New Journal of Chemistry

Synthesis and mechanism of novel fluorescent coumarin-dihydropyrimidinone dyads obtained by Biginelli multicomponent reaction.

Felipe Vitório[a,b], Thiago Moreira Pereira[a], Rosane Nora Castro[b], Guilherme Pereira Guedes[b], Cedric Stephan Graebin[a,b] and Arthur Eugen Kummerle*[,a,b]

[a] Laboratório de Diversidade Molecular e Química Medicinal (LaDMol-QM, Molecular Diversity and Medicinal Chemistry Laboratory), Departament of Chemistry, Universidade Federal Rural do Rio de Janeiro, Seropédica, Rio de Janeiro, 239897-000, Brazil.

[b] Programa de Pós-Gradução em Química (PPGQ), Universidade Federal Rural do Rio de Janeiro, Seropédica, Rio de Janeiro, 239897-000, Brazil.

Email: akummerle@ufrrj.br

Supporting Information

Contents

Copies of ^{1}H , $^{13}CNMR$ and Mass Spectra for all products ---------- 2-43

HPLC data analysis ---------- 44-48

Crystal Structure analysis ---------- 49-50

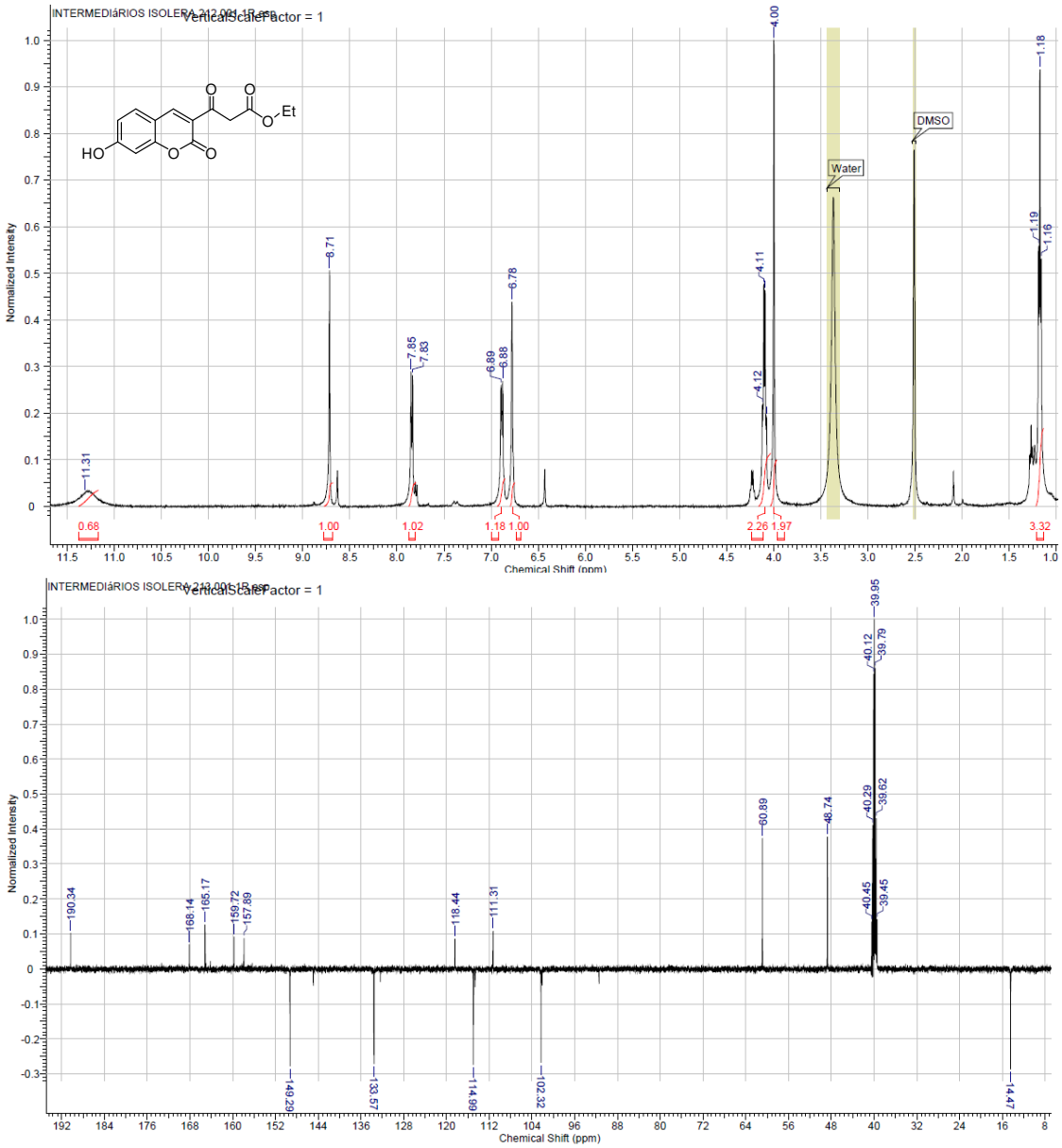


Fig. S1 ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) spectra of **3a** in DMSO-*d6*.

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Negative	Alternating Ion Polarity	off
Mass Range Mode	Enhanced	Scan Begin	100 m/z	Scan End	700 m/z
Capillary Exit	Resolution	n/a	n/a	Trap Drive	68.9
Accumulation Time	175 µs	Averages	5 Spectra	Auto MS/MS	off

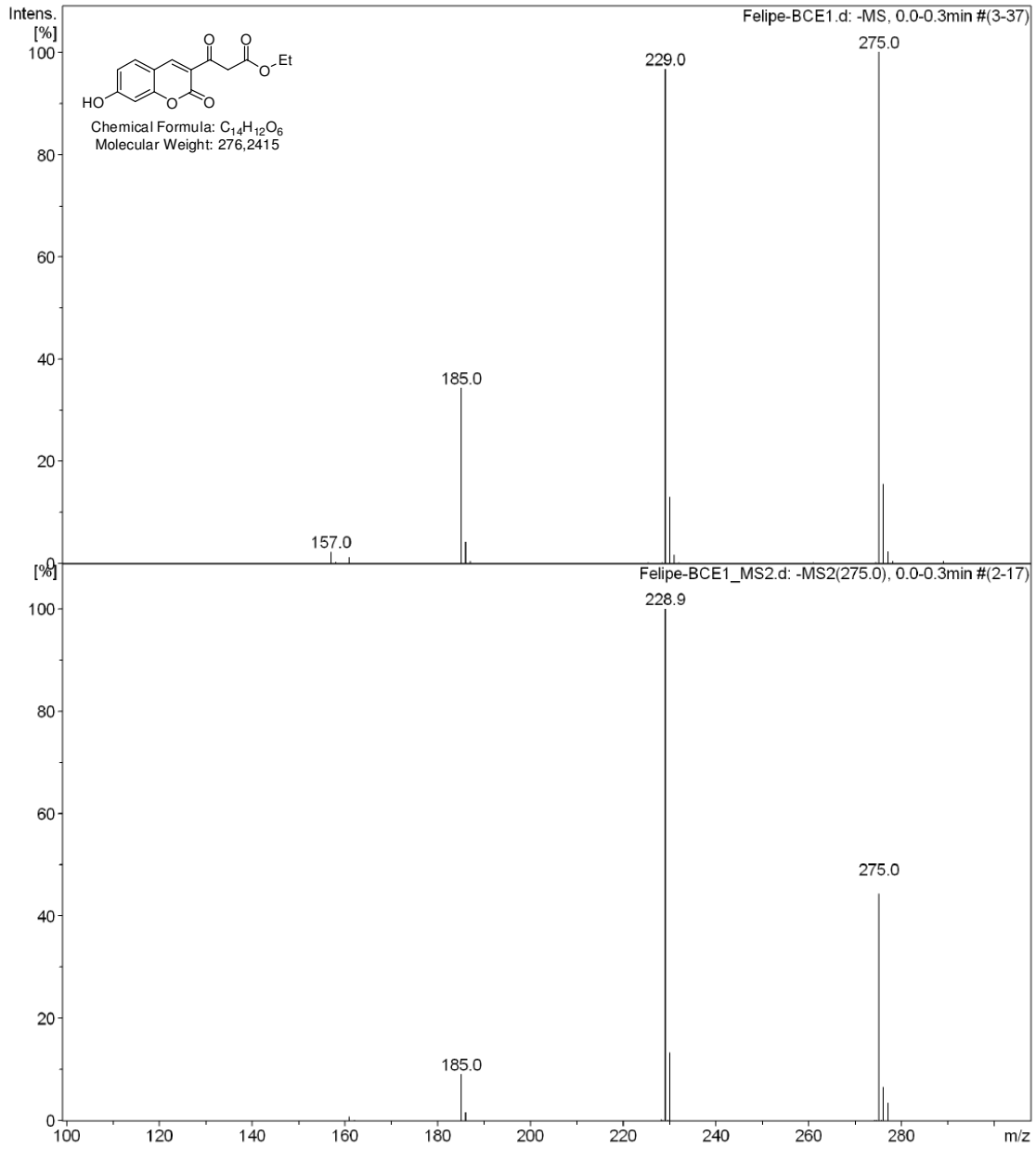


Fig. S2 ESI spectra of **3a**.

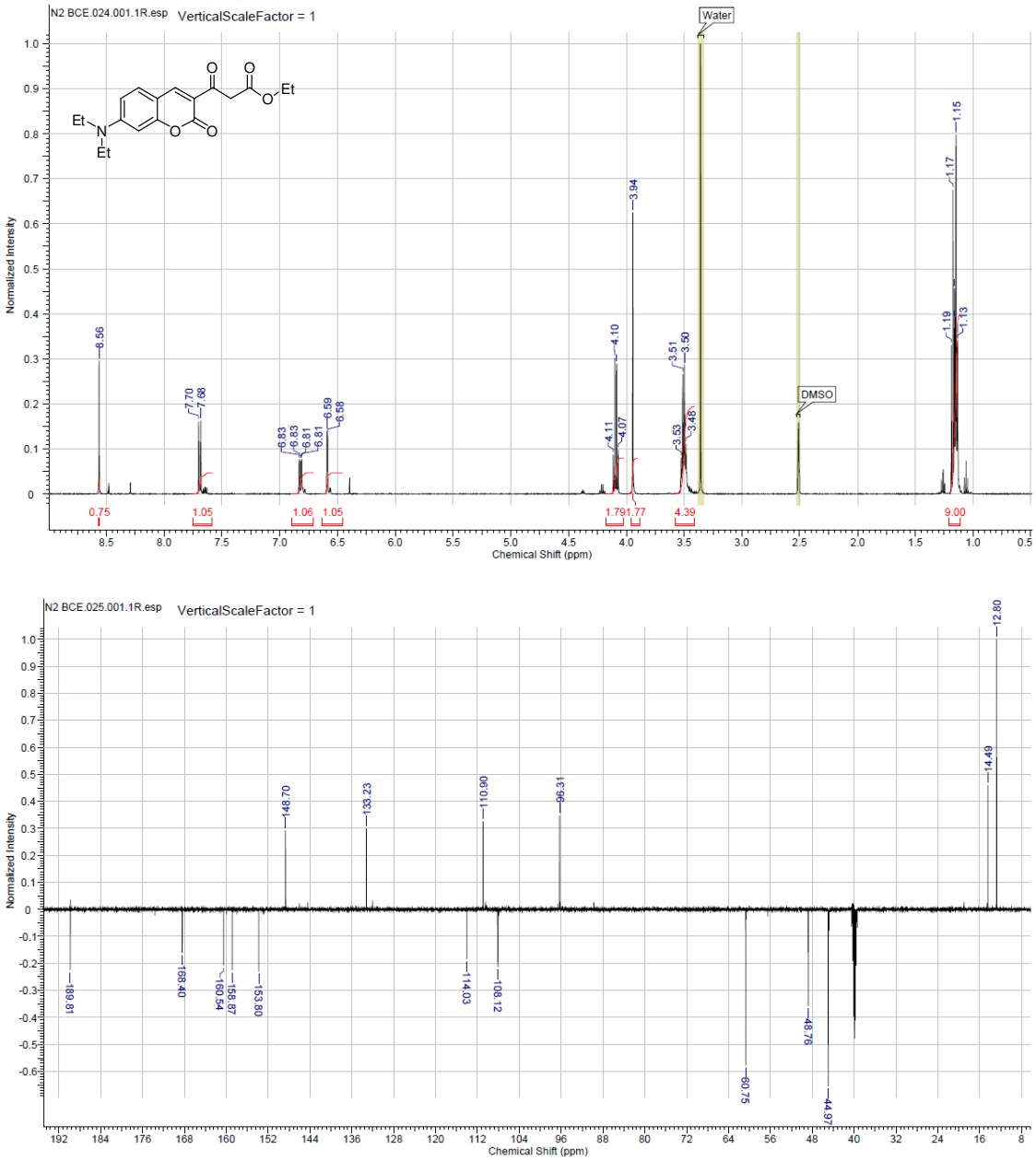


Fig. S3 ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) spectra of **3b** in DMSO-*d6*.

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Negative	Alternating Ion Polarity	off
Mass Range Mode	Enhanced	Scan Begin	100 m/z	Scan End	700 m/z
Capillary Exit	Resolution	n/a	n/a	Trap Drive	68.9
Accumulation Time	2130 µs	Averages	5 Spectra	Auto MS/MS	off

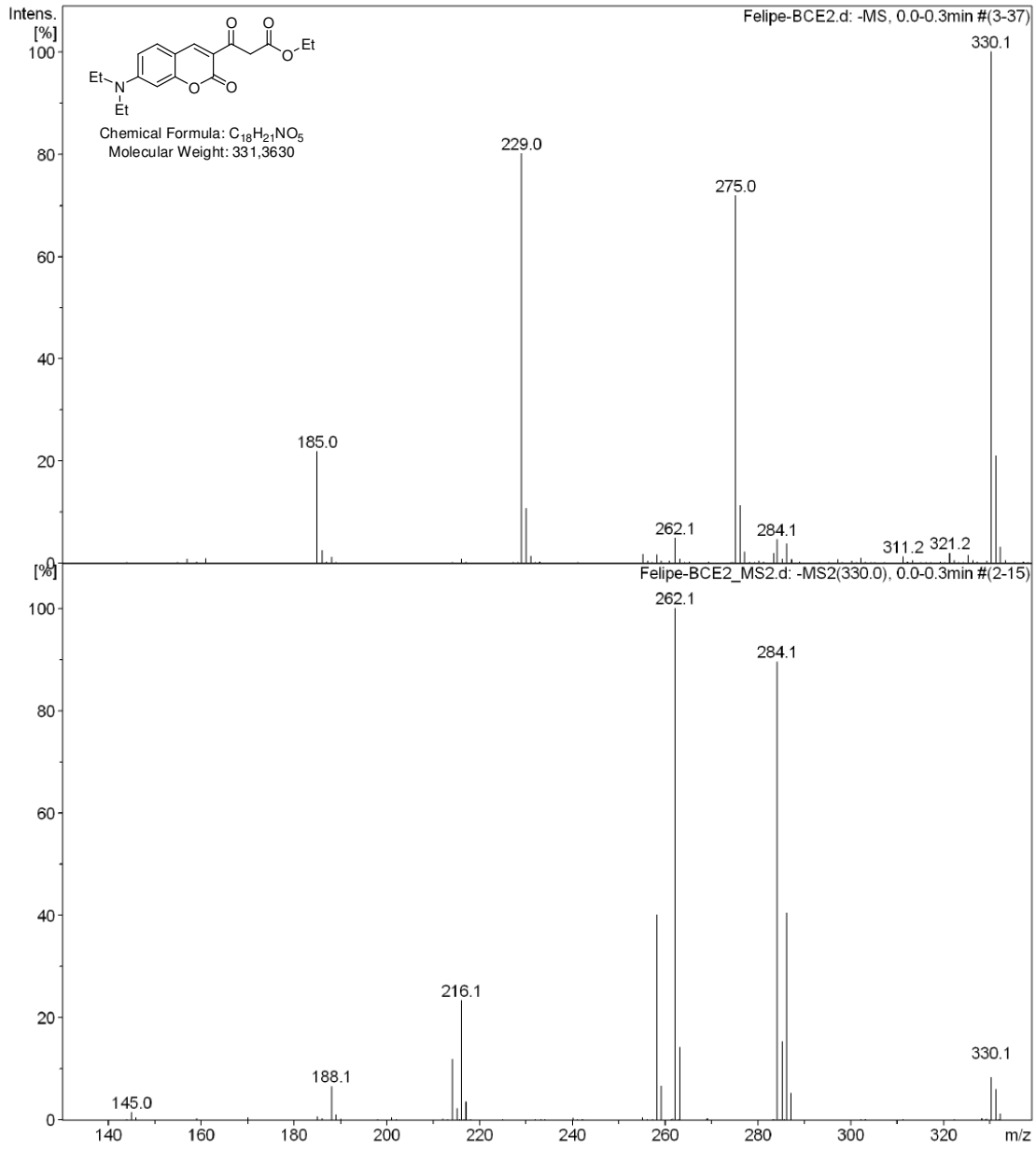


Fig. S4 ESI spectra of **3b**.

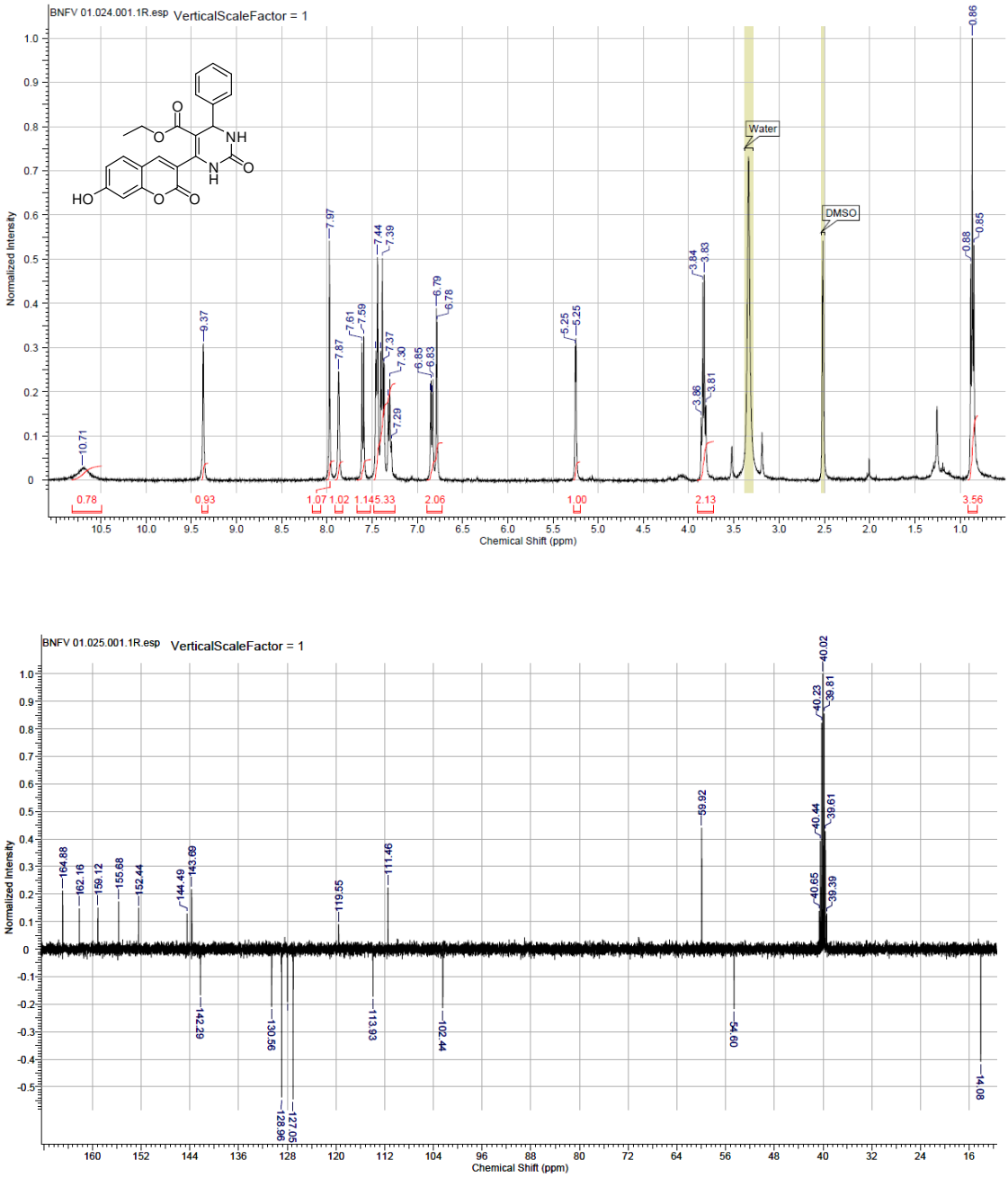


Fig. S5 ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) spectra of **4a** in DMSO-*d6*.

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Negative	Alternating Ion Polarity	off
Mass Range Mode	Enhanced	Scan Begin	100 m/z	Scan End	700 m/z
Capillary Exit	Resolution	n/a	n/a	Trap Drive	68.9
Accumulation Time	219 µs	Averages	5 Spectra	Auto MS/MS	off

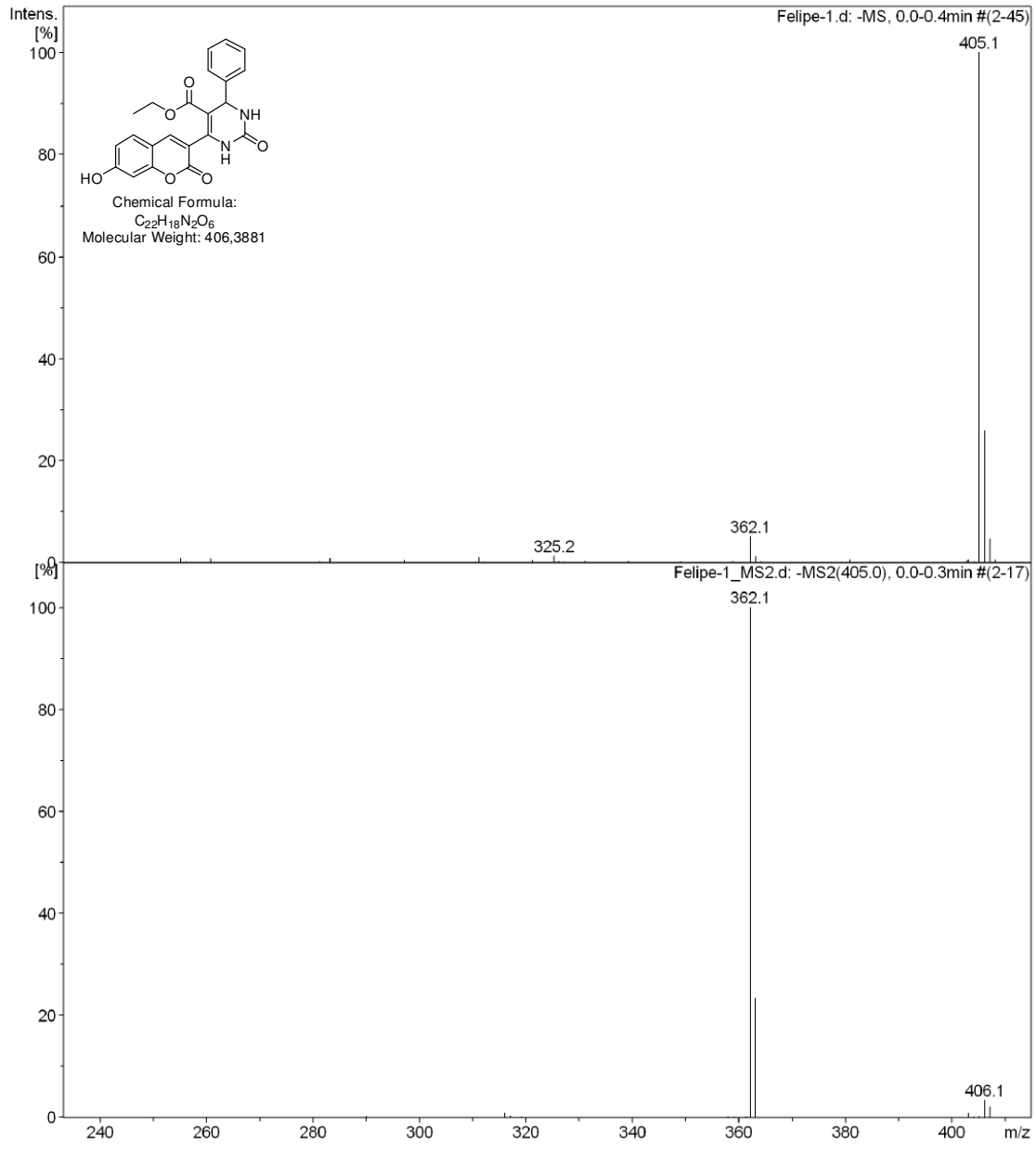


Fig. S6 ESI spectra of **4a**.

