Supplementary information

The study of photochemical behavior of 5-aryl-2,3-dihydropyrazine 1,4-dioxides

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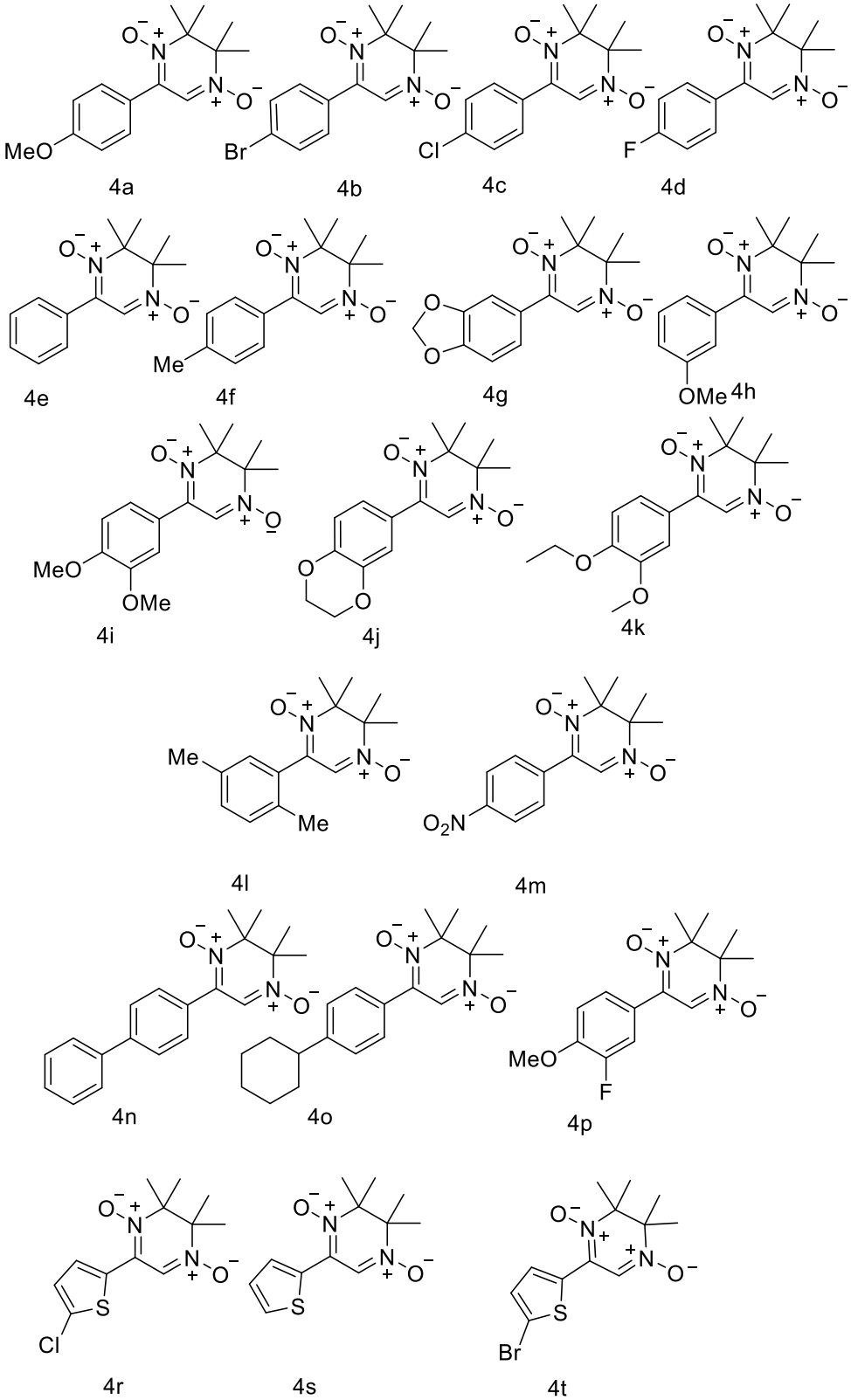
1. General information.

Unless otherwise stated, all starting chemicals were commercially available and were used as received. NMR spectra were recorded with Bruker AM 300 (300 MHz) spectrometers in DMSO-d6. Chemical shifts (ppm) are given relative to solvent signals (DMSO-d6: 2.50 ppm [^{1}H NMR] and 39.52 ppm [^{13}C NMR]). High-resolution mass spectra (HRMS) were obtained on a Bruker micrOTOF II instrument using electrospray ionization (ESI). The melting points were determined on a Kofler hot stage. Photochemical reactions were performed in common glassware. Irradiation was carried out with a Vilber Lourmat VL-6.LM lamp (365 nm, 6 W) and with a strip of 24 W 450 nm LED at room temperature in air atmosphere.

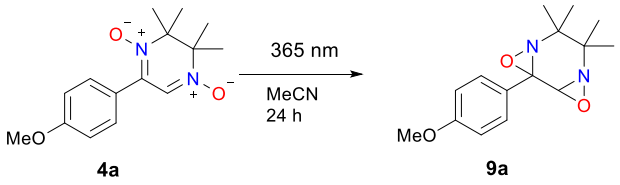
2. Starting compounds.

All starting compounds were prepared by the known literature method[1]



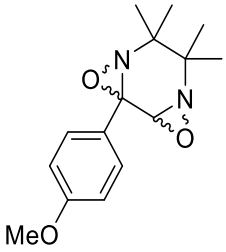
[1] N. A. Bakuleva, B. V. Lichitsky, D. V. Tsyganov, A. N. Komogortsev, V. G. Melekhina and E. V. Tretyakov, Synthesis of substituted 5-aryl-2,3-dihydropyrazine1,4-dioxides based on condensation of N,N'-(2,3-dimethylbutane-2,3-diyl)bis(hydroxylamine) with various arylglyoxals, *J. Heterocyclic Chem.*, 2024, **61**, 1057–1065.

3. Experimental procedure for the synthesis of 1-(4-methoxyphenyl)-5,5,6,6-tetramethyl-3,8-dioxa-4,7-diazatricyclo[5.1.0.02,4]octane 9a.



4a **9a**

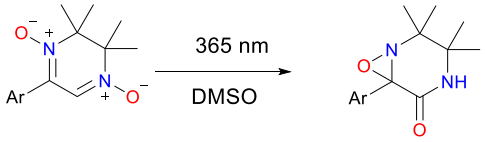
A solution of compound **4a** (1 mmol, 0.28 g) in acetonitrile (5 ml) was irradiated with a Vilber Lourmat VL-6.LM lamp (365 nm, 6 W) for 24 hours at room temperature in common laboratory glassware. The resulting mixture was evaporated in vacuum and obtained residue was purified using column chromatography (eluent EtOAc-hexane 2:1).



1-(4-methoxyphenyl)-5,5,6,6-tetramethyl-3,8-dioxa-4,7-diazatricyclo[5.1.0.02,4]octane **9a**, mixture of diastereomers (1:5)

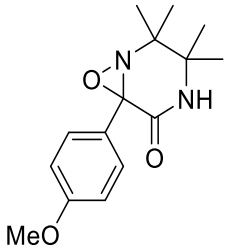
Yellow oil; yield 89% (0.25 g);
^{1}H NMR (300 MHz, DMSO-d_6) δ 7.53 (d, J = 8.6 Hz, 1.66H), 7.45 (d, J = 8.6 Hz, 0.34H), 7.02 (d, J = 8.6 Hz, 2H), 5.32 (s, 0.17H), 5.24 (s, 0.83H), 3.78 (s, 3H), 1.35 – 1.12 (m, 12H).
^{13}C NMR (76 MHz, DMSO-d_6) δ 160.51, 160.31, 128.34, 128.09, 127.67, 114.20, 75.28, 72.65, 72.07, 60.19, 59.15, 58.88, 57.93, 55.34, 26.33, 26.24, 26.13, 24.82, 24.61, 24.50, 23.31, 23.29.

4. General experimental procedure for the synthesis of 6-aryl-2,2,3,3-tetramethyl-7-oxa-1,4-diazabicyclo[4.1.0]heptan-5-ones 5.



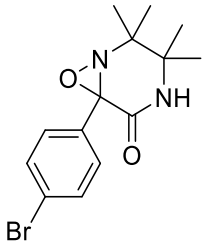
4 5

A solution of compound **4** (1 mmol) in DMSO (5 ml) was irradiated with a Vilber Lourmat VL-6.LM lamp (365 nm, 6 W) for 48 hours at room temperature in common laboratory glassware. The reaction mixture was diluted with water (50 ml) and extracted with diethyl ether (3x20 ml). The ether solution was separated and washed with water (3x30 ml). Then, the solvent was evaporated in vacuum and obtained residue was purified using column chromatography (eluent EtOAc-hexane 2:1).



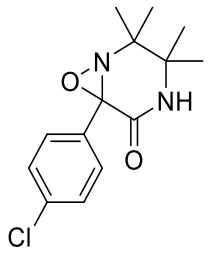
6-(4-methoxyphenyl)-2,2,3,3-tetramethyl-7-oxa-1,4-diazabicyclo[4.1.0]heptan-5-one **5a**

Yellow powder; yield 71% (0.20 g); mp 168-170 °C.
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.34 (s, 1H), 7.32 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 3.76 (s, 3H), 1.33 (s, 3H), 1.27 (s, 3H), 1.22 (s, 3H), 1.13 (s, 3H).
^{13}C NMR (76 MHz, DMSO-d_6) δ 164.41, 159.66, 128.81, 126.05, 113.19, 75.08, 61.37, 55.67, 55.17, 27.55, 27.31, 21.98, 21.95.
HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{15}H_{21}N_2O_3$: 277.1547; Found: 277.1548.



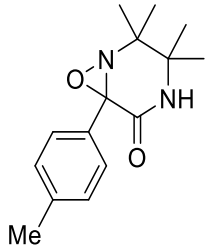
6-(4-bromophenyl)-2,2,3,3-tetramethyl-7-oxa-1,4-diazabicyclo[4.1.0]heptan-5-one **5b**

Yellow powder; yield 67% (0.22 g); mp 236-238 °C.
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.46 (s, 1H), 7.59 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 1.35 (s, 3H), 1.29 (s, 3H), 1.22 (s, 3H), 1.14 (s, 3H).
^{13}C NMR (76 MHz, DMSO-d_6) δ 163.84, 133.55, 130.80, 129.52, 122.31, 75.15, 61.55, 55.70, 27.88, 27.33, 22.06, 21.64.
HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{14}H_{18}BrN_2O_2$: 325.0546; Found: 325.0546



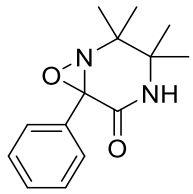
6-(4-chlorophenyl)-2,2,3,3-tetramethyl-7-oxa-1,4-diazabicyclo[4.1.0]heptan-5-one **5c**

Yellow powder; yield 73% (0.21 g); mp 206-208°C.
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.46 (s, 1H), 7.45 (d, J = 8.5 Hz, 2H), 7.40 (d, J = 8.7 Hz, 2H), 1.35 (s, 3H), 1.30 (s, 3H), 1.22 (s, 3H), 1.14 (s, 3H).
^{13}C NMR (76 MHz, DMSO-d_6) δ 163.88, 133.66, 133.13, 129.25, 127.89, 75.07, 61.55, 55.71, 27.88, 27.33, 22.06, 21.65.
HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{14}H_{18}ClN_2O_2$: 281.1051; Found: 281.1057



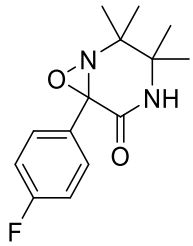
2,2,3,3-tetramethyl-6-(p-tolyl)-7-oxa-1,4-diazabicyclo[4.1.0]heptan-5-one **5d**

Yellow powder; yield 54% (0.14 g); mp 187-189°C.
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.35 (s, 1H), 7.26 (d, J = 8.2 Hz, 2H), 7.18 (d, J = 7.9 Hz, 2H), 2.31 (s, 3H), 1.34 (s, 3H), 1.28 (s, 3H), 1.22 (s, 3H), 1.14 (s, 3H).
^{13}C NMR (76 MHz, DMSO-d_6) δ 164.39, 138.28, 131.28, 128.30, 127.21, 75.45, 61.40, 55.68, 27.69, 27.34, 22.04, 21.87, 20.87.
HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{15}H_{21}N_2O_2$: 261.1598; Found: 261.1608



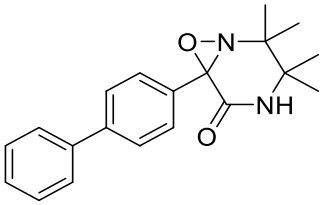
2,2,3,3-tetramethyl-6-phenyl-7-oxa-1,4-diazabicyclo[4.1.0]heptan-5-one **5e**

Yellow powder; yield 51% (0.13 g); mp 184-186°C.
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.39 (s, 1H), 7.40 – 7.33 (m, 5H), 1.35 (s, 3H), 1.29 (s, 3H), 1.23 (s, 3H), 1.15 (s, 3H).
^{13}C NMR (76 MHz, DMSO-d_6) δ 164.30, 134.23, 128.85, 127.77, 127.21, 75.60, 61.45, 55.69, 27.81, 27.36, 22.07, 21.78.
HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{14}H_{19}N_2O_2$: 247.1441; Found: 247.1445



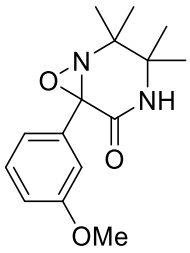
6-(4-fluorophenyl)-2,2,3,3-tetramethyl-7-oxa-1,4-diazabicyclo[4.1.0]heptan-5-one **5f**

Yellow powder; yield 58% (0.15 g); mp 176-178°C.
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.43 (s, 1H), 7.48 – 7.39 (m, 2H), 7.26 – 7.16 (m, 2H), 1.35 (s, 3H), 1.29 (s, 3H), 1.23 (s, 3H), 1.14 (s, 3H).
^{13}C NMR (76 MHz, DMSO-d_6) δ 164.07, 162.33 (d, J = 245.4 Hz), 130.42 (d, J = 3.0 Hz), 129.65 (d, J = 8.7 Hz), 114.75 (d, J = 21.8 Hz), 75.03, 61.51, 55.71, 27.84, 27.34, 22.07, 21.72.
HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{14}H_{19}FN_2O_2$: 265.1347; Found: 265.1358



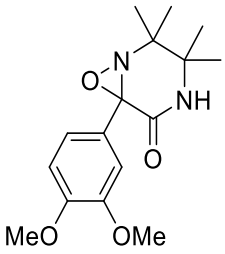
6-([1,1'-biphenyl]-4-yl)-2,2,3,3-tetramethyl-7-oxa-1,4-diazabicyclo[4.1.0]heptan-5-one **5g**

Yellow powder; yield 65% (0.21 g); mp 179-181°C.
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.44 (s, 1H), 7.72 – 7.62 (m, 4H), 7.51 – 7.37 (m, 5H), 1.37 (s, 3H), 1.31 (s, 3H), 1.26 (s, 3H), 1.16 (s, 3H).
^{13}C NMR (76 MHz, DMSO-d_6) δ 164.22, 140.76, 139.70, 133.28, 128.99, 127.88, 127.70, 126.79, 126.13, 75.38, 61.48, 55.69, 27.78, 27.35, 22.05, 21.79.
HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{20}H_{23}N_2O_2$: 323.1754; Found: 323.1749



6-(3-methoxyphenyl)-2,2,3,3-tetramethyl-7-oxa-1,4-diazabicyclo[4.1.0]heptan-5-one **5h**

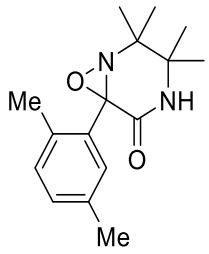
Yellow powder; yield 47% (0.13 g); mp 137-139°C.
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.38 (s, 1H), 7.34 – 7.24 (m, 1H), 6.98 – 6.89 (m, 2H), 6.88 – 6.83 (m, 1H), 3.75 (s, 3H), 1.34 (s, 3H), 1.28 (s, 3H), 1.23 (s, 3H), 1.14 (s, 3H).
^{13}C NMR (76 MHz, DMSO-d_6) δ 164.16, 158.76, 135.72, 129.02, 119.50, 114.35, 112.70, 75.51, 61.46, 55.67, 55.16, 27.77, 27.34, 22.06, 21.76.
HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{15}H_{21}N_2O_3$: 277.1547; Found: 277.1552



6-(3,4-dimethoxyphenyl)-2,2,3,3-tetramethyl-7-oxa-1,4-diazabicyclo[4.1.0]heptan-5-one **5i**

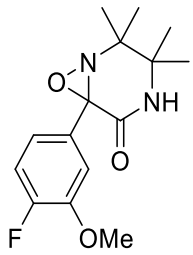
Yellow powder; yield 52% (0.16 g); mp 162-164°C.
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.33 (s, 1H), 6.99 – 6.91 (m, 2H), 6.89 (s, 1H), 3.75 (s, 3H), 3.73 (s, 3H), 1.32 (s, 3H), 1.27 (s, 3H), 1.23 (s, 3H), 1.14 (s, 3H).

^{13}C NMR (76 MHz, DMSO-d_6) δ 164.41, 149.39, 148.18, 126.40, 120.25, 111.14, 110.76, 75.28, 61.49, 55.75, 55.64, 55.57, 27.55, 27.34, 22.03.
HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{16}H_{23}N_2O_4$: 307.1652; Found: 307.1656



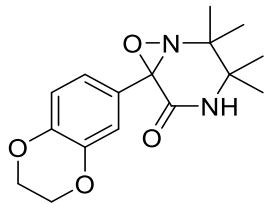
6-(2,5-dimethylphenyl)-2,2,3,3-tetramethyl-7-oxa-1,4-diazabicyclo[4.1.0]heptan-5-one **5j**

Yellow powder; yield 44% (0.12 g); mp 119-121°C.
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.31 (s, 1H), 7.11 – 7.00 (m, 2H), 6.96 (s, 1H), 2.25 (s, 3H), 2.19 (s, 3H), 1.41 (s, 3H), 1.33 (s, 3H), 1.28 (s, 3H), 1.13 (s, 3H).
^{13}C NMR (76 MHz, DMSO-d_6) δ 164.26, 133.99, 133.30, 133.18, 129.58, 128.99, 127.38, 76.79, 61.20, 55.36, 28.93, 27.41, 22.61, 21.88, 20.46, 18.58.
HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{16}H_{23}N_2O_2$: 275.1754; Found: 275.1760



6-(4-fluoro-3-methoxyphenyl)-2,2,3,3-tetramethyl-7-oxa-1,4-diazabicyclo[4.1.0]heptan-5-one **5k**

Yellow powder; yield 69% (0.20 g); mp 146-148°C.
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.40 (s, 1H), 7.27 – 7.10 (m, 3H), 3.85 (s, 3H), 1.33 (s, 3H), 1.28 (s, 3H), 1.22 (s, 3H), 1.13 (s, 3H).
^{13}C NMR (76 MHz, DMSO-d_6) δ 163.92, 150.71 (d, J = 243.6 Hz), 147.66 (d, J = 10.4 Hz), 126.68 (d, J = 6.5 Hz), 124.03 (d, J = 3.5 Hz), 115.10 (d, J = 19.7 Hz), 113.16 (d, J = 2.0 Hz), 74.50, 61.49, 56.07, 55.67, 27.68, 27.29, 22.01, 21.76.
HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{15}H_{20}FN_2O_3$: 295.1452; Found: 295.1453

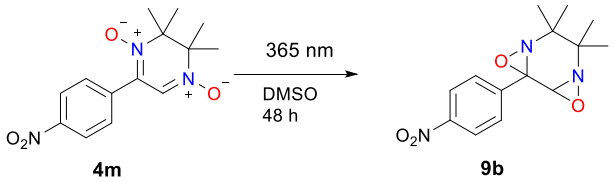


6-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-2,2,3,3-tetramethyl-7-oxa-1,4-diazabicyclo[4.1.0]heptan-5-one **5l**

White powder; yield 59% (0.18 g); mp 159-161°C

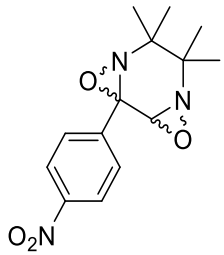
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.34 (s, 1H), 6.83 (s, 3H), 4.23 (s, 4H), 1.31 (s, 3H), 1.25 (s, 3H), 1.20 (s, 3H), 1.12 (s, 3H).
^{13}C NMR (76 MHz, DMSO-d_6) δ 164.27, 144.00, 142.72, 127.00, 120.35, 116.49, 116.36, 74.91, 64.20, 64.09, 61.45, 55.72, 27.56, 27.34, 22.00, 21.96.
HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{16}H_{21}N_2O_4$: 305.1496; Found: 305.1500

4. Experimental procedure for the synthesis of 1-(4-nitrophenyl)-5,5,6,6-tetramethyl-3,8-dioxa-4,7-diazatricyclo[5.1.0.02,4]octane 9b.



4m **9b**

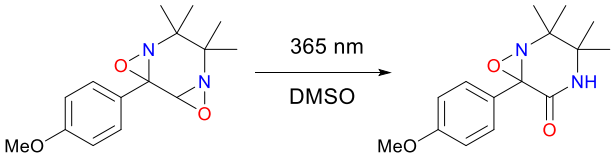
A solution of compound **4m** (1 mmol, 0.29 g) in DMSO (5 ml) was irradiated with a Vilber Lourmat VL-6.LM lamp (365 nm, 6 W) for 48 hours at room temperature in common laboratory glassware. The reaction mixture was diluted with water (50 ml) and extracted with diethyl ether (3x20 ml). The ether solution was separated and washed with water (3x30 ml). Then, the solvent was evaporated in vacuum and obtained residue was purified using column chromatography (eluent EtOAc-hexane 2:1).



1-(4-nitrophenyl)-5,5,6,6-tetramethyl-3,8-dioxa-4,7-diazatricyclo[5.1.0.02,4]octane **9b**, mixture of diastereomers (1:4)

Yellow oil; yield 38% (0.11 g);
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.34 (d, J = 8.5 Hz, 2H), 7.91 (d, J = 8.5 Hz, 1.6H), 7.81 (d, J = 8.5 Hz, 0.4H), 5.45 (s, 0.2H), 5.35 (s, 0.8H), 1.41 – 1.20 (m, 12H).
^{13}C NMR (76 MHz, DMSO-d_6) δ 148.73, 142.91, 128.78, 128.54, 124.43, 124.34, 75.70, 72.47, 72.01, 60.99, 60.16, 59.44, 26.62, 26.54, 26.38, 25.49, 24.93, 24.85, 23.72, 23.69.

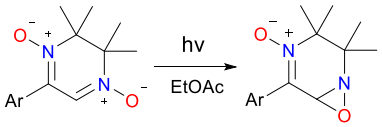
5. Experimental procedure for the synthesis of 6-(4-methoxyphenyl)-2,2,3,3-tetramethyl-7-oxa-1,4-diazabicyclo[4.1.0]heptan-5-one 5a



9a **5a**

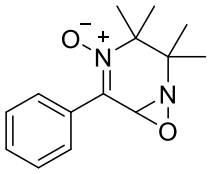
A solution of compound **9a** (1 mmol, 0.28 g) in DMSO (5 ml) was irradiated with a Vilber Lourmat VL-6.LM lamp (365 nm, 6 W) for 48 hours at room temperature in common laboratory glassware. The reaction mixture was diluted with water (50 ml) and extracted with diethyl ether (3x20 ml). The ether solution was separated and washed with water (3x30 ml). Then, the solvent was evaporated in vacuum and obtained residue was purified using column chromatography (eluent EtOAc-hexane 2:1).

6. General experimental procedure for the synthesis of 5-aryl-2,2,3,3-tetramethyl-7-oxa-1,4-diazabicyclo[4.1.0]hept-4-ene 4-oxides 6



4 6

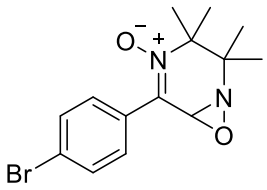
A solution of compound **4** (1 mmol) in EtOAc (5 ml) was irradiated with a a strip of 24 W 450 nm LED for 24 hours at room temperature in common laboratory glassware. The reaction mixture was evaporated in vacuum and obtained residue was purified using column chromatography (eluent EtOAc-hexane 2:1).



2,2,3,3-tetramethyl-5-phenyl-7-oxa-1,4-diazabicyclo[4.1.0]hept-4-ene 4-oxide **6a**

Yellow powder; yield 46% (0.11 g); mp 110-112 °C.

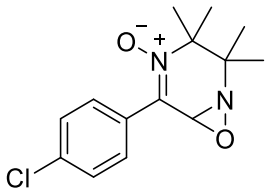
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 – 7.96 (m, 2H), 7.53 – 7.37 (m, 3H), 5.00 (s, 1H), 1.64 (s, 3H), 1.50 (s, 6H), 1.29 (s, 3H).
^{13}C NMR (76 MHz, $CDCl_3$) δ 133.00, 131.77, 130.06, 128.57, 128.45, 75.23, 71.24, 63.16, 26.99, 24.71, 23.63, 22.96.
HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{14}H_{19}N_2O_2$: 247.1441; Found: 247.1449.



5-(4-bromophenyl)-2,2,3,3-tetramethyl-7-oxa-1,4-diazabicyclo[4.1.0]hept-4-ene 4-oxide **6b**

Yellow powder; yield 58% (0.19 g); mp 143-145 °C.

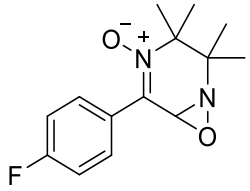
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 8.7 Hz, 2H), 4.95 (s, 1H), 1.61 (s, 3H), 1.48 (s, 6H), 1.28 (s, 3H).
^{13}C NMR (76 MHz, $CDCl_3$) δ 132.18, 131.74, 130.51, 129.90, 124.08, 75.54, 70.85, 63.16, 26.80, 24.63, 23.50, 23.01.
HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{14}H_{18}BrN_2O_2$: 325.0546; Found: 325.0541.



5-(4-chlorophenyl)-2,2,3,3-tetramethyl-7-oxa-1,4-diazabicyclo[4.1.0]hept-4-ene 4-oxide **6c**

Yellow powder; yield 61% (0.17 g); mp 128-130 °C.

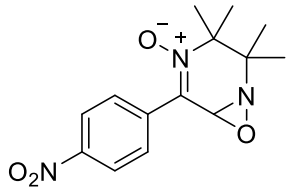
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 8.8 Hz, 2H), 4.96 (s, 1H), 1.62 (s, 3H), 1.49 (s, 6H), 1.29 (s, 3H).
^{13}C NMR (76 MHz, $CDCl_3$) δ 135.78, 132.15, 130.10, 129.77, 128.81, 75.52, 70.96, 63.21, 26.84, 24.68, 23.54, 23.06.
HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{14}H_{18}ClN_2O_2$: 281.1051; Found: 281.1050.



5-(4-fluorophenyl)-2,2,3,3-tetramethyl-7-oxa-1,4-diazabicyclo[4.1.0]hept-4-ene 4-oxide **6d**

Yellow powder; yield 52% (0.14 g); mp 115-117 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 – 8.00 (m, 2H), 7.20 – 7.11 (m, 2H), 4.97 (s, 1H), 1.62 (s, 3H), 1.50 (s, 6H), 1.29 (s, 3H).
^{13}C NMR (76 MHz, $CDCl_3$) δ 163.13 (d, *J* = 252.1 Hz), 132.20, 130.73 (d, *J* = 8.3 Hz), 127.88, 115.70 (d, *J* = 21.7 Hz), 75.29, 71.08, 63.22, 26.83, 24.69, 23.55, 23.06.
HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{14}H_{18}FN_2O_2$: 265.1347; Found: 265.1348.

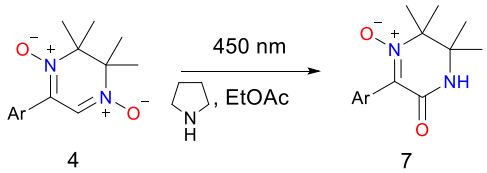


2,2,3,3-tetramethyl-5-(4-nitrophenyl)-7-oxa-1,4-diazabicyclo[4.1.0]hept-4-ene 4-oxide **6e**

Yellow powder; yield 62% (0.18 g); mp 135-137 °C.

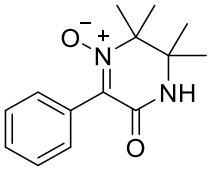
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.32 (s, 4H), 5.36 (s, 1H), 1.52 (s, 3H), 1.42 (s, 3H), 1.40 (s, 3H), 1.25 (s, 3H).
^{13}C NMR (76 MHz, DMSO-d_6) δ 147.50, 137.99, 131.64, 130.01, 123.74, 75.97, 70.33, 63.13, 26.64, 24.69, 23.49, 23.17.
HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for : $C_{14}H_{18}N_3O_4$: 292.1292; Found: 292.1285.

7. General experimental procedure for the synthesis of target 6-aryl-2,2,3,3-tetramethyl-5-oxo-2,3,4,5-tetrahydropyrazine 1-oxides 7



4 7

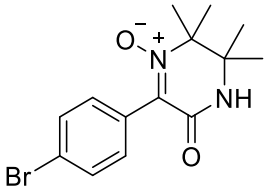
A solution of compound **4** (1 mmol) and pyrrolidine (3 mmol, 0.22 g) in EtOAc (5 ml) was irradiated with a a strip of 24 W 450 nm LED for 24 hours at room temperature in common laboratory glassware. The resulting mixture was evaporated in vacuum and obtained residue was purified using column chromatography (eluent EtOAc-hexane 2:1).



2,2,3,3-tetramethyl-5-oxo-6-phenyl-2,3,4,5-tetrahydropyrazine 1-oxide **7a**

Yellow powder; yield 42% (0.10 g); mp 208-210 °C.

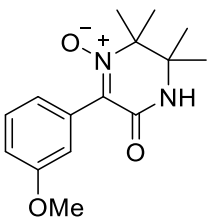
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.48 (s, 1H), 7.51 – 7.45 (m, 2H), 7.39 – 7.34 (m, 3H), 1.40 (s, 6H), 1.30 (s, 6H).
^{13}C NMR (76 MHz, DMSO-d_6) δ 159.07, 135.09, 130.21, 129.81, 128.65, 127.26, 75.78, 54.25, 24.09, 20.90.
HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{14}H_{19}N_2O_2$: 247.1441; Found: 247.1449.



6-(4-bromophenyl)-2,2,3,3-tetramethyl-5-oxo-2,3,4,5-tetrahydropyrazine 1-oxide **7b**

Yellow powder; yield 43% (0.14 g); mp 237-239 °C.

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.52 (s, 1H), 7.59 (d, J = 8.2 Hz, 2H), 7.48 (d, J = 8.3 Hz, 2H), 1.40 (s, 6H), 1.29 (s, 6H).
^{13}C NMR (76 MHz, DMSO-d_6) δ 158.80, 134.33, 132.46, 130.36, 128.90, 121.97, 76.14, 54.31, 24.11, 20.91.
HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{14}H_{18}BrN_2O_2$: 325.0546; Found: 325.0542.

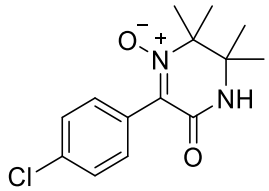


6-(3-methoxyphenyl)-2,2,3,3-tetramethyl-5-oxo-2,3,4,5-tetrahydropyrazine 1-oxide **7c**

Yellow powder; yield 37% (0.10 g); mp 224-226 °C.

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.47 (s, 1H), 7.35 – 7.24 (m, 1H), 7.08 – 6.98 (m, 2H), 6.99 – 6.90 (m, 1H), 3.75 (s, 3H), 1.40 (s, 6H), 1.29 (s, 6H).
^{13}C NMR (76 MHz, DMSO-d_6) δ 158.98, 158.30, 134.98, 131.02, 128.34, 122.55, 115.85, 114.20, 75.87, 55.14, 54.23, 24.08, 20.87.

HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{15}H_{21}N_2O_3$: 277.1547; Found: 277.1555.

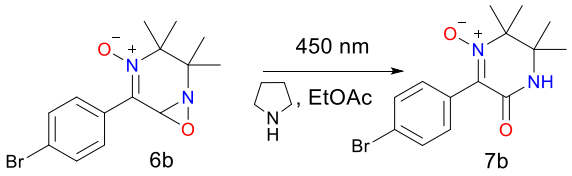


6-(4-chlorophenyl)-2,2,3,3-tetramethyl-5-oxo-2,3,4,5-tetrahydropyrazine 1-oxide **7d**

Yellow powder; yield 49% (0.14 g); mp 233-235 °C.

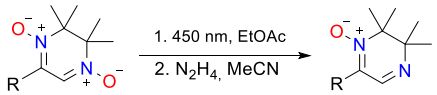
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.54 (s, 1H), 7.57 (d, J = 8.7 Hz, 2H), 7.45 (d, J = 8.7 Hz, 2H), 1.40 (s, 6H), 1.29 (s, 6H).
^{13}C NMR (76 MHz, DMSO-d_6) δ 158.78, 134.15, 133.15, 132.19, 128.46, 127.34, 76.04, 54.24, 24.07, 20.87.
HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{14}H_{18}ClN_2O_2$: 281.1051; Found: 281.1052.

8. Synthesis of 6-(4-bromophenyl)-2,2,3,3-tetramethyl-5-oxo-2,3,4,5-tetrahydropyrazine 1-oxide 7b from 6b.



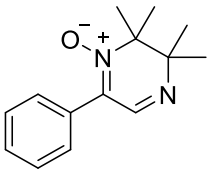
A solution of compound **6b** (1 mmol, 0.33 g) and pyrrolidine (3 mmol, 0.22 g) in EtOAc (5 ml) was irradiated with a a strip of 24 W 450 nm LED for 24 hours at room temperature in common laboratory glassware. The resulting mixture was evaporated in vacuum and obtained residue was purified using column chromatography (eluent EtOAc-hexane 2:1).

9. General experimental procedure for the synthesis of 6-aryl-2,2,3,3-tetramethyl-2,3-dihydropyrazine 1-oxides 8



4 8

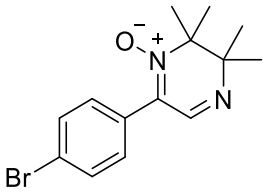
A solution of compound **4** (1 mmol) in EtOAc (5 ml) was irradiated with a strip of 24 W 450 nm LED lamp (450 nm, 6 W) for 24 hours at room temperature in common laboratory glassware. Then, the solvent was evaporated and the residue was dissolved in MeCN (5 ml). Next, hydrazine hydrate (4 mmol, 0.2 g) was added and the resulting mixture was stirred for 24 h at room temperature. Then, the solvent was evaporated in vacuum and obtained residue was purified using column chromatography (eluent EtOAc-hexane 3:1).



2,2,3,3-tetramethyl-6-phenyl-2,3-dihydropyrazine 1-oxide **8a**

Yellow powder; yield 58% (0.14 g); mp 55-57°C.

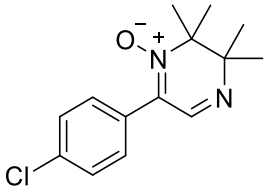
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.16 (s, 1H), 7.96 – 7.89 (m, 2H), 7.50 – 7.42 (m, 3H), 1.33 (s, 6H), 1.24 (s, 6H).
^{13}C NMR (76 MHz, DMSO-d_6) δ 150.24, 130.65, 130.08, 129.57, 128.25, 127.99, 71.87, 61.05, 23.26, 20.09.
HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{14}H_{19}N_2O$: 231.1492; Found: 231.1486



6-(4-bromophenyl)-2,2,3,3-tetramethyl-2,3-dihydropyrazine 1-oxide **8b**

Yellow powder; yield 79% (0.25 g); mp 115-117°C.

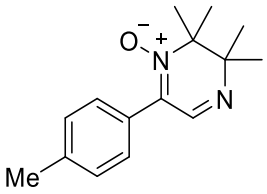
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.16 (s, 1H), 7.92 (d, J = 8.7 Hz, 2H), 7.66 (d, J = 8.7 Hz, 2H), 1.32 (s, 6H), 1.23 (s, 6H).
^{13}C NMR (76 MHz, DMSO-d_6) δ 149.76, 131.23, 130.01, 129.15, 122.61, 72.13, 61.06, 23.23, 20.05.
HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{14}H_{18}BrN_2O$: 309.0597; Found: 309.0610.



6-(4-chlorophenyl)-2,2,3,3-tetramethyl-2,3-dihydropyrazine 1-oxide **8c**

Yellow powder; yield 76% (0.20 g); mp 105-107°C.

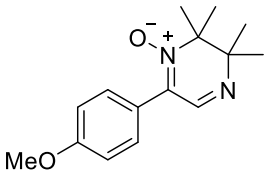
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.17 (s, 1H), 8.00 (d, J = 8.7 Hz, 2H), 7.53 (d, J = 8.7 Hz, 2H), 1.33 (s, 6H), 1.23 (s, 6H).
^{13}C NMR (76 MHz, DMSO-d_6) δ 149.82, 133.85, 129.94, 129.83, 128.81, 128.30, 72.10, 61.07, 23.24, 20.07.
HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{14}H_{18}ClN_2O$: 265.1102; Found: 265.1105.



2,2,3,3-tetramethyl-6-(p-tolyl)-2,3-dihydropyrazine 1-oxide **8d**

Yellow powder; yield 61% (0.15 g); mp 63-65°C.

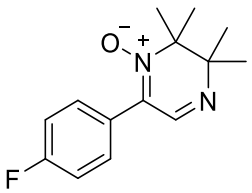
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.16 (s, 1H), 7.86 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 2.34 (s, 3H), 1.32 (s, 6H), 1.22 (s, 6H).
^{13}C NMR (76 MHz, DMSO-d_6) δ 150.30, 139.37, 130.56, 128.79, 127.86, 127.27, 71.73, 61.02, 23.27, 21.04, 20.11.
HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{15}H_{21}N_2O$: 245.1648; Found: 245.1647



6-(4-methoxyphenyl)-2,2,3,3-tetramethyl-2,3-dihydropyrazine 1-oxide **8e**

Yellow powder; yield 53% (0.14 g); mp 83-85°C.

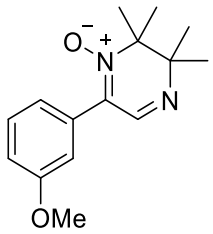
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.18 (s, 1H), 7.99 (d, J = 9.0 Hz, 2H), 7.01 (d, J = 9.0 Hz, 2H), 3.80 (s, 3H), 1.31 (s, 6H), 1.22 (s, 6H).
^{13}C NMR (76 MHz, DMSO-d_6) δ 159.92, 150.33, 130.19, 129.64, 122.46, 113.63, 71.51, 61.02, 55.31, 23.30, 20.14.
HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{15}H_{21}N_2O_2$: 261.1598; Found: 261.1595



6-(4-fluorophenyl)-2,2,3,3-tetramethyl-2,3-dihydropyrazine 1-oxide **8f**

Yellow powder; yield 72% (0.18 g); mp 78-80°C.

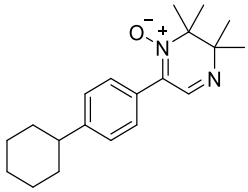
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.18 (s, 1H), 8.11 – 8.00 (m, 2H), 7.38 – 7.26 (m, 2H), 1.34 (s, 6H), 1.25 (s, 6H).
^{13}C NMR (76 MHz, DMSO-d_6) δ 162.09 (d, J = 248.5 Hz), 150.02, 130.54 (d, J = 8.3 Hz), 129.93, 126.52 (d, J = 3.4 Hz), 115.22 (d, J = 21.5 Hz), 71.86, 61.06, 23.24, 20.07.
HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{14}H_{17}FN_2O$: 249.1398; Found: 249.1405



6-(3-methoxyphenyl)-2,2,3,3-tetramethyl-2,3-dihydropyrazine 1-oxide **8g**

Yellow powder; yield 67% (0.17 g); mp 70-72°C.

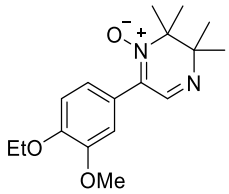
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.17 (s, 1H), 7.58 (s, 1H), 7.49 – 7.33 (m, 2H), 7.06 – 6.98 (m, 1H), 3.78 (s, 3H), 1.33 (s, 6H), 1.23 (s, 6H).
^{13}C NMR (76 MHz, DMSO-d_6) δ 158.89, 150.24, 131.27, 130.57, 129.34, 120.27, 115.47, 113.28, 72.01, 60.95, 55.21, 23.26, 20.08.
HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{15}H_{21}N_2O_2$: 261.1598; Found: 261.1601



6-(4-cyclohexylphenyl)-2,2,3,3-tetramethyl-2,3-dihydropyrazine 1-oxide **8h**

Yellow powder; yield 74% (0.23 g); mp 87-89°C.

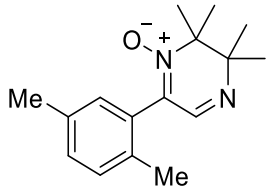
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.18 (s, 1H), 7.90 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 2.54-2.49 (m, 1H in DMSO-d_6), 1.85 – 1.67 (m, 5H), 1.55 – 1.27 (m, 11H), 1.24 (s, 6H).
^{13}C NMR (76 MHz, DMSO-d_6) δ 150.31, 149.27, 130.52, 127.99, 127.67, 126.51, 71.68, 61.00, 43.71, 33.69, 26.25, 25.52, 23.24, 20.08.
HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{20}H_{28}N_2O$: 313.2274; Found: 313.2276



6-(4-ethoxy-3-methoxyphenyl)-2,2,3,3-tetramethyl-2,3-dihydropyrazine 1-oxide **8i**

Yellow powder; yield 57% (0.17 g); mp 116-118°C.

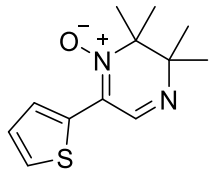
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.24 (s, 1H), 7.78 (s, 1H), 7.55 (d, J = 8.5 Hz, 1H), 7.02 (d, J = 8.5 Hz, 1H), 4.07 (q, J = 7.0 Hz, 2H), 3.78 (s, 3H), 1.39 – 1.27 (m, 9H), 1.22 (s, 6H).
^{13}C NMR (76 MHz, DMSO-d_6) δ 150.41, 149.04, 148.03, 130.26, 122.50, 121.34, 112.03, 111.48, 71.63, 63.72, 60.93, 55.52, 23.33, 20.16, 14.64.
HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{17}H_{25}N_2O_3$: 305.1860; Found: 305.1857



6-(2,5-dimethylphenyl)-2,2,3,3-tetramethyl-2,3-dihydropyrazine 1-oxide **8j**

Brown oil; yield 45% (0.12 g);

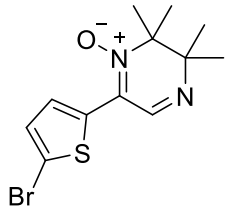
^{1}H NMR (300 MHz, DMSO-d_6) δ 7.79 (s, 1H), 7.17 (s, 2H), 7.04 (s, 1H), 2.30 (s, 3H), 2.11 (s, 3H), 1.35 (s, 6H), 1.29 (s, 6H).
^{13}C NMR (76 MHz, DMSO-d_6) δ 150.76, 134.87, 134.65, 133.32, 130.36, 129.93, 129.85, 128.66, 71.47, 61.43, 23.25, 20.37, 20.05, 18.69.
HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{16}H_{23}N_2O$: 259.1805; Found: 259.1815



2,2,3,3-tetramethyl-6-(thiophen-2-yl)-2,3-dihydropyrazine 1-oxide **8k**

Yellow powder; yield 64% (0.15 g); mp 90-92°C.

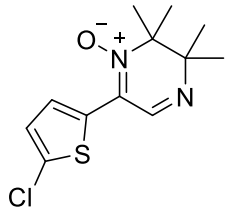
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.69 (s, 1H), 8.05 (d, J = 4.0 Hz, 1H), 7.68 (d, J = 5.1 Hz, 1H), 7.29 – 7.23 (m, 1H), 1.33 (s, 6H), 1.21 (s, 6H).
^{13}C NMR (76 MHz, DMSO-d_6) δ 148.11, 130.87, 128.53, 127.52, 127.48, 126.96, 70.10, 61.33, 23.25, 20.20.
HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{12}H_{17}N_2OS$: 237.1056; Found: 237.1063



6-(5-bromothiophen-2-yl)-2,2,3,3-tetramethyl-2,3-dihydropyrazine 1-oxide **8l**

Brown powder; yield 51% (0.16 g); mp 87-89°C.

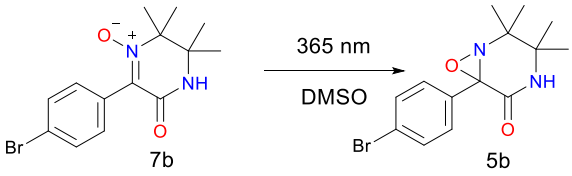
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.42 (d, J = 4.3 Hz, 1H), 7.16 (d, J = 4.3 Hz, 1H), 1.42 (s, 6H), 1.30 (s, 6H).
^{13}C NMR (76 MHz, $CDCl_3$) δ 147.13, 132.80, 129.54, 127.97, 126.01, 117.66, 71.05, 62.19, 23.57, 20.51.
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcld for $C_{12}H_{16}BrN_2OS$: 315.0161; Found: 315.0159



6-(5-chlorothiophen-2-yl)-2,2,3,3-tetramethyl-2,3-dihydropyrazine 1-oxide **8m**

Brown powder; yield 50% (0.14 g); mp 82-84°C
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.68 (s, 1H), 7.97 (d, J = 4.4 Hz, 1H), 7.32 (d, J = 4.4 Hz, 1H), 3.33 (s, 3H), 1.34 (s, 6H), 1.22 (s, 6H).
^{13}C NMR (76 MHz, DMSO-d_6) δ 147.03, 130.74, 129.48, 127.28, 127.21, 126.68, 70.12, 61.47, 23.19, 20.14.
HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{12}H_{15}ClN_2OS$: 271.0666; Found: 271.0673

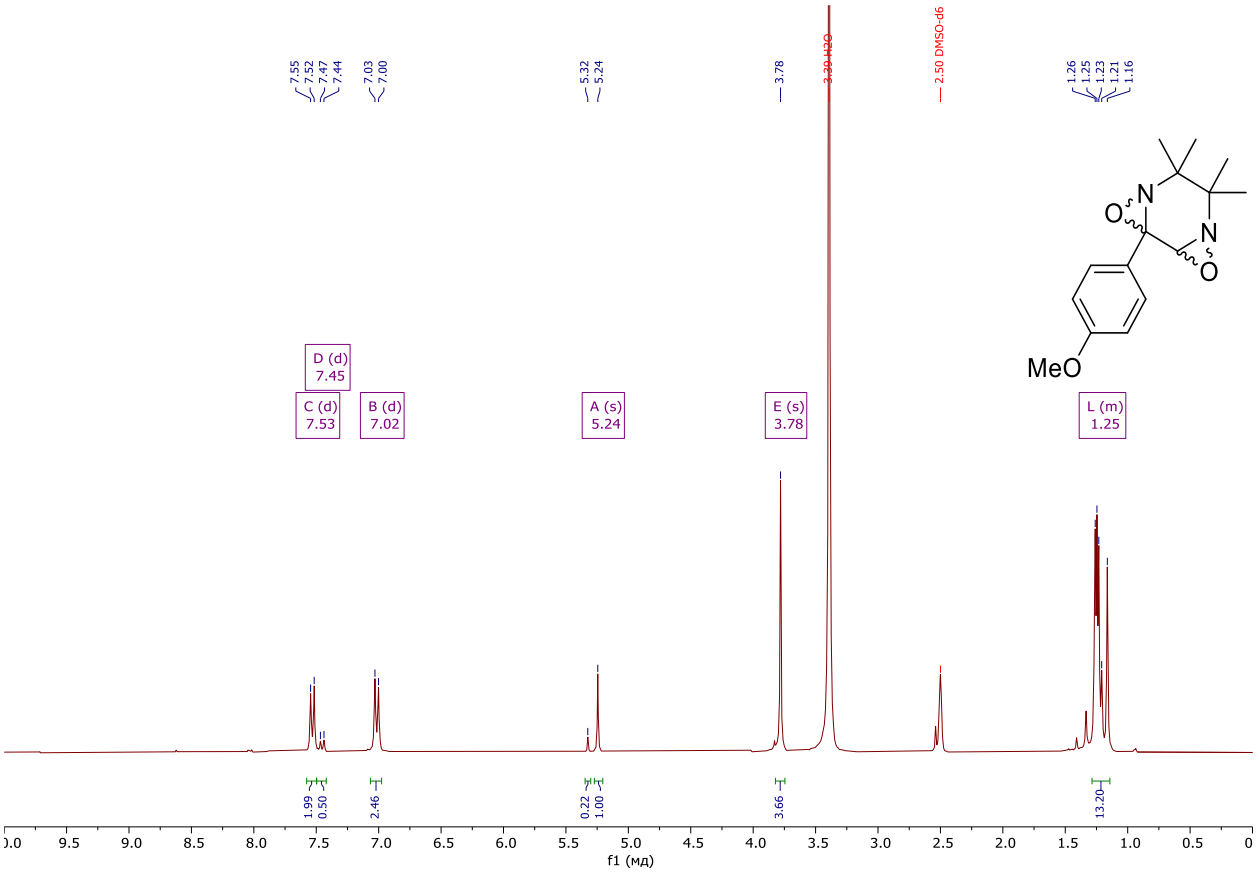
10. Experimental procedure for the synthesis of 6-(4-methoxyphenyl)-2,2,3,3-tetramethyl-7-oxa-1,4-diazabicyclo[4.1.0]heptan-5-one 5a



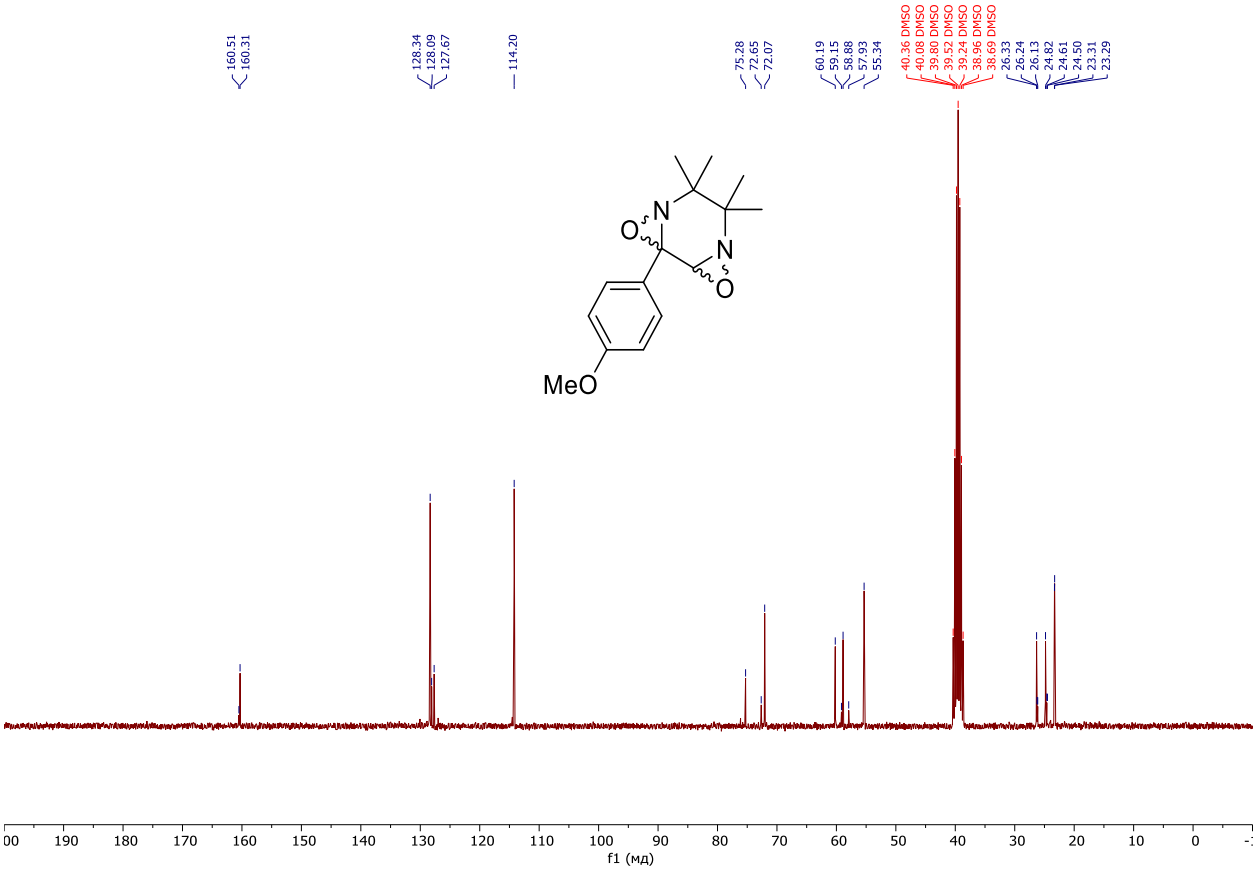
A solution of compound **7** (1 mmol, 0.33 g) in DMSO (5 ml) was irradiated with a Vilber Lourmat VL-6.LM lamp (365 nm, 6 W) for 24 hours at room temperature in common laboratory glassware. The reaction mixture was diluted with water (50 ml) and extracted with diethyl ether (3x20 ml). The ether solution was separated and washed with water (3x30 ml). Then, the solvent was evaporated in vacuum and obtained residue was purified using column chromatography (eluent EtOAc-hexane 2:1).

