

Supplementary Information for
Quinone Methide Chemistry of Prekinamycins: ^{13}C -labeling, Spectral Global Fitting and In Vitro
Studies

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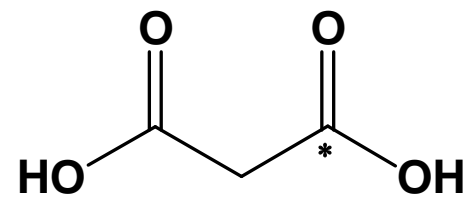
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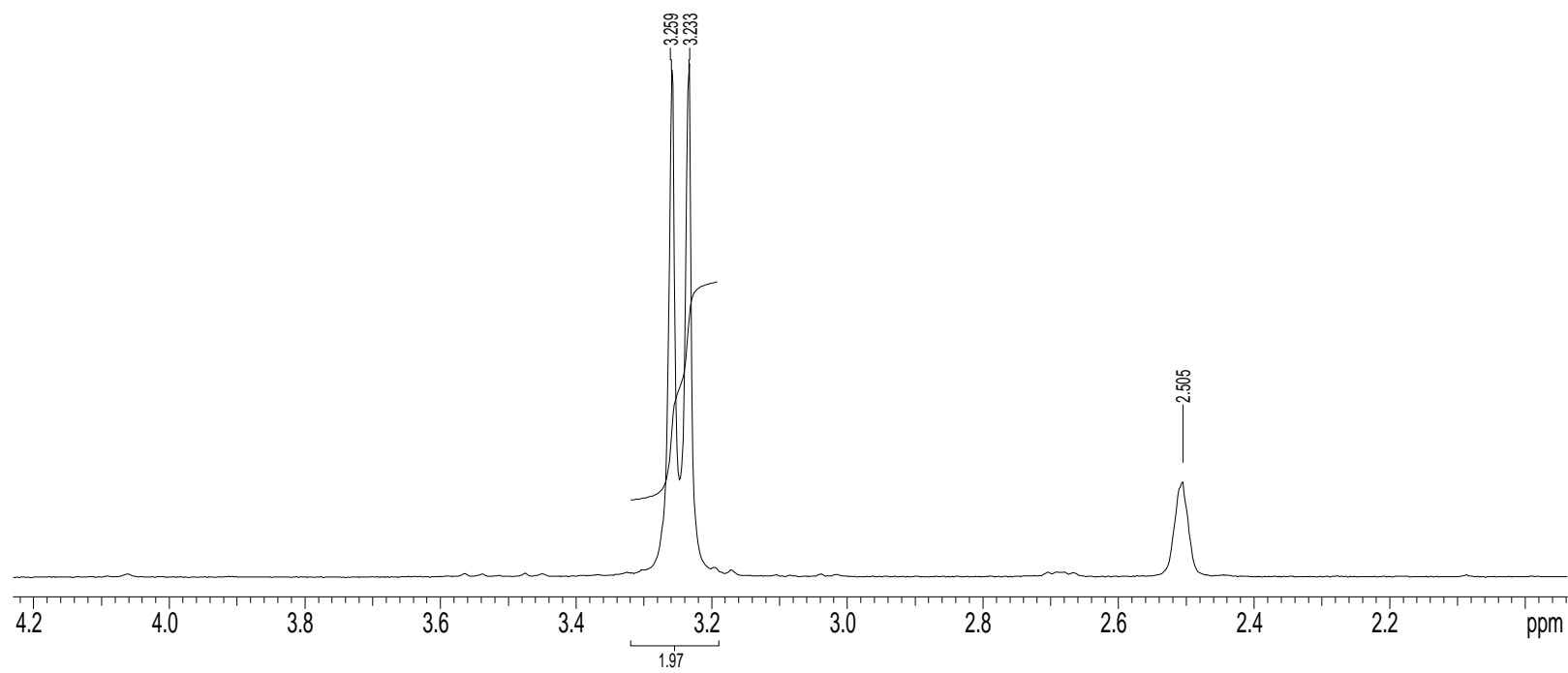
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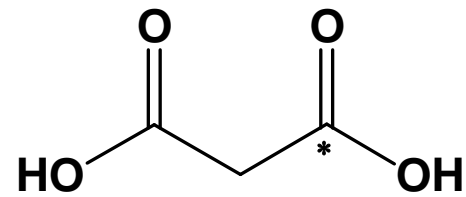
General Experimental Methods

All analytically pure compounds were dried under high vacuum in a drying pistol over refluxing methanol. Elemental analyses (CHN) were obtained for intermediates and final products. Melting points and decomposition points were determined for all intermediates and final products. All TLCs were performed on silica gel plates using a variety of solvent systems and a fluorescent indicator for visualization. IR spectra were taken as KBr pellets and only the strongest absorbances were reported. ¹H NMR spectra were obtained with a 300 or 500 MHz spectrometer. All chemical shifts are reported relative to TMS. High-resolution mass spectra were obtained using MALDI or EI mode.

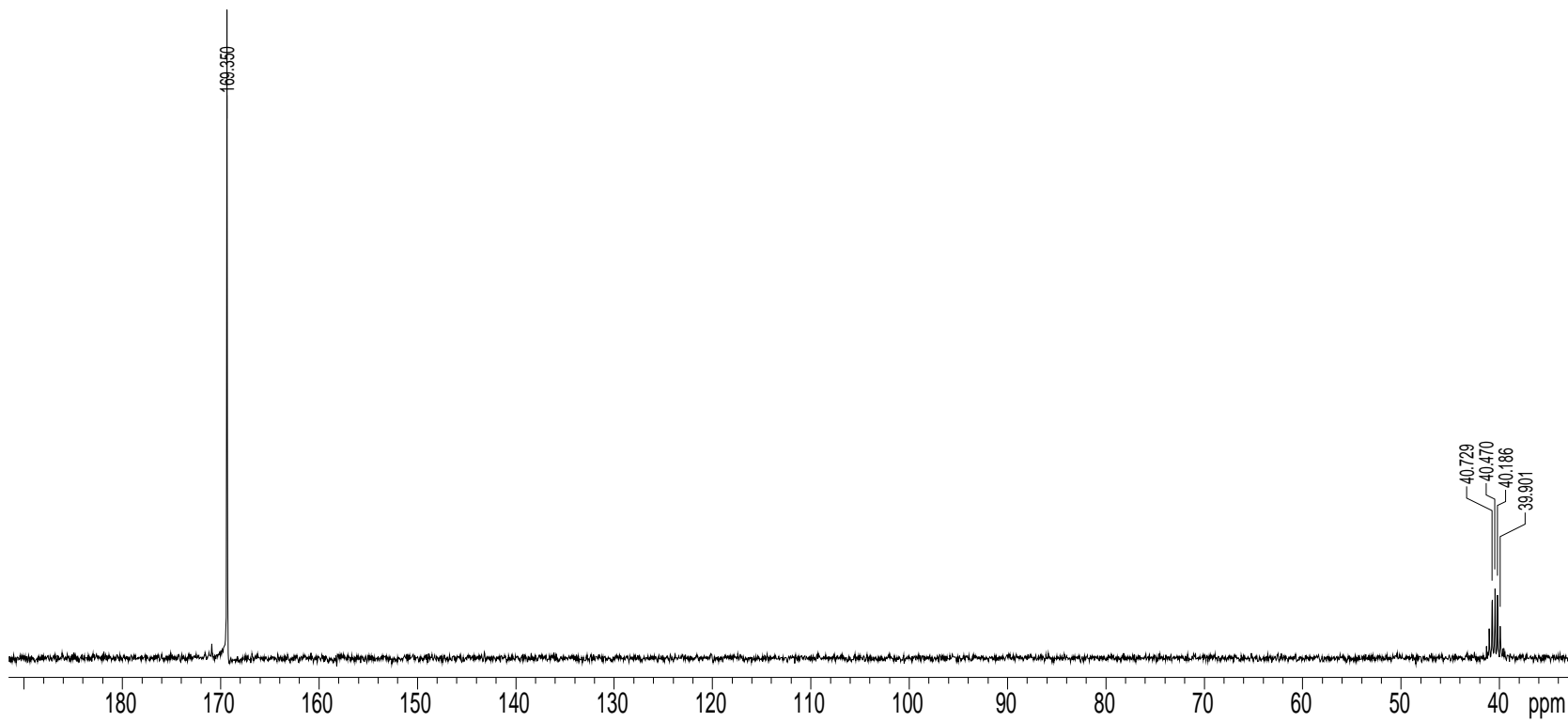


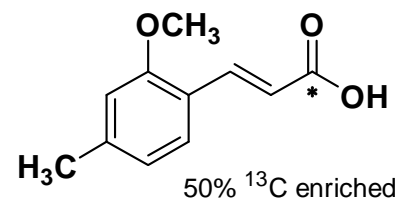
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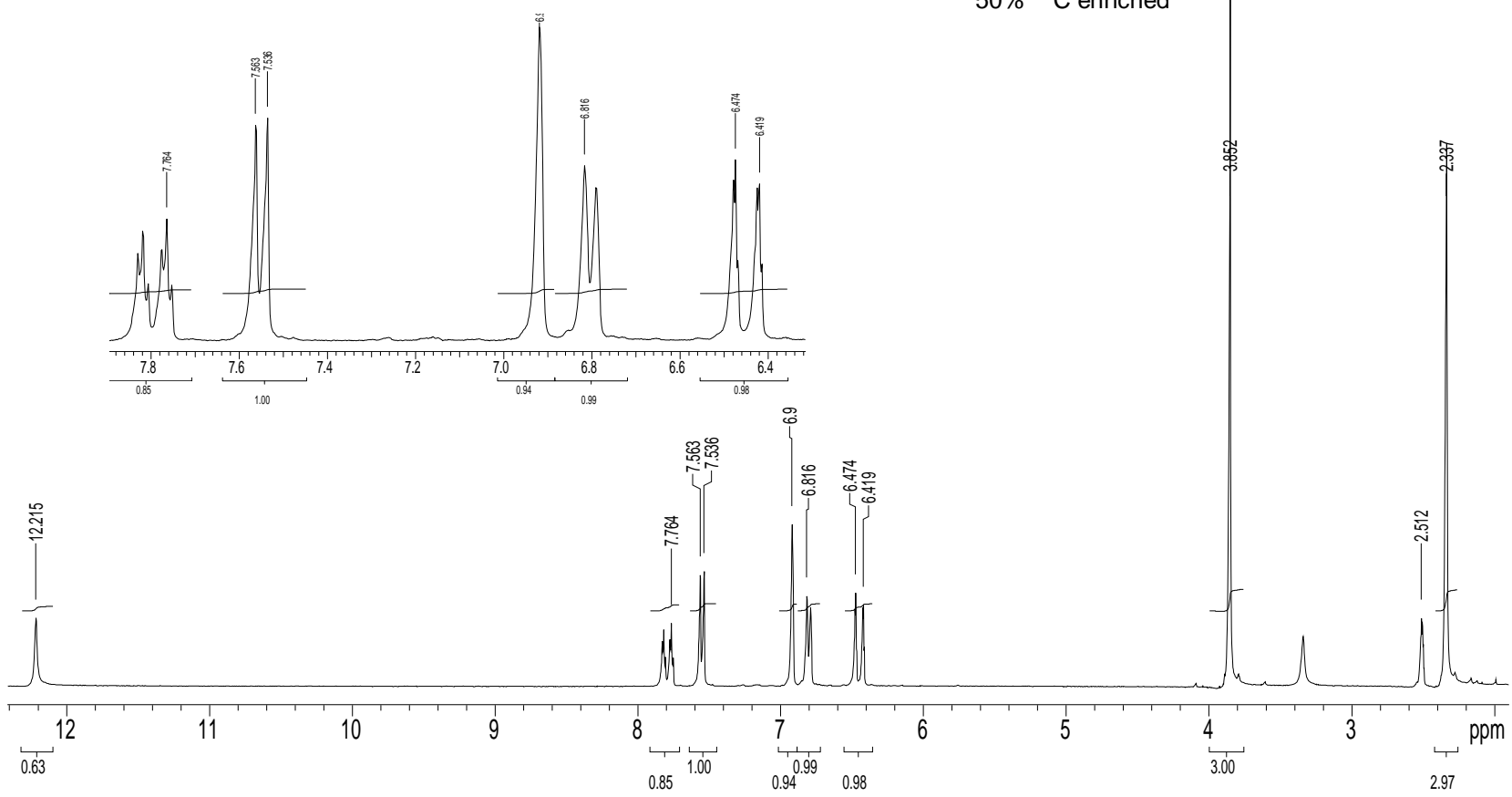


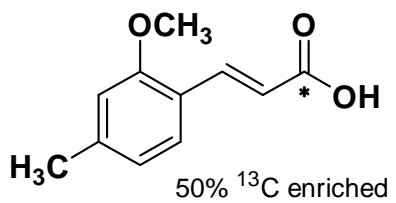
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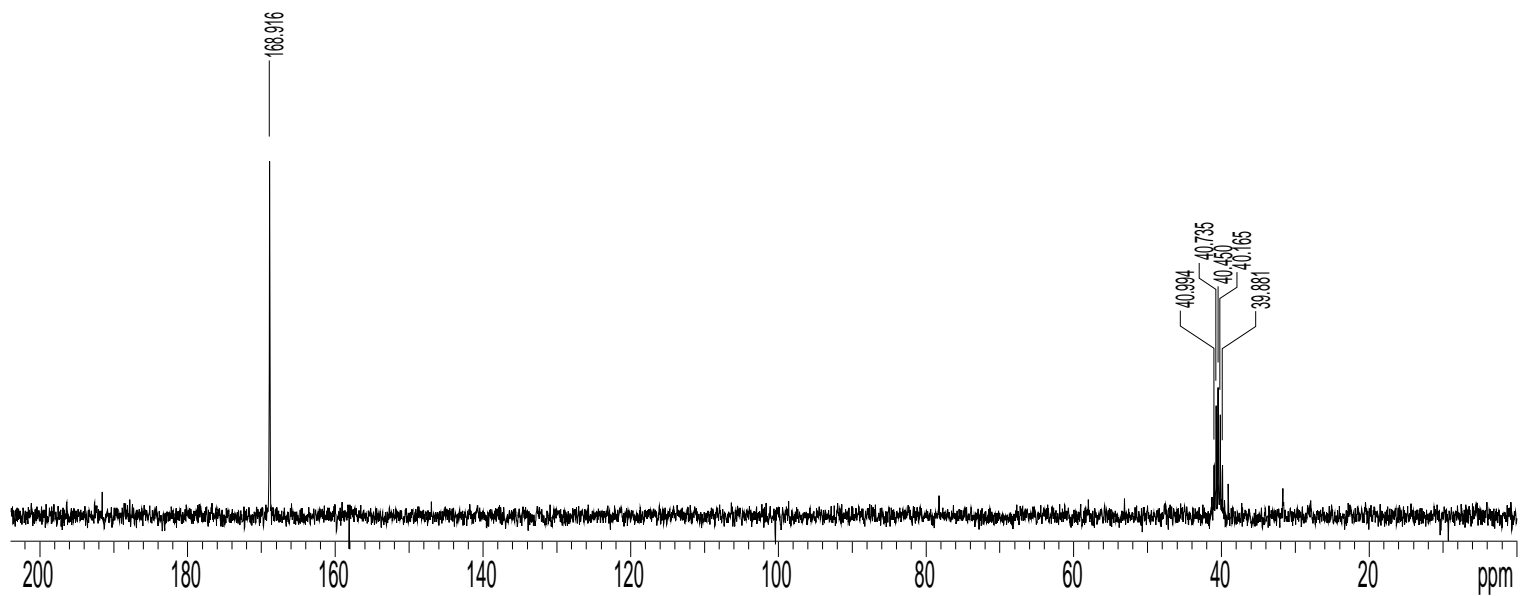