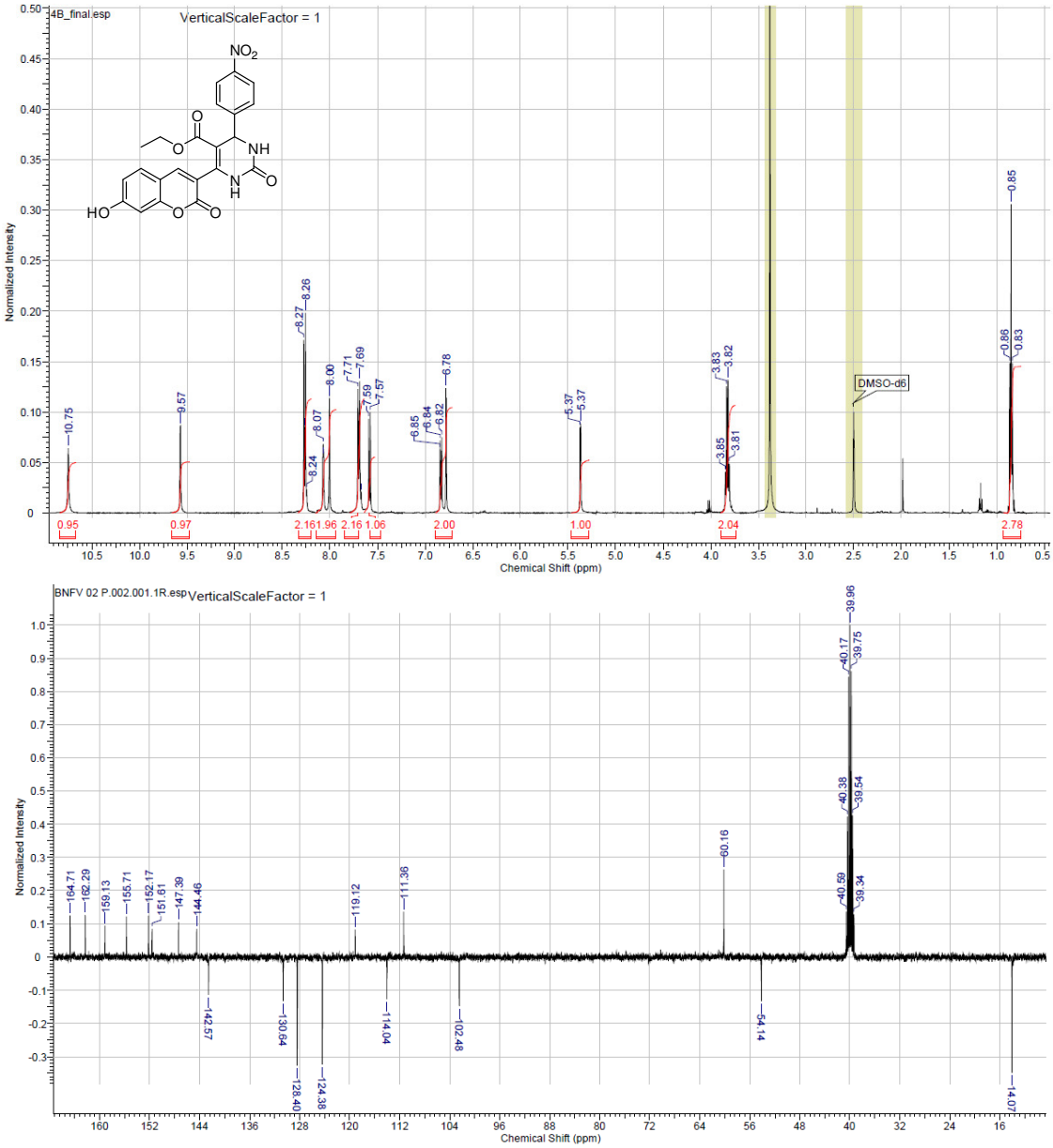


Fig. S7 ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) spectra of **4b** in DMSO-*d6*.

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Negative	Alternating Ion Polarity	off
Mass Range Mode	Enhanced	Scan Begin	100 m/z	Scan End	700 m/z
Capillary Exit	Resolution	n/a	n/a	Trap Drive	68.9
Accumulation Time	13906 µs	Averages	5 Spectra	Auto MS/MS	off

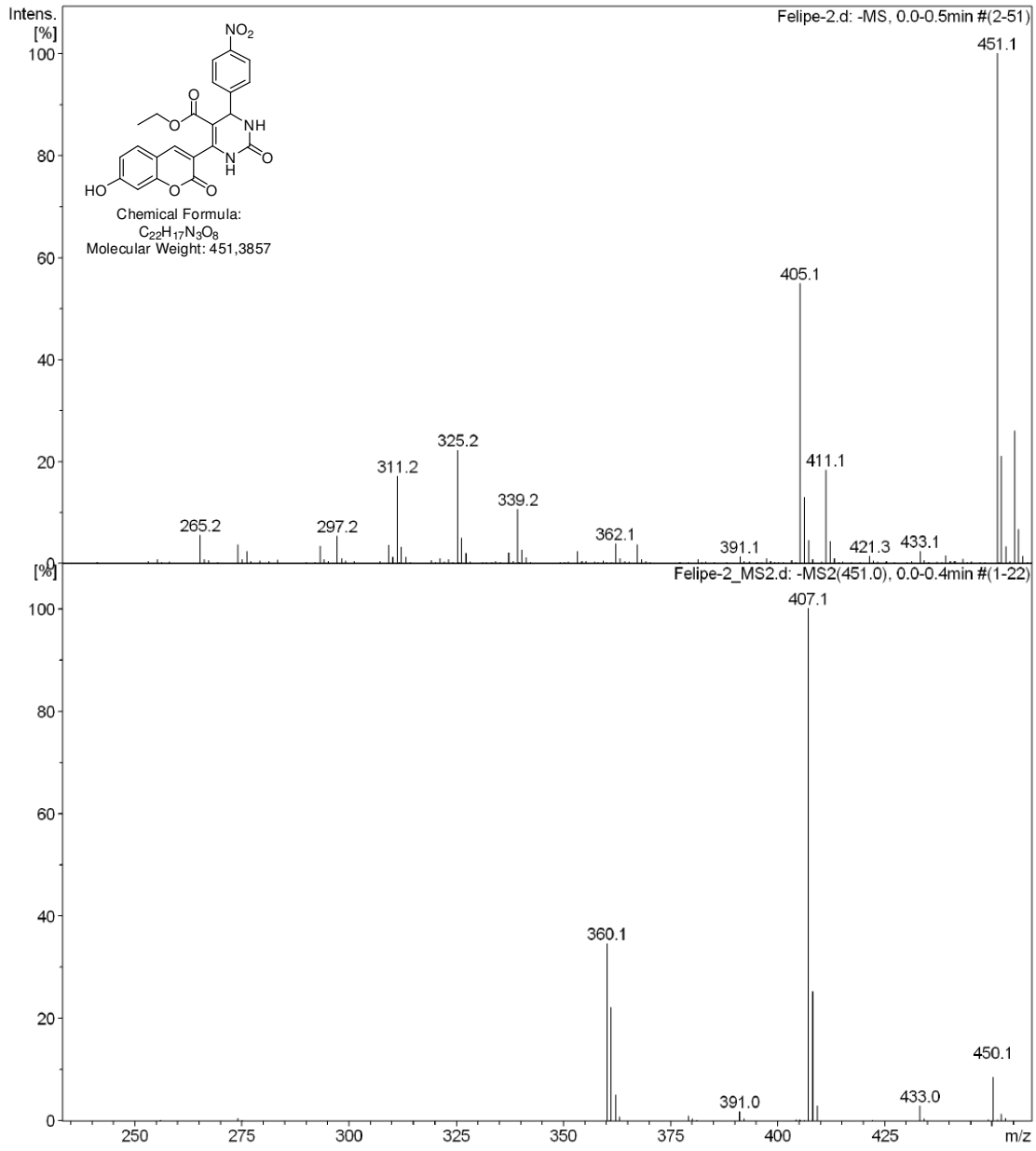


Fig. S8 ESI spectra of **4b**.

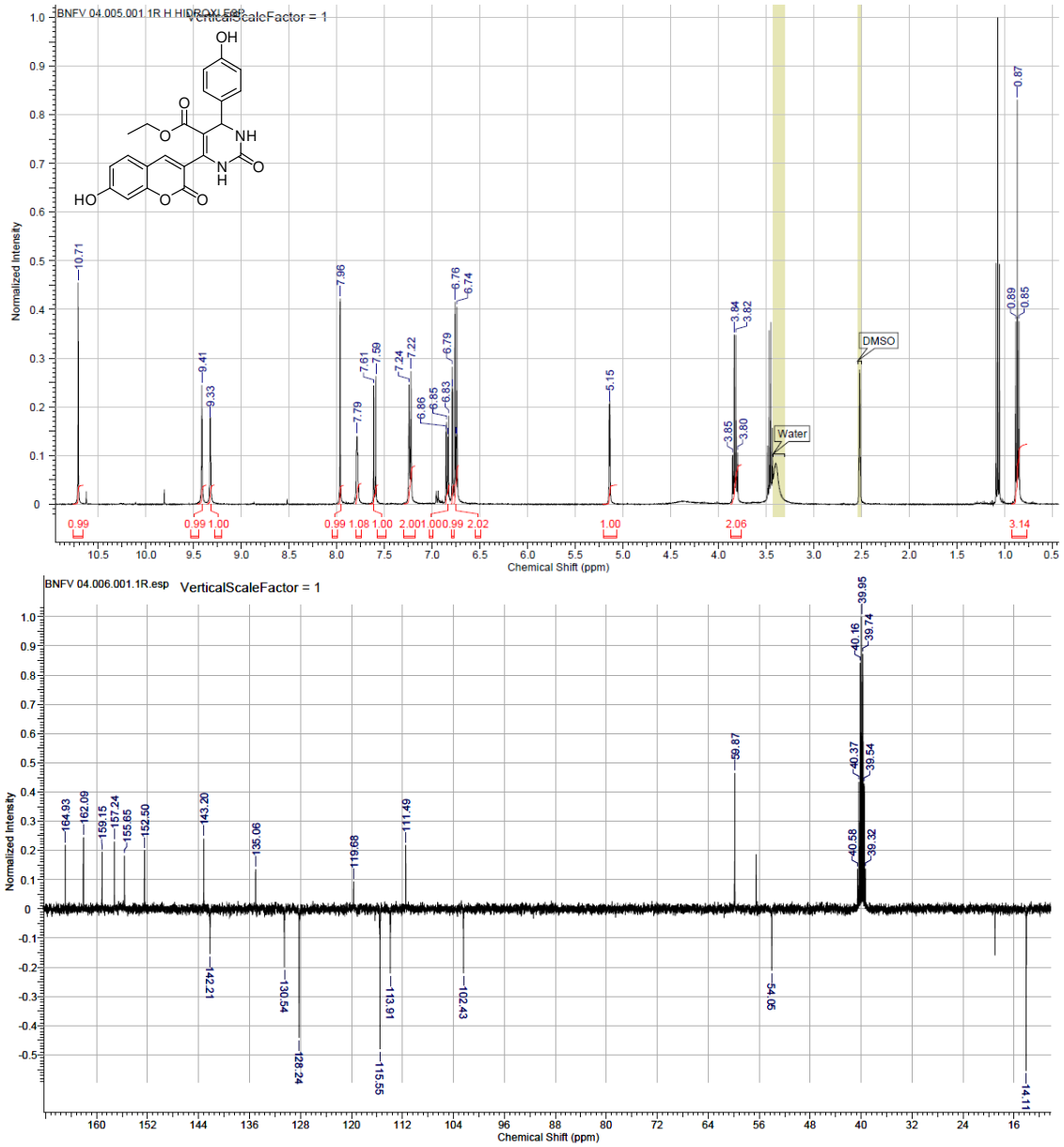


Fig. S9 ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) spectra of **4c** in DMSO-*d6*.

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Negative	Alternating Ion Polarity	off
Mass Range Mode	Enhanced	Scan Begin	100 m/z	Scan End	700 m/z
Capillary Exit	Resolution	n/a	n/a	Trap Drive	68.9
Accumulation Time	332 µs	Averages	5 Spectra	Auto MS/MS	off

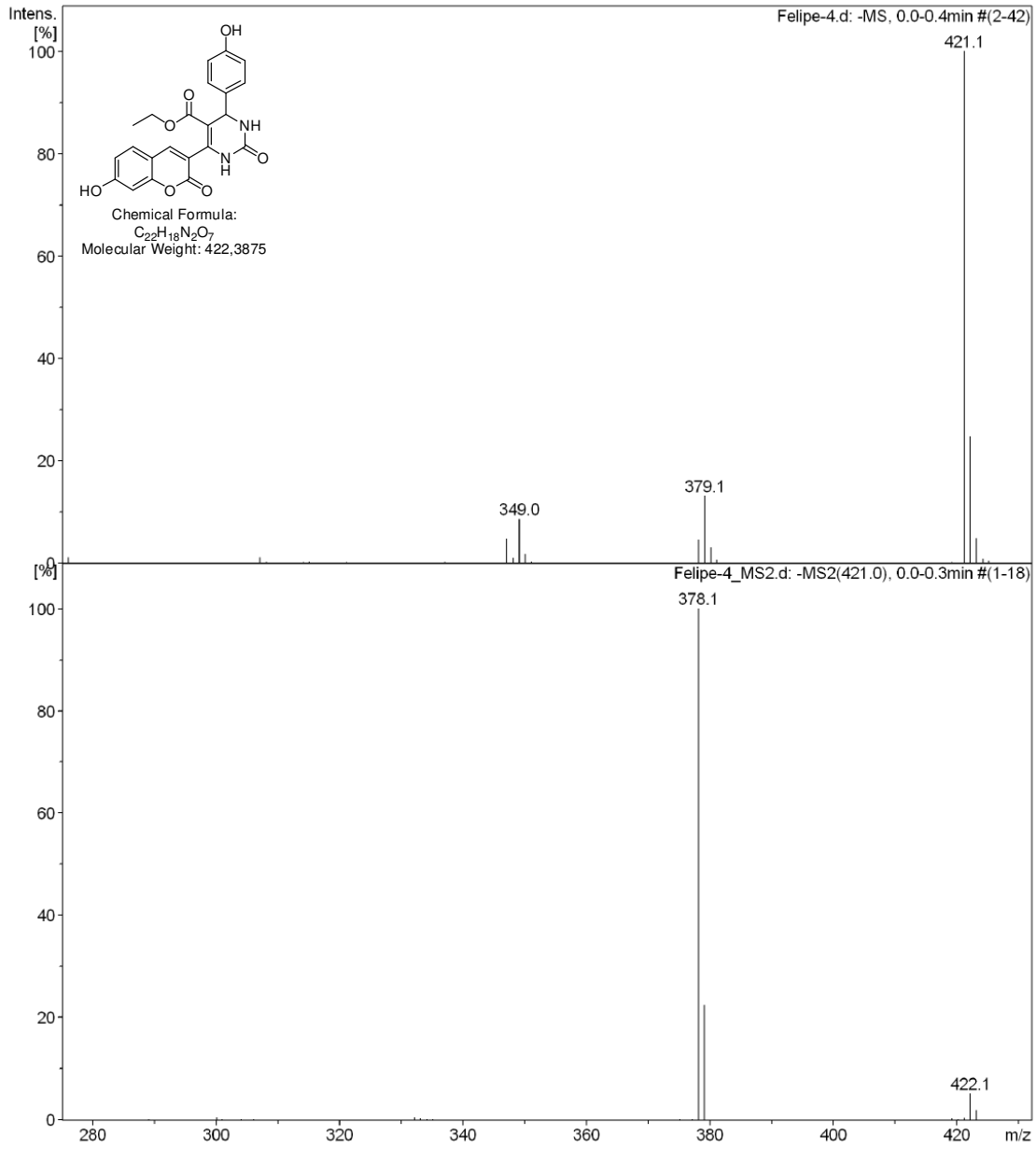


Fig. S10 ESI spectra of **4c**.

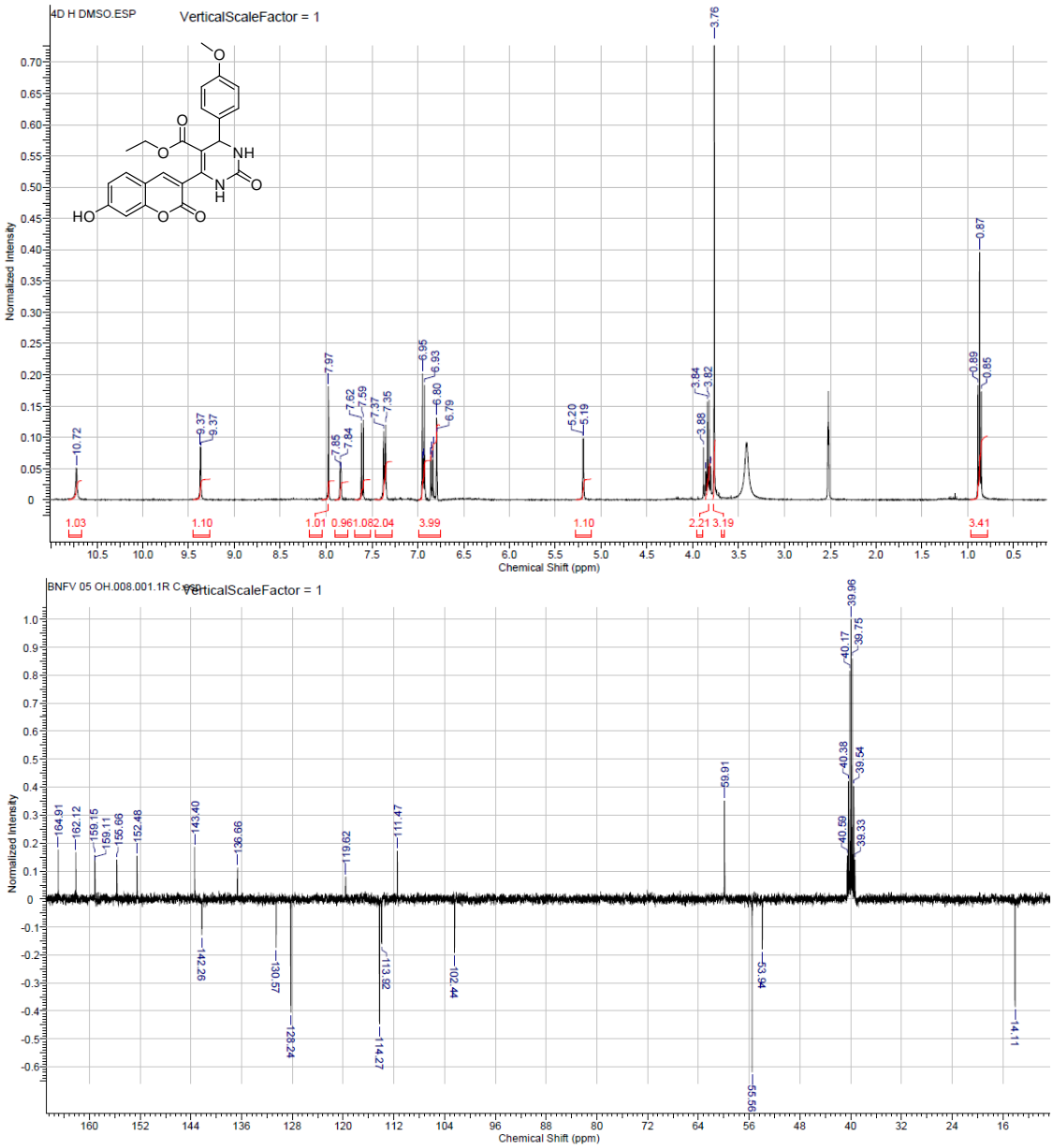


Fig. S11 ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) spectra of **4d** in DMSO-*d6*.

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Negative	Alternating Ion Polarity	off
Mass Range Mode	Enhanced	Scan Begin	100 m/z	Scan End	700 m/z
Capillary Exit	Resolution	n/a	n/a	Trap Drive	68.9
Accumulation Time	139 µs	Averages	5 Spectra	Auto MS/MS	off

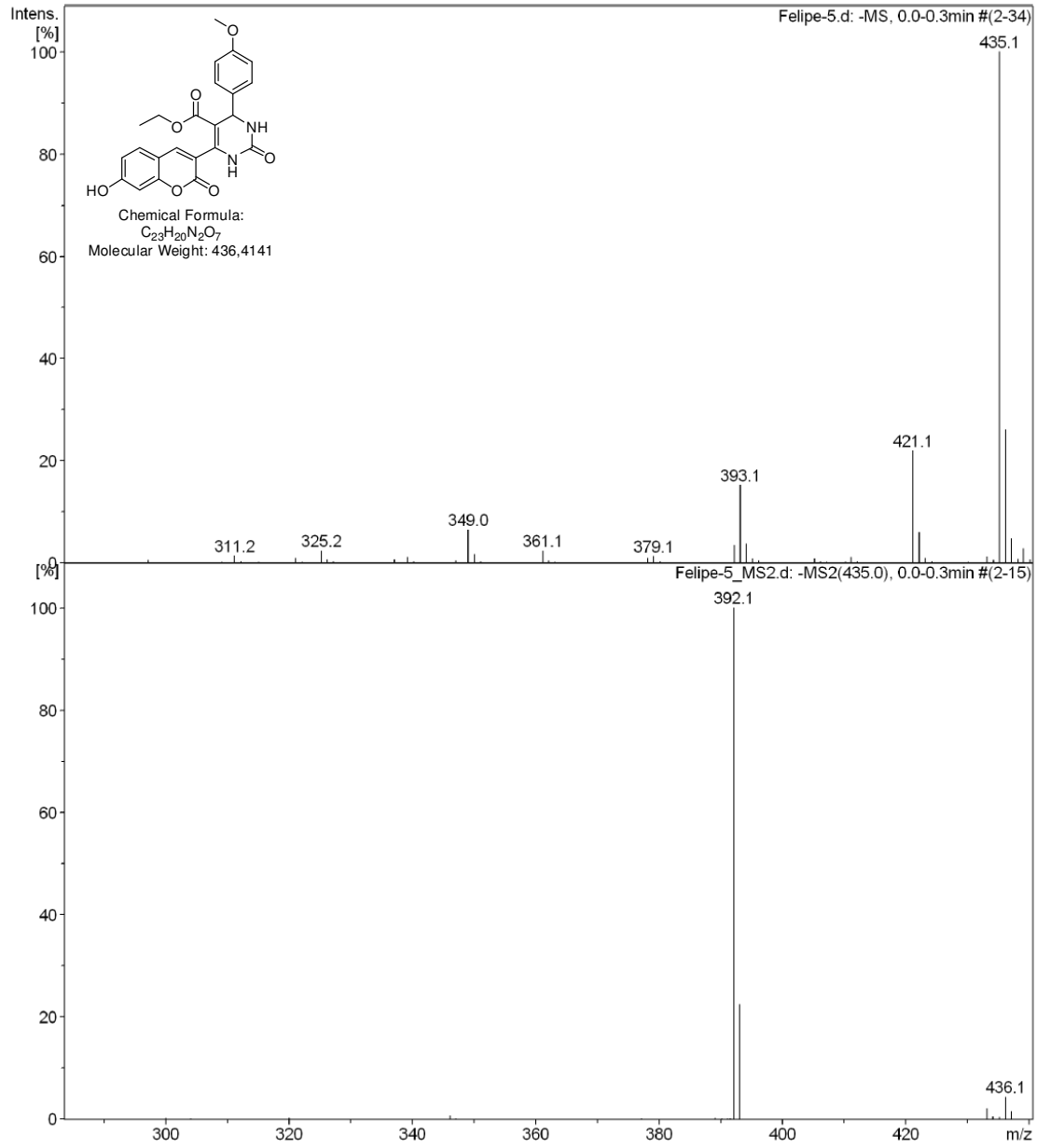


Fig. S12 ESI spectra of **4d**.

