Supplementary information

Construction of a 1,2-diazetidine core based on a multicomponent reaction of *N*,*N*′-(2,3-dimethylbutane-2,3-diyl)bis(hydroxylamine), arylglyoxals, and Meldrum's acid

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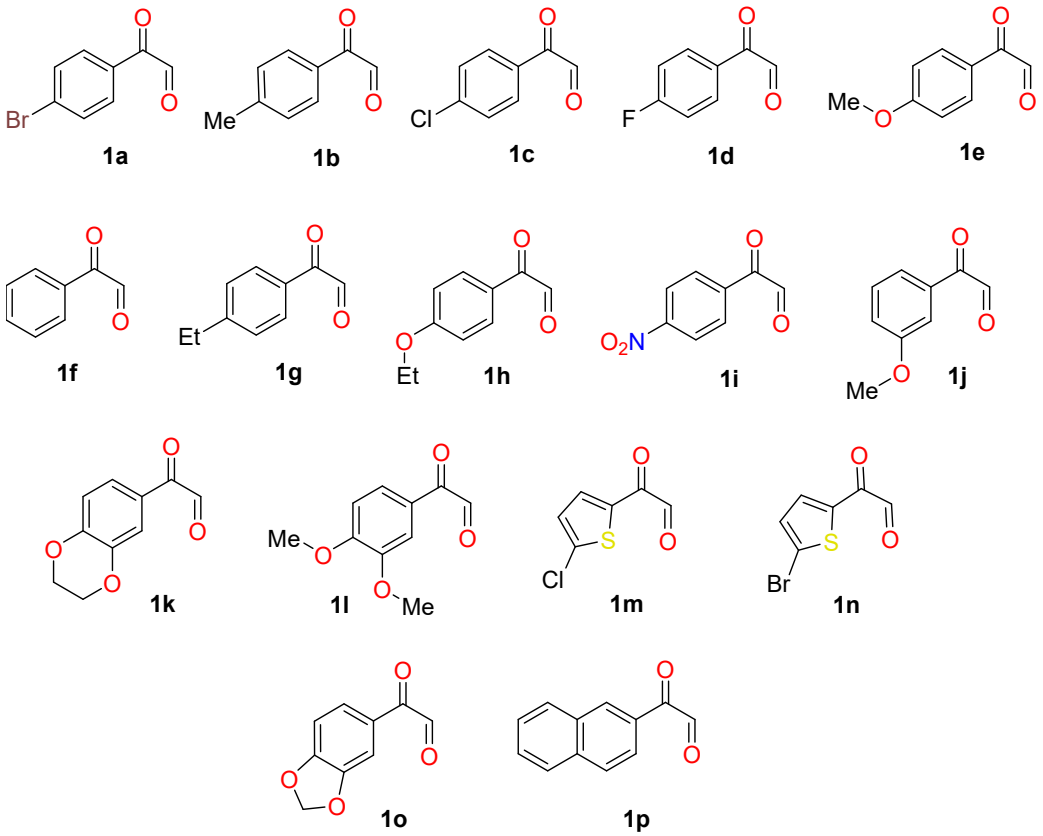
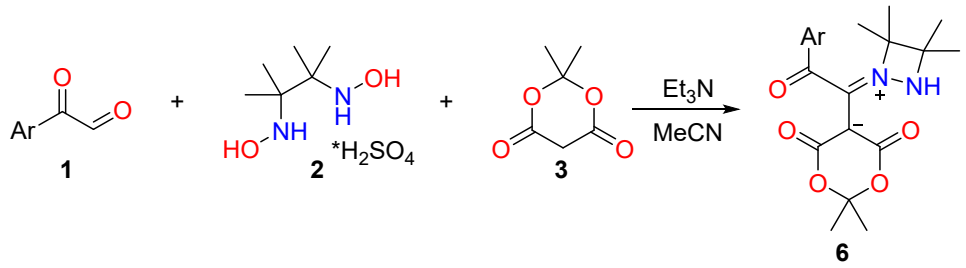
1. General Information

Arylglyoxals **1a-p** were prepared by the known literature method were prepared by the known literature method.[1] *N*,*N*′-(2,3-Dimethylbutane-2,3-diyl)bis(hydroxylamine) sulfate **2** was synthesized according with a previously described procedure.[2] Other chemicals were commercially available and were used as received. NMR spectra were recorded with Bruker AM 300 (300 MHz) spectrometers in DMSO-d_6. Chemical shifts (ppm) are given relative to solvent signals (DMSO-d_6: 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.

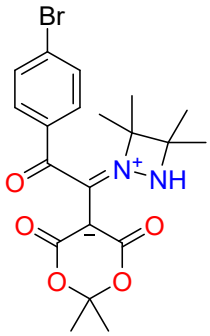


1. N. A. Bakuleva, B. V. Lichitsky, D. V. Tsyganov, A. N. Komogortsev, V. G. Melekhina and E. V. Tretyakov, Synthesis of substituted 5-aryl-2,3-dihydropyrazine1,4-dioxides based on condensation of *N*,*N*'-(2,3-dimethylbutane-2,3-diyl)bis(hydroxylamine) with various arylglyoxals, *J. Heterocycl. Chem.*, 2024, **61**, 1057–1065.
2. V. I. Ovcharenko, S. V. Fokin, G. V. Romanenko, I. V. Korobkov and P. Rey, Synthesis of vicinal bishydroxylamine, *Russ. Chem. Bull.,* 1999, **48**, 1519–1525.

2. General Experimental Procedure and Characterization of 2,2-Dimethyl-5-(2-oxo-2-aryl-1-(3,3,4,4-tetramethyl-1,2-diazetidin-1-yl)ethylidene)-1,3-dioxane-4,6-diones 6a-p



A mixture of appropriate arylglyoxal **1** (1 mmol), Meldrum's acid **3** (1.1 mmol, 0.16 g), and Et_3N (8 mmol, 0.81 g) was stirred in MeCN (2 ml) at r.t. for 15 min. Next, *N*,*N*′-(2,3-dimethylbutane-2,3-diyl)bis (hydroxylamine) sulfate **2** (1.7 mmol, 0.42 g) was added, and the mixture was stirred for 3 h at r.t. Then, the resulting solution was acidified with acetic acid (10 mmol, 0.6 g) and diluted with water (4 ml). The precipitated product was filtered off and washed with 25% aqueous MeCN (3 × 5 ml).



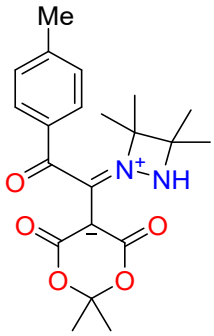
(E)-5-(2-(4-bromophenyl)-2-oxo-1-(3,3,4,4-tetramethyl-1,2-diazetidin-1-ium-1-ylidene)ethyl)-2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ide **6a**

Gray powder; yield 45% (0.20 g); mp 212-214 °C.

^{1}H NMR (300 MHz, DMSO-d_6) δ 7.87 (s, 1H), 7.82 (d, J = 8.2 Hz, 2H), 7.69 (d, J = 8.3 Hz, 2H), 1.65 – 1.38 (m, 18H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 186.08, 149.31, 134.69, 132.36, 129.91, 128.58, 103.18, 83.67, 78.44, 63.33, 25.82, 22.57.

HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{20}H_{24}BrN_2O_5$: 451.0863; Found: 451.0851.



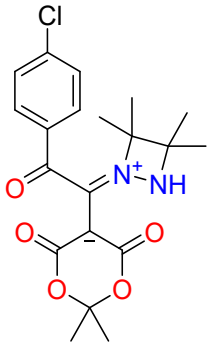
(E)-2,2-dimethyl-4,6-dioxo-5-(2-oxo-1-(3,3,4,4-tetramethyl-1,2-diazetidin-1-ium-1-ylidene)-2-(p-tolyl)ethyl)-1,3-dioxan-5-ide **6b**

Gray powder; yield 41% (0.16 g); mp 158-160 °C.

^{1}H NMR (300 MHz, DMSO-d_6) δ 7.81 (br. s, 1H), 7.66 (d, J = 7.8 Hz, 2H), 7.39 (d, J = 7.8 Hz, 2H), 2.40 (s, 3H), 1.79 – 1.20 (m, 18H).

^{13}C NMR (76 MHz, DMSO-d_6) δ 186.37, 161.70, 145.12, 133.30, 129.65, 128.24, 102.91, 83.38, 78.48, 63.15, 25.60, 22.57, 21.34.

HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{21}H_{27}N_2O_5$: 387.1920; Found: 387.1904.



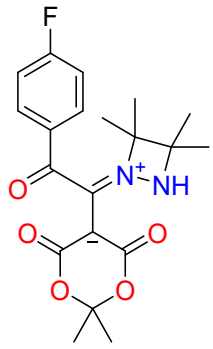
(E)-5-(2-(4-chlorophenyl)-2-oxo-1-(3,3,4,4-tetramethyl-1,2-diazetidin-1-ium-1-ylidene)ethyl)-2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ide **6c**

Gray powder; yield 44% (0.18 g); mp 210-212 °C.

^{1}H NMR (300 MHz, DMSO-d_6) δ 7.84 (s, 1H), 7.76 (d, J = 8.3 Hz, 2H), 7.65 (d, J = 8.2 Hz, 2H), 1.64 – 1.38 (m, 18H).

^{13}C NMR (76 MHz, DMSO-d_6) δ 185.59, 138.99, 134.31, 129.63, 129.09, 102.83, 83.53, 78.43, 63.03, 25.45, 23.42, 22.34.

HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{20}H_{24}ClN_2O_5$: 407.1368; Found: 407.1360.



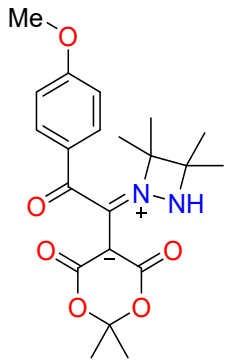
(E)-5-(2-(4-fluorophenyl)-2-oxo-1-(3,3,4,4-tetramethyl-1,2-diazetidin-1-ium-1-ylidene)ethyl)-2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ide **6d**

Gray powder; yield 38% (0.15 g); mp 190-192 °C.

^{1}H NMR (300 MHz, DMSO-d_6) δ 7.88 – 7.78 (m, 3H), 7.47 – 7.35 (m, 2H), 1.64 – 1.34 (m, 18H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 185.49, 165.51 (d, J = 253.9 Hz), 149.67, 132.43 (d, J = 2.8 Hz), 131.18 (d, J = 9.8 Hz), 116.46 (d, J = 22.4 Hz), 103.12, 83.60, 78.43, 63.28, 25.70, 23.19.

HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{20}H_{24}FN_2O_5$: 391.1664; Found: 391.1660.



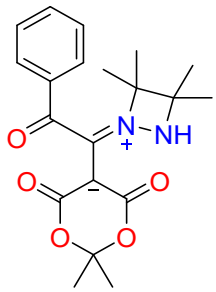
(E)-5-(2-(4-methoxyphenyl)-2-oxo-1-(3,3,4,4-tetramethyl-1,2-diazetidin-1-ium-1-ylidene)ethyl)-2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ide **6e**

Gray powder; yield 42% (0.17 g); mp 160-162 °C.

^{1}H NMR (300 MHz, DMSO-d_6) δ 7.77 – 7.67 (m, 3H), 7.09 (d, J = 8.5 Hz, 2H), 3.85 (s, 3H), 1.68 – 1.32 (m, 18H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 185.26, 164.05, 150.70, 130.61, 128.57, 114.50, 102.86, 83.23, 78.53, 63.07, 55.75, 26.37, 21.59.

HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{21}H_{27}N_2O_6$: 403.1864; Found: 403.1855.



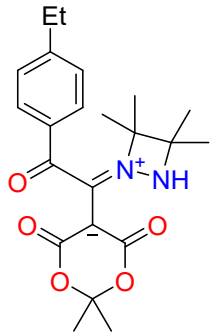
(E)-2,2-dimethyl-4,6-dioxo-5-(2-oxo-2-phenyl-1-(3,3,4,4-tetramethyl-1,2-diazetidin-1-ium-1-ylidene)ethyl)-1,3-dioxan-5-ide **6f**

Gray powder; yield 38% (0.14 g); mp 193-195 °C.

^{1}H NMR (300 MHz, DMSO-d_6) δ 7.87 – 7.52 (m, 6H), 1.66 – 1.37 (m, 18H).

^{13}C NMR (76 MHz, DMSO-d_6) δ 186.84, 161.51, 150.14, 135.63, 134.37, 129.11, 128.11, 103.03, 83.49, 78.54, 63.19, 25.58, 22.55.

HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{20}H_{25}N_2O_5$: 373.1758; Found: 373.1761.



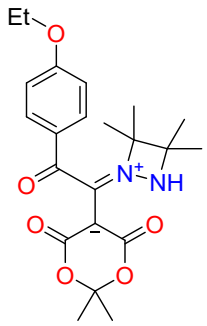
(E)-5-(2-(4-ethylphenyl)-2-oxo-1-(3,3,4,4-tetramethyl-1,2-diazetidin-1-ium-1-ylidene)ethyl)-2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ide **6g**

Gray powder; yield 34% (0.14 g); mp 205-207 °C.

^{1}H NMR (300 MHz, DMSO-d_6) δ 7.79 (s, 1H), 7.67 (d, J = 7.8 Hz, 2H), 7.40 (d, J = 7.9 Hz, 2H), 2.68 (q, J = 7.6 Hz, 2H), 1.66 – 1.34 (m, 18H), 1.20 (t, J = 7.5 Hz, 3H).

^{13}C NMR (76 MHz, DMSO-d_6) δ 186.43, 151.05, 150.45, 133.46, 128.52, 128.34, 102.97, 83.39, 78.55, 63.15, 28.31, 25.64, 22.58, 14.90.

HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{22}H_{29}N_2O_5$: 401.2071; Found: 401.2069.



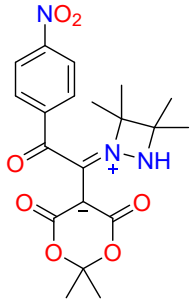
(E)-5-(2-(4-ethoxyphenyl)-2-oxo-1-(3,3,4,4-tetramethyl-1,2-diazetidin-1-ium-1-ylidene)ethyl)-2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ide **6h**

Gray powder; yield 33% (0.14 g); mp 178-180 °C.

^{1}H NMR (300 MHz, DMSO-d_6) δ 7.83 – 7.59 (m, 3H), 7.07 (d, J = 9.0 Hz, 2H), 4.13 (q, J = 6.9 Hz, 2H), 1.63 – 1.25 (m, 21H).

^{13}C NMR (76 MHz, DMSO-d_6) δ 185.26, 163.43, 150.83, 130.68, 128.44, 114.84, 102.88, 83.28, 78.59, 63.88, 63.08, 25.62, 22.46, 14.50.

HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{22}H_{29}N_2O_6$: 417.2020; Found: 417.2014.



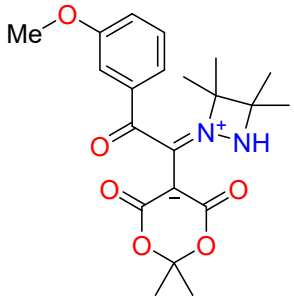
(E)-2,2-dimethyl-5-(2-(4-nitrophenyl)-2-oxo-1-(3,3,4,4-tetramethyl-1,2-diazetidin-1-ium-1-ylidene)ethyl)-4,6-dioxo-1,3-dioxan-5-ide **6i**

Gray powder; yield 45% (0.18 g); mp 200-202 °C.

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.39 (d, J = 8.4 Hz, 2H), 8.01 (d, J = 8.4 Hz, 2H), 7.96 (s, 1H), 1.69 – 1.18 (m, 18H).

^{13}C NMR (76 MHz, DMSO) δ 185.77, 150.46, 148.54, 140.12, 129.39, 124.41, 103.46, 84.06, 78.40, 63.54, 25.34, 22.52.

HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{20}H_{24}N_3O_7$: 418.1609; Found: 418.1599.



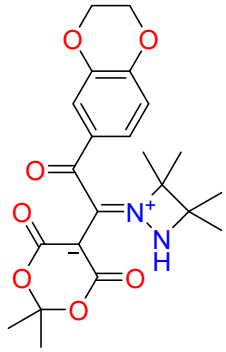
(E)-5-(2-(3-methoxyphenyl)-2-oxo-1-(3,3,4,4-tetramethyl-1,2-diazetidin-1-ium-1-ylidene)ethyl)-2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ide **6j**

Gray powder; yield 39% (0.16 g); mp 156-158 °C.

^{1}H NMR (300 MHz, DMSO-d_6) δ 7.77 (br. s, 1H), 7.55 – 7.43 (m, 1H), 7.33 – 7.23 (m, 3H), 3.81 (s, 3H), 1.73 – 1.22 (m, 18H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 186.54, 159.51, 150.13, 136.97, 130.53, 120.82, 120.42, 112.49, 103.20, 83.60, 78.71, 63.32, 55.49, 26.23, 22.33.

HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{21}H_{27}N_2O_6$: 403.1864; Found: 403.1867.



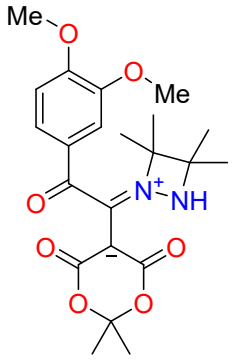
(E)-5-(2-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-2-oxo-1-(3,3,4,4-tetramethyl-1,2-diazetidin-1-ium-1-ylidene)ethyl)-2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ide **6k**

Gray powder; yield 41% (0.18 g); mp 208-210 °C.

^{1}H NMR (300 MHz, DMSO-d_6) δ 7.71 (s, 1H), 7.29 – 7.18 (m, 2H), 7.02 (d, J = 8.5 Hz, 1H), 4.34 – 4.30 (m, 4H), 1.87 – 0.90 (m, 18H).

^{13}C NMR (76 MHz, DMSO-d_6) δ 185.06, 161.41, 150.43, 149.06, 143.40, 129.15, 122.45, 117.69, 116.75, 102.94, 83.33, 78.62, 64.69, 63.98, 63.12, 25.59, 22.53.

HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{22}H_{27}N_2O_7$: 431.1813; Found: 431.1808.



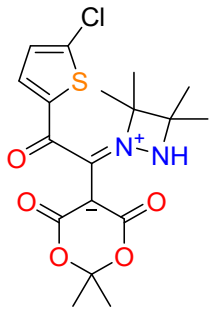
(E)-5-(2-(3,4-dimethoxyphenyl)-2-oxo-1-(3,3,4,4-tetramethyl-1,2-diazetidin-1-ium-1-ylidene)ethyl)-2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ide **6l**

Gray powder; yield 37% (0.16 g); mp 215-217 °C.

^{1}H NMR (300 MHz, DMSO-d_6) δ 7.72 (s, 1H), 7.37 (s, 1H), 7.29 (d, J = 8.4 Hz, 1H), 7.14 (d, J = 8.4 Hz, 1H), 3.87 (s, 3H), 3.83 (s, 3H), 2.00 – 0.86 (m, 18H).

^{13}C NMR (76 MHz, DMSO-d_6) δ 185.15, 161.41, 154.14, 150.85, 148.96, 128.57, 123.53, 111.20, 109.60, 102.86, 83.27, 78.79, 63.08, 55.95, 55.54, 25.61, 22.82.

HRMS (ESI-TOF) *m/z*: [M+H]$^+$ Calcld for $C_{22}H_{29}N_2O_7$: 433.1969; Found: 433.1966.



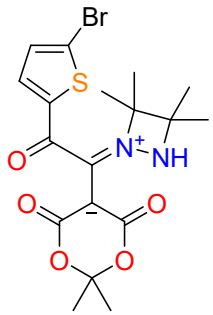
(E)-5-(2-(5-chlorothiophen-2-yl)-2-oxo-1-(3,3,4,4-tetramethyl-1,2-diazetidin-1-ium-1-ylidene)ethyl)-2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ide **6m**

Gray powder; yield 34% (0.14 g); mp 188-190 °C.

^{1}H NMR (300 MHz, DMSO-d_6) δ 7.77 (s, 1H), 7.52 (d, J = 4.1 Hz, 1H), 7.33 (d, J = 4.1 Hz, 1H), 1.66 – 1.32 (m, 18H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 178.22, 162.66, 148.05, 140.59, 139.34, 134.25, 129.51, 103.30, 83.98, 78.39, 63.46, 25.69, 22.54.

HRMS (ESI-TOF) *m/z*: [M+H]$^+$ Calcld for $C_{18}H_{22}ClN_2O_5S$: 413.0932; Found: 413.0925.



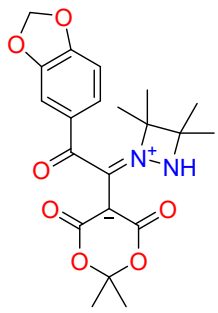
(E)-5-(2-(5-bromothiophen-2-yl)-2-oxo-1-(3,3,4,4-tetramethyl-1,2-diazetidin-1-ium-1-ylidene)ethyl)-2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ide **6n**

Gray powder; yield 43% (0.20 g); mp 184-186 °C.

^{1}H NMR (300 MHz, DMSO-d_6) δ 7.76 (s, 1H), 7.46 (d, J = 4.2 Hz, 1H), 7.42 (d, J = 4.1 Hz, 1H), 1.64 – 1.34 (m, 18H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 178.00, 148.19, 143.25, 134.84, 132.92, 123.86, 103.33, 84.01, 78.39, 63.49, 24.39, 22.57.

HRMS (ESI-TOF) *m/z*: [M+H]$^+$ Calcld for $C_{18}H_{22}BrN_2O_5S$: 457.0427; Found: 457.0420.



(E)-5-(2-(benzo[d][1,3]dioxol-5-yl)-2-oxo-1-(3,3,4,4-tetramethyl-1,2-diazetidin-1-ium-1-ylidene)ethyl)-2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ide **6o**

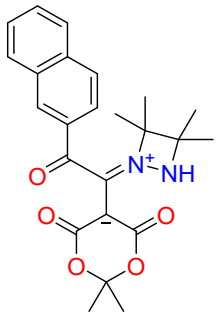
Gray powder; yield 42% (0.18 g); mp 196-198 °C.

^{1}H NMR (300 MHz, DMSO-d_6) δ 7.73 (s, 1H), 7.32 – 7.21 (m, 2H), 7.07 (d, J = 8.1 Hz, 1H), 6.17 (s, 2H), 1.87 – 0.95 (m, 18H).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.48 – 7.30 (m, 2H), 6.81 (d, J = 8.1 Hz, 1H), 6.04 (s, 2H), 1.84 (s, 3H), 1.69 – 1.53 (m, 9H), 1.38 (s, 3H), 1.21 (s, 3H).

^{13}C NMR (76 MHz, DMSO-d_6) δ 184.91, 161.48, 152.67, 150.41, 148.22, 130.33, 125.40, 108.48, 106.92, 102.96, 102.60, 83.40, 78.68, 63.15, 25.62, 22.71.

HRMS (ESI-TOF) *m/z*: [M+H]$^+$ Calcld for $C_{21}H_{25}N_2O_7$:417.1656; Found: 417.1646.



(E)-2,2-dimethyl-5-(2-(naphthalen-2-yl)-2-oxo-1-(3,3,4,4-tetramethyl-1,2-diazetidin-1-ium-1-ylidene)ethyl)-4,6-dioxo-1,3-dioxan-5-ide **6p**

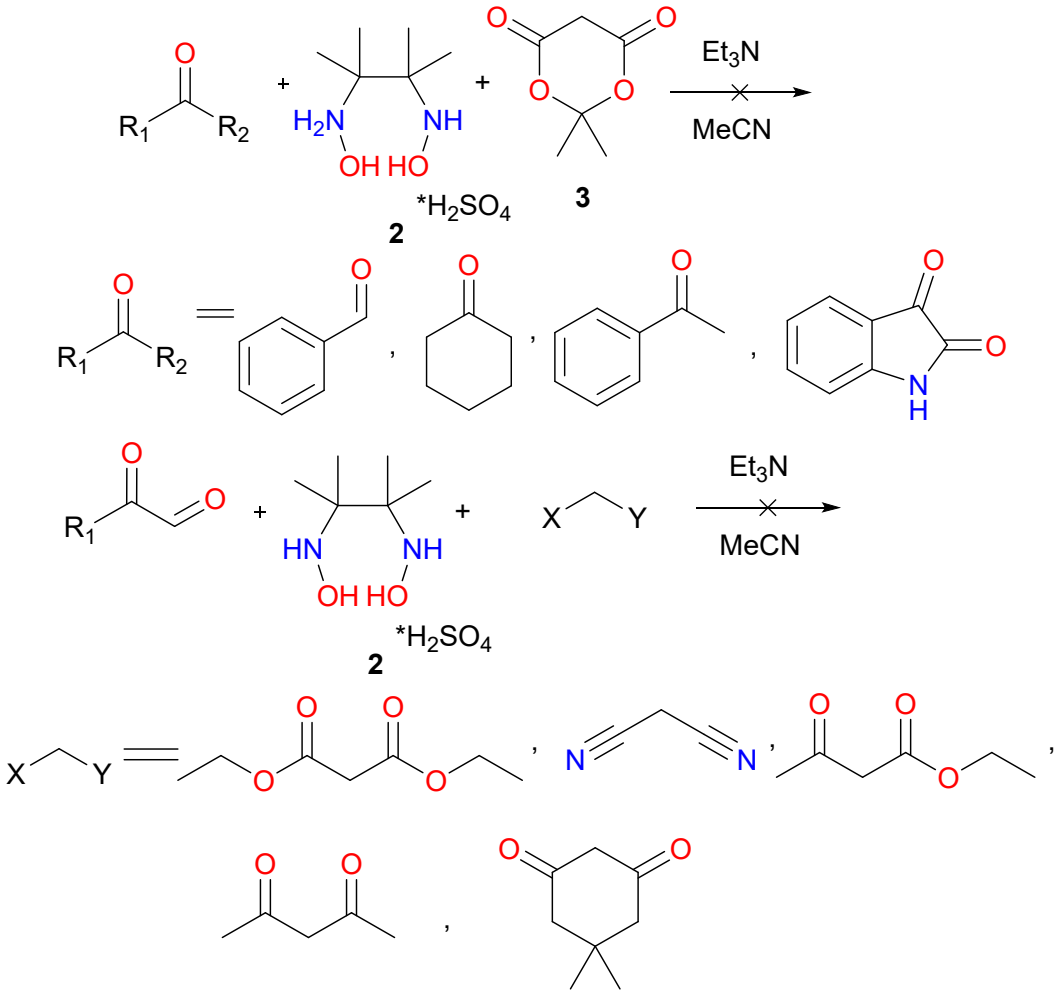
Gray powder; yield 32% (0.14 g); mp 207-209 °C.

