whereupon the initial suspension changed into a solution followed by the gradual appearance of yellow precipitates. The reaction mixture was stirred for 2 h, and the resulting precipitates were collected and recrystallized to give the 4-diazomethylcoumarins.

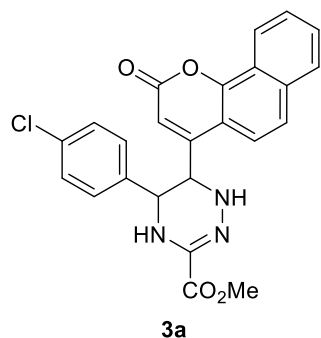
General procedure 2 for the synthesis of coumarin-decorated tetrahydro-triazines **3 from the corresponding glycine imino esters**



A 10 mL Schlenk tube equipped with a stirring bar and capped with a rubber septum was charged with coumarin-diazo reagents (**1**, 0.2 mmol, 1.0 equiv.), glycine imino esters (**2**, 0.3 mmol, 1.5 equiv.), and Cs₂CO₃ (13 mg, 0.04 mmol, 0.2 equiv.). CH₂Cl₂ (2.0 mL) was transferred into the tube. The reaction mixture was stirred under an air atmosphere at rt for 12 h. After the reaction completed (detected by TLC), the reaction mixture was purified by flash chromatography on silica gel (eluting with ethyl acetate / petroleum ether = 1:1) to give the desired product **3**.

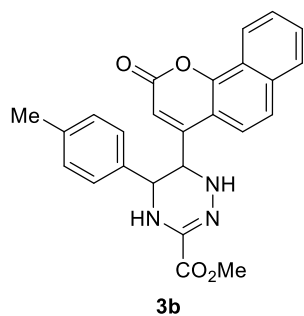
Characterization Data of the Products

Methyl 5-(4-chlorophenyl)-6-(2-oxo-2*H*-benzo[*h*]chromen-4-yl)-1,4,5,6-tetrahydro-1,2,4-triazine-3-carboxylate (3a)



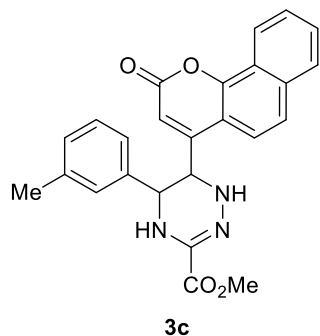
Obtained as a yellow solid after column chromatography (EtOAc/petroleum ether = 2:1, R_f = 0.5), 83.3 mg, 93% yield, m.p. 145-147 °C. **¹H NMR** (600 MHz, CDCl₃): δ 8.52 – 8.49 (m, 1H), 7.82 – 7.80 (m, 1H), 7.66 – 7.61 (m, 2H), 7.49 (d, J = 8.8 Hz, 1H), 7.27 – 7.17 (m, 3H), 7.12 (d, J = 8.1 Hz, 2H), 6.56 (s, 1H), 5.87 (s, 1H), 5.73 (d, J = 3.4 Hz, 1H), 4.78 – 4.63 (m, 1H), 4.23 – 4.10 (m, 1H), 3.95 (s, 3H) ppm. **¹³C NMR** (151 MHz, CDCl₃): δ 162.1, 160.4, 152.5, 151.1, 136.5, 135.9, 135.1, 134.6, 129.4, 129.3, 128.3, 127.7, 127.5, 124.4, 123.2, 122.8, 119.2, 115.0, 113.1, 59.5, 56.0, 53.4 ppm. **HRMS** (ESI-TOF) m/z : [M+H] calcd. For C₂₄H₁₉N₃O₄Cl 448.1064, found 448.1064.

Methyl 6-(2-oxo-2*H*-benzo[*h*]chromen-4-yl)-5-(*p*-tolyl)-1,4,5,6-tetrahydro-1,2,4-triazine-3-carboxylate (3b)



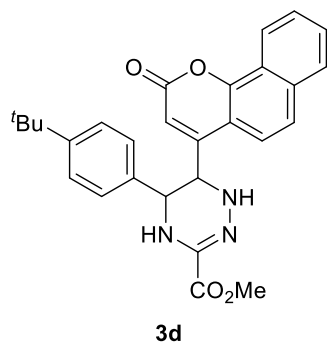
Obtained as a yellow solid after column chromatography (EtOAc/petroleum ether = 2:1, R_f = 0.5), 71.0 mg, 83% yield, m.p. 142-144 °C. **¹H NMR** (600 MHz, CDCl₃): δ 8.54 – 8.42 (m, 1H), 7.80 – 7.73 (m, 1H), 7.64 – 7.55 (m, 2H), 7.44 (d, J = 8.8 Hz, 1H), 7.29 (s, 1H), 7.09 – 6.94 (m, 4H), 6.51 (s, 1H), 5.85 (s, 1H), 5.72 (s, 1H), 4.66 (d, J = 6.2 Hz, 1H), 4.10 (d, J = 6.2 Hz, 1H), 3.93 (s, 3H), 2.22 (s, 3H) ppm. **¹³C NMR** (151 MHz, CDCl₃): δ 162.2, 160.5, 152.9, 151.0, 139.1, 136.4, 134.7, 134.6, 129.8, 129.1, 127.6, 127.3, 126.8, 124.1, 123.2, 122.8, 119.8, 115.1, 113.4, 60.2, 56.4, 53.3, 21.1 ppm. **HRMS** (ESI-TOF) m/z : [M+H] calcd. For C₂₅H₂₂N₃O₄ 428.1610, found 428.1609.

Methyl 6-(2-oxo-2*H*-benzo[*h*]chromen-4-yl)-5-(*m*-tolyl)-1,4,5,6-tetrahydro-1,2,4-triazine-3-carboxylate (3c)



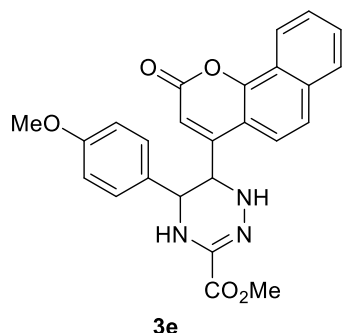
Obtained as a yellow solid after column chromatography (EtOAc/petroleum ether = 2:1, R_f = 0.5), 71.8 mg, 84% yield, m.p. 149-151 °C. **^1H NMR** (600 MHz, CDCl_3): δ 8.46 (dd, J = 7.6, 1.9 Hz, 1H), 7.76 (dd, J = 7.3, 1.9 Hz, 1H), 7.62 – 7.57 (m, 2H), 7.43 (d, J = 8.8 Hz, 1H), 7.25 (s, 1H), 7.08 (t, J = 7.6 Hz, 1H), 7.00 (d, J = 7.7 Hz, 1H), 6.96 (s, 1H), 6.93 (d, J = 7.7 Hz, 1H), 6.53 (s, 1H), 5.88 (s, 1H), 5.73 (s, 1H), 4.64 – 4.63 (m, 1H), 4.17 – 4.10 (m, 1H), 3.93 (s, 3H), 2.20 (s, 3H) ppm. **^{13}C NMR** (151 MHz, CDCl_3): δ 162.2, 160.6, 152.9, 150.9, 139.0, 137.7, 136.3, 134.5, 129.9, 129.1, 129.0, 127.6, 127.4, 127.3, 124.1, 124.0, 123.1, 122.7, 119.6, 114.9, 113.4, 60.4, 55.8, 53.3, 21.4 ppm. **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{H}]$ calcd. For $\text{C}_{25}\text{H}_{22}\text{N}_3\text{O}_4$ 428.1610, found 428.1611.

Methyl 5-(4-(*tert*-butyl)phenyl)-6-(2-oxo-2*H*-benzo[*h*]chromen-4-yl)-1,4,5,6-tetrahydro-1,2,4-triazine-3-carboxylate (3d)



Obtained as a yellow solid after column chromatography (EtOAc/petroleum ether = 2:1, R_f = 0.5), 90.2 mg, 96% yield, m.p. 140-142 °C. **^1H NMR** (600 MHz, CDCl_3): δ 8.55 – 8.40 (m, 1H), 7.75 – 7.69 (m, 1H), 7.63 – 7.55 (m, 2H), 7.33 (d, J = 8.9 Hz, 1H), 7.21-7.19 (m, 2H), 7.07-7.06 (m, 3H), 6.59 (s, 1H), 5.88 (s, 1H), 5.73 (s, 1H), 4.62 (d, J = 5.9 Hz, 1H), 4.20 – 4.06 (m, 1H), 3.92 (s, 3H), 1.17 (s, 9H) ppm. **^{13}C NMR** (151 MHz, CDCl_3): δ 162.1, 160.6, 153.2, 152.5, 150.8, 136.3, 134.7, 134.4, 129.0, 127.5, 127.3, 126.6, 126.0, 123.8, 123.1, 122.7, 119.6, 114.8, 113.4, 60.4, 55.7, 53.3, 34.6, 31.2 ppm. **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{H}]$ calcd. For $\text{C}_{28}\text{H}_{28}\text{N}_3\text{O}_4$ 470.2080, found 470.2082.

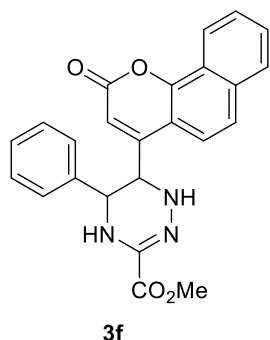
Methyl 5-(4-methoxyphenyl)-6-(2-oxo-2*H*-benzo[*h*]chromen-4-yl)-1,4,5,6-tetrahydro-1,2,4-triazine-3-carboxylate (3e)



Obtained as a yellow solid after column chromatography (EtOAc/petroleum ether = 2:1, R_f = 0.5), 84.3 mg, 95% yield, m.p. 148-150 °C. **^1H NMR** (600 MHz, CDCl_3): δ 8.50 – 8.42 (m, 1H), 7.81 – 7.73 (m, 1H), 7.65 – 7.54 (m, 2H), 7.44 (d, J = 8.8 Hz, 1H), 7.26 (s, 1H), 7.12 – 7.01 (m, 2H), 6.76 – 6.67 (m, 2H), 6.51 (s, 1H), 5.84 (s, 1H), 5.72 (s, 1H), 4.63 (d, J = 6.3 Hz, 1H), 4.09 (d, J = 6.4 Hz, 1H),

3.93 (s, 3H), 3.67 (s, 3H) ppm. **^{13}C NMR** (151 MHz, CDCl_3): δ 162.1, 160.5, 160.1, 153.0, 150.9, 136.4, 134.5, 129.6, 129.1, 128.1, 127.6, 127.3, 124.1, 123.1, 122.7, 119.7, 115.1, 114.5, 113.4, 60.0, 55.9, 55.3, 53.2 ppm. **HRMS** (ESI-TOF) m/z : [M+H] calcd. For $\text{C}_{25}\text{H}_{22}\text{N}_3\text{O}_5$ 444.1559, found 444.1558.

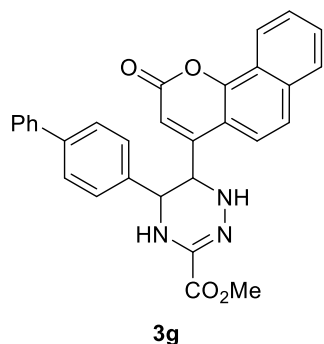
Methyl 6-(2-oxo-2*H*-benzo[*h*]chromen-4-yl)-5-phenyl-1,4,5,6-tetrahydro-1,2,4-triazine-3-carboxylate (3f)



Obtained as a yellow solid after column chromatography (EtOAc/petroleum ether = 2:1, R_f = 0.5), 78.6 mg, 95% yield, m.p. 140-142 °C. **^1H NMR** (400 MHz, CDCl_3): δ 8.50 – 8.40 (m, 1H), 7.81 – 7.70 (m, 1H), 7.62-7.55 (m, 2H), 7.40 (d, J = 8.8 Hz, 1H), 7.26 – 7.10 (m, 6H), 6.54 (s, 1H), 5.92 (s, 1H), 5.75 (s, 1H), 4.67 (d, J = 6.1 Hz, 1H), 4.13 (d, J = 6.1 Hz, 1H), 3.92 (s, 3H) ppm. **^{13}C NMR** (101 MHz, CDCl_3): δ 162.1, 160.5, 152.9, 150.9,

137.7, 136.3, 134.5, 129.2, 129.2, 129.1, 127.6, 127.3, 126.9, 124.1, 123.1, 122.7, 119.5, 115.0, 113.3, 60.5, 55.8, 53.3 ppm. **HRMS** (ESI-TOF) m/z : [M+H] calcd. For $\text{C}_{24}\text{H}_{20}\text{N}_3\text{O}_4$ 414.1454, found 414.1458.

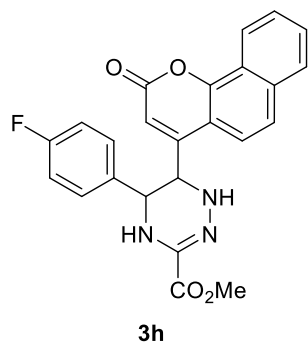
Methyl 5-(4-(tert-butyl)phenyl)-6-(2-oxo-2H-benzo[h]chromen-4-yl)-1,4,5,6-tetrahydro-1,2,4-triazine-3-carboxylate (3g)



Obtained as a yellow solid after column chromatography (EtOAc/petroleum ether = 2:1, R_f = 0.5), 95.9 mg, 98% yield, m.p. 152-154 °C. **^1H NMR** (600 MHz, CDCl_3): δ 8.53 – 8.45 (m, 1H), 7.74-7.73 (m, 1H), 7.62 – 7.56 (m, 2H), 7.44 – 7.35 (m, 7H), 7.34 – 7.29 (m, 1H), 7.27 (s, 1H), 7.22 (d, J = 7.9 Hz, 2H), 6.59 (s, 1H), 5.94 (s, 1H), 5.74 (s, 1H), 4.73 (d, J = 5.1 Hz, 1H), 4.19 (d, J = 6.1 Hz, 1H), 3.94 (s, 3H)

ppm. **^{13}C NMR** (151 MHz, CDCl_3): δ 162.1, 160.6, 152.9, 151.0, 142.2, 140.2, 136.8, 136.2, 134.6, 129.1, 128.9, 127.9, 127.7, 127.6, 127.4, 127.4, 127.1, 124.1, 123.2, 122.8, 119.5, 114.9, 113.3, 60.1, 56.0, 53.3 ppm. **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{H}]$ calcd. For $\text{C}_{30}\text{H}_{24}\text{N}_3\text{O}_4$ 490.1767, found 490.1768.

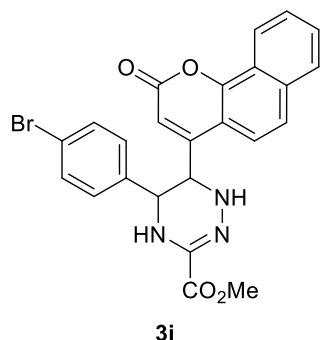
Methyl 5-(4-fluorophenyl)-6-(2-oxo-2H-benzo[h]chromen-4-yl)-1,4,5,6-tetrahydro-1,2,4-triazine-3-carboxylate (3h)



Obtained as a yellow solid after column chromatography (EtOAc/petroleum ether = 2:1, R_f = 0.5), 82.8 mg, 96% yield, m.p. 137-139 °C. **^1H NMR** (600 MHz, CDCl_3): δ 8.53-8.52 (m, 1H), 7.81-7.79 (m, 1H), 7.66-7.62 (m, 2H), 7.47 (d, J = 8.8 Hz, 1H), 7.17-7.15 (m, 3H), 6.94-6.91 (m, 2H), 6.58 (s, 1H), 5.86 (s, 1H), 5.67 (s, 1H), 4.70 (d, J = 6.2 Hz, 1H), 4.15 (d, J = 6.0 Hz, 1H), 3.96 (s, 3H) ppm. **^{19}F NMR** (565 MHz, CDCl_3): δ -111.68 ppm. **^{13}C NMR** (151 MHz, CDCl_3): δ 163.0 (d, J = 248.6 Hz), 162.1,

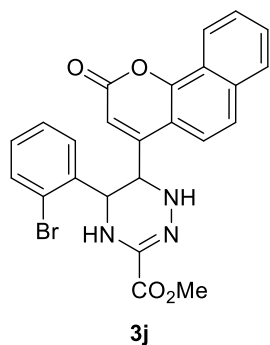
160.5, 152.6, 151.0, 136.1, 134.6, 133.6, 129.2, 128.7 (d, J = 8.4 Hz), 127.7, 127.5, 124.3, 123.2, 122.8, 119.3, 116.2 (d, J = 21.6 Hz), 115.0, 113.1, 59.7, 55.6, 53.4 ppm. **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{H}]$ calcd. For $\text{C}_{24}\text{H}_{19}\text{N}_3\text{O}_4\text{F}$ 432.1360, found 432.1361.

Methyl 5-(4-bromophenyl)-6-(2-oxo-2H-benzo[h]chromen-4-yl)-1,4,5,6-tetrahydro-1,2,4-triazine-3-carboxylate (3i)



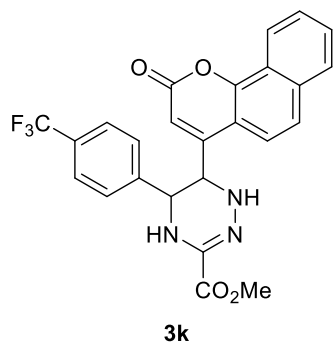
Obtained as a yellow solid after column chromatography (EtOAc/petroleum ether = 2:1, R_f = 0.5), 83.7 mg, 85% yield, m.p. 146-148 °C. **¹H NMR** (600 MHz, CDCl₃): δ 8.46 (d, J = 7.9 Hz, 1H), 7.81 – 7.77 (m, 1H), 7.65 – 7.57 (m, 2H), 7.48 (d, J = 9.4 Hz, 1H), 7.37 – 7.33 (m, 2H), 7.23 (s, 1H), 7.05 (d, J = 8.7 Hz, 2H), 6.53 (s, 1H), 5.90 (s, 1H), 5.78 (s, 1H), 4.67 (d, J = 5.3 Hz, 1H), 4.15 (d, J = 5.8 Hz, 1H), 3.92 (s, 3H) ppm. **¹³C NMR** (151 MHz, CDCl₃): δ 162.0, 160.4, 152.5, 151.1, 137.2, 135.8, 134.6, 132.3, 129.2, 128.6, 127.7, 127.5, 124.4, 123.2, 122.7, 119.2, 114.9, 113.1, 59.4, 55.6, 53.4 ppm. **HRMS** (ESI-TOF) m/z : [M+H] calcd. For C₂₄H₁₉N₃O₄Br 492.0559, found 492.0556.

Methyl 5-(2-bromophenyl)-6-(2-oxo-2H-benzo[h]chromen-4-yl)-1,4,5,6-tetrahydro-1,2,4-triazine-3-carboxylate (3j)



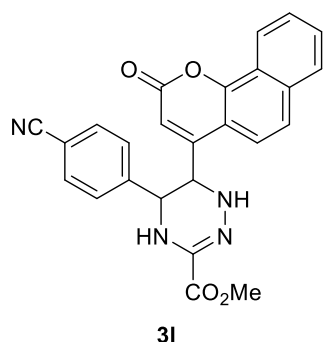
Obtained as a yellow solid after column chromatography (EtOAc/petroleum ether = 2:1, R_f = 0.5), 92.6 mg, 94% yield, m.p. 147-149 °C. **¹H NMR** (600 MHz, DMSO-*d*₆): δ 8.42 – 8.35 (m, 1H), 8.06 – 7.98 (m, 1H), 7.81 (d, J = 8.9 Hz, 1H), 7.75 (d, J = 8.9 Hz, 1H), 7.73-7.71 (m, 2H), 7.48 (dd, J = 8.0, 1.2 Hz, 1H), 7.46 – 7.42 (m, 2H), 7.40 – 7.37 (m, 2H), 7.21 – 7.18 (m, 1H), 6.84(s, 1H), 5.10 – 5.06 (m, 1H), 4.55 (d, J = 3.4 Hz, 1H), 3.78 (s, 3H) ppm. **¹³C NMR** (151 MHz, DMSO-*d*₆): δ 162.3, 160.2, 154.2, 150.5, 141.1, 134.8, 134.7, 132.9, 130.1, 129.5, 128.6, 128.4, 128.1, 124.4, 122.8, 122.5, 122.2, 121.5, 113.9, 113.6, 56.0, 52.8, 51.6 ppm. **HRMS** (ESI-TOF) m/z : [M+H] calcd. For C₂₄H₁₉N₃O₄Br 492.0559, found 492.0561.

Methyl 6-(2-oxo-2H-benzo[h]chromen-4-yl)-5-(4-(trifluoromethyl)phenyl)-1,4,5,6-tetrahydro-1,2,4-triazine-3-carboxylate (3k)



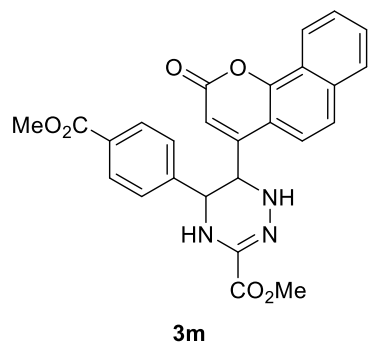
Obtained as a yellow solid after column chromatography (EtOAc/petroleum ether = 2:1, R_f = 0.5), 88.6 mg, 92% yield, m.p. 138-140 °C. **¹H NMR** (600 MHz, CDCl₃): δ 8.53 – 8.44 (m, 1H), 7.82 – 7.76 (m, 1H), 7.66 – 7.59 (m, 2H), 7.51 (d, J = 8.1 Hz, 2H), 7.45 (d, J = 8.9 Hz, 1H), 7.33 (d, J = 7.9 Hz, 2H), 7.17 (s, 1H), 6.59 (s, 1H), 5.95 (s, 1H), 5.80 (s, 1H), 4.79 (d, J = 5.3 Hz, 1H), 4.23 (d, J = 5.6 Hz, 1H), 3.94 (s, 3H) ppm. **¹⁹F NMR** (565 MHz, CDCl₃): δ -62.65 ppm. **¹³C NMR** (151 MHz, CDCl₃): δ 162.0, 160.4, 152.3, 151.1, 142.4, 135.6, 134.6, 131.4 (q, J = 32.7 Hz), 129.3, 127.7 (q, J = 11.2 Hz), 127.4, 126.2 (q, J = 3.7 Hz), 124.4, 123.7 (q, J = 272.3 Hz), 123.2, 122.7, 118.9, 114.8, 112.9, 59.3, 55.3, 53.4 ppm. **HRMS** (ESI-TOF) m/z : [M+H] calcd. For C₂₅H₁₉N₃O₄F₃ 482.1328, found 482.1327.

Methyl 5-(4-cyanophenyl)-6-(2-oxo-2H-benzo[h]chromen-4-yl)-1,4,5,6-tetrahydro-1,2,4-triazine-3-carboxylate (3l)



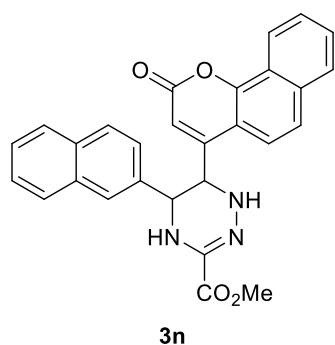
Obtained as a yellow solid after column chromatography (EtOAc/petroleum ether = 2:1, R_f = 0.5), 73.7 mg, 84% yield, m.p. 210-212 °C. **¹H NMR** (600 MHz, DMSO-*d*₆): δ 8.33 (d, J = 7.6 Hz, 1H), 8.00 (d, J = 7.6 Hz, 1H), 7.78 (t, J = 7.5 Hz, 3H), 7.71-7.67 (m, 3H), 7.55 – 7.45 (m, 3H), 7.35 (d, J = 3.7 Hz, 1H), 6.41 (s, 1H), 4.77 (s, 1H), 4.66 (s, 1H), 3.74 (s, 3H) ppm. **¹³C NMR** (151 MHz, DMSO-*d*₆): δ 162.3, 160.3, 154.8, 150.6, 148.2, 134.6, 134.0, 132.8, 129.6, 128.5, 128.2, 124.7, 122.8, 122.2, 121.1, 119.3, 113.6, 113.3, 110.8, 56.2, 53.0, 52.8 ppm. **HRMS** (ESI-TOF) m/z : [M+H] calcd. For C₂₅H₁₉N₄O₄ 439.1406, found 439.1405.

Methyl 5-(4-(methoxycarbonyl)phenyl)-6-(2-oxo-2H-benzo[h]chromen-4-yl)-1,4,5,6-tetrahydro-1,2,4-triazine-3-carboxylate (3m)



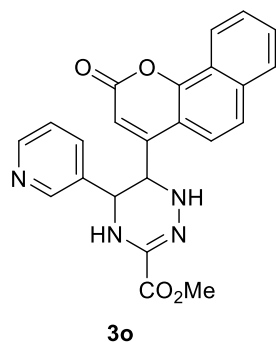
Obtained as a yellow solid after column chromatography (EtOAc/petroleum ether = 2:1, R_f = 0.5), 80.1 mg, 85% yield, m.p. 189-191 °C. **¹H NMR** (600 MHz, DMSO-*d*₆): δ 8.36 – 8.27 (m, 1H), 8.00 – 7.96 (m, 1H), 7.87 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 8.8 Hz, 1H), 7.68-7.65 (m, 3H), 7.48 (d, J = 1.7 Hz, 1H), 7.42 (d, J = 8.1 Hz, 2H), 7.27 (d, J = 3.6 Hz, 1H), 6.41 (s, 1H), 4.76 (d, J = 3.8 Hz, 1H), 4.62 – 4.58 (m, 1H), 3.78 (s, 3H), 3.74 (s, 3H) ppm. **¹³C NMR** (151 MHz, DMSO-*d*₆): δ 166.6, 162.3, 160.3, 154.9, 150.6, 147.9, 134.6, 134.2, 129.8, 129.5, 129.3, 128.4, 128.1, 127.8, 124.7, 122.8, 122.2, 121.0, 113.6, 113.4, 56.5, 53.5, 52.7, 52.7 ppm. **HRMS** (ESI-TOF) m/z : [M+H] calcd. For C₂₆H₂₂N₃O₆ 472.1509, found 472.1509.

Methyl 5-(naphthalen-2-yl)-6-(2-oxo-2H-benzo[h]chromen-4-yl)-1,4,5,6-tetrahydro-1,2,4-triazine-3-carboxylate (3n)



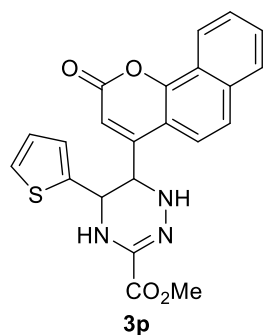
Obtained as a yellow solid after column chromatography (EtOAc/petroleum ether = 2:1, R_f = 0.5), 82.5 mg, 89% yield, m.p. 145-147 °C. **¹H NMR** (600 MHz, CDCl₃): δ 8.37 (d, J = 7.9 Hz, 1H), 7.80 (s, 1H), 7.70-7.64 (m, 3H), 7.57-7.52 (m, 3H), 7.41 (s, 1H), 7.29 (s, 2H), 7.22 (s, 1H), 7.00 (s, 1H), 6.66 (s, 1H), 6.04 (s, 1H), 5.72 (s, 1H), 5.49 (s, 1H), 4.44 (s, 1H), 3.94 (s, 3H) ppm. **¹³C NMR** (151 MHz, CDCl₃): δ 162.1, 160.5, 153.1, 150.8, 136.2, 134.4, 133.8, 133.6, 130.7, 129.8, 129.2, 129.0, 127.5, 127.2, 126.8, 126.0, 125.5, 123.8, 123.0, 122.7, 121.7, 119.1, 114.6, 113.3, 56.0, 54.2, 53.4 ppm. **HRMS** (ESI-TOF) m/z : [M+H] calcd. For C₂₈H₂₂N₃O₄ 464.1610, found 464.1607.

Methyl 6-(2-oxo-2*H*-benzo[*h*]chromen-4-yl)-5-(pyridin-3-yl)-1,4,5,6-tetrahydro-1,2,4-triazine-3-carboxylate (3o)



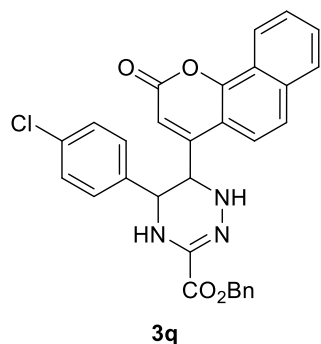
Obtained as a yellow solid after column chromatography (EtOAc/petroleum ether = 10:1, R_f = 0.2), 77.9 mg, 94% yield, m.p. 118-120 °C. **^1H NMR** (600 MHz, CDCl_3): δ 8.57 – 8.33 (m, 3H), 7.78-7.76 (m, 1H), 7.65 – 7.57 (m, 2H), 7.55-7.53 (m, 1H), 7.49 (d, J = 8.8 Hz, 1H), 7.24 (s, 1H), 7.20 (dd, J = 7.9, 4.8 Hz, 1H), 6.57 (s, 1H), 6.05 – 6.00 (m, 1H), 5.92 (s, 1H), 4.74 (d, J = 5.3 Hz, 1H), 4.29 (d, J = 5.4 Hz, 1H), 3.92 (s, 3H) ppm. **^{13}C NMR** (151 MHz, CDCl_3): δ 161.9, 160.4, 152.2, 151.2, 150.5, 148.4, 135.4, 134.7, 134.6, 134.4, 129.3, 127.7, 127.6, 124.5, 124.0, 123.2, 122.8, 118.9, 114.7, 112.8, 57.2, 55.1, 53.4 ppm. **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{H}]$ calcd. For $\text{C}_{23}\text{H}_{19}\text{N}_4\text{O}_4$ 415.1406, found 415.1404.

Methyl 6-(2-oxo-2*H*-benzo[*h*]chromen-4-yl)-5-(thiophen-2-yl)-1,4,5,6-tetrahydro-1,2,4-triazine-3-carboxylate (3p)



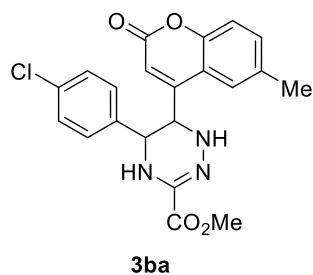
Obtained as a yellow solid after column chromatography (EtOAc/petroleum ether = 2:1, R_f = 0.5), 76.3 mg, 91% yield, m.p. 146-148 °C. **^1H NMR** (600 MHz, CDCl_3): δ 8.49 (d, J = 7.7 Hz, 1H), 7.79 (d, J = 7.4 Hz, 1H), 7.64-7.58 (m, 2H), 7.51 (d, J = 7.2 Hz, 1H), 7.34 (s, 1H), 7.22 – 7.15 (m, 1H), 6.90 – 6.82 (m, 1H), 6.79-6.78 (m, 1H), 6.57 (s, 1H), 5.94 (s, 1H), 5.81 (s, 1H), 5.02 (s, 1H), 4.32 (s, 1H), 3.91 (s, 3H) ppm. **^{13}C NMR** (151 MHz, CDCl_3): δ 161.9, 160.5, 152.7, 151.0, 141.2, 135.4, 134.6, 129.1, 127.7, 127.4, 127.2, 126.2, 126.1, 124.4, 123.2, 122.8, 119.2, 114.8, 113.3, 56.2, 55.8, 53.3 ppm. **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{H}]$ calcd. For $\text{C}_{22}\text{H}_{18}\text{N}_3\text{O}_4\text{S}$ 420.1018, found 420.1018.

Benzyl **5-(4-chlorophenyl)-6-(2-oxo-2*H*-benzo[*h*]chromen-4-yl)-1,4,5,6-tetrahydro-1,2,4-triazine-3-carboxylate (3q)**



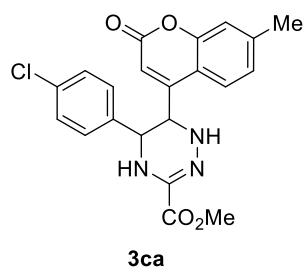
Obtained as a yellow solid after column chromatography (EtOAc/petroleum ether = 2:1, R_f = 0.5), 95.4 mg, 91% yield, m.p. 173-175 °C. **¹H NMR** (600 MHz, CDCl₃): δ 8.52 – 8.42 (m, 1H), 7.81 – 7.76 (m, 1H), 7.66 – 7.57 (m, 2H), 7.49 – 7.43 (m, 3H), 7.41 – 7.32 (m, 3H), 7.20 – 7.16 (m, 3H), 7.08 (d, J = 8.1 Hz, 2H), 6.51 (s, 1H), 5.85 (s, 1H), 5.74 (d, J = 3.1 Hz, 1H), 5.38 (d, J = 12.0, 1H), 5.32 (d, J = 12.0 Hz, 1H), 4.66 (s, 1H), 4.15 – 3.95 (m, 1H) ppm. **¹³C NMR** (151 MHz, CDCl₃): δ 161.5, 160.4, 151.1, 136.4, 136.0, 135.1, 135.0, 134.6, 129.4, 129.2, 129.0, 128.8, 128.3, 127.7, 127.5, 124.3, 123.2, 122.8, 119.3, 115.1, 113.1, 68.2, 59.6, 29.8 ppm. **HRMS** (ESI-TOF) m/z : [M+H] calcd. For C₃₀H₂₃N₃O₄Cl 524.1377, found 524.1376.

Methyl **5-(4-chlorophenyl)-6-(6-methyl-2-oxo-2*H*-chromen-4-yl)-1,4,5,6-tetrahydro-1,2,4-triazine-3-carboxylate (3ba)**



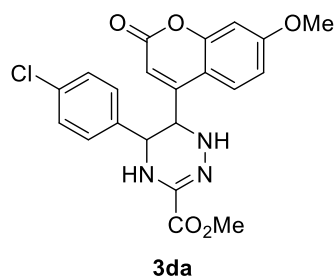
Obtained as a white solid after column chromatography (EtOAc/petroleum ether = 2:1, R_f = 0.5), 70.8 mg, 86% yield, m.p. 140-142 °C. **¹H NMR** (600 MHz, CDCl₃) δ 7.26-7.24 (m, 1H), 7.23 – 7.19 (m, 2H), 7.16 (d, J = 8.5 Hz, 1H), 7.13 – 7.08 (m, 2H), 6.84 (s, 1H), 6.51 (s, 1H), 5.89 (s, 1H), 5.65 (s, 1H), 4.59 (d, J = 6.0 Hz, 1H), 4.03 (d, J = 6.1 Hz, 1H), 3.92 (s, 3H), 2.22 (s, 3H) ppm. **¹³C NMR** (151 MHz, CDCl₃): δ 162.1, 160.6, 151.7, 151.5, 136.5, 136.0, 135.1, 133.9, 133.1, 129.2, 128.3, 123.7, 117.4, 117.2, 115.5, 59.9, 55.0, 53.3, 20.8 ppm. **HRMS** (ESI-TOF) m/z : [M+H] calcd. For C₂₁H₁₉N₃O₄Cl 412.1064, found 412.1064.

Methyl 5-(4-chlorophenyl)-6-(7-methyl-2-oxo-2H-chromen-4-yl)-1,4,5,6-tetrahydro-1,2,4-triazine-3-carboxylate (3ca)



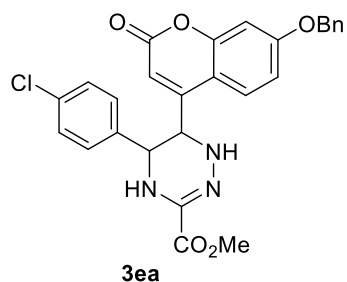
Obtained as a white solid after column chromatography (EtOAc/petroleum ether = 2:1, R_f = 0.5), 68.4 mg, 83% yield, m.p. 132-134 °C. **^1H NMR** (600 MHz, CDCl_3): δ 7.22 (d, J = 8.0 Hz, 2H), 7.13 (s, 1H), 7.12 – 7.06 (m, 3H), 6.91 (d, J = 8.1 Hz, 1H), 6.39 (s, 1H), 5.88 (s, 1H), 5.70 (s, 1H), 4.63 (d, J = 5.8 Hz, 1H), 4.03 (d, J = 5.8 Hz, 1H), 3.91 (s, 3H), 2.39 (s, 3H) ppm. **^{13}C NMR** (151 MHz, CDCl_3): δ 162.0, 160.6, 153.7, 151.5, 143.6, 136.6, 135.9, 135.0, 129.3, 128.3, 125.6, 123.6, 117.7, 115.3, 114.6, 59.4, 55.4, 53.3, 21.6 ppm. **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{H}]$ calcd. For $\text{C}_{21}\text{H}_{19}\text{N}_3\text{O}_4\text{Cl}$ 412.1064, found 412.1064.

Methyl 5-(4-chlorophenyl)-6-(7-methoxy-2-oxo-2H-chromen-4-yl)-1,4,5,6-tetrahydro-1,2,4-triazine-3-carboxylate (3da)



Obtained as a white solid after column chromatography (EtOAc/petroleum ether = 2:1, R_f = 0.5), 74.4 mg, 87% yield, m.p. 154-156 °C. **^1H NMR** (600 MHz, $\text{DMSO}-d_6$) δ 7.56 (d, J = 9.0 Hz, 1H), 7.37 (s, 1H), 7.35 – 7.31 (m, 2H), 7.27 – 7.22 (m, 2H), 7.14 (d, J = 3.5 Hz, 1H), 6.97 (d, J = 2.5 Hz, 1H), 6.86 (dd, J = 9.0, 2.6 Hz, 1H), 6.11 (s, 1H), 4.58 (d, J = 4.2 Hz, 1H), 4.37 (d, J = 3.5 Hz, 1H), 3.80 (s, 3H), 3.72 (s, 3H) ppm. **^{13}C NMR** (151 MHz, $\text{DMSO}-d_6$): δ 162.7, 162.3, 160.8, 155.6, 154.4, 141.6, 134.1, 132.6, 129.3, 128.7, 126.6, 112.9, 111.5, 110.5, 101.6, 56.5, 56.2, 53.4, 52.7 ppm. **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{H}]$ calcd. For $\text{C}_{21}\text{H}_{19}\text{N}_3\text{O}_5\text{Cl}$ 428.1013, found 428.1012.

Methyl 6-(7-(benzyloxy)-2-oxo-2H-chromen-4-yl)-5-(4-chlorophenyl)-1,4,5,6-tetrahydro-1,2,4-triazine-3-carboxylate (3ea)

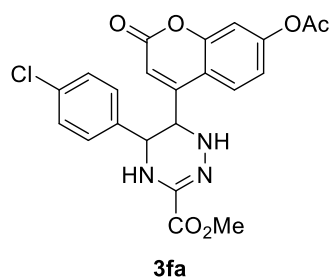


0.2 equiv. of AgOAc was also added for this example following General Procedure 2. Obtained as a yellow solid after column chromatography (EtOAc/petroleum ether = 2:1, R_f = 0.5), 84.7 mg, 84% yield, m.p. 157-159 °C. ^1H

NMR (600 MHz, CDCl_3): δ 7.44 – 7.37 (m, 4H), 7.36-

7.33 (m, 1H), 7.21 (d, J = 8.3 Hz, 2H), 7.14 (s, 1H), 7.08 (d, J = 8.1 Hz, 2H), 6.79 (d, J = 2.5 Hz, 1H), 6.71 (dd, J = 9.0, 2.6 Hz, 1H), 6.27 (s, 1H), 5.89 (s, 1H), 5.71 (s, 1H), 5.06 (s, 2H), 4.60 (d, J = 6.0 Hz, 1H), 3.96 (d, J = 6.0 Hz, 1H), 3.88 (s, 3H) ppm. ^{13}C **NMR** (151 MHz, CDCl_3): δ 162.0, 161.8, 160.8, 155.4, 151.6, 136.6, 135.9, 135.6, 135.0, 129.3, 128.9, 128.5, 128.3, 127.6, 125.1, 113.1, 112.4, 111.4, 102.3, 70.6, 59.4, 55.6, 53.3 ppm. **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{H}]$ calcd. For $\text{C}_{27}\text{H}_{23}\text{N}_3\text{O}_5\text{Cl}$ 504.1326, found 504.1329.

Methyl 6-(7-acetoxy-2-oxo-2H-chromen-4-yl)-5-(4-chlorophenyl)-1,4,5,6-tetrahydro-1,2,4-triazine-3-carboxylate (3fa)



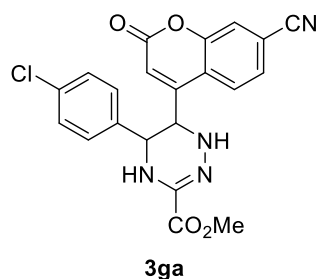
0.2 equiv. of AgOAc was also added for this example following General Procedure 2. Obtained as a yellow solid after column chromatography (EtOAc/petroleum ether = 2:1, R_f = 0.5), 45.6 mg, 50% yield, m.p. 121-123 °C. ^1H

NMR (600 MHz, CDCl_3): δ 7.31 (s, 1H), 7.25 (d, J = 8.2

Hz, 2H), 7.10 (d, J = 7.7 Hz, 3H), 6.89 (d, J = 8.5 Hz, 1H), 6.41 (s, 1H), 5.86 (s, 1H), 5.66 (s, 1H), 4.65 (d, J = 5.8 Hz, 1H), 4.02 (d, J = 6.0 Hz, 1H), 3.93 (s, 3H), 2.32 (s, 3H) ppm. ^{13}C **NMR** (151 MHz, CDCl_3): δ 168.6, 162.0, 159.9, 154.4, 153.3, 151.0, 136.4, 136.0, 135.2, 129.5, 128.2, 124.9, 118.2, 115.4, 115.3, 111.0, 59.2, 55.9, 53.4,

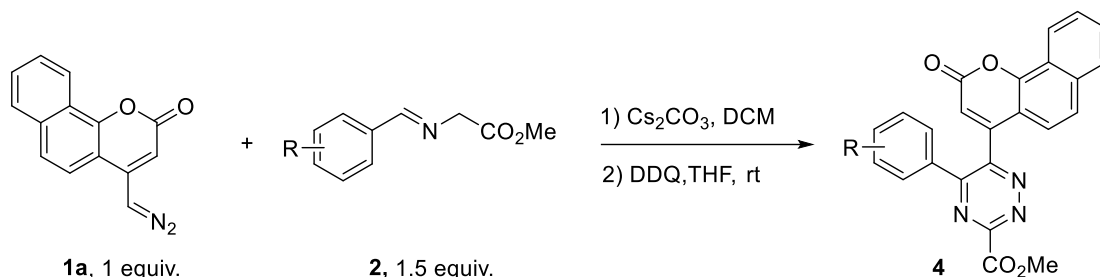
21.2 ppm. **HRMS** (ESI-TOF) m/z : [M+H] calcd. For C₂₂H₁₉N₃O₆Cl 456.0962, found 456.0960.

Methyl 5-(4-chlorophenyl)-6-(7-cyano-2-oxo-2H-chromen-4-yl)-1,4,5,6-tetrahydro-1,2,4-triazine-3-carboxylate (3ga)



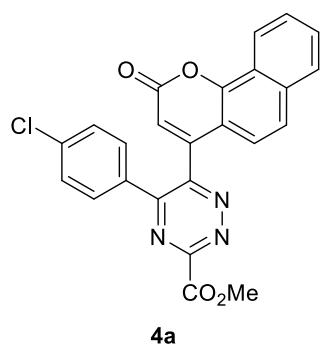
Obtained as a yellow solid after column chromatography (EtOAc/petroleum ether = 2:1, R_f = 0.5), 61.7 mg, 73% yield, m.p. 138-140 °C. **¹H NMR** (600 MHz, CDCl₃): δ 7.57 (s, 1H), 7.34 (d, J = 7.5 Hz, 2H), 7.26 (d, J = 8.1 Hz, 2H), 7.10 (d, J = 8.1 Hz, 2H), 6.60 (s, 1H), 5.92 (s, 1H), 5.70 (s, 1H), 4.61 (d, J = 5.8 Hz, 1H), 4.04 (d, J = 6.0 Hz, 1H), 3.93 (s, 3H) ppm. **¹³C NMR** (151 MHz, CDCl₃): δ 161.8, 158.6, 153.1, 150.4, 136.1, 135.9, 135.5, 129.6, 128.2, 127.2, 125.2, 121.3, 121.2, 118.9, 117.0, 115.2, 59.6, 55.4, 53.5 ppm. **HRMS** (ESI-TOF) m/z : [M+H] calcd. For C₂₁H₁₆N₄O₄Cl 423.0860, found 423.0867.

