Supporting Information

Table of contents

General remarks. NMR spectra of ^{1}H, ^{13}C, ^{19}F, and ^{11}B were recorded on a Bruker Avance 400 spectrometer 400.1 (^{1}H), 100.6 (^{13}C), 376.3 (^{19}F) and 128.3 (^{11}B) MHz respectively in D_2O, $CDCl_3$ or DMSO-d_6. The IR spectra were recorded on a Nicolet iS5 FTIR spectrometer (Thermo Scientific) using a prefix for disturbed total internal reflection (DTIR) with a nominal angle of incidence of 45°. The resolution is 4 cm^{-1}, the number of scans is 32. HRMS (ESI-TOF) spectra were measured with an MicroTof Bruker Daltonics and Orbitrap Elite instrument. Melting points were determined on an Electrothermal 9100 apparatus. All reagents were of reagent grade and were used as such or distilled prior to use. Acetonitrile was absolutized over phosphorus pentoxide, followed by distillation over anhydrous potash.[1]

Meta-nitrobenzotrifluoride (p.a., Acros Organics) and kerosene were used as solvents for extraction studies. The composition of the aqueous phase included nitric acid (a.g., Chemmed), potassium pertechnetate (125 MBq/l, JSC Isotope, Russia).

Synthesis of dicationic pyridinium bromides 13-21 (general procedure). Corresponding pyridine (2.2 eq.), dry acetonitrile in an amount of 1 ml per 10 mmol, and dibromalcane (1 eq.) were loaded into vials with a screw cap. The reaction mixture was stirred on a magnetic stirrer at 80 ° C for 1-30 hours until the container was filled with sediment. After cooling the reaction mixture to room temperature, the precipitate was filtered, washed with acetone on a filter, and dried to a constant weight. Most compounds are spectrally pure products. Compounds **14a**, **15a** and **18a** were recrystallized from ethanol to obtain spectrally pure products.

1,1'-(etane-1,2-diyl)bis(1-pyridinium) dibromide (**13a**). White powder, m.p. 295-296 °C dec. (lit.[2] 278−280 °C dec.), yield 2.84 g (82%). ^{1}H NMR (400 MHz, D_2O): δ 8.96 – 8.87 (m, 4H, Py-$H^{2,6}$), 8.70 (tt, J = 7.9, 1.4 Hz, 2H, Py-H^{4}), 8.22 – 8.14 (m, 4H, Py-$H^{3,5}$), 5.40 (s, 4H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 147.1, 144.3, 128.7, 59.7. ^{1}H and ^{13}C NMR data of **13a** are in agreement with those in the literature[2].

1,1'-(propane-1,3-diyl)bis(1-pyridinium) dibromide (**13b**). White powder, m.p. 247-251°C, yield 3.50 g (97%). ^{1}H NMR (400 MHz, D_2O): δ 9.03 – 8.92 (m, 4H, Py-$H^{2,6}$), 8.62 (t, *J* = 7.9 Hz, 2H, Py-H^{4}), 8.21 – 8.07 (m, 4H, Py-$H^{3,5}$), 4.93 – 4.81 (m, 4H, N-CH_2), 2.86 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 145.9, 144.0, 128.2, 57.7, 31.4. ^{1}H NMR data of **13b** are in agreement with those in the literature[3].

1,1'-(butane-1,4-diyl)bis(1-pyridinium) dibromide (**13c**). White powder, m.p. 241-242 °C, yield 3.70 g (99%). ^{1}H NMR (400 MHz, D_2O): δ 8.93 – 8.82 (m, 4H, Py-$H^{2,6}$), 8.57 (t, J = 7.9 Hz, 2H, Py-H^{4}), 8.09 (t, J = 7.1 Hz, 4H, Py-$H^{3,5}$), 4.75 – 4.67 (m, 4H, N-CH_2), 2.16 (m, 4H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 145.9, 143.8, 128.0, 60.4, 26.9. ^{1}H NMR data of **13c** are in agreement with those in the literature[3].

1,1'-(etane-1,2-diyl)bis(3-metylpyridin-1-ium) dibromide (**14a**). Slightly pinkish crystals, m.p. 254-255 °C, yield 1.89 g (33%). ^{1}H NMR (400 MHz, D_2O): δ 8.76 (s, 2H, Py-H^{2}), 8.63 (d, J = 6.1

Hz, 2H, Py-H^6), 8.52 (d, J = 8.1 Hz, 2H, Py-H^4), 8.01 (dd, J = 8.0 Hz, J = 6.2 Hz, 2H, Py-H^5), 5.31 (s, 4H, N-CH_2), 2.55 (s, 6H, CH_3); ^{13}C NMR (100 MHz, D_2O): δ 147.6, 143.7, 141.4, 140.6, 127.9, 59.6, 17.4. HRMS (ESI-TOF): m/z $[M - Br^-]^+$ Calcd for $C_{14}H_{18}{}^{79}BrN_2^+$: 293.0648; found: 293.0650; calcd for $C_{14}H_{18}{}^{81}BrN_2^+$: 295.0628; found: 295.0628.

1,1'-(propane-1,3-diyl)bis(3-metylpyridin-1-ium) dibromide (**14b**). White powder, m.p. 213-215 °C, yield 2.25 g (96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.51 (s, 2H, Py-H^2), 9.41 (d, J = 6.0 Hz, 2H, Py-H^6), 8.13 (d, J = 8.0 Hz, 2H, Py-H^4), 7.85 (dd, J = 8.0 Hz, J = 6.1 Hz, 2H, Py-H^5), 5.18-5.05 (m, 4H, N-CH_2), 3.06-2.94 (m, 2H, CH_2), 2.46 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.7, 144.4, 142.0, 139.5, 127.5, 56.9, 34.1, 18.4. HRMS (ESI-TOF): m/z $[M - Br^-]^+$ Calcd for $C_{15}H_{20}{}^{79}BrN_2^+$: 307.0805; found: 307.0809; calcd for $C_{15}H_{20}{}^{81}BrN_2^+$: 309.0784; found: 309.0784.

1,1'-(butane-1,4-diyl)bis(3-metylpyridin-1-ium) dibromide (**14c**). White powder, m.p. 217-220 °C, yield 2.61 g (94%). ^{1}H NMR (400 MHz, D_2O): δ 9.45 (s, 2H, Py-H^2), 9.37 (d, J = 6.0 Hz, 2H, Py-H^6), 8.13 (d, J = 8.0 Hz, 2H, Py-H^4), 7.82 (dd, J = 7.8 Hz, J = 6.2 Hz, 2H, Py-H^5), 4.98 (t, J = 6.0 Hz, 4H, N-CH_2), 2.47 (s, 6H, CH_3), 2.21 (brs, 4H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 145.5, 144.3, 141.9, 139.3, 127.3, 59.4, 27.4, 18.3. HRMS (ESI-TOF): m/z $[M - Br^-]^+$ Calcd for $C_{16}H_{22}{}^{79}BrN_2^+$: 321.0961; found: 321.0967; calcd for $C_{16}H_{22}{}^{81}BrN_2^+$: 323.0941; found: 323.0941.

1,1'-(etane-1,2-diyl)bis(4-metylpyridin-1-ium) dibromide (**15a**). Pale beige crystals, m.p. 296-296.5°C, yield 2.29 g (31%). ^{1}H NMR (400 MHz, D_2O): δ 8.61 (d, J = 6.7 Hz, 4H, Py-$H^{2,6}$), 7.93 (d, J = 6.5 Hz, 4H, Py-$H^{3,5}$), 5.24 (s, 4H, N-CH_2), 2.68 (s, 6H, CH_3); ^{13}C NMR (100 MHz, D_2O) δ 162.0, 142.9, 129.1, 59.0, 21.3. HRMS (ESI-TOF): m/z $[M - Br^-]^+$ Calcd for $C_{14}H_{18}{}^{79}BrN_2^+$: 293.0648; found: 293.0650; calcd for $C_{14}H_{18}{}^{81}BrN_2^+$: 295.0628; found: 295.0629.

1,1'-(propane-1,3-diyl)bis(4-metylpyridin-1-ium) dibromide (**15b**). Beige powder, m.p. 246-247 °C, yield 1.98 g (85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.44 (d, J = 6.7 Hz, 4H, Py-$H^{2,6}$), 7.73 (d, J = 6.4 Hz, 4H, Py-$H^{3,5}$), 5.17-5.00 (m, 4H, N-CH_2), 3.03-2.87 (m, 2H, CH_2), 2.53 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 144.2, 128.7, 56.5, 34.5, 22.2. HRMS (ESI-TOF): m/z $[M - Br^-]^+$ Calcd for $C_{15}H_{20}{}^{79}BrN_2^+$: 307.0805; found: 307.0808; calcd for $C_{15}H_{20}{}^{81}BrN_2^+$: 309.0784; found: 309.0784.

1,1'-(butane-1,4-diyl)bis(4-metylpyridin-1-ium) dibromide (**15c**). Pale pink powder, m.p. 221-224 °C, yield 2.61 g (93%). ^{1}H NMR (400 MHz, D_2O): δ 8.66 (d, J = 4.5 Hz, 4H, Py-$H^{2,6}$), 7.88 (d, J = 5.9 Hz, 4H, Py-$H^{3,5}$), 4.61 (brs, 4H, N-CH_2), 2.65 (s, 6H, CH_3), 2.09 (brs, 4H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 159.9, 142.7, 128.4, 59.5, 26.8, 21.0. HRMS (ESI-TOF): m/z $[M - Br^-]^+$ Calcd for $C_{16}H_{22}{}^{79}BrN_2^+$: 321.0961; found: 321.0966; calcd for $C_{16}H_{22}{}^{81}BrN_2^+$: 323.0941; found: 323.0941.

1,1'-(propane-1,3-diyl)bis(2,4-dimetylpyridin-1-ium) dibromide (**16b**). Pale beige powder, m.p. 227-228 °C, yield 1.81 g (87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.84 (d, J = 6.5 Hz, 2H, Py-

H^6), 7.62 (s, 2H, Py-H^3), 7.52 (d, J = 6.4 Hz, 2H, Py-H^5), 5.24-5.09 (m, 4H, N-CH_2), 3.09 (s, 6H, CH_3), 2.69-2.57 (m, 2H, CH_2), 2.48 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 154.5, 145.1, 130.2, 126.3, 52.9, 31.5, 21.8. HRMS (ESI-TOF): m/z $[M - Br^-]^+$ Calcd for $C_{17}H_{24}{}^{79}BrN_2^+$: 335.1118; found: 335.1120; calcd for $C_{17}H_{24}{}^{81}BrN_2^+$: 337.1097; found: 337.1096.

1,1'-(propane-1,3-diyl)bis(2,5-dimetylpyridin-1-ium) dibromide (**17b**). Pale beige powder, m.p. 333-334 °C, yield 2.15 g (72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.19 (s, 2H, Py-H^6), 7.99 (dd, J = 8.1 Hz, J = 0.9 Hz, 2H, Py-H^4), 7.66 (d, J = 8.2 Hz, 2H, Py-H^3), 5.28-5.18 (m, 4H, N-CH_2), 3.18 (s, 6H, CH_3), 2.88-2.76 (m, 2H, CH_2), 2.51 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.4, 145.6, 145.2, 136.7, 129.1, 53.3, 31.2, 21.1, 17.4. HRMS (ESI-TOF): m/z $[M - Br^-]^+$ Calcd for $C_{17}H_{24}{}^{79}BrN_2^+$: 335.1118; found: 335.1123; calcd for $C_{17}H_{24}{}^{81}BrN_2^+$: 337.1097; found: 337.1099.

1,1'-(etane-1,2-diyl)bis(3,4-dimetylpyridin-1-ium) dibromide (**18a**). White powder, m.p. 289.5-290.5 °C, yield 1.55 g (20%). ^{1}H NMR (400 MHz, D_2O): δ 8.50 (s, 2H, Py-H^2), 8.35 (d, J = 6.3 Hz, 2H, Py-H^6), 7,80 (d, J = 6.3 Hz, 2H, Py-H^5), 5.15 (s, 4H, N-CH_2), 2.56 (s, 6H, CH_3), 2.39 (s, 6H, CH_3); ^{13}C NMR (100 MHz, D_2O): δ 160.7, 142.0, 140.5, 139.3, 128.5, 59.0, 19.4, 15.7. HRMS (ESI-TOF): m/z $[M - Br^-]^+$ Calcd for $C_{16}H_{22}{}^{79}BrN_2^+$: 321.0961; found: 321.0963; calcd for $C_{16}H_{22}{}^{81}BrN_2^+$: 323.0941; found: 323.0941.

1,1'-(propane-1,3-diyl)bis(3,4-dimetylpyridin-1-ium) dibromide (**18b**). White powder, m.p. 225-227 °C, yield 1.77 g (86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.39 (s, 2H, Py-H^2), 9.23 (d, J = 6.2 Hz, 2H, Py-H^6), 7.63 (d, J = 6.2 Hz, 2H, Py-H^5), 5.04-4.94 (m, 4H, N-CH_2), 3.02-2.89 (m, 2H, CH_2), 2.40 (s, 6H, CH_3), 2.34 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.8, 143.1, 141.5, 138.1, 128.1, 56.1, 33.9, 20.1, 16.6. HRMS (ESI-TOF): m/z $[M - Br^-]^+$ Calcd for $C_{17}H_{24}{}^{79}BrN_2^+$: 335.1118; found: 335.1121; calcd for $C_{17}H_{24}{}^{81}BrN_2^+$: 337.1097; found: 337.1097.

1,1'-(butane-1,4-diyl)bis(3,4-dimetylpyridin-1-ium) dibromide (**18c**). White powder, m.p. 192-193.7 °C, yield 3.40 g (99%). ^{1}H NMR (400 MHz, D_2O): δ 8.58 (s, 2H, Py-H^2), 8.52 (d, J = 6.3 Hz, 2H, Py-H^6), 7.82 (d, J = 6.3 Hz, 2H, Py-H^5), 4.58 (brs, 4H, N-CH_2), 2.56 (s, 6H, CH_3), 2.45 (s, 6H, CH_3), 2.13-2.03 (m, 4H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 158.6, 141.9, 140.3, 138.4, 127.9, 59.3, 26.8, 19.2, 15.8. HRMS (ESI-TOF): m/z $[M - Br^-]^+$ Calcd for $C_{18}H_{26}{}^{79}BrN_2^+$: 349.1274; found: 349.1282; calcd for $C_{18}H_{26}{}^{81}BrN_2^+$: 351.1254; found: 351.1256.

1,1'-(propane-1,3-diyl)bis(5-ethyl-2-metylpyridin-1-ium) dibromide (**19b**). White powder, m.p. 204-206 °C, yield 1.73 g (91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.01 (s, 2H, Py-H^6), 8.03 (dd, J = 8.2 Hz, J = 1.4 Hz, 2H, Py-H^4), 7.75 (d, J = 8.2 Hz, 2H, Py-H^3), 5.29-5.14 (m, 4H, N-CH_2), 3.14 (s, 6H, CH_3), 2.82-2.71 (m, 6H, CH_2), 1.24 (t, J = 7.6 Hz, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9, 145.2, 144.6, 142.9, 129.7, 53.7, 31.8, 25.2, 21.7, 14.4. HRMS (ESI-TOF): m/z $[M - Br^-]^+$ Calcd for $C_{19}H_{28}{}^{79}BrN_2^+$: 363.1431; found: 363.1435; calcd for $C_{19}H_{28}{}^{81}BrN_2^+$: 365.1410; found: 365.1410.

1,1'-(propane-1,3-diyl)bis(3-cyanopyridine-1-ium) dibromide (**20b**). White powder, m.p. 260-262 °C dec., yield 1.73 g (87%). ^{1}H NMR (400 MHz, D_2O): δ 9.66 (s, 2H, Py-H^2), 9.31 (d, J = 6.3 Hz, 2H, Py-H^6), 9.02 (d, J = 8.2 Hz, 2H, Py-H^4), 8.36 (dd, J = 7.9 Hz, J = 6.6 Hz, 2H, Py-H^5), 5.02-4.94 (m, 4H, N-CH_2), 2.97-2.86 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 149.1, 148.2, 147.9, 129.0, 113.9, 112.7, 58.4, 30.9. HRMS (ESI-TOF): m/z [M − Br^-]$^+$ Calcd for $C_{15}H_{14}{}^{79}BrN_4{}^+$: 329.0397; found: 329.0400; calcd for $C_{15}H_{14}{}^{81}BrN_4{}^+$: 331.0376; found: 331.0379.

1,1'-(prolpan-1,3-diyl)bis(4-(dimethylamino)pyridine-1-ium) dibromide (**21b**). White powder, m.p. 146-148 °C, yield 1.60 g (98%). ^{1}H NMR (400 MHz, D_2O): δ 7.97 (d, J = 7.9 Hz, 4H, Py-$H^{2,6}$), 6.82 (d, J = 7.9 Hz, 4H, Py-$H^{3,5}$), 4.28 (t, J = 6.9 Hz, 4H, N-CH_2), 3.17 (s, 12H, CH_3), 2.51 (p, 2H, CH_2, J = 6.9 Hz); ^{13}C NMR (100 MHz, D_2O): δ 155.8, 140.7, 107.5, 54.3, 39.0, 29.5. HRMS (ESI-TOF): m/z [M − Br^-]$^+$ Calcd for $C_{17}H_{26}{}^{79}BrN_4{}^+$: 365.1336; found: 365.1342; calcd for $C_{19}H_{28}{}^{81}BrN_2{}^+$: 367.1315; found: 367.1317.

Synthesis of dicationic pyridinium bromides 22-23. To a solution of the corresponding pyridine (2.2 eq.) in toluene (2 ml per 10 mmol) placed in a vial with a screw cap, dibromopropane (1 eq.) was added. The reaction mixture was stirred on a magnetic stirrer at 110 ° C for 12-19 hours for **22** and **23**, respectively, until a stable volume of oily liquid formed at the bottom. Upon completion of the reaction, the solvent was removed by decantation. The oily liquid was dissolved in ethanol. Acetone was added to the solution until stable turbidity was formed (~1:20). The formed precipitate was filtered a day later, washed with acetone on a filter, and dried in air to a constant mass, obtaining spectrally pure products.

1,1'-(propane-1,3-diyl)bis(3,5-dimetylpyridin-1-ium) dibromide (**22**). Pale beige crystals, m.p. 111-113 °C, yield 2.74 g (33%). ^{1}H NMR (400 MHz, D_2O): δ 8.70 (d, J = 6.3 Hz, 2H, Py), 8.31 (d, J = 7.9 Hz, 2H, Py), 7.84-7.77 (m, 2H, Py-H^4), 4.92-4.82 (m, 4H, N-CH_2), 2.83 (s, 6H, CH_3), 2.70-2.61 (m, 2H, CH_2), 2.56 (s, 6H, CH_3); ^{13}C NMR (100 MHz, D_2O): δ 154.3, 145.7, 142.1, 139.4, 124.6, 54.6, 29.2, 18.9, 16.1. HRMS (ESI-TOF): m/z [M − Br^-]$^+$ Calcd for $C_{17}H_{24}{}^{79}BrN_2{}^+$: 335.1118; found: 335.1121; calcd for $C_{17}H_{24}{}^{81}BrN_2{}^+$: 337.1097; found: 337.1098.

1,1'-(propane-1,3-diyl)bis(2,3-dimetylpyridin-1-ium) dibromide (**23**). Pale beige crystals, m.p. 111.5-112.5 °C, yield 2.79 g (28%). ^{1}H NMR (400 MHz, D_2O): δ 8.70 (d, J = 6.0 Hz, 2H, Py-H^6), 8.31 (d, J = 7.9 Hz, 2H, Py-H^4), 7.84-7.78 (m, 2H, Py-H^5), 4.94-4.83 (m, 4H, N-CH_2), 2.84 (s, 6H, CH_3), 2.71-2.61 (m, 2H, CH_2), 2.56 (s, 6H, CH_3); ^{13}C NMR (100 MHz, D_2O): δ 154.3, 145.7, 142.1, 139.4, 124.6, 54.6, 29.2, 19.0, 16.1. HRMS (ESI-TOF): m/z [M − Br^-]$^+$ Calcd for $C_{17}H_{24}{}^{79}BrN_2{}^+$: 335.1118; found: 335.1120; calcd for $C_{17}H_{24}{}^{81}BrN_2{}^+$: 337.1097; found: 337.1098.

Synthesis of dicationic pyridinium nitrates 24-33 (general procedure). To a solution of 2.5-3.0 mmol (1 eq.) of dibromide in 1-1.5 ml of water at room temperature, a solution of 5-6 mmol (2 eq.) of silver nitrate in 1-1.5 ml of H2O was added with stirring. The precipitate was filtered.

The water from the filtrate was distilled in a vacuum of a water jet pump (10 mmHg). The precipitate was washed with diethyl ether and dried to a constant weight. The compounds are spectrally pure products to a constant weight.

1,1'-(propane-1,3-diyl)bis(3-methylpyridine-1-ium) dinitrate (**24**). White crystals, m.p. 150-152.5 °C, yield 0.85 g (95%). ^{1}H NMR (400 MHz, D_2O): δ 8.73 (s, 2H, Py-H^{2}), 8.69 (d, J = 6.1 Hz, 2H, Py-H^{6}), 8.39 (d, J = 8.1 Hz, 2H, Py-H^{4}), 7.96 (dd, J = 7.9 Hz, J = 6.3 Hz, 2H, Py-H^{5}), 4.77-4.69 (m, 4H, N-CH_2), 2.83-2.74 (m, 2H, CH_2), 2.54 (s, 6H, CH_3); ^{13}C NMR (100 MHz, D_2O): δ 146.2, 143.4, 141.0, 140.0, 127.3, 57.5, 31.2, 17.2. HRMS (ESI-TOF): m/z [M – NO_3^-]$^+$ Calcd for $C_{15}H_{20}N_3O_3^+$: 290.1500; found: 290.1503.

1,1'-(propane-1,3-diyl)bis(4-methylpyridine-1-ium) dinitrate (**25**). Pale beige powder, m.p. 129-132 °C dec., yield 1.014 g (94%). ^{1}H NMR (400 MHz, D_2O): δ 8.66 (d, J = 6.4 Hz, 4H, Py-H^{2,6}), 7.88 (d, J = 6.3 Hz, 4H, Py-H^{3,5}), 4.73-4.65 (m, 4H, N-CH_2), 2.78-2.68 (m, 2H, CH_2), 2.64 (s, 6H, CH_3); ^{13}C NMR (100 MHz, D_2O): δ 160.4, 142.7, 128.5, 56.8, 31.1, 20.9. HRMS (ESI-TOF): m/z [M – NO_3^-]$^+$ Calcd for $C_{15}H_{20}N_3O_3^+$: 290.1500; found: 290.1501.

1,1'-(propane-1,3-diyl)bis(2,3-dimethylpyridine-1-ium) dinitrate (**26**). White-beige powder, m.p. 138-141 °C, yield 0.85 g (95%). ^{1}H NMR (400 MHz, D_2O): δ 8.60 (d, J = 6.2 Hz, 2H, Py-H^{6}), 8.26 (d, J = 7.8 Hz, 2H, Py-H^{4}), 7.78-7.72 (m, 2H, Py-H^{5}), 4.84-4.76 (m, 4H, N-CH_2), 2.77 (s, 6H, CH_3), 2.64-2.54 (m, 2H, CH_2), 2.51 (s, 6H, CH_3); ^{13}C NMR (100 MHz, D_2O): δ 154.2, 145.6, 142.0, 139.3, 124.5, 54.5, 29.0, 18.7, 15.6. HRMS (ESI-TOF): m/z [M – NO_3^-]$^+$ Calcd for $C_{17}H_{24}N_3O_3^+$: 318.1813; found: 318.1816.

1,1'-(propane-1,3-diyl)bis(2,4-dimethylpyridine-1-ium) dinitrate (**27**). Light beige powder, m.p. 157-159 °C dec., yield 0.98 g (93%). ^{1}H NMR (400 MHz, D_2O): δ 8.55 (d, J = 6.4 Hz, 2H, Py-H^{6}), 7.73 (s, 2H, Py-H^{3}), 7.68 (d, J = 6.2 Hz, 2 H, Py-H^{5}), 4.72-4.63 (m, 4H, N-CH_2), 2.78 (s, 6H, CH_3), 2.60-2.47 (m, 2H, CH_2), 2.56 (s, 6H, CH_3); ^{13}C NMR (100 MHz, D_2O): δ 159.7, 153.6, 143.1, 130.1, 126.2, 52.8, 29.0, 20.5, 18.6. HRMS (ESI-TOF): m/z [M – NO_3^-]$^+$ Calcd for $C_{17}H_{24}N_3O_3^+$: 318.1813; found: 318.1815.

1,1'-(propane-1,3-diyl)bis(2,5-dimethylpyridine-1-ium) dinitrate (**28**). White powder, m.p. 155.5-158.5 °C, yield 1.01 g (93%). ^{1}H NMR (400 MHz, D_2O): δ 8.61 (s, 2H, Py-H^{6}), 8.22 (dd, J = 8.2 Hz, J = 1.3 Hz, 2H, Py-H^{4}), 7.80 (d, J = 8.2 Hz, 2H, Py-H^{3}), 4.76-4.68 (m, 4H, N-CH_2), 2.81 (s, 6H, CH_3), 2.64-2.54 (m, 2H, CH_2), 2.47 (s, 6H, CH_3); ^{13}C NMR (100 MHz, D_2O): δ 151.9, 146.1, 143.5, 137.1, 129.2, 53.5, 29.0, 18.4, 16.6. HRMS (ESI-TOF): m/z [M – NO_3^-]$^+$ Calcd for $C_{17}H_{24}N_3O_3^+$: 318.1813; found: 318.1815.

1,1'-(propane-1,3-diyl)bis(3,4-dimethylpyridine-1-ium) dinitrate (**29**). White crystals, m.p. 171-174 °C, yield 1.04 g (97%). ^{1}H NMR (400 MHz, D_2O): δ 8.54 (s, 2H, Py-H^{2}), 8.51 (d, J = 6.3 Hz, 2H, Py-H^{6}), 7.80 (d, J = 6.3 Hz, 2H, Py-H^{5}), 4.69-4.61 (m, 4H, N-CH_2), 2.78-2.68 (m, 2H, CH_2), 2.54 (s, 6H, CH_3), 2.41 (s, 6H, CH_3); ^{13}C NMR (100 MHz, D_2O): δ 159.1, 141.9, 140.3,

138.6, 128.0, 56.7, 31.0, 19.0, 15.6. HRMS (ESI-TOF): m/z [M – NO_3^-]$^+$ Calcd for $C_{17}H_{24}N_3O_3^+$: 318.1813; found: 318.1815.

1,1'-(propane-1,3-diyl)bis(3,5-dimethylpyridine-1-ium) dinitrate (**30**). Light beige powder, m.p. 129-132 °C, yield 0.91 g (80%). ^{1}H NMR (400 MHz, D_2O): δ 8.61 (d, J = 6.3 Hz, 2H, Py), 8.26 (d, J = 7.9 Hz, 2H, Py), 7.75 (t, J = 7.1 Hz, 2H, Py-H^4), 4.84-4.77 (m, 4H, N-CH_2), 2.78 (s, 6H, CH_3), 2.65-2.54 (m, 2H, CH_2), 2.51 (s, 6H, CH_3); ^{13}C NMR (100 MHz, D_2O): δ 154.2, 145.6, 142.0, 139.3, 124.5, 54.5, 29.0, 18.7, 15.6. HRMS (ESI-TOF): m/z [M – NO_3^-]$^+$ Calcd for $C_{17}H_{24}N_3O_3^+$: 318.1813; found.1815.

1,1'-(propane-1,3-diyl)bis(5-ethyl-2-metylpyridin-1-ium) dinitrate (**31**). Pale lilac-grey powder, m.p. 155-158 °C, yield 1.08 g (90%). ^{1}H NMR (400 MHz, D_2O): δ 8.61 (*pseudo*-d, J = 1.1 Hz, 2H, Py-H^6), 8.26 (dd, J = 8.3 Hz, J = 1.5 Hz, 2H, Py-H^4), 7.82 (d, J = 8.3 Hz, 2H, Py-H^3), 4.76-4.68 (m, 4H, N-CH_2), 2.84-2.76 (m, 4H, CH_2), 2.80 (s, 6H, CH_3), 2.65-2.54 (m, 2H, CH_2), 1.25 (t, J = 7.6 Hz, 6H, CH_3,); ^{13}C NMR (100 MHz, D_2O): δ 152.1, 145.1, 142.84, 142.75, 129.4, 53.5, 29.1, 24.5, 18.4, 13.1. HRMS (ESI-TOF): m/z [M – NO_3^-]$^+$ Calcd for $C_{19}H_{28}N_3O_3^+$: 346.2126; found: 346.2129.

1,1'-(propane-1,3-diyl)bis(3-cyanopyridine-1-ium) dinitrate (**32**). Light beige powder, m.p. 222-226 °C, yield 0.72 g (77%). ^{1}H NMR (400 MHz, D_2O): δ 9.63 (s, 2H, Py-H^2), 9.29 (d, J = 5.9 Hz, 2H, Py-H^6), 9.04 (d, J = 7.9 Hz, 2H, Py-H^4), 8.37 (d, J = 7.1 Hz, 2H, Py-H^5), 5.08-4.93 (m, 4H, N-CH_2), 2.98-2.78 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 149.6, 148.7, 148.4, 129.5, 114.5, 113.3, 59.0, 31.4. HRMS (ESI-TOF): m/z [M – NO_3^-]$^+$ Calcd for $C_{15}H_{14}N_5O_3^+$: 312.1092; found: 312.1092.

1,1'-(prolpan-1,3-diyl)bis(4-(dimethylamino)pyridine-1-ium) dinitrate (**33**). Light beige powder, m.p. 150-152.5 °C, yield 1.02 g (95%). ^{1}H NMR (400 MHz, D_2O): δ 7.94 (d, J = 7.8 Hz, 4H, Py-H^{2,6}), 6.80 (d, J = 7.8 Hz, 4H, Py-H^{3,5}), 4.24 (t, J = 6.9 Hz, 4H, N-CH_2), 3.15 (s, 12H, CH_3), 2.48 (p, J = 6.9 Hz, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 155.8, 140.6, 107.3, 54.2, 38.9, 29.6. HRMS (ESI-TOF): m/z [M – NO_3^-]$^+$ Calcd for $C_{17}H_{26}N_5O_3^+$: 348.2030; found: 348.2036.

Method of synthesis of pyridinium dihydrosulfate. Concentrated H_2SO_4 (4.4 mmol) was added to a solution of dibromide **13b** (2 mmol) in H_2O (2 ml) placed in a vial with a screw cap. The reaction mixture was kept at room temperature for 48 hours with the lid ajar, stirring occasionally. Water and the formed HBr were distilled in a vacuum of a water jet pump (10 mmHg) to a constant mass, crystallized from ethanol, obtaining a spectrally pure product.

1,1'-(propane-1,3-diyl)bis(1-pyridinium) dihydrosulfate (**34**). White crystals, m.p. 158-160 °C, yield 0.78 g (98%). ^{1}H NMR (400 MHz, D_2O): δ 8.90 –8,82 (m, 4H, Py-H^{2,6}), 8.58 – 8.49 (m, 2H, Py-H^4), 8.12 – 8.00 (m, 4H, Py-H^{3,5}), 4.80 – 4.72 (m, 4H, N-CH_2), 2.85-2.68 (m, 2H, CH_2); ^{13}C

NMR (100 MHz, D_2O): δ 145.8, 143.9, 128.1, 57.6, 31.3. HRMS (ESI-TOF): m/z [M – HSO_4^-]$^+$ Calcd for $C_{13}H_{17}N_2O_4S^+$: 297.0904; found: 297.0904.

Synthesis by substitution of bromide ion in acetonitrile (general procedure). A mixed suspension of dibromide **13b** (2 mmol) in acetonitrile (40 ml) containing the corresponding sodium acetate, sodium tetraphenylborate or ammonium thiocyanate (4.4 mmol) was boiled in a reflux refrigerator for 24 hours. After cooling the mixture, the resulting crude product was filtered, washed with acetonitrile, dried, and crystallized from isopropanol. The compounds are spectrally pure products.

Synthesis by substitution of bromide ion in propanol-2 (general procedure). A vial with a screw cap was loaded with dibromide **13b** (2 mmol), corresponding sodium acetate, potassium tetrafluoroborate, ammonium thiocyanate (4.4 mmol) or sodium succinate (2.2 mmol) and propanol-2 in an amount of 10 ml per 1 mmol. The suspension was stirred on a magnetic stirrer at 81 ° C for 51-63 hours. After cooling the mixture, the resulting crude product was filtered, washed with propanol-2, dried and crystallized from the corresponding alcohol. Recrystallization is not required for compound **40**. The compounds are spectrally pure products.

1,1'-(propane-1,3-diyl)bis(1-pyridinium) ditetrafenylborate (**35**). Beige powder, m.p. 211-213 °C, yield 1.80 g (86.5%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.98 (d, *J* = 5.6 Hz, 4H, Py-$H^{2,6}$), 8.56 (t, *J* = 7.8 Hz, 2H, Py-H^4), 8.18 – 8.04 (m, 4H, Py-$H^{3,5}$), 7.25-7.13 (m, 16H, Ph), 6.94 (t, *J* = 7.4 Hz, 16H, Ph), 6.80 (t, *J* = 7.2 Hz, 8H, Ph), 4.64 (t, *J* = 7.4 Hz, 4H, N-CH_2), 2.62-2.52 (m, 2H, CH_2); ^{13}C NMR (100 MHz, DMSO-d_6): δ 164.2, 163.7, 163.2, 162.7, 145.9, 144.9, 135.6, 128.3, 125.5, 125.42, 125.40, 125.37, 121.6, 57.6, 31.6; ^{11}B NMR (128.3 MHz, DMSO-d_6): δ -6.71. HRMS (ESI-TOF): m/z [M – $B(C_6H_5)_4^-$]$^+$ Calcd for $C_{37}H_{36}BN_2^+$: 519.2967; found: 519.2964.

1,1'-(propane-1,3-diyl)bis(1-pyridinium) ditetrafluoroborate (**36**). White powder, m.p. 232-234 °C, yield 0.61 g (81%), recrystallization from ethanol. ^{1}H NMR (400 MHz, D_2O): δ 8.92 (d, *J* = 5.5 Hz, 4H, Py-$H^{2,6}$), 8.59 (tt, *J* = 7.9 Hz, *J* = 1.2 Hz, 2H, Py-H^4), 8.14 – 8.06 (m, 4H, Py-$H^{3,5}$), 4.85-4.80 (m, 4H, N-CH_2), 2.90-2.75 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 145.9, 144.0, 128.2, 57.6, 31.3; ^{19}F NMR (376.3 MHz, D_2O): δ -150.23 (d), -150.28 (q); ^{11}B NMR (128.3 MHz, D_2O): δ -1.43. HRMS (ESI-TOF): m/z [M – BF_4^-]$^+$ Calcd for $C_{13}H_{16}BF_4N_2^+$: 287.1338; found: 287.1336[2].

1,1'-(propane-1,3-diyl)bis(3-cyanopyridine-1-ium) ditetrafluoroborate (**37**). Beige powder, m.p. 222-226 °C, yield 0.77 g (63%), recrystallization from methanol. ^{1}H NMR (400 MHz, D_2O): δ 9.63 (s, 2H, Py-H^2), 9.28 (d, 2H, Py-H^6, J = 6.3 Hz), 9.02 (d, 2H, Py-H^4, J = 8.2 Hz), 8.48-4.15 (m, 2H, Py-H^5), 5.01-4.91 (m, 4H, N-CH_2), 2.99-2.79 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 149.1, 148.2, 147.9, 128.9, 113.9, 112.7, 58.4, 30.9; ^{19}F NMR (376.3 MHz, D_2O): δ -150.20

(*pseudo*-s), -150.25 (q); ^{11}B NMR (128.3 MHz, D_2O): δ -1.44. HRMS (ESI-TOF): m/z [M – BF_4^-]$^+$ Calcd for $C_{15}H_{14}BF_4N_4^+$: 337.1243; found: 337.1255.

1,1'-(propane-1,3-diyl)bis(1-pyridinium) diacetate (**38**). Beige powder, m.p. 220-223 °C, yield 0.42 g (66%) propanol-2, 0.29 g (45.5%) acetonitrile (recrystallization from propanol-2). ^{1}H NMR (400 MHz, D_2O): δ 8.95 – 8.88 (m, 4H, Py-H^{2,6}), 8.58 (t, *J* = 7.9 Hz, 2H, Py-H^4), 8.15 – 8.03 (m, 4H, Py-H^{3,5}), 4.84 – 4.76 (m, 4H, N-CH_2), 2.88-2.73 (m, 2H, CH_2), 1.87 (s, 3H, CH_3); ^{13}C NMR (100 MHz, D_2O): δ 181.0, 145.9, 144.0, 128.2, 57.6, 31.3, 22.8. IR (v, cm^{-1}): 3398 (O-H); 3037, 3020, 3002, 2934 (C-H); 1622, (C=N,); 1574 (C=C); 1484 (C-C); 1408(-COO^-); 1211 (O-C-C); 1181 (C-N); 784, 686, 645 (propyl CH).

1,1'-(propane-1,3-diyl)bis(1-pyridinium) succinate (**39**). White powder, m.p. 245-248 °C, yield 0.61 g (96%). ^{1}H NMR (400 MHz, D_2O): δ 8.92 (d, *J* = 5.6 Hz, 4H, Py-H^{2,6}), 8.59 (t, *J* = 7.9 Hz, 2H, Py-H^4), 8.11 (d, *J* = 7.2 Hz, 4H, Py-H^{3,5}), 4.85 – 4.79 (m, 4H, N-CH_2), 2.87-2.74 (m, 2H, CH_2), 2.41 (s, 4H, CH_2-COO); ^{13}C NMR (100 MHz, D_2O): δ 180.9, 145.9, 144.0, 128.2, 57.6, 32.7, 31.3. IR (v, cm^{-1}): 3037, 3020, 3002, 2973, 2947 (C-H); 1629, 1621 (C=N); 1558 (C=O); 1485 (C-C); 1431(-COO^-); 1211 (O-C-C); 1181 (C-N); 783, 687, 659 (propyl CH).

1,1'-(propane-1,3-diyl)bis(1-pyridinium) dithiocyanate (**40**). Light peach powder, m.p. 98-99 °C, yield 0.53 g (84%) propanol-2, 0.49 g (63%) acetonitrile (recrystallization from propanol-2).. ^{1}H NMR (400 MHz, D_2O): δ 8.93 (d, *J* = 5.6 Hz, 4H, Py-H^{2,6}), 8.61 (t, *J* = 7.9 Hz, 2H, Py-H^4), 8.13 (t, *J* = 7.1 Hz, 4H, Py-H^{3,5}), 4.87 – 4.81 (m, 4H, N-CH_2), 2.89-2.76 (m, 2H, CH_2); ^{13}C NMR (100 MHz, D_2O): δ 145.9, 144.0, 128.2, 57.6, 31.3. IR (v, cm^{-1}): 3126, 3087, 3031, 3013, 2867, 2796 (C-H); 2055 (SNC); 1633, (C=N); 1582 (C=C); 1487, 1453 (C-H); 1373, 1323, 1220, 1175 (C-N); 779, 738, 686 (propyl CH). HRMS (ESI-TOF): m/z [M – NCS^-]$^+$ Calcd for $C_{14}H_{16}N_3S^+$: 258.1060; found: 258.1063.

Synthesis of perrenates in alcohols (general procedure). A derivative of 1,1'-(propane-1,3-diyl)bis(1-pyridinium) dibromide (0.1 mmol), sodium perrenate (0.22 mmol) and propanol-2 (**41**) in an amount of 2 ml or 1 ml of ethanol (**42**) was loaded into a vial with a screw cap. The suspension was stirred on a magnetic stirrer at 81 °C (78 °C) for 24 (85) hours hours. After cooling the mixture, the resulting crude product was filtered, washed with propanol-2 or ethanol, and dried. The compounds are spectrally pure products.

Synthesis of perrenates in water (general procedure). A solution of 0.22 mmol of $NaReO_4$ in 0.5 ml of water was added drop by drop to a solution of 0.1 mmol of the 1,1'-(propane-1,3-diyl) bis(1-pyridinium) dibromide derivative in 0.5 ml of water. They waited for sediment or crystals to form, and filtered them.

1,1'-(propane-1,3-diyl)bis(1-pyridinium) perrenate (**41**). White powder, m.p. 158-160 °C, yield 0.0674 g (96%) propanol-2, 0.0686 g (98%) water. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.13

(d, *J* = 7.8 Hz, 4H, Py-$H^{2,6}$), 8.64 (t, *J* = 7.8 Hz, 2H, Py-H^4), 8.27 – 8.06 (m, 4H, Py-$H^{3,5}$), 4.76 (t, *J* = 7.84 Hz, 4H, N-CH_2), 2.74-2.59 (m, 2H, CH_2); ^{13}C NMR (100 MHz, DMSO-d_6): δ 145.9, 145.0, 128.3, 57.6, 31.8. HRMS (ESI-TOF): m/z [M – ReO_4^-]$^+$ Calcd for $C_{13}H_{16}N_2O_4Re^+$: 451.0663; found: 451.0670.

1,1'-(propane-1,3-diyl)bis(2,4-dimetylpyridin-1-ium) perrenate (**42**). Beige crystals, m.p. 151-154 °C, yield 0.0496 g (66%) ethanol, 0.0448 g (59%) water. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.80 (d, J = 6.5 Hz, 2H, Py-H^6), 7.91 (s, 2H, Py-H^3), 7.84 (dd, J = 6.5 Hz, J = 1.7 Hz, 2H, Py-H^5), 4.66-4.52 (m, 4H, N-CH_2), 2.80 (s, 6H, CH_3), 2.56 (s, 6H, CH_3), 2.47-2.30 (m, 2H, CH_2); ^{13}C NMR (100 MHz, DMSO-d_6): δ 158.6, 154.3, 144.5, 130.1, 126.2, 53.3, 29.4, 21.2, 19.5. HRMS (ESI-TOF): m/z [M – ReO_4^-]$^+$ Calcd for $C_{17}H_{24}N_2O_4Re^+$: 507.1289; found: 507.1285.

Computational details. The geometries of molecules were fully optimized by means of density functional theory (DFT) calculations. We used first-principles GGA PBE functional[4] and scalar-relativistic theory were used, the latter employing the four-component spin-free Hamiltonian derived by Dyall[5] and applied variationally. The full electron basis sets L1 was used, where L1 stands for double set size.[6,7,8] The numbers of contracted and primitive functions used in L1 are respectively {2,1}/{6,2} for H, {3,2,1}/{10,7,3} for C, N, and O, { 7, 6, 4, 1}/{ 26,23,16, 5} for Tc. Stationary points on the potential energy surface (PES) were identified by analyzing Hessians. The thermodynamic functions (Gibbs energies, G) at 298.15 K were calculated using an approximation of restricted rotator and harmonic oscillator. The atomic charges were calculated according to Hirschfeld.[9] The topological analysis was performed in the frame of Bader theory.[10] [46]. All calculations were performed with the use of the PRIRODA04 program written by Laikov.[11]

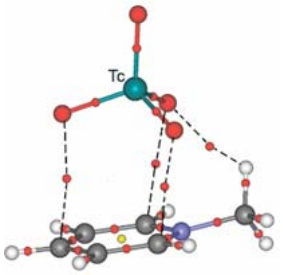


Fig. S1. QTAIM-diagram for complex **1**.

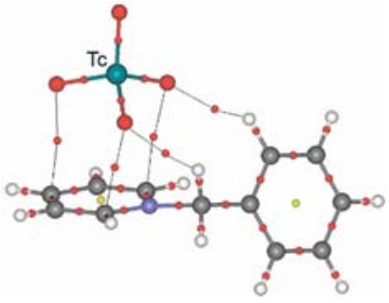


Fig. S2. QTAIM-diagram for complex **2**.

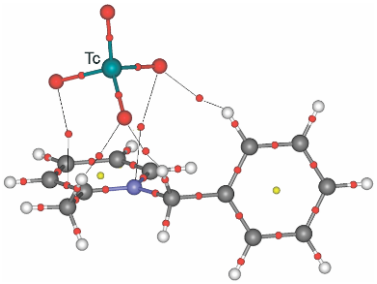


Fig. S3. QTAIM-diagram for complex **3**.

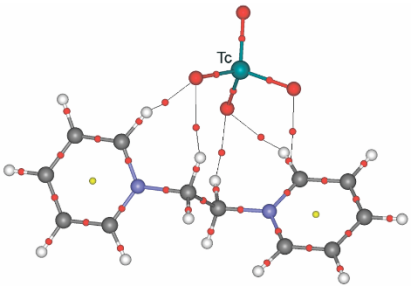


Fig. S4. QTAIM-diagram for complex **6**.

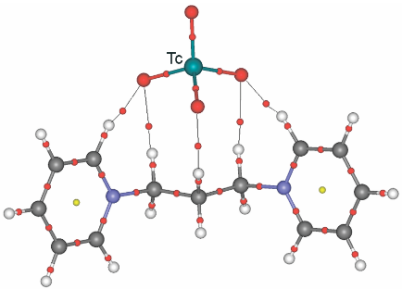


Fig. S5. QTAIM-diagram for complex **7**.

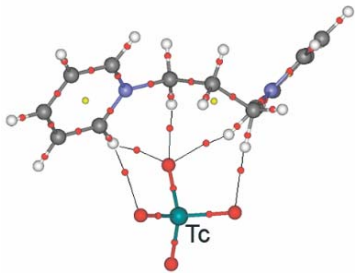


Fig. S6. QTAIM-diagram for complex **8**.

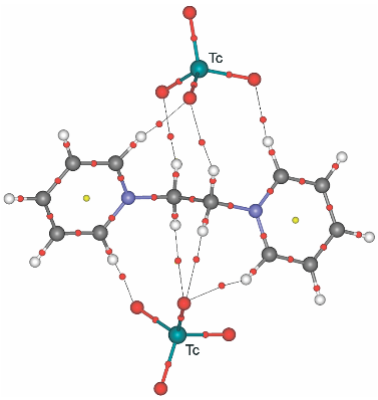


Fig. S7. QTAIM-diagram for complex **9**.