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.34 (s, 1H), 8.16 – 7.96 (m, 3H), 7.90 (s, 1H), 7.81 (d, J = 8.5 Hz, 1H), 7.77 – 7.59 (m, 2H), 1.97 – 0.88 (m, 18H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 186.94, 150.29, 135.57, 133.20, 131.91, 130.03, 129.96, 129.56, 129.05, 127.97, 127.58, 123.56, 103.19, 83.69, 78.77, 63.37, 25.47, 22.57.

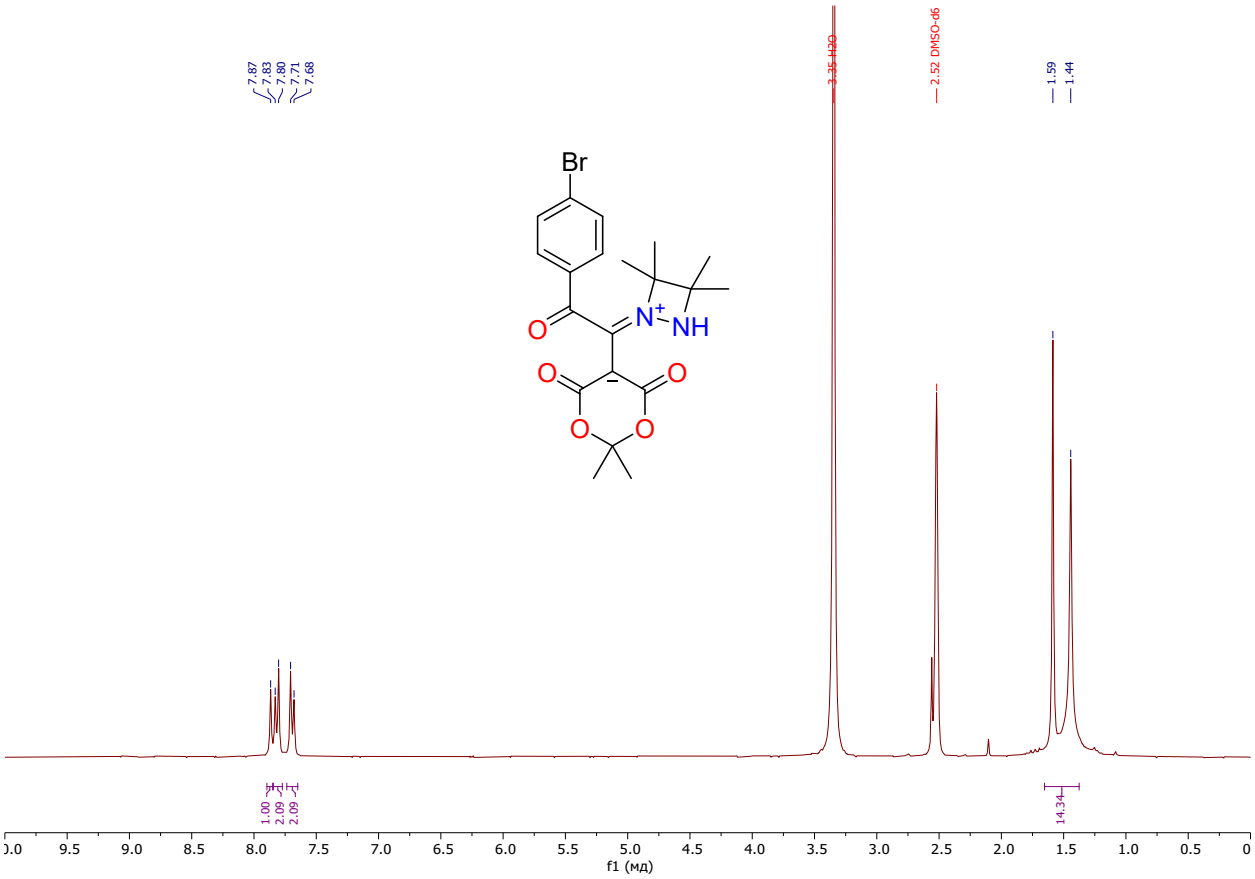
HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{24}H_{27}N_2O_5$: 423.1914; Found: 423.1901.

3. Unsuccessful experiments.

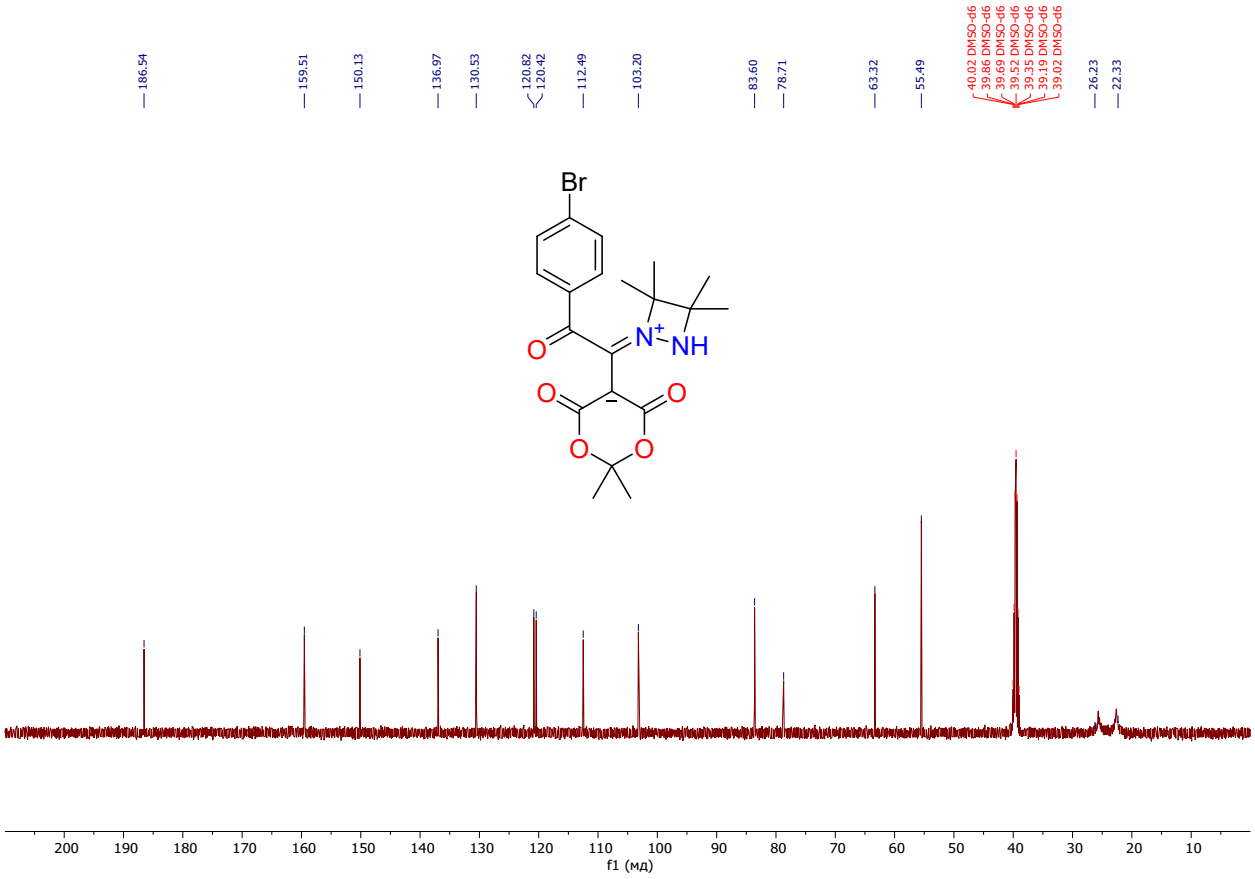


4. Copies of ^{1}H, ^{13}C NMR and HRMS for Compounds 6a-p

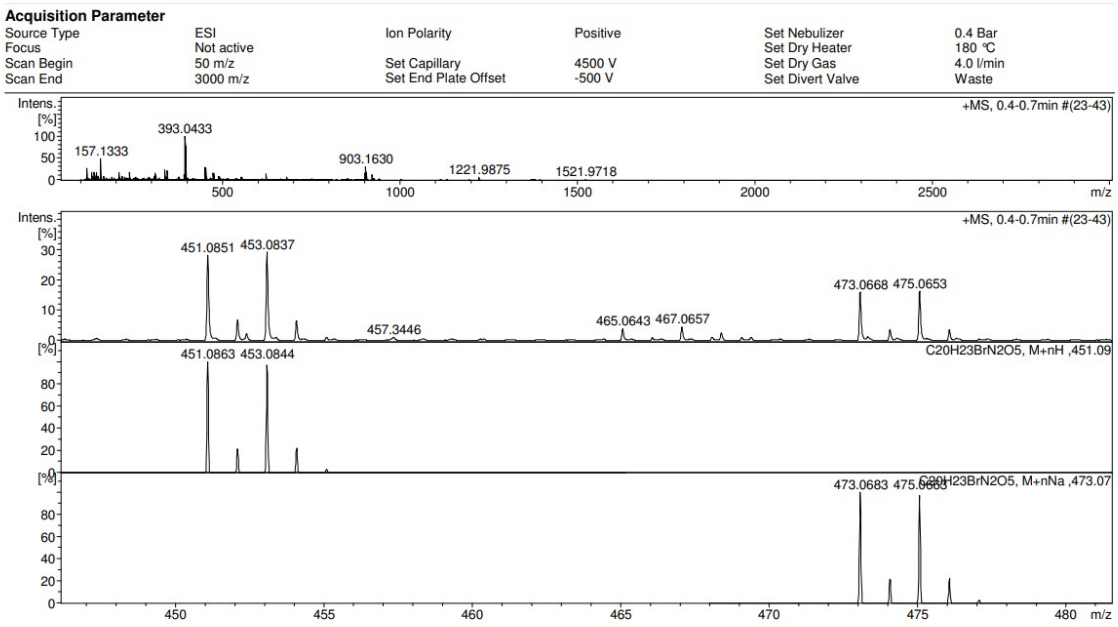
^{1}H NMR spectrum (300 MHz) of **6a** in DMSO-d_6



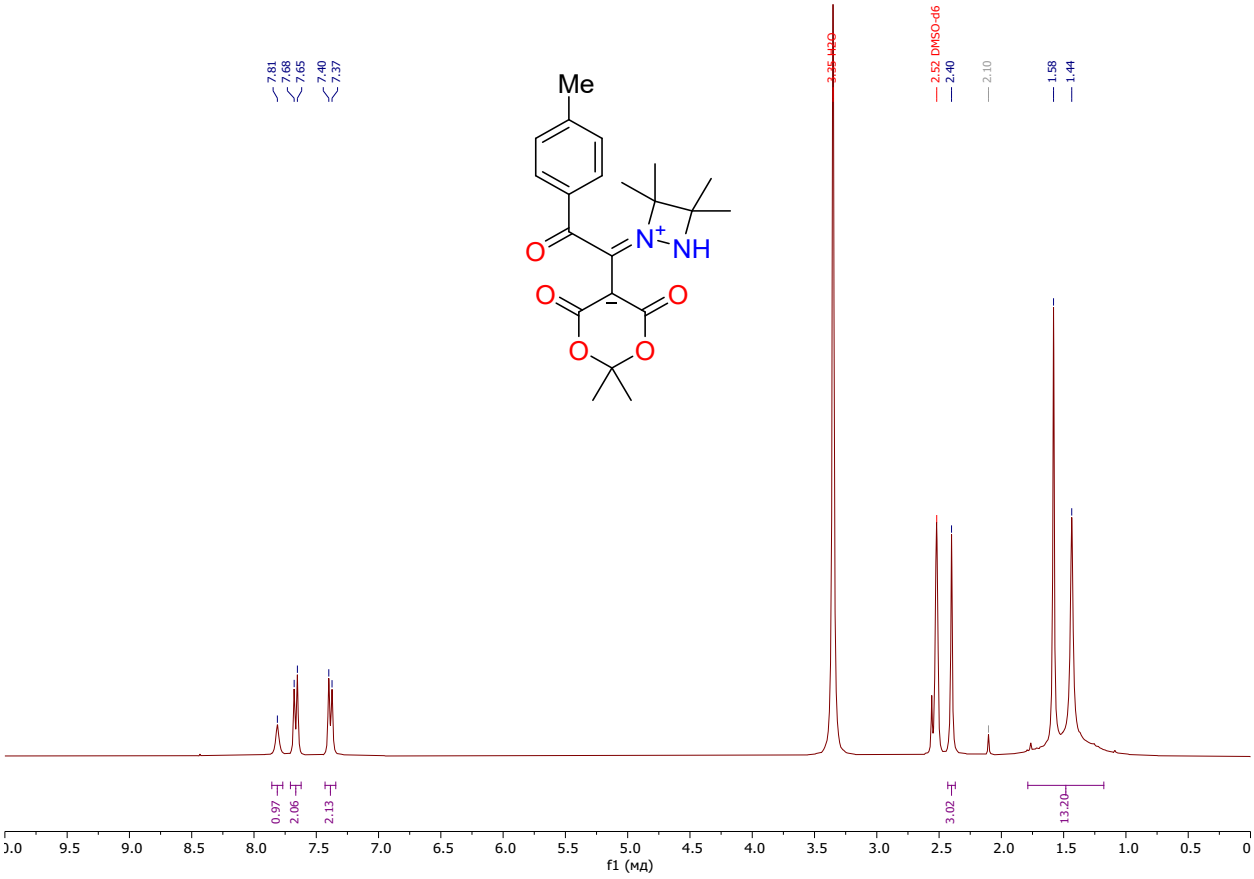
^{13}C {^{1}H} NMR spectrum (76 MHz) of **6a** in DMSO-d_6



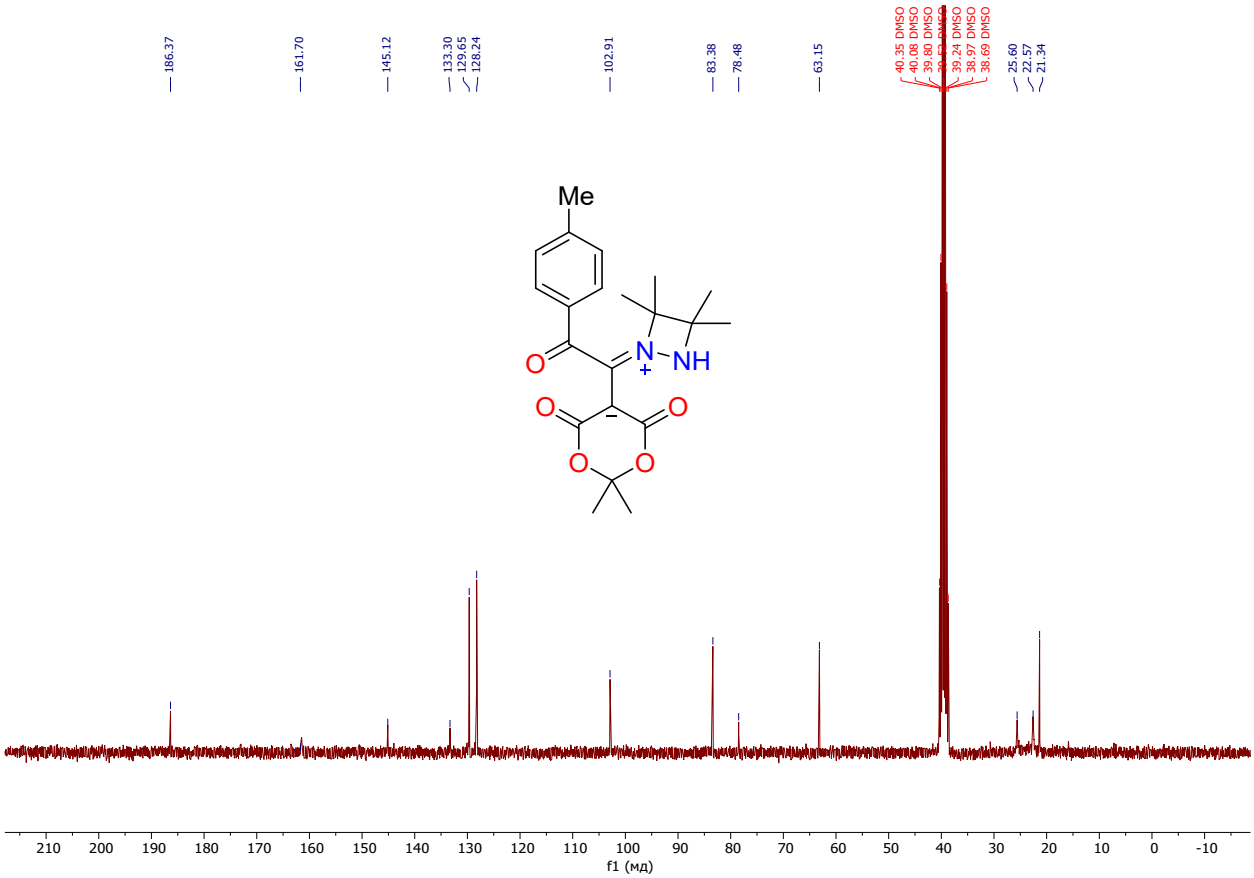
HRMS for compound **6a**



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



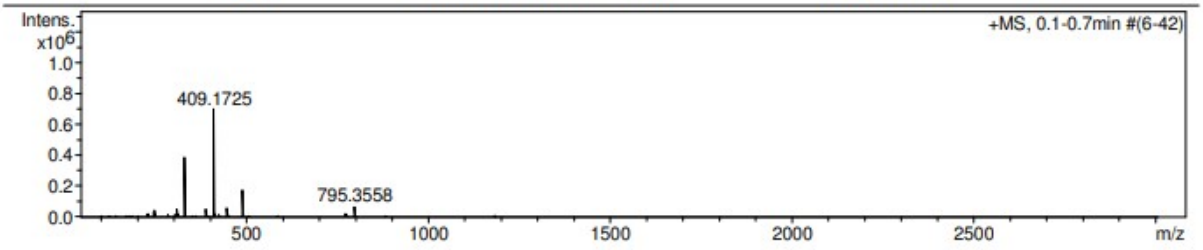
^{13}C {^{1}H} NMR spectrum (76 MHz) of **6b** in DMSO-d_6