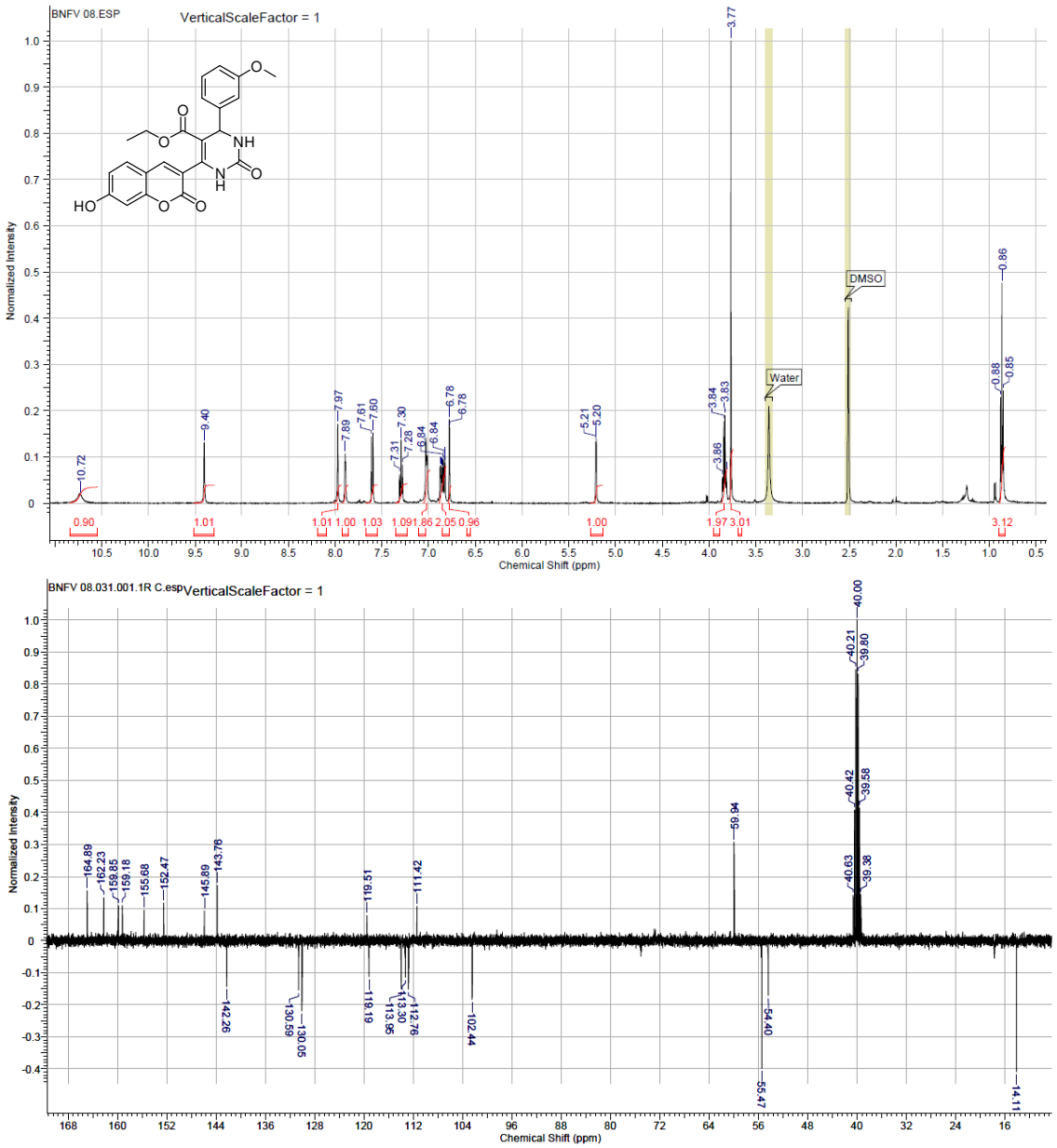


Fig. S13 ^{1}H NMR (500 MHz), ^{13}C NMR (100 MHz) spectra of **4e** in DMSO-*d6*.

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Negative	Alternating Ion Polarity	off
Mass Range Mode	Enhanced	Scan Begin	100 m/z	Scan End	700 m/z
Capillary Exit	Resolution	n/a	n/a	Trap Drive	68.9
Accumulation Time	110 µs	Averages	5 Spectra	Auto MS/MS	off

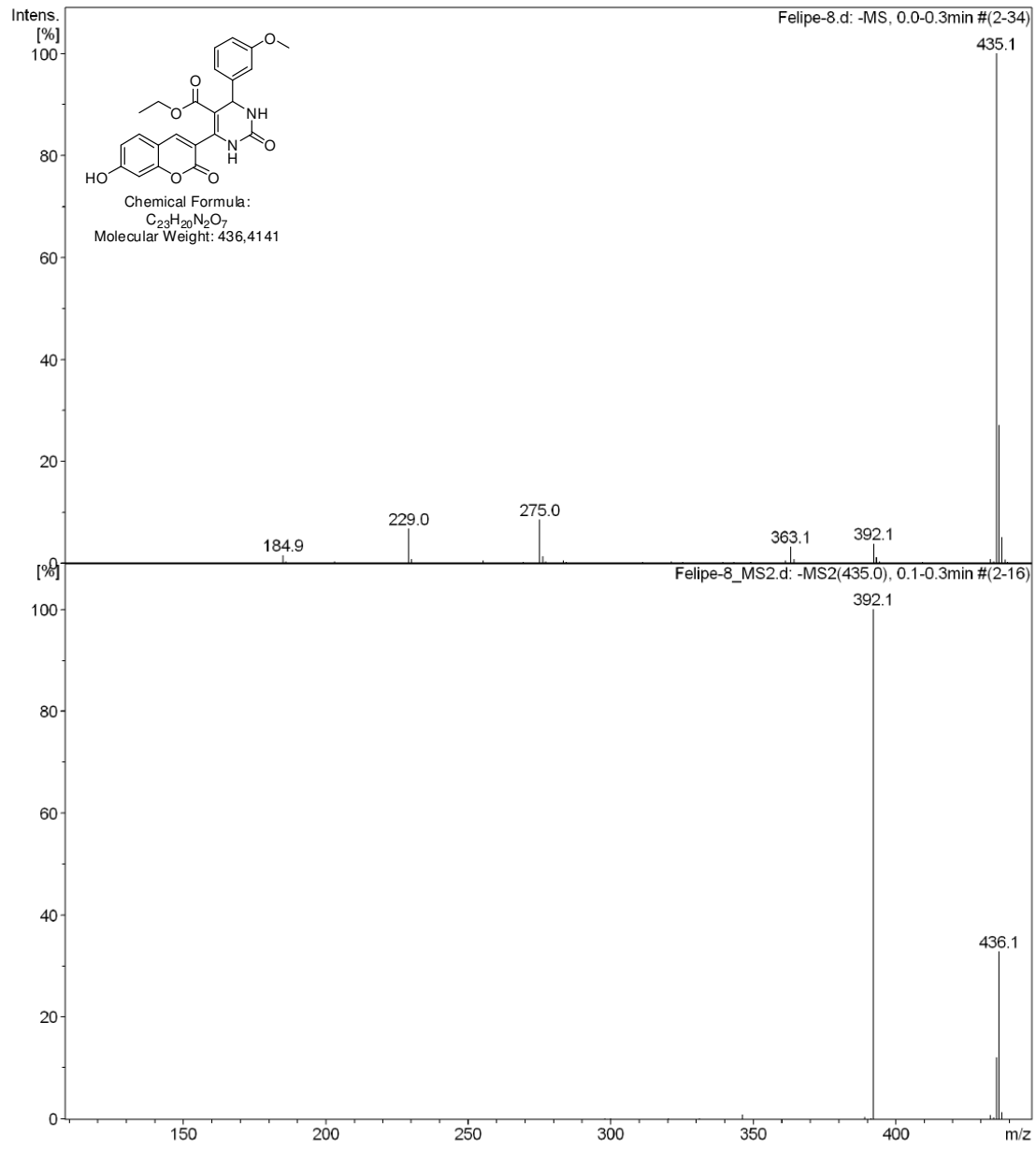


Fig. S14 ESI spectra of **4e**.

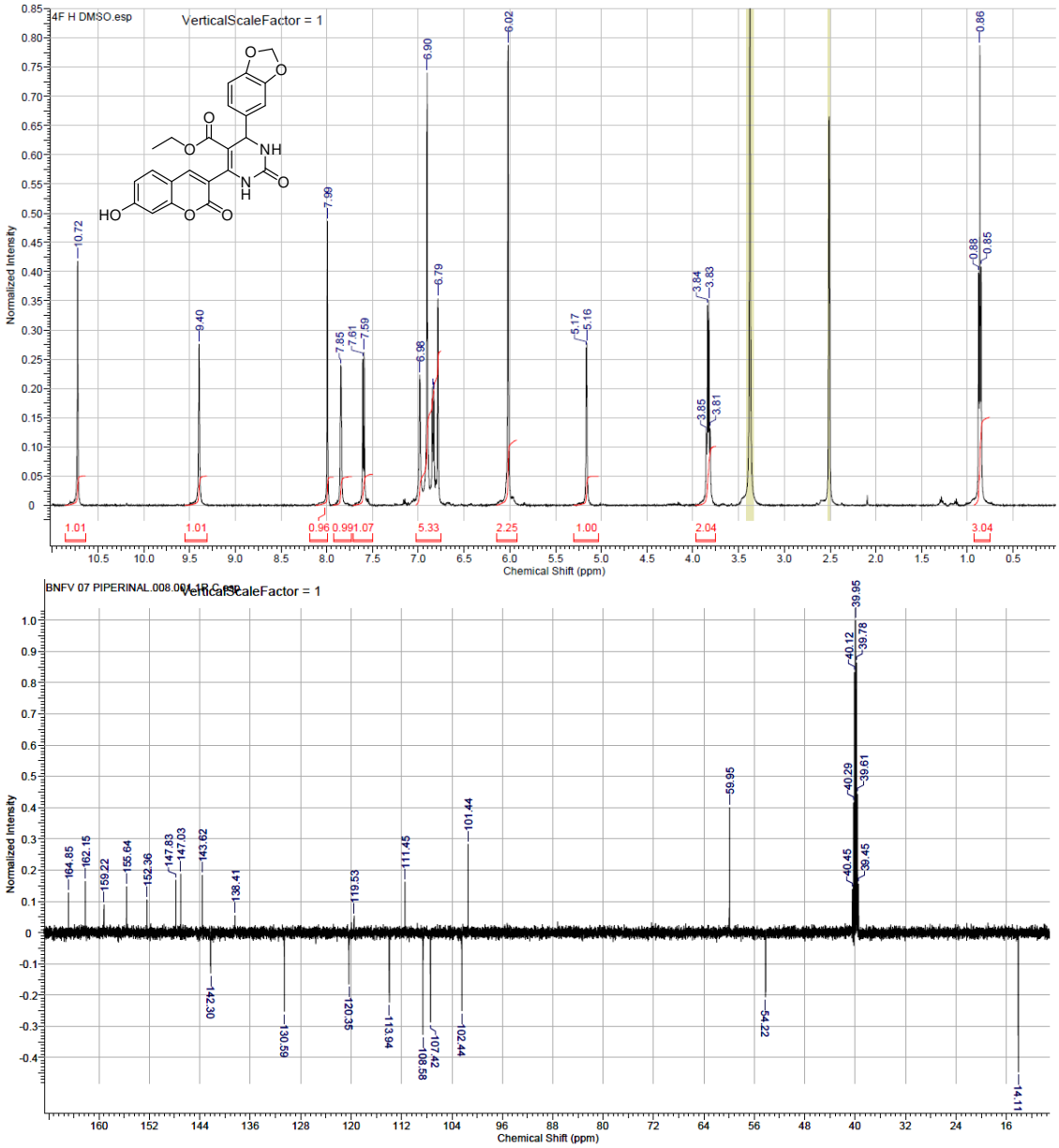


Fig. S15 ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) spectra of **4f** in DMSO-*d6*.

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Negative	Alternating Ion Polarity	off
Mass Range Mode	Enhanced	Scan Begin	100 m/z	Scan End	700 m/z
Capillary Exit	Resolution	n/a	n/a	Trap Drive	68.9
Accumulation Time	187 µs	Averages	5 Spectra	Auto MS/MS	off

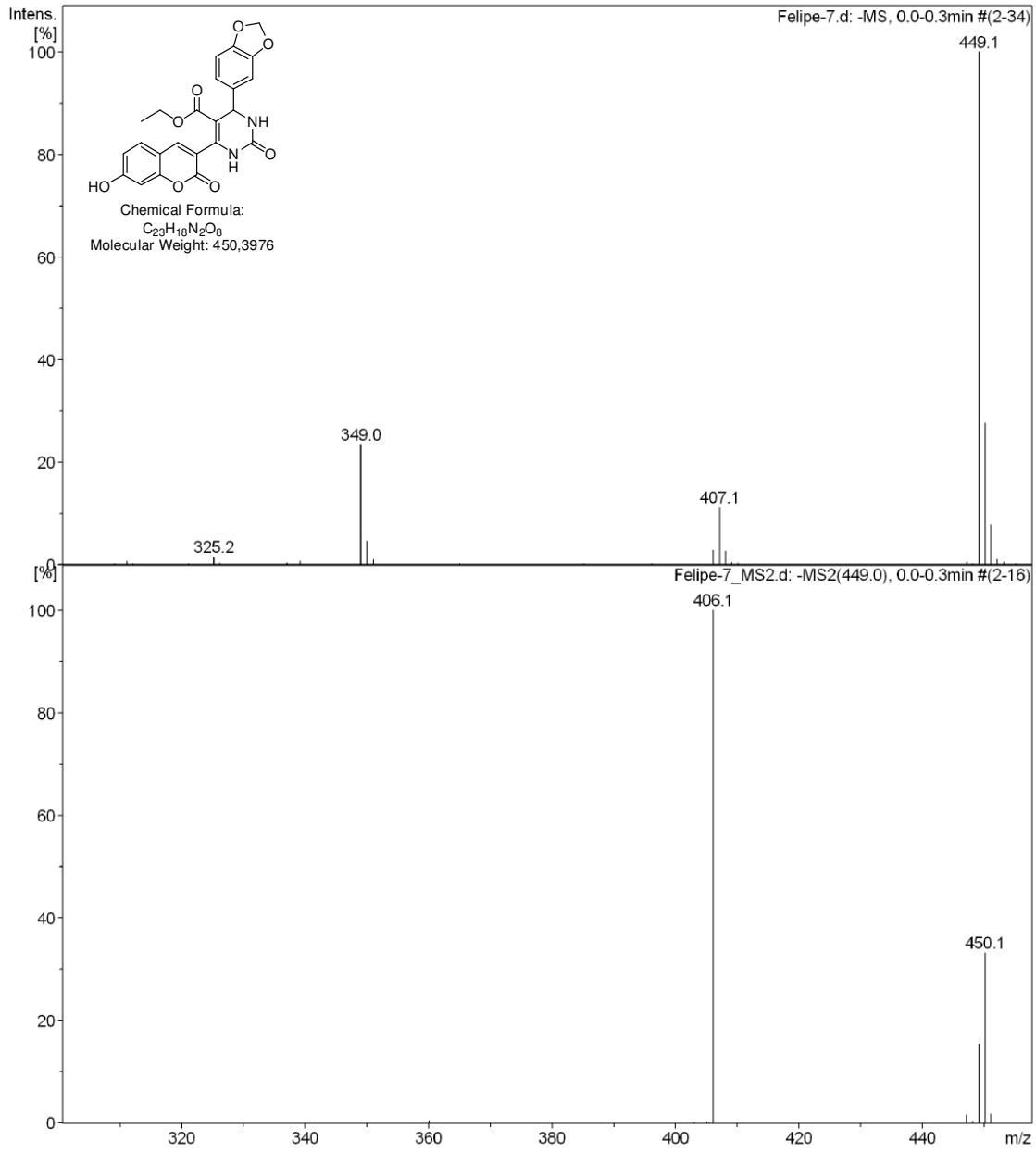


Fig. S16 ESI spectra of **4f**.

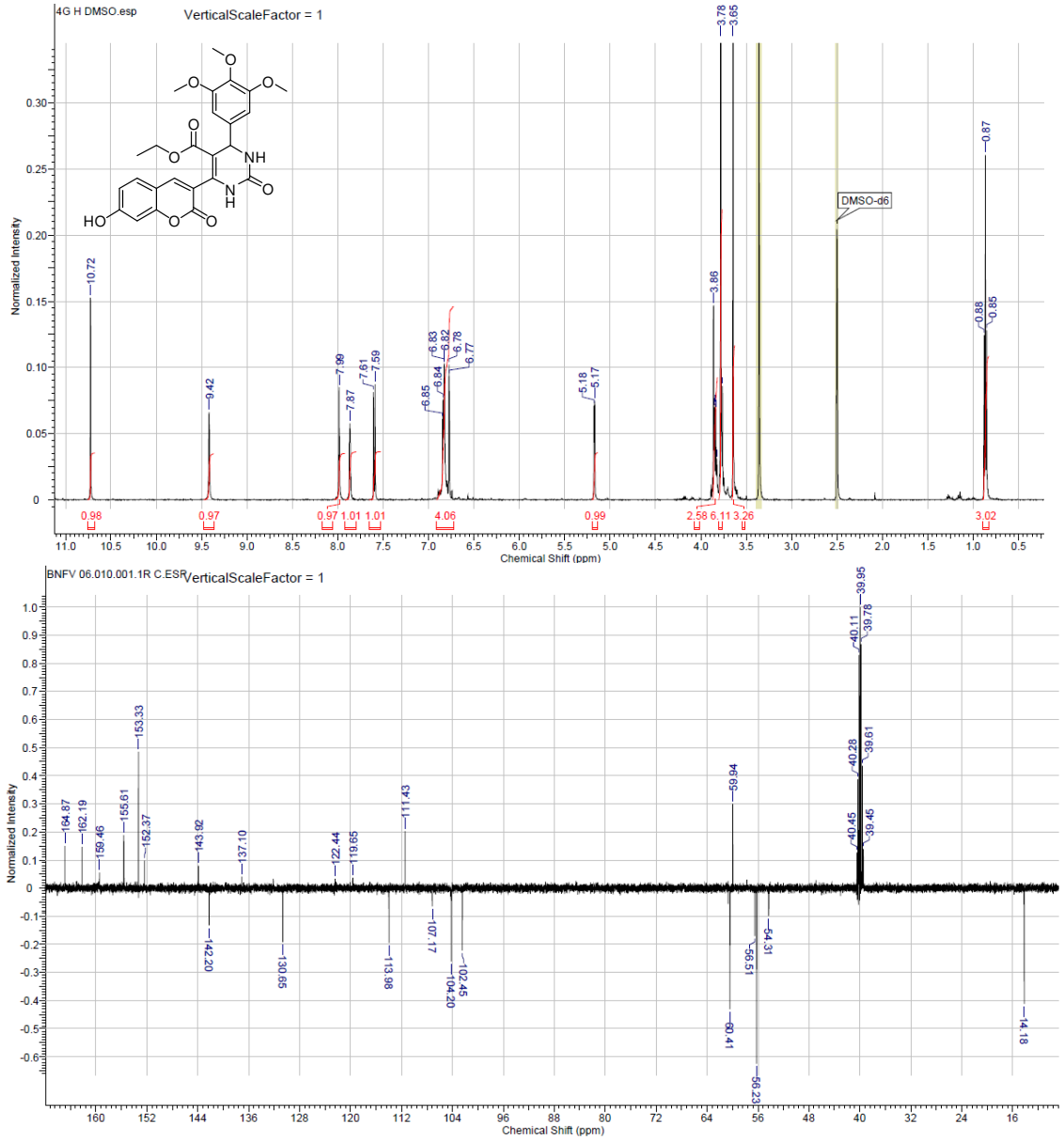


Fig. S17 ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) spectra of **4g** in DMSO-*d6*.

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Negative	Alternating Ion Polarity	off
Mass Range Mode	Enhanced	Scan Begin	100 m/z	Scan End	700 m/z
Capillary Exit	Resolution	n/a	n/a	Trap Drive	68.9
Accumulation Time	2620 µs	Averages	5 Spectra	Auto MS/MS	off

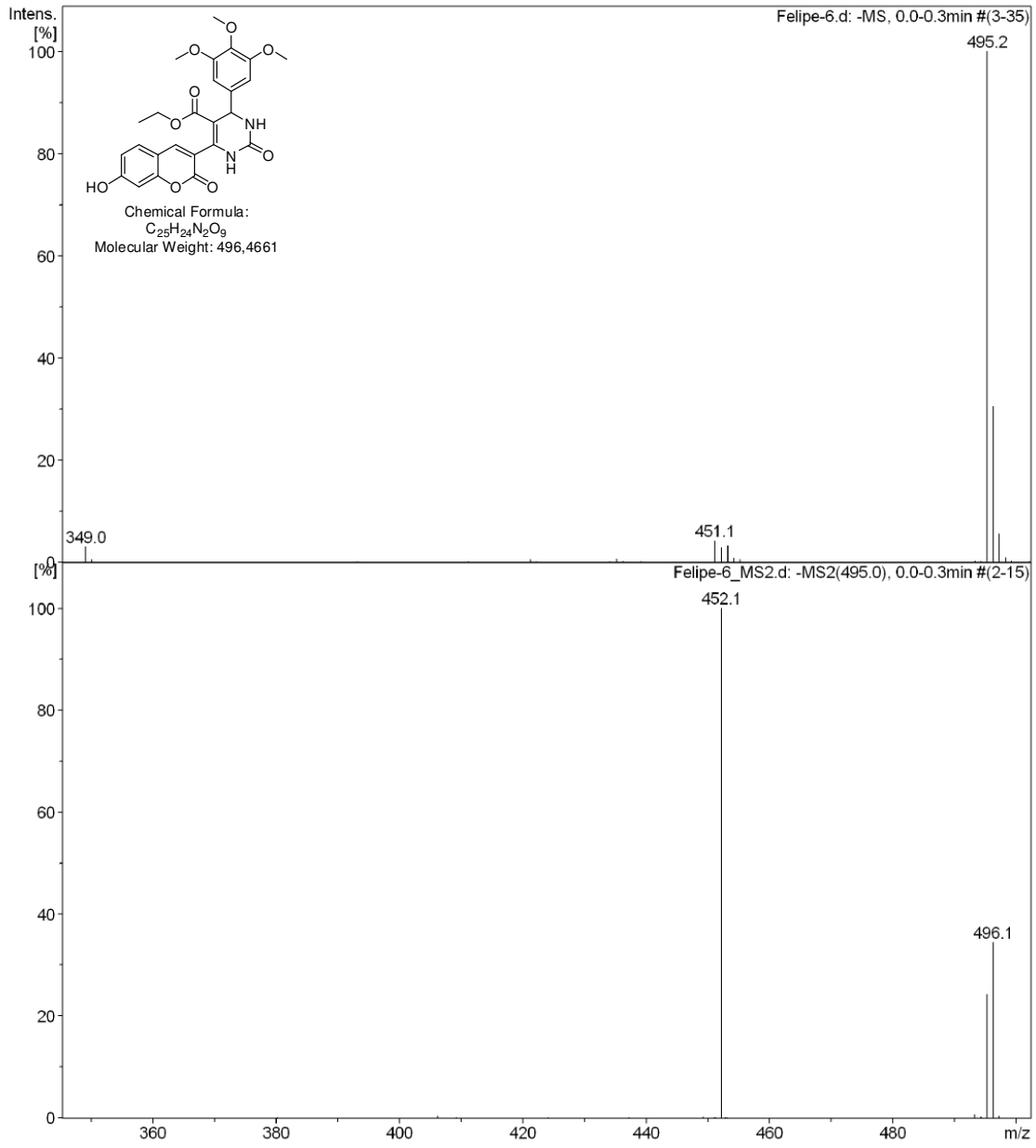


Fig. S18 ESI spectra of **4g**.