11. Copies of ^{1}H, ^{13}C NMR and HRMS for compound 9a.

^{1}H NMR spectrum (300 MHz) of **9a** in DMSO-d_6



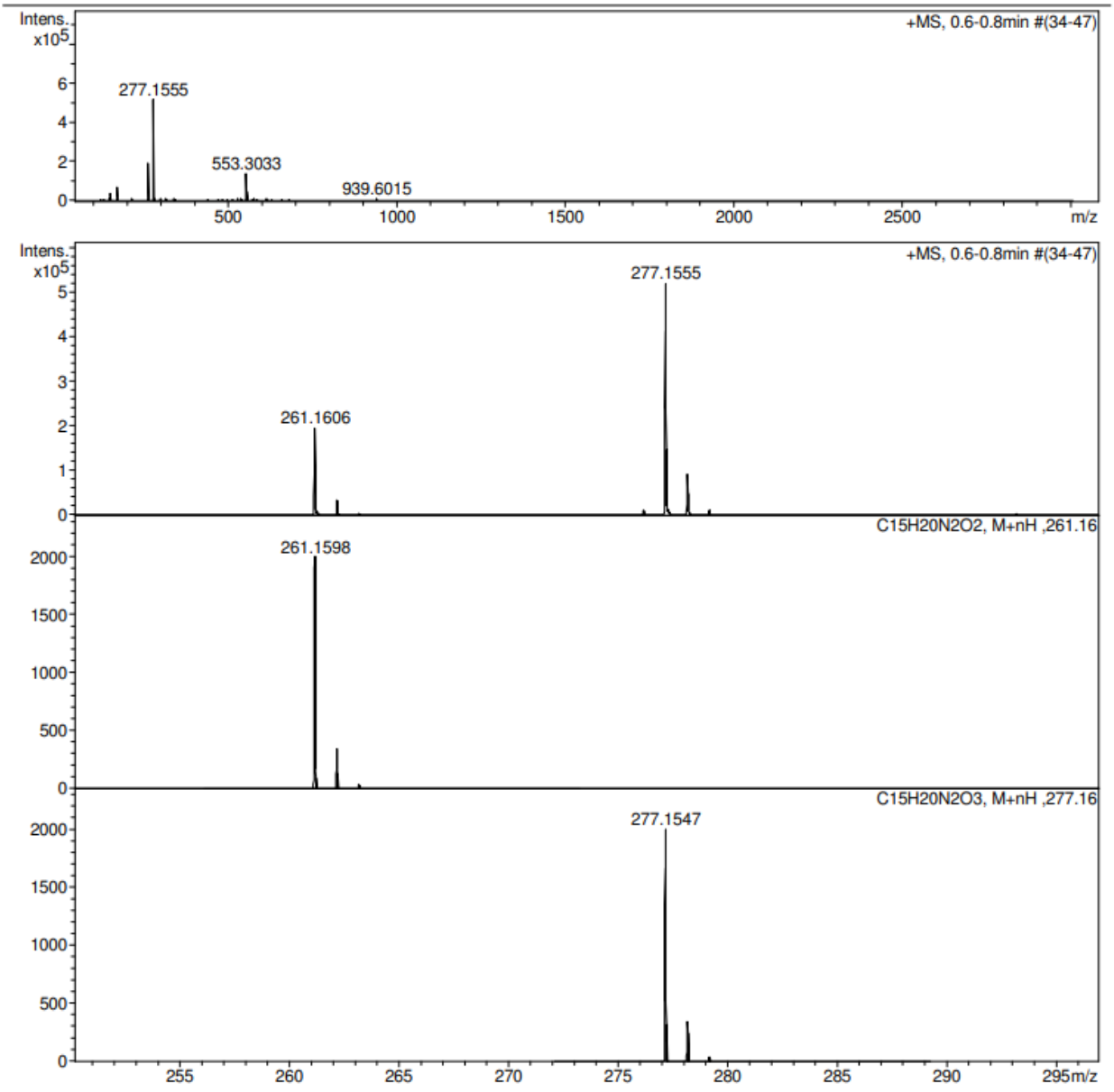
^{13}C {^{1}H} NMR spectrum (76 MHz) of **9a** in DMSO-d_6



HRMS for compound **9a**

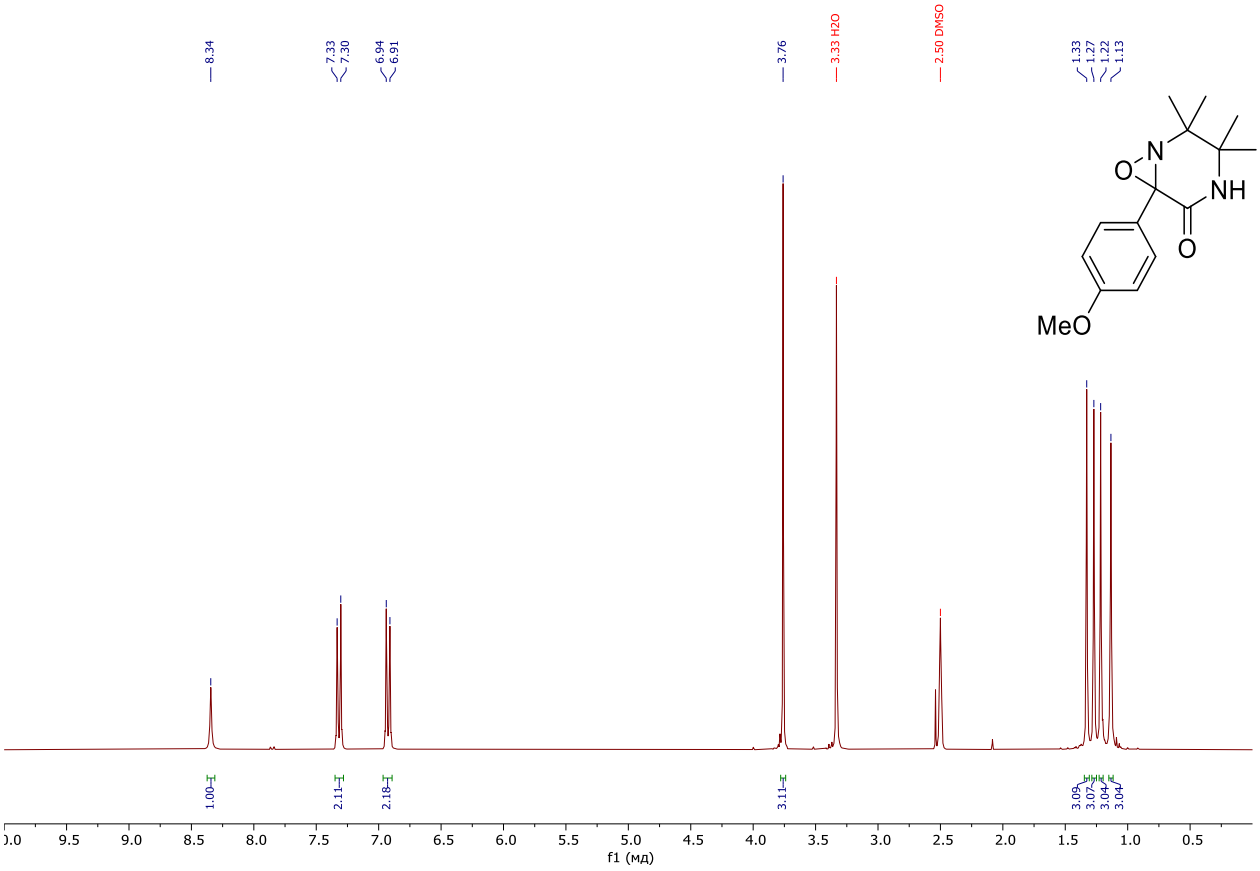
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

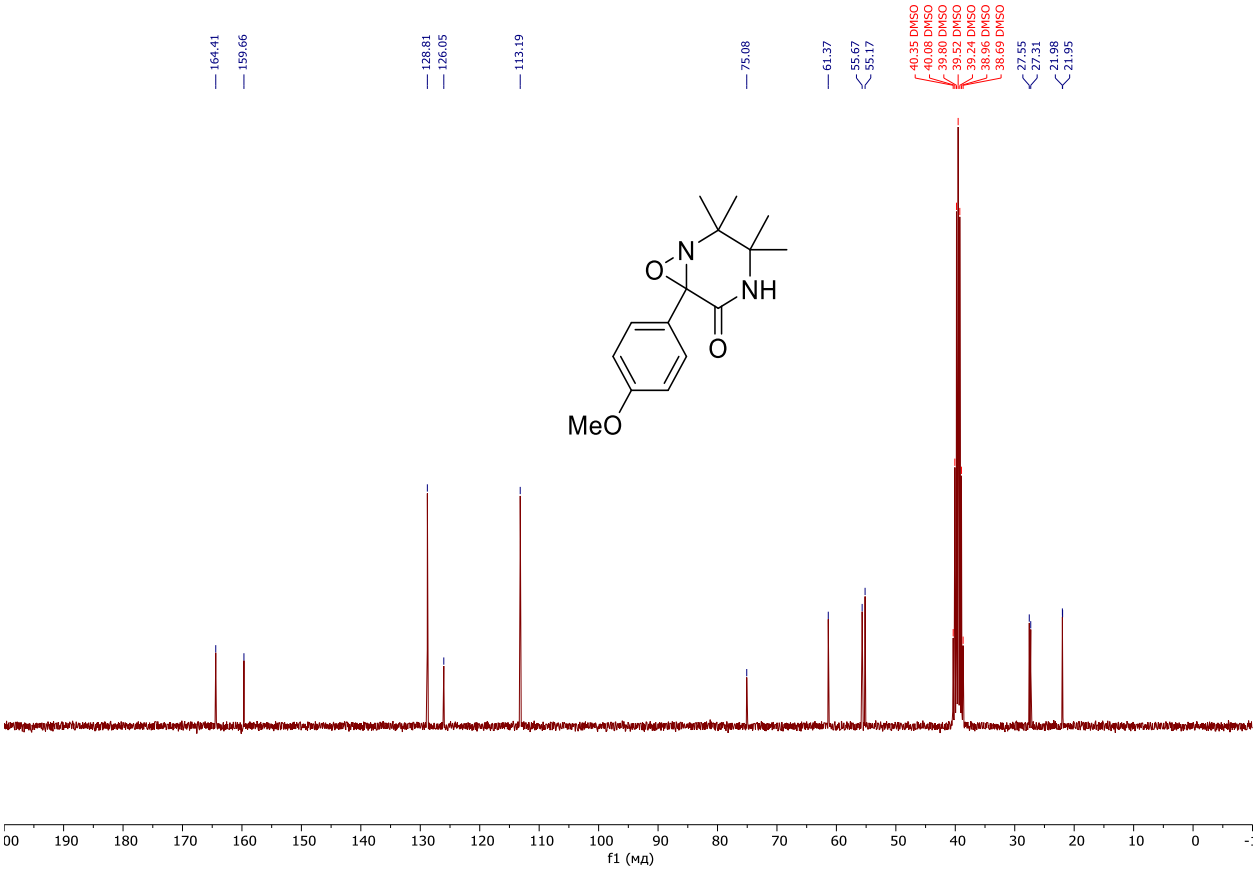


12. Copies of ^{1}H, ^{13}C NMR and HRMS for amides 5.

^{1}H NMR spectrum (300 MHz) of **5a** in DMSO-d_6



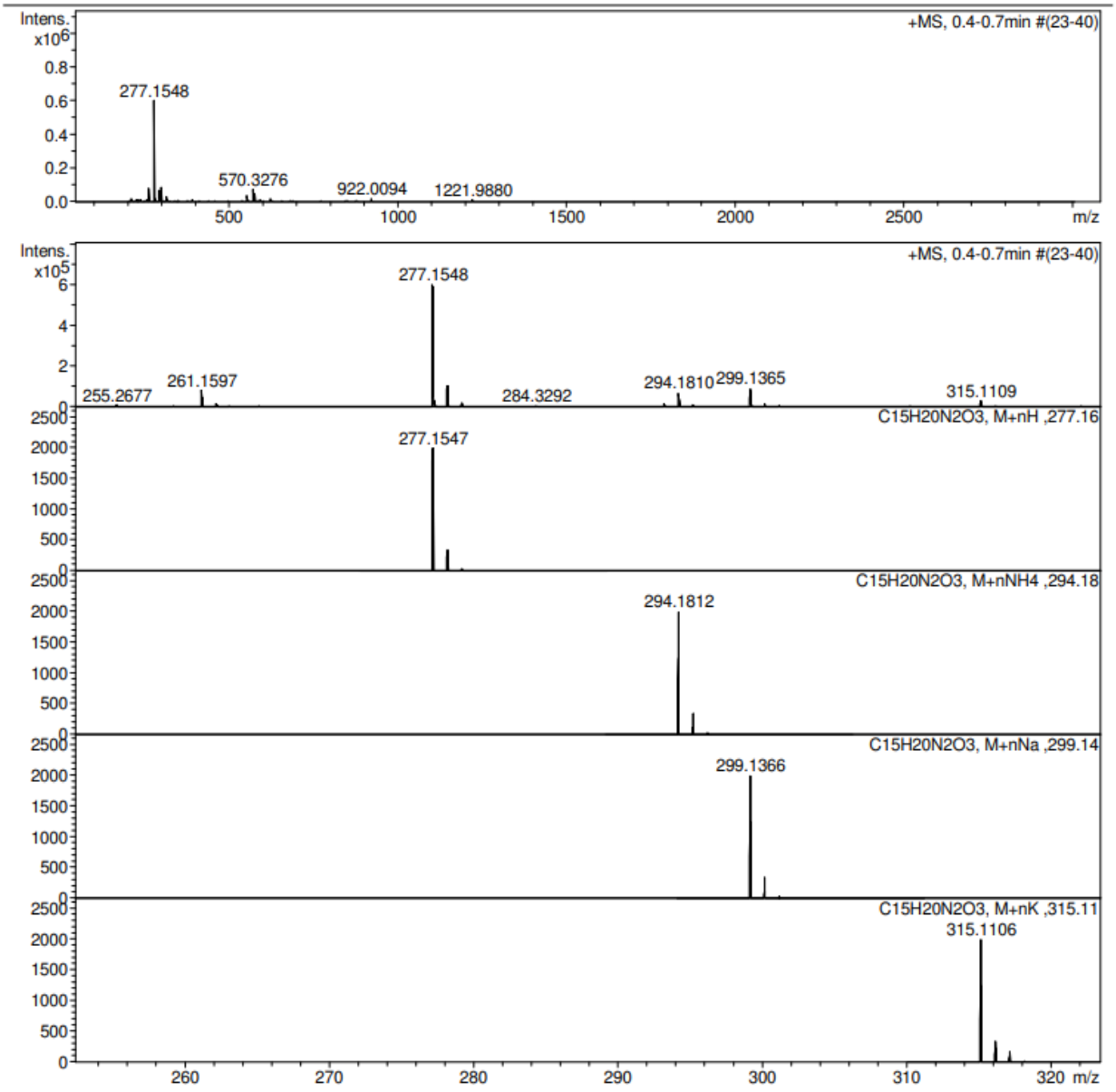
^{13}C {^{1}H} NMR spectrum (76 MHz) of **5a** in DMSO-d_6



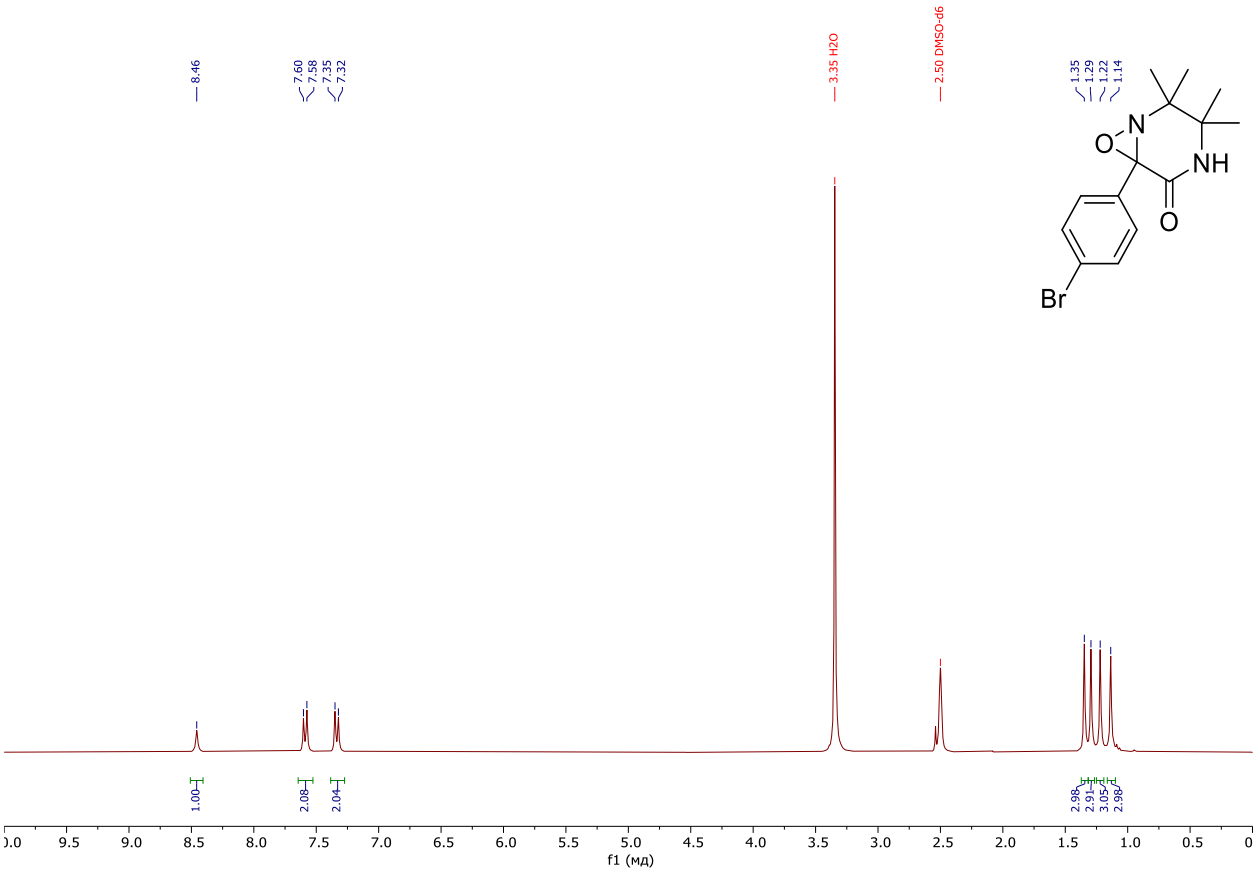
HRMS for compound **5a**

Acquisition Parameter

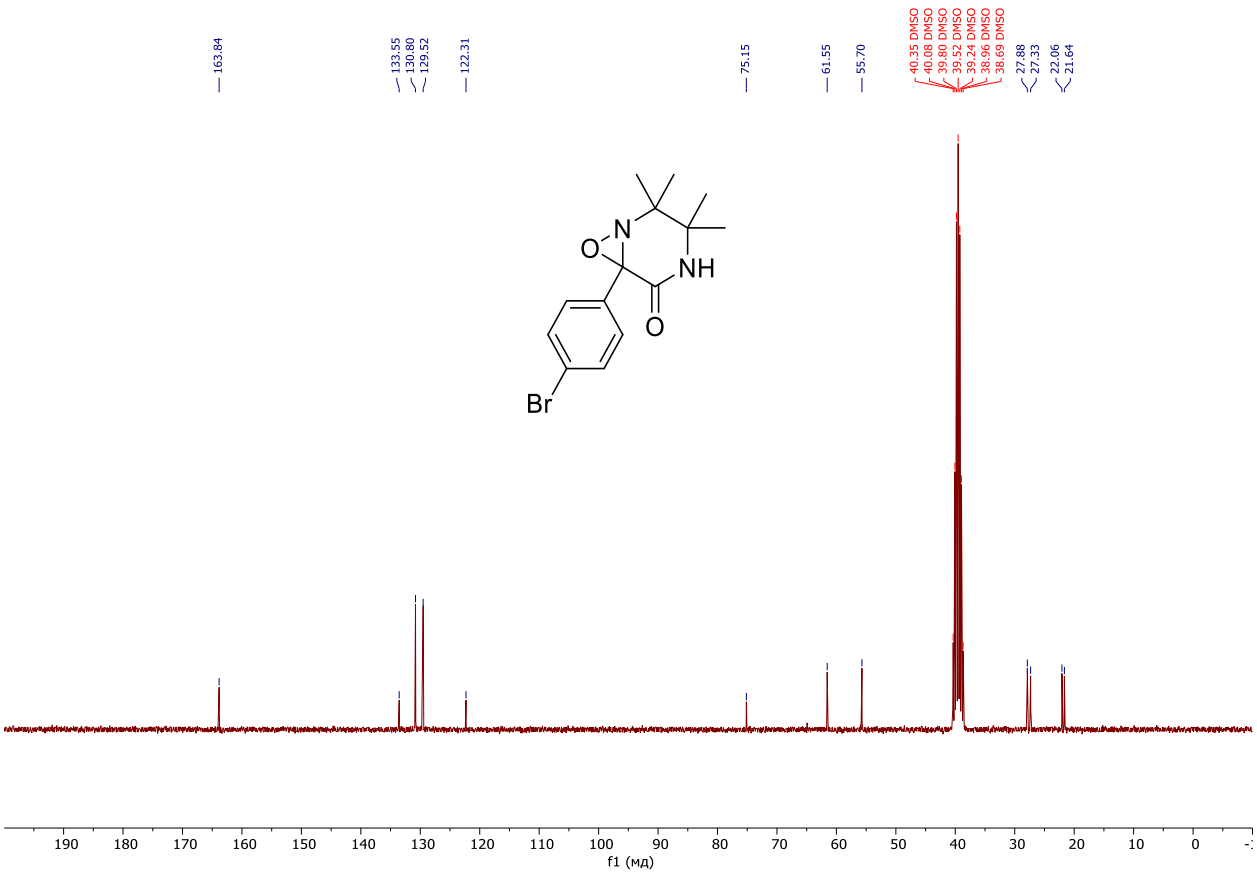
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



^{1}H NMR spectrum (300 MHz) of **5b** in DMSO-d_6



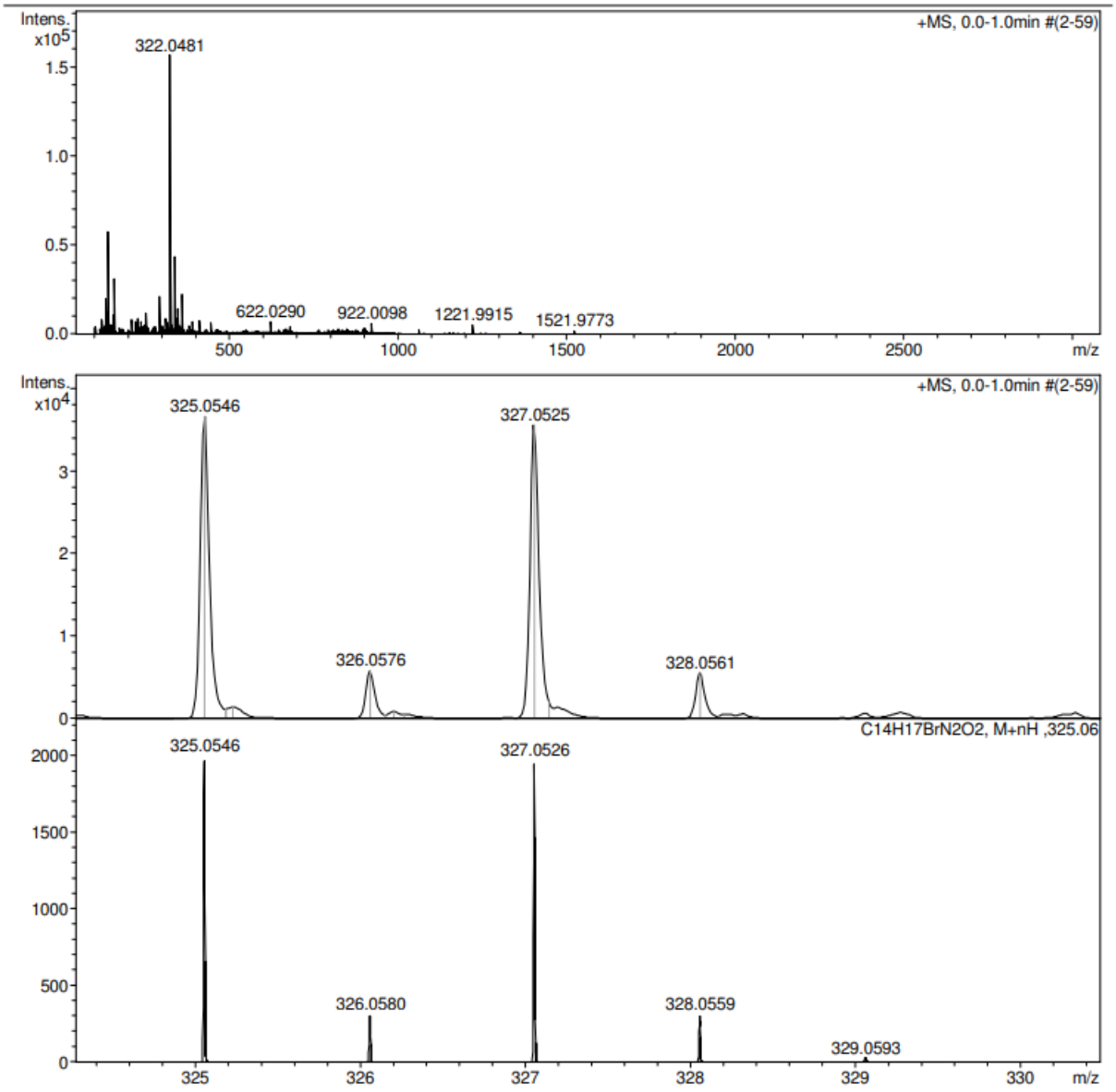
^{13}C {^{1}H} NMR spectrum (76 MHz) of **5b** in DMSO-d_6



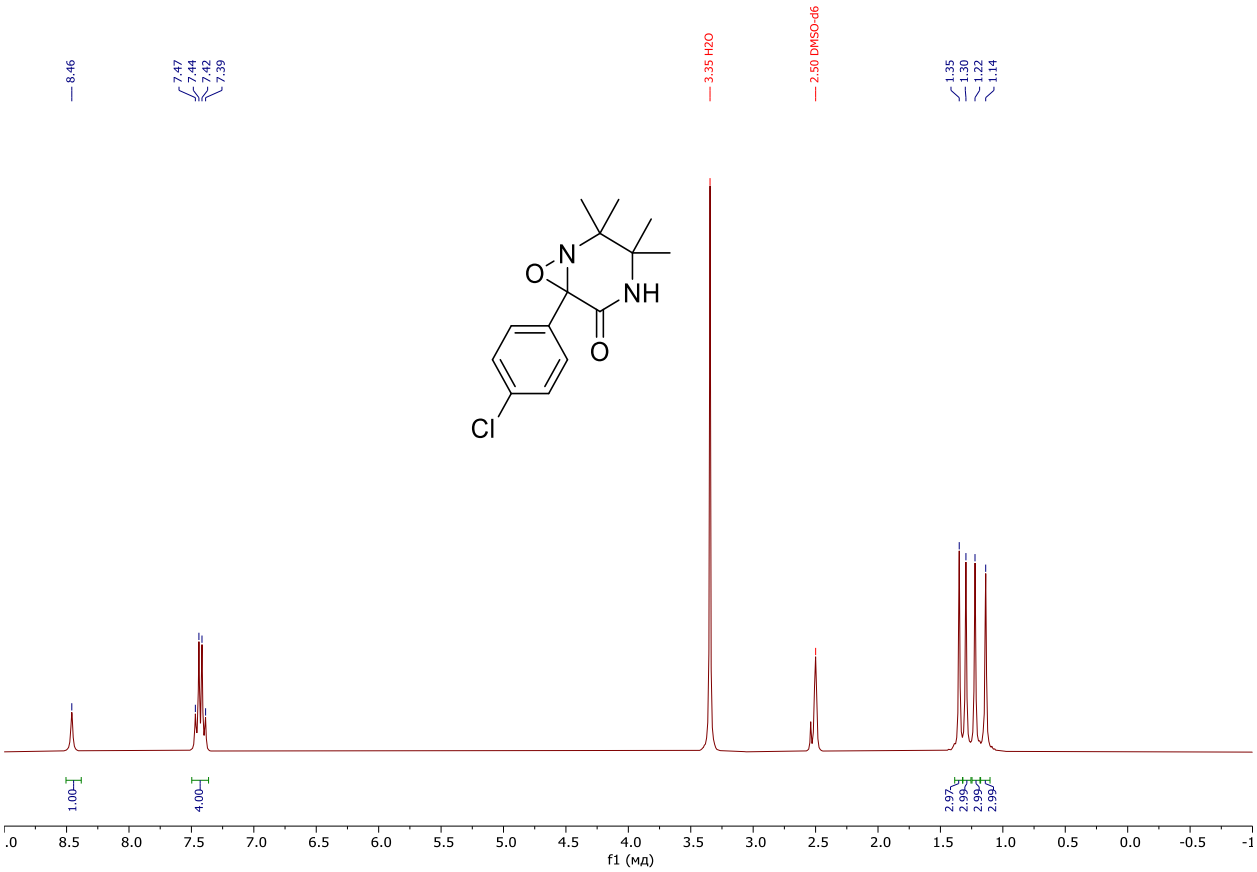
HRMS for compound **5b**

Acquisition Parameter

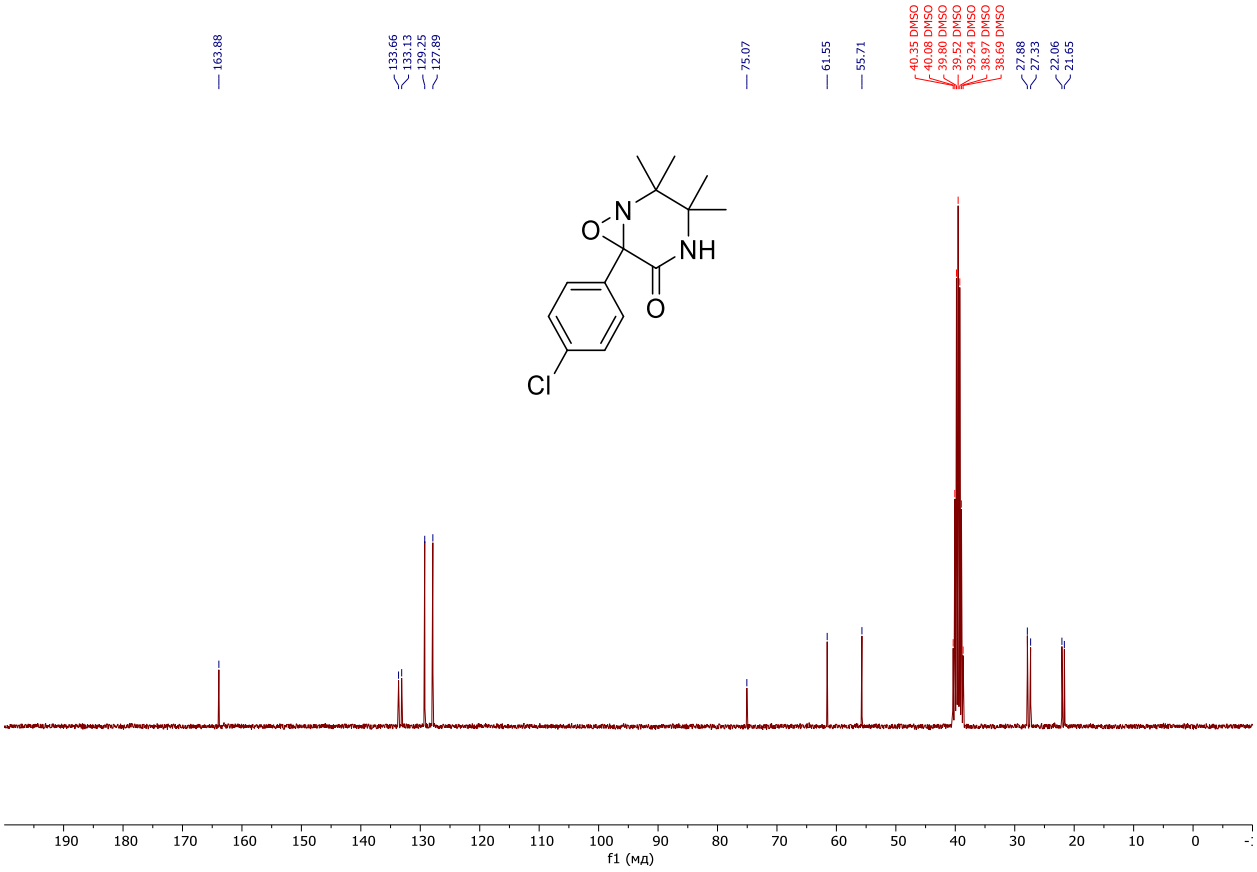
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



^{1}H NMR spectrum (300 MHz) of **5c** in DMSO-d_6



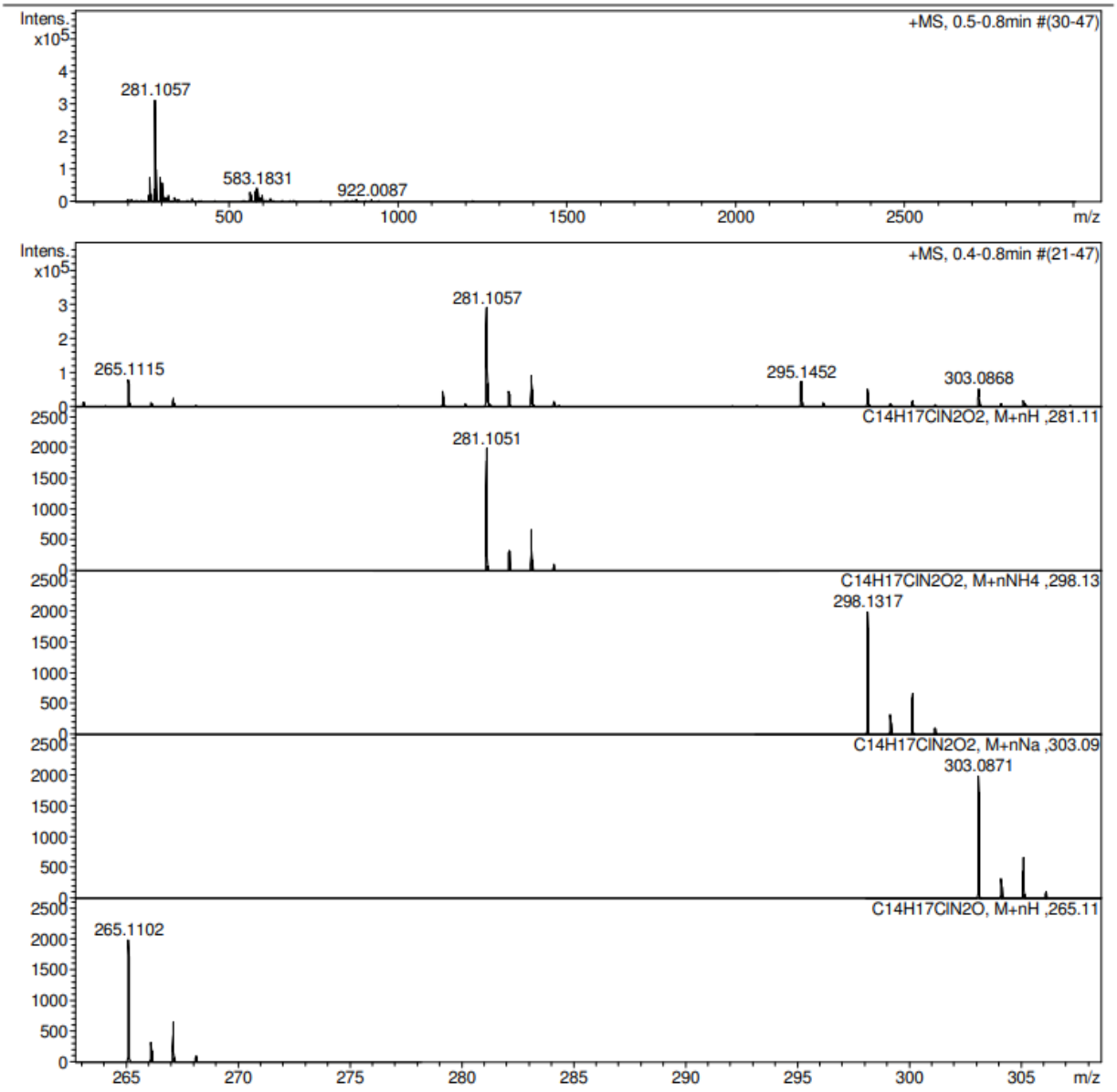
^{13}C {^{1}H} NMR spectrum (76 MHz) of **5c** in DMSO-d_6



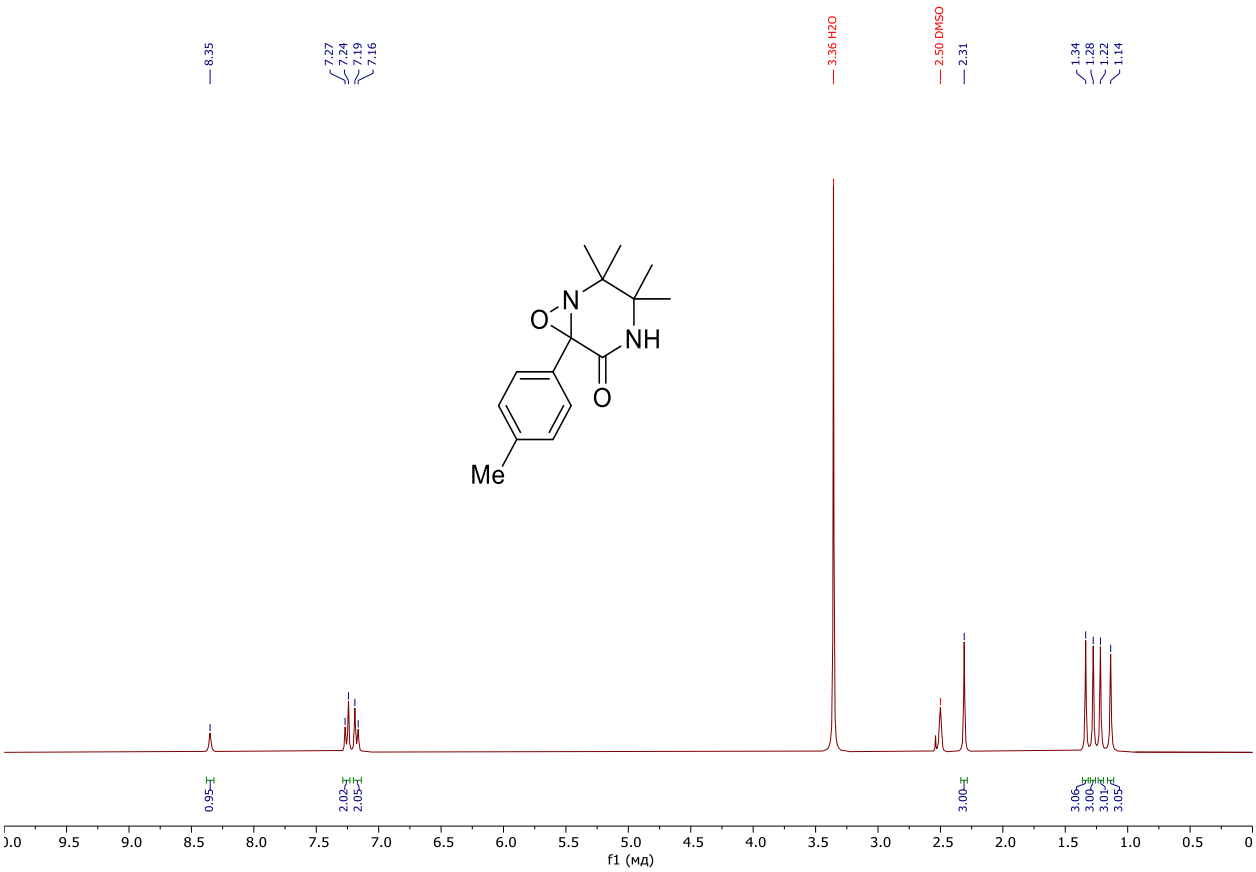
HRMS for compound **5c**

Acquisition Parameter

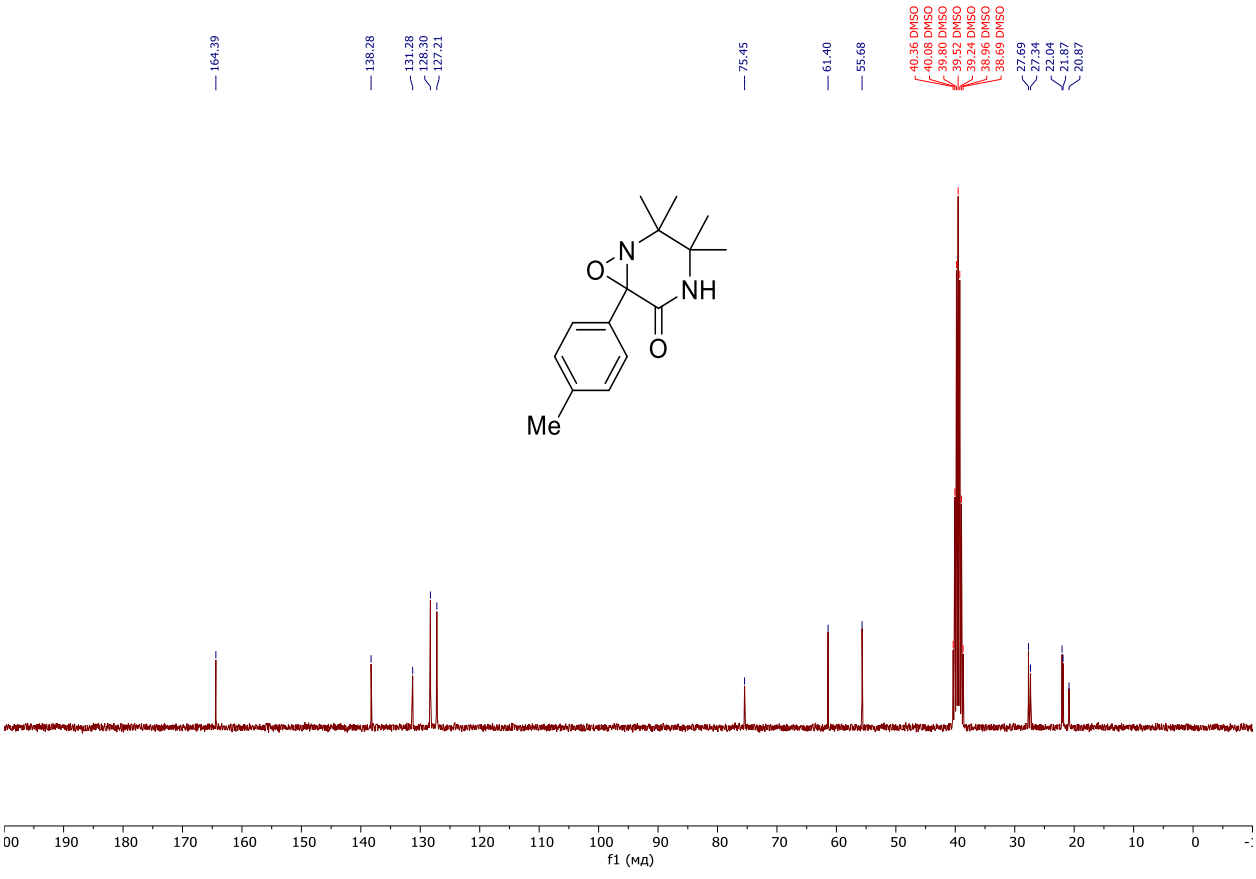
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



^{1}H NMR spectrum (300 MHz) of **5d** in DMSO-d_6



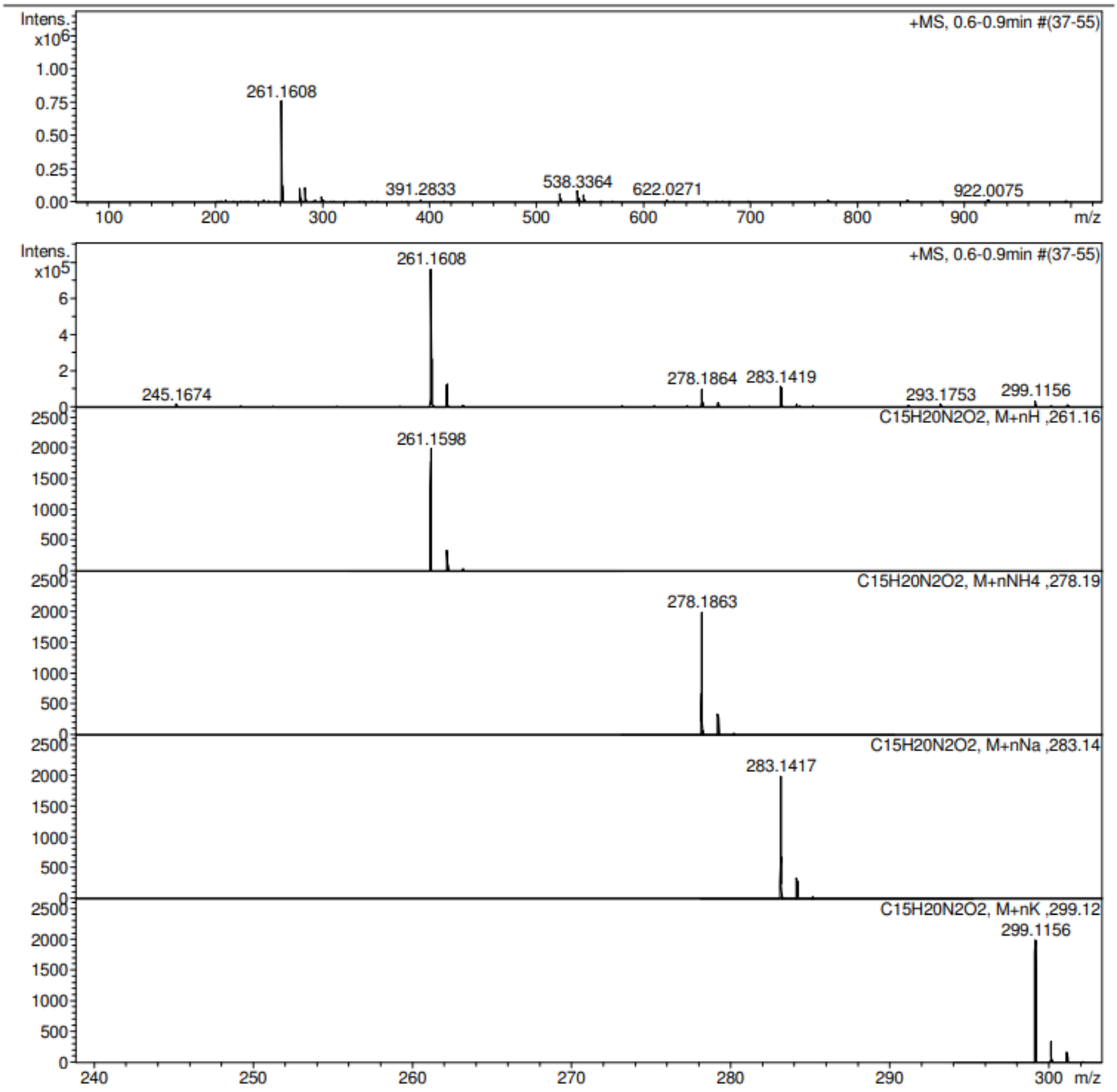
^{13}C {^{1}H} NMR spectrum (76 MHz) of **5d** in DMSO-d_6



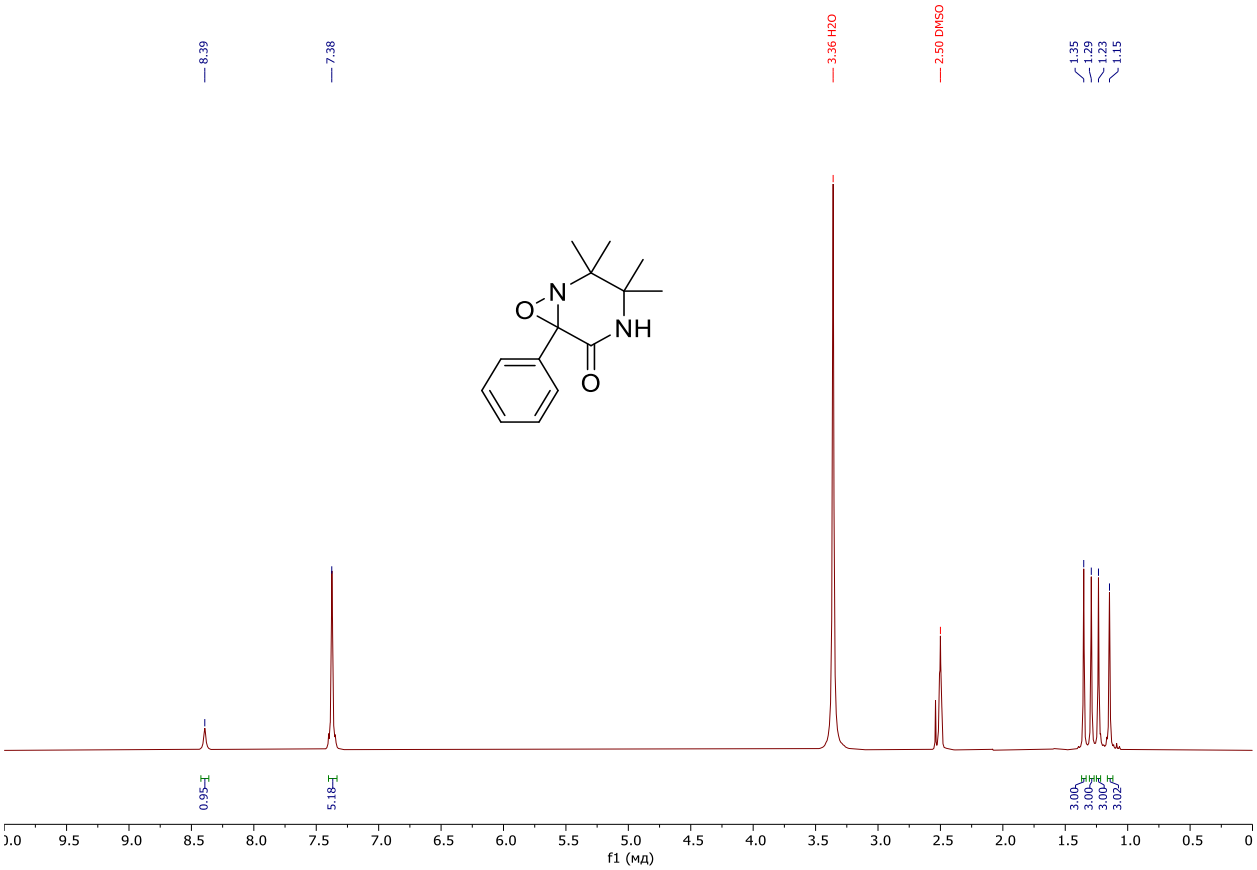
HRMS for compound **5d**

Acquisition Parameter

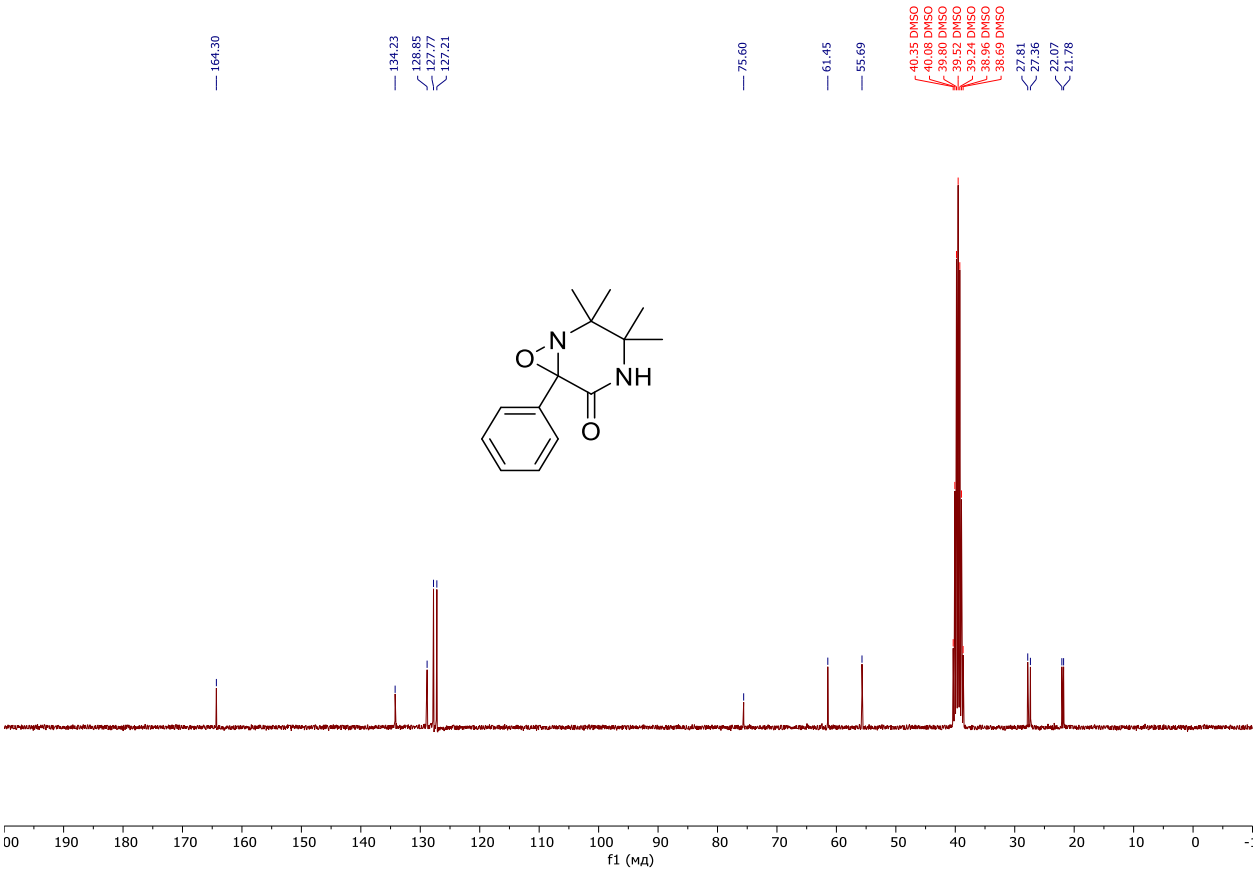
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



^{1}H NMR spectrum (300 MHz) of **5e** in DMSO-d_6



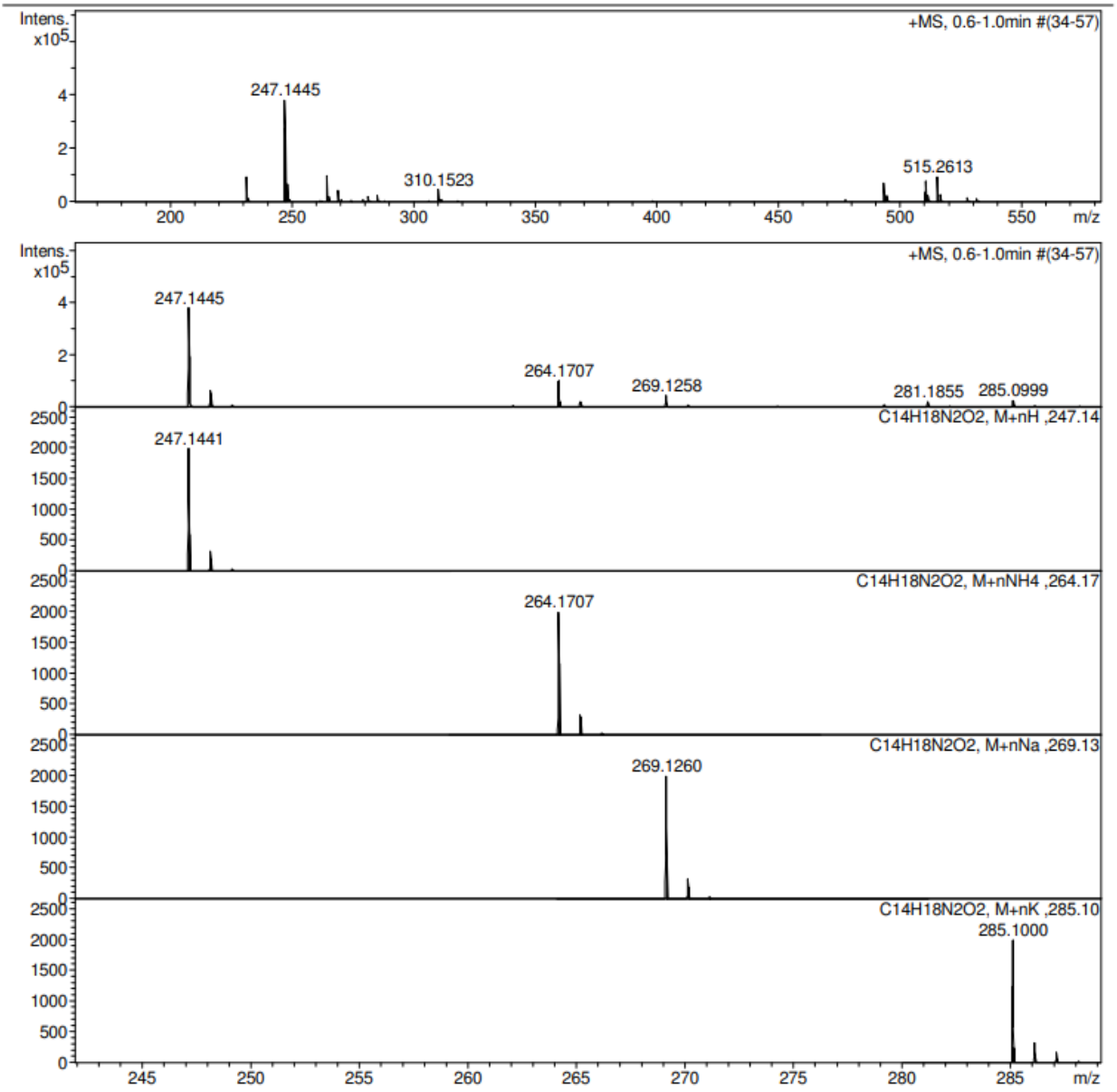
^{13}C {^{1}H} NMR spectrum (76 MHz) of **5e** in DMSO-d_6



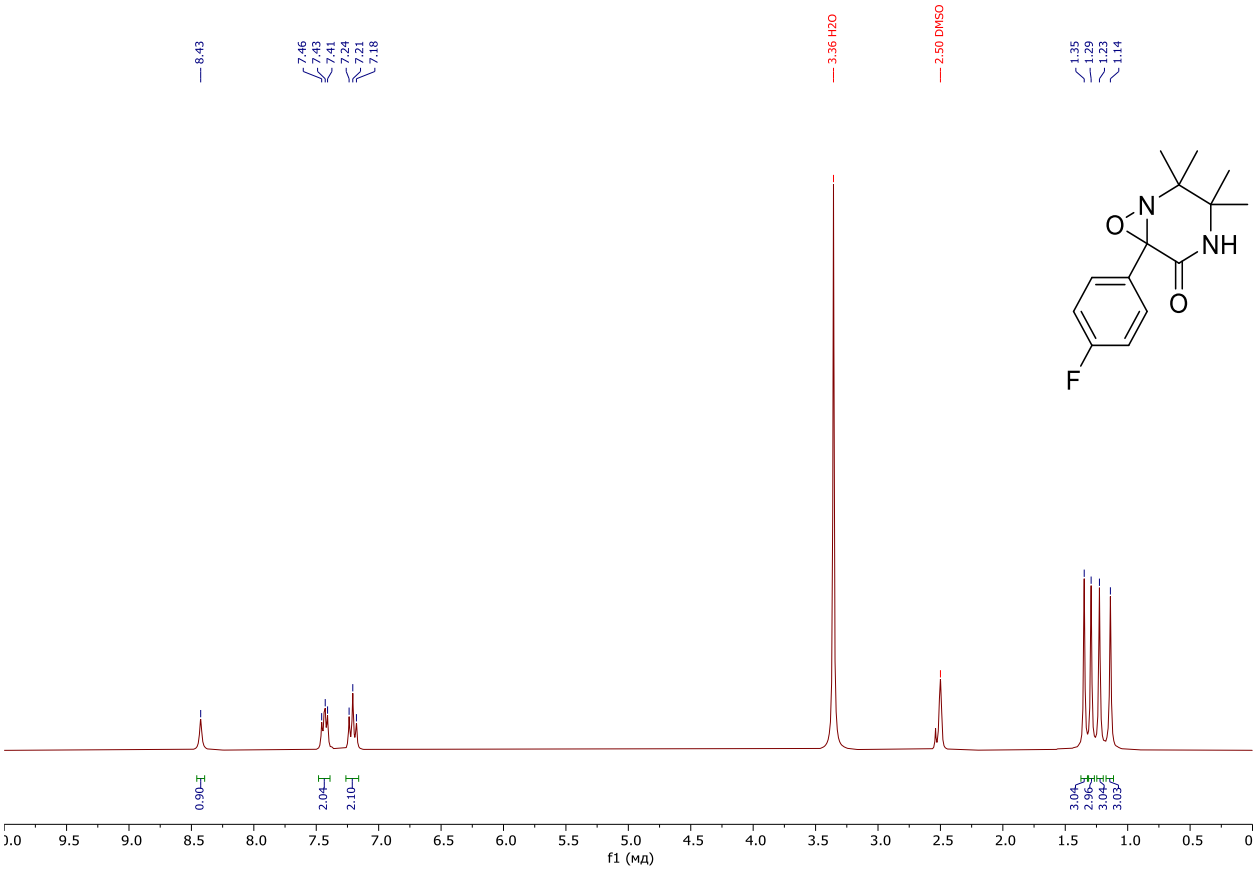
HRMS for compound **5e**

Acquisition Parameter

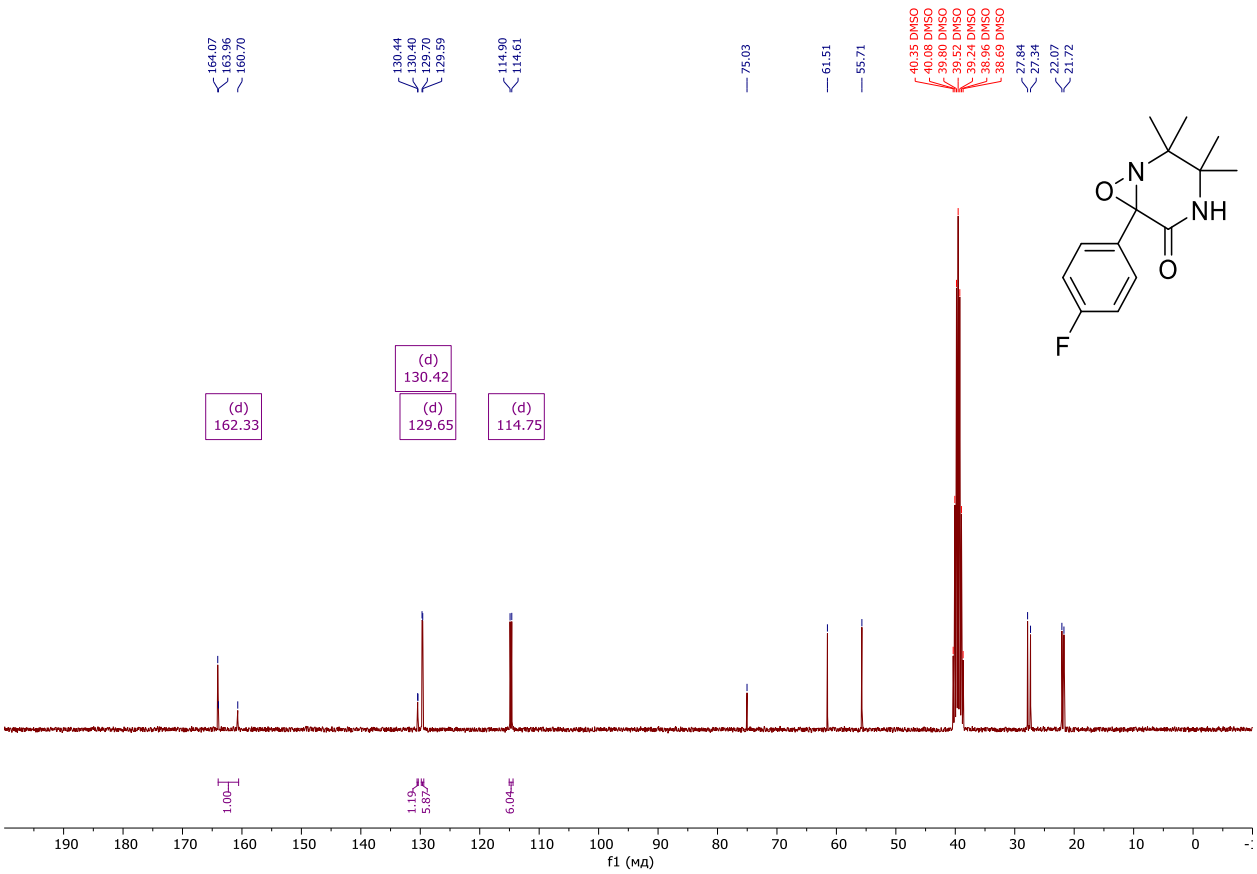
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



^{1}H NMR spectrum (300 MHz) of **5f** in DMSO-d_6



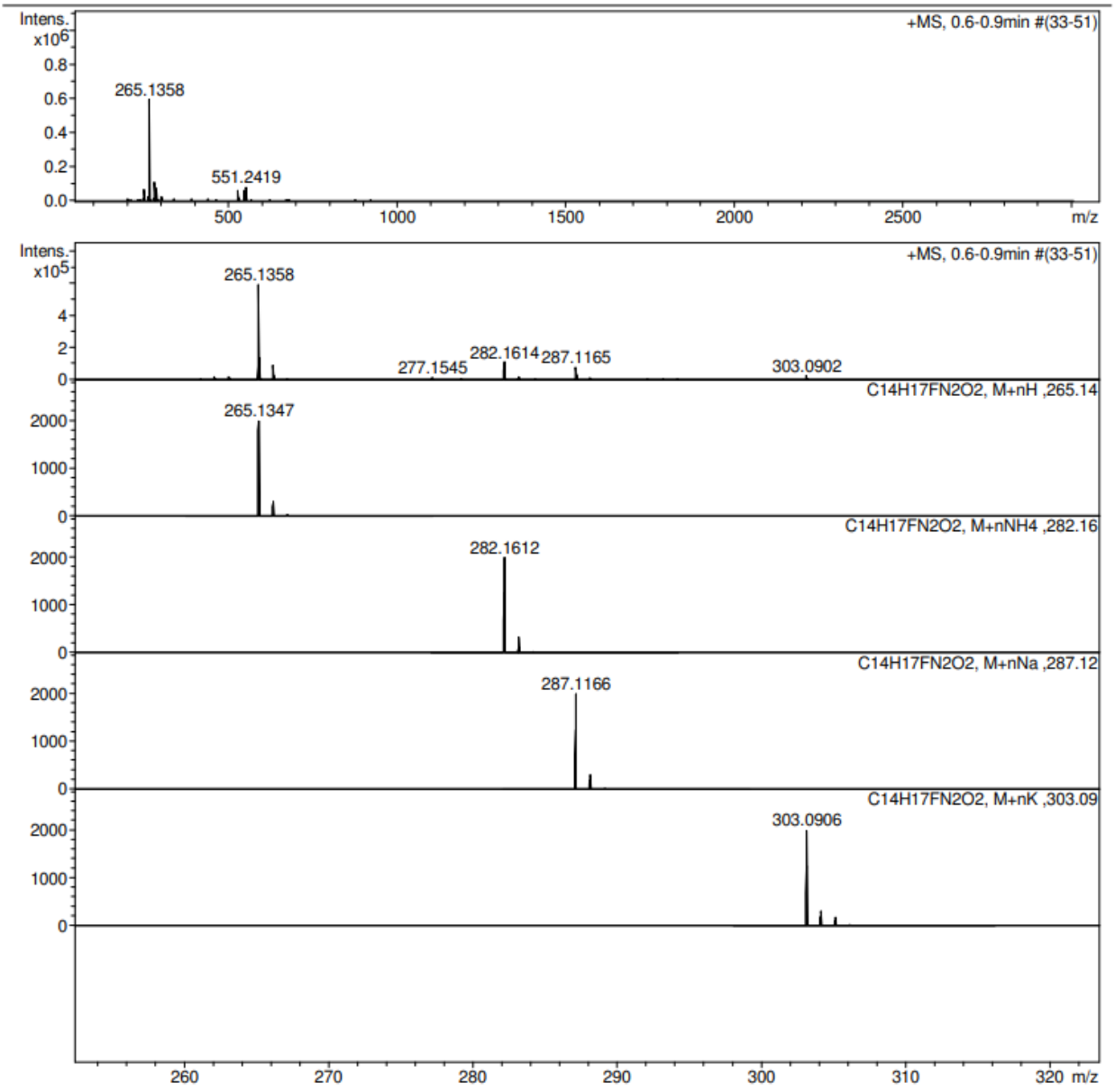
^{13}C {^{1}H} NMR spectrum (76 MHz) of **5f** in DMSO-d_6