One-pot transformation to access 1,2,4-triazines **4**



A 10 mL Schlenk tube equipped with a stirring bar and capped with a rubber septum was charged with 4-(diazomethyl)-2H-benzo[h]chromen-2-one **1a** (52.6 mg, 0.2 mmol, 1.0 equiv.), glycine imino esters (**2**, 0.3 mmol, 1.5 equiv.), and Cs₂CO₃ (13 mg, 0.04 mmol, 0.2 equiv.). CH₂Cl₂ (2.0 mL) was transferred into the tube. The resulting mixture was stirred under an air atmosphere at rt for 12 h. After the reaction completed (detected by TLC), CH₂Cl₂ was removed by evaporation under reduced pressure. Then DDQ (136.2 mg, 0.6 mmol, 3.0 equiv.) and THF (3.0 mL) was added. The resulting mixture was stirred at rt for 12 h until the tetrahydro-1,2,4-triazine intermediate disappeared. Then the reaction mixture was poured into saturated aqueous solution of NaHCO₃, and extracted with ethyl acetate (3 times). The combined organic layers were washed with saturated NaHCO₃ solution (2 times) and brine sequentially, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by a silica gel chromatography (PE: EA = 1: 1) to yield the corresponding triazines **4**.

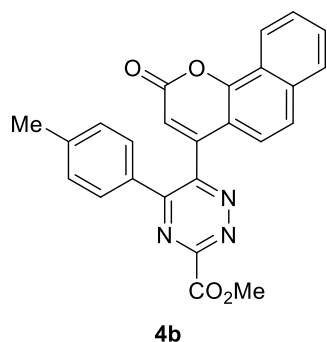
Methyl 5-(4-chlorophenyl)-6-(2-oxo-2H-benzo[h]chromen-4-yl)-1,2,4-triazine-3-carboxylate (**4a**)



Obtained as a yellow solid after column chromatography (EtOAc/petroleum ether = 1:1, R_f = 0.5), 69.2 mg, 78% yield, m.p. 146-148 °C. ¹H NMR (600 MHz, CDCl₃): δ 8.68 – 8.57 (m, 1H), 7.92 – 7.84 (m, 1H), 7.80 – 7.75 (m, 2H), 7.75 – 7.68 (m, 2H), 7.57 (d, *J* = 9.0 Hz, 1H), 7.37 – 7.31 (m, 2H), 7.05 (d, *J* = 8.8 Hz, 1H), 6.64 (s, 1H), 4.21 (s, 3H) ppm. ¹³C

NMR (151 MHz, CDCl₃): δ 162.6, 159.5, 156.3, 156.0, 154.4, 152.1, 149.9, 139.6, 135.2, 131.3, 130.9, 129.9, 129.8, 128.0, 127.9, 125.1, 123.3, 122.8, 120.7, 117.5, 112.3, 54.3 ppm. **HRMS** (ESI-TOF) m/z : [M+H] calcd. For C₂₄H₁₅N₃O₄Cl 444.0751, found 444.0750.

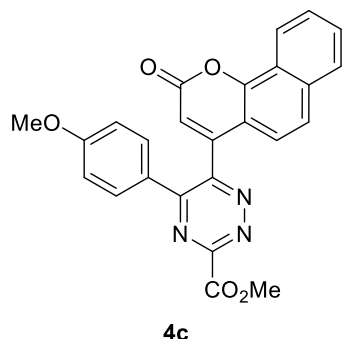
Methyl 6-(2-oxo-2H-benzo[h]chromen-4-yl)-5-(*p*-tolyl)-1,2,4-triazine-3-carboxylate (4b)



Obtained as a yellow solid after column chromatography (EtOAc/petroleum ether = 1:1, R_f = 0.5), 42.3 mg, 50% yield, m.p. 136-138 °C. **¹H NMR** (600 MHz, CDCl₃): δ 8.64 – 8.55 (m, 1H), 7.85-7.83 (m, 1H), 7.73 – 7.65 (m, 4H), 7.55 (d, J = 8.7 Hz, 1H), 7.14 (d, J = 8.1 Hz, 2H), 7.10 (d, J = 8.8 Hz, 1H), 6.63 (s, 1H), 4.19 (s, 3H), 2.31 (s, 3H) ppm.

¹³C NMR (151 MHz, CDCl₃): δ 162.9, 159.7, 157.5, 156.0, 154.5, 152.0, 150.4, 143.8, 135.2, 130.2, 130.0, 129.7, 129.6, 127.9, 127.7, 124.9, 123.3, 122.8, 121.0, 117.4, 112.7, 54.1, 21.7 ppm. **HRMS** (ESI-TOF) m/z : [M+H] calcd. For C₂₅H₁₈N₃O₄ 424.1297, found 424.1291.

Methyl 5-(4-methoxyphenyl)-6-(2-oxo-2H-benzo[h]chromen-4-yl)-1,2,4-triazine-3-carboxylate (4c)

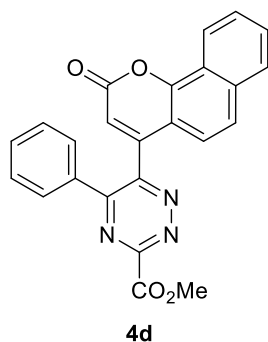


Obtained as a yellow solid after column chromatography (EtOAc/petroleum ether = 1:1, R_f = 0.5), 36.0 mg, 41% yield, m.p. 137-139 °C. **¹H NMR** (600 MHz, CDCl₃): δ 8.65 – 8.56 (m, 1H), 7.88 – 7.79 (m, 3H), 7.74 – 7.66 (m, 2H), 7.54 (d, J = 8.8 Hz, 1H), 7.08 (d, J = 8.7 Hz, 1H), 6.86 – 6.80 (m, 2H), 6.67 (s, 1H), 4.19 (s, 3H), 3.77 (s, 3H) ppm. **¹³C NMR** (151 MHz, CDCl₃): δ 163.5, 163.0, 159.8,

156.6, 155.8, 153.9, 152.0, 150.8, 135.2, 131.8, 129.6, 128.0, 127.7, 124.9, 124.8, 123.3,

122.8, 121.0, 117.2, 115.0, 112.6, 55.6, 54.1 ppm. **HRMS** (ESI-TOF) m/z : $[M+H]^+$ calcd. For $C_{25}H_{18}N_3O_5$ 440.1246, found 440.1247.

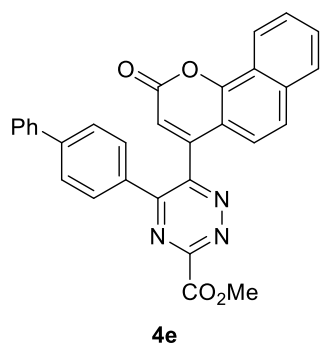
Methyl 6-(2-oxo-2H-benzo[h]chromen-4-yl)-5-phenyl-1,2,4-triazine-3-carboxylate (4d)



Obtained as a yellow solid after column chromatography (EtOAc/petroleum ether = 1:1, R_f = 0.5), 39.3 mg, 48% yield, m.p. 143-145 °C. **1H NMR** (600 MHz, $CDCl_3$): δ 8.63 – 8.54 (m, 1H), 7.85 – 7.82 (m, 1H), 7.82 – 7.77 (m, 2H), 7.72 – 7.65 (m, 2H), 7.54 (d, J = 8.8 Hz, 1H), 7.44 (t, J = 7.4 Hz, 1H), 7.35 (t, J = 7.7 Hz, 2H), 7.09 (d, J = 8.7 Hz, 1H), 6.62 (s, 1H), 4.20 (s, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$): δ 162.7, 159.6, 157.6, 156.0,

154.7, 151.9, 150.1, 135.1, 132.9, 132.7, 129.7, 129.6, 129.4, 127.9, 127.7, 124.9, 123.3, 122.8, 120.9, 117.5, 112.6, 54.2 ppm. **HRMS** (ESI-TOF) m/z : $[M+H]^+$ calcd. For $C_{24}H_{16}N_3O_4$ 410.1141, found 410.1142.

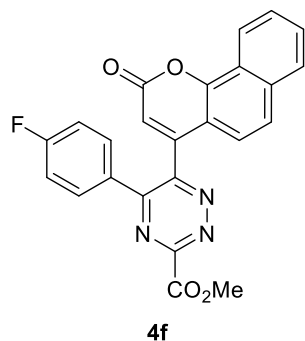
Methyl 5-([1,1'-biphenyl]-4-yl)-6-(2-oxo-2H-benzo[h]chromen-4-yl)-1,2,4-triazine-3-carboxylate (4e)



Obtained as a yellow solid after column chromatography (EtOAc/petroleum ether = 1:1, R_f = 0.5), 38.8 mg, 40% yield, m.p. 130-132 °C. **1H NMR** (600 MHz, $CDCl_3$): δ 8.66 – 8.57 (m, 1H), 7.90 (d, J = 8.5 Hz, 2H), 7.84-7.82 (m, 1H), 7.70-7.66 (m, 2H), 7.57 (dd, J = 8.7, 3.3 Hz, 3H), 7.51 (d, J = 7.4 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.37-7.34 (m, 1H), 7.14 (d, J = 8.7 Hz, 1H), 6.67 (s, 1H), 4.21 (s, 3H) ppm. **^{13}C NMR**

(151 MHz, $CDCl_3$): δ 162.8, 159.6, 157.1, 156.0, 154.5, 152.0, 150.3, 145.5, 139.1, 135.2, 131.5, 130.3, 129.6, 129.1, 128.6, 128.0, 128.0, 127.8, 127.3, 125.0, 123.3, 122.8, 121.0, 117.5, 112.7, 54.2 ppm. **HRMS** (ESI-TOF) m/z : $[M+H]^+$ calcd. For $C_{30}H_{20}N_3O_4$ 486.1454, found 486.1454.

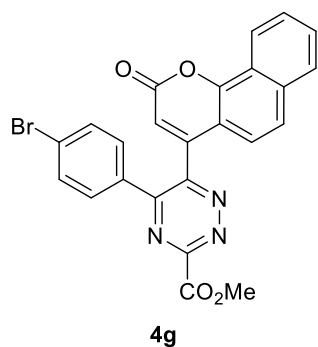
Methyl 5-(4-fluorophenyl)-6-(2-oxo-2H-benzo[h]chromen-4-yl)-1,2,4-triazine-3-carboxylate (4f)



Obtained as a yellow solid after column chromatography (EtOAc/petroleum ether = 1:1, R_f = 0.5), 48.7 mg, 57% yield, m.p. 139-141 °C. **^1H NMR** (600 MHz, CDCl_3): δ 8.67 – 8.55 (m, 1H), 7.93 – 7.81 (m, 3H), 7.77 – 7.64 (m, 2H), 7.55 (d, J = 8.8 Hz, 1H), 7.07-7.04 (m, 3H), 6.66 (s, 1H), 4.20 (s, 3H) ppm. **^{19}F NMR** (565 MHz, CDCl_3): δ -104.50 ppm. **^{13}C NMR** (151 MHz, CDCl_3): δ 165.4 (d, J = 256.4 Hz), 162.7, 159.5,

156.3, 156.0 154.4, 152.1, 150.0, 135.2, 132.1 (d, J = 9.2 Hz), 129.8, 129.0 (d, J = 3.1 Hz), 128.0, 127.9, 125.0, 123.3, 122.8, 120.7, 117.5, 116.9 (d, J = 22.2 Hz), 112.3, 54.2 ppm. **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{H}]$ calcd. For $\text{C}_{24}\text{H}_{15}\text{N}_3\text{O}_4\text{F}$ 428.1047, found 428.1048.

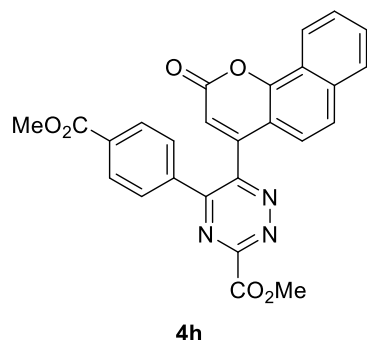
Methyl 5-(4-bromophenyl)-6-(2-oxo-2H-benzo[h]chromen-4-yl)-1,2,4-triazine-3-carboxylate (4g)



Obtained as a yellow solid after column chromatography (EtOAc/petroleum ether = 1:1, R_f = 0.5), 53.7 mg, 55% yield, m.p. 153-155 °C. **^1H NMR** (600 MHz, CDCl_3): δ 8.64 – 8.56 (m, 1H), 7.88 – 7.81 (m, 1H), 7.73 – 7.65 (m, 4H), 7.56 (d, J = 8.8 Hz, 1H), 7.51 – 7.47 (m, 2H), 7.04 (d, J = 8.8 Hz, 1H), 6.64 (s, 1H), 4.20 (s, 3H) ppm. **^{13}C NMR** (151 MHz, CDCl_3): δ 162.6, 159.4, 156.4, 156.0, 154.4, 152.1, 149.9,

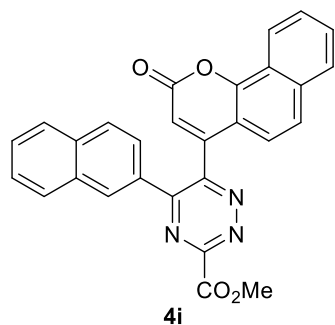
135.2, 132.8, 131.7, 131.0, 129.8, 128.2, 128.0, 127.9, 125.1, 123.3, 122.8, 120.7, 117.5, 112.3, 54.2 ppm. **HRMS** (ESI-TOF) m/z : $[\text{M}+\text{H}]$ calcd. For $\text{C}_{24}\text{H}_{15}\text{N}_3\text{O}_4\text{Br}$ 488.0246, found 488.0247.

Methyl 5-(4-(methoxycarbonyl)phenyl)-6-(2-oxo-2*H*-benzo[*h*]chromen-4-yl)-1,2,4-triazine-3-carboxylate (4h)



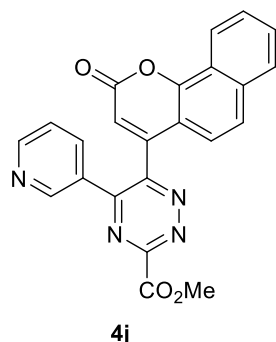
Obtained as a yellow solid after column chromatography (EtOAc/petroleum ether = 1:1, R_f = 0.5), 58.0 mg, 62% yield, m.p. 154-156 °C. **¹H NMR** (600 MHz, CDCl₃): δ 8.65 – 8.56 (m, 1H), 8.00 (d, J = 8.2 Hz, 2H), 7.87 (d, J = 8.2 Hz, 2H), 7.84 – 7.82 (m, 1H), 7.73 – 7.65 (m, 2H), 7.54 (d, J = 8.8 Hz, 1H), 7.04 (d, J = 8.8 Hz, 1H), 6.64 (s, 1H), 4.21 (s, 3H), 3.88 (s, 3H) ppm. **¹³C NMR** (151 MHz, CDCl₃): δ 165.8, 162.5, 159.4, 156.7, 156.1, 154.8, 152.0, 149.6, 137.0, 135.2, 133.6, 130.4, 129.8, 129.6, 128.0, 127.9, 125.0, 123.3, 122.8, 120.6, 117.7, 112.3, 54.3, 52.6 ppm. **HRMS** (ESI-TOF) m/z : [M+H] calcd. For C₂₆H₁₈N₃O₆ 468.1196, found 468.1199.

Methyl 5-(naphthalen-2-yl)-6-(2-oxo-2*H*-benzo[*h*]chromen-4-yl)-1,2,4-triazine-3-carboxylate (4i)



Obtained as a yellow solid after column chromatography (EtOAc/petroleum ether = 1:1, R_f = 0.5), 37.7 mg, 41% yield, m.p. 145-145 °C. **¹H NMR** (600 MHz, CDCl₃): δ 8.50 – 8.45 (m, 1H), 7.89 (d, J = 8.2 Hz, 1H), 7.84 (d, J = 8.1 Hz, 1H), 7.81 (d, J = 7.5 Hz, 2H), 7.66-7.61 (m, 2H), 7.54 – 7.48 (m, 2H), 7.48 – 7.42 (m, 2H), 7.39 – 7.34 (m, 1H), 7.31 (d, J = 8.8 Hz, 1H), 6.37 (s, 1H), 4.20 (s, 3H) ppm. **¹³C NMR** (151 MHz, CDCl₃): δ 162.7, 159.3, 159.3, 157.0, 155.9, 151.7, 149.1, 135.0, 133.7, 132.4, 130.4, 130.3, 129.5, 129.2, 129.0, 128.2, 127.9, 127.6, 127.1, 125.0, 124.6, 123.8, 123.1, 122.7, 121.0, 117.3, 112.7, 54.3 ppm. **HRMS** (ESI-TOF) m/z : [M+H] calcd. For C₂₈H₁₈N₃O₄ 460.1297, found 460.1296.

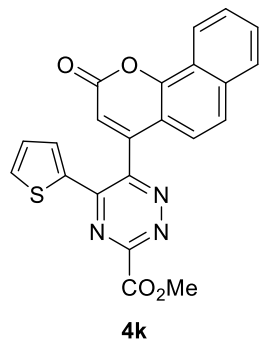
Methyl 6-(2-oxo-2H-benzo[h]chromen-4-yl)-5-(pyridin-3-yl)-1,2,4-triazine-3-carboxylate (4j)



Obtained as a yellow solid after column chromatography (EtOAc/petroleum ether = 2:1, R_f = 0.5), 48.4 mg, 59% yield, m.p. 126-128 °C. **¹H NMR** (600 MHz, CDCl₃): δ 8.95 (d, J = 2.4 Hz, 1H), 8.64 (d, J = 4.8 Hz, 1H), 8.59 – 8.53 (m, 1H), 8.16–8.14 (m, 1H), 7.87 – 7.78 (m, 1H), 7.71 – 7.63 (m, 2H), 7.53 (d, J = 8.7 Hz, 1H), 7.32 (dd, J = 8.1, 4.8 Hz, 1H), 7.01 (d, J = 8.7 Hz, 1H), 6.60 (s, 1H), 4.19 (s, 3H) ppm. **¹³C NMR** (151 MHz,

CDCl₃): δ 162.4, 159.3, 156.1, 155.2, 154.8, 153.2, 152.2, 150.0, 149.3, 136.7, 135.2, 129.9, 129.3, 128.0, 125.2, 124.0, 123.3, 122.8, 120.5, 117.7, 112.2, 54.3 ppm. **HRMS** (ESI-TOF) m/z : [M+H] calcd. For C₂₅H₁₈N₃O₅ 440.1246, found 440.1247.

Methyl 6-(2-oxo-2H-benzo[h]chromen-4-yl)-5-(thiophen-2-yl)-1,2,4-triazine-3-carboxylate (4k)

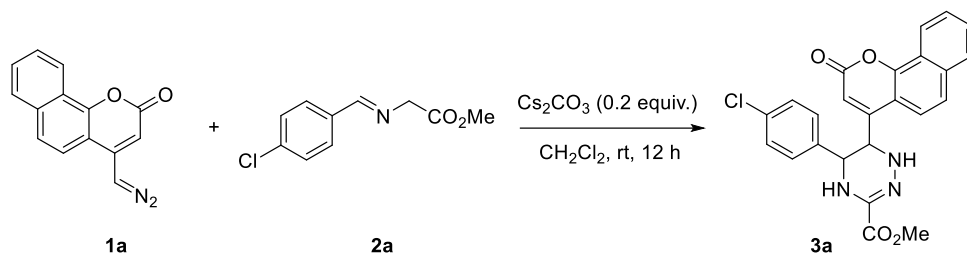


Obtained as a yellow solid after column chromatography (EtOAc/petroleum ether = 1:1, R_f = 0.5), 54.8 mg, 66% yield, m.p. 138-140 °C. **¹H NMR** (600 MHz, CDCl₃): δ 8.63-8.61 (m, 1H), 7.85-7.82 (m, 1H), 7.71-7.68 (m, 2H), 7.65-7.60 (m, 2H), 7.54 (d, J = 8.7, 1H), 6.97 (t, J = 4.7 Hz, 1H), 6.95 – 6.91 (m, 1H), 6.79 (s, 1H), 4.18 (s, 3H) ppm. **¹³C NMR** (151 MHz, CDCl₃): δ 162.7, 159.6, 156.1, 152.0, 151.6, 150.6, 150.2, 136.8,

135.7, 135.3, 134.3, 129.7, 129.6, 128.0, 127.8, 125.2, 123.3, 122.7, 120.6, 117.3, 112.6, 54.1 ppm. **HRMS** (ESI-TOF) m/z : [M+H] calcd. For C₂₂H₁₄N₃O₄S 416.0705, found 416.0704.

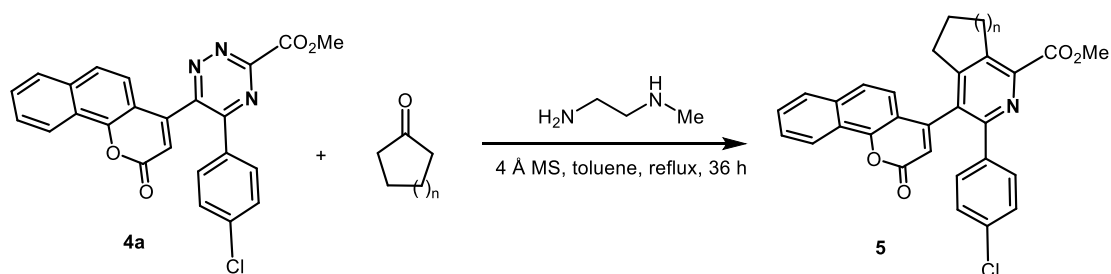
Gram-experiment and Synthetic Transformation

Gram-experiment



A 100 mL round-bottomed flask equipped with a stirring bar and capped with a rubber septum was charged with 4-(diazomethyl)-2*H*-benzo[*h*]chromen-2-one **1a** (1.05 g, 1.0 equiv., 4.0 mmol), methyl (*E*)-2-((4-chlorobenzylidene)amino)acetate **2a** (1.27 g, 1.5 equiv., 6.0 mmol), and Cs₂CO₃ (0.26 g, 0.2 equiv., 0.8 mmol). CH₂Cl₂ (40.0 mL) was transferred into the flask. The reaction mixture was stirred under an air atmosphere at rt for 12 h. After the reaction completed, the reaction solution was quenched with water and extracted with CH₂Cl₂ (20 mL×3). The organic phase was washed with saturated brine, and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the residue was further purified by silica gel column chromatography using EtOAc/petroleum ether as an eluent to obtain **3a** (1.45 g, 81% yield).

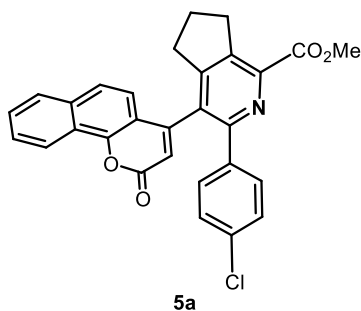
Synthetic Transformation⁶



To a solution of 1,2,4-triazines **4a** (44.4 mg, 0.1 mmol, 1.0 equiv.) in toluene (1.0 mL) was added powdered 4 Å molecular sieves (100 mg), ketone (0.60 mmol, 6.0 equiv.)

and *N*-methylethylenediamine (22.2 mg, 0.30 mmol, 3.0 equiv.). The reaction mixture was heated at reflux for 36 h. The reaction mixture was then cooled, filtered through a cotton wool plug and concentrated in vacuo to furnish the crude product. Purification by column chromatography on silica gel (petrol ether: ethyl acetate = 5 : 1) gave the title compound **5**.

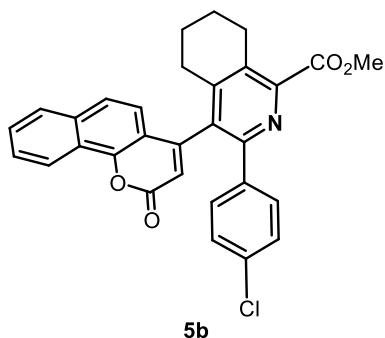
Methyl 3-(4-chlorophenyl)-4-(2-oxo-2*H*-benzo[*h*]chromen-4-yl)-6,7-dihydro-5*H*-cyclopenta[*c*]pyridine-1-carboxylate (5a**)**



Obtained as a white solid, 21.7 mg, 45% yield, m.p. 102-104 °C. ¹H NMR (600 MHz, CDCl₃): δ 8.69 – 8.54 (m, 1H), 7.88 – 7.85 (m, 1H), 7.73 – 7.66 (m, 2H), 7.59 (dd, *J* = 8.7, 3.0 Hz, 1H), 7.38 (dd, *J* = 8.6, 1.8 Hz, 2H), 7.21 – 7.12 (m, 2H), 7.03 (d, *J* = 8.6 Hz, 1H), 6.27 (s, 1H), 4.04 (s, 3H), 3.52 – 3.44 (m, 2H), 2.91 – 2.76 (m, 1H),

2.69-2.64 (m, 1H), 2.19-2.11 (m, 2H) ppm. ¹³C NMR (151 MHz, CDCl₃): δ 166.0, 160.2, 156.7, 154.1, 153.5, 151.5, 144.0, 142.3, 137.1, 135.2, 135.1, 130.4, 129.4, 128.8, 127.9, 127.7, 125.0, 123.4, 122.8, 121.2, 115.9, 113.7, 52.9, 32.8, 32.4, 24.6 ppm. HRMS (ESI-TOF) *m/z*: [M+H] calcd. For C₂₉H₂₁NO₄Cl 482.1159, found 482.1156.

Methyl 3-(4-chlorophenyl)-4-(2-oxo-2*H*-benzo[*h*]chromen-4-yl)-5,6,7,8-tetrahydroisoquinoline-1-carboxylate (5b**)**



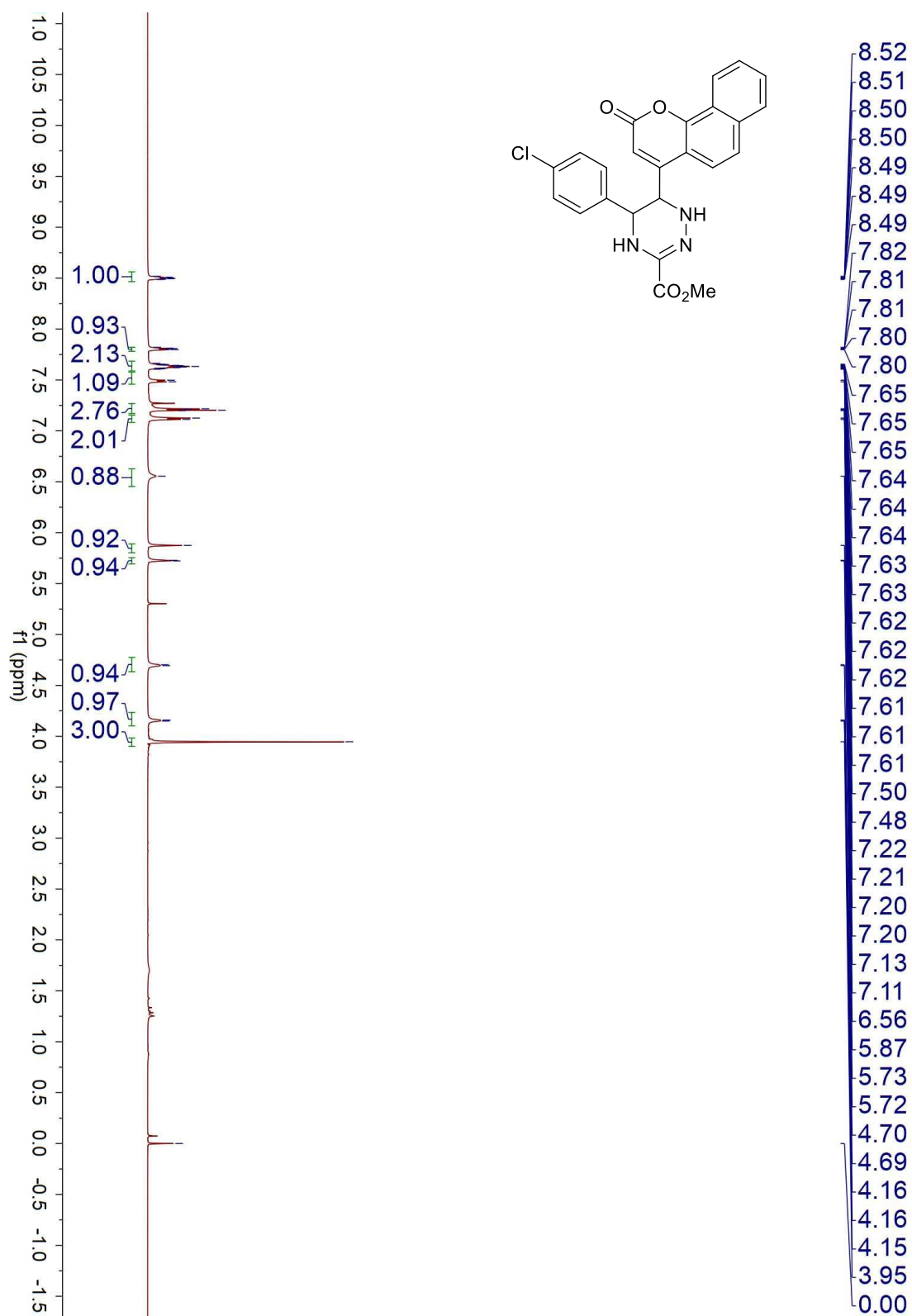
Obtained as a white solid, 9.9 mg, 20% yield, m.p. 113-115 °C. ¹H NMR (600 MHz, CDCl₃): δ 8.60-8.58 (m, 1H), 7.89-7.87 (m, 1H), 7.71-7.67 (m, 2H), 7.63 (dd, *J* = 9.1, 4.1 Hz, 1H), 7.26-7.22 (m, 2H), 7.16-7.10 (m, 2H), 7.06 (dd, *J* = 9.0, 4.0 Hz, 1H), 6.21 (s, 1H), 4.02 (s, 3H), 3.11-3.09 (m, 2H), 2.63-2.58 (m, 1H), 2.42-2.37 (m, 1H), 1.86-1.82 (m, 2H), 1.74-1.69 (m, 2H) ppm. ¹³C NMR (151 MHz, CDCl₃): δ 167.0, 160.2, 153.6, 152.8, 151.3, 149.6,

147.1, 137.2, 135.2, 134.9, 132.1, 131.3, 130.2, 129.4, 128.6, 127.9, 127.7, 125.2, 123.4, 122.8, 121.1, 116.4, 114.4, 53.0, 28.1, 26.2, 21.9, 21.7 ppm.

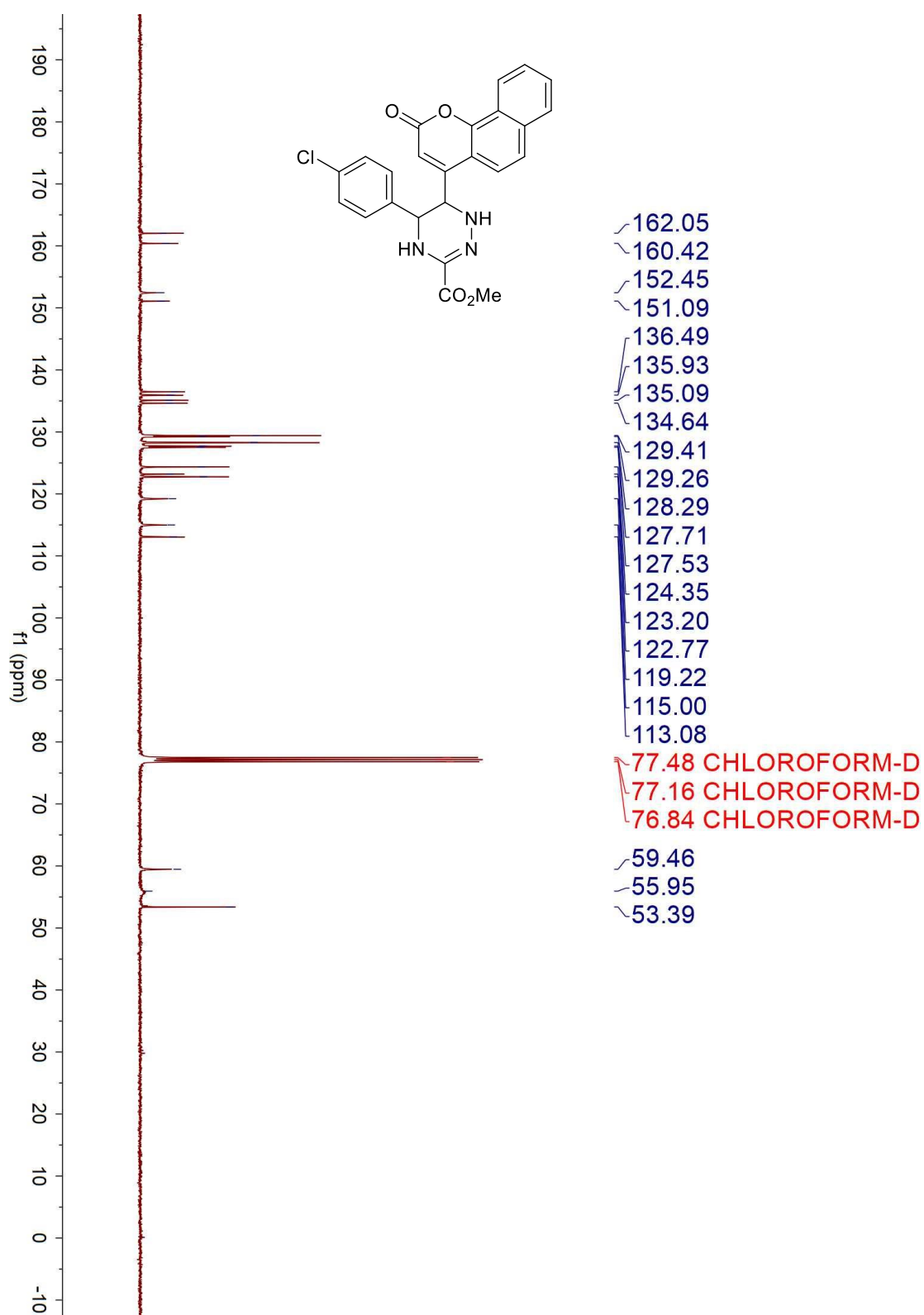
References

- 1) Zhang, C.; Yang, J.; Zhou, W.; Tan, Q.; Yang, Z.; He, L.; Zhang, M. *Org. Lett.* **2019**, *21*, 8620.
- 2) Liang, G.; Tong, M.-C.; Wang, C.-J. *Adv. Syn. Catal.* **2009**, *351*, 3101.
- 3) Liu, X.-Y.; Zhai, S.-J.; Feng, F.-F.; Zhang, F.-G.; Ma, J.-A. *ChemCatChem* **2020**, *12*, 5623.
- 4) Ito, K.; Sawanobori, J. *Synth. Commun.* **1982**, *12*, 665.
- 5) Ito, K.; Sawanobori, J. *Chem. Pharm. Bull.* **1983**, *31*, 3014.
- 6) Raw, S. A.; Taylor, R, J. K. *Chem. Commun.* **2004**, 508.

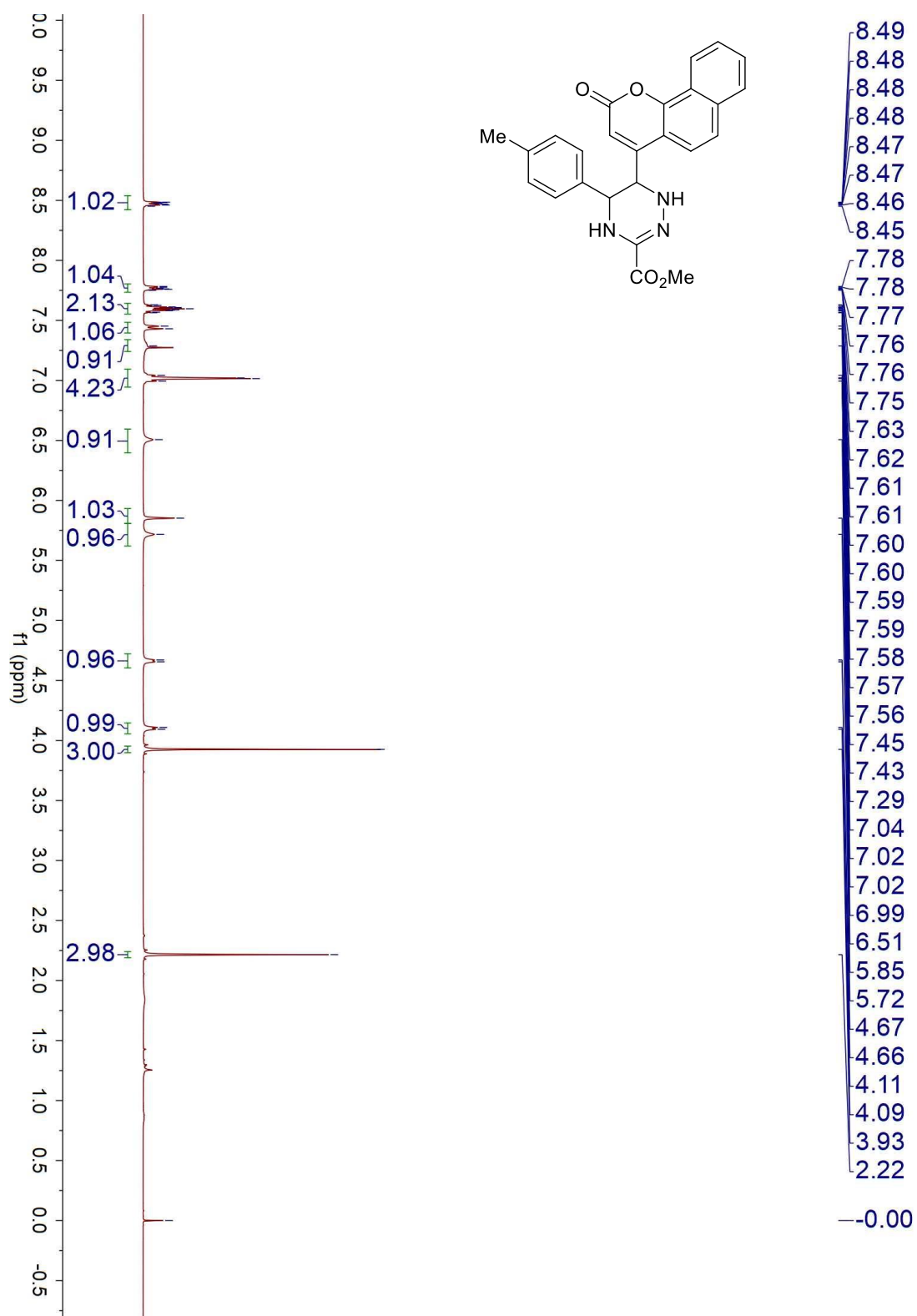
Spectra of Products

¹H-NMR spectra of compound **3a** (CDCl₃, 600 MHz)

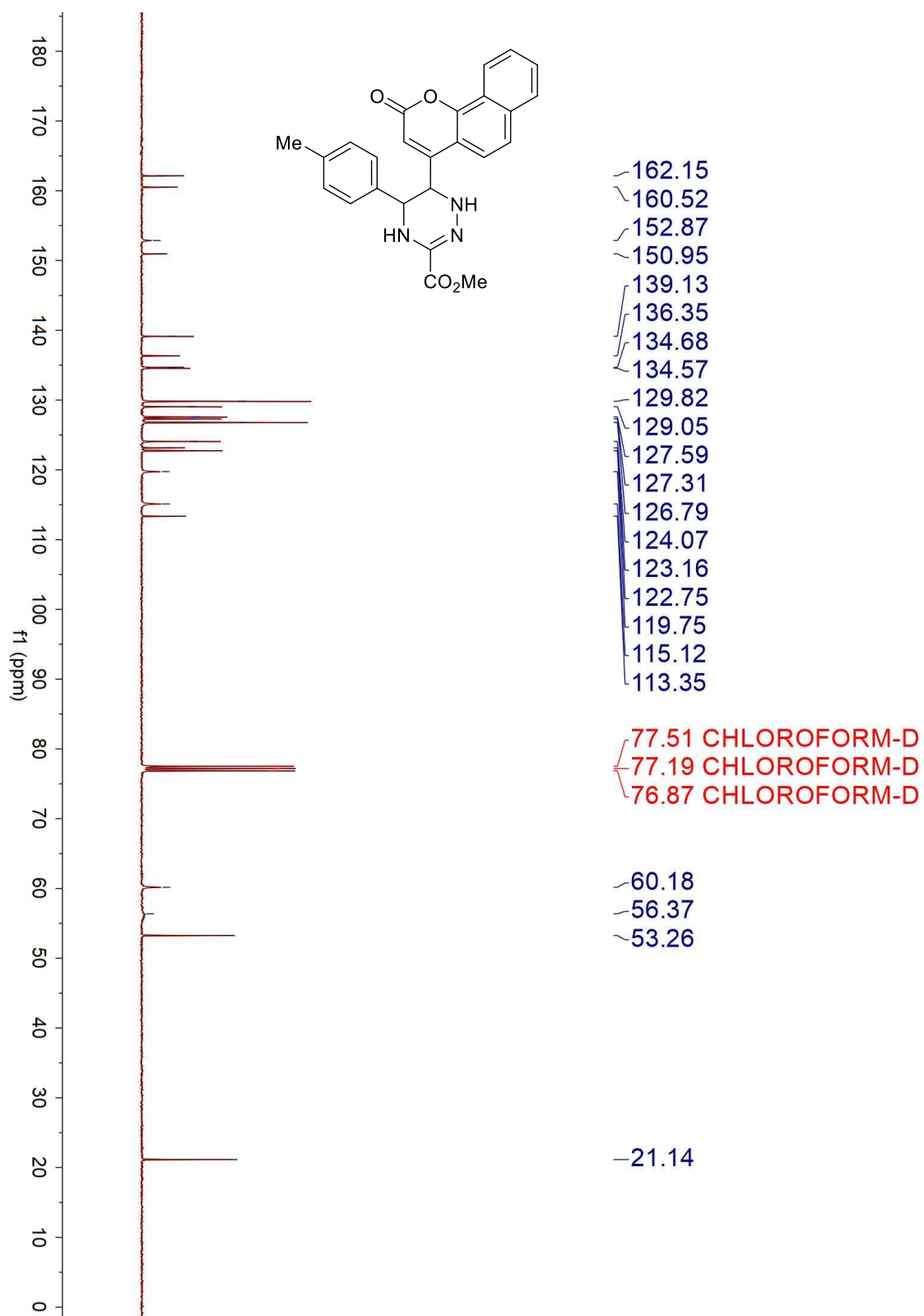
^{13}C -NMR spectra of compound **3a** (CDCl_3 , 151 MHz)



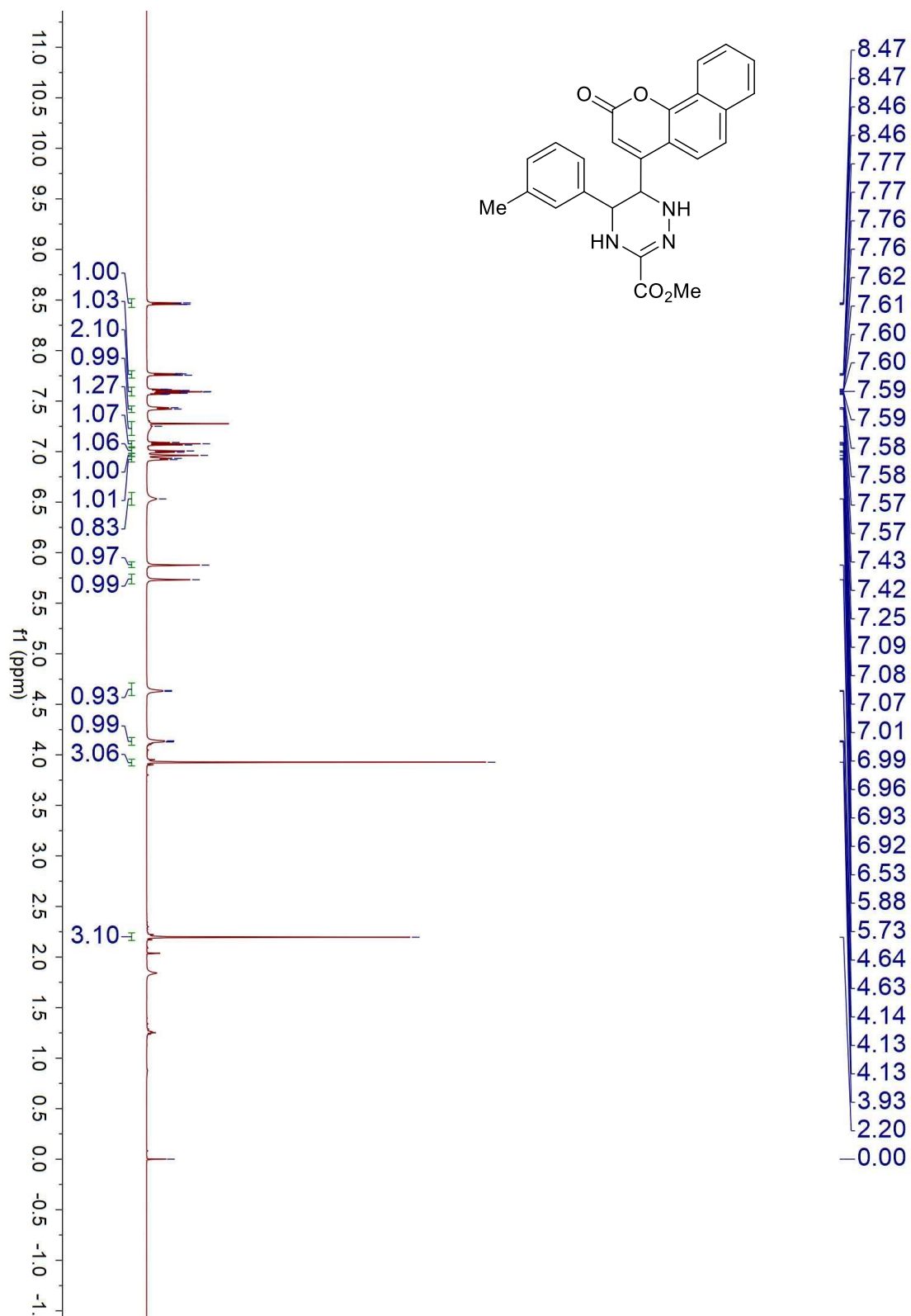
^1H -NMR spectra of compound **3b** (CDCl_3 , 600 MHz)



