Supplementary Material

Novel combinatorial approach to the synthesis of dihydropyridine (quinoline) based merocyanine dyes

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1. Experimental section

^{1}H NMR spectra were recorded on a Bruker AVANCE 600 spectrometer (600.13 MHz). Chemical shifts for 1H NMR were reported as δ values and coupling constants were in hertz (Hz). The following abbreviations were used for spin multiplicity: s = singlet, d = doublet, t = triplet, dd = double doublet, m = multiplet, bs = broad singlet. Chemical shifts for ^{13}C NMR reported in ppm relative to the solvent peak. Chemical shifts are given in ppm relative to $SiMe_4$. The IR spectra recorded on a "Bruker Alpha" in KBr pellets. Melting points were measured on Kofler bench. UV spectra were recorded on an Shimadzu UV-2600 instrument in quartz cells with a light pathlength of 1 cm with the concentration of the substance $C_M = 10^{-5}$ [M] (solvent acetone). The reactions were monitored by thin layer chromatography (TLC). Thin layer chromatography was performed on Fluka precoated silica gel plates (0.20 mm thick, particle size 25 μm). Reagents were available from commercial suppliers and used without any purification unless otherwise noted.

2. General Procedure

Synthesis of salts 3-12. General Experimental Procedure.

Dimethylformamide dimethyl acetal (5.36 g, 45.0 mmol) was added to the solution of the corresponding picolinium or quinolinium salts **1** (30.0 mmol) in DMF (25 ml), the resulting mixture was stirred at room temperature for 16 h. The solution was evaporated to near dryness in vacuo. The crude product was purified by precipitation from boiling metanol–diethyl ether to obtain a grey solid **3-12** which was filtered off, washed with diethyl ether and dried.

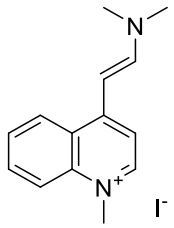
Synthesis of dyes 23, 24, 28, 29, 30, 33, 36, 37, 39, 40, 42, 43, 45. General Experimental Procedure.

Compounds **13, 17, 18** (1.36 mmol) were added to the solution of the corresponding salts **3-12** (1.46 mmol) in DMF (5-6 ml), the resulting mixture was stirred at room temperature for 12 h. The reaction mixture was diluted with water (50 mL) and left to stand at room temperature for 12 h. The precipitated product was filtered off, washed with water and air-dried. The products were obtained in good yield without further purification.

Synthesis of dyes 19, 20, 21, 22, 25, 26, 27, 31, 32, 34, 35, 38 41, 44. General Experimental Procedure.

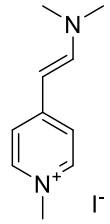
Compounds **14, 15, 16** (1.36 mmol) and sodium acetate (1.36 mmol) were added to the solution of the corresponding salts **3-12** (1.46 mmol) in DMF (5-6 ml), the resulting mixture was heated at 60 °C for 5 h and then cooled to room temperature. The reaction mixture was diluted with water (50 mL). The resulting precipitate was filtered off, washed with water and air-dried. The products were obtained in good yield without further purification.

1. *4-(2-(dimethylamino)vinyl)-1-methylquinolin-1-ium iodide* ***(3)****:*



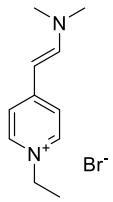
Yield: 95% ***^{1}H NMR:*** (600 MHz, DMSO-*d*^{6}) δ 8.66 (d, J = 8.4 Hz, 1H), 8.56 (d, J = 12.3 Hz, 1H), 8.41 (d, J = 7.3 Hz, 1H), 8.04 – 7.99 (m, 2H), 7.75 – 7.71 (m, 1H), 7.62 (d, J = 7.3 Hz, 1H), 6.27 (d, J = 12.3 Hz, 1H), 4.14 (s, 3H), 3.44 (s, 3H), 3.28 (s, 3H). ***^{13}C NMR:*** (151 MHz, DMSO-*d*^{6}) δ 154.6, 153.4, 142.4, 137.9, 132.8, 125.6, 125.3, 122.3, 117.2, 105.8, 90.0, 45.1, 41.2, 37.3. ***Anal. calcd*** for $C_{14}H_{17}IN_2$ (340,21): C, 49.43; H, 5.04; N, 8.23 Found: C, 49,27; H, 4,93; N, 7,99;

2. *4-(2-(dimethylamino)vinyl)-1-methylpyridin-1-ium iodide* ***(4)*** *:*



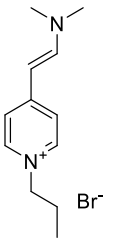
Yield: 98% ***^{1}H NMR:*** (600 MHz, DMSO-*d*^{6}) δ 8.12 – 8.00 (m, 3H), 7.67 – 7.02 (s, 2H), 5.31 (d, J = 13.0 Hz, 1H), 3.88 (s, 3H), 3.20 (s, 3H), 2.93 (s, 3H). ***^{13}C NMR:*** (151 MHz, DMSO-*d*^{6}) δ 155.0, 152.2, 141.7, 127.9, 92.1, 44.7, 44.5, 37.0. ***Anal. calcd*** for $C_{10}H_{15}IN_2$ (290,15): C, 41.40; H, 5.21; N, 9.66 Found: C, 41,18; H, 5,02; N, 9,51;

3.*4-(2-(dimethylamino)vinyl)-1-ethylpyridin-1-ium bromide* ***(5)****:*



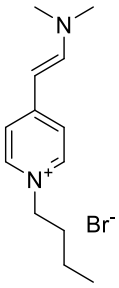
Yield: 99% ***^{1}H NMR:*** (600 MHz, DMSO-*d*^{6}) δ 8.19 (d, J = 6.9 Hz, 2H), 8.15 (d, J = 13.0 Hz, 1H), 7.67 – 7.10 (m, 2H), 5.31 (d, J = 13.0 Hz, 1H), 4.16 (q, J = 7.4 Hz, 2H), 3.21 (s, 3H), 2.94 (s, 3H), 1.38 (t, J = 7.4 Hz, 3H). ***^{13}C NMR:*** (151 MHz, DMSO-*d*^{6}) δ 155.2, 152.4, 140.6, 92.2, 52.5, 44.6, 36.9, 34.2, 16.0. ***Anal. calcd*** for $C_{11}H_{17}BrN_2$ (257,18): C, 51.37; H, 6.66; N, 10.89; Found: C, 51,12; H, 6,49; N, 10,63;

4**.** *4-(2-(dimethylamino)vinyl)-1-propylpyridin-1-ium bromide* ***(6)****:*



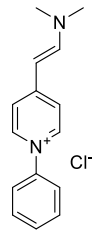
Yield: 96% ***^{1}H NMR:*** (600 MHz, DMSO-*d*^{6}) δ 8.32 – 8.23 (m, 3H), 7.47 (s, 2H), 5.41 (d, J = 12.9 Hz, 1H), 4.19 (t, J = 7.3 Hz, 2H), 3.29 (s, 3H), 3.01 (s, 3H), 1.85 (q, J = 7.3 Hz, 2H), 0.90 (t, J = 7.3 Hz, 3H). ***^{13}C NMR:*** (151 MHz, DMSO-*d*^{6}) δ 154.7, 152.0, 140.3, 115.54, 91.7, 57.8, 44.1, 36.4, 23.1, 9.7. ***Anal. calcd*** for $C_{12}H_{19}BrN_2$ (271,02): C, 53.15; H, 7.06; N, 10.34 Found: C, 52,92; H, 6,98; N, 9,96;

5. *1-butyl-4-(2-(dimethylamino)vinyl)pyridin-1-ium bromide* ***(7)****:*



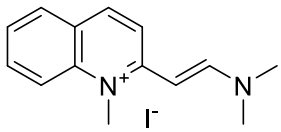
Yield: 97% ***^{1}H NMR:*** (600 MHz, DMSO-*d*^{6}) δ 8.16 (d, J = 7.0 Hz, 2H), 8.11 (d, J = 12.9 Hz, 1H), 7.35 (s, 1H), 5.31 (d, J = 12.9 Hz, 1H), 4.11 (t, J = 7.3 Hz, 2H), 3.20 (s, 3H), 2.94 (s, 3H), 1.74 (p, J = 7.4 Hz, 2H), 1.26 (hept, J = 7.4 Hz, 2H), 0.89 (t, J = 7.4 Hz, 3H). ***^{13}C NMR:*** (151 MHz, DMSO-*d*^{6}) δ 155.2, 152.5, 140.9, 92.2, 56.9, 44.7, 36.9, 34.2, 32.22, 18.774, 13.3. ***Anal. calcd*** for $C_{13}H_{21}BrN_2$ (285,23): C, 54.74; H, 7.42; N, 9.82; Found: C, 54,5; H, 7,28; N, 9,53;

6. *4-(2-(dimethylamino)vinyl)-1-phenylpyridin-1-ium chloride* ***(8)****:*



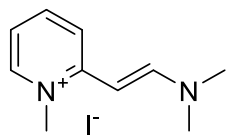
Yield: 93% ***^{1}H NMR:*** (600 MHz, DMSO-*d*^{6}) δ 8.59 (d, J = 12.8 Hz, 1H), 8.44 (d, J = 7.4 Hz, 2H), 8.03 – 7.83 (m, 1H), 7.78 (d, J = 7.8 Hz, 2H), 7.68 (t, J = 7.8 Hz, 2H), 7.61 (t, J = 7.3 Hz, 1H), 7.46 – 7.03 (m, 1H), 5.59 (d, J = 12.8 Hz, 1H), 3.37 (s, 3H), 3.08 (s, 3H). ***^{13}C NMR:*** (151 MHz, DMSO-*d*^{6}) δ 154.8, 153.8, 141.5, 139.1, 138.6, 129.5, 128.5, 122.5, 118.7, 113.3, 92.8, 44.4, 36.7. ***Anal. calcd*** for $C_{15}H_{17}ClN_2$ (260,77): C, 69.09; H, 6.57; N, 10.74 Found: C, 68,95; H, 6,46; N, 10,46;

7. *2-(2-(dimethylamino)vinyl)-1-methylquinolin-1-ium iodide* ***(9)****:*



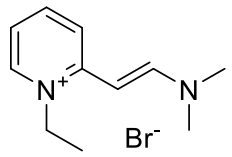
Yield: 93% ***^{1}H NMR:*** (600 MHz, DMSO-*d*^{6}) δ 8.50 (d, J = 12.2 Hz, 1H), 8.13 (d, J = 9.5 Hz, 1H), 7.99 (d, J = 8.8 Hz, 1H), 7.96 (d, J = 9.6 Hz, 1H), 7.89 (d, J = 7.8 Hz, 1H), 7.78 (t, J = 7.9 Hz, 1H), 7.51 (t, J = 7.4 Hz, 1H), 5.56 (d, J = 12.2 Hz, 1H), 3.94 (s, 3H), 3.37 (s, 3H), 3.18 (s, 3H). ***^{13}C NMR:*** (151 MHz, DMSO-*d*^{6}) δ 156.9, 156.2, 139.1, 137.1, 132.4, 129.1, 125.2, 123.9, 118.1, 117.0, 89.1, 54.4, 45.8, 38.0, 36.9. ***Anal. calcd*** for $C_{14}H_{17}IN_2$ (340,21): C, 49.43; H, 5.04; N, 8.23 Found: C, 49,22; H, 4,91; N, 8,03;

8. *2-(2-(dimethylamino)vinyl)-1-methylpyridin-1-ium iodide* ***(10)****:*



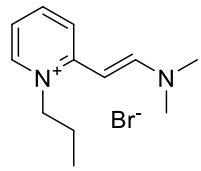
Yield: 98% ***^{1}H NMR:*** (600 MHz, DMSO-*d*^{6}) δ 8.21 (d, J = 6.5 Hz, 1H), 8.18 (d, J = 12.6 Hz, 1H), 7.94 (d, J = 8.9 Hz, 1H), 7.79 (t, J = 7.9 Hz, 1H), 6.99 (t, J = 6.8 Hz, 1H), 5.13 (d, J = 12.6 Hz, 1H), 3.86 (s, 3H), 3.25 (s, 3H), 3.02 (s, 3H). ***^{13}C NMR:*** (151 MHz, DMSO-*d*^{6}) δ 155.1, 153.3, 142.6, 139.2, 119.2, 115.7, 84.8, 54.4, 54.4, 54.4, 45.0, 44.2, 37.4. ***Anal. calcd*** for $C_{10}H_{15}IN_2$ (290,15): C, 41.40; H, 5.21; N, 9.66 Found: C, 41,22; H, 5,04; N, 9,53;

9. *2-(2-(dimethylamino)vinyl)-1-ethylpyridin-1-ium bromide* ***(11)****:*



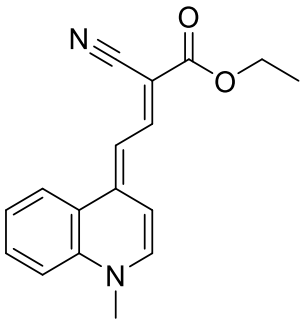
Yield: 98% ***^{1}H NMR:*** (600 MHz, DMSO-*d*^{6}) δ 8.30 – 8.21 (m, 2H), 8.00 (d, J = 8.9 Hz, 1H), 7.78 (t, J = 7.8 Hz, 1H), 7.03 (t, J = 6.7 Hz, 1H), 5.21 (d, J = 12.5 Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 3.26 (s, 3H), 3.03 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H) ***^{13}C NMR:*** (151 MHz, DMSO-*d*^{6}) δ 154.2, 153.6, 141.7, 139.2, 119.8, 116.3, 84.4, 50.7, 44.9, 37.3, 13.6. ***Anal. calcd*** for $C_{11}H_{17}BrN_2$ (257,18): C, 51.37; H, 6.66; N, 10.89 Found: C, 51,18; H, 6,46; N, 10,69;

10. *2-(2-(dimethylamino)vinyl)-1-propylpyridin-1-ium bromide* ***(12)****:*



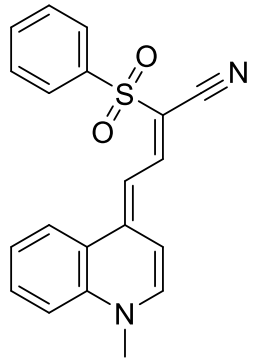
Yield: 96% ***^{1}H NMR:*** (600 MHz, DMSO-*d*^{6}) δ 8.29 – 8.24 (m, 2H), 8.02 (d, J = 8.8 Hz, 1H), 7.78 (t, J = 7.9 Hz, 1H), 7.01 (td, J = 6.9, 1.2 Hz, 1H), 5.19 (d, J = 12.5 Hz, 1H), 4.30 (t, J = 7.4 Hz, 2H), 3.25 (s, 3H), 3.02 (s, 3H), 1.78 – 1.71 (m, 2H), 0.90 (t, J = 7.4 Hz, 3H). ***^{13}C NMR:*** (151 MHz, DMSO-*d*^{6}) δ 154.4, 153.5, 142.3, 139.2, 119.9, 115.9, 84.6, 56.5, 44.9, 37.3, 20.9, 10.4. ***Anal. calcd*** for $C_{12}H_{19}BrN_2$ (271,02): C, 53.15; H, 7.06; N, 10.33 Found: C, 52,96; H, 6,9; N, 10,06;

11. E*thyl 2-cyano-4-(1-methylquinolin-4(1H)-ylidene)but-2-enoate* ***(19)***:



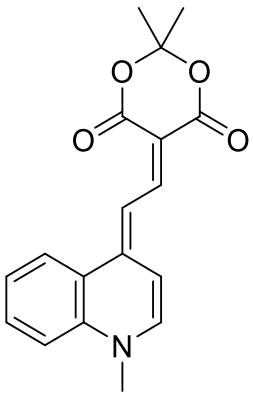
Yield: 75% ***mp:*** 209-211°C ***^{1}H NMR:*** (600 MHz, DMSO-*d*^{6}) δ 8.38 (d, J = 13.6 Hz, 1H), 8.24 (d, J = 8.1 Hz, 1H), 7.99 (d, J = 7.3 Hz, 1H), 7.90 (t, J = 7.8 Hz, 1H), 7.83 (d, J = 8.6 Hz, 1H), 7.63 (t, J = 7.6 Hz, 1H), 7.24 (d, J = 7.4 Hz, 1H), 6.52 (d, J = 13.6 Hz, 1H), 4.23 (q, J = 7.1 Hz, 2H), 3.98 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H). ***^{13}C NMR:*** (151 MHz, DMSO-*d*^{6}) δ 164.7, 148.9, 147.2, 140.6, 138.2, 132.0, 125.1, 123.7, 122.1, 118.4, 116.7, 105.6, 98.6, 81.3, 59.1, 40.5, 13.9. ***Anal. calcd*** for $C_{17}H_{16}N_2O_2$ (280,12): C, 72.84; H, 5.75; N, 9.99; Found: C, 72,65; H, 5,63; N, 9,82; ***λ_{max}*** [nm] (acetone):542 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 7,95

12. *4-(1-methylquinolin-4(1H)-ylidene)-2-(phenylsulfonyl)but-2-enenitrile* ***(20)***:



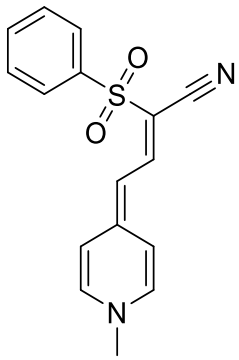
Yield: 86% ***mp:*** 253-255°C ***IR*** (KBr),ν, cm^{-1}: 3449, 2188, 1621, 1522, 1370, 1276, 1227, 1137, 1081, 1029, 823, 757, 717, 694, 608, 573, 528. ***^{1}H NMR:*** (600 MHz, DMSO-d^6) δ 8.27 (d, J = 8.4 Hz, 1H), 8.24 (d, J = 13.6 Hz, 1H), 8.17 (d, J = 7.2 Hz, 1H), 7.99 – 7.89 (m, 4H), 7.73 – 7.64 (m, 4H), 7.45 (d, J = 7.3 Hz, 1H), 6.40 (d, J = 13.6 Hz, 1H), 4.07 (s, 3H) ***^{13}C NMR:*** (151 MHz, DMSO-d^6) δ 150.3, 144.6, 142.6, 141.5, 138.1, 132.3, 132.0, 128.9, 125.6, 125.5, 124.0, 122.1, 117.0, 116.3, 106.5, 97.5, 88.8, 40.9. ***Anal. calcd*** for $C_{20}H_{16}N_2O_2S$ (348,09): C, 68.94; H, 4.63; N, 8.04; Found: C, 68,70; H, 4,43; N, 7,91; ***λ_{max}*** [nm] (acetone):531 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 6,54

13. *(E)-2,2-dimethyl-5-(2-(1-methylquinolin-4(1H)-ylidene)ethylidene)-1,3-dioxane-4,6-dione* ***(21)***:



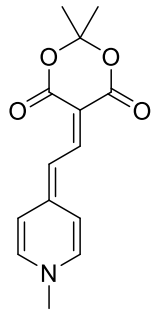
Yield: 93% ***mp:*** 234-237°C ***IR*** (KBr),ν, cm^{-1}: 3532, 3471, 1629, 1556, 1519, 1426, 1369, 1360, 1323, 1267, 1220, 1160, 1111, 976, 929. ***^{1}H NMR:*** (600 MHz, DMSO-d^6) δ 8.32 (d, J = 7.1 Hz, 1H), 8.30 (d, J = 14.6 Hz, 1H), 8.25 (d, J = 8.4 Hz, 1H), 7.99 – 7.93 (m, 2H), 7.91 (d, J = 14.6 Hz, 1H), 7.71 (t, J = 6.3 Hz, 1H), 7.55 (d, J = 7.1 Hz, 1H), 4.10 (s, 3H), 1.59 (s, 6H). ***^{13}C NMR:*** (151 MHz, DMSO-d^6) δ 153.9, 144.7, 143.4, 138.7, 133.3, 126.8, 124.7, 123.9, 118.0, 108.2, 104.3, 101.6, 89.5, 42.1, 26.5. The signal of C(4) is overlapped with CH(beta). ***Anal. calcd*** for $C_{18}H_{17}NO_4$ (311,12): C, 69.44; H, 5.50; N, 4.50; Found: C, 69,26; H, 5,30; N, 4,25; ***λ_{max}*** [nm] (acetone):542,00 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 7,29

14**.** *4-(1-methylpyridin-4(1H)-ylidene)-2-(phenylsulfonyl)but-2-enenitrile* ***(22)***:



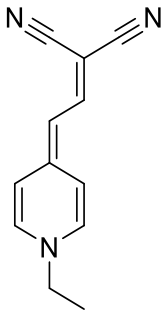
Yield: 66% ***mp:*** 277-280°C ***IR*** (KBr),ν, cm^{-1}: 3423, 2170, 1646, 1548, 1480, 1387, 1311, 1269, 1198, 1135, 1088, 1037, 852, 753, 603. ***^{1}H NMR:*** (600 MHz, DMSO-d^6) δ 8.02 (d, J = 6.8 Hz, 2H), 7.90 – 7.80 (m, 3H), 7.64 (d, J = 7.4 Hz, 3H), 7.55 – 7.09 (s, 2H), 5.63 (d, J = 14.4 Hz, 1H), 3.91 (s, 3H). ***^{13}C NMR:*** (151 MHz, DMSO-d^6) δ 152.6, 144.1, 142.2, 141.3, 131.2, 128.6, 125.0, 117.7, 100.3, 80.8, 43.6. The signal of C(CN) is overlapped with hetaryl. ***Anal. calcd*** for $C_{16}H_{14}N_2O_2S$ (298,08): C, 64.41; H, 4.73; N, 9.39; Found: C, 64,24; H, 4,55; N, 9,21; ***λ_{max}*** [nm] (acetone):474 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 2,71

15. *2,2-dimethyl-5-(2-(1-methylpyridin-4(1H)-ylidene)ethylidene)-1,3-dioxane-4,6-dione* ***(23)***:



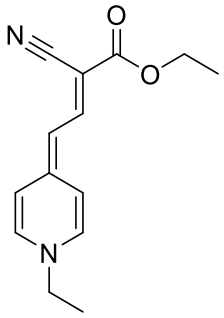
Yield: 62% ***mp:*** 281-283°C ***IR*** (KBr),ν, cm^{-1}: 3440, 1682, 1638, 1558, 1539, 1479, 1402, 1344, 1263, 1185, 1124 ***^{1}H NMR:*** (600 MHz, DMSO-*d*^{6}) δ 8.12 (d, J = 7.0 Hz, 2H), 7.93 (d, J = 15.2 Hz, 1H), 7.44 (d, J = 5.9 Hz, 2H), 7.01 (d, J = 15.2 Hz, 1H), 3.93 (s, 3H), 1.53 (s, 6H). ***^{13}C NMR:*** (151 MHz, DMSO-*d*^{6}) δ 155.6, 142.2, 141.6, 118.4, 108.3, 100.9, 85.1, 44.8, 26.3. The signal of C(4) is overlapped with hetaryl. ***Anal. calcd*** for $C_{14}H_{15}NO_4$ (261,10): C, 64.36; H, 5.79; N, 5.36; Found: C, 64,12; H, 5,60; N, 5,07; ***λ_{max}*** [nm] (acetone):474 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 6,54

16. *2-(2-(1-ethylpyridin-4(1H)-ylidene)ethylidene)malononitrile* ***(24)***:



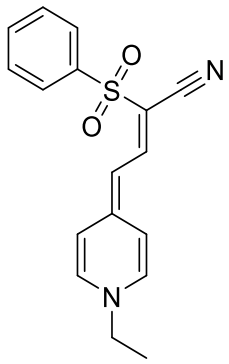
Yield: 57% ***mp:*** 183-185°C ***IR*** (KBr),ν, cm^{-1}: ***^{1}H NMR:*** (600 MHz, DMSO-*d*^{6}) δ 7.98 (d, J = 7.3 Hz, 2H), 7.73 (d, J = 14.2 Hz, 1H), 7.69 – 6.65 (m, 2H), 5.65 (d, J = 14.2 Hz, 1H), 4.07 (q, J = 7.2 Hz, 2H), 1.35 (t, J = 7.3 Hz, 3H). ***^{13}C NMR:*** (151 MHz, DMSO-*d*^{6}) δ 152.6, 147.5, 140.5 (br), 121.2, 119.0, 102.1, 52.2, 47.4, 15.9. ***Anal. calcd*** for $C_{12}H_{11}N_3$ (197,10): C, 73.07; H, 5.62; N, 21.30 Found: C, 72,94; H, 5,46; N, 21,17; ***λ_{max}*** [nm] (acetone):479 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 9,88

17. *Ethyl-2-cyano-4-(1-ethylpyridin-4(1H)-ylidene)-but-2-enoate* ***(25)****:*



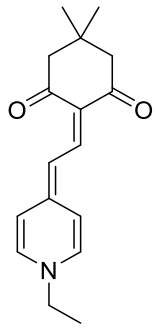
Yield: 48% ***mp:*** 163-166°C ***IR*** (KBr),ν, cm^{-1}: 3445, 2186, 1664, 1648, 1542, 1485, 1415, 1326, 1248, 1223, 1180, 1094, 1029, 945 ***^{1}H NMR:*** (600 MHz, DMSO-*d*^{6}) δ 7.96 (d, J = 14.4 Hz, 1H), 7.89 (d, J = 7.1 Hz, 2H), 7.44 – 6.79 (m, 2H), 5.63 (d, J = 14.4 Hz, 1H), 4.21 – 3.89 (m, 4H), 1.34 (t, J = 7.2 Hz, 3H), 1.19 (t, J = 7.1 Hz, 3H). ***^{13}C NMR:*** (151 MHz, DMSO-*d*^{6}) δ 166.2, 152.8, 145.7, 139.7(br), 120.4, 101.4, 74.1, 58.8, 51.9, 15.9, 14.6. ***Anal. calcd*** for $C_{14}H_{16}N_2O_2$ (244,12): C, 68.83; H, 6.60; N, 11.47; Found: C, 68,61; H, 6,46; N, 11,24; ***λ_{max}*** [nm] (acetone):488 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 10,00

18. *4-(1-ethylpyridin-4(1H)-ylidene)-2-(phenylsulfonyl)but-2-enenitrile* ***(26)***:



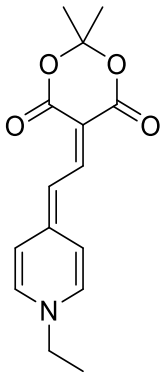
Yield: 66% ***mp:*** 231-234°C ***IR*** (KBr),ν, cm^{-1}: 3459, 2172, 1644, 1553, 1478, 1445, 1387, 1311, 1271, 1185, 1134, 1085, 1034, 604, 578 ***^{1}H NMR:*** (600 MHz, DMSO-*d*^{6}) δ 8.02 (d, J = 7.1 Hz, 2H), 7.84 – 7.72 (m, 3H), 7.64 – 7.47 (m, 3H), 7.44 – 7.04 (m, 2H), 5.56 (d, J = 14.4 Hz, 1H), 4.10 (q, J = 7.2 Hz, 2H), 1.36 (t, J = 7.2 Hz, 3H). ***^{13}C NMR:*** (151 MHz, DMSO-*d*^{6}) δ 153.4, 144.6, 142.9, 140.2, 131.8, 129.2, 125.5, 118.2, 107,7, 100.9, 81.6, 52.3, 16.0. ***Anal. calcd*** for $C_{17}H_{16}N_2O_2S$ (312,09): C, 65.36; H, 5.16; N, 8.97; Found: C, 65,11; H, 4,99; N, 8,74; ***λ_{max}*** [nm] (acetone):475 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 8,73

19. *2-(2-(1-ethylpyridin-4(1H)-ylidene)ethylidene)-5,5-dimethylcyclohexane-1,3-dione* ***(27)***:



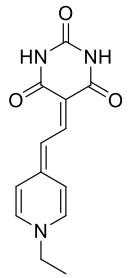
Yield: 47% ***mp:*** >300°C ***IR*** (KBr),ν, cm^{-1}: 3443, 2958, 1644, 1635, 1548, 1531, 1508, 1478, 1396, 1354, 1264, 1174, 1120, 989, 886 ***^{1}H NMR:*** (600 MHz, DMSO-*d*^{6}) δ 8.14 (d, J = 7.0 Hz, 2H), 8.01 (d, J = 15.1 Hz, 1H), 7.46 (d, J = 15.1 Hz, 1H), 7.37 (d, J = 5.4 Hz, 2H), 4.17 (q, J = 7.2 Hz, 2H), 2.15 (s, 4H), 1.39 (t, J = 7.2 Hz, 3H), 0.94 (s, 6H). ***^{13}C NMR:*** (151 MHz, DMSO-*d*^{6}) δ 193.5, 157.0, 140.7, 139.9, 118.3, 111.5, 108.8, 52.6, 51.9, 30.5, 28.4, 16.0. ***Anal. calcd*** for $C_{17}H_{21}NO_2$ (271,16): C, 75.25; H, 7.80; N, 5.16; Found: C, 75,04; H, 7,60; N, 4,98; ***λ_{max}*** [nm] (acetone):501 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 10,24

20**.** *5-(2-(1-ethylpyridin-4(1H)-ylidene)ethylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione* ***(28)***:



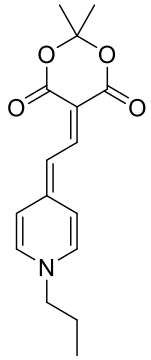
Yield: 66% ***mp:*** 258-261°C ***IR*** (KBr),ν, cm^{-1}: 3460, 3052, 2988, 1681, 1642, 1548, 1531, 1476, 1397, 1347, 1261, 1201, 1167, 989, 935, 892, 772. ***^{1}H NMR:*** (600 MHz, DMSO-*d*^{6}) δ 8.22 (d, J = 7.0 Hz, 2H), 7.95 (d, J = 15.2 Hz, 1H), 7.45 (d, J = 5.1 Hz, 2H), 7.02 (d, J = 15.2 Hz, 1H), 4.21 (q, J = 7.2 Hz, 2H), 1.53 (s, 6H), 1.40 (t, J = 7.2 Hz, 3H). ***^{13}C NMR:*** (151 MHz, DMSO-*d*^{6}) δ 155.8, 141.8, 141.1, 118.6, 108.3, 101.0, 85.2, 52.9, 26.3, 16.0. The signal of C(4) is overlapped with hetaryl. ***Anal. calcd*** for $C_{15}H_{17}NO_4$ (275,12): C, 65.44; H, 6.22; N, 5.09; Found: C, 65,22; H, 6,06; N, 4,92; ***λ_{max}*** [nm] (acetone):475 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 1,93

21. *5-(2-(1-ethylpyridin-4(1H)-ylidene)ethylidene)pyrimidine-2,4,6(1H,3H,5H)-trione hydrate* ***(29)****:*



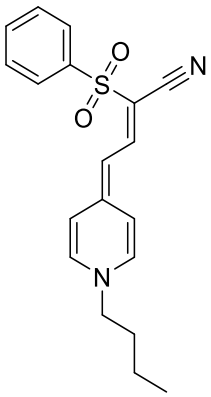
Yield: 65% ***mp:*** >300°C ***IR*** *(KBr),v, cm^{-1}:* 3164, 3065, 1718, 1697, 1644, 1601, 1559, 1426, 1333, 1310, 1273, 1170, 1038, 979, 528. ***^{1}H NMR:*** (600 MHz, DMSO-*d*^{6}) δ 9.95 – 9.84 (m, 2H), 8.19 (d, J = 7.1 Hz, 2H), 8.00 (d, J = 15.2 Hz, 1H), 7.44 (d, J = 5.7 Hz, 2H), 7.29 (d, J = 15.2 Hz, 1H), 4.19 (q, J = 7.3 Hz, 2H), 1.40 (t, J = 7.3 Hz, 3H). ***^{13}C NMR:*** (151 MHz, DMSO-*d*^{6}) δ 168.7, 155.9, 151.1, 140.9, 140.8, 118.4, 108.3, 92.8, 52.8, 16.0. ***Anal. calcd*** for $C_{13}H_{15}N_3O_4$ (277,11): C, 56.31; H, 5.45; N, 15.15; Found: C, 56,16; H, 5,31; N, 14,97; ***λ$_{max}$*** [nm] (acetone):487 ε $_{max}$ ×10^{-4} [M $^{-1}$ ×cm $^{-1}$]: 4,03

22. *2,2-dimethyl-5-(2-(1-propylpyridin-4(1H)-ylidene)ethylidene)-1,3-dioxane-4,6-dione* ***(30)****:*



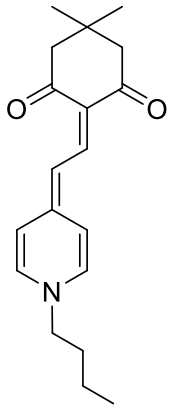
Yield: 74% ***mp:*** 245-247°C ***IR*** (KBr),ν,cm–1: 3564, 3491, 3075, 2979, 1687, 1679, 1645, 1632, 1553, 1538, 1409, 1349, 1270, 1181. ***^{1}H NMR:*** (600 MHz, DMSO-*d*^{6}) δ 8.20 (d, J = 6.9 Hz, 2H), 7.95 (d, J = 15.2 Hz, 1H), 7.46 (d, J = 6.5 Hz, 2H), 7.02 (d, J = 15.2 Hz, 1H), 4.14 (t, J = 7.3 Hz, 2H), 1.80 (q, J = 7.3 Hz, 2H), 1.53 (s, 6H), 0.85 (t, J = 7.3 Hz, 3H). ***^{13}C NMR:*** (151 MHz, DMSO-*d*^{6})δ 155.9, 141.9, 141.3, 118.5, 108.3, 100.9, 85.4, 58.9, 40.0, 26.3, 23.7, 10.3. ***Anal. calcd*** for $C_{16}H_{19}NO_4$ (289,33): C, 66.42; H, 6.62; N, 4.84; Found: C, 66,21; H, 6,5; N, 4,65; ***λ$_{max}$*** [nm] (acetone):476 ε $_{max}$ ×10^{-4} [M $^{-1}$ ×cm $^{-1}$]: 8,24

23. *4-(1-butylpyridin-4(1H)-ylidene)-2-(phenylsulfonyl)but-2-enenitrile* ***(31)***:



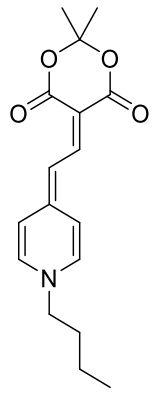
Yield: 73% ***mp:*** 176-178°C ***IR*** (KBr),ν, cm^{-1}: 3436, 2172, 1642, 1545, 1539, 1508, 1478, 1390, 1314, 1267, 1181, 1134, 1082, 1029, 843, 759, 713, 607. ***^{1}H NMR:*** (600 MHz, DMSO-*d*^{6}) δ 8.01 (d, J = 7.1 Hz, 2H), 7.84 – 7.71 (m, 3H), 7.61 – 7.50 (m, 3H), 7.45 – 6.83 (m, 2H), 5.56 (d, J = 14.4 Hz, 1H), 4.07 (t, J = 7.2 Hz, 2H), 1.78 – 1.64 (m, 2H), 1.28 – 1.20 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H). ***^{13}C NMR:*** (151 MHz, DMSO-*d*^{6}) δ 153.4, 144.5, 143.0, 140.5, 131.8, 129.2, 125.5, 118.2, 100.9, 81.8, 56.7, 32.3, 18.7, 13.3. The signal of C(CN) is overlapped with hetaryl. ***Anal. calcd*** for $C_{19}H_{20}N_2O_2S$ (340,12): C, 67.03; H, 5.92; N, 8.23; Found: C, 66,80; H, 5,75; N, 8,08; ***λ$_{max}$*** [nm] (acetone):476 ε $_{max}$ ×10^{-4} [M $^{-1}$ ×cm $^{-1}$]: 7,99

24. *2-(2-(1-butylpyridin-4(1H)-ylidene)ethylidene)-5,5-dimethylcyclohexane-1,3-dione* ***(32)***:



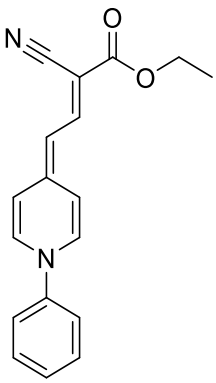
Yield: 76% ***mp:*** >300°C ***IR*** (KBr),ν, cm^{-1}: 3425, 2955, 1645, 1625, 1555, 1470, 1405, 1359, 1277, 1185, 975, 872. ***^{1}H NMR:*** (600 MHz, DMSO-*d*^{6}) δ 8.12 (d, J = 7.1 Hz, 2H), 8.00 (d, J = 15.1 Hz, 1H), 7.46 (d, J = 15.1 Hz, 1H), 7.40 – 7.33 (m, 2H), 4.14 (t, J = 7.3 Hz, 2H), 2.15 (s, 4H), 1.78 – 1.72 (m, 2H), 1.30 – 1.23 (m, 2H), 0.94 (s, 6H), 0.90 (t, J = 7.4 Hz, 3H). ***^{13}C NMR:*** (151 MHz, DMSO-*d*^{6}) δ 193.5, 157.0, 140.9, 139.9, 111.5, 108.9, 57.0, 51.9, 40.4, 32.3, 30.5, 28.4, 18.8, 13.3. ***Anal. calcd*** for $C_{19}H_{25}NO_2$ (299,19): C, 76.22; H, 8.42; N, 4.68; Found: C, 76,02; H, 8,22; N, 4,53; ***λ_{max}*** [nm] (acetone):507 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 3,65

25. *5-(2-(1-butylpyridin-4(1H)-ylidene)ethylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione* ***(33)***:



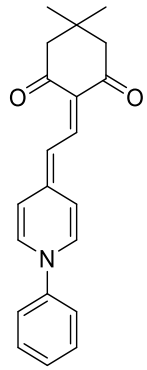
Yield: 85% ***mp:*** 262-265°C ***IR*** (KBr),ν, cm^{-1}: 3433, 3067, 2958, 1705, 1649, 1566, 1542, 1479, 1416, 1352, 1277, 1206, 1188, 966, 936, 863. ***^{1}H NMR:*** (600 MHz, DMSO-*d*^{6}) δ 8.20 (d, J = 7.0 Hz, 2H), 7.95 (d, J = 15.2 Hz, 1H), 7.45 (d, J = 5.6 Hz, 2H), 7.02 (d, J = 15.2 Hz, 1H), 4.17 (t, J = 7.2 Hz, 2H), 1.80 – 1.72 (m, 2H), 1.53 (s, 6H), 1.30 – 1.21 (m, 2H), 0.89 (t, J = 7.4 Hz, 3H). ***^{13}C NMR:*** (151 MHz, DMSO-*d*^{6}) δ 155.8, 141.9, 141.3, 118.5, 108.3, 101.0, 85.4, 57.3, 32.3, 26.3, 18.8, 13.3. The signal of C(4) is overlapped with hetaryl. ***Anal. calcd*** for $C_{17}H_{21}NO_4$ (303,15): C, 67.31; H, 6.98; N, 4.62; Found: C, 67,18; H, 6,85; N, 4,44; ***λ_{max}*** [nm] (acetone):476 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 7,90

26. *Ethyl 2-cyano-4-(1-phenylpyridin-4(1H)-ylidene)but-2-enoate* ***(34)***:



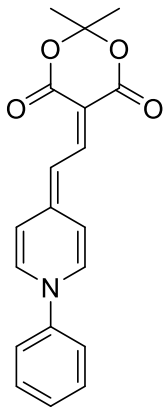
Yield: 91% ***mp:*** 205-208°C ***IR*** (KBr),ν, cm^{-1}: 3449, 2186, 1671, 1646, 1536, 1505, 1480, 1420, 1246, 1190, 1173, 1087. ***^{1}H NMR:*** (600 MHz, DMSO-*d*^{6}) δ 8.10 (d, J = 14.1 Hz, 1H), 8.04 (d, J = 16.7 Hz, 2H), 7.63 (d, J = 7.5 Hz, 3H), 7.59 (t, J = 7.8 Hz, 2H), 7.50 (t, J = 7.2 Hz, 1H), 7.41 – 7.30 (s, 1H), 7.02 – 6.91 (s, 1H), 5.78 (d, J = 14.1 Hz, 1H), 4.11 (q, J = 7.1 Hz, 2H), 1.21 (t, J = 7.1 Hz, 3H). ***^{13}C NMR:*** (151 MHz, DMSO-*d*^{6}) δ 165.6, 151.7, 147.1, 142.2, 138.4, 137.7, 130.0, 128.6, 122.6, 119.4, 118.5, 113.24, 102.3, 78.7, 59.3, 14.5. ***Anal. calcd*** for $C_{18}H_{16}N_2O_2$ (292,12): C, 73.95; H, 5.52; N, 9.58; Found: C, 73,82; H, 5,37; N, 9,35; ***λ_{max}*** [nm] (acetone):503 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 8,12

27. *5,5-dimethyl-2-(2-(1-phenylpyridin-4(1H)-ylidene)ethylidene)cyclohexane-1,3-dione* ***(35)***:



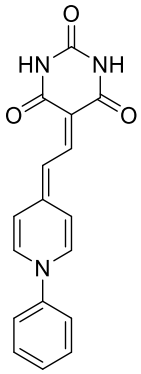
Yield: 79% ***mp:*** >300°C ***IR*** (KBr),ν, cm^{-1}: 3423, 3045, 2954, 1642, 1634, 1561, 1528, 1475, 1400, 1354, 1254, 1184, 1165, 976. ***^{1}H NMR:*** (600 MHz, DMSO-*d*^{6}) δ 8.28 (d, J = 7.3 Hz, 2H), 8.12 (d, J = 14.9 Hz, 1H), 7.70 (d, J = 7.6 Hz, 2H), 7.63 (t, J = 7.8 Hz, 2H), 7.56 (t, J = 7.3 Hz, 1H), 7.51 (d, J = 14.9 Hz, 1H), 7.47 – 7.29 (m, 2H), 2.21 (s, 4H), 0.96 (s, 6H). ***^{13}C NMR:*** (151 MHz, DMSO-*d*^{6}) δ 194.4, 156.7, 142.2, 141.4, 139.4, 130.1, 129.2, 123.1, 113.3, 108.7, 40.0, 30.4, 28.4, 27.9. ***Anal. calcd*** for $C_{21}H_{21}NO_2$ (319,16): C, 78.97; H, 6.63; N, 4.39; Found: C, 78,74; H, 6,45; N, 4,16; ***λ$_{max}$*** [nm] (acetone):523 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 4,92

28. *2,2-dimethyl-5-(2-(1-phenylpyridin-4(1H)-ylidene)ethylidene)-1,3-dioxane-4,6-dione* ***(36)***:



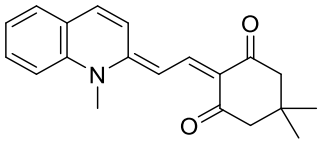
Yield: 78% ***mp:*** 272-274°C ***IR*** (KBr),ν, cm^{-1}: 3443, 3051, 1698, 1649, 1541, 1525, 1509, 1478, 1409, 1349, 1253, 1180, 1125, 931, 762, 511. ***^{1}H NMR:*** (600 MHz, DMSO-*d*^{6}) δ 8.46 (d, J = 7.4 Hz, 2H), 8.18 (d, J = 15.0 Hz, 1H), 7.80 (d, J = 8.1 Hz, 2H), 7.71 (t, J = 7.8 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.63 – 7.51 (s, 2H), 7.19 (d, J = 15.0 Hz, 1H), 1.64 (s, 6H). ***^{13}C NMR:*** (151 MHz, DMSO-*d*^{6}) δ 155.2, 143.2, 141.6, 139.5, 129.5, 128.8, 122.7, 122.7, 107.7, 100.8, 87.2, 25.9. The signal of C(4) is overlapped with hetaryl. ***Anal. calcd*** for $C_{19}H_{17}NO_4$ (323,12): C, 70.58; H, 5.30; N, 4.33; Found: C, 70,39; H, 5,13; N, 4,08; ***λ$_{max}$*** [nm] (acetone):495 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 9,11

29. *5-(2-(1-phenylpyridin-4(1H)-ylidene)ethylidene)pyrimidine-2,4,6(1H,3H,5H)-trione* ***(37)***:



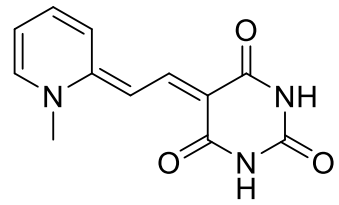
Yield: 89% ***mp:*** >300°C ***IR*** (KBr),ν, cm^{-1}: 3433, 2361, 2342, 1699, 1639, 1605, 1542, 1510, 1475, 1423, 1323, 1260, 1227, 1175, 975, 858, 606, 518. ***^{1}H NMR:*** (600 MHz, DMSO-*d*^{6}) δ 10.27 – 10.04 (m, 2H), 8.41 (d, J = 7.2 Hz, 2H), 8.22 (d, J = 14.9 Hz, 1H), 7.79 (d, J = 7.9 Hz, 2H), 7.71 (t, J = 7.7 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.60 – 7.48 (s, 2H), 7.44 (d, J = 14.9 Hz, 1H). ***^{13}C NMR:*** (151 MHz, DMSO-*d*^{6}) 155.2, 150.4, 142.2, 141.6, 139.2, 129.5, 129.5, 128.7, 122.6, 122.6, 107.6, 94.6. ***Anal. calcd*** for $C_{17}H_{13}N_3O_3$ (307,10): C, 66.44; H, 4.26; N, 13.67; Found: C, 66,28; H, 4,13; N, 13,43; ***λ$_{max}$*** [nm] (acetone):511 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 3,39

30. *5,5-dimethyl-2-(2-(1-methylquinolin-2(1H)-ylidene)ethylidene)cyclohexane-1,3-dione* ***(38)***:



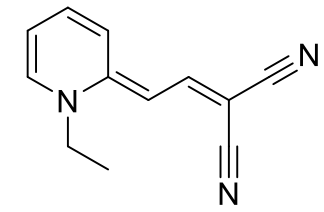
Yield: 91% ***mp:*** 257-259°C ***IR*** (KBr),ν, cm^{-1}: 3473, 3385, 2951, 2865, 1619, 1541, 1508, 1366, 1269, 1240, 1234, 1224, 966. ***^{1}H NMR:*** (600 MHz, DMSO-*d*^{6}) δ 8.37 (d, J = 14.4 Hz, 1H), 8.29 (d, J = 14.3 Hz, 1H), 8.22 (d, J = 8.3 Hz, 1H), 8.17 (d, J = 7.1 Hz, 1H), 7.94 – 7.78 (m, 2H), 7.70 – 7.59 (m, 1H), 7.44 (d, J = 7.3 Hz, 1H), 4.02 (s, 3H), 2.27 (s, 4H), 0.97 (s, 6H). ***^{13}C NMR:*** (151 MHz, DMSO-*d*^{6}) δ 195.0, 154.7, 142.5, 142.0, 138.7, 133.0, 126.3, 124.6, 124.1, 117.8, 114.6, 107.7, 105.0, 53.4 – 50.2, 41.8, 30.4, 28.3. ***Anal. calcd*** for $C_{20}H_{21}NO_2$ (307,39): C, 78.15; H, 6.89; N, 4.56; Found: C, 77,90; H, 6,77; N, 4,37; ***λ_{max}*** [nm] (acetone):574 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 6,3

31. *-5-(2-(1-methylpyridin-2(1H)-ylidene)ethylidene)pyrimidine-2,4,6(1H,3H,5H)-trione dihydrate* ***(39)***:



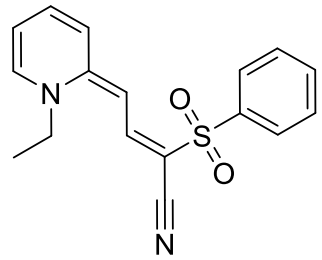
Yield: 68% ***mp:*** >300°C ***IR*** (KBr),ν, cm^{-1}: 3391, 3185, 2793, 1691, 1648, 1607, 1543, 1427, 1397, 1343, 1271, 1165, 1038, 848, 770, 515. ***^{1}H NMR:*** (600 MHz, DMSO-*d*^{6}) δ 10.18 – 9.86 (m, 2H), 8.28 (d, J = 6.2 Hz, 1H), 8.07 (d, J = 14.7 Hz, 1H), 7.96 (d, J = 8.7 Hz, 1H), 7.84 (t, J = 7.8 Hz, 1H), 7.46 (d, J = 14.7 Hz, 1H), 7.09 (t, J = 6.7 Hz, 1H), 3.88 (s, 3H). ***^{13}C NMR:*** (151 MHz, DMSO-*d*^{6}) δ 164.6 (br), 155.8, 151.1, 143.1, 142.1, 139.8, 120.3, 117.1, 100.1, 93.4, 44.1. ***Anal. calcd*** for $C_{12}H_{15}N_3O_5$ (281,27): C, 51.24; H, 5.38; N, 14.94; Found: C, 51,04; H, 5,19; N, 14,76; ***λ_{max}*** [nm] (acetone):457 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 2,67

32. *2-(2-(1-ethylpyridin-2(1H)-ylidene)ethylidene)malononitrile* ***(40)***:



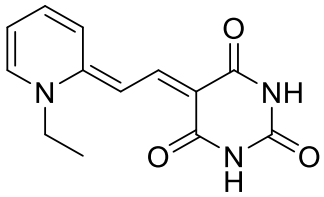
Yield: 75% ***^{1}H NMR:*** (600 MHz, DMSO-*d*^{6}) δ 8.08 (d, J = 6.4 Hz, 1H), 7.92 (d, J = 8.9 Hz, 1H), 7.88 (d, J = 13.8 Hz, 1H), 7.63 (t, J = 7.9 Hz, 1H), 6.93 – 6.83 (m, 1H), 5.57 (d, J = 13.8 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 1.33 (t, J = 7.2 Hz, 3H). ***^{13}C NMR:*** (151 MHz, DMSO-*d*^{6}) δ 152.2, 149.0, 141.1, 138.2, 120.7, 120.7, 118.6, 115.3, 92.9, 50.4, 48.4, 13.4. ***Anal. calcd*** for $C_{12}H_{11}N_3$ (197,10): C, 73.07; H, 5.62; N, 21.30 Found: C, 72,84; H, 5,49; N, 21,16; ***λ_{max}*** [nm] (acetone):450 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 6,30

33. *4-(1-ethylpyridin-2(1H)-ylidene)-2-(phenylsulfonyl)but-2-enenitrile* ***(41)****:*



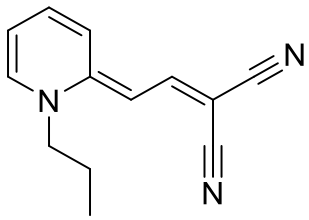
Yield: 70% ***mp:*** 184-186°C ***IR*** (KBr),ν, cm^{-1}: 3442, 2172, 1634, 1526, 1440, 1397, 1316, 1300, 1273, 1223, 1140, 1085, 1032, 621, 601, 577. ***^{1}H NMR:*** (600 MHz, DMSO-*d*^{6}) δ 8.12 (t, J = 6.6 Hz, 1H), 7.94 – 7.86 (m, 2H), 7.84 – 7.79 (m, 2H), 7.72 – 7.67 (m, 1H), 7.60 – 7.54 (m, 3H), 6.95 (t, J = 6.8 Hz, 1H), 5.48 (d, J = 14.0 Hz, 1H), 4.18 (q, J = 7.2 Hz, 2H), 1.31 (t, J = 7.2 Hz, 3H). ***^{13}C NMR:*** (151 MHz, DMSO-*d*^{6}) δ 152.8, 144.3, 144.3, 141.4, 138.7, 131.9, 129.2, 125.7, 120.7, 117.8, 115.8, 91.7, 82.7, 50.4, 13.5. ***Anal. calcd*** for $C_{17}H_{16}N_2O_2S$ (312,09): C, 65.36; H, 5.16; N, 8.97; Found: C, 65,11; H, 4,98; N, 8,75; ***λ$_{max}$*** [nm] (acetone):448 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 5,00

34. *5-(2-(1-ethylpyridin-2(1H)-ylidene)ethylidene)pyrimidine-2,4,6(1H,3H,5H)-trione hydrate* ***(42)****:*



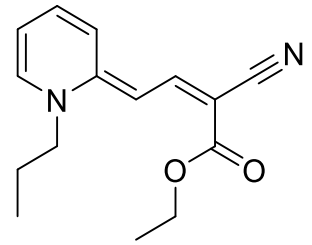
Yield: 87% ***mp:*** >300°C ***IR*** (KBr),ν, cm^{-1}: 3450, 3141, 1689, 1636, 1606, 1542, 1433, 1405, 1337, 1293, 1143, 762, 524 ***^{1}H NMR:*** (600 MHz, DMSO-*d*^{6}) δ 10.16 – 9.82 (m, 2H), 8.31 (d, J = 6.3 Hz, 1H), 8.08 (d, J = 14.6 Hz, 1H), 7.99 (d, J = 8.7 Hz, 1H), 7.85 (t, J = 7.8 Hz, 1H), 7.60 (d, J = 14.6 Hz, 1H), 7.14 (t, J = 6.6 Hz, 1H), 4.29 (q, J = 6.9 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H). ***^{13}C NMR:*** (151 MHz, DMSO-*d*^{6}) δ 164.5 (br), 154.9, 151.1, 142.3, 142.1, 139.8, 120.9, 117.6, 99.7, 93.3, 51.2, 13.8. ***Anal. calcd*** for $C_{13}H_{15}N_3O_4$ (277,28): C, 56.31; H, 5.45; N, 15.15; Found: C, 56,06; H, 5,29; N, 15,01; ***λ$_{max}$*** [nm] (acetone):464 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 2,37

35. *2-(2-(1-propylpyridin-2(1H)-ylidene)ethylidene)malononitrile* ***(43)****:*



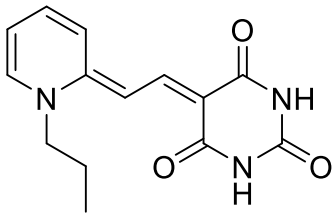
Yield: 58% ***mp:*** 147-149°C ***IR*** (KBr),ν, cm^{-1}: 3432, 2191, 1665, 1624, 1541, 1518, 1462, 1372, 1324, 1284, 1206, 1154, 1090, 825, 766. ***^{1}H NMR:*** (600 MHz, DMSO-*d*^{6}) δ 8.06 (d, J = 6.2 Hz, 1H), 7.93 (d, J = 8.9 Hz, 1H), 7.90 (d, J = 13.8 Hz, 1H), 7.63 (t, J = 7.7 Hz, 1H), 6.87 (t, J = 6.4 Hz, 1H), 5.54 (d, J = 13.8 Hz, 1H), 4.10 (t, J = 7.0 Hz, 2H), 1.90 – 1.56 (m, 2H), 0.91 (t, J = 7.2 Hz, 3H). ***^{13}C NMR:*** (151 MHz, DMSO-*d*^{6}) δ 152.3, 149.0, 141.7, 138.2, 120.7, 120.6, 118.5, 114.9, 93.1, 56.4, 48.5, 20.7, 10.4. ***Anal. calcd*** for $C_{13}H_{13}N_3$ (211,11): C, 73.91; H, 6.20; N, 19.89 Found: C, 73,76; H, 6,03; N, 19,63; ***λ$_{max}$*** [nm] (acetone):452 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 3,42

36. *Ethyl 2-cyano-4-(1-propylpyridin-2(1H)-ylidene)but-2-enoate* ***(44)****:*

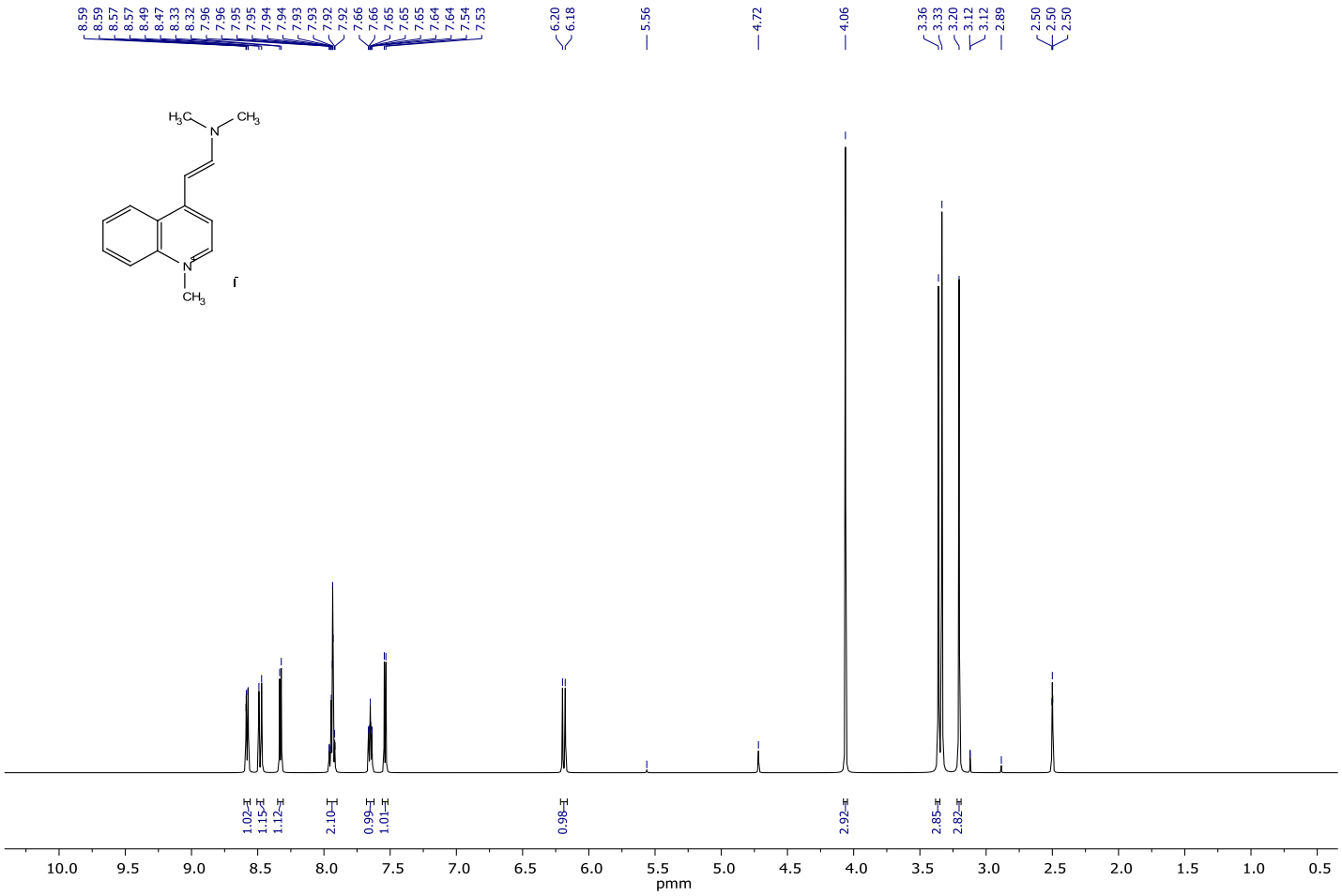


Yield: 63% ***mp:*** 162-165°C ***IR*** (KBr),ν, cm^{-1}: 3450, 2969, 2182, 1669, 1635, 1532, 1449, 1412, 1310, 1241, 1217, 1155, 1100, 1078, 803, 757. ***^{1}H NMR:*** (600 MHz, DMSO-*d*^{6}) δ 8.08 (d, J = 14.0 Hz, 1H), 8.01 (d, J = 6.4 Hz, 1H), 7.75 (d, J = 9.0 Hz, 1H), 7.57 (t, J = 7.9 Hz, 1H), 6.79 (t, J = 6.6 Hz, 1H), 5.53 (d, J = 14.0 Hz, 1H), 4.14 – 4.01 (m, 4H), 1.85 – 1.65 (m, 2H), 1.20 (t, J = 7.1 Hz, 3H), 0.92 (t, J = 7.4 Hz, 3H). ***^{13}C NMR:*** (151 MHz, DMSO-*d*^{6}) δ 165.9, 152.7, 146.9, 141.6, 137.8, 120.3, 120.0, 114.0, 92.2, 75.1, 58.9, 56.1, 20.6, 14.6, 10.4. ***Anal. calcd*** for $C_{15}H_{18}N_2O_2$ (258,14): C, 69.74; H, 7.02; N, 10.84; Found: C, 69,53; H, 6,88; N, 10,65; ***λ$_{max}$*** [nm] (acetone):456 ε $_{max}$ ×10^{-4} [M^{-1} ×cm^{-1}]: 4,11

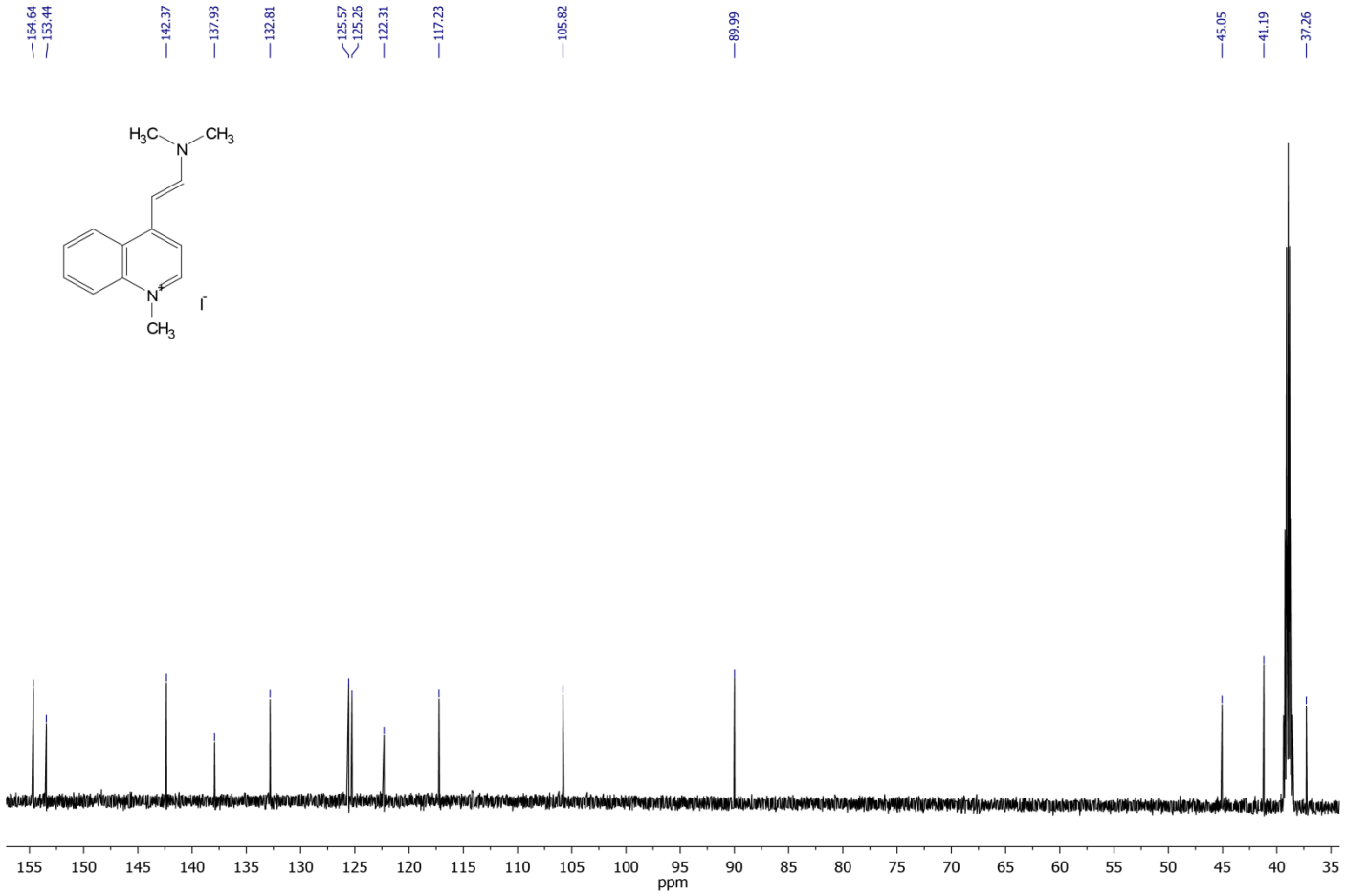
37. *5-(2-(1-propylpyridin-2(1H)-ylidene)ethylidene)pyrimidine-2,4,6(1H,3H,5H)-trione hydrate* ***(45)****:*



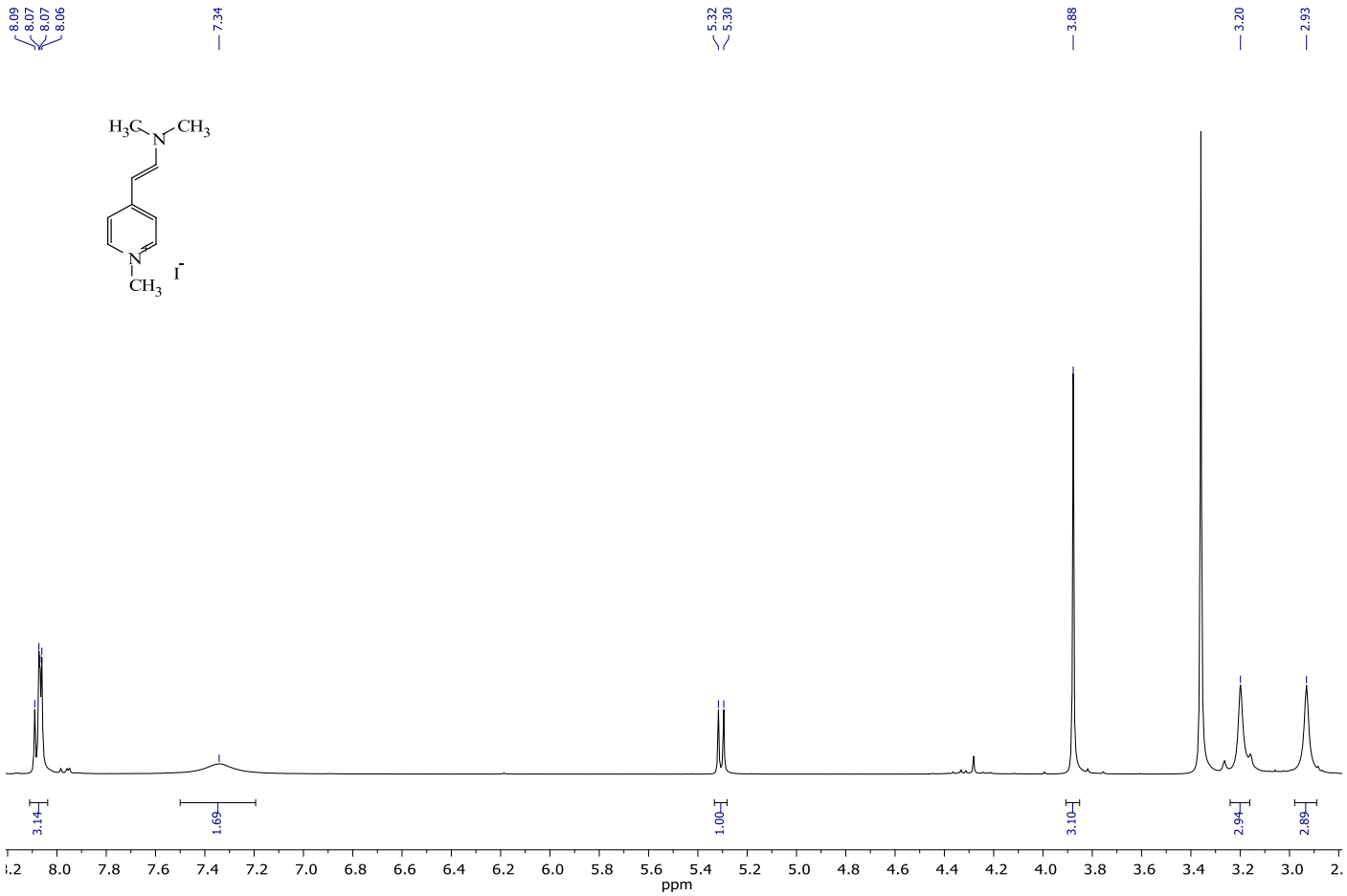
Yield: 77% ***mp:*** >300°C ***IR*** (KBr),ν, cm^{-1}: 3526, 3410, 3153, 1685, 1636, 1606, 1542, 1432, 1400, 1336, 1300, 1273, 1158, 755, 523. ***^{1}H NMR:*** (600 MHz, DMSO-*d*^{6}) δ 10.14 – 9.81 (m, 2H), 8.29 (d, J = 6.2 Hz, 1H), 8.08 (d, J = 14.6 Hz, 1H), 8.00 (d, J = 8.7 Hz, 1H), 7.84 (t, J = 7.7 Hz, 1H), 7.61 (d, J = 14.6 Hz, 1H), 7.12 (t, J = 6.6 Hz, 1H), 4.21 (t, J = 7.2 Hz, 2H), 1.83 (q, J = 7.3 Hz, 2H), 0.95 (t, J = 7.3 Hz, 3H). ***^{13}C NMR:*** (151 MHz, DMSO-*d*^{6}) δ 164.6 (br), 155.0, 151.1, 142.5, 142.2, 139.8, 120.8, 117.2, 99.9, 93.3, 57.2, 21.2, 10.5. ***Anal. calcd*** for $C_{14}H_{17}N_3O_4$ (291,31): C, 57.72; H, 5.88; N, 14.42; Found: C, 57,3; H, 5,54; N, 13,93; ***λ$_{max}$*** [nm] (acetone):463 ε $_{max}$ ×10^{-4} [M^{-1} ×cm^{-1}]: 8,85



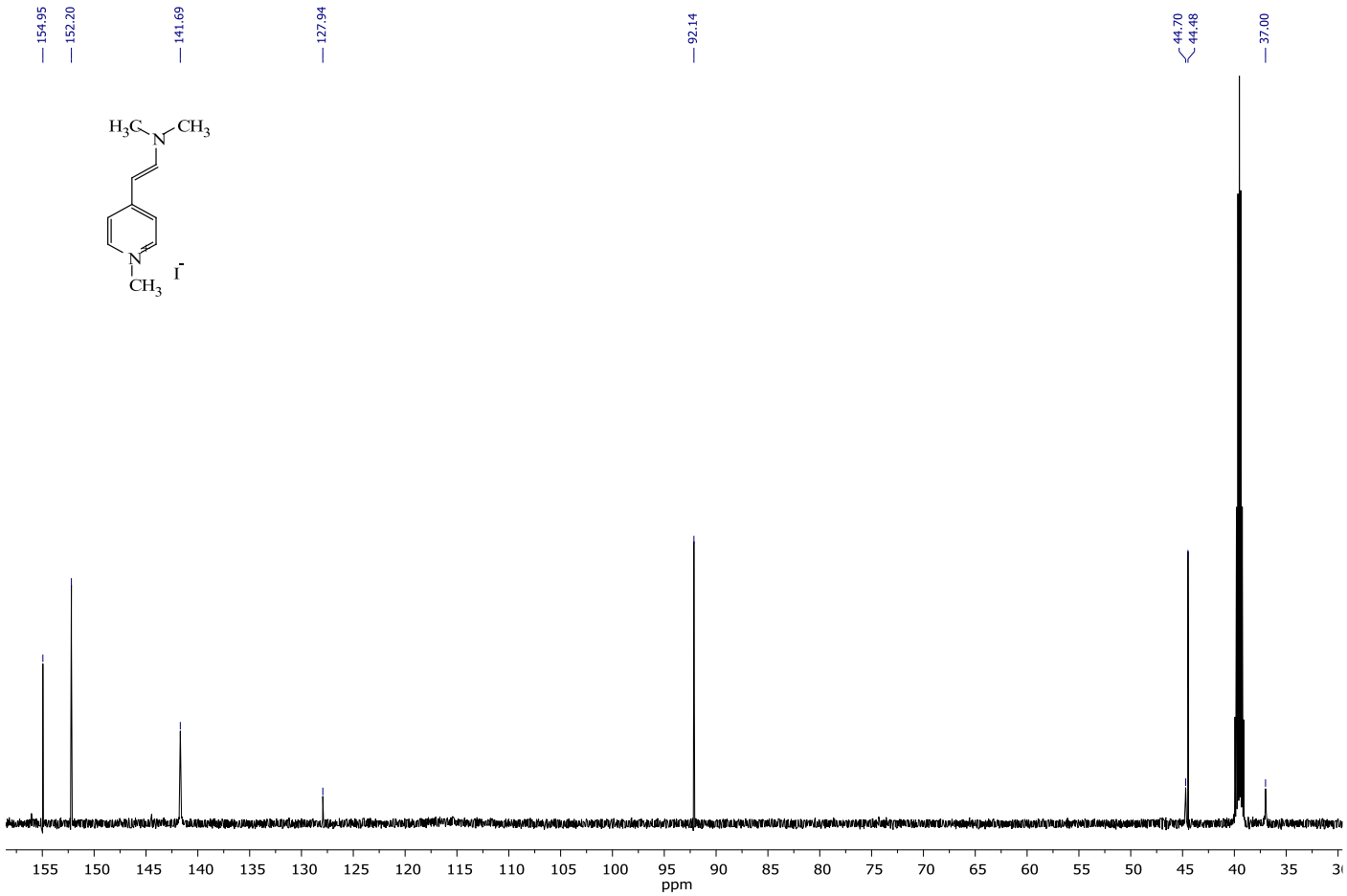
^{1}H NMR spectrum of the compound **3**



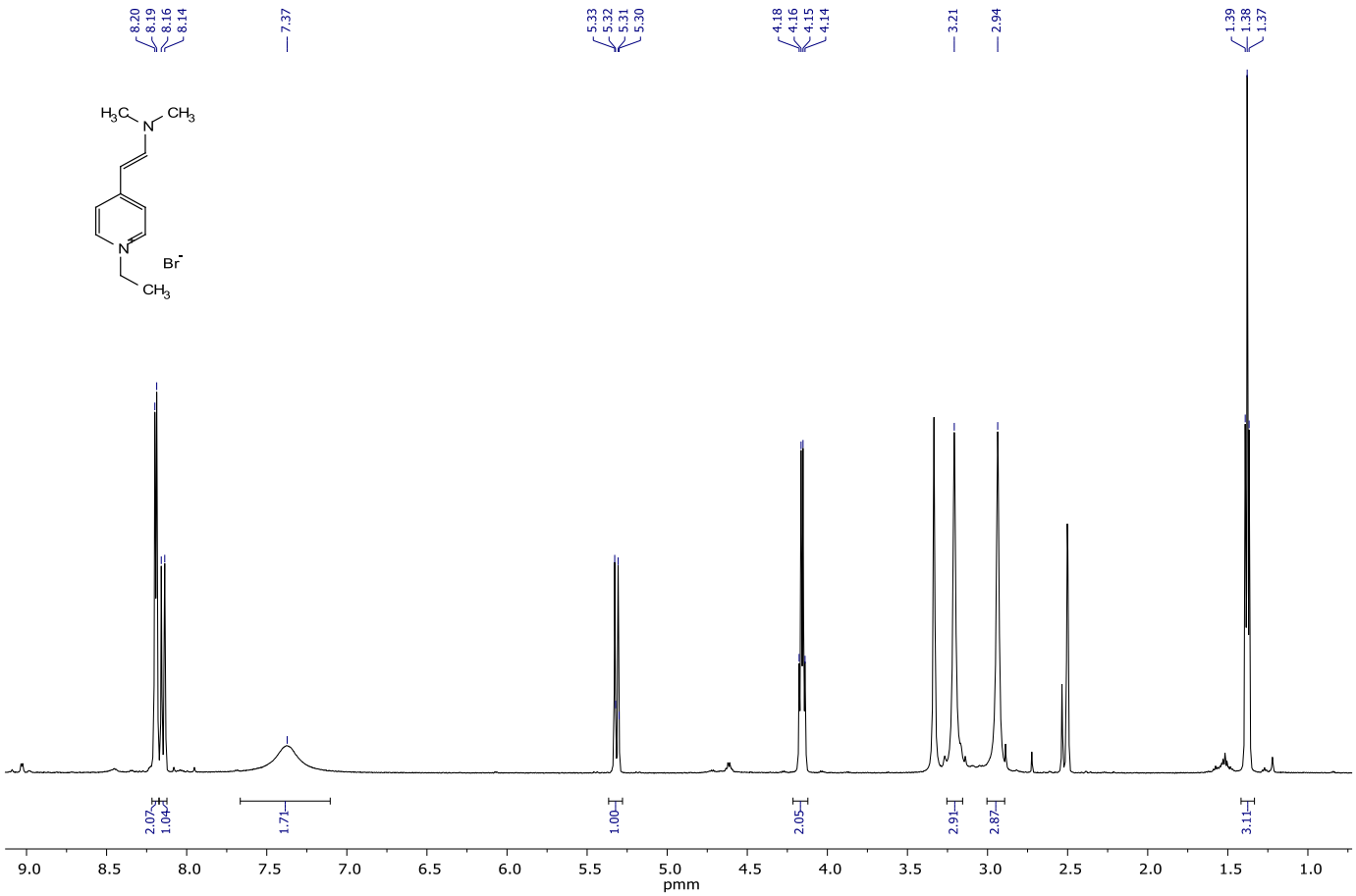
^{13}C NMR spectrum of the compound **3**



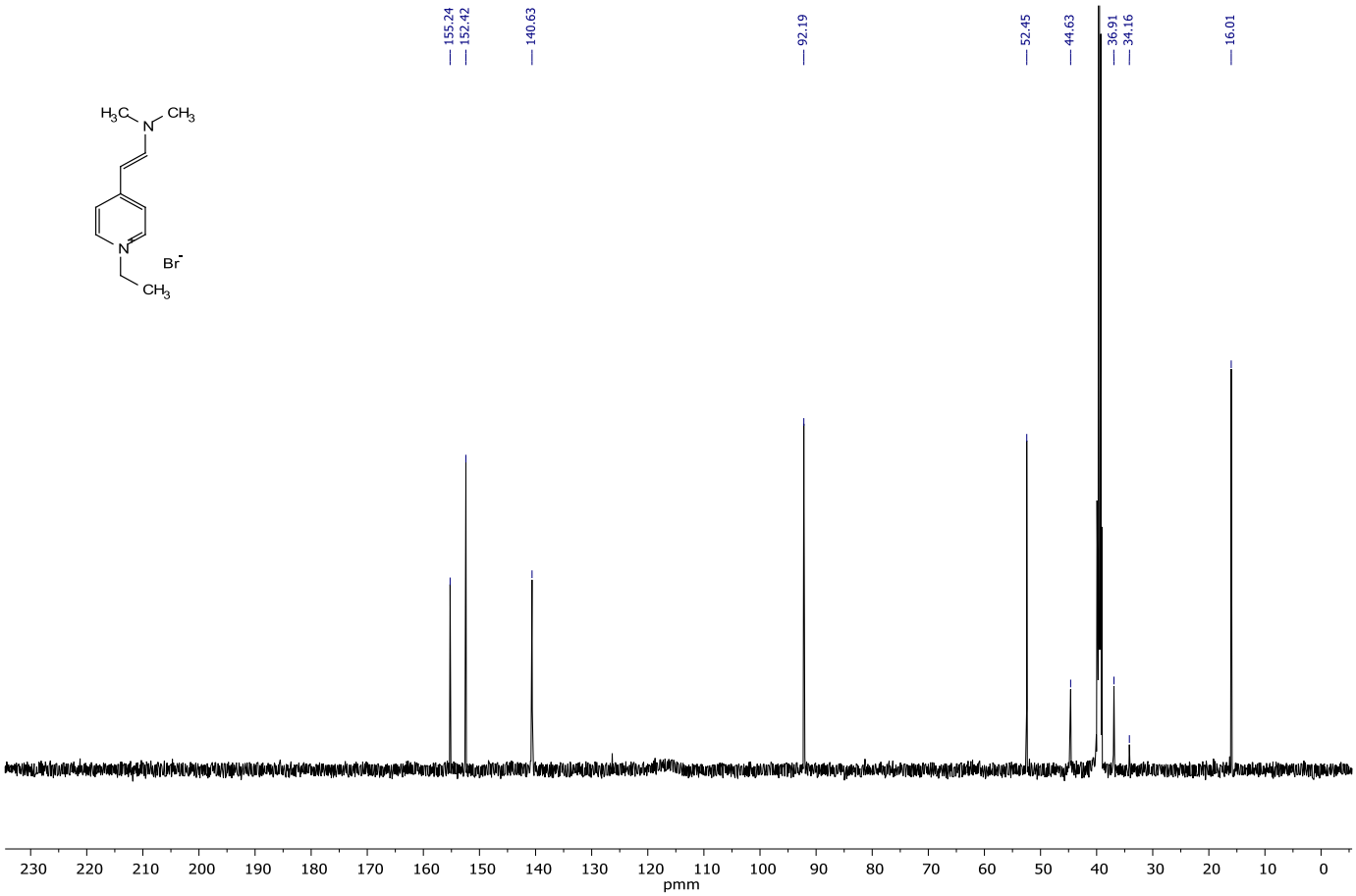
^{1}H NMR spectrum of the compound **4**



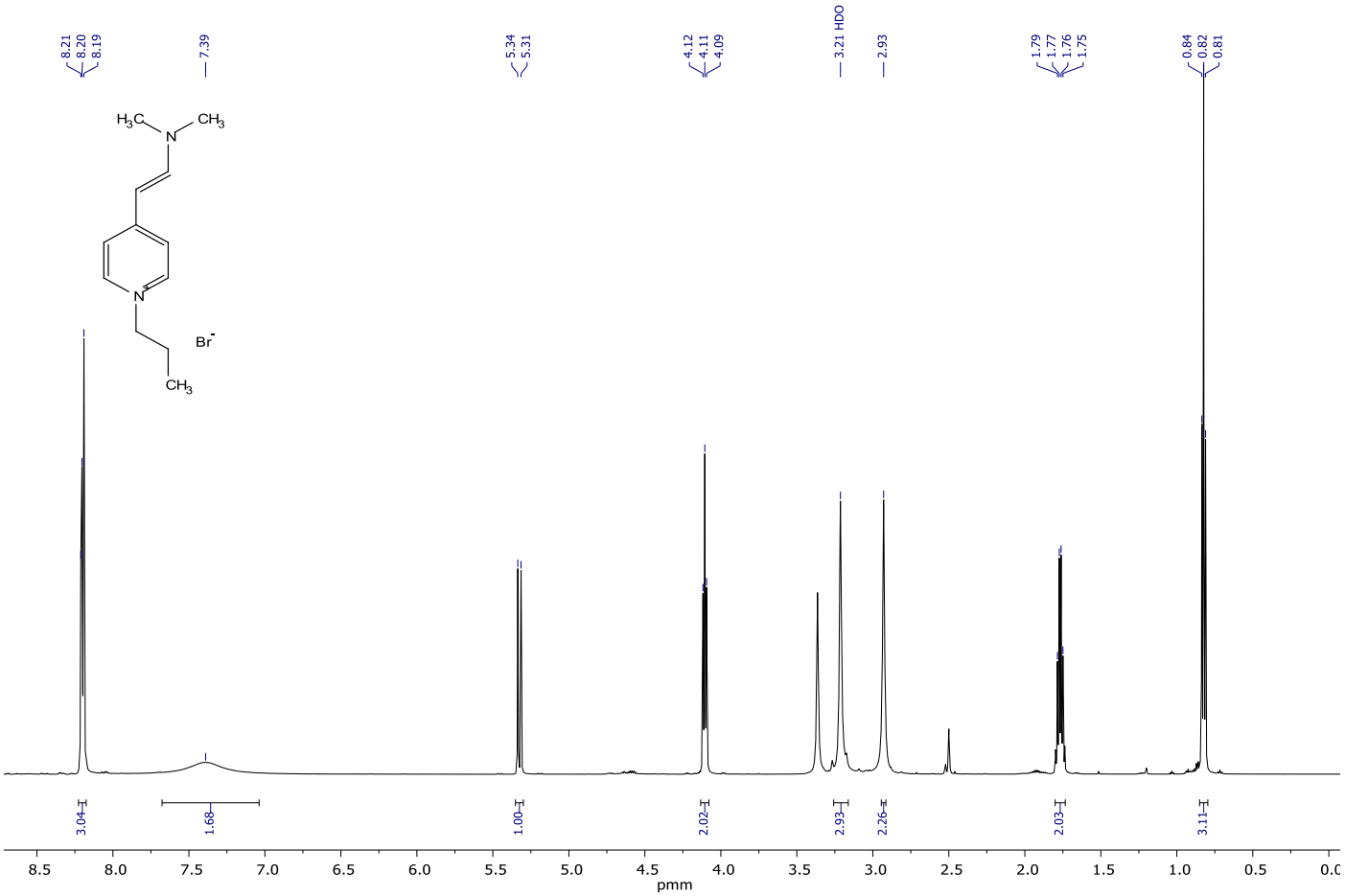
^{13}C NMR spectrum of the compound **4**