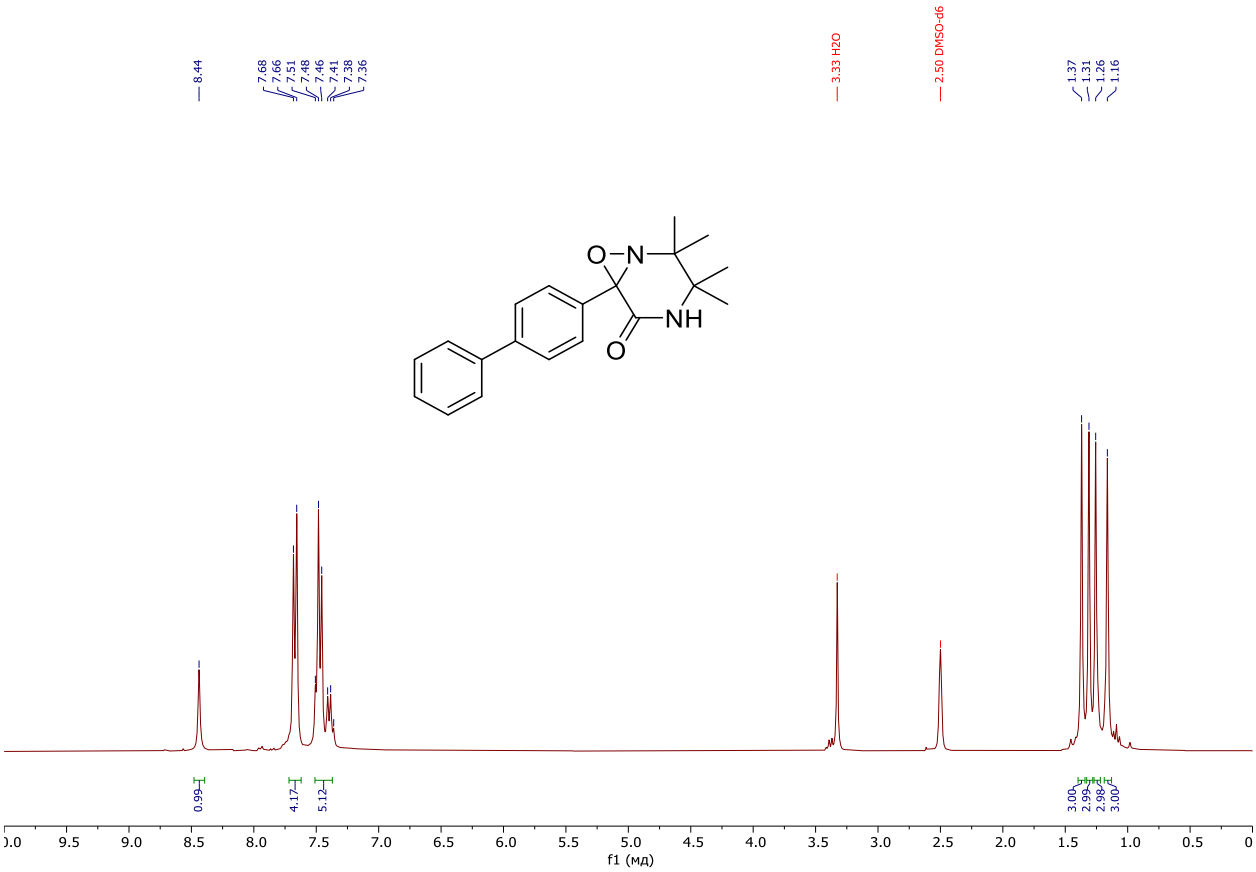
HRMS for compound **5f**

Acquisition Parameter

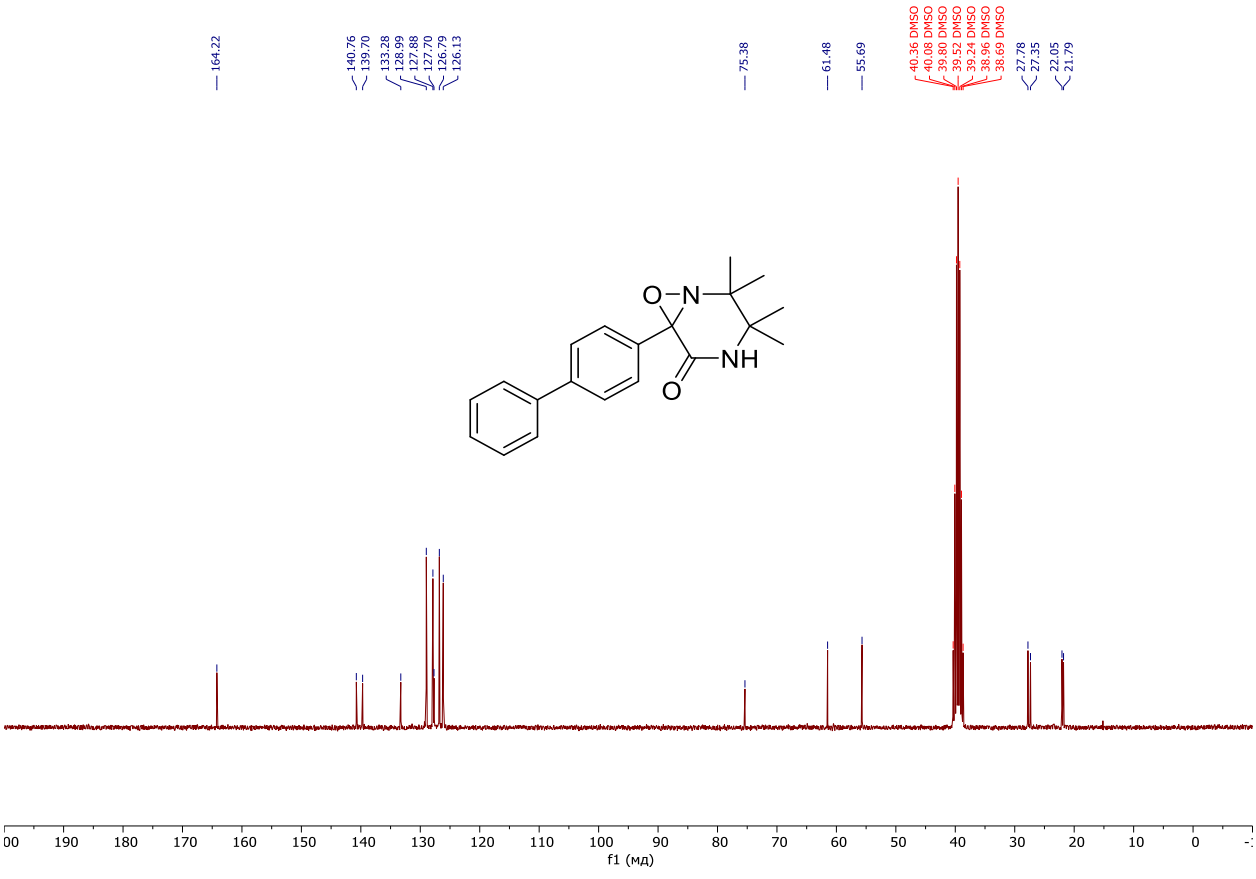
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



^{1}H NMR spectrum (300 MHz) of **5g** in DMSO-d_6



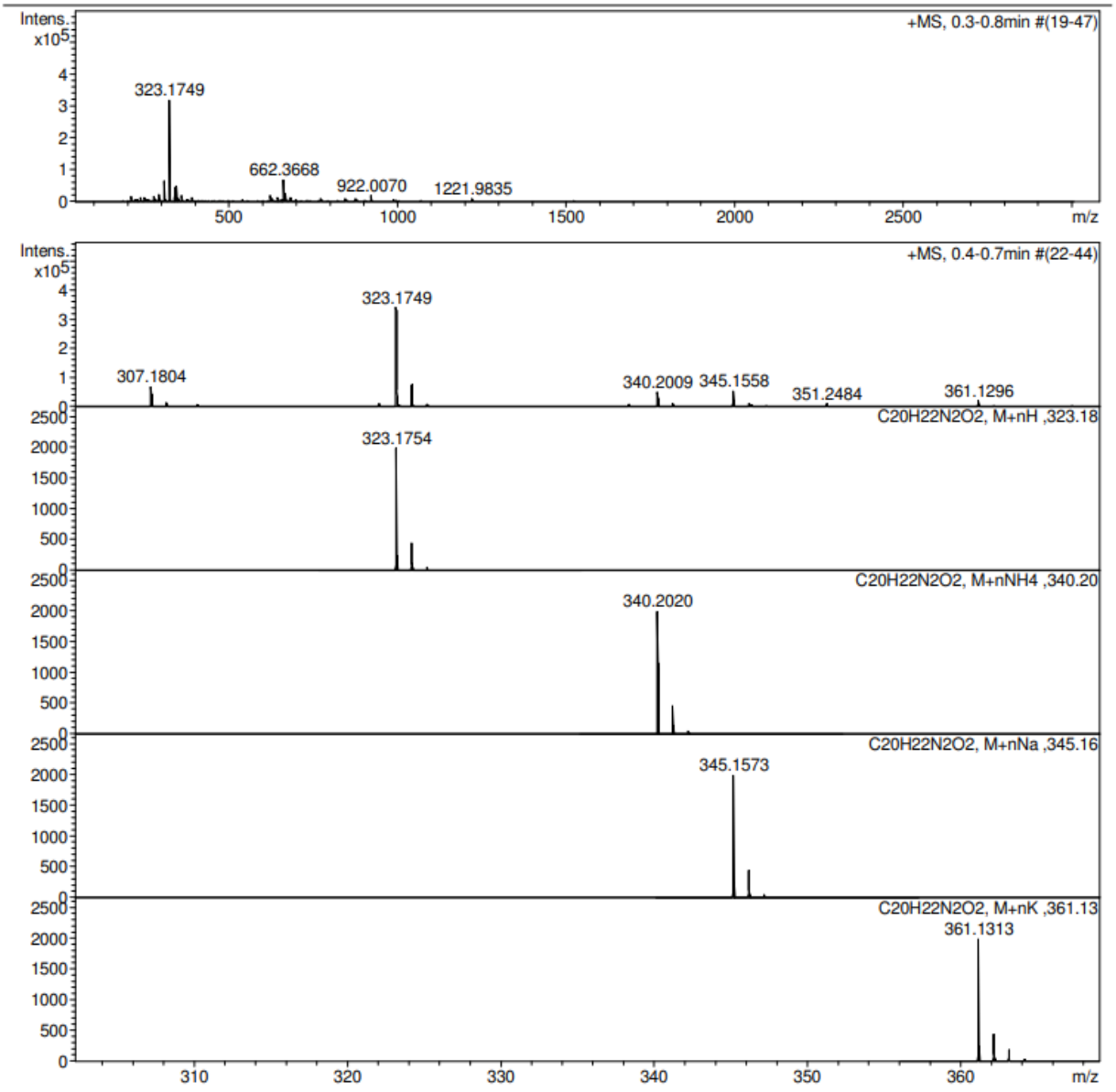
^{13}C {^{1}H} NMR spectrum (76 MHz) of **5g** in DMSO-d_6



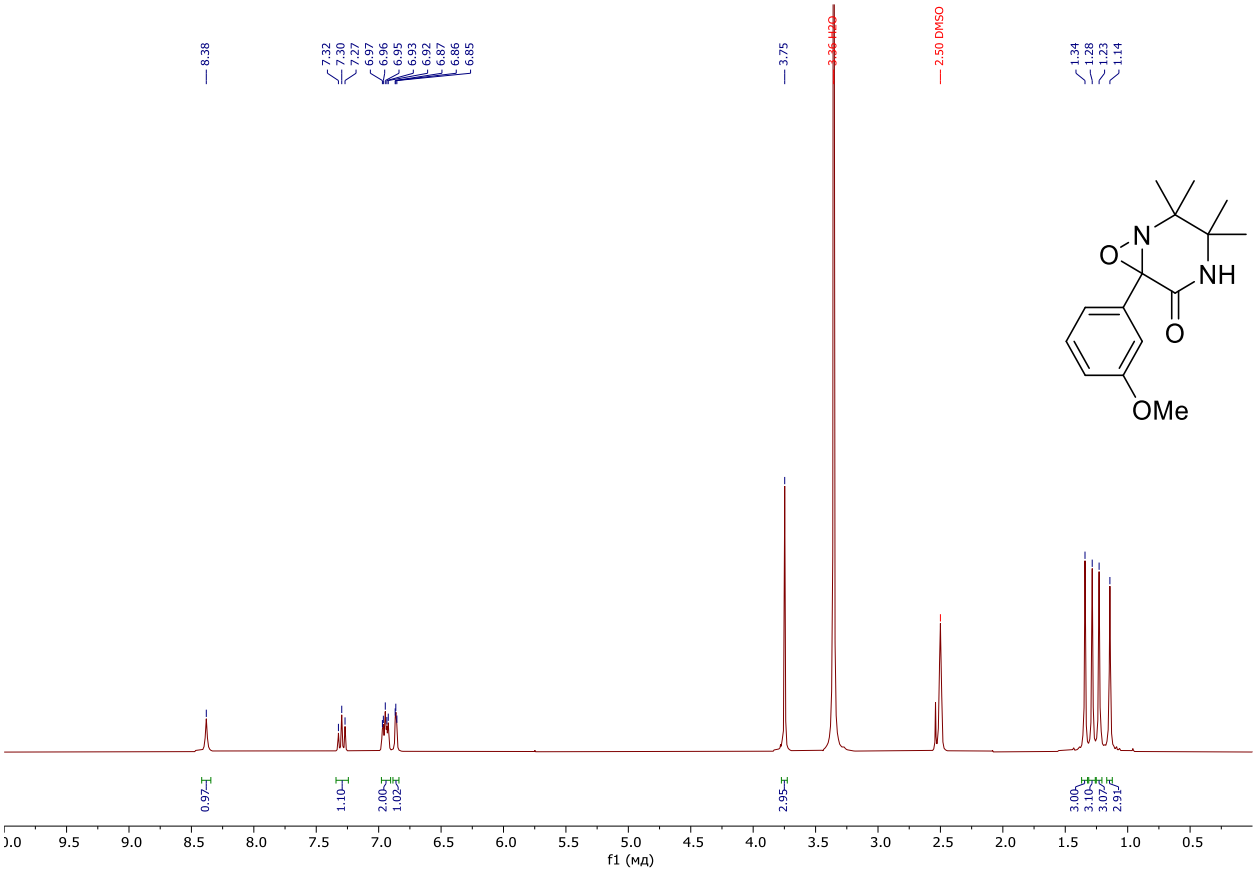
HRMS for compound **5g**

Acquisition Parameter

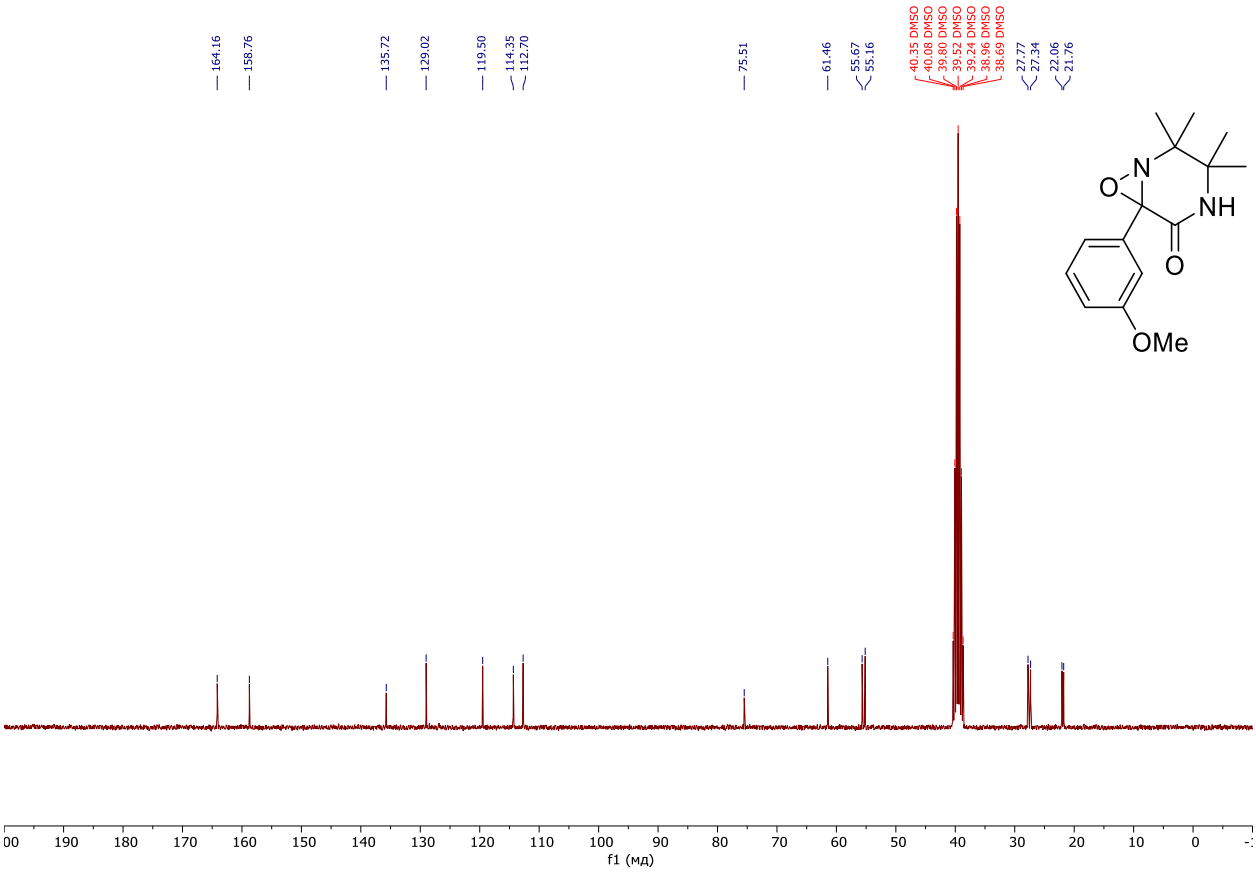
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



^{1}H NMR spectrum (300 MHz) of **5h** in DMSO-d_6



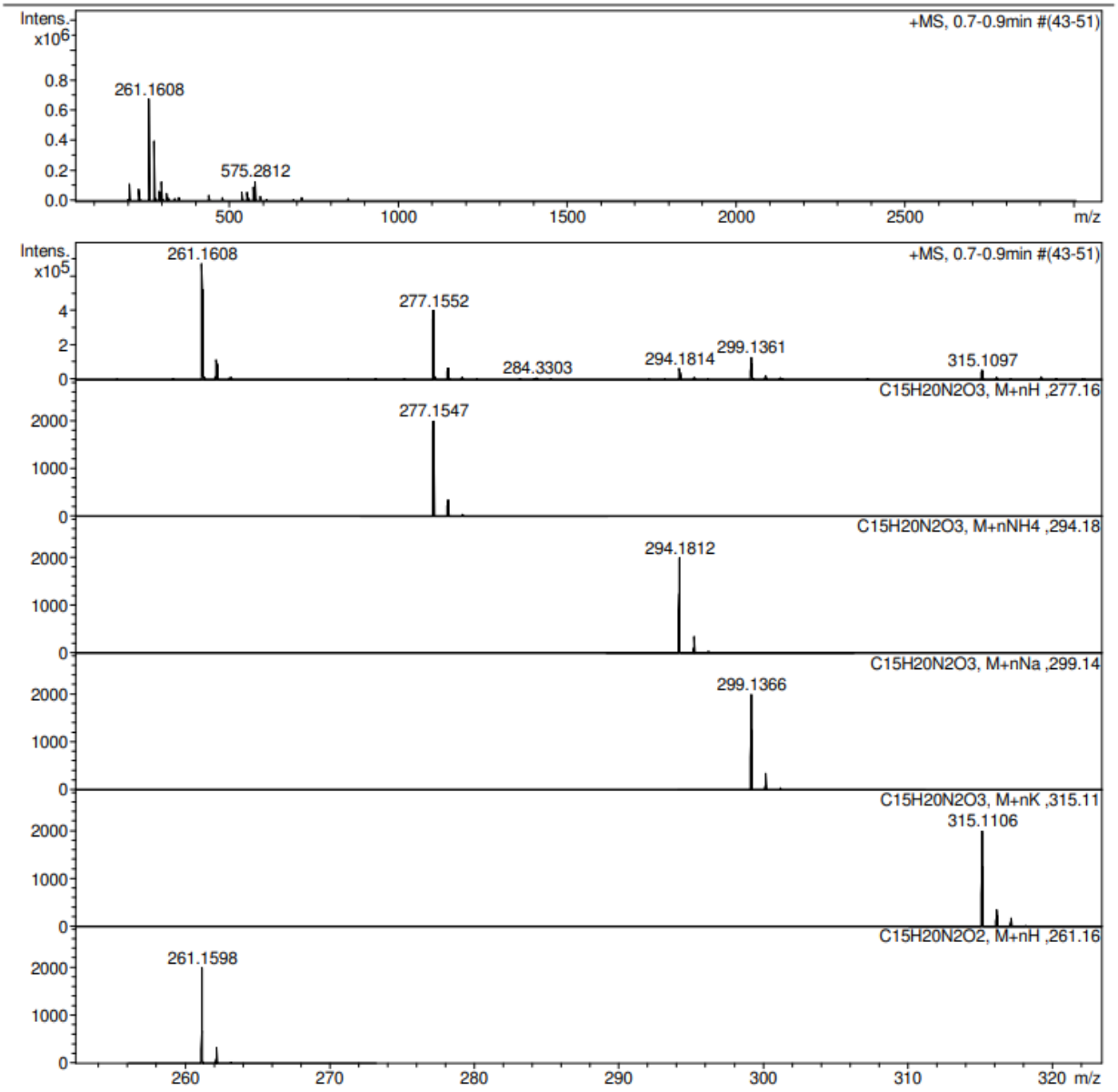
^{13}C {^{1}H} NMR spectrum (76 MHz) of **5h** in DMSO-d_6



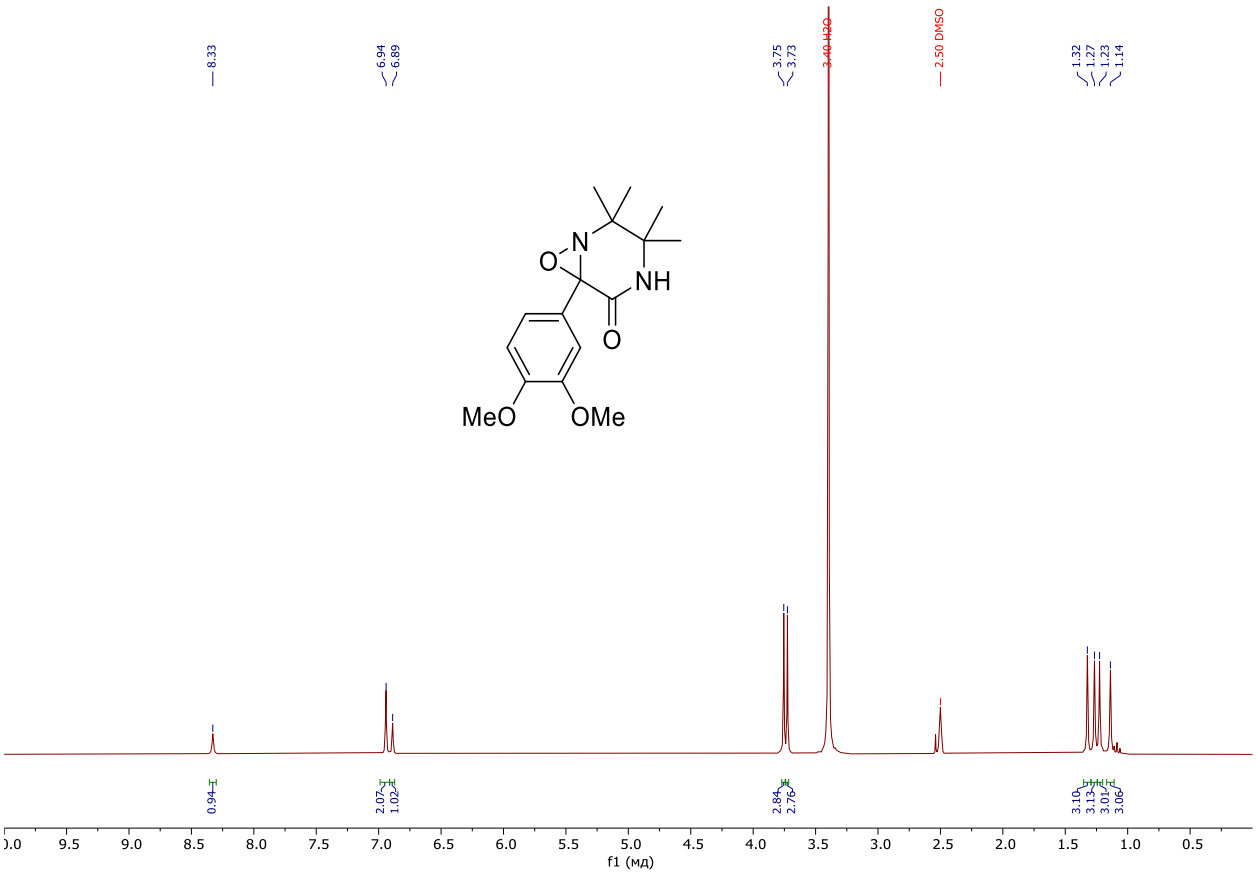
HRMS for compound **5h**

Acquisition Parameter

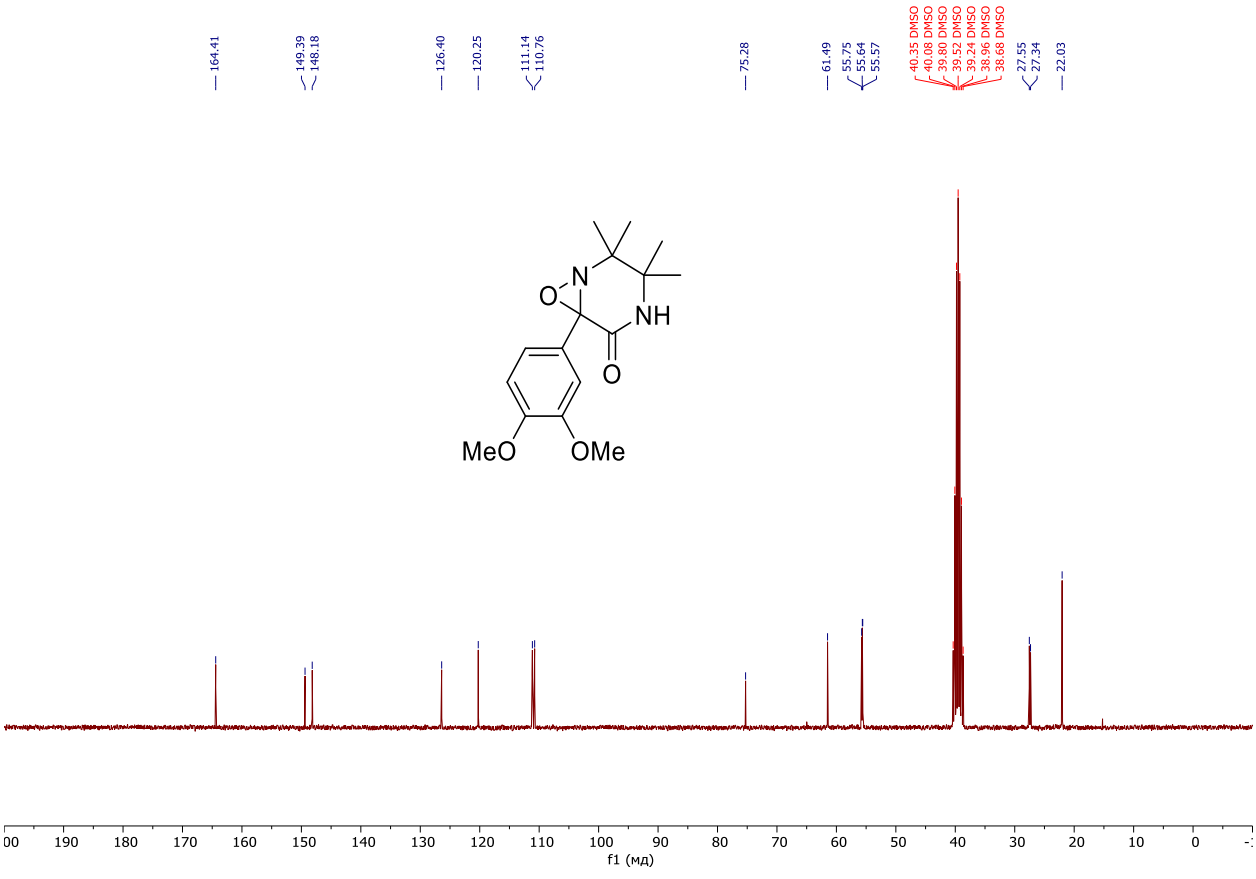
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



^{1}H NMR spectrum (300 MHz) of **5i** in DMSO-d_6



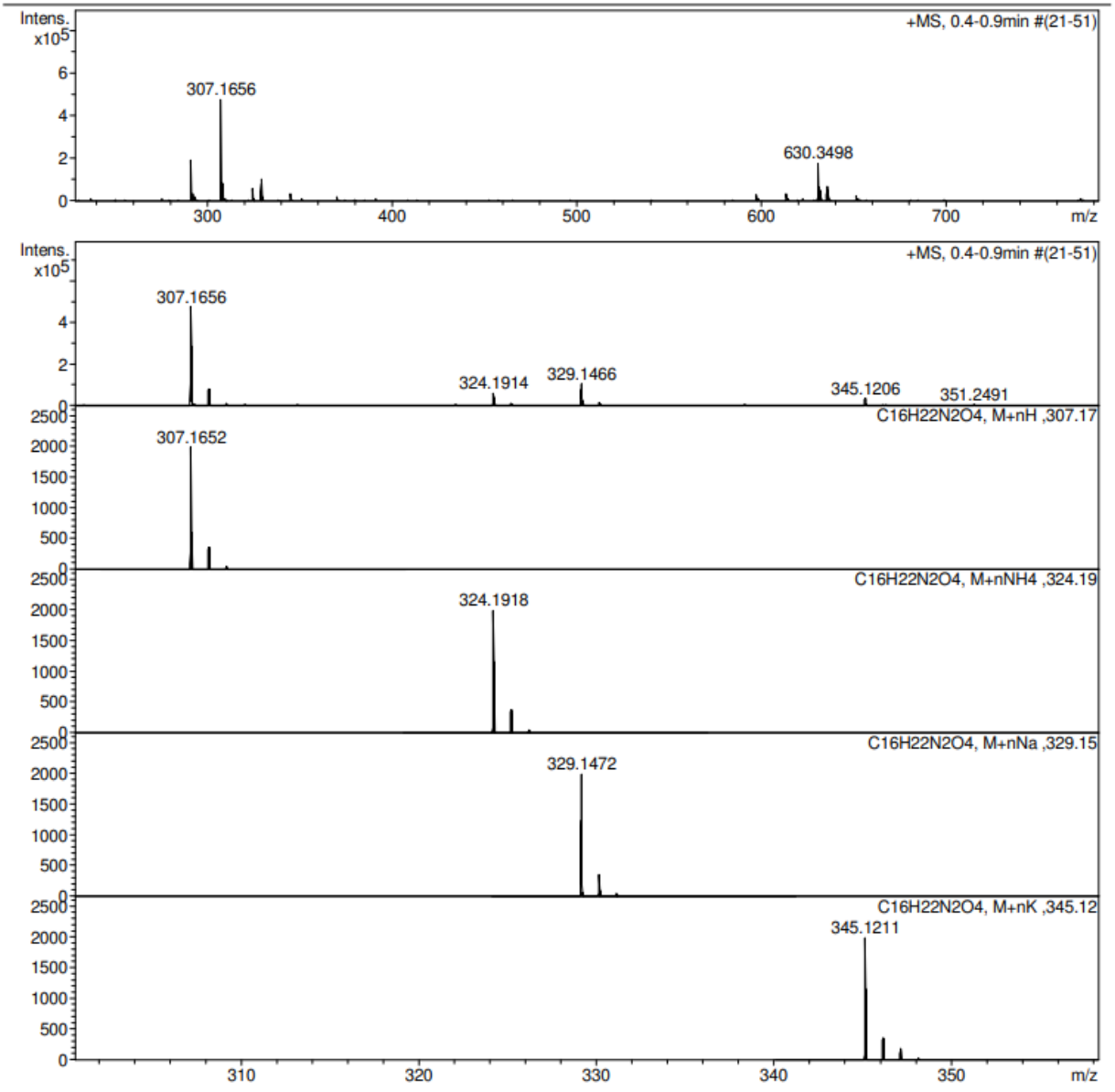
^{13}C {^{1}H} NMR spectrum (76 MHz) of **5i** in DMSO-d_6



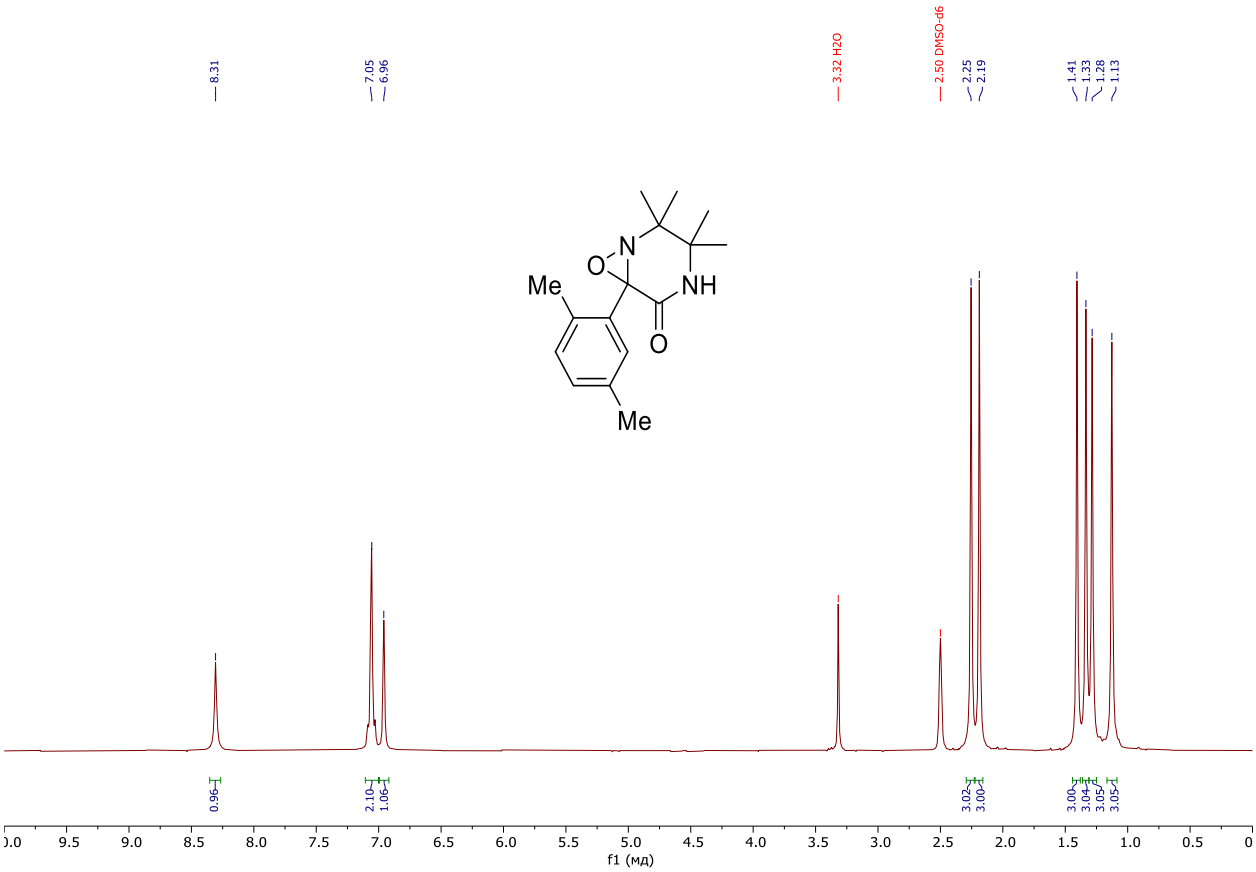
HRMS for compound **5i**

Acquisition Parameter

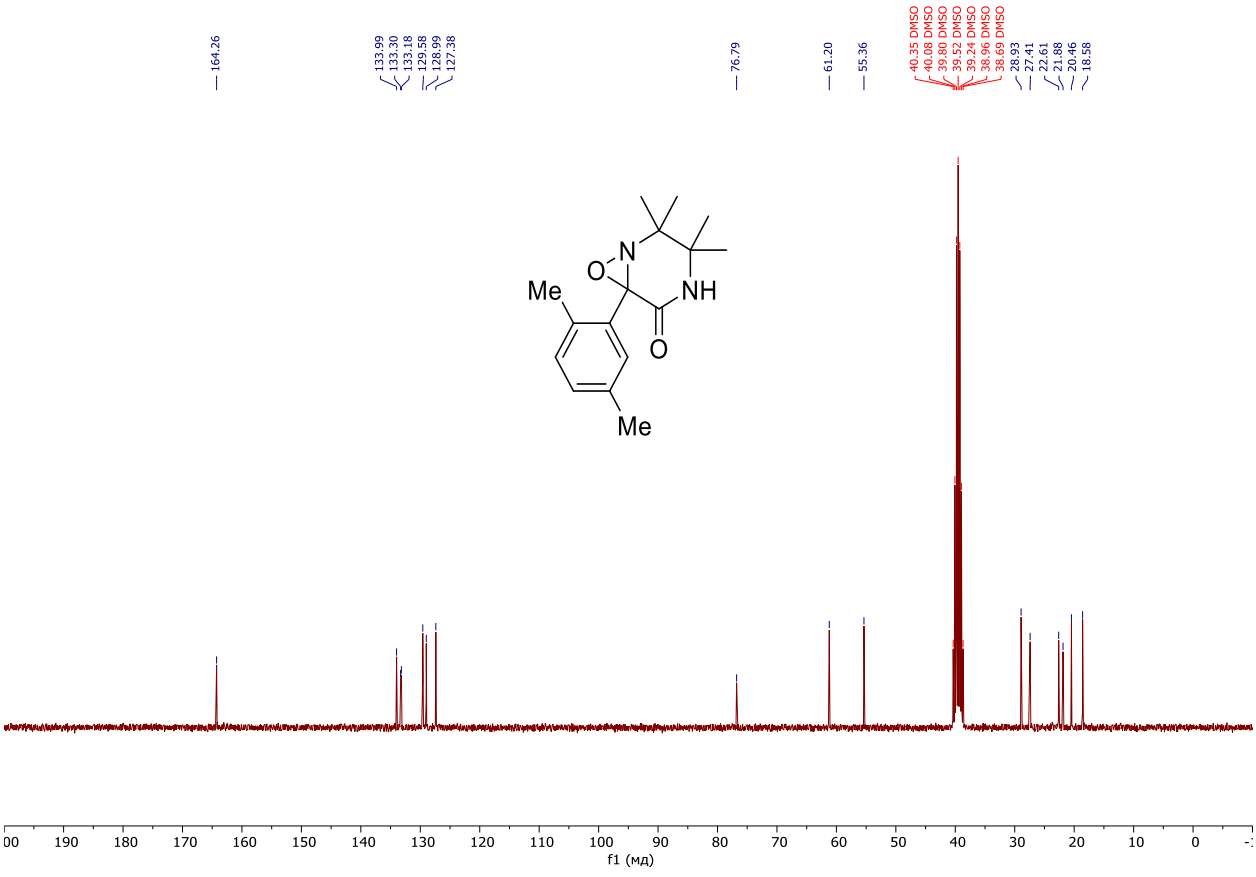
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



^{1}H NMR spectrum (300 MHz) of **5j** in DMSO-d_6



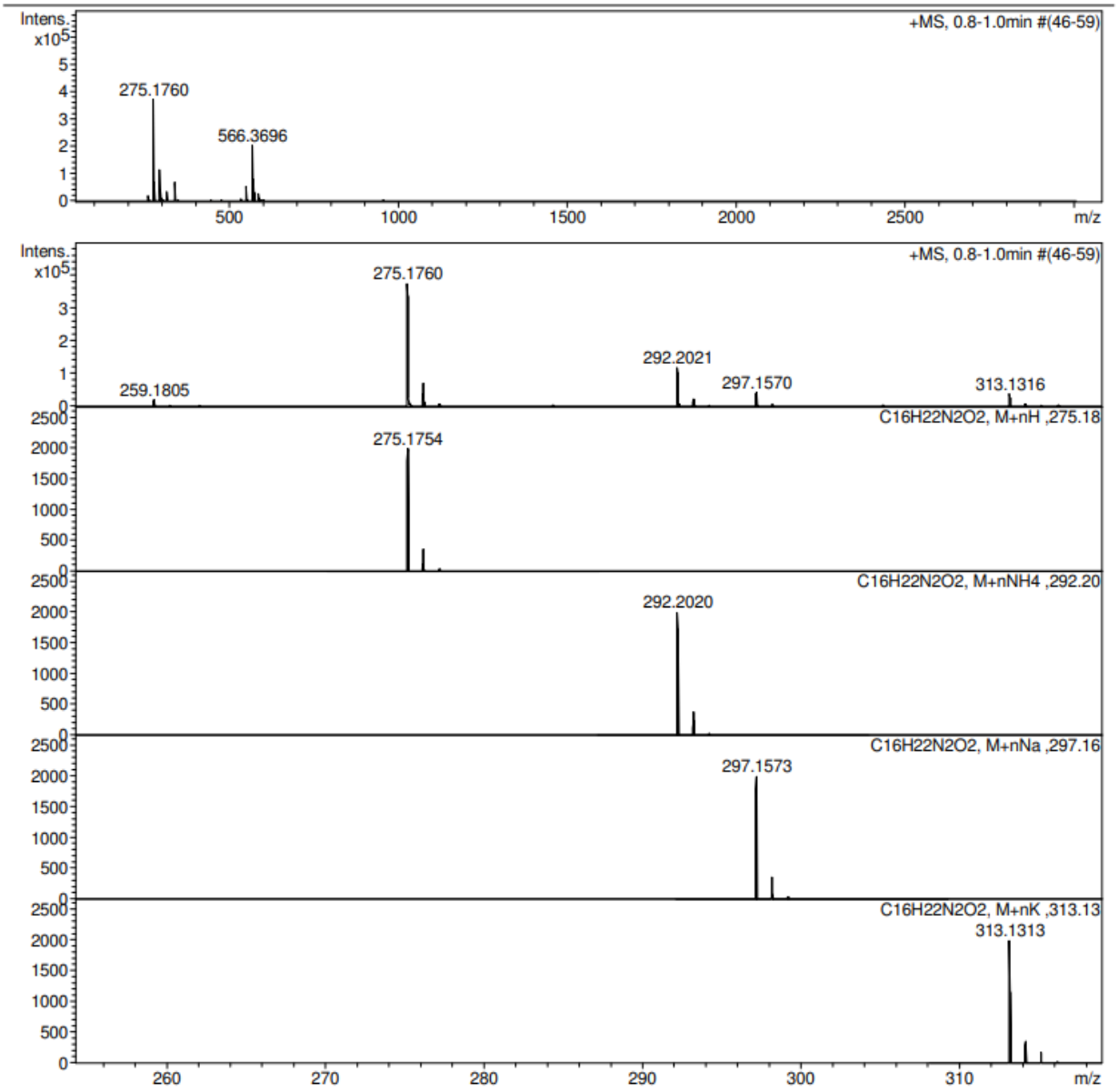
^{13}C {^{1}H} NMR spectrum (76 MHz) of **5j** in DMSO-d_6



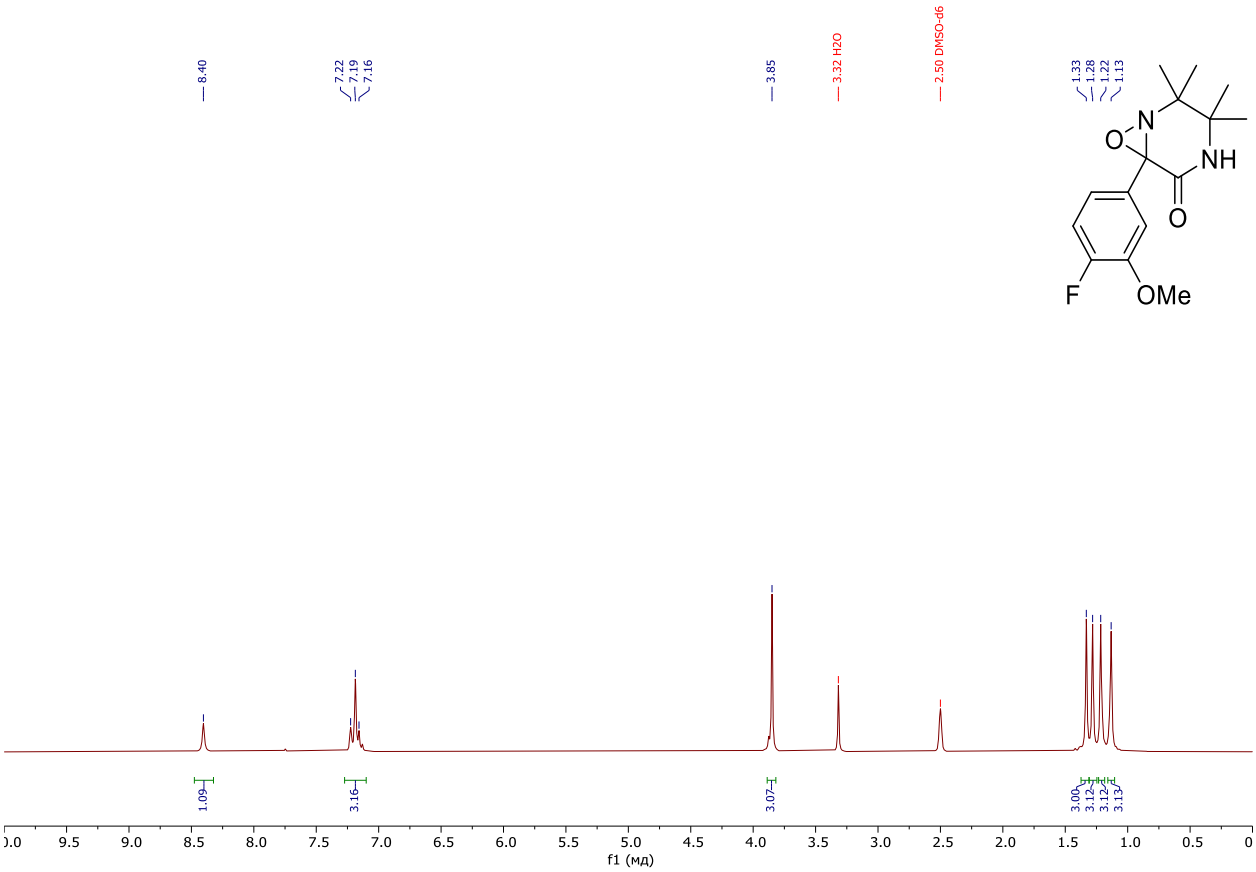
HRMS for compound **5j**

Acquisition Parameter

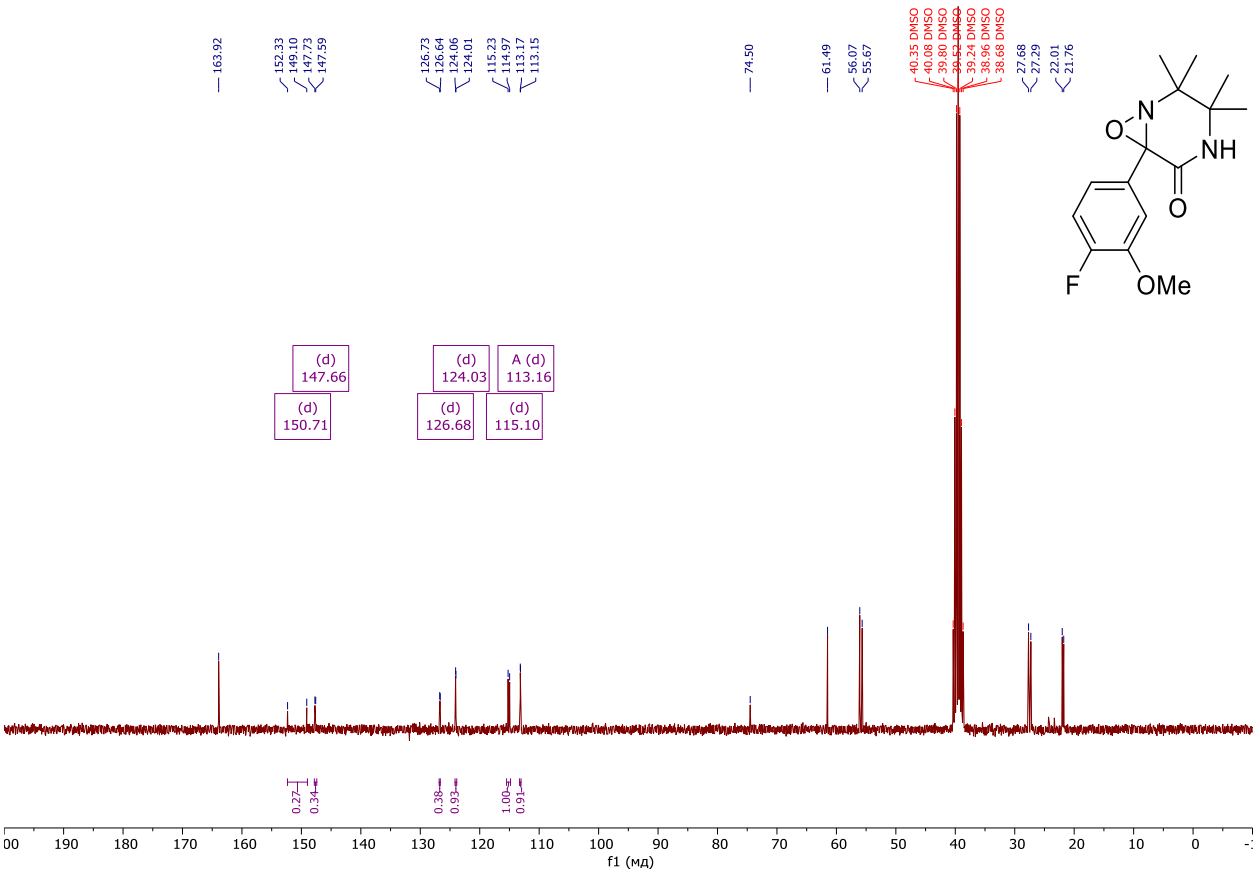
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



^{1}H NMR spectrum (300 MHz) of **5k** in DMSO-d_6



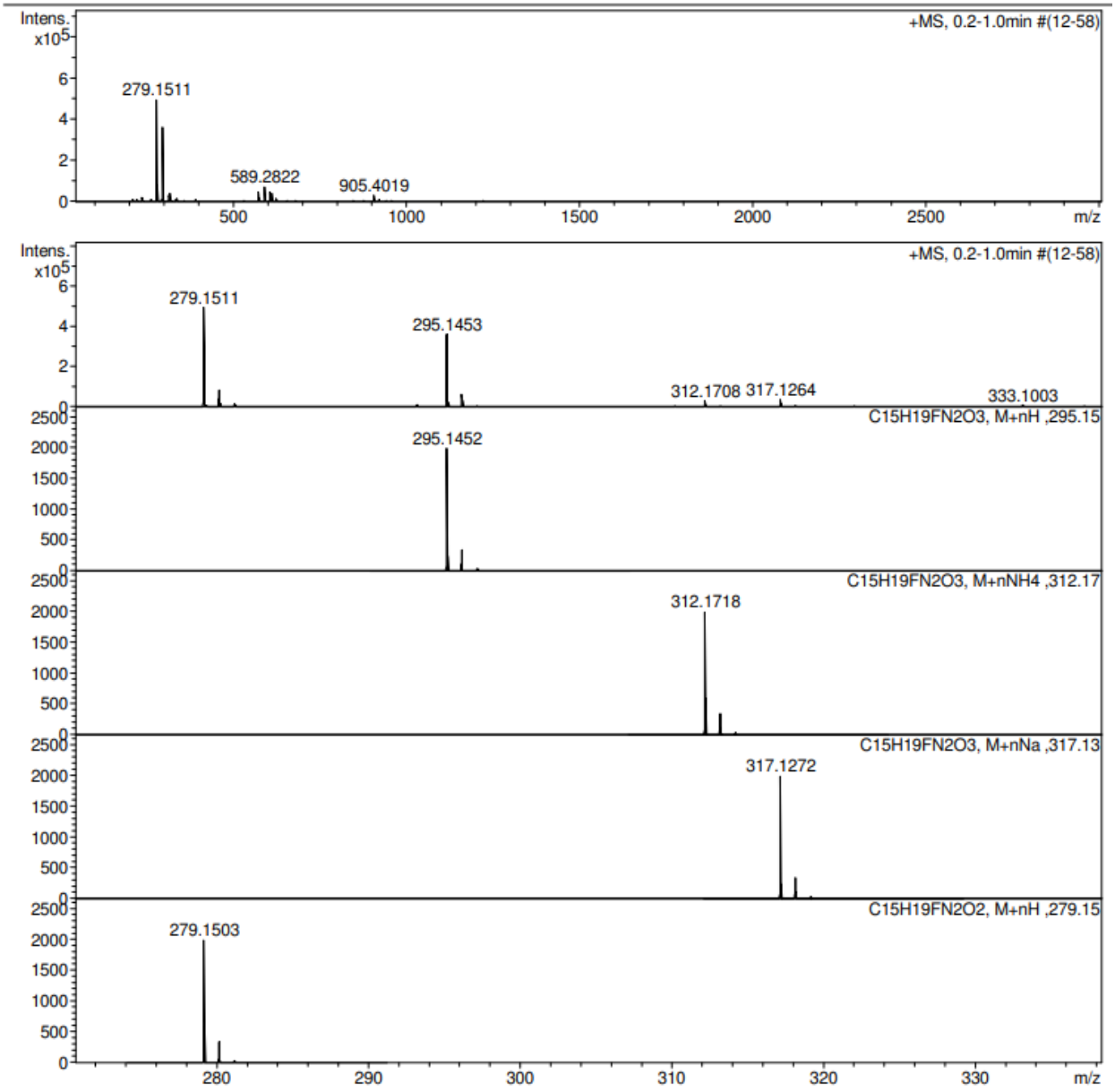
^{13}C {^{1}H} NMR spectrum (76 MHz) of **5k** in DMSO-d_6



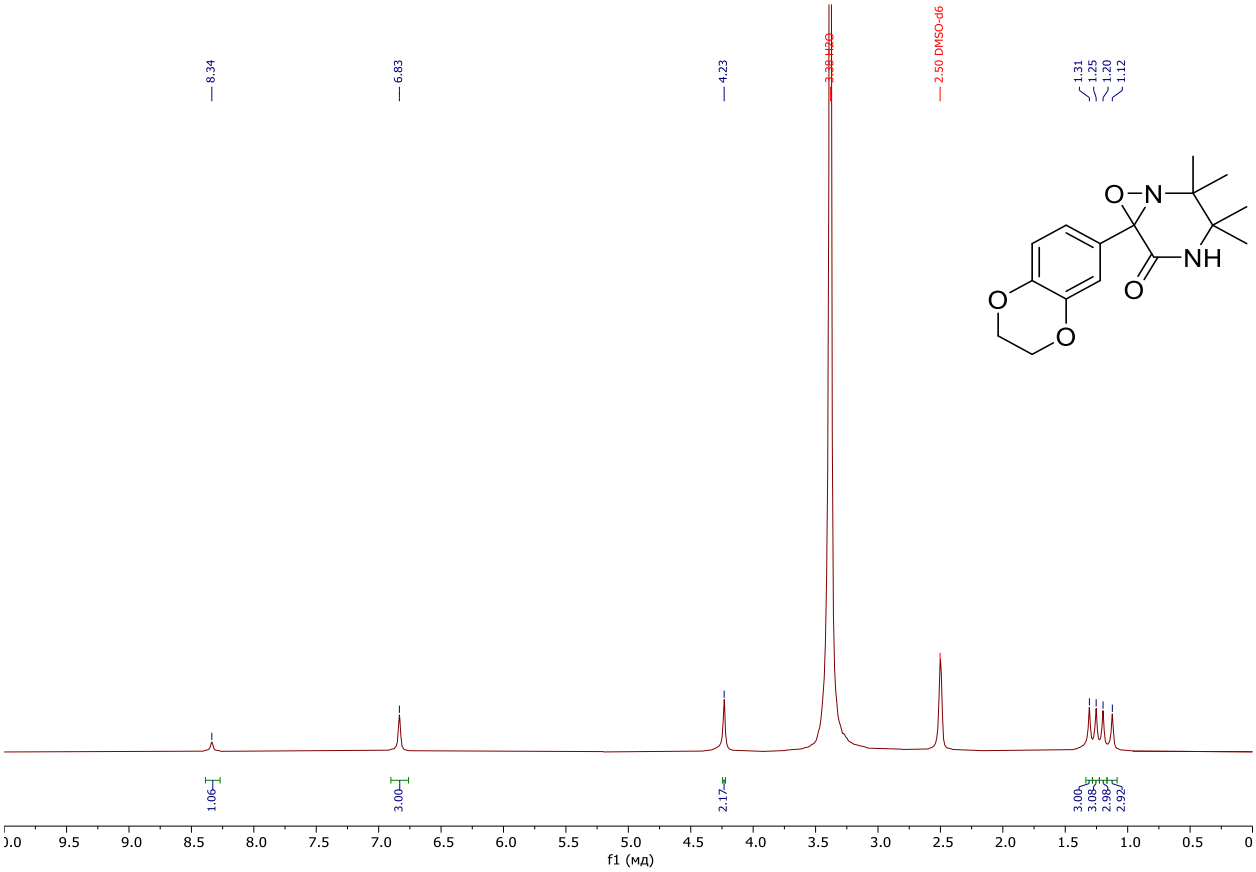
HRMS for compound **5k**

Acquisition Parameter

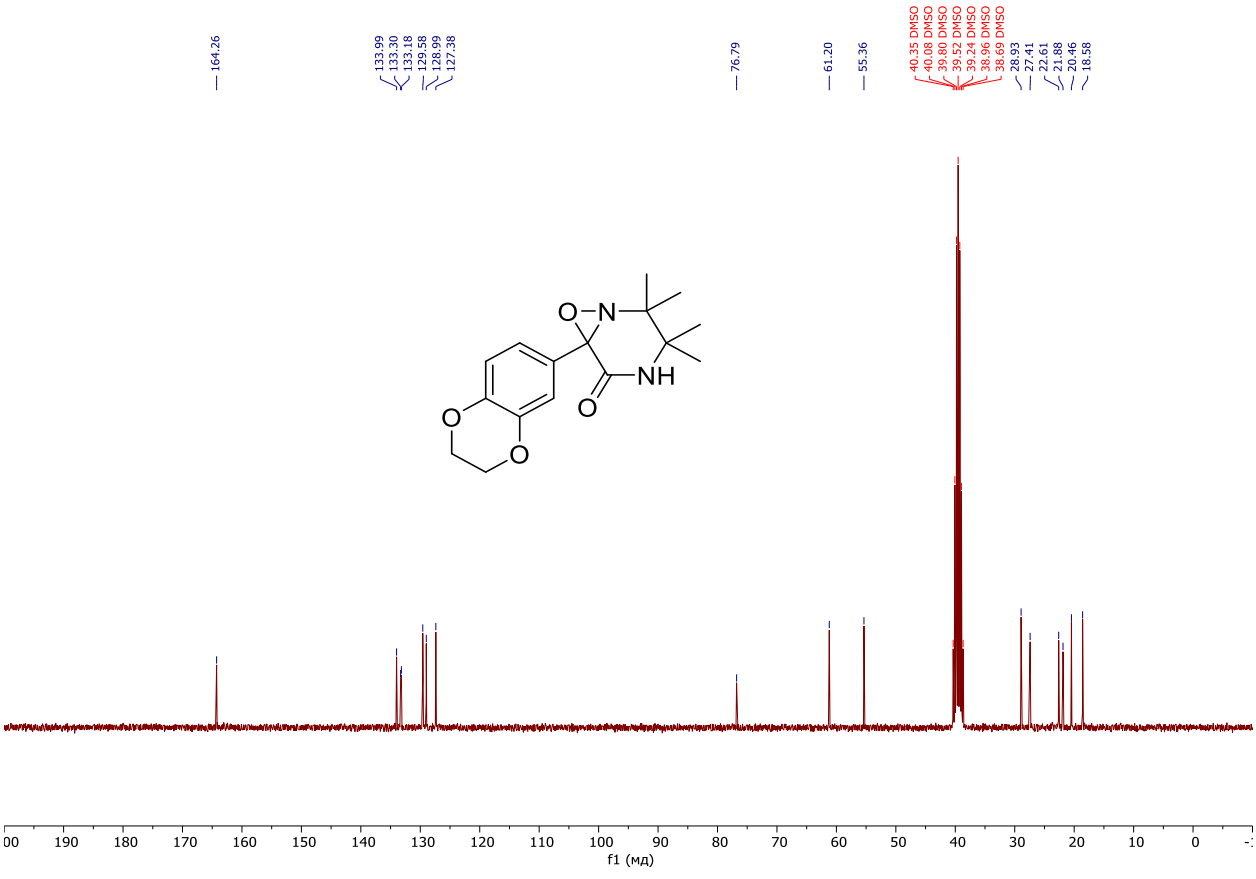
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