H-NMR of the Carboxylic Acid Derivative of 8*

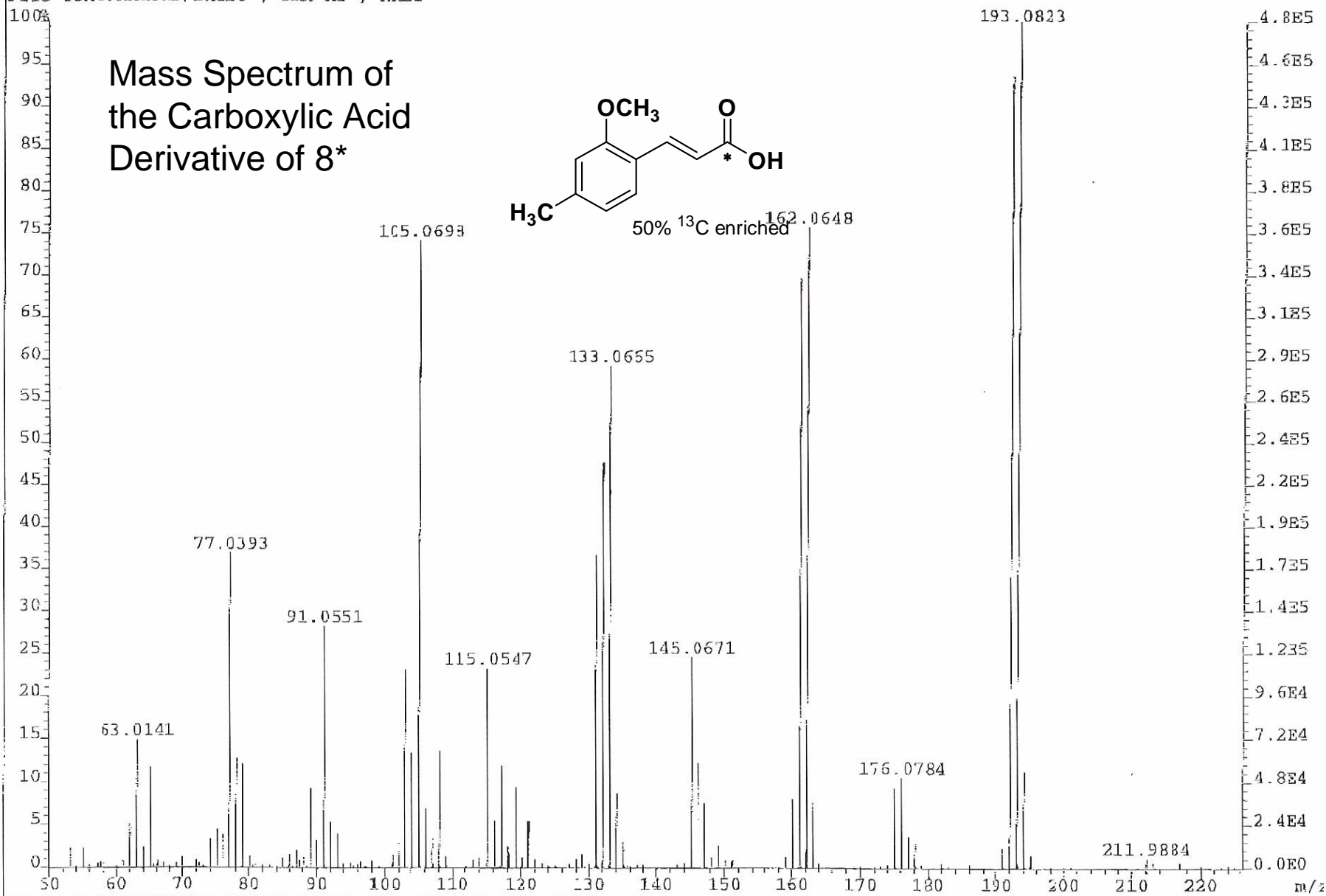




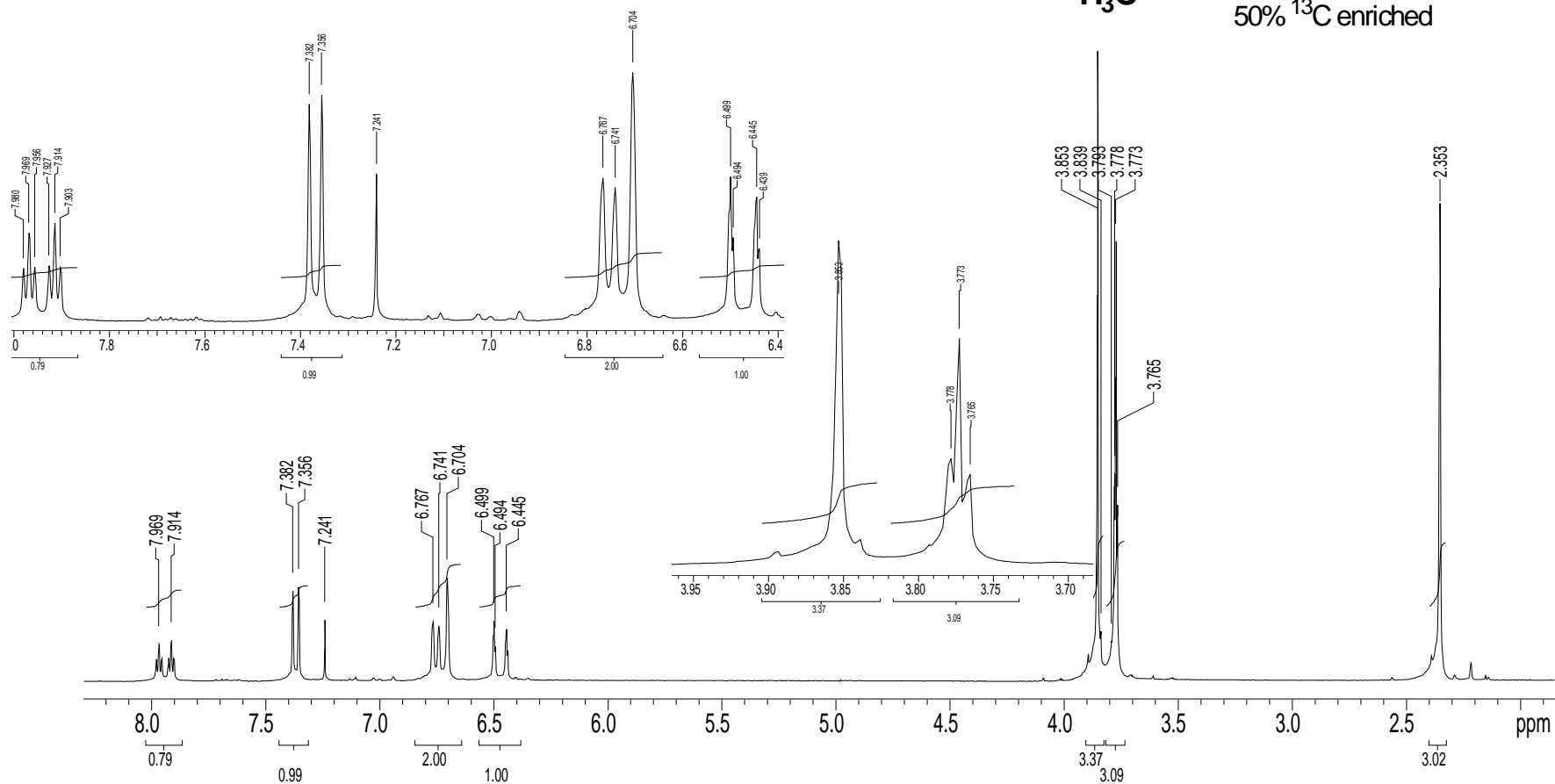
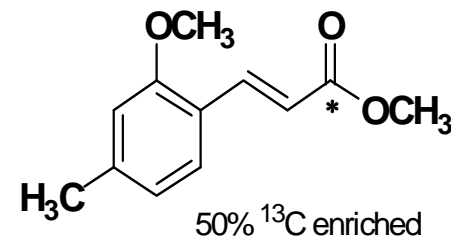
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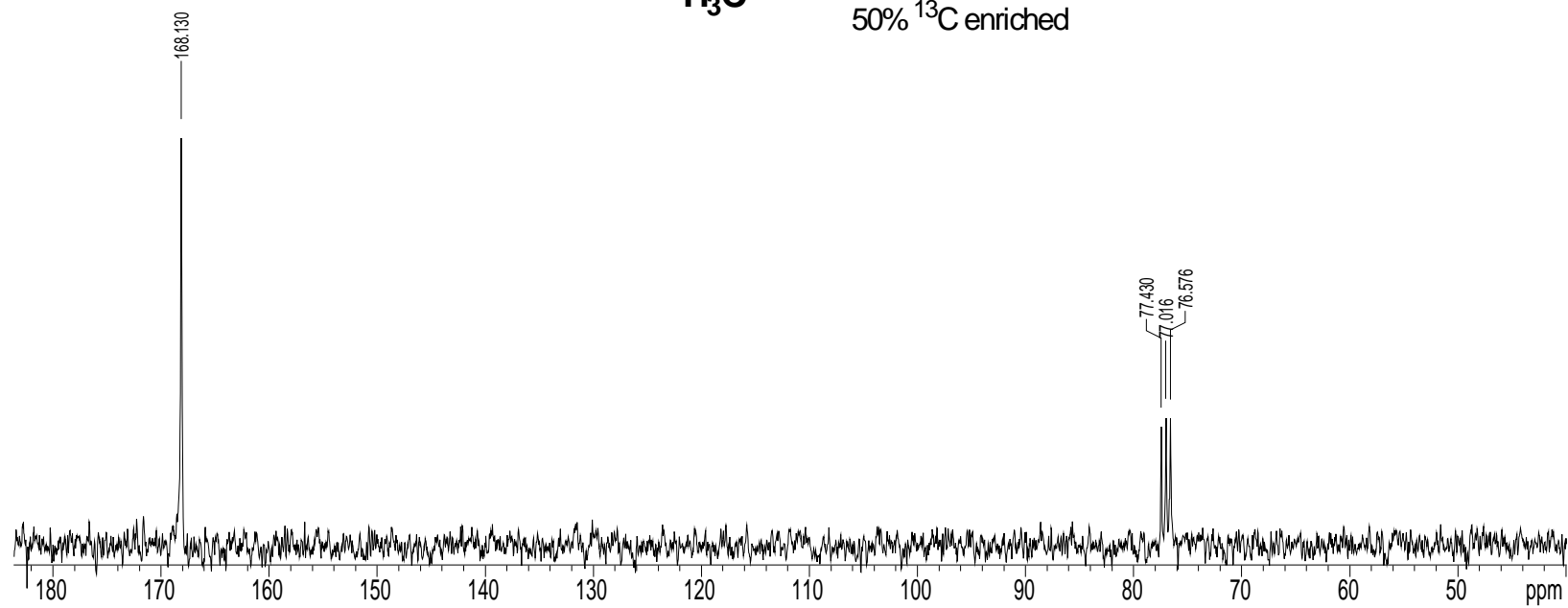
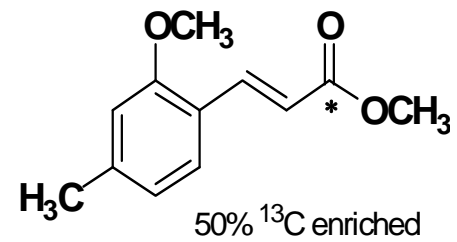
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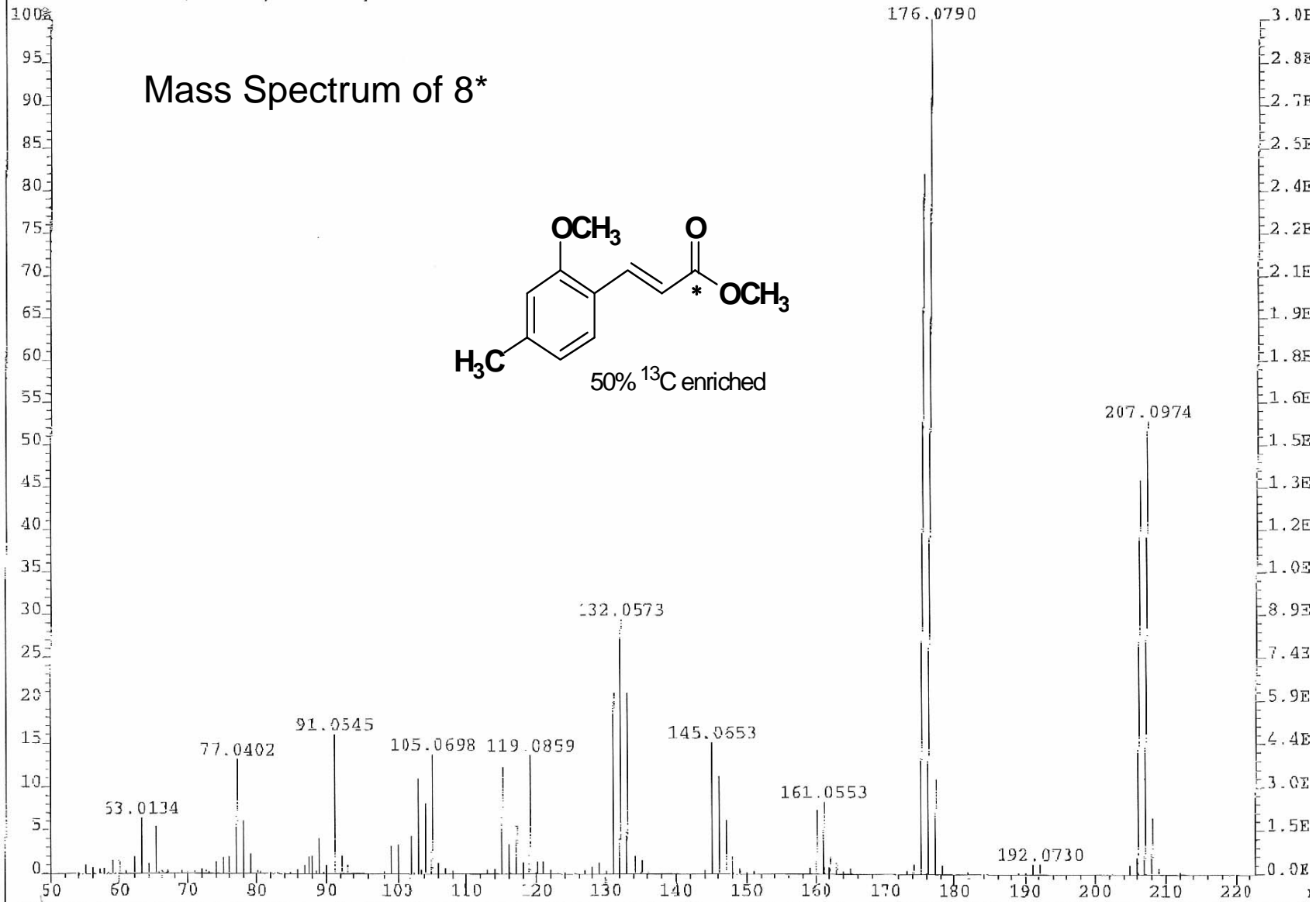
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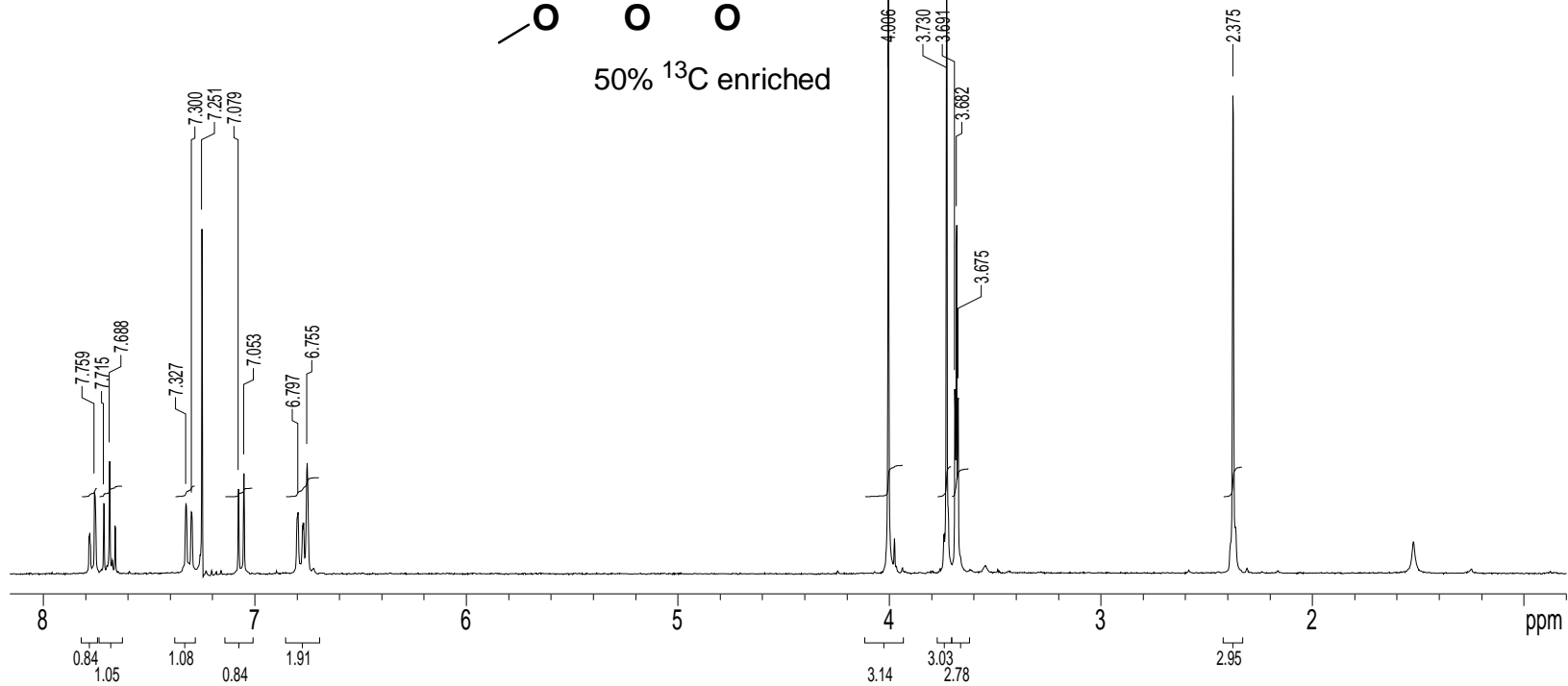
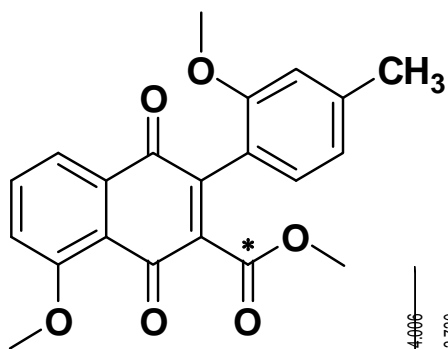
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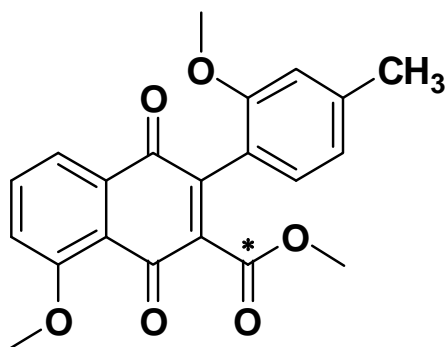
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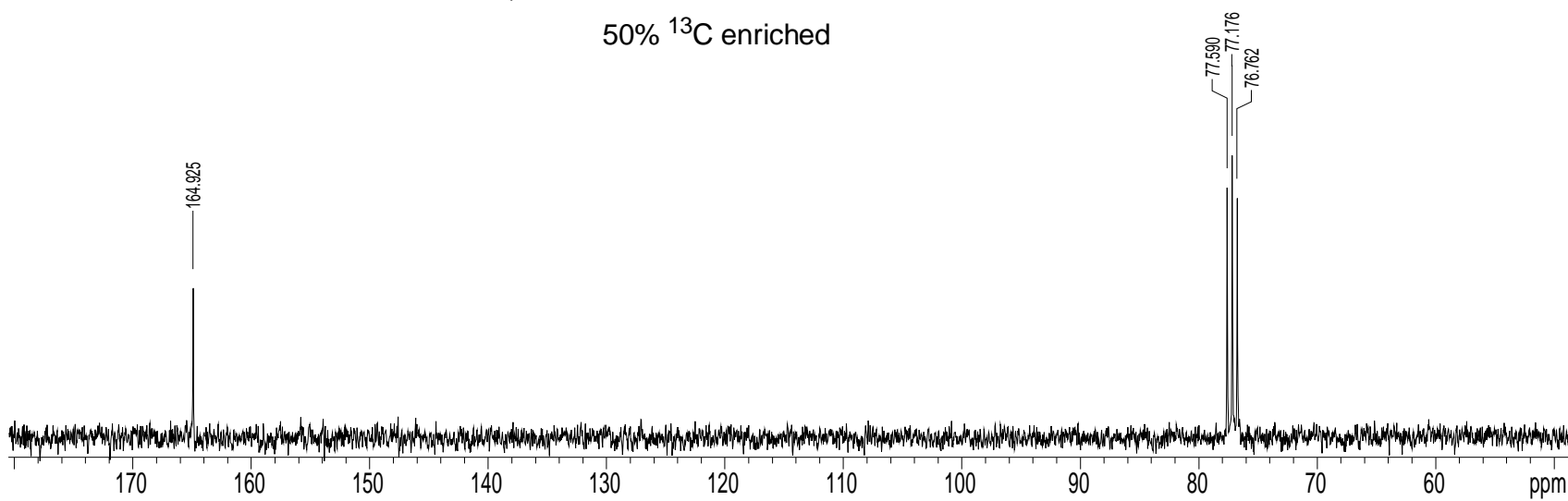
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^{13}C -NMR of **10***

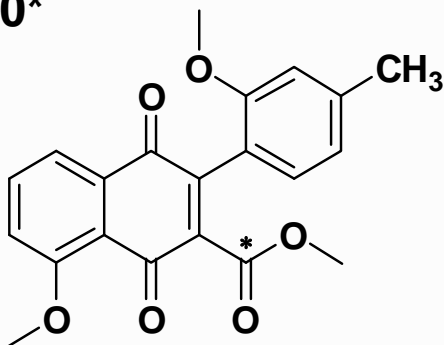


50% ^{13}C enriched

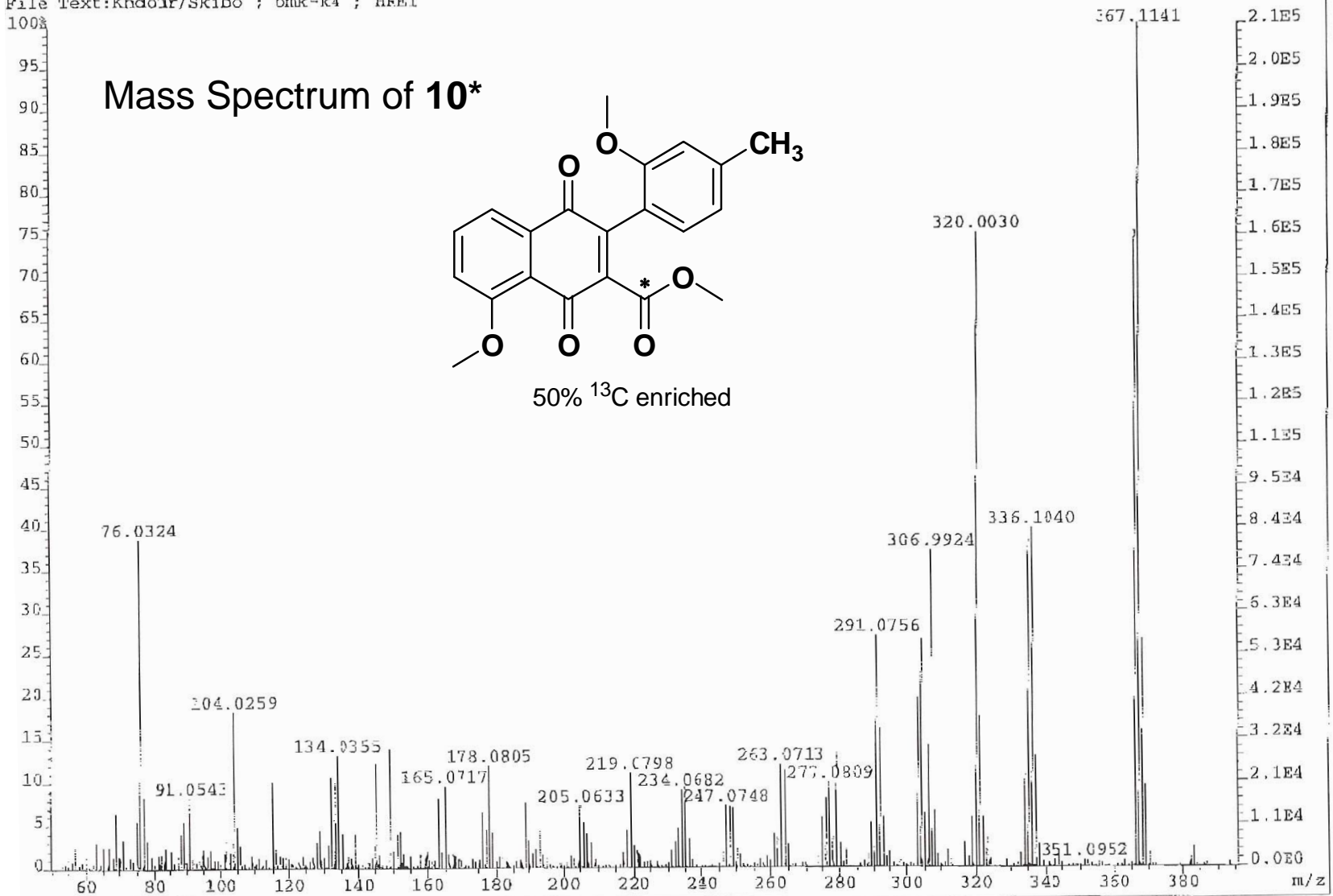


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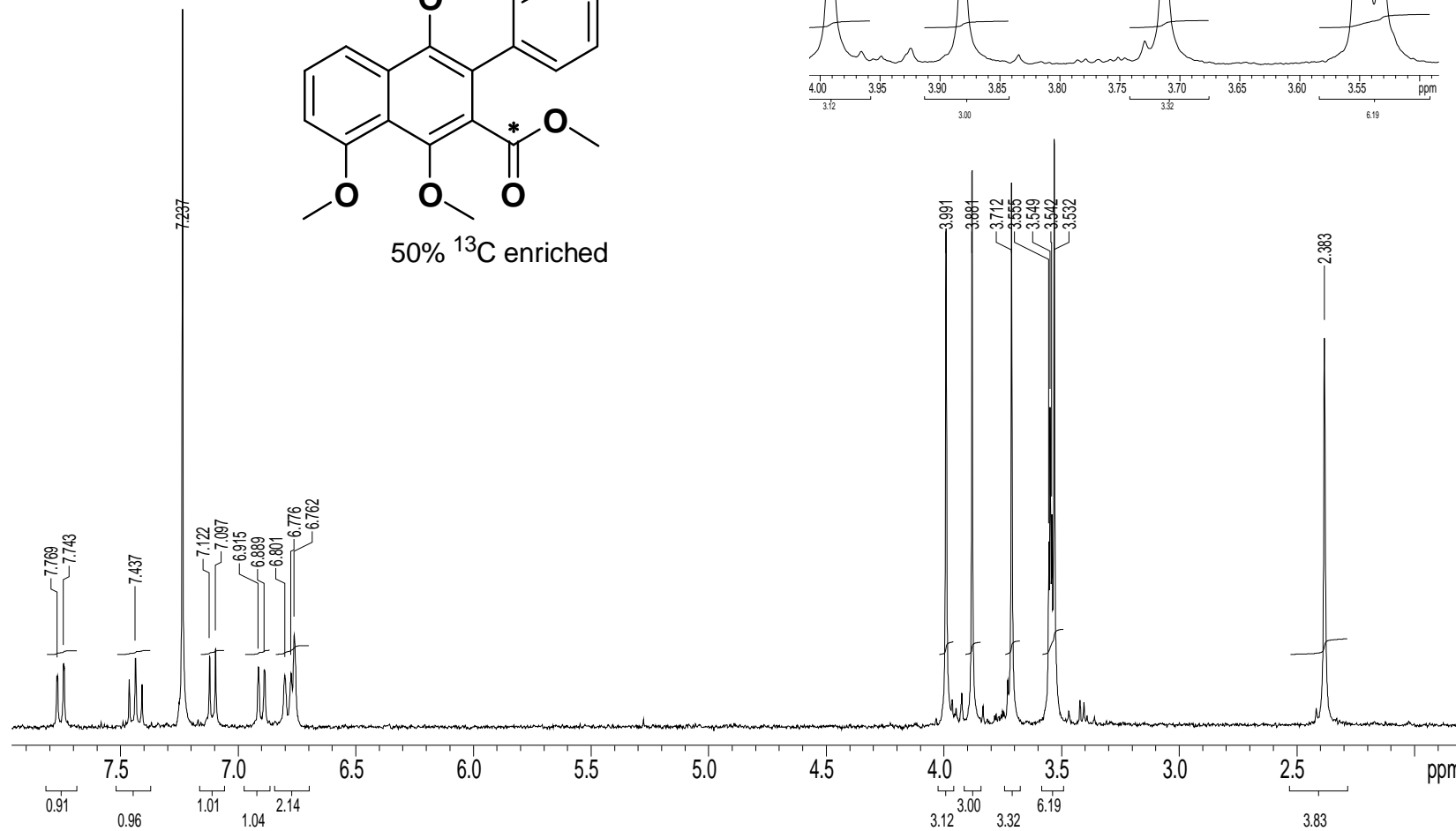
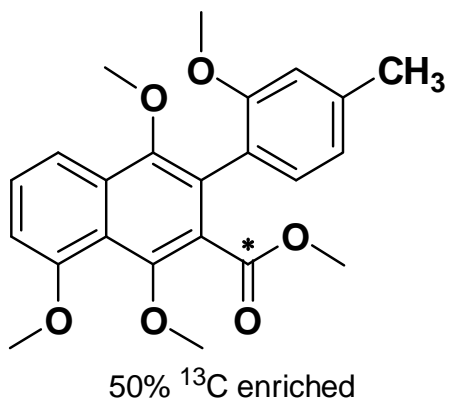
Mass Spectrum of 10*