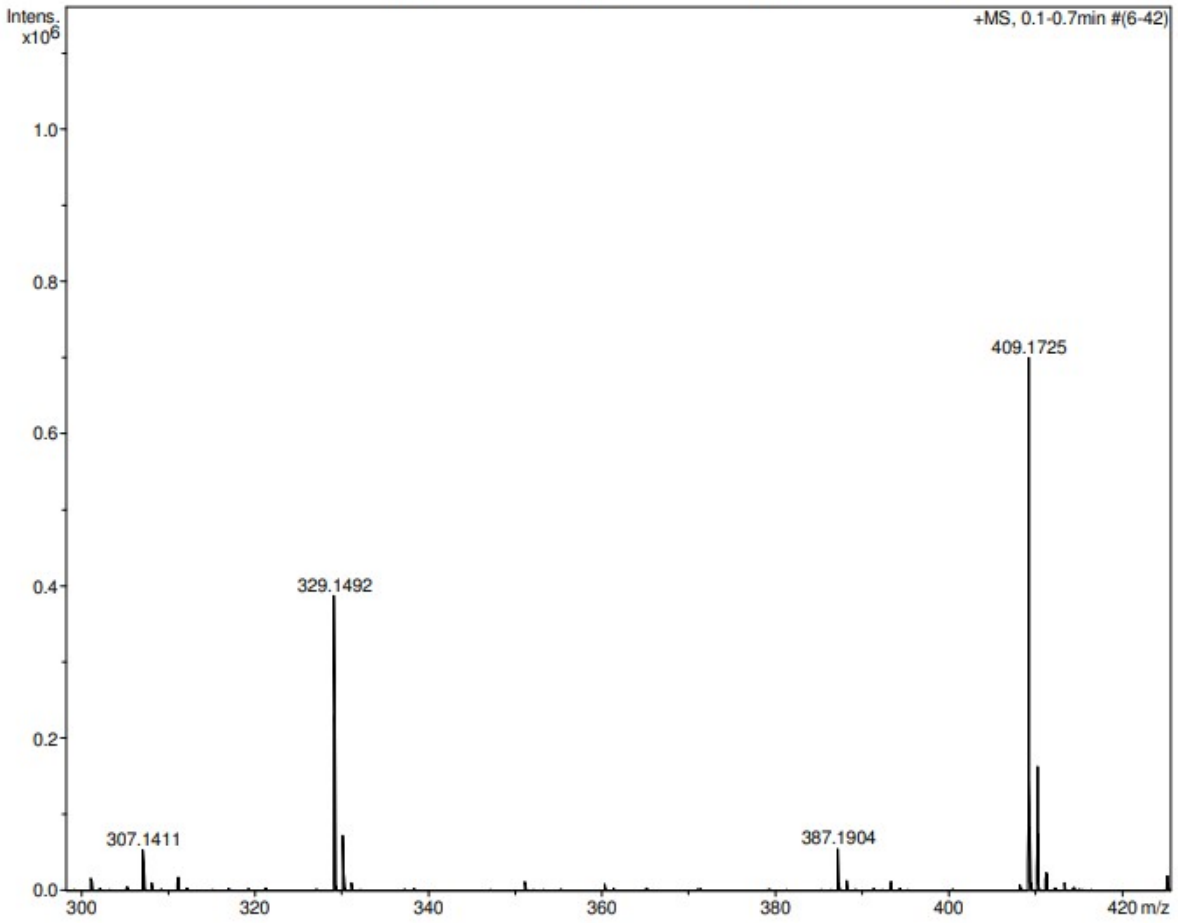


HRMS for compound **6b**

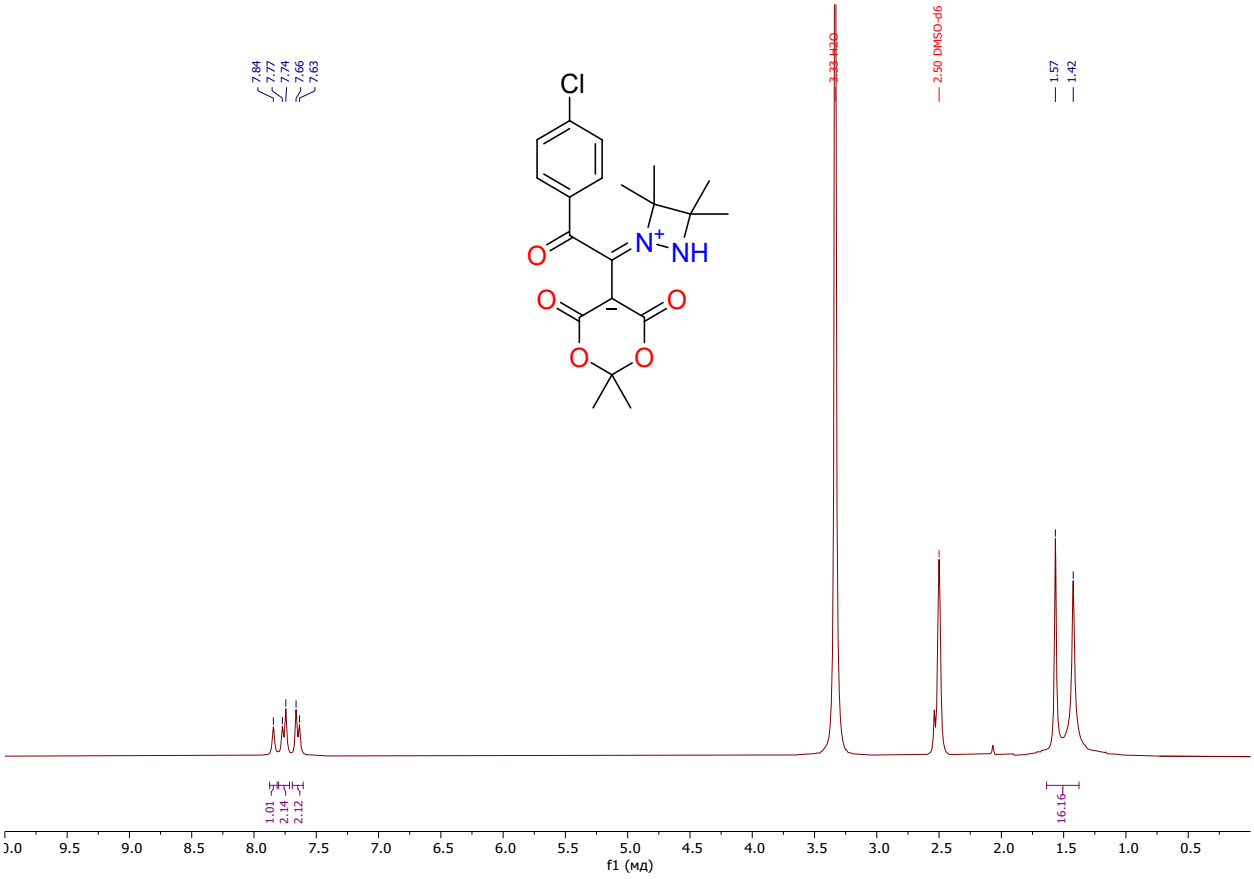
Acquisition Parameter

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

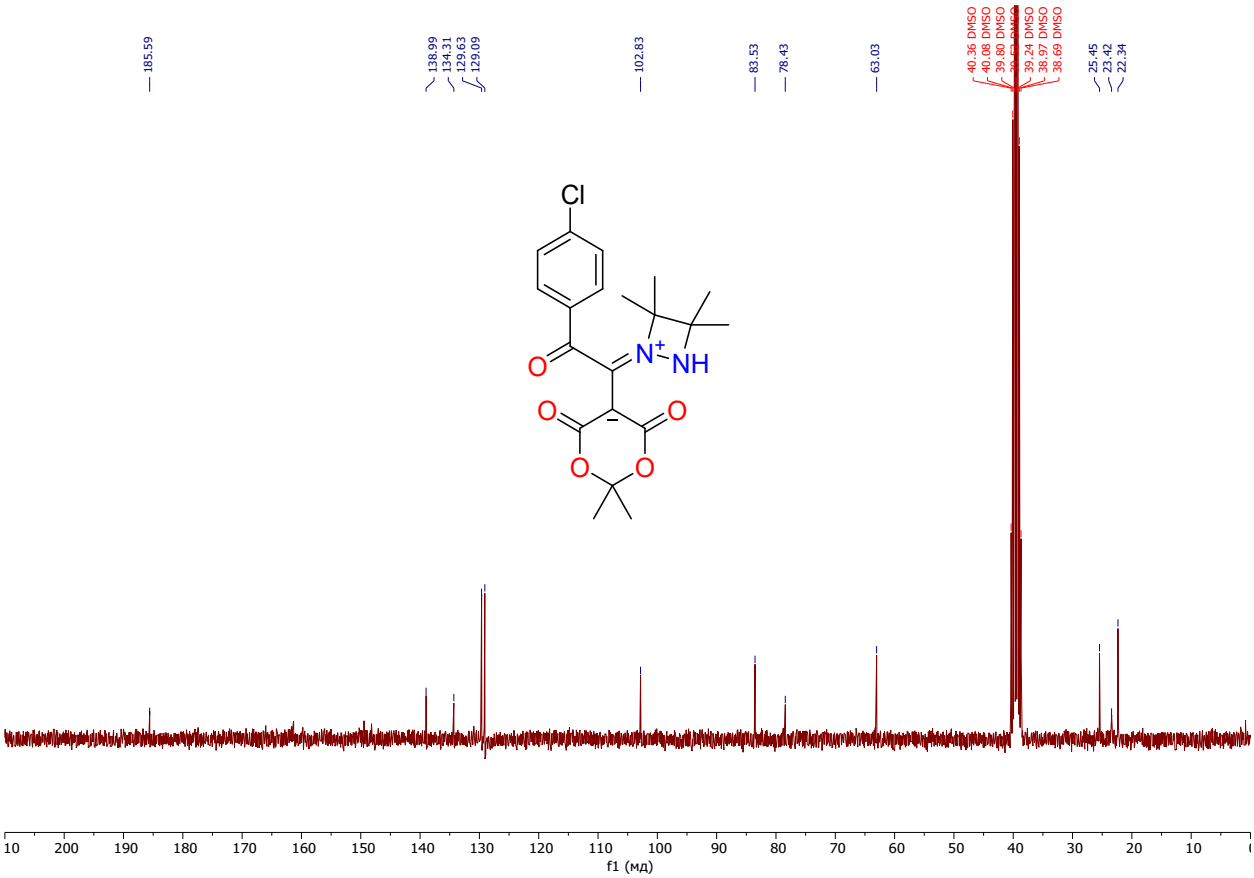




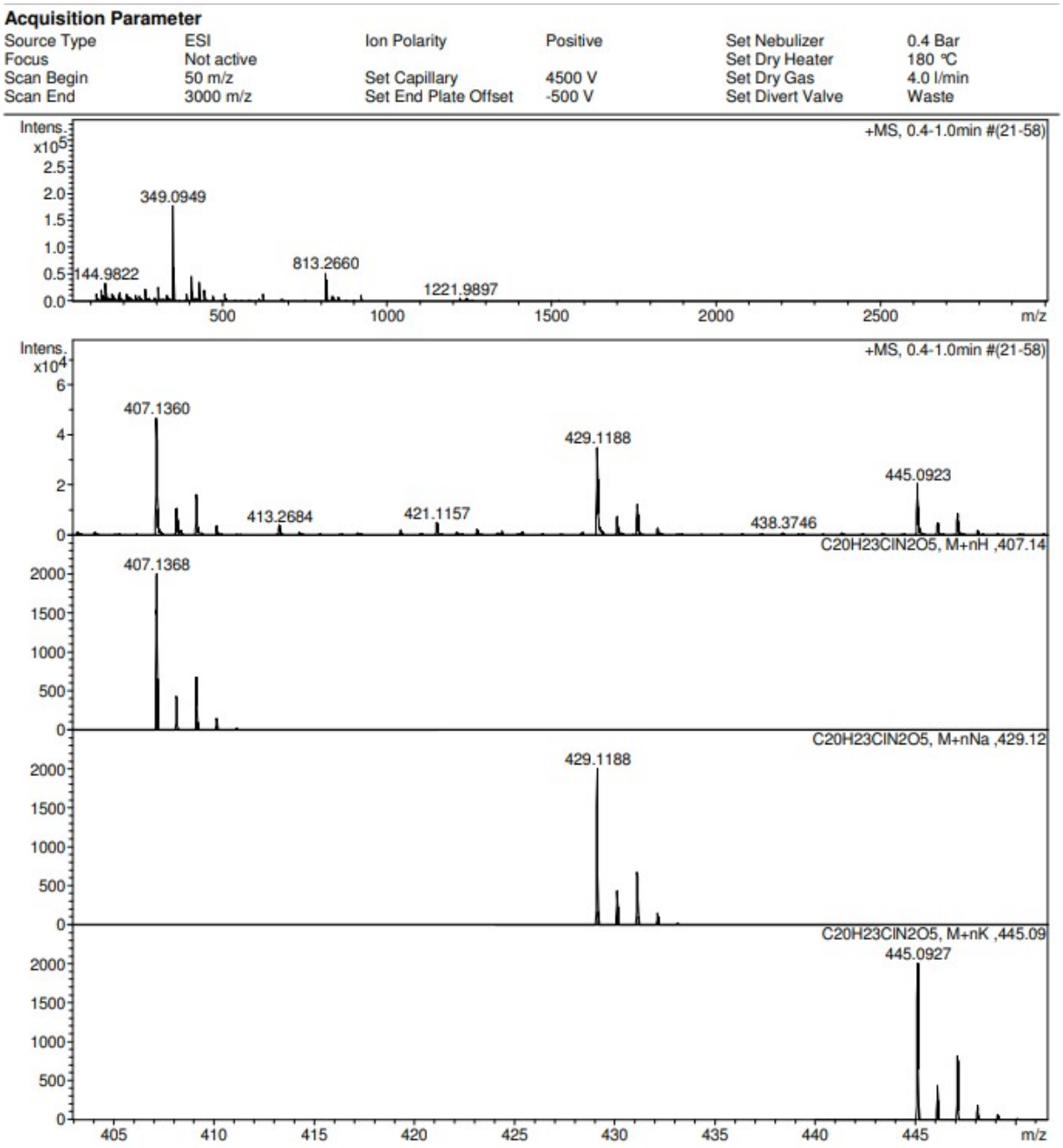
^{1}H NMR spectrum (300 MHz) of **6c** in DMSO-d_6



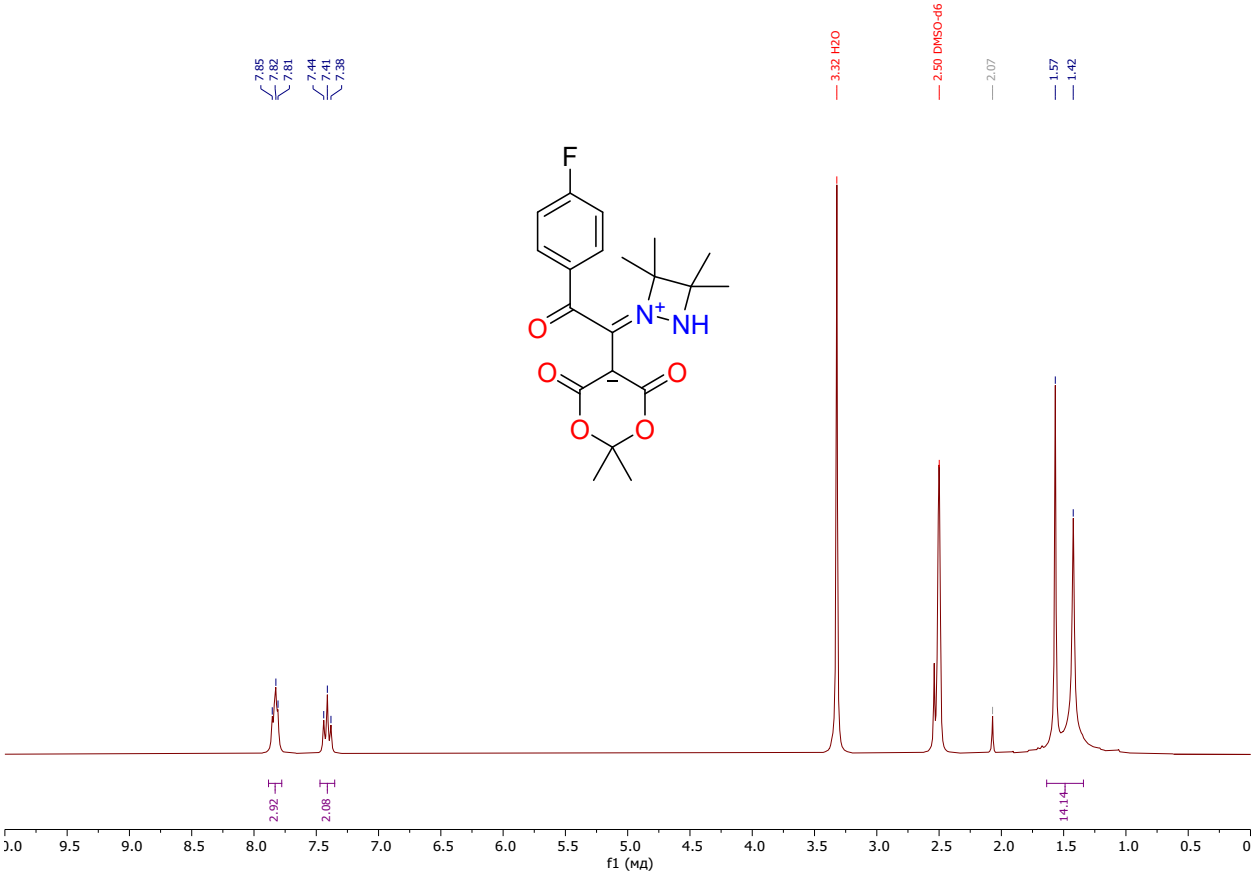
^{13}C {^{1}H} NMR spectrum (76 MHz) of **6c** in DMSO-d_6



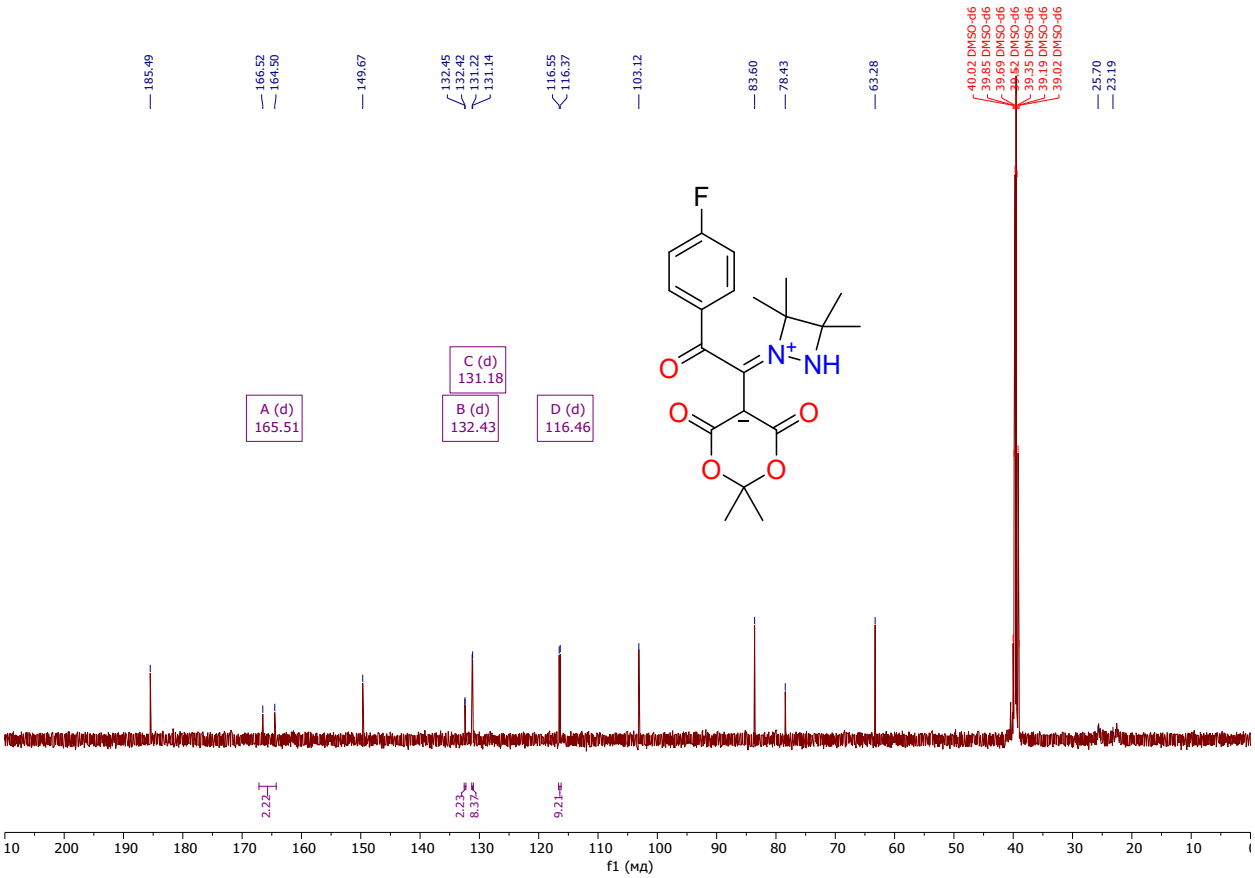
HRMS for compound **6c**



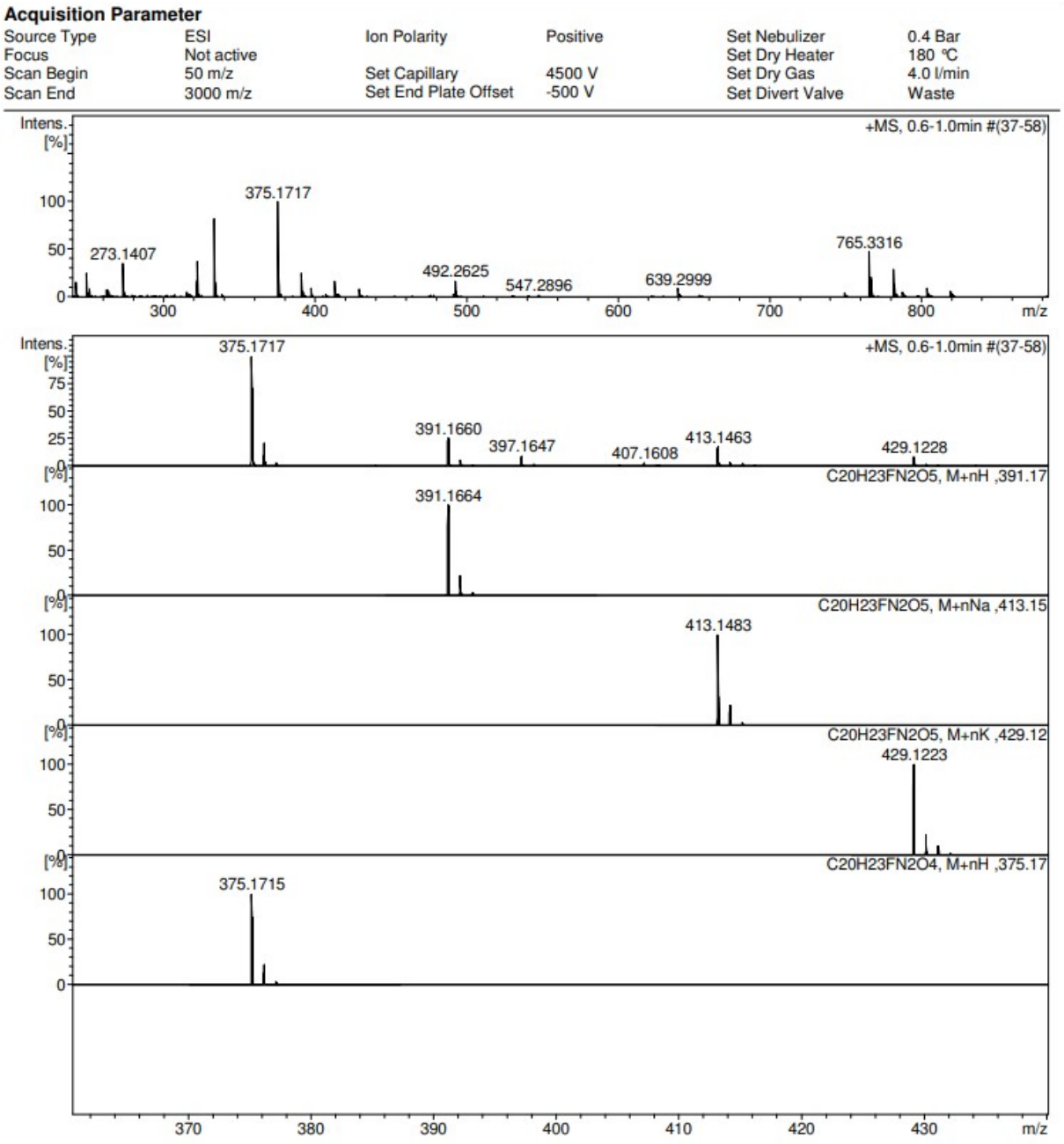
^{1}H NMR spectrum (300 MHz) of **6d** in DMSO-d_6



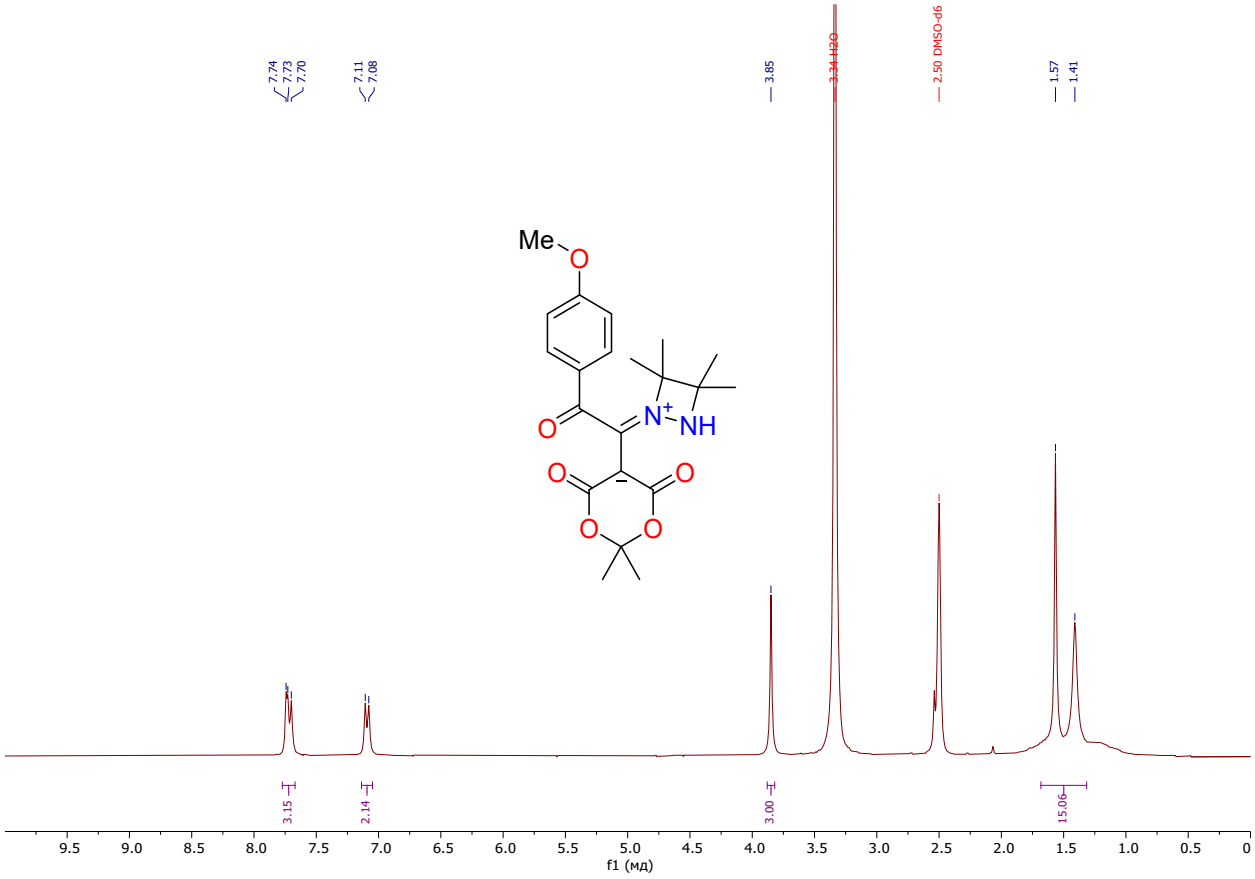
^{13}C {^{1}H} NMR spectrum (76 MHz) of **6d** in DMSO-d_6



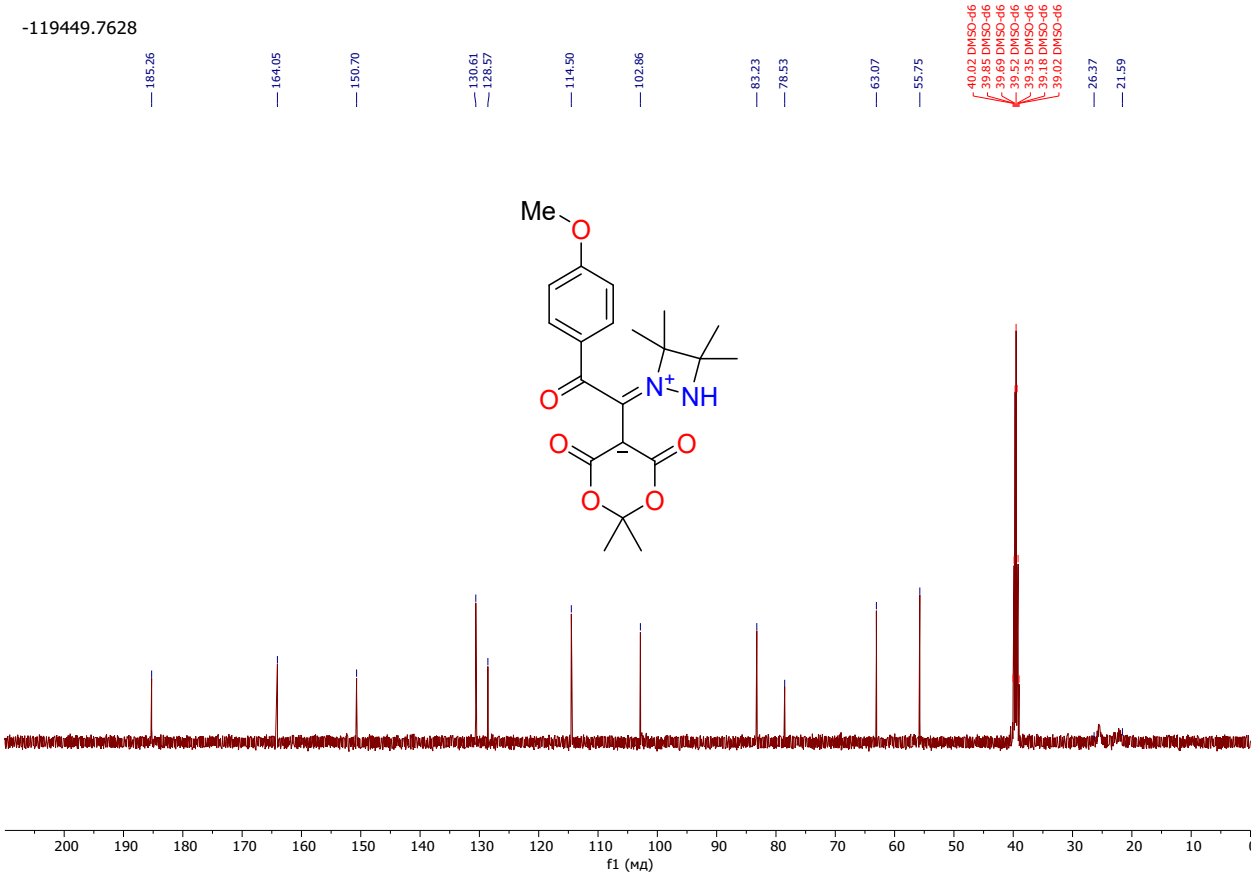
HRMS for compound **6d**



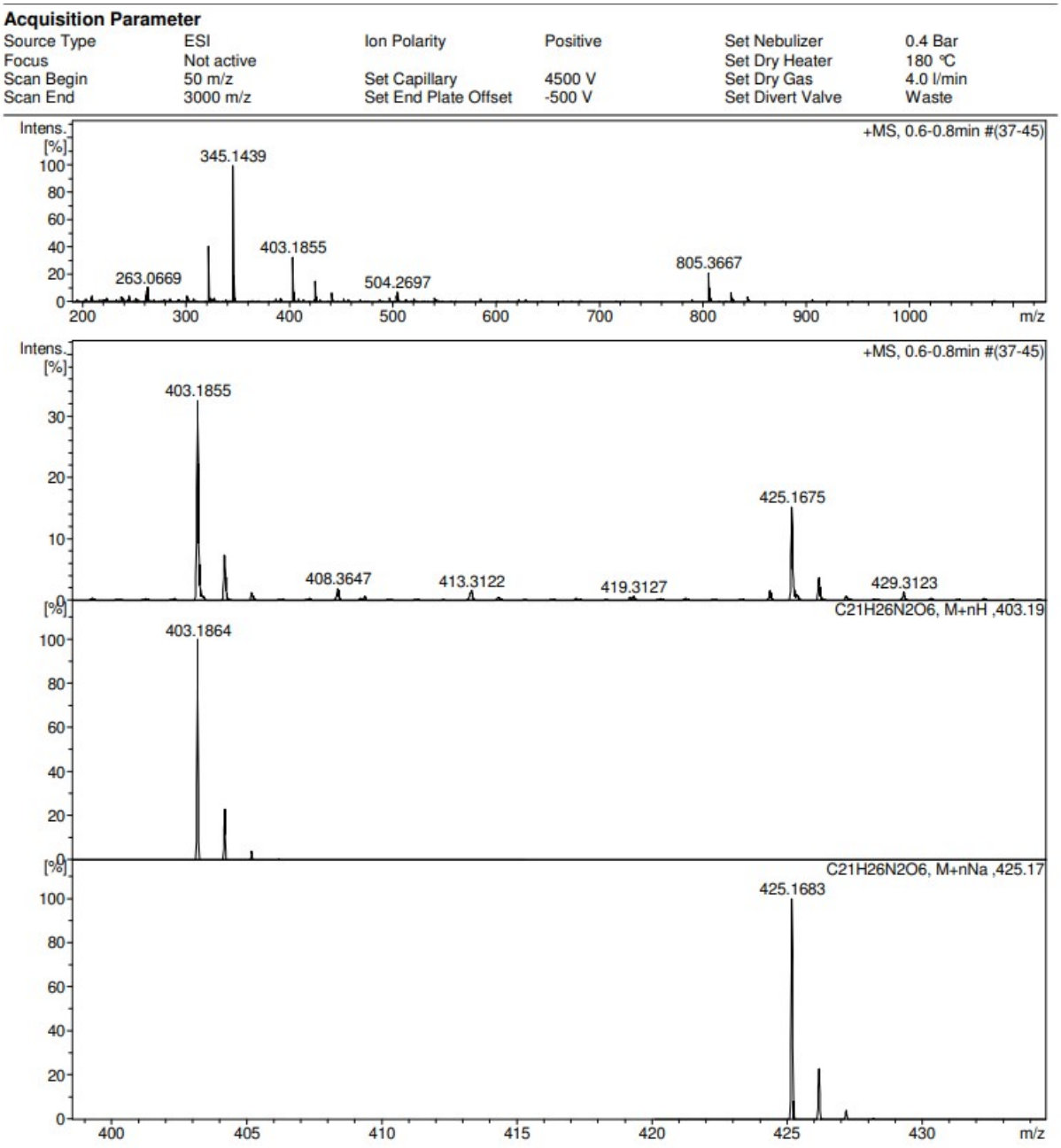
^{1}H NMR spectrum (300 MHz) of **6e** in DMSO-d_6