^{1}H NMR spectrum (300 MHz) of **5l** in DMSO-d_6



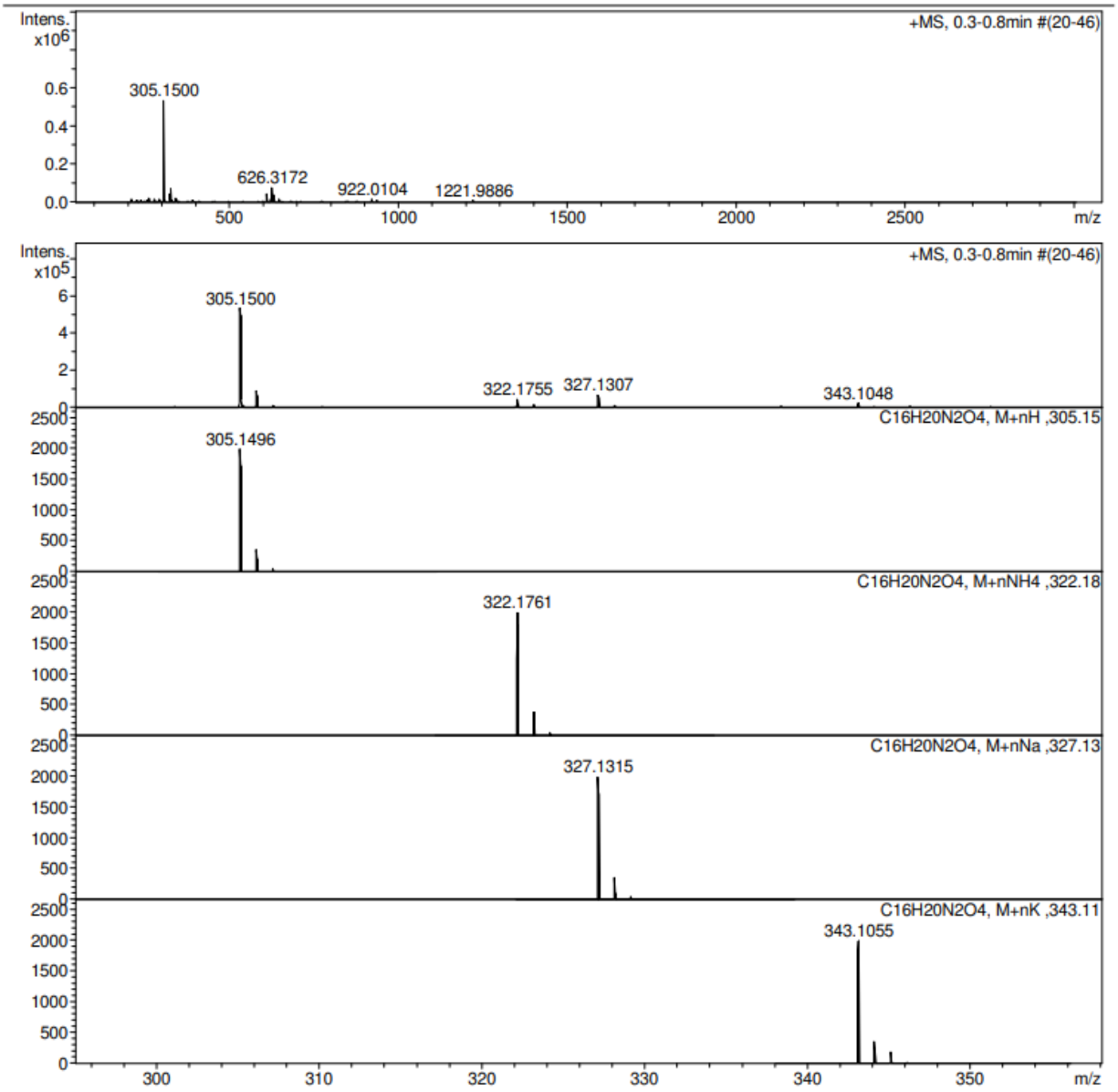
^{13}C {^{1}H} NMR spectrum (76 MHz) of **5l** in DMSO-d_6



HRMS for compound **5l**

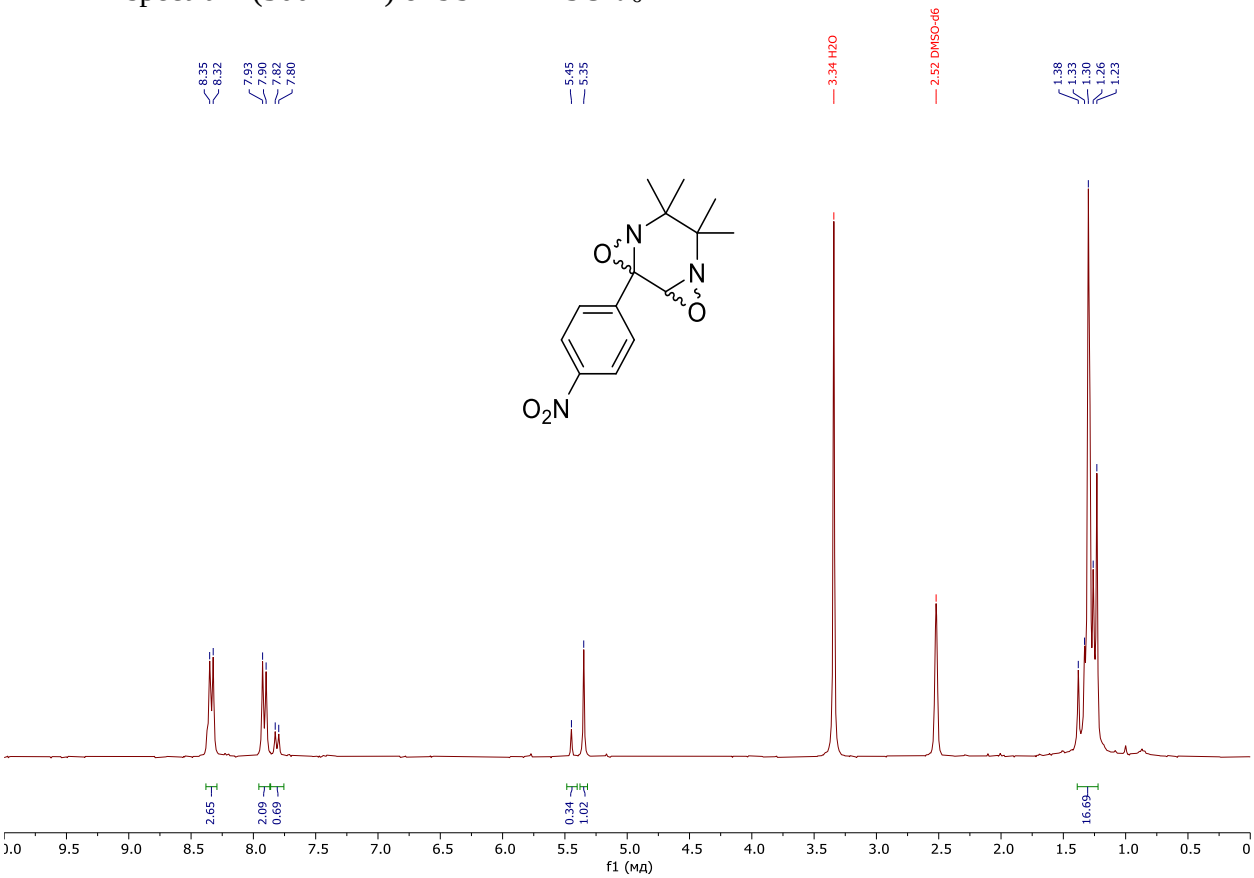
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

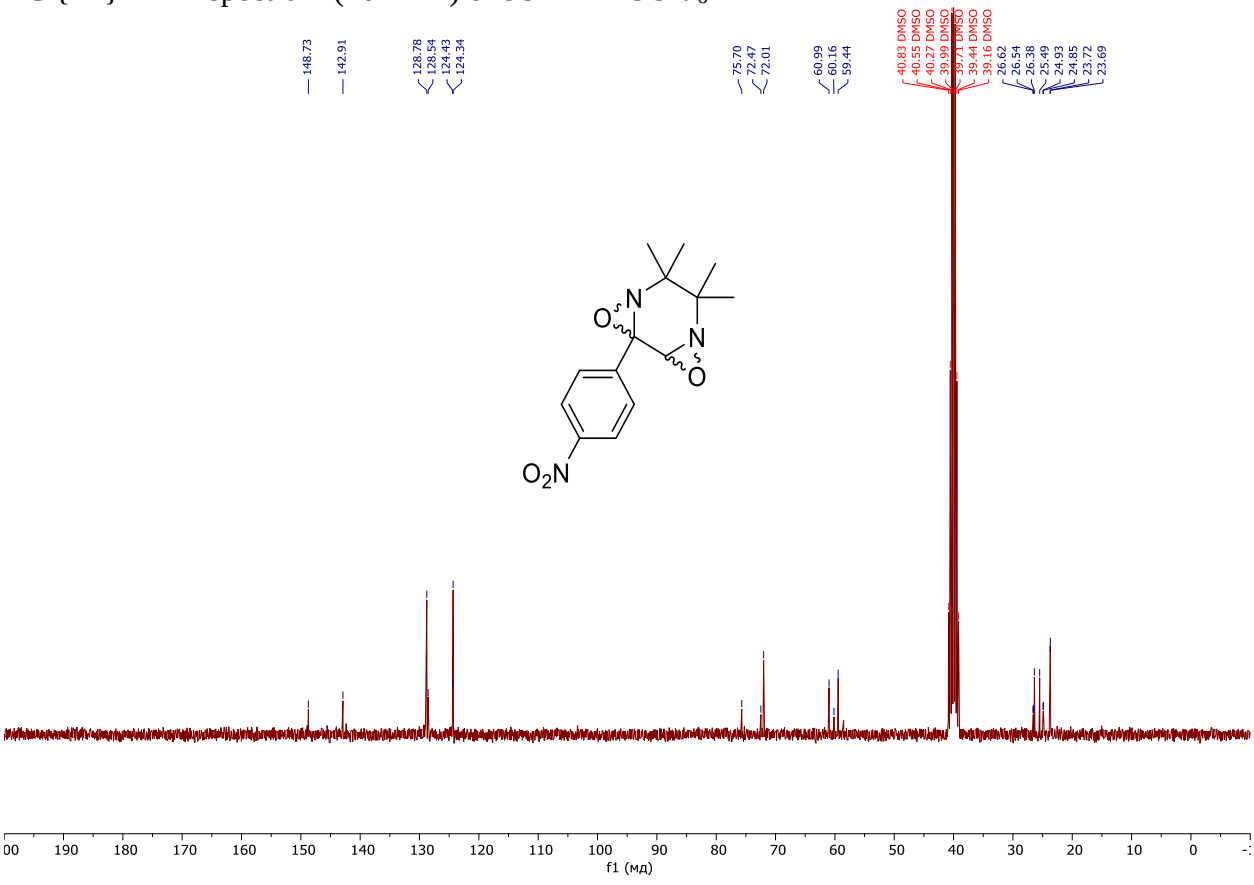


13. Copies of ^{1}H, ^{13}C NMR and HRMS for 1-(4-nitrophenyl)-5,5,6,6-tetramethyl-3,8-dioxa-4,7-diazatricyclo[5.1.0.02,4]octane 9b

^{1}H NMR spectrum (300 MHz) of **9b** in DMSO-d_6



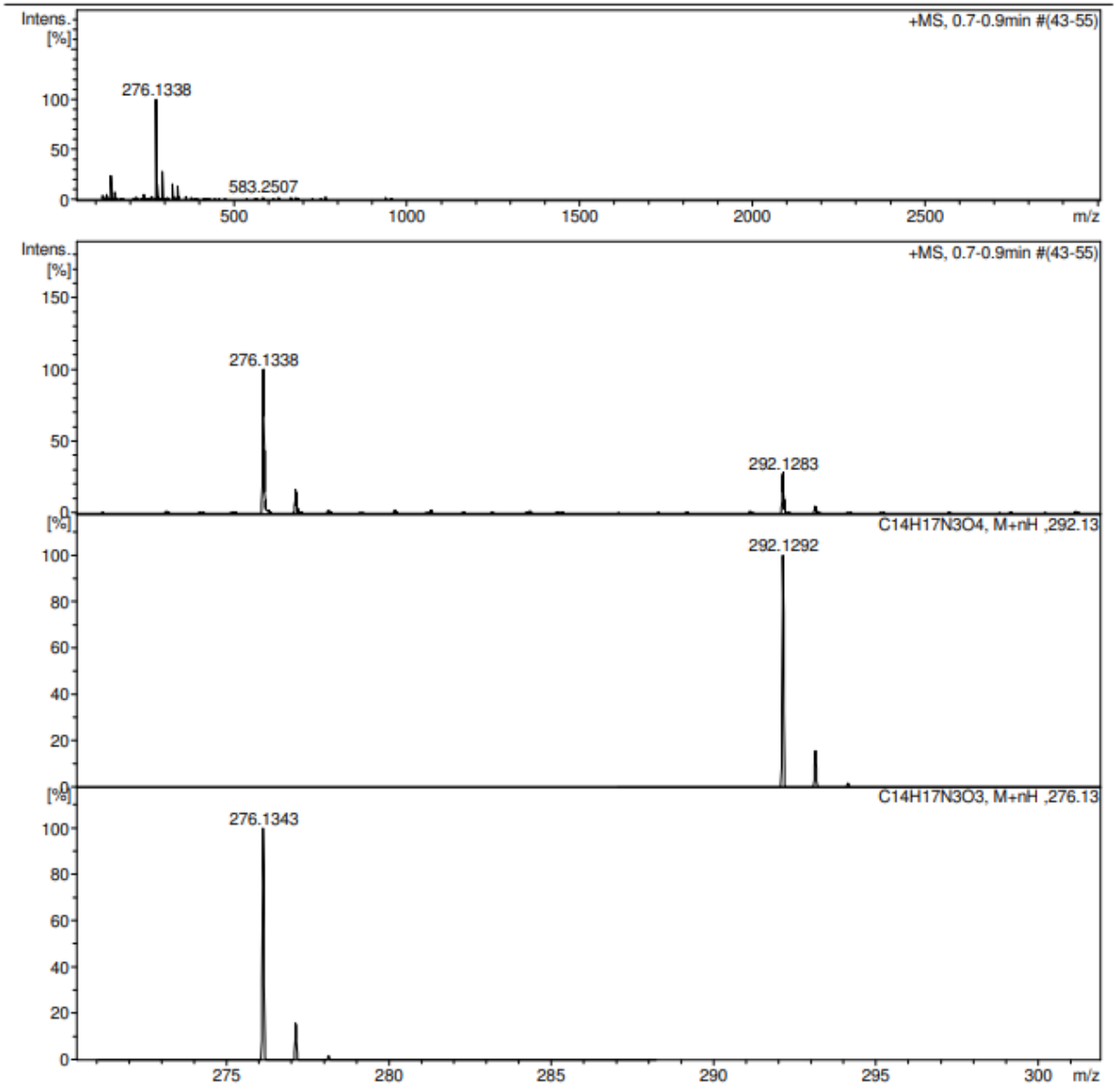
^{13}C {^{1}H} NMR spectrum (76 MHz) of **9b** in DMSO-d_6



HRMS for compound **9b**

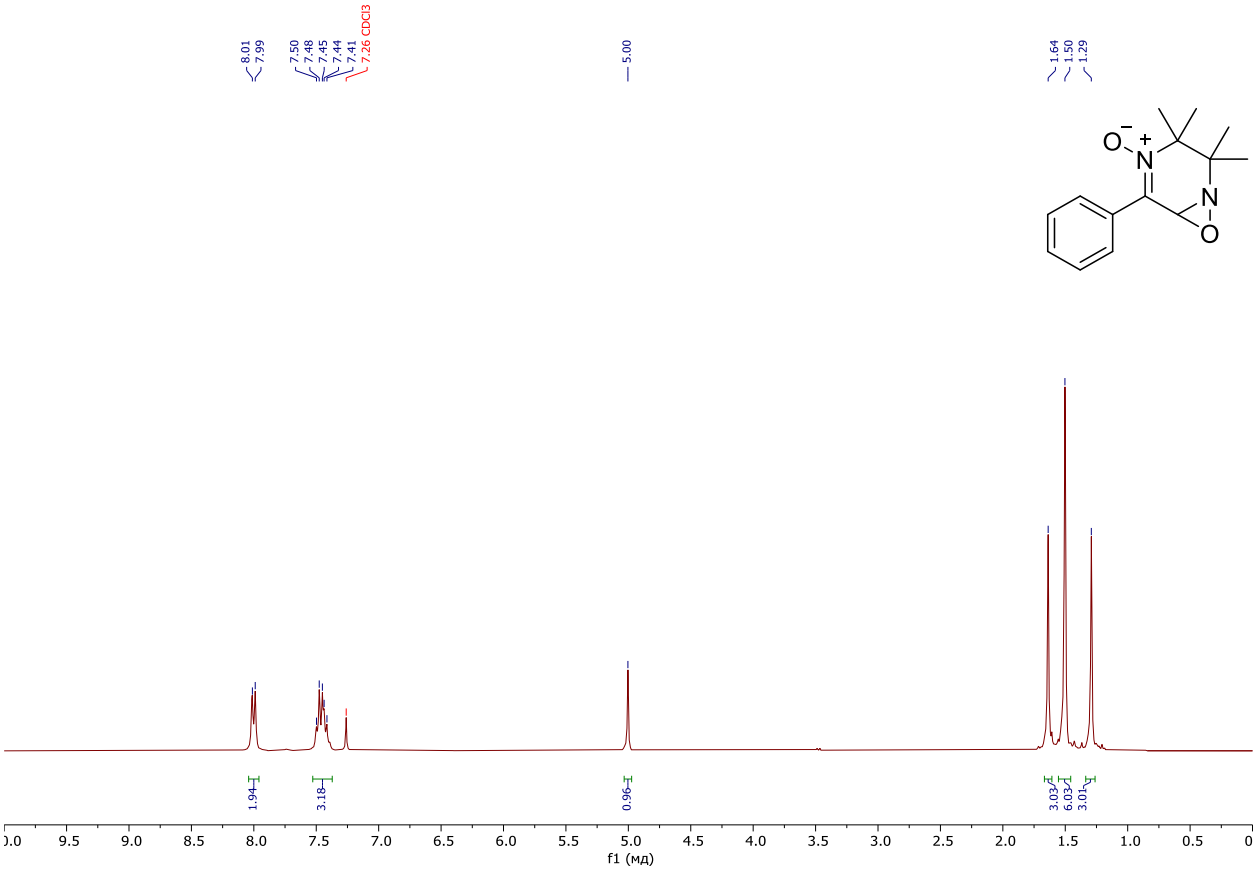
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

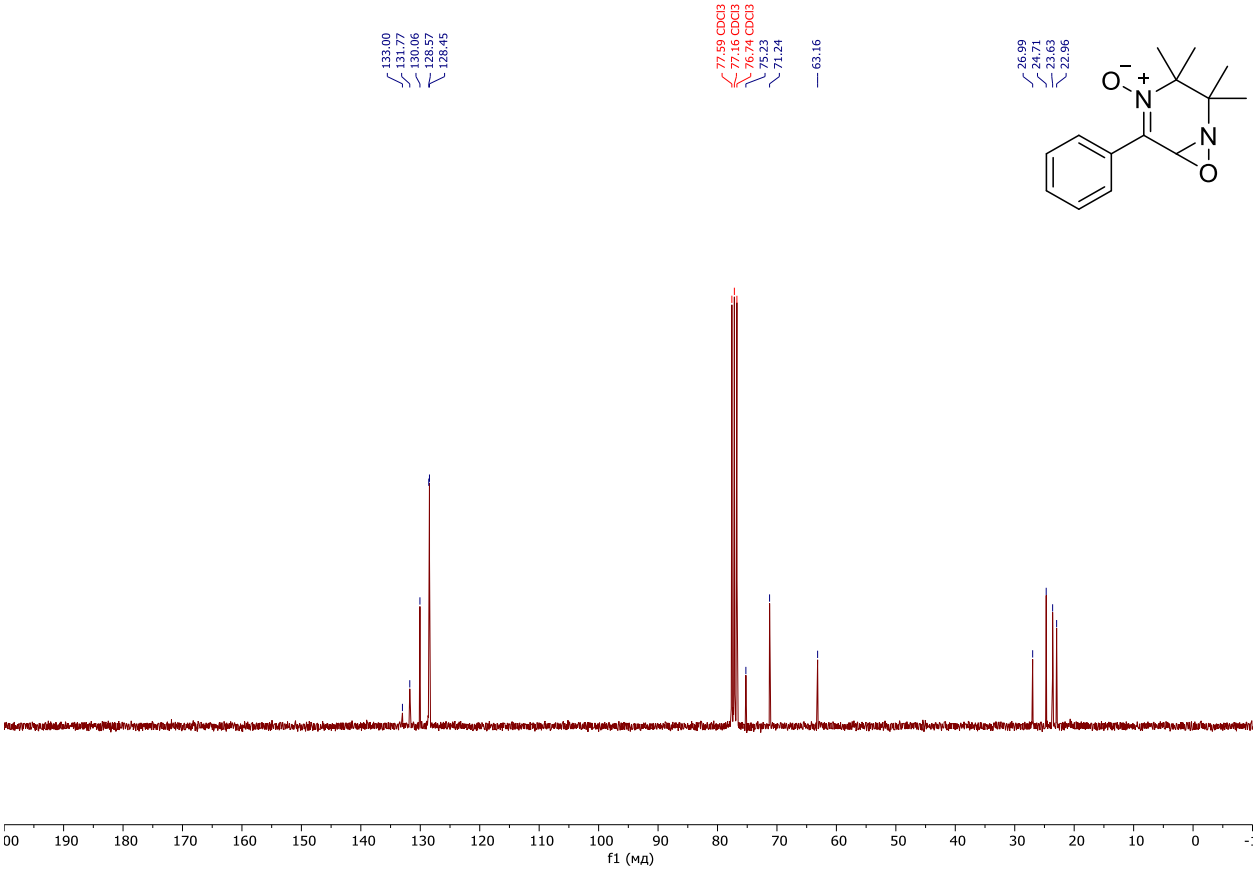


14. Copies of ^{1}H, ^{13}C NMR and HRMS for monooxaziridines 6.

^{1}H NMR spectrum (300 MHz) of **6a** in DMSO-d_6



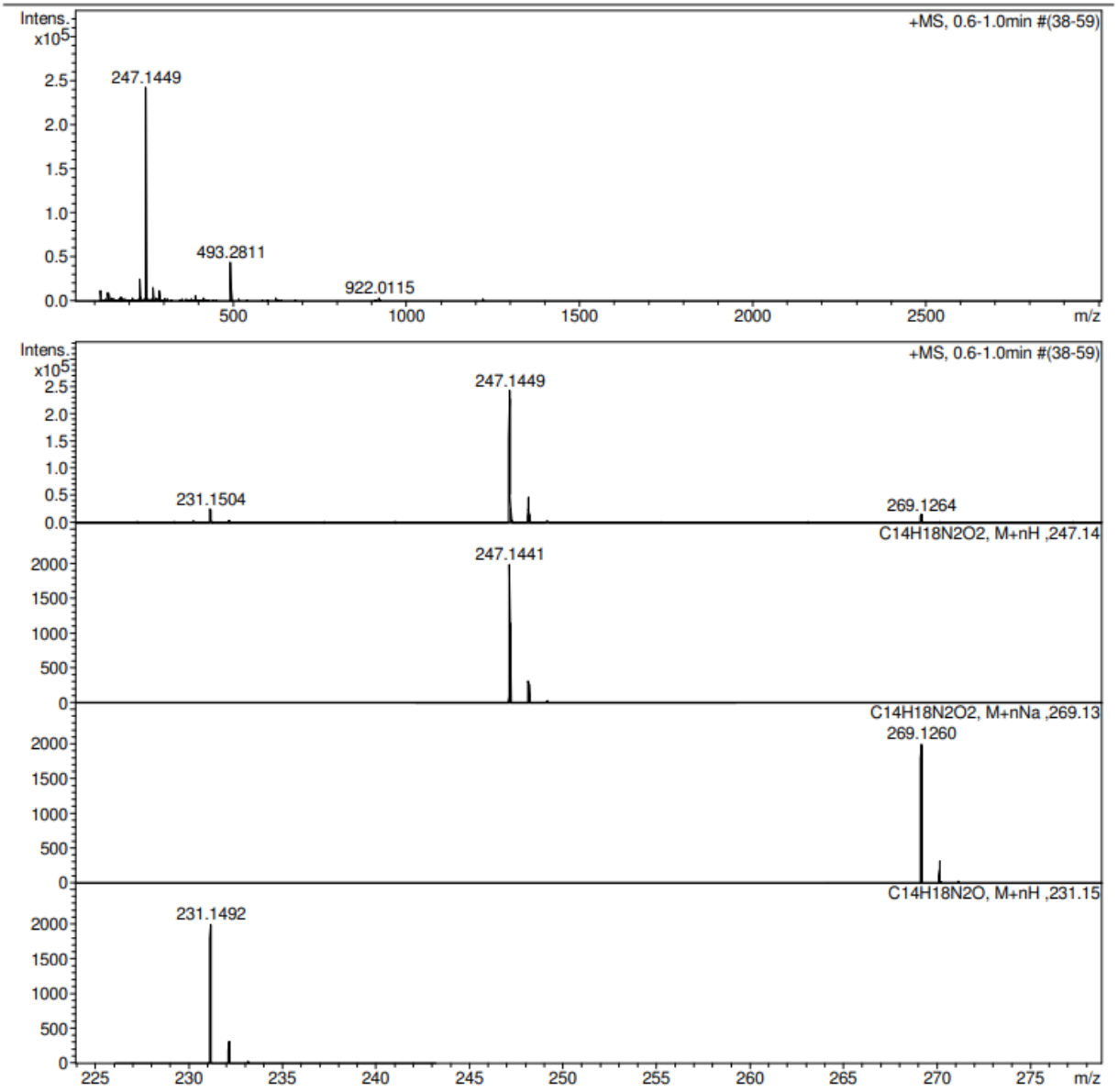
^{13}C {^{1}H} NMR spectrum (76 MHz) of **6a** in DMSO-d_6



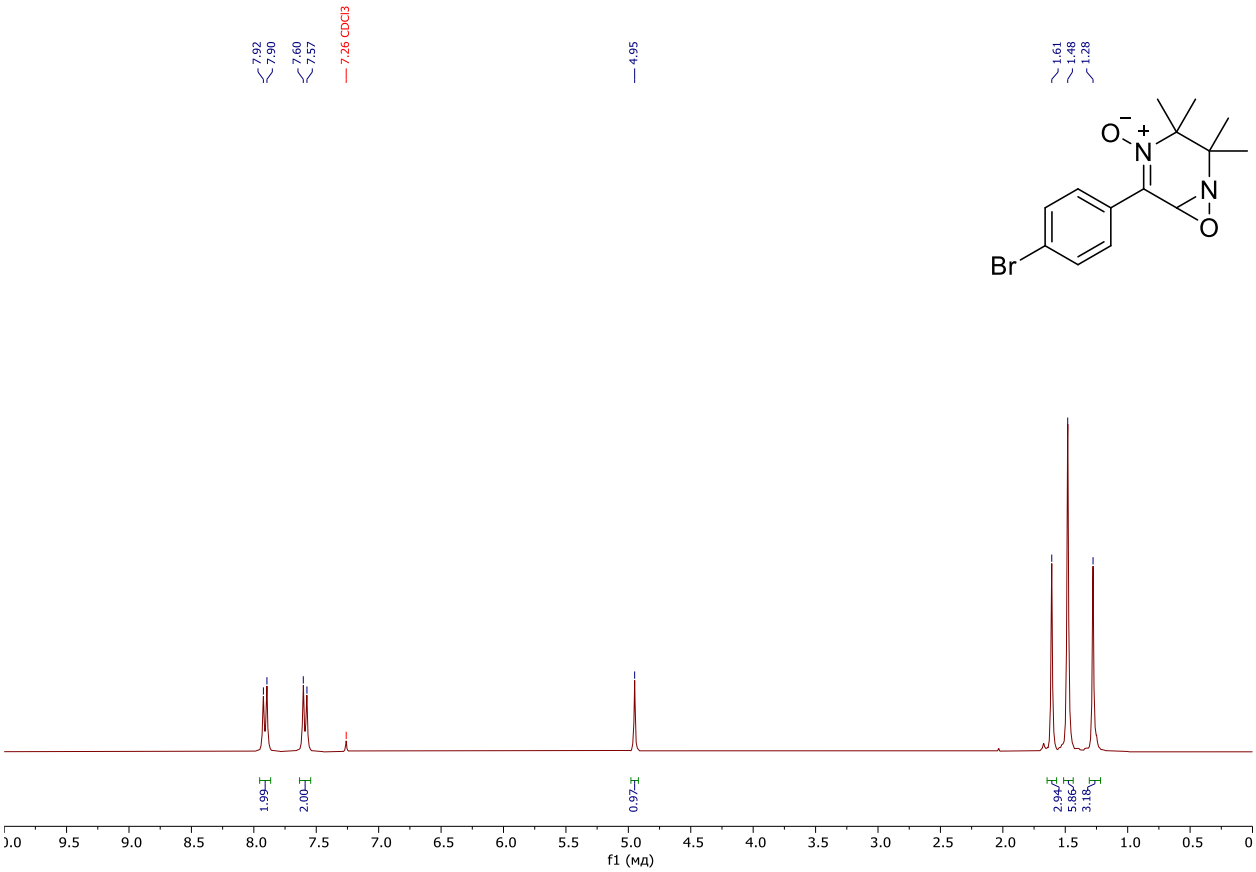
HRMS for compound **6a**

Acquisition Parameter

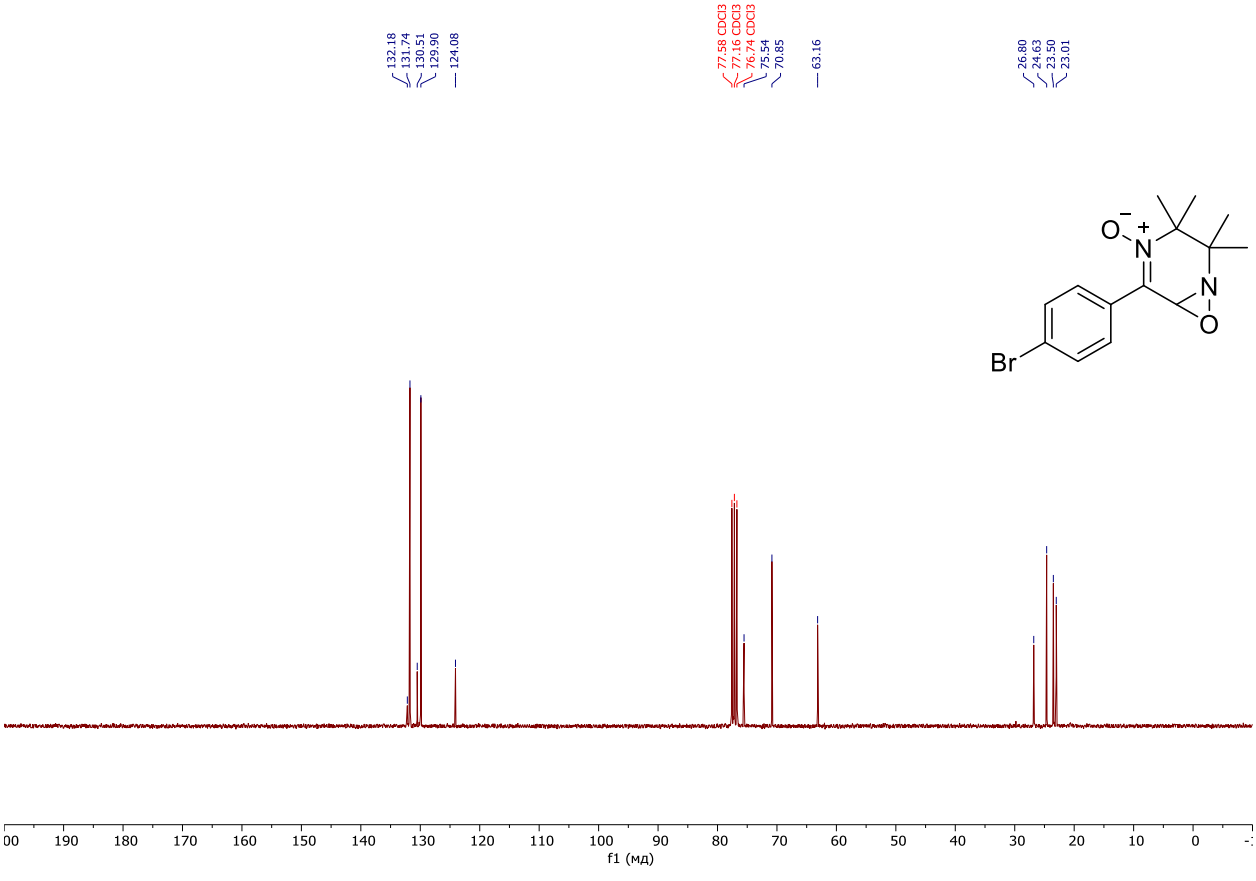
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



^{1}H NMR spectrum (300 MHz) of **6b** in $CDCl_3$



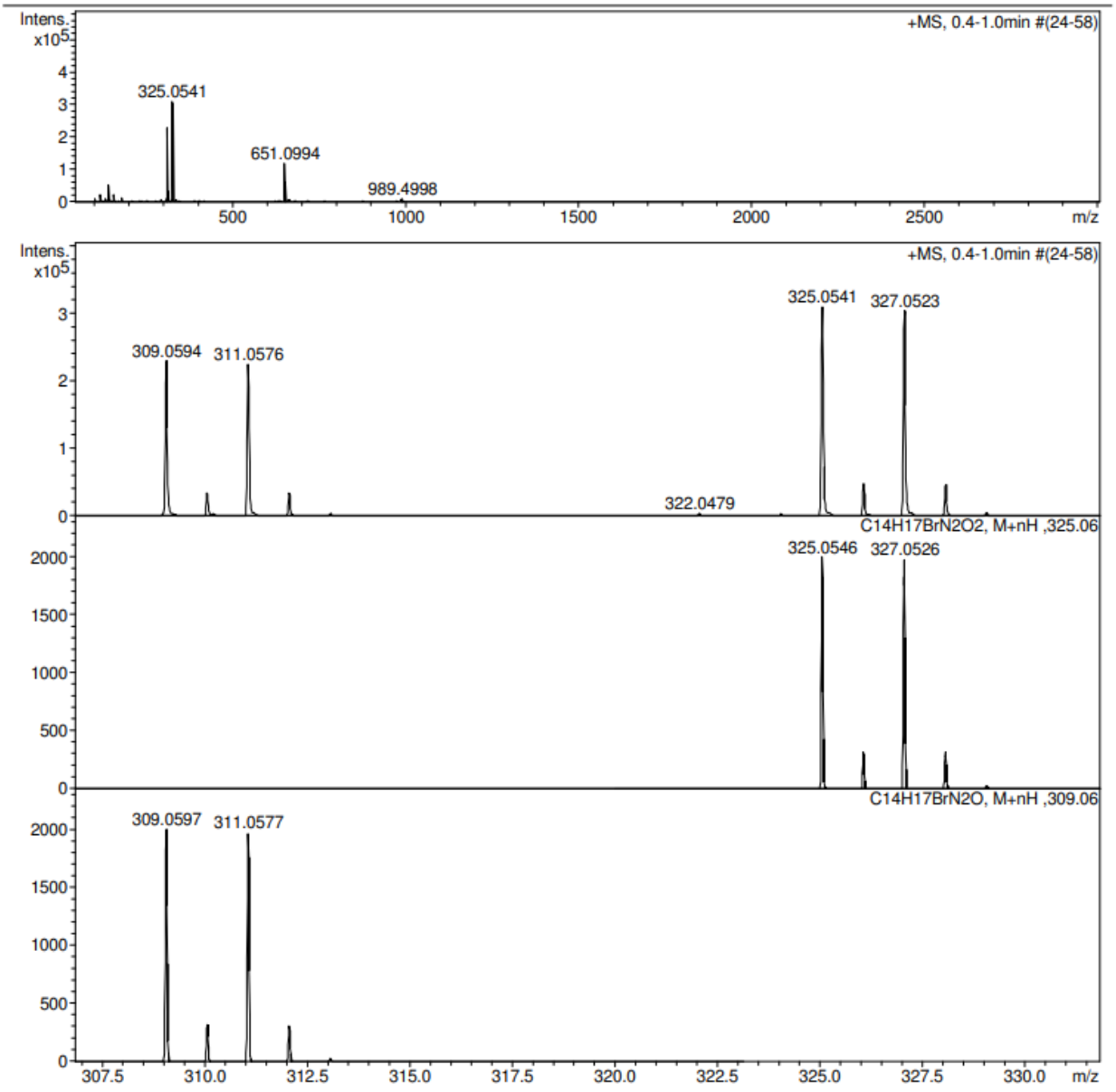
^{13}C {^{1}H} NMR spectrum (76 MHz) of **6b** in $CDCl_3$



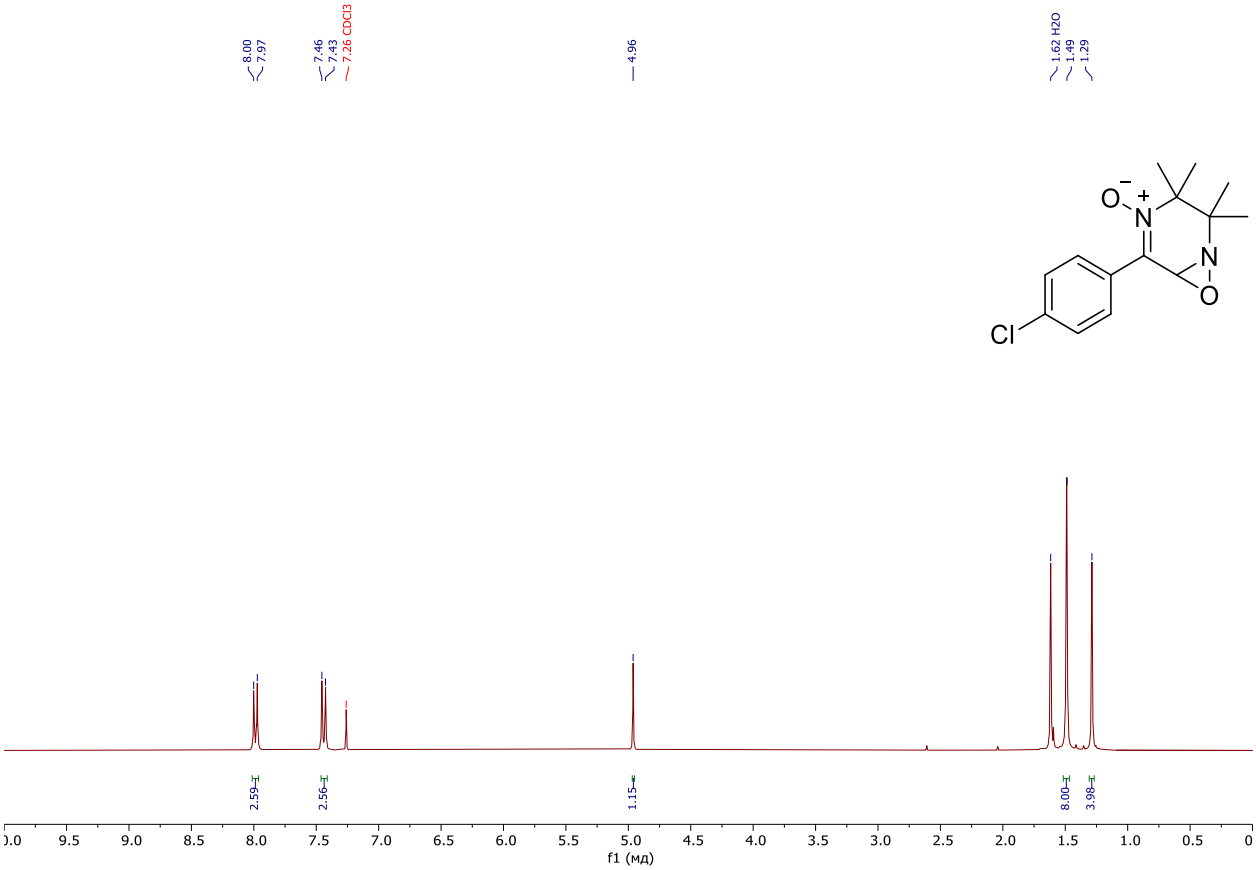
HRMS for compound **6b**

Acquisition Parameter

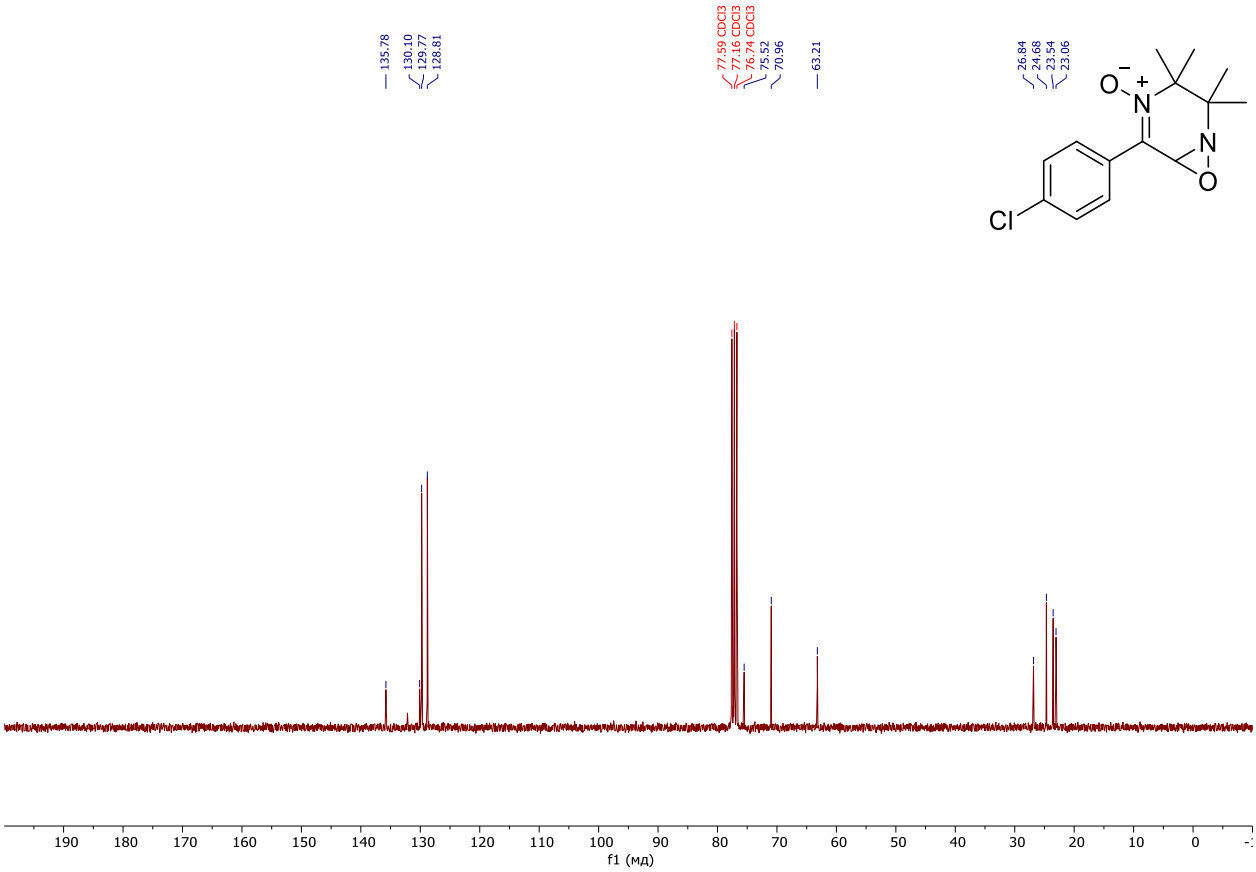
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



^{1}H NMR spectrum (300 MHz) of **6c** in $CDCl_3$



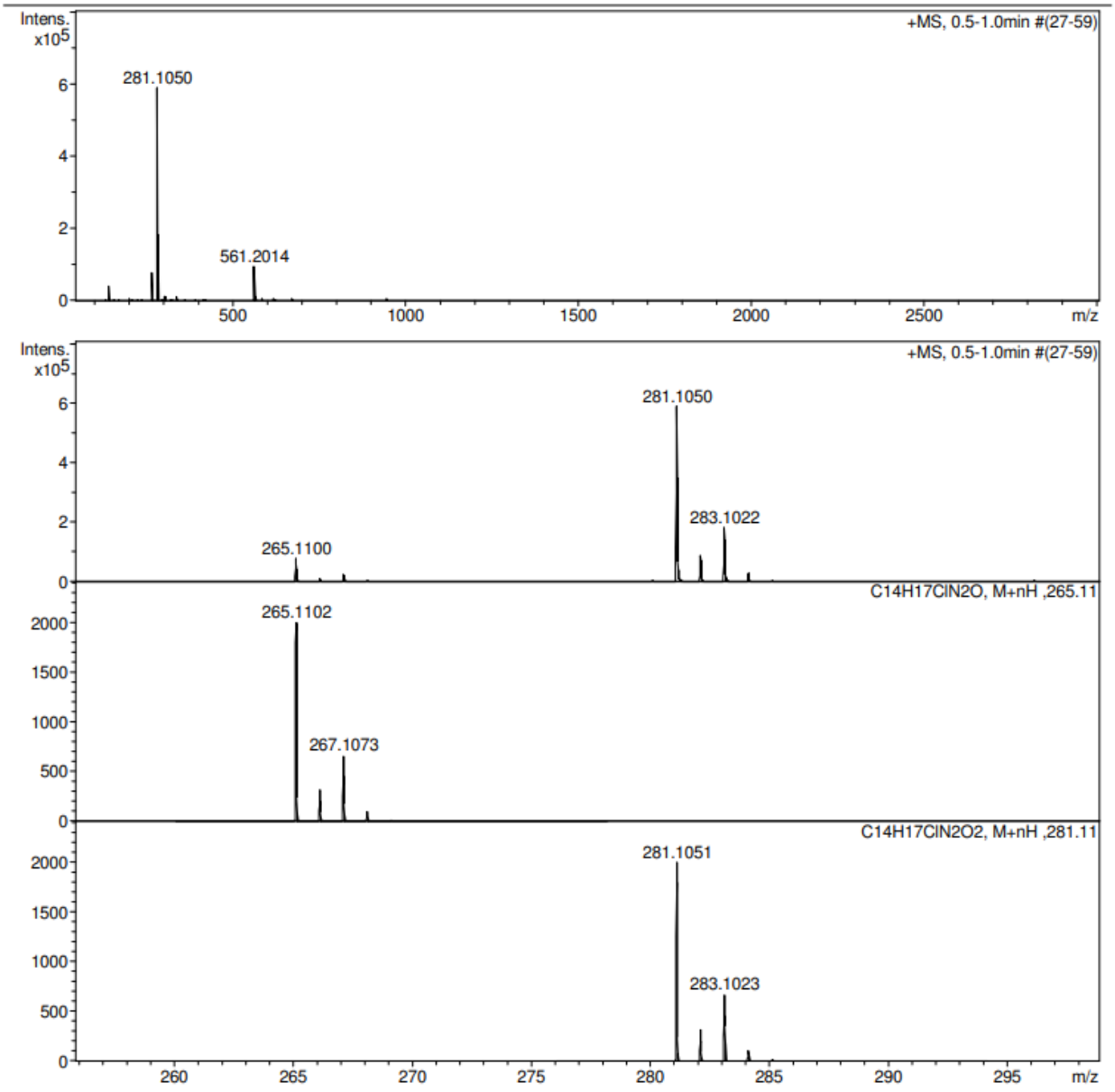
^{13}C {^{1}H} NMR spectrum (76 MHz) of **6c** in $CDCl_3$



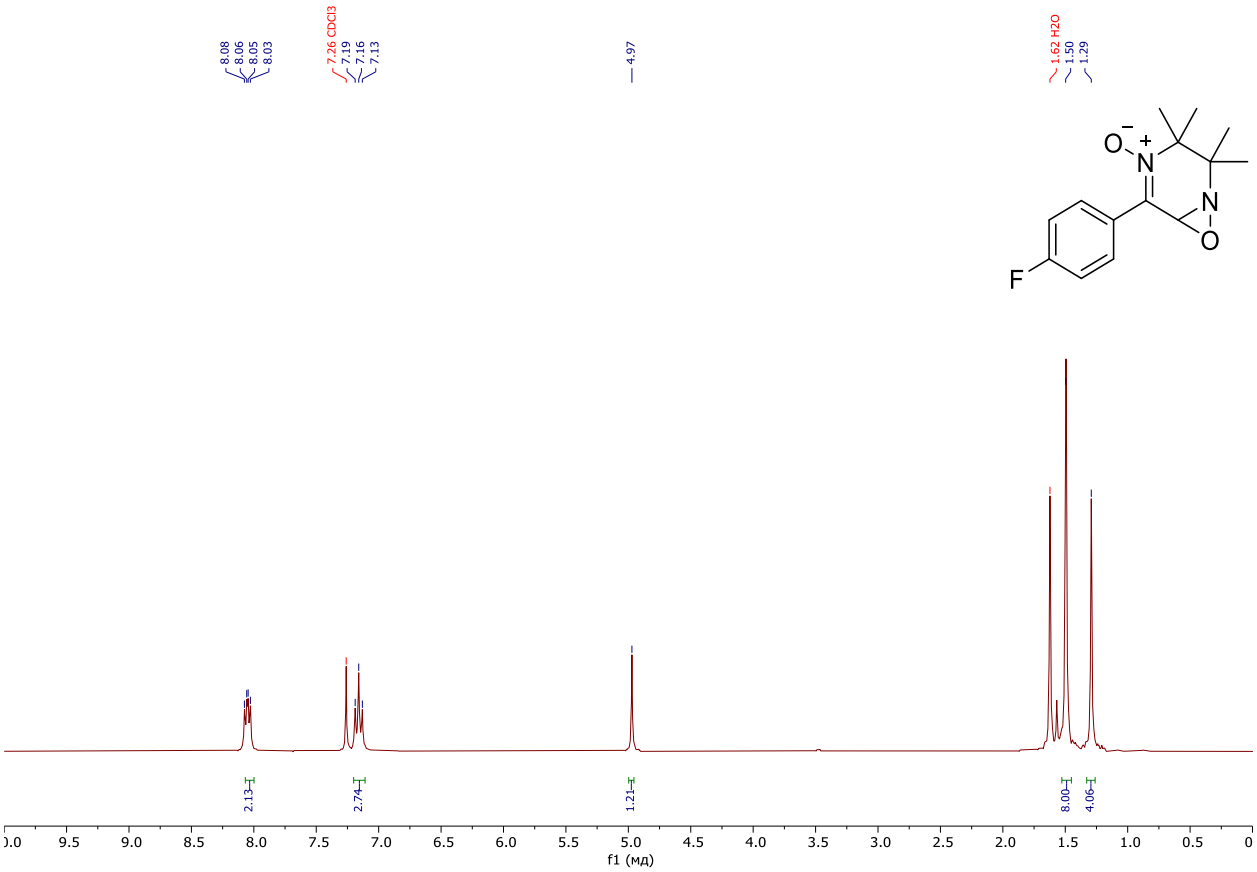
HRMS for compound **6c**

Acquisition Parameter

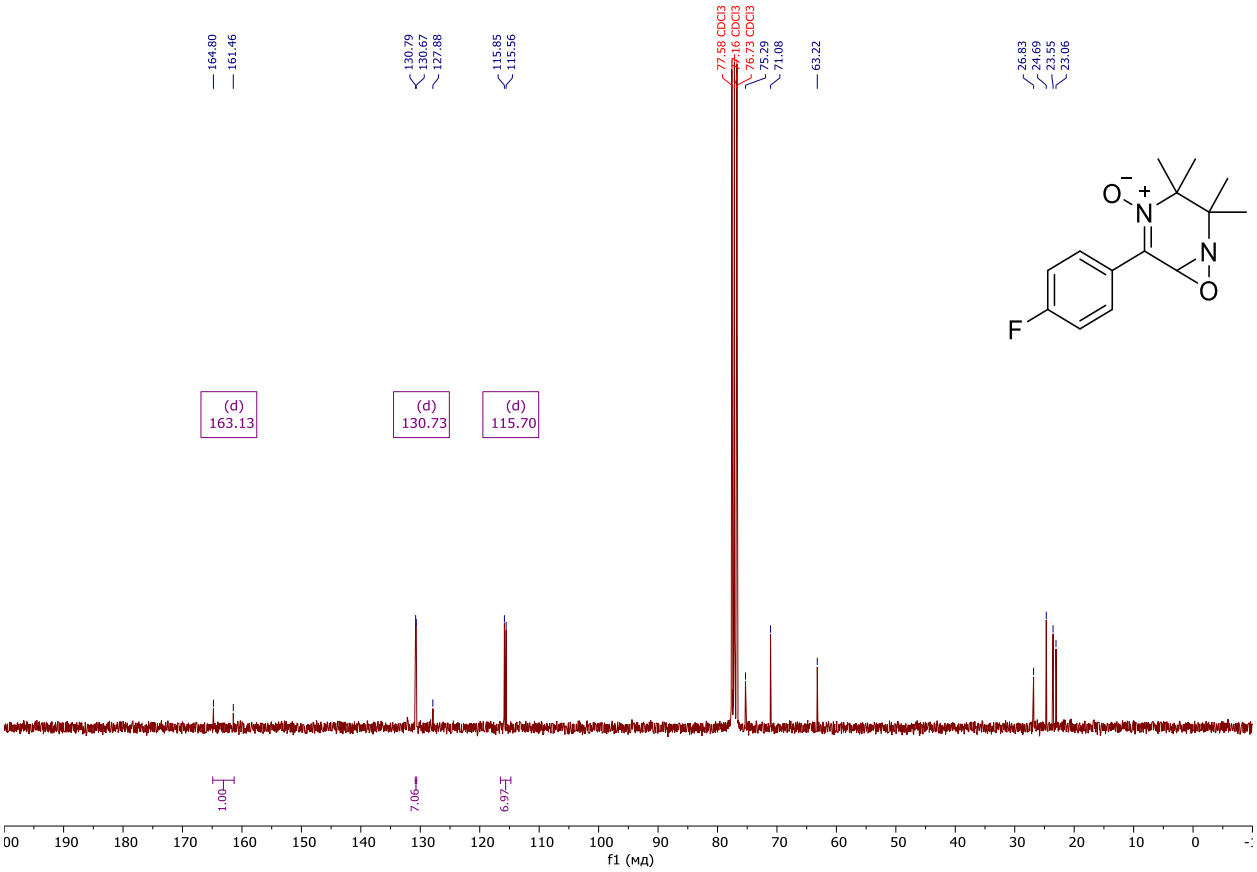
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



^{1}H NMR spectrum (300 MHz) of **6d** in $CDCl_3$



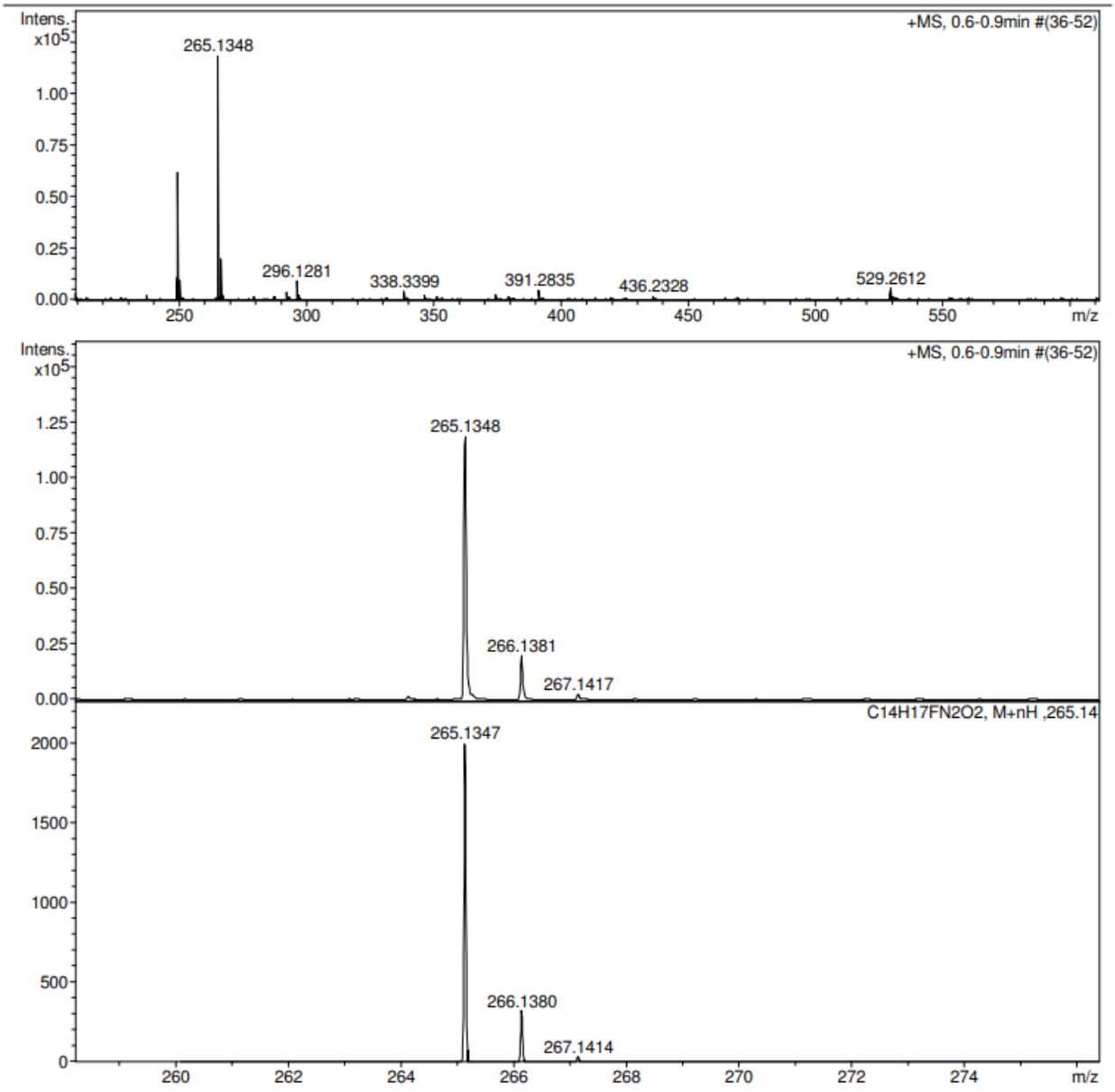
^{13}C {^{1}H} NMR spectrum (76 MHz) of **6d** in $CDCl_3$