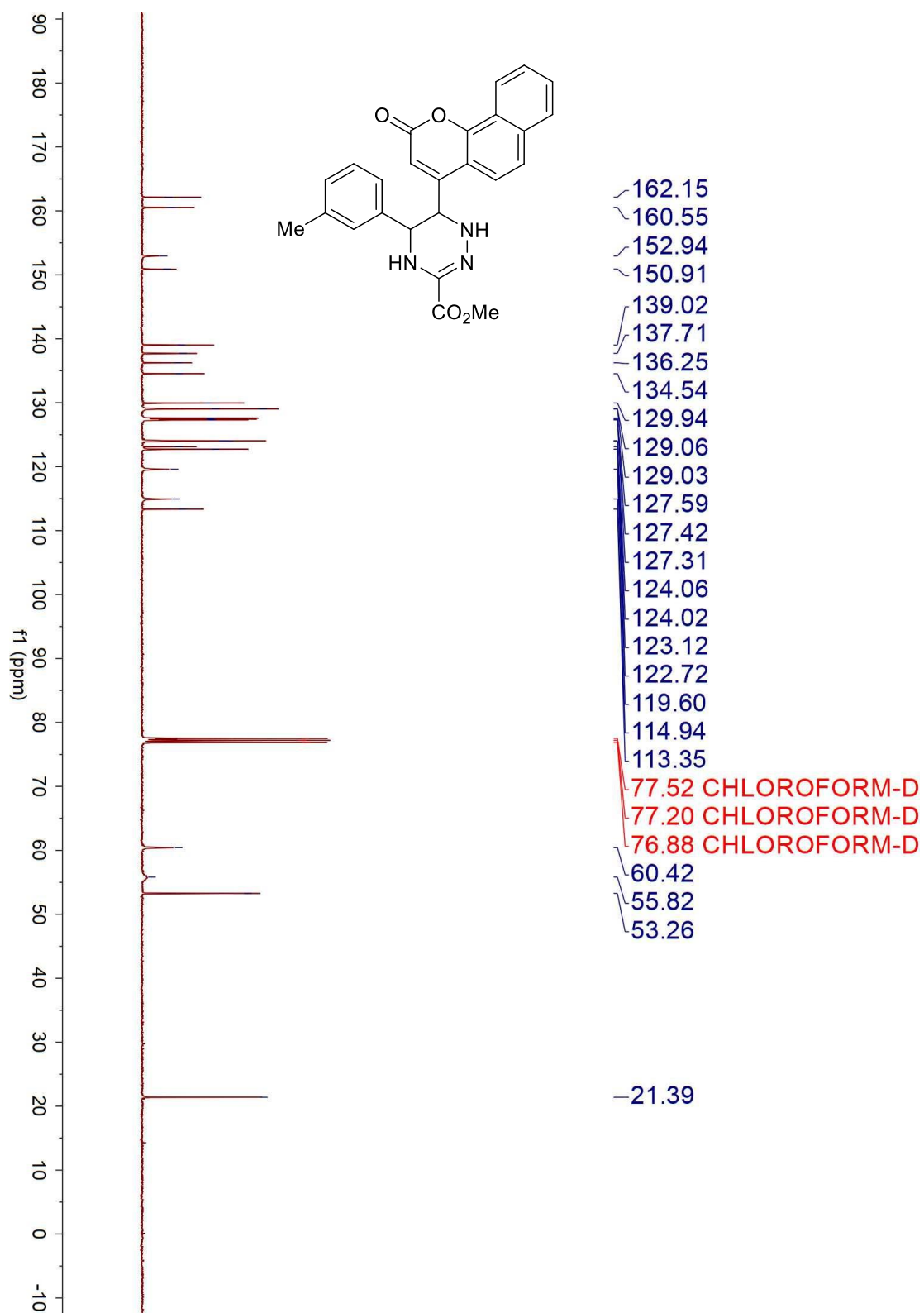
^{13}C -NMR spectra of compound **3b** (CDCl_3 , 151 MHz)



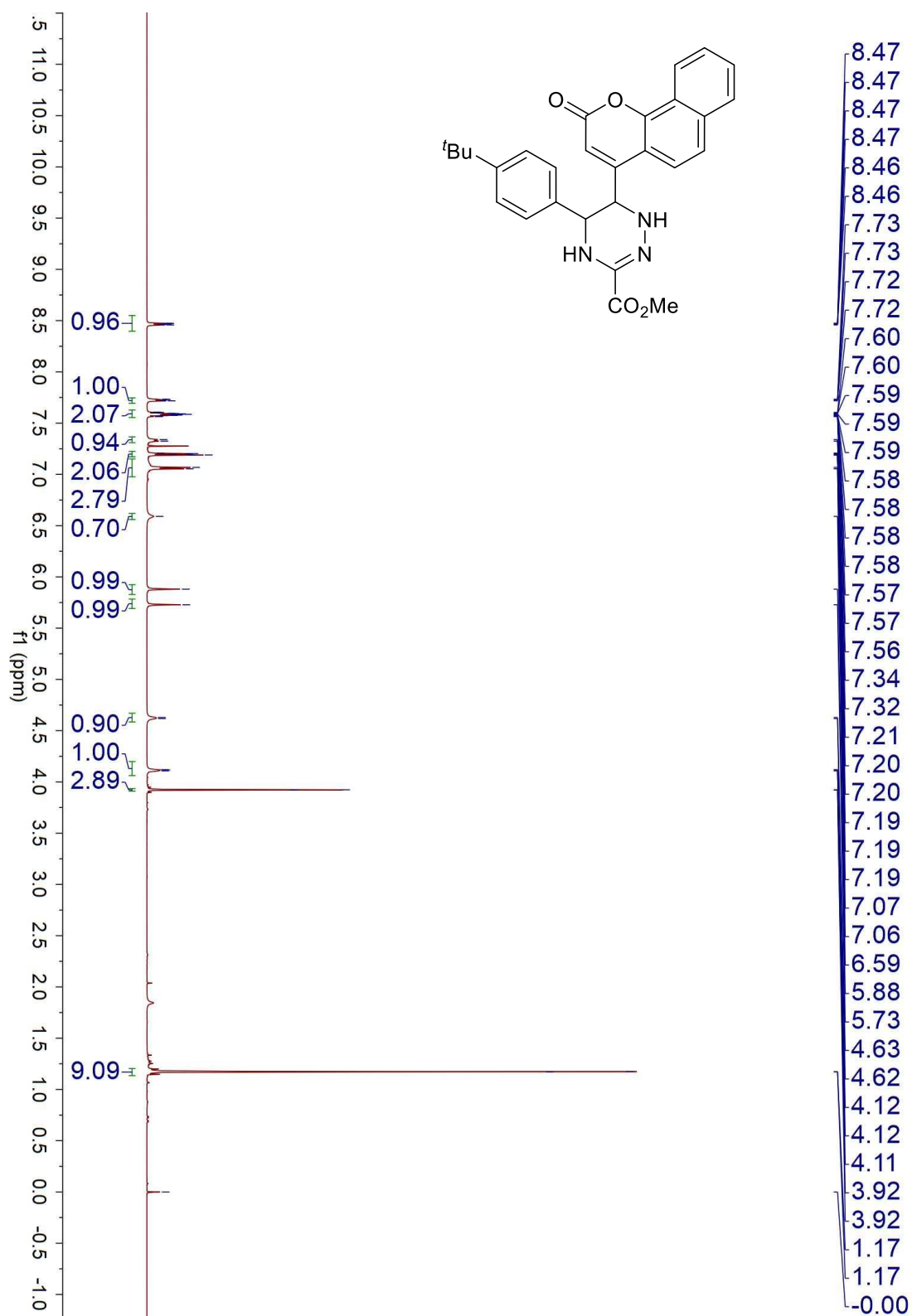
¹H-NMR spectra of compound **3c** (CDCl₃, 600 MHz)



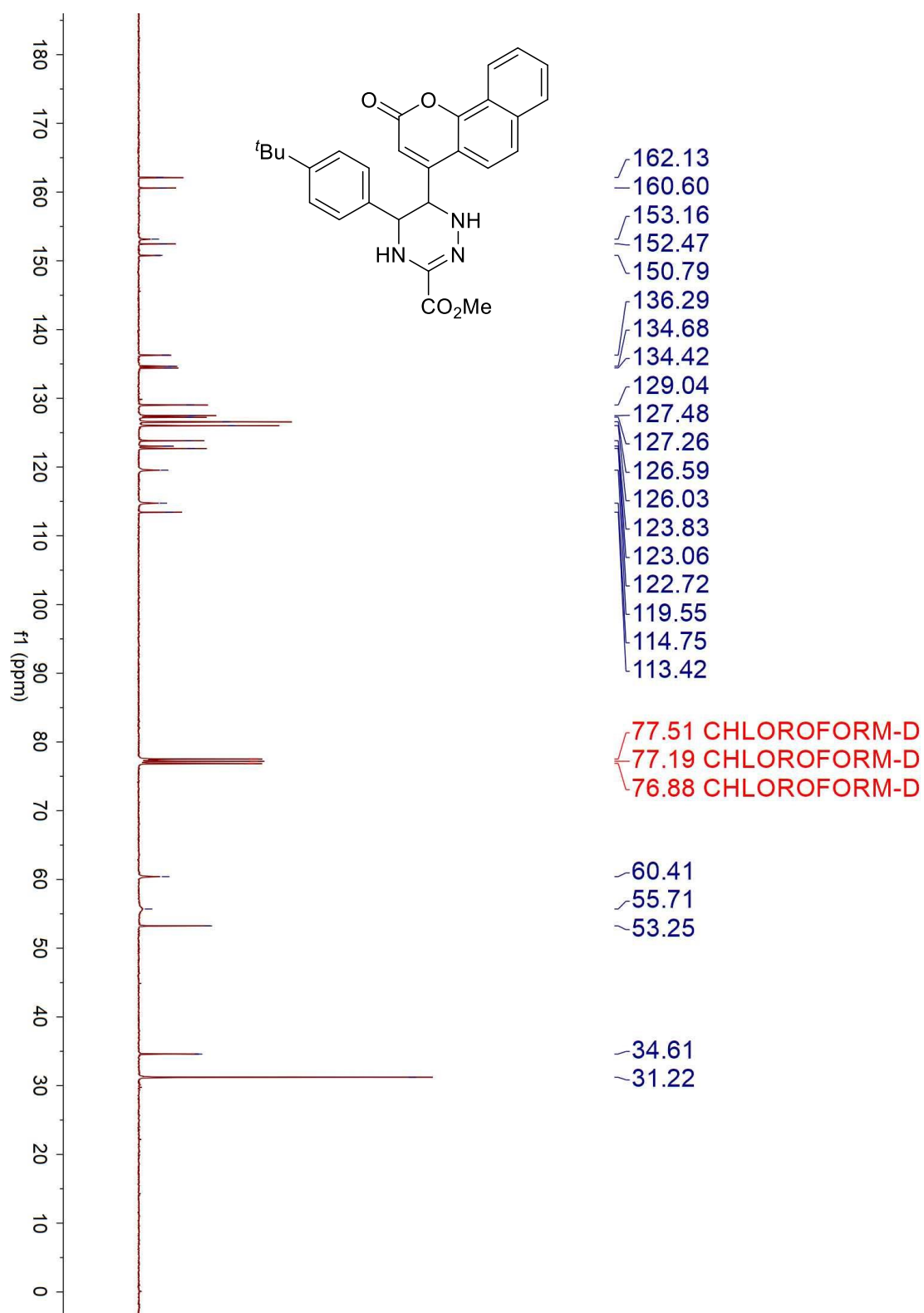
^{13}C -NMR spectra of compound **3c** (CDCl_3 , 151 MHz)



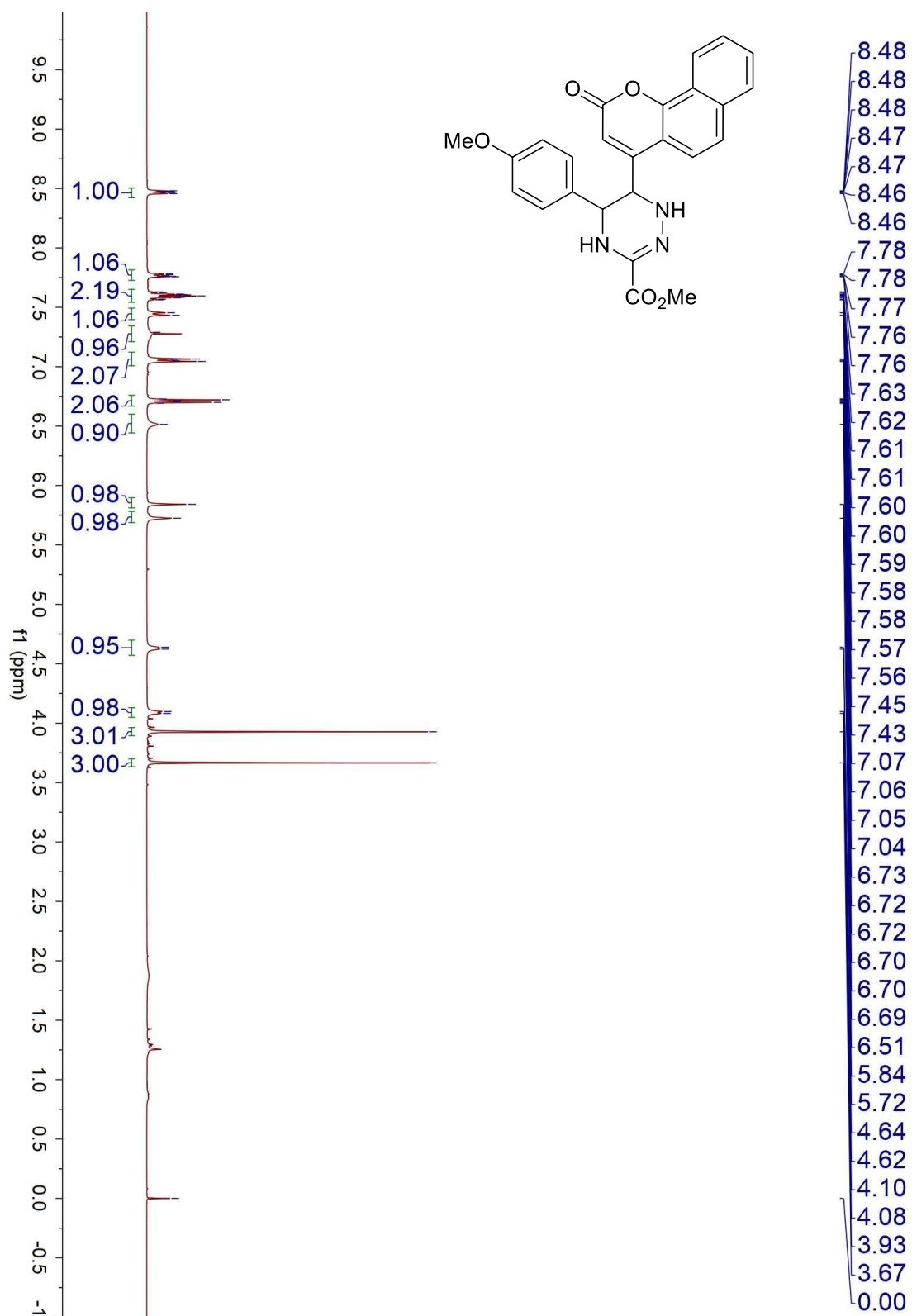
¹H-NMR spectra of compound **3d** (CDCl₃, 600 MHz)



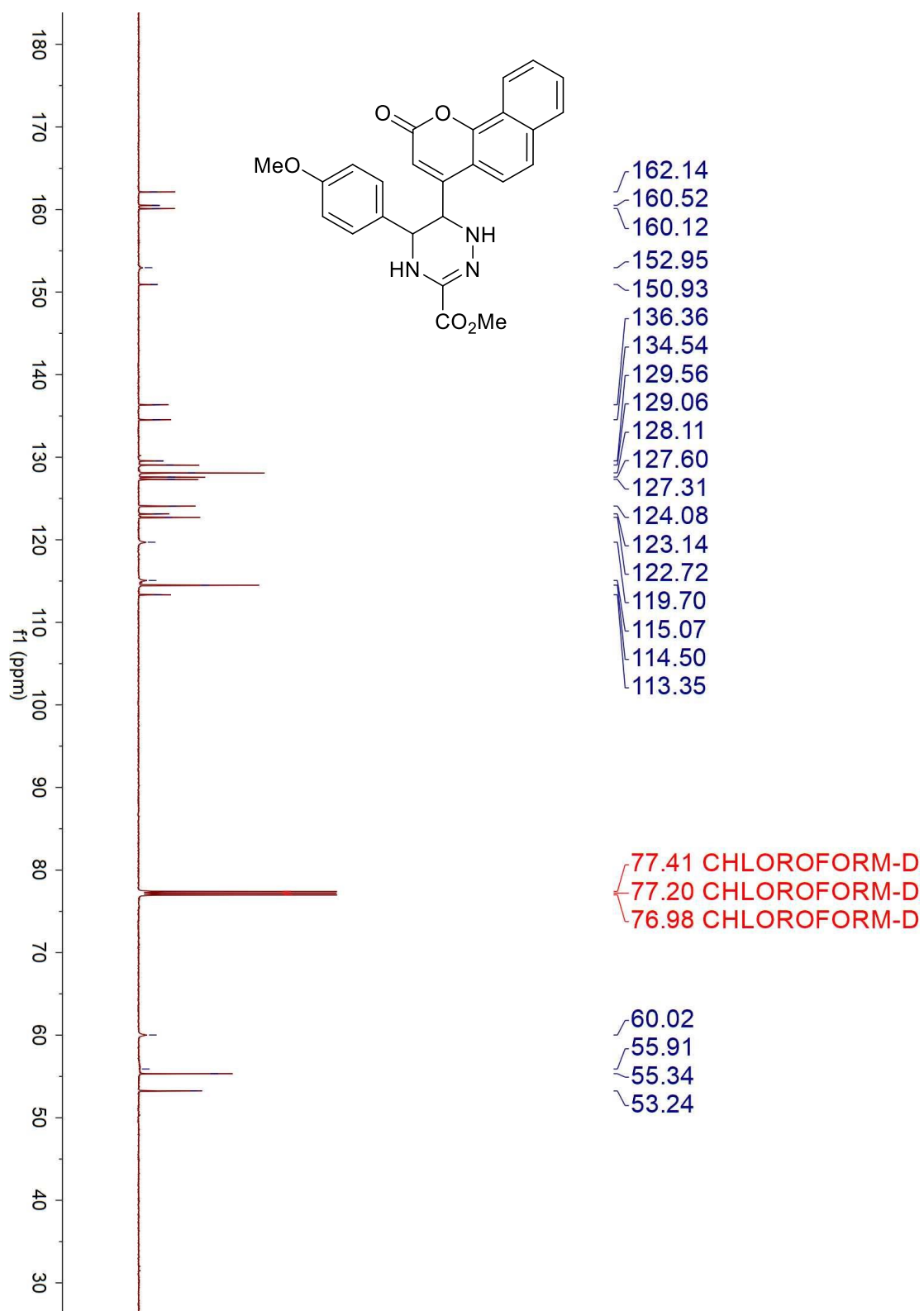
^{13}C -NMR spectra of compound **3d** (CDCl_3 , 151 MHz)



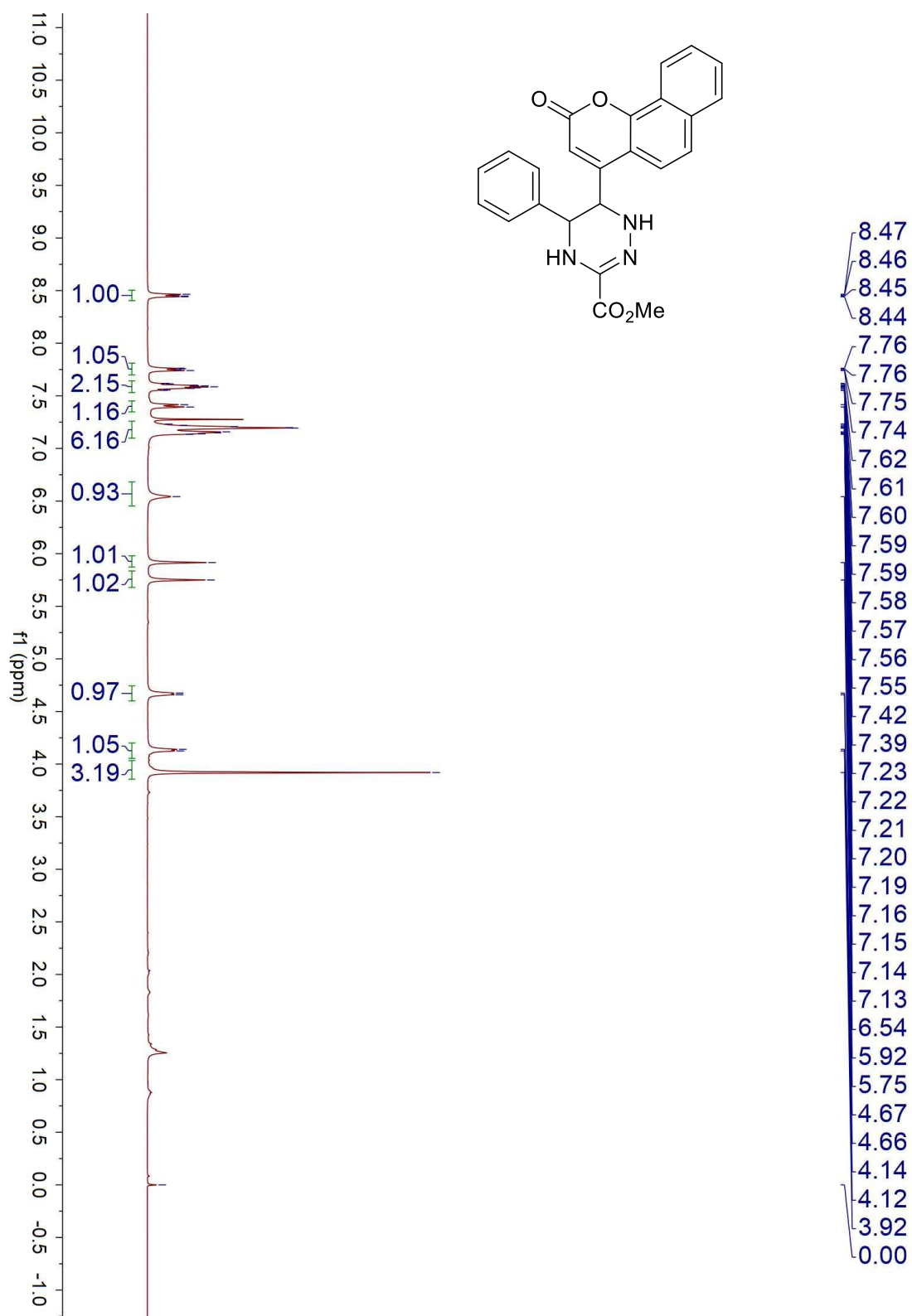
¹H-NMR spectra of compound **3e** (CDCl₃, 600 MHz)



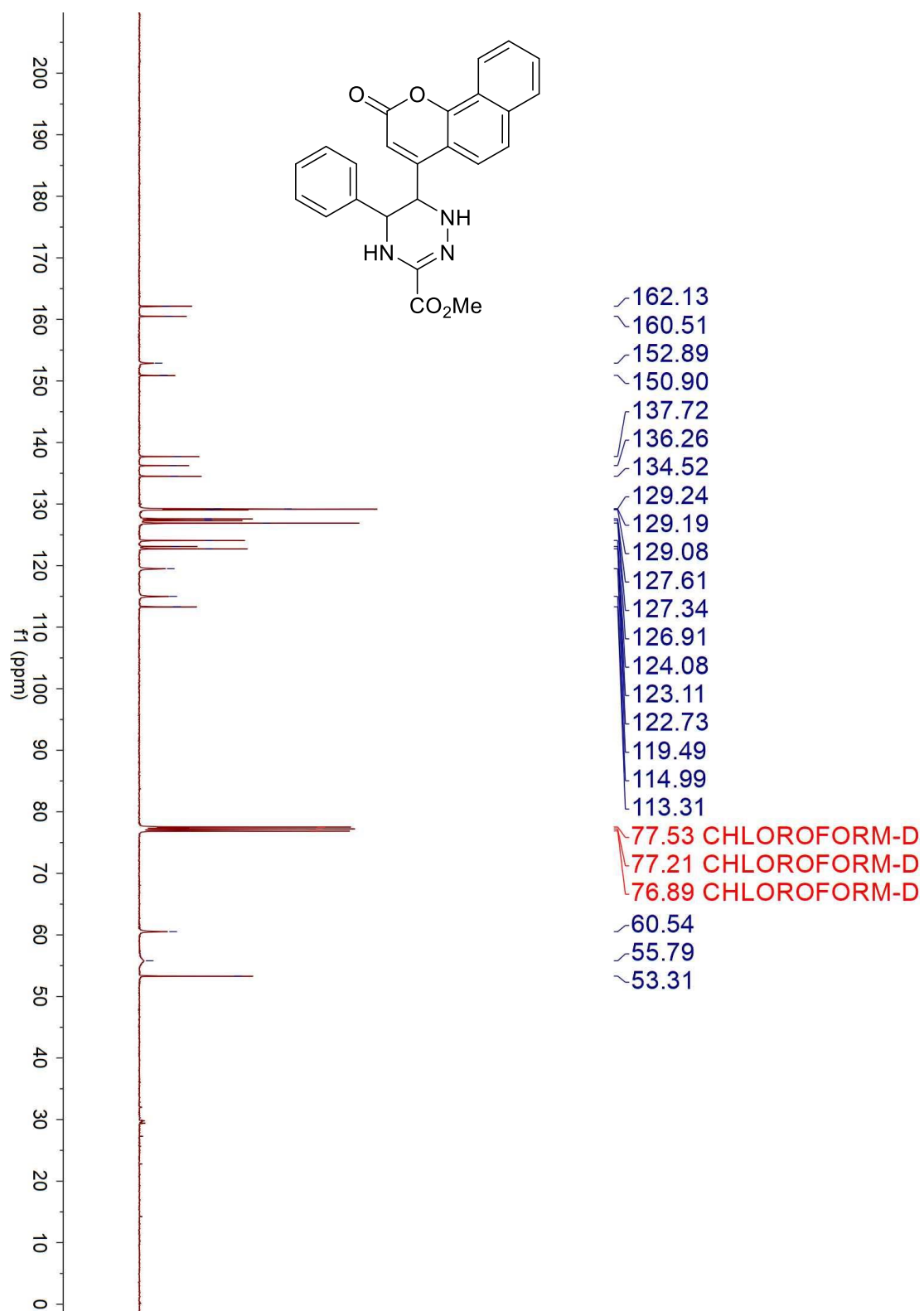
^{13}C -NMR spectra of compound **3e** (CDCl_3 , 151 MHz)



¹H-NMR spectra of compound **3f** (CDCl₃, 600 MHz)



^{13}C -NMR spectra of compound **3f** (CDCl_3 , 151 MHz)



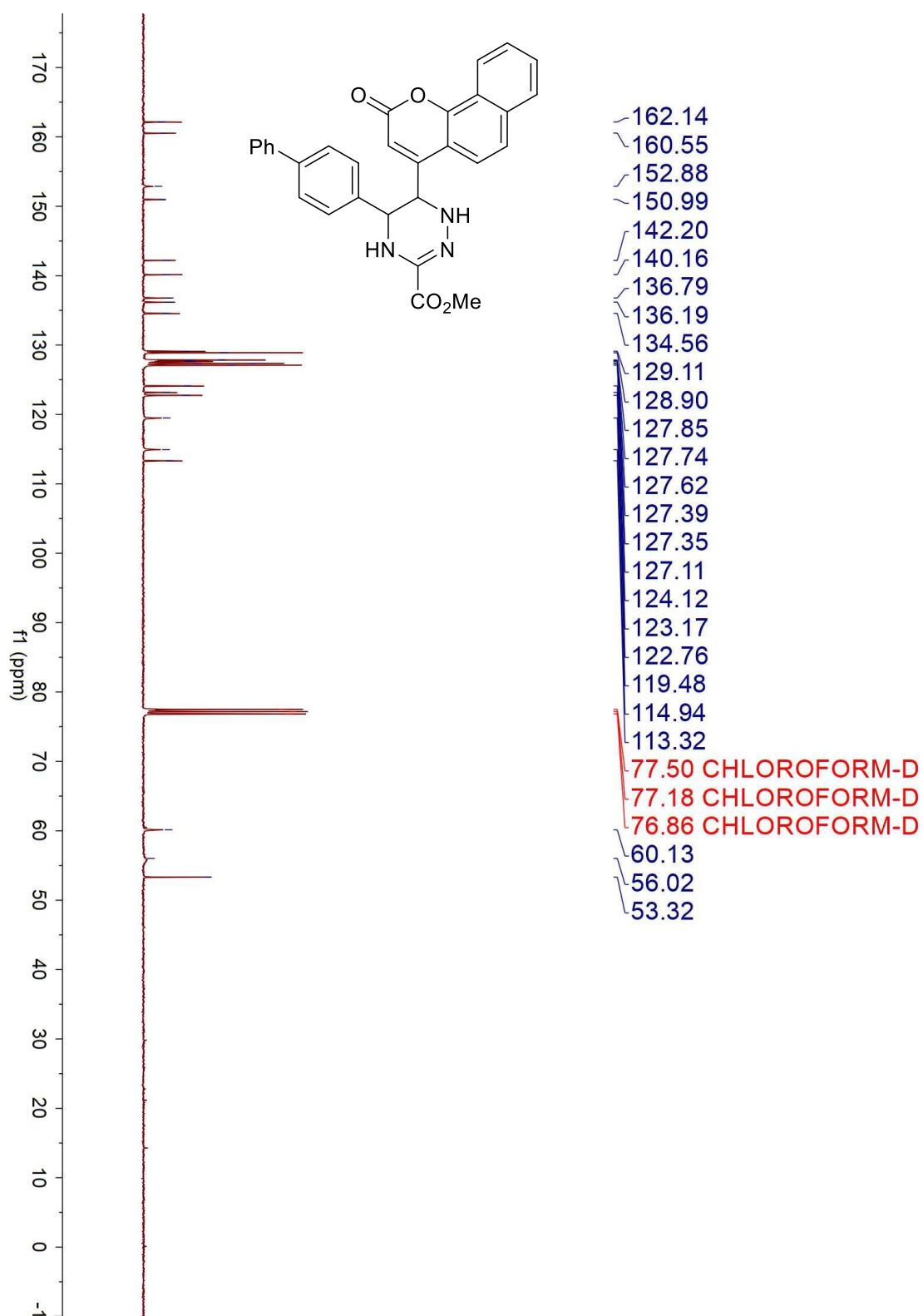
Chemical structure of the compound is shown above the spectrum. The spectrum displays chemical shifts (ppm) on the x-axis and integration values on the y-axis.

Chemical structure: CCOC(=O)N1C(=NNC1C(c2ccccc2)c3ccccc3)c4cc5ccccc5oc(=O)c4

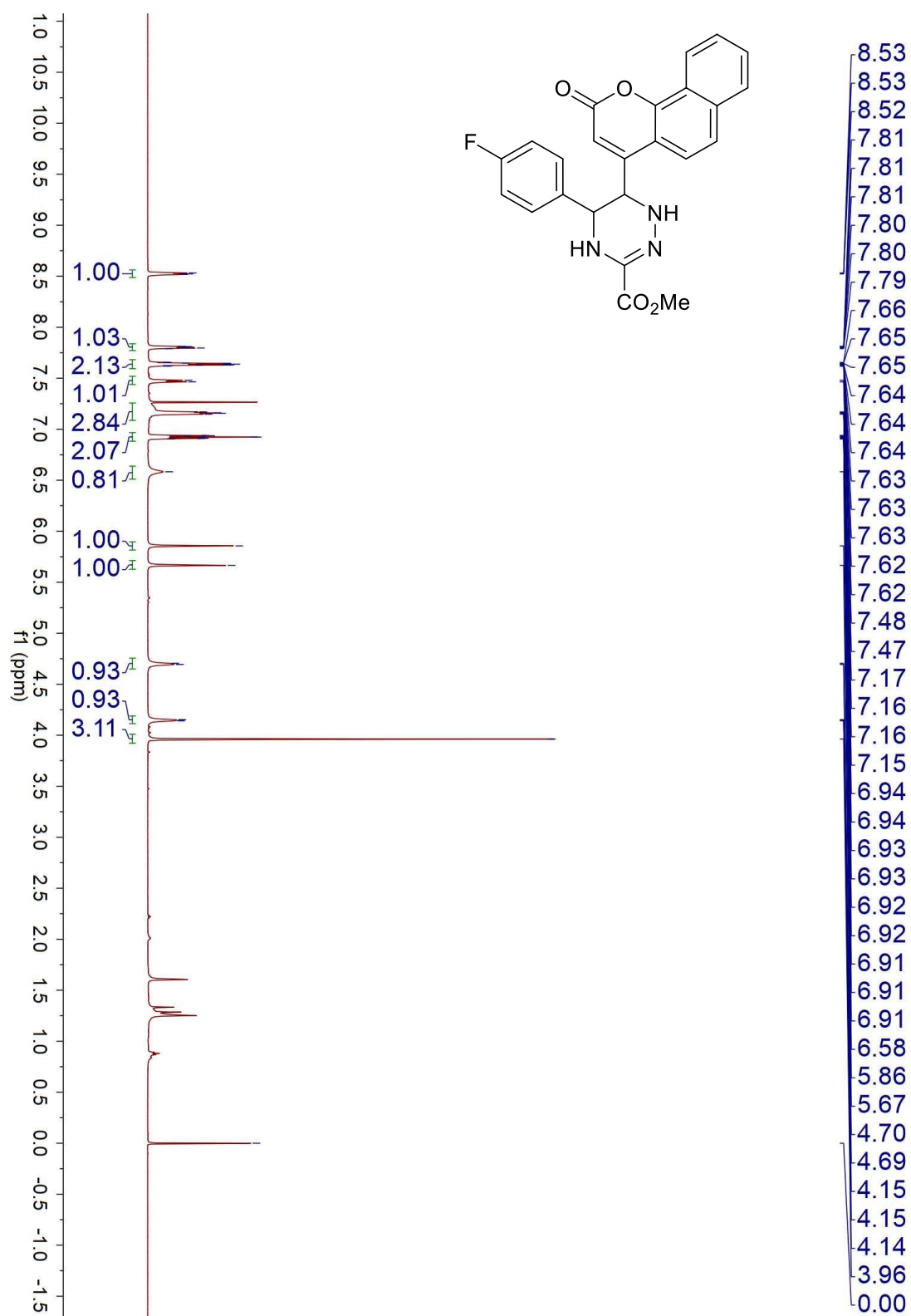
Integration values (from top to bottom):

Chemical Shift (ppm)	Integration Value
8.49	1.00
8.48	1.04
8.48	2.11
8.48	7.35
8.48	1.12
8.48	0.71
8.48	2.31
8.48	0.88
7.60	1.00
7.60	1.00
7.43	0.94
7.42	0.93
7.42	3.11
7.41	
7.41	
7.40	
7.40	
7.39	
7.38	
7.37	
7.37	
7.36	
7.33	
7.33	
7.33	
7.32	
7.32	
7.31	
7.27	
7.23	
7.22	
5.94	
5.74	
4.73	
4.72	
4.20	
4.19	
3.94	
-0.00	

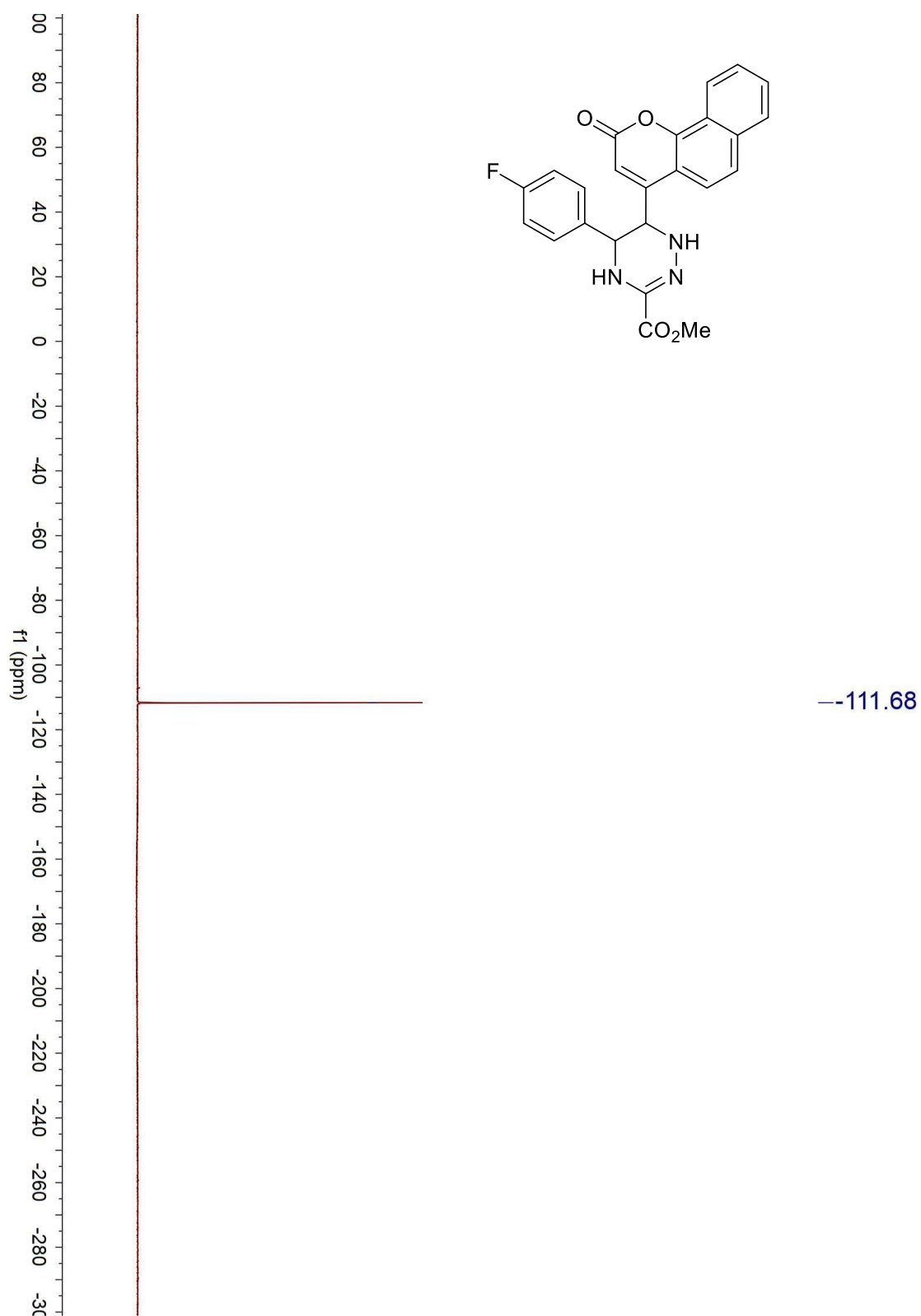
^{13}C -NMR spectra of compound **3g** (CDCl_3 , 151 MHz)



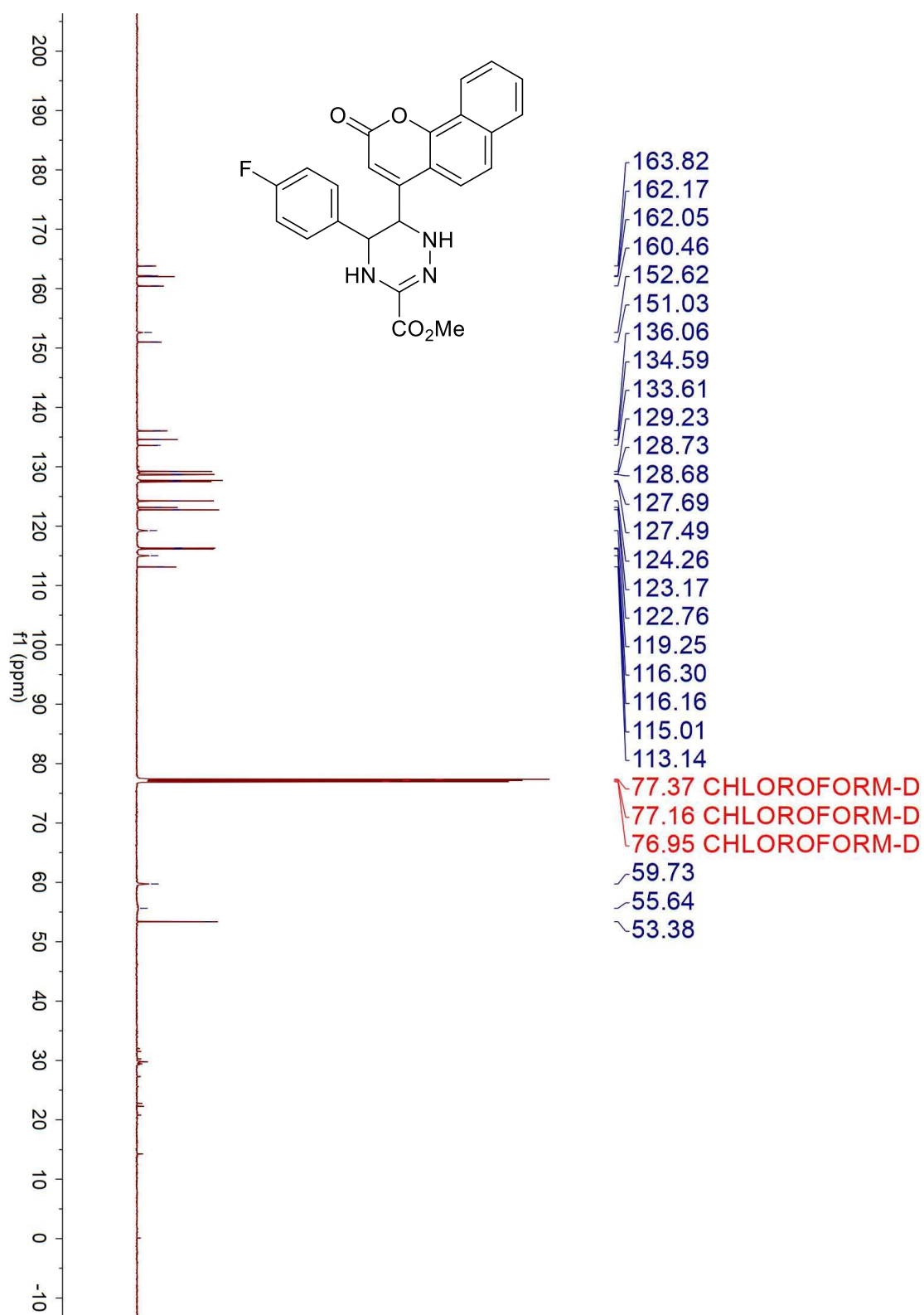
^1H -NMR spectra of compound **3h** (CDCl_3 , 600 MHz)