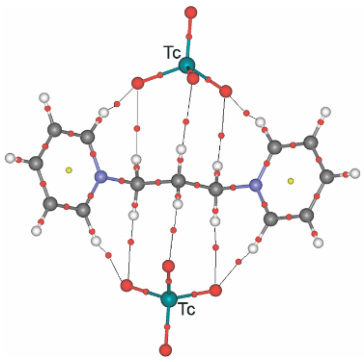


Fig. S8. QTAIM-diagram for complex **10**.

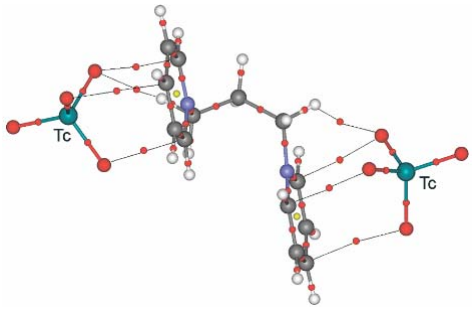


Fig. S9. QTAIM-diagram for complex **11**.

X-ray diffraction analysis. The data of **41** and **42** were collected by using STOE diffractometer Pilatus100K detector, focusing mirror collimation Mo Kα (0.71073Å) radiation, rotation method mode. STOE X-AREA software was used for cells refinement and data reduction. Data collection and image processing was performed with X-Area 1.67 (STOE & Cie GmbH, Darmstadt, Germany, 2013). Intensity data were scaled with LANA (part of X-Area) in order to minimize differences of intensities of symmetry-equivalent reflections (multi-scan method)."

The structures were solved and refined with SHELX[12] program. The non-hydrogen atoms were refined by using the anisotropic full matrix least-square procedure. **H**ydrogen atoms were placed in the calculated positions and allowed to ride on their parent atoms

Molecular geometry calculations were performed with the SHELX program, and the molecular graphics were prepared by using DIAMOND[13] software.

The main crystallographic parameters are listed in Table 1-6 respectively.

Table 1. Crystal data and structure refinement for 41.

Identification code	sza384new1	
Empirical formula	C13 H16 N2 O8 Re2	
Formula weight	700.68	
Temperature	295(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 12.7103(5) Å	α= 90°.

	b = 12.8430(5) Å	β= 90.590(4)°.
	c = 10.8220(4) Å	γ = 90°.
Volume	1766.47(12) $Å^3$	
Z	4	
Density (calculated)	2.635 Mg/m^3	
Absorption coefficient	13.736 mm^{-1}	
F(000)	1288	
Theta range for data collection	2.254 to 25.994°.	
Index ranges	-15<=h<=15, -15<=k<=15, -13<=l<=13	
Reflections collected	43408	
Independent reflections	3472 [R(int) = 0.0731]	
Completeness to theta = 25.242°	100.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3472 / 0 / 227	
Goodness-of-fit on F2	0.787	
Final R indices [I>2sigma(I)]	R1 = 0.0283, wR2 = 0.0445	
R indices (all data)	R1 = 0.0585, wR2 = 0.0480	
Extinction coefficient	0.00108(4)	
Largest diff. peak and hole	0.988 and -0.855 $e.Å^{-3}$	

Table 2. Bond lengths [Å] and angles [°] for 41.

Re(1)-O(2)	1.694(6)
Re(1)-O(3)	1.713(6)
Re(1)-O(1)	1.714(5)
Re(1)-O(4)	1.715(5)
Re(2)-O(6)	1.699(5)
Re(2)-O(8)	1.700(5)
Re(2)-O(5)	1.710(5)
Re(2)-O(7)	1.711(6)
N(1)-C(5)	1.334(9)
N(1)-C(1)	1.345(9)
N(1)-C(13)	1.482(9)
N(2)-C(6)	1.325(9)
N(2)-C(10)	1.336(10)
N(2)-C(11)	1.483(8)
C(1)-C(2)	1.365(11)
C(2)-C(3)	1.376(12)
C(3)-C(4)	1.360(12)

C(4)-C(5)	1.389(12)
C(6)-C(7)	1.362(10)
C(7)-C(8)	1.354(11)
C(8)-C(9)	1.379(12)
C(9)-C(10)	1.383(11)
C(11)-C(12)	1.514(11)
C(12)-C(13)	1.520(9)

O(2)-Re(1)-O(3)	109.9(3)
O(2)-Re(1)-O(1)	108.5(3)
O(3)-Re(1)-O(1)	110.2(3)
O(2)-Re(1)-O(4)	109.7(3)
O(3)-Re(1)-O(4)	108.7(3)
O(1)-Re(1)-O(4)	109.8(3)
O(6)-Re(2)-O(8)	109.7(3)
O(6)-Re(2)-O(5)	108.7(3)
O(8)-Re(2)-O(5)	109.3(3)
O(6)-Re(2)-O(7)	109.9(3)
O(8)-Re(2)-O(7)	109.3(3)
O(5)-Re(2)-O(7)	109.9(4)
C(5)-N(1)-C(1)	121.5(7)
C(5)-N(1)-C(13)	119.2(6)
C(1)-N(1)-C(13)	119.2(6)
C(6)-N(2)-C(10)	120.3(7)
C(6)-N(2)-C(11)	120.3(6)
C(10)-N(2)-C(11)	119.3(7)
N(1)-C(1)-C(2)	120.5(8)
C(1)-C(2)-C(3)	119.4(8)
C(3)-C(4)-C(5)	120.4(9)
N(2)-C(6)-C(7)	121.8(7)
C(8)-C(7)-C(6)	119.3(8)
C(7)-C(8)-C(9)	119.3(8)
C(8)-C(9)-C(10)	119.2(8)
N(2)-C(10)-C(9)	120.0(8)
N(2)-C(11)-C(12)	113.2(5)
C(11)-C(12)-C(13)	115.5(6)

N(1)-C(13)-C(12) 113.8(6)

Table 3. Torsion angles [°] for 41.

C(5)-N(1)-C(1)-C(2)	-0.5(11)
C(13)-N(1)-C(1)-C(2)	-177.2(7)
N(1)-C(1)-C(2)-C(3)	0.0(11)
C(1)-C(2)-C(3)-C(4)	0.7(12)
C(2)-C(3)-C(4)-C(5)	-0.9(12)
C(1)-N(1)-C(5)-C(4)	0.3(11)
C(13)-N(1)-C(5)-C(4)	177.0(6)
C(3)-C(4)-C(5)-N(1)	0.4(12)
C(10)-N(2)-C(6)-C(7)	-1.4(10)
C(11)-N(2)-C(6)-C(7)	-178.9(6)
N(2)-C(6)-C(7)-C(8)	1.7(11)
C(6)-C(7)-C(8)-C(9)	-1.1(12)
C(7)-C(8)-C(9)-C(10)	0.3(12)
C(6)-N(2)-C(10)-C(9)	0.6(11)
C(11)-N(2)-C(10)-C(9)	178.1(6)
C(8)-C(9)-C(10)-N(2)	-0.1(11)
C(6)-N(2)-C(11)-C(12)	-65.7(8)
C(10)-N(2)-C(11)-C(12)	116.8(7)
N(2)-C(11)-C(12)-C(13)	-61.8(8)
C(5)-N(1)-C(13)-C(12)	116.2(7)
C(1)-N(1)-C(13)-C(12)	-67.0(9)
C(11)-C(12)-C(13)-N(1)	-63.4(8)

Table 4. Crystal data and structure refinement for 42.

Identification code	sza618new1.	
Empirical formula	C8.50 H12 N O4 Re	
Formula weight	378.39	
Temperature	295(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 20.9788(17) Å	α= 90°.
	b = 4.9855(3) Å	β= 98.868(7)°.
	c = 20.7240(19) Å	γ = 90°.
Volume	2141.6(3) $Å^3$	

Z	8
Density (calculated)	2.347 Mg/m^3
Absorption coefficient	11.339 mm^{-1}
F(000)	1416
Theta range for data collection	1.965 to 23.991°.
Index ranges	-24<=h<=24, -5<=k<=4, -23<=l<=23
Reflections collected	9643
Independent reflections	1681 [R(int) = 0.0892]
Completeness to theta = 23.991°	99.6 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1681 / 52 / 162
Goodness-of-fit on F^2	0.654
Final R indices [I>2sigma(I)]	R1 = 0.0337, wR2 = 0.0468
R indices (all data)	R1 = 0.0974, wR2 = 0.0549
Largest diff. peak and hole	0.660 and -0.796 $e.Å^{-3}$

Table 5. Bond lengths [Å] and angles [°] for 42.

Re(1)-O(3)	1.677(8)
Re(1)-O(2)	1.678(8)
Re(1)-O(1)	1.693(8)
Re(1)-O(4)	1.695(7)
N(1)-C(1)	1.343(10)
N(1)-C(5)	1.356(11)
N(1)-C(6)	1.465(11)
C(9)-C(6)#1	1.515(10)
C(9)-C(6)	1.515(10)
C(1)-C(2)	1.382(11)
C(1)-C(7)	1.495(12)
C(2)-C(3)	1.361(14)
C(5)-C(4)	1.379(13)
C(3)-C(4)	1.365(15)
C(3)-C(8)	1.512(12)
O(1A)-Re(1A)	1.690(9)
O(3A)-Re(1A)	1.673(8)
O(2A)-Re(1A)	1.678(8)
O(4A)-Re(1A)	1.691(8)

O(3)-Re(1)-O(2)	109.5(9)
O(3)-Re(1)-O(1)	108.2(10)
O(2)-Re(1)-O(1)	108.9(8)
O(3)-Re(1)-O(4)	107.3(10)
O(2)-Re(1)-O(4)	115.0(10)
O(1)-Re(1)-O(4)	107.8(9)
C(1)-N(1)-C(5)	121.5(9)
C(1)-N(1)-C(6)	121.7(9)
C(5)-N(1)-C(6)	116.5(9)
C(6)#1-C(9)-C(6)	113.5(11)
N(1)-C(1)-C(2)	118.0(9)
N(1)-C(1)-C(7)	121.3(9)
C(2)-C(1)-C(7)	120.7(10)
C(3)-C(2)-C(1)	121.5(10)
N(1)-C(5)-C(4)	120.5(10)
N(1)-C(6)-C(9)	110.2(7)
C(2)-C(3)-C(4)	119.5(11)
C(2)-C(3)-C(8)	120.7(12)
C(4)-C(3)-C(8)	119.7(12)
C(3)-C(4)-C(5)	118.9(11)
O(3A)-Re(1A)-O(2A)	110.5(13)
O(3A)-Re(1A)-O(1A)	108.1(14)
O(2A)-Re(1A)-O(1A)	107.6(12)
O(3A)-Re(1A)-O(4A)	111.5(16)
O(2A)-Re(1A)-O(4A)	111.3(14)
O(1A)-Re(1A)-O(4A)	107.7(15)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+1/2

Table 6. Torsion angles [°] for 42.

C(5)-N(1)-C(1)-C(2)	1.4(14)
C(6)-N(1)-C(1)-C(2)	175.3(8)
C(5)-N(1)-C(1)-C(7)	-179.7(9)
C(6)-N(1)-C(1)-C(7)	-5.8(14)
N(1)-C(1)-C(2)-C(3)	-4.4(14)

C(7)-C(1)-C(2)-C(3)	176.7(10)
C(1)-N(1)-C(5)-C(4)	0.5(15)
C(6)-N(1)-C(5)-C(4)	-173.7(8)
C(1)-N(1)-C(6)-C(9)	-92.7(10)
C(5)-N(1)-C(6)-C(9)	81.5(10)
C(6)#1-C(9)-C(6)-N(1)	178.1(9)
C(1)-C(2)-C(3)-C(4)	5.4(16)
C(1)-C(2)-C(3)-C(8)	-179.3(8)
C(2)-C(3)-C(4)-C(5)	-3.3(16)
C(8)-C(3)-C(4)-C(5)	-178.7(9)
N(1)-C(5)-C(4)-C(3)	0.4(15)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+1/2

When deciphering the structure of **42** it was revealed that the anion ReO4 is disordered, which resulted in a sharp drop in the intensity of the diffraction.

Although the experiment was recorded up to 27 Θ°, only reflections with a diffraction angle of no more than 22° were used to refine the molecular parameters (resolution 0.99).

Based on the analysis of variance for reflections employed in refinement from the Table 7 (shelx.lst) and the graph of the dependence of F2/sigma(F2) versus, Sin(Θ)/λ (Fig. S10) the refinement was carried out with a resolution of 0.84Å.

Analysis of variance for reflections employed in refinemen.

Table 7. Data for 42.

Resolution(A)	0.78	0.81	0.84	0.88	0.93	0.98	1.06	1.17	1.34	1.67
Number in group	243	230	234	235	232	232	233	230	234	234
R1	0.52	0.47	0.41	0.33	0.25	0.17	0.11	0.07	0.04	0.021

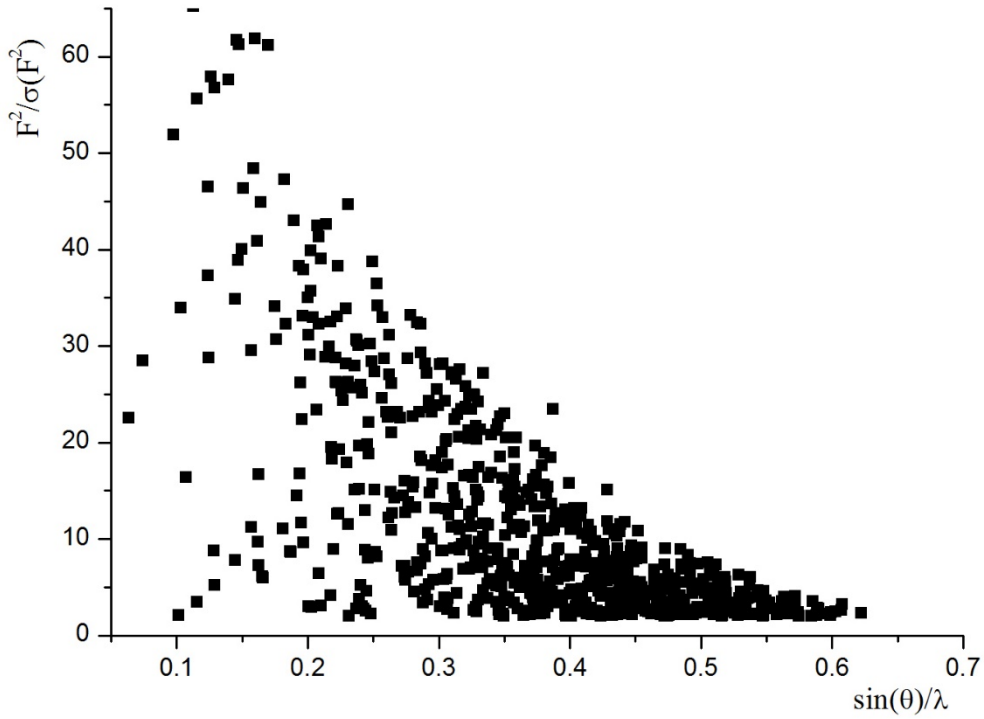


Fig. S10. Graph of the dependence of F2/sigma(F2) versus, Sin(Θ)/λ for **42**.

CCDC 2497803 for (**41**) and 2467578 for (**42**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge CrystallographicData Centre via www.ccdc.cam.ac.uk/data_request/cif.

Liquid extraction (general procedure). The organic and aqueous phases of equal volumes (0.5 ml) were contacted for 30 minutes on a Multi-Vortex V-32 shaker (BioSan, Latvia) in 1.5 ml polypropylene tubes. Extraction was performed at a temperature of 25 ± 1 °C in a TSO-1/80 SPU dry-air cooling thermostat (Russia). The phases were separated on a Centrifuge 5418 centrifuge (Eppendorf, Austria), then 400 µl of the aqueous phase was taken for further analysis by liquid scintillation spectroscopy. The organic phase contained 0.1 mol/l of tetran-n-octylamide of diglycolic acid in meta-nitrobenzotrifluoride or 30% vol. of tri-n-butyl phosphate in kerosene. The aqueous phase contained a label of the pertechnetate anion with an activity of 40 kBq/l, as well as 3 mol/l of nitric acid and 0.1 mol/l of a water-soluble ligand.

The distribution coefficient was calculated using the following formula:

$$D = \frac{C_{org}}{C_{wtr}} = \frac{C_0 - C_{wtr}}{C_{wtr}},$$

where C_0 – is the initial concentration of the pertechnetate anion in solution, C_{wtr} – концентрация в водной фазе после экстракции, C_{org} – concentration in the organic phase after extraction.

To determine the effectiveness of suppression of pertechnetate anion extraction, the suppression coefficient (K) was calculated, which characterizes how many times the technetium distribution coefficient decreases with the introduction of a water-soluble ligand compared with a system without a ligand.

Liquid scintillation spectroscopy. To quantify the pertechnetate anion, 3 ml of UltimaGold scintillator (PerkinElmer, USA) was added to 400 µl of the sample, measured on a Tri-Carb 2810 TR spectrometer (PerkinElmer, USA), the registration time was 30 minutes. In the case of the TBP/kerosene system, the content of pertechnetate in both the organic and aqueous phases was determined after extraction, whereas for the TODGA/F-3 system, only the aqueous phase was measured due to strong quenching caused by meta-nitrobenzotrifluoride, and the concentration of pertechnetate in the organic phase was determined as the difference between its concentration in the initial solution and in the aqueous phase after extraction.

References

[1] Walden P., Birr E. J., *Z. physik. Chem.*, **1929**, 144A, 269

[2] Nikolai A. Tcyrulnikov, Ramkumar Varadharajan, Anastasiia A. Tikhomirova, Mahesh Pattabiraman, Vaidhyanathan Ramamurthy and R. Marshall Wilson, Modulation of Reduction Potentials of Bis(pyridinium)alkane Dications through Encapsulation within Cucurbit[7]uril J. Org. Chem. 2019, 84, 8759−8765. DOI: 10.1021/acs.joc.9b01049

[3] Jui-Cheng Changa, Wen-Yueh Hob, I-Wen Suna, Yu-Kai Choub, Hsin-Hsiu Hsiehb, Tzi-Yi Wu, Synthesis and properties of new tetrachlorocobaltate (II) and tetrachloromanganate (II) anion salts with dicationic counterions Polyhedron 30 (2011) 497–507, doi:10.1016/j.poly.2010.11.009

[4] Perdew, J. P.; Burke, K.; Ernzerhof, M. Phys. Rev. Lett. 1996, 77, 3865−3868.

[5] Dyall, K. G. J. Chem. Phys. 1994, 100, 2118−2127.

[6] Laikov, D. N. A new class of atomic basis functions for accurate electronic structure calculations of molecules. *Chem. Phys. Lett*. 2005, 416, 116−120.

[7] Laikov, D. N. Atomic Basis Functions for Molecular Electronic Structure Calculations. *Theor. Chem. Acc*. 2019, 138, 40.

[8] Laikov, D. N. Optimization of atomic density-fitting basis functions for molecular two-electron integral approximations. *J. Chem. Phys*. 2020, 153, 114121.

[9] Hirshfeld, F.L. Bonded-Atom Fragments for Describing Molecular Charge Densities. *Theoret. Chim. Acta (Berl.)* 1977, 44, 129-138.

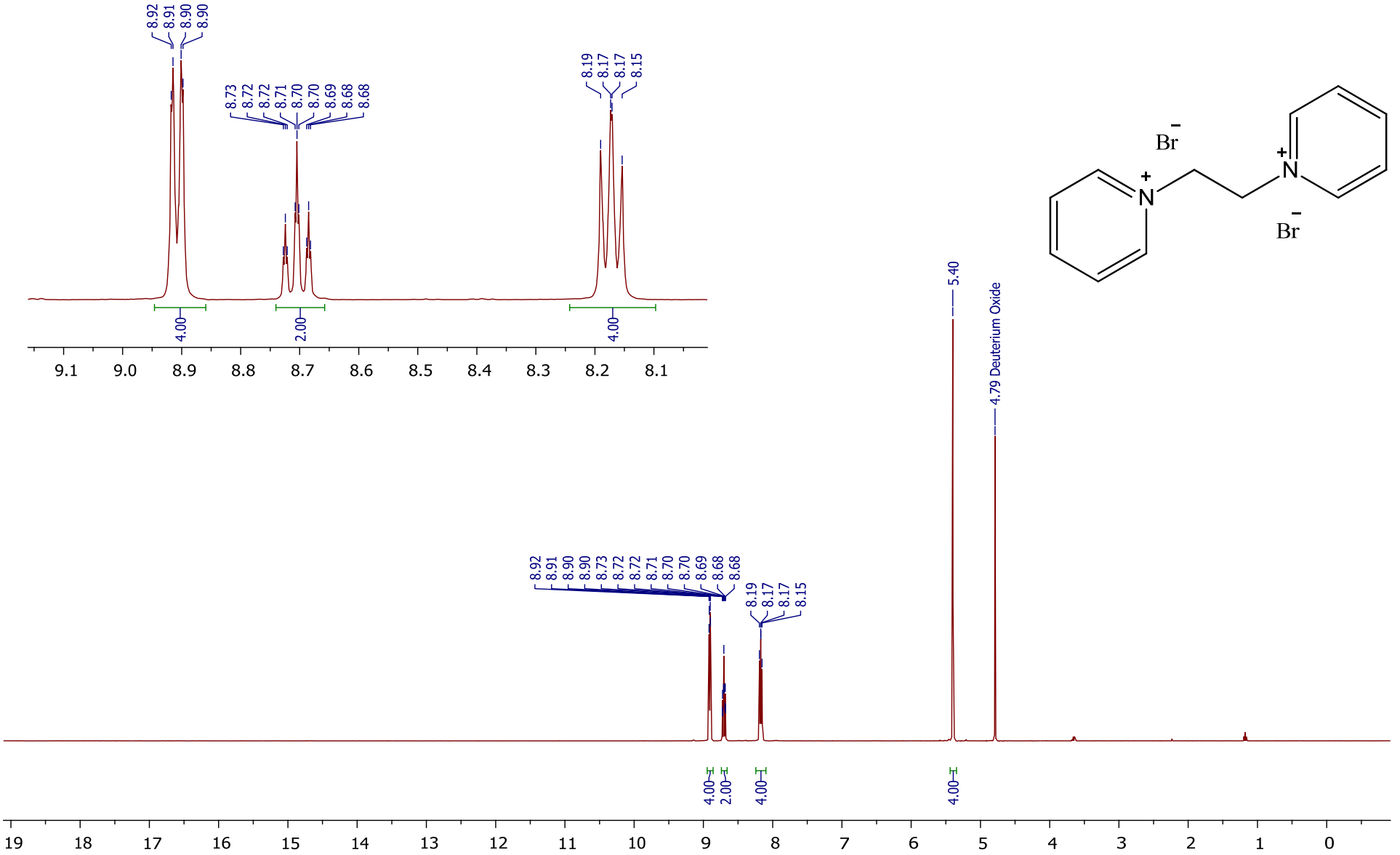
[10] Bader, R.W.F. *Atoms in Molecules: A Quantum Theory*; Oxford University Press: Oxford, UK, 1990.

[11] Laikov, D. N.; Ustynyuk, Yu. A. Russ. Chem. Bull., Int. Ed. 2005, 54, 820−826.

[12] Sheldrick, G. M. Acta Crystallogr. 2008, A64, 112-122.

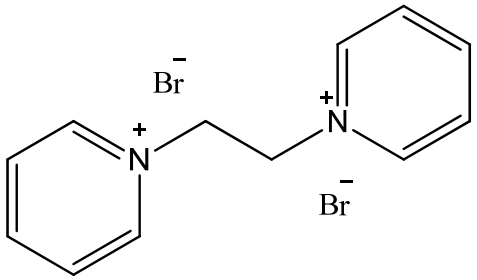
[13] Brandenburg, K. DIAMOND, Release 2.1d; Crystal Impact GbR: Bonn, Germany, 2000.