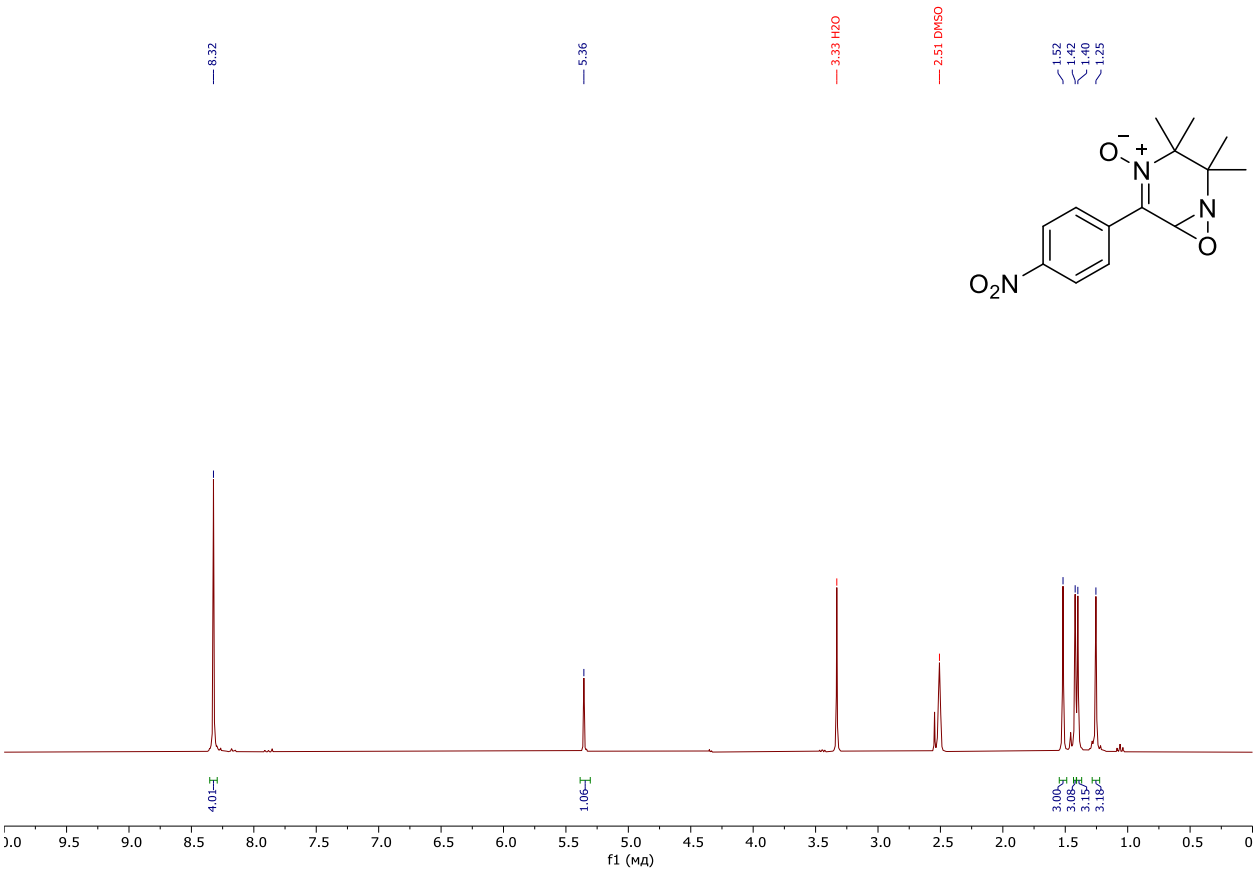
HRMS for compound **6d**

Acquisition Parameter

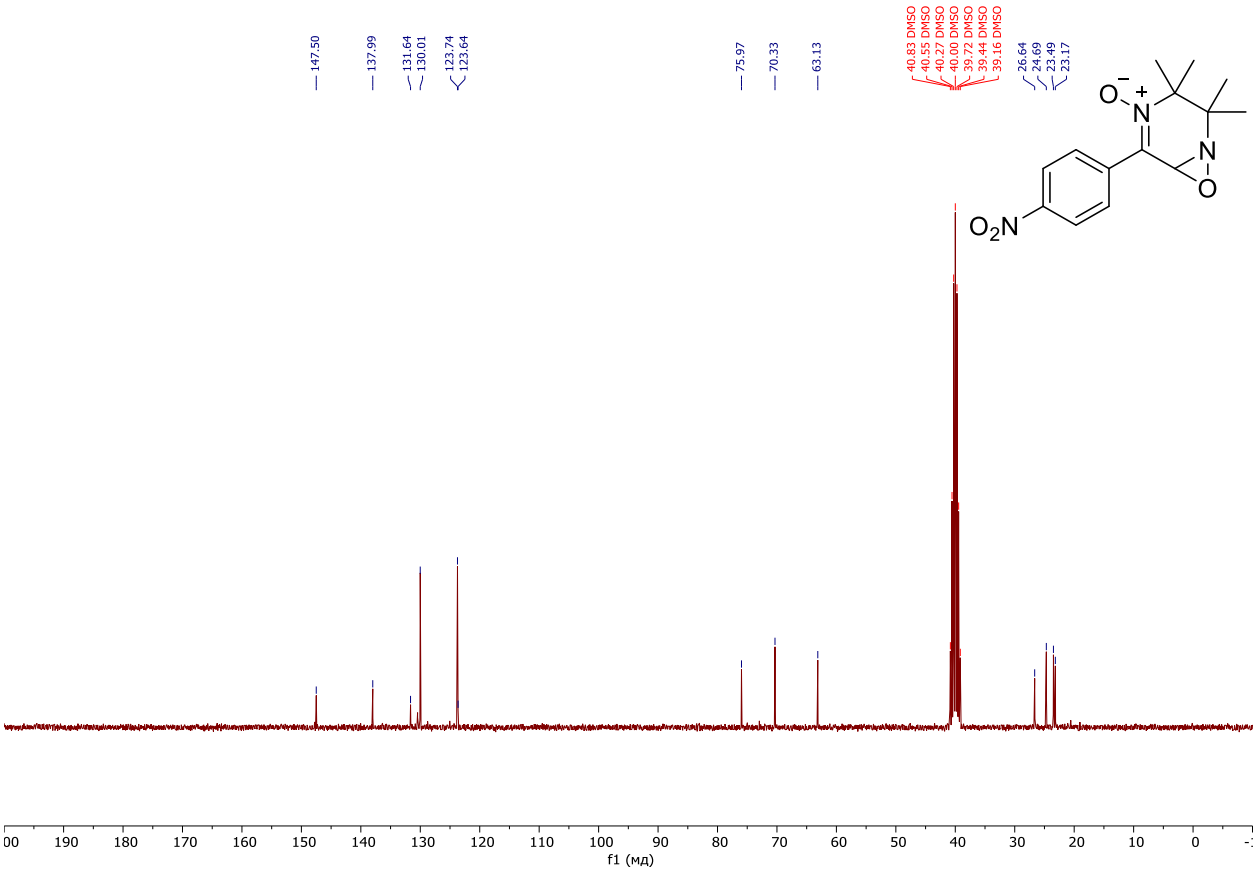
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



^{1}H NMR spectrum (300 MHz) of **6e** in DMSO-d_6



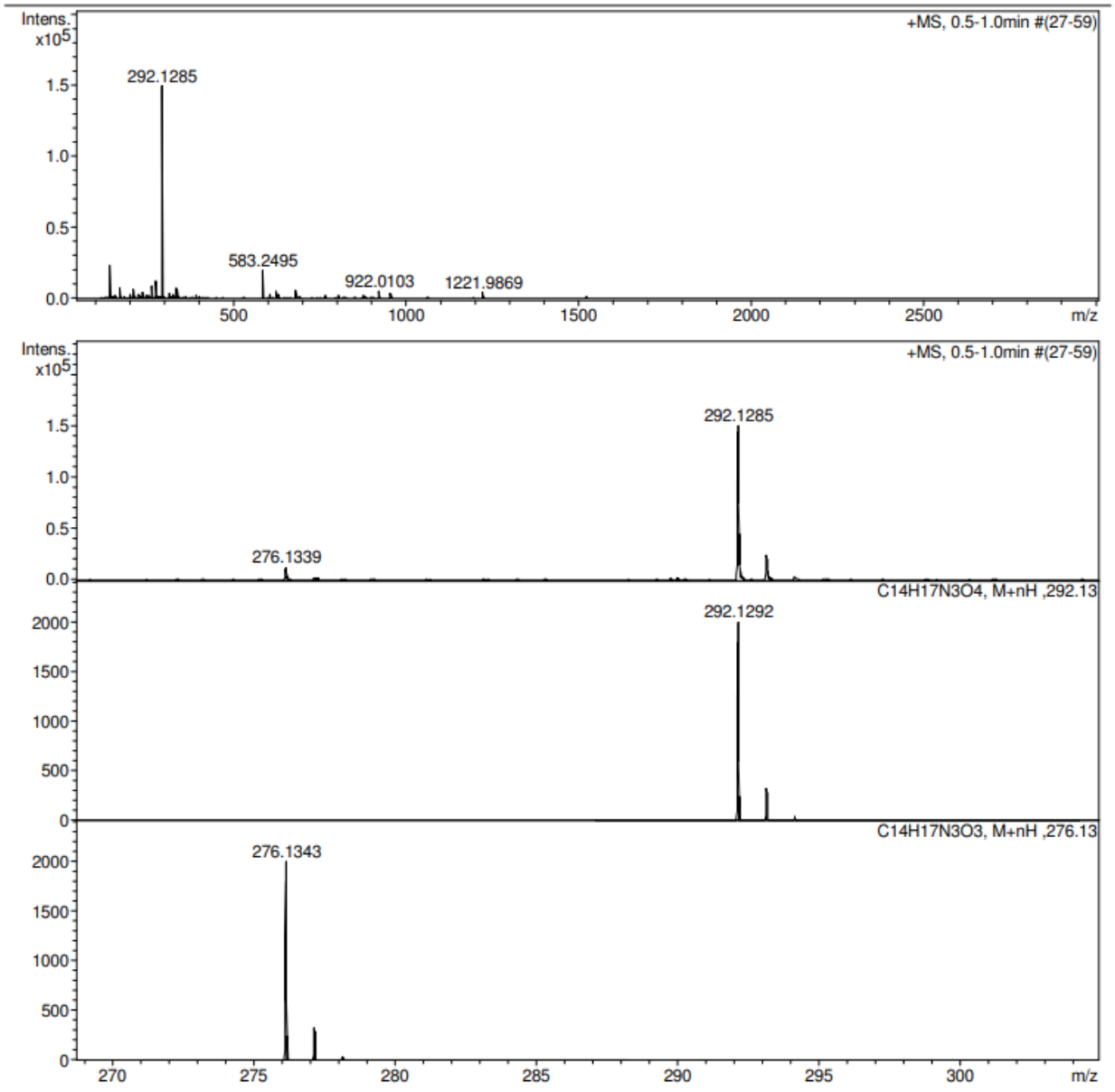
^{13}C {^{1}H} NMR spectrum (76 MHz) of **6e** in DMSO-d_6



HRMS for compound **6e**

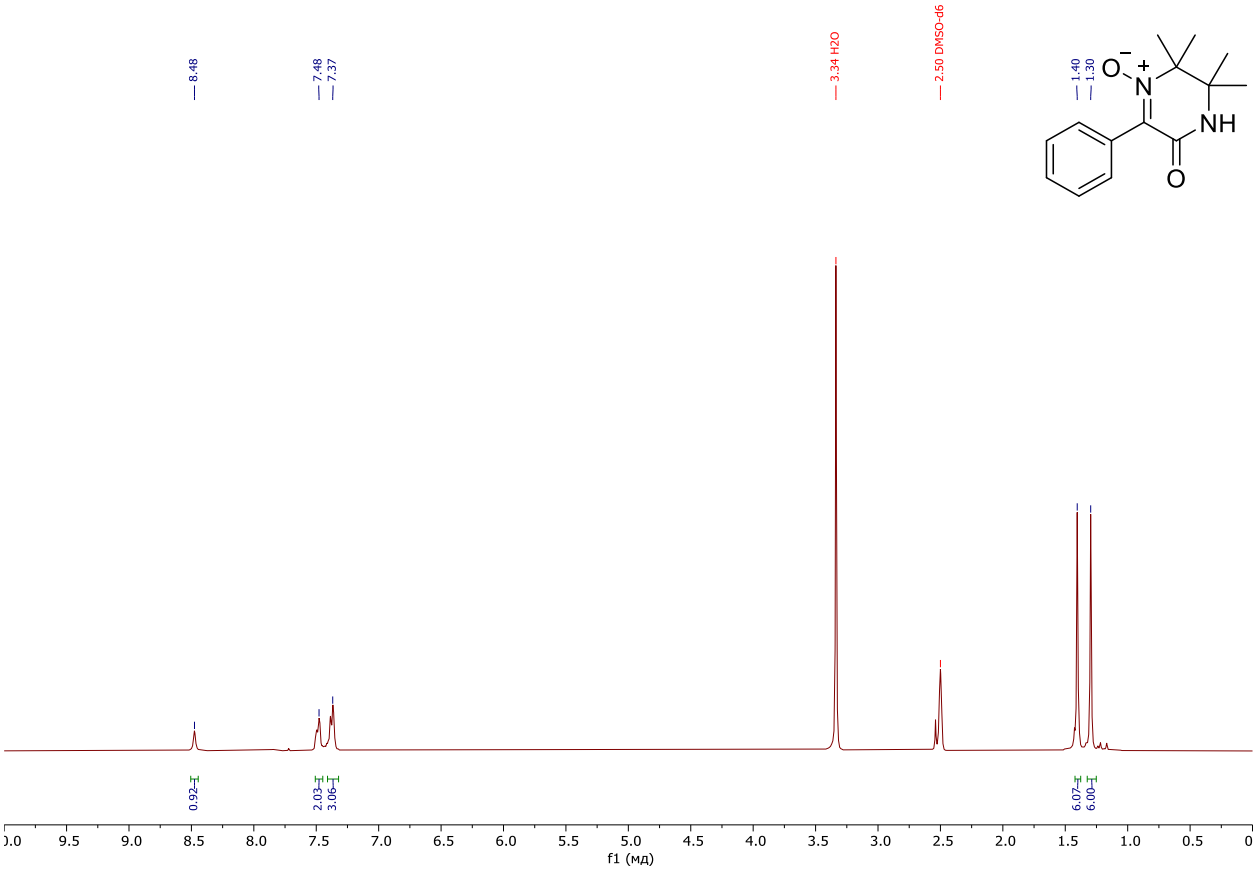
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

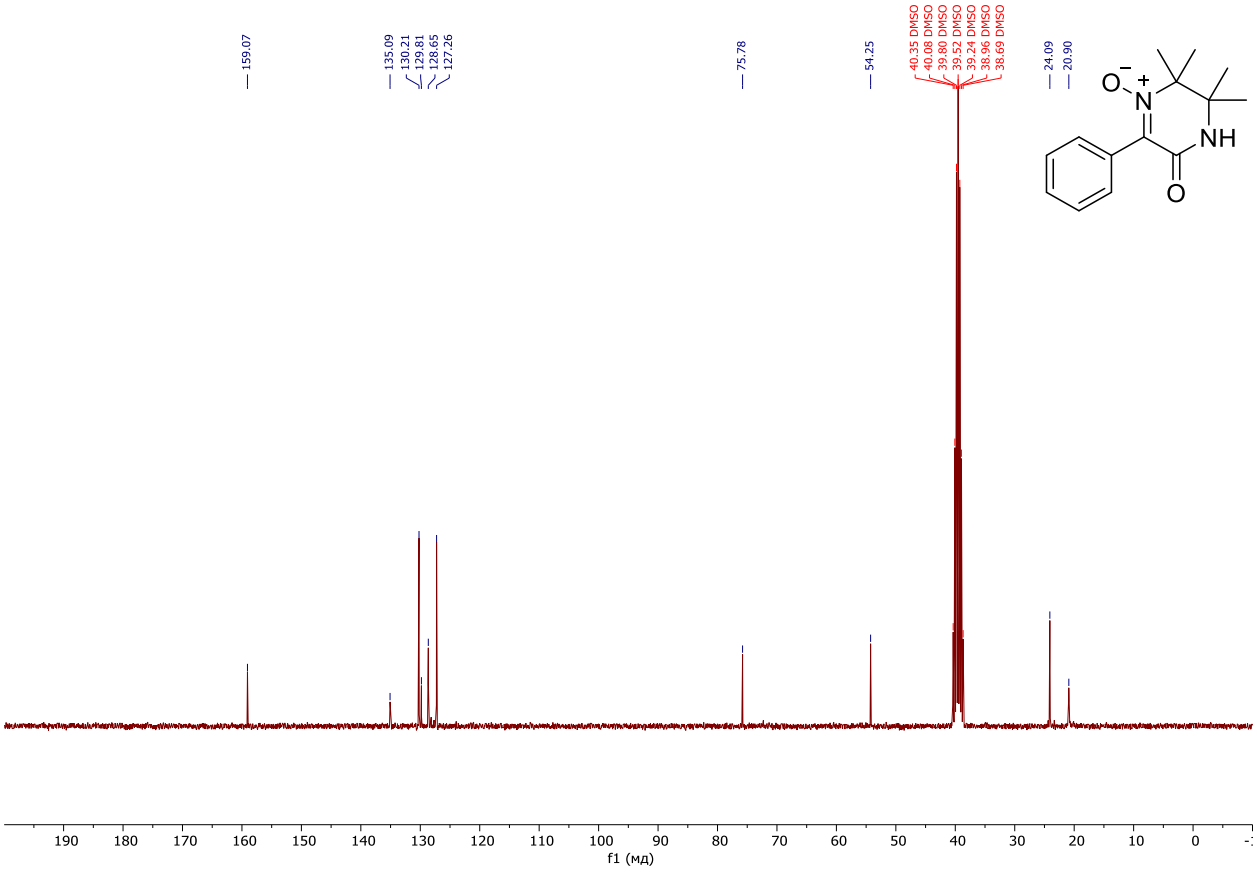


15. Copies of ^{1}H, ^{13}C NMR and HRMS for monoamides 7.

^{1}H NMR spectrum (300 MHz) of **7a** in DMSO-d_6



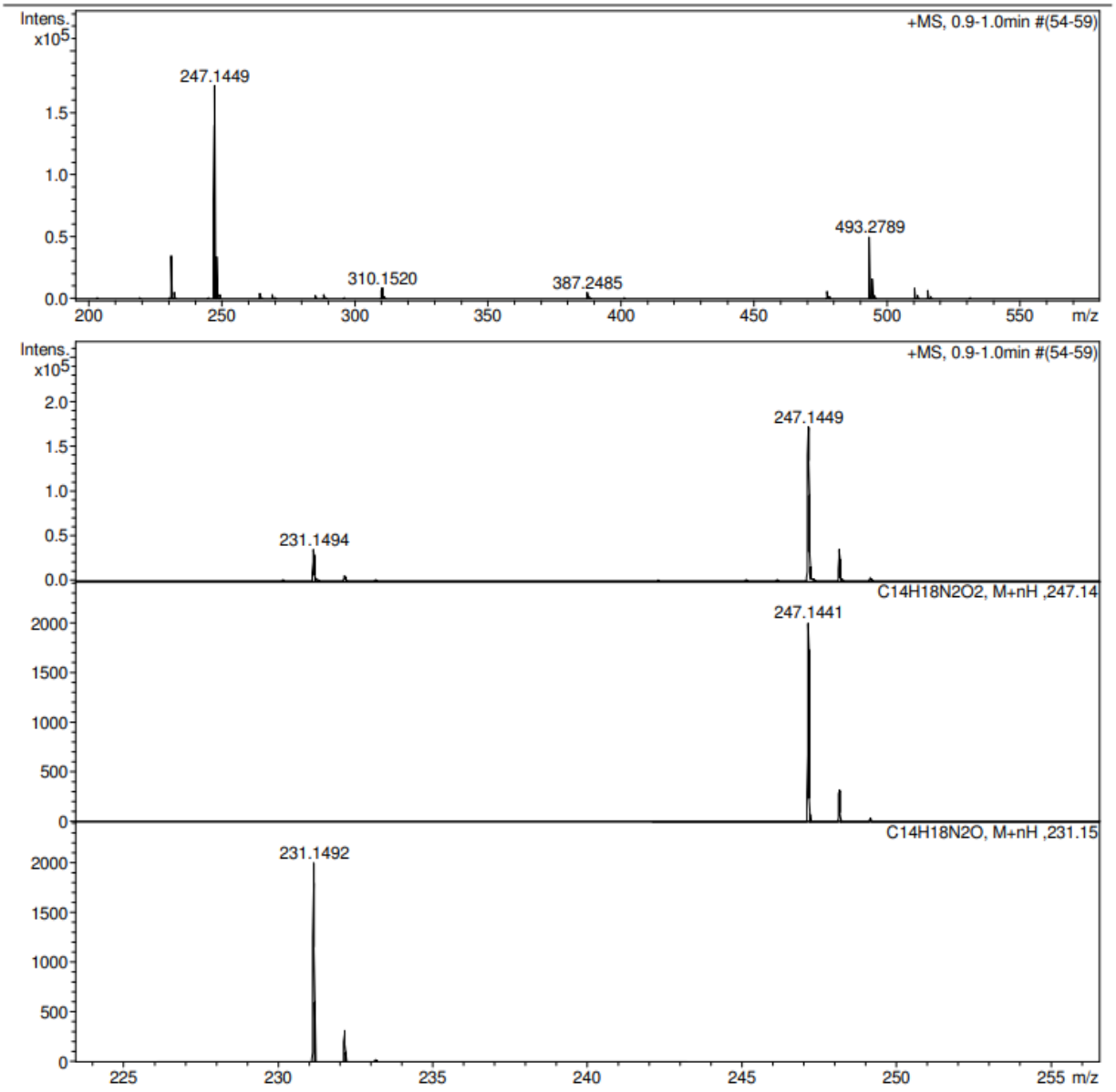
^{13}C {^{1}H} NMR spectrum (76 MHz) of **7a** in DMSO-d_6



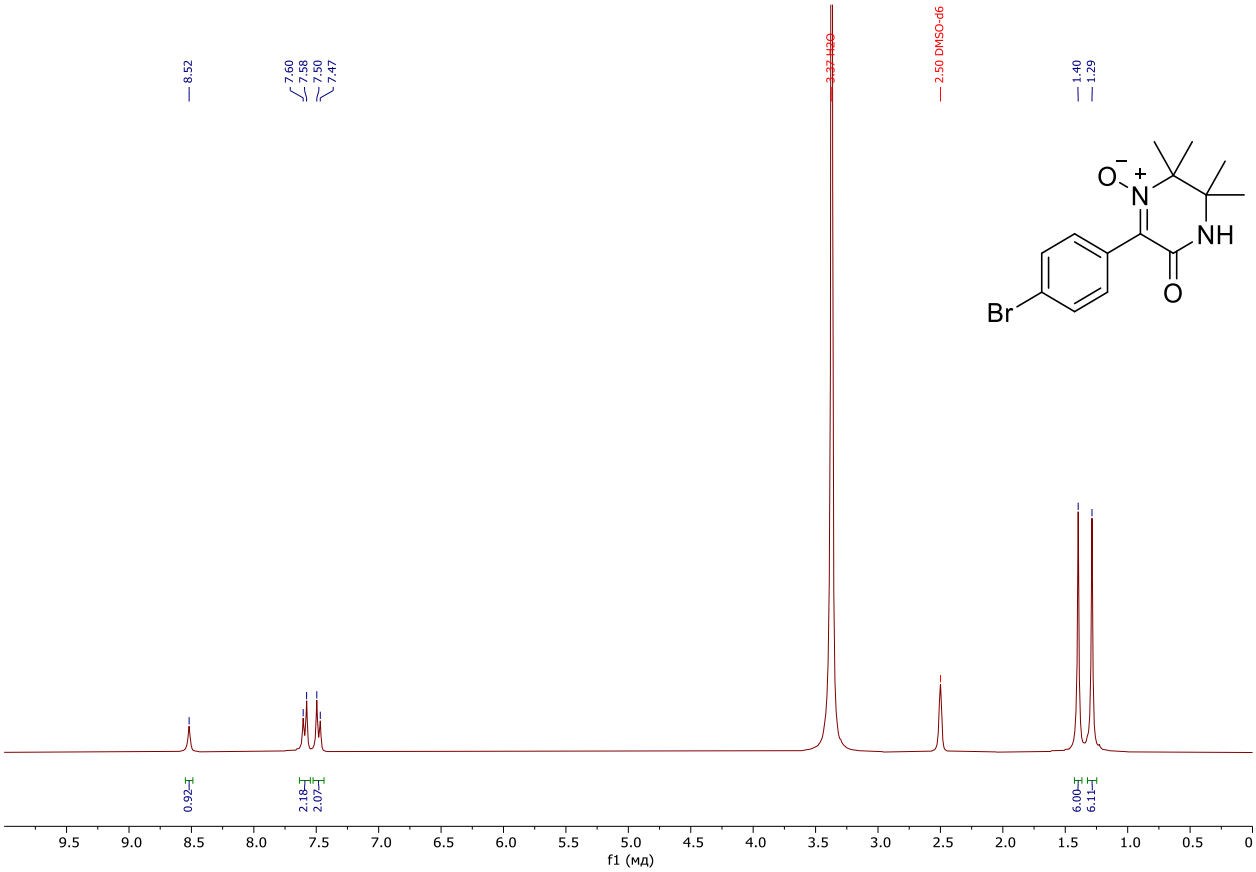
HRMS for compound **7a**

Acquisition Parameter

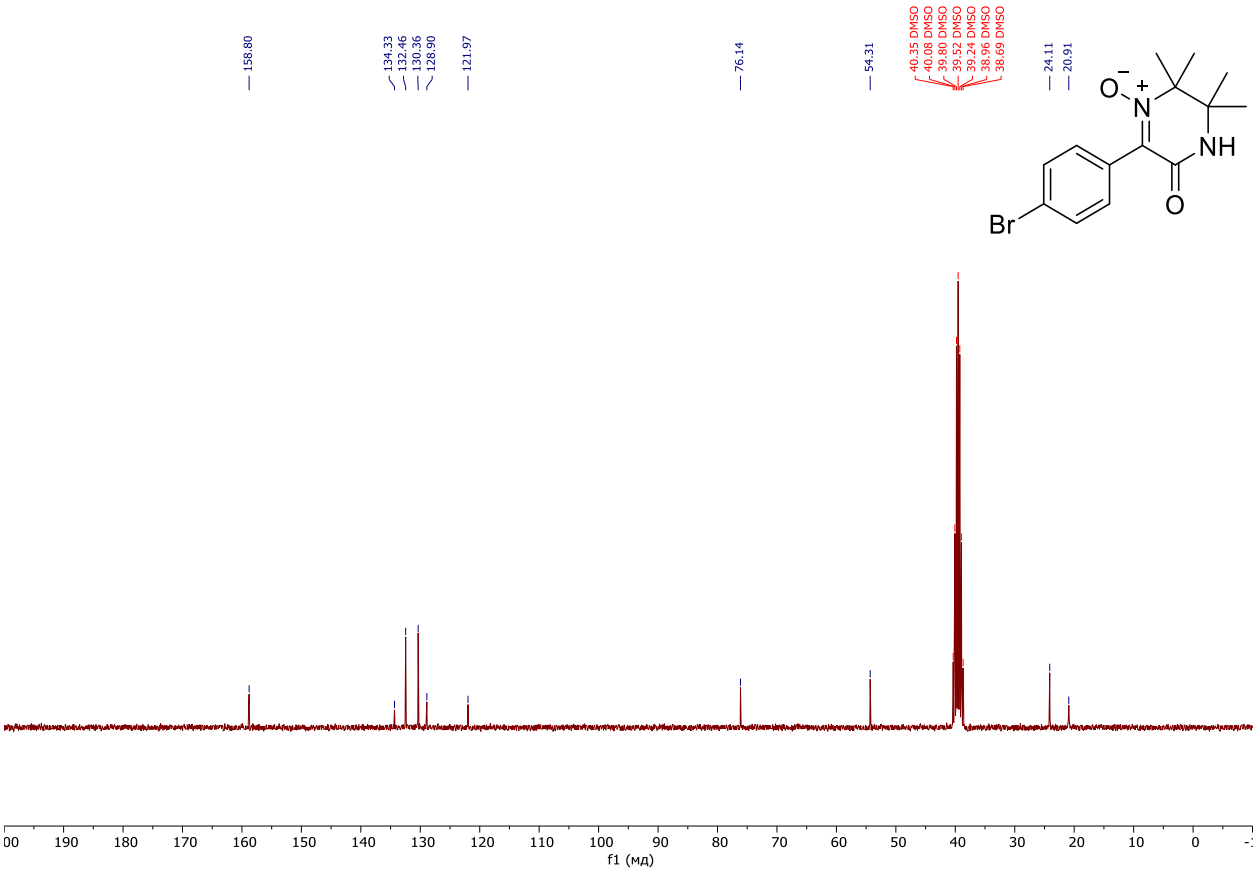
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



^{1}H NMR spectrum (300 MHz) of **7b** in DMSO-d_6



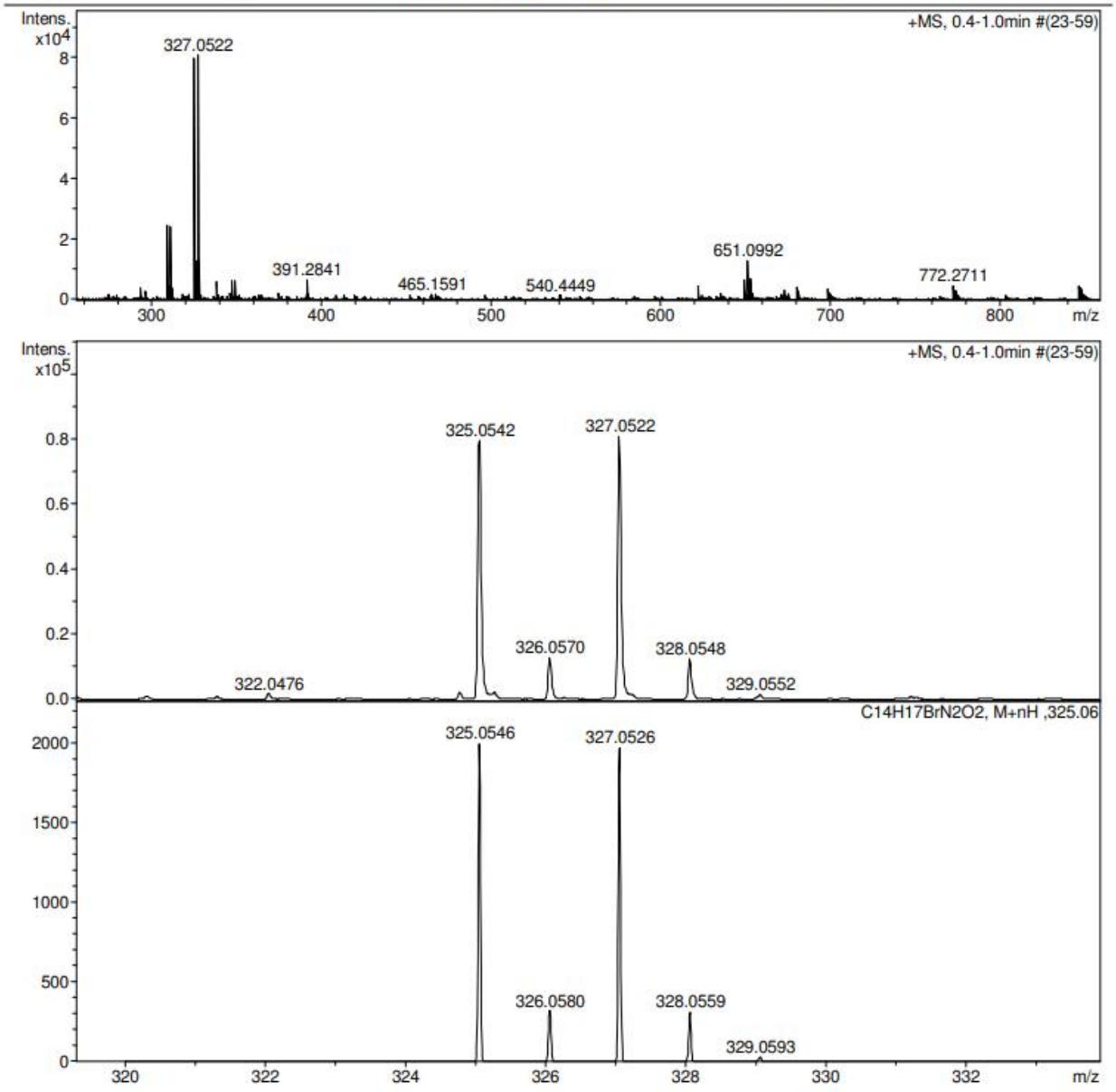
^{13}C {^{1}H} NMR spectrum (76 MHz) of **7b** in DMSO-d_6



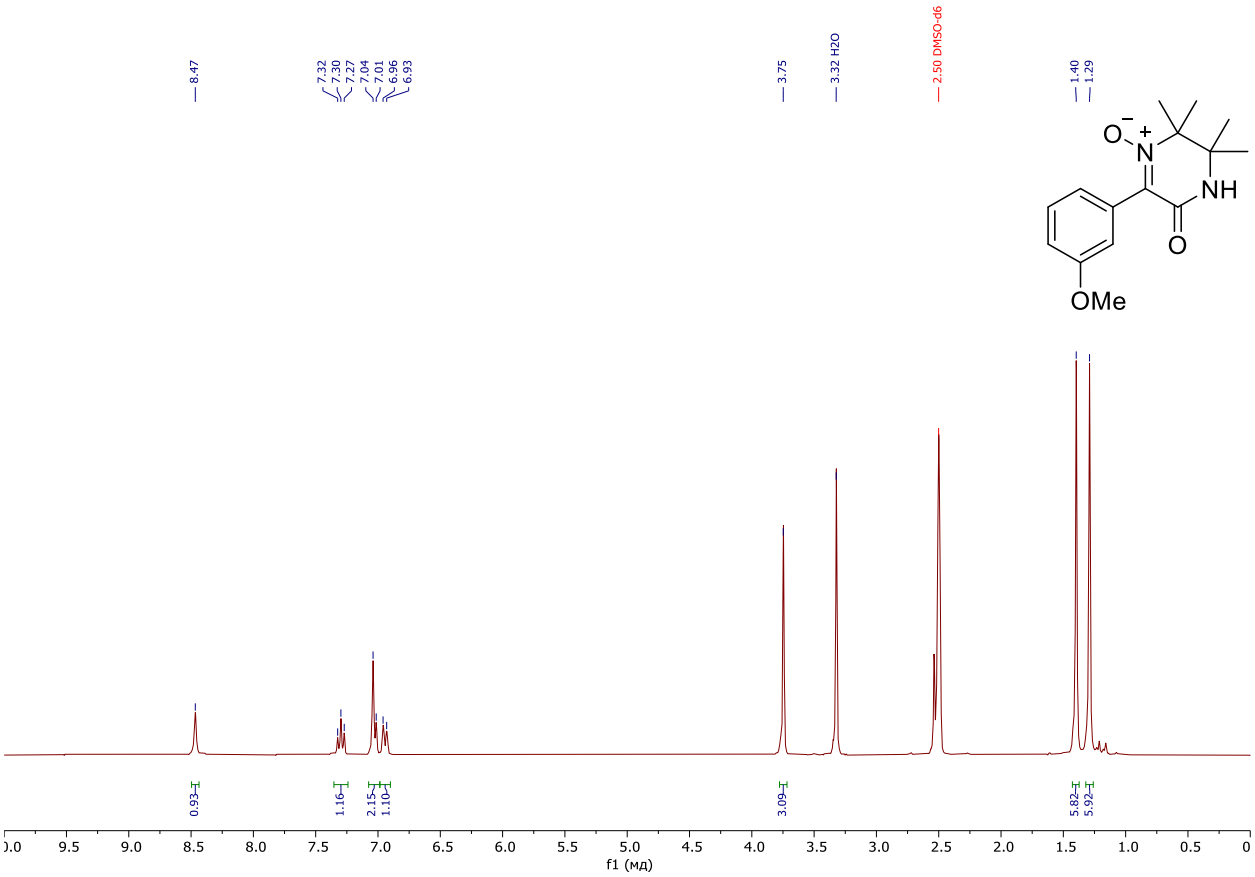
HRMS for compound **7b**

Acquisition Parameter

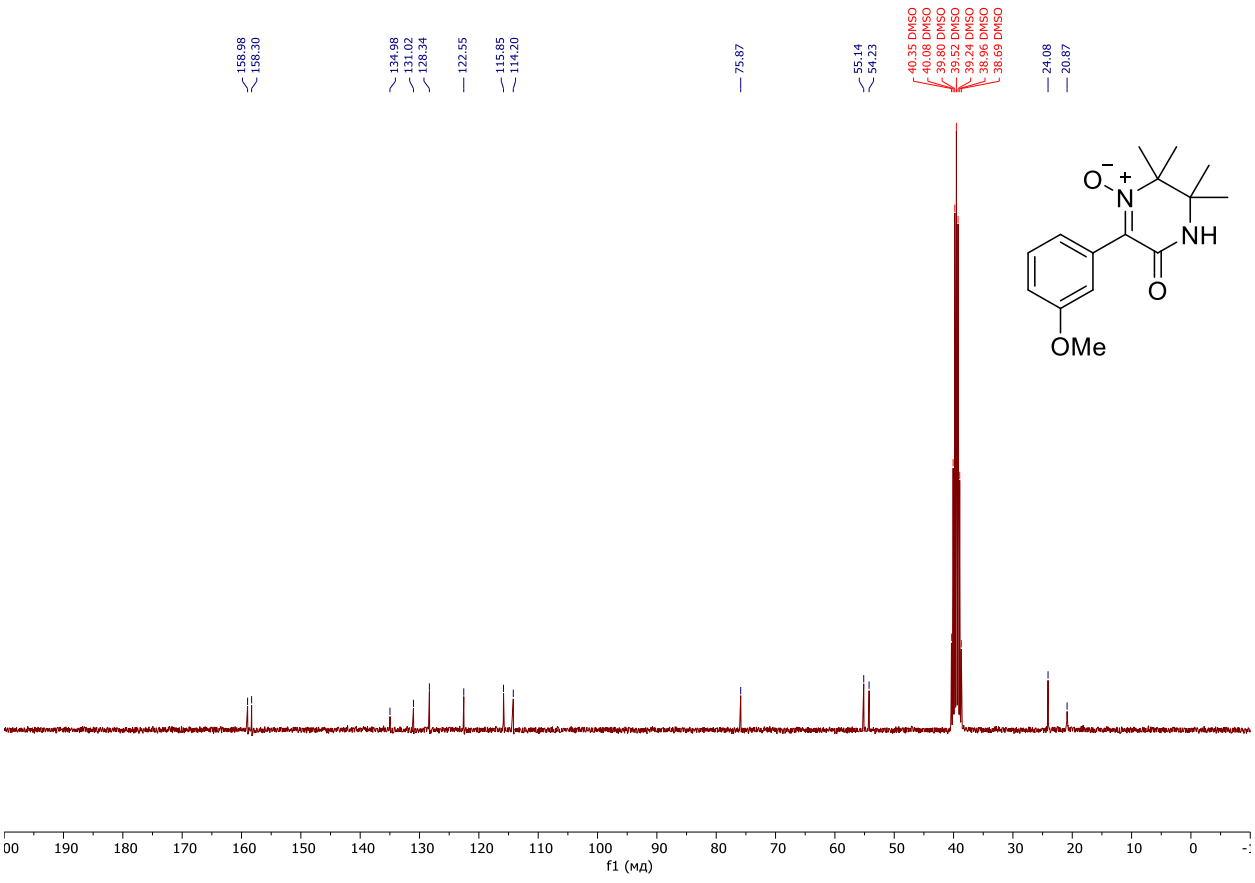
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



^{1}H NMR spectrum (300 MHz) of **7c** in DMSO-d_6



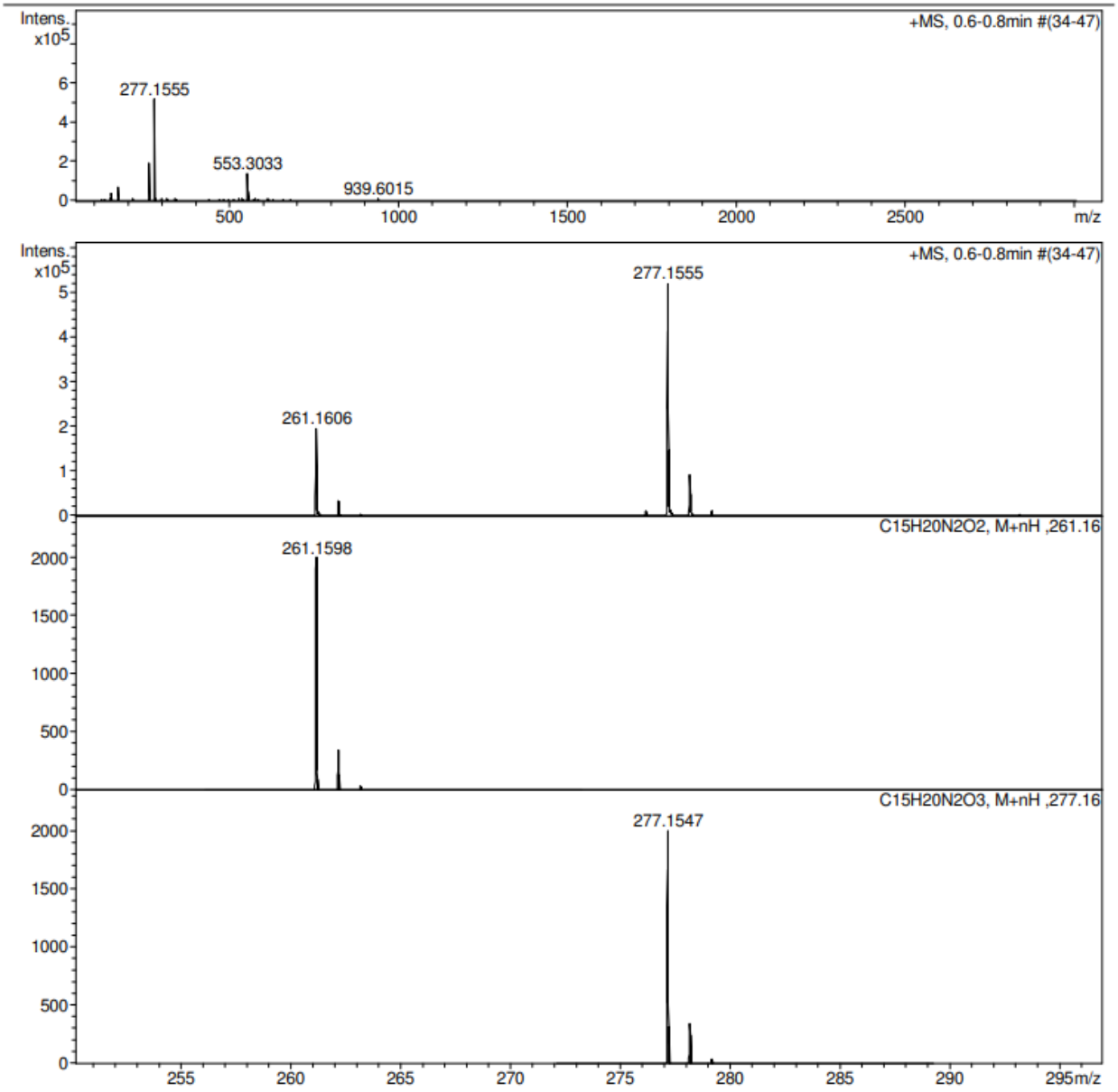
^{13}C {^{1}H} NMR spectrum (76 MHz) of **7c** in DMSO-d_6



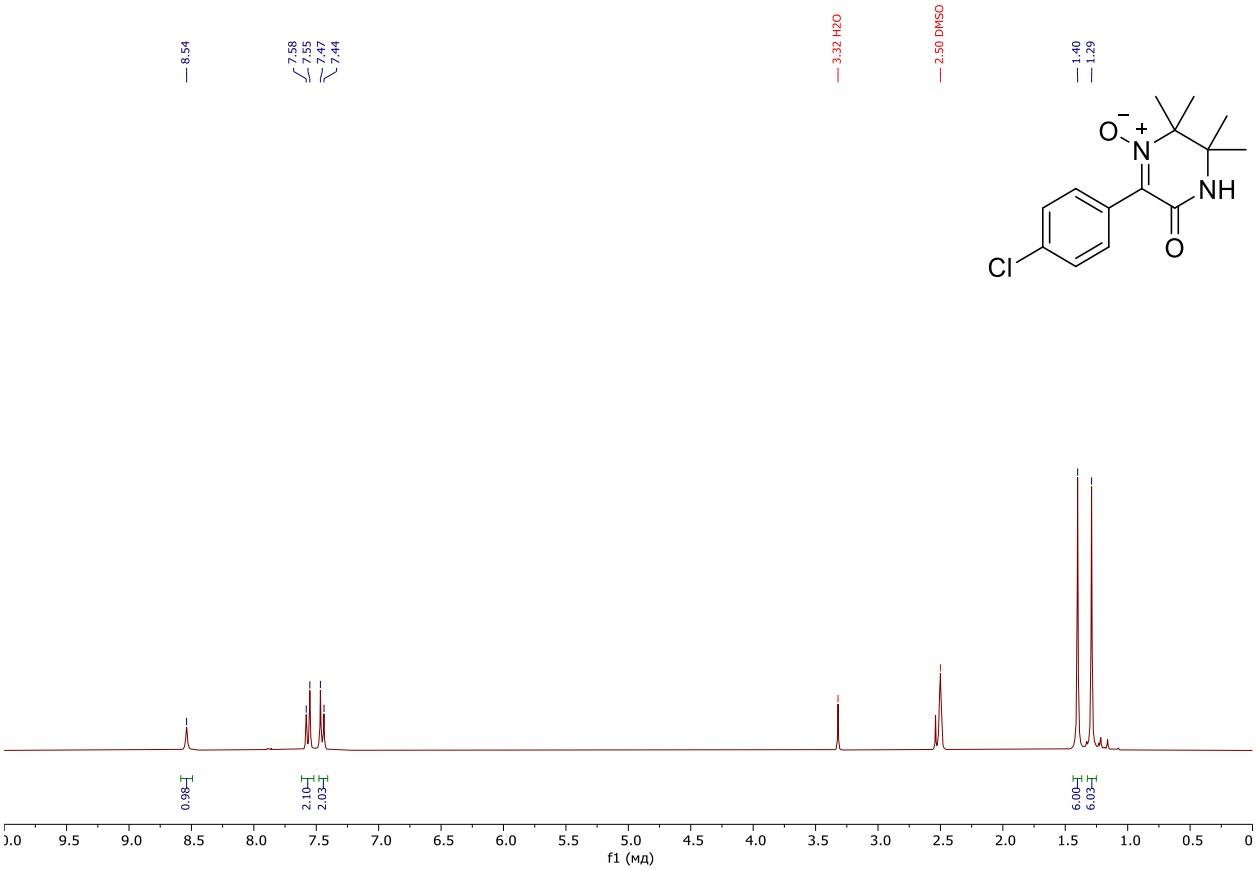
HRMS for compound **7c**

Acquisition Parameter

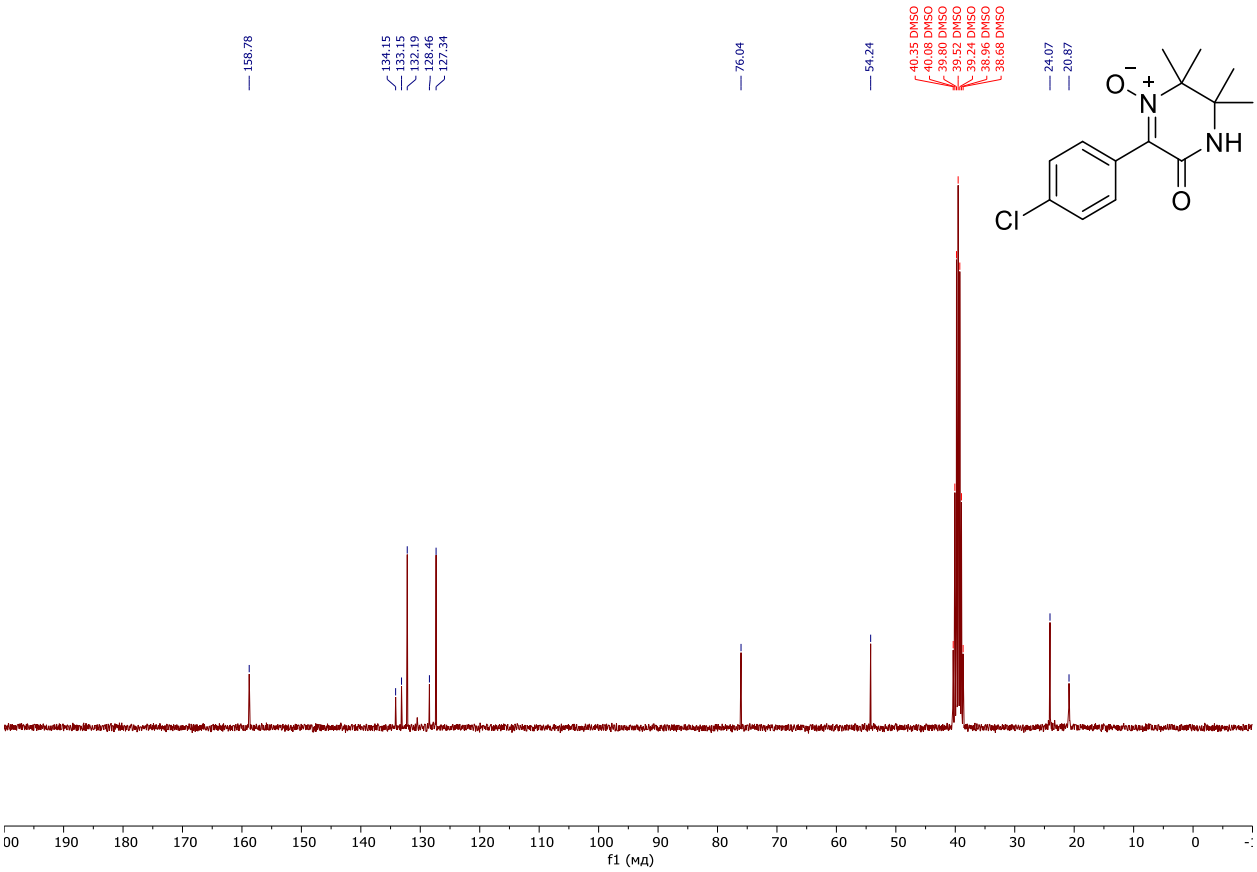
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



^{1}H NMR spectrum (300 MHz) of **7d** in DMSO-d_6



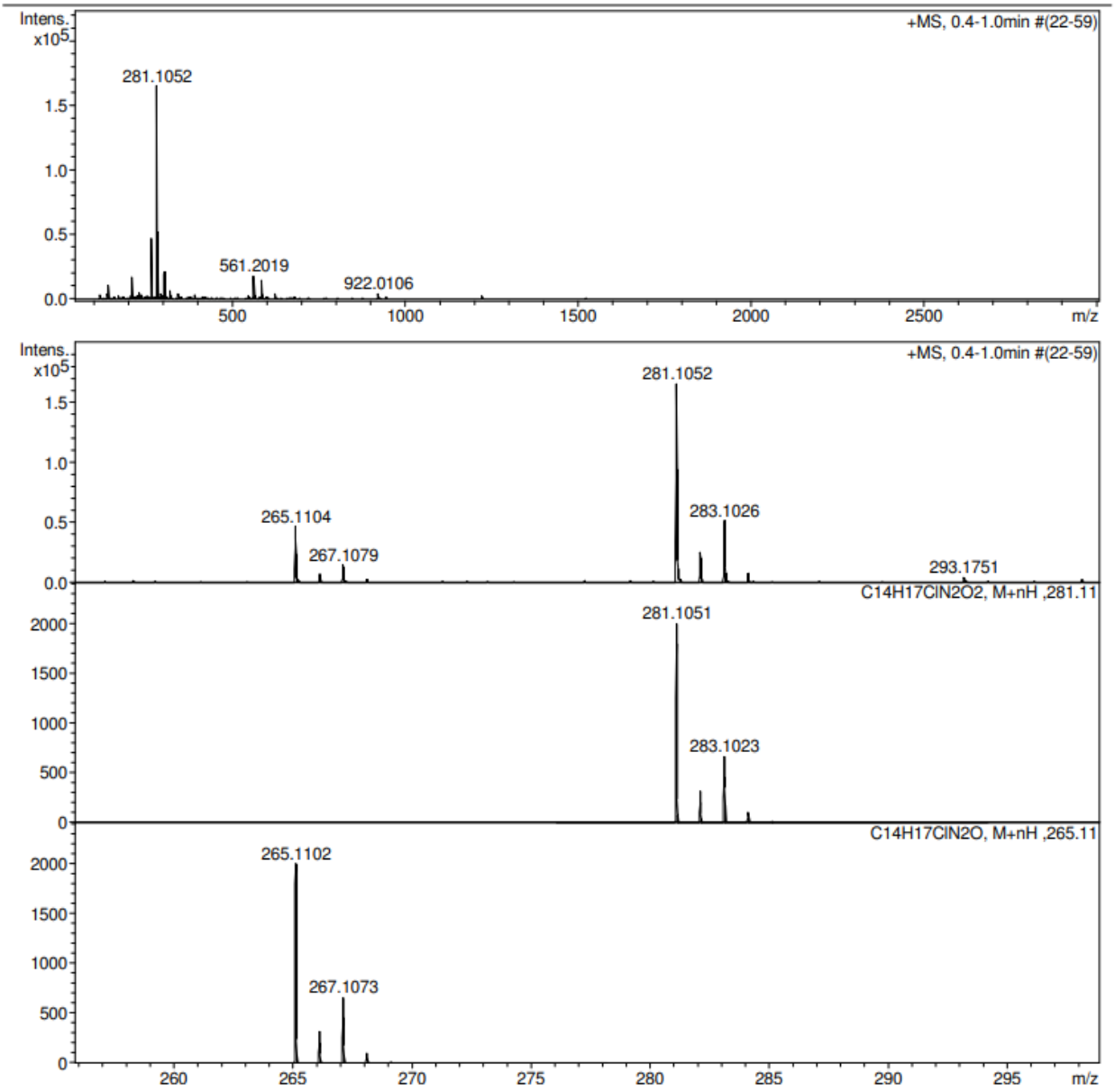
^{13}C {^{1}H} NMR spectrum (76 MHz) of **7d** in DMSO-d_6



HRMS for compound **7d**

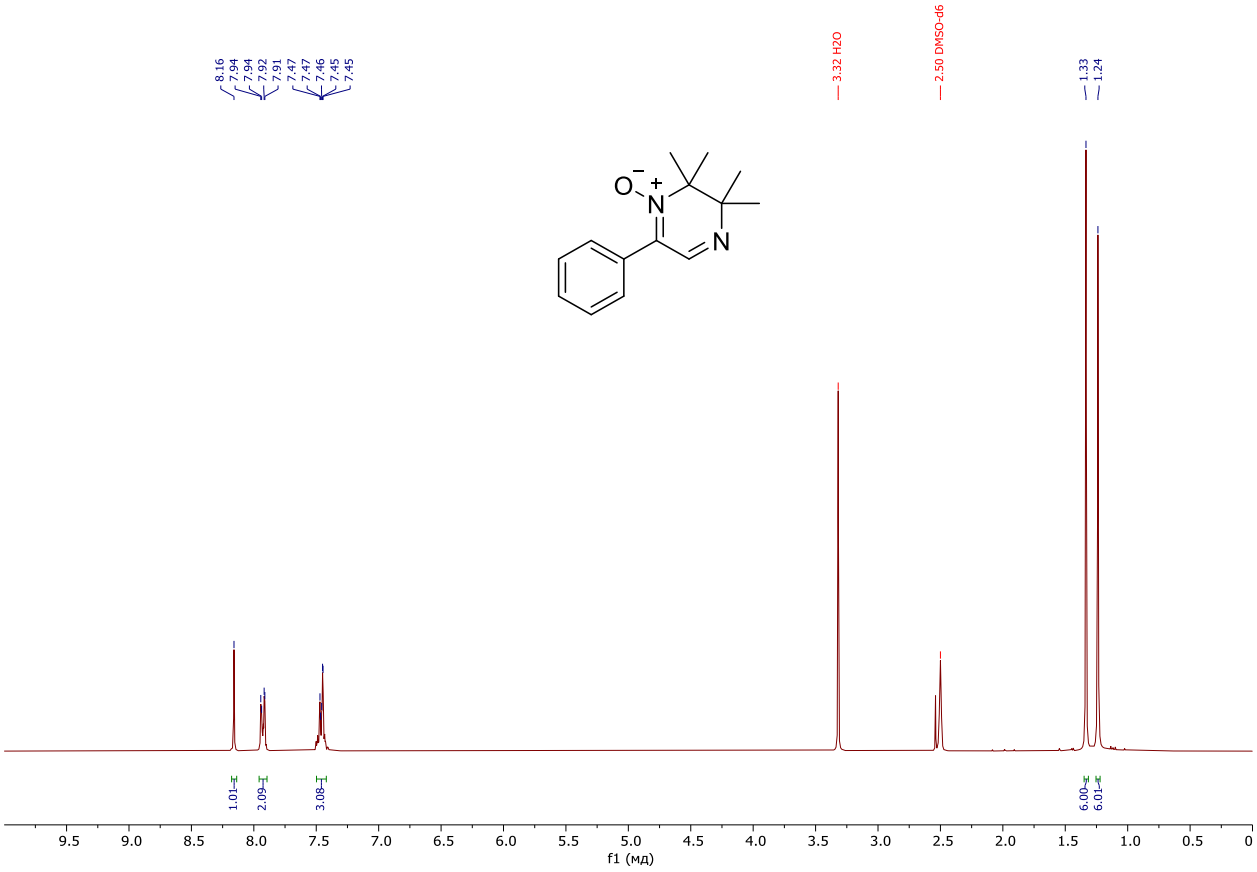
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

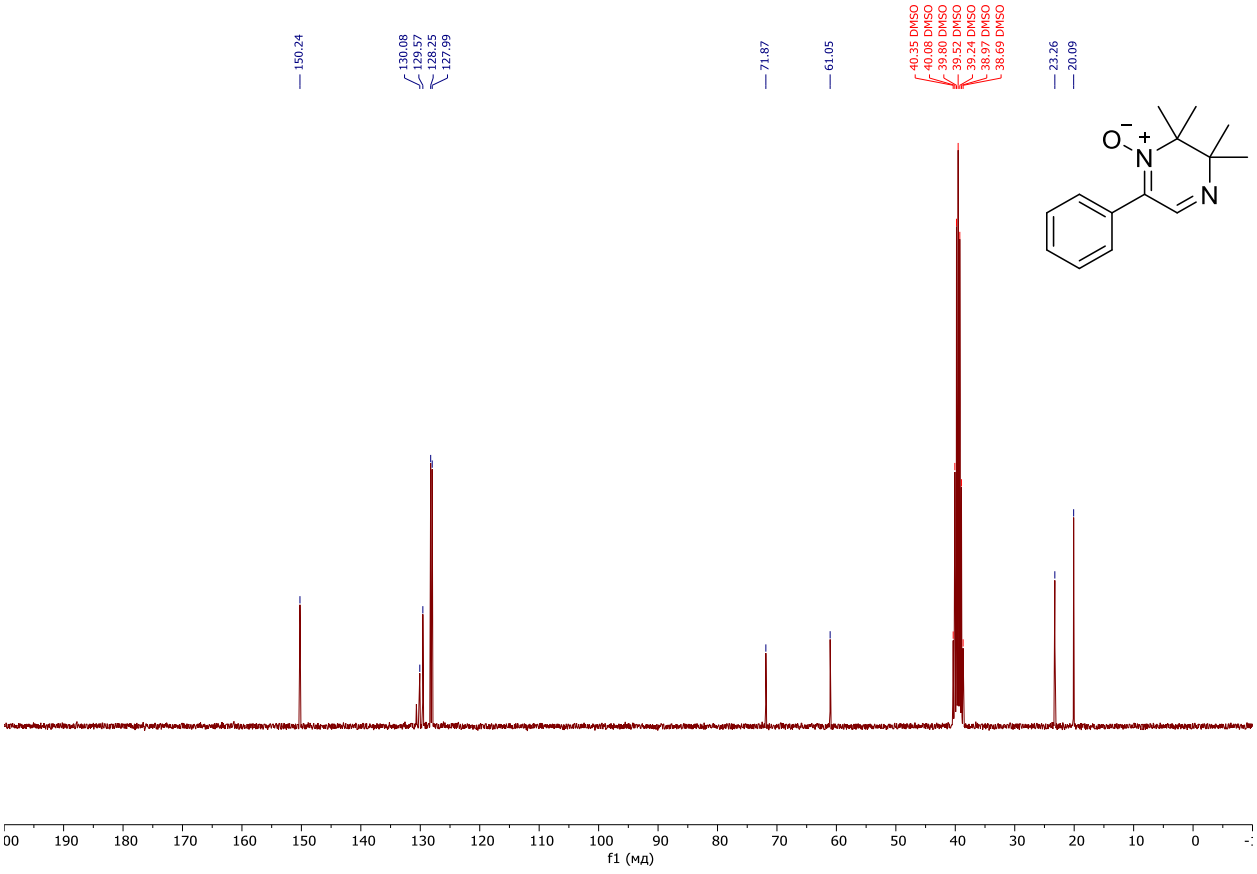


16. Copies of ^{1}H, ^{13}C NMR and HRMS for imines 8.

^{1}H NMR spectrum (300 MHz) of **8a** in DMSO-d_6



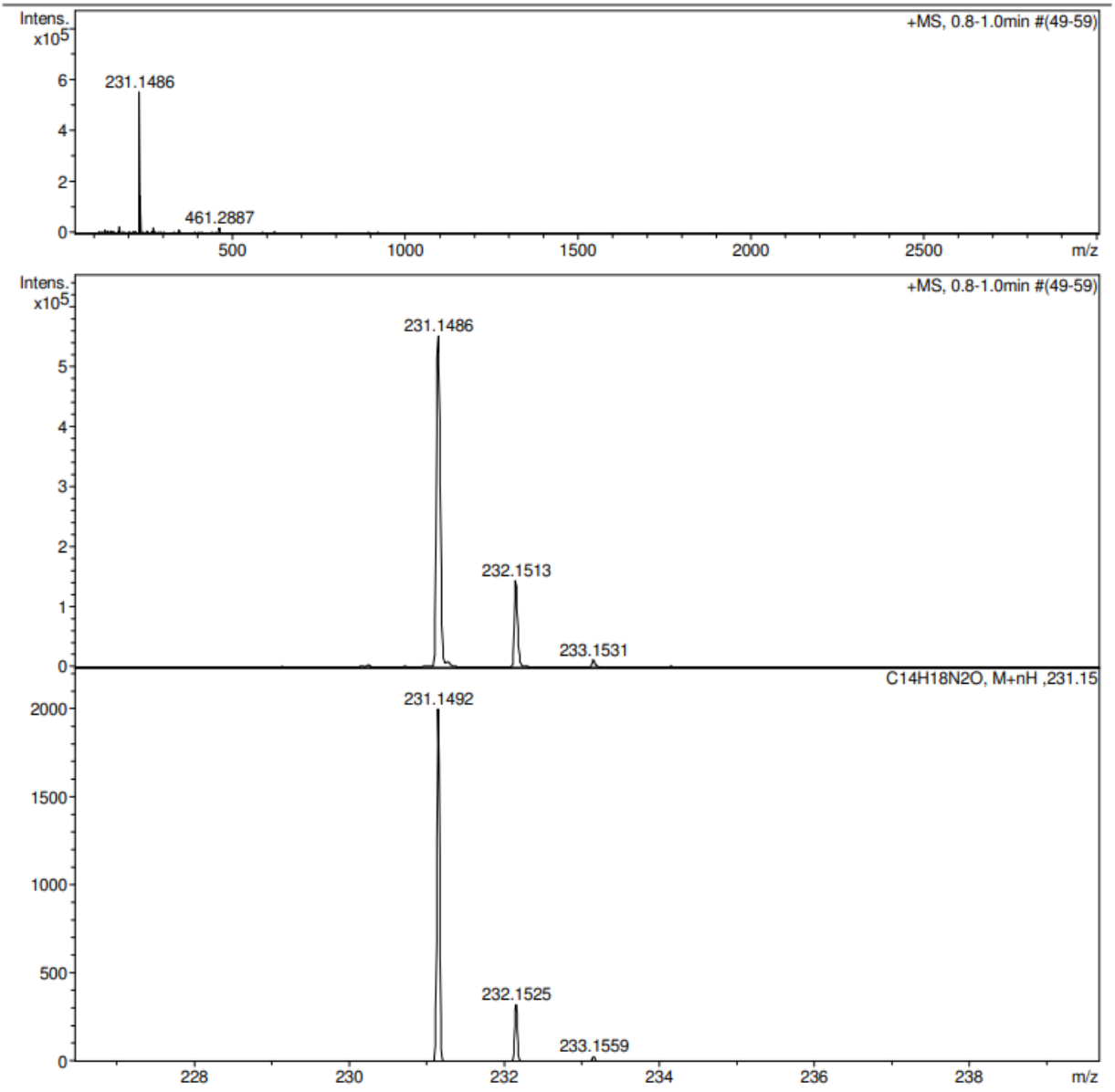
^{13}C {^{1}H} NMR spectrum (76 MHz) of **8a** in DMSO-d_6