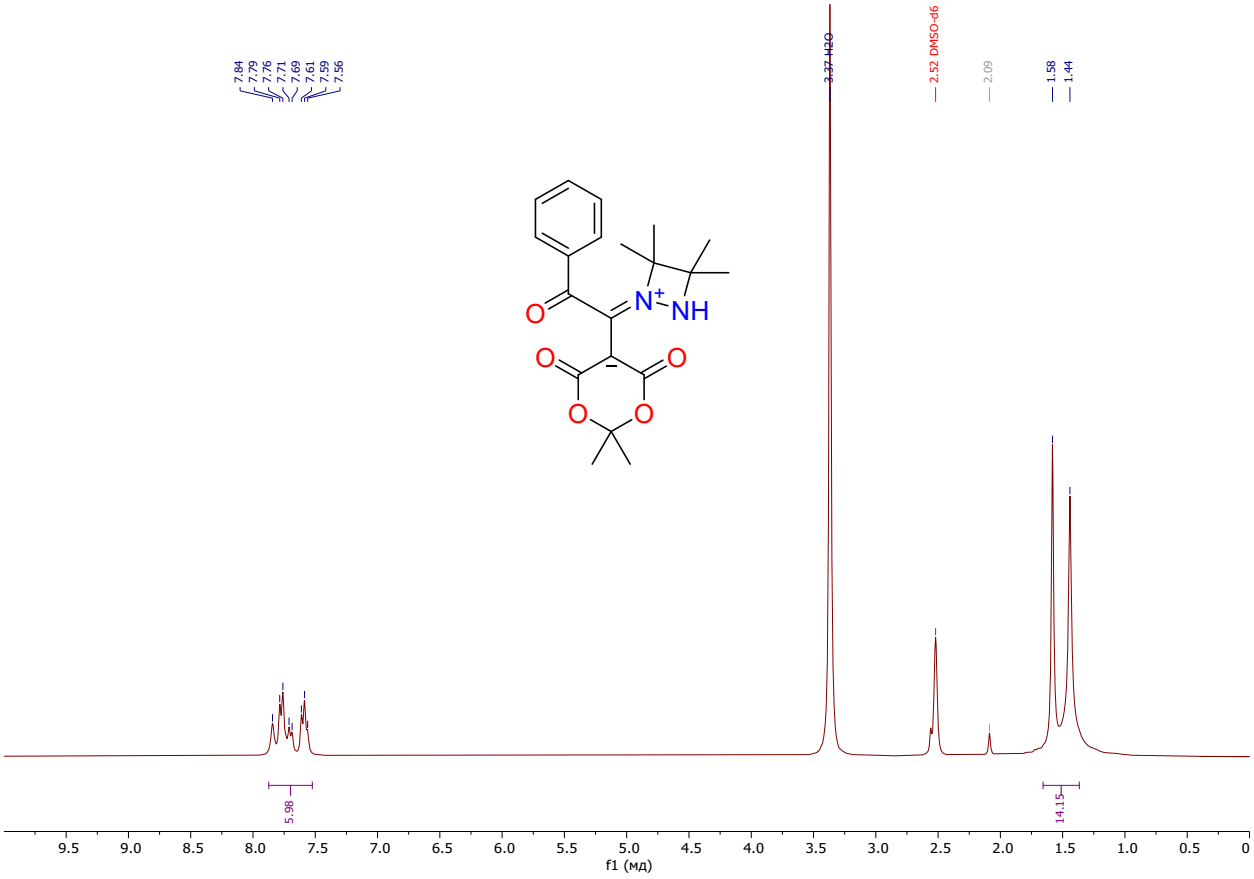
^{13}C {^{1}H} NMR spectrum (76 MHz) of **6e** in DMSO-d_6



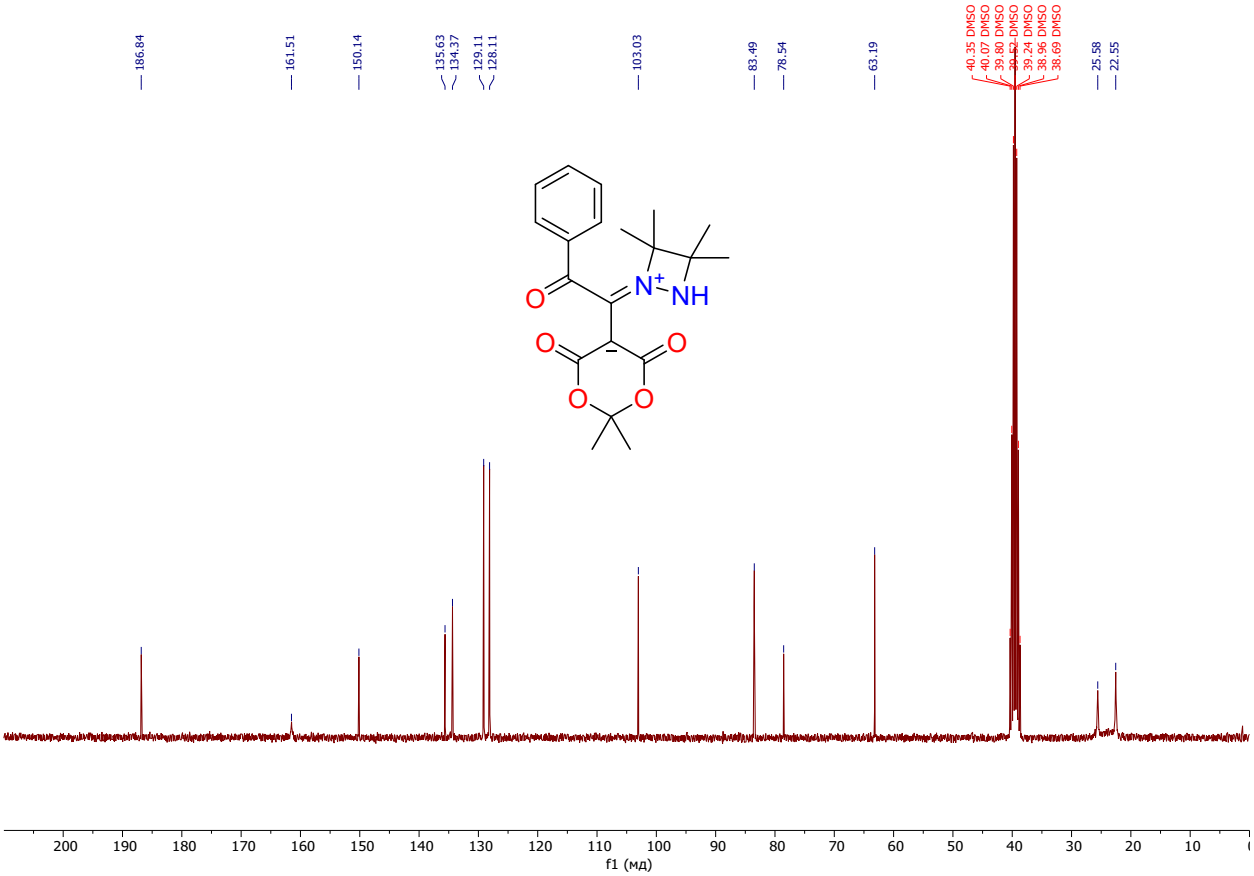
HRMS for compound **6e**



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



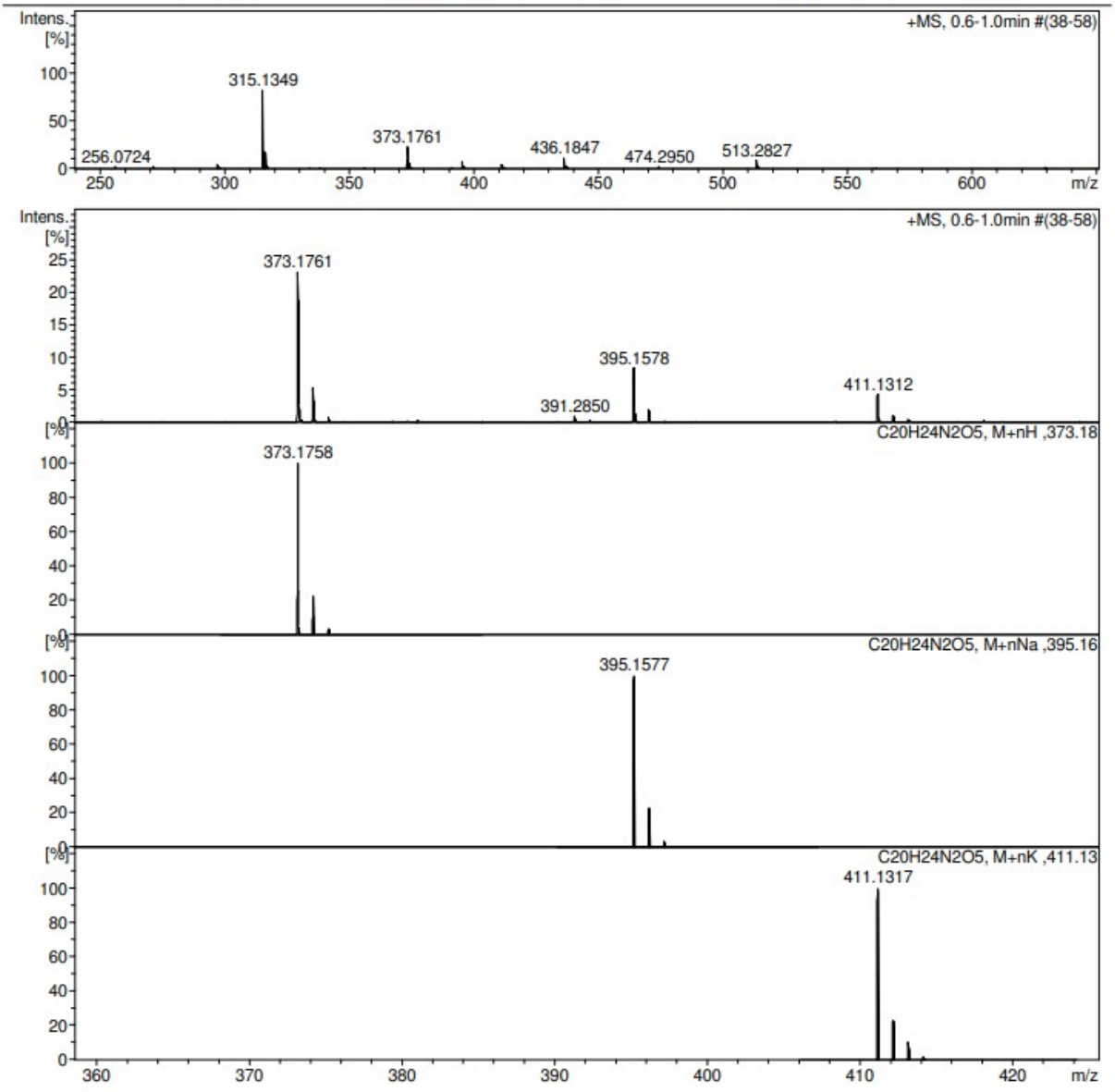
^{13}C {^{1}H} NMR spectrum (76 MHz) of **6f** in DMSO-d_6



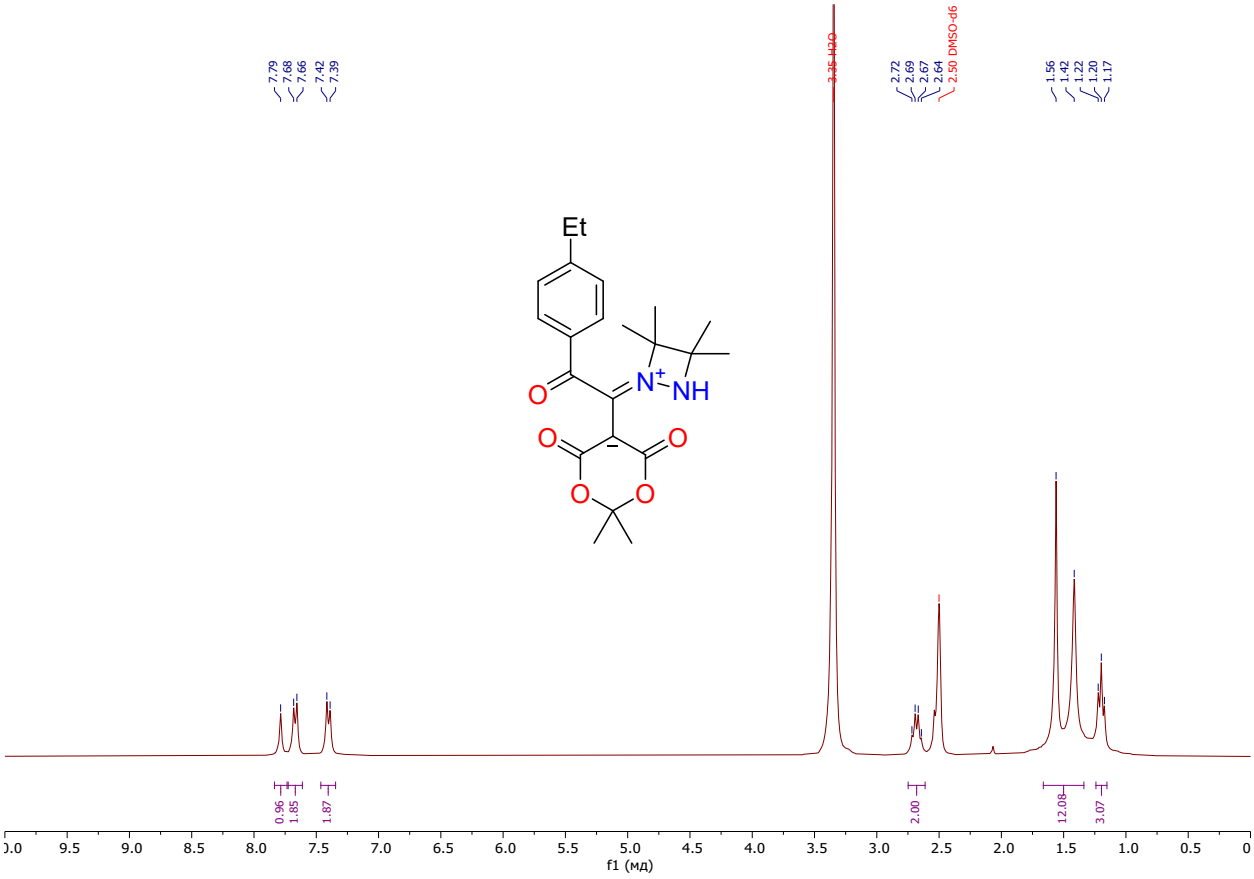
HRMS for compound **6f**

Acquisition Parameter

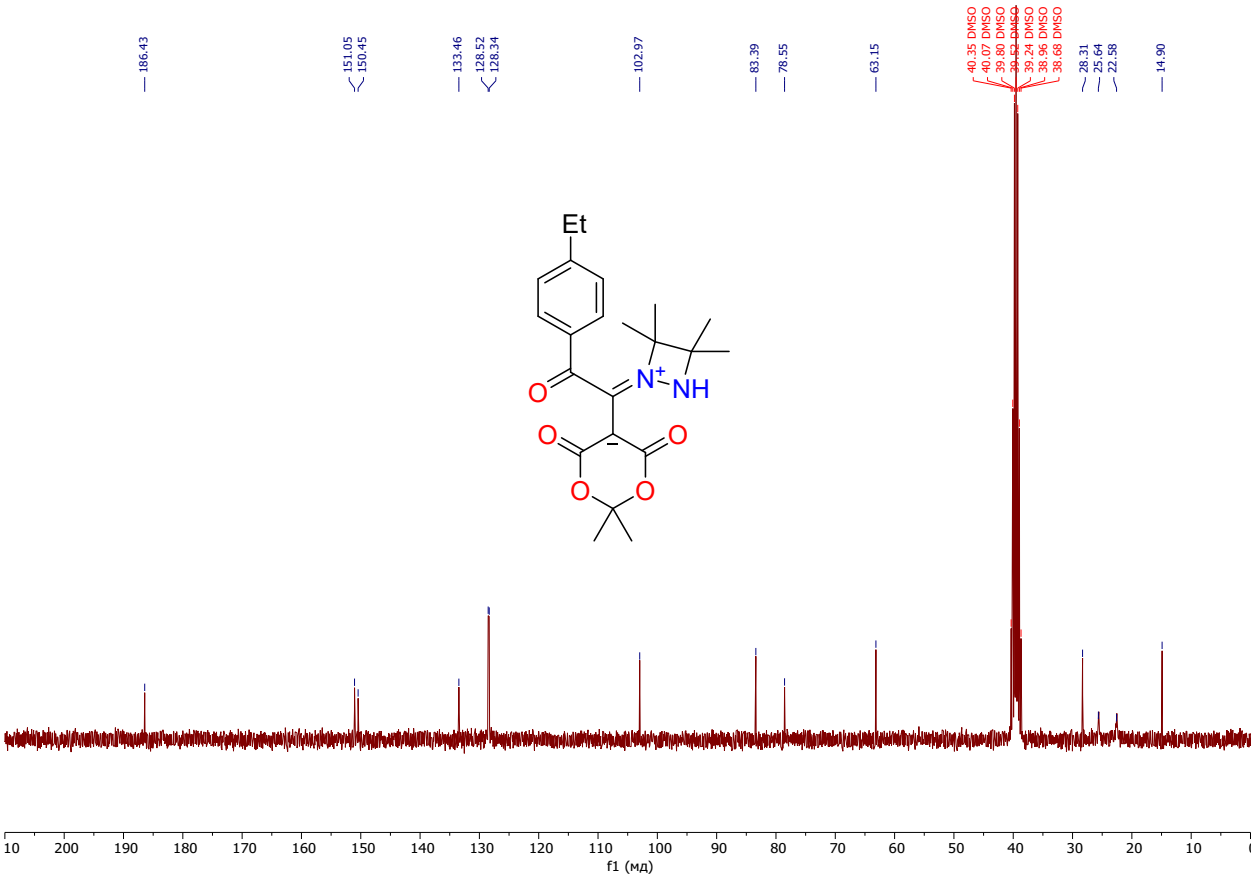
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



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



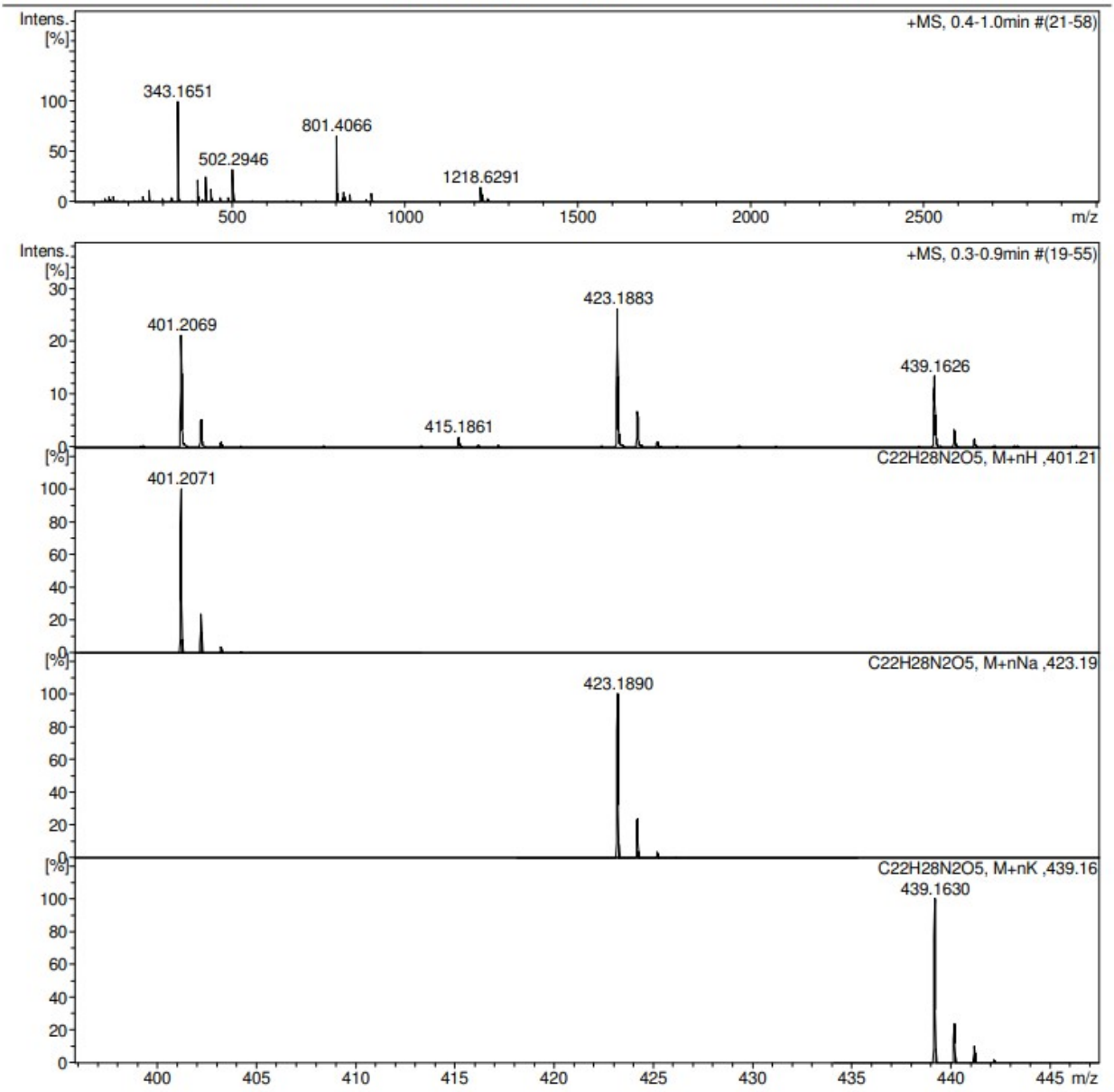
^{13}C {^{1}H} NMR spectrum (76 MHz) of **6g** in DMSO-d_6