JIK-008.H



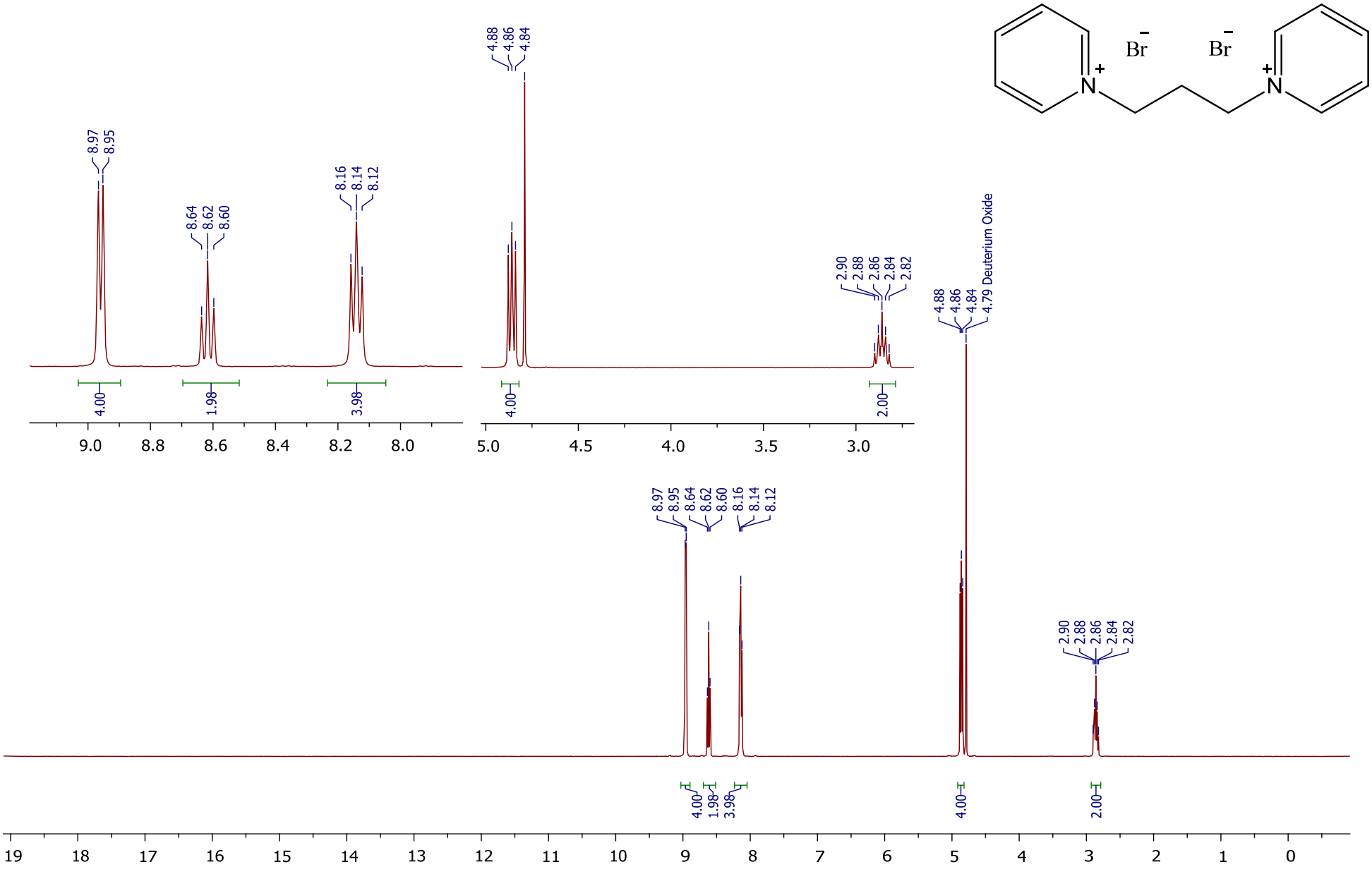
^{1}H NMR spectrum of **13a** in D_2O

JIL-008.C



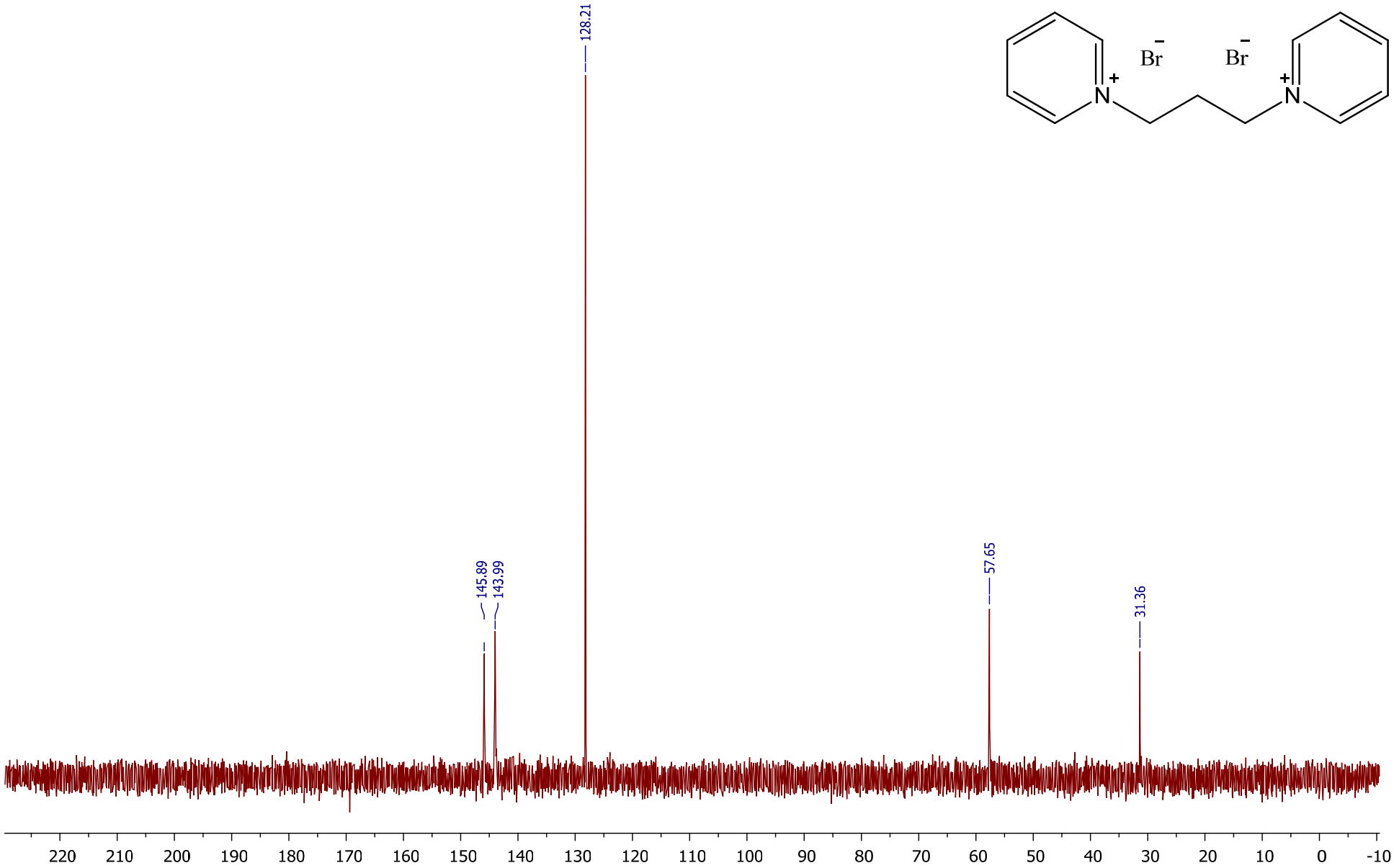
^{13}C NMR spectrum of **13a** in D_2O

JIK-015.H



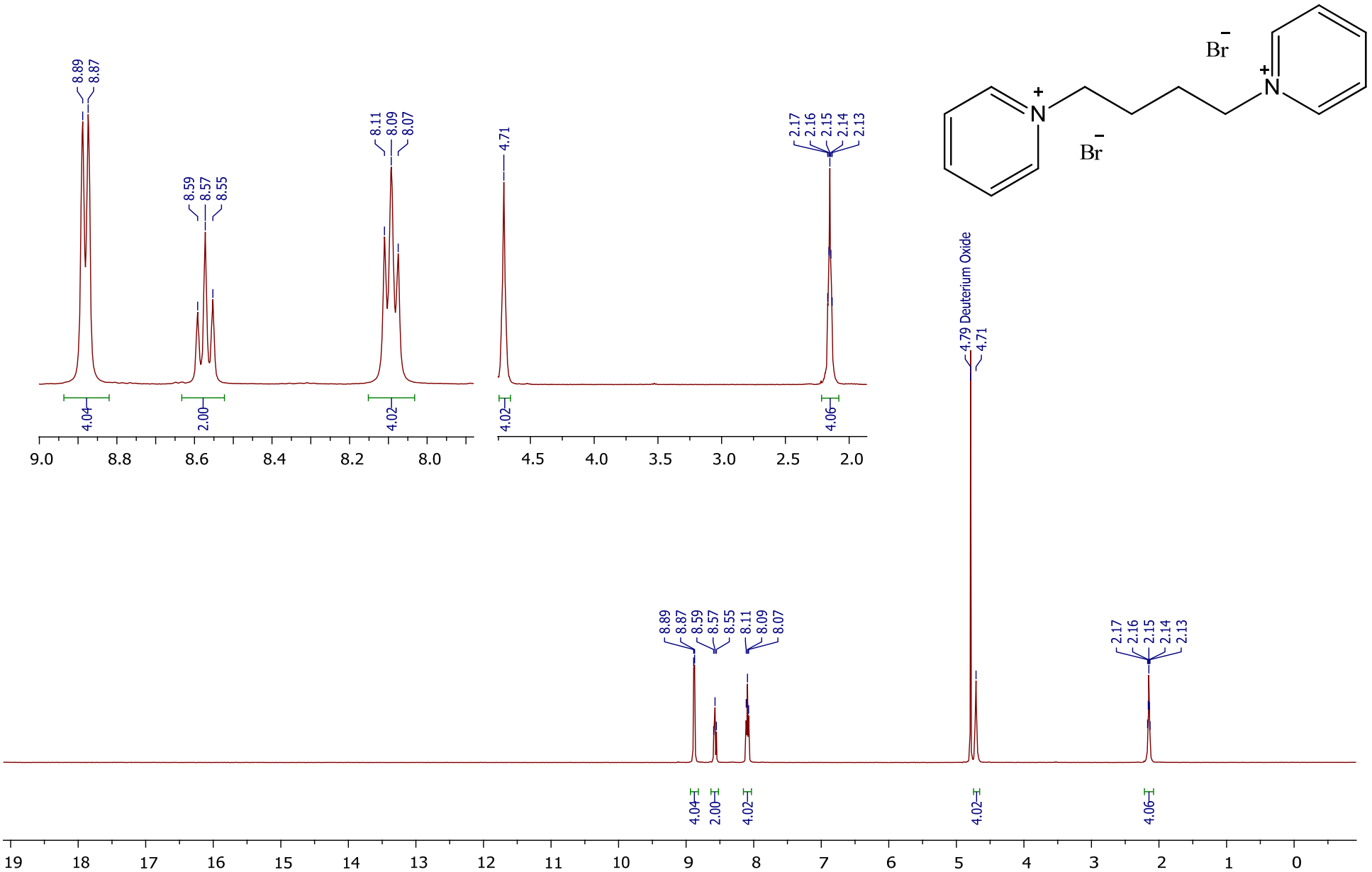
^{1}H NMR spectrum of **13b** in D_2O

JIK-015.C



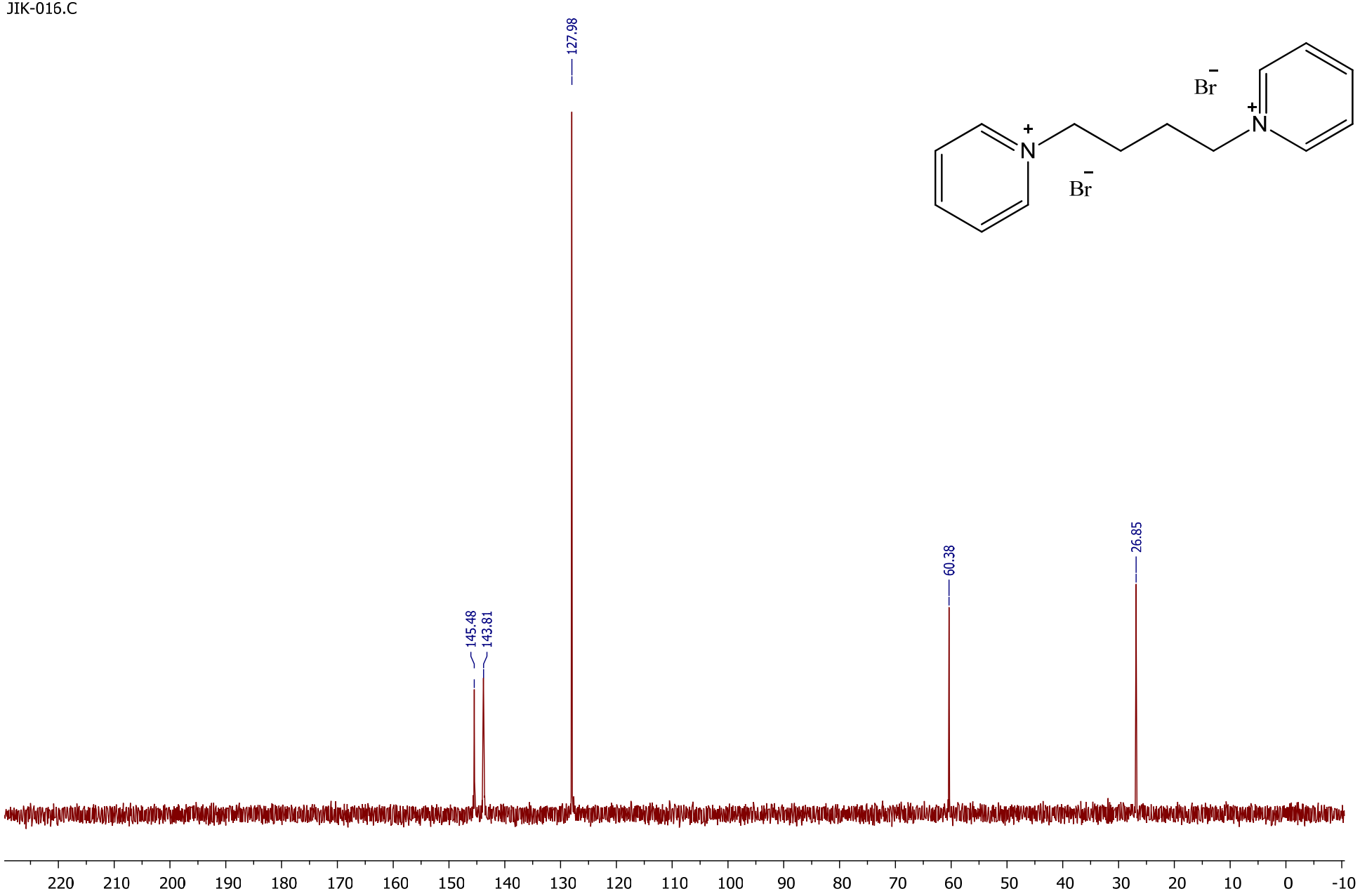
^{13}C NMR spectrum of **13b** in D_2O

JIK-016.H

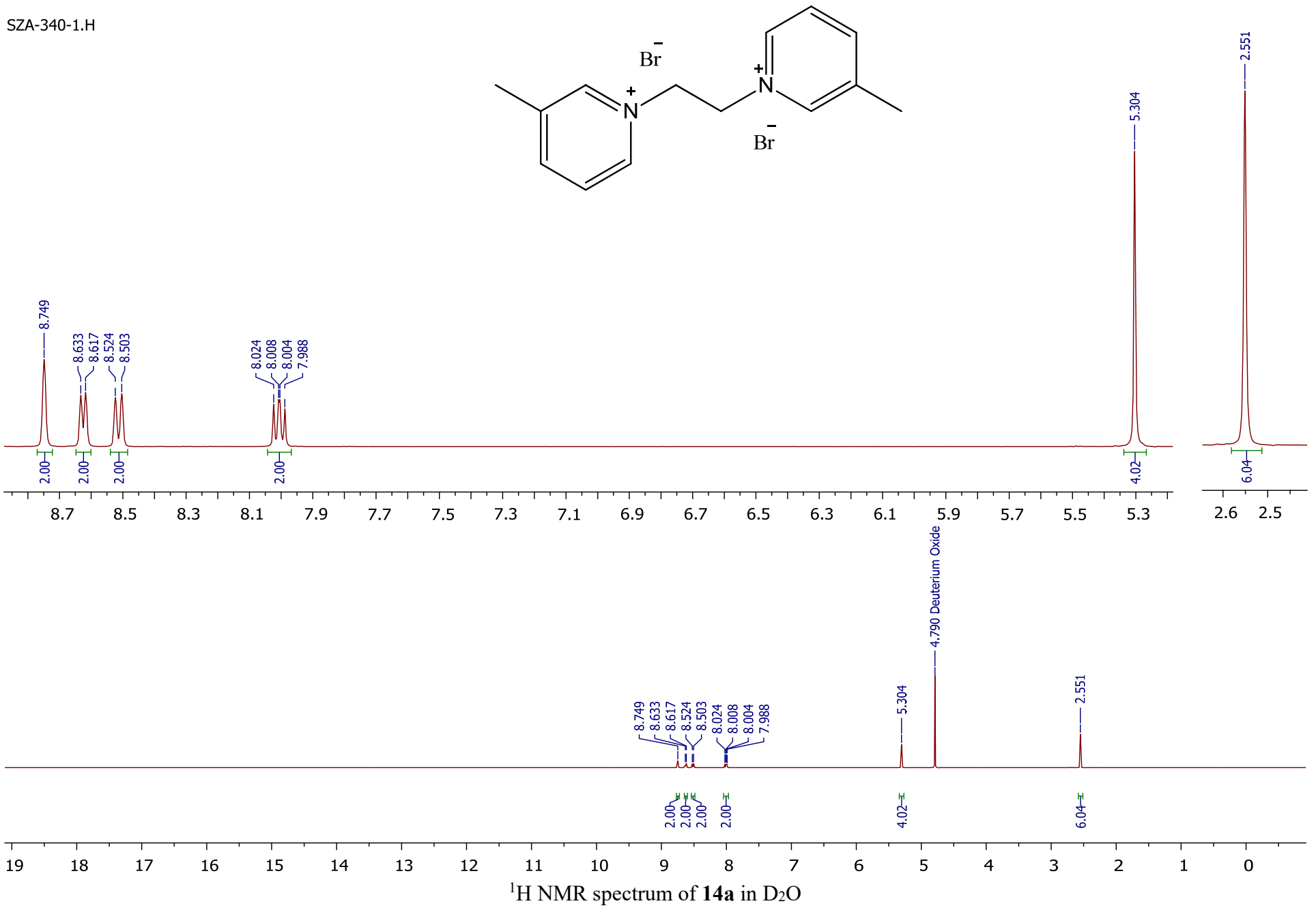


^{1}H NMR spectrum of **13c** in D_2O

JIK-016.C

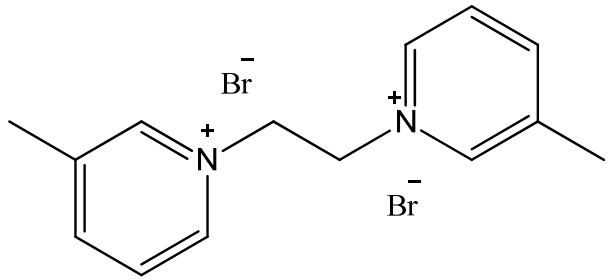


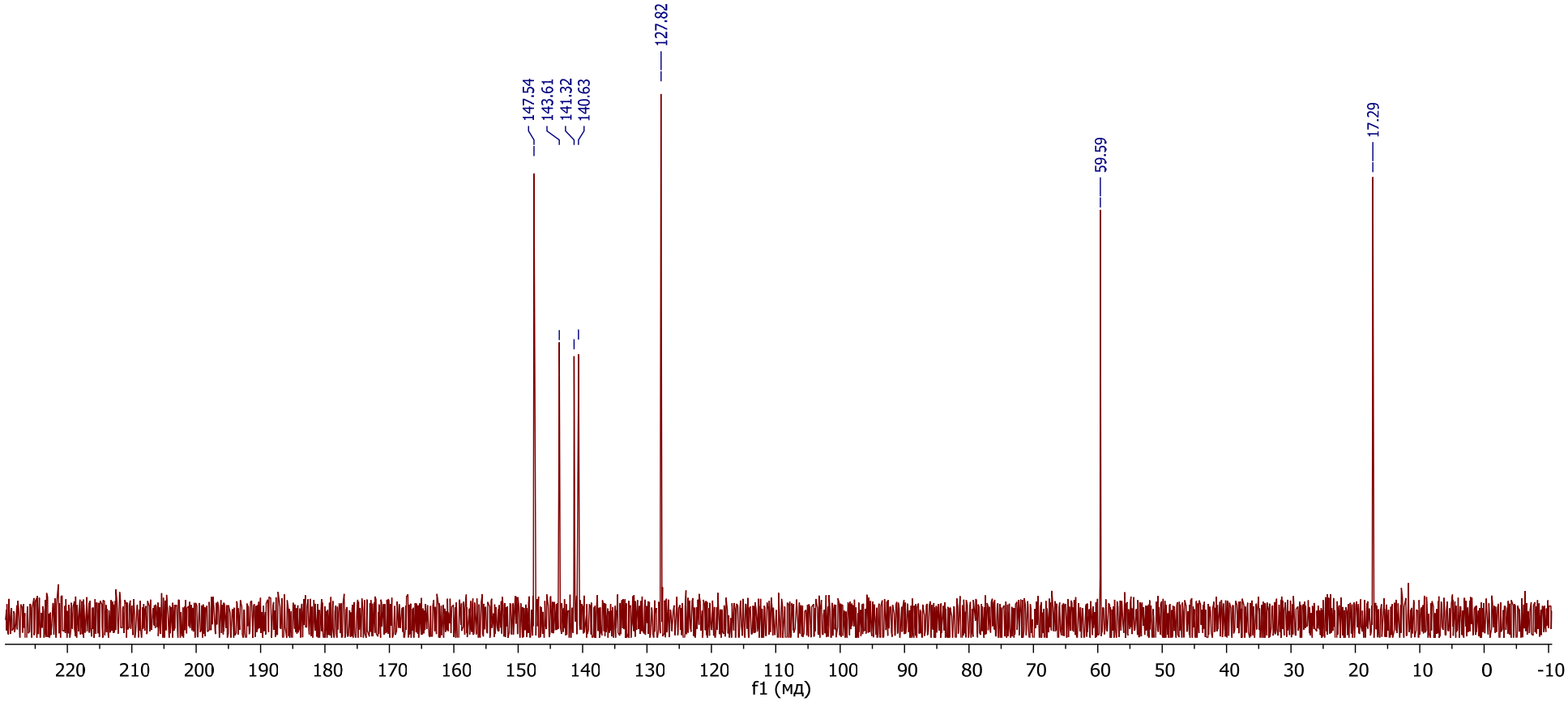
^{13}C NMR spectrum of **13c** in D_2O



^{1}H NMR spectrum of **14a** in D_2O

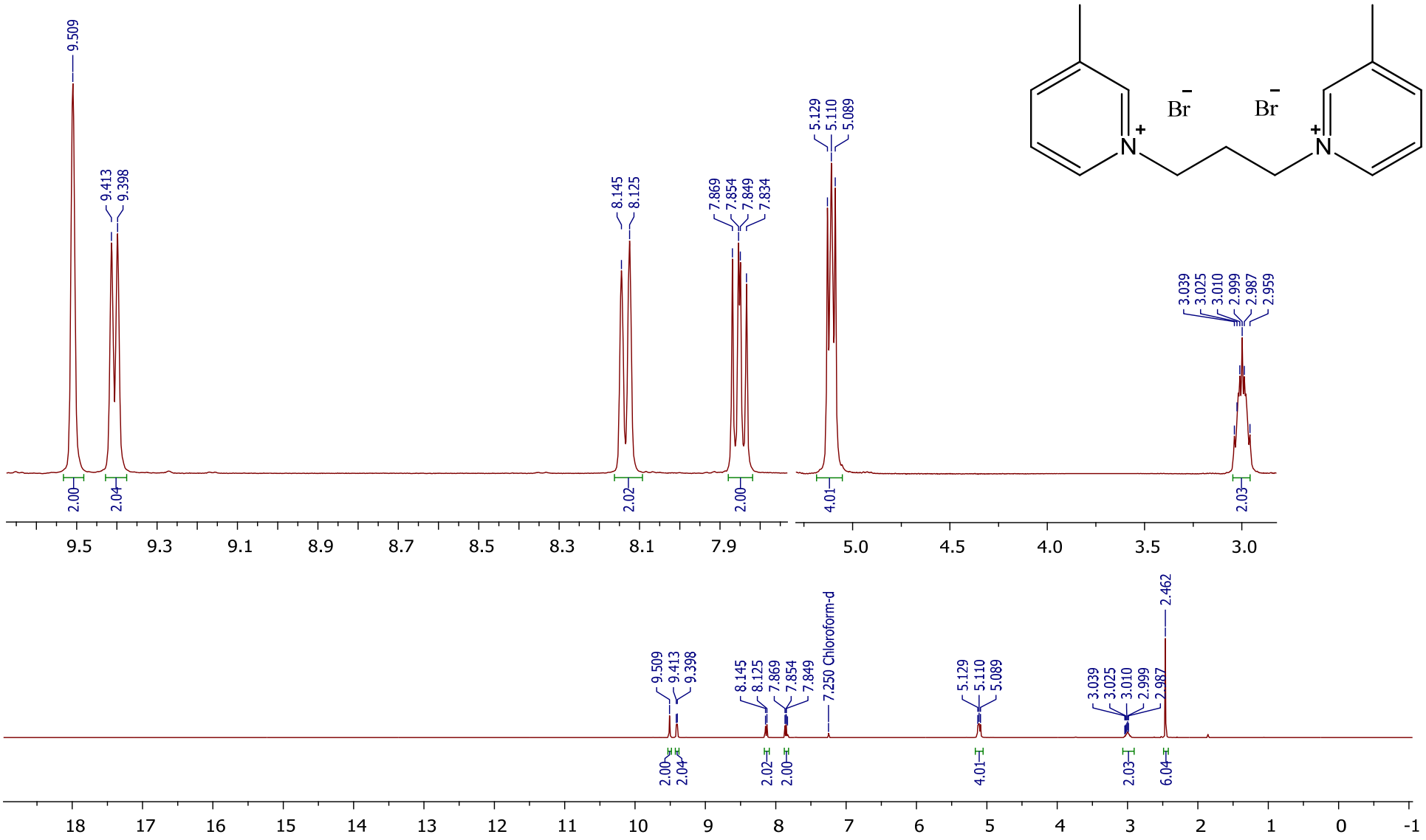
SZA-340-1.C



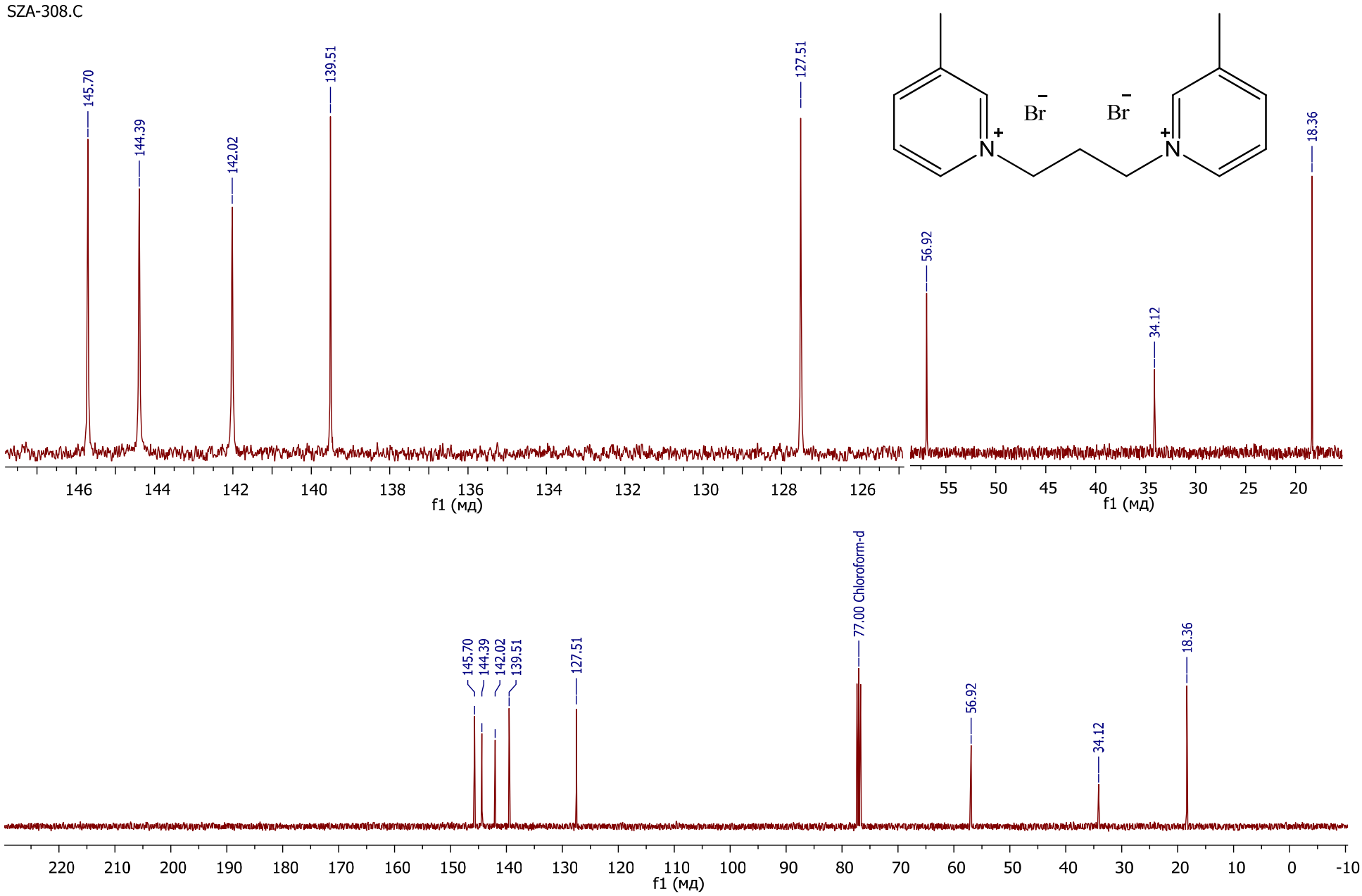


^{13}C NMR spectrum of **14a** in D_2O

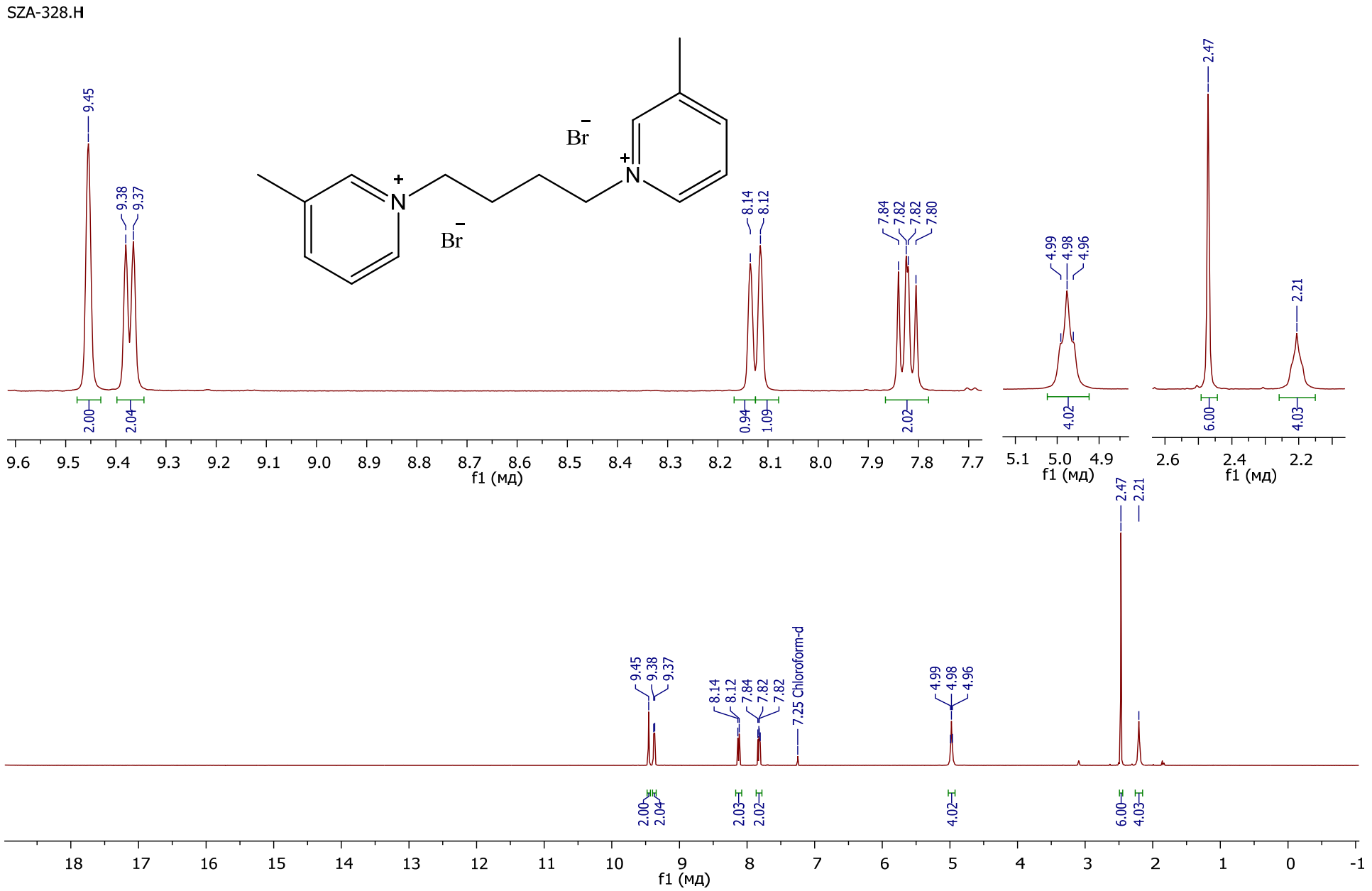
SZA-308.H



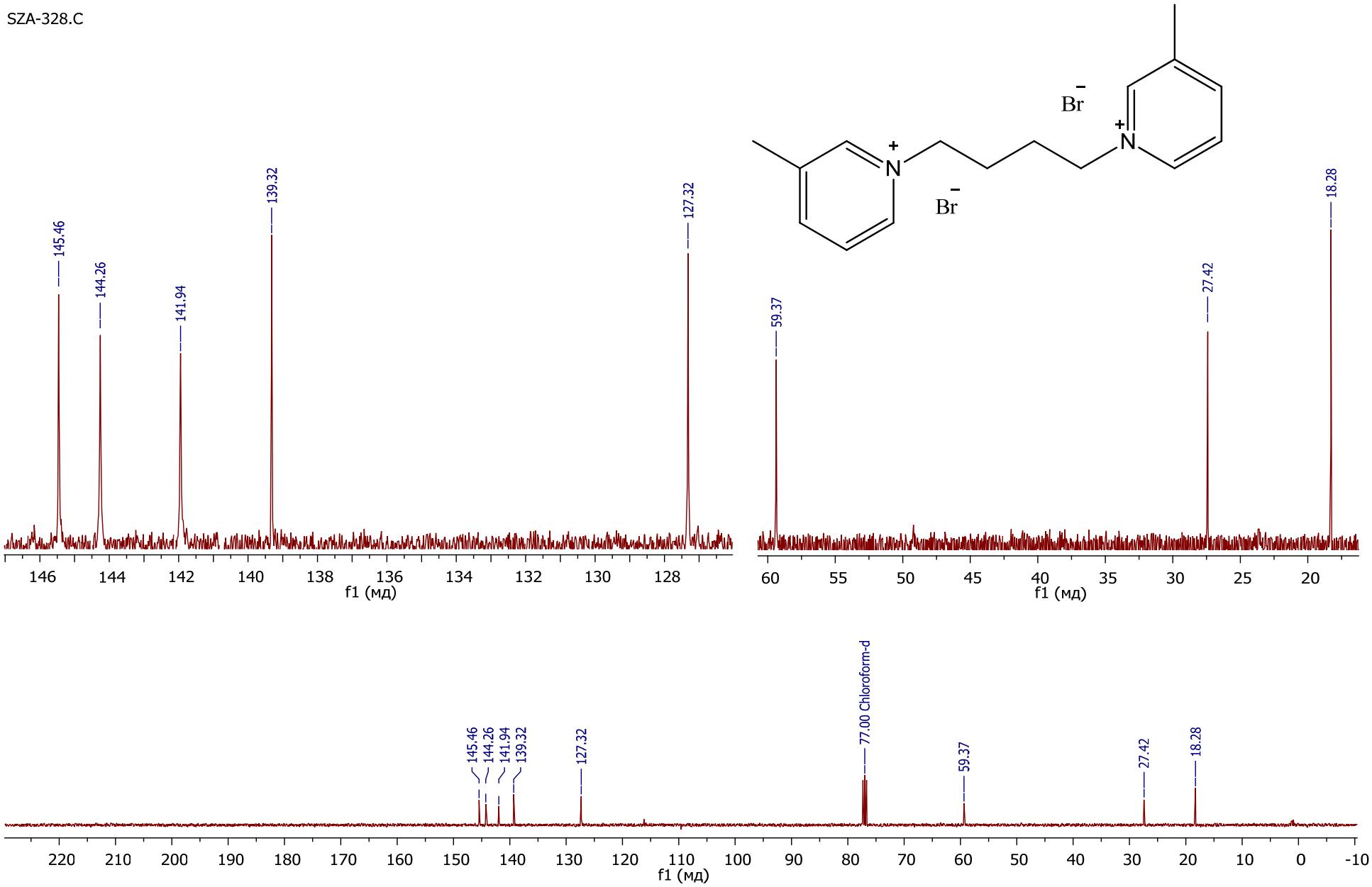
^{1}H NMR spectrum of **14b** in $CDCl_3$



^{13}C NMR spectrum of **14b** in $CDCl_3$

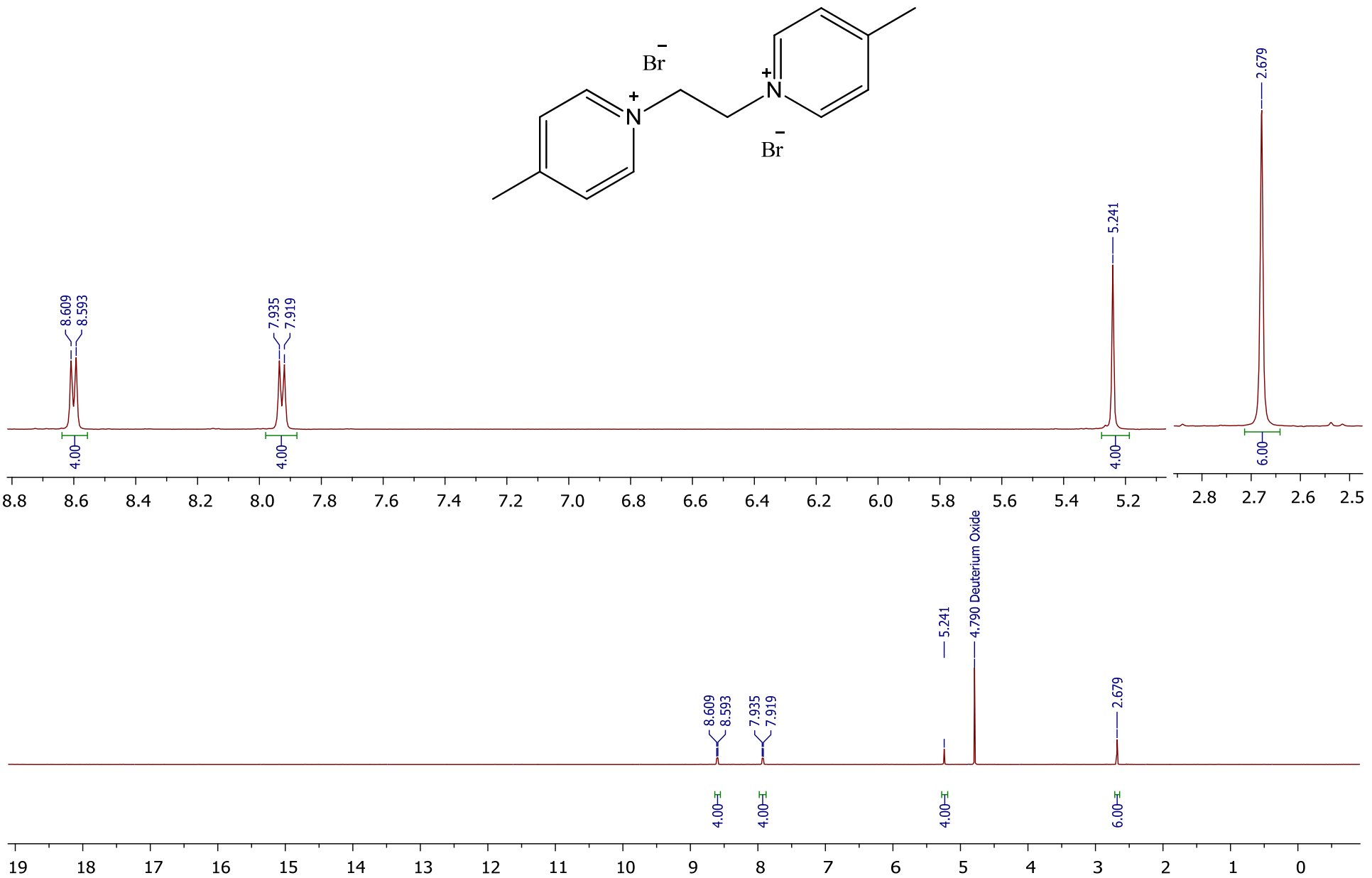


^{1}H NMR spectrum of **14c** in $CDCl_3$



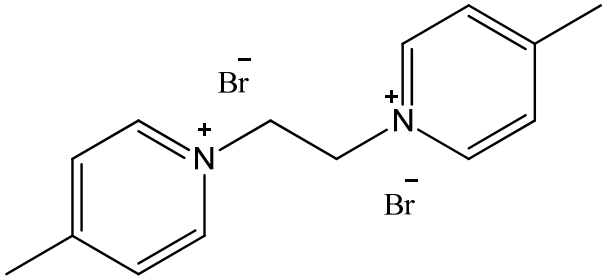
^{13}C NMR spectrum of **14c** in $CDCl_3$

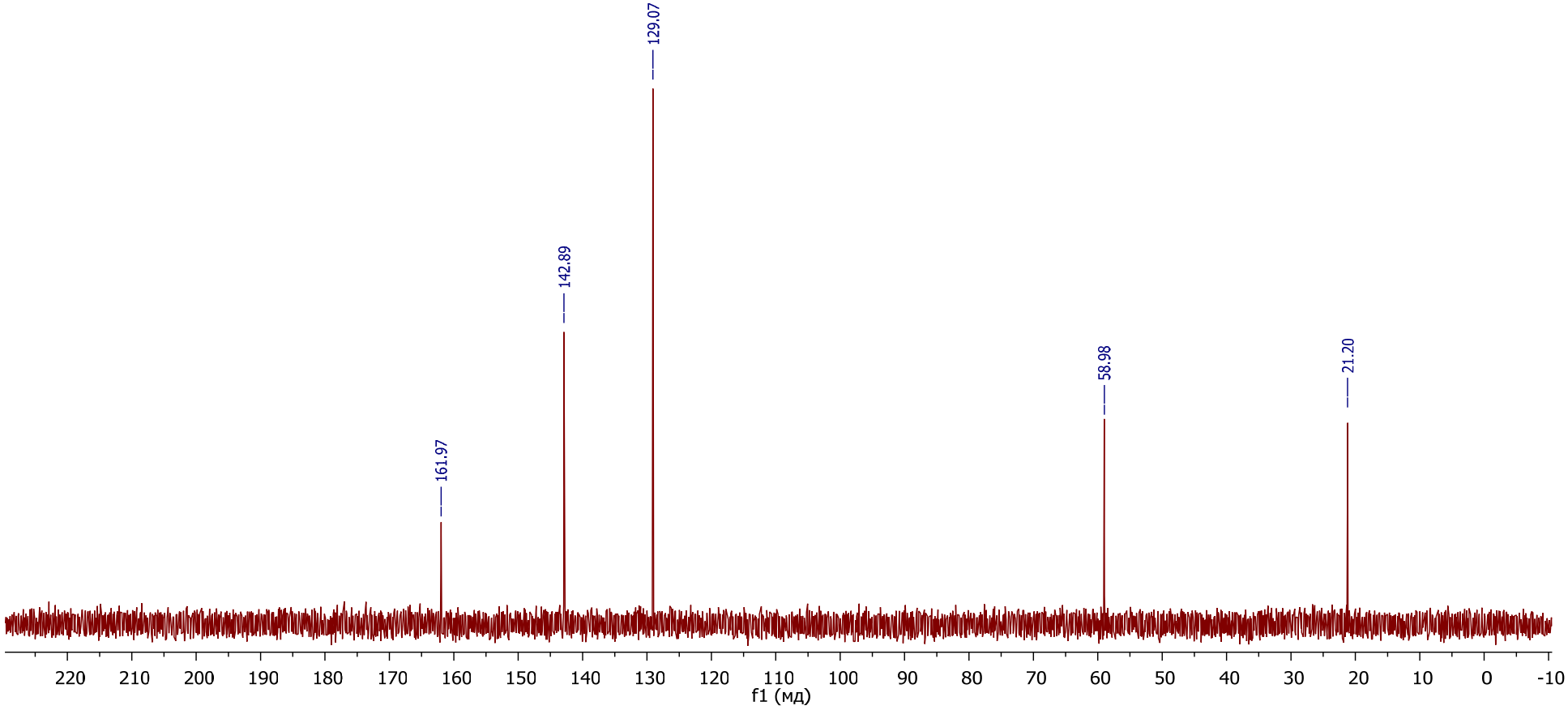
SZA-339-1.H



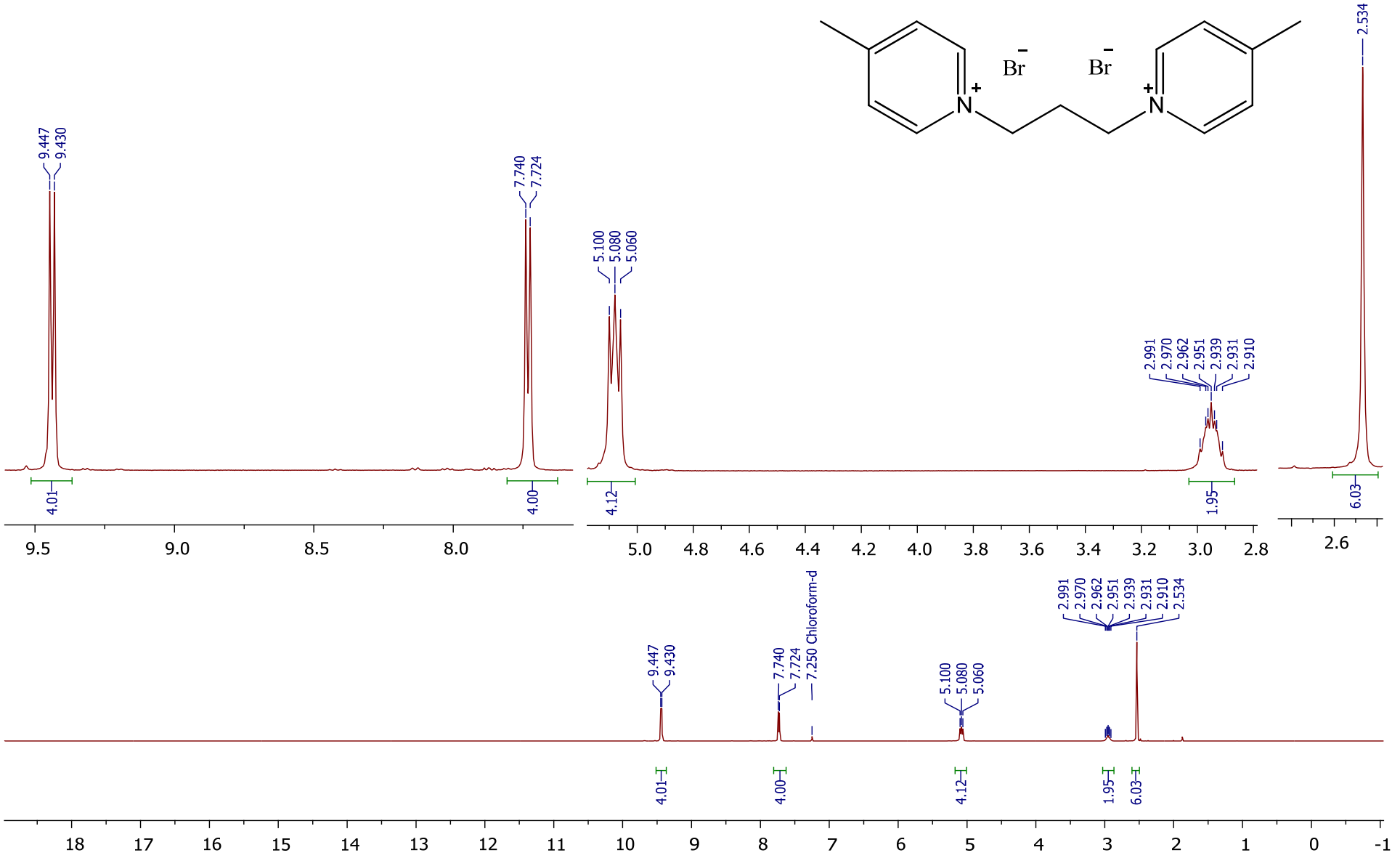
^{1}H NMR spectrum of **15a** in D_2O

SZA-339-1.C



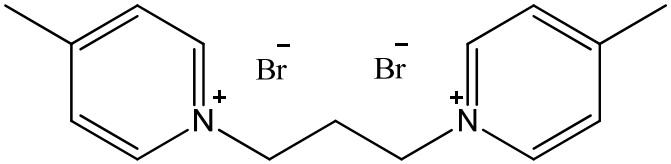


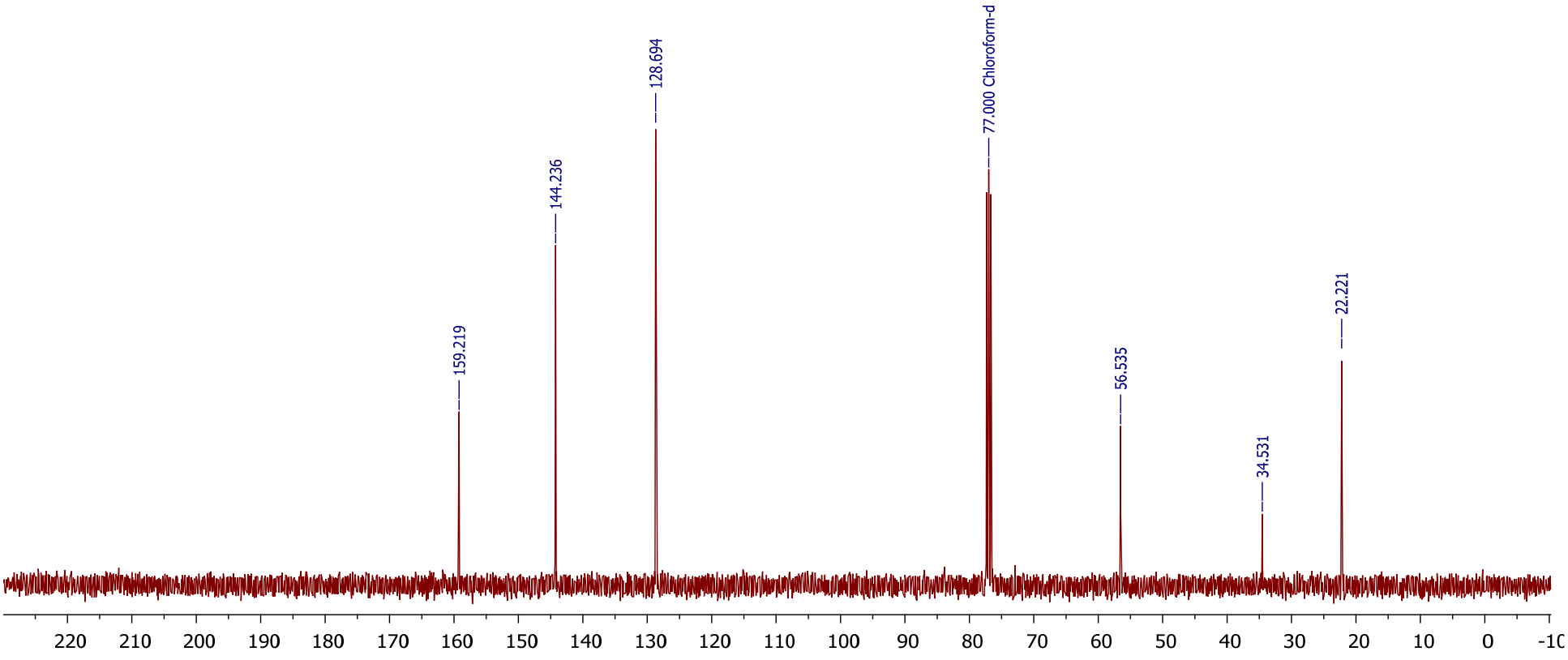
^{13}C NMR spectrum of **15a** in D_2O



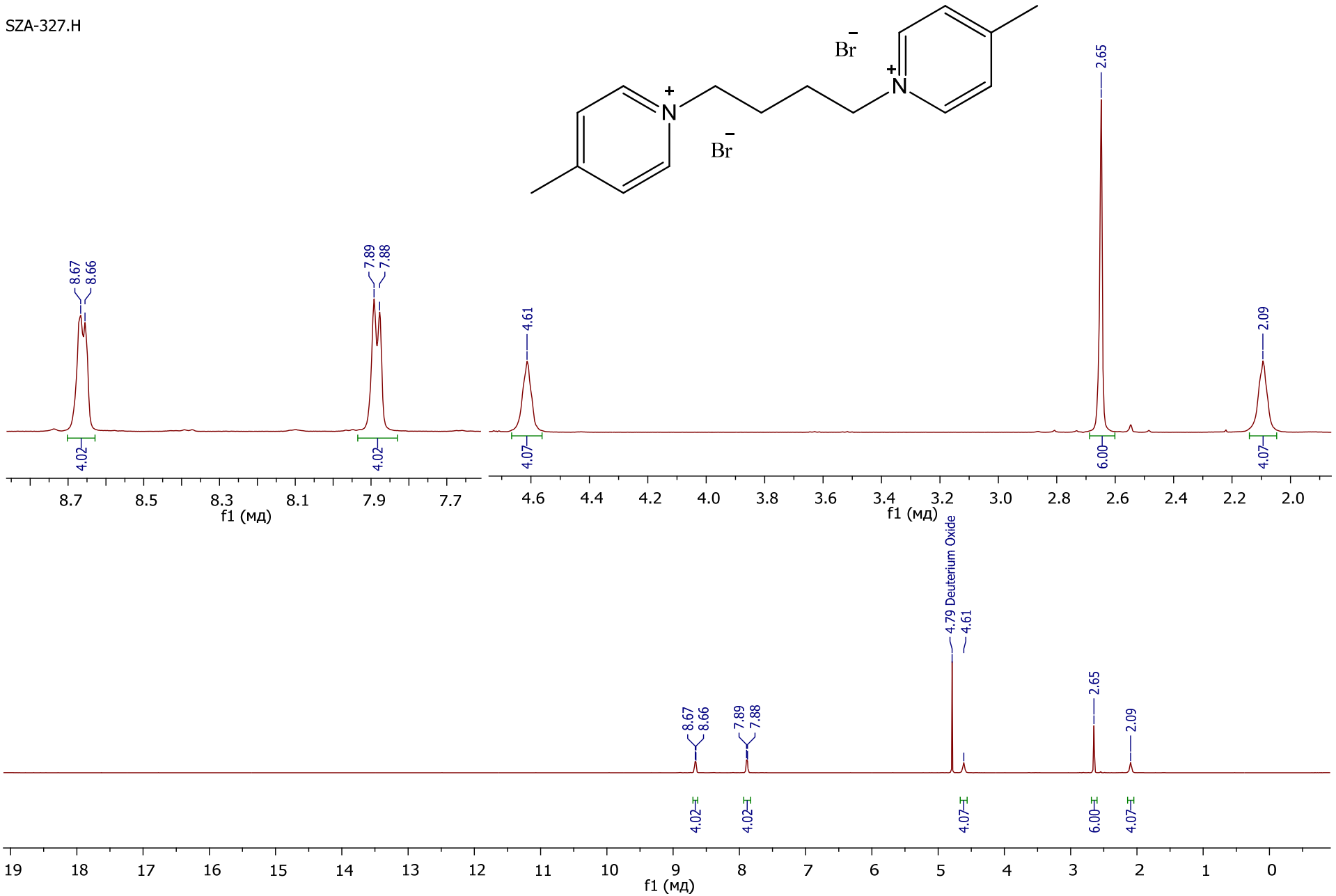
^{1}H NMR spectrum of **15b** in $CDCl_3$

SZA-303.C

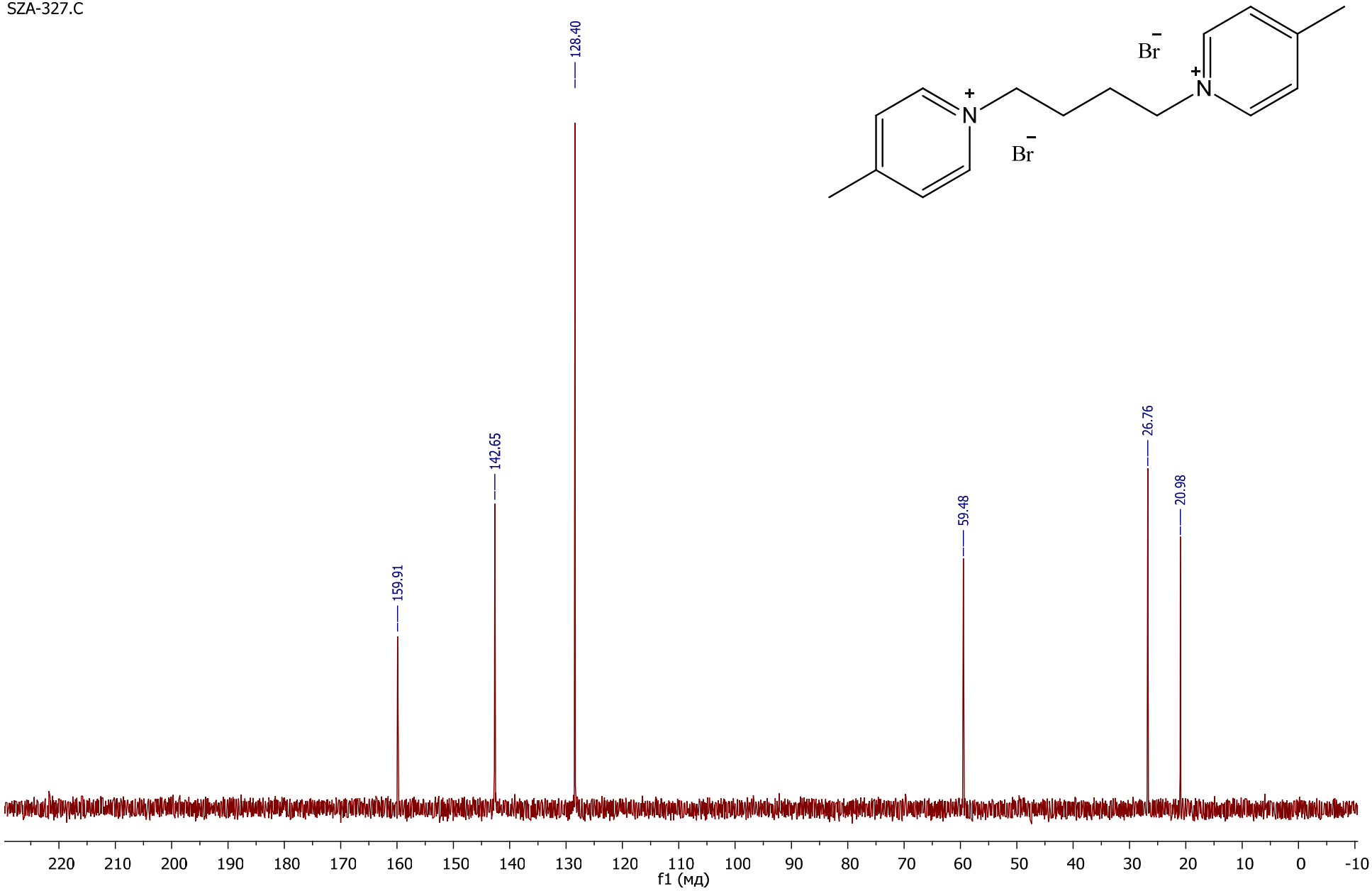




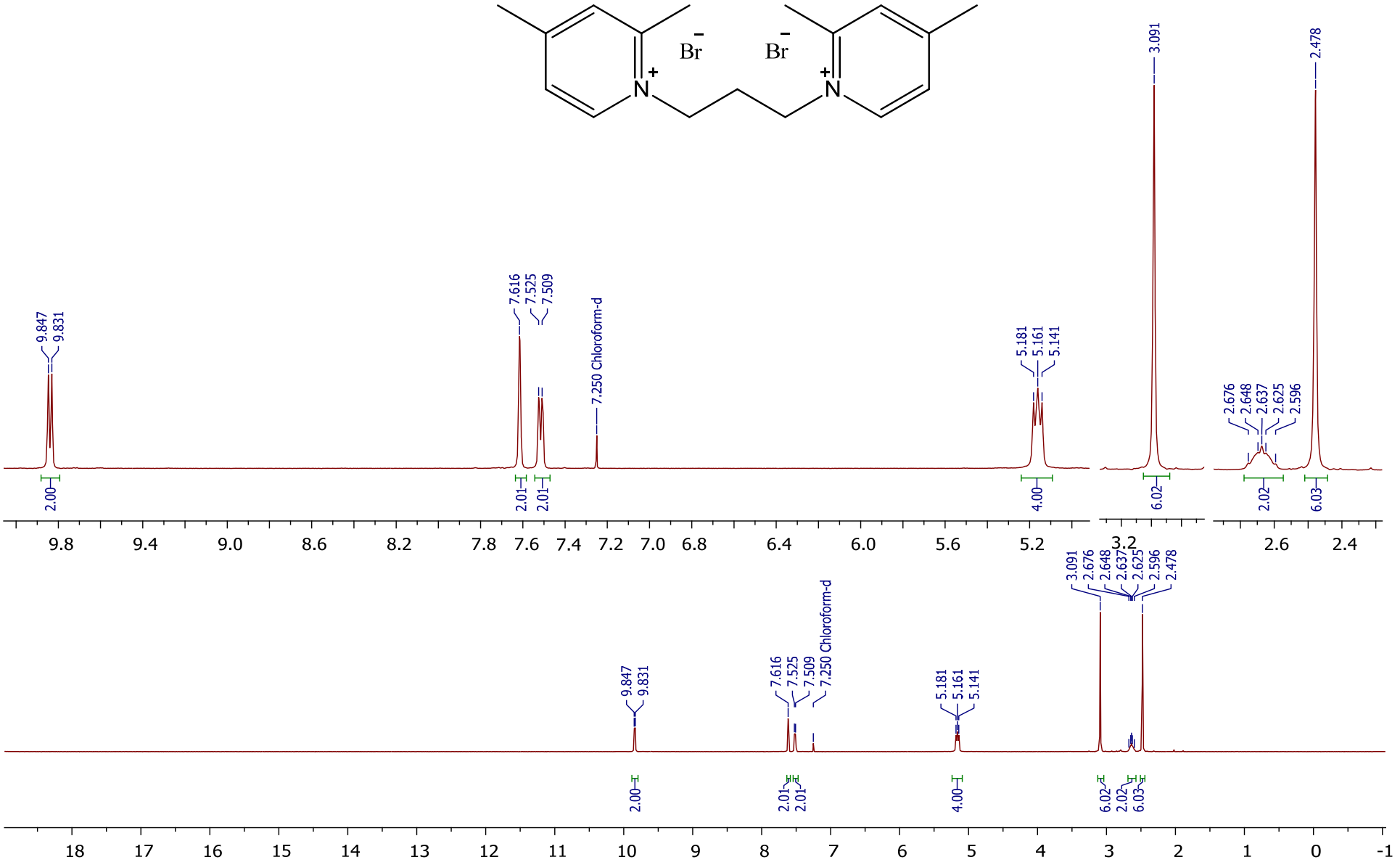
^{13}C NMR spectrum of **15b** in $CDCl_3$