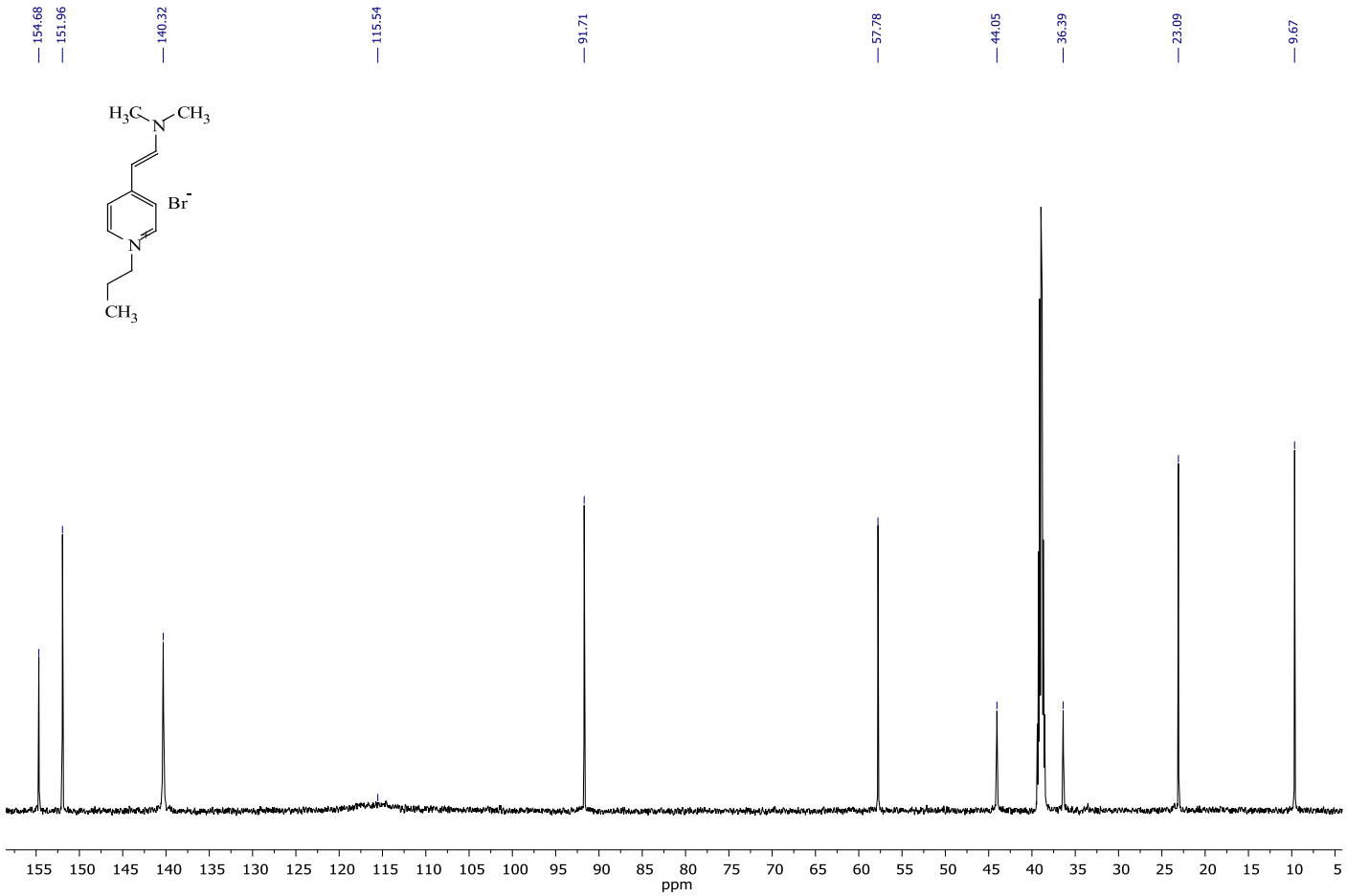
^{1}H NMR spectrum of the compound **5**



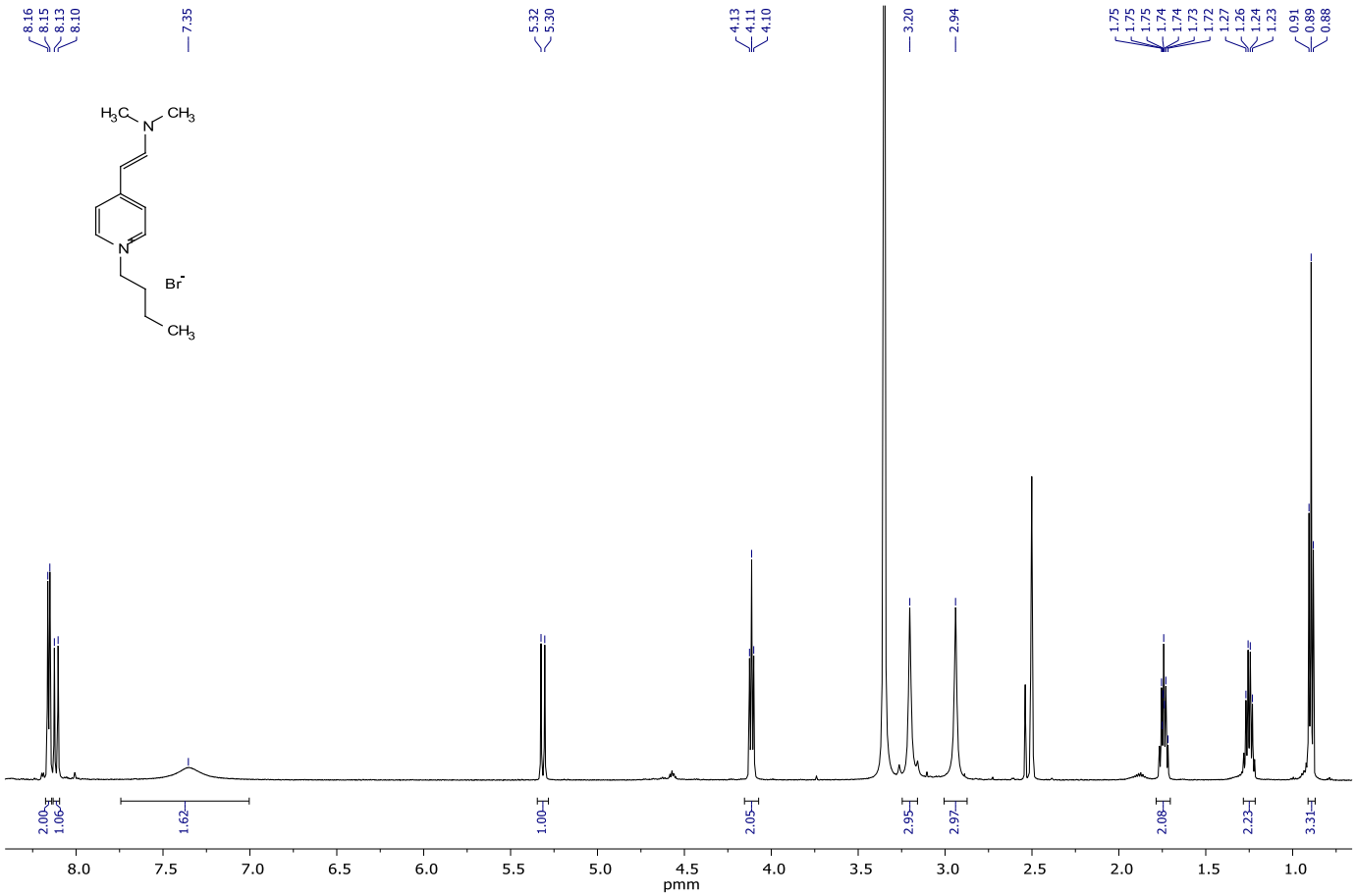
^{13}C NMR spectrum of the compound **5**



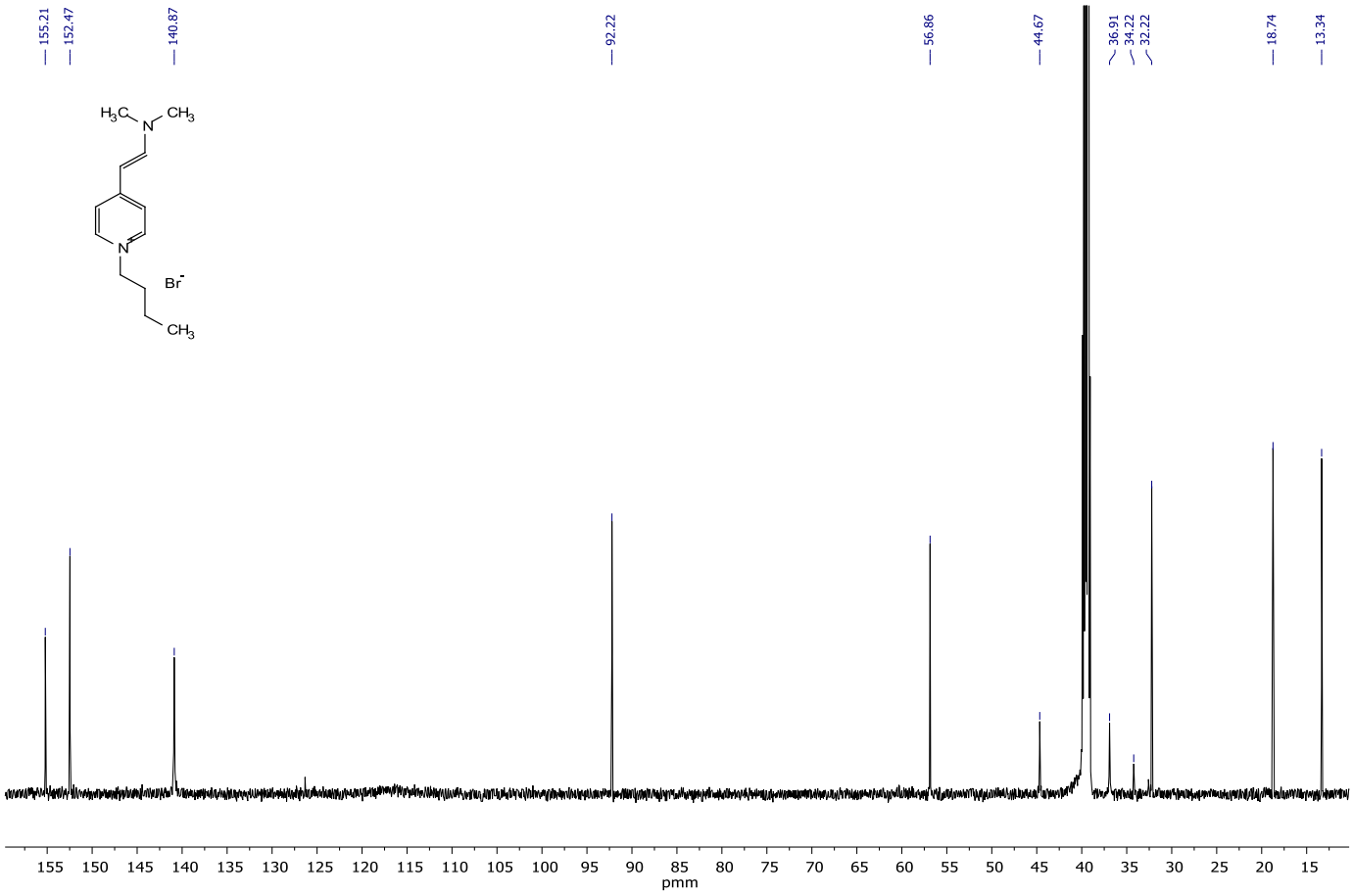
^{1}H NMR spectrum of the compound **6**



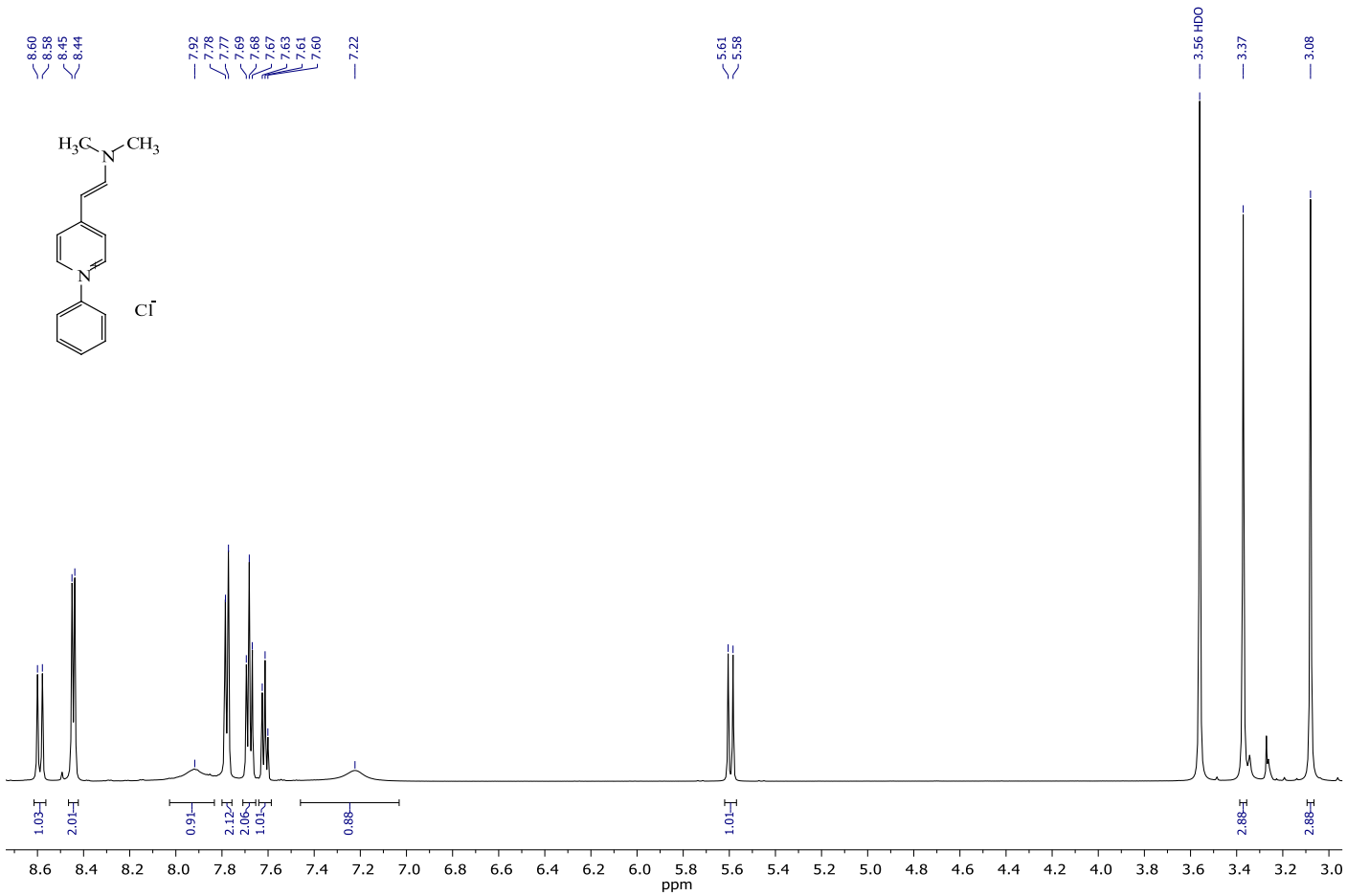
^{13}C NMR spectrum of the compound **6**



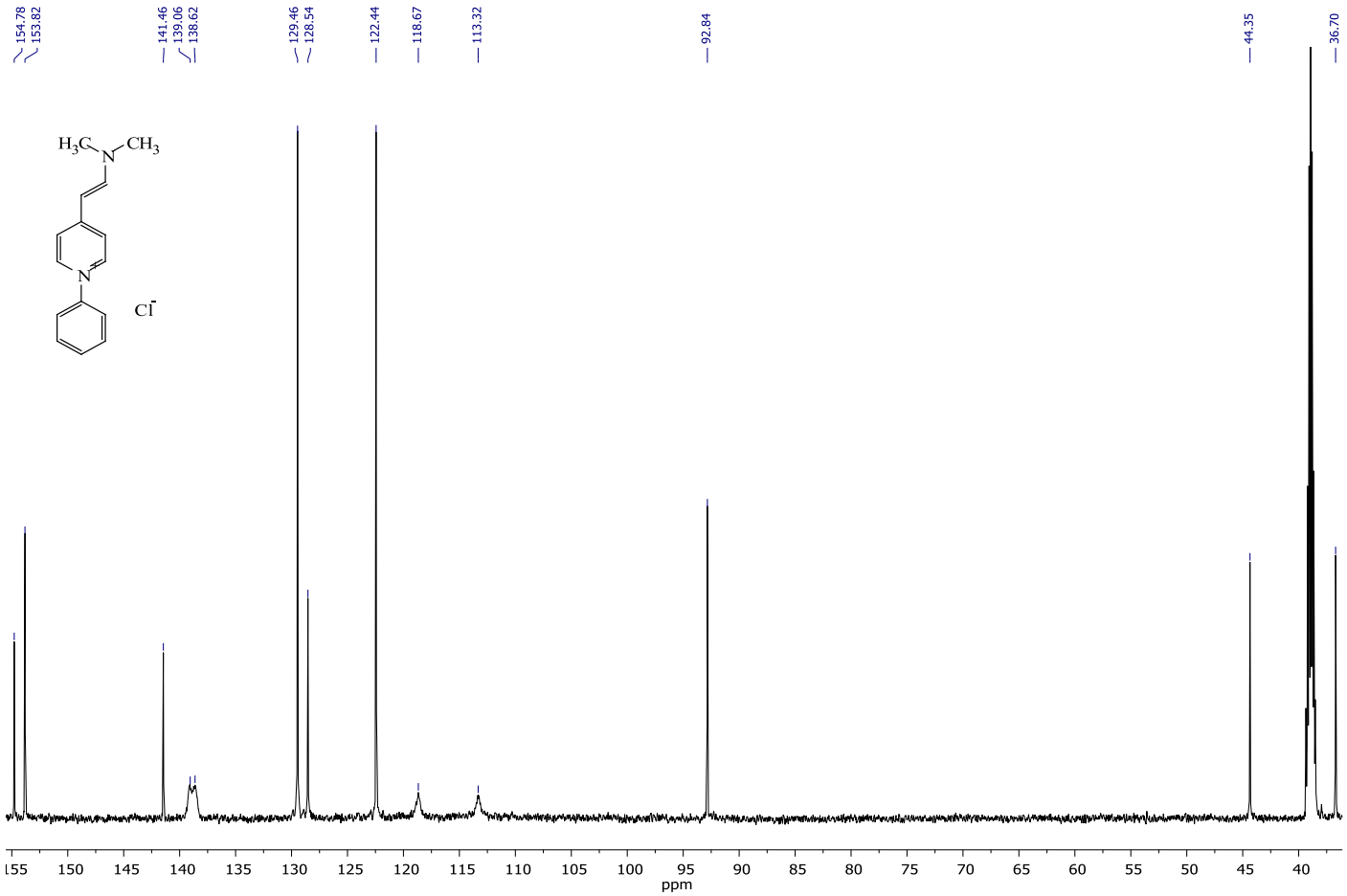
^{1}H NMR spectrum of the compound **7**



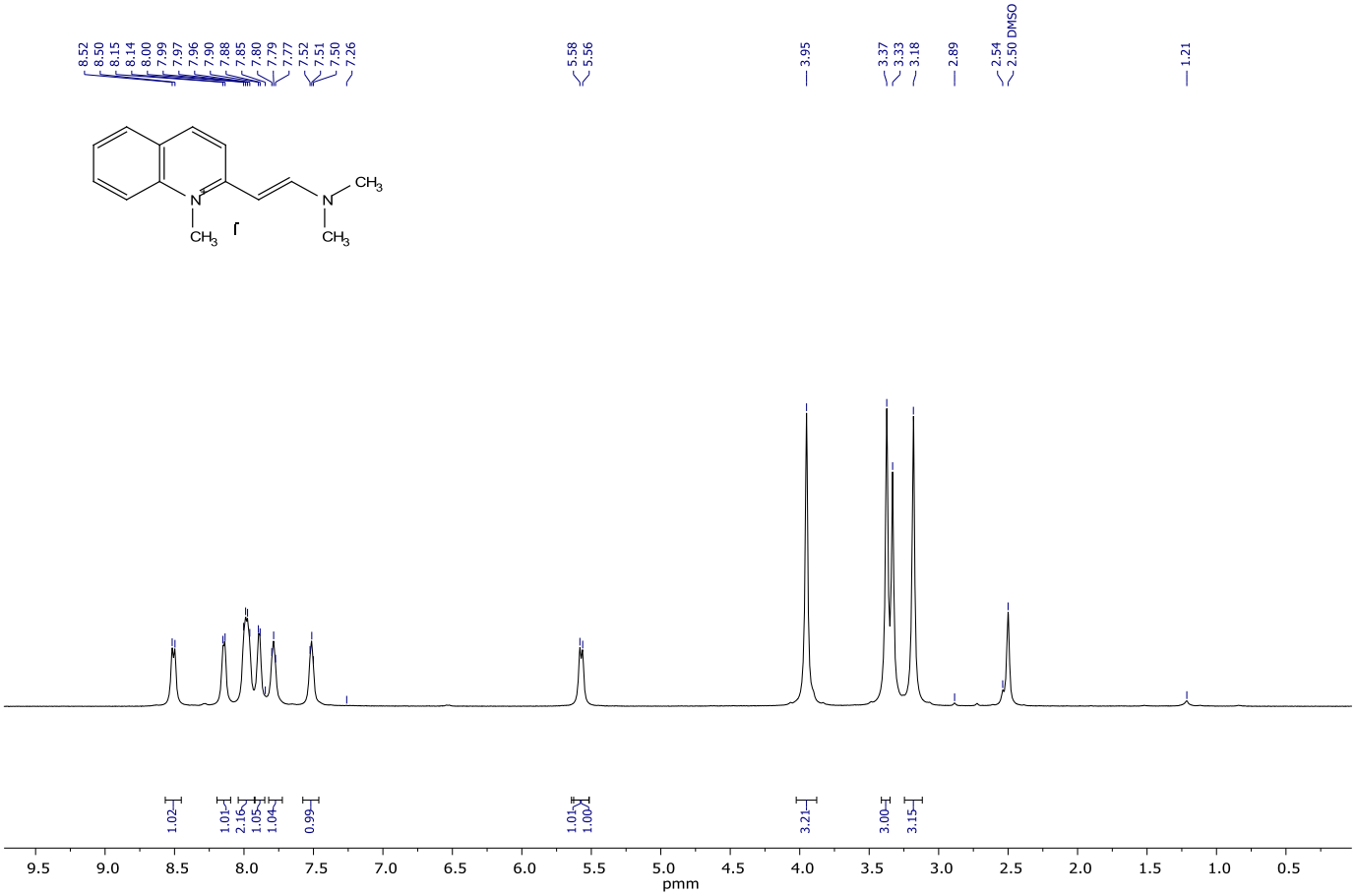
^{13}C NMR spectrum of the compound **7**



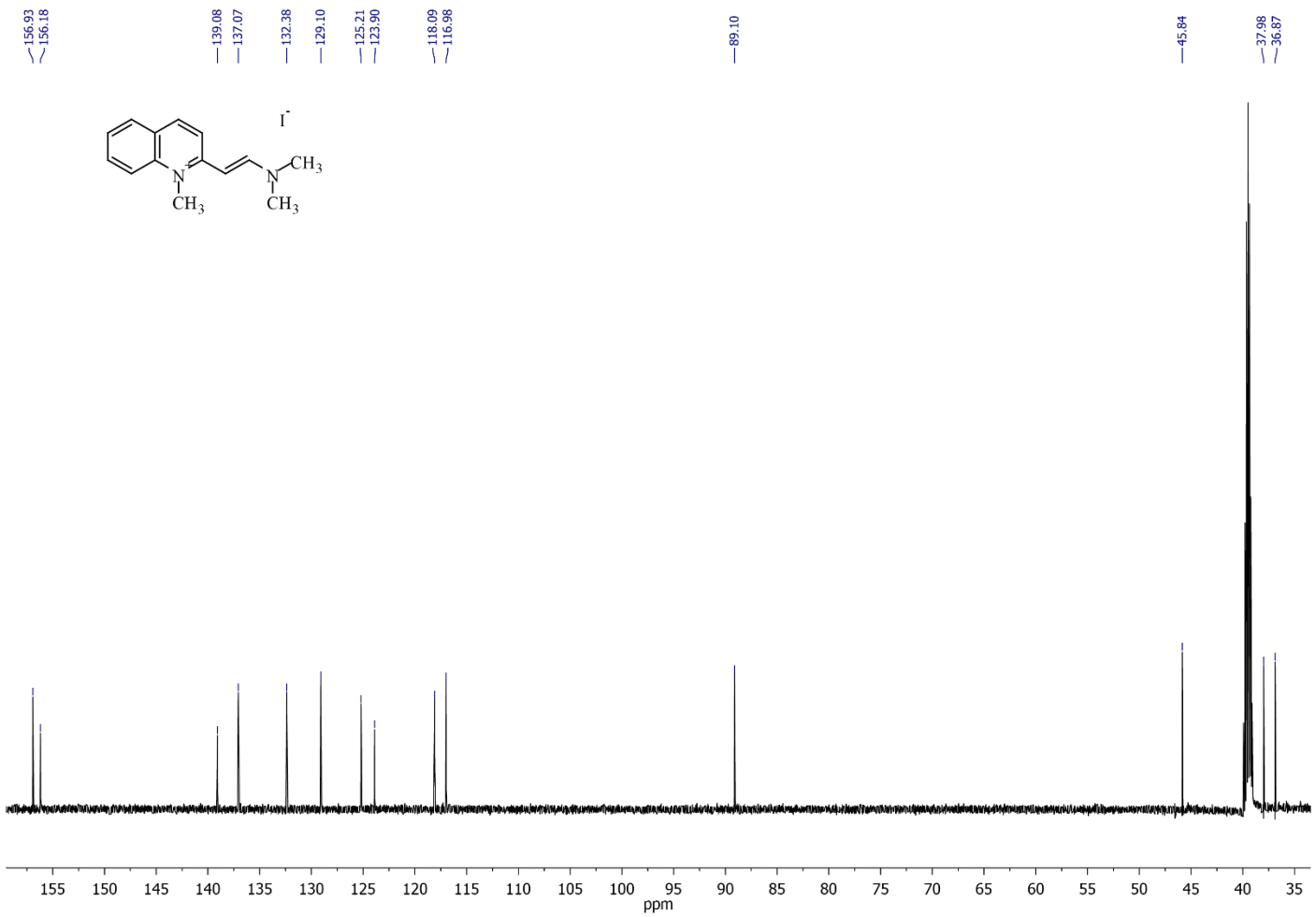
^{1}H NMR spectrum of the compound **8**



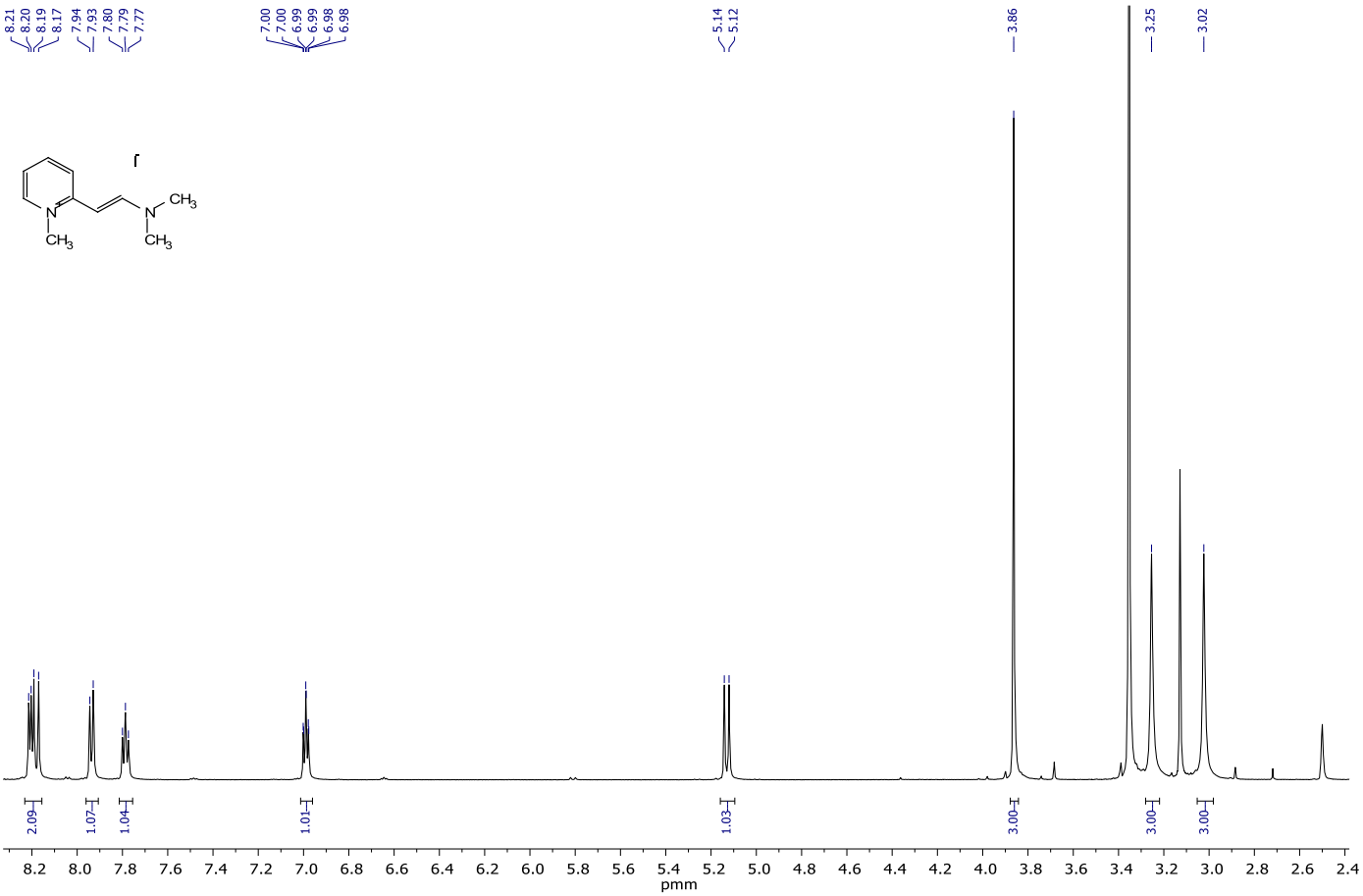
^{13}C NMR spectrum of the compound **8**



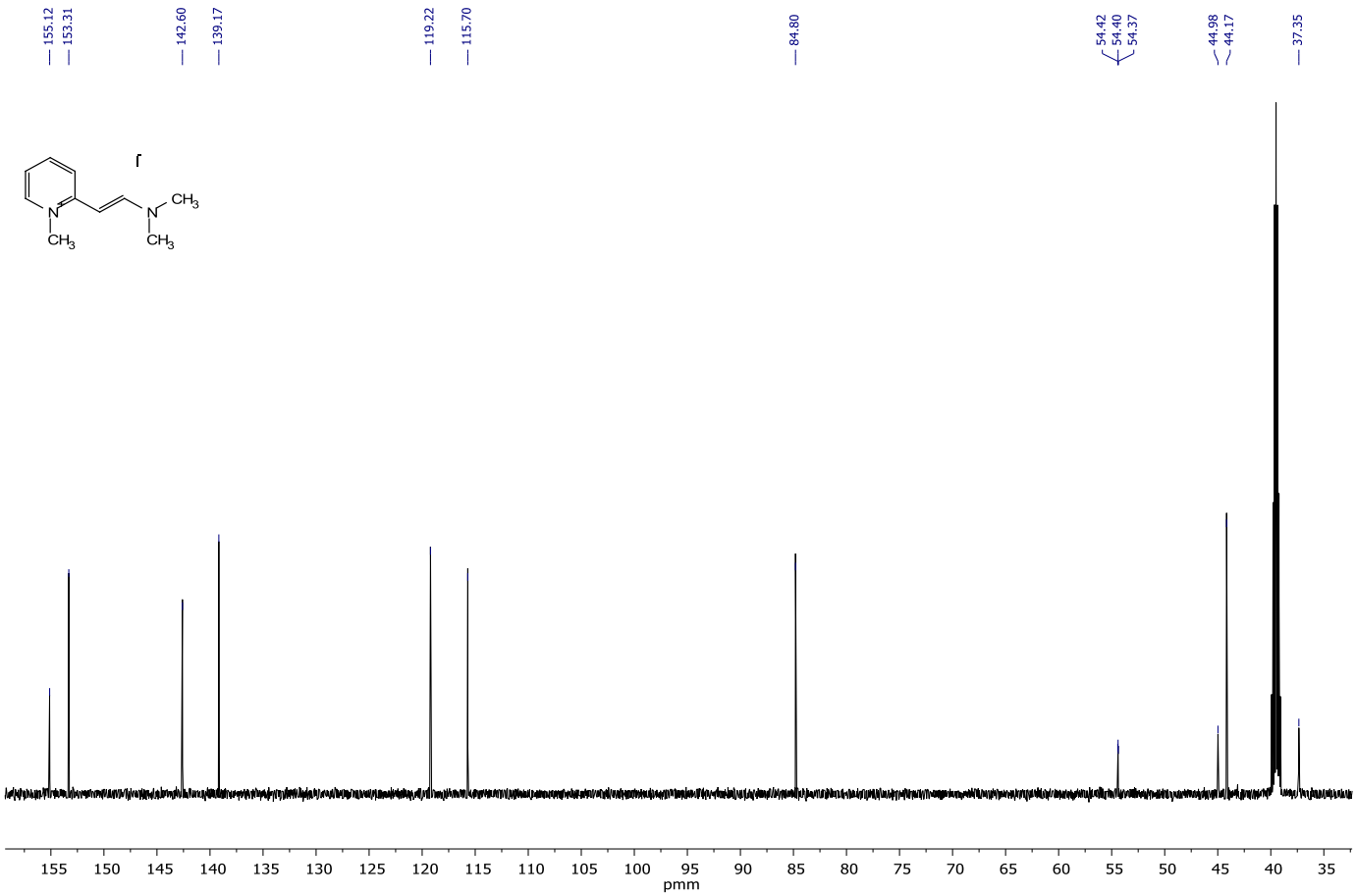
^{1}H NMR spectrum of the compound **9**



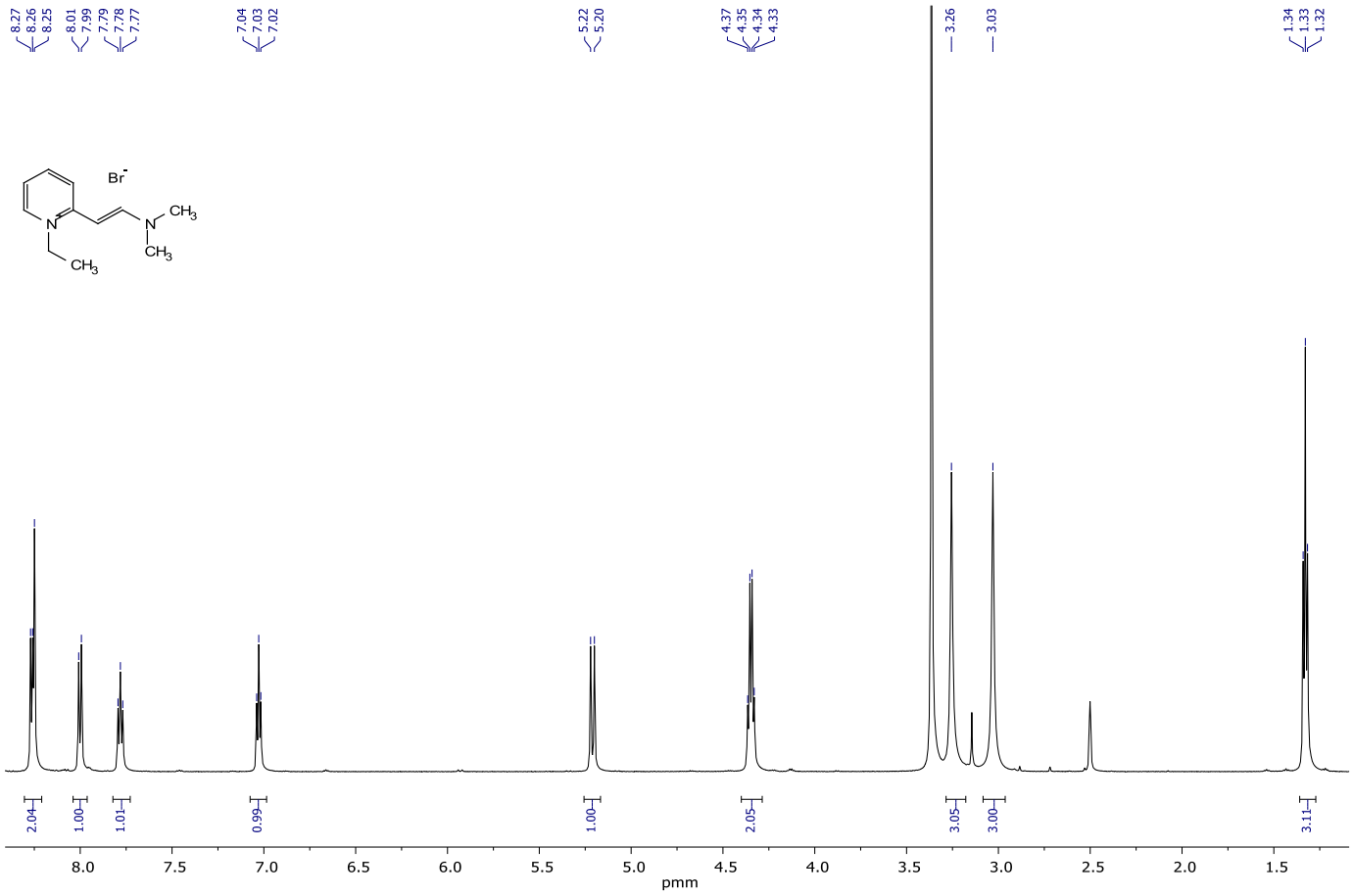
^{13}C NMR spectrum of the compound **9**



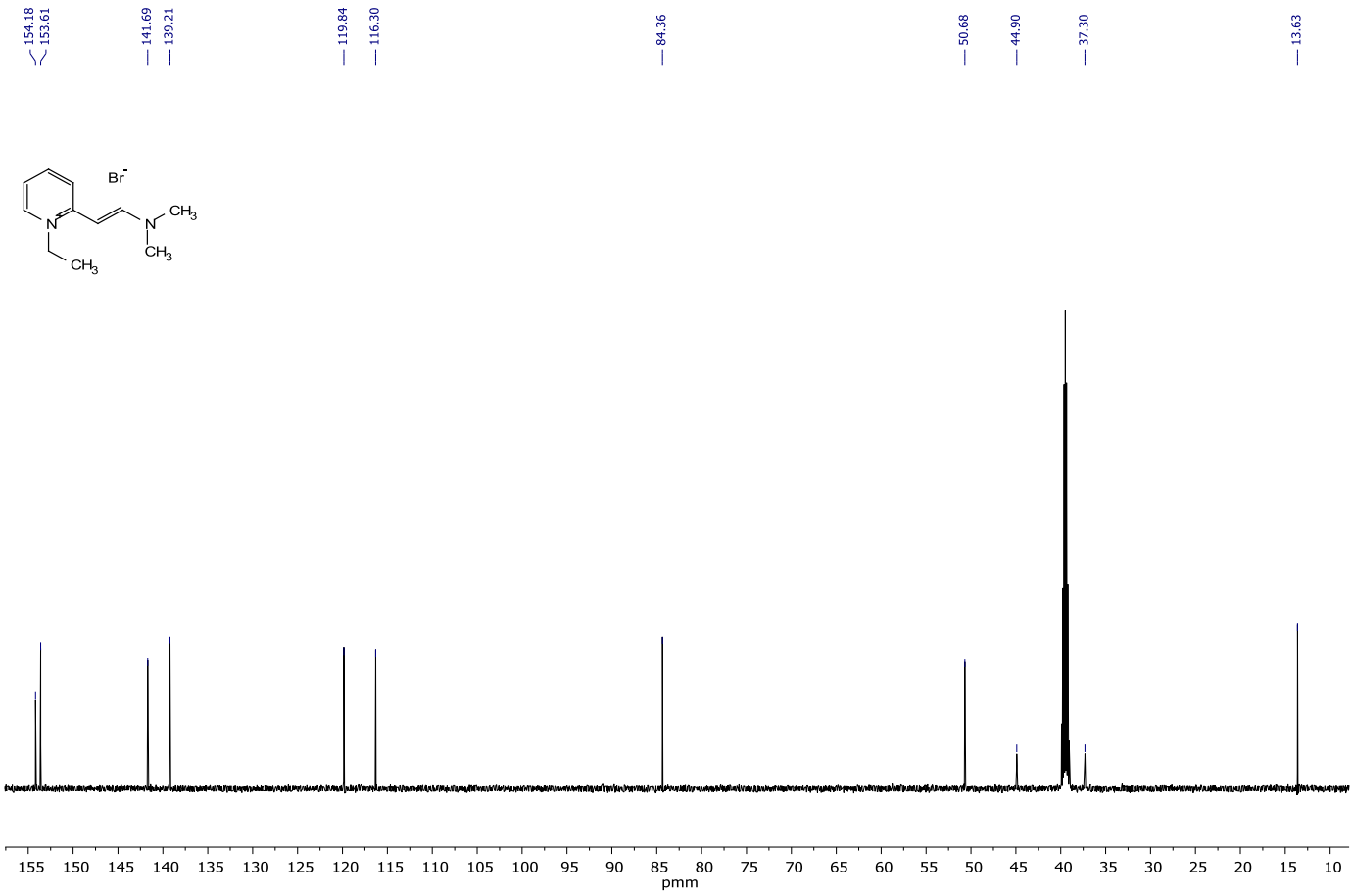
^{1}H NMR spectrum of the compound **10**



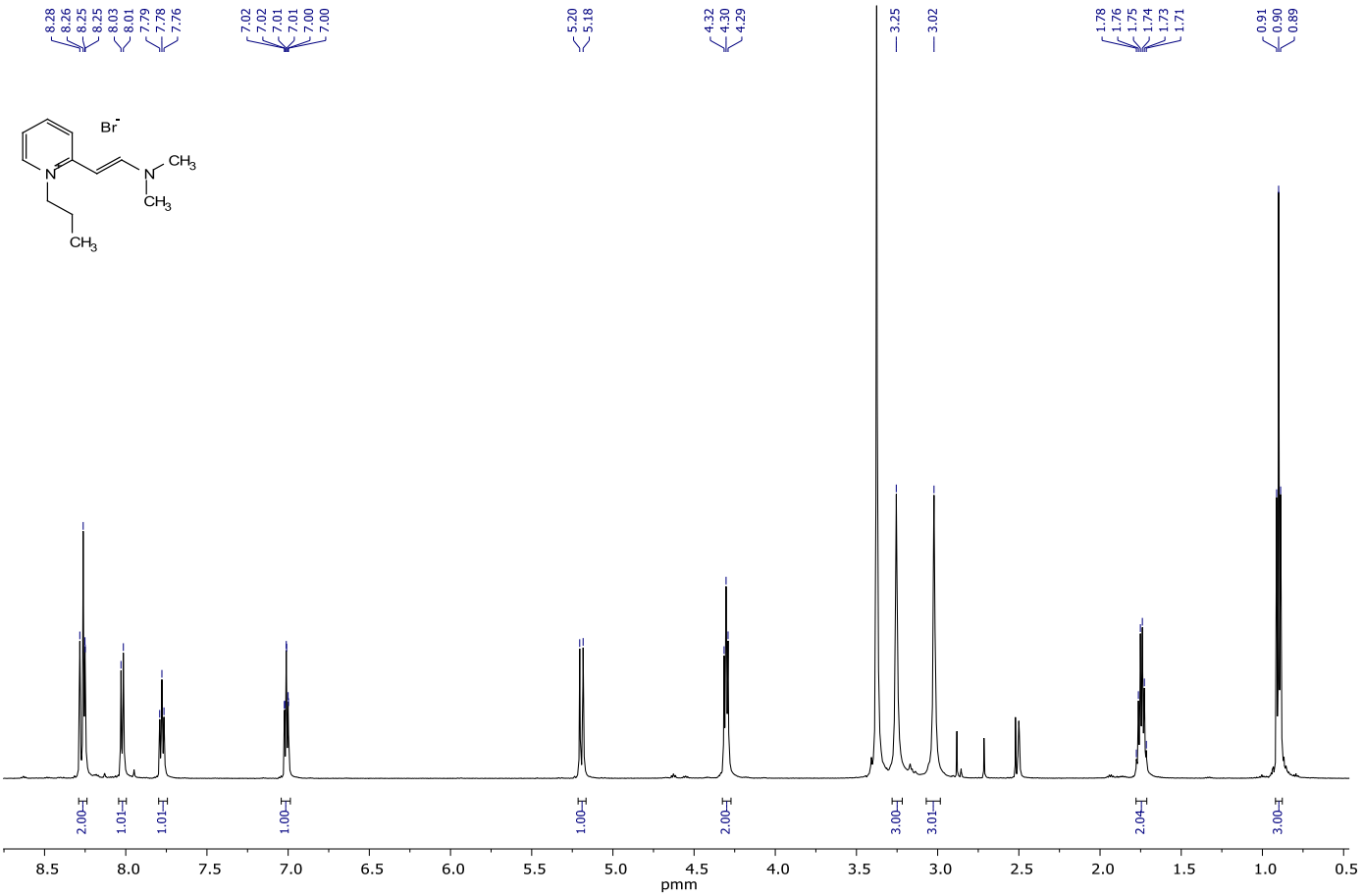
^{13}C NMR spectrum of the compound **10**



