SUPPORTING INFORMATION FOR:

Direct transition-metal-free synthesis of 2-heteroaryl-4-quinolones via ANRORC type rearrangement of 3-(2-(2-nitrophenyl)-2-oxoethyl)quinoxalin-2(1*H*)-ones

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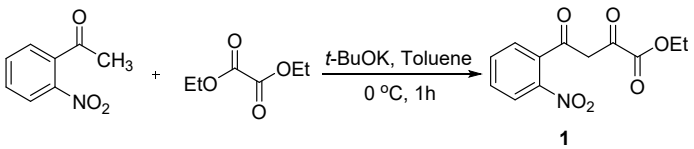
Experimental section

General Methods. The melting points were determined on a Boetius hot-stage apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Bruker Vector-22 spectrometer. The pH of the reaction mixtures was measured using universal indicator paper pH 0-12 (Lachema o.p. Brno, plant Neratovice) and using the HANNA instruments pH 211−Laboratory pH−meter. (State Register of SI No. 20738-00). Nuclear magnetic resonance (NMR) spectra were recorded on Brucer spectrometer Avance III-500.1 (500.1 MHz for ^{1}H, 125.8 MHz for ^{13}C, and 50.7 MHz for ^{15}N) in DMSO-d_6 at 303 K. The spectrometer was equipped with a pulsed gradient unit capable of producing magnetic field pulse gradients in the z-direction of 53.5 G cm^{-1}. All the spectra were obtained in a 5-mm gradient broadband probehead. Chemical shifts are reported on the δ (ppm) scale and referred to the solvent DMSO-d_6 (2.50 ppm for ^{1}H and 39.5 ppm for ^{13}C NMR) and to external MeCN (235.5 for ^{15}N NMR). The ^{1}H and ^{13}C NMR spectra of synthesized compounds were completely assigned by using a combination of 2D NMR experiments, which included ^{1}H-^{1}H COSY, HSQC and HMBC sequences. For a number of compounds **2f**, **2l**, **4a**, **4f**, **4h**, **6b**, **7b** the chemical shifts of nitrogen atoms were also established by HSQC (^{1}H-^{15}N) and HMBC (^{1}H-^{15}N) experiments. The high-resolution mass spectra (HRMS) with electrospray ionization (ESI) were obtained on ESI-QTOF Impact II mass spectrometer (Bruker Daltonik GmbH, Germany). The relative error in determining the exact mass values was no more than 3 ppm.

General Procedure for the Synthesis of Ethyl 4-(2-nitrophenyl)-2,4-dioxobutanoate (1): To a stirred mixture of diethyl oxalate (2.90 g, 2 mmol, 1.0 equiv), 1-(2-nitrophenyl)ethan-1-one (2 mmol, 1.0 equiv) in anhydrous toluene (25 mL) *t*-BuOK (2 mmol, 1.0 equiv) was added in three portions at 0 °C for 1 h under argon. The reaction mixture was stirred for 5 h at room temperature and left overnight. Ice (50 mL) was added and stirred until the ice dissolved, the rection mixture was neutralized by addition of acetic acid (2 mmol, 1.0 equiv). After completion, the reaction mixture was extracted with toluene (3×50 mL), dried over Na_2SO_4 and evaporated in vacuo to afford crude product which was used in further synthesis without purification.



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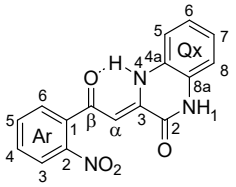
General Procedure for the Synthesis of (*Z*)-3-(2-(2-Nitrophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-ones 2a-l: Ethyl 4-(2-nitrophenyl)-2,4-dioxobutanoate **(1)** (1.0 g, 4 mmol, 1.0 equiv) was dissolved in acetic acid (30 mL) and benzene-1,2-diamine (4 mmol, 1.0 equiv) was added in a 50 mL reaction flask. The reaction mixture was stirred for one day at room temperature. Ice (15 mL) was added to the rection mixture and the mixture was neutralized by addition of 5% aqueous solution of $NaHCO_3$. This afforded a precipitate, which was filtered, washed with water (3×10 mL), dried in air to afford the pure desired products **(2)** as solids.



(*Z*)-3-(2-(2-Nitrophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (2a). The compound was obtained by the same procedure starting from ethyl 4-(2-nitrophenyl)-2,4-dioxobutanoate **(1)** (1.0 g, 3.77 mmol, 1.0 equiv) and benzene-1,2-diamine (0.41 g, 3.77 mmol, 1.0 equiv) in acetic acid (30 mL) following the general procedure. Yield 0.85 g, 73%; orange solid; mp 274−275 °C. IR (KBr, cm^{-1}): ν_{max} 3001, 2902, 1687, 1610, 1528, 1391, 1354, 1268, 1055, 934, 838, 790, 758, 575. NMR data for **2a**:^{1}H NMR (500.1 MHz, DMSO-d_6): δ 13.12 (brs, 1H, N(4)H-Qx), 12.11 (s, 1H, N(1)H-Qx), 7.95 (dd, J = 8.1 Hz, J = 2.5 Hz, 1H, H3-Ar), 7.82-7.79 (m, 1H, H6-Ar), 7.79 (ddd, J = 8.1 Hz, J = 8.0 Hz, J = 2.5 Hz, 1H, H5-Ar), 7.72 (ddd, J = 8.1 Hz, J = 8.0 Hz, J = 2.5 Hz, 1H, H4-Ar), 7.59 (dd, J = 7.8 Hz, J = 2.5 Hz, 1H, H5-Qx), 7.17 (tr, J = 7.8 Hz, 1H, H6-Qx), 7.15 (d, J = 7.8 Hz, 1H, H8-Qx), 7.13 (ddd, J = 8.0 Hz, J = 7.8 Hz, J = 2.5 Hz, 1H, H7-Qx), 6.42 (s, 1H, Hα-Sp). ^{13}C{^{1}H} NMR (125.8 MHz, DMSO-d_6): δ 187.9 (Cβ-Sp), 155.2 (C2-Qx), 148.0 (C2-Ar), 145.9 (C3-Qx), 135.3 (C1-Ar), 133.1 (C5-Ar), 131.4 (C4-Ar), 128.8 (C6-Ar), 126.9 (C8a-Qx), 124.6 (C6-Qx), 124.2 (C3-Ar), 123.8 (C7-Qx), 123.6 (C4a-Qx), 116.9 (C5-Qx), 115.5 (C8-Qx), 91.2 (Cα-Sp). HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{16}H_{12}N_3O_4$ 310.0822, found 310.0817.

(*Z*)-7,8-Dichloro-3-(2-(2-nitrophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (2b). The compound was obtained by the same procedure starting from ethyl 4-(2-nitrophenyl)-2,4-dioxobutanoate **(1)** (1.0 g, 3.77 mmol, 1.0 equiv) and 4,5-dichlorobenzene-1,2-diamine (0.54 g, 3.77 mmol, 1.0 equiv) in acetic acid (30 mL) following the general procedure. Yield 0.98 g, 69%; orange solid; mp 292−293 °C. IR (KBr, cm^{-1}): ν_{max} 3414, 3335, 3051, 2922, 1675, 1618, 1580, 1530, 1491, 1394, 1359, 1295, 1243, 1125, 1048, 957, 876, 804. NMR data for **2b**:^{1}H NMR (500.1 MHz, DMSO-d_6): δ 12.77 (brs, 1H, N(4)H-Qx), 12.15 (s, 1H, N(1)H-Qx), 8.12 (s, 1H, H5-Qx), 7.98 (dd, J = 8.1 Hz, J = 1.5 Hz, 1H, H3-Ar), 7.82 (dd, J = 8.1 Hz, J = 1.5 Hz, 1H, H6-Ar), 7.81 (dd, J = 8.1 Hz, J = 1.5 Hz, 1H, H5-Ar), 7.74 (dd, J = 8.1 Hz, J = 1.5 Hz, 1H, H4-Ar), 7.26 (s, 1H, H8-Qx), 6.47 (s, 1H, Hα-Sp). ^{13}C{^{1}H} NMR (125.8 MHz, DMSO-d_6): δ 188.3 (Cβ-Sp), 155.1 (C2-Qx), 147.9 (C2-Ar), 144.7 (C3-Qx), 135.0 (C1-Ar), 133.1 (C5-Ar), 131.6 (C4-Ar), 128.8 (C6-Ar), 126.9 (C8a-Qx), 125.4 (C7-Qx), 125.0 (C6-Qx), 124.2 (C3-Ar), 124.2 (C4a-Qx), 118.3 (C5-Qx), 116.0 (C8-Qx), 92.5 (Cα-Sp). HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{16}H_{10}{}^{35}Cl_2N_3O_4$ 378.0043, found 378.0044; $[M+H]^+$ calcd for $C_{16}H_{10}{}^{37}Cl_2N_3O_4$ 380.0016, found 380.0017.

(*Z*)-6-Chloro-3-(2-(2-nitrophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (2c) and **(*Z*)-7-chloro-3-(2-(2-nitrophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (2′c)** was obtained and characterized as the mixture of regioisomers in percentage ratio 33:67, respectively. The compound was obtained by the same procedure starting from ethyl 4-(2-nitrophenyl)-2,4-dioxobutanoate **(1)** (1.0 g, 3.77 mmol, 1.0 equiv) and 4-chlorobenzene-1,2-diamine (0.54 g, 3.77 mmol, 1.0 equiv) in acetic acid (30 mL) following the general procedure. Yield 0.95 g, 73%; brown solid; mp 276−277 °C. IR (KBr, cm^{-1}): ν_{max} 3442, 2921, 1690, 1600, 1537, 1359, 1261, 1168, 1117, 1051, 811, 609, 418.
NMR data for **2c**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 12.98 (brs, 1H, N(4)H-Qx), 12.14 (brs, 1H, N(1)H-Qx), 7.96 (d, J = 7.8 Hz, 1H, H3-Ar), 7.82-7.78 (m, 1H, H6-Ar), 7.80-7.76 (m, 1H, H5-Ar), 7.75-7.71 (m, 1H, H4-Ar), 7.68 (d, J = 8.8 Hz, 1H, H8-Qx), 7.16 (dd, J = 8.8 Hz, J = 2.5 Hz, 1H, H7-Qx), 7.14 (d, J = 2.5 Hz, 1H, H5-Qx), 6.45 (s, 1H, Hα-Sp). ^{13}C{^{1}H} NMR (125.8 MHz, DMSO-d_6): δ 188.0 (Cβ-Sp), 155.2 (C2-Qx), 148.0 (C2-Ar), 145.2 (C3-Qx), 135.1 (C1-Ar), 133.0 (C5-Ar), 131.4 (C4-Ar), 128.8 (C6-Ar), 128.0 (C6-Qx), 127.9 (C8a-Qx), 124.1 (C3-Ar), 123.3 (C7-Qx), 122.9 (C4a-Qx), 118.5 (C8-Qx), 114.9 (C5-Qx), 91.7 (Cα-Sp). ^{15}N NMR (50.7 MHz, DMSO-d_6): δ 141.0 (N1-Qx), 126.0 (N4-Qx). NMR data for **2′c**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 12.85 (brs, 1H, N(4)H-Qx), 12.14 (brs, 1H, N(1)H-Qx), 7.97 (d, J = 7.8 Hz, 1H, H3-Ar), 7.86 (d, J = 2.2 Hz, 1H, H8-Qx), 7.80-7.78 (m, 1H, H6-Ar), 7.80-7.76 (m, 1H, H5-Ar), 7.75-7.71 (m, 1H, H4-Ar), 7.19 (dd, J = 8.6 Hz, J = 2.2 Hz, 1H, H6-Qx), 7.12 (d, J = 8.6 Hz, 1H, H5-Qx), 6.45 (s, 1H, Hα-Sp). ^{13}C{^{1}H} NMR (125.8 MHz, DMSO-d_6): δ 188.1 (Cβ-Sp), 155.1 (C2-Qx), 148.1 (C2-Ar), 145.1 (C3-Qx), 135.1 (C1-Ar), 133.1 (C5-Ar), 131.5 (C4-Ar), 128.8 (C6-Ar), 127.3 (C7-Qx), 125.7 (C4a-Qx), 125.0 (C8a-Qx), 124.1 (C3-Ar), 123.9 (C6-Qx), 116.7 (C8-Qx), 116.5 (C5-Qx), 91.7 (Cα-Sp). ^{15}N NMR (50.7 MHz, DMSO-d_6): δ 141.0 (N1-Qx), 124.7 (N4-Qx). HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{16}H_{11}{}^{35}ClN_3O_4$ 344.0433, found 344.0436; $[M+H]^+$ calcd for $C_{16}H_{11}{}^{37}ClN_3O_4$ 346.0409, found 346.0410.

(*Z*)-7,8-Dimethyl-3-(2-(2-nitrophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (2d). The compound was obtained by the same procedure starting from ethyl 4-(2-nitrophenyl)-2,4-dioxobutanoate **(1)** (1.0 g, 3.77 mmol, 1.0 equiv) and 4,5-dimethylbenzene-1,2-diamine (0.51 g, 3.77 mmol, 1.0 equiv) in acetic acid (30 mL) following the general procedure. Yield 0.81 g, 64%; orange solid; mp 284−285 °C. IR (KBr, cm^{-1}): ν_{max} 3446, 2983, 1671, 1602, 1534, 1449, 1400, 1361, 1301, 1254, 1053, 1006, 955, 867. NMR data for **2d**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 13.30 (brs, 1H, N(4)H-Qx), 12.04 (s, 1H, N(1)H-Qx), 7.94 (dd, J = 8.1 Hz, J = 1.5 Hz, 1H, H3-Ar), 7.82 (dd, J = 8.1 Hz, J = 1.5 Hz, 1H, H6-Ar), 7.78 (dd, J = 8.1 Hz, J = 1.5 Hz, 1H, H5-Ar), 7.71 (dd, J = 8.1 Hz, J = 1.5 Hz, 1H, H4-Ar), 7.40 (s, 1H, H5-Qx), 6.94 (s, 1H, H8-Qx), 6.39 (s, 1H, Hα-Sp), 2.22 (s, 6H, $CH_3$6 and $CH_3$7-Qx). ^{13}C{^{1}H} NMR (125.8 MHz, DMSO-d_6): δ 187.1 (Cβ-Sp), 155.0 (C2-Qx), 148.1 (C2-Ar), 146.1 (C3-Qx), 135.1 (C1-Ar), 133.3 (C7-Qx), 132.9 (C5-Ar), 132.2 (C6-Qx), 131.2 (C4-Ar), 128.8 (C6-Ar), 124.8 (C8a-Qx), 124.0 (C3-Ar), 121.3 (C4a-Qx), 117.4 (C5-Qx), 115.9 (C8-Qx), 90.6 (Cα-Sp), 19.1 ($CH_3$7-Qx), 18.9 ($CH_3$6-Qx). HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{18}H_{16}N_3O_4$ 338.1135, found 338.1136.

(*Z*)-6-Methyl-3-(2-(2-nitrophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (2e) and **(*Z*)-7-methyl-3-(2-(2-nitrophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (2′e)** was obtained and characterized as the mixture of regioisomers in percentage ratio 40:60, respectively. The compound was obtained by the same procedure starting from ethyl 4-(2-nitrophenyl)-2,4-dioxobutanoate **(1)** (1.0 g, 3.77 mmol, 1.0 equiv) and 4-methylbenzene-1,2-diamine (0.46 g, 3.77 mmol, 1.0 equiv) in acetic acid (30 mL) following the general procedure. Yield 0.80 g, 66%; orange solid; mp 271−272 °C. IR (KBr, cm^{-1}): ν_{max} 3424, 1922, 1677, 1608, 1531, 1453, 1366, 1266, 1139, 1052, 806, 609, 576, 433. NMR data for **2e**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 12.19 (brs, 1H, N(4)H-Qx), 12.09 (brs, 1H, N(1)H-Qx), 7.95 (d, J = 8.1 Hz, 1H, H3-Ar), 7.82-7.78 (m, 1H, H6-Ar), 7.89-7.76 (m, 1H, H5-Ar), 7.74-7.70 (m, 1H,

H4-Ar), 7.39 (d, *J* = 1.1 Hz, 1H, H5-Qx), 7.06 (d, *J* = 8.2 Hz, 1H, H8-Qx), 7.00 (dd, *J* = 8.2 Hz, *J* = 1.1 Hz, 1H, H7-Qx), 6.41 (s, 1H, Hα-Sp), 2.29 (s, 3H, $CH_3$6-Qx). $^{13}C\{^1H\}$ NMR (125.8 MHz, DMSO-d_6): δ 187.7 (Cβ-Sp), 155.0 (C2-Qx), 148.1 (C2-Ar), 145.9 (C3-Qx), 135.2 (C1-Ar), 133.3 (C6-Qx), 133.0 (C5-Ar), 131.4 (C4-Ar), 128.8 (C6-Ar), 125.5 (C7-Qx), 124.6 (C8a-Qx), 124.1 (C3-Ar), 123.4 (C4a-Qx), 116.9 (C5-Qx), 115.3 (C8-Qx), 91.1 (Cα-Sp), 20.5 ($CH_3$6-Qx). NMR data for **2′e**: ^1H NMR (500.1 MHz, DMSO-d_6): δ 13.18 (brs, 1H, N(4)H-Qx), 12.06 (brs, 1H, N(1)H-Qx), 7.94 (d, *J* = 7.8 Hz, 1H, H3-Ar), 7.81-7.77 (m, 1H, H6-Ar), 7.80-7.76 (m, 1H, H5-Ar), 7.74-7.70 (m, 1H, H4-Ar), 7.48 (d, *J* = 8.2 Hz, 1H, H5-Qx), 6.97 (dd, *J* = 8.2 Hz, *J* = 1.1 Hz, 1H, H6-Qx), 6.96 (d, *J* = 1.1 Hz, 1H, H8-Qx), 6.39 (s, 1H, Hα-Sp), 2.30 (s, 3H, $CH_3$7-Qx). $^{13}C\{^1H\}$ NMR (125.8 MHz, DMSO-d_6): δ 187.3 (Cβ-Sp), 155.0 (C2-Qx), 148.1 (C2-Ar), 145.9 (C3-Qx), 135.2 (C1-Ar), 134.3 (C7-Qx), 133.0 (C5-Ar), 131.3 (C4-Ar), 128.8 (C6-Ar), 126.8 (C8a-Qx), 124.6 (C6-Qx), 124.1 (C3-Ar), 121.4 (C4a-Qx), 116.8 (C5-Qx), 115.4 (C8-Qx), 90.7 (Cα-Sp), 20.7 ($CH_3$7-Qx). HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{17}H_{14}N_3O_4$ 324.0979, found 324.0980.

(*Z*)-5-Methyl-3-(2-(2-nitrophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (2f) and **(*Z*)-8-methyl-3-(2-(2-nitrophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (2′f)** was obtained and characterized as the mixture of regioisomers in percentage ratio 45:55, respectively. The compound was obtained by the same procedure starting from ethyl 4-(2-nitrophenyl)-2,4-dioxobutanoate **(1)** (1.0 g, 3.77 mmol, 1.0 equiv) and 3-methylbenzene-1,2-diamine (0.46 g, 3.77 mmol, 1.0 equiv) in acetic acid (30 mL) following the general procedure. Yield 0.58 g, 48%; solid; mp 282−283 °C. IR (KBr, cm^{-1}): ν_{max} 3435, 1676, 1608, 1536, 1452, 1369, 1275, 1048, 777, 729, 597. NMR data for **2f**: ^1H NMR (500.1 MHz, DMSO-d_6): δ 13.64 (brs, 1H, N(4)H-Qx), 12.15 (s, 1H, N(1)H-Qx), 7.95 (dd, *J* = 8.1 Hz, *J* = 1.0 Hz, 1H, H3-Ar), 7.84-7.81 (m, 1H, H6-Ar), 7.82-7.78 (m, 1H, H5-Ar), 7.72 (ddd, *J* = 8.0 Hz, *J* = 8.0 Hz, *J* = 1.4 Hz, 1H, H4-Ar), 7.12-7.08 (m, 1H, H7-Qx), 7.07-7.04 (m, 1H, H8-Qx), 7.05-7.02 (m, 1H, H6-Qx), 6.44 (s, 1H, Hα-Sp), 2.41 (s, 3H, $CH_3$5-Qx). $^{13}C\{^1H\}$ NMR (125.8 MHz, DMSO-d_6): δ 188.2 (Cβ-Sp), 154.9 (C2-Qx), 147.9 (C2-Ar), 146.2 (C3-Qx), 135.1 (C1-Ar), 133.1 (C5-Ar), 131.3 (C4-Ar), 128.9 (C6-Ar), 127.0 (C8a-Qx), 124.4 (C7-Qx), 124.2 (C3-Ar), 124.0 (C5-Qx), 123.5 (C6-Qx), 121.9 (C4a-Qx), 113.6 (C8-Qx), 91.3 (Cα-Sp), 16.0 ($CH_3$5-Qx). ^{15}N NMR (50.7 MHz, DMSO-d_6): δ 374.6 ($NO_2$2-Ar), 143.0 (N1-Qx), 127.6 (N4-Qx). NMR data for **2′f**: ^1H NMR (500.1 MHz, DMSO-d_6): δ 13.17 (brs, 1H, N(4)H-Qx), 11.42 (s, 1H, N(1)H-Qx), 7.98 (dd, *J* = 8.1 Hz, *J* = 1.0 Hz, 1H, H3-Ar), 7.85-7.81 (m, 1H, H6-Ar), 7.81-7.77 (m, 1H, H5-Ar), 7.72 (ddd, *J* = 8.0 Hz, *J* = 7.9 Hz, *J* = 1.4 Hz, 1H, H4-Ar), 7.42 (dd, *J* = 7.7 Hz, *J* = 7.6 Hz, 1H, H5-Qx), 7.10-7.06 (m, 1H, H6-Qx), 7.05-7.01 (m, 1H, H7-Qx), 6.43 (s, 1H, Hα-Sp), 2.37 (s, 3H, $CH_3$8-Qx). $^{13}C\{^1H\}$ NMR (125.8 MHz, DMSO-d_6): δ 187.7 (Cβ-Sp), 155.7 (C2-Qx), 148.0 (C2-Ar), 145.6 (C3-Qx), 135.1 (C1-Ar), 133.1 (C5-Ar), 131.3 (C4-Ar), 128.8 (C6-Ar), 126.2 (C7-Qx), 125.2 (C8a-Qx), 124.9 (C6-Qx), 124.3 (C8-Qx), 124.1 (C3-Ar), 123.4 (C4a-Qx), 114.8 (C5-Qx), 90.8 (Cα-Sp), 17.0 ($CH_3$8-Qx). ^{15}N NMR (50.7 MHz, DMSO-d_6): δ 372.7 ($NO_2$2-Ar), 139.4 (N1-Qx), 128.9 (N4-Qx). HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{17}H_{14}N_3O_4$ 324.0979, found 324.0979.

(*Z*)-6,7-Difluoro-3-(2-(2-nitrophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (2g). The compound was obtained by the same procedure starting from ethyl 4-(2-nitrophenyl)-2,4-dioxobutanoate **(1)** (1.0 g, 3.77 mmol, 1.0 equiv) and 4,5-difluorobenzene-1,2-diamine (0.54 g, 3.77 mmol, 1.0 equiv) in acetic acid (30 mL) following the general procedure. Yield 0.86 g, 66%; orange solid; mp 293−295 °C. IR (KBr, cm^{-1}): ν_{max} 3443, 3112, 2859, 1689, 1621, 1530, 1346, 1305, 1245, 1061, 966, 856, 788, 675, 548. NMR data for **2g**: ^1H NMR (500.1 MHz, DMSO-d_6): δ 12.89 (brs, 1H, N(4)H-Qx), 12.12 (s, 1H, N(1)H-Qx), 7.96 (d, *J* = 7.9 Hz, 1H, H3-Ar), 7.93 (dd, *J*(HF) = 11.2 Hz, *J*(HF) = 7.3 Hz, 1H, H8-Qx), 7.84-7.79 (m, 1H, H6-Ar), 7.81-7.77 (m, 1H, H5-Ar), 7.74-7.70 (m, 1H, H4-Ar), 7.09 (dd, *J*(HF) = 11.0 Hz, *J*(HF) = 7.6 Hz, 1H, H5-Qx), 6.43 (s, 1H, Hα-Sp). $^{13}C\{^1H\}$ NMR (125.8 MHz, DMSO-d_6): δ 188.0 (Cβ-Sp), 155.2 (C2-Qx), 148.1 (C2-Ar), 146.0 (dd, *J*(CF) = 239.4 Hz, *J*(CF) = 13.6 Hz, C7-Qx), 146.0 (dd, *J*(CF) = 240.4 Hz, *J*(CF) = 13.8 Hz, C6-Qx), 145.2 (C3-Qx), 135.1 (C1-Ar), 133.2 (C5-Ar), 131.6 (C4-Ar), 128.9 (C6-Ar), 124.2 (C3-Ar), 123.6 (d, *J*(CF) = 9.0 Hz, C8a-Qx), 120.6 (d, *J*(CF) = 8.3 Hz, C4a-Qx), 106.2 (d, *J*(CF) = 23.4 Hz, C8-Qx), 103.9 (d, *J*(CF) = 22.4 Hz, C5-Qx), 91.9 (Cα-Sp). HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{16}H_{10}F_2N_3O_4$ 346.0634, found 346.0637.

(*Z*)-6-Fluoro-3-(2-(2-nitrophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (2h) and **(*Z*)-7-fluoro-3-(2-(2-nitrophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (2′h)** was obtained and characterized as the mixture of regioisomers in percentage ratio 85:15, respectively. The compound was obtained by the same procedure starting from ethyl 4-(2-nitrophenyl)-2,4-dioxobutanoate **(1)** (1.0 g, 3.77 mmol, 1.0 equiv) and 4-fluorobenzene-1,2-diamine (0.48 g, 3.77 mmol, 1.0 equiv) in acetic acid (30 mL) following the general procedure. Yield 0,79 g, 64%; olive solid; mp 279−280 °C. IR (KBr, cm^{-1}): ν_{max} 3442, 2921, 1690, 1600, 1537, 1359, 1261, 1168, 1117, 1051, 811, 609, 418. NMR data for **2h**: ^1H NMR (500.1 MHz, DMSO-d_6): δ 13.10 (brs, 1H, N(4)H-Qx), 12.17 (s, 1H, N(1)H-Qx), 7.95 (d, *J* = 7.8 Hz, 1H, H3-Ar), 7.82-7.78 (m, 1H, H6-Ar), 7.80-7.76 (m, 1H, H5-Ar), 7.75-7.71 (m, 1H, H4-Ar),

7.72-7.68 (m, 1H, H8-Qx), 7.00 (ddd, *J*(HF) =8.9 Hz, *J* = 8.8 Hz, *J* = 2.5 Hz, 1H, H7-Qx), 6.93 (dd, *J*(HF) =9.3 Hz, *J* = 2.6 Hz, 1H, H5-Qx), 6.40 (s, 1H, Hα-Sp). $^{13}C\{^{1}H\}$ NMR (125.8 MHz, DMSO-d_6): δ 187.5 (Cβ-Sp), 158.6 (d, *J*(CF)= 241.0 Hz, C6-Qx), 155.3 (C2-Qx), 148.0 (C2-Ar), 145.3 (C3-Qx), 135.1 (C1-Ar), 133.0 (C5-Ar), 131.4 (C4-Ar), 128.8 (C6-Ar), 128.1 (d, *J*(CF) =11.7 Hz, C8a-Qx), 124.1 (C3-Ar), 120.6 (d, *J*(CF) = 1.9 Hz, C4a-Qx), 118.6 (d, *J*(CF) =9.5 Hz, C8-Qx), 110.5 (d, *J*(CF) =23.5 Hz, C7-Qx), 102.0 (d, *J*(CF) =27.3 Hz, C5-Qx), 91.0 (Cα-Sp). ^{15}N NMR (50.7 MHz, DMSO-d_6): δ 142.1 (N1-Qx), 126.0 (N4-Qx). NMR data for **2′h**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 12.91 (brs, 1H, N(4)H-Qx), 12.09 (s, 1H, N(1)H-Qx), 7.95 (d, *J* = 7.8 Hz, 1H, H3-Ar), 7.78-7.75 (m, 1H, H5-Ar), 7.78-7.74 (m, 1H, H5-Qx), 7.70-7.74 (m, 1H, H4-Ar), 7.15-7.12 (m, 1H, H6-Ar), 7.14 (dd, *J*(HF) =8.9 Hz, *J* = 8. Hz, 1H, H8-Qx), 7.03-6.98 (m, 1H, H6-Qx), 6.45 (s, 1H, Hα-Sp). $^{13}C\{^{1}H\}$ NMR (125.8 MHz, DMSO-d_6): δ 188.1 (Cβ-Sp), 158.1 (d, *J*(CF)= 238.5 Hz, C7-Qx), 154.9 (C2-Qx), 148.0 (C2-Ar), 145.3 (C3-Qx), 135.1 (C1-Ar), 133.1 (C5-Ar), 131.5 (C4-Ar), 128.8 (C6-Ar), 124.7 (d, *J*(CF) =12.2 Hz, C4a-Qx), 124.1 (C3-Ar), 123.4 (d, *J*(CF) =1.8 Hz, C8a-Qx), 116.5 (d, *J*(CF) =9.4 Hz, C8-Qx), 111.2 (d, *J*(CF) =24.1 Hz, C6-Qx), 103.7 (d, *J*(CF) =28.1 Hz, C5-Qx), 92.0 (Cα-Sp). ^{15}N NMR (50.7 MHz, DMSO-d_6): δ 142.1 (N1-Qx), 124.2 (N4-Qx). HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{16}H_{11}FN_3O_4$ 328.0728, found 328.0728.

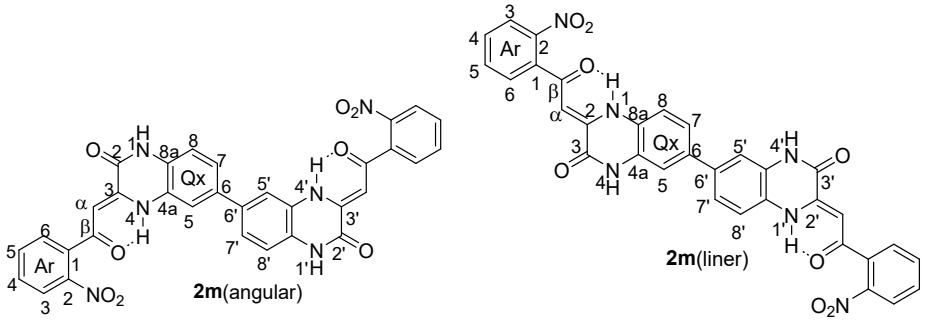
(*Z*)-6-Bromo-3-(2-(2-nitrophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (2i) and **(*Z*)-7-bromo-3-(2-(2-nitrophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (2′i)** was obtained and characterized as the mixture of regioisomers in percentage ratio 36:64, respectively. The compound was obtained by the same procedure starting from ethyl 4-(2-nitrophenyl)-2,4-dioxobutanoate **(1)** (1.0 g, 3.77 mmol, 1.0 equiv) and 4-bromobenzene-1,2-diamine (0.70 g, 3.77 mmol, 1.0 equiv) in acetic acid (30 mL) following the general procedure. Yield 0.82 g, 56%; olive solid; mp 278−279 °C. IR (KBr, cm^{-1}): ν_{max} 3442, 3051, 2927, 1687, 1618, 1525, 1351, 1247, 1059, 942, 861, 812, 597. NMR data for **2i**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 12.84 (brs, 1H, N(4)H-Qx), 12.13 (brs, 1H, N(1)H-Qx), 8.00-7.96 (d, *J* = 2.5 Hz, 1H, H5-Qx), 7.99-7.95 (d, *J* = 7.8 Hz, 1H, H3-Ar), 7.92-7.78 (m, 1H, H6-Ar), 7.81-7.77 (m, 1H, H5-Ar), 7.75-7.71 (m, 1H, H4-Ar), 7.31 (dd, *J* = 8.6 Hz, *J* = 2.5 Hz, 1H, H7-Qx), 7.07 (d, *J* = 8.6 Hz, 1H, H8-Qx), 6.45 (s, 1H, Hα-Sp). $^{13}C\{^{1}H\}$ NMR (125.8 MHz, DMSO-d_6): δ 188.1 (Cβ-Sp), 155.1 (C2-Qx), 148.0 (C2-Ar), 145.1 (C3-Qx), 135.1 (C1-Ar), 133.1 (C5-Ar), 131.5 (C4-Ar), 128.8 (C6-Ar), 126.7 (C8a-Qx), 126.1 (C7-Qx), 125.3 (C4a-Qx), 124.2 (C3-Ar), 119.3 (C5-Qx), 117.5 (C8-Qx), 115.0 (C6-Qx), 92.0 (Cα-Sp). NMR data for **2′i**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 12.96 (brs, 1H, N(4)H-Qx), 12.13 (brs, 1H, N(1)H-Qx), 7.96 (d, *J* = 7.9 Hz, 1H, H3-Ar), 7.83-7.79 (m, 1H, H6-Ar), 7.82-7.78 (m, 1H, H5-Ar), 7.75-7.71 (m, 1H, H4-Ar), 7.62 (d, *J* = 9.0 Hz, 1H, H5-Qx), 7.28 (dd, *J* = 9.0 Hz, *J* = 2.2 Hz, 1H, H6-Qx), 7.27 (d, *J* = 2.2 Hz, 1H, H8-Qx), 6.43 (s, 1H, Hα-Sp). $^{13}C\{^{1}H\}$ NMR (125.8 MHz, DMSO-d_6): δ 188.0 (Cβ-Sp), 155.2 (C2-Qx), 148.0 (C2-Ar), 145.2 (C3-Qx), 135.1 (C1-Ar), 133.1 (C5-Ar), 131.5 (C4-Ar), 128.8 (C6-Ar), 128.3 (C8a-Q), 126.1 (C6-Qx), 124.2 (C3-Ar), 123.3 (C4a-Qx), 118.8 (C5-Qx), 117.5 (C8-Qx), 115.7 (C7-Qx), 91.7 (Cα-Sp). HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{16}H_{11}{}^{79}BrN_3O_4$ 387.9927, found 387.9927; $[M+H]^+$ calcd for $C_{16}H_{11}{}^{81}BrN_3O_4$ 389.9909, found 389.9908.

(*Z*)-3-(2-(2-Nitrophenyl)-2-oxoethylidene)-2-oxo-1,2,3,4-tetrahydroquinoxaline-6-carboxylic acid (2j). The compound was obtained by the same procedure starting from ethyl 4-(2-nitrophenyl)-2,4-dioxobutanoate **(1)** (1.0 g, 3.77 mmol, 1.0 equiv) and 3,4-diaminobenzoic acid (0.57 g, 3.77 mmol, 1.0 equiv) in acetic acid (30 mL) following the general procedure. Yield 0.57 g, 44%; yellow solid; mp 317−319 °C. IR (KBr, cm^{-1}): ν_{max} 3092, 2906, 1719, 1690, 1613, 1527, 1359, 1268, 1209, 1107, 1054, 851, 785, 724, 697, 582. NMR data for **2j**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 12.98 (brs, 1H, N(4)H-Qx), 12.31 (brs, 1H, N(1)H-Qx), 8.17 (d, *J* = 1.5 Hz, 1H, H5-Qx), 7.97 (d, *J* = 7.8 Hz, 1H, H3-Ar), 7.84-7.78 (m, 1H, H6-Ar), 7.83-7.77 (m, 1H, H5-Ar), 7.72 (dd, *J* = 8.4 Hz, *J* = 1.5 Hz, 1H, H7-Qx), 7.36-7.30 (m, 1H, H4-Ar), 7.21 (d, *J* = 8.4 Hz, 1H, H8-Qx), 6.43 (s, 1H, Hα-Sp). $^{13}C\{^{1}H\}$ NMR (125.8 MHz, DMSO-d_6): δ 188.0 (Cβ-Sp), 166.5 (C6a (C(O)OH)-Qx), 155.6 (C2-Qx), 147.9 (C2-Ar), 145.3 (C3-Qx), 135.2 (C1-Ar), 133.1 (C5-Ar), 131.4 (C4-Ar), 130.3 (C8a-Qx), 128.8 (C6-Ar), 116.0 (C6-Qx), 125.4 (C7-Qx), 124.2 (C3-Ar), 123.7 (C4a-Qx), 118.1 (C5-Qx), 115.3 (C8-Qx), 91.8 (Cα-Sp). HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{17}H_{12}N_3O_6$ 354.0720, found 354.0718.

(*Z*)-6-Nitro-3-(2-(2-nitrophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (2k) and **(*Z*)-7-nitro-3-(2-(2-nitrophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (2′k)** was obtained and characterized as the mixture of regioisomers in percentage ratio 55:45 respectively. The compound was obtained by the same procedure starting from ethyl 4-(2-nitrophenyl)-2,4-dioxobutanoate **(1)** (1.0 g, 3.77 mmol, 1.0 equiv) and 4-nitrobenzene-1,2-diamine (0,58 g, 3.77 mmol, 1.0 equiv) in acetic acid (30 mL) following the general procedure. Yield 0.80 g, 60%; orange solid; mp 281−282 °C. IR (KBr, cm^{-1}): ν_{max} 3302, 3085, 1698, 1524, 1335, 1251, 1136, 1088, 1047, 968, 829,

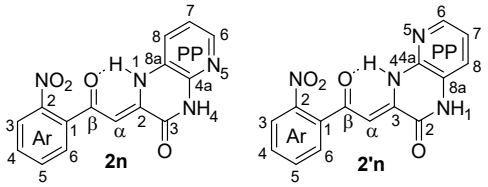
745, 627, 573, 460. NMR data for **2k**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 12.79 (brs, 1H, N(4)H-Qx), 12.37 (s, 1H, N(1)H-Qx), 8.75 (d, J = 2.0 Hz, 1H, H5-Qx), 7.99 (d, J = 8.7 Hz, 1H, H7-Qx), 7.97 (d, J = 8.1 Hz, 1H, H3-Ar), 7.83 (d, J = 8.1 Hz, 1H, H6-Ar), 7.81 (dd, J = 8.1 Hz, 1H, H5-Ar), 7.75 (dd, J = 8.1 Hz, Hz, 1H, H4-Ar), 7.25 (d, J = 8.7 Hz, 1H, H8-Qx), 6.48 (s, 1H, Hα-Sp). ^{13}C{^{1}H} NMR (125.8 MHz, DMSO-d_6): δ 188.3 (Cβ-Sp), 155.8 (C2-Qx), 147.9 (C2-Ar), 144.4 (C3-Qx), 142.7 (C6-Qx), 135.1 (C1-Ar), 133.2 (C5-Ar), 132.2 (C8a-Qx), 131.6 (C4-Ar), 128.8 (C6-Ar), 124.3 (C4a-Qx), 124.2 (C3-Ar), 119.3 (C7-Qx), 115.6 (C8-Qx), 112.7 (C5-Qx), 92.7 (Cα-Sp). NMR data for **2′k**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 12.79 (brs, 1H, N(4)H-Qx), 12.37 (s, 1H, N(1)H-Qx), 8.75 (d, J = 2.0 Hz, 1H, H5-Qx), 7.99 (d, J = 8.7 Hz, 1H, H7-Qx), 7.97 (d, J = 8.1 Hz, 1H, H3-Ar), 7.83 (d, J = 8.1 Hz, 1H, H6-Ar), 7.81 (dd, J = 8.1 Hz, 1H, H5-Ar), 7.75 (dd, J = 8.1 Hz, Hz, 1H, H4-Ar), 7.25 (d, J = 8.7 Hz, 1H, H8-Qx), 6.48 (s, 1H, Hα-Sp). ^{13}C{^{1}H} NMR (125.8 MHz, DMSO-d_6): δ 189.1 (Cβ-Sp), 155.2 (C2-Qx), 147.8 (C2-Ar), 144.2 (C3-Qx), 142.4 (C7-Qx), 135.0 (C1-Ar), 133.3 (C5-Ar), 131.7 (C4-Ar), 129.7 (C4a-Qx), 128.8 (C6-Ar), 126.9 (C8a-Qx), 124.2 (C3-Ar), 118.9 (C6-Qx), 117.2 (C5-Qx), 110.4 (C9-Qx), 94.1 (Cα-Sp). HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{16}H_{11}N_4O_6$ 355.0673, found 355.0676.

(*Z*)-6-Benzoyl-3-(2-(2-nitrophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (2l) and **(*Z*)-7-benzoyl-3-(2-(2-nitrophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (2′l)** was obtained and characterized as the mixture of regioisomers in percentage ratio 65:35, respectively. The compound was obtained by the same procedure starting from ethyl 4-(2-nitrophenyl)-2,4-dioxobutanoate **(1)** (1.0 g, 3.77 mmol, 1.0 equiv) and (3,4-diaminophenyl)(phenyl)methanone (0.80 g, 3.77 mmol, 1.0 equiv) in acetic acid (30 mL) following the general procedure. Yield 1.26 g, 81%; brown solid; mp 293−294 °C. IR (KBr, cm^{-1}): ν_{max} 3444, 3049, 2924, 1681, 1610, 1531, 1448, 1360, 1276, 1129, 1043, 908, 713, 578. NMR data for **2l**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 12.89 (s, 1H, N(4)H-Qx), 12.36 (s, 1H, N(1)H-Qx), 8.12 (d, J = 1.7 Hz, 1H, H5-Qx), 7.96 (d, J = 8.1 Hz, 1H, H3-Ar1), 7.83-7.79 (m, 1H, H6-Ar1), 7.82-7.78 (m, 1H, H5-Ar1), 7.76-7.72 (m, 2H, H2 and H6-Ar2), 7.70-7.66 (m, 1H, H4-Ar1), 7.56-7.52 (m, 1H, H7-Qx), 7.61-7.55 (m, 1H, H3 and H5-Ar2), 7.57 (dd, J = 7.5 Hz, J = 7.5 Hz, 1H, H4-Ar2), 7.28 (d, J = 8.4 Hz, 1H, H8-Qx), 6.46 (s, 1H, Hα-Sp). ^{13}C{^{1}H} NMR (125.8 MHz, DMSO-d_6): δ 194.3 (C=O), 187.9 (Cβ-Sp), 155.6 (C2-Qx), 147.9 (C2-Ar1), 145.1 (C3-Qx), 137.2 (C1-Ar2), 135.2 (C1-Ar1), 133.1 (C5-Ar1), 132.4 (C4-Ar2), 132.0 (C6-Qx), 131.4 (C4-Ar1), 130.3 (C8a-Qx), 129.5 (C2 and C6-Ar2), 128.8 (C6-Ar1), 128.5 (C3 and C5-Ar2), 125.8 (C7-Qx), 124.1 (C3-Ar1), 123.6 (C4a-Qx), 119.1 (C5-Qx), 115.4 (C8-Qx), 91.9 (Cα-Sp). ^{15}N NMR (50.7 MHz, DMSO-d_6): δ 375.8 (N2a-Ar1), 143.4 (N1-Qx), 125.1 (N4-Qx). NMR data for **2′l**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 12.94 (s, 1H, N(4)H-Qx), 12.13 (s, 1H, N(1)H-Qx), 8.00-7.98 (d, J = 8.09 Hz, 1H, H3-Ar1), 7.83-7.79 (m, 1H, H6-Ar1), 7.82-7.78 (m, 1H, H5-Ar1), 7.78 (d, J = 8.4 Hz, 1H, H5-Qx), 7.77-7.71 (m, 2H, H2 and H6-Ar2), 7.66-7.62 (m, 1H, H4-Ar1), 7.62-7.56 (m, 1H, H3 and H5-Ar2), 7.61 (d, J = 1.7 Hz,1H, H8-Qx), 7.56 (dd, J = 7.5 Hz, J = 7.5 Hz, 1H, H4-Ar2), 7.50 (dd, J = 8.4 Hz, J = 1.7 Hz 1H, H6-Qx), 6.52 (s, 1H, Hα-Sp). ^{13}C{^{1}H} NMR (125.8 MHz, DMSO-d_6): δ 195.7 (C=O), 188.7 (Cβ-Sp), 155.2 (C2-Qx), 147.9 (C2-Ar1), 145.0 (C3-Qx), 137.3 (C1-Ar2), 135.1 (C1-Ar1), 133.2 (C5-Ar1), 132.6 (C4-Ar2), 131.9 (C7-Qx), 131.4 (C4-Ar), 129.6 (C2 and C6-Ar2), 128.8 (C6-Ar), 128.5 (C3 and C5-Ar2), 127.6 (C4a-Qx), 126.6 (C8a-Qx), 125.6 (C6-Qx), 124.2 (C3-Ar1), 117.0 (C8-Qx), 116.7 (C5-Qx), 93.0 (Cα-Sp). ^{15}N NMR (50.7 MHz, DMSO-d_6): δ 371.5 (N2a-Ar), 141.9 (N1-Qx), 125.0 (N4-Qx). HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{23}H_{16}N_3O_5$ 414.1084, found 414.1084.

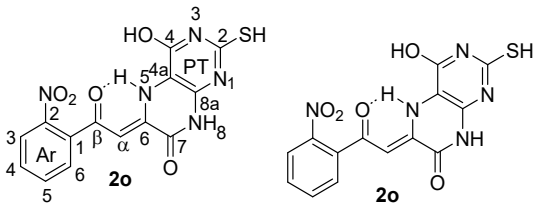


(3*Z*,3′*Z*)-3,3′-Bis(2-(2-nitrophenyl)-2-oxoethylidene)-3,3′,4,4′-tetrahydro-[6,6′-biquinoxaline]-2,2′(1*H*,1′*H*)-dione (2m) and **(2*Z*,2′*Z*)-2,2′-bis(2-(2-nitrophenyl)-2-oxoethylidene)-1,1′,4,4′-tetrahydro-[6,6′-biquinoxaline]-3,3′(2*H*,2′*H*)-dione (2′m)** were obtained and characterized as the mixture of regioisomers in percentage ratio 35:35:15:15, respectively. The compound was obtained by the same procedure starting from ethyl 4-(2-nitrophenyl)-2,4-dioxobutanoate **(1)** (1.0 g, 3.77 mmol, 1.0 equiv) and [1,1′-biphenyl]-3,3′,4,4′-tetraamine (0.81 g, 3.77 mmol, 1.0 equiv) in acetic acid (30 mL) following the general procedure. Yield 1.63 g, 70%; brown solid; mp 244−245°C. IR (KBr, cm^{-1}): ν_{max} 3428, 3158, 1681, 1610, 1528, 1453, 1355, 1302, 1250, 1103, 1052, 959, 859, 808,

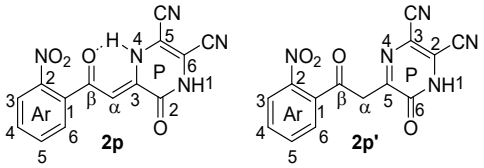
784, 748, 700, 648, 610, 577, 476. HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{32}H_{21}N_6O_8$ 617.1415, found 617.1419. NMR data for **2m(C6-C6′-angular)**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 13.24 (s, 1H, N(4)H-Qx), 12.16 (s, 1H, N(1)H-Qx), 8.08 and 8.05 (d, J = 1.7 Hz, 1H, H5-Qx), 7.96 (d, J = 8.1 Hz, 1H, H3-Ar), 7.85-7.81 (m, 1H, H6-Ar), 7.81-7.77 (m, 1H, H5-Ar), 7.76-7.72 (m, 1H, H4-Ar), 7.60 and 7.43 (dd, J = 8.5 Hz, J = 1.0 Hz, 1H, H7-Qx), 7.23 and 7.22 (d, J = 8.5 Hz, 1H, H8-Qx), 6.46 (s, 1H, Hα-Sp). ^{13}C{^{1}H} NMR (125.8 MHz, DMSO-d_6): δ 187.8 (Cβ-Sp), 155.2 (C2-Qx), 148.1 (C2-Ar), 145.6 (C3-Qx), 135.1 (C1-Ar), 134.6 and 134.2 (C6-Qx), 133.0 (C5-Ar), 131.4 (C4-Ar), 128.8 (C6-Ar), 126.4 (C8a-Qx), 124.2 (C4a-Qx), 124.1 (C3-Ar), 122.5 (C7-Qx), 115.8 (C8-Qx), 114.8 and 114.4 (C5-Qx), 91.3 (Cα-Sp). ^{15}N NMR (50.7 MHz, DMSO-d_6): δ 375.6 (N2a-Ar), 142.6 (N1-Qx), 127.2 (N4-Qx). NMR data for **2′m(C6-C6′-liner)**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 13.16 (s, 1H, N(4)H-Qx), 12.19 (s, 1H, N(1)H-Qx), 7.96 (d, J = 8.1 Hz, 1H, H3-Ar), 7.83-7.81 (m, 1H, H6-Ar), 7.81-7.78 (m, 1H, H5-Ar), 7.76-7.72 (m, 1H, H4-Ar), 7.71-7.66 (m, 1H, H5-Qx), 7.42-7.38 (m, 1H, H6-Qx), 7.38 and 7.36 (d, J = 1.5 Hz, 1H, H8-Qx), 6.45 (s, 1H, Hα-Sp). ^{13}C{^{1}H} NMR (125.8 MHz, DMSO-d_6): δ 187.7 (Cβ-Sp), 155.1 (C2-Qx), 148.1 (C2-Ar), 145.9 (C3-Qx), 135.2 (C7-Qx), 135.1 (C1-Ar), 133.0 (C5-Ar), 131.4 (C4-Ar), 128.8 (C6-Ar), 127.4 (C8a-Qx), 124.1 (C3-Ar), 123.2 (C4a-Qx), 122.1 (C6-Qx), 117.4 (C5-Qx), 112.7 (C8-Qx), 91.3 (Cα-Sp). ^{15}N NMR (50.7 MHz, DMSO-d_6): δ 375.4 (N2a-Ar), 142.6 (N1-Qx), 127.0 (N4-Qx). NMR data for other isomer of **2m(C6-C6′-angular)**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 13.23 (s, 1H, N(4)H-Qx), 12.17 (s, 1H, N(1)H-Qx), 8.03 (d, J = 1.7 Hz, 1H, H5-Qx), 7.96 (d, J = 8.1 Hz, 1H, H3-Ar), 7.84-7.81 (m, 1H, H6-Ar), 7.81-7.77 (m, 1H, H5-Ar), 7.76-7.72 (m, 1H, H4-Ar), 7.53-7.51 (m, 1H, H7-Qx), 7.23 (d, J = 8.5 Hz, 1H, H8-Qx), 6.46 (s, 1H, Hα-Sp). ^{13}C{^{1}H} NMR (125.8 MHz, DMSO-d_6): δ 187.8 (Cβ-Sp), 155.2 (C2-Qx), 148.1 (C2-Ar), 145.6 (C3-Qx), 136.9 (C6-Qx), 135.1 (C1-Ar), 133.0 (C5-Ar), 131.4 (C4-Ar), 128.8 (C6-Ar), 125.6 (C8a-Qx), 123.0 (C4a-Qx), 124.1 (C3-Ar), 122.6 (C7-Qx), 116.0 (C8-Qx), 114.8 (C5-Qx), 91.3 (Cα-Sp). NMR data for for other isomer of **2m(C6-C6′-liner)**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 13.16 (s, 1H, N(4)H-Qx), 12.18 (s, 1H, N(1)H-Qx), 7.96 (d, J = 8.1 Hz, 1H, H3-Ar), 7.84-7.81 (m, 1H, H6-Ar), 7.81-7.77 (m, 1H, H5-Ar), 7.76-7.72 (m, 1H, H4-Ar), 7.69-7.65 (m, 1H, H5-Qx), 7.47 (dd, J = 8.5 Hz, J = 1.9 Hz, 1H, H6-Qx), 7.45-7.41 (m, 1H, H8-Qx), 6.45 (s, 1H, Hα-Sp). ^{13}C{^{1}H} NMR (125.8 MHz, DMSO-d_6): δ 187.7 (Cβ-Sp), 155.2 (C2-Qx), 148.1 (C2-Ar), 145.9 (C3-Qx), 135.1 (C1-Ar), 133.0 (C5-Ar), 132.5 (C7-Qx), 131.4 (C4-Ar), 128.8 (C6-Ar), 128.2 (C8a-Qx), 124.1 (C3-Ar), 123.0 (C4a-Qx), 122.4 (C6-Qx), 117.6 (C5-Qx), 113.1 (C8-Qx), 91.3 (Cα-Sp). HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{32}H_{21}N_6O_8$ 617.1415, found 617.1419.



(*Z*)-2-(2-(2-Nitrophenyl)-2-oxoethylidene)-1,4-dihydropyrido[2,3-*b*]pyrazin-3(2*H*)-one (2n) and **(*Z*)-3-(2-(2-nitrophenyl)-2-oxoethylidene)-3,4-dihydropyrido[2,3-*b*]pyrazin-2(1*H*)-one (2n′)** were obtained and characterized as the mixture of regioisomers in percentage ratio 45:55, respectively. The compound was obtained by the same procedure starting from ethyl 4-(2-nitrophenyl)-2,4-dioxobutanoate **(1)** (1.0 g, 3.77 mmol, 1.0 equiv) and pyridine-2,3-diamine (0.41 g, 3.77 mmol, 1.0 equiv) in acetic acid (30 mL) following the general procedure. Yield 1.03 g, 88%; olive solid; mp 280−281 °C. IR (KBr, cm^{-1}): ν_{max} 3442, 3065, 2851, 1693, 1626, 1527, 1364, 1250, 1060, 862, 750, 584. NMR data for **2n**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 12.96 (brs, 1H, N(1)H-PP), 12.15 (s, 1H, N(4)H-PP), 8.14 (dd, J = 4.3 Hz, J = 1.5 Hz, 1H, H6-PP), 8.01 (dd, J = 8.0 Hz, J = 1.0 Hz, 1H, H3-Ar), 7.85-7.81 (m, 1H, H6-Ar), 7.84-7.80 (m, 1H, H5-Ar), 7.76-7.7.62 (m, 1H, H4-Ar), 7.11 (dd, J = 8.0 Hz, J = 4.3 Hz, 1H, H7-PP), 7.06 (dd, J = 8.0 Hz, J = 1.5 Hz, 1H, H8-PP), 6.45 (s, 1H, Hα-Sp). ^{13}C{^{1}H} NMR (125.8 MHz, DMSO-d_6): δ 189.6 (Cβ-Sp), 155.0 (C2-PP), 147.7 (C2-Ar), 145.9 (C3-PP), 143.1 (C6-PP), 136.8 (C4a-PP), 135.1 (C1-Ar), 133.3 (C5-Ar), 131.7 (C4-Ar), 128.8 (C6-Ar), 124.2 (C3-Ar), 122.9 (C8-PP), 122.8 (C8a-PP), 120.1 (C7-PP), 92.7 (Cα-Sp). NMR data for **2n′**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 12.87 (brs, 1H, N(1)H-PP), 12.49 (s, 1H, N(4)H-PP), 8.13 (dd, J = 4.3 Hz, J = 1.5 Hz, 1H, H7-PP), 8.09 (dd, J = 8.0 Hz, J = 1.5 Hz, 1H, H8-PP), 7.97 (dd, J = 8.0 Hz, J = 1.0 Hz, 1H, H3-Ar), 7.85-7.81 (m, 1H, H6-Ar), 7.84-7.80 (m, 1H, H5-Ar), 7.76-7.72 (m, 1H, H4-Ar), 7.10 (dd, J = 8.0 Hz, J = 4.3 Hz, 1H, H6-PP), 6.47 (s, 1H, Hα-Sp). ^{13}C{^{1}H} NMR (125.8 MHz, DMSO-d_6): δ 188.1 (Cβ-Sp), 156.6 (C2-PP), 148.0 (C2-Ar), 145.2 (C3-PP), 143.3 (C7-PP), 139.9 (C8a-PP), 135.0 (C1-Ar), 133.1 (C5-Ar), 131.5 (C4-Ar), 128.8 (C6-Ar), 124.3 (C6-PP), 124.2 (C3-Ar), 120.4 (C4a-PP), 119.5 (C6-PP), 92.2 (Cα-Sp). HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{15}H_{11}N_4O_4$ 311.0775, found 311.0775.

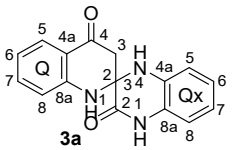


(*Z*)-4-Hydroxy-2-mercapto-6-(2-(2-nitrophenyl)-2-oxoethylidene)-5,8-dihydropteridin-7(6*H*)-one (2o). The compound was obtained by the same procedure starting from ethyl 4-(2-nitrophenyl)-2,4-dioxobutanoate **(1)** (1.0 g, 3.77 mmol, 1.0 equiv) and 4,5-diamino-6-hydroxy-2-mercaptopyrimidin (0.60 g, 3.77 mmol, 1.0 equiv) in acetic acid (30 mL) following the general procedure. Yield 0.47 g, 35%; brown solid; mp 279−280°C. IR (KBr, cm^{-1}): ν_{max} 3437, 3099, 2915, 1669, 1575, 1528, 1458, 1437, 1244, 1147, 1052, 1002, 965, 857, 788, 753, 703, 633, 640, 550, 469, 430. NMR data for **2o**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 7.88 (dd, J = 8.0 Hz, J = 1.5 Hz, 1H, H3-Ar), 7.78 (dd, J = 8.0 Hz, J = 1.5 Hz, 1H, H6-Ar), 7.74 (dd, J = 8.0 Hz, J = 1.5 Hz, 1H, H5-Ar), 7.66 (dd, J = 8.0 Hz, J = 1.5 Hz, 1H, H4-Ar), 6.13 (s, 1H, Hα-Sp). The signals of (O(8)H-PT, S(6)H-PT, N(1)H-PT, N(4)H-PT) have not been observed. ^{13}C{^{1}H} NMR (125.8 MHz, DMSO-d_6): δ 187.7 (Cβ-Sp), 159.2 (C8-PT), 158.1 (C6-PT), 155.6 (C2-PT), 150.7 (C3-PT), 148.3 (C2-Ar), 148.3 (C4a-PT), 133.6 (C1-Ar), 132.6 (C5-Ar), 130.8 (C4-Ar), 129.0 (C6-Ar), 124.0 (C8a-PT), 123.9 (C3-Ar), 90.5 (Cα-Sp). HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{14}H_{10}N_5O_5S$ 360.0397, found 360.0401.

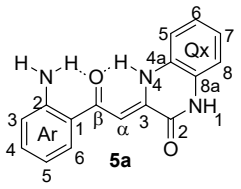


(*E*)-3-(2-(2-nitrophenyl)-2-oxoethylidene)-3,4-dihydropyrazin-2(1*H*)-one-5,6-dicarbonitrile (2p) and **5-(2-(2-nitrophenyl)-2-oxoethyl)-6-oxo-1,6-dihydropyrazine-2,3-dicarbonitrile (2p′)** were obtained and characterized as the mixture of tautomers in percentage ratio 65:35, respectively. The compound was obtained by the same procedure starting from ethyl 4-(2-nitrophenyl)-2,4-dioxobutanoate **(1)** (1.0 g, 3.77 mmol, 1.0 equiv) and 2,3-diaminomaleonitrile (0.41 g, 3.77 mmol, 1.0 equiv) in acetic acid (30 mL) following the general procedure. Data for **2p** and **2p′**: yield 1.23 g, 95%; orange solid; mp 197−198 °C (compare with lit. 197−198 °C[1]). Spectroscopic data for the title compound were consistent with those reported in the literature.[1] HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{14}H_8N_5O_4$ 310.0571, found 310.0574.

Sodium Dithionite Reduction of (*Z*)-3-(2-(2-Nitrophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (2a) in a Mixture of EtOH:H_2O (3:1): (*Z*)-3-(2-(2-Nitrophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one **(2a)** (1.0 g, 3.23 mmol, 1.0 equiv), sodium dithionite (1.97 g, 11.32 mmol, 3.5 equiv) and a mixture of EtOH:H_2O (3:1) as solvent were taken in a 25 mL reaction flask. The resulting reaction mixture was stirred at 80 °C in an oil bath for 2.5 h. After the reaction mixture was allowed to cool to room temperature, diluted with cold water (20 mL). This afforded a precipitate, which was filtered, washed with water (3×10 mL), in air dried and was chromatographed on silica gel column using a mixture of cyclohexane-EtOAc as eluent to give two products, namely **3a** and **5a**.



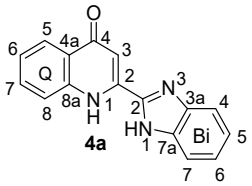
1',4'-Dihydro-1*H*,3'*H*-spiro[quinoline-2,2'-quinoxaline]-3',4(3*H*)-dione (3a). Chromatographic eluent: $CHCl_3$; yield 0.1 g, 14%; brown solid; mp 375−378°C. IR (KBr, cm^{-1}): ν_{max} 3461, 1686, 1614, 1571, 1495, 1369, 1229, 1041, 740, 638, 594. NMR data for **3a**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 10.55 (s, 1H, N(1)H-Qx), 7.56 (dd, J = 7.9 Hz, J = 1.0 Hz, 1H, H5-Q), 7.33 (s, 1H, N(4)H-Qx), 7.26 (s, 1H, N(1)H-Q), 7.25-7.21 (m, 1H, H7-Q), 6.87-6.84 (m, 2H, H7 and H5-Qx), 6.84-6.80 (m, 2H, H8-Q and H8-Qx), 6.72 (ddd, J = 7.5 Hz, J = 7.5 Hz, J = 1.0 Hz, 1H, H6-Qx), 6.63 (dd, J =7.4 Hz, J = 1.2 Hz, 1H, H6-Q), 3.01 (d, J_{AB} = 16.2 Hz, 1H, $CH_A\underline{H}_B$-Q), 2.85 (d, J_{AB} = 16.2 Hz, 1H, $C\underline{H}_AH_B$-Q). ^{13}C{^{1}H} NMR (125.8 MHz, DMSO-d_6): δ 194.2 (C4-Q), 164.3 (C2-Qx), 149.2 (C8a-Q), 135.2 (C7-Q), 131.3 (C4a-Qx), 125.3 (C8a-Qx and C5-Q), 119.2 (C7-Qx), 118.0 (C4a-Q), 117.0 (C6-Q and C6-Qx), 116.1 (C8-Q), 115.0 (C8-Qx), 114.2 (C5-Qx), 69.3 (C3-Qx and C2-Q), 46.1 (C3-Q). HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{16}H_{14}N_3O_2$ 280.1081, found 280.1081.



5a

(*Z*)-3-(2-(2-Aminophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (5a). Chromatographic eluent: $CHCl_3$/MeOH (9/1); yield 0.63 g, 86%; brown solid; mp 163−164°C. IR (KBr, cm^{-1}): ν_{max} 3422, 3276, 1670, 1623, 1601, 1568, 1521, 1370, 1309, 1228, 1014, 746, 611. NMR data for **5a**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 13.19 (s, 1H, N(4)H-Qx), 11.87 (s, 1H, N(1)H-Qx), 7.76 (dd, J = 8.1 Hz, J = 1.5 Hz, 1H, H3-Ar), 7.69 (dd, J = 8.3 Hz, J = 1.5 Hz, 1H, H6-Ar), 7.42 (d, J = 7.8 Hz, 1H, H8-Qx), 7.20 (dd, J =7.8 Hz, J = 1.5 Hz, 1H, H4-Ar), 7.12-7.07 (m, 1H, H8-Qx), 7.11-7.09 (m, 1H, H6-Qx), 7.10-7.07 (m, 1H, H7-Qx), 7.07 (s, 2H, NH_2-Ar), 6.76 (s, 1H, Hα-Sp), 6.57 (dd, J = 7.6 Hz, J = 1.5 Hz, 1H, H5-Ar). ^{13}C{^{1}H} NMR (125.8 MHz, DMSO-d_6): δ 192.3 (Cβ-Sp), 156.0 (C2-Qx), 150.7 (C2-Ar), 143.7 (C3-Qx), 133.0 (C4-Ar), 129.3 (C6-Ar), 126.2 (C8a-Qx), 124.3 (C4a-Qx), 123.6 (C6-Qx), 123.3 (C7-Qx), 118.7 (C1-Ar), 117.0 (C3-Ar), 115.9 (C5-Qx), 115.3 (C8-Qx), 114.8 (C5-Ar), 90.4 (Cα-Sp). ^{15}N NMR (50.7 MHz, DMSO-d_6): δ 140.4 (N1-Qx), 120.1 (N4-Qx), 70.0 (NH_2-Ar). HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{16}H_{14}N_3O_2$ 280.1081, found 280.1081.

General Procedure for the Synthesis of 2-(Benzimidazol-2-yl)quinolin-4(1*H*)-ones 4a-l: (*Z*)-3-(2-(2-Nitrophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one **(2)** (3.2 mmol, 1.0 equiv), sodium dithionite (11.2 mmol, 3.5 equiv) and a mixture of DMF:H_2O (5:1) as solvent were taken in a 25 mL reaction flask. The resulting reaction mixture was stirred at 90 °C in an oil bath for 7 h. After completion, the reaction mixture was allowed to cool to room temperature, diluted with cold water (20 mL). This afforded a precipitate, which was filtered, washed with water (3×10 mL), dried in air (and recrystallized from AcOH (5.0 mL) to give the analytically pure compound (**4)** as solids.) to afford the desired products (**4)** as solids.



4a

2-(1*H*-Benzimidazol-2-yl)quinolin-4(1*H*)-one (4a). The compound was obtained by the same procedure starting from (*Z*)-3-(2-(2-nitrophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one **(2a)** (1.0 g, 3.23 mmol, 1.0 equiv) and sodium dithionite (1.97 g, 11.32 mmol, 3.5 equiv) in DMF:H_2O (5:1) (6.34 mL) following the general procedure. Yield 0.82 g, 97%; gray solid; mp >400 °C. IR (KBr, cm^{-1}): ν_{max} 3363, 3064, 2884, 2748, 1633, 1609, 1568, 1516, 1433, 1352, 1306, 1233, 1144, 1009, 924, 864, 745, 619, 563, 526, 467. NMR data for **4a**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 8.14 (dd, J = 8.2 Hz, J = 1.1 Hz, 1H, H5-Q), 8.05 (d, J = 8.4 Hz, 1H, H8-Q), 7.73 (dd, J = 7.5 Hz, 1H, H7-Q), 7.75-7.72 (m, 2H, H3 and H7-Bi), 7.43 (dd, J = 7.5 Hz, 1H, H6-Q), 7.38-7.34 (m, 2H, H5 and H6-Bi), 7.12 (s, 1H, H3-Q). The signals of (NH-Q and NH-NBi) have not been observed. ^{13}C{^{1}H} NMR (125.8 MHz, DMSO-d_6): δ 174.7 (C4-Q), 146.4 (C2-Bi), 141.8 (C8a-Q), 140.7 (C2-Q), 138.8 (C3a and C7a-Bi), 132.1 (C7-Q), 124.6 (C6-Q), 124.2 (C4a-Q), 124.1 (C5-Q), 123.6 (C5 and C6-Bi), 120.9 (C8-Q), 115.8 (C3 and C7-Bi), 105.9 (C3-Q). HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{16}H_{12}N_3O$ 262.0975, found 262.0976.

2-(5,6-Dichloro-1*H*-benzimidazol-2-yl)quinolin-4(1*H*)-one (4b). The compound was obtained by the same procedure starting from (*Z*)-7,8-dichloro-3-(2-(2-nitrophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (**2b**) (1.0 g, 2.64 mmol, 1.0 equiv) and sodium dithionite (1.61 g, 9.25 mmol, 3.5 equiv) in DMF:H_2O (5:1) (5.19 mL) following the general procedure. Yield 0.80 g, 92%; beige solid; mp >400 °C. IR (KBr, cm^{-1}): ν_{max} 3101, 2990, 1698, 1602, 1575, 1538, 1497, 1473, 1393, 1293, 1144, 1101, 1008, 971, 914, 864, 810, 756, 730, 662, 627, 532, 500, 453. NMR data for **4b**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 13.54 (brs, 1H, NH-Bi), 12.38 (brs, 1H, NH-Q), 8.12 (d, J = 8.1 Hz, 1H, H5-Q), 8.04 (d, J = 8.1 Hz, 1H, H8-Q), 7.95 (brs, 2H, H4 and H7-Bi), 7.72 (dd, J = 8.1 Hz, J = 8.1 Hz, 1H, H7-Q), 7.41 (brs, 1H, H6-Q), 7.10 (brs, 1H, H3-Q). ^{13}C{^{1}H} NMR (125.8 MHz, DMSO-d_6): δ 176.9 (C4-Q), 149.1 (C2-Bi), 141.5 (C2-Q), 141.0 (C8a-Q), 131.8 (C7-Q), 125.7 (C6 and C5-Bi), 124.1 (C5-Q), 124.0 (C6-Q), 123.1 (C4a-Q), 119.5 (C8-Q), (C4 and C7-Bi), 106.8 (C3-Q). The signals of (C3a, C7a, C4 and C7-Bi) have not been

observed. HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{16}H_{10}{}^{35}Cl_2N_3O$ 330.0195, found 330.0195; $[M+H]^+$ calcd for $C_{16}H_{10}{}^{37}Cl_2N_3O$ 332.0168, found 332.0166.

2-(5-Chloro-1*H*-benzimidazol-2-yl)quinolin-4(1*H*)-one (4c). The compound was obtained by the same procedure starting from regioisomeric mixture of (*Z*)-6- **(2c)** and 7-chloro-3-(2-(2-nitrophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-ones **(2′c)** (1.0 g, 2.91 mmol, 1.0 equiv) and sodium dithionite (1.77 g, 10.18 mmol, 3.5 equiv) in DMF:H_2O (5:1) (5.88 mL) following the general procedure. Yield 0.82 g, 95%; beige solid; mp 394−396 °C. IR (KBr, cm^{-1}): ν_{max} 3436, 3169, 3073, 2990, 2854, 2609, 1703, 1616, 1565, 1514, 1430, 1368, 1326, 1286, 1152, 1060, 1006, 932, 867, 796, 761, 626, 521, 429. NMR data for **4c**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 8.13 (dd, J = 8.0 Hz, J = 1.1 Hz, 1H, H5-Q), 8.05 (d, J = 8.0 Hz, 1H, H8-Q), 7.75 (d, J = 2.0 Hz, 1H, H4-Bi), 7.73 (dd, J = 8.0 Hz, J = 8.2 Hz, 1H, H7-Q), 7.72 (d, J = 8.6 Hz, 1H, H7-Bi), 7.41 (dd, J = 8.4 Hz, J = 8.2 Hz, 1H, H6-Q), 7.35 (dd, J = 8.6 Hz, J = 2.0 Hz, 1H, H6-Bi), 7.13 (brs, 1H, H3-Q). The signals of (NH-Q and NH-NBi) have not been observed. $^{13}C\{^1H\}$ NMR (125.8 MHz, DMSO-d_6): δ 174.4 (C4-Q), 148.1 (C2-Bi), 142.0 (C8a-Q), 140.8 (C3a-Bi), 140.7 (C2-Q), 139.5 (C7a-Bi), 132.0 (C7-Q), 127.7 (C5-Bi), 124.5 (C4a-Q), 124.4 (C5-Q), 124.2 (C6-Q), 123.8 (C6-Bi), 121.2 (C8-Q), 117.0 (C7-Bi), 115.3 (C4-Bi), 106.0 (C3-Q). HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{16}H_{11}{}^{35}ClN_3O$ 296.0585, found 296.0588; $[M+H]^+$ calcd for $C_{16}H_{11}{}^{37}ClN_3O$ 298.0560, found 298.0559.

2-(5,6-Dimethyl-1*H*-benzimidazol-2-yl)quinolin-4(1*H*)-one (4d). The compound was obtained by the same procedure starting from (*Z*)-7,8-dimethyl-3-(2-(2-nitrophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one **(2d)** (1.0 g, 2.96 mmol, 1.0 equiv) and sodium dithionite (1.81 g, 10.37 mmol, 3.5 equiv) in DMF:H_2O (5:1) (5.81 mL) following the general procedure. Yield 0.82 g, 95%; yellow solid; mp >400 °C. IR (KBr, cm^{-1}): ν_{max} 3436, 1695, 1611, 1563, 1517, 1283, 1005, 760, 544. NMR data for **4d**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 12.47 (brs, 1H, NH-Bi), 12.47 (brs,1H, NH-Q), 8.12 (dd, J = 8.1 Hz, J = 1.5 Hz, J = 1.2 Hz, 1H, H5-Q), 8.05 (dd, J = 8.1 Hz, J = 1.1 Hz, 1H, H8-Q), 7.70 (ddd, J = 8.1 Hz, J = 8.0 Hz, J = 1.6 Hz, 1H, H7-Q), 7.48 (brs, 2H, H4 and H7-Bi), 7.39 (dd, J = 8.1 Hz, J = 8.1 Hz, 1H, H6-Q), 7.38 (brs, 1H, H3-Q), 2.37 (s, 6H, $CH_3$5 and $CH_3$6-Bi). $^{13}C\{^1H\}$ NMR (125.8 MHz, DMSO-d_6): δ 171.9 (C4-Q), 145.3 (C2-Bi), 141.6 (C8a-Q), 140.1 (C2-Q), 137.3 (C3a-Bi), 136.2 (C7a-Bi), 132.6 (C6-Bi and C5-Bi), 131.9 (C7-Q), 124.8 (C4a-Q),124.2 (C5-Q), 123.8 (C6-Q), 120.6 (C8-Q), 115.3 (C4 and C7-Bi), 105.6 (C3-Q), 20.0 ($CH_3$5 and $CH_3$6-Bi). HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{18}H_{16}N_3O$ 290.1288, found 290.1288.

2-(5-Methyl-1*H*-benzimidazol-2-yl)quinolin-4(1*H*)-one (4e). The compound was obtained by the same procedure starting from regioisomeric mixture of (*Z*)-6- **(2e)** and 7-methyl-3-(2-(2-nitrophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-ones **(2′e)** (1.0 g, 3.09 mmol, 1.0 equiv) and sodium dithionite (1.89 g, 10.83 mmol, 3.5 equiv) in DMF:H_2O (5:1) (6.07 mL) following the general procedure. Yield 0.83 g, 97%; beige solid; mp 372−273 °C. IR (KBr, cm^{-1}): ν_{max} 3441, 3175, 3066, 2984, 2918, 2863, 2664, 1698, 1628, 1613, 1569, 1520, 1436, 1370, 1296, 1151, 1072, 1027, 1008, 927, 867, 799, 758, 734, 693, 664, 627, 597, 536, 456, 428. NMR data for **4e**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 8.13 (dd, J = 8.0 Hz, J = 1.1 Hz, 1H, H5-Q), 8.06 (d, J = 8.0 Hz, 1H, H8-Q), 7.71 (dd, J = 8.4 Hz, J = 8.5 Hz, 1H, H7-Q), 7.61 (d, J = 8.6 Hz, 1H, H7-Bi), 7.49 (d, J = 2.0 Hz, 1H, H4-Bi), 7.39 (dd, J = 8.0 Hz, J = 8.0 Hz, 1H, H6-Q), 7.16 (d, J = 8.2 Hz, 1H, H6-Bi), 7.07 (s, 1H, H3-Q), 2.47 (s, 3H, CH_3-Bi). The signals of (NH-Q and NH-Bi) have not been observed. $^{13}C\{^1H\}$ NMR (125.8 MHz, DMSO-d_6): δ 174.3 (C4-Q), 146.0 (C2-Bi), 141.7 (C8a-Q), 140.5 (C2-Q), 138.3 (C3a-Bi), 137.1 (C7a-Bi), 133.2 (C5-Bi), 132.0 (C7-Q), 125.2 (C6-Bi), 124.6 (C4a-Q), 124.2 (C5-Q), 124.0 (C6-Q), 120.7 (C8-Q), 115.8 (C7-Bi), 114.7 (C4-Bi), 105.7 (C3-Q). HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{17}H_{14}N_3O$ 276.1131, found 276.1135.

2-(7-Methyl-1*H*-benzimidazol-2-yl)quinolin-4(1*H*)-one (4f). The compound was obtained by the same procedure starting from regioisomeric mixture of (*Z*)-5- **(2f)** and 8-methyl-3-(2-(2-nitrophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-ones **(2′f)** (1.0 g, 3.09 mmol, 1.0 equiv) and sodium dithionite (1.89 g, 10.83 mmol, 3.5 equiv) in DMF:H_2O (5:1) (6.07 mL) following the general procedure. Yield 0.82 g, 96%; beige solid; mp >400 °C. IR (KBr, cm^{-1}): ν_{max} 3437, 3249, 3171, 3074, 2985, 1699, 1632, 1572, 1520, 1435, 1367, 1295, 1146, 1006, 865, 784, 747, 664, 627, 549. NMR data for **4f**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 8.13 (dd, J = 8.1 Hz, J = 1.2 Hz, 1H, H5-Q), 8.07 (dd, J = 8.1 Hz, J = 1.1 Hz, 1H, H8-Q), 7.71 (ddd, J = 8.1 Hz, J = 8.0 Hz, J = 1.0 Hz, 1H, H7-Q), 7.54 (brd, J = 8.1 Hz, Hz, 1H, H4-Bi), 7.38 (dd, J = 8.1 Hz, J = 8.0 Hz, 1H, H6-Q), 7.22 (dd, J = 7.9 Hz, J = 7.2 Hz, 1H, H5-Bi), 7.14 (s, 1H, H3-Q), 7.12 (d, J = 7.2 Hz, 1H, H6-Bi), 2.63 (s, 3H, CH_3-Bi). The signals of (NH-Q and NH-Bi) have not been observed. $^{13}C\{^1H\}$ NMR (125.8 MHz, DMSO-d_6): δ 176.8 (C4-Q), 145.8 (C2-Bi), 140.8 (C8a-Q), 140.6 (C3a-Bi), 140.5 (C2-Q), 132.2 (C7a-Bi), 131.9 (C7-Q), 124.8 (C4a-Q), 124.3 (C5-Q), 123.8 (C6-Bi), 123.8 (C6-Q), 123.3 (C5-Bi), 120.3 (C8-Q), 114.2 (C4-Bi), 106.4 (C3-Q), 16.9 (CH_3-Bi). HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{17}H_{14}N_3O$ 276.1131, found 276.1134.

2-(5,6-Difluoro-1*H*-benzimidazol-2-yl)quinolin-4(1*H*)-one (4g). The compound was obtained by the same procedure starting from (*Z*)-6,7-difluoro-3-(2-(2-nitrophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (**2g**) (1.0 g, 2.896 mmol, 1.0 equiv) and sodium dithionite (1.76 g, 10.14 mmol, 3.5 equiv) in DMF:H_2O (5:1) (5.68 mL) following the general procedure. Yield 0.84 g, 98%; gray solid; mp >400 °C. IR (KBr, cm^{-1}): ν_{max} 3451, 3300, 3154, 3111, 3077, 2992, 2872, 2689, 1650, 1636, 1602, 1546, 1498, 1472, 1435, 1413, 1365, 1319, 1287, 1240, 1167, 1128, 1026, 1001, 913, 889, 852, 829, 786, 756, 726, 651, 618, 553, 518, 482, 457, 425, 406. NMR data for **4g**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 8.13 (dd, J = 8.0 Hz, J = 1.5 Hz, 1H, H5-Q), 8.04 (d, J = 8.0 Hz, 1H, H8-Q), 7.75 (dd, J = 9.4 Hz, J(HF) = 9.0 Hz, 2H, H4 and H7-Bi), 7.73 (ddd, J = 8.0 Hz, J = 8.0 Hz, J = 1.5 Hz, 1H, H7-Q), 7.42 (dd, J = 8.0 Hz, J = 8.0 Hz, 1H, H6-Q), 7.11 (s, 1H, H3-Q). The signals of (NH-Q and NH-Bi) have not been observed. ^{13}C{^{1}H} NMR (125.8 MHz, DMSO-d_6): δ 174.1 (C4-Q), 148.7 (C2-Bi), 147.8 (dd, *J(CF)* = 240.1 Hz, *J(CF)* = 17.5 Hz, C6-Bi and C5-Bi, 142.0 (C8a-Q), 140.9 (C2-Q), 134.6 (C7a-Bi), 134.6 (C3a-Bi), 132.2 (C7-Q), 124.5 (C4a-Q), 124.4 (C5-Q), 124.2 (C6-Q), 121.2 (C8-Q), 105.7 (C3-Q), 103.4 (d, *J(CF)* = 26.1 Hz, C7 and C4-Bi). HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{16}H_{10}F_2N_3O$ 298.0786, found 298.0789.

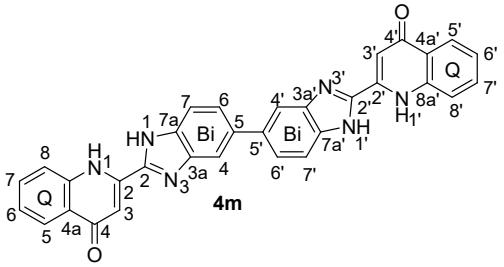
2-(6-Fluoro-1*H*-benzimidazol-2-yl)quinolin-4(1*H*)-one (4h). The compound was obtained by the same procedure starting from regioisomeric mixture of (*Z*)-6- **(2h)** and 7-fluoro-3-(2-(2-nitrophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-ones **(2′h)** (1.0 g, 3.06 mmol, 1.0 equiv) and sodium dithionite (1.86 g, 10.70 mmol, 3.5 equiv) in DMF:H_2O (5:1) (5.99 mL) following the general procedure. Yield 0.82 g, 96%; gray solid; mp >400°C. IR (KBr, cm^{-1}): ν_{max} 3173, 3068, 2992, 2871, 2608, 1836, 1787, 1708, 1621, 1567, 1519, 1487, 1435, 1401, 1370, 1355, 1330, 1283, 1262, 1222, 1145, 1116, 1028, 1007, 961, 926, 894, 836, 810, 793, 761, 736, 694, 664, 645, 628, 606, 547, 536, 482, 454, 434. NMR data for **4h**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 8.13 (dd, J = 8.0 Hz, 1H, H5-Q), 8.05 (d, J = 8.0 Hz, 1H, H8-Q), 7.72 (dd, J(HF) = 3.1 Hz, J = 9.4 Hz, 1H, H7-Bi), 7.72 (ddd, J = 8.0 Hz, J = 8.0 Hz, J = 1.5 Hz, 1H, H7-Q), 7.50 (dd, J(HF) = 9.2 Hz, J = 2.5 Hz, 1H, H4-Bi), 7.40 (ddd, J = 8.0 Hz, J = 8.0 Hz, J = 1.1 Hz, 1H, H6-Q), 7.20 (ddd, J = 9.4 Hz, J(HF) = 9.4 Hz, J = 2.5 Hz, 1H, H5-Bi), 7.09 (brs, 1H, H3-Q). The signals of (NH-Q and NH-Bi) have not been observed. ^{13}C{^{1}H} NMR (125.8 MHz, DMSO-d_6): δ 174.4 (C4-Q), 159.3 (d, *J(CF)* = 237.2 Hz, C6-Bi), 147.9 (C2-Bi), 141.8 (C8a-Q), 140.6 (C2-Q), 139.1 (C7a-Bi), 135.7 (C3a-Bi), 132.1 (C7-Q), 124.6 (C4a-Q), 124.2 (C5-Q), 124.11 (C6-Q), 120.9 (C8-Q), 117.1 (C7-Bi), 111.9 (d, J(CF) = 26.1 Hz, C5-Bi), 105.9 (C3-Q), 101.4 (C7-Bi). HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{16}H_{11}FN_3O$ 280.0881, found 280.0883.

2-(6-Bromo-1*H*-benzimidazol-2-yl)quinolin-4(1*H*)-one (4i). The compound was obtained by the same procedure starting from regioisomeric mixture of (*Z*)-6- **(2i)** and 7-bromo-3-(2-(2-nitrophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-ones **(2′i)** (1.0 g, 2.58 mmol, 1.0 equiv) and sodium dithionite (1.57 g, 9.02 mmol, 3.5 equiv) in DMF:H_2O (5:1) (5.05 mL) following the general procedure. Yield 0.82 g, 93%; gray solid; mp 374−375°C. IR (KBr, cm^{-1}): ν_{max} 3435, 3256, 3171, 3071, 2991, 2855, 2607, 1699, 1632, 1603, 1514, 1469, 1433, 1368, 1326, 1299, 1251, 1223, 1150, 1124, 1047, 1027, 1005, 961, 913, 854, 795, 759, 665, 630, 588, 534, 518, 475, 453, 425. NMR data for **4i**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 8.13 (dd, J = 8.0 Hz, J = 1.1 Hz, 1H, H5-Q), 8.05 (d, J = 8.0 Hz, 1H, H8-Q), 7.89 (d, J = 1.6 Hz, 1H, H7-Bi), 7.72 (ddd, J = 8.5 Hz, J = 7.0 Hz, J = 1.5 Hz, 1H, H7-Q), 7.67 (d, J = 8.6 Hz, 1H, H4-Bi), 7.46 (dd, J = 8.6 Hz, J = 1.6 Hz, 1H, H5-Bi), 7.41 (ddd, J = 8.5 Hz, J = 8.0 Hz, J = 1.6 Hz, 1H, H6-Q), 7.12 (brs, 1H, H3-Q). The signals of (NH-Q and NH-Bi) have not been observed. ^{13}C{^{1}H} NMR (125.8 MHz, DMSO-d_6): δ 174.3 (C4-Q), 148.0 (C2-Bi), 142.1 (C8a-Q), 140.7 (C7a-Bi), 140.2 (C2-Q), 138.1 (C7a-Bi), 132.1 (C7-Q), 126.4 (C5-Bi), 124.5 (C4a-Q), 124.2 (C6-Q), 124.2 (C5-Q), 121.1 (C8-Q), 118.5 (C7-Bi), 117.4 (C4-Bi), 115.6 (C6-Bi), 106.0 (C3-Q). HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{16}H_{11}{}^{79}BrN_3O$ 340.0080, found 340.0079; $[M+H]^+$ calcd for $C_{16}H_{11}{}^{81}BrN_3O$ 342.0061, found 342.0059.

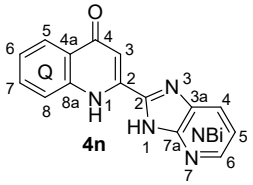
2-(6-Oxo-1,4-dihydroquinolin-2-yl)-1*H*-benzimidazole-5-carboxylic acid (4j). The compound was obtained by the same procedure starting from (*Z*)-3-(2-(2-nitrophenyl)-2-oxoethylidene)-2-oxo-1,2,3,4-tetrahydroquinoxaline-6-carboxylic acid **(2j)** (1.0 g, 2.83 mmol, 1.0 equiv) and sodium dithionite (1.73 g, 9.91 mmol, 3.5 equiv) in DMF:H_2O (5:1) (5.55 mL) following the general procedure. Yield 0.77 g, 89%; brown solid; mp >400 °C. IR (KBr, cm^{-1}): ν_{max} 3430, 3067, 2986, 2907, 1692, 1604, 1573, 1516, 1474, 1438, 1418, 1354, 1309, 1293, 1239, 1227, 1143, 1088, 1032, 1008, 947, 925, 906, 839, 823, 771, 748, 696, 671, 623, 578, 550, 527, 461, 438, 424. NMR data for **4j**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 8.15 (dd, J = 8.4 Hz, J = 1.1 Hz, 1H, H5-Q), 8.10 (d, J = 8.4 Hz, 1H, H8-Q), 7.95 (d, J = 8.5 Hz, 1H, H7-Bi), 7.84 (d, J = 1.0 Hz, 1H, H4-Bi), 7.74 (dd, J = 7.5 Hz, 1H, H7-Q), 7.72 (dd, J = 8.5 Hz, J = 1.0 Hz, 1H, H5-Bi), 7.43 (dd, J = 7.5 Hz, 1H, H6-Q), 7.17 (s, 1H, H3-Q). The signals of (NH-Q and NH-Bi) have not been observed. ^{13}C{^{1}H} NMR (125.8 MHz, DMSO-d_6): δ 174.2 (C4-Q), 147.1 (C2-Bi), 142.1 (C8a-Q), 141.5 (C3a-Bi), 140.7 (C2-Q), 132.1 (C7-Q), 131.6 (C7a-Bi), 125.1 (C5-Bi), 124.5 (C4a-Q), 124.2 (C6-Q), 124.1 (C5-Q), 123.6 (C6-Bi), 121.0 (C8-Q), 116.6 (C4-Bi), 113.8 (C7-Bi), 105.8 (C3-Q). The signal of (C-sp) has not been observed. HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{17}H_{12}N_3O_3$ 306.0873, found 306.0873.

2-(6-Aminobenzimidazol-2-yl)quinolin-4(1*H*)-one (4k). The compound was obtained by the same procedure starting from regioisomeric mixture of **(***Z*)-6- **(2k)** and 7-nitro-3-(2-(2-nitrophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-ones **(2′k)** (1.0 g, 2.82 mmol, 1.0 equiv) and sodium dithionite (1.72 g, 9.88 mmol, 3.5 equiv) in DMF:H_2O (5:1) (5.57 mL) following the general procedure. Yield 0.28 g, 36%; brown solid; mp >400 °C. IR (KBr, cm^{-1}): ν_{max} 3419, 3177, 1702, 1629, 1602, 1517, 1437, 1370, 1292, 1256, 1143, 1010, 810, 757. NMR data for **4k**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 10.07 (brs, 1H, NH-Bi), 8.19 (d, J = 1.9 Hz, 1H, H7-Bi), 8.11 (dd, J = 8.2 Hz, J = 1.5 Hz, 1H, H5-Q), 8.03 (d, J = 8.0 Hz, 1H, H8-Q), 7.69 (ddd, J = 7.7 Hz, J = 7.7 Hz, J = 1.6 Hz, 1H, H7-Q), 7.65 (d, J = 8.6 Hz, J = 8.1 Hz, 1H, H4-Bi), 7.37 (dd, J = 8.0 Hz, J = 7.9 Hz, 1H, H6-Q), 7.35 (dd, J = 8.6 Hz, J = 1.6 Hz, 1H, H5-Bi), 6.99 (s, 1H, H3-Q). The signale of NH-Q has not been observed. ^{13}C{^{1}H} NMR (125.8 MHz, DMSO-d_6): δ 175.5 (C4-Q), 146.5 (C2-Bi), 146.3 (C2-Q), 141.6 (C8a-Q), 137.3 (C7a-Bi), 136.9 (C3a-Bi), 135.7 (C6-Bi), 131.9 (C7-Q), 125.0 (C4a-Q), 124.3 (C5-Q), 123.6 (C6-Q), 120.3 (C8-Q), 117.2 (C4-Bi), 116.1 (C5-Bi), 105.9 (C3-Q). 103.9 (C7-Bi). HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{16}H_{13}N_4O$ 277.1084, found 277.1085. The synthesis of 2-(6-amino-benzimidazol-2-yl)quinolin-4(1*H*)-one **(4k)** from(*Z*)-6-amino-3-(2-(2-aminophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one **(5k)**. A solution (*Z*)-6-amino-3-(2-(2-aminophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (**5k**) (0.5 g, 1.7 mmol) in 5 mL acetic acid was heated at reflux with stirring for 2 h. After cooling the solvent was removed under vacuum and the residue was treated with 5% water solution of $NaHCO_3$. The precipitate was separated by a Buchner funnel washed with water (3×10 mL) and dried in air. Yield 0.46 g, 100%. The characteristic data (mp., IR, NMR and HRMS (ESI)) of the compound were identical with those obtained above.

2-(6-Benzoyl-1*H*-benzo[*d*]imidazol-2-yl)quinolin-4(1*H*)-one (4l). The compound was obtained by the same procedure starting from regioisomeric mixture of (*Z*)-6- **(2l)** and 7-benzoyl-3-(2-(2-nitrophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-ones **(2′l)** (1.0 g, 2.42 mmol, 1.0 equiv) and sodium dithionite (1.47 g, 8.47 mmol, 3.5 equiv) in DMF:H_2O (5:1) (4.74 mL) following the general procedure. Yield 0.86 g, 97%; brown solid; mp 384−385°C. IR (KBr, cm^{-1}): ν_{max} 3456, 3293, 3057, 2979, 2884, 2797, 1704, 1634, 1610, 1569, 1517, 1440, 1417, 1355, 1330, 1311, 1235, 1181, 1140, 1111, 1077, 1029, 1002, 962, 922, 895, 833, 784, 760, 718, 661, 640, 620, 582, 529, 468, 435. NMR data for **4l**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 8.17 (dd, J = 8.4 Hz, J = 1.1 Hz, 1H, H5-Q), 8.10 (d, J = 8.4 Hz, 1H, H8-Q), 8.08 (d, J = 1.0 Hz, 1H, H7-Bi), 7.88 (d, J = 8.5 Hz, 1H, H4-Bi), 7.79 (dd, J = 8.5 Hz, J = 1.0 Hz, 1H, H5-Bi), 7.78 (dd, J = 7.5 Hz, J = 7.5 Hz, 1H, H7-Q), 7.78 (d, J = 7.7 Hz, 2H, H2 and H6-Ar), 7.70 (dd, J = 7.7 Hz, J = 7.5 Hz, 1H, H4-Ar), 7.59 (dd, J = 7.7 Hz, J = 7.6 Hz, 2H, H3 and H7-Ar), 7.48 (dd, J = 7.5 Hz, J = 7.5 Hz, 1H, H6-Q), 7.26 (s, 1H, H3-Q). The signals of (NH-Q and NH-Bi) have not been observed. ^{13}C{^{1}H} NMR (125.8 MHz, DMSO-d_6): δ 195.6 (C=O), 173.1 (C4-Q), 149.3 (C2-Bi), 142.3 (C2-Q), 141.5 (C3a-Bi), 141.4 (C8a-Q), 138.7 (C6-Bi), 137.8 (C1-Ar), 132.5 (C4-Ar), 132.5 (C7a-Bi), 132.4 (C7-Q), 129.6 (C2 and C6-Ar), 128.6 (C3 and C5-Ar), 125.4 (C5-Bi), 125.0 (C6-Q), 124.1 (C5-Q), 124.0 (C4a-Q), 121.7 (C8-Q), 118.9 (C7-Bi), 115.7 (C7-Bi), 105.8 (C3-Q). HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{23}H_{16}N_3O_2$ 366.1237, found 366.1234.

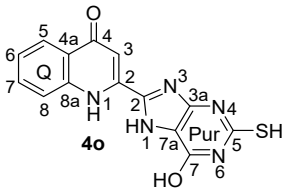


2,2'-(1*H*,1'*H*-[5,5'-Bibenzo[*d*]imidazole]-2,2'-diyl)bis(quinolin-4(1*H*)-one) (4m). The compound was obtained by the same procedure starting from regioisomeric mixture of (3*Z*,3'*Z*)-3,3'-bis(2-(2-nitrophenyl)-2-oxoethylidene)-3,3',4,4'-tetrahydro-[6,6'-biquinoxaline]-2,2'(1*H*,1'*H*)-dione **(2m)** and (2*Z*,2'*Z*)-2,2'-bis(2-(2-nitrophenyl)-2-oxoethylidene)-1,1',4,4'-tetrahydro-[6,6'-biquinoxaline]-3,3'(2*H*,2'*H*)-dione **(2′m)** (1.0 g, 1.62 mmol, 1.0 equiv) and sodium dithionite (0.99 g, 5.68 mmol, 3.5 equiv) in DMF:H_2O (5:1) (3.18 mL) following the general procedure. Yield 0.80 g, 75%; brown solid; mp >400°C. IR (KBr, cm^{-1}): ν_{max} 3416, 3067, 1625, 1603, 1571, 1513, 1473, 1434, 1298, 1222, 1143, 1030, 1003, 923, 854, 800, 756, 732, 695, 666, 612, 527, 472, 427. NMR data for **4m**: ^{1}H NMR (500.1 MHz, CF_3CO_2D): δ 8.79-8.75 (d, J = 8.2 Hz, 2H, H5-Q), 8.47-8.43 (m, 2H, H8-Q), 8.39 (brs, 2H, H3-Q), 8.36-8.33 (m, 2H, H4-Bi), 8.26-8.24 (m, 2H, H7-Bi), 8.25-8.22 (m, 2H, H7-Q), 8.20-8.10 (m, 2H, H6-Q), 8.10-7.95 (m, 2H, H6-Bi). The signals of NH-Q and NH-Bi have not been observed. ^{13}C{^{1}H} NMR (125.8 MHz, CF_3CO_2D): δ 173.1 (C4-Q), 153.2 (C2-Bi), 142.1 (C8a-Q), 139.4 (C7-Q), 137.1 (C3a-Bi), 133.7 (C7a-Bi), 133.2 (C2-Q), 132.2 (C6-Q), 131.1 (C5-Bi), 128.4 (C6-Bi), 125.5 (C5-Q), 122.4 (C4a-Q), 121.3 (C8-Q), 114.4 (C7-Bi), 111.9 (C4-Bi), 107.8 (C3-Q). HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{32}H_{21}N_6O_2$ 521.1721, found 521.1714.



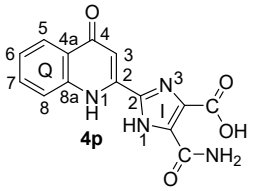
4n

2-(3*H*-imidazo[4,5-*b*]pyridin-2-yl)quinolin-4(1*H*)-one (4n). The compound was obtained by the same procedure starting from regioisomeric mixture of (*Z*)-3-(2-(2-nitrophenyl)-2-oxoethylidene)-3,4-dihydropyrido[2,3-*b*]pyrazin-2(1*H*)-one **(2n)** and (*Z*)-2-(2-(2-nitrophenyl)-2-oxoethylidene)-1,4-dihydropyrido[2,3-*b*]pyrazin-3(2*H*)-one **(2′n)** (1.0 g, 3.12 mmol, 1.0 equiv) and sodium dithionite (1.90 g, 10.93 mmol, 3.5 equiv) in DMF:H_2O (5:1) (6.12 mL) following the general procedure. Yield 0.67 g, 82%; gray solid; mp 381−382°C. IR (KBr, cm^{-1}): ν_{max} 3436, 3165, 3068, 2986, 2613, 1695, 1628, 1606, 1514, 1434, 1389, 1323, 1280, 1148, 1121, 1031, 999, 920, 872, 778, 761, 694, 664, 642, 620, 568, 543, 512, 479, 453. NMR data for **4n**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 13.94 (brs, 1H, NH-NBi), 12.33 (brs,1H, NH-Q), 8.49 (d, J = 4.6 Hz, 1H, H6-NBi), 8.15 (brs, 1H, H4-NBi), 8.13 (dd, J = 8.0 Hz, J = 1.1 Hz, 1H, H5-Q), 8.05 (d, J = 8.0 Hz, 1H, H8-Q), 7.71 (dd, J = 7.8 Hz, J = 7.7 Hz, 1H, H7-Q), 7.40 (brs, 1H, H5-NBi), 7.37 (dd, J = 8.2 Hz, J = 8.1 Hz, 1H, H6-Q), 7.10 (brs, 1H, H3-Q). ^{13}C{^{1}H} NMR (125.8 MHz, DMSO-d_6): δ 177.3 (C4-Q), 149.5 (C7a-NBi), 147.5 (C2-NBi), 145.5 (C6-NBi), 140.5 (C8a-Q), 139.2 (C2-Q), 132.1 (C7-Q), 132.1 (C3a-NBi), 126.0 (C4a-Q), 125.6 (C4-NBi), 124.4 (C5-Q), 123.9 (C6-Q), 119.9 (C5-NBi), 119.2 (C8-Q), 106.9 (C3-Q). HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{15}H_{11}N_4O$ 263.0927, found 263.0929.



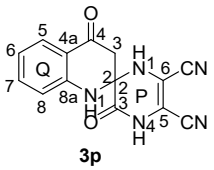
4o

2-(6-Hydroxy-2-mercapto-7*H*-purin-8-yl)quinolin-4(1*H*)-one (4o). The compound was obtained by the same procedure starting from (*Z*)-4-hydroxy-2-mercapto-6-(2-(2-nitrophenyl)-2-oxoethylidene)-5,8-dihydropteridin-7(6*H*)-one **(2o)** (1.0 g, 2.78 mmol, 1.0 equiv) and sodium dithionite (1.17 g, 9.74 mmol, 3.5 equiv) in DMF:H_2O (5:1) (5.46 mL) following the general procedure. Yield 0.65 g, 75%; gray solid; mp >400°C. IR (KBr, cm^{-1}): ν_{max} 3435, 2923, 2111, 1636, 1126, 637, 615. NMR data for **4o**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 13.46 (brs, 1H, OH-Pur), 12.38 (brs, 1H, NH-Q), 8.06 (dd, J = 8.1 Hz, J = 1.2 Hz, 1H, H5-Q), 7.97 (d, J = 8.4 Hz, 1H, H8-Q), 7.71 (ddd, J = 7.7 Hz, J = 7.7 Hz, J = 1.5 Hz, 1H, H7-Q), 7.40 (dd, J = 7.6 Hz, J = 7.5 Hz, 1H, H6-Q), 7.04 (s, 1H, H3-Q), 7.04 (brs, 1H, SH-Pur). ^{13}C{^{1}H} NMR (125.8 MHz, DMSO-d_6): δ 173.9 (C4-Q), 148.6 (C2-Pur), 142.6 (C8a-Q), 141.2 (C2-Q), 132.0 (C7-Q), 124.8 (C4a-Q), 124.2 (C5-Q), 124.1 (C6-Q), 120.9 (C8-Q), 106.3 (C3-Q). The signals of (C3a, C7a, C5 and C7-Pur) have not been observed. HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{14}H_{10}N_5O_2S$ 312.0550, found 312.0553.



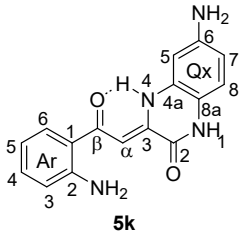
4p

5-Carbamoyl-2-(4-oxo-1,4-dihydroquinolin-2-yl)-1*H*-imidazole-4-carboxylic acid (4p). The compound was obtained by the same procedure starting from tautomeric mixture of (*Z*)-5-(2-(2-nitrophenyl)-2-oxoethylidene)-6-oxo-1,4,5,6-tetrahydropyrazine-2,3-dicarbonitrile **(2p)** and 5-(2-(2-nitrophenyl)-2-oxoethyl)-6-oxo-1,6-dihydropyrazine-2,3-dicarbonitrile **(2p′)** (1.0 g, 3.23 mmol, 1.0 equiv) and sodium dithionite (1.97 g, 11.32 mmol, 3.5 equiv) in DMF:H_2O (5:1) (6.34 mL) following the general procedure. Yield 0.36 g, 43%; brown solid; mp 377−378°C. IR (KBr, cm^{-1}): ν_{max} 3424, 3328, 1671, 1600, 1523, 1443, 1390, 1359, 1234, 1147, 1078, 1032, 870, 806, 760, 621, 554, 505. NMR data for **4p**: ^{1}H NMR (500.1 MHz, DMSO-d_6 and CF_3COOD): δ 8.31 (d, J = 8.1 Hz, 1H, H5-Q), 8.31 (d, J = 8.1 Hz, 1H, H8-Q), 7.93 (dd, J = 8.1 Hz, 1H, H7-Q), 7.72 (s, 1H, H3-Q), 7.68 (dd, J = 8.1 Hz, 1H, H6-Q). The signals of N(1)H-Q and N(1)H-I have not been observed. ^{13}C{^{1}H} NMR (125.8 MHz, DMSO-d_6 and CF_3COOD): δ 172.5 (C4-Q), 170.7 (CO_2H) , 168.6 ($CONH_2$), 159.3 (C3-Q), 146.9 (C2-I), 141.0 (C8a-Q), 140.5 (C4a-Q), 136.2 (C7-Q), 129.3 (C6-Q), 124.7 (C5-Q), 122.3 (C8-Q), 119.6 (C4a and C5a-I), 105.9 (C3-Q), 98.9 (C4 and C5-I). HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{14}H_8N_5O$ 262.0723, found 262.0724.



3p

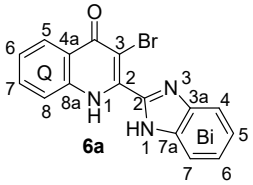
3,4'-Dioxo-3,3',4,4'-tetrahydro-1*H*,1'*H*-spiro[pyrazine-2,2'-quinoline]-5,6-dicarbonitrile (3p). 5-(2-(2-Nitrophenyl)-2-oxoethyl)-6-oxo-1,6-dihydropyrazine-2,3-dicarbonitrile **(2p)** (1.0 g, 3.23 mmol, 1.0 equiv) was dissolved in methanol/ethyl acetate (20:80, 150 mL) and palladium on carbon (0.23 g, 10% palladium (by wt%)) was added. The reaction mixture was stirred under a hydrogen atmospheric for 5 h (1 atm, balloon) pressure. After 5 h, the expected volume of hydrogen had been taken up and the solution of the reaction mixture was changed from green to brown. The Pd/C was then filtered off and the filtrate was evaporated. A reaction mixture was obtained, which was purified using column chromatography (EtOAc/MeOH:10/1). Yield 0.52 g, 58%; beige solid; mp 222−223°C. IR (KBr, cm^{-1}): ν_{max} 3366, 3251, 3146, 2929, 2232, 1688, 1673, 1634, 1609, 1521, 1480, 1365, 1310, 1002, 779. NMR data for **3p**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 11.29 (s, 1H, N(1)H-P), 8.97 (s, 1H, N(4)H-P), 7.64 (s, 1H, N(1)H-Q), 7.59 (dd, J = 7.9 Hz, J = 1.6 Hz, 1H, H5-Q), 7.35 (ddd, J = 7.7 Hz, J = 7.7 Hz, J = 1.7 Hz, 1H, H7-Q), 6.77 (d, J = 8.1 Hz, 1H, H8-Q), 6.73 (ddd, J = 7.5 Hz, J = 7.4 Hz, J = 1.1 Hz, 1H, H6-Q), 3.06 (d, J_{AB} = 16.6 Hz, 1H, $CH_A\underline{H}_B$-Q), 2.79 (d, J_{AB} = 16.6 Hz, 1H, $C\underline{H}_AH_B$-Q). ^{13}C{^{1}H} NMR (125.8 MHz, DMSO-d_6): δ 189.6 (C4-Q), 160.6 (C3-P), 147.6 (C8a-Q), 135.3 (C7-Q), 128.5 (C5-Q), 117.9 (C6-Q), 117.5 (C4a-Q), 115.6 (C8-Q), 113.0 (C6a-P), 112.6 (C5a-P), 109.8 (C5-P), 99.2 (C6-P), 67.9 (C2-Q), 43.9 (C3-Q). HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{14}H_{10}N_5O_2$ 280.0829, found 280.0833.



5k

(*Z*)-6-Amino-3-(2-(2-aminophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one (**5k**). (*Z*)-6- **(2k)** and 7-nitro-3-(2-(2-nitrophenyl)-2-oxoethylidene)-3,4-dihydroquinoxalin-2(1*H*)-one **(2′k)** (1.0 g, 2.82 mmol, 1.0 equiv) was dissolved in methanol/ethyl acetate (20:80, 150 mL) and palladium on carbon (0.23 g, 10% palladium (by wt%)) was added. The reaction mixture was stirred under a hydrogen atmospheric for 5 h (1 atm, balloon) pressure. After 5 h, the expected volume of hydrogen had been taken up and the solution of the reaction mixture was changed from orange to brown. Filtration (Celite) and concentration of the filtrate without delay afforded the diamine (**5k**). Yield 0.83 g, 100%; dark burgundy color solid; mp 219−220 °C. IR (KBr, cm^{-1}): ν_{max} 3419, 1664, 1617, 1564, 1507, 1368, 1259, 1226, 1160, 1039, 747. NMR data for **5k**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 13.27 (s, 1H, N(4)H-Qx), 11.60 (s, 1H, N(1)H-Qx), 7.66 (dd, J = 8.2 Hz, J = 1.5 Hz, 1H, H6-Ar), 7.19 (ddd, J = 8.4 Hz, J = 6.9 Hz, J = 1.5 Hz, 1H, H4-Ar), 7.01 (s, 2H, $NH_2$2-Ar), 6.85 (d, J = 8.5 Hz, 1H, H8-Qx), 6.75 (d, J = 8.3 Hz, 1H, H3-Ar), 6.70 (s, 1H, Hα-Sp), 6.56 (ddd, J = 7.4 Hz, J = 7.4 Hz, J = 1.1 Hz, 1H, H5-Ar), 6.47 (d, J = 2.2 Hz, 1H, H5-Qx), 6.40 (dd, J = 8.5 Hz, J = 2.2 Hz, 1H, H7-Qx), 5.11 (s, 2H, $NH_2$6-Qx). ^{13}C{^{1}H} NMR (125.8 MHz, DMSO-d_6): δ 192.0 (Cβ-Sp), 154.9 (C2-Qx), 150.5 (C2-Ar), 145.5 (C6-Qx), 144.4 (C3-Qx), 132.8 (C4-Ar), 129.2 (C6-Ar), 124.8 (C4a-Qx), 118.9 (C1-Ar), 117.0 (C3-Ar), 116.8 (C8a-Qx), 116.0 (C8-Qx), 114.8 (C5-Ar), 110.7 (C7-Qx), 99.4 (C5-Qx), 89.9 (Cα-Sp). HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{16}H_{15}N_4O_2$ 295.1190, found 295.1190.

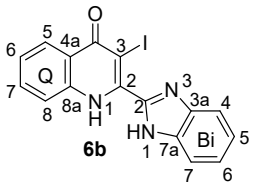
Functionalization of 2-(1*H*-Benzimidazol-2-yl)quinolin-4(1*H*)-one (4a).



6a

2-(1*H*-benzimidazol-2-yl)-3-bromoquinolin-4(1*H*)-one (6a). The compound was obtained by the same procedure starting from 2-(1*H*-benzo[*d*]imidazol-2-yl)quinolin-4(1*H*)-one (**4a**) (1.0 g, 3.83 mmol, 1.0 equiv) and Br_2 (0.61 g, 3.83 mmol, 1.0 equiv) in DMSO (5mL) at room temperature for 48 h. Yield 1.24 g, 95%; brown solid; mp 347−348°C. IR (KBr, cm^{-1}): ν_{max} 3292, 1598, 1567, 1515, 1418, 1315, 1256, 1237, 1177, 1128, 1019, 926, 875, 822, 741, 641, 509, 476, 429. NMR data for **6a**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 12.68 (brs,1H, NH-Q), 8.20 (dd, J = 8.1 Hz, J = 1.2

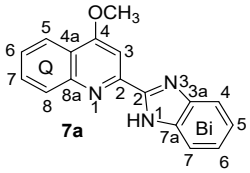
Hz, 1H, H5-Q), 7.84 (d, *J* = 8.1 Hz, 1H, H8-Q), 7.77 (ddd, *J* = 8.1 Hz, *J* = 8.1 Hz, *J* = 1.5 Hz, 1H, H7-Q), 7.76 (brs, 2H, H4 and H7-Bi), 7.46 (ddd, *J* = 8.1 Hz, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H, H6-Q), 7.40-7.33 (m, 2H, H6 and H5-Bi). The signale of NH-Bi has not been observed. $^{13}C\{^{1}H\}$ NMR (125.8 MHz, DMSO-d_6): δ 171.8 (C4-Q), 145.0 (C2-Bi), 140.1 (C2-Q), 139.1 (C8a-Q), 132.6 (C7-Q), 125.3 (C5-Q), 124.5 (C6-Q), 123.3 (C6 and C5-Bi), 123.1 (C4a-Q), 118.9 (C8-Q), 105.8 (C3-Q). The signals of (C3a, C7a, C4 and C7-Bi) have not been observed. HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{16}H_{11}{}^{79}BrN_3O$ 340.0080, found 340.0079; $[M+H]^+$ calcd for $C_{16}H_{11}{}^{81}BrN_3O$ 342.0061, found 342.0059.



6b

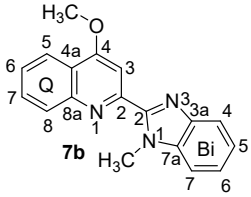
2-(1*H*-benzimidazol-2-yl)-3-iodoquinolin-4(1*H*)-one (6b). The compound was obtained by the same procedure starting from 2-(1*H*-benzo[*d*]imidazol-2-yl)quinolin-4(1*H*)-one (**4a**) (1.0 g, 3.83 mmol, 1.0 equiv) and I_2 (0.97 g, 3.83 mmol, 1.0 equiv) in DMSO (5mL) at room temperature for 48 h. Yield 1.44 g, 97%; brown solid; mp 361−362°C. IR (KBr, cm^{-1}): ν_{max} 3449, 3286, 3171, 3057, 2917, 1621, 1551, 1493, 1470, 1416, 1334, 1210, 1131, 1018, 864, 753, 691, 569, 510. NMR data for **6b**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 12.71 (brs,1H, NH-Q), 8.19 (dd, *J* = 8.1 Hz, *J* = 1.2 Hz, 1H, H5-Q), 7.77 (dd, *J* = 8.1 Hz, *J* = 8.1 Hz, 1H, H7-Q), 7.75-7.72 (brs, 2H, H4 and H7-Bi), 7.73 (dd, *J* = 8.1 Hz, *J* = 1.2 Hz, 1H, H8-Q), 7.47 (ddd, *J* = 8.1 Hz, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H, H6-Q), 7.40-7.36 (m, 2H, H6 and H5-Bi). The signal of NH-Bi was not been observed. $^{13}C\{^{1}H\}$ NMR (125.8 MHz, DMSO-d_6): δ 173.5 (C4-Q), 146.8 (C2-Bi), 143.5 (C2-Q), 139.3 (C8a-Q), 137.7 (C3a and C7a-Bi), 132.7 (C7-Q), 125.5 (C5-Q), 124.7 (C6-Q), 123.4 (C6 and C5-Bi), 121.2 (C4a-Q), 118.5 (C8-Q), 115.8 (C4 and C7-Bi), 85.9 (C3-Q). HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{16}H_{11}IN_3O$ 387.9941, found 387.9940.

General Procedure for the Synthesis of 7a-b: potassium hydroxide (0.64 g, 11.48 mmol, 3.0 equiv) and **4a** (1.0 g, 3.83 mmol, 1.0 equiv) were dissolved in ethanol (10 ml). CH_3I (1.74 g, 12.26 mmol, 3.2 equiv) was added to the resulting solution with stirring and cooling at 0 °C over 30 min and the mixture was stirred for another 30 min. at the same temperature. After that, stirring was continued at room temperature for 7 hours. After separating the potassium iodide, the filtrate was evaporated in a vacuum, first at a low temperature and finally at an elevated temperature. The resulting oily residue was purified by column chromatography using a mixture of hexane–EtOAc as eluent gave the *O*- (**7a**) and *O*,*N*-methylated (**7b**) products.



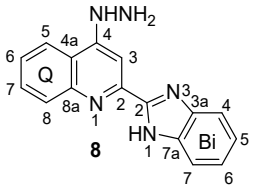
7a

2-(Benzimidazol-2-yl)-4-methoxyquinoline (**7a**). Chromatographic eluent: hexane–EtOAc (100/1), R_f=0.25. Compound was obtained in 0.1g, 33% yield as a white powder, mp 263−264°C. IR (KBr, cm^{-1}): ν_{max} 3446, 2925, 2854, 1729, 1591, 1509, 1461, 1408, 1216, 1112, 984, 897, 765, 750, 557, 472, 432. NMR data for **7a**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 13.13 (s, 1H, N(1)H-Bi), 8.20 (dd, *J* = 8.1 6Hz, *J* = 1.0 Hz, 1H, H5-Q), 8.10 (dd, , *J* = 8.1 Hz, *J* = 1.0 Hz, 1H, H8-Q), 7.93 (s, 1H, H3-Q), 7.84 (dd, *J* = 8.1 Hz, *J* = 1.0 Hz, 1H, H7-Q), 7.76 (dd, *J* = 7.9 Hz, *J* = 1.1 Hz, 1H, H4-Bi), 7.63 (dd, *J* = 8.1 Hz, *J* = 1.0 Hz, 1H, H6-Q), 7.62 (dd, *J* = 7.9 Hz, *J* = 1.1 Hz, 1H, H7-Bi), 7.30 (dd, *J* = 7.9 Hz, *J* = 1.1 Hz, 1H, H6-Bi), 7.26 (dd, *J* = 7.9 Hz, *J* = 1.1 Hz, 1H, H5-Bi), 4.20 (s, 3H, OCH_3). $^{13}C\{^{1}H\}$ NMR (125.8 MHz, DMSO-d_6): δ162.3 (C4-Q), 150.9 (C2-Bi), 149.9 (C2-Q), 148.2 (C8a-Q), 143.7 (C4a-Bi), 135.1 (C7a-Bi), 130.6 (C7-Q), 128.5 (C8-Q), 126.5 (C6-Q), 123.5 (C6-Bi), 122.0 (C5-Bi), 121.7 (C5-Q), 120.9 (C4a-Q), 119.4 (C4-Bi), 112.3 (C7-Bi), 98.3 (C3-Q), 56.3 (C4a-Q (CH3)). HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{17}H_{14}N_3O$ 276.1131, found 276.1131.



7b

4-Methoxy-2-(1-methylbenzimidazol-2-yl)quinoline (**7b**). Chromatographic eluent: hexane– EtOAc (10/8), R_f=0.28. Compound was obtained in 0.22g, 62% yield as a white powder, mp 130−131°C. IR (KBr, cm^{-1}): ν_{max} 3197, 2925, 2854, 1619, 1599, 1461, 1401, 1327, 1204, 1159, 1109, 1077, 986, 919, 906, 765, 743, 733, 433. NMR data for **7b**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 8.20 (brdd, J = 8.3 Hz, J = 1.1 Hz, 1H, H5-Q), 8.12 (brd, J = 8.0 Hz, 1H, H8-Q), 7.94 (s, 1H, H3-Q), 7.84 (ddd, J = 7.7 Hz, J = 7.7 Hz, J = 1.4 Hz, 1H, H7-Q), 7.79 (brd, J = 7.8 Hz, 1H, H4-Bi), 7.71 (brd, J = 8.0 Hz, 1H, H7-Bi), 7.65 (ddd, J = 7.6 Hz, J = 7.6 Hz, J = 1.2 Hz, 1H, H6-Q), 7.38 (ddd, J = 7.5 Hz, J = 7.1 Hz, J = 1.1 Hz, 1H, H6-Bi), 7.32 (ddd, J = 7.8 Hz, J = 7.5 Hz, J = 1.1 Hz, 1H, H5-Bi), 4.43 (s, 3H, NCH_3-Bi), 4.18 (s, 3H, OCH_3-Q). ^{13}C{^{1}H} NMR (125.8 MHz, DMSO-d_6): δ 162.0 (C4-Q), 151.5 (C2-Q), 149.5 (C2-Bi), 147.7 (C8a-Q), 141.9 (C3a), 137.4 (C7a-Bi), 130.5 (C7-Q), 129.0 (C8-Q), 126.8 (C6-Q), 123.5 (C6-Bi), 122.5 (C5-Bi), 121.4 (C5-Q), 120.3 (C4a-Q), 119.6 (C4-Bi), 110.9 (C7-Bi), 100.5 (C3-Q), 56.3 (C4a-Q (CH3)), 33.0 (C1a-Bi). HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{18}H_{16}N_3O$ 290.1288, found 290.1292.



8

2-(1*H*-benzimidazol-2-yl)-4-hydrazineylquinoline (8). 2-(1*H*-Benzimidazol-2-yl)quinolin-4(1*H*)-one (**4a**) (1.0 g, 3.83 mmol) in 7 mL 64% hydrazine hydrate was stirred at 120 °C for 10 h. The mixture was left overnight. The precipitate was filtered off and washed with water (3×10 mL), dried in air to obtain 10 as a beige powder. Yield 0.79 g, 75%; mp 147−149°C. IR (KBr, cm^{-1}): ν_{max} 3421, 3308, 1590, 1563, 1523, 1416, 1351, 1069, 916, 849, 765, 738. NMR data for **8**: ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 8.63 (brs,1H, NH-Q), 8.19 (dd, J = 8.4 Hz, J = 1.0 Hz, 1H, H5-Q), 7.95 (s, 1H, H3-Q), 7.94 (d, J = 8.4 Hz, 1H, H8-Q), 7.68 (ddd, J = 8.0 Hz, J = 8.0 Hz, J = 1.3 Hz, 1H, H7-Q), 7.69-7.64 (m, 2H, H3 and H7-Bi), 7.43 (ddd, J = 8.0 Hz, J = 8.0 Hz, J = 1.3 Hz, 1H, H6-Q), 7.24-7.21 (m, 2H, H5 and H6-Bi). The signal of NH-Bi was not been observed. ^{13}C{^{1}H} NMR (125.8 MHz, DMSO-d_6): δ 153.5 (C4-Q), 152.0 (C2-Bi), 149.0 (C2-Q), 147.7 (C8a-Q), 138.7 (C3a and C7a-Bi), 129.3 (C7-Q), 128.7 (C8-Q), 124.3 (C6-Q), 124.1 (C5 and C6-Bi), 121.6 (C5-Q), 116.0 (C3 and C7-Bi), 117.4 (C4a-Q), 95.9 (C3-Q). HRMS (ESI), *m/z*: $[M+H]^+$ calcd for $C_{16}H_{14}N_5$ 276.1244, found 276.1245.

References:

1.V. A. Mamedov, V. R. Galimullina, Z.-W. Qu, H. Zhu, V. V. Syakaev, D. V. Nikolaeva, I. Kh. Rizvanov, A. T. Gubaidullin, O. G. Sinyashina, S. Grimme, ANRORC type rearrangement/intermolecular cyclocondensation cascade of 5,6-dicyano-3-(2-oxo-2-ethyl)pyrazin-2(1*H*)-ones with hydrazine hydrate for the synthesis of 2-(pyrazol-3-yl)imidazo[4,5-d]pyridazines, *Org. Biomol. Chem.*, 2025, **23**, 2180–2189.

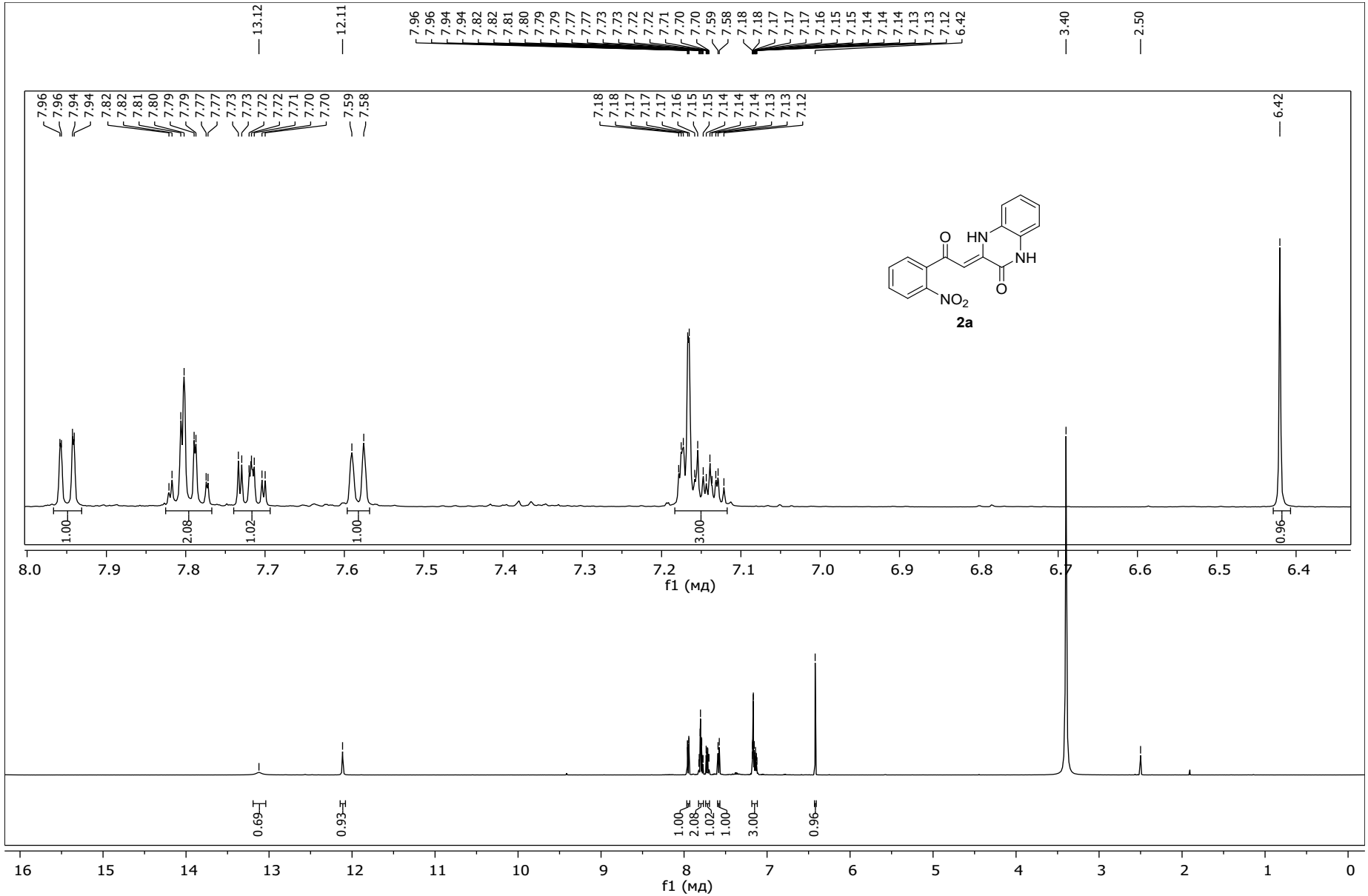


Figure S1. 1D ^{1}H NMR spectrum of **2a** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

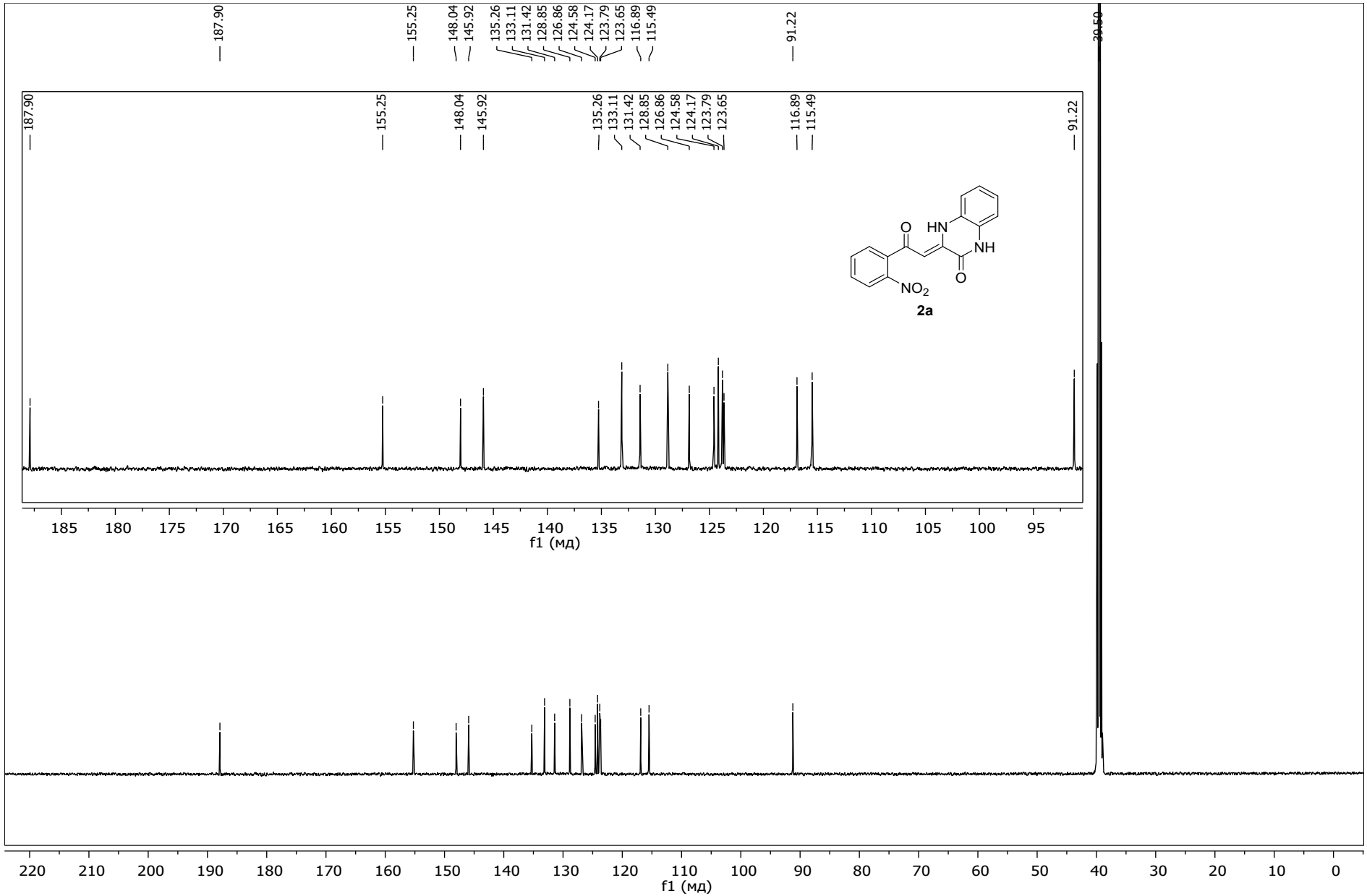


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **2a** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

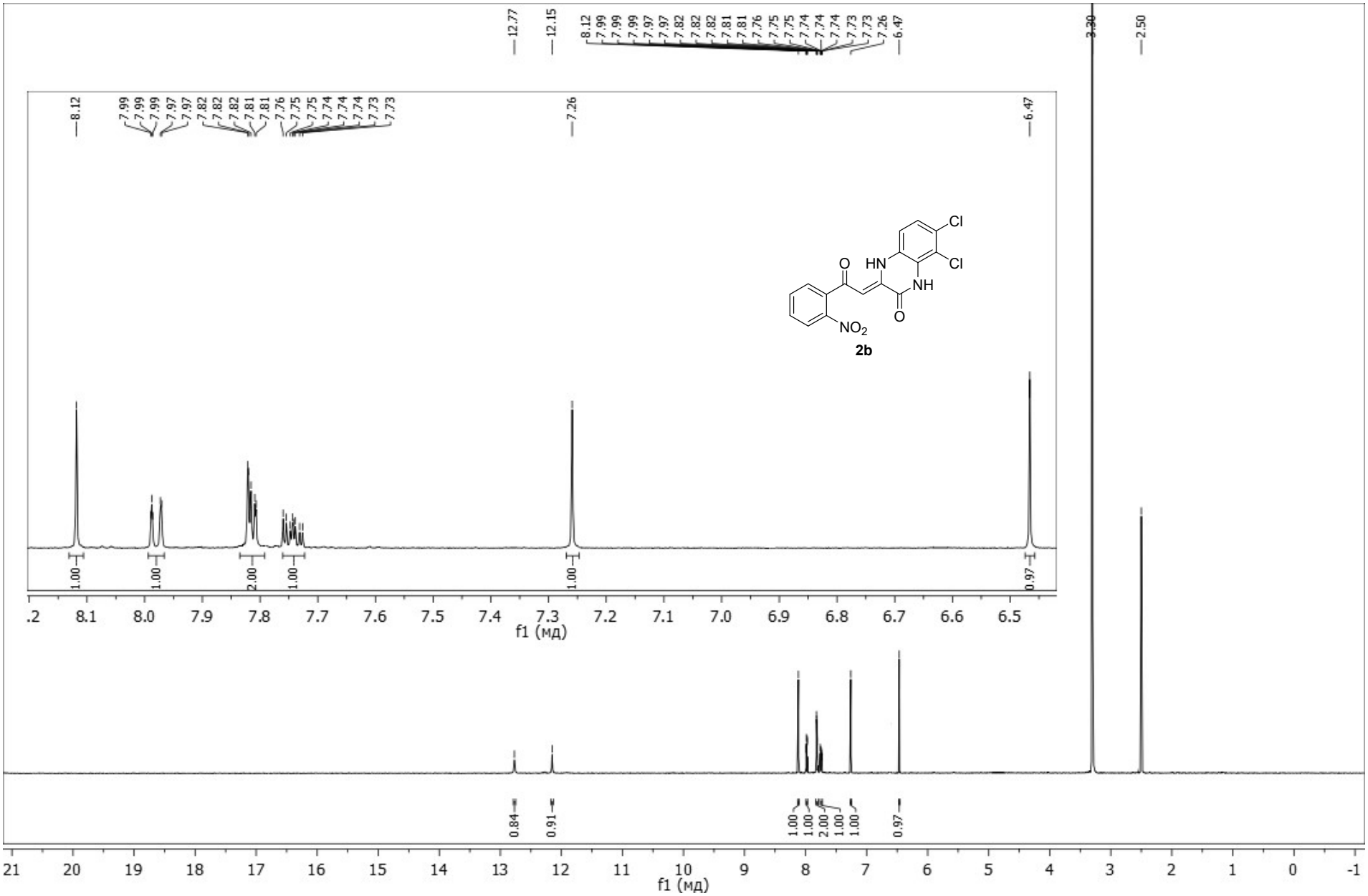


Figure S3. 1D ^{1}H NMR spectrum of **2b** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

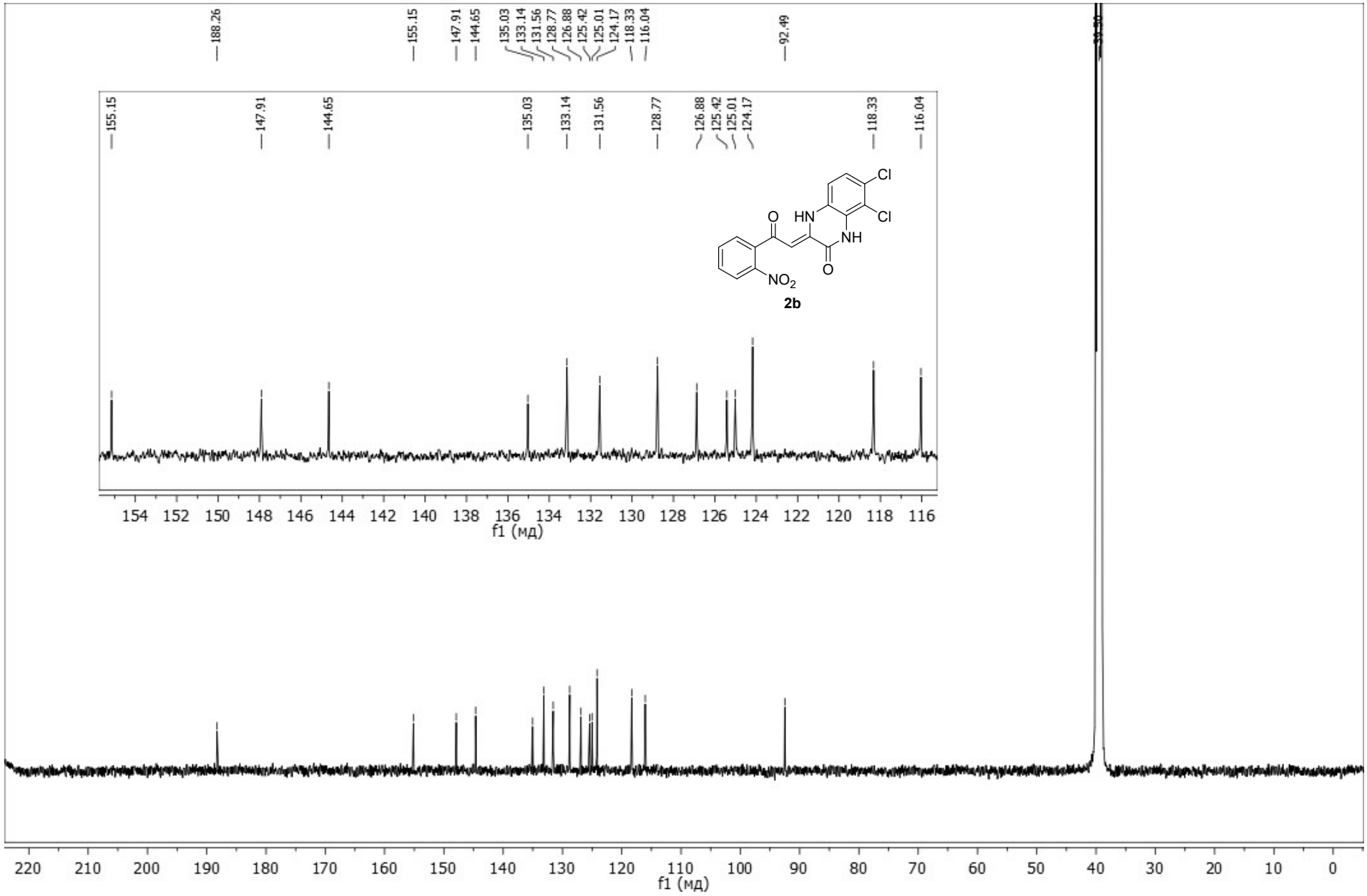


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of **2b** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

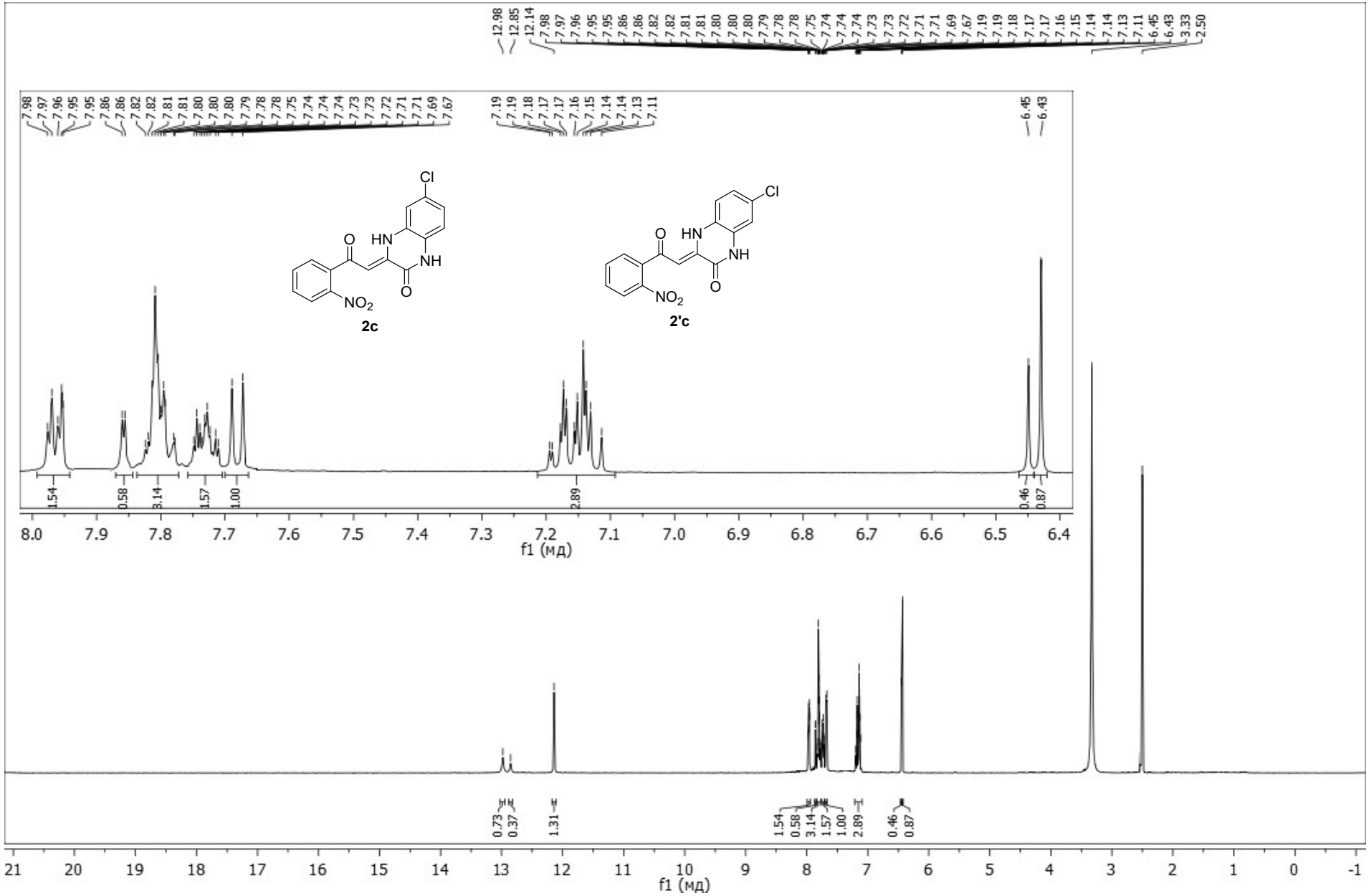


Figure S5. 1D ^{1}H NMR spectrum of **2c** and **2′c** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

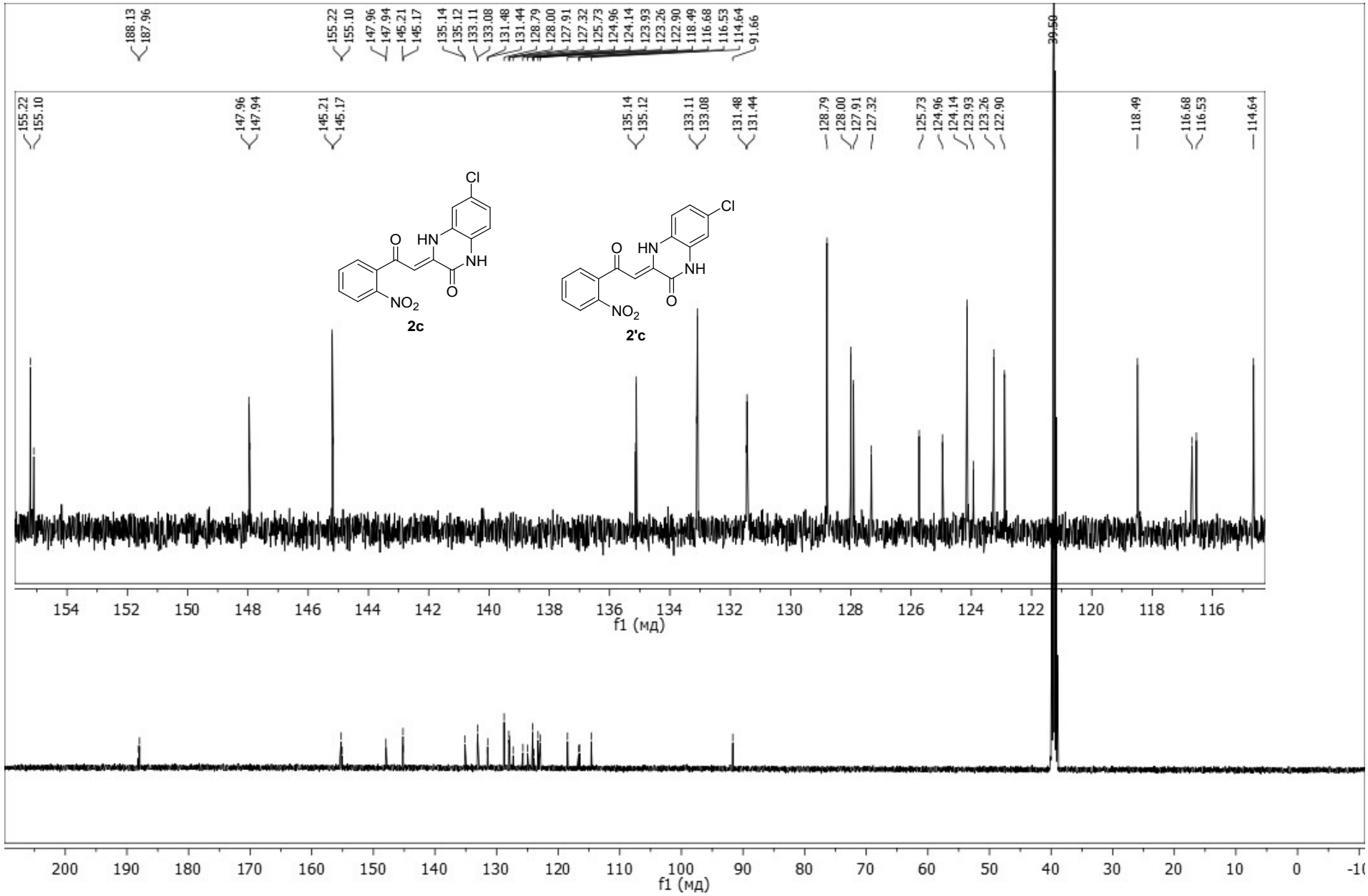


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **2c** and **2′c** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

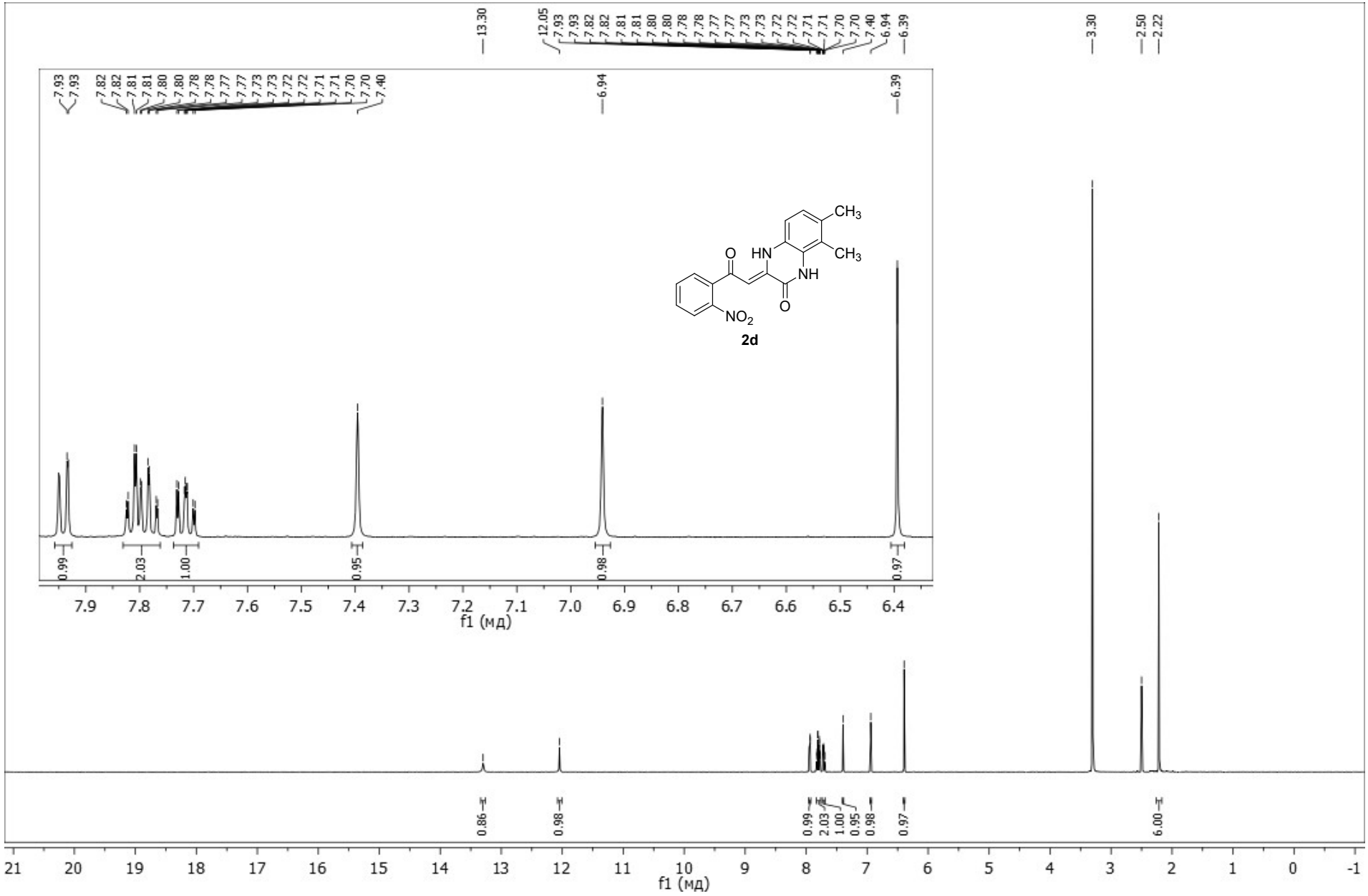


Figure S7. 1D ^{1}H NMR spectrum of **2d** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

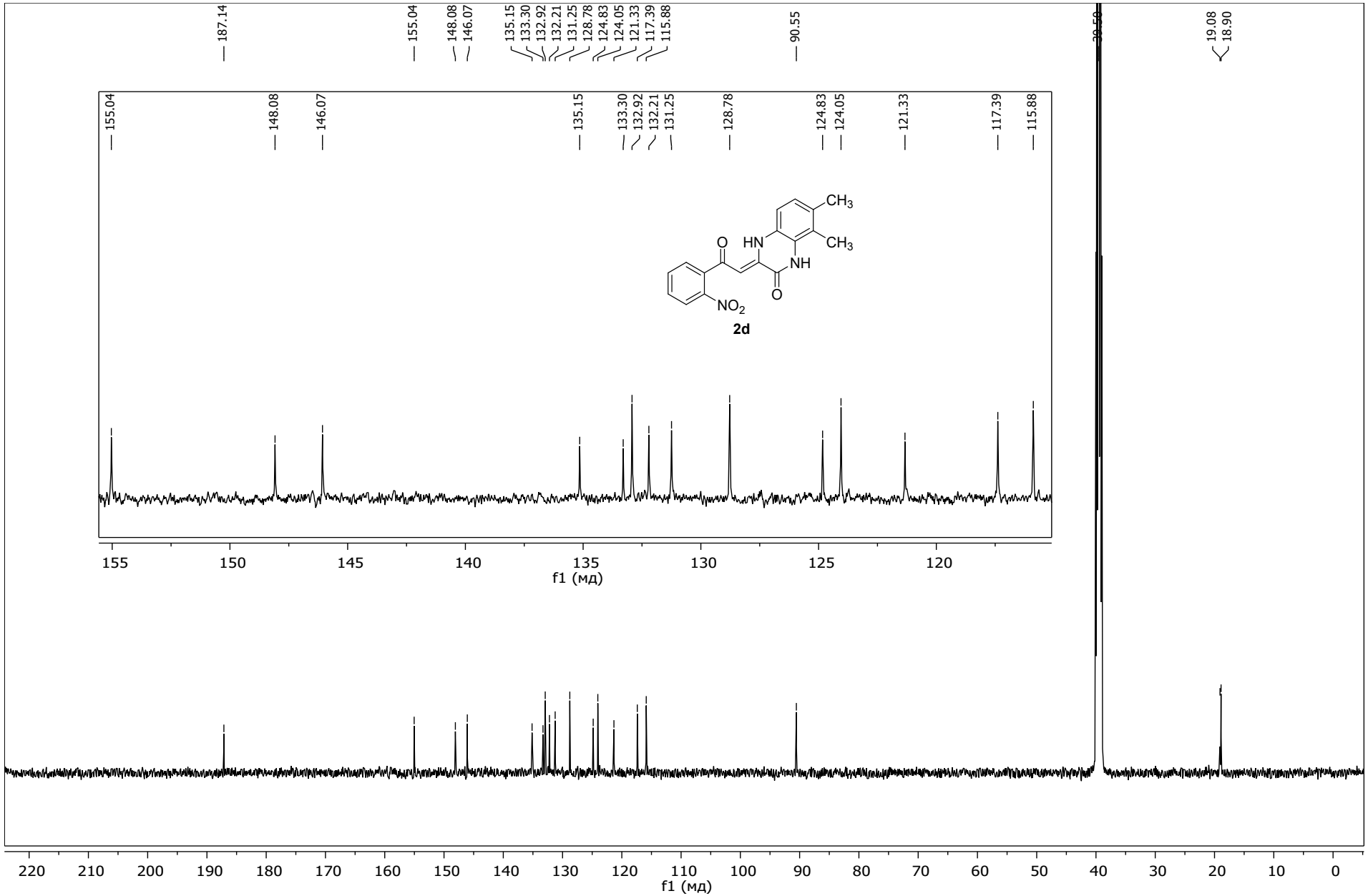


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of **2d** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

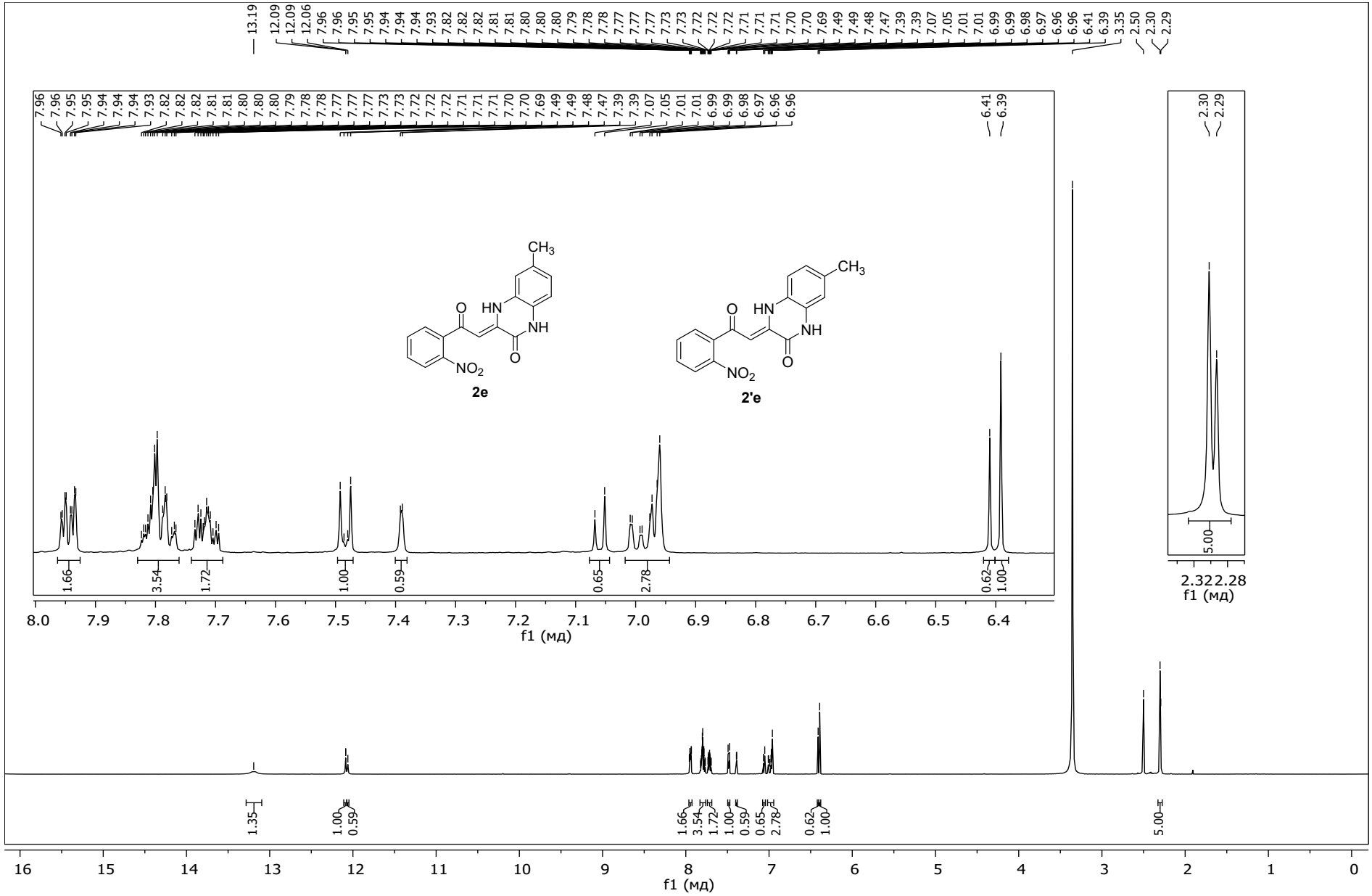


Figure S9. 1D ^{1}H NMR spectrum of **2e** and **2′e** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

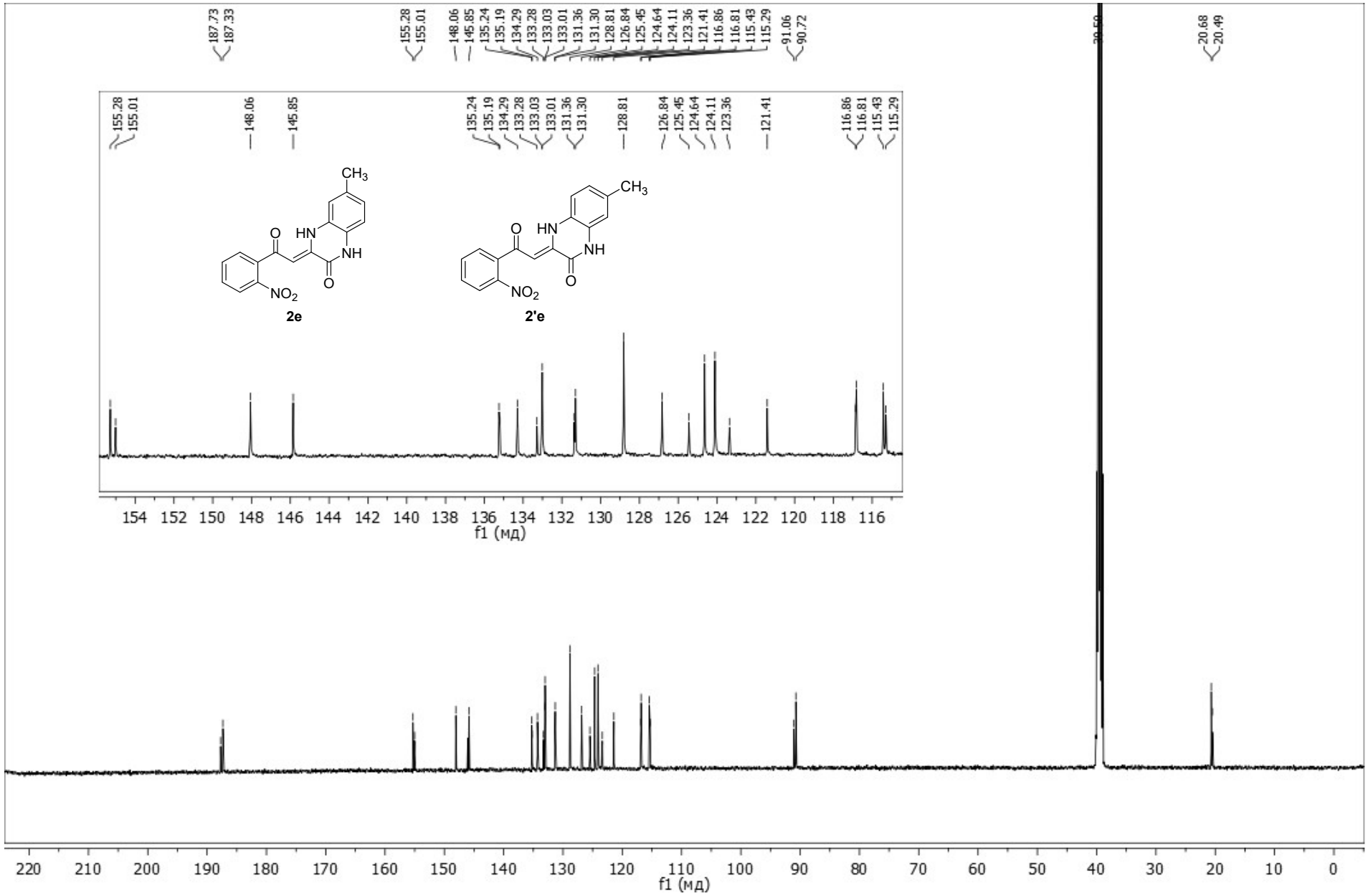


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of **2e** and **2′e** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

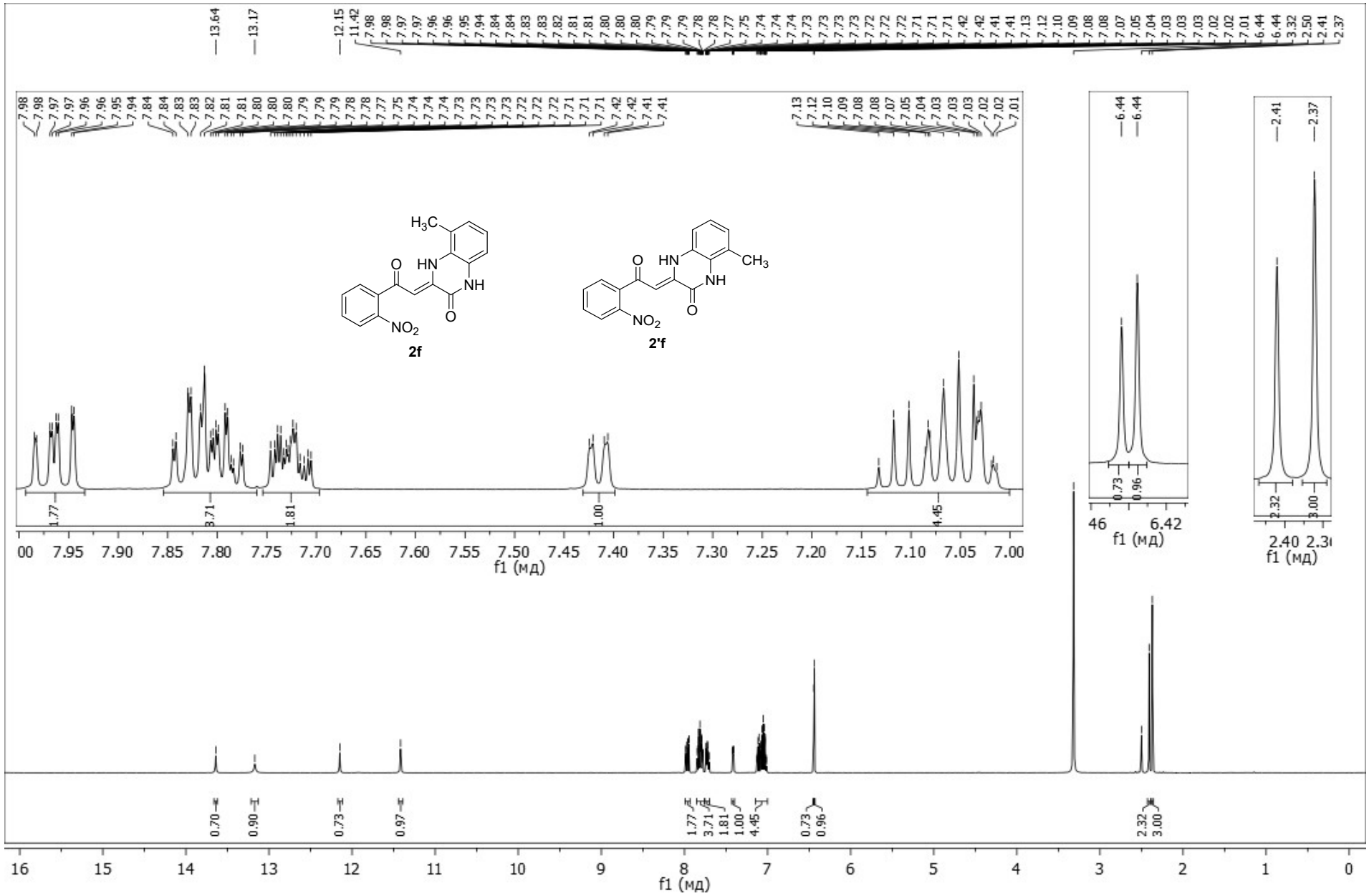


Figure S11. 1D ^{1}H NMR spectrum of **2f** and **2′f** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

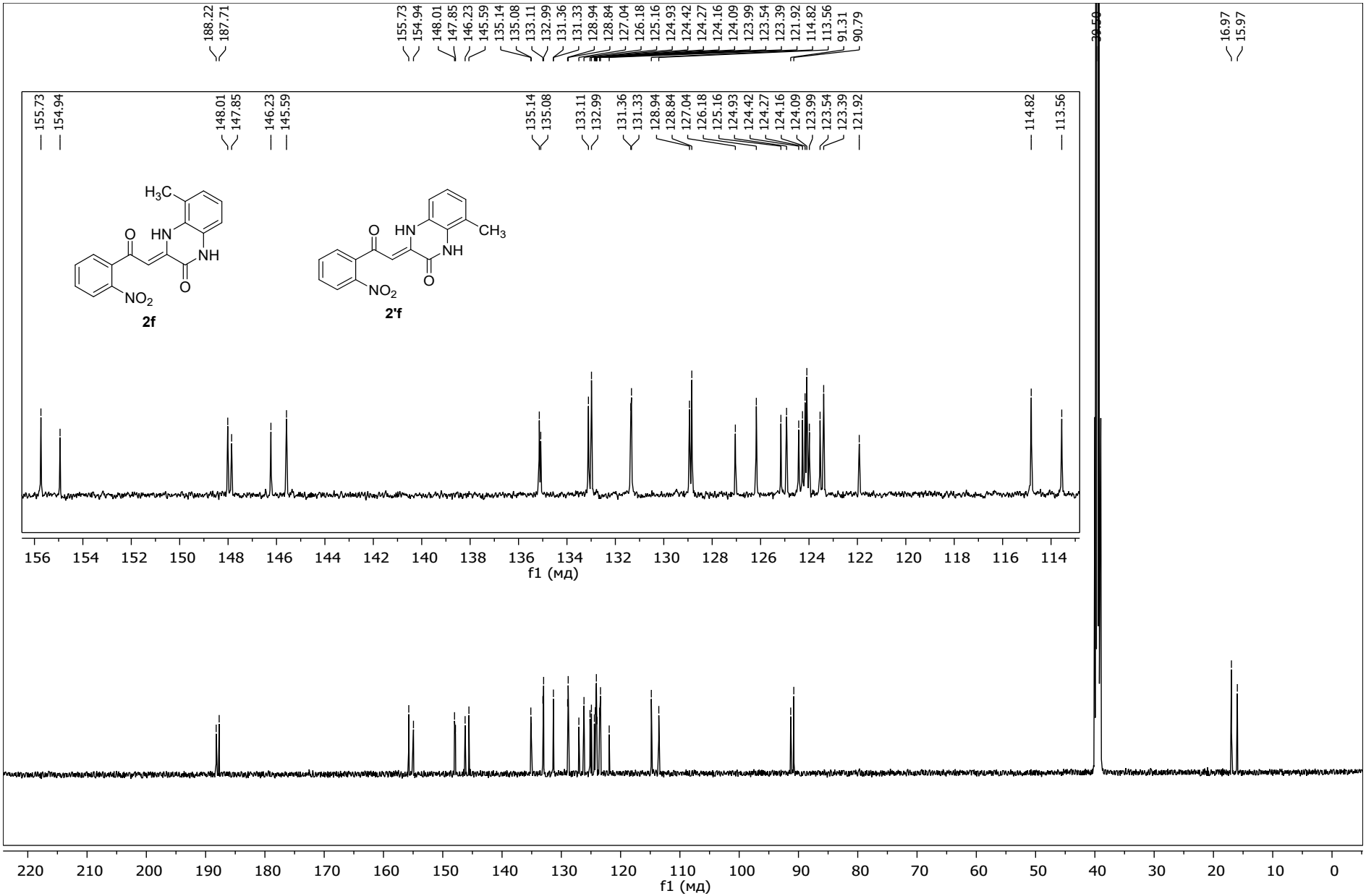


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of **2f** and **2′f** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

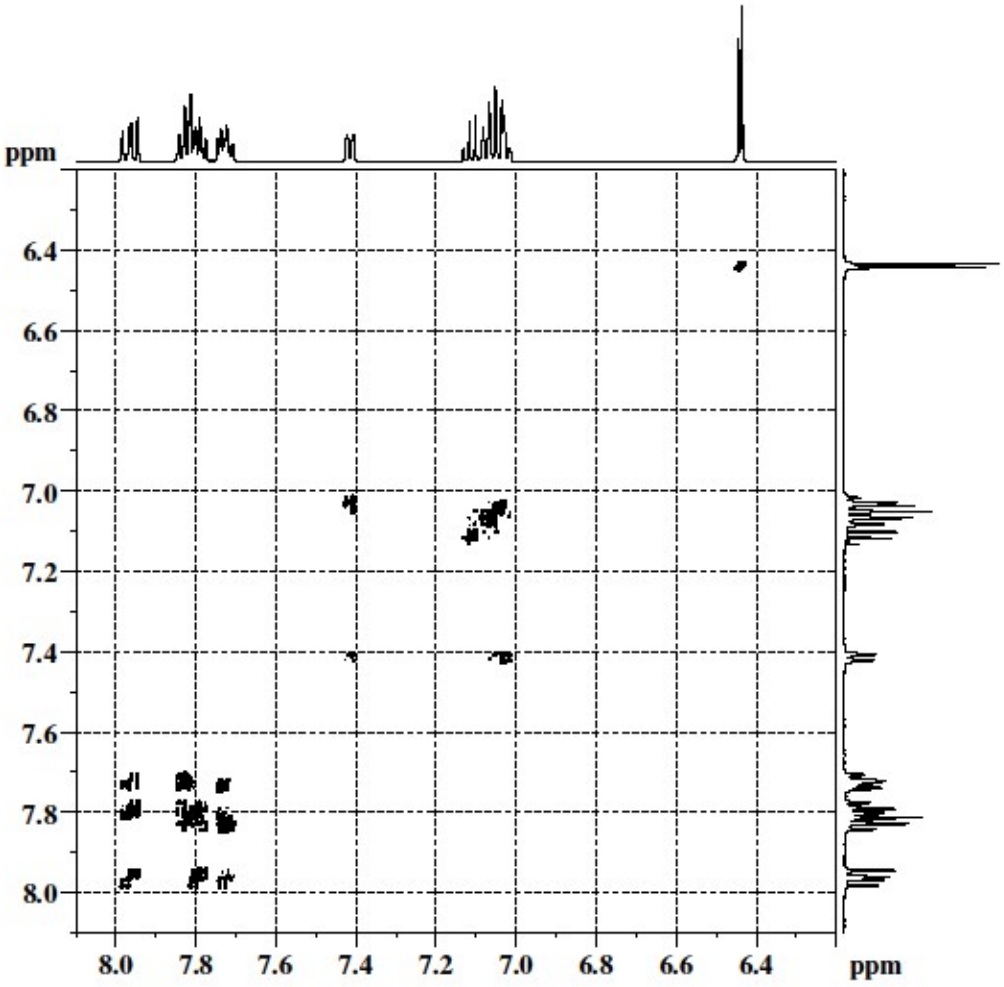


Figure S13. 2D ^{1}H-^{1}H COSY NMR spectrum of **2f** and **2′f** in DMSO-d_6 at T = 303 K.

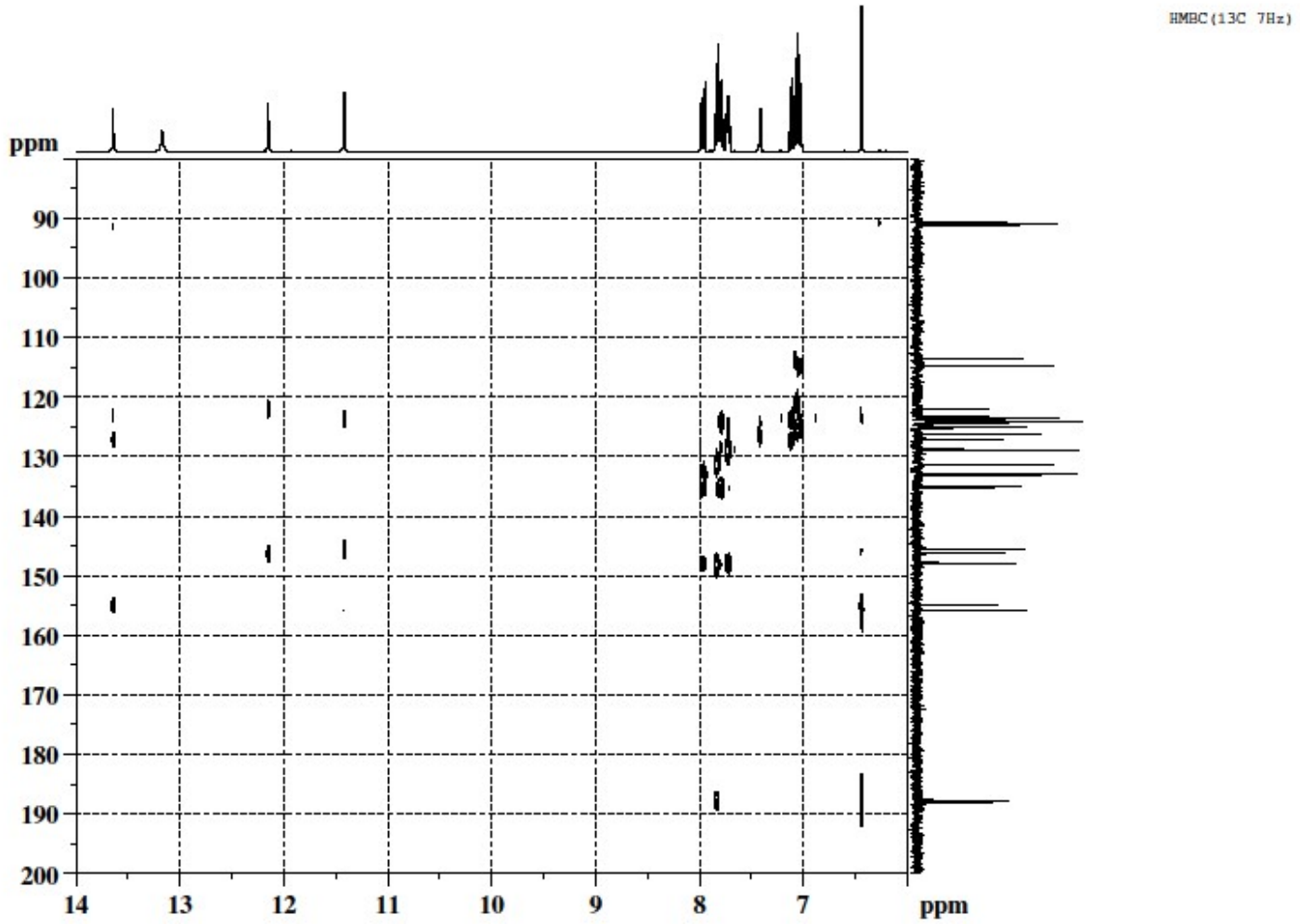


Figure S14. 2D ^{1}H-^{13}C HMBC NMR spectrum of **2f** and **2′f** in DMSO-d_6 at T = 303 K.

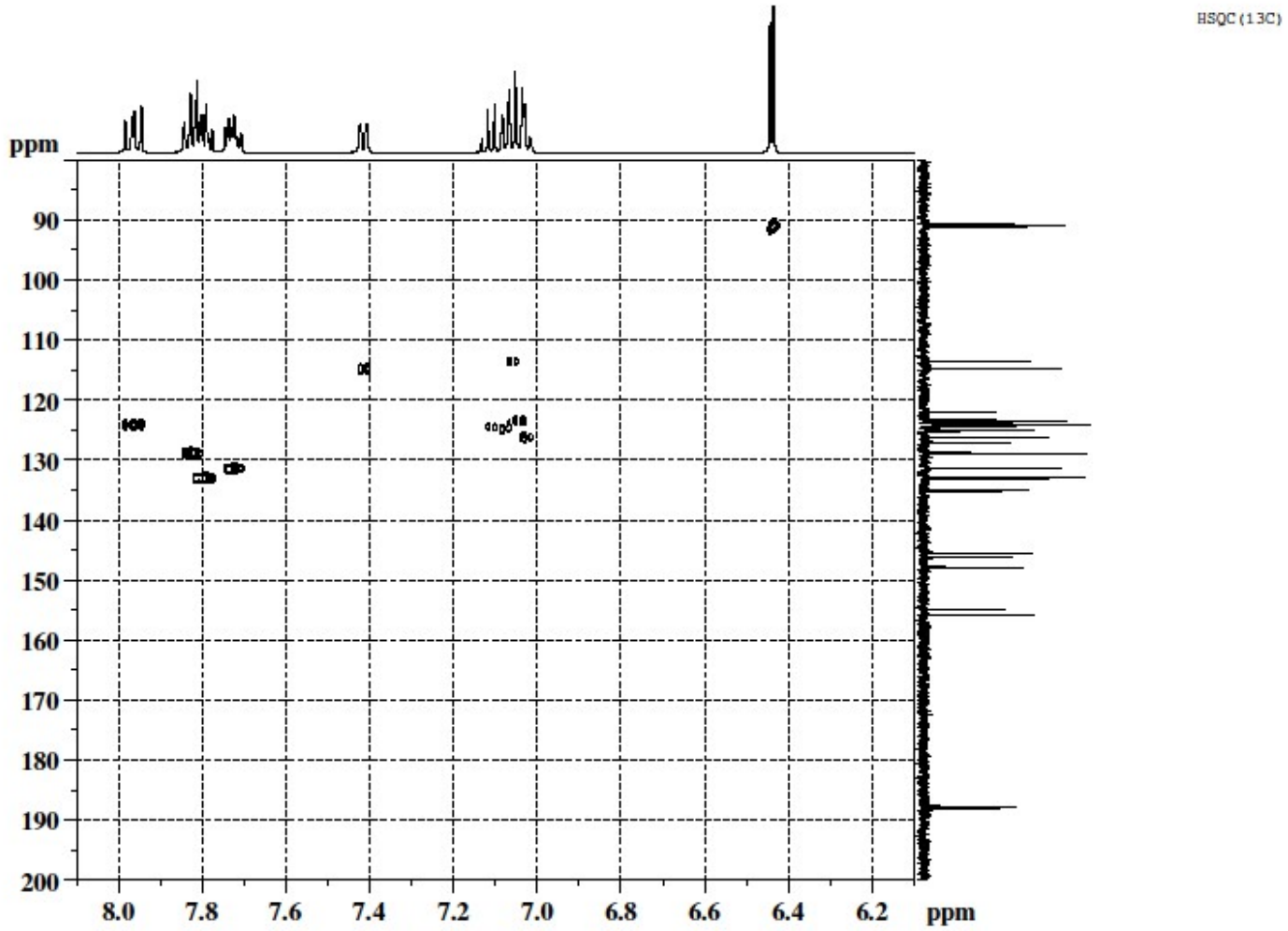


Figure S15. 2D 1H-^{13}C HSQC NMR spectrum of **2f** and **2′f** in DMSO-d_6 at T = 303 K.

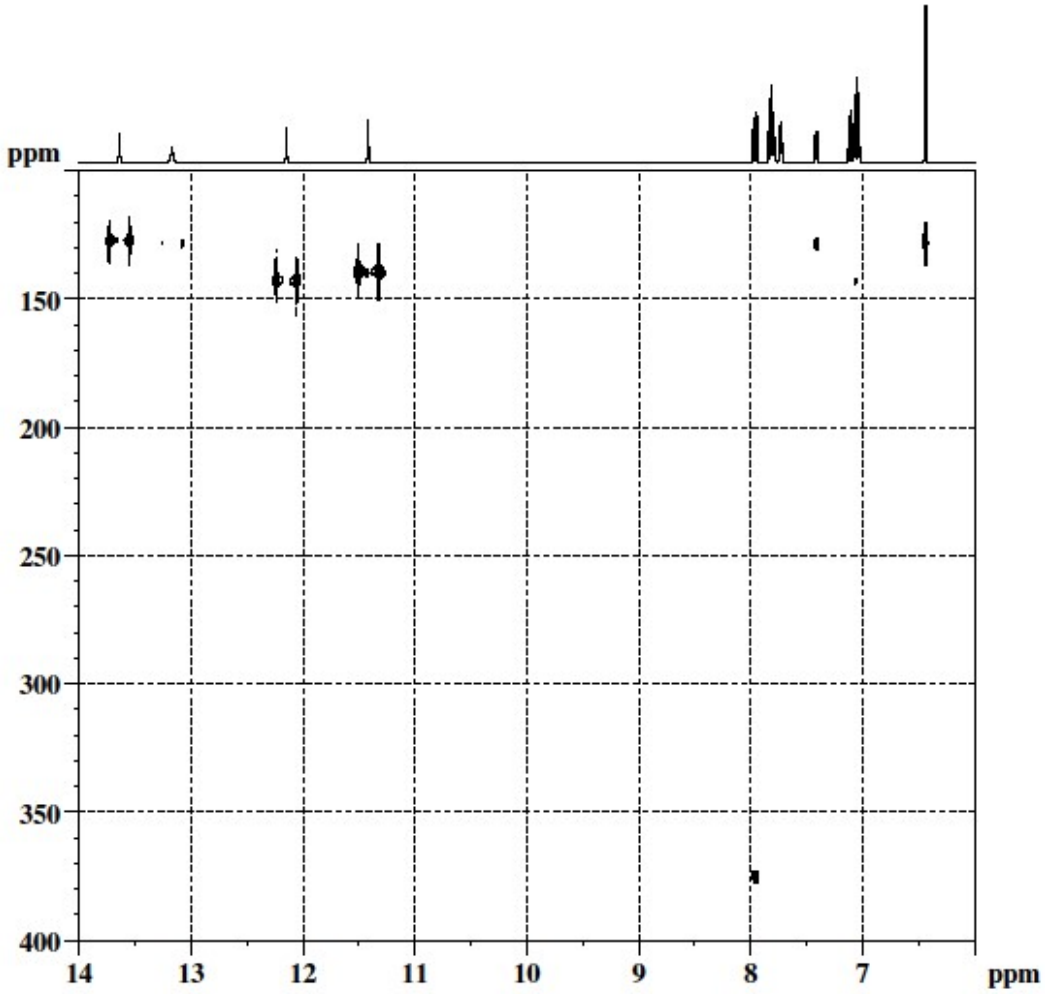


Figure S16. 2D ^{1}H-^{15}N HMBC NMR spectrum of **2f** and **2′f** in DMSO-d_6 at T = 303 K.

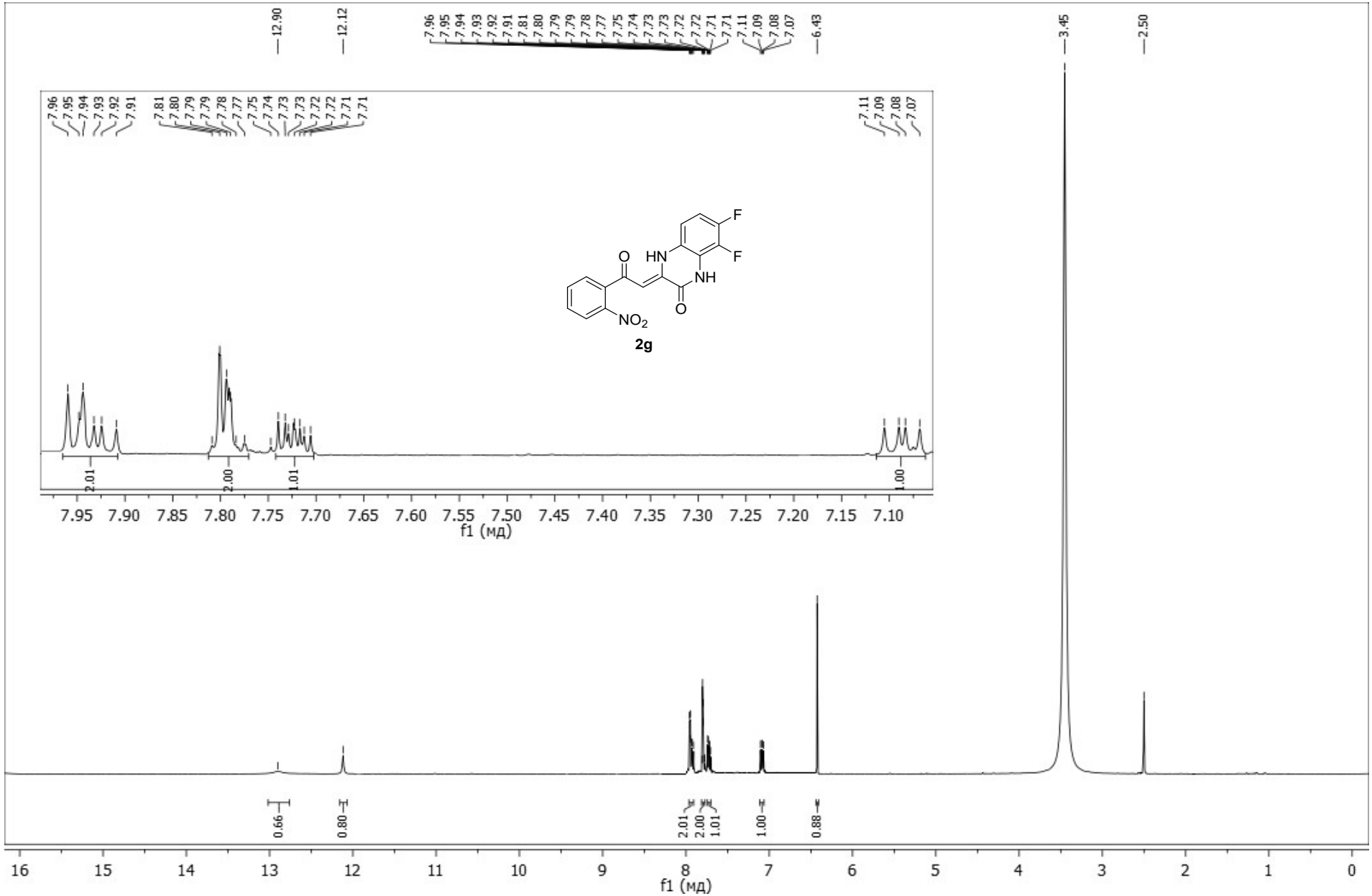


Figure S17. 1D ^{1}H NMR spectrum of **2g** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

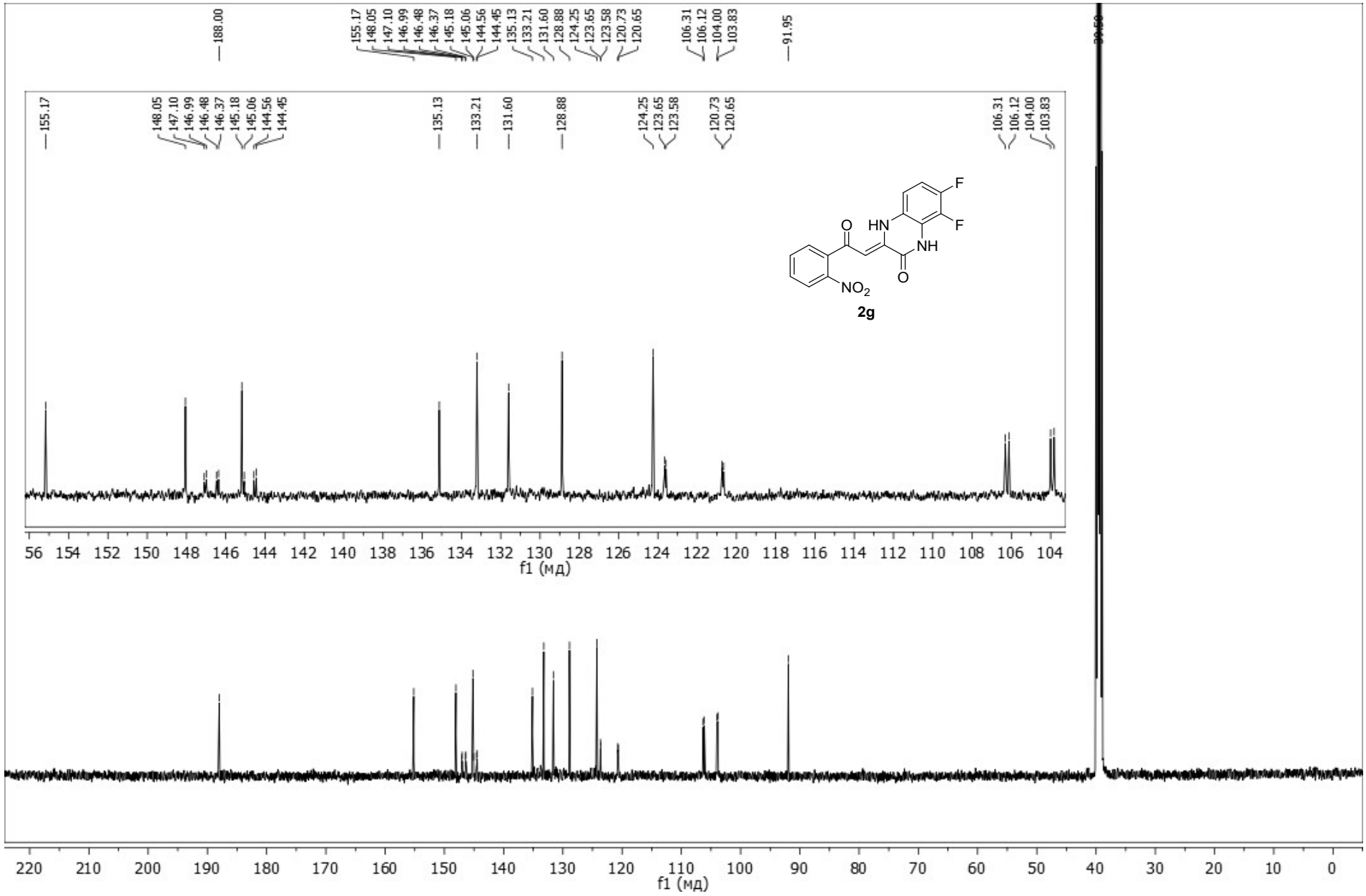


Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum of **2g** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

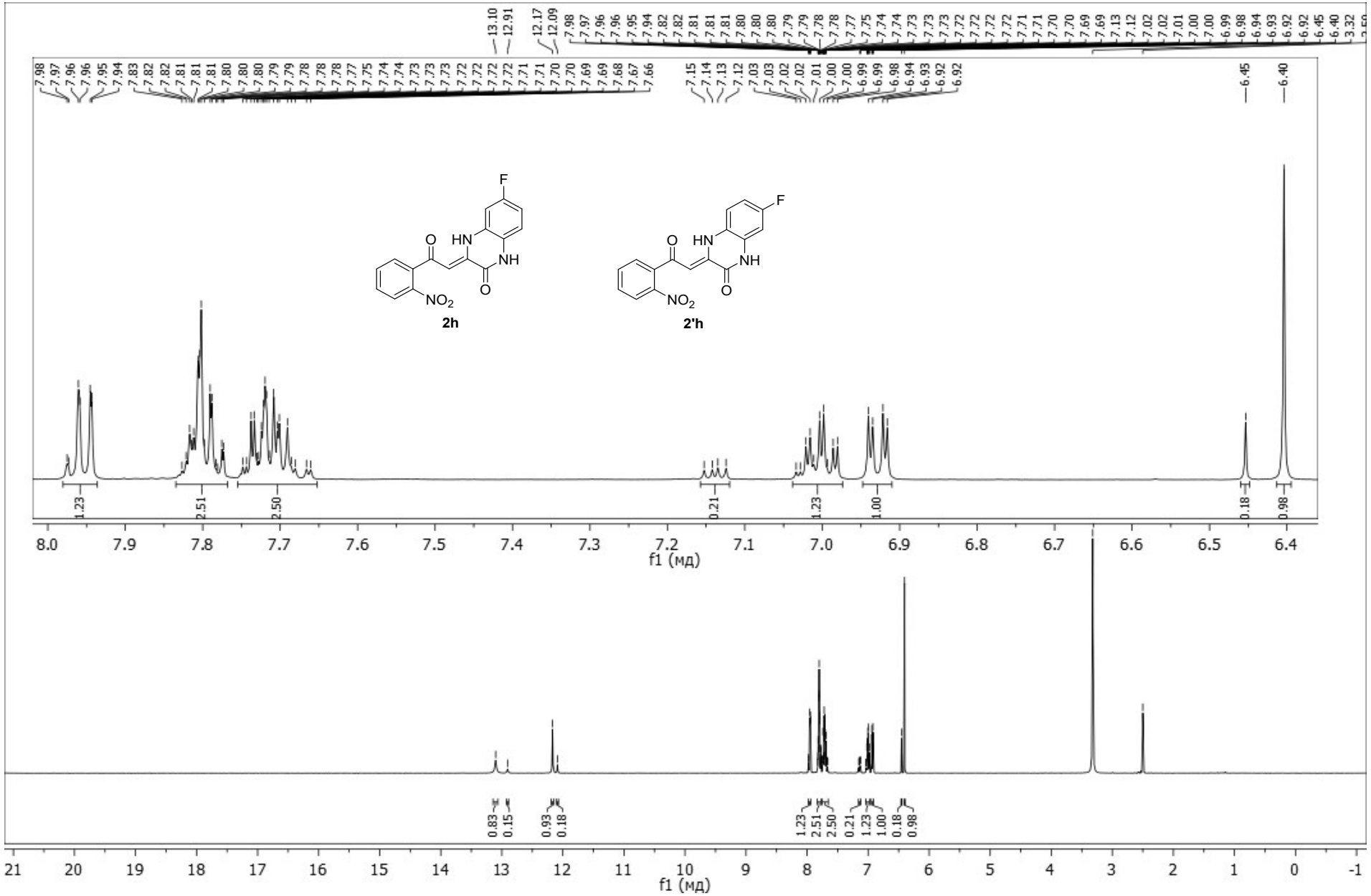


Figure S19. 1D ^{1}H NMR spectrum of **2h** and **2′h** in DMSO-d_6 at T = 303 K. Chemical shifts are given in Hz (Bruker spectrometer at 500.1 MHz).

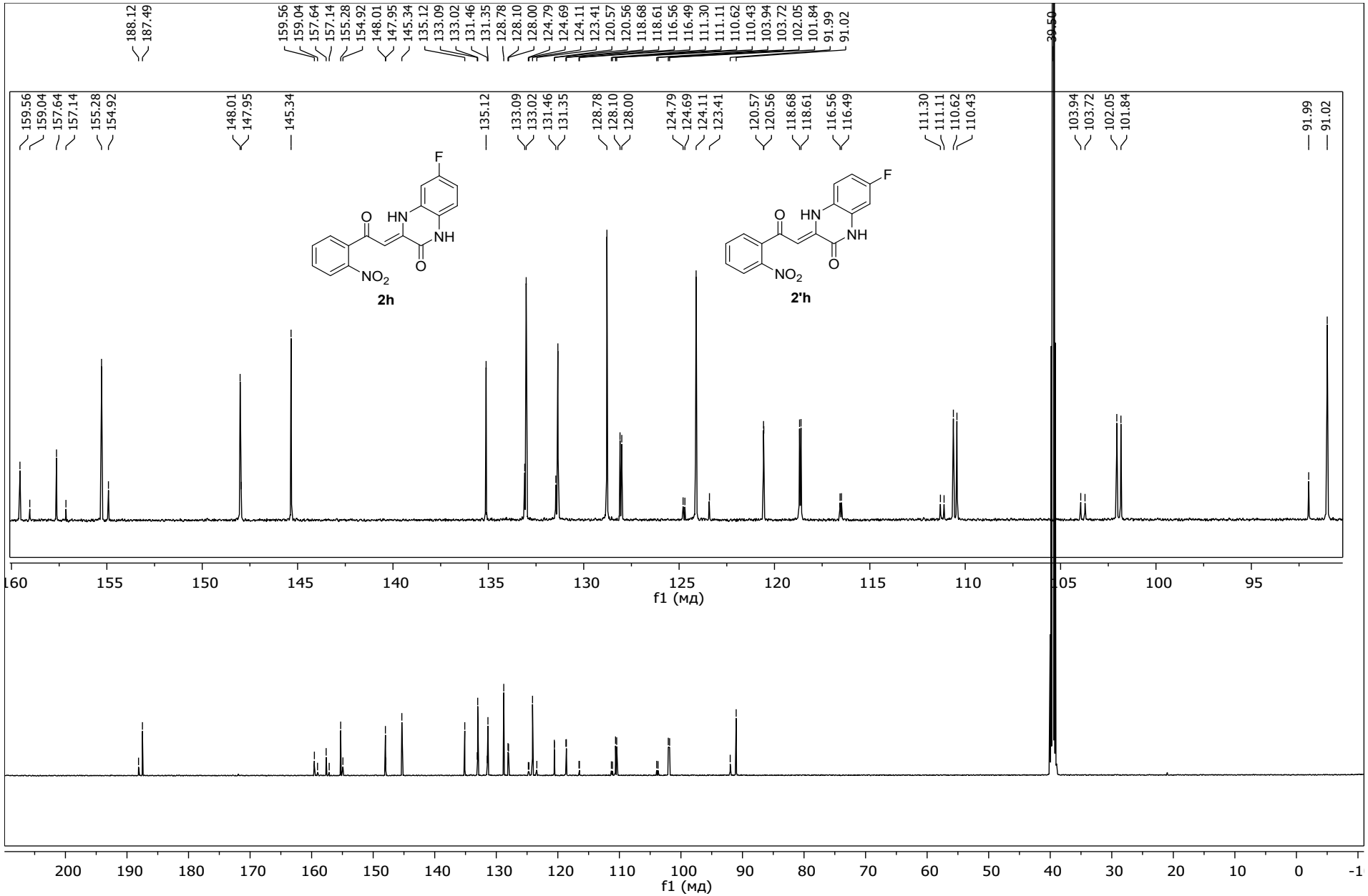


Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum of **2h** and **2′h** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

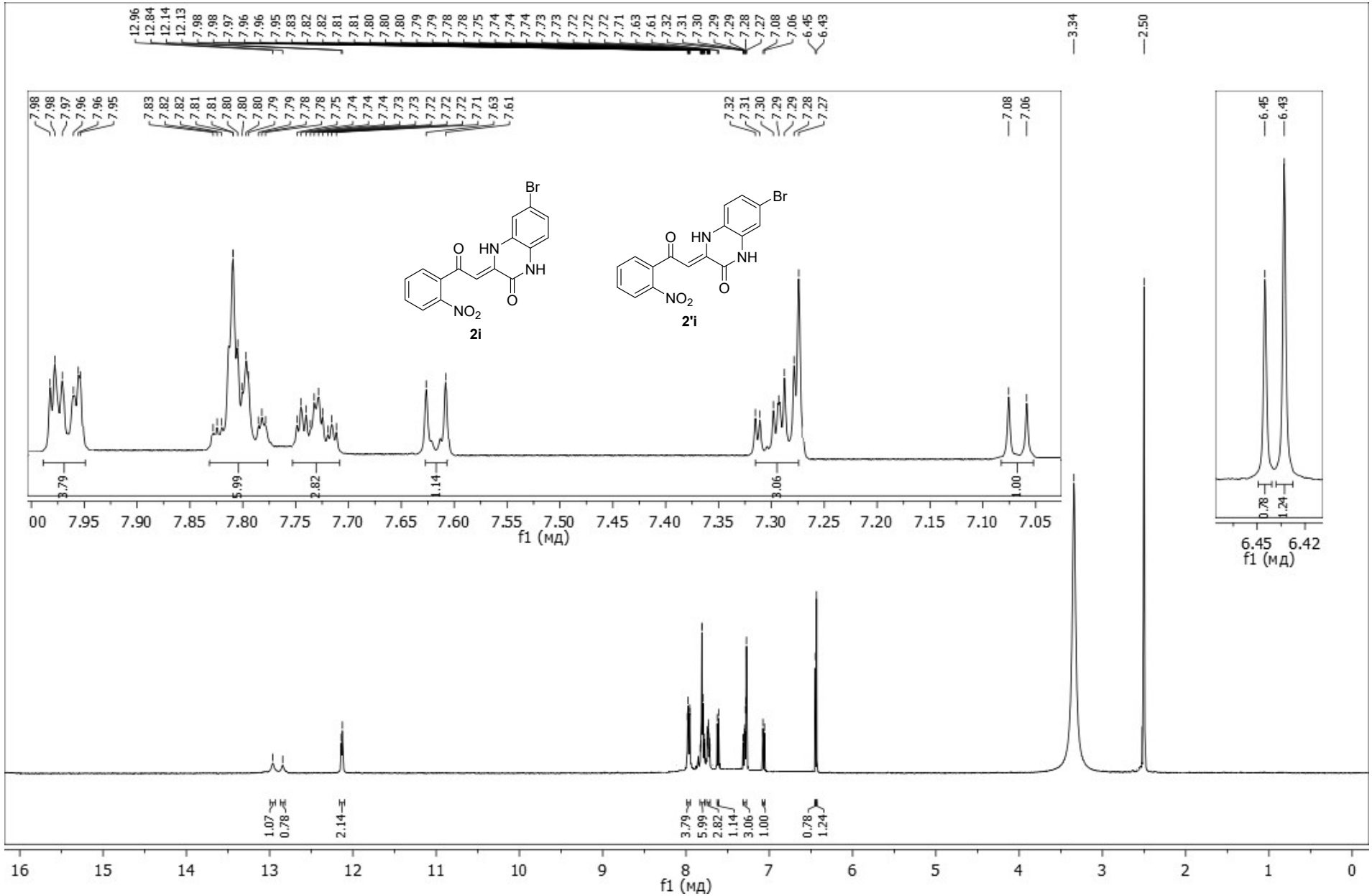


Figure S21. 1D ^{1}H NMR spectrum of **2i** and **2′i** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

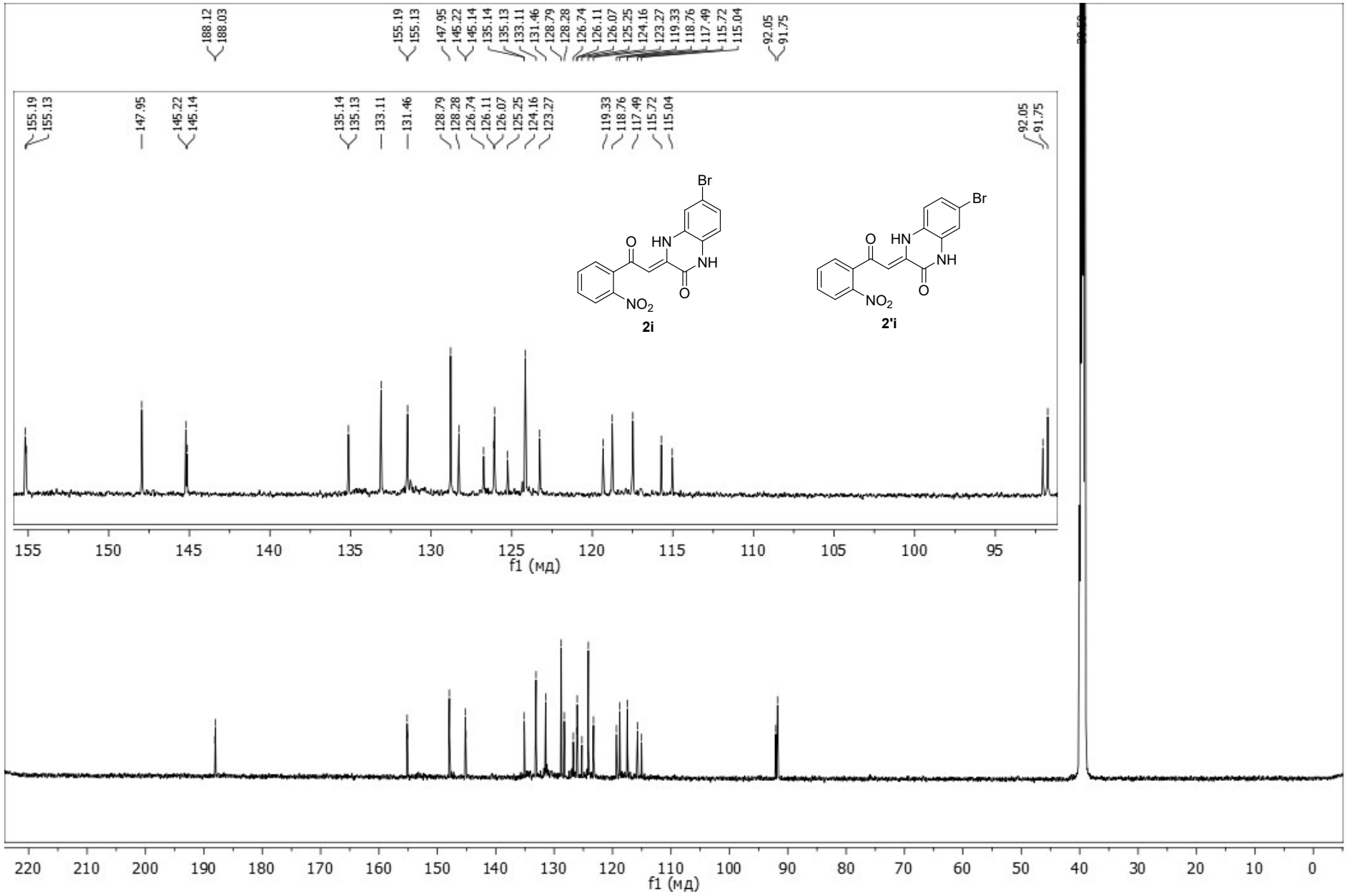


Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum of **2i** and **2′i** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

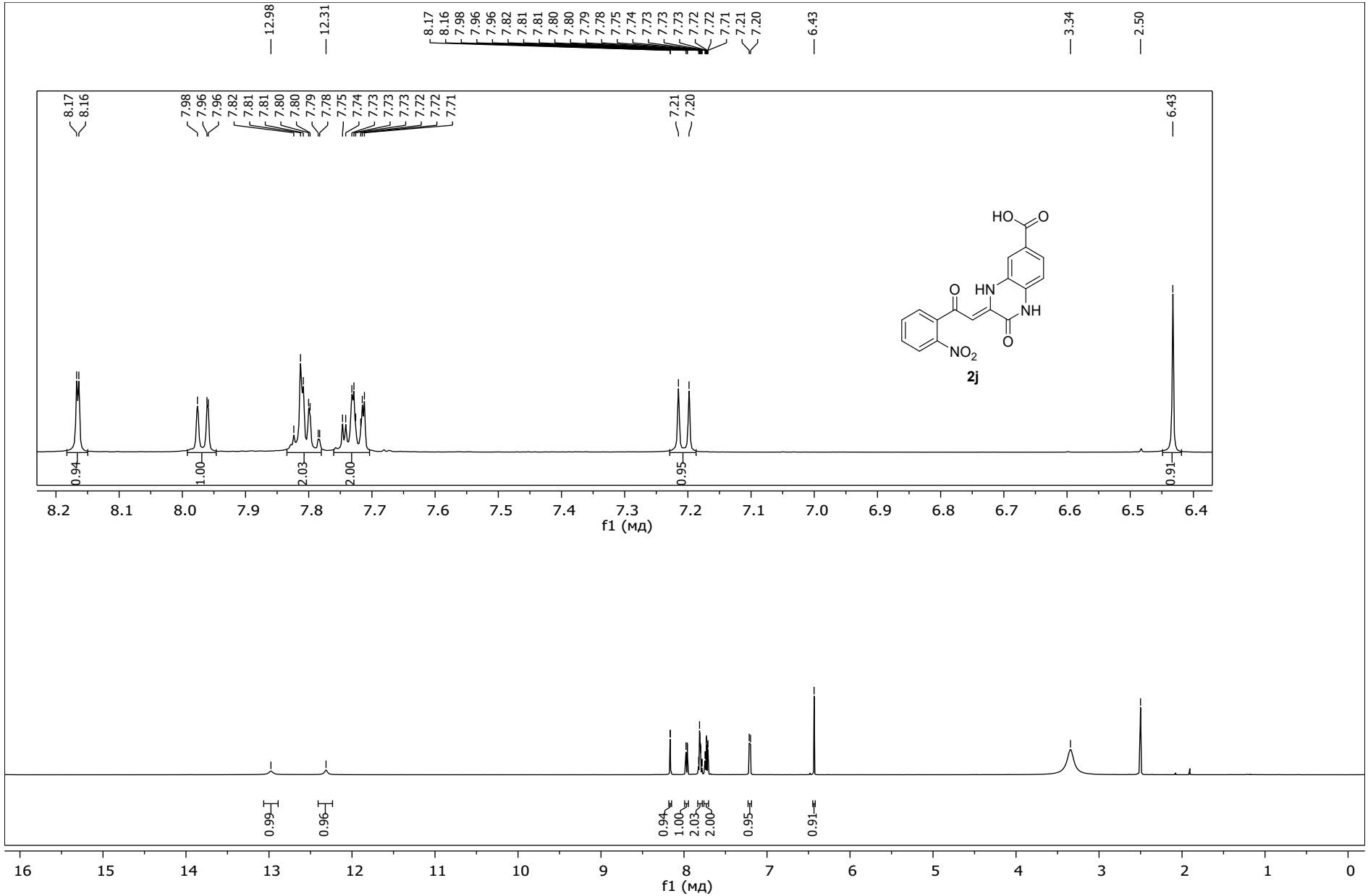


Figure S23. 1D ^{1}H NMR spectrum of **2j** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

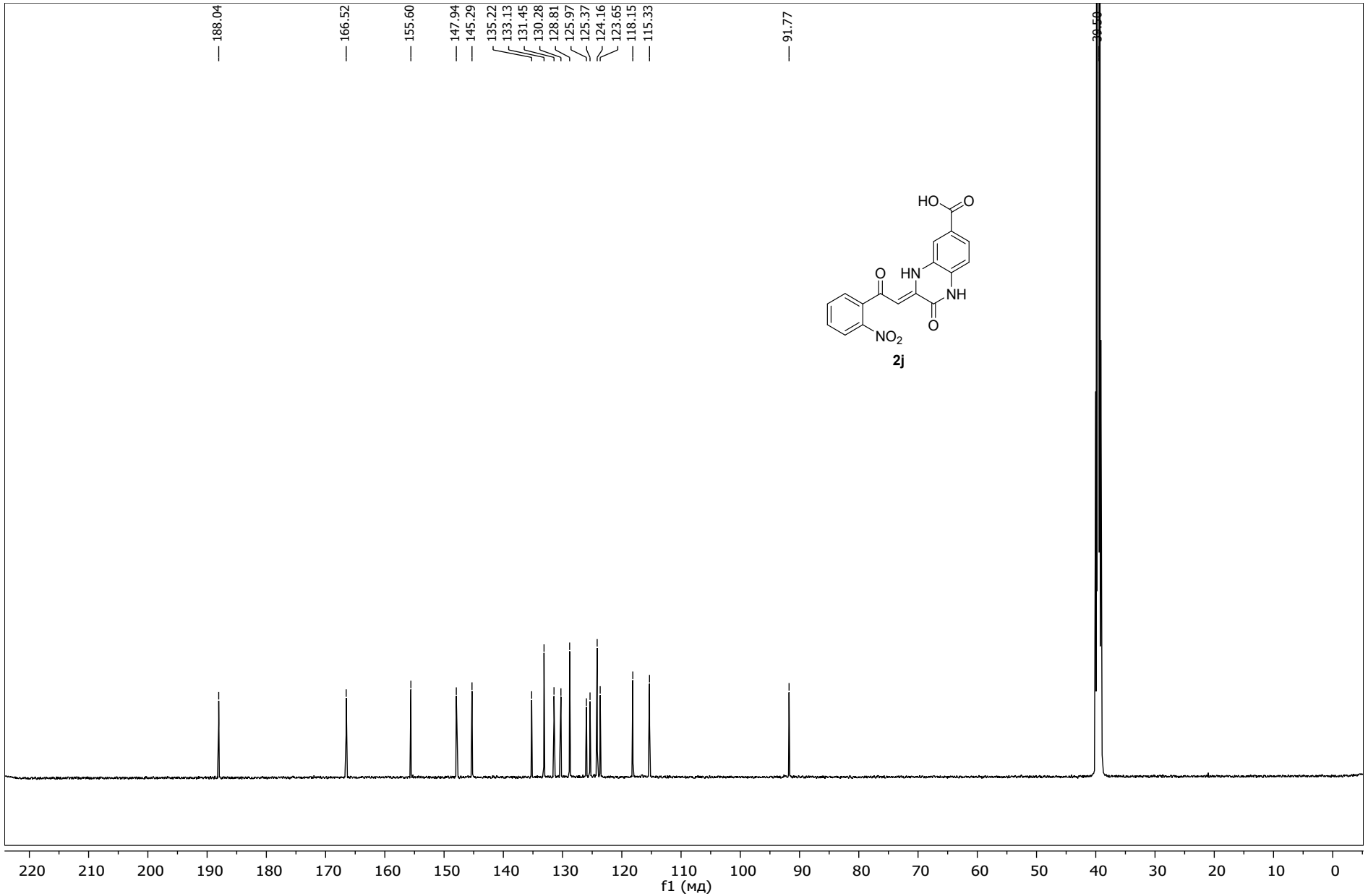


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum of **2j** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

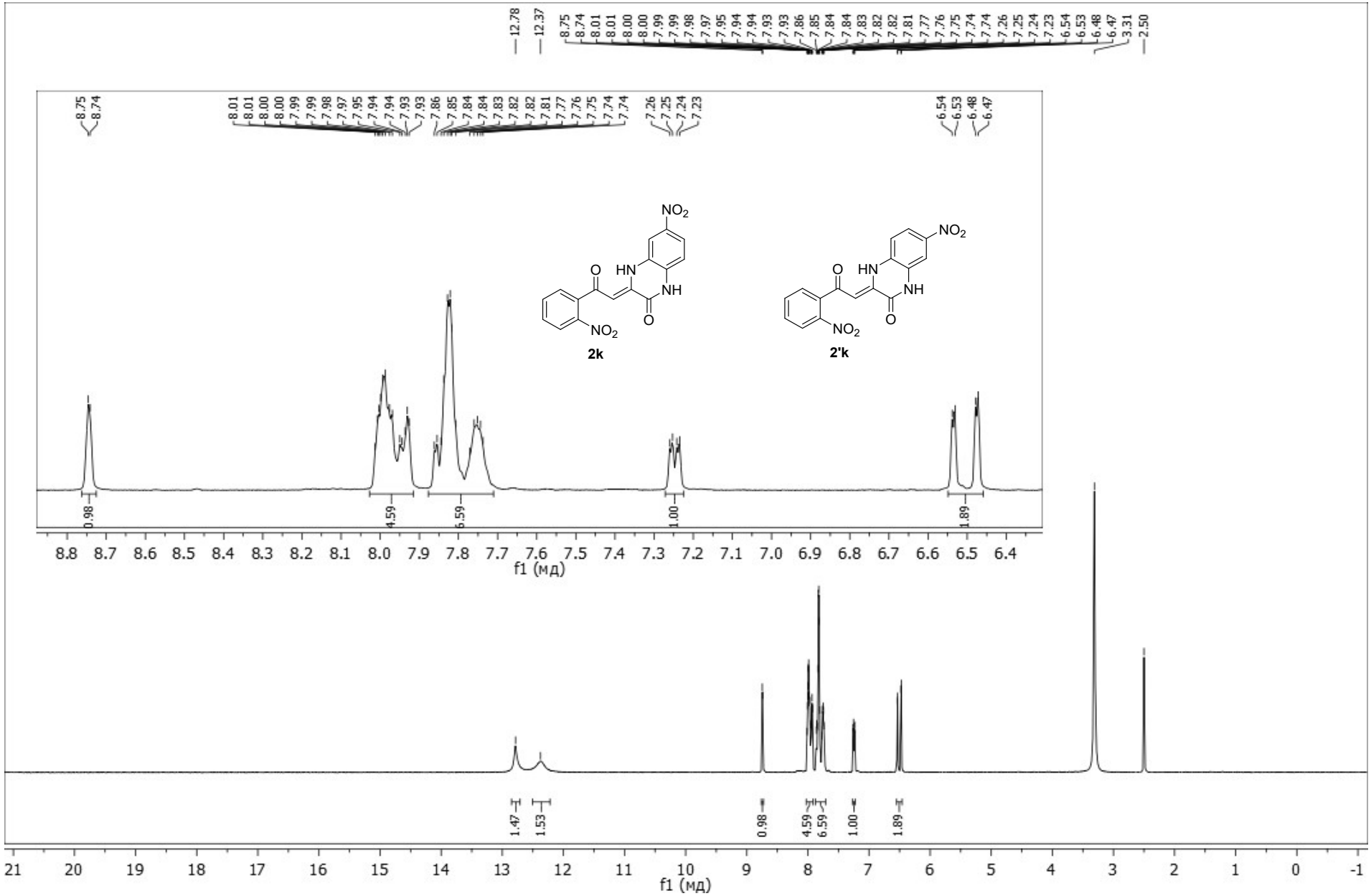


Figure S25. 1D ^{1}H NMR spectrum of **2k** and **2′k** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

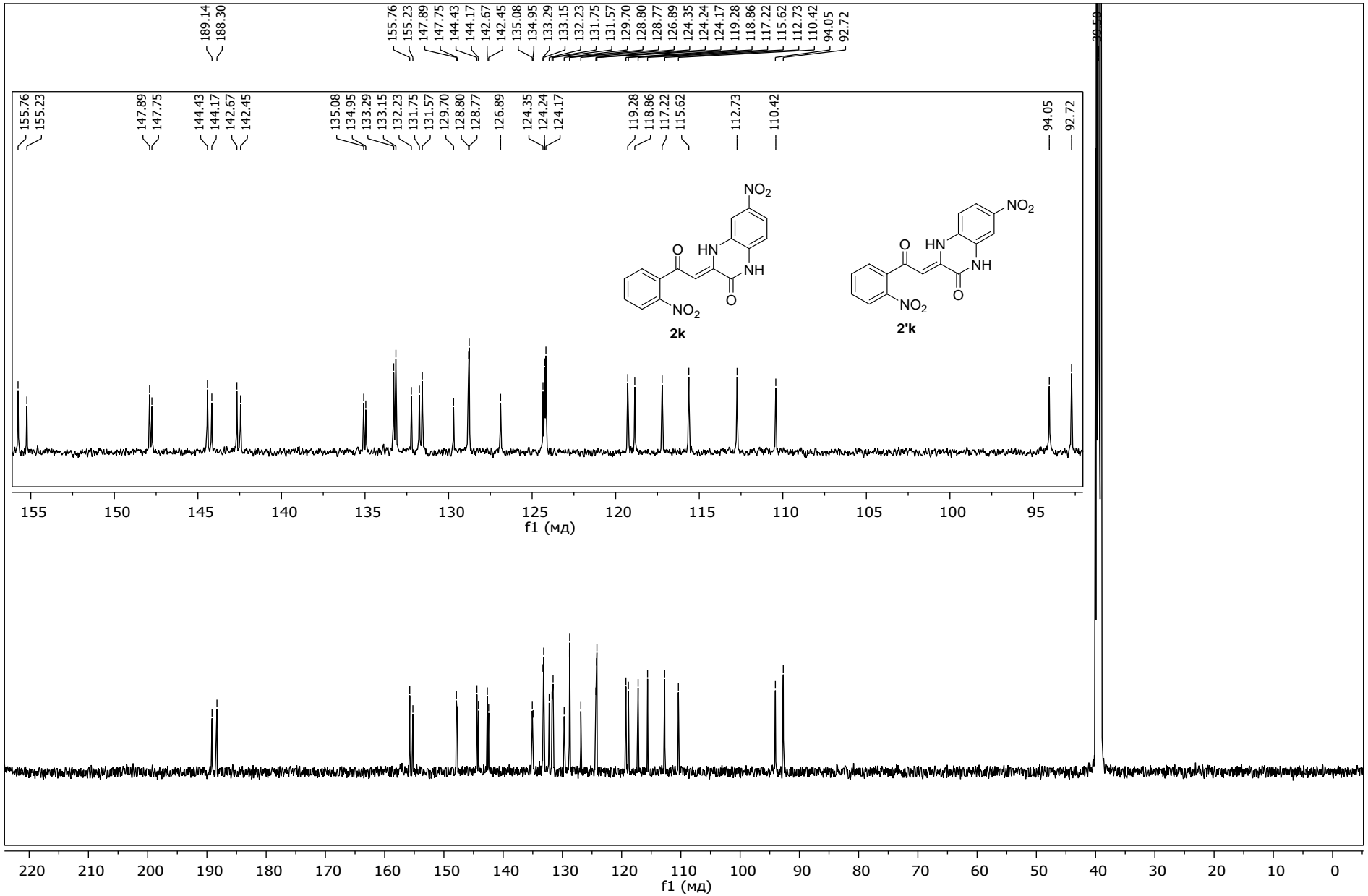


Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum of **2k** and **2′k** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

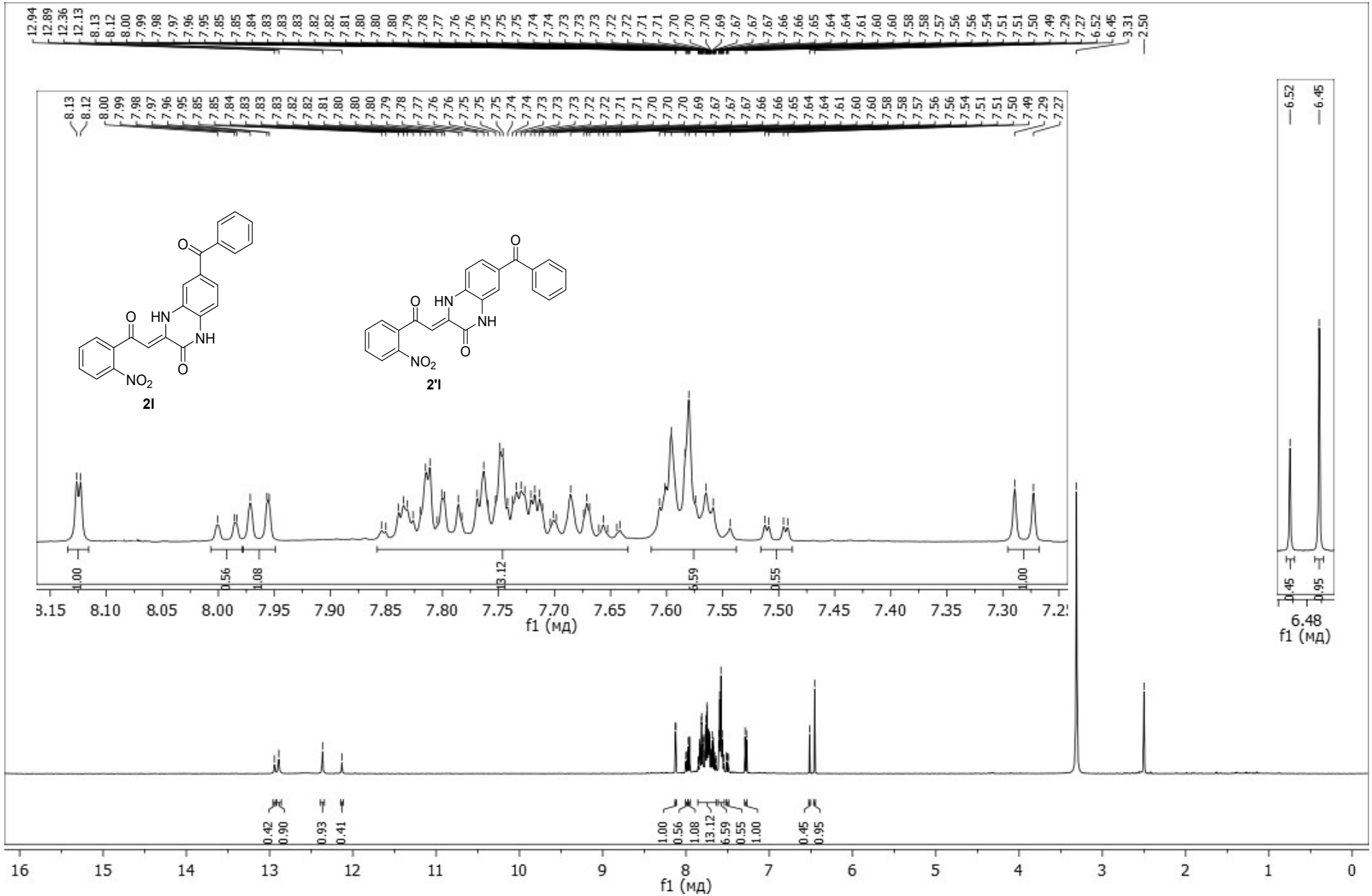


Figure S27. 1D ^{1}H NMR spectrum of **2l** and **2′l** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

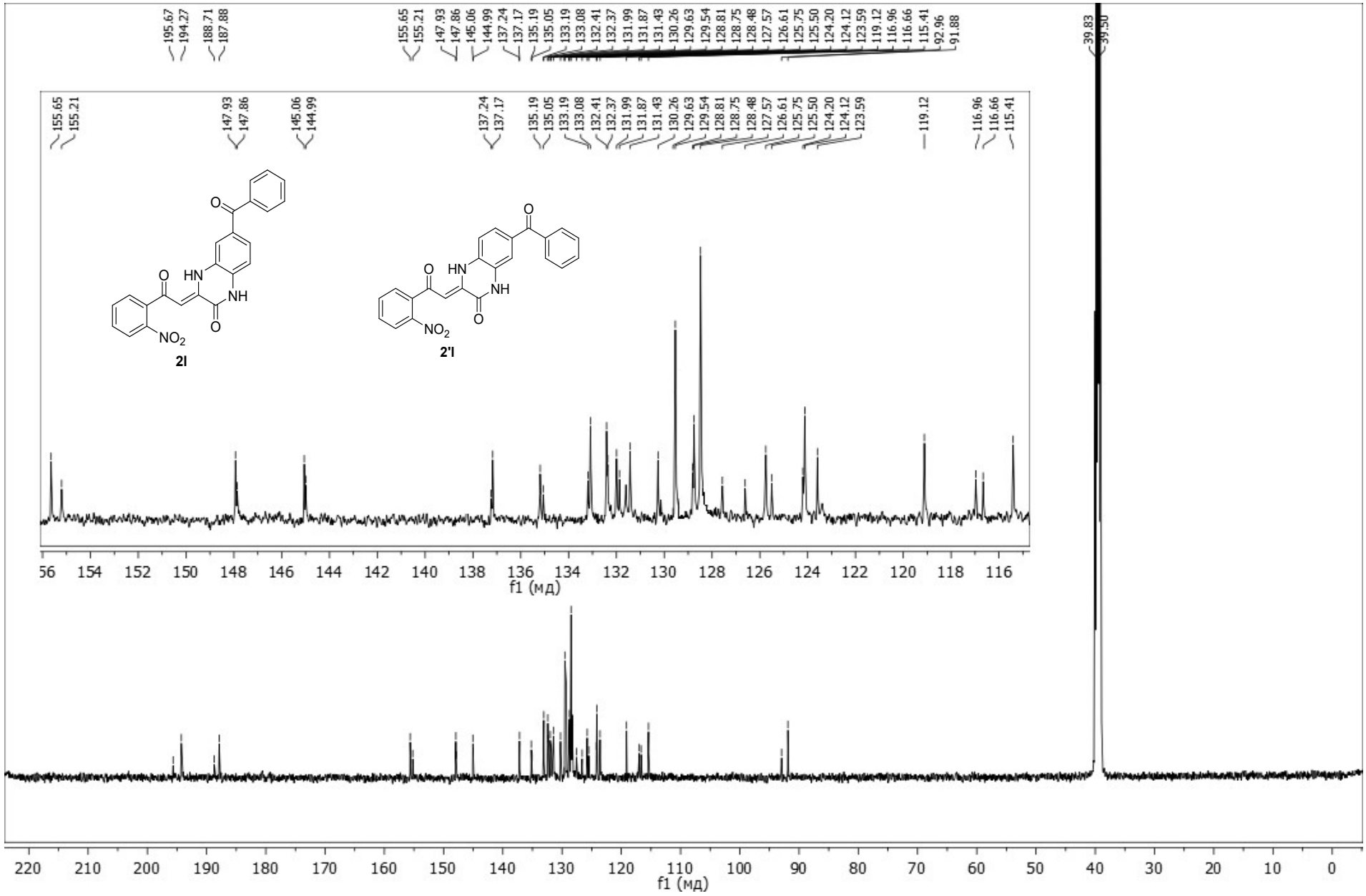


Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum of **2l** and **2′l** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

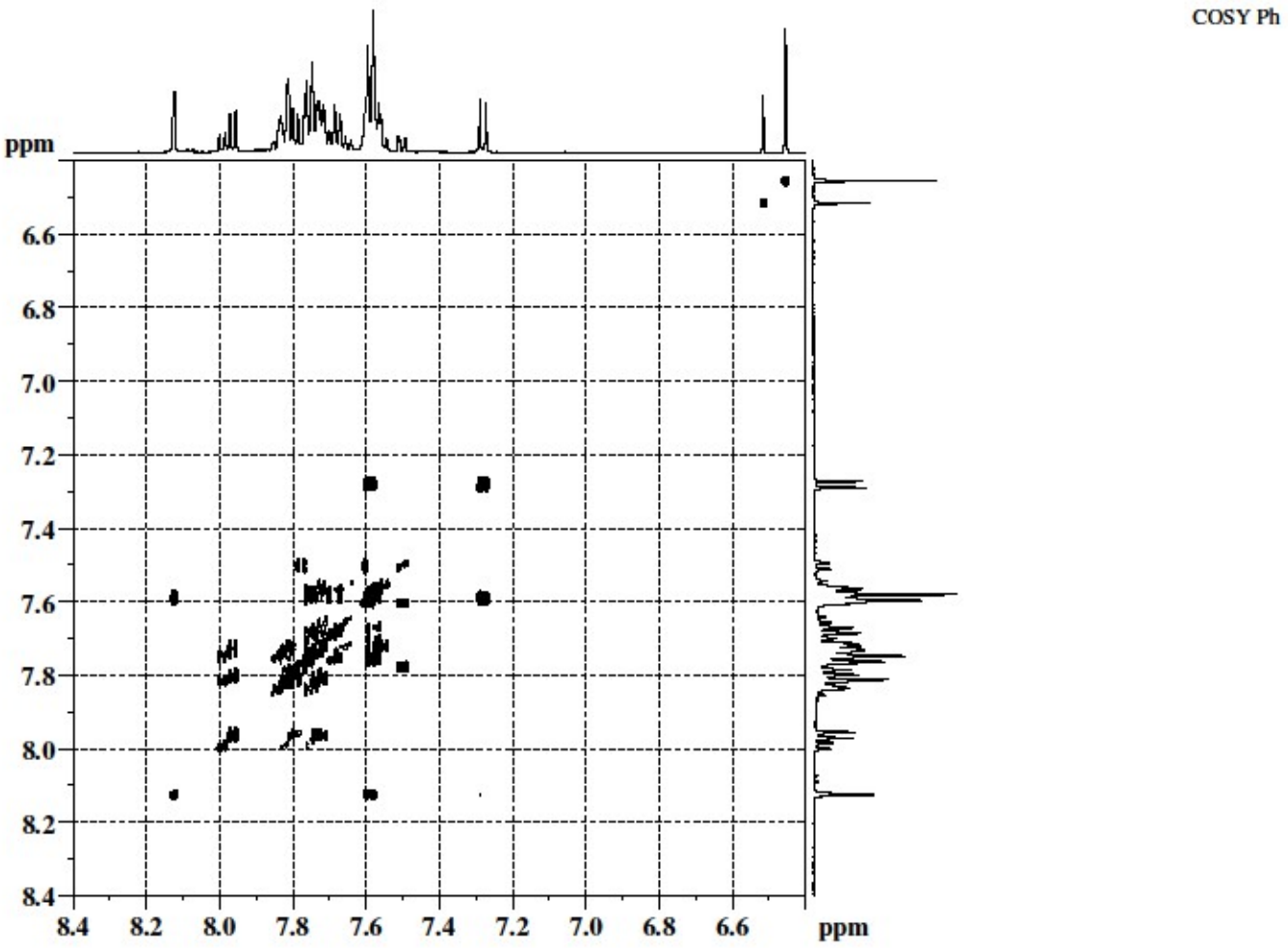


Figure S29. 2D ^{1}H-^{1}H COSY NMR spectrum of **2l** and **2′l** in DMSO-d_6 at T = 303 K.

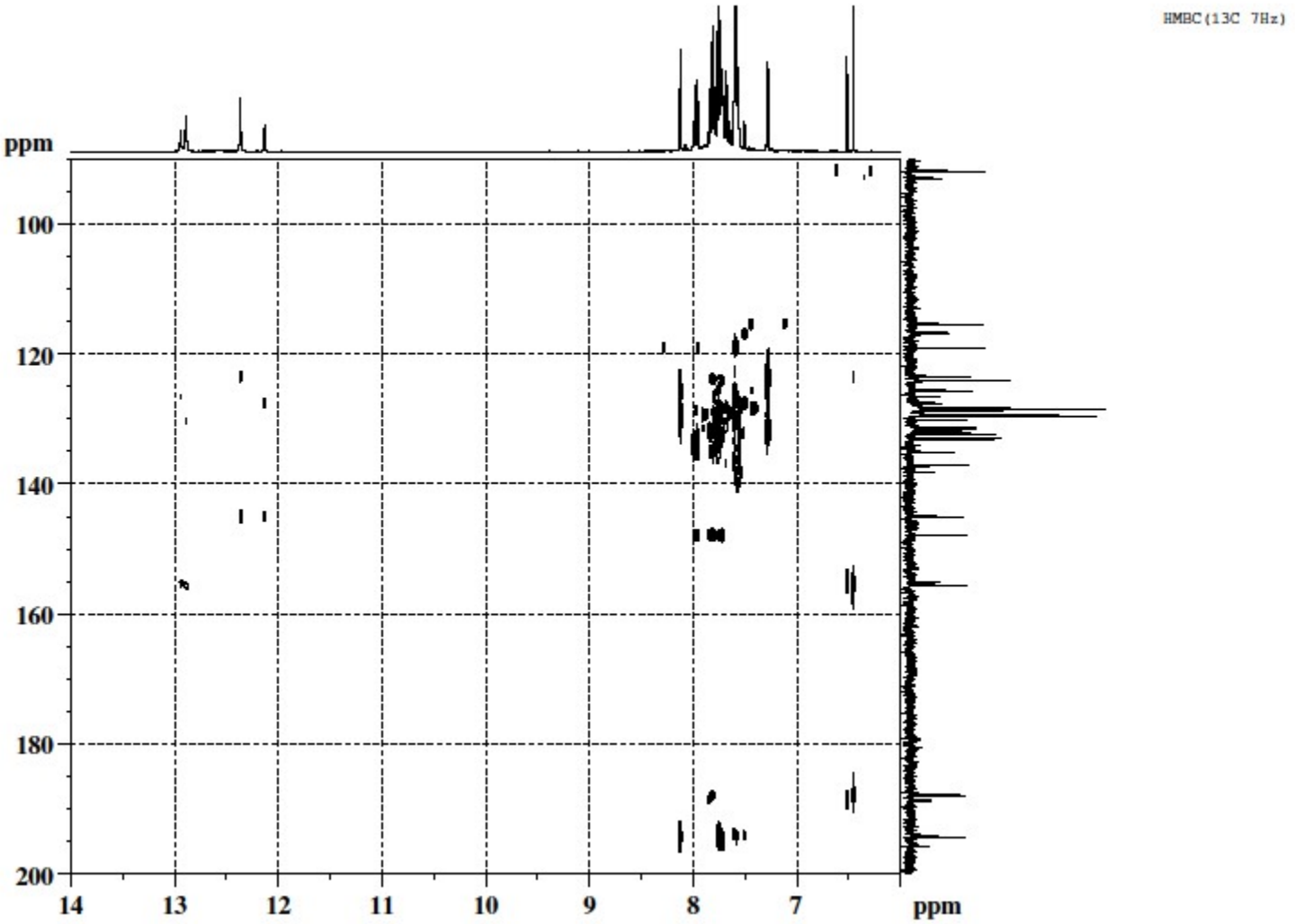


Figure S30. 2D ^{1}H-^{13}C HMBC NMR spectrum of **2l** and **2′l** in DMSO-d_6 at T = 303 K.

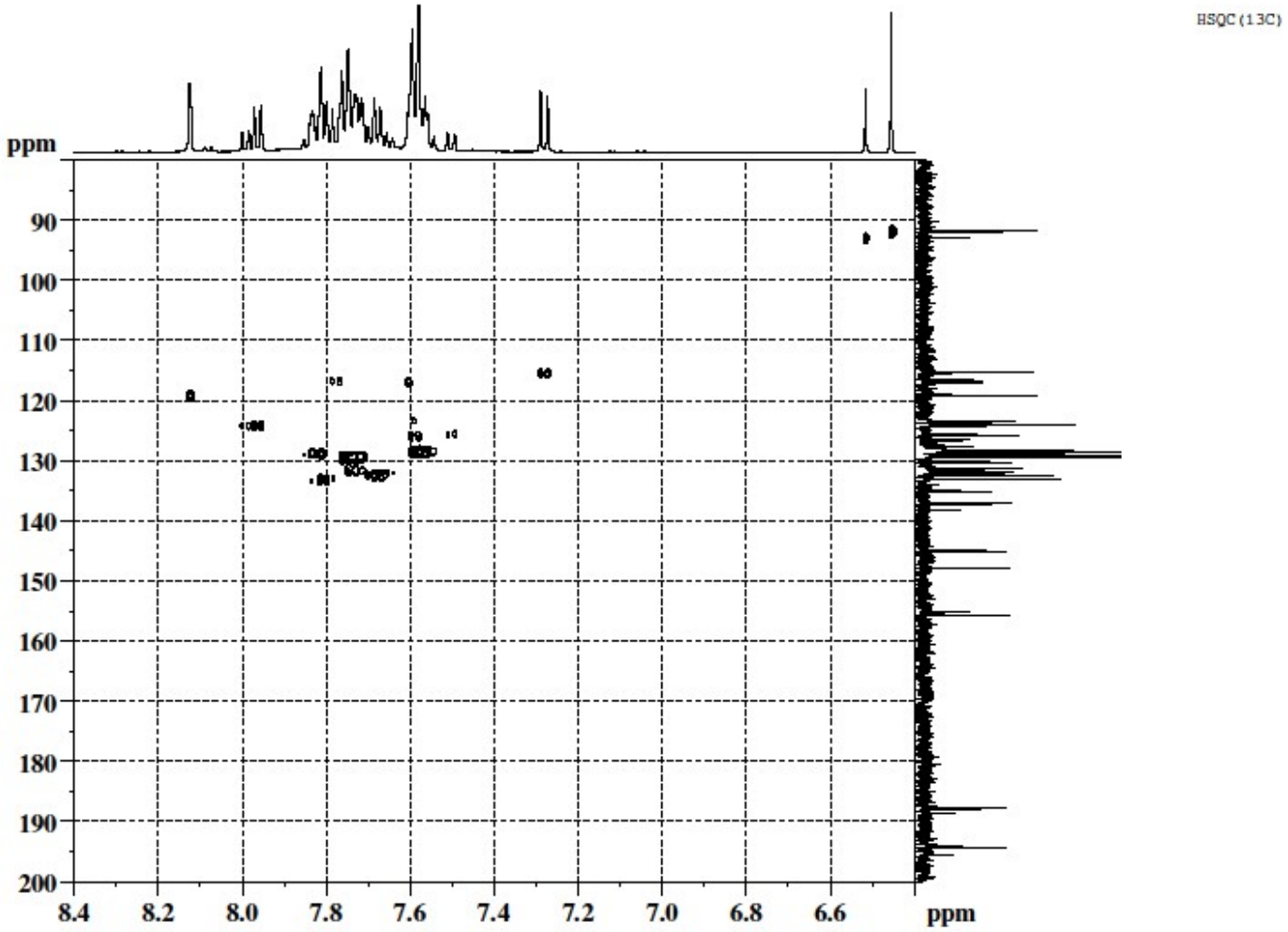


Figure S31. 2D 1H-^{13}C HSQC NMR spectrum of **2l** and **2′l** in DMSO-d_6 at T = 303 K.

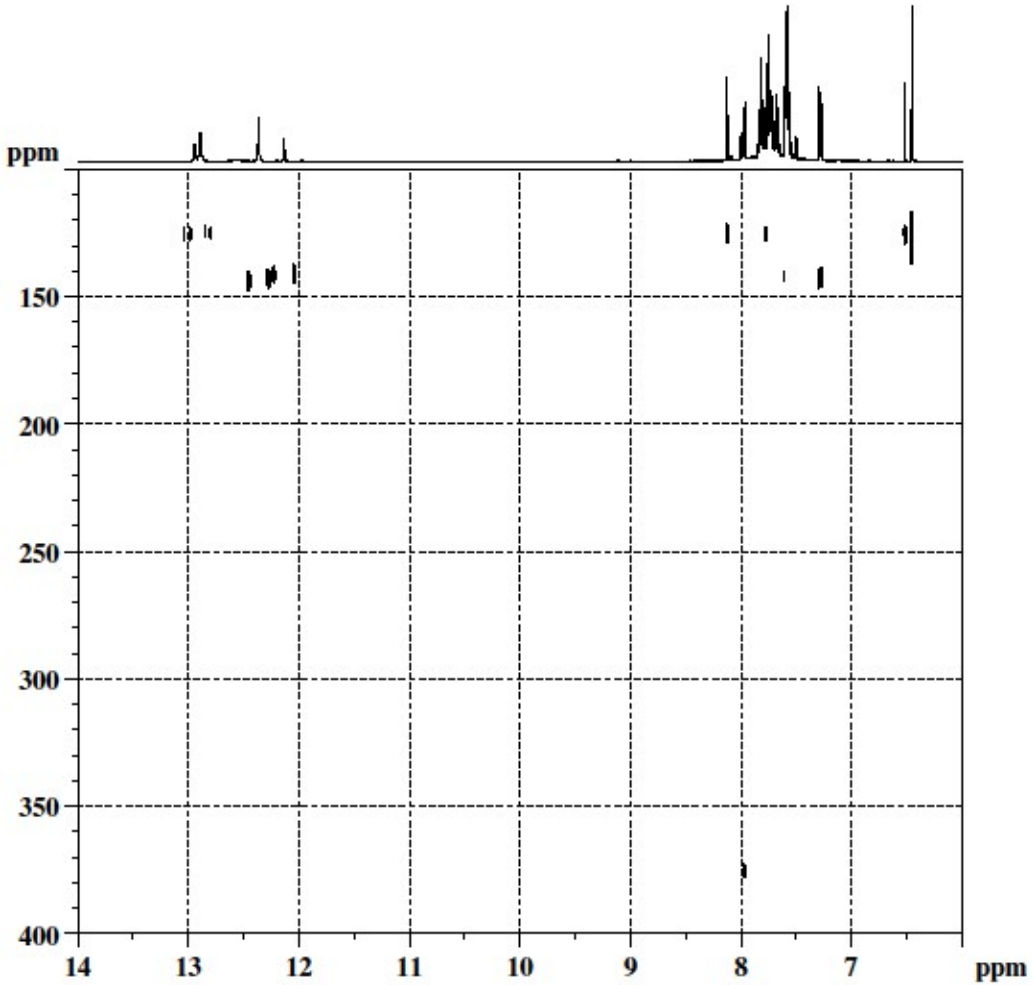


Figure S32. 2D ^{1}H-^{15}N HMBC NMR spectrum of **2l** and **2′l** in DMSO-d_6 at T = 303 K.

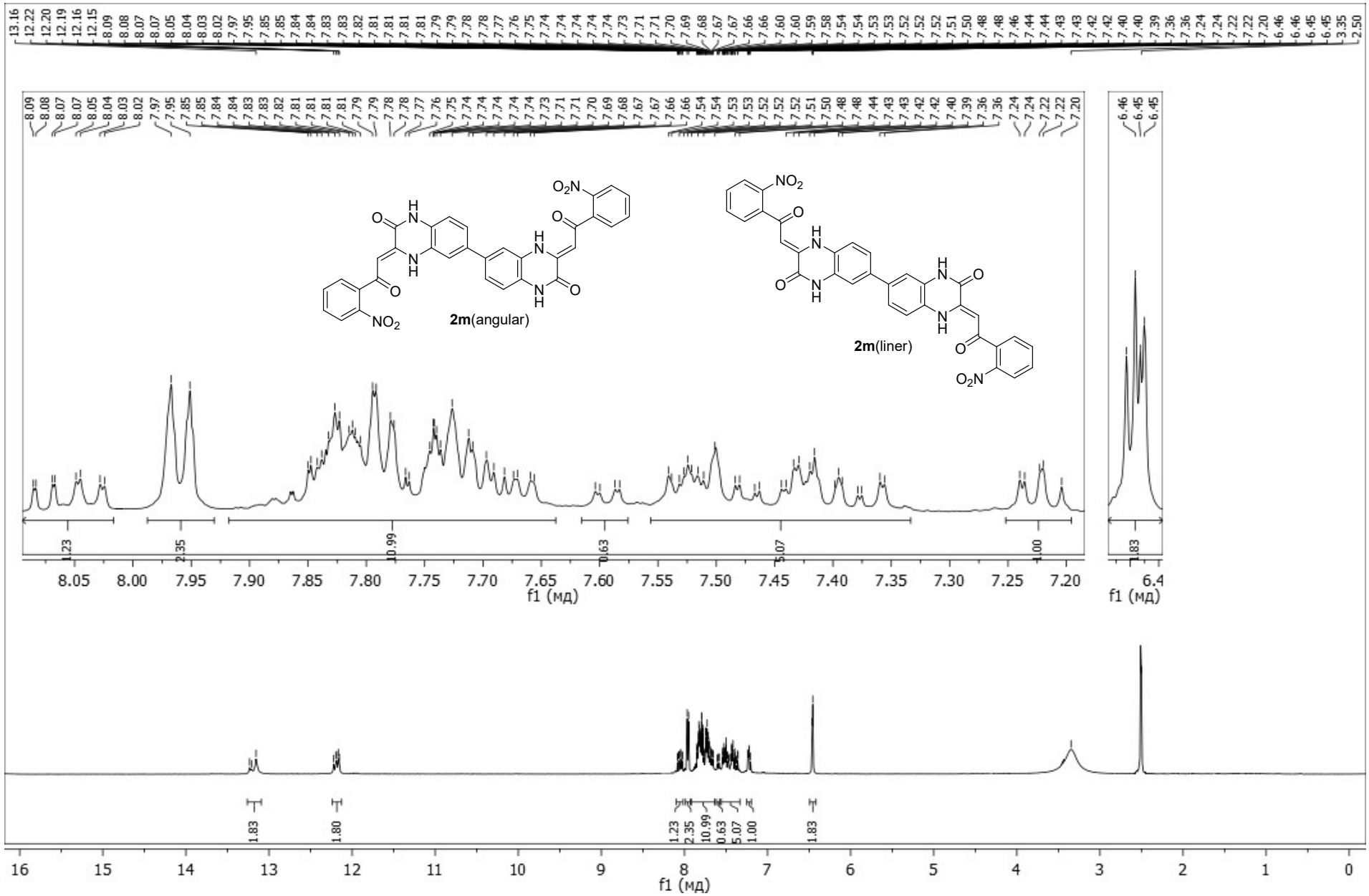


Figure S33. 1D ^{1}H NMR spectrum of **2m**(angular) and **2m**(liner) in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

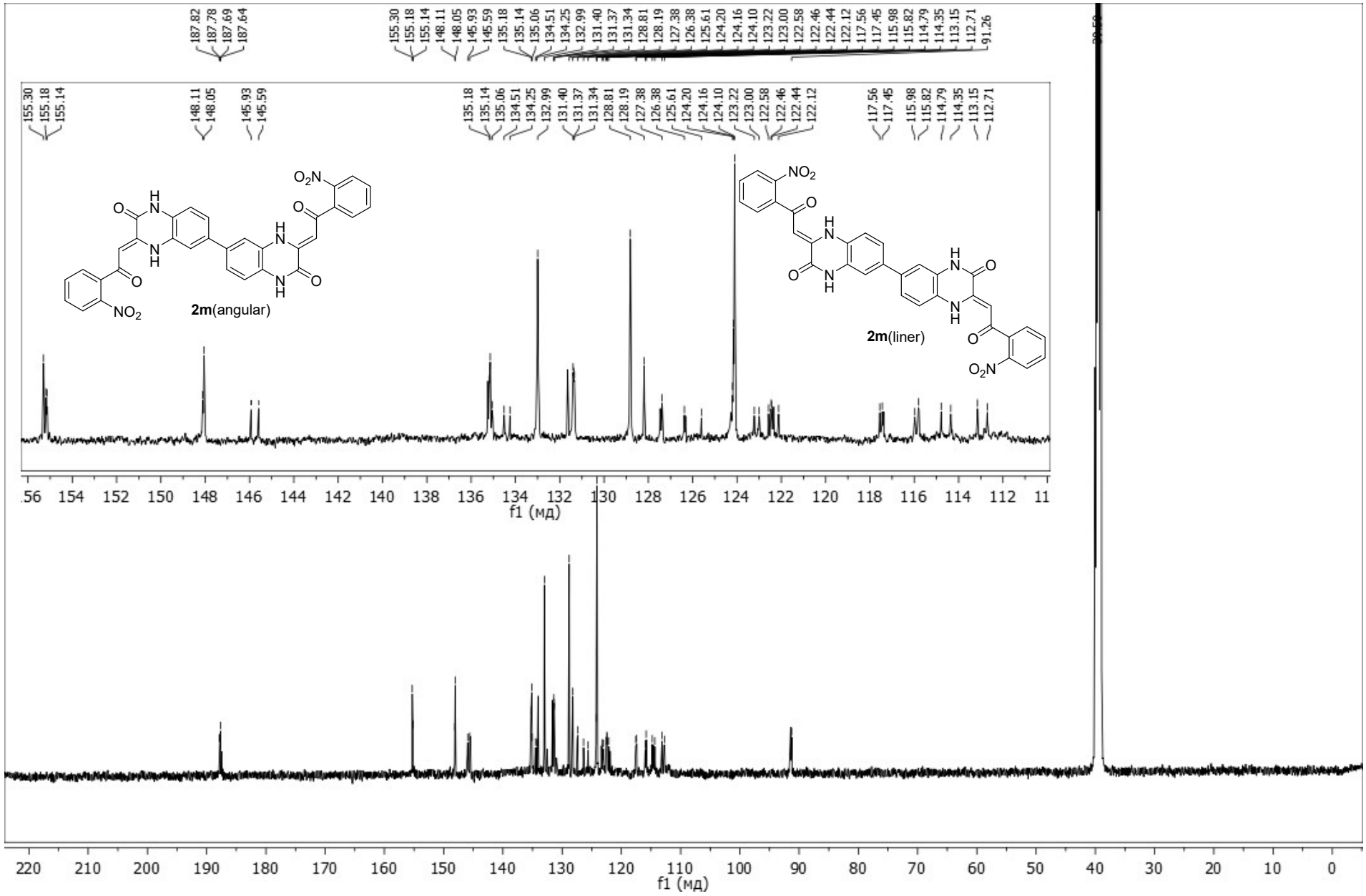


Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum of **2m**(angular) and **2m**(liner) in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

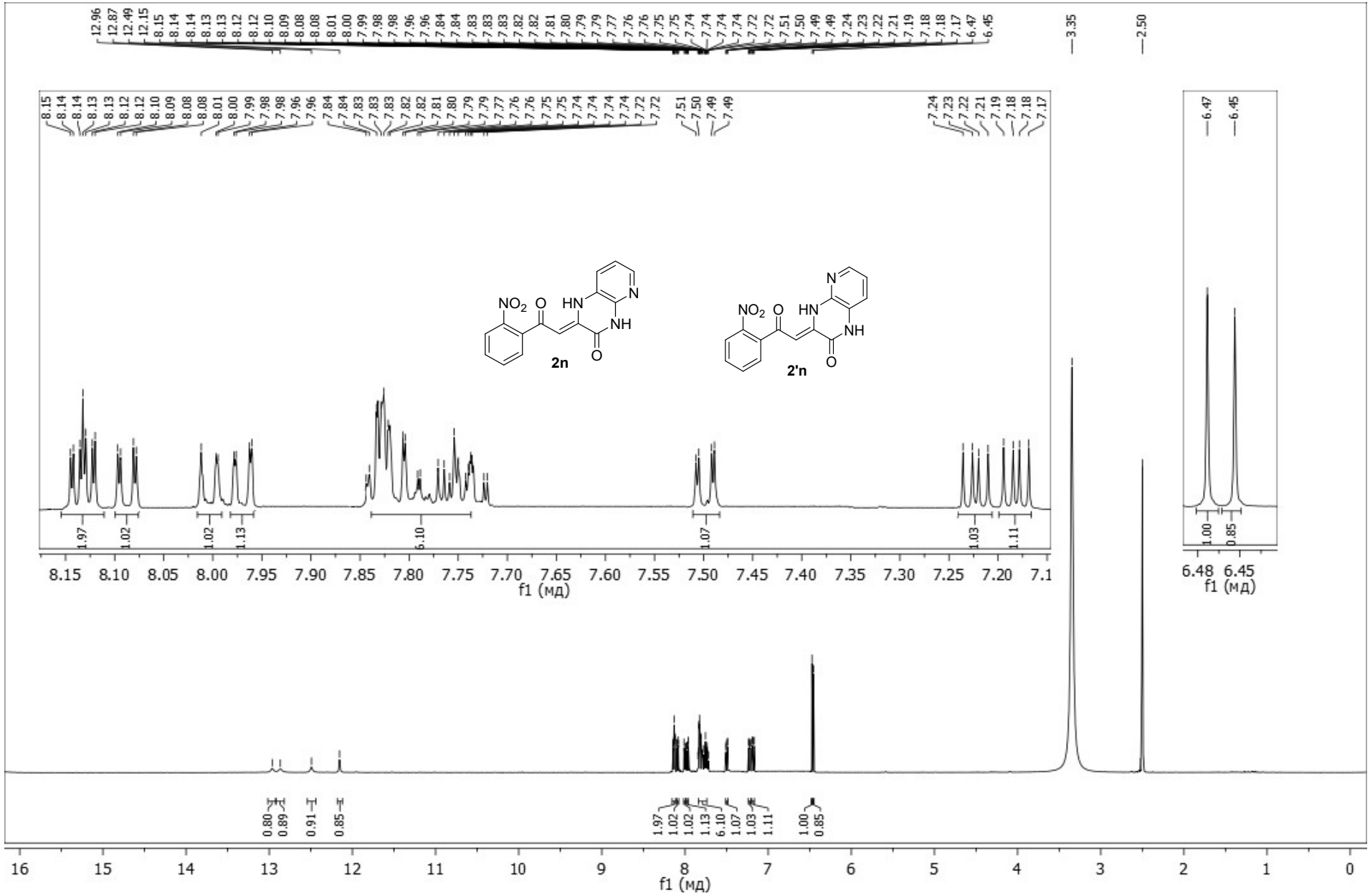


Figure S35. 1D ^{1}H NMR spectrum of **2n** and **2′n** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

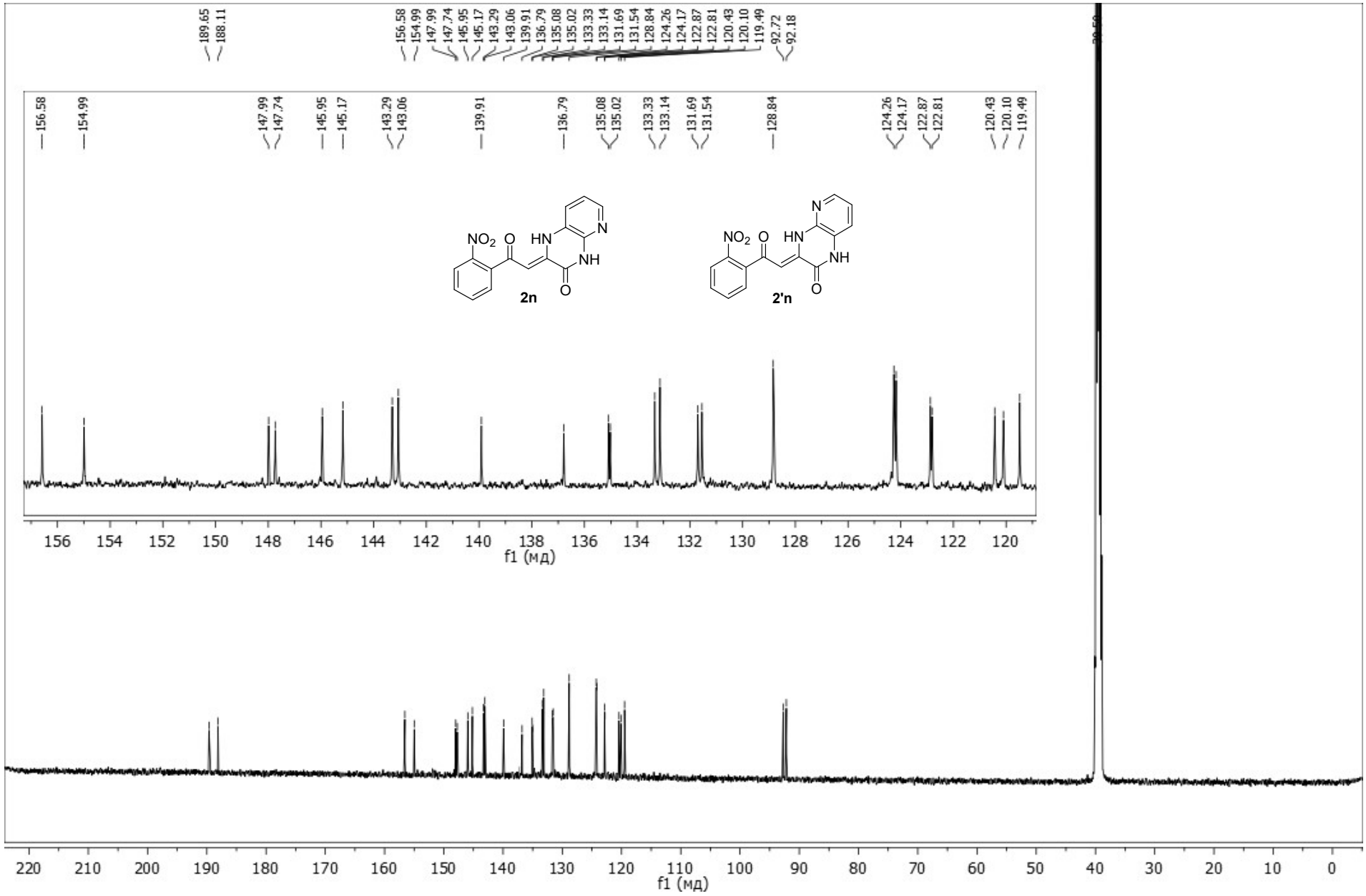


Figure S36. $^{13}C\{^{1}H\}$ NMR spectrum of **2n** and **2′n** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

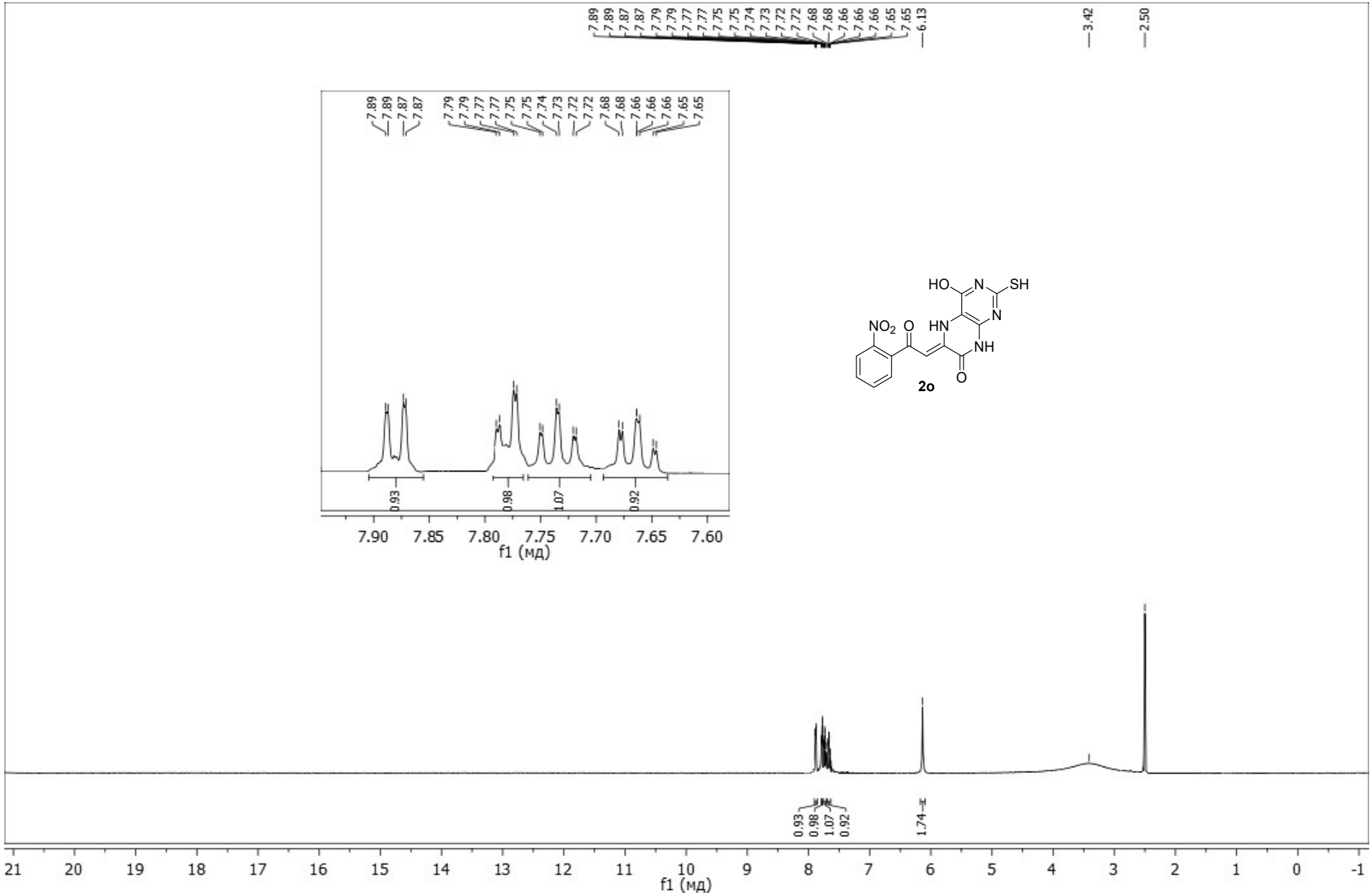


Figure S37. 1D ^{1}H NMR spectrum of **2o** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

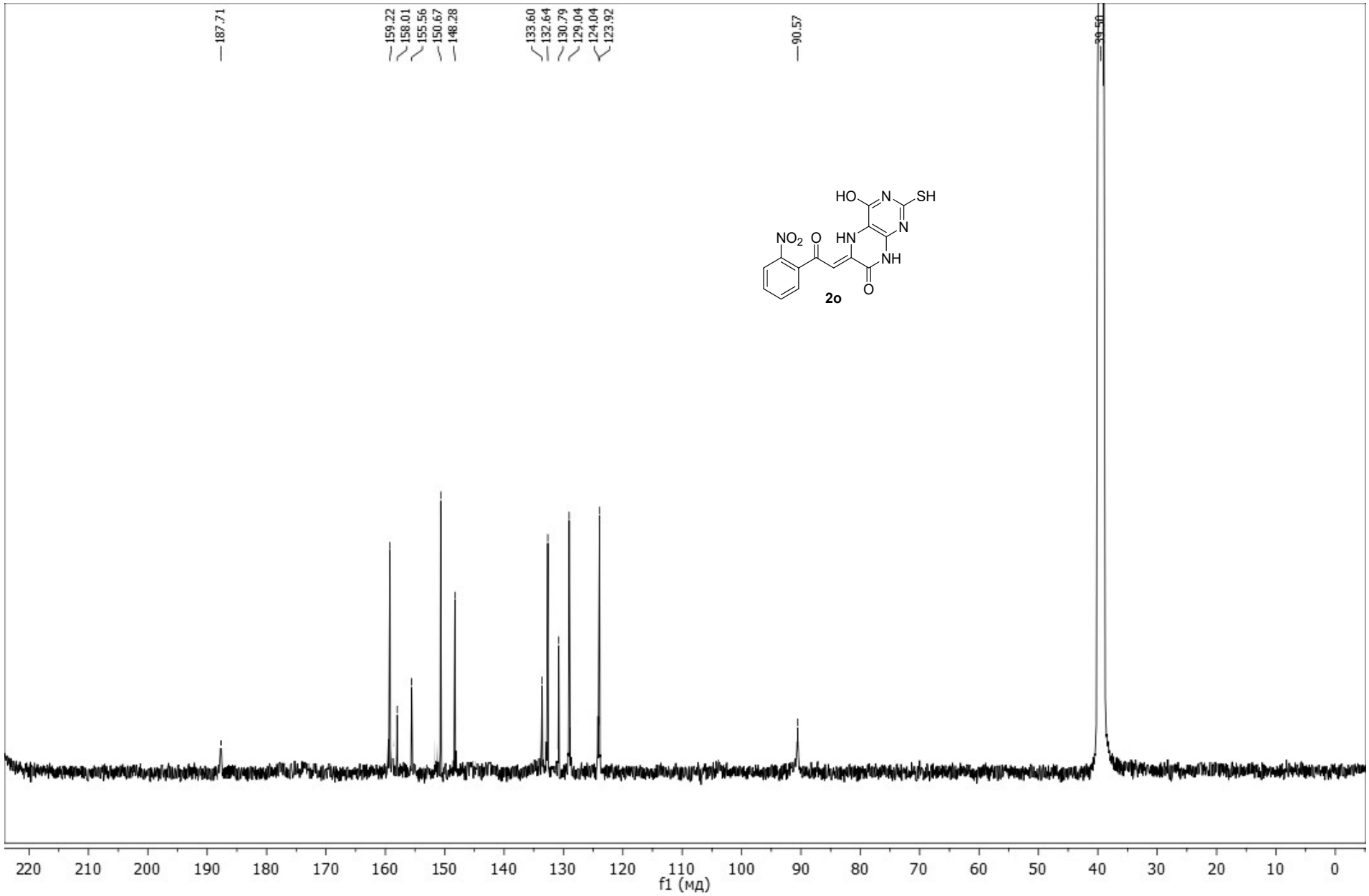


Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum of **2o** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

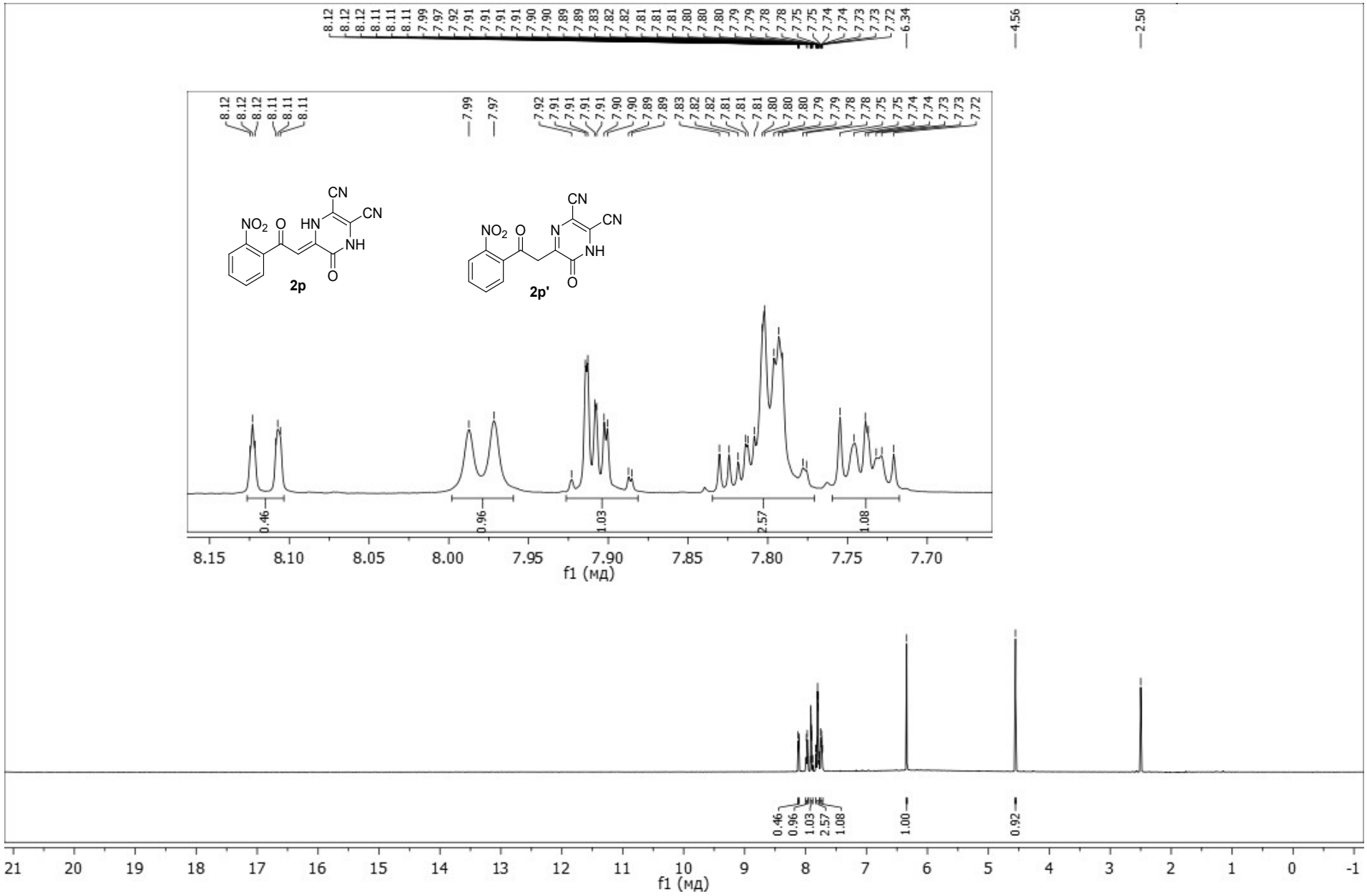


Figure S39. 1D ^{1}H NMR spectrum of **2p** and **2p′** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

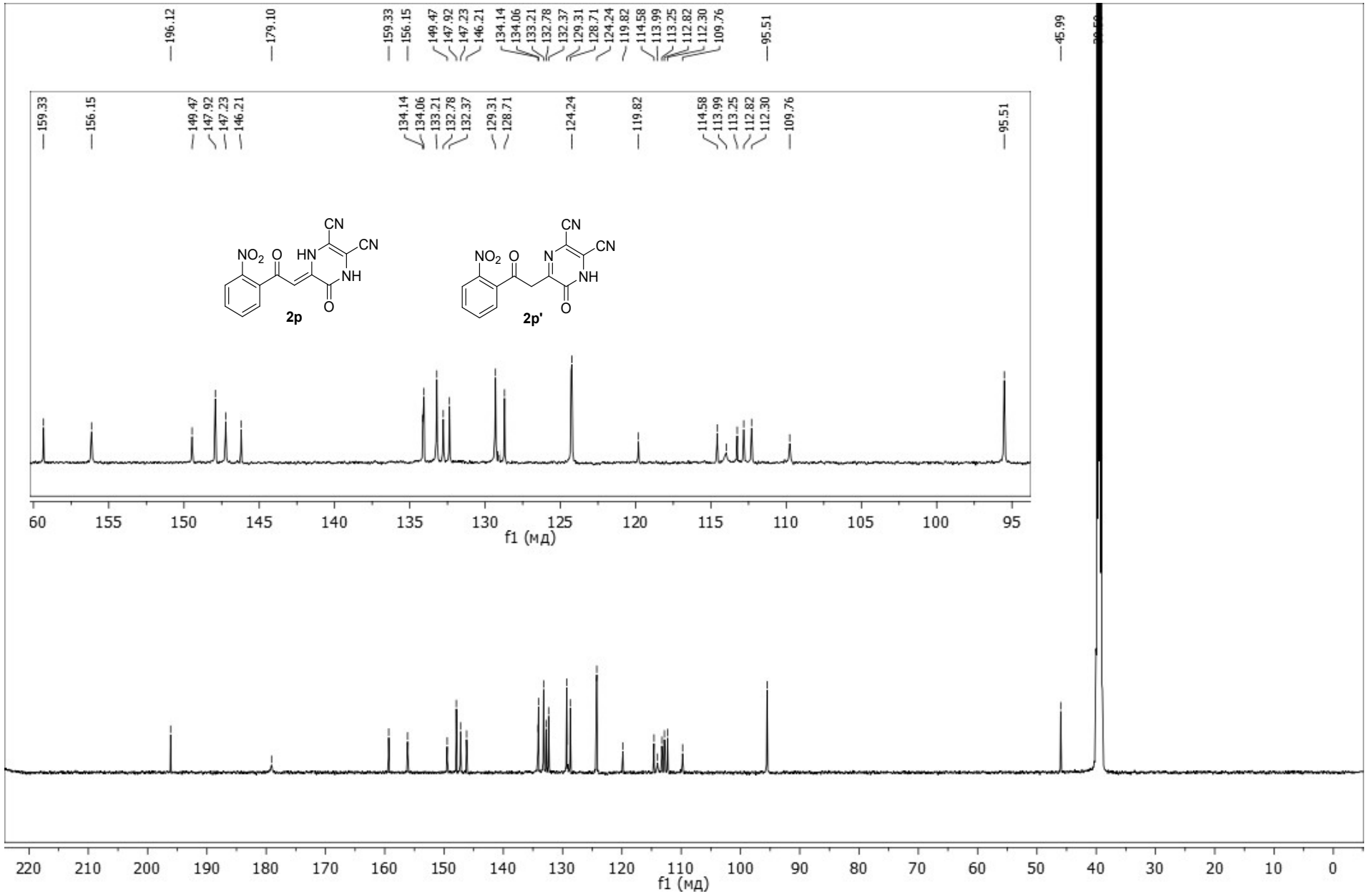


Figure S40. $^{13}C\{^{1}H\}$ NMR spectrum of **2p** and **2p′** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

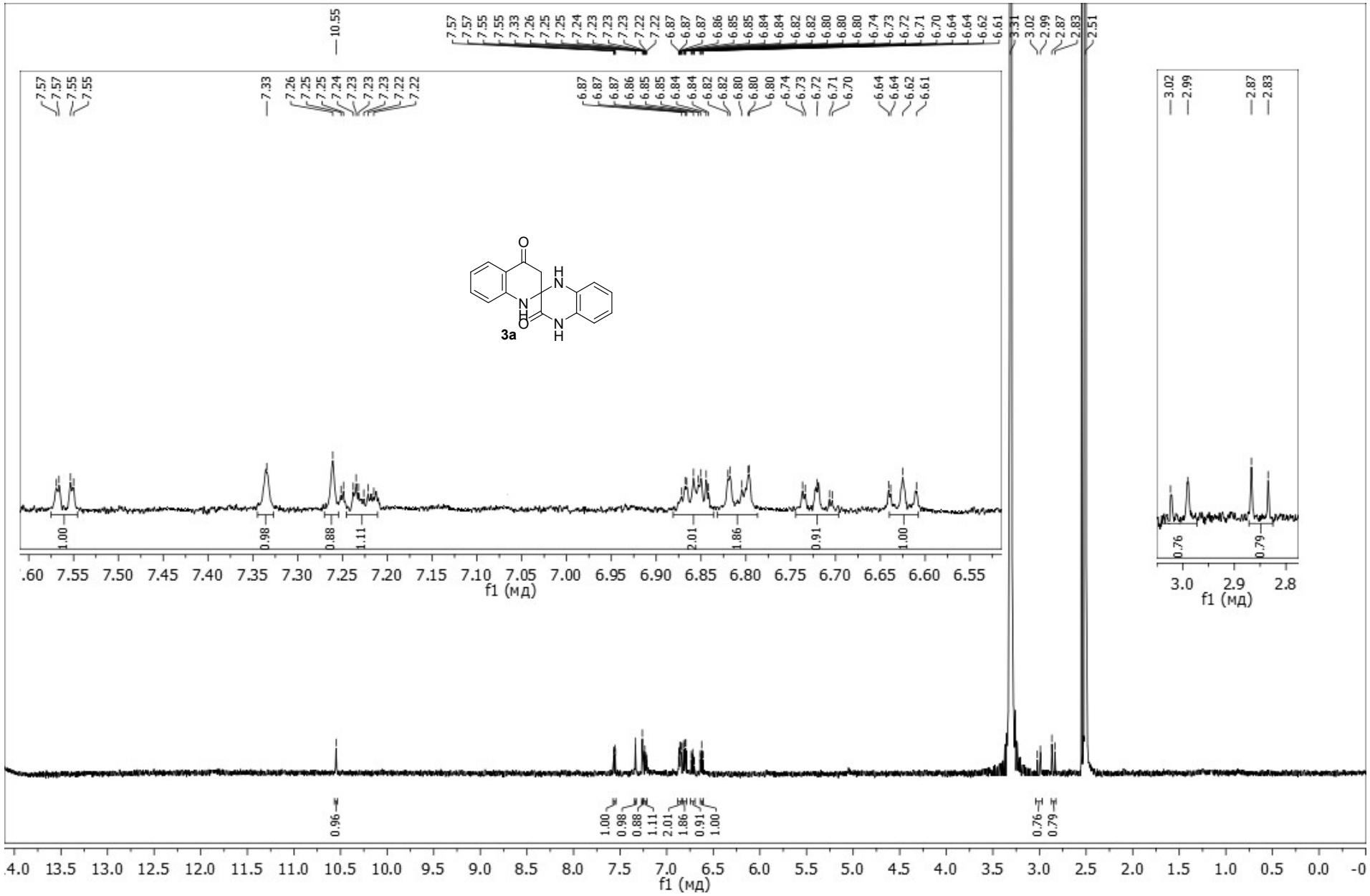


Figure S41. 1D ^{1}H NMR spectrum of **3a** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

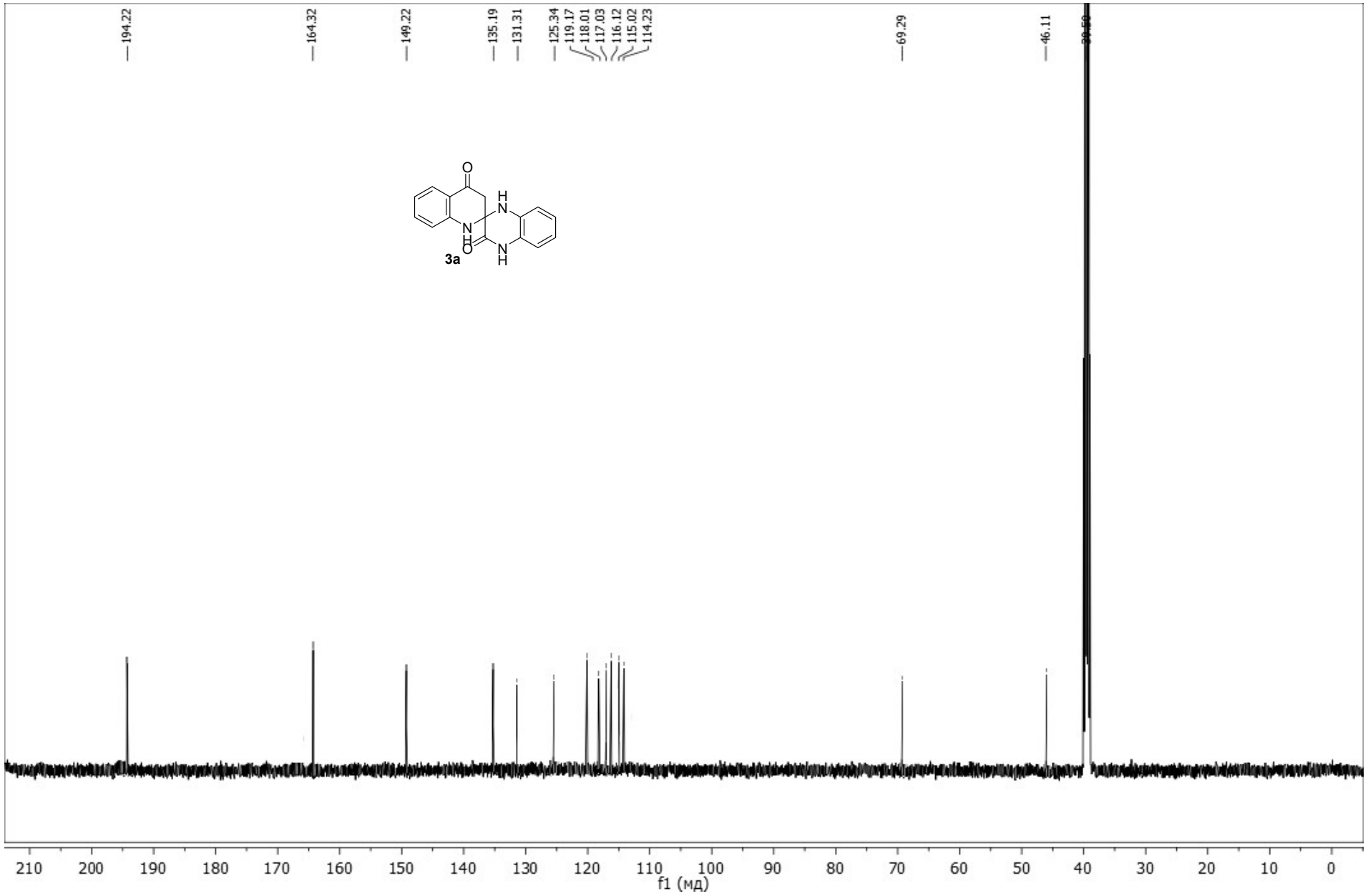


Figure S42. $^{13}C\{^{1}H\}$ NMR spectrum of **3a** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

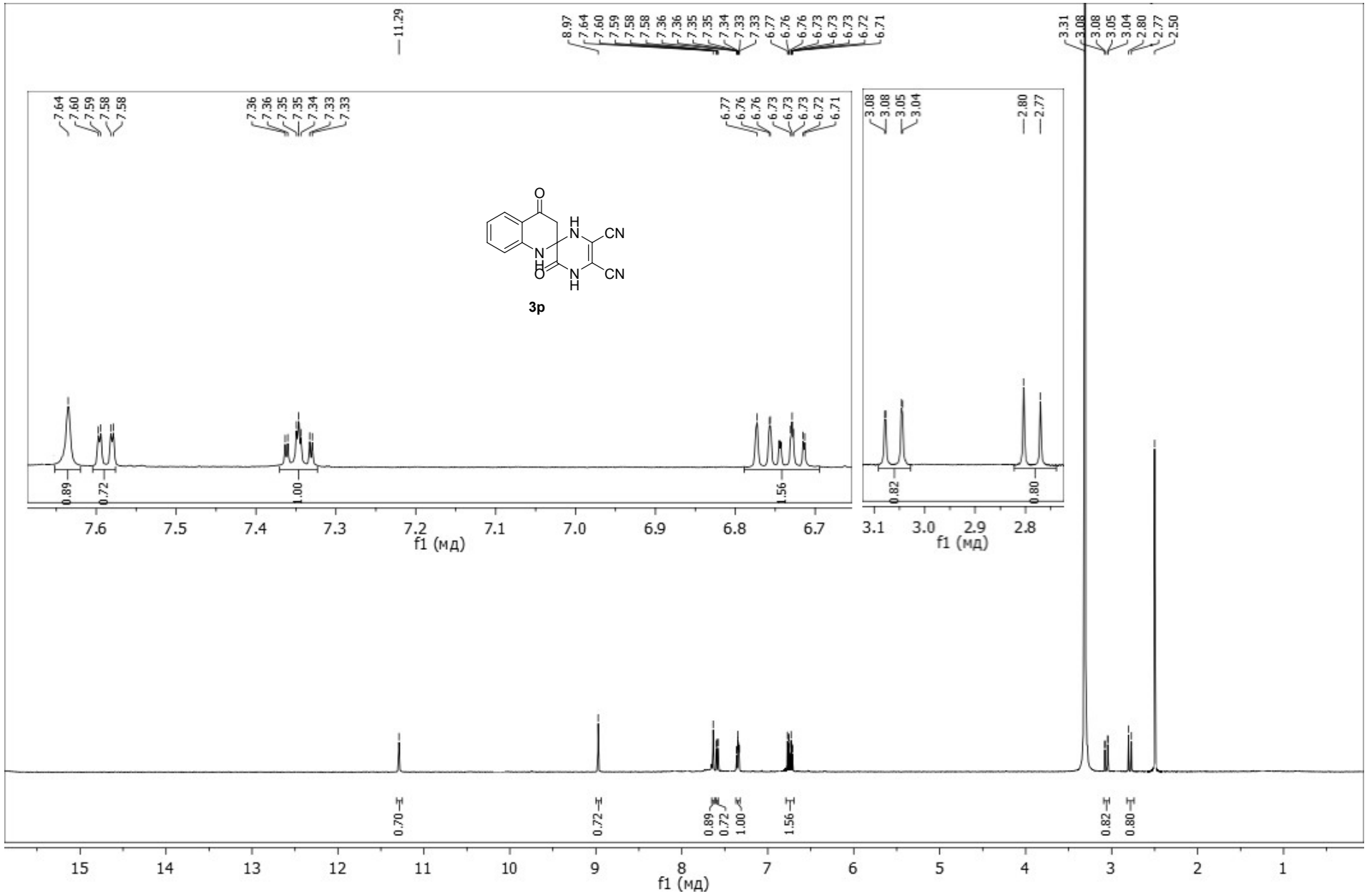


Figure S43. 1D ^{1}H NMR spectrum of **3p** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

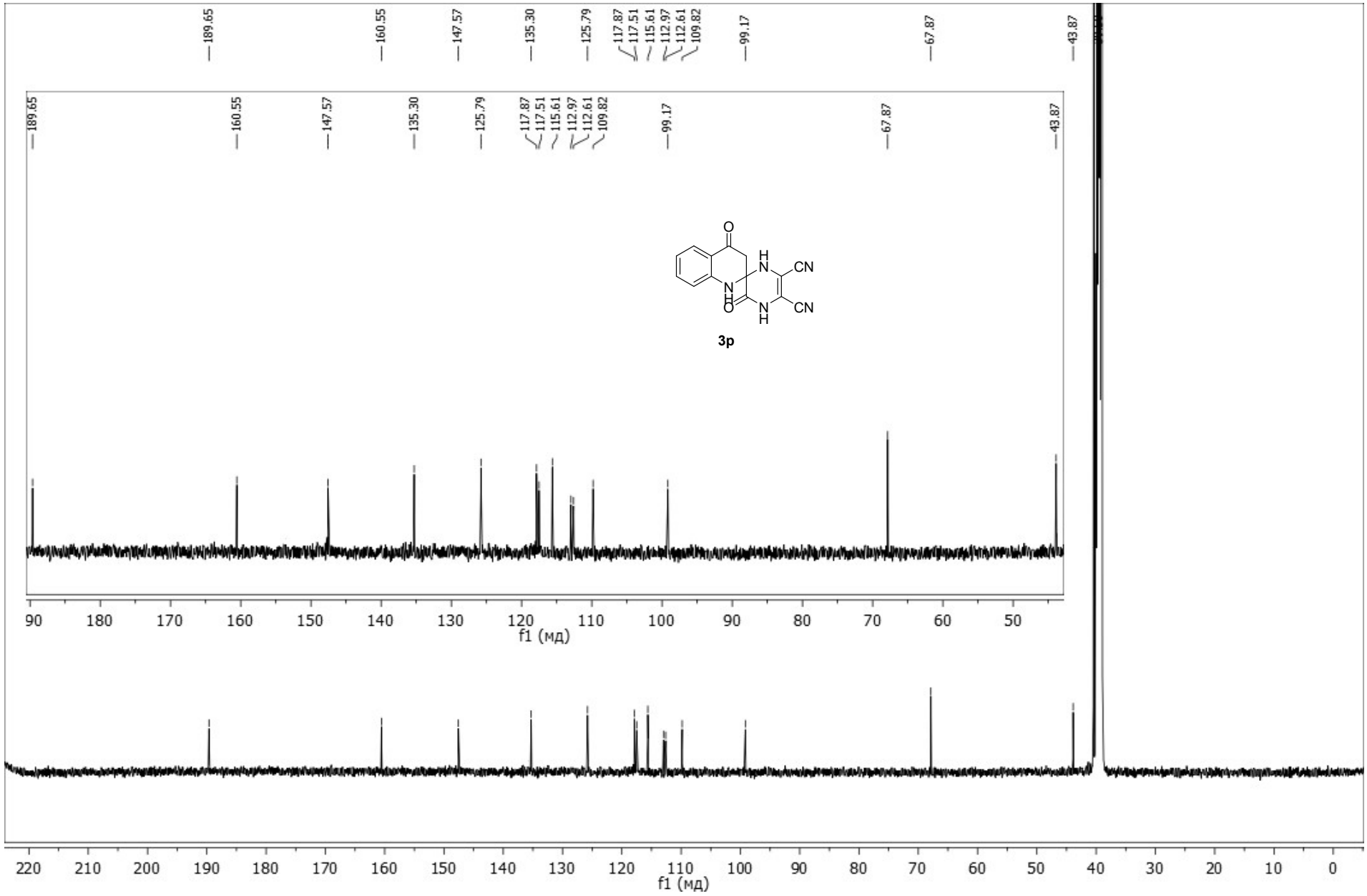


Figure S44. $^{13}C\{^{1}H\}$ NMR spectrum of **3p** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

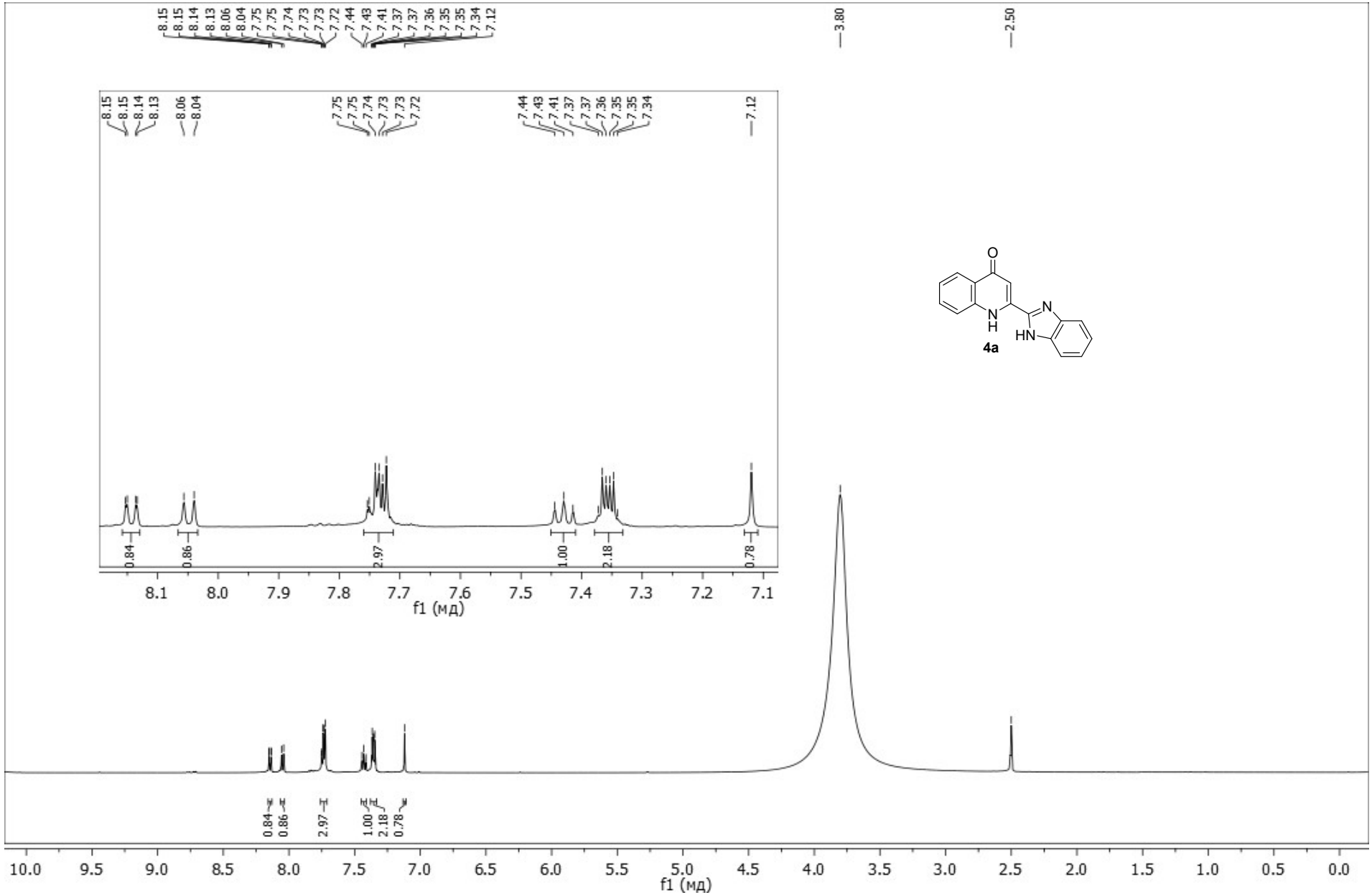


Figure S45. 1D ^{1}H NMR spectrum of **4a** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

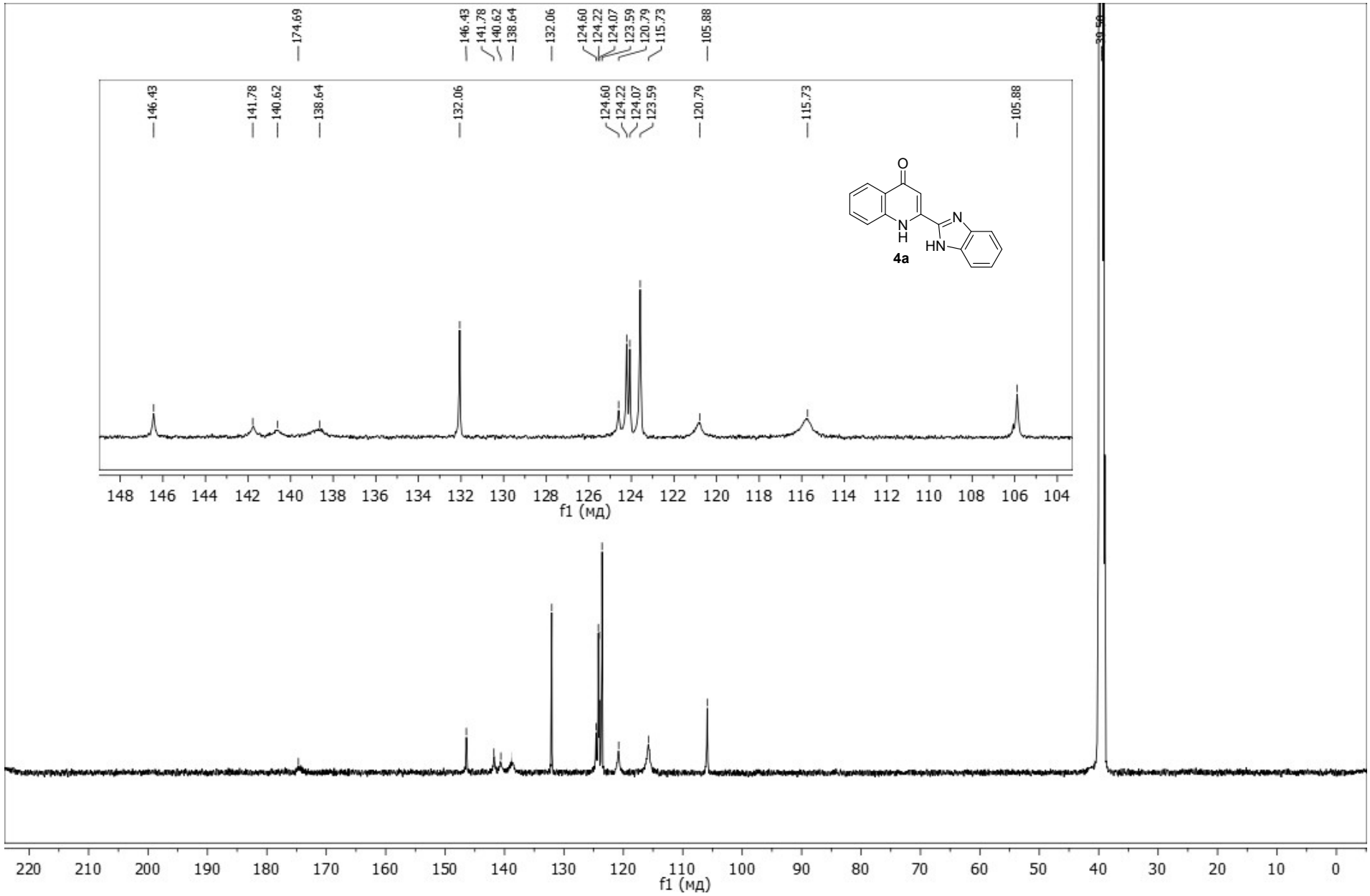


Figure S46. $^{13}C\{^{1}H\}$ NMR spectrum of **4a** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

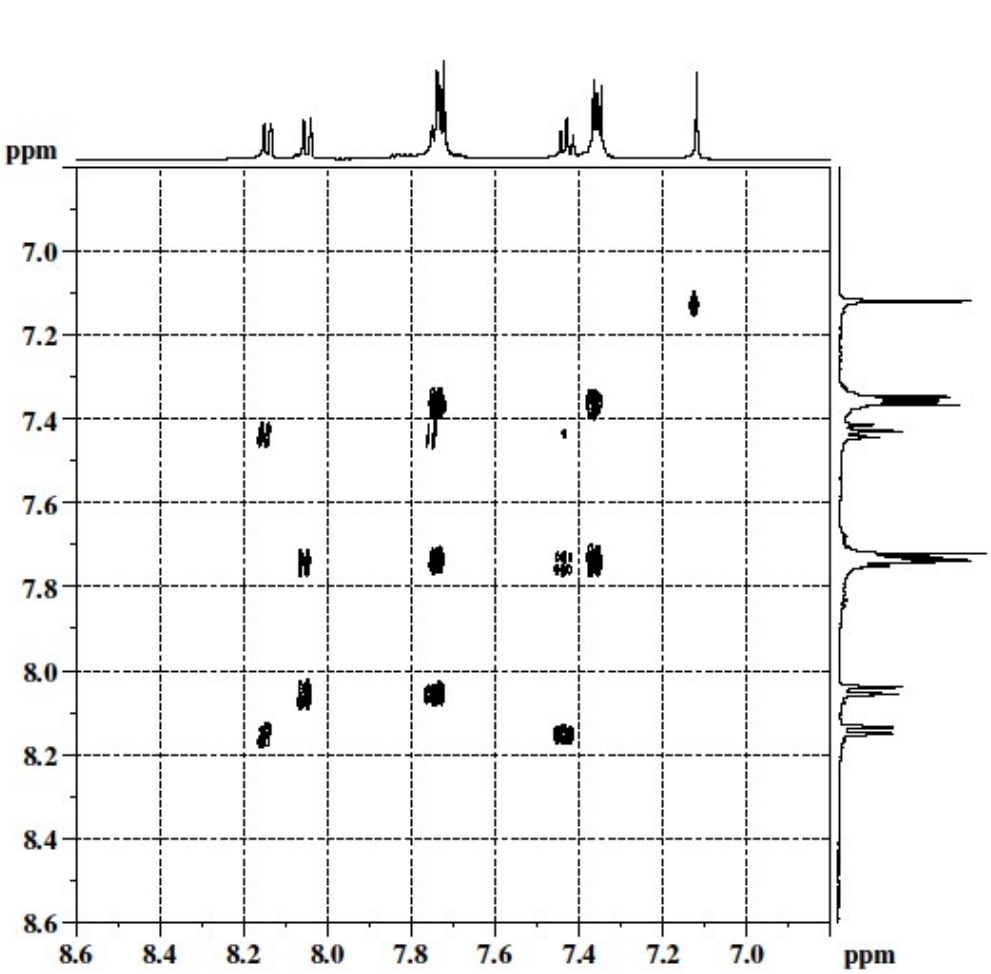


Figure S47. 2D ^{1}H-^{1}H COSY NMR spectrum of **4a** in DMSO-d_6 at T = 303 K.

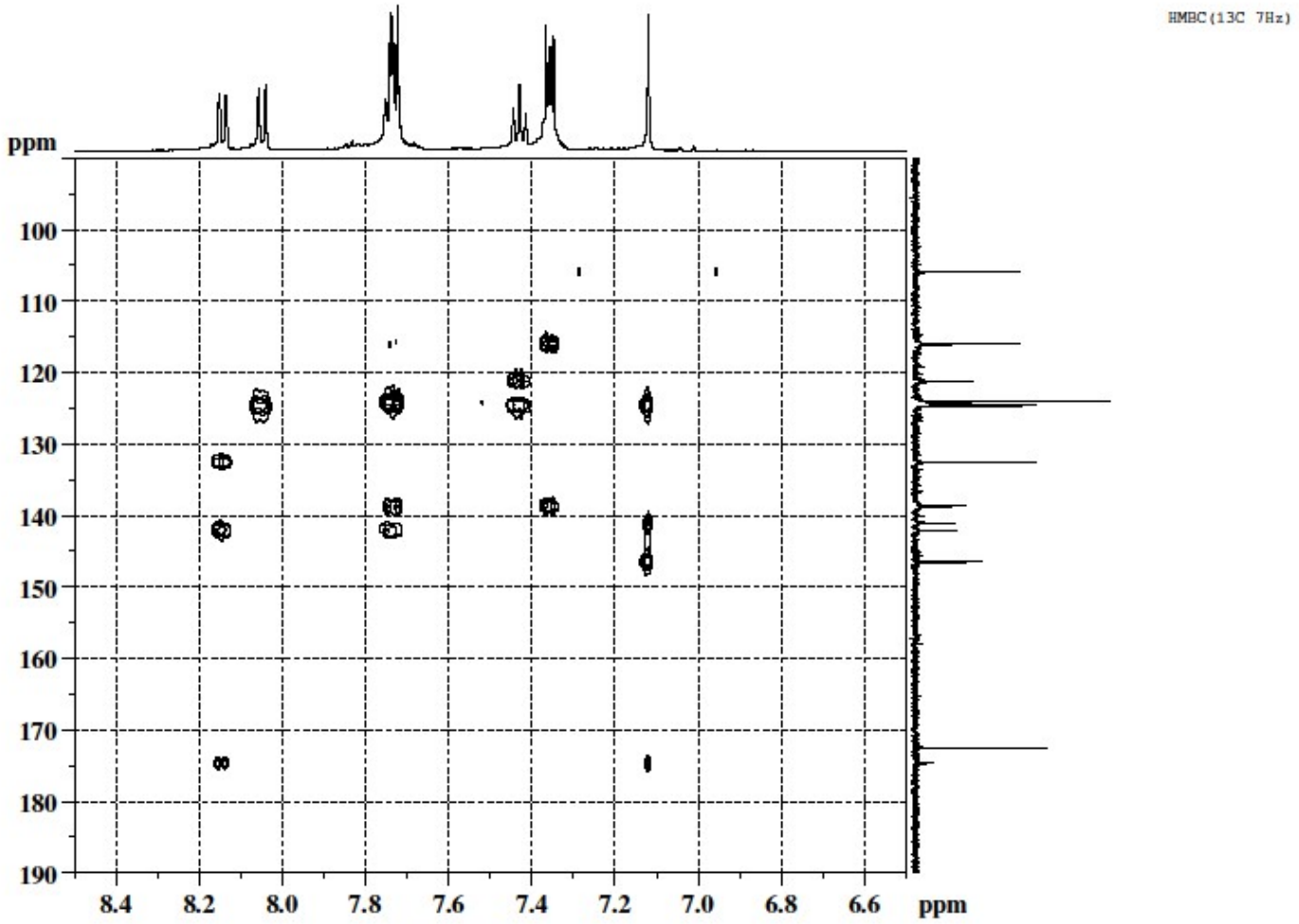


Figure S48. 2D ^{1}H-^{13}C HMBC NMR spectrum of **4a** in DMSO-d_6 at T = 303 K.

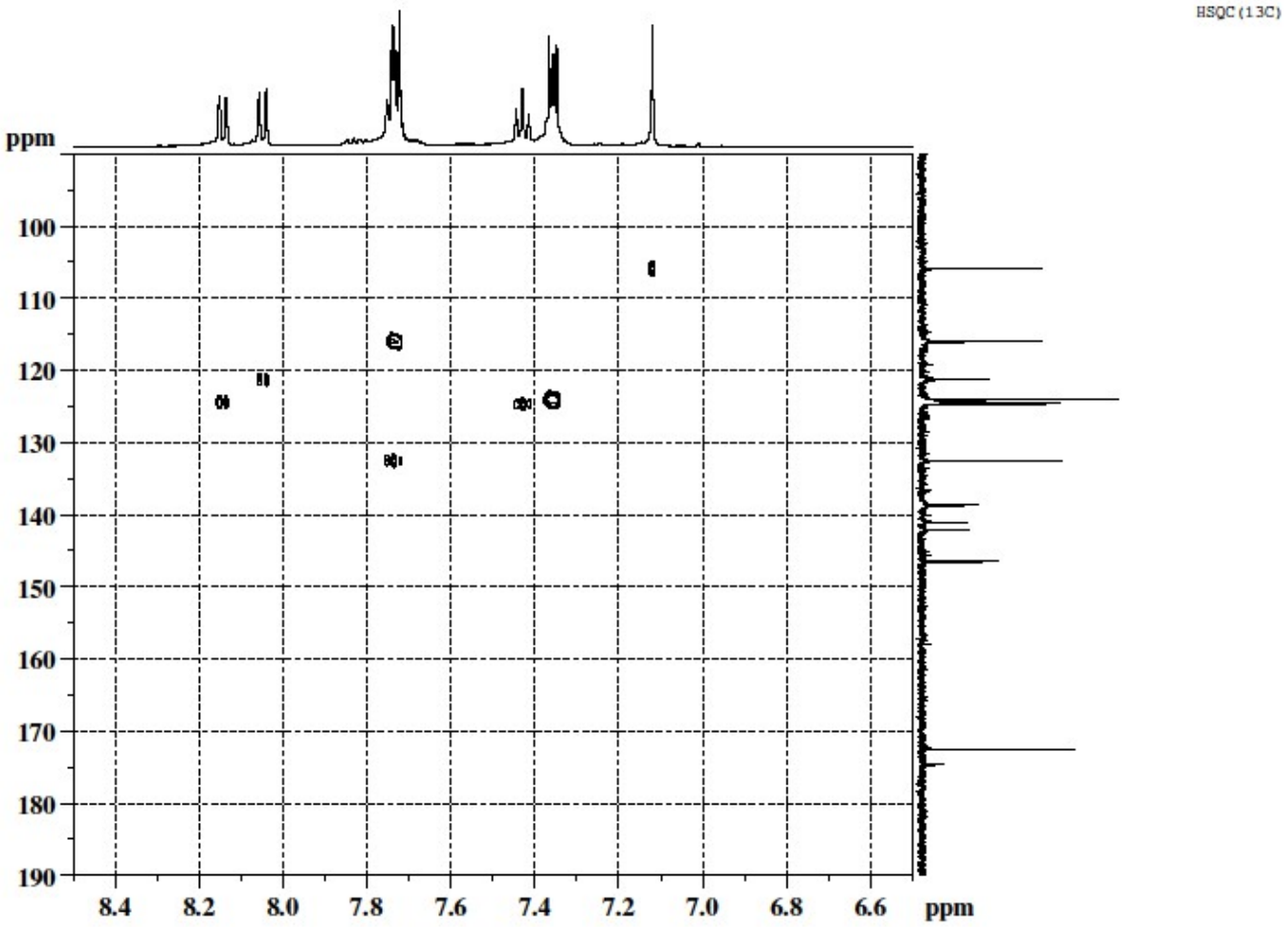


Figure S49. 2D 1H-^{13}C HSQC NMR spectrum of **4a** in DMSO-d_6 at T = 303 K.

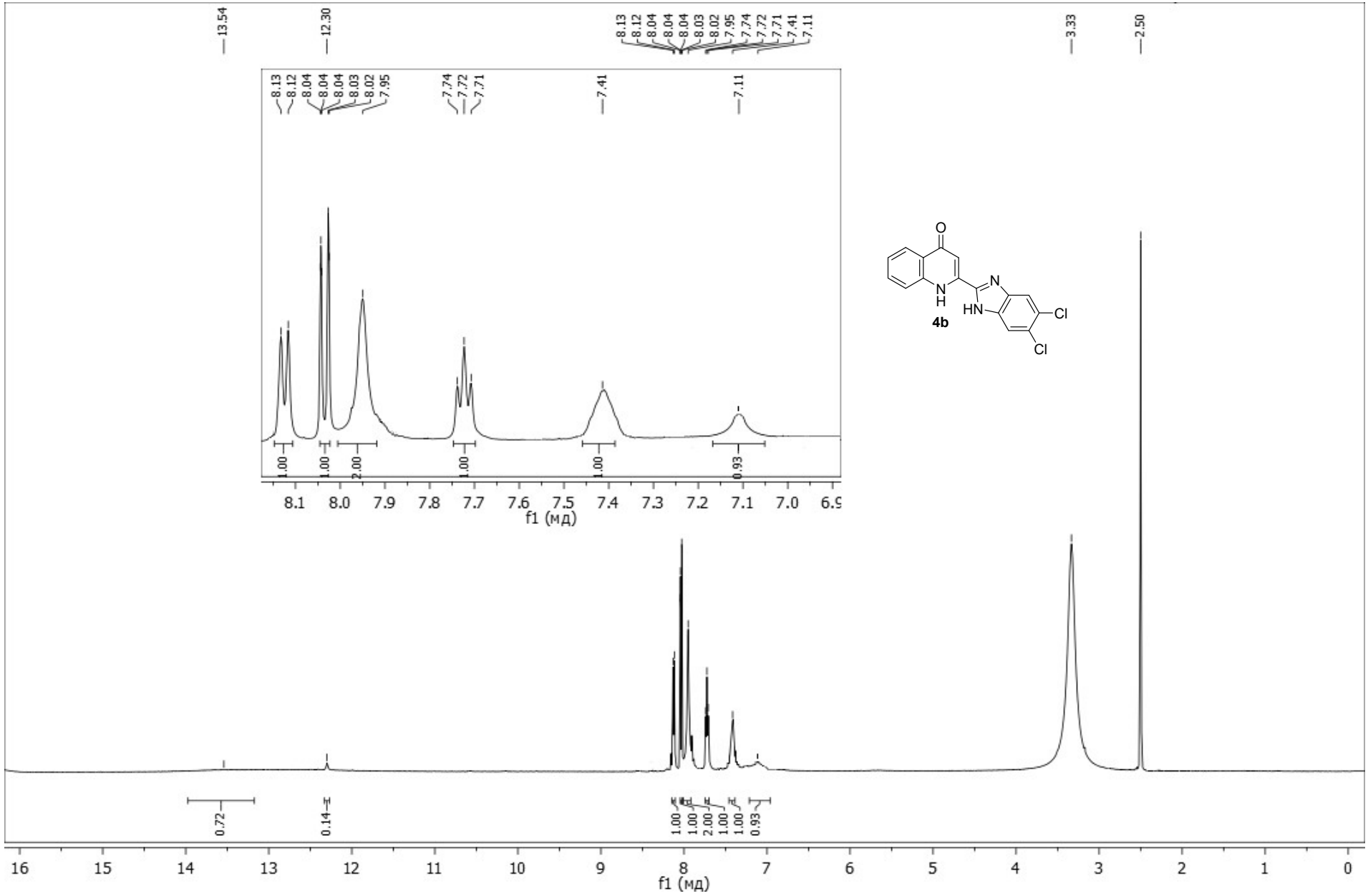


Figure S50. 1D ^{1}H NMR spectrum of **4b** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

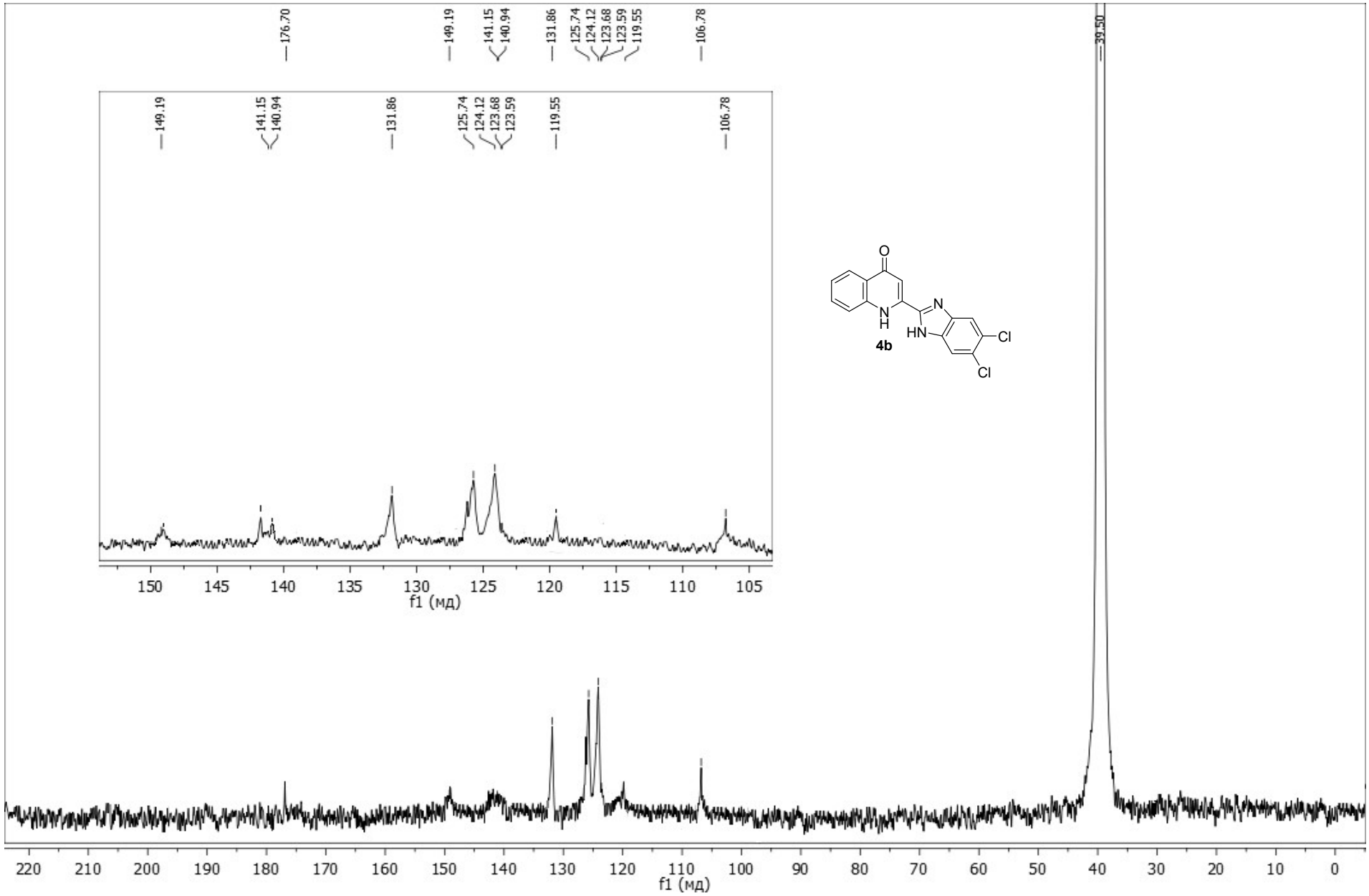


Figure S51. $^{13}C\{^{1}H\}$ NMR spectrum of **4b** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

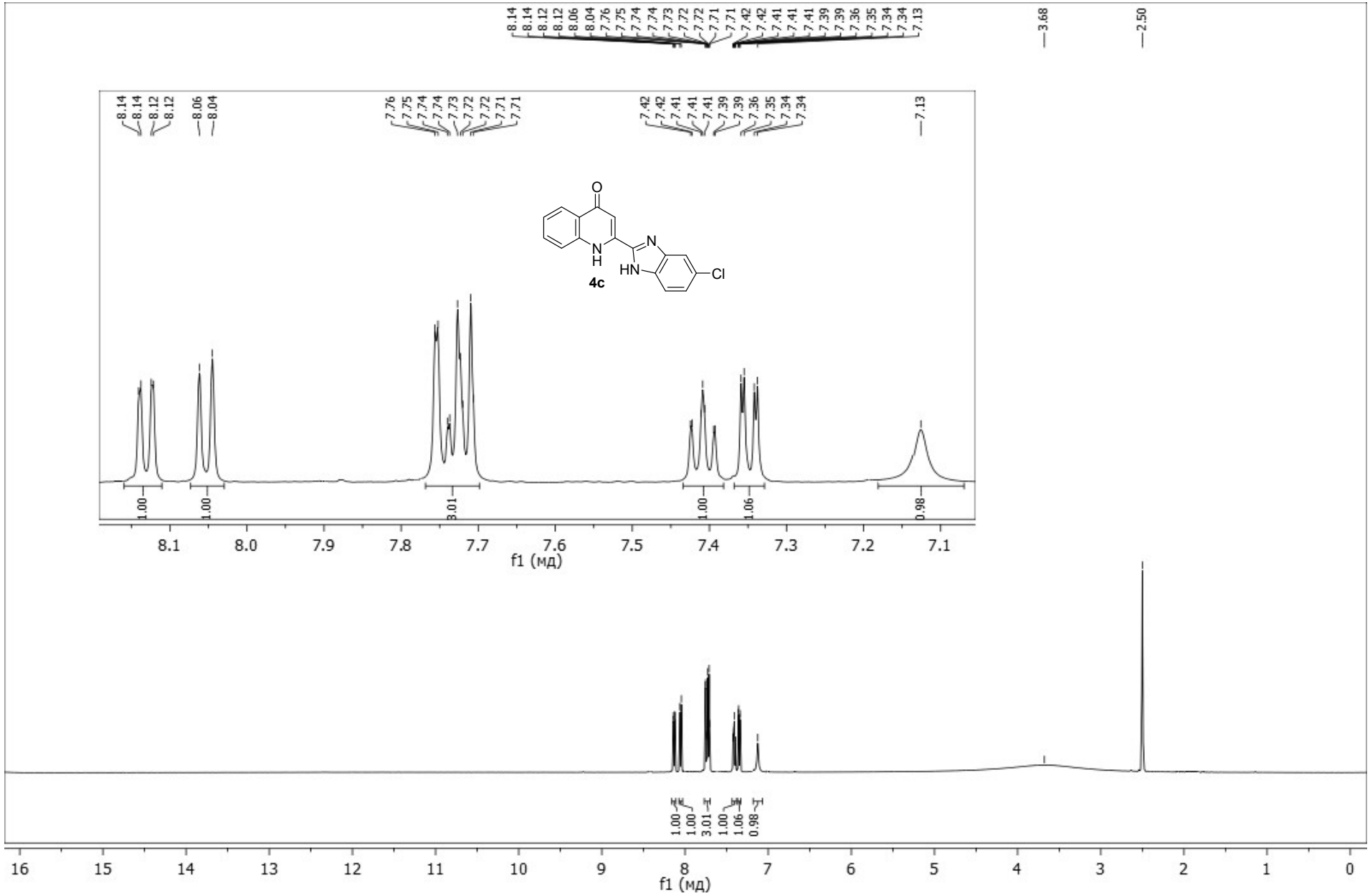


Figure S52. 1D ^{1}H NMR spectrum of **4c** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

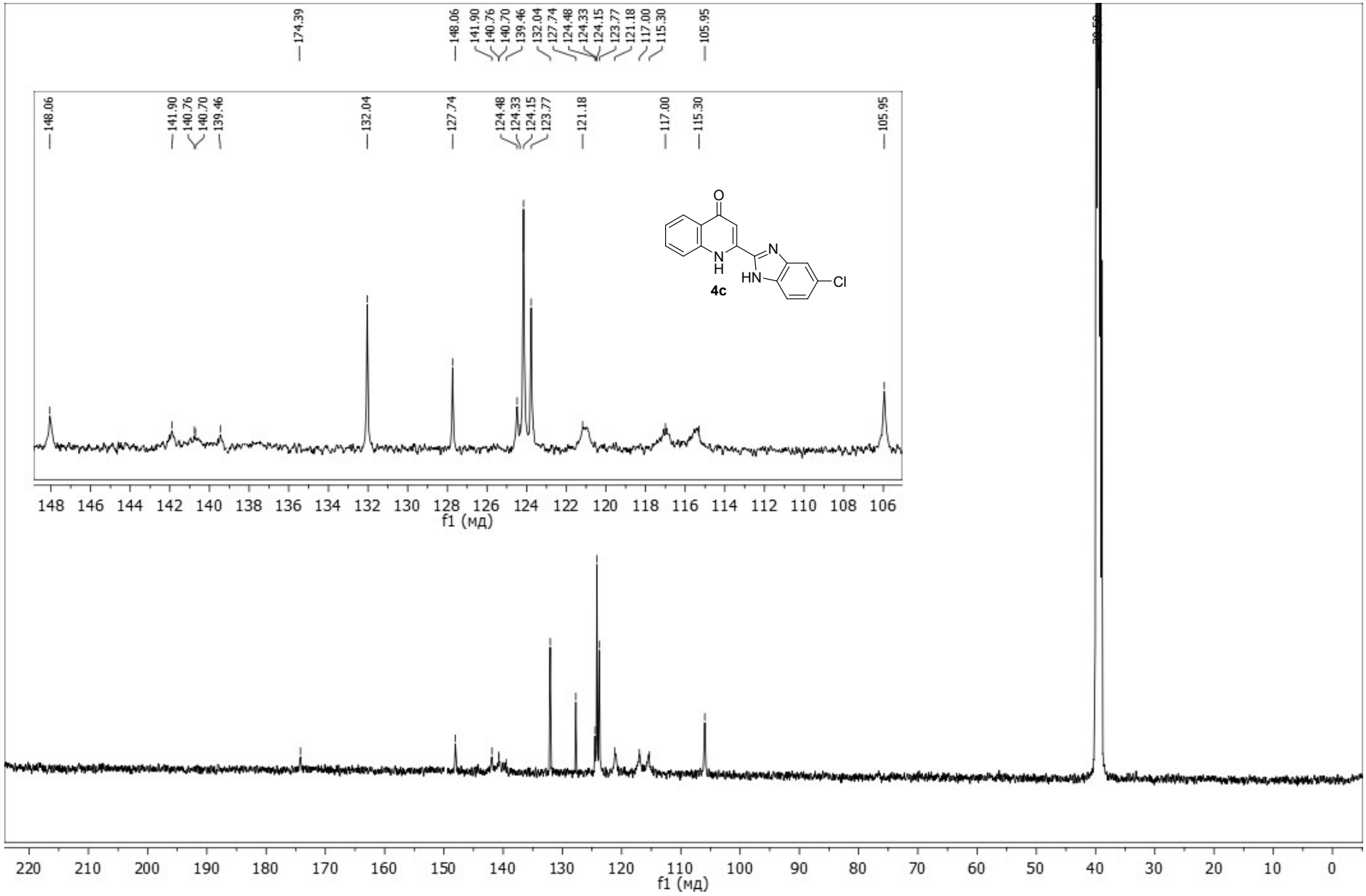


Figure S53. $^{13}C\{^{1}H\}$ NMR spectrum of **4c** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

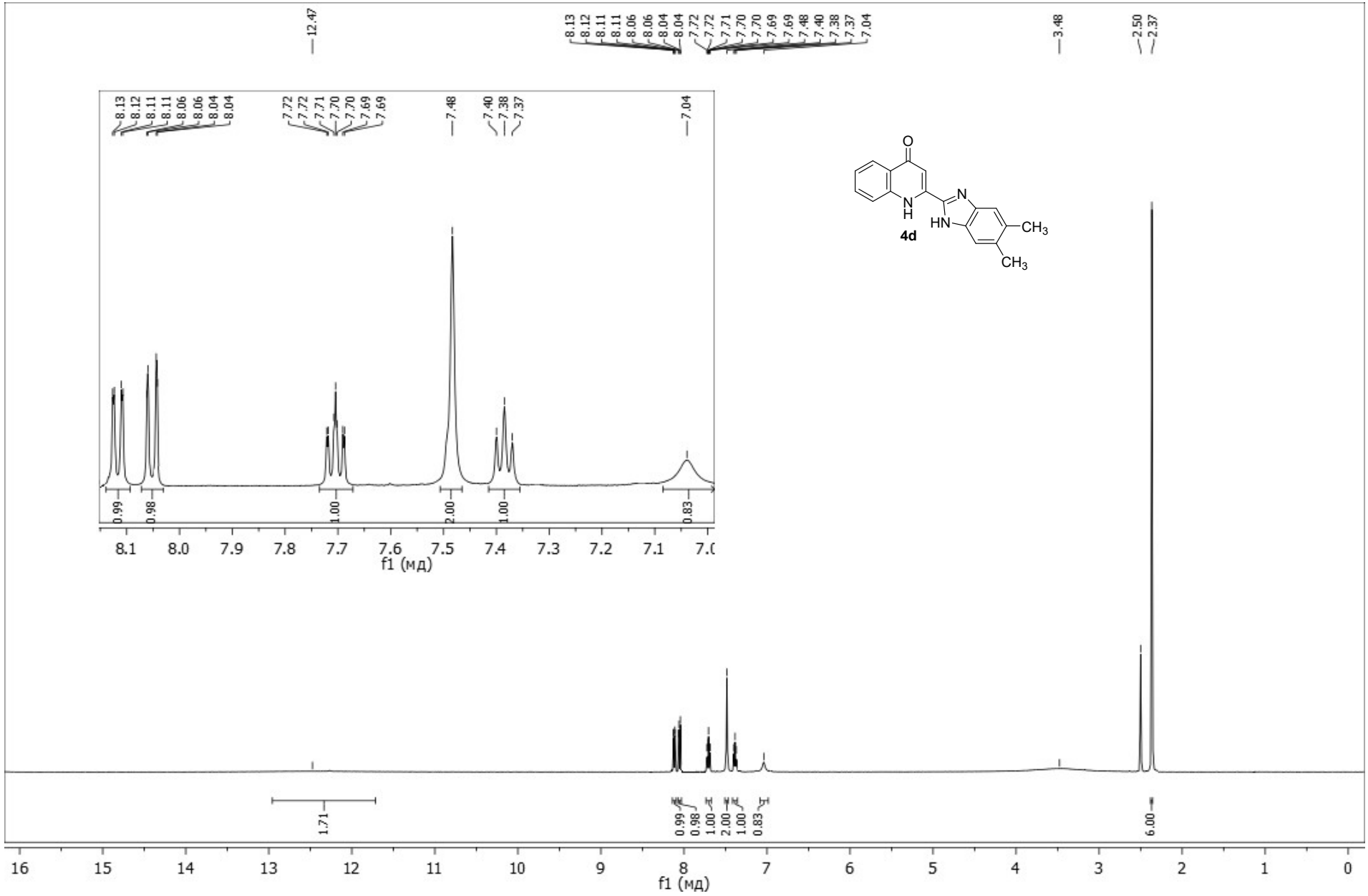


Figure S54. 1D ^{1}H NMR spectrum of **4d** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

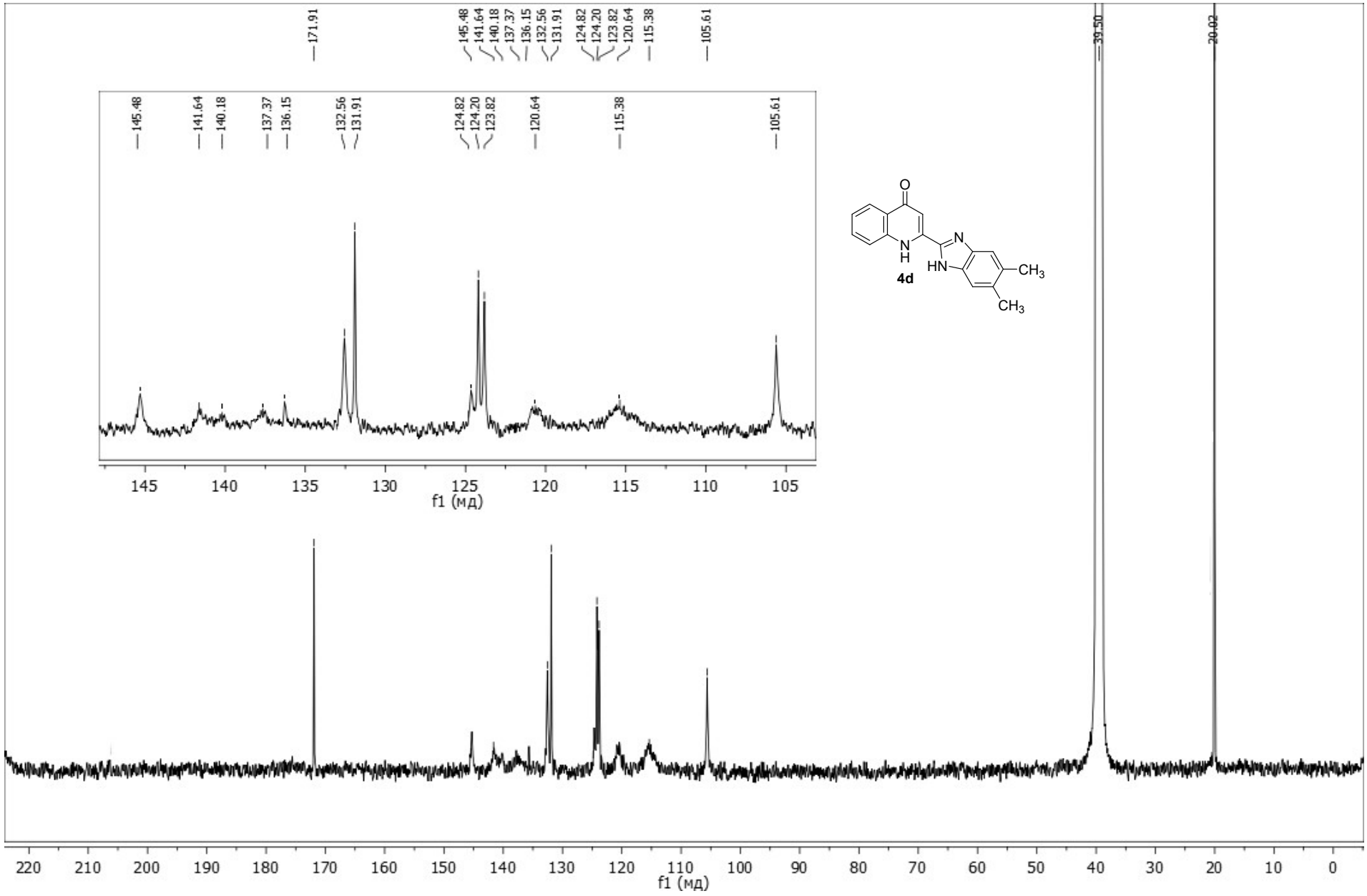


Figure S55. $^{13}C\{^{1}H\}$ NMR spectrum of **4d** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

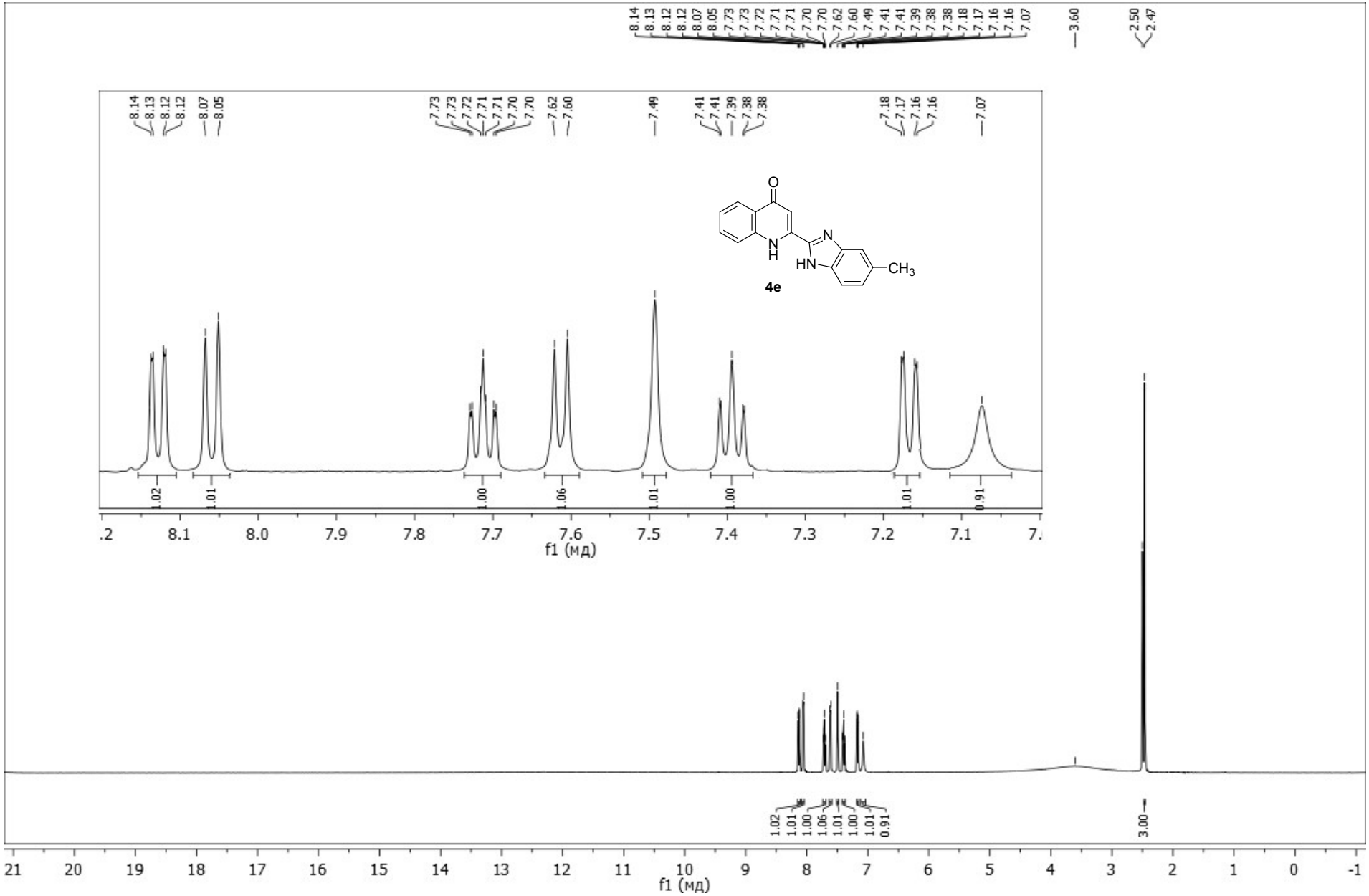


Figure S56. 1D ^{1}H NMR spectrum of **4e** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

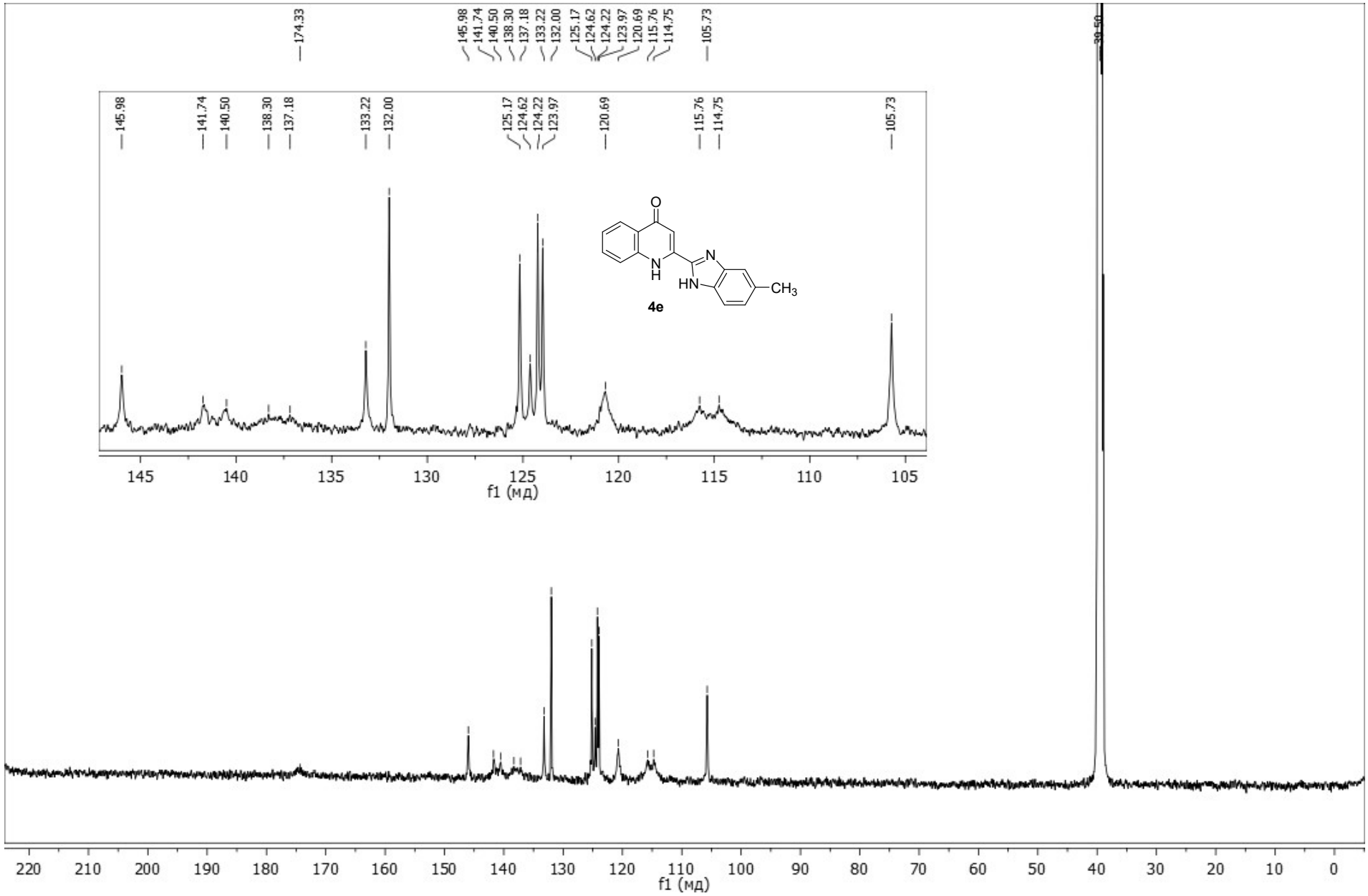


Figure S57. $^{13}C\{^{1}H\}$ NMR spectrum of **4e** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

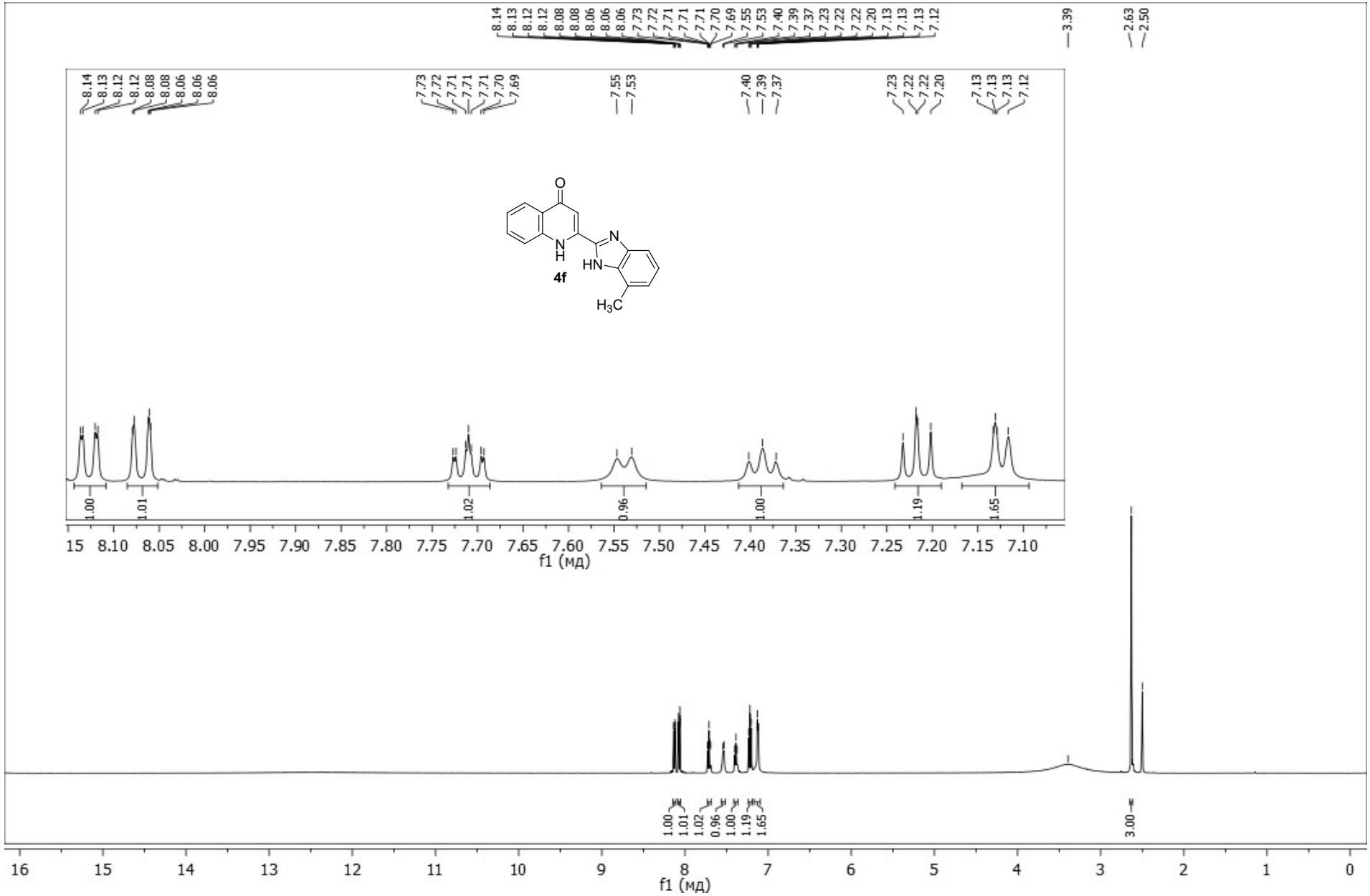


Figure S58. 1D ^{1}H NMR spectrum of **4f** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

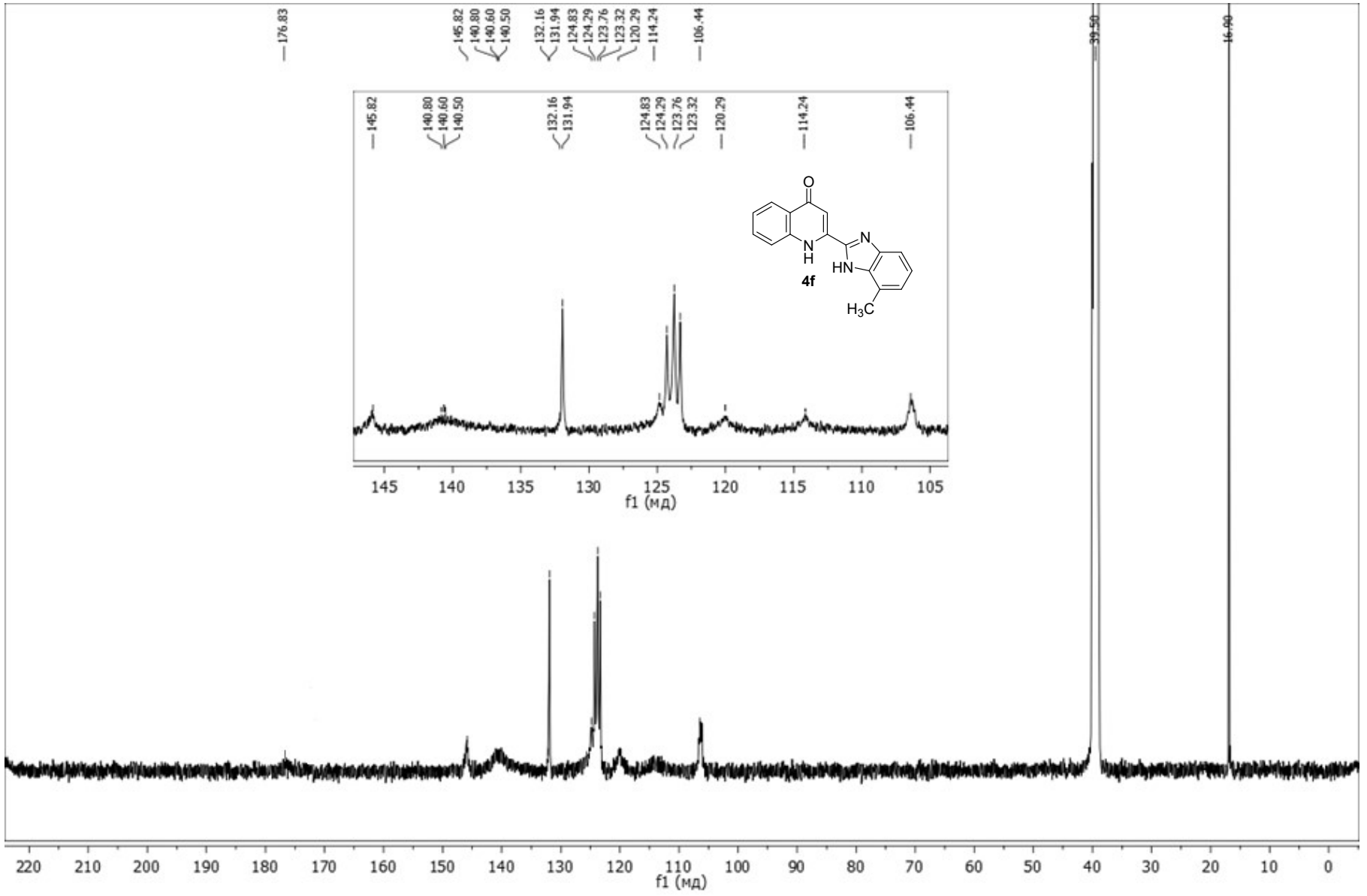


Figure S59. $^{13}C\{^{1}H\}$ NMR spectrum of **4f** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

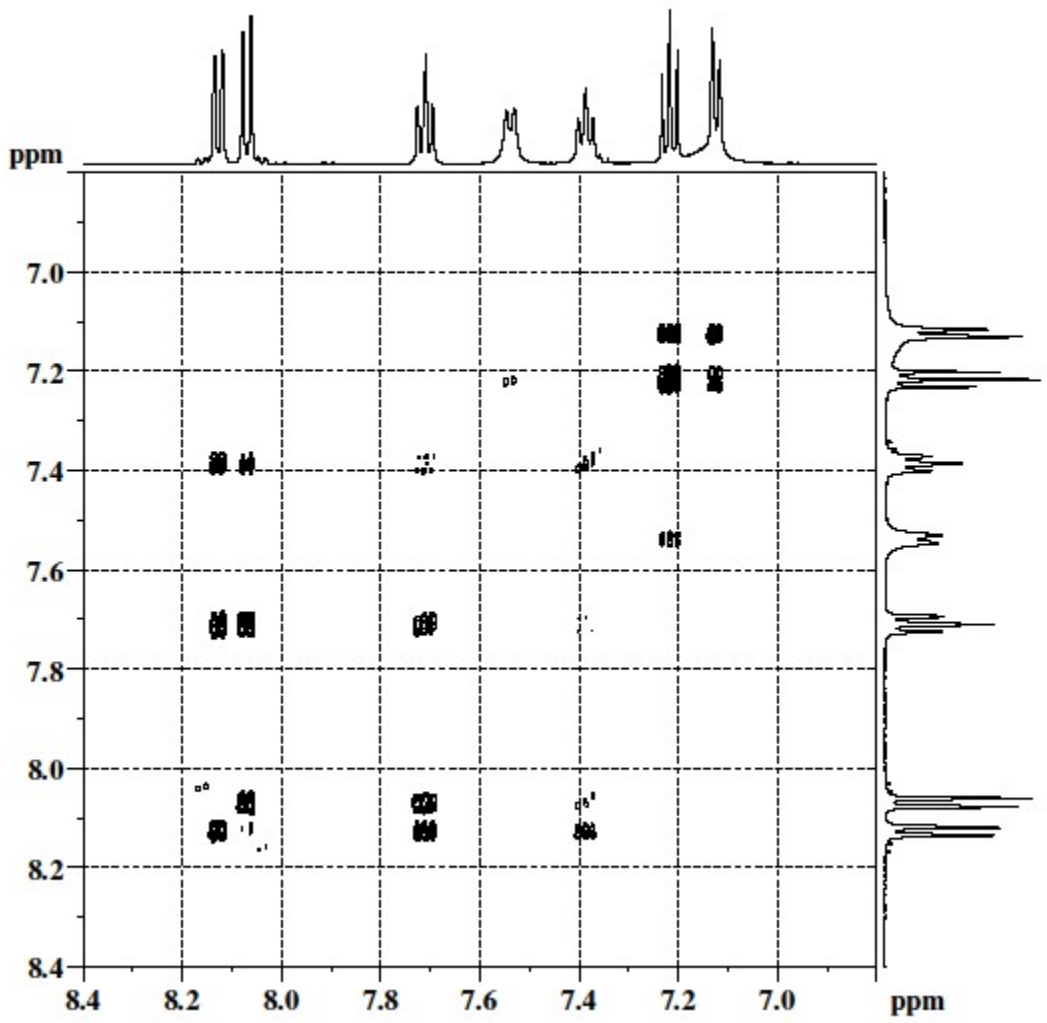


Figure S60. 2D ^{1}H-^{1}H COSY NMR spectrum of **4f** in DMSO-d_6 at T = 303 K.

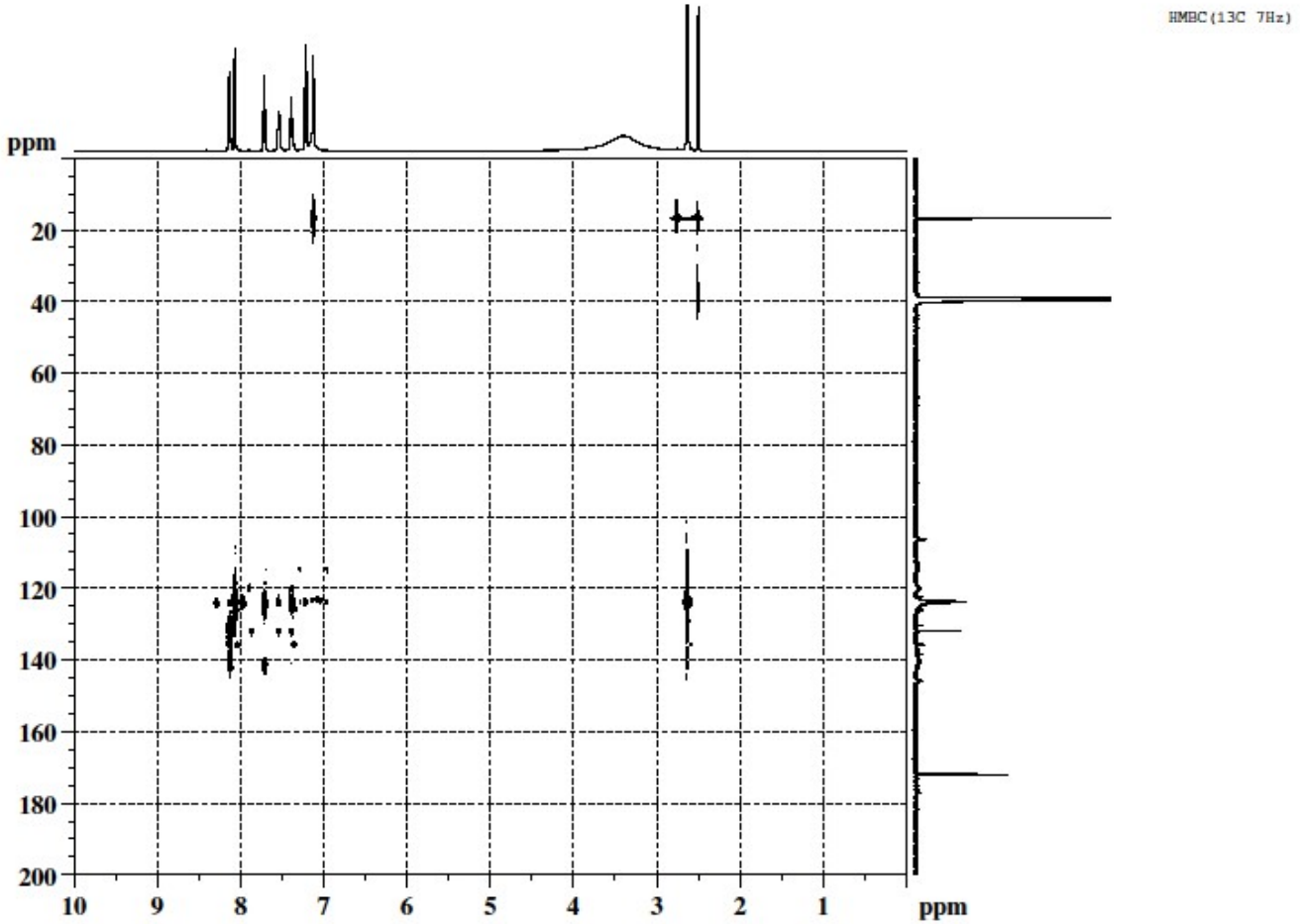


Figure S61. 2D ^{1}H-^{13}C HMBC NMR spectrum of **4f** in DMSO-d_6 at T = 303 K.

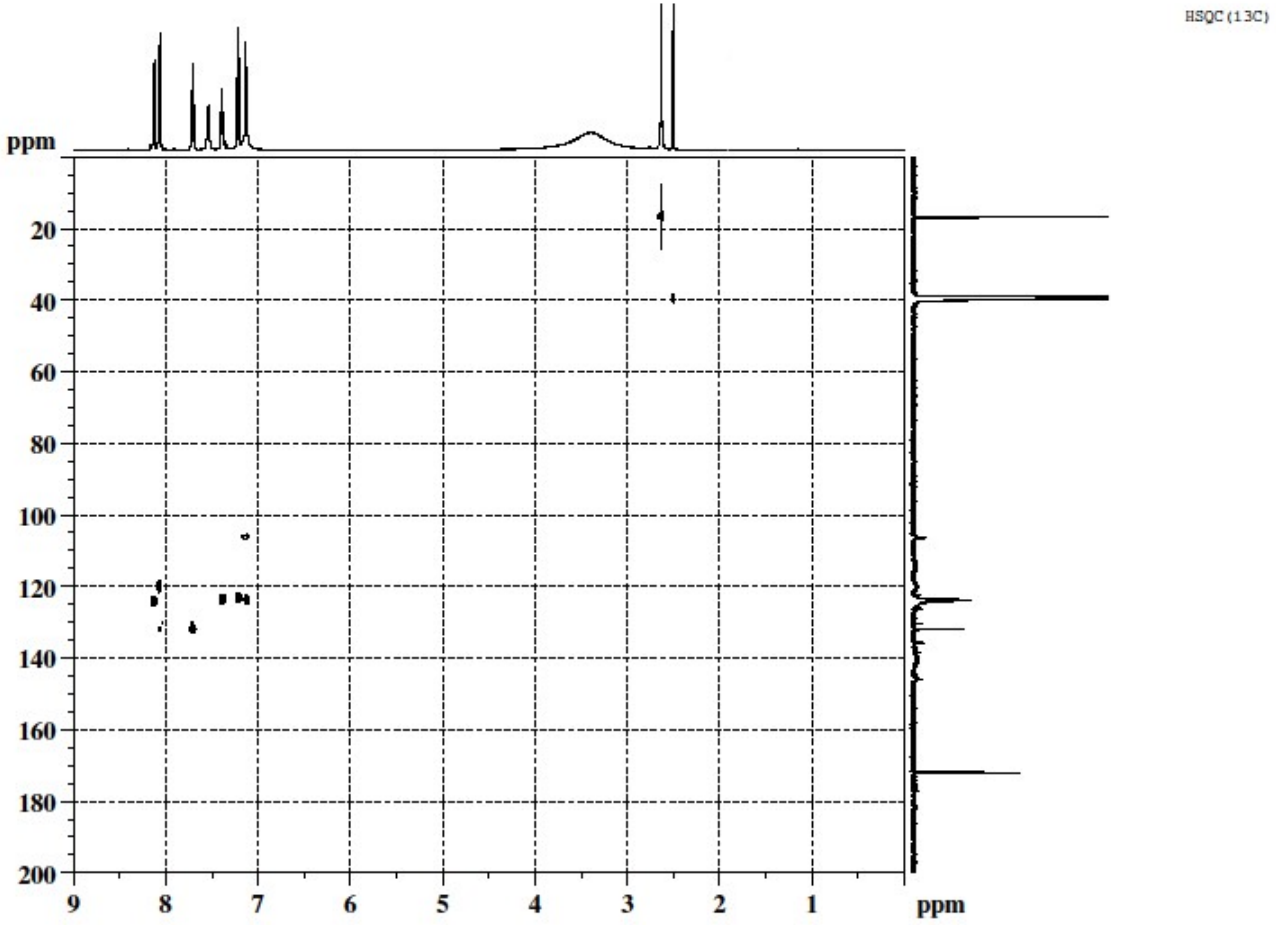


Figure S62. 2D 1H-^{13}C HSQC NMR spectrum of **4f** in DMSO-d_6 at T = 303 K.

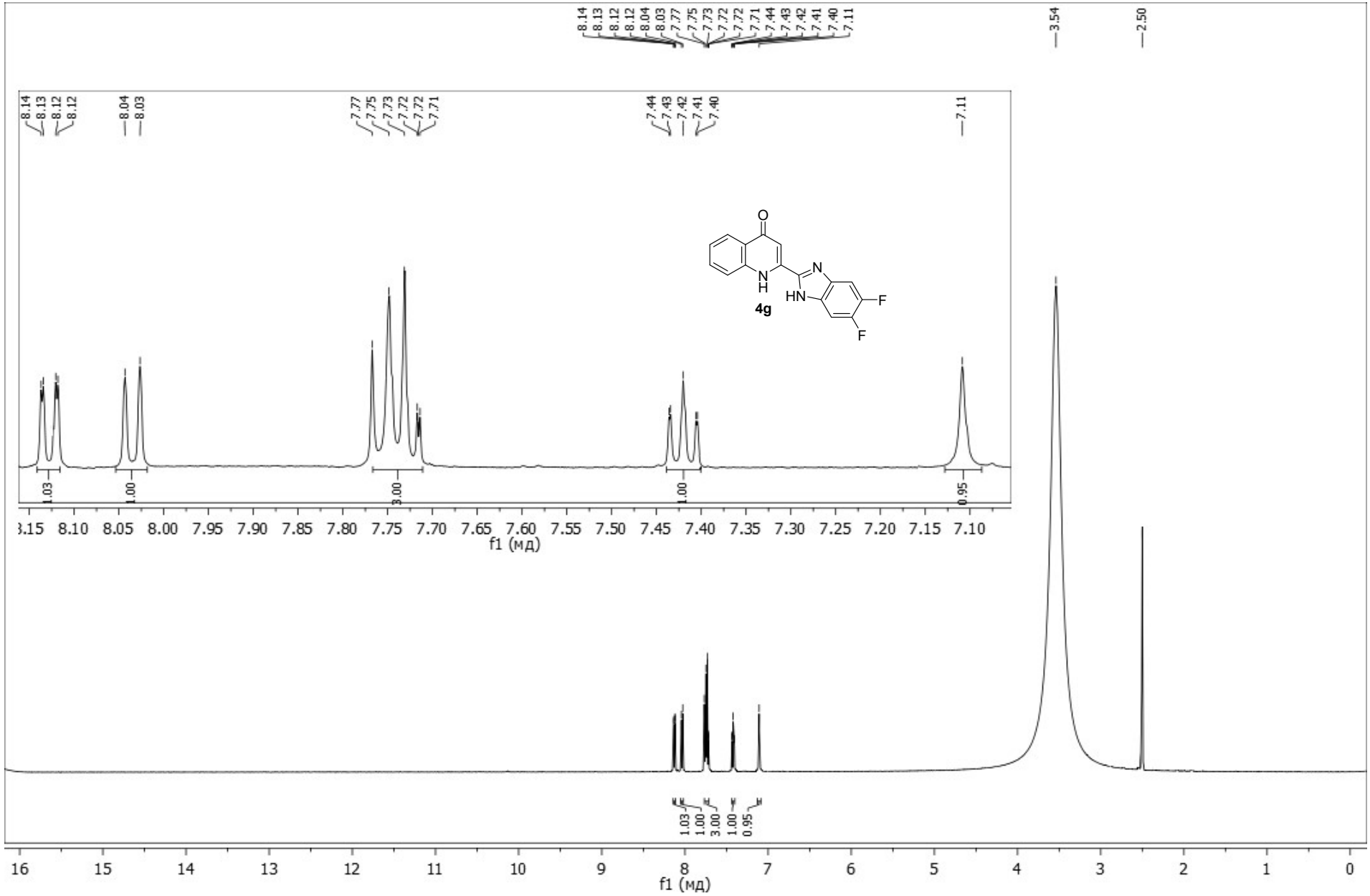


Figure S63. 1D ^{1}H NMR spectrum of **4g** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

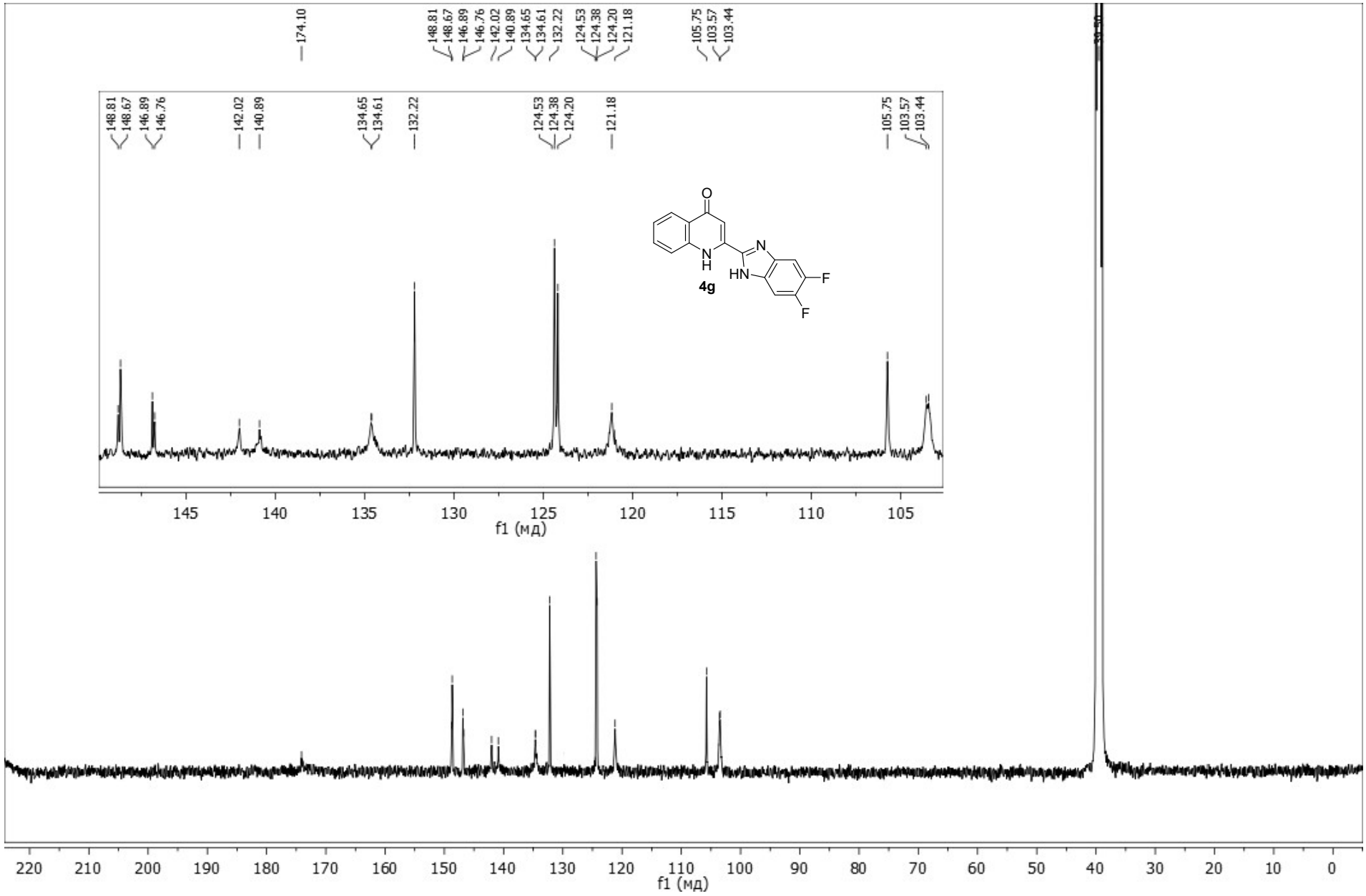


Figure S64. $^{13}C\{^{1}H\}$ NMR spectrum of **4g** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

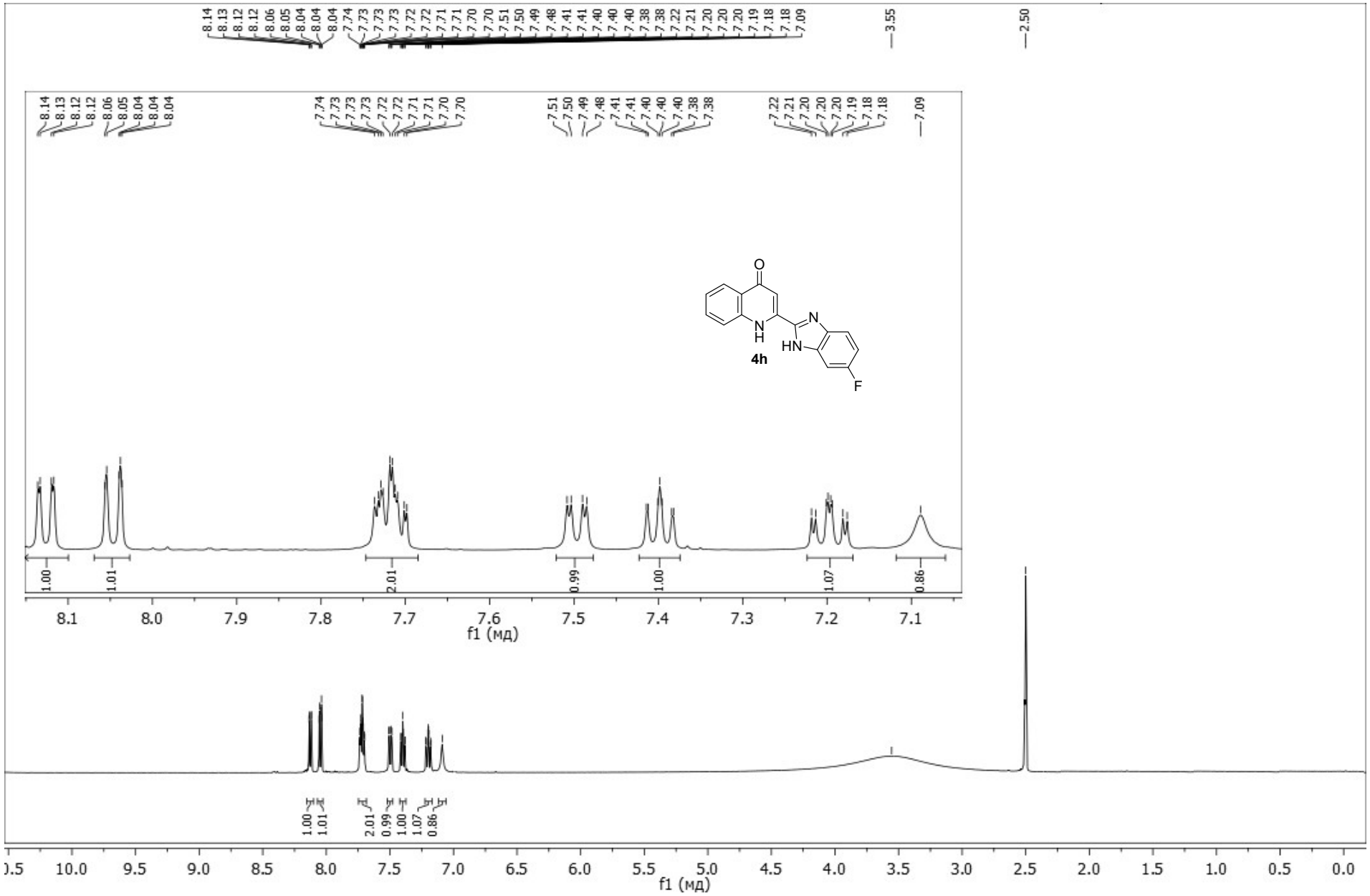


Figure S65. 1D ^{1}H NMR spectrum of **4h** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

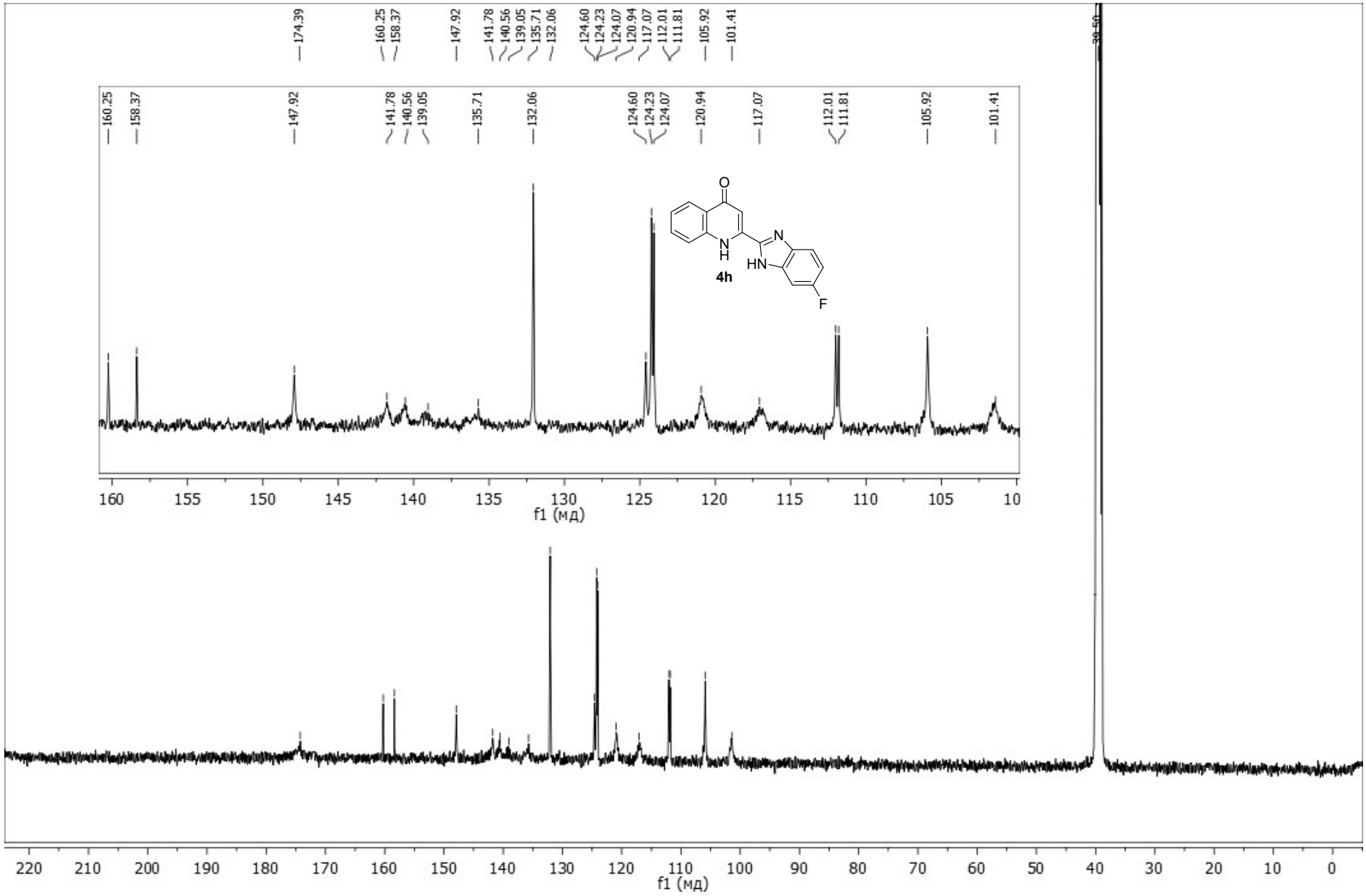


Figure S66. $^{13}C\{^{1}H\}$ NMR spectrum of **4h** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

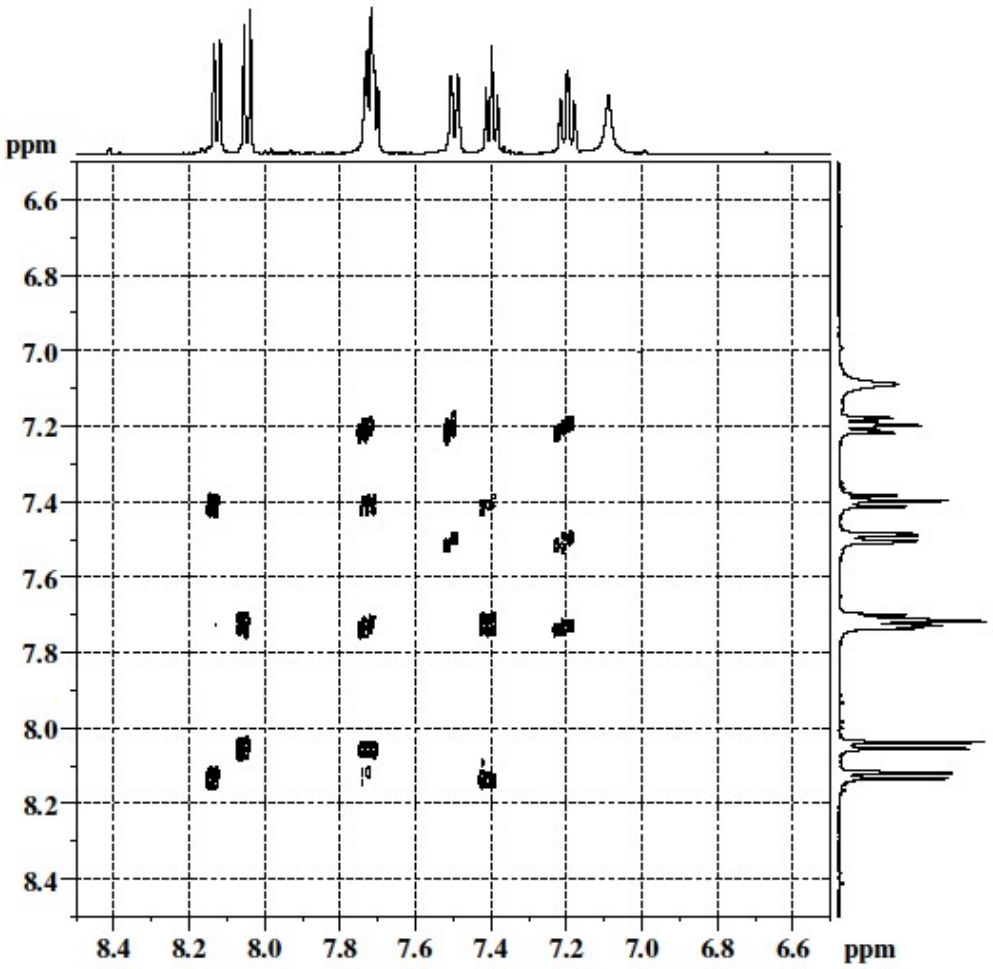


Figure S67. 2D ^{1}H-^{1}H COSY NMR spectrum of **4h** in DMSO-d_6 at T = 303 K.

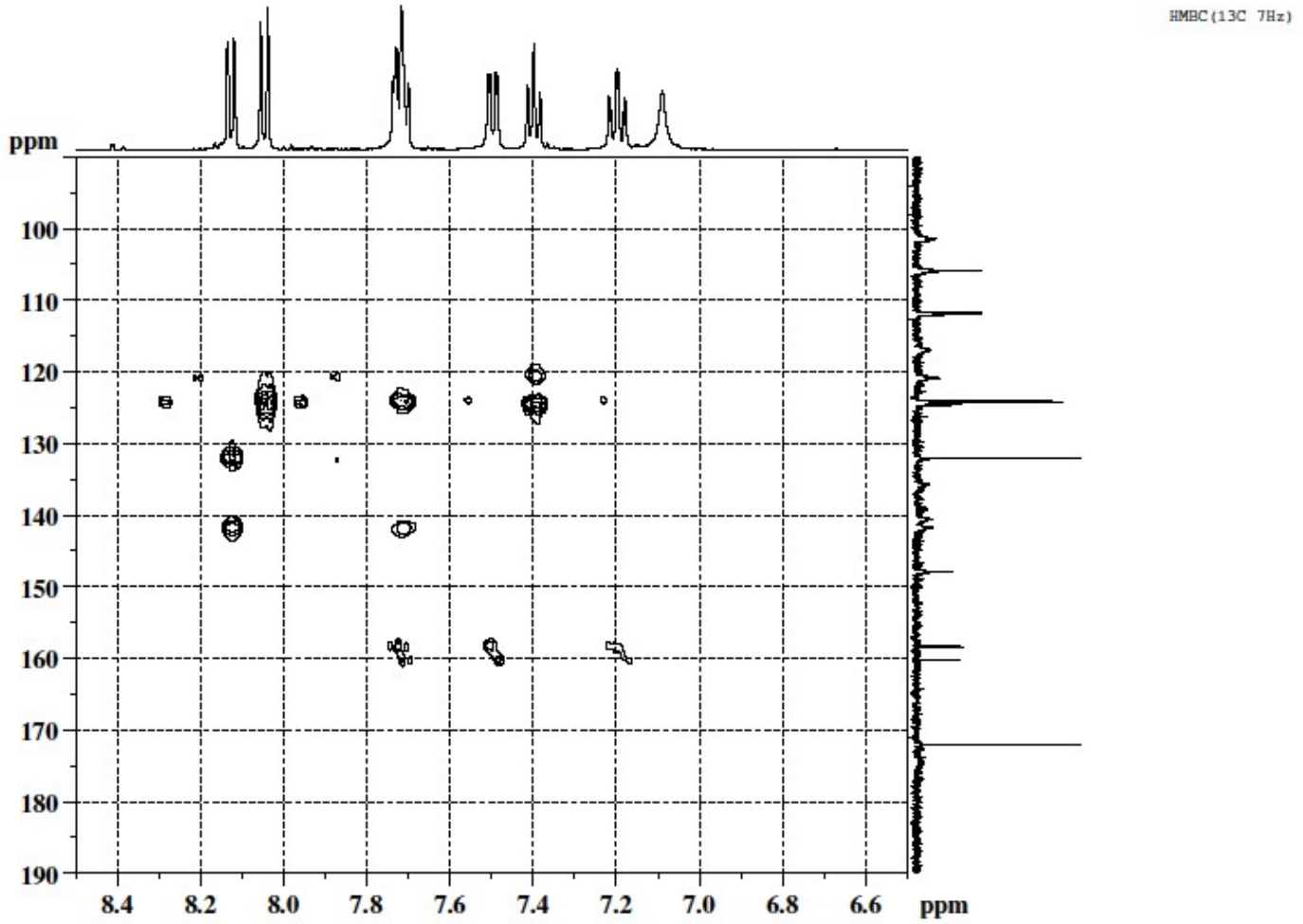


Figure S68. 2D ^{1}H-^{13}C HMBC NMR spectrum of **4h** in DMSO-d_6 at T = 303 K.

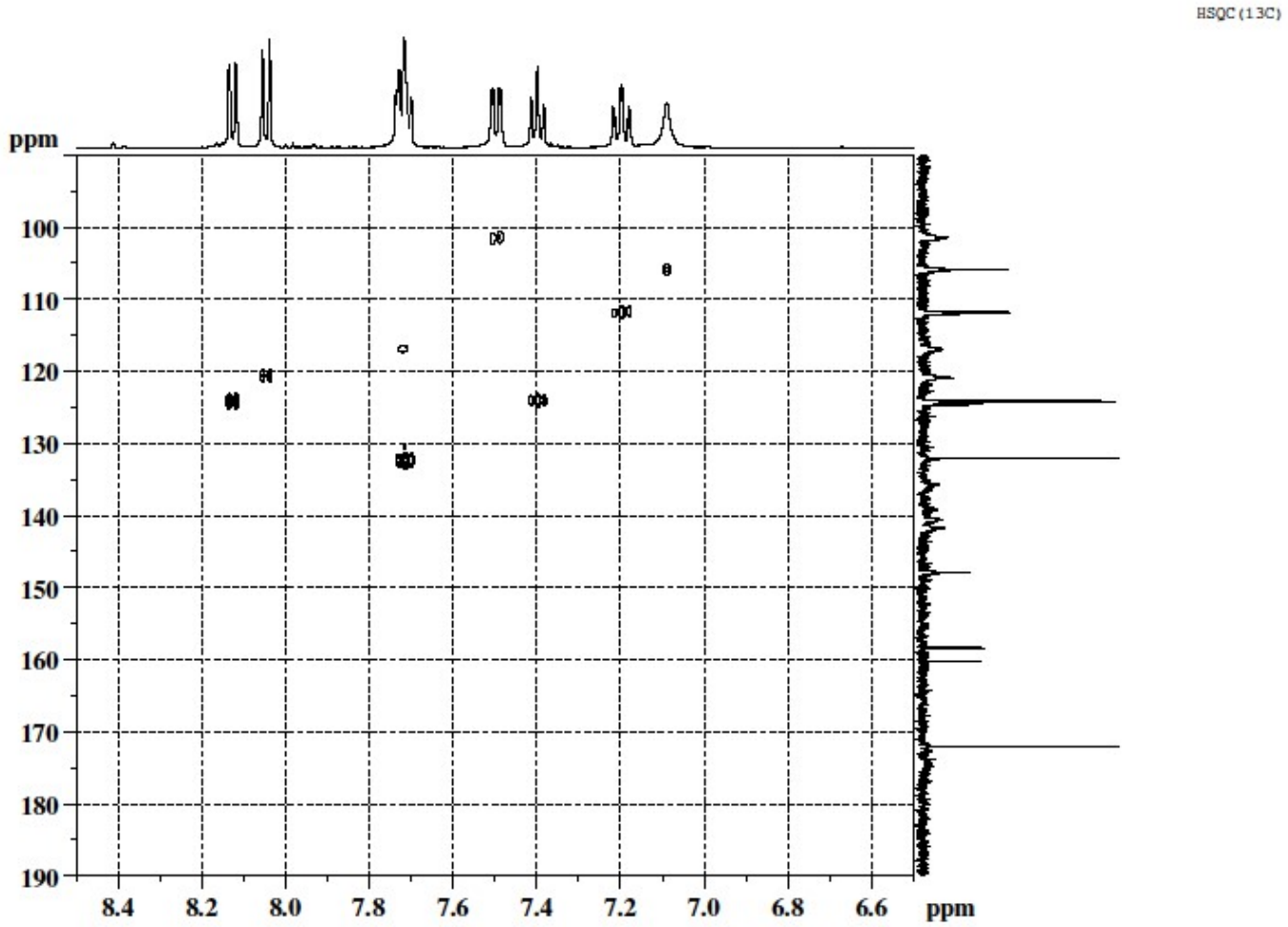


Figure S69. 2D 1H-^{13}C HSQC NMR spectrum of **4h** in DMSO-d_6 at T = 303 K.

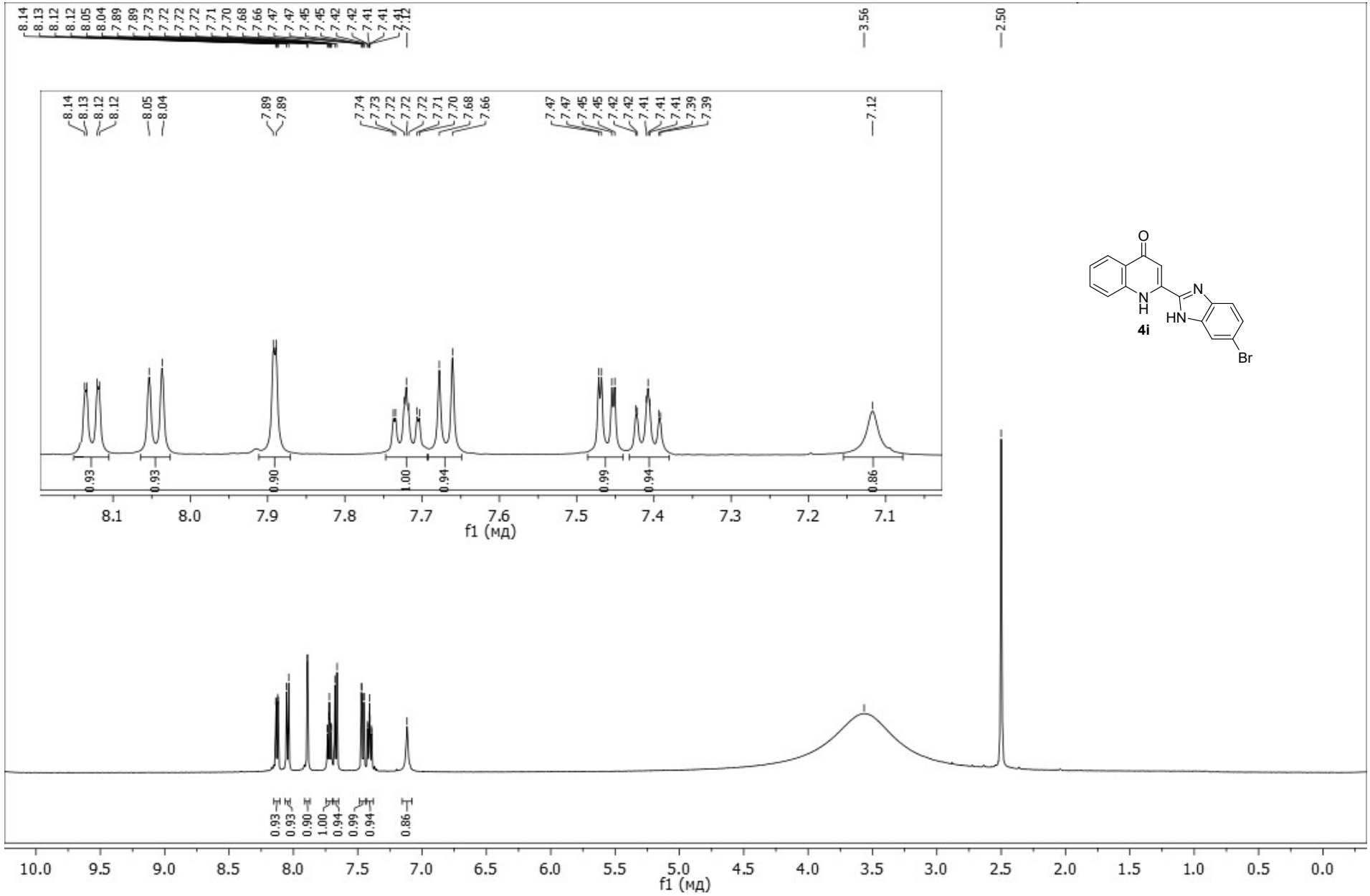


Figure S70. 1D ^{1}H NMR spectrum of **4i** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

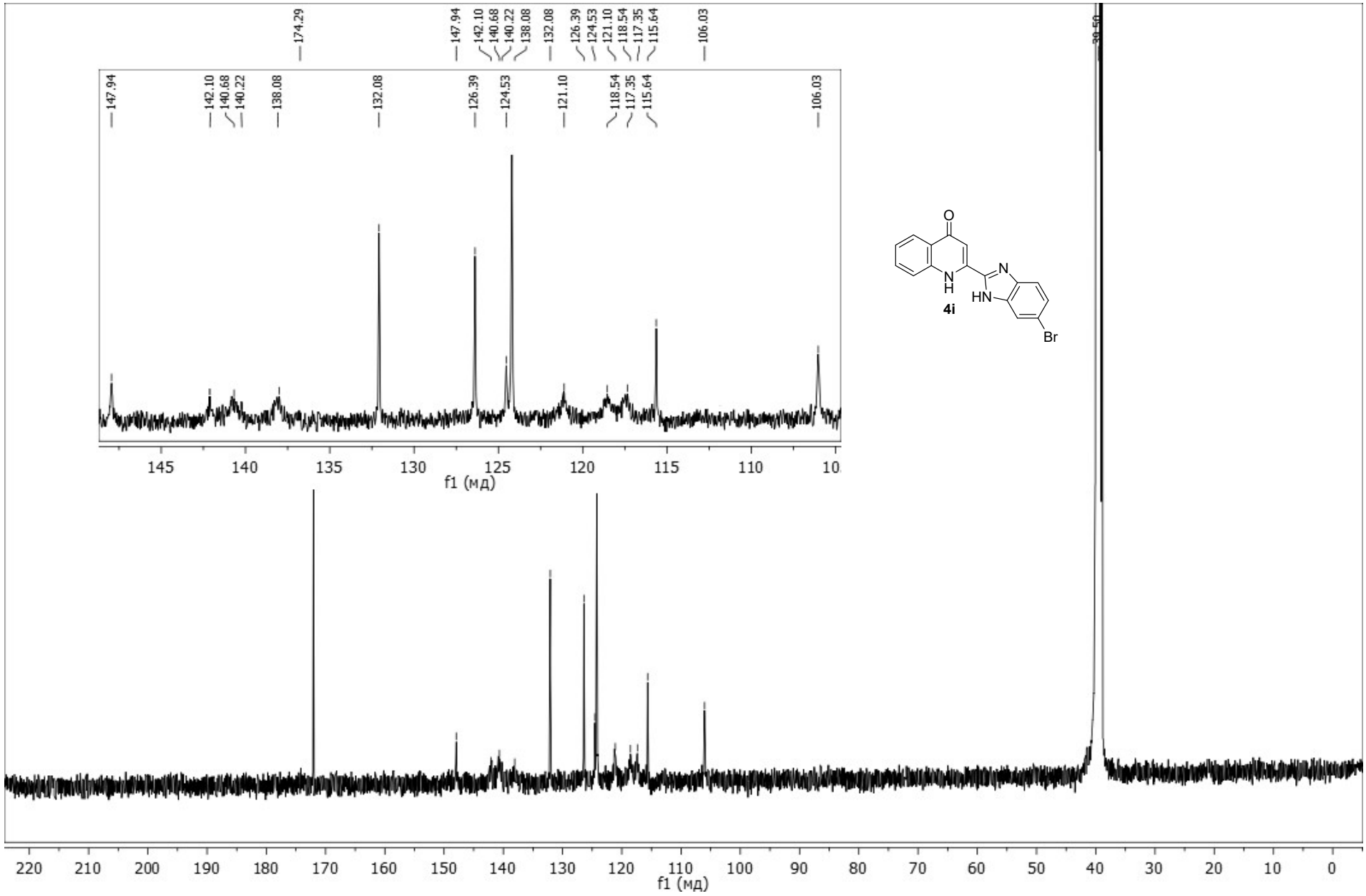


Figure S71. $^{13}C\{^{1}H\}$ NMR spectrum of **4i** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

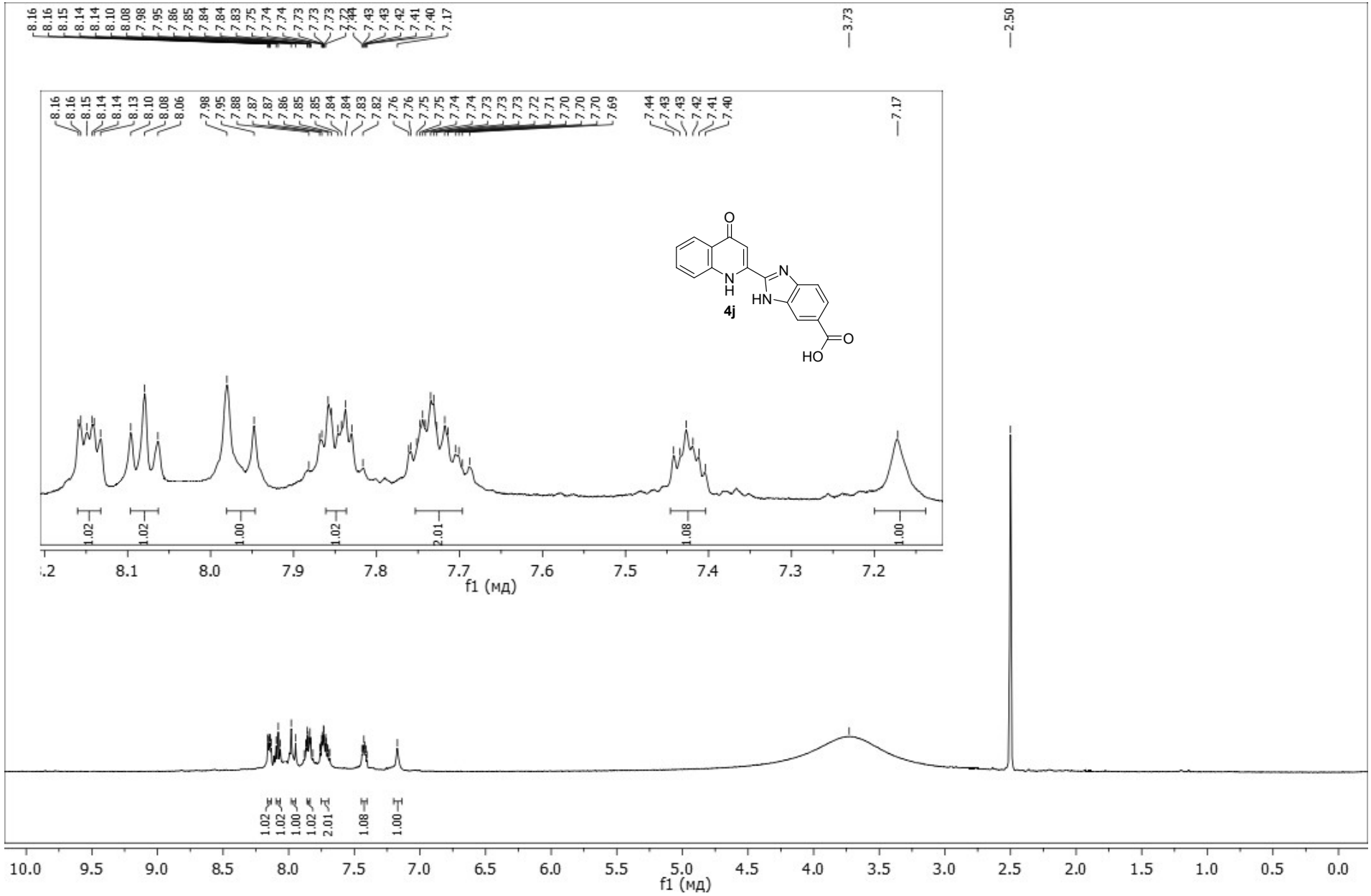


Figure S72. 1D ^{1}H NMR spectrum of **4j** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

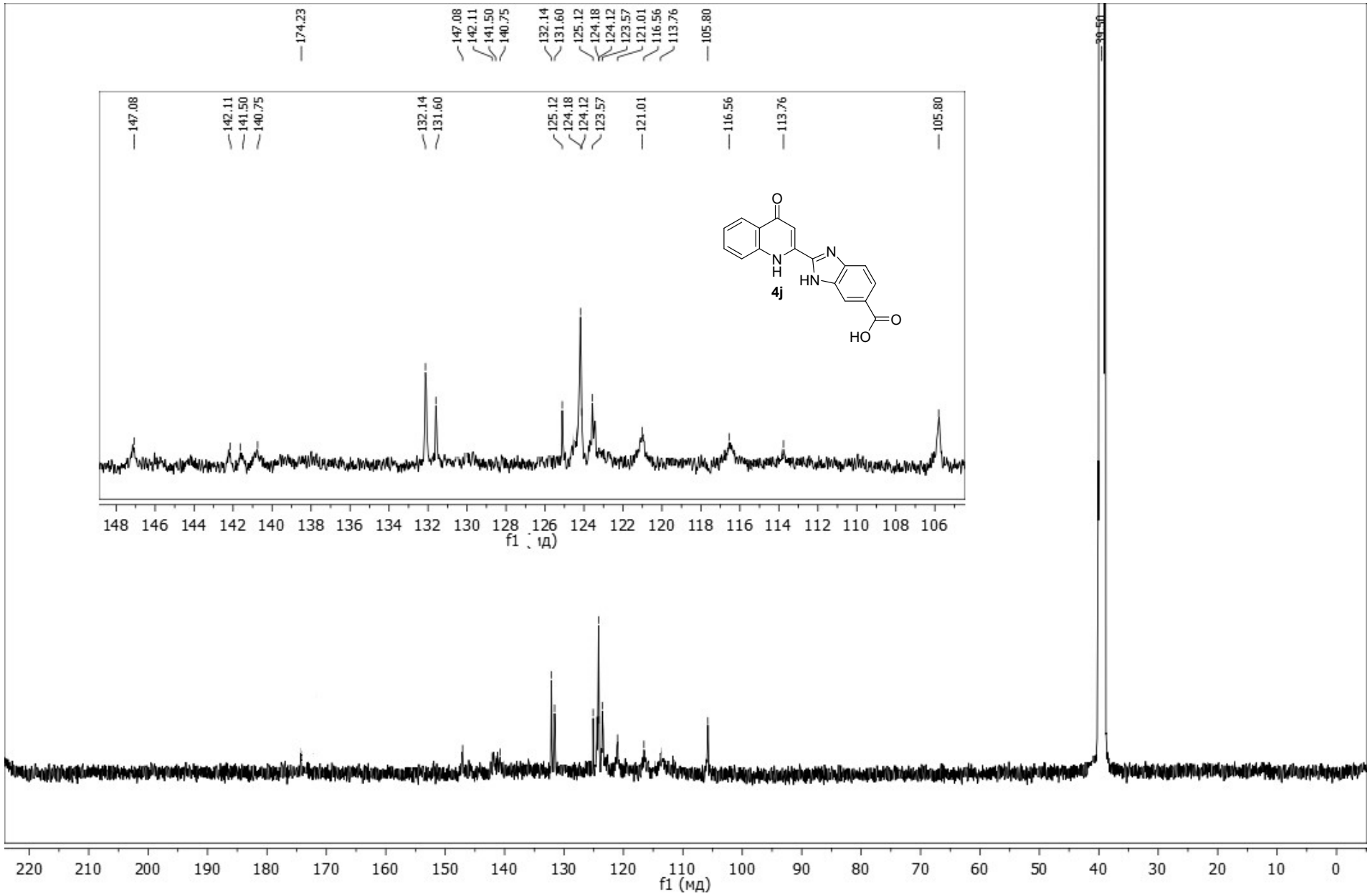


Figure S73. $^{13}C\{^{1}H\}$ NMR spectrum of **4j** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

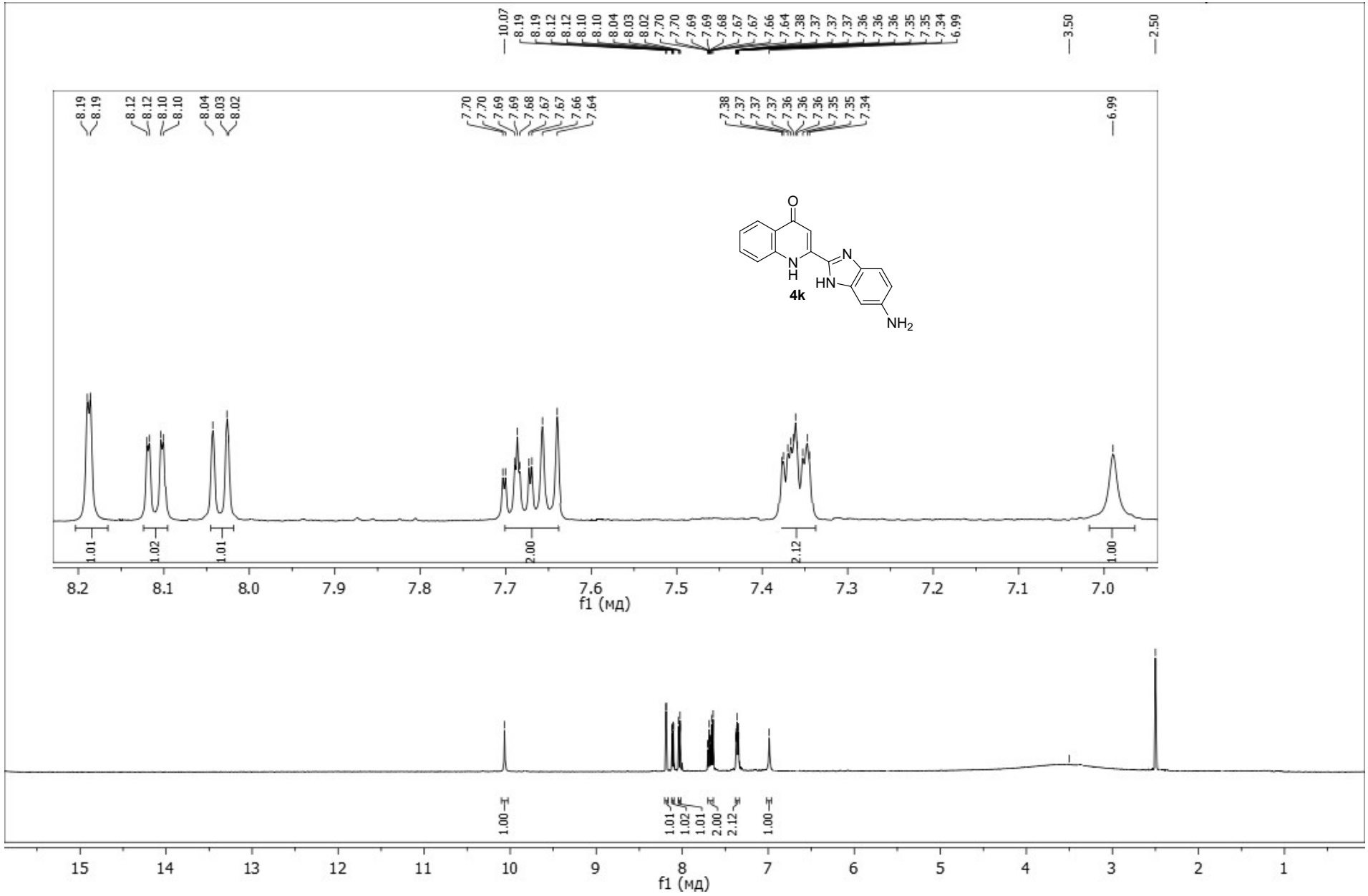


Figure S74. 1D ^{1}H NMR spectrum of **4k** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

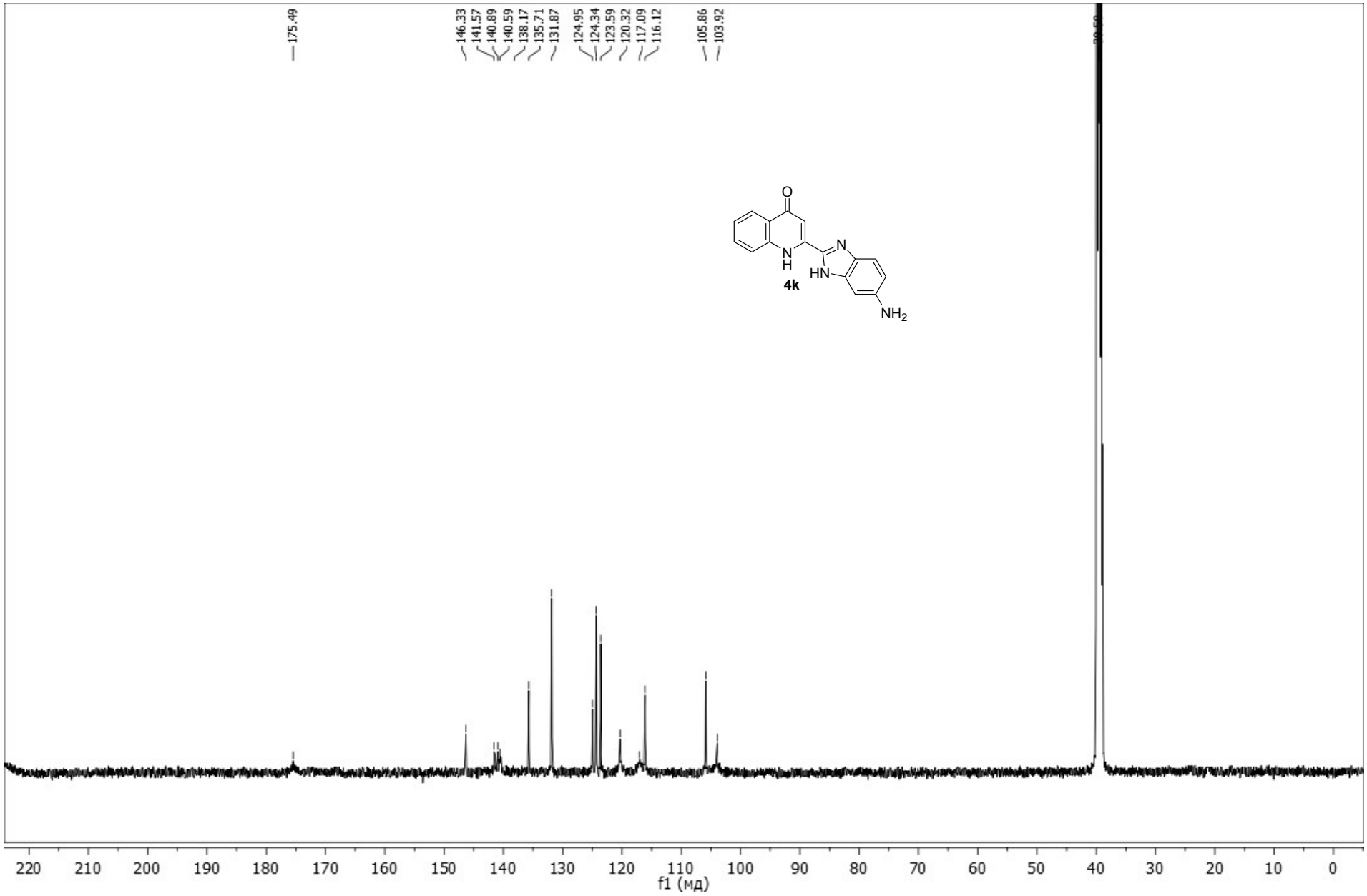


Figure S75. $^{13}C\{^{1}H\}$ NMR spectrum of **4k** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

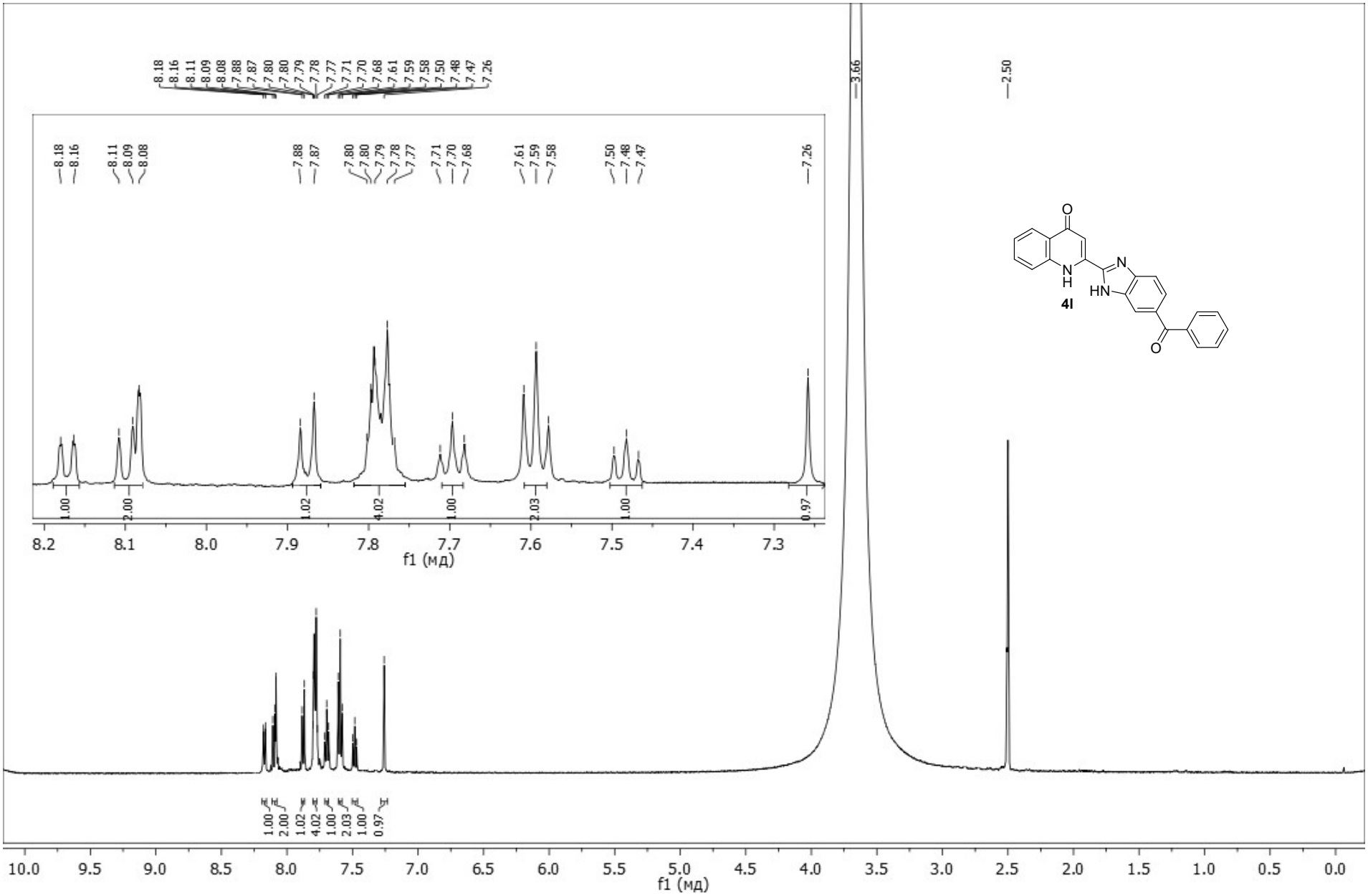


Figure S76. 1D ^{1}H NMR spectrum of **4l** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

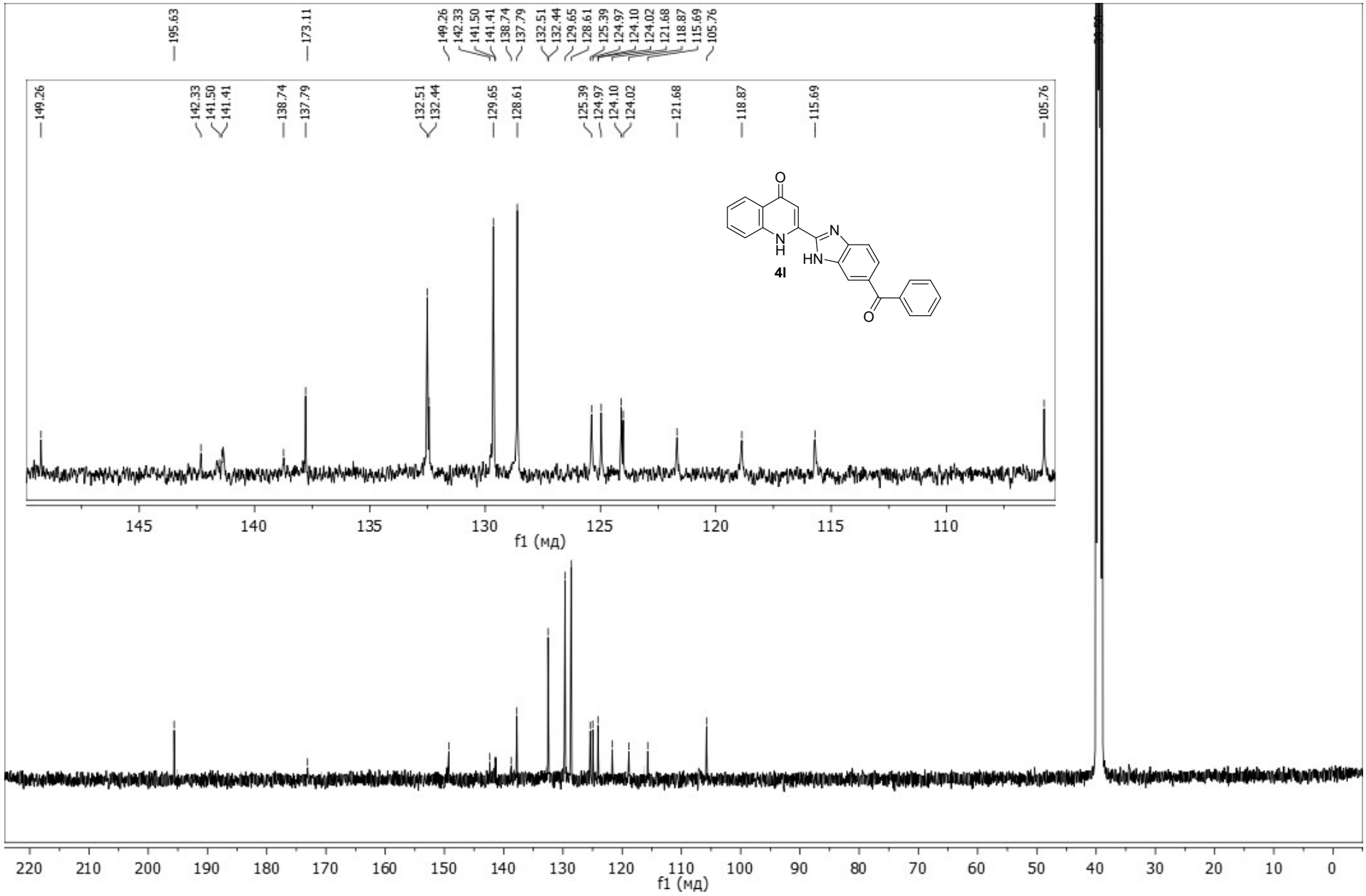


Figure S77. $^{13}C\{^{1}H\}$ NMR spectrum of **4l** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

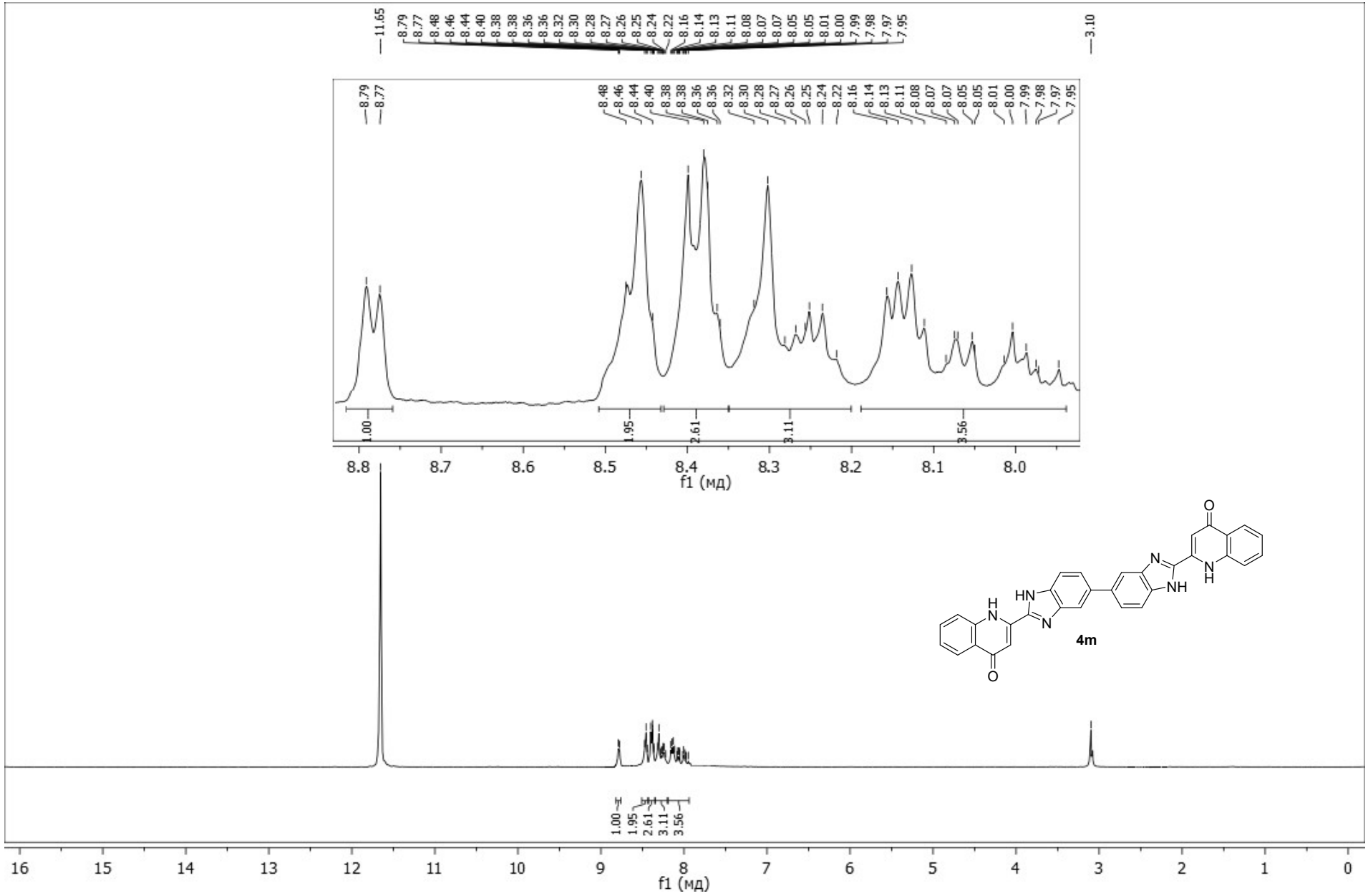


Figure S78. 1D ^{1}H NMR spectrum of **4m** in CF_3COOD at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

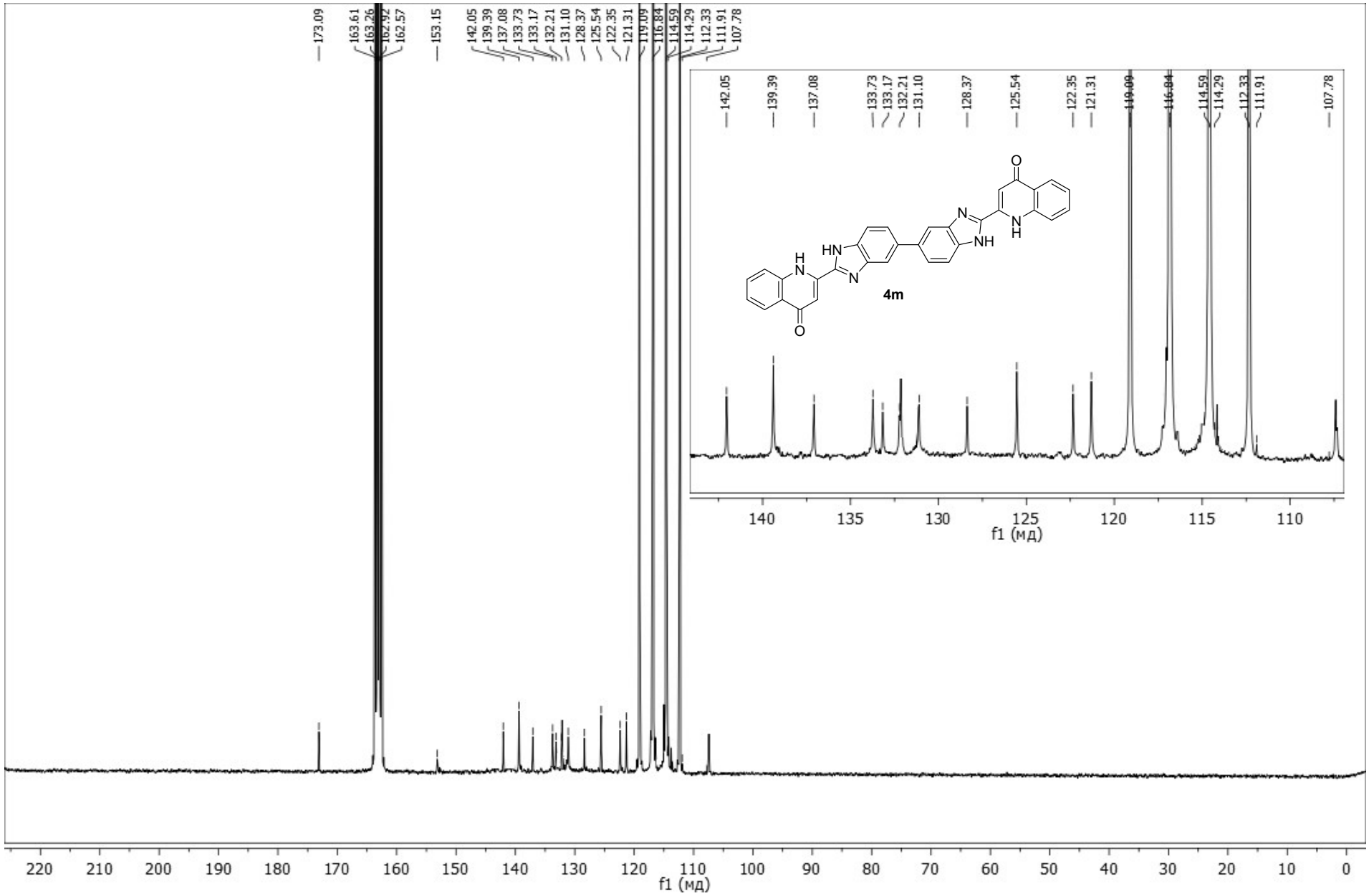


Figure S79. $^{13}C\{^{1}H\}$ NMR spectrum of **4m** in CF_3COOD at T = 303 K (Bruker spectrometer at 125.7 MHz).

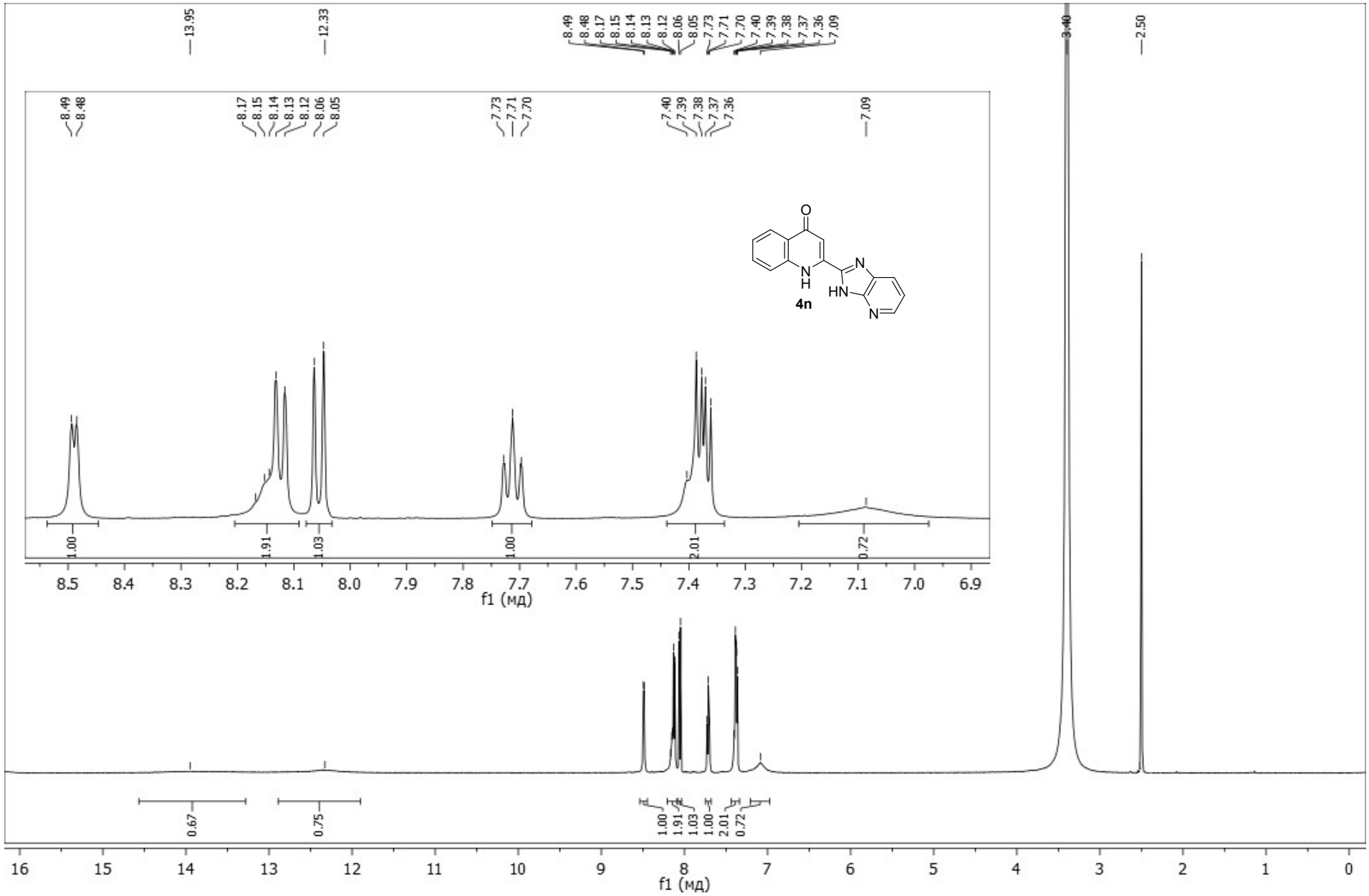


Figure S80. 1D ^{1}H NMR spectrum of **4n** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

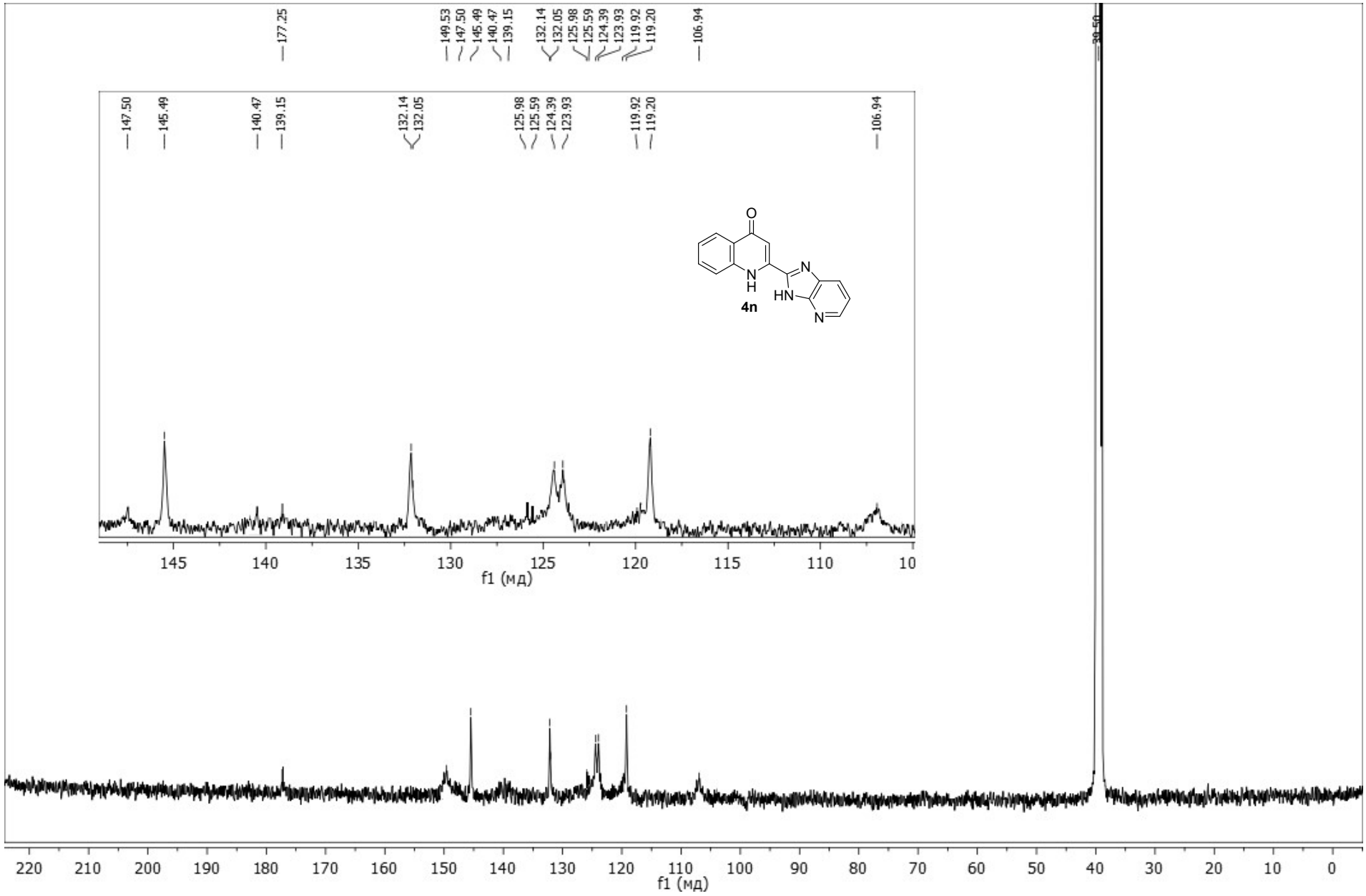


Figure S81. $^{13}C\{^{1}H\}$ NMR spectrum of **4n** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

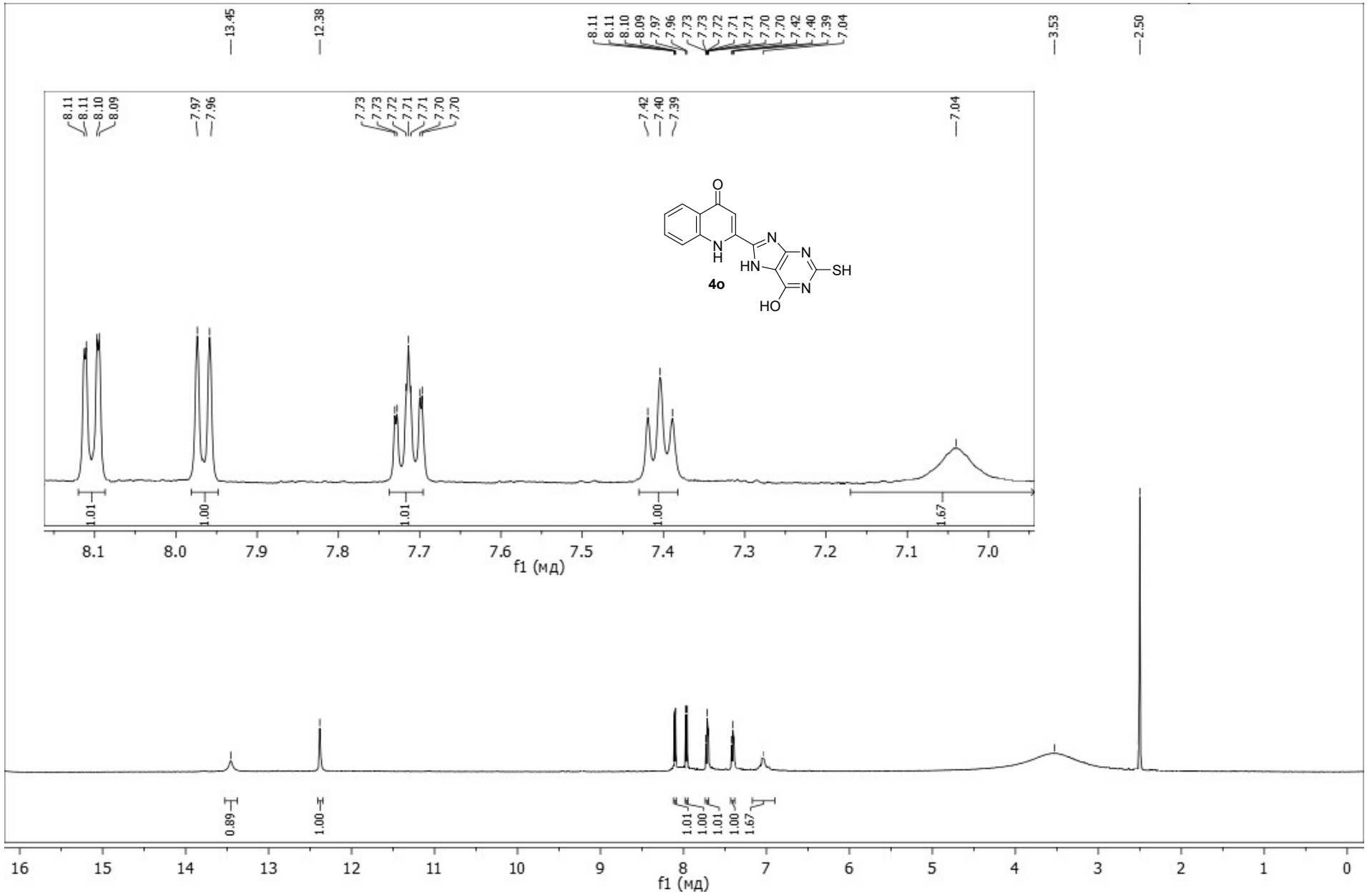


Figure S82. 1D ^{1}H NMR spectrum of **4o** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

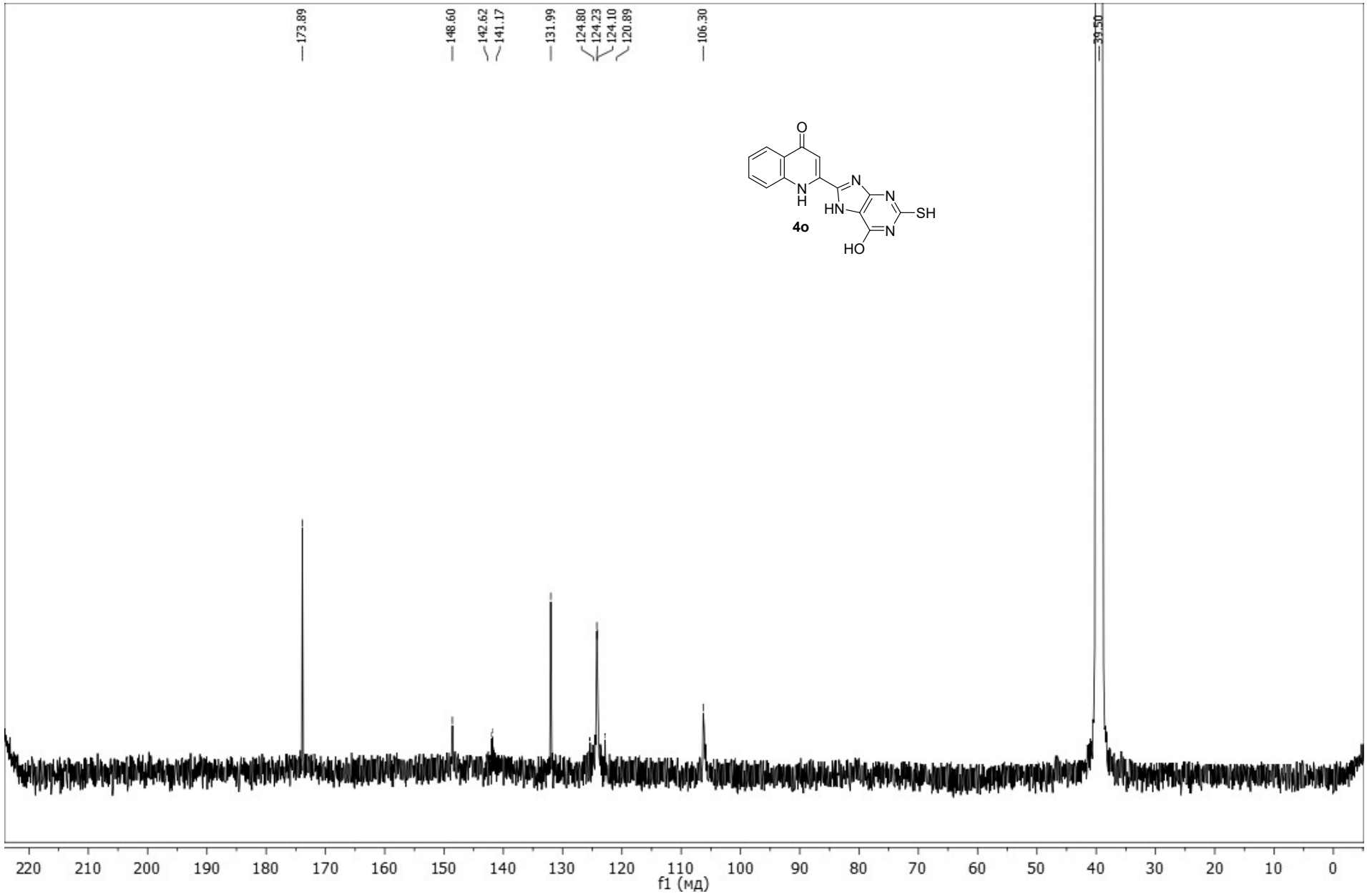


Figure S83. $^{13}C\{^{1}H\}$ NMR spectrum of **4o** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

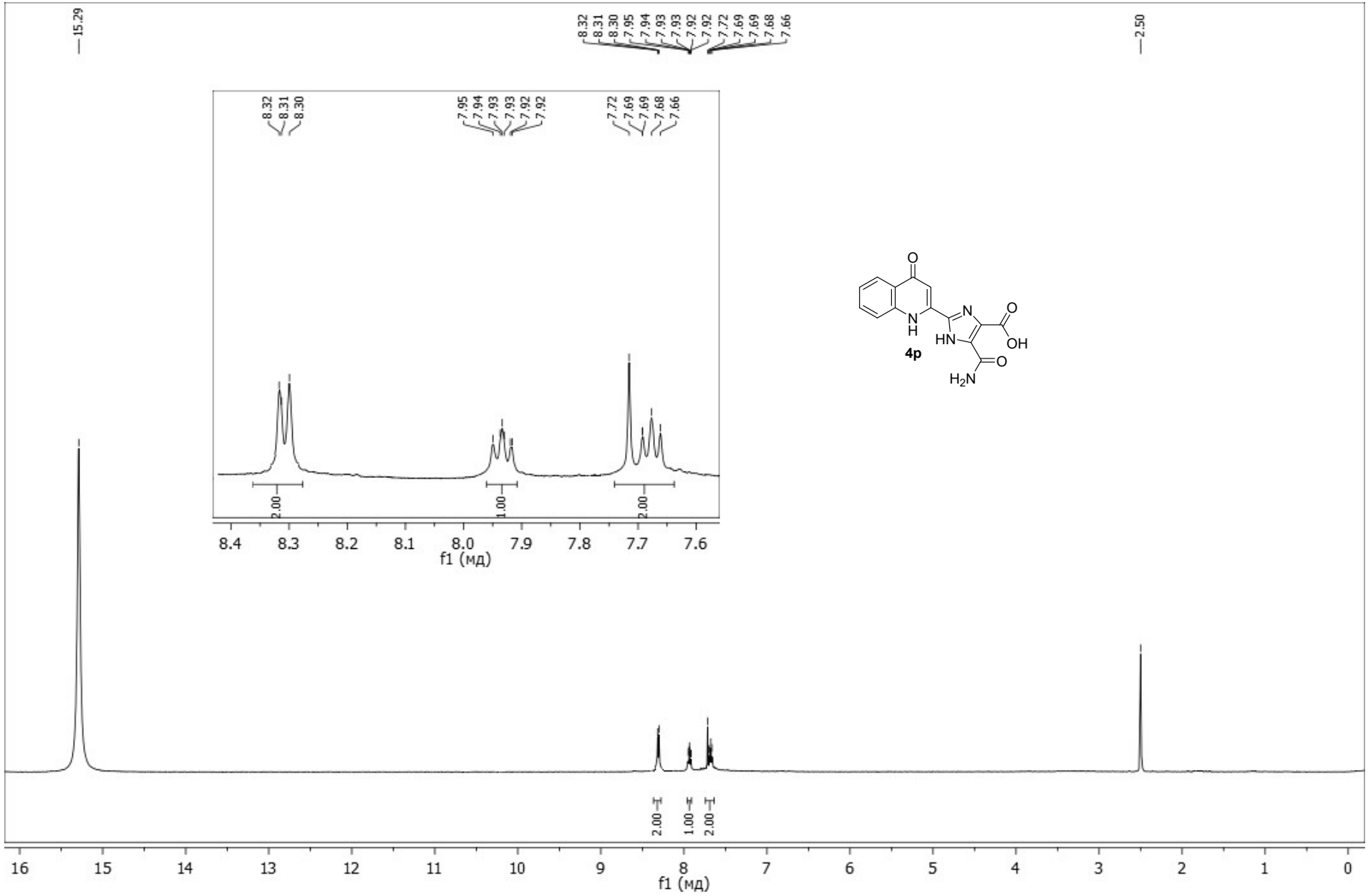


Figure S84. 1D ^{1}H NMR spectrum of **4p** in DMSO-d_6 and CF_3COOD at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

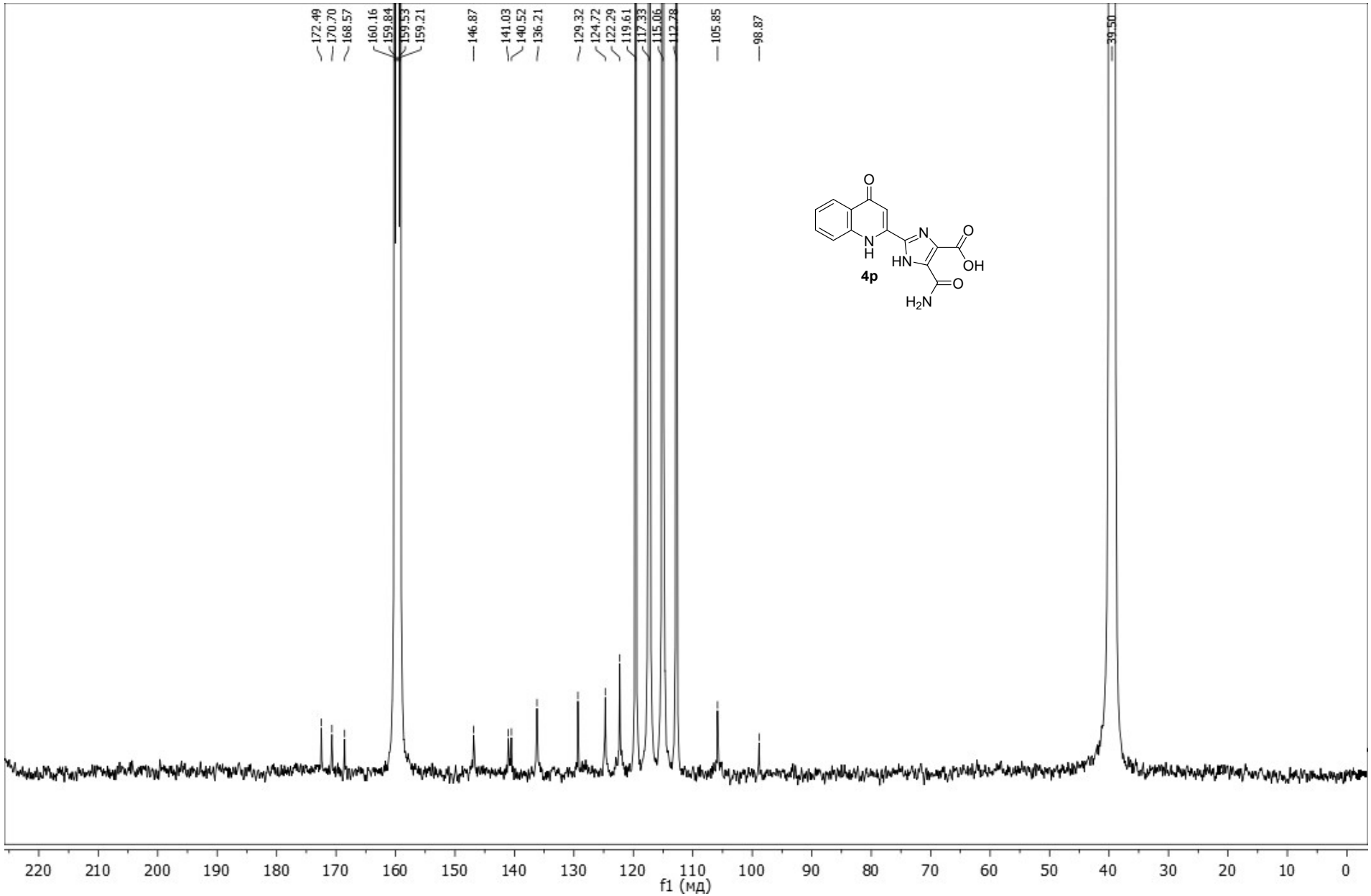


Figure S85. $^{13}C\{^{1}H\}$ NMR spectrum of **4p** in DMSO-d_6 and CF_3COOD at T = 303 K (Bruker spectrometer at 125.7 MHz).

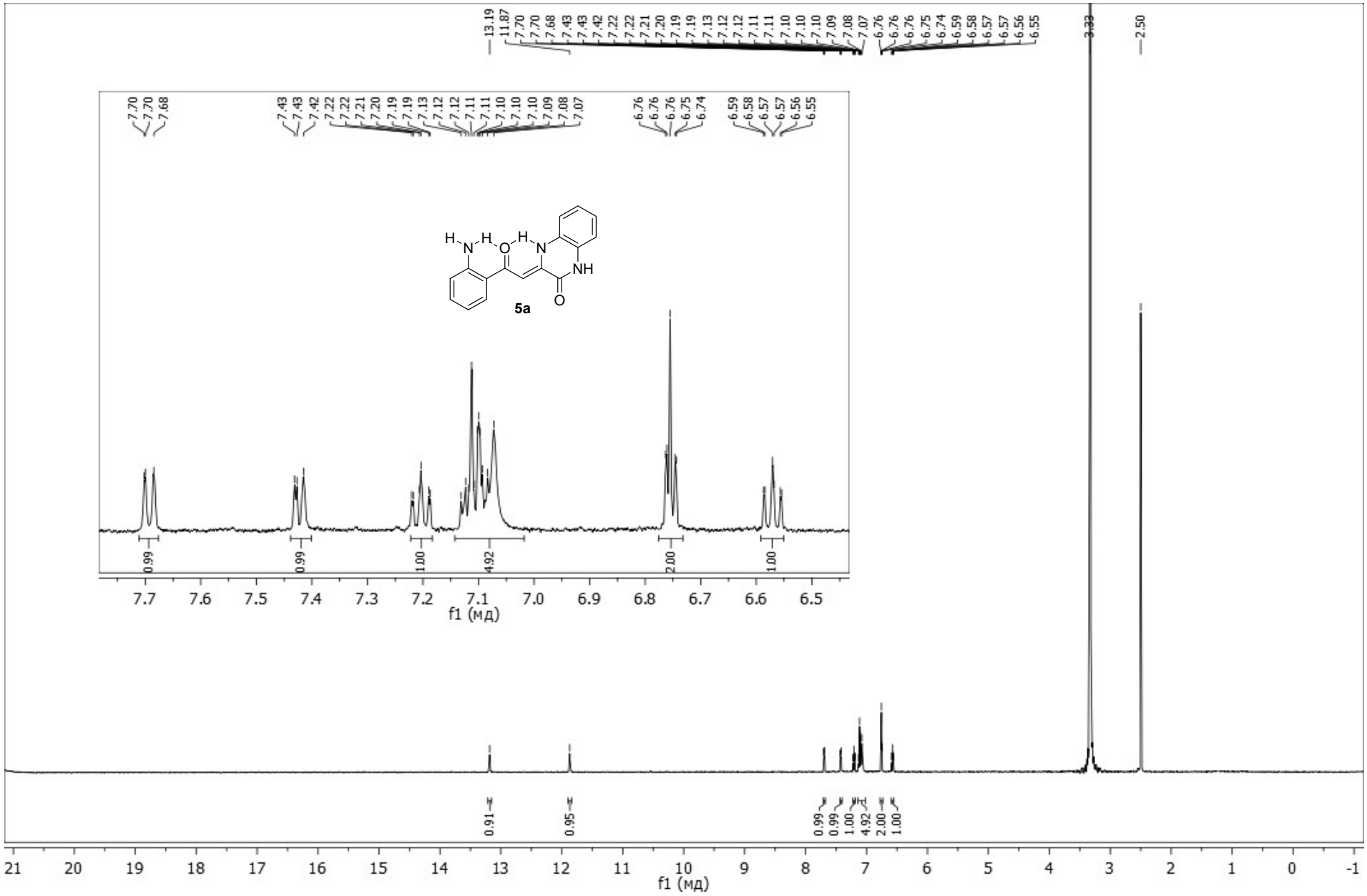


Figure S86. 1D ^{1}H NMR spectrum of **5a** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

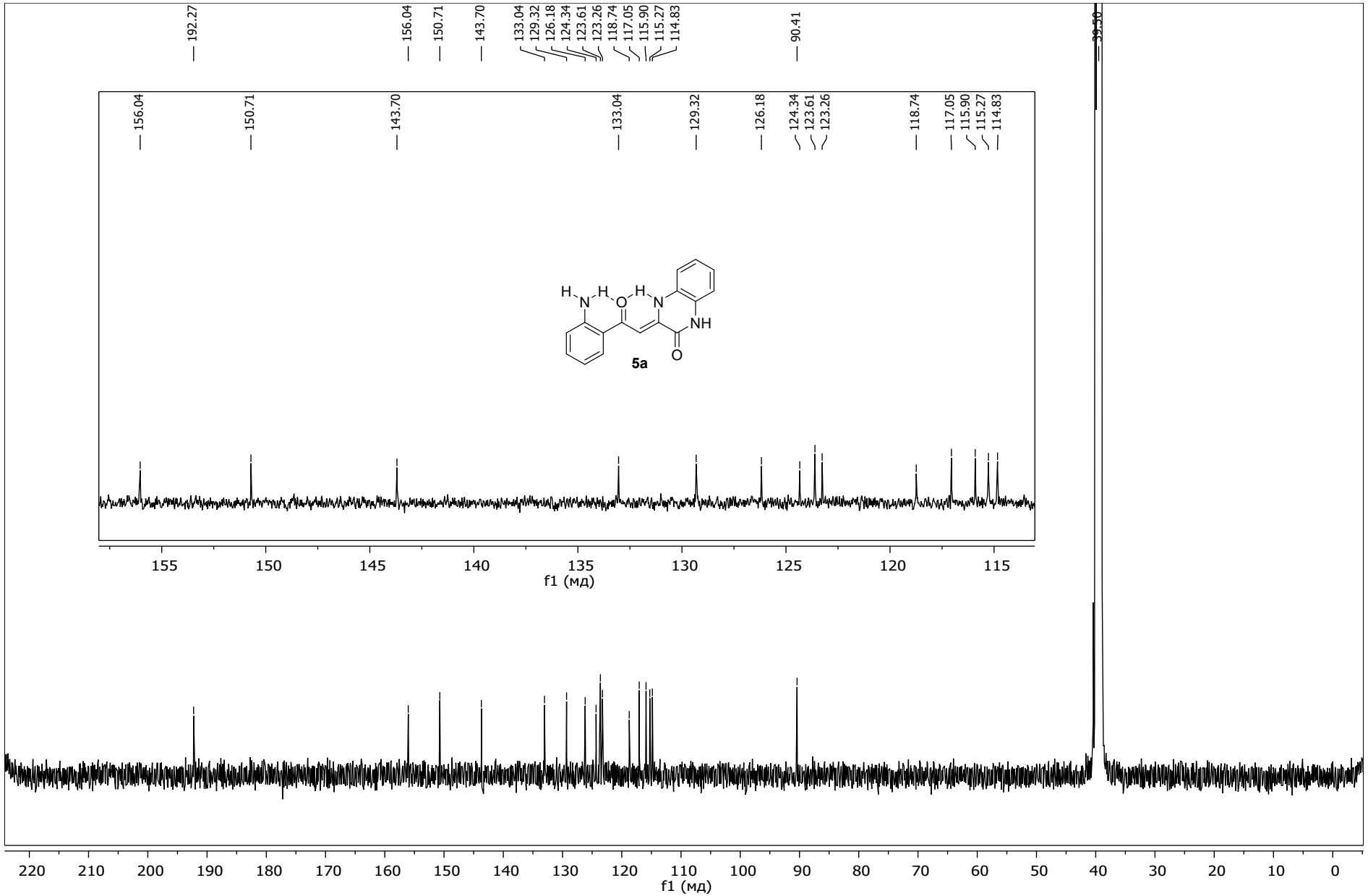


Figure S87. $^{13}C\{^{1}H\}$ NMR spectrum of **5a** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

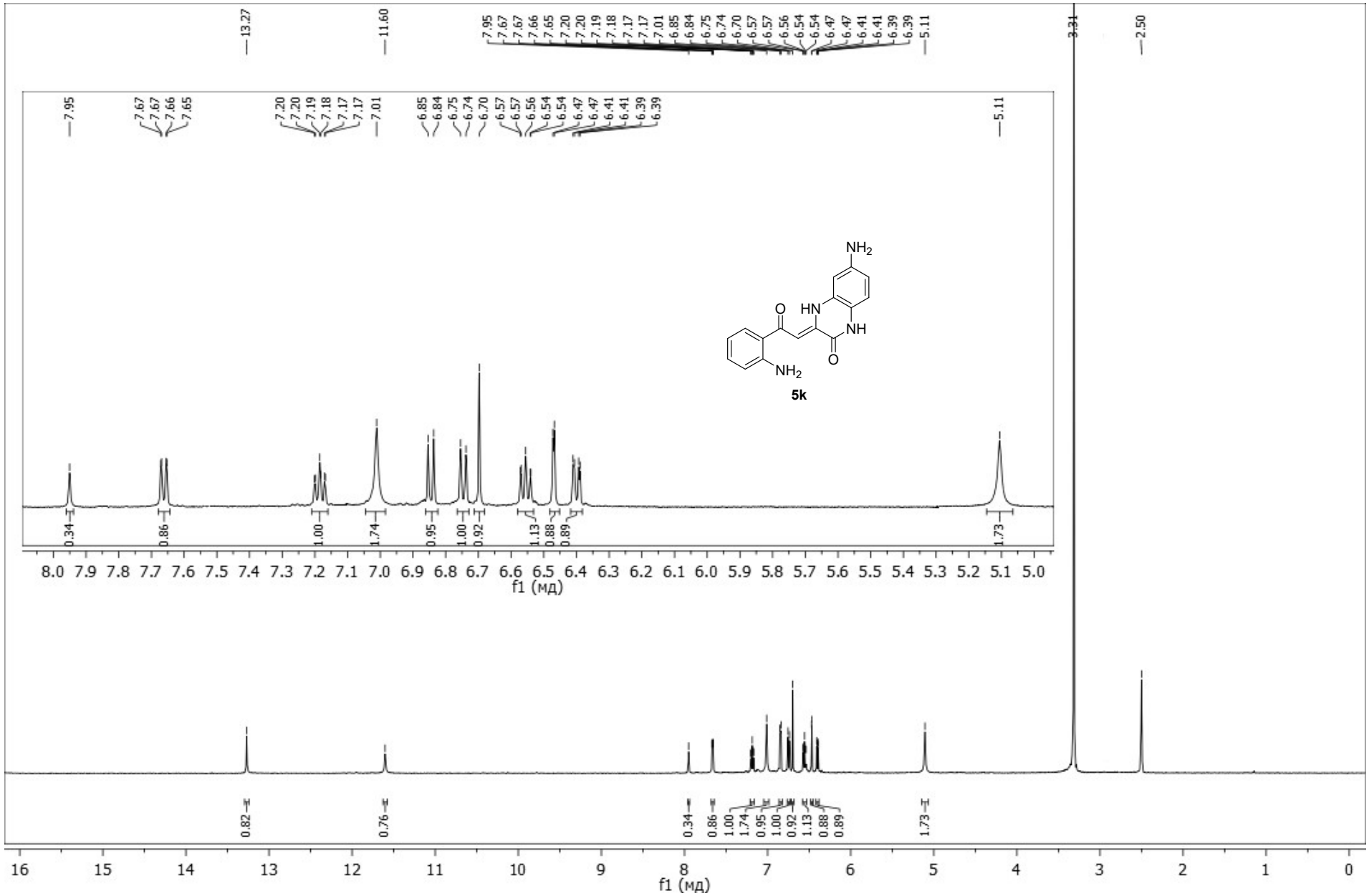


Figure S88. 1D ^{1}H NMR spectrum of **5k** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

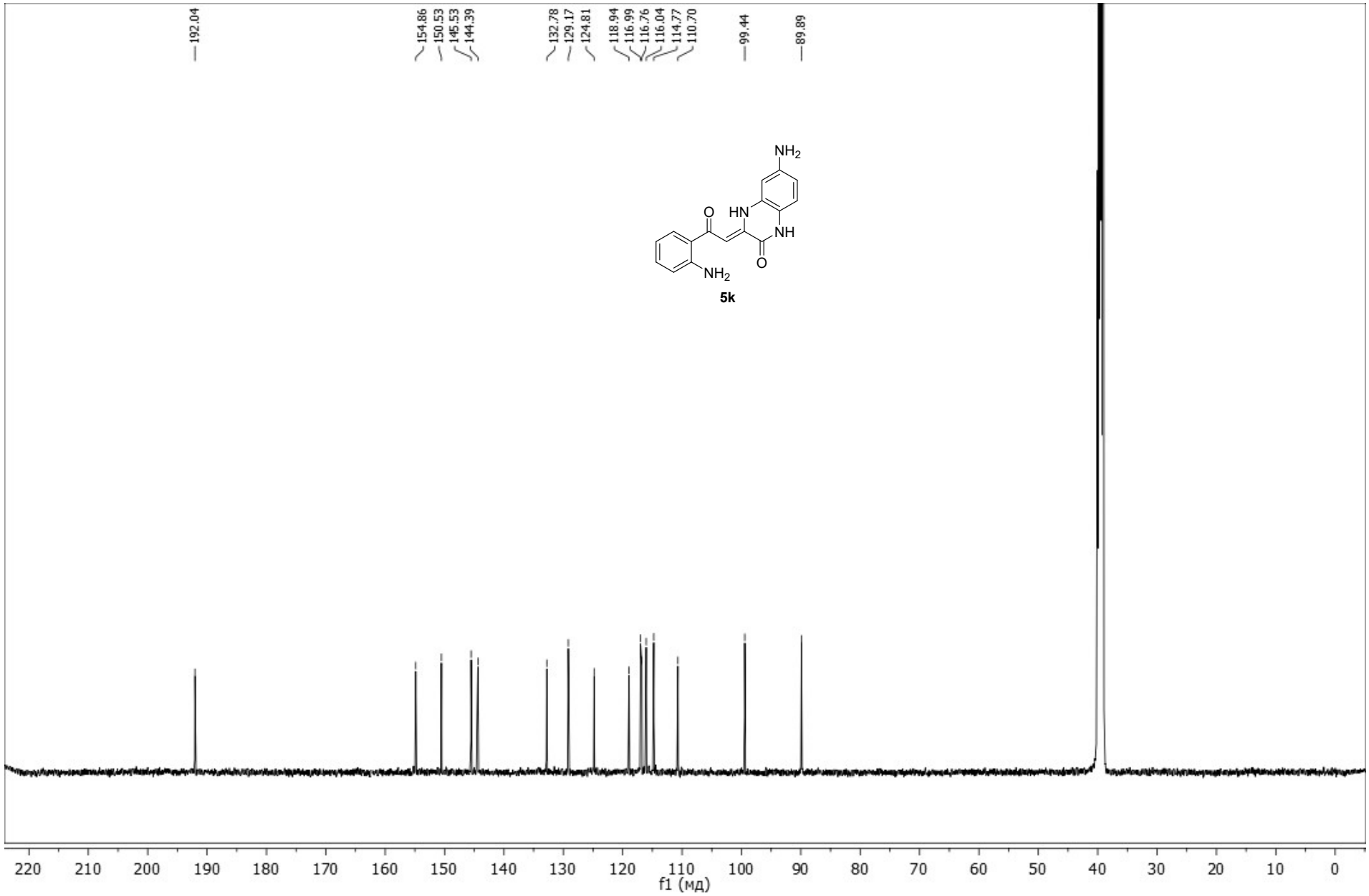


Figure S89. $^{13}C\{^{1}H\}$ NMR spectrum of **5k** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

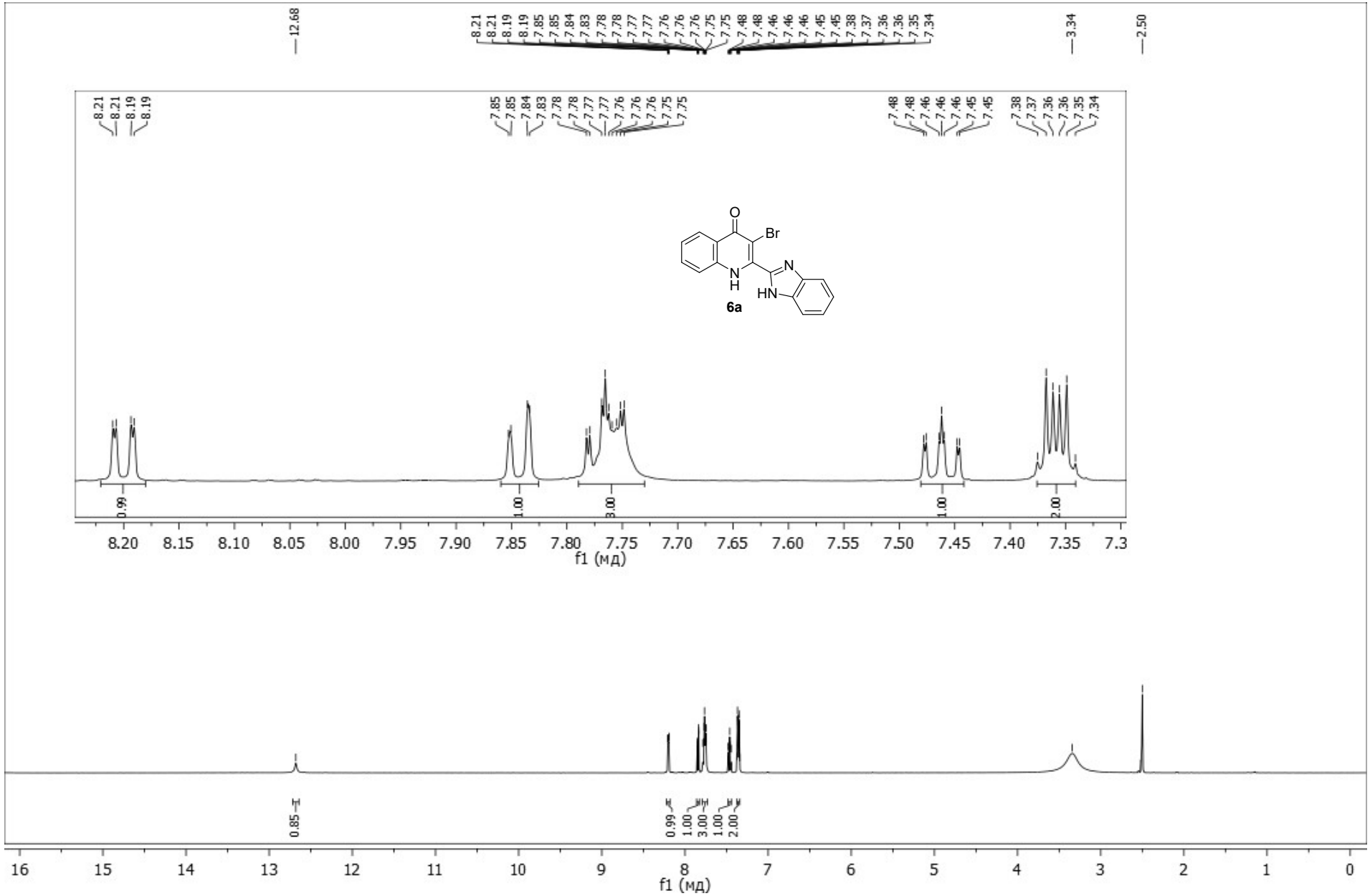


Figure S90. 1D ^{1}H NMR spectrum of **6a** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

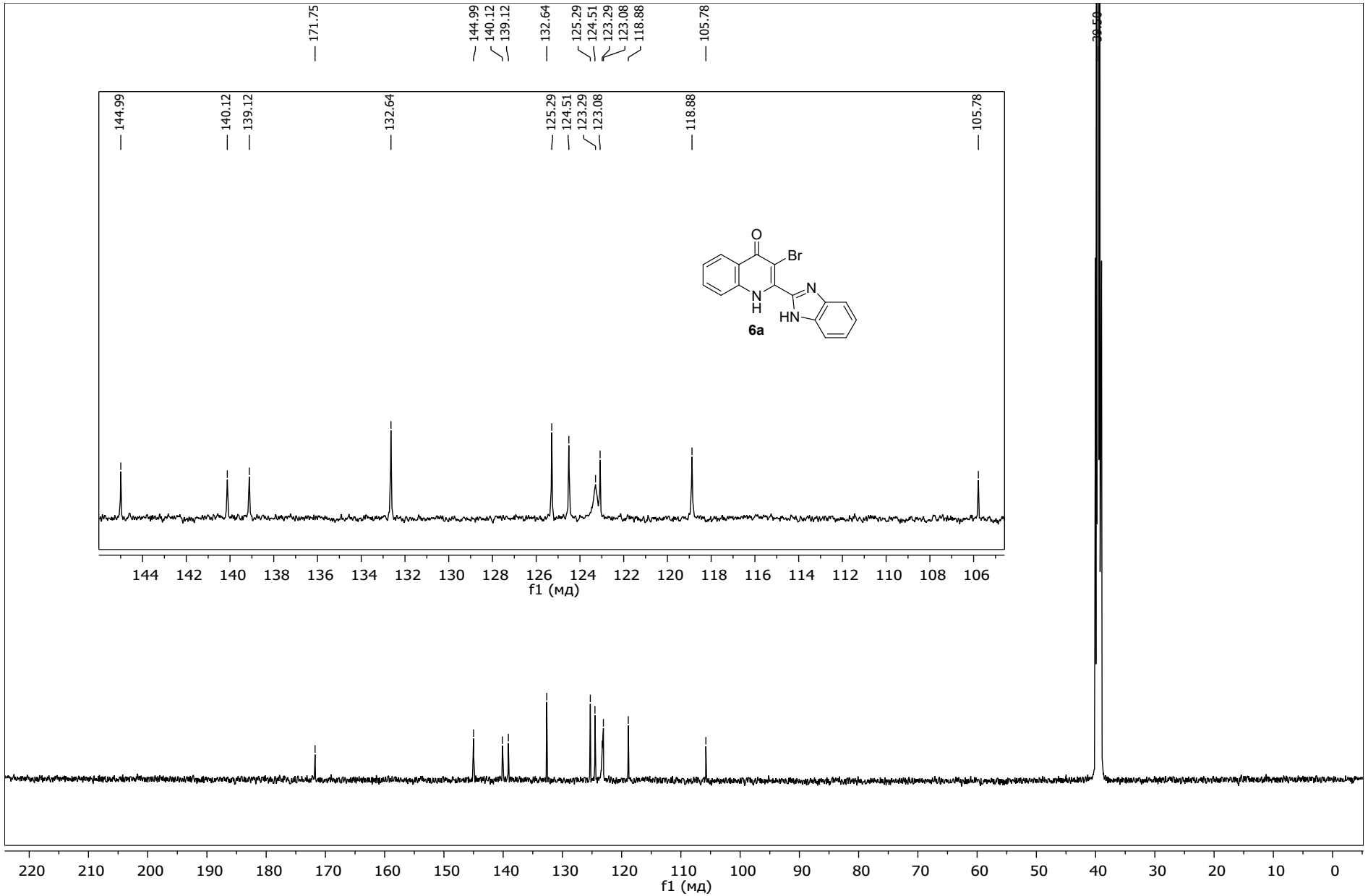


Figure S91. $^{13}C\{^{1}H\}$ NMR spectrum of **6a** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

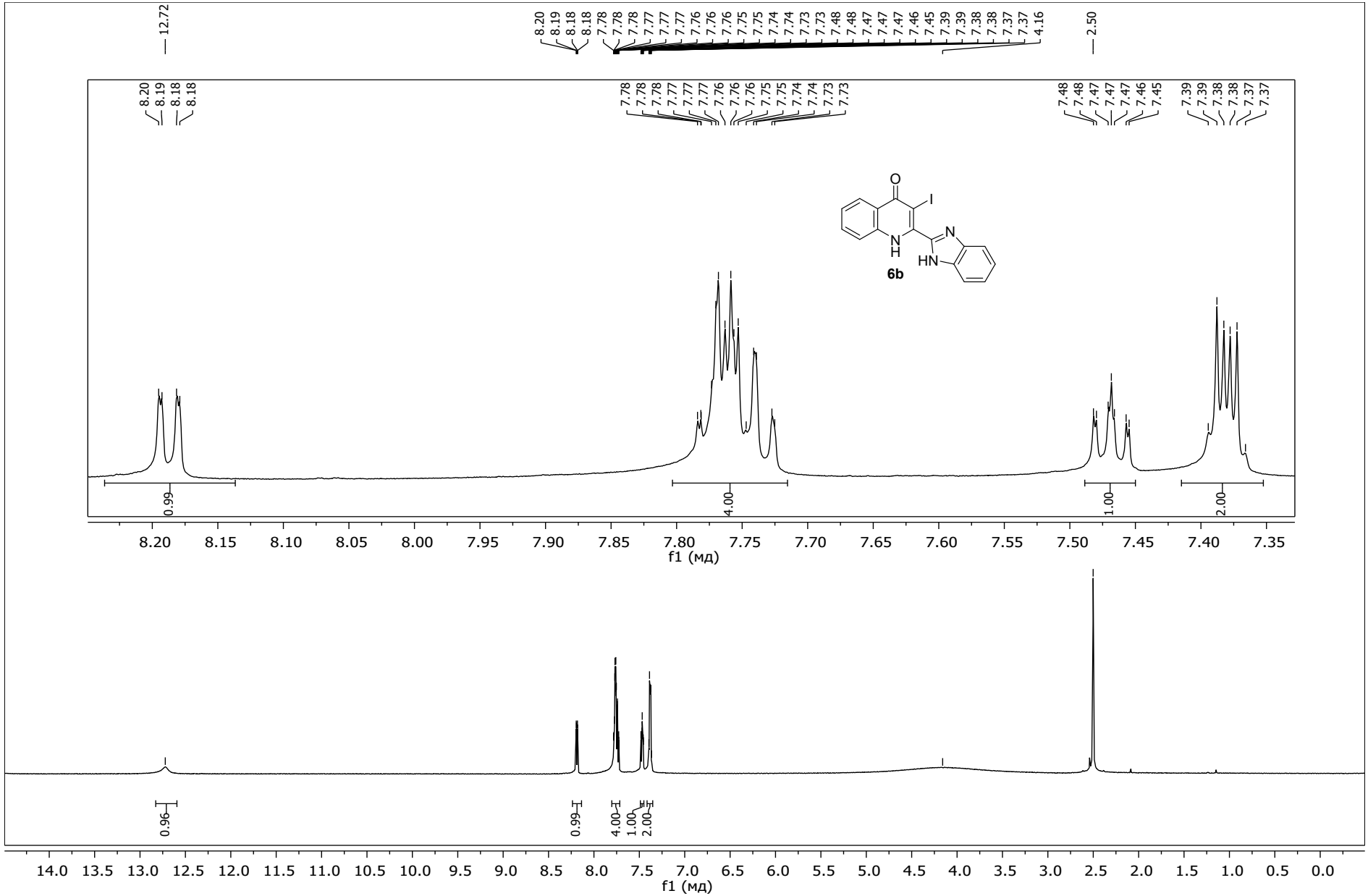


Figure S92. 1D ^{1}H NMR spectrum of **6b** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

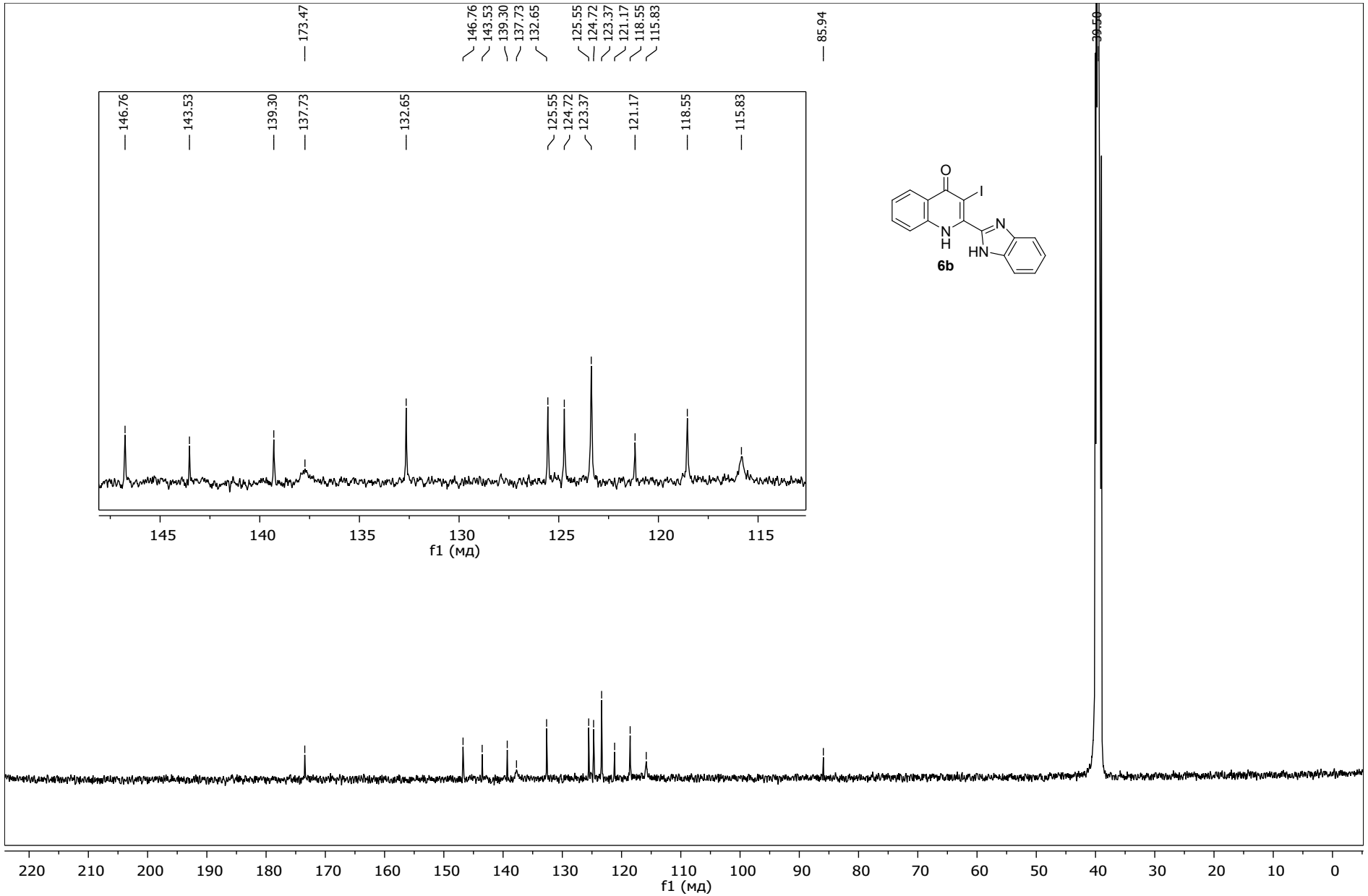


Figure S93. $^{13}C\{^{1}H\}$ NMR spectrum of **6b** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

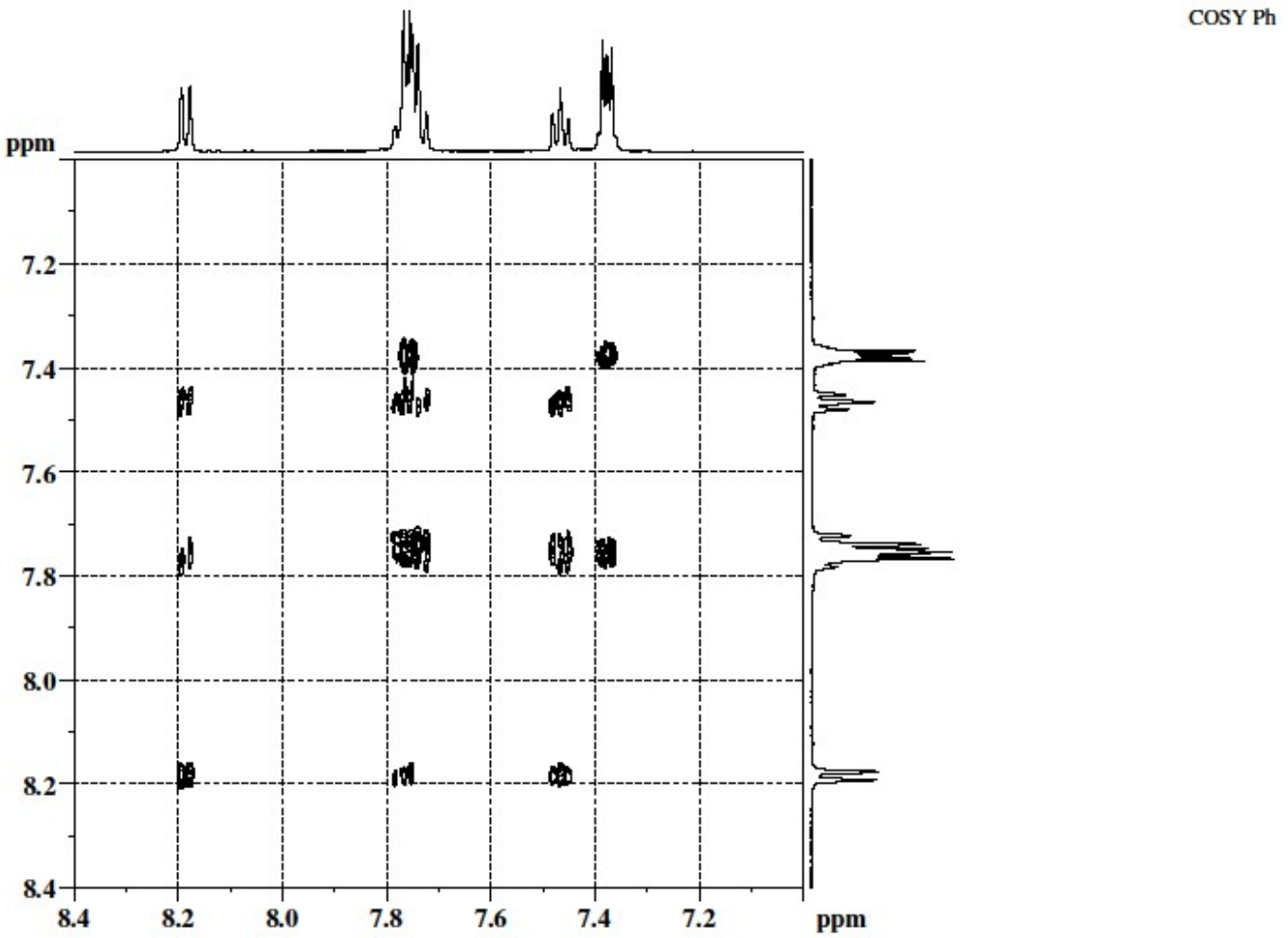


Figure S94. 2D ^{1}H-^{1}H COSY NMR spectrum of **6b** in DMSO-d_6 at T = 303 K.

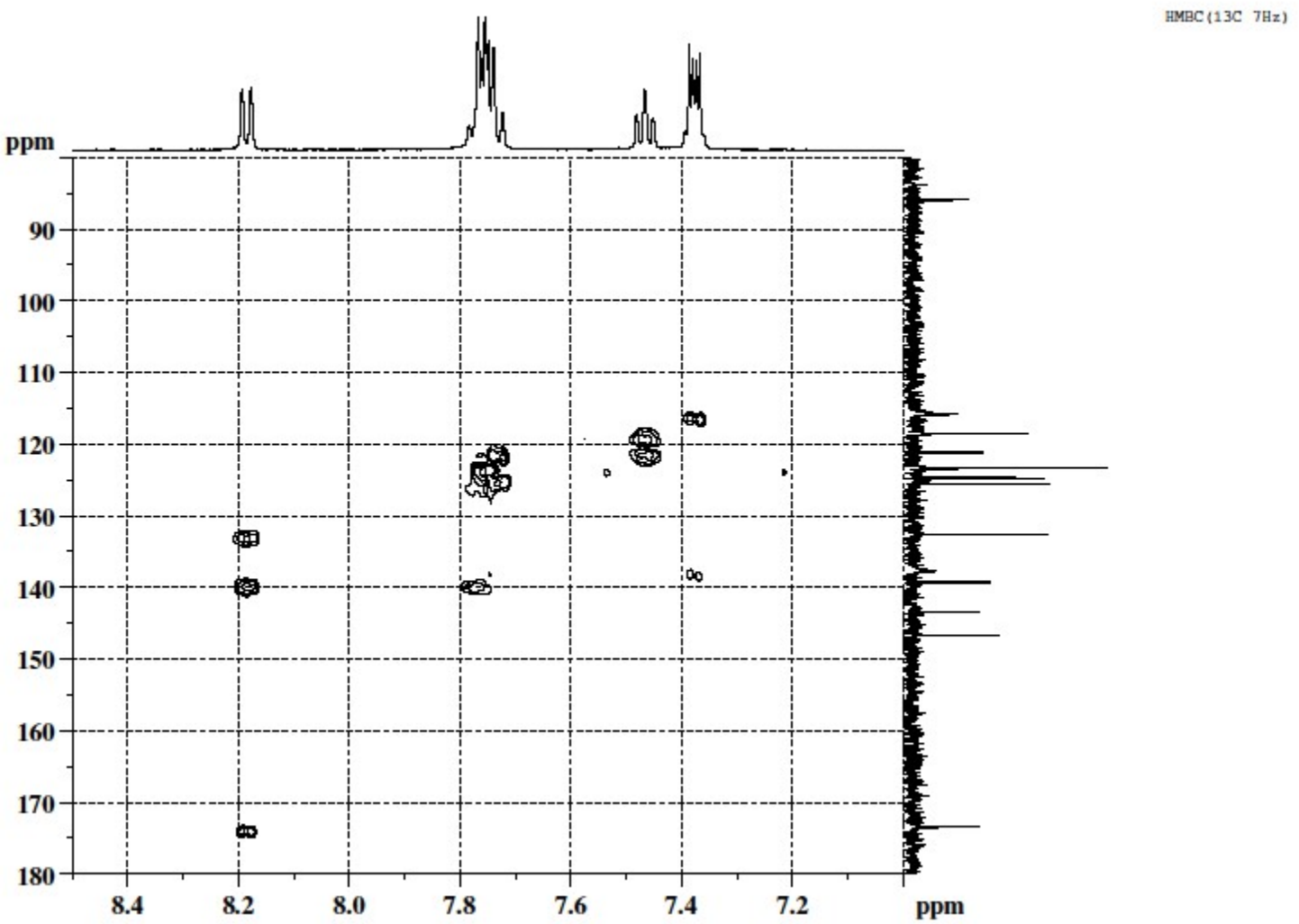


Figure S95. 2D ^{1}H-^{13}C HMBC NMR spectrum of **6b** in DMSO-d_6 at T = 303 K.

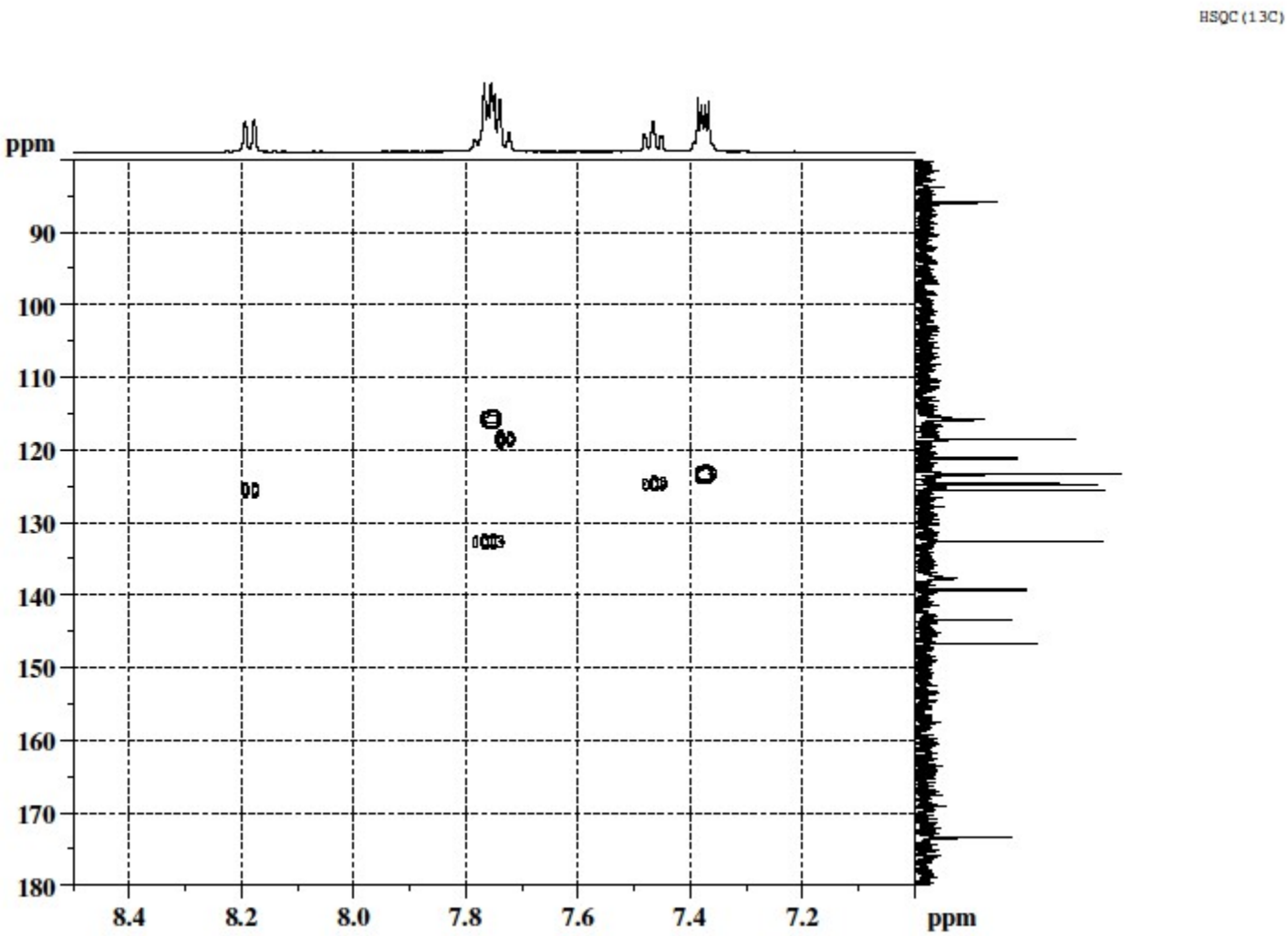


Figure S96. 2D ^{1}H-^{13}C HMBC NMR spectrum of **6b** in DMSO-d_6 at T = 303 K.

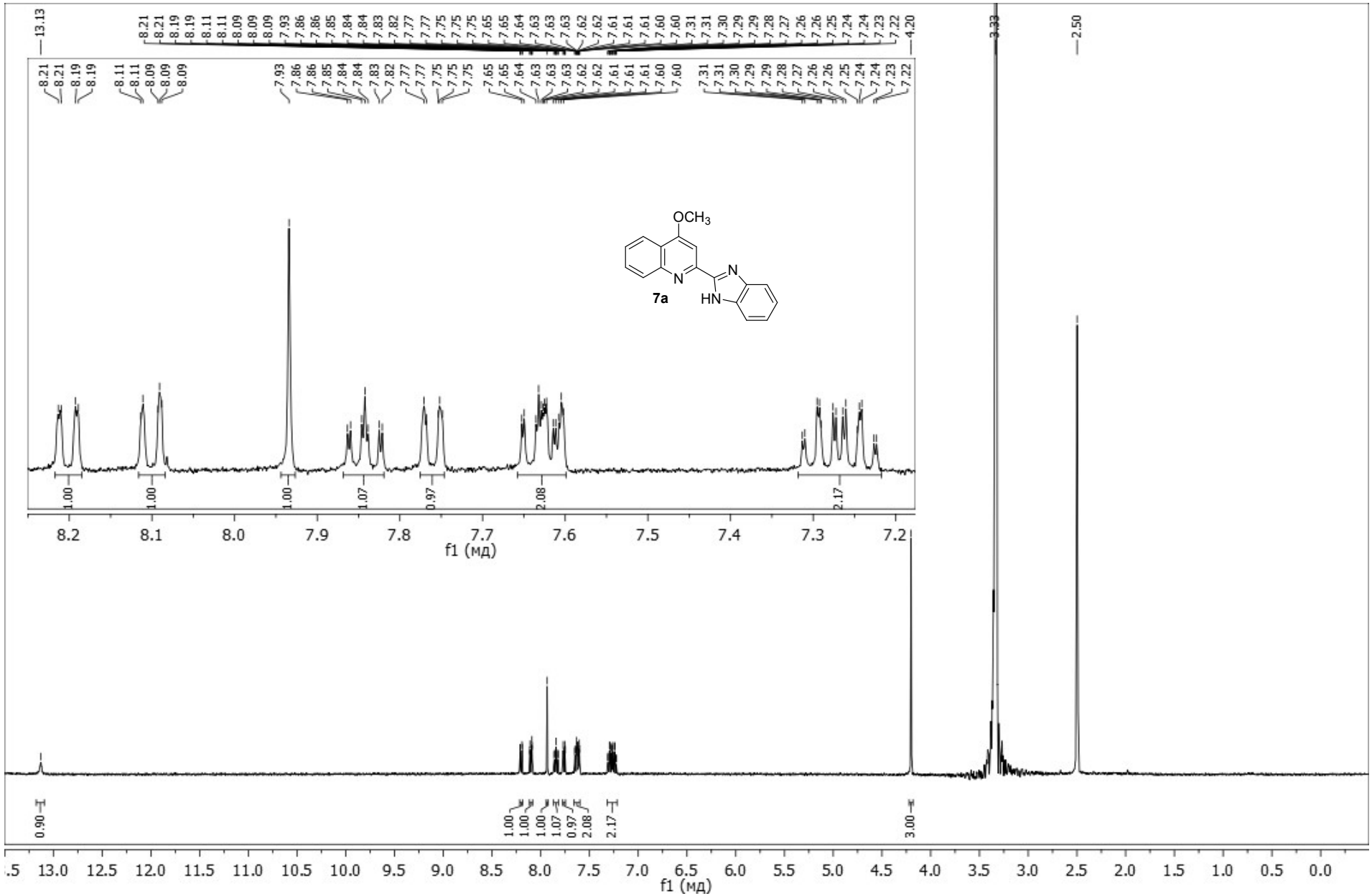


Figure S97. 1D ^{1}H NMR spectrum of **7a** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

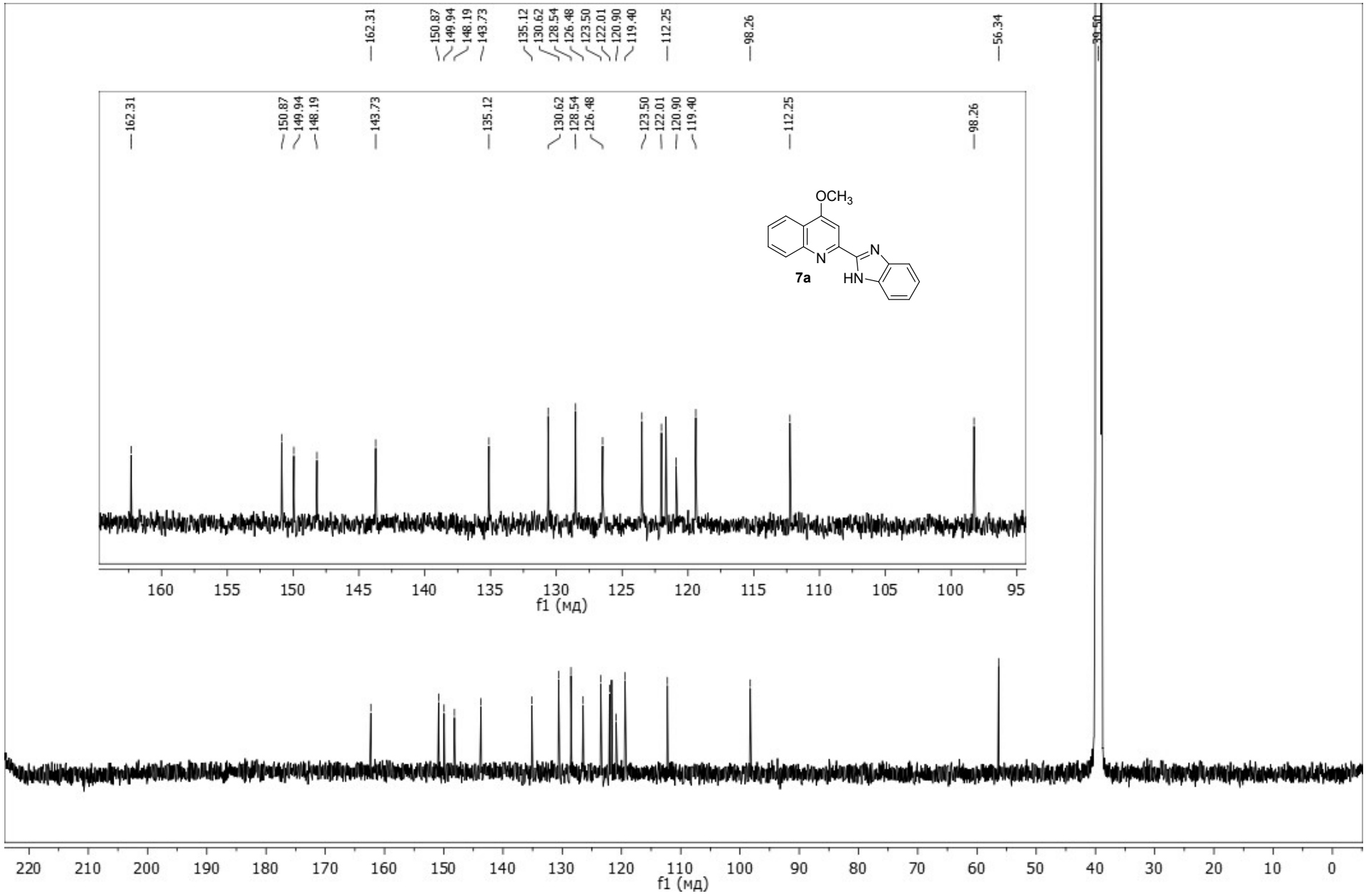


Figure S98. $^{13}C\{^{1}H\}$ NMR spectrum of **7a** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

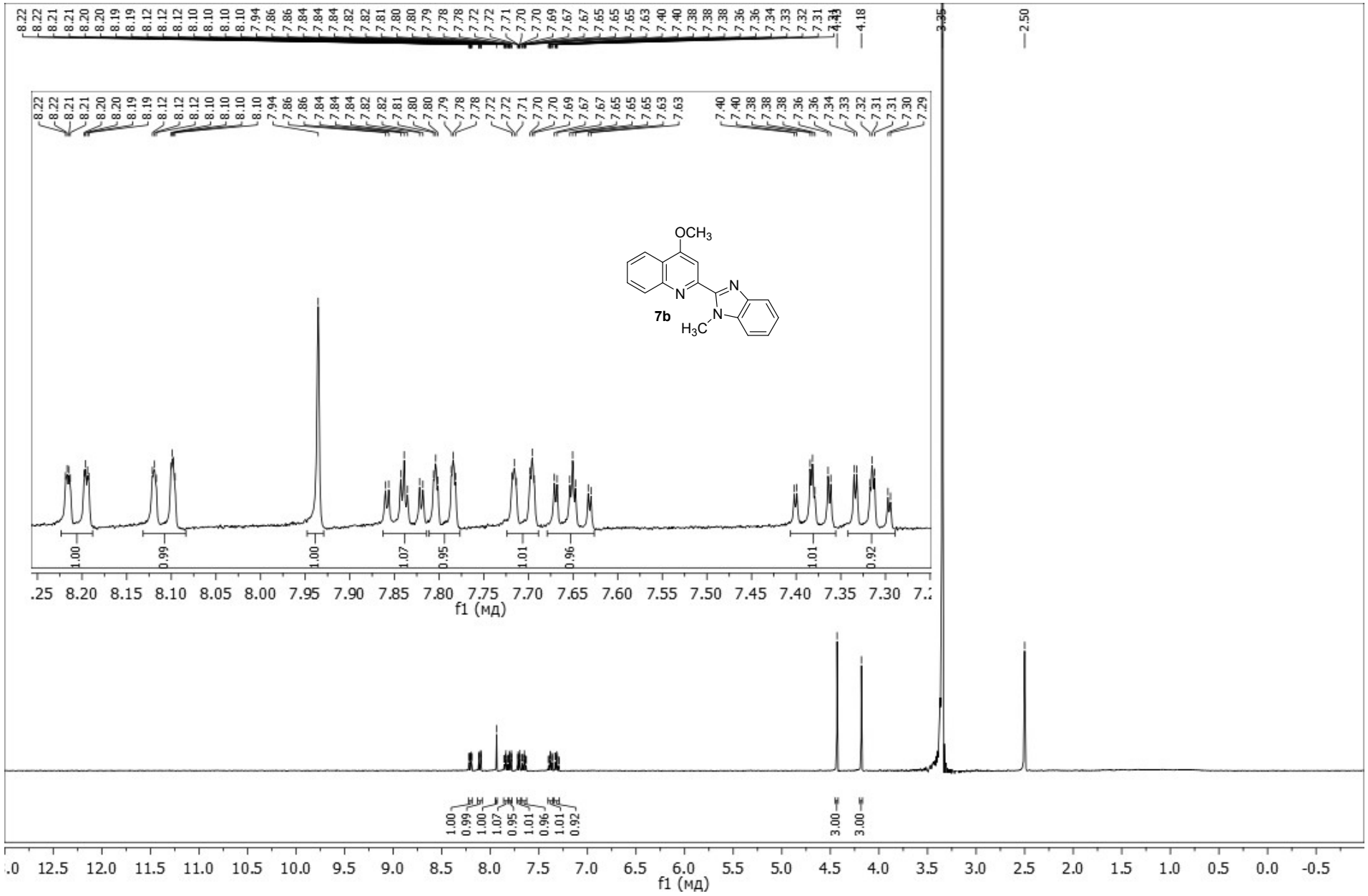


Figure S99. 1D ^{1}H NMR spectrum of **7b** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

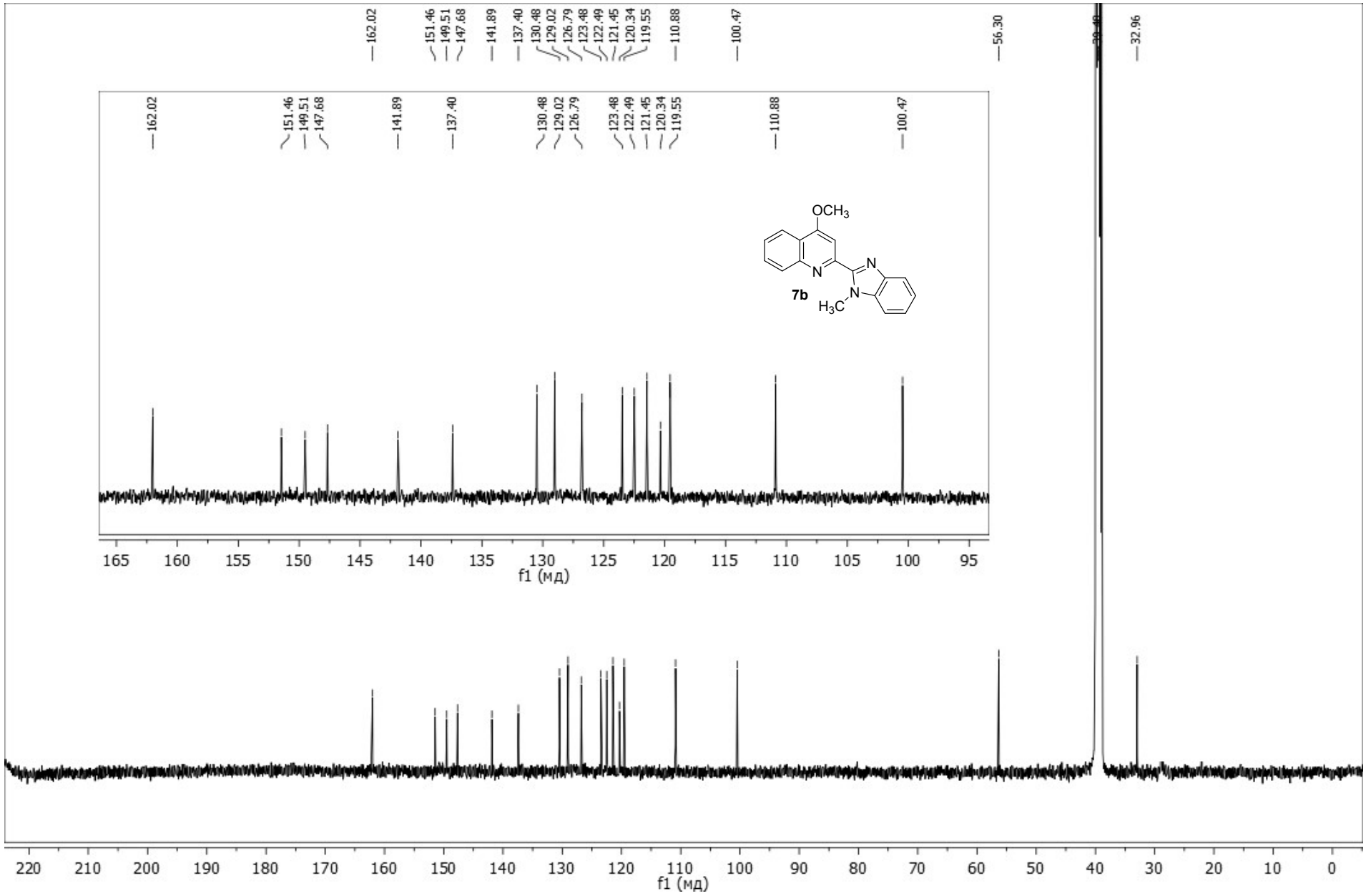


Figure S100. $^{13}C\{^{1}H\}$ NMR spectrum of **7b** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).

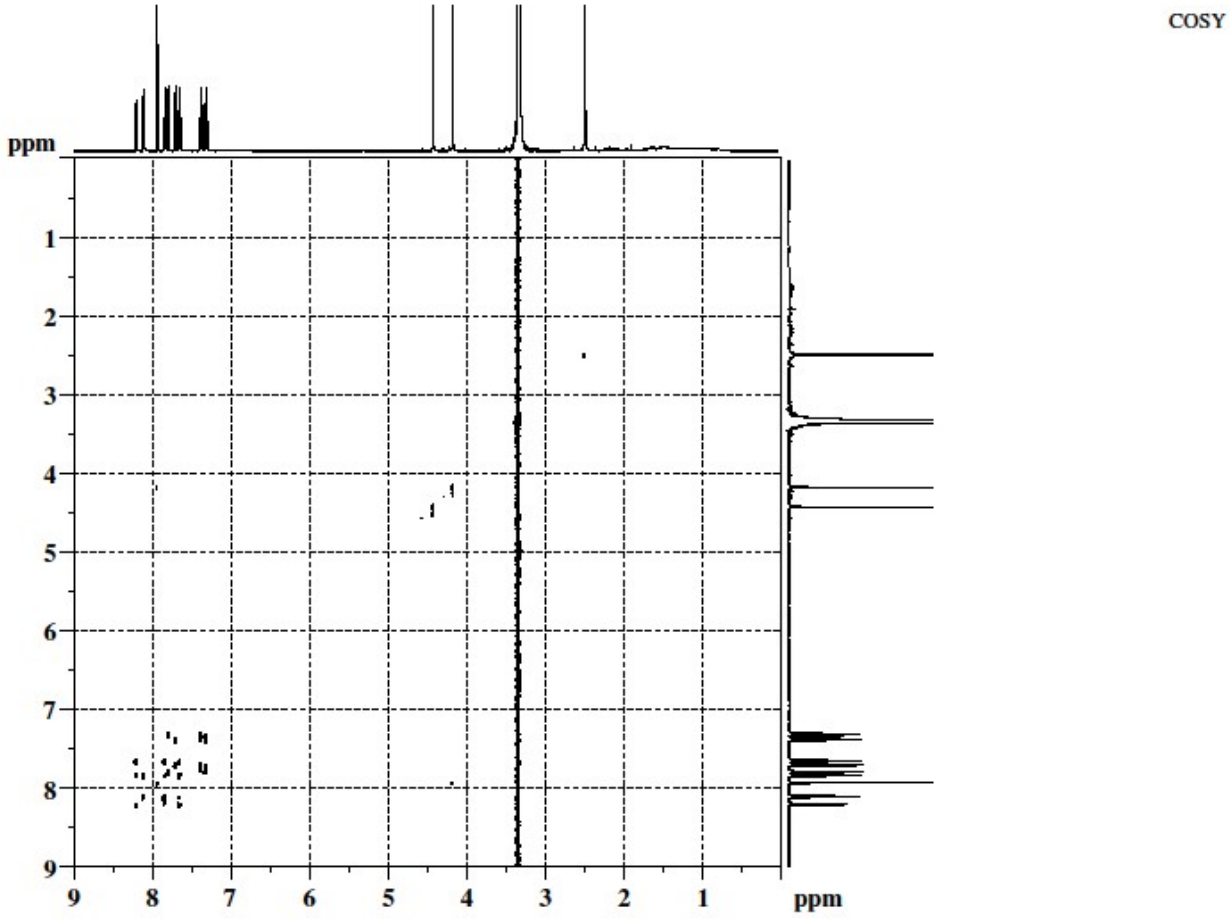


Figure S101. 2D ^{1}H-^{1}H COSY NMR spectrum of **7b** in DMSO-d_6 at T = 303 K.

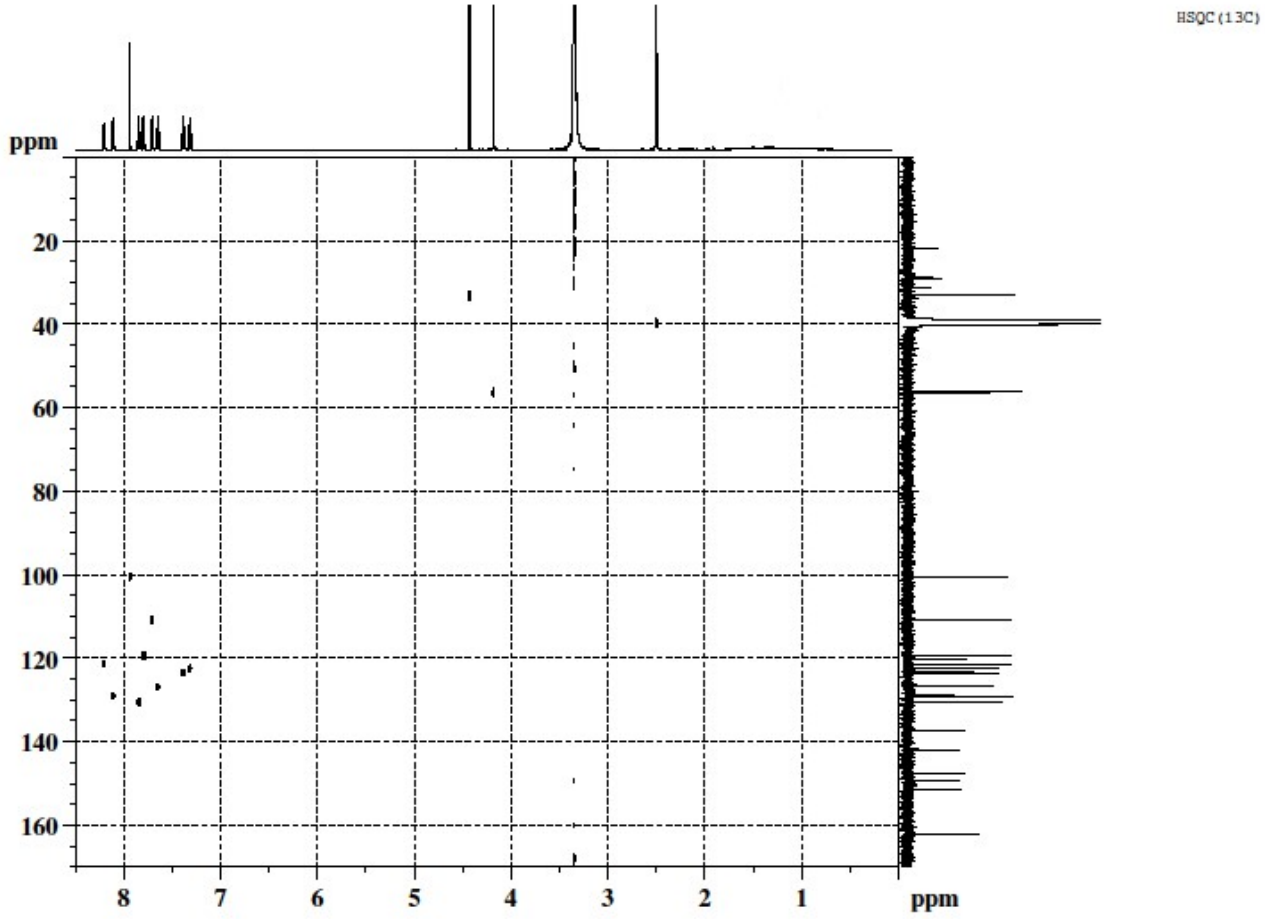


Figure S102. 2D 1H-^{13}C HSQC NMR spectrum of **7b** in DMSO-d_6 at T = 303 K.

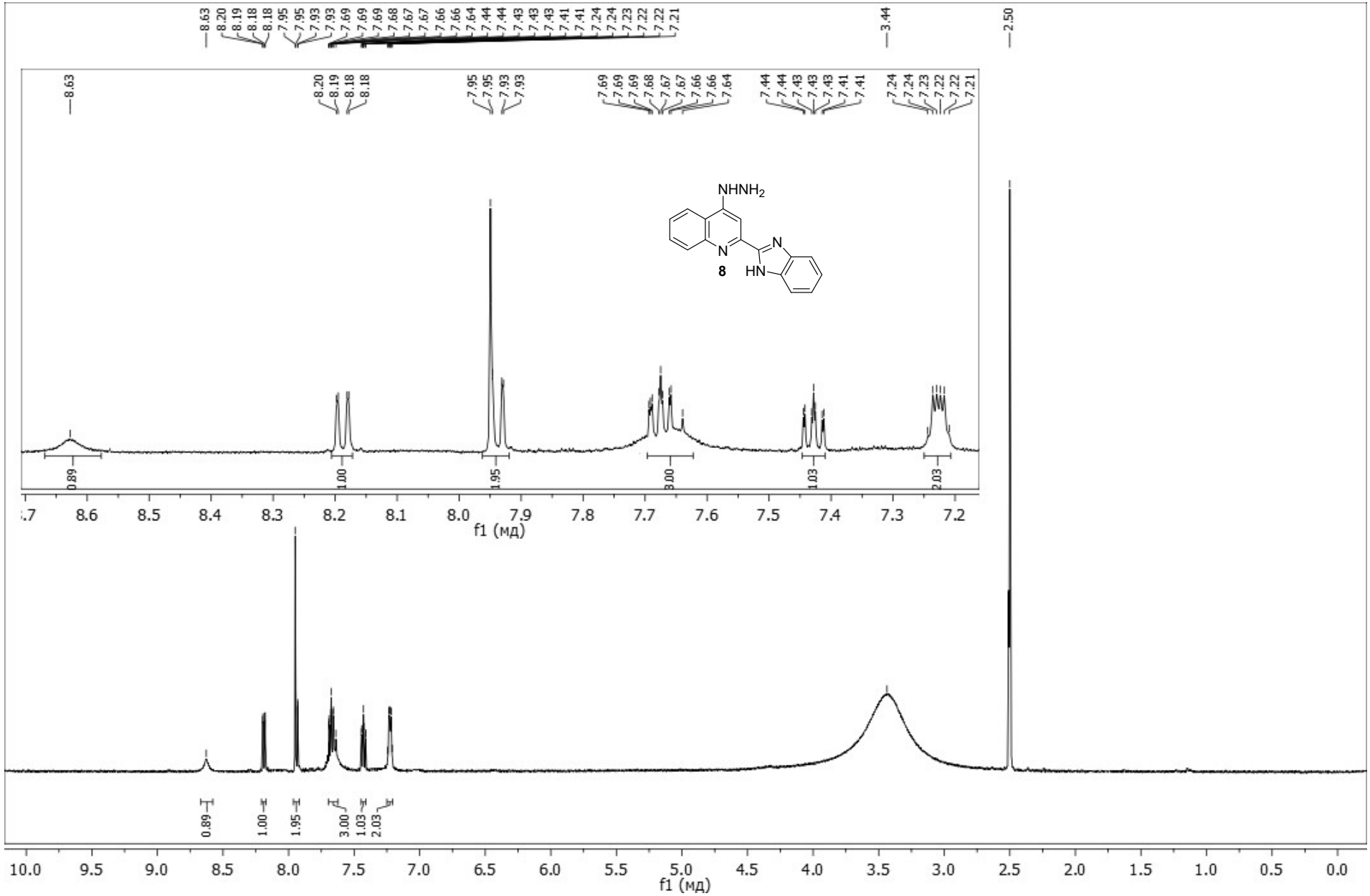


Figure S103. 1D ^{1}H NMR spectrum of **8** in DMSO-d_6 at T = 303 K. Chemical shifts are given in ppm (Bruker spectrometer at 500.1 MHz).

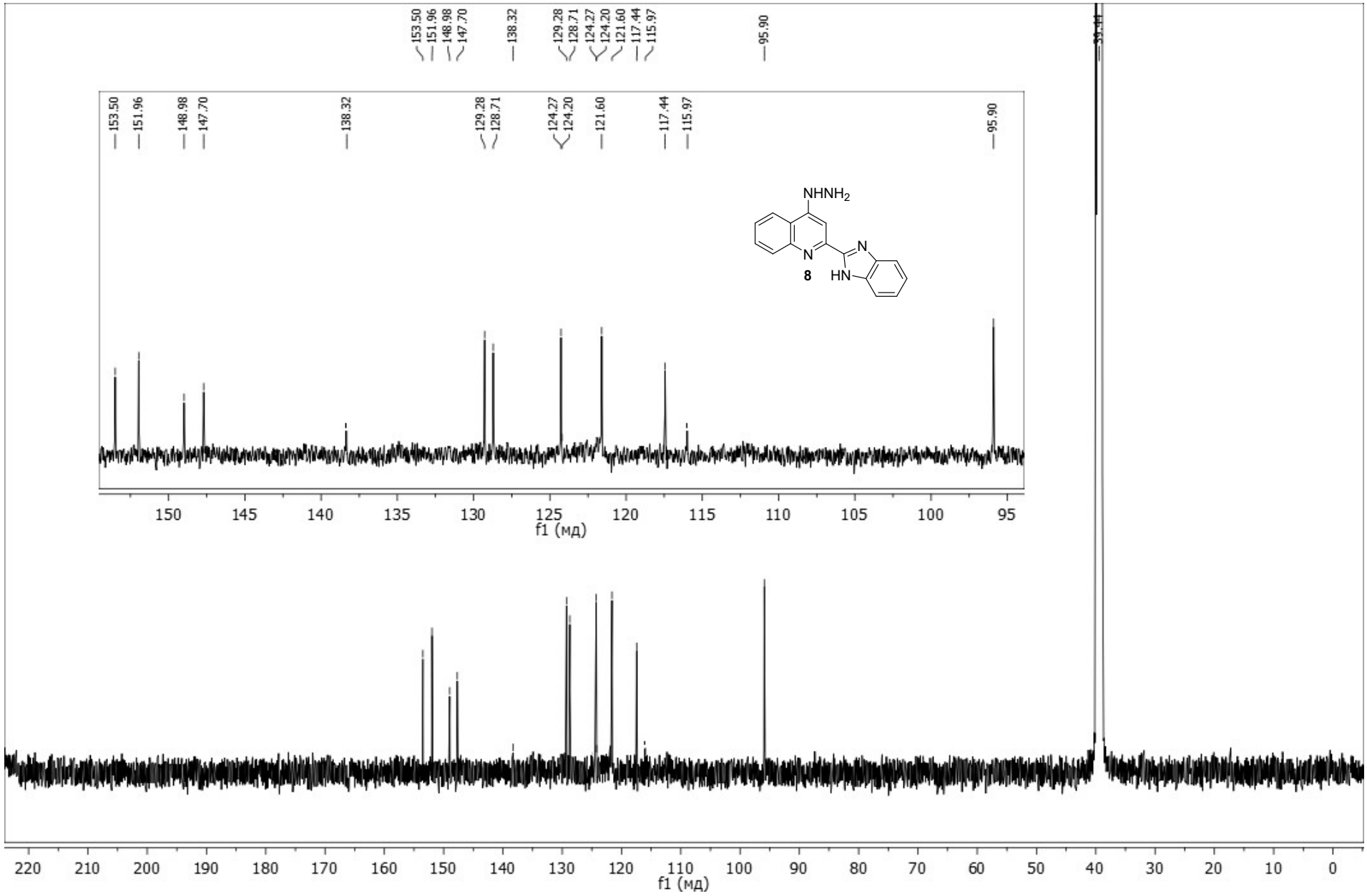


Figure S104. $^{13}C\{^{1}H\}$ NMR spectrum of **8** in DMSO-d_6 at T = 303 K (Bruker spectrometer at 125.7 MHz).