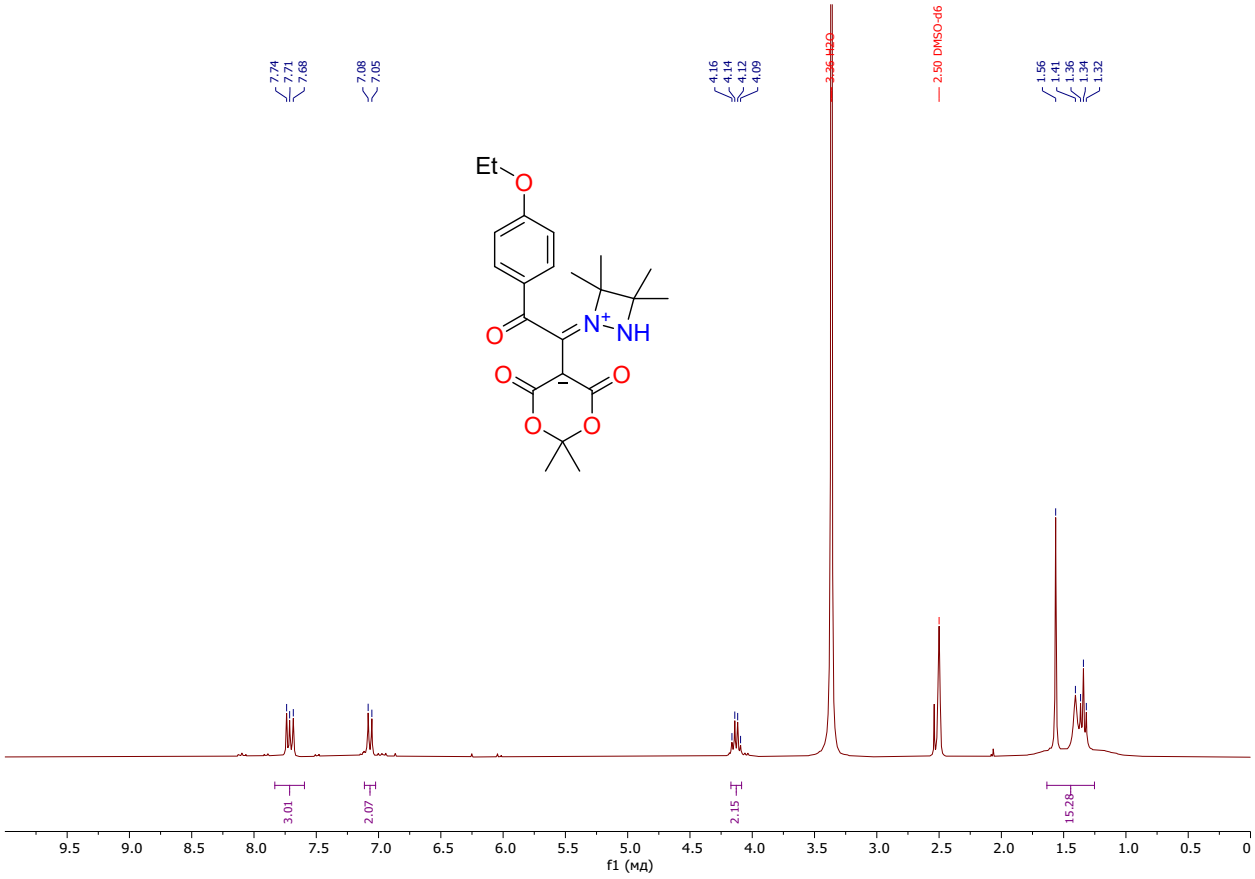
HRMS for compound **6g**

Acquisition Parameter

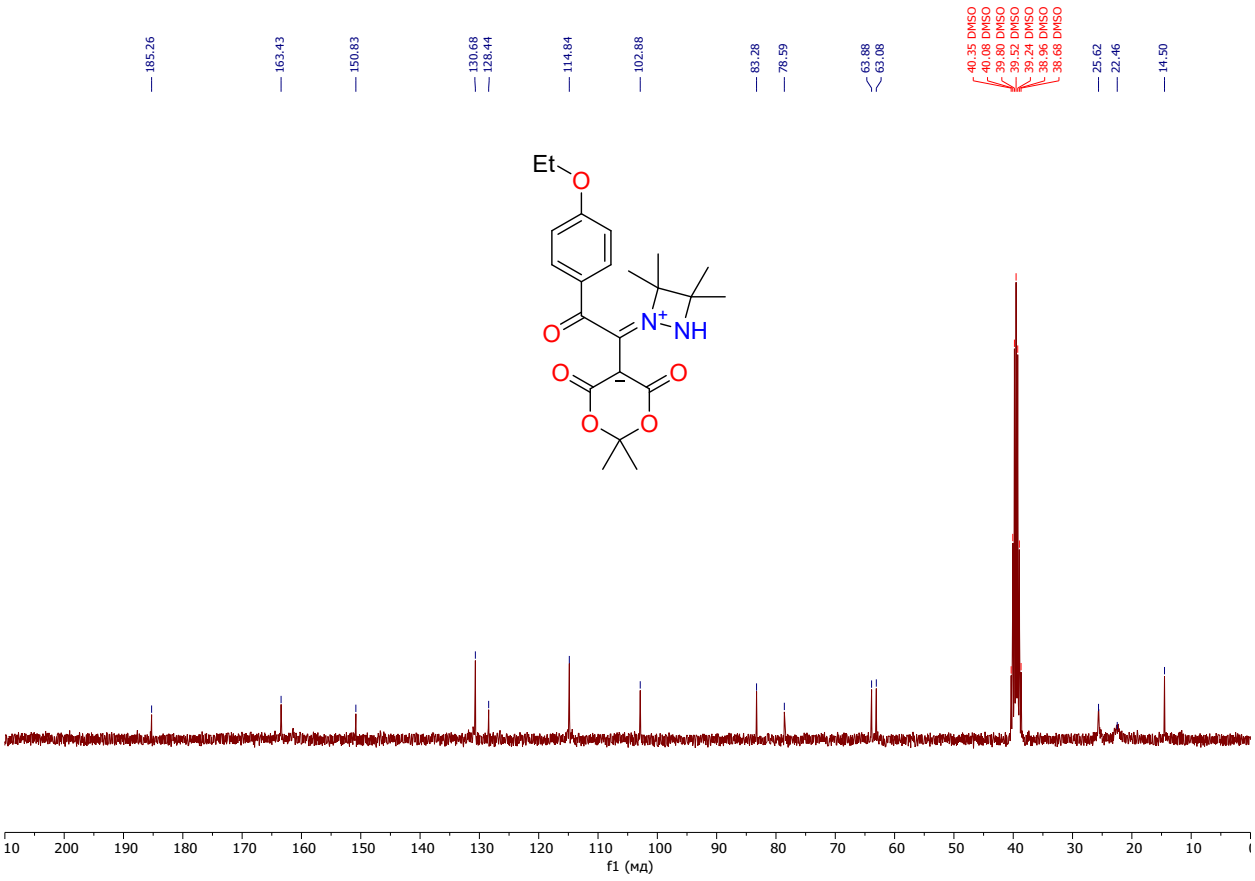
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



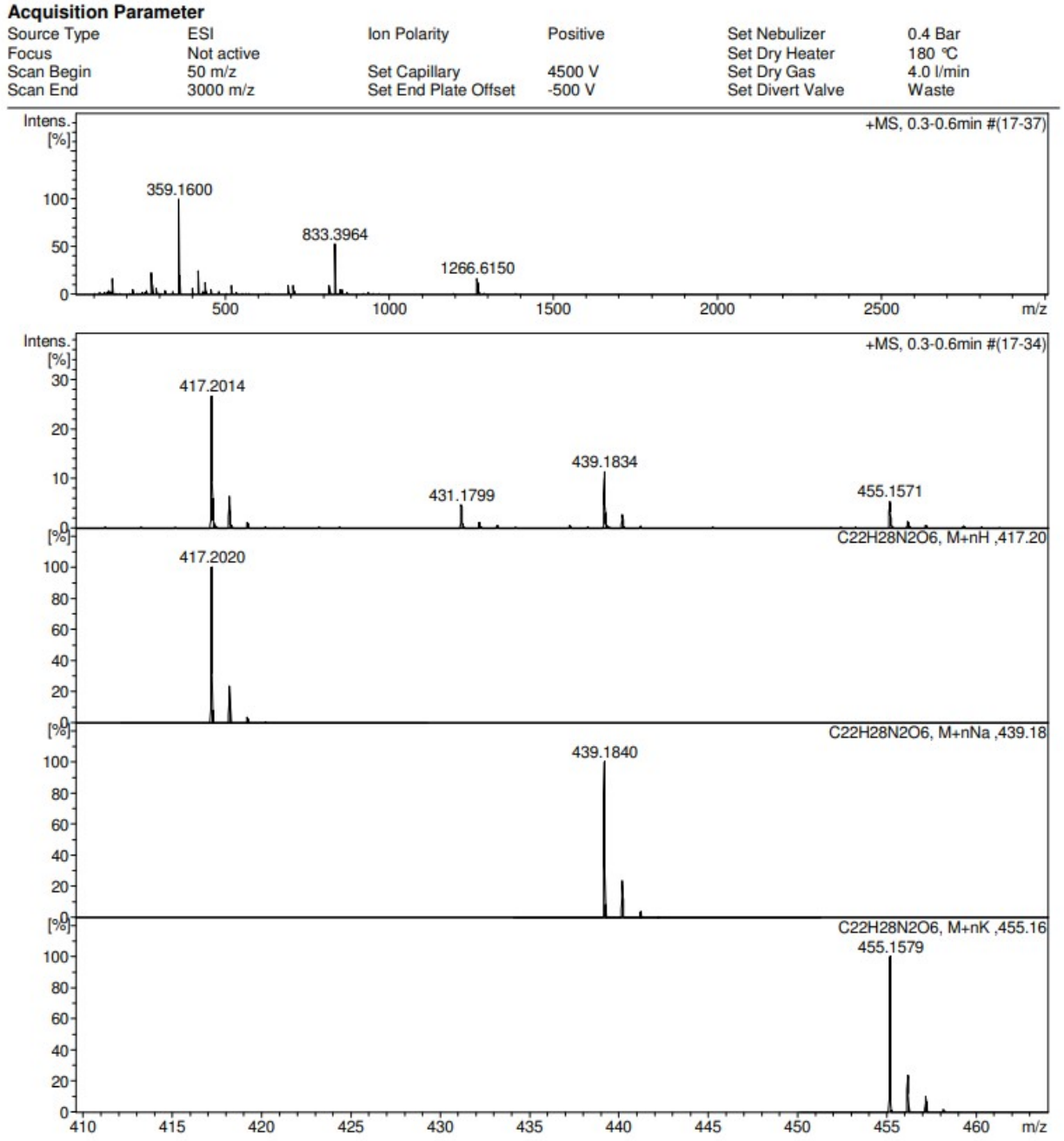
^{1}H NMR spectrum (300 MHz) of **6h** in DMSO-d_6



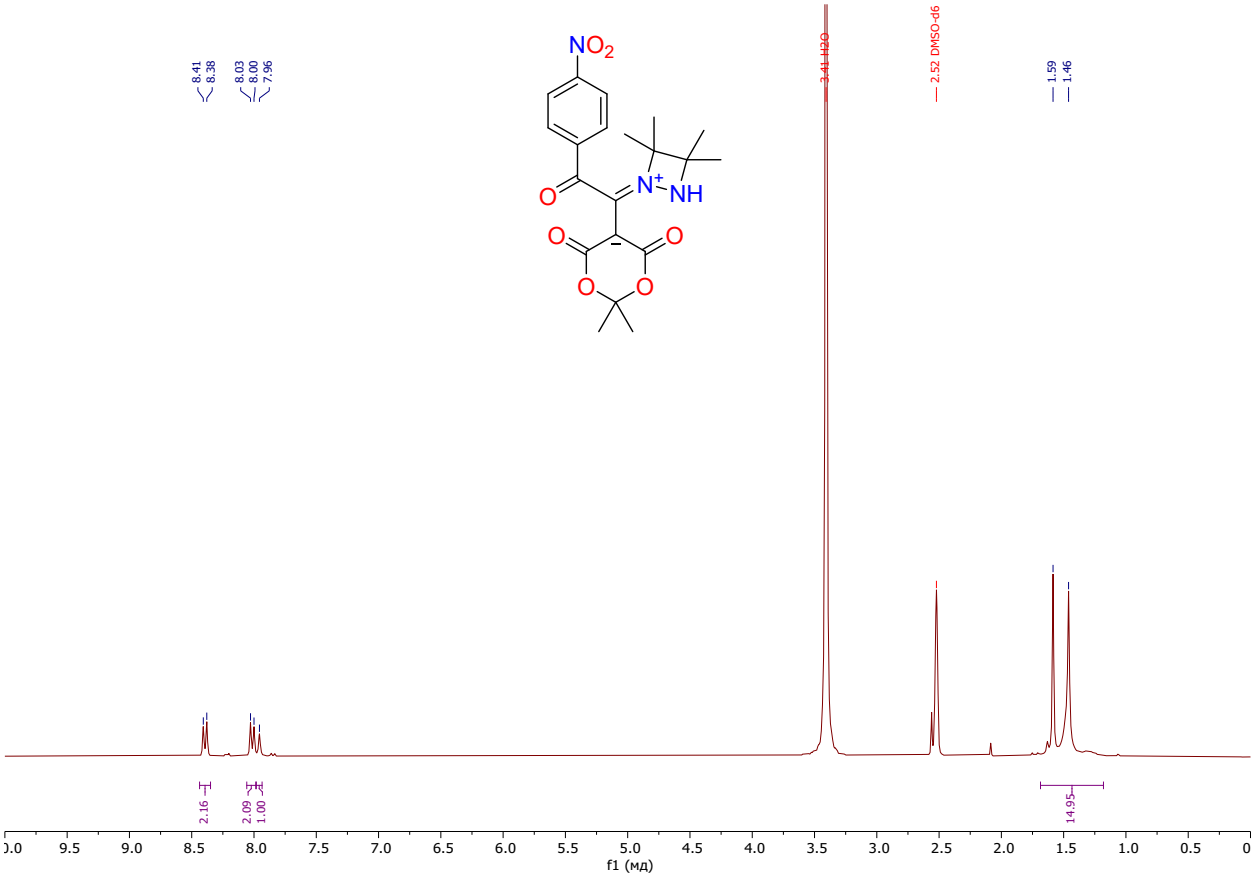
^{13}C {^{1}H} NMR spectrum (76 MHz) of **6h** in DMSO-d_6



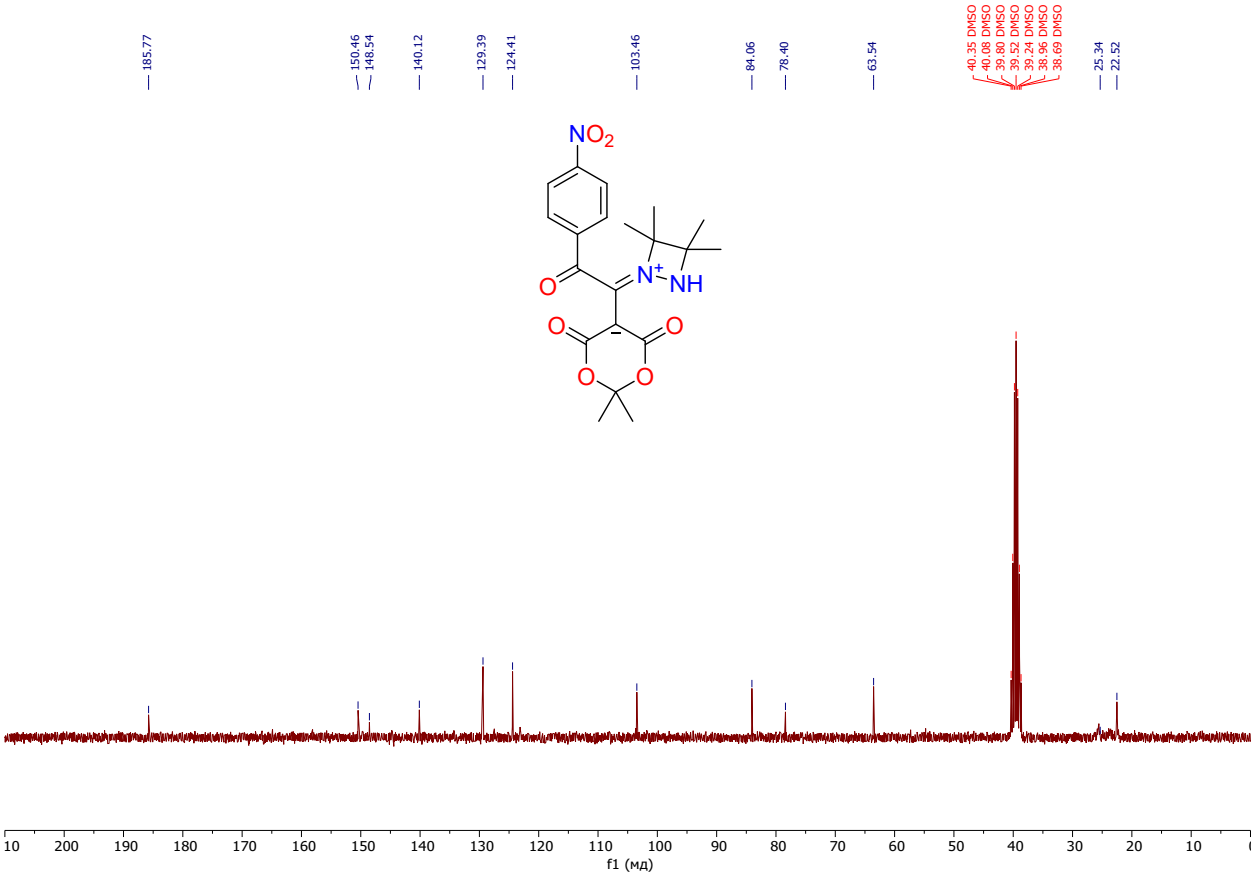
HRMS for compound **6h**



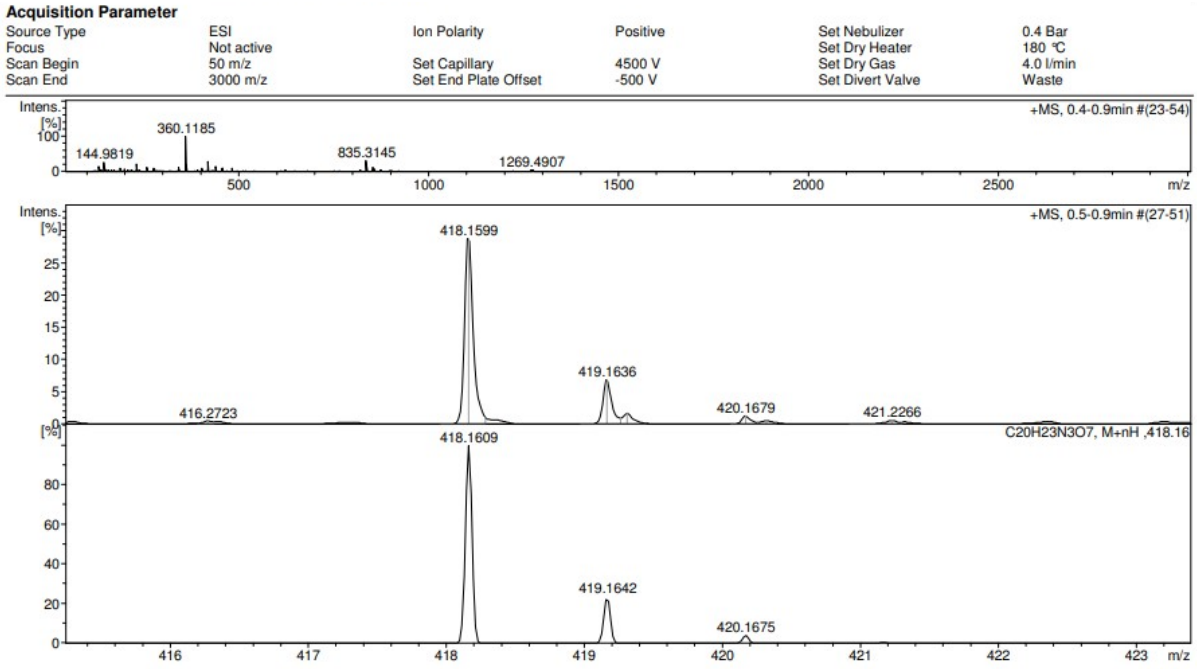
^{1}H NMR spectrum (300 MHz) of **6i** in DMSO-d_6



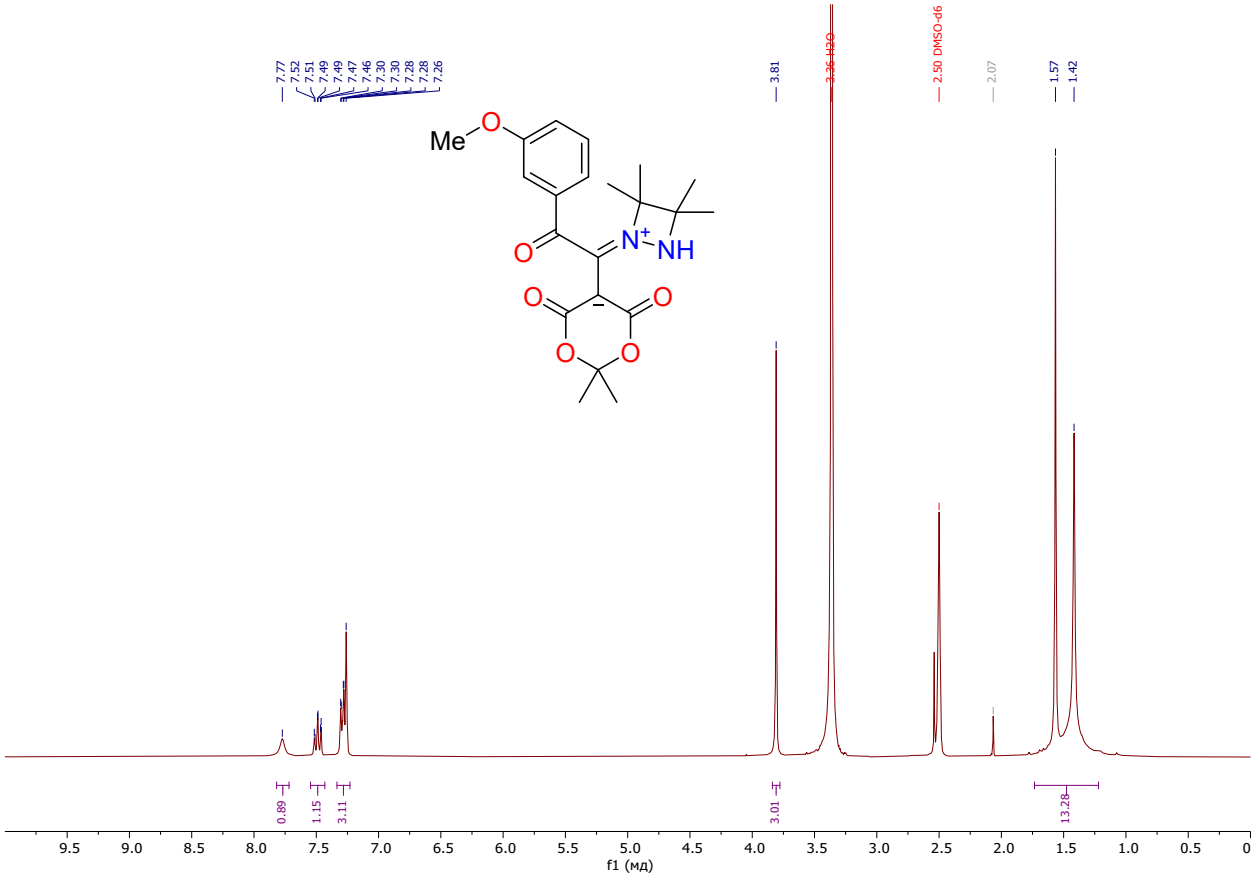
^{13}C {^{1}H} NMR spectrum (76 MHz) of **6i** in DMSO-d_6



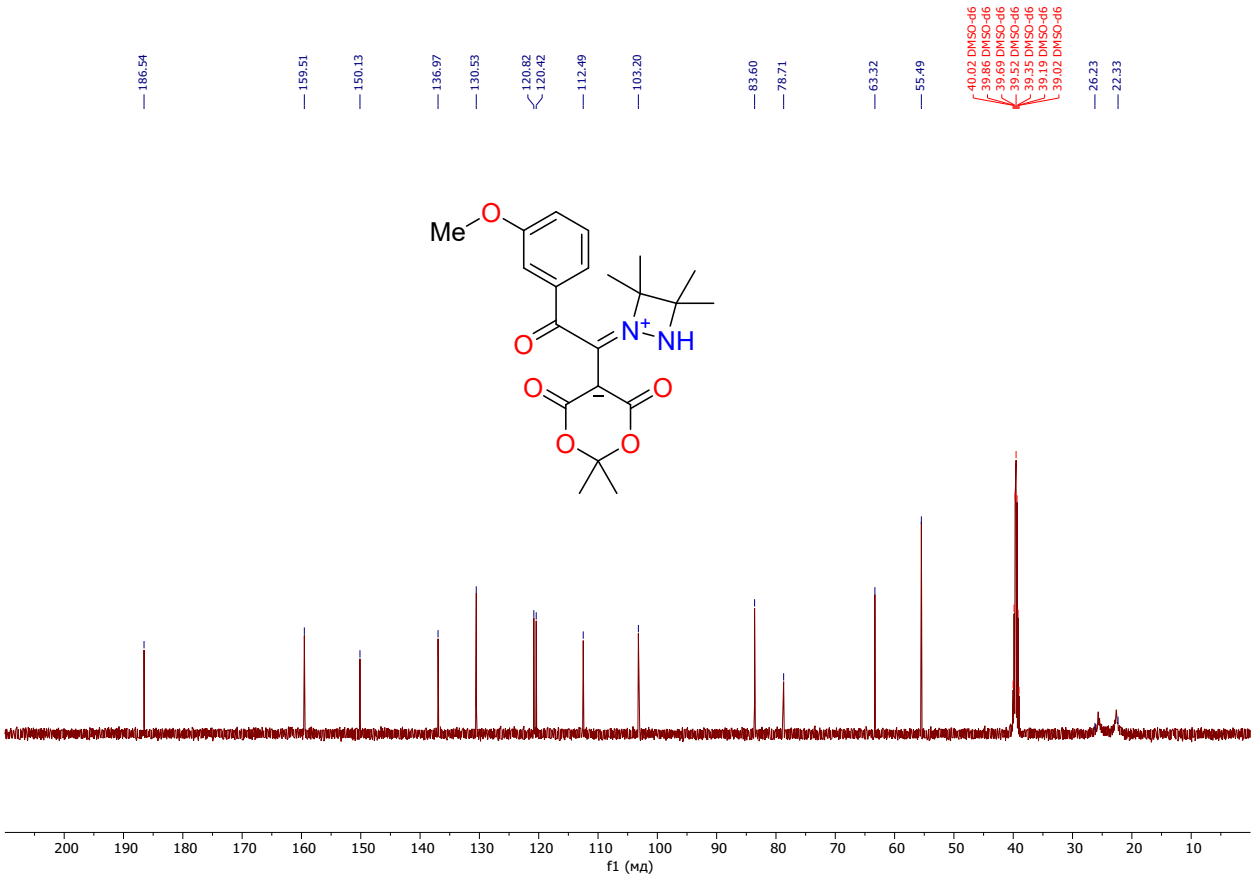
HRMS for compound **6i**



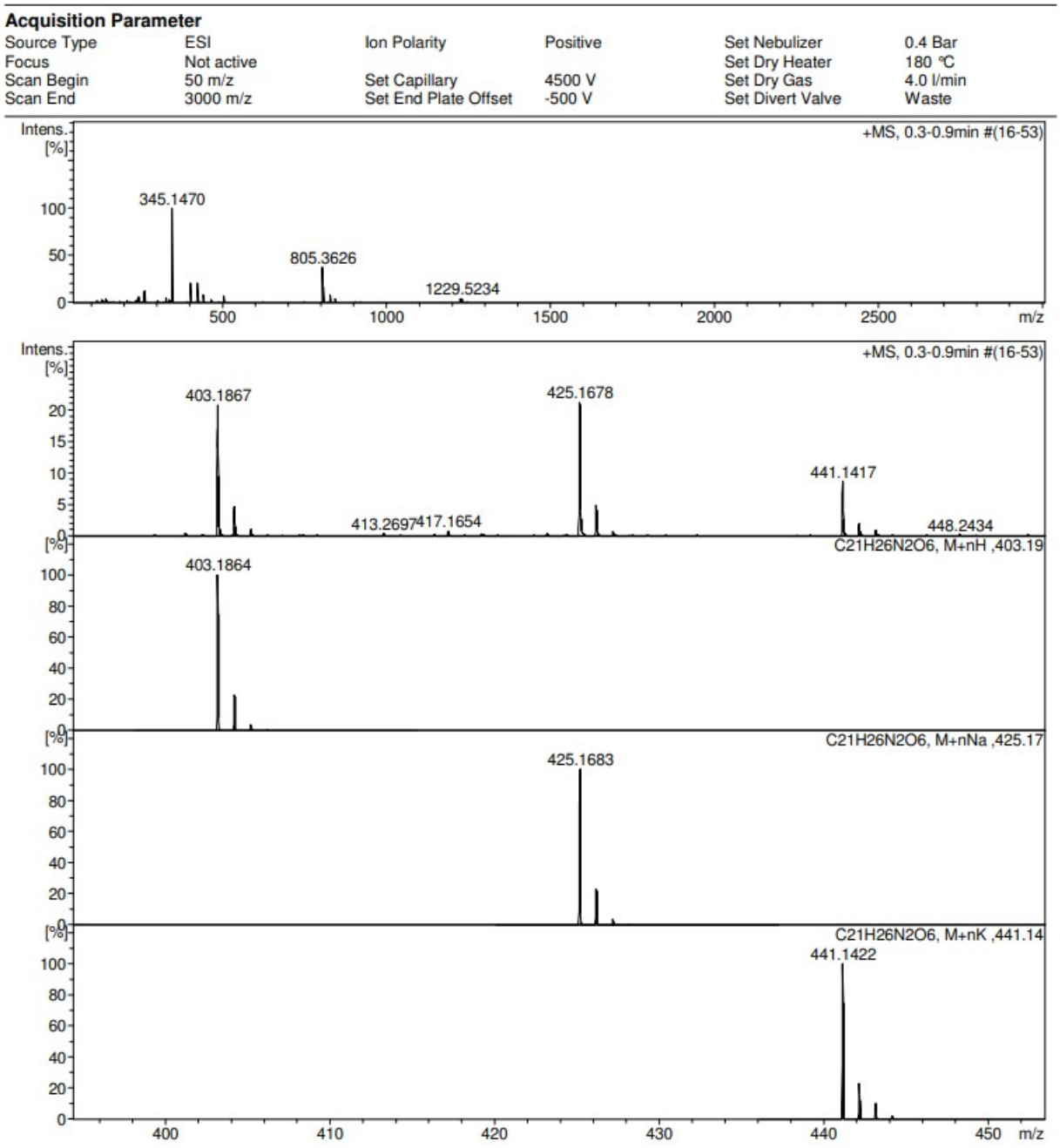
^{1}H NMR spectrum (300 MHz) of **6j** in DMSO-d_6