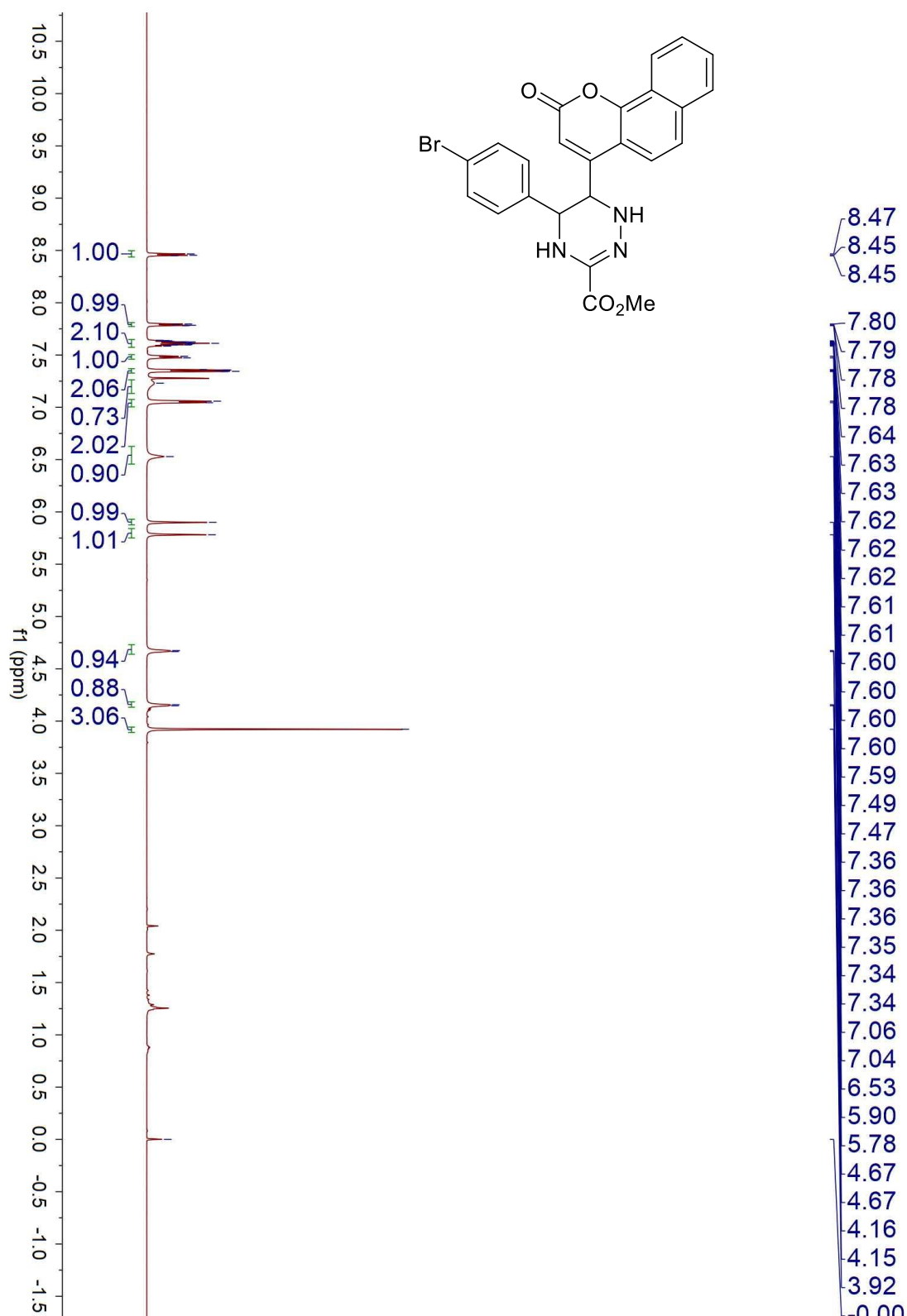
^{19}F -NMR spectra of compound **3h** (CDCl_3 , 565 MHz)



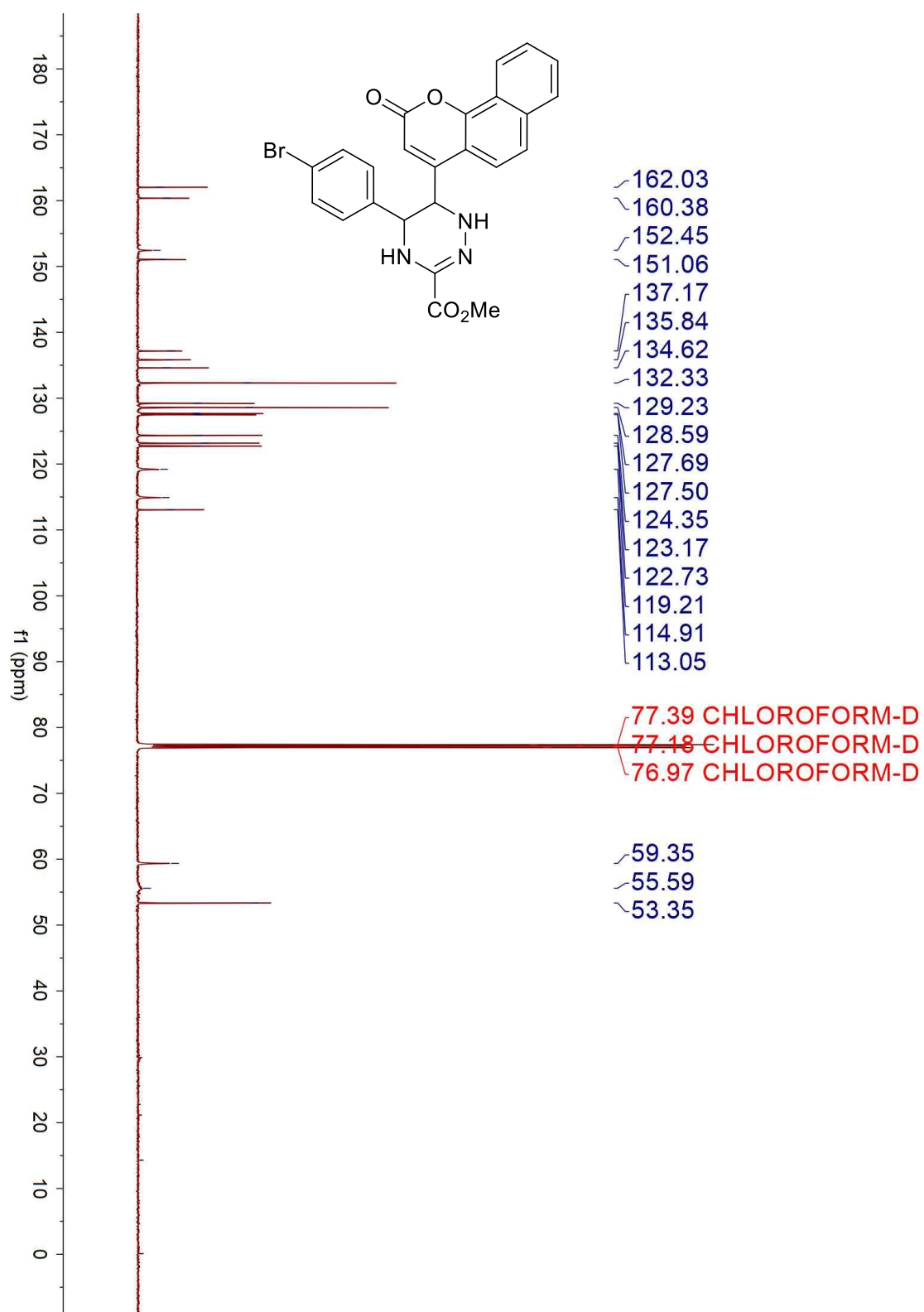
^{13}C -NMR spectra of compound **3h** (CDCl_3 , 151 MHz)



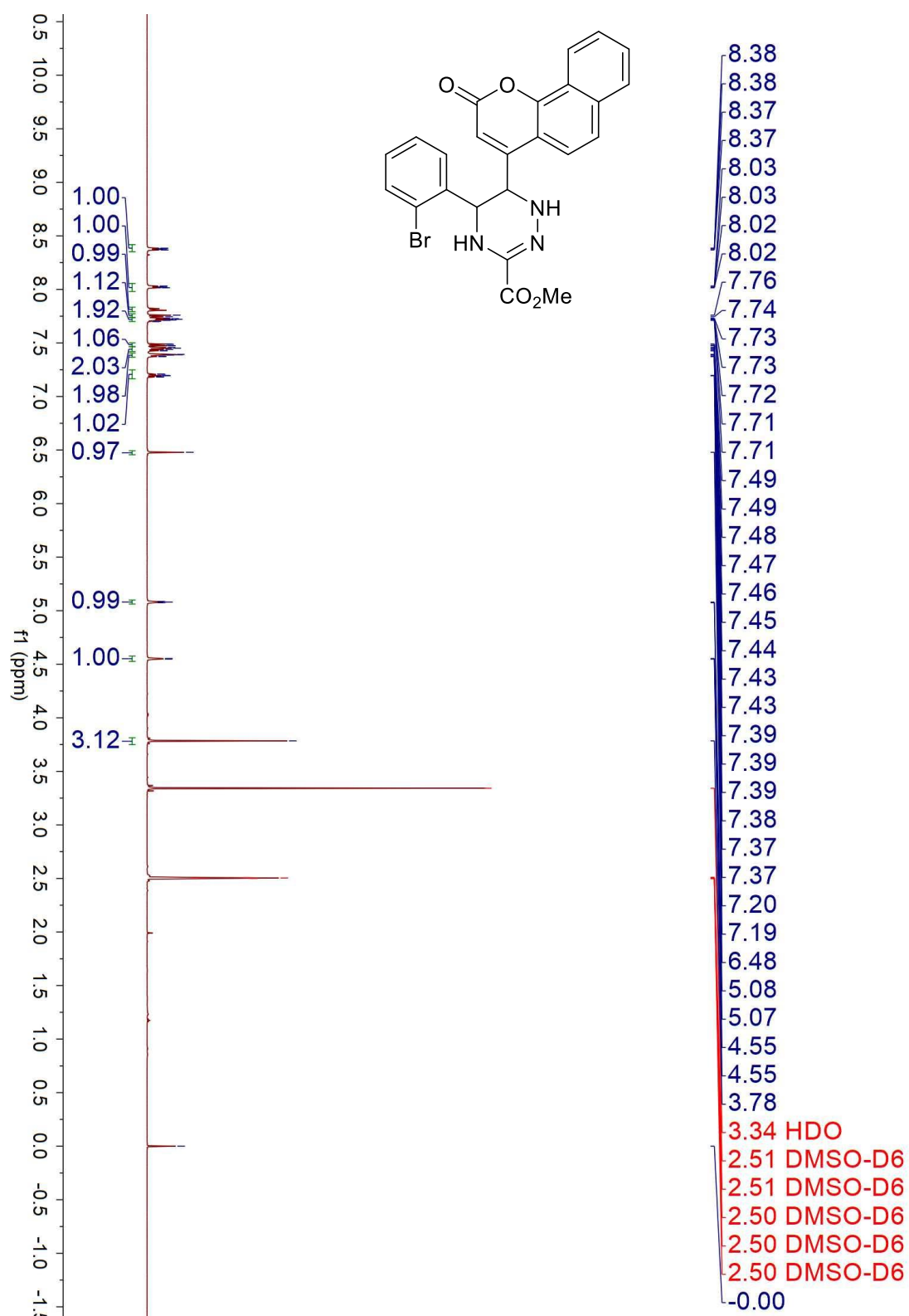
¹H-NMR spectra of compound **3i** (CDCl₃, 600 MHz)



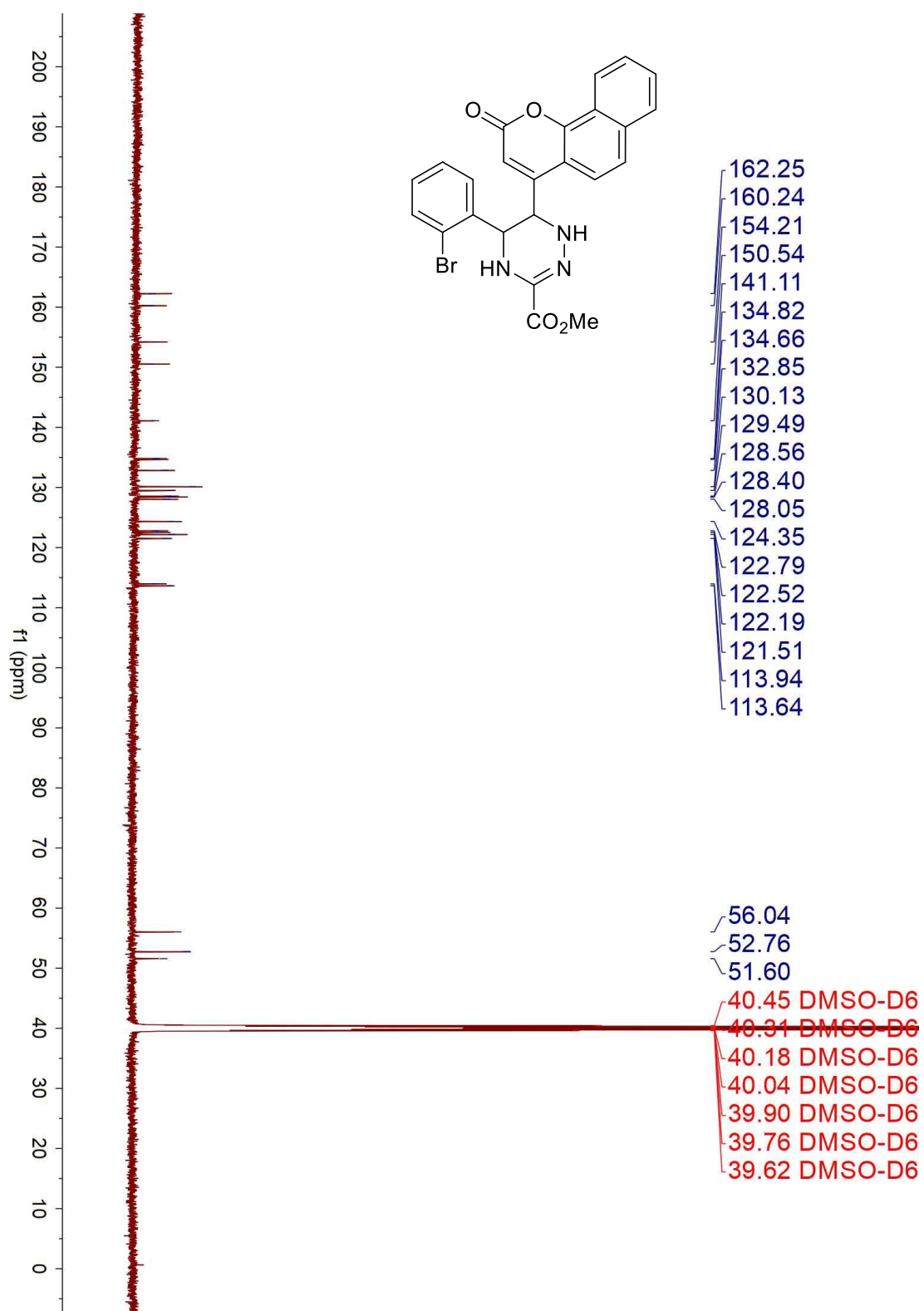
^{13}C -NMR spectra of compound **3i** (CDCl_3 , 151 MHz)



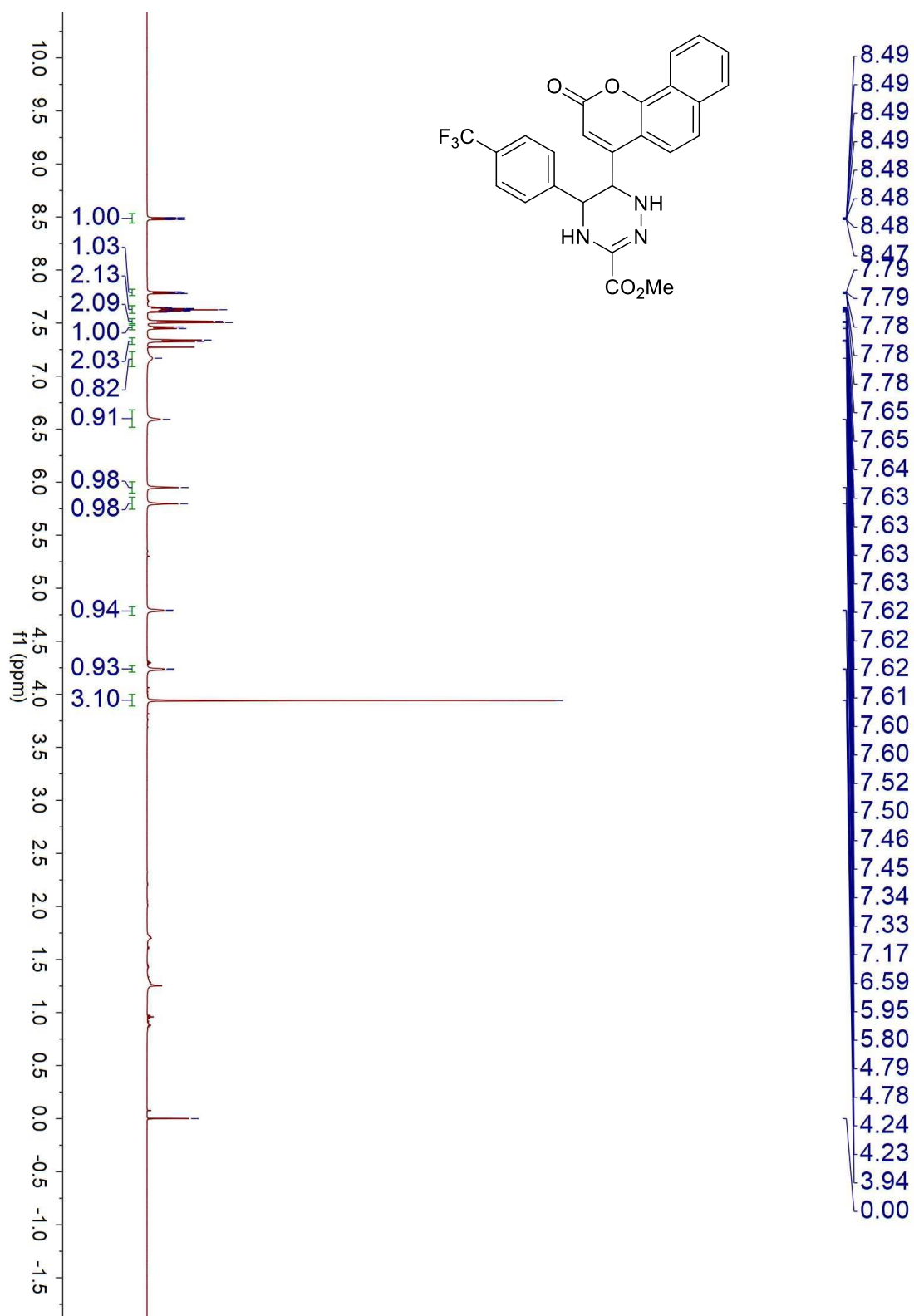
¹H-NMR spectra of compound **3j** (DMSO-*d*₆, 600 MHz)



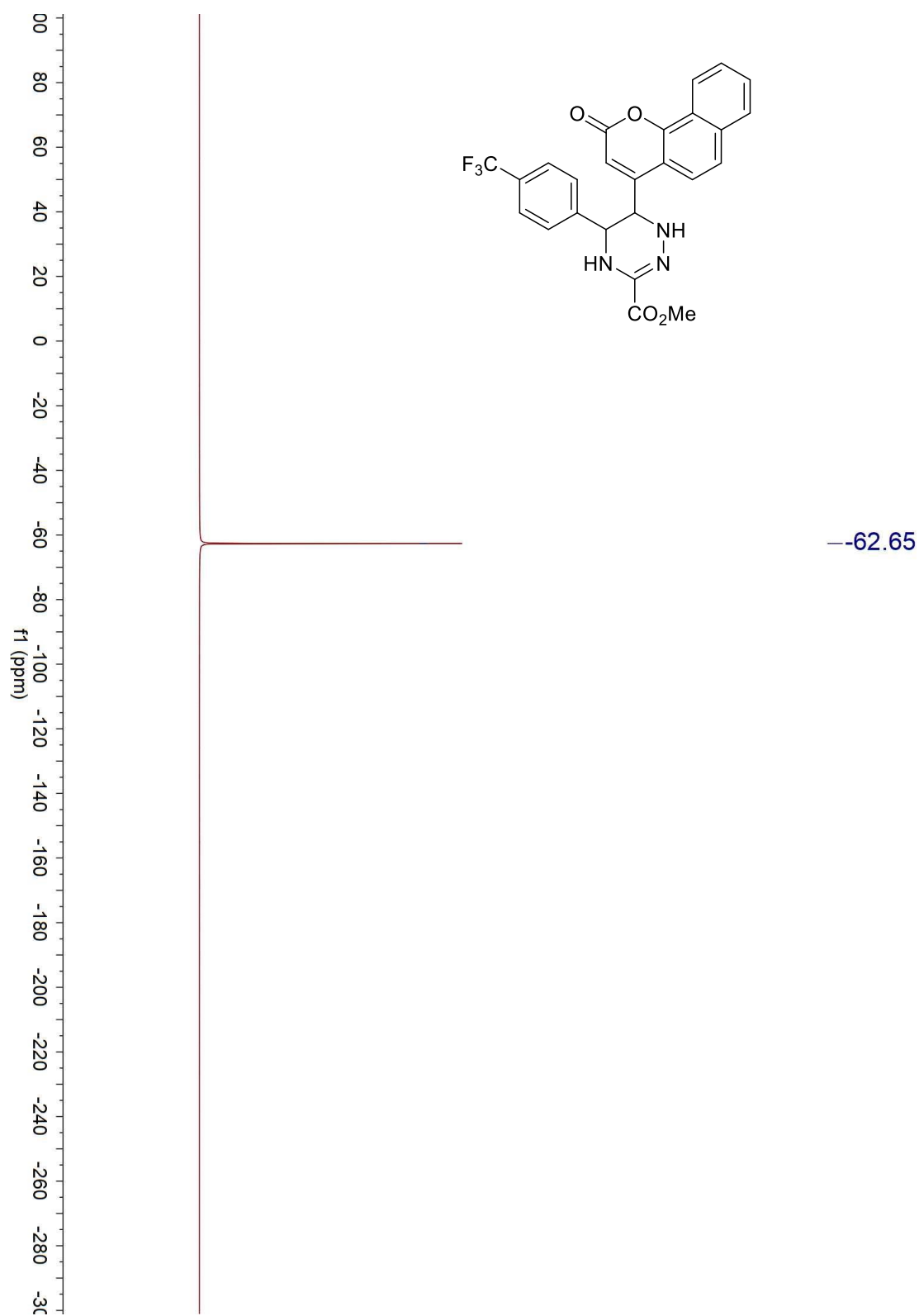
^{13}C -NMR spectra of compound **3j** (DMSO- d_6 , 151 MHz)



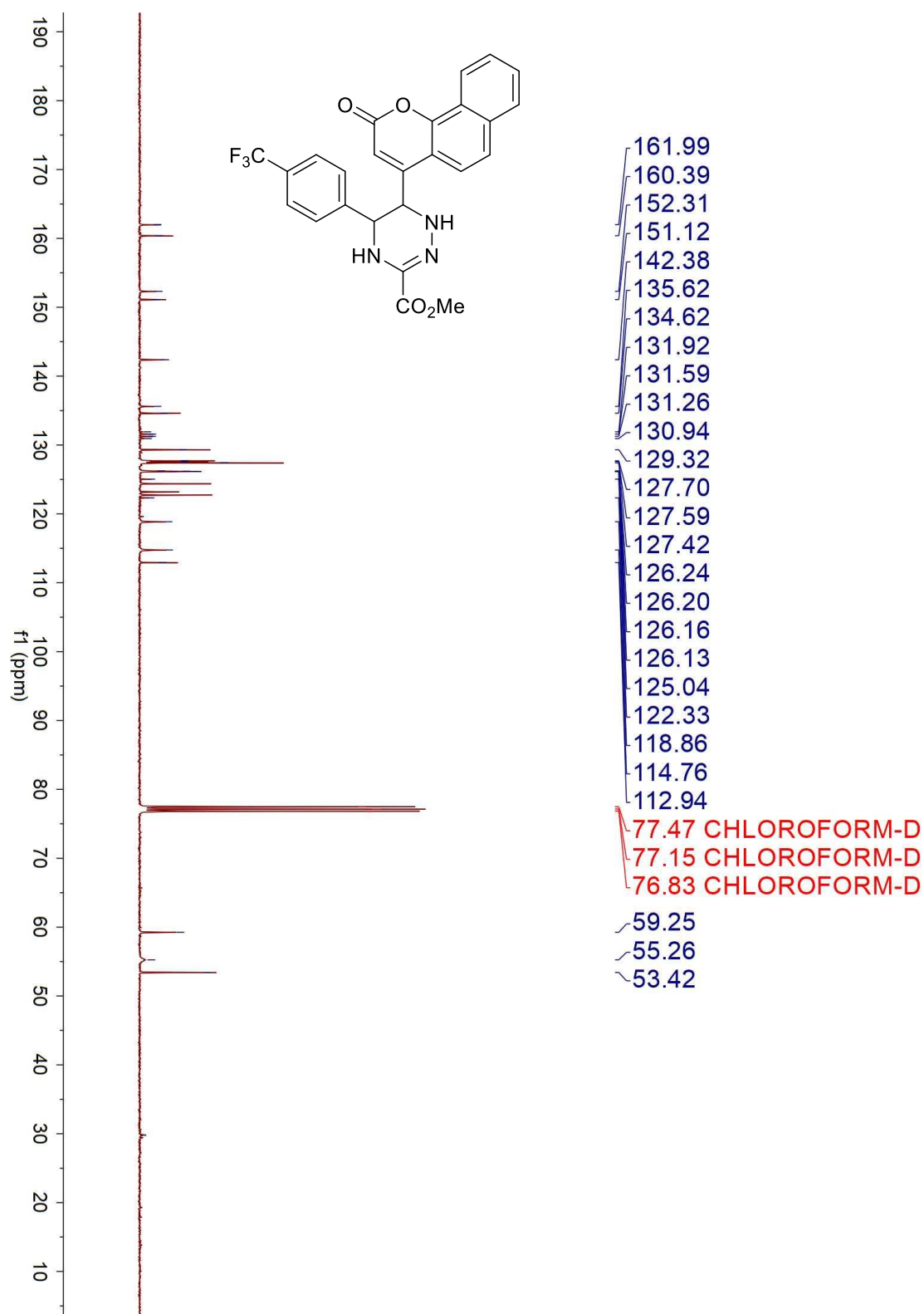
¹H-NMR spectra of compound **3k** (CDCl₃, 600 MHz)



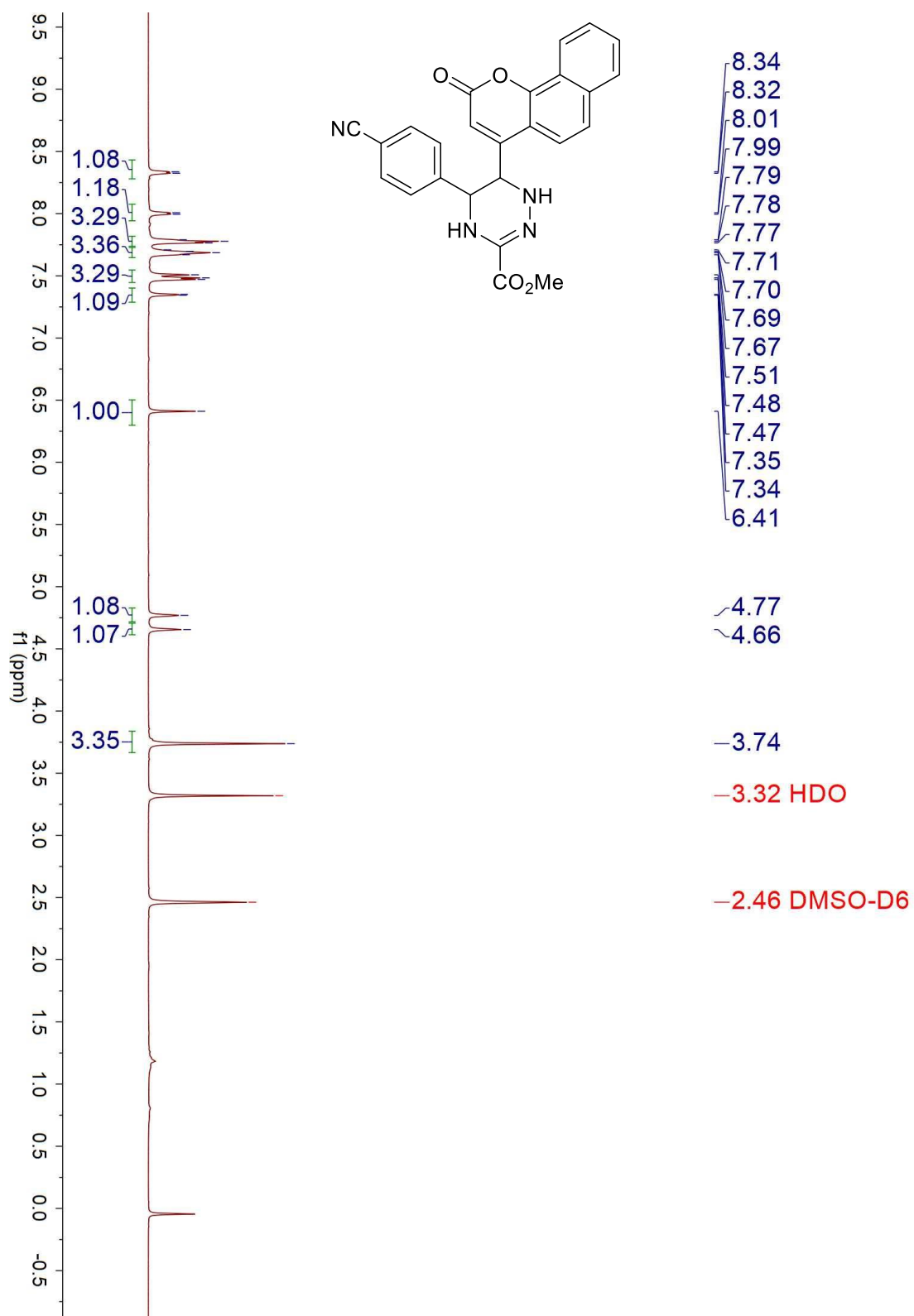
^{19}F -NMR spectra of compound **3k** (CDCl_3 , 565 MHz)



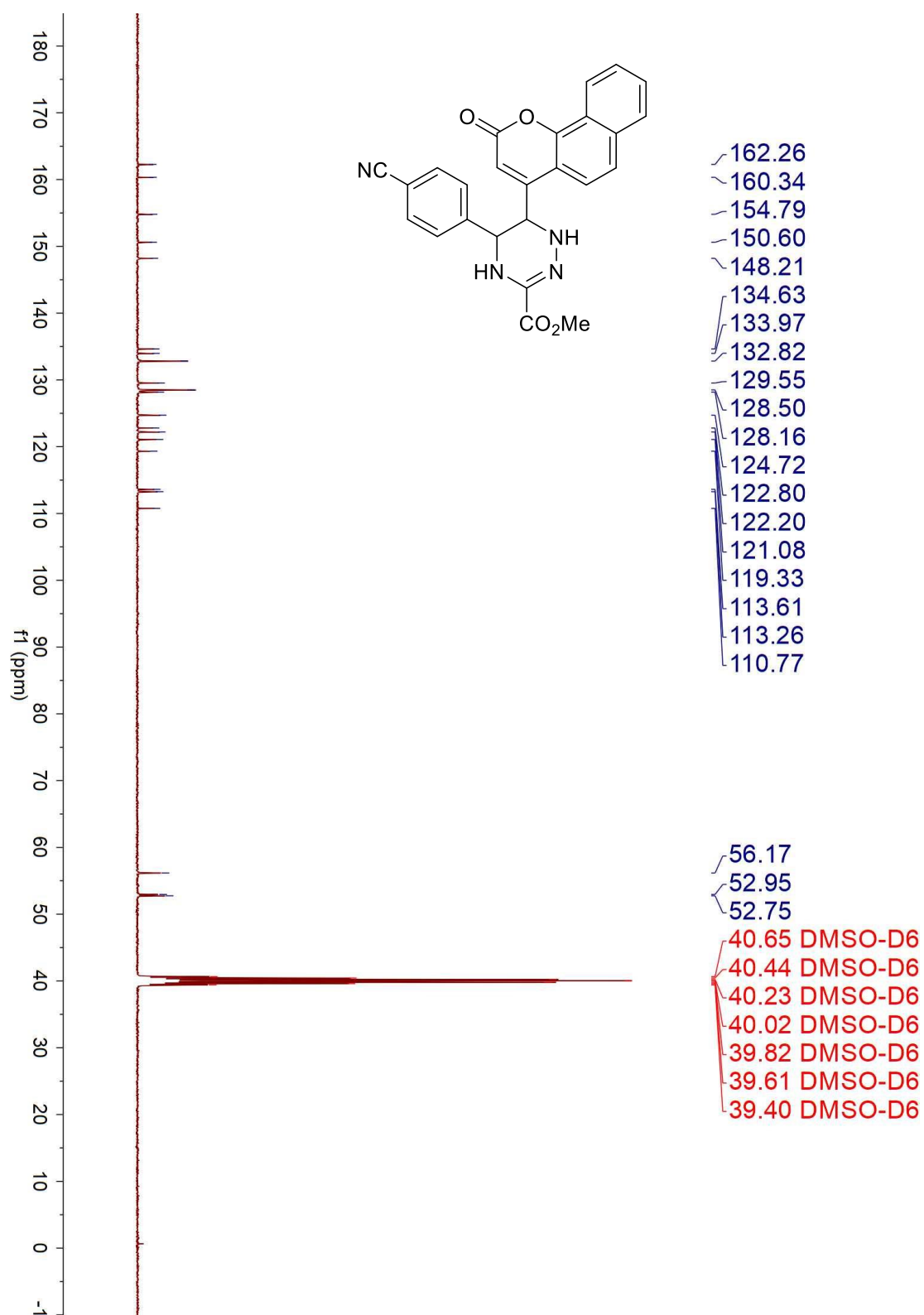
^{13}C -NMR spectra of compound **3k** (CDCl_3 , 151 MHz)



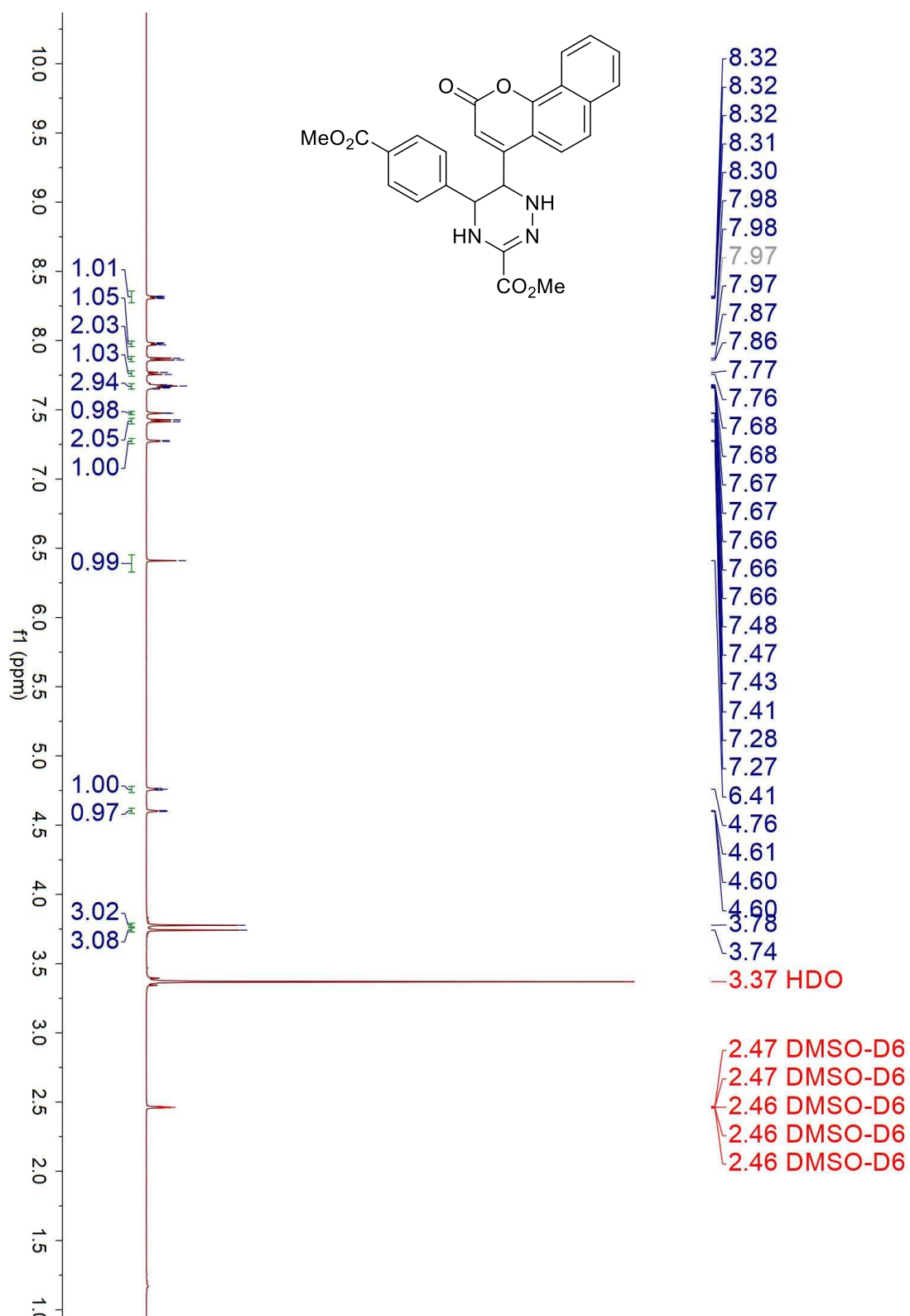
¹H-NMR spectra of compound **3I** (DMSO-*d*₆, 600 MHz)



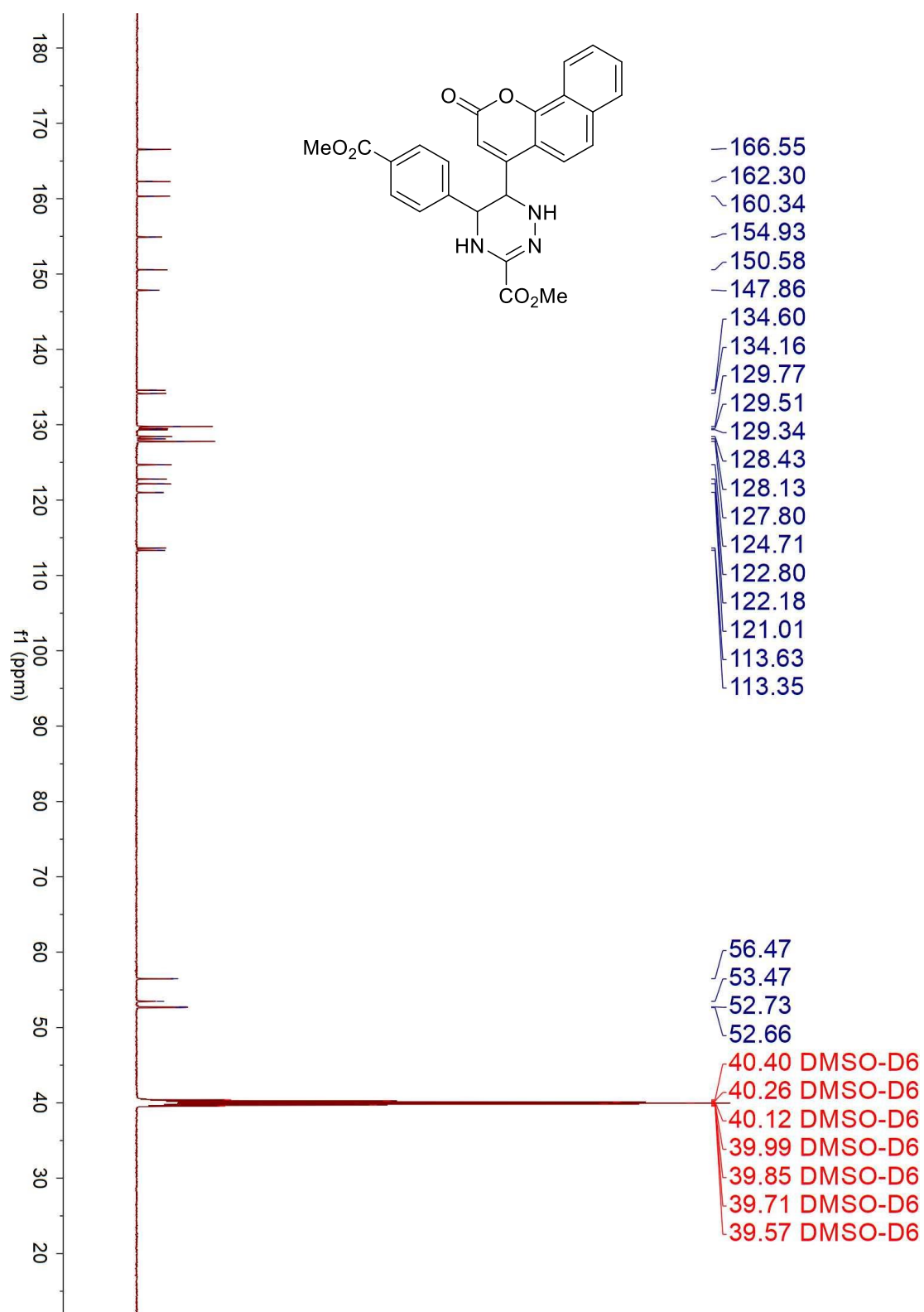
^{13}C -NMR spectra of compound **31** (DMSO- d_6 , 151 MHz)



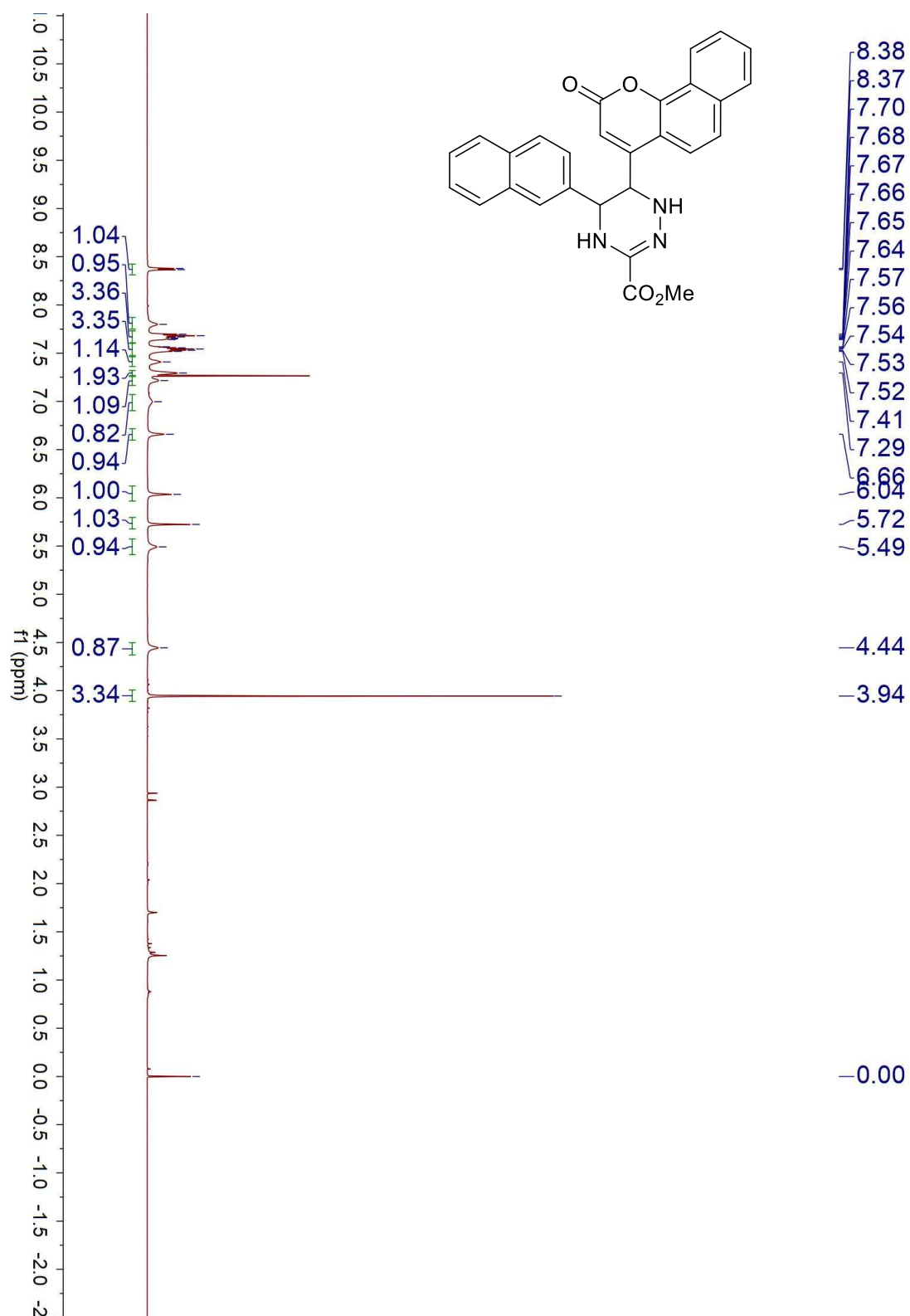
¹H-NMR spectra of compound **3m** (DMSO-*d*₆, 600 MHz)