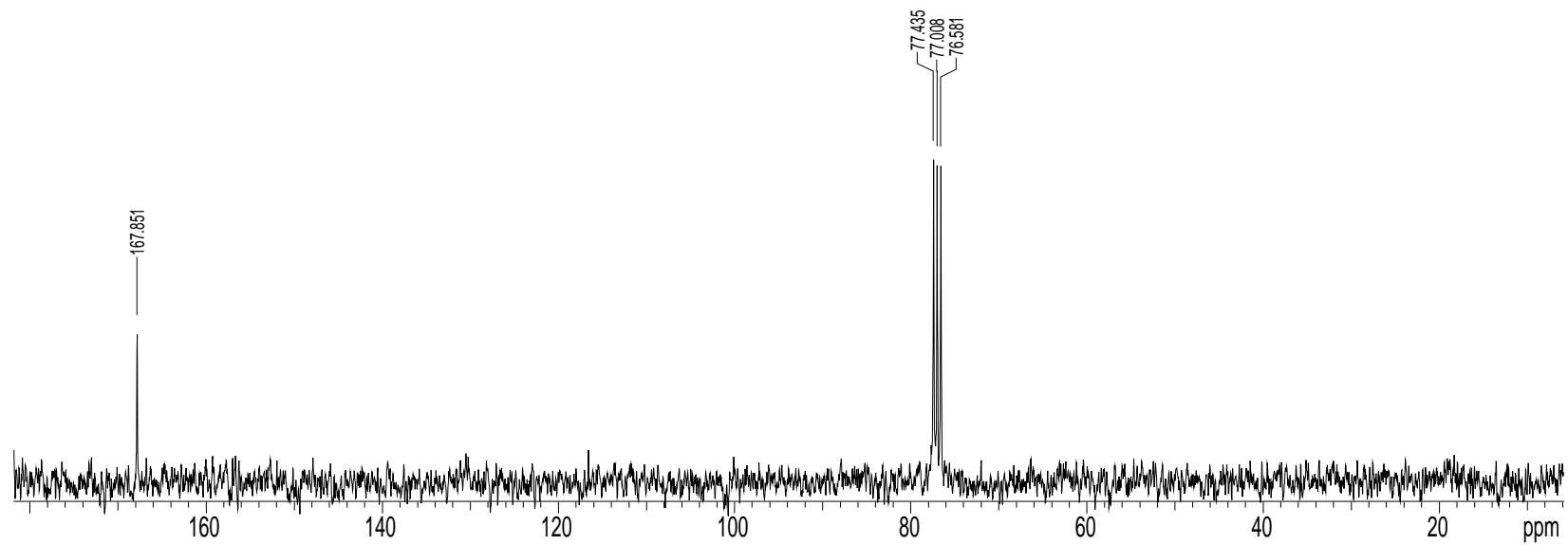
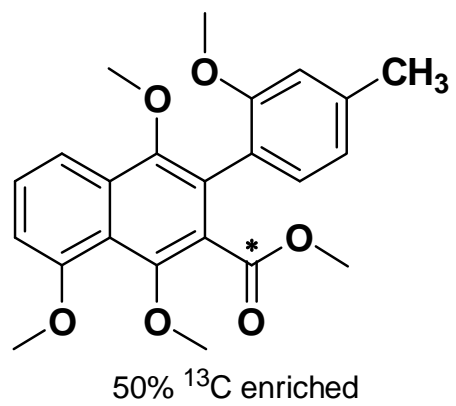
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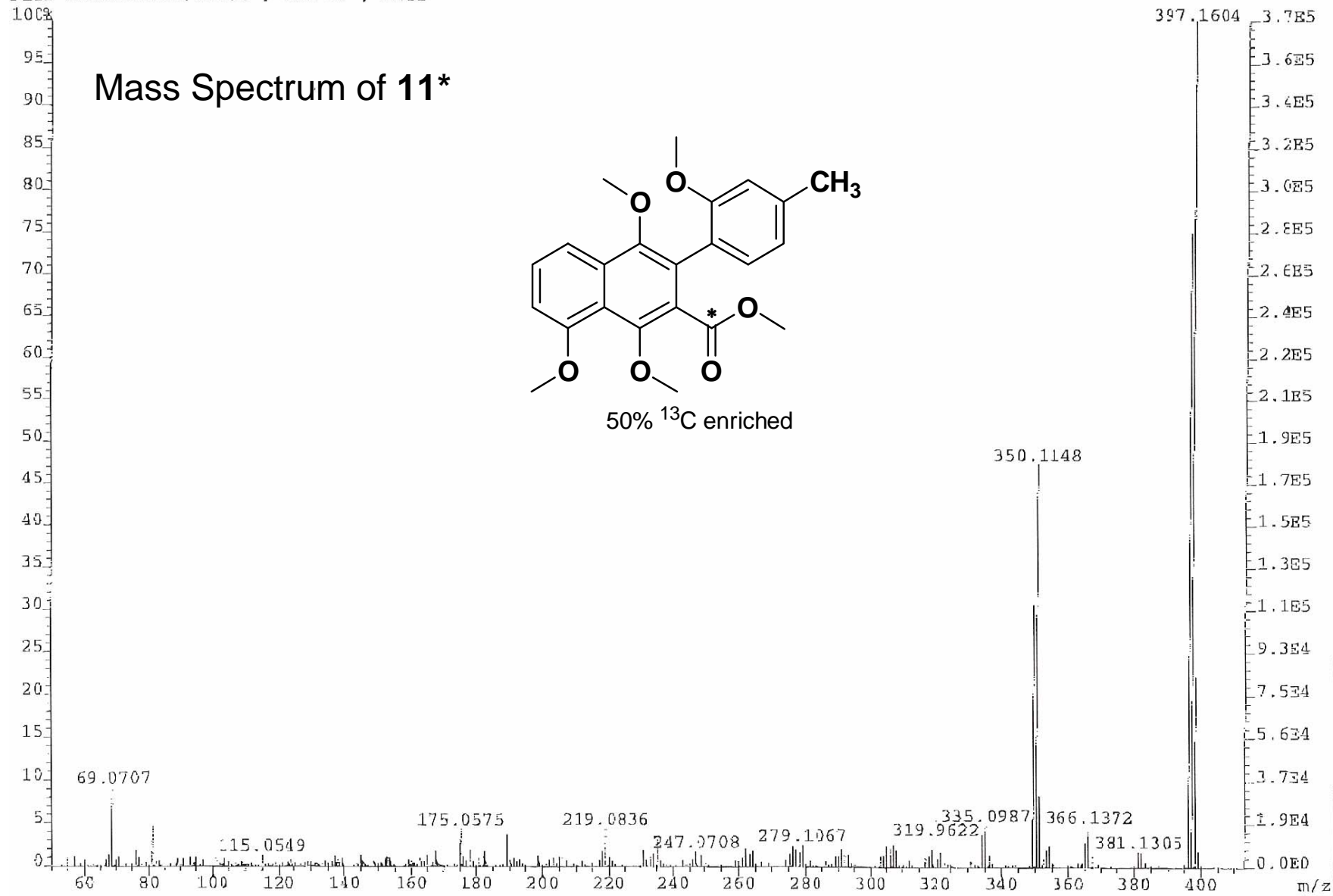
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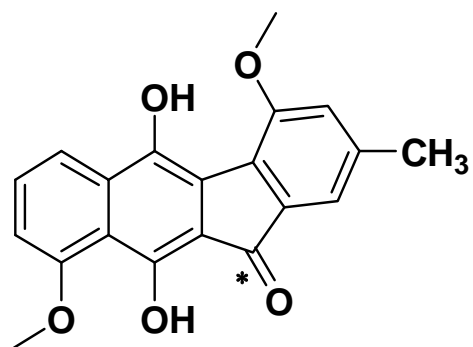
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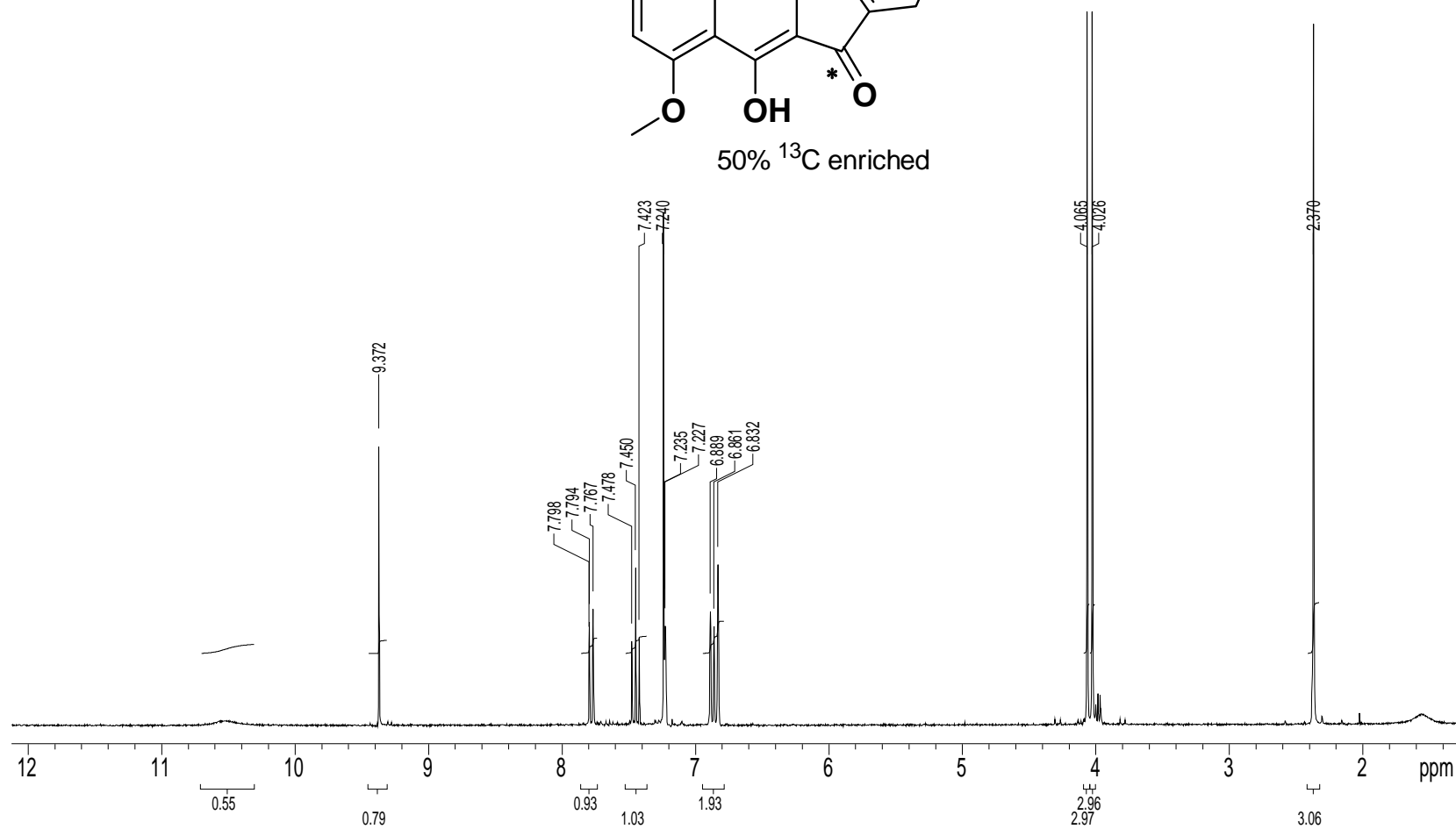
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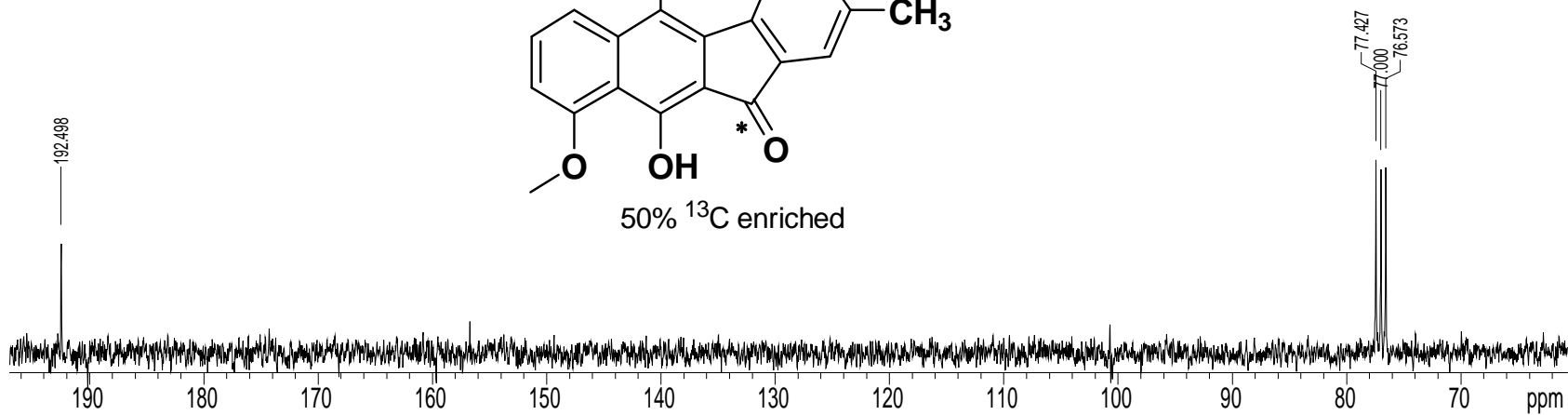
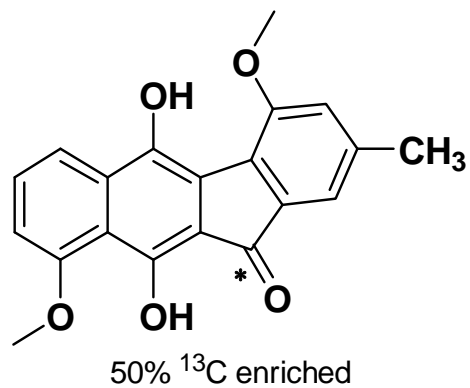
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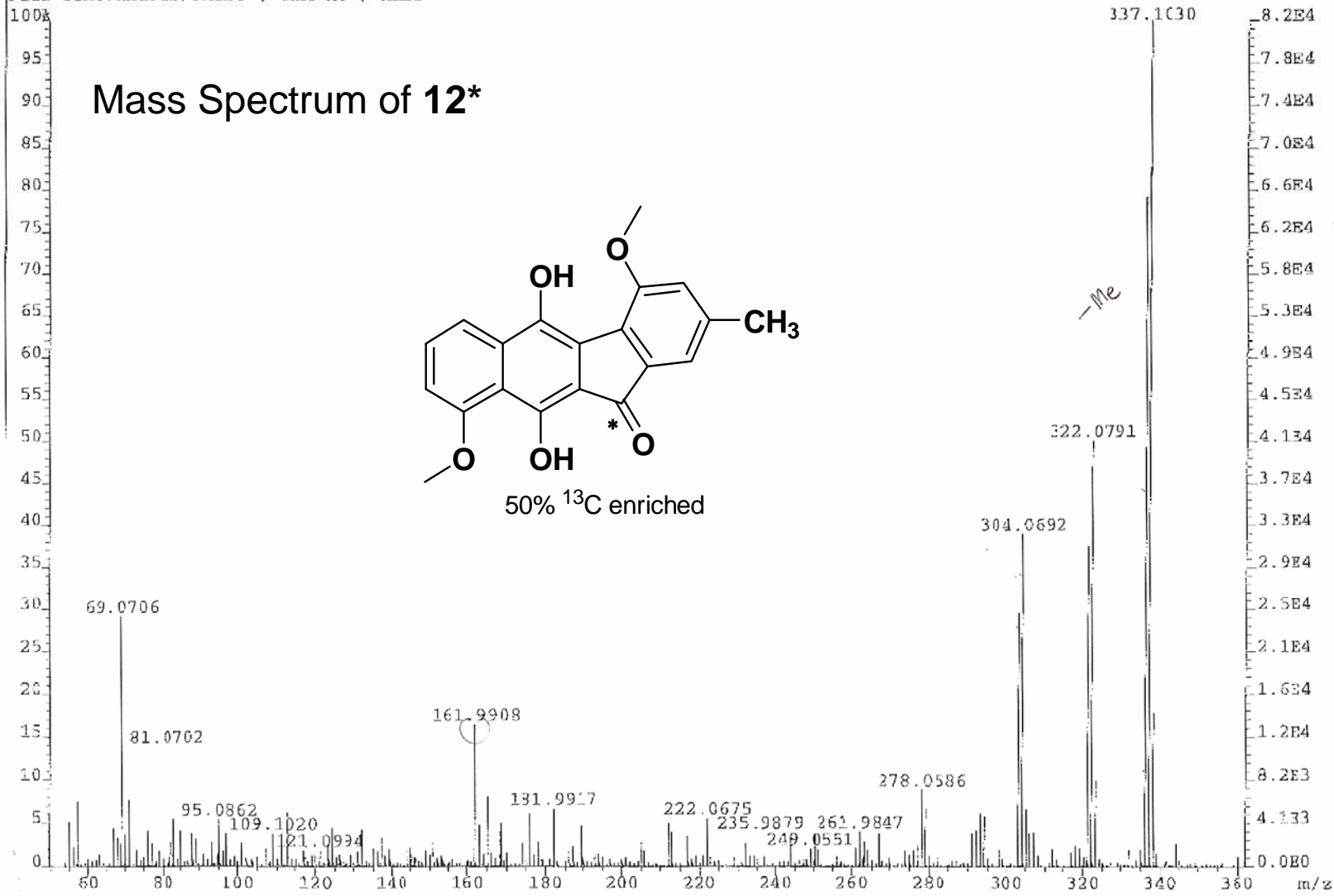
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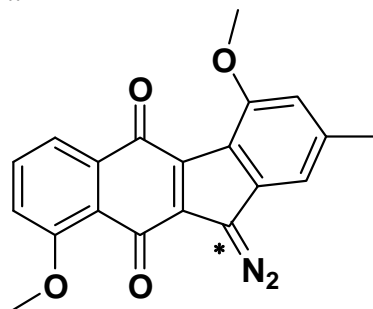
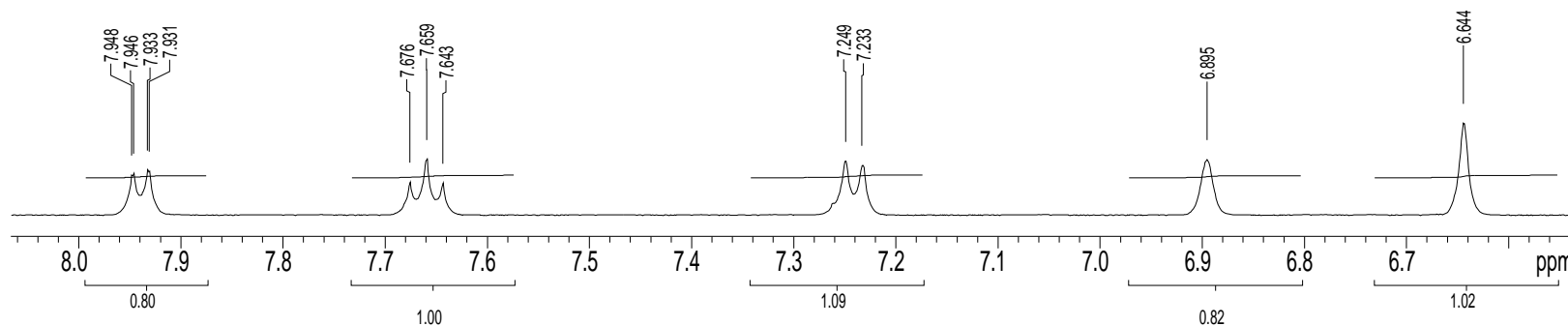
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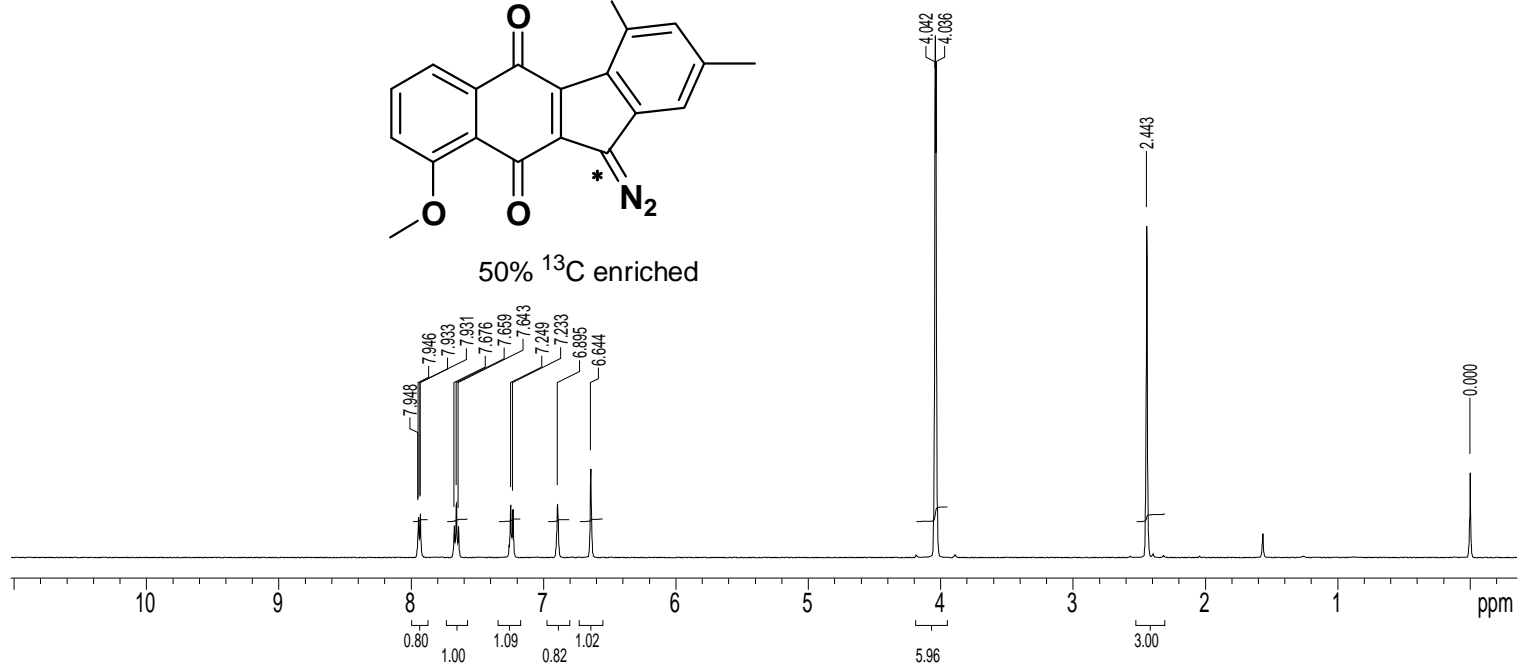
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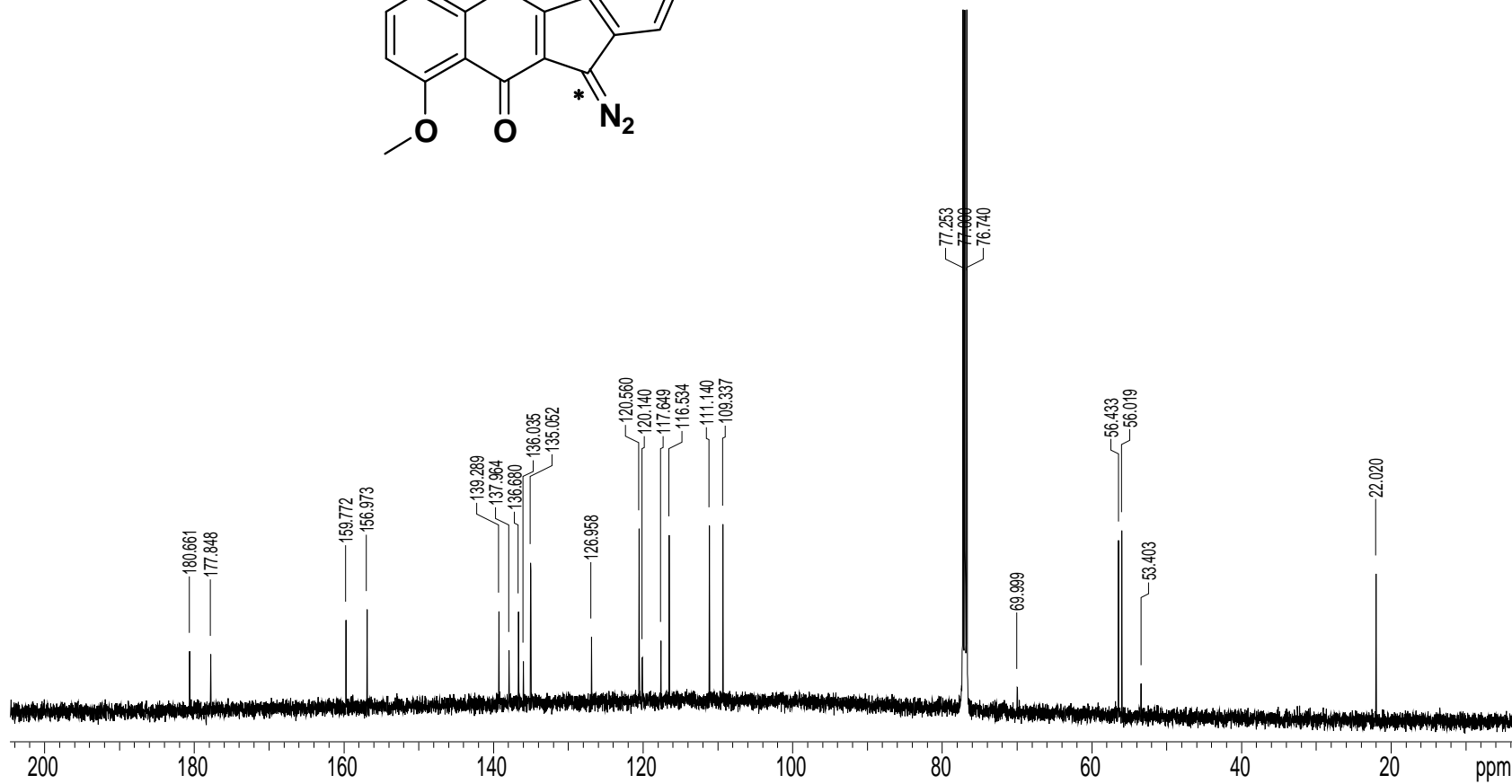
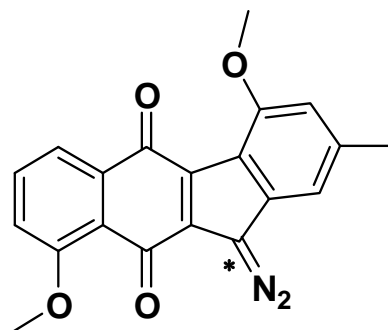
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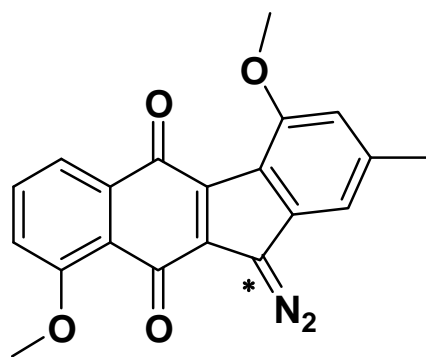
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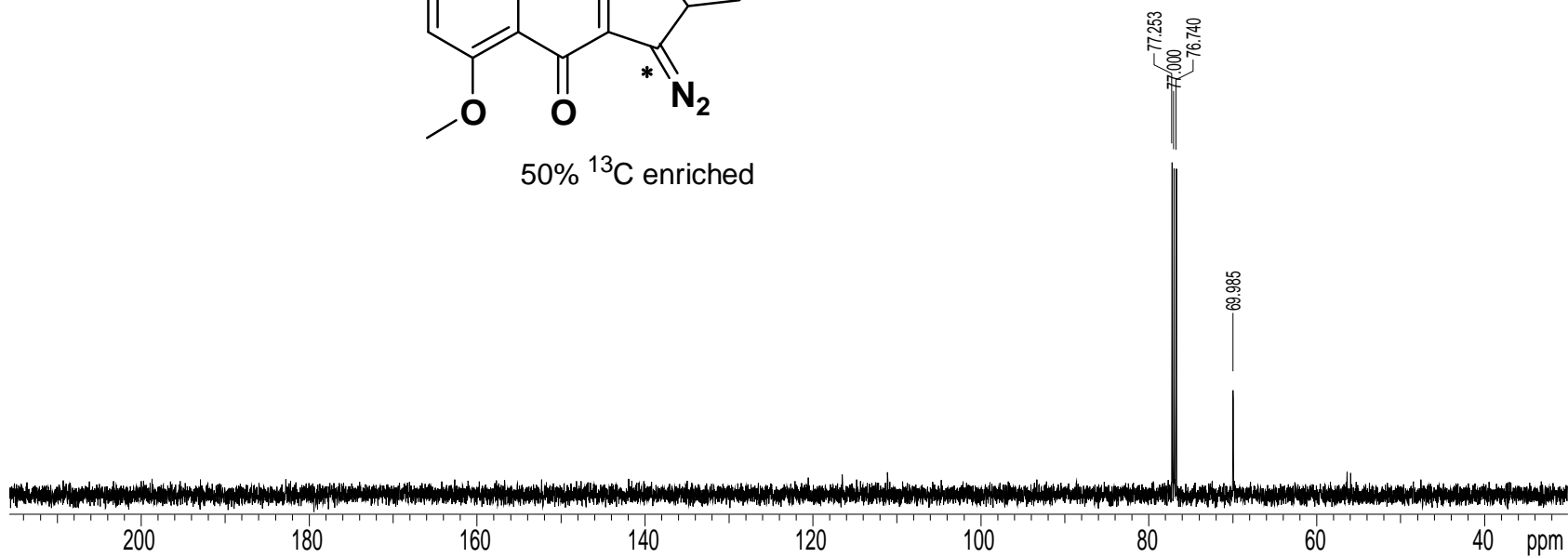
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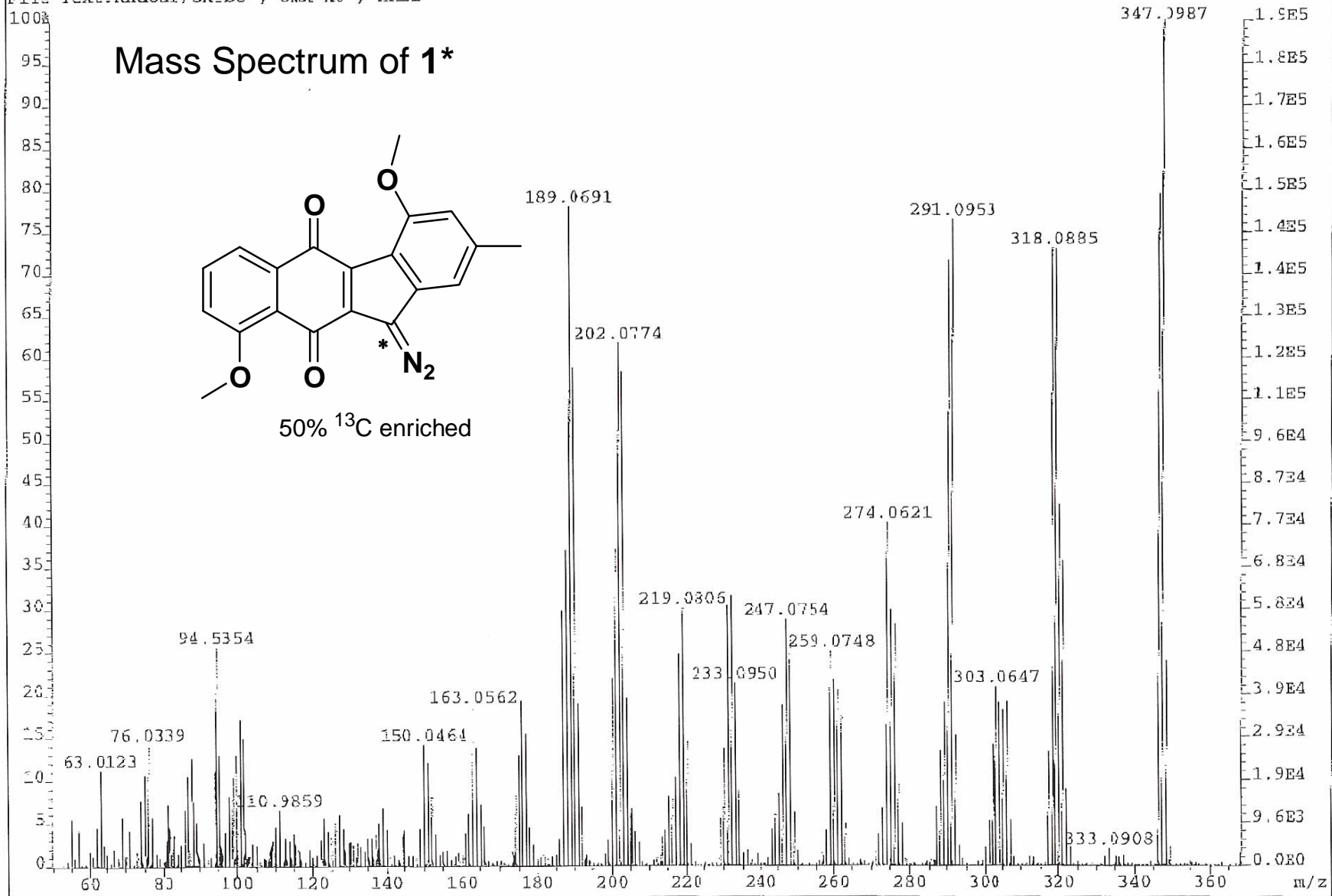
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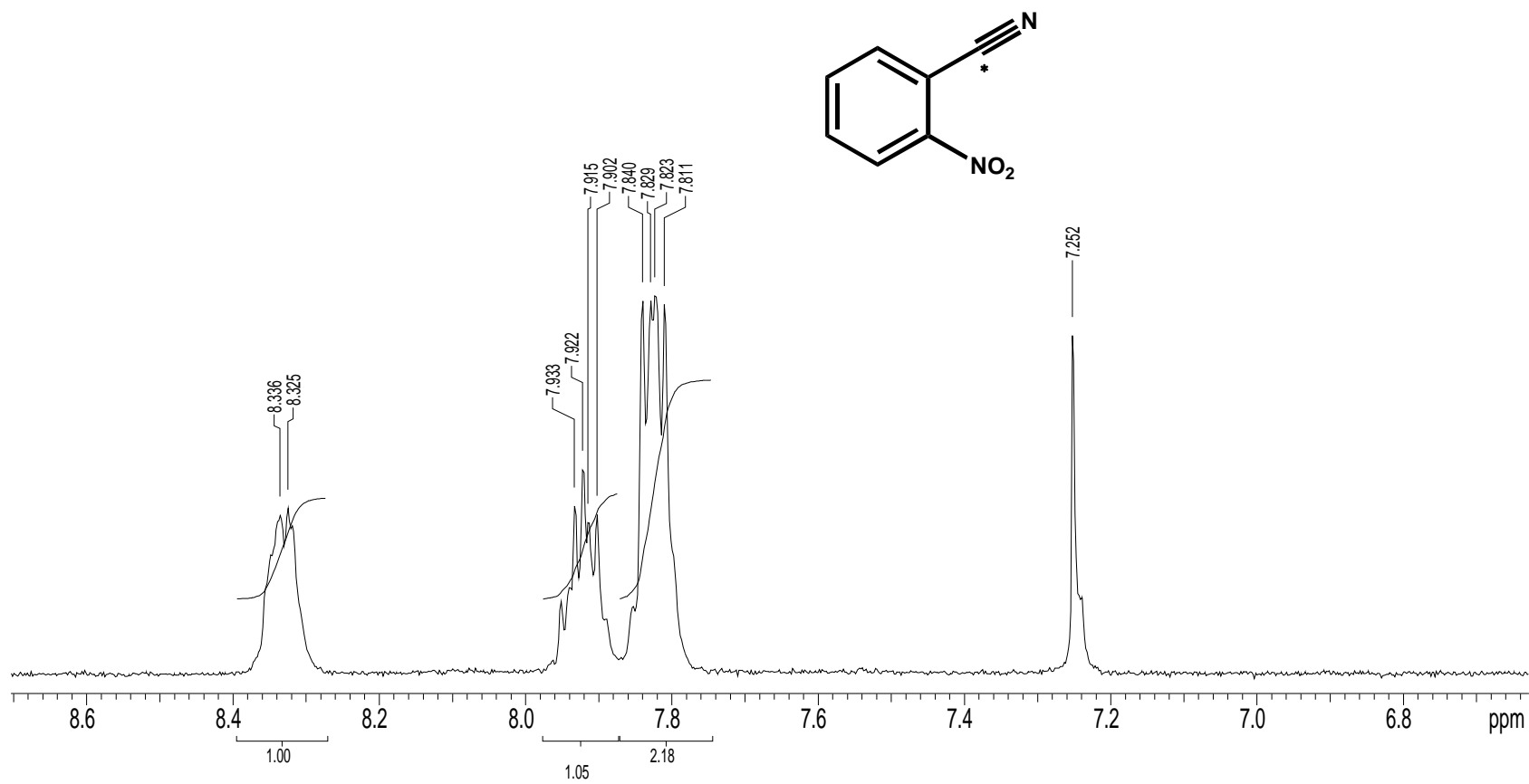
