Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting information

Photoinduced assembly of 3,4,4a,7a-tetrahydro-1*H*-cyclopenta[*b*]pyridine-2,7-dione core on the basis of allomaltol derivatives

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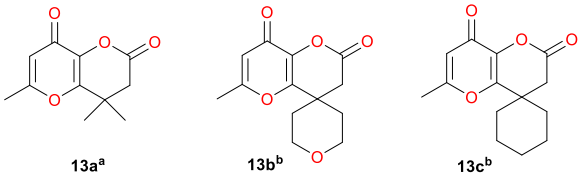
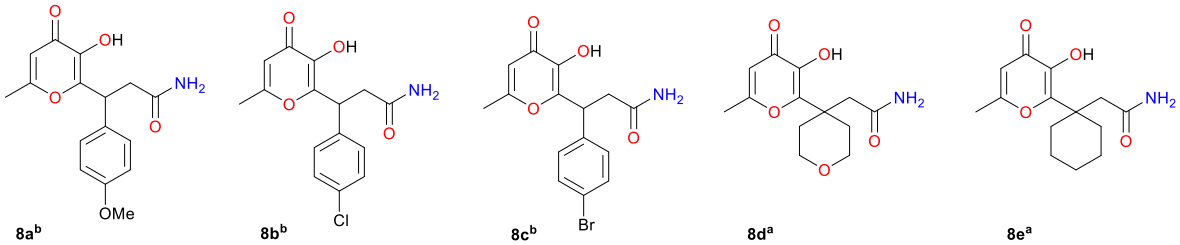
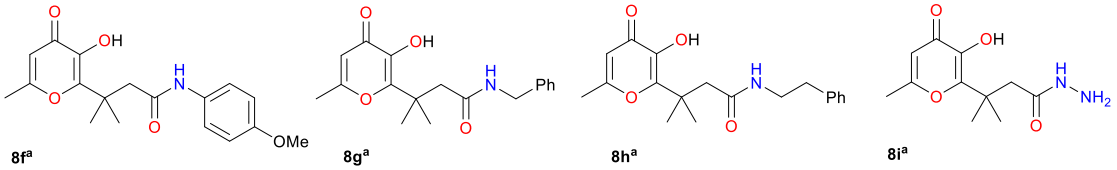
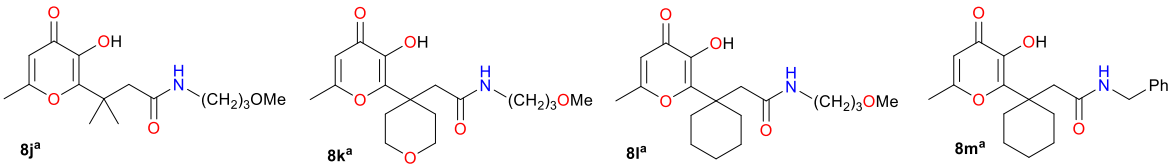
1. General information

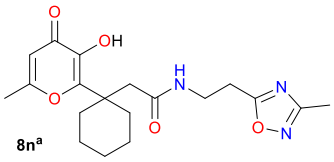
All synthesized starting compounds











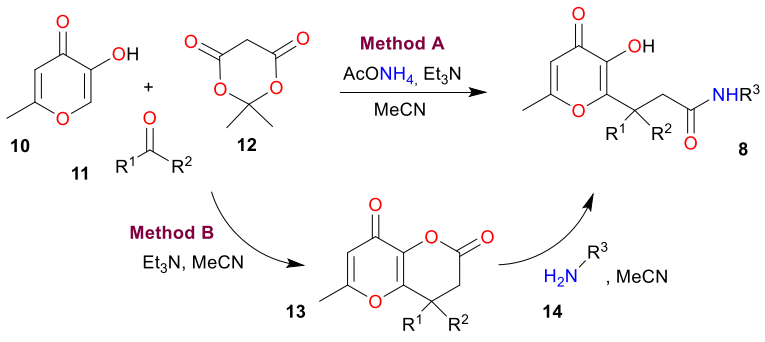
[a] New compounds

[b] Compounds synthesized previously[1]

1. A. N. Komogortsev, B. V. Lichitsky, A. D. Tretyakov, A. A. Dudinov and M. M. Krayushkin, *Chem. Heterocycl. Compd.*, 2019, **55**, 818–822

2. General procedures for the synthesis of compounds 8, 13, 9 and 16.

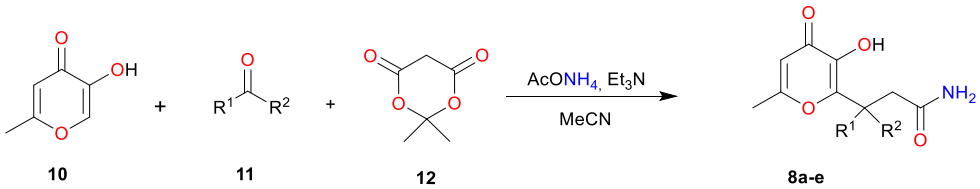
2.1 Synthesis of starting compounds **8:**



Compounds **8a-e** were synthesized *via* Method A.

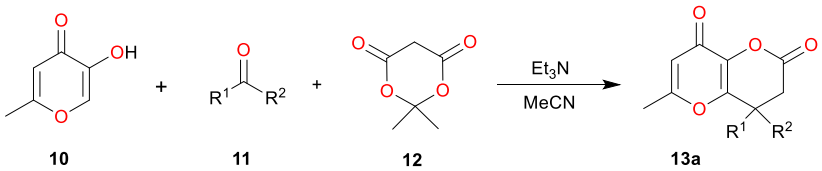
Compounds **8f-n** were synthesized *via* Method B.

Method A:

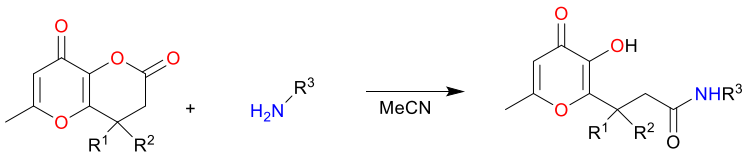


A mixture of 5-hydroxy2-methyl-4*H*-pyran-4-one **10** (3 mmol, 0.38 g), the appropriate carbonyl compound **11** (3.3 mmol), Meldrum's acid **12** (3.6 mmol, 0.52 g), $AcONH_4$ (9 mmol, 0.7 g), and Et_3N (3.3 mmol, 0.33 g) in MeCN (5 ml) was refluxed for 1 h. The reaction mixture was cooled to room temperature, and the precipitate formed was filtered off and washed with MeCN (3×5 ml) and H_2O (3×3) ml.

Method B:



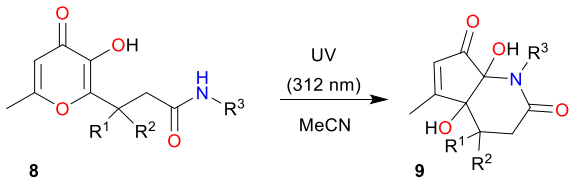
1) A mixture of allomaltol **10** (3 mmol, 0.38 g), carbonyl compound **11** (4 mmol), Meldrum's acid **12** (3.6 mmol, 0.52 g), and Et_3N (3.3 mmol, 0.33 g) in MeCN (5 ml) was refluxed for 20 min. Then the reaction mixture was evaporated in vacuo, and residue was triturated with *i*-PrOH. The precipitate formed was filtered off and washed with *i*-PrOH (3×5 ml).



13 14 8f-n

2) A mixture of lactone **13** (1 mmol) and the corresponding amine **14** (1.1 mmol) (or amine hydrochloride (1.1 mmol) and Et_3N (1.1 mmol, 0.11 g)) was reflux in acetonitrile for 2 h (or left overnight at r.t. for compound **8i**). For compounds **8f-h,m,n** the resulting solution was cooled, the precipitate formed was filtered off, washed with acetonitrile (3 × 5 ml) and water (3 x 5 ml). For compound **8i** the precipitate formed was filtered off, washed with acetonitrile (3 × 5 ml). For compounds **8j-l** the solution was evaporated in vacuum, the resulting residue was triturated with diethyl ether.

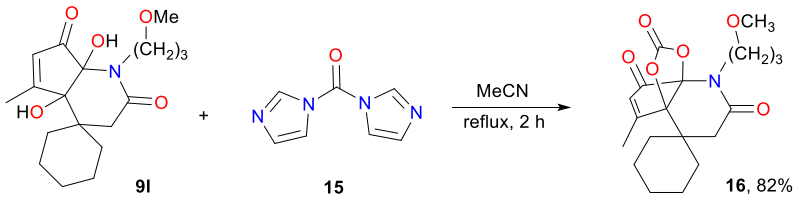
2.2 Experimental procedure for the synthesis of photoproducts **9**.



8 9

A solution of compound **8** (1 mmol) in 20 ml of acetonitrile was irradiated with a Vilber Lourmat VL-6.LM lamp (312 nm, 6 W) for 72 hours at room temperature in common laboratory glassware. The resulting mixture was evaporated in vacuum and recrystallized from isopropanol (for compounds **9a-i**,**m**), from a mixture of isopropanol and water (1: 1) (for compounds **9k**,**l**), from a mixture of diethyl ether and isopropanol (3: 1) (for compound **9j**) or from diethyl ether (for compound **9n**). The resulting product was filtered off and washed with an appropriate solvent or an appropriate mixture of solvents (3 × 5 ml).

2.3 Experimental procedure for the synthesis of 1'-(3-methoxypropyl)-5'-methyl-3'-hydro-1'*H*,7'*H*-spiro[cyclohexane-1,4'-[4a,7a](epoxymethanooxy)cyclopenta[*b*]pyridine]-2',7',9'-trione **16.**

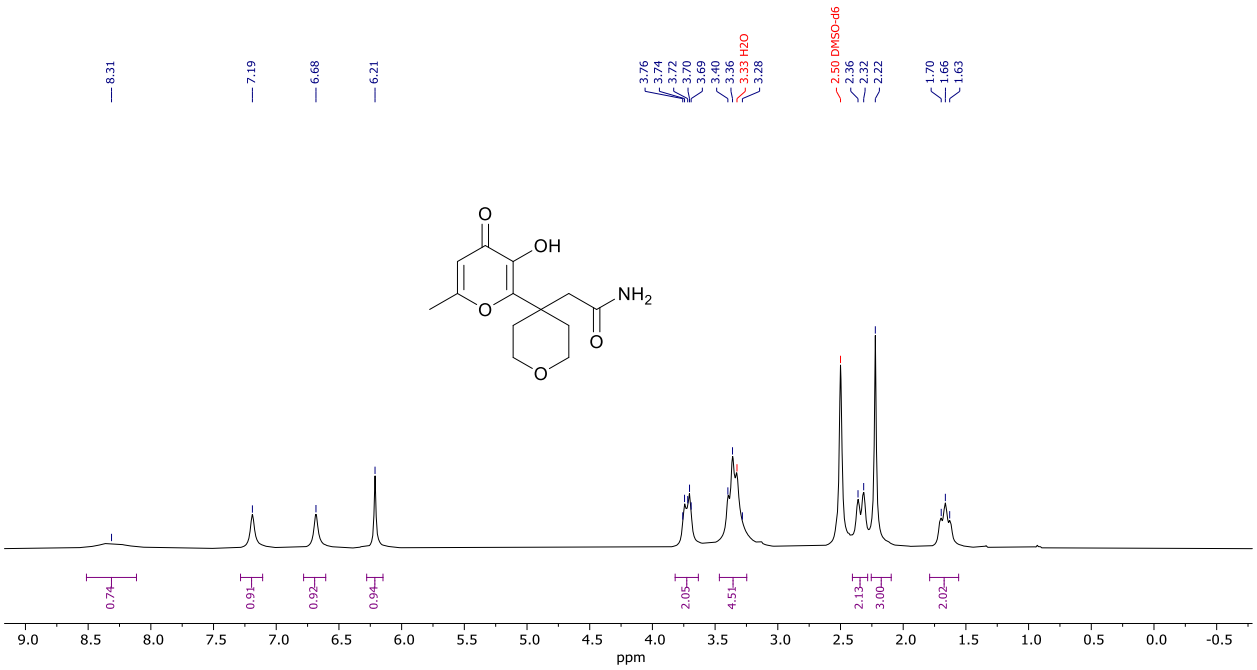


9l 15 16, 82%

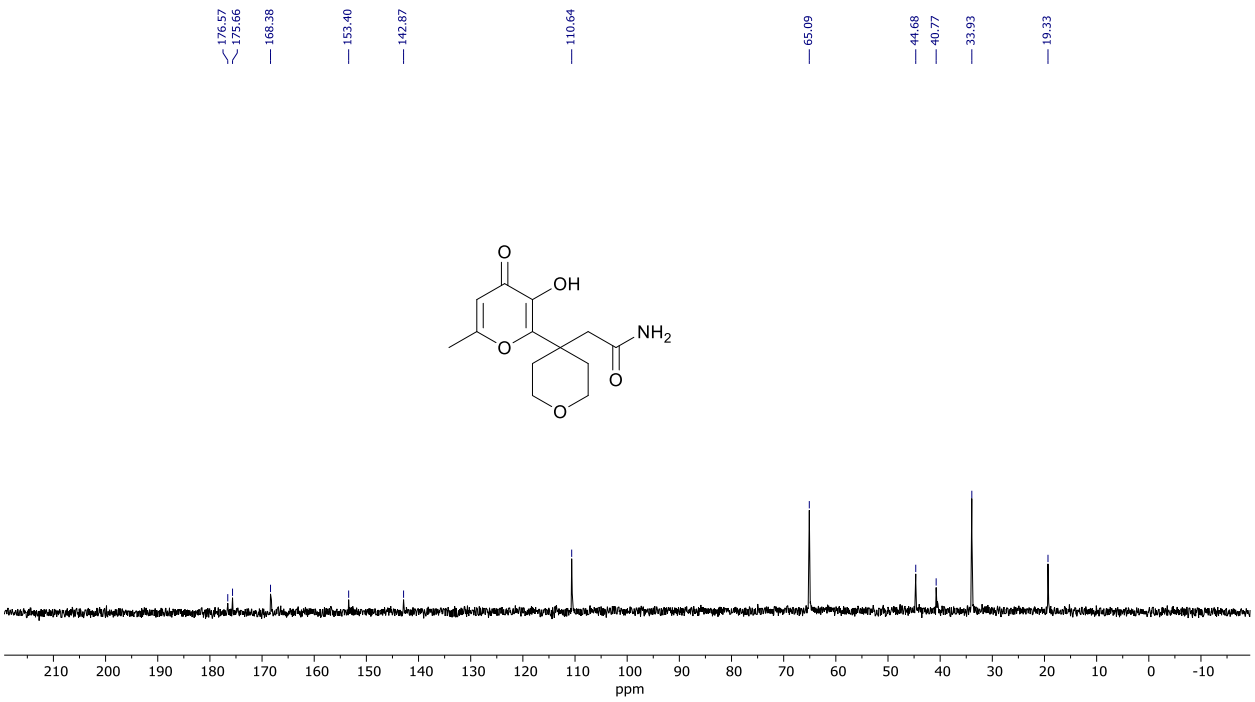
A mixture of **9l** (1 mmol, 0.34 g) and CDI (4 mmol, 0.65 g) in MeCN (5 ml) was reflux for 2 h. The reaction mixture was cooled to room temperature, poured into water (30 ml) and extracted with $CHCl_3$ (3×15 ml). The combined $CHCl_3$ extract was washed with 2% HCl (2×15 ml), H_2O (3×15 ml) and dried over Na_2SO_4. The organic layer was evaporated in vacuum to give the target product **16**.

3. Copies of ^{1}H and ^{13}C NMR spectra for compounds 8 and 13.

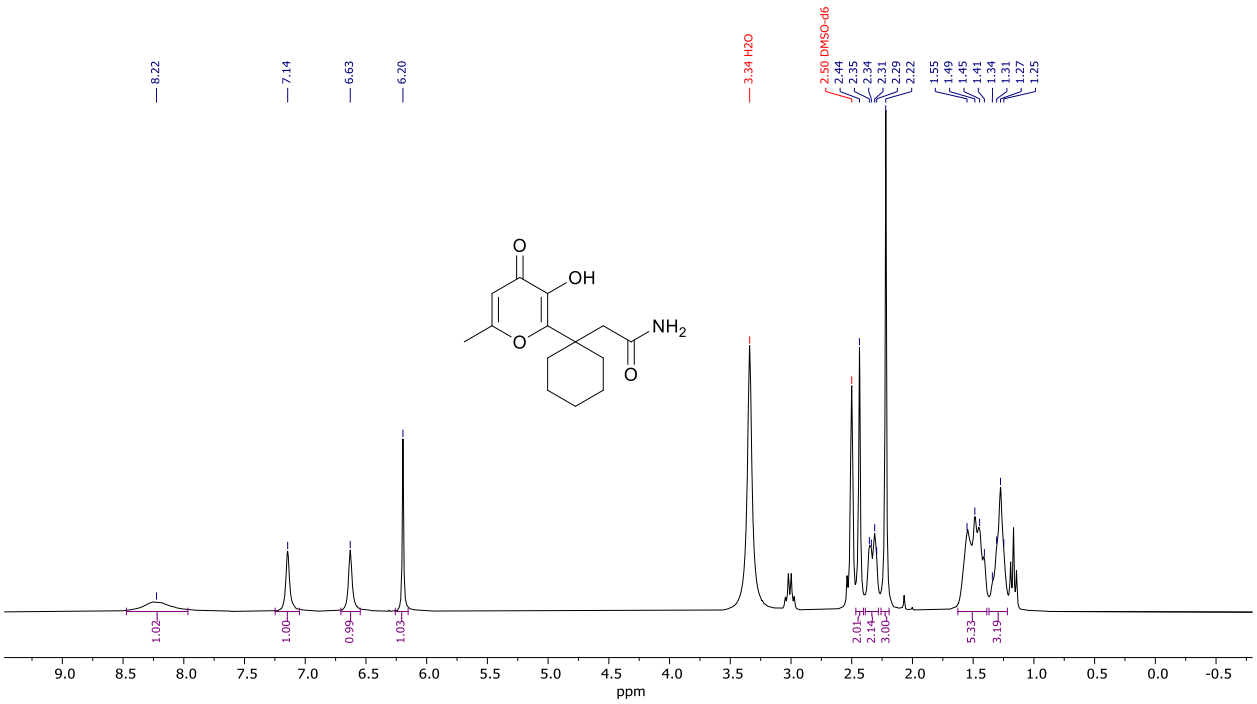
^{1}H NMR spectrum (300 MHz) of **8d** in DMSO-d_6



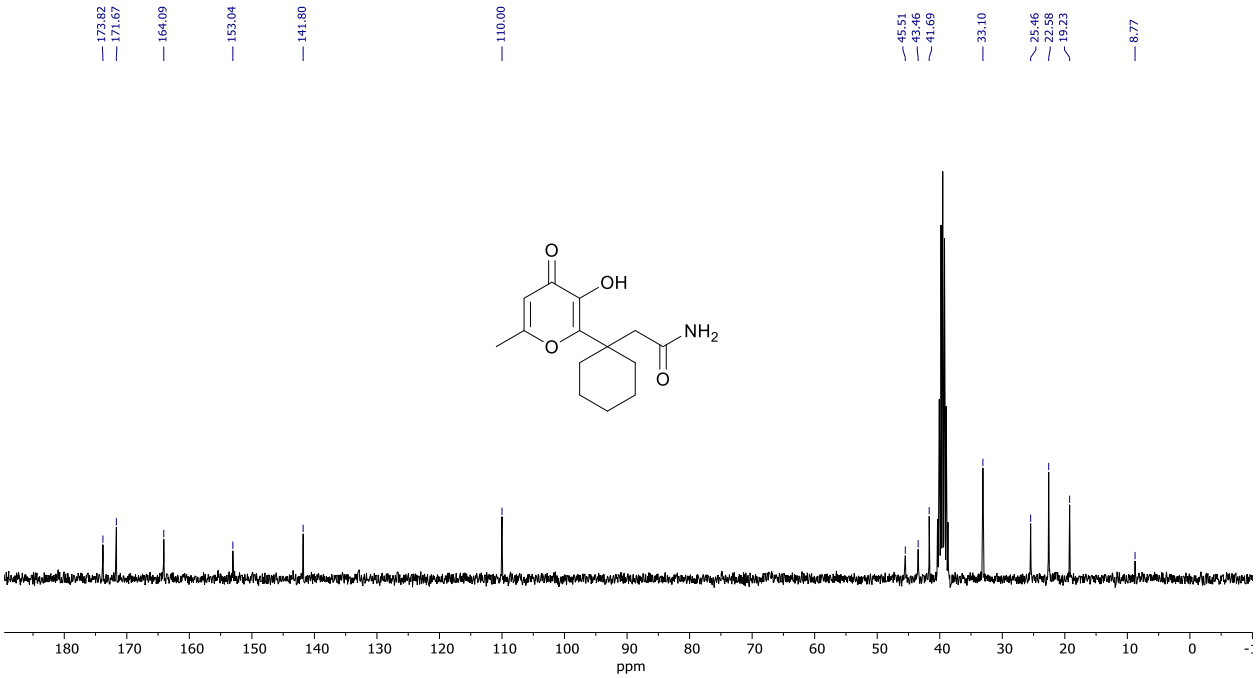
^{13}C {^{1}H} NMR spectrum (75 MHz) of **8d** in D_2O



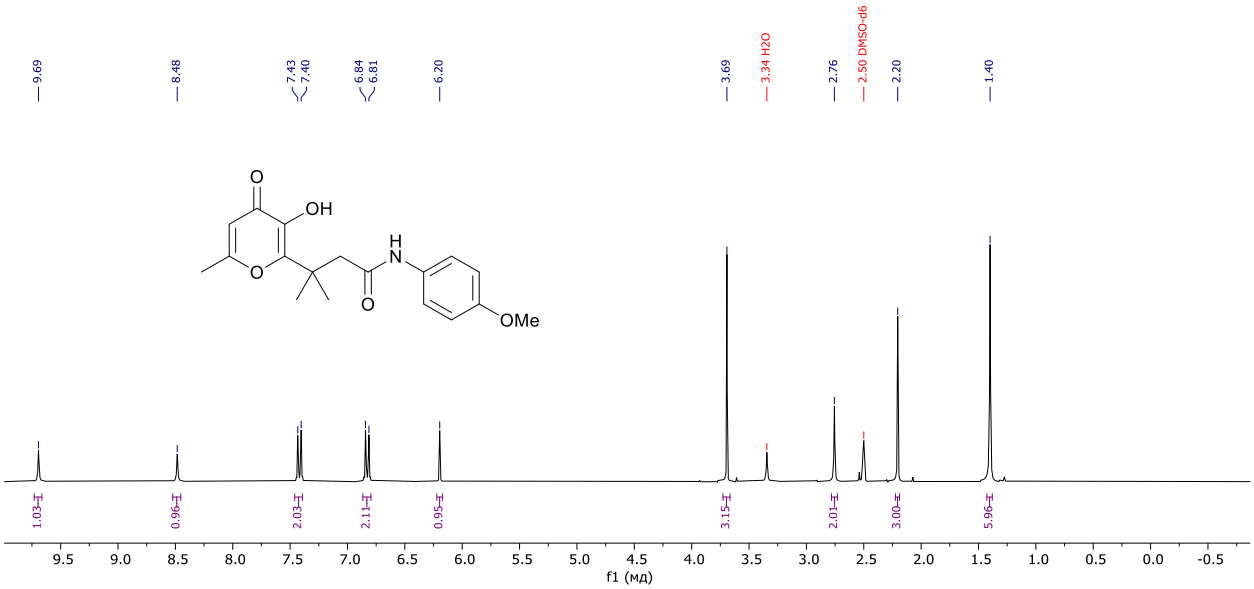
^{1}H NMR spectrum (300 MHz) of **8e** in DMSO-d_6



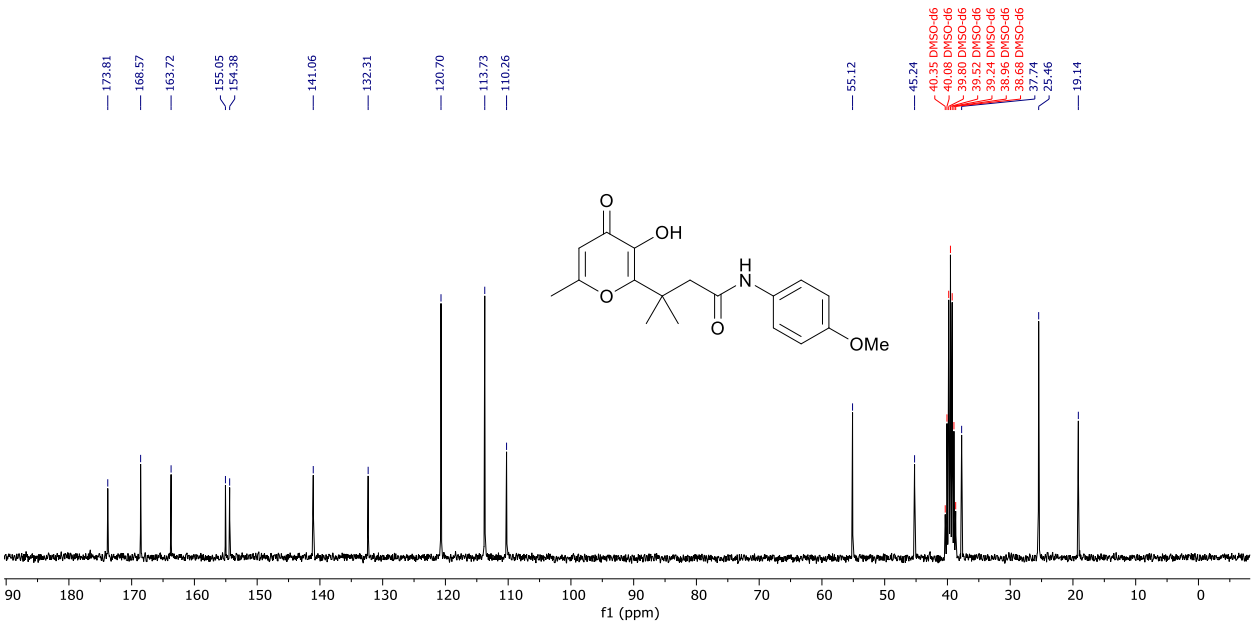
^{13}C {^{1}H} NMR spectrum (75 MHz) of **8e** in DMSO-d_6



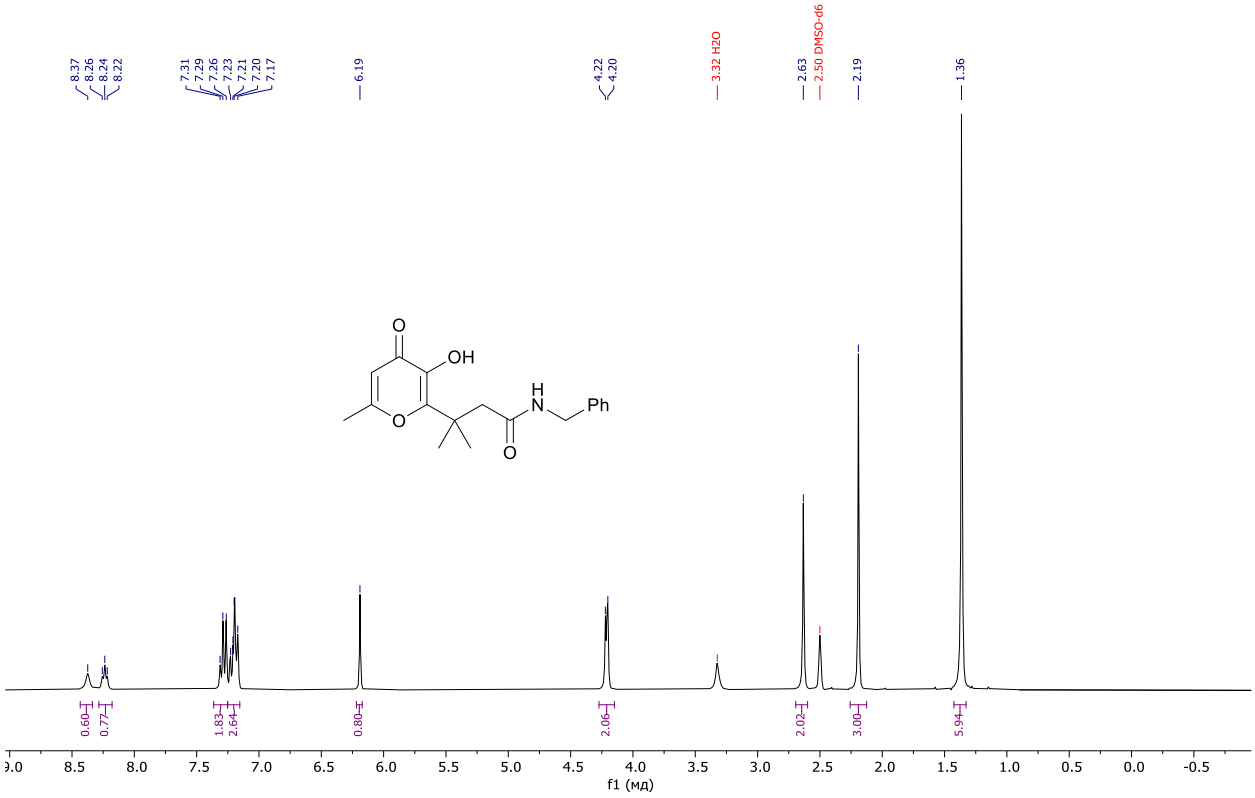
^{1}H NMR spectrum (300 MHz) of **8f** in DMSO-d_6



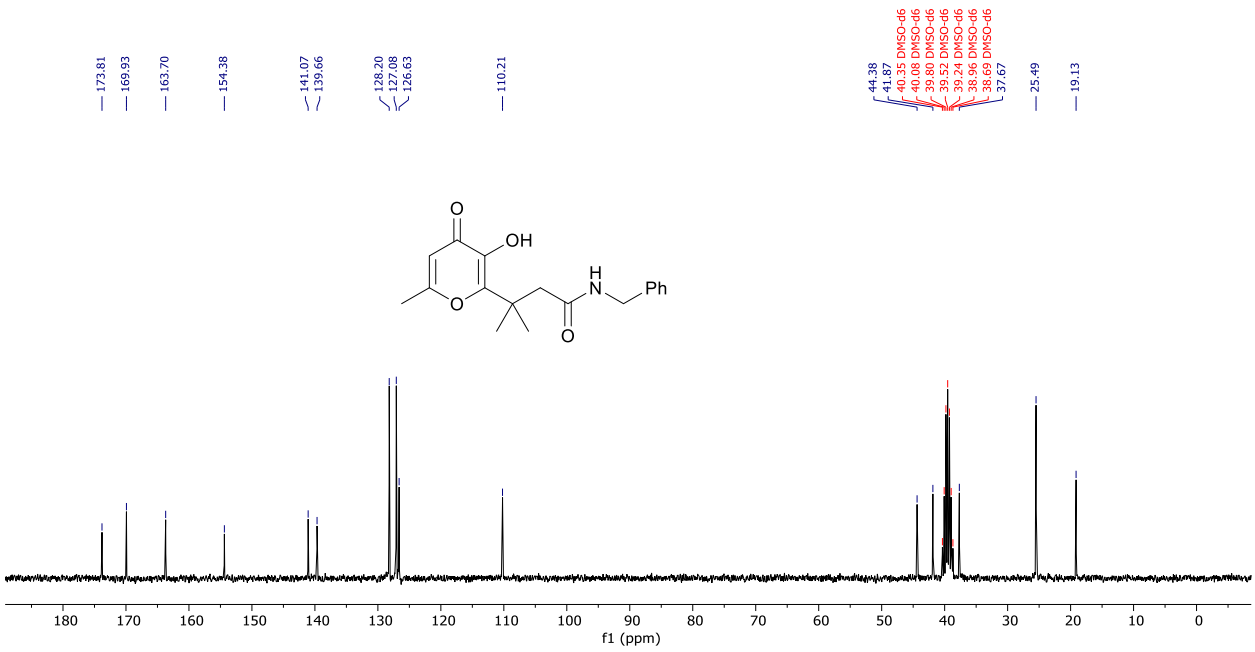
^{13}C {^{1}H} NMR spectrum (75 MHz) of **8f** in DMSO-d_6



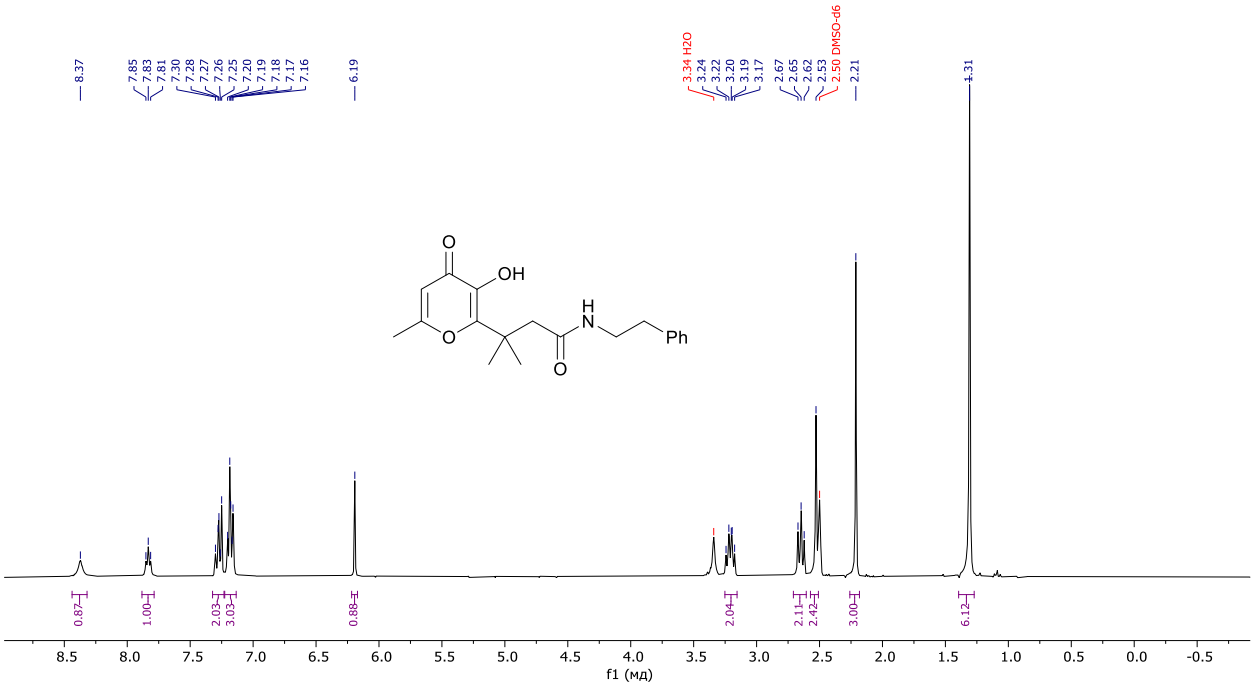
^{1}H NMR spectrum (300 MHz) of **8g** in DMSO-d_6



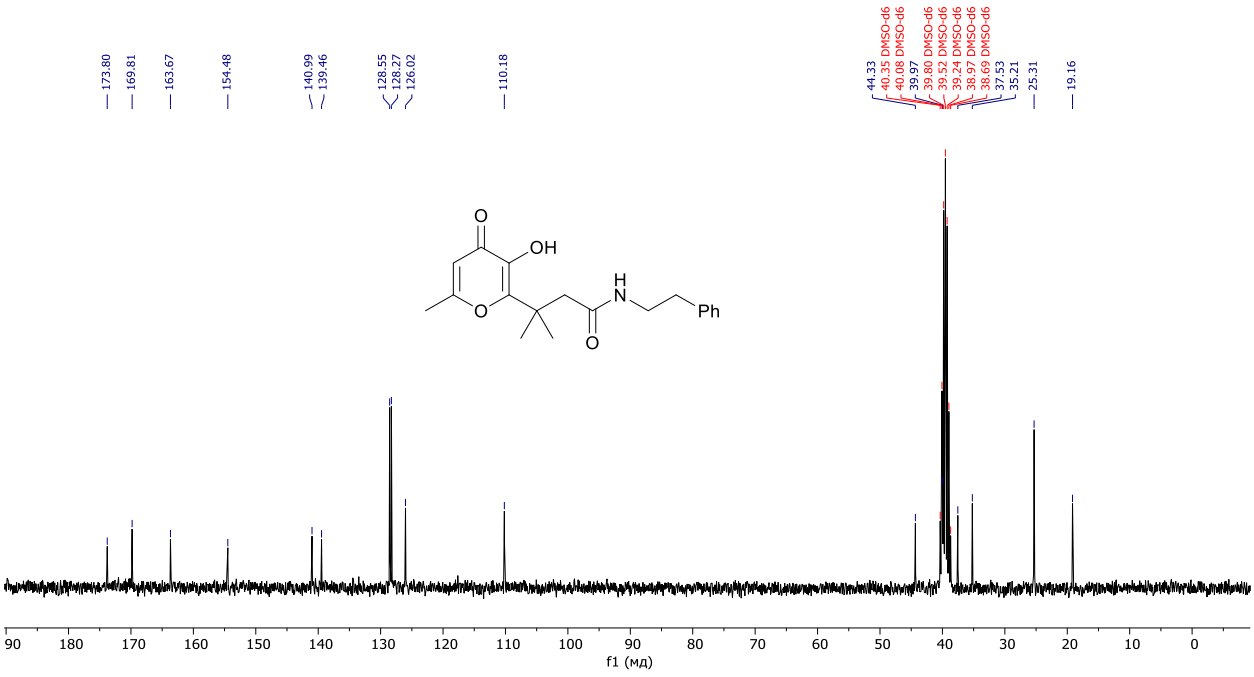
^{13}C {^{1}H} NMR spectrum (75 MHz) of **8g** in DMSO-d_6