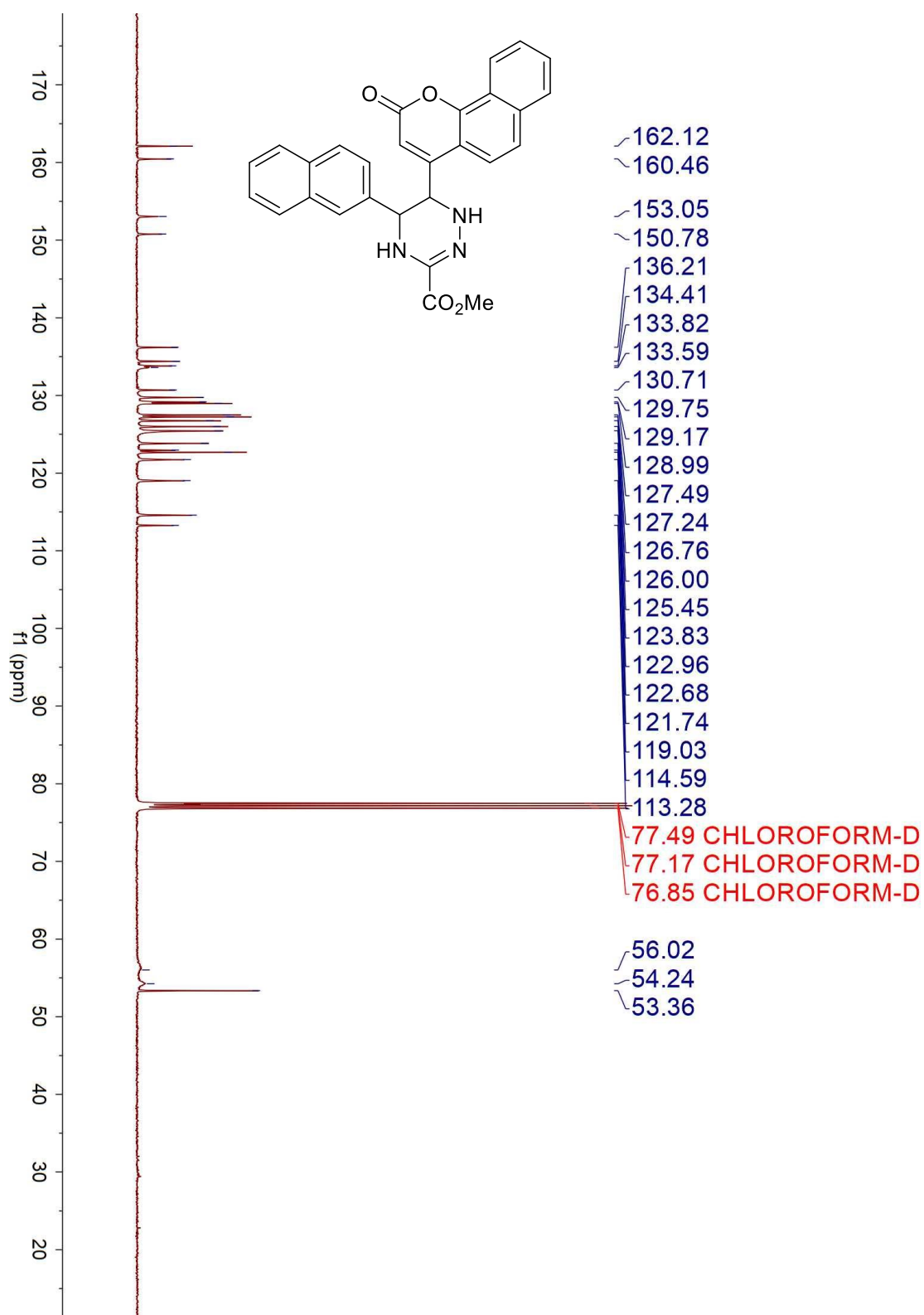
^{13}C -NMR spectra of compound **3m** (DMSO- d_6 , 151 MHz)



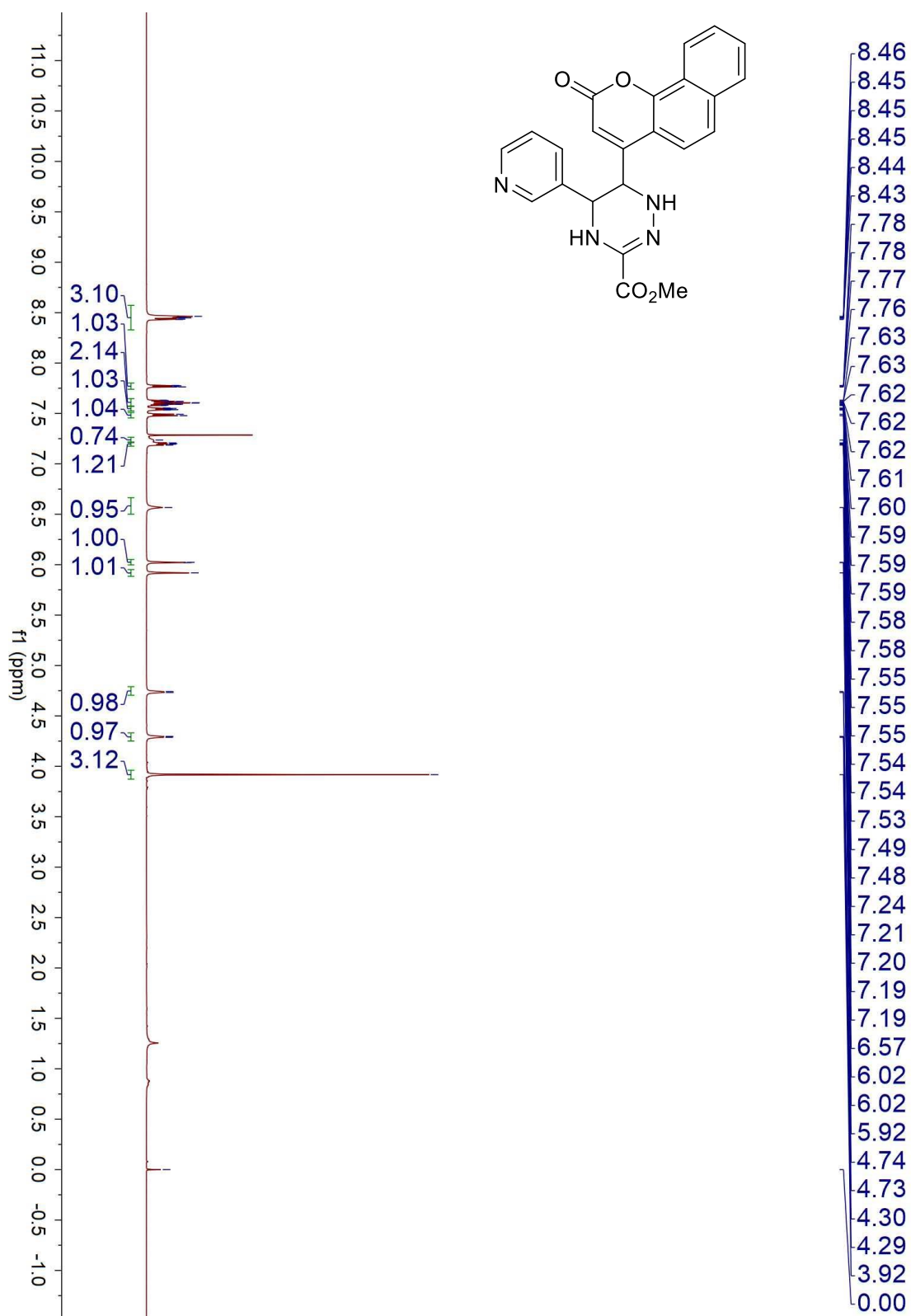
¹H-NMR spectra of compound **3n** (CDCl₃, 600 MHz)



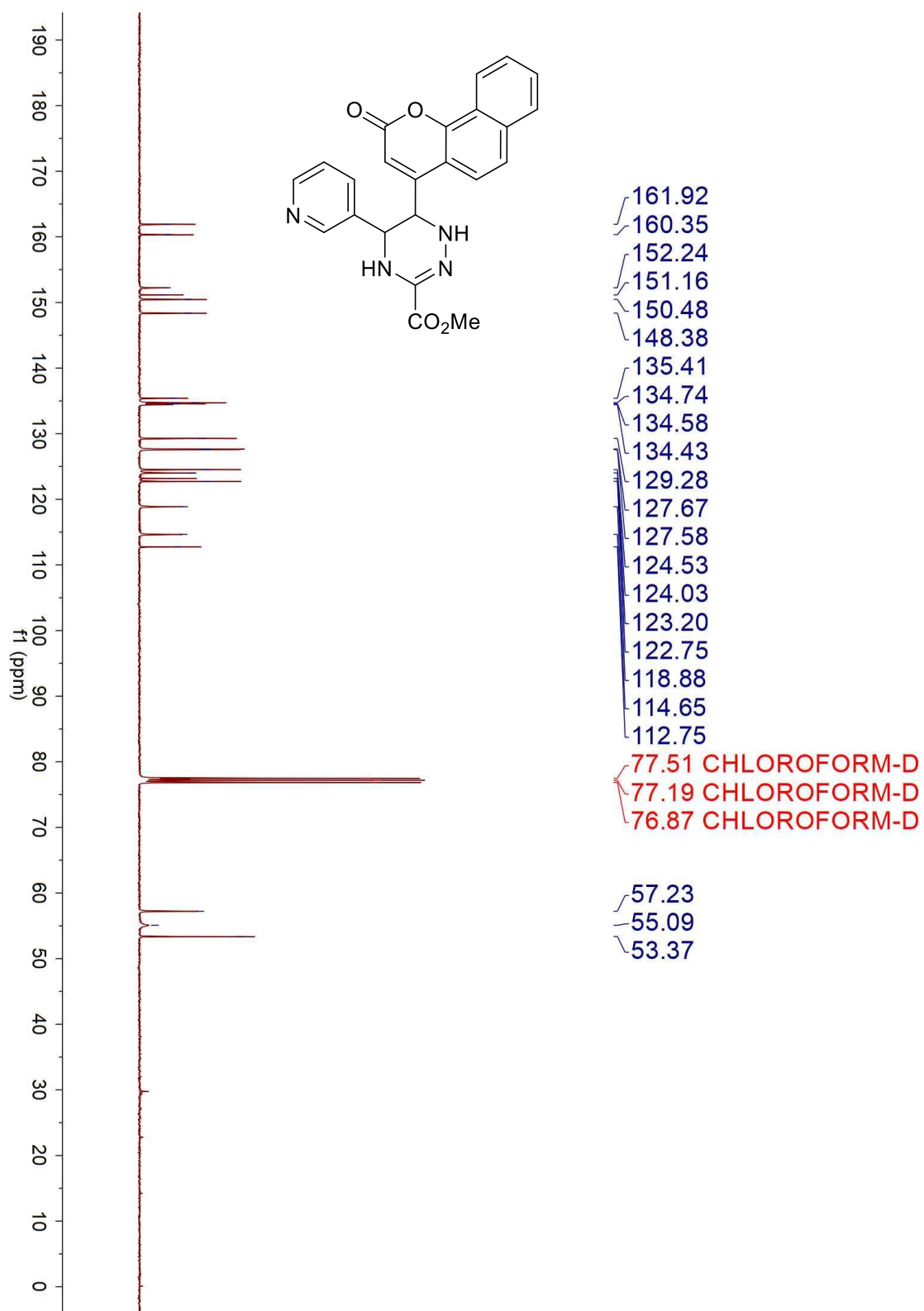
^{13}C -NMR spectra of compound **3n** (CDCl_3 , 151 MHz)



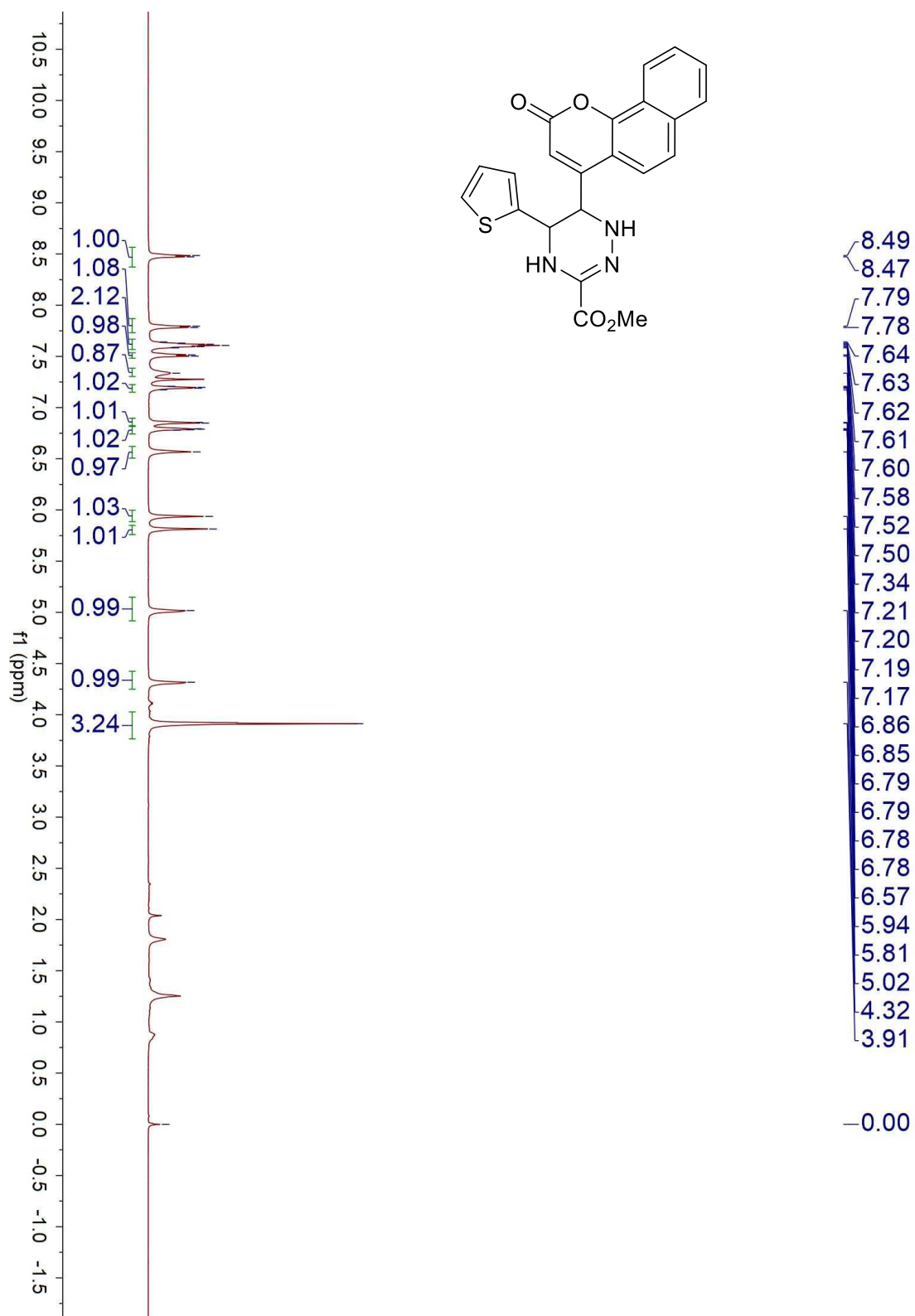
¹H-NMR spectra of compound **3o** (CDCl₃, 600 MHz)



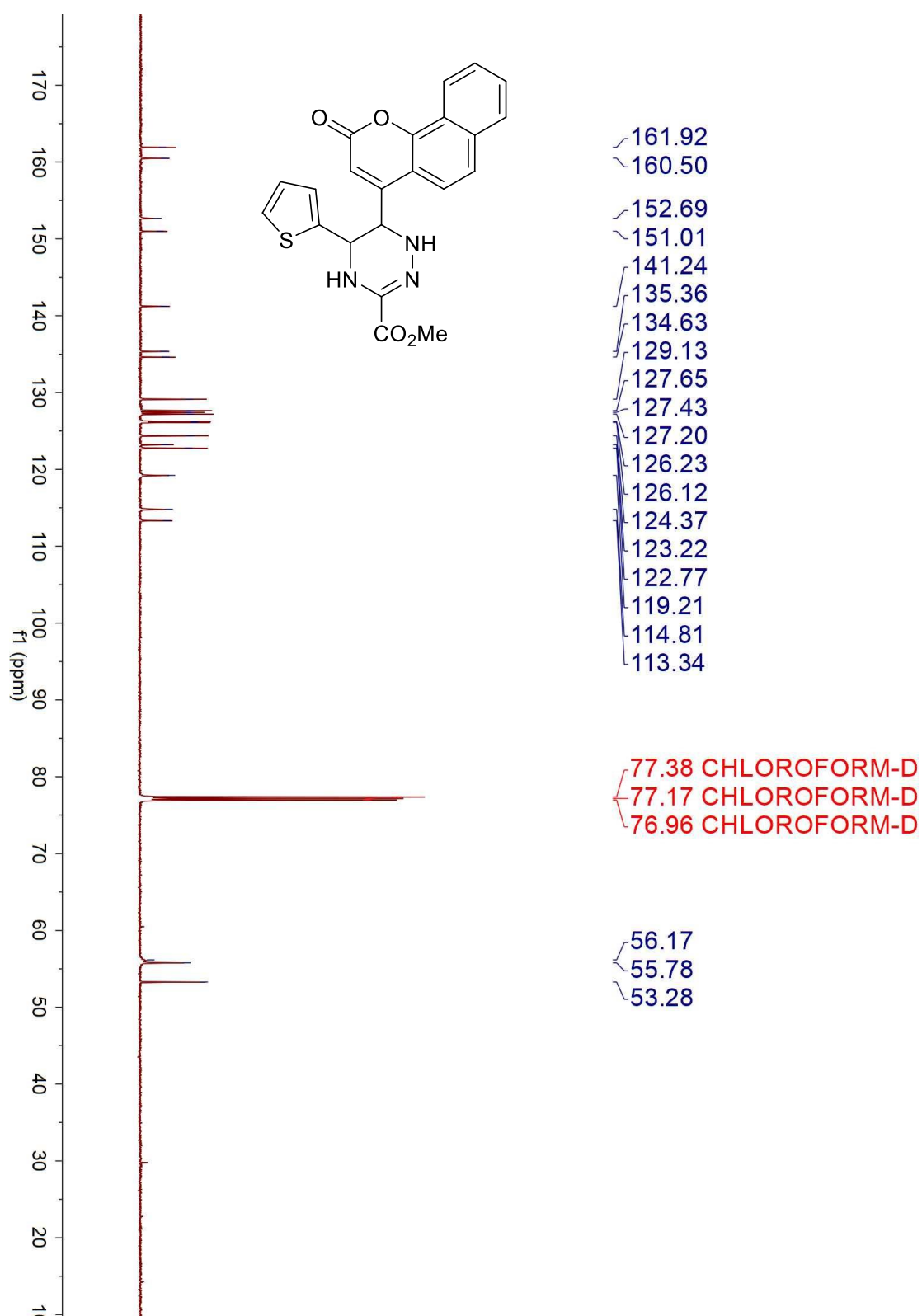
^{13}C -NMR spectra of compound **3o** (CDCl_3 , 151 MHz)



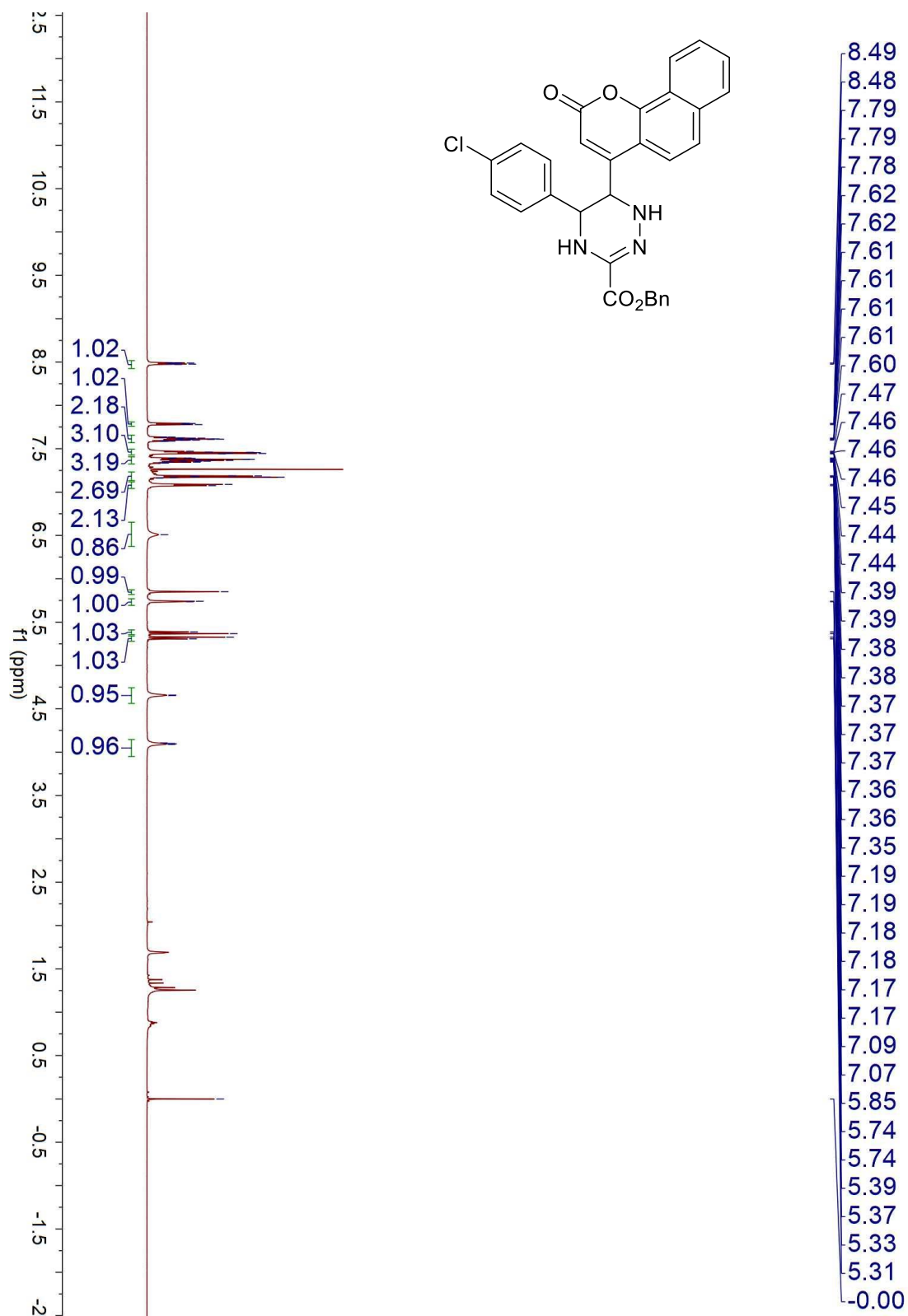
¹H-NMR spectra of compound **3p** (CDCl₃, 600 MHz)



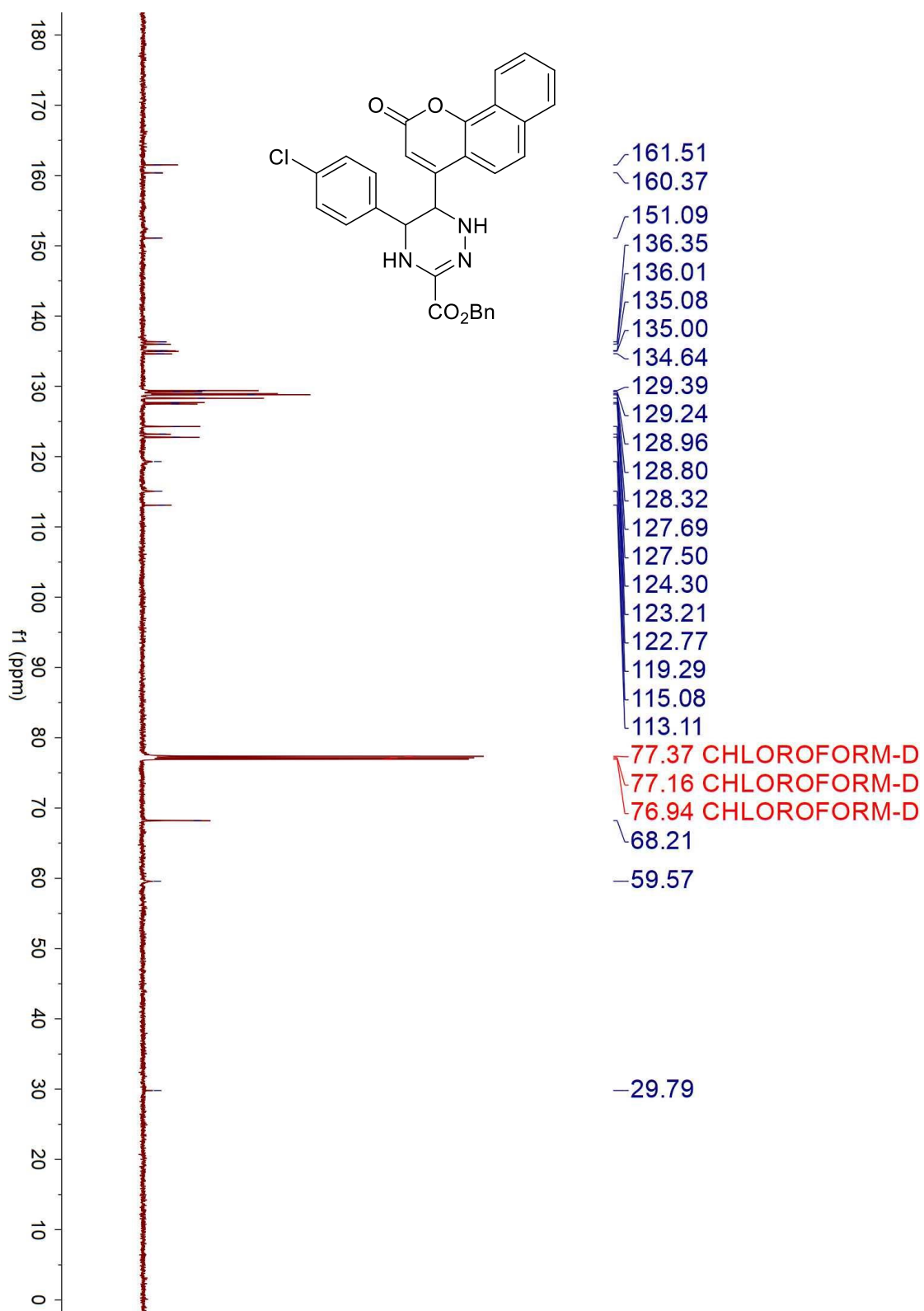
^{13}C -NMR spectra of compound **3p** (CDCl_3 , 151 MHz)



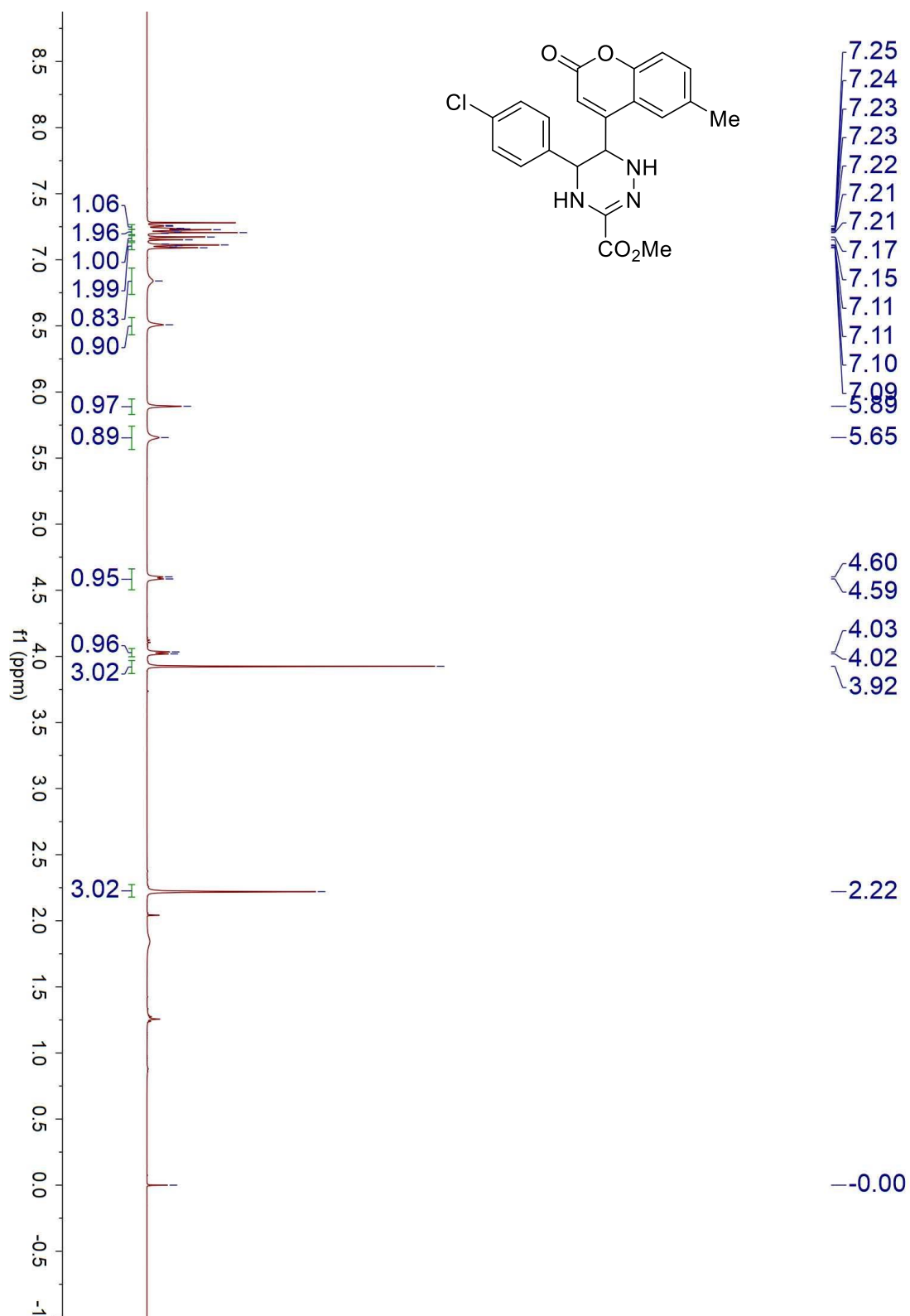
¹H-NMR spectra of compound **3q** (CDCl₃, 600 MHz)



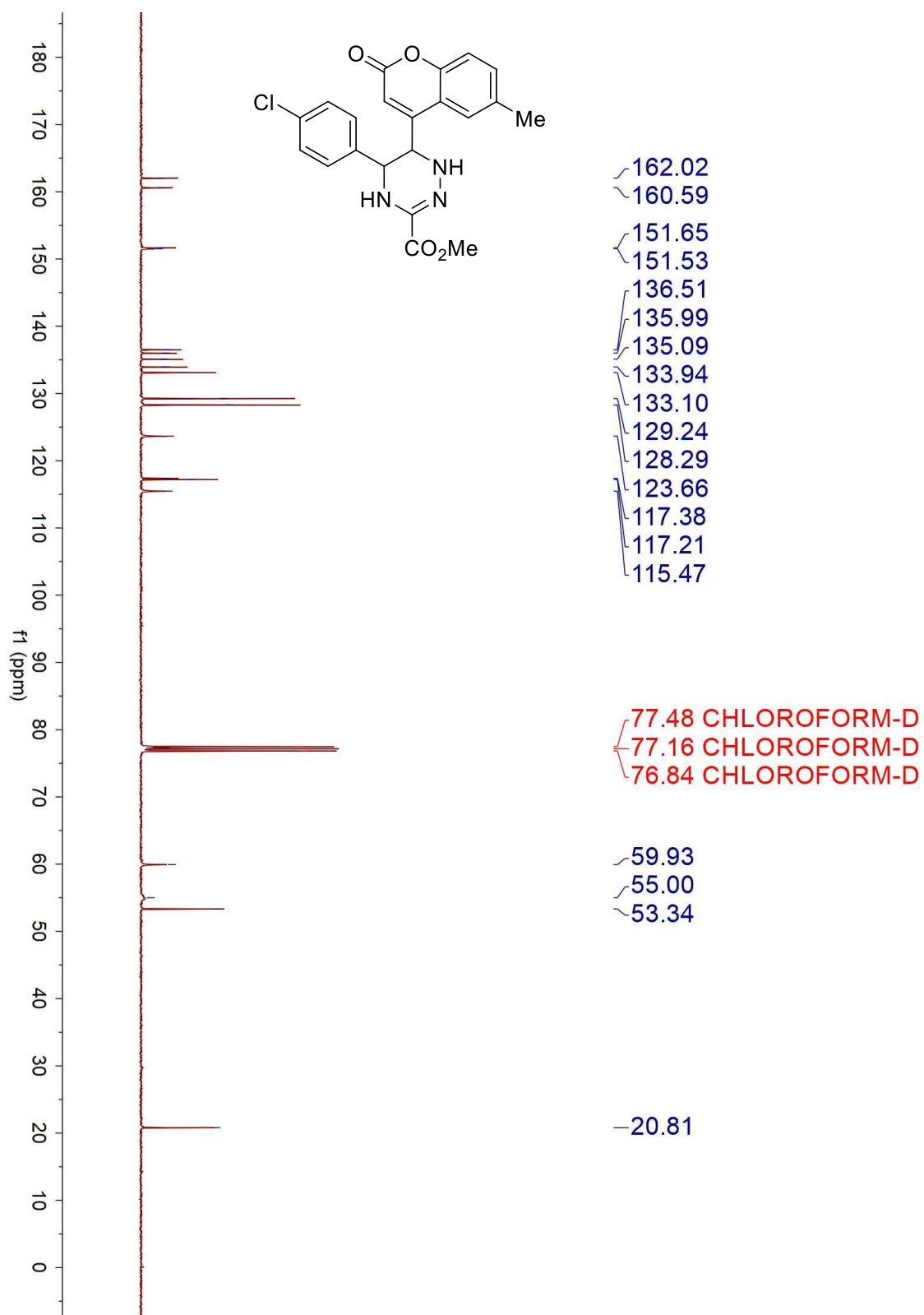
^{13}C -NMR spectra of compound **3q** (CDCl_3 , 151 MHz)



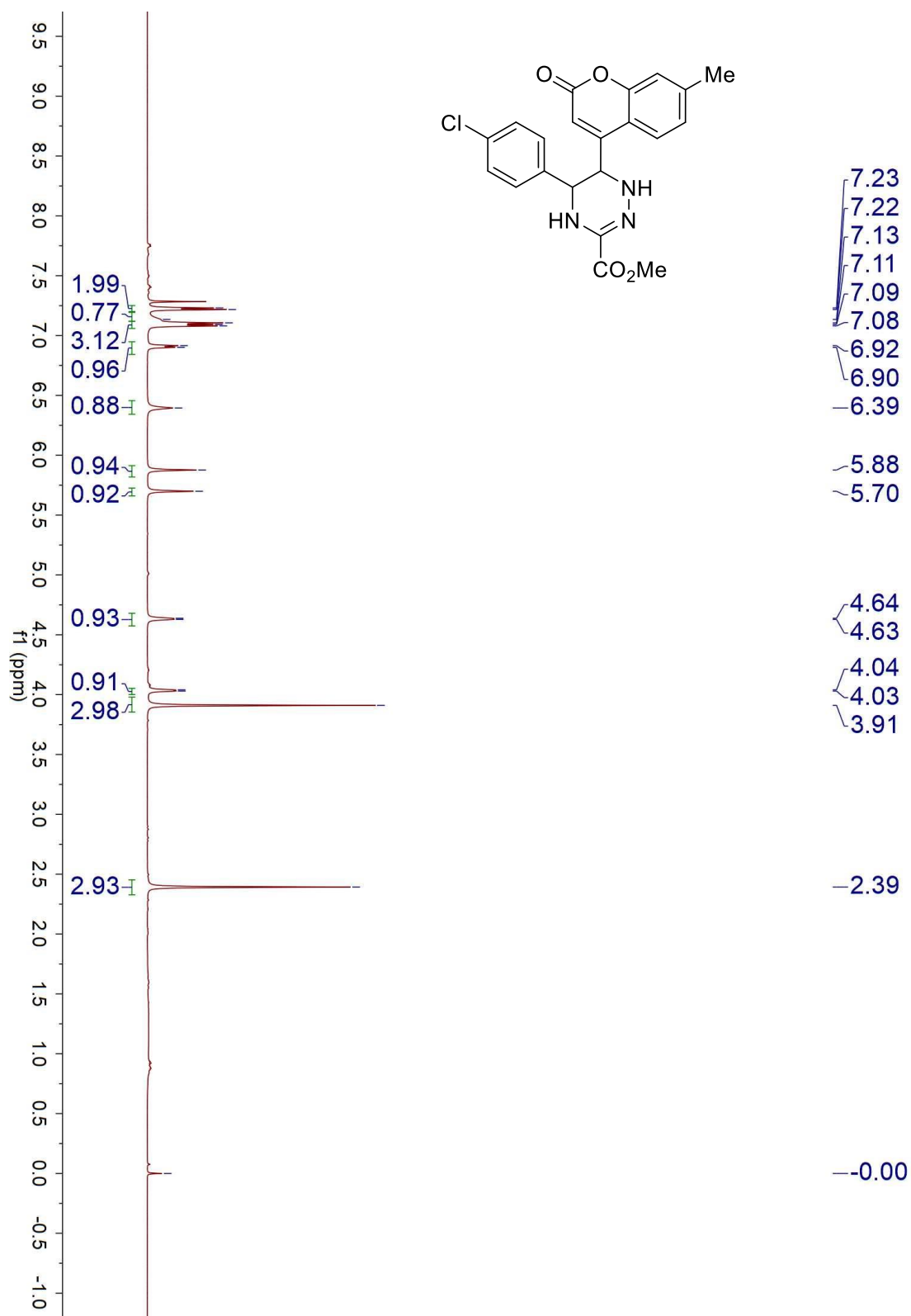
^1H -NMR spectra of compound **3ba** (CDCl_3 , 600 MHz)



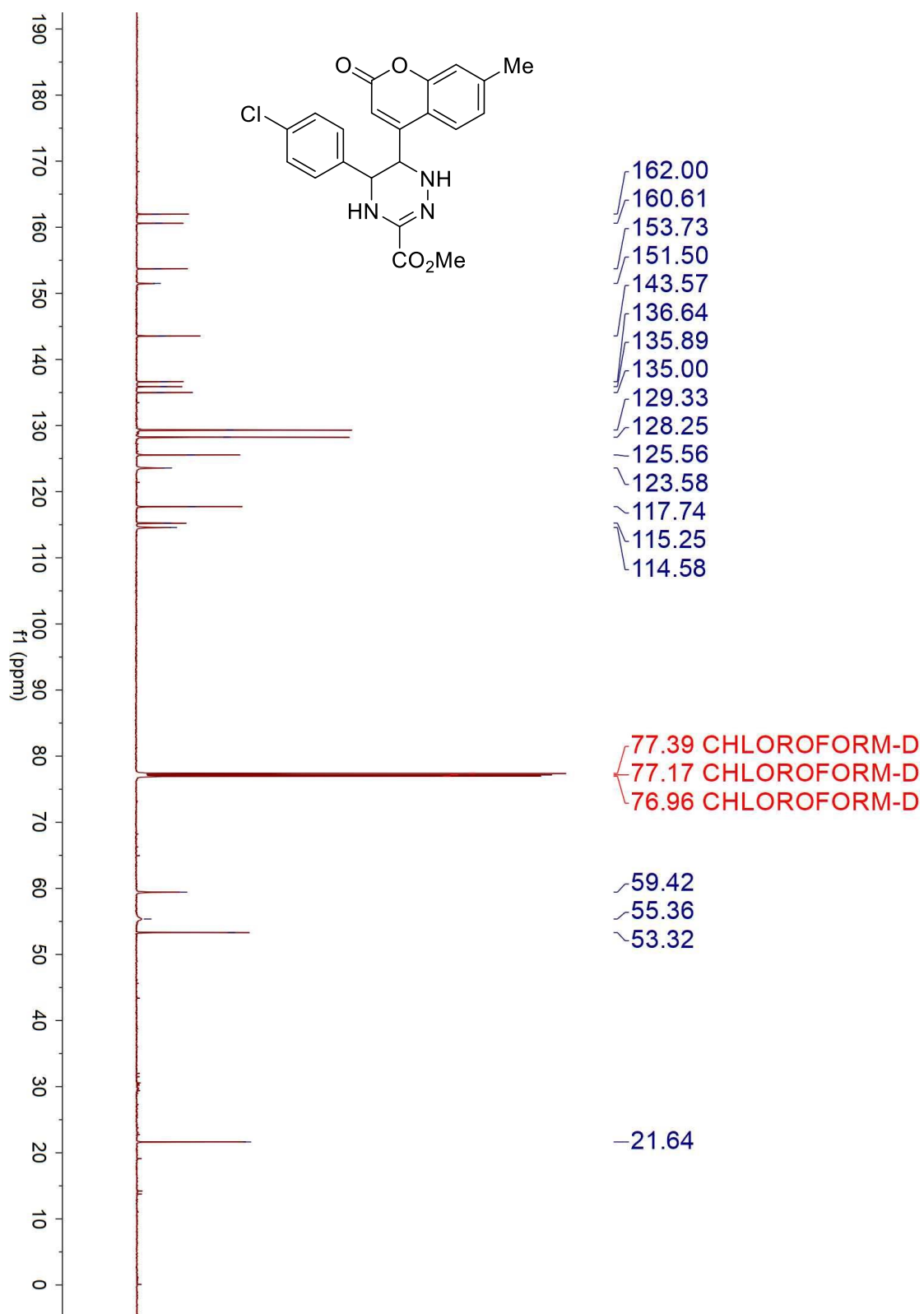
^{13}C -NMR spectra of compound **3ba** (CDCl_3 , 151 MHz)



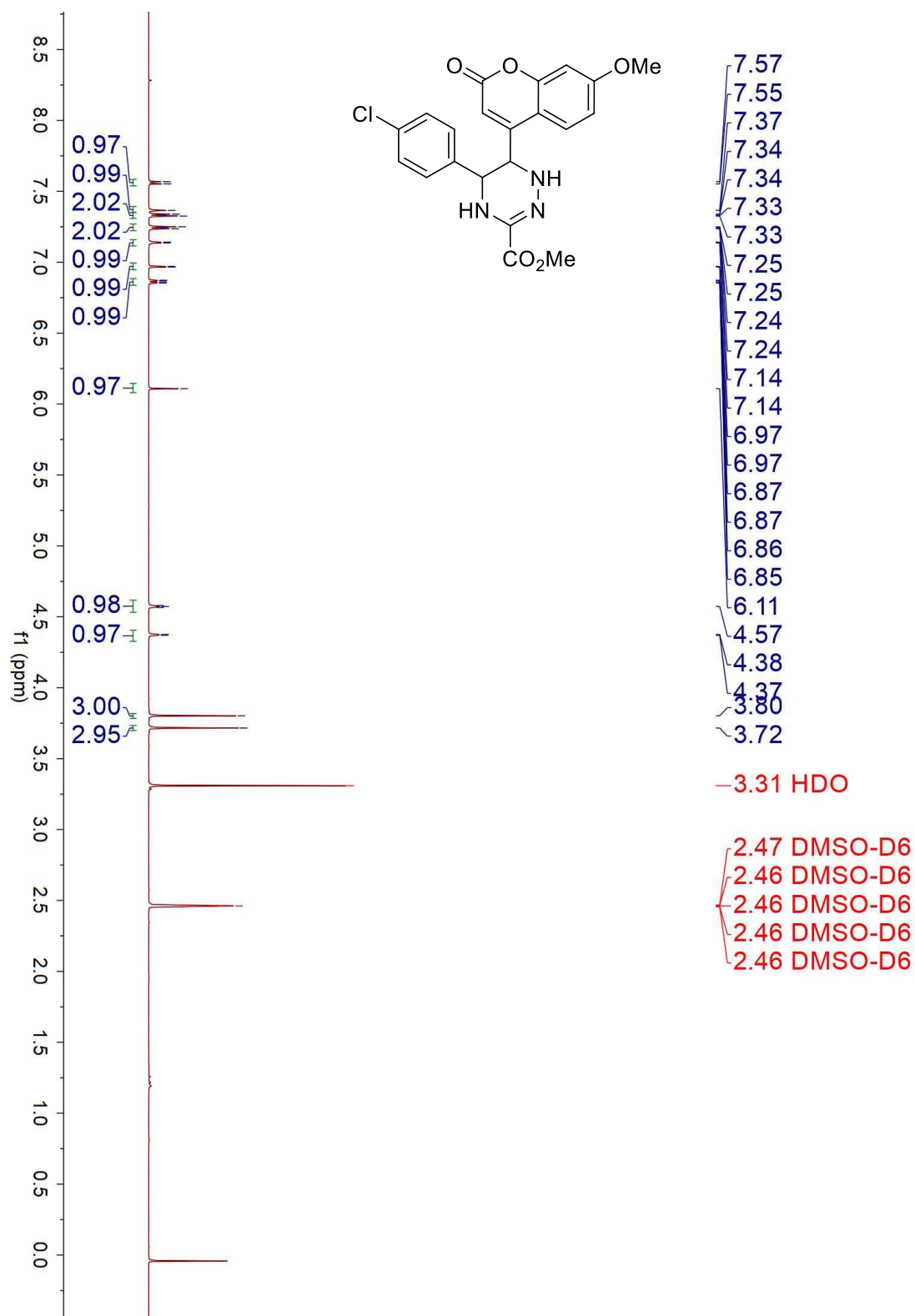
¹H-NMR spectra of compound **3ca** (CDCl₃, 600 MHz)