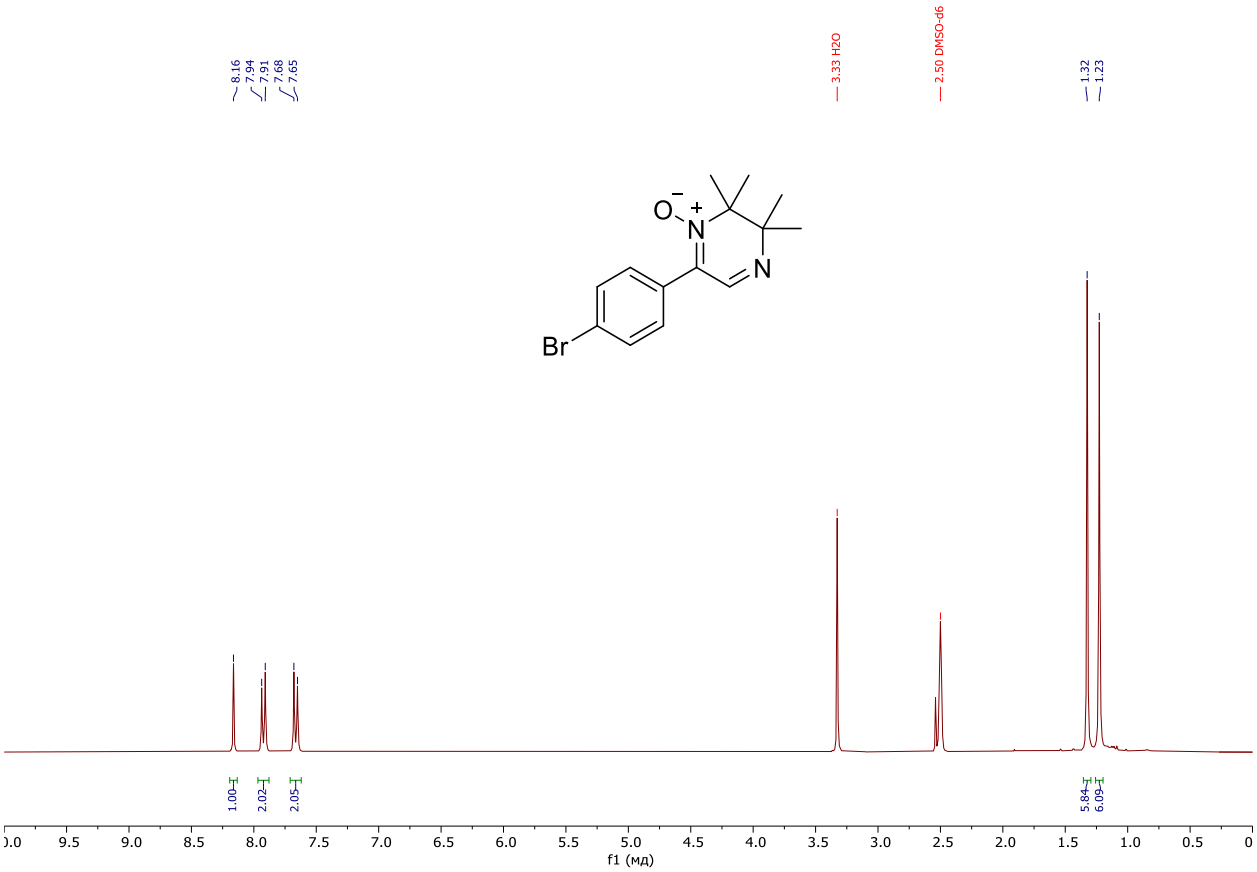
HRMS for compound **8a**

Acquisition Parameter

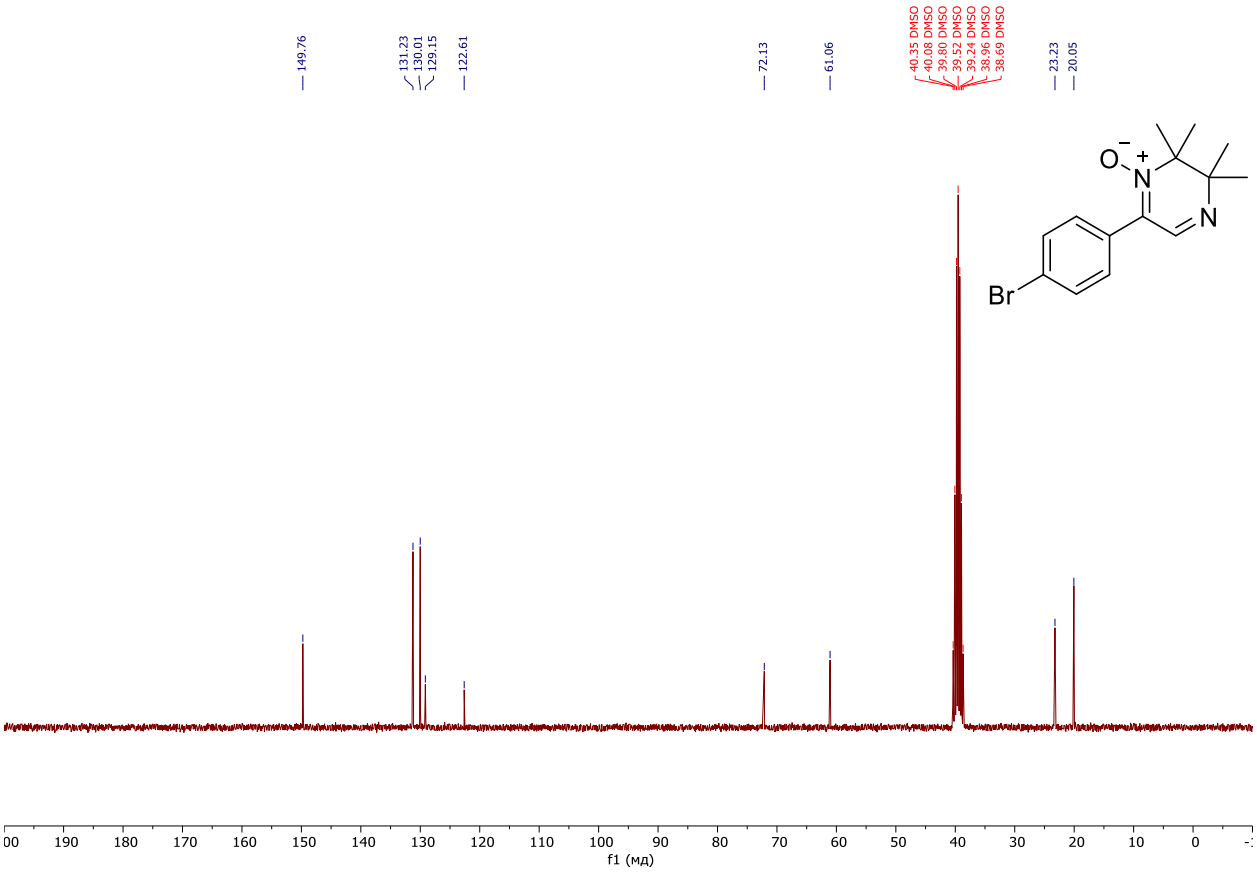
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



^{1}H NMR spectrum (300 MHz) of **8b** in DMSO-d_6



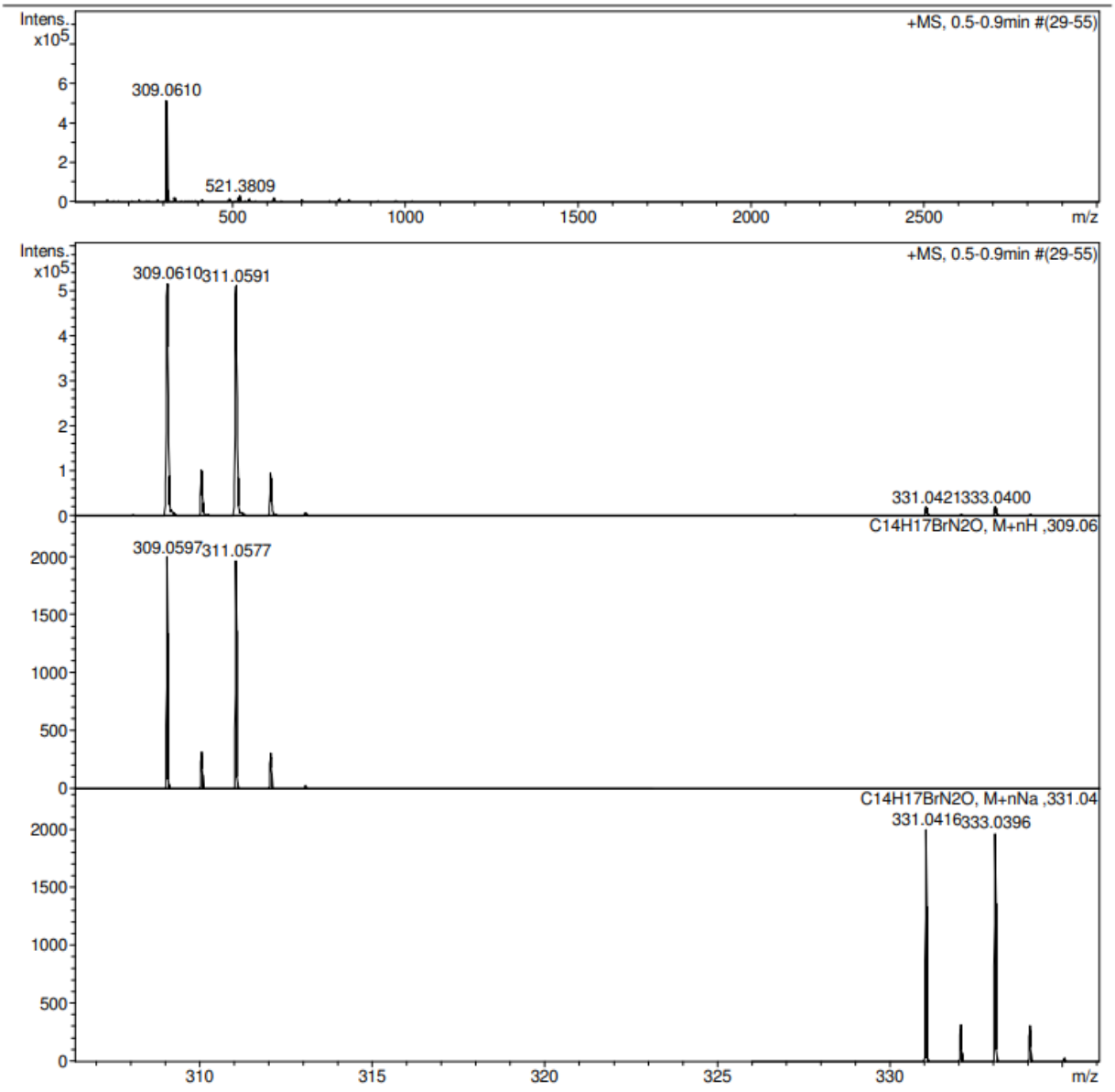
^{13}C {^{1}H} NMR spectrum (76 MHz) of **8b** in DMSO-d_6



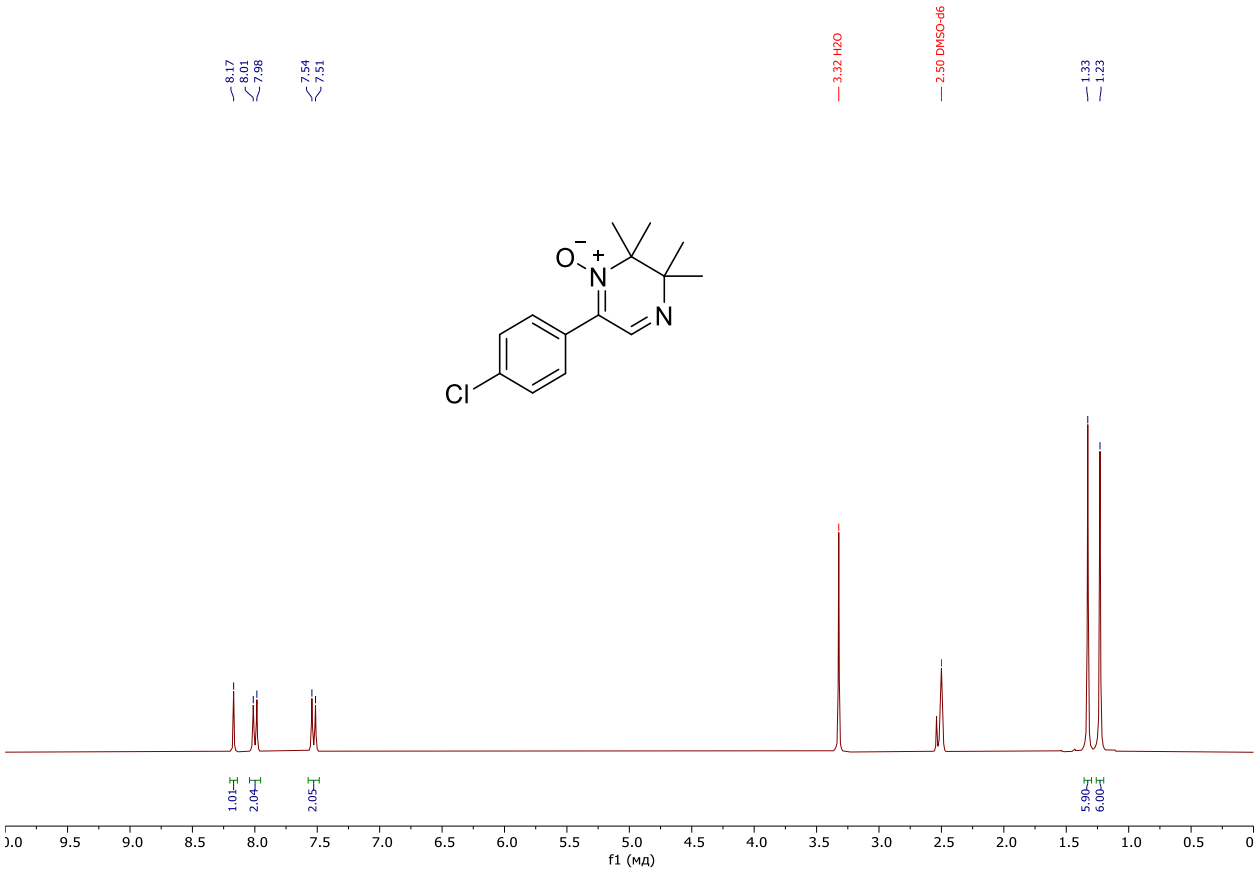
HRMS for compound **8b**

Acquisition Parameter

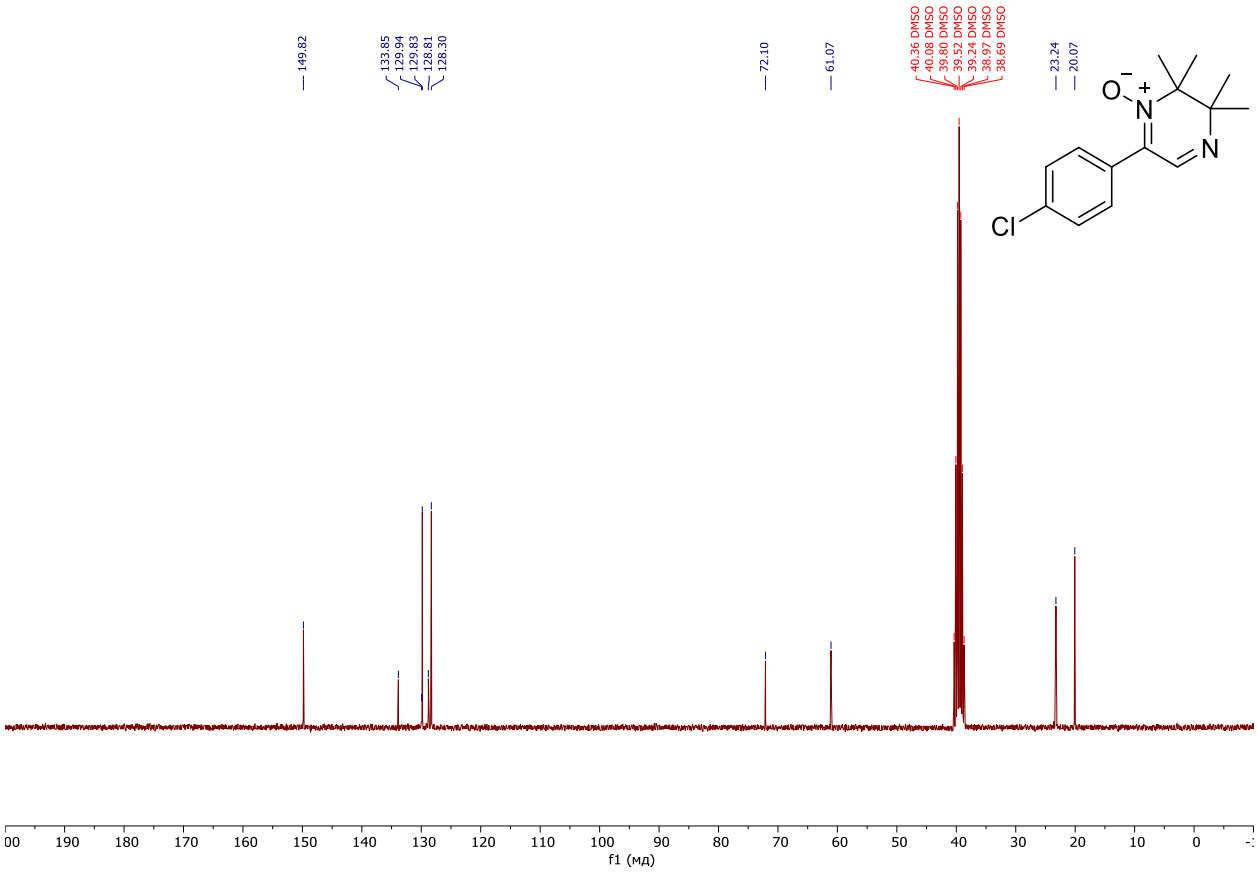
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



^{1}H NMR spectrum (300 MHz) of **8c** in DMSO-d_6



^{13}C {^{1}H} NMR spectrum (76 MHz) of **8c** in DMSO-d_6



HRMS for compound **8c**

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
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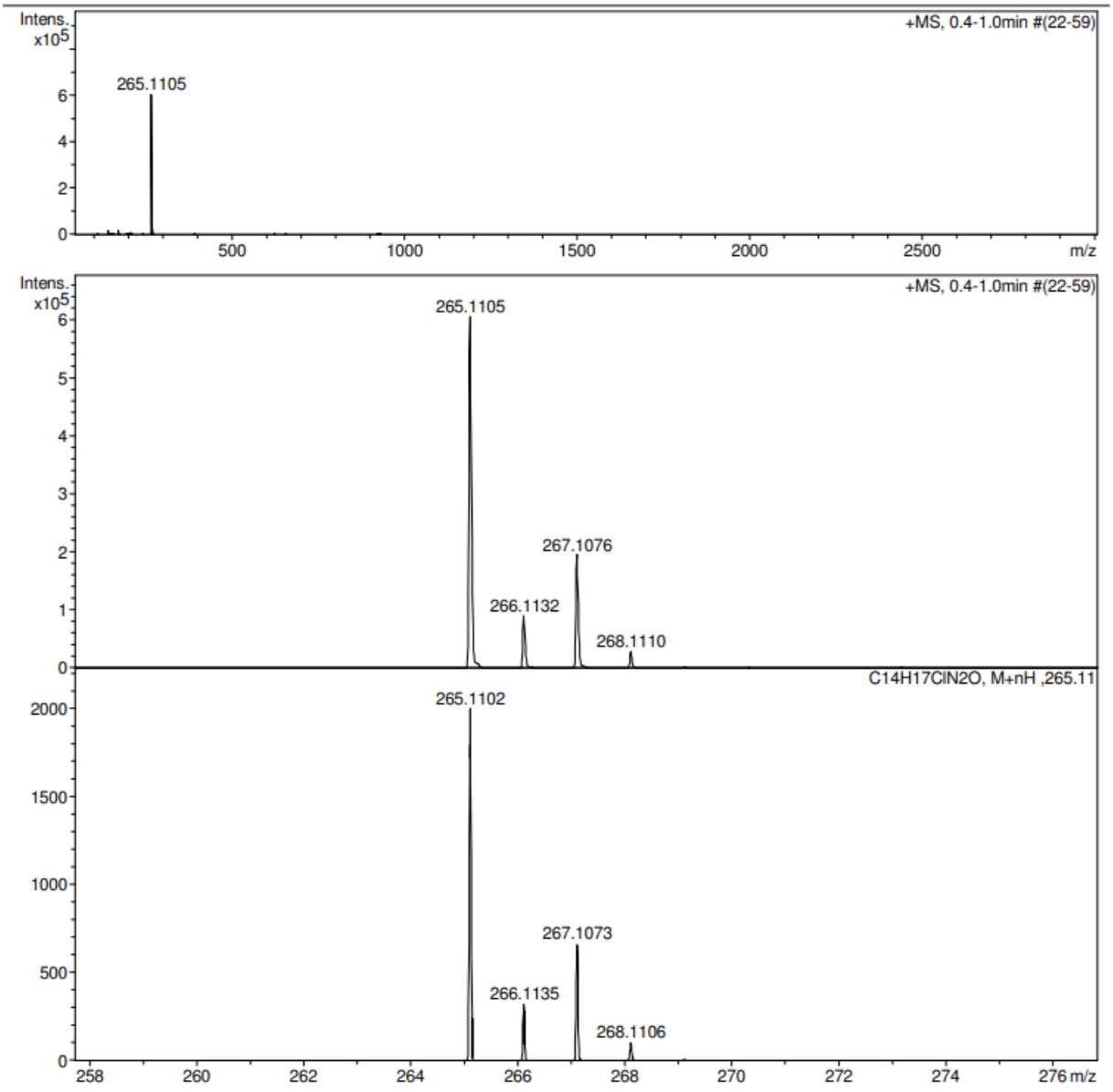
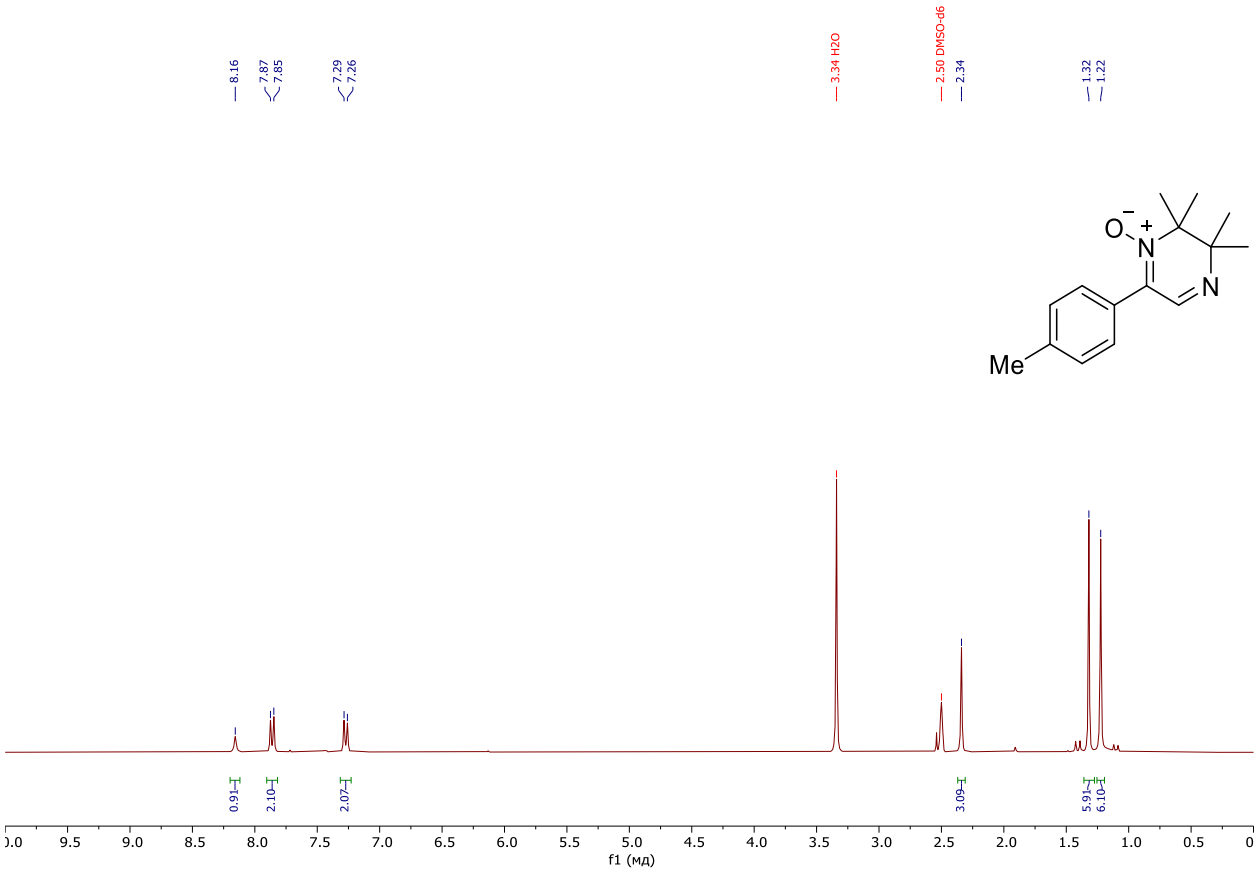
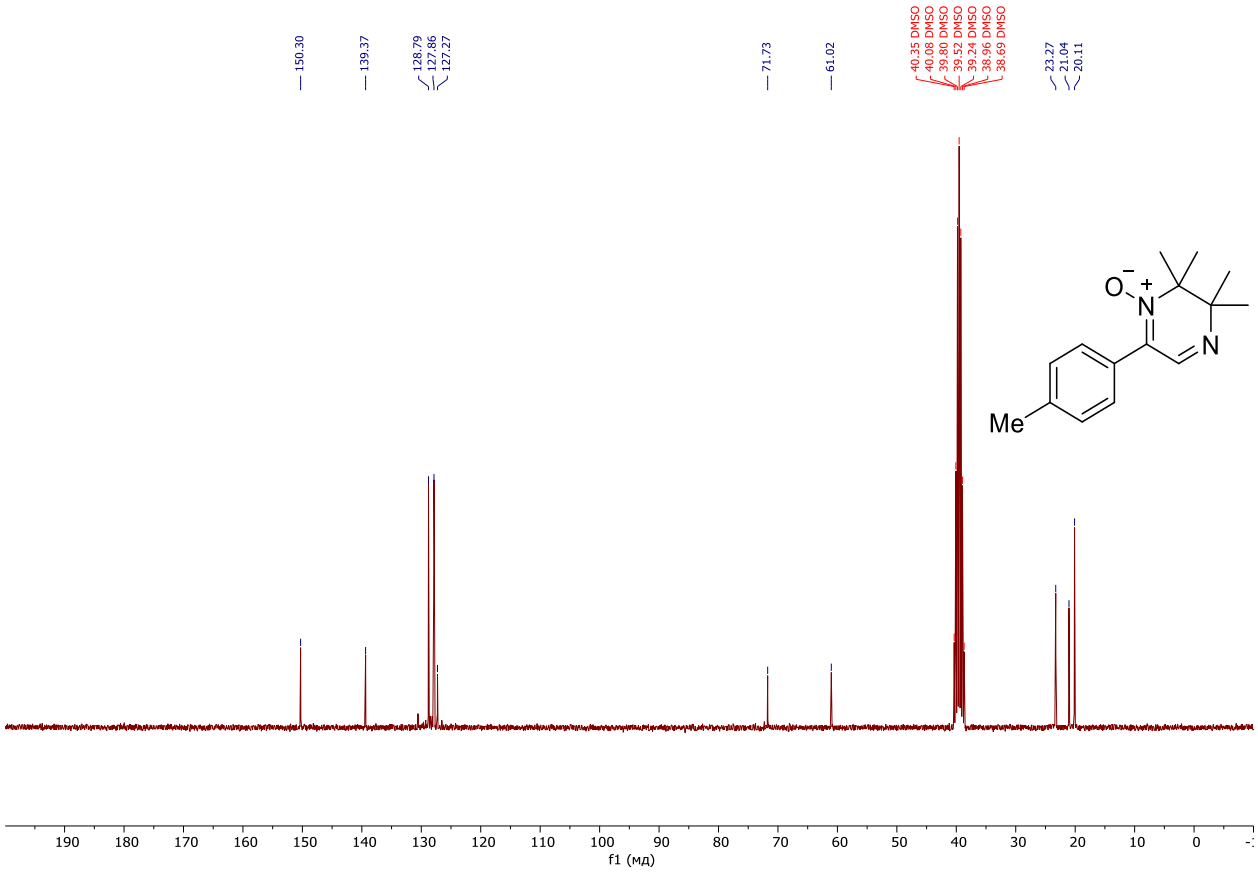
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



^{1}H NMR spectrum (300 MHz) of **8d** in DMSO-d_6



^{13}C {^{1}H} NMR spectrum (76 MHz) of **8d** in DMSO-d_6



HRMS for compound **8d**

Acquisition Parameter

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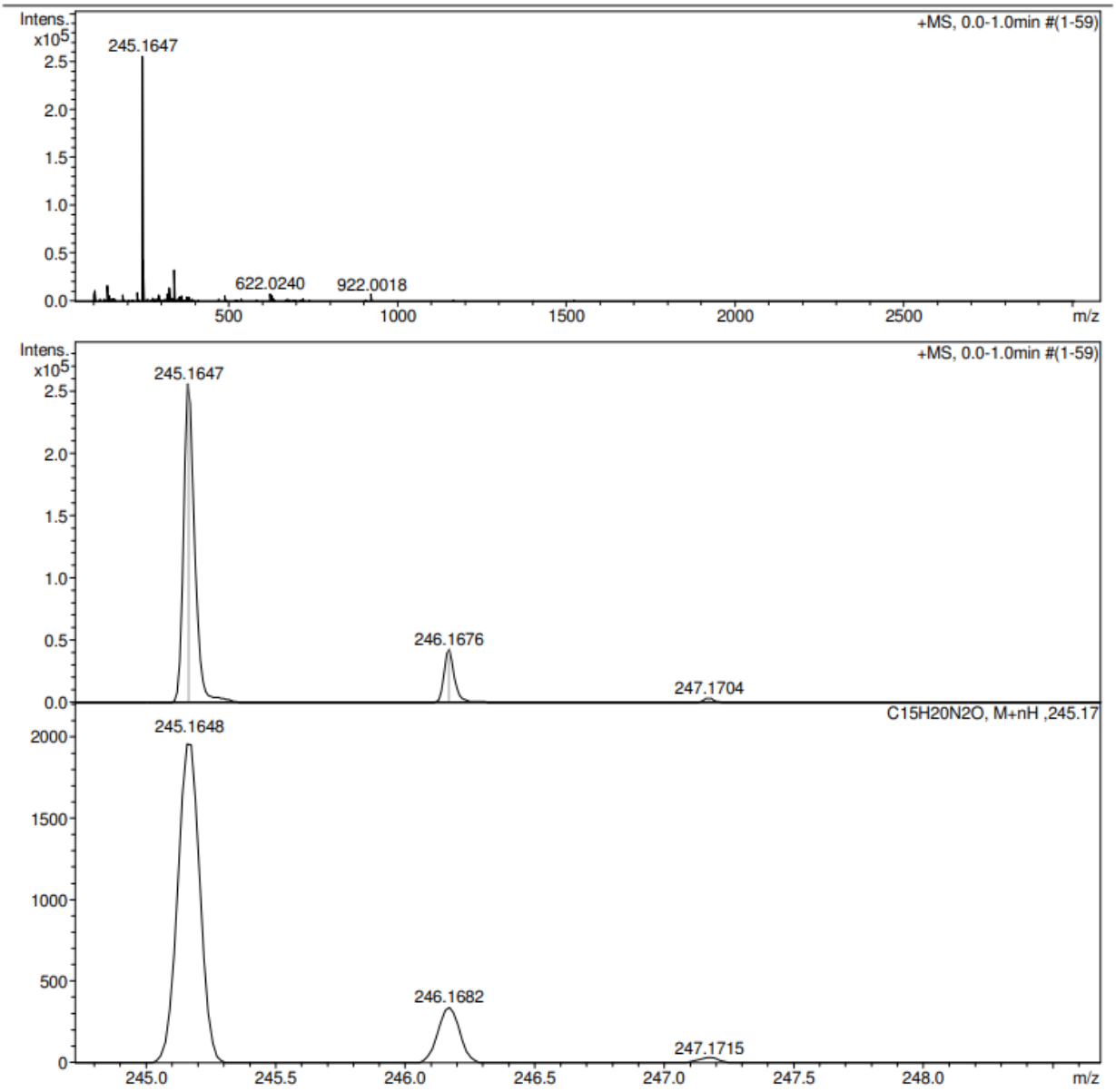
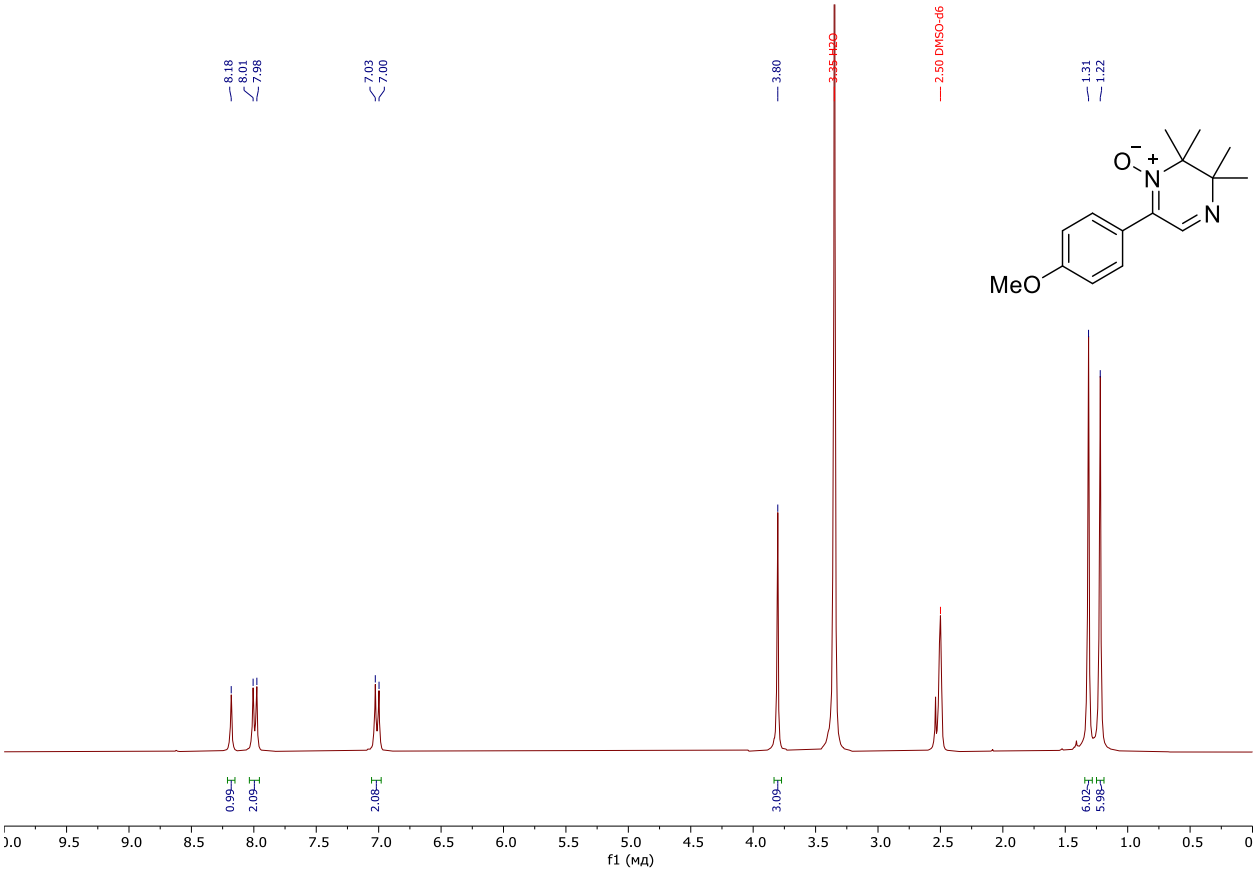
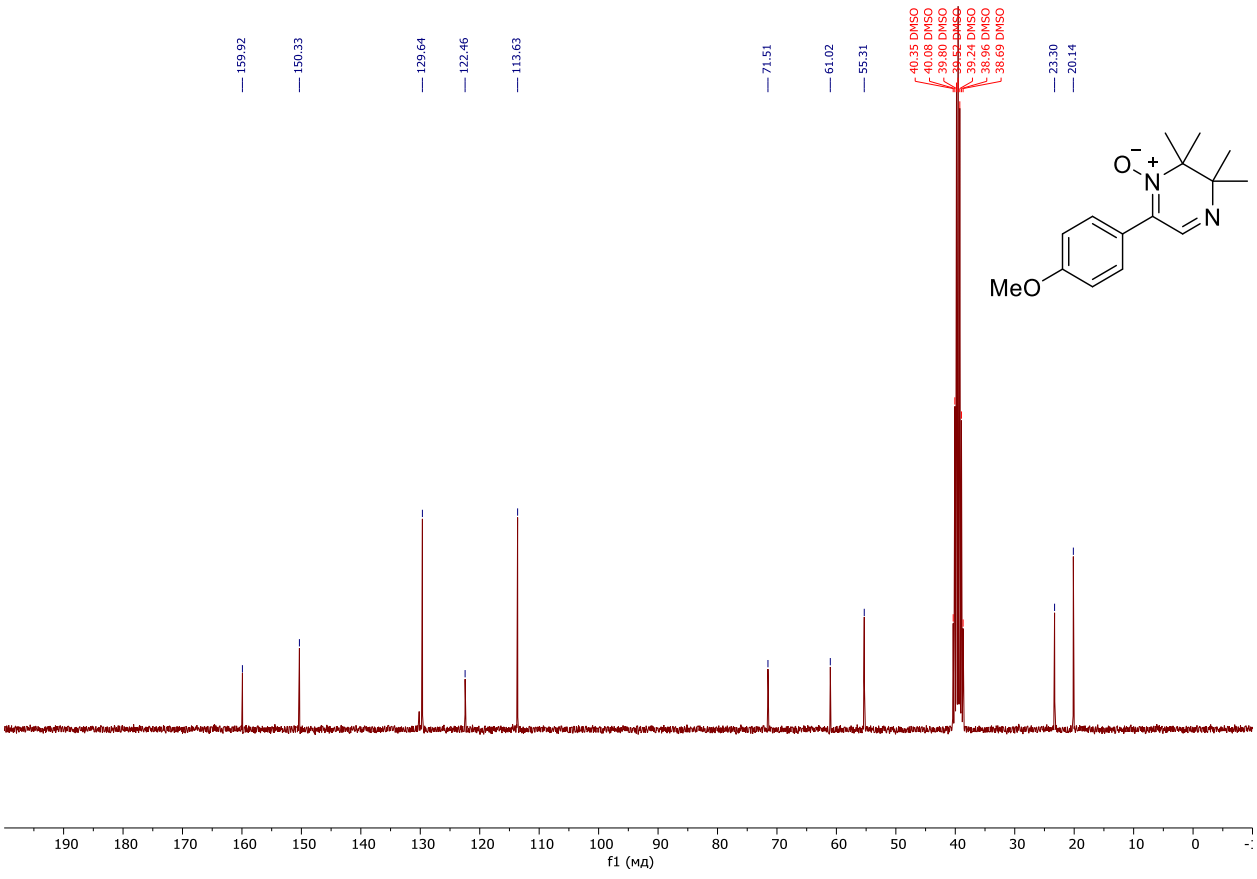


^{1}H NMR spectrum (300 MHz) of **8e** in DMSO-d_6



^{13}C {^{1}H} NMR spectrum (76 MHz) of **8e** in DMSO-d_6



HRMS for compound **8e**

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
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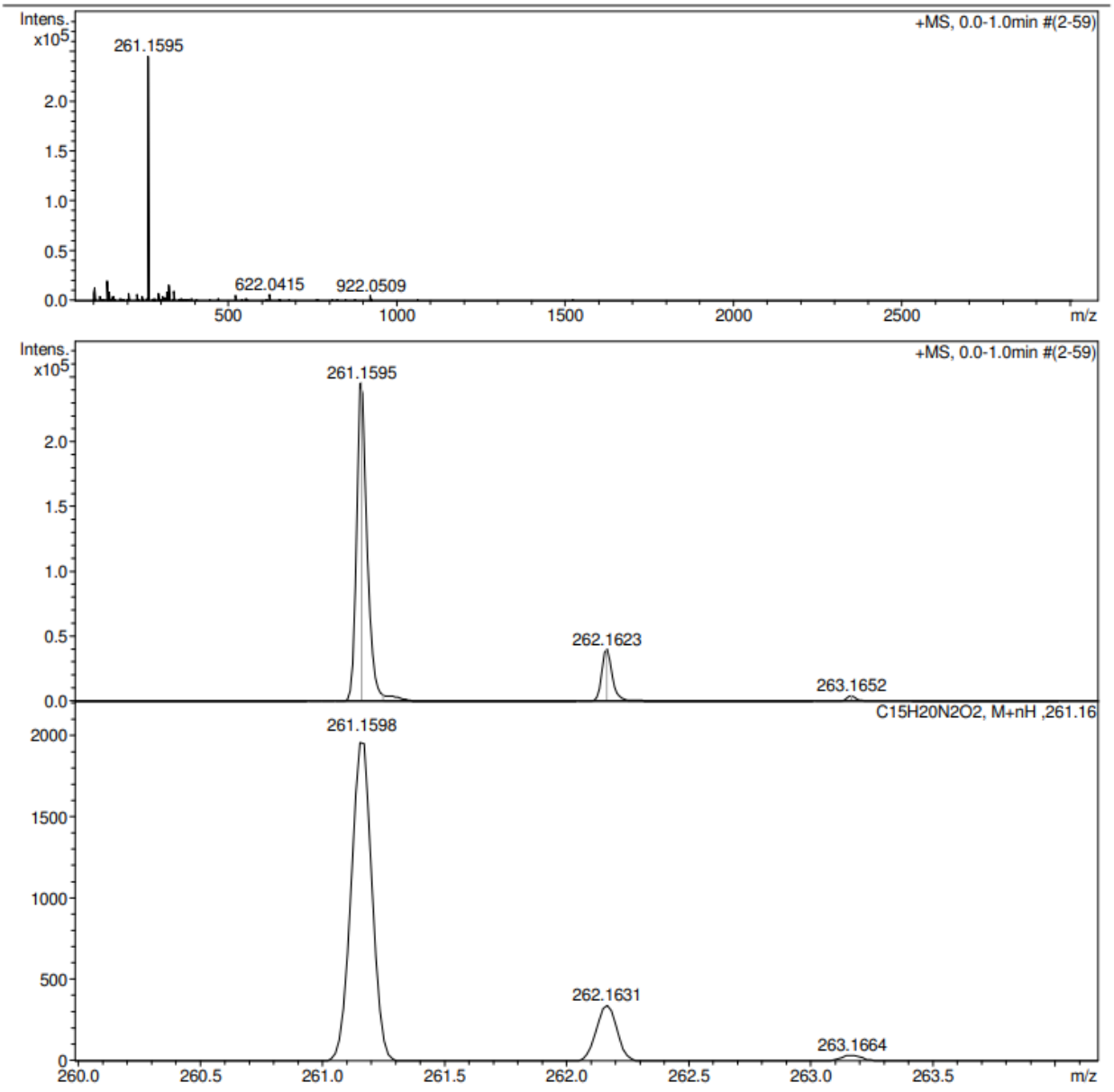
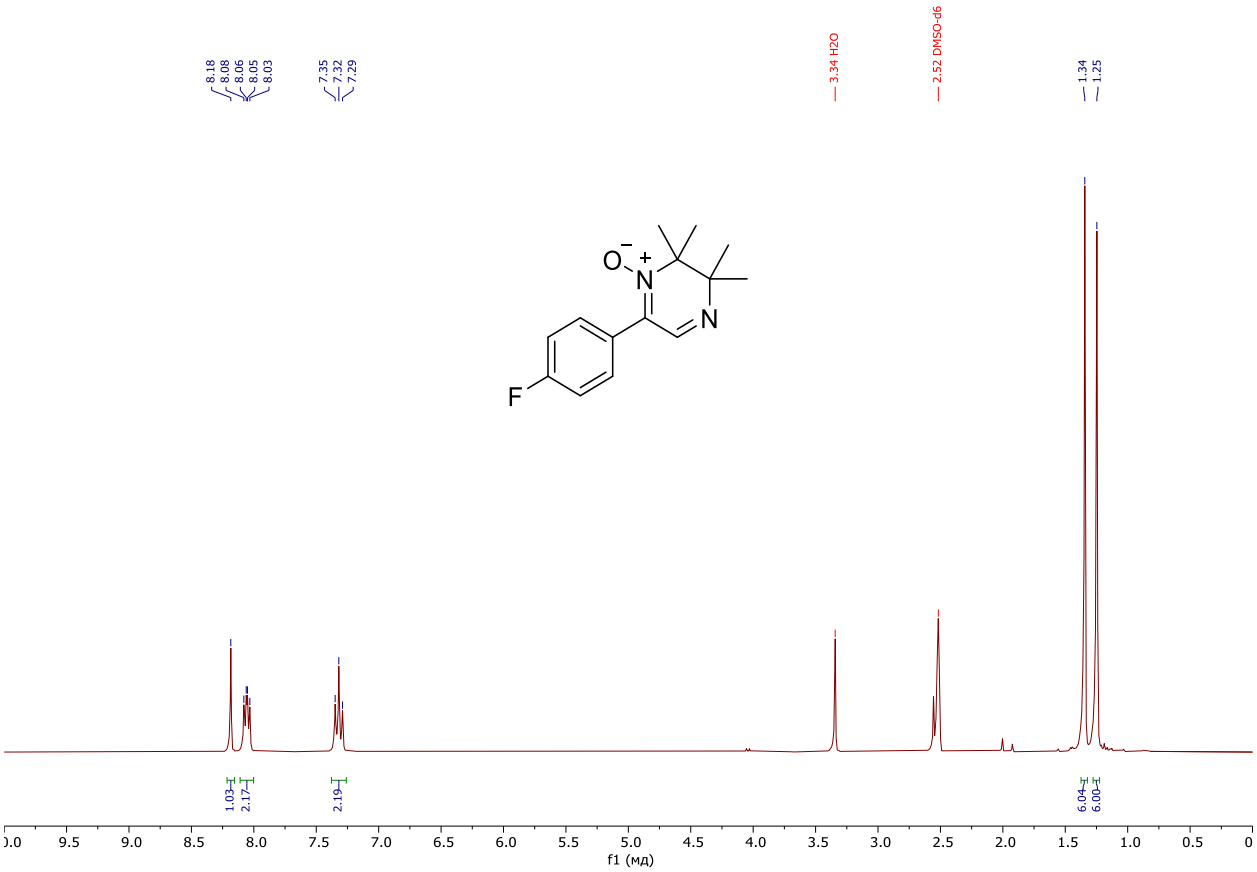
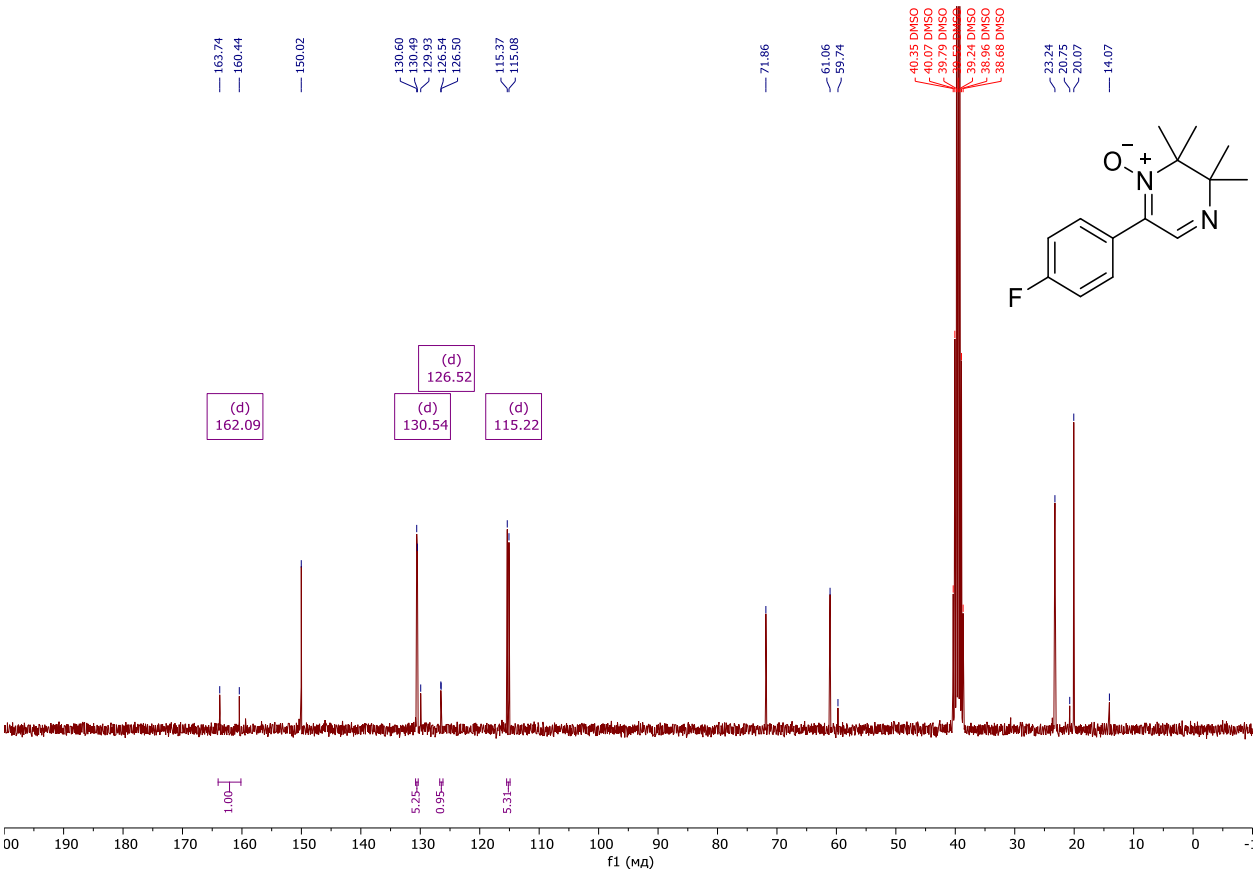
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



^{1}H NMR spectrum (300 MHz) of **8f** in DMSO-d_6



^{13}C {^{1}H} NMR spectrum (76 MHz) of **8f** in DMSO-d_6



HRMS for compound **8f**

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
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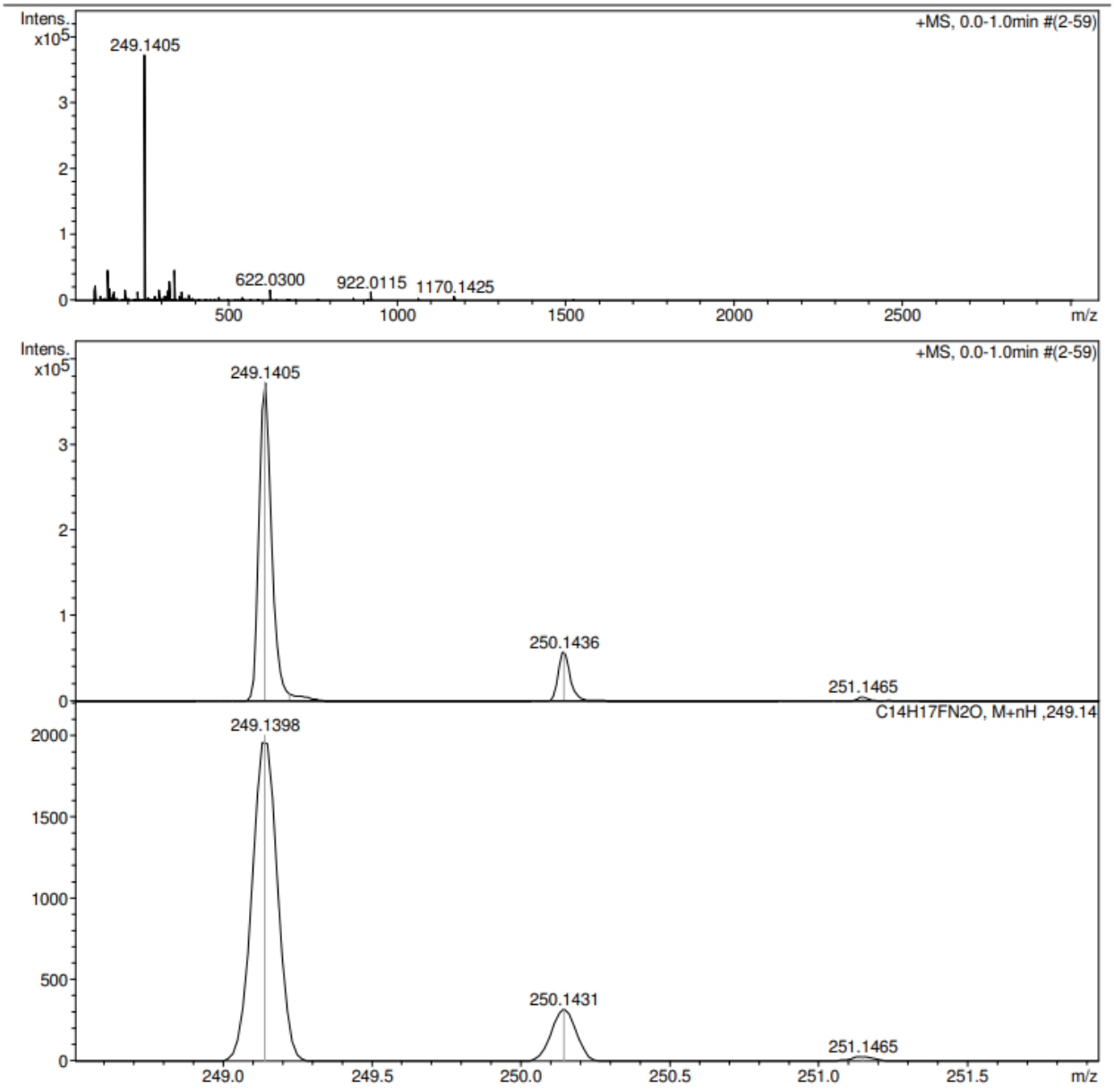
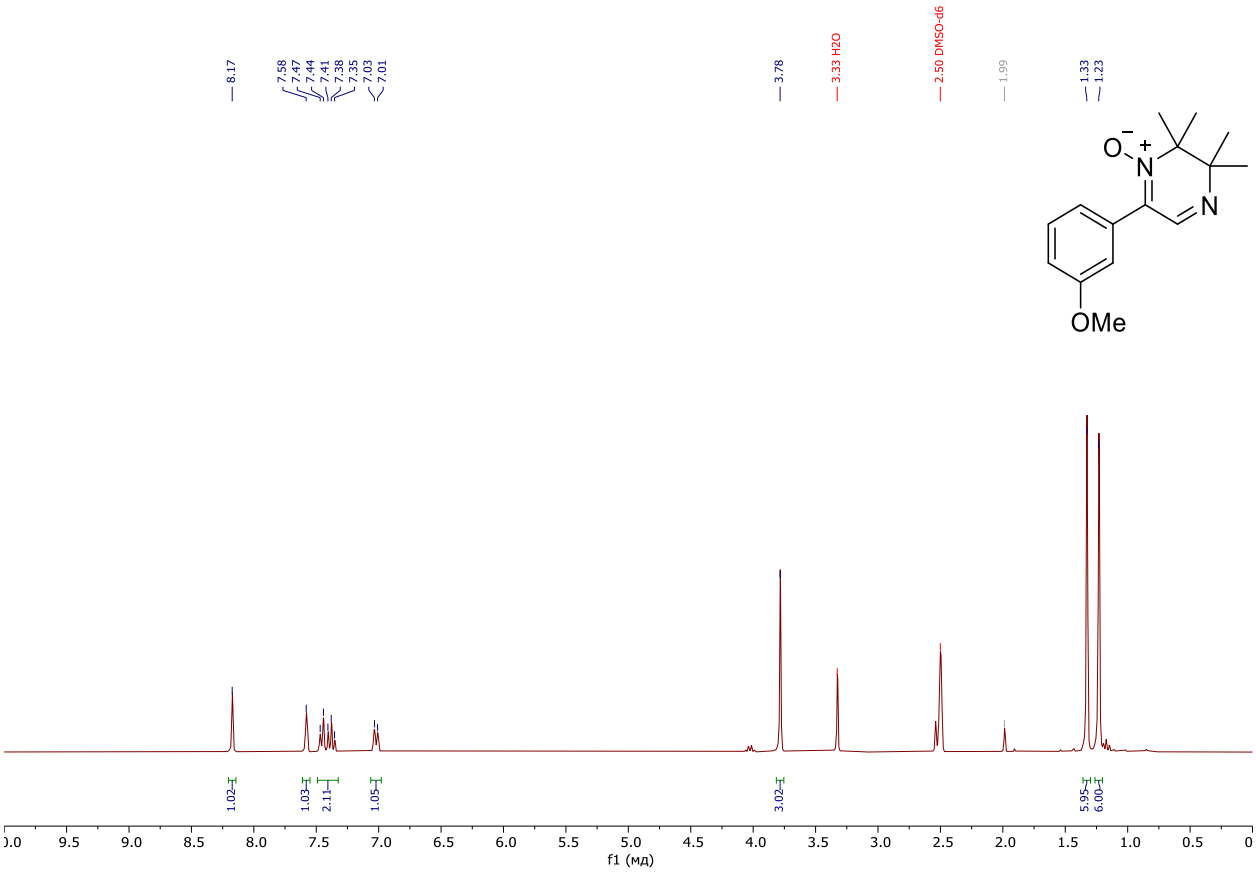
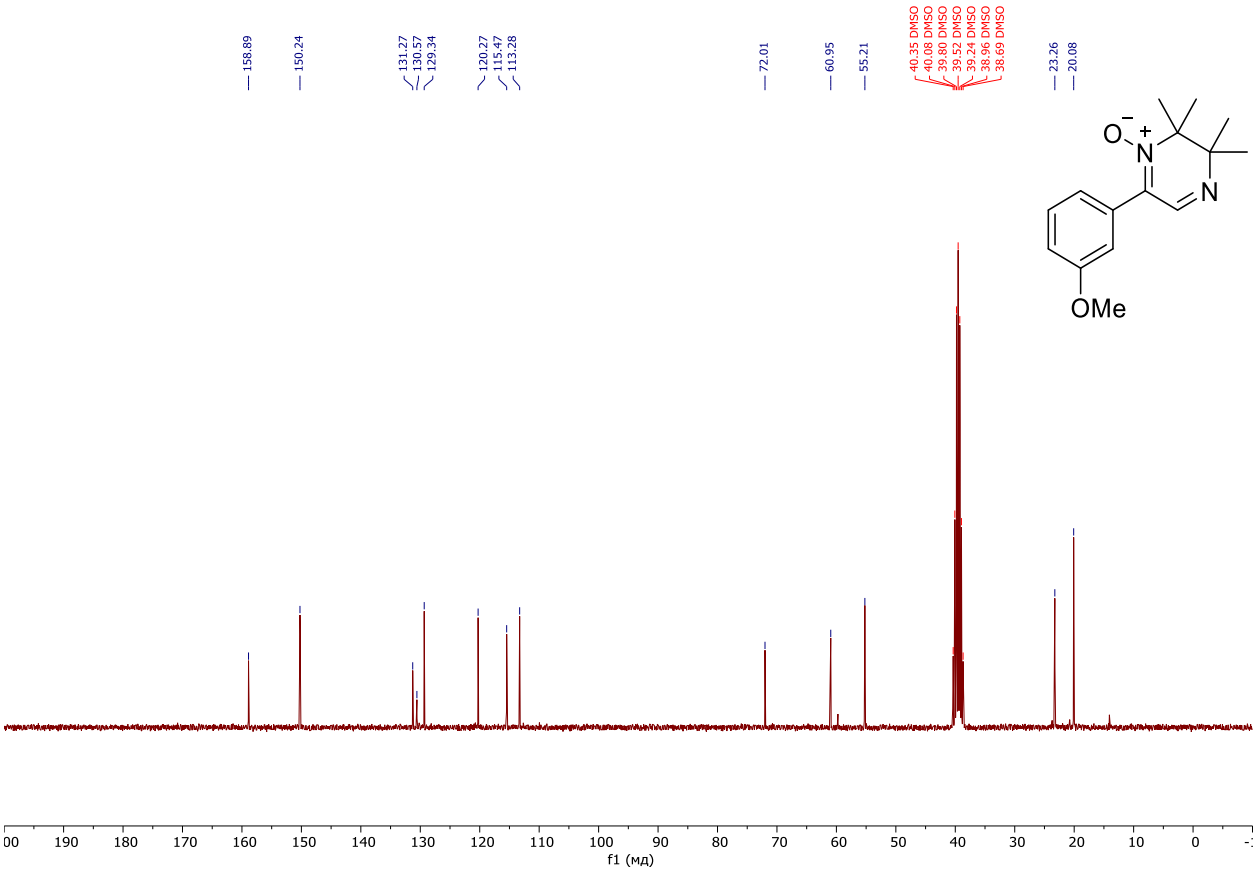
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