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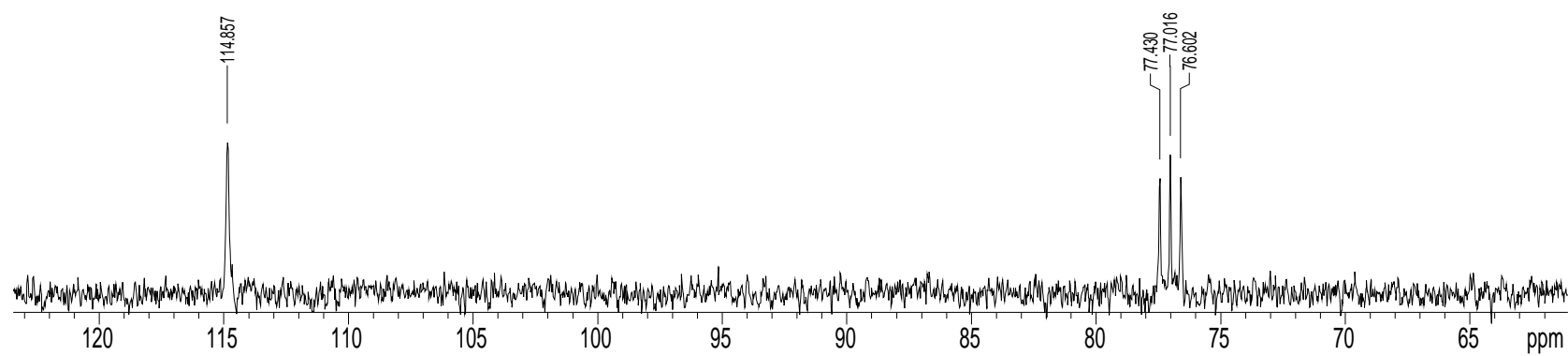
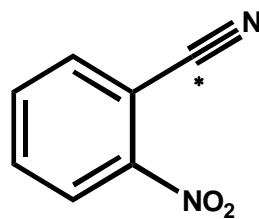
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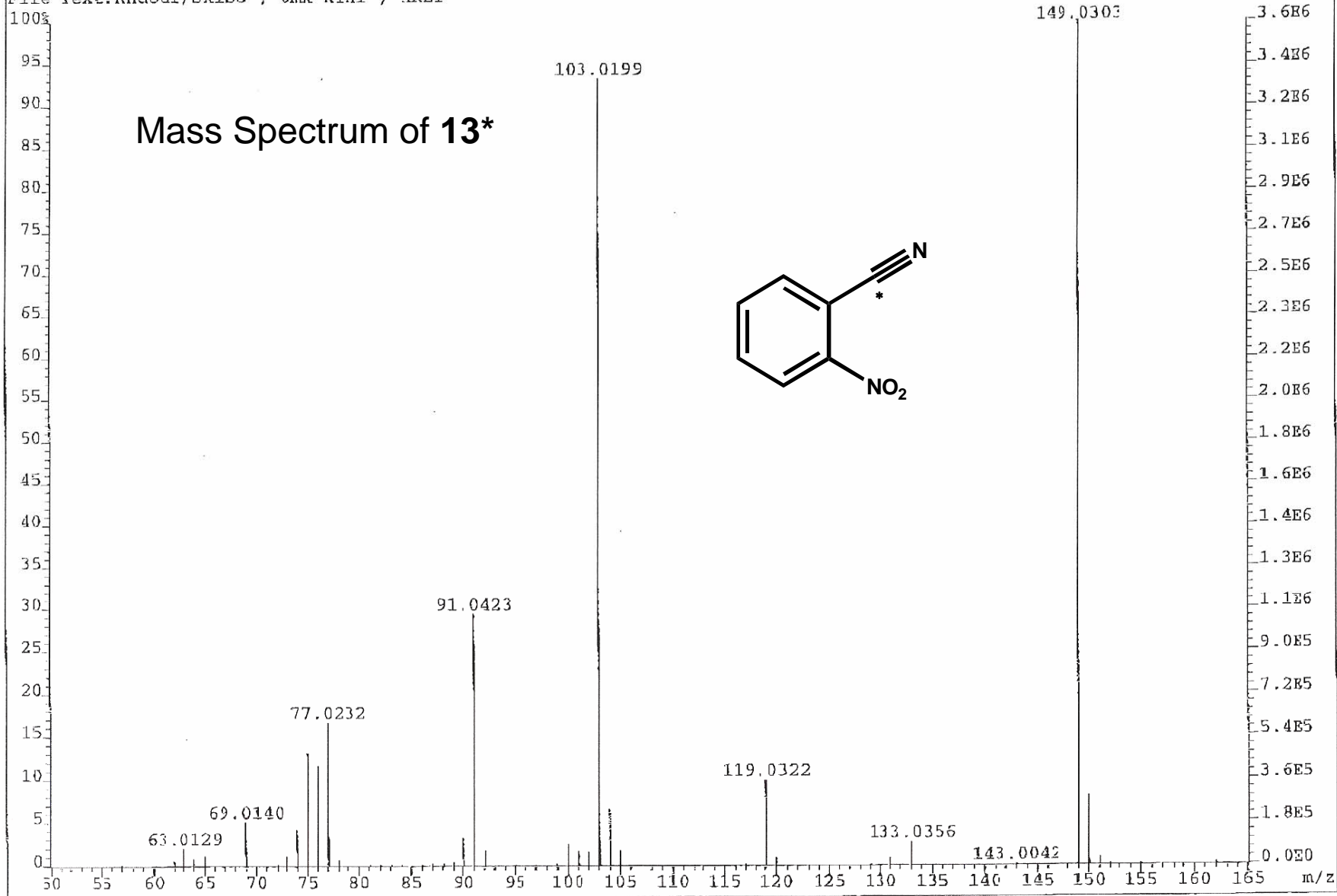
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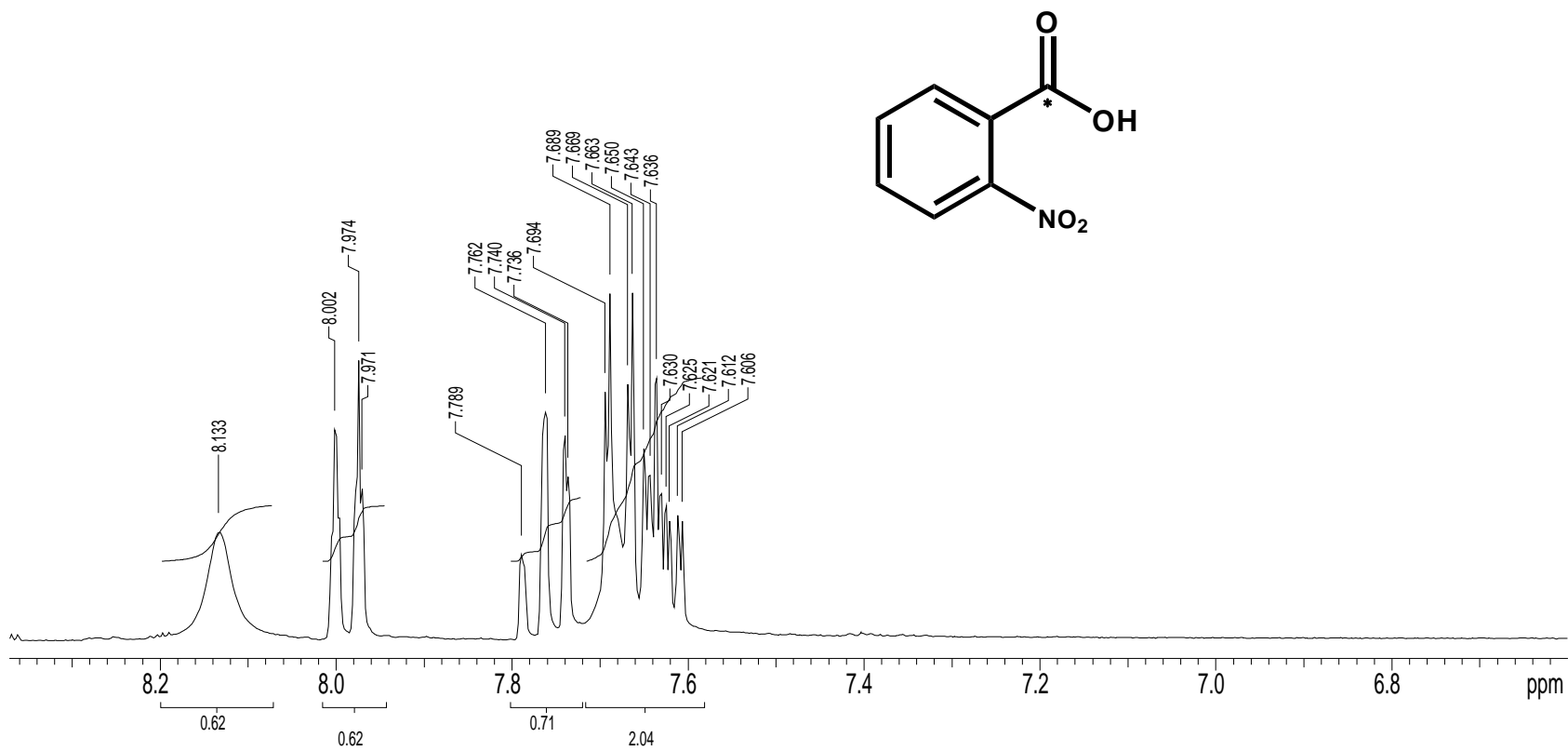
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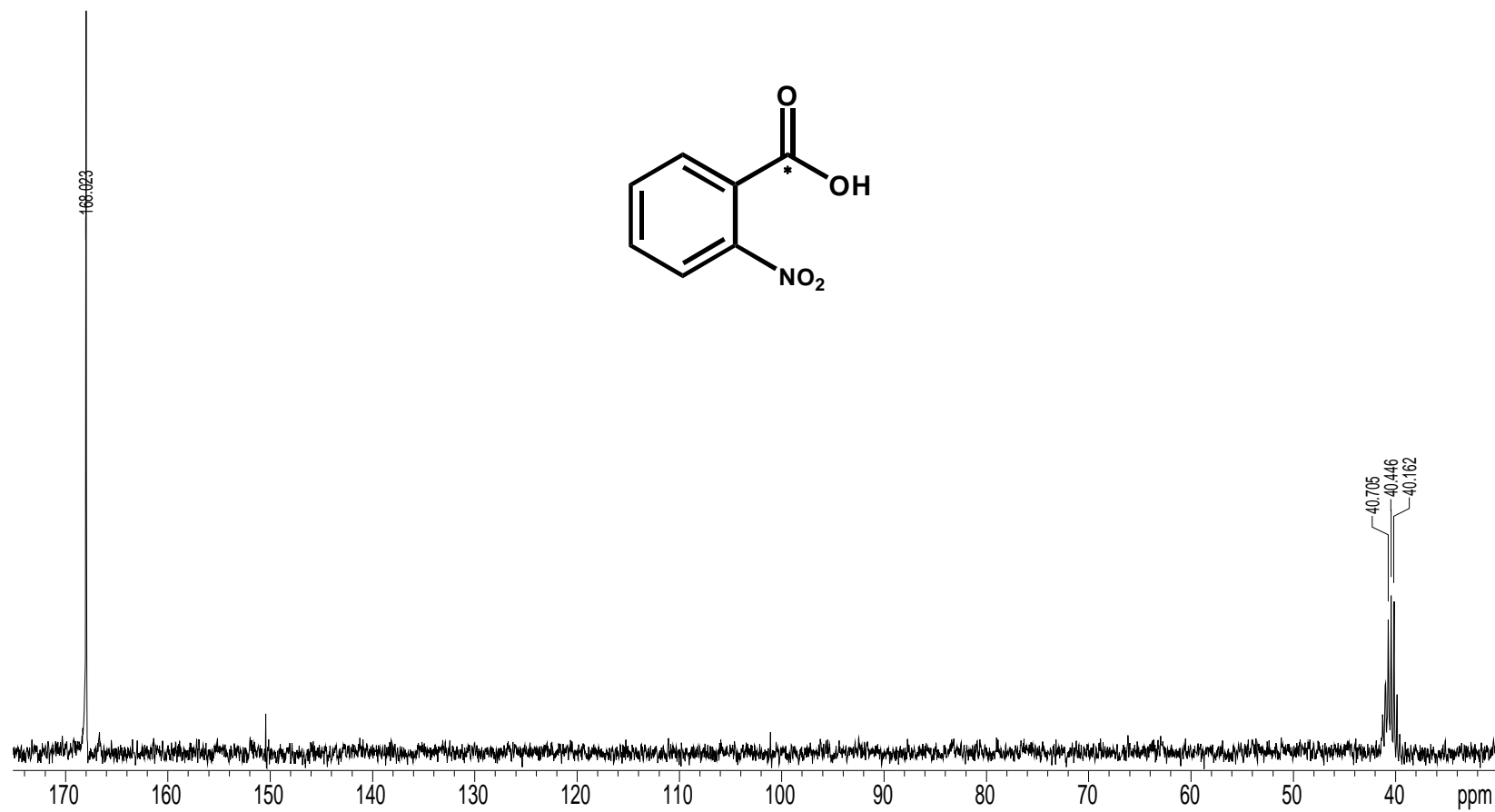
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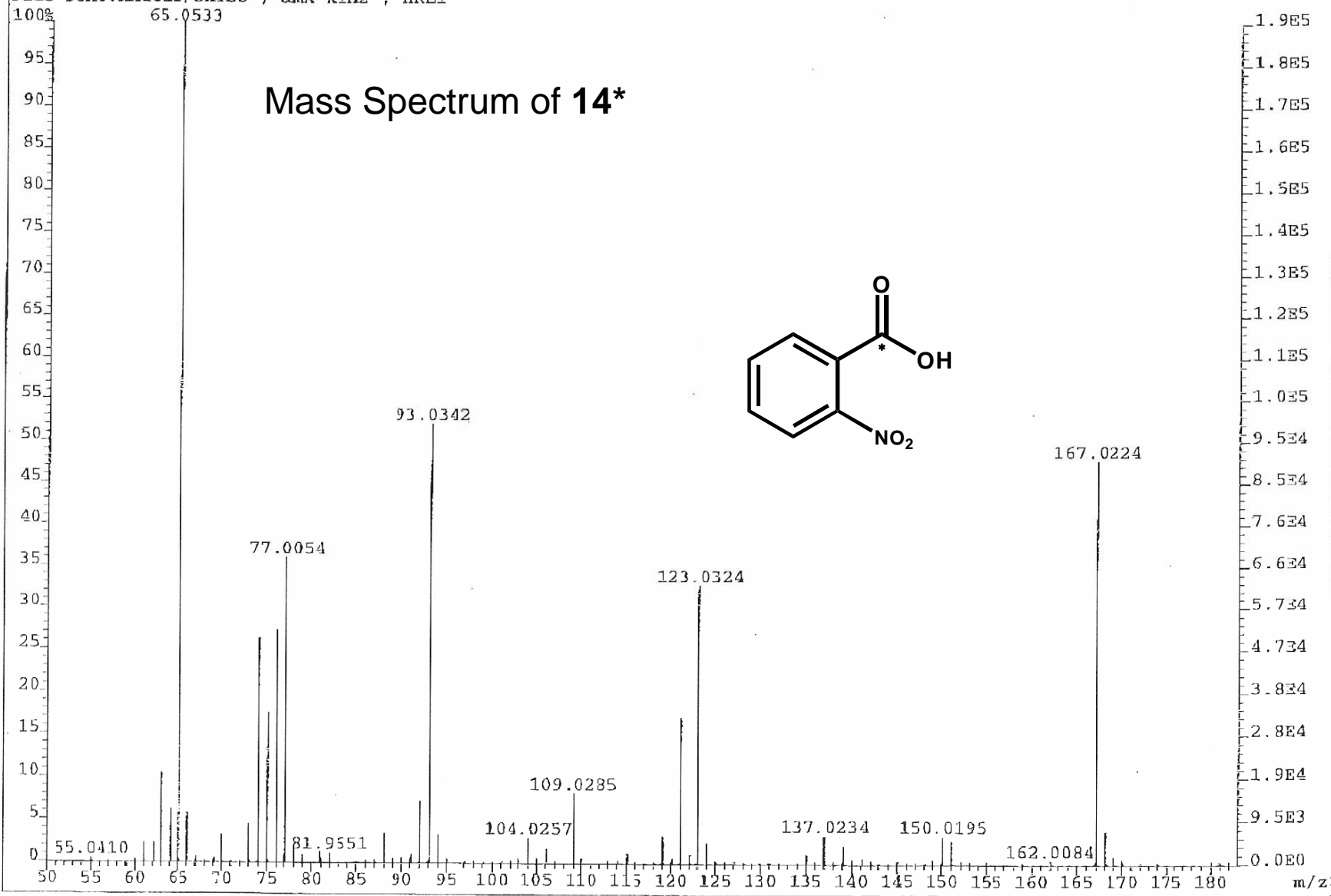
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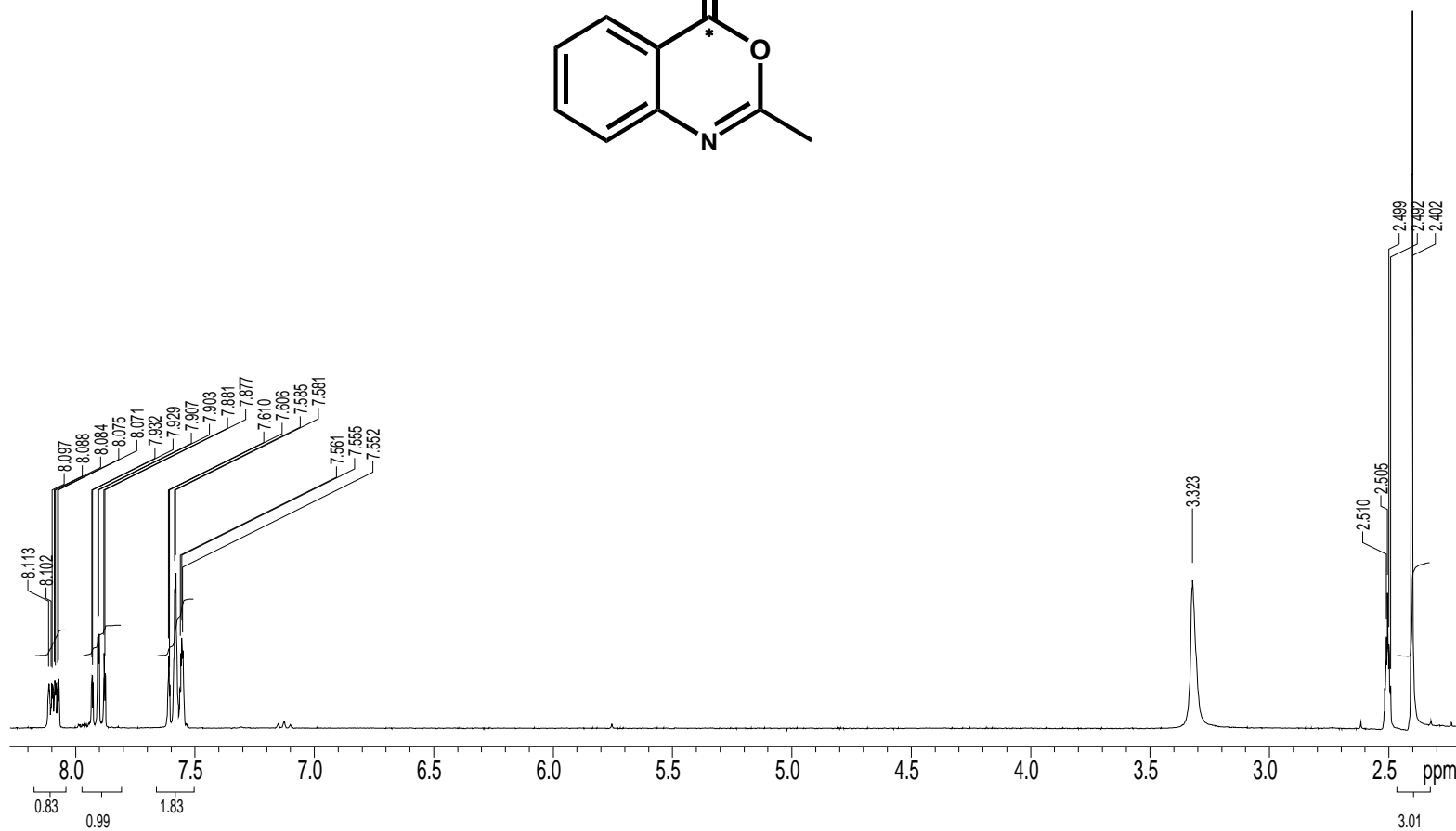
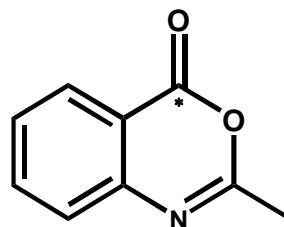
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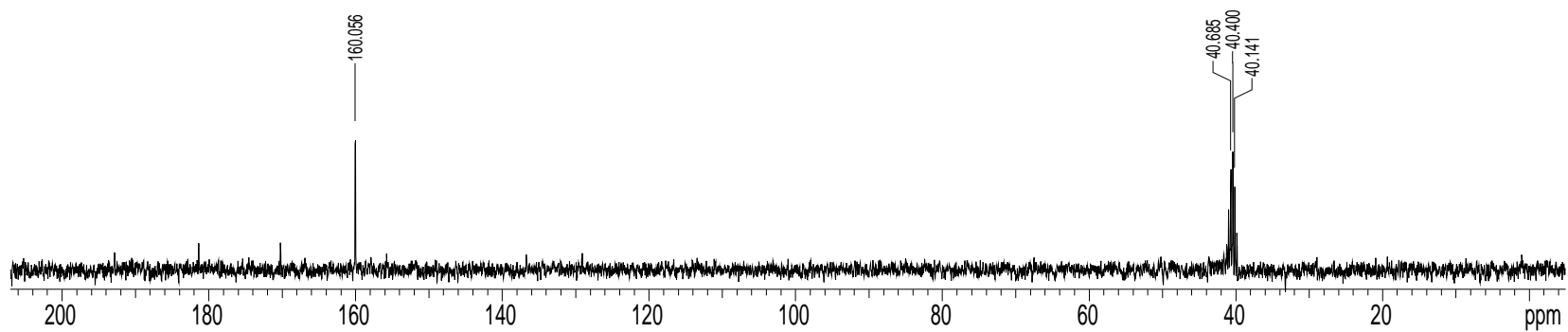
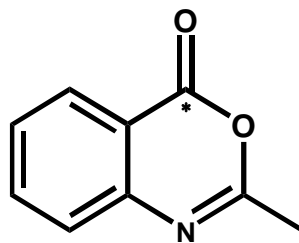
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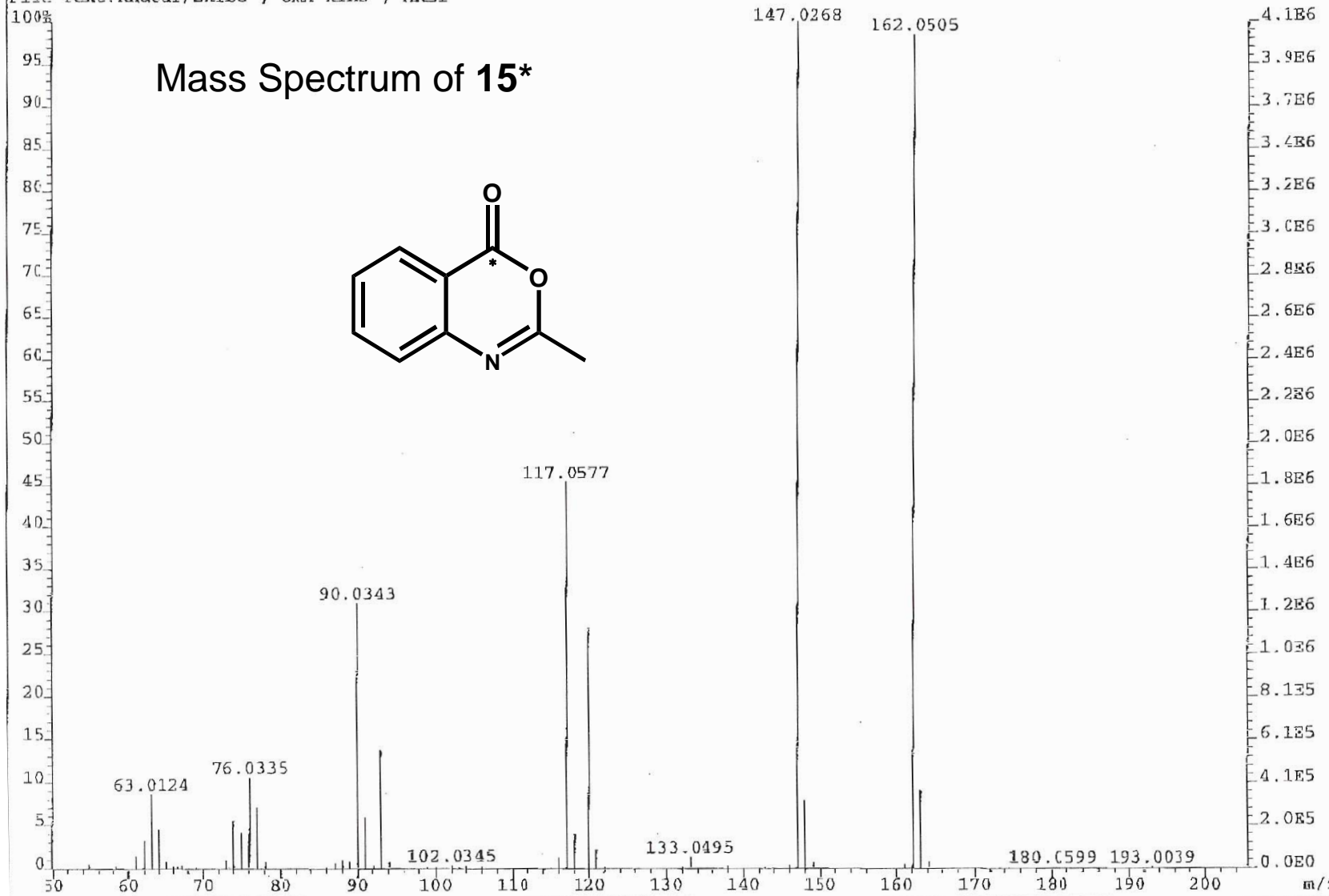
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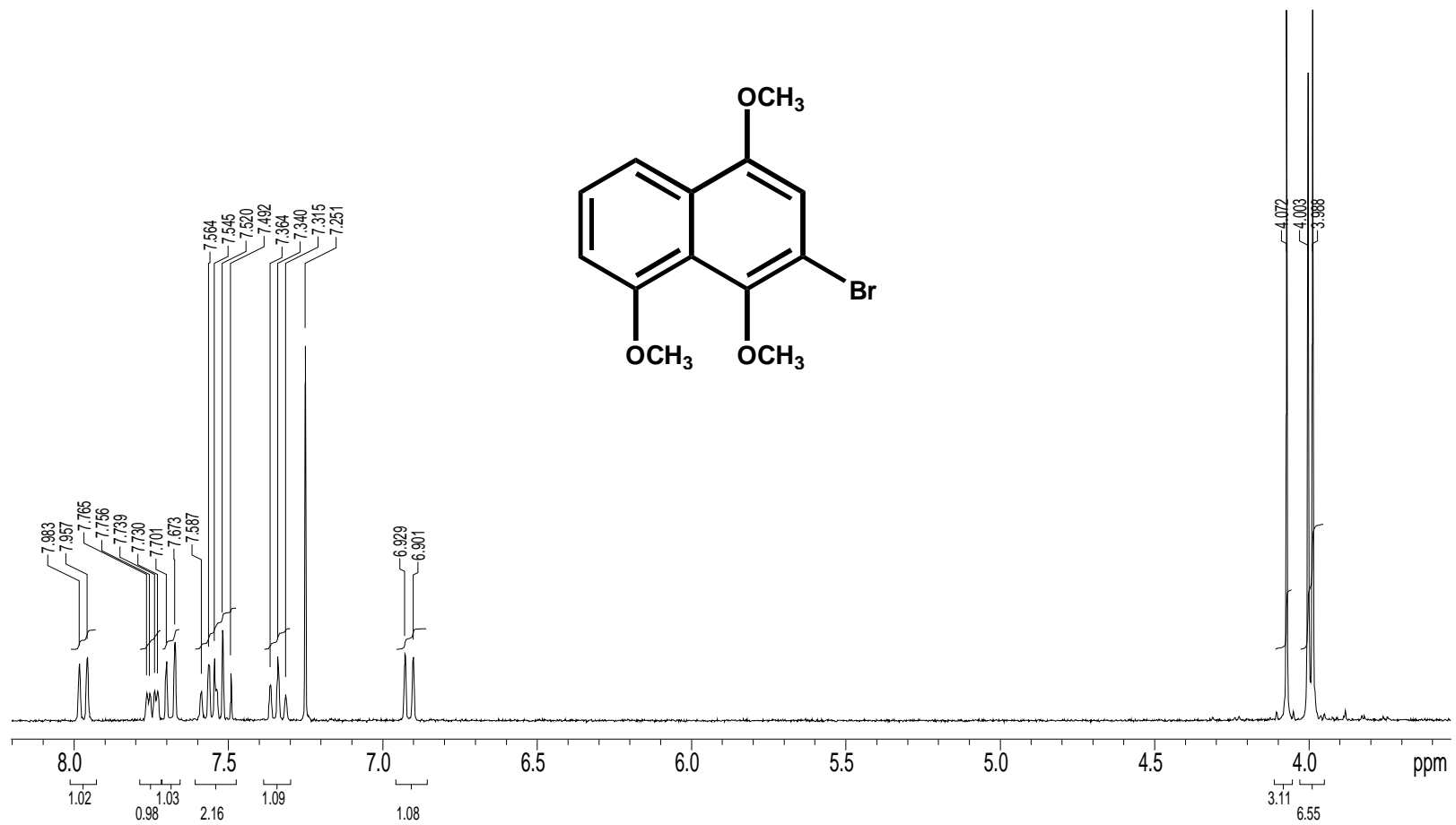
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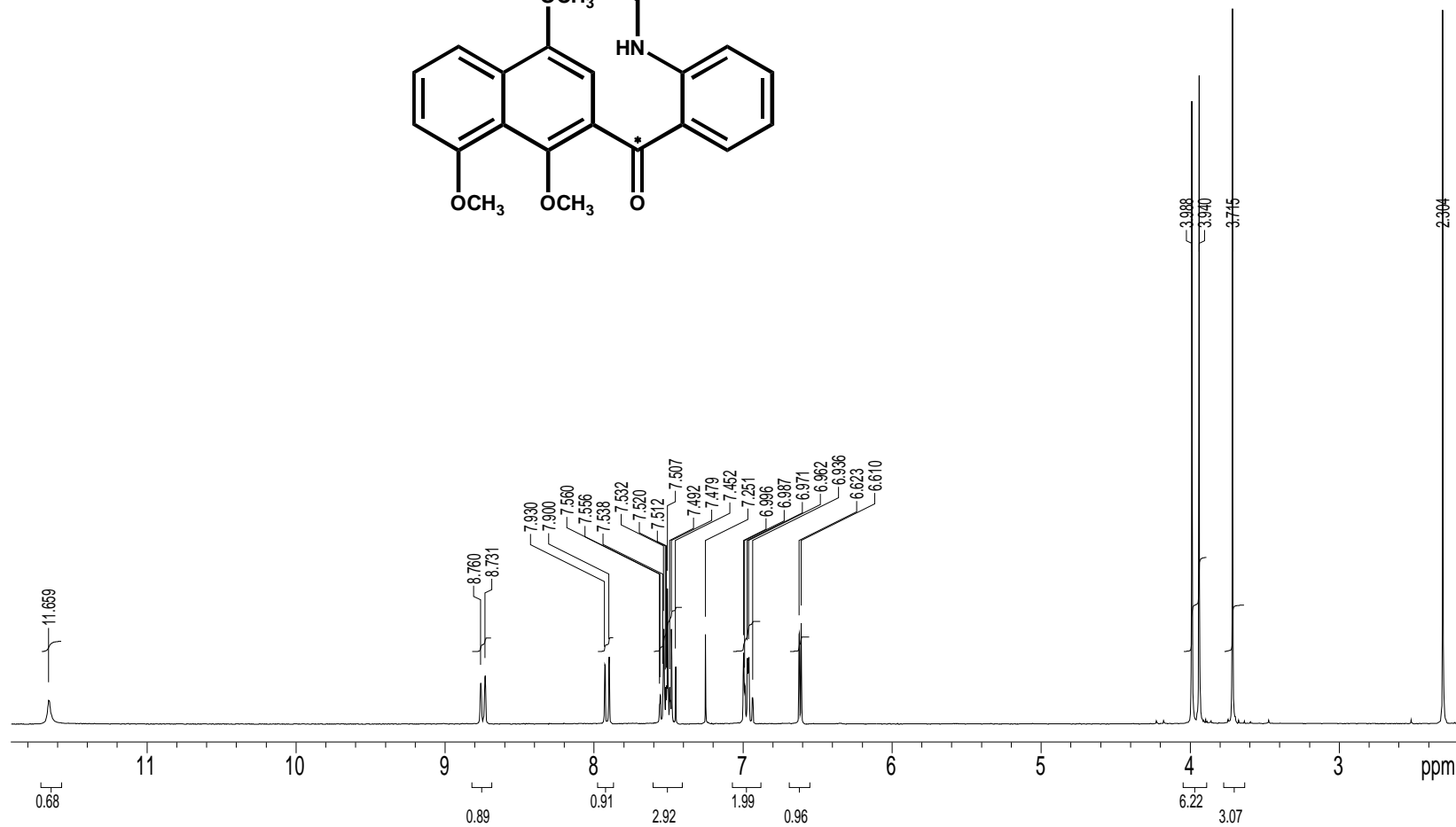
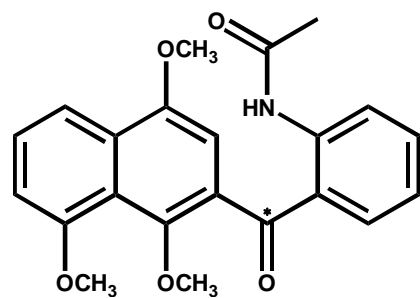
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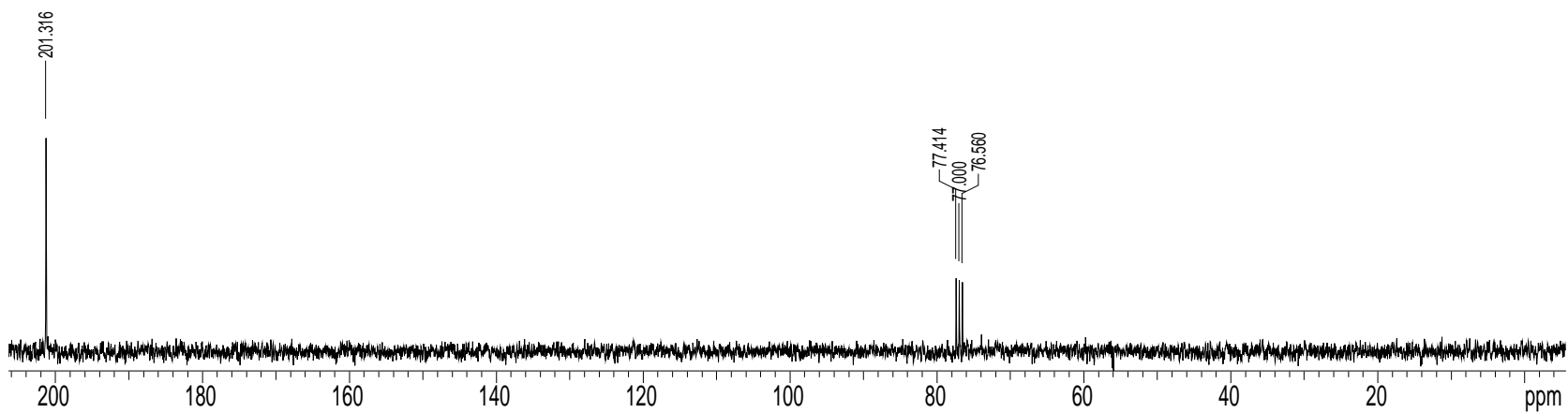
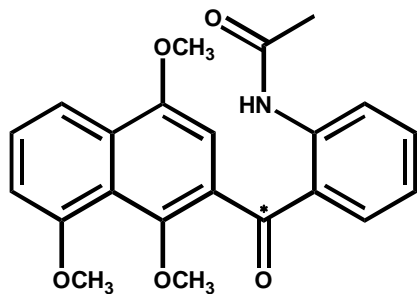
H-NMR of 16