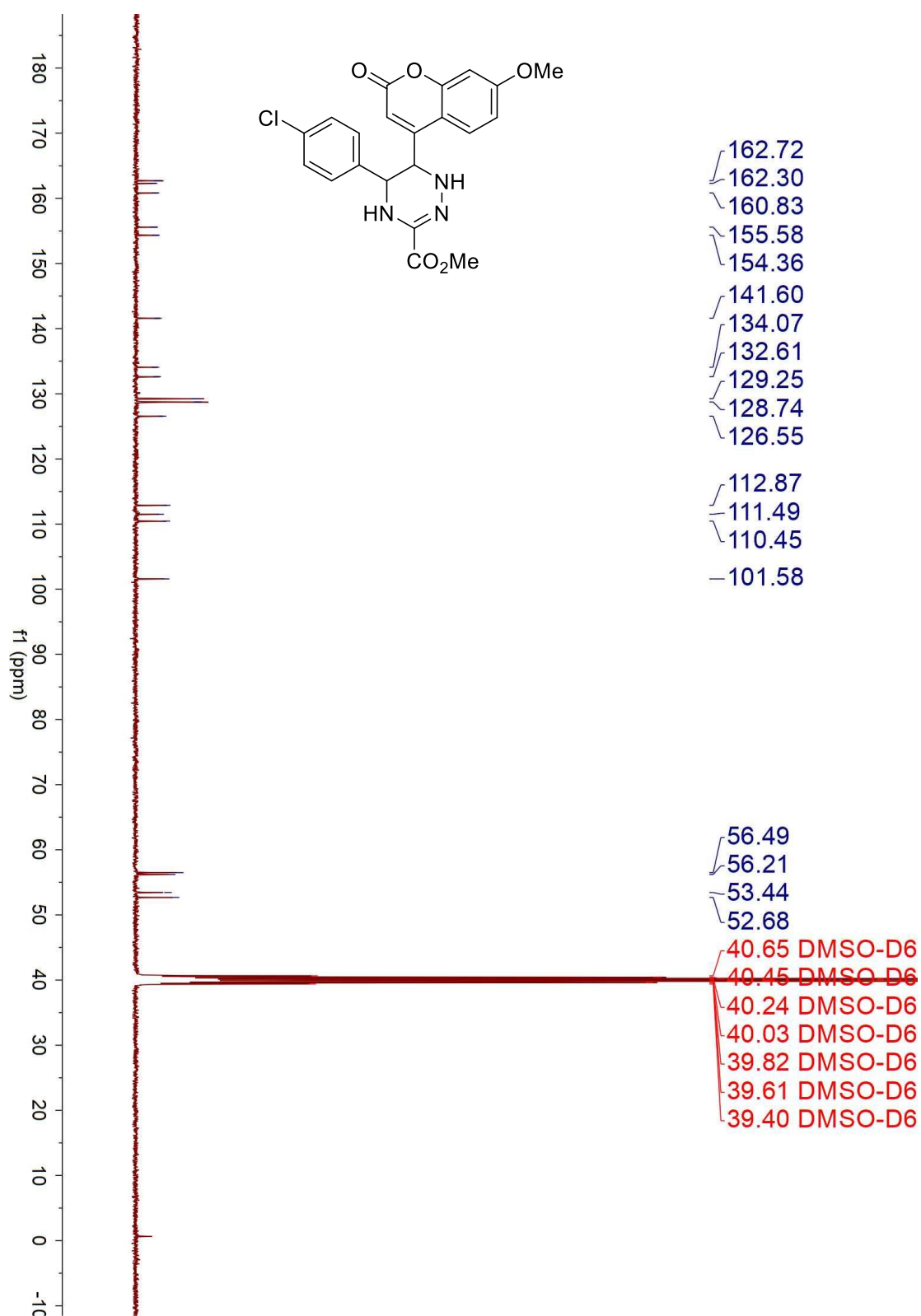
^{13}C -NMR spectra of compound **3ca** (CDCl_3 , 151 MHz)



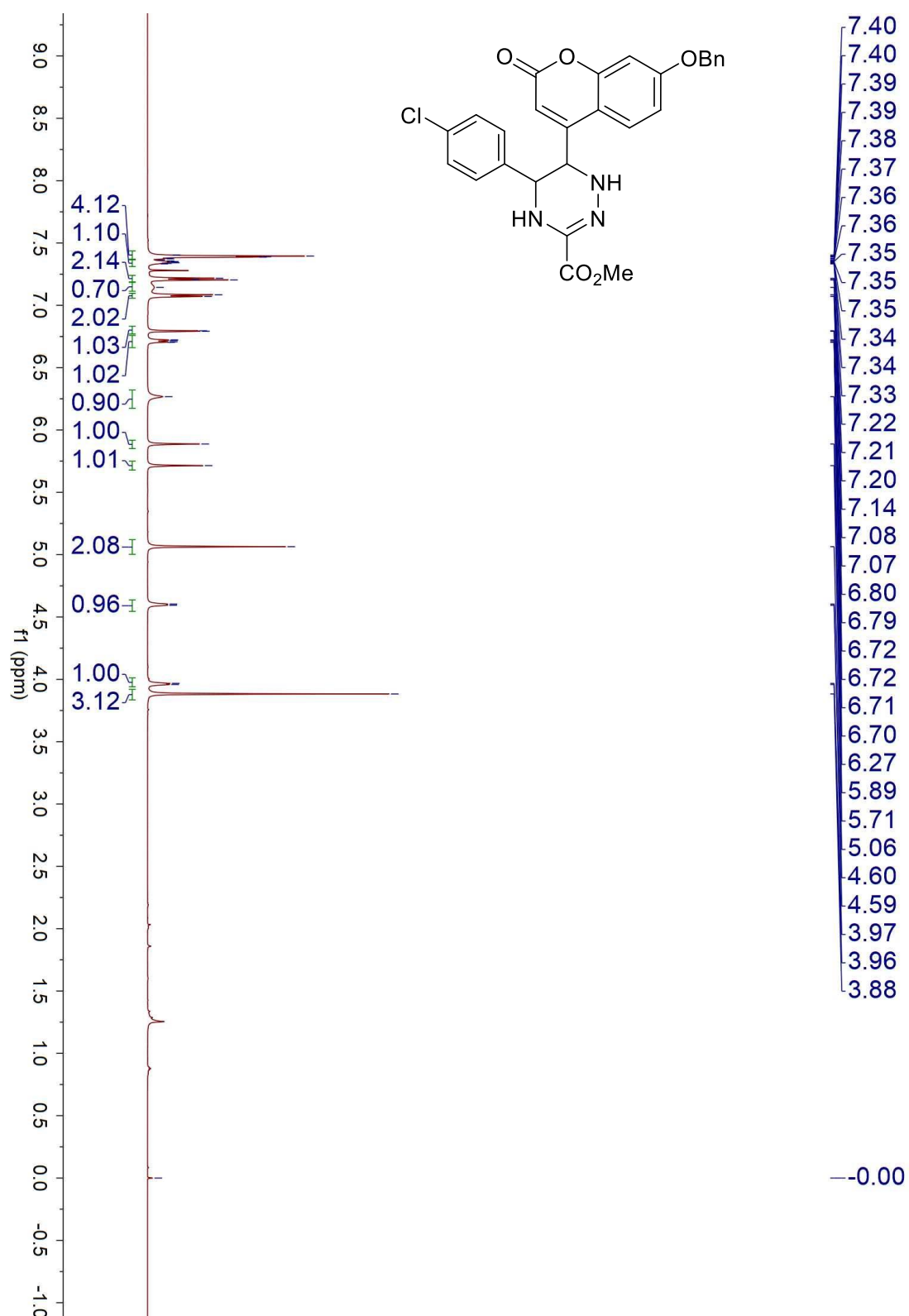
¹H-NMR spectra of compound **3da** (DMSO-*d*₆, 600 MHz)



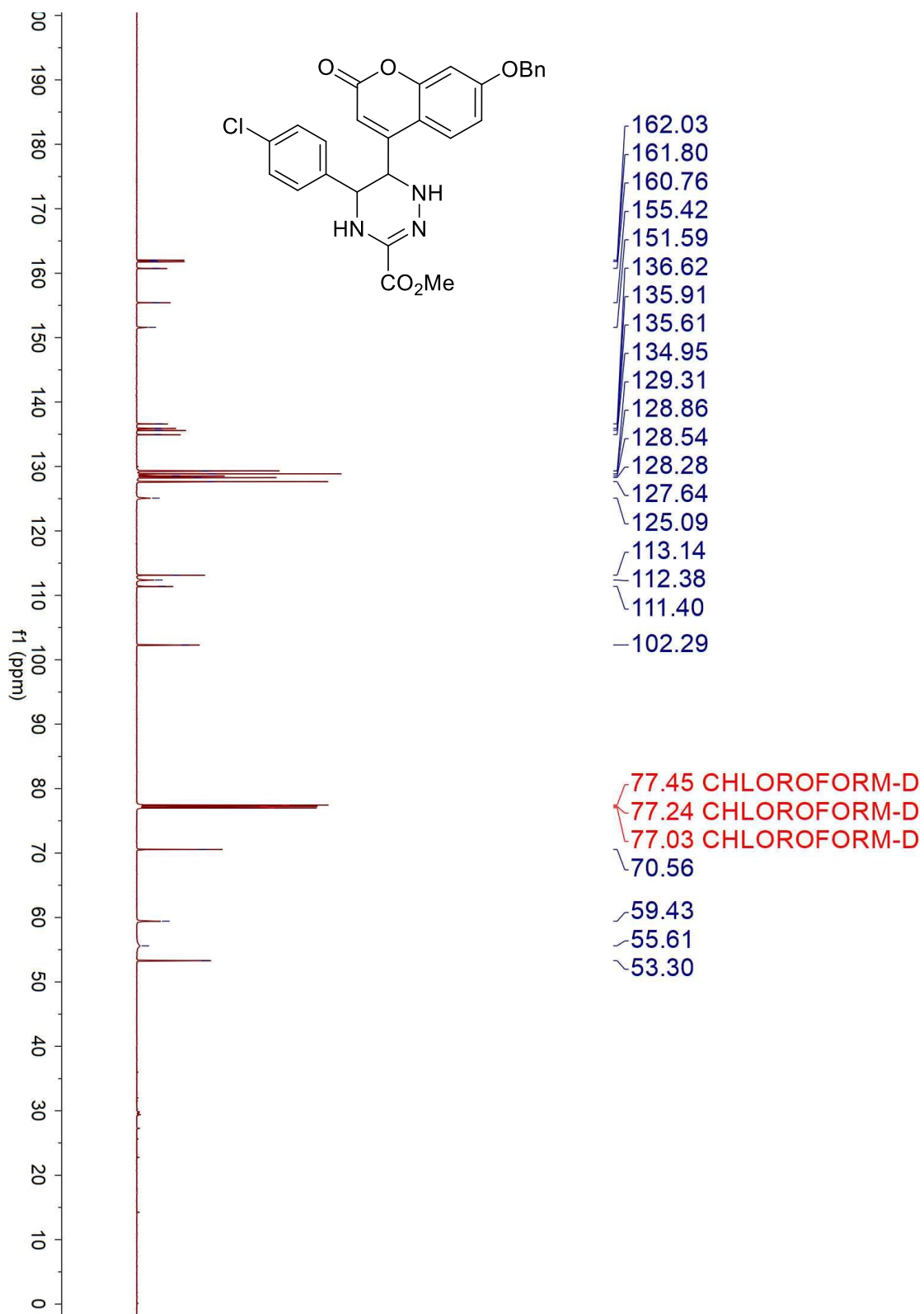
^{13}C -NMR spectra of compound **3da** (DMSO- d_6 , 151 MHz)



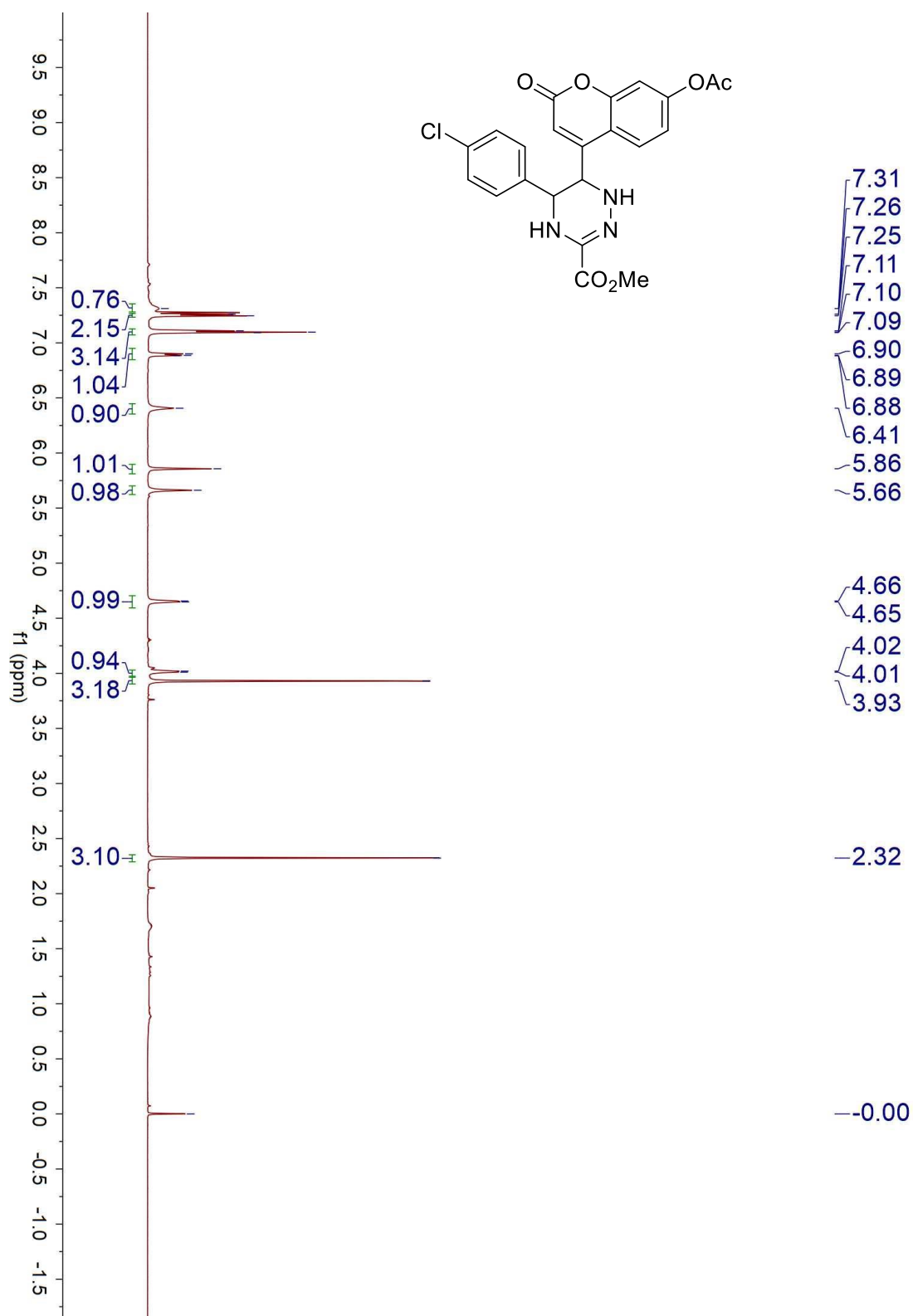
¹H-NMR spectra of compound **3ea** (CDCl₃, 600 MHz)



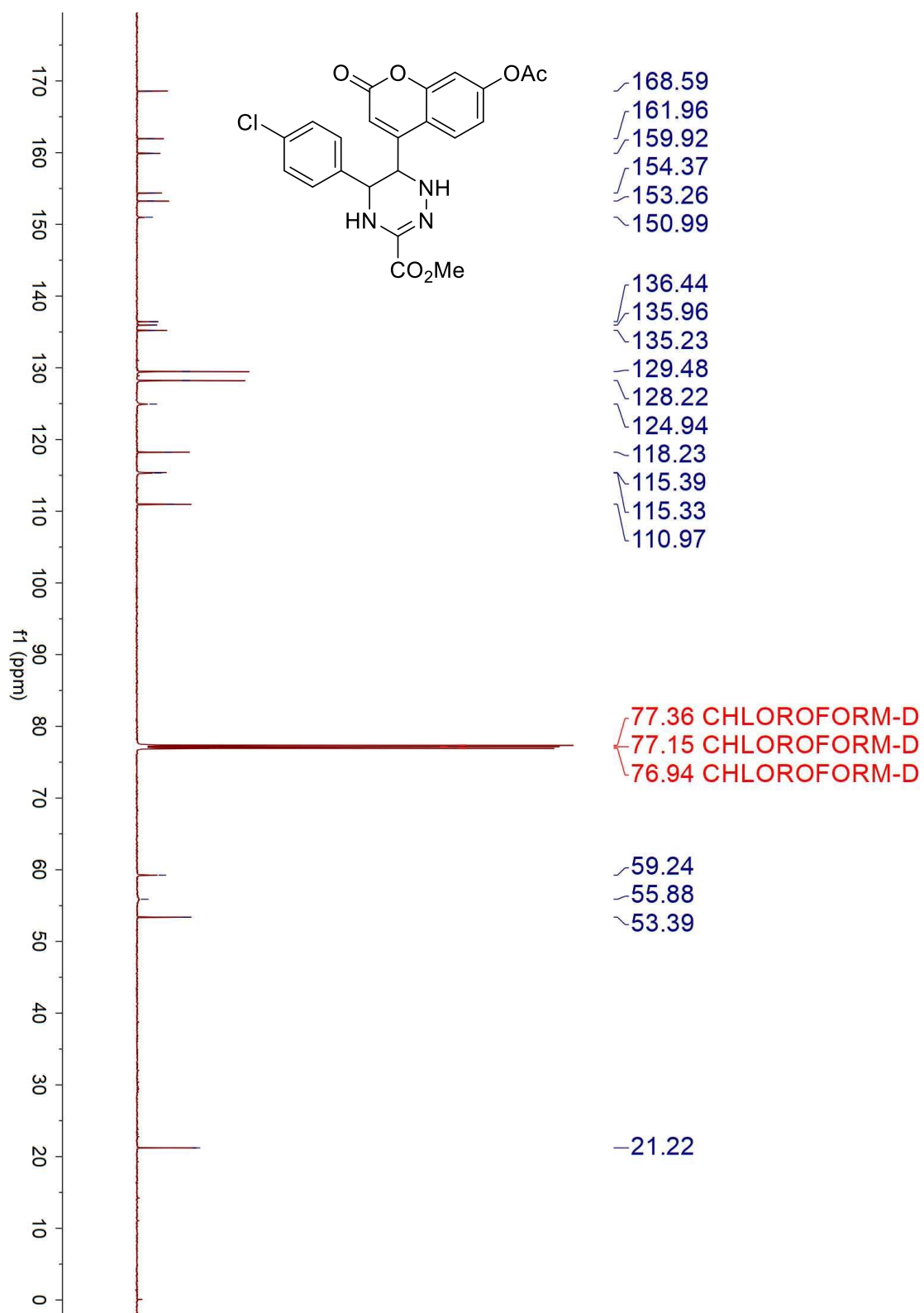
^{13}C -NMR spectra of compound **3ea** (CDCl_3 , 151 MHz)



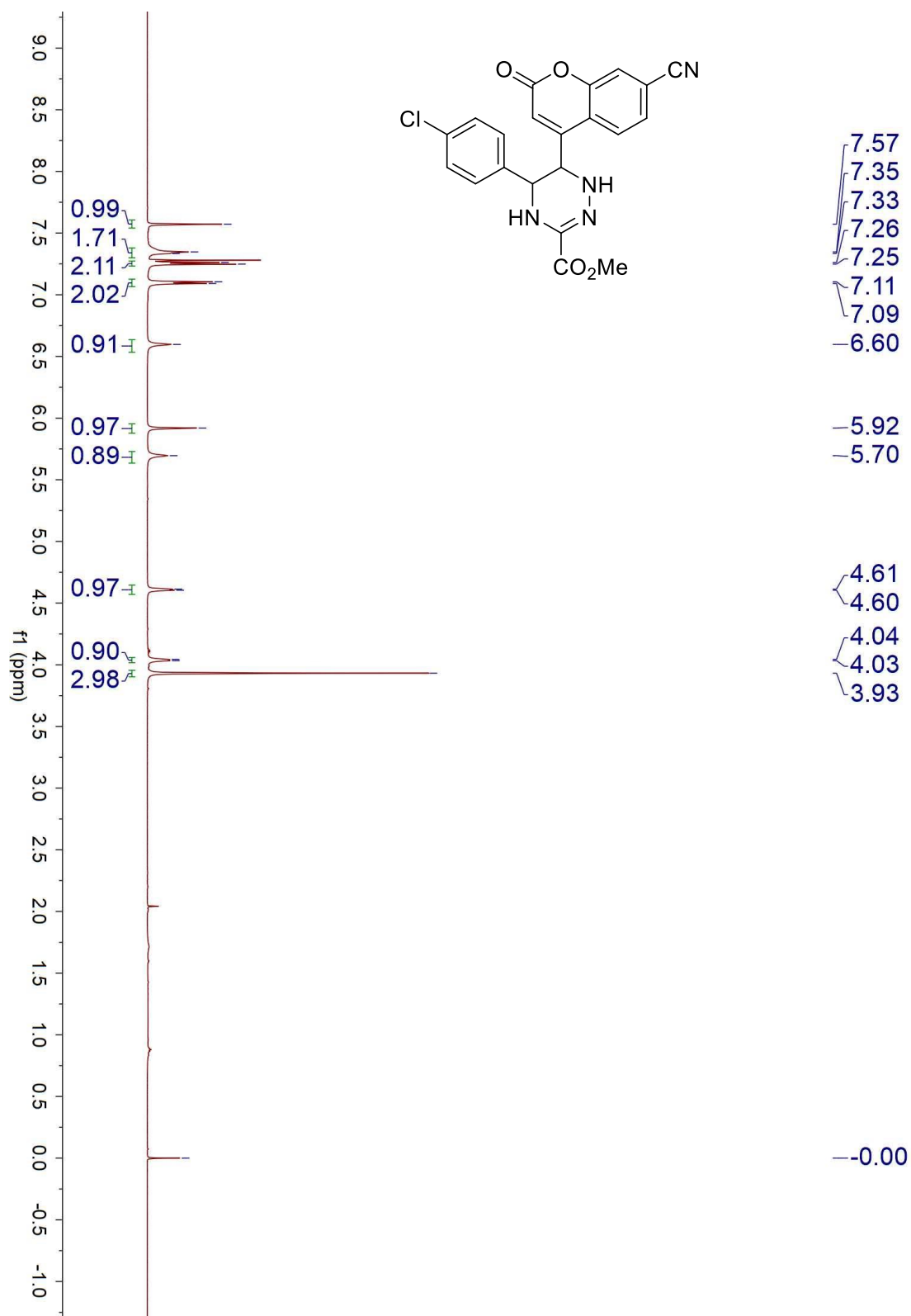
¹H-NMR spectra of compound **3fa** (CDCl₃, 600 MHz)



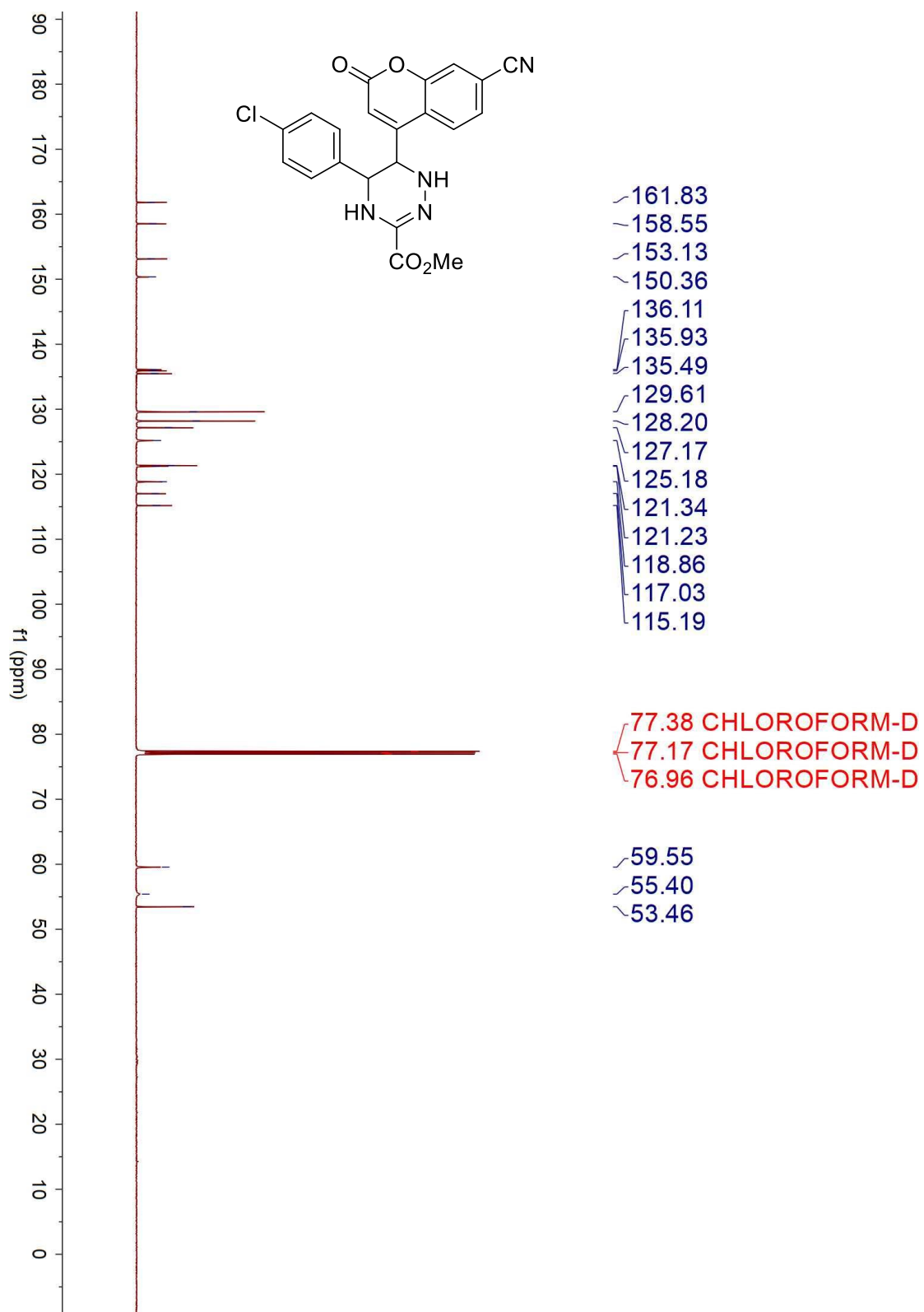
^{13}C -NMR spectra of compound **3fa** (CDCl_3 , 151 MHz)



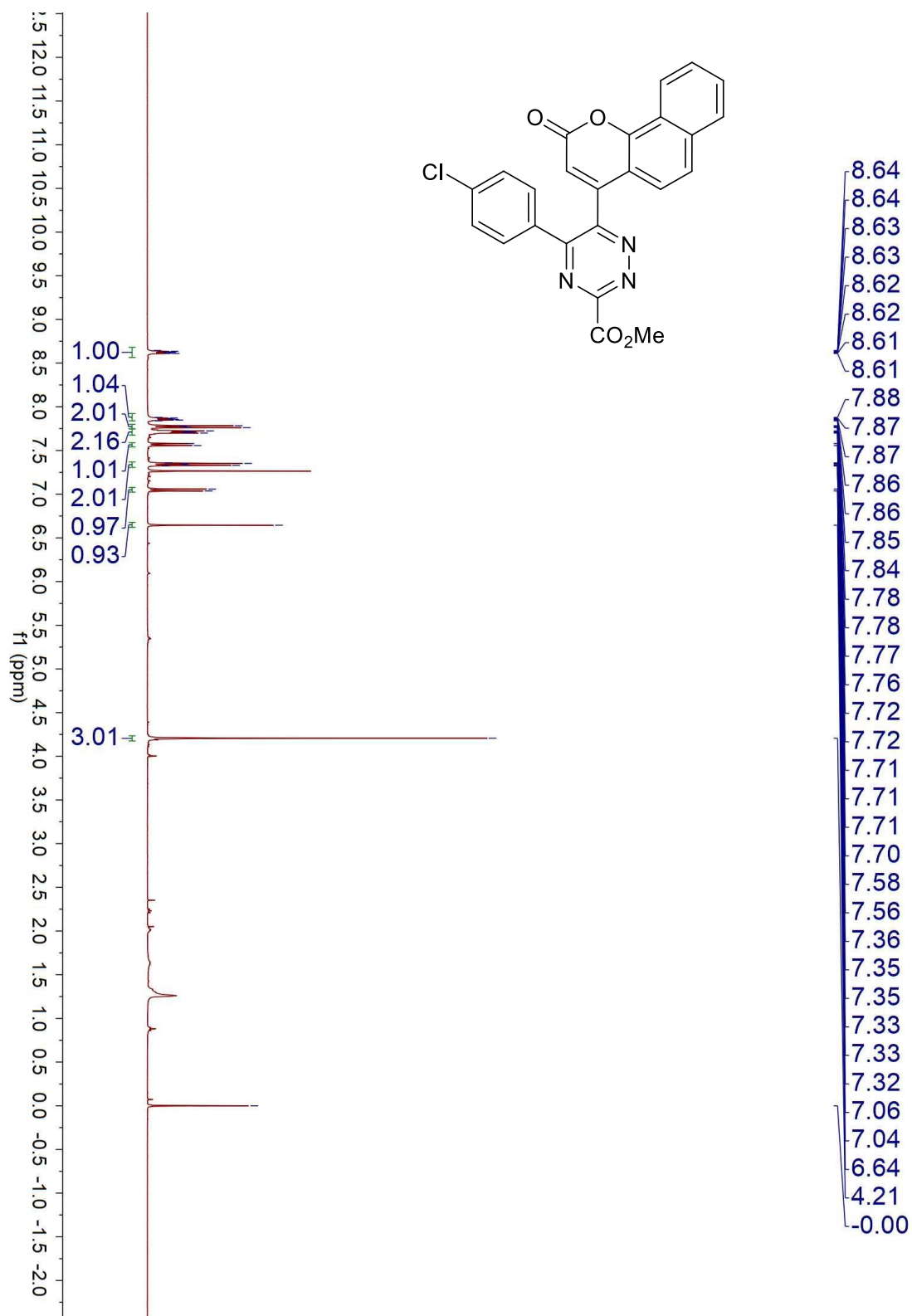
¹H-NMR spectra of compound **3ga** (CDCl₃, 600 MHz)



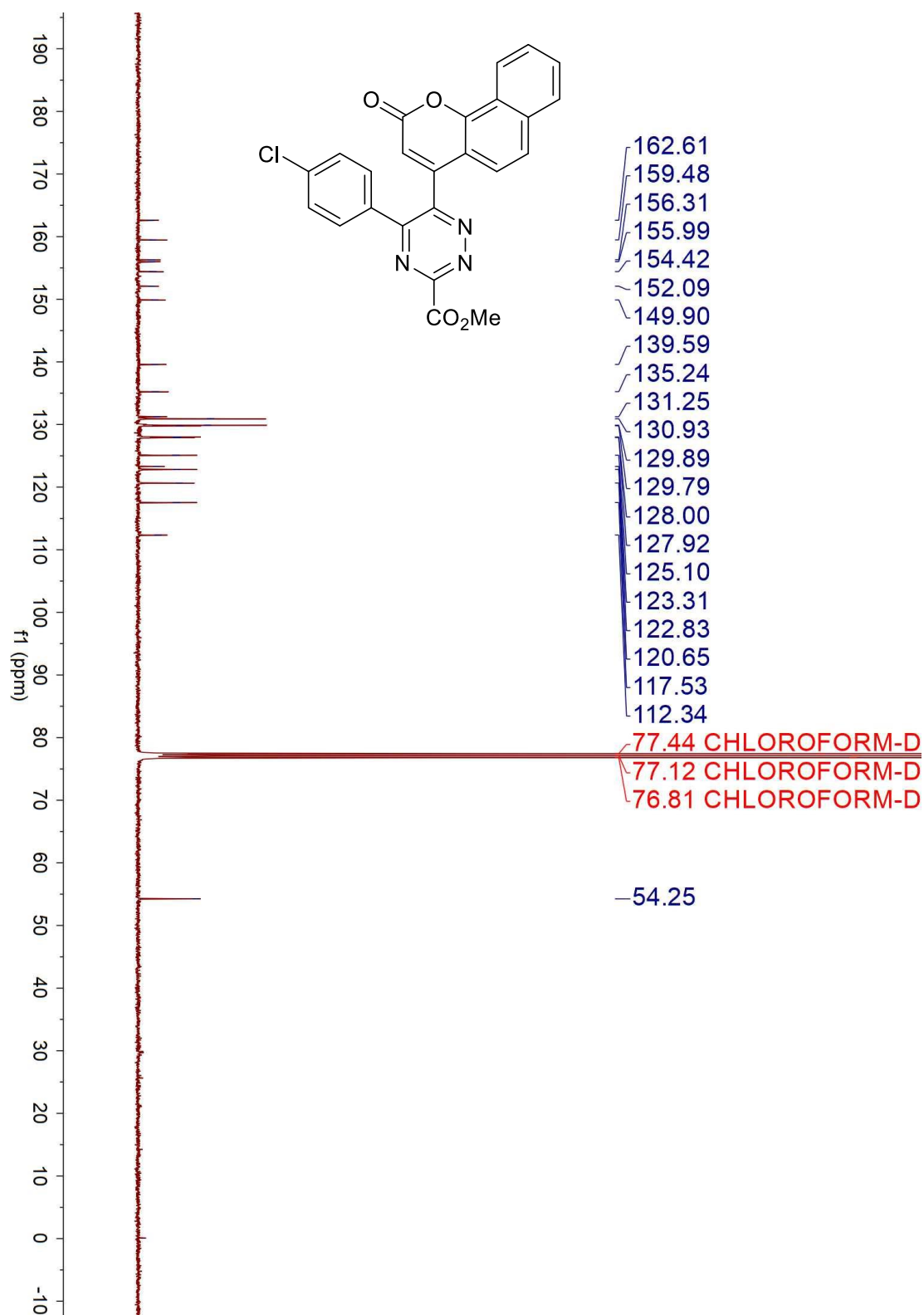
^{13}C -NMR spectra of compound **3ga** (CDCl_3 , 151 MHz)



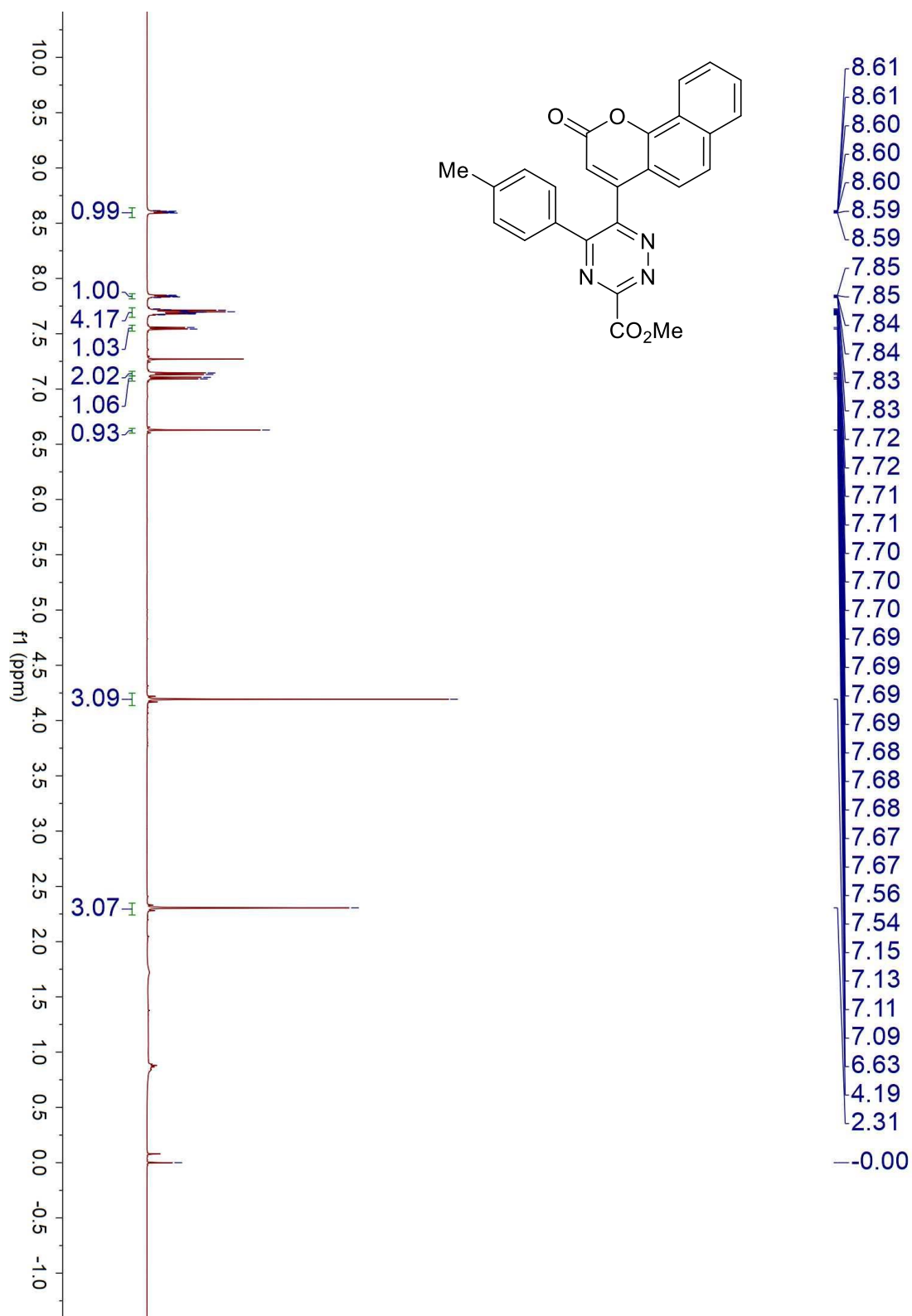
^1H -NMR spectra of compound **4a** (CDCl_3 , 600 MHz)



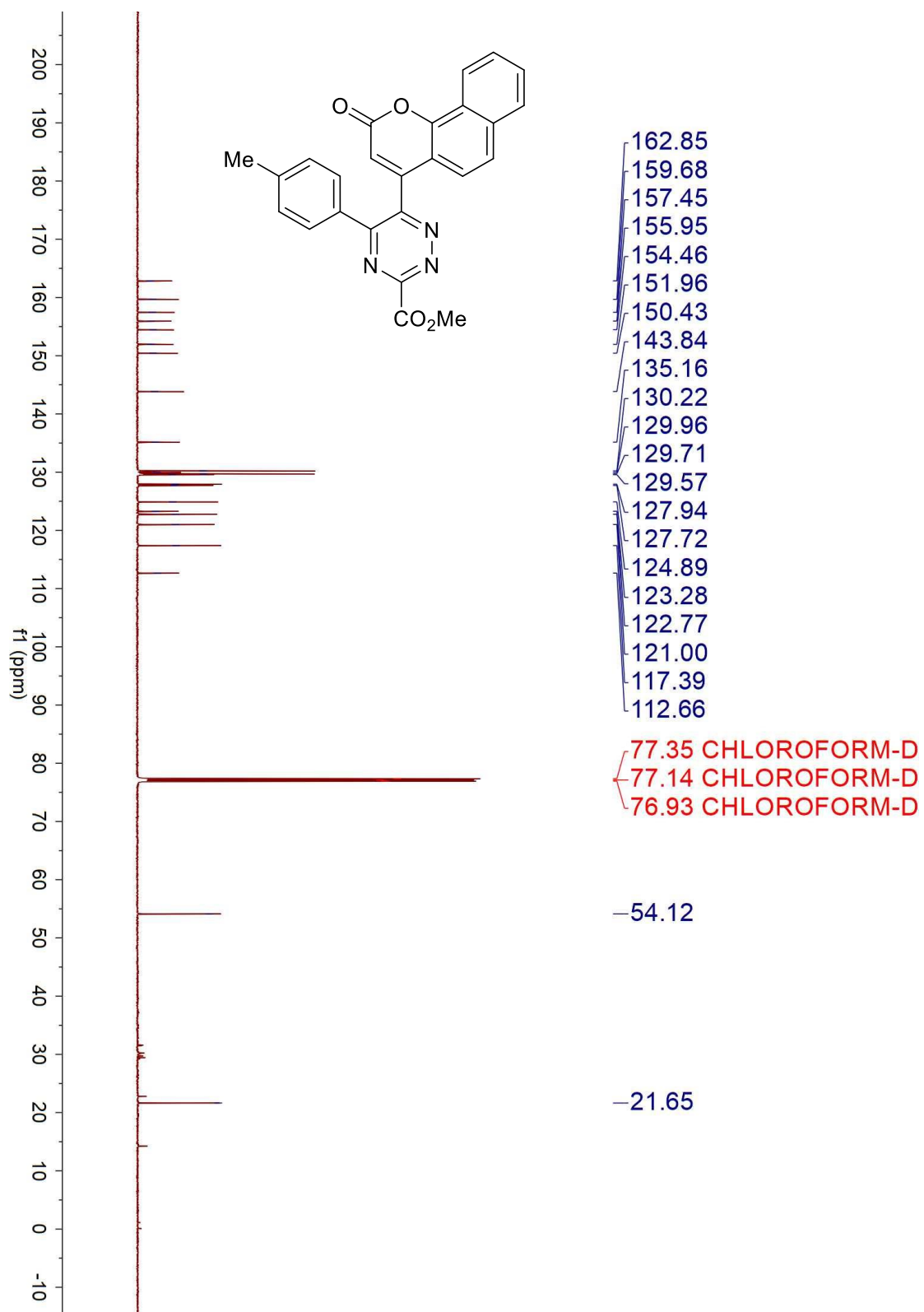
^{13}C -NMR spectra of compound **4a** (CDCl_3 , 151 MHz)



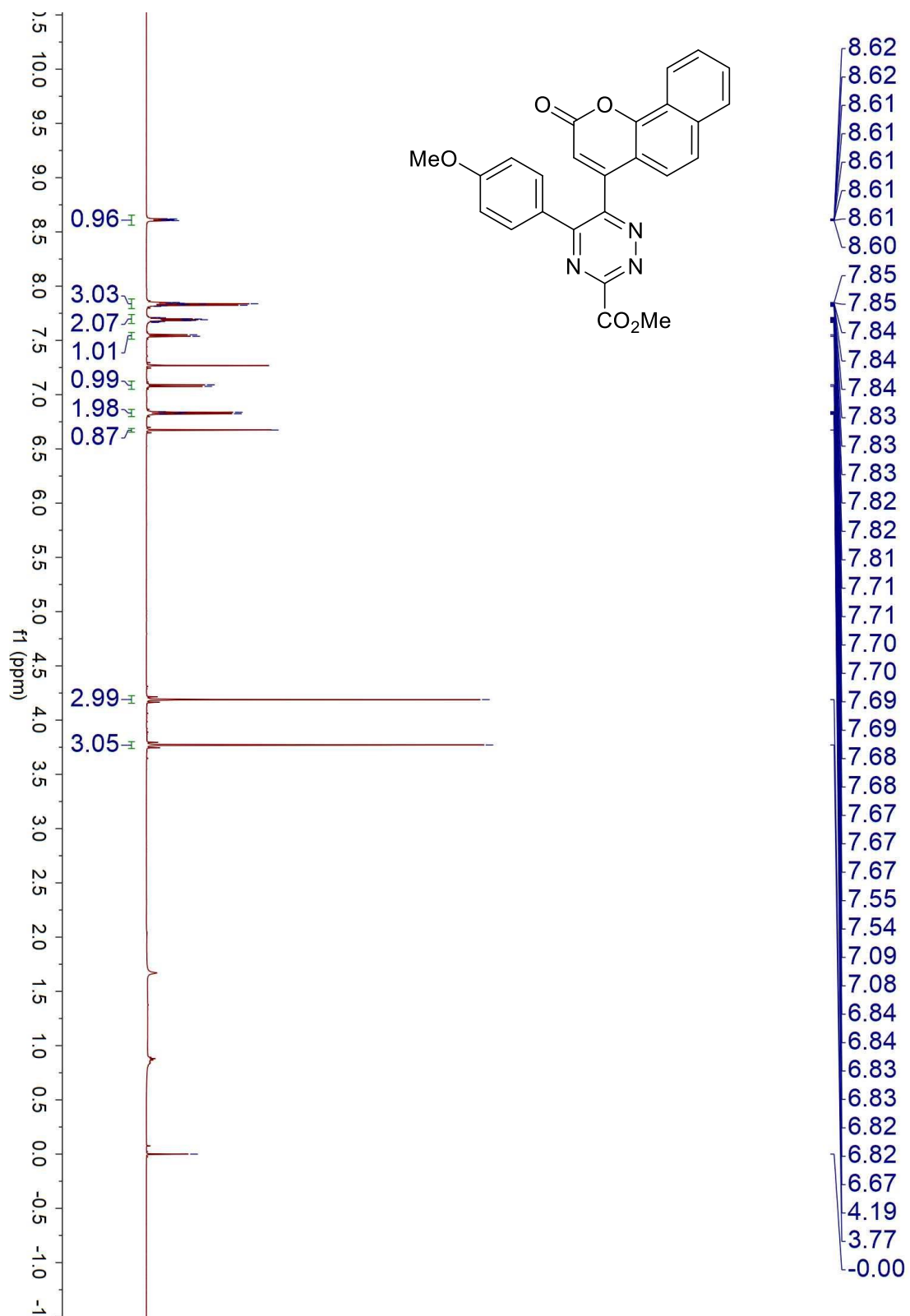
¹H-NMR spectra of compound **4b** (CDCl₃, 600 MHz)



