Electronic supplementary materials *Mendeleev Commun.*, 2025, **35**, 720–722

First synthesis of 1,10-phenanthroline-2,9-diamine dioxides, a novel family of phenanthroline-based ligands

Vasiliy M. Muzalevskiy, Javokhirmirzo K. Isomiddinov, Konstantin A. Lyssenko and Valentine G. Nenajdenko

Table of contents

Experimental part

General remarks.

General remarks. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker AVANCE 400 MHz spectrometer in $CDCl_3$ and D_2O at 400.1 and 100.6 MHz respectively. Chemical shifts (δ) in ppm are reported with the use of the residual chloroform and H_2O signals (7.25 and 4.75 for ^{1}H and 77.0 for ^{13}C ($CDCl_3$)) as internal reference. The coupling constants (*J*) are given in Hertz (Hz). HRMS spectra were measured at MicroTof Bruker Daltonics instrument. TLC analysis was performed on "Macherey-Nagel ALUGRAM Xtra SIL G/UV_{254}" plates. Column chromatography was performed on silica gel "Macherey-Nagel 0.063-0.2nm (Silica 60)". All reagents were of reagent grade and were used as such or were distilled prior to use. Phenantroline diamines **1** were prepared as reported previously [V. M. Muzalevskiy, J. K. Isomiddinov, K. A. Lyssenko, V. G. Nenajdenko, *Russ Chem. Bull.* submitted]

Synthesis of *N,N'*-dioxides 2 (general procedure). A 4 mL vial with a screw cup was charged with 1 mmol of corresponding diamine **1**, 2 mL of $CHCl_3$, mCPBA (2.2 mmo1, 70%), and this was stirred overnight. Next *N*-oxide was isolated *via* procedure A or B.

A: The reaction mixture was passed through silica gel pad using subsequent elation with mixtures of CH_2Cl_2 and MeOH (30:1, 10:1) and mixture of CH_2Cl_2, MeOH and $NH_{3(sat)}$ (100:10:1). Evaporation of solvents *in vacuo* affords the corresponding *N*,*N*′-dioxide **2′**.

B: The reaction mixture was poured into 10 mL of 2 M HCl and extracted with CH_2Cl_2 (2×10 mL). The water layer was evaporated to leave *N*,*N*′-dioxide as a dihydrochloride of **2**.

4,4′-(1,10-Phenanthroline-2,9-diyl)bis(morpholine 4-oxide) 2′a. Obtained from 2,9-dimorpholin-4-yl-1,10-phenanthroline **1a** (0.298 g). Yield 0.320 g (98%), pale beige solid, m.p. 141-144 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 8.88 (d, 2H, *J* = 8.6), 8.53 (d, 2H, *J* = 8.6), 7.94 (s, 2H), 4.72-4.66 (m, 4H), 4.56-4.50 (m, 4H), 3.99-3.96 (m, 4H), 3.13-3.10 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 163.9, 142.3, 140.2, 129.1, 126.8, 116.0, 65.4, 61.5. ESI-MS (m/z): calcd $C_{20}H_{23}N_4O_4$ [M+H$^+$] 383.1714, found 383.1722.

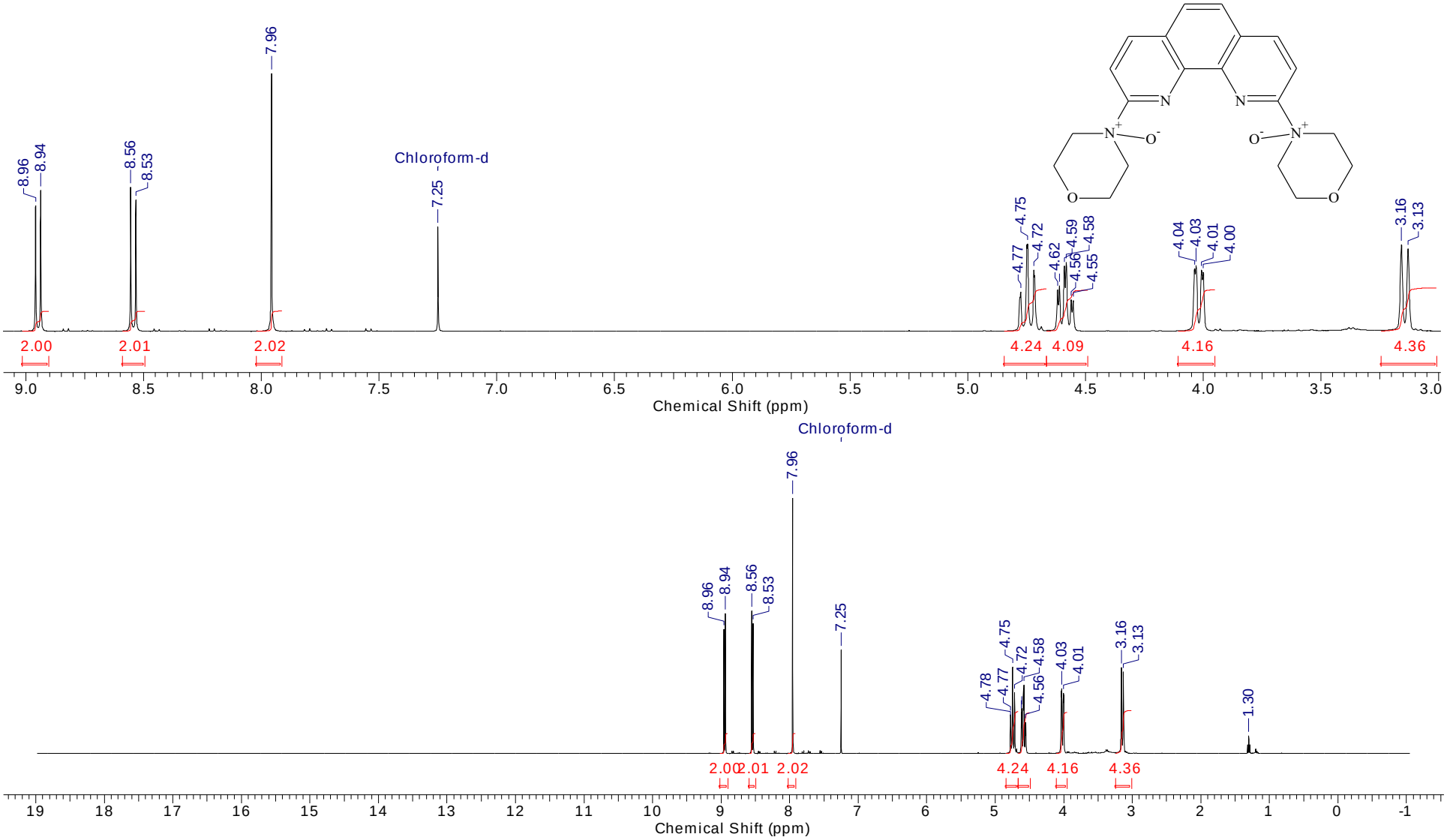
4,4′-(1,10-Phenanthroline-2,9-diyl)bis(morpholine 4-oxide) dihydrochloride 2a (**2′a**·HCl): obtained from 0.094 g of **1a**, yield 0.117 g (96%), brown sticky mass. ^{1}H NMR (D_2O): δ 8.66 (d, 2H, *J* = 8.8), 8.18 (d, 2H, *J* = 8.8), 7.96 (s, 2H), 4.52-4.46 (m, 4H), 4.25-4.20 (m, 4H), 4.04-4.00 (m, 4H), 3.93-3.90 (m, 4H). ^{13}C NMR (D_2O): δ 155.2, 142.0, 141.2, 129.7, 127.3, 113.9, 62.8, 60.3.

1,10-Phenanthroline-2,9-diylbis(dimethylamine oxide) dihydrochloride 2b. Obtained from *N*,*N*,*N*′,*N*′-tetramethyl-1,10-phenanthroline-2,9-diamine **1b** (0.043 g), yield 0.059 g (98%). Brown sticky solid, m.p. 152-155 °C (decomp.). brown sticky mass. ^{1}H NMR (D_2O): δ 8.47 (d, 2H, *J* = 8.7), 8.15 (d, 2H, *J* = 8.7), 7.71 (s, 2H), 3.89 (s, 12H). ^{13}C NMR (D_2O): δ 156.2, 142.2, 141.3, 130.0, 127.5, 113.9, 57.5. ESI-MS (m/z): calcd $C_{16}H_{19}N_4O_2$ [M+H$^+$] 299.1503, found 299.1505.

1,10-Phenanthroline-2,9-diylbis(diethylamine oxide) dihydrochloride 2c. Obtained from *N*,*N*,*N*′,*N*′-tetraethyl-1,10-phenanthroline-2,9-diamine **1c** (0.080 g), yield 0.105 g (99%). Yellow-brown sticky solid, m.p. 170-172 °C (decomp.). ^{1}H NMR (D_2O): δ 8.47 (d, 2H, *J* = 8.7), 8.15 (d, 2H, *J* = 8.7), 7.71 (s, 2H), 3.89 (s, 12H). ^{13}C NMR (D_2O): δ 152.4, 142.1, 141.6, 129.8, 127.6, 116.1, 64.6, 6.9. ESI-MS (m/z): calcd $C_{20}H_{27}N_4O_2$ [M+H$^+$] 355.2129, found 355.2131.

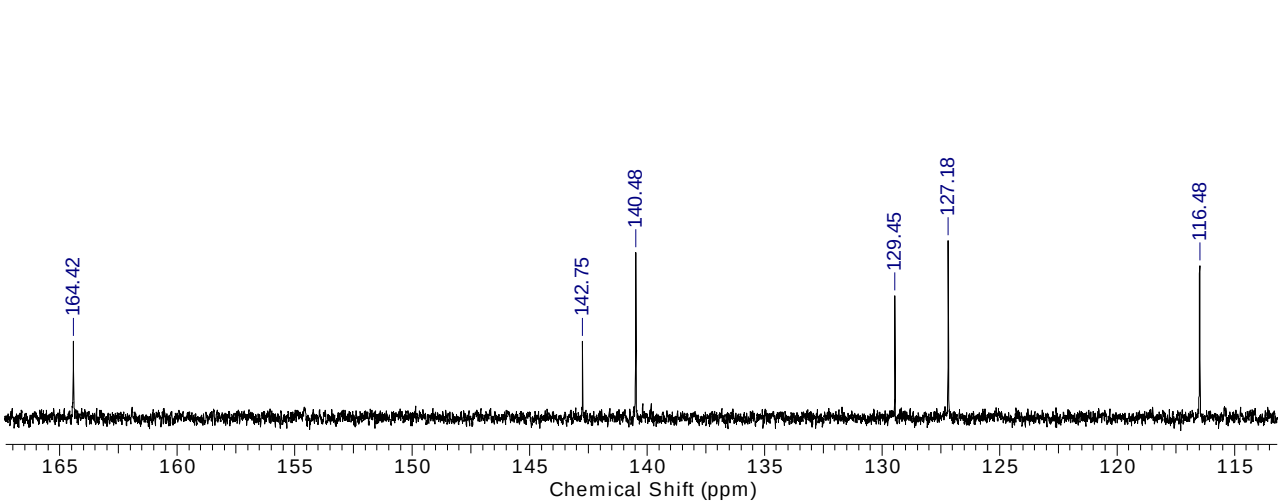
Synthesis of complex 3: To a solution of **4,4'-(1,10-phenanthroline-2,9-diyl)bis(morpholine 4-oxide) 2′a** (0.022 g, 0.058 mmol) in chloroform (1 mL), a solution of $HgCl_2$ (0.0158 g, 0.058 mmol) in acetonitrile (1 mL) was added, and this was left overnight. Colourless crystals thus formed were used for X-ray investigations (for X-ray data see main text).