H-NMR of 17*

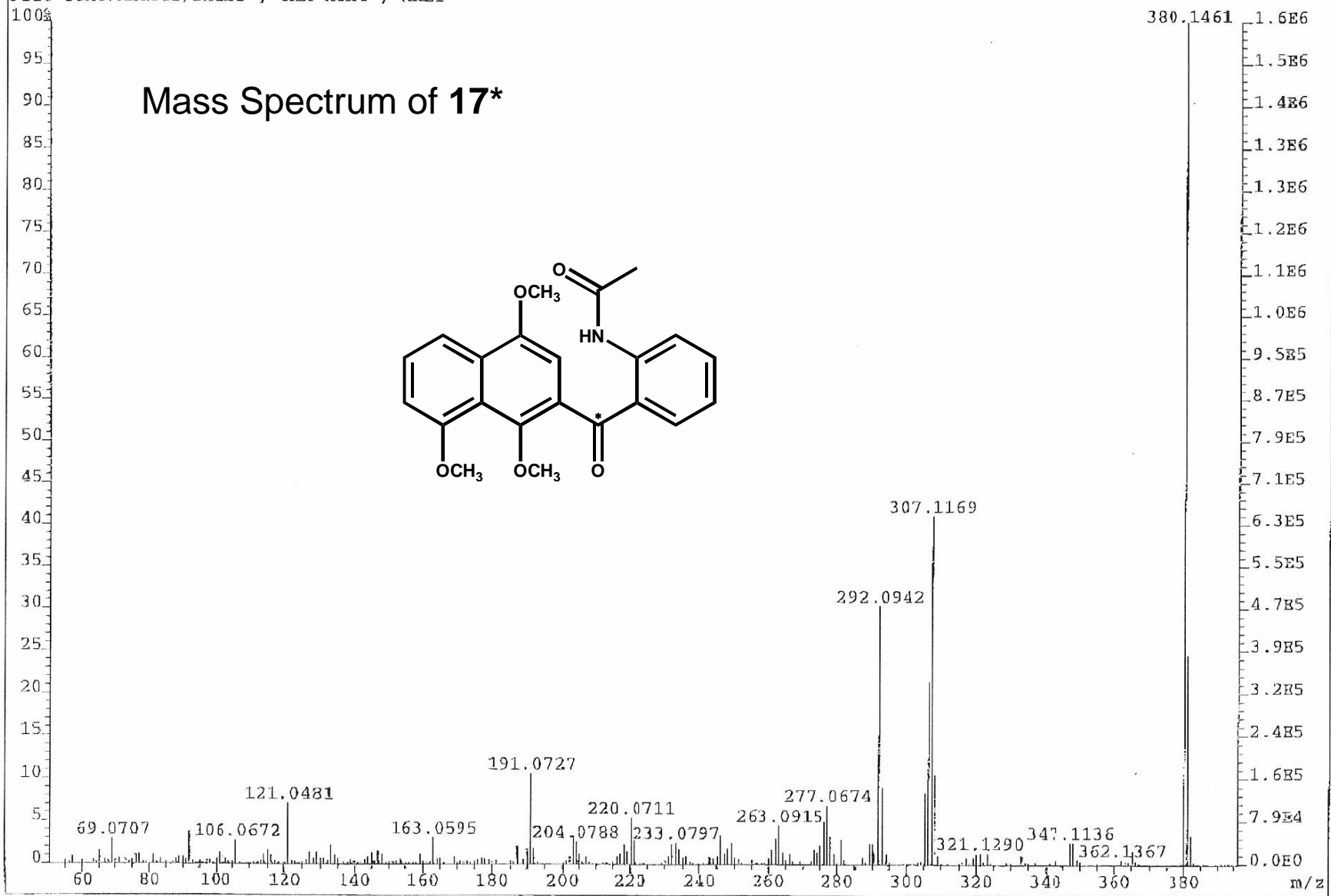
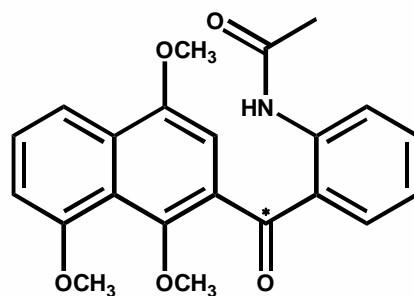