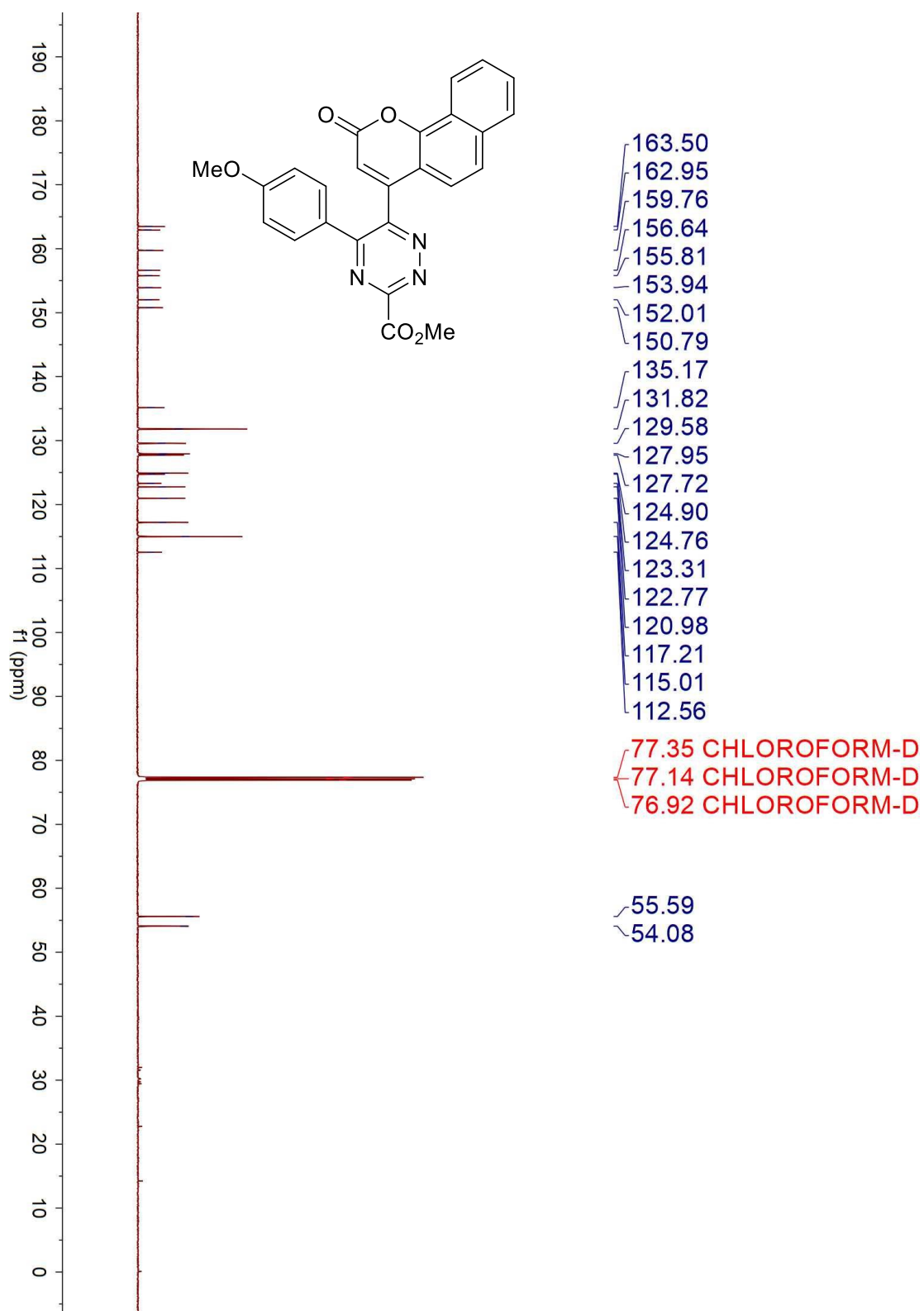
^{13}C -NMR spectra of compound **4b** (CDCl_3 , 151 MHz)



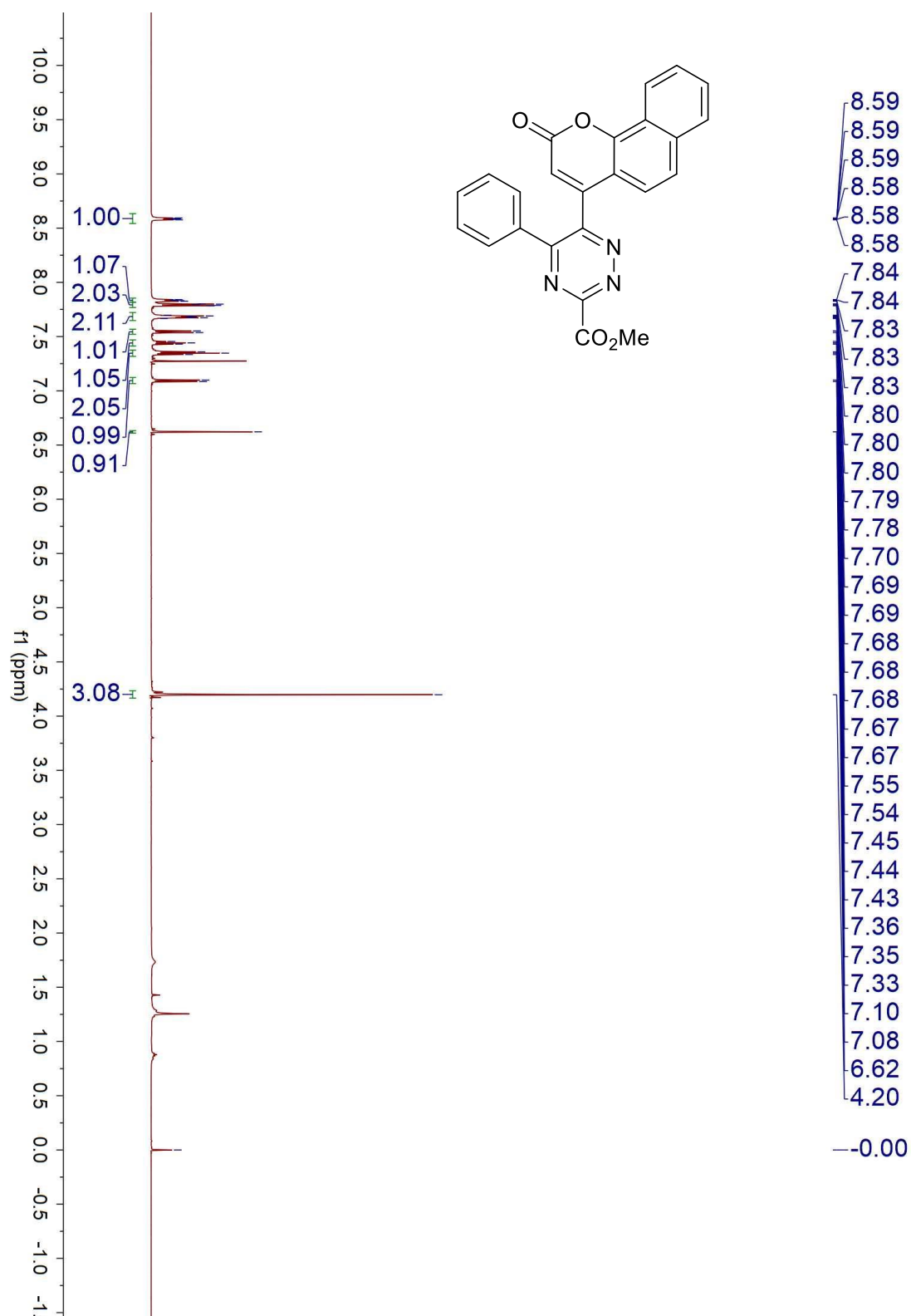
^1H -NMR spectra of compound **4c** (CDCl_3 , 600 MHz)



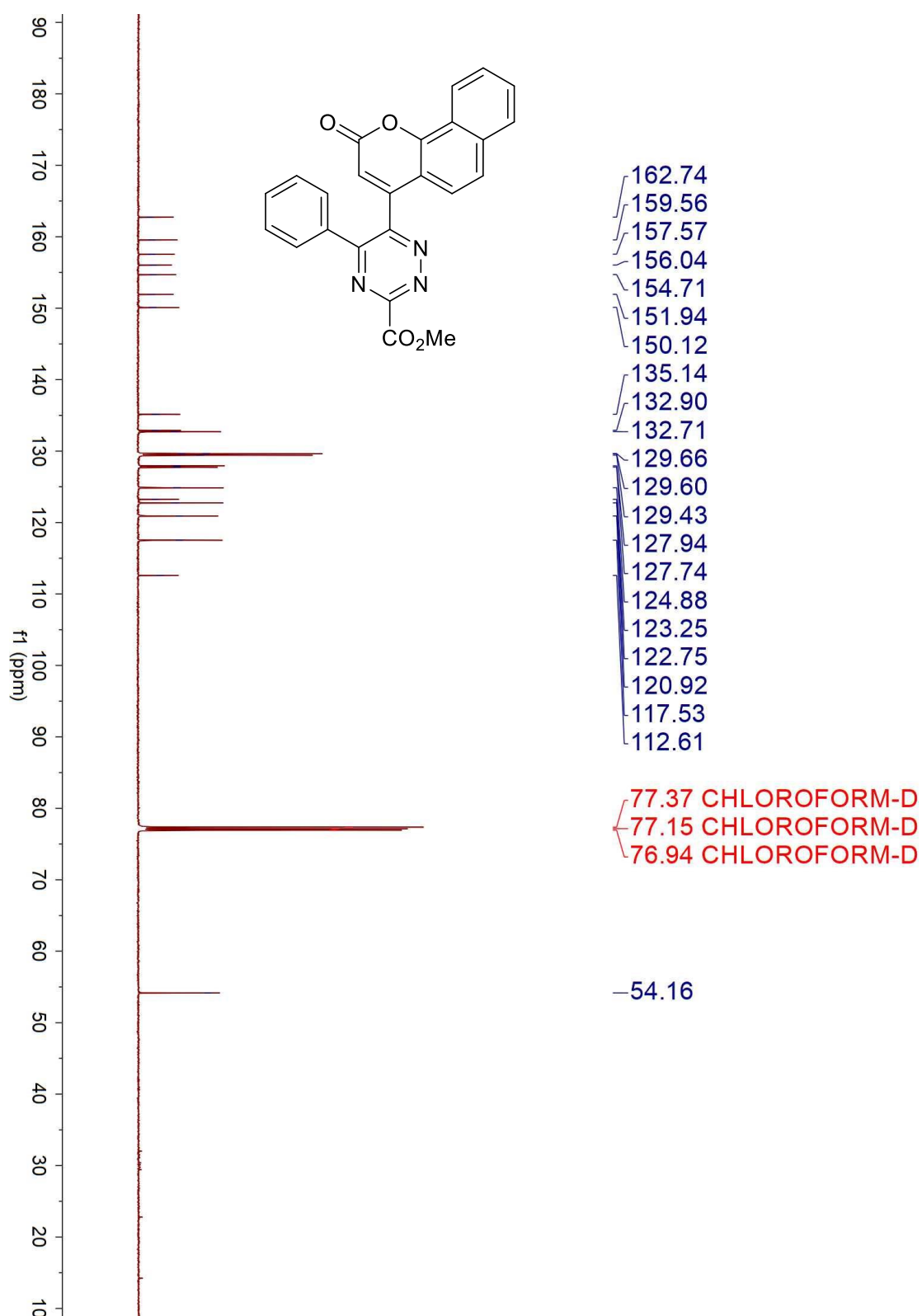
^{13}C -NMR spectra of compound **4c** (CDCl_3 , 151 MHz)



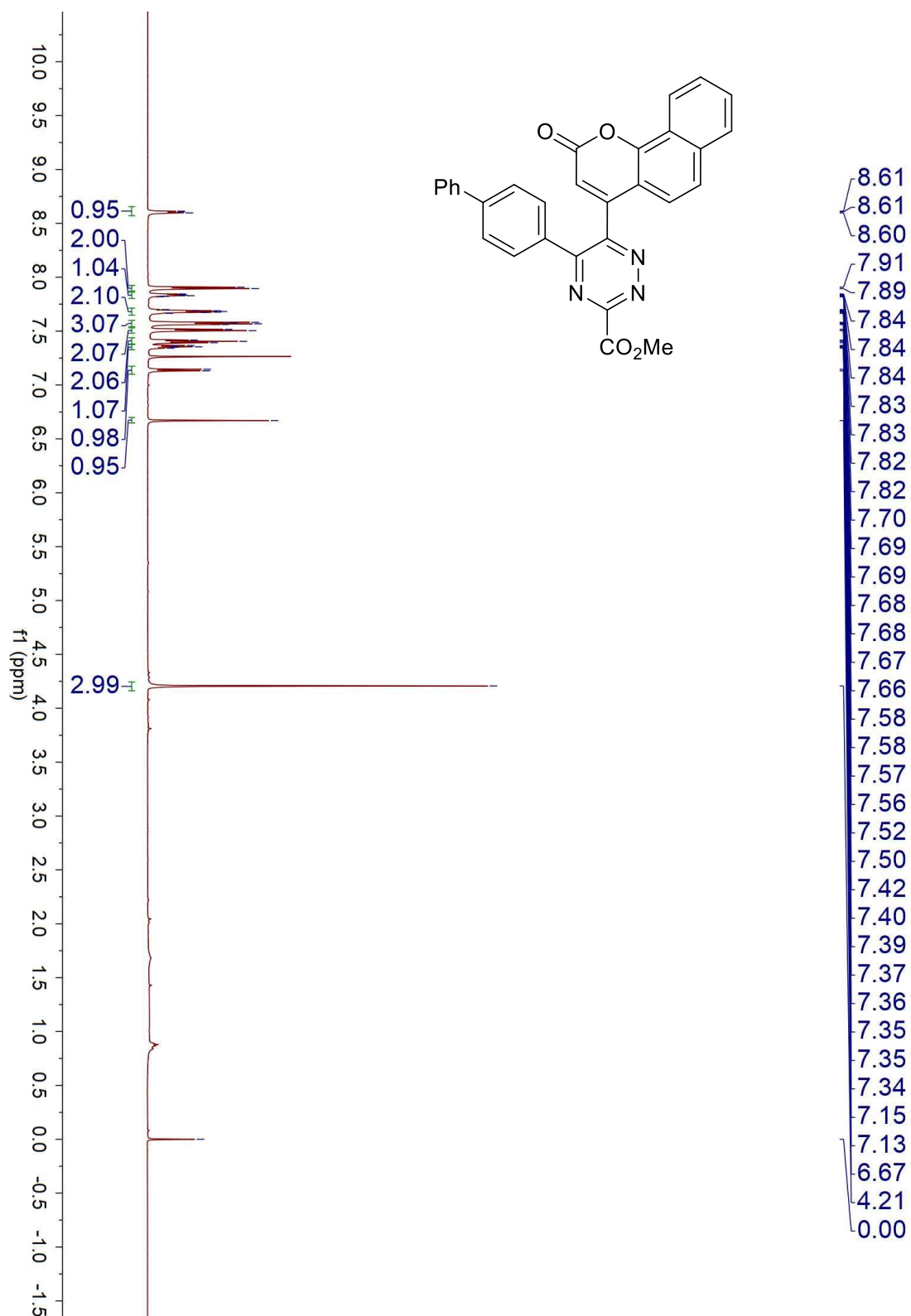
^1H -NMR spectra of compound **4d** (CDCl_3 , 600 MHz)



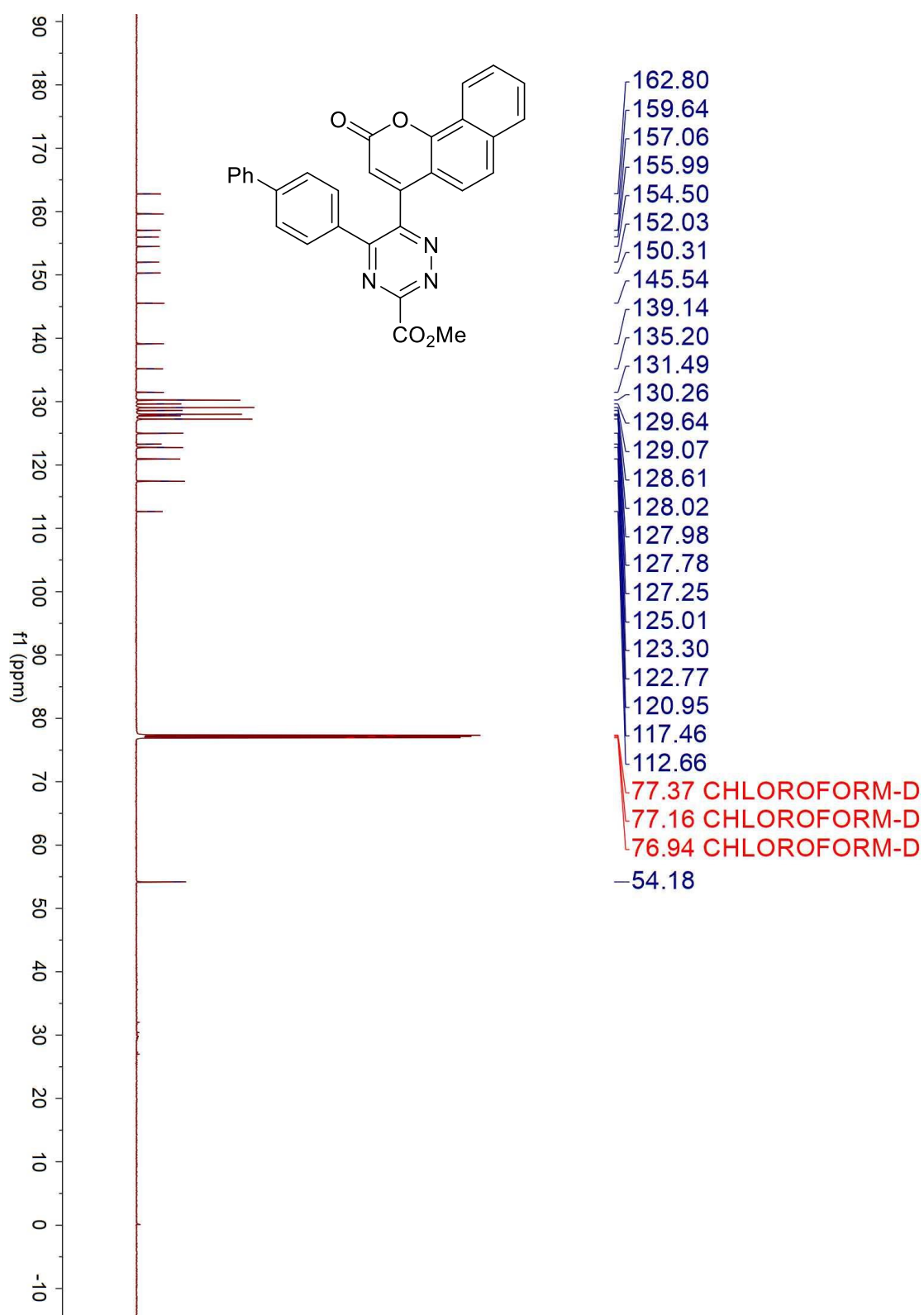
^{13}C -NMR spectra of compound **4d** (CDCl_3 , 151 MHz)



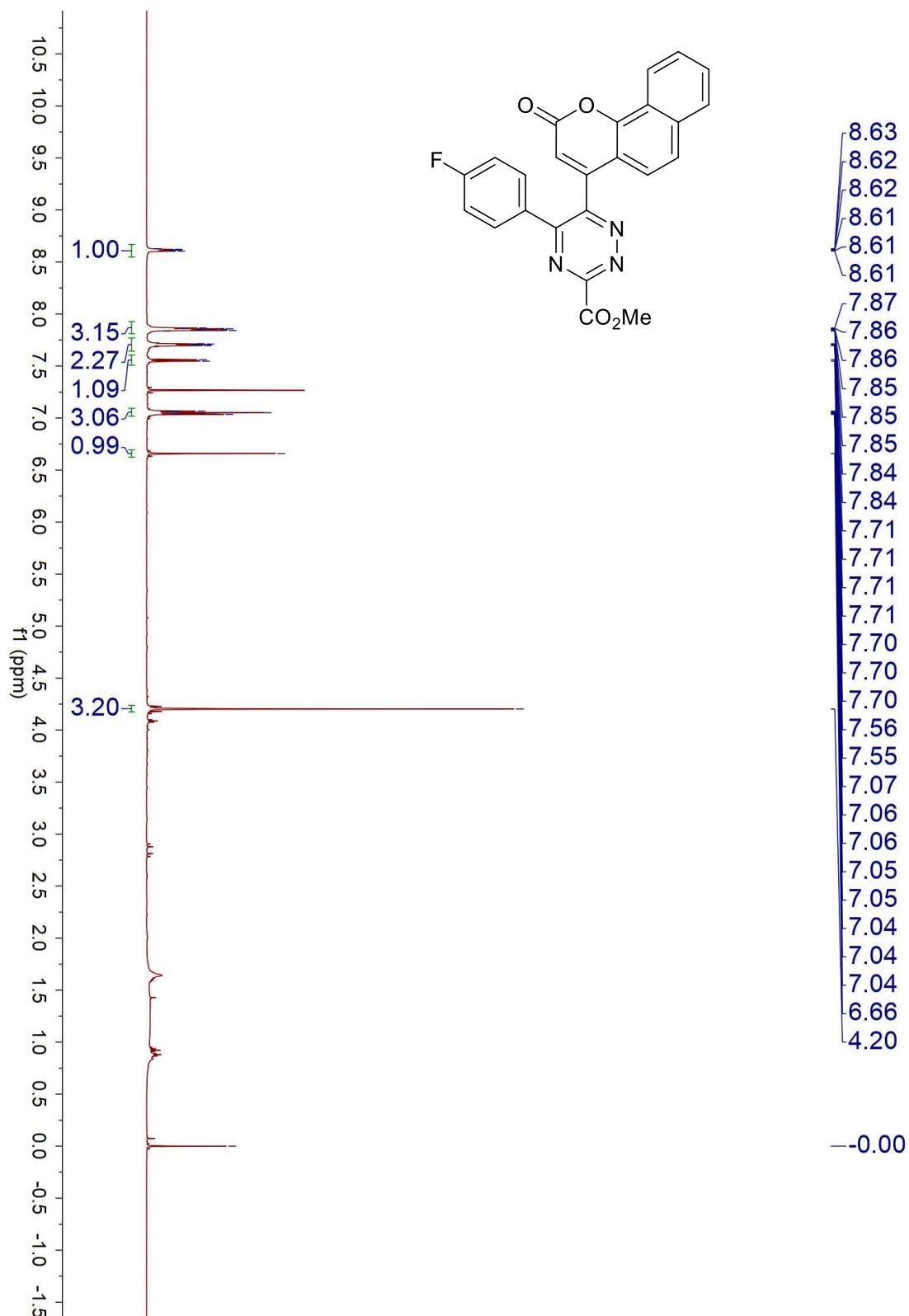
¹H-NMR spectra of compound **4e** (CDCl₃, 600 MHz)



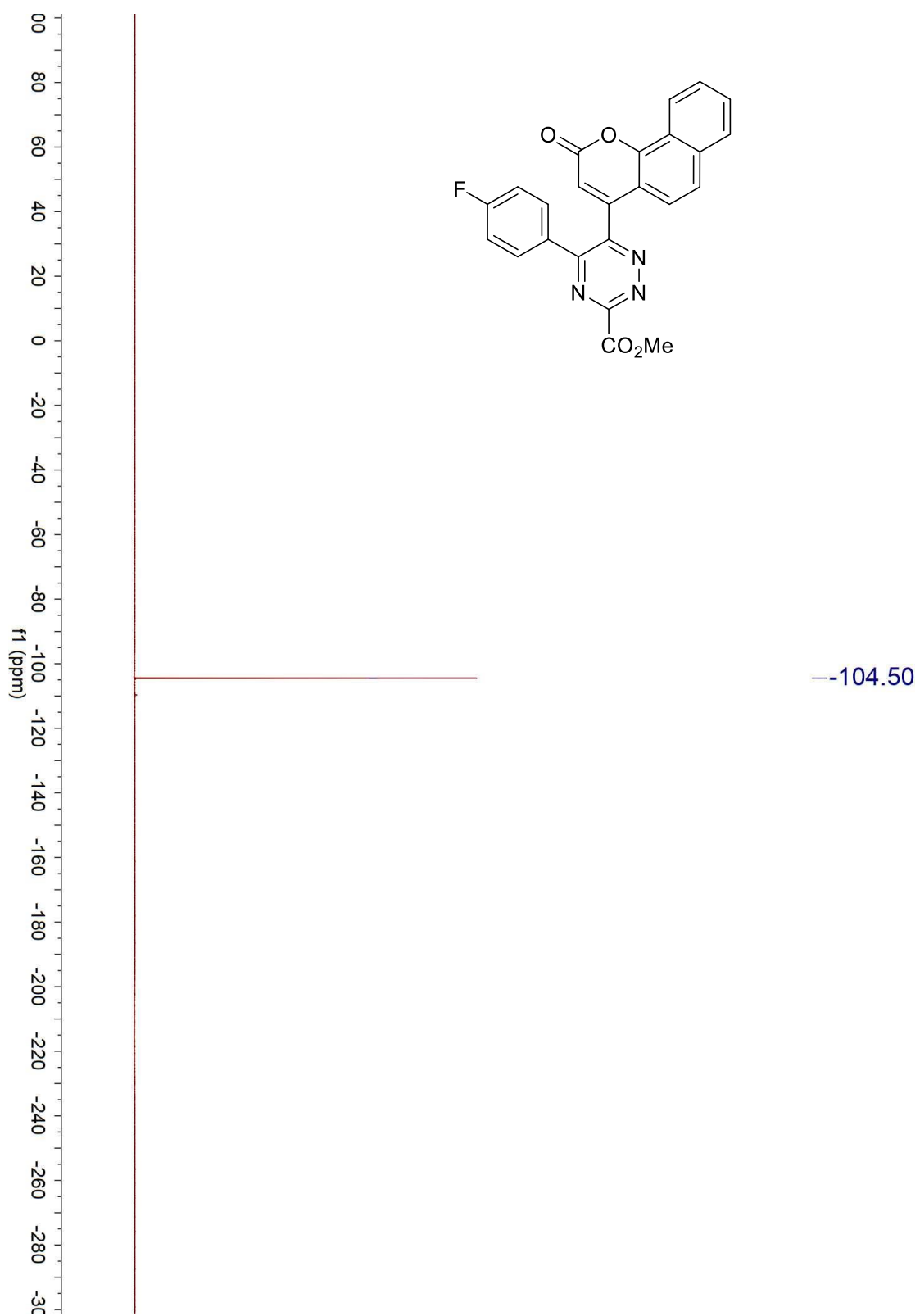
^{13}C -NMR spectra of compound **4e** (CDCl_3 , 151 MHz)



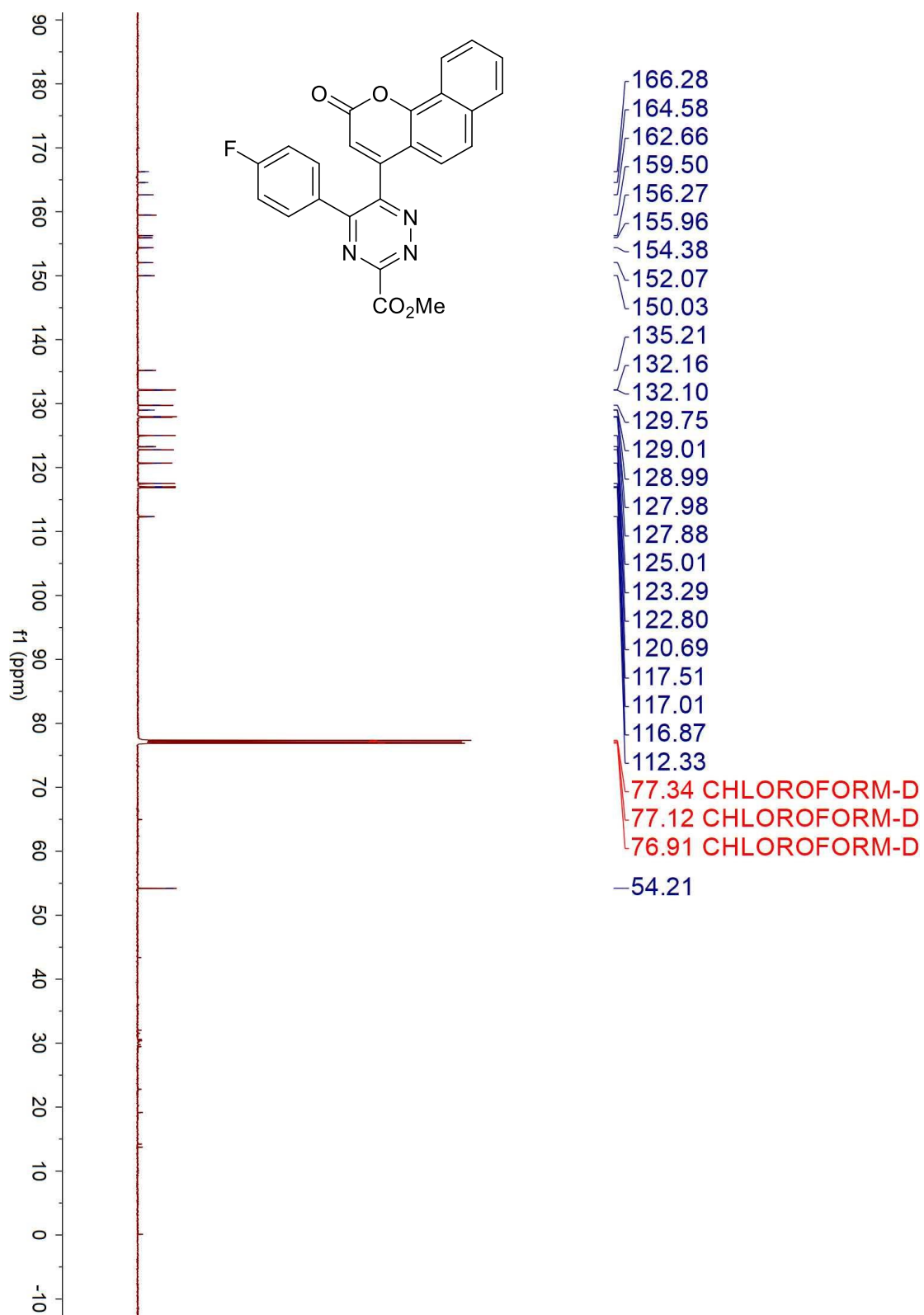
^1H -NMR spectra of compound **4f** (CDCl_3 , 600 MHz)



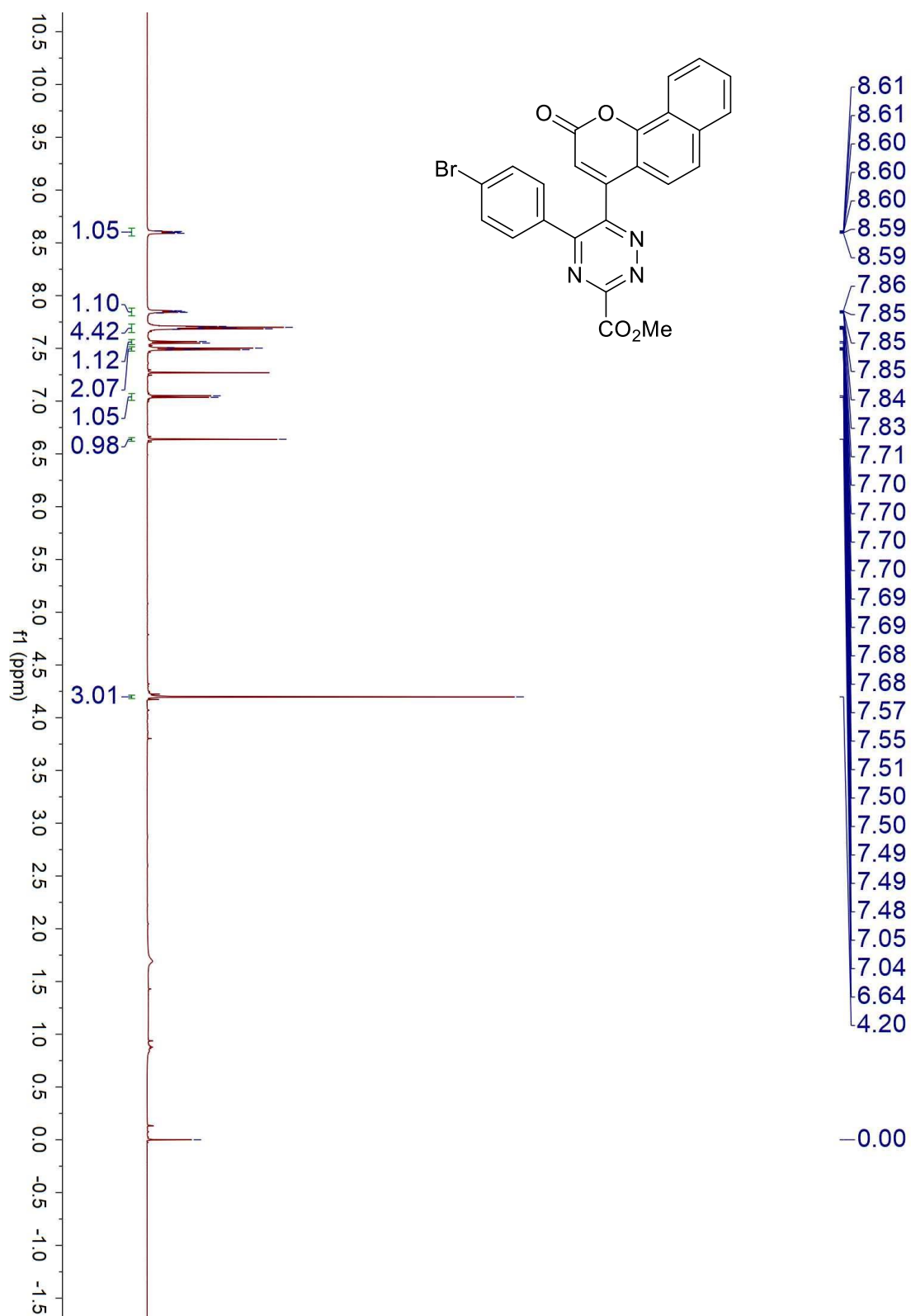
^{19}F -NMR spectra of compound **4f** (CDCl_3 , 565 MHz)



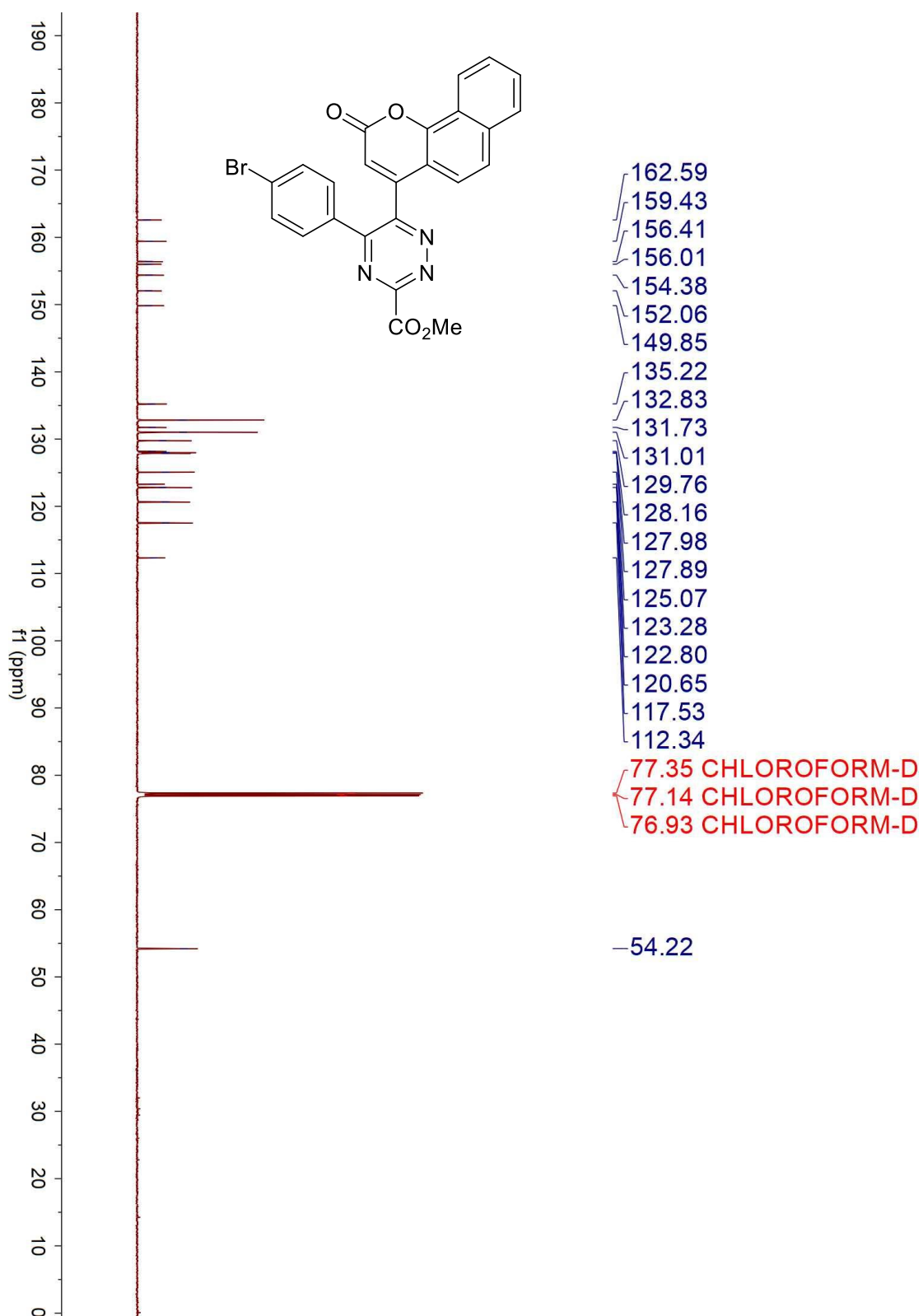
^{13}C -NMR spectra of compound **4f** (CDCl_3 , 151 MHz)



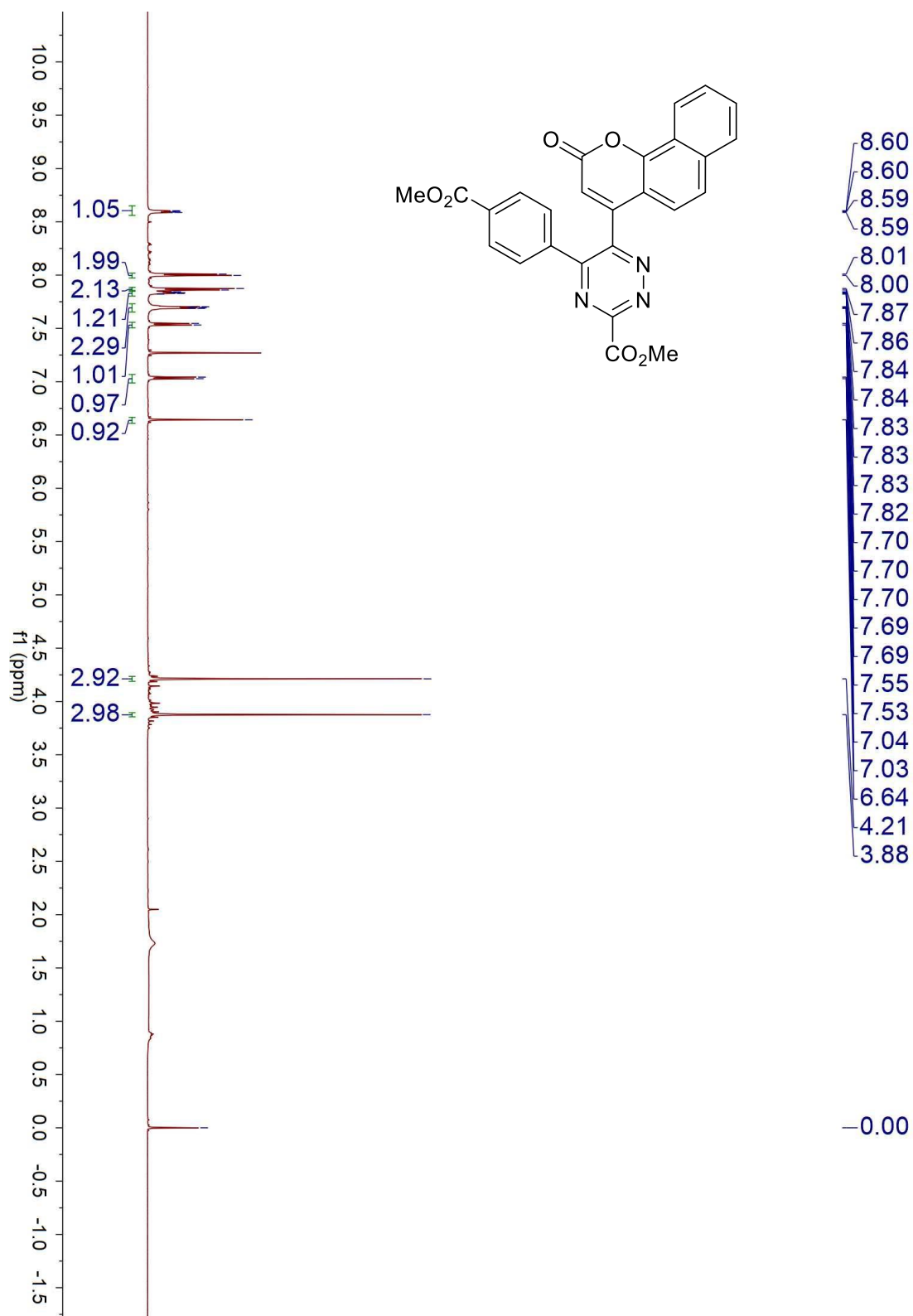
^1H -NMR spectra of compound **4g** (CDCl_3 , 600 MHz)