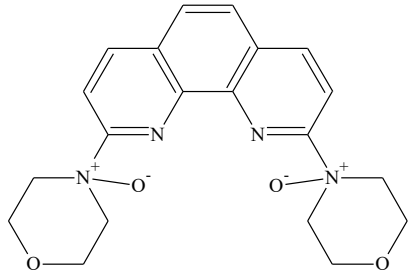
Acquisition Time (sec)	4.0894	***Comment***	Imported from UXNMR.			***Date***	02 Apr 2024 20:53:50
File Name	C:\DOCS\BM\ЯМР_СОСЕДИ\2024\BM-J-051-2p\BM-J-051-2p_001001r					***Frequency (MHz)***	400.13
Nucleus	1H	***Number of Transients***	8	***Original Points Count***	32768	***Points Count***	131072
Pulse Sequence	zg30	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	8012.82
Temperature (degree C)	27.000						

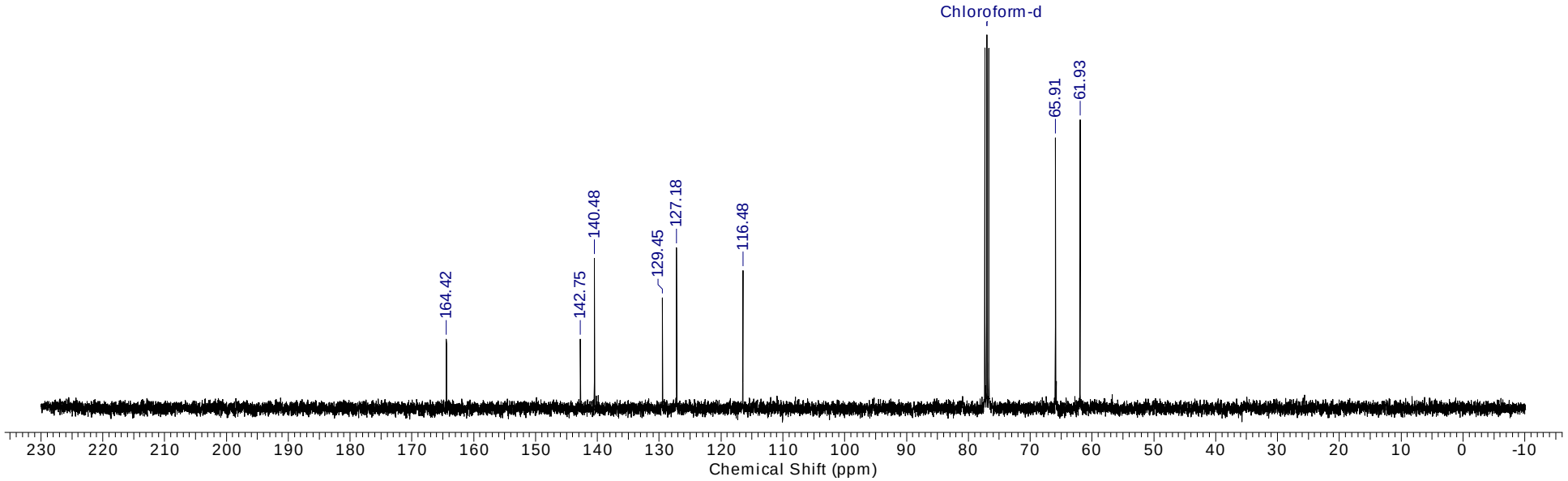


^{1}H NMR spectrum of **2a** (400.1 MHz, $CDCl_3$)

Acquisition Time (sec)	0.6783	***Comment***	Imported from UXNMR.			***Date***	04 Apr 2024 11:43:10
File Name	C:\DOCS\OUTPUT_301\2024\04.апрель\BM-J-051-3p.C_002001r					***Frequency (MHz)***	100.61
Nucleus	13C	***Number of Transients***	95	***Original Points Count***	16384	***Points Count***	131072
Pulse Sequence	zgpg30	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	24154.59
Temperature (degree C)	27.000						

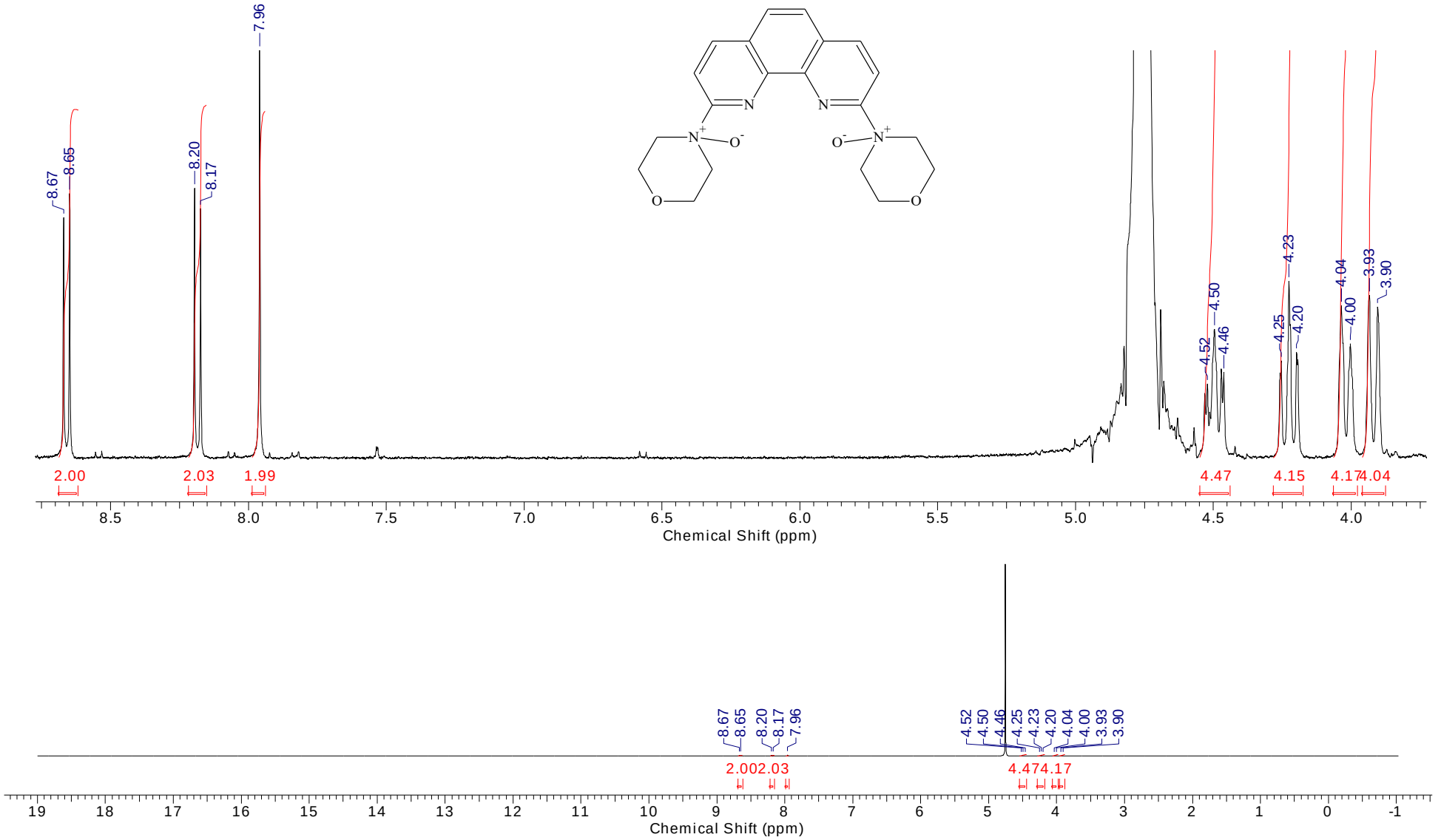






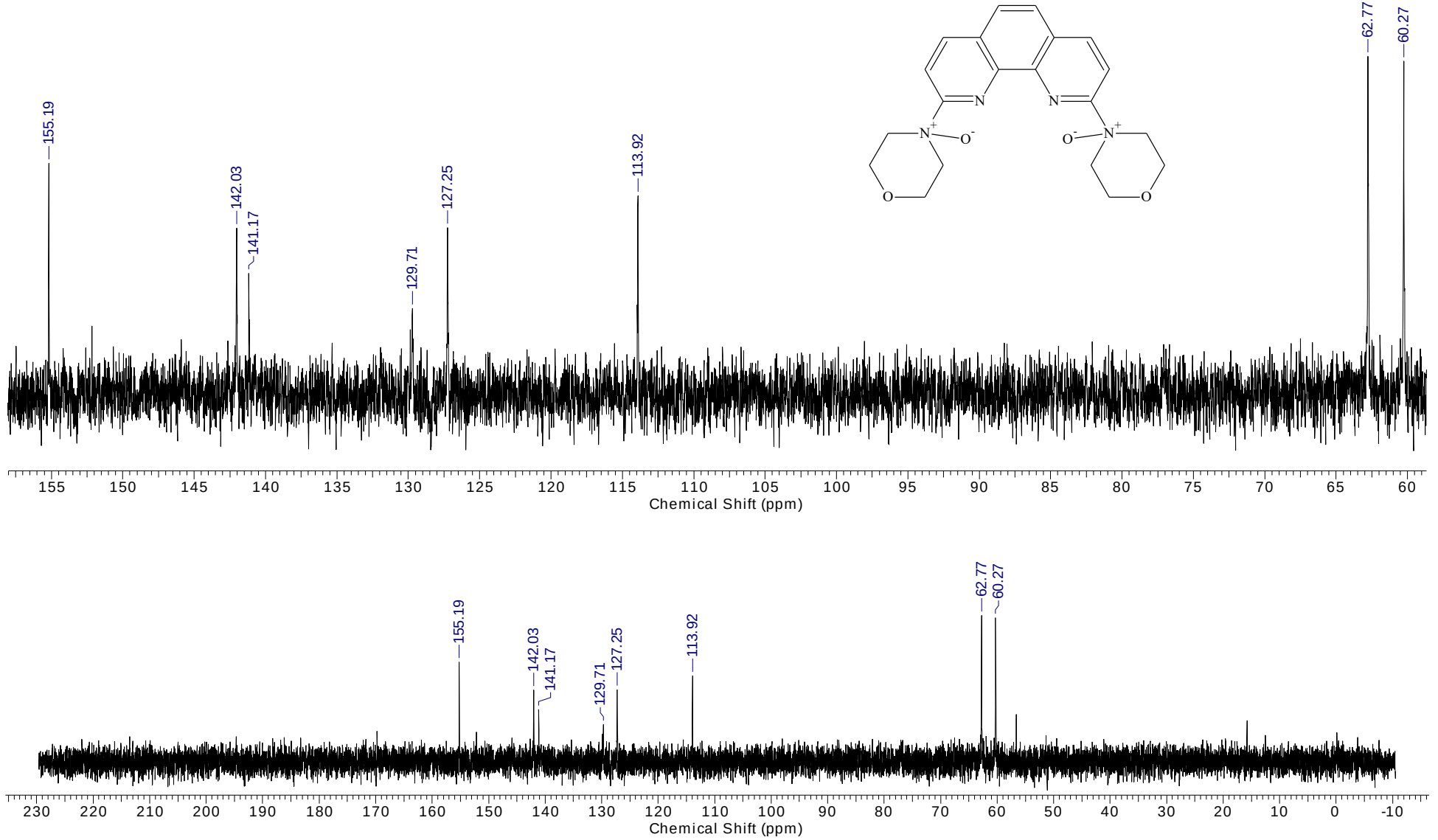
^{13}C NMR spectrum of **2a** (100.6 MHz, $CDCl_3$)

Acquisition Time (sec)	4.0894	***Comment***	Imported from UXNMR.			***Date***	11 Oct 2024 15:12:20
File Name	C:\DOCS\OUTPUT_301\2024\10.октябрь\BM-J-082-84-D2O.H_001001r					***Frequency (MHz)***	400.13
Nucleus	1H	***Number of Transients***	4	***Original Points Count***	32768	***Points Count***	131072
Pulse Sequence	zg30	***Solvent***	DEUTERIUM OXIDE			***Sweep Width (Hz)***	8012.82
Temperature (degree C)	27.000						



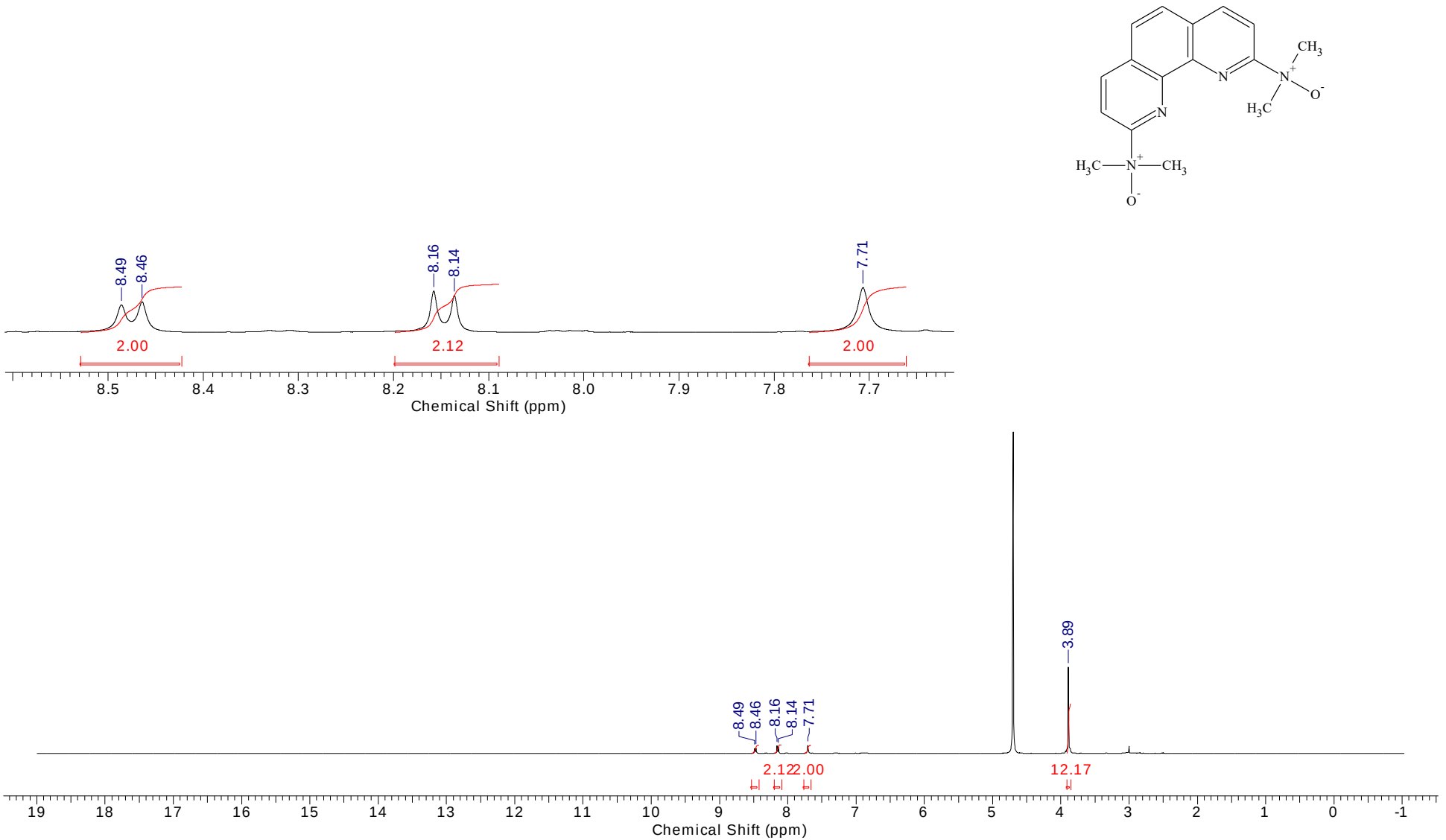
^{1}H NMR spectrum of **2a** (400.1 MHz, D_2O)

Acquisition Time (sec)	0.6783	***Comment***	Imported from UXNMR.			***Date***	11 Oct 2024 15:25:22
File Name	C:\DOCS\OUTPUT_301\2024\10.октябрь\BM-J-091-D2O.C_002001r					***Frequency (MHz)***	100.61
Nucleus	13C	***Number of Transients***	77	***Original Points Count***	16384	***Points Count***	131072
Pulse Sequence	zgpg30	***Solvent***	DEUTERIUM OXIDE			***Sweep Width (Hz)***	24154.59
Temperature (degree C)	27.000						



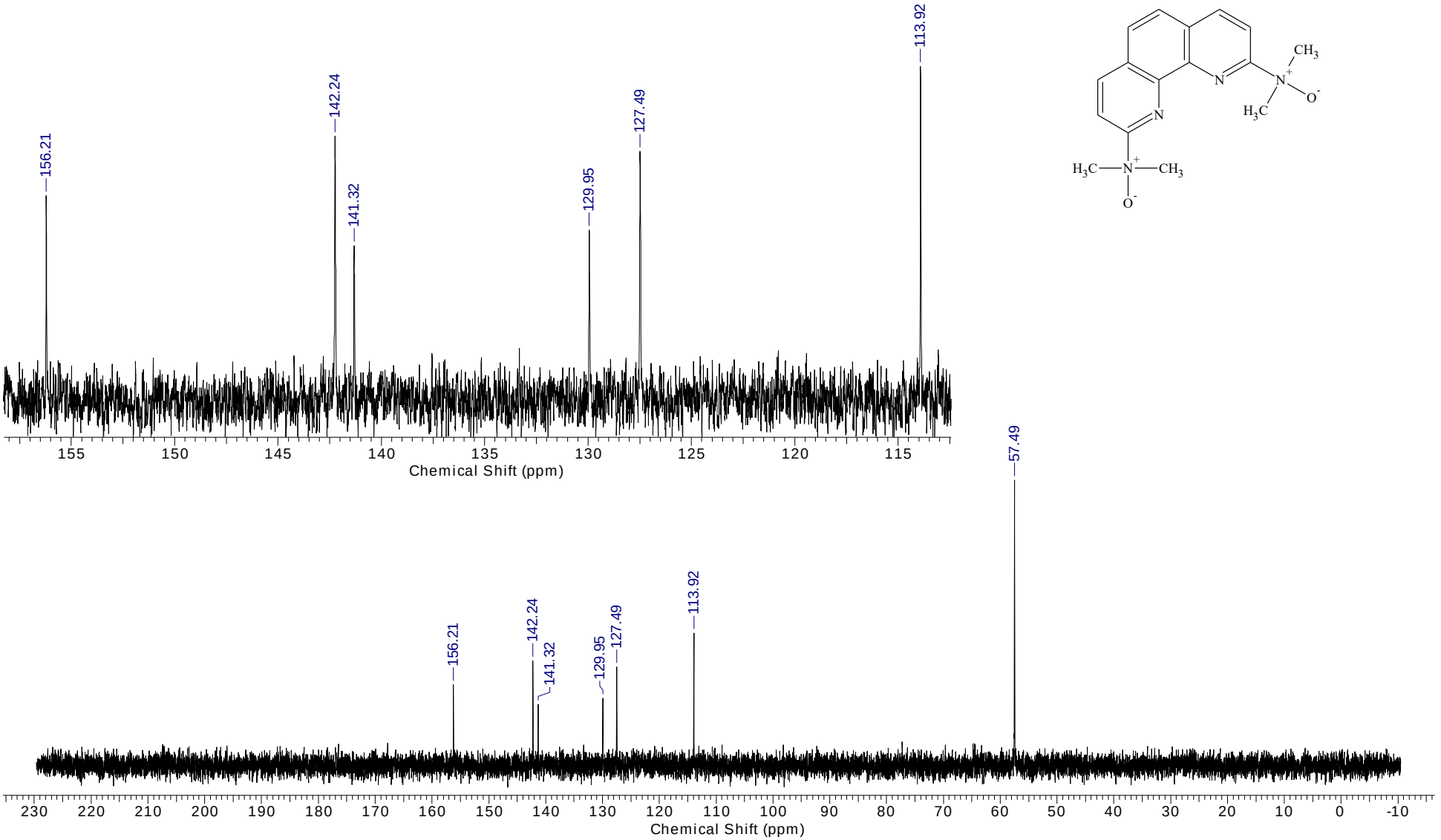
^{13}C NMR spectrum of **2a** (100.6 MHz, D_2O)

Acquisition Time (sec)	4.0894	***Comment***	Imported from UXNMR.			***Date***	12 Oct 2024 12:47:22
File Name	C:\DOCS\BM\ЯМР_СОСЕДИ\2024\241012\BM-J-090_001001r					***Frequency (MHz)***	400.13
Nucleus	1H	***Number of Transients***	8	***Original Points Count***	32768	***Points Count***	131072
Pulse Sequence	zg30	***Solvent***	DEUTERIUM OXIDE			***Sweep Width (Hz)***	8012.82
Temperature (degree C)	27.000						



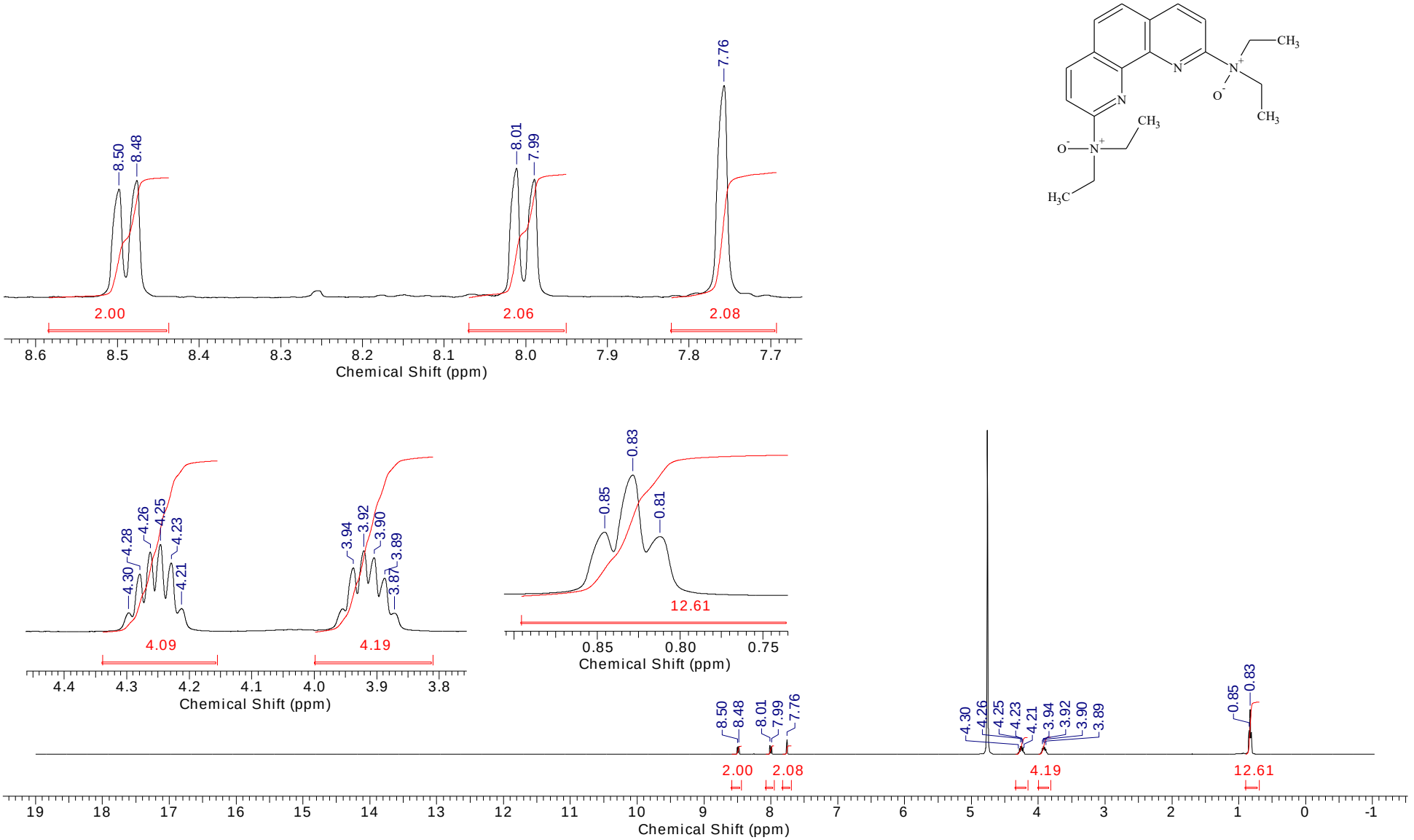
^{1}H NMR spectrum of **2b** (400.1 MHz, D_2O)

Acquisition Time (sec)	0.6783	***Comment***	Imported from UXNMR.			***Date***	12 Oct 2024 12:51:54
File Name	C:\DOCS\BM\ЯМР_СОСЕДИ\2024\241012\BM-J-090_002001r					***Frequency (MHz)***	100.61
Nucleus	13C	***Number of Transients***	64	***Original Points Count***	16384	***Points Count***	131072
Pulse Sequence	zgpg30	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	24154.59
Temperature (degree C)	27.000						



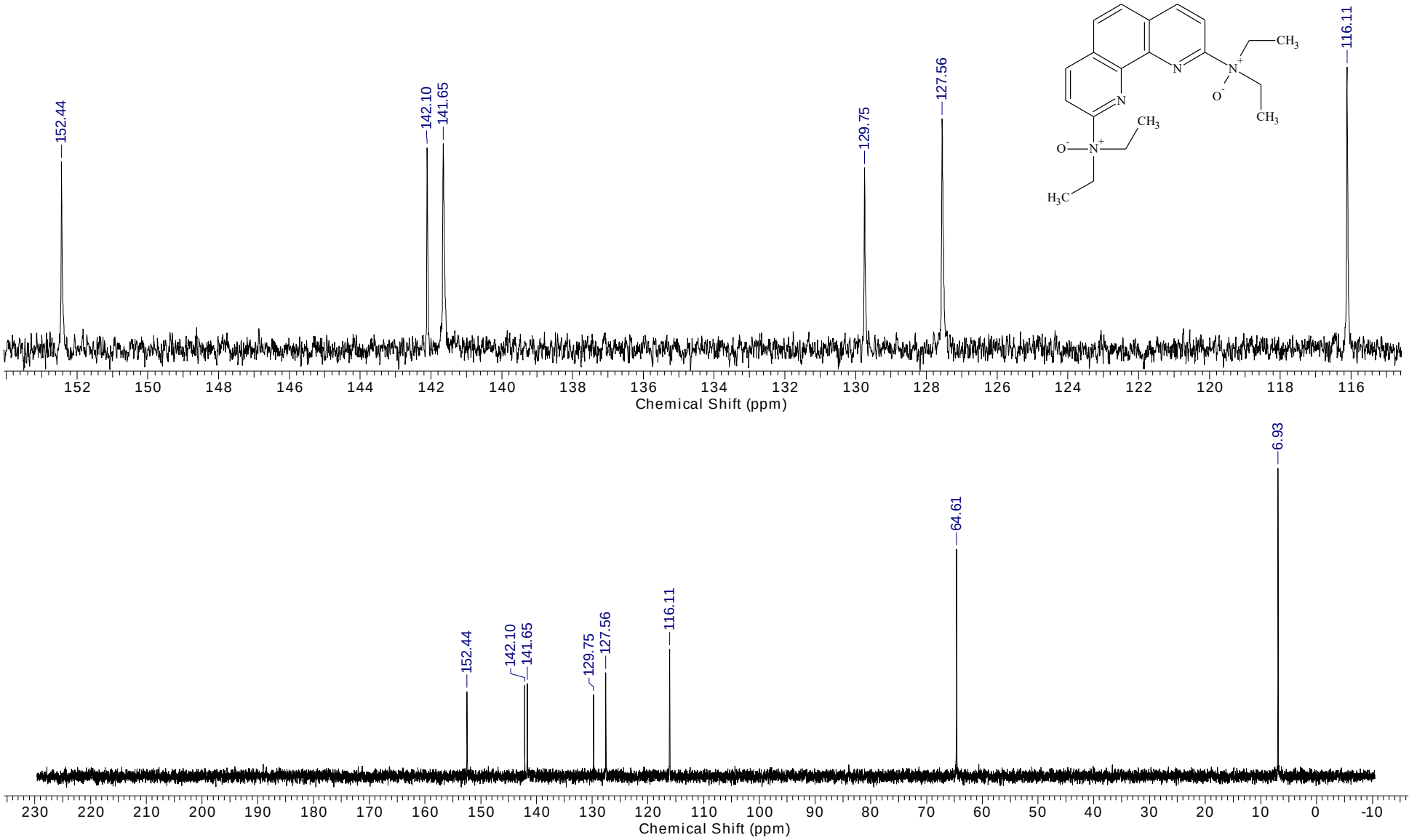
^{13}C NMR spectrum of **2b** (100.6 MHz, D_2O)

Acquisition Time (sec)	4.0894	***Comment***	Imported from UXNMR.			***Date***	19 Oct 2024 13:11:04
File Name	C:\DOCS\BM\ЯМР_СОСЕДИ\2024\19-10-2024_14-01-56\BM-J-118\BM-J-118_001001r					***Frequency (MHz)***	400.13
Nucleus	1H	***Number of Transients***	8	***Original Points Count***	32768	***Points Count***	131072
Pulse Sequence	zg30	***Solvent***	DMSO-D6	***Sweep Width (Hz)***	8012.82	***Temperature (degree C)***	27.000