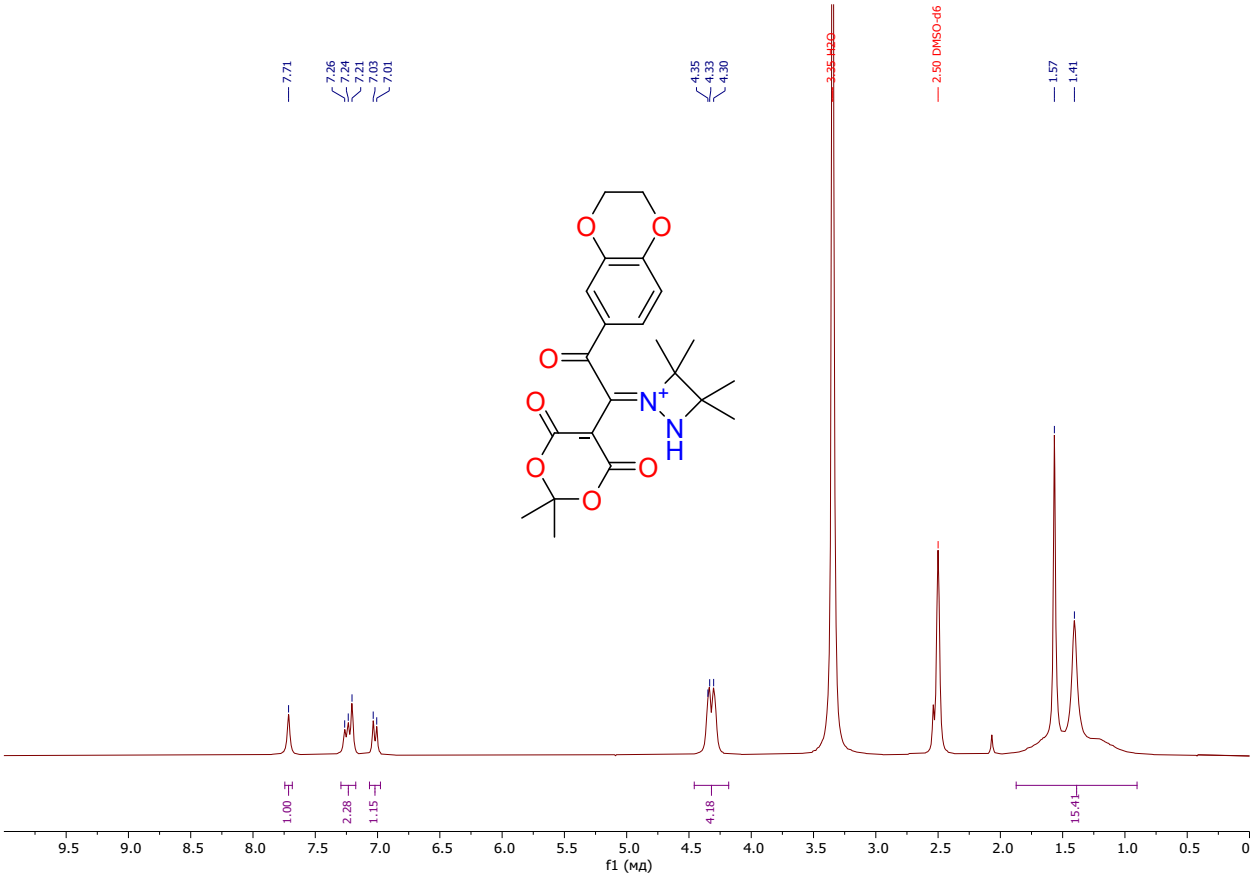
^{13}C {^{1}H} NMR spectrum (76 MHz) of **6j** in DMSO-d_6



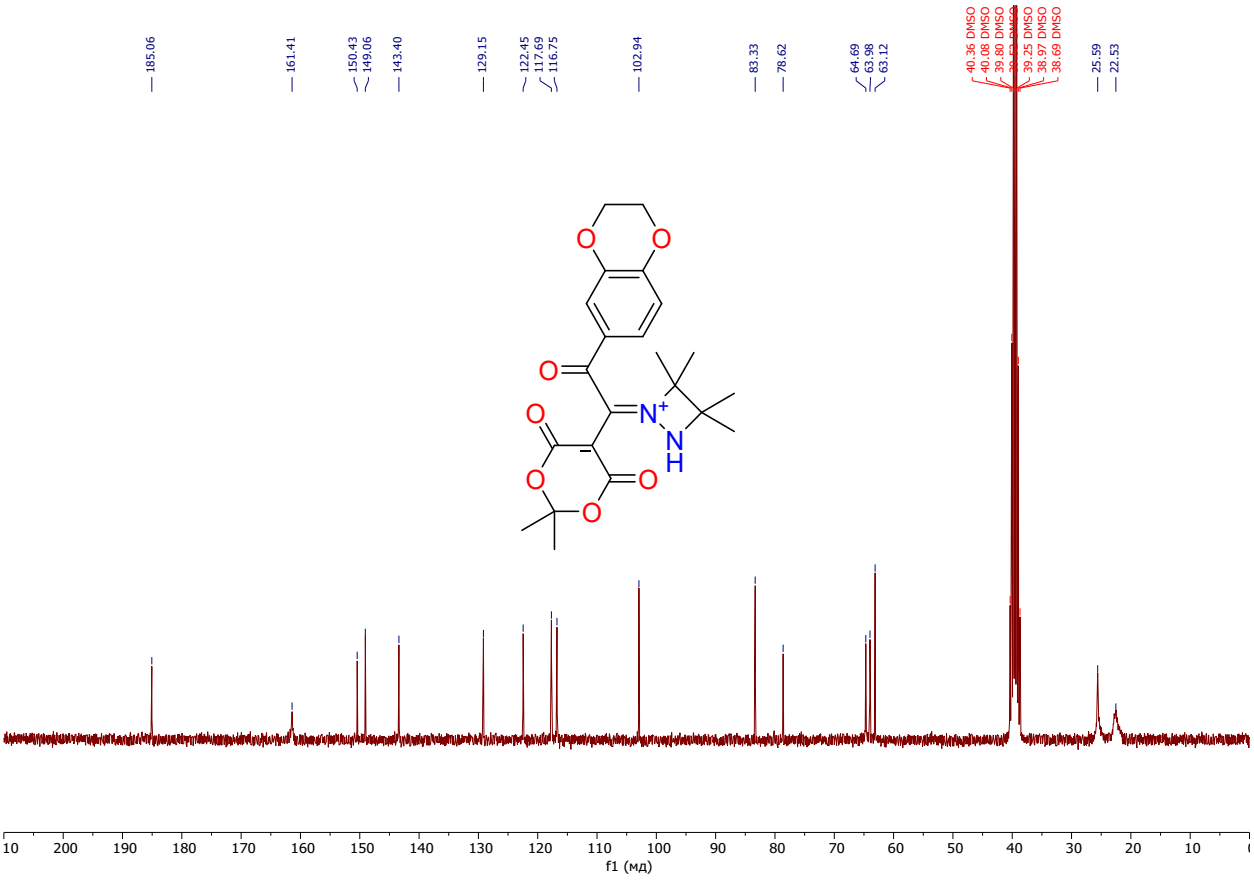
HRMS for compound **6j**



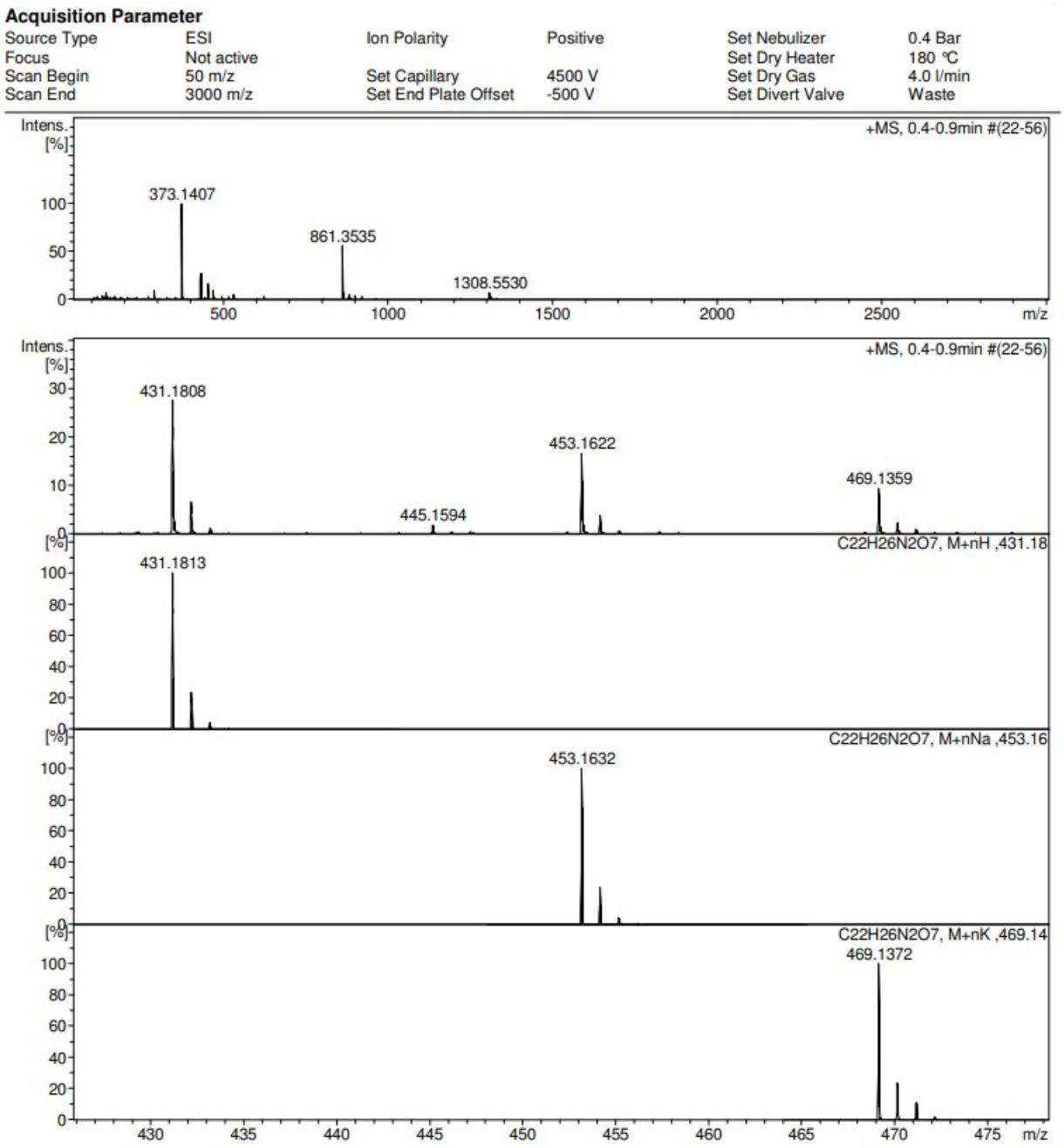
^{1}H NMR spectrum (300 MHz) of **6k** in DMSO-d_6



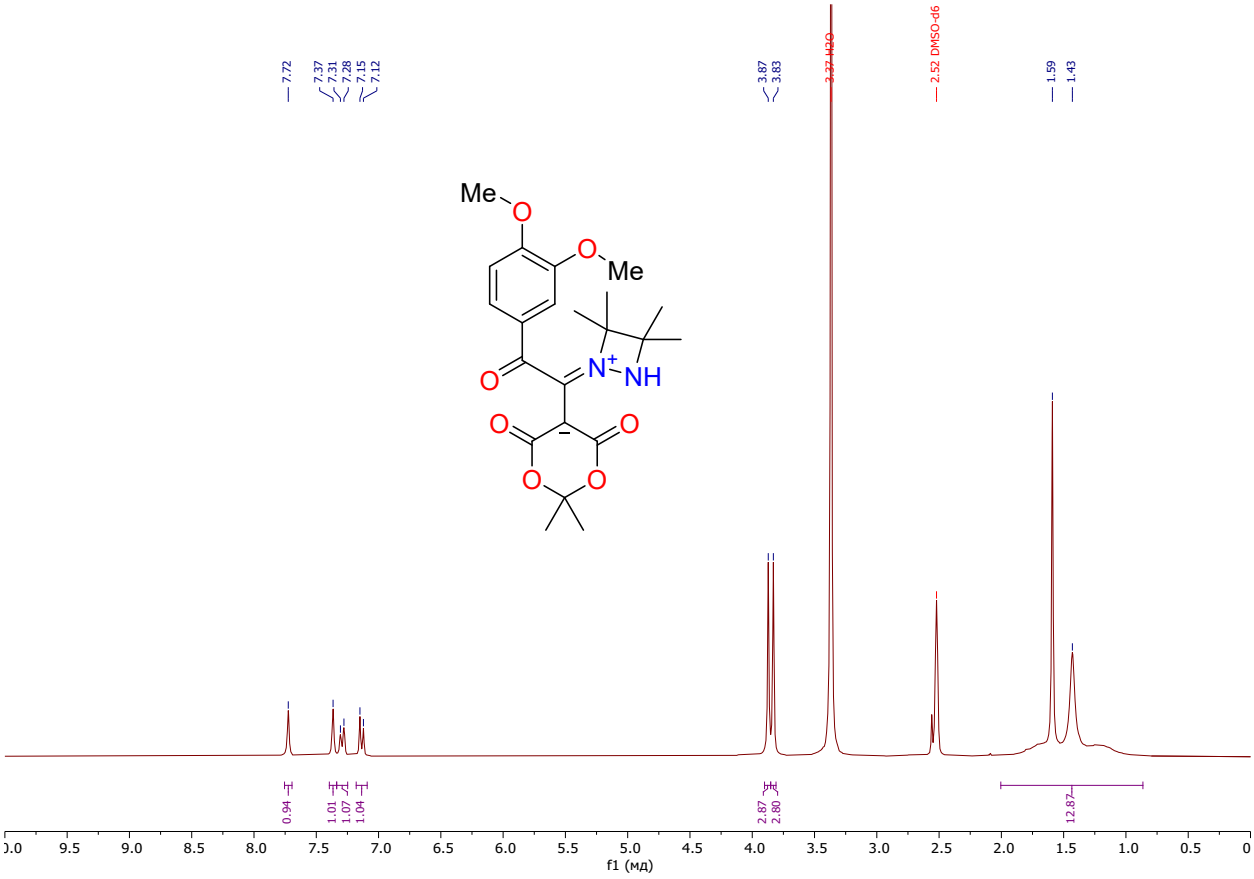
^{13}C {^{1}H} NMR spectrum (76 MHz) of **6k** in DMSO-d_6



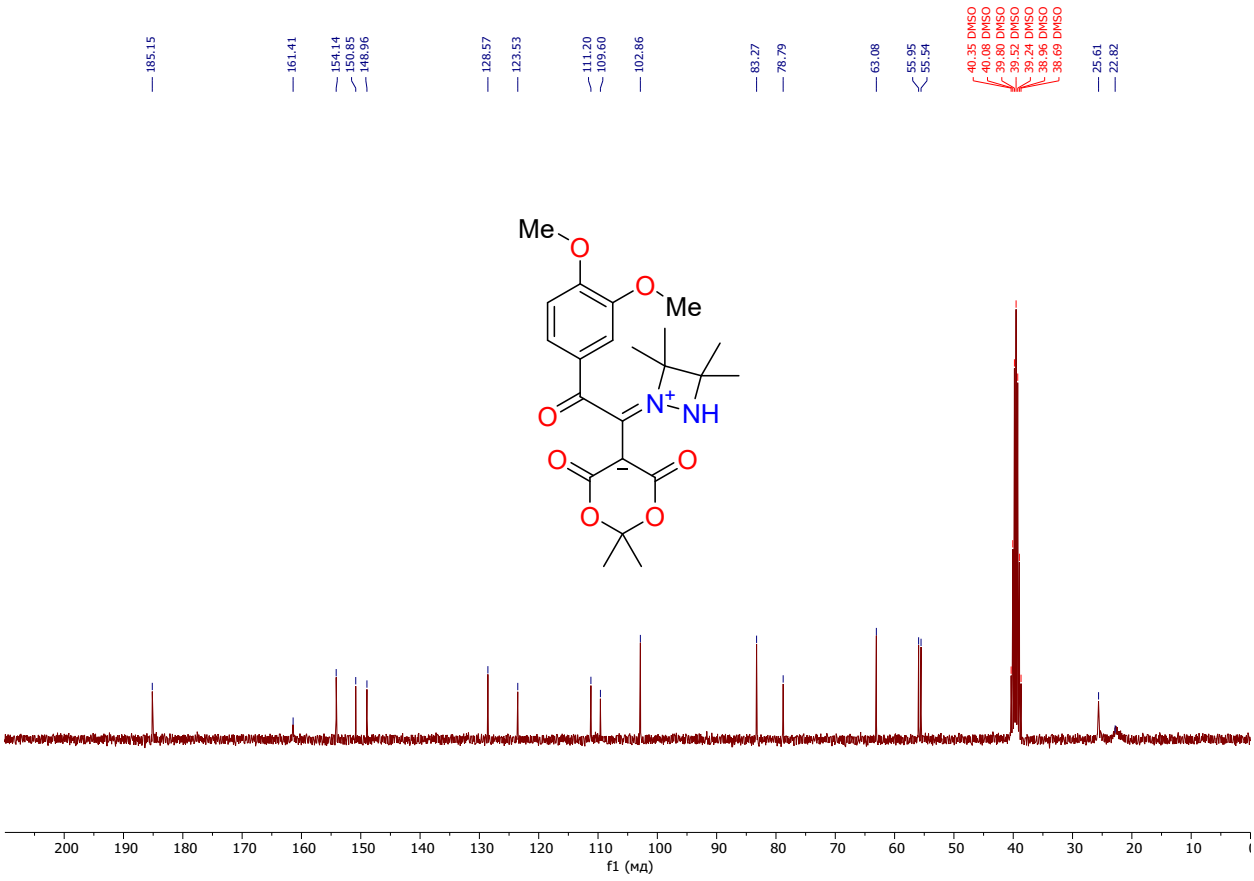
HRMS for compound **6k**



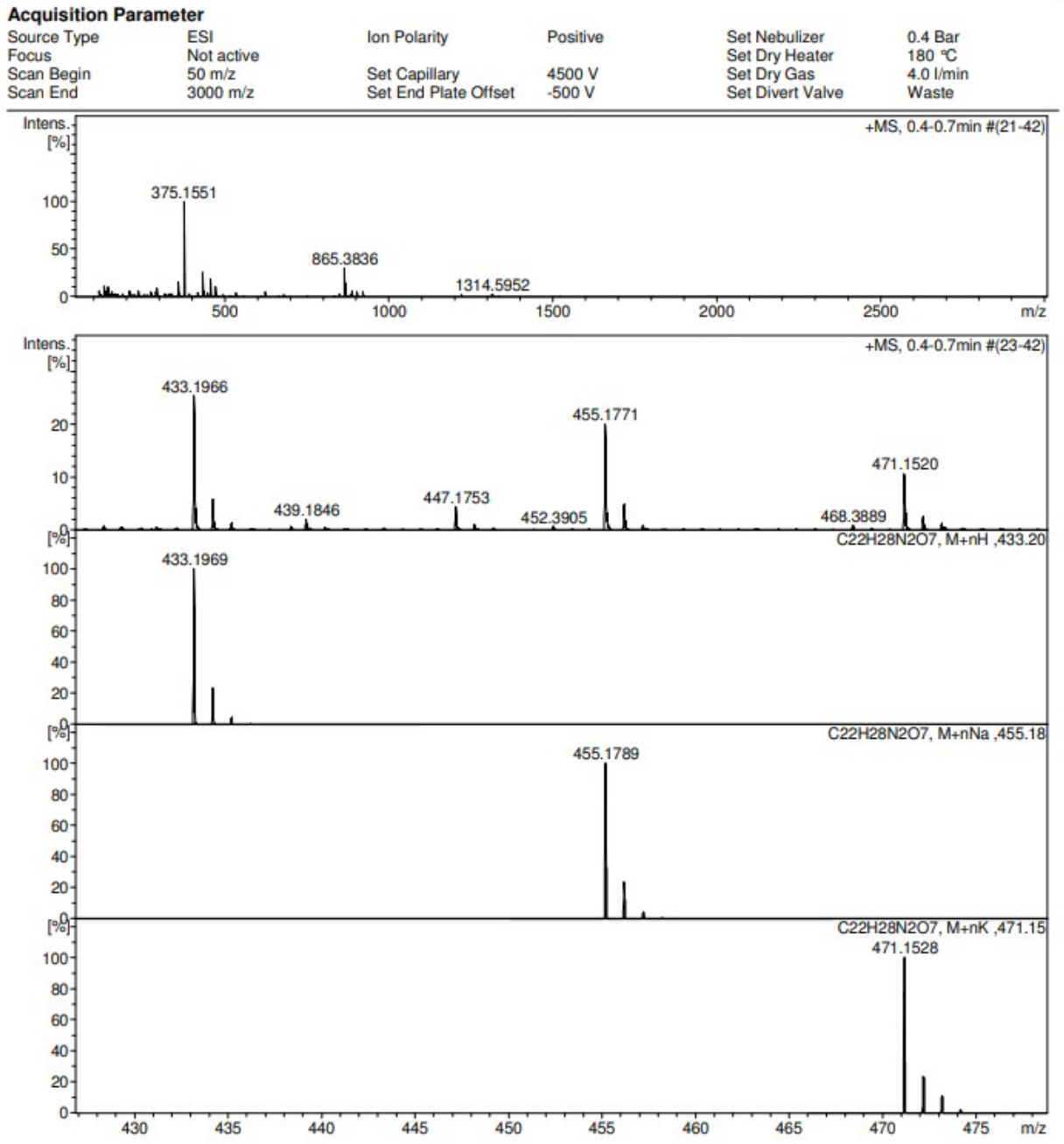
^{1}H NMR spectrum (300 MHz) of **6l** in DMSO-d_6