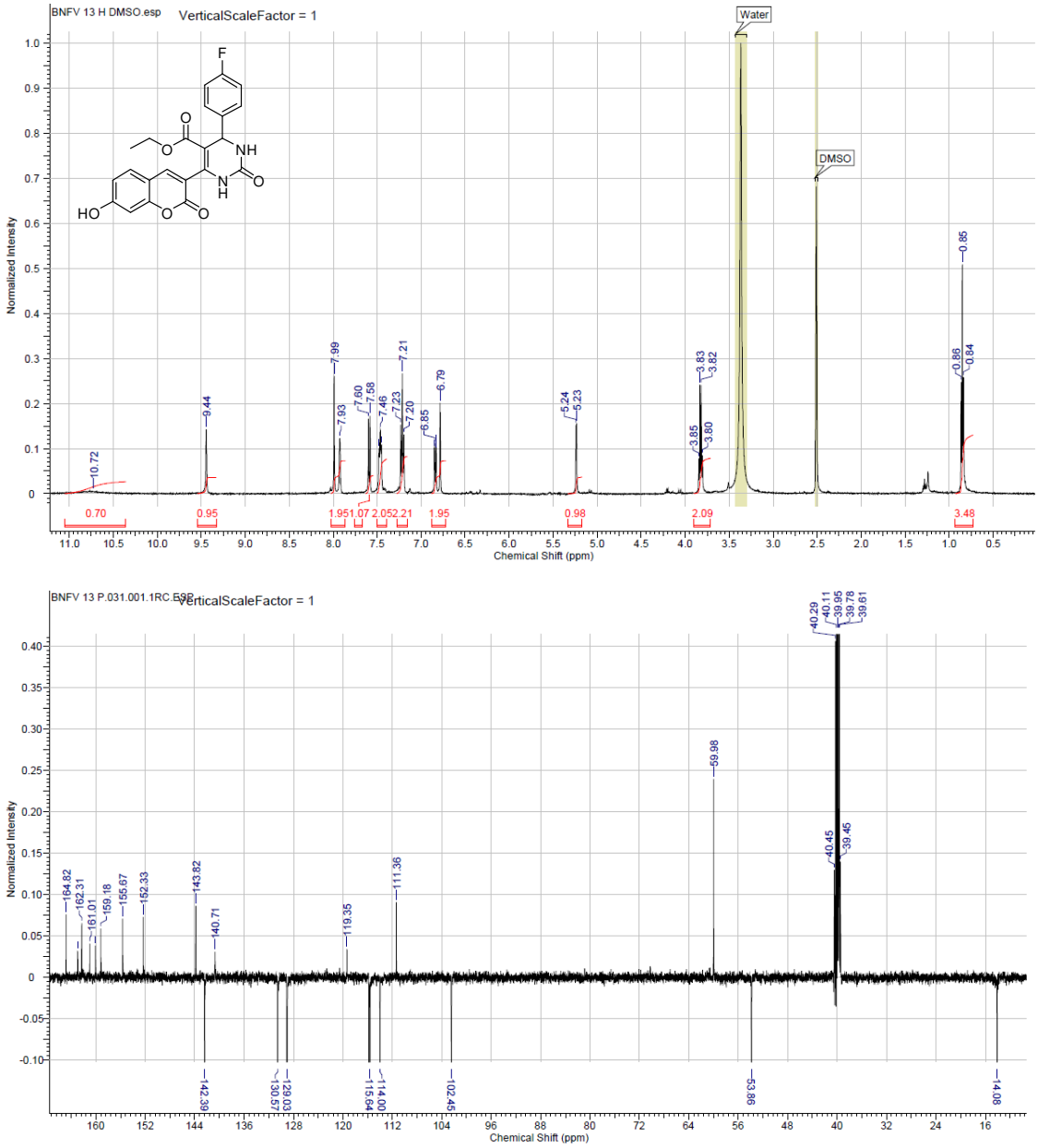


Fig. S19 1H NMR (500 MHz), 13C NMR (125 MHz) spectra of **4h** in DMSO-*d6*.

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Negative	Alternating Ion Polarity	off
Mass Range Mode	Enhanced	Scan Begin	100 m/z	Scan End	700 m/z
Capillary Exit	Resolution	n/a	n/a	Trap Drive	68.9
Accumulation Time	169 µs	Averages	5 Spectra	Auto MS/MS	off

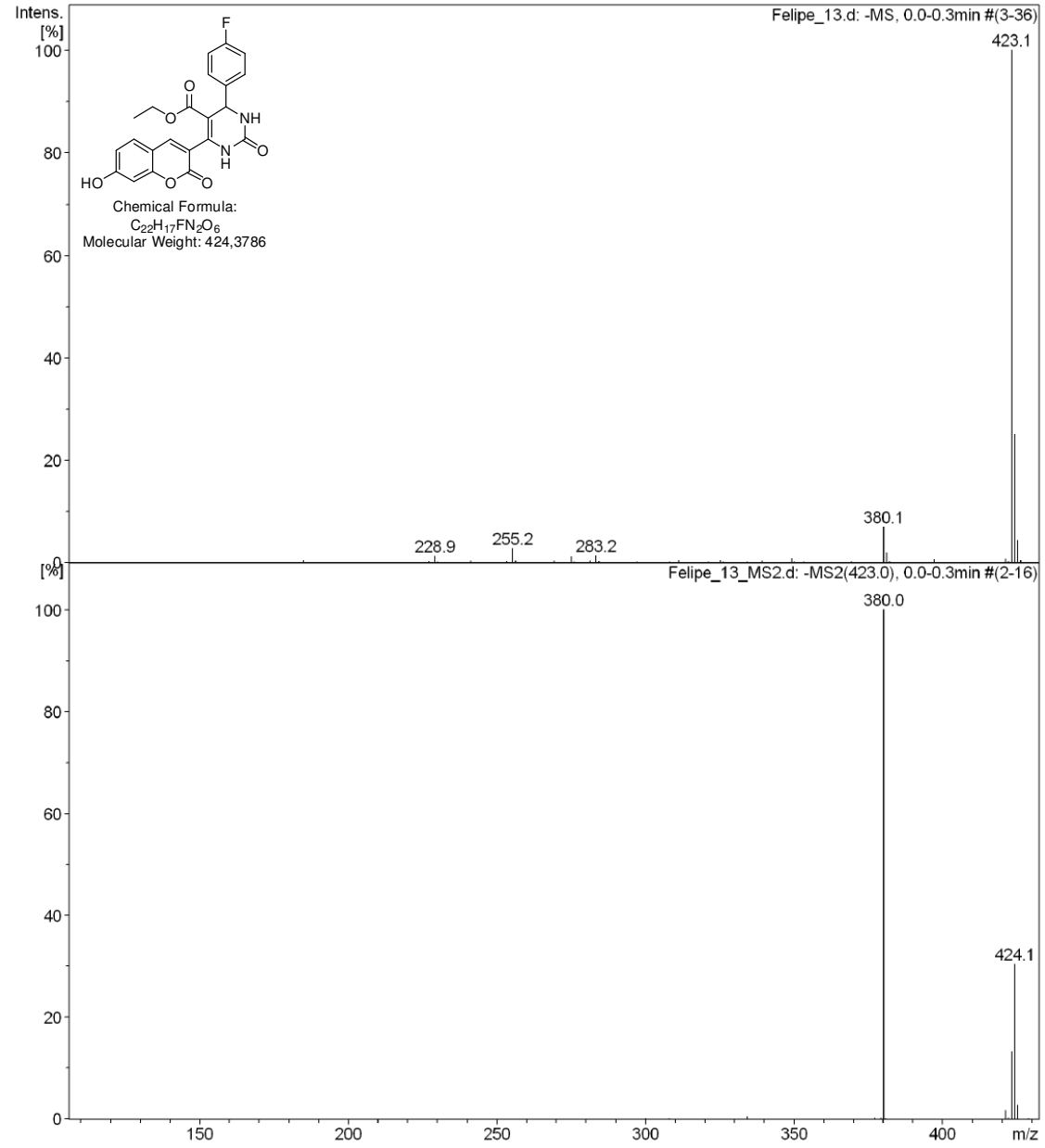


Fig. S20 ESI spectra of **4h**.

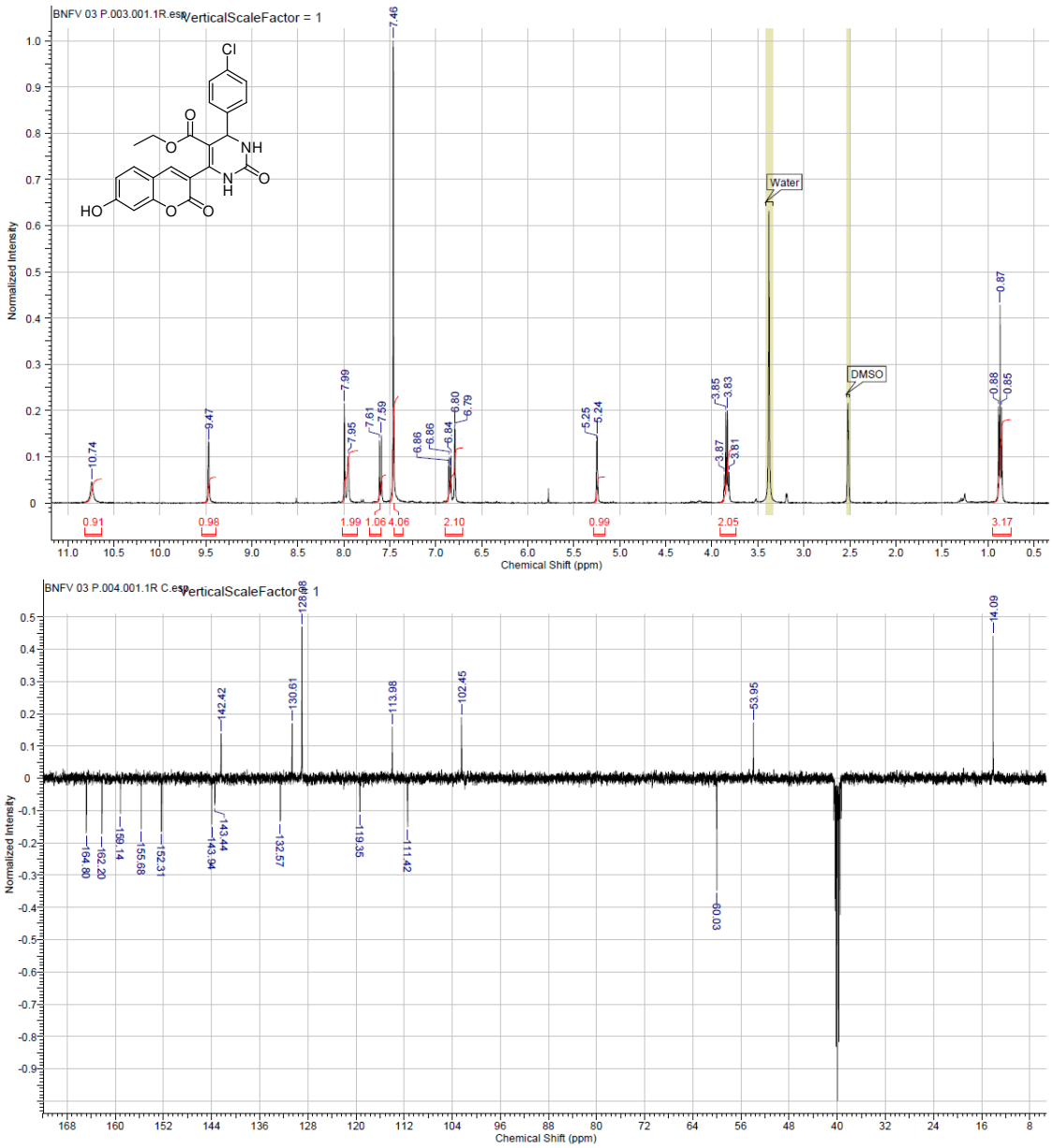


Fig. 21 ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) spectra of **4i** in DMSO-*d6*.

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Negative	Alternating Ion Polarity	off
Mass Range Mode	Enhanced	Scan Begin	100 m/z	Scan End	700 m/z
Capillary Exit	Resolution	n/a	n/a	Trap Drive	68.9
Accumulation Time	527 µs	Averages	5 Spectra	Auto MS/MS	off

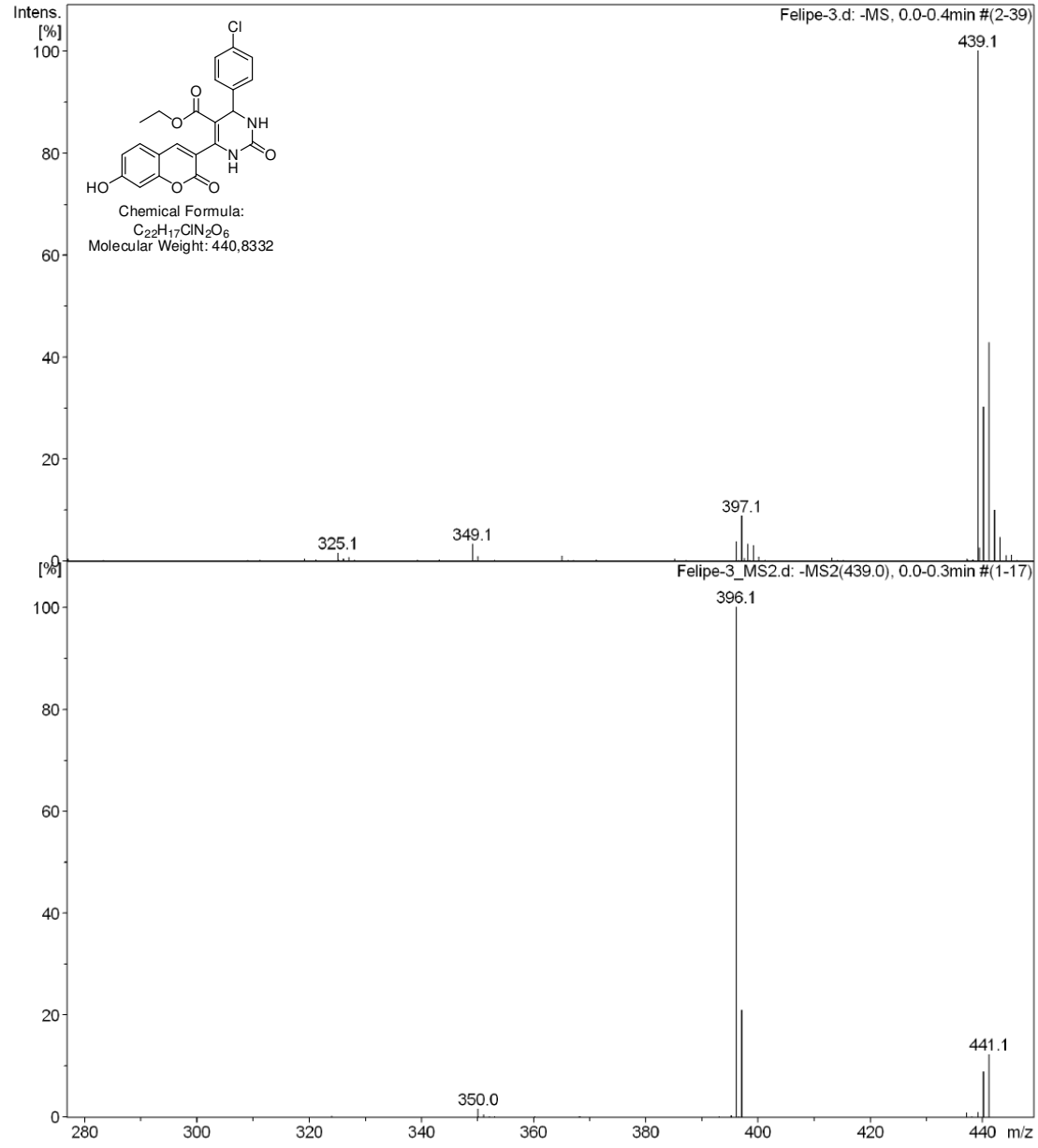


Fig. S22 ESI spectra of **4i**.

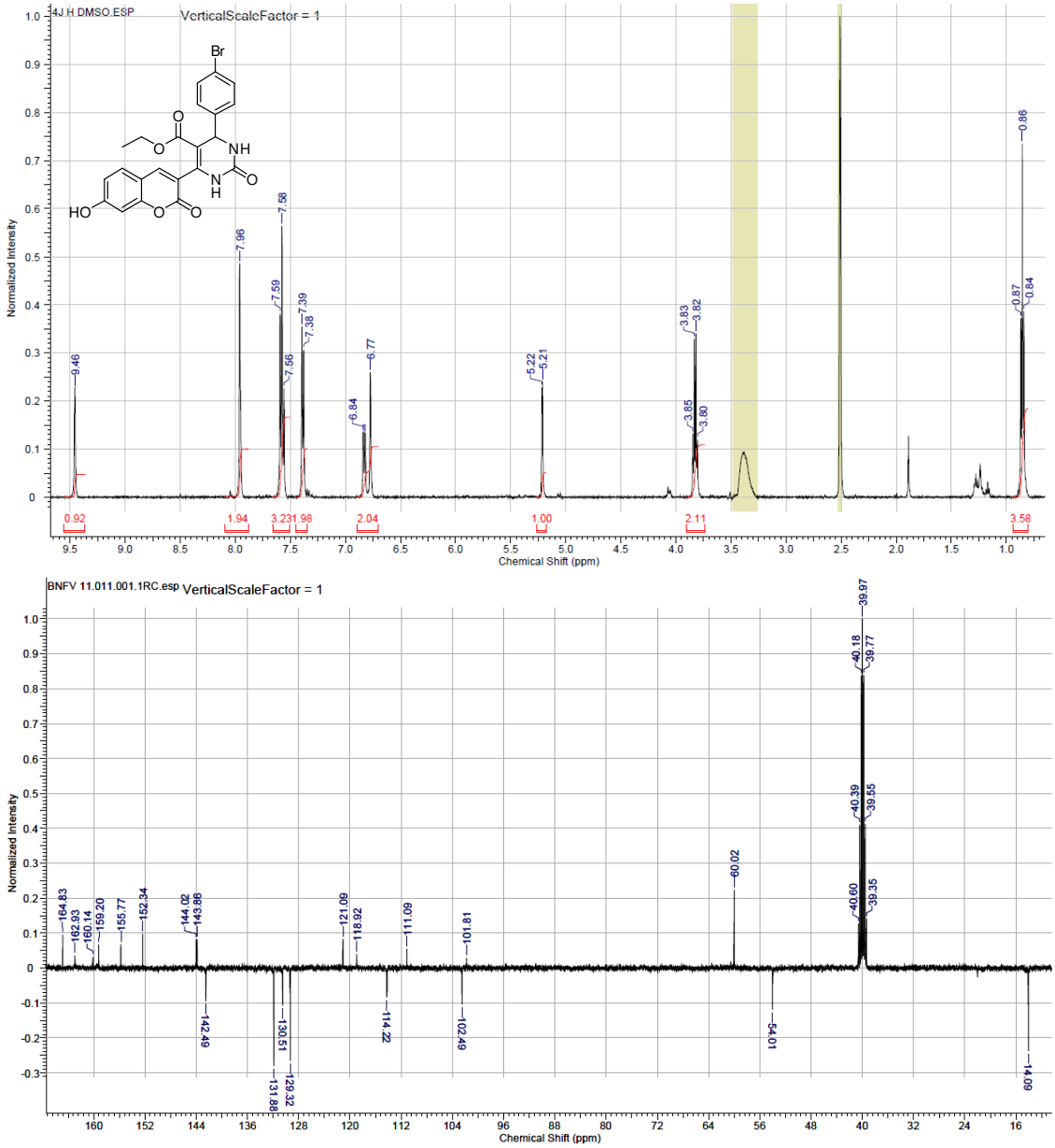


Fig. 23 ^{1}H NMR (500 MHz), ^{13}C NMR (100 MHz) spectra of **4j** in DMSO-*d6*.

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Negative	Alternating Ion Polarity	off
Mass Range Mode	Enhanced	Scan Begin	100 m/z	Scan End	700 m/z
Capillary Exit	Resolution	n/a	n/a	Trap Drive	68.9
Accumulation Time	3267 µs	Averages	5 Spectra	Auto MS/MS	off

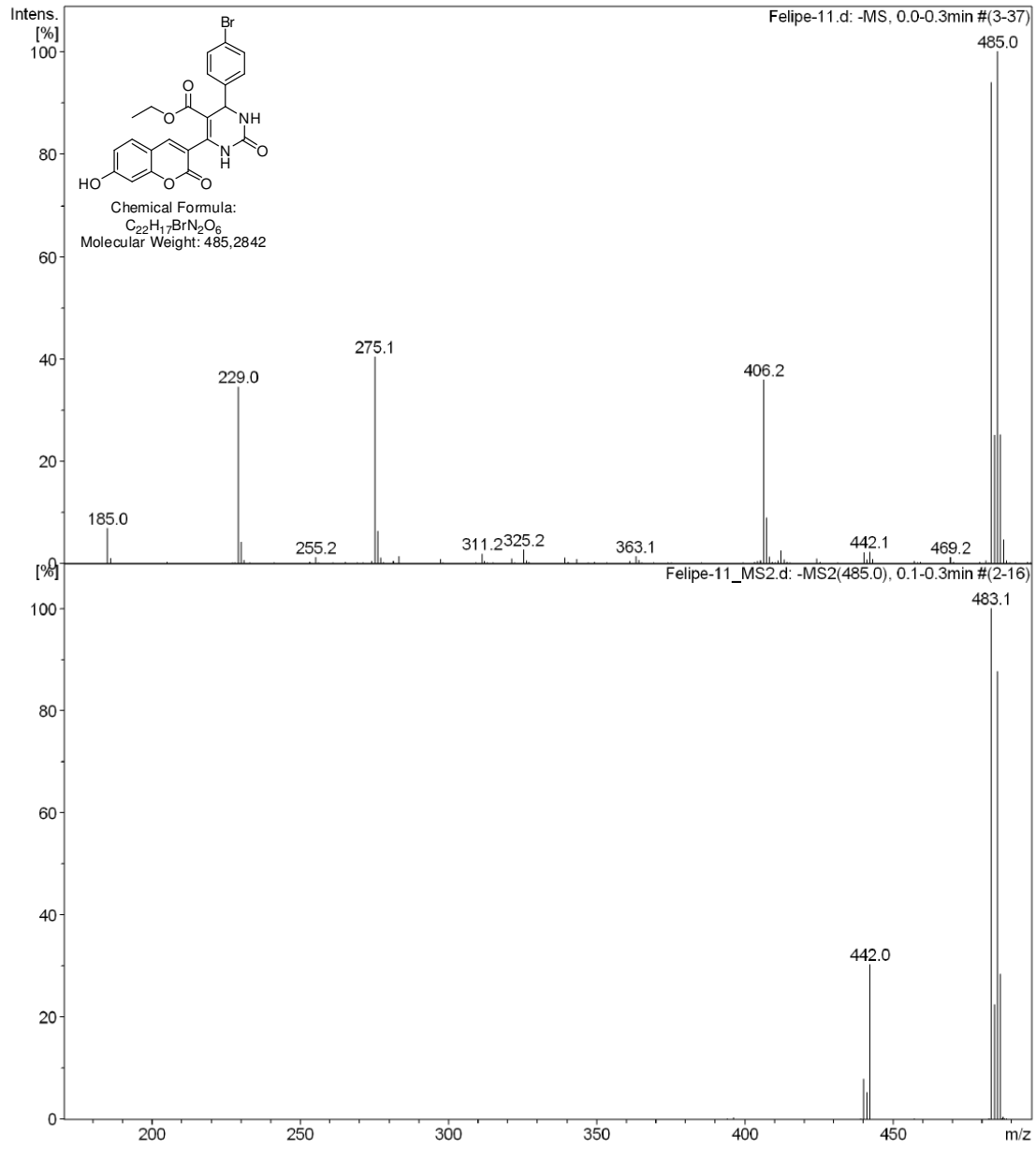


Fig. S24 ESI spectra of **4j**.

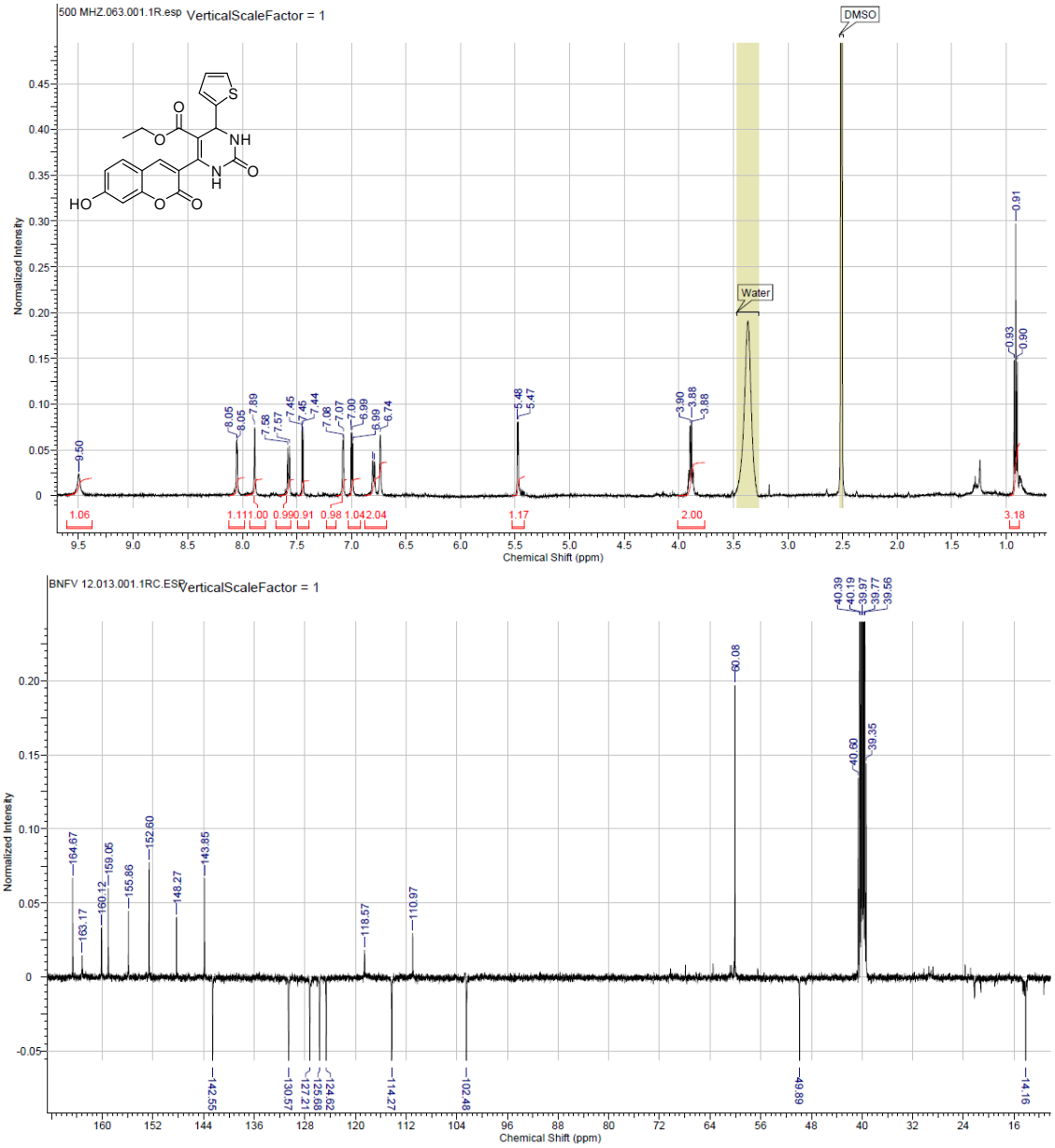


Fig. 25 ^{1}H NMR (500 MHz), ^{13}C NMR (100 MHz) spectra of **4k** in DMSO-*d6*.