^{1}H NMR spectrum of **15c** in D_2O

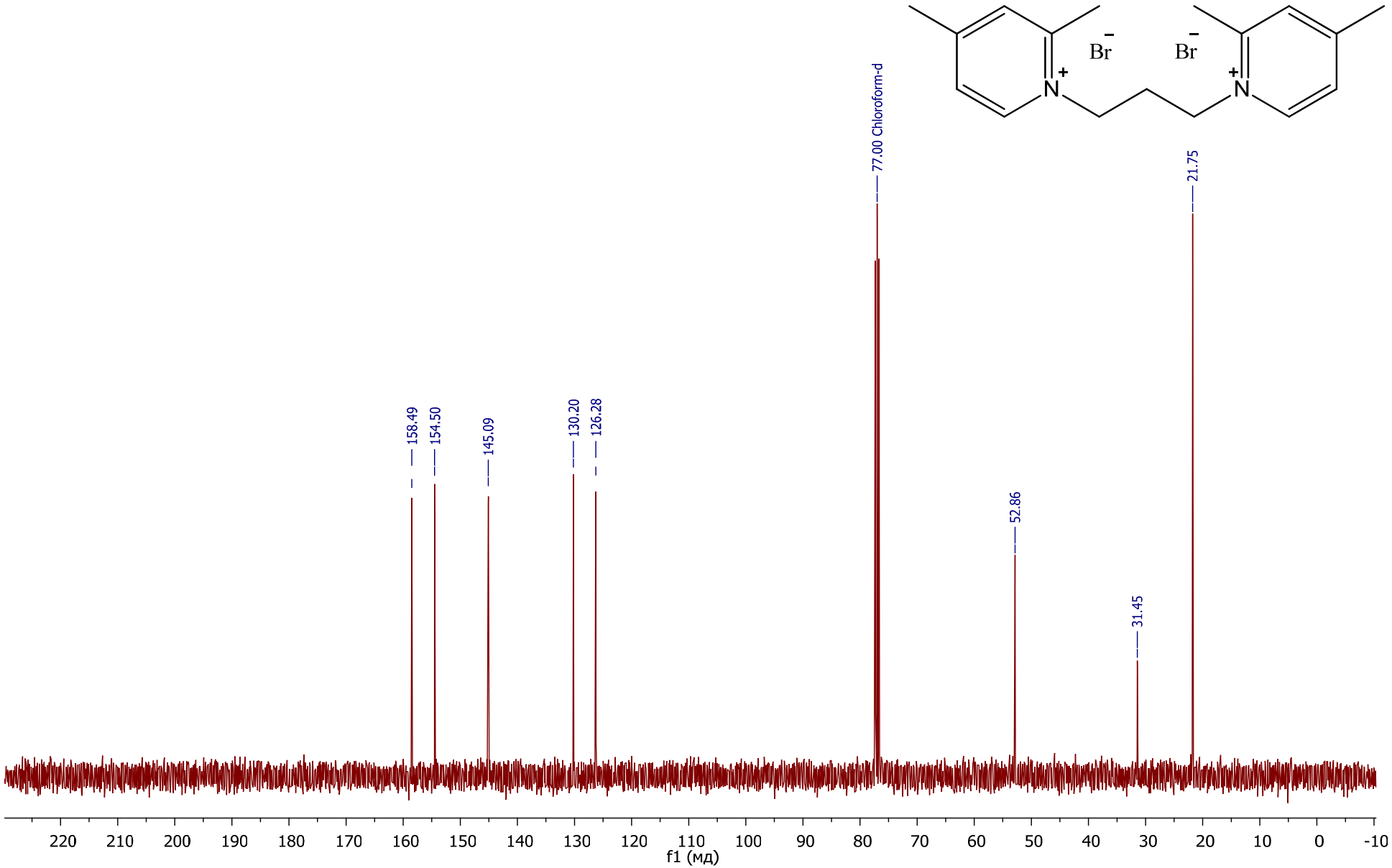


^{13}C NMR spectrum of **15c** in D_2O

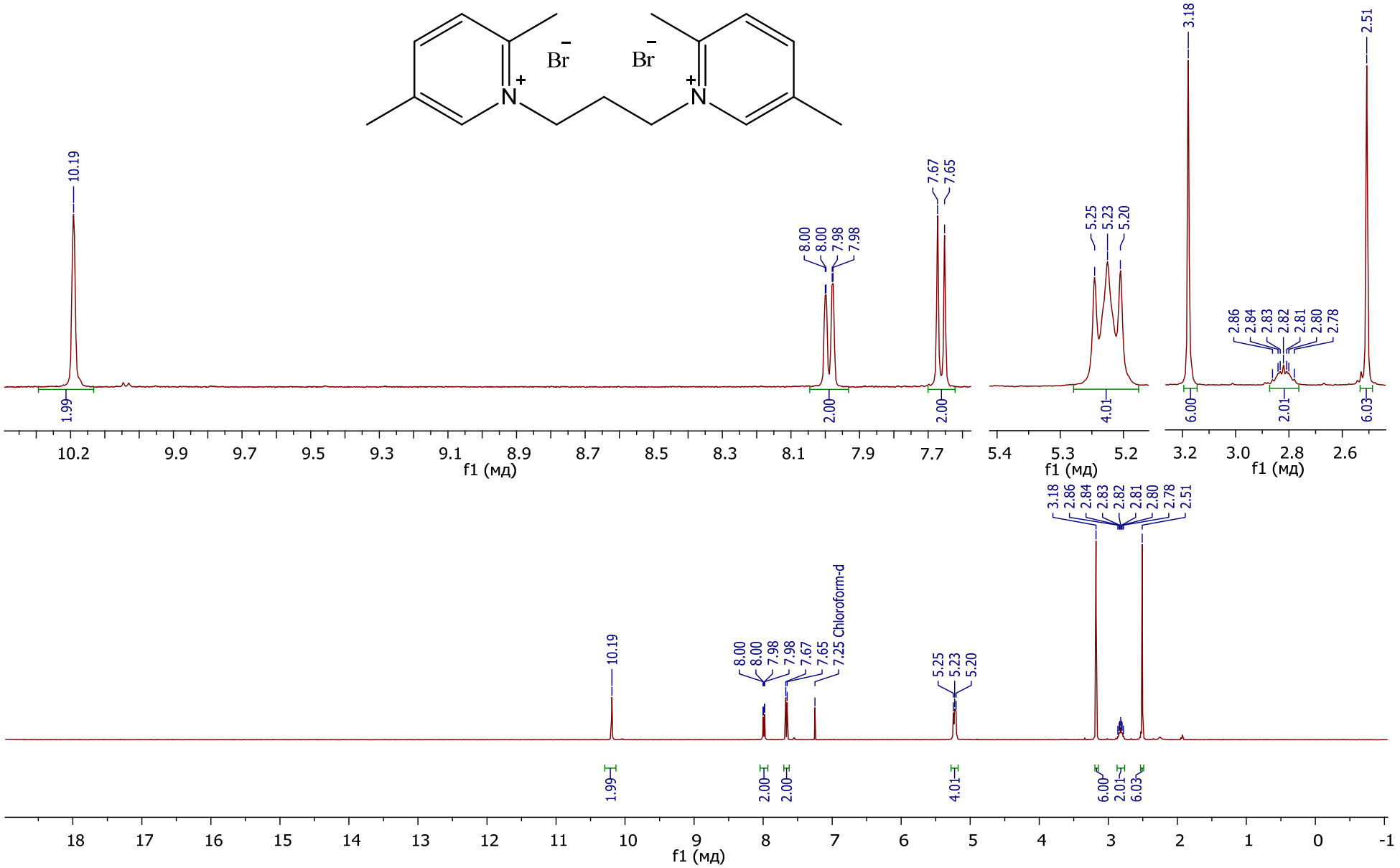


^{1}H NMR spectrum of **16b** in $CDCl_3$

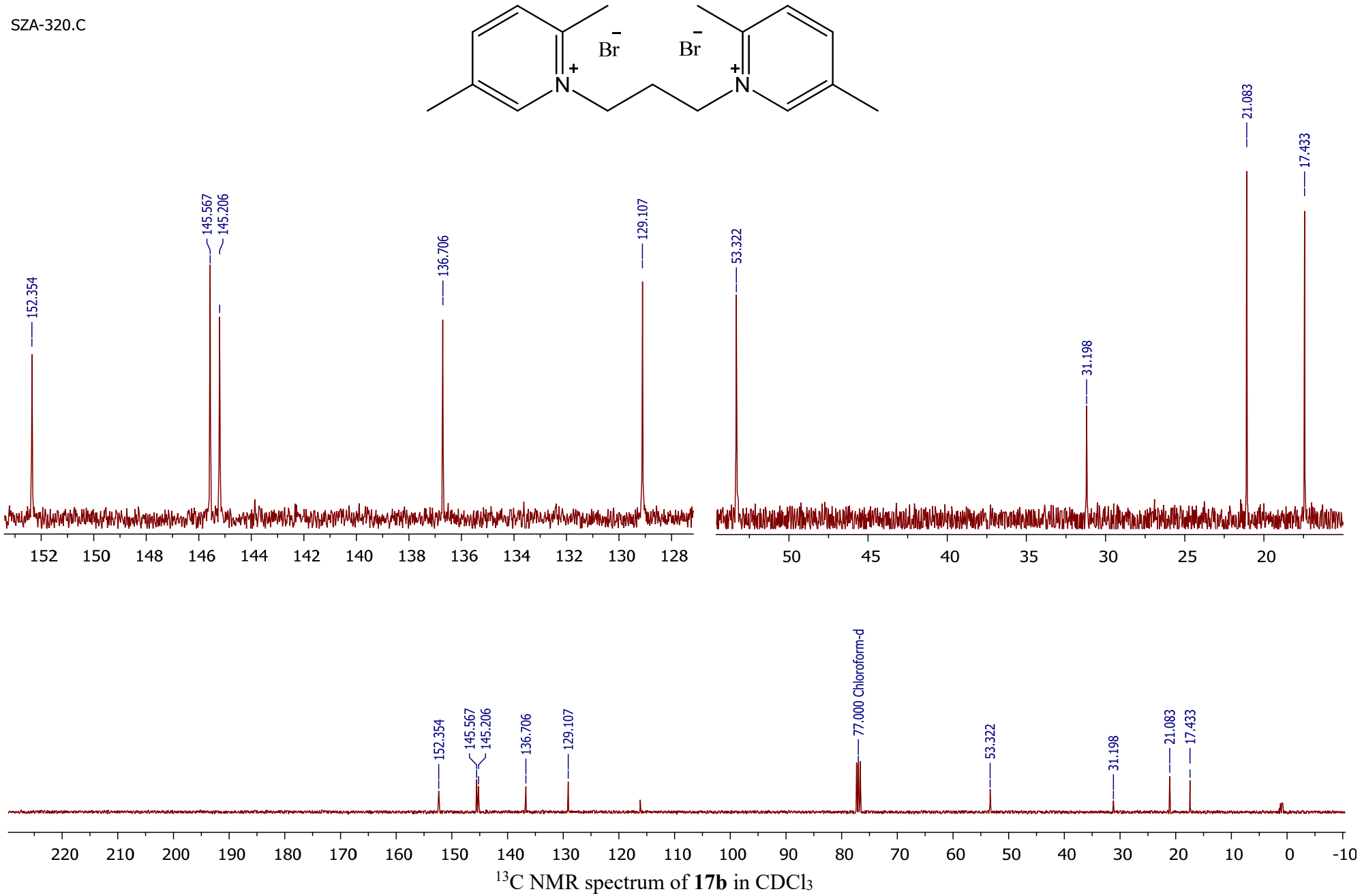
SZA-309.C



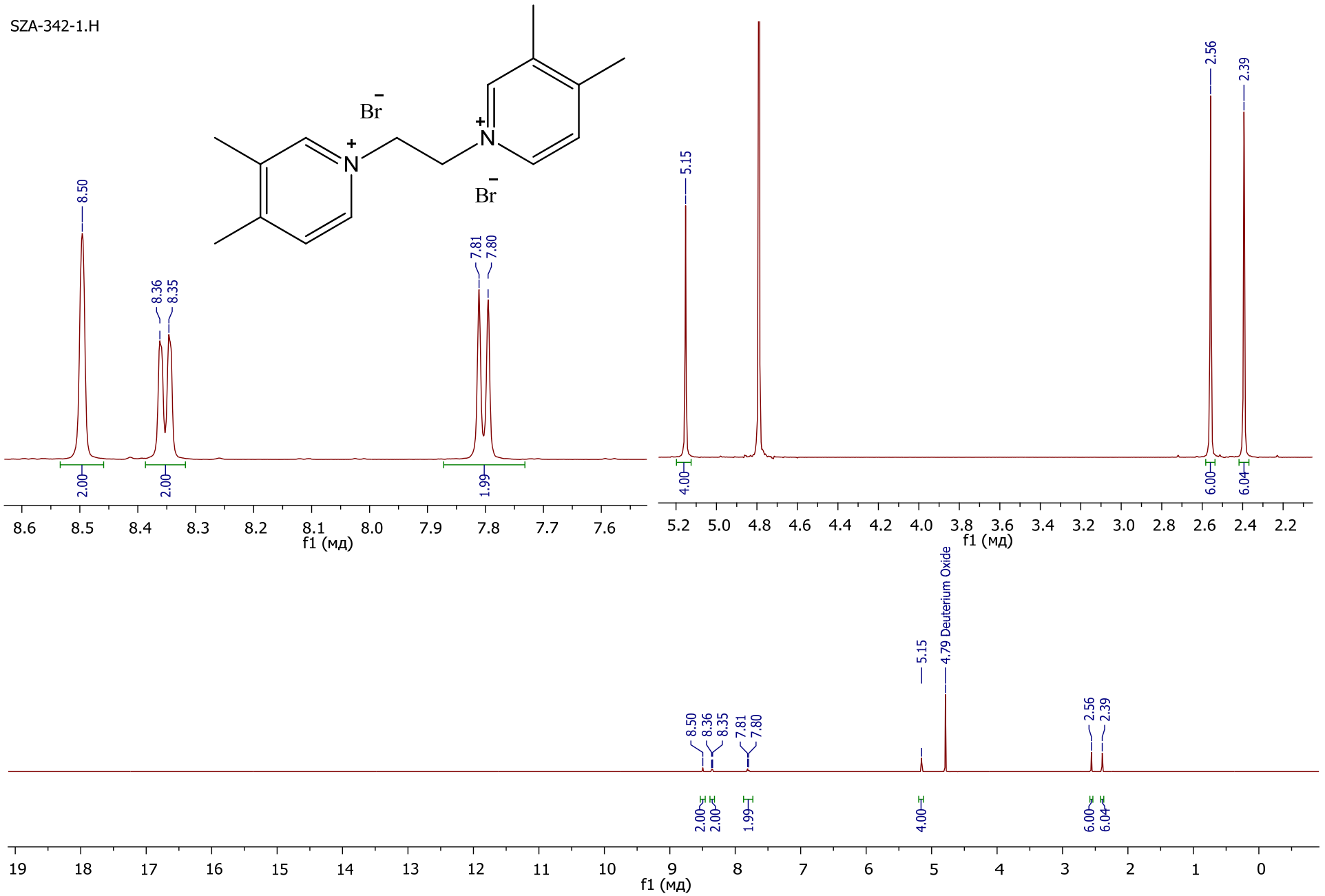
^{13}C NMR spectrum of **16b** in $CDCl_3$



^{1}H NMR spectrum of **17b** in $CDCl_3$

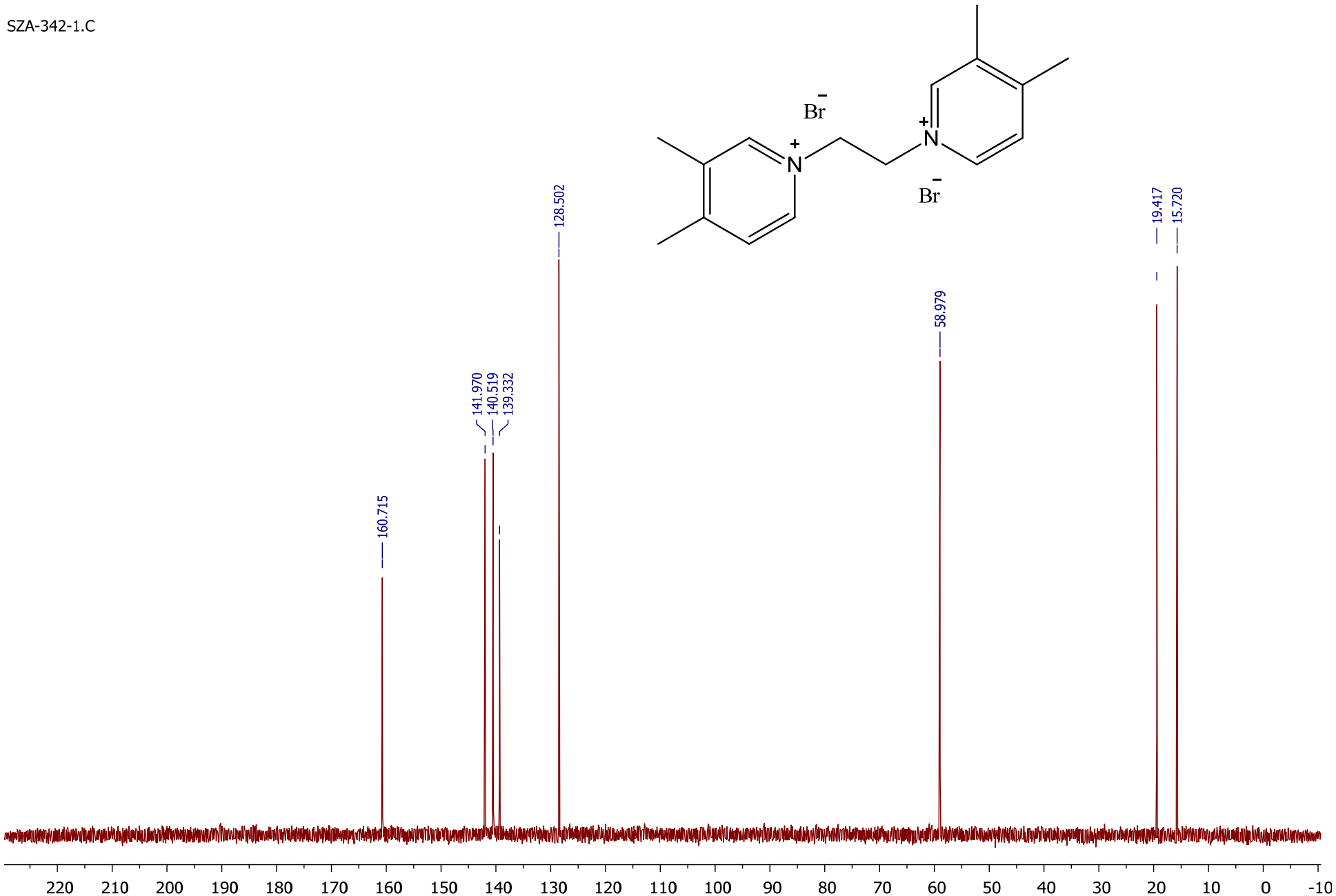


^{13}C NMR spectrum of **17b** in $CDCl_3$

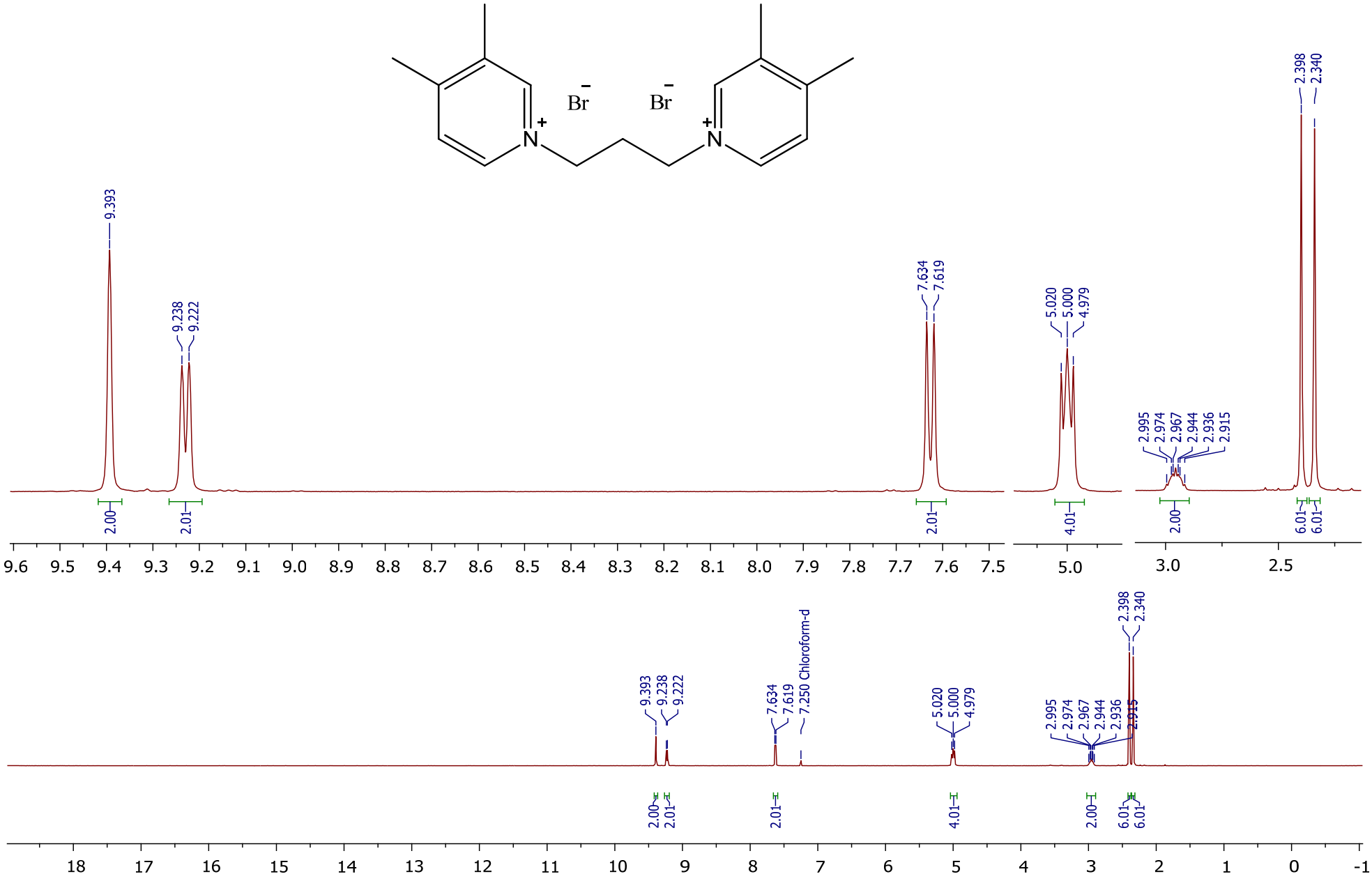


^{1}H NMR spectrum of **18a** in D_2O

SZA-342-1.C

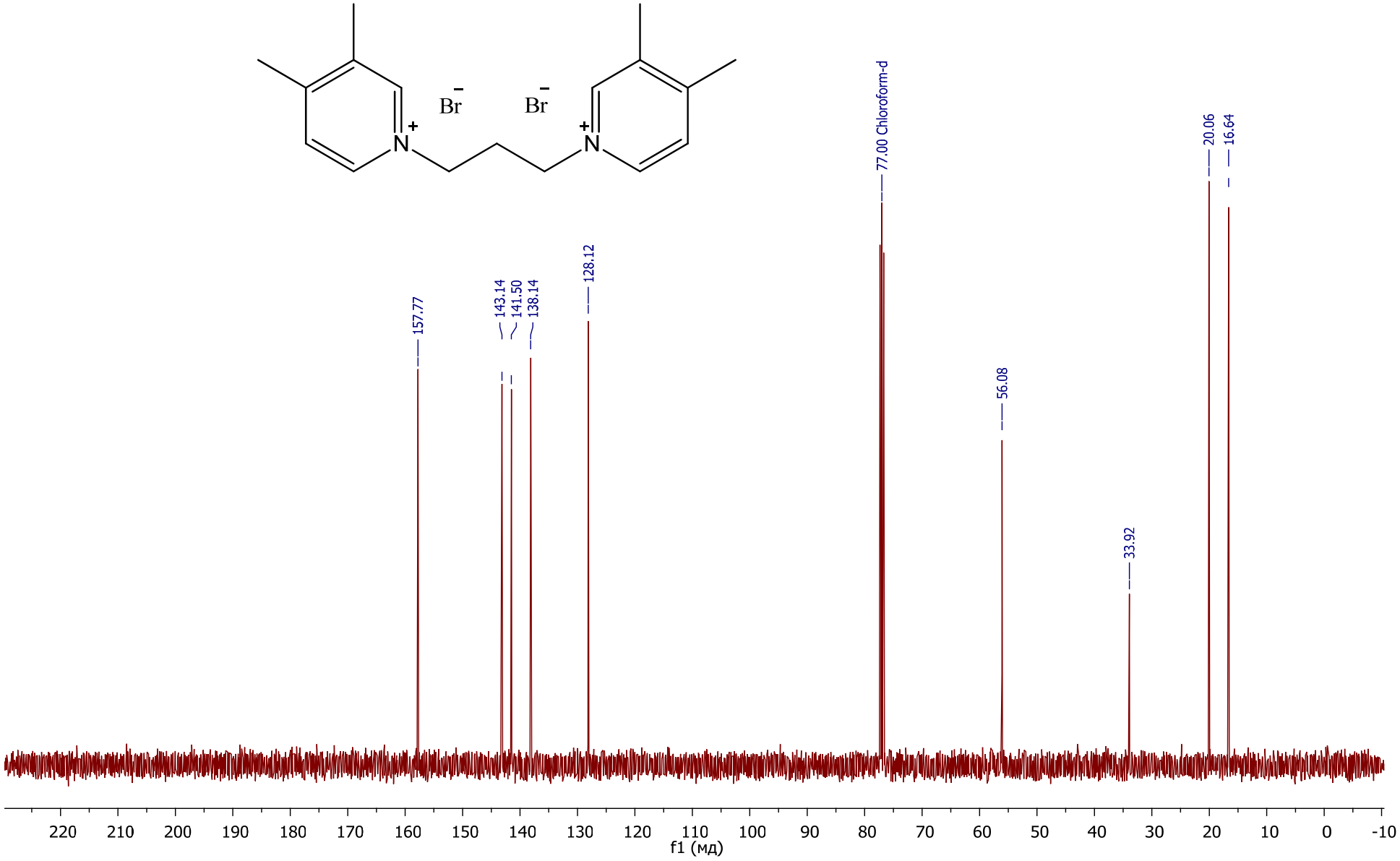


^{13}C NMR spectrum of **18a** in D_2O

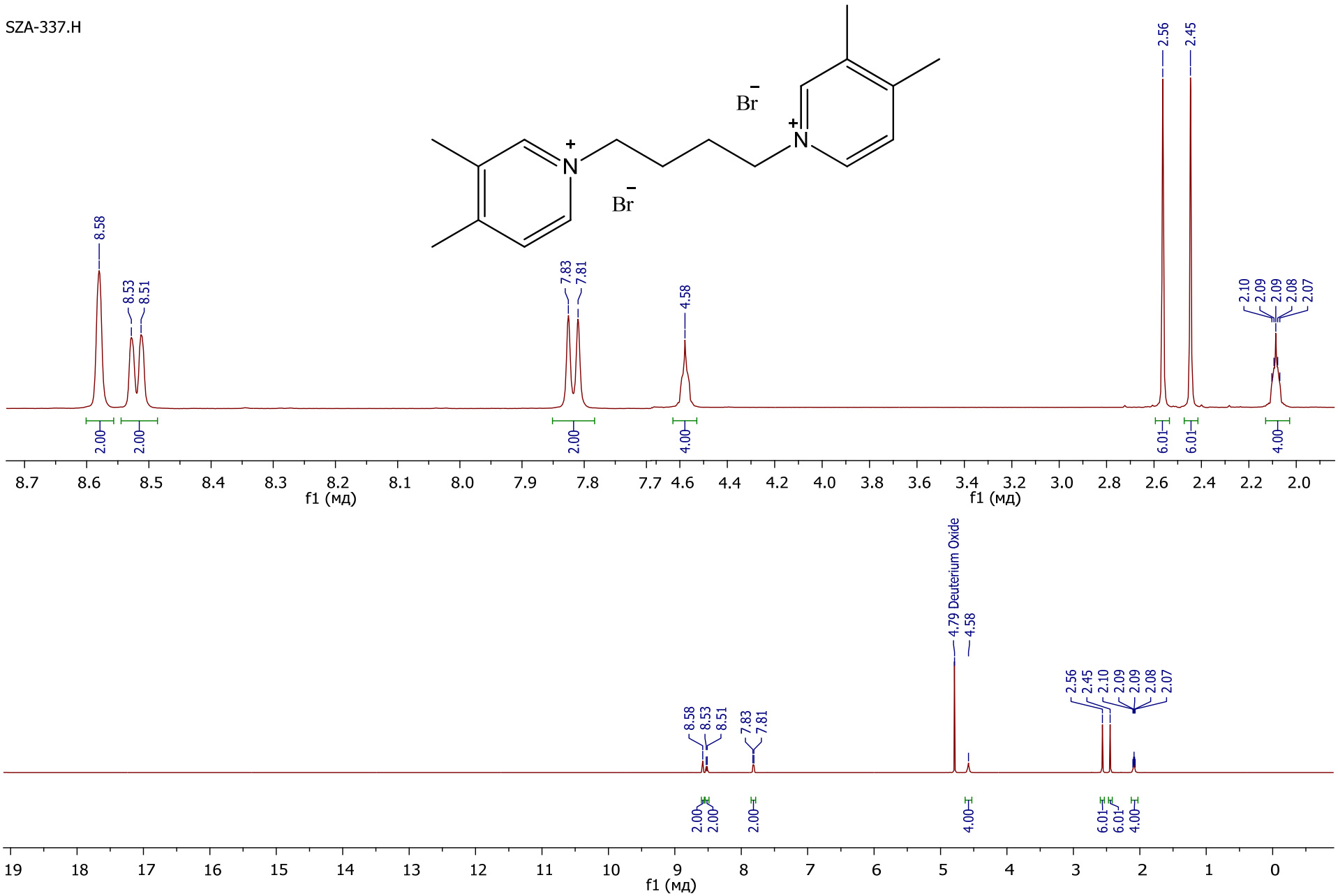


^{1}H NMR spectrum of **18b** in $CDCl_3$

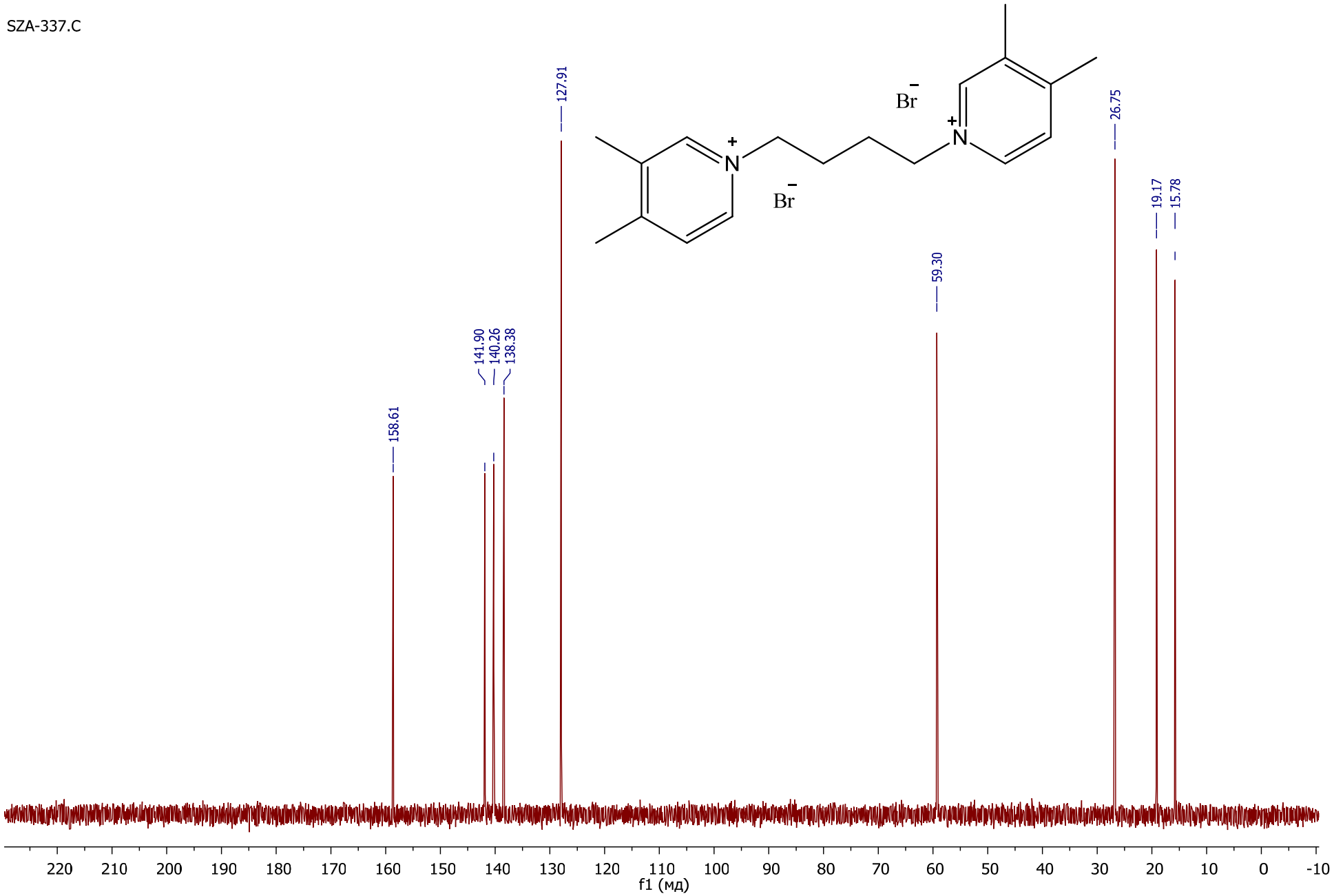
SZA-310.C



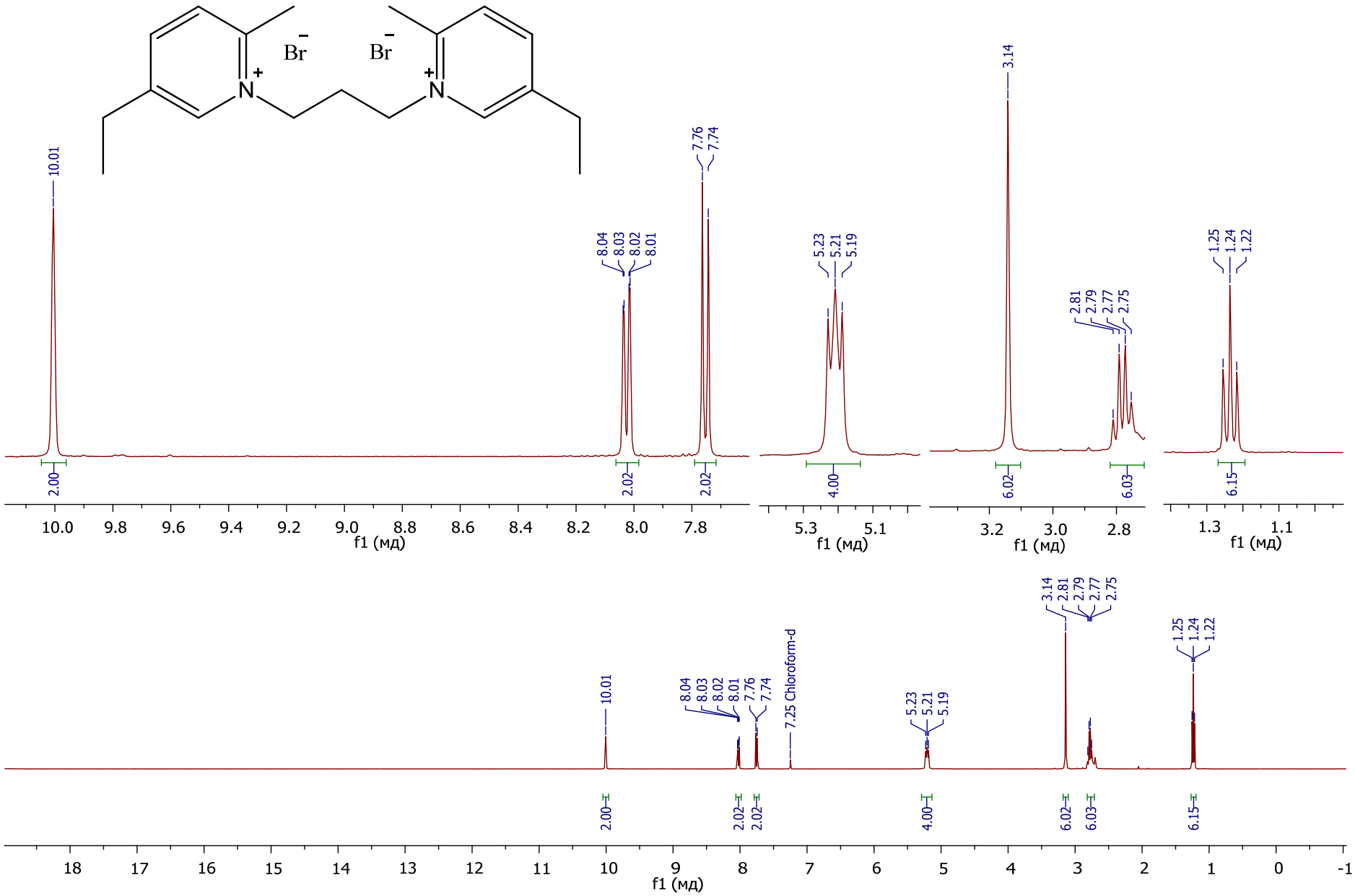
^{13}C NMR spectrum of **18b** in $CDCl_3$



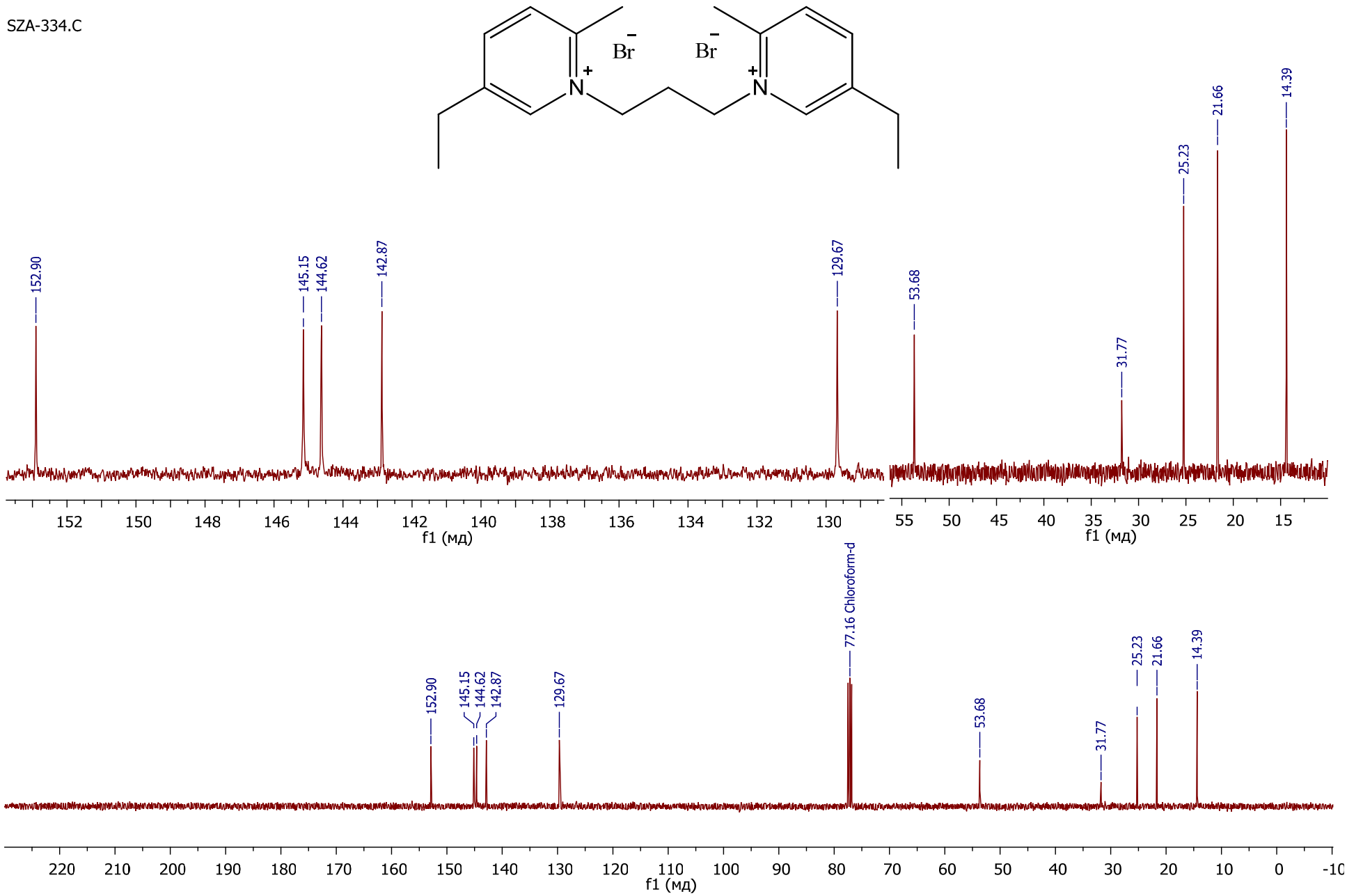
^{1}H NMR spectrum of **18c** in D_2O



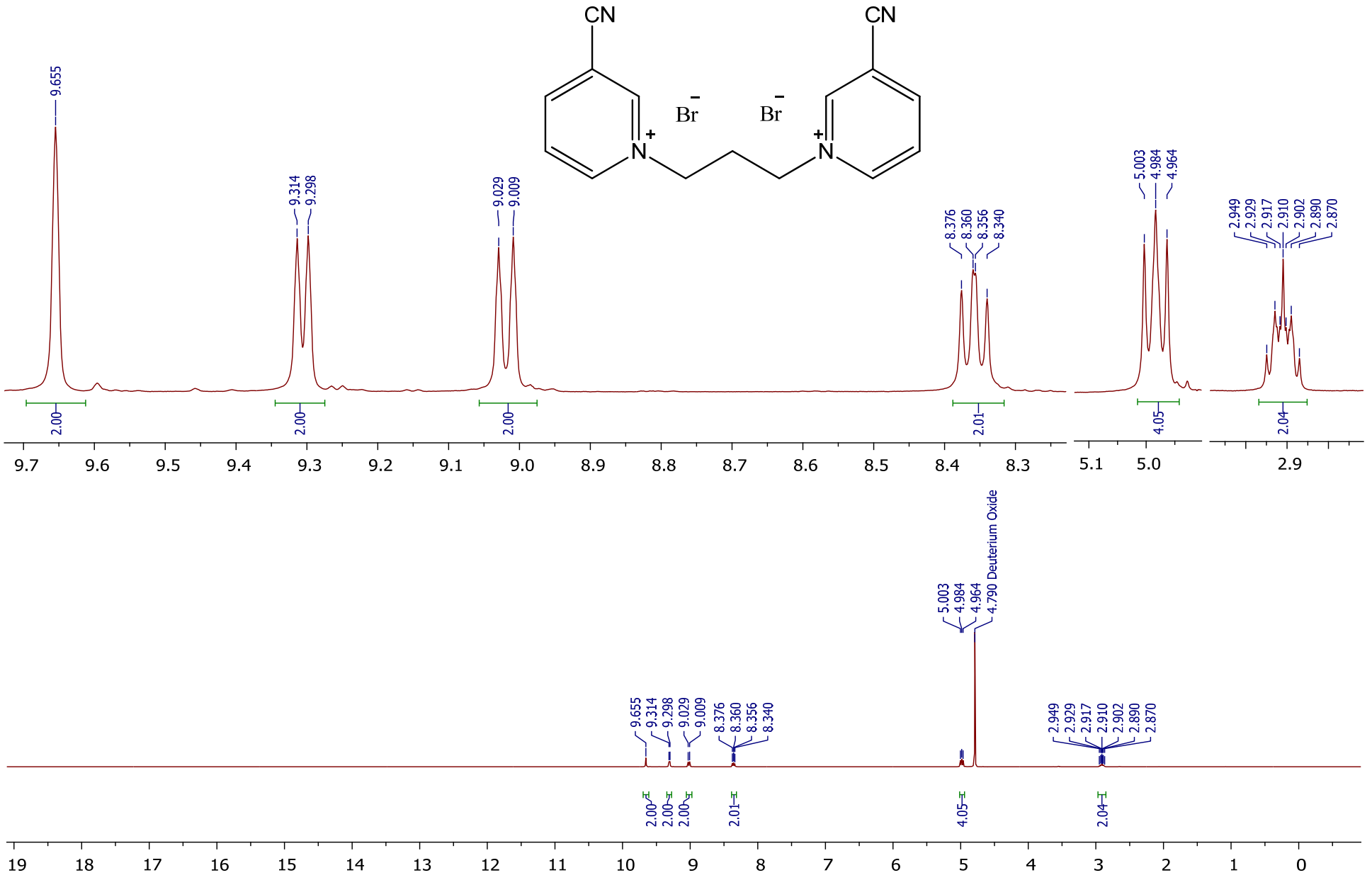
^{13}C NMR spectrum of **18c** in D_2O



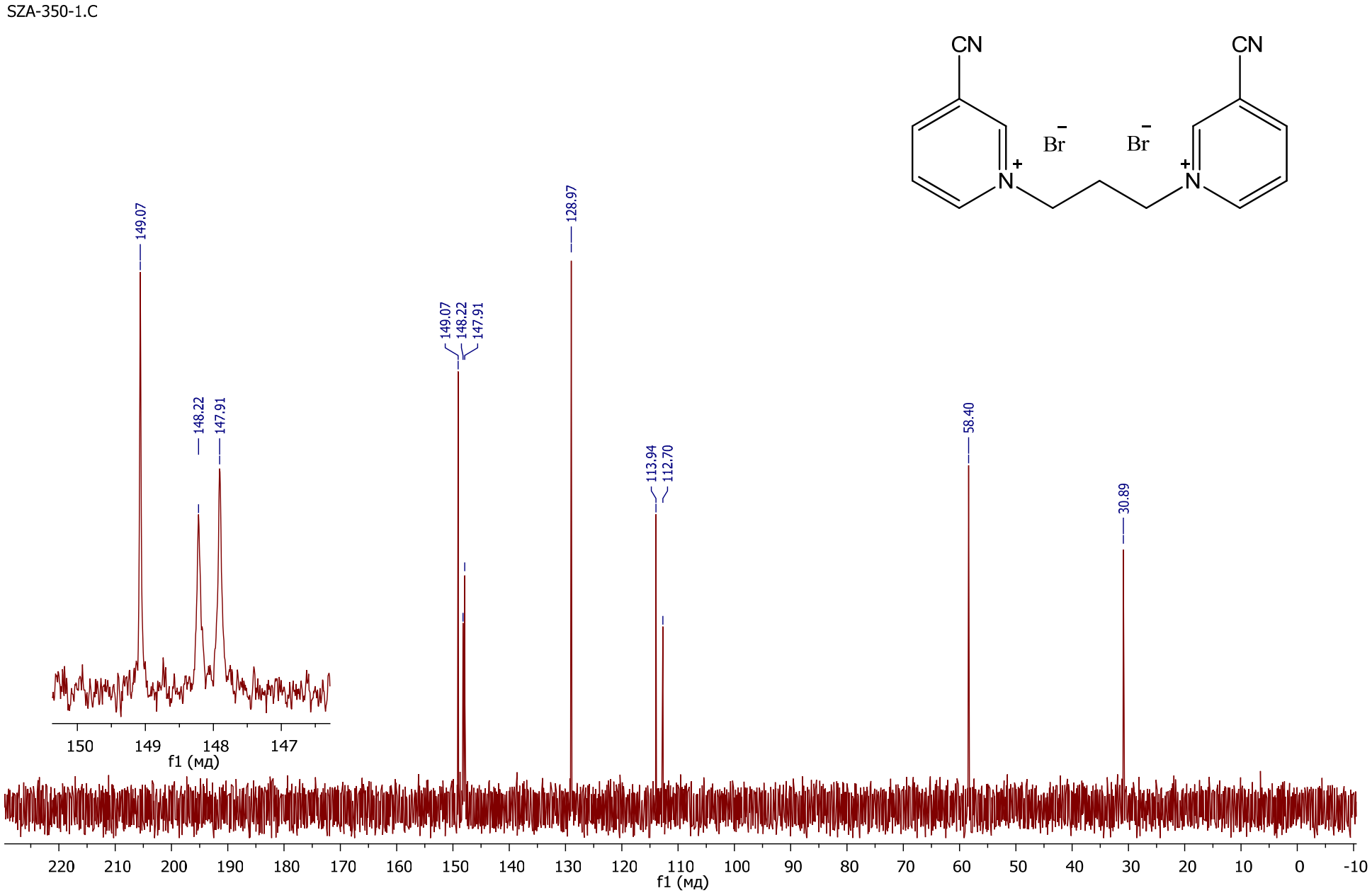
^{1}H NMR spectrum of **19b** in $CDCl_3$



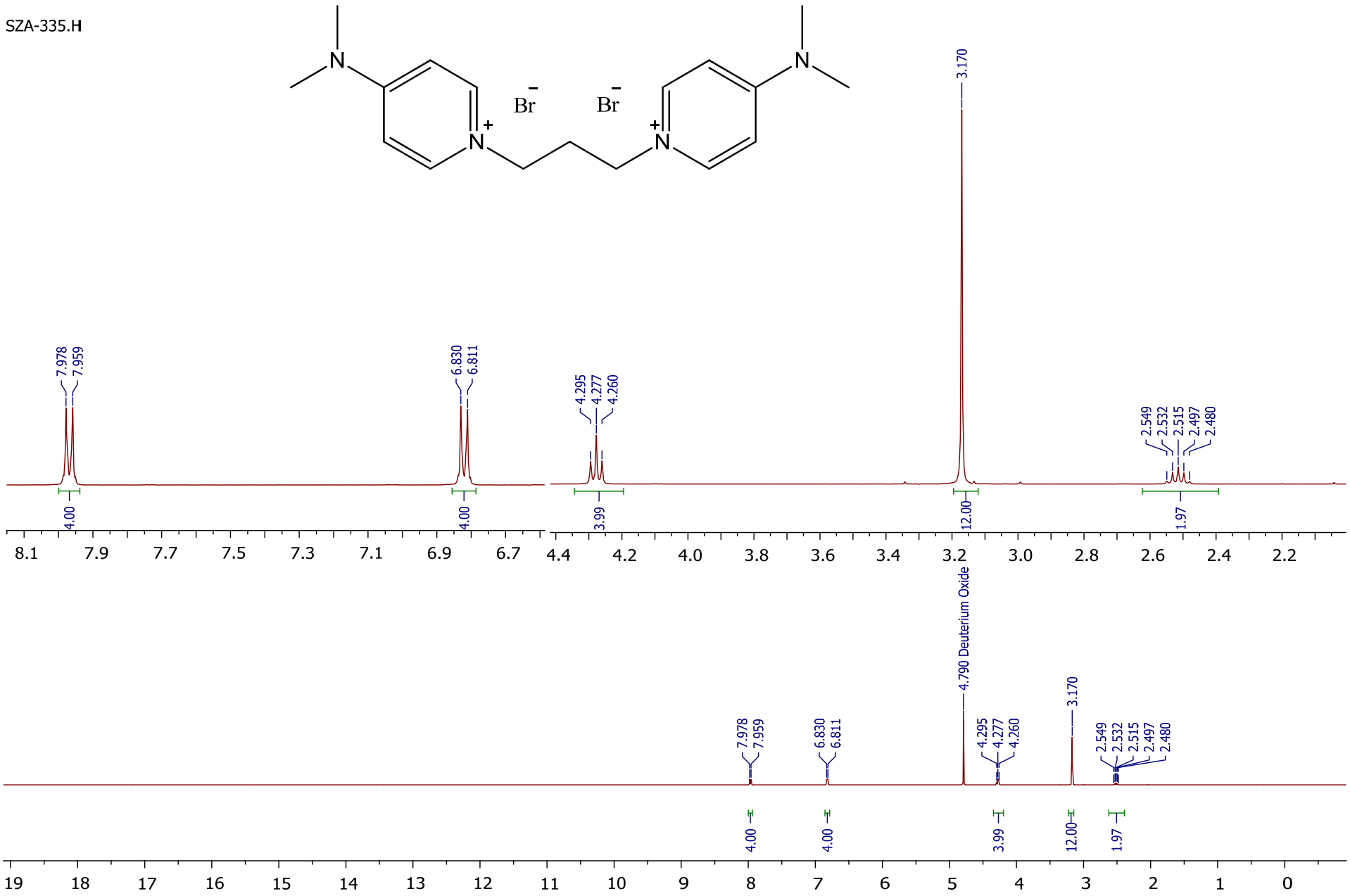
^{13}C NMR spectrum of **19b** in $CDCl_3$



^{1}H NMR spectrum of **20b** in D_2O

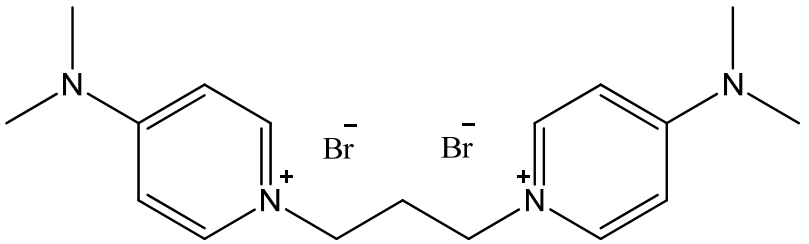


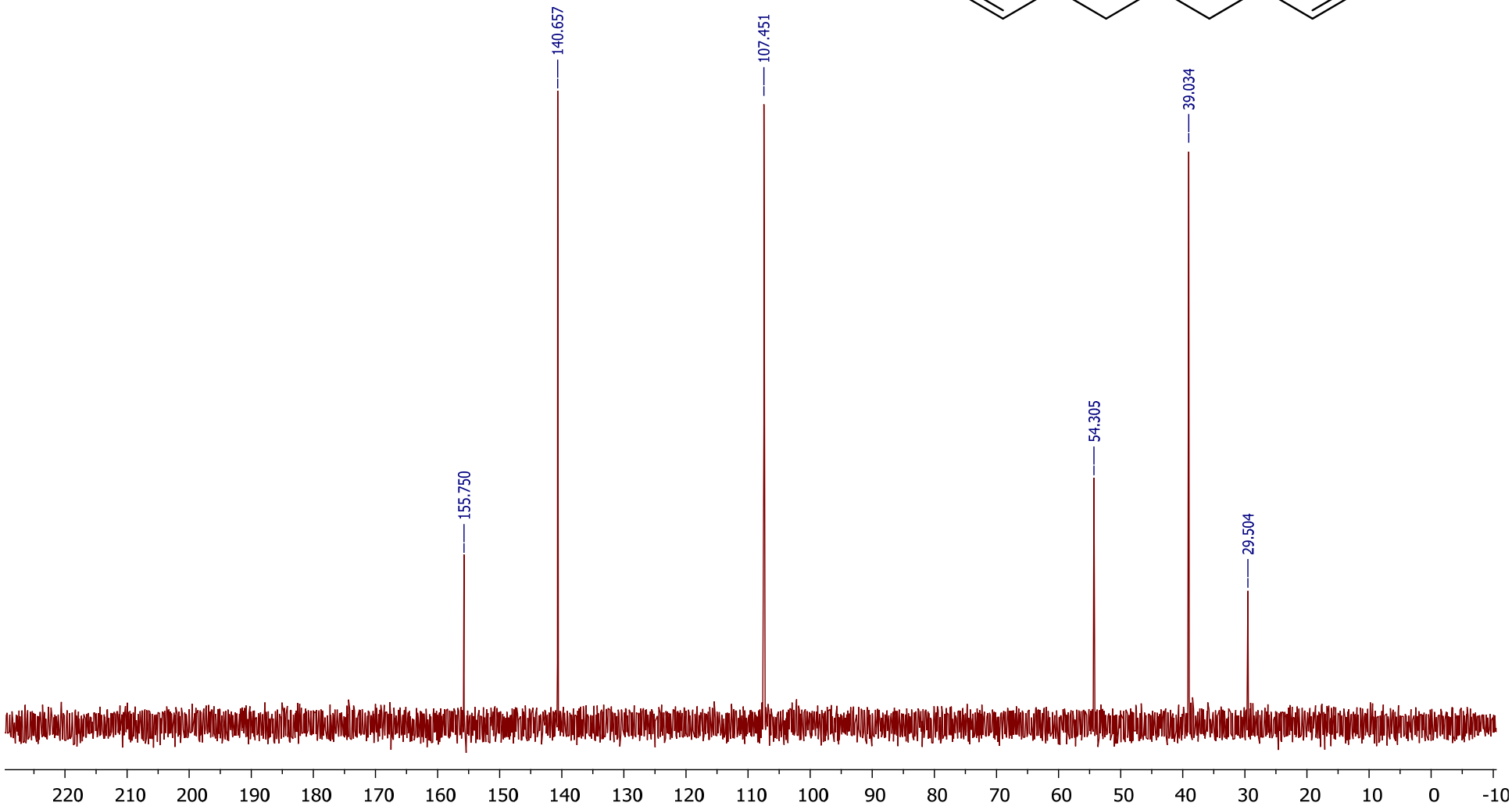
^{13}C NMR spectrum of **20b** in D_2O



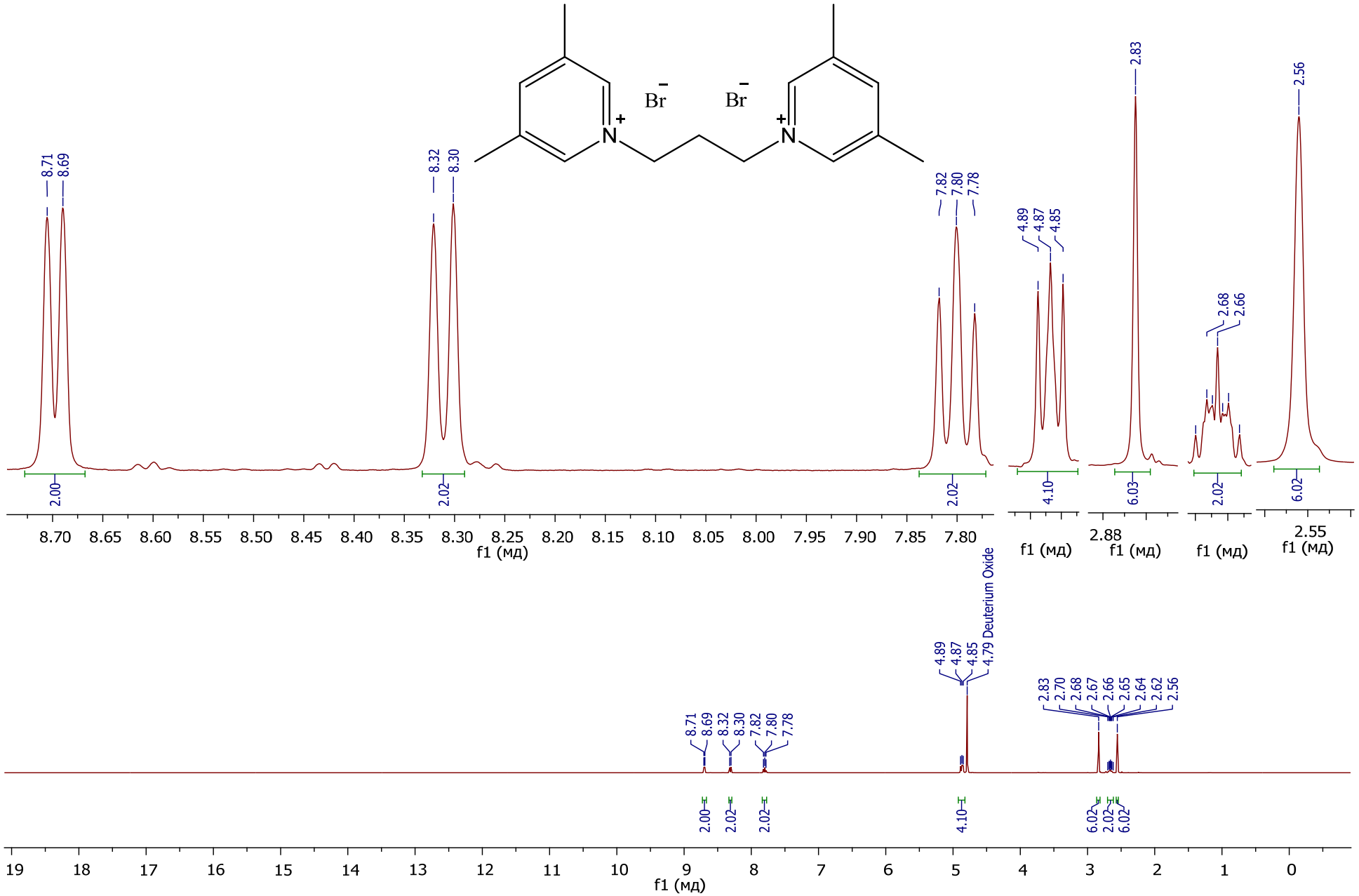
^{1}H NMR spectrum of **21b** in D_2O

SZA-335.C



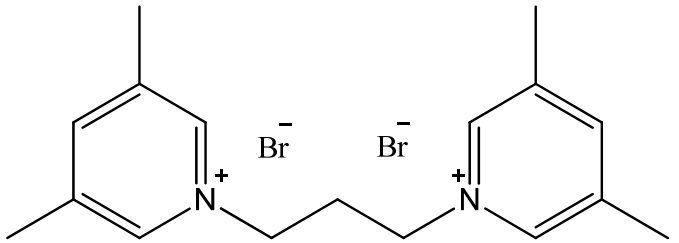


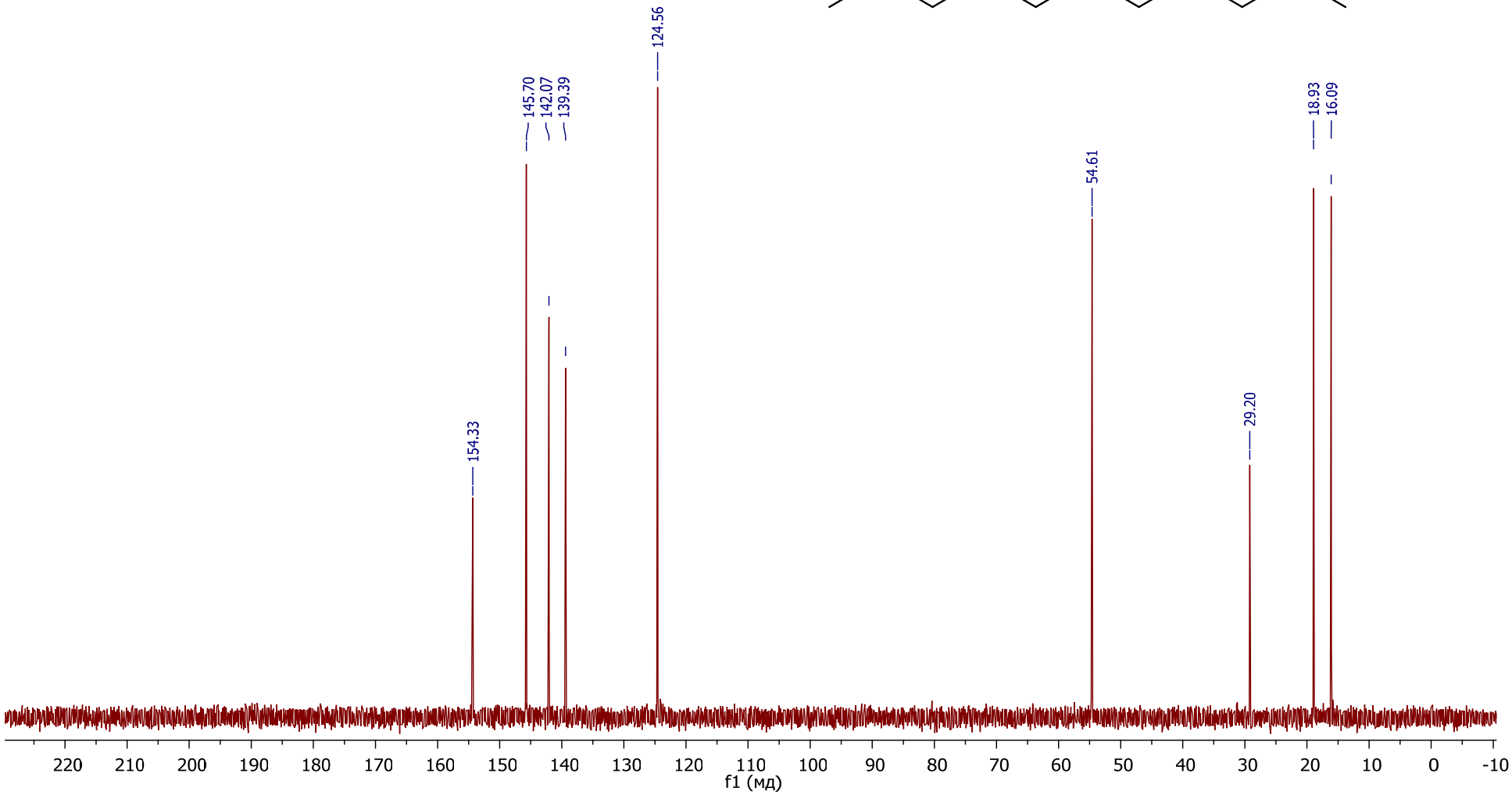
^{13}C NMR spectrum of **21b** in D_2O



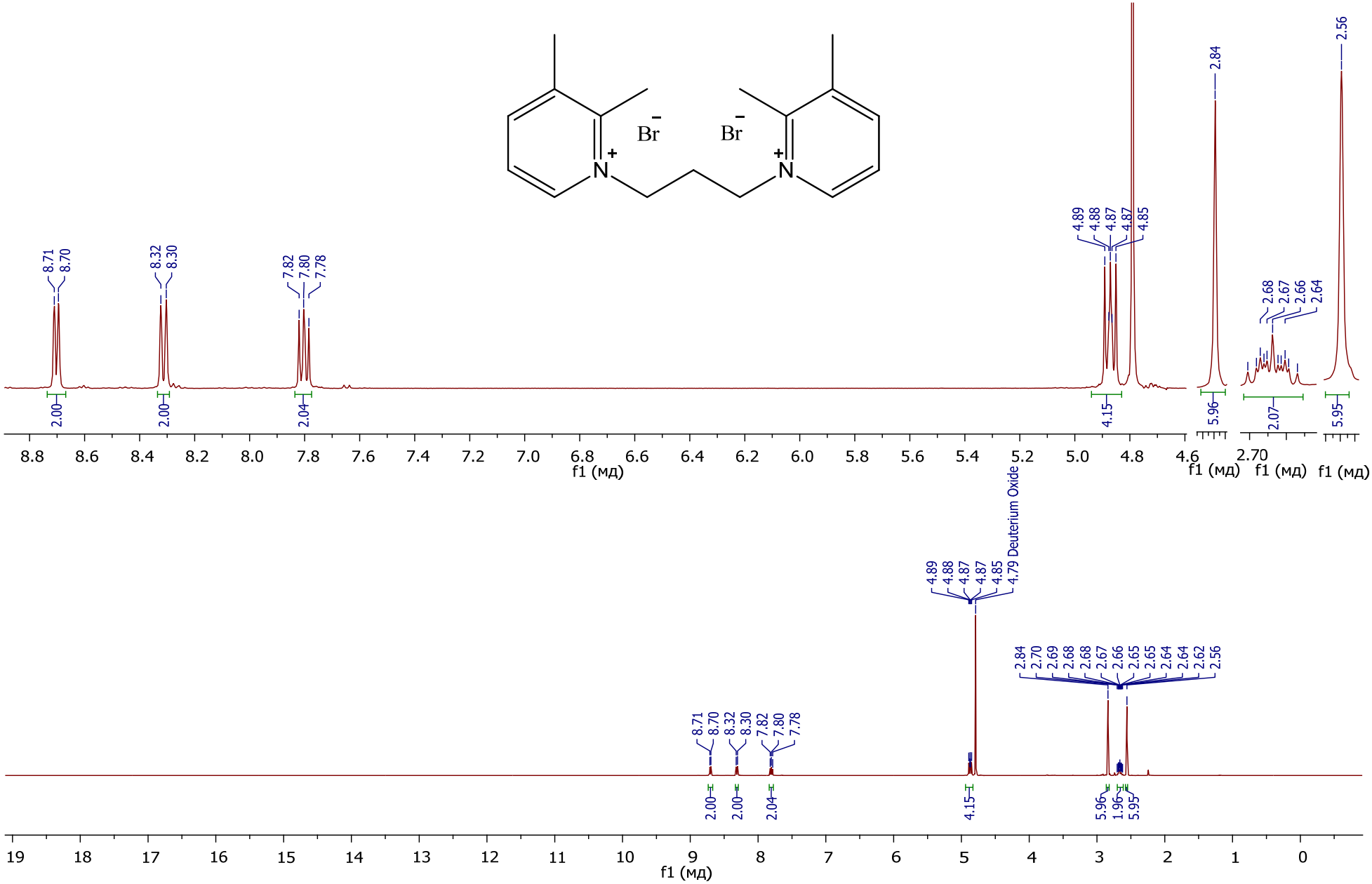
[1]H NMR spectrum of **22** in D_2O

SZA-333.C



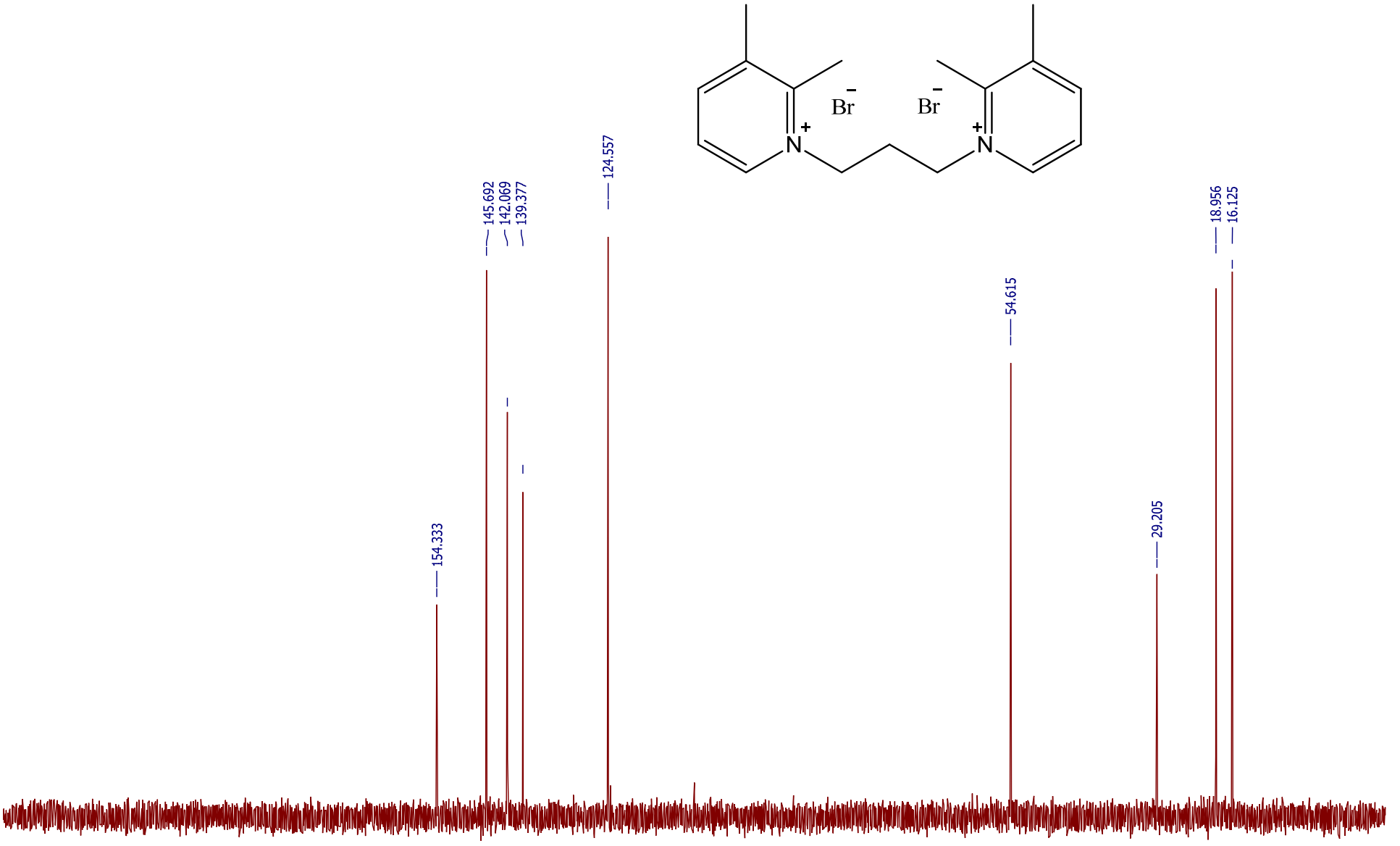


^{13}C NMR spectrum of **22** in D_2O

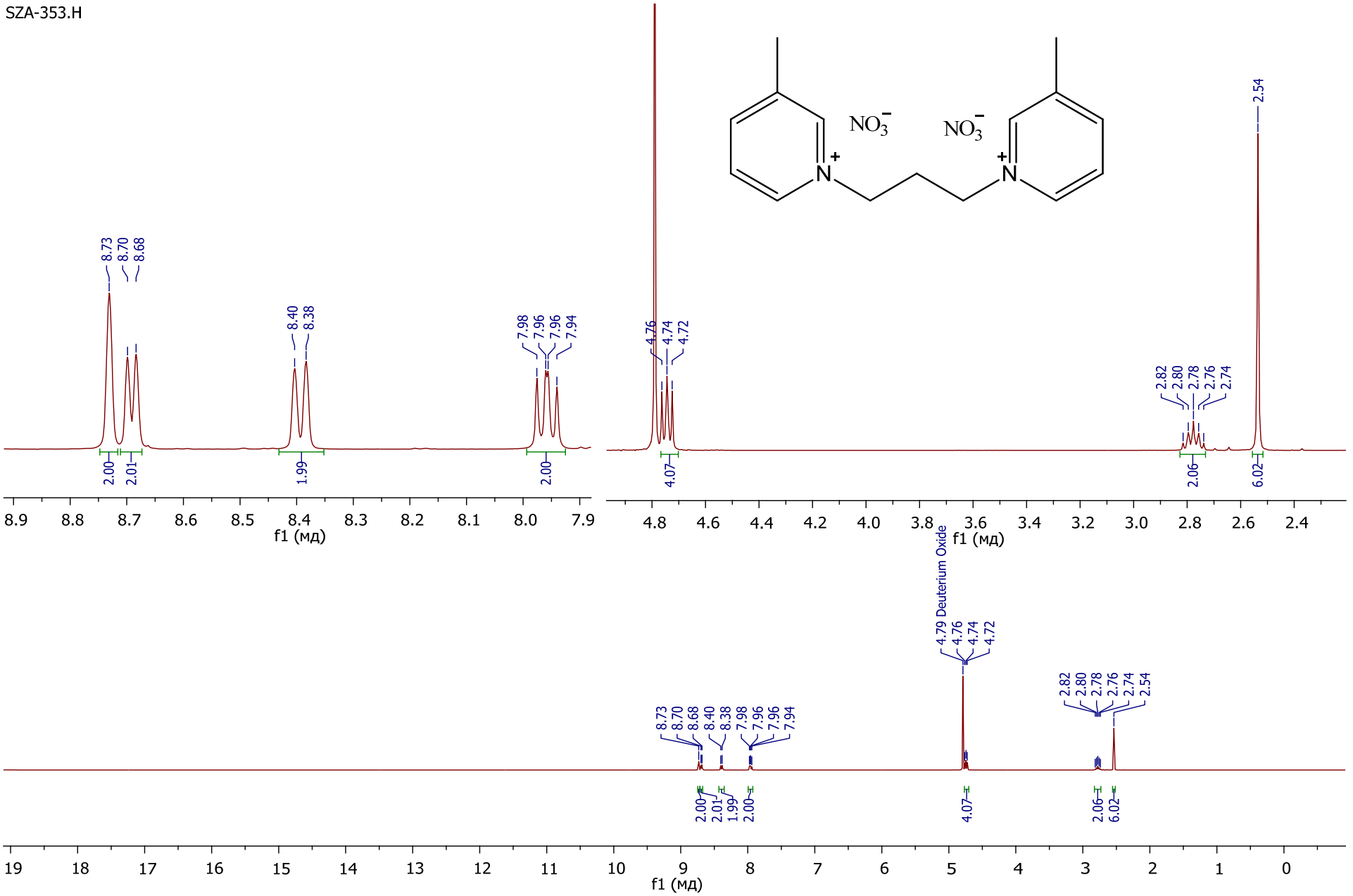


[1]H NMR spectrum of **23** in D_2O

SZA-336.C

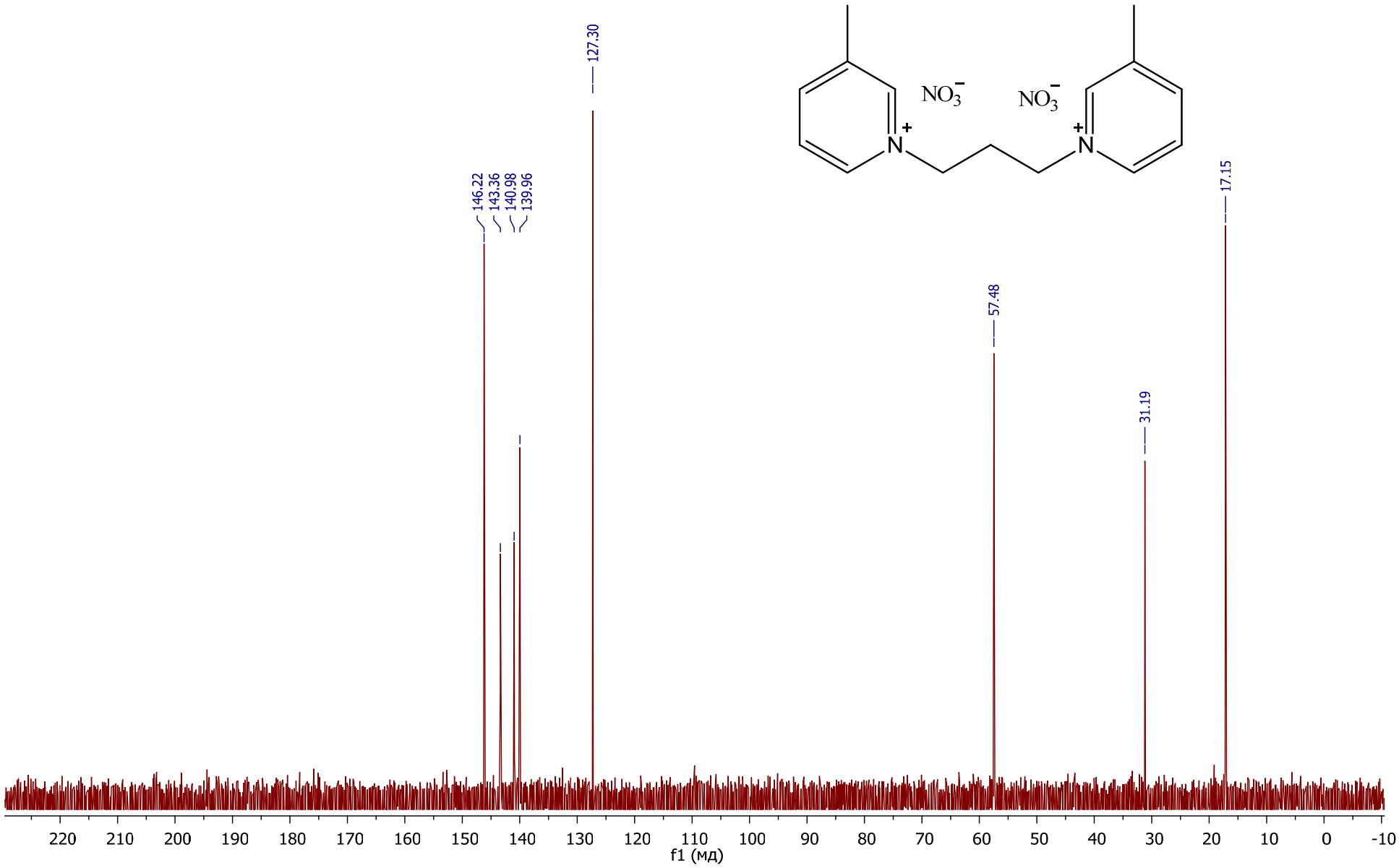


^{13}C NMR spectrum of **23** in D_2O

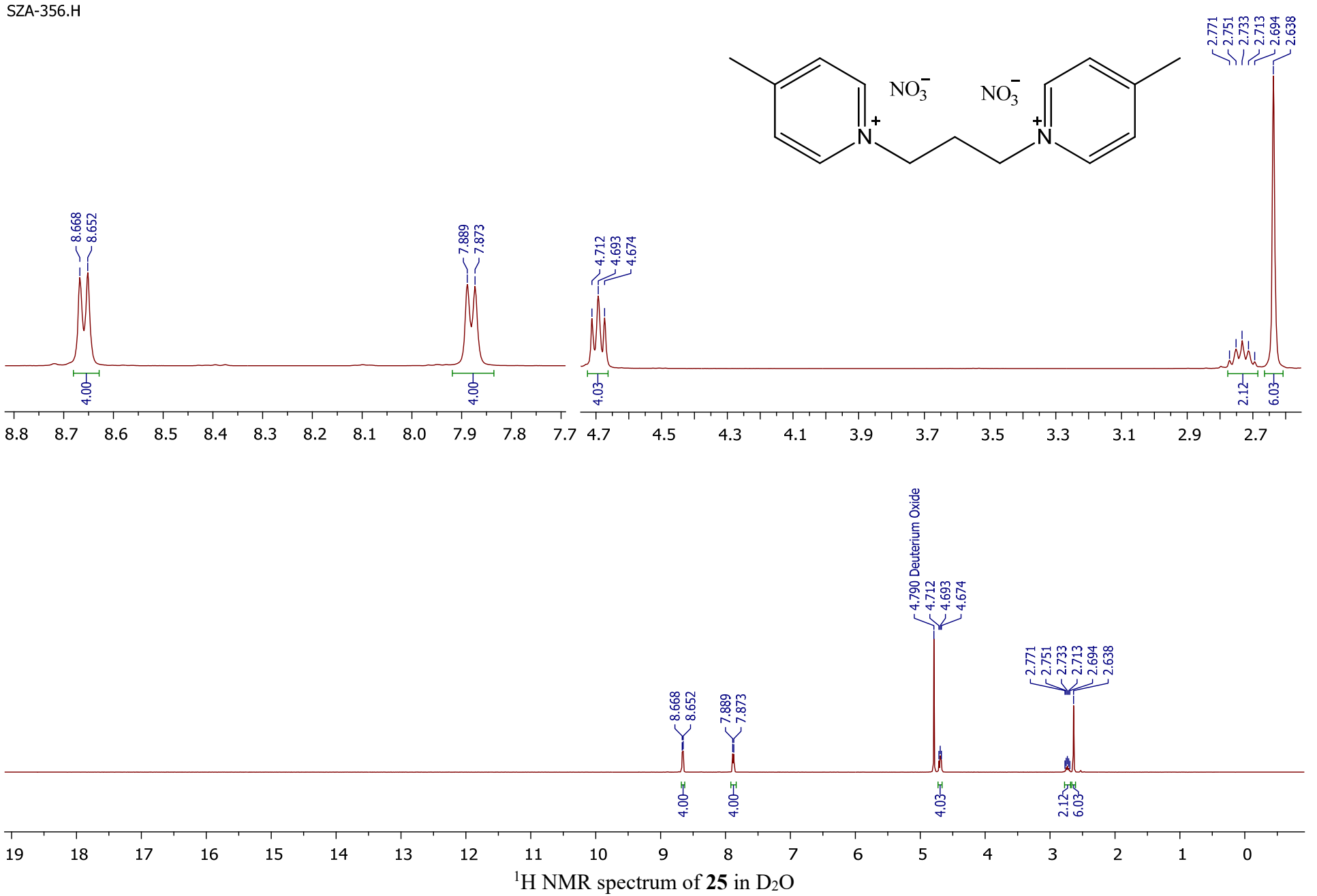


^{1}H NMR spectrum of **24** in D_2O

SZA-353.C

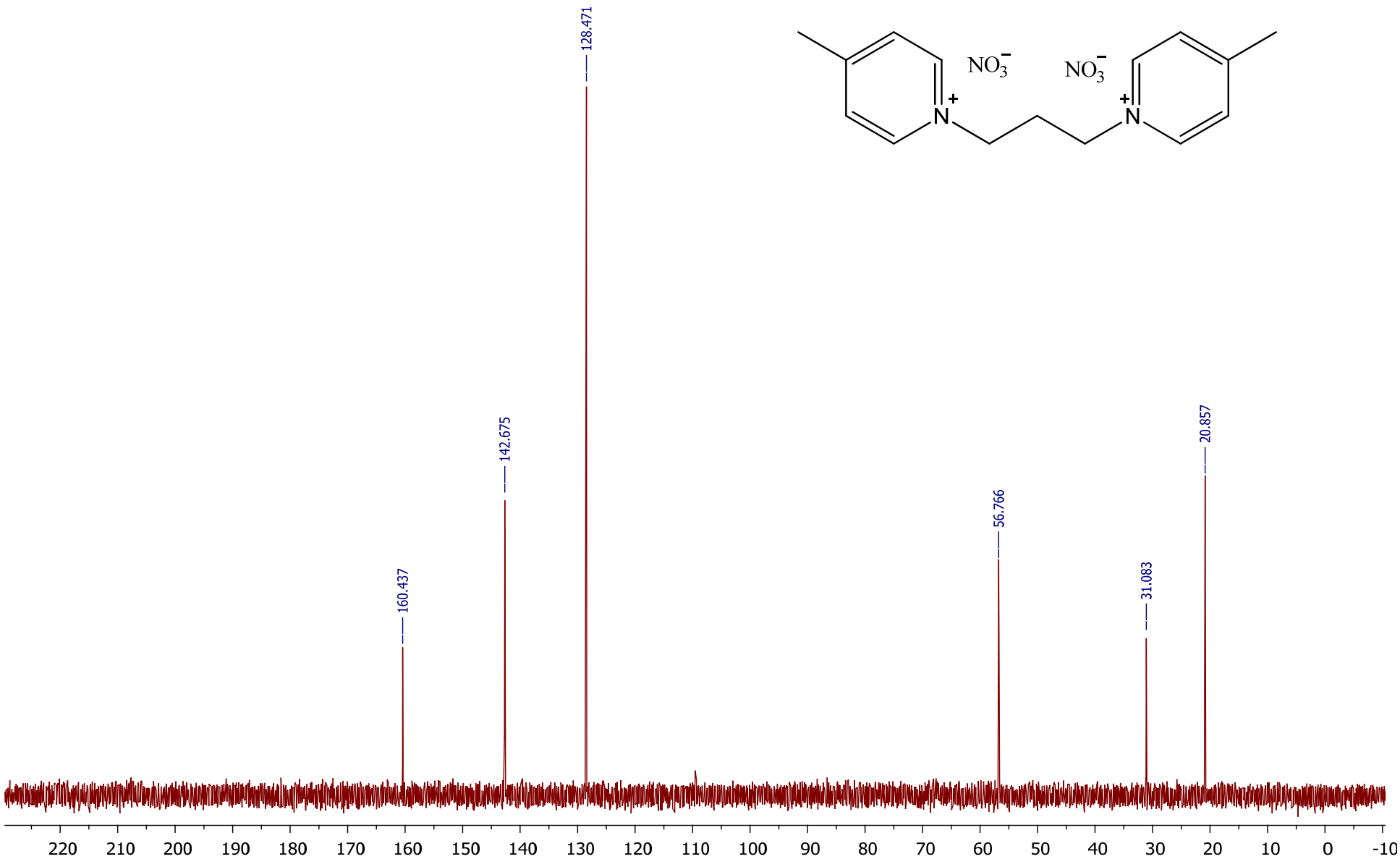


^{13}C NMR spectrum of **24** in D_2O

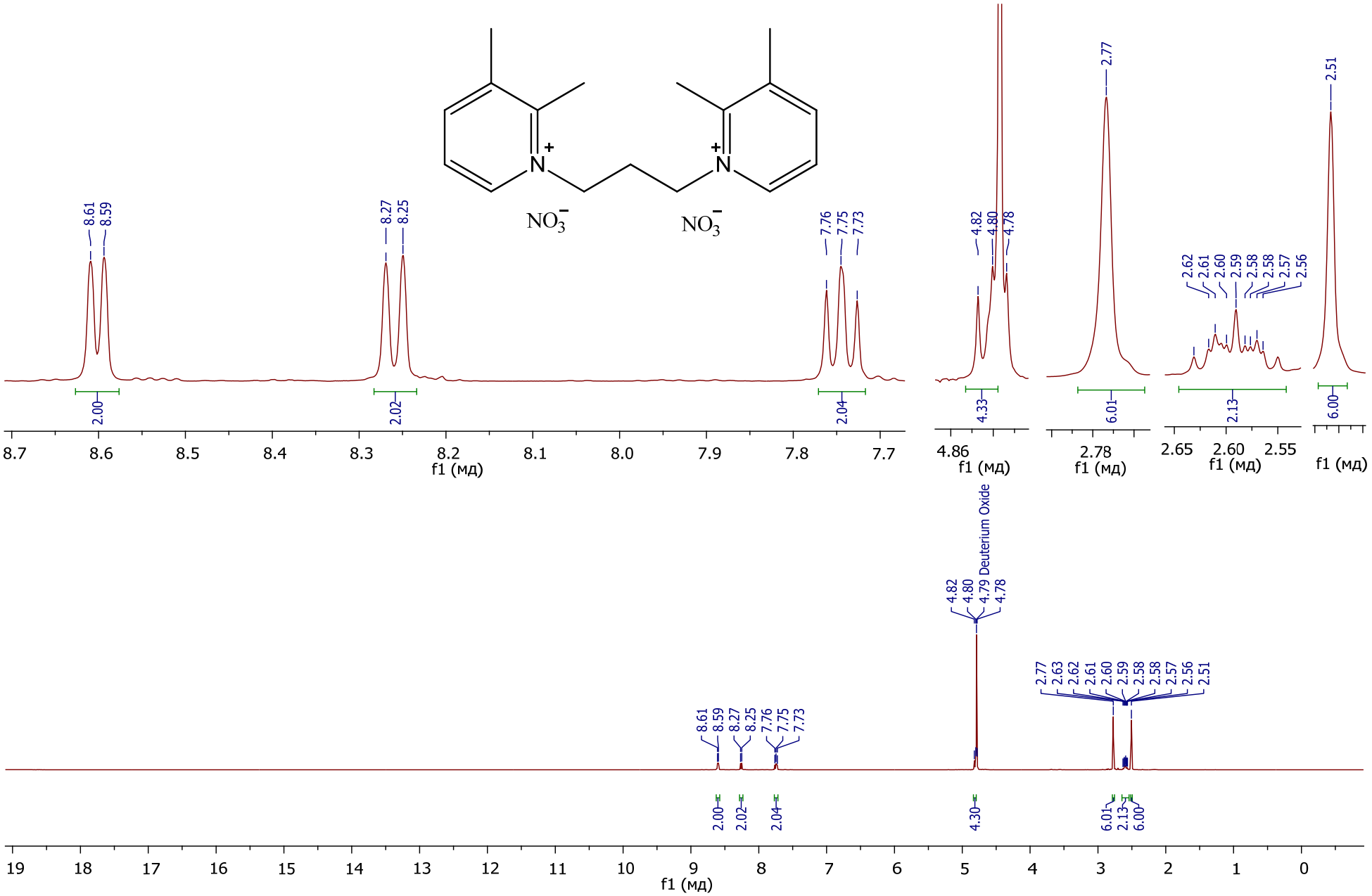


^{1}H NMR spectrum of **25** in D_2O

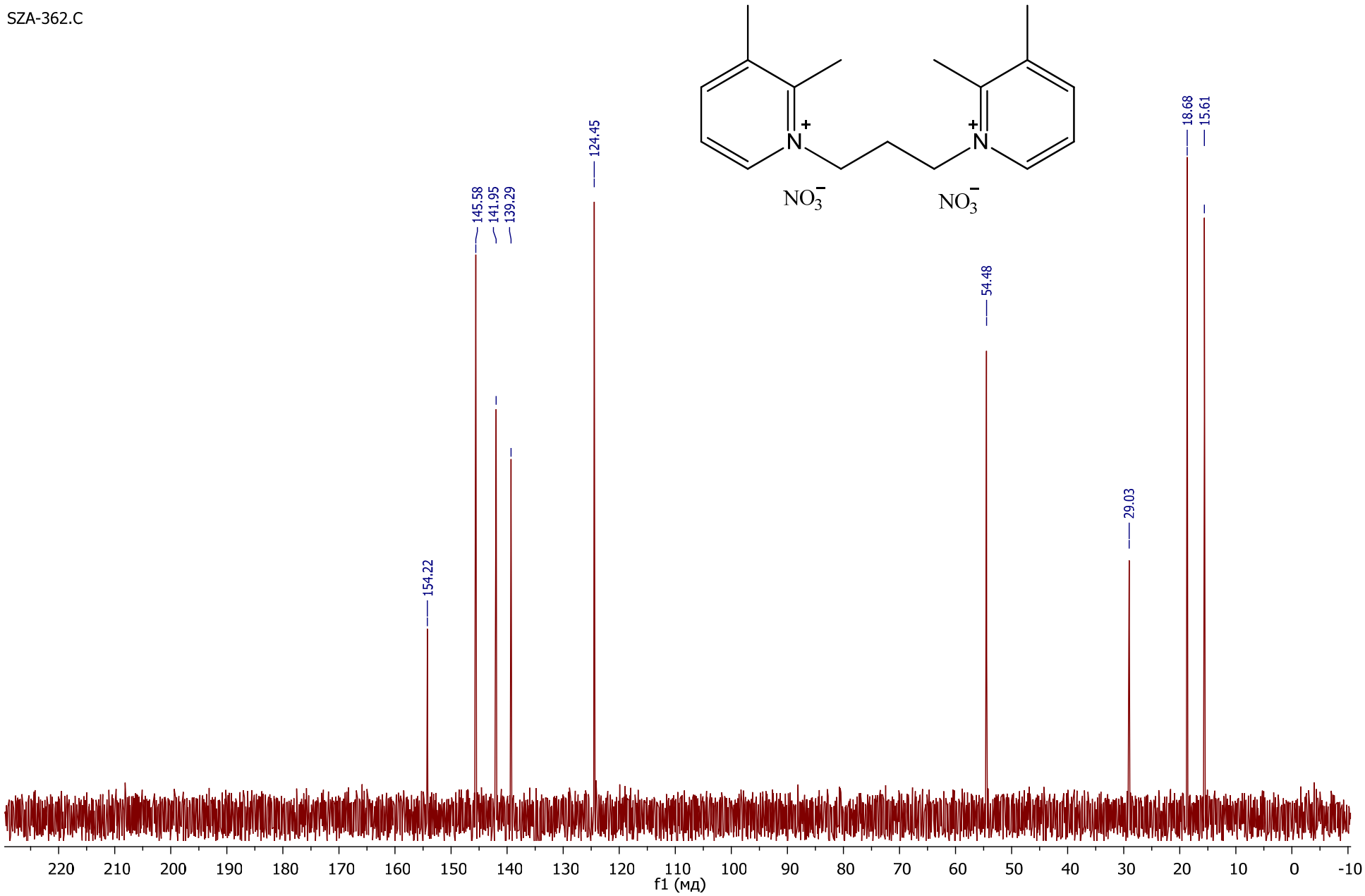
SZA-356.C



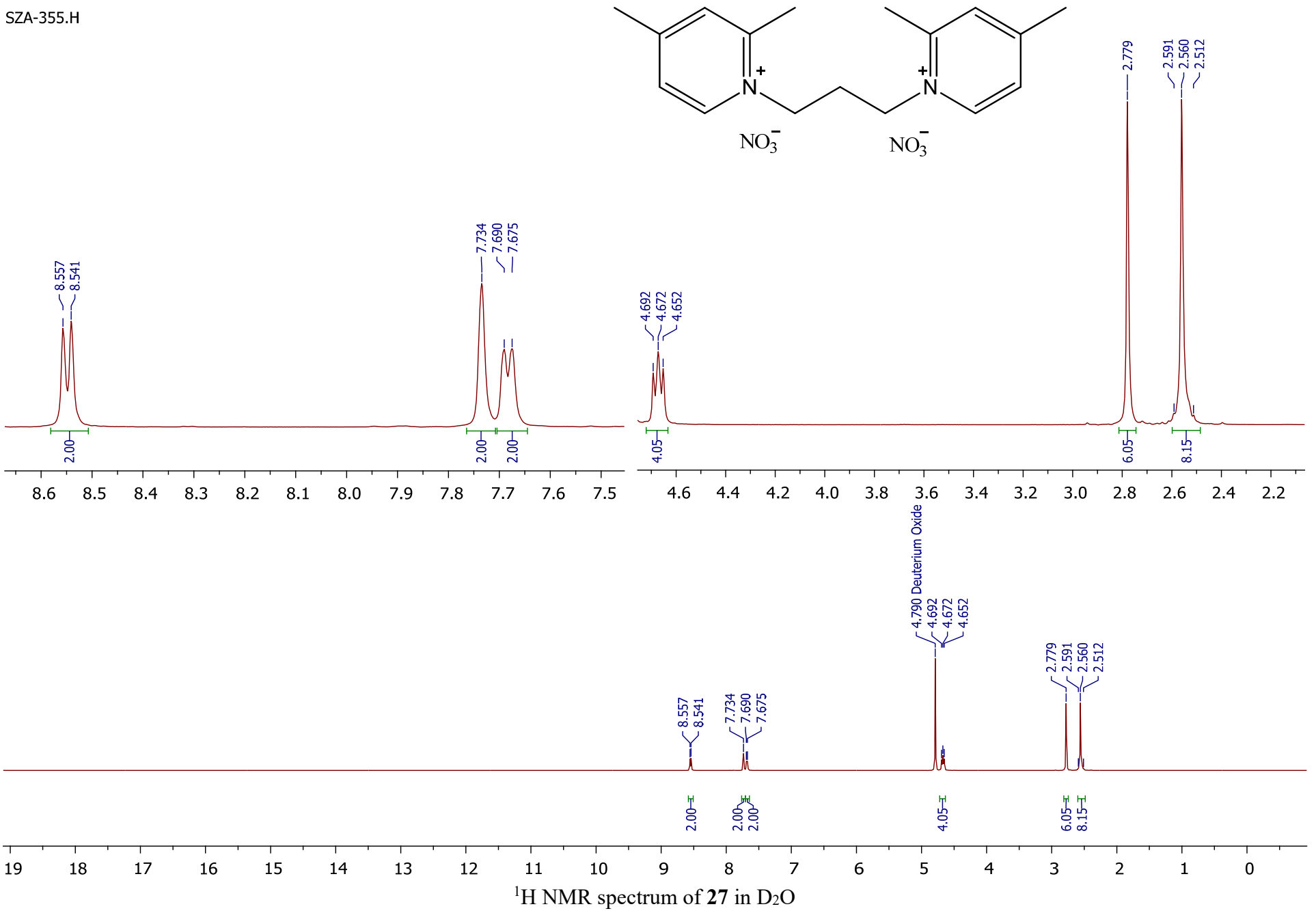
^{13}C NMR spectrum of **25** in D_2O



[1]H NMR spectrum of **26** in D_2O

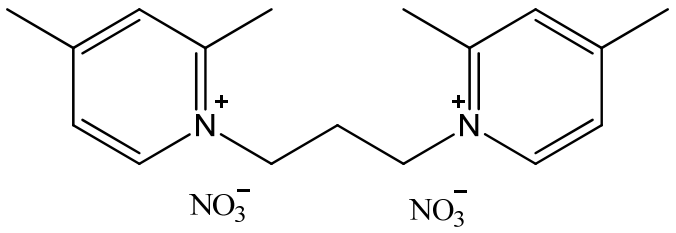


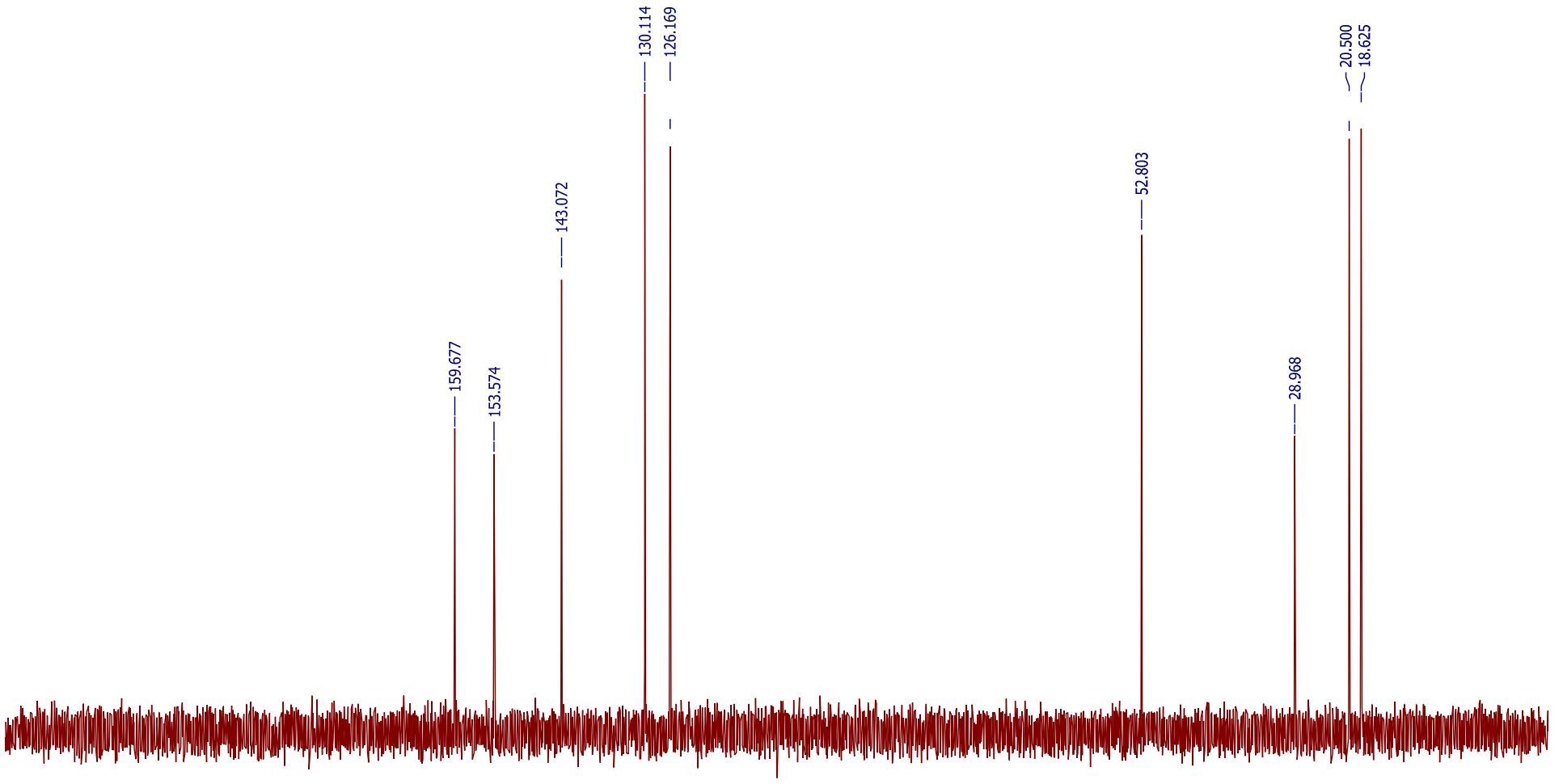
^{13}C NMR spectrum of **26** in D_2O



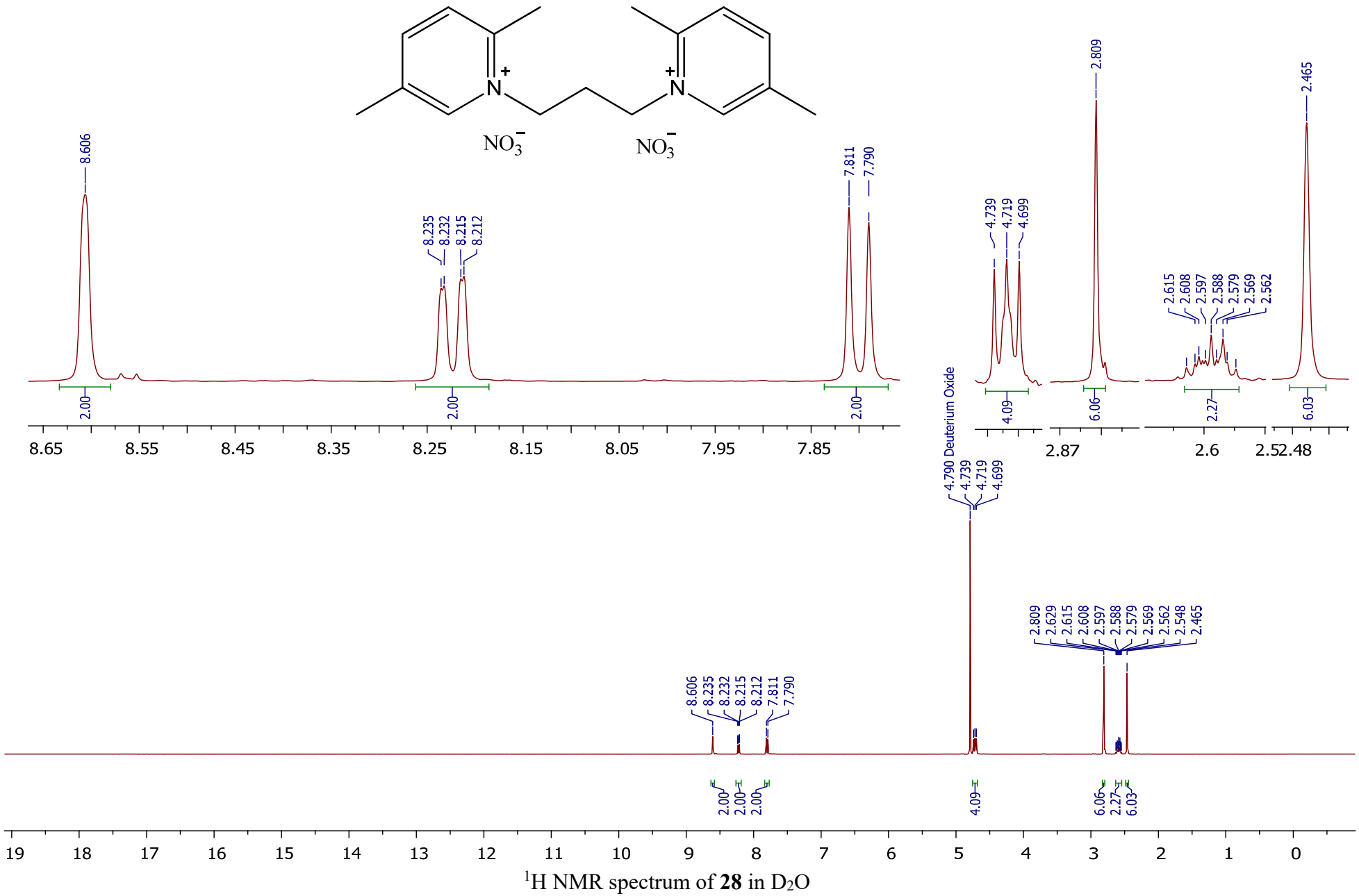
^{1}H NMR spectrum of **27** in D_2O

SZA-355.C



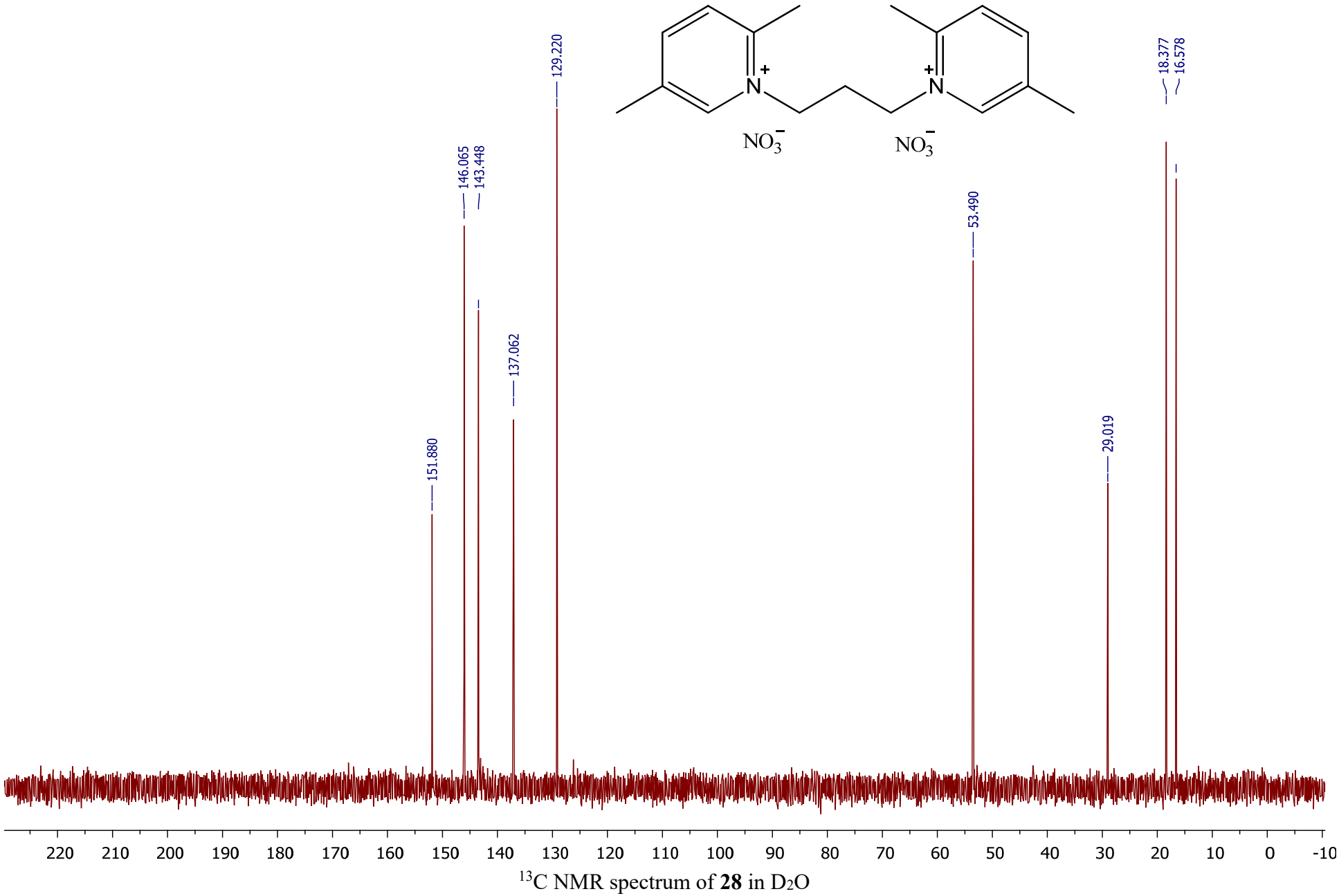


^{13}C NMR spectrum of **27** in D_2O

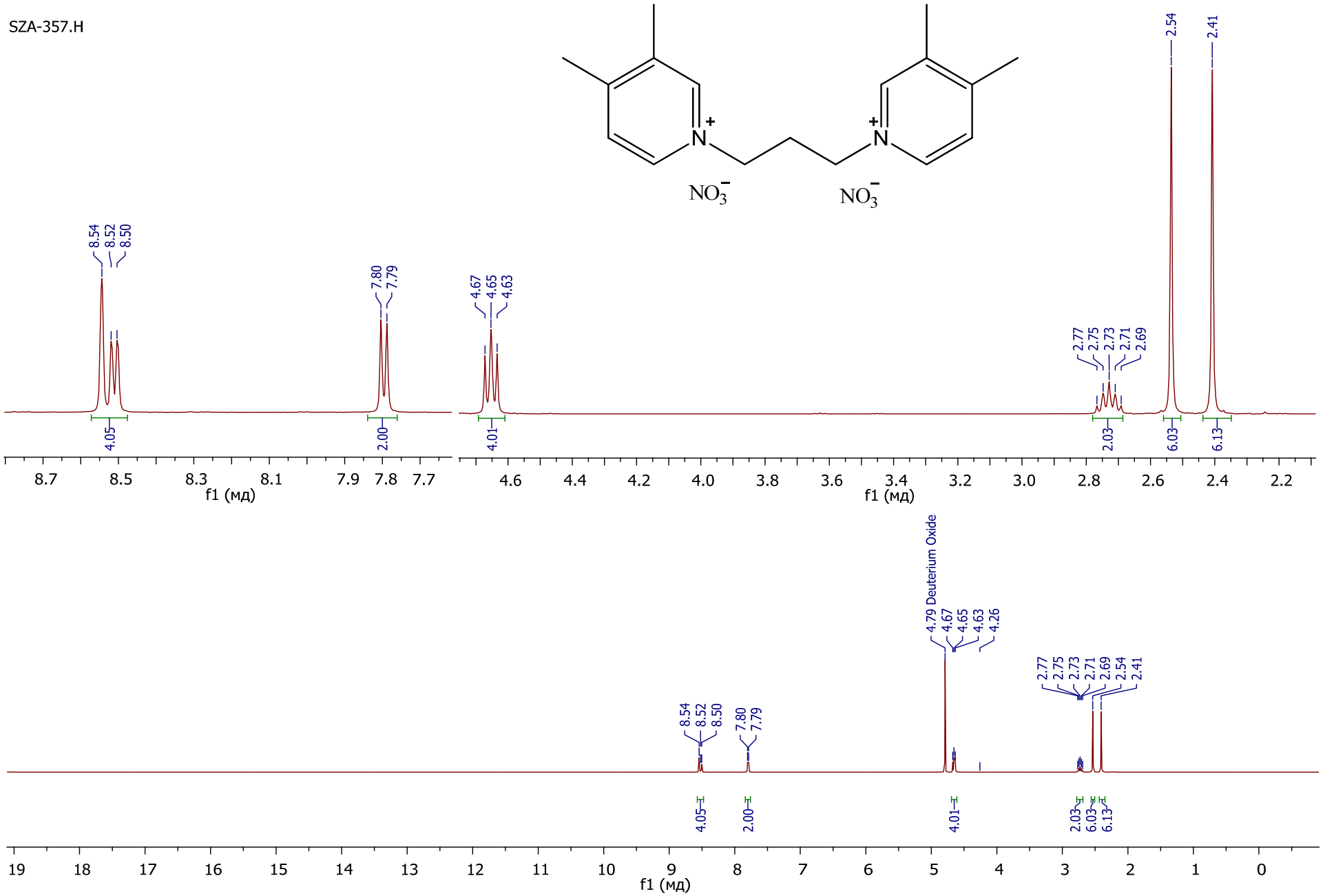


[1]H NMR spectrum of **28** in D_2O

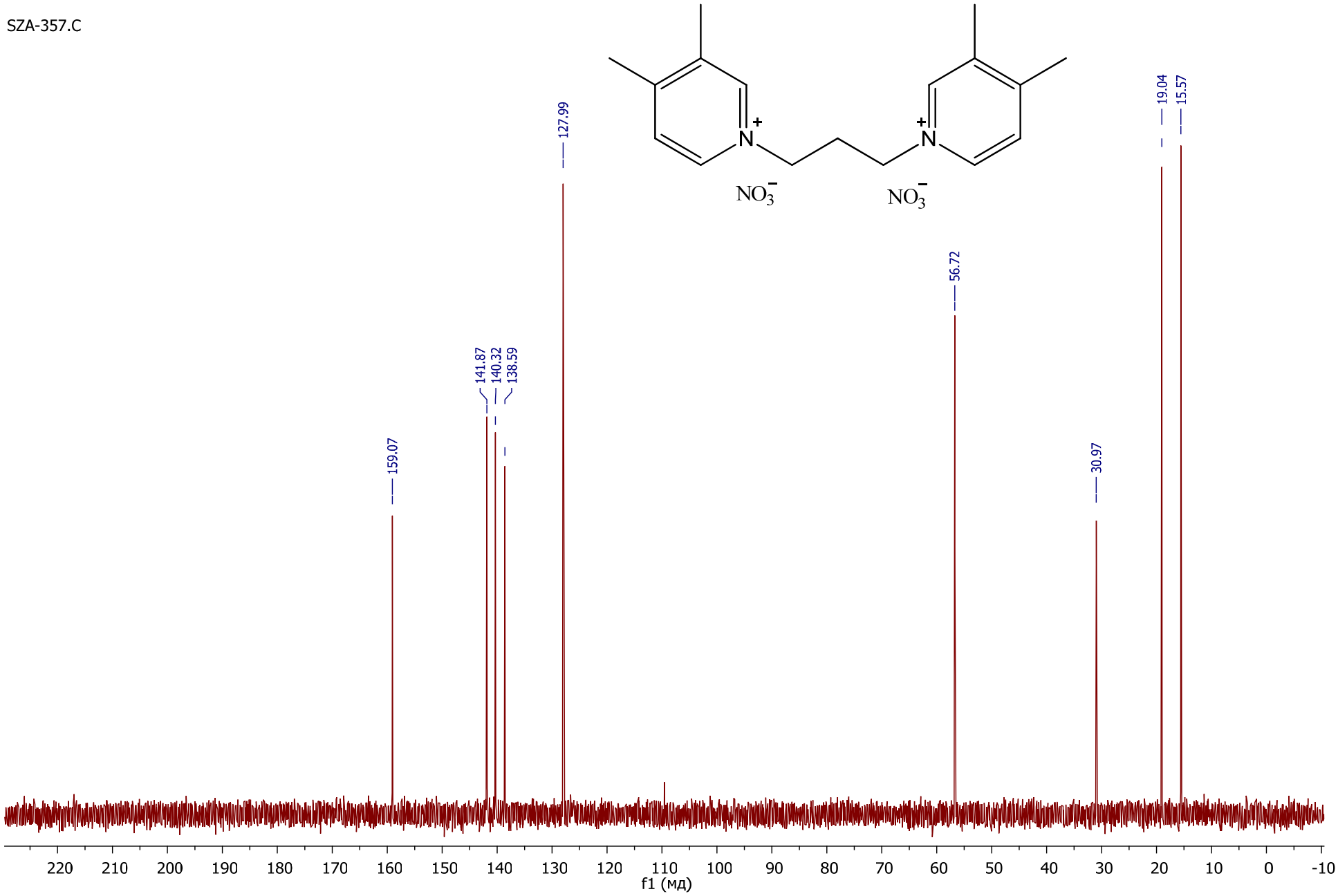
SZA-358.C



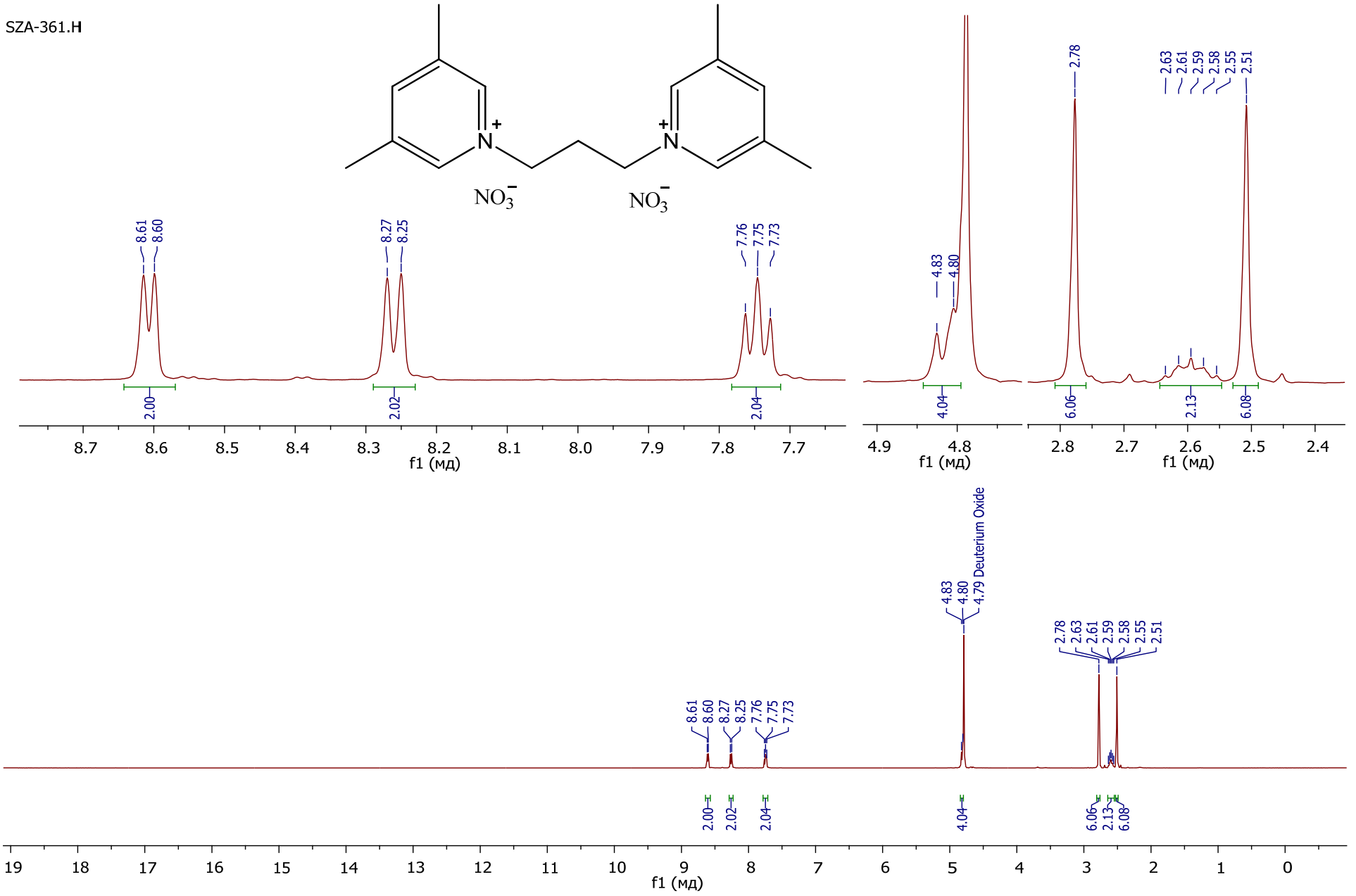
^{13}C NMR spectrum of **28** in D_2O



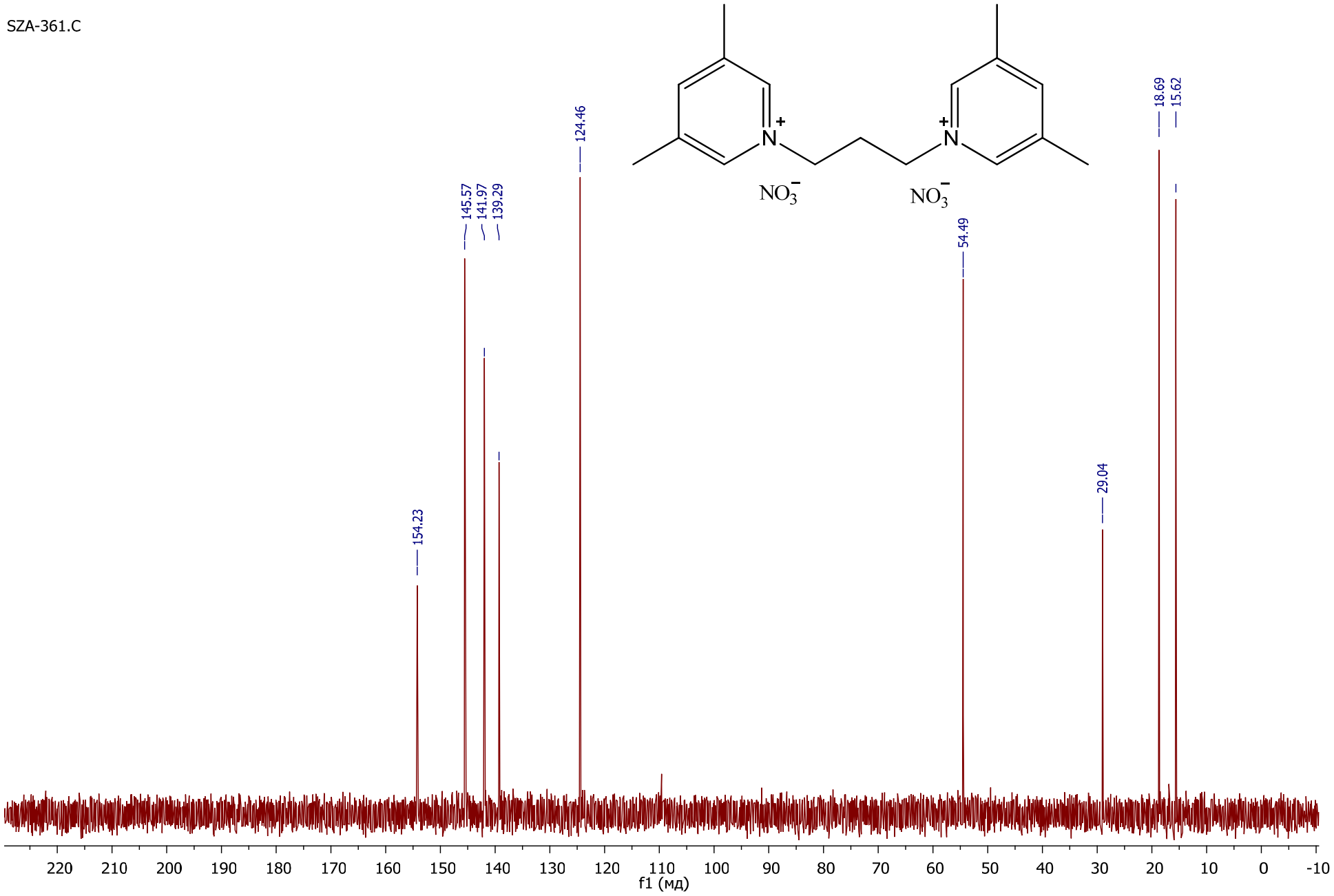
^{1}H NMR spectrum of **29** in D_2O



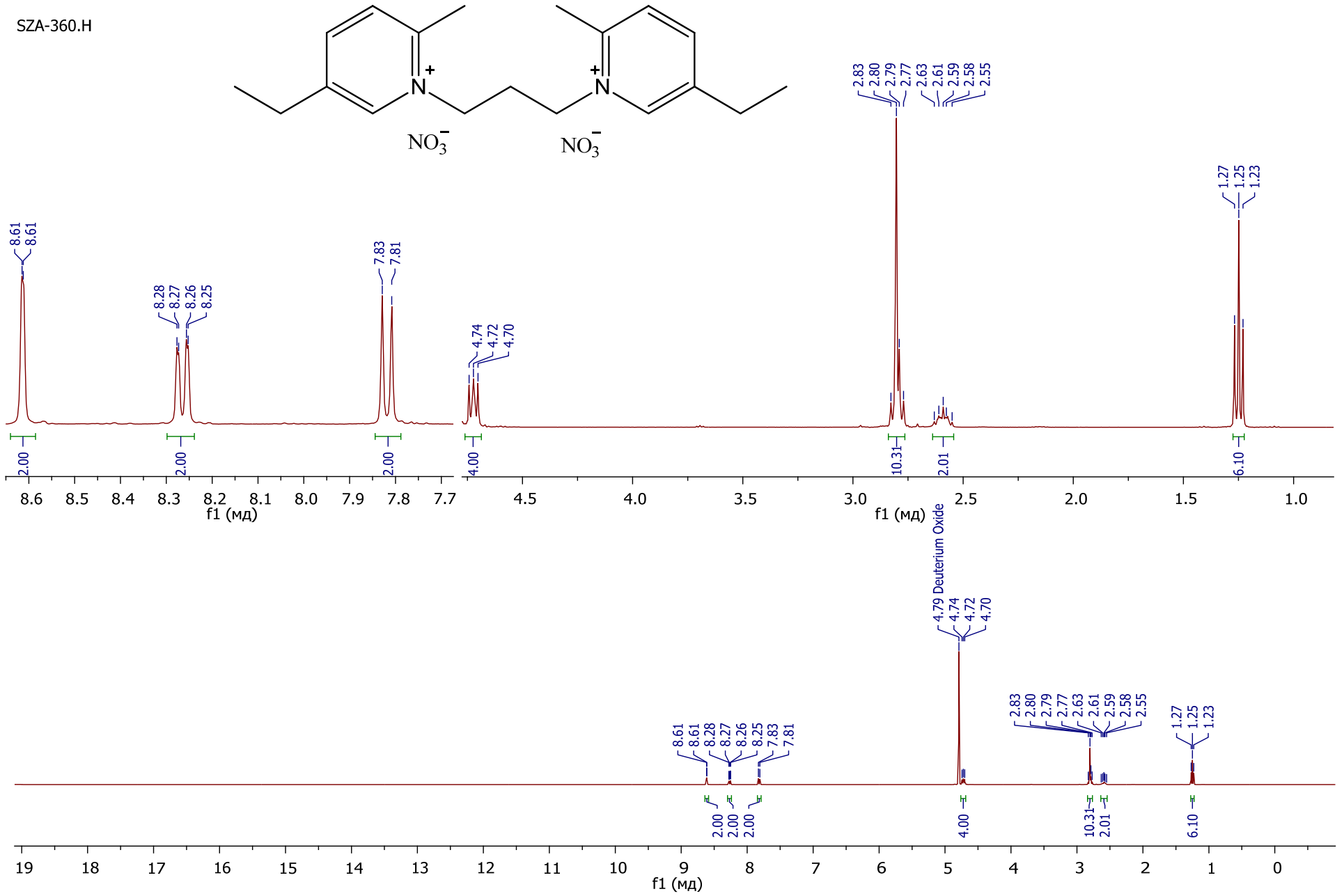
^{13}C NMR spectrum of **29** in D_2O



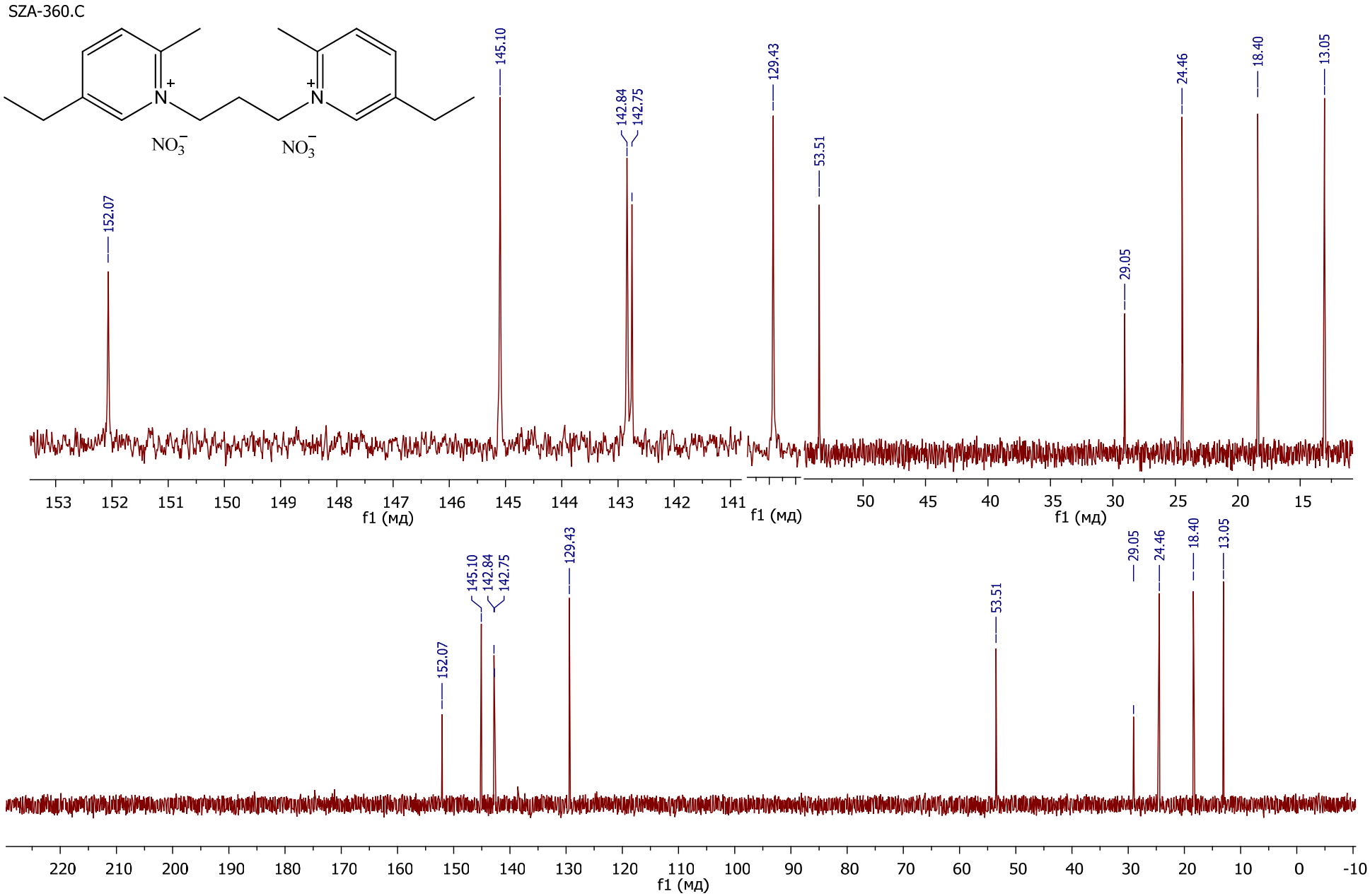
^{1}H NMR spectrum of **30** in D_2O



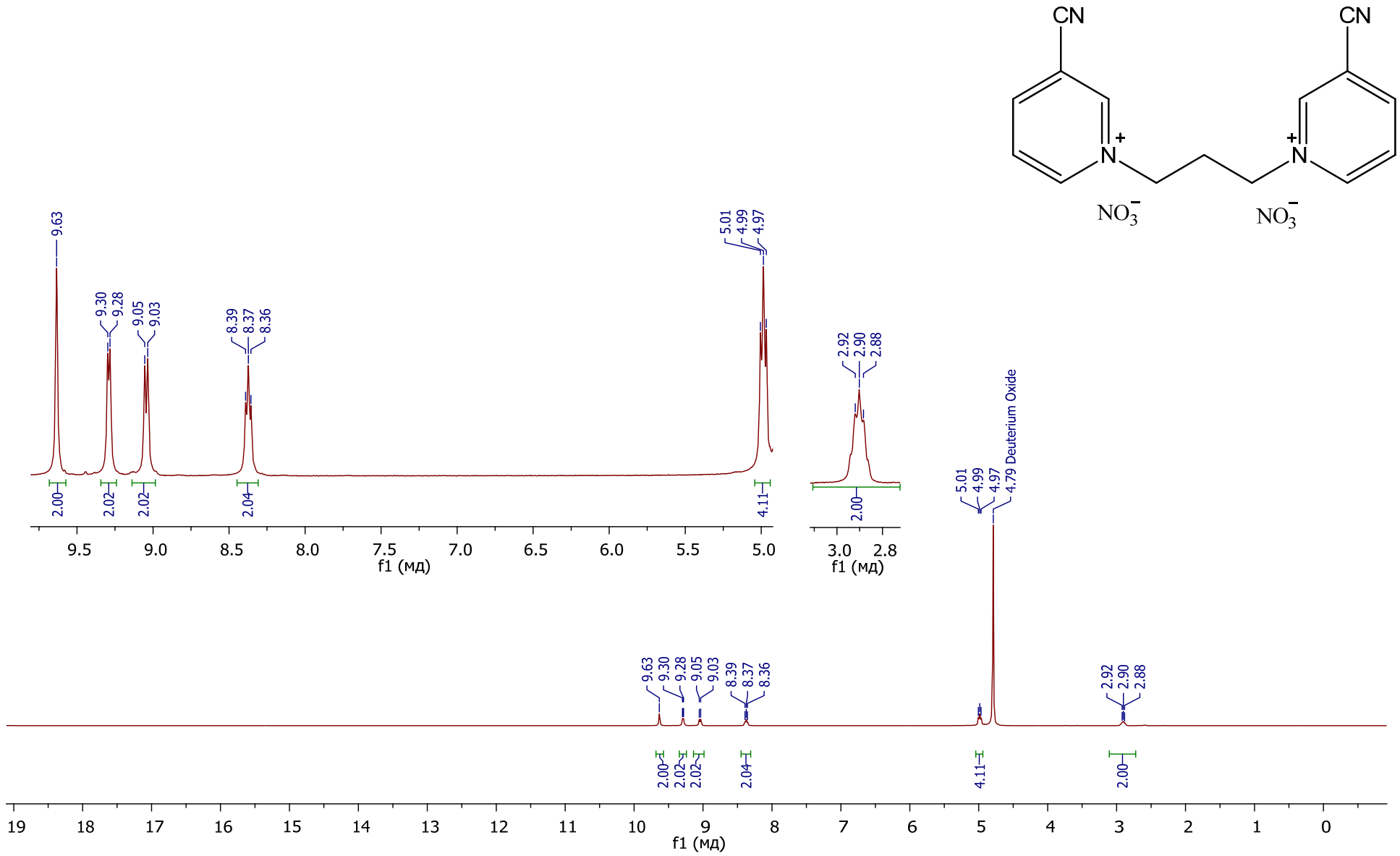
^{13}C NMR spectrum of **30** in D_2O



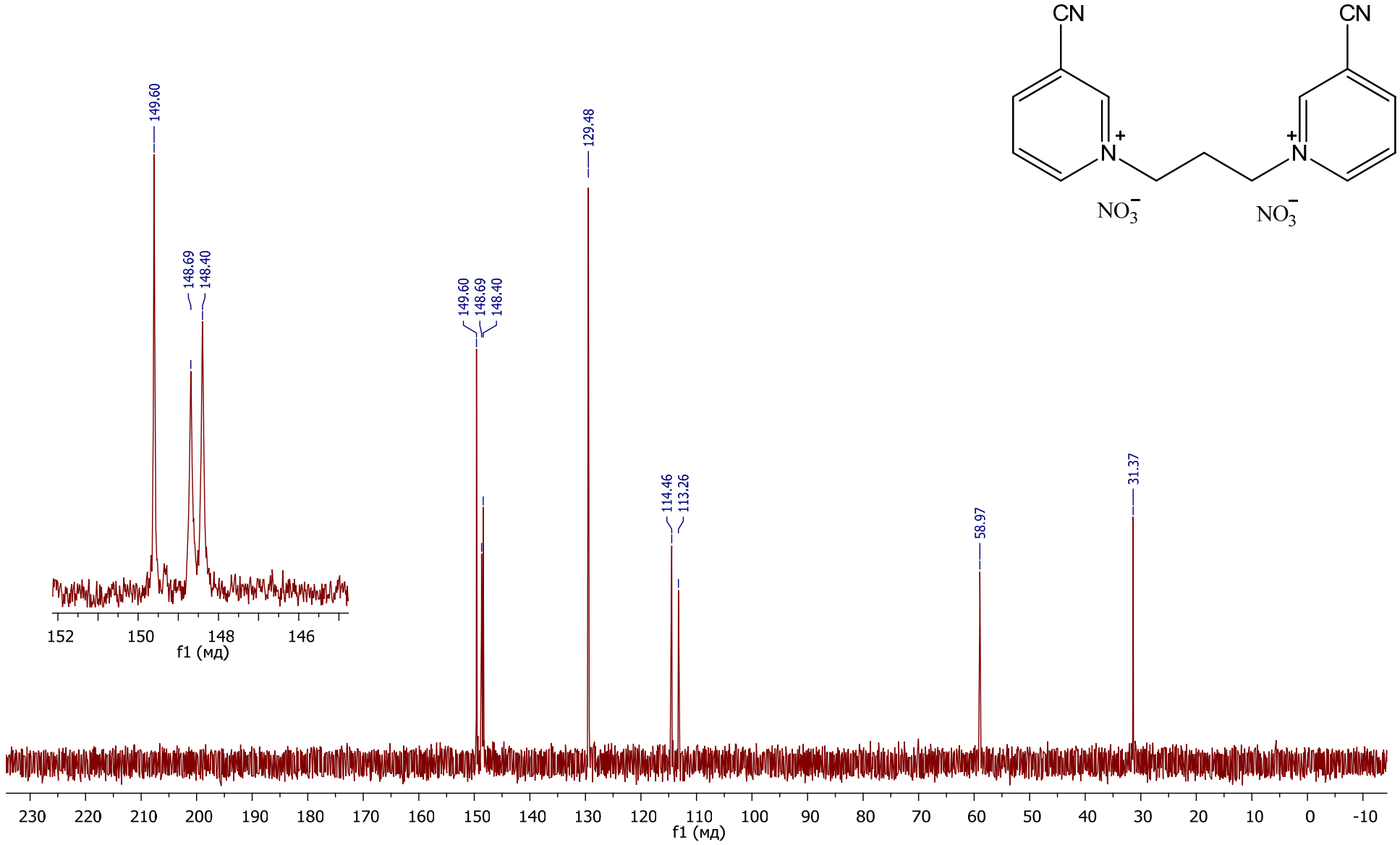
^{1}H NMR spectrum of **31** in D_2O



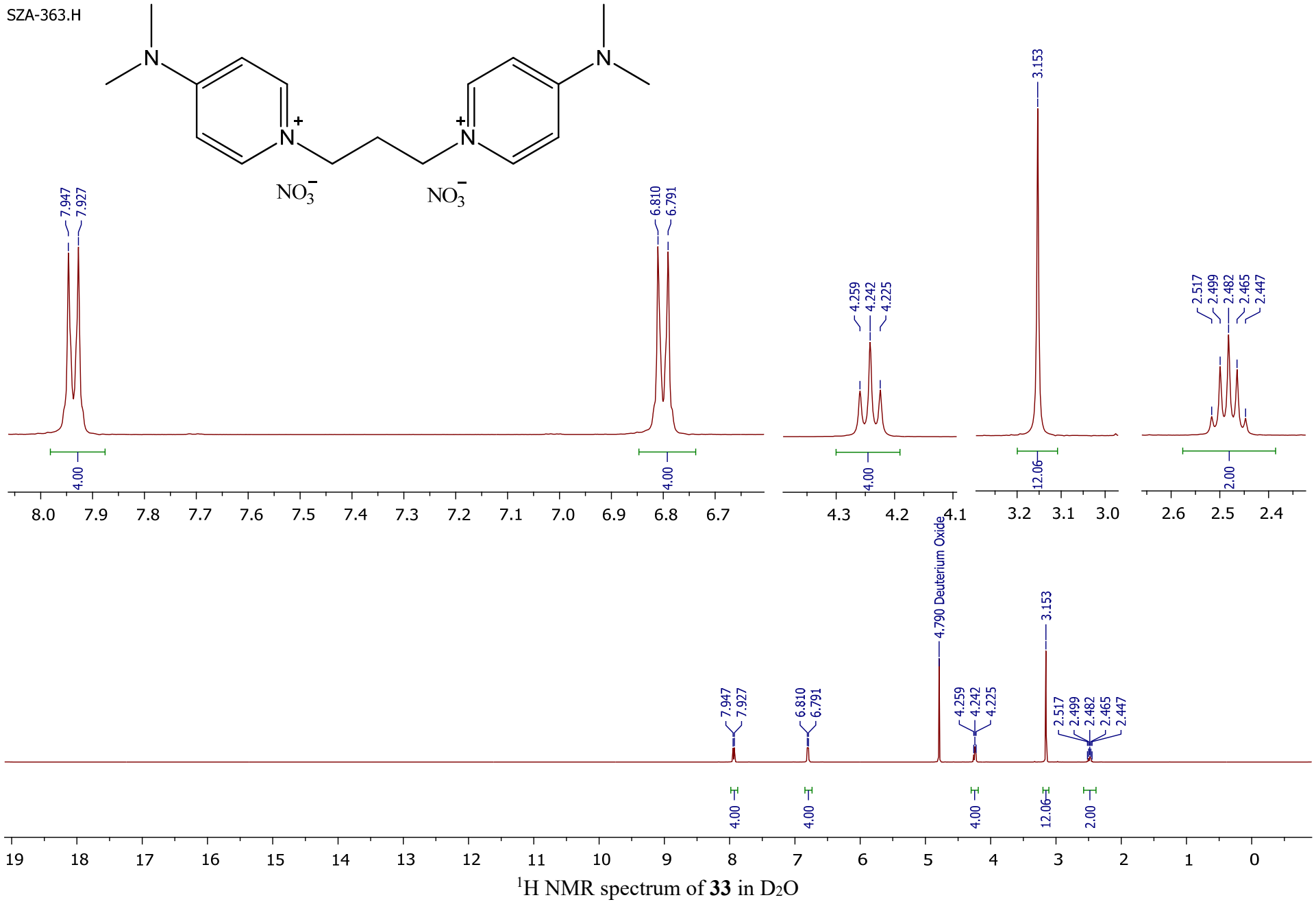
^{13}C NMR spectrum of **31** in D_2O



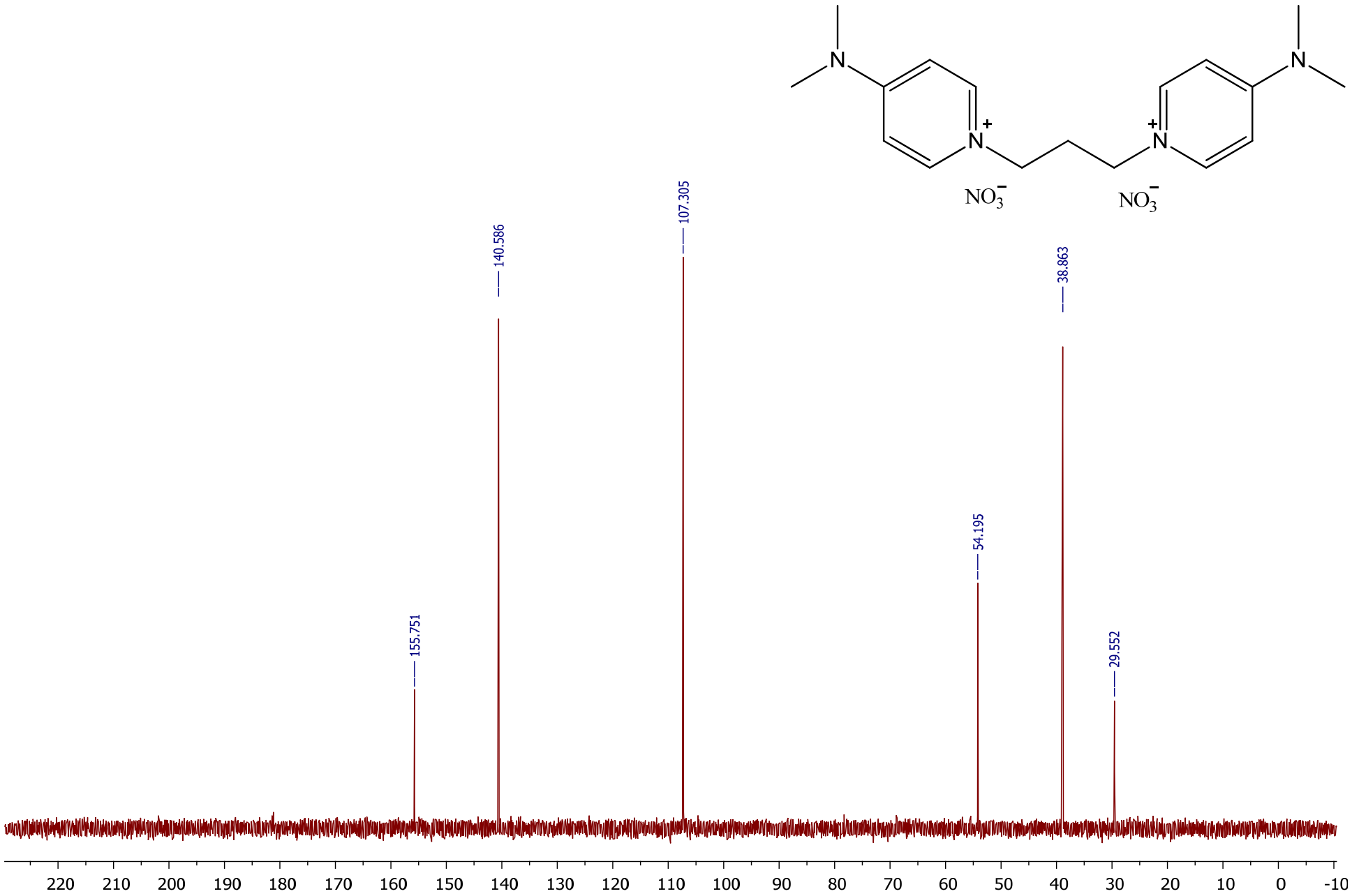
^{1}H NMR spectrum of **32** in D_2O



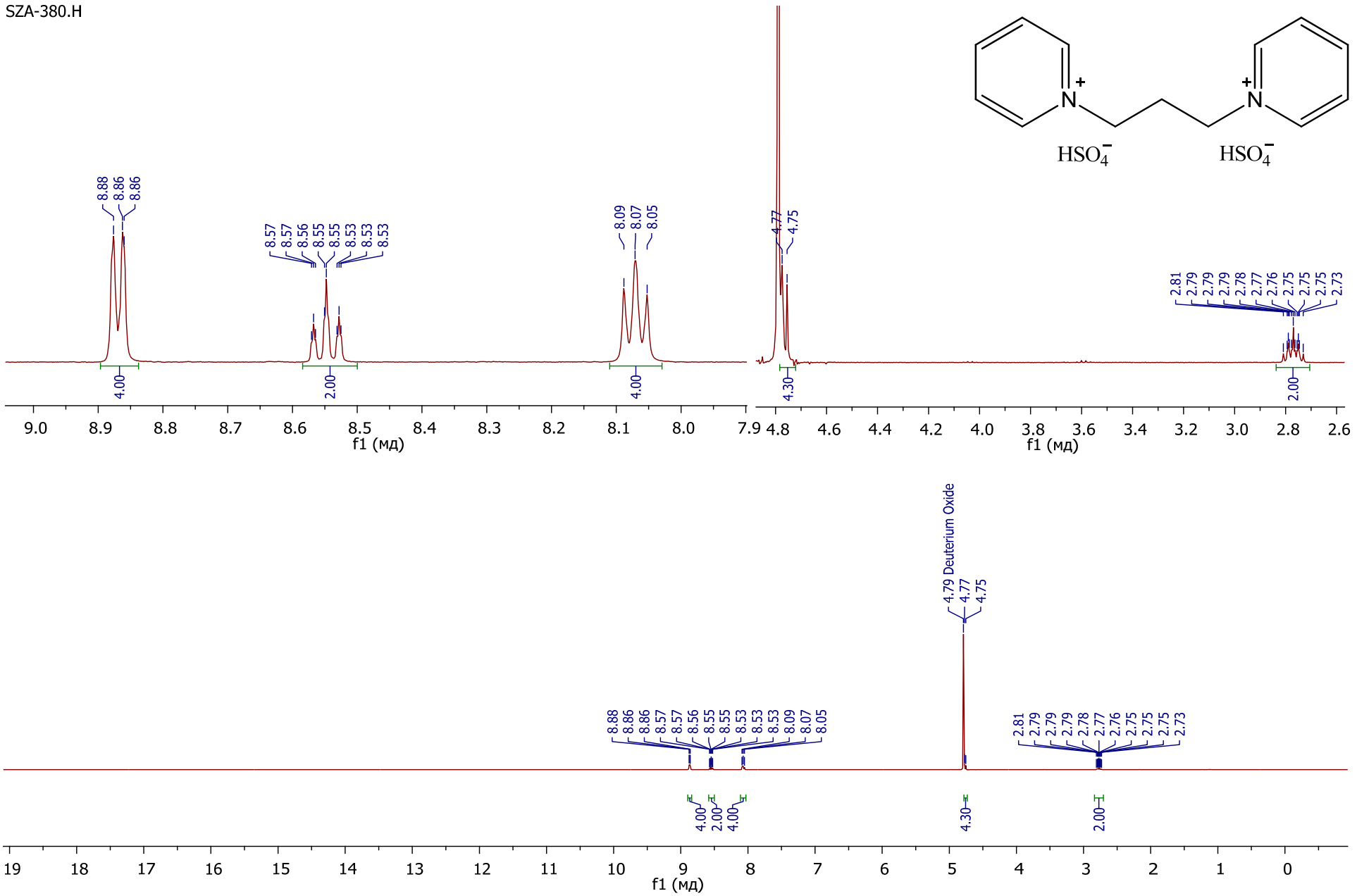
^{13}C NMR spectrum of **32** in D_2O



^{1}H NMR spectrum of **33** in D_2O

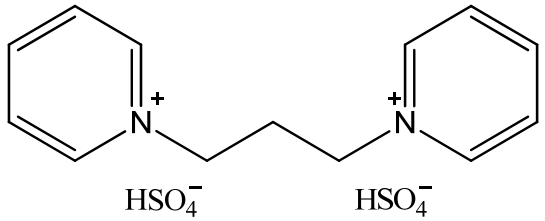


^{13}C NMR spectrum of **33** in D_2O

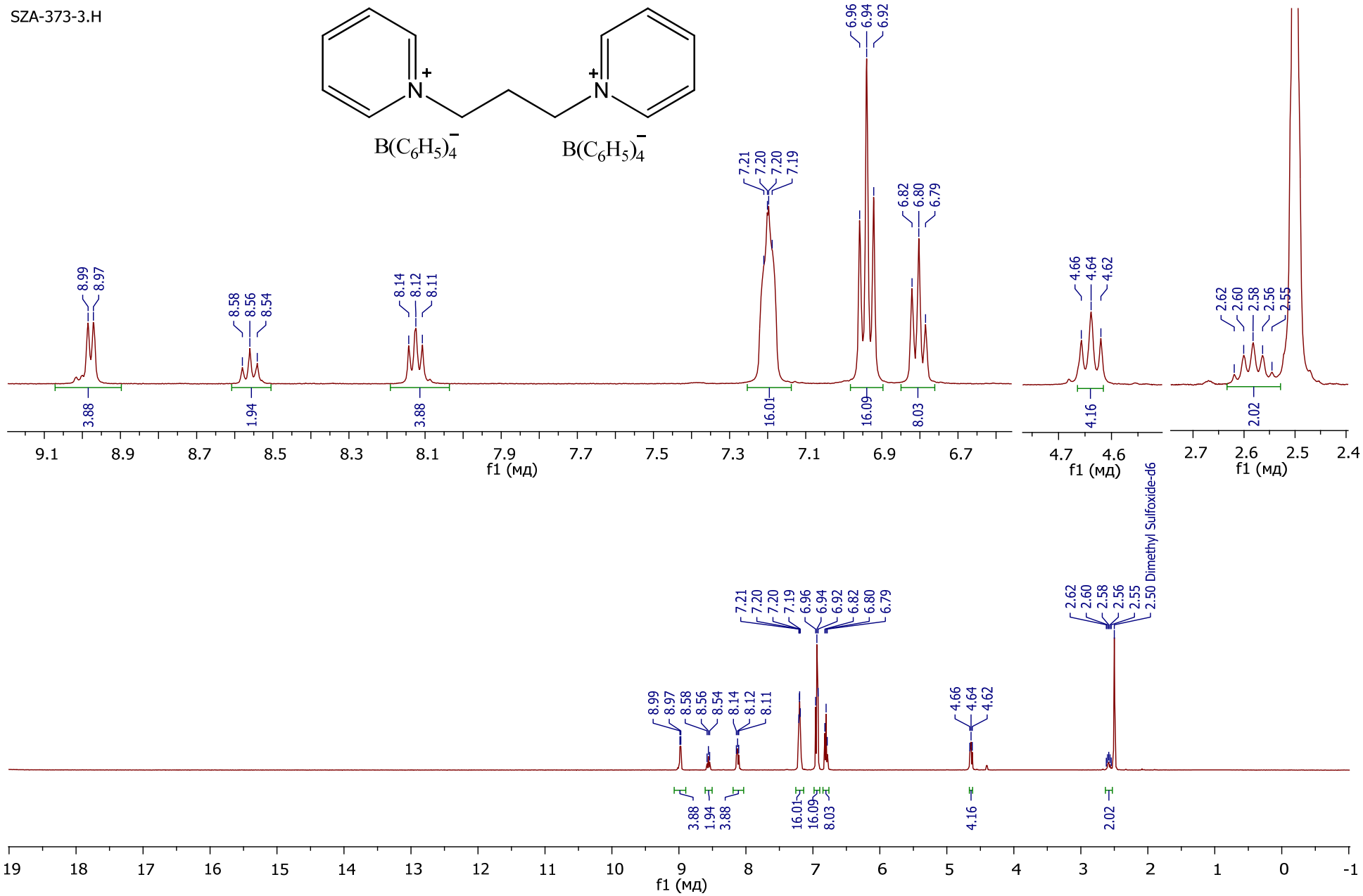


^{1}H NMR spectrum of **34** in D_2O

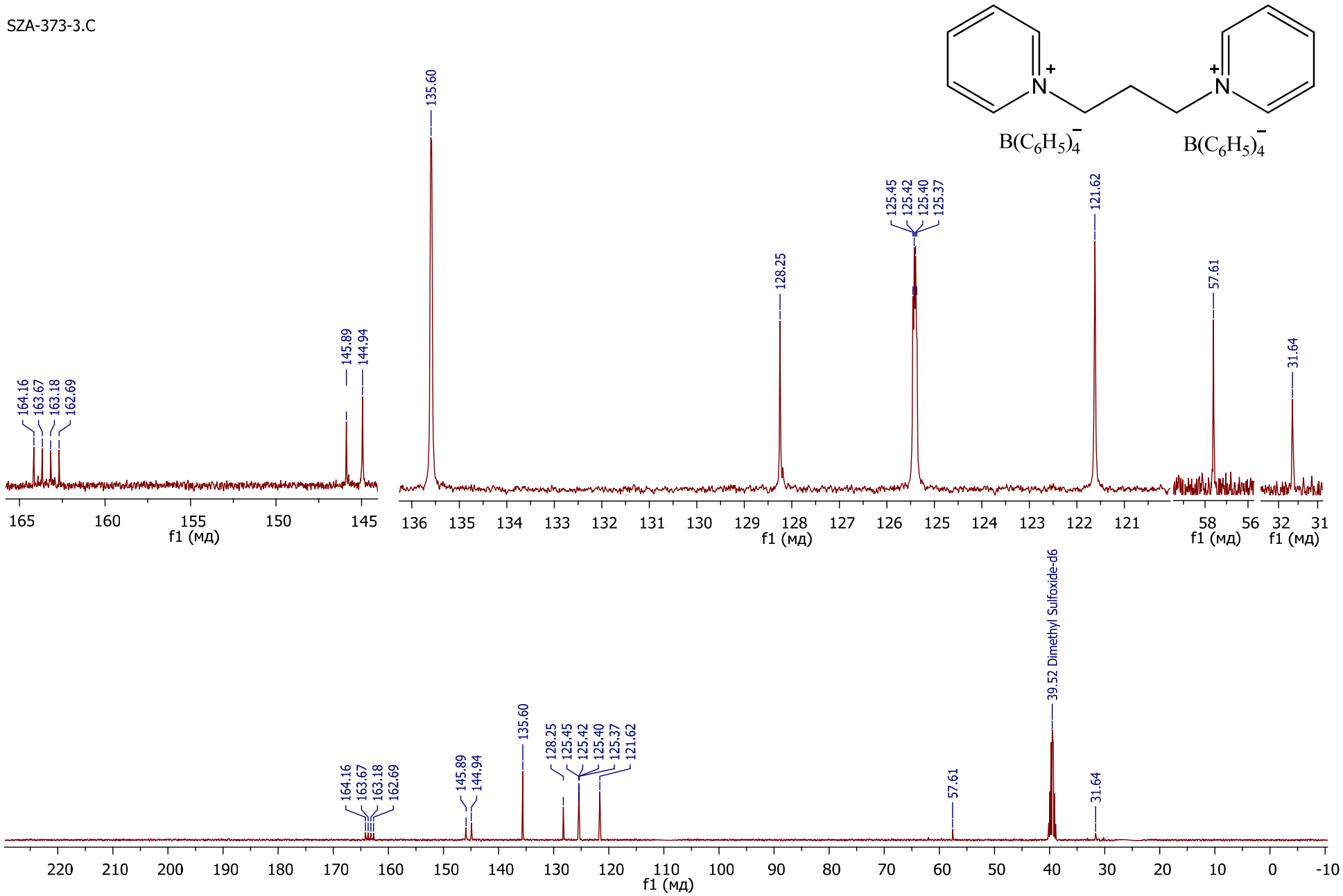
SZA-380.C



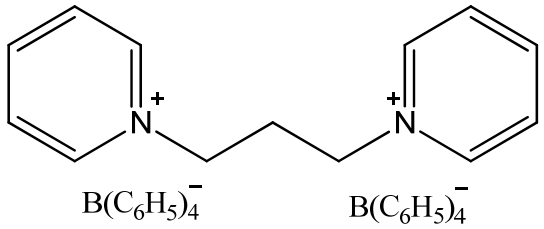
^{13}C NMR spectrum of **34** in D_2O

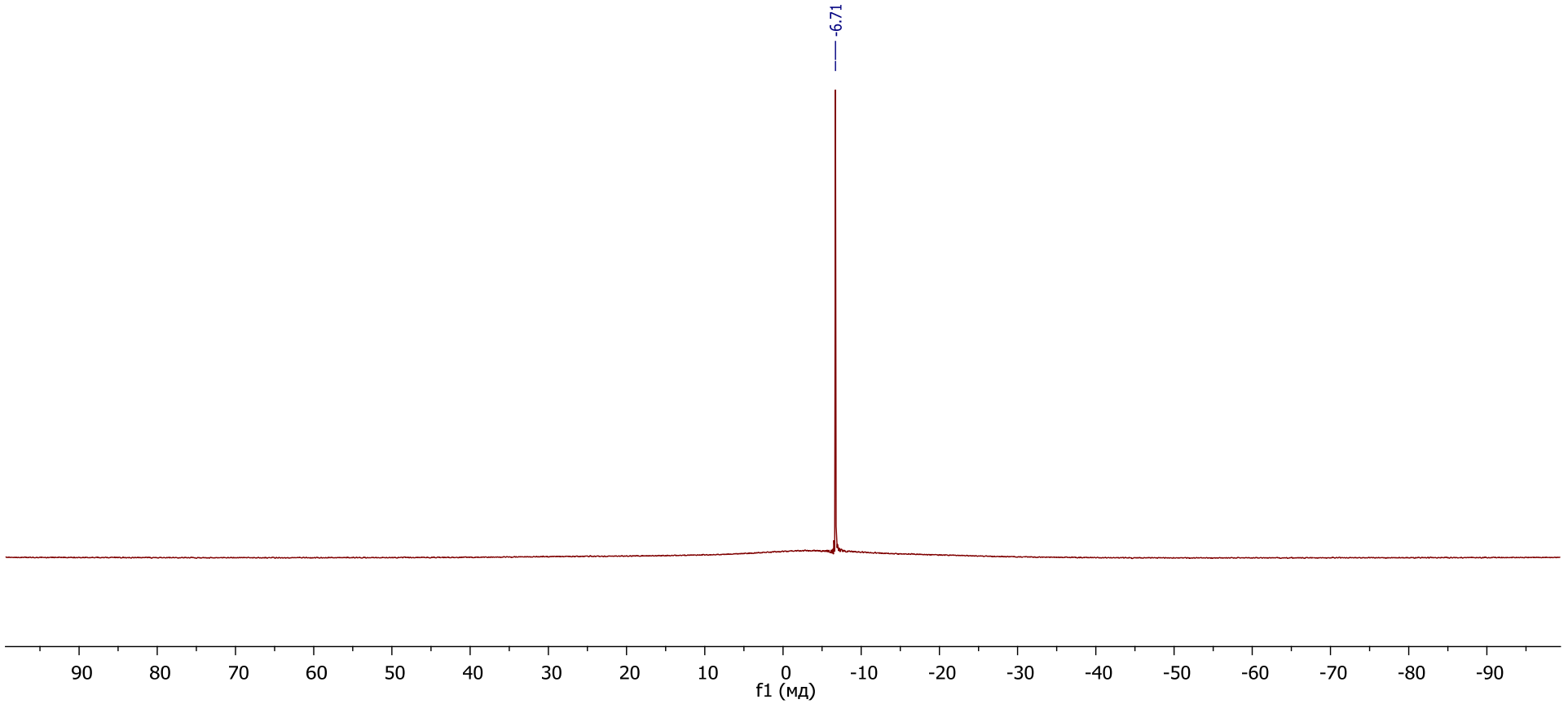


^{1}H NMR spectrum of **35** in DMSO-d$_6$

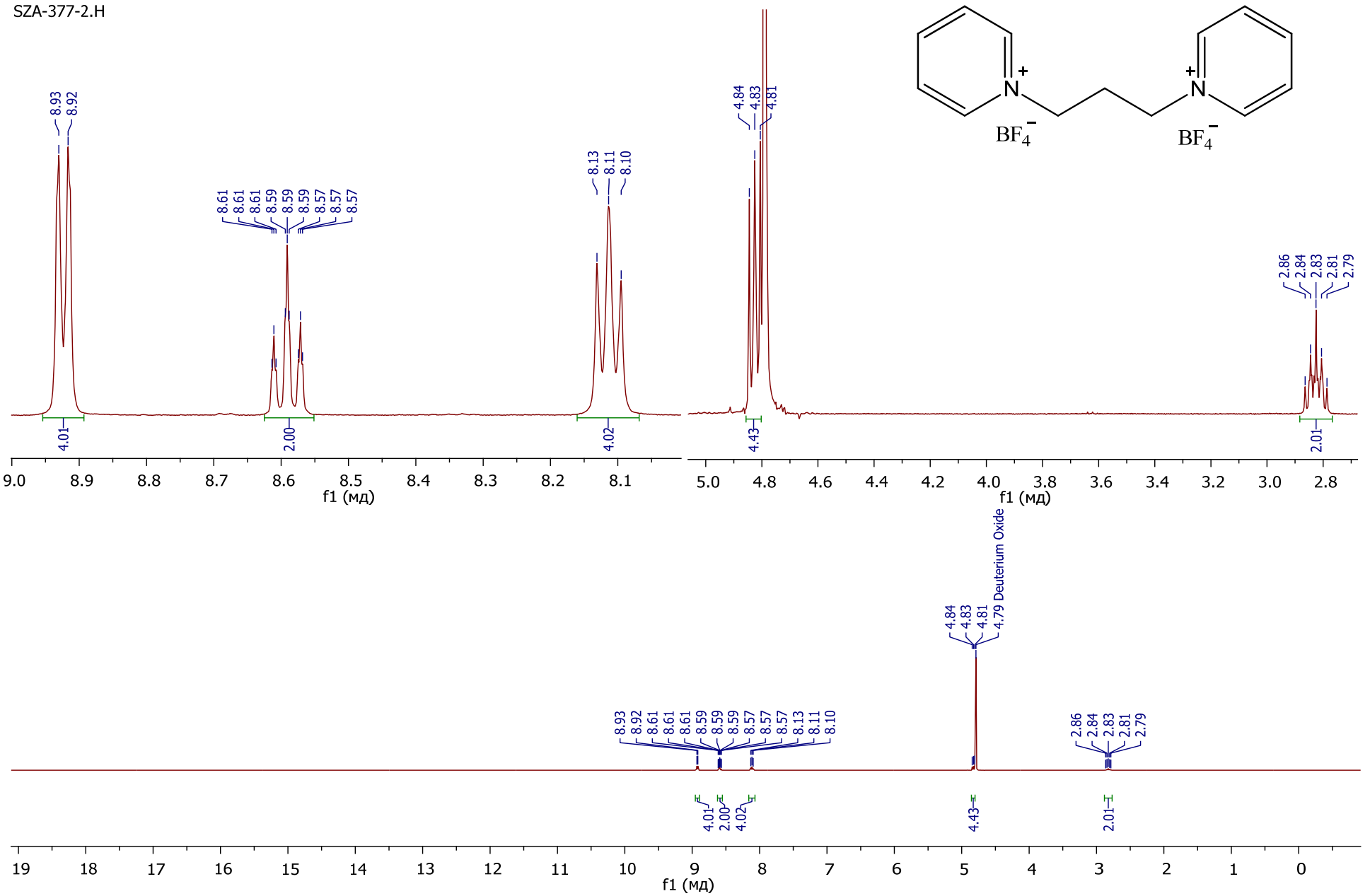


^{13}C NMR spectrum of **35** in DMSO-d$_6$



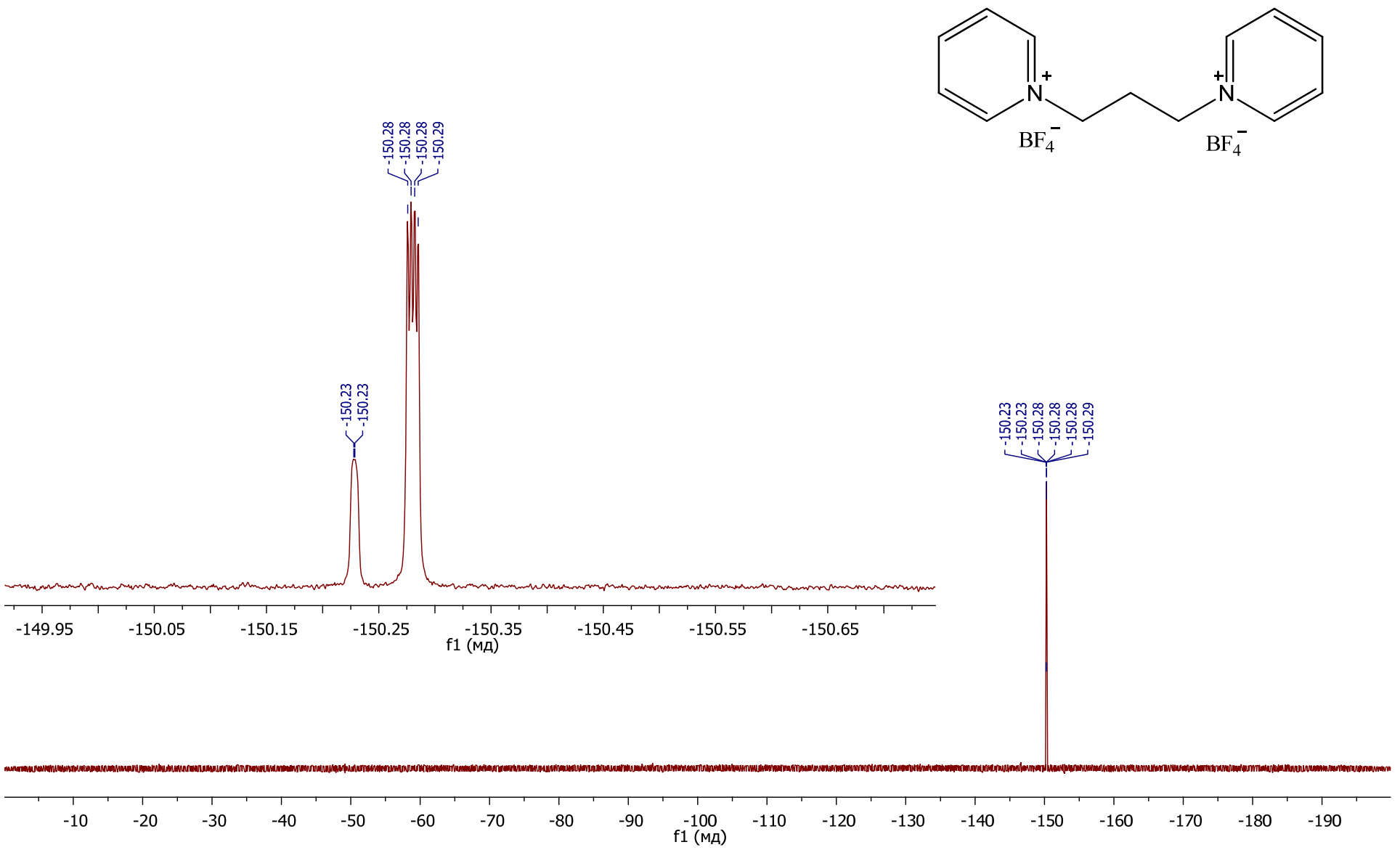


^{11}B NMR spectrum of **35** in DMSO-d_6



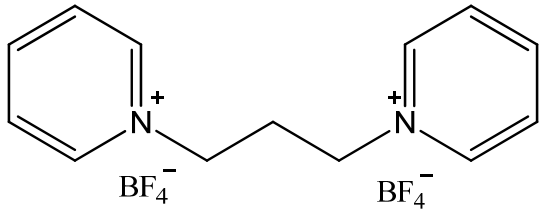
^{1}H NMR spectrum of **36** in D_2O

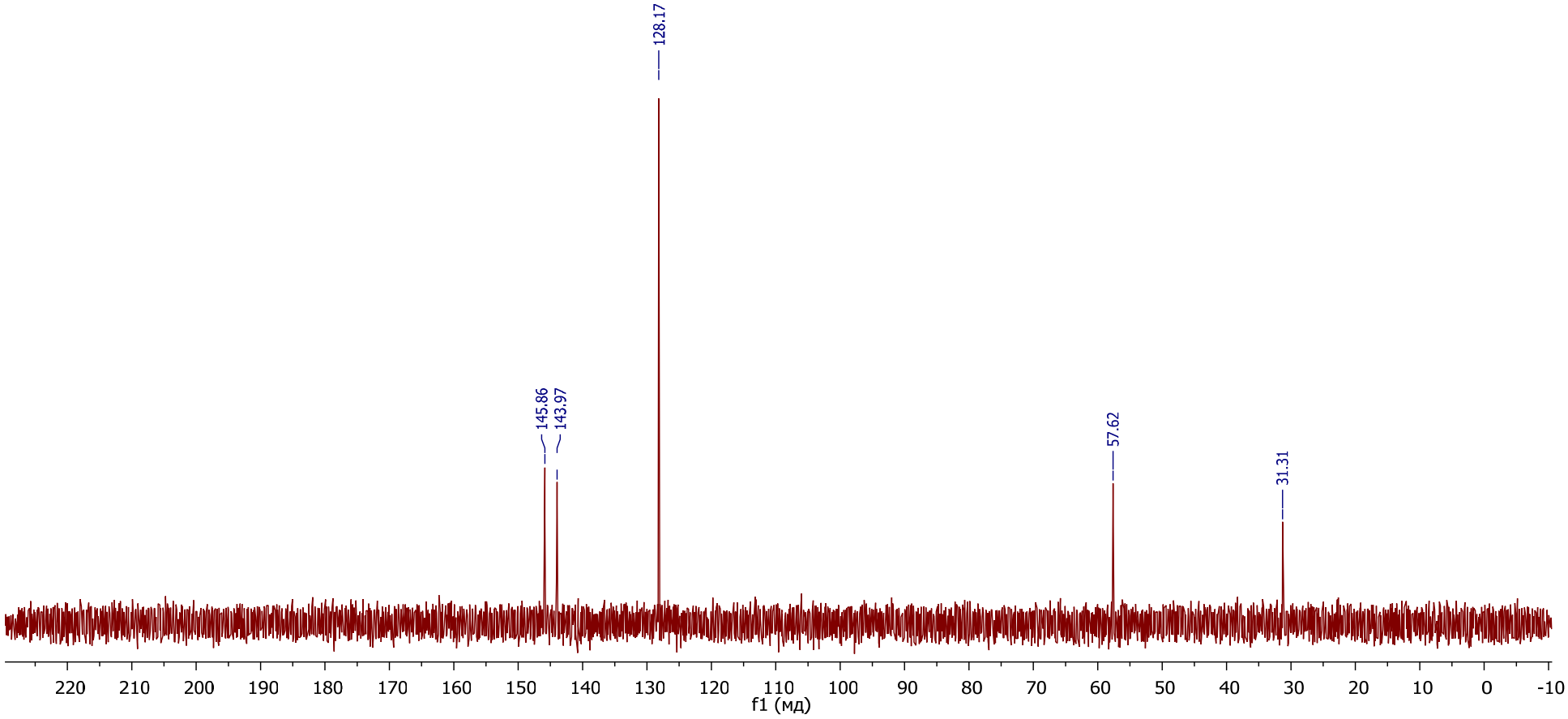
SZA-377-2.F



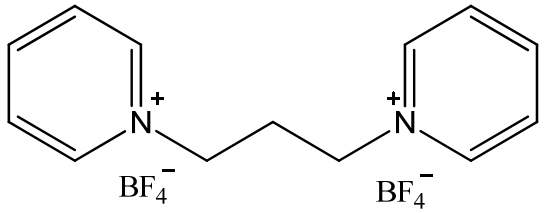
^{19}F NMR spectrum of **36** in D_2O

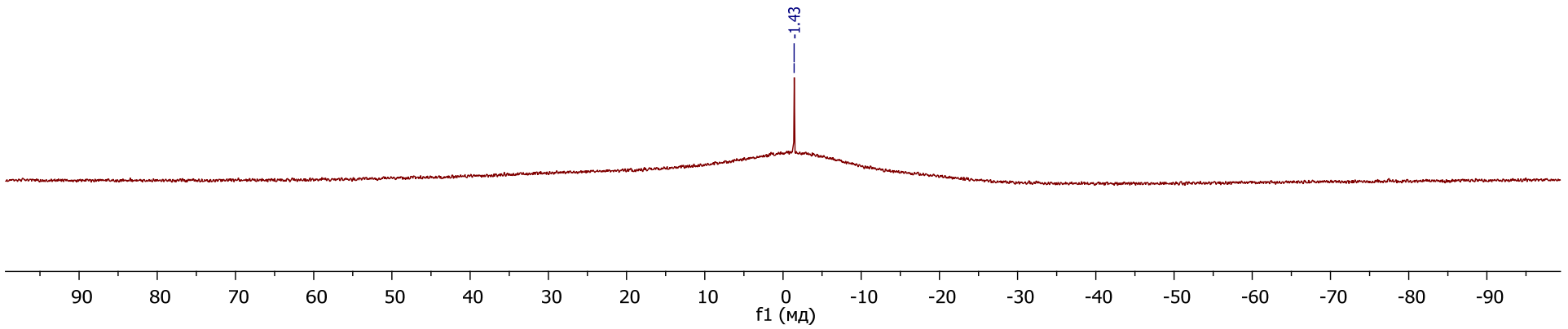
SZA-377-2.C



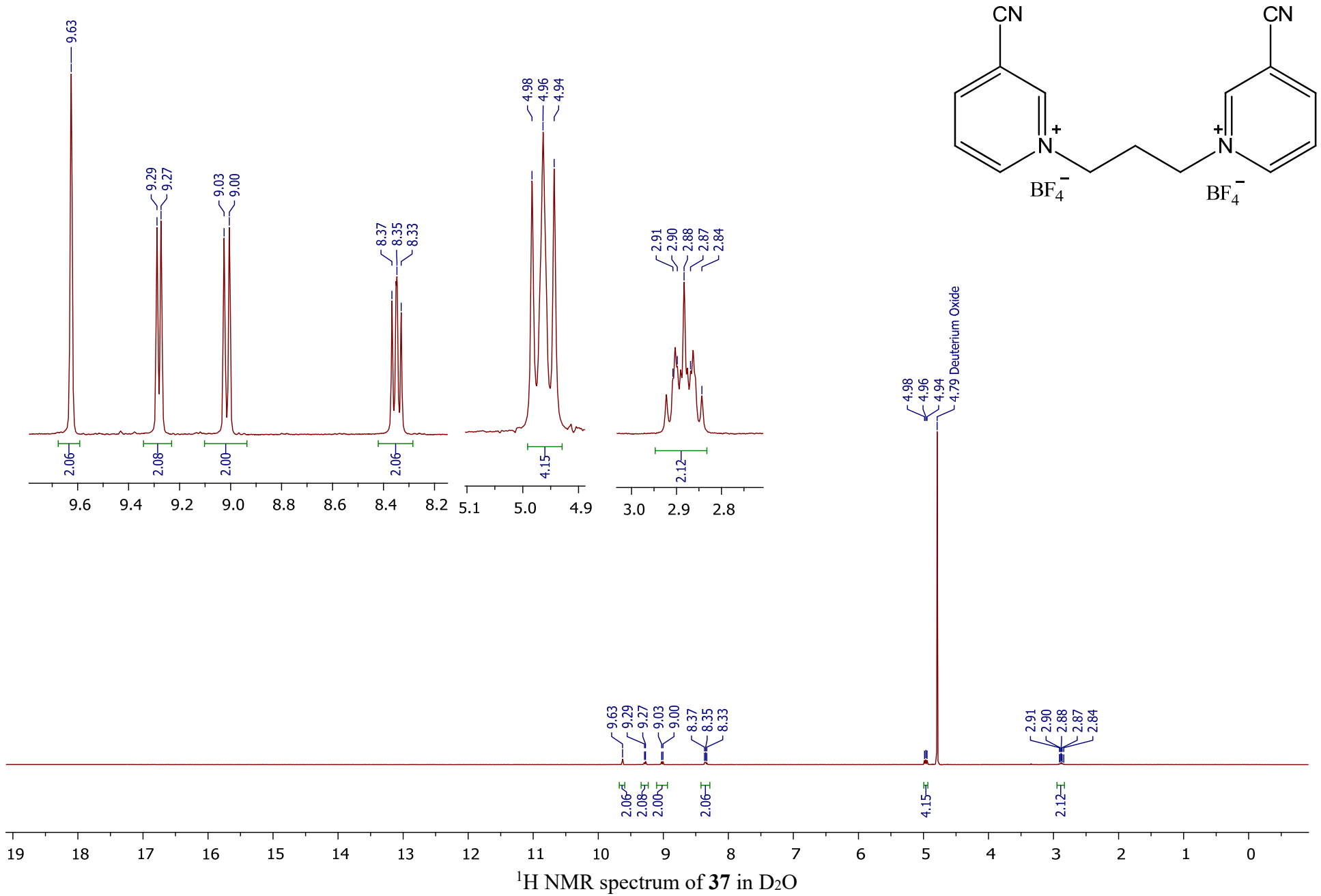


^{13}C NMR spectrum of **36** in D_2O

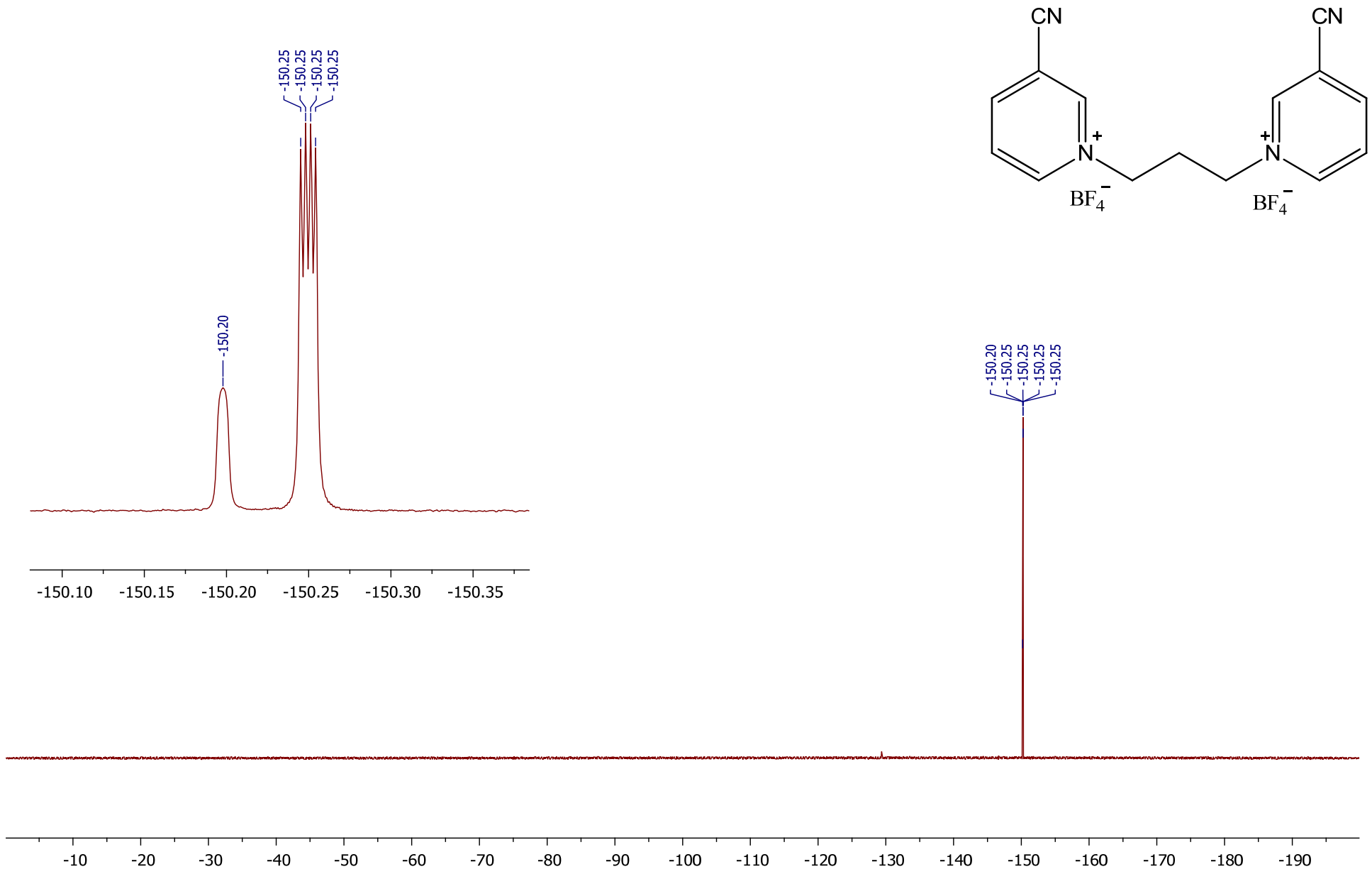




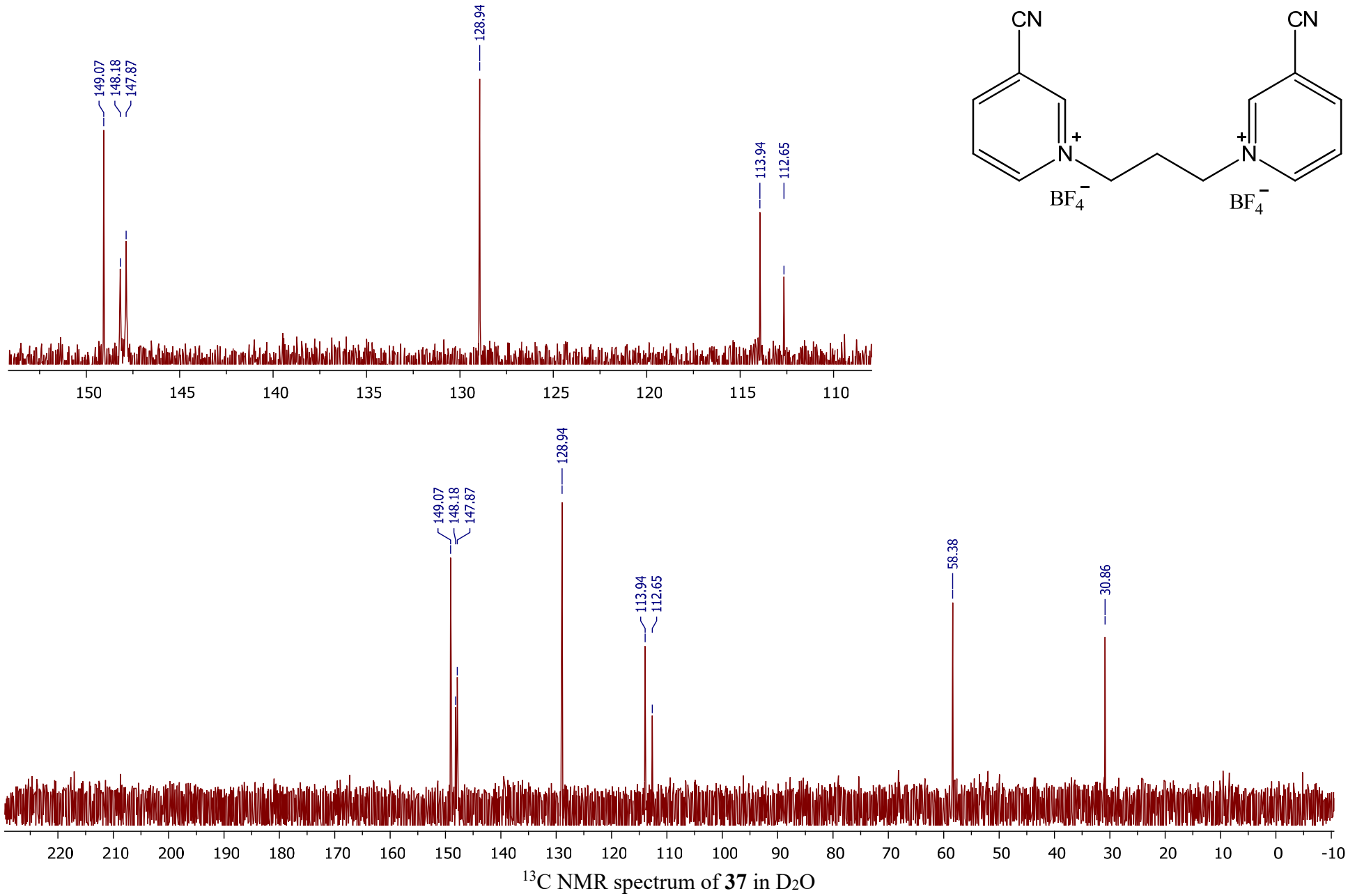
^{11}B NMR spectrum of **36** in D_2O



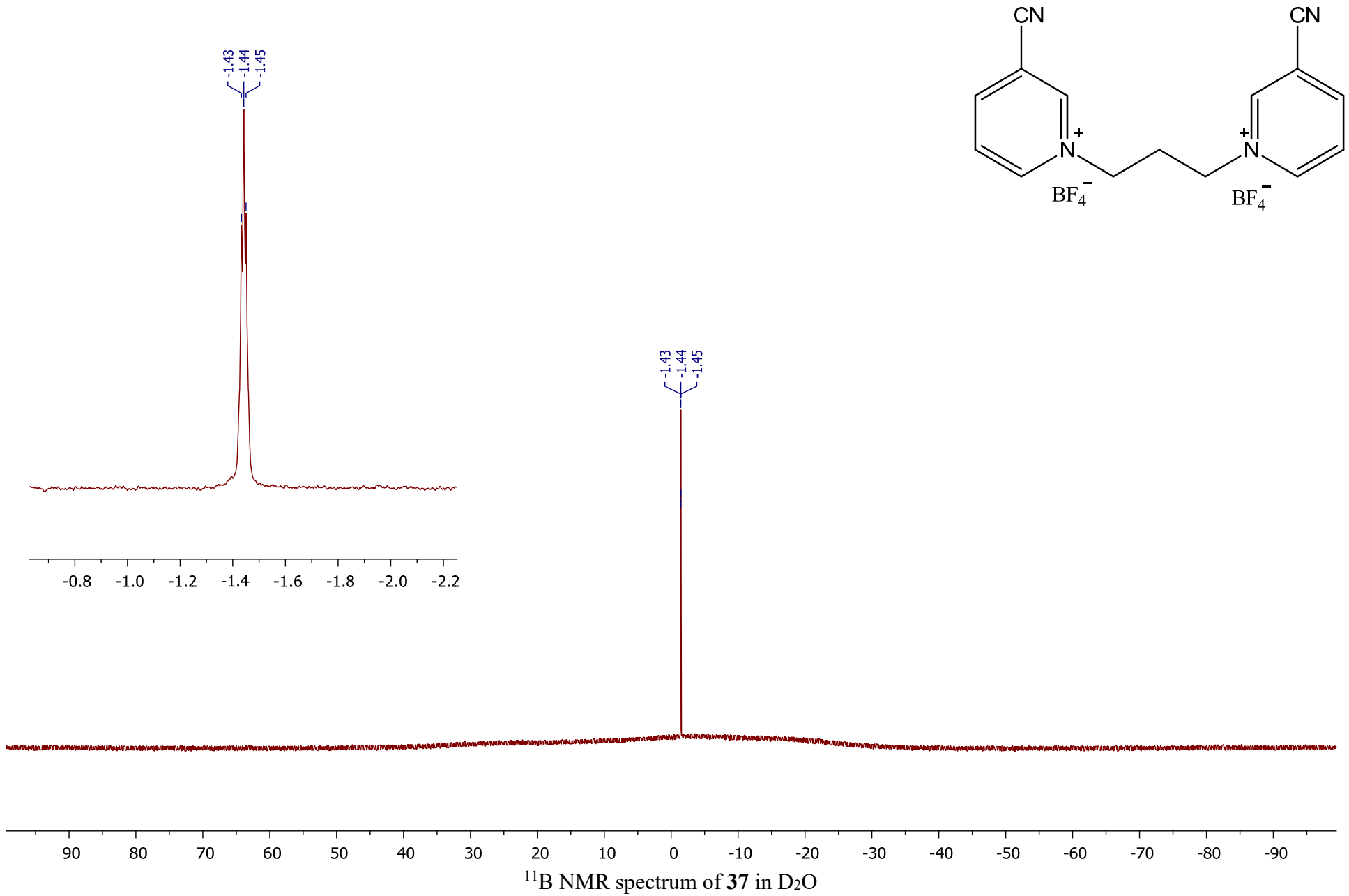
^{1}H NMR spectrum of **37** in D_2O



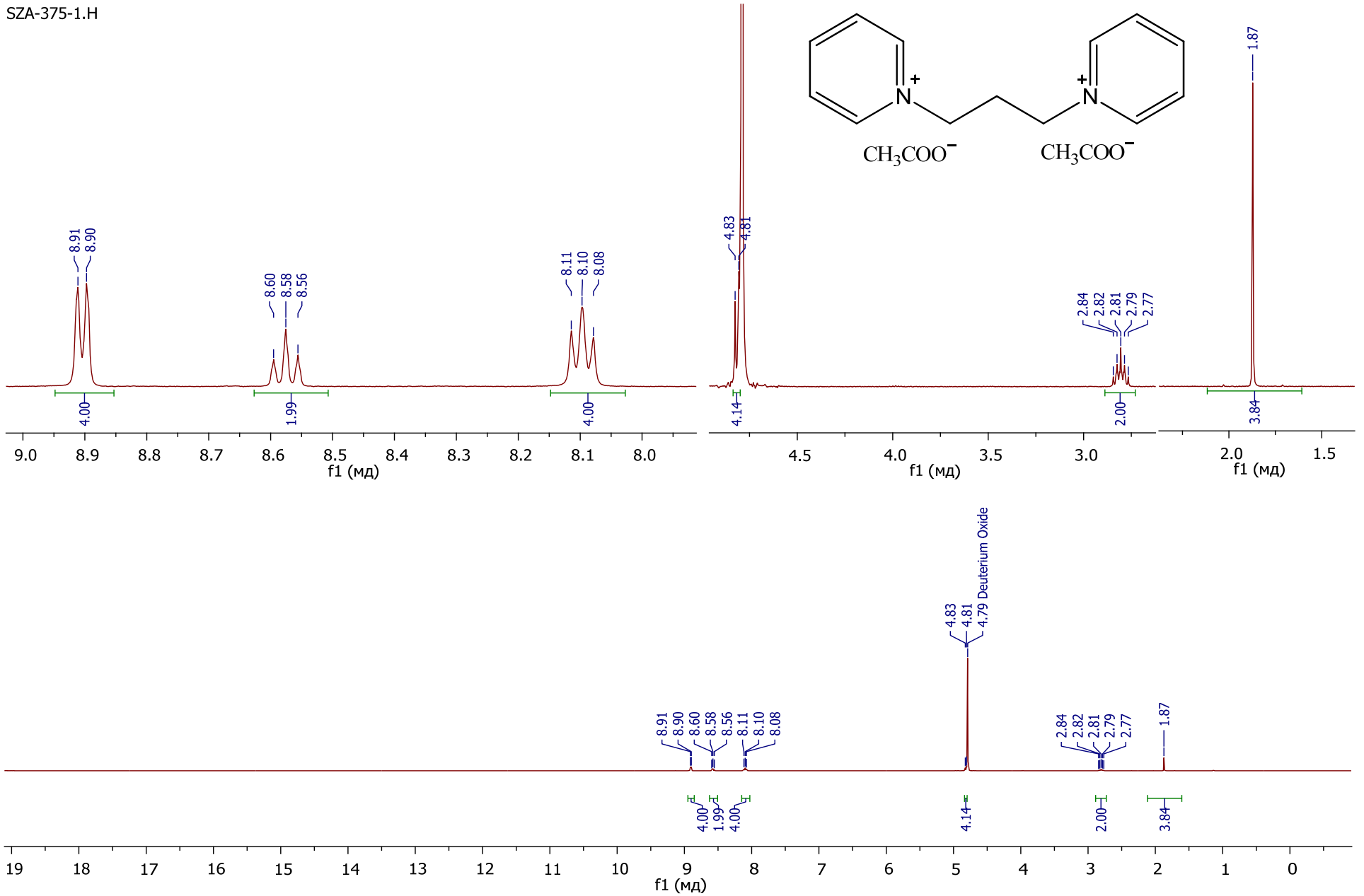
^{19}F NMR spectrum of **37** in D_2O



^{13}C NMR spectrum of **37** in D_2O

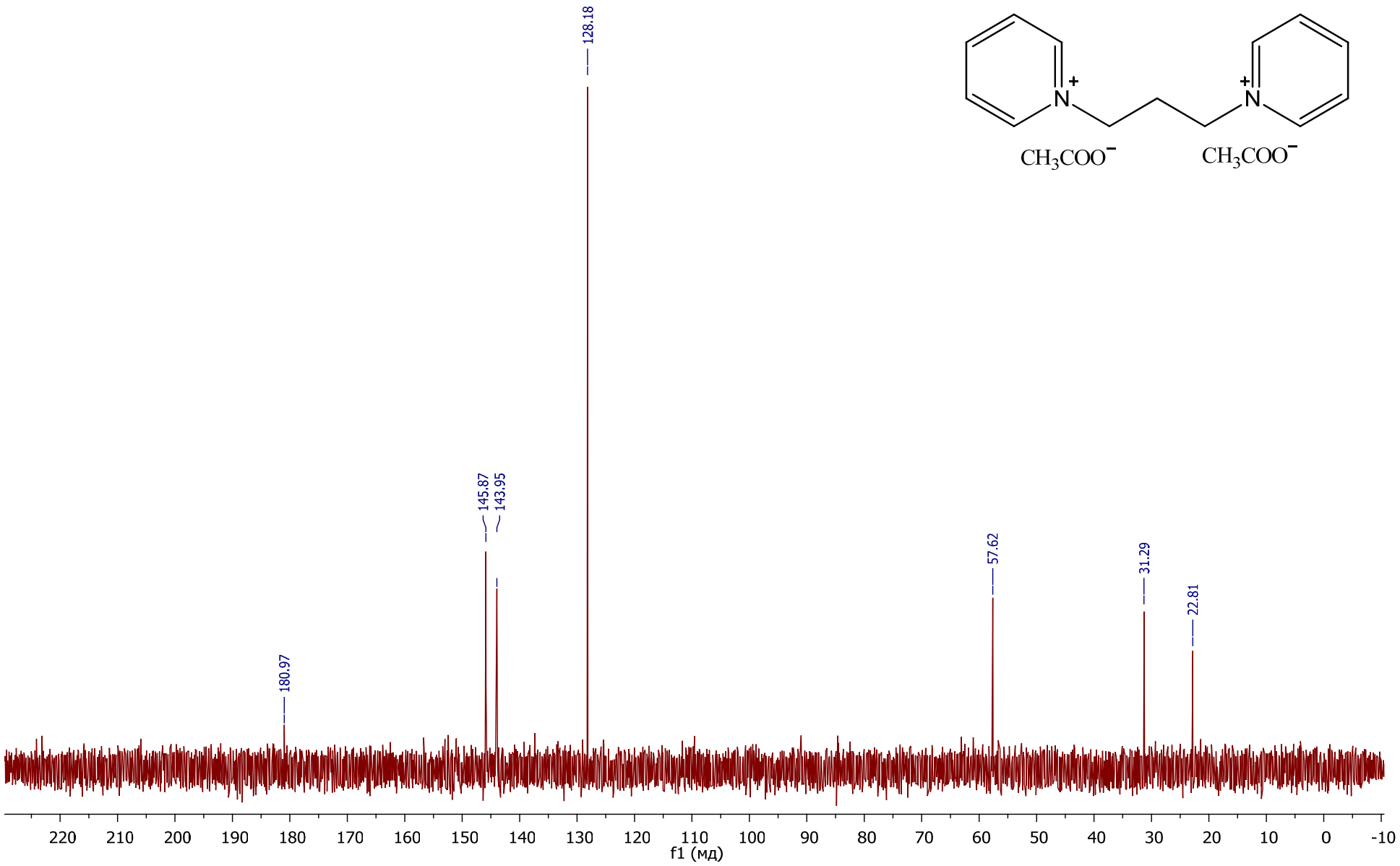


^{11}B NMR spectrum of **37** in D_2O

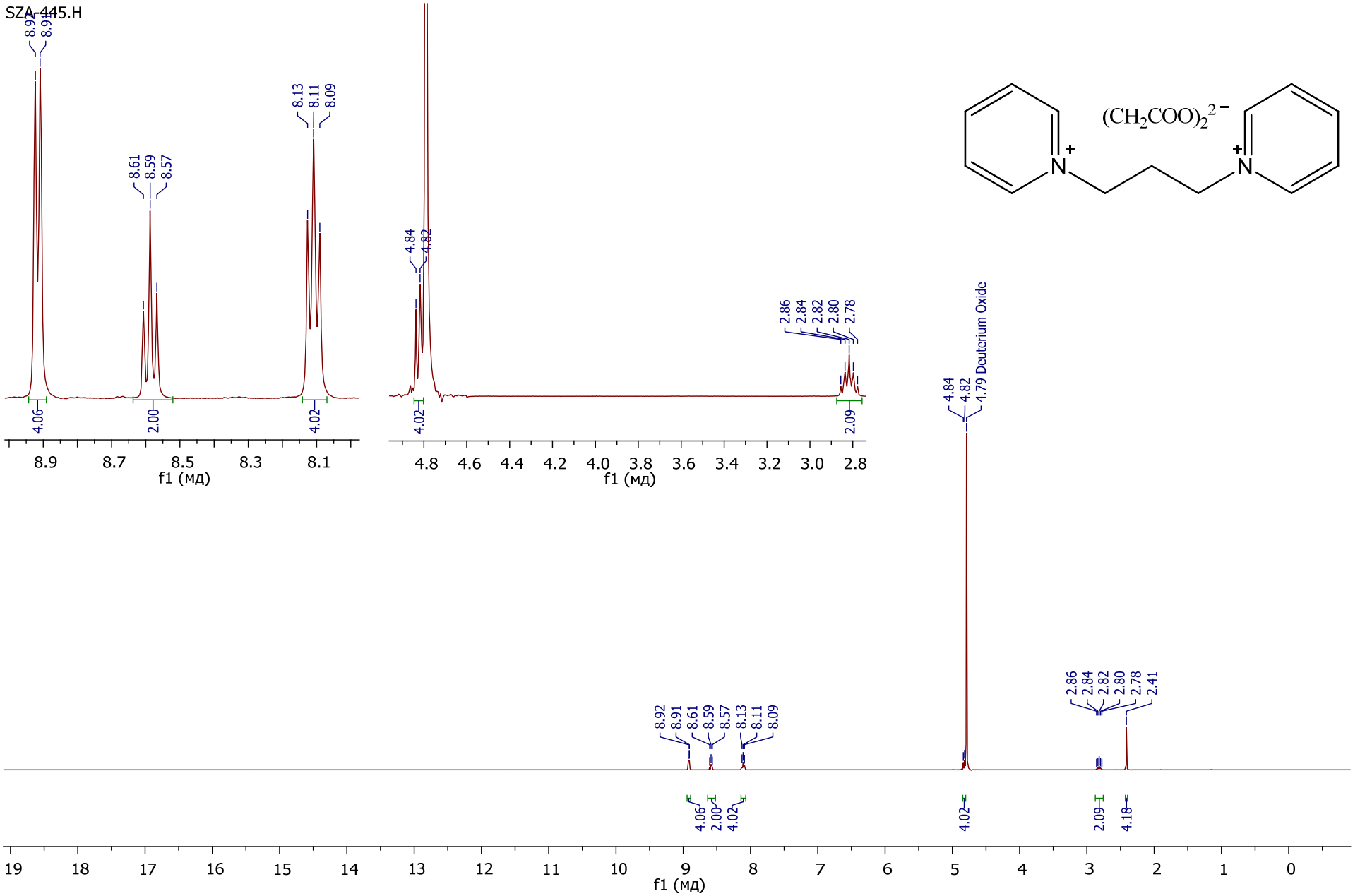


^{1}H NMR spectrum of **38** in D_2O

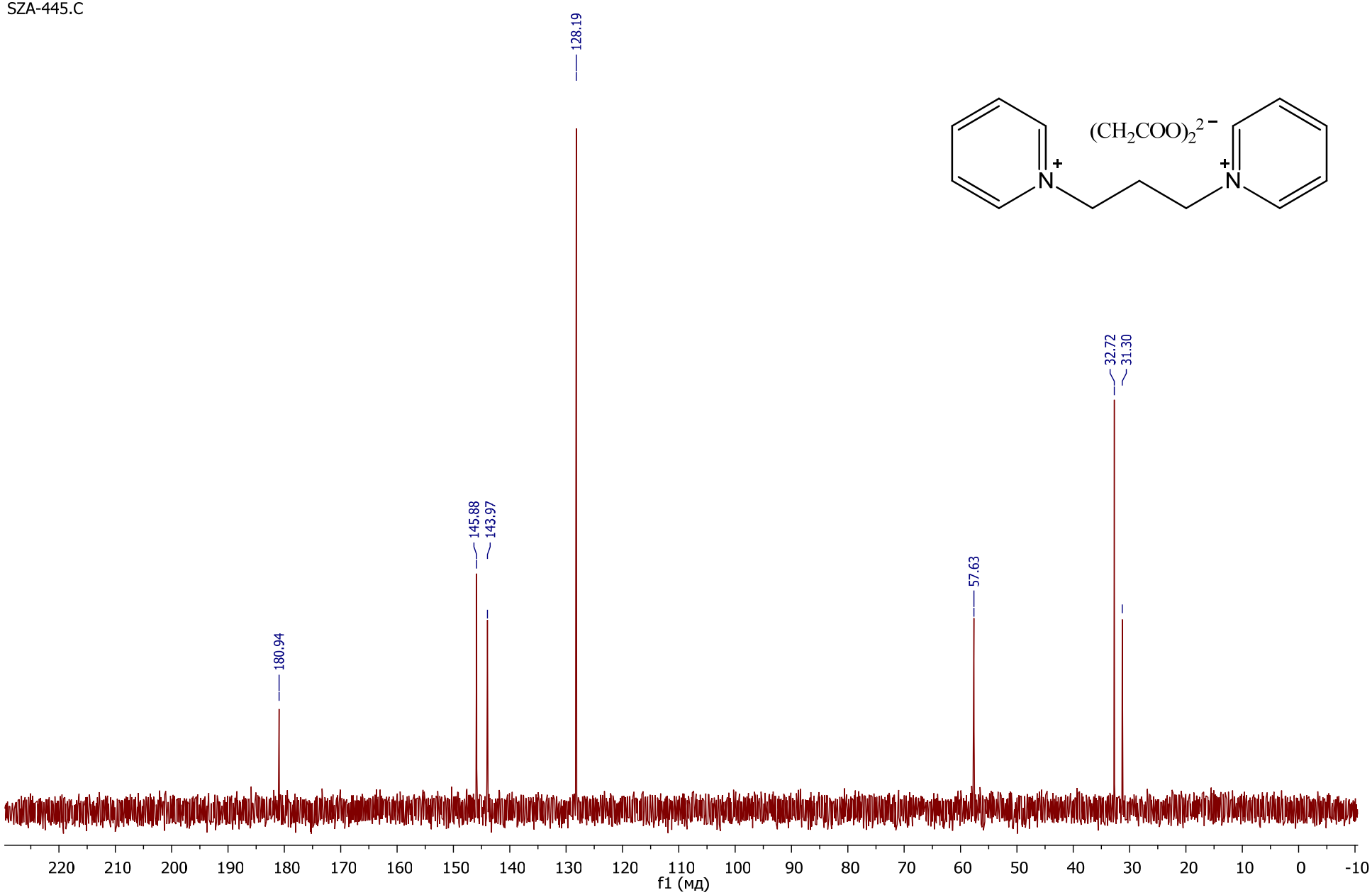
SZA-375-1.C



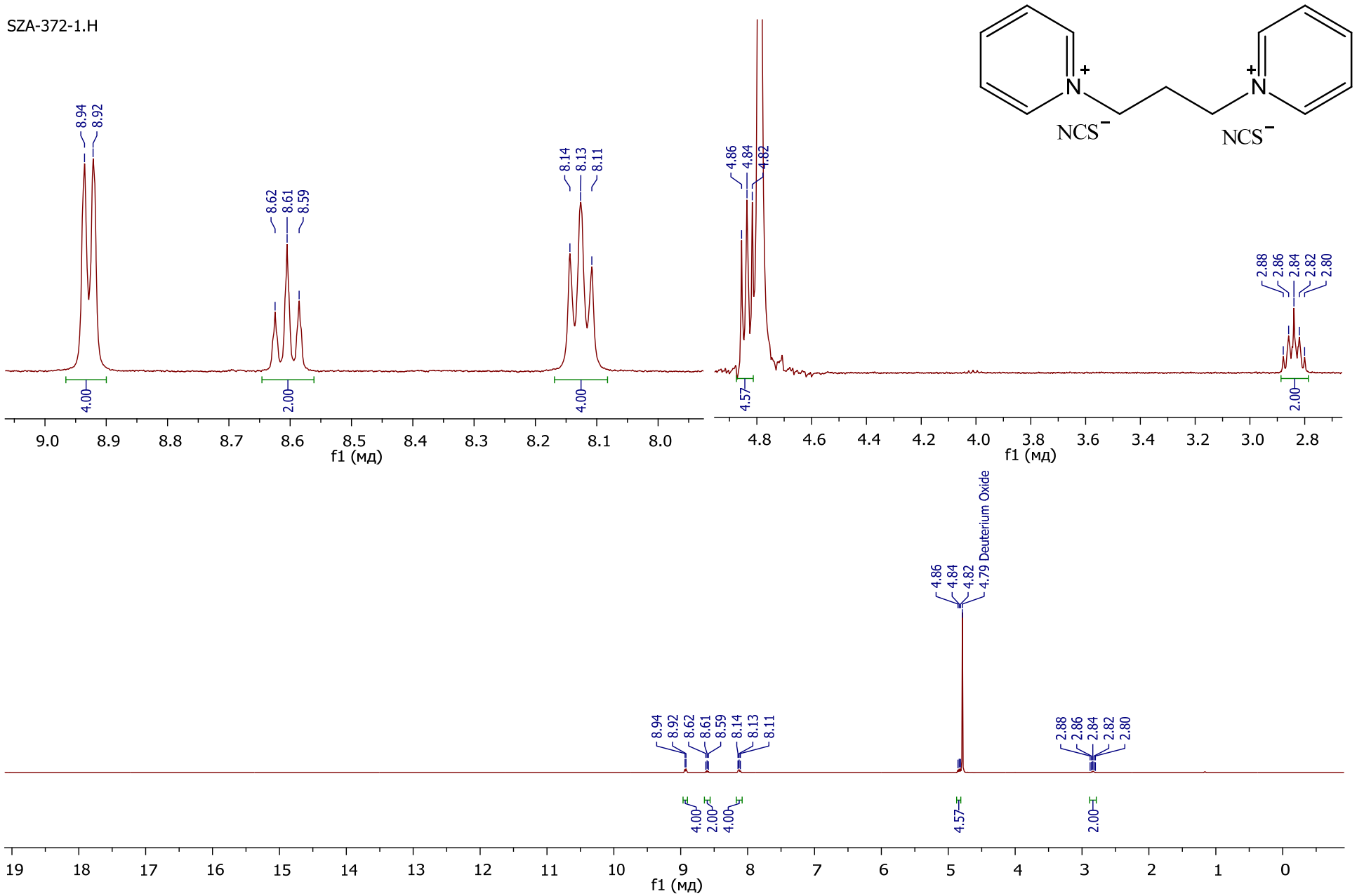
^{13}C NMR spectrum of **38** in D_2O



^{1}H NMR spectrum of **39** in D_2O

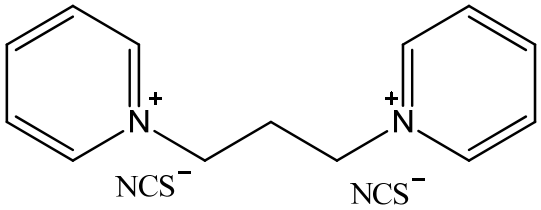


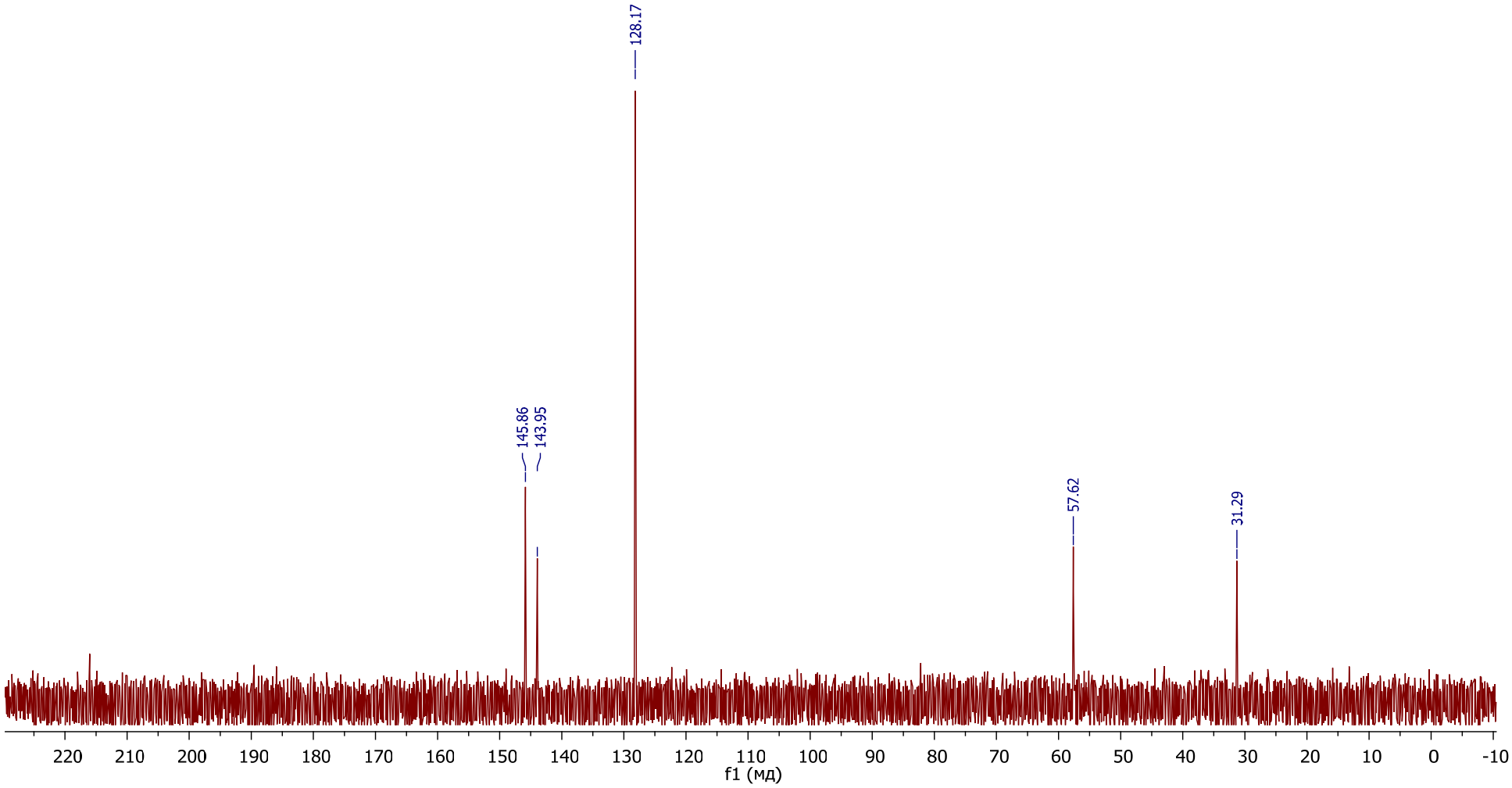
^{13}C NMR spectrum of **39** in D_2O



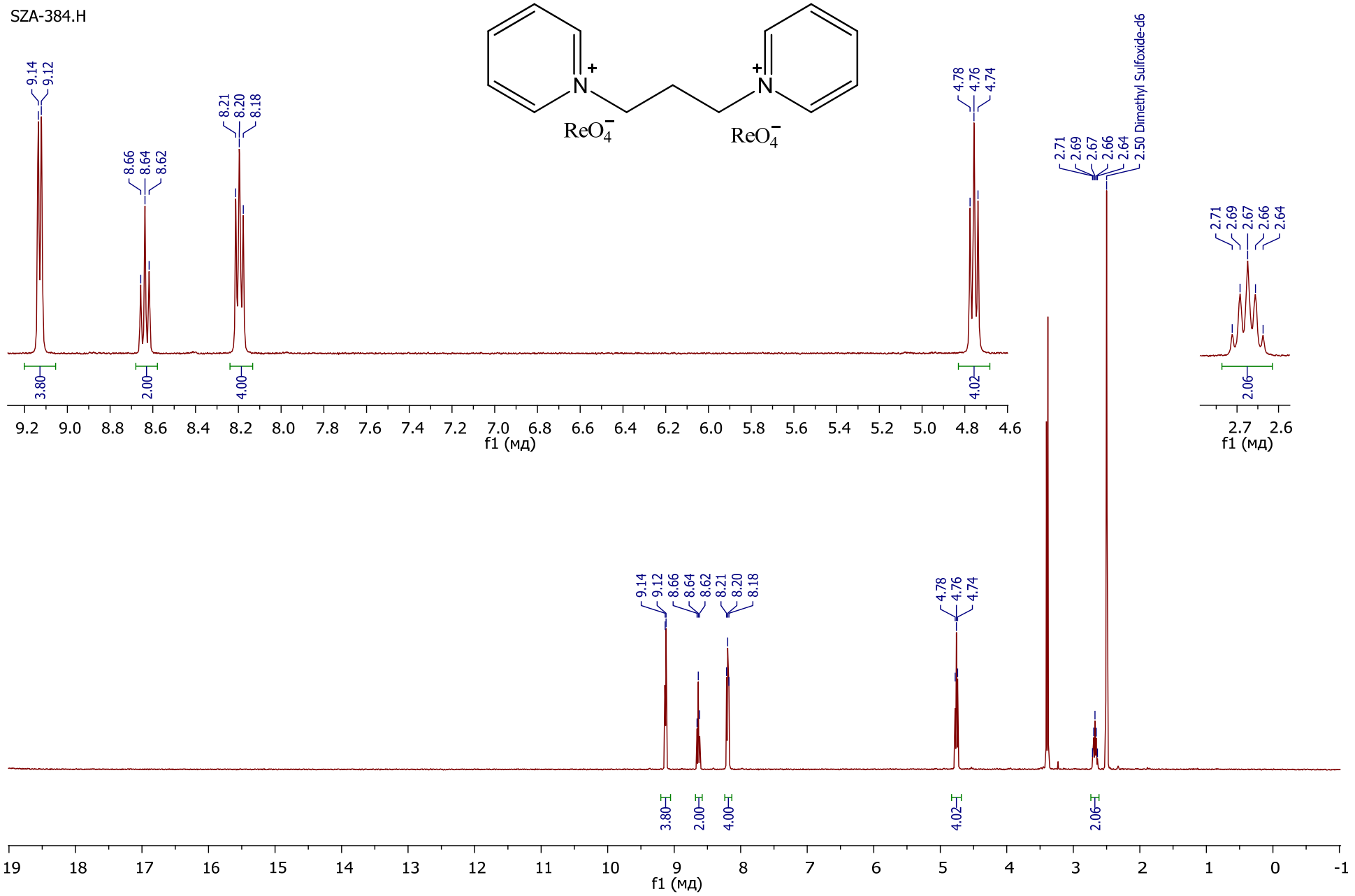
^{1}H NMR spectrum of **40** in D_2O

SZA-372-1.C



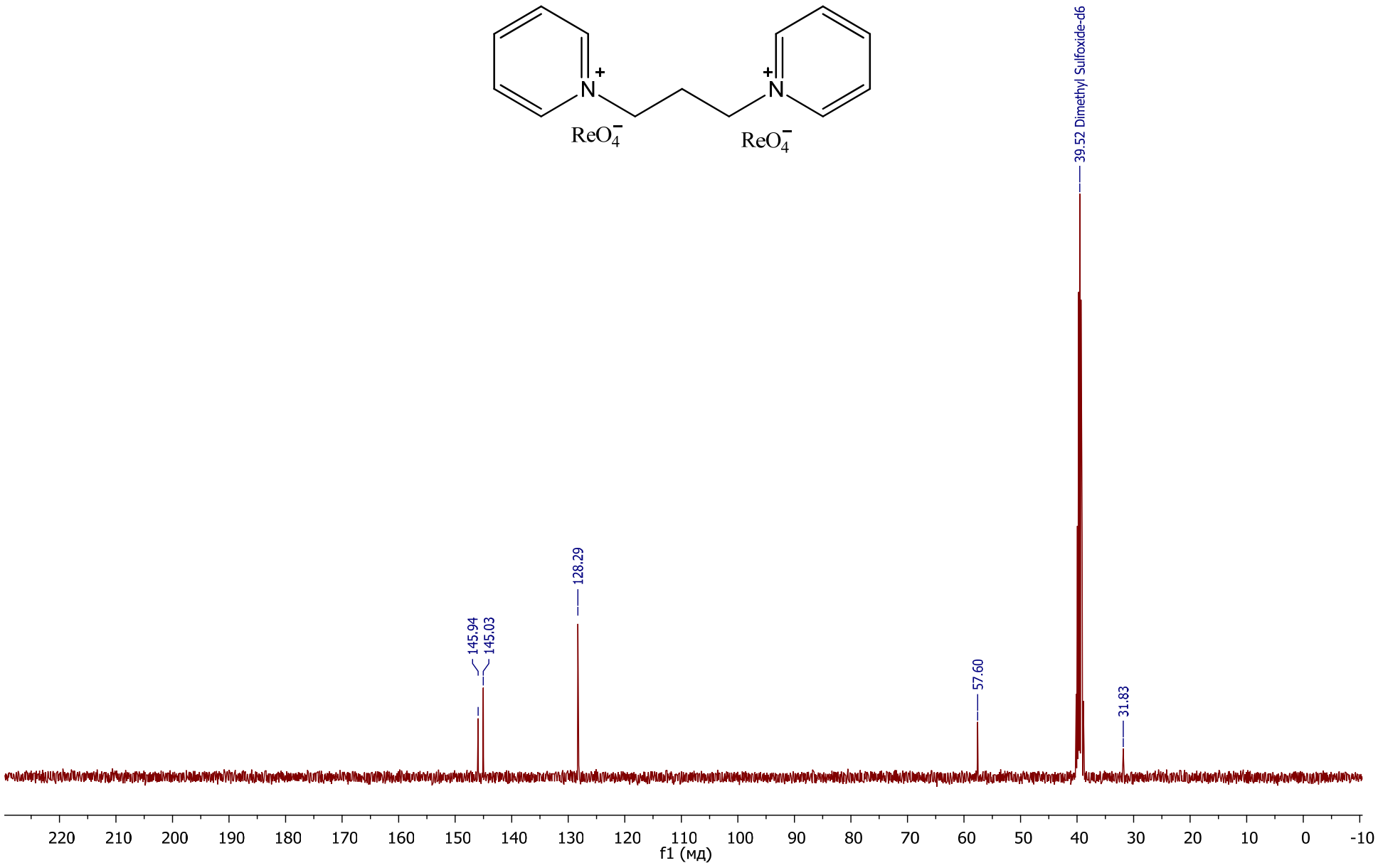


^{13}C NMR spectrum of **40** in D_2O



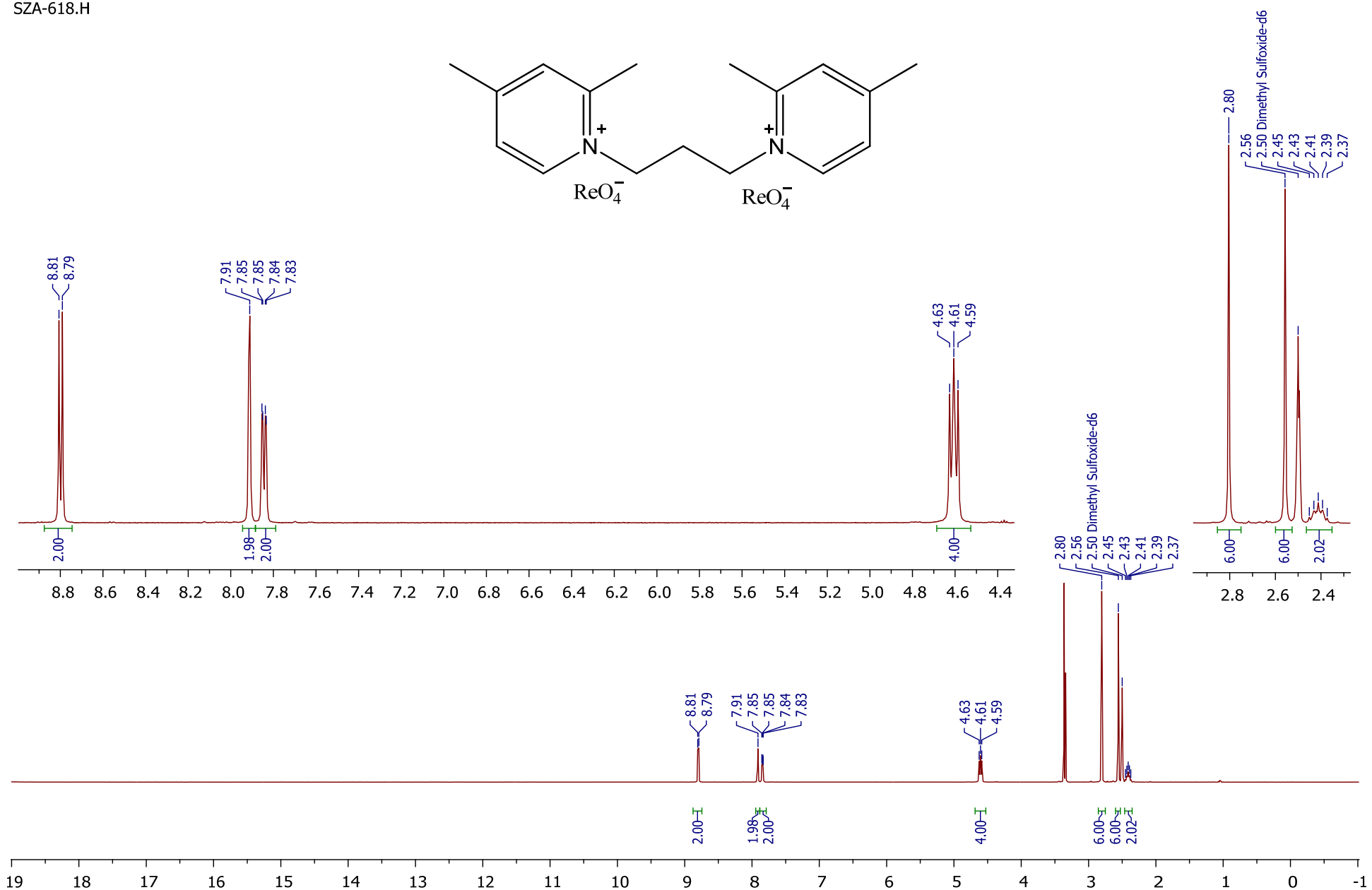
[1]H NMR spectrum of **41** in DMSO-d6

SZA-384.C



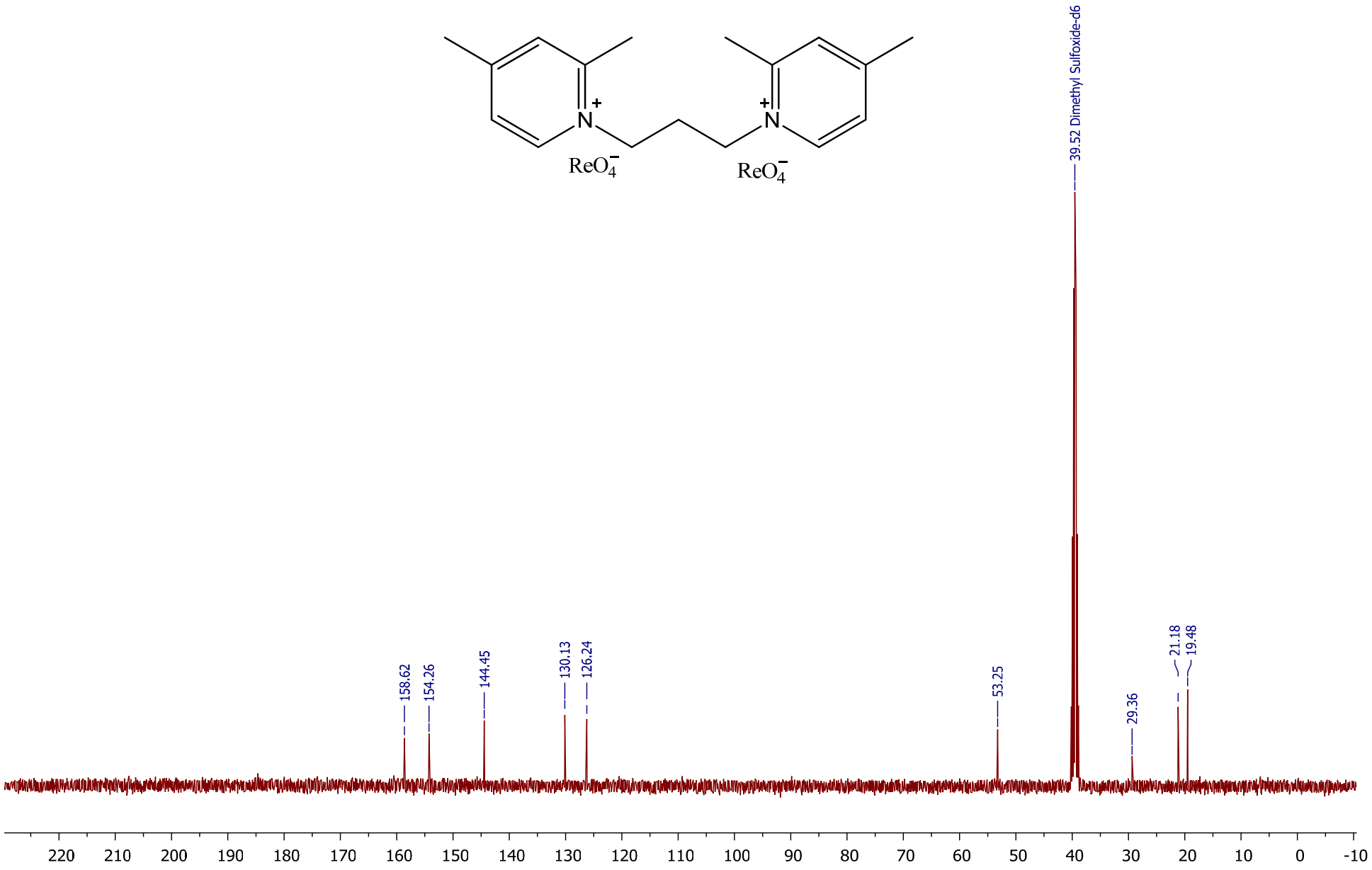
^{13}C NMR spectrum of **41** in DMSO-d$_6$

SZA-618.H



^{1}H NMR spectrum of **42** in DMSO-d$_6$

SZA-618.C



^{13}C NMR spectrum of **42** in DMSO-d$_6$