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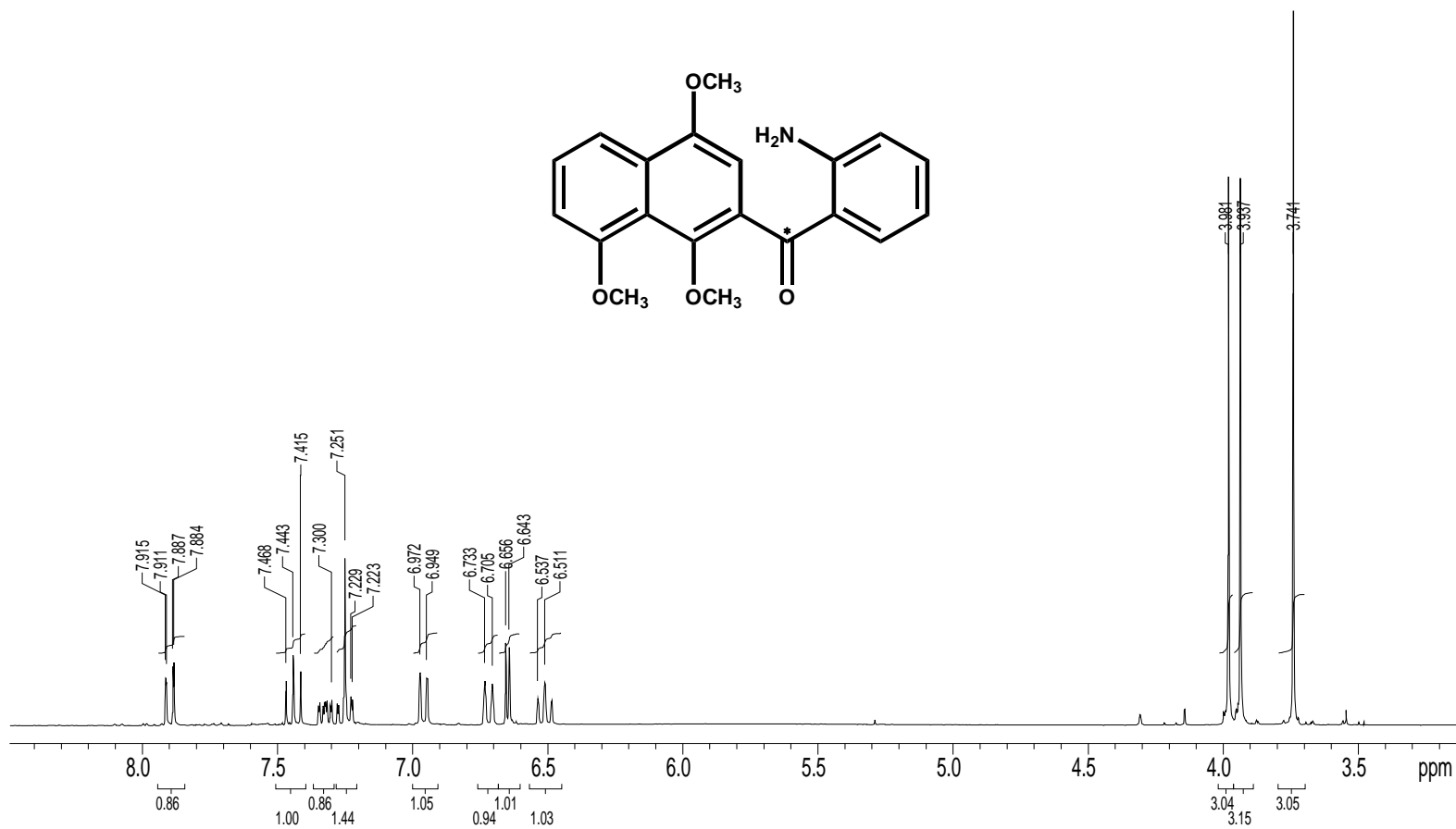
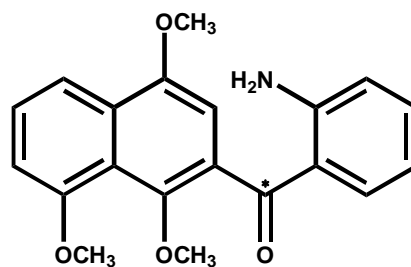


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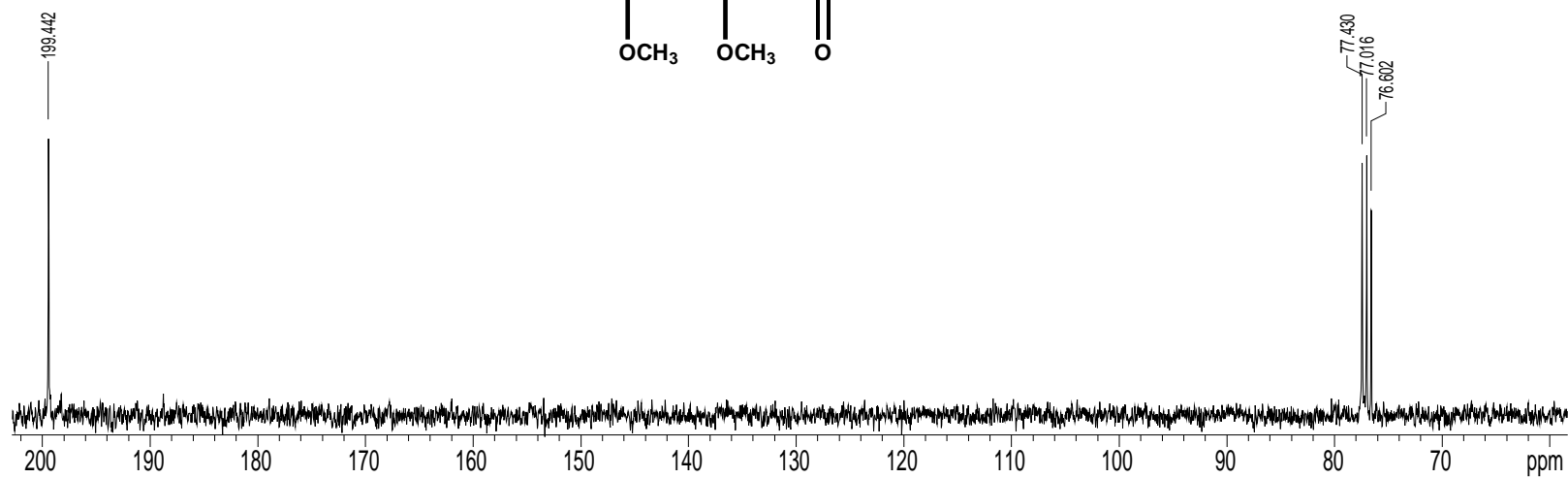
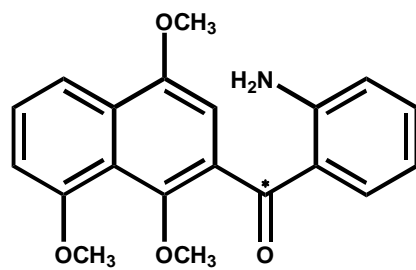
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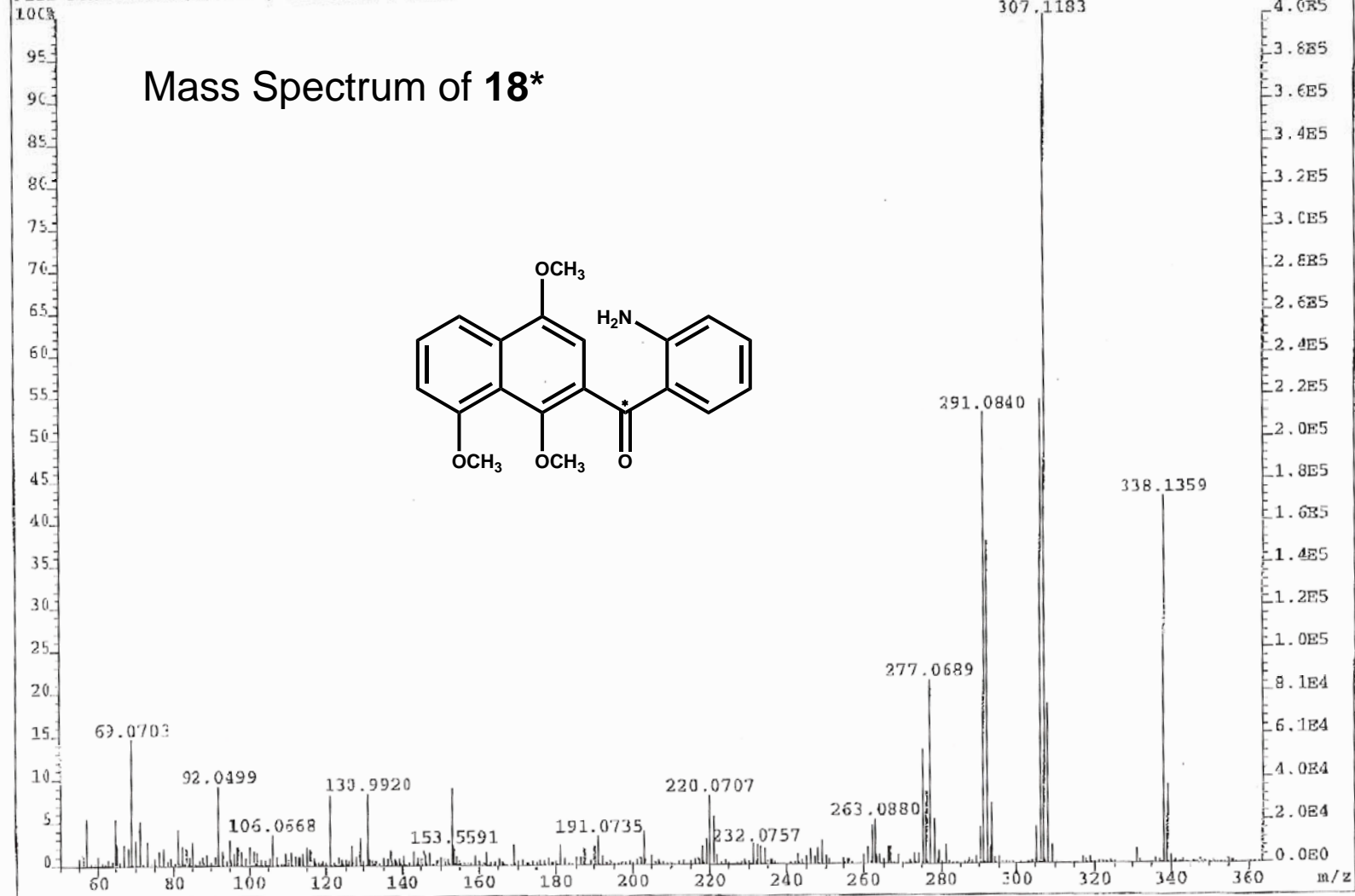
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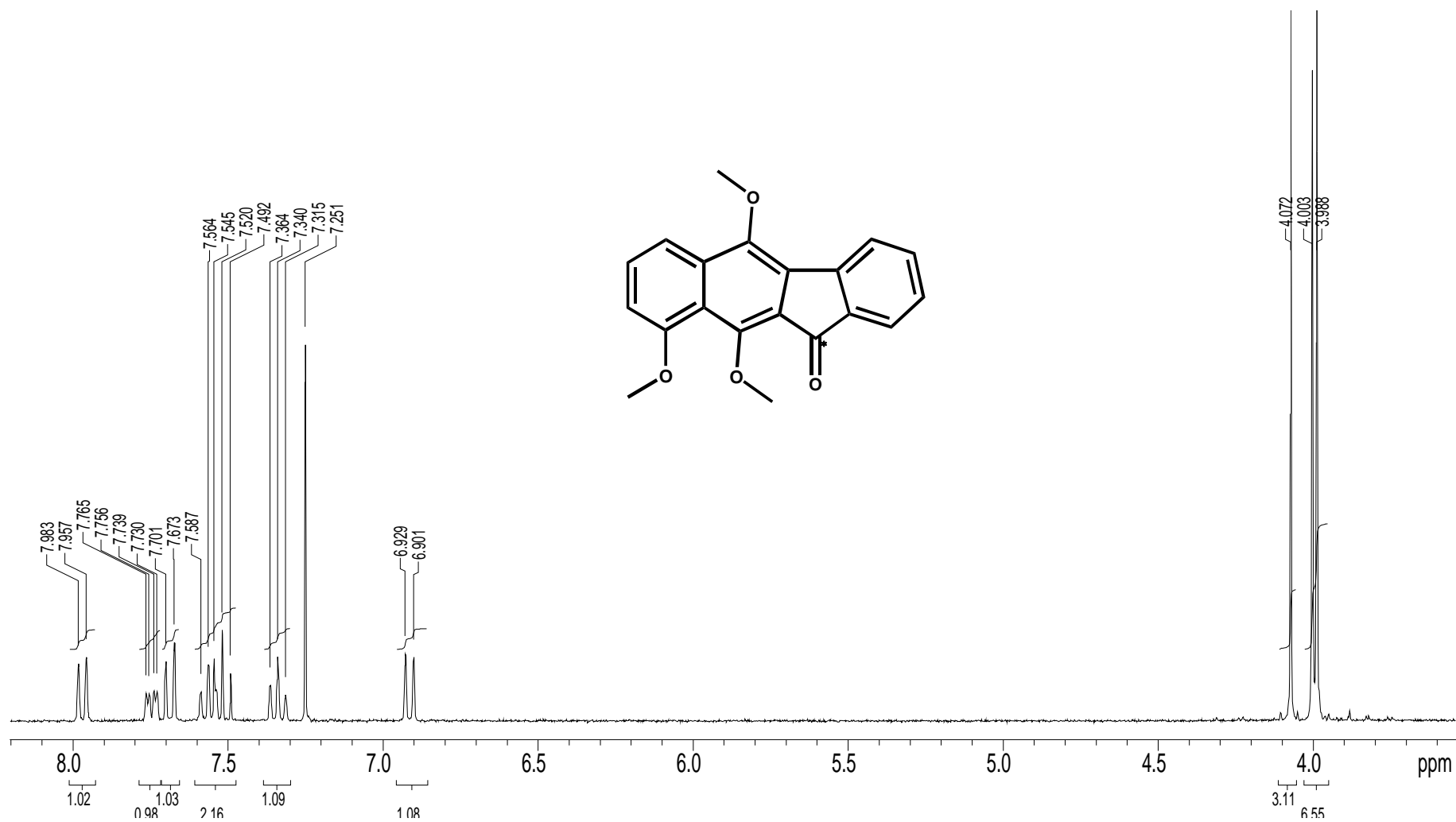
^{13}C -NMR of **18***



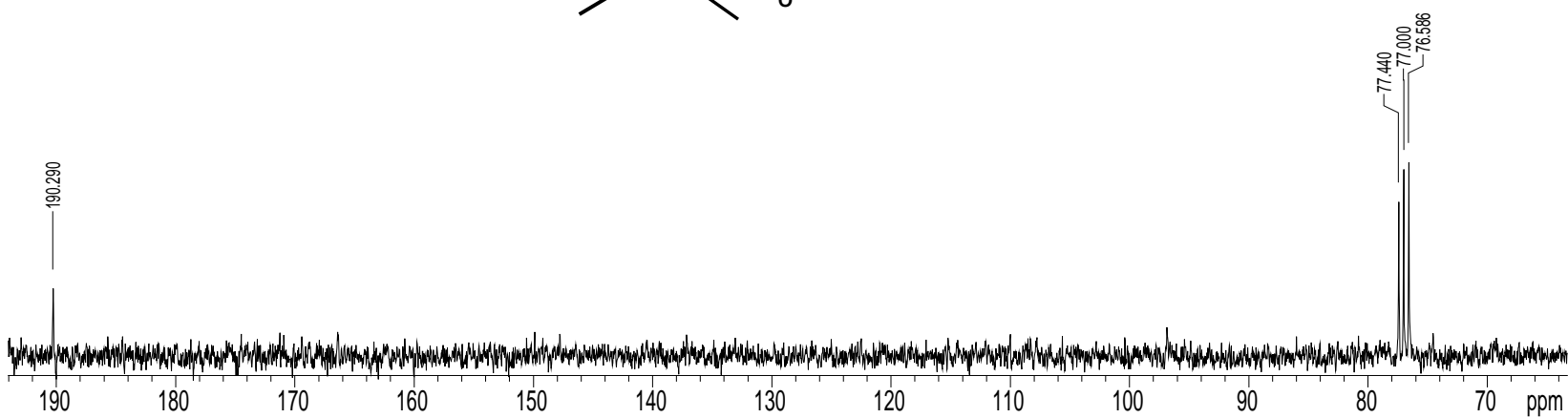
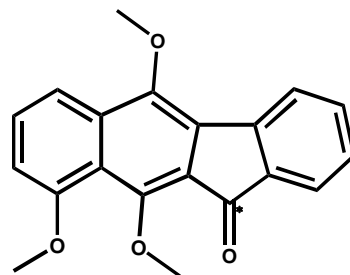
File:54115 Ident:15_25-1_11 Win 100PPM Acq:16-AUG-2006 16:32:50 +4:21 Cal:54115
AutoSpecETOFFPD EI+ Magnet BpM:307 BpI:404803 TIC:4732572 Flags:ACC
File Text:Khdour/Skibo ; omk-kin5 ; HREI



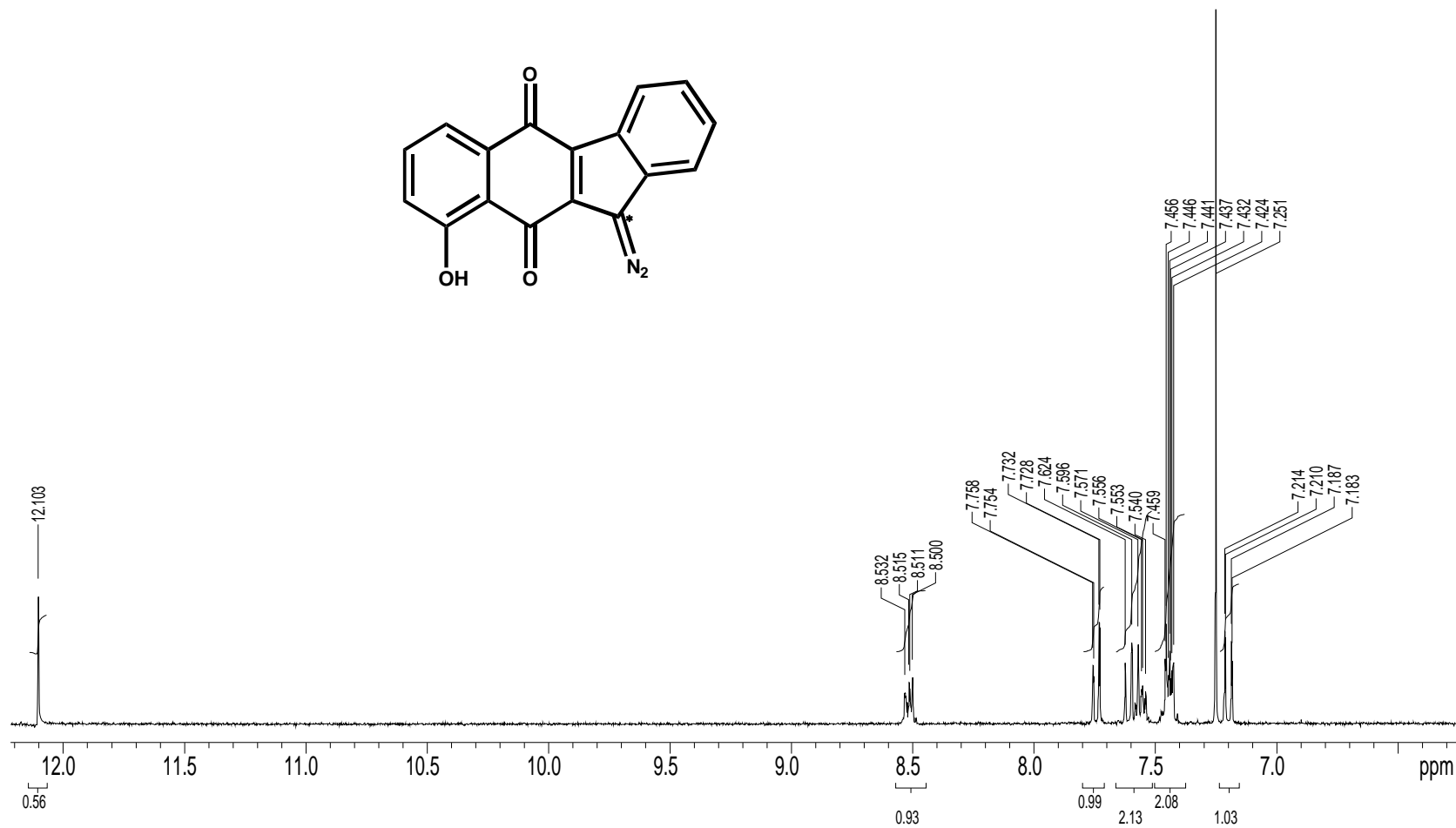
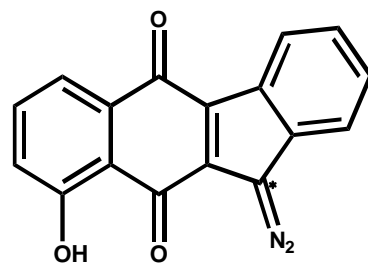
H-NMR of 19*



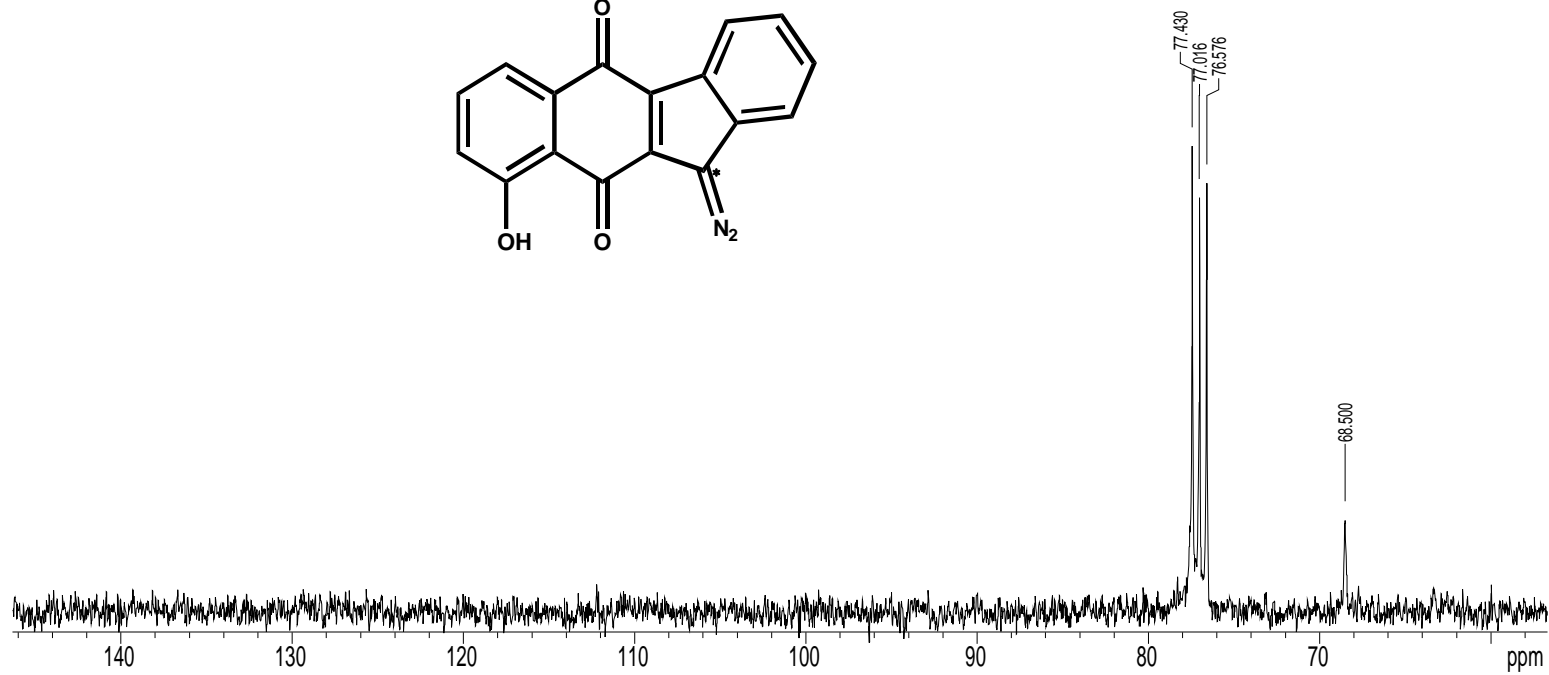
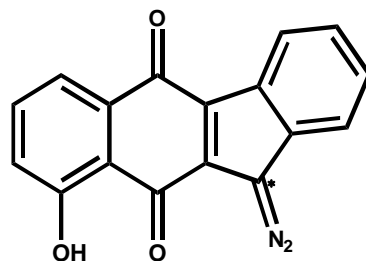
^{13}C -NMR of **19***



H-NMR of 2*

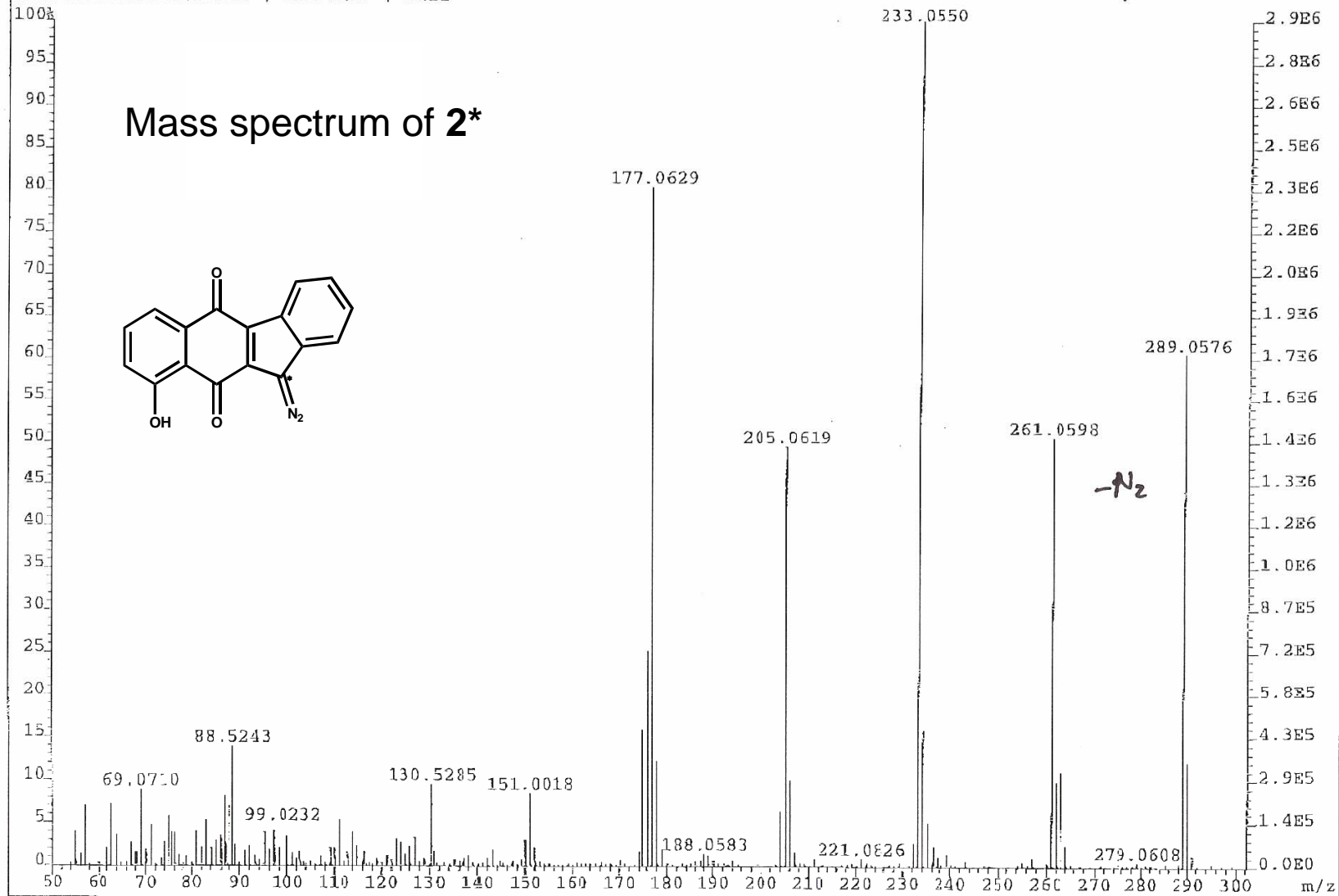


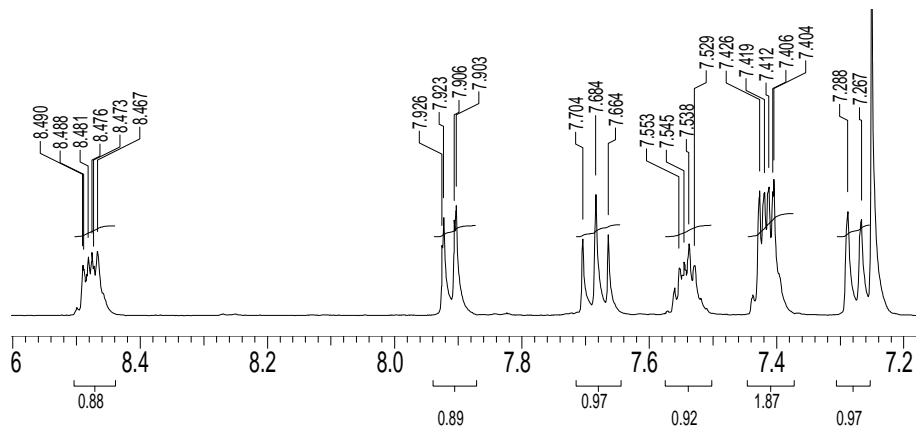
^{13}C -NMR of **2***



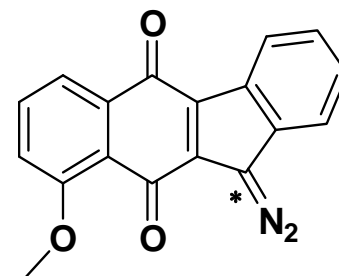
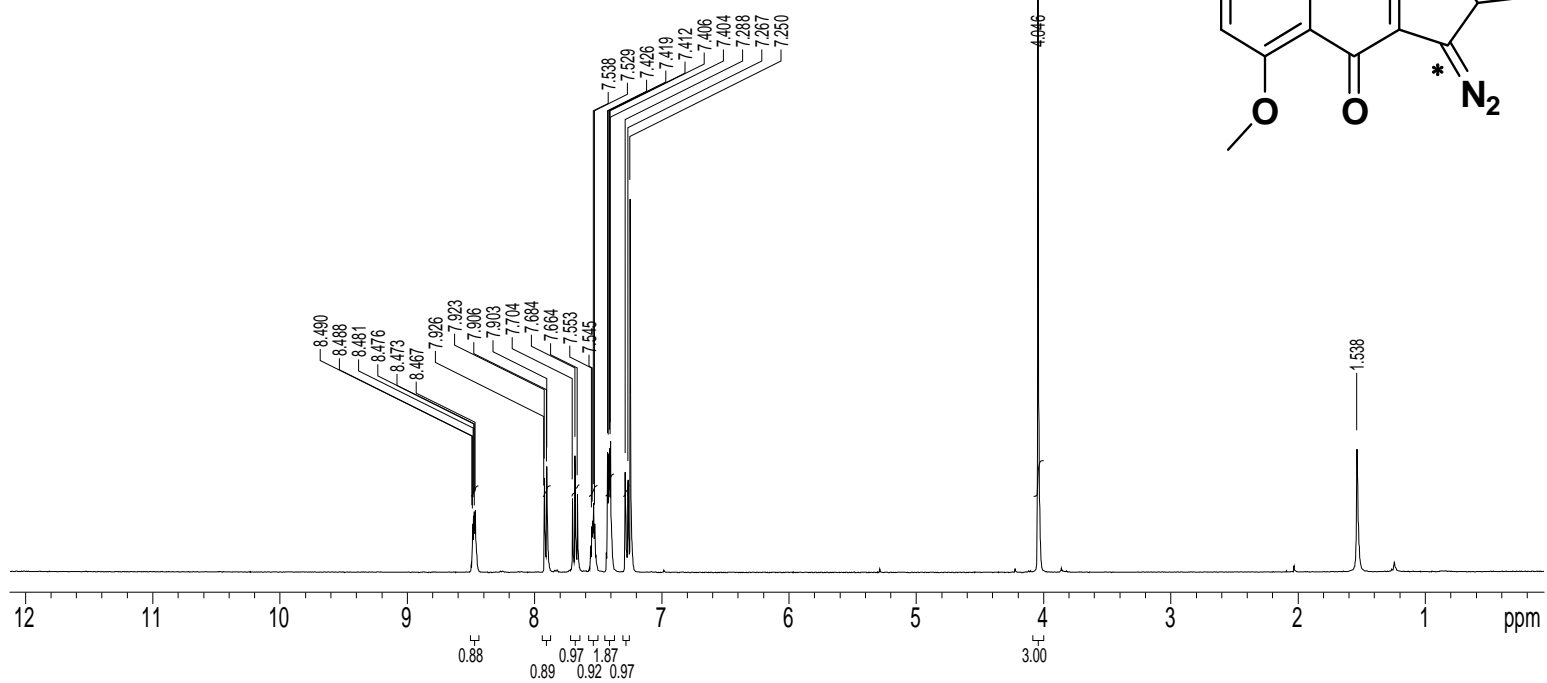
File:54117A Ident:47_52-1_12 Win 100PPM Acq:17-AUG-2006 10:01:17 +10:29 Cal:54117A
AutoSpecFTOPFPD EI+ Magnet BpM:233 BpI:2897558 TIC:28580344 Flags:ACC
File Text:Khmour/Skibo ; omk-kin7 ; HREI

$^{12}\text{C}, ^{13}\text{C}, \text{H}, \text{N}, \text{O}_2$ 289.0569

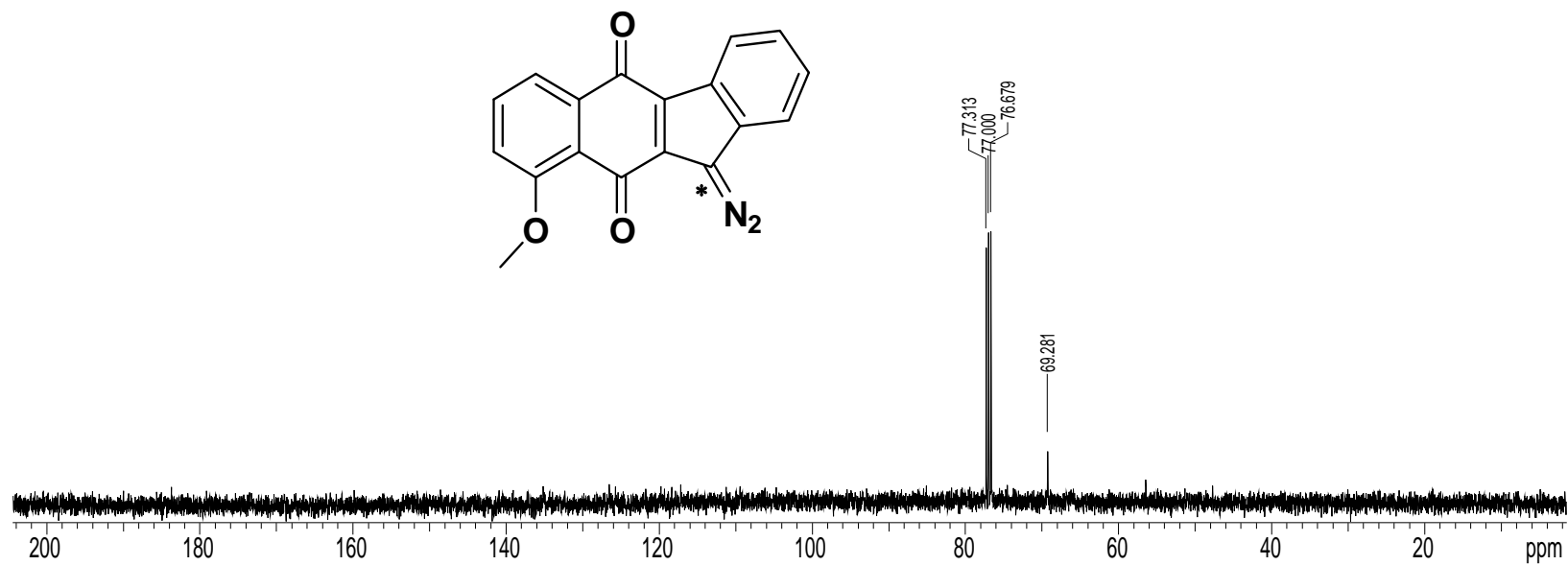




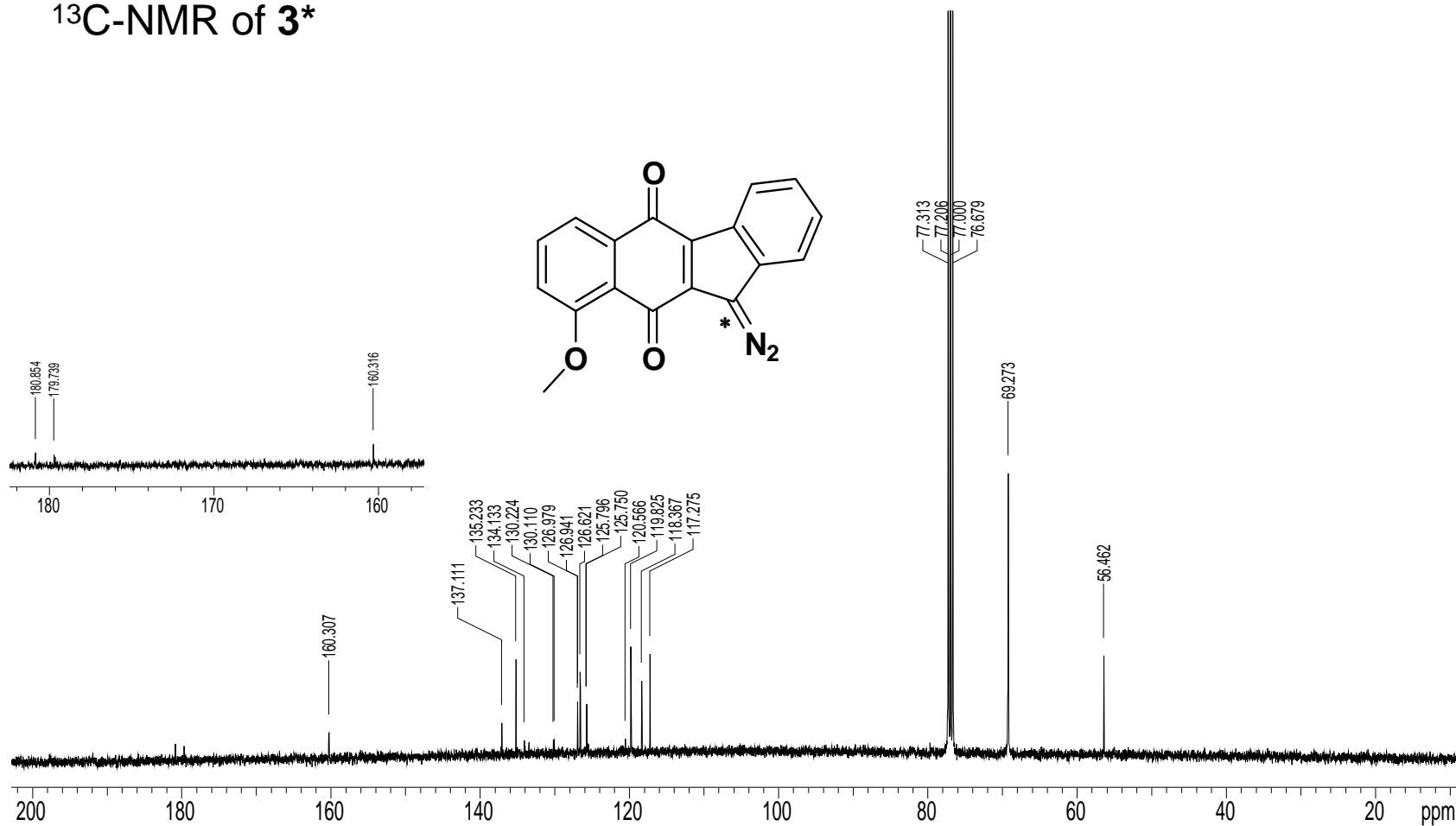
H-NMR of 3*



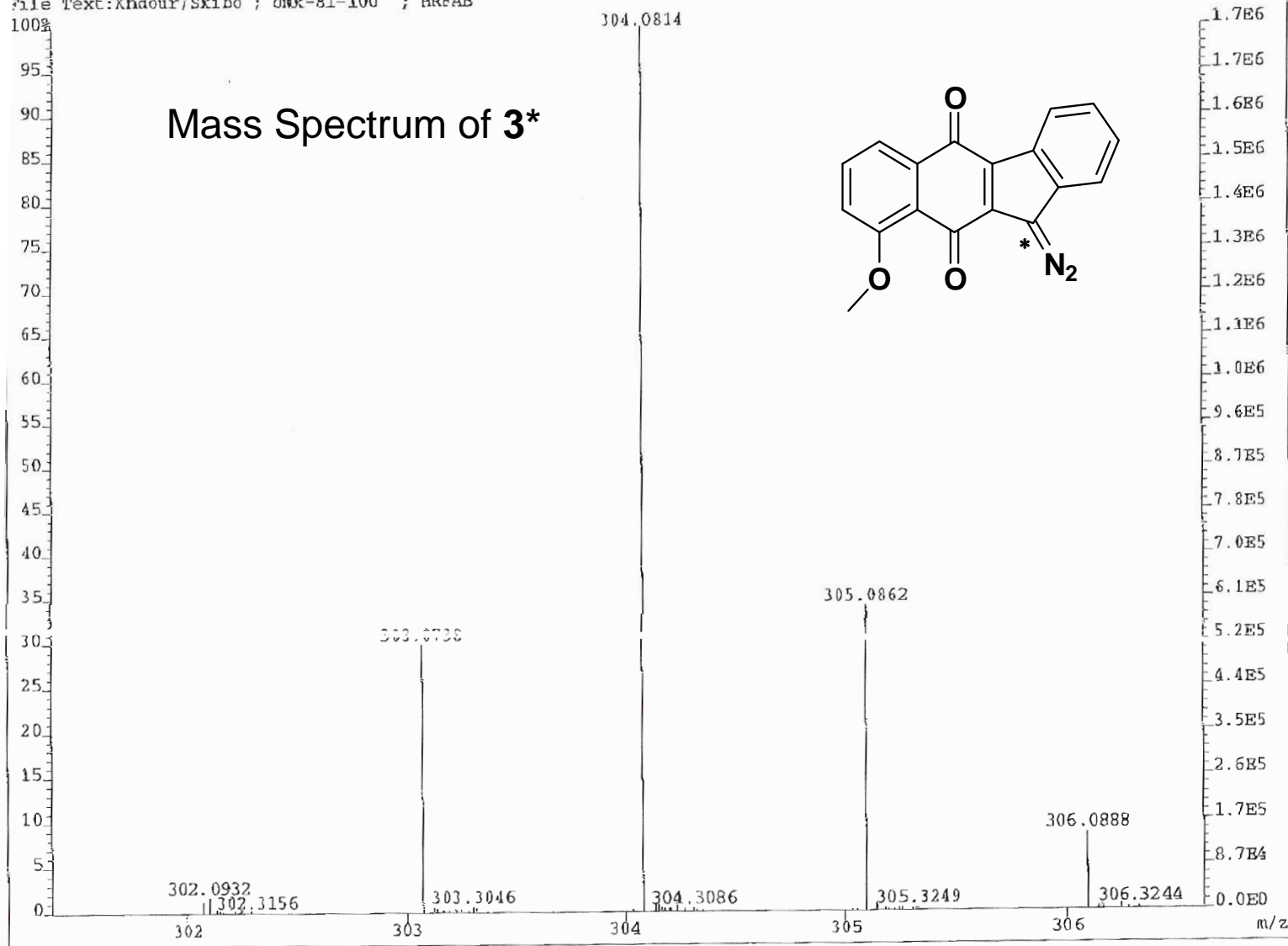
^{13}C -NMR of **3***



^{13}C -NMR of **3***

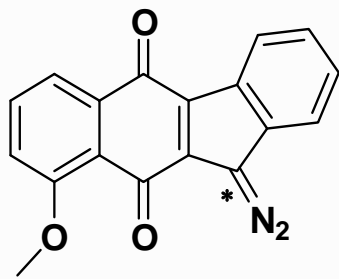
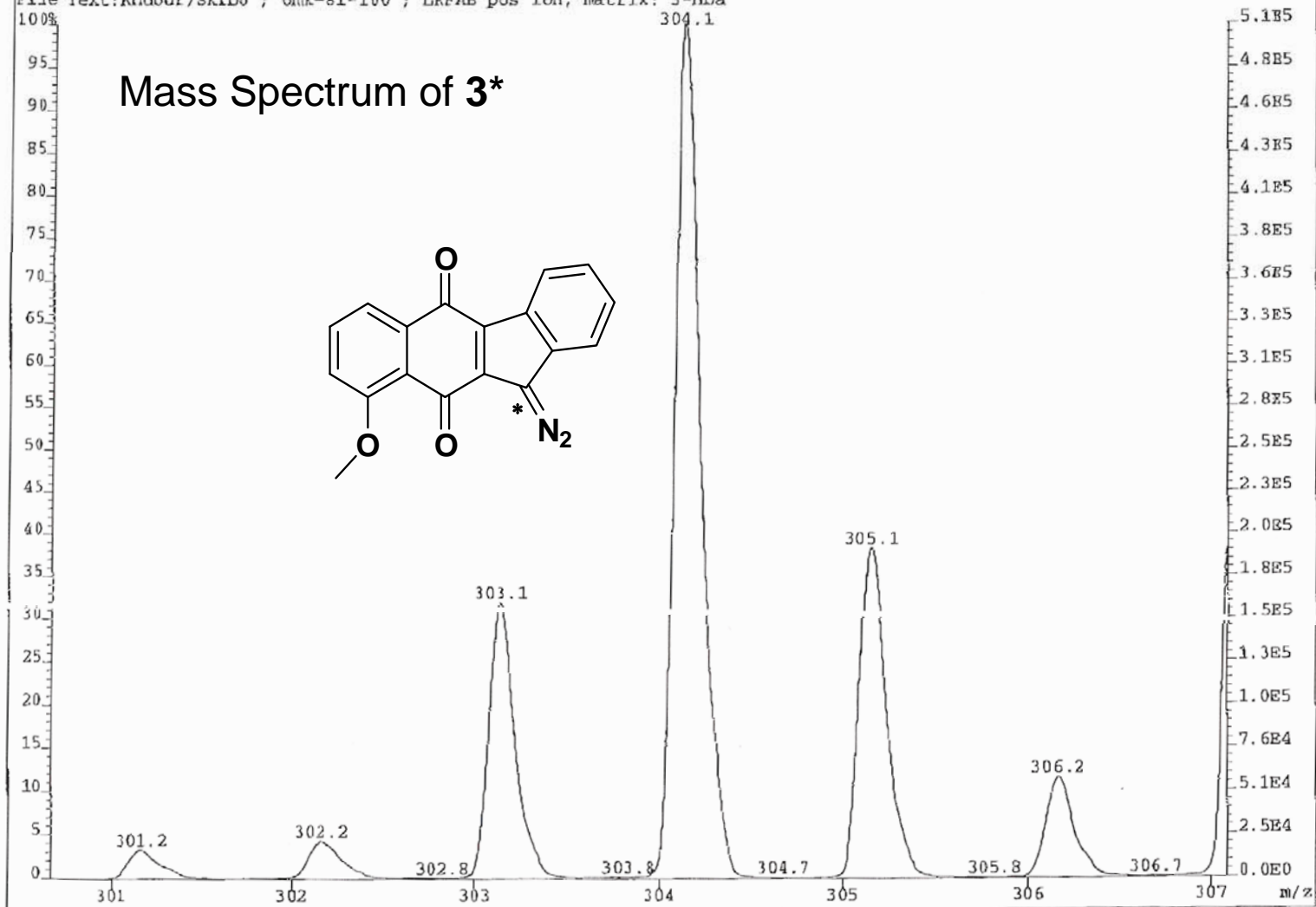


File: 54296 Ident: 50_60 SMO(1,7) PKD(7,4,7,0.00%,0.0,65.00%,F,F) SPEC(Heights, Centroid) Acq: 31-OCT-2006 14:36:38 +11:11 >
AutoSpecEToFPPD FAB+ Voltage BpI: 2470752 TIC: 213505360 Flags: NORM
File Text: Khmour/Skibo ; omk-81-100 ; HRFAB