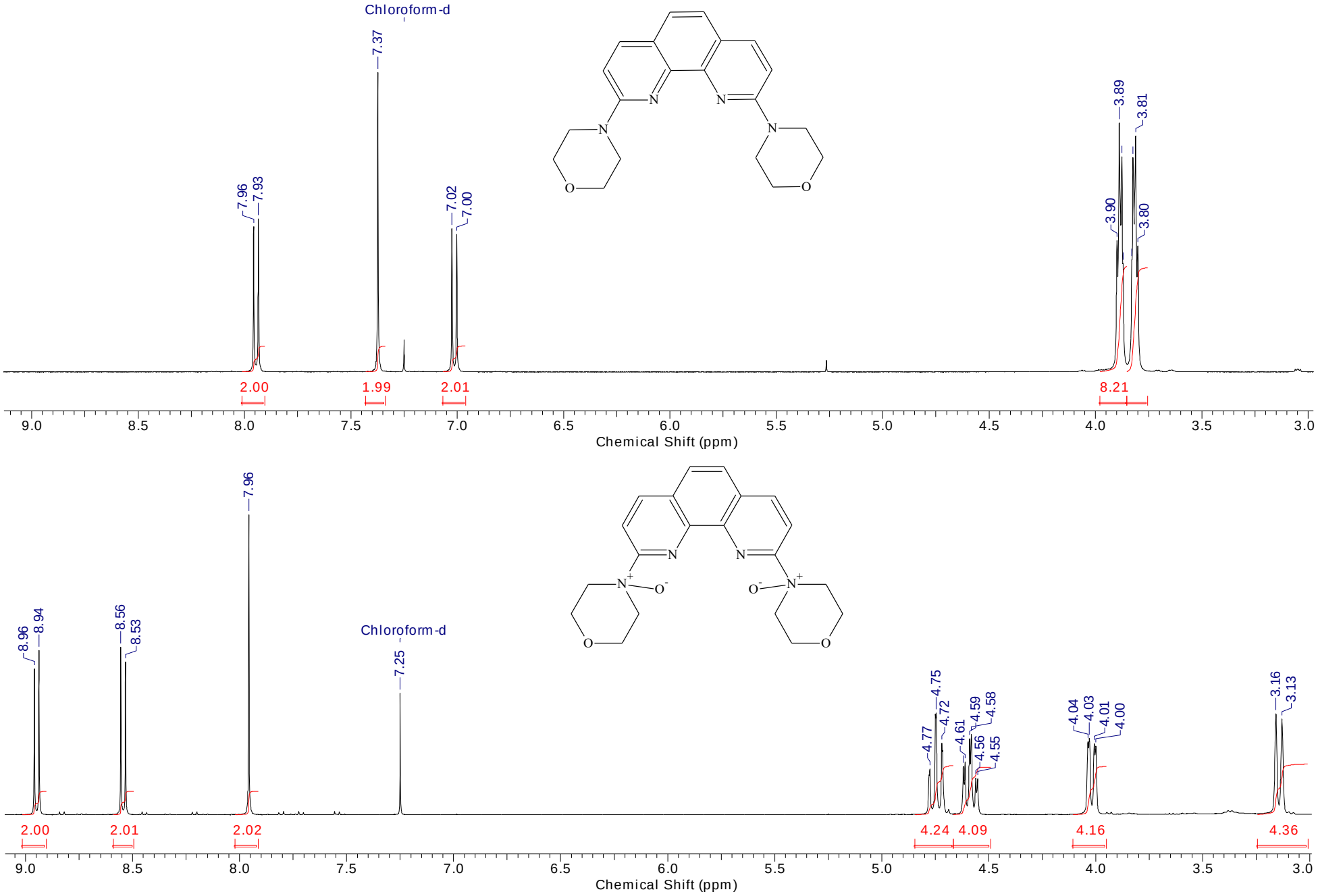


^{1}H NMR spectrum of **2c** (400.1 MHz, D_2O)

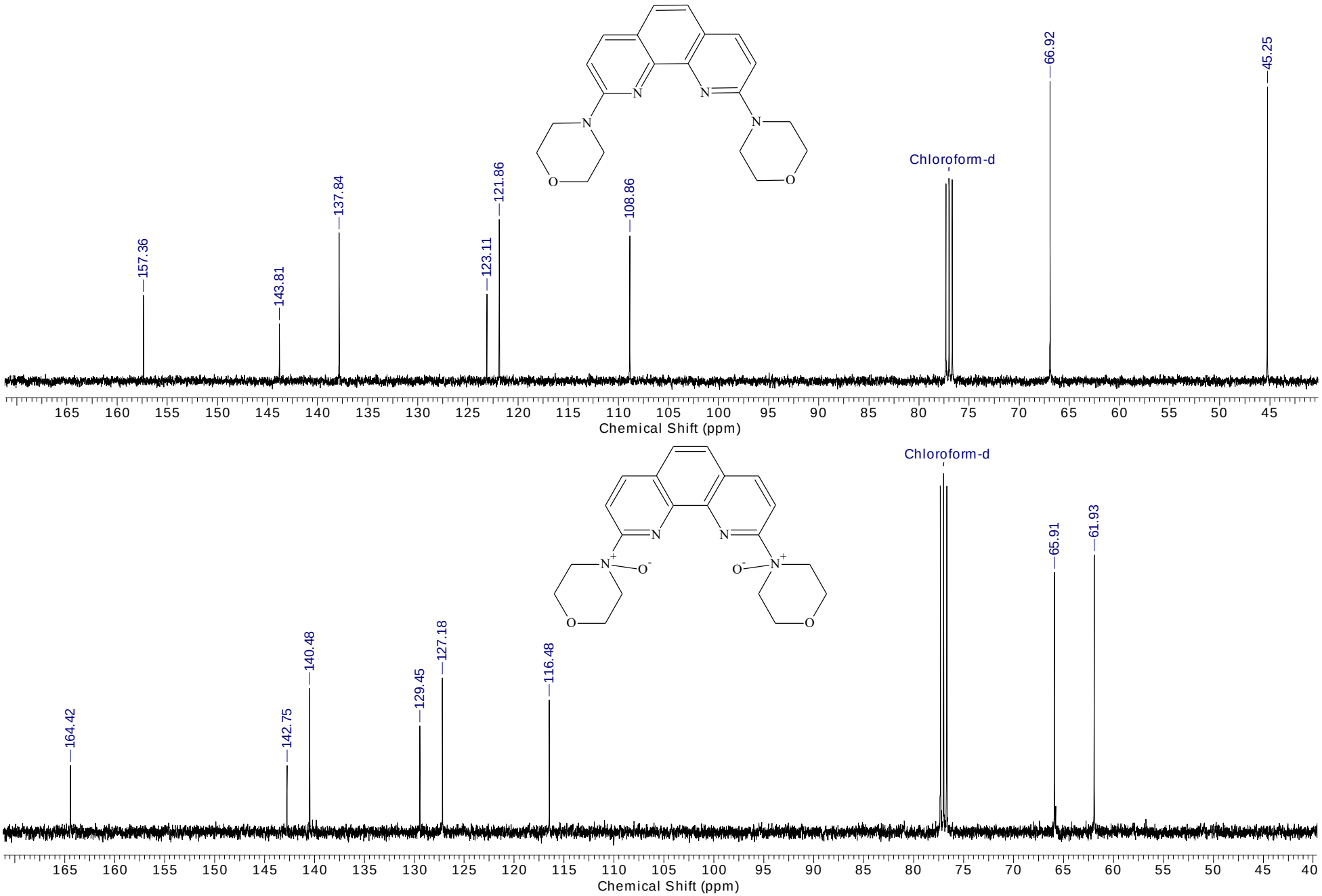
Acquisition Time (sec)	0.6783	***Comment***	Imported from UXNMR.			***Date***	19 Oct 2024 13:09:10
File Name	C:\DOCS\BM\ЯМР_СОСЕДИ\2024\19-10-2024_14-01-56\BM-J-118\BM-J-118_002001r					***Frequency (MHz)***	100.61
Nucleus	13C	***Number of Transients***	144	***Original Points Count***	16384	***Points Count***	131072
Pulse Sequence	zgpg30	***Solvent***	CHLOROFORM-D	***Sweep Width (Hz)***	24154.59	***Temperature (degree C)***	27.000



^{13}C NMR spectrum of **2c** (100.6 MHz, D_2O)



Comparison of ^{1}H NMR spectra of **1a** and **2a** (400.1 MHz, $CDCl_3$)



Comparison of ^{13}C NMR spectra of **1a** and **2a** (100.6 MHz, $CDCl_3$)