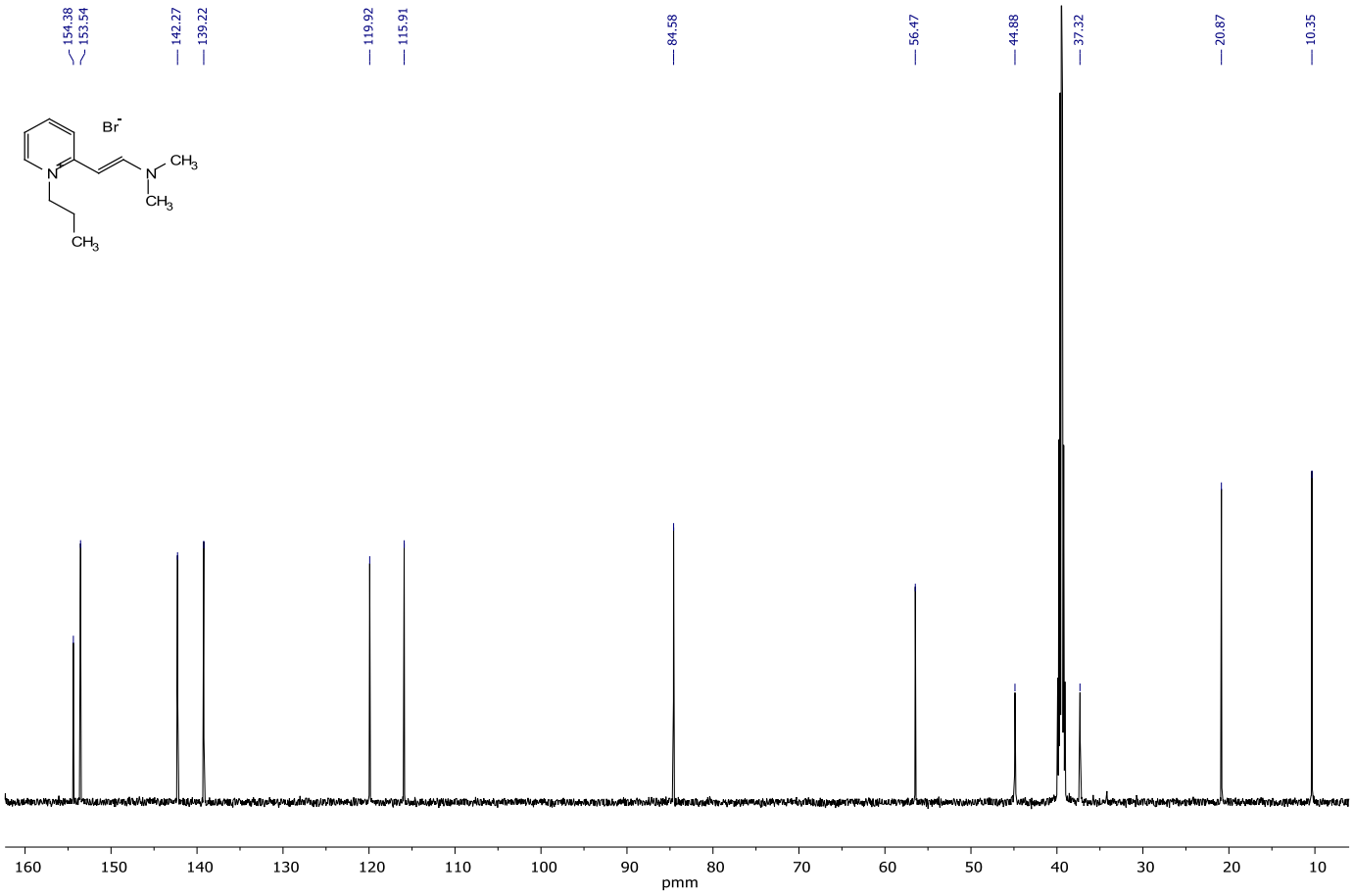
^{1}H NMR spectrum of the compound **11**



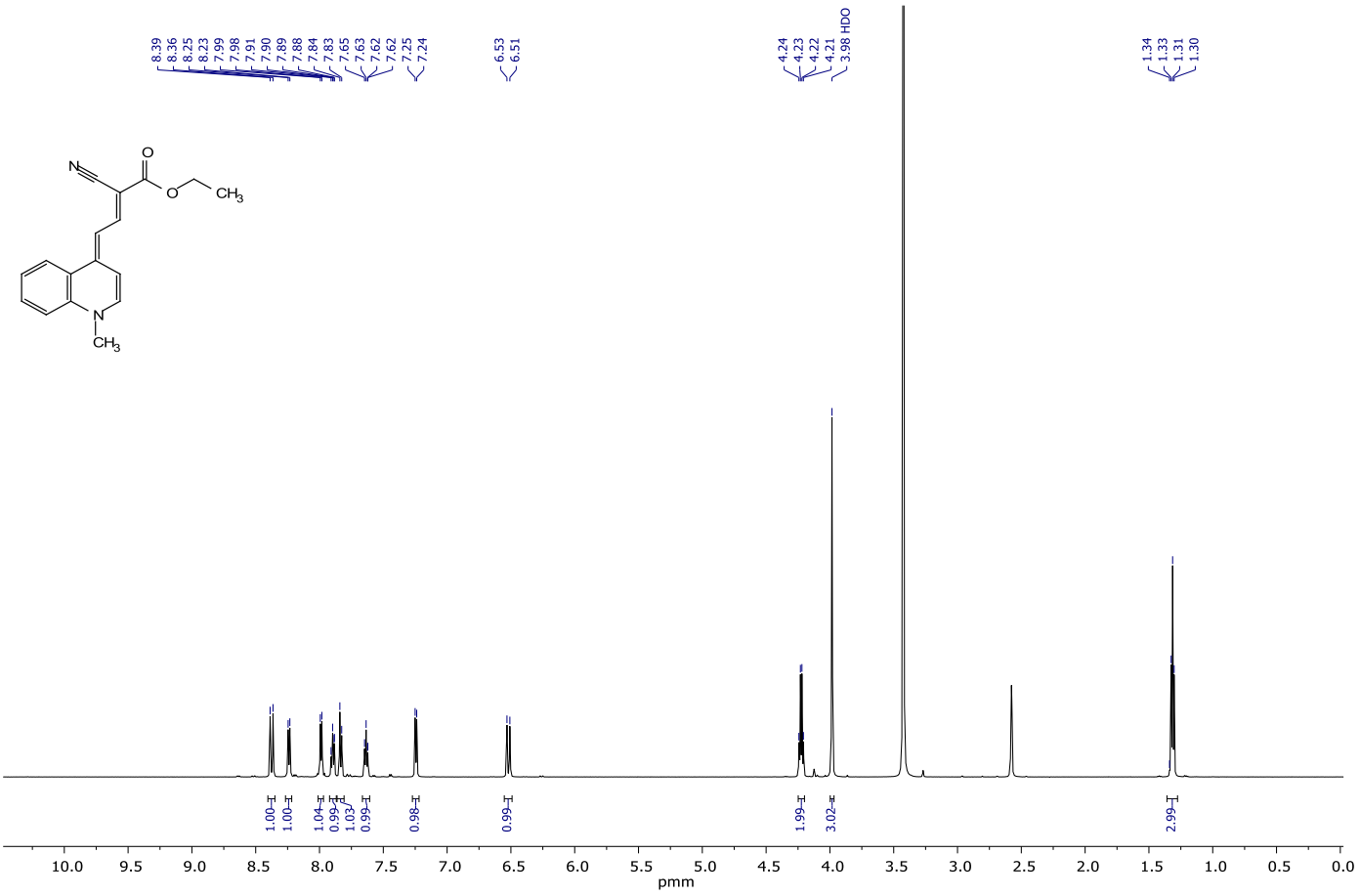
^{13}C NMR spectrum of the compound **11**



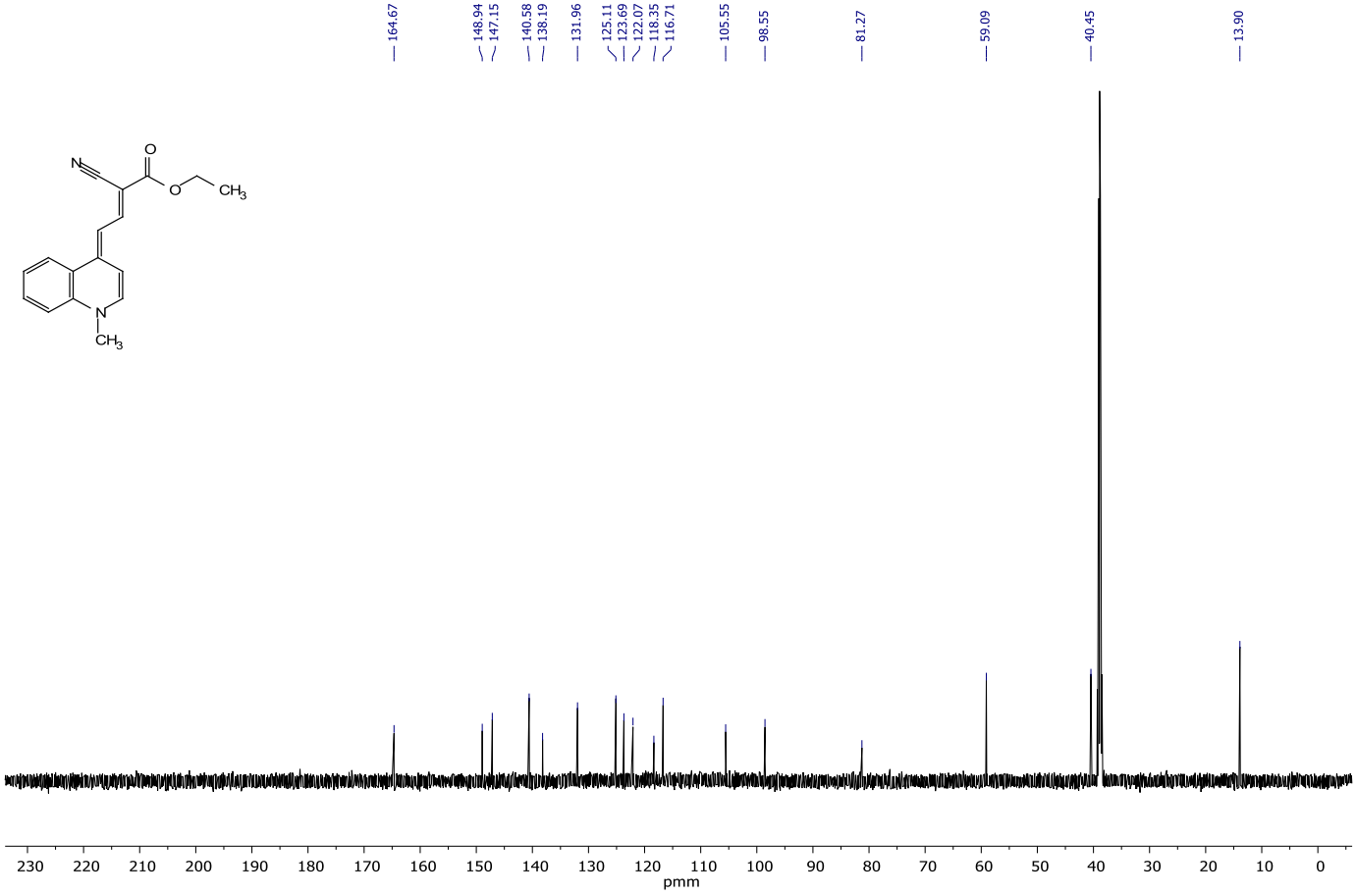
^{1}H NMR spectrum of the compound **12**



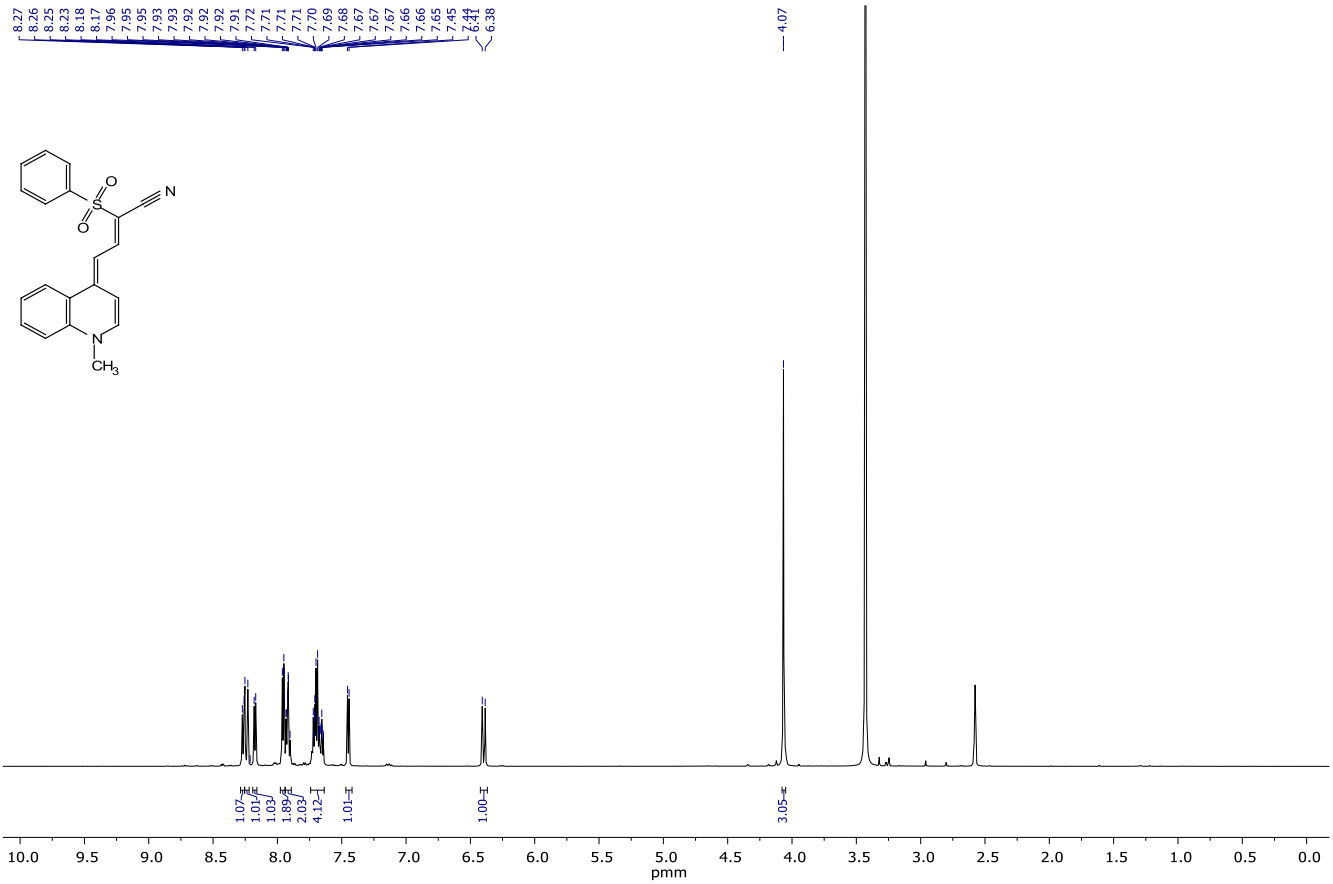
^{13}C NMR spectrum of the compound **12**



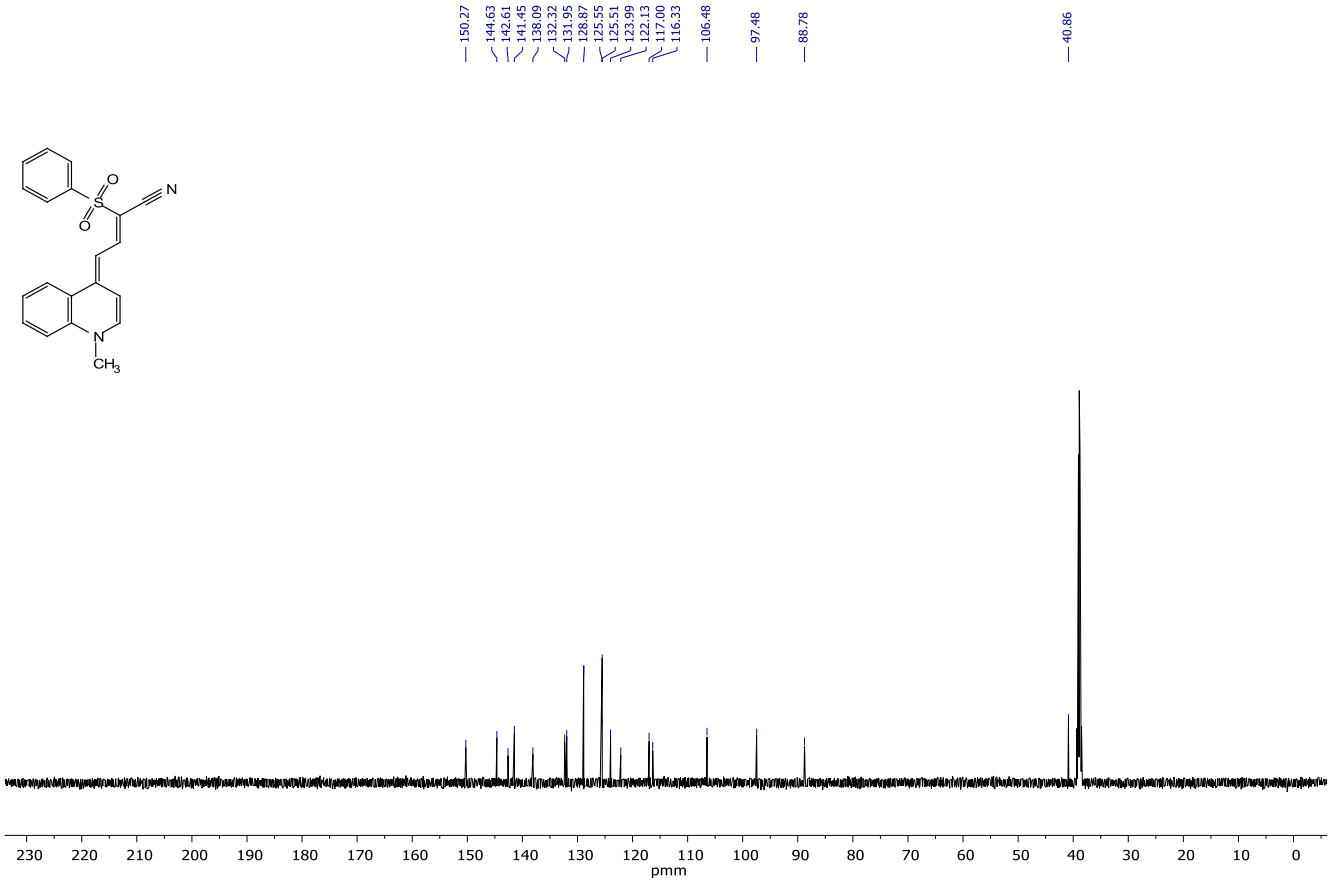
^{1}H NMR spectrum of the compound **19**



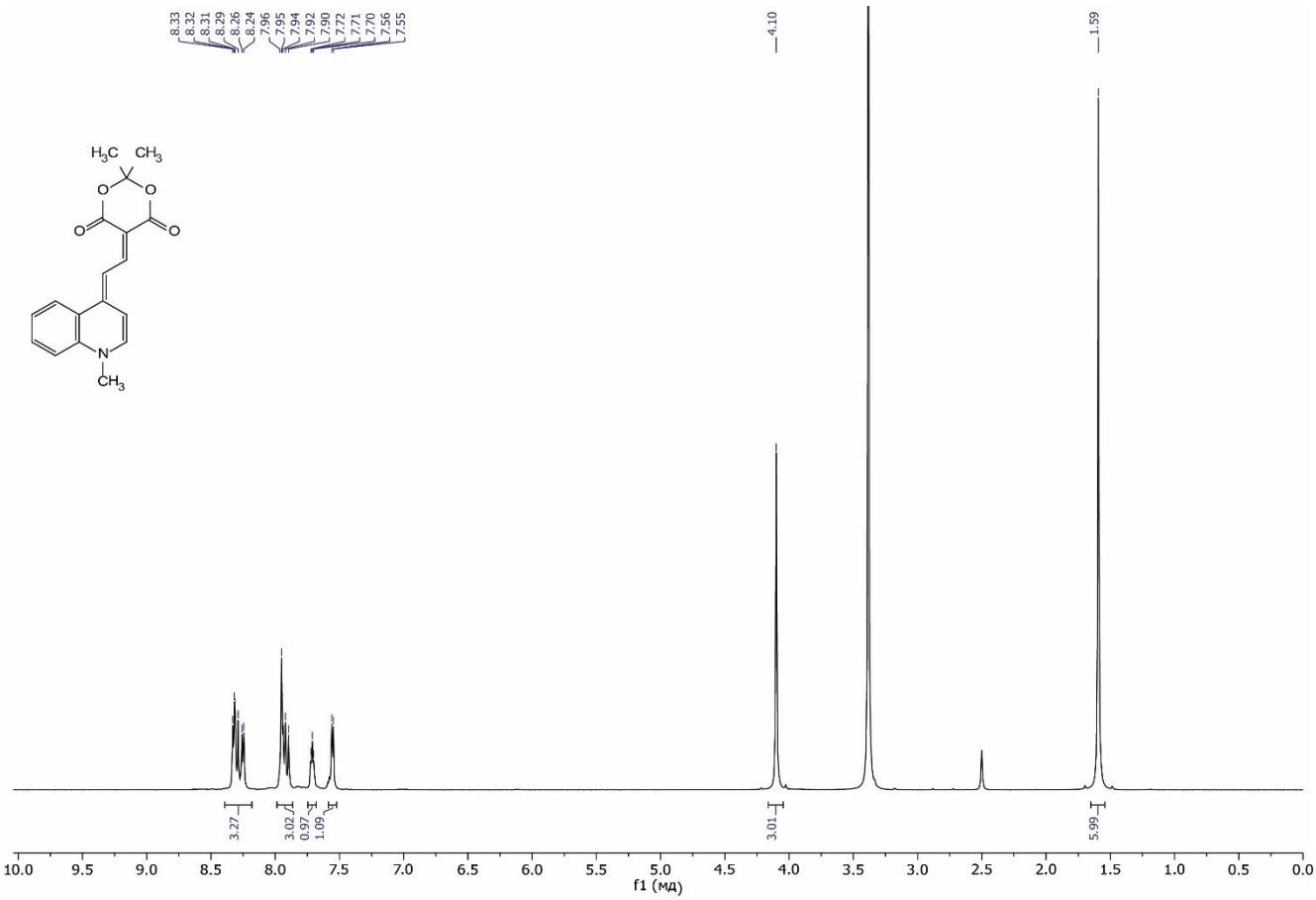
^{13}C NMR spectrum of the compound **19**



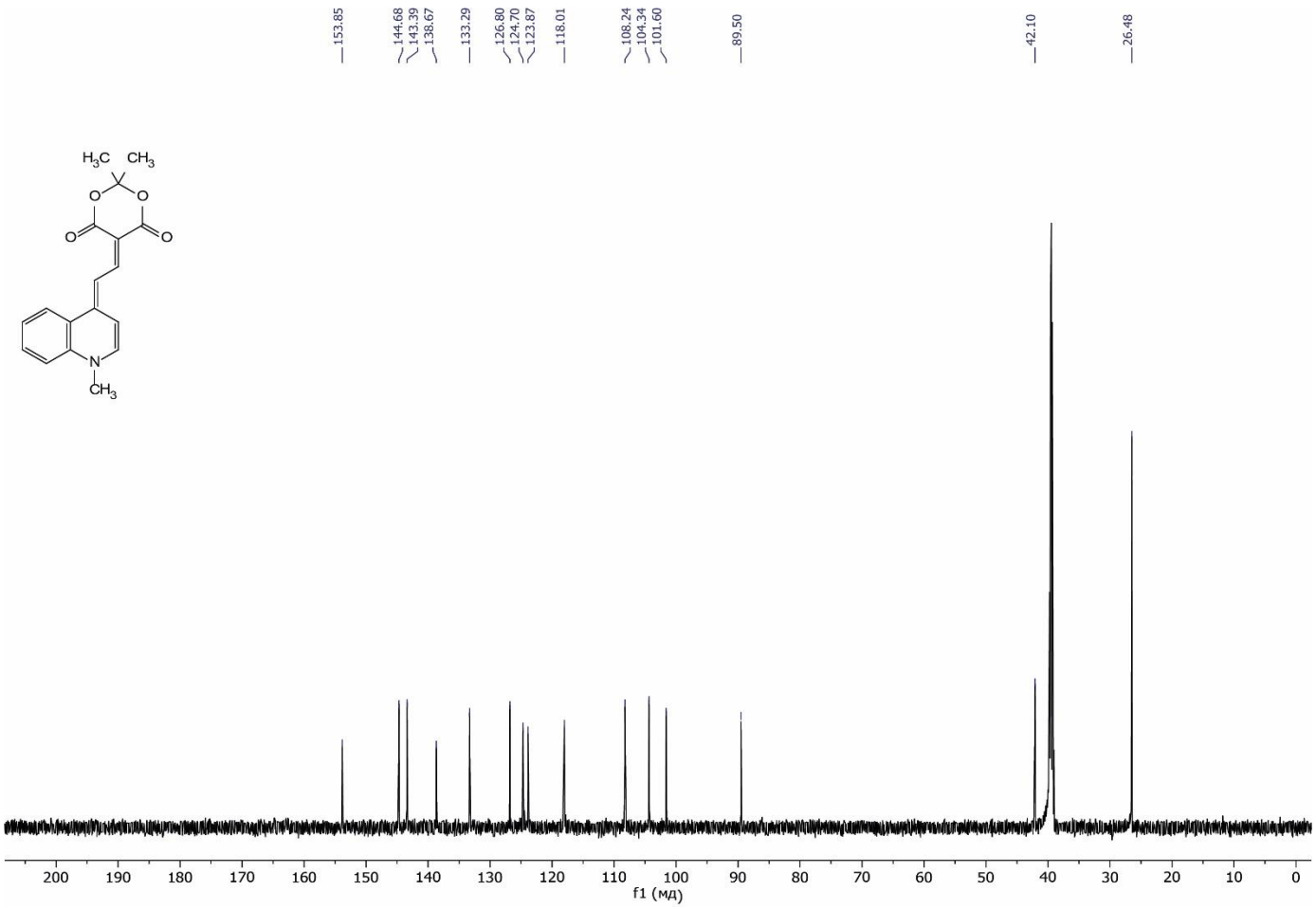
^{1}H NMR spectrum of the compound **20**



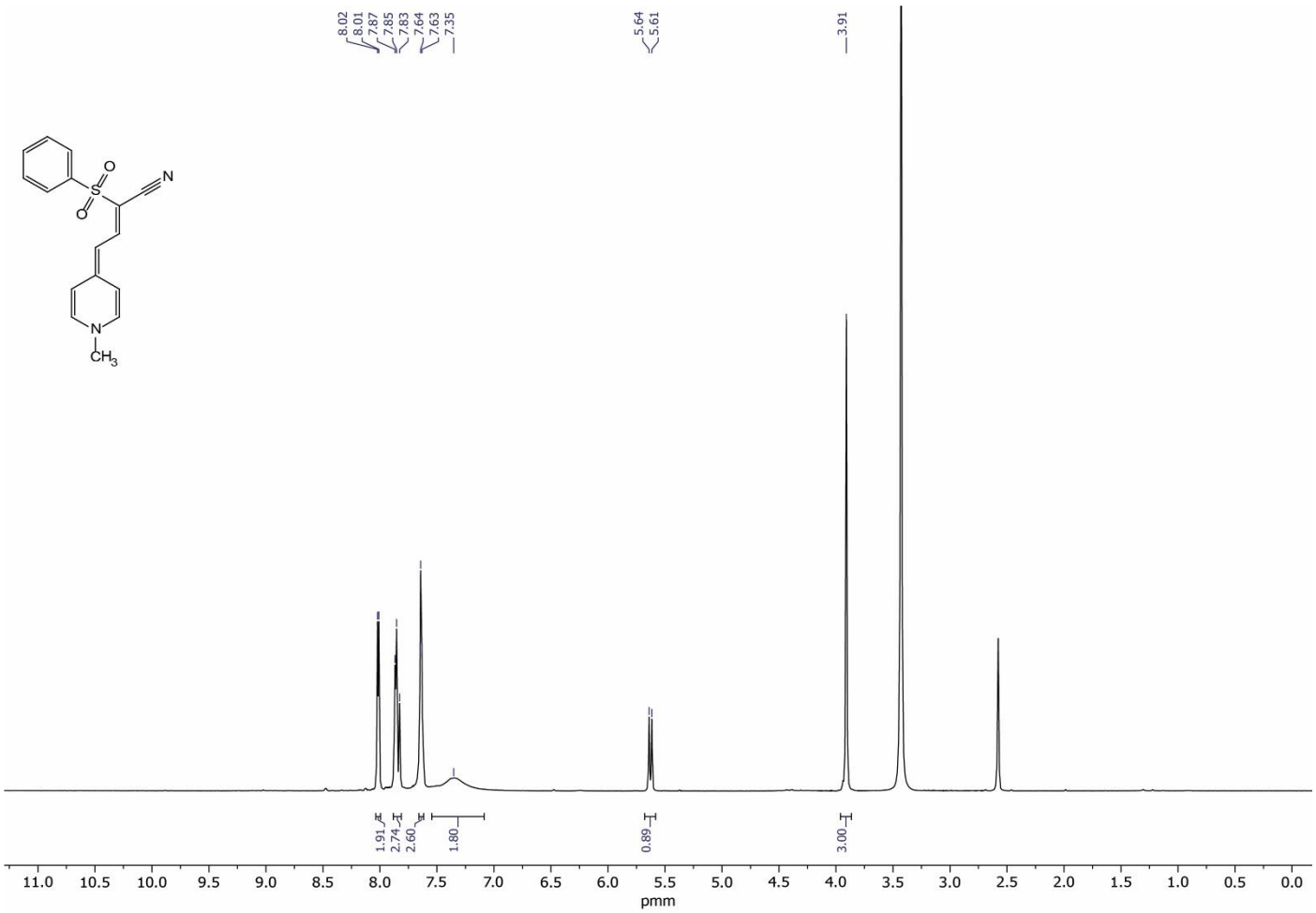
^{13}C NMR spectrum of the compound **20**



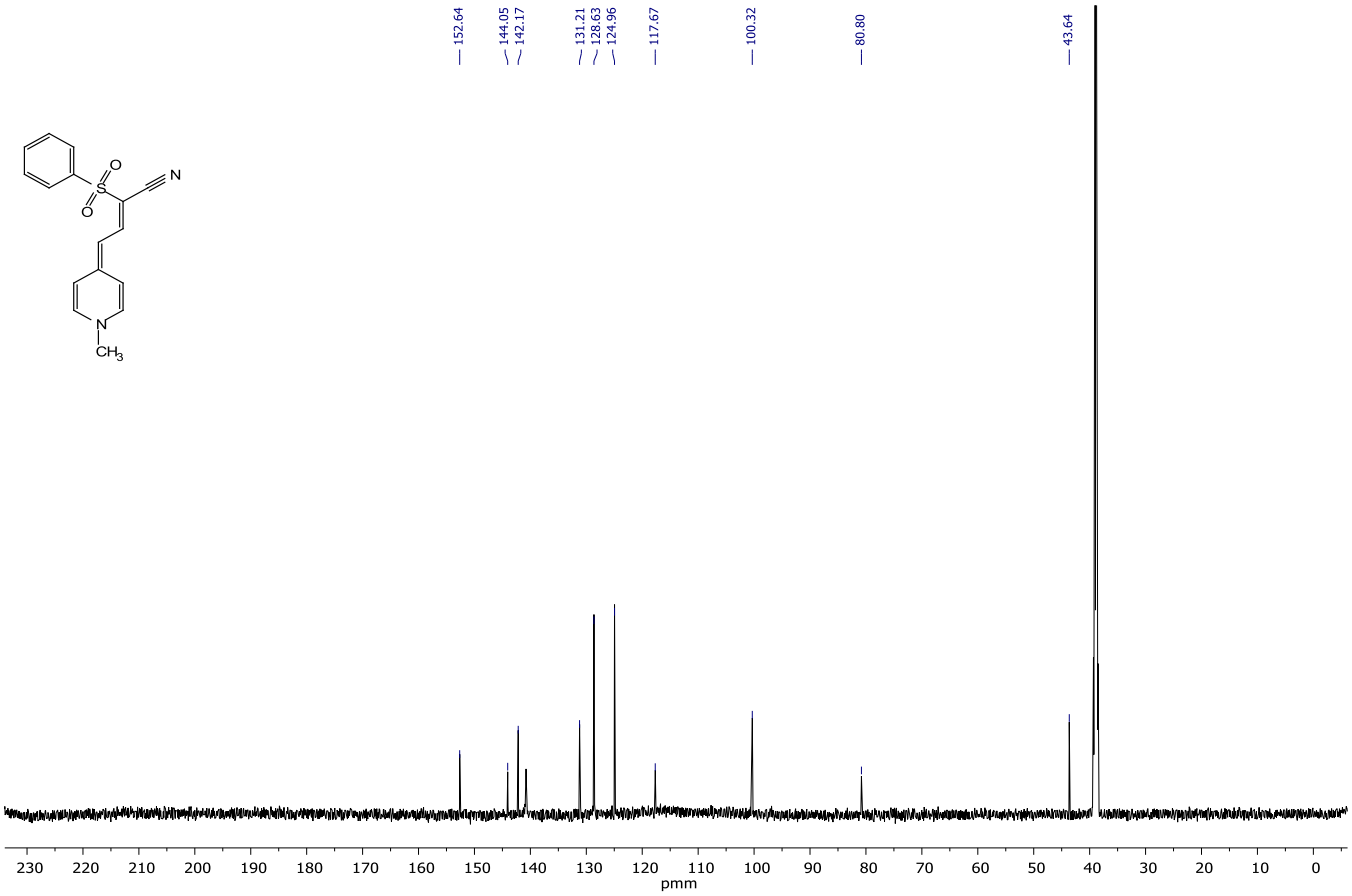
^{1}H NMR spectrum of the compound **21**



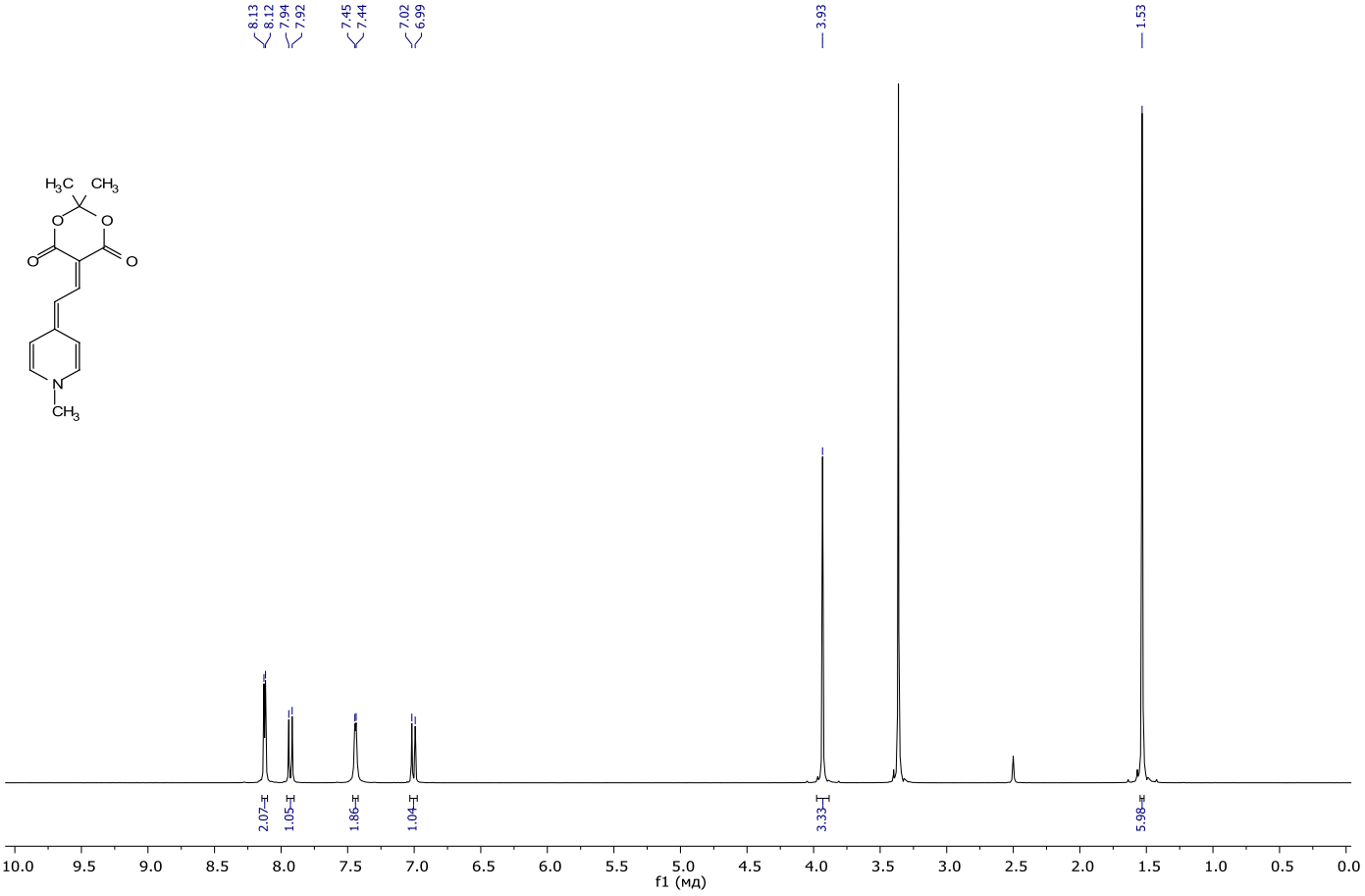
^{13}C NMR spectrum of the compound **21**



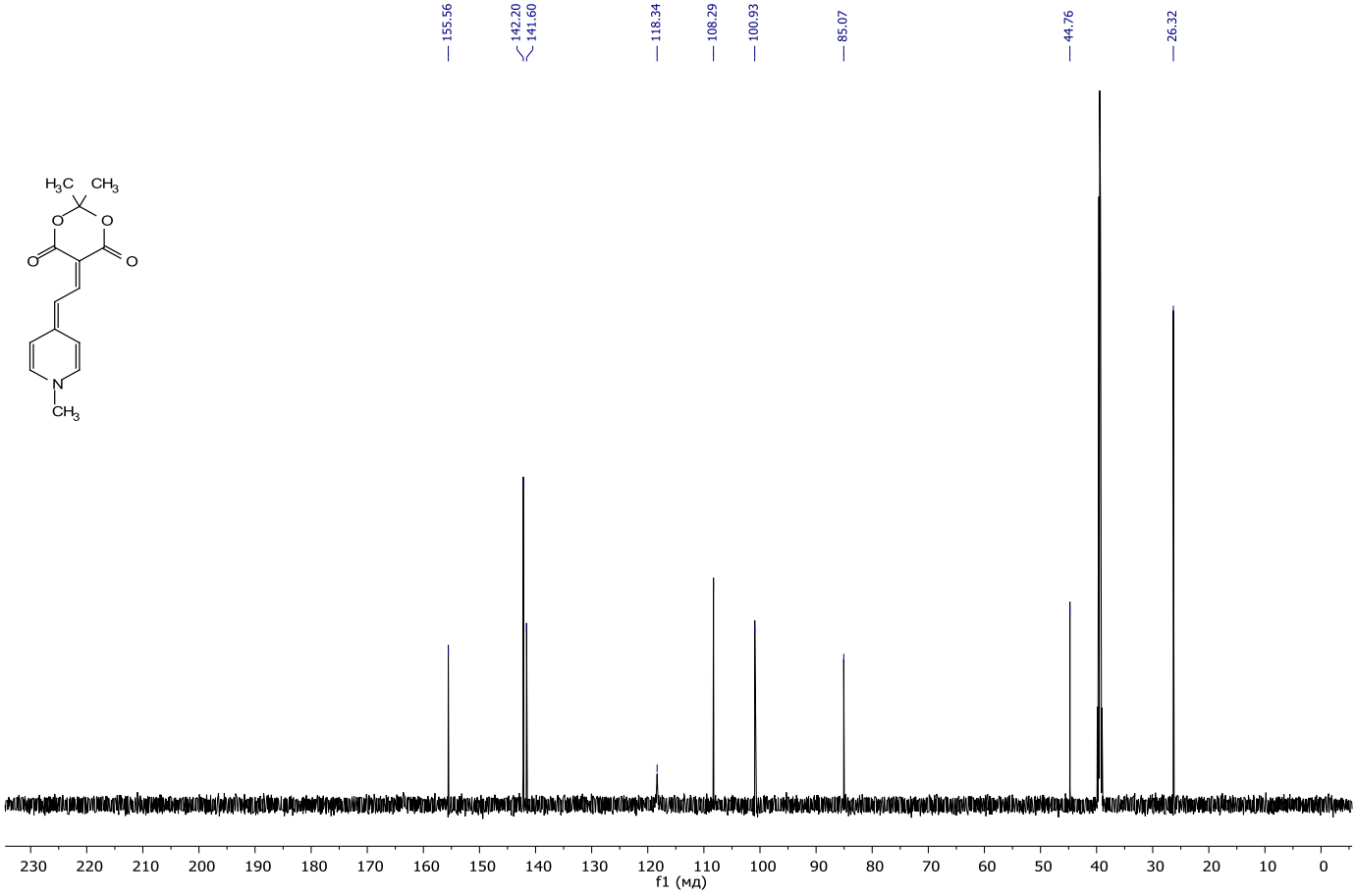
^{1}H NMR spectrum of the compound **22**