^{1}H NMR spectrum (300 MHz) of **8g** in DMSO-d_6



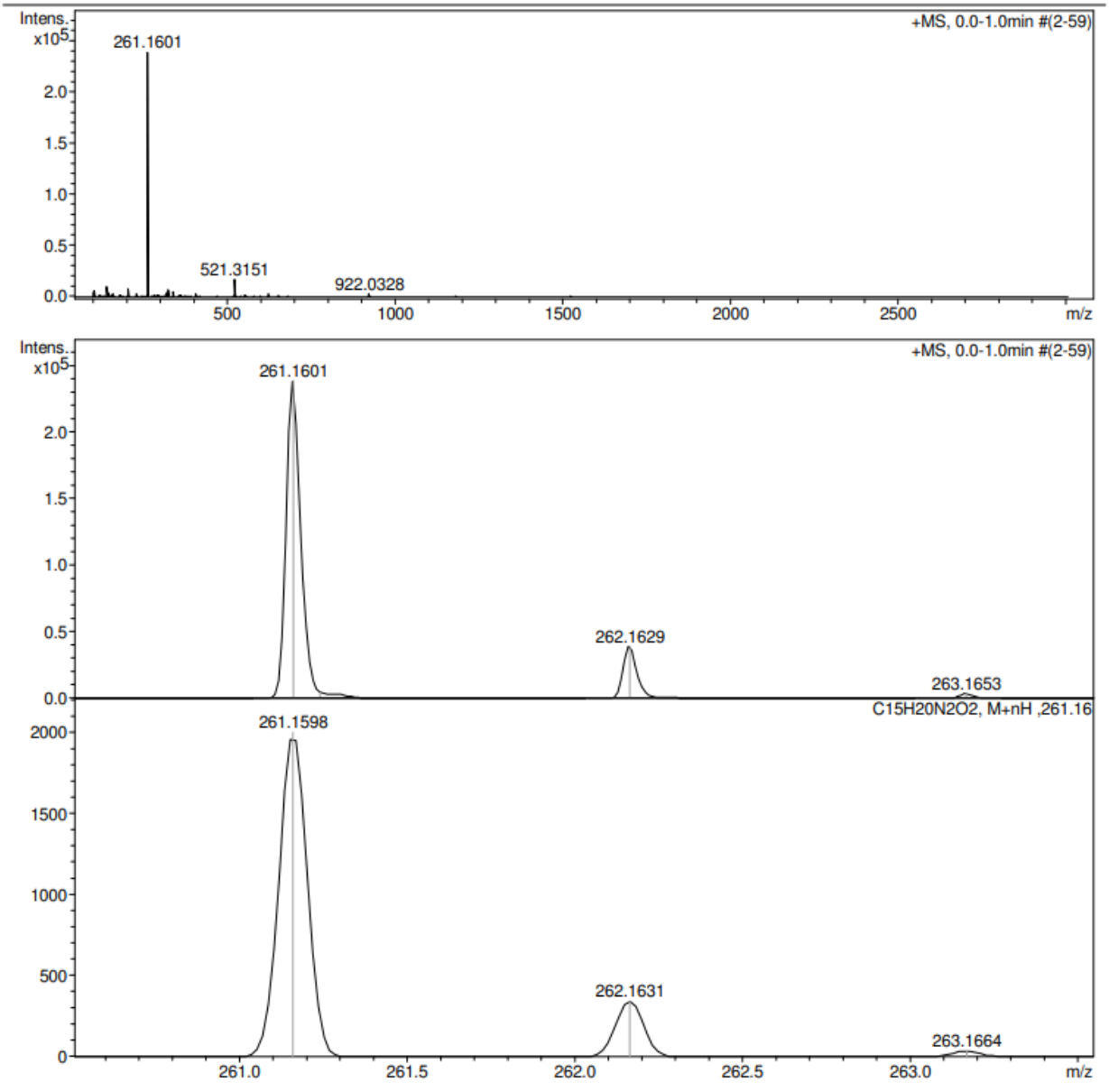
^{13}C {^{1}H} NMR spectrum (76 MHz) of **8g** in DMSO-d_6



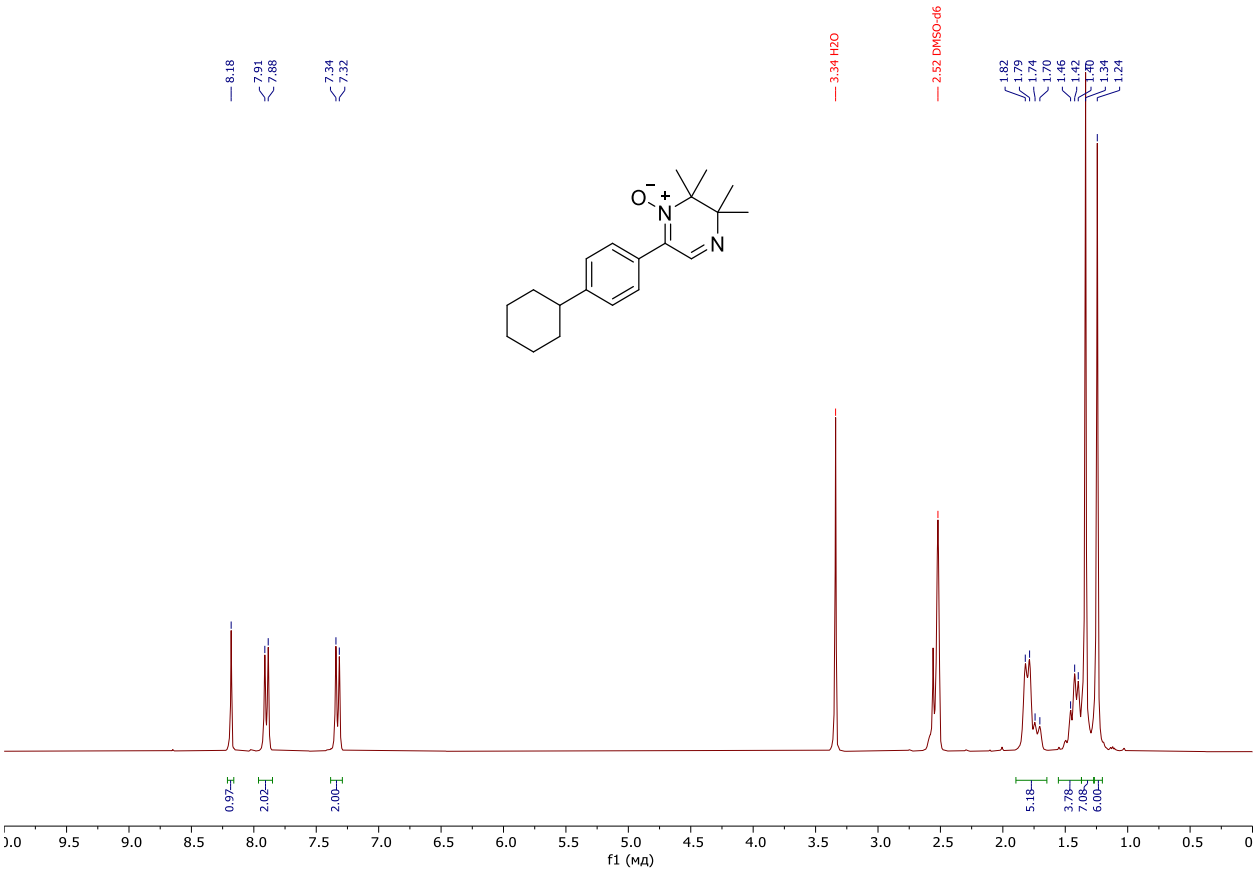
HRMS for compound **8g**

Acquisition Parameter

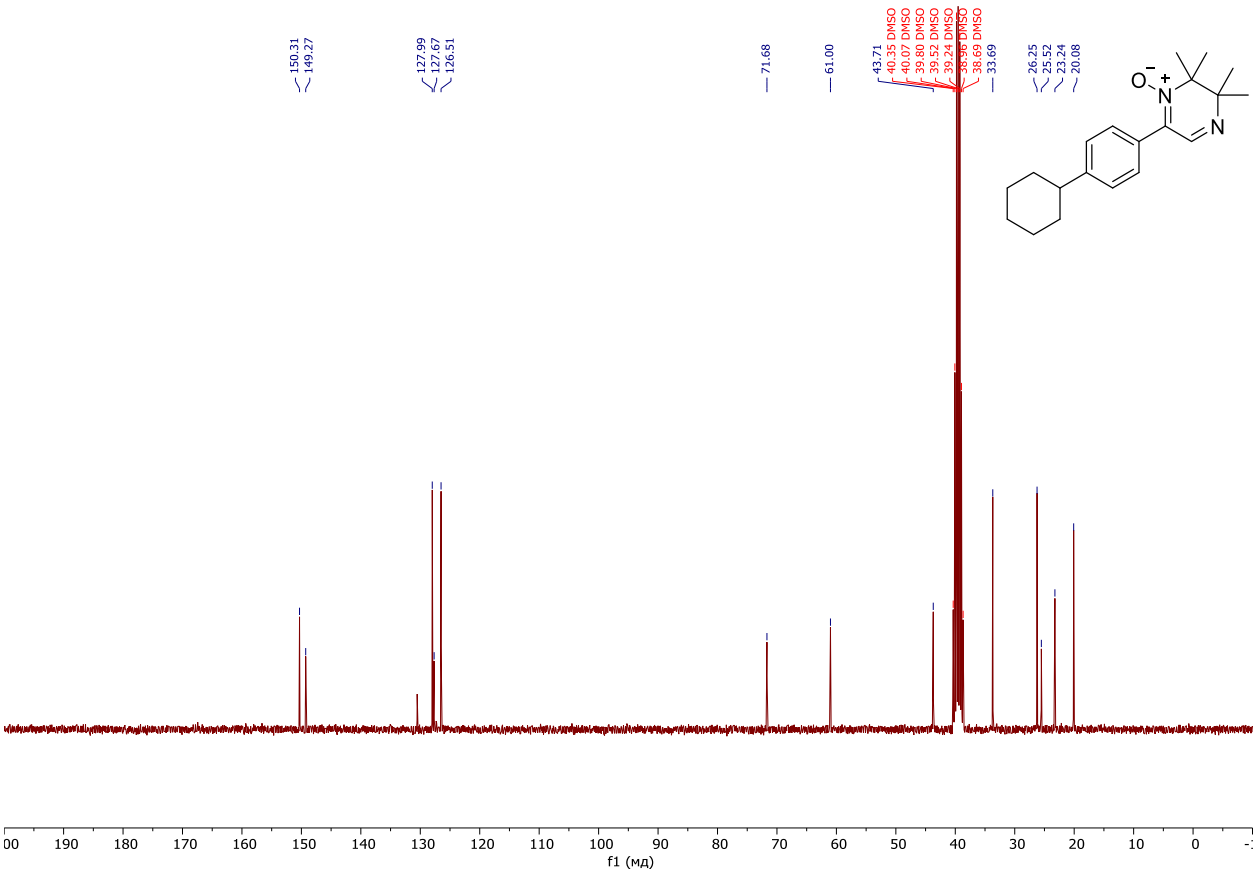
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



^{1}H NMR spectrum (300 MHz) of **8h** in DMSO-d_6



^{13}C {^{1}H} NMR spectrum (76 MHz) of **8h** in DMSO-d_6



HRMS for compound **8h**

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
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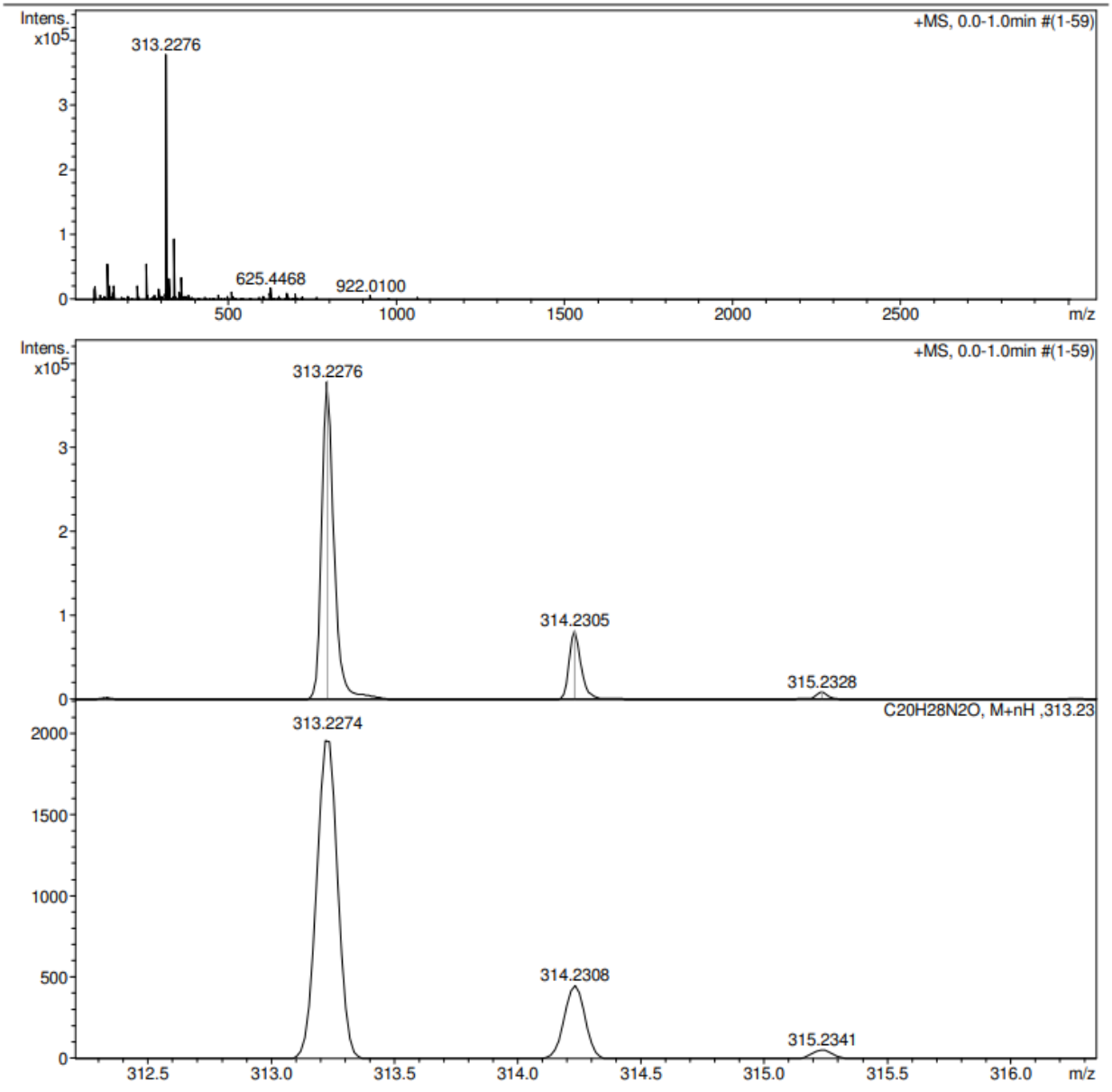
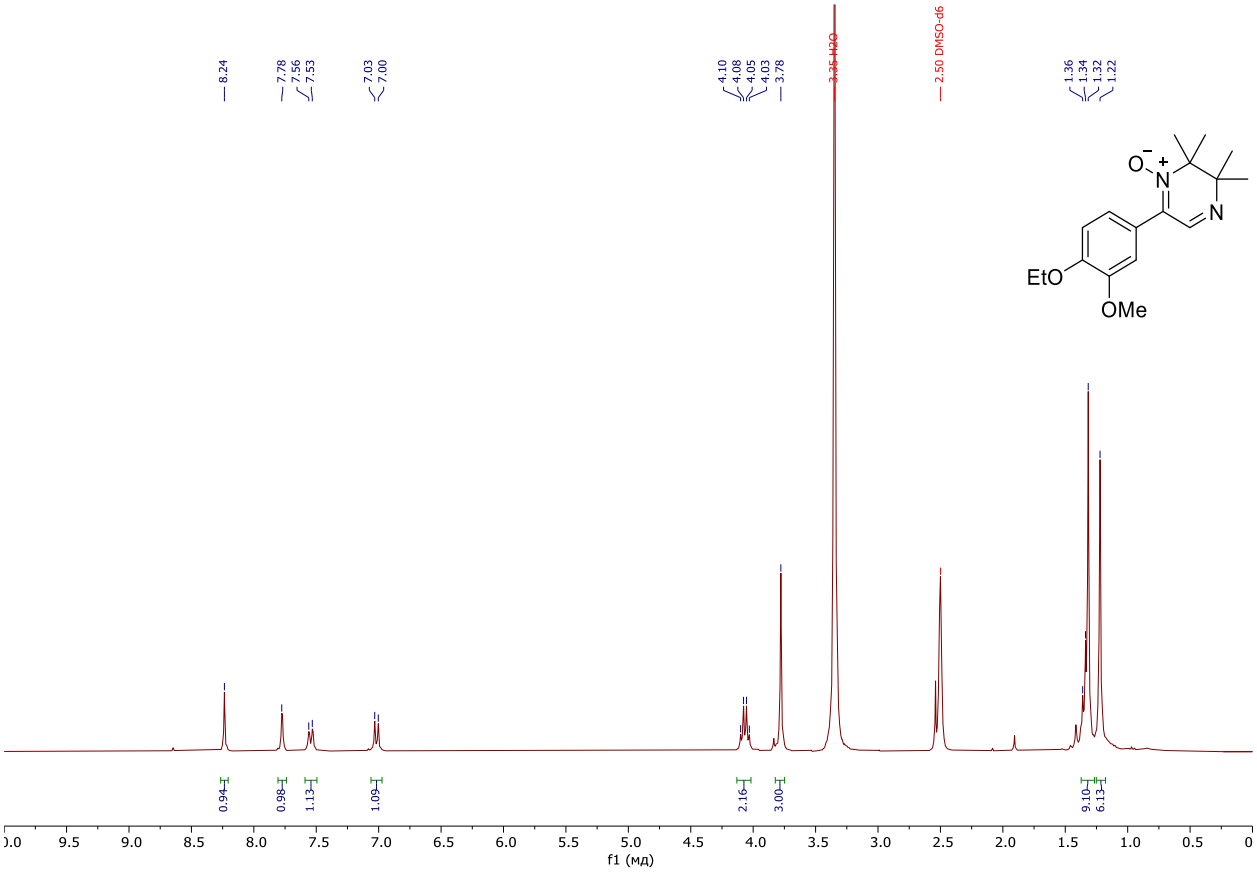
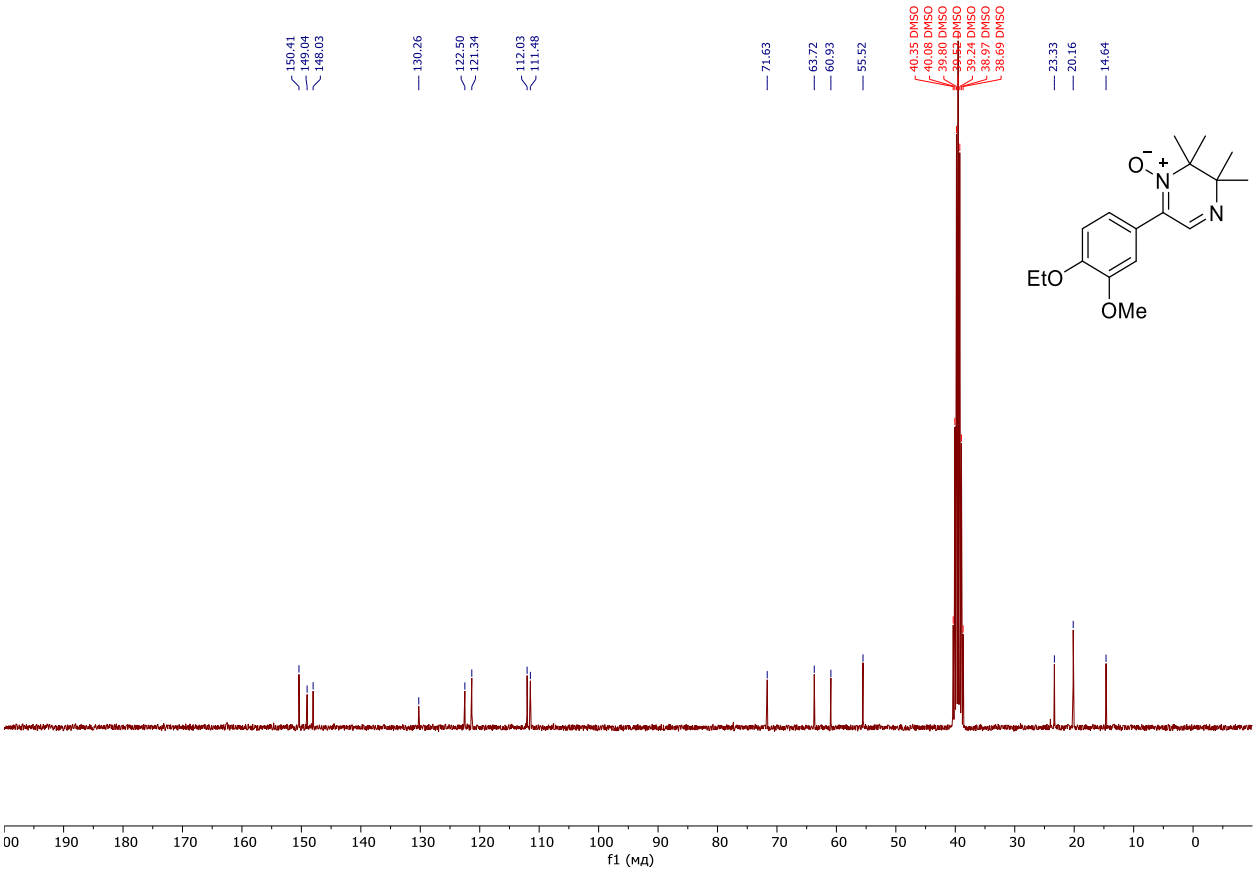


^{1}H NMR spectrum (300 MHz) of **8i** in DMSO-d_6



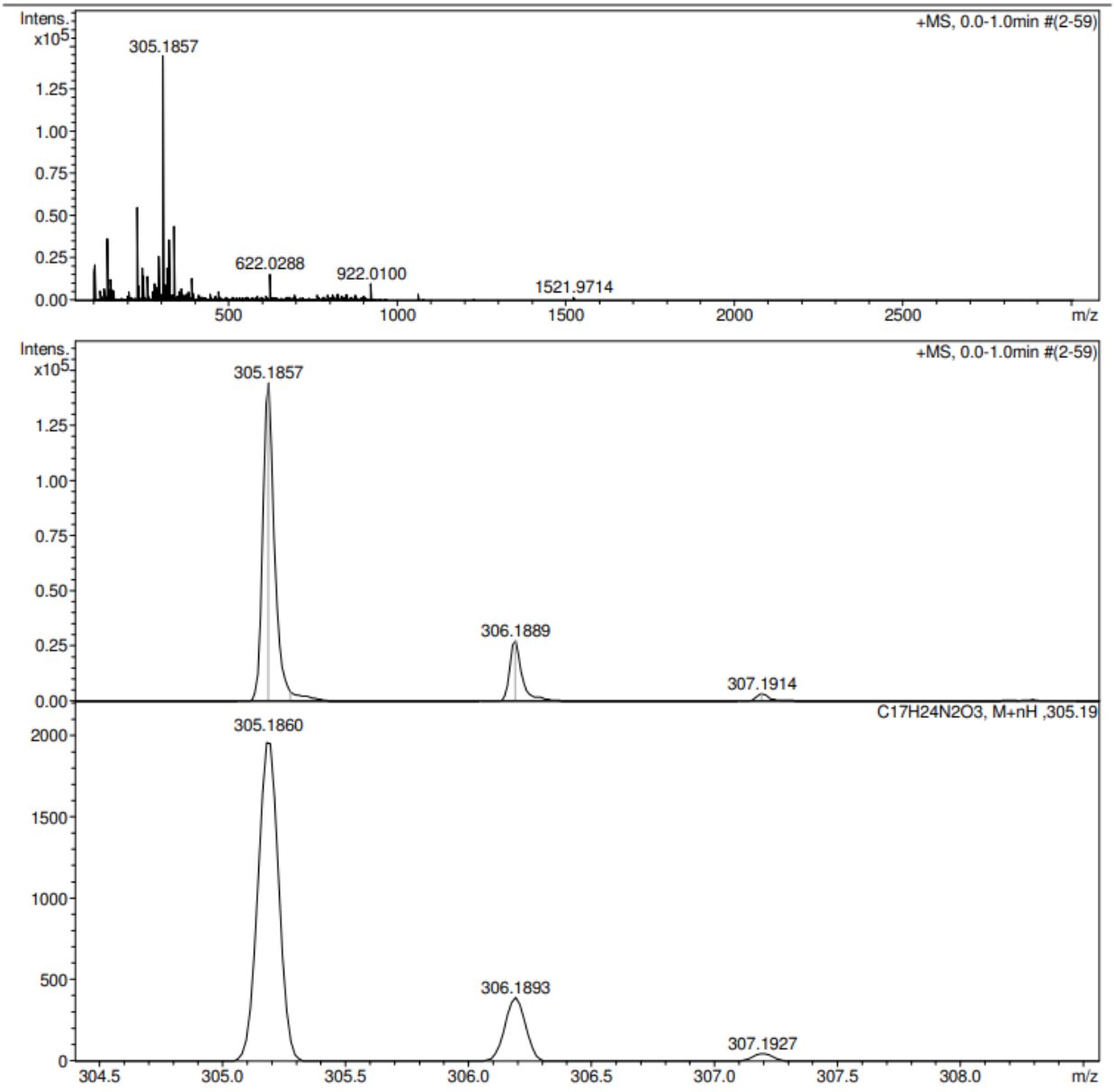
^{13}C {^{1}H} NMR spectrum (76 MHz) of **8i** in DMSO-d_6



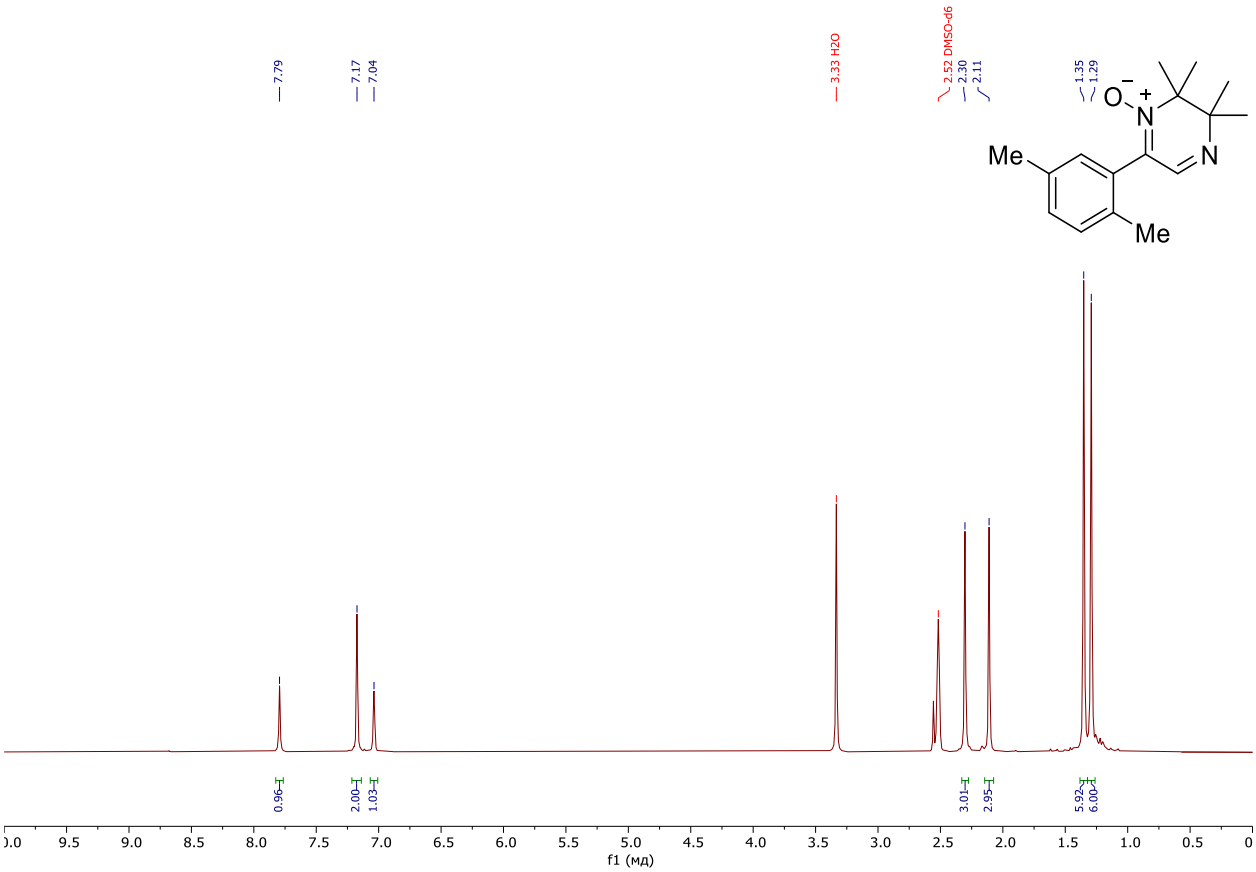
HRMS for compound **8i**

Acquisition Parameter

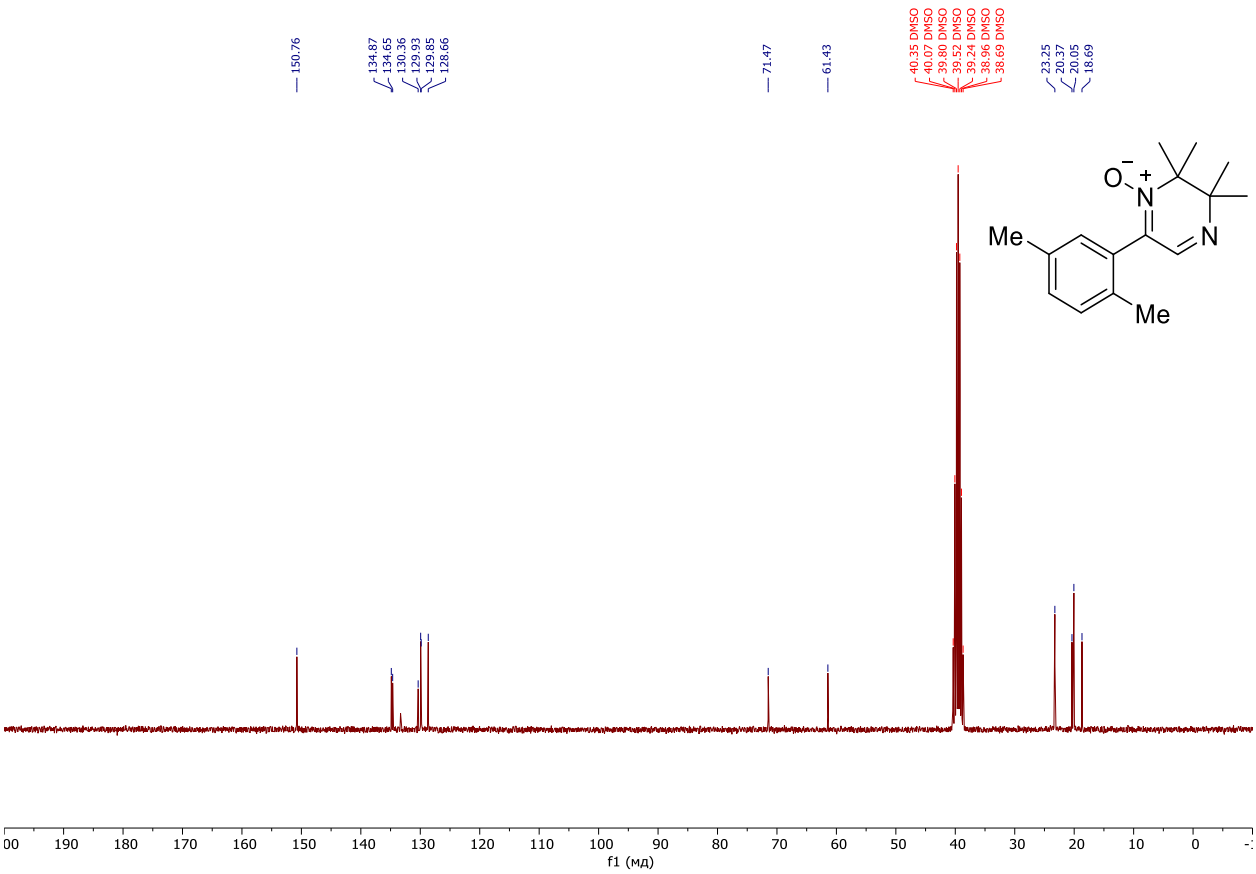
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



^{1}H NMR spectrum (300 MHz) of **8j** in DMSO-d_6



^{13}C {^{1}H} NMR spectrum (76 MHz) of **8j** in DMSO-d_6



HRMS for compound **8j**

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
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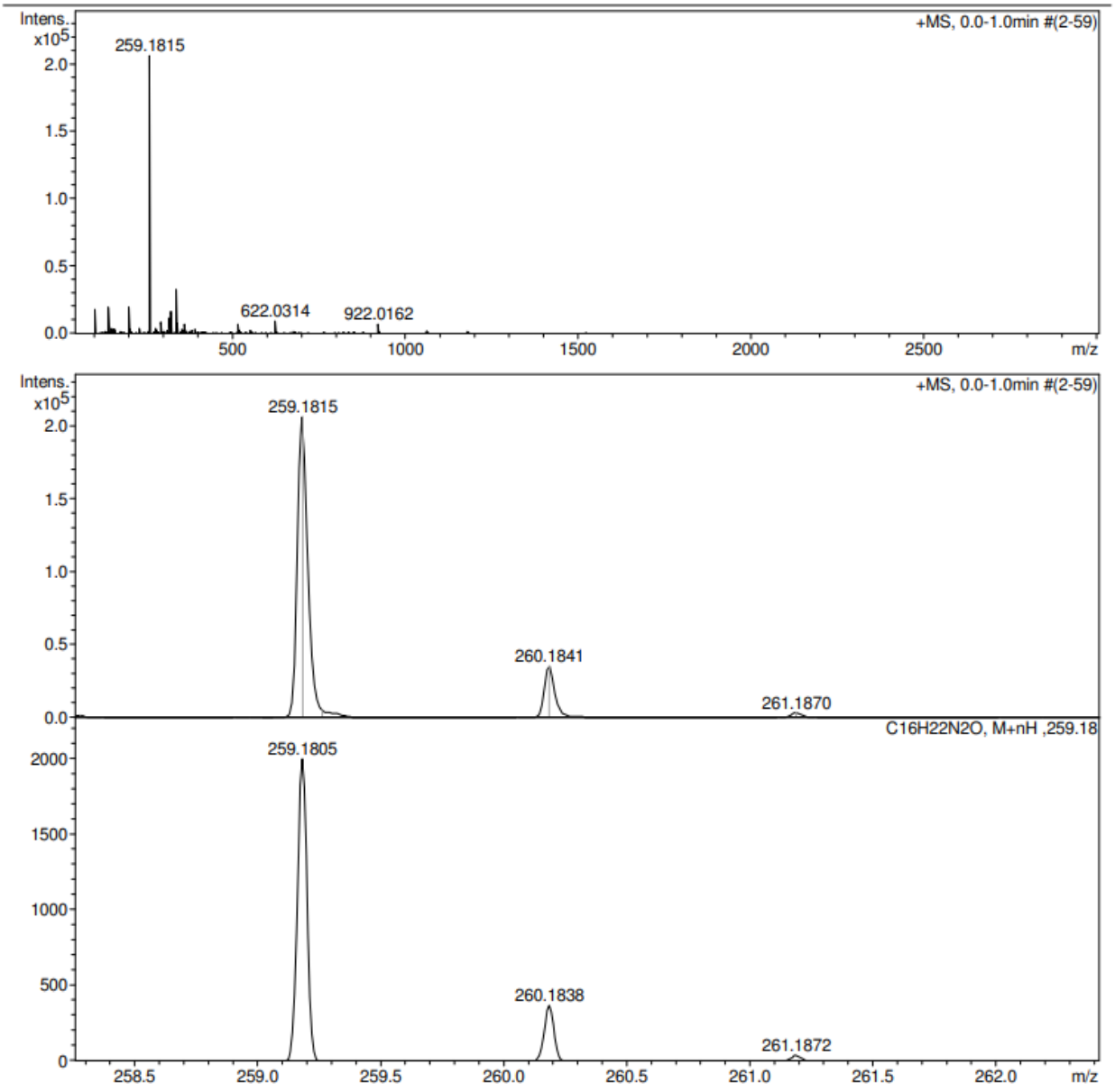
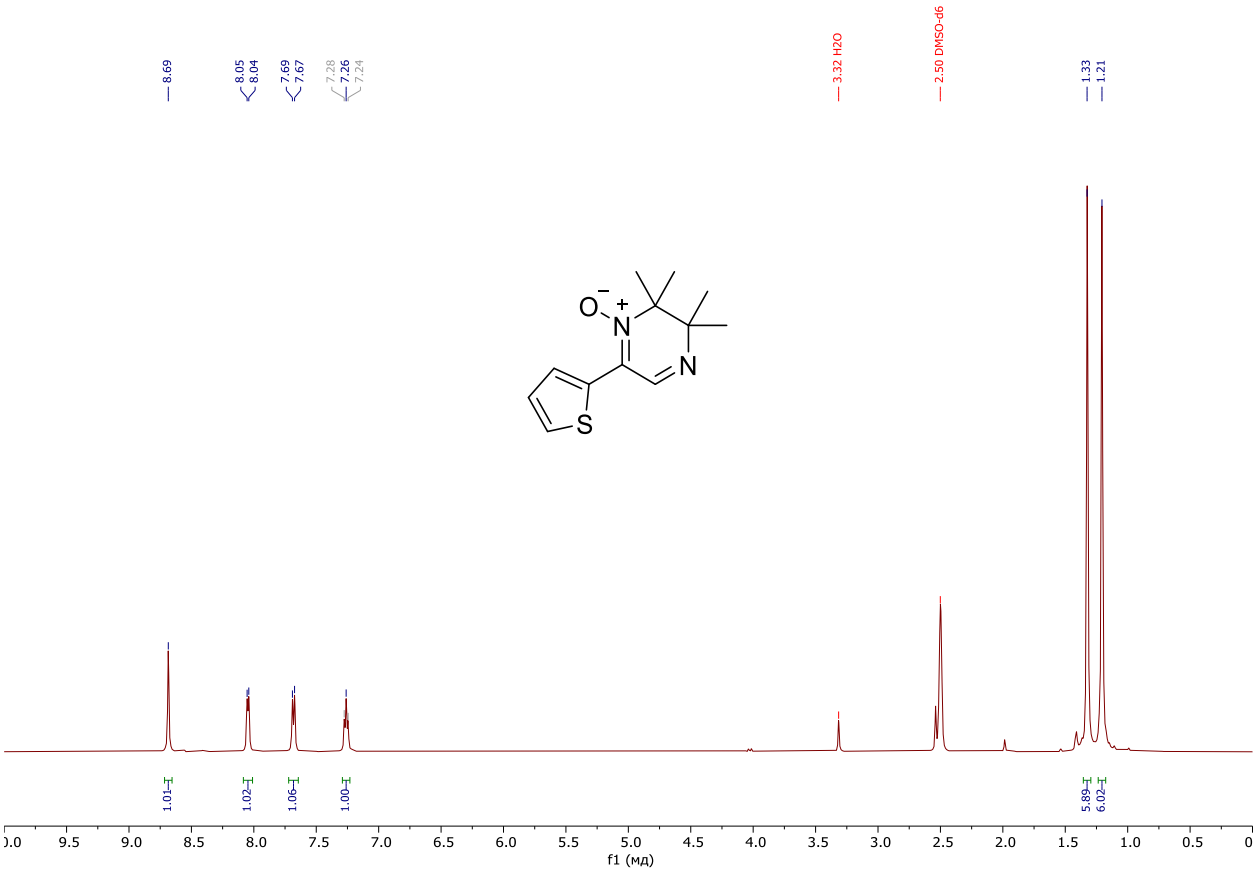
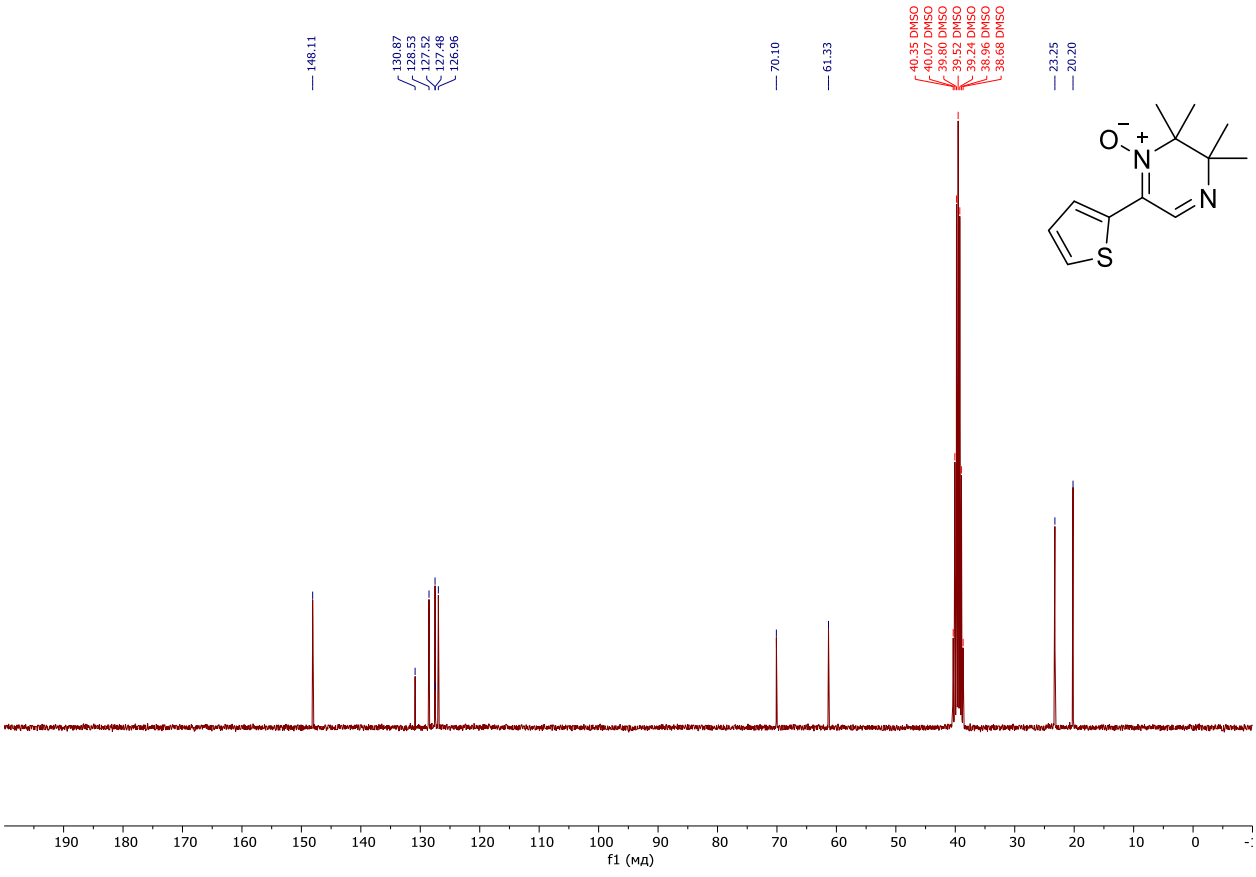
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



^{1}H NMR spectrum (300 MHz) of **8k** in DMSO-d_6



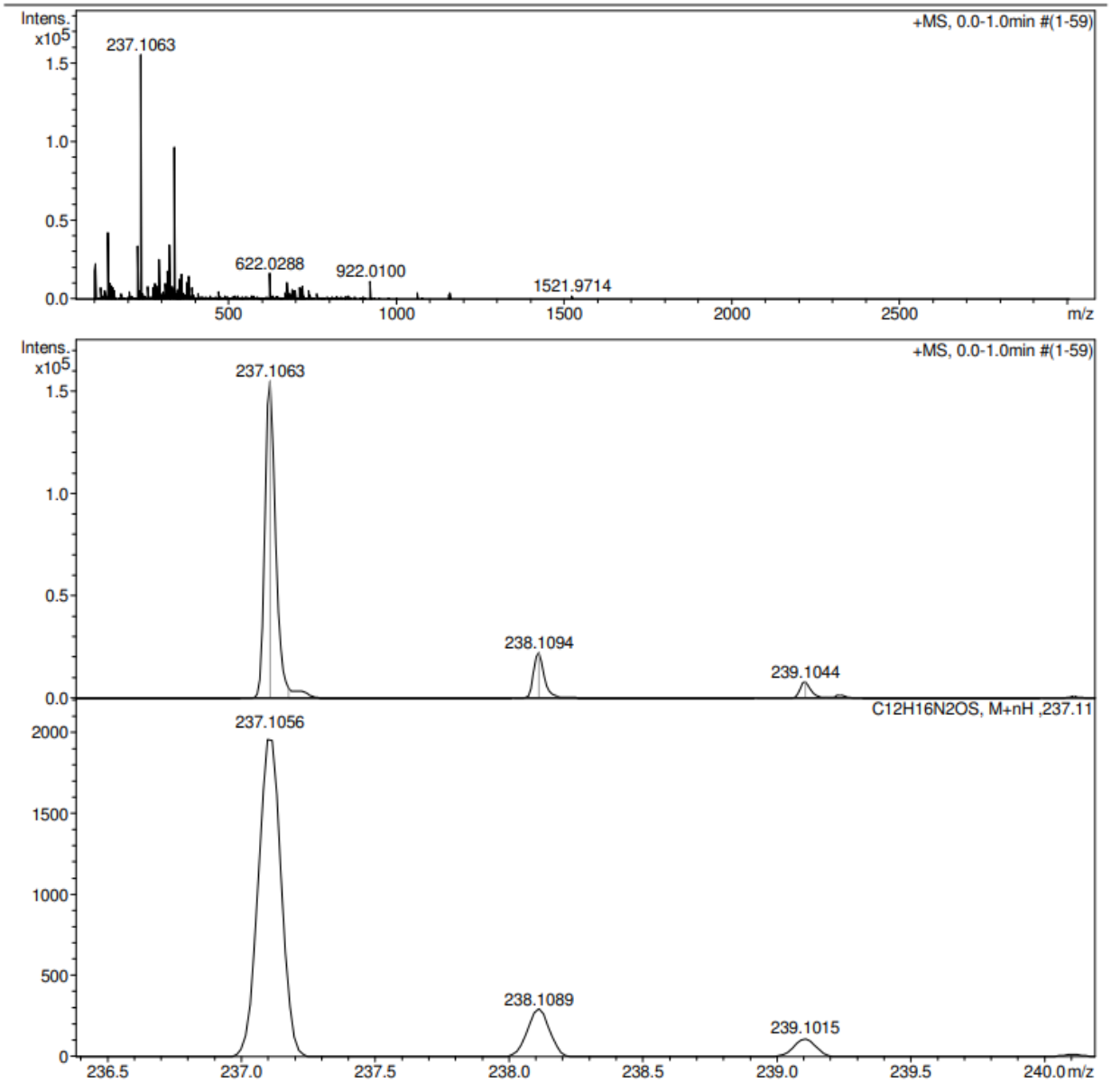
^{13}C {^{1}H} NMR spectrum (76 MHz) of **8k** in DMSO-d_6



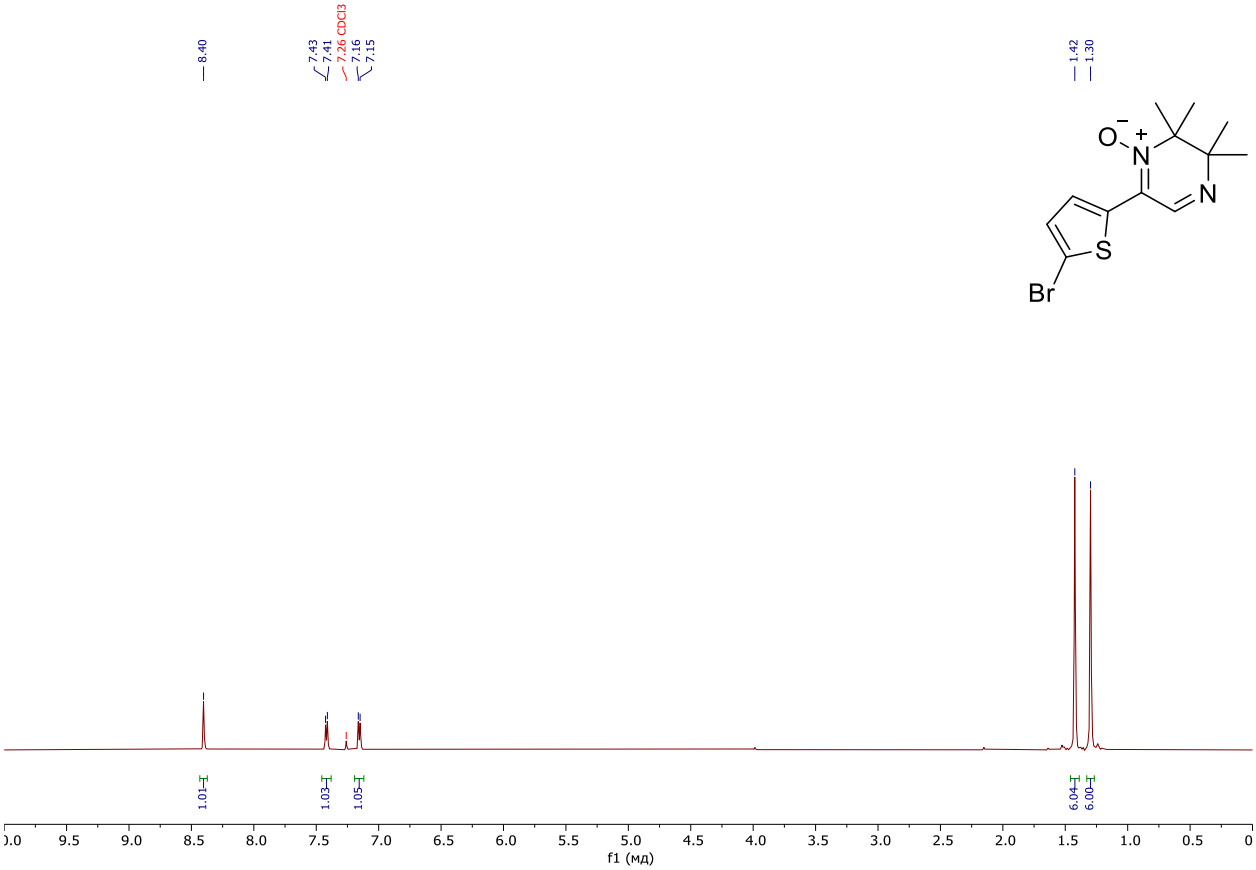
HRMS for compound **8k**

Acquisition Parameter

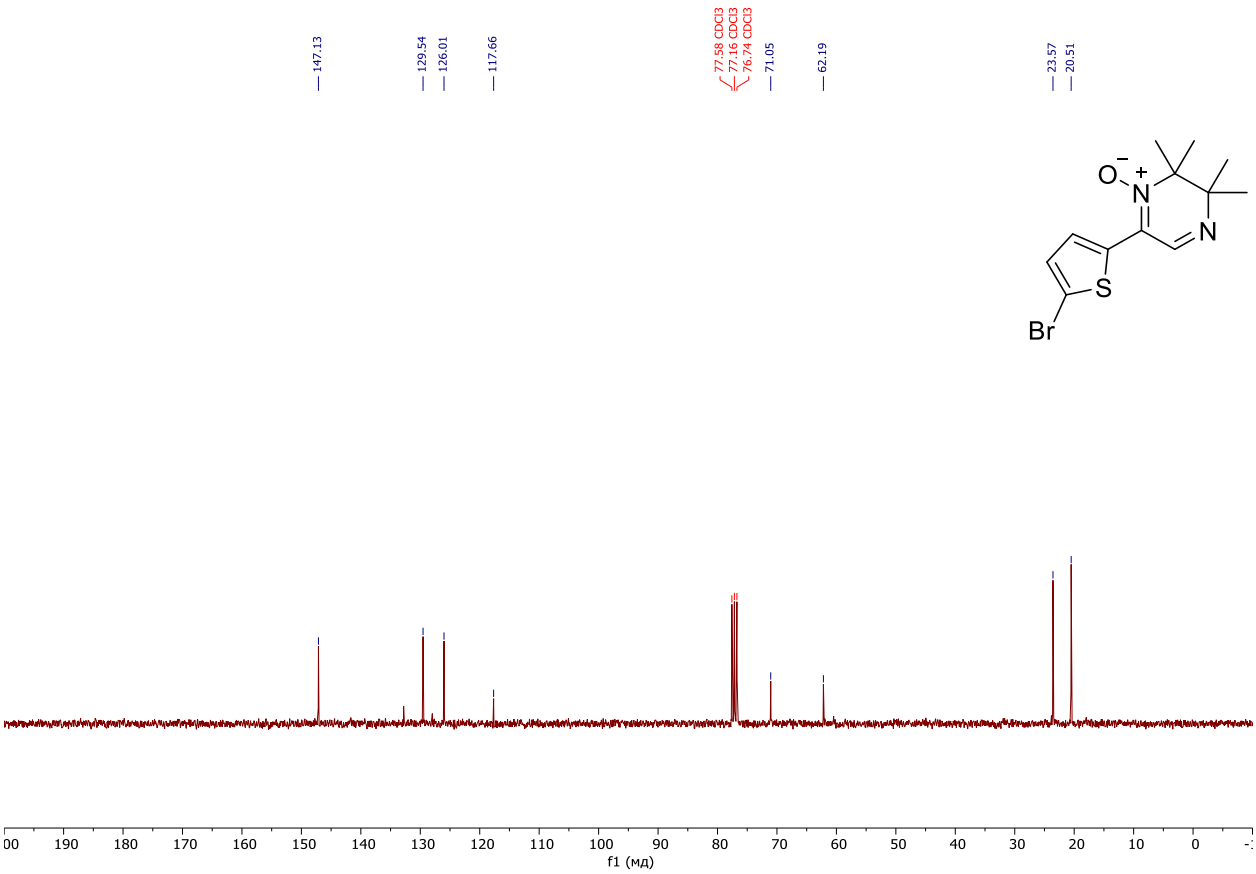
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



^{1}H NMR spectrum (300 MHz) of **8l** in $CDCl_3$



^{13}C {^{1}H} NMR spectrum (76 MHz) of **8l** in $CDCl_3$



HRMS for compound **8l**

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
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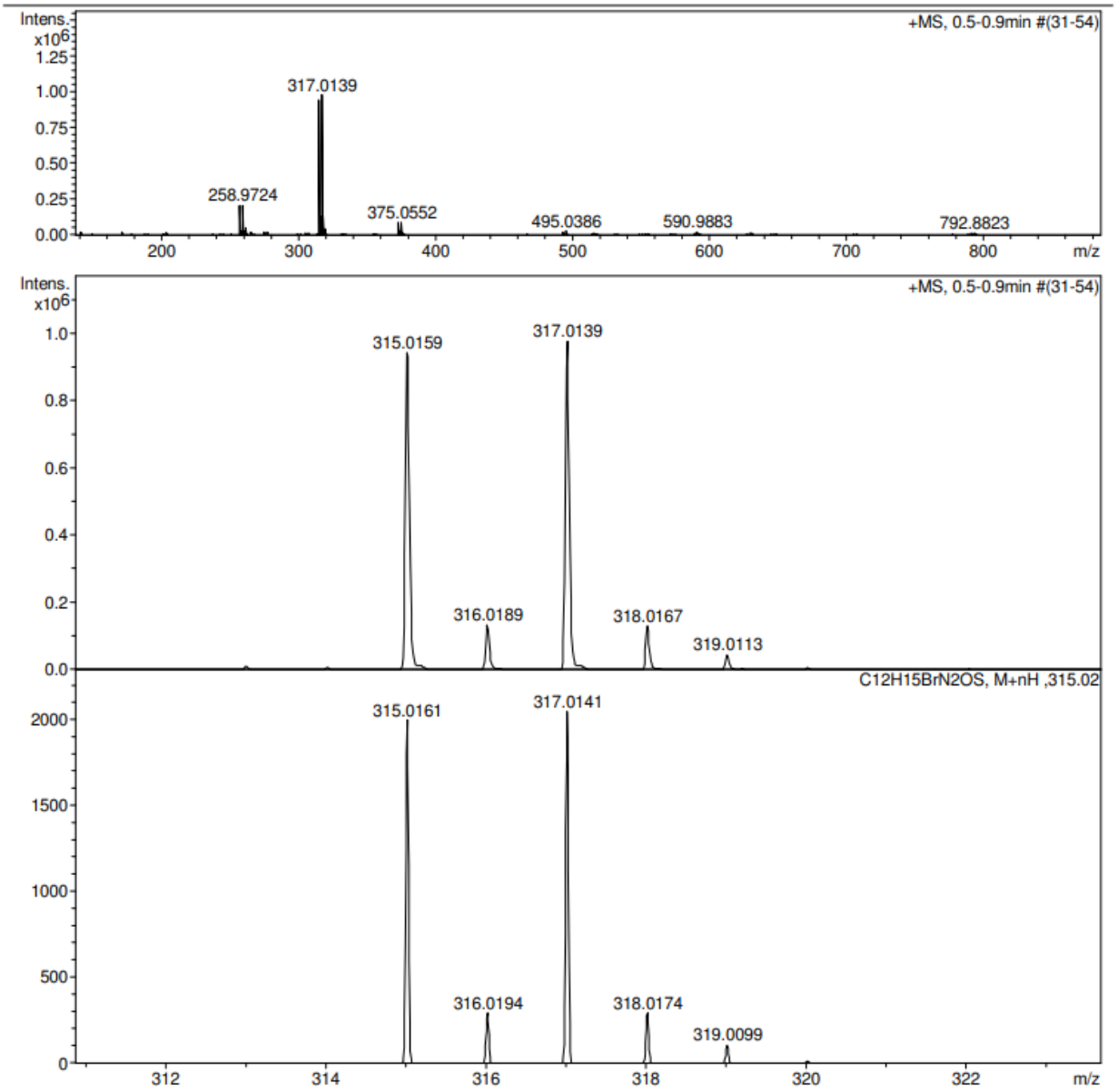
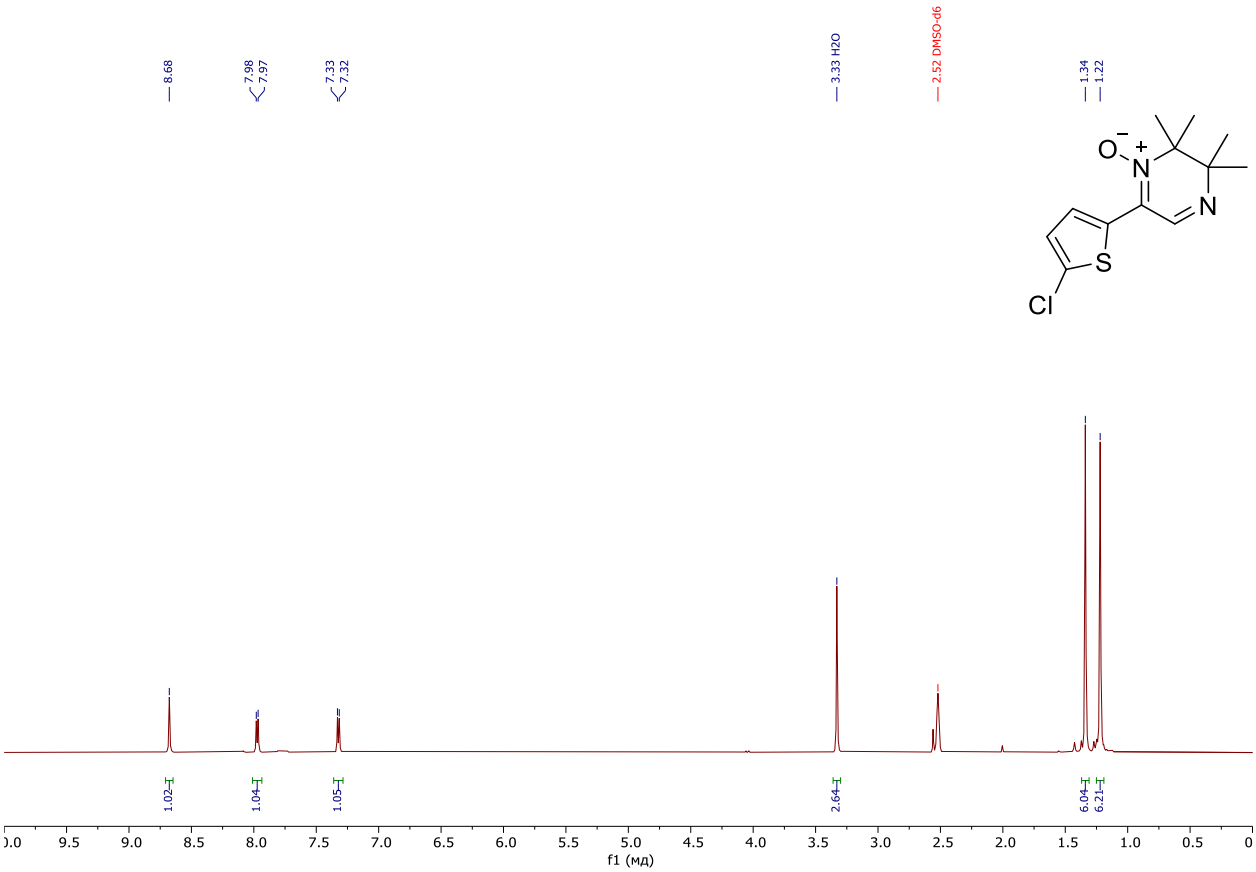
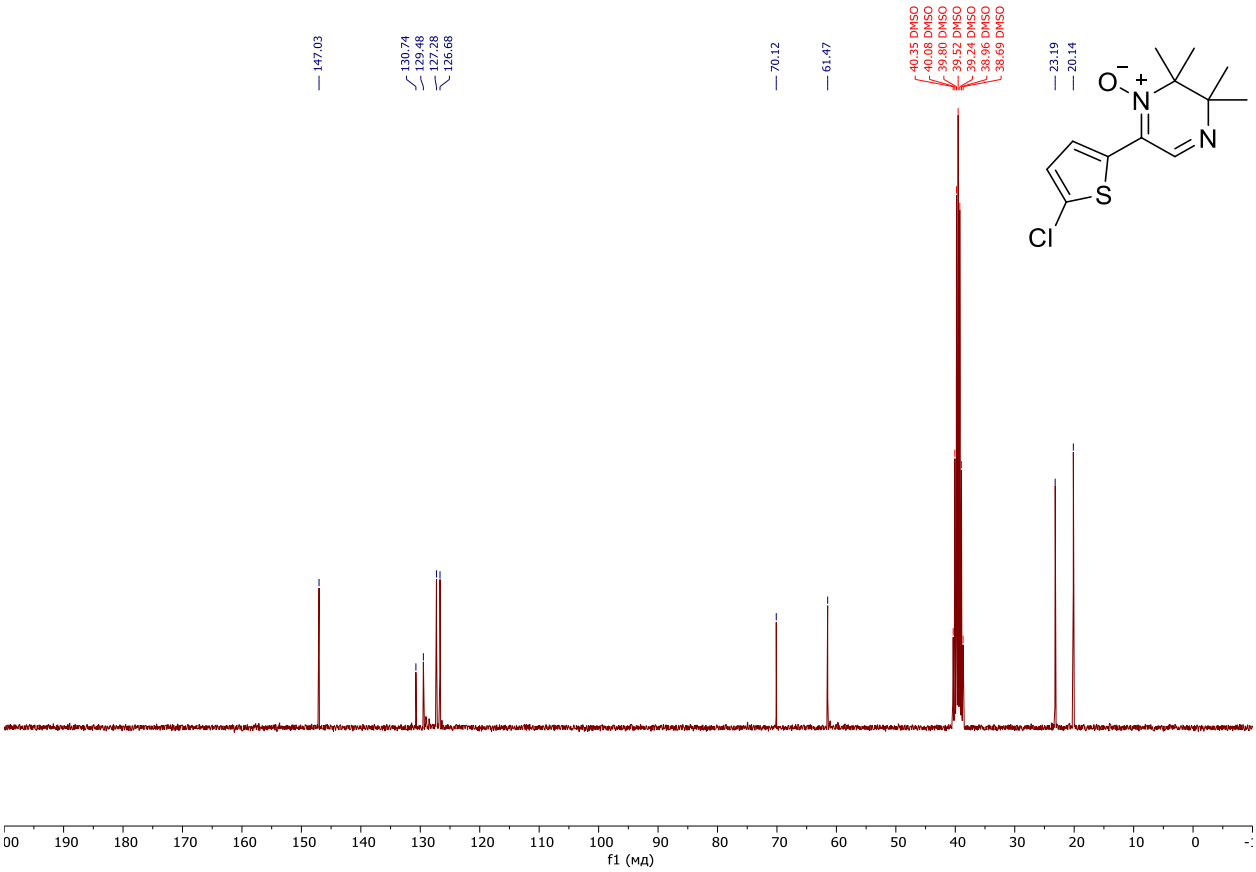


^{1}H NMR spectrum (300 MHz) of **8m** in DMSO-d_6



^{13}C {^{1}H} NMR spectrum (76 MHz) of **8m** in DMSO-d_6



HRMS for compound **8m**

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
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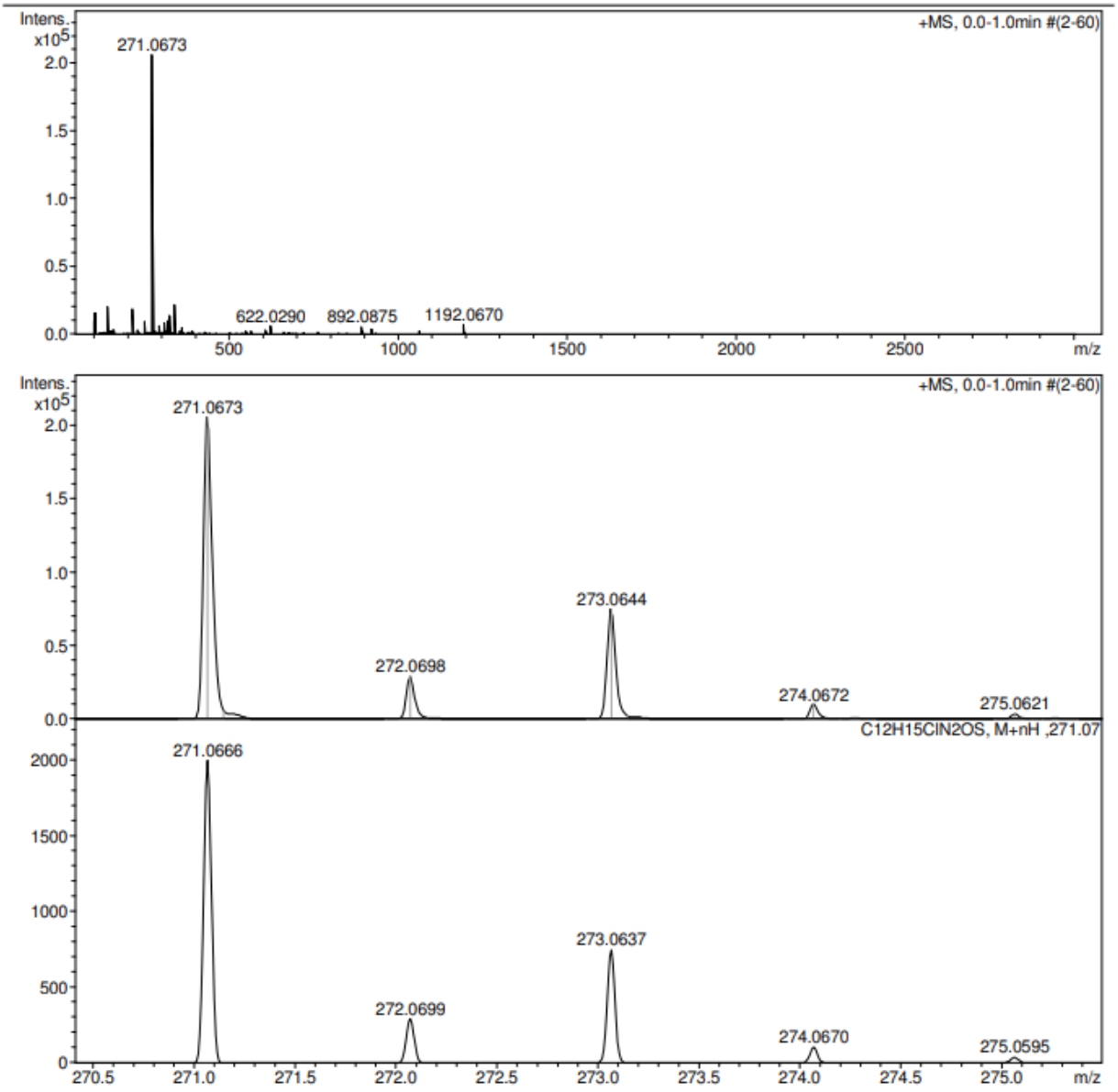

17. X-ray crystallographic data, refinement details and computational methods.

DFT calculations were carried out at the B3LYP level of density functional theory with the 6-311G(d,p) basis set. For calculations, the ORCA 5.0.5 software package was used[2].

X-ray diffraction data were collected at 100K on a four-circle Rigaku Synergy S diffractometer equipped with a HyPix6000HE area-detector (kappa geometry, shutterless ω-scan technique), using monochromatized Cu K_α-radiation. The intensity data were integrated and corrected for absorption and decay by the CrysAlisPro program[1]. The structure was solved by direct methods using SHELXT[2] and refined on F^2 using SHELXL-2018[3] in the OLEX2 program.[4] All non-hydrogen atoms were refined with individual anisotropic displacement parameters. Location of amino hydrogen atom (H2) for compound **5i** and location of hydrogen atom (H1) for compound **7b** were found from the electron density-difference map; these hydrogen atoms were refined with individual isotropic displacement parameters. All other hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters. The Mercury program suite[5] was used for molecular graphics.

Acknowledgment

Crystal structure determination was performed in the Department of Structural Studies of Zelinsky Institute of Organic Chemistry, Moscow.

1. CrysAlisPro. Version 1.171.41.106a. *Rigaku Oxford Diffraction*, **2021**.
2. Sheldrick, G. M. SHELXT - Integrated space-group and crystal-structure determination. *Acta Cryst.* **2015**, A71(1), 3-8. http://doi.org/10.1107/S2053273314026370
3. Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Cryst.* **2015**, C71(1), 3-8. http://doi.org/10.1107/S2053229614024218
4. Dolomanov O.V.; Bourhis L.J.; Gildea R.J.; Howard J.A.K.; Puschmann H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, 42(2), 339-341. http://doi.org/10.1107/S0021889808042726
5. Macrae, C. F.; Sovago, I.; Cottrell, S. J.; Galek, P. T. A.; McCabe, P.; Pidcock, E.; Platings, M.; Shields, G. P.; Stevens, J. S.; Towler, M.; Wood, P. A. Mercury 4.0: from visualization to analysis, design and prediction. *J. Appl. Cryst.* **2020**, 53, 226-235. https://doi.org/10.1107/S1600576719014092

[2] Neese, F. Software update: The ORCA program system—Version 5.0. WIREs Comput. Mol. Sci. 2022, 12, e1606.

Table S1. Crystal data and structure refinement for **5i**.

Identification code	2366252	
Empirical formula	C_{16} H_{22} N_2 O_4	
Formula weight	306.35	
Temperature	100.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 10.76900(10) Å	α= 90°.
	b = 12.7670(2) Å	β= 90°.
	c = 22.6802(3) Å	γ= 90°.
Volume	3118.25(7) $Å^3$	
Z	8	
Density (calculated)	1.305 g/cm^3	
Absorption coefficient	0.773 mm^{-1}	
F(000)	1312	
Crystal size	0.1 x 0.04 x 0.03 mm^3	
Theta range for data collection	3.898 to 80.784°.	
Index ranges	-12<=h<=13, -16<=k<=16, -29<=l<=29	
Reflections collected	20617	
Independent reflections	3415 [R(int) = 0.0283]	
Observed reflections	3126	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.81207	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3415 / 0 / 210	
Goodness-of-fit on F^2	1.081	
Final R indices [I>2sigma(I)]	R1 = 0.0347, wR2 = 0.0920	
R indices (all data)	R1 = 0.0375, wR2 = 0.0939	
Extinction coefficient	0.00062(10)	
Largest diff. peak and hole	0.328 and -0.188 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **5i**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	3858(1)	5808(1)	5078(1)	18(1)
O(2)	1103(1)	5150(1)	4413(1)	19(1)
O(3)	2862(1)	7458(1)	2622(1)	32(1)
O(4)	4491(1)	6091(1)	2272(1)	26(1)
N(1)	3460(1)	6935(1)	4989(1)	17(1)
N(2)	1206(1)	5902(1)	5318(1)	16(1)
C(1)	2956(1)	6083(1)	4651(1)	15(1)
C(2)	1663(1)	5674(1)	4788(1)	15(1)
C(3)	1814(1)	6527(1)	5781(1)	16(1)
C(4)	2680(1)	7349(1)	5479(1)	18(1)
C(5)	766(1)	7073(1)	6119(1)	21(1)
C(6)	2489(1)	5796(1)	6214(1)	20(1)
C(7)	1932(1)	8207(1)	5162(1)	24(1)
C(8)	3599(1)	7839(1)	5915(1)	26(1)
C(9)	3356(1)	6032(1)	4020(1)	16(1)
C(10)	2871(1)	6760(1)	3622(1)	19(1)
C(11)	3269(1)	6770(1)	3042(1)	21(1)
C(12)	4160(1)	6032(1)	2853(1)	19(1)
C(13)	4632(1)	5316(1)	3251(1)	19(1)
C(14)	4231(1)	5314(1)	3839(1)	18(1)
C(15)	1987(1)	8226(1)	2816(1)	39(1)
C(16)	5445(1)	5392(1)	2081(1)	27(1)

Table S3. Bond lengths [Å] and angles [°] for **5i**.

O(1)-N(1)	1.5146(11)
O(1)-C(1)	1.4168(12)
O(2)-C(2)	1.2390(13)
O(3)-C(11)	1.3666(13)
O(3)-C(15)	1.4301(15)
O(4)-C(12)	1.3660(13)
O(4)-C(16)	1.4280(14)
N(1)-C(1)	1.4380(13)
N(1)-C(4)	1.4909(13)
N(2)-H(2)	0.890(16)
N(2)-C(2)	1.3305(13)
N(2)-C(3)	1.4734(13)
C(1)-C(2)	1.5196(13)
C(1)-C(9)	1.4952(14)
C(3)-C(4)	1.5621(14)
C(3)-C(5)	1.5325(14)
C(3)-C(6)	1.5370(14)
C(4)-C(7)	1.5378(15)
C(4)-C(8)	1.5317(15)
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-C(10)	1.3967(14)
C(9)-C(14)	1.3776(14)
C(10)-H(10)	0.9500
C(10)-C(11)	1.3860(15)
C(11)-C(12)	1.4118(15)
C(12)-C(13)	1.3824(15)
C(13)-H(13)	0.9500

C(13)-C(14)	1.4011(15)
C(14)-H(14)	0.9500
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800

C(1)-O(1)-N(1)	58.64(6)
C(11)-O(3)-C(15)	115.94(9)
C(12)-O(4)-C(16)	116.47(9)
C(1)-N(1)-O(1)	57.28(6)
C(1)-N(1)-C(4)	116.99(8)
C(4)-N(1)-O(1)	113.39(7)
C(2)-N(2)-H(2)	115.4(10)
C(2)-N(2)-C(3)	126.74(9)
C(3)-N(2)-H(2)	117.9(10)
O(1)-C(1)-N(1)	64.08(6)
O(1)-C(1)-C(2)	113.75(8)
O(1)-C(1)-C(9)	116.53(8)
N(1)-C(1)-C(2)	119.75(8)
N(1)-C(1)-C(9)	115.76(8)
C(9)-C(1)-C(2)	116.47(8)
O(2)-C(2)-N(2)	123.97(9)
O(2)-C(2)-C(1)	119.32(9)
N(2)-C(2)-C(1)	116.70(9)
N(2)-C(3)-C(4)	108.48(8)
N(2)-C(3)-C(5)	106.02(8)
N(2)-C(3)-C(6)	109.63(8)
C(5)-C(3)-C(4)	110.71(8)
C(5)-C(3)-C(6)	107.76(8)
C(6)-C(3)-C(4)	113.95(8)
N(1)-C(4)-C(3)	115.14(8)
N(1)-C(4)-C(7)	101.51(8)
N(1)-C(4)-C(8)	105.18(8)
C(7)-C(4)-C(3)	111.77(8)
C(8)-C(4)-C(3)	112.13(9)
C(8)-C(4)-C(7)	110.46(9)
C(3)-C(5)-H(5A)	109.5

C(3)-C(5)-H(5B)	109.5
C(3)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
C(3)-C(6)-H(6A)	109.5
C(3)-C(6)-H(6B)	109.5
C(3)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(4)-C(7)-H(7A)	109.5
C(4)-C(7)-H(7B)	109.5
C(4)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(4)-C(8)-H(8A)	109.5
C(4)-C(8)-H(8B)	109.5
C(4)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(10)-C(9)-C(1)	118.74(9)
C(14)-C(9)-C(1)	120.76(9)
C(14)-C(9)-C(10)	120.43(10)
C(9)-C(10)-H(10)	119.9
C(11)-C(10)-C(9)	120.26(10)
C(11)-C(10)-H(10)	119.9
O(3)-C(11)-C(10)	124.66(10)
O(3)-C(11)-C(12)	115.82(9)
C(10)-C(11)-C(12)	119.53(10)
O(4)-C(12)-C(11)	115.63(10)
O(4)-C(12)-C(13)	124.82(10)
C(13)-C(12)-C(11)	119.56(10)
C(12)-C(13)-H(13)	119.7
C(12)-C(13)-C(14)	120.63(10)
C(14)-C(13)-H(13)	119.7
C(9)-C(14)-C(13)	119.59(10)
C(9)-C(14)-H(14)	120.2

C(13)-C(14)-H(14)	120.2
O(3)-C(15)-H(15A)	109.5
O(3)-C(15)-H(15B)	109.5
O(3)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
O(4)-C(16)-H(16A)	109.5
O(4)-C(16)-H(16B)	109.5
O(4)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **5i**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	17(1)	20(1)	18(1)	-1(1)	-2(1)	3(1)
O(2)	18(1)	23(1)	17(1)	-1(1)	-1(1)	-6(1)
O(3)	39(1)	39(1)	18(1)	9(1)	6(1)	18(1)
O(4)	27(1)	36(1)	15(1)	-1(1)	4(1)	4(1)
N(1)	17(1)	16(1)	18(1)	0(1)	0(1)	-2(1)
N(2)	14(1)	18(1)	16(1)	0(1)	1(1)	-2(1)
C(1)	15(1)	15(1)	16(1)	1(1)	0(1)	0(1)
C(2)	15(1)	14(1)	16(1)	2(1)	-1(1)	0(1)
C(3)	16(1)	16(1)	16(1)	-2(1)	1(1)	0(1)
C(4)	19(1)	16(1)	18(1)	-3(1)	2(1)	-2(1)
C(5)	21(1)	21(1)	21(1)	-1(1)	5(1)	4(1)
C(6)	21(1)	22(1)	16(1)	1(1)	0(1)	3(1)
C(7)	30(1)	17(1)	26(1)	2(1)	5(1)	1(1)
C(8)	26(1)	28(1)	23(1)	-8(1)	2(1)	-9(1)
C(9)	14(1)	18(1)	15(1)	-1(1)	0(1)	-4(1)
C(10)	17(1)	21(1)	18(1)	0(1)	1(1)	2(1)
C(11)	20(1)	25(1)	17(1)	3(1)	-1(1)	2(1)
C(12)	18(1)	25(1)	15(1)	-2(1)	2(1)	-2(1)
C(13)	17(1)	21(1)	19(1)	-3(1)	1(1)	1(1)
C(14)	18(1)	19(1)	18(1)	0(1)	-1(1)	0(1)
C(15)	47(1)	44(1)	26(1)	13(1)	9(1)	25(1)
C(16)	25(1)	35(1)	21(1)	-6(1)	7(1)	-1(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **5i**.

	x	y	z	U(eq)
H(2)	467(15)	5625(12)	5398(7)	29(4)
H(5A)	253	7475	5843	32
H(5B)	1123	7547	6414	32
H(5C)	251	6547	6317	32
H(6A)	1903	5275	6367	29
H(6B)	2825	6208	6542	29
H(6C)	3169	5439	6009	29
H(7A)	2477	8589	4891	36
H(7B)	1590	8694	5454	36
H(7C)	1252	7885	4940	36
H(8A)	4202	7309	6040	39
H(8B)	3147	8101	6260	39
H(8C)	4036	8420	5724	39
H(10)	2265	7251	3751	23
H(13)	5234	4820	3125	23
H(14)	4560	4820	4110	22
H(15A)	1796	8704	2490	58
H(15B)	2342	8624	3145	58
H(15C)	1224	7877	2946	58
H(16A)	5605	5502	1660	40
H(16B)	5178	4668	2146	40
H(16C)	6206	5528	2305	40

Table S6. Torsion angles [°] for **5i**.

O(1)-N(1)-C(1)-C(2)	103.77(10)
O(1)-N(1)-C(1)-C(9)	-108.47(9)
O(1)-N(1)-C(4)-C(3)	-33.02(11)
O(1)-N(1)-C(4)-C(7)	-153.92(8)
O(1)-N(1)-C(4)-C(8)	90.94(9)
O(1)-C(1)-C(2)-O(2)	-126.37(10)
O(1)-C(1)-C(2)-N(2)	53.04(12)
O(1)-C(1)-C(9)-C(10)	-145.73(9)
O(1)-C(1)-C(9)-C(14)	31.16(13)
O(3)-C(11)-C(12)-O(4)	-0.74(15)
O(3)-C(11)-C(12)-C(13)	179.22(10)
O(4)-C(12)-C(13)-C(14)	-179.76(10)
N(1)-O(1)-C(1)-C(2)	-112.89(9)
N(1)-O(1)-C(1)-C(9)	107.30(9)
N(1)-C(1)-C(2)-O(2)	161.00(9)
N(1)-C(1)-C(2)-N(2)	-19.59(13)
N(1)-C(1)-C(9)-C(10)	-73.28(12)
N(1)-C(1)-C(9)-C(14)	103.61(11)
N(2)-C(3)-C(4)-N(1)	-44.88(11)
N(2)-C(3)-C(4)-C(7)	70.26(10)
N(2)-C(3)-C(4)-C(8)	-165.08(9)
C(1)-O(1)-N(1)-C(4)	108.05(9)
C(1)-N(1)-C(4)-C(3)	30.84(12)
C(1)-N(1)-C(4)-C(7)	-90.07(10)
C(1)-N(1)-C(4)-C(8)	154.80(9)
C(1)-C(9)-C(10)-C(11)	176.66(10)
C(1)-C(9)-C(14)-C(13)	-176.99(9)
C(2)-N(2)-C(3)-C(4)	29.83(13)
C(2)-N(2)-C(3)-C(5)	148.76(10)
C(2)-N(2)-C(3)-C(6)	-95.17(12)
C(2)-C(1)-C(9)-C(10)	75.56(12)
C(2)-C(1)-C(9)-C(14)	-107.55(11)
C(3)-N(2)-C(2)-O(2)	-179.30(9)
C(3)-N(2)-C(2)-C(1)	1.31(15)
C(4)-N(1)-C(1)-O(1)	-101.67(9)
C(4)-N(1)-C(1)-C(2)	2.09(13)
C(4)-N(1)-C(1)-C(9)	149.85(9)
C(5)-C(3)-C(4)-N(1)	-160.81(9)

C(5)-C(3)-C(4)-C(7)	-45.67(11)
C(5)-C(3)-C(4)-C(8)	78.99(11)
C(6)-C(3)-C(4)-N(1)	77.54(11)
C(6)-C(3)-C(4)-C(7)	-167.32(9)
C(6)-C(3)-C(4)-C(8)	-42.67(12)
C(9)-C(1)-C(2)-O(2)	13.46(13)
C(9)-C(1)-C(2)-N(2)	-167.12(9)
C(9)-C(10)-C(11)-O(3)	-179.23(10)
C(9)-C(10)-C(11)-C(12)	0.65(17)
C(10)-C(9)-C(14)-C(13)	-0.15(15)
C(10)-C(11)-C(12)-O(4)	179.36(10)
C(10)-C(11)-C(12)-C(13)	-0.67(17)
C(11)-C(12)-C(13)-C(14)	0.28(16)
C(12)-C(13)-C(14)-C(9)	0.13(16)
C(14)-C(9)-C(10)-C(11)	-0.24(16)
C(15)-O(3)-C(11)-C(10)	1.64(18)
C(15)-O(3)-C(11)-C(12)	-178.24(11)
C(16)-O(4)-C(12)-C(11)	176.36(10)
C(16)-O(4)-C(12)-C(13)	-3.60(16)

Table S7. Hydrogen bonds for **5i** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2)...O(2)#1	0.890(16)	2.005(16)	2.8910(11)	173.7(14)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z+1

Table S8. Crystal data and structure refinement for **6c**.

Identification code	2366250	
Empirical formula	C_{14} H_{17} Cl N_2 O_2	
Formula weight	280.74	
Temperature	100.01(10) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 2_1/c	
Unit cell dimensions	a = 9.58470(10) Å	α= 90°.
	b = 11.18550(10) Å	β= 102.1830(10)°.
	c = 13.06700(10) Å	γ = 90°.
Volume	1369.36(2) $Å^3$	
Z	4	
Density (calculated)	1.362 g/cm^3	
Absorption coefficient	2.472 mm^{-1}	
F(000)	592	
Crystal size	0.82 x 0.44 x 0.22 mm^3	
Theta range for data collection	4.720 to 79.911°.	
Index ranges	-11<=h<=12, -13<=k<=14, -16<=l<=16	
Reflections collected	22397	
Independent reflections	2983 [R(int) = 0.0315]	
Observed reflections	2964	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.296	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2983 / 0 / 177	
Goodness-of-fit on F^2	1.055	
Final R indices [I>2sigma(I)]	R1 = 0.0311, wR2 = 0.0810	
R indices (all data)	R1 = 0.0313, wR2 = 0.0812	
Extinction coefficient	0.0013(2)	
Largest diff. peak and hole	0.371 and -0.204 $e.Å^{-3}$	

Table S9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **6c**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	8033(1)	914(1)	5795(1)	20(1)
O(1)	8987(1)	6316(1)	2140(1)	19(1)
O(2)	5258(1)	5757(1)	3393(1)	20(1)
N(1)	9095(1)	7290(1)	2963(1)	16(1)
N(2)	6440(1)	6143(1)	3191(1)	15(1)
C(1)	7963(1)	2274(1)	5137(1)	16(1)
C(2)	7171(1)	3202(1)	5433(1)	16(1)
C(3)	7044(1)	4265(1)	4876(1)	15(1)
C(4)	7750(1)	4424(1)	4051(1)	14(1)
C(5)	8577(1)	3486(1)	3789(1)	16(1)
C(6)	8673(1)	2401(1)	4318(1)	17(1)
C(7)	7653(1)	5558(1)	3465(1)	14(1)
C(8)	8970(1)	6053(1)	3203(1)	16(1)
C(9)	7757(1)	7994(1)	2863(1)	16(1)
C(10)	6326(1)	7286(1)	2552(1)	16(1)
C(11)	7942(1)	8537(1)	3962(1)	22(1)
C(12)	7842(1)	8983(1)	2071(1)	24(1)
C(13)	5092(1)	8018(1)	2810(1)	21(1)
C(14)	5911(1)	6907(1)	1395(1)	24(1)

Table S10. Bond lengths [Å] and angles [°] for **6c**.

Cl(1)-C(1)	1.7422(11)
O(1)-N(1)	1.5184(12)
O(1)-C(8)	1.4235(14)
O(2)-N(2)	1.2904(12)
N(1)-C(8)	1.4292(15)
N(1)-C(9)	1.4870(14)
N(2)-C(7)	1.3153(15)
N(2)-C(10)	1.5188(14)
C(1)-C(2)	1.3883(16)
C(1)-C(6)	1.3901(16)
C(2)-H(2)	0.9500
C(2)-C(3)	1.3856(16)
C(3)-H(3)	0.9500
C(3)-C(4)	1.4006(15)
C(4)-C(5)	1.3999(16)
C(4)-C(7)	1.4747(15)
C(5)-H(5)	0.9500
C(5)-C(6)	1.3910(16)
C(6)-H(6)	0.9500
C(7)-C(8)	1.4827(15)
C(8)-H(8)	1.0000
C(9)-C(10)	1.5623(15)
C(9)-C(11)	1.5348(16)
C(9)-C(12)	1.5277(16)
C(10)-C(13)	1.5337(15)
C(10)-C(14)	1.5380(16)
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800

C(8)-O(1)-N(1)	58.03(7)
C(8)-N(1)-O(1)	57.66(7)
C(8)-N(1)-C(9)	114.91(9)
C(9)-N(1)-O(1)	112.88(8)
O(2)-N(2)-C(7)	122.82(10)
O(2)-N(2)-C(10)	115.39(9)
C(7)-N(2)-C(10)	121.69(9)
C(2)-C(1)-Cl(1)	118.75(9)
C(2)-C(1)-C(6)	121.58(11)
C(6)-C(1)-Cl(1)	119.66(9)
C(1)-C(2)-H(2)	120.4
C(3)-C(2)-C(1)	119.21(10)
C(3)-C(2)-H(2)	120.4
C(2)-C(3)-H(3)	119.7
C(2)-C(3)-C(4)	120.62(10)
C(4)-C(3)-H(3)	119.7
C(3)-C(4)-C(7)	121.39(10)
C(5)-C(4)-C(3)	118.96(10)
C(5)-C(4)-C(7)	119.64(10)
C(4)-C(5)-H(5)	119.5
C(6)-C(5)-C(4)	120.90(10)
C(6)-C(5)-H(5)	119.5
C(1)-C(6)-C(5)	118.66(10)
C(1)-C(6)-H(6)	120.7
C(5)-C(6)-H(6)	120.7
N(2)-C(7)-C(4)	121.62(10)
N(2)-C(7)-C(8)	119.85(10)
C(4)-C(7)-C(8)	118.52(10)
O(1)-C(8)-N(1)	64.32(7)
O(1)-C(8)-C(7)	119.19(10)
O(1)-C(8)-H(8)	114.2
N(1)-C(8)-C(7)	121.83(10)
N(1)-C(8)-H(8)	114.2
C(7)-C(8)-H(8)	114.2
N(1)-C(9)-C(10)	116.60(9)
N(1)-C(9)-C(11)	101.54(9)
N(1)-C(9)-C(12)	105.95(9)
C(11)-C(9)-C(10)	111.46(9)
C(12)-C(9)-C(10)	111.14(10)

C(12)-C(9)-C(11)	109.57(10)
N(2)-C(10)-C(9)	109.04(9)
N(2)-C(10)-C(13)	107.35(9)
N(2)-C(10)-C(14)	106.44(9)
C(13)-C(10)-C(9)	110.28(9)
C(13)-C(10)-C(14)	108.17(10)
C(14)-C(10)-C(9)	115.22(9)
C(9)-C(11)-H(11A)	109.5
C(9)-C(11)-H(11B)	109.5
C(9)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(9)-C(12)-H(12A)	109.5
C(9)-C(12)-H(12B)	109.5
C(9)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(10)-C(13)-H(13A)	109.5
C(10)-C(13)-H(13B)	109.5
C(10)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(10)-C(14)-H(14A)	109.5
C(10)-C(14)-H(14B)	109.5
C(10)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5

Table S11. Crystal data and structure refinement for **7b**.

Identification code	2366249	
Empirical formula	C_{14} H_{17} Br N_2 O_2	
Formula weight	325.20	
Temperature	99.98(10) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 2_1/n	
Unit cell dimensions	a = 10.54497(6) Å	α= 90°.
	b = 7.19449(4) Å	β= 100.3895(6)°.
	c = 18.56940(11) Å	γ= 90°.
Volume	1385.683(13) $Å^3$	
Z	4	
Density (calculated)	1.559 g/cm^3	
Absorption coefficient	4.048 mm^{-1}	
F(000)	664	
Crystal size	0.79 x 0.18 x 0.12 mm^3	
Theta range for data collection	4.507 to 80.048°.	
Index ranges	-13<=h<=13, -9<=k<=8, -23<=l<=23	
Reflections collected	22811	
Independent reflections	3026 [R(int) = 0.0301]	
Observed reflections	3017	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.426	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3026 / 0 / 181	
Goodness-of-fit on F^2	1.099	
Final R indices [I>2sigma(I)]	R1 = 0.0270, wR2 = 0.0695	
R indices (all data)	R1 = 0.0272, wR2 = 0.0696	
Extinction coefficient	0.00080(12)	
Largest diff. peak and hole	0.474 and -0.469 e.$Å^{-3}$	

Table S12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **7b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	9646(1)	1142(1)	6906(1)	21(1)
O(1)	3517(1)	4097(2)	6647(1)	22(1)
O(2)	5892(1)	7946(2)	5382(1)	18(1)
N(1)	3894(2)	8835(2)	5537(1)	15(1)
N(2)	3672(1)	5509(2)	6256(1)	14(1)
C(1)	8146(2)	2653(3)	6693(1)	16(1)
C(2)	6976(2)	1810(3)	6416(1)	17(1)
C(3)	5883(2)	2911(3)	6247(1)	15(1)
C(4)	5960(2)	4839(2)	6337(1)	14(1)
C(5)	7150(2)	5646(3)	6620(1)	16(1)
C(6)	8250(2)	4557(3)	6808(1)	17(1)
C(7)	4801(2)	6003(2)	6104(1)	14(1)
C(8)	4898(2)	7682(2)	5648(1)	14(1)
C(9)	2769(2)	8636(2)	5898(1)	15(1)
C(10)	2439(2)	6541(3)	5919(1)	15(1)
C(11)	3085(2)	9486(3)	6670(1)	19(1)
C(12)	1678(2)	9737(3)	5431(1)	21(1)
C(13)	1428(2)	6148(3)	6391(1)	21(1)
C(14)	2023(2)	5678(3)	5157(1)	19(1)

Table S13. Bond lengths [Å] and angles [°] for **7b**.

Br(1)-C(1)	1.9014(17)
O(1)-N(2)	1.276(2)
O(2)-C(8)	1.251(2)
N(1)-C(8)	1.332(2)
N(1)-C(9)	1.472(2)
N(1)-H(1)	0.95(2)
N(2)-C(7)	1.322(2)
N(2)-C(10)	1.529(2)
C(1)-C(2)	1.387(3)
C(1)-C(6)	1.388(3)
C(2)-H(2)	0.9500
C(2)-C(3)	1.387(3)
C(3)-H(3)	0.9500
C(3)-C(4)	1.398(3)
C(4)-C(5)	1.396(2)
C(4)-C(7)	1.480(2)
C(5)-H(5)	0.9500
C(5)-C(6)	1.391(3)
C(6)-H(6)	0.9500
C(7)-C(8)	1.488(2)
C(9)-C(10)	1.549(2)
C(9)-C(11)	1.537(2)
C(9)-C(12)	1.531(2)
C(10)-C(13)	1.525(2)
C(10)-C(14)	1.535(2)
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800

C(8)-N(1)-C(9)	123.51(15)
C(8)-N(1)-H(1)	122.3(14)
C(9)-N(1)-H(1)	114.0(14)
O(1)-N(2)-C(7)	123.27(15)
O(1)-N(2)-C(10)	115.65(14)
C(7)-N(2)-C(10)	120.93(15)
C(2)-C(1)-Br(1)	118.55(14)
C(2)-C(1)-C(6)	121.93(16)
C(6)-C(1)-Br(1)	119.51(14)
C(1)-C(2)-H(2)	120.6
C(3)-C(2)-C(1)	118.75(17)
C(3)-C(2)-H(2)	120.6
C(2)-C(3)-H(3)	119.6
C(2)-C(3)-C(4)	120.83(16)
C(4)-C(3)-H(3)	119.6
C(3)-C(4)-C(7)	119.98(15)
C(5)-C(4)-C(3)	119.06(16)
C(5)-C(4)-C(7)	120.92(16)
C(4)-C(5)-H(5)	119.6
C(6)-C(5)-C(4)	120.85(17)
C(6)-C(5)-H(5)	119.6
C(1)-C(6)-C(5)	118.54(17)
C(1)-C(6)-H(6)	120.7
C(5)-C(6)-H(6)	120.7
N(2)-C(7)-C(4)	120.92(15)
N(2)-C(7)-C(8)	119.79(15)
C(4)-C(7)-C(8)	119.16(15)
O(2)-C(8)-N(1)	122.87(16)
O(2)-C(8)-C(7)	119.74(16)
N(1)-C(8)-C(7)	117.38(15)
N(1)-C(9)-C(10)	107.98(14)
N(1)-C(9)-C(11)	109.17(15)
N(1)-C(9)-C(12)	106.05(14)
C(11)-C(9)-C(10)	112.09(15)
C(12)-C(9)-C(10)	111.63(15)
C(12)-C(9)-C(11)	109.69(15)
N(2)-C(10)-C(9)	107.75(14)
N(2)-C(10)-C(14)	105.20(14)
C(13)-C(10)-N(2)	107.78(14)
C(13)-C(10)-C(9)	112.19(15)

C(13)-C(10)-C(14)	109.99(15)
C(14)-C(10)-C(9)	113.50(15)
C(9)-C(11)-H(11A)	109.5
C(9)-C(11)-H(11B)	109.5
C(9)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(9)-C(12)-H(12A)	109.5
C(9)-C(12)-H(12B)	109.5
C(9)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(10)-C(13)-H(13A)	109.5
C(10)-C(13)-H(13B)	109.5
C(10)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(10)-C(14)-H(14A)	109.5
C(10)-C(14)-H(14B)	109.5
C(10)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S14. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **7b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	17(1)	28(1)	17(1)	0(1)	2(1)	9(1)
O(1)	22(1)	19(1)	25(1)	7(1)	7(1)	0(1)
O(2)	16(1)	21(1)	19(1)	4(1)	5(1)	0(1)
N(1)	15(1)	15(1)	15(1)	4(1)	4(1)	1(1)
N(2)	14(1)	14(1)	15(1)	2(1)	2(1)	1(1)
C(1)	16(1)	21(1)	11(1)	2(1)	3(1)	6(1)
C(2)	20(1)	16(1)	14(1)	0(1)	3(1)	1(1)
C(3)	16(1)	17(1)	14(1)	0(1)	3(1)	-2(1)
C(4)	16(1)	16(1)	11(1)	1(1)	4(1)	1(1)
C(5)	19(1)	15(1)	13(1)	-1(1)	5(1)	-2(1)
C(6)	16(1)	23(1)	12(1)	-2(1)	3(1)	-1(1)
C(7)	15(1)	13(1)	12(1)	0(1)	3(1)	-1(1)
C(8)	15(1)	14(1)	12(1)	0(1)	1(1)	-2(1)
C(9)	14(1)	16(1)	13(1)	1(1)	3(1)	4(1)
C(10)	12(1)	19(1)	14(1)	2(1)	2(1)	2(1)
C(11)	23(1)	19(1)	16(1)	-2(1)	6(1)	2(1)
C(12)	17(1)	24(1)	21(1)	6(1)	4(1)	6(1)
C(13)	16(1)	26(1)	22(1)	5(1)	7(1)	1(1)
C(14)	18(1)	22(1)	16(1)	-2(1)	0(1)	-2(1)

Table S15. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **7b**.

	x	y	z	U(eq)
H(2)	6924	503	6344	20
H(3)	5073	2348	6068	18
H(5)	7209	6954	6685	19
H(6)	9055	5105	7010	20
H(11A)	3774	8765	6970	29
H(11B)	2314	9459	6896	29
H(11C)	3370	10774	6635	29
H(12A)	1910	11056	5438	31
H(12B)	884	9583	5630	31
H(12C)	1540	9275	4927	31
H(13A)	1205	4824	6362	31
H(13B)	654	6889	6215	31
H(13C)	1774	6477	6901	31
H(14A)	2628	6053	4840	29
H(14B)	1155	6111	4945	29
H(14C)	2021	4321	5199	29
H(1)	3880(20)	9920(30)	5244(13)	15(5)

Table S16. Torsion angles [°] for **7b**.

Br(1)-C(1)-C(2)-C(3)	-178.78(13)
Br(1)-C(1)-C(6)-C(5)	177.37(13)
O(1)-N(2)-C(7)-C(4)	4.7(3)
O(1)-N(2)-C(7)-C(8)	-179.42(15)
O(1)-N(2)-C(10)-C(9)	145.67(15)
O(1)-N(2)-C(10)-C(13)	24.4(2)
O(1)-N(2)-C(10)-C(14)	-92.94(17)
N(1)-C(9)-C(10)-N(2)	52.18(17)
N(1)-C(9)-C(10)-C(13)	170.66(14)
N(1)-C(9)-C(10)-C(14)	-63.89(18)
N(2)-C(7)-C(8)-O(2)	-165.74(16)
N(2)-C(7)-C(8)-N(1)	13.4(2)
C(1)-C(2)-C(3)-C(4)	1.5(3)
C(2)-C(1)-C(6)-C(5)	-1.7(3)
C(2)-C(3)-C(4)-C(5)	-1.8(3)
C(2)-C(3)-C(4)-C(7)	175.63(16)
C(3)-C(4)-C(5)-C(6)	0.4(3)
C(3)-C(4)-C(7)-N(2)	44.2(2)
C(3)-C(4)-C(7)-C(8)	-131.70(17)
C(4)-C(5)-C(6)-C(1)	1.3(3)
C(4)-C(7)-C(8)-O(2)	10.2(2)
C(4)-C(7)-C(8)-N(1)	-170.67(15)
C(5)-C(4)-C(7)-N(2)	-138.38(18)
C(5)-C(4)-C(7)-C(8)	45.7(2)
C(6)-C(1)-C(2)-C(3)	0.3(3)
C(7)-N(2)-C(10)-C(9)	-38.7(2)
C(7)-N(2)-C(10)-C(13)	-159.94(16)
C(7)-N(2)-C(10)-C(14)	82.73(19)
C(7)-C(4)-C(5)-C(6)	-177.05(16)
C(8)-N(1)-C(9)-C(10)	-40.2(2)
C(8)-N(1)-C(9)-C(11)	81.9(2)
C(8)-N(1)-C(9)-C(12)	-160.03(17)
C(9)-N(1)-C(8)-O(2)	-174.38(16)
C(9)-N(1)-C(8)-C(7)	6.5(2)
C(10)-N(2)-C(7)-C(4)	-170.63(15)
C(10)-N(2)-C(7)-C(8)	5.3(2)
C(11)-C(9)-C(10)-N(2)	-68.12(18)
C(11)-C(9)-C(10)-C(13)	50.4(2)

C(11)-C(9)-C(10)-C(14)	175.82(15)
C(12)-C(9)-C(10)-N(2)	168.37(14)
C(12)-C(9)-C(10)-C(13)	-73.15(19)
C(12)-C(9)-C(10)-C(14)	52.3(2)

Symmetry transformations used to generate equivalent atoms:

Table S17. Hydrogen bonds for **7b** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(2)#1	0.95(2)	1.97(2)	2.909(2)	171(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+2,-z+1

Table S18. Crystal data and structure refinement for **8b**.

Identification code	2366251	
Empirical formula	C_{14} H_{17} Br N_2 O	
Formula weight	309.20	
Temperature	99.97(16) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 12.47732(7) Å	α= 90°.
	b = 10.43720(5) Å	β= 114.5849(6)°.
	c = 11.94409(6) Å	γ= 90°.
Volume	1414.450(14) $Å^3$	
Z	4	
Density (calculated)	1.452 g/cm^3	
Absorption coefficient	3.880 mm^{-1}	
F(000)	632	
Crystal size	0.38 x 0.27 x 0.17 mm^3	
Theta range for data collection	3.896 to 80.001°.	
Index ranges	-15<=h<=15, -13<=k<=13, -15<=l<=15	
Reflections collected	43942	
Independent reflections	3082 [R(int) = 0.0310]	
Observed reflections	3065	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.328	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3082 / 6 / 191	
Goodness-of-fit on F^2	1.070	
Final R indices [I>2sigma(I)]	R1 = 0.0255, wR2 = 0.0609	
R indices (all data)	R1 = 0.0255, wR2 = 0.0610	
Extinction coefficient	0.00268(14)	
Largest diff. peak and hole	0.470 and -0.425 $e.Å^{-3}$	

Table S19. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **8b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	1719(1)	6730(1)	6646(1)	36(1)
O(1)	4152(4)	3731(5)	3211(5)	32(1)
O(1A)	4282(9)	4067(10)	3139(10)	32(1)
N(1)	3323(1)	4144(2)	2179(1)	33(1)
N(2)	1389(1)	4553(2)	-112(1)	34(1)
C(1)	1923(1)	6170(1)	5232(1)	25(1)
C(2)	949(1)	5809(2)	4187(1)	27(1)
C(3)	1115(1)	5350(2)	3181(1)	25(1)
C(4)	2251(1)	5235(1)	3220(1)	21(1)
C(5)	3214(1)	5627(1)	4287(1)	24(1)
C(6)	3053(1)	6101(1)	5292(1)	25(1)
C(7)	2380(1)	4764(2)	2120(1)	24(1)
C(8)	3483(2)	3987(3)	954(2)	26(1)
C(8A)	3233(4)	3330(5)	1042(4)	26(1)
C(9)	2258(2)	3532(2)	0(2)	23(1)
C(9A)	2645(4)	4276(4)	-31(4)	23(1)
C(10)	1437(1)	4979(2)	896(1)	26(1)
C(11)	4455(2)	2983(2)	1228(2)	36(1)
C(12)	3862(3)	5276(3)	611(3)	37(1)
C(12A)	2517(6)	2088(6)	875(6)	37(1)
C(13)	1889(3)	2253(2)	373(3)	30(1)
C(13A)	3378(5)	5489(5)	108(5)	30(1)
C(14)	2226(9)	3394(11)	-1289(5)	29(1)
C(14A)	2425(14)	3647(14)	-1272(11)	29(1)

Table S20. Bond lengths [Å] and angles [°] for **8b**.

Br(1)-C(1)	1.9020(14)
O(1)-N(1)	1.310(5)
O(1A)-N(1)	1.269(10)
N(1)-C(7)	1.318(2)
N(1)-C(8)	1.566(3)
N(1)-C(8A)	1.565(5)
N(2)-C(9)	1.486(3)
N(2)-C(9A)	1.556(4)
N(2)-C(10)	1.262(2)
C(1)-C(2)	1.384(2)
C(1)-C(6)	1.383(2)
C(2)-H(2)	0.9500
C(2)-C(3)	1.387(2)
C(3)-H(3)	0.9500
C(3)-C(4)	1.404(2)
C(4)-C(5)	1.400(2)
C(4)-C(7)	1.4734(19)
C(5)-H(5)	0.9500
C(5)-C(6)	1.388(2)
C(6)-H(6)	0.9500
C(7)-C(10)	1.463(2)
C(8)-C(9)	1.553(3)
C(8)-C(11)	1.531(3)
C(8)-C(12)	1.537(4)
C(8A)-C(9A)	1.541(6)
C(8A)-C(11)	1.491(5)
C(8A)-C(12A)	1.540(7)
C(9)-C(13)	1.537(3)
C(9)-C(14)	1.530(6)
C(9A)-C(13A)	1.530(6)
C(9A)-C(14A)	1.538(11)
C(10)-H(10)	0.9500
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(11)-H(11D)	0.9800
C(11)-H(11E)	0.9800
C(11)-H(11F)	0.9800

C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(12A)-H(12D)	0.9800
C(12A)-H(12E)	0.9800
C(12A)-H(12F)	0.9800
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(13A)-H(13D)	0.9800
C(13A)-H(13E)	0.9800
C(13A)-H(13F)	0.9800
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(14A)-H(14D)	0.9800
C(14A)-H(14E)	0.9800
C(14A)-H(14F)	0.9800

O(1)-N(1)-C(7)	123.4(3)
O(1)-N(1)-C(8)	119.2(3)
O(1A)-N(1)-C(7)	124.4(6)
O(1A)-N(1)-C(8A)	116.7(7)
C(7)-N(1)-C(8)	117.29(14)
C(7)-N(1)-C(8A)	118.7(2)
C(10)-N(2)-C(9)	115.10(15)
C(10)-N(2)-C(9A)	111.11(19)
C(2)-C(1)-Br(1)	119.55(11)
C(6)-C(1)-Br(1)	118.69(11)
C(6)-C(1)-C(2)	121.74(13)
C(1)-C(2)-H(2)	120.5
C(1)-C(2)-C(3)	118.93(14)
C(3)-C(2)-H(2)	120.5
C(2)-C(3)-H(3)	119.5
C(2)-C(3)-C(4)	120.92(14)
C(4)-C(3)-H(3)	119.5
C(3)-C(4)-C(7)	118.85(13)
C(5)-C(4)-C(3)	118.48(13)
C(5)-C(4)-C(7)	122.60(13)
C(4)-C(5)-H(5)	119.5

C(6)-C(5)-C(4)	120.93(14)
C(6)-C(5)-H(5)	119.5
C(1)-C(6)-C(5)	118.96(13)
C(1)-C(6)-H(6)	120.5
C(5)-C(6)-H(6)	120.5
N(1)-C(7)-C(4)	122.80(13)
N(1)-C(7)-C(10)	117.30(13)
C(10)-C(7)-C(4)	119.91(13)
C(9)-C(8)-N(1)	104.39(17)
C(11)-C(8)-N(1)	105.59(17)
C(11)-C(8)-C(9)	113.45(19)
C(11)-C(8)-C(12)	110.6(2)
C(12)-C(8)-N(1)	109.3(2)
C(12)-C(8)-C(9)	113.0(2)
C(9A)-C(8A)-N(1)	102.2(3)
C(11)-C(8A)-N(1)	107.6(3)
C(11)-C(8A)-C(9A)	112.5(3)
C(11)-C(8A)-C(12A)	108.5(4)
C(12A)-C(8A)-N(1)	113.4(4)
C(12A)-C(8A)-C(9A)	112.4(4)
N(2)-C(9)-C(8)	107.76(18)
N(2)-C(9)-C(13)	110.72(19)
N(2)-C(9)-C(14)	105.3(3)
C(13)-C(9)-C(8)	112.0(2)
C(14)-C(9)-C(8)	111.9(4)
C(14)-C(9)-C(13)	108.9(5)
C(8A)-C(9A)-N(2)	106.8(3)
C(13A)-C(9A)-N(2)	113.2(3)
C(13A)-C(9A)-C(8A)	112.5(4)
C(13A)-C(9A)-C(14A)	108.5(6)
C(14A)-C(9A)-N(2)	104.4(7)
C(14A)-C(9A)-C(8A)	111.1(7)
N(2)-C(10)-C(7)	126.72(14)
N(2)-C(10)-H(10)	116.6
C(7)-C(10)-H(10)	116.6
C(8)-C(11)-H(11A)	109.5
C(8)-C(11)-H(11B)	109.5
C(8)-C(11)-H(11C)	109.5
C(8A)-C(11)-H(11D)	109.5
C(8A)-C(11)-H(11E)	109.5

C(8A)-C(11)-H(11F)	109.5
H(11A)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
H(11D)-C(11)-H(11E)	109.5
H(11D)-C(11)-H(11F)	109.5
H(11E)-C(11)-H(11F)	109.5
C(8)-C(12)-H(12A)	109.5
C(8)-C(12)-H(12B)	109.5
C(8)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(8A)-C(12A)-H(12D)	109.5
C(8A)-C(12A)-H(12E)	109.5
C(8A)-C(12A)-H(12F)	109.5
H(12D)-C(12A)-H(12E)	109.5
H(12D)-C(12A)-H(12F)	109.5
H(12E)-C(12A)-H(12F)	109.5
C(9)-C(13)-H(13A)	109.5
C(9)-C(13)-H(13B)	109.5
C(9)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(9A)-C(13A)-H(13D)	109.5
C(9A)-C(13A)-H(13E)	109.5
C(9A)-C(13A)-H(13F)	109.5
H(13D)-C(13A)-H(13E)	109.5
H(13D)-C(13A)-H(13F)	109.5
H(13E)-C(13A)-H(13F)	109.5
C(9)-C(14)-H(14A)	109.5
C(9)-C(14)-H(14B)	109.5
C(9)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(9A)-C(14A)-H(14D)	109.5
C(9A)-C(14A)-H(14E)	109.5
C(9A)-C(14A)-H(14F)	109.5

H(14D)-C(14A)-H(14E)	109.5
H(14D)-C(14A)-H(14F)	109.5
H(14E)-C(14A)-H(14F)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S21. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **8b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	48(1)	37(1)	29(1)	-10(1)	22(1)	-2(1)
O(1)	21(1)	51(3)	20(1)	-1(2)	4(1)	9(2)
O(1A)	21(1)	51(3)	20(1)	-1(2)	4(1)	9(2)
N(1)	22(1)	55(1)	18(1)	-6(1)	5(1)	10(1)
N(2)	32(1)	47(1)	20(1)	-1(1)	7(1)	14(1)
C(1)	34(1)	21(1)	22(1)	-2(1)	15(1)	1(1)
C(2)	26(1)	29(1)	29(1)	-3(1)	14(1)	1(1)
C(3)	22(1)	29(1)	23(1)	-3(1)	8(1)	-1(1)
C(4)	22(1)	23(1)	19(1)	0(1)	9(1)	1(1)
C(5)	22(1)	25(1)	22(1)	-1(1)	8(1)	-1(1)
C(6)	28(1)	23(1)	21(1)	-2(1)	6(1)	-2(1)
C(7)	19(1)	31(1)	20(1)	-2(1)	7(1)	1(1)
C(8)	26(1)	32(1)	22(1)	-3(1)	13(1)	0(1)
C(8A)	26(1)	32(1)	22(1)	-3(1)	13(1)	0(1)
C(9)	26(1)	24(1)	21(1)	1(1)	11(1)	3(1)
C(9A)	26(1)	24(1)	21(1)	1(1)	11(1)	3(1)
C(10)	22(1)	34(1)	20(1)	-3(1)	6(1)	4(1)
C(11)	31(1)	50(1)	29(1)	0(1)	15(1)	12(1)
C(12)	42(2)	41(2)	37(1)	-7(1)	24(1)	-14(1)
C(12A)	42(2)	41(2)	37(1)	-7(1)	24(1)	-14(1)
C(13)	38(1)	27(1)	32(1)	-4(1)	20(1)	-7(1)
C(13A)	38(1)	27(1)	32(1)	-4(1)	20(1)	-7(1)
C(14)	33(3)	35(3)	21(1)	0(1)	13(1)	2(2)
C(14A)	33(3)	35(3)	21(1)	0(1)	13(1)	2(2)

Table S22. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **8b**.

	x	y	z	U(eq)
H(2)	179	5874	4159	32
H(3)	451	5111	2455	30
H(5)	3987	5567	4324	28
H(6)	3709	6374	6011	30
H(10)	793	5492	857	32
H(11A)	5217	3359	1762	54
H(11B)	4477	2702	455	54
H(11C)	4293	2247	1643	54
H(11D)	4964	3738	1509	54
H(11E)	4448	2678	450	54
H(11F)	4755	2305	1849	54
H(12A)	3230	5905	438	56
H(12B)	4020	5165	-121	56
H(12C)	4578	5578	1298	56
H(12D)	2839	1592	1641	56
H(12E)	2565	1579	208	56
H(12F)	1692	2301	669	56
H(13A)	1980	2307	1227	45
H(13B)	2389	1564	299	45
H(13C)	1064	2073	-170	45
H(13D)	2909	6123	-506	45
H(13E)	4086	5278	-18	45
H(13F)	3609	5843	936	45
H(14A)	1448	3085	-1859	43
H(14B)	2830	2780	-1264	43
H(14C)	2380	4228	-1570	43
H(14D)	1857	2946	-1434	43
H(14E)	3169	3307	-1243	43
H(14F)	2110	4286	-1930	43

Table S23. Torsion angles [°] for **8b**.

Br(1)-C(1)-C(2)-C(3)	-177.24(12)
Br(1)-C(1)-C(6)-C(5)	176.50(11)
O(1)-N(1)-C(7)-C(4)	9.8(3)
O(1)-N(1)-C(7)-C(10)	-170.0(2)
O(1)-N(1)-C(8)-C(9)	137.2(3)
O(1)-N(1)-C(8)-C(11)	17.3(3)
O(1)-N(1)-C(8)-C(12)	-101.7(3)
O(1A)-N(1)-C(7)-C(4)	-12.1(5)
O(1A)-N(1)-C(7)-C(10)	168.0(5)
O(1A)-N(1)-C(8A)-C(9A)	-137.1(5)
O(1A)-N(1)-C(8A)-C(11)	-18.4(6)
O(1A)-N(1)-C(8A)-C(12A)	101.6(6)
N(1)-C(7)-C(10)-N(2)	5.4(3)
N(1)-C(8)-C(9)-N(2)	61.6(2)
N(1)-C(8)-C(9)-C(13)	-60.4(2)
N(1)-C(8)-C(9)-C(14)	177.0(4)
N(1)-C(8A)-C(9A)-N(2)	-64.6(3)
N(1)-C(8A)-C(9A)-C(13A)	60.3(4)
N(1)-C(8A)-C(9A)-C(14A)	-177.8(7)
C(1)-C(2)-C(3)-C(4)	0.9(2)
C(2)-C(1)-C(6)-C(5)	-1.6(2)
C(2)-C(3)-C(4)-C(5)	-1.7(2)
C(2)-C(3)-C(4)-C(7)	-178.92(14)
C(3)-C(4)-C(5)-C(6)	1.0(2)
C(3)-C(4)-C(7)-N(1)	-151.68(16)
C(3)-C(4)-C(7)-C(10)	28.2(2)
C(4)-C(5)-C(6)-C(1)	0.7(2)
C(4)-C(7)-C(10)-N(2)	-174.49(17)
C(5)-C(4)-C(7)-N(1)	31.3(2)
C(5)-C(4)-C(7)-C(10)	-148.86(15)
C(6)-C(1)-C(2)-C(3)	0.8(2)
C(7)-N(1)-C(8)-C(9)	-47.0(2)
C(7)-N(1)-C(8)-C(11)	-166.91(17)
C(7)-N(1)-C(8)-C(12)	74.1(2)
C(7)-N(1)-C(8A)-C(9A)	48.6(4)
C(7)-N(1)-C(8A)-C(11)	167.3(2)
C(7)-N(1)-C(8A)-C(12A)	-72.7(4)
C(7)-C(4)-C(5)-C(6)	178.03(14)

C(8)-N(1)-C(7)-C(4)	-165.74(16)
C(8)-N(1)-C(7)-C(10)	14.4(2)
C(8A)-N(1)-C(7)-C(4)	161.6(2)
C(8A)-N(1)-C(7)-C(10)	-18.3(3)
C(9)-N(2)-C(10)-C(7)	13.1(3)
C(9A)-N(2)-C(10)-C(7)	-25.1(3)
C(10)-N(2)-C(9)-C(8)	-47.9(2)
C(10)-N(2)-C(9)-C(13)	74.9(2)
C(10)-N(2)-C(9)-C(14)	-167.5(5)
C(10)-N(2)-C(9A)-C(8A)	56.7(3)
C(10)-N(2)-C(9A)-C(13A)	-67.7(4)
C(10)-N(2)-C(9A)-C(14A)	174.5(6)
C(11)-C(8)-C(9)-N(2)	176.04(17)
C(11)-C(8)-C(9)-C(13)	54.0(3)
C(11)-C(8)-C(9)-C(14)	-68.6(5)
C(11)-C(8A)-C(9A)-N(2)	-179.8(3)
C(11)-C(8A)-C(9A)-C(13A)	-54.9(5)
C(11)-C(8A)-C(9A)-C(14A)	67.0(7)
C(12)-C(8)-C(9)-N(2)	-57.1(2)
C(12)-C(8)-C(9)-C(13)	-179.1(2)
C(12)-C(8)-C(9)-C(14)	58.3(5)
C(12A)-C(8A)-C(9A)-N(2)	57.4(4)
C(12A)-C(8A)-C(9A)-C(13A)	-177.8(4)
C(12A)-C(8A)-C(9A)-C(14A)	-55.9(8)

Symmetry transformations used to generate equivalent atoms:

Table 1. Crystal data and structure refinement for **5i**, **6c**, **7b**, and **8b**.

	5i	**6c**	**7b**	**8b**
Brutto formula	$C_{16}H_{22}N_2O_4$	$C_{14}H_{17}ClN_2O_2$	$C_{14}H_{17}BrN_2O_2$	$C_{14}H_{17}BrN_2O$
Formula weight	306.35	280.74	325.20	309.20
Crystal size, mm	0.1 × 0.04 × 0.03	0.82 × 0.44 × 0.22	0.79 × 0.18 × 0.12	0.38 × 0.27 × 0.17
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
a, Å	10.76900(10)	9.58470(10)	10.54497(6)	12.47732(7)
b, Å	12.7670(2)	11.18550(10)	7.19449(4)	10.43720(5)
c, Å	22.6802(3)	13.06700(10)	18.56940(11)	11.94409(6)
α, °	90	90	90	90
β, °	90	102.1830(10)	100.3895(6)	114.5849(6)
γ, °	90	90	90	90
Volume, Å³	3118.25(7)	1369.36(2)	1385.683(13)	1414.450(14)
Density, gcm^{-3}	1.305	1.362	1.559	1.452
T_{min}/T_{max}	0.81207/1.00000	0.296/1.000	0.426/1.000	0.328/1.000
μ, mm^{-1}	0.773	2.472	4.048	3.880
Space group	Pbca	P 2_1/c	P 2_1/n	P 2_1/c
Z	8	4	4	4
F(000)	1312	592	664	632
Reflections collected	20617	22397	22811	43942
Independent reflections	3415	2983	3026	3082
Observed reflections	3126	2964	3017	3065
Parameters	210	177	181	191
R_{int}	0.0283	0.0315	0.0301	0.0310
$2\theta_{min}$ - $2\theta_{max}$, °	3.898 – 80.784	4.720 – 79.911	4.507 – 80.048	3.896 – 80.001
wR_2 (all reflections)	0.0939	0.0812	0.0696	0.0610
R_1 (I>σ(I))	0.0347	0.0311	0.0270	0.0255
GOF	1.081	1.055	1.099	1.070
ρ_{min}/ρ_{max}, eÅ^{-3}	–0.188/0.328	–0.204/0.371	–0.469/0.474	–0.425/0.470
Restraints	0	0	0	6