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Negative	Alternating Ion Polarity	off
Mass Range Mode	Enhanced	Scan Begin	100 m/z	Scan End	700 m/z
Capillary Exit	Resolution	n/a	n/a	Trap Drive	68.9
Accumulation Time	918 µs	Averages	5 Spectra	Auto MS/MS	off

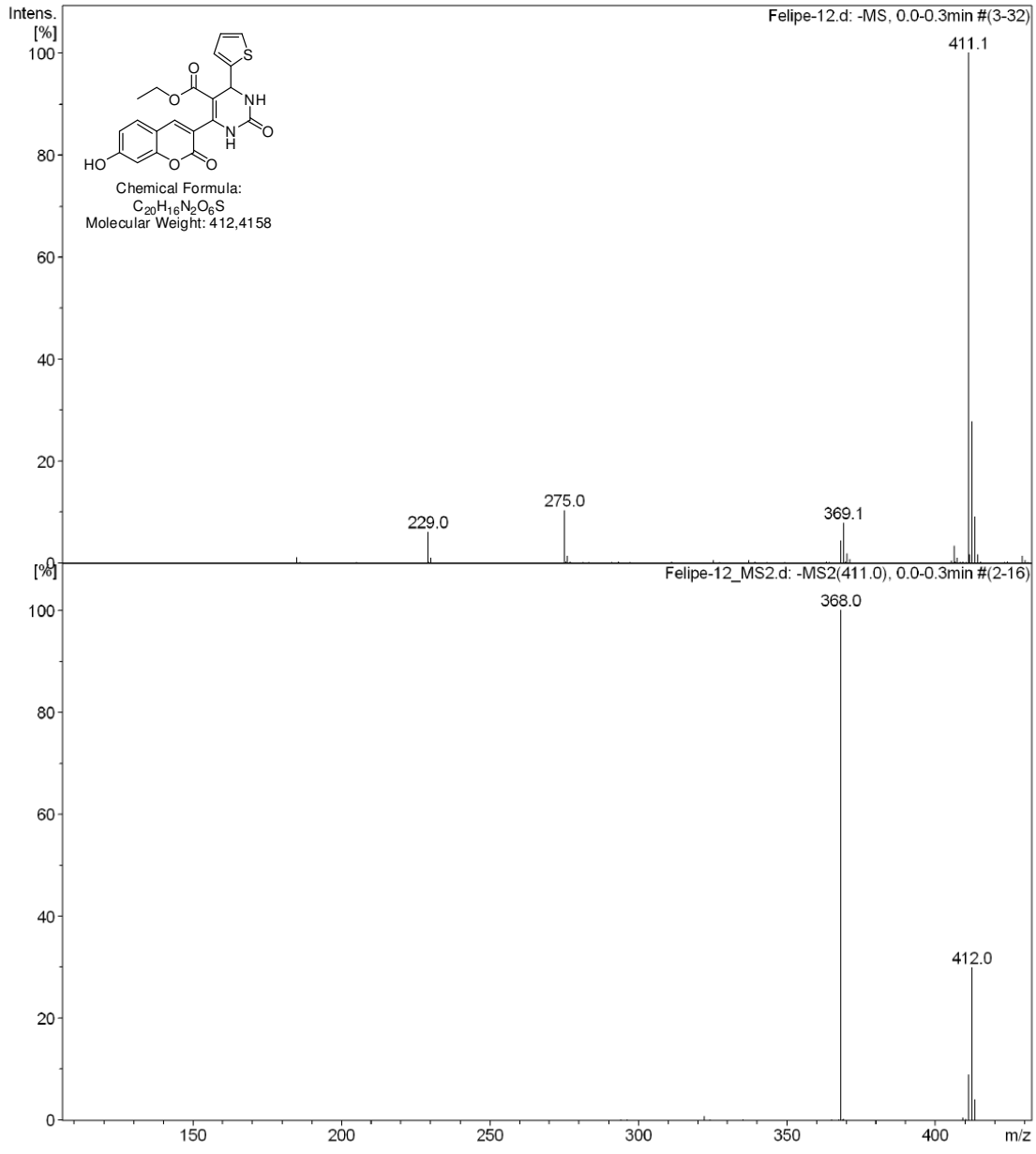


Fig. S26 ESI spectra of **4k**.

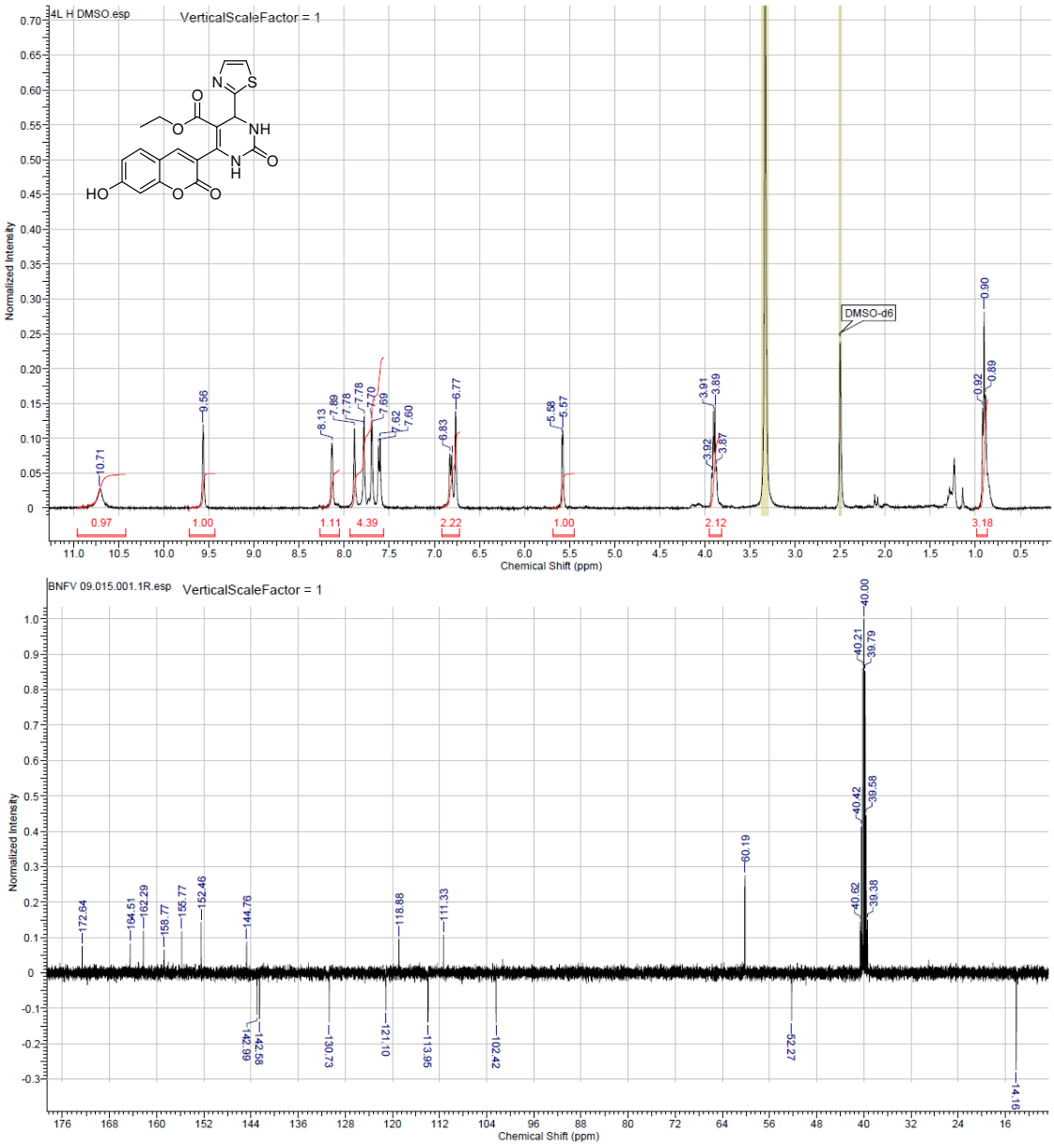


Fig. S27 ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) spectra of **4l** in DMSO-*d6*.

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Negative	Alternating Ion Polarity	off
Mass Range Mode	Enhanced	Scan Begin	100 m/z	Scan End	700 m/z
Capillary Exit	Redacted	n/a	n/a	Trap Drive	68.9
Accumulation Time	199 µs	Averages	5 Spectra	Auto MS/MS	off

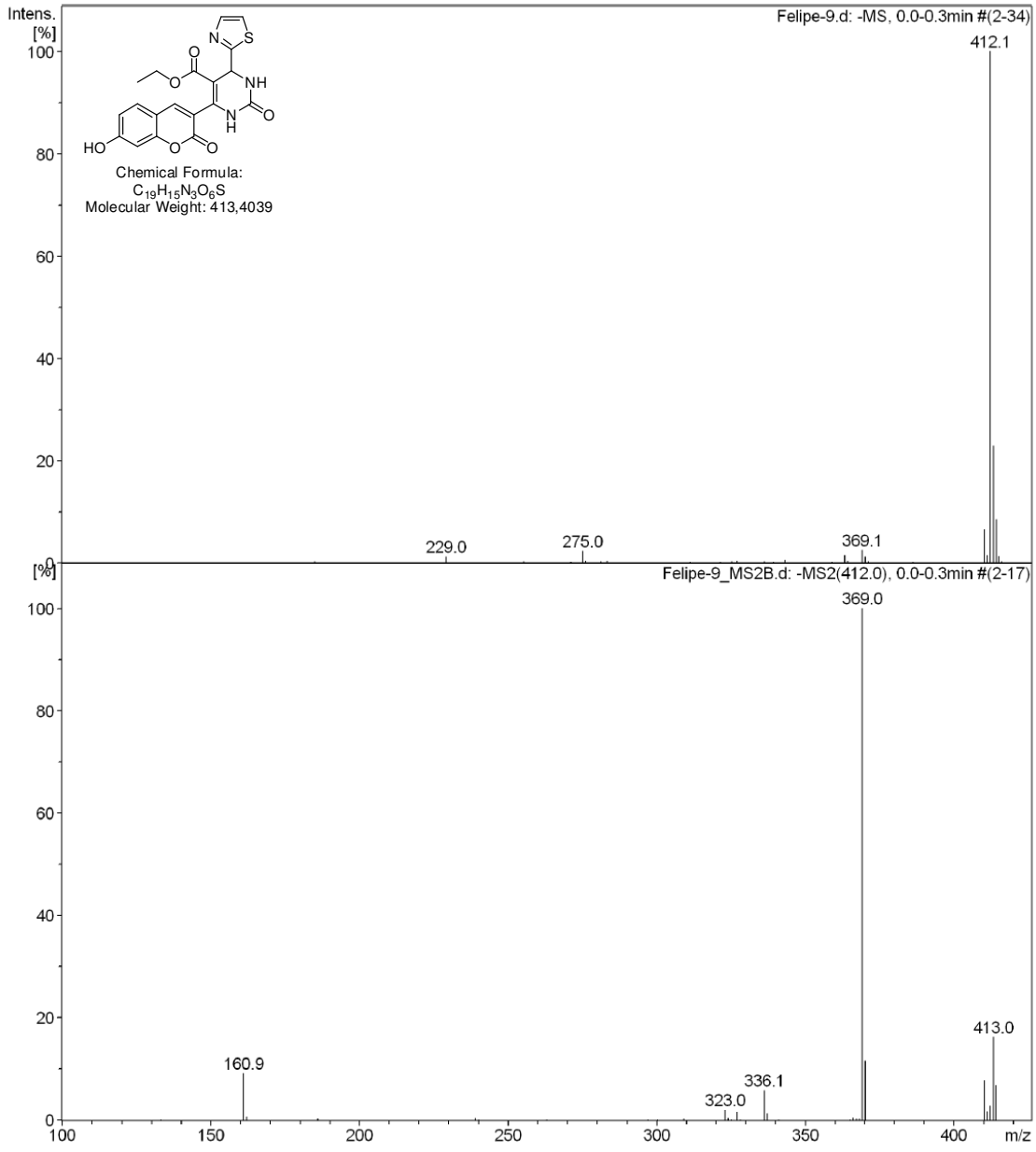


Fig. S28 ESI spectra of **4l**.

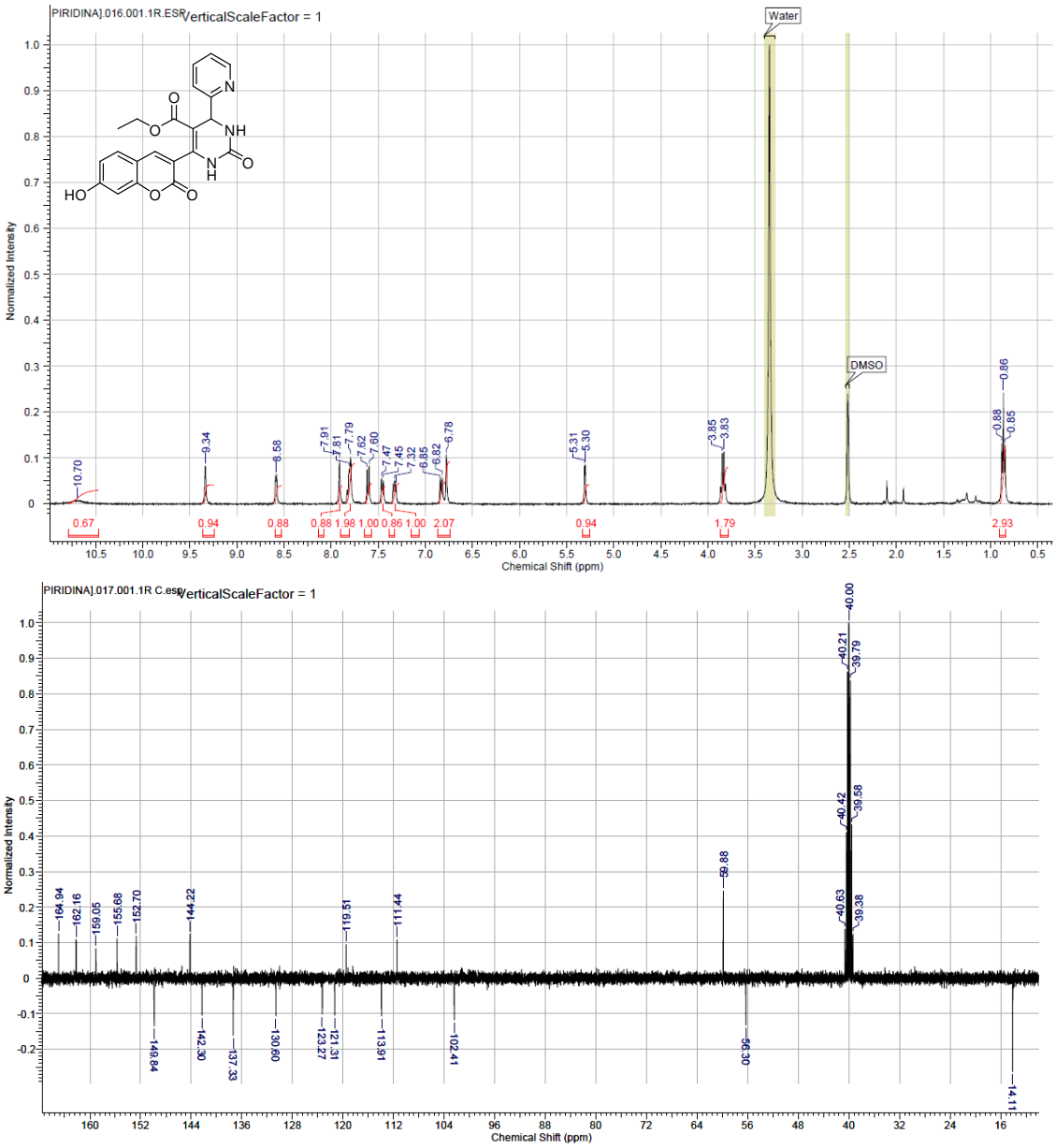


Fig. S29 ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) spectra of **4m** in DMSO-*d6*.

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Negative	Alternating Ion Polarity	off
Mass Range Mode	Enhanced	Scan Begin	100 m/z	Scan End	700 m/z
Capillary Exit	Resolution	n/a	n/a	Trap Drive	68.9
Accumulation Time	94 µs	Averages	5 Spectra	Auto MS/MS	off

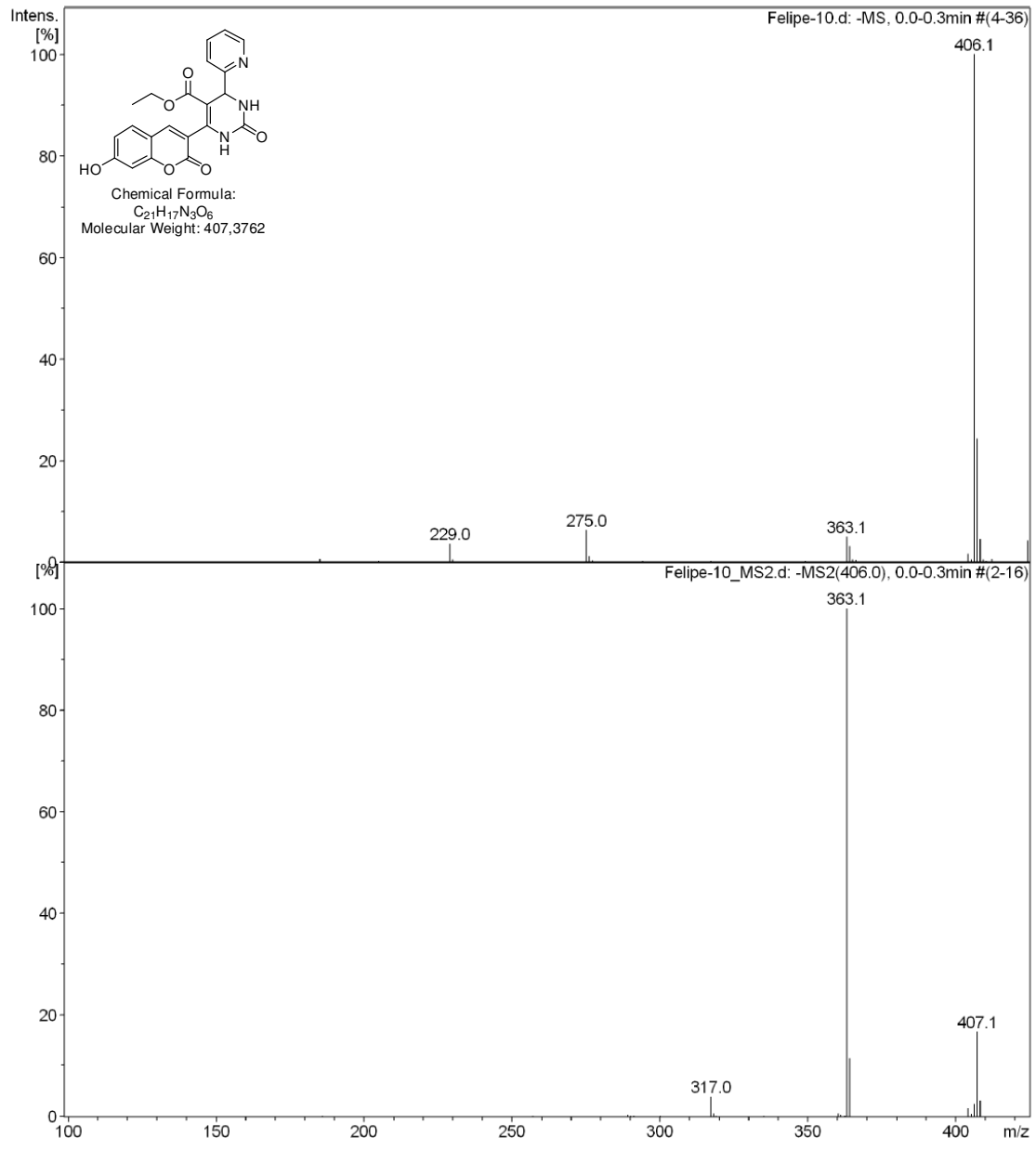


Fig. S30 ESI spectra of **4m**.

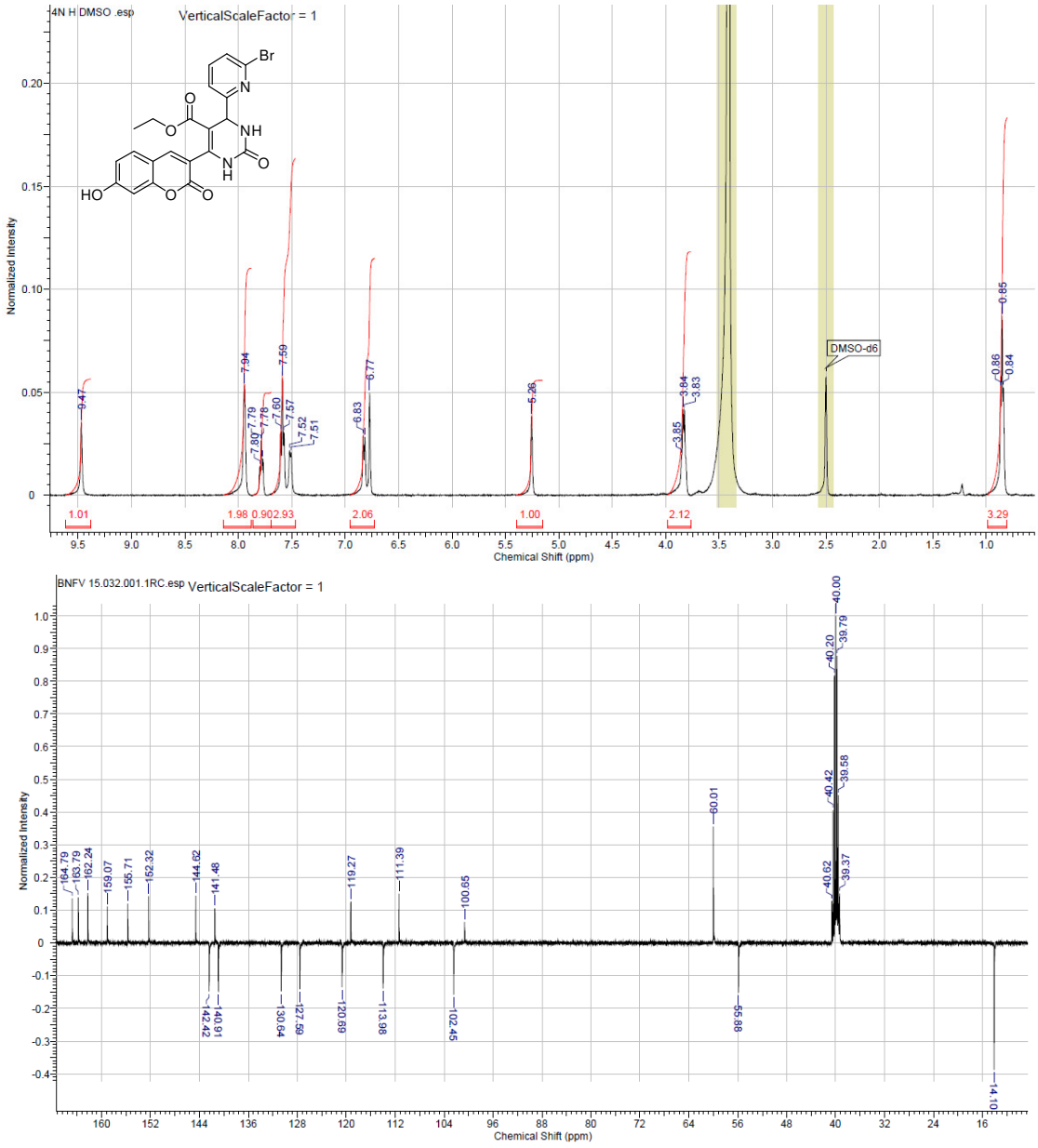


Fig. S31 ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) spectra of **4n** in DMSO-*d6*.