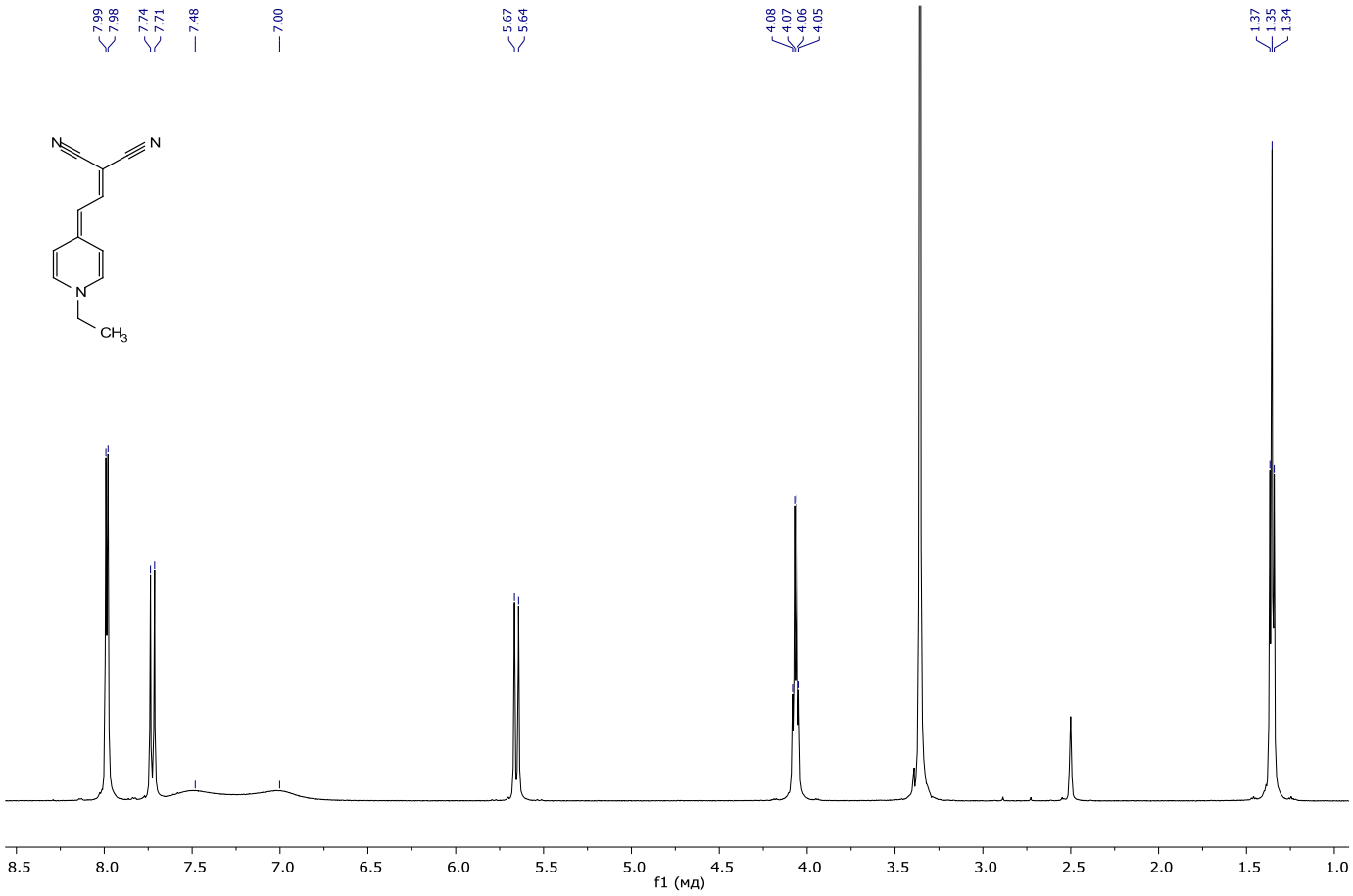
^{13}C NMR spectrum of the compound **22**



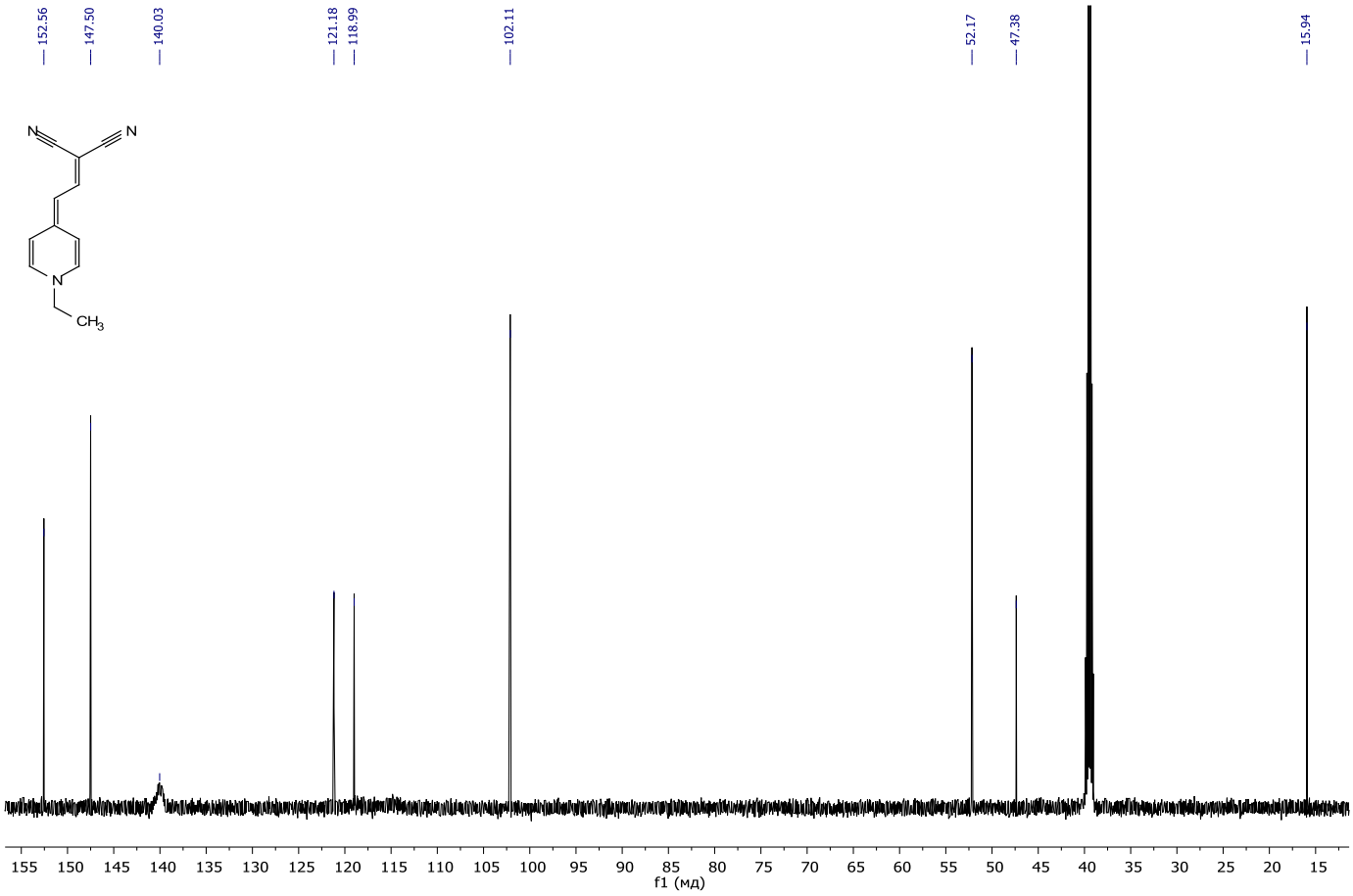
^{1}H NMR spectrum of the compound **23**



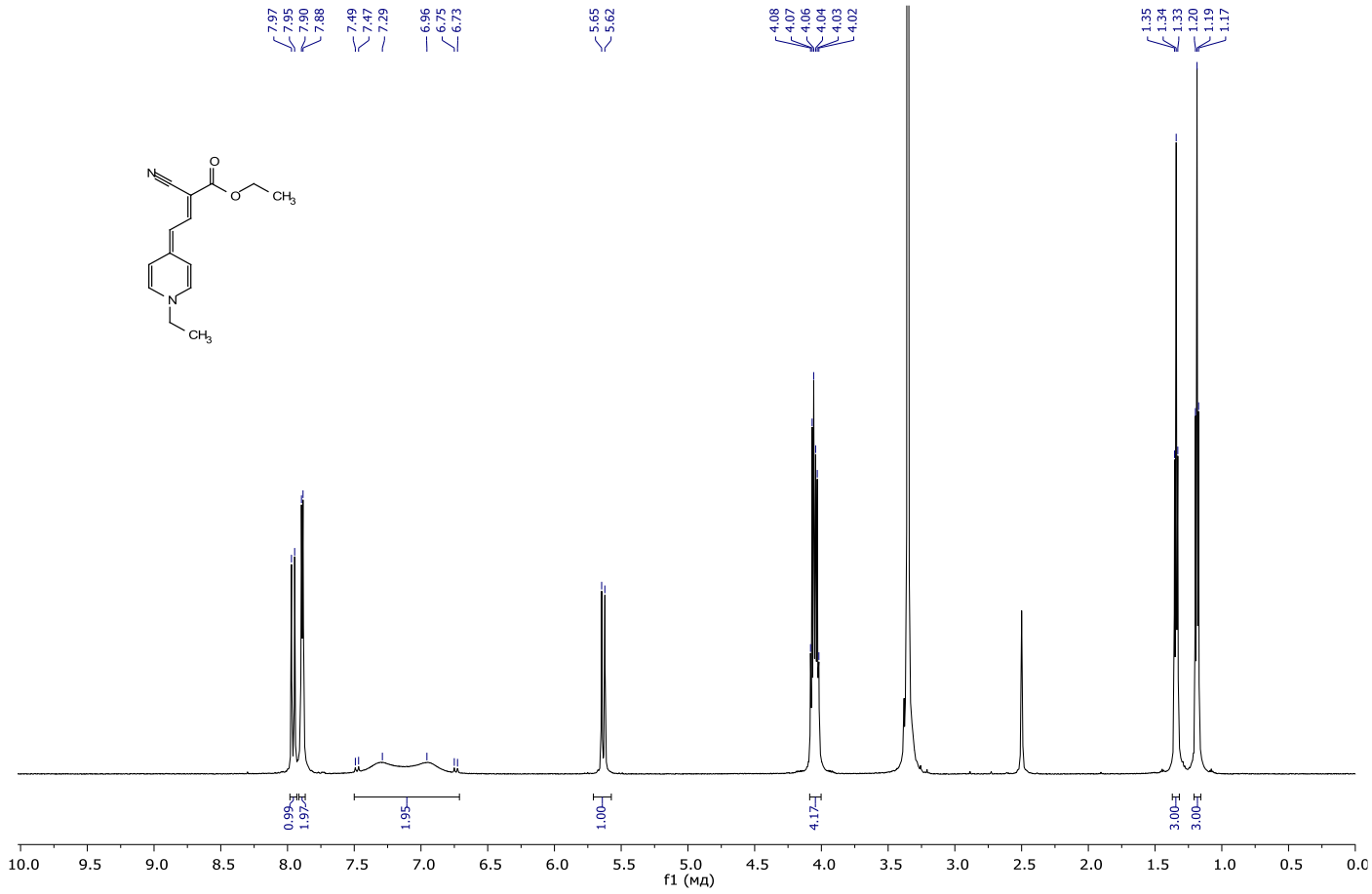
^{13}C NMR spectrum of the compound **23**



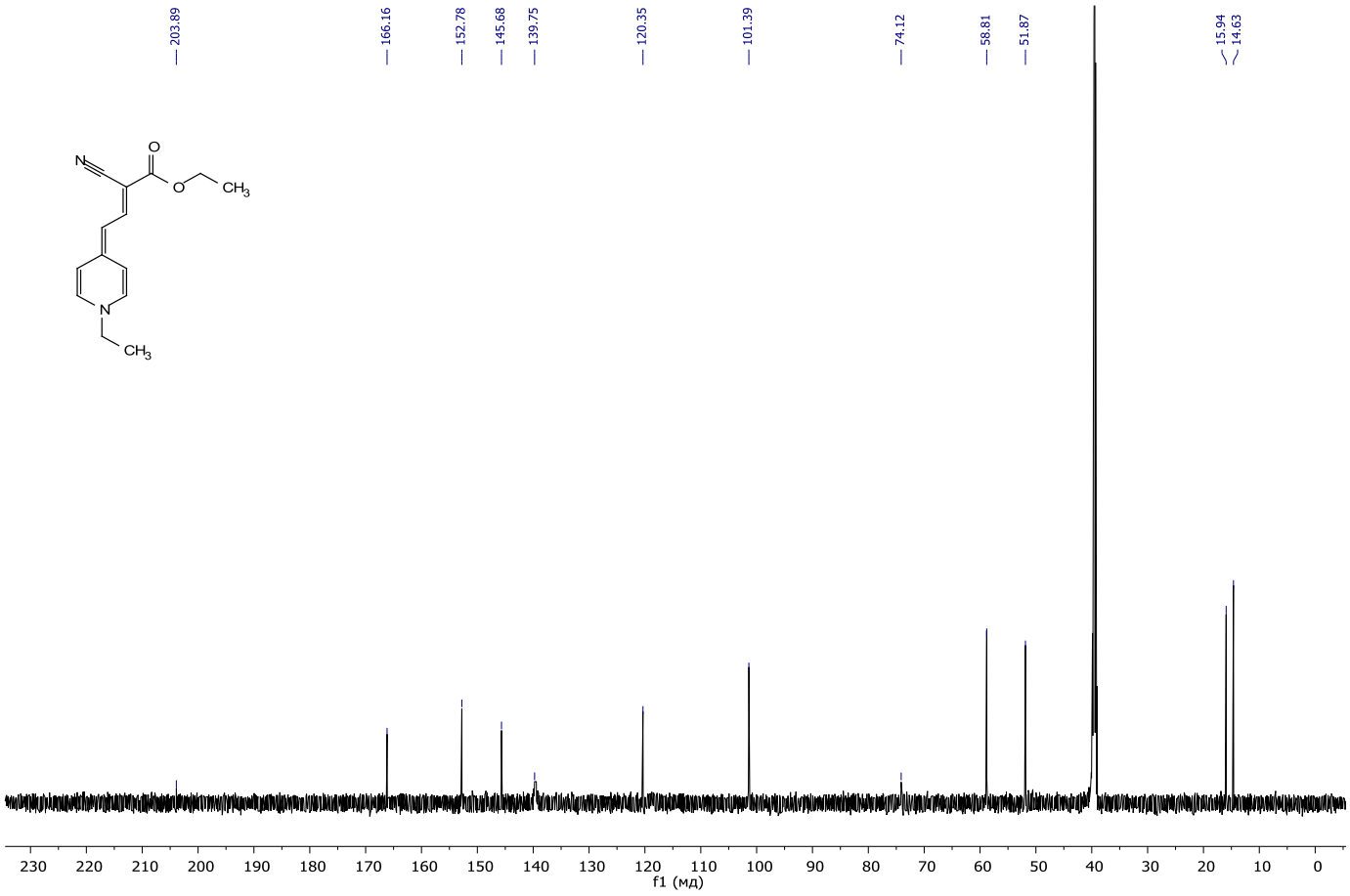
^{1}H NMR spectrum of the compound **24**



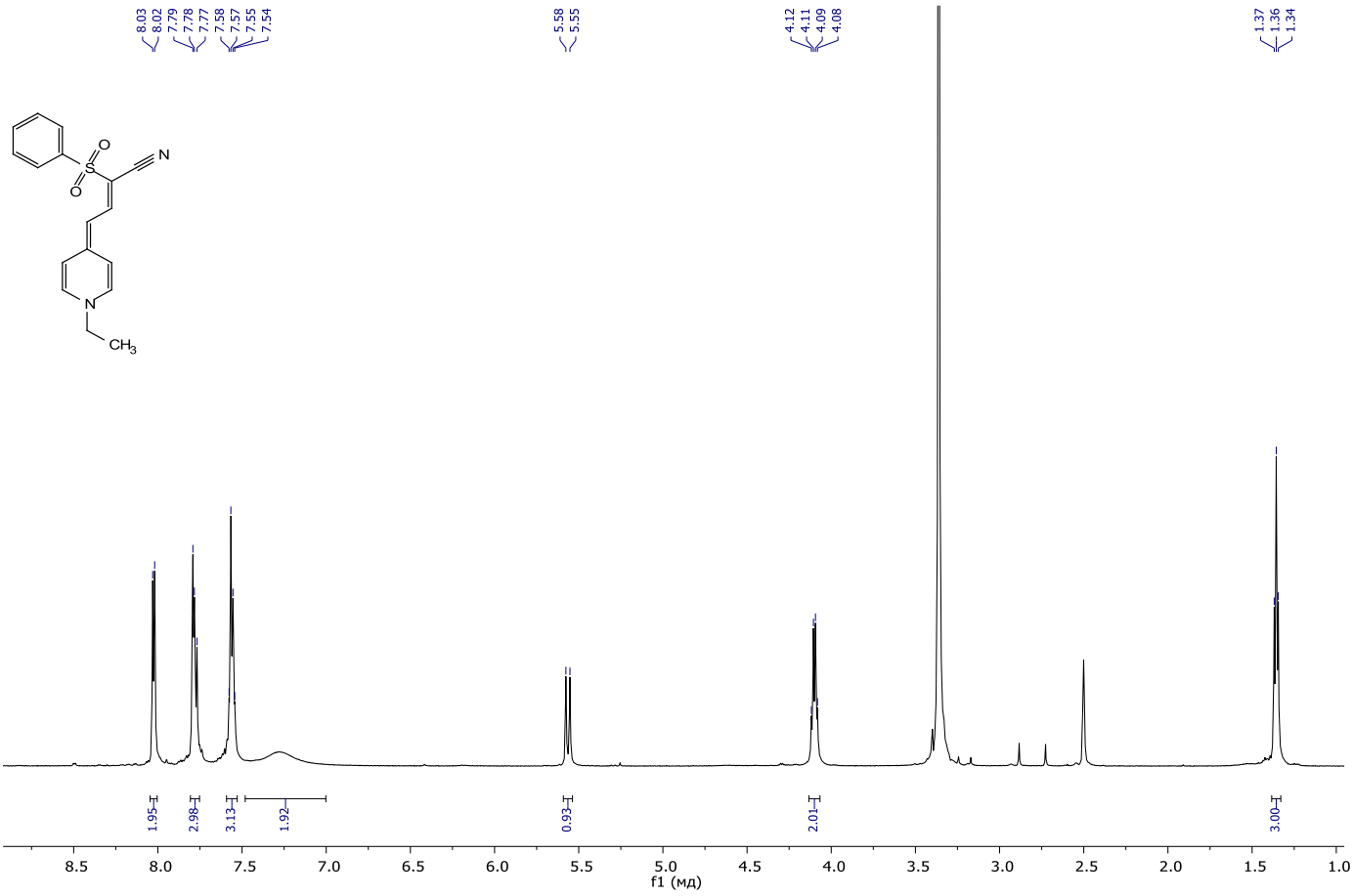
^{13}C NMR spectrum of the compound **24**



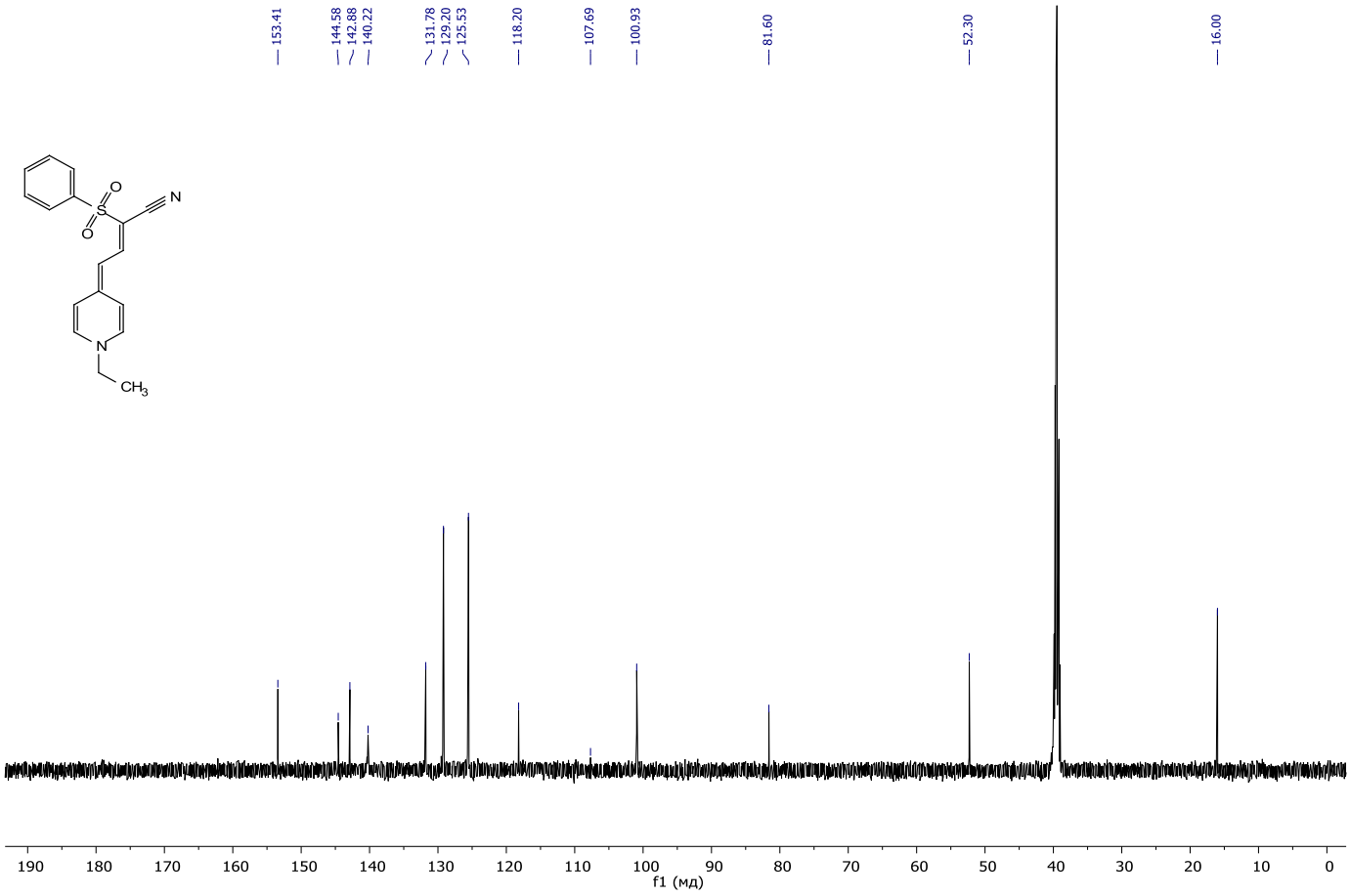
^{1}H NMR spectrum of the compound **25**



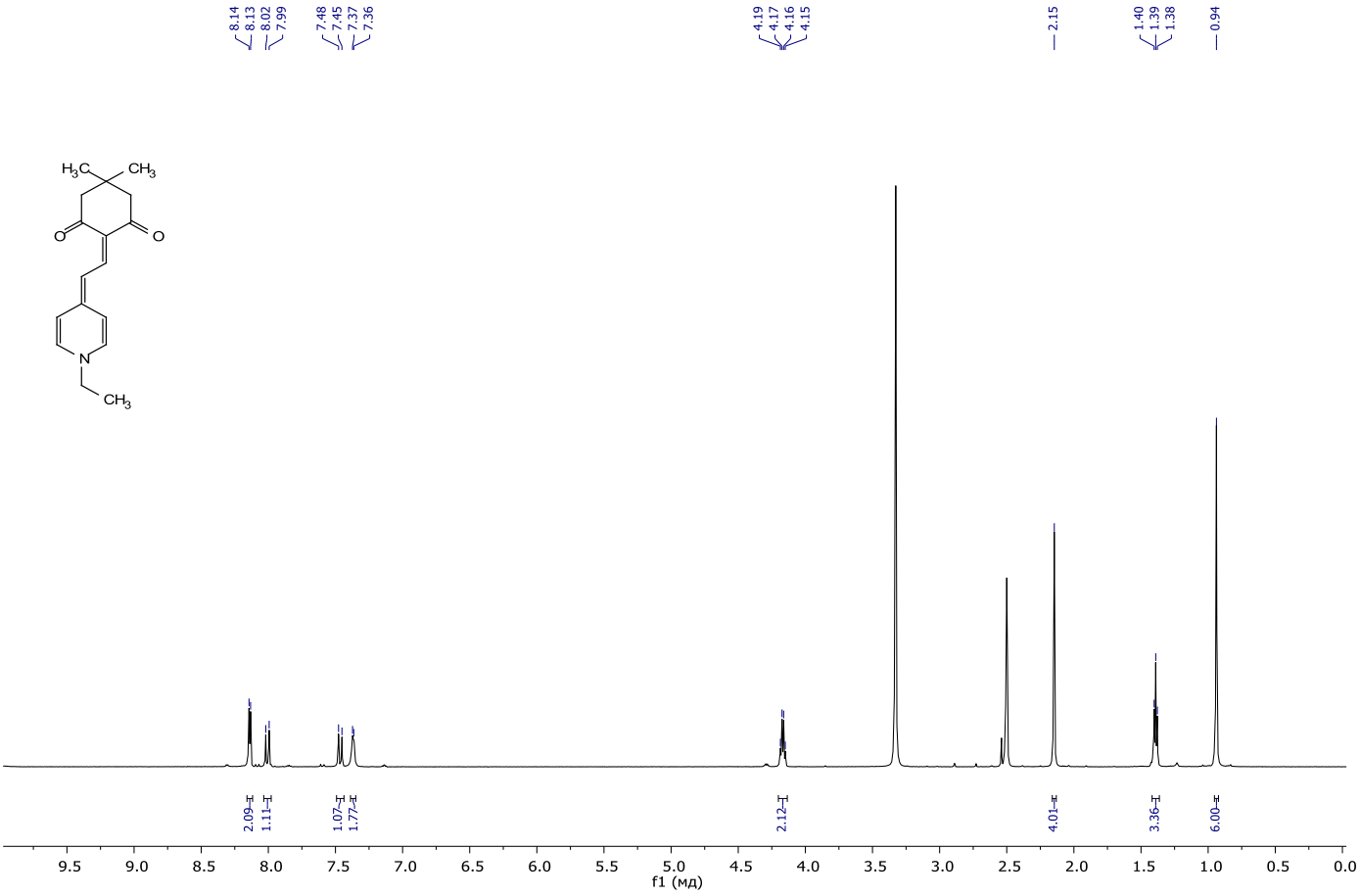
^{13}C NMR spectrum of the compound **25**



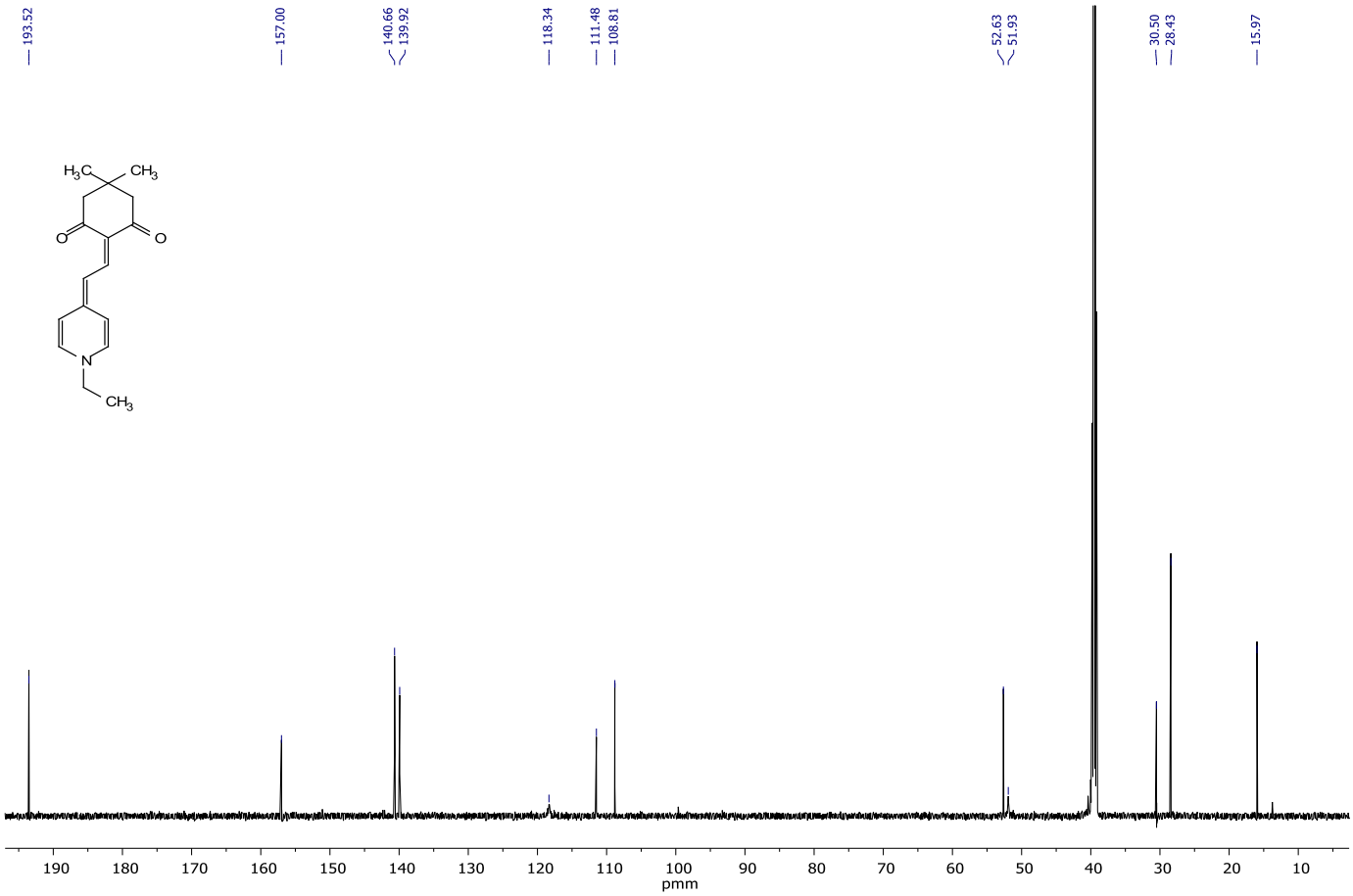
^{1}H NMR spectrum of the compound **26**



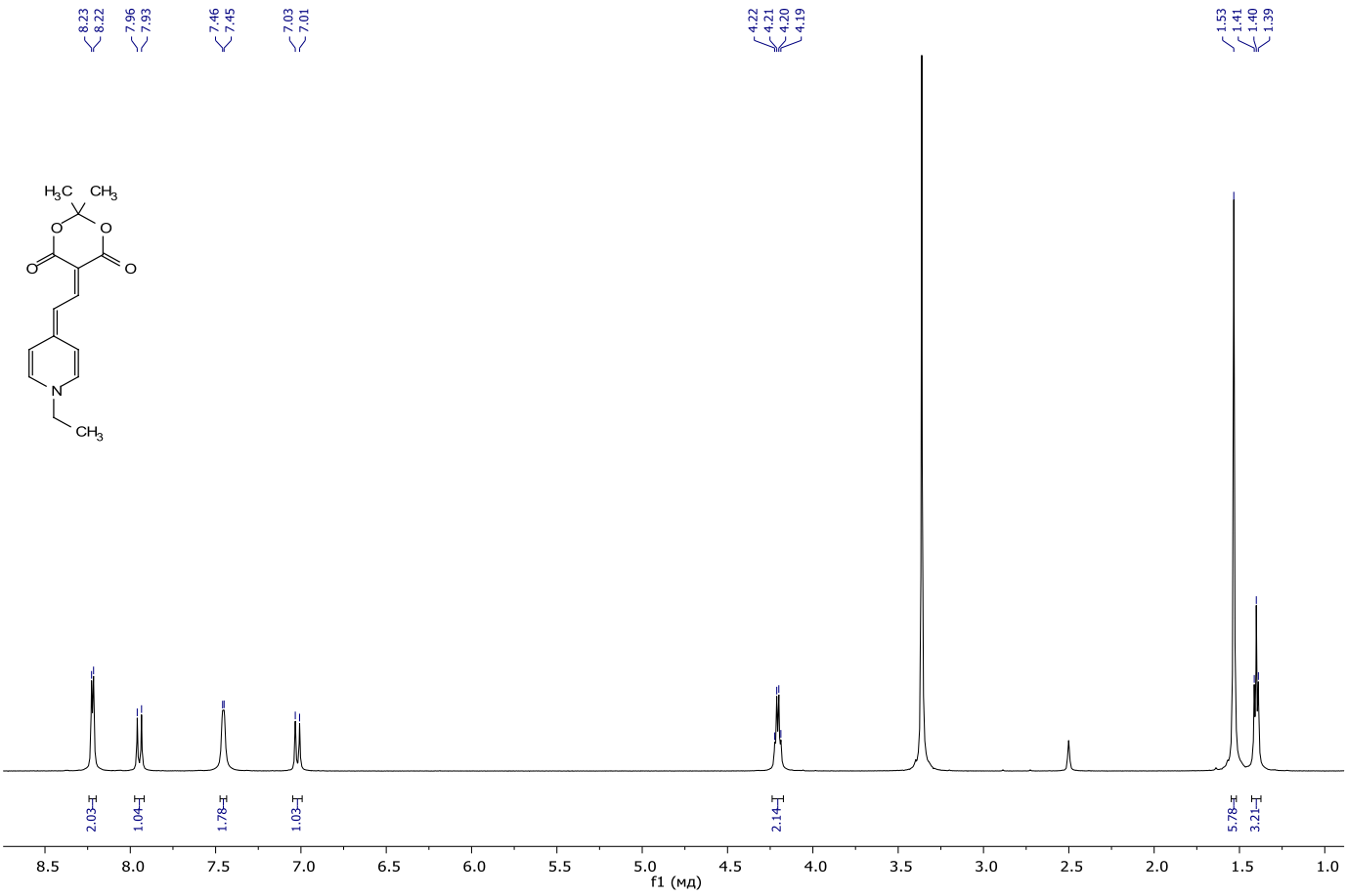
^{13}C NMR spectrum of the compound **26**



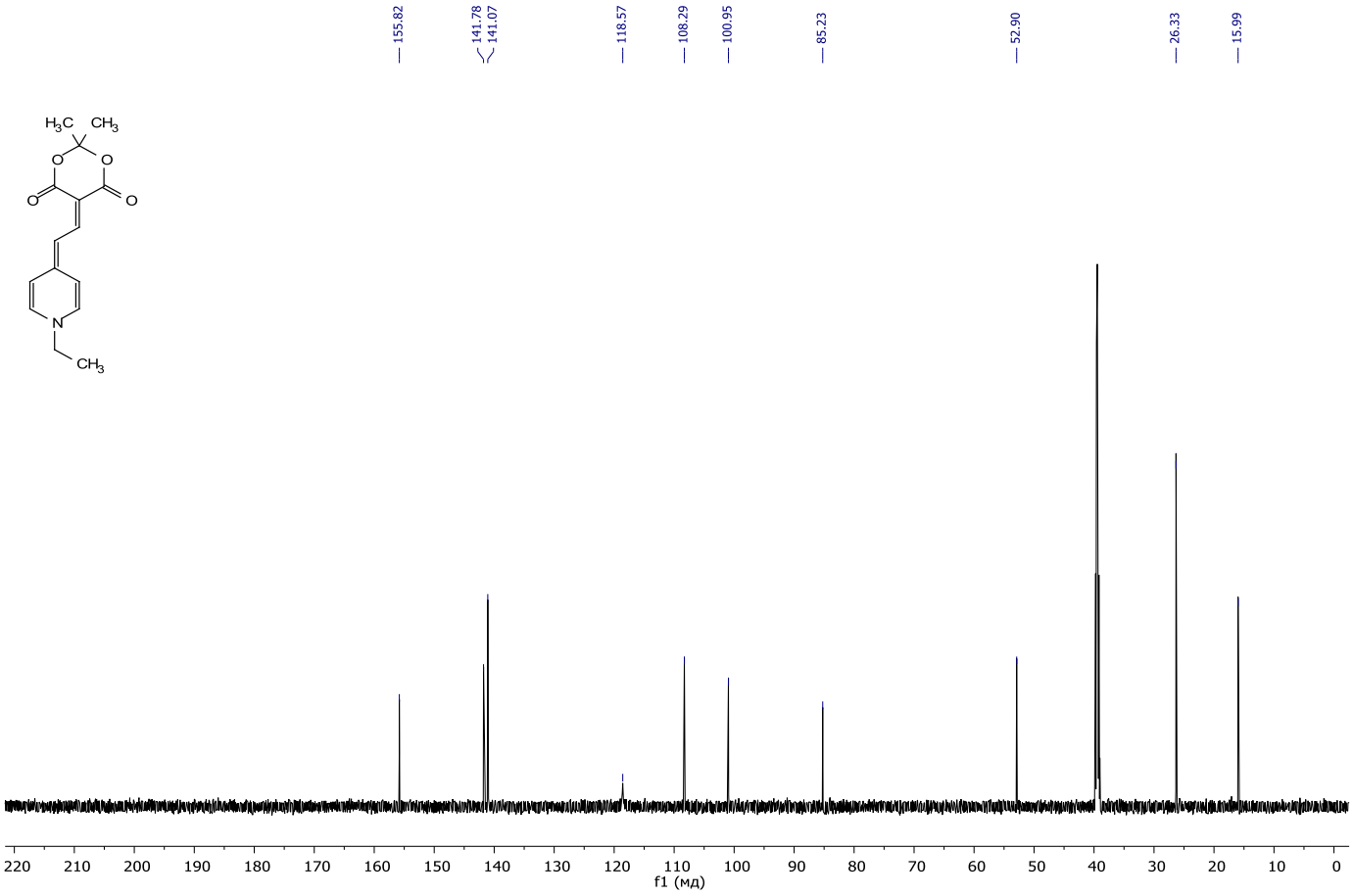
^{1}H NMR spectrum of the compound **27**



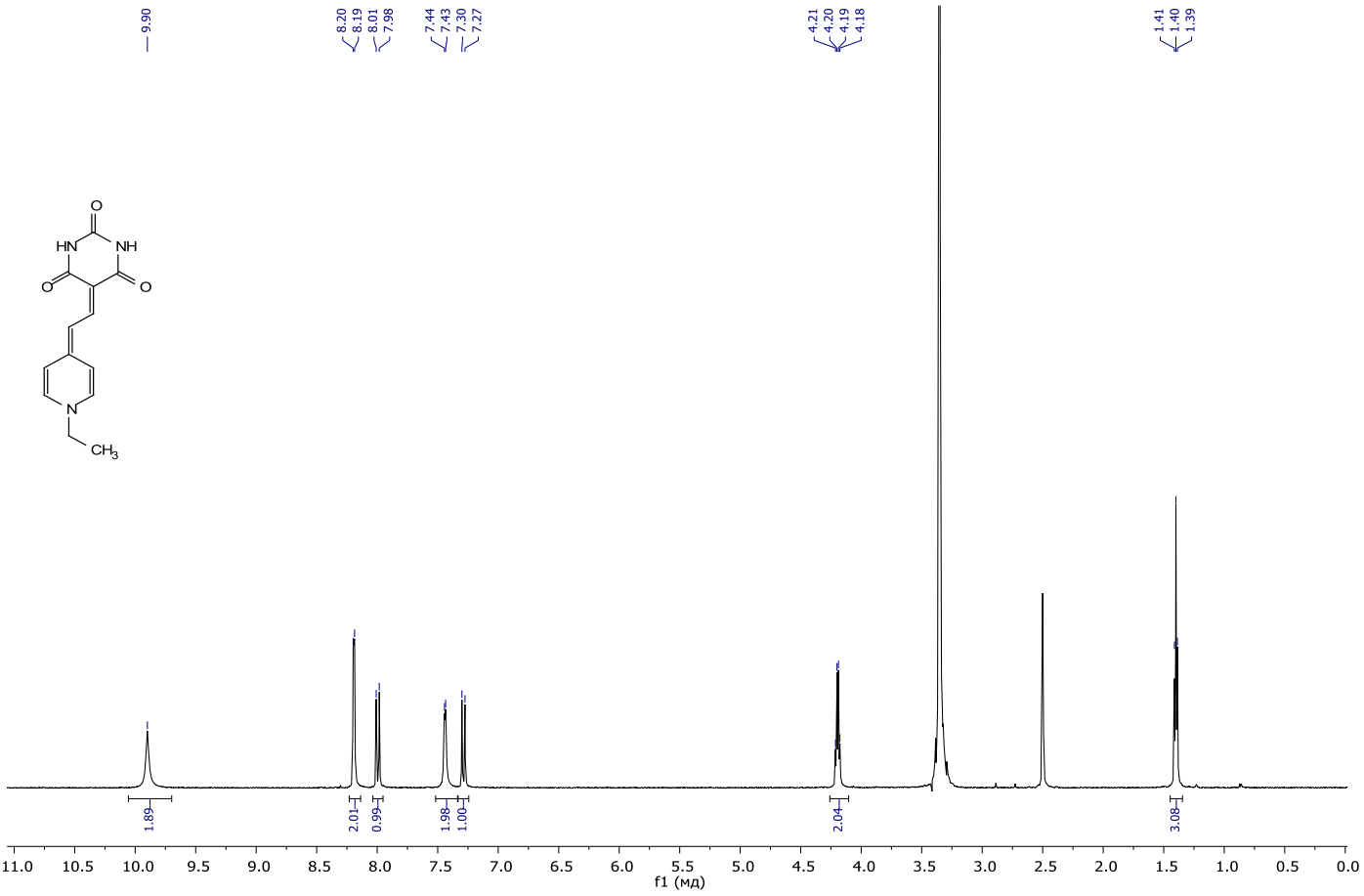
^{13}C NMR spectrum of the compound **27**