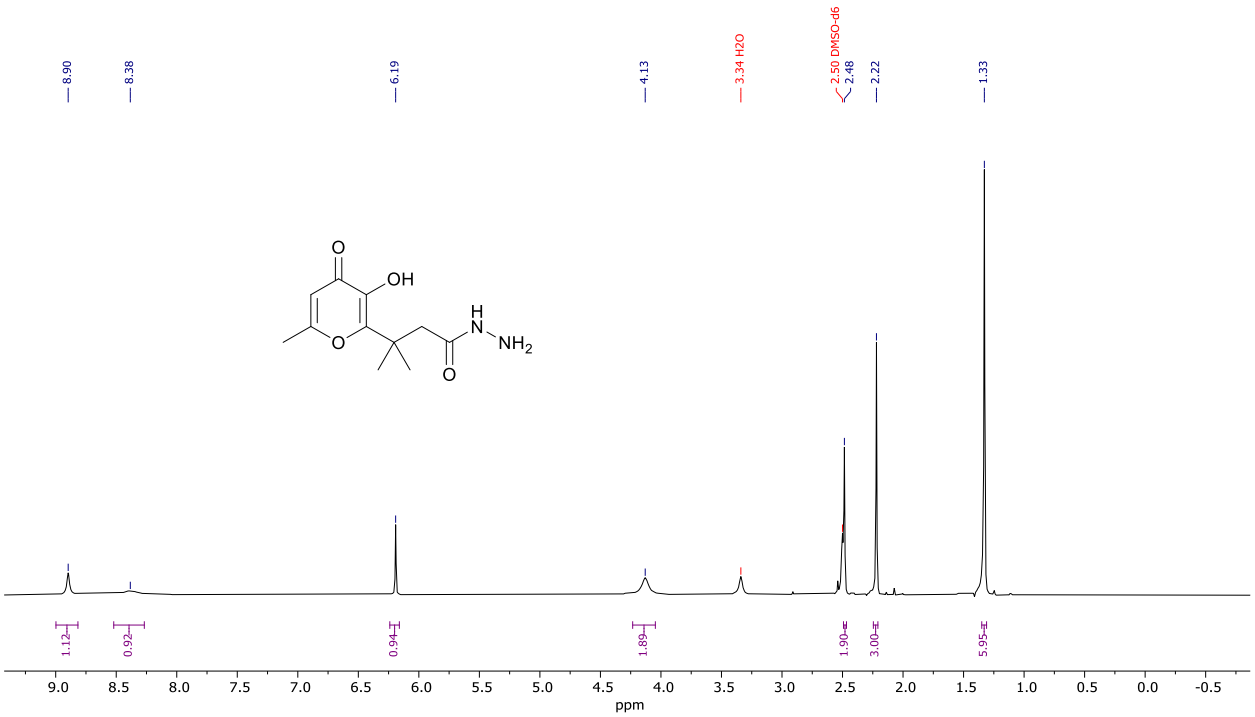
^{1}H NMR spectrum (300 MHz) of **8h** in DMSO-d_6



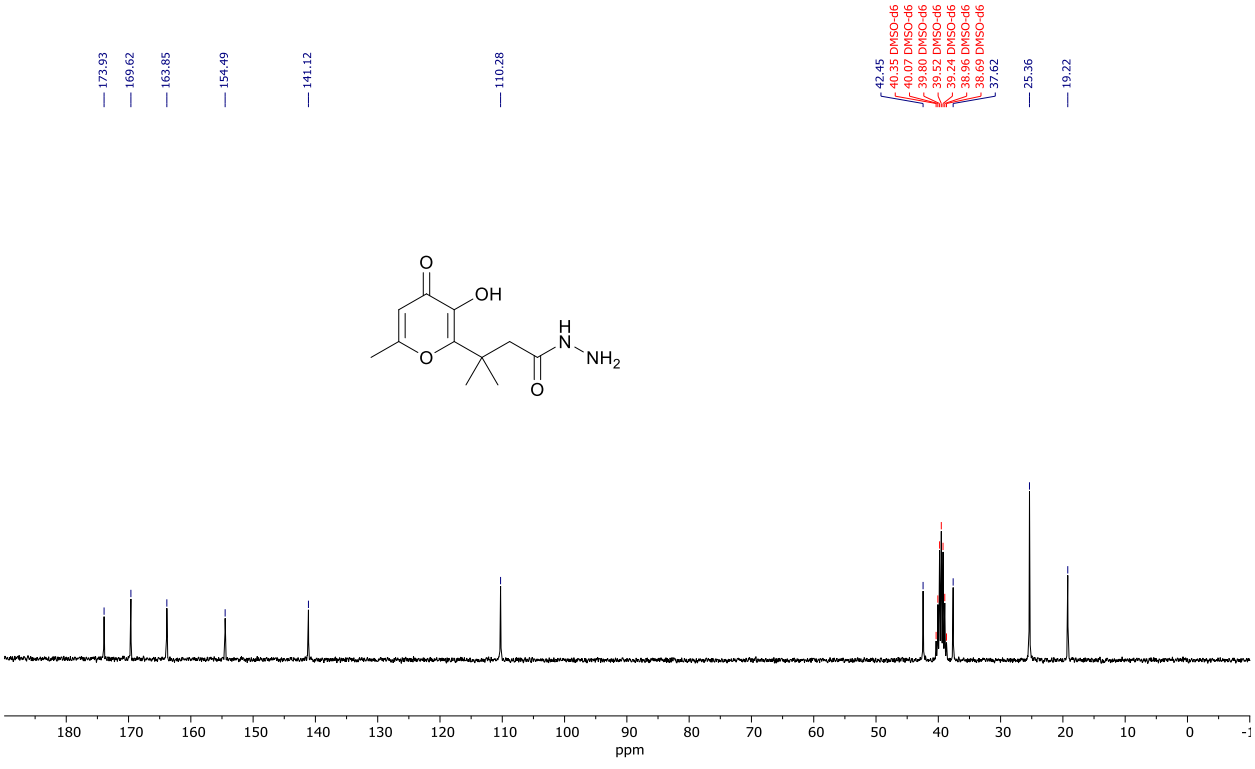
^{13}C {^{1}H} NMR spectrum (75 MHz) of **8h** in DMSO-d_6



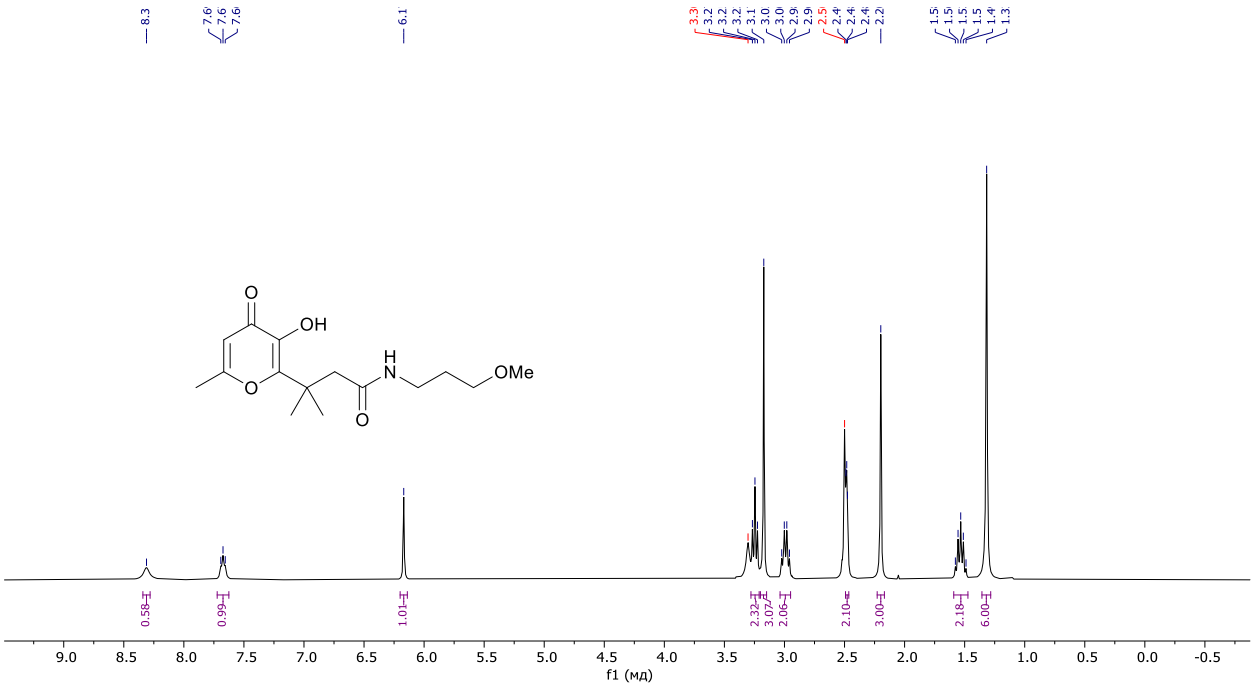
^{1}H NMR spectrum (300 MHz) of **8i** in DMSO-d_6



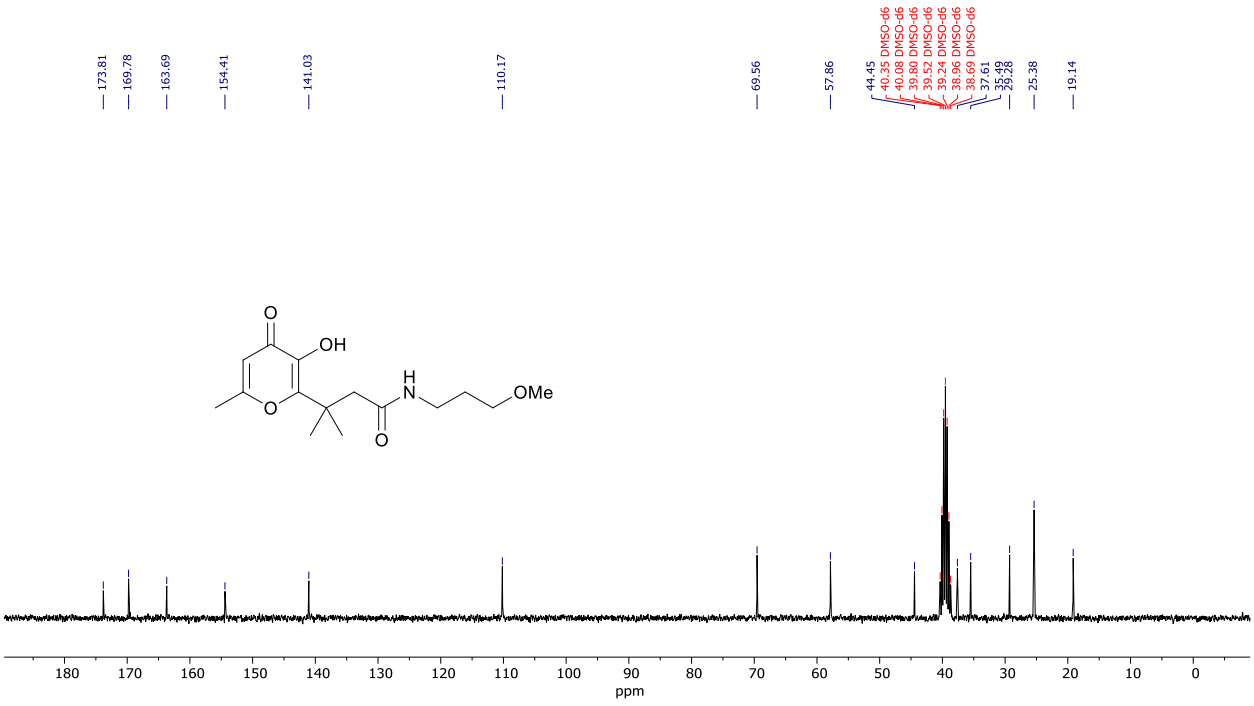
^{13}C {^{1}H} NMR spectrum (75 MHz) of **8i** in DMSO-d_6



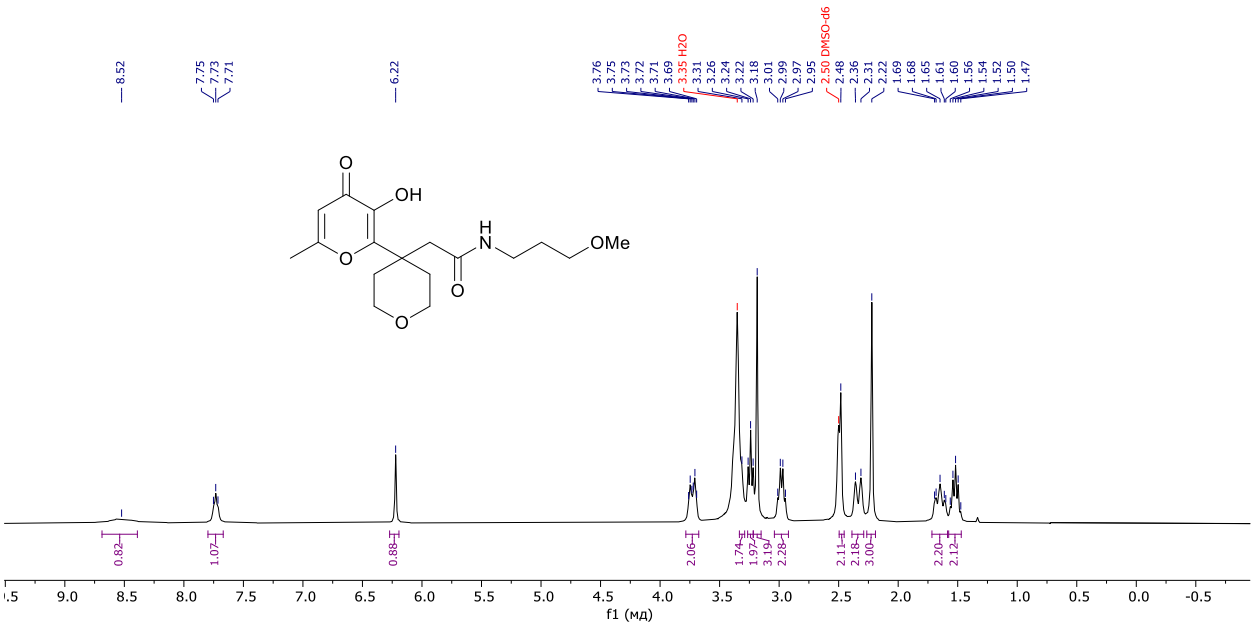
^{1}H NMR spectrum (300 MHz) of **8j** in DMSO-d_6



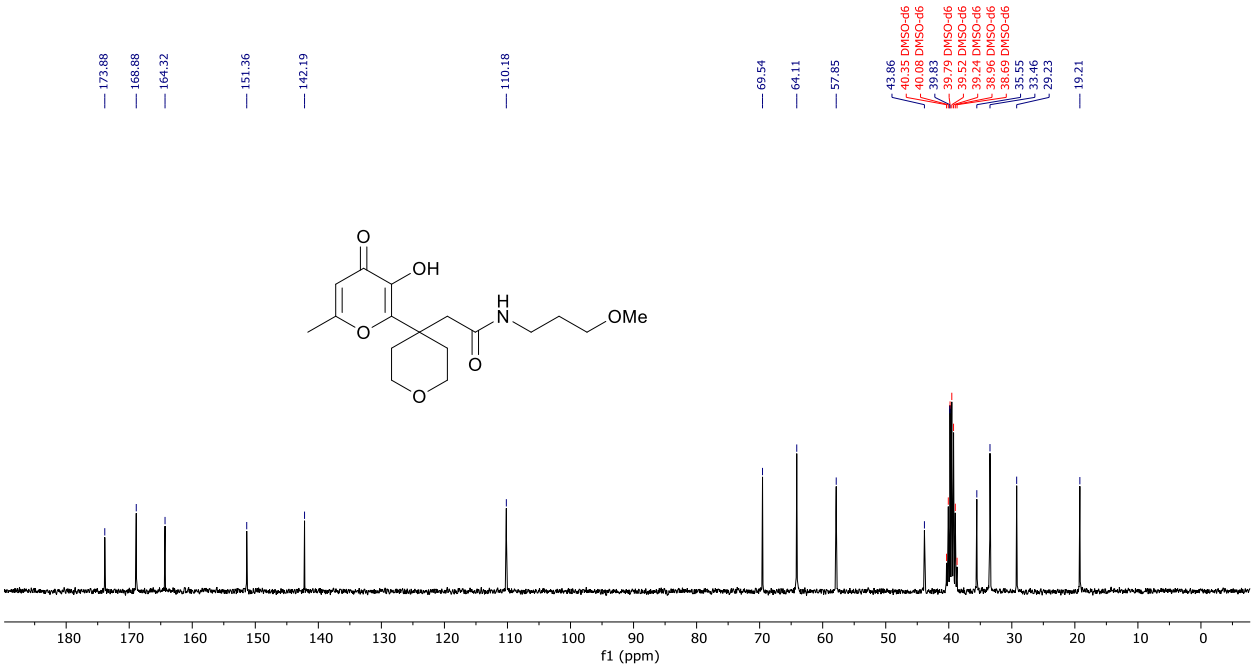
^{13}C {^{1}H} NMR spectrum (75 MHz) of **8j** in DMSO-d_6



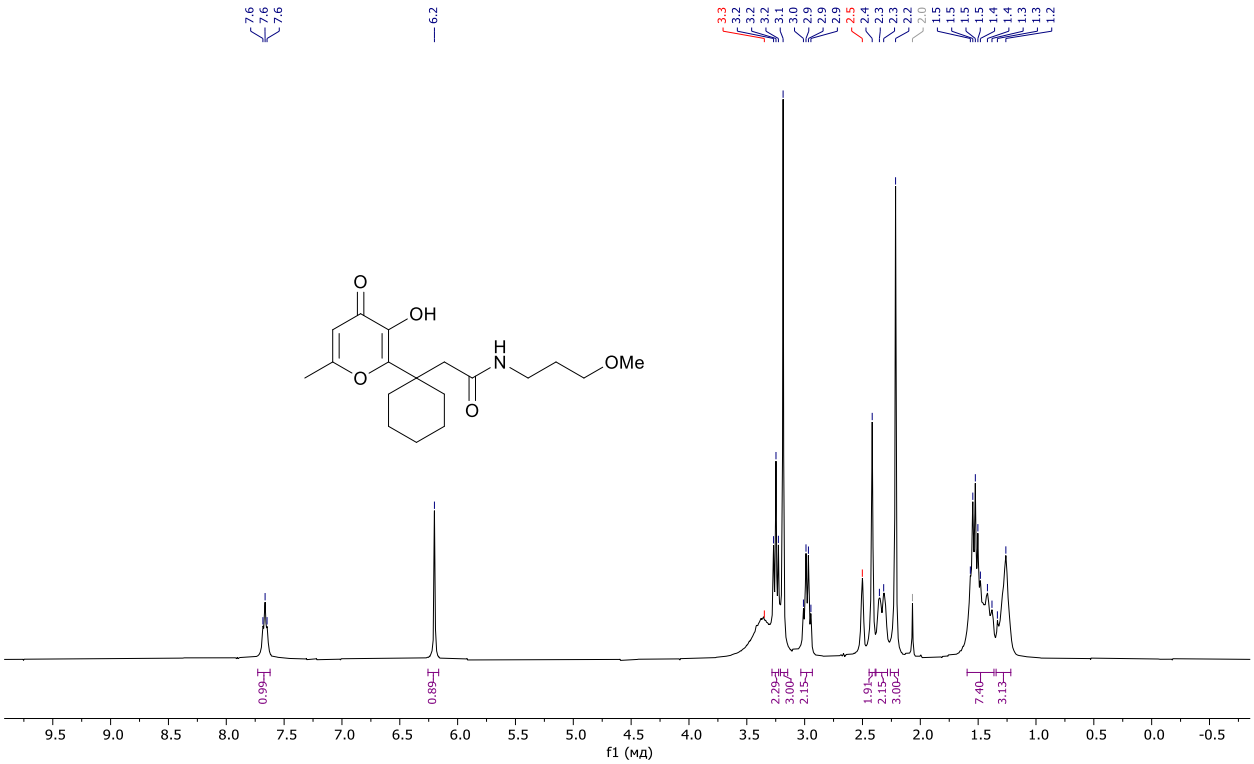
^{1}H NMR spectrum (300 MHz) of **8k** in DMSO-d_6



^{13}C {^{1}H} NMR spectrum (75 MHz) of **8k** in DMSO-d_6



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



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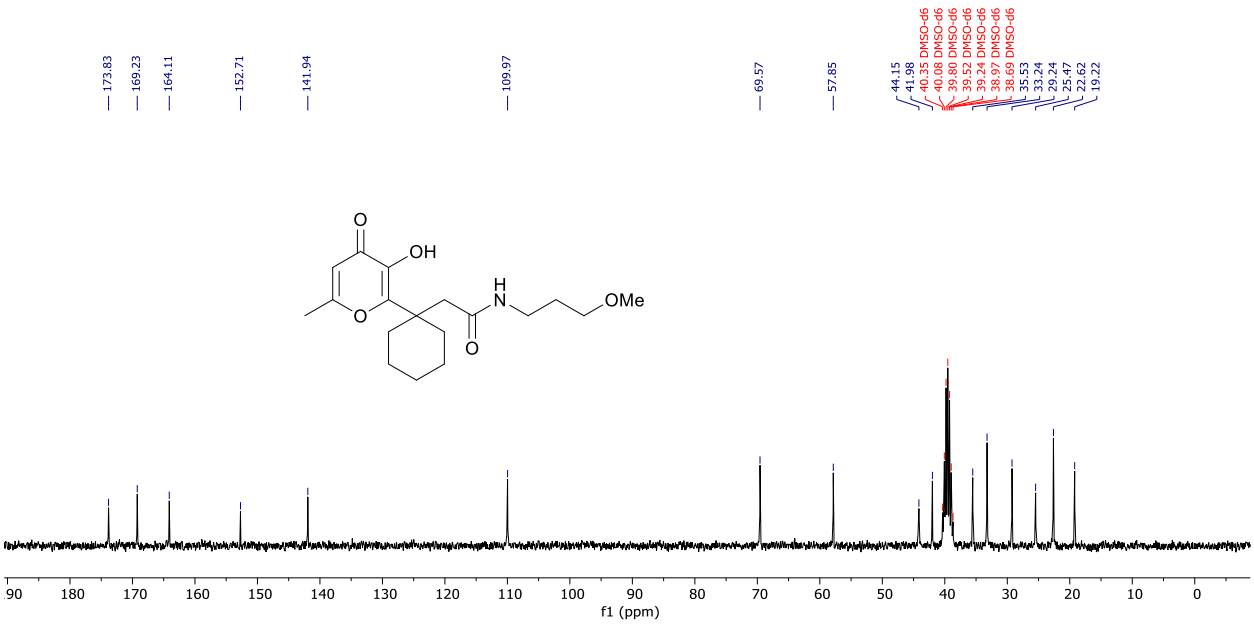
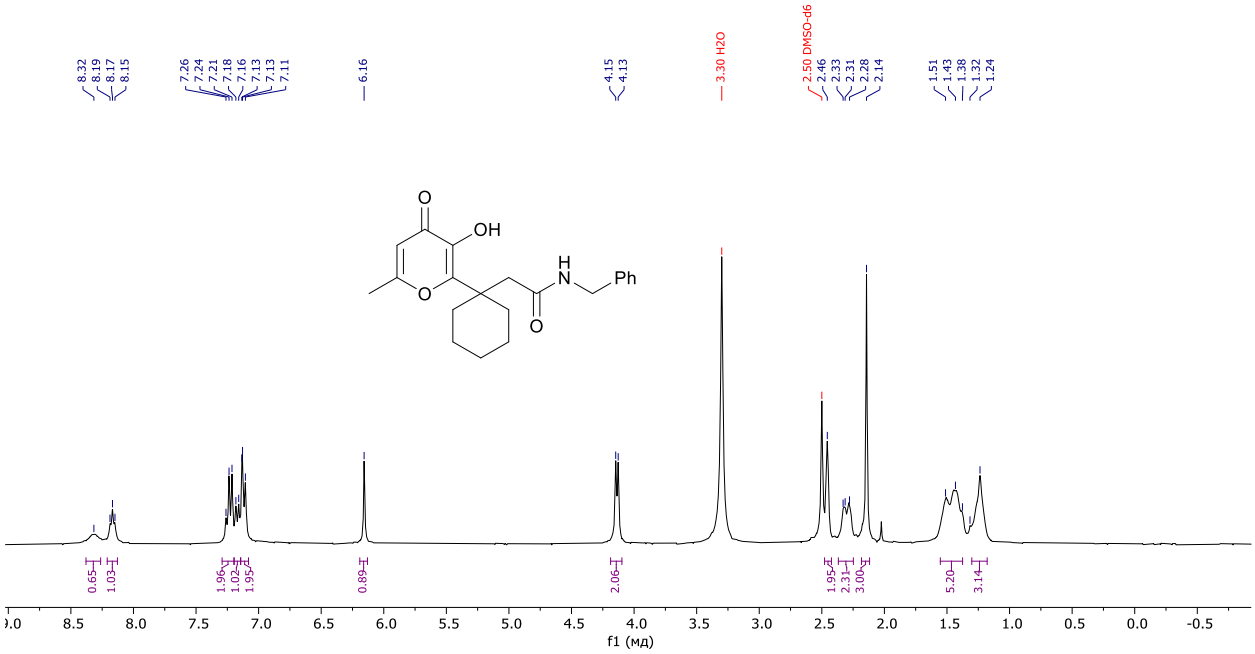
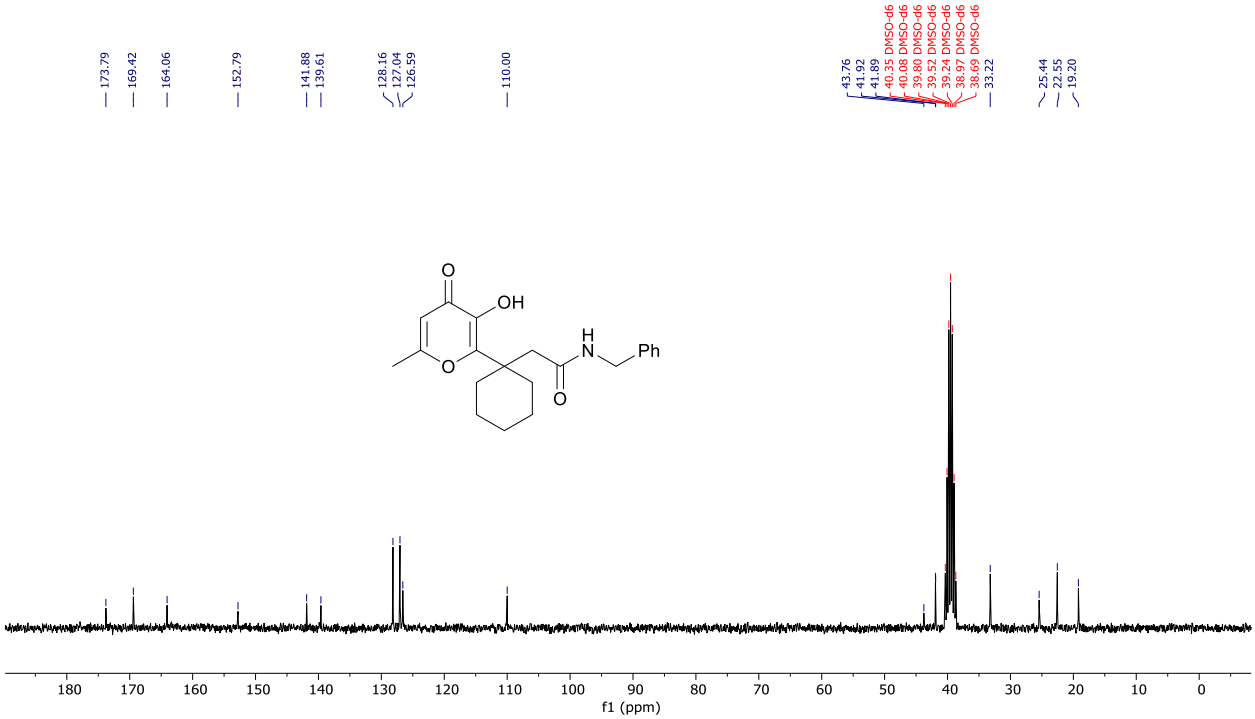


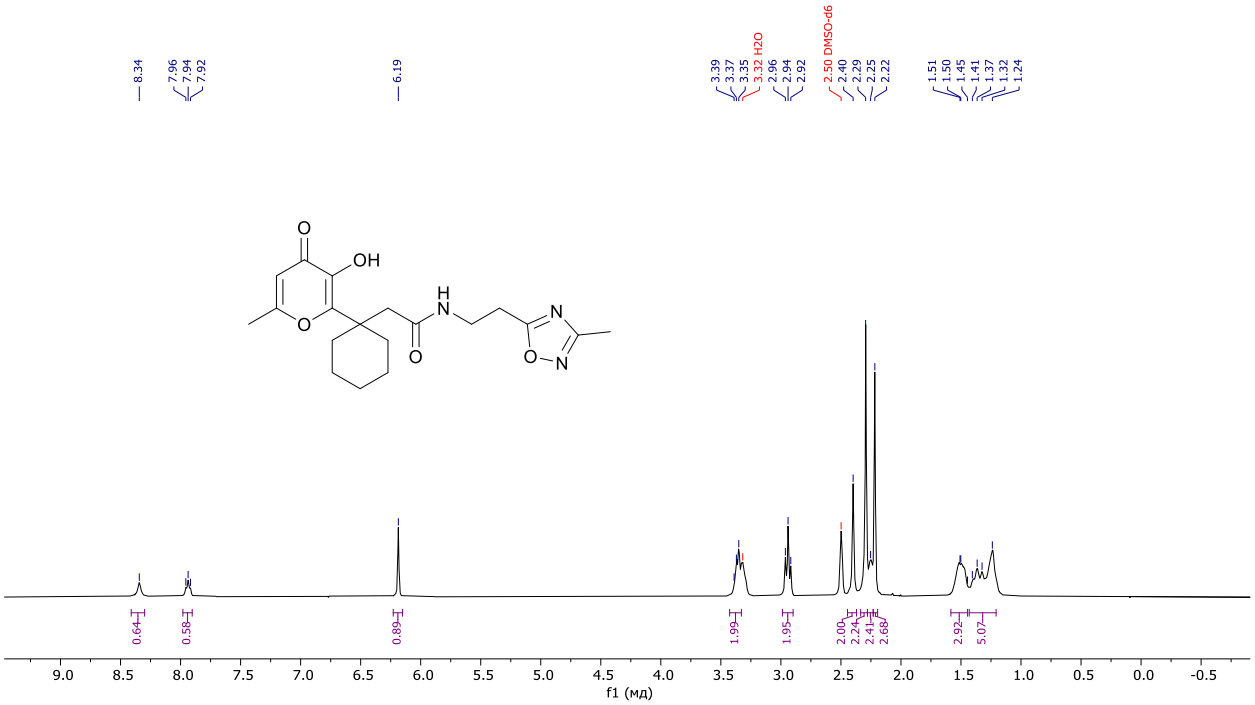
^{1}H NMR spectrum (300 MHz) of **8m** in DMSO-d_6



^{13}C {^{1}H} NMR spectrum (75 MHz) of **8m** in DMSO-d_6



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



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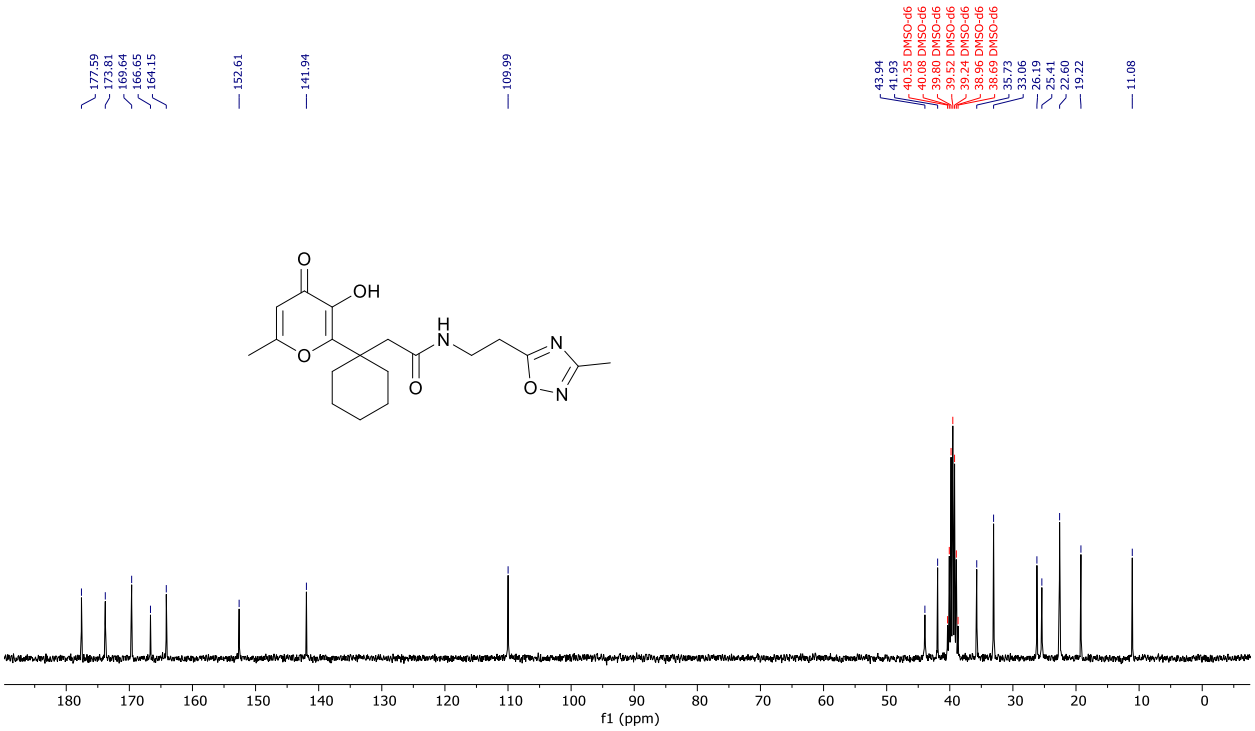
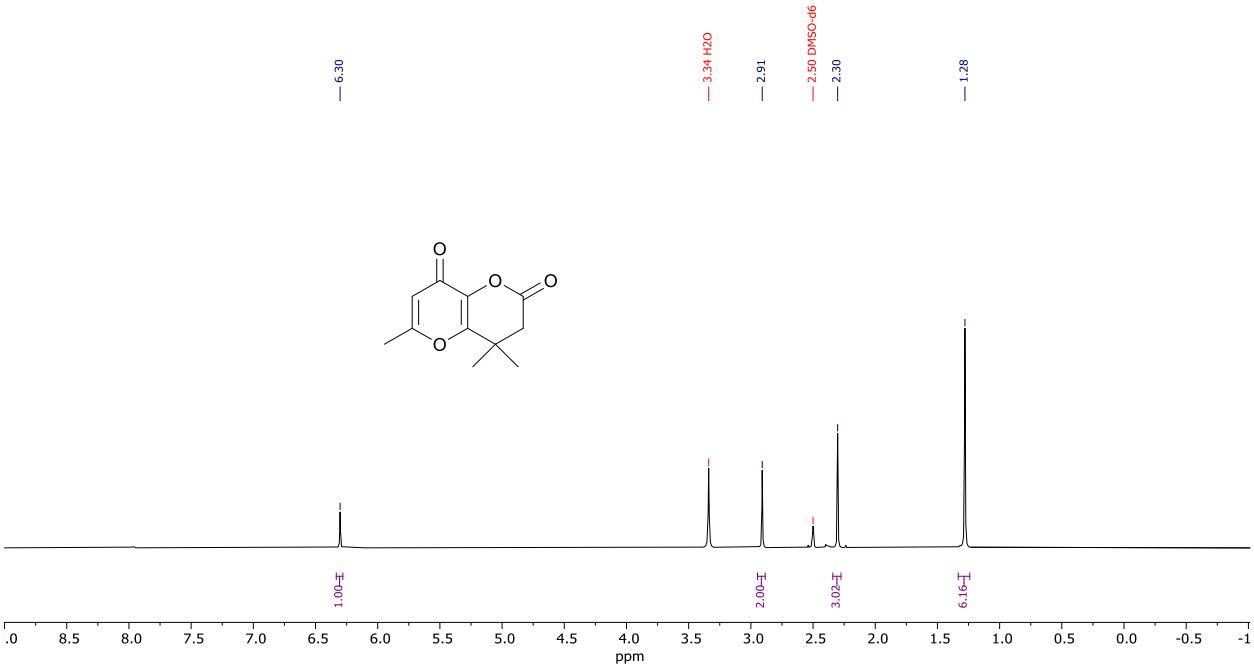
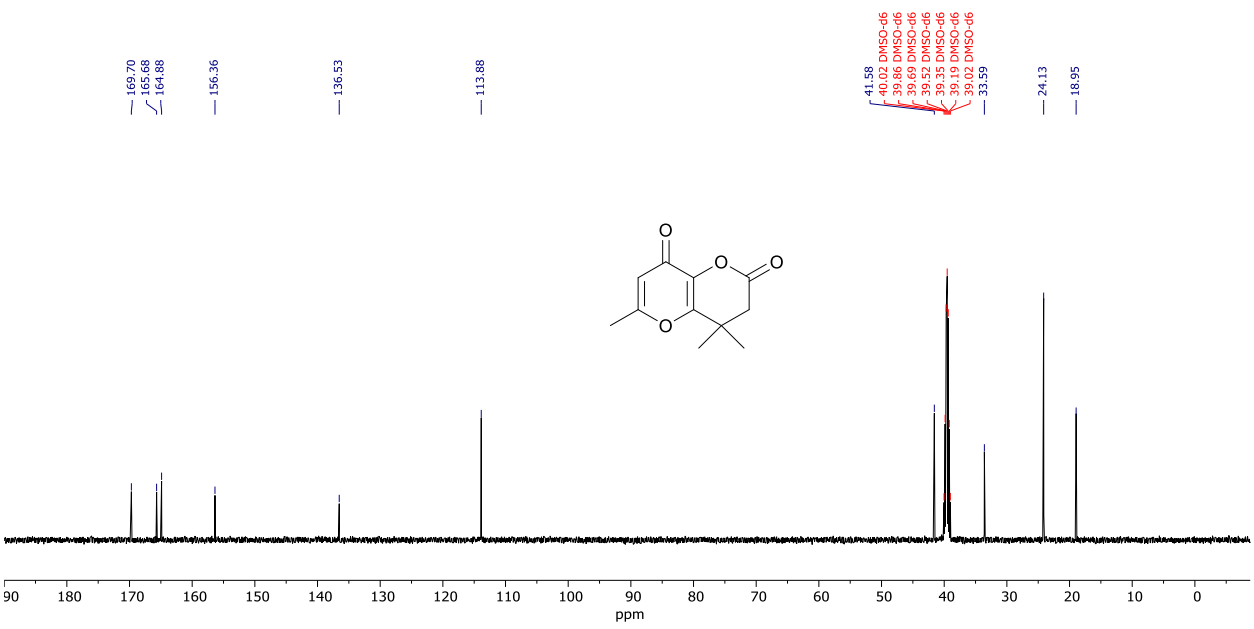


^{1}H NMR spectrum (500 MHz) of **13a** in DMSO-d_6

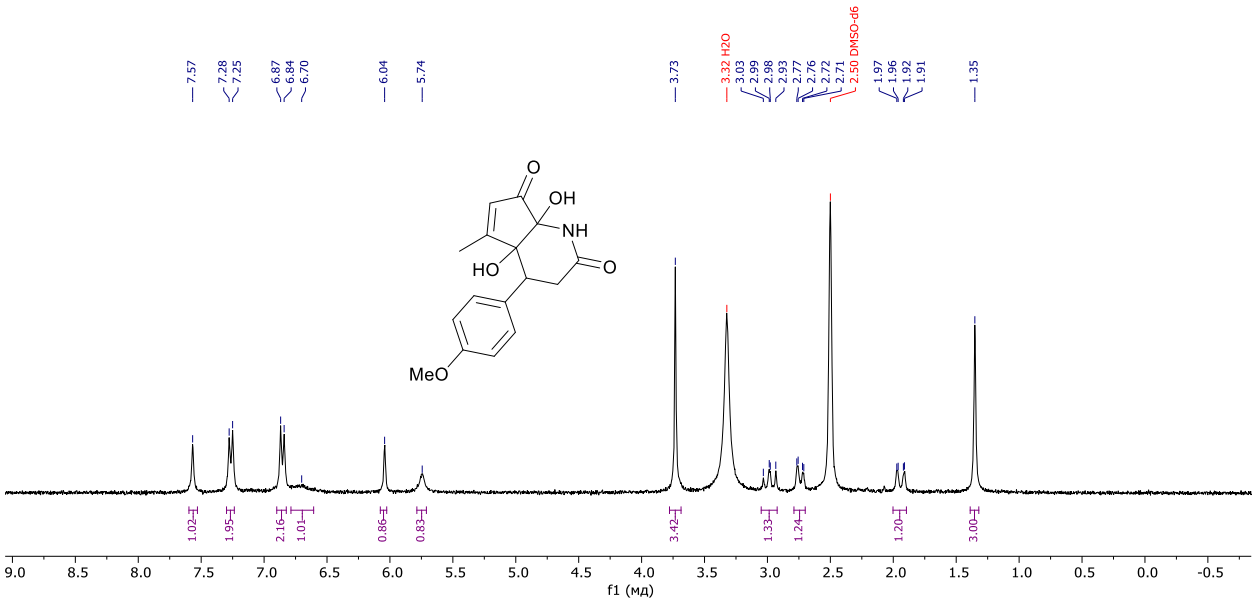


^{13}C {^{1}H} NMR spectrum (126 MHz) of **13a** in DMSO-d_6

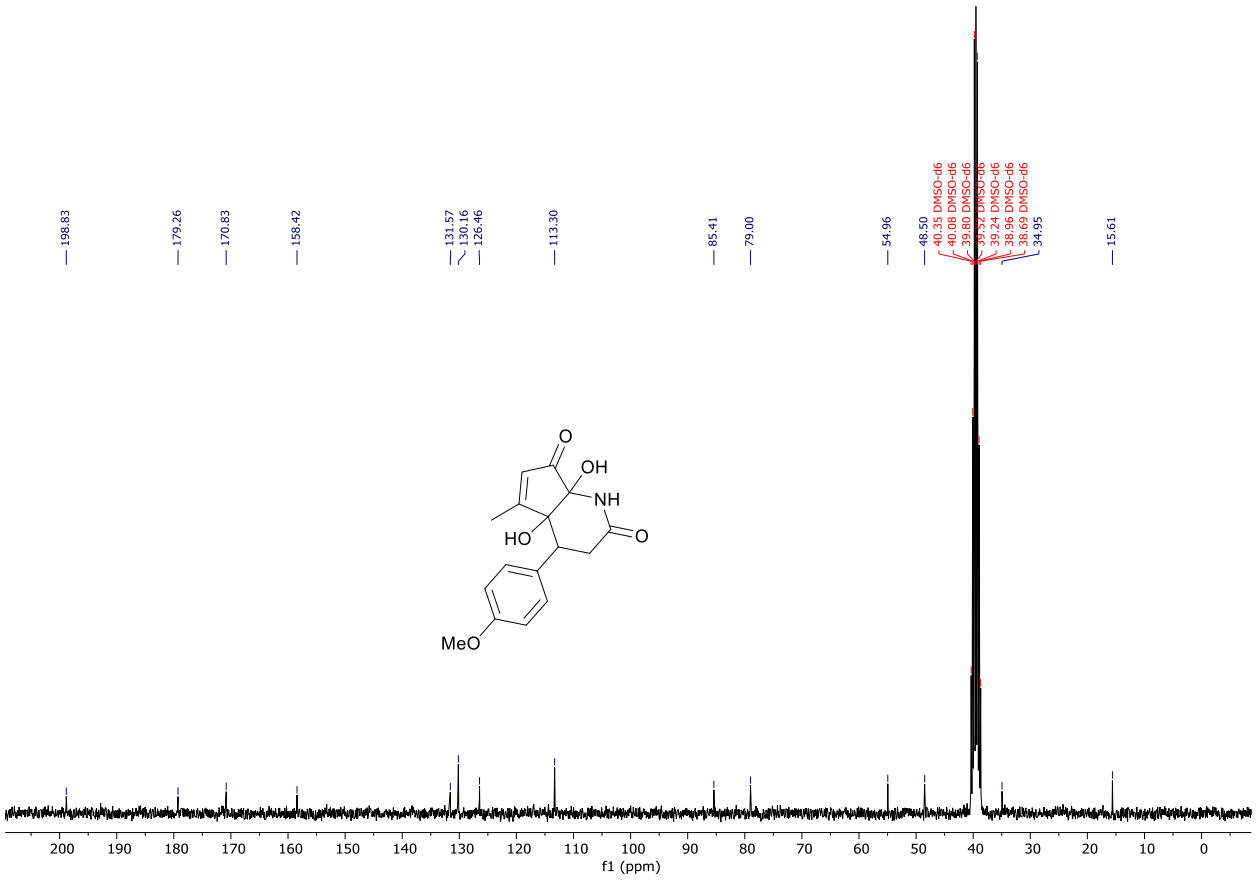


4. Copies of ^{1}H and ^{13}C NMR spectra for photoproducts 9

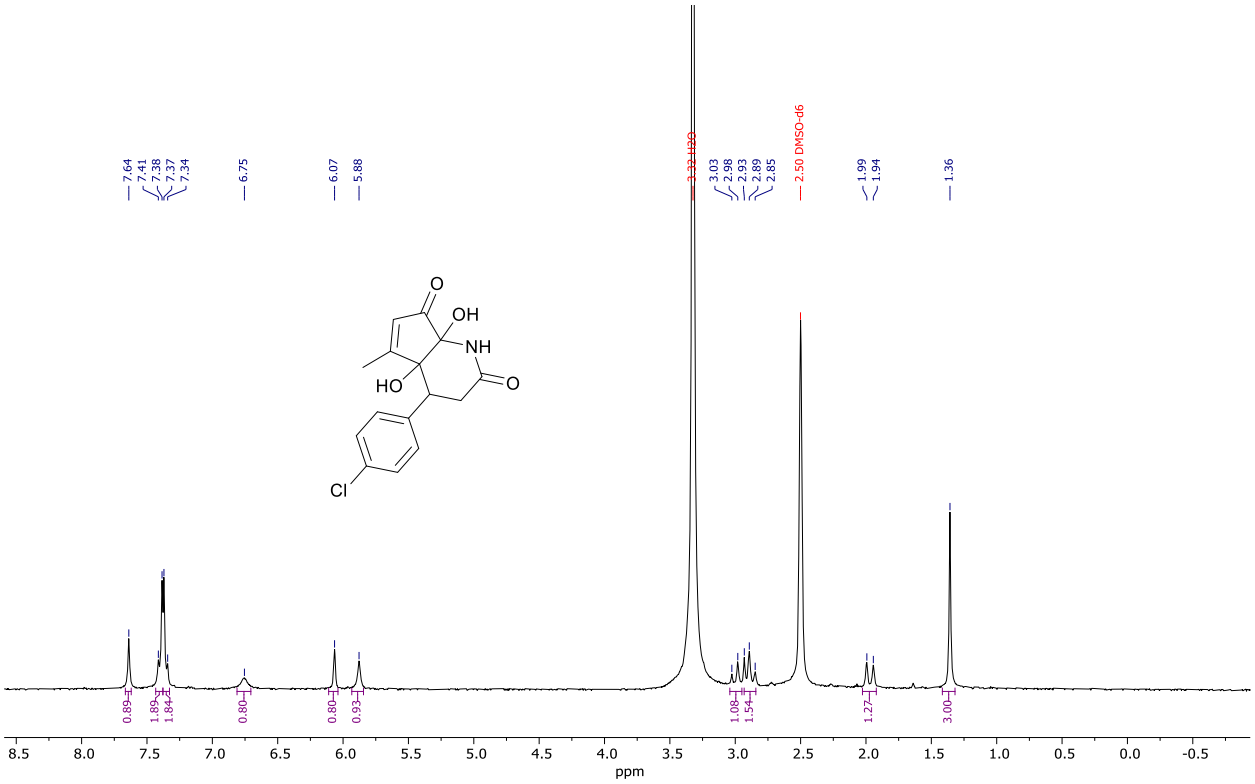
^{1}H NMR spectrum (300 MHz) of **9a** in DMSO-d_6



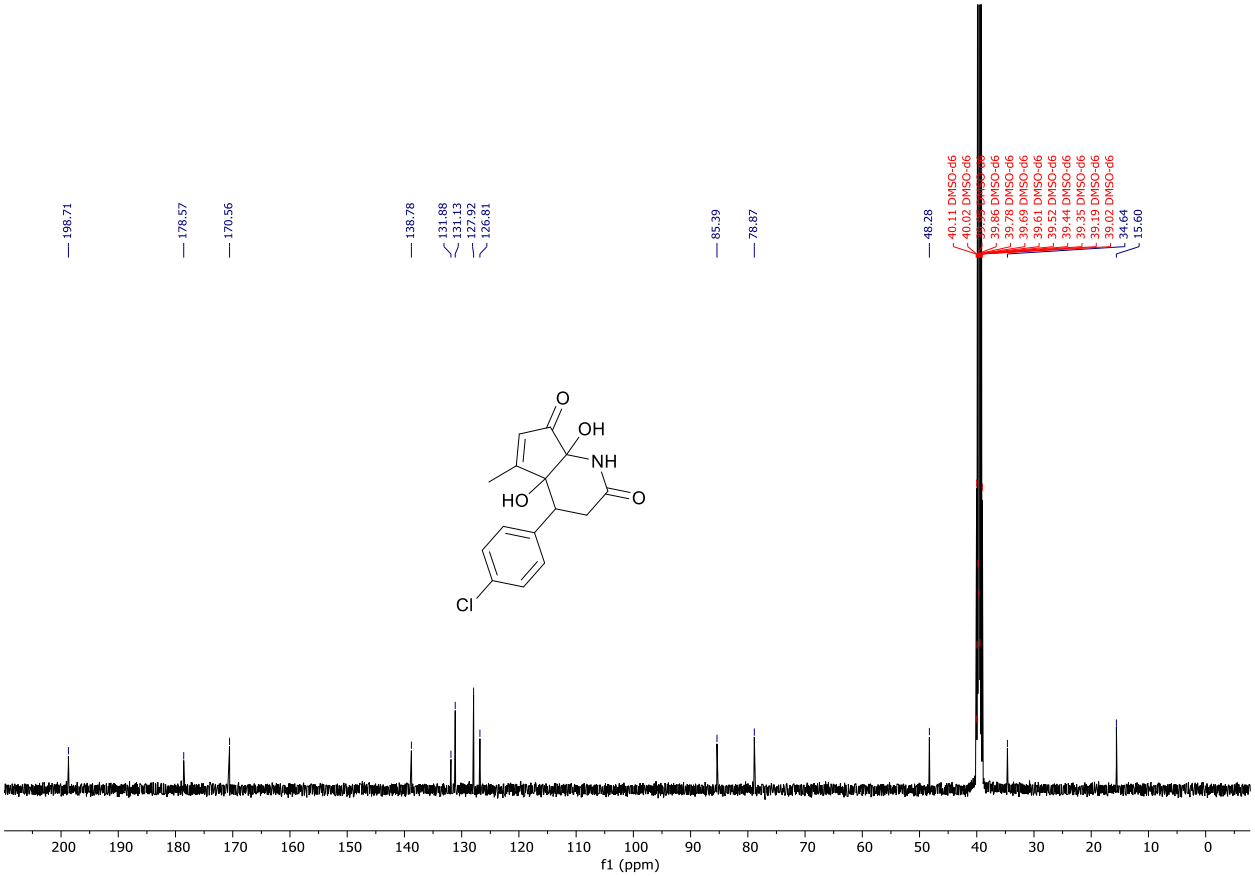
^{13}C {^{1}H} NMR spectrum (75 MHz) of **9a** in DMSO-d_6



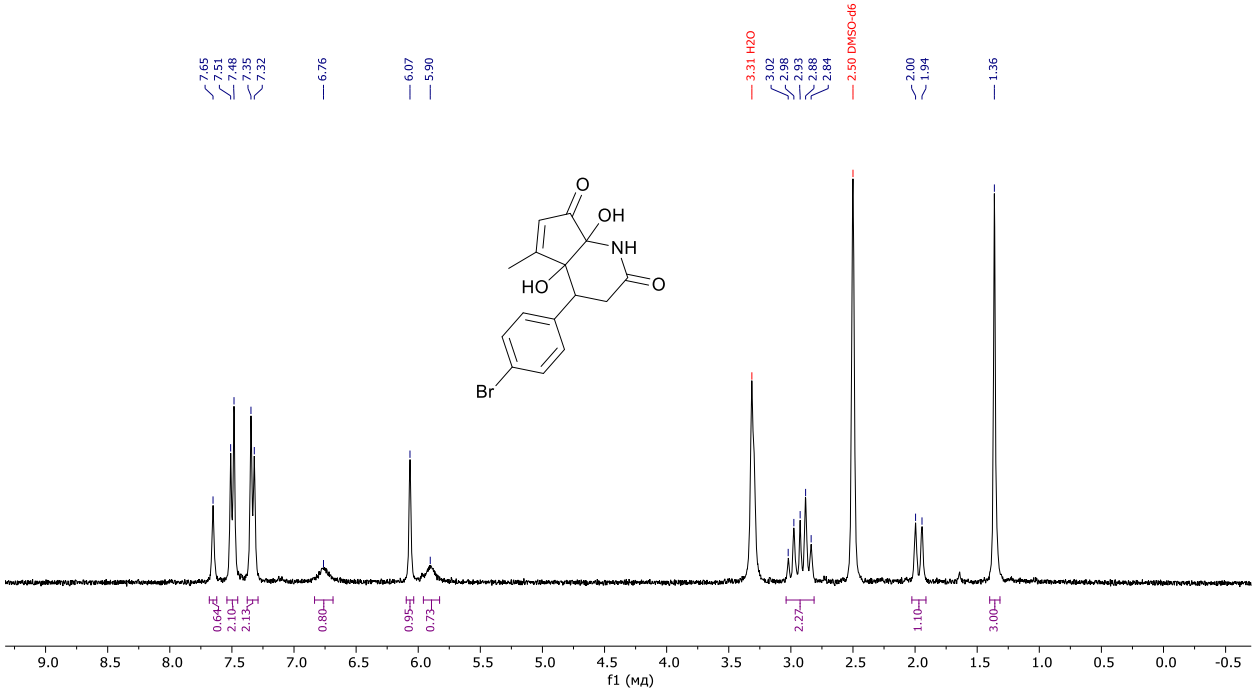
^{1}H NMR spectrum (500 MHz) of **9b** in DMSO-d_6



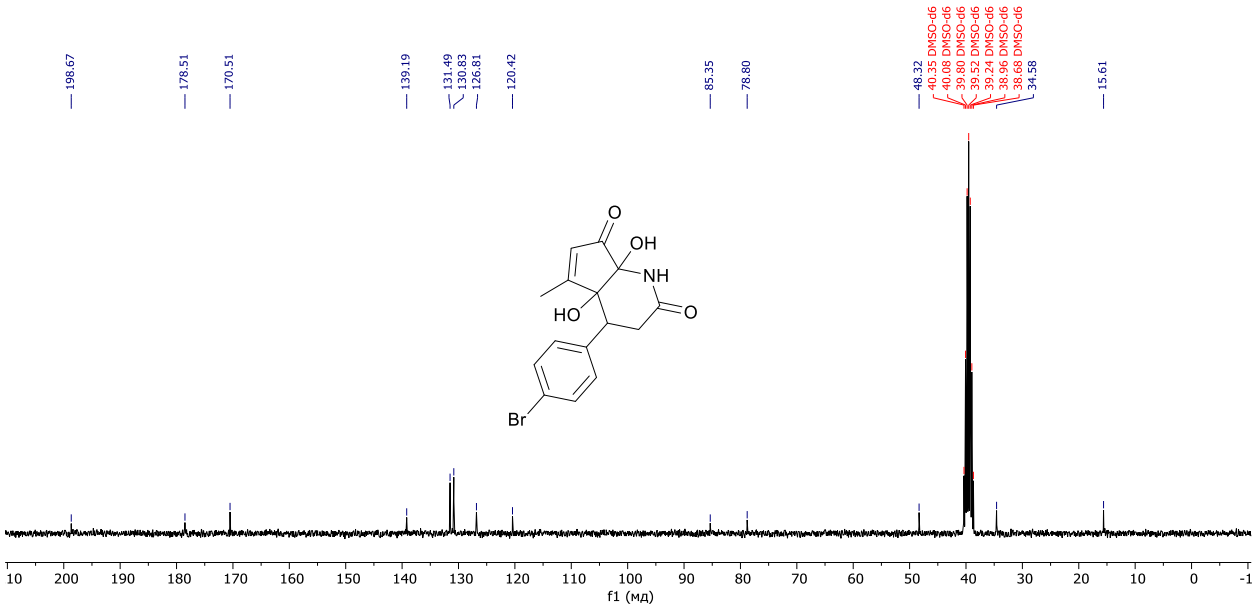
^{13}C {^{1}H} NMR spectrum (126 MHz) of **9b** in DMSO-d_6



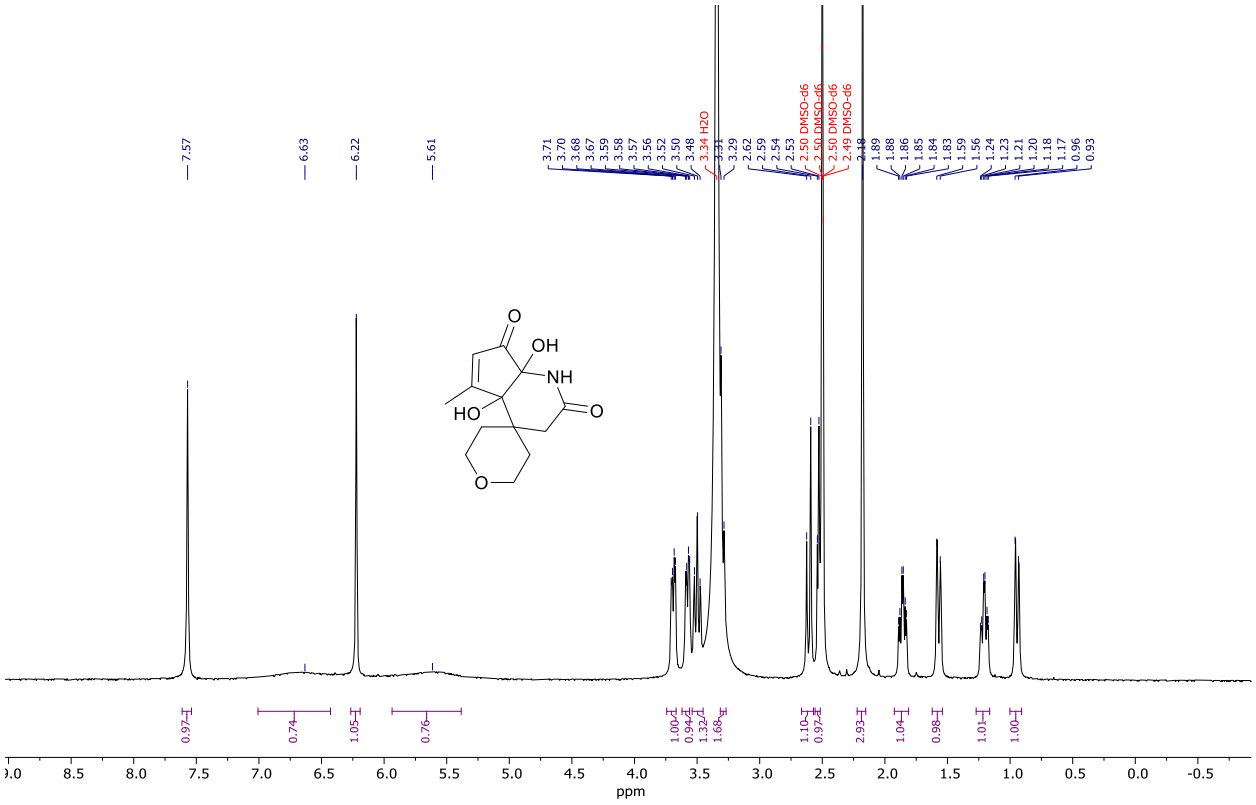
^{1}H NMR spectrum (300 MHz) of **9c** in DMSO-d_6



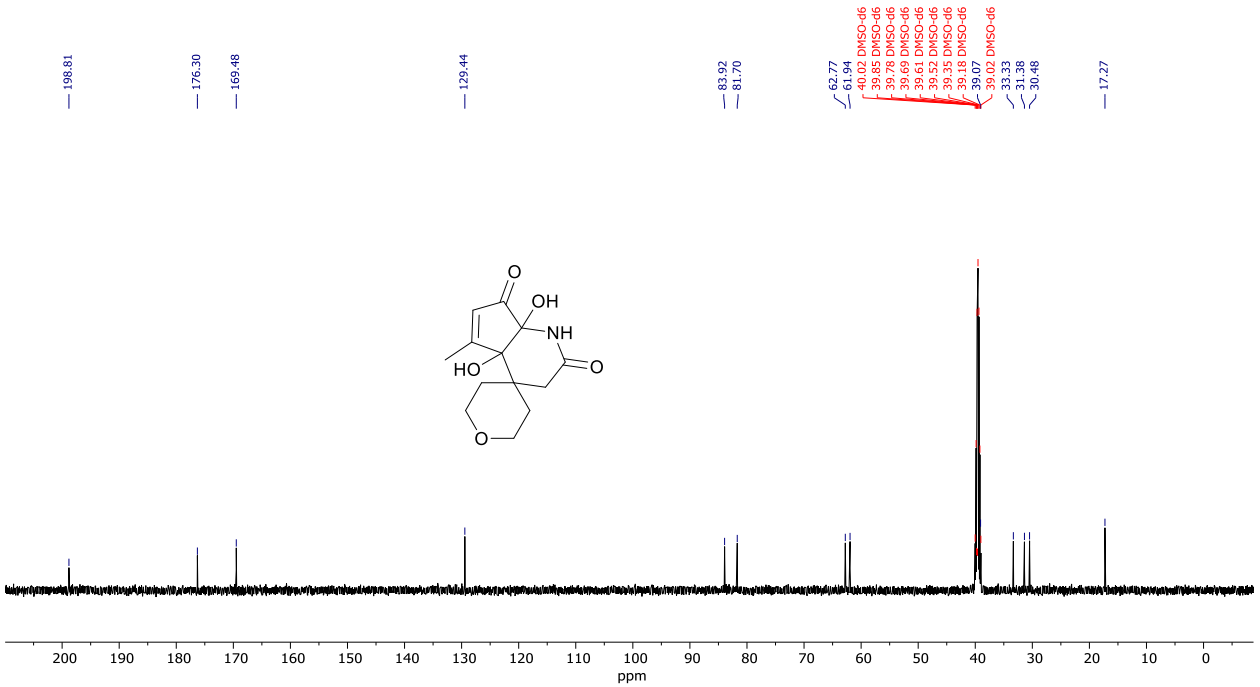
^{13}C {^{1}H} NMR spectrum (75 MHz) of **9c** in DMSO-d_6



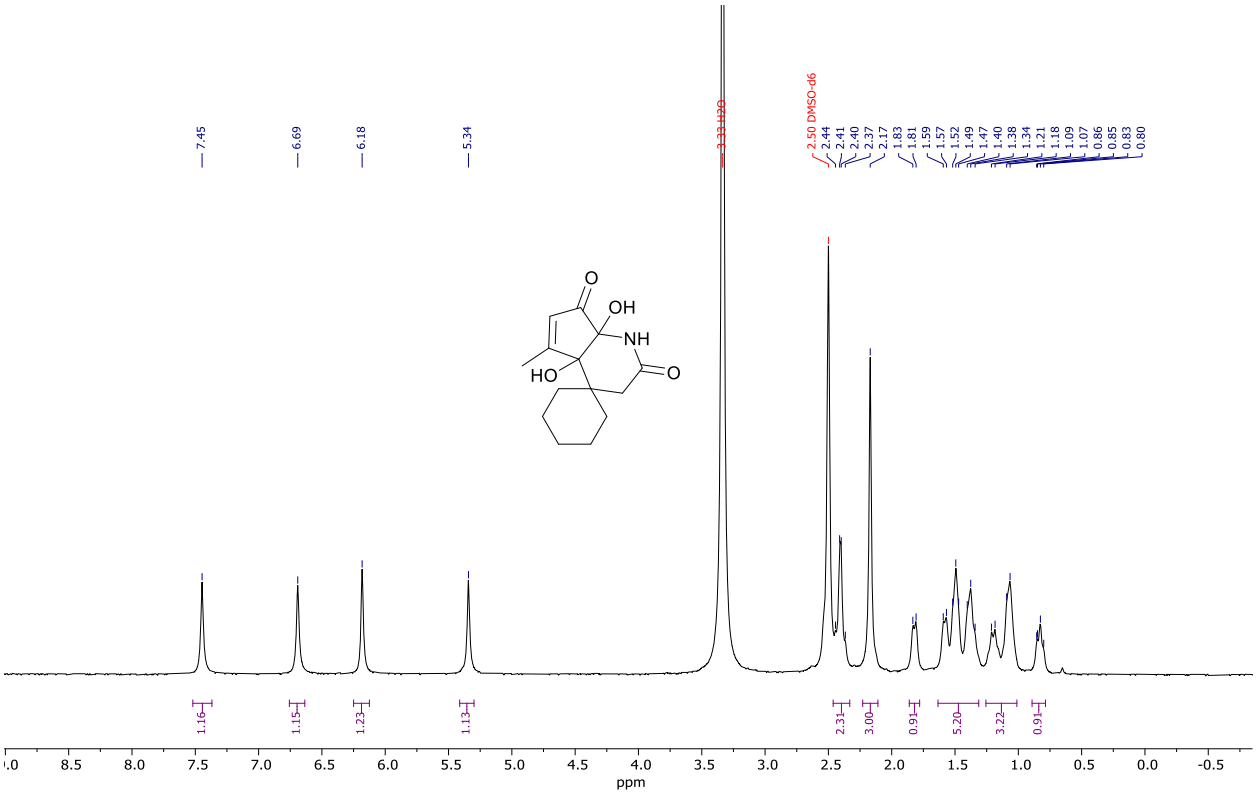
^{1}H NMR spectrum (500 MHz) of **9d** in DMSO-d_6



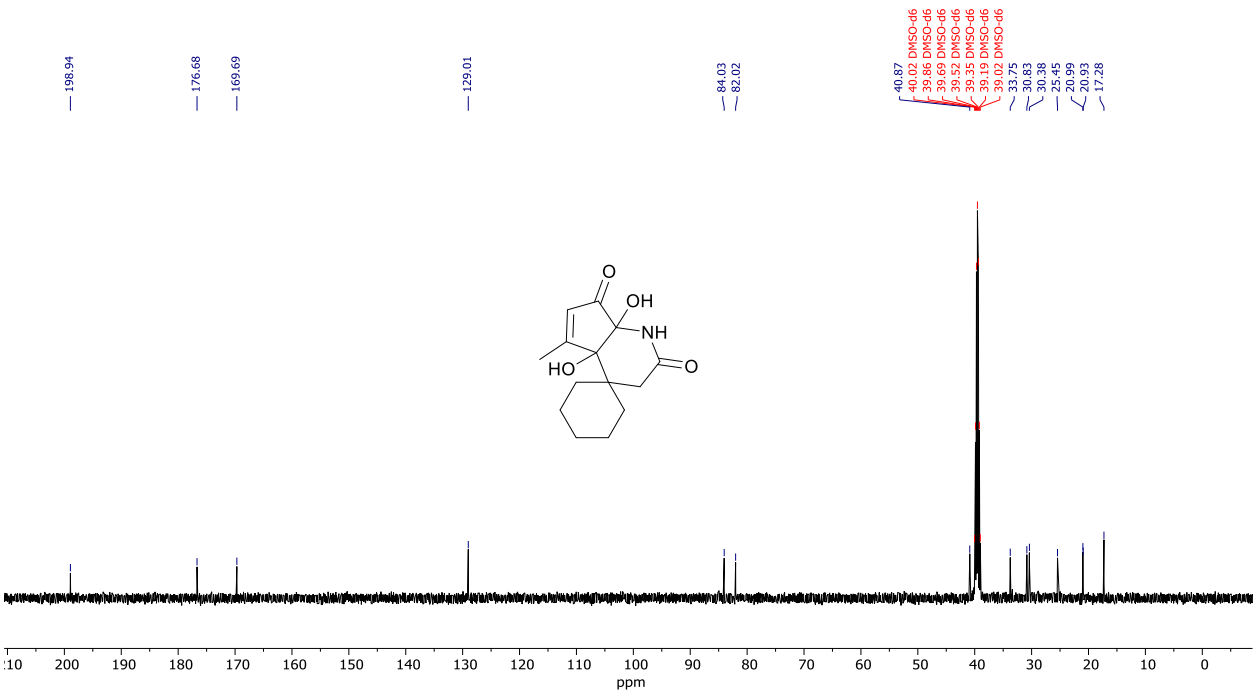
^{13}C {^{1}H} NMR spectrum (126 MHz) of **9d** in DMSO-d_6



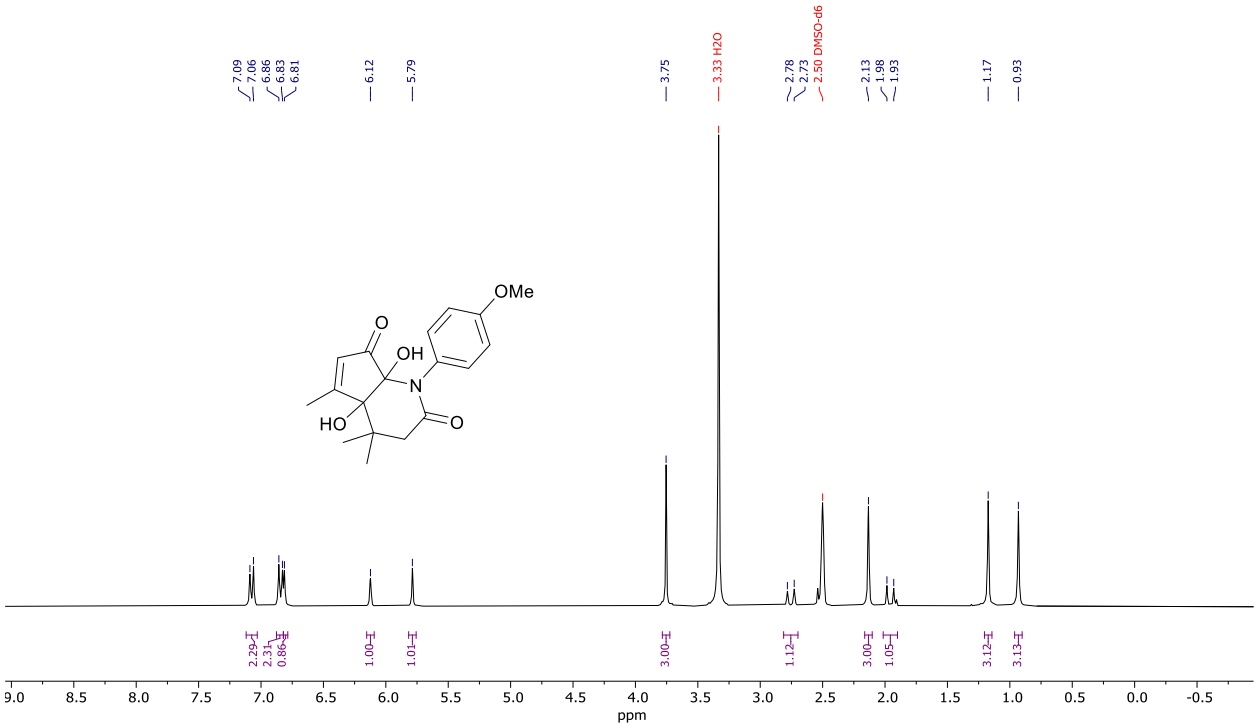
^{1}H NMR spectrum (500 MHz) of **9e** in DMSO-d_6



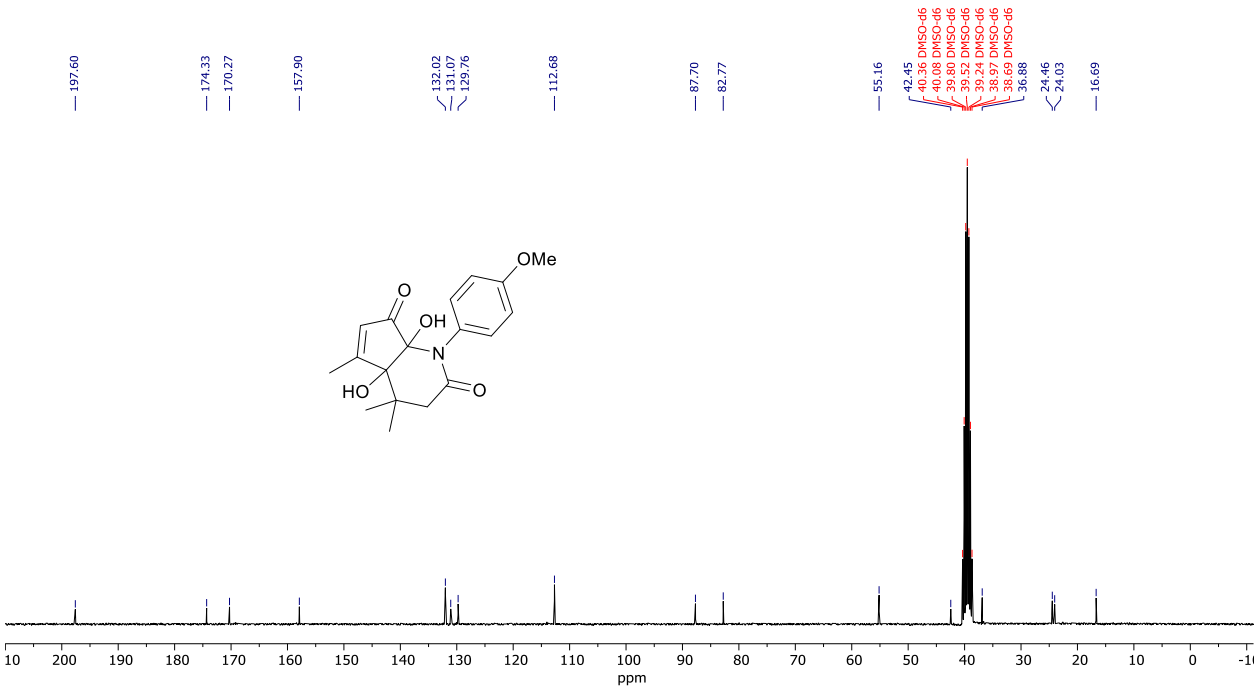
^{13}C {^{1}H} NMR spectrum (126 MHz) of **9e** in DMSO-d_6



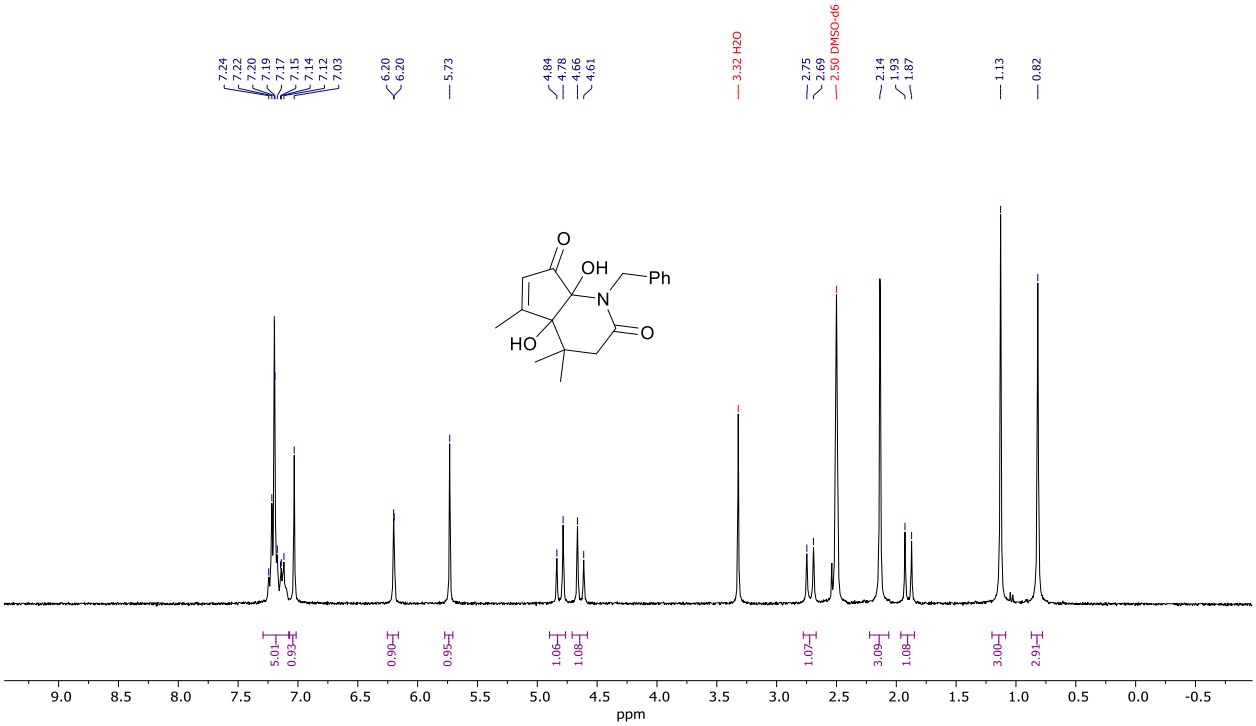
^{1}H NMR spectrum (300 MHz) of **9f** in DMSO-d_6



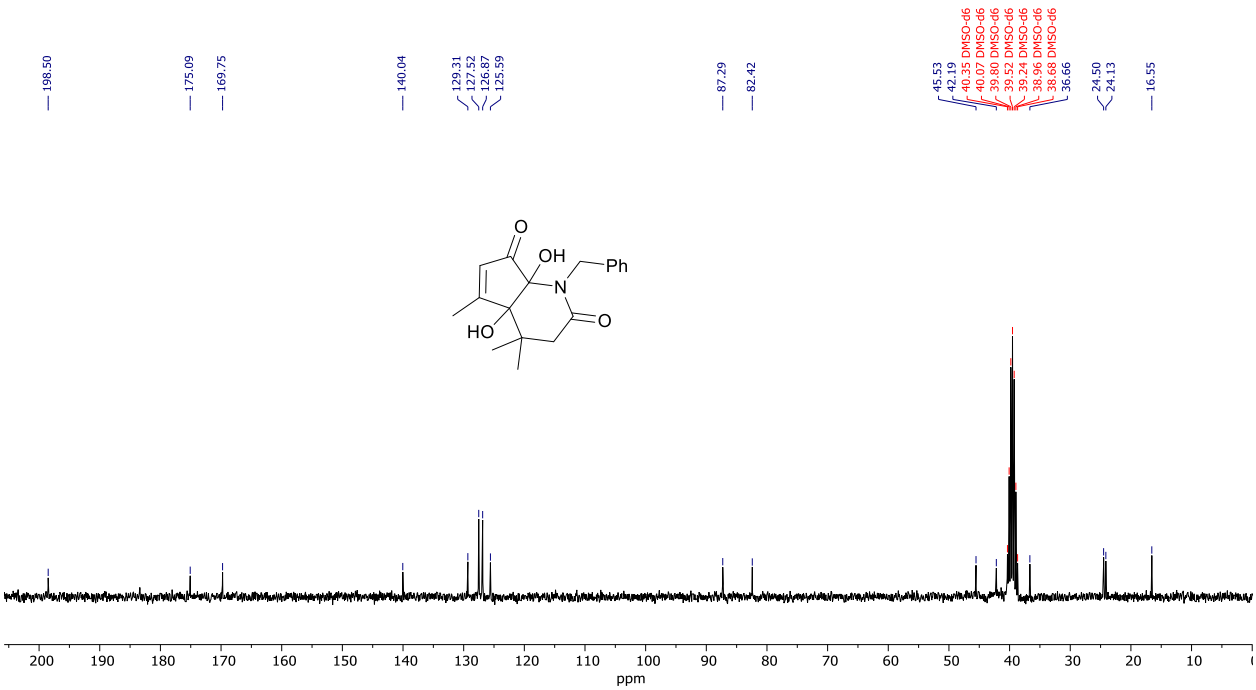
^{13}C {^{1}H} NMR spectrum (76 MHz) of **9f** in DMSO-d_6



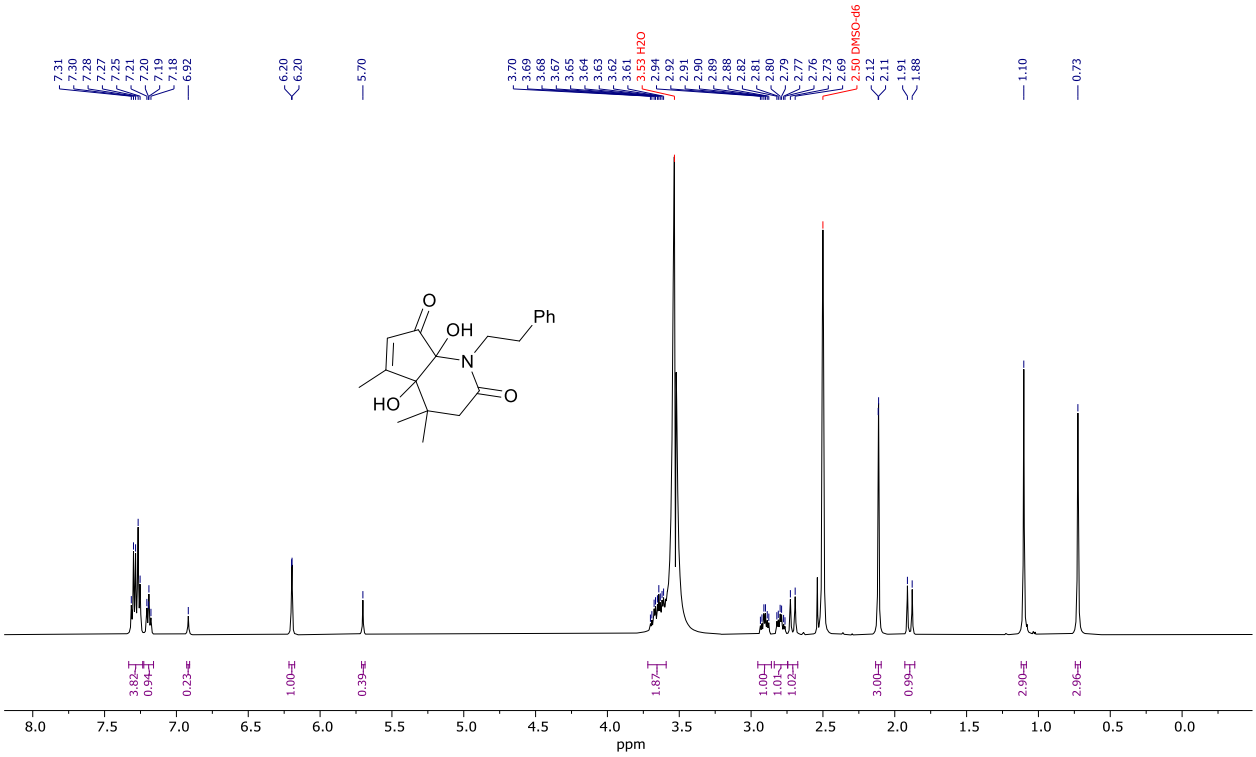
^{1}H NMR spectrum (300 MHz) of **9g** in DMSO-d_6



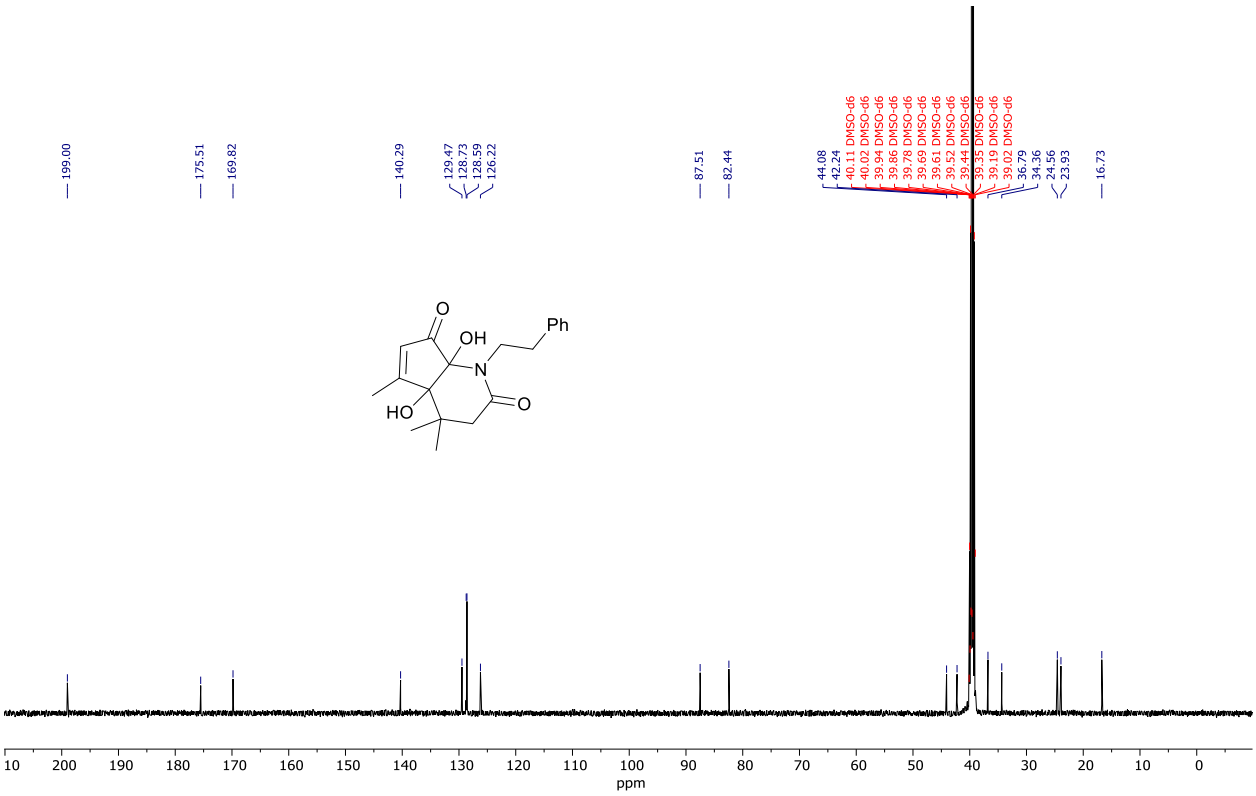
^{13}C {^{1}H} NMR spectrum (75 MHz) of **9g** in DMSO-d_6



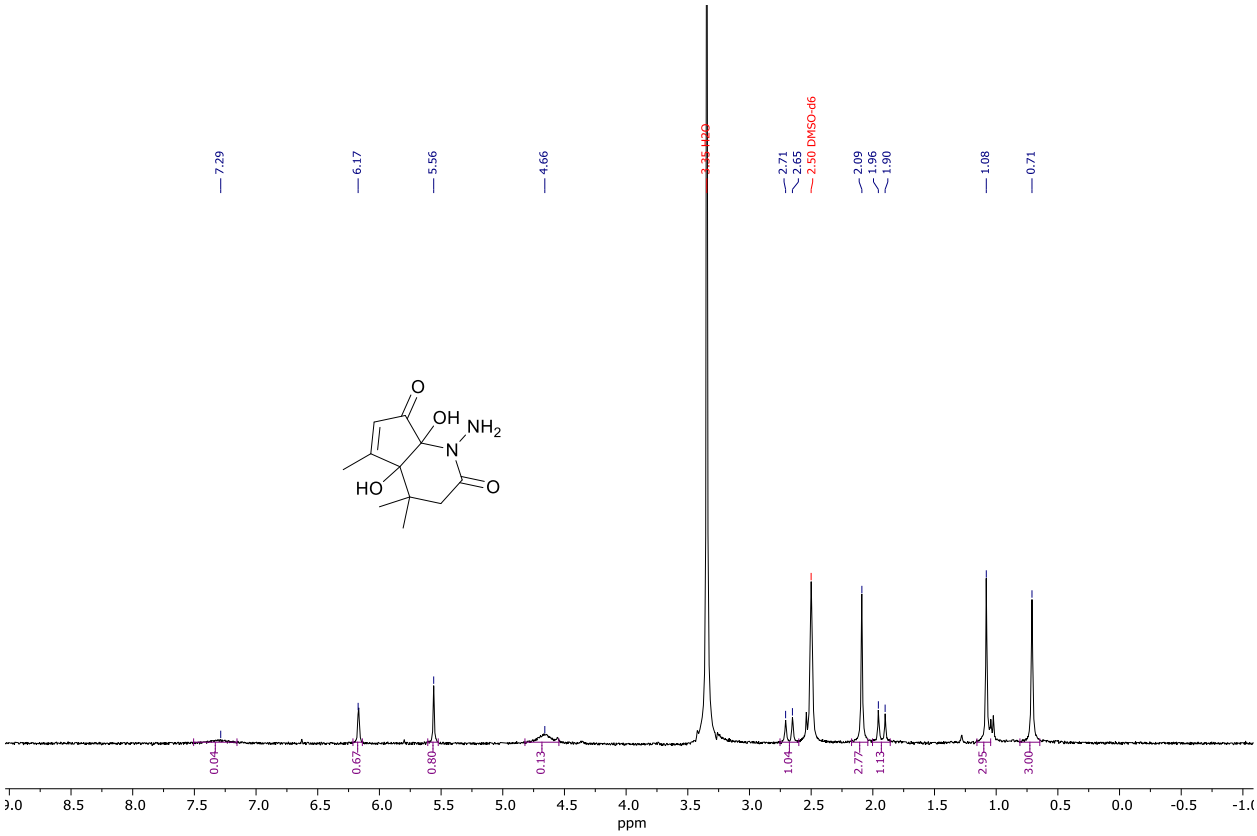
^{1}H NMR spectrum (500 MHz) of **9h** in DMSO-d_6



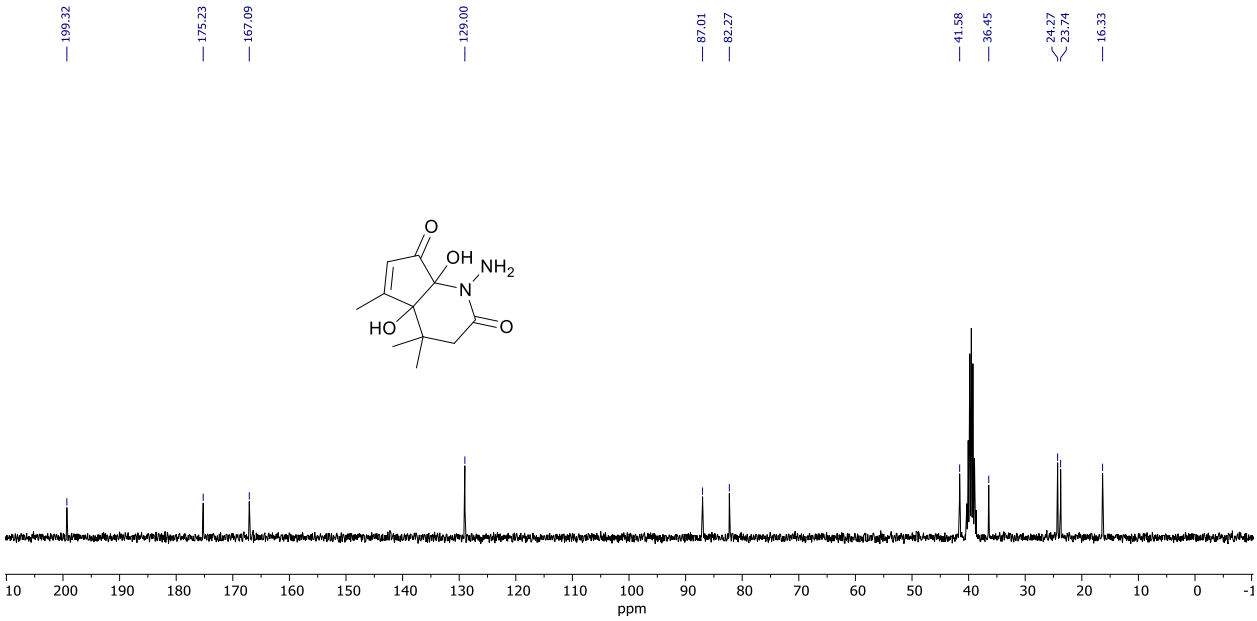
^{13}C {^{1}H} NMR spectrum (126 MHz) of **9h** in DMSO-d_6



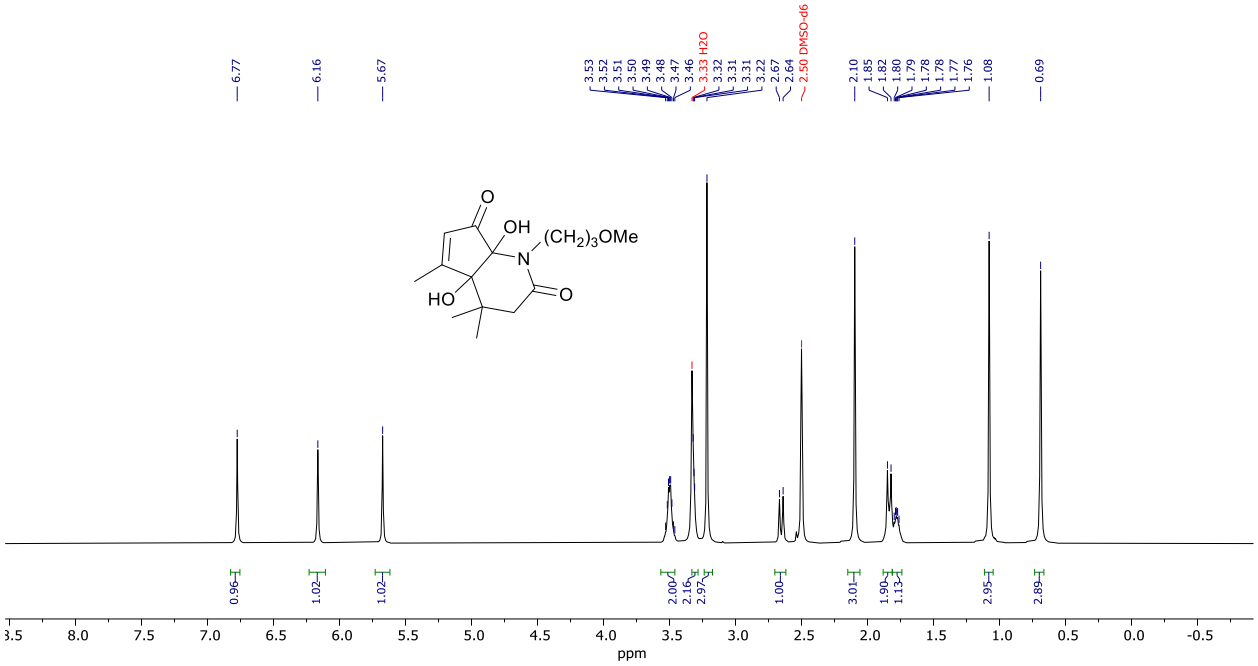
^{1}H NMR spectrum (300 MHz) of **9i** in DMSO-d_6



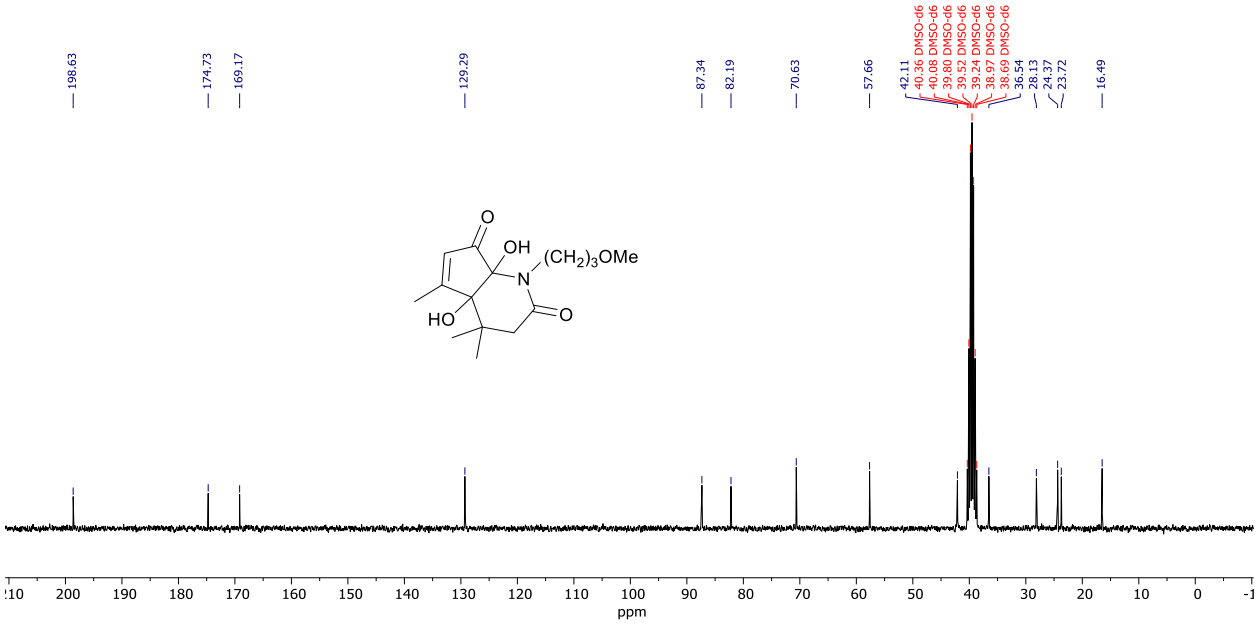
^{13}C {^{1}H} NMR spectrum (75 MHz) of **9i** in DMSO-d_6



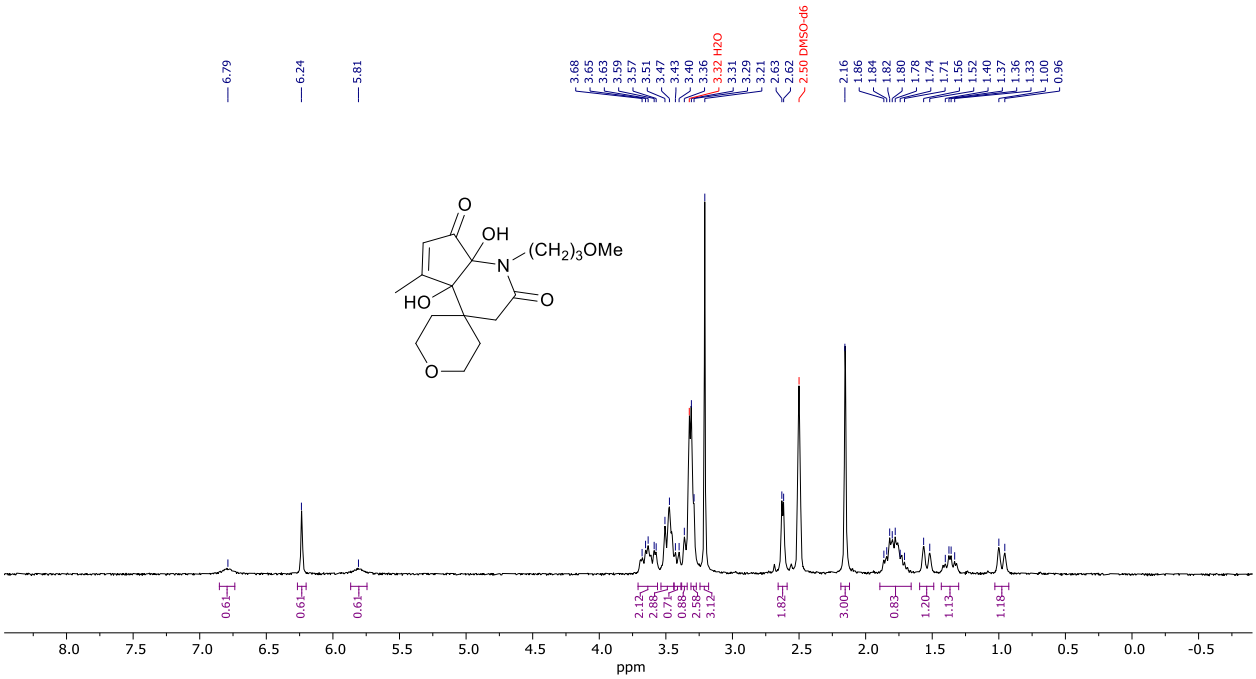
^{1}H NMR spectrum (600 MHz) of **9j** in DMSO-d_6



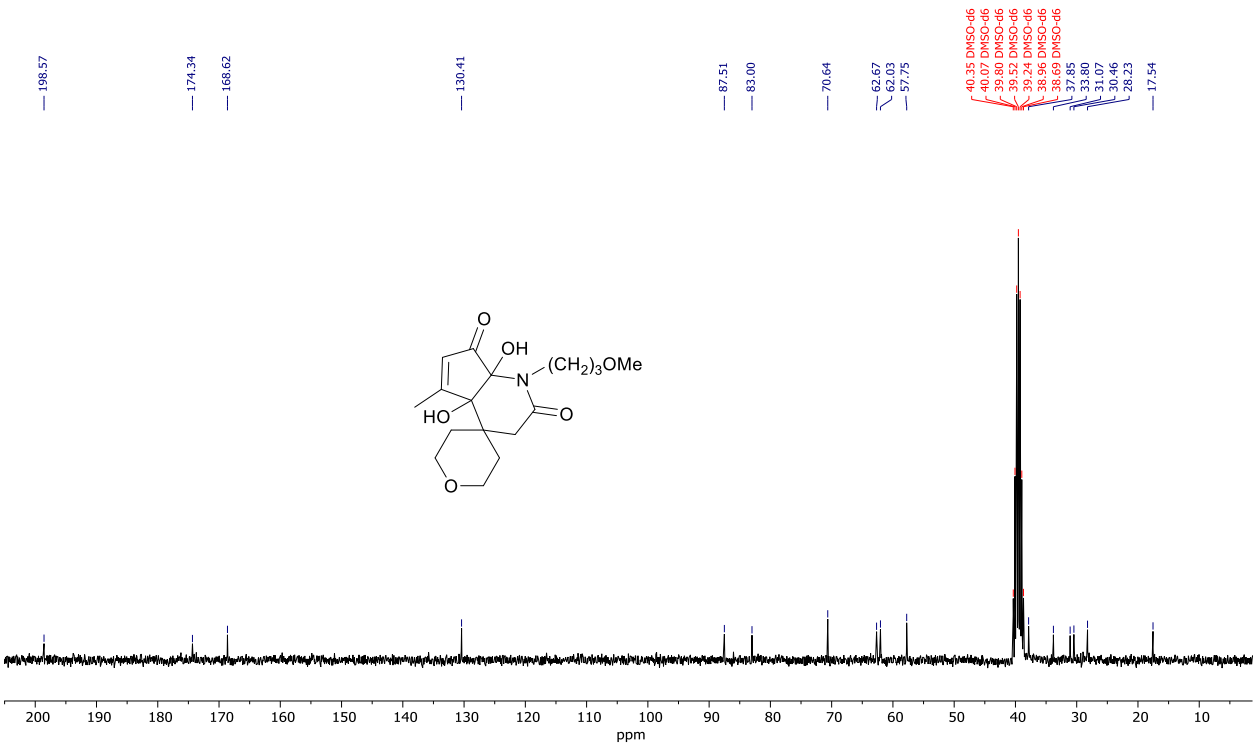
^{13}C {^{1}H} NMR spectrum (75 MHz) of **9j** in DMSO-d_6



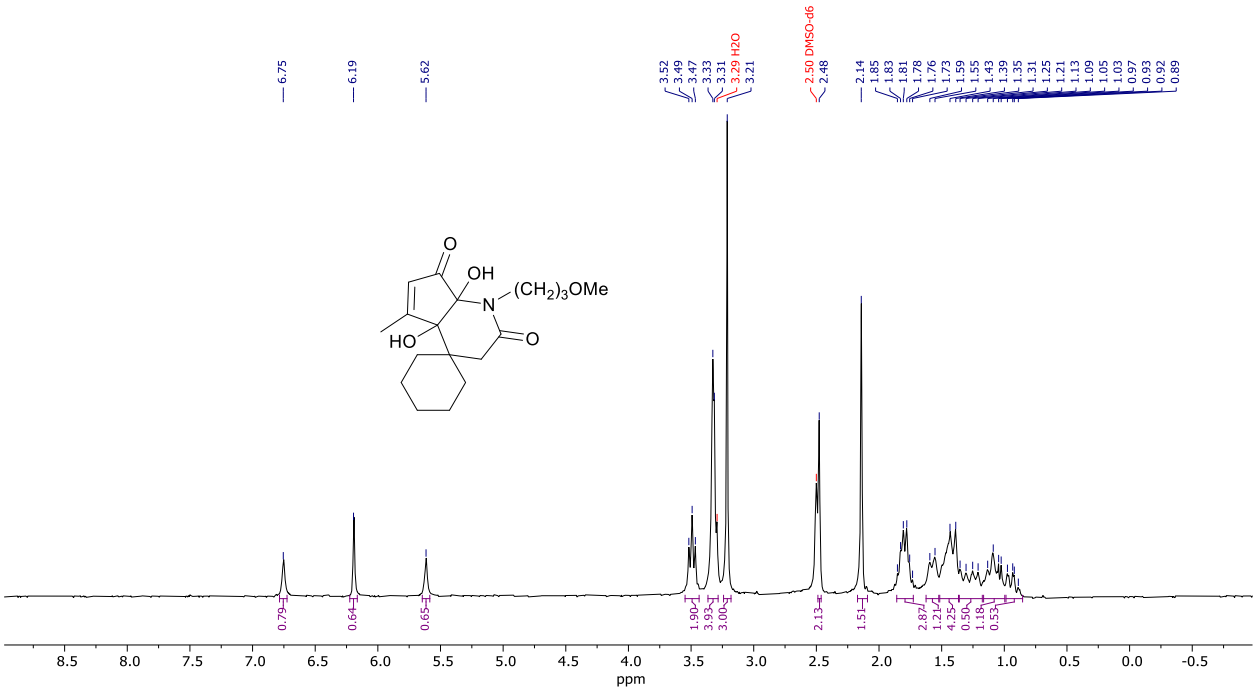
^{1}H NMR spectrum (300 MHz) of **9k** in DMSO-d_6



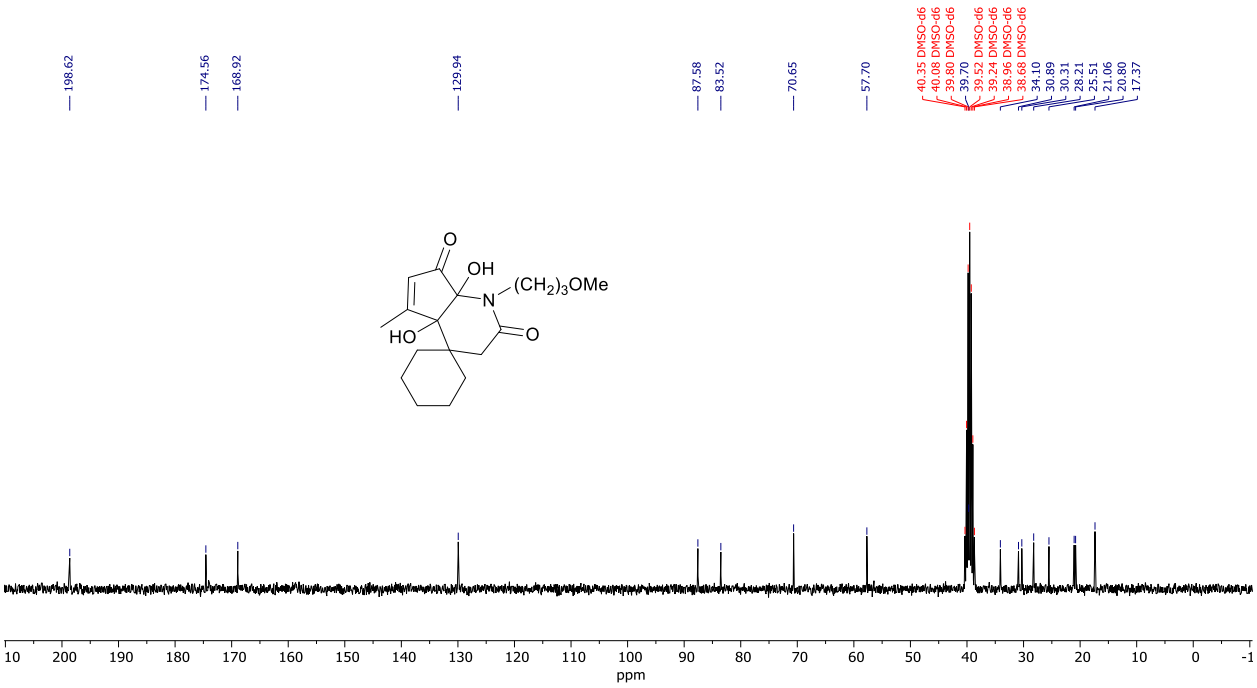
^{13}C {^{1}H} NMR spectrum (75 MHz) of **9k** in DMSO-d_6



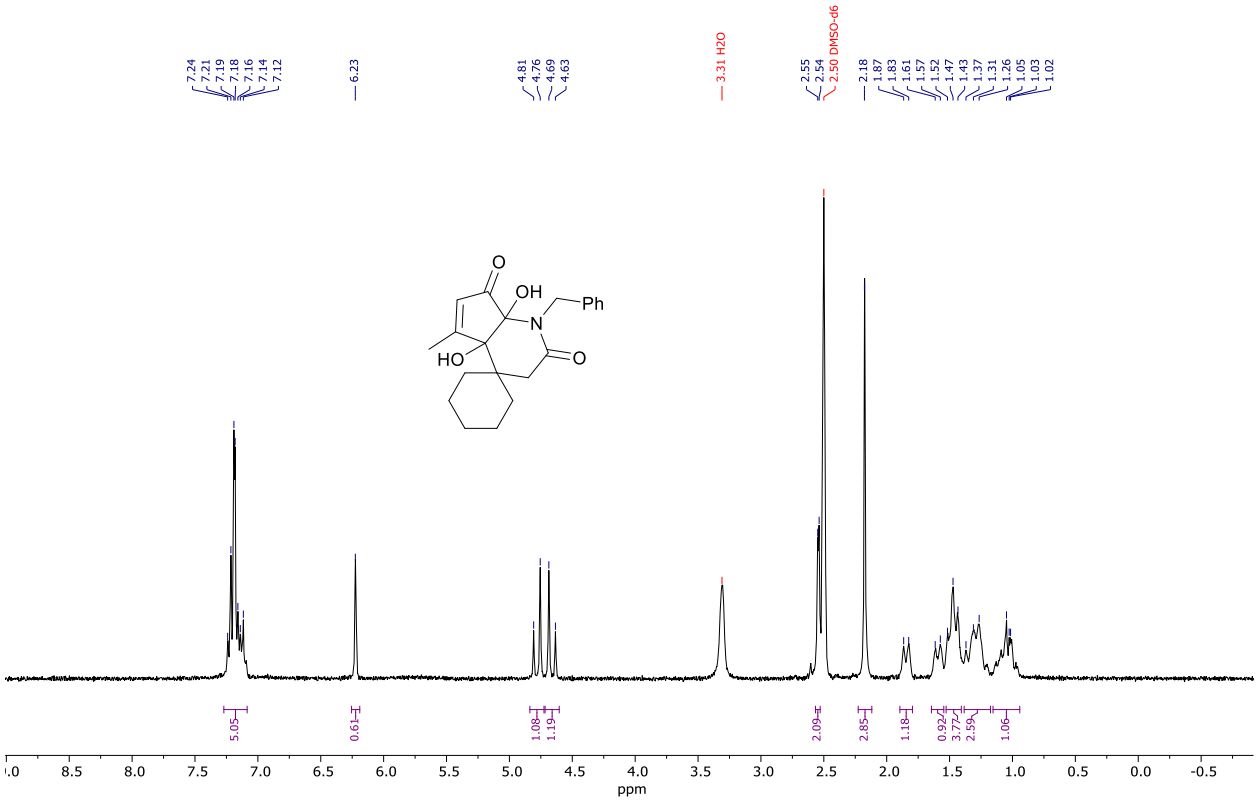
^{1}H NMR spectrum (300 MHz) of **9l** in DMSO-d_6



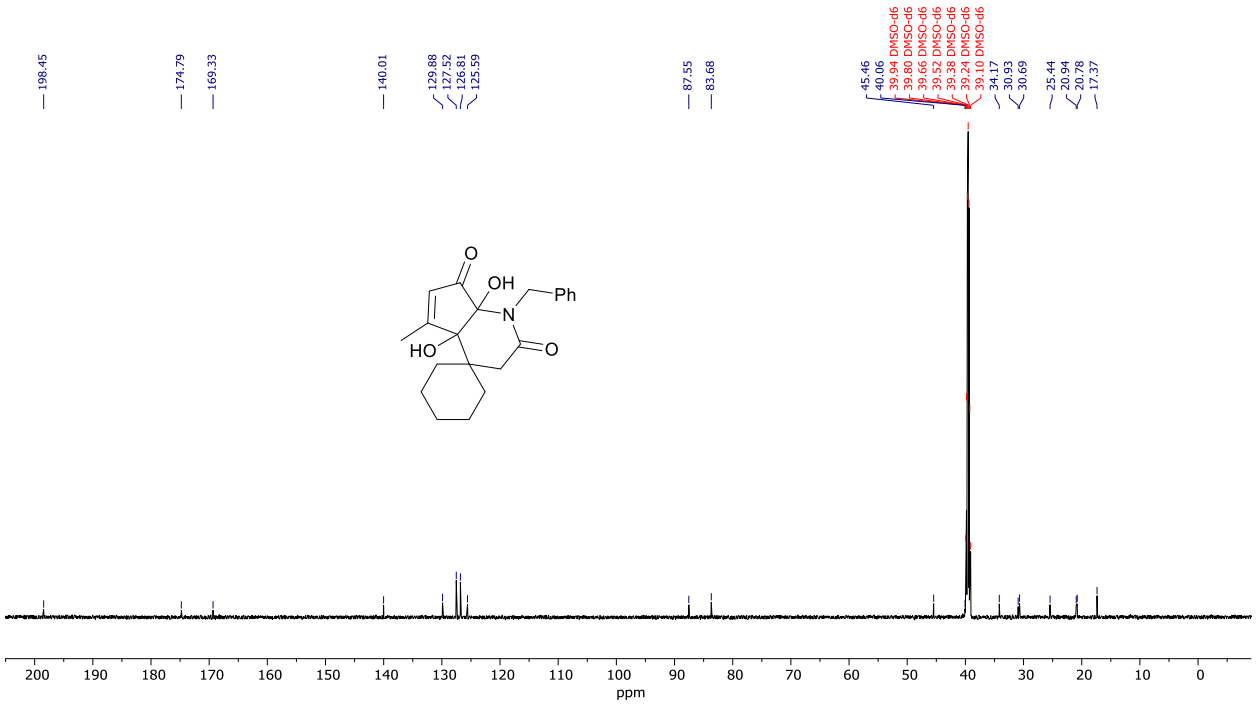
^{13}C {^{1}H} NMR spectrum (75 MHz) of **9l** in DMSO-d_6



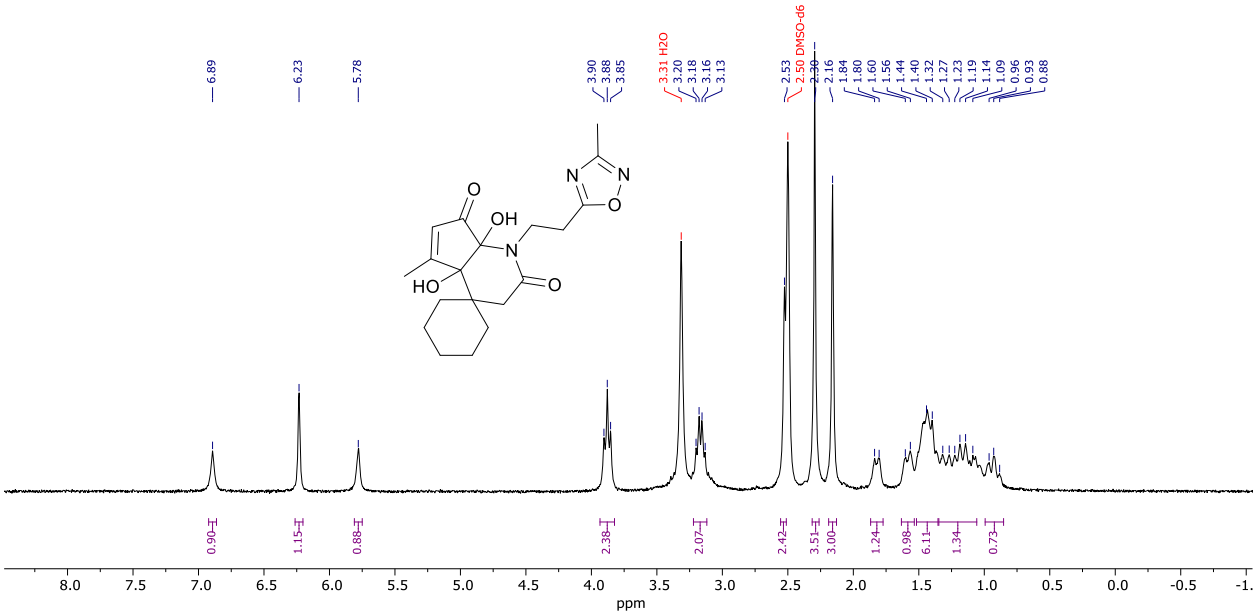
^{1}H NMR spectrum (300 MHz) of **9m** in DMSO-d_6



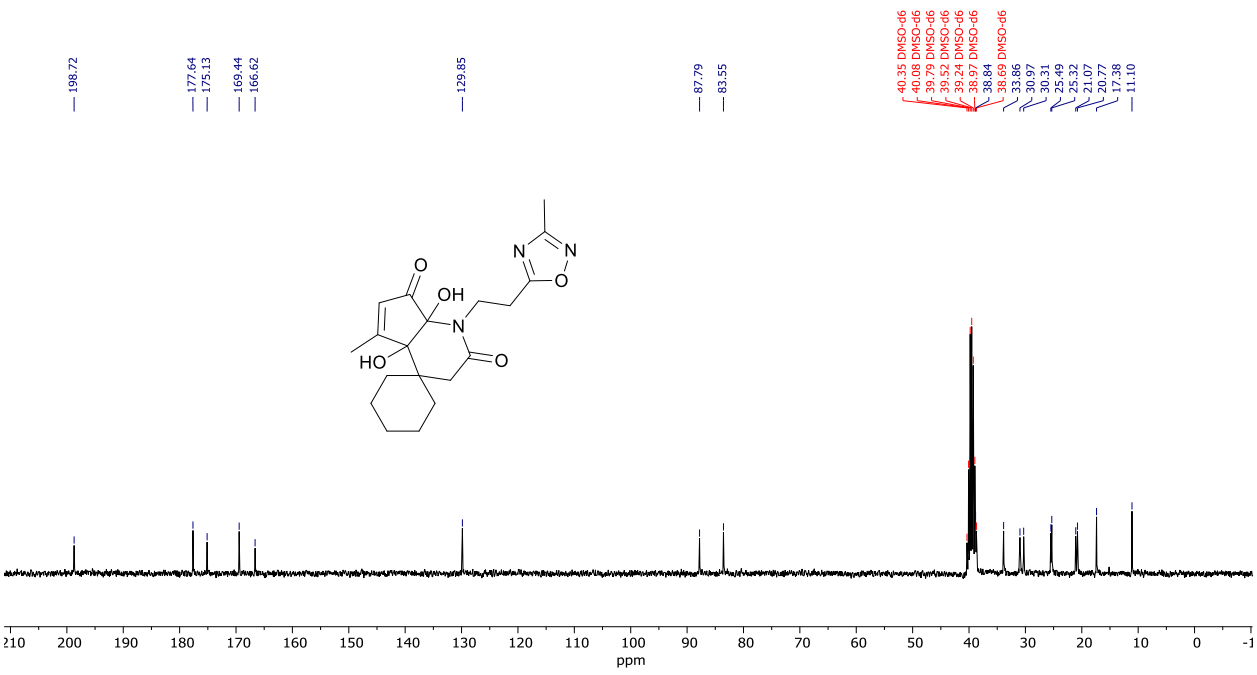
^{13}C {^{1}H} NMR spectrum (75 MHz) of **9m** in DMSO-d_6



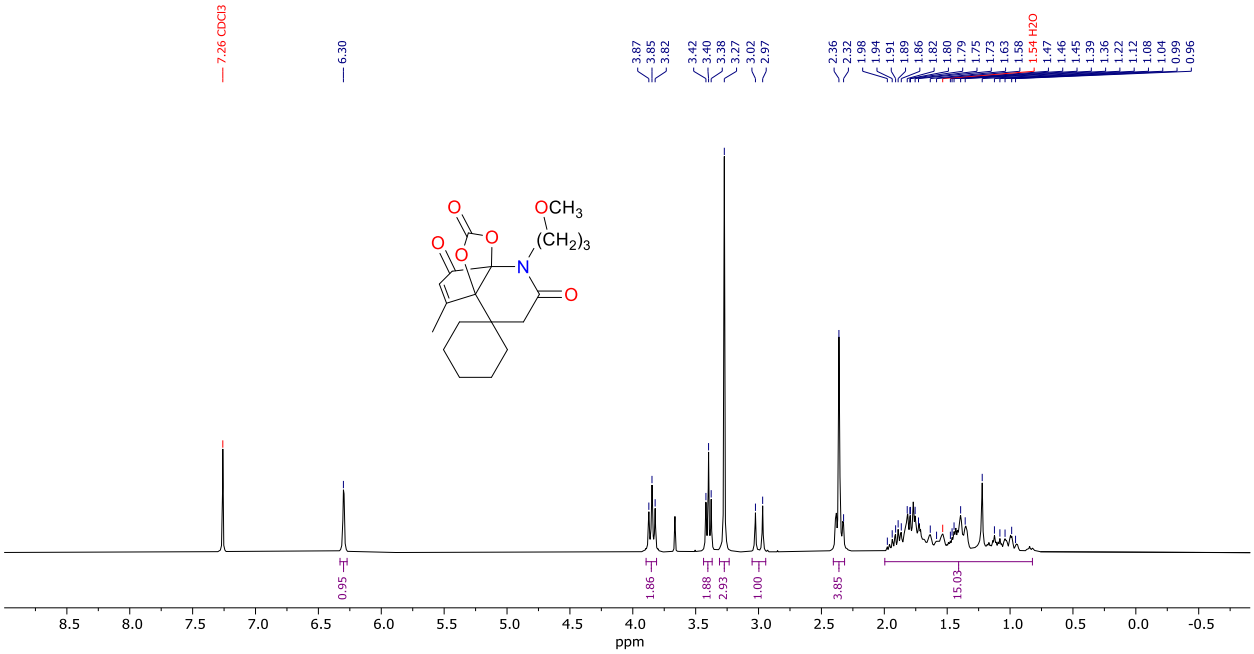
^{1}H NMR spectrum (300 MHz) of **9n** in DMSO-d_6



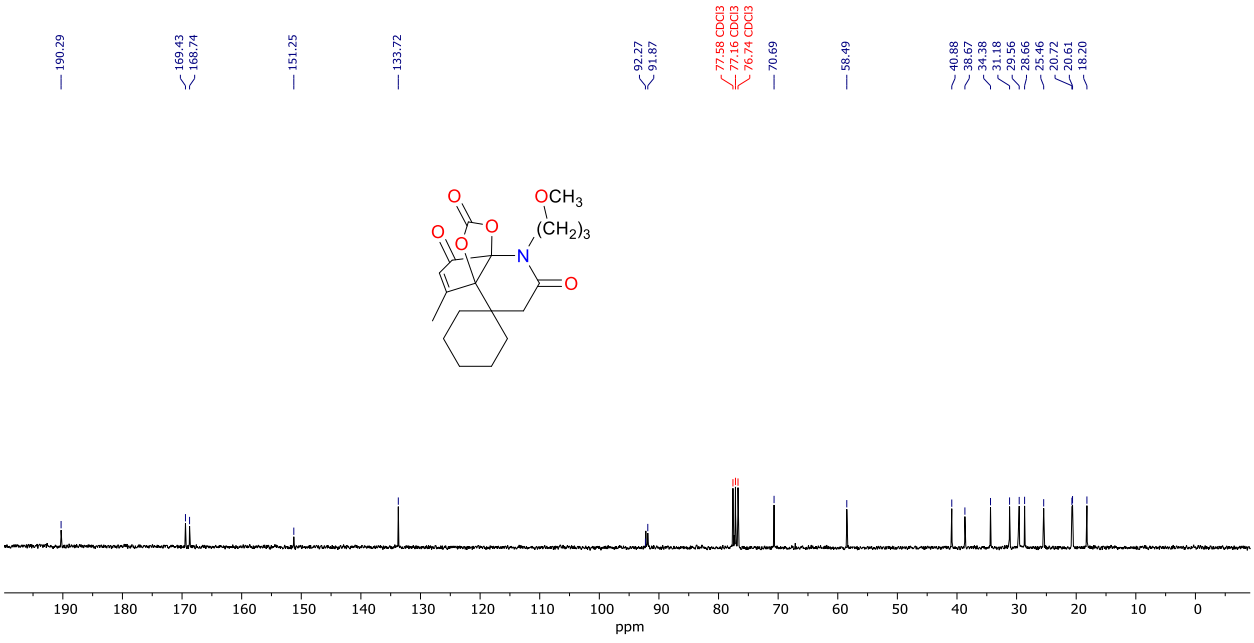
^{13}C {^{1}H} NMR spectrum (75 MHz) of **9n** in DMSO-d_6



^{1}H NMR spectrum (300 MHz) of **16** in $CDCl_3$



^{13}C {^{1}H} NMR spectrum (75 MHz) of **16** in $CDCl_3$



5. ^{1}H NMR monitoring of the photoreactions.

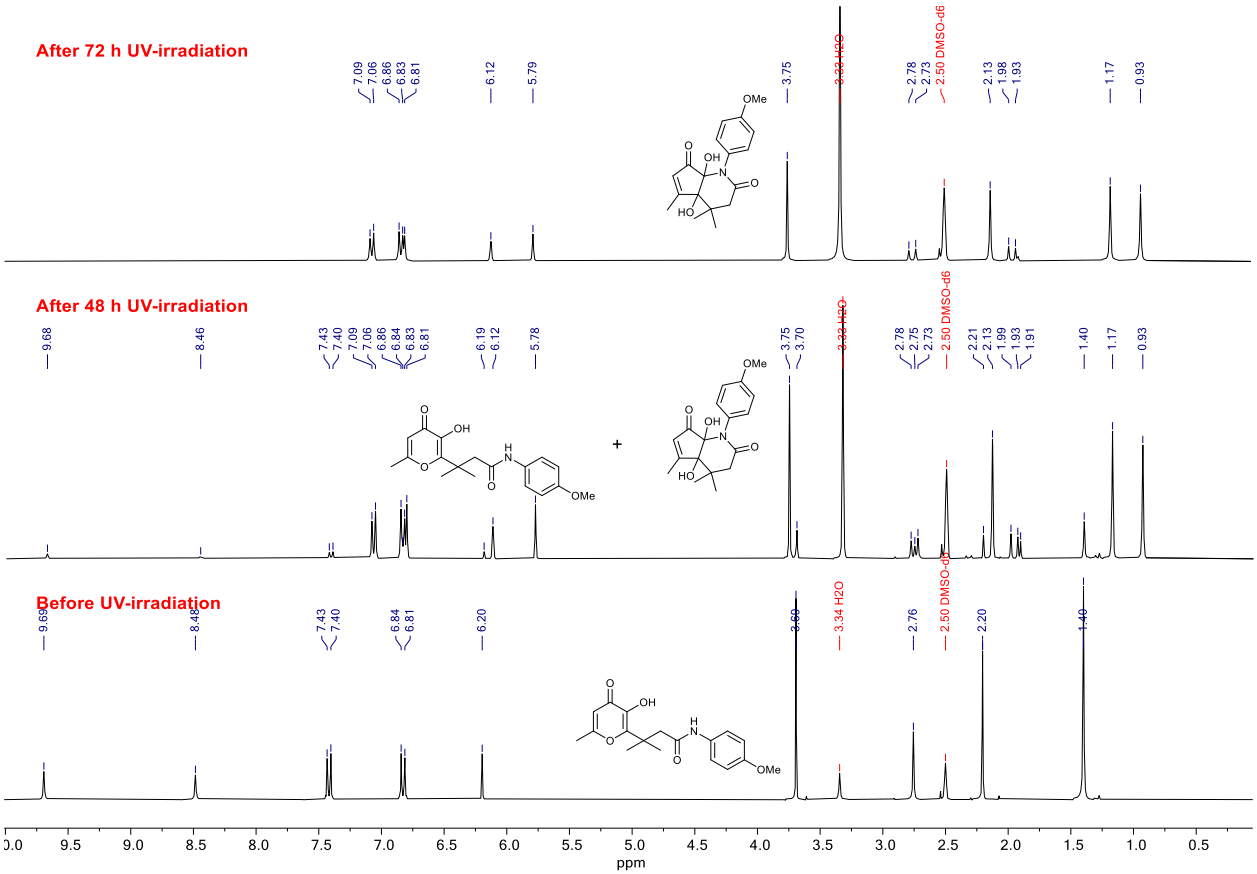
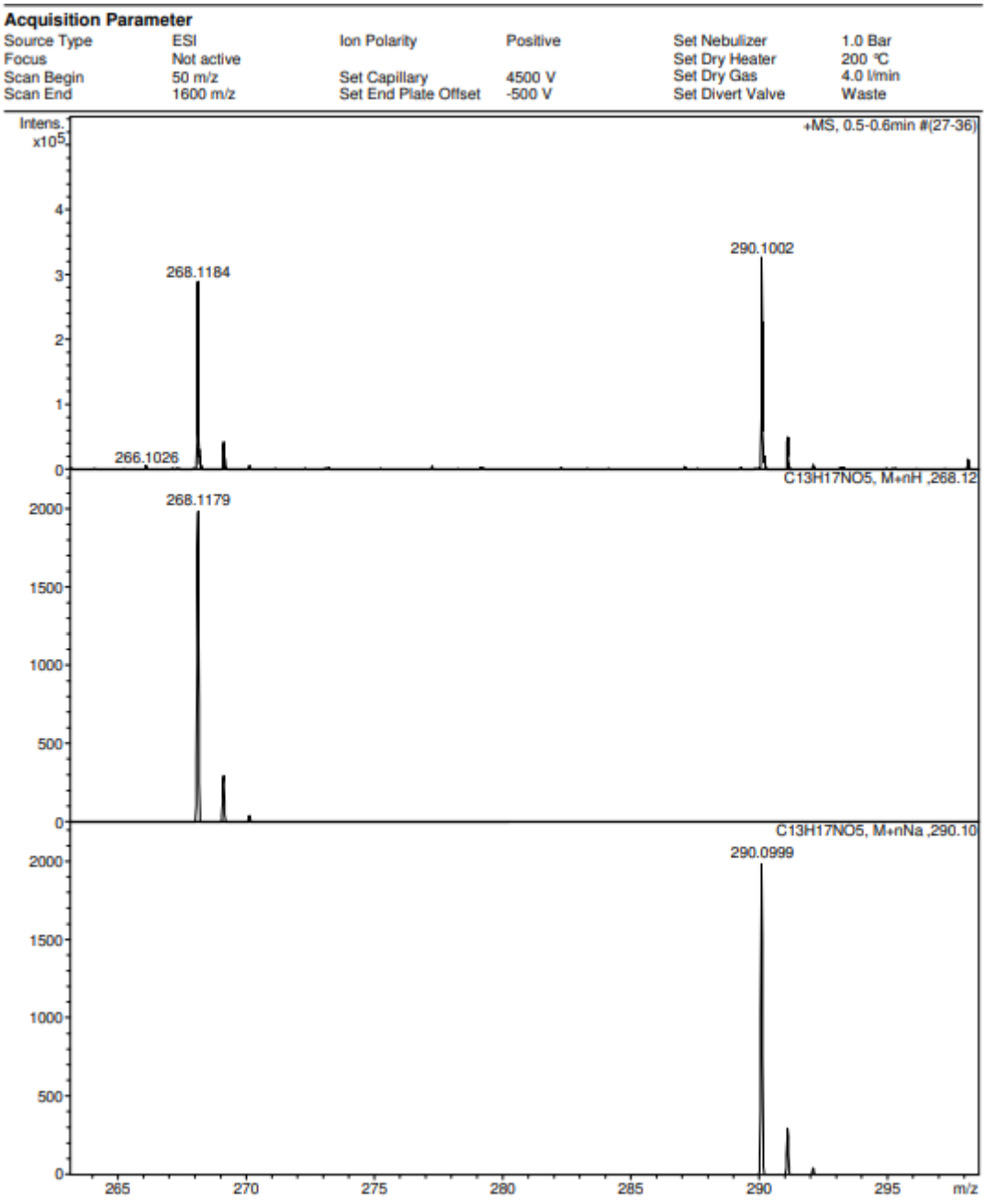


Fig. S1. ^{1}H NMR monitoring of the photoreaction of compound **8f** under UV-irradiation (312 nm) in DMSO-d_6 solution.

6. Copies of HRMS for all compounds

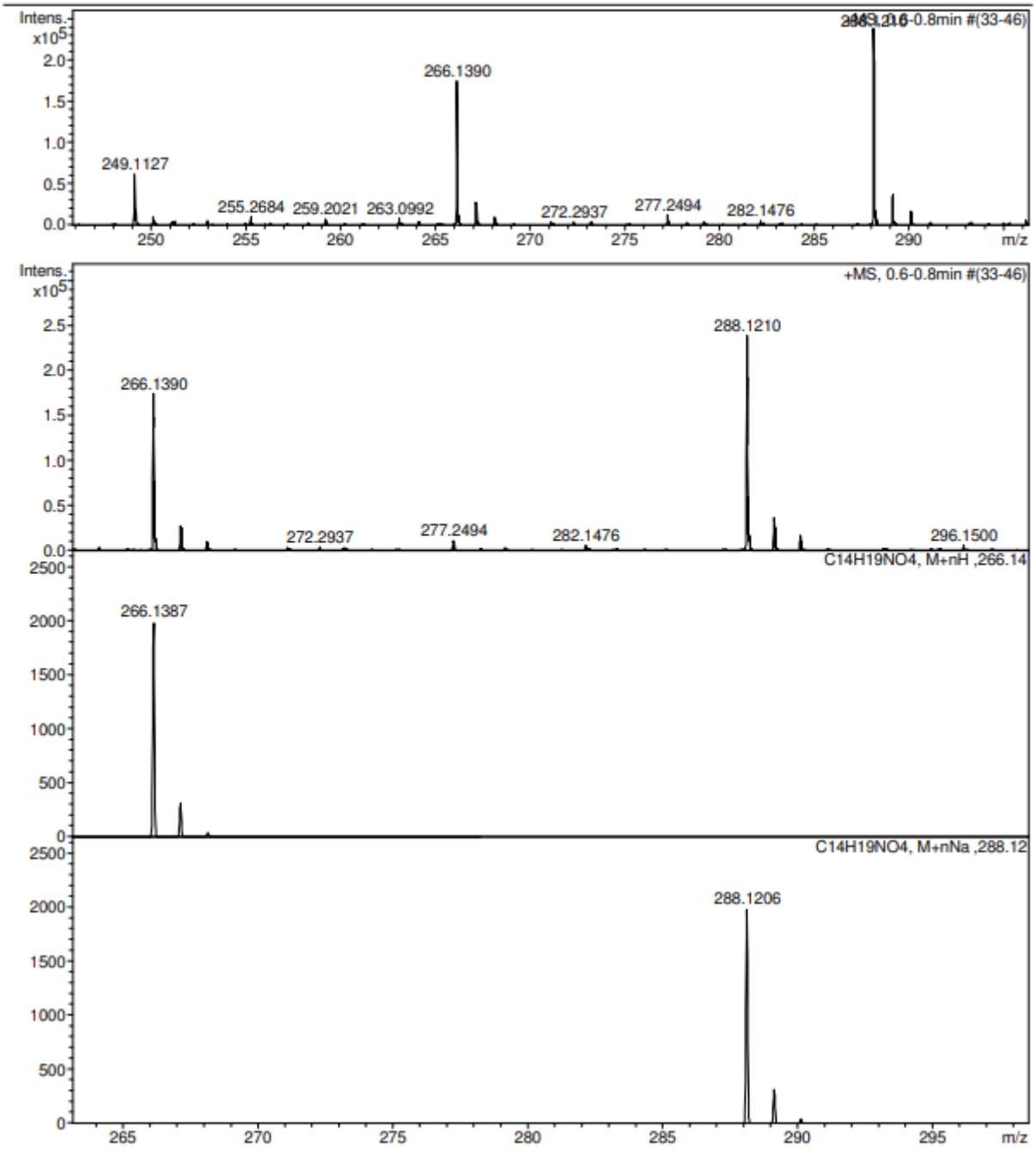
HRMS for compound **8d**



HRMS for compound **8e**

Acquisition Parameter

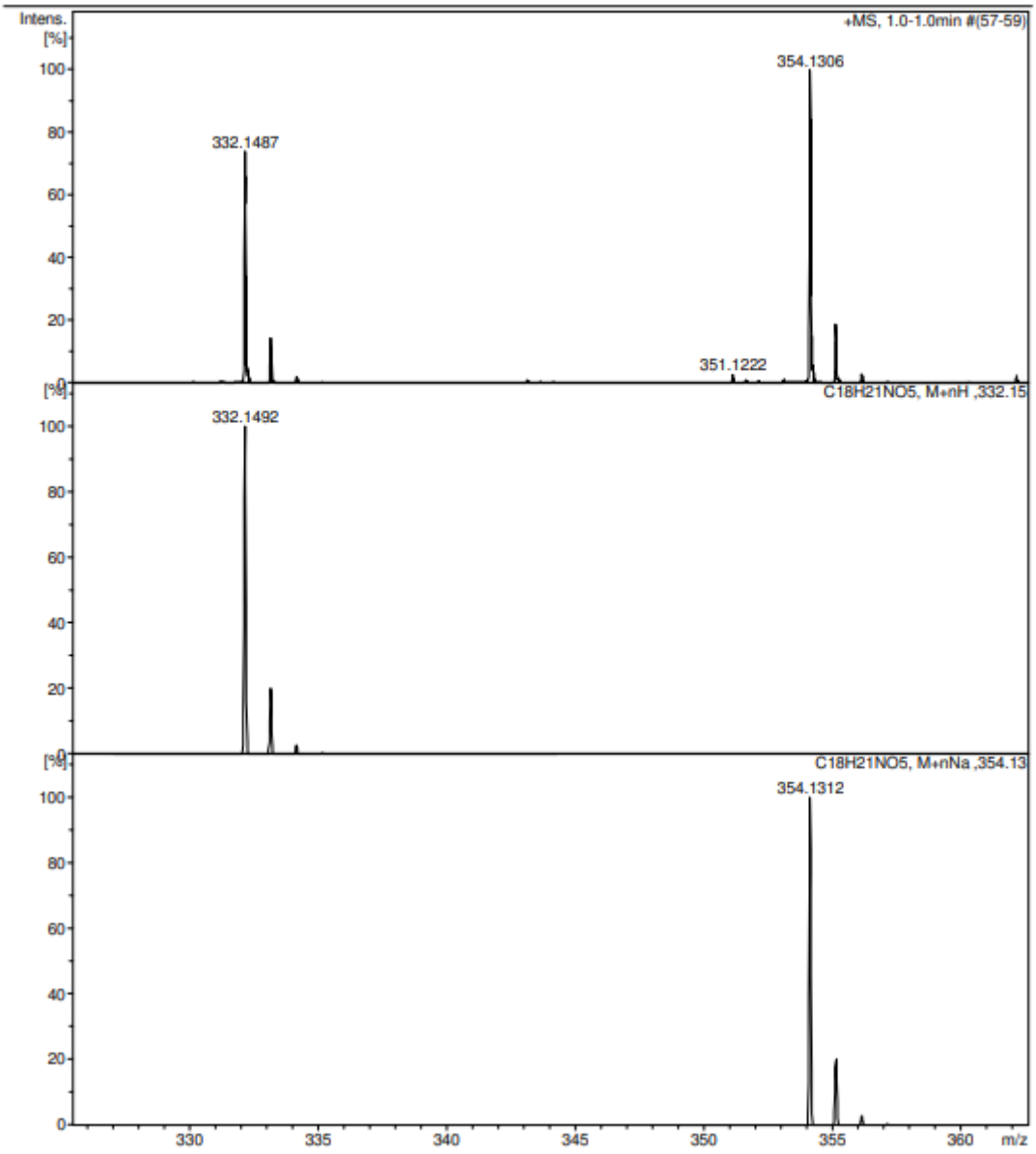
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



HRMS for compound **8f**

Acquisition Parameter

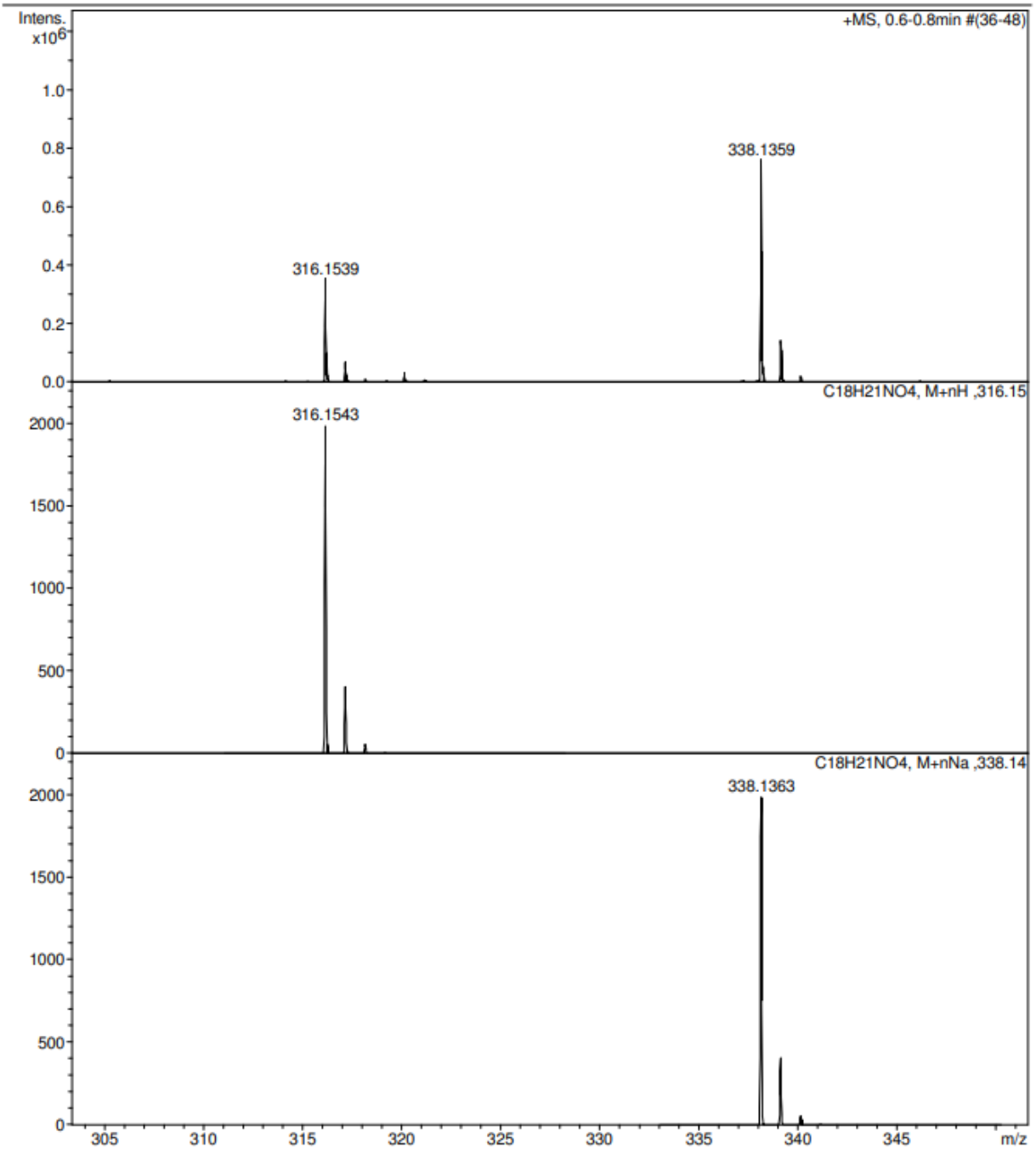
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



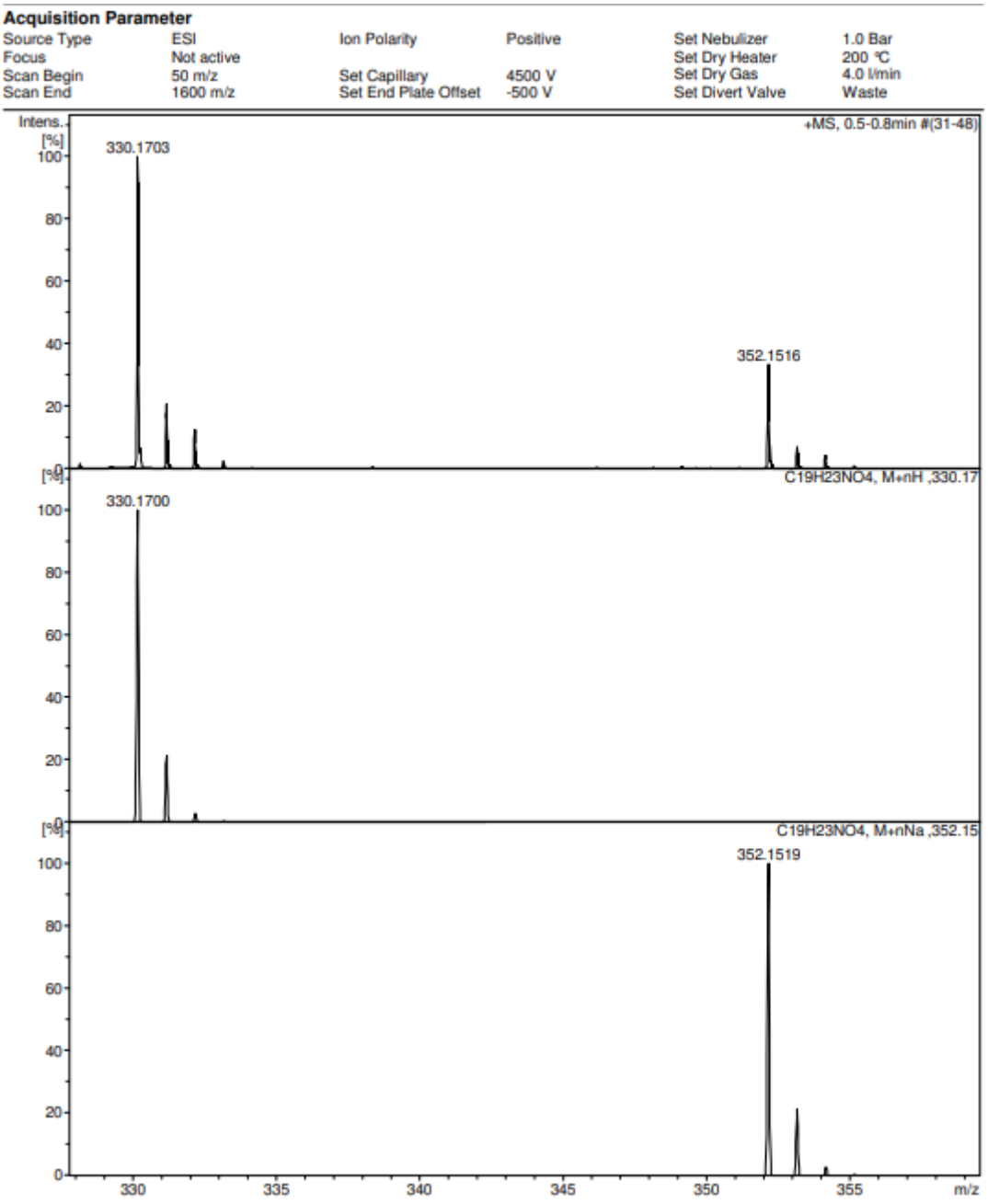
HRMS for compound **8g**

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



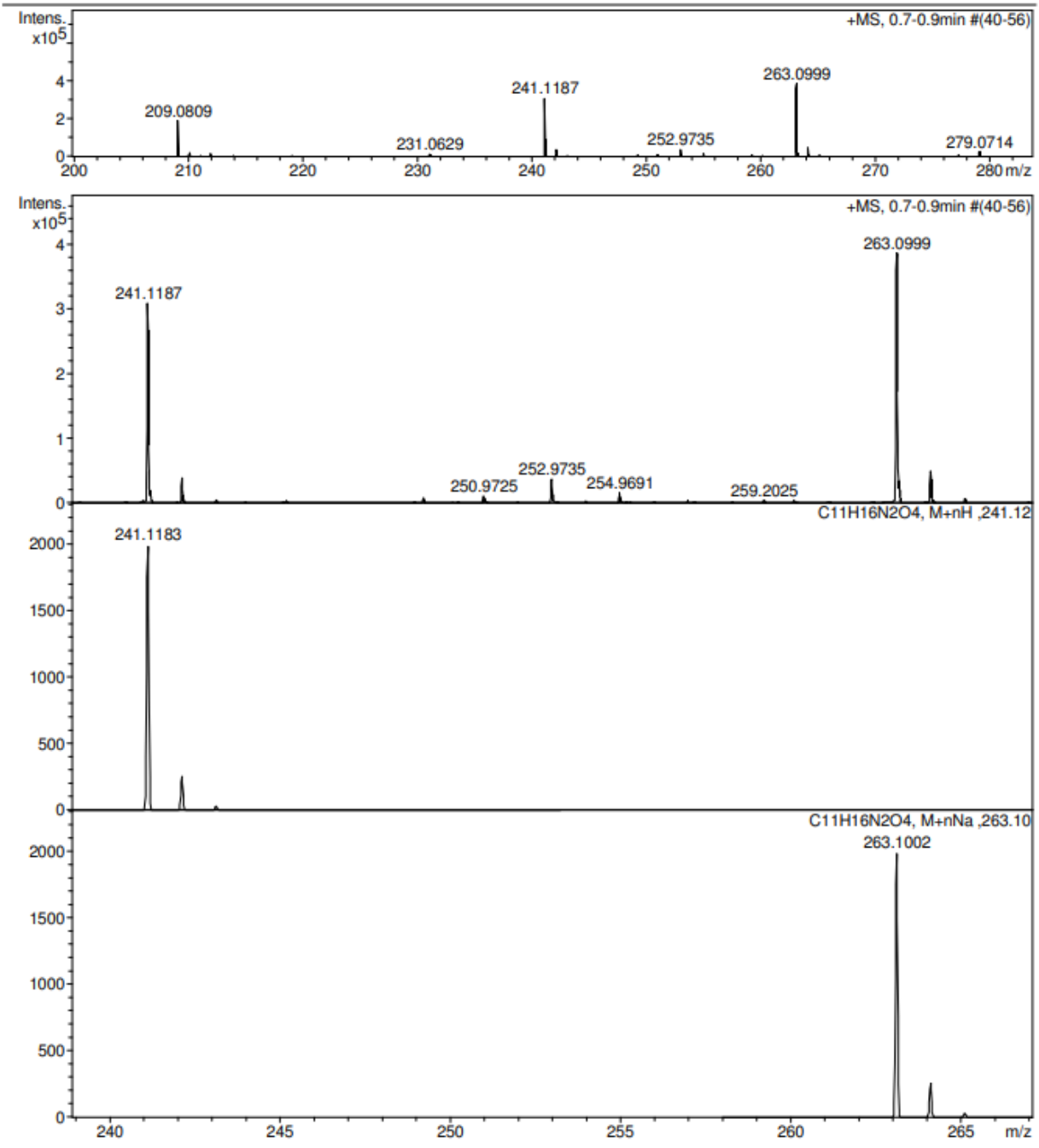
HRMS for compound **8h**



HRMS for compound **8i**

Acquisition Parameter

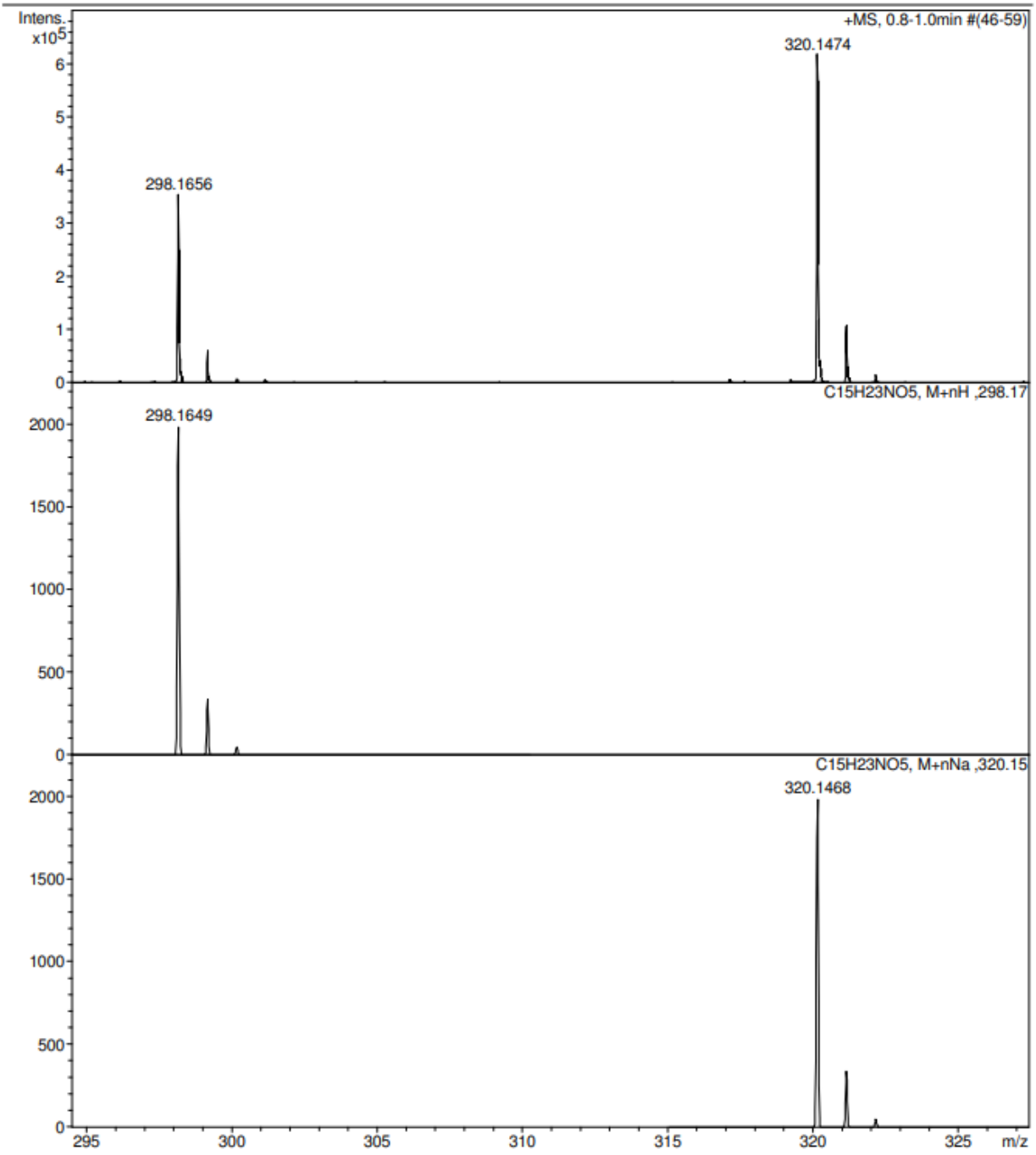
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



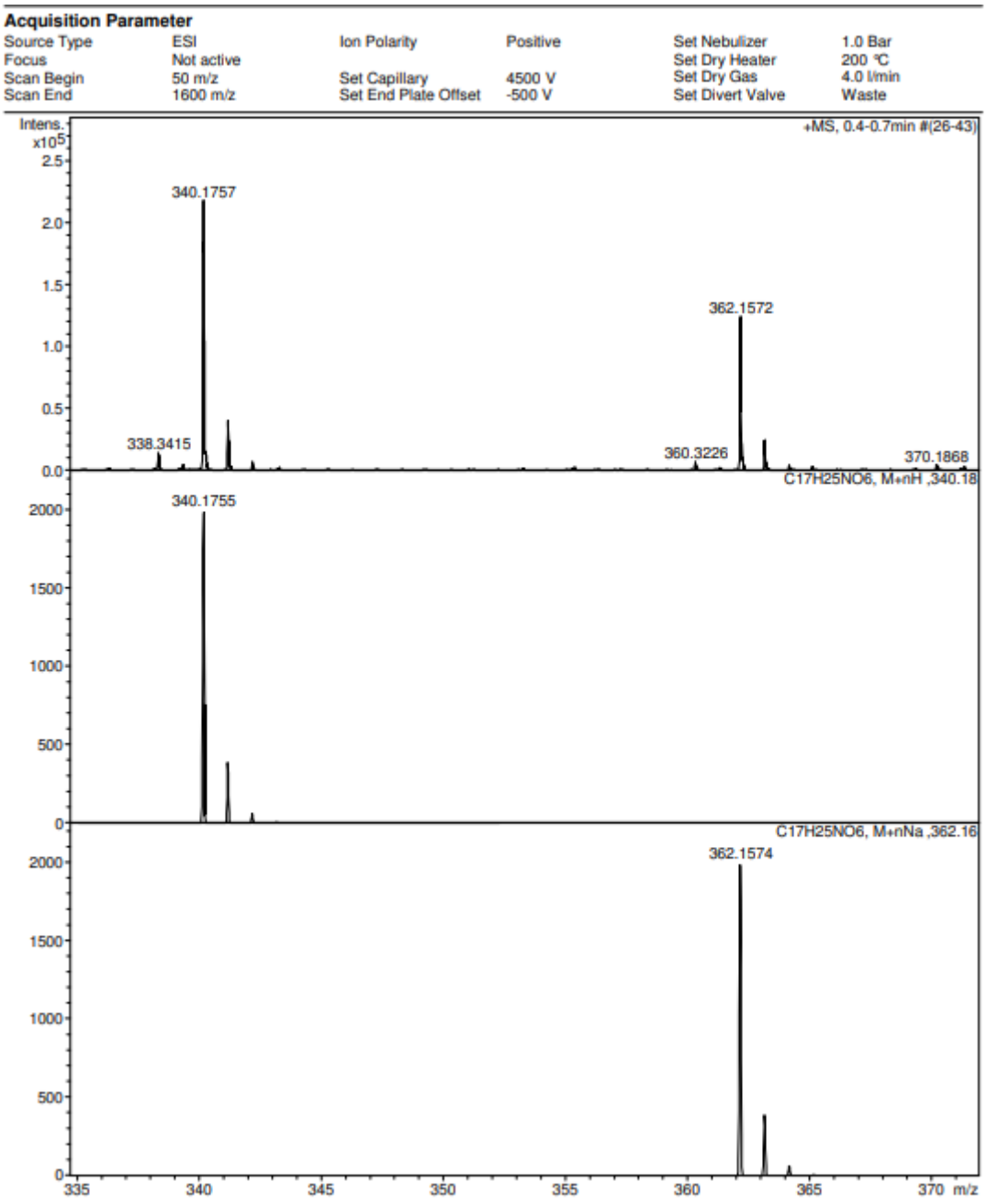
HRMS for compound **8j**

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



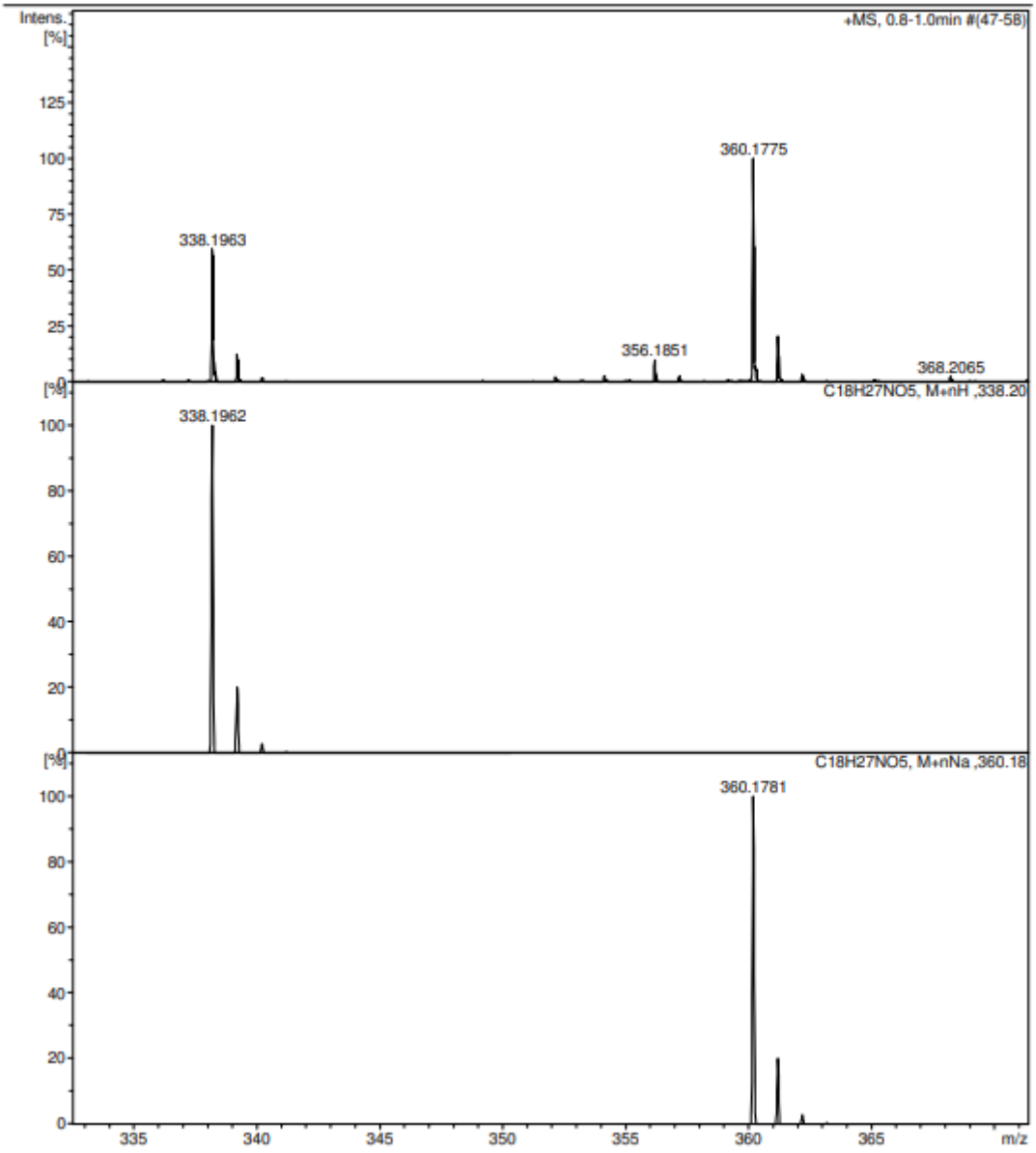
HRMS for compound **8k**



HRMS for compound **8l**

Acquisition Parameter

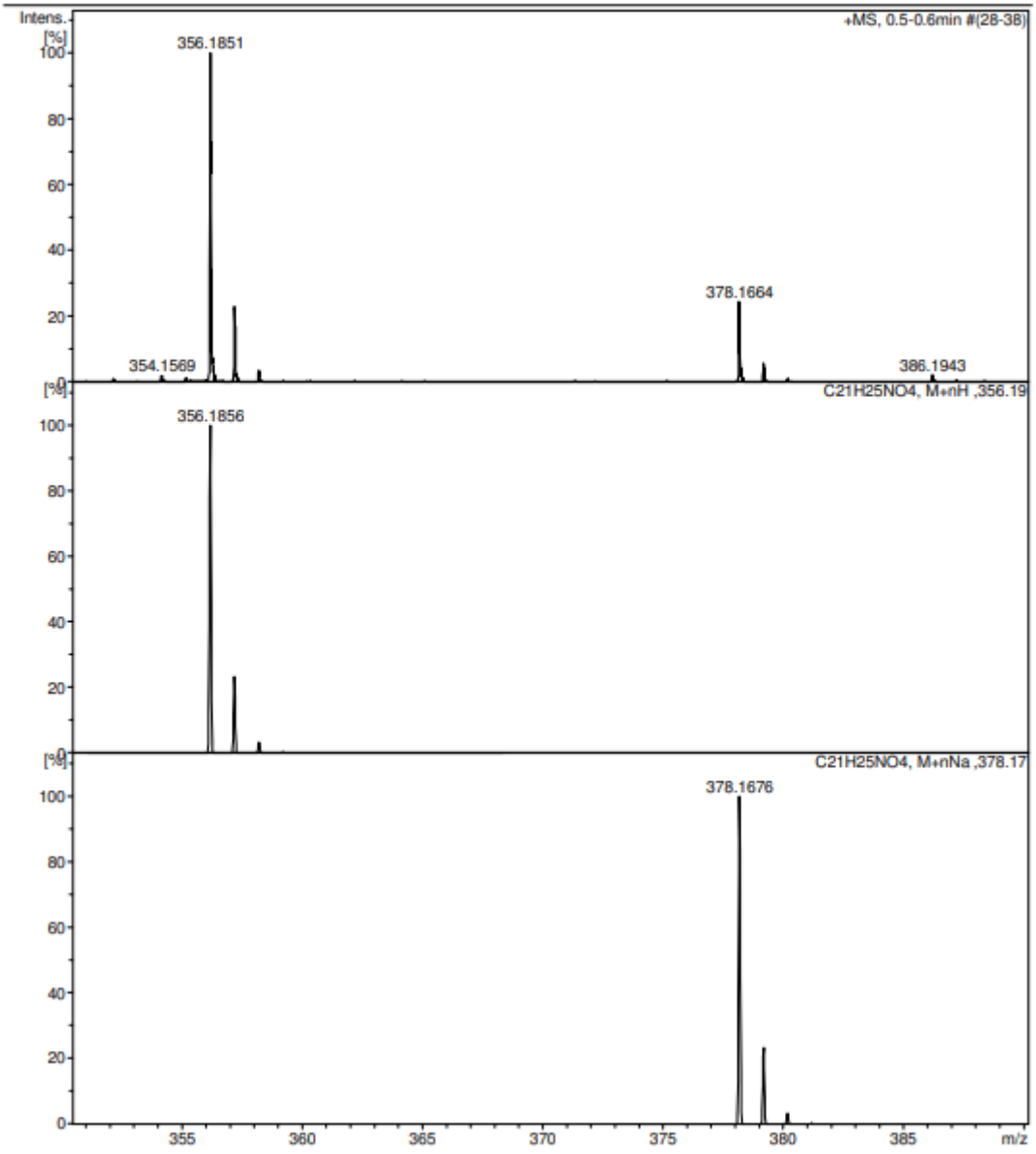
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



HRMS for compound **8m**

Acquisition Parameter

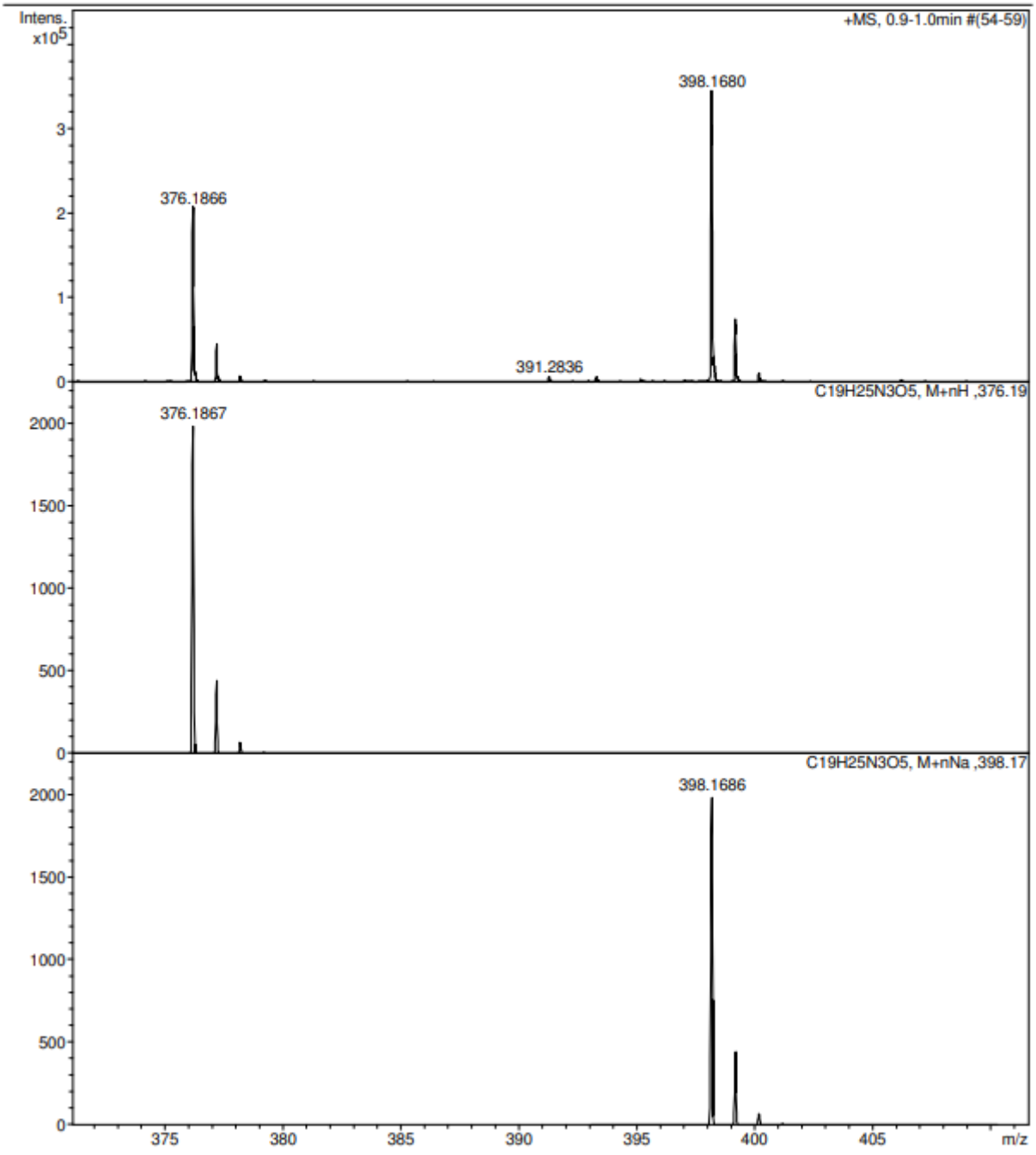
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



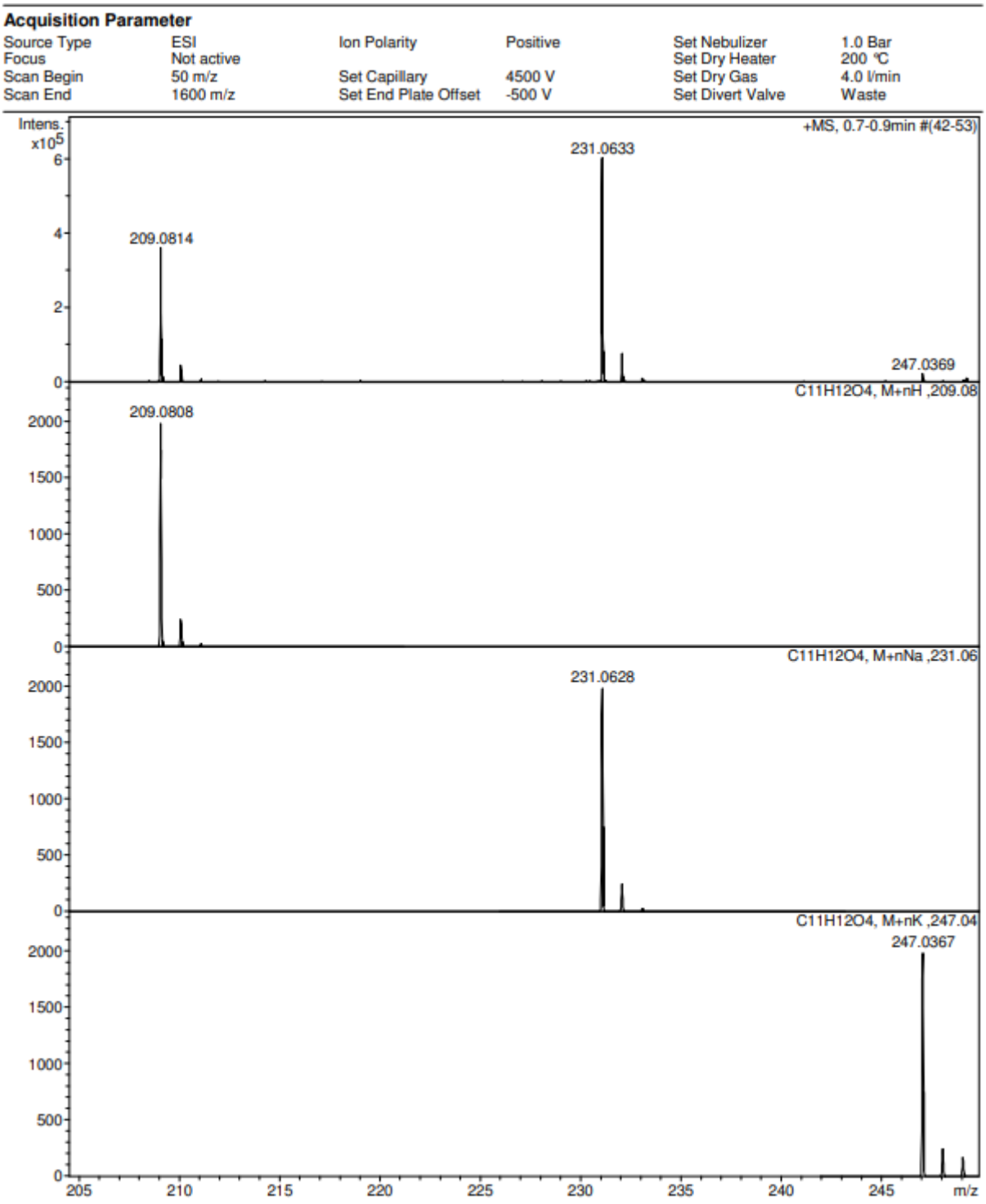
HRMS for compound **8n**

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



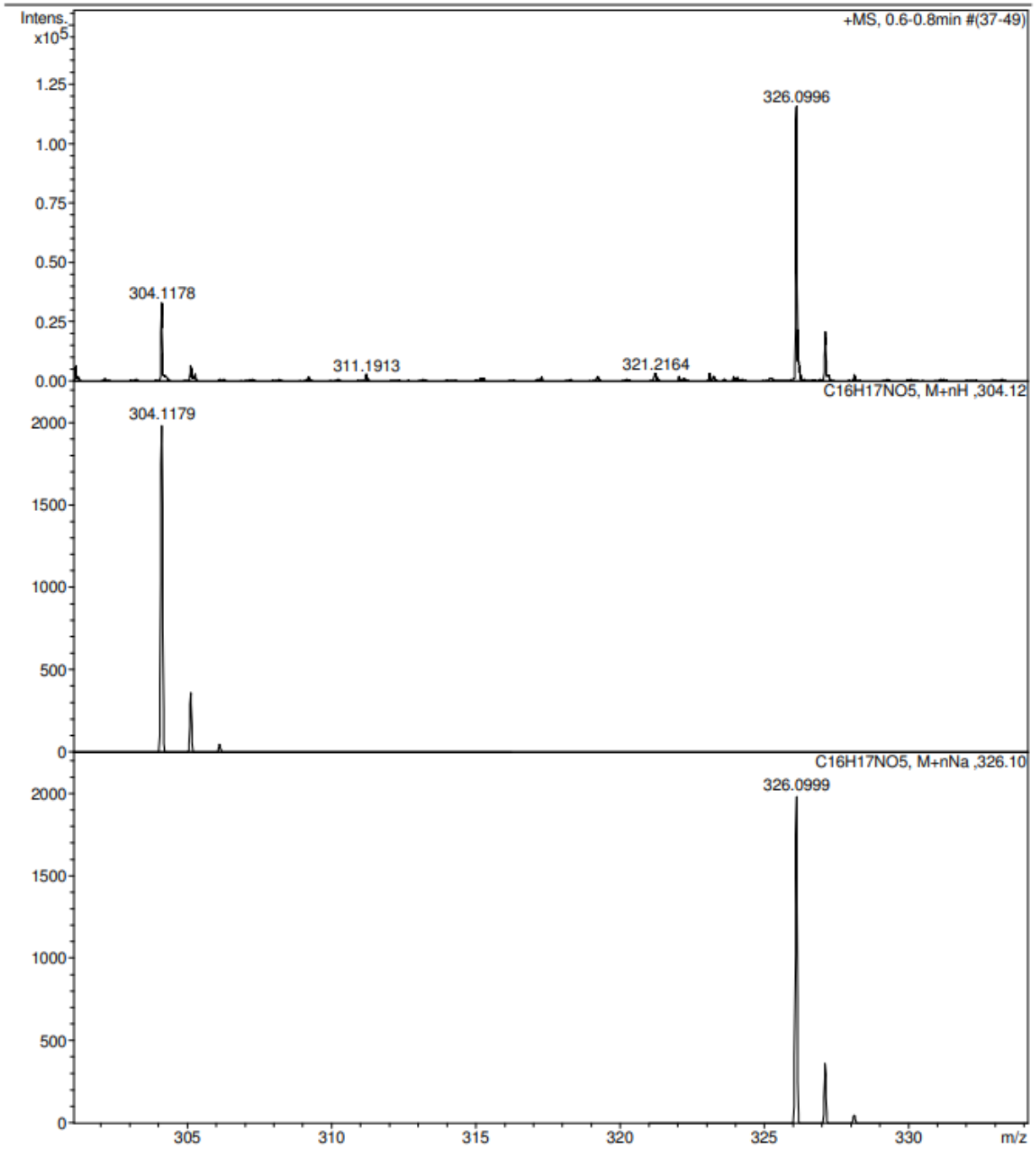
HRMS for compound **13a**



HRMS for compound **9a**

Acquisition Parameter

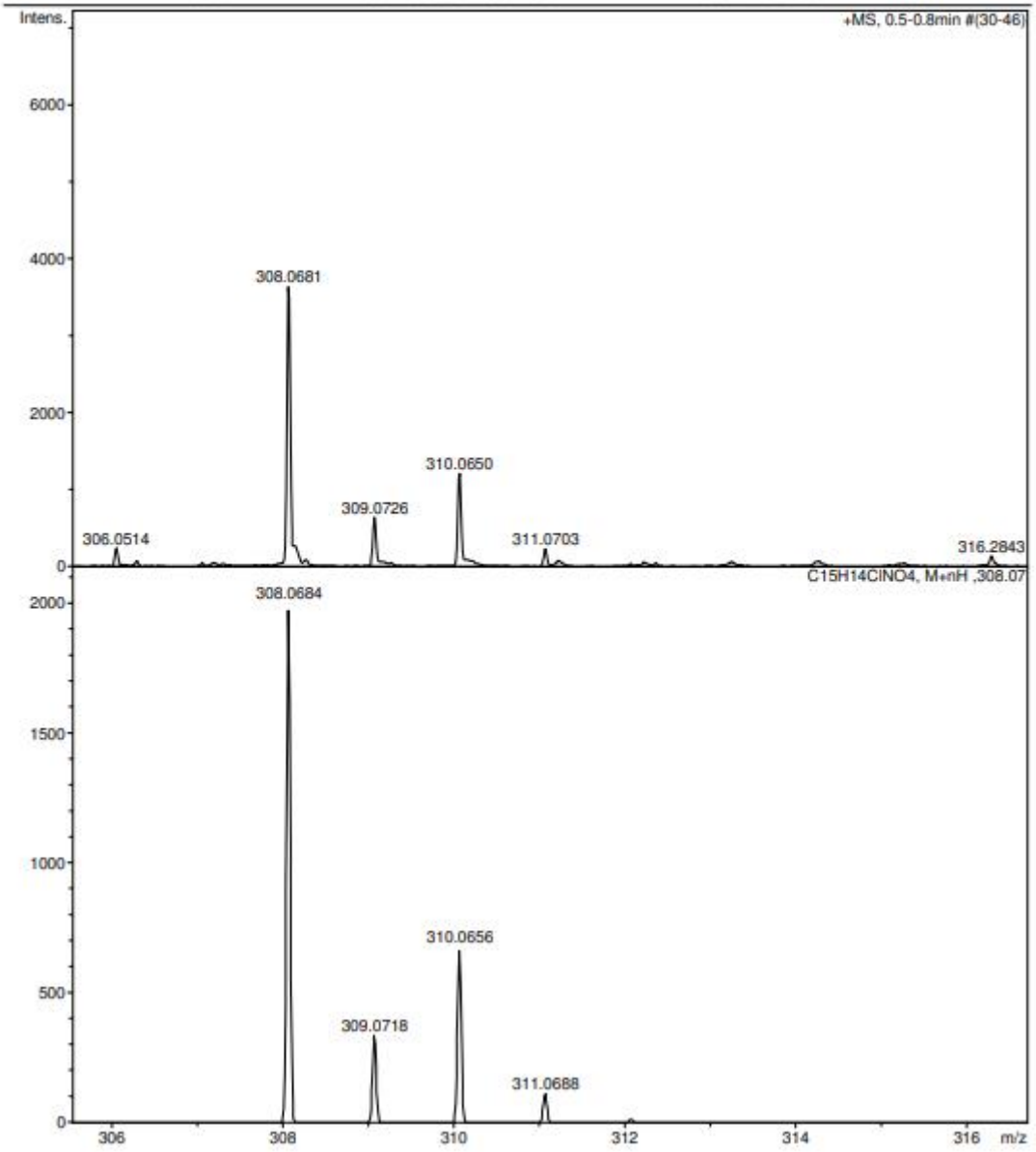
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



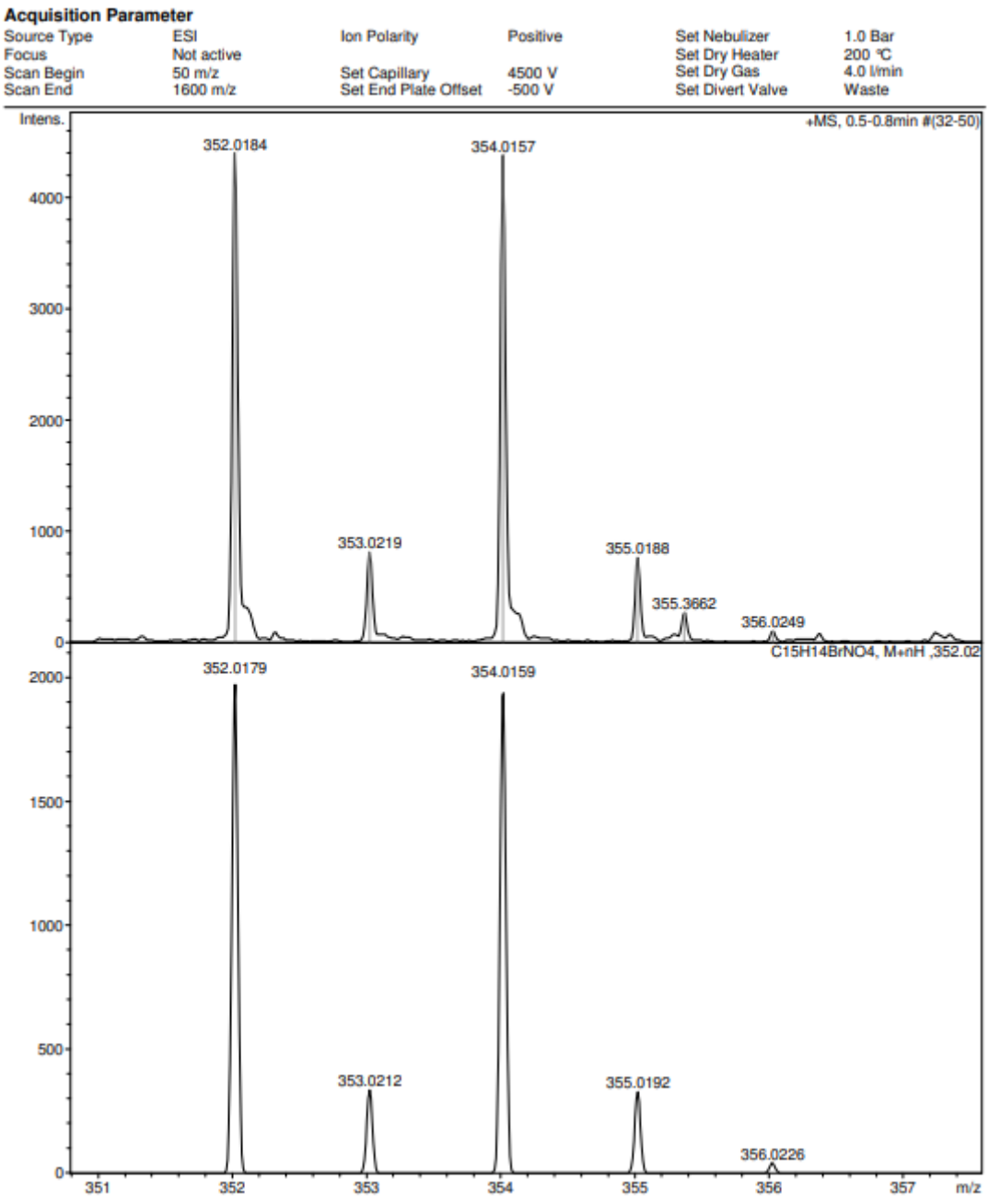
HRMS for compound **9b**

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



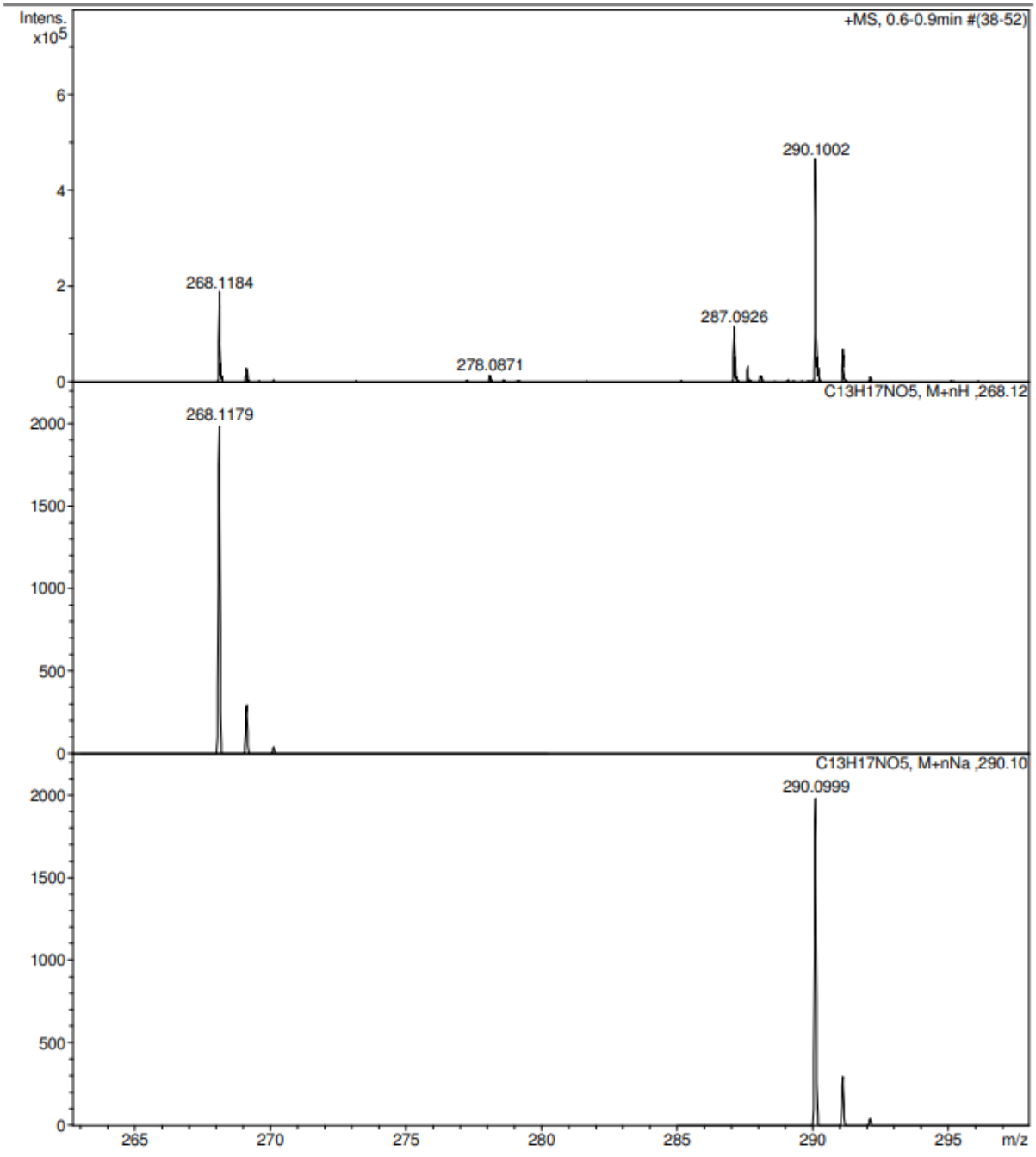
HRMS for compound **9c**



HRMS for compound **9d**

Acquisition Parameter

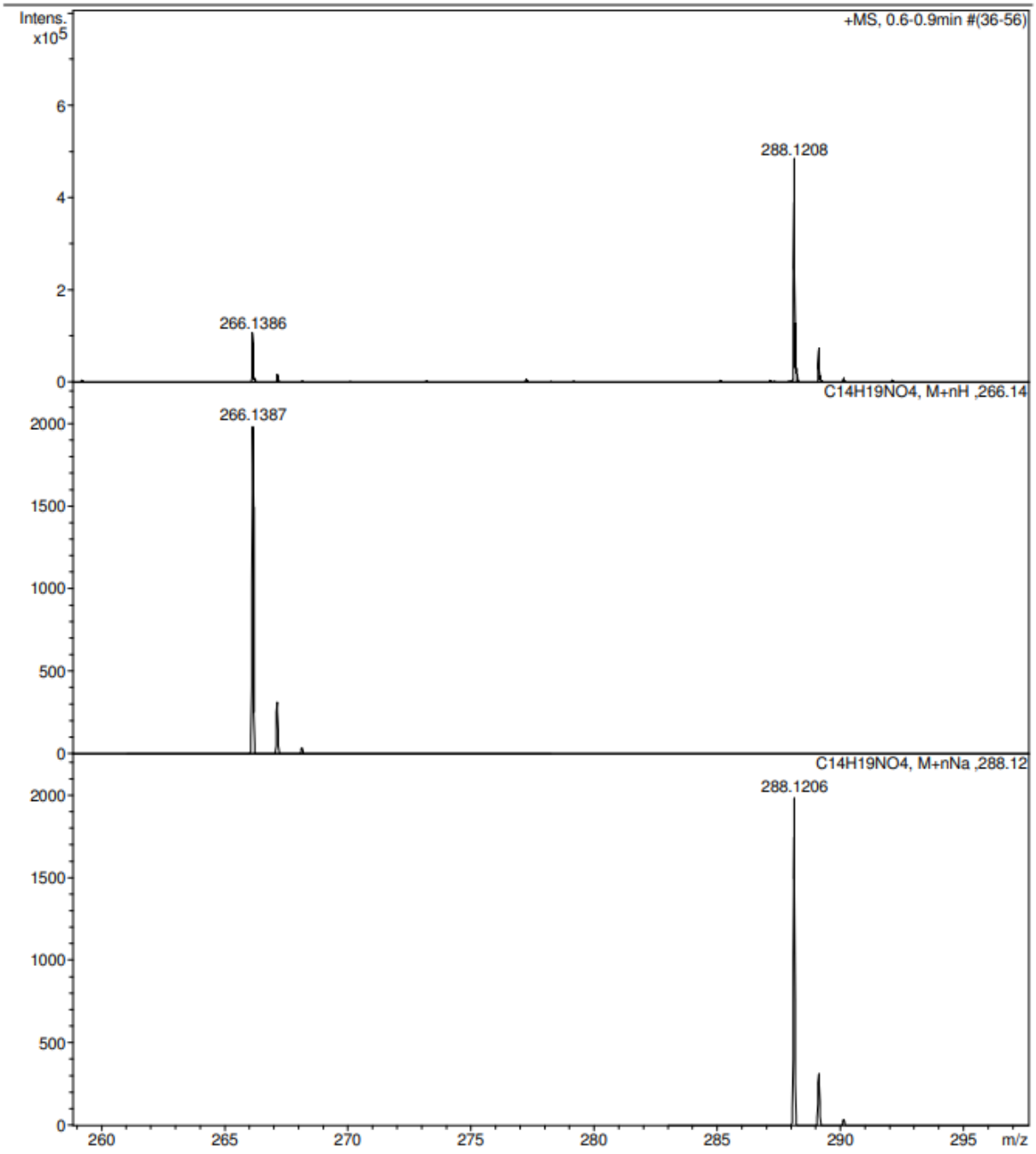
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



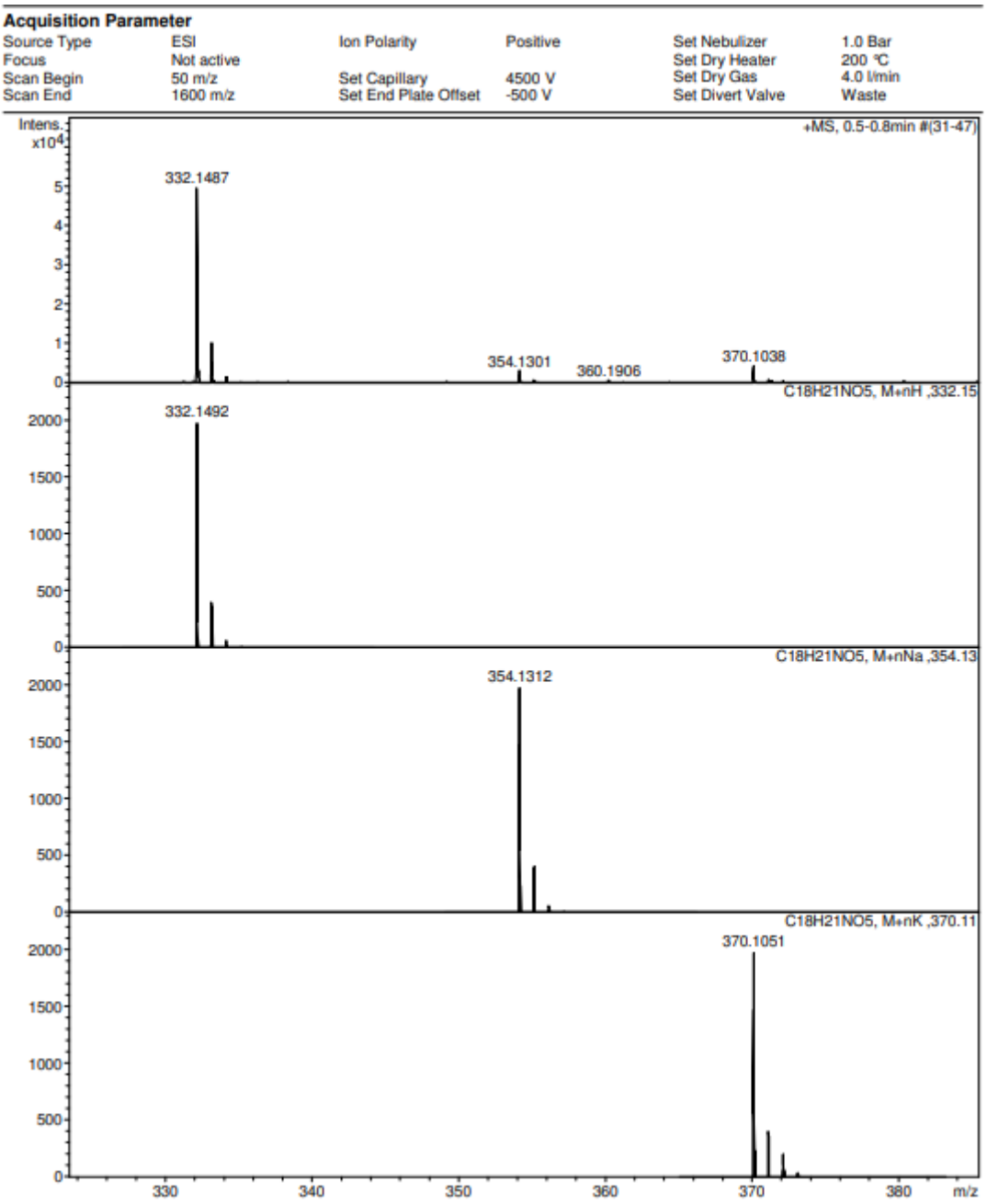
HRMS for compound **9e**

Acquisition Parameter

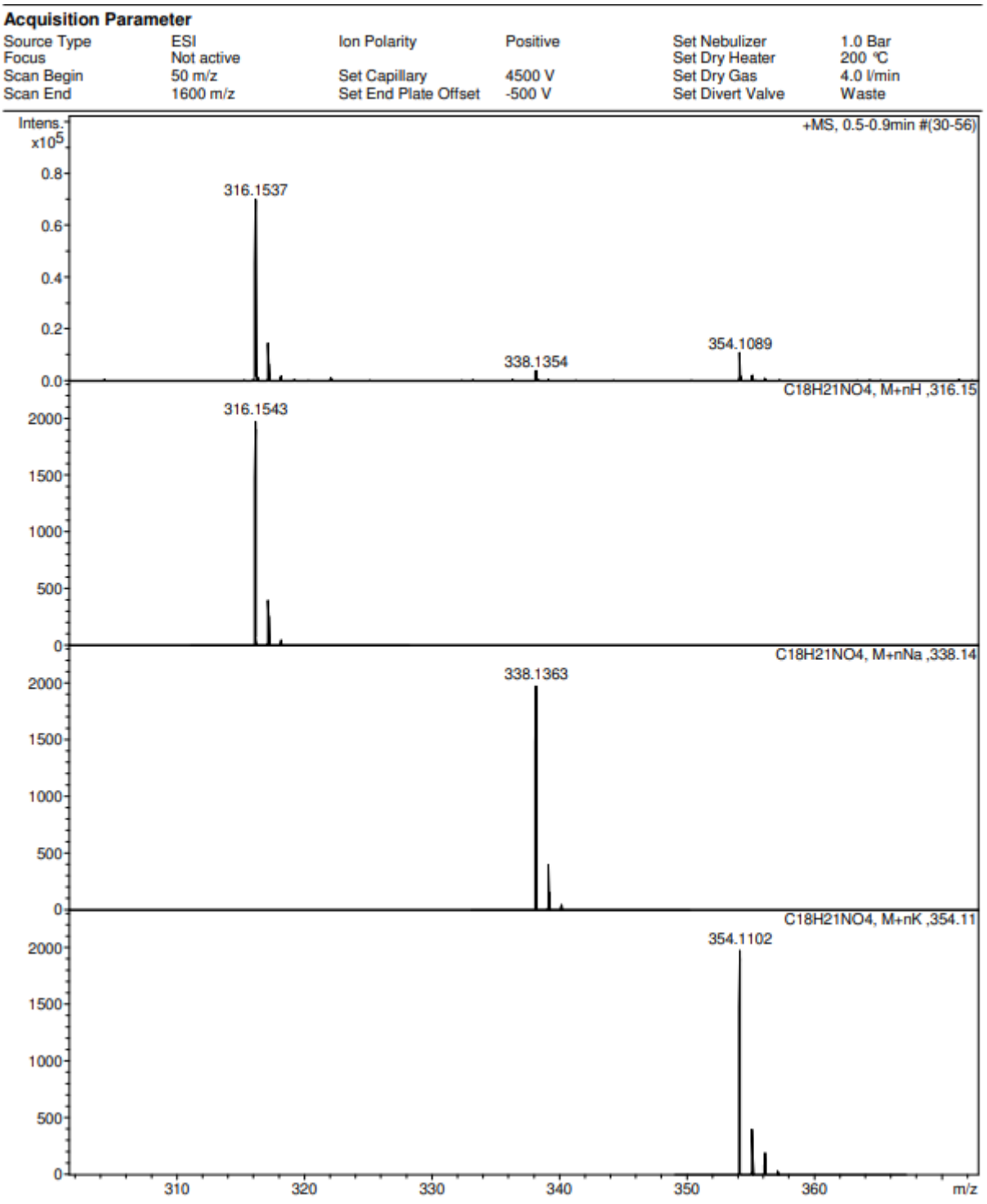
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



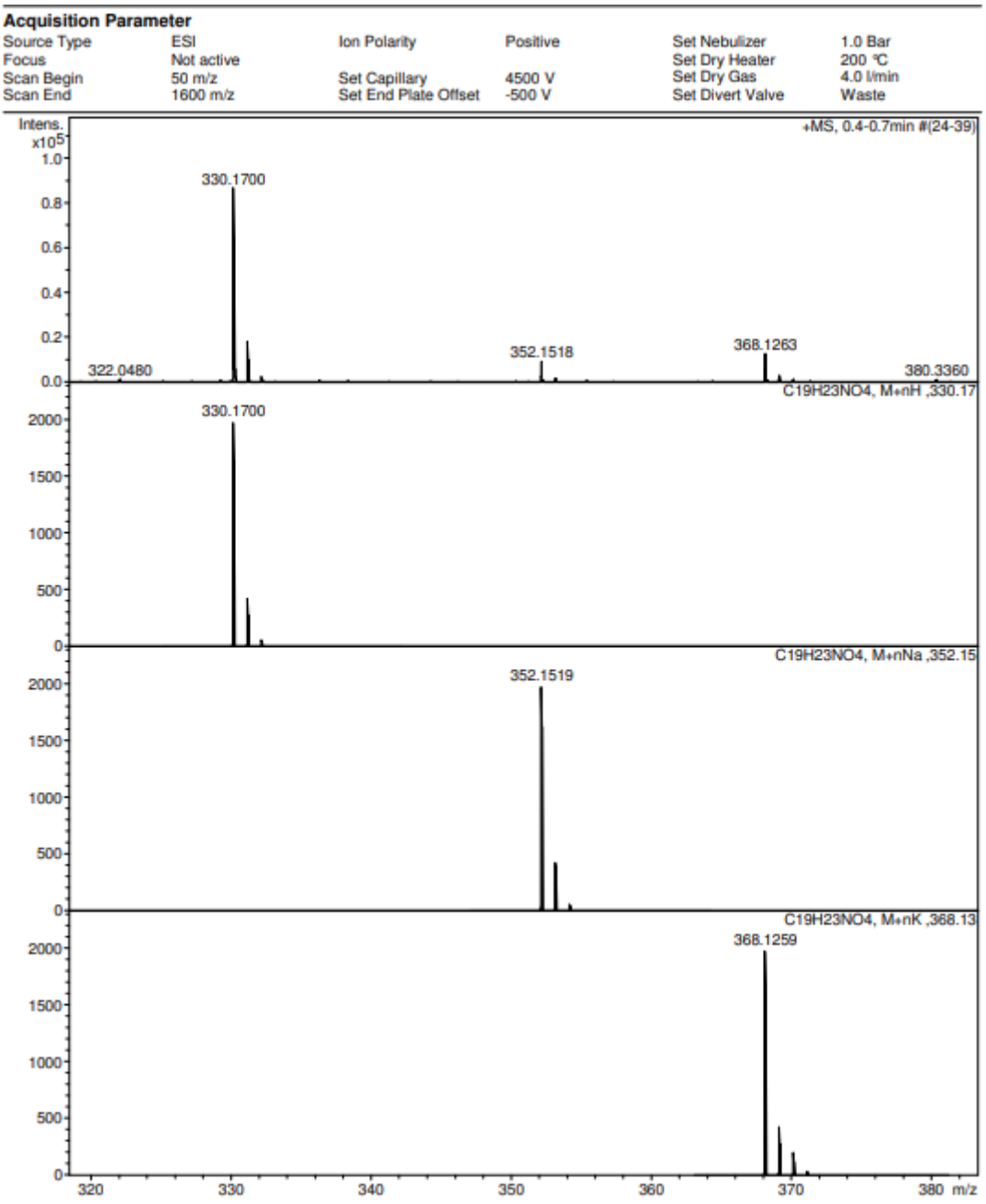
HRMS for compound **9f**



HRMS for compound **9g**



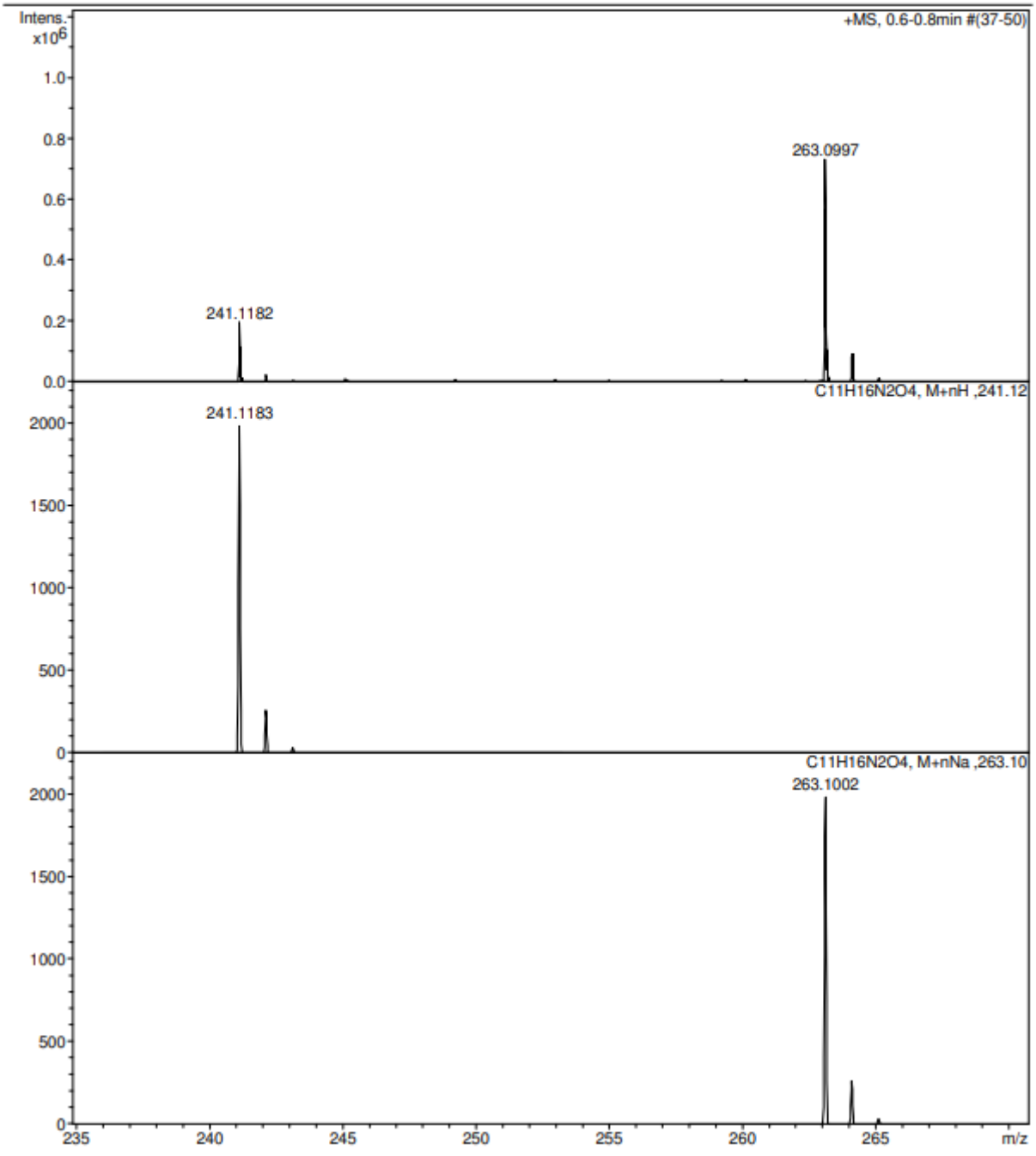
HRMS for compound **9h**



HRMS for compound **9i**

Acquisition Parameter

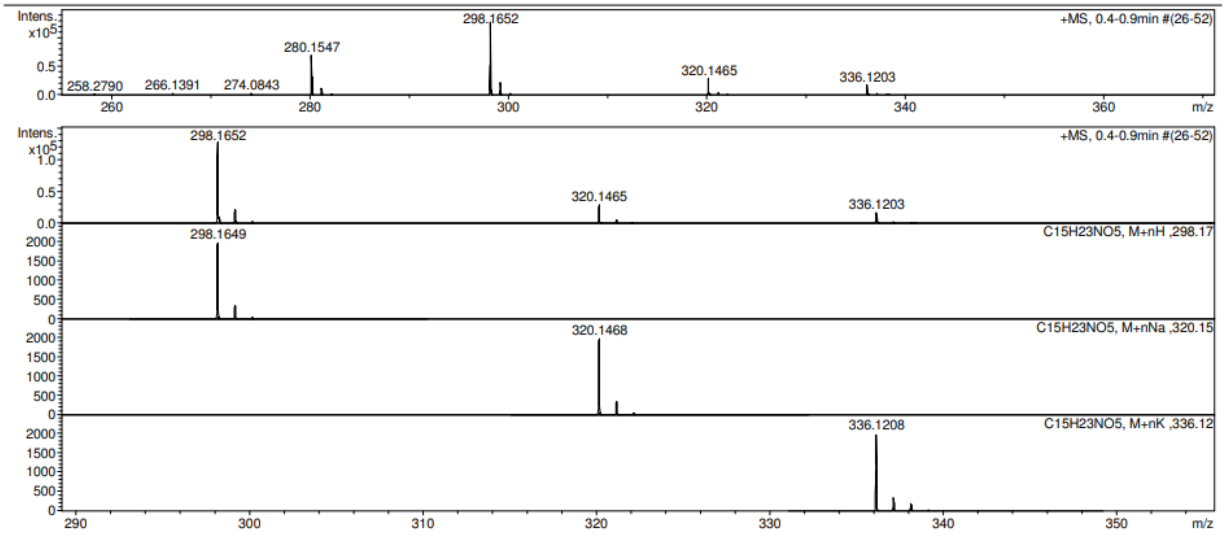
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



HRMS for compound **9j**

Acquisition Parameter

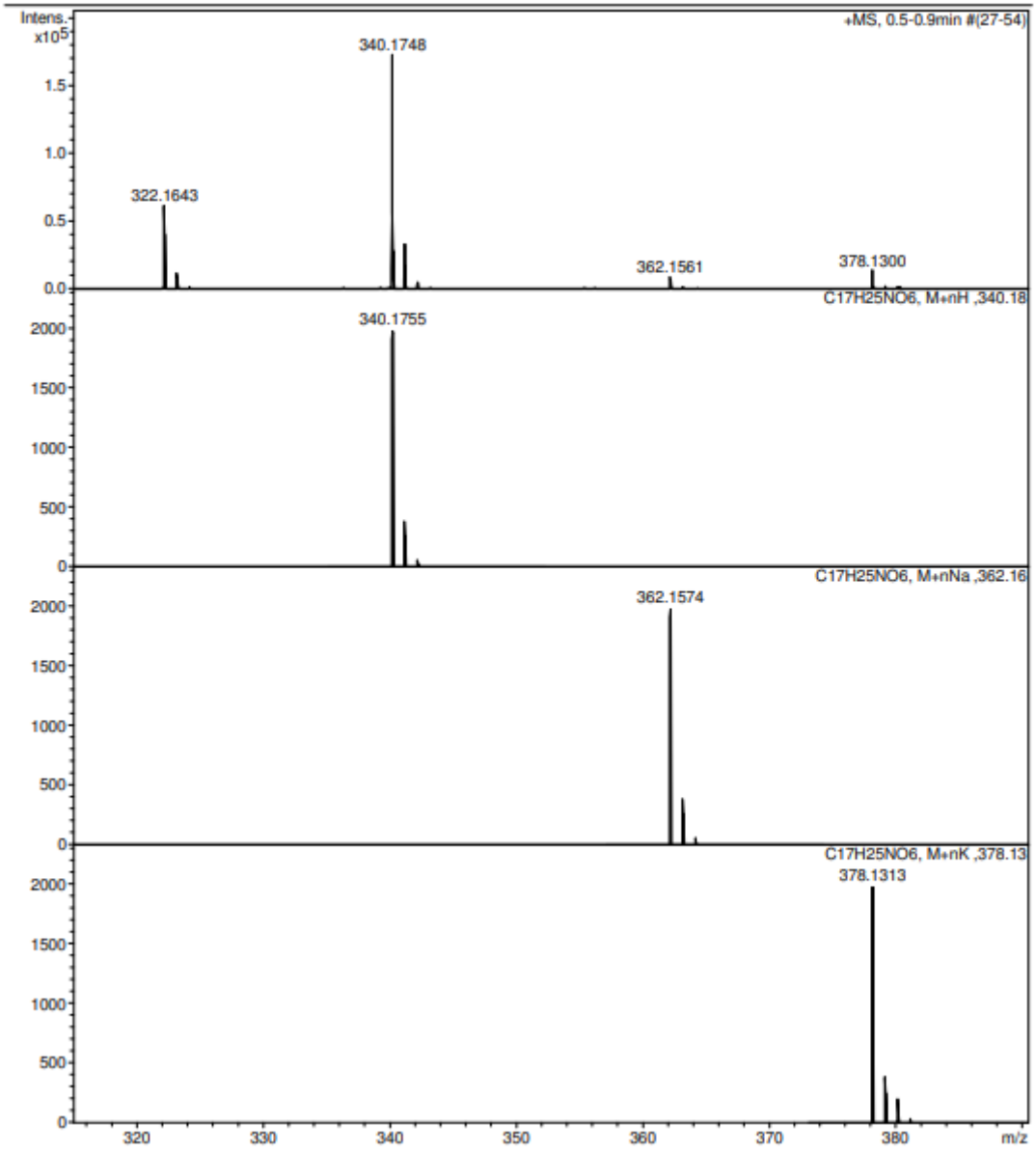
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



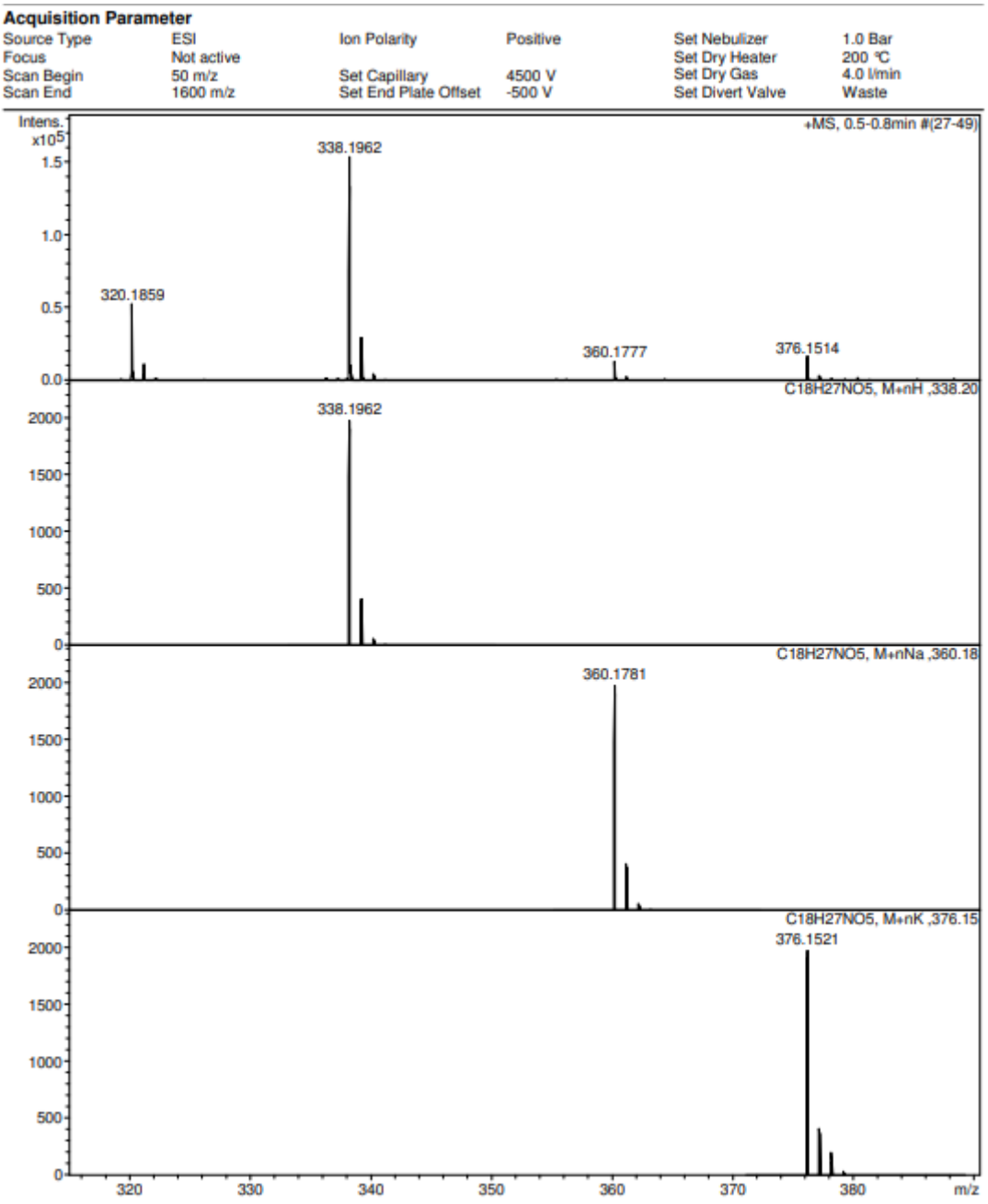
HRMS for compound **9k**

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



HRMS for compound 9l



HRMS for compound 9m

Acquisition Parameter

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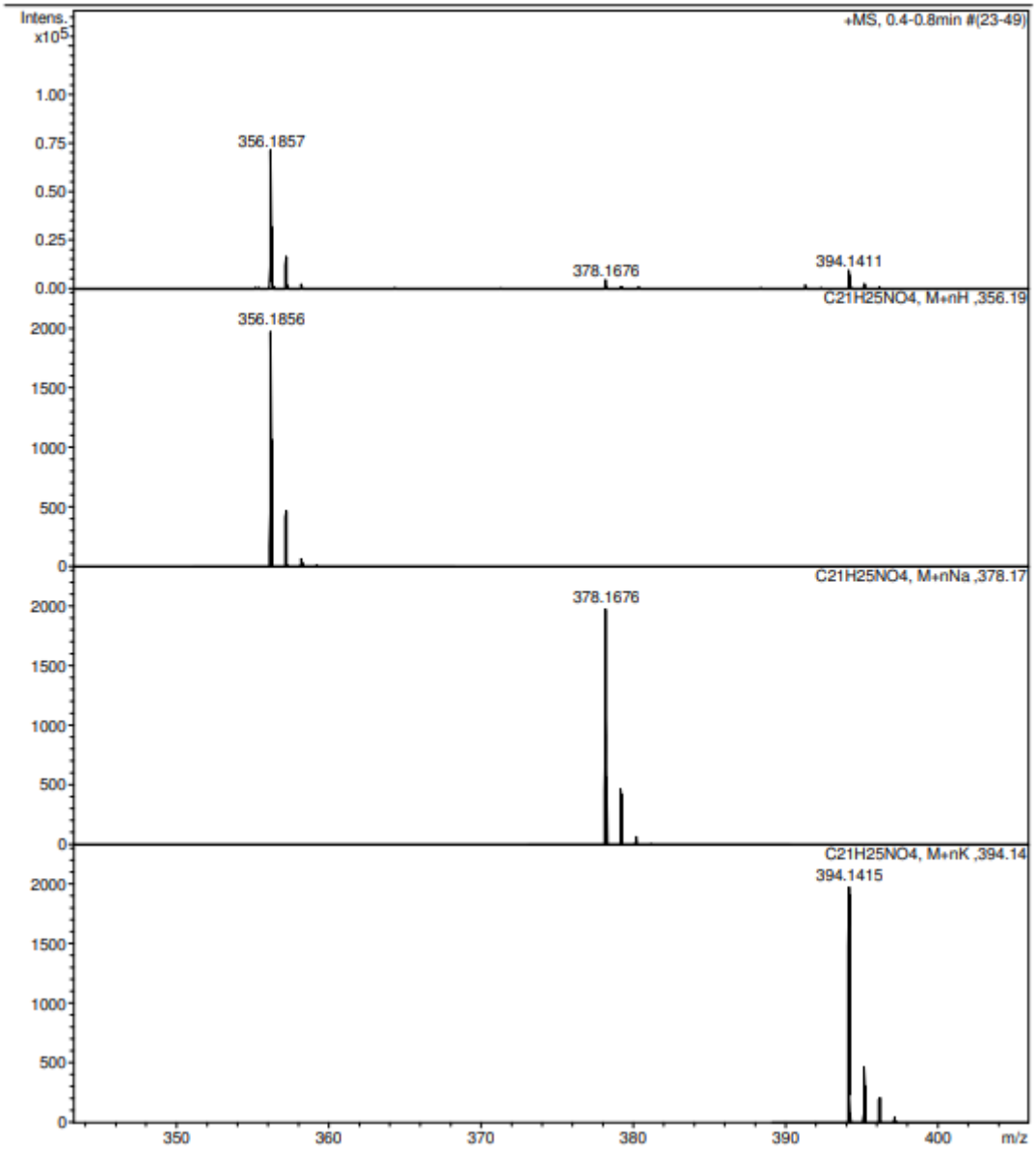
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



HRMS for compound 9n

Acquisition Parameter

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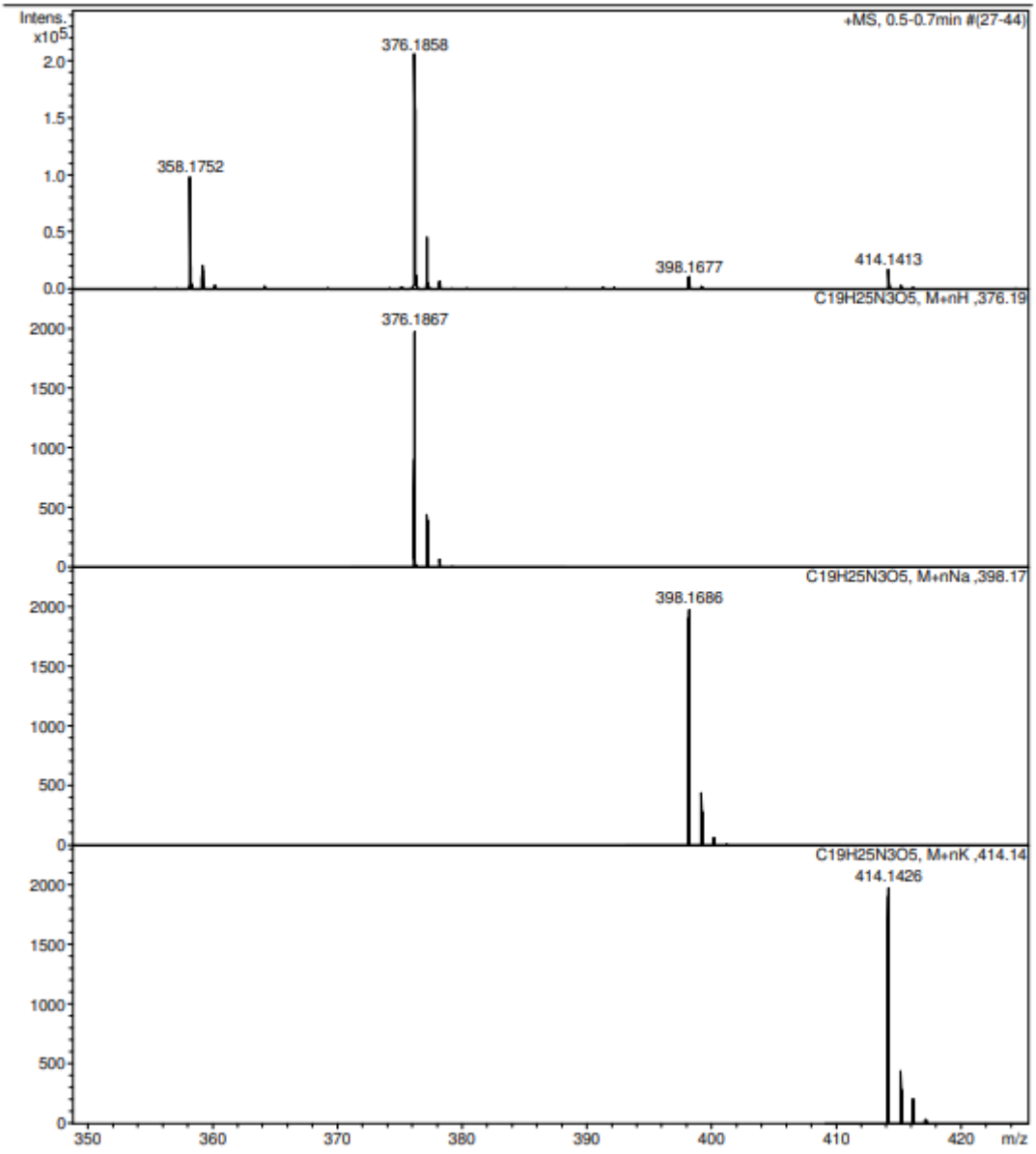
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



HRMS for compound 16

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
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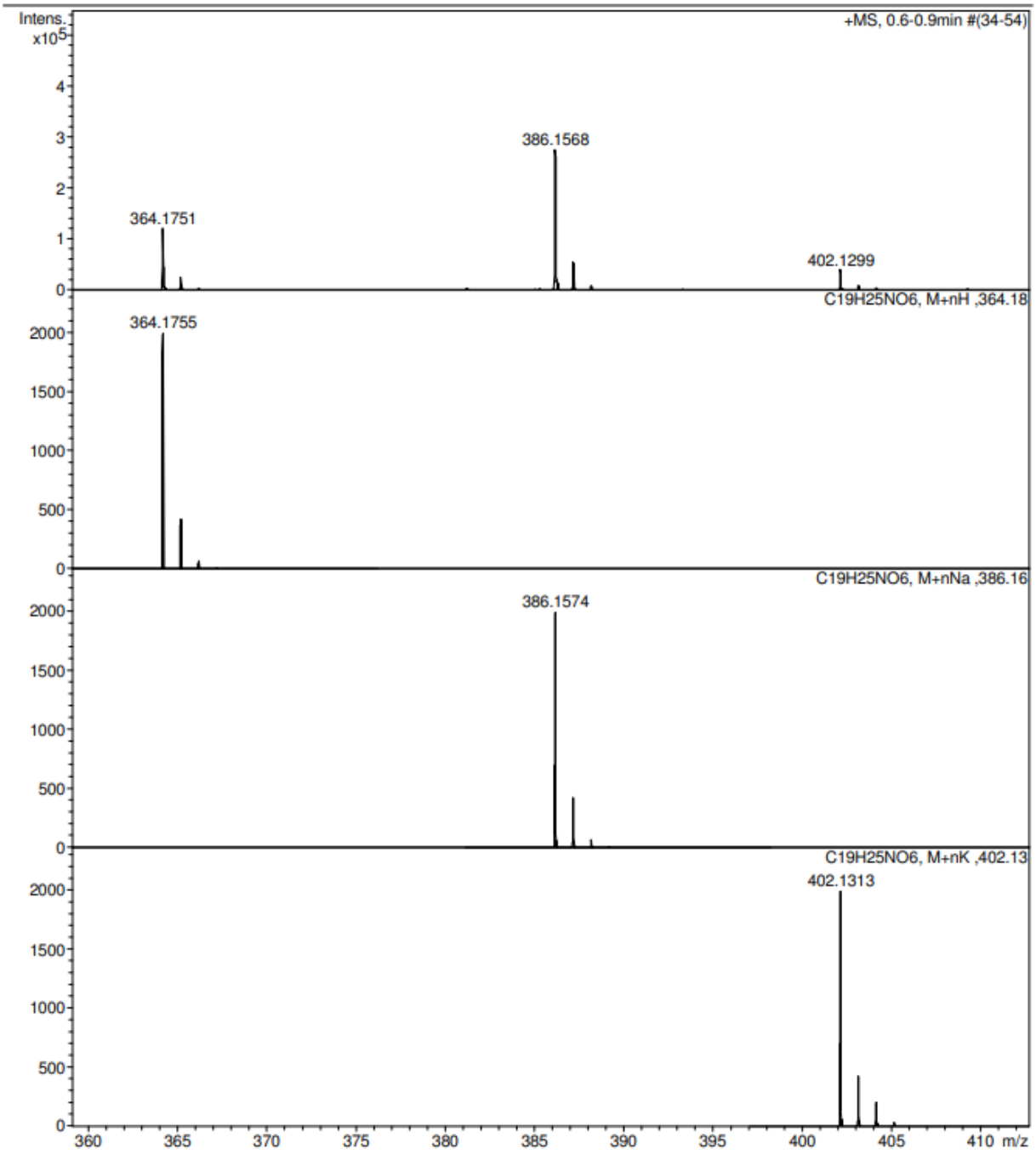
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



7. X-ray crystallographic data and refinement details

Crystals of **9c**, grown under various conditions from different solvents over weeks, were always very thin twinned needles. A monocrystal suitable for X-ray studies was obtained by cutting a thin twinned crystal in halves along the longest dimension under polarized light. X-ray diffraction data for **9c** were collected on a Rigaku Synergy S diffractometer equipped with a HyPix600HE area-detector (kappa geometry, shutterless ω-scan technique), using monochromatized Cu Kα-radiation. X-ray diffraction data for **9n** were collected on a Bruker Quest D8 diffractometer equipped with a Photon-III area-detector (shutterless ϕ- and ω-scan technique), using graphite monochromatized Mo Kα-radiation. The intensity data of collected reflections were integrated by the CrysAlisPro program[1] for **9c** and the SAINT program[2] for **9n**. The intensity data were corrected for absorption by multi-scan methods basing on measurements of equivalent reflections, using the CrysAlisPro program[1] for **9c** and SADABS[3] for **9n**. The structures were solved by direct and dual space methods using SHELXT[4] and refined by the full-matrix least-squares method on F^2 using SHELXL-2018[5] in the OLEX2 program[6] for **9c** and in the APEX-III program suite[2] for **9n**. Positions of all atoms were found from the electron density-difference map. Atoms were refined with individual anisotropic (non-hydrogen atoms) or isotropic (hydrogen atoms) displacement parameters.

1. CrysAlisPro. Version 1.171.41.106a. *Rigaku Oxford Diffraction*, 2021.
2. Bruker. APEX-III. *Bruker AXS Inc.*, Madison, Wisconsin, USA, 2020.
3. Krause, L.; Herbst-Irmer, R.; Sheldrick, G. M.; Stalke, D. Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination. *J. Appl. Cryst.* 2015, 48, 3-10. http://doi.org/10.1107/S1600576714022985
4. Sheldrick, G. M. SHELXT - Integrated space-group and crystal-structure determination. *Acta Cryst.* 2015, A71(1), 3-8. http://doi.org/10.1107/S2053273314026370
5. Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Cryst.* 2015, C71(1), 3-8. http://doi.org/10.1107/S2053229614024218
6. 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), 229-341. http://doi.org/10.1107/S0021889808042726

Table S1. Crystal data and structure refinement for **9c** and **9n**.

Identification code	**9c**	**9n**
Empirical formula	$C_{15}H_{14}BrNO_4$	$C_{19}H_{27}N_3O_6$
Formula weight	352.18	393.43
Temperature, K	100	100
Wavelength, Å	1.54184	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
Unit cell dimensions		
a, Å	6.70863(6)	9.2023(3)
b, Å	31.0104(3)	10.5800(3)
c, Å	6.93722(7)	20.2538(5)
β, °	110.1997(10)	101.5857(8)
Volume, $Å^3$	1354.43(2)	1931.74(10)
Z	4	4
Calcd. Density, g/cm^3	1.727	1.353
Absorption coefficient, mm^{-1}	4.296	0.101
F(000)	712	840
Crystal size, mm	0.08 x 0.005 x 0.004	0.57 x 0.23 x 0.19
θ range for data collection	2.850 to 79.301°.	2.053 to 34.497°
Index ranges	-8<=h<=5, -39<=k<=38, -8<=l<=8	-14<=h<=14, -16<=k<=16, -32<=l<=32
Reflections		
collected	16633	79433
independent	2906 [R(int) = 0.0289]	8190 [R(int) = 0.0397]
observed	2758	6789
Completeness to θ_{full}	100.0 %	100.0 %
Data / restraints / parameters	2906 / 0 / 246	8190 / 0 / 361
Goodness-of-fit on F2	1.101	1.056
Final R1, wR2 indices with I>2σ(I)	0.0247, 0.0675	0.0466, 0.1198
Final R1, wR2 indices (all data)	0.0257, 0.0681	0.0596, 0.1298
Largest diff. peak, hole, $ē·Å^{-3}$	0.426, -0.511	0.520, -0.291
CCDC deposition number	**2110941**	**2110942**

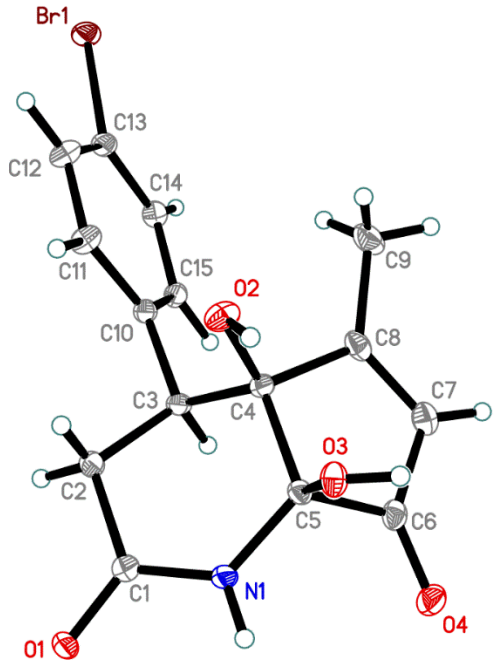


Fig. S2. The structure of **9c**. The thermal ellipsoids are set to a 50% probability level.

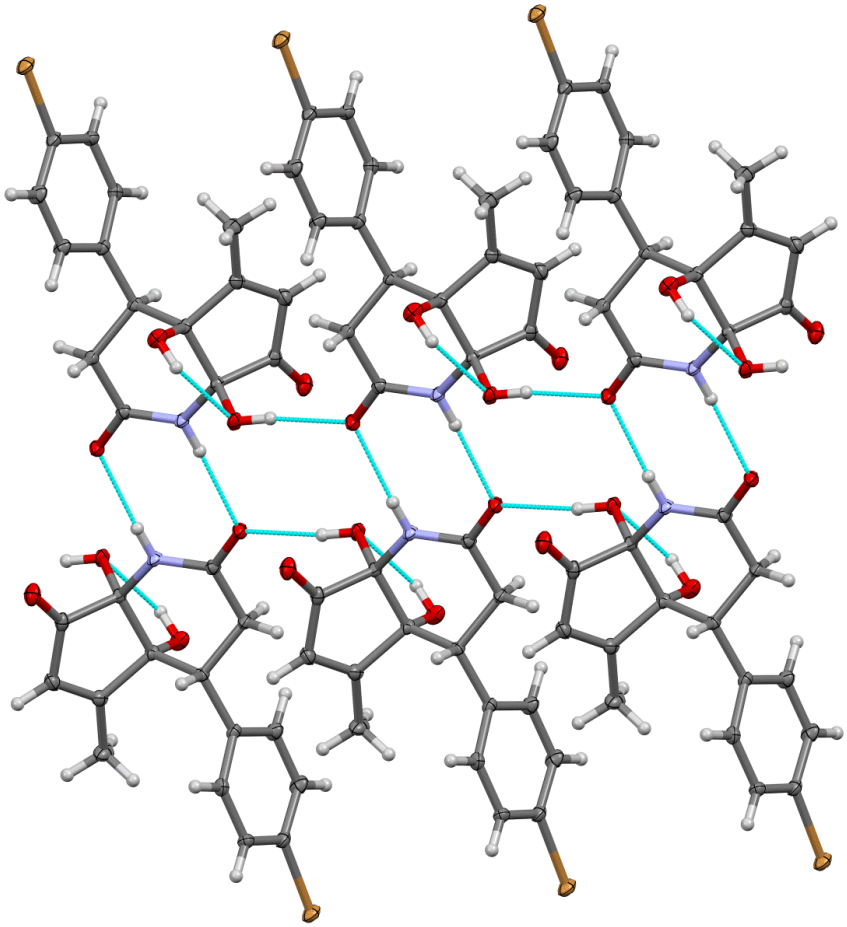


Fig. S3. Hydrogen bonding in **9c**. A fragment of 1D chain is shown. The thermal ellipsoids are set to a 50% probability level.

Table S2. Bond lengths [Å] for **9c**.

Br(1)-C(13)	1.8971(17)	C(4)-C(5)	1.556(2)	C(9)-H(9C)	0.93(3)
N(1)-H(1)	0.84(3)	C(4)-C(8)	1.531(2)	C(10)-C(11)	1.395(2)
N(1)-C(1)	1.337(2)	O(2)-H(2)	0.81(3)	C(10)-C(15)	1.396(2)
N(1)-C(5)	1.442(2)	C(5)-O(3)	1.4240(19)	C(11)-H(11)	0.96(2)
C(1)-O(1)	1.246(2)	C(5)-C(6)	1.546(2)	C(11)-C(12)	1.389(2)
C(1)-C(2)	1.505(2)	O(3)-H(3A)	0.80(3)	C(12)-H(12)	0.96(2)
C(2)-H(2A)	1.00(2)	C(6)-O(4)	1.215(2)	C(12)-C(13)	1.388(2)
C(2)-H(2B)	0.98(2)	C(6)-C(7)	1.459(2)	C(13)-C(14)	1.387(2)
C(2)-C(3)	1.530(2)	C(7)-H(7)	0.92(3)	C(14)-H(14)	0.89(2)
C(3)-H(3)	0.97(2)	C(7)-C(8)	1.341(3)	C(14)-C(15)	1.390(2)
C(3)-C(4)	1.549(2)	C(8)-C(9)	1.486(2)	C(15)-H(15)	0.94(2)
C(3)-C(10)	1.516(2)	C(9)-H(9A)	0.92(4)		
C(4)-O(2)	1.4168(19)	C(9)-H(9B)	0.94(3)		

Table S3. Bond angles [°] for **9c**.

C(1)-N(1)-H(1)	116.7(18)	O(4)-C(6)-C(7)	129.85(16)
C(1)-N(1)-C(5)	126.67(14)	C(7)-C(6)-C(5)	106.72(14)
C(5)-N(1)-H(1)	116.6(18)	C(6)-C(7)-H(7)	123.2(16)
N(1)-C(1)-C(2)	117.58(14)	C(8)-C(7)-C(6)	110.61(15)
O(1)-C(1)-N(1)	121.21(15)	C(8)-C(7)-H(7)	126.2(16)
O(1)-C(1)-C(2)	121.20(15)	C(7)-C(8)-C(4)	111.98(15)
C(1)-C(2)-H(2A)	106.1(13)	C(7)-C(8)-C(9)	126.69(16)
C(1)-C(2)-H(2B)	106.2(12)	C(9)-C(8)-C(4)	121.33(16)
C(1)-C(2)-C(3)	112.13(14)	C(8)-C(9)-H(9A)	114(2)
H(2A)-C(2)-H(2B)	111.6(18)	C(8)-C(9)-H(9B)	112.0(18)
C(3)-C(2)-H(2A)	109.2(13)	C(8)-C(9)-H(9C)	109.1(19)
C(3)-C(2)-H(2B)	111.5(12)	H(9A)-C(9)-H(9B)	105(3)
C(2)-C(3)-H(3)	107.6(12)	H(9A)-C(9)-H(9C)	109(3)
C(2)-C(3)-C(4)	107.70(13)	H(9B)-C(9)-H(9C)	107(3)
C(4)-C(3)-H(3)	107.5(12)	C(11)-C(10)-C(3)	122.17(14)
C(10)-C(3)-C(2)	112.93(13)	C(11)-C(10)-C(15)	118.19(15)
C(10)-C(3)-H(3)	107.8(12)	C(15)-C(10)-C(3)	119.59(15)
C(10)-C(3)-C(4)	113.02(13)	C(10)-C(11)-H(11)	120.4(14)

C(3)-C(4)-C(5)	110.25(13)	C(12)-C(11)-C(10)	121.48(16)
O(2)-C(4)-C(3)	108.95(13)	C(12)-C(11)-H(11)	118.1(14)
O(2)-C(4)-C(5)	111.53(13)	C(11)-C(12)-H(12)	121.4(14)
O(2)-C(4)-C(8)	112.54(13)	C(13)-C(12)-C(11)	118.69(16)
C(8)-C(4)-C(3)	111.62(13)	C(13)-C(12)-H(12)	119.9(13)
C(8)-C(4)-C(5)	101.81(13)	C(12)-C(13)-Br(1)	119.52(14)
C(4)-O(2)-H(2)	103.4(19)	C(14)-C(13)-Br(1)	119.17(13)
N(1)-C(5)-C(4)	115.67(13)	C(14)-C(13)-C(12)	121.30(16)
N(1)-C(5)-C(6)	111.79(13)	C(13)-C(14)-H(14)	121.5(14)
O(3)-C(5)-N(1)	107.53(13)	C(13)-C(14)-C(15)	118.93(15)
O(3)-C(5)-C(4)	108.68(13)	C(15)-C(14)-H(14)	119.5(14)
O(3)-C(5)-C(6)	109.72(13)	C(10)-C(15)-H(15)	117.5(14)
C(6)-C(5)-C(4)	103.34(12)	C(14)-C(15)-C(10)	121.21(16)
C(5)-O(3)-H(3A)	112.3(19)	C(14)-C(15)-H(15)	121.3(14)
O(4)-C(6)-C(5)	123.39(15)		

Table S4. Torsion angles [°] for **9c**.

Br(1)-C(13)-C(14)-C(15)	174.96(12)	O(2)-C(4)-C(5)-O(3)	-26.36(17)
N(1)-C(1)-C(2)-C(3)	30.3(2)	O(2)-C(4)-C(5)-C(6)	-142.86(13)
N(1)-C(5)-C(6)-O(4)	-36.7(2)	O(2)-C(4)-C(8)-C(7)	138.58(15)
N(1)-C(5)-C(6)-C(7)	145.29(14)	O(2)-C(4)-C(8)-C(9)	-40.8(2)
C(1)-N(1)-C(5)-C(4)	-4.3(2)	C(5)-N(1)-C(1)-O(1)	-176.44(15)
C(1)-N(1)-C(5)-O(3)	117.28(17)	C(5)-N(1)-C(1)-C(2)	2.8(2)
C(1)-N(1)-C(5)-C(6)	-122.24(17)	C(5)-C(4)-C(8)-C(7)	19.06(18)
C(1)-C(2)-C(3)-C(4)	-59.35(17)	C(5)-C(4)-C(8)-C(9)	-160.33(15)
C(1)-C(2)-C(3)-C(10)	175.15(13)	C(5)-C(6)-C(7)-C(8)	-9.11(19)
O(1)-C(1)-C(2)-C(3)	-150.45(15)	O(3)-C(5)-C(6)-O(4)	82.48(19)
C(2)-C(3)-C(4)-O(2)	-66.26(16)	O(3)-C(5)-C(6)-C(7)	-95.52(15)
C(2)-C(3)-C(4)-C(5)	56.45(16)	C(6)-C(7)-C(8)-C(4)	-6.6(2)
C(2)-C(3)-C(4)-C(8)	168.84(13)	C(6)-C(7)-C(8)-C(9)	172.75(16)
C(2)-C(3)-C(10)-C(11)	51.4(2)	O(4)-C(6)-C(7)-C(8)	173.06(17)
C(2)-C(3)-C(10)-C(15)	-131.05(16)	C(8)-C(4)-C(5)-N(1)	-145.11(14)
C(3)-C(4)-C(5)-N(1)	-26.53(18)	C(8)-C(4)-C(5)-O(3)	93.87(14)
C(3)-C(4)-C(5)-O(3)	-147.55(13)	C(8)-C(4)-C(5)-C(6)	-22.62(15)

C(3)-C(4)-C(5)-C(6)	95.96(14)	C(10)-C(3)-C(4)-O(2)	59.19(17)
C(3)-C(4)-C(8)-C(7)	-98.54(17)	C(10)-C(3)-C(4)-C(5)	-178.10(13)
C(3)-C(4)-C(8)-C(9)	82.06(19)	C(10)-C(3)-C(4)-C(8)	-65.71(18)
C(3)-C(10)-C(11)-C(12)	173.41(16)	C(10)-C(11)-C(12)-C(13)	0.9(3)
C(3)-C(10)-C(15)-C(14)	-174.07(15)	C(11)-C(10)-C(15)-C(14)	3.5(2)
C(4)-C(3)-C(10)-C(11)	-71.1(2)	C(11)-C(12)-C(13)-Br(1)	-175.53(13)
C(4)-C(3)-C(10)-C(15)	106.38(17)	C(11)-C(12)-C(13)-C(14)	3.1(3)
C(4)-C(5)-C(6)-O(4)	-161.76(15)	C(12)-C(13)-C(14)-C(15)	-3.7(3)
C(4)-C(5)-C(6)-C(7)	20.24(16)	C(13)-C(14)-C(15)-C(10)	0.3(2)
O(2)-C(4)-C(5)-N(1)	94.65(16)	C(15)-C(10)-C(11)-C(12)	-4.1(3)

Table S5. Hydrogen bonds for **9c** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(1)#1	0.84(3)	2.06(3)	2.9047(19)	174(2)
O(2)-H(2)...O(3)	0.81(3)	2.02(3)	2.6039(18)	128(3)
O(3)-H(3A)...O(1)#2	0.80(3)	1.97(3)	2.7550(17)	167(3)

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

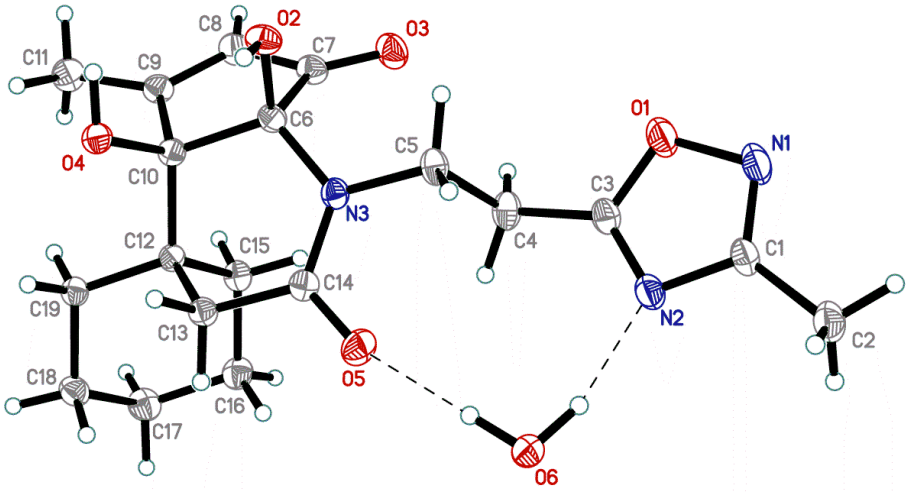


Fig. S4. The structure of **9n**. The thermal ellipsoids are set to a 50% probability level.

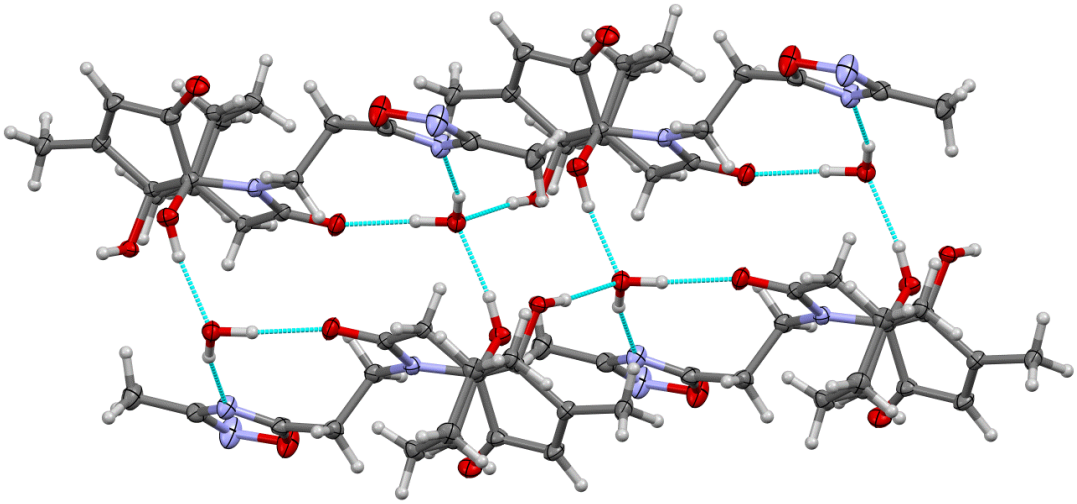


Fig. S5. Hydrogen bonding in **9n**. A fragment of 1D chain is shown. The thermal ellipsoids are set to a 50% probability level.

Table S6. Bond lengths [Å] for **9n**.

O(1)-C(3)	1.3352(13)	C(4)-C(5)	1.5366(14)	C(13)-C(14)	1.4973(13)
O(1)-N(1)	1.4279(13)	C(4)-H(4A)	0.984(15)	C(13)-H(13A)	0.958(15)
O(2)-C(6)	1.4056(11)	C(4)-H(4B)	0.987(16)	C(13)-H(13B)	0.970(16)
O(2)-H(2)	0.894(17)	C(5)-H(5A)	0.992(15)	C(15)-C(16)	1.5346(14)
O(3)-C(7)	1.2167(12)	C(5)-H(5B)	0.948(15)	C(15)-H(15A)	1.013(16)
O(4)-C(10)	1.4128(11)	C(6)-C(7)	1.5486(13)	C(15)-H(15B)	0.996(15)
O(4)-H(4)	0.91(2)	C(6)-C(10)	1.5772(13)	C(16)-C(17)	1.5295(15)
O(5)-C(14)	1.2350(11)	C(7)-C(8)	1.4554(14)	C(16)-H(16A)	0.976(17)
N(1)-C(1)	1.2955(14)	C(8)-C(9)	1.3430(14)	C(16)-H(16B)	0.937(16)
N(2)-C(3)	1.2944(13)	C(8)-H(8)	0.991(17)	C(17)-C(18)	1.5243(15)
N(2)-C(1)	1.3811(13)	C(9)-C(11)	1.4954(14)	C(17)-H(17A)	0.965(17)
N(3)-C(14)	1.3583(12)	C(9)-C(10)	1.5290(12)	C(17)-H(17B)	0.973(17)
N(3)-C(6)	1.4604(12)	C(10)-C(12)	1.5576(12)	C(18)-C(19)	1.5329(14)
N(3)-C(5)	1.4721(12)	C(11)-H(11A)	0.943(19)	C(18)-H(18A)	1.008(16)
C(1)-C(2)	1.4813(15)	C(11)-H(11B)	0.973(19)	C(18)-H(18B)	0.960(16)
C(2)-H(2A)	0.95(2)	C(11)-H(11C)	0.977(18)	C(19)-H(19A)	1.019(15)
C(2)-H(2B)	0.99(2)	C(12)-C(13)	1.5320(12)	C(19)-H(19B)	0.965(15)
C(2)-H(2C)	0.980(18)	C(12)-C(19)	1.5413(13)	O(6)-H(6A)	0.94(2)
C(3)-C(4)	1.4824(14)	C(12)-C(15)	1.5457(13)	O(6)-H(6B)	0.92(2)

Table S7. Bond angles [°] for **9n**.

C(3)-O(1)-N(1)	106.12(8)	C(9)-C(11)-H(11A)	112.3(11)
C(6)-O(2)-H(2)	114.0(11)	C(9)-C(11)-H(11B)	111.5(11)
C(10)-O(4)-H(4)	106.4(12)	H(11A)-C(11)-H(11B)	108.9(16)
C(1)-N(1)-O(1)	103.63(9)	C(9)-C(11)-H(11C)	108.4(11)
C(3)-N(2)-C(1)	103.65(8)	H(11A)-C(11)-H(11C)	106.2(15)
C(14)-N(3)-C(6)	123.56(8)	H(11B)-C(11)-H(11C)	109.4(15)
C(14)-N(3)-C(5)	116.77(8)	C(13)-C(12)-C(19)	108.64(7)
C(6)-N(3)-C(5)	118.53(8)	C(13)-C(12)-C(15)	111.71(7)
N(1)-C(1)-N(2)	113.72(9)	C(19)-C(12)-C(15)	108.48(7)
N(1)-C(1)-C(2)	123.20(9)	C(13)-C(12)-C(10)	104.03(7)
N(2)-C(1)-C(2)	123.08(9)	C(19)-C(12)-C(10)	111.81(7)
C(1)-C(2)-H(2A)	109.6(12)	C(15)-C(12)-C(10)	112.11(7)

C(1)-C(2)-H(2B)	110.3(11)
H(2A)-C(2)-H(2B)	107.3(16)
C(1)-C(2)-H(2C)	111.8(10)
H(2A)-C(2)-H(2C)	106.5(15)
H(2B)-C(2)-H(2C)	111.2(15)
N(2)-C(3)-O(1)	112.87(9)
N(2)-C(3)-C(4)	127.83(9)
O(1)-C(3)-C(4)	119.27(9)
C(3)-C(4)-C(5)	111.23(8)
C(3)-C(4)-H(4A)	107.0(9)
C(5)-C(4)-H(4A)	110.0(8)
C(3)-C(4)-H(4B)	110.8(9)
C(5)-C(4)-H(4B)	109.8(9)
H(4A)-C(4)-H(4B)	107.9(13)
N(3)-C(5)-C(4)	110.79(8)
N(3)-C(5)-H(5A)	107.0(9)
C(4)-C(5)-H(5A)	109.8(9)
N(3)-C(5)-H(5B)	106.8(9)
C(4)-C(5)-H(5B)	113.2(9)
H(5A)-C(5)-H(5B)	109.1(13)
O(2)-C(6)-N(3)	109.84(7)
O(2)-C(6)-C(7)	102.41(7)
N(3)-C(6)-C(7)	113.88(8)
O(2)-C(6)-C(10)	110.81(7)
N(3)-C(6)-C(10)	115.39(7)
C(7)-C(6)-C(10)	103.65(7)
O(3)-C(7)-C(8)	128.37(9)
O(3)-C(7)-C(6)	125.03(9)
C(8)-C(7)-C(6)	106.49(8)
C(9)-C(8)-C(7)	111.23(8)
C(9)-C(8)-H(8)	124.5(10)
C(7)-C(8)-H(8)	124.2(10)
C(8)-C(9)-C(11)	124.82(9)
C(8)-C(9)-C(10)	112.49(8)
C(14)-C(13)-C(12)	113.51(7)
C(14)-C(13)-H(13A)	107.3(9)
C(12)-C(13)-H(13A)	109.3(9)
C(14)-C(13)-H(13B)	107.4(9)
C(12)-C(13)-H(13B)	112.6(9)
H(13A)-C(13)-H(13B)	106.4(13)
O(5)-C(14)-N(3)	121.27(9)
O(5)-C(14)-C(13)	120.47(8)
N(3)-C(14)-C(13)	118.26(8)
C(16)-C(15)-C(12)	112.39(8)
C(16)-C(15)-H(15A)	107.3(9)
C(12)-C(15)-H(15A)	108.4(9)
C(16)-C(15)-H(15B)	108.7(9)
C(12)-C(15)-H(15B)	111.5(9)
H(15A)-C(15)-H(15B)	108.5(12)
C(17)-C(16)-C(15)	111.47(8)
C(17)-C(16)-H(16A)	110.0(10)
C(15)-C(16)-H(16A)	109.6(10)
C(17)-C(16)-H(16B)	110.1(10)
C(15)-C(16)-H(16B)	109.3(10)
H(16A)-C(16)-H(16B)	106.3(14)
C(18)-C(17)-C(16)	111.80(8)
C(18)-C(17)-H(17A)	109.0(10)
C(16)-C(17)-H(17A)	107.6(10)
C(18)-C(17)-H(17B)	109.8(10)
C(16)-C(17)-H(17B)	110.3(10)
H(17A)-C(17)-H(17B)	108.2(14)
C(17)-C(18)-C(19)	112.07(8)
C(17)-C(18)-H(18A)	111.7(9)
C(19)-C(18)-H(18A)	109.3(9)
C(17)-C(18)-H(18B)	109.8(9)
C(19)-C(18)-H(18B)	109.7(9)
H(18A)-C(18)-H(18B)	104.1(12)
C(18)-C(19)-C(12)	112.96(8)

C(11)-C(9)-C(10)	122.66(8)	C(18)-C(19)-H(19A)	110.1(8)
O(4)-C(10)-C(9)	111.25(7)	C(12)-C(19)-H(19A)	109.6(8)
O(4)-C(10)-C(12)	106.55(7)	C(18)-C(19)-H(19B)	108.1(9)
C(9)-C(10)-C(12)	114.49(7)	C(12)-C(19)-H(19B)	107.9(9)
O(4)-C(10)-C(6)	111.13(7)	H(19A)-C(19)-H(19B)	107.9(12)
C(9)-C(10)-C(6)	101.51(7)	H(6A)-O(6)-H(6B)	102.9(17)
C(12)-C(10)-C(6)	112.00(7)		

Table S8. Torsion angles [°] for **9n**.

C(3)-O(1)-N(1)-C(1)	-0.10(13)	N(3)-C(6)-C(10)-O(4)	95.95(9)
O(1)-N(1)-C(1)-N(2)	-0.33(14)	C(7)-C(6)-C(10)-O(4)	-138.86(7)
O(1)-N(1)-C(1)-C(2)	179.54(11)	O(2)-C(6)-C(10)-C(9)	88.71(8)
C(3)-N(2)-C(1)-N(1)	0.65(13)	N(3)-C(6)-C(10)-C(9)	-145.68(8)
C(3)-N(2)-C(1)-C(2)	-179.22(10)	C(7)-C(6)-C(10)-C(9)	-20.49(9)
C(1)-N(2)-C(3)-O(1)	-0.70(12)	O(2)-C(6)-C(10)-C(12)	-148.71(7)
C(1)-N(2)-C(3)-C(4)	-178.73(10)	N(3)-C(6)-C(10)-C(12)	-23.10(10)
N(1)-O(1)-C(3)-N(2)	0.53(13)	C(7)-C(6)-C(10)-C(12)	102.10(8)
N(1)-O(1)-C(3)-C(4)	178.75(9)	O(4)-C(10)-C(12)-C(13)	-64.94(8)
N(2)-C(3)-C(4)-C(5)	96.48(13)	C(9)-C(10)-C(12)-C(13)	171.63(7)
O(1)-C(3)-C(4)-C(5)	-81.44(12)	C(6)-C(10)-C(12)-C(13)	56.77(9)
C(14)-N(3)-C(5)-C(4)	78.43(10)	O(4)-C(10)-C(12)-C(19)	52.11(9)
C(6)-N(3)-C(5)-C(4)	-113.33(9)	C(9)-C(10)-C(12)-C(19)	-71.31(9)
C(3)-C(4)-C(5)-N(3)	-159.45(8)	C(6)-C(10)-C(12)-C(19)	173.82(7)
C(14)-N(3)-C(6)-O(2)	113.57(9)	O(4)-C(10)-C(12)-C(15)	174.20(7)
C(5)-N(3)-C(6)-O(2)	-53.82(10)	C(9)-C(10)-C(12)-C(15)	50.77(10)
C(14)-N(3)-C(6)-C(7)	-132.25(9)	C(6)-C(10)-C(12)-C(15)	-64.09(9)
C(5)-N(3)-C(6)-C(7)	60.36(11)	C(19)-C(12)-C(13)-C(14)	178.86(8)
C(14)-N(3)-C(6)-C(10)	-12.53(12)	C(15)-C(12)-C(13)-C(14)	59.23(10)
C(5)-N(3)-C(6)-C(10)	-179.92(7)	C(10)-C(12)-C(13)-C(14)	-61.90(9)
O(2)-C(6)-C(7)-O(3)	80.59(12)	C(6)-N(3)-C(14)-O(5)	-171.44(9)
N(3)-C(6)-C(7)-O(3)	-37.92(13)	C(5)-N(3)-C(14)-O(5)	-3.85(13)
C(10)-C(6)-C(7)-O(3)	-164.08(10)	C(6)-N(3)-C(14)-C(13)	9.28(13)
O(2)-C(6)-C(7)-C(8)	-95.75(9)	C(5)-N(3)-C(14)-C(13)	176.88(8)
N(3)-C(6)-C(7)-C(8)	145.73(8)	C(12)-C(13)-C(14)-O(5)	-148.55(9)

C(10)-C(6)-C(7)-C(8)	19.57(10)	C(12)-C(13)-C(14)-N(3)	30.73(12)
O(3)-C(7)-C(8)-C(9)	173.25(11)	C(13)-C(12)-C(15)-C(16)	63.72(10)
C(6)-C(7)-C(8)-C(9)	-10.57(12)	C(19)-C(12)-C(15)-C(16)	-56.00(10)
C(7)-C(8)-C(9)-C(11)	174.62(10)	C(10)-C(12)-C(15)-C(16)	-179.96(8)
C(7)-C(8)-C(9)-C(10)	-3.72(13)	C(12)-C(15)-C(16)-C(17)	56.21(11)
C(8)-C(9)-C(10)-O(4)	134.08(9)	C(15)-C(16)-C(17)-C(18)	-53.26(12)
C(11)-C(9)-C(10)-O(4)	-44.30(12)	C(16)-C(17)-C(18)-C(19)	52.34(12)
C(8)-C(9)-C(10)-C(12)	-105.05(10)	C(17)-C(18)-C(19)-C(12)	-54.43(11)
C(11)-C(9)-C(10)-C(12)	76.57(12)	C(13)-C(12)-C(19)-C(18)	-66.56(10)
C(8)-C(9)-C(10)-C(6)	15.80(11)	C(15)-C(12)-C(19)-C(18)	55.06(10)
C(11)-C(9)-C(10)-C(6)	-162.58(9)	C(10)-C(12)-C(19)-C(18)	179.20(7)
O(2)-C(6)-C(10)-O(4)	-29.66(9)		

Table S9. Hydrogen bonds for **9n** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(2)...O(6)#1	0.894(17)	1.812(18)	2.6926(10)	168.1(16)
O(4)-H(4)...O(6)#2	0.91(2)	1.82(2)	2.7307(10)	171.4(18)
O(6)-H(6A)...N(2)	0.94(2)	1.91(2)	2.8324(11)	164.3(18)
O(6)-H(6B)...O(5)	0.92(2)	1.78(2)	2.6990(10)	175.8(19)

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