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Negative	Alternating Ion Polarity	off
Mass Range Mode	Enhanced	Scan Begin	100 m/z	Scan End	700 m/z
Capillary Exit	Resolution	n/a	n/a	Trap Drive	68.9
Accumulation Time	2189 µs	Averages	5 Spectra	Auto MS/MS	off

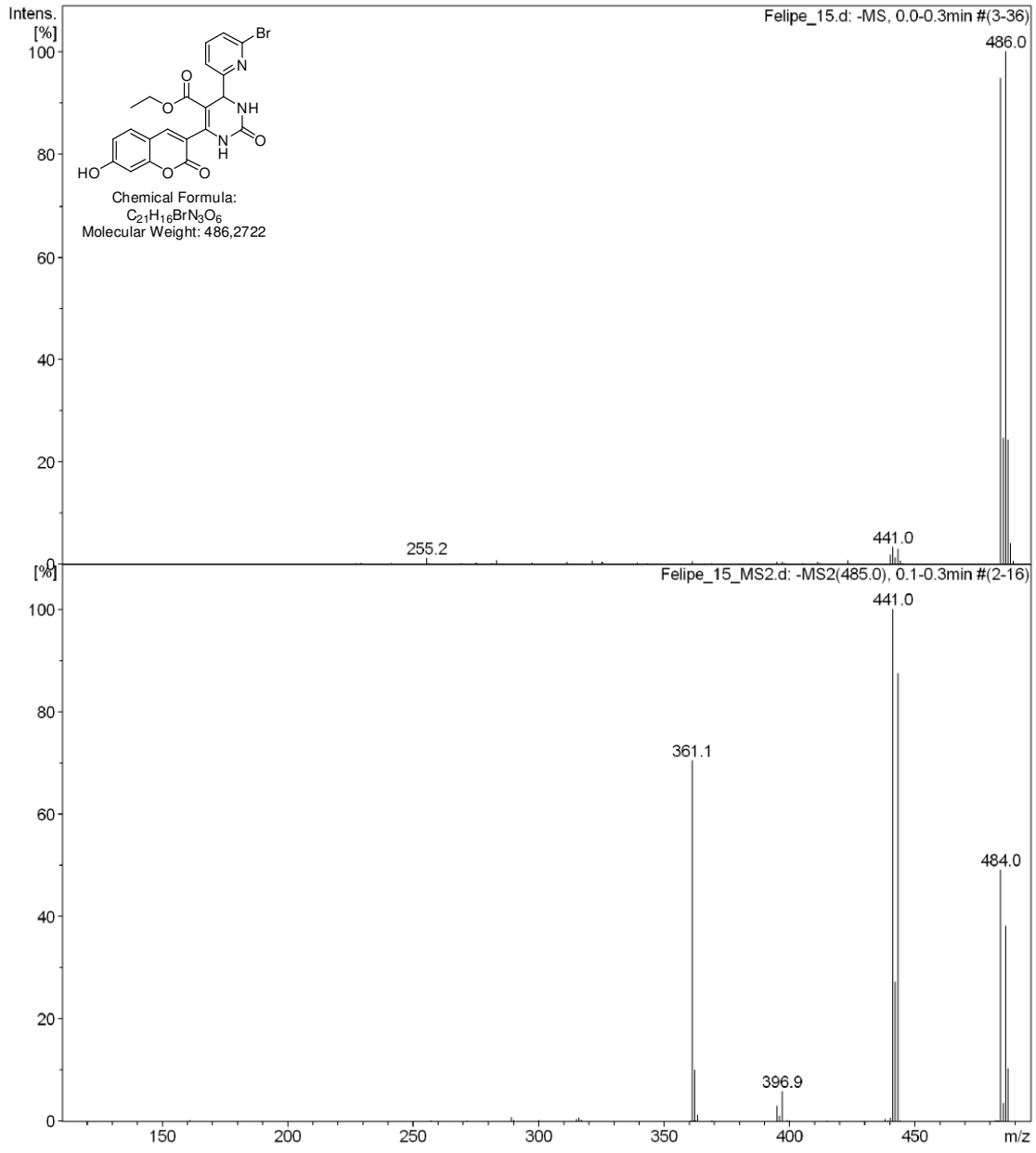


Fig. S32 ESI spectra of **4n**.

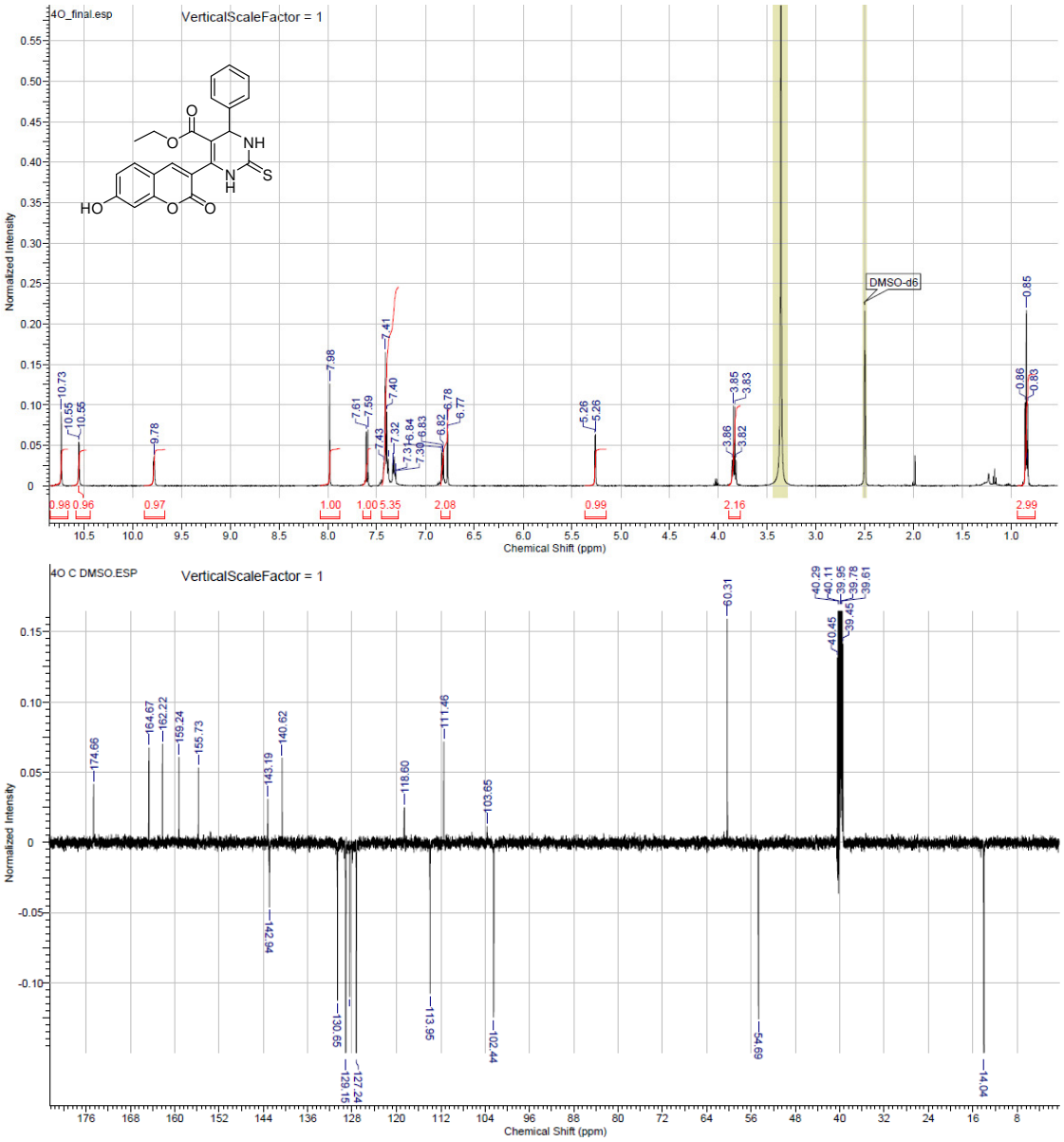


Fig. S33 ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) spectra of **4o** in DMSO-*d6*.

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Negative	Alternating Ion Polarity	off
Mass Range Mode	Enhanced	Scan Begin	100 m/z	Scan End	700 m/z
Capillary Exit	Redouti	n/a	n/a	Trap Drive	68.9
Accumulation Time	413 µs	Averages	5 Spectra	Auto MS/MS	off

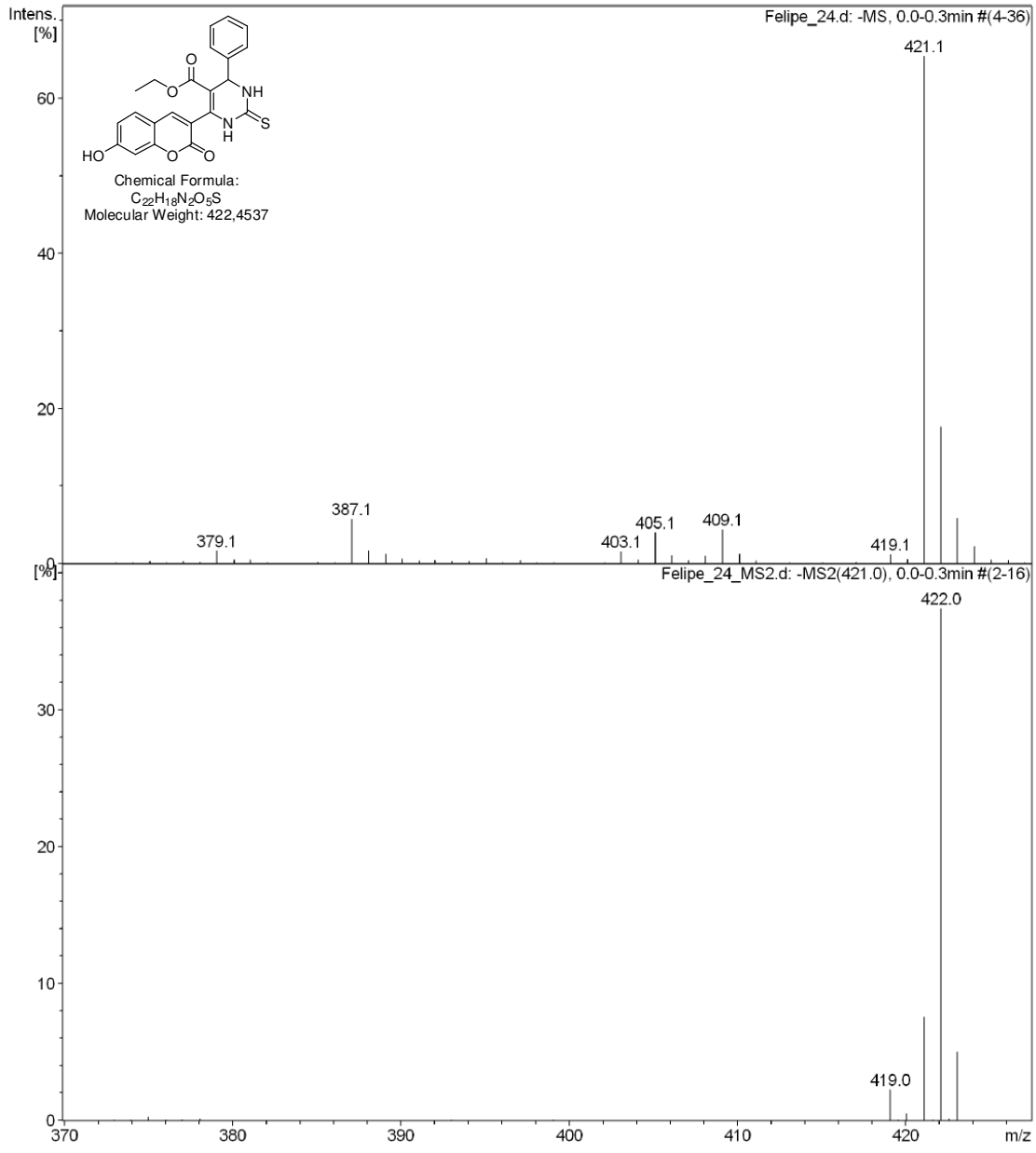


Fig. S34 ESI spectra of **4o**.

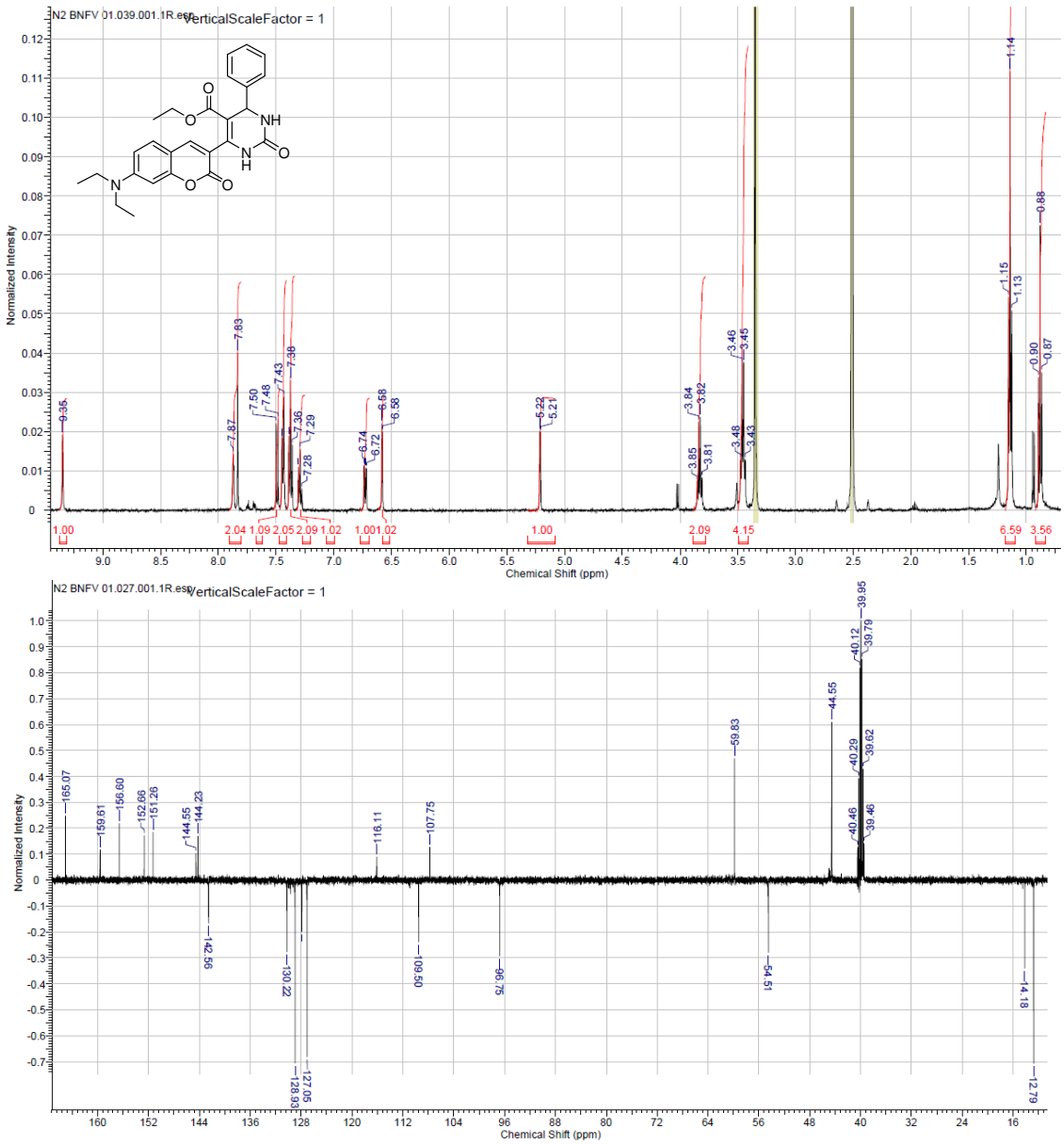


Fig. S35 ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) spectra of **4p** in DMSO-*d6*.

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Negative	Alternating Ion Polarity	off
Mass Range Mode	Enhanced	Scan Begin	100 m/z	Scan End	700 m/z
Capillary Exit	Resolution	n/a	n/a	Trap Drive	68.9
Accumulation Time	2722 µs	Averages	5 Spectra	Auto MS/MS	off

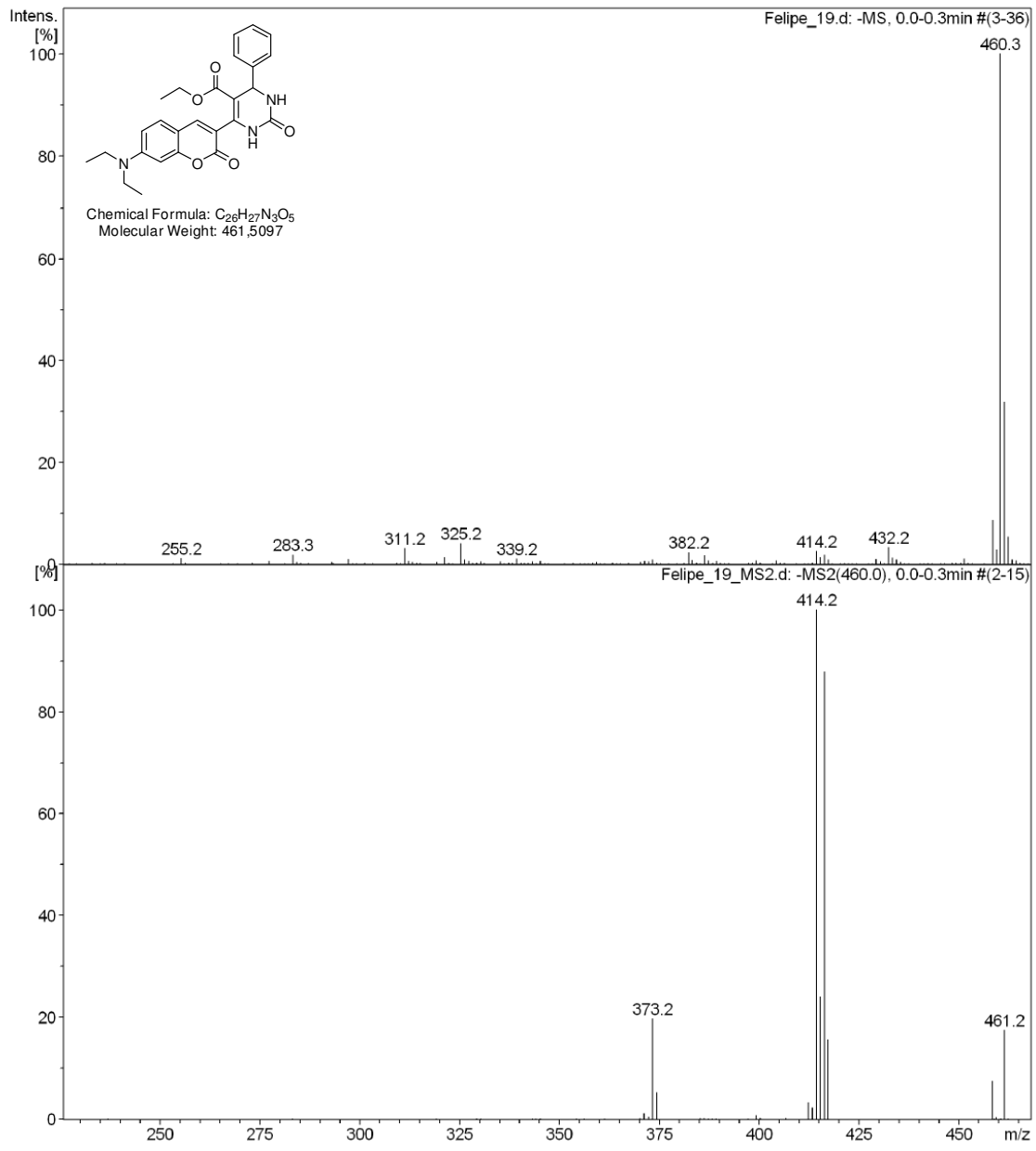


Fig. S36 ESI spectra of **4p**.

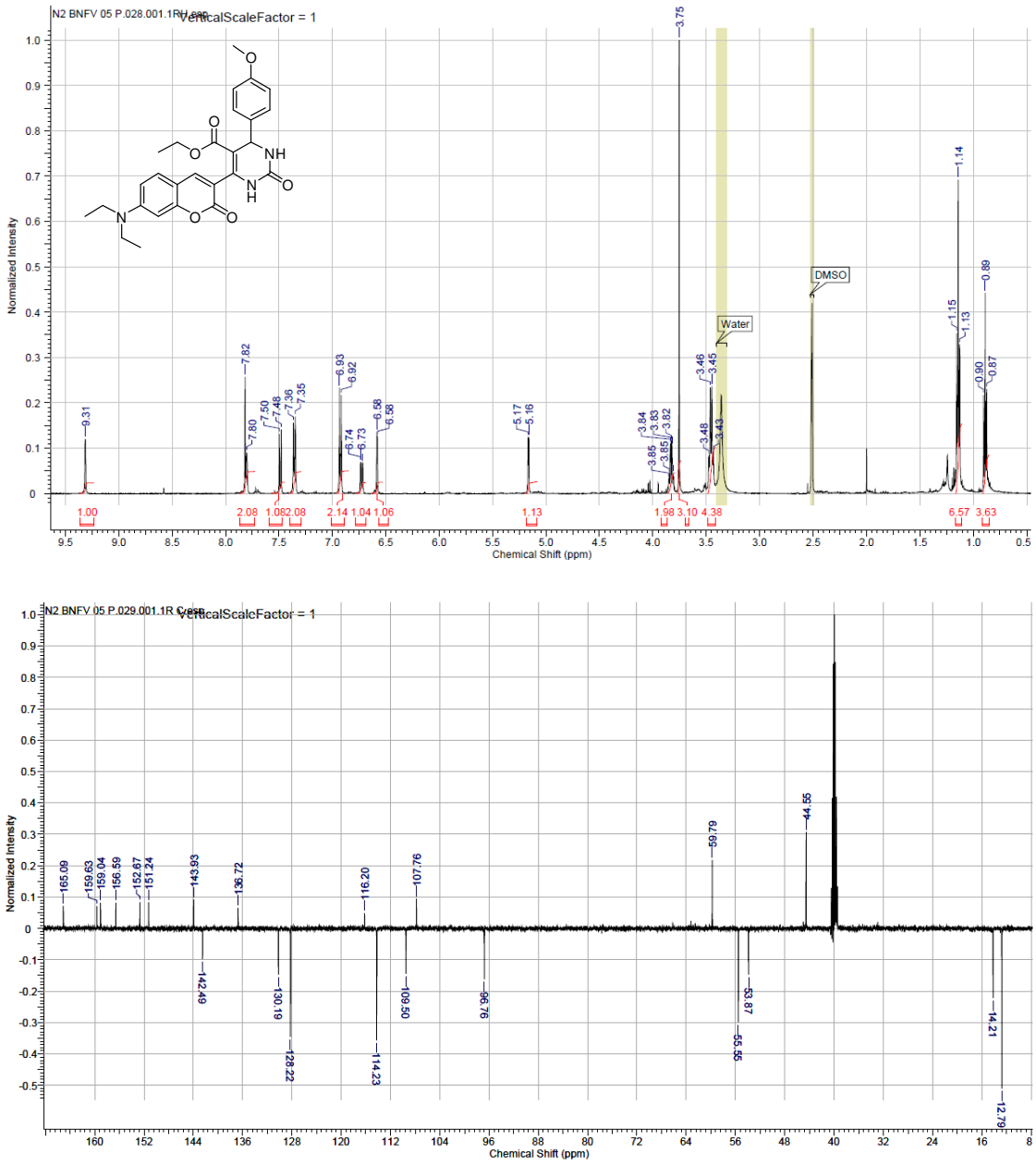


Fig. S37 ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) spectra of **4q** in DMSO-*d6*.