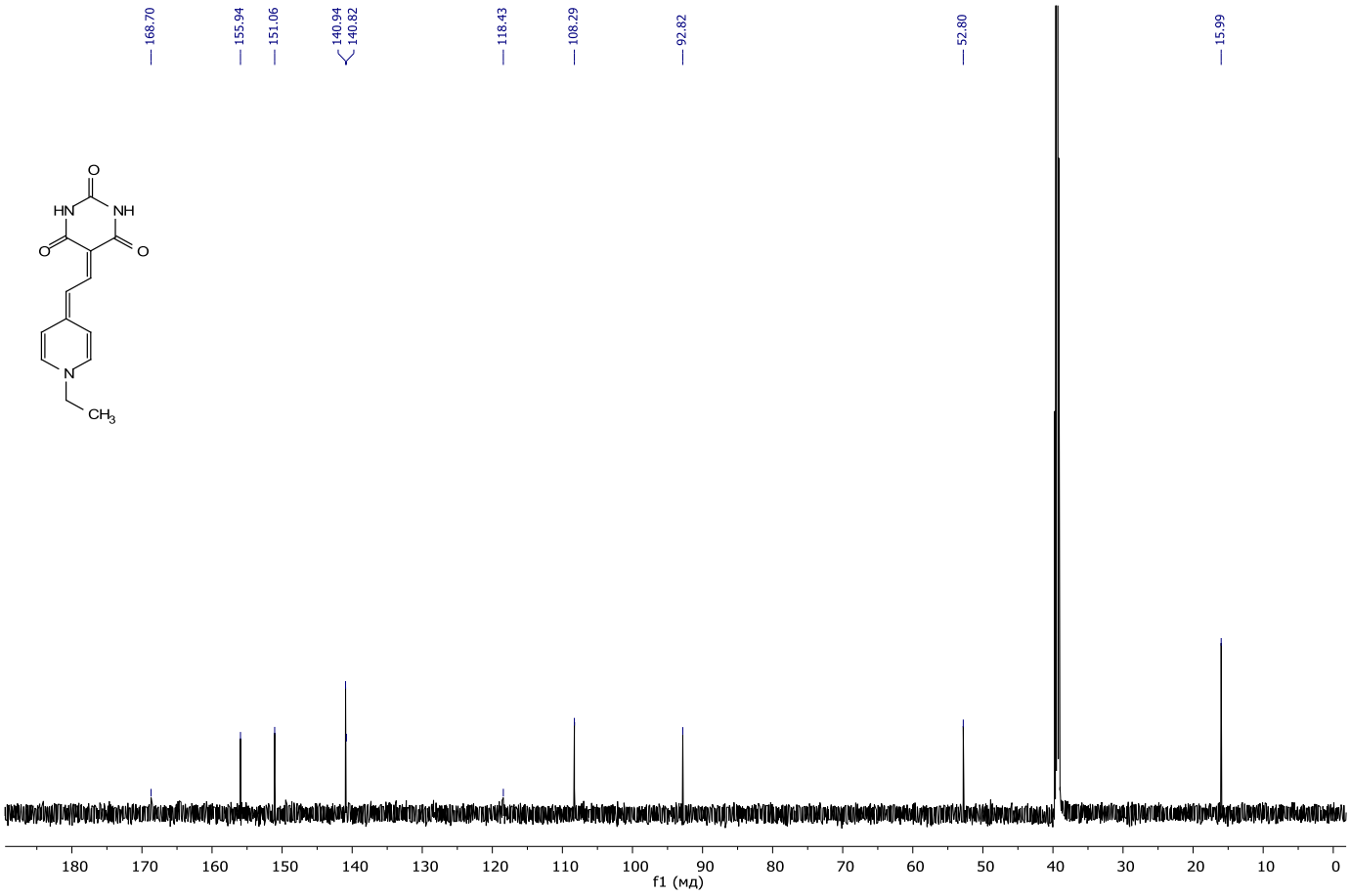
^{1}H NMR spectrum of the compound **28**



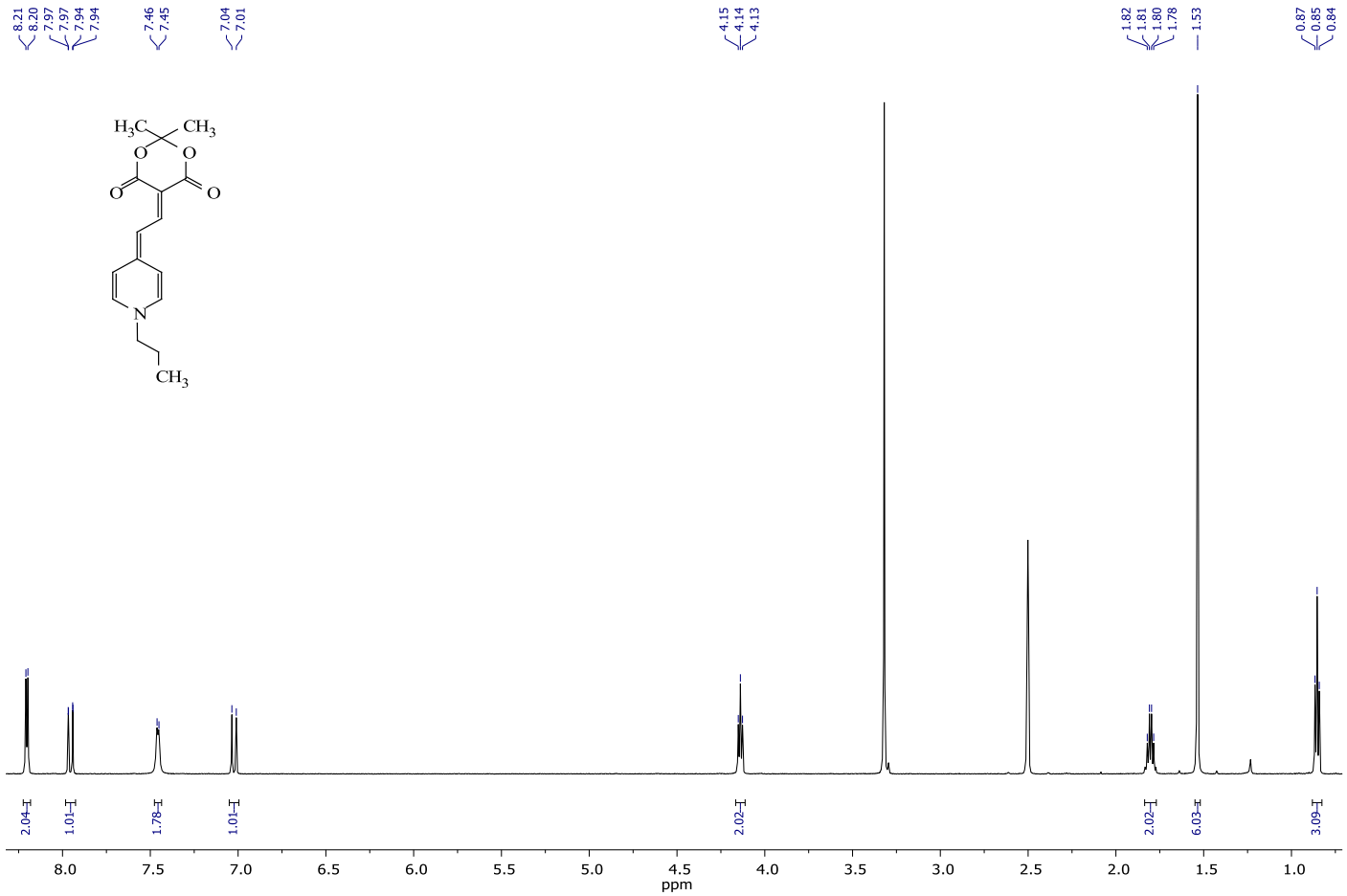
^{13}C NMR spectrum of the compound **28**



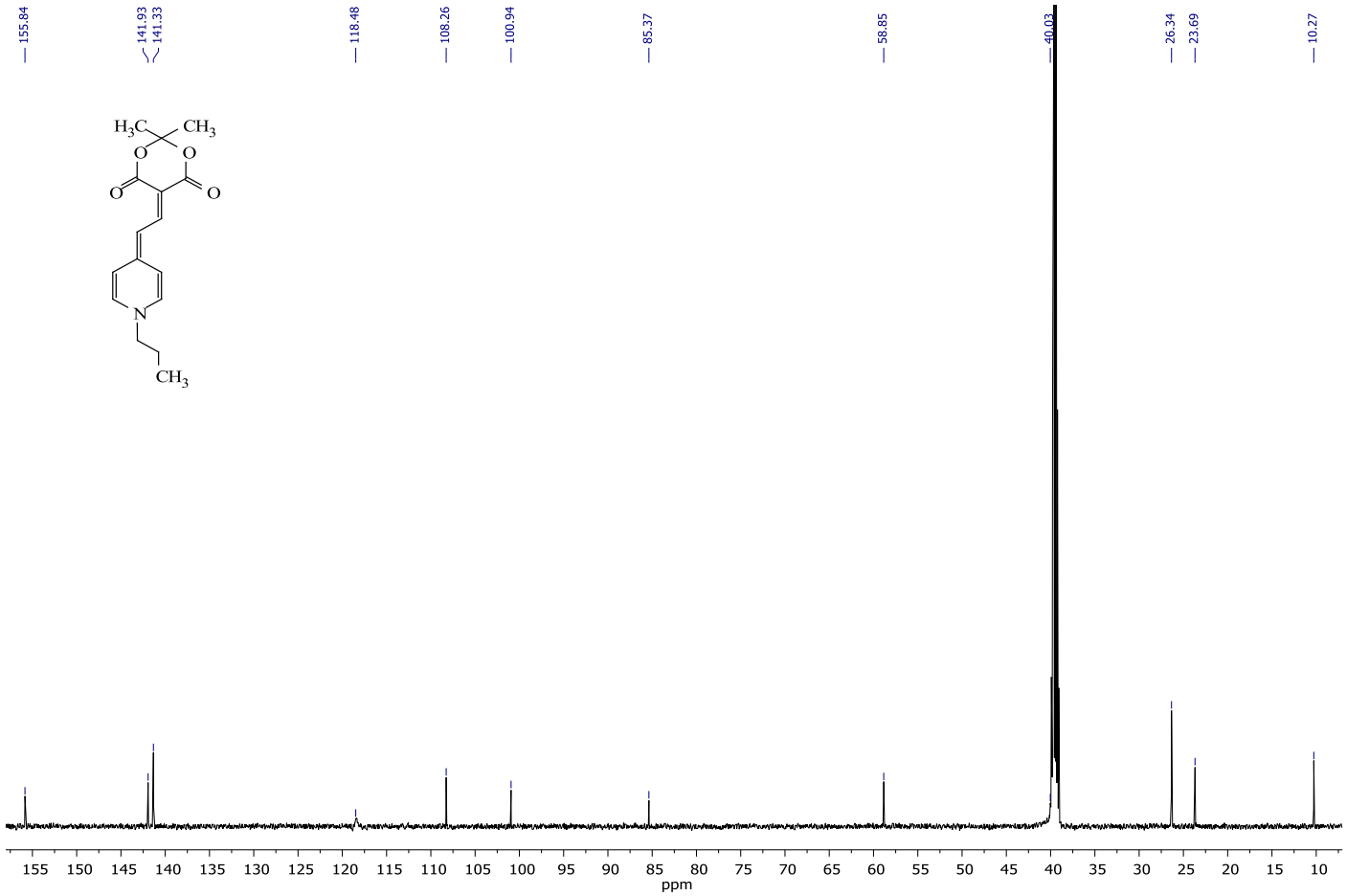
^{1}H NMR spectrum of the compound **29**



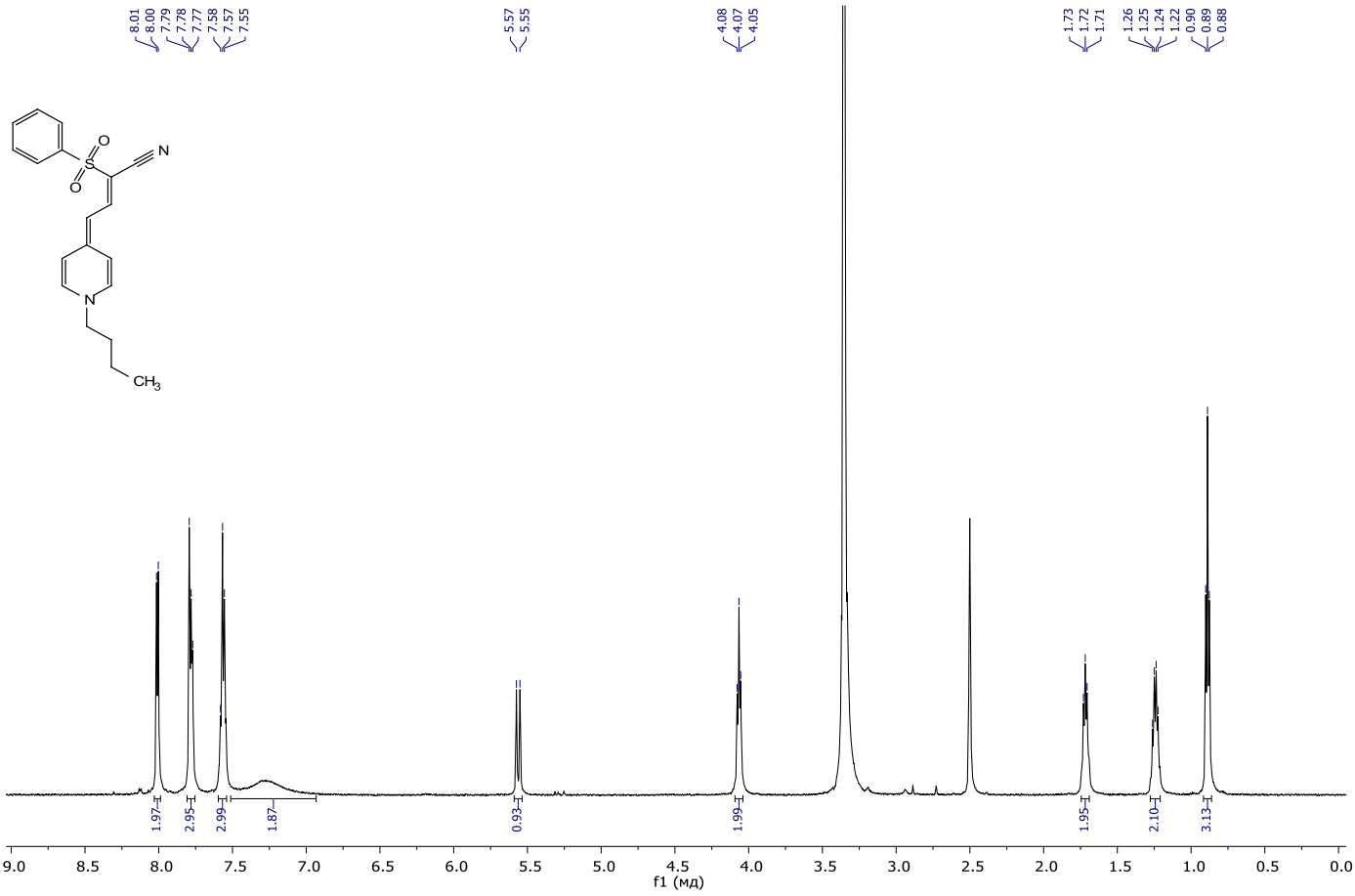
^{13}C NMR spectrum of the compound **29**



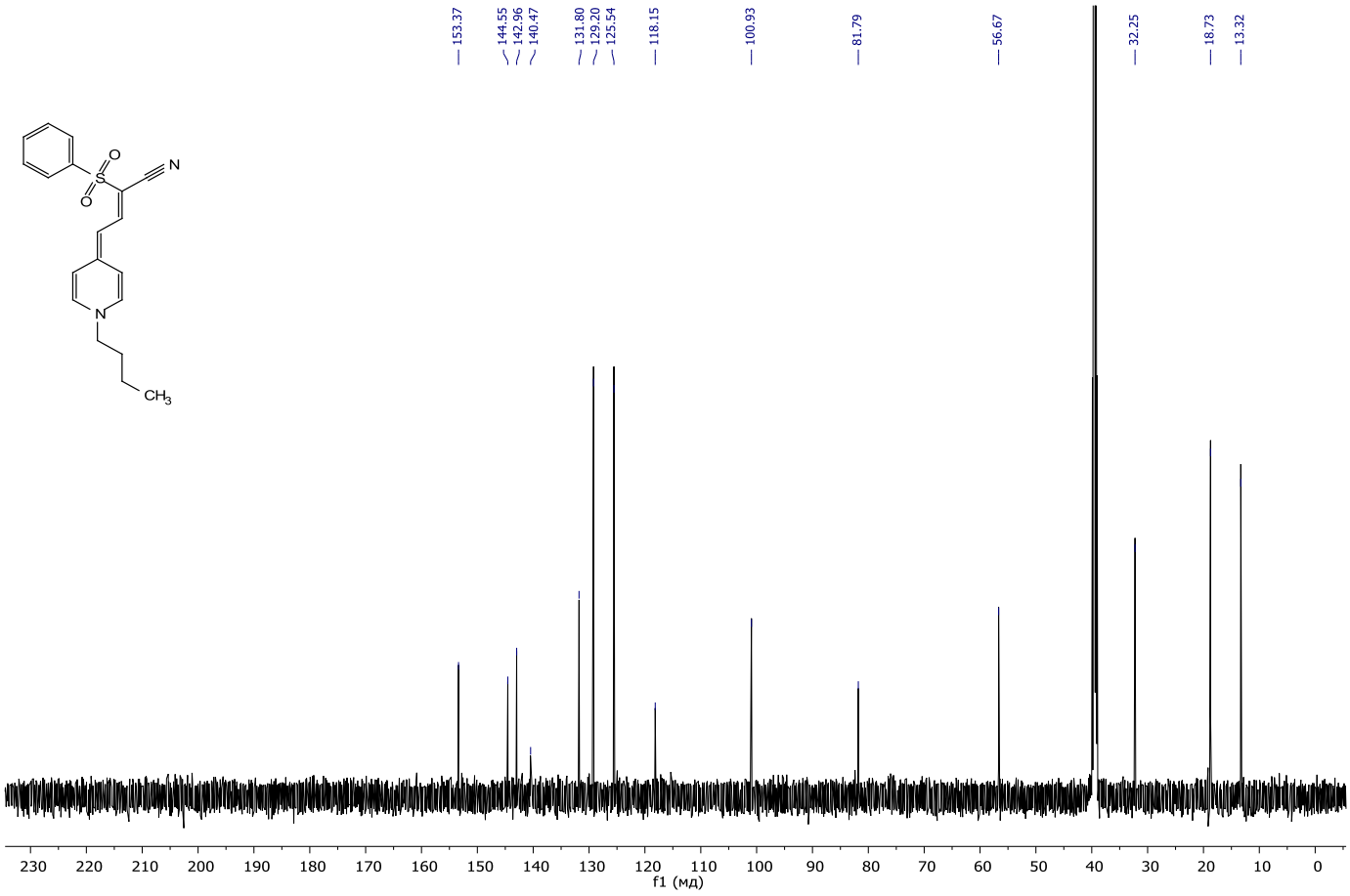
^{1}H NMR spectrum of the compound **30**



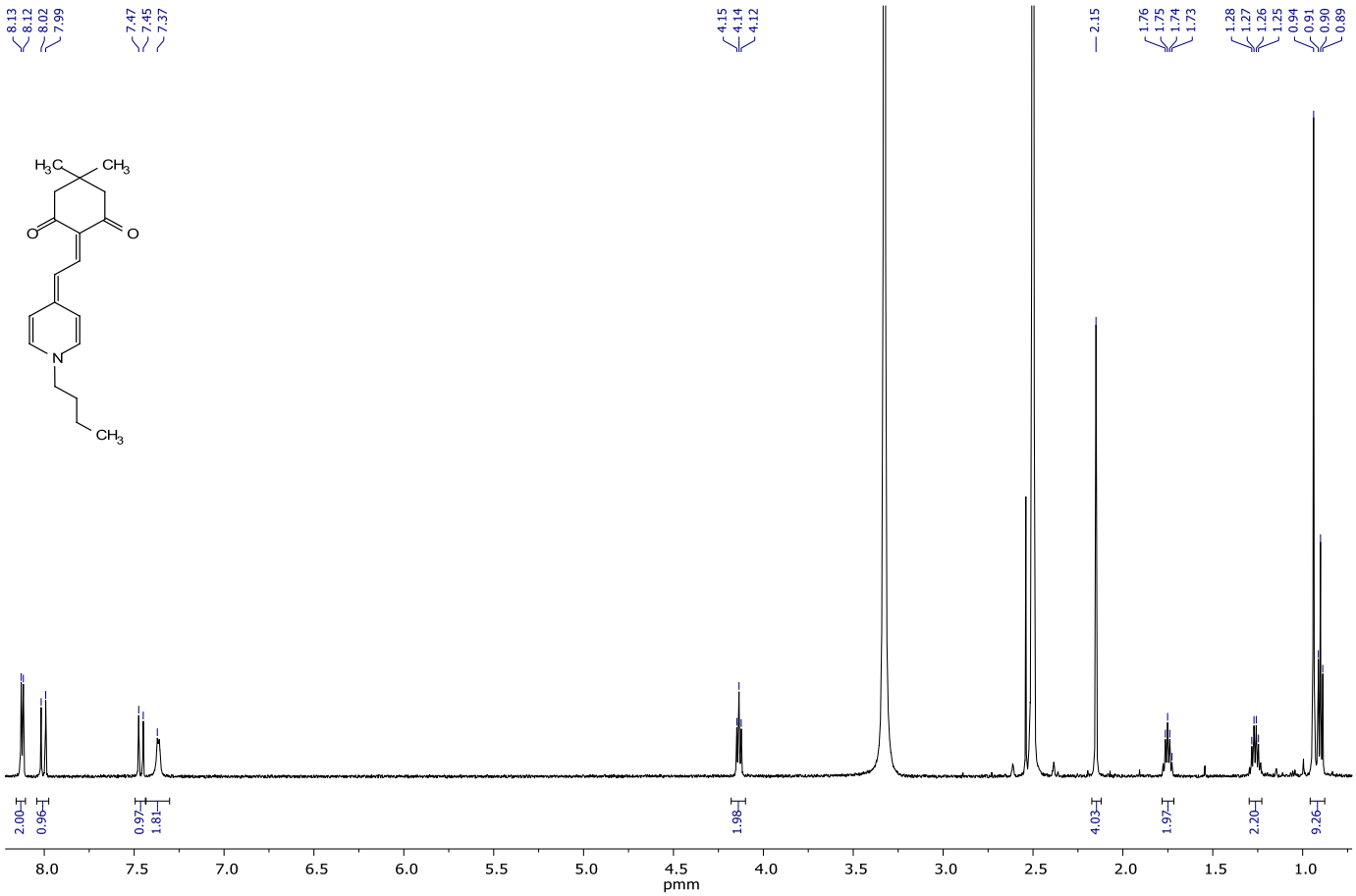
^{13}C NMR spectrum of the compound **30**



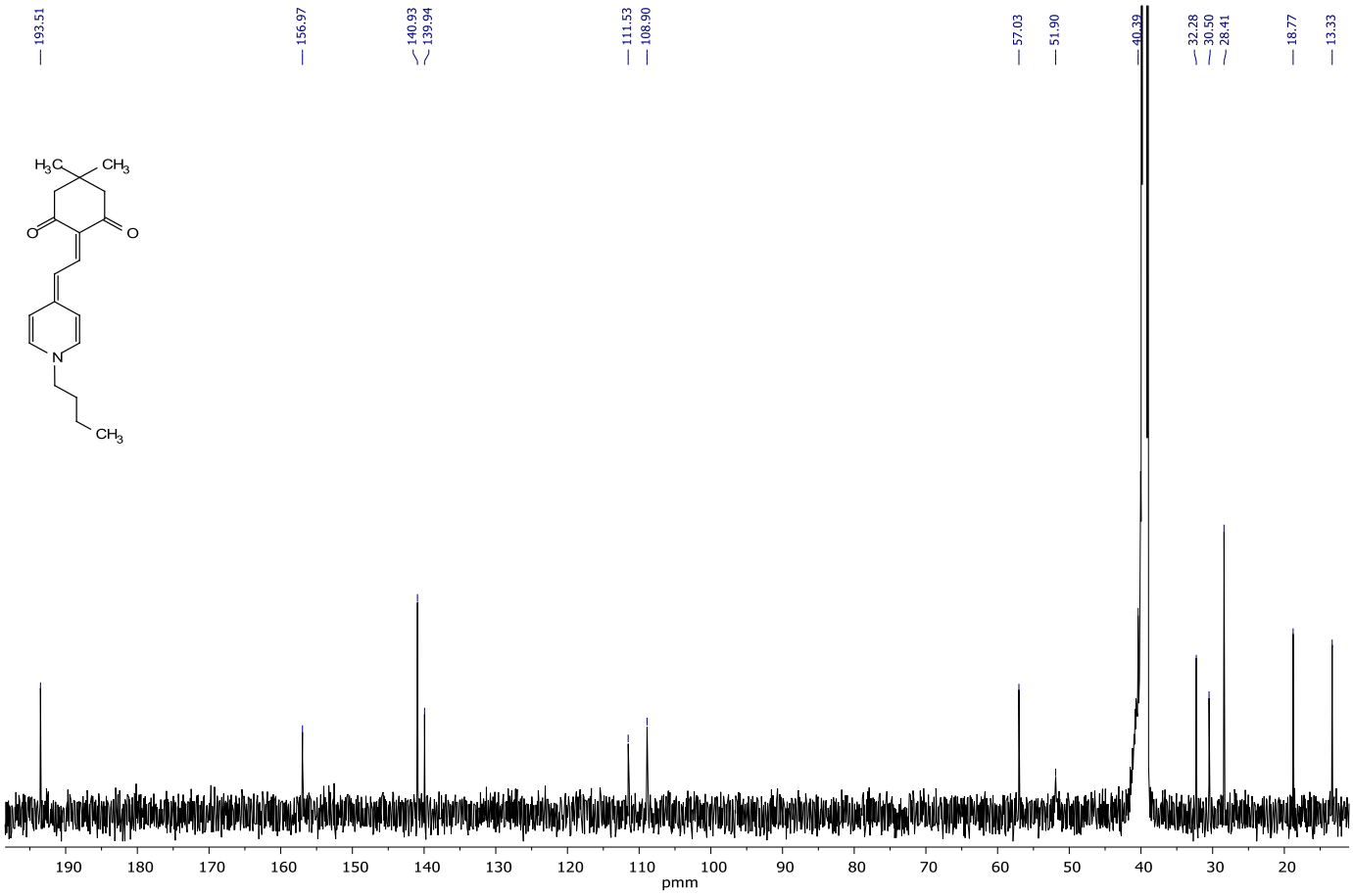
^{1}H NMR spectrum of the compound **31**



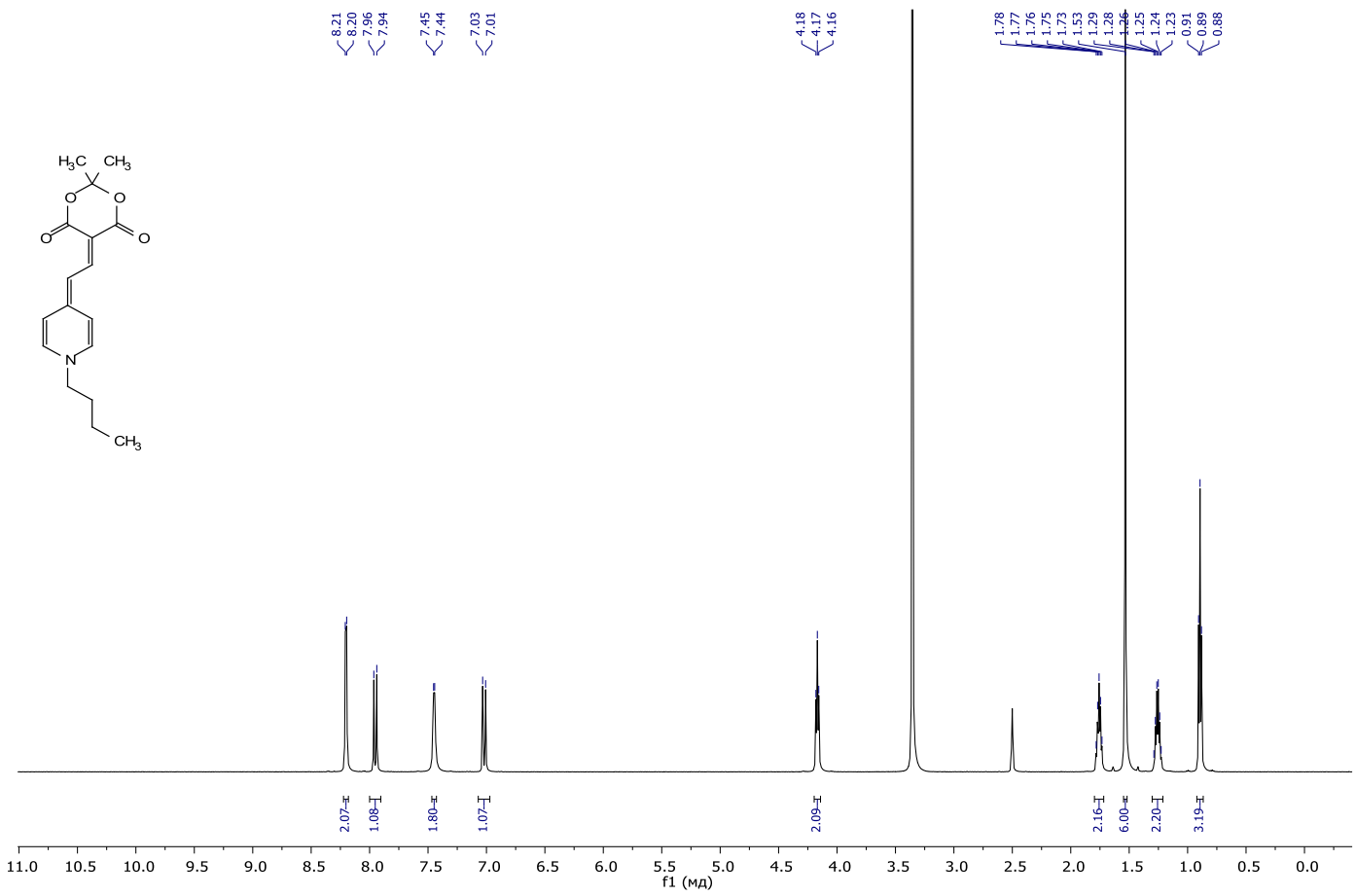
^{13}C NMR spectrum of the compound **31**



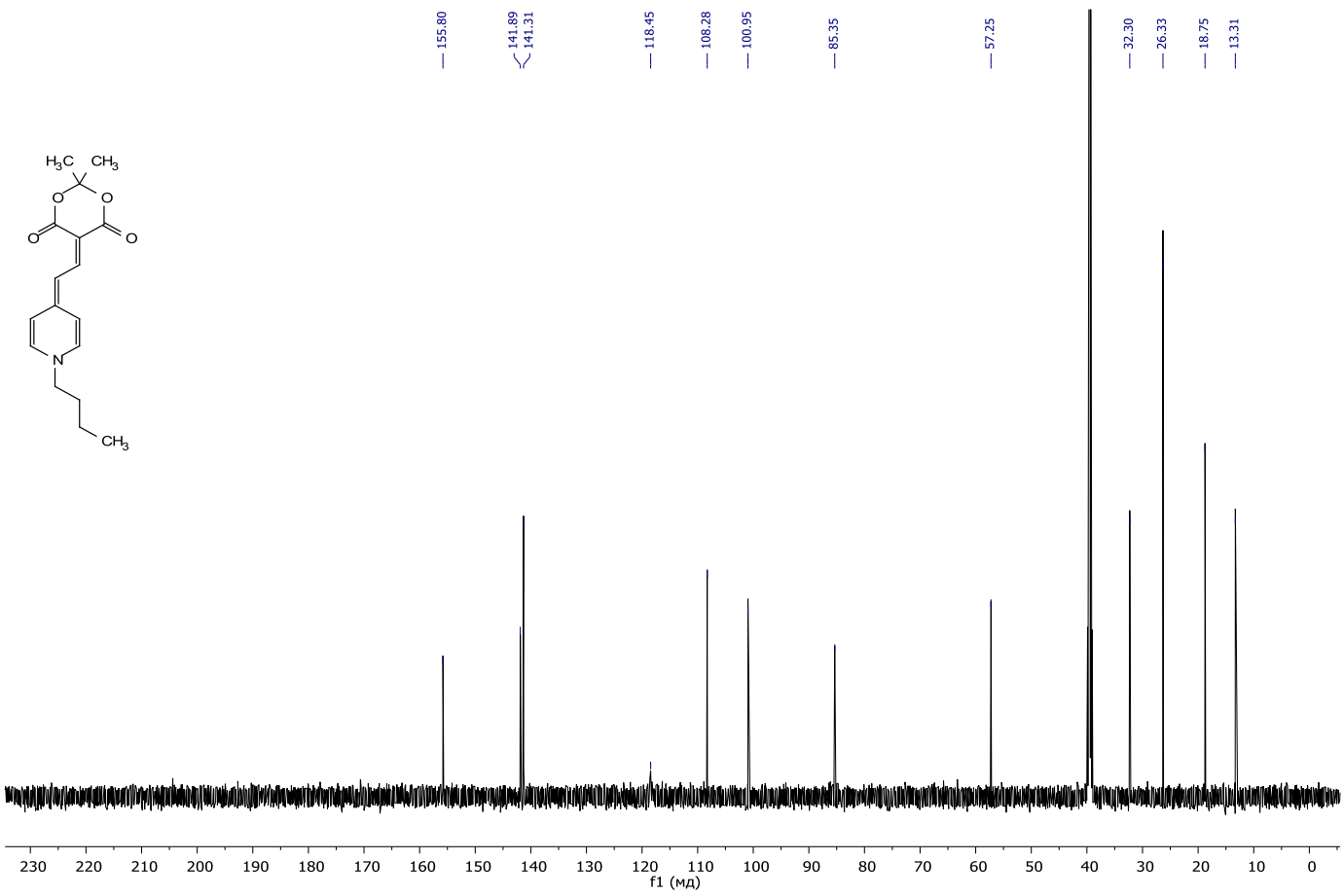
^{1}H NMR spectrum of the compound **32**



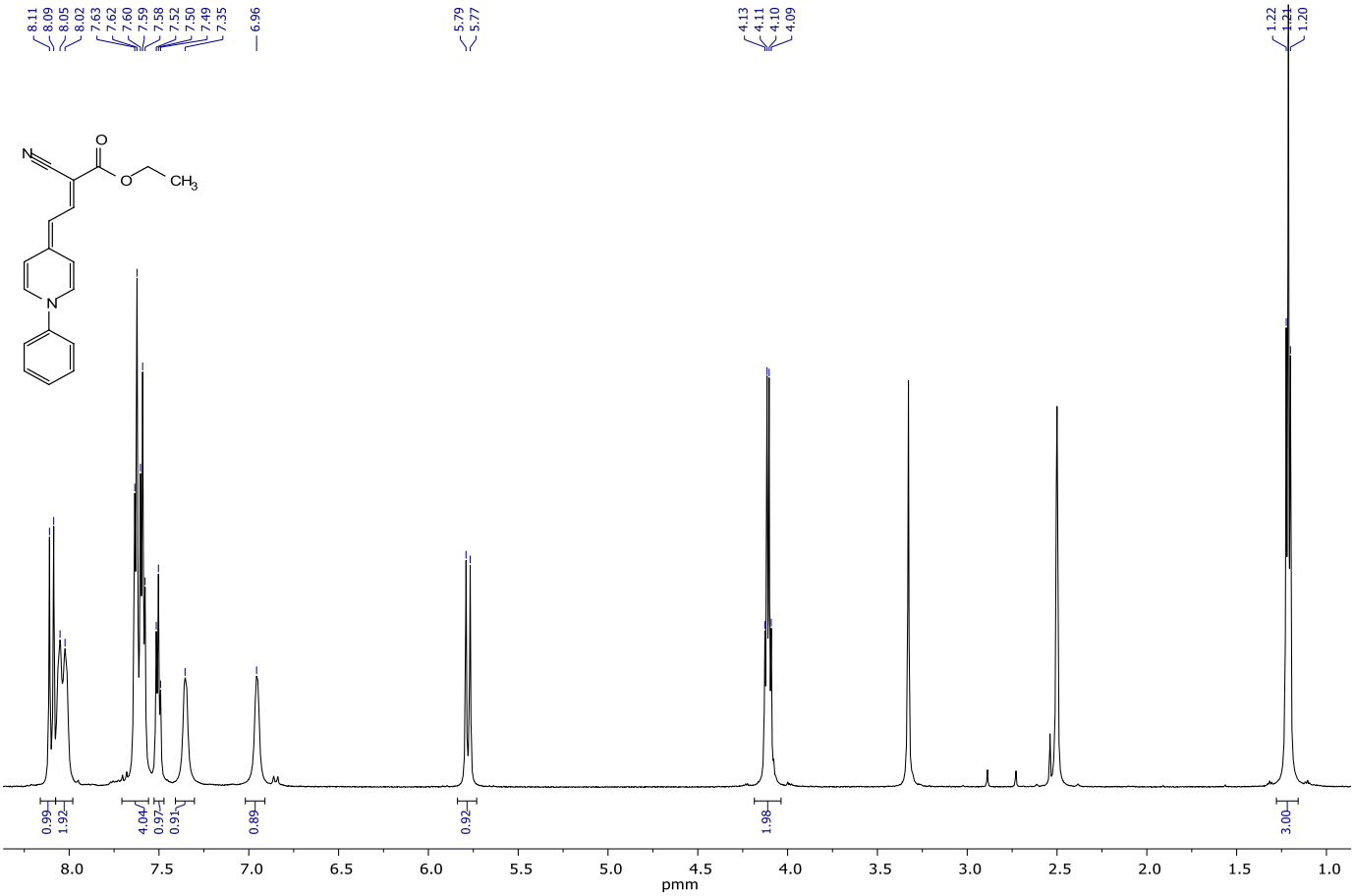
^{13}C NMR spectrum of the compound **32**



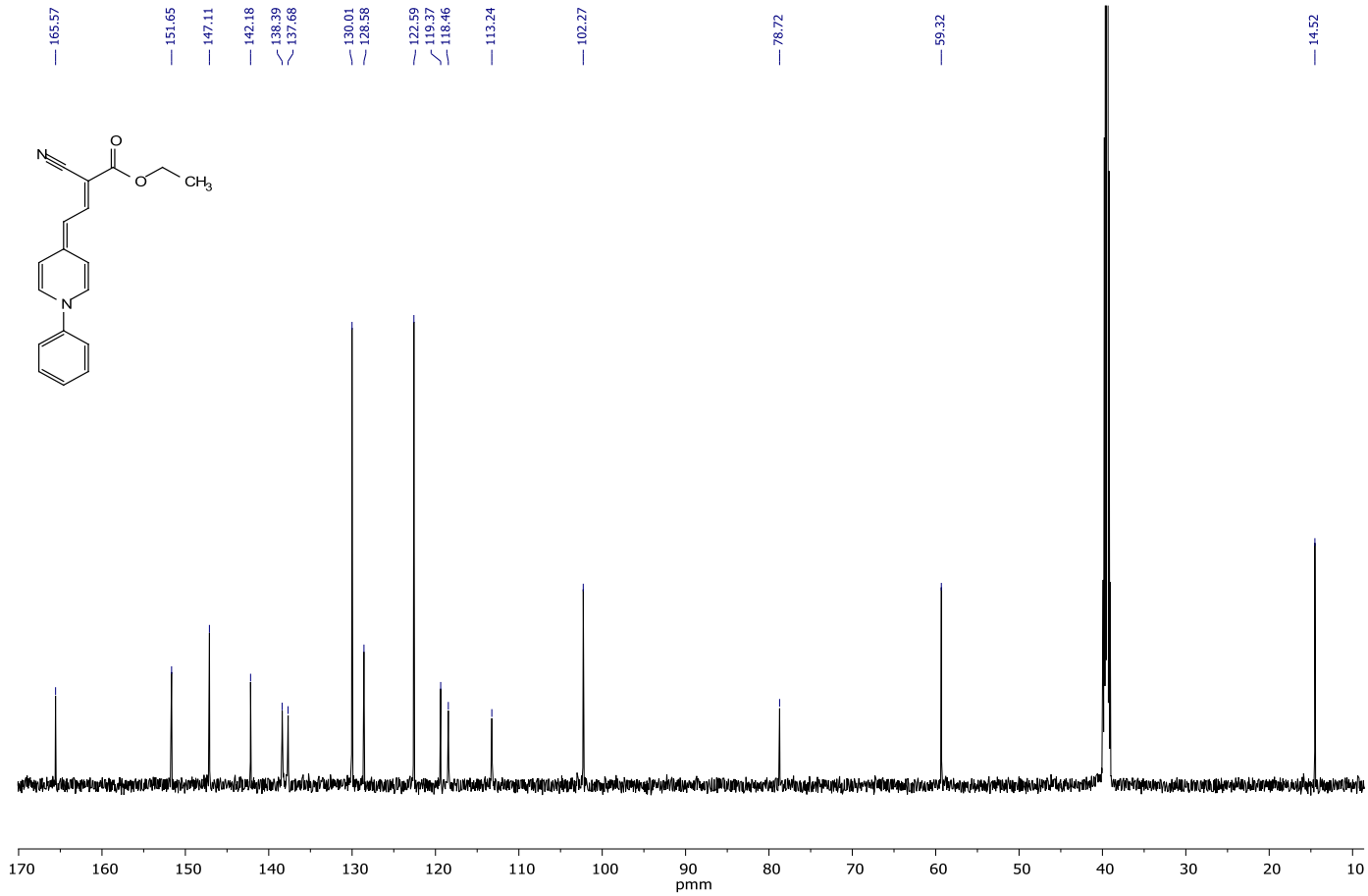
^{1}H NMR spectrum of the compound **33**



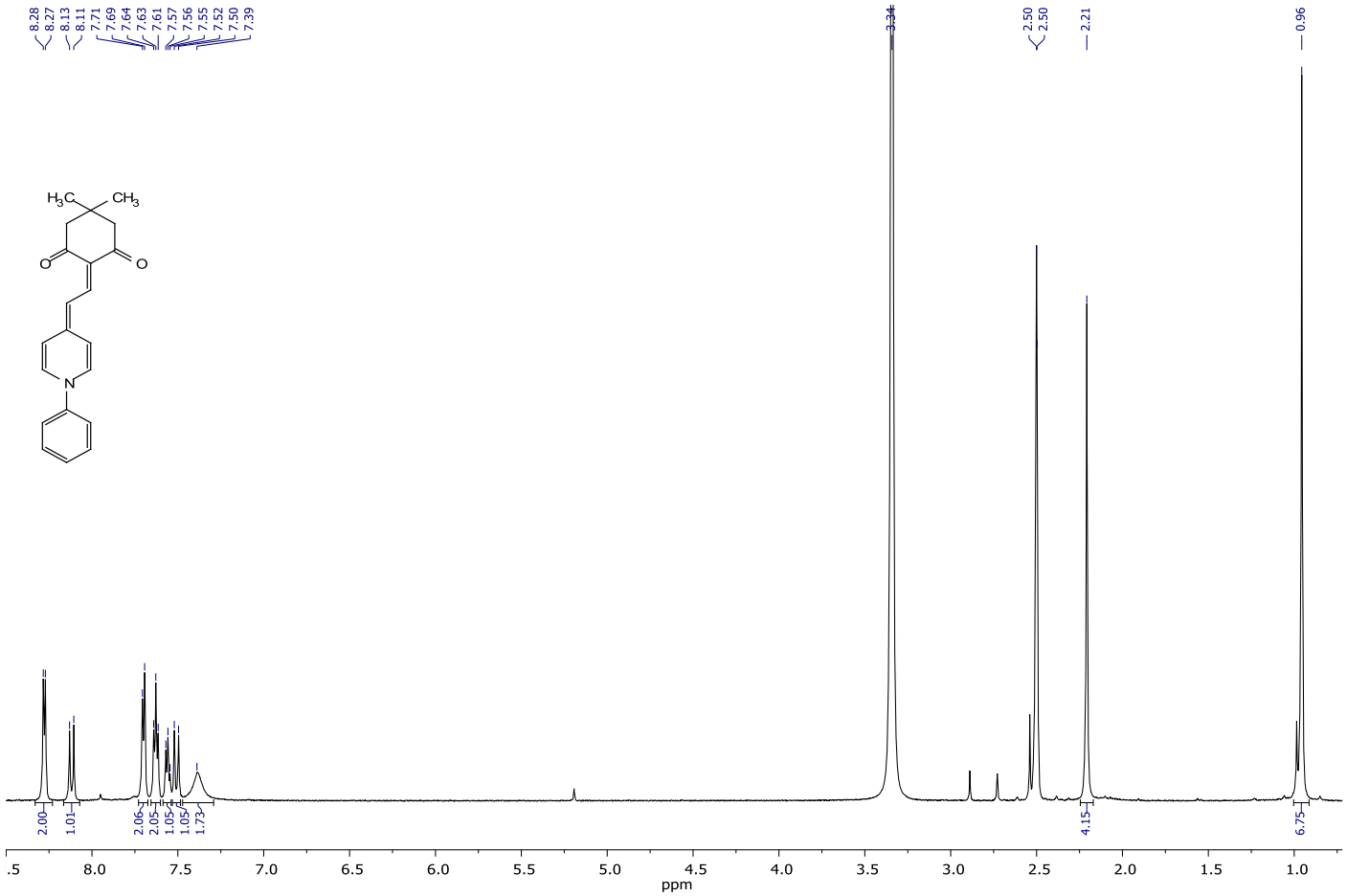
^{13}C NMR spectrum of the compound **33**



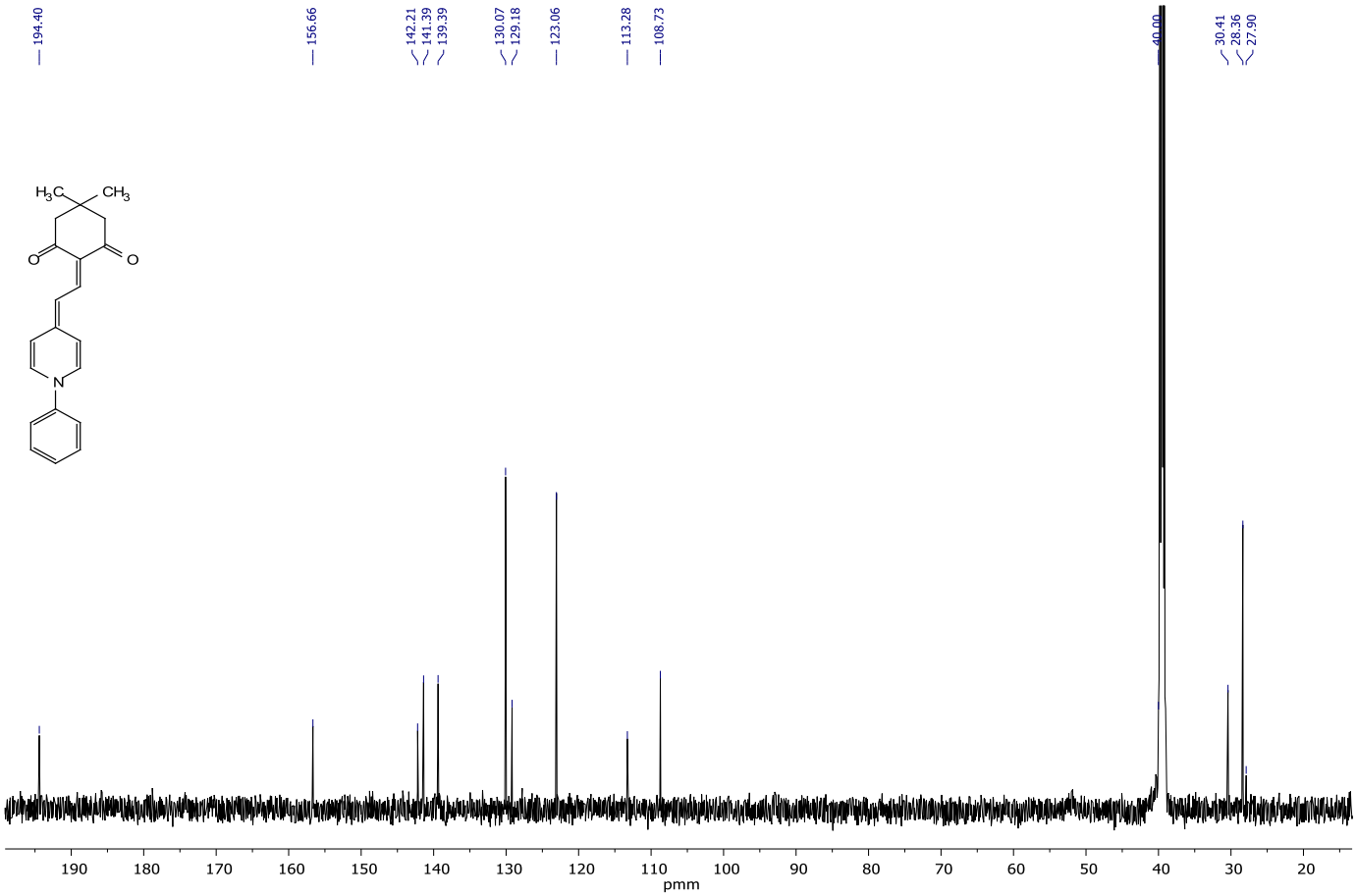
^{1}H NMR spectrum of the compound **34**



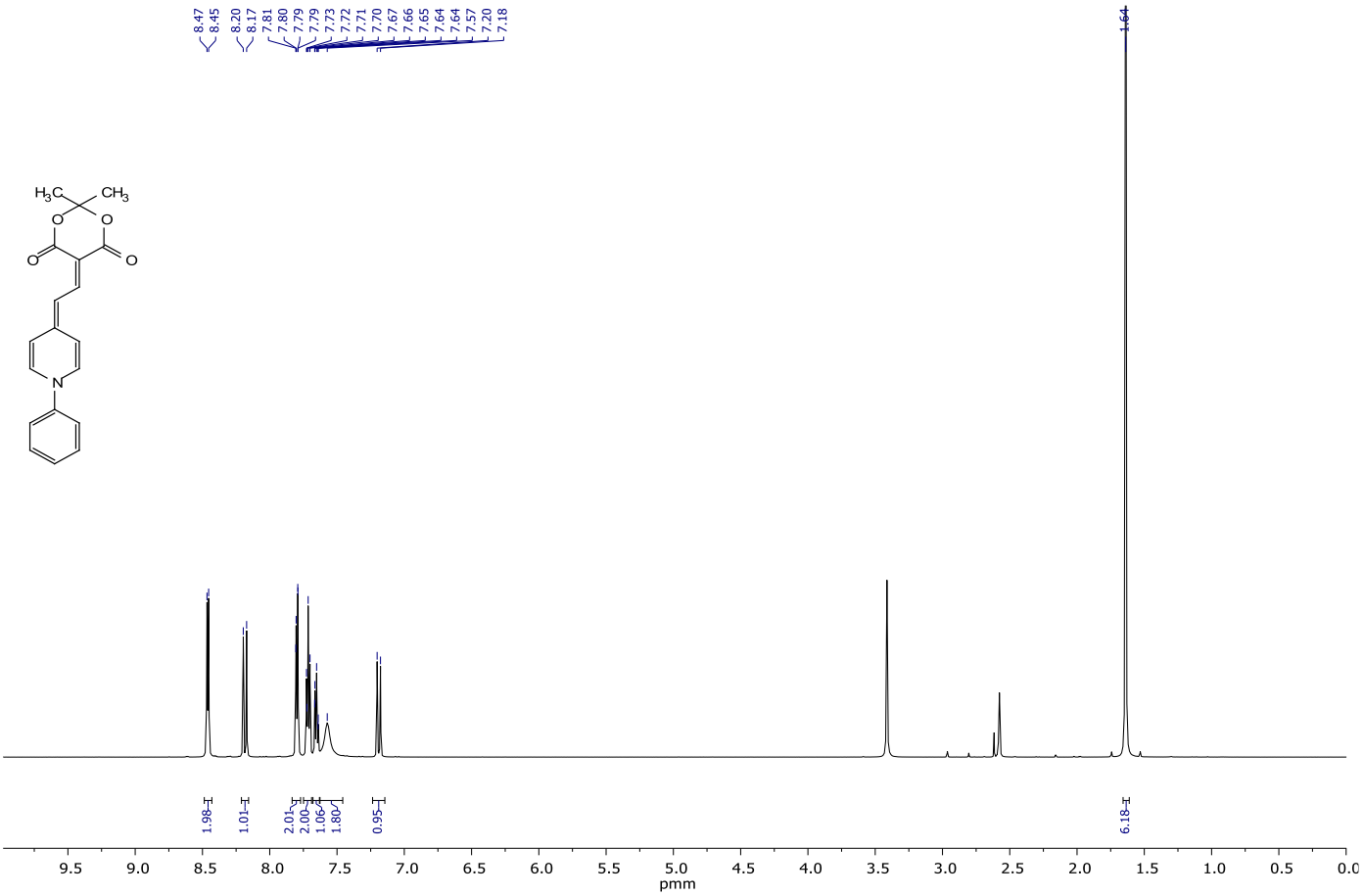
^{13}C NMR spectrum of the compound **34**



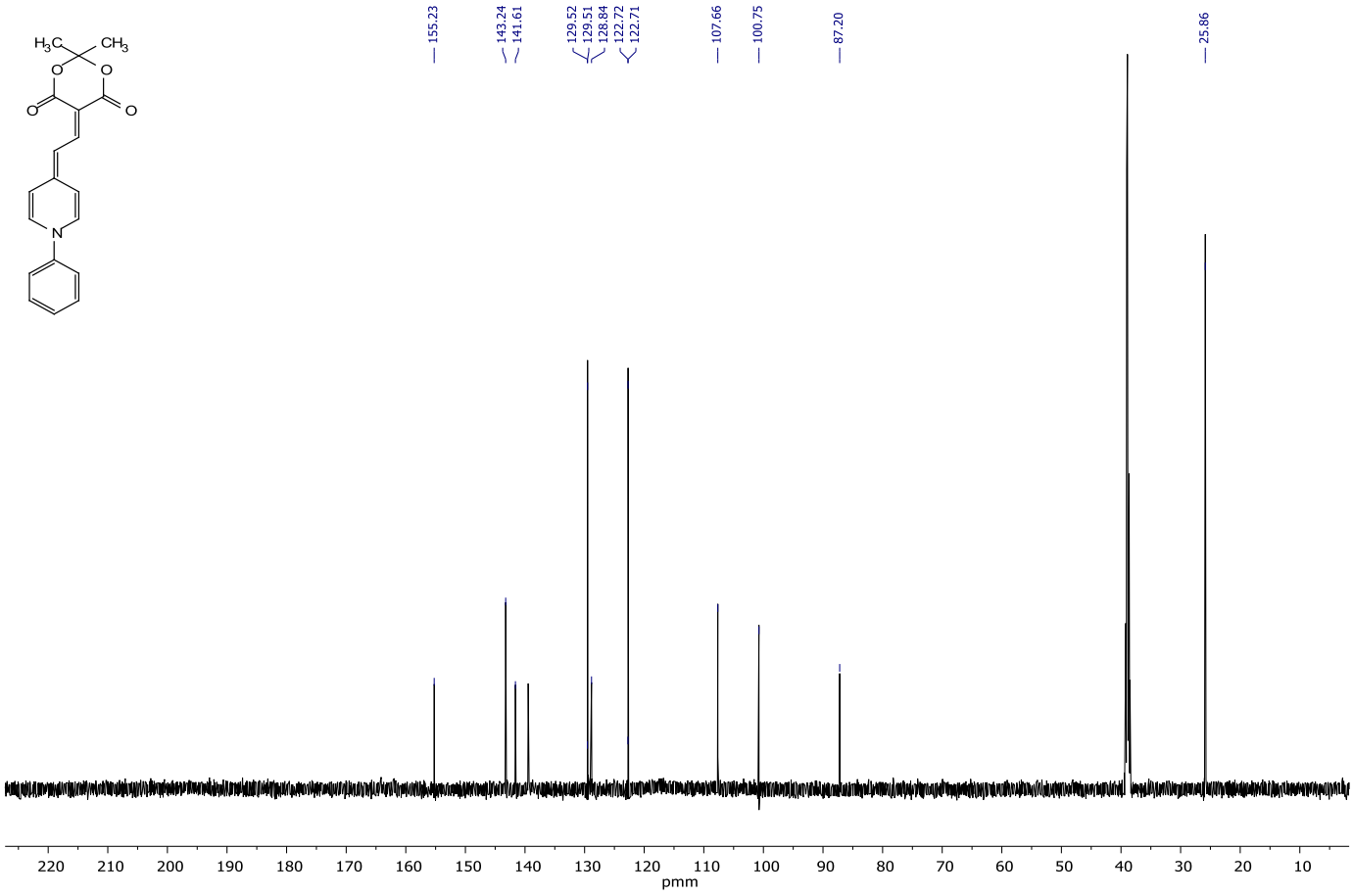
^{1}H NMR spectrum of the compound **35**



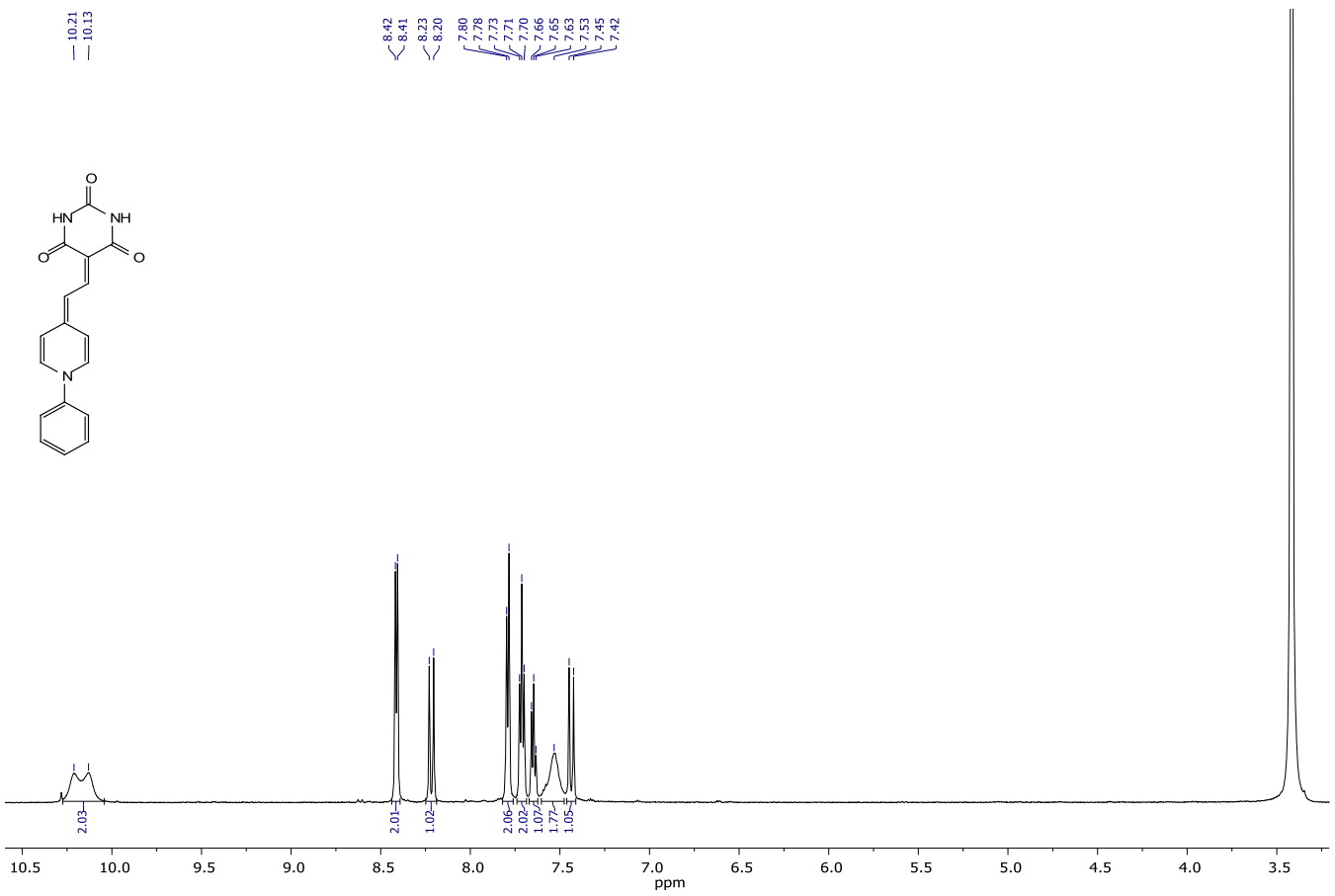
^{13}C NMR spectrum of the compound **35**



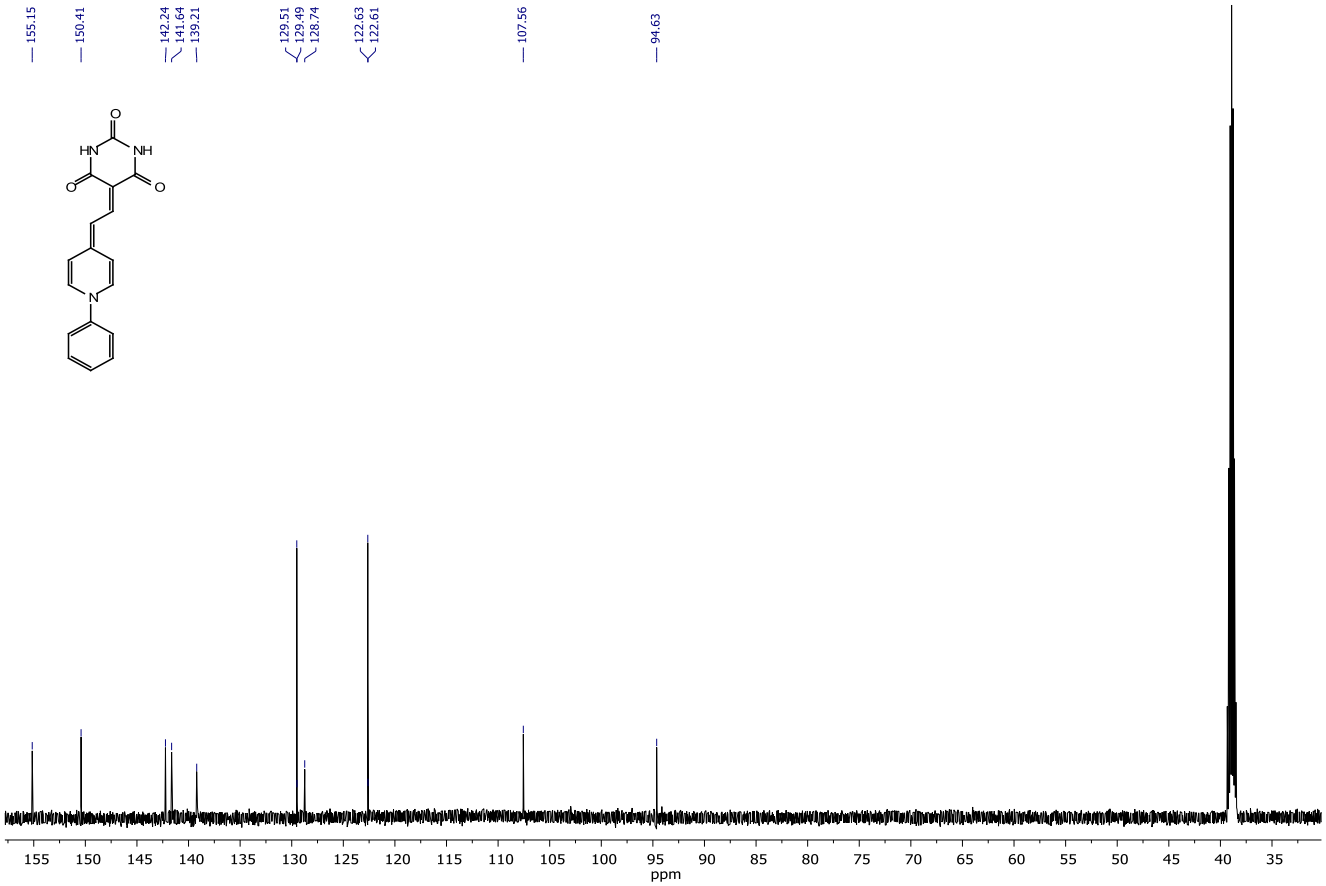
^{1}H NMR spectrum of the compound **36**



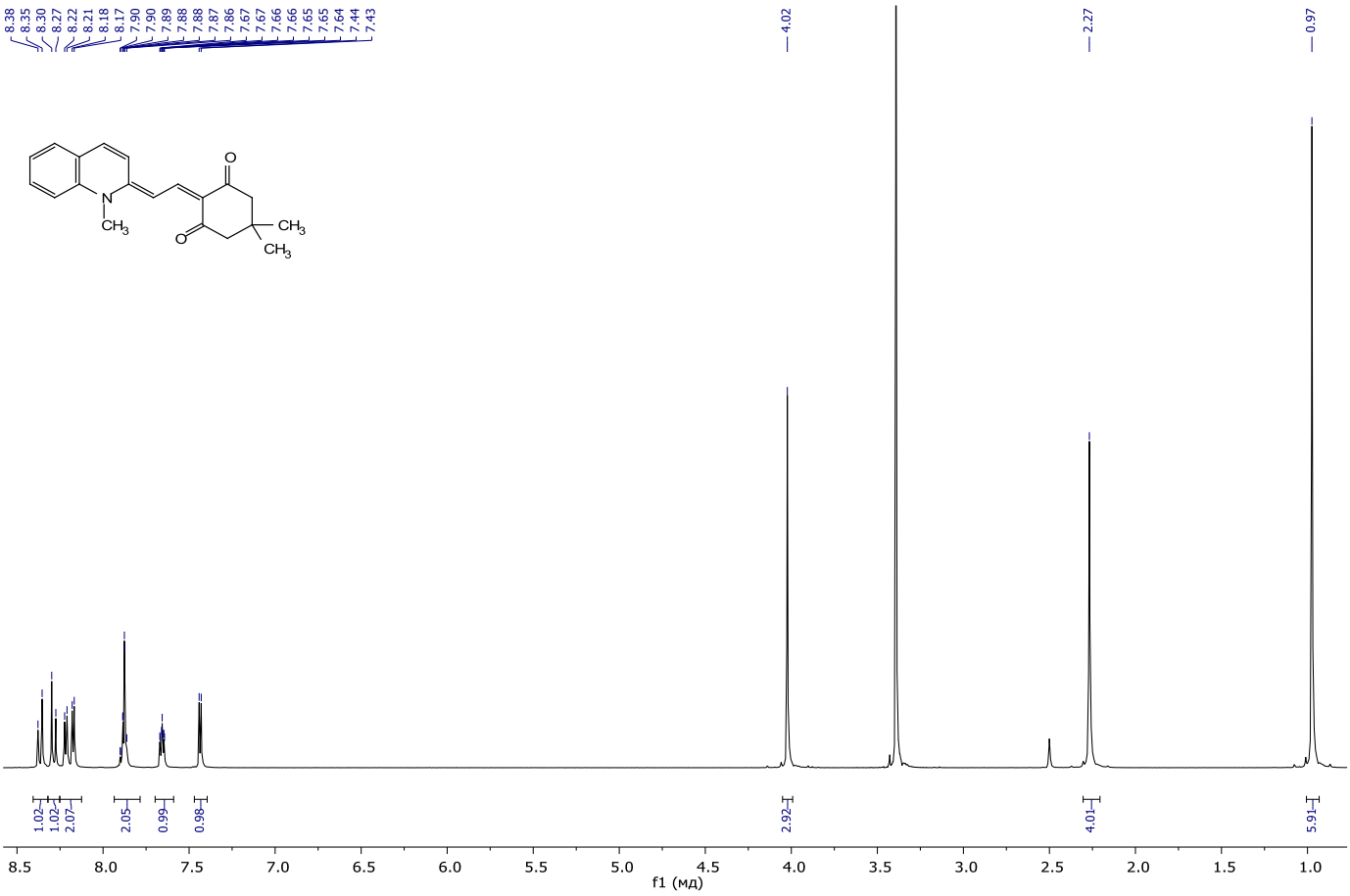
^{13}C NMR spectrum of the compound **36**



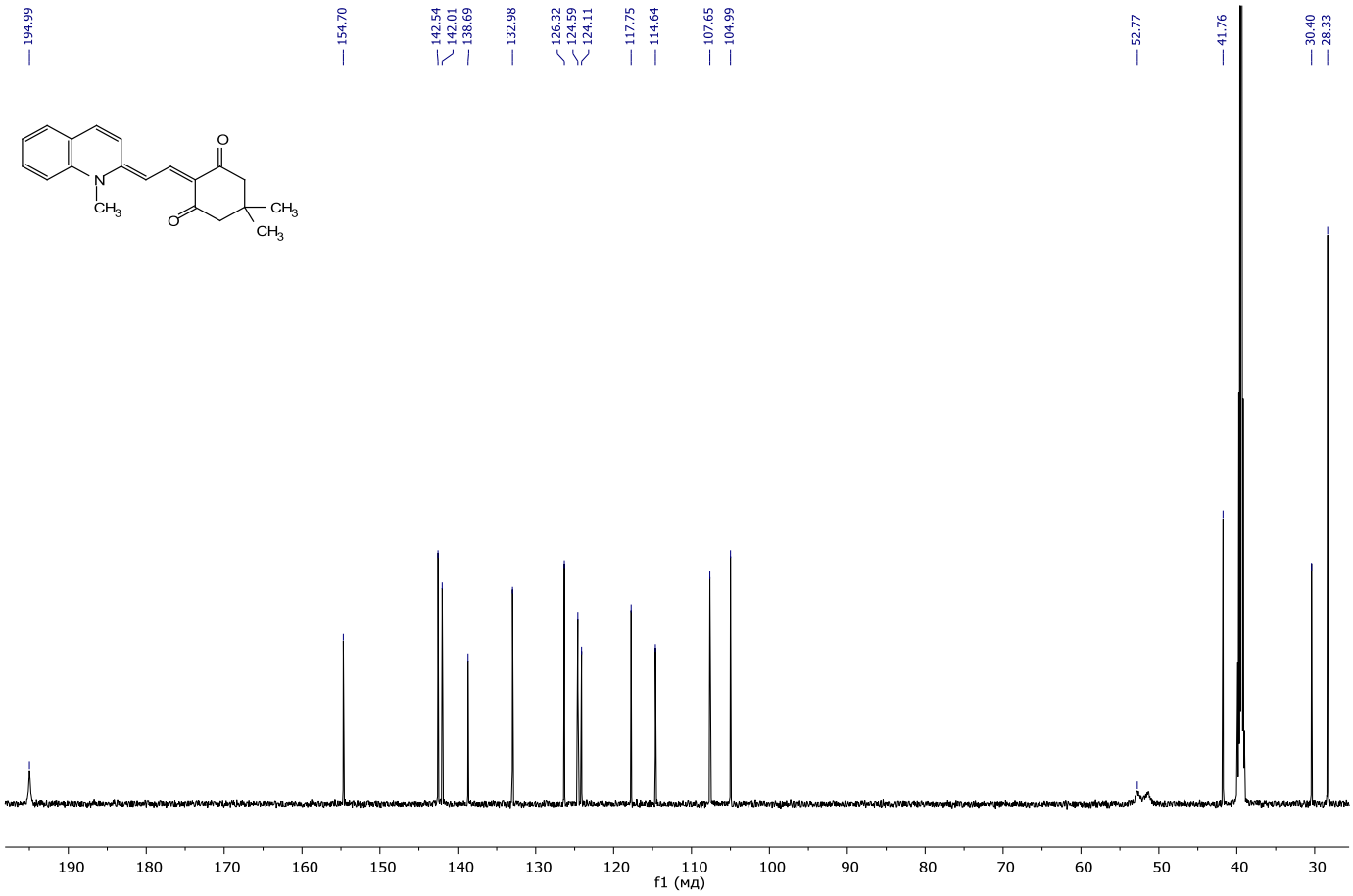
^{1}H NMR spectrum of the compound **37**



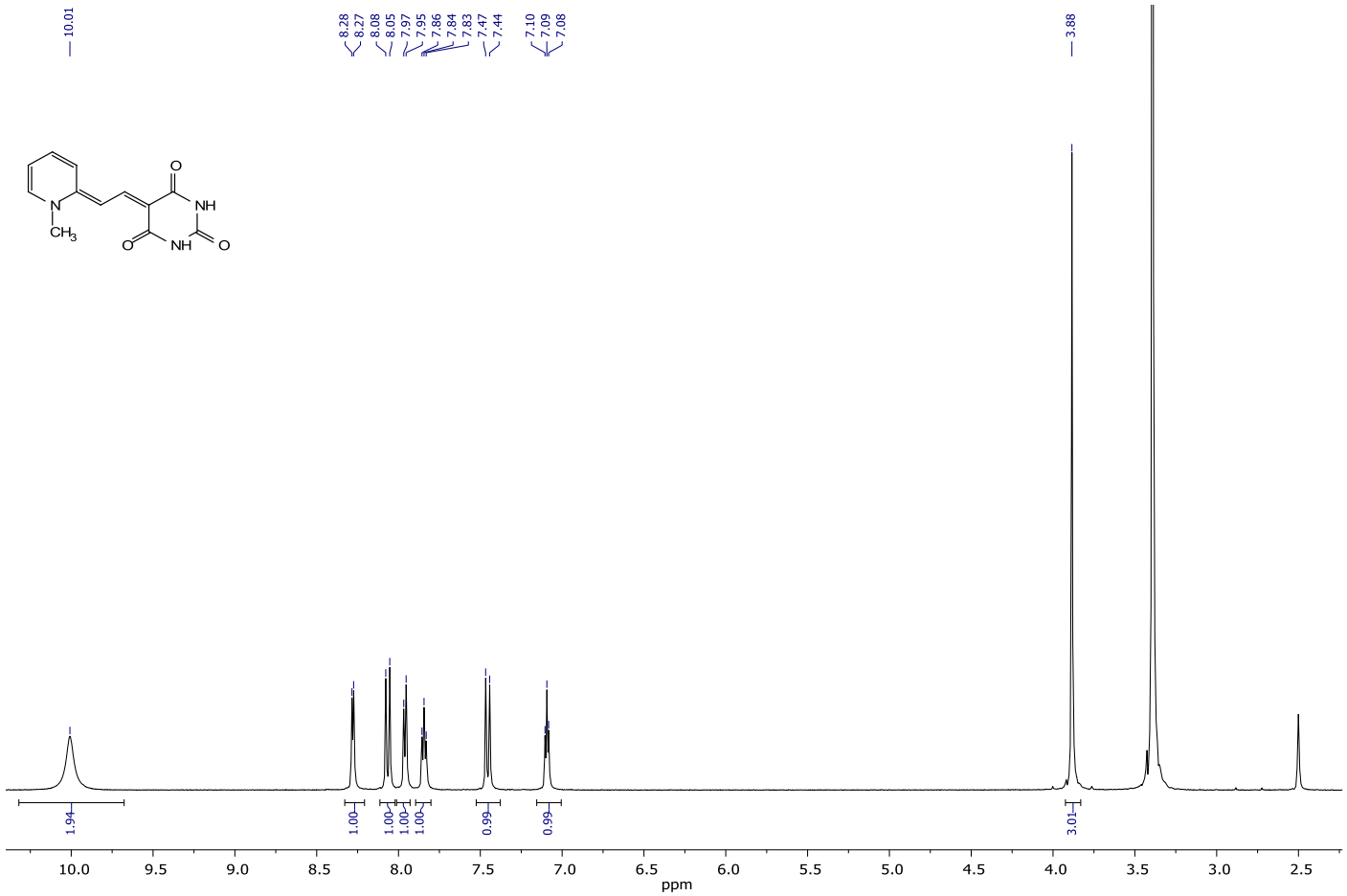
^{13}C NMR spectrum of the compound **37**



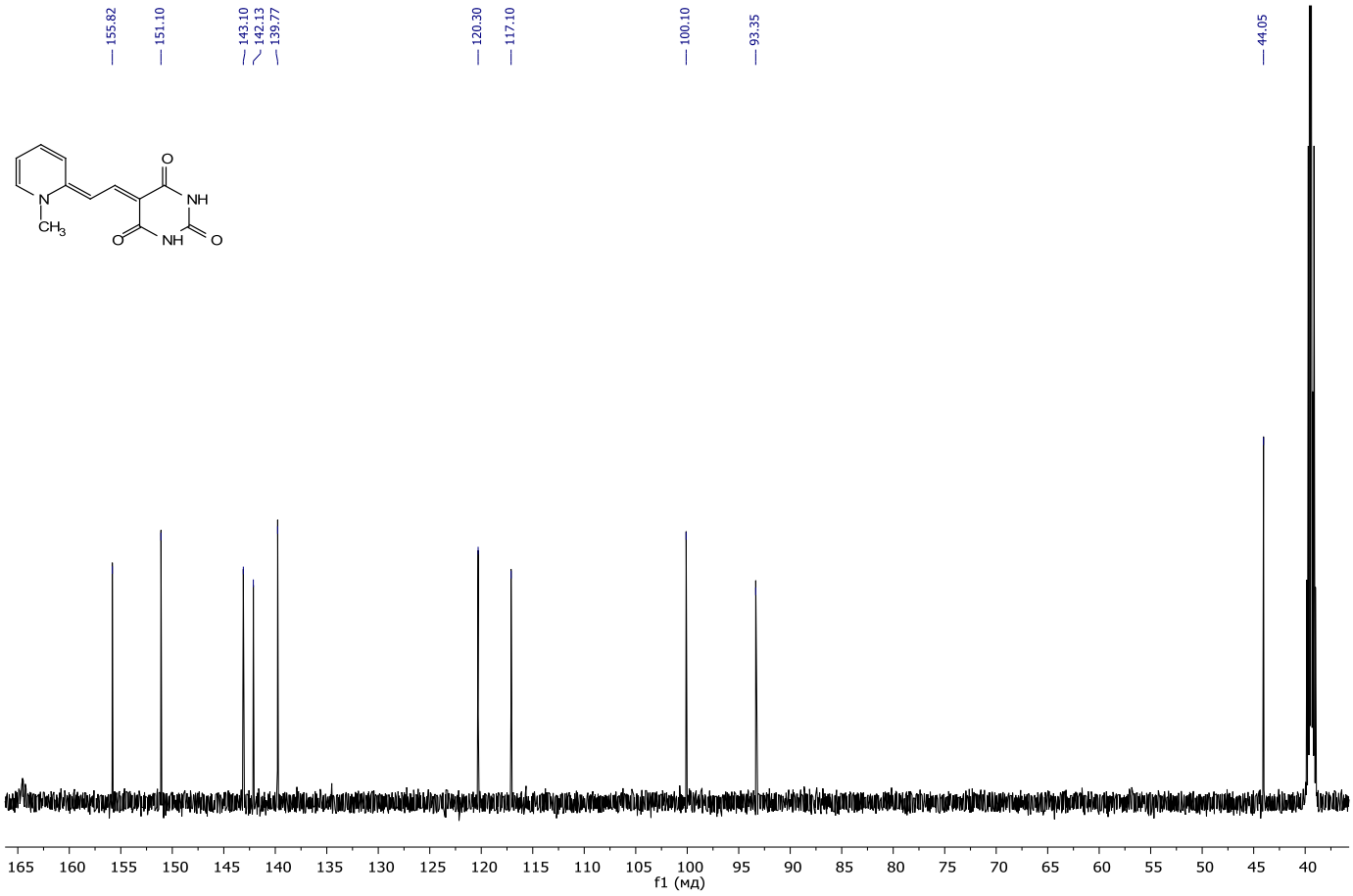
^{1}H NMR spectrum of the compound **38**



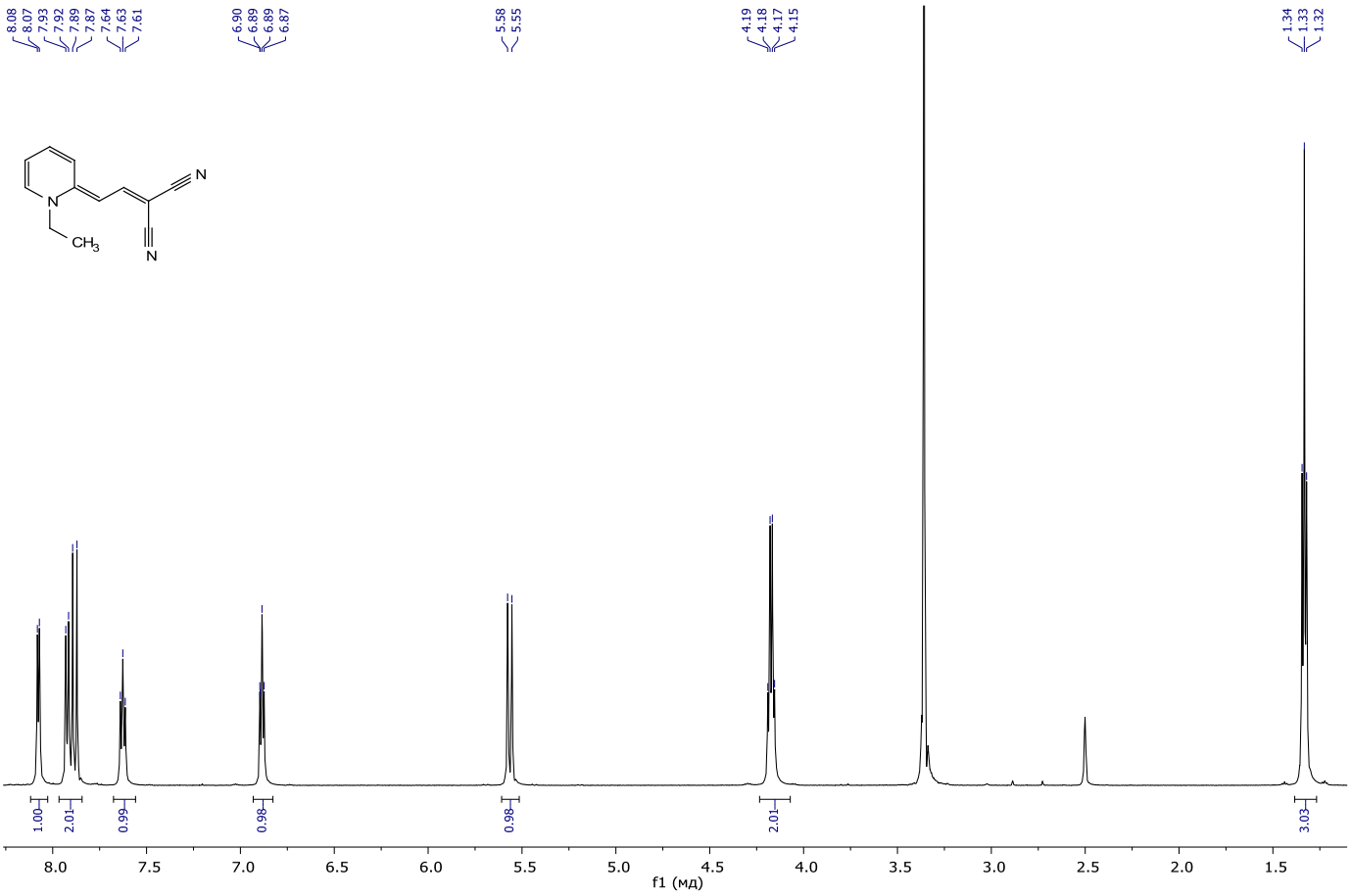
^{13}C NMR spectrum of the compound **38**



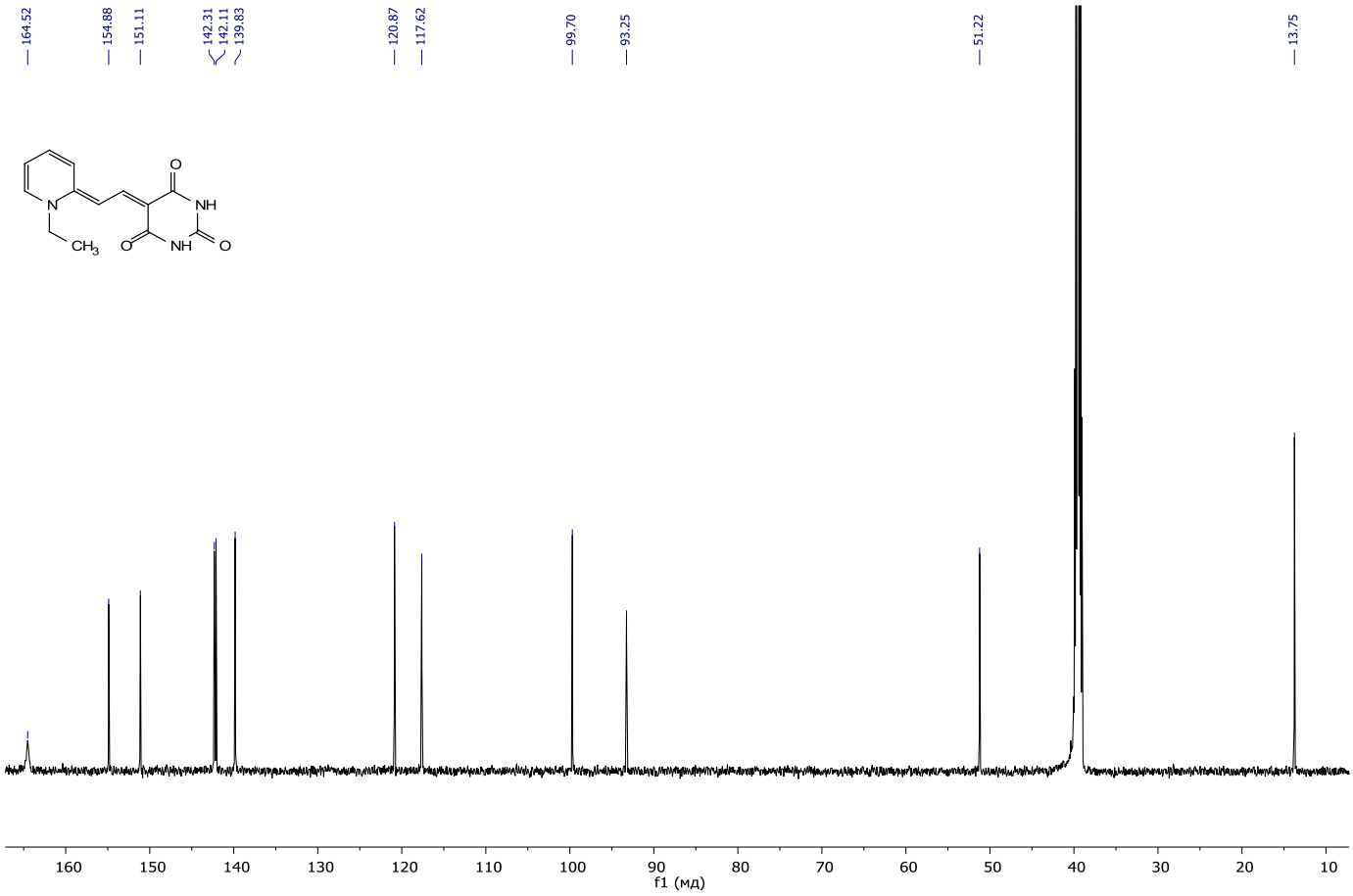
^{1}H NMR spectrum of the compound **39**