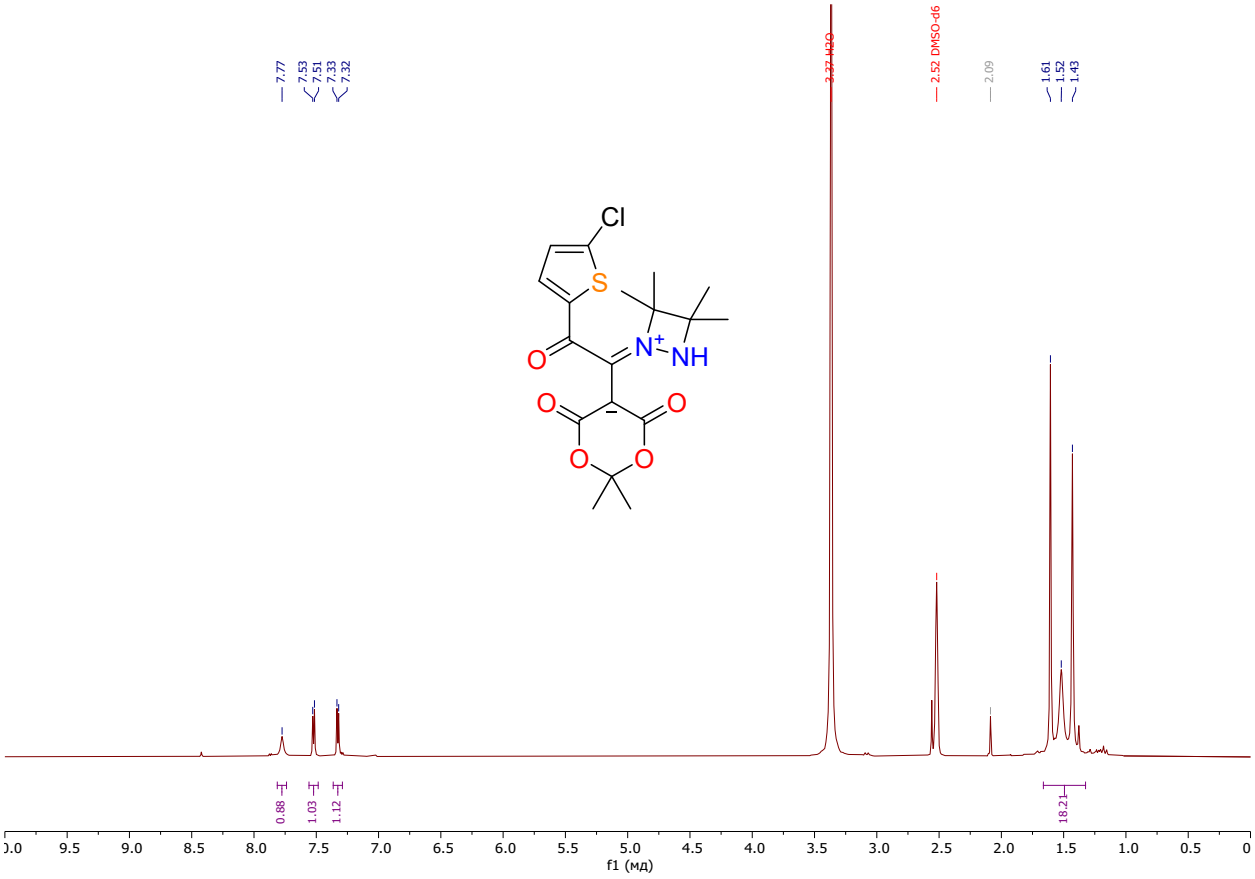
^{13}C {^{1}H} NMR spectrum (76 MHz) of **6l** in DMSO-d_6



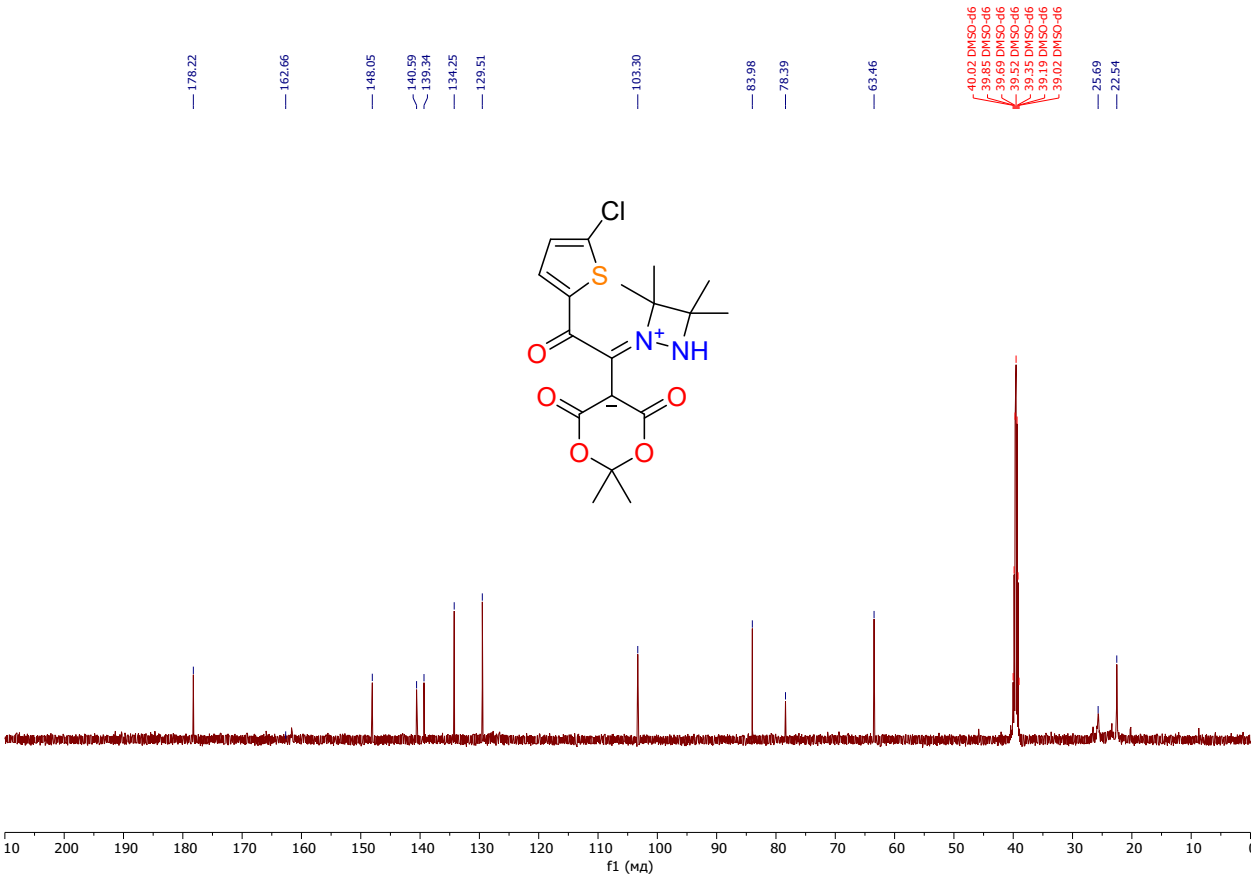
HRMS for compound **6l**



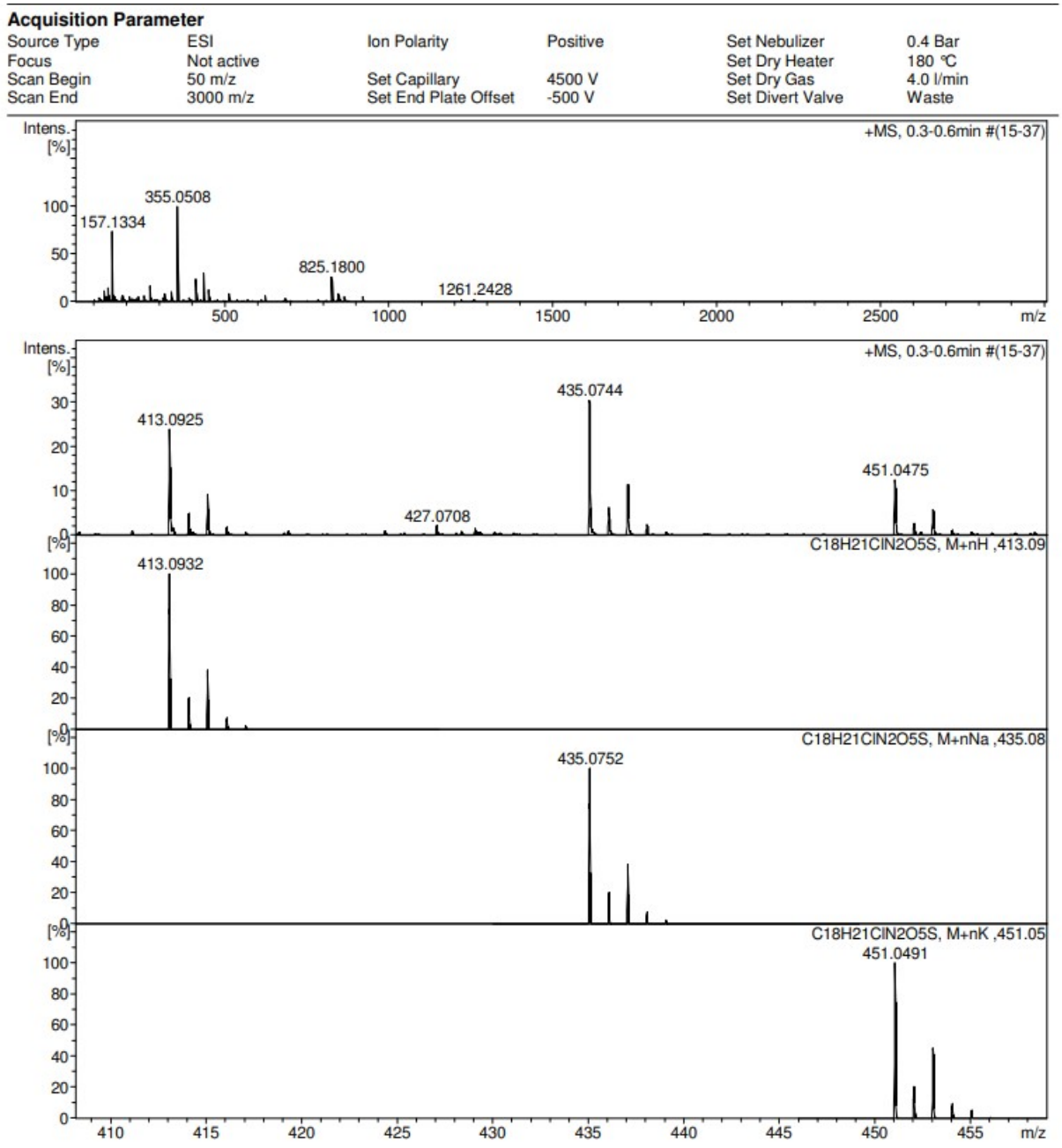
^{1}H NMR spectrum (300 MHz) of **6m** in DMSO-d_6



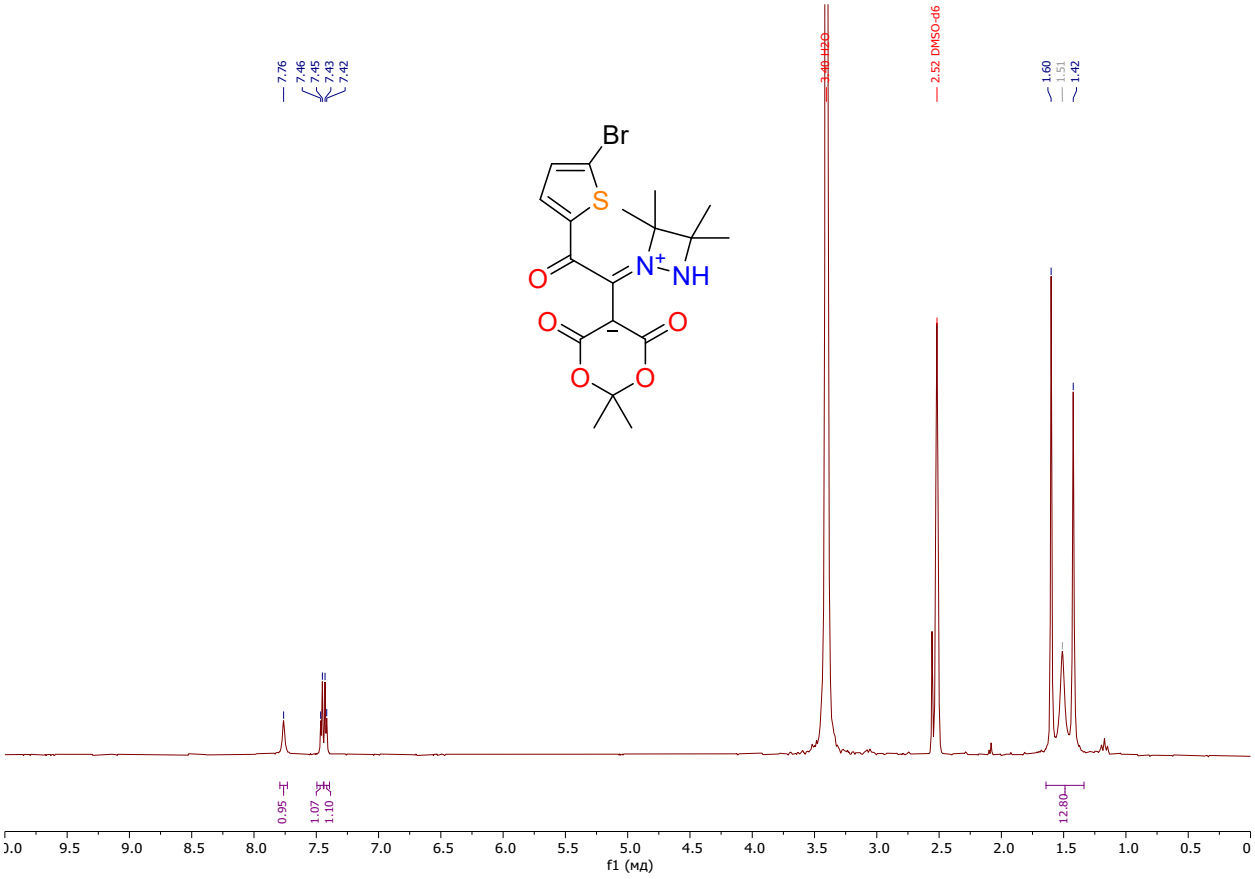
^{13}C {^{1}H} NMR spectrum (76 MHz) of **6m** in DMSO-d_6



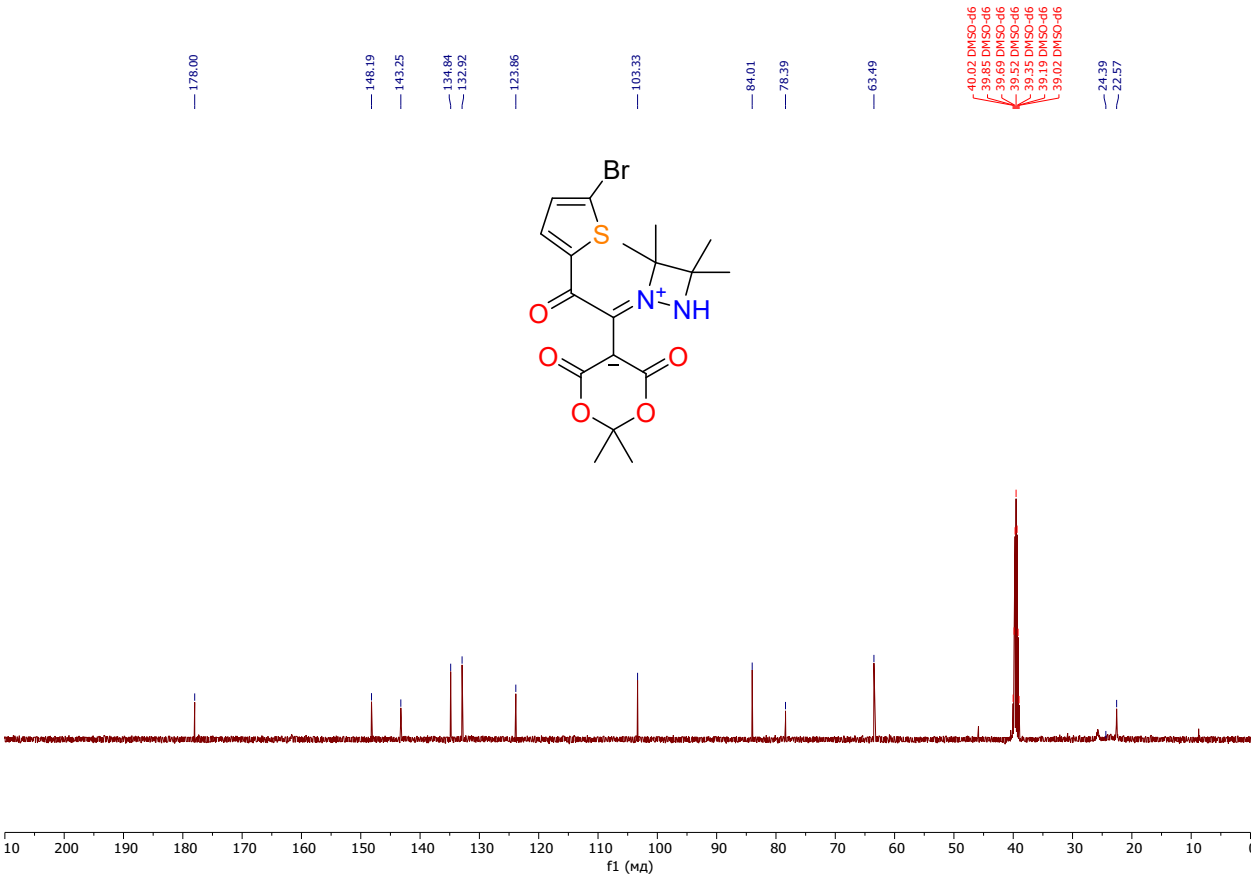
HRMS for compound **6m**



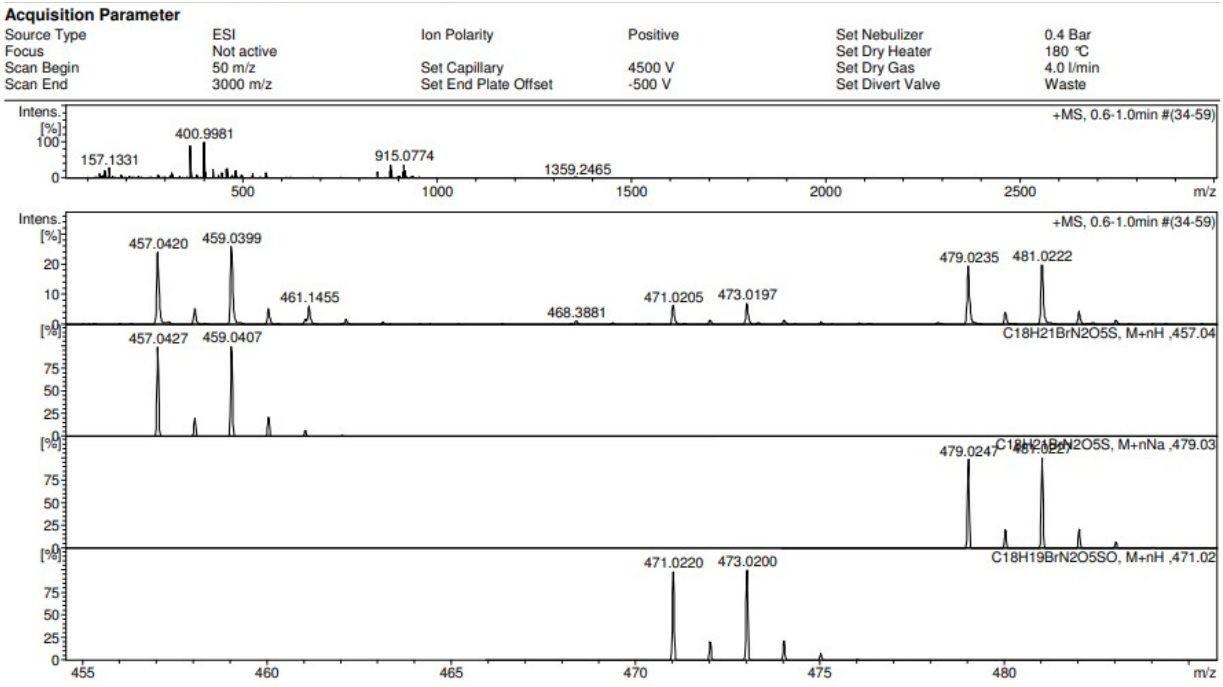
^{1}H NMR spectrum (300 MHz) of **6n** in DMSO-d_6



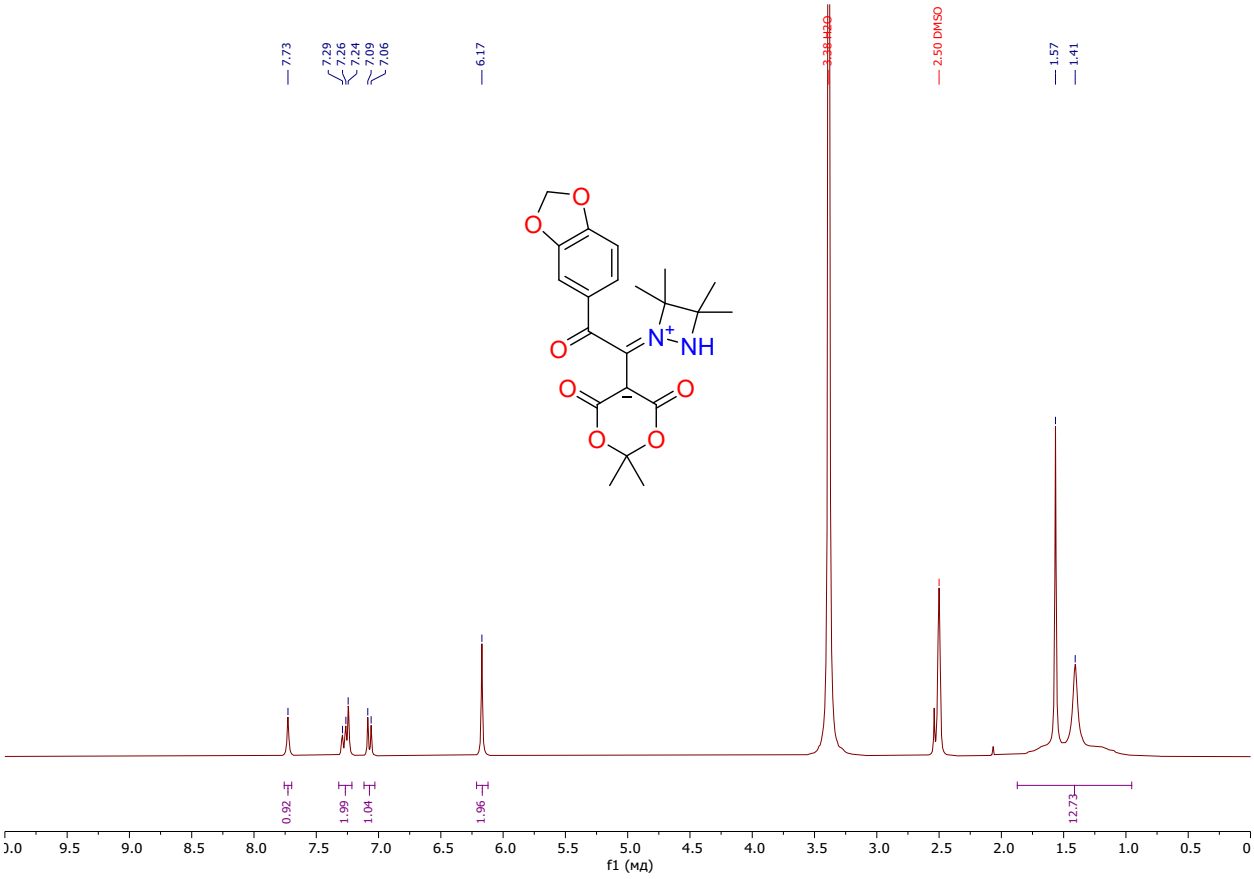
^{13}C {^{1}H} NMR spectrum (76 MHz) of **6n** in DMSO-d_6