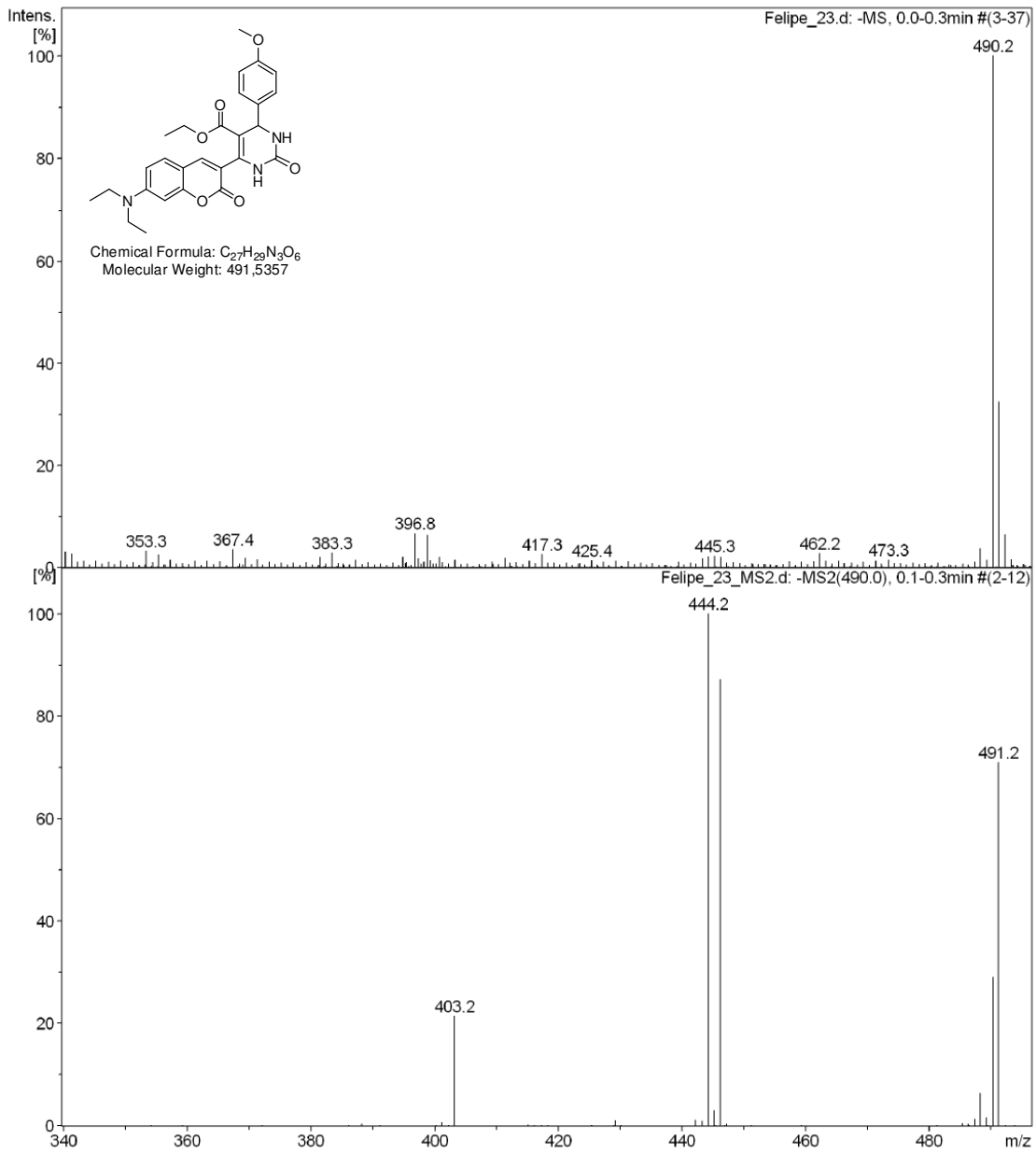


Fig. S38 ESI spectra of **4q**.

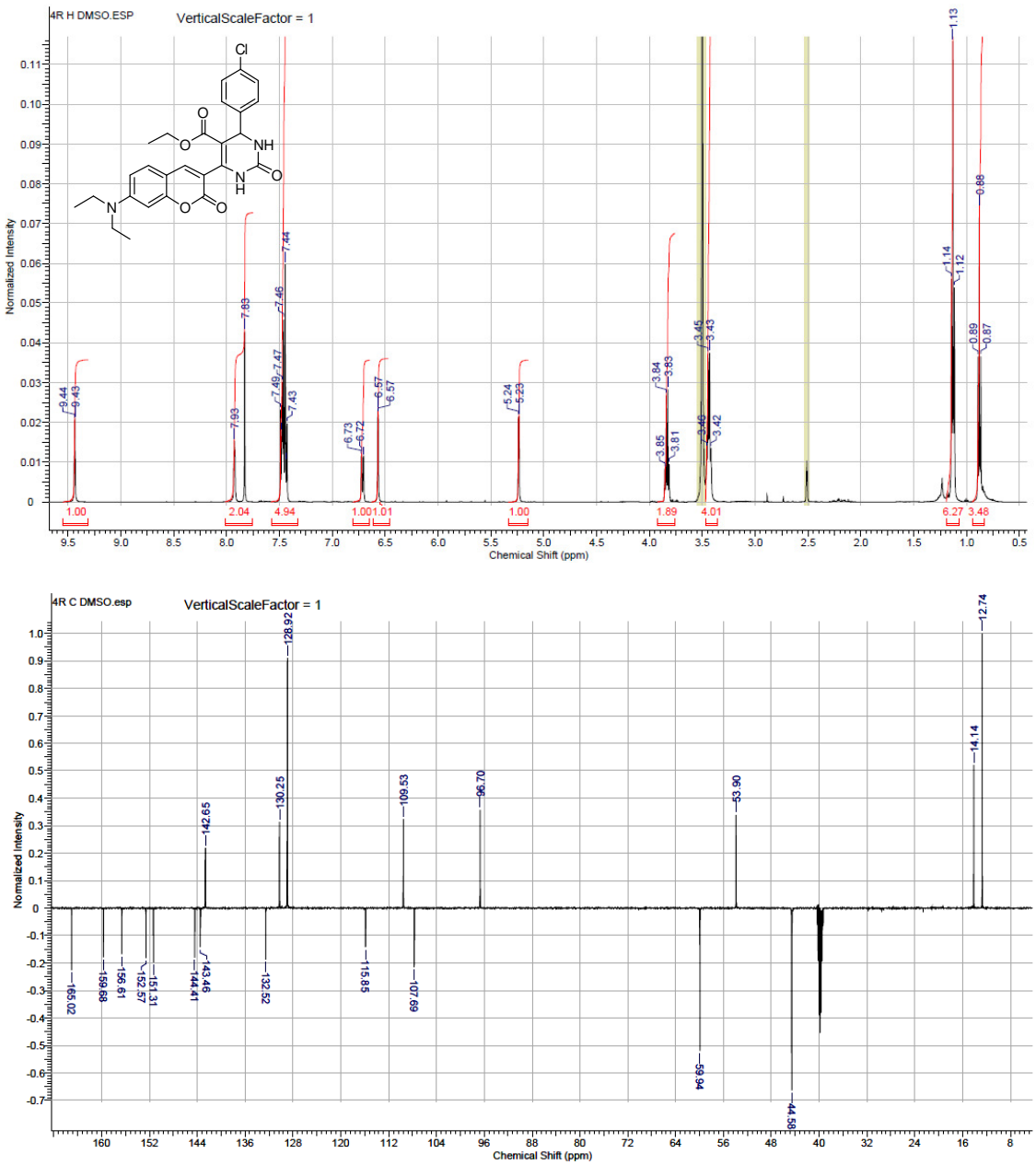


Fig. S39 ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) spectra of **4r** in DMSO-*d6*.

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Negative	Alternating Ion Polarity	off
Mass Range Mode	Enhanced	Scan Begin	100 m/z	Scan End	700 m/z
Capillary Exit	Reduction	n/a	n/a	Trap Drive	68.9
Accumulation Time	74854 µs	Averages	5 Spectra	Auto MS/MS	off

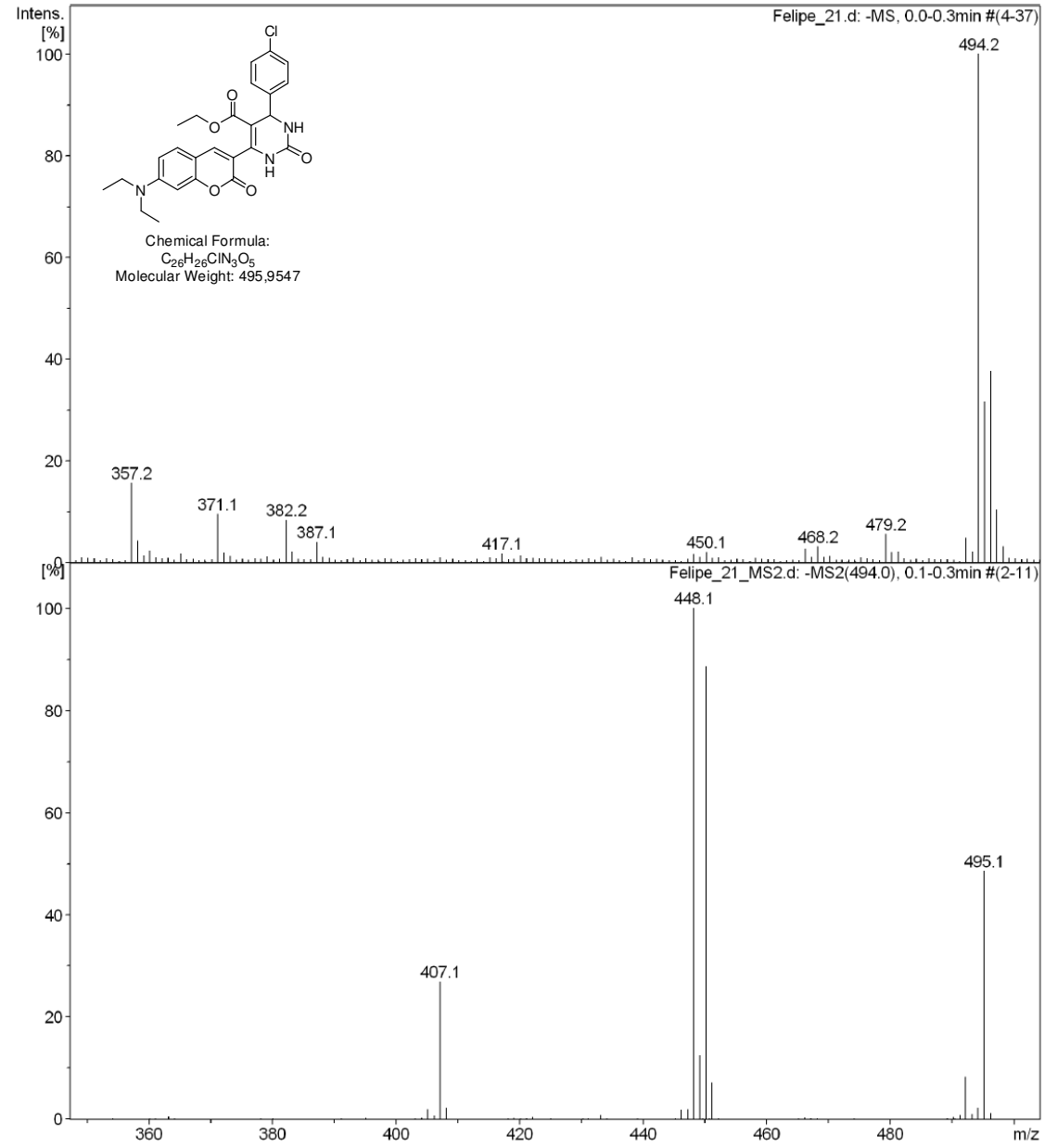


Fig. S40 ESI spectra of **4r**.

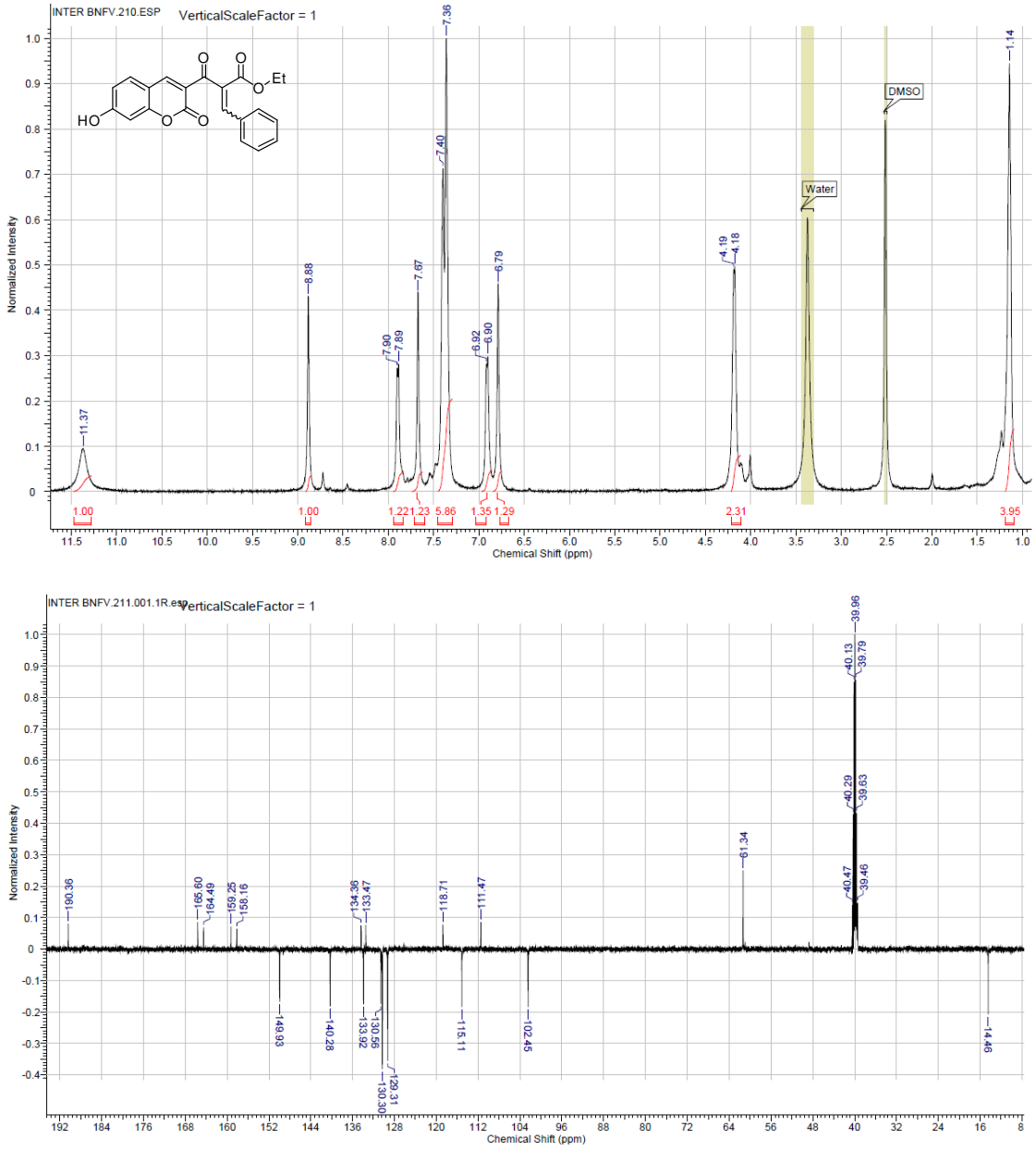


Fig. S41 ^{1}H NMR (500 MHz), ^{13}C NMR(125 MHz) spectra of **5** in DMSO-*d6*.

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Negative	Alternating Ion Polarity	off
Mass Range Mode	Enhanced	Scan Begin	100 m/z	Scan End	700 m/z
Capillary Exit	Ramp On	n/a	n/a	Trap Drive	68.9
Accumulation Time	602 µs	Averages	5 Spectra	Auto MS/MS	off

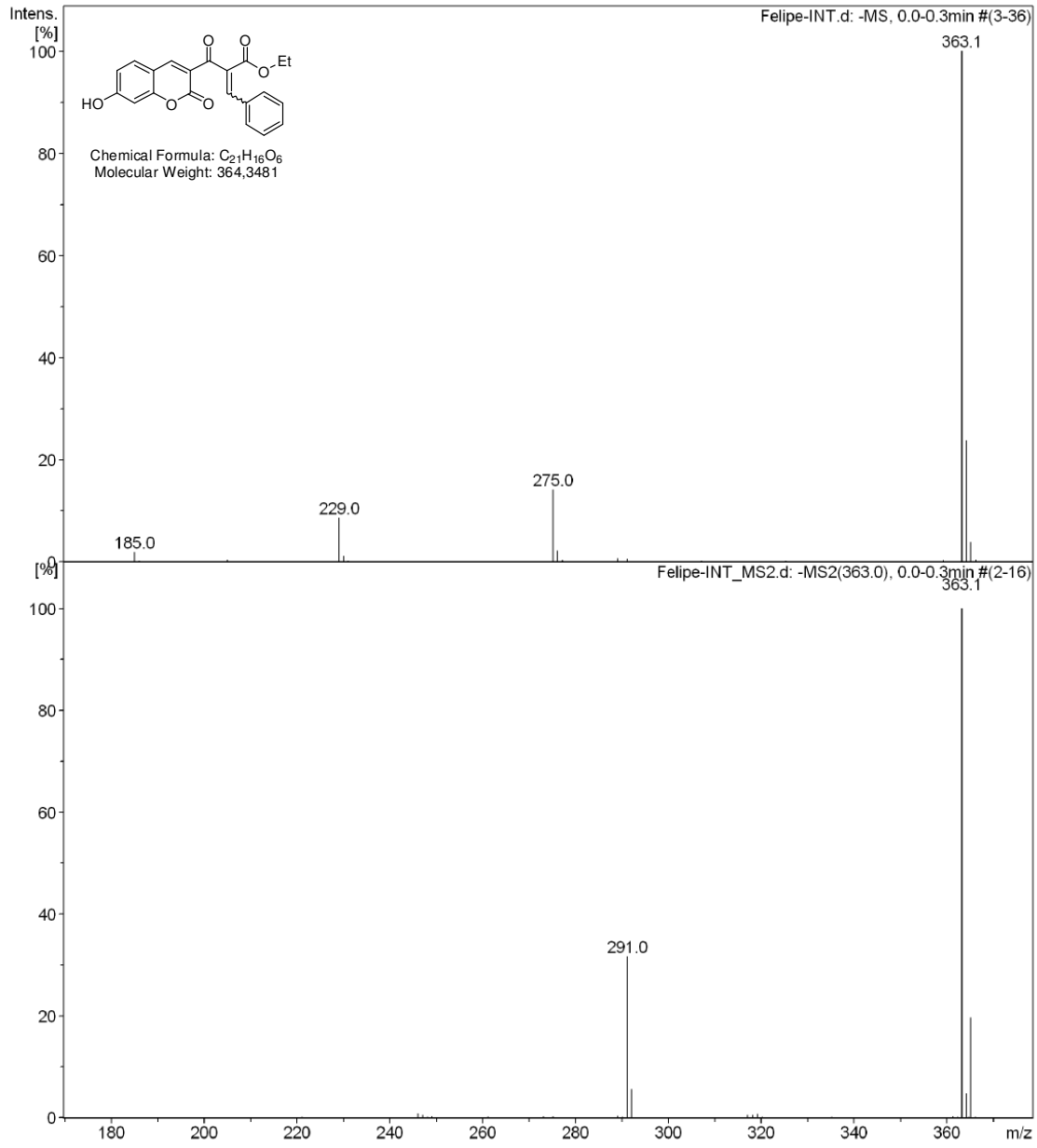
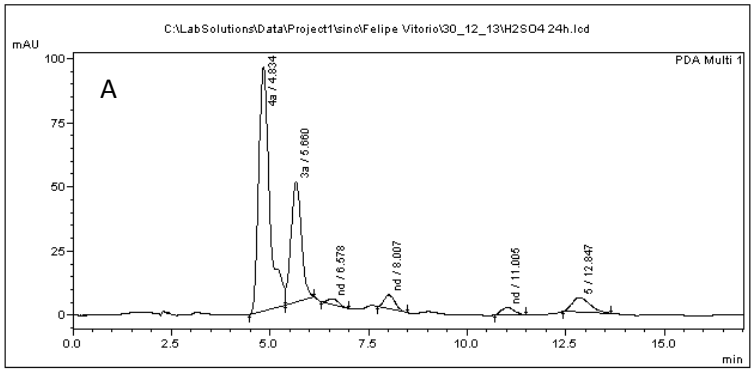


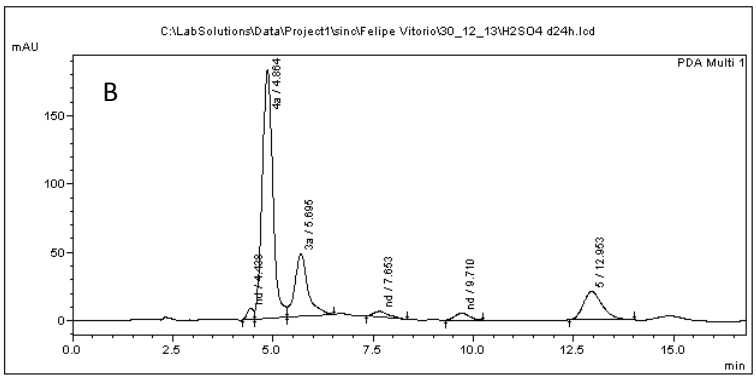
Fig. S42 ESI spectra of **5**.

HPLC data analysis



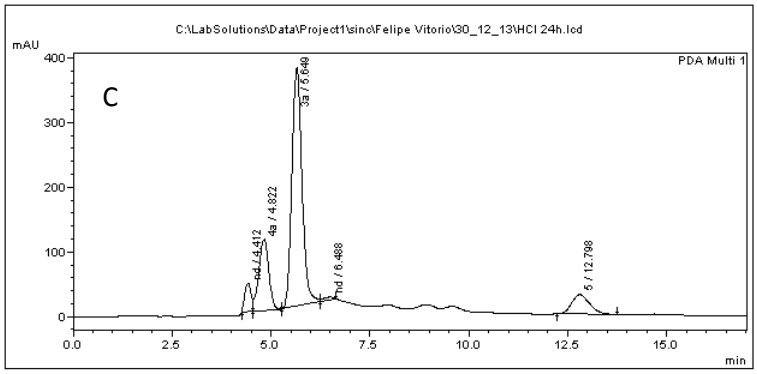
PDA Ch1 370nm 4nm

Name	Ret. Time	Area %	Height %
4a	4.834	59.303	60.119
3a	5.660	28.032	29.618
nd	6.578	1.338	1.428
nd	8.007	3.399	3.462
nd	11.005	2.075	1.775
5	12.847	5.852	3.598
		100.000	100.000



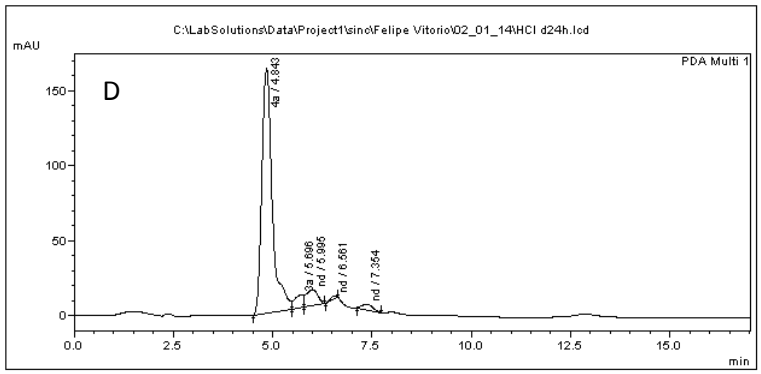
PDA Ch1 370nm 4nm

Name	Ret. Time	Area %	Height %
nd	4.438	1.602	3.106
4a	4.864	62.448	68.499
3a	5.695	18.934	17.237
nd	7.653	1.937	1.495
nd	9.710	2.315	1.889
5	12.953	12.763	7.774
		100.000	100.000



PDA Ch1 370nm 4nm

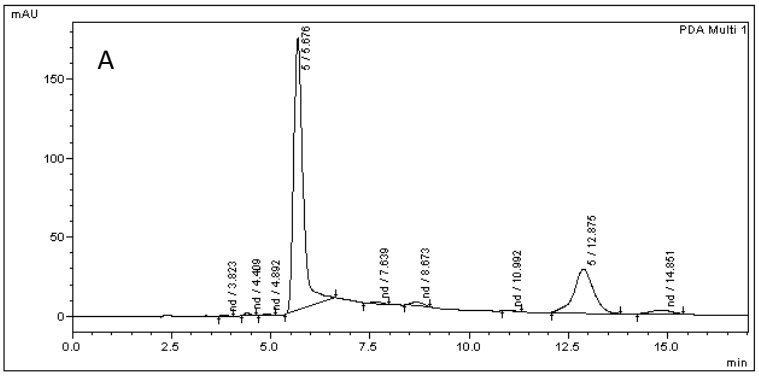
Name	Ret. Time	Area %	Height %
nd	4.412	4.922	7.927
4a	4.822	19.095	19.651
3a	5.649	65.719	66.310
nd	6.488	0.796	0.731
5	12.798	9.467	5.382
		100.000	100.000



PDA Ch1 370nm 4nm

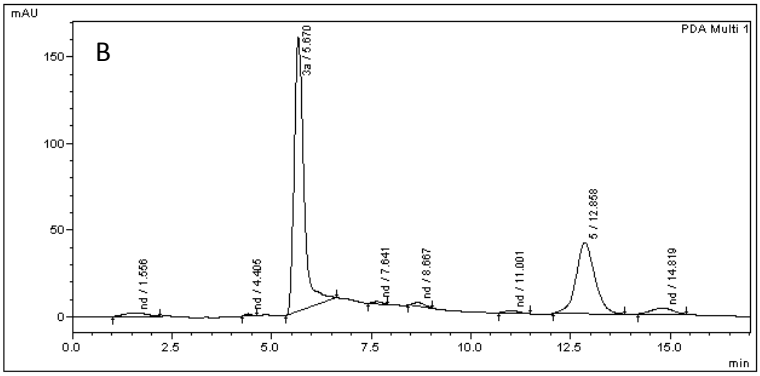
Name	Ret. Time	Area %	Height %
4a	4.843	86.818	86.924
3a	5.696	4.098	4.432
nd	5.995	6.416	5.692
nd	6.561	0.681	1.077
nd	7.354	1.988	1.875
		100.000	100.000

Fig. S43 Comparison of reaction catalyzed conditions. A – H_2SO_4 (25 µL); B – H_2SO_4 (12.5 µL); C – HCl (25 µL); D – HCl (12.5 µL). nd – not determined product.



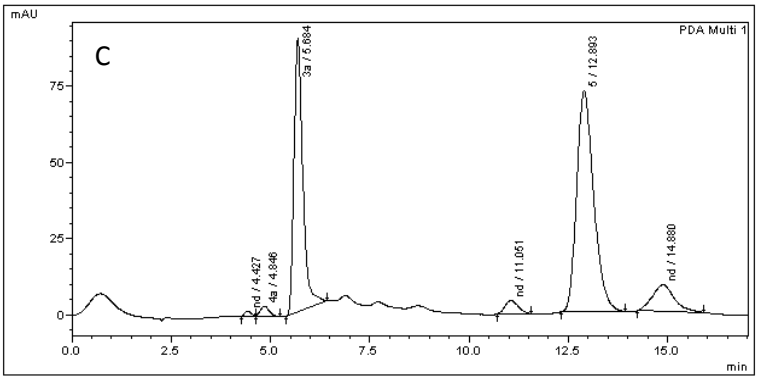
PDA Ch1 370nm 4nm

Name	Ret. Time	Area %	Height %
nd	3.823	0.203	0.394
nd	4.409	0.448	0.786
nd	4.892	0.253	0.313
5	5.676	71.347	82.140
nd	7.639	0.486	0.598
nd	8.673	1.231	1.113
nd	10.992	0.195	0.202
5	12.875	23.688	13.281
nd	14.851	2.148	1.172
		100.000	100.000



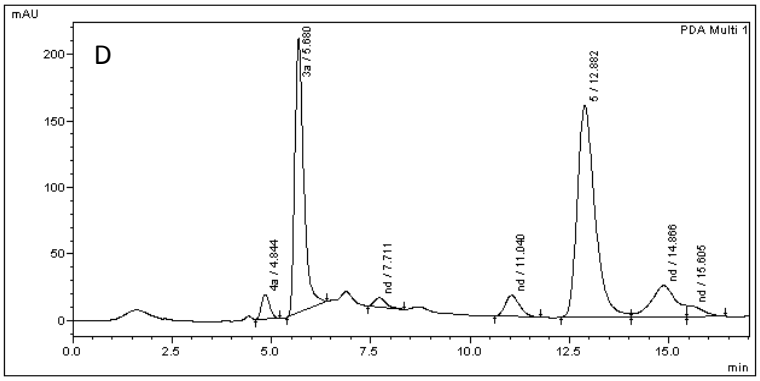
PDA Ch1 370nm 4nm

Name	Ret. Time	Area %	Height %
nd	1.556	2.104	1.059
nd	4.405	0.346	0.654
3a	5.670	61.588	74.874
nd	7.641	0.425	0.573
nd	8.667	1.034	1.020
nd	11.001	0.805	0.706
5	12.858	30.823	19.480
nd	14.819	2.875	1.635
		100.000	100.000



PDA Ch1 370nm 4nm

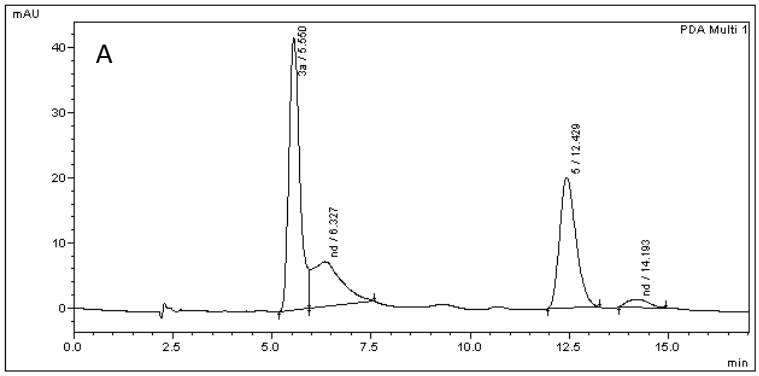
Name	Ret. Time	Area %	Height %
nd	4.427	0.501	0.949
4a	4.846	1.322	1.860
3a	5.684	34.330	49.686
nd	11.051	2.540	2.447
5	12.893	53.004	40.219
nd	14.880	8.302	4.838
		100.000	100.000



PDA Ch1 370nm 4nm

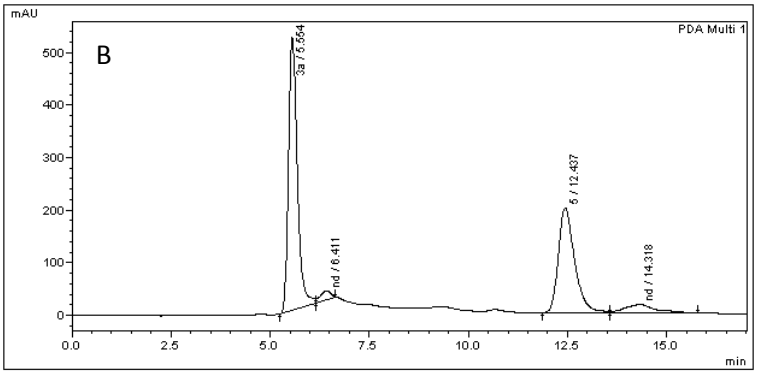
Name	Ret. Time	Area %	Height %
4a	4.844	2.614	4.204
3a	5.680	31.783	47.102
nd	7.711	1.274	1.555
nd	11.040	3.920	3.610
5	12.882	48.302	36.409
nd	14.866	9.913	5.335
nd	15.605	2.194	1.785
		100.000	100.000

Fig. S44 Reaction conditions: non-catalyzed. A – 2 hours time reaction; B – 4 hours time reaction; C – 10 hours time reaction and D – 24 hours time reaction; nd – not determinate.



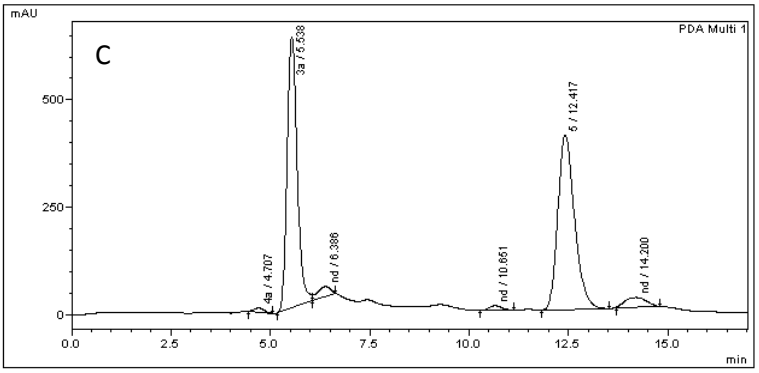
PDA Ch1 370nm 4nm

Name	Ret. Time	Area %	Height %
3a	5.550	45.178	59.719
nd	6.327	19.925	9.895
5	12.429	32.365	28.653
nd	14.193	2.532	1.733
		100.000	100.000



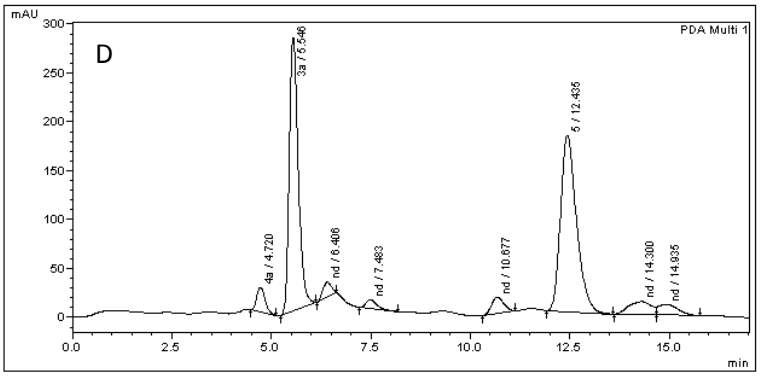
PDA Ch1 370nm 4nm

Name	Ret. Time	Area %	Height %
3a	5.554	54.136	69.060
nd	6.411	2.022	2.236
5	12.437	38.253	26.595
nd	14.318	5.589	2.110
		100.000	100.000



PDA Ch1 370nm 4nm

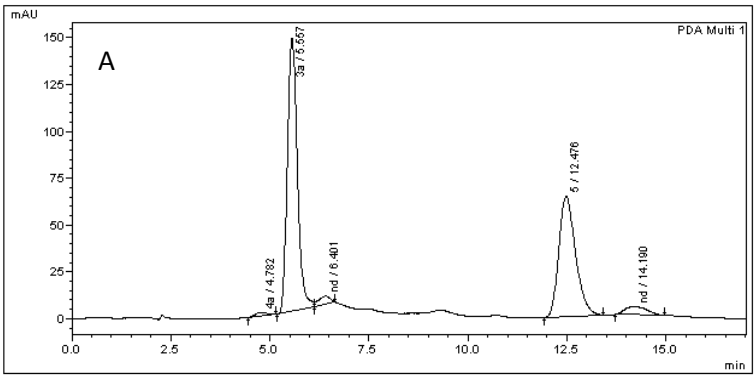
Name	Ret. Time	Area %	Height %
4a	4.707	0.658	0.855
3a	5.538	44.979	57.166
nd	6.386	2.143	2.095
nd	10.651	0.943	0.950
5	12.417	47.954	36.933
nd	14.200	3.322	2.000
		100.000	100.000



PDA Ch1 370nm 4nm

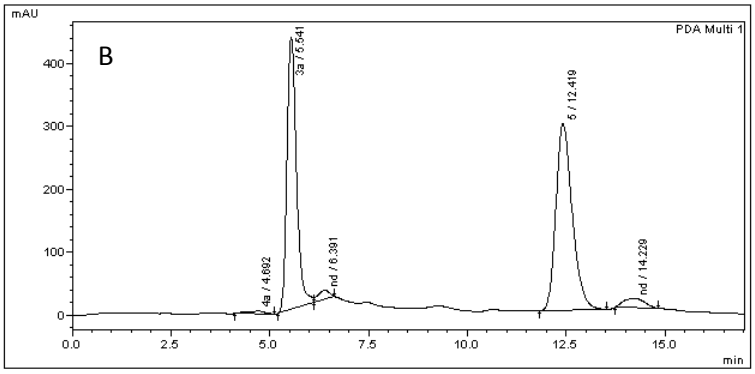
Name	Ret. Time	Area %	Height %
4a	4.720	3.127	4.486
3a	5.546	38.422	50.794
nd	6.406	1.985	2.795
nd	7.483	1.458	1.599
nd	10.677	3.192	3.100
5	12.435	43.994	32.830
nd	14.300	4.559	2.396
nd	14.935	3.264	2.002
		100.000	100.000

Fig. S45 Reaction conditions: acetic acid as catalyst. A – 2 hours time reaction; B – 4 hours time reaction; C – 10 hours time reaction and D – 24 hours time reaction; nd – not determinated.



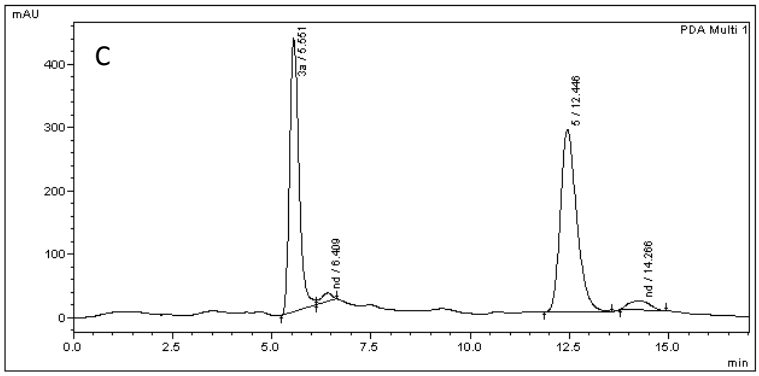
PDA Ch1 370nm 4nm

Name	Ret. Time	Area %	Height %
4a	4.782	0.800	0.850
3a	5.557	54.077	66.101
nd	6.401	1.758	1.838
5	12.476	39.740	29.225
nd	14.190	3.625	1.986
		100.000	100.000



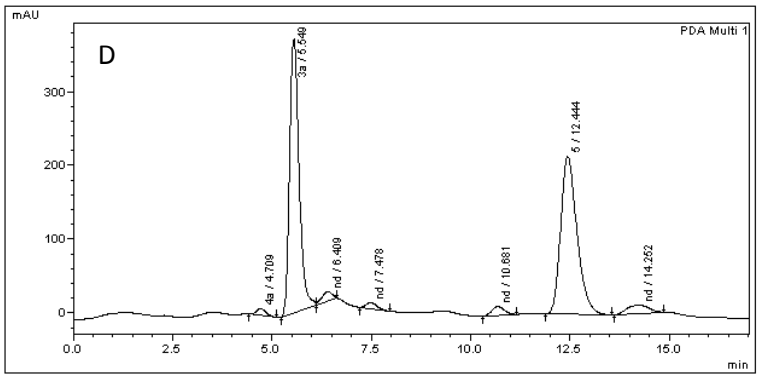
PDA Ch1 370nm 4nm

Name	Ret. Time	Area %	Height %
4a	4.692	0.712	0.548
3a	5.541	43.293	56.659
nd	6.391	1.788	1.913
5	12.419	50.800	38.905
nd	14.229	3.406	1.975
		100.000	100.000



PDA Ch1 370nm 4nm

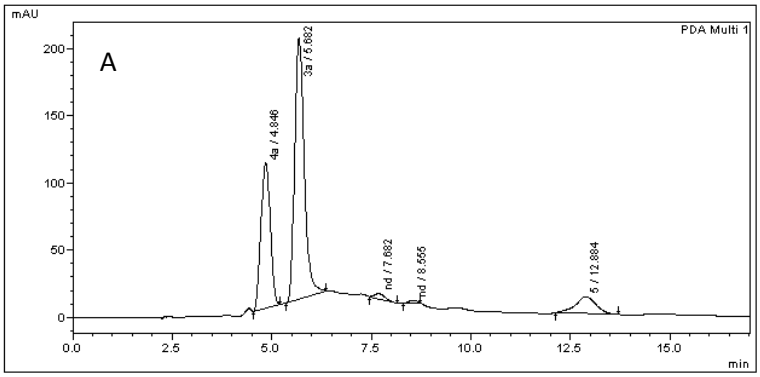
Name	Ret. Time	Area %	Height %
3a	5.551	44.153	57.820
nd	6.409	1.617	1.802
5	12.446	50.972	38.501
nd	14.266	3.258	1.877
		100.000	100.000



PDA Ch1 370nm 4nm

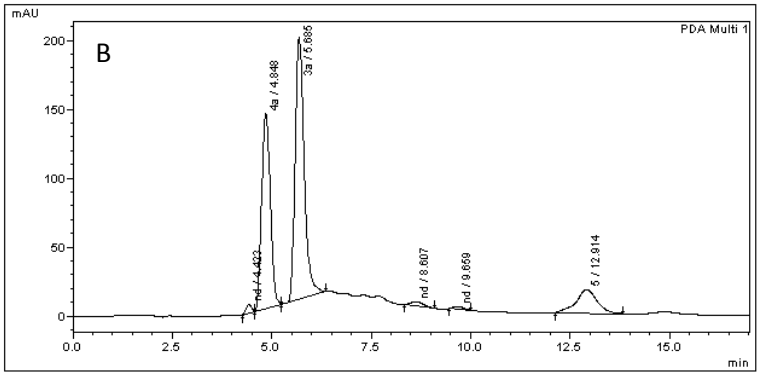
Name	Ret. Time	Area %	Height %
4a	4.709	1.044	1.352
3a	5.549	45.747	58.294
nd	6.409	1.720	1.954
nd	7.478	1.140	1.279
nd	10.681	1.947	1.872
5	12.444	45.294	33.562
nd	14.252	3.109	1.687
		100.000	100.000

Fig. S46 Reaction conditions: Lewis acid as catalyst (CaF_2): A – 2 hours time reaction; B – 4 hours time reaction; C – 10 hours time reaction and D – 24 hours time reaction; nd – not determinated.



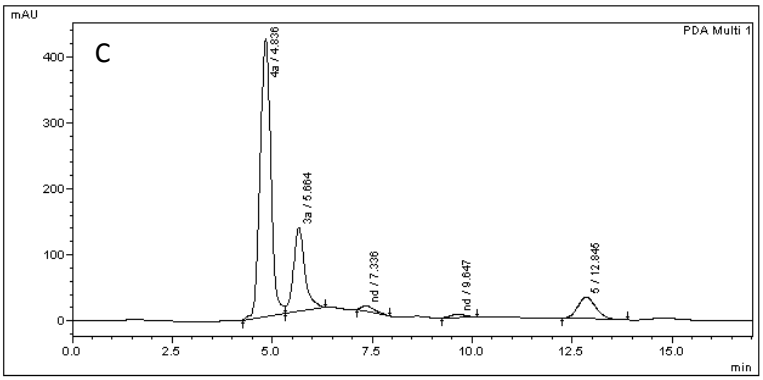
PDA Ch1 370nm 4nm

Name	Ret. Time	Area %	Height %
4a	4.846	31.880	33.746
3a	5.682	58.137	60.544
nd	7.682	1.225	1.144
nd	8.555	0.538	0.620
5	12.884	8.220	3.945
		100.000	100.000



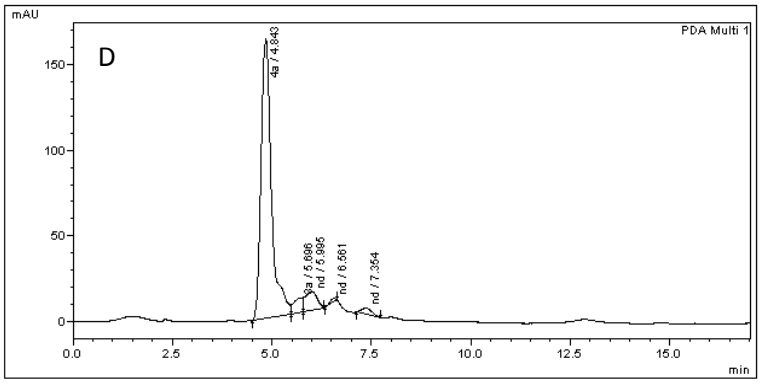
PDA Ch1 370nm 4nm

Name	Ret. Time	Area %	Height %
nd	4.423	1.018	1.770
4a	4.848	36.175	39.383
3a	5.685	50.599	52.732
nd	8.607	1.223	0.862
nd	9.659	0.586	0.529
5	12.914	10.399	4.724
		100.000	100.000



PDA Ch1 370nm 4nm

Name	Ret. Time	Area %	Height %
4a	4.836	66.784	70.806
3a	5.664	21.578	21.415
nd	7.336	1.685	1.390
nd	9.647	1.029	0.816
5	12.845	8.924	5.573
		100.000	100.000



PDA Ch1 370nm 4nm

Name	Ret. Time	Area %	Height %
4a	4.843	86.818	86.924
3a	5.696	4.098	4.432
nd	5.995	6.416	5.692
nd	6.561	0.681	1.077
nd	7.354	1.988	1.875
		100.000	100.000

Fig. S47 Reaction conditions: HCl as catalyst (12.5µL): A – 2 hours time reaction; B – 4 hours time reaction; C – 10 hours time reaction and D – 24 hours time reaction; nd – not determinated.

X-ray diffraction

Single crystal X-ray diffraction data for compound **4c** were collected on an Bruker D8 Venture diffractometer at room temperature, using graphite monochromatic MoKα radiation (λ = 0.71069 Å). Data collection and cell refinement were performed with Bruker Instrument Service v4.2.2 and APEX2 [i], respectively. Data reduction was carried out using SAINT [ii]. Empirical multiscan absorption correction using equivalent reflections was performed with the SADABS program [iii]. The structure solutions and full-matrix least-squares refinements based on F^2 were performed with the SHELXS-97 and SHELXL-97 program packages [iv]. All atoms except hydrogen were refined anisotropically. Hydrogen atoms were treated by a mixture of independent and constrained refinement. The structure was drawn by Mercury program [v]. Details of data collection and refinement are listed in Table S1.

Table S1: Summary of crystal data and structure refinement of compound **4c**.

Empirical formula	$C_{49}H_{36}N_4O_{14}$	
Formula weight	904.82	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P* -1	
Unit cell dimensions	a = 9.2503(5) Å	α= 76.141(2)°
	b = 10.6790(6) Å	β= 77.031(2)°
	c = 13.4211(6) Å	γ = 64.664(2)°
Volume	1152.10(10) $Å^3$	
Z	1	
Density (calculated)	1.304 Mg/m^3	
Absorption coefficient	0.10 mm^{-1}	
F(000)	470	
Crystal size	0.28 x 0.17 x 0.05 mm^3	

Theta range for data collection	2.1 to 25.0°
Index ranges	-10<=h<=10,
	-12<=k<=12,
	-15<=l<=15
Reflections collected	32147
Independent reflections	4053 [R(int) = 0.075]
Completeness to theta = 25.06°	100 %
Max. and min. transmission	0.980 and 0.995
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4048 / 0 / 312
Goodness-of-fit on F^2	1.06
Final R indices [I>2sigma(I)]	R_1 = 0.062, wR_2 = 0.199
R indices (all data)	R_1 = 0.099, wR_2 = 0.171
Largest diff. peak and hole	0.52 and -0.23 e.Å^{-3}

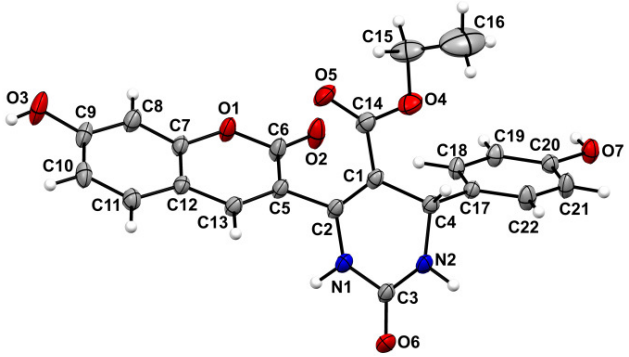


Fig. S48 Molecular structure of compound **4c**. Thermal ellipsoids are drawn at 40 % of probability. Crystallization solvent molecule was omitted for sake of clarity.

[i] Bruker (2007). APEX2 v2014.5-0. Bruker AXS Inc., Madison, Wisconsin, USA.

[ii] Bruker (2013). SAINT v8.34A. Bruker AXS Inc., Madison, Wisconsin, USA.

[iii] Sheldrick, G.M. SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Germany, 1996.

[iv] Sheldrick, G.M. *Acta Cryst*. **2008**, *A64*, 112-122.

[ᵞ]Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J., *J. Appl. Cryst.* **2006**, 39, 453-457.