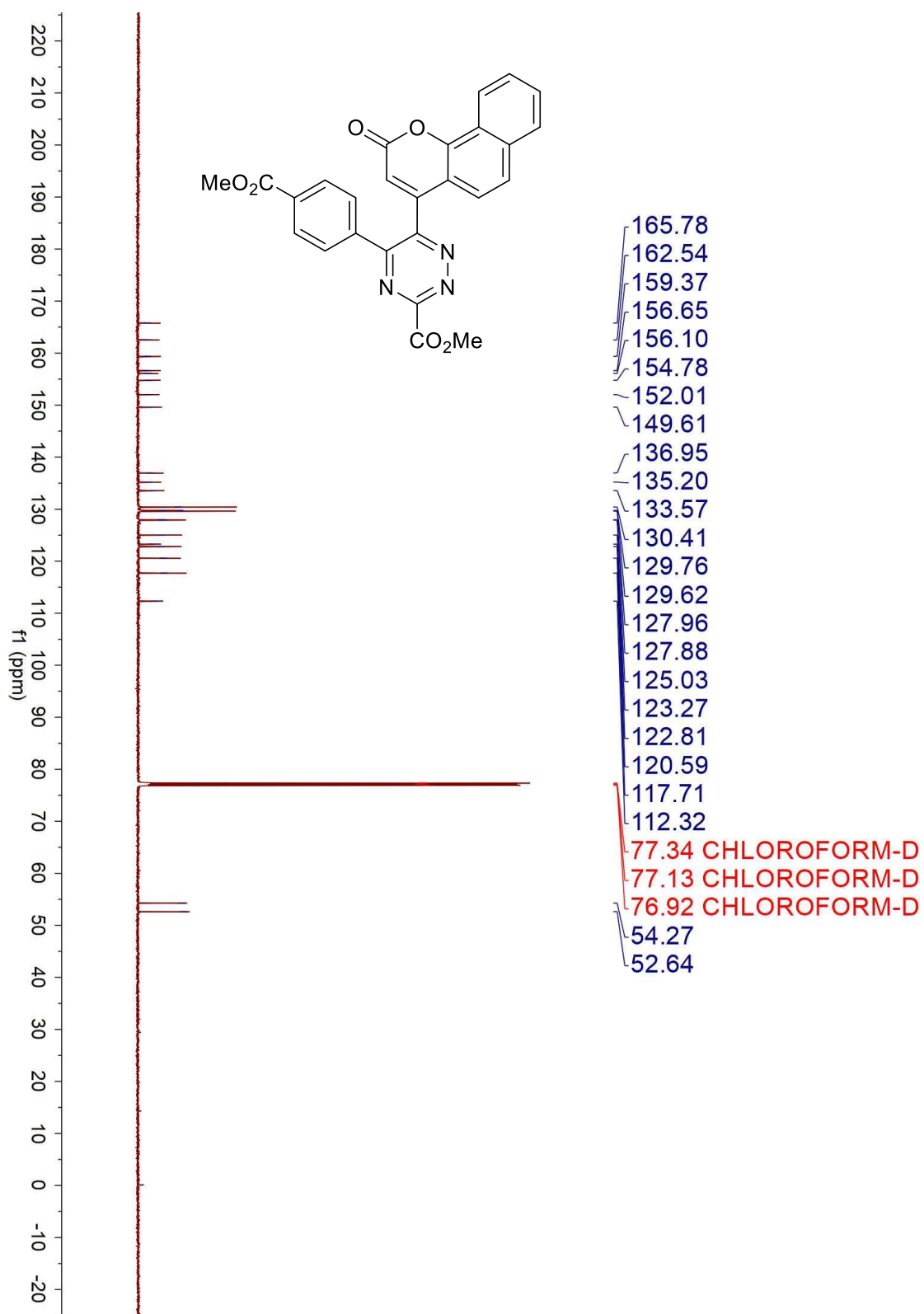
^{13}C -NMR spectra of compound **4g** (CDCl_3 , 151 MHz)



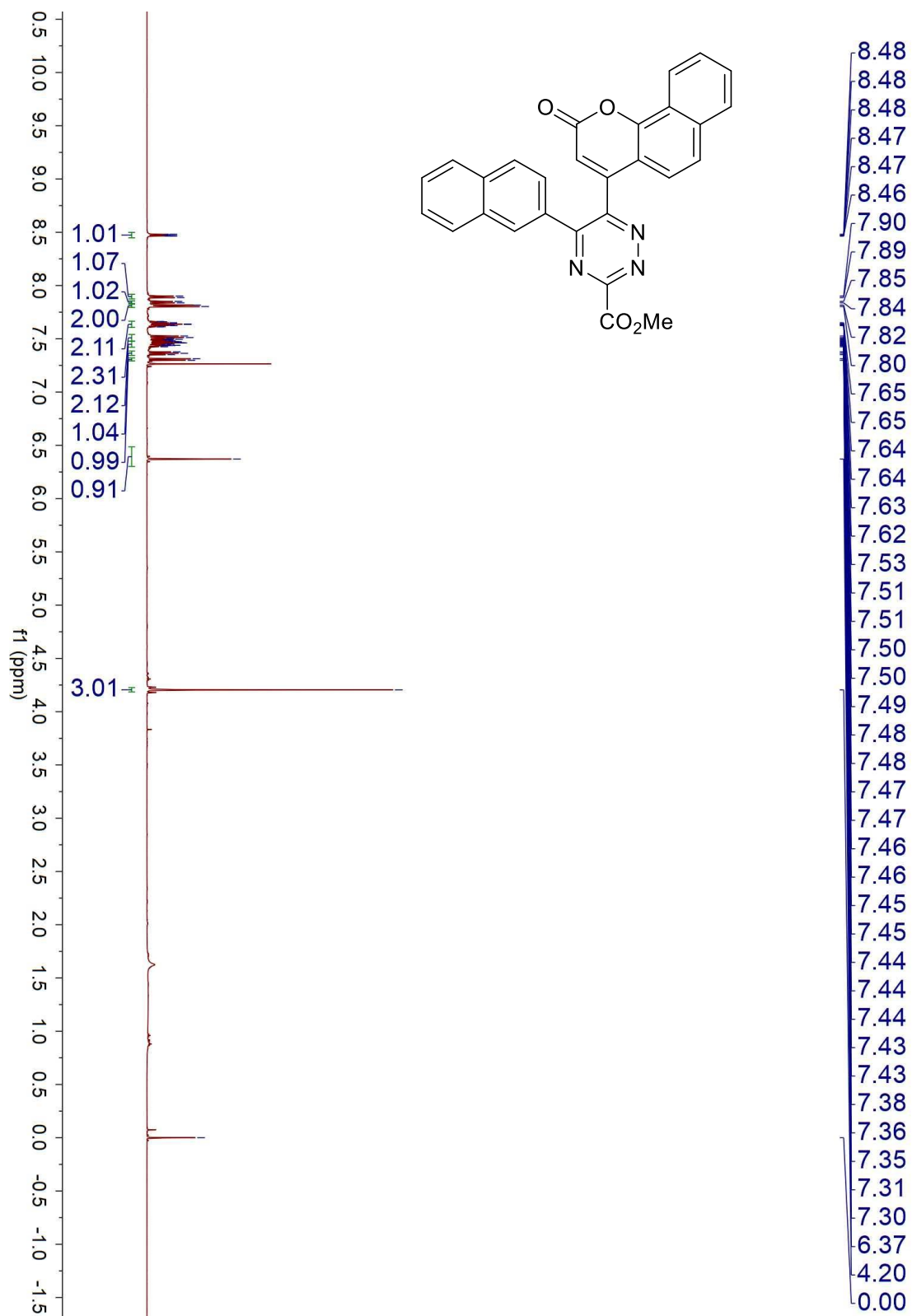
¹H-NMR spectra of compound **4h** (CDCl₃, 600 MHz)



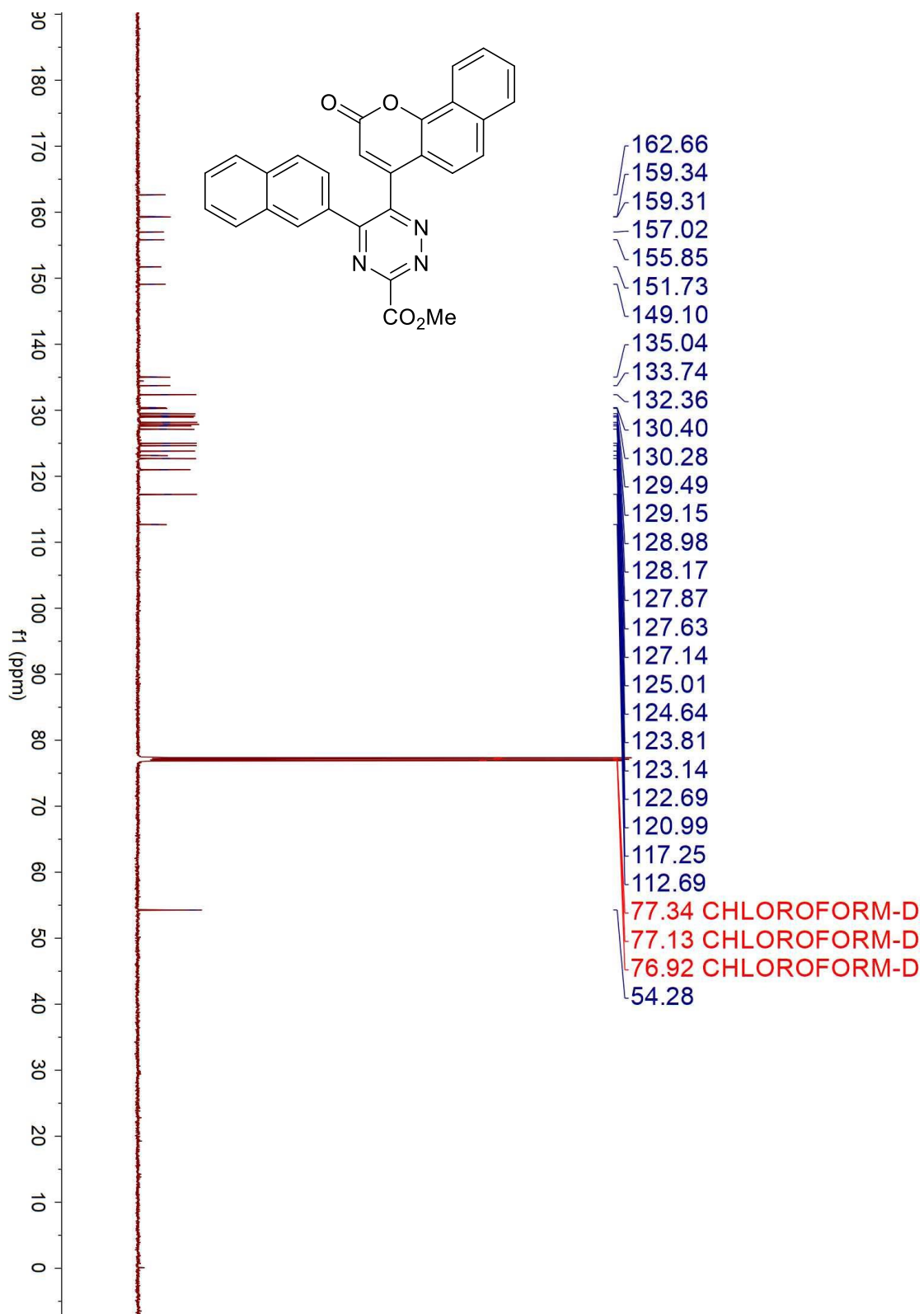
^{13}C -NMR spectra of compound **4h** (CDCl_3 , 151 MHz)



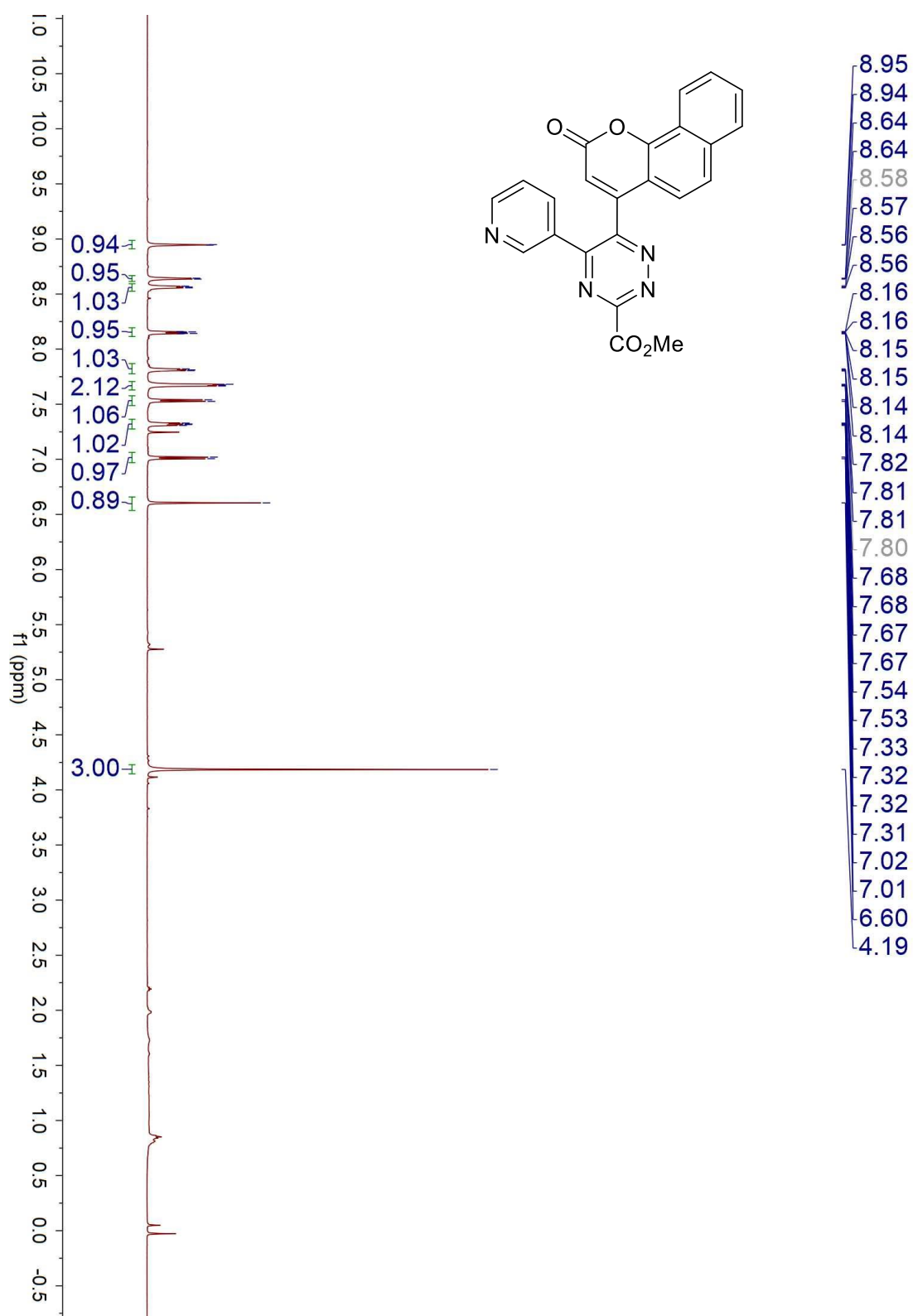
¹H-NMR spectra of compound **4i** (CDCl₃, 600 MHz)



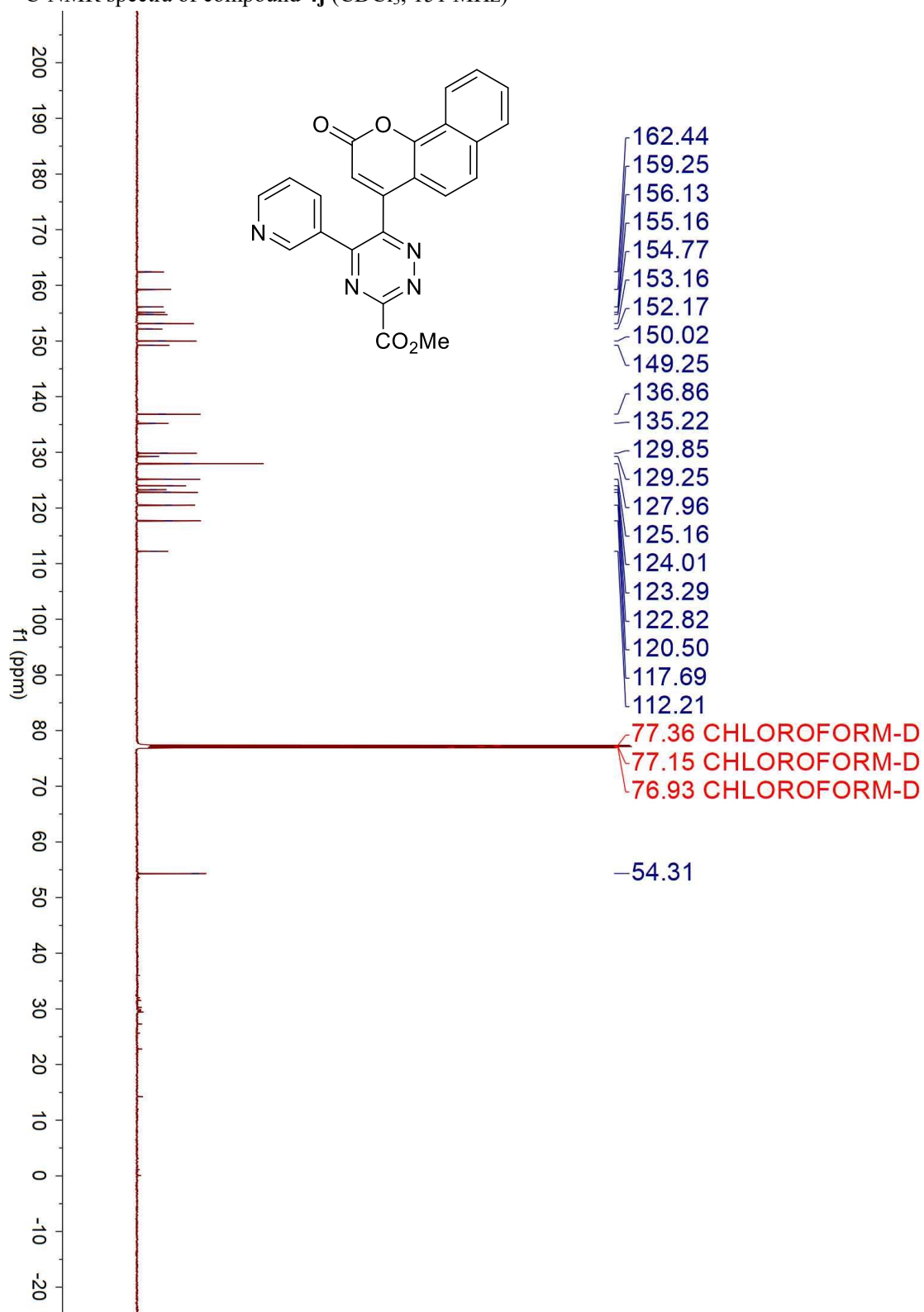
^{13}C -NMR spectra of compound **4i** (CDCl_3 , 151 MHz)



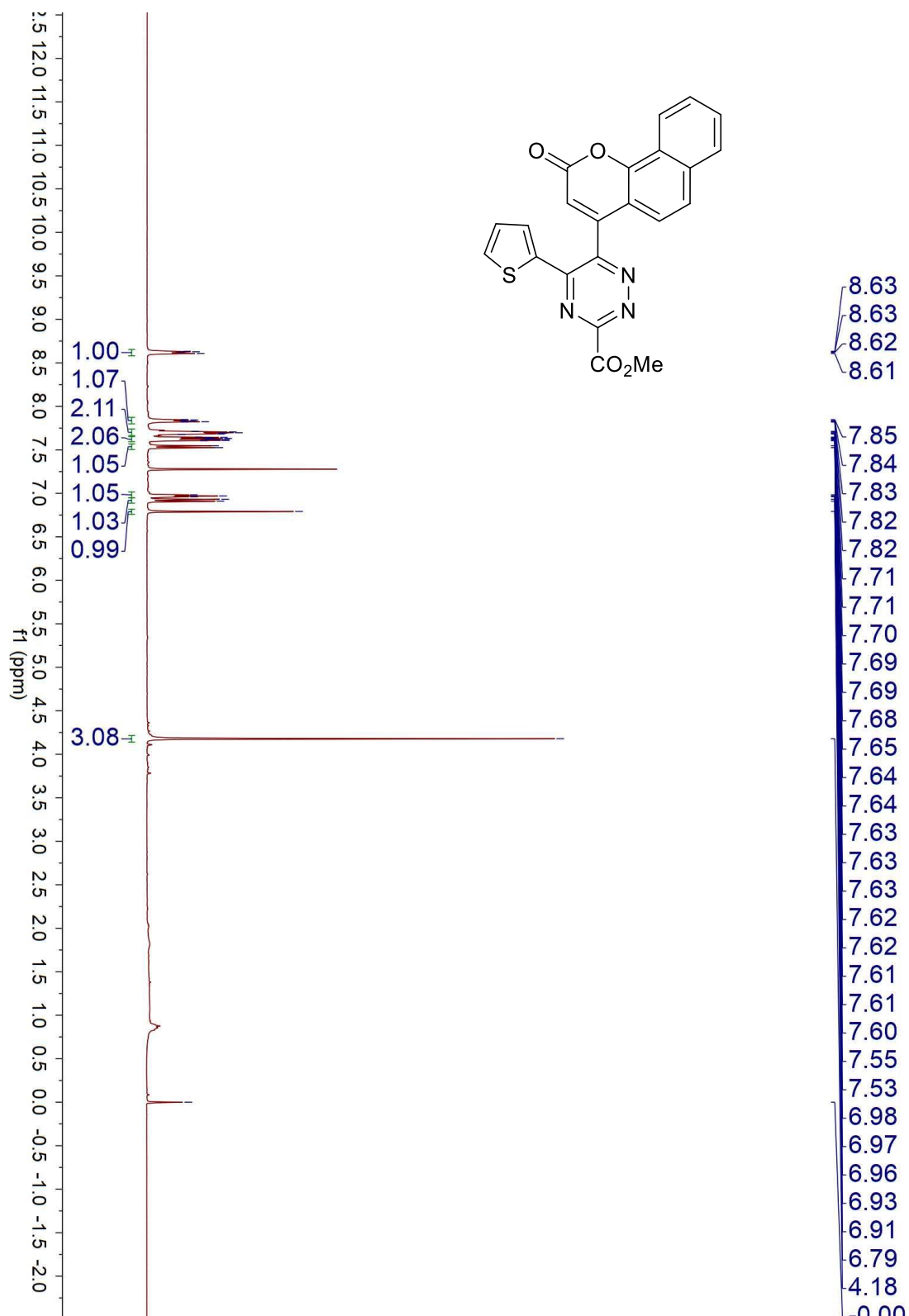
¹H-NMR spectra of compound **4j** (CDCl₃, 600 MHz)



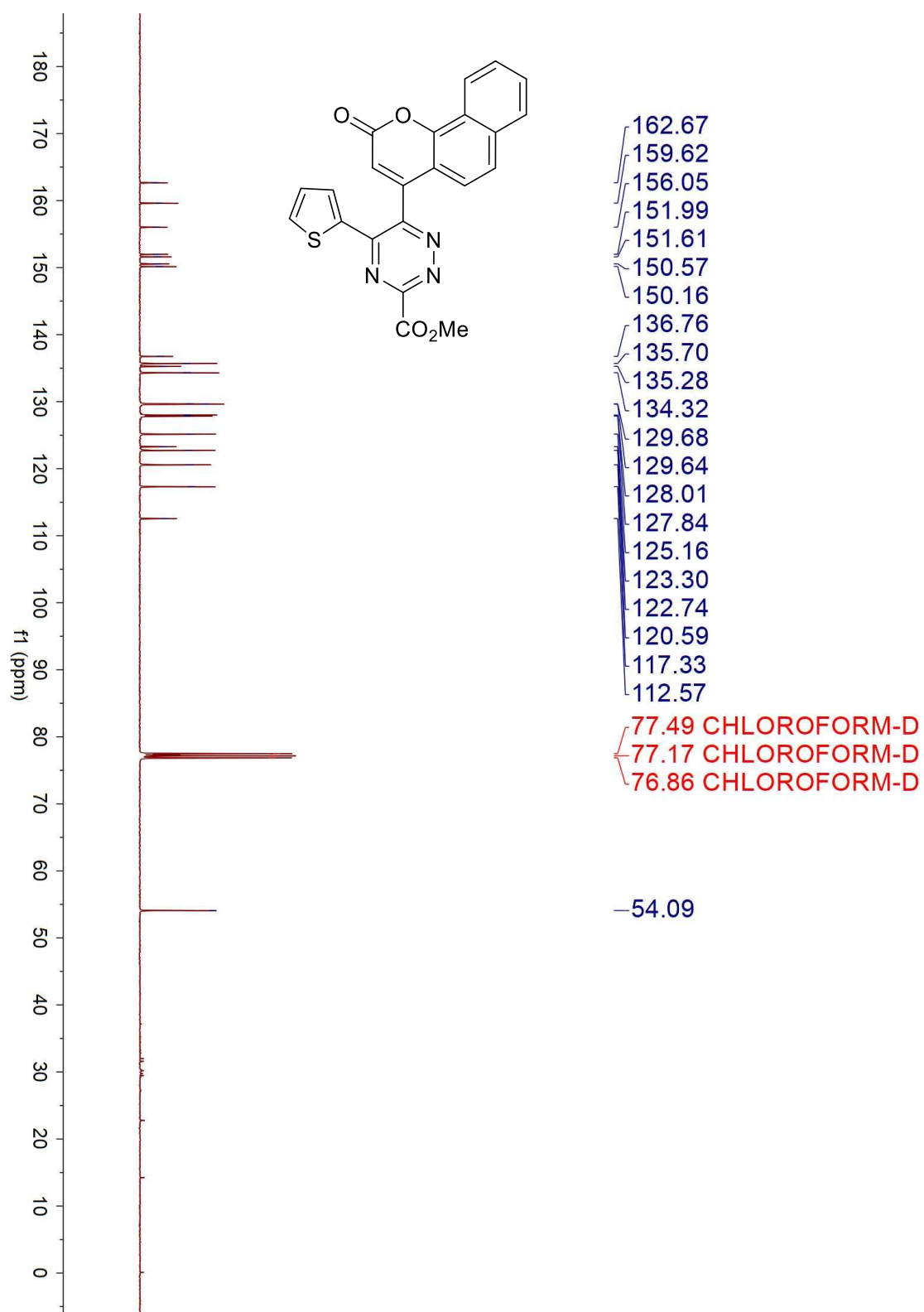
^{13}C -NMR spectra of compound **4j** (CDCl_3 , 151 MHz)



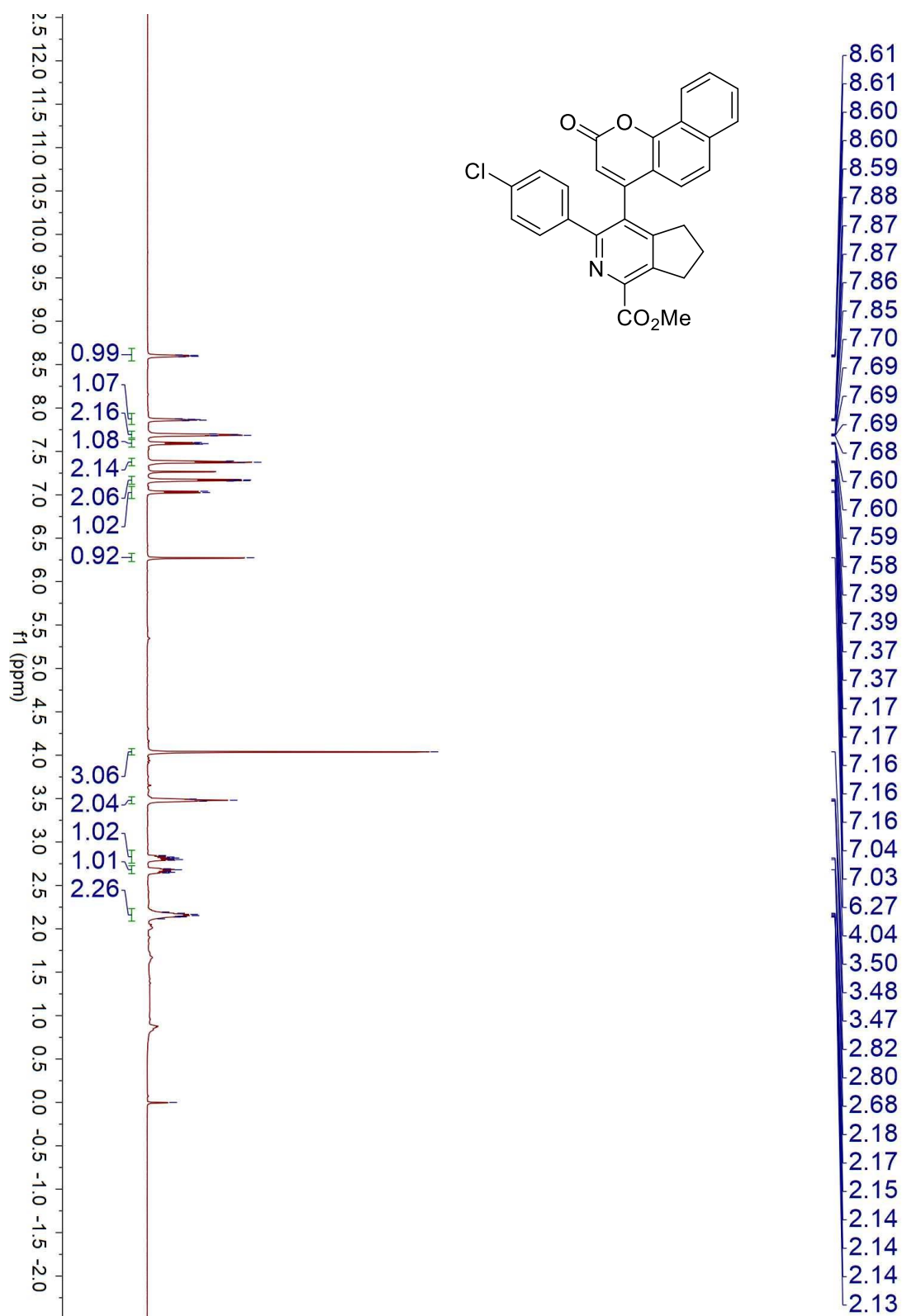
^1H -NMR spectra of compound **4k** (CDCl_3 , 600 MHz)



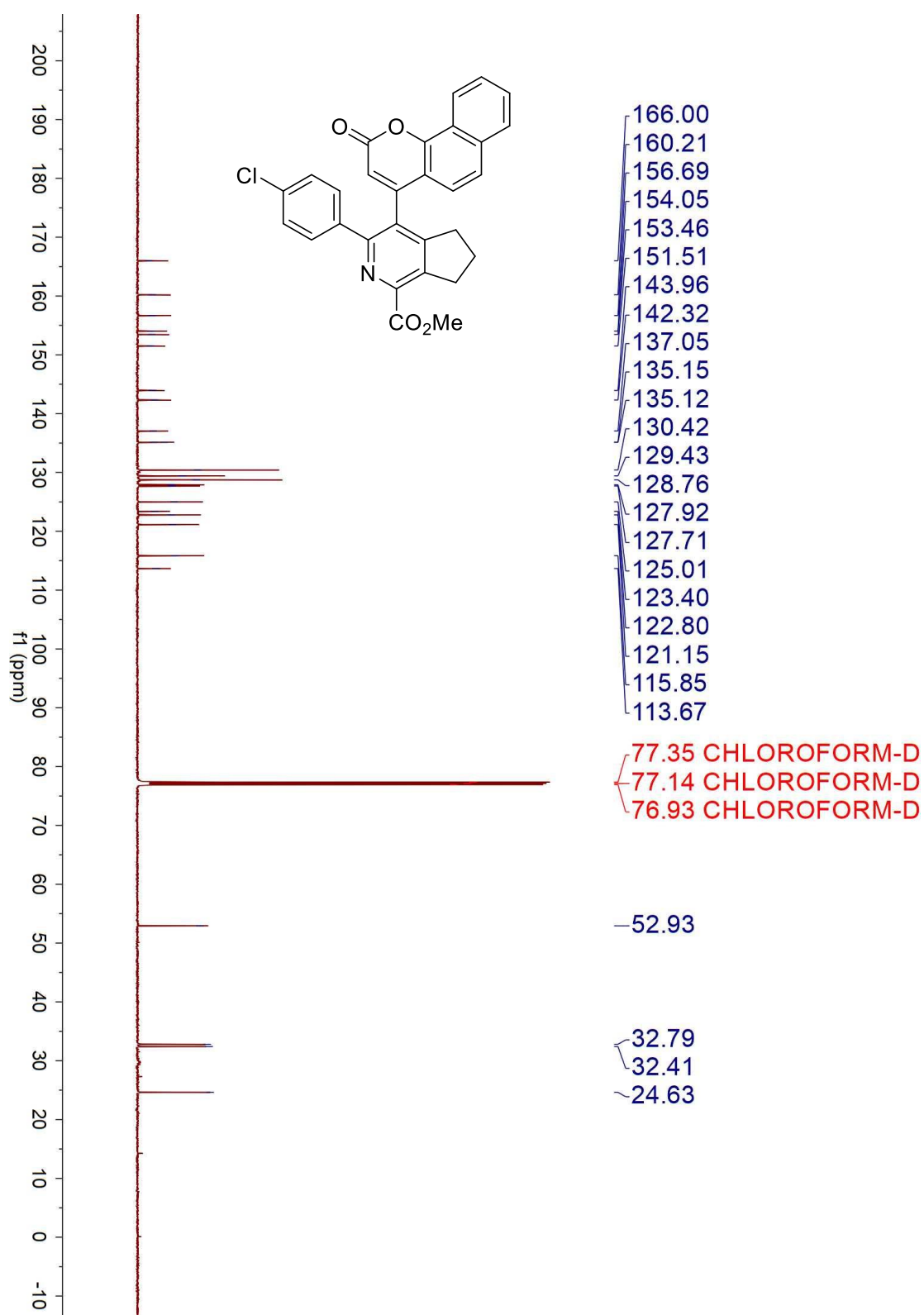
^{13}C -NMR spectra of compound **4k** (CDCl_3 , 151 MHz)



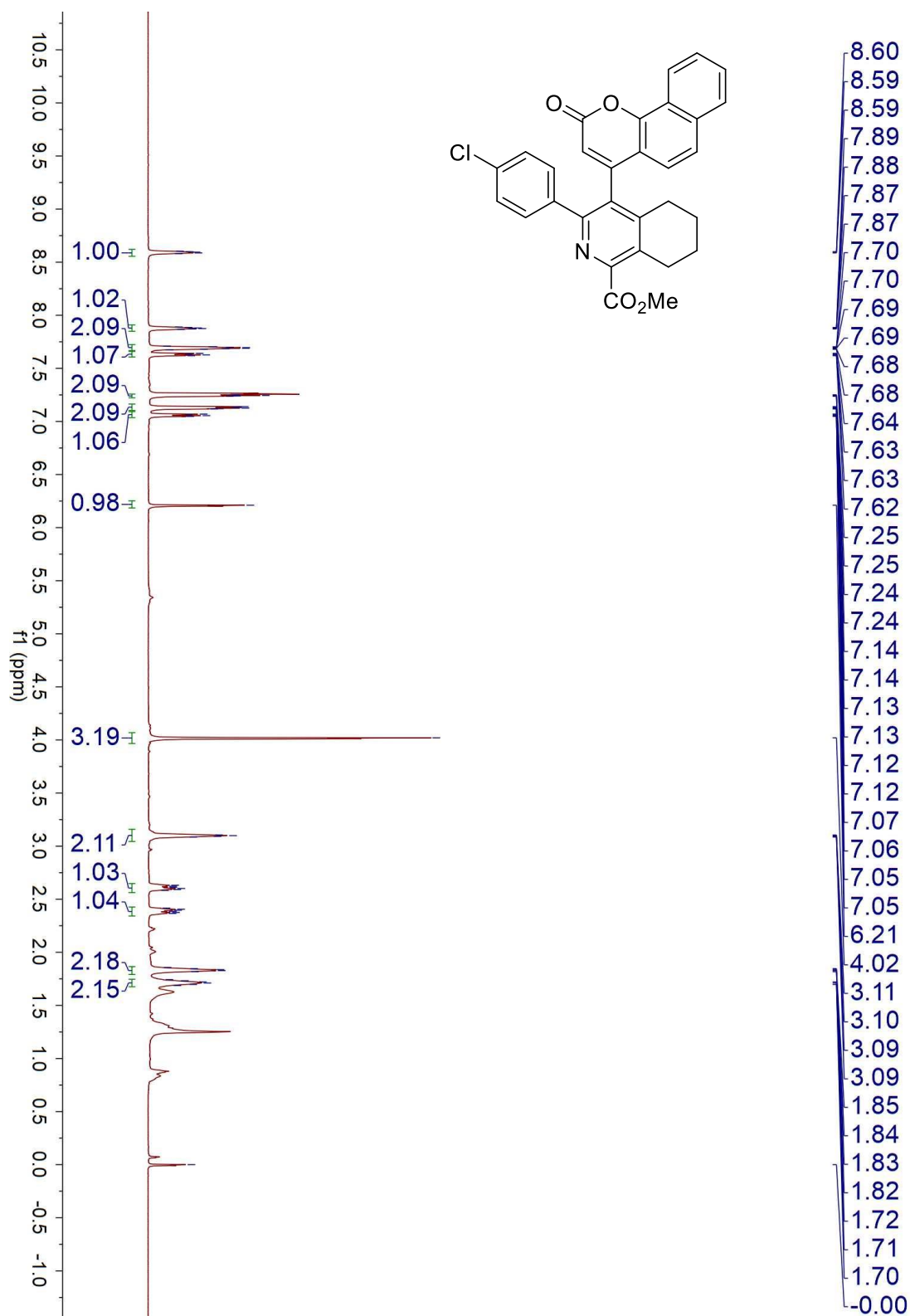
^1H -NMR spectra of compound **5a** (CDCl_3 , 600 MHz)



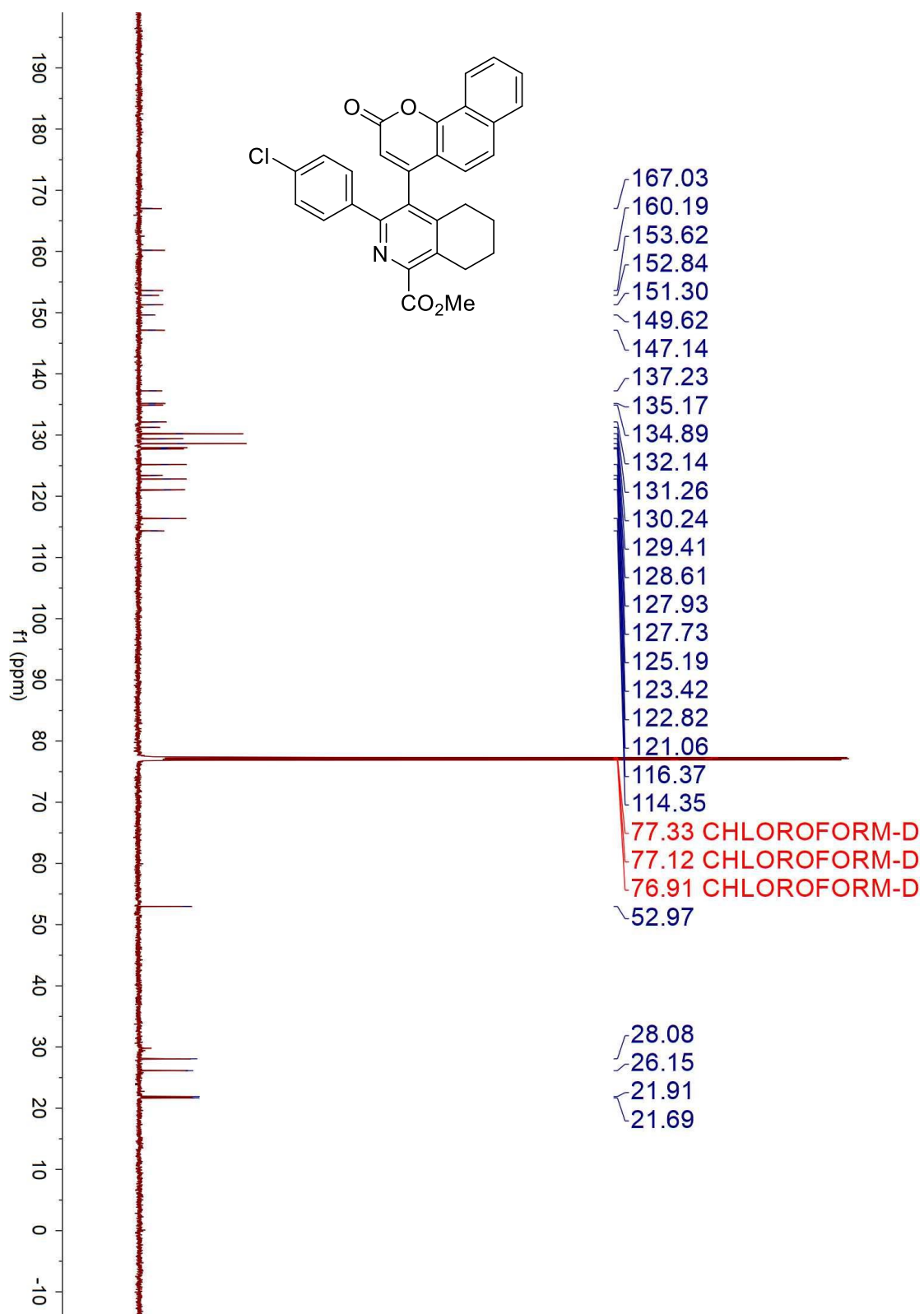
^{13}C -NMR spectra of compound **5a** (CDCl_3 , 151 MHz)



¹H-NMR spectra of compound **5b** (CDCl₃, 600 MHz)

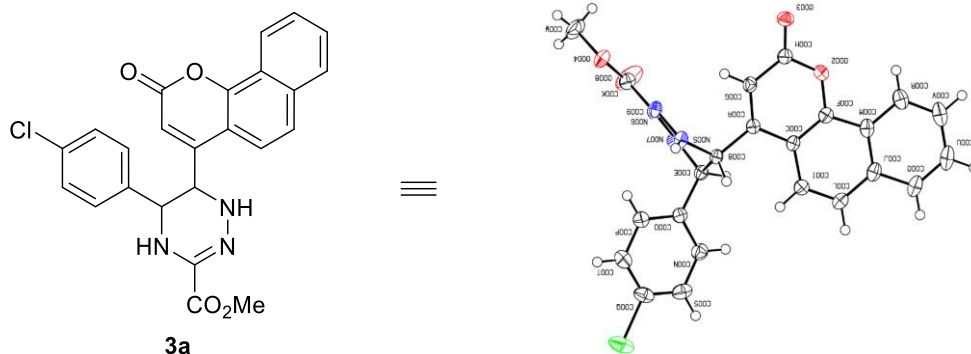


^{13}C -NMR spectra of compound **5b** (CDCl_3 , 151 MHz)



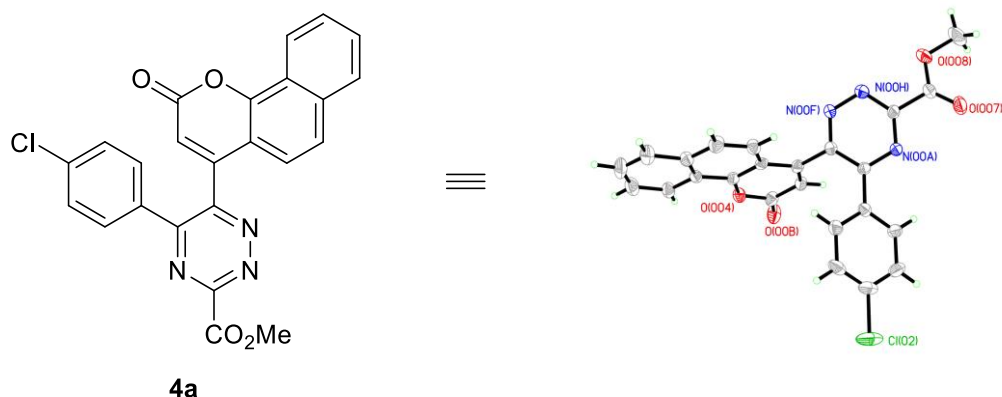
X-Ray Crystallographic Data

The X-ray crystallographic structure for ketal compound (**3a**). Crystal data has been deposited to CCDC, number 2153601.



Empirical formula	C ₂₄ H ₁₈ ClN ₃ O ₄
Formula weight	447.86
Temperature/K	296.15
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	7.3437(3)
b/Å	24.9898(11)
c/Å	11.9263(5)
α/°	90
β/°	95.490(2)
γ/°	90
Volume/Å ³	2178.65(16)
Z	4
ρ _{calc} /cm ³	1.365
μ/mm ⁻¹	0.212
F(000)	928.0
Crystal size/mm ³	0.28 × 0.17 × 0.12
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	3.798 to 59.28
Index ranges	-10 ≤ h ≤ 10, -34 ≤ k ≤ 34, -15 ≤ l ≤ 16
Reflections collected	56535
Independent reflections	6134 [R _{int} = 0.0929, R _{sigma} = 0.0524]
Data/restraints/parameters	6134/0/290
Goodness-of-fit on F ²	1.040
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0465, wR ₂ = 0.1070
Final R indexes [all data]	R ₁ = 0.0792, wR ₂ = 0.1185
Largest diff. peak/hole / e Å ⁻³	0.59/-0.59

The X-ray crystallographic structure for ketal compound (**4a**). Crystal data has been deposited to CCDC, number 2153602.



Empirical formula	C ₂₄ H ₁₄ ClN ₃ O ₄
Formula weight	486.29
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	7.6152(7)
b/Å	14.5507(17)
c/Å	21.281(2)
α/°	104.024(9)
β/°	94.922(8)
γ/°	101.334(9)
Volume/Å ³	2221.0(4)
Z	4
ρ _{calc} /g/cm ³	1.454
μ/mm ⁻¹	0.331
F(000)	996.0
Crystal size/mm ³	0.32 × 0.26 × 0.21
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	3.984 to 50.046
Index ranges	-9 ≤ h ≤ 9, -17 ≤ k ≤ 17, -25 ≤ l ≤ 25
Reflections collected	29435
Independent reflections	7793 [R _{int} = 0.1049, R _{sigma} = 0.1311]
Data/restraints/parameters	7793/0/607
Goodness-of-fit on F ²	1.049
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0864, wR ₂ = 0.2438
Final R indexes [all data]	R ₁ = 0.1734, wR ₂ = 0.2842
Largest diff. peak/hole / e Å ⁻³	0.55/-0.47