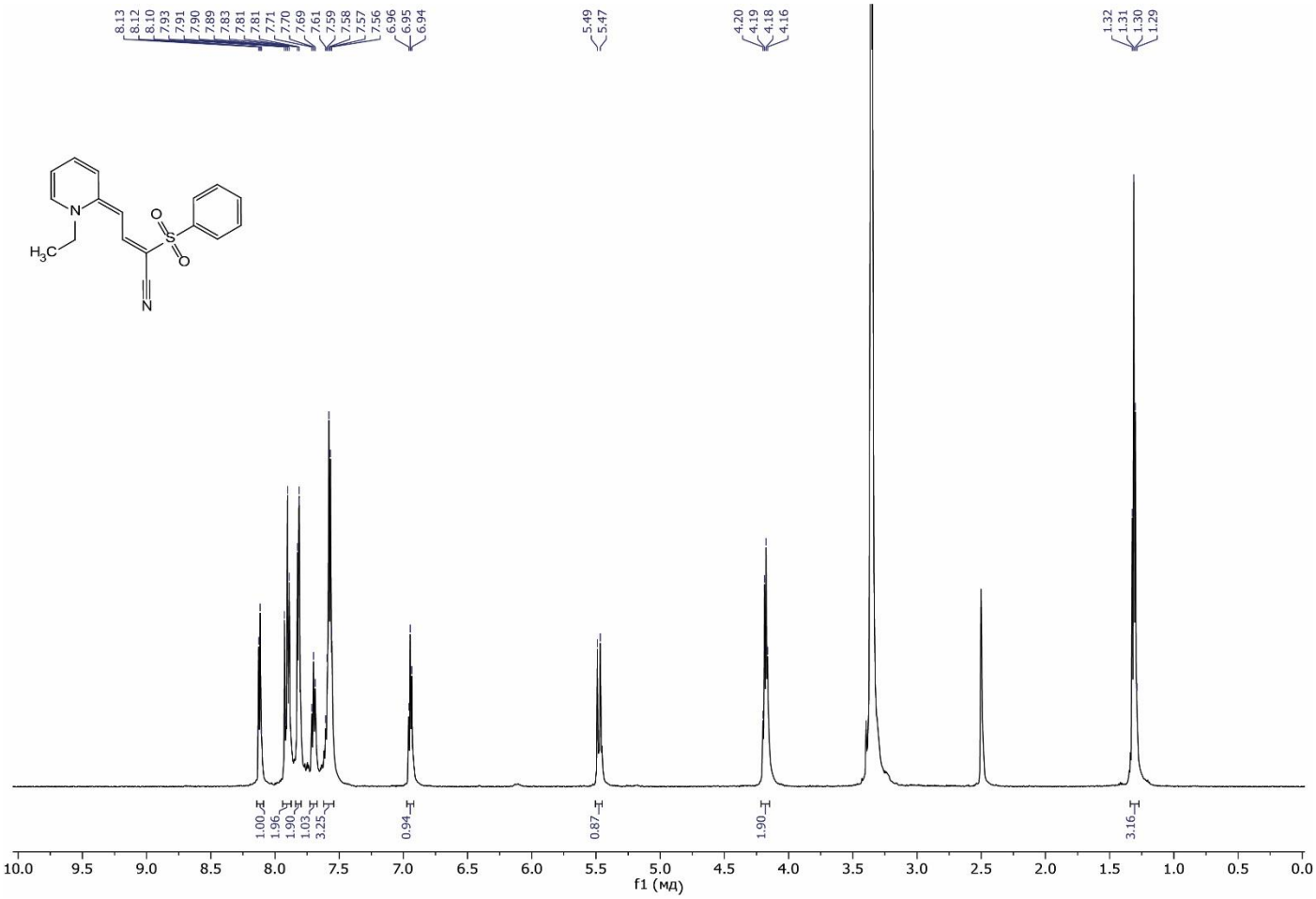
^{13}C NMR spectrum of the compound **39**



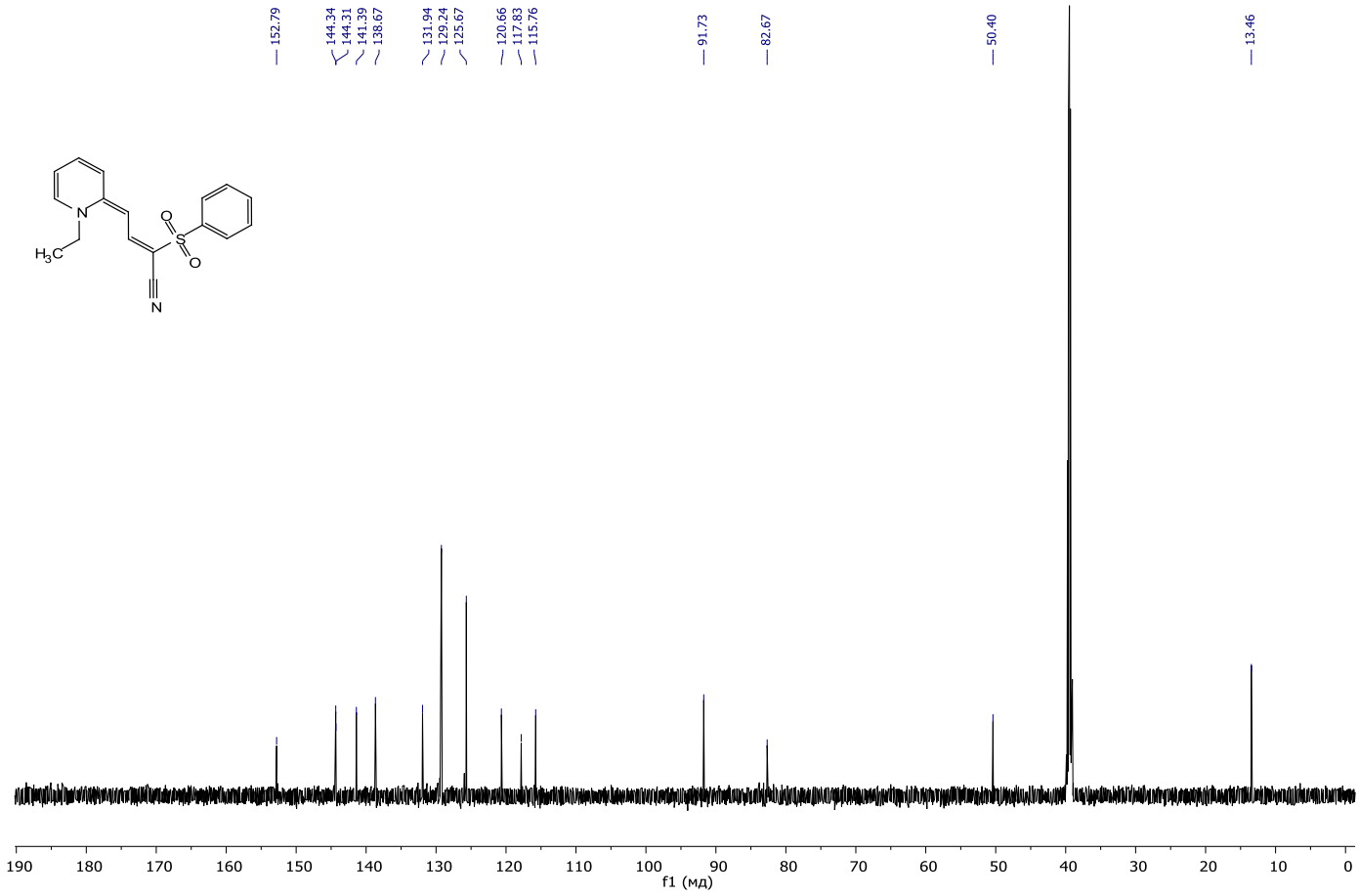
^{1}H NMR spectrum of the compound **40**



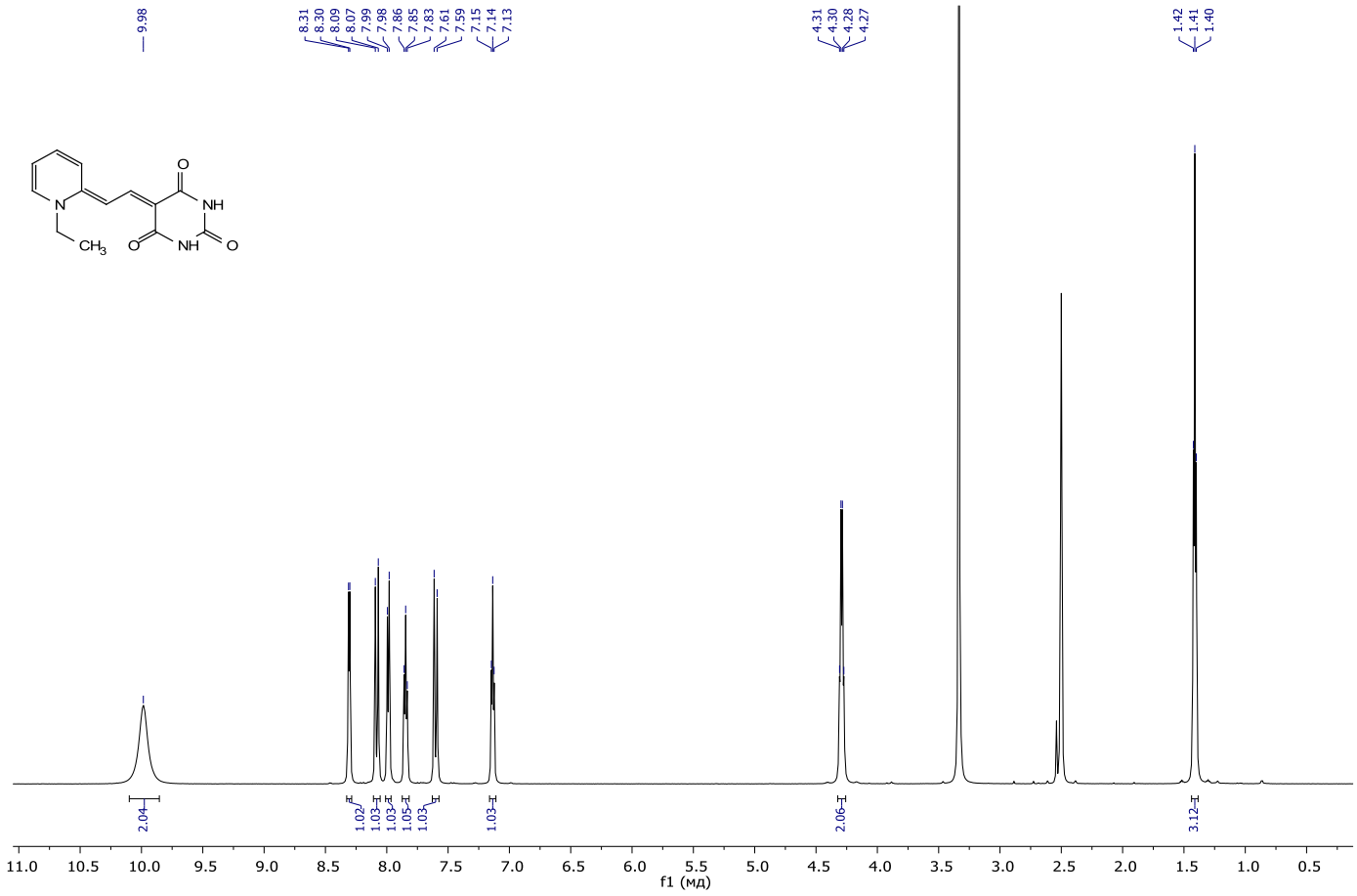
^{13}C NMR spectrum of the compound **40**



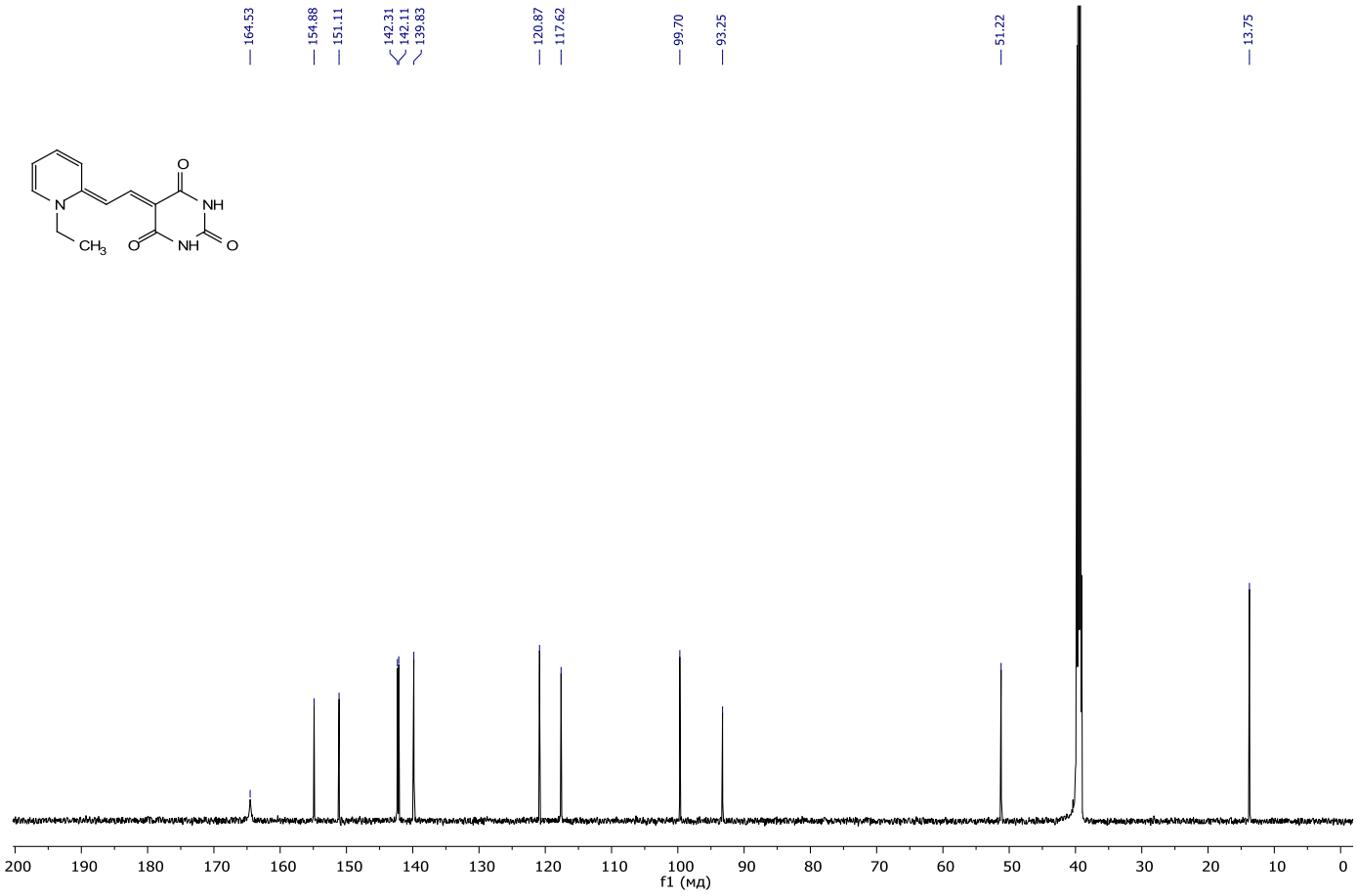
^{1}H NMR spectrum of the compound **41**



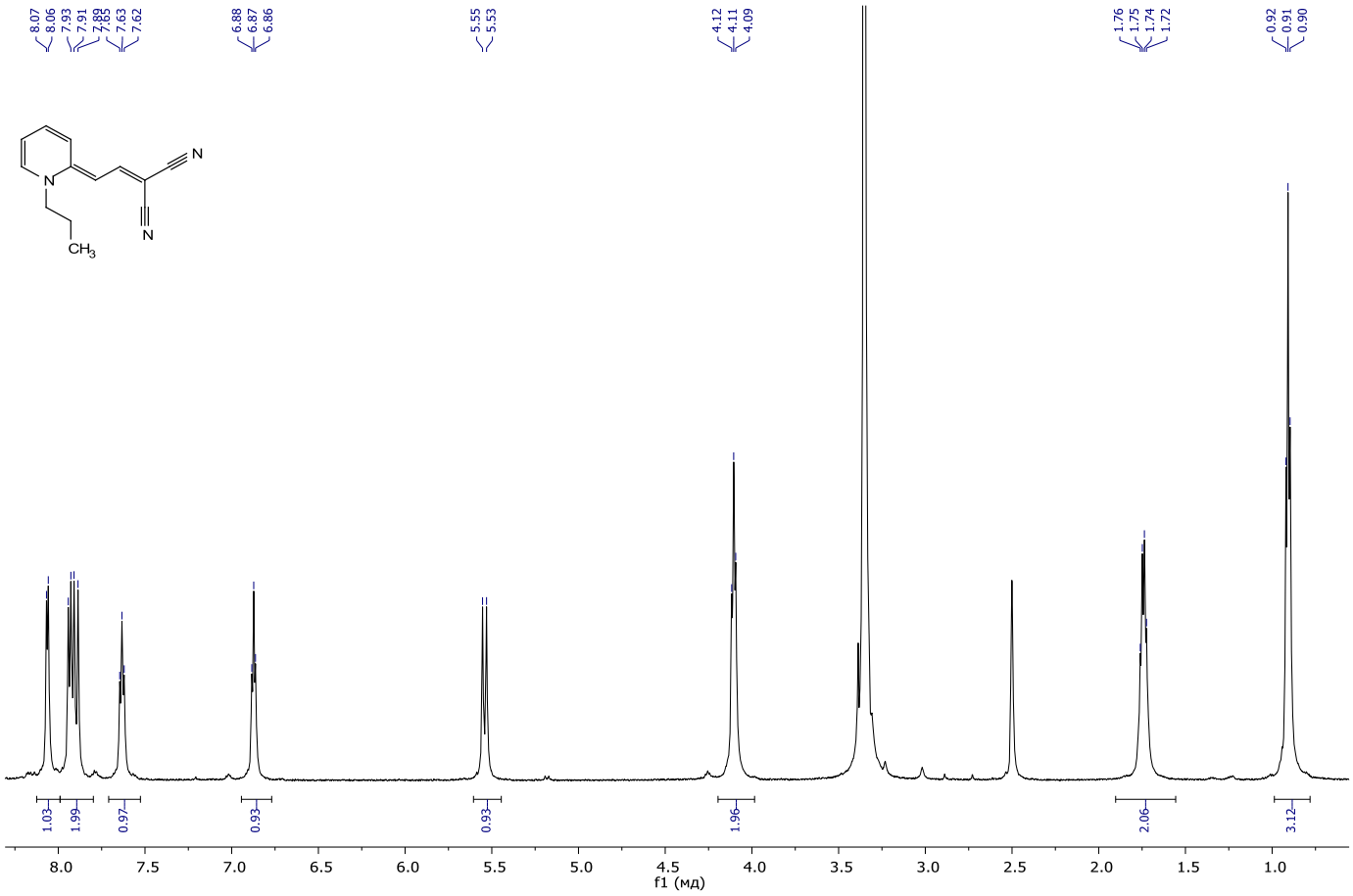
^{13}C NMR spectrum of the compound **41**



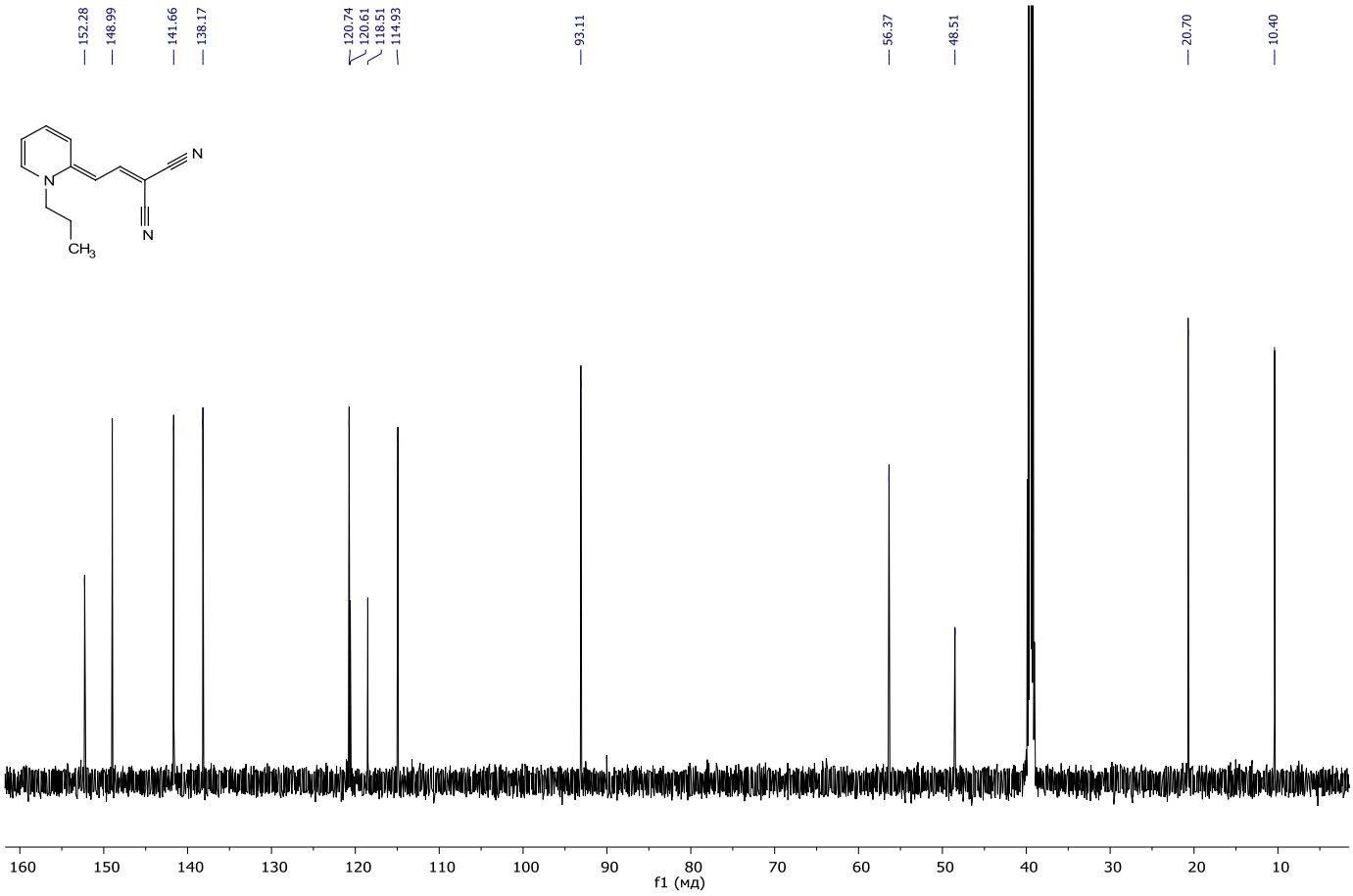
^{1}H NMR spectrum of the compound **42**



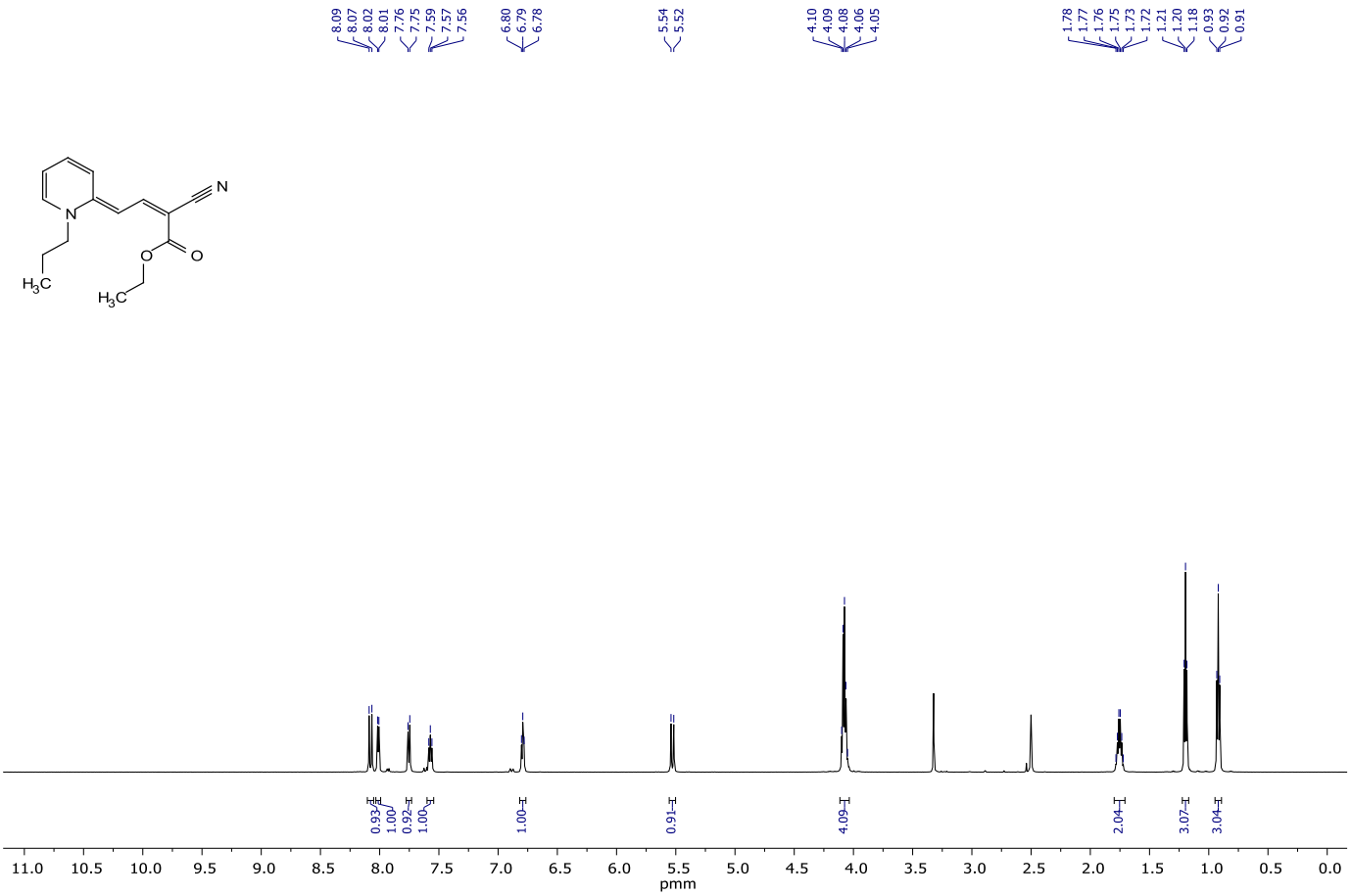
^{13}C NMR spectrum of the compound **42**



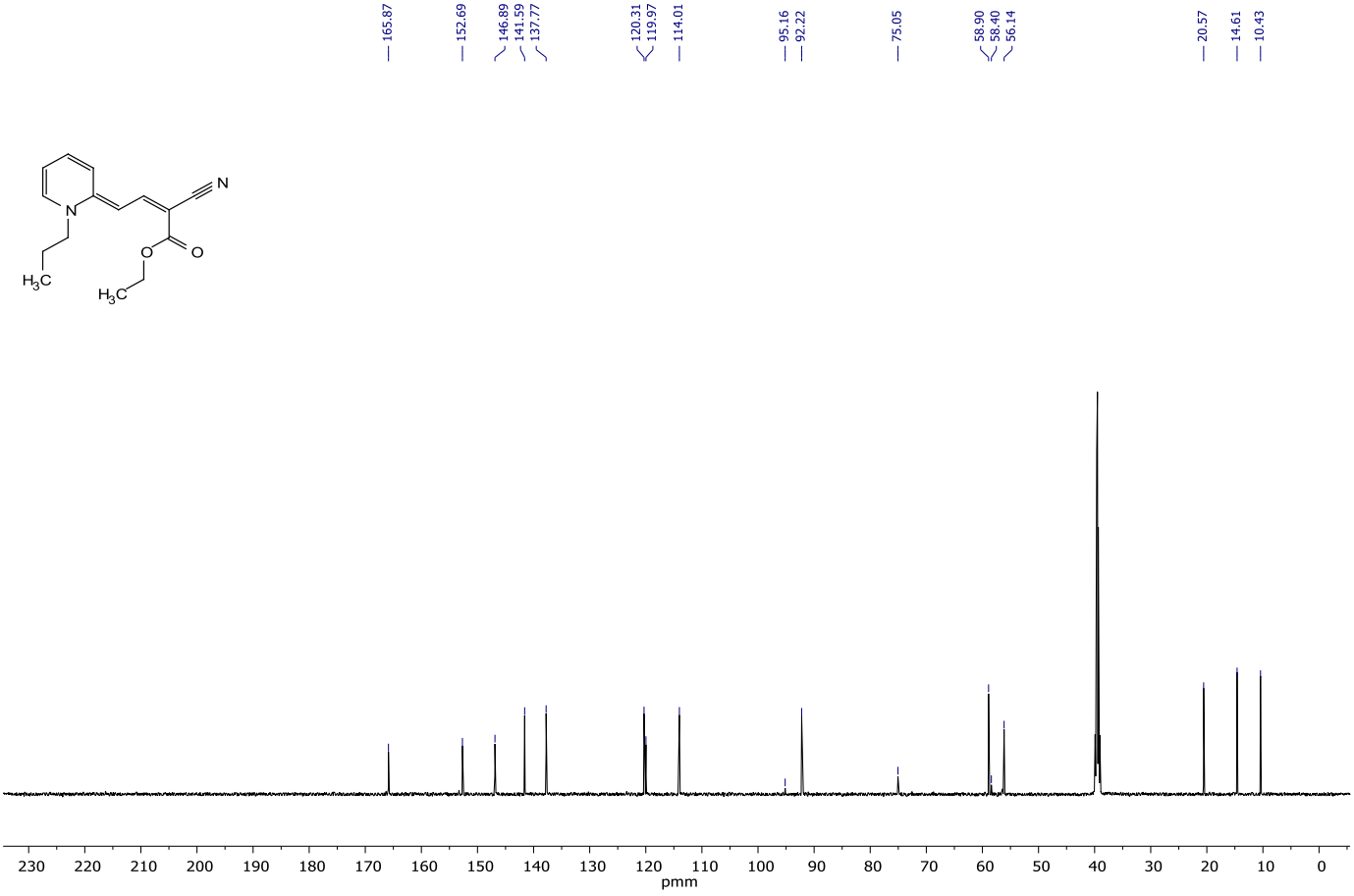
^{1}H NMR spectrum of the compound **43**



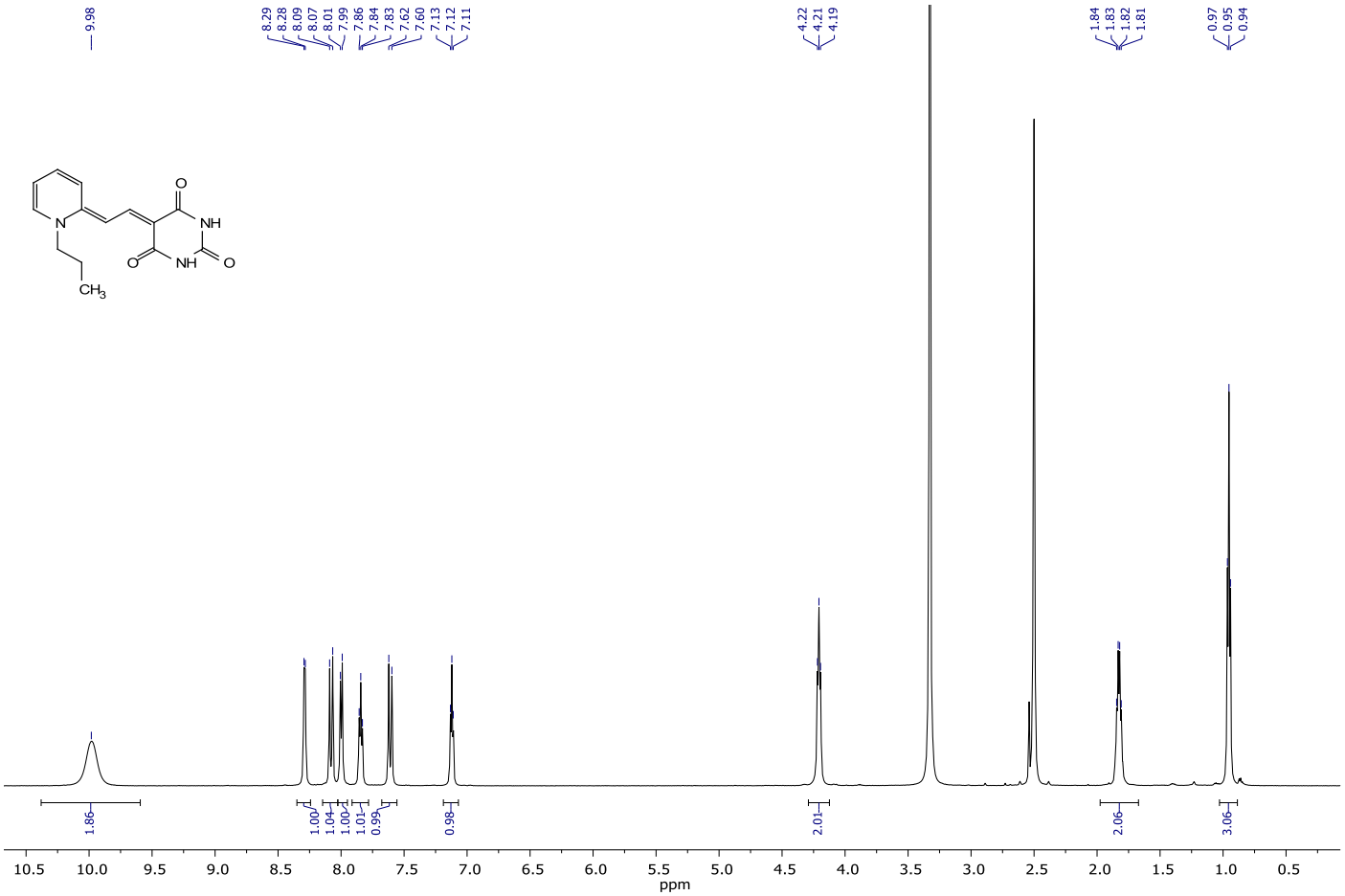
^{13}C NMR spectrum of the compound **43**



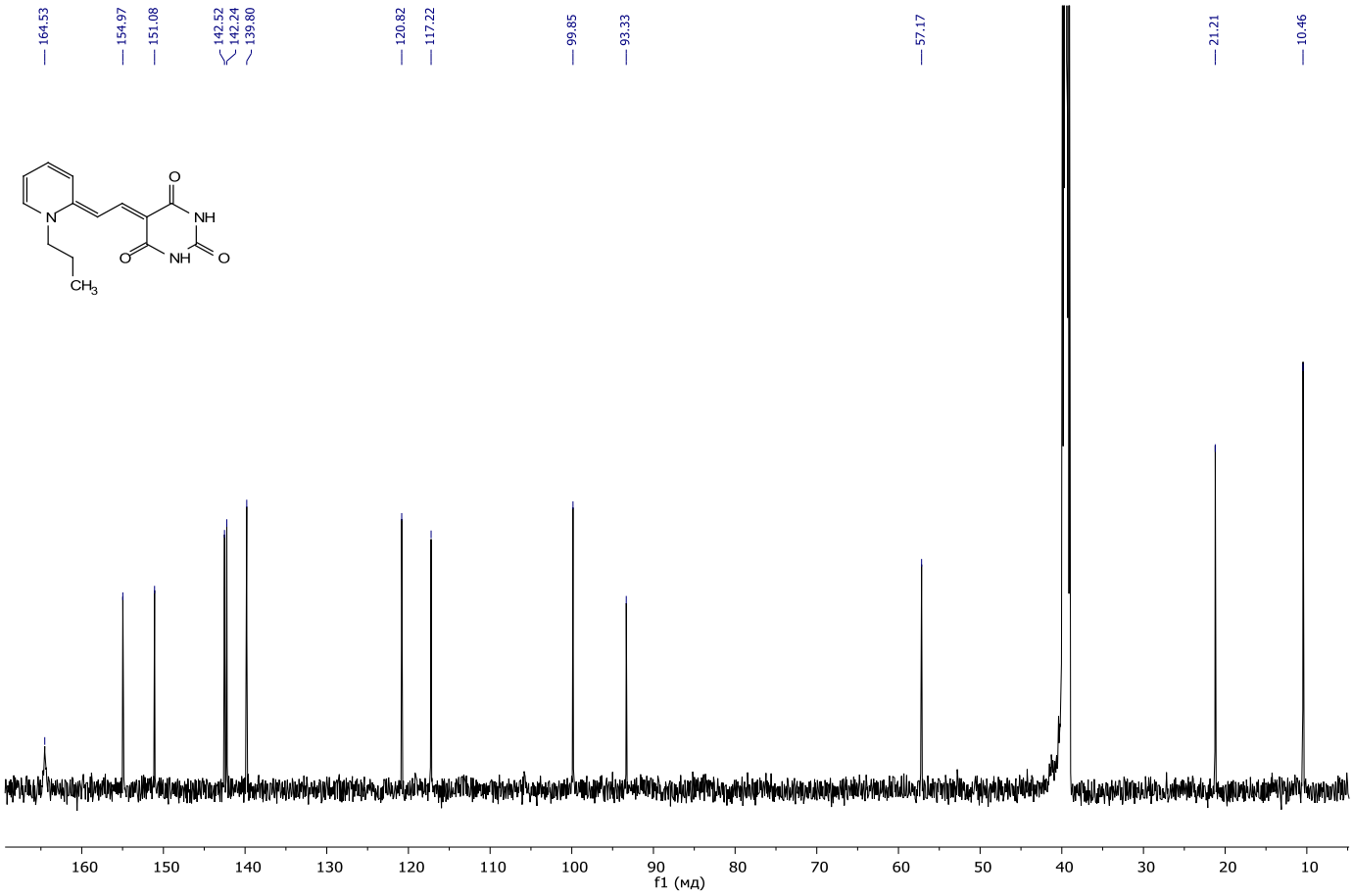
^{1}H NMR spectrum of the compound **44**



^{13}C NMR spectrum of the compound **44**



^{1}H NMR spectrum of the compound **45**



^{13}C NMR spectrum of the compound **45**

3. Crystal structure determination

X-ray diffraction data were collected on a APEX II DUO CCD diffractometer using molybdenum radiation [λ(MoKα) = 0.71072 Å, ω-scans]. The substantial redundancy in data allowed empirical absorption correction to be applied with SADABS by multiple measurements of equivalent reflections. The structures were solved by direct methods and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. C-H hydrogen atoms in all structures were placed in calculated positions and refined within the riding model. The hydrogen atoms of water molecules and N-H groups were located from the Fourier density synthesis and refined in anisotropic approximation. All calculations were performed with the SHELXTL software package.[1] Crystal data and structure refinement parameters are listed in Table 1. Crystallographic data for the structures reported in this paper have been deposited to the Cambridge Crystallographic Data Centre. These data can be obtained free of charge from The Cambridge Crystallographic Data via www.ccdc.cam.ac.uk/data_request/cif.

[1] M. Sheldrick, *Acta. Cryst.,* **2008**, A64, 112.

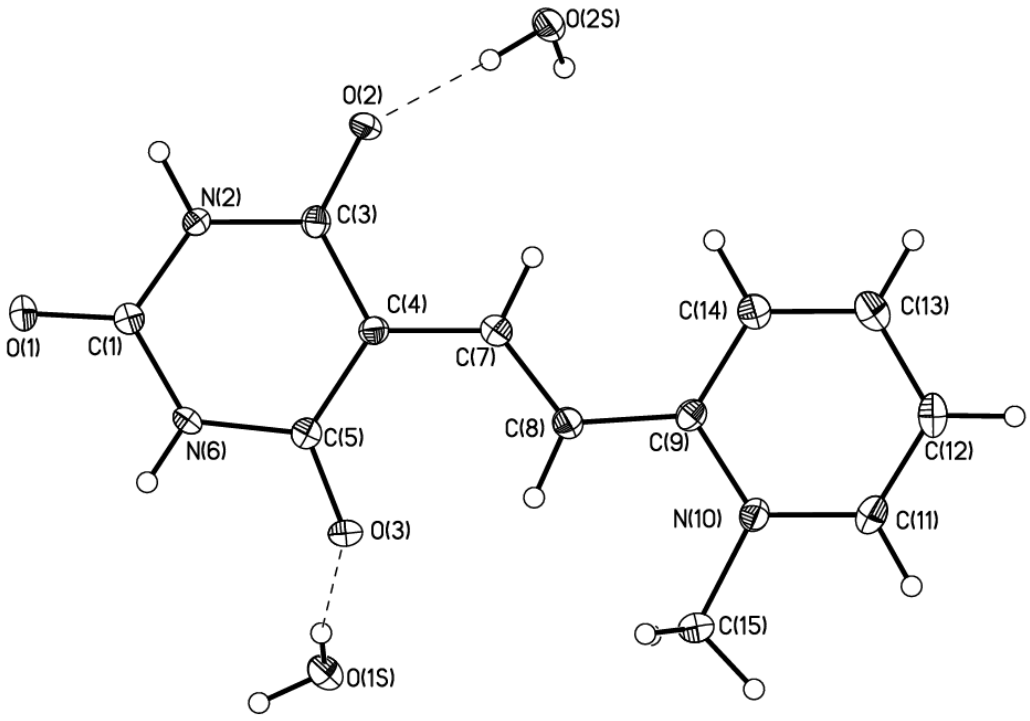


Figure S1. General view of **39** in a crystal in representation of non-hydrogen atoms by probability ellipsoids of atomic displacements (p=50%).

Table S1. Crystal data and structure refinement parameters

Compound	**5**{*8, 6*}
CCDC	1850463
Formula	$C_{12}H_{15}N_3O_5$
MW	281.27
T, K	120
Crystal system	Triclinic
Space group	P-1
Z(Z')	2(1)
a, Å	4.5087(16)
b, Å	9.696(3)
c, Å	14.245(5)
α, °	86.206(7)
β, °	84.513(7)
γ, °	89.489(7)
V, Å^3	618.5(4)
d_{calc}, g cm^{-3}	1.510
μ, cm^{-1}	1.19
F(000)	296
$2\theta_{max}$, °(completeness,%)	58 (99.9)
Reflections collected	8078
Independent reflections	3282
Reflections with I>2σ(I)	2517
Parameters	206
R1	0.0439
wR2	0.1246
GOF	1.052
Residual electron density, e·Å^{-3} (ρ_{max}/ρ_{min})	0.494/-0.231