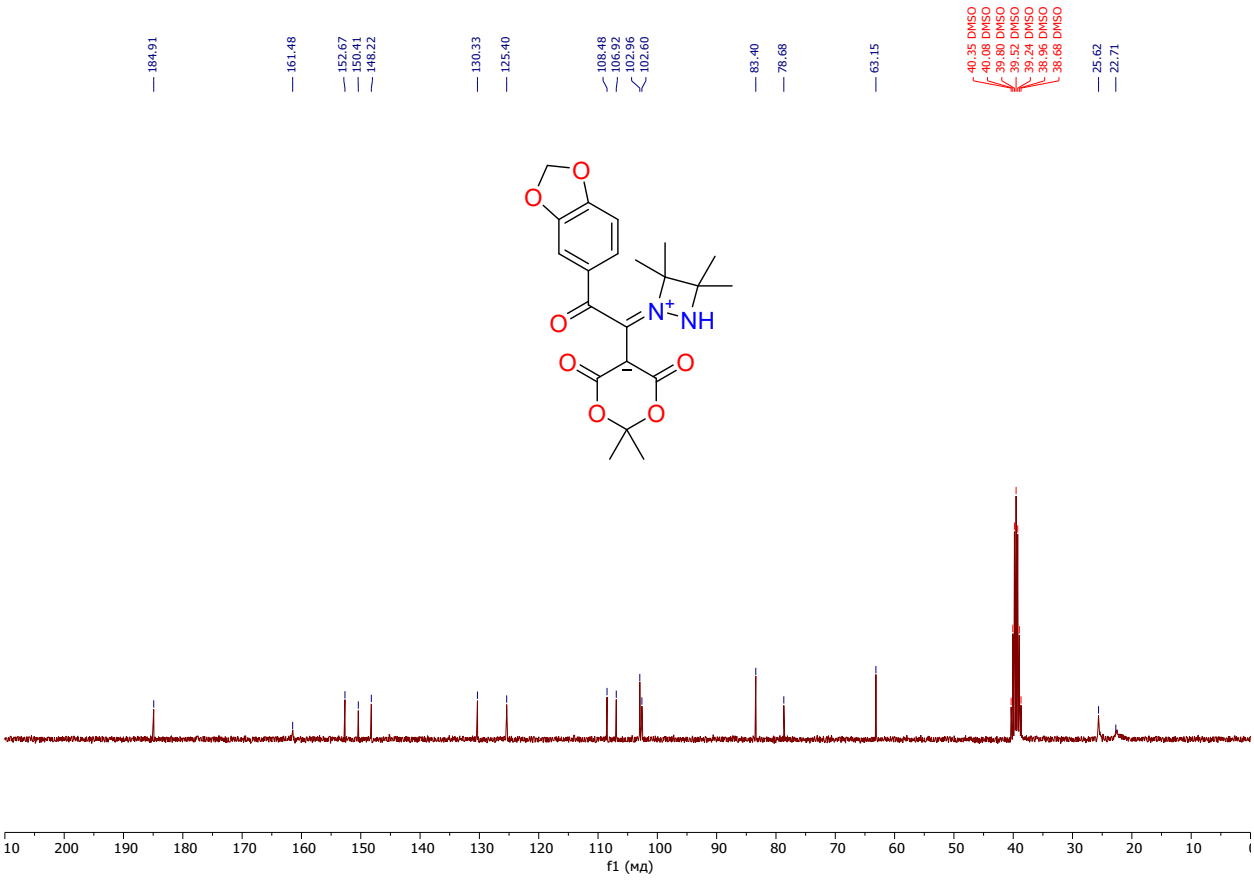
HRMS for compound **6n**



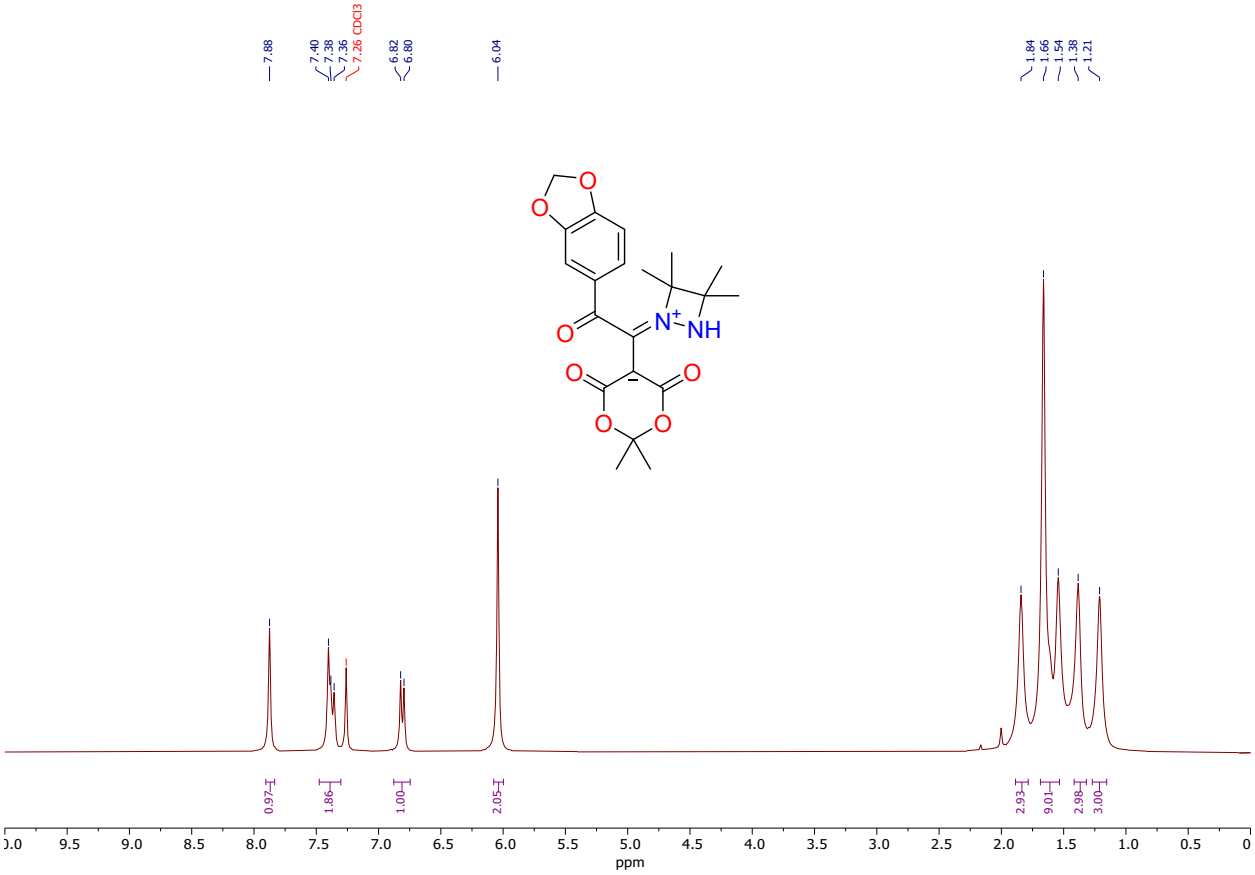
^{1}H NMR spectrum (300 MHz) of **6o** in DMSO-d_6



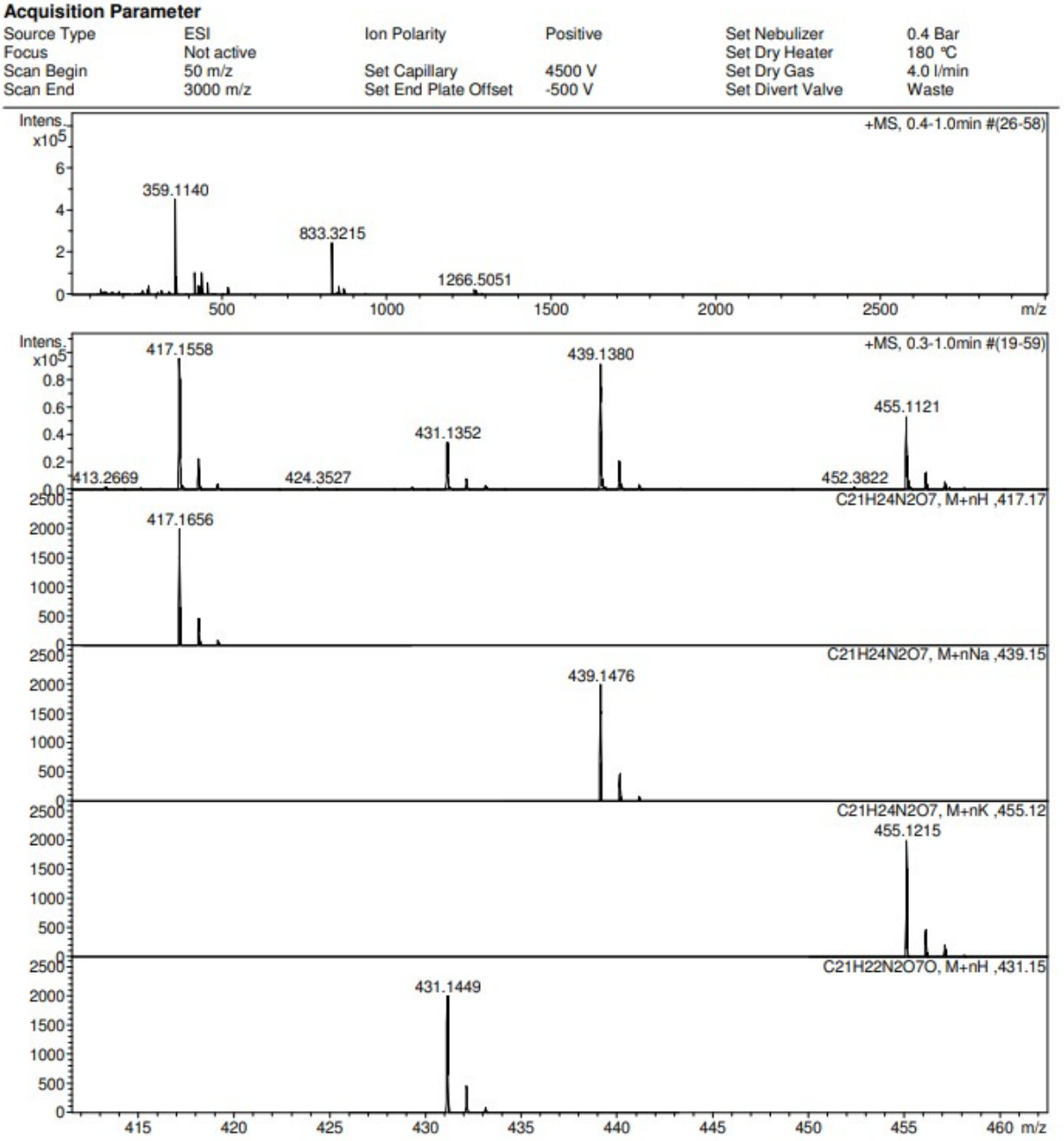
^{13}C {^{1}H} NMR spectrum (76 MHz) of **6o** in DMSO-d_6



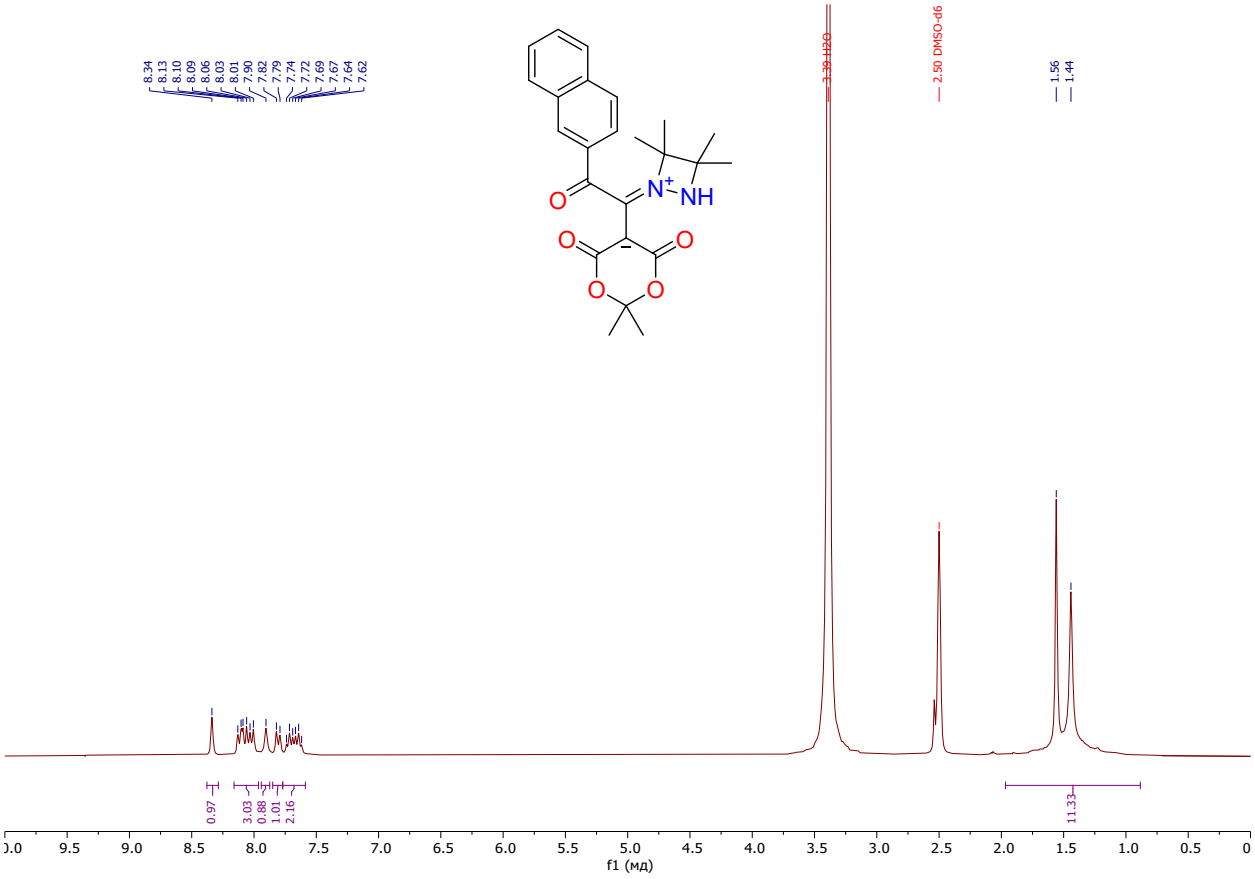
^{1}H NMR spectrum (300 MHz) of **6o** in $CDCl_3$.



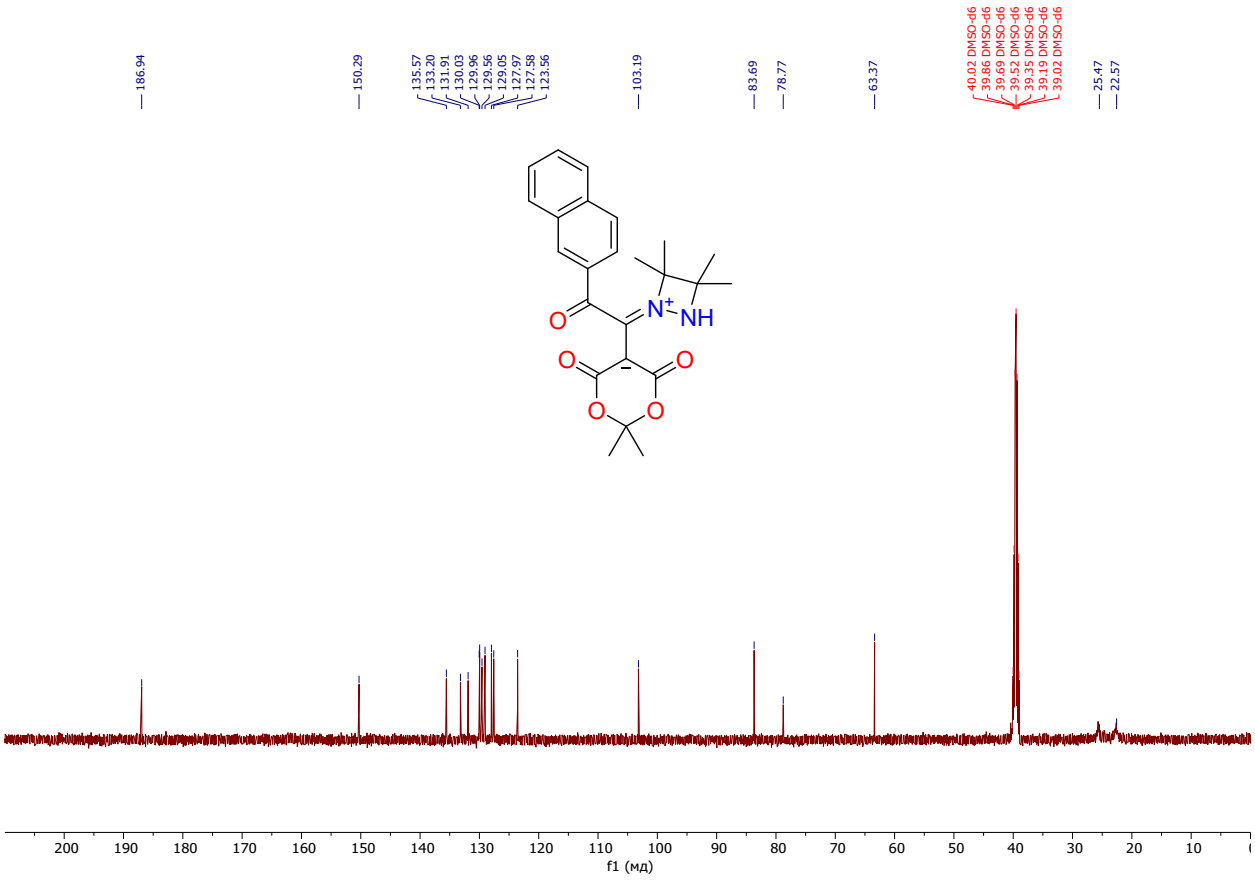
HRMS for compound **6o**



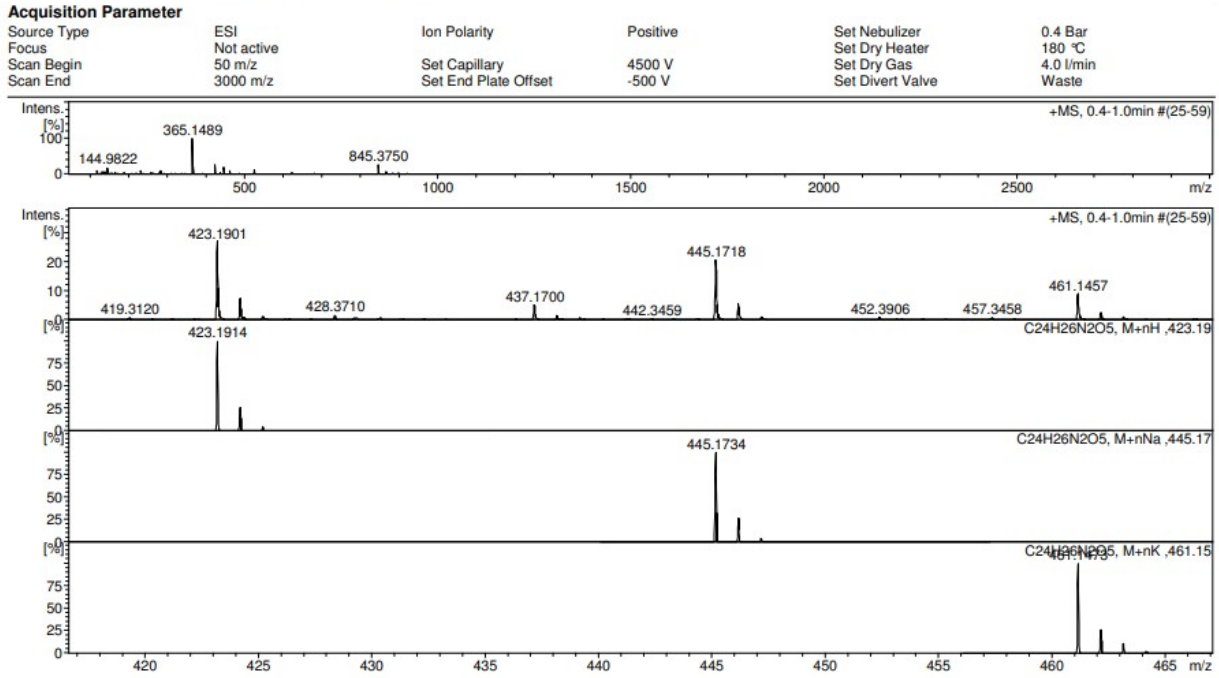
^{1}H NMR spectrum (300 MHz) of **6p** in DMSO-d_6



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



HRMS for compound **6p**



5. Geometric Parameters for compound 6a

Table S1. Selected bond lengths [Å] and angles [°] for **6a**.

Br(1)-C(16)	1.8978(13)	C(6)-O(1)-C(2)	117.79(10)
O(1)-C(2)	1.4410(15)	C(4)-O(3)-C(2)	117.68(10)
O(1)-C(6)	1.3598(16)	N(8)-N(7)-C(10)	93.25(9)
O(3)-C(2)	1.4442(15)	C(11)-N(7)-N(8)	129.77(11)
O(3)-C(4)	1.3684(16)	C(11)-N(7)-C(10)	136.98(11)
O(4)-C(4)	1.2260(17)	N(7)-N(8)-C(9)	90.44(9)
O(6)-C(6)	1.2173(17)	N(7)-N(8)-H(8)	108.2(13)
O(12)-C(12)	1.2136(17)	C(9)-N(8)-H(8)	115.0(12)
N(7)-N(8)	1.4159(15)	O(1)-C(2)-O(3)	109.42(10)
N(7)-C(10)	1.5193(16)	O(1)-C(2)-C(19)	105.48(11)
N(7)-C(11)	1.3004(17)	O(1)-C(2)-C(20)	111.32(10)
N(8)-C(9)	1.5103(17)	O(3)-C(2)-C(19)	107.00(10)
N(8)-H(8)	0.90(2)	O(3)-C(2)-C(20)	110.17(11)
C(2)-C(19)	1.5075(19)	C(19)-C(2)-C(20)	113.24(11)
C(2)-C(20)	1.5122(19)	O(3)-C(4)-C(5)	116.88(11)
C(4)-C(5)	1.4345(17)	O(4)-C(4)-O(3)	116.16(11)
C(5)-C(6)	1.4496(17)	O(4)-C(4)-C(5)	126.81(12)
C(5)-C(11)	1.4255(18)	C(4)-C(5)-C(6)	119.34(11)
C(9)-C(10)	1.5751(18)	C(11)-C(5)-C(4)	123.46(12)
C(9)-C(21)	1.5133(19)	C(11)-C(5)-C(6)	116.49(11)
C(9)-C(22)	1.5262(19)	O(1)-C(6)-C(5)	116.75(11)
C(10)-C(23)	1.5262(19)	O(6)-C(6)-O(1)	117.61(12)
C(10)-C(24)	1.5160(18)	O(6)-C(6)-C(5)	125.61(12)
C(11)-C(12)	1.5380(18)	N(8)-C(9)-C(10)	87.53(9)
C(12)-C(13)	1.4848(18)	N(8)-C(9)-C(21)	112.51(11)
C(13)-C(14)	1.3987(18)	N(8)-C(9)-C(22)	111.11(11)
C(13)-C(18)	1.3952(18)	C(21)-C(9)-C(10)	117.79(12)
C(14)-C(15)	1.384(2)	C(21)-C(9)-C(22)	111.42(12)
C(15)-C(16)	1.3898(19)	C(22)-C(9)-C(10)	114.29(11)
C(16)-C(17)	1.3891(18)	N(7)-C(10)-C(9)	84.35(9)
C(17)-C(18)	1.3915(19)	N(7)-C(10)-C(23)	110.54(10)

C(27)-C(26)	1.46(3)	C(23)-C(10)-C(9)	114.41(11)
N(25)-C(26)	1.142(5)	C(24)-C(10)-N(7)	114.98(11)
		C(24)-C(10)-C(9)	117.62(11)
		C(24)-C(10)-C(23)	112.08(12)
		N(7)-C(11)-C(5)	125.54(12)
		N(7)-C(11)-C(12)	113.96(11)
		C(5)-C(11)-C(12)	120.40(11)
		O(12)-C(12)-C(11)	119.00(12)
		O(12)-C(12)-C(13)	123.39(12)
		C(13)-C(12)-C(11)	117.47(11)
		C(14)-C(13)-C(12)	118.08(12)
		C(18)-C(13)-C(12)	122.06(12)
		C(18)-C(13)-C(14)	119.82(12)
		C(15)-C(14)-C(13)	120.29(12)
		C(14)-C(15)-C(16)	118.90(12)
		C(15)-C(16)-Br(1)	118.82(10)
		C(17)-C(16)-Br(1)	119.14(10)
		C(17)-C(16)-C(15)	122.04(12)
		C(16)-C(17)-C(18)	118.49(12)
		C(17)-C(18)-C(13)	120.44(12)
		N(25)-C(26)-C(27)	178.9(5)

Table S2. Torsion angles [°] for **6a**.

Br(1)-C(16)-C(17)-C(18)	179.12(10)	C(5)-C(11)-C(12)-C(13)	72.76(16)
O(3)-C(4)-C(5)-C(6)	13.53(17)	C(6)-O(1)-C(2)-O(3)	49.97(15)
O(3)-C(4)-C(5)-C(11)	-176.51(11)	C(6)-O(1)-C(2)-C(19)	164.76(11)
O(4)-C(4)-C(5)-C(6)	-161.84(13)	C(6)-O(1)-C(2)-C(20)	-72.04(14)
O(4)-C(4)-C(5)-C(11)	8.1(2)	C(6)-C(5)-C(11)-N(7)	-158.35(13)
O(12)-C(12)-C(13)-C(14)	15.8(2)	C(6)-C(5)-C(11)-C(12)	17.71(17)
O(12)-C(12)-C(13)-C(18)	-162.05(13)	C(10)-N(7)-N(8)-C(9)	16.58(10)
N(7)-N(8)-C(9)-C(10)	-15.96(10)	C(10)-N(7)-C(11)-C(5)	-173.78(13)
N(7)-N(8)-C(9)-C(21)	-135.12(12)	C(10)-N(7)-C(11)-C(12)	9.9(2)
N(7)-N(8)-C(9)-C(22)	99.16(12)	C(11)-N(7)-N(8)-C(9)	-162.87(13)
N(7)-C(11)-C(12)-O(12)	64.99(16)	C(11)-N(7)-C(10)-C(9)	163.42(15)
N(7)-C(11)-C(12)-C(13)	-110.75(13)	C(11)-N(7)-C(10)-C(23)	-82.61(18)
N(8)-N(7)-C(10)-C(9)	-15.95(9)	C(11)-N(7)-C(10)-C(24)	45.5(2)
N(8)-N(7)-C(10)-C(23)	98.02(11)	C(11)-C(5)-C(6)-O(1)	176.20(11)
N(8)-N(7)-C(10)-C(24)	-133.86(12)	C(11)-C(5)-C(6)-O(6)	-5.8(2)
N(8)-N(7)-C(11)-C(5)	5.4(2)	C(11)-C(12)-C(13)-C(14)	-168.65(12)
N(8)-N(7)-C(11)-C(12)	-170.88(12)	C(11)-C(12)-C(13)-C(18)	13.49(18)
N(8)-C(9)-C(10)-N(7)	14.92(9)	C(12)-C(13)-C(14)-C(15)	-178.99(12)
N(8)-C(9)-C(10)-C(23)	-95.10(12)	C(12)-C(13)-C(18)-C(17)	177.97(12)
N(8)-C(9)-C(10)-C(24)	130.21(12)	C(13)-C(14)-C(15)-C(16)	1.0(2)
C(2)-O(1)-C(6)-O(6)	161.93(12)	C(14)-C(13)-C(18)-C(17)	0.1(2)
C(2)-O(1)-C(6)-C(5)	-19.95(16)	C(14)-C(15)-C(16)-Br(1)	179.97(10)
C(2)-O(3)-C(4)-O(4)	-165.11(11)	C(14)-C(15)-C(16)-C(17)	0.0(2)
C(2)-O(3)-C(4)-C(5)	19.02(16)	C(15)-C(16)-C(17)-C(18)	-0.9(2)
C(4)-O(3)-C(2)-O(1)	-49.46(15)	C(16)-C(17)-C(18)-C(13)	0.84(19)
C(4)-O(3)-C(2)-C(19)	-163.27(11)	C(18)-C(13)-C(14)-C(15)	-1.1(2)
C(4)-O(3)-C(2)-C(20)	73.23(14)	C(21)-C(9)-C(10)-N(7)	129.15(12)
C(4)-C(5)-C(6)-O(1)	-13.14(17)	C(21)-C(9)-C(10)-C(23)	19.13(17)
C(4)-C(5)-C(6)-O(6)	164.81(13)	C(21)-C(9)-C(10)-C(24)	-115.56(14)
C(4)-C(5)-C(11)-N(7)	31.4(2)	C(22)-C(9)-C(10)-N(7)	-97.16(12)
C(4)-C(5)-C(11)-C(12)	-152.52(12)	C(22)-C(9)-C(10)-C(23)	152.82(12)
C(5)-C(11)-C(12)-O(12)	-111.50(14)	C(22)-C(9)-C(10)-C(24)	18.12(17)

Table S3. Hydrogen bonds for **6a** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(8)-H(8)...O(4)	0.90(2)	1.88(2)	2.6873(16)	148.6(18)

Symmetry transformations used to generate equivalent atoms: