Supporting Information

Anionic photochemical rearrangement of 3-hydroxypyran-4-ones bearing oxazol-2-one fragment

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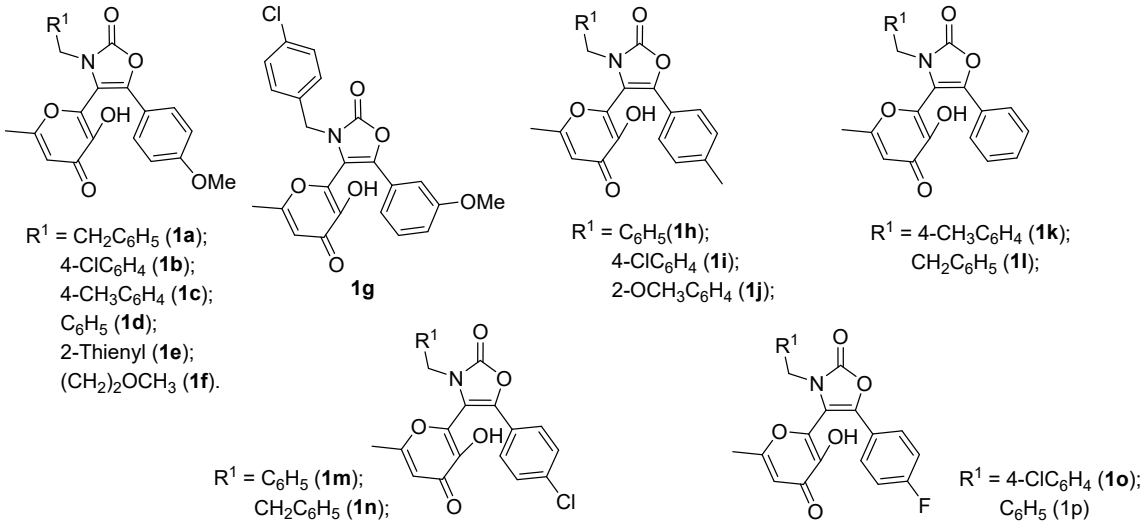
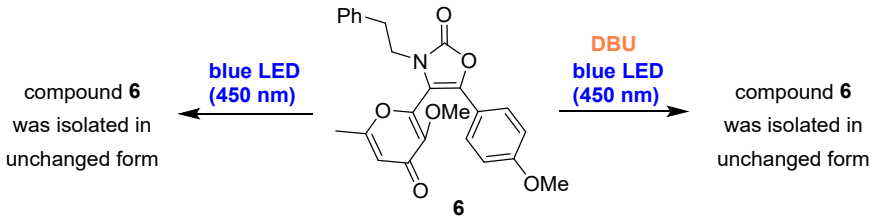
1. General information

Unless otherwise stated, all starting chemicals were commercially available and were used as received. Compounds **1** were prepared according to a procedure described previously.[1] NMR spectra were recorded with Bruker AM 300 (300 MHz), Bruker DRX 500 (500 MHz) and Bruker AV 600 (600 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. Magnetic stirrer IKA C-MAG HS 7 was used for the reactions that require heating. UV/Vis spectra were recorded with Agilent Cary 60.

Photochemical reactions were performed in common glassware. Irradiation was carried out with a strip of 24 W 450 nm LED at room temperature in air atmosphere.

Compounds **1**:





Scheme S1. Photochemical behavior of compound **6**

2. Experimental procedure

General experimental procedure for the synthesis of target photoproducts 4

The mixture of compound **1** (0.5 mmol) and DBU (0.5 mmol, 0.08 g) in DMSO (5 mL) was irradiated in common glassware with a strip of 24 W 450 nm LED for 6 h. Then AcOH (2 mmol, 0.12 g) was added to the obtained solution. Further, the reaction mixture was poured into water (100 mL) and left overnight. The formed precipitate was filtered off and washed with H_2O (3 × 15 mL) to give the target product **4**.

Experimental procedure for the synthesis of methylated derivative 7

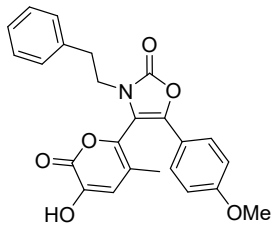
A mixture of compound **4h** (1 mmol, 0,39 g), K_2CO_3 (2 mmol, 0.27 g) and MeI (3 mmol, 0.43 g) in DMF (5 mL) was stirred at room temperature for 8 h. Then the solvent was removed under reduced pressure, H_2O (20 mL) was added to the obtained residue and left overnight. The resulting precipitate was filtered off and washed with H_2O (3 × 15 mL) to give the product **7**.

Experimental procedure for the synthesis of compound 10

A mixture of compound **4a** (1 mmol, 0.42 g), 4-methoxyphenylglyoxal hydrate **8** (1.5 mmol, 0.27 g), Meldrum's acid **9** (2 mmol, 0.29 g) and Et_3N (2 mmol, 0.2 g) in MeCN (6 mL) was kept for 24 h at room temperature. Then, the reaction mixture was evaporated in vacuo. To obtained residue HCl_{conc} (2 mL) and of AcOH (4 mL) were added and the solution was refluxed for 15 min. The resulting solution was poured into water (100 mL) and the formed precipitate was collected by filtration. The target product was recrystallized from MeCN (3 mL).

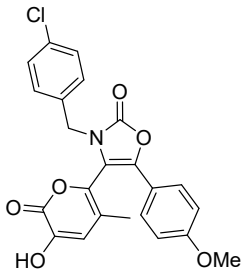
3. Characterization data for starting compounds 4

*4-(3-Hydroxy-5-methyl-2-oxo-2H-pyran-6-yl)-5-(4-methoxyphenyl)-3-phenethyloxazol-2(3H)-one (**4a**)*



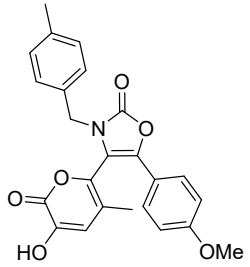
Yellowish powder; yield 88% (0.18 g); mp 94-96 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.59 (br.s, 1H), 7.28 (d, *J* = 8.8 Hz, 2H), 7.26 – 7.10 (m, 5H), 6.97 (d, *J* = 8.9 Hz, 2H), 6.60 (s, 1H), 3.76 (s, 3H), 3.75 – 3.69 (m, 2H), 2.87 (t, *J* = 7.3 Hz, 2H), 1.58 (s, 3H). ^{13}C {^{1}H} NMR (151 MHz, DMSO-d_6) δ 159.6, 158.8, 152.9, 143.7, 137.6, 136.9, 133.9, 128.6, 128.5, 126.5, 125.9, 119.6, 119.1, 119.0, 114.6, 113.0, 55.2, 43.6, 33.9, 15.5. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{24}H_{22}NO_6$: 420.1442; Found: 420.1449.

*3-(4-Chlorobenzyl)-4-(3-hydroxy-5-methyl-2-oxo-2H-pyran-6-yl)-5-(4-methoxyphenyl)oxazol-2(3H)-one (**4b**)*



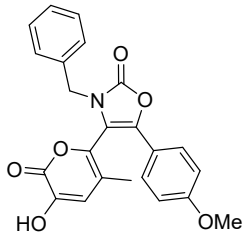
Yellowish powder; yield 90% (0.2 g); mp 109-111 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.40 – 7.25 (m, 4H), 7.19 (d, *J* = 8.2 Hz, 2H), 6.97 (d, *J* = 8.5 Hz, 2H), 6.49 (s, 1H), 4.71 (s, 2H), 3.75 (s, 3H), 1.52 (s, 3H). ^{13}C {^{1}H} NMR (151 MHz, DMSO-d_6) δ 159.7, 158.8, 153.3, 144.1, 137.3, 135.0, 133.4, 132.4, 129.2, 128.4, 125.9, 119.9, 119.0, 118.3, 114.7, 112.7, 55.2, 45.0, 15.3. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{23}H_{19}ClNO_6$: 440.0895; Found: 440.0894.

*4-(3-Hydroxy-5-methyl-2-oxo-2H-pyran-6-yl)-5-(4-methoxyphenyl)-3-(4-methylbenzyl)oxazol-2(3H)-one (**4c**)*



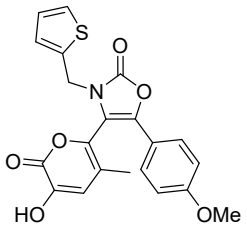
Yellowish powder; yield 85% (0.18 g); mp 85-87 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.29 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 2H), 7.03 – 6.88 (m, 4H), 6.47 (s, 1H), 4.77 – 4.54 (m, 2H), 3.75 (s, 3H), 2.24 (s, 3H), 1.49 (s, 3H). ^{13}C {^{1}H} NMR (75 MHz, DMSO-d_6) δ 159.7, 158.9, 153.3, 144.0, 137.2, 137.0, 133.5, 132.9, 129.0, 127.3, 125.8, 119.8, 119.0, 118.4, 114.7, 112.8, 55.2, 45.4, 20.7, 15.2. HRMS (ESI-TOF) *m/z*: $[M+K]^+$ Calcld for $C_{24}H_{21}NO_6K$: 458.1000; Found: 458.0988.

*3-Benzyl-4-(3-hydroxy-5-methyl-2-oxo-2H-pyran-6-yl)-5-(4-methoxyphenyl)oxazol-2(3H)-one (**4d**)*



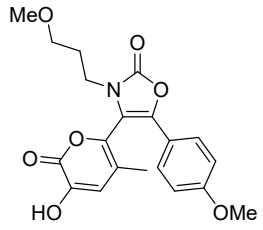
Yellowish powder; yield 85% (0.17 g); mp 119-121 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.35 – 7.22 (m, 5H), 7.13 (d, *J* = 6.9 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.39 (s, 1H), 4.83 – 4.60 (m, 2H), 3.75 (s, 3H), 1.47 (s, 3H). ^{13}C {^{1}H} NMR (151 MHz, DMSO-d_6) δ 159.7, 158.8, 153.4, 143.9, 137.3, 136.0, 133.6, 128.5, 127.8, 127.3, 125.9, 119.8, 119.0, 118.5, 114.7, 112.8, 55.3, 45.7, 15.3. HRMS (ESI-TOF) *m/z*: $[M+K]^+$ Calcld for $C_{23}H_{19}NO_6K$: 444.0844; Found: 444.0835.

*4-(3-Hydroxy-5-methyl-2-oxo-2H-pyran-6-yl)-5-(4-methoxyphenyl)-3-(thiophen-2-ylmethyl)oxazol-2(3H)-one (**4e**)*



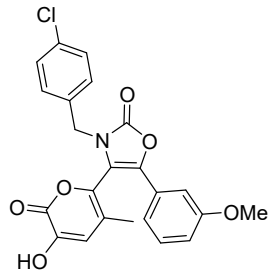
Yellowish powder; yield 86% (0.18 g); mp 155-157 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.66 (br.s, 1H), 7.53 – 7.22 (m, 3H), 7.14 – 6.77 (m, 4H), 6.56 (s, 1H), 4.89 (s, 2H), 3.75 (s, 3H), 1.56 (s, 3H). ^{13}C {^{1}H} NMR (75 MHz, DMSO-d_6) δ 159.7, 158.8, 152.8, 143.9, 137.9, 137.3, 133.5, 127.2, 126.9, 126.6, 125.9, 119.9, 118.9, 118.6, 114.7, 112.5, 55.2, 40.5, 15.3. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{21}H_{18}NO_6S$: 412.0849; Found: 412.0858.

*4-(3-Hydroxy-5-methyl-2-oxo-2H-pyran-6-yl)-5-(4-methoxyphenyl)-3-(3-methoxypropyl)oxazol-2(3H)-one (**4f**)*



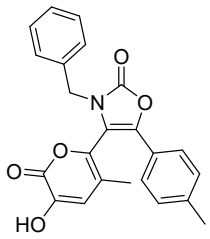
Yellowish powder; yield 78% (0.15 g); mp 88-90 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.64 (br.s, 1H), 7.30 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 8.5 Hz, 2H), 6.66 (s, 1H), 3.76 (s, 3H), 3.62 – 3.47 (m, 3H), 3.34 – 3.24 (m, 3H), 3.14 (s, 3H), 1.75 (s, 3H). ^{13}C {^{1}H} NMR (126 MHz, DMSO-d_6) δ 159.6, 158.9, 153.1, 143.8, 137.0, 134.0, 125.8, 119.7, 119.2, 118.9, 114.7, 113.1, 68.8, 57.9, 55.2, 39.69, 28.2, 15.5. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{20}H_{22}NO_7$: 388.1391; Found: 388.1393.

*3-(4-Chlorobenzyl)-4-(3-hydroxy-5-methyl-2-oxo-2H-pyran-6-yl)-5-(3-methoxyphenyl)oxazol-2(3H)-one (**4g**)*



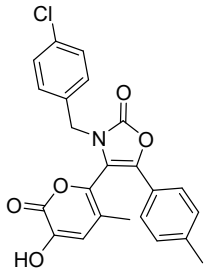
Yellowish powder; yield 81% (0.18 g); mp 96-98 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.65 (br. s, 1H), 7.40 – 7.29 (m, 3H), 7.21 (d, *J* = 8.2 Hz, 2H), 6.93 (d, *J* = 8.5 Hz, 2H), 6.86 (s, 1H), 6.52 (s, 1H), 4.73 (s, 2H), 3.71 (s, 3H), 1.56 (s, 3H). ^{13}C {^{1}H} NMR (75 MHz, DMSO-d_6) δ 159.5, 158.6, 153.2, 144.0, 136.8, 134.9, 133.1, 132.4, 130.5, 129.2, 128.5, 127.7, 120.2, 118.3, 116.4, 114.8, 114.7, 109.2, 55.1, 45.0, 15.3. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{23}H_{19}ClNO_6$: 440.0895; Found: 440.0891.

*3-Benzyl-4-(3-hydroxy-5-methyl-2-oxo-2H-pyran-6-yl)-5-(p-tolyl)oxazol-2(3H)-one (**4h**)*



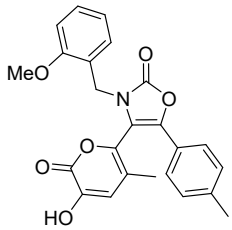
Yellowish powder; yield 82% (0.16 g); mp 124-126 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.57 (br.s, 1H), 7.33 – 7.14 (m, 9H), 6.46 (s, 1H), 4.84 – 4.58 (m, 2H), 2.28 (s, 3H), 1.47 (s, 3H). ^{13}C {^{1}H} NMR (75 MHz, DMSO-d_6) δ 158.7, 153.3, 143.8, 138.7, 137.2, 135.9, 133.5, 129.7, 128.5, 127.7, 127.3, 124.1, 123.8, 119.8, 118.5, 113.7, 45.7, 20.9, 15.2. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{23}H_{20}NO_5$: 390.1336; Found: 390.1336.

*3-(4-Chlorobenzyl)-4-(3-hydroxy-5-methyl-2-oxo-2H-pyran-6-yl)-5-(p-tolyl)oxazol-2(3H)-one (**4i**)*



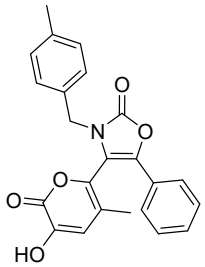
Yellowish powder; yield 92% (0.2 g); mp 101-103 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.35 (d, *J* = 8.1 Hz, 2H), 7.28 – 7.14 (m, 6H), 6.49 (s, 1H), 4.72 (s, 2H), 2.28 (s, 3H), 1.52 (s, 3H). ^{13}C {^{1}H} NMR (126 MHz, DMSO-d_6) δ 158.7, 153.3, 144.0, 138.8, 137.3, 135.0, 133.3, 132.4, 129.8, 129.2, 128.5, 124.1, 123.8, 119.9, 118.4, 113.7, 45.0, 20.9, 15.6. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{23}H_{19}ClNO_5$: 424.0946; Found: 424.0935.

*4-(3-Hydroxy-5-methyl-2-oxo-2H-pyran-6-yl)-3-(2-methoxybenzyl)-5-(p-tolyl)oxazol-2(3H)-one (**4j**)*



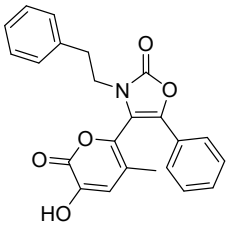
Yellowish powder; yield 79% (0.17 g); mp 103-105 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.36 – 7.14 (m, 5H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.91 (d, *J* = 8.3 Hz, 1H), 6.87 – 6.79 (m, 1H), 6.43 (s, 1H), 4.73 (s, 2H), 3.64 (s, 3H), 2.28 (s, 3H), 1.40 (s, 3H). ^{13}C {^{1}H} NMR (126 MHz, DMSO-d_6) δ 158.8, 156.6, 153.4, 143.7, 138.7, 136.9, 133.7, 129.8, 129.4, 128.9, 124.0, 123.9, 123.2, 120.3, 119.4, 118.5, 113.9, 110.8, 55.4, 40.9, 20.9, 15.0. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{24}H_{21}NO_6$: 420.1442; Found: 420.1439.

*4-(3-Hydroxy-5-methyl-2-oxo-2H-pyran-6-yl)-3-(4-methylbenzyl)-5-phenyloxazol-2(3H)-one (**4k**)*



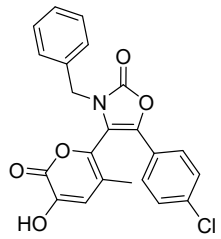
Yellowish powder; yield 80% (0.16 g); mp 94-96 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.51 – 7.29 (m, 5H), 7.09 (d, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 7.8 Hz, 2H), 6.49 (s, 1H), 4.81 – 4.50 (m, 2H), 2.24 (s, 3H), 1.50 (s, 3H). ^{13}C {^{1}H} NMR (75 MHz, DMSO-d_6) δ 158.7, 153.3, 144.0, 137.1, 136.9, 133.3, 132.8, 129.2, 129.0, 128.9, 127.3, 126.5, 124.1, 120.0, 118.4, 114.5, 45.5, 20.7, 15.2. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{23}H_{20}NO_5$: 390.1336; Found: 390.1327.

*4-(3-Hydroxy-5-methyl-2-oxo-2H-pyran-6-yl)-3-phenethyl-5-phenyloxazol-2(3H)-one (**4l**)*



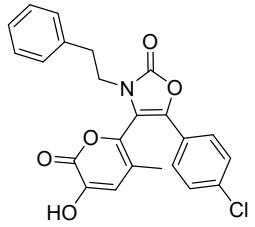
Yellowish powder; yield 84% (0.16 g); mp 82-84 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.70 (br.s, 1H), 7.44 – 7.32 (m, 5H), 7.26 – 7.17 (m, 3H), 7.13 (d, *J* = 7.4 Hz, 2H), 6.61 (s, 1H), 3.75 (t, *J* = 7.3 Hz, 2H), 2.88 (t, *J* = 7.3 Hz, 2H), 1.58 (s, 3H). ^{13}C {^{1}H} NMR (75 MHz, DMSO-d_6) δ 158.8, 152.9, 143.9, 137.6, 136.6, 133.6, 129.3, 128.9, 128.6, 128.5, 126.6, 126.6, 124.2, 119.8, 118.9, 114.8, 43.7, 33.9, 15.5. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{23}H_{20}NO_5$: 390.1336; Found: 390.1330.

*3-Benzyl-5-(4-chlorophenyl)-4-(3-hydroxy-5-methyl-2-oxo-2H-pyran-6-yl)oxazol-2(3H)-one (**4m**)*



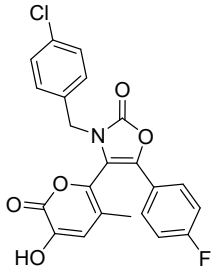
Yellowish powder; yield 85% (0.17 g); mp 91-93 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.47 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 7.32 – 7.18 (m, 4H), 7.15 (d, *J* = 6.9 Hz, 2H), 6.45 (s, 1H), 4.84 – 4.62 (m, 2H), 1.49 (s, 3H). ^{13}C {^{1}H} NMR (75 MHz, DMSO-d_6) δ 158.6, 153.2, 144.0, 135.9, 135.7, 133.4, 132.9, 129.3, 128.5, 127.8, 127.3, 125.9, 125.4, 120.1, 118.3, 114.8, 45.8, 15.2. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{22}H_{17}ClNO_5$: 410.0790; Found: 410.0785.

*5-(4-Chlorophenyl)-4-(3-hydroxy-5-methyl-2-oxo-2H-pyran-6-yl)-3-phenethyloxazol-2(3H)-one (**4n**)*



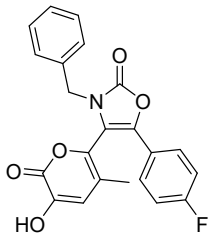
Yellowish powder; yield 88% (0.19 g); mp 118-120 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.51 – 7.44 (m, 2H), 7.35 (d, J = 8.7 Hz, 2H), 7.28 – 7.18 (m, 3H), 7.12 (d, J = 6.5 Hz, 2H), 6.54 (s, 1H), 3.74 (t, J = 7.3 Hz, 2H), 2.88 (t, J = 7.3 Hz, 2H), 1.58 (s, 3H). ^{13}C {^{1}H} NMR (126 MHz, DMSO-d_6) δ 152.8, 137.6, 135.5, 133.2, 129.2, 129.0, 128.7, 128.6, 128.5, 126.6, 125.9, 125.5, 124.0, 120.1, 118.4, 115.5, 43.8, 33.9 15.5. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{23}H_{19}ClNO_5$: 424.0946; Found: 424.0940.

*3-(4-Chlorobenzyl)-5-(4-fluorophenyl)-4-(3-hydroxy-5-methyl-2-oxo-2H-pyran-6-yl)oxazol-2(3H)-one (**4o**)*



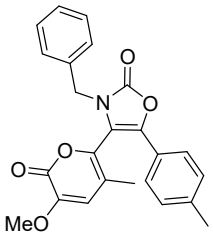
Yellowish powder; yield 82% (0.18 g); mp 173-175 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.49 – 7.31 (m, 4H), 7.31 – 7.16 (m, 4H), 6.49 (s, 1H), 4.72 (s, 2H), 1.53 (s, 3H). ^{13}C {^{1}H} NMR (126 MHz, DMSO-d_6) δ 162.1 (d, J_{CF} = 247.6 Hz), 158.7, 153.3, 144.1, 136.4, 135.0, 133.0, 132.5, 129.3, 128.5, 126.7 (d, J_{CF} = 8.5 Hz), 123.2 (d, J_{CF} = 3.3 Hz), 120.1, 118.4, 116.4 (d, J_{CF} = 22.1 Hz), 114.3, 45.1, 15.3. ^{19}F NMR (282 MHz, DMSO-d_6) δ -111.27. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{22}H_{16}ClFNO_5$: 428.0696; Found: 428.0684.

*3-Benzyl-5-(4-fluorophenyl)-4-(3-hydroxy-5-methyl-2-oxo-2H-pyran-6-yl)oxazol-2(3H)-one (**4p**)*



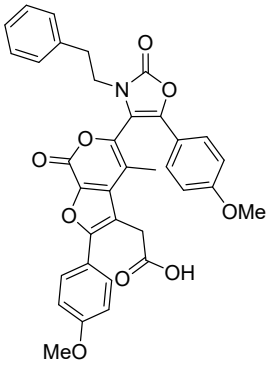
Yellowish powder; yield 79% (0.16 g); mp 93-95 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.48 – 7.36 (m, 2H), 7.34 – 7.19 (m, 5H), 7.17 – 7.08 (m, 2H), 6.45 (s, 1H), 4.86 – 4.57 (m, 2H), 1.48 (s, 3H). ^{13}C {^{1}H} NMR (126 MHz, DMSO-d_6) δ 162.1 (d, J_{CF} = 247.2 Hz), 158.7, 153.3, 144.0, 136.3, 135.9, 133.2, 128.5, 127.8, 127.3, 126.6 (d, J_{CF} = 8.4 Hz), 123.2 (d, J_{CF} = 3.3 Hz), 120.0, 118.4, 116.4 (d, J_{CF} = 22.1 Hz), 114.3, 45.8, 15.2. ^{19}F NMR (282 MHz, DMSO) δ -111.33. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{22}H_{17}FNO_5$: 394.1085; Found: 394.1096.

*3-Benzyl-4-(3-methoxy-5-methyl-2-oxo-2H-pyran-6-yl)-5-(p-tolyl)oxazol-2(3H)-one (**7**)*



Yellowish powder; yield 94% (0.38 g); mp 105-107 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.31 – 7.12 (m, 9H), 6.66 (s, 1H), 4.72 (d, *J* = 27.6 Hz, 2H), 3.77 (s, 3H), 2.29 (s, 3H), 1.53 (s, 3H). ^{13}C {^{1}H} NMR (75 MHz, DMSO-d_6) δ 157.0, 153.3, 145.8, 138.8, 137.3, 135.8, 134.3, 129.7, 128.5, 127.8, 127.3, 124.2, 123.7, 119.0, 116.5, 113.6, 56.3, 45.7, 20.8, 15.4. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{24}H_{22}NO_5$: 404.1492; Found: 404.1473.

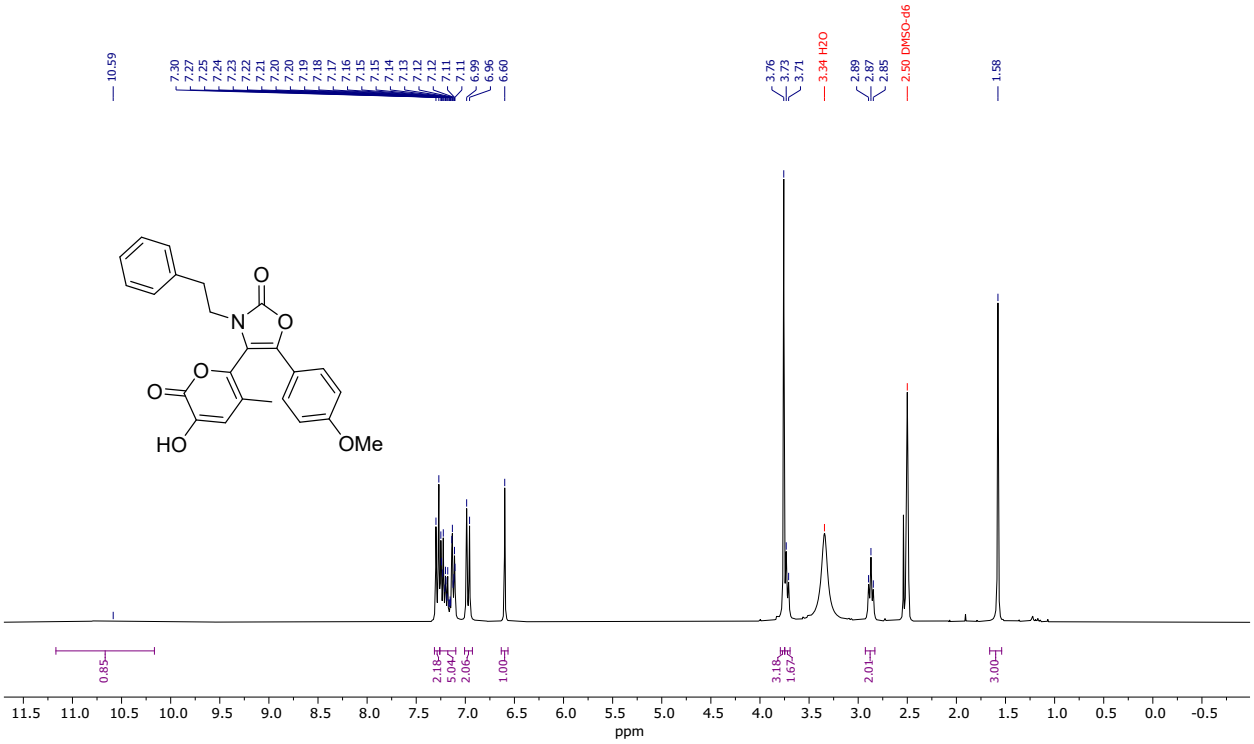
*2-(2-(4-Methoxyphenyl)-5-(5-(4-methoxyphenyl)-2-oxo-3-phenethyl-2,3-dihydrooxazol-4-yl)-4-methyl-7-oxo-7H-furo[2,3-c]pyran-3-yl)acetic acid (**10**)*



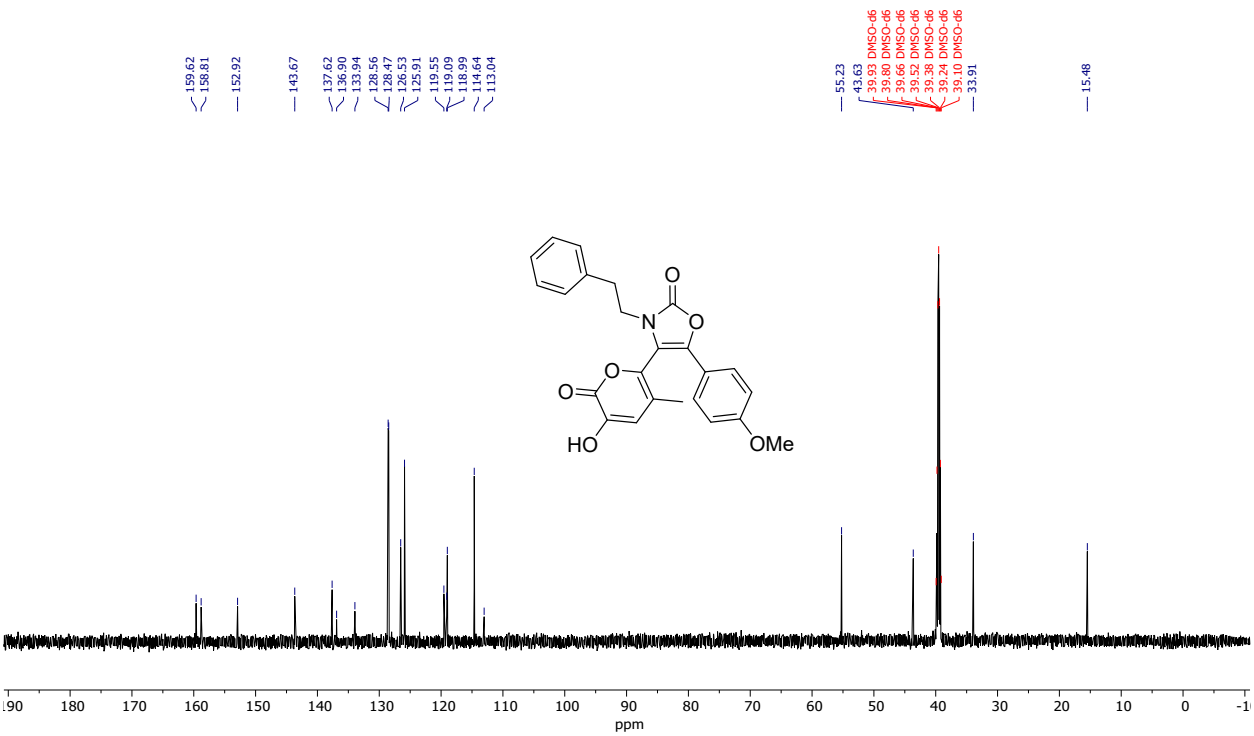
Yellowish powder; yield 68% (0.41 g); mp 249-251 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.93 (br.s, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.22 – 7.09 (m, 7H), 6.95 (d, *J* = 8.4 Hz, 2H), 3.86 (s, 3H), 3.84 – 3.78 (m, 4H), 3.76 (s, 3H), 2.91 (t, *J* = 7.4 Hz, 2H), 1.92 (s, 3H). ^{13}C {^{1}H} NMR (126 MHz, DMSO-d_6) δ 172.0, 160.8, 159.7, 158.6, 153.0, 152.1, 139.4, 137.6, 137.2, 136.6, 136.4, 129.2, 128.6, 128.4, 126.5, 126.1, 120.4, 118.9, 115.5, 114.9, 114.7, 112.8, 111.7, 55.4, 55.2, 43.7, 33.9, 30.4, 12.8. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcld for $C_{35}H_{30}NO_9$: 608.1915; Found: 608.1895.

4. Copies of ^{1}H and ^{13}C NMR spectra for all compounds

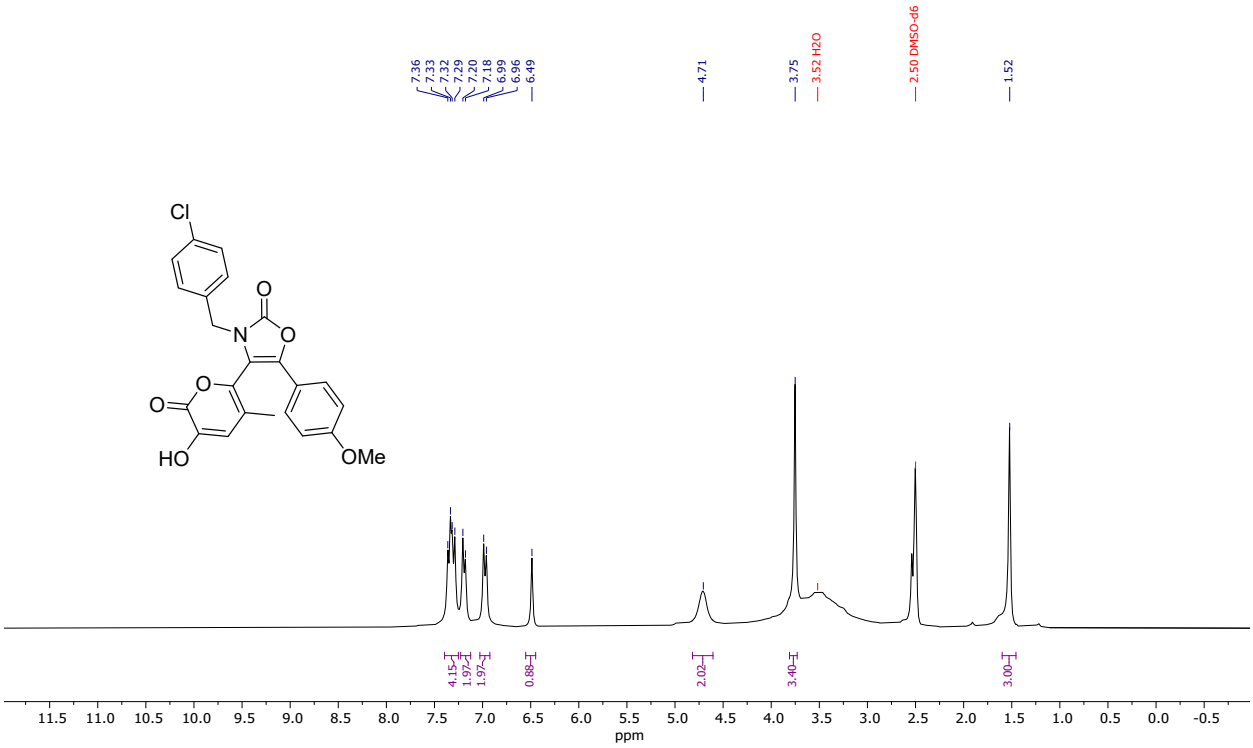
^{1}H NMR spectrum (300 MHz) of **4a** in DMSO-d_6



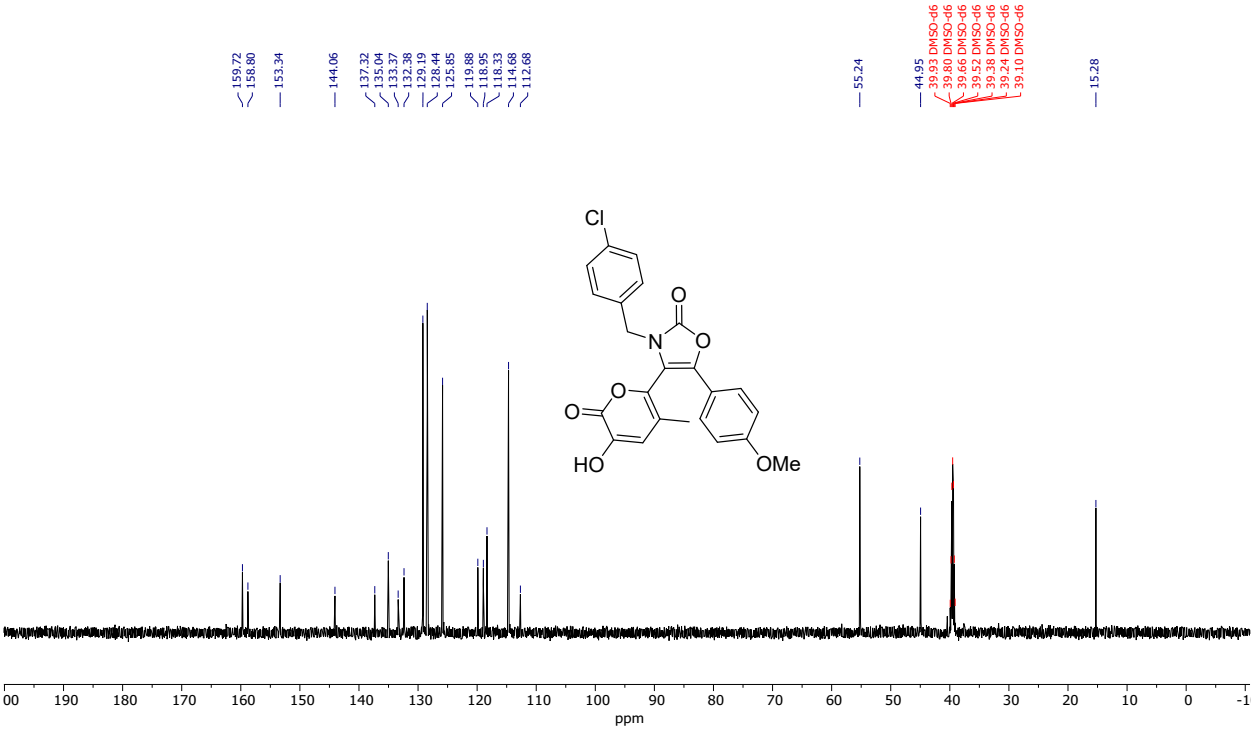
^{13}C {^{1}H} NMR spectrum (151 MHz) of **4a** in DMSO-d_6



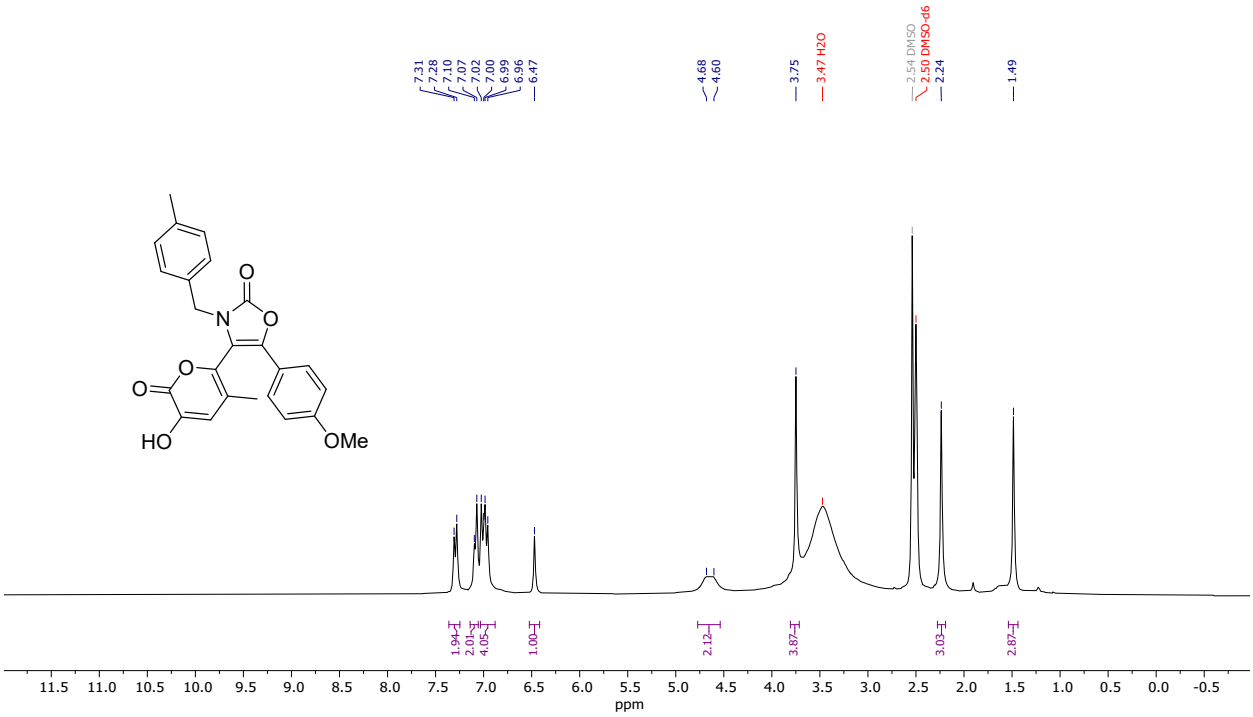
^{1}H NMR spectrum (300 MHz) of **4b** in DMSO-d_6



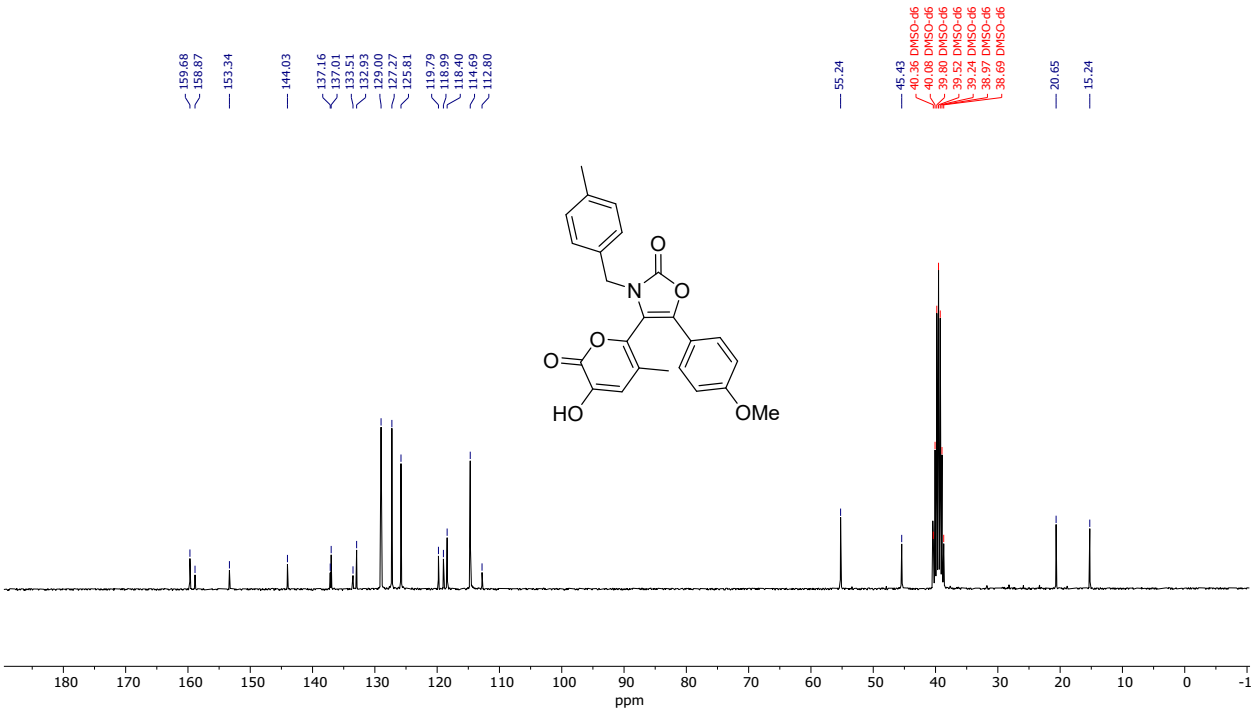
^{13}C {^{1}H} NMR spectrum (151 MHz) of **4b** in DMSO-d_6



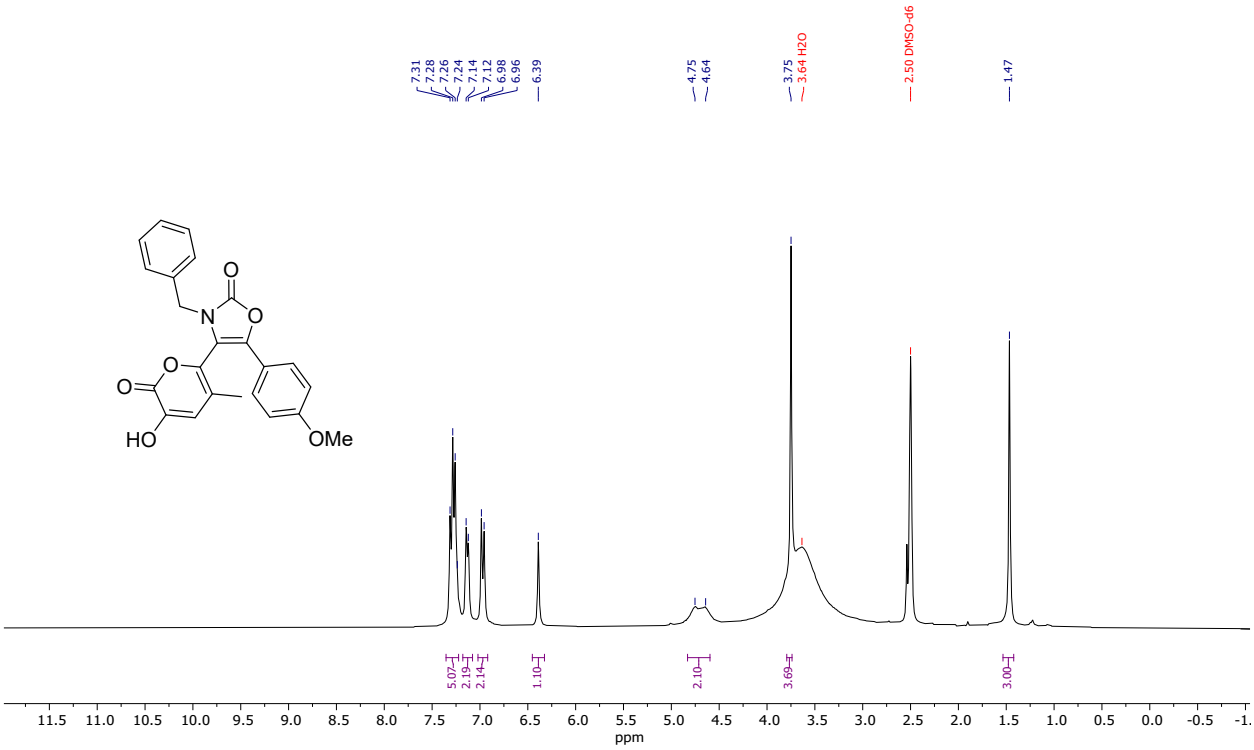
^{1}H NMR spectrum (300 MHz) of **4c** in DMSO-d_6



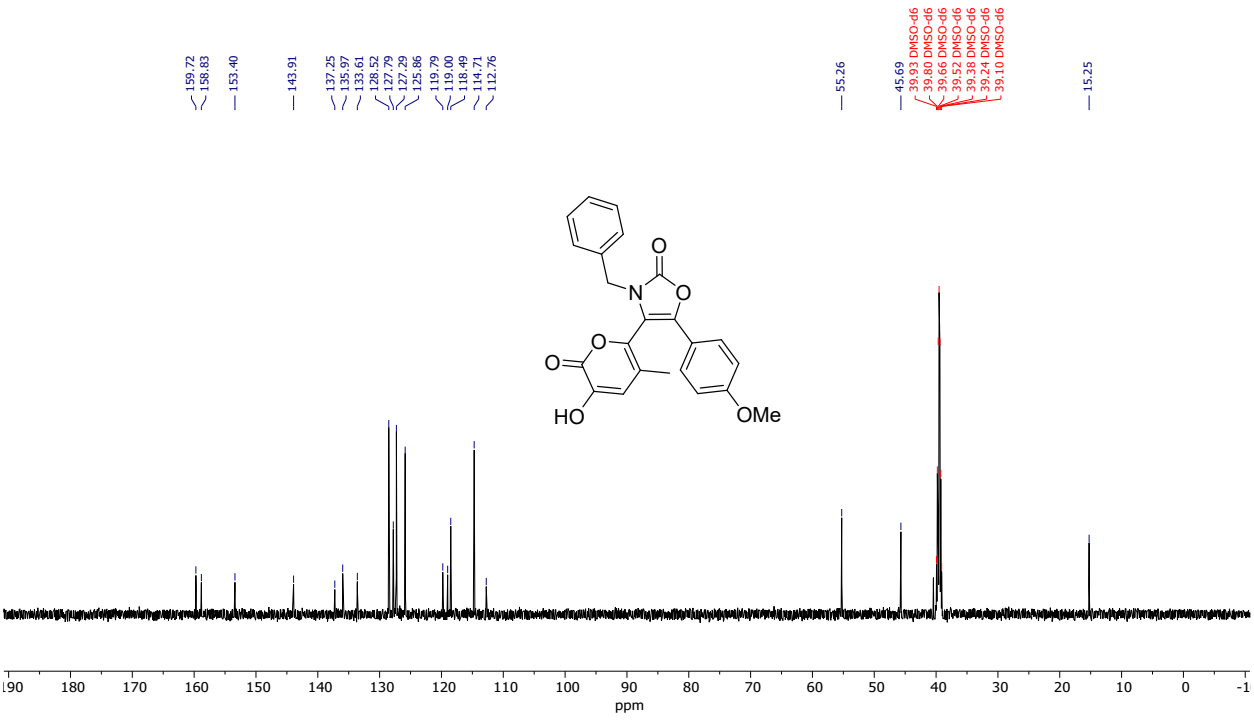
^{13}C {^{1}H} NMR spectrum (75 MHz) of **4c** in DMSO-d_6



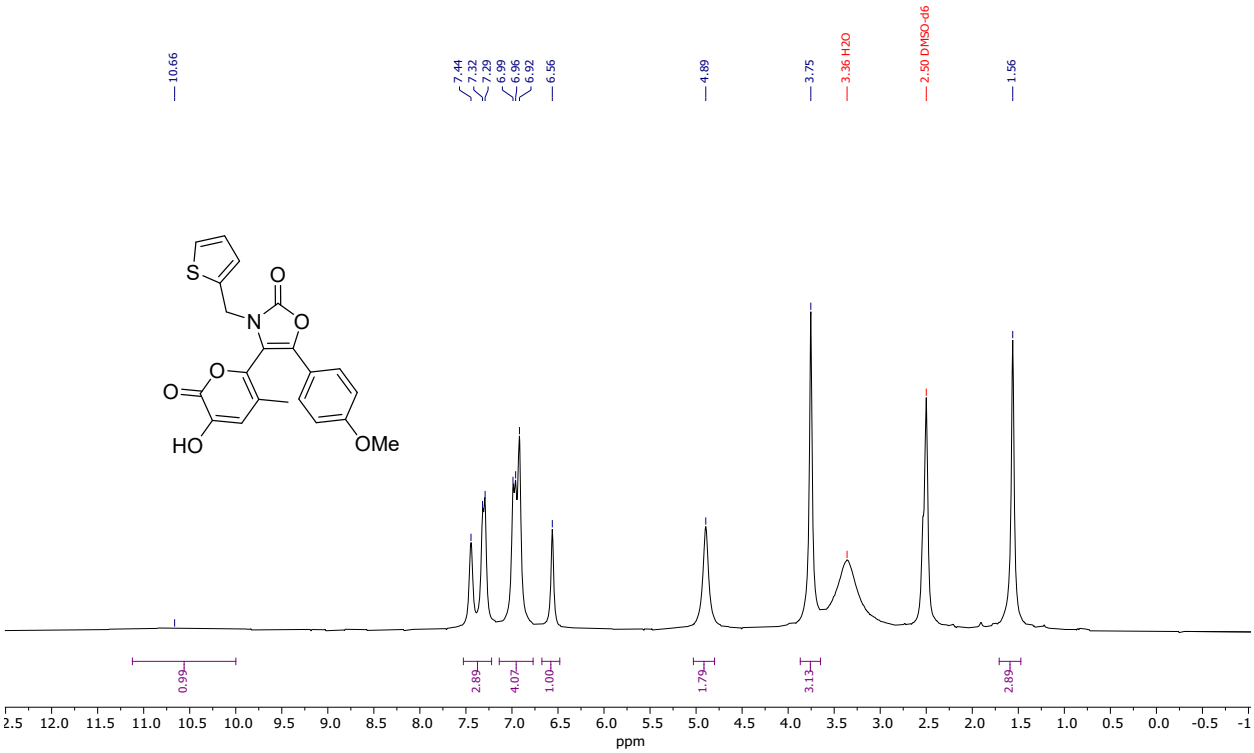
^{1}H NMR spectrum (300 MHz) of **4d** in DMSO-d_6



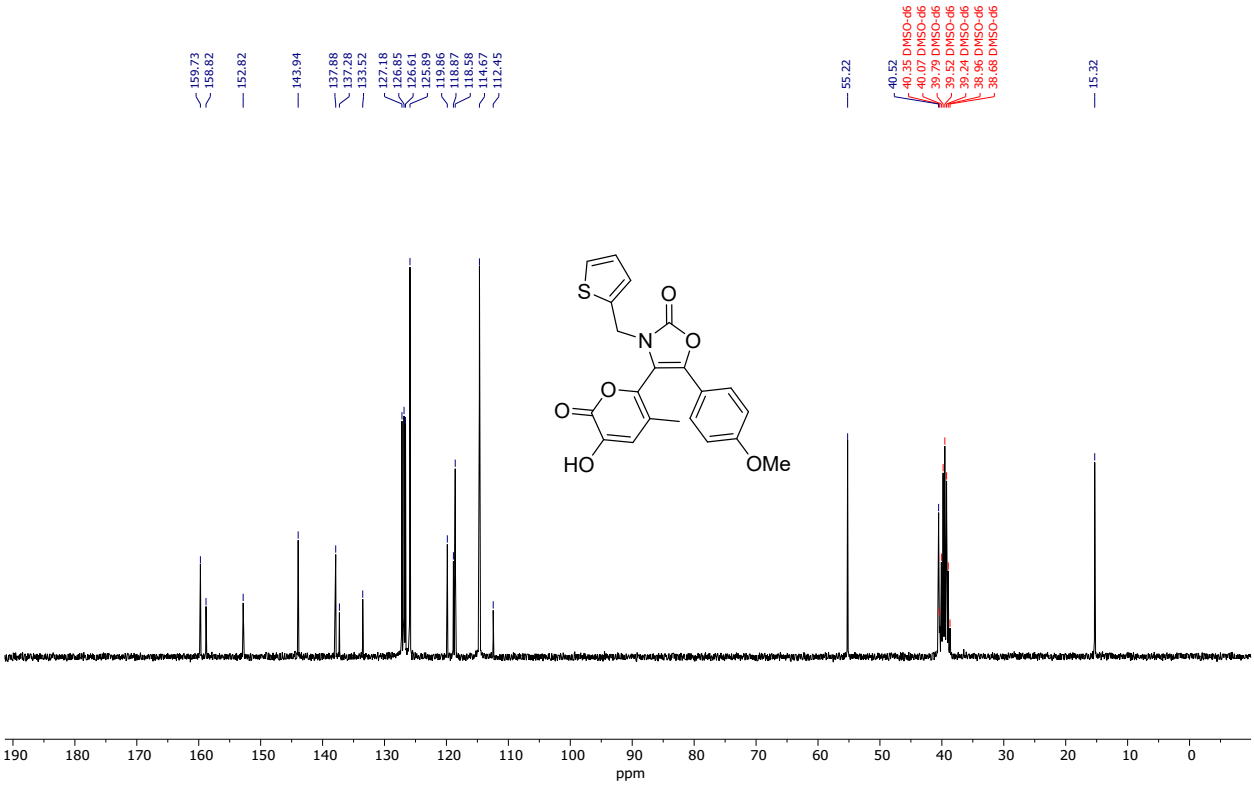
^{13}C {^{1}H} NMR spectrum (151 MHz) of **4d** in DMSO-d_6



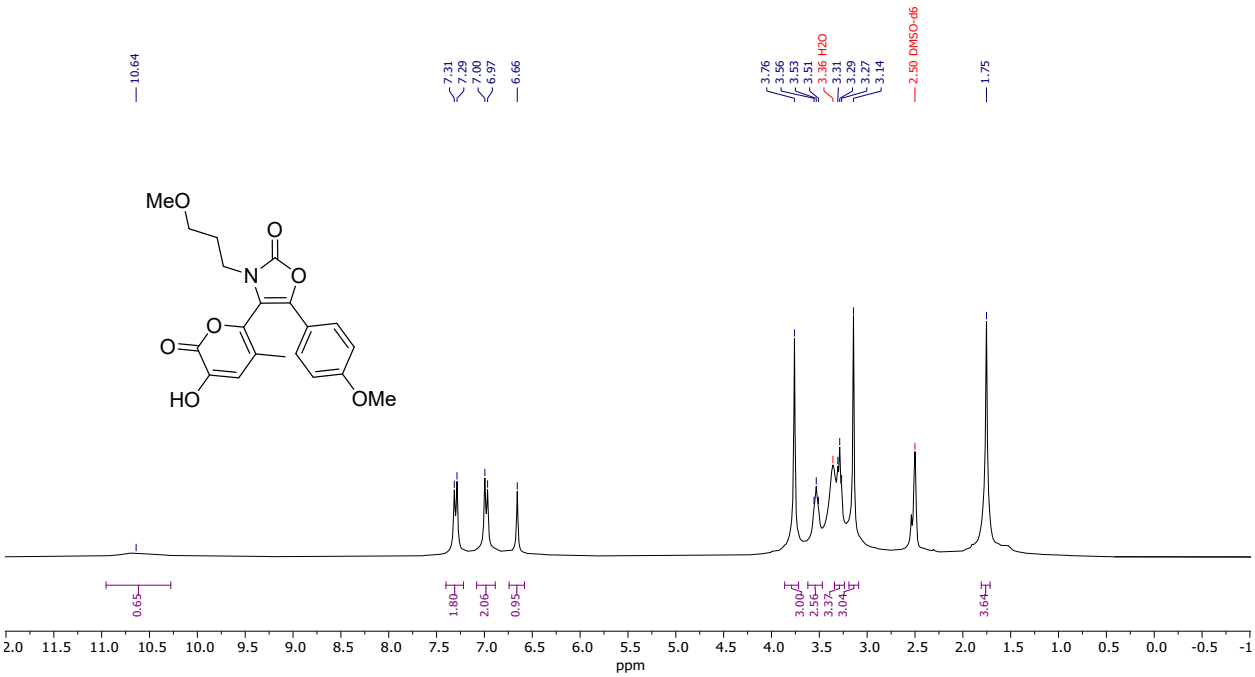
^{1}H NMR spectrum (300 MHz) of **4e** in DMSO-d_6



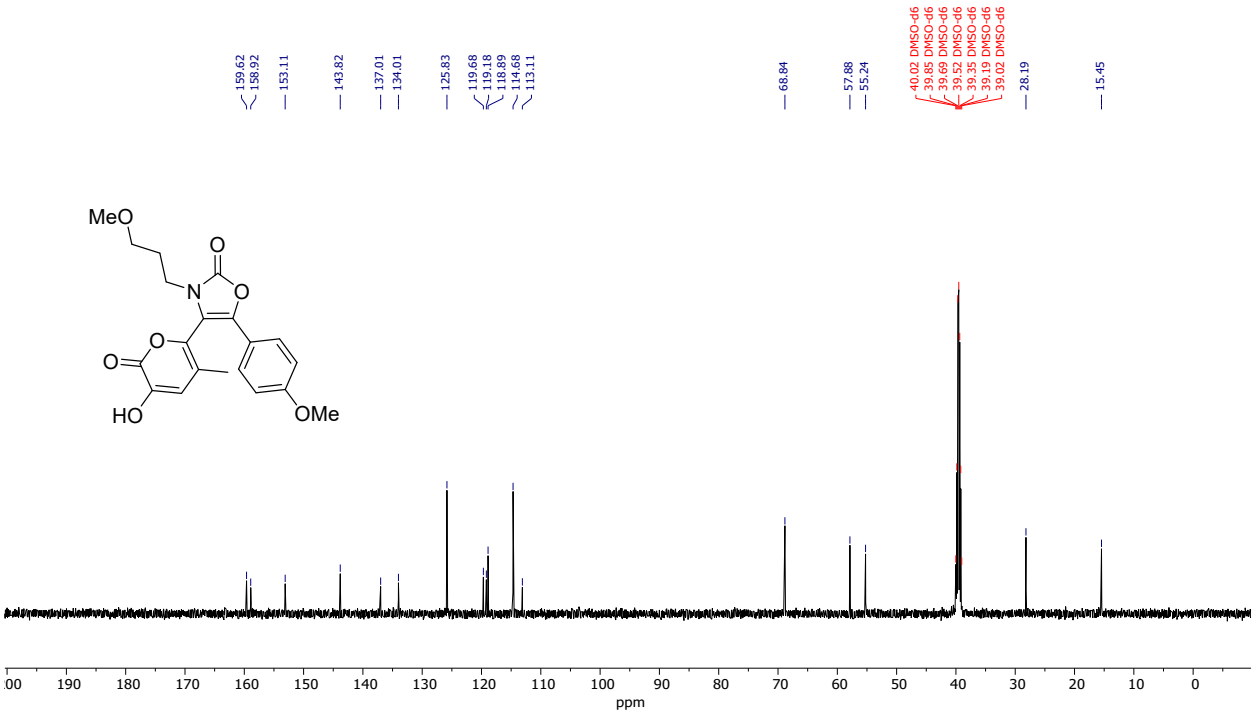
^{13}C {^{1}H} NMR spectrum (75 MHz) of **4e** in DMSO-d_6



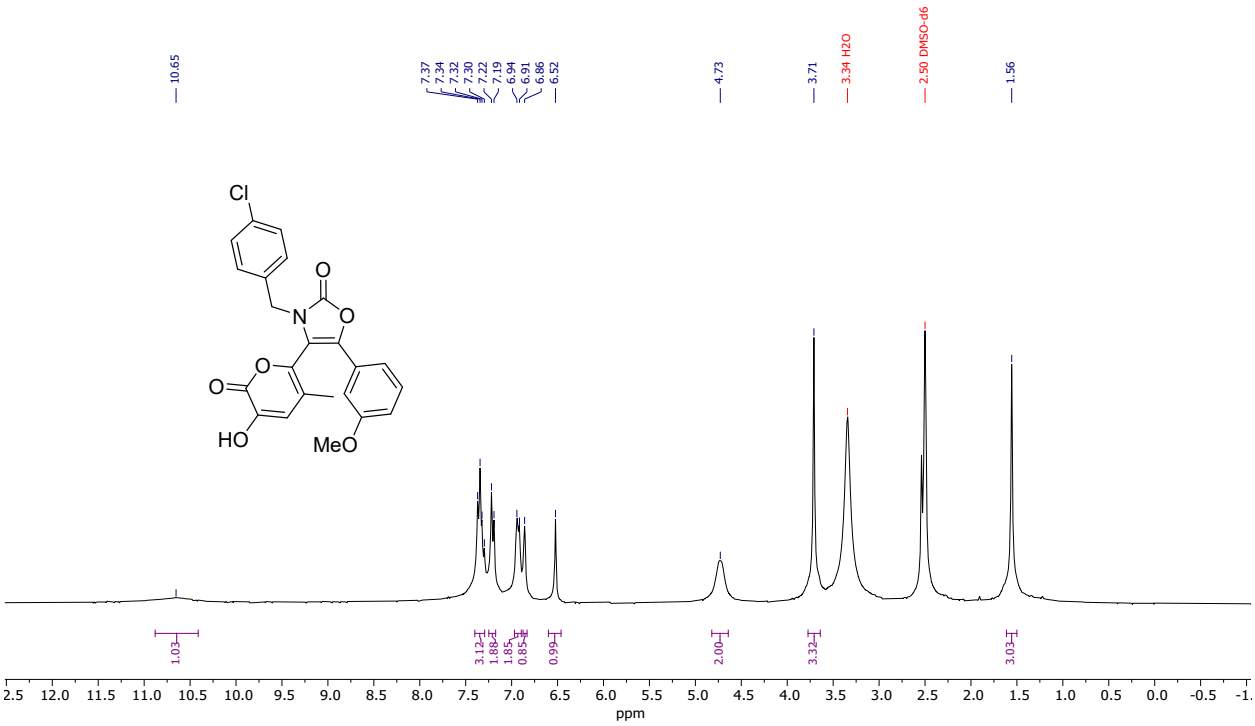
^{1}H NMR spectrum (300 MHz) of **4f** in DMSO-d_6



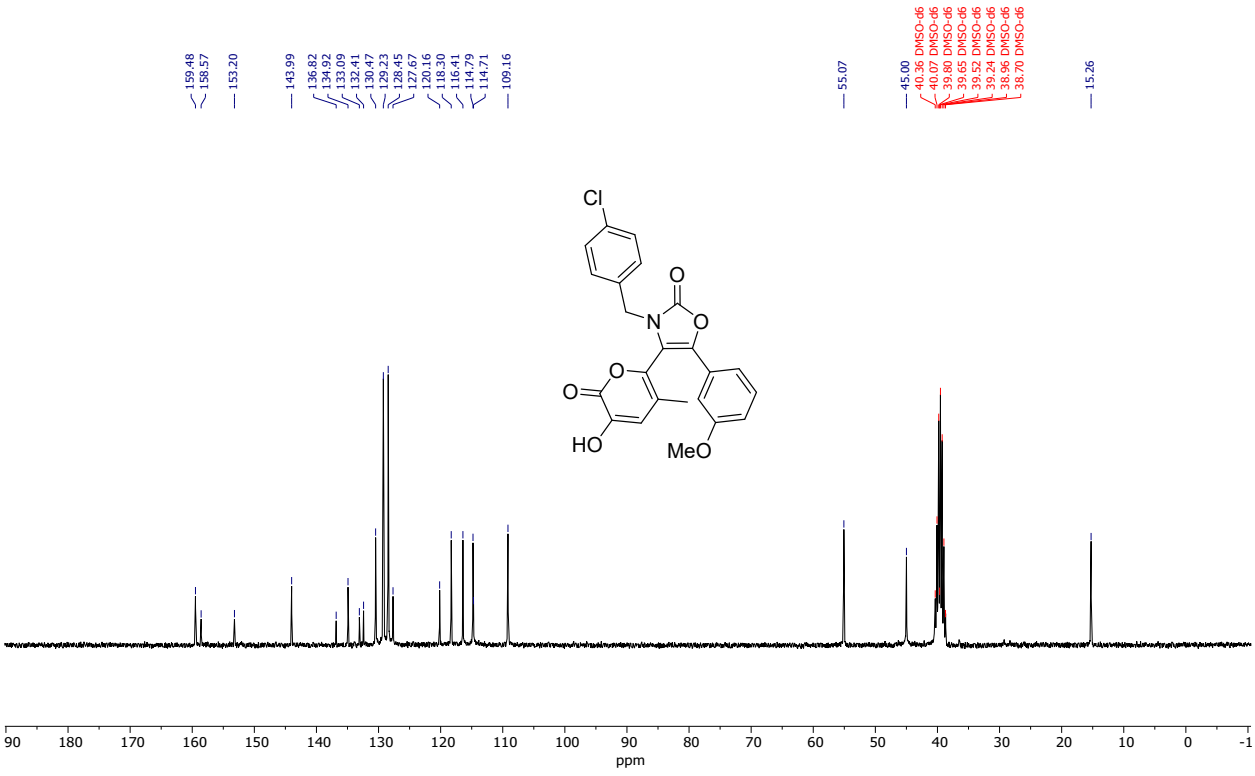
^{13}C {^{1}H} NMR spectrum (126 MHz) of **4f** in DMSO-d_6



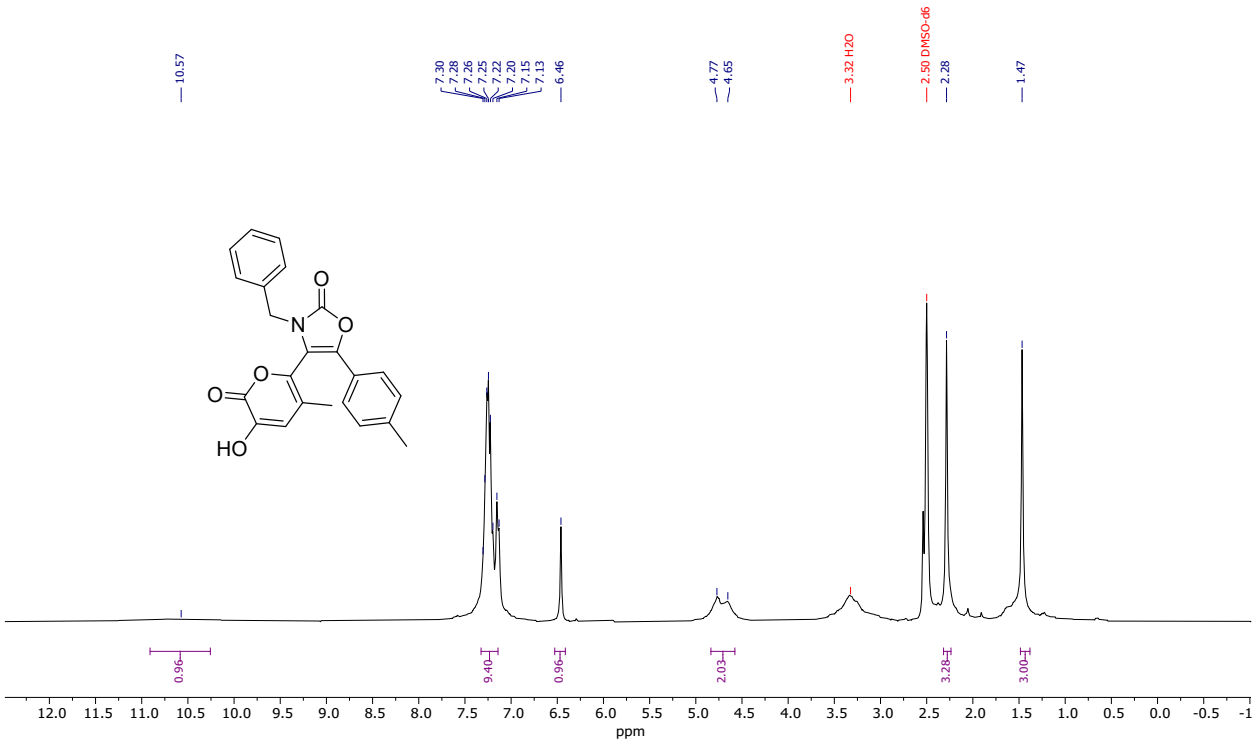
^{1}H NMR spectrum (300 MHz) of **4g** in DMSO-d_6



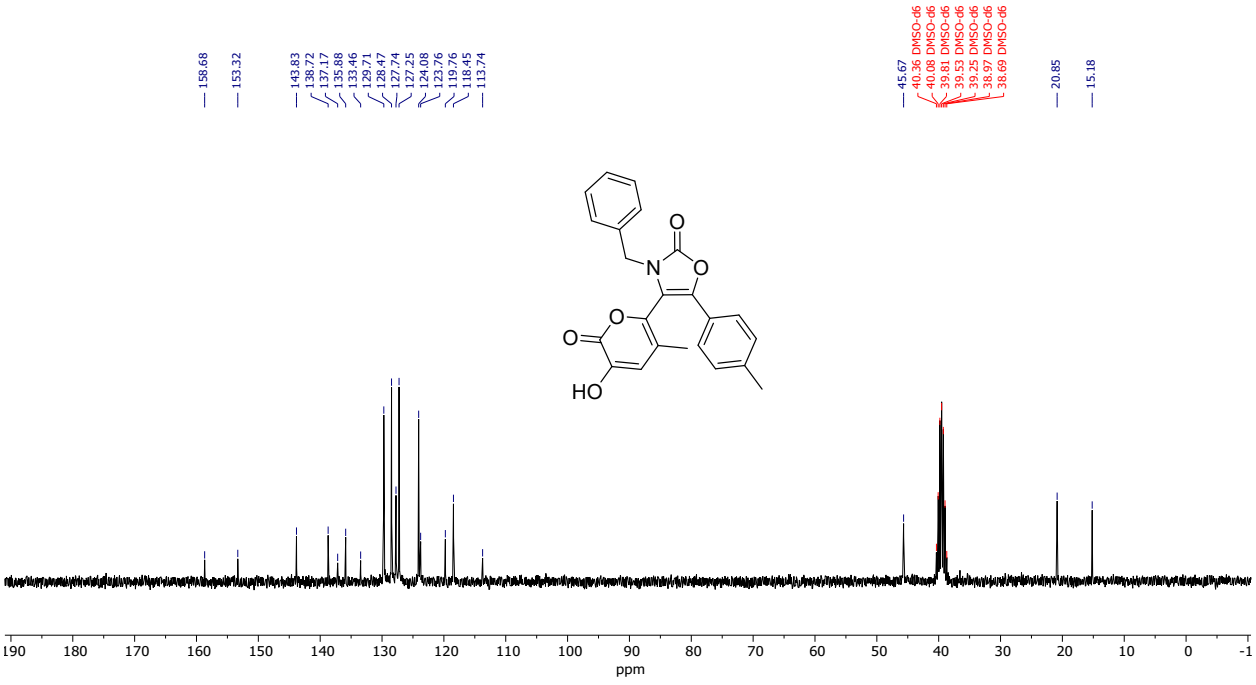
^{13}C {^{1}H} NMR spectrum (75 MHz) of **4g** in DMSO-d_6



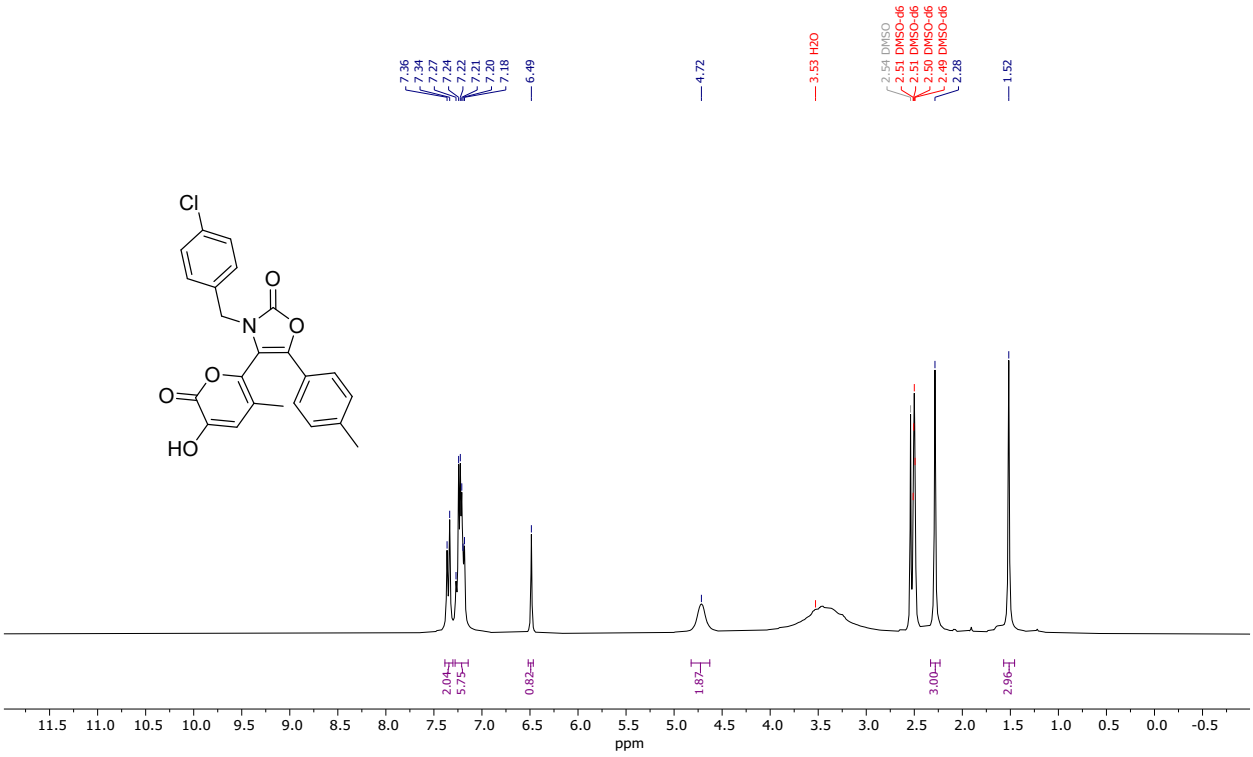
^{1}H NMR spectrum (300 MHz) of **4h** in DMSO-d_6



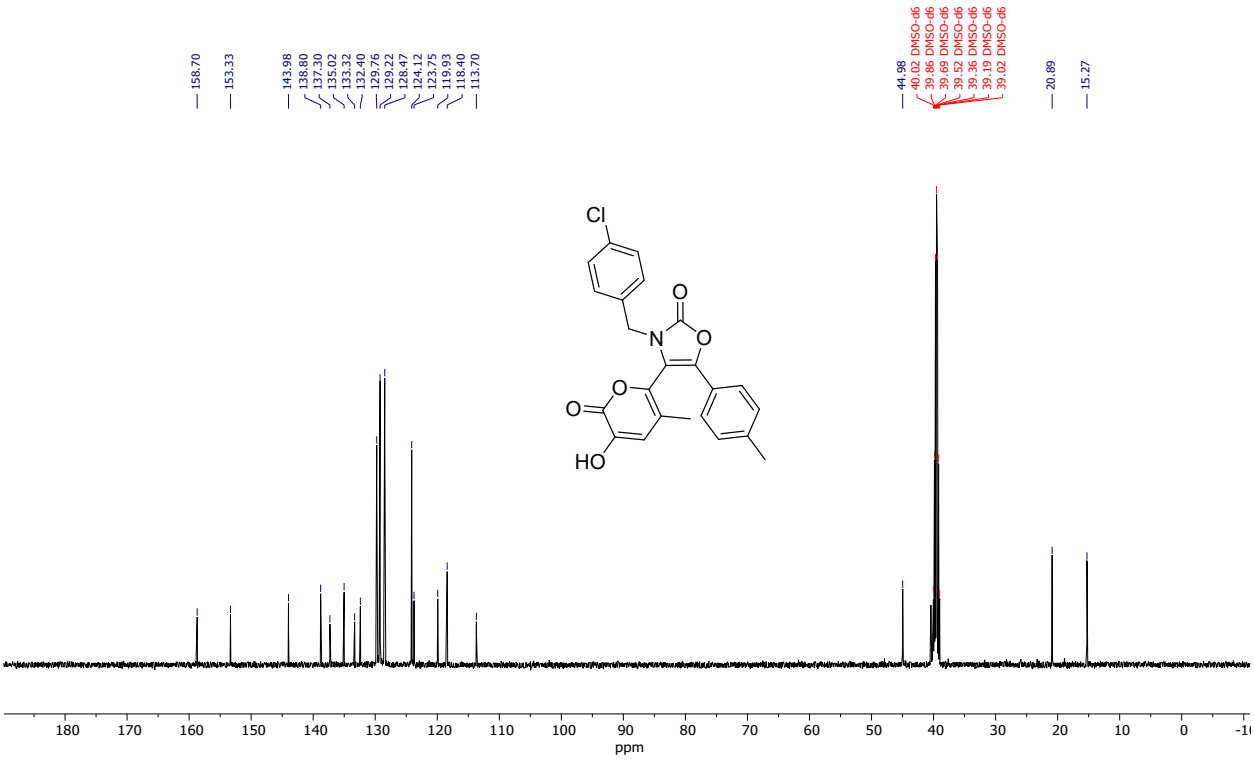
^{13}C {^{1}H} NMR spectrum (75 MHz) of **4h** in DMSO-d_6



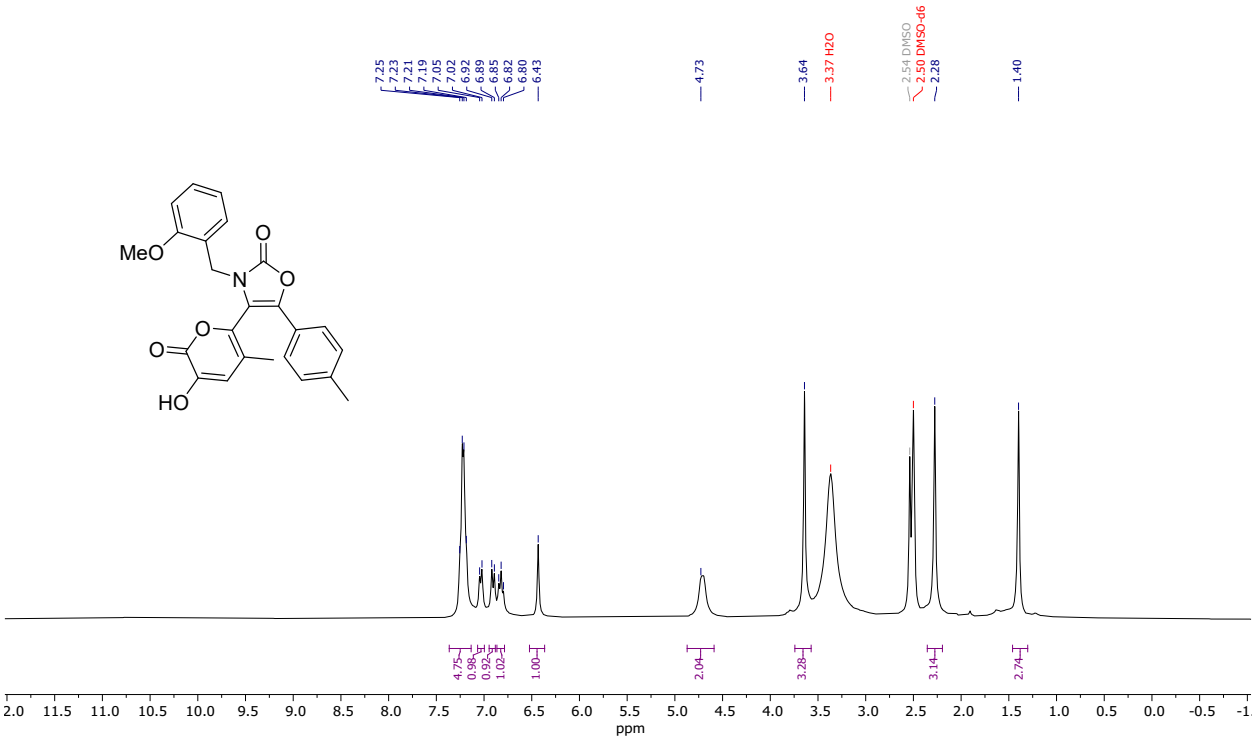
^{1}H NMR spectrum (300 MHz) of **4i** in DMSO-d_6



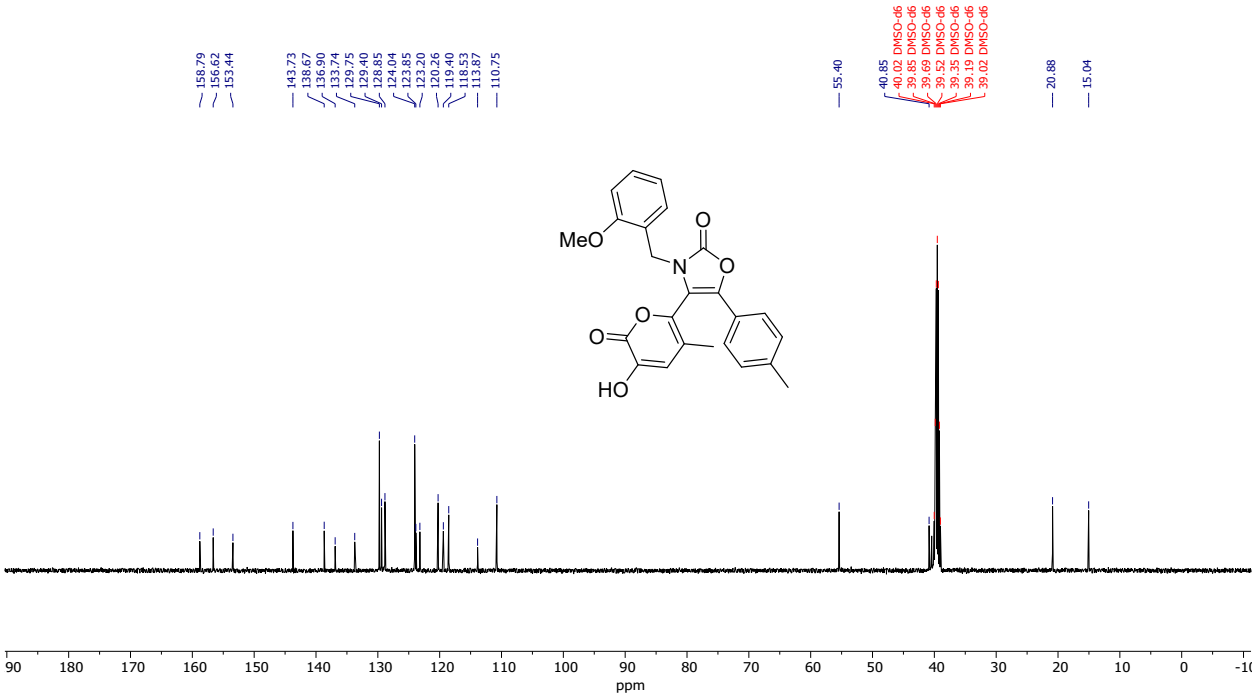
^{13}C {^{1}H} NMR spectrum (126 MHz) of **4i** in DMSO-d_6



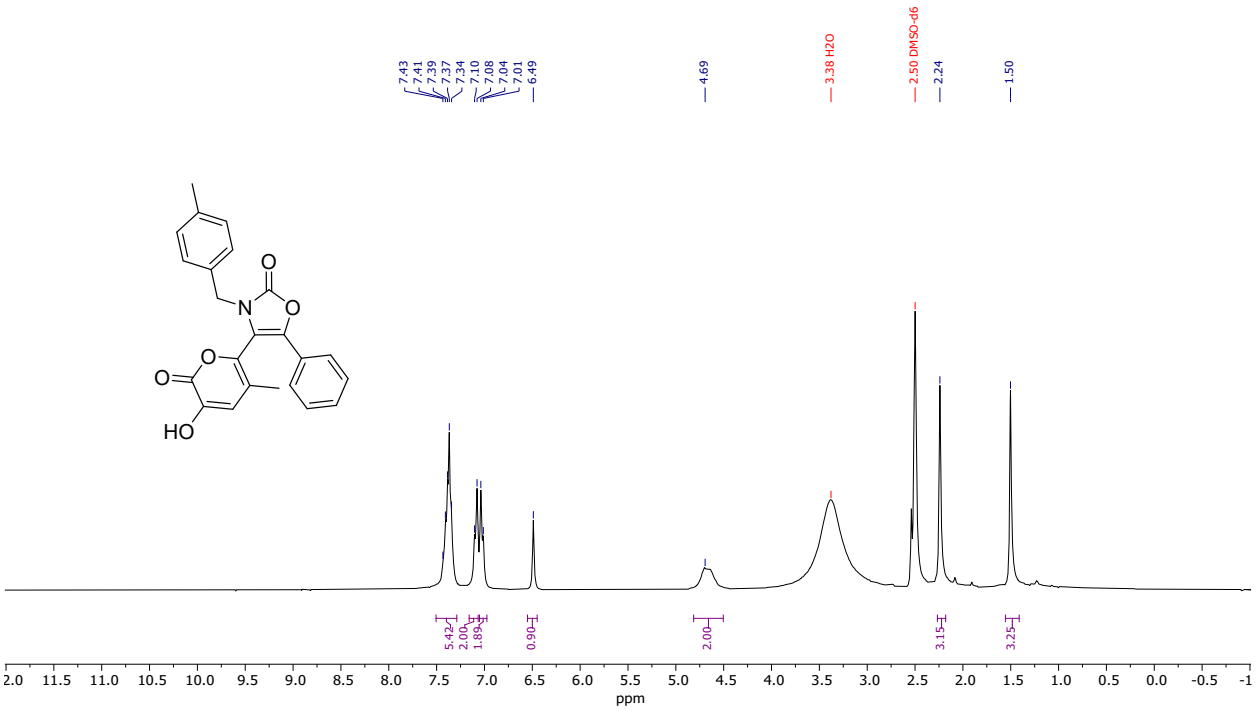
^{1}H NMR spectrum (300 MHz) of **4j** in DMSO-d_6



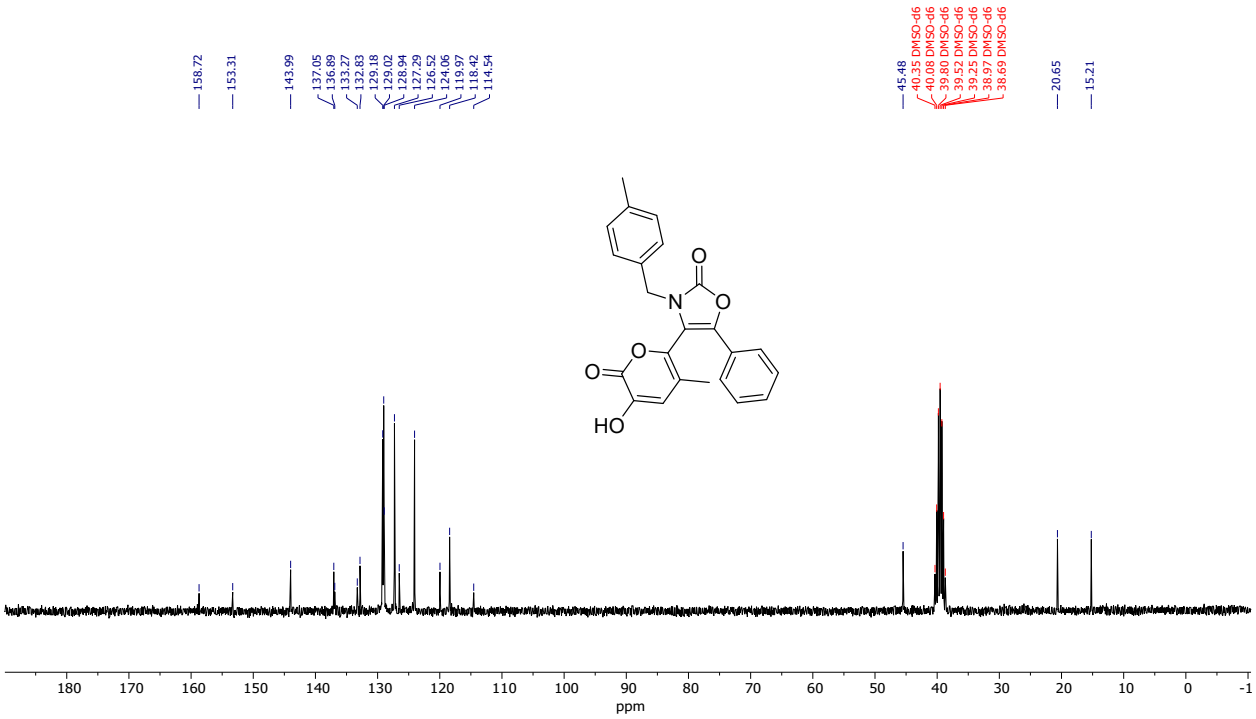
^{13}C {^{1}H} NMR spectrum (126 MHz) of **4j** in DMSO-d_6



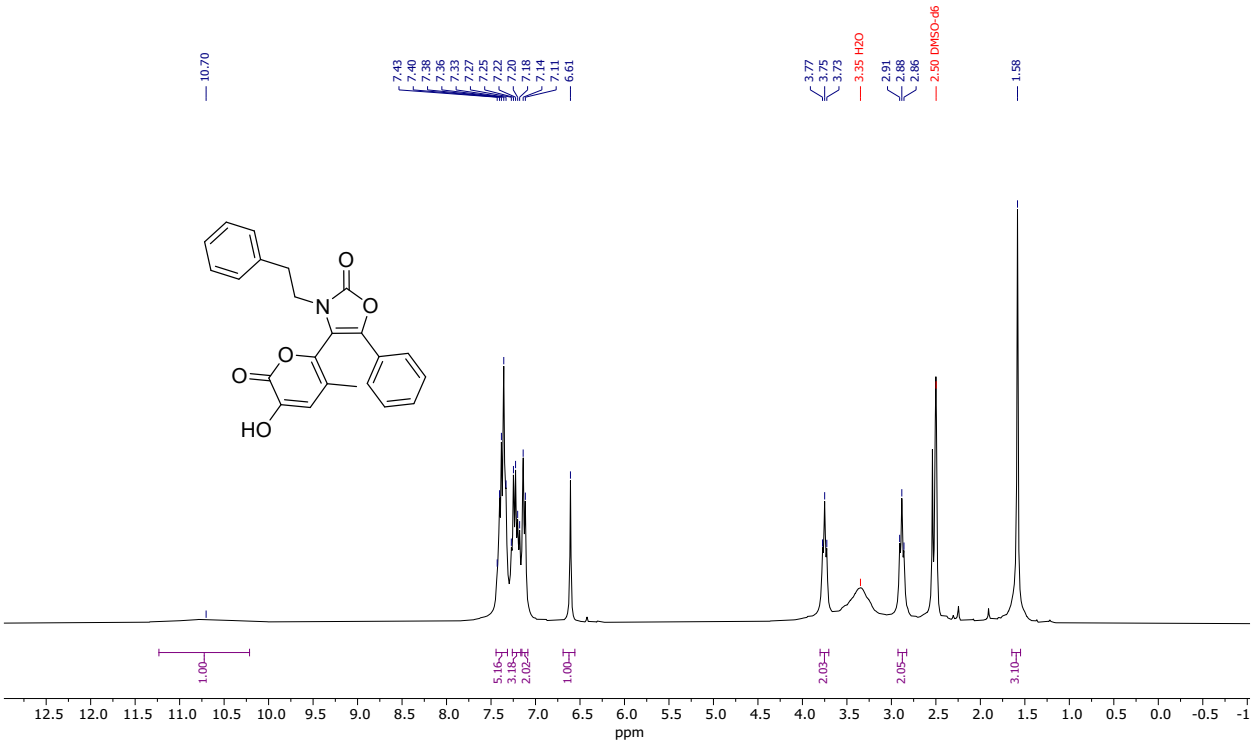
^{1}H NMR spectrum (300 MHz) of **4k** in DMSO-d_6



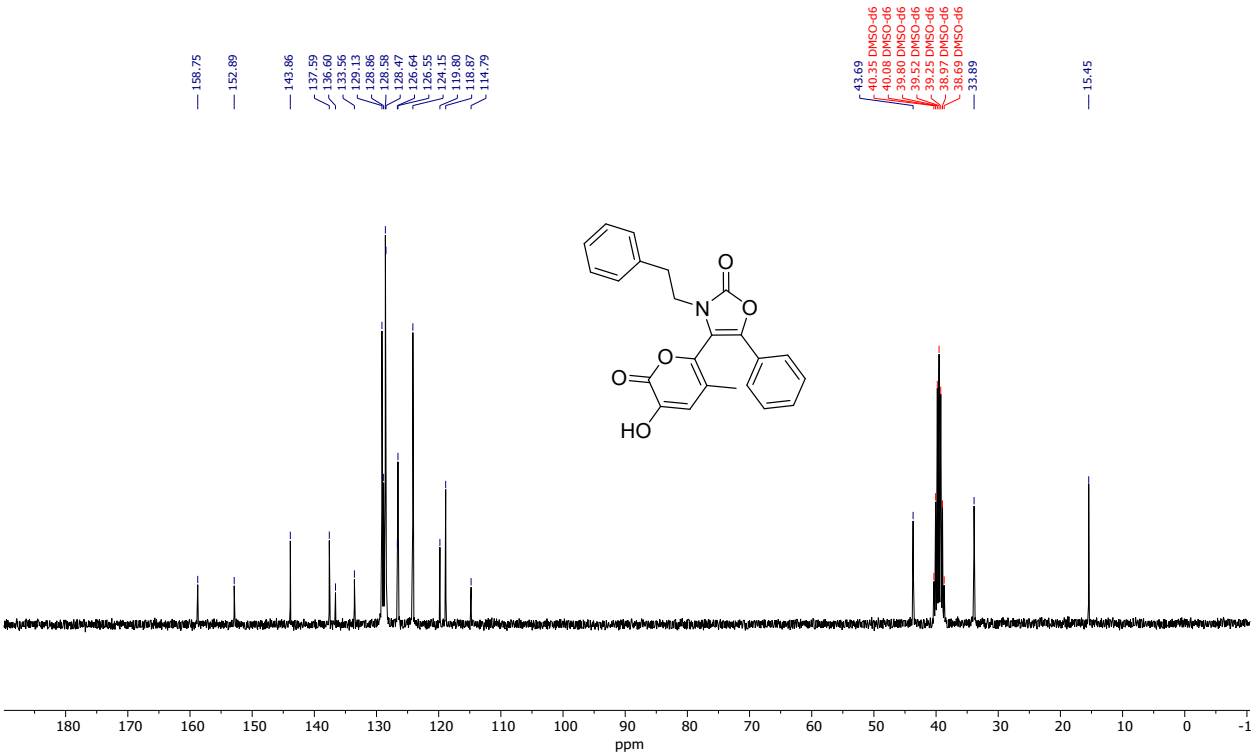
^{13}C {^{1}H} NMR spectrum (75 MHz) of **4k** in DMSO-d_6



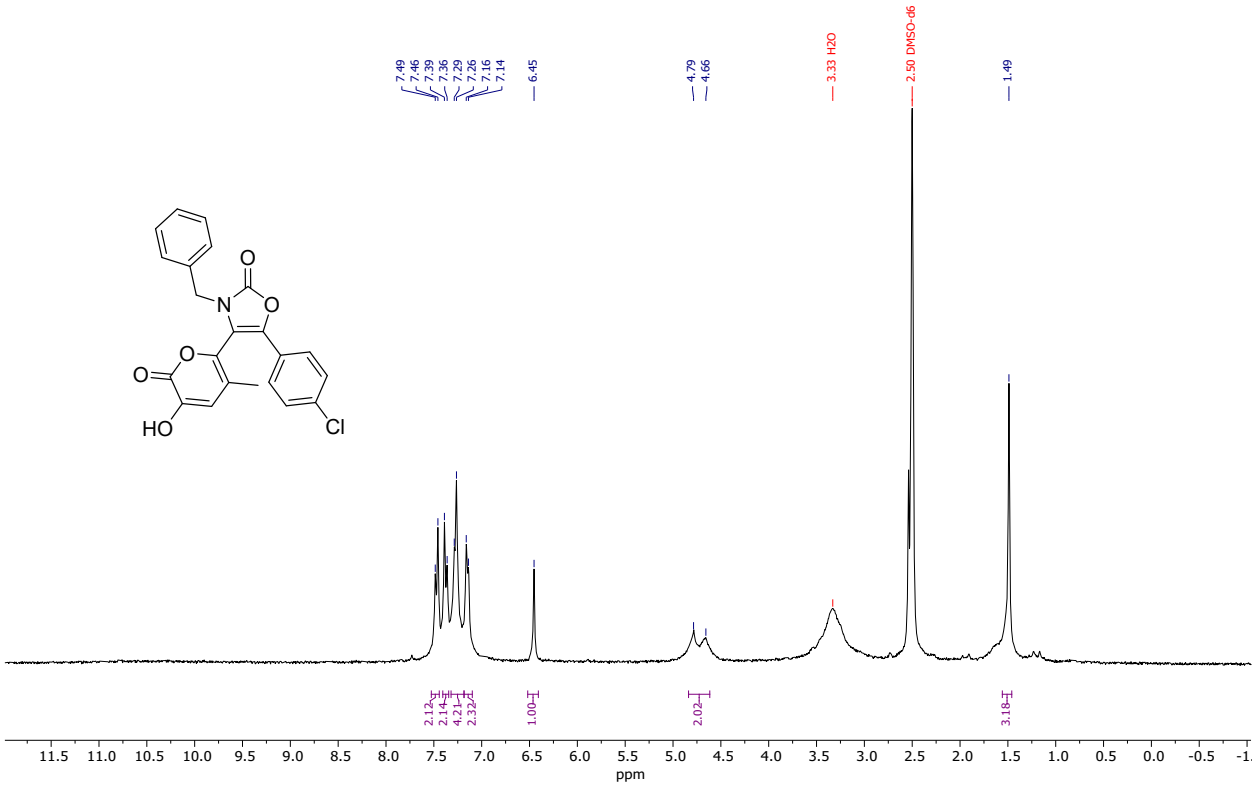
^{1}H NMR spectrum (300 MHz) of **4l** in DMSO-d_6



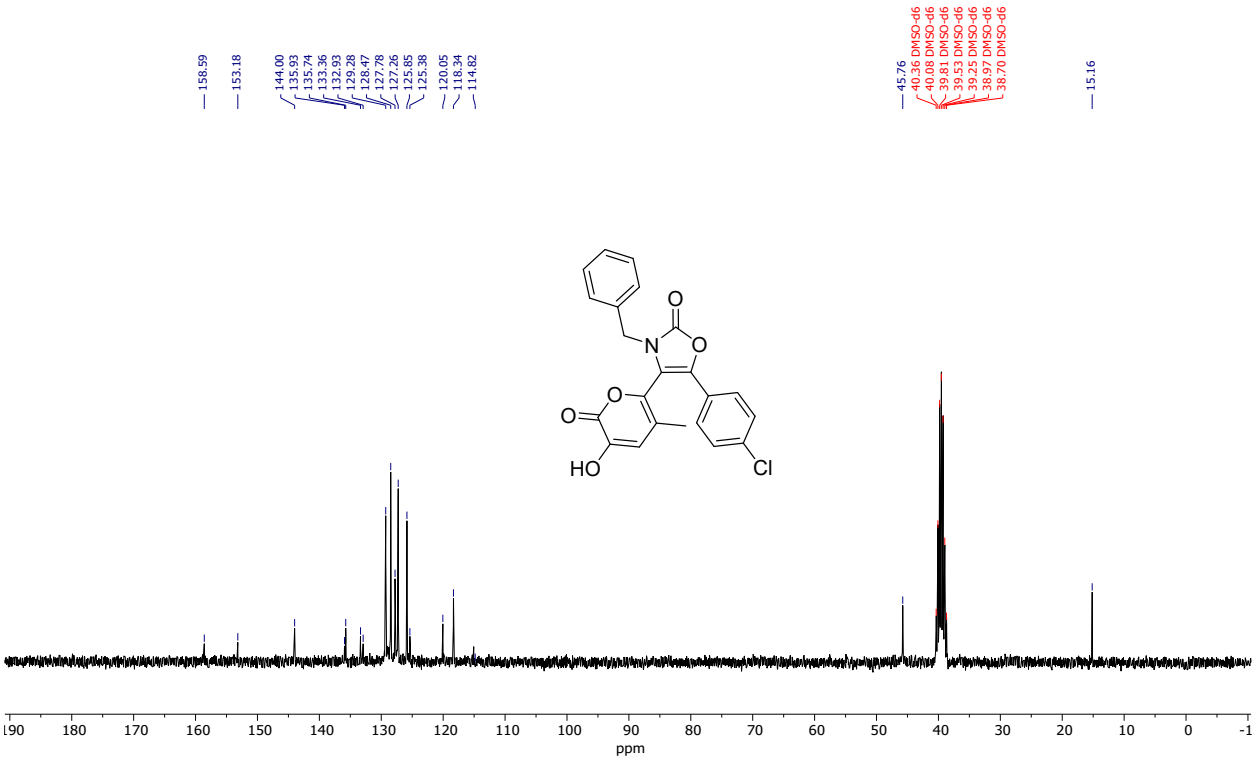
^{13}C {^{1}H} NMR spectrum (75 MHz) of **4l** in DMSO-d_6



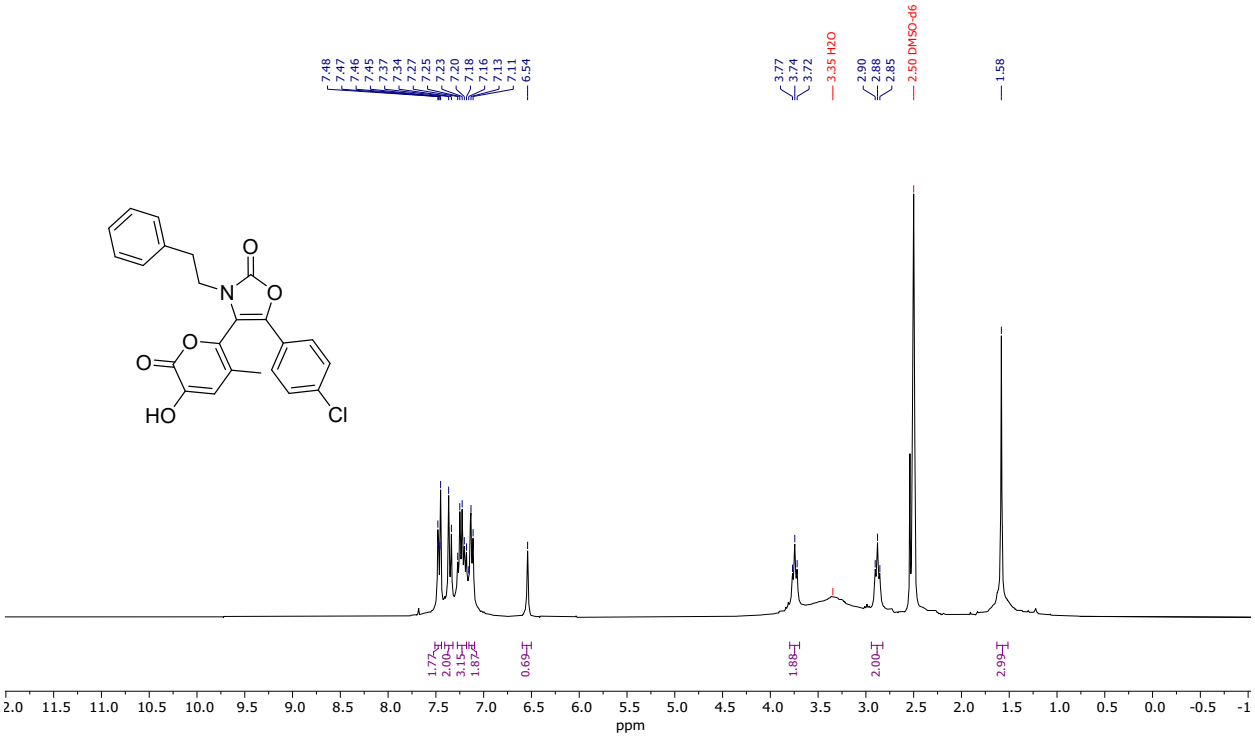
^{1}H NMR spectrum (300 MHz) of **4m** in DMSO-d_6



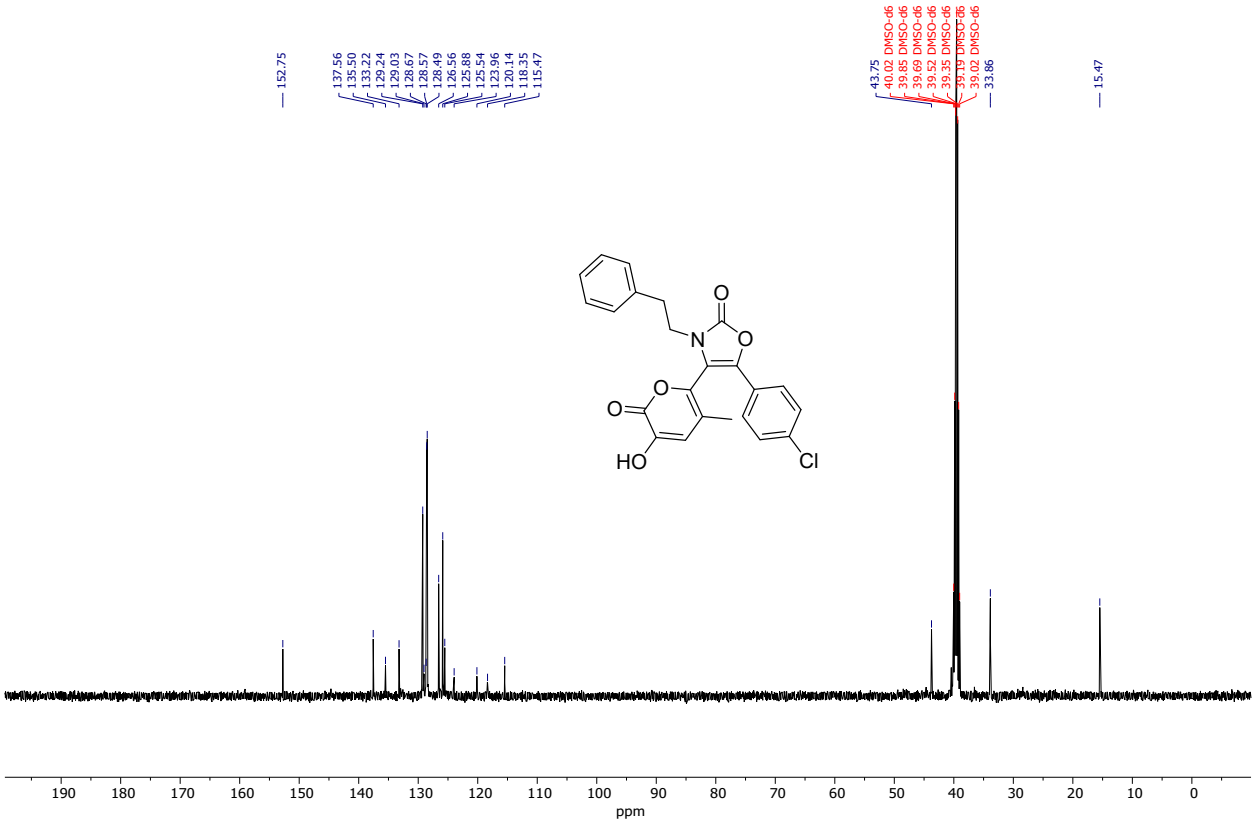
^{13}C {^{1}H} NMR spectrum (75 MHz) of **4m** in DMSO-d_6



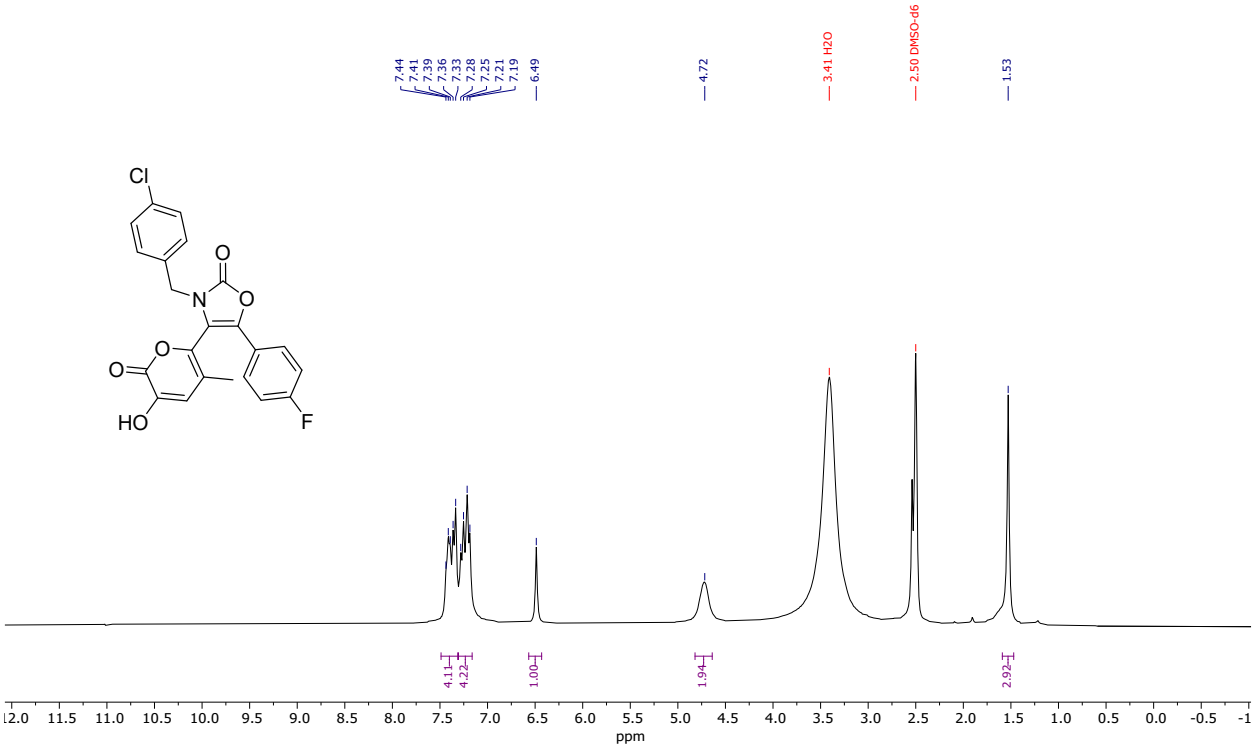
^{1}H NMR spectrum (300 MHz) of **4n** in DMSO-d_6



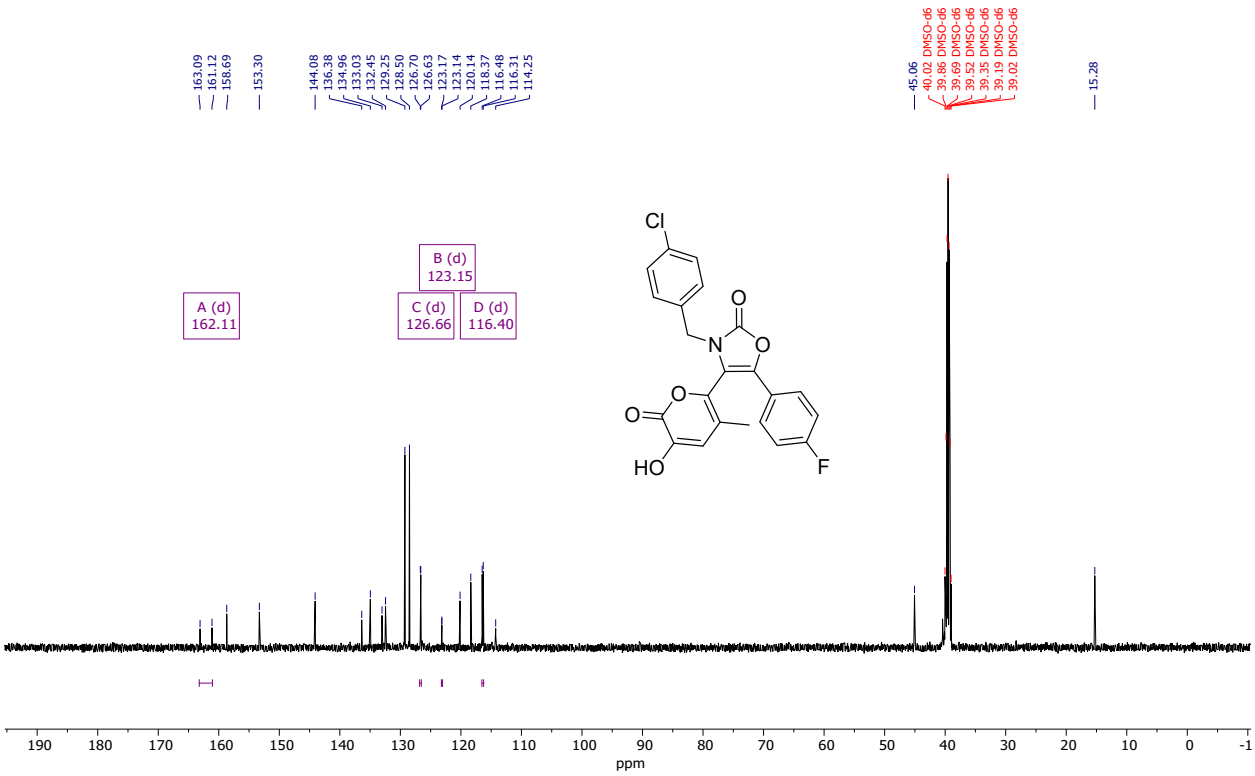
^{13}C {^{1}H} NMR spectrum (126 MHz) of **4n** in DMSO-d_6



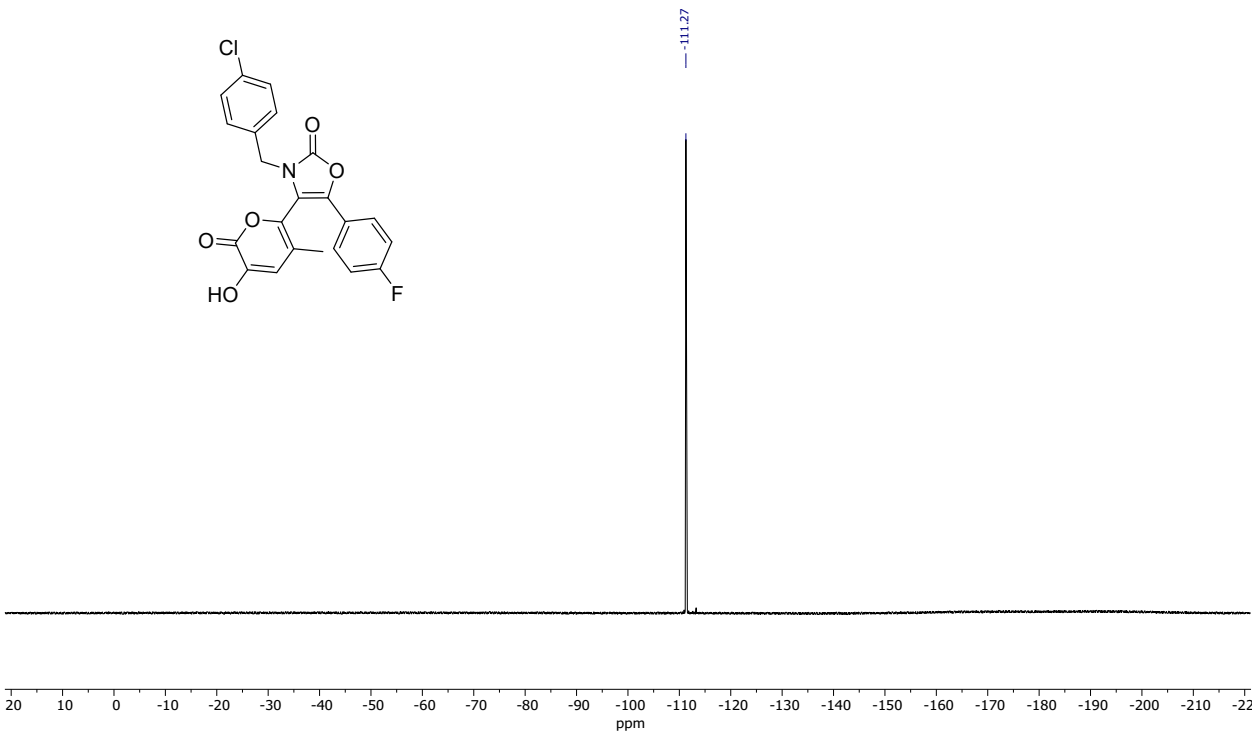
^{1}H NMR spectrum (300 MHz) of **4o** in DMSO-d_6



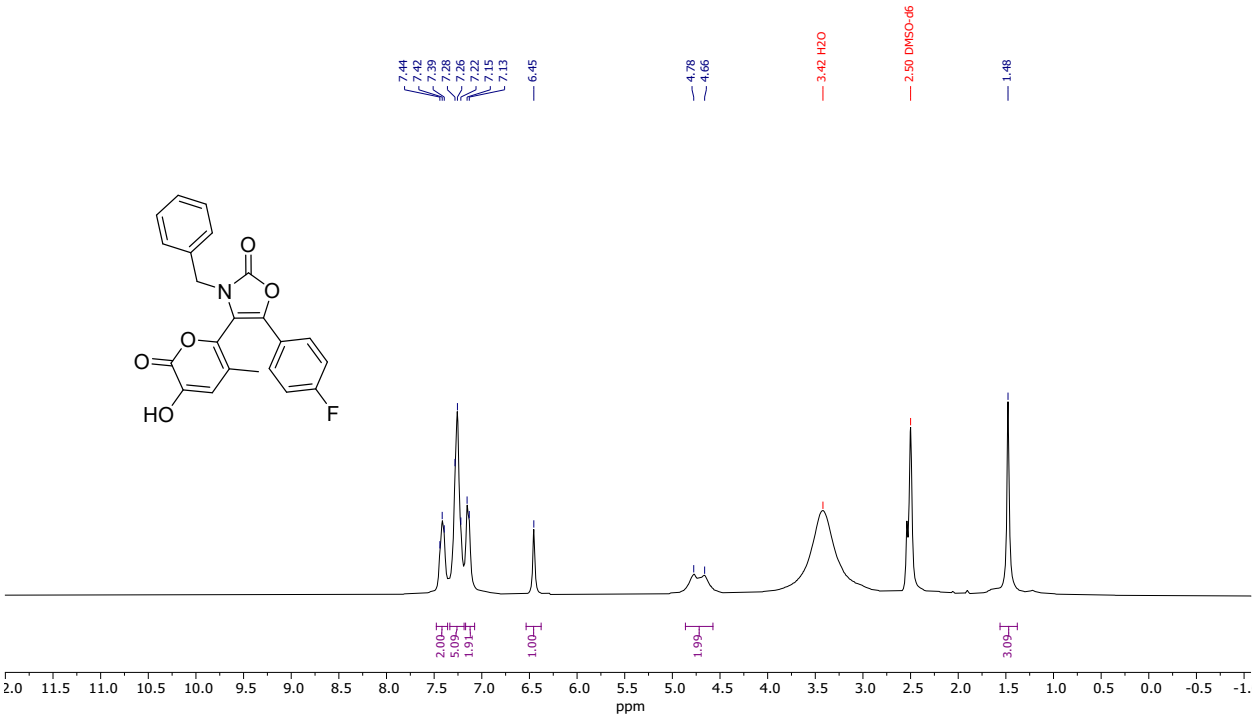
^{13}C {^{1}H} NMR spectrum (126 MHz) of **4o** in DMSO-d_6



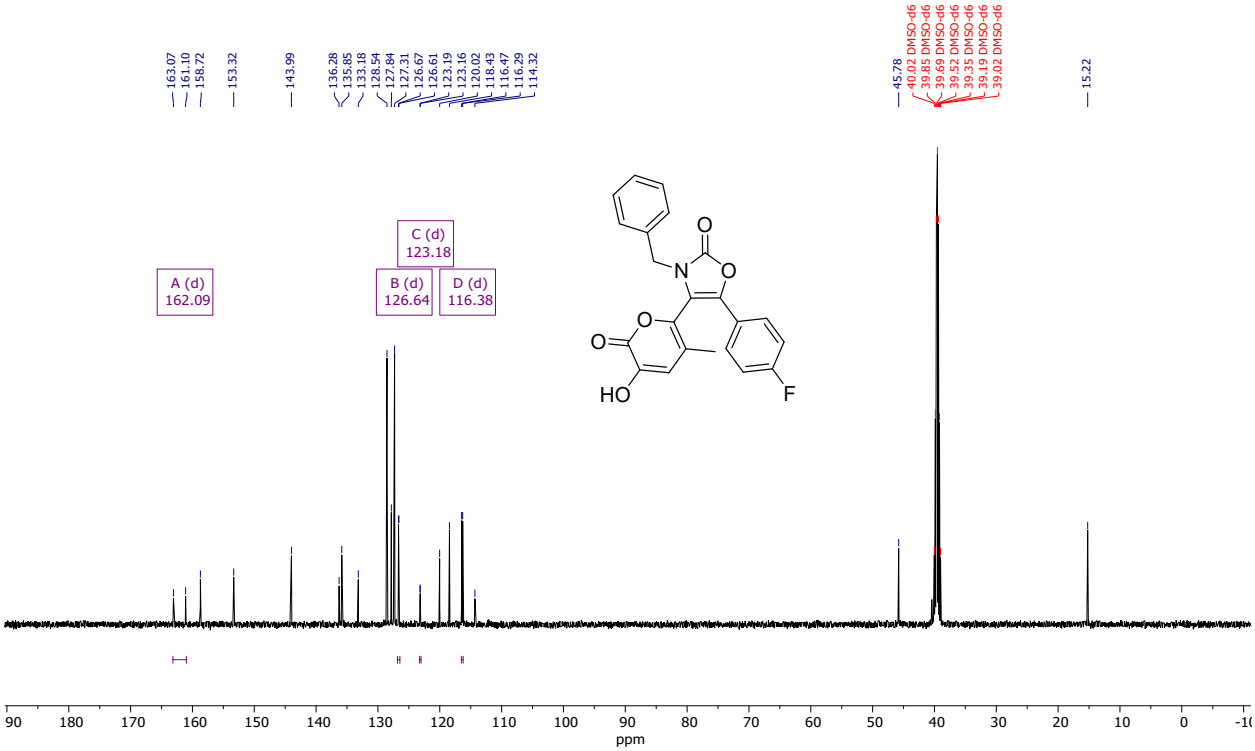
^{19}F NMR spectrum (282 MHz) of **4o** in DMSO-d_6



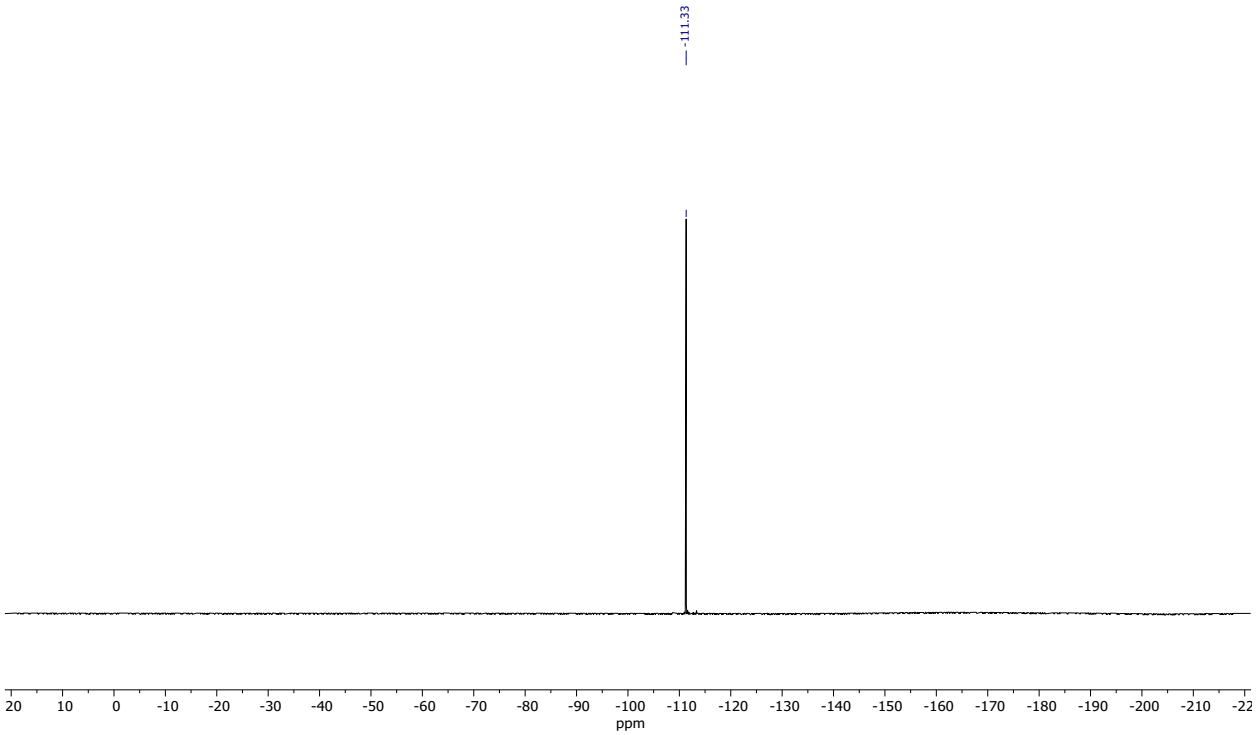
^{1}H NMR spectrum (300 MHz) of **4p** in DMSO-d_6



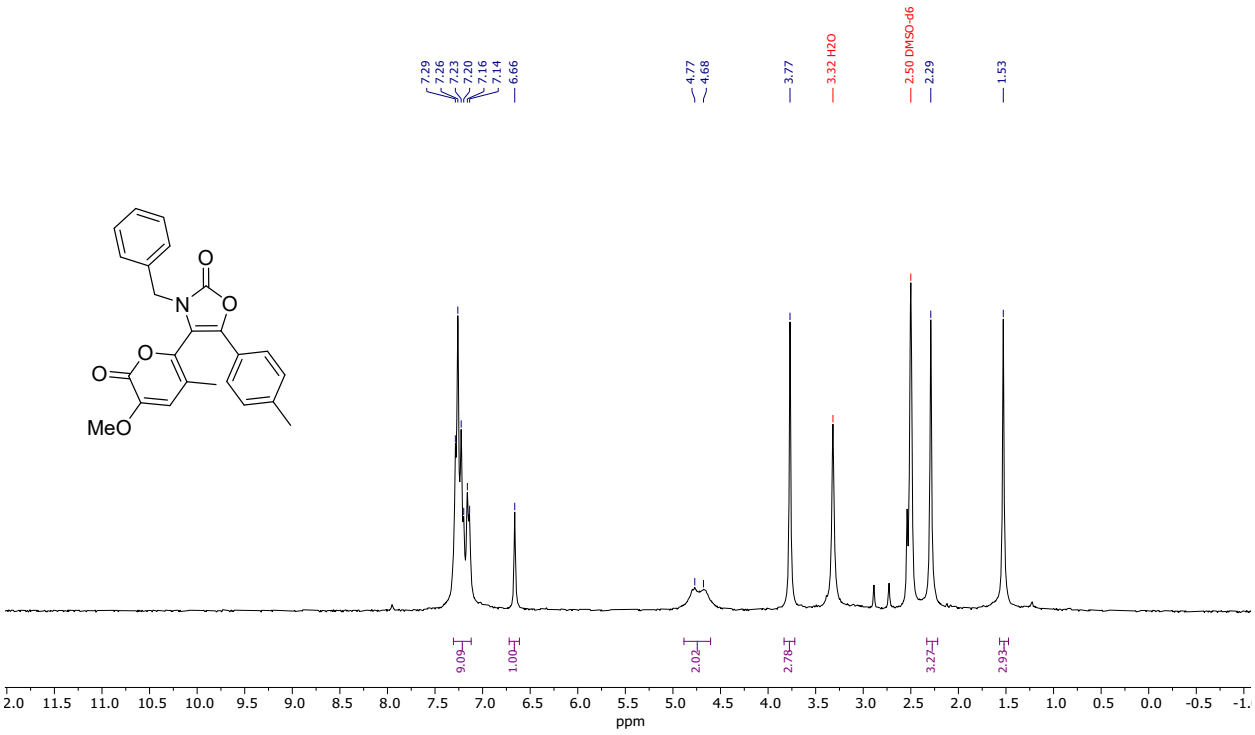
^{13}C {^{1}H} NMR spectrum (126 MHz) of **4p** in DMSO-d_6



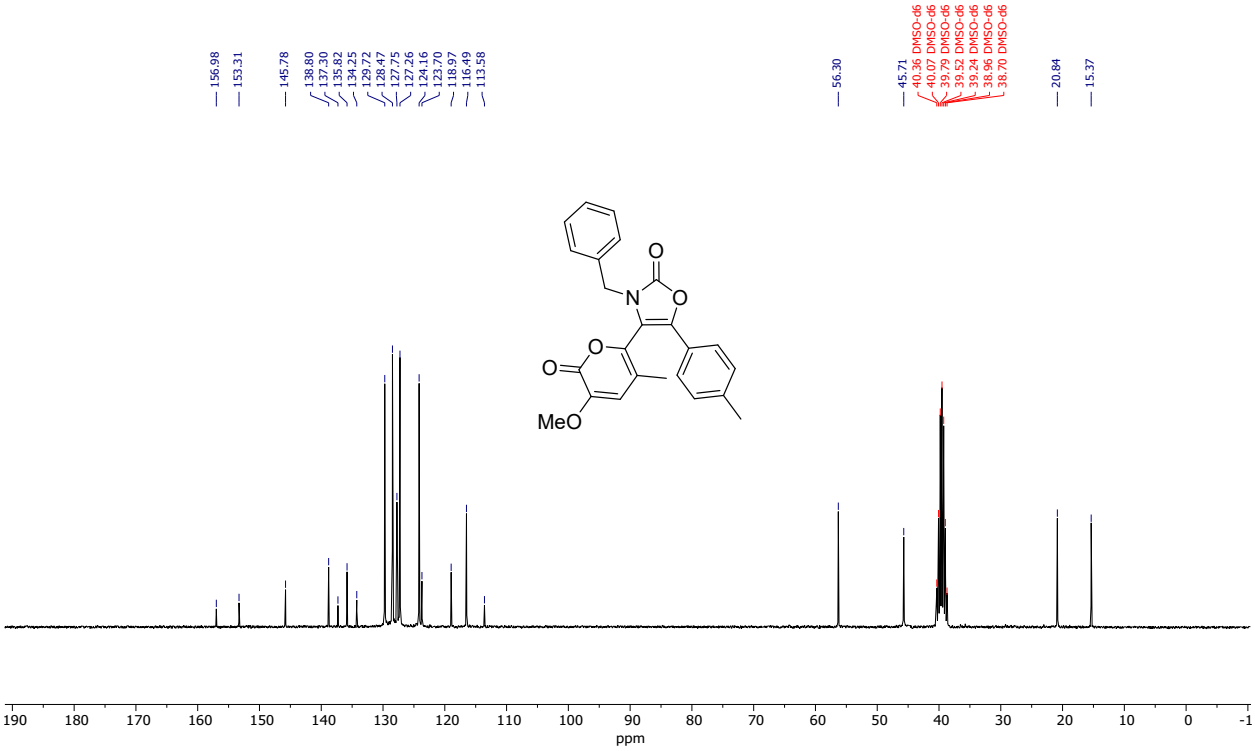
^{19}F NMR spectrum (282 MHz) of **4p** in DMSO-d_6



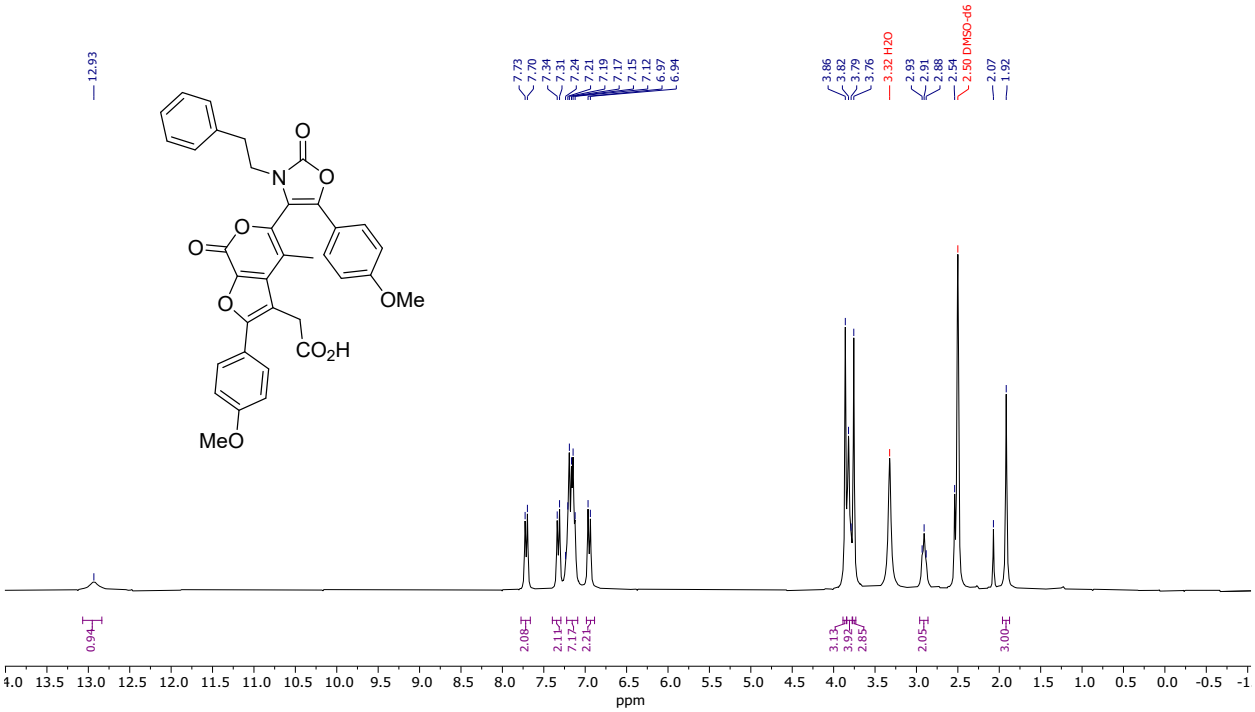
^{1}H NMR spectrum (300 MHz) of **7** in DMSO-d_6



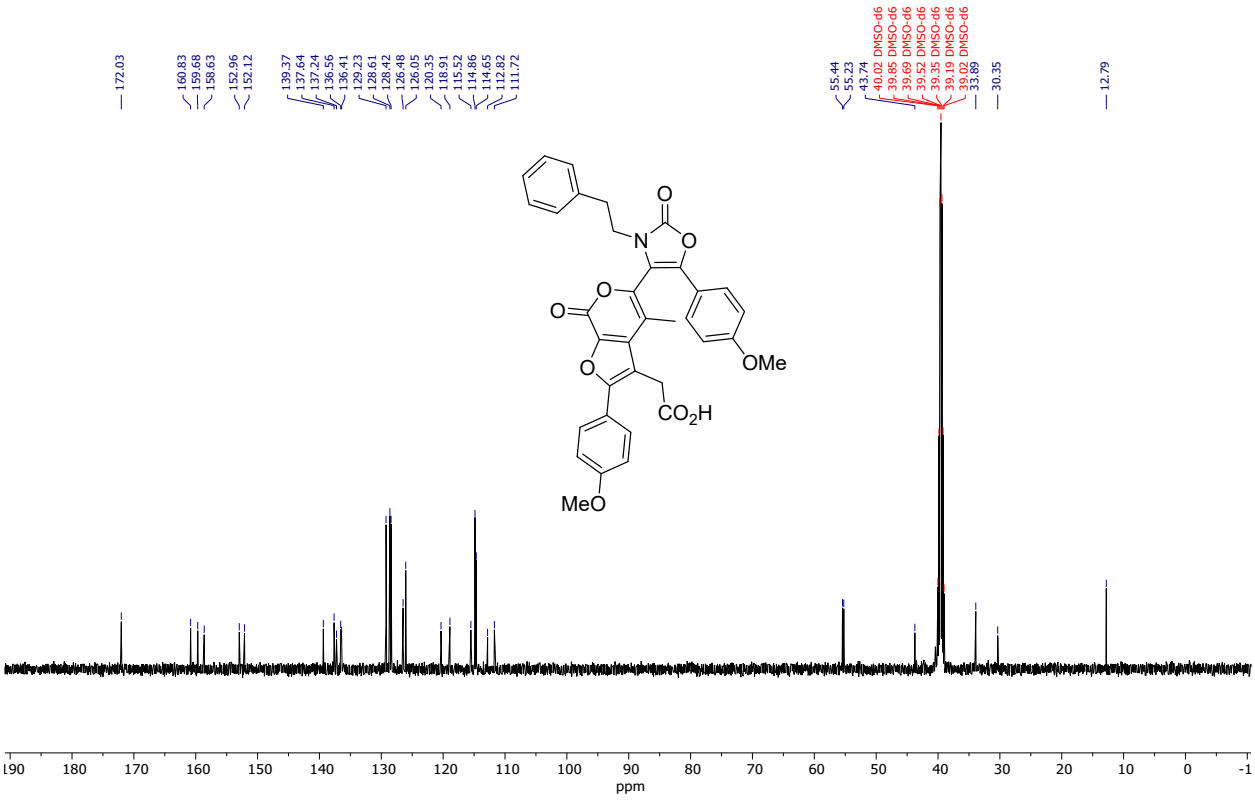
^{13}C {^{1}H} NMR spectrum (75 MHz) of **7** in DMSO-d_6



^{1}H NMR spectrum (300 MHz) of **10** in DMSO-d_6

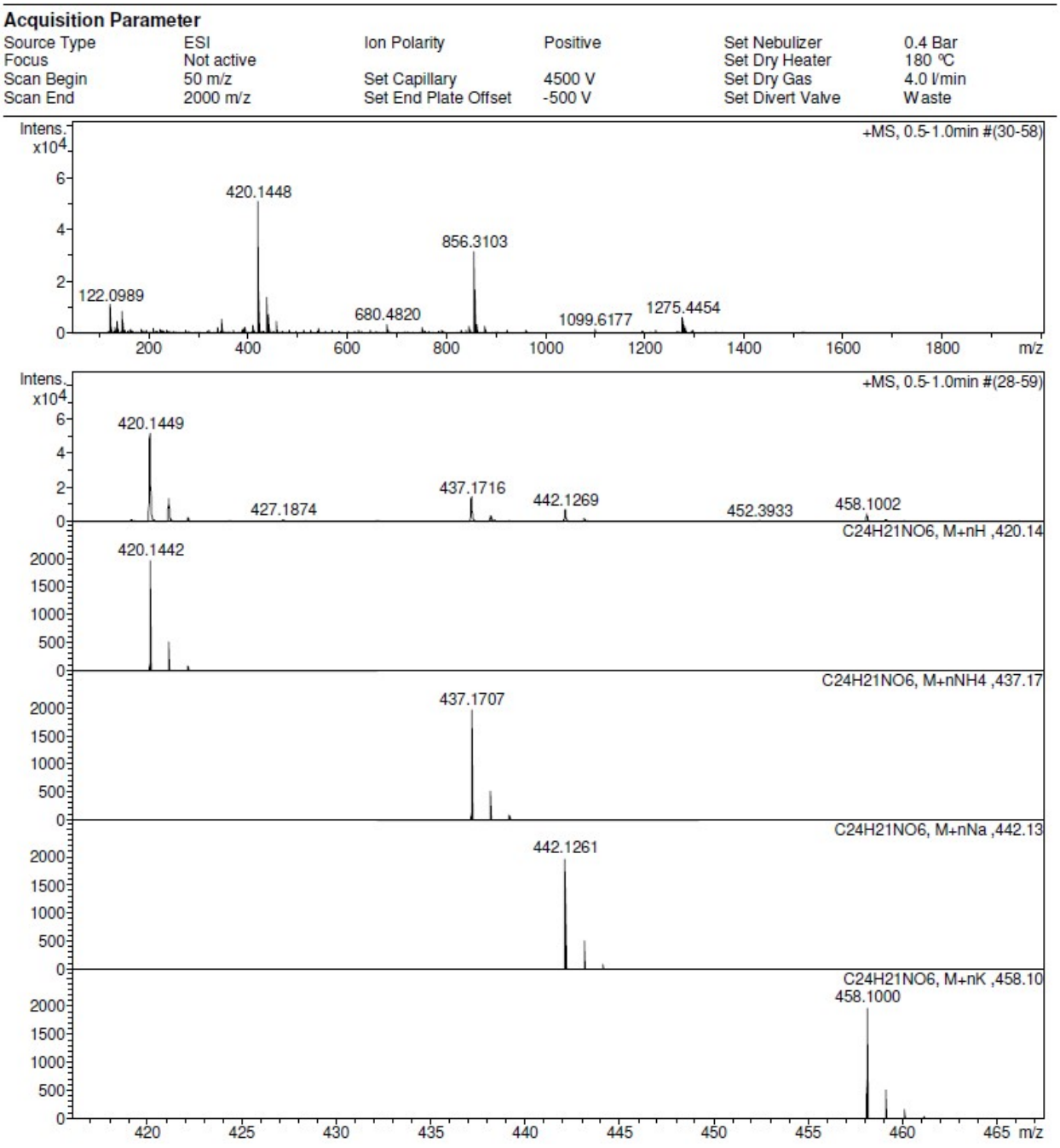


^{13}C {^{1}H} NMR spectrum (126 MHz) of **10** in DMSO-d_6



5. Copies of HRMS for all compounds

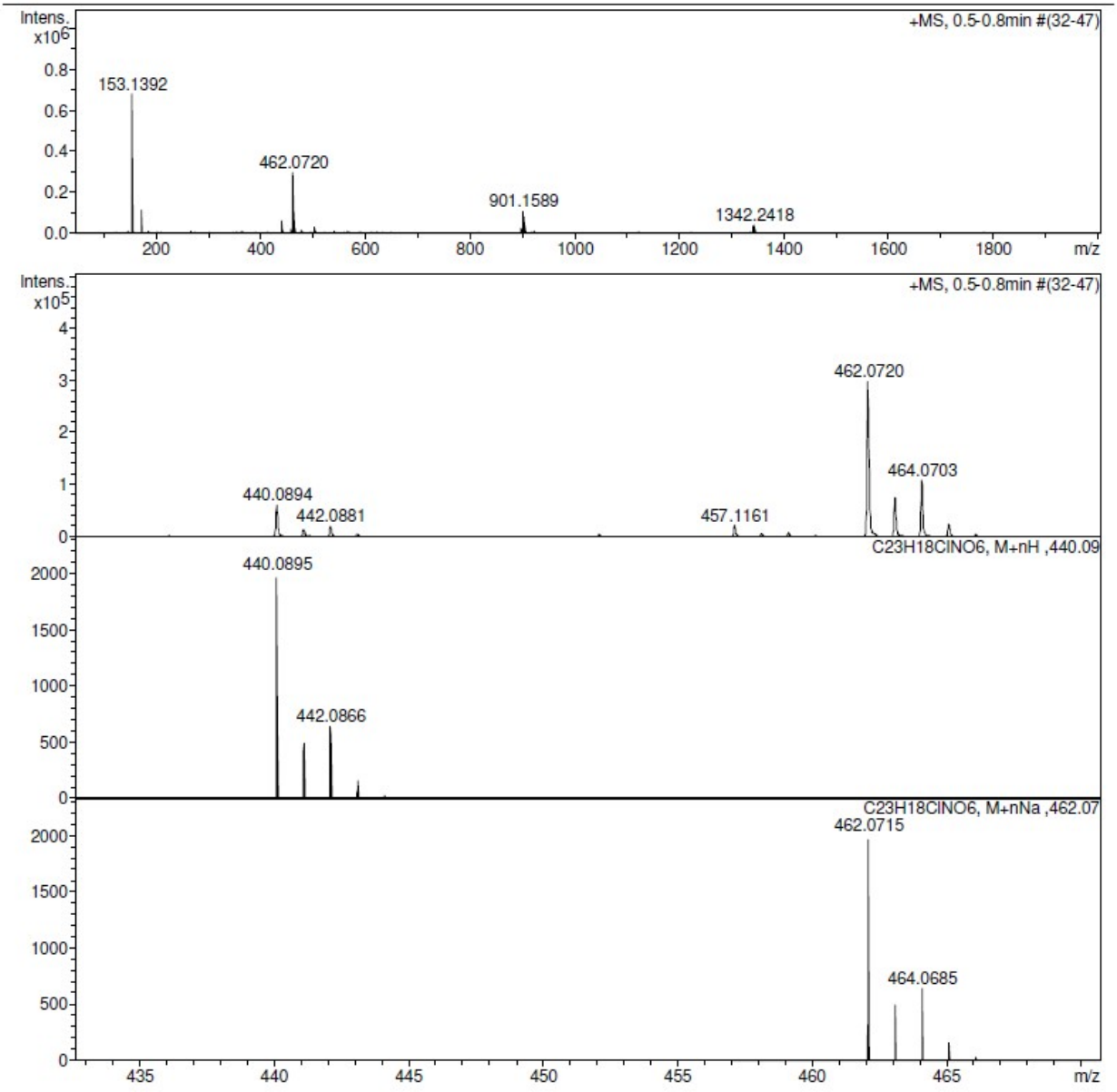
HRMS for compound **4a**



HRMS for compound **4b**

Acquisition Parameter

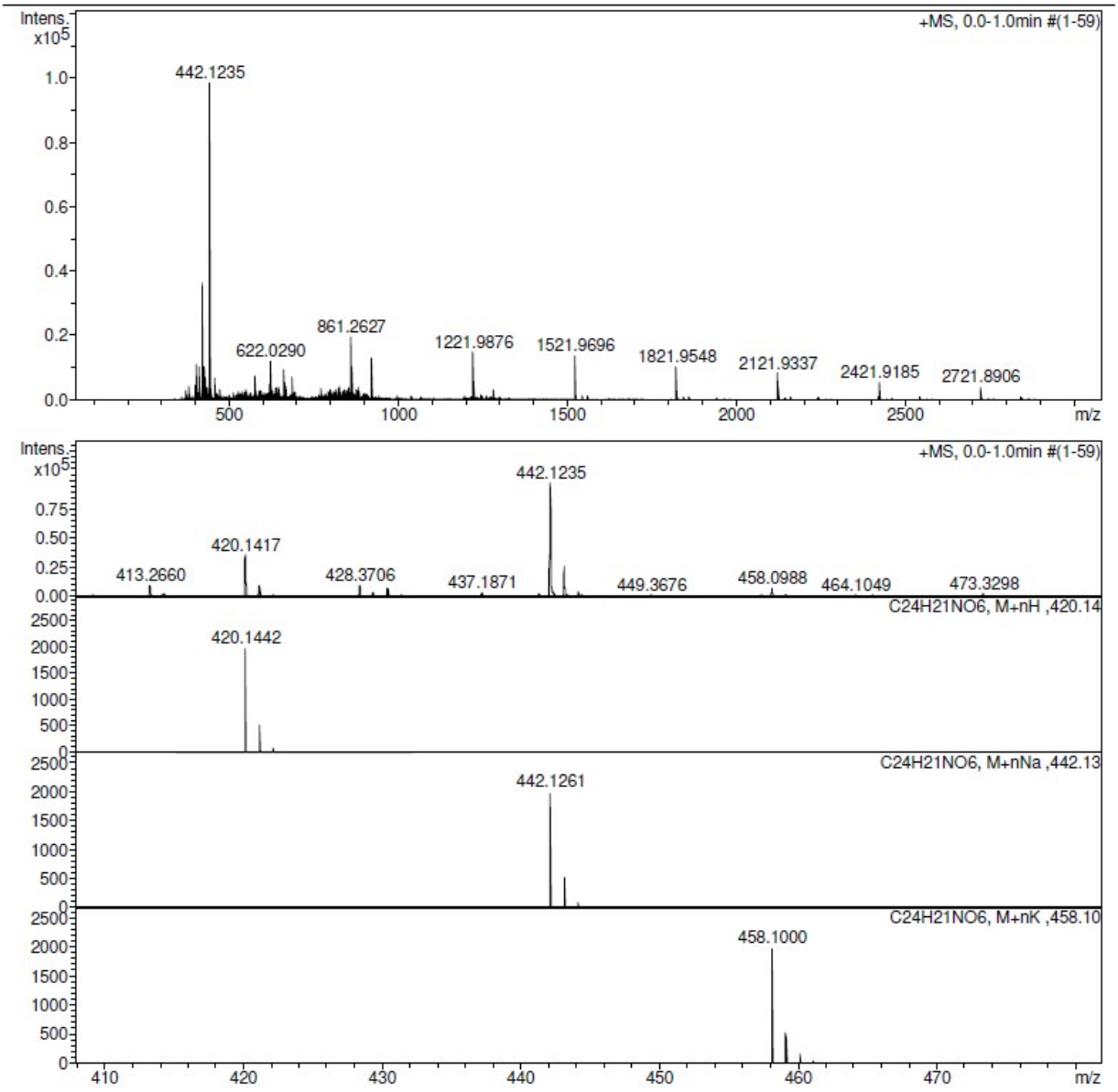
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	2000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



HRMS for compound **4c**

Acquisition Parameter

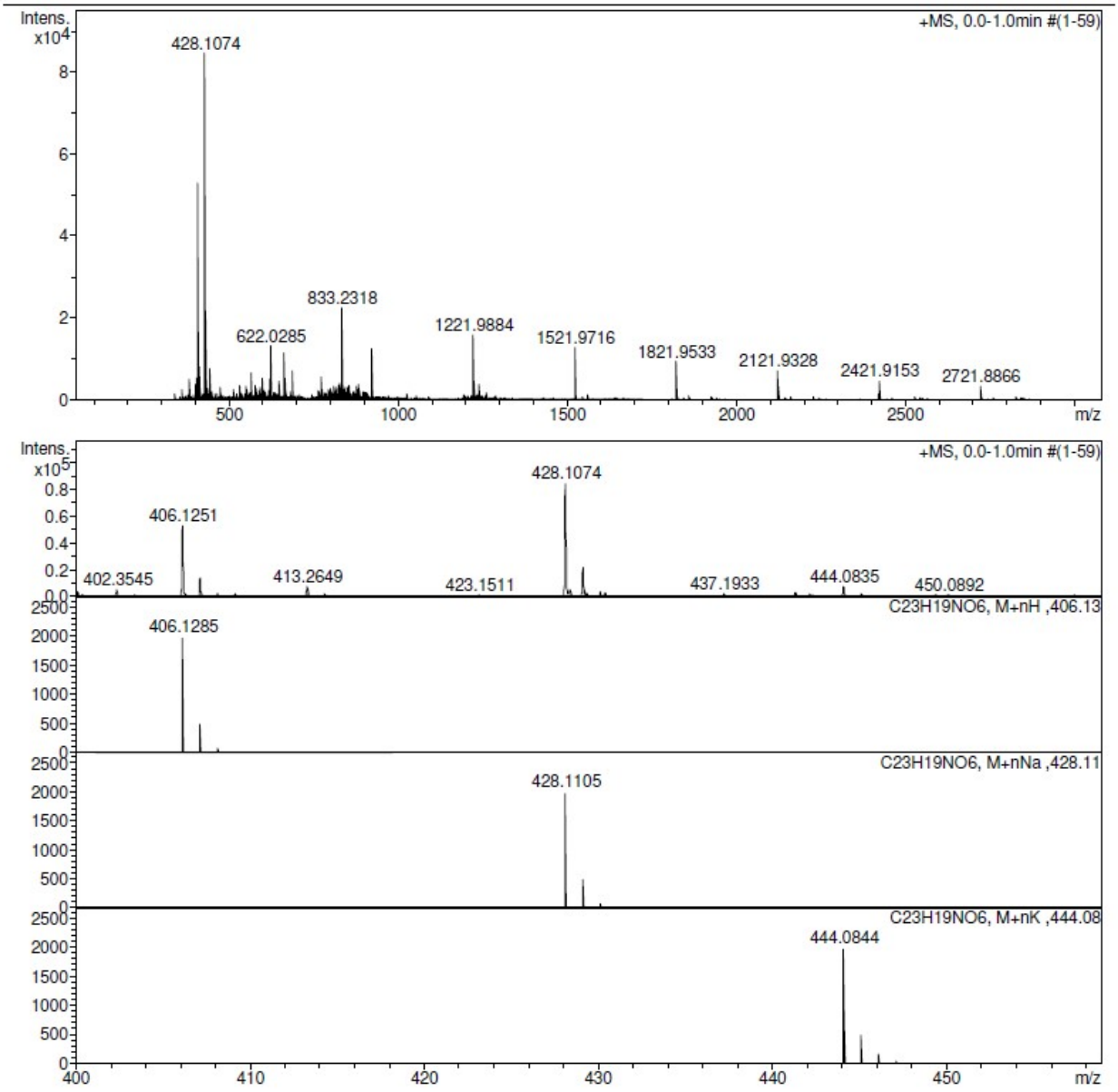
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



HRMS for compound **4d**

Acquisition Parameter

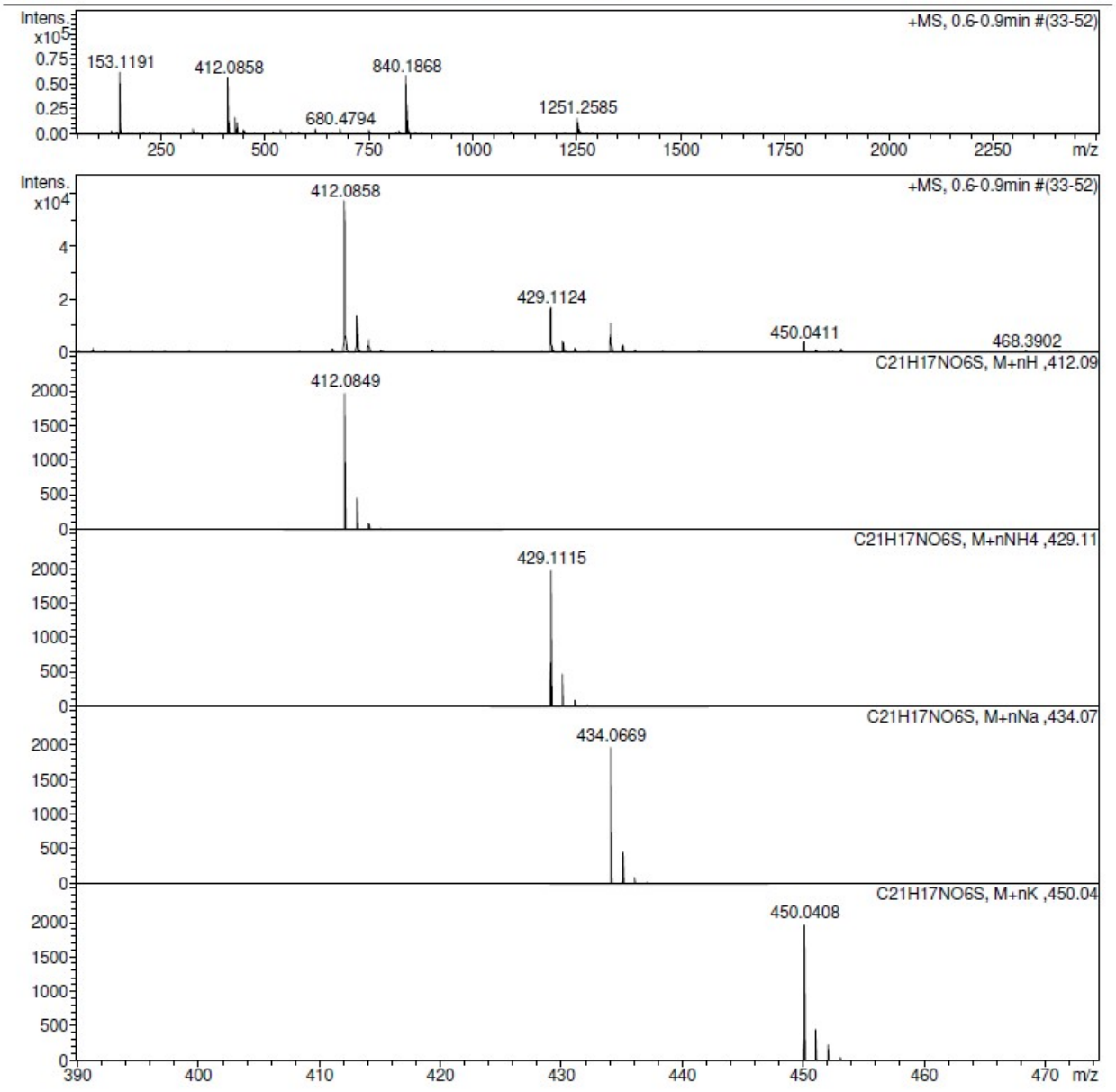
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



HRMS for compound **4e**

Acquisition Parameter

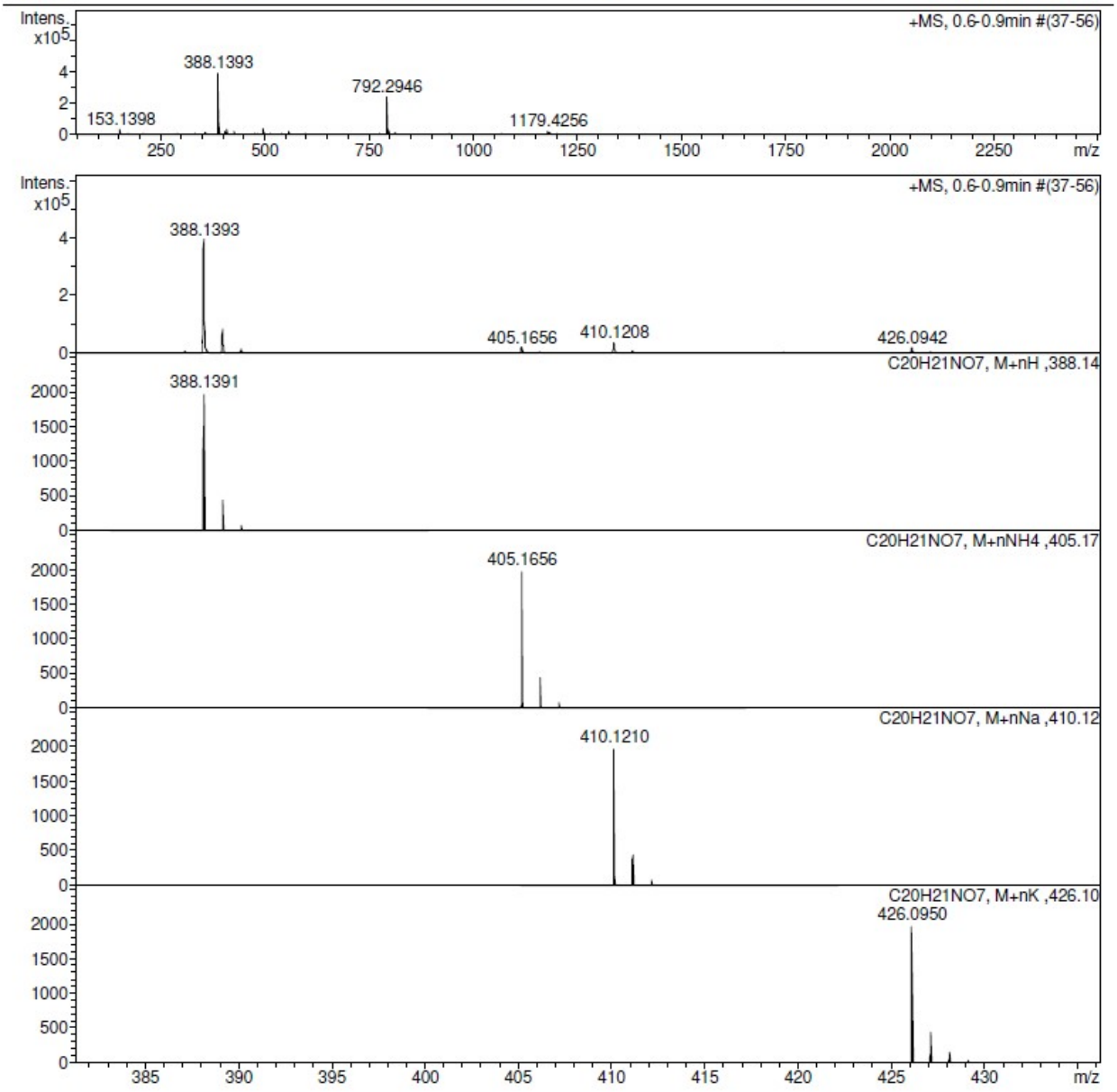
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	2500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



HRMS for compound **4f**

Acquisition Parameter

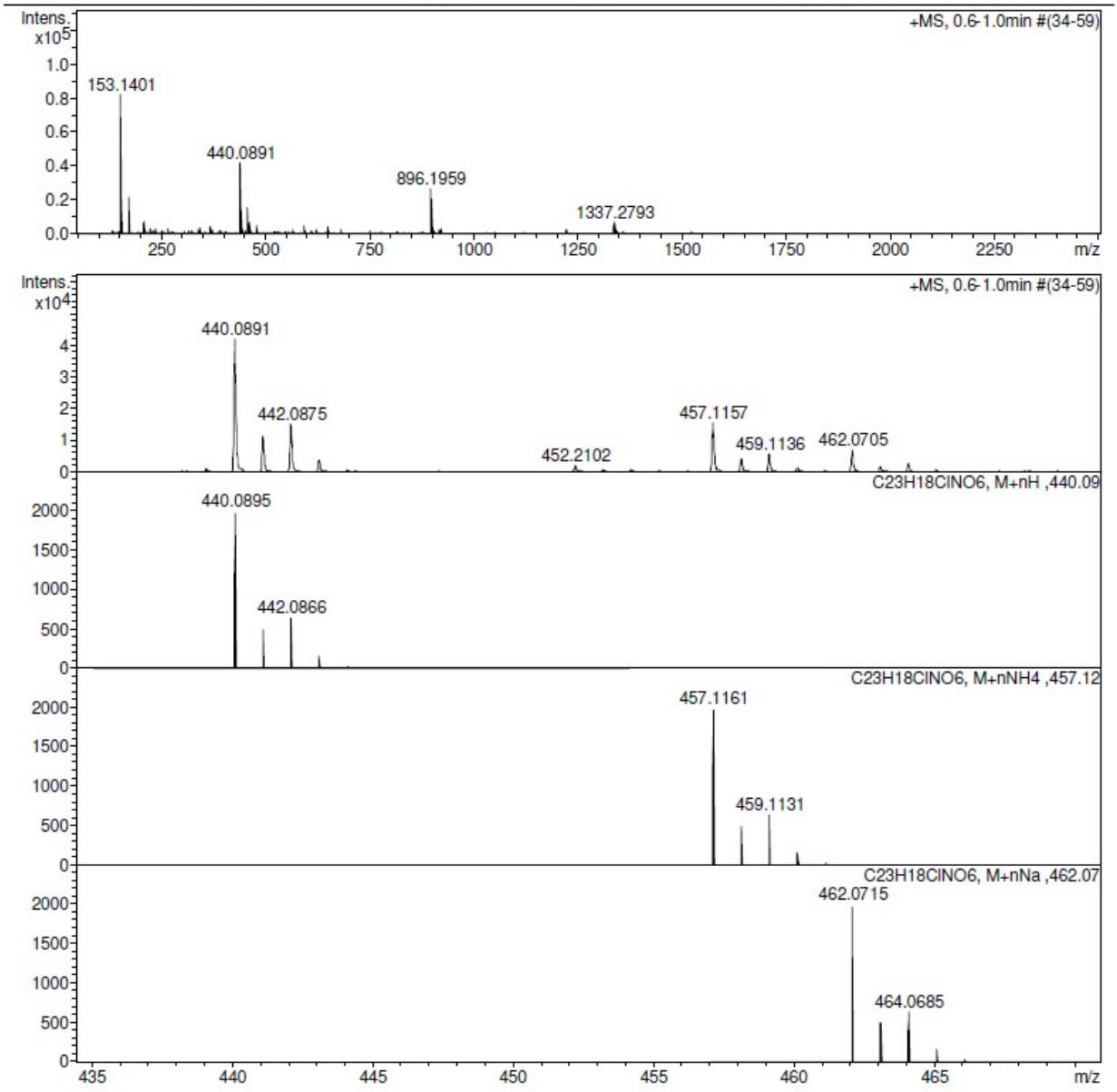
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	2500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



HRMS for compound **4g**

Acquisition Parameter

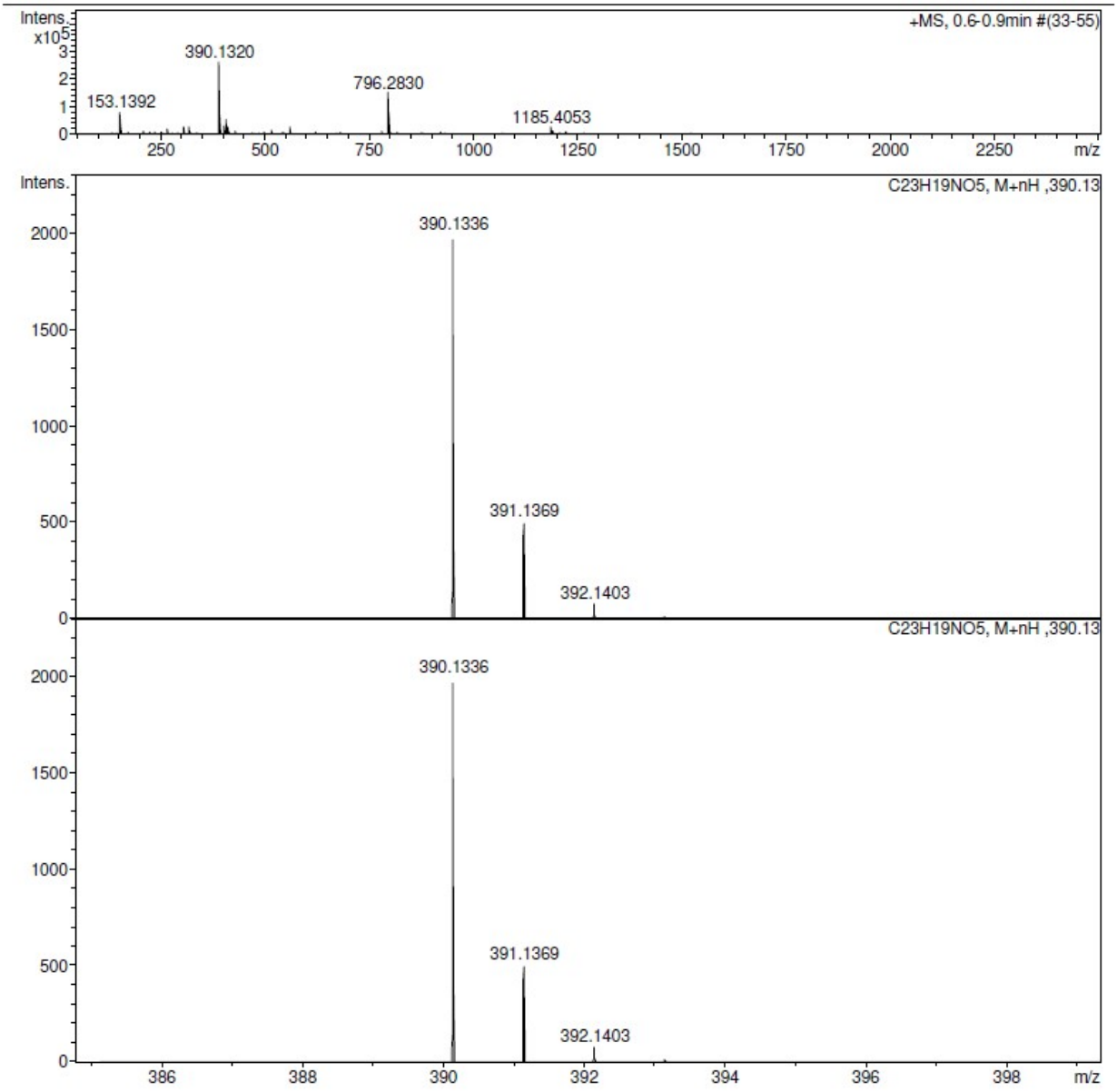
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	2500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



HRMS for compound **4h**

Acquisition Parameter

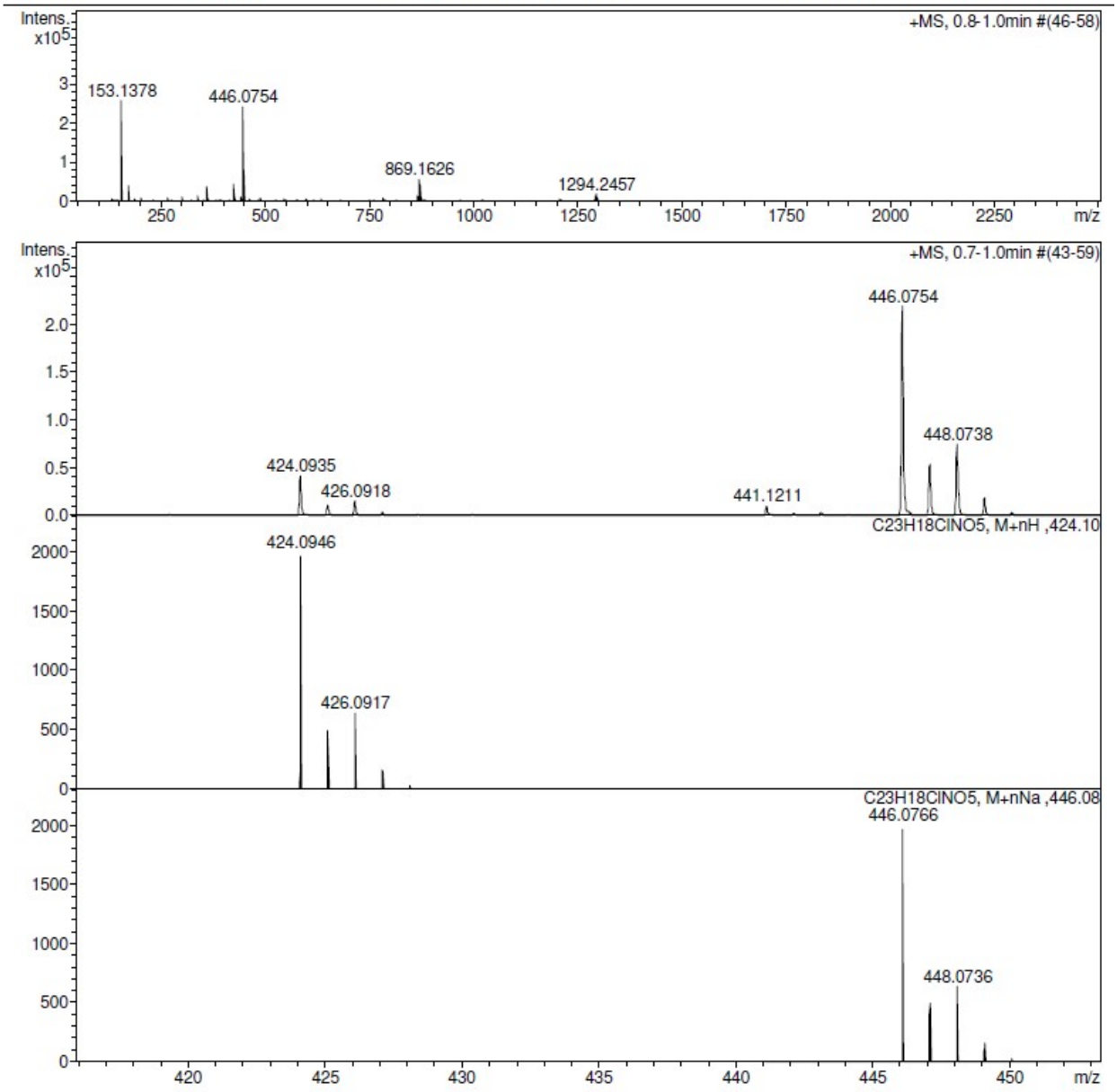
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	2500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



HRMS for compound **4i**

Acquisition Parameter

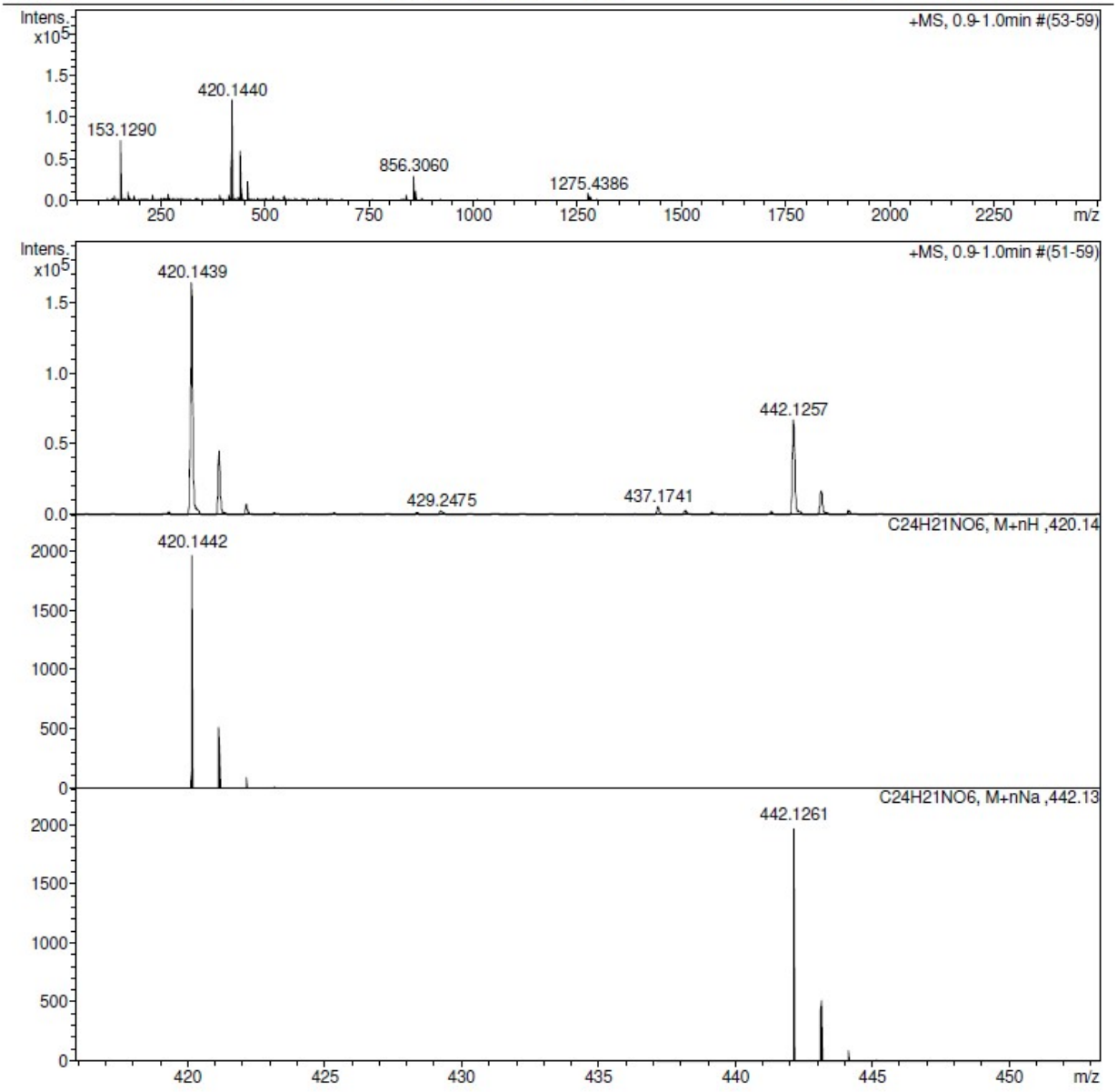
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	2500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



HRMS for compound **4j**

Acquisition Parameter

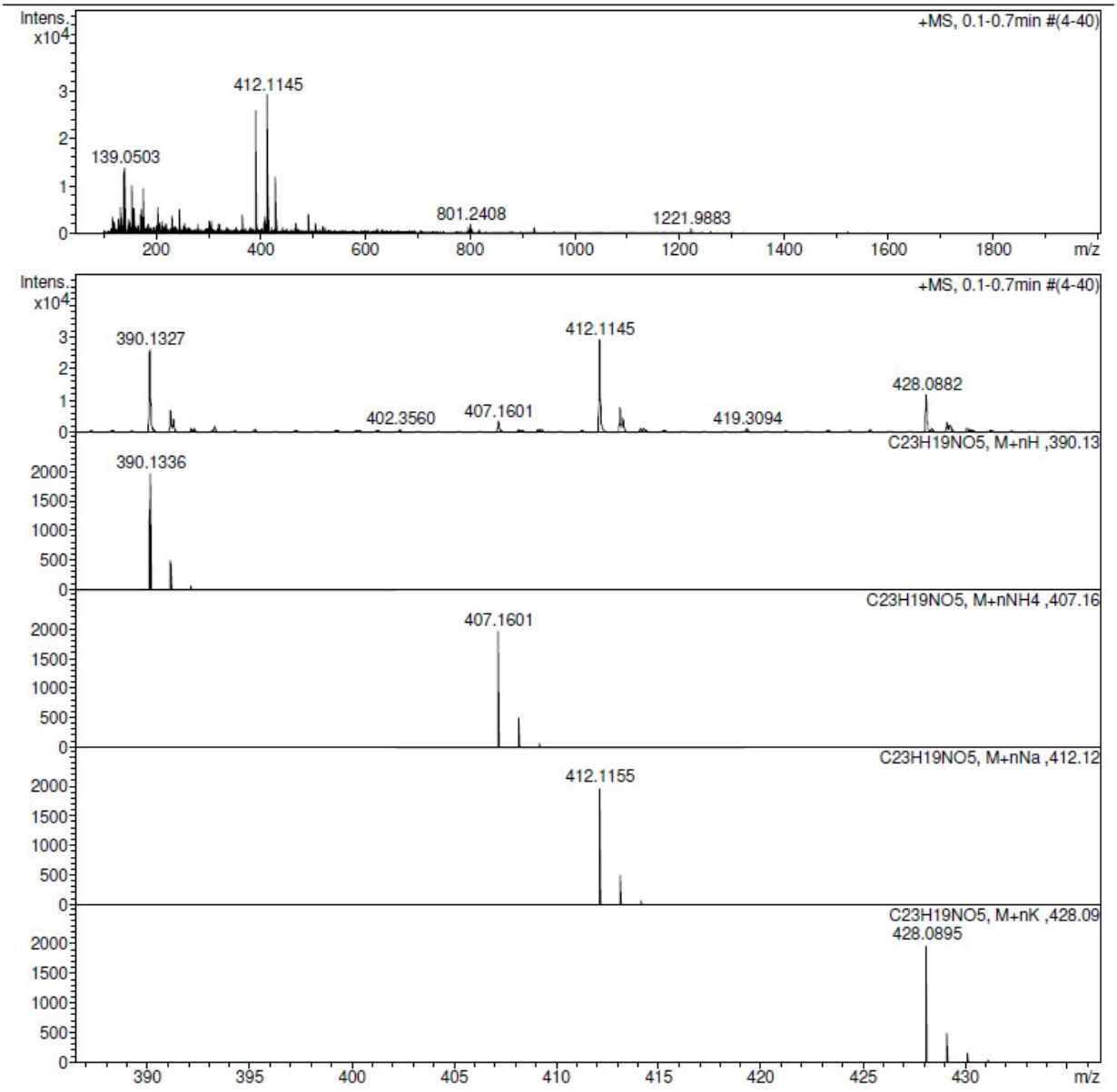
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	2500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



HRMS for compound **4k**

Acquisition Parameter

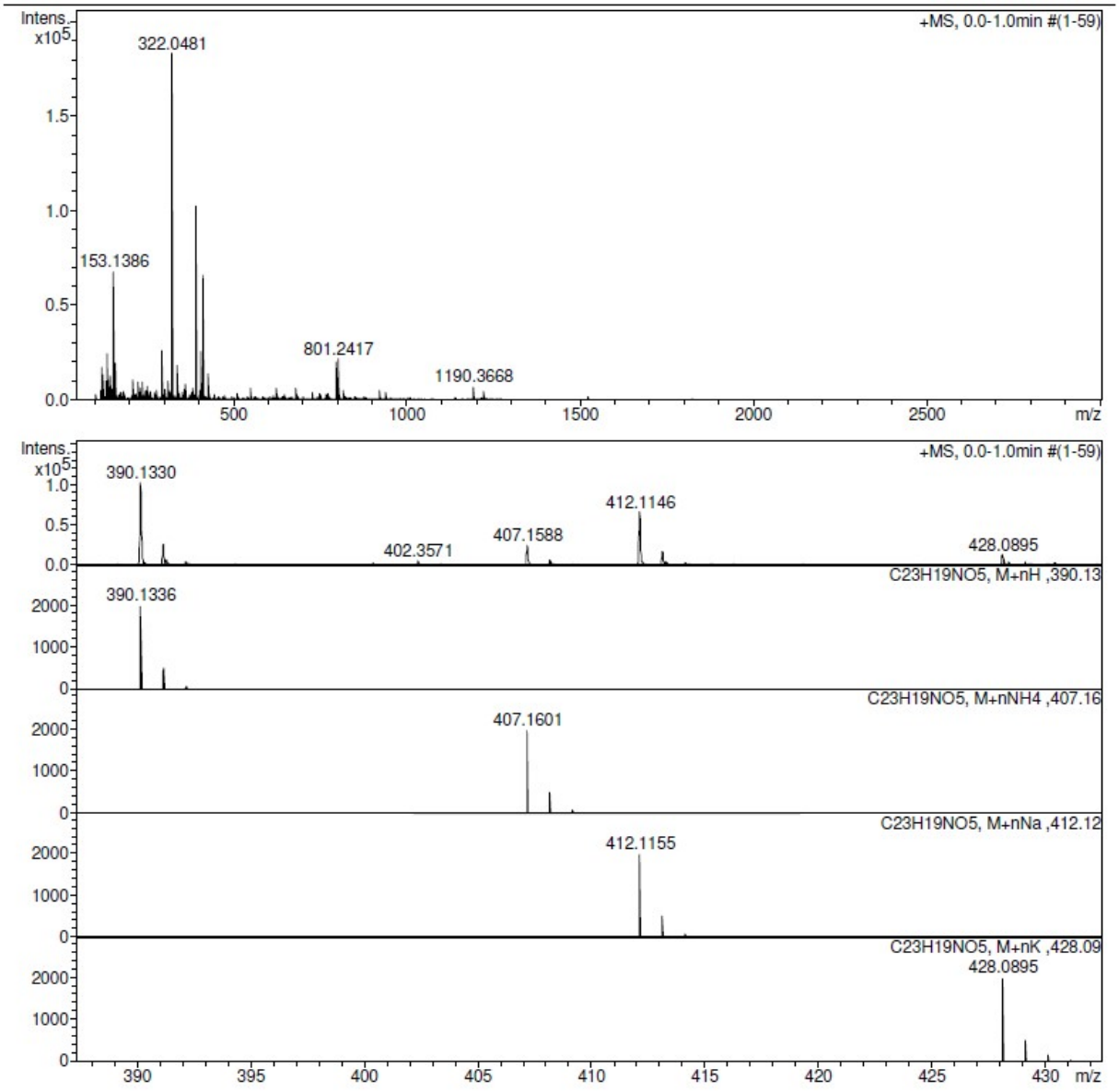
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	2000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



HRMS for compound **4l**

Acquisition Parameter

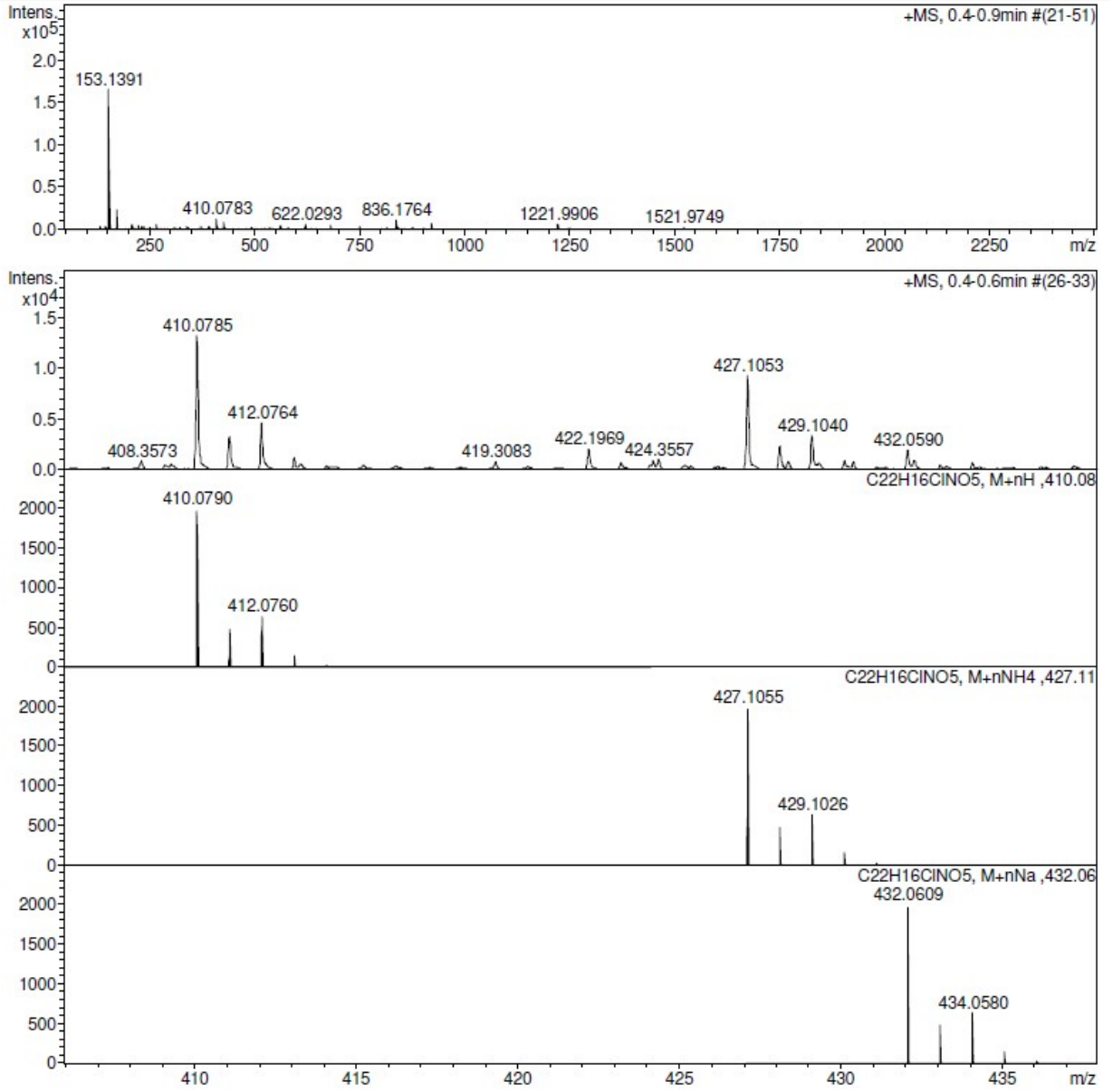
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



HRMS for compound **4m**

Acquisition Parameter

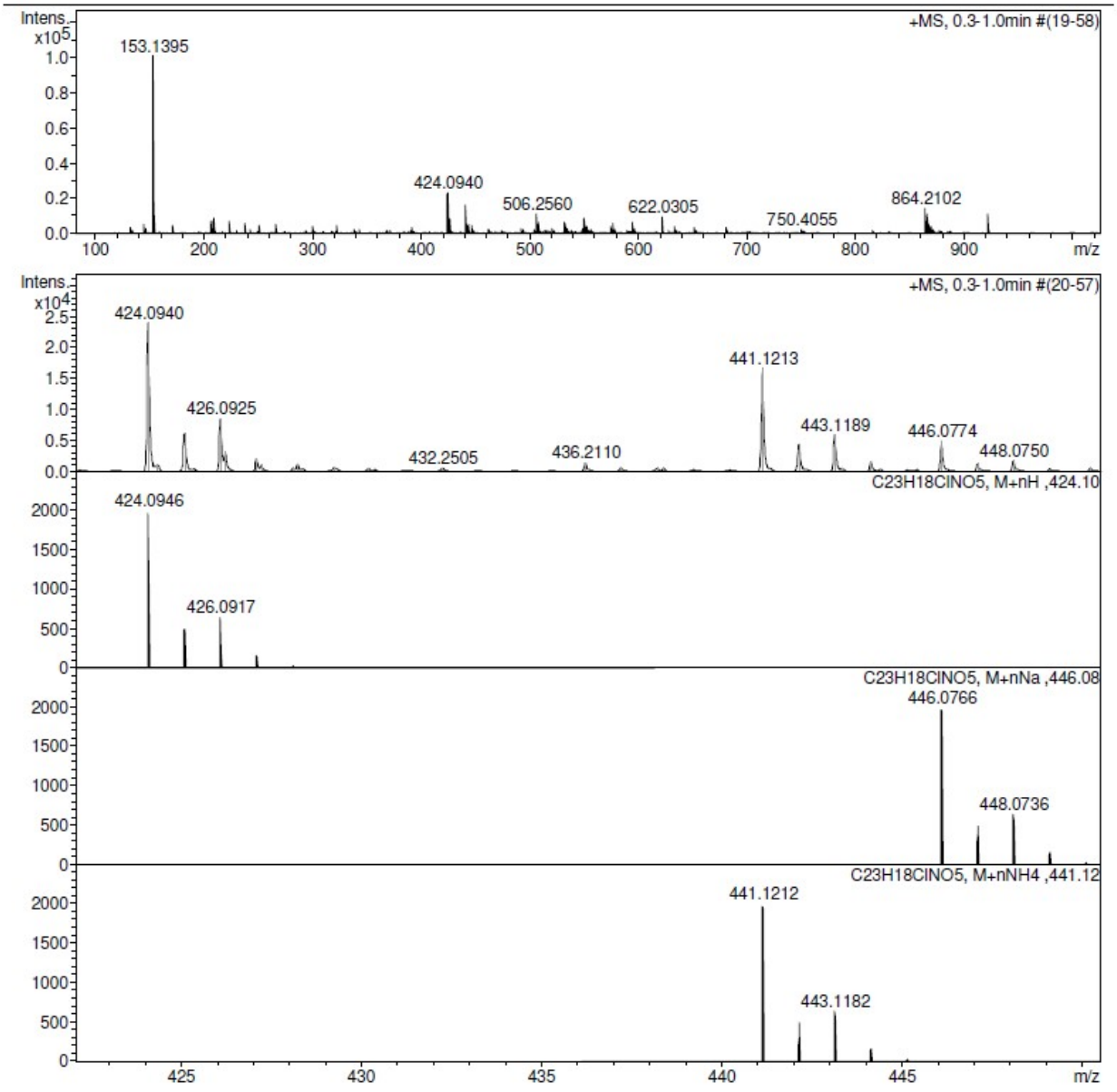
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	2500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



HRMS for compound **4n**

Acquisition Parameter

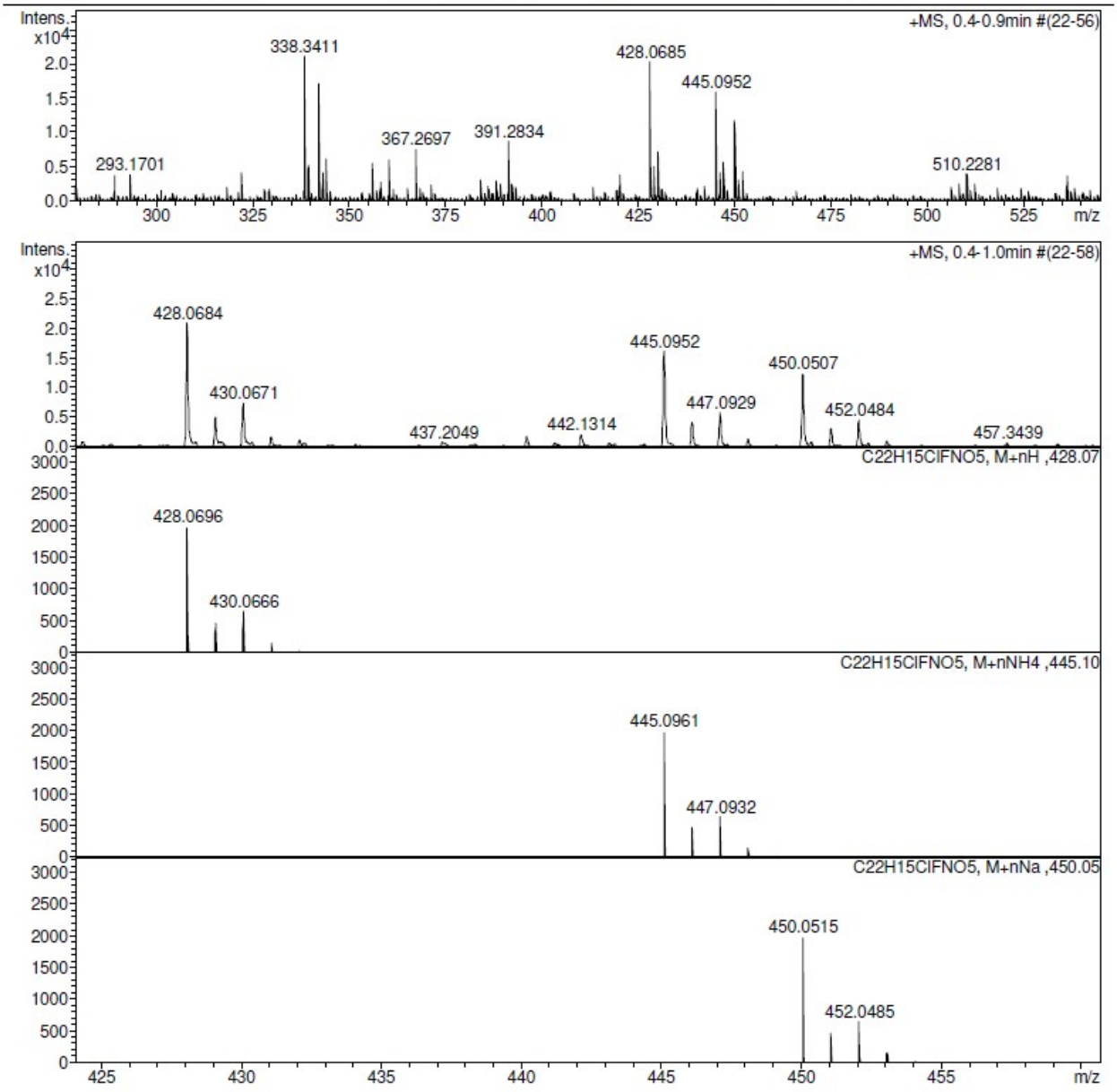
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	2500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



HRMS for compound **4o**

Acquisition Parameter

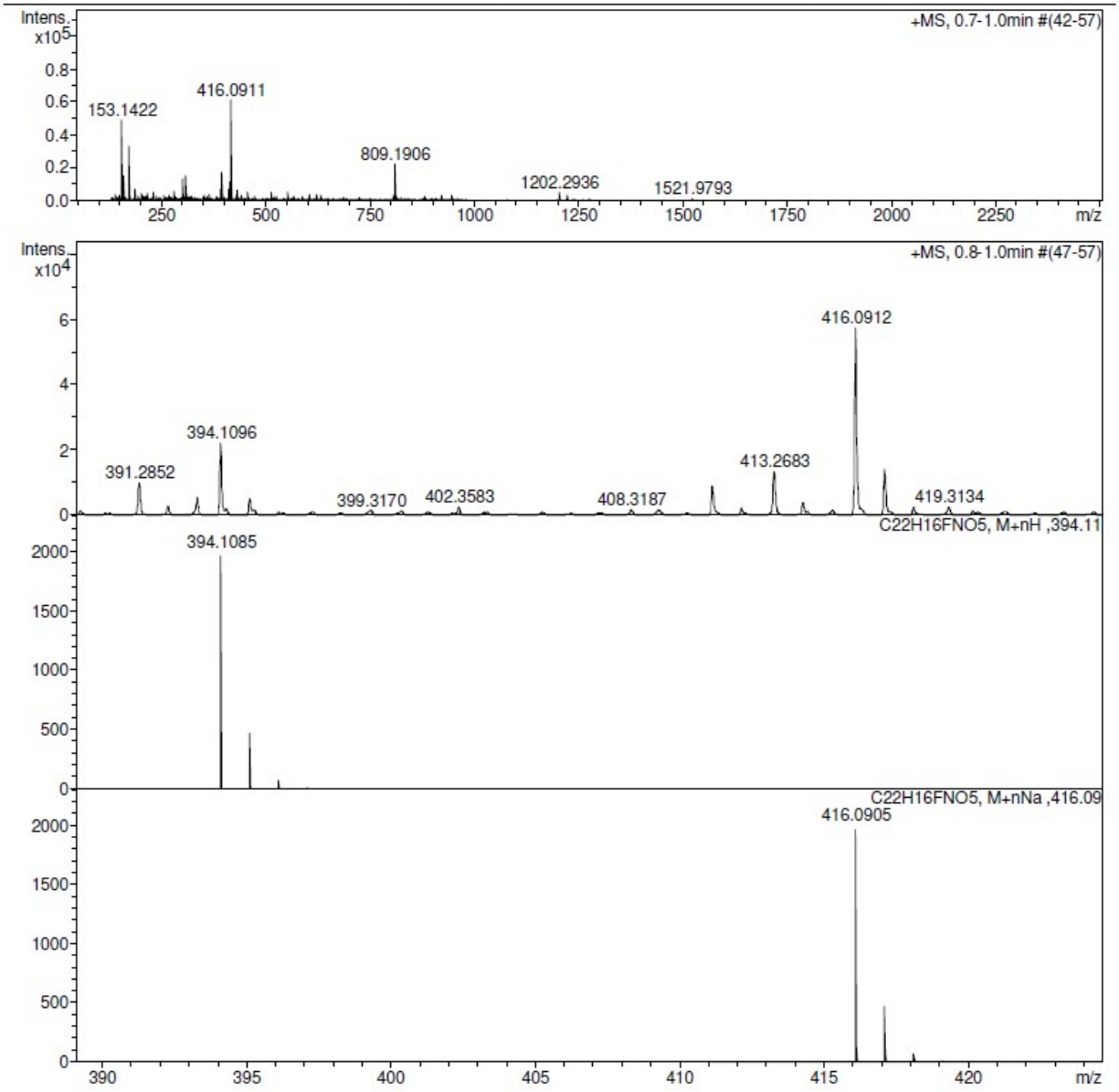
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	2500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



HRMS for compound **4p**

Acquisition Parameter

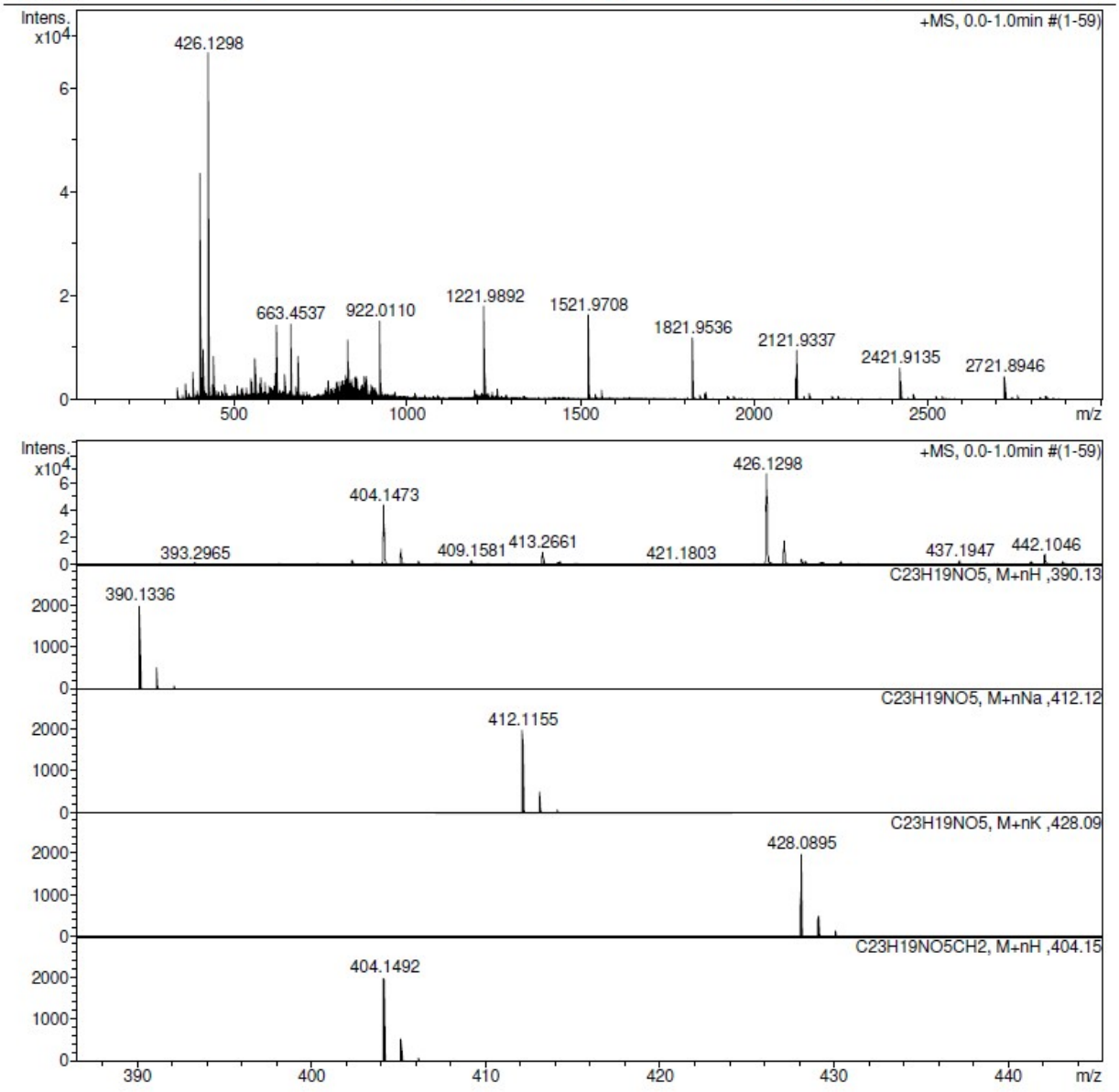
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	2500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



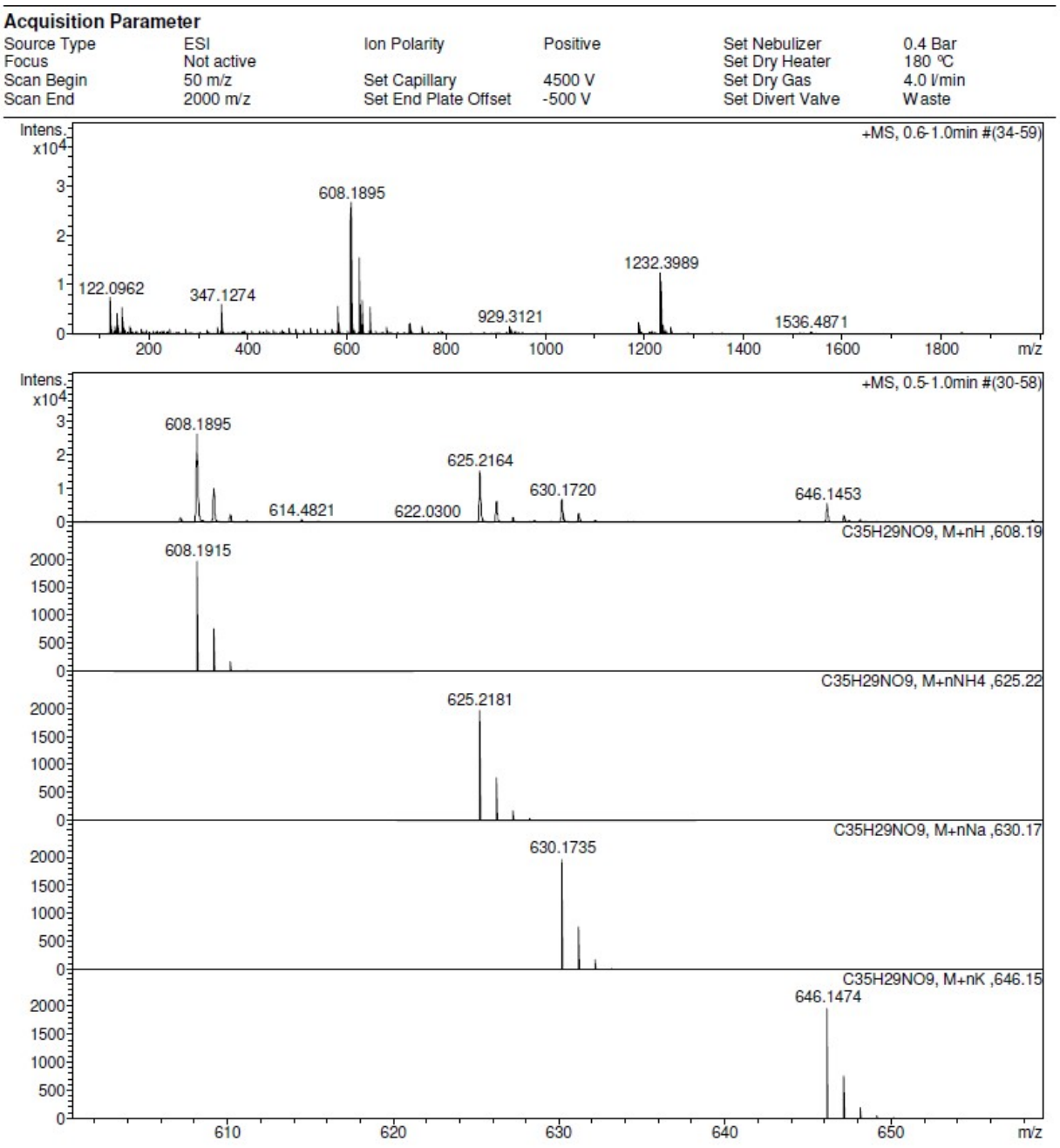
HRMS for compound **7**

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



HRMS for compound **10**



6. X-ray crystallographic data and refinement details for compound 4a

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.[2] The structure was solved by direct methods using SHELXT[3] and refined on F^2 using SHELXL-2018[4] in the OLEX2 program.[5] All non-hydrogen atoms were refined with individual anisotropic displacement parameters. Locations of hydroxy hydrogen atom (H5) was found from the electron density-difference map; this hydrogen atom was 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.

Table S1. Crystal data and structure refinement for **4a**.

Identification code	**4a**	
Empirical formula	C27 H24 N O6	
Formula weight	458.47	
Temperature	100.0(3) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 2_1/c	
Unit cell dimensions	a = 17.2259(2) Å	α= 90°.
	b = 19.8037(2) Å	β= 94.1260(10)°.
	c = 7.83380(10) Å	γ= 90°.
Volume	2665.47(5) $Å^3$	
Z	4	
Density (calculated)	1.142 g/cm^3	
Absorption coefficient	0.666 mm^{-1}	
F(000)	964	
Crystal size	0.17 x 0.06 x 0.06 mm^3	
Theta range for data collection	2.572 to 77.064°.	
Index ranges	-21<=h<=21, -16<=k<=24, -9<=l<=9	
Reflections collected	33501	
Independent reflections	5572 [R(int) = 0.0342]	
Observed reflections	4965	
Completeness to theta = 67.684°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.78302	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5572 / 3 / 314	
Goodness-of-fit on F^2	1.041	
Final R indices [I>2sigma(I)]	R1 = 0.0480, wR2 = 0.1347	
R indices (all data)	R1 = 0.0519, wR2 = 0.1377	
Extinction coefficient	0.00104(17)	
Largest diff. peak and hole	0.221 and -0.207 $e.Å^{-3}$	
CCDC	2304109	

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

	x	y	z	U(eq)
O(1)	5421(1)	5492(1)	6876(1)	42(1)
O(2)	4196(1)	5612(1)	7771(2)	47(1)
O(3)	5450(1)	3258(1)	7213(1)	38(1)
O(4)	5140(1)	2190(1)	6617(2)	46(1)
O(5)	6483(1)	1730(1)	8437(2)	46(1)
O(6)	8906(1)	5505(1)	4640(2)	56(1)
N(1)	4882(1)	4606(1)	8004(2)	40(1)
C(1)	5961(1)	4963(1)	6915(2)	40(1)
C(2)	5637(1)	4418(1)	7615(2)	39(1)
C(3)	4766(1)	5263(1)	7572(2)	41(1)
C(4)	6719(1)	5114(1)	6316(2)	40(1)
C(5)	7152(1)	4618(1)	5532(2)	44(1)
C(6)	7872(1)	4766(1)	4997(2)	48(1)
C(7)	8183(1)	5416(1)	5222(2)	46(1)
C(8)	7763(1)	5910(1)	5990(2)	45(1)
C(9)	7036(1)	5761(1)	6533(2)	42(1)
C(10)	9234(1)	6165(1)	4796(3)	68(1)
C(11)	5946(1)	3741(1)	7969(2)	37(1)
C(12)	5599(1)	2580(1)	7329(2)	37(1)
C(13)	6317(1)	2391(1)	8298(2)	36(1)
C(14)	6791(1)	2865(1)	9035(2)	38(1)
C(15)	6607(1)	3573(1)	8887(2)	37(1)
C(16)	7159(1)	4077(1)	9748(2)	44(1)
C(17)	4321(1)	4221(1)	8937(2)	40(1)
C(18)	3675(1)	3921(1)	7739(2)	45(1)
C(19)	3067(1)	3579(1)	8725(2)	45(1)
C(20)	2337(1)	3862(1)	8816(2)	51(1)
C(21)	1764(1)	3542(1)	9683(2)	68(1)
C(22)	1931(2)	2931(1)	10488(2)	79(1)
C(23)	2654(2)	2657(1)	10439(2)	77(1)
C(24)	3226(1)	2968(1)	9575(2)	60(1)
C(25)	9315(1)	4892(2)	9063(3)	86(1)
C(26)	9347(1)	4848(2)	10817(3)	88(1)
C(27)	10033(1)	4956(1)	11756(3)	65(1)

Table S3. Bond lengths [Å] and angles [°] for **4a**.

O(1)-C(1)	1.3992(17)	C(17)-H(17A)	0.9900
O(1)-C(3)	1.365(2)	C(17)-H(17B)	0.9900
O(2)-C(3)	1.2190(19)	C(17)-C(18)	1.525(2)
O(3)-C(11)	1.3877(16)	C(18)-H(18A)	0.9900
O(3)-C(12)	1.3679(16)	C(18)-H(18B)	0.9900
O(4)-C(12)	1.2119(17)	C(18)-C(19)	1.506(2)
O(5)-H(5)	0.91(3)	C(19)-C(20)	1.382(3)
O(5)-C(13)	1.3432(16)	C(19)-C(24)	1.398(2)
O(6)-C(7)	1.367(2)	C(20)-H(20)	0.9500
O(6)-C(10)	1.426(2)	C(20)-C(21)	1.390(3)
N(1)-C(2)	1.407(2)	C(21)-H(21)	0.9500
N(1)-C(3)	1.3558(18)	C(21)-C(22)	1.386(3)
N(1)-C(17)	1.467(2)	C(22)-H(22)	0.9500
C(1)-C(2)	1.350(2)	C(22)-C(23)	1.361(4)
C(1)-C(4)	1.451(2)	C(23)-H(23)	0.9500
C(2)-C(11)	1.4605(18)	C(23)-C(24)	1.380(3)
C(4)-C(5)	1.402(2)	C(24)-H(24)	0.9500
C(4)-C(9)	1.398(2)	C(25)-H(25)	0.9500
C(5)-H(5A)	0.9500	C(25)-C(26)	1.374(2)
C(5)-C(6)	1.369(2)	C(25)-C(27)#1	1.366(2)
C(6)-H(6)	0.9500	C(26)-H(26)	0.9500
C(6)-C(7)	1.400(2)	C(26)-C(27)	1.364(2)
C(7)-C(8)	1.381(2)	C(27)-H(27)	0.9500
C(8)-H(8)	0.9500	C(3)-O(1)-C(1)	108.10(11)
C(8)-C(9)	1.384(2)	C(12)-O(3)-C(11)	122.82(11)
C(9)-H(9)	0.9500	C(13)-O(5)-H(5)	112.8(15)
C(10)-H(10A)	0.9800	C(7)-O(6)-C(10)	117.10(15)
C(10)-H(10B)	0.9800	C(2)-N(1)-C(17)	128.50(12)
C(10)-H(10C)	0.9800	C(3)-N(1)-C(2)	108.84(12)
C(11)-C(15)	1.344(2)	C(3)-N(1)-C(17)	122.15(13)
C(12)-C(13)	1.453(2)	O(1)-C(1)-C(4)	116.83(12)
C(13)-C(14)	1.346(2)	C(2)-C(1)-O(1)	108.30(14)
C(14)-H(14)	0.9500	C(2)-C(1)-C(4)	134.78(14)
C(14)-C(15)	1.4399(19)	N(1)-C(2)-C(11)	122.14(13)
C(15)-C(16)	1.5046(19)	C(1)-C(2)-N(1)	106.92(13)
C(16)-H(16A)	0.9800	C(1)-C(2)-C(11)	130.95(15)
C(16)-H(16B)	0.9800	O(2)-C(3)-O(1)	124.06(13)
C(16)-H(16C)	0.9800	O(2)-C(3)-N(1)	128.11(15)

N(1)-C(3)-O(1)	107.82(13)	C(15)-C(16)-H(16A)	109.5
C(5)-C(4)-C(1)	121.11(13)	C(15)-C(16)-H(16B)	109.5
C(9)-C(4)-C(1)	120.13(14)	C(15)-C(16)-H(16C)	109.5
C(9)-C(4)-C(5)	118.75(15)	H(16A)-C(16)-H(16B)	109.5
C(4)-C(5)-H(5A)	119.8	H(16A)-C(16)-H(16C)	109.5
C(6)-C(5)-C(4)	120.36(14)	H(16B)-C(16)-H(16C)	109.5
C(6)-C(5)-H(5A)	119.8	N(1)-C(17)-H(17A)	109.2
C(5)-C(6)-H(6)	119.8	N(1)-C(17)-H(17B)	109.2
C(5)-C(6)-C(7)	120.35(16)	N(1)-C(17)-C(18)	111.97(12)
C(7)-C(6)-H(6)	119.8	H(17A)-C(17)-H(17B)	107.9
O(6)-C(7)-C(6)	115.23(15)	C(18)-C(17)-H(17A)	109.2
O(6)-C(7)-C(8)	124.82(15)	C(18)-C(17)-H(17B)	109.2
C(8)-C(7)-C(6)	119.96(16)	C(17)-C(18)-H(18A)	109.4
C(7)-C(8)-H(8)	120.1	C(17)-C(18)-H(18B)	109.4
C(7)-C(8)-C(9)	119.78(14)	H(18A)-C(18)-H(18B)	108.0
C(9)-C(8)-H(8)	120.1	C(19)-C(18)-C(17)	111.32(12)
C(4)-C(9)-H(9)	119.6	C(19)-C(18)-H(18A)	109.4
C(8)-C(9)-C(4)	120.80(15)	C(19)-C(18)-H(18B)	109.4
C(8)-C(9)-H(9)	119.6	C(20)-C(19)-C(18)	120.81(14)
O(6)-C(10)-H(10A)	109.5	C(20)-C(19)-C(24)	118.32(17)
O(6)-C(10)-H(10B)	109.5	C(24)-C(19)-C(18)	120.87(17)
O(6)-C(10)-H(10C)	109.5	C(19)-C(20)-H(20)	119.3
H(10A)-C(10)-H(10B)	109.5	C(19)-C(20)-C(21)	121.37(18)
H(10A)-C(10)-H(10C)	109.5	C(21)-C(20)-H(20)	119.3
H(10B)-C(10)-H(10C)	109.5	C(20)-C(21)-H(21)	120.4
O(3)-C(11)-C(2)	110.29(12)	C(22)-C(21)-C(20)	119.3(2)
C(15)-C(11)-O(3)	121.92(12)	C(22)-C(21)-H(21)	120.4
C(15)-C(11)-C(2)	127.79(13)	C(21)-C(22)-H(22)	120.2
O(3)-C(12)-C(13)	115.85(12)	C(23)-C(22)-C(21)	119.6(2)
O(4)-C(12)-O(3)	118.82(13)	C(23)-C(22)-H(22)	120.2
O(4)-C(12)-C(13)	125.32(13)	C(22)-C(23)-H(23)	119.2
O(5)-C(13)-C(12)	117.56(12)	C(22)-C(23)-C(24)	121.6(2)
O(5)-C(13)-C(14)	121.69(13)	C(24)-C(23)-H(23)	119.2
C(14)-C(13)-C(12)	120.74(13)	C(19)-C(24)-H(24)	120.1
C(13)-C(14)-H(14)	119.3	C(23)-C(24)-C(19)	119.8(2)
C(13)-C(14)-C(15)	121.40(13)	C(23)-C(24)-H(24)	120.1
C(15)-C(14)-H(14)	119.3	C(26)-C(25)-H(25)	119.7
C(11)-C(15)-C(14)	117.26(13)	C(27)#1-C(25)-H(25)	119.7
C(11)-C(15)-C(16)	123.97(13)	C(27)#1-C(25)-C(26)	120.61(19)
C(14)-C(15)-C(16)	118.77(13)	C(25)-C(26)-H(26)	120.0

C(27)-C(26)-C(25)	120.0(2)	C(26)-C(27)-C(25)#1	119.40(18)
C(27)-C(26)-H(26)	120.0	C(26)-C(27)-H(27)	120.3
C(25)#1-C(27)-H(27)	120.3		

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

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4a**. 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)	58(1)	22(1)	42(1)	4(1)	-9(1)	0(1)
O(2)	57(1)	26(1)	56(1)	1(1)	-10(1)	3(1)
O(3)	49(1)	22(1)	42(1)	0(1)	-8(1)	-1(1)
O(4)	54(1)	26(1)	56(1)	-4(1)	-12(1)	-3(1)
O(5)	55(1)	22(1)	58(1)	-1(1)	-12(1)	2(1)
O(6)	61(1)	54(1)	53(1)	3(1)	2(1)	-8(1)
N(1)	51(1)	22(1)	44(1)	3(1)	-7(1)	-1(1)
C(1)	58(1)	22(1)	36(1)	0(1)	-9(1)	1(1)
C(2)	52(1)	25(1)	38(1)	1(1)	-7(1)	-2(1)
C(3)	54(1)	26(1)	42(1)	0(1)	-10(1)	0(1)
C(4)	60(1)	27(1)	31(1)	3(1)	-7(1)	-3(1)
C(5)	66(1)	30(1)	35(1)	0(1)	-5(1)	-3(1)
C(6)	67(1)	38(1)	38(1)	0(1)	-1(1)	1(1)
C(7)	58(1)	45(1)	34(1)	4(1)	-6(1)	-6(1)
C(8)	65(1)	34(1)	36(1)	2(1)	-8(1)	-10(1)
C(9)	64(1)	29(1)	33(1)	1(1)	-7(1)	-4(1)
C(10)	70(1)	61(1)	73(1)	1(1)	4(1)	-20(1)
C(11)	50(1)	22(1)	39(1)	0(1)	-4(1)	-4(1)
C(12)	49(1)	23(1)	38(1)	0(1)	-2(1)	-1(1)
C(13)	49(1)	23(1)	38(1)	2(1)	-1(1)	1(1)
C(14)	46(1)	29(1)	39(1)	2(1)	-5(1)	0(1)
C(15)	49(1)	26(1)	36(1)	1(1)	-3(1)	-4(1)

C(16)	55(1)	30(1)	45(1)	1(1)	-10(1)	-6(1)
C(17)	53(1)	26(1)	38(1)	1(1)	-8(1)	-1(1)
C(18)	57(1)	36(1)	38(1)	2(1)	-10(1)	-5(1)
C(19)	64(1)	33(1)	34(1)	3(1)	-13(1)	-12(1)
C(20)	66(1)	46(1)	38(1)	5(1)	-6(1)	-11(1)
C(21)	76(1)	80(1)	48(1)	-5(1)	1(1)	-29(1)
C(22)	118(2)	78(2)	41(1)	0(1)	0(1)	-60(2)
C(23)	132(2)	50(1)	45(1)	16(1)	-25(1)	-42(1)
C(24)	91(1)	36(1)	49(1)	8(1)	-24(1)	-13(1)
C(25)	70(1)	121(2)	63(1)	13(1)	-15(1)	-12(1)
C(26)	65(1)	137(2)	63(1)	22(1)	-1(1)	3(1)
C(27)	75(1)	70(1)	49(1)	3(1)	-4(1)	19(1)

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

	x	y	z	U(eq)
H(5)	6102(14)	1464(13)	7940(30)	76(7)
H(5A)	6945	4176	5370	53
H(6)	8162	4426	4471	57
H(8)	7973	6351	6145	54
H(9)	6748	6102	7060	51
H(10A)	8897	6486	4142	102
H(10B)	9751	6165	4350	102
H(10C)	9280	6299	6004	102
H(14)	7256	2729	9666	46
H(16A)	7296	3934	10930	66
H(16B)	6909	4521	9751	66
H(16C)	7632	4103	9126	66
H(17A)	4089	4522	9772	48
H(17B)	4597	3853	9584	48
H(18A)	3428	4283	7020	53
H(18B)	3901	3588	6971	53
H(20)	2225	4283	8274	61
H(21)	1264	3741	9723	82

H(22)	1542	2704	11072	95
H(23)	2767	2242	11012	93
H(24)	3727	2768	9558	72
H(25)	8836	4816	8414	103
H(26)	8890	4742	11375	106
H(27)	10058	4927	12969	78

Table S6. Torsion angles [°] for **4a**.

O(1)-C(1)-C(2)-N(1)	0.53(15)	C(2)-C(11)-C(15)-C(14)	-179.26(14)
O(1)-C(1)-C(2)-C(11)	-179.34(13)	C(2)-C(11)-C(15)-C(16)	0.4(3)
O(1)-C(1)-C(4)-C(5)	-149.06(13)	C(3)-O(1)-C(1)-C(2)	0.43(15)
O(1)-C(1)-C(4)-C(9)	31.68(18)	C(3)-O(1)-C(1)-C(4)	-176.65(12)
O(3)-C(11)-C(15)-C(14)	1.1(2)	C(3)-N(1)-C(2)-C(1)	-1.32(16)
O(3)-C(11)-C(15)-C(16)	-179.27(13)	C(3)-N(1)-C(2)-C(11)	178.57(13)
O(3)-C(12)-C(13)-O(5)	-179.90(12)	C(3)-N(1)-C(17)-C(18)	85.16(17)
O(3)-C(12)-C(13)-C(14)	0.6(2)	C(4)-C(1)-C(2)-N(1)	176.86(15)
O(4)-C(12)-C(13)-O(5)	-0.9(2)	C(4)-C(1)-C(2)-C(11)	-3.0(3)
O(4)-C(12)-C(13)-C(14)	179.65(15)	C(4)-C(5)-C(6)-C(7)	-0.2(2)
O(5)-C(13)-C(14)-C(15)	-179.70(13)	C(5)-C(4)-C(9)-C(8)	-0.2(2)
O(6)-C(7)-C(8)-C(9)	-179.88(13)	C(5)-C(6)-C(7)-O(6)	179.98(13)
N(1)-C(2)-C(11)-O(3)	54.64(17)	C(5)-C(6)-C(7)-C(8)	0.1(2)
N(1)-C(2)-C(11)-C(15)	-125.04(17)	C(6)-C(7)-C(8)-C(9)	0.0(2)
N(1)-C(17)-C(18)-C(19)	-175.07(12)	C(7)-C(8)-C(9)-C(4)	0.1(2)
C(1)-O(1)-C(3)-O(2)	177.62(13)	C(9)-C(4)-C(5)-C(6)	0.3(2)
C(1)-O(1)-C(3)-N(1)	-1.25(15)	C(10)-O(6)-C(7)-C(6)	178.12(15)
C(1)-C(2)-C(11)-O(3)	-125.50(16)	C(10)-O(6)-C(7)-C(8)	-2.0(2)
C(1)-C(2)-C(11)-C(15)	54.8(2)	C(11)-O(3)-C(12)-O(4)	-179.26(13)
C(1)-C(4)-C(5)-C(6)	-179.00(13)	C(11)-O(3)-C(12)-C(13)	-0.15(19)
C(1)-C(4)-C(9)-C(8)	179.10(13)	C(12)-O(3)-C(11)-C(2)	179.57(12)
C(2)-N(1)-C(3)-O(1)	1.59(15)	C(12)-O(3)-C(11)-C(15)	-0.7(2)
C(2)-N(1)-C(3)-O(2)	-177.23(14)	C(12)-C(13)-C(14)-C(15)	-0.2(2)
C(2)-N(1)-C(17)-C(18)	-103.99(16)	C(13)-C(14)-C(15)-C(11)	-0.6(2)
C(2)-C(1)-C(4)-C(5)	34.8(2)	C(13)-C(14)-C(15)-C(16)	179.72(14)
C(2)-C(1)-C(4)-C(9)	-144.41(17)	C(17)-N(1)-C(2)-C(1)	-173.14(13)

C(17)-N(1)-C(2)-C(11)	6.7(2)	C(20)-C(19)-C(24)-C(23)	1.6(2)
C(17)-N(1)-C(3)-O(1)	174.03(11)	C(20)-C(21)-C(22)-C(23)	0.9(3)
C(17)-N(1)-C(3)-O(2)	-4.8(2)	C(21)-C(22)-C(23)-C(24)	-1.2(3)
C(17)-C(18)-C(19)-C(20)	108.20(16)	C(22)-C(23)-C(24)-C(19)	0.0(3)
C(17)-C(18)-C(19)-C(24)	-71.64(19)	C(24)-C(19)-C(20)-C(21)	-1.9(2)
C(18)-C(19)-C(20)-C(21)	178.24(15)	C(25)-C(26)-C(27)-C(25)#1	0.0(5)
C(18)-C(19)-C(24)-C(23)	-178.56(15)	C(27)#1-C(25)-C(26)-C(27)	0.0(5)
C(19)-C(20)-C(21)-C(22)	0.7(3)		

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

Table S7. Hydrogen bonds for **4a** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(5)-H(5)...O(2)#2	0.91(3)	1.84(3)	2.6477(15)	147(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y+1,-z+2 #2 -x+1,y-1/2,-z+3/2

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