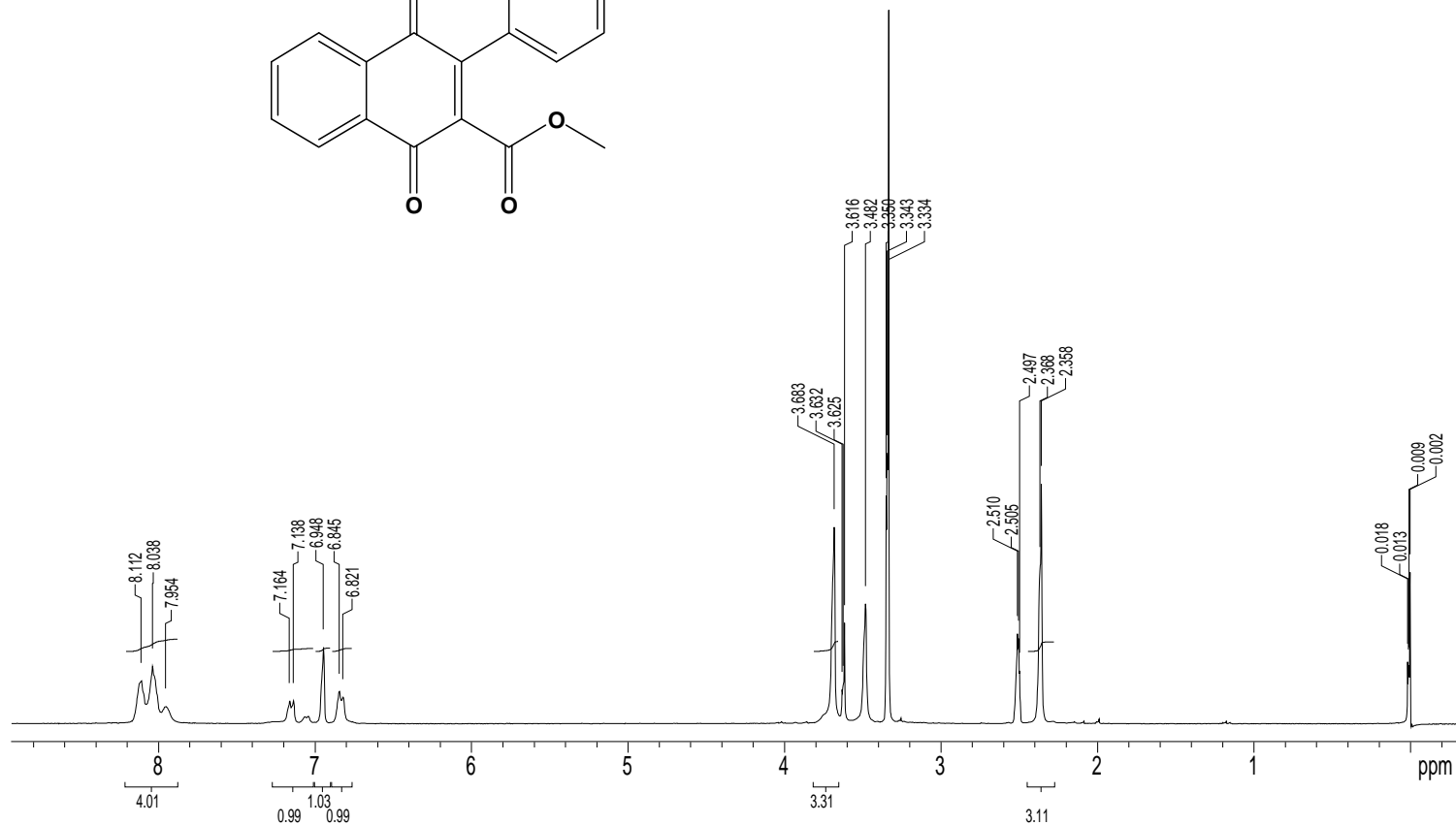
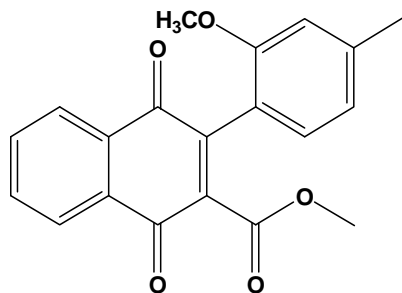


File:54256C Ident:32_41 SMO(1,11) Acq:24-OCT-2006 15:34:09 +8:17 Cal:SERCAL102406
AutoSpecETOFPPD FAB+ Magnet BpI:2643712 TIC:522632160
File Text:Khgour/Skibo ; omk-81-100 ; LRFAB pos ion, matrix: 3-nba

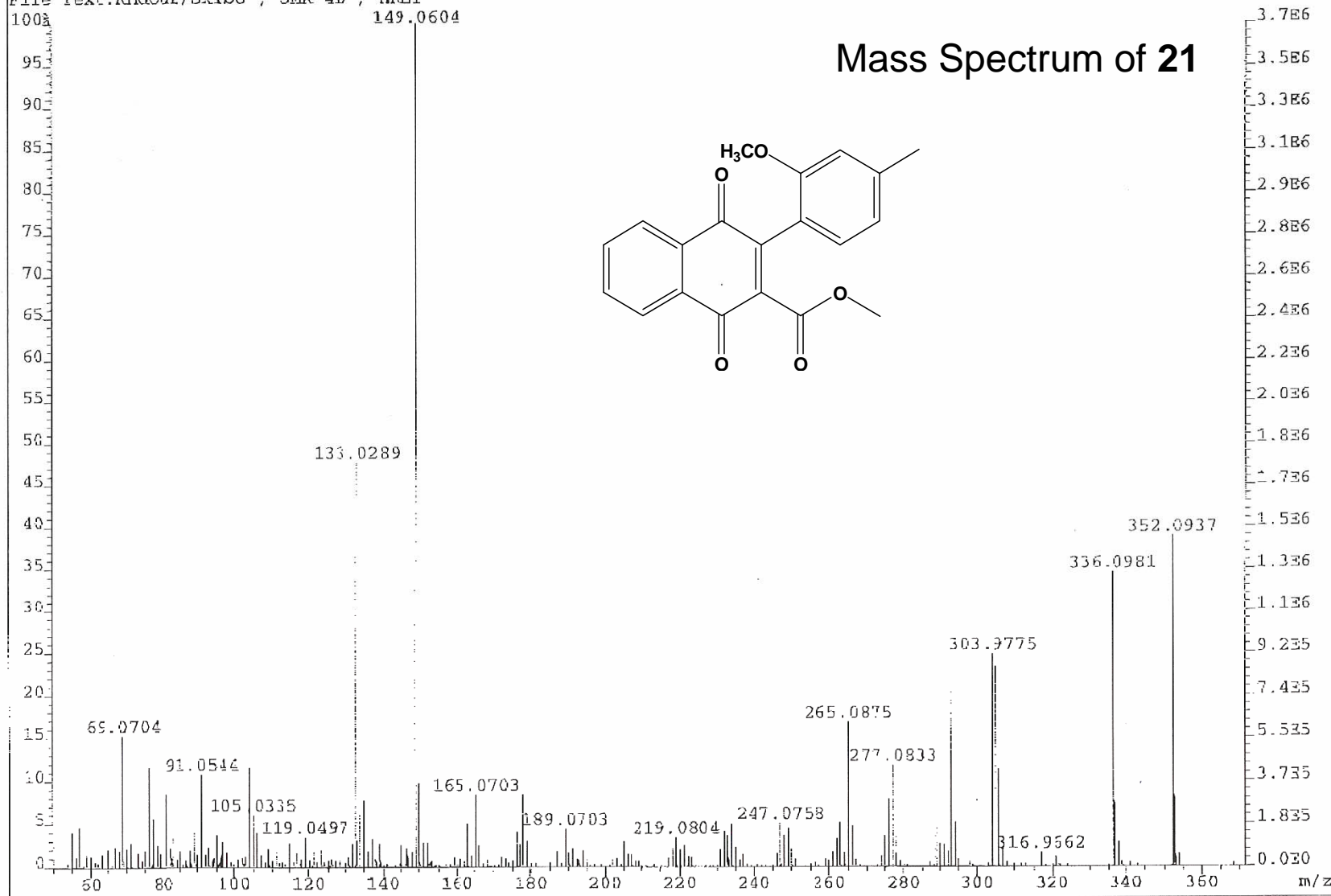
Mass Spectrum of 3*



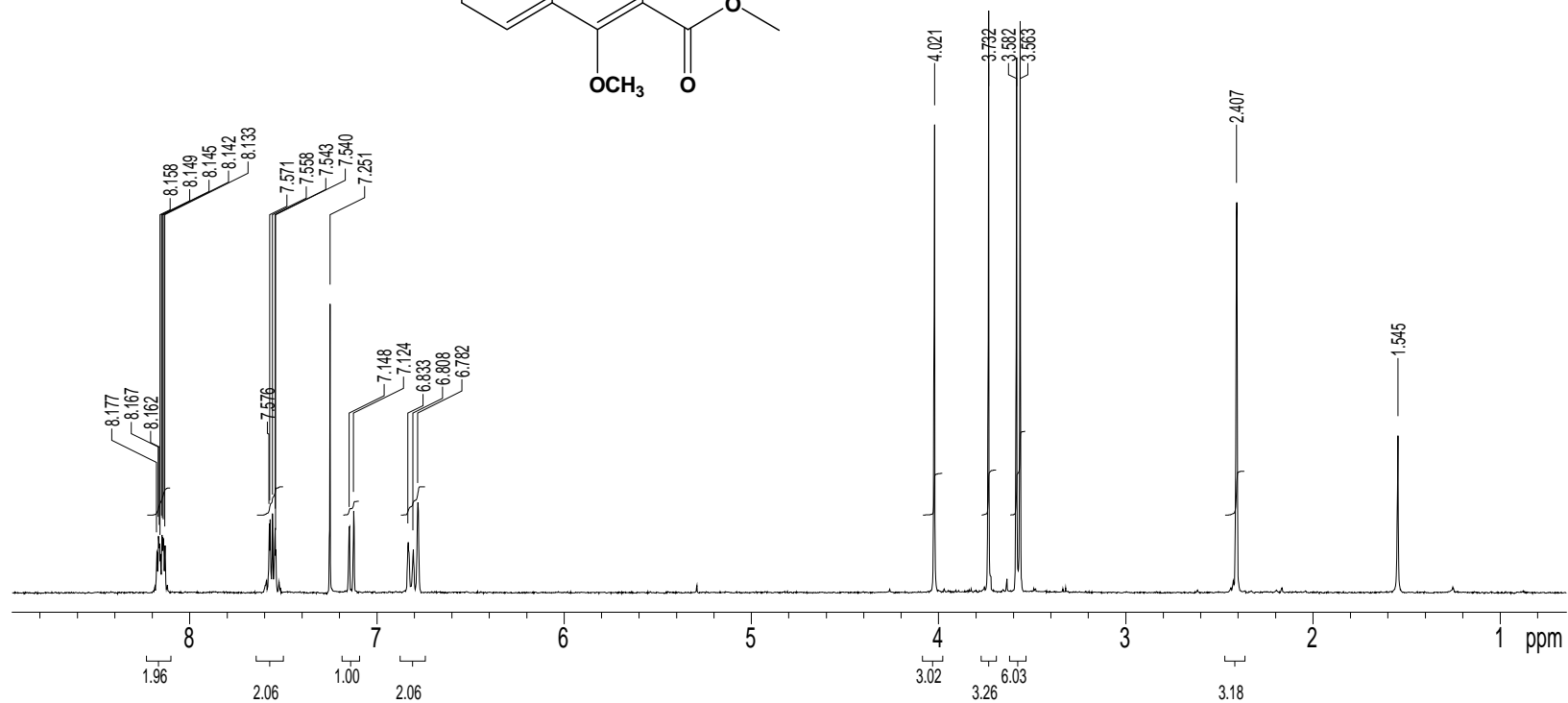
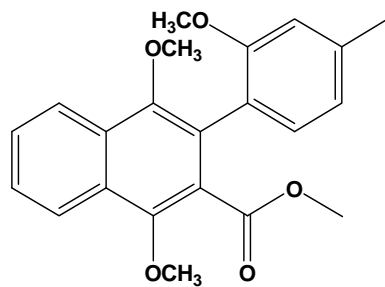
H-NMR of 21



File:54343 Ident:33_43-1_11 Win 100FPM Acq: 9-NOV-2006 16:48:35 +8:07 Cal:54343
AutoSpecTTOFFPD EI+ Magnet BpM:149 EpI:3637097 TIC:34779260 Flags:ACC
File Text:Khdour/Skibo ; DMK-4b ; HREI

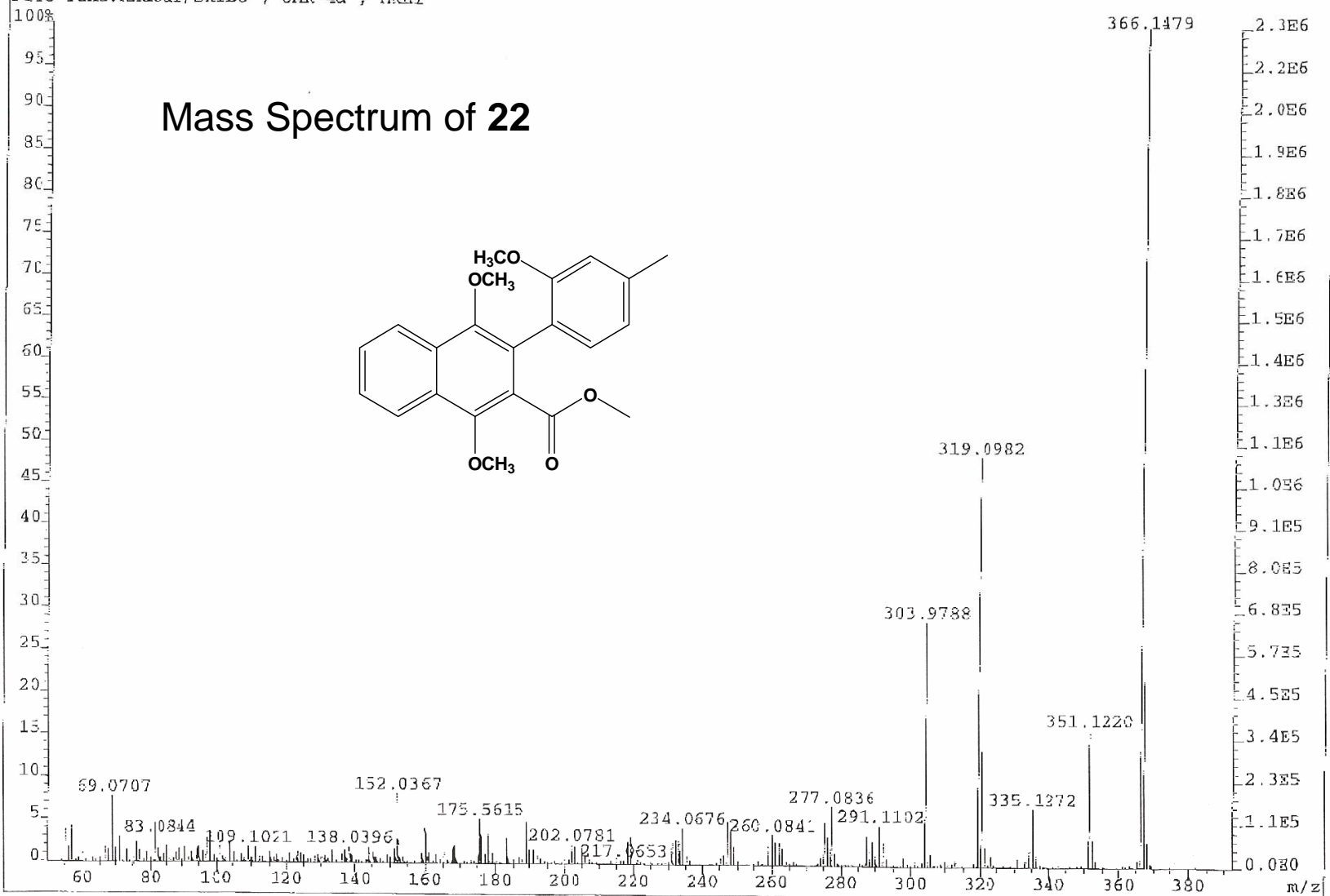
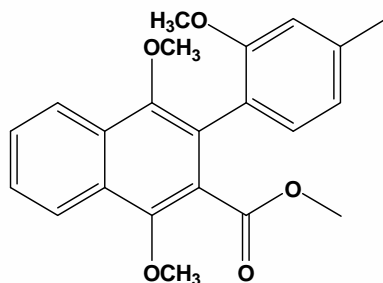


H-NMR of 22

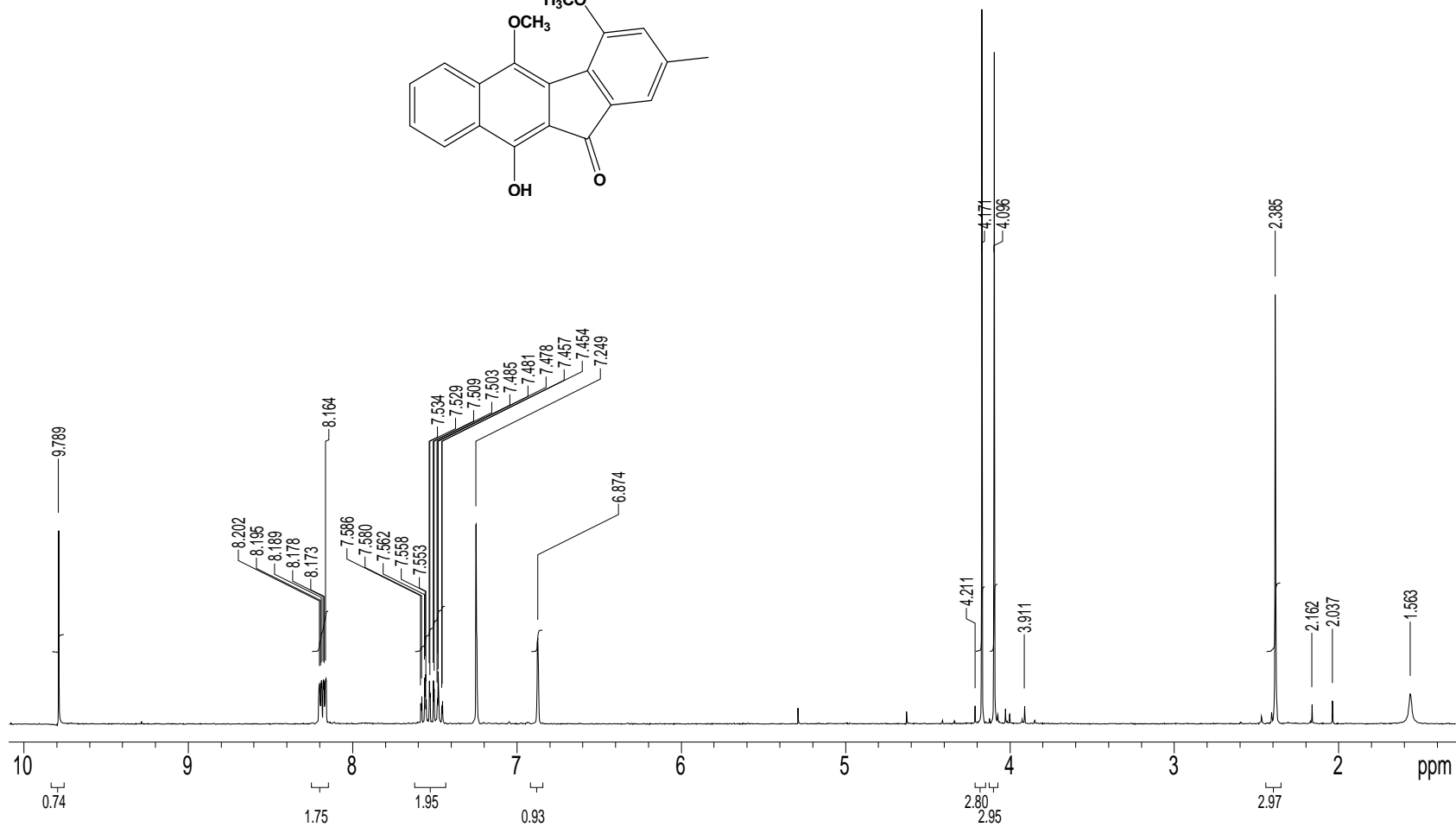
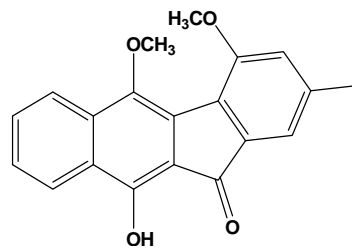


File:54344 Ident:21_31-1_11 Win 1003PM Acq: 9-NOV-2006 17:05:31 +5:37 Cal:54344
AutoSpecETOFPPD EI+ Magnet BpM:366 SpI:2274283 TIC:17260016 Flags:ACC
File Text:Khdour/Skibo ; OMK-4a ; HRRT

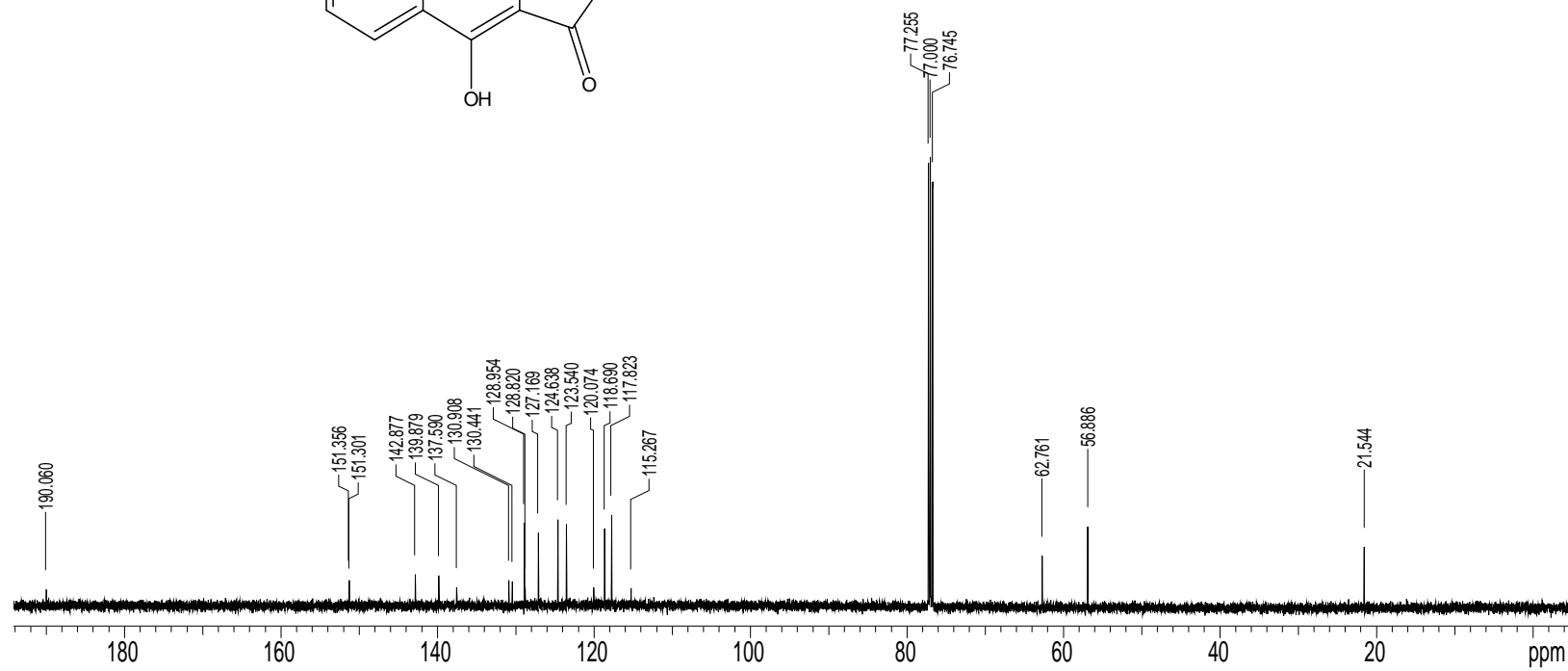
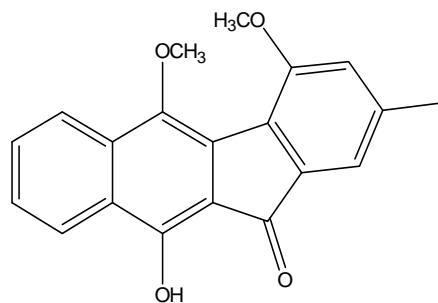
Mass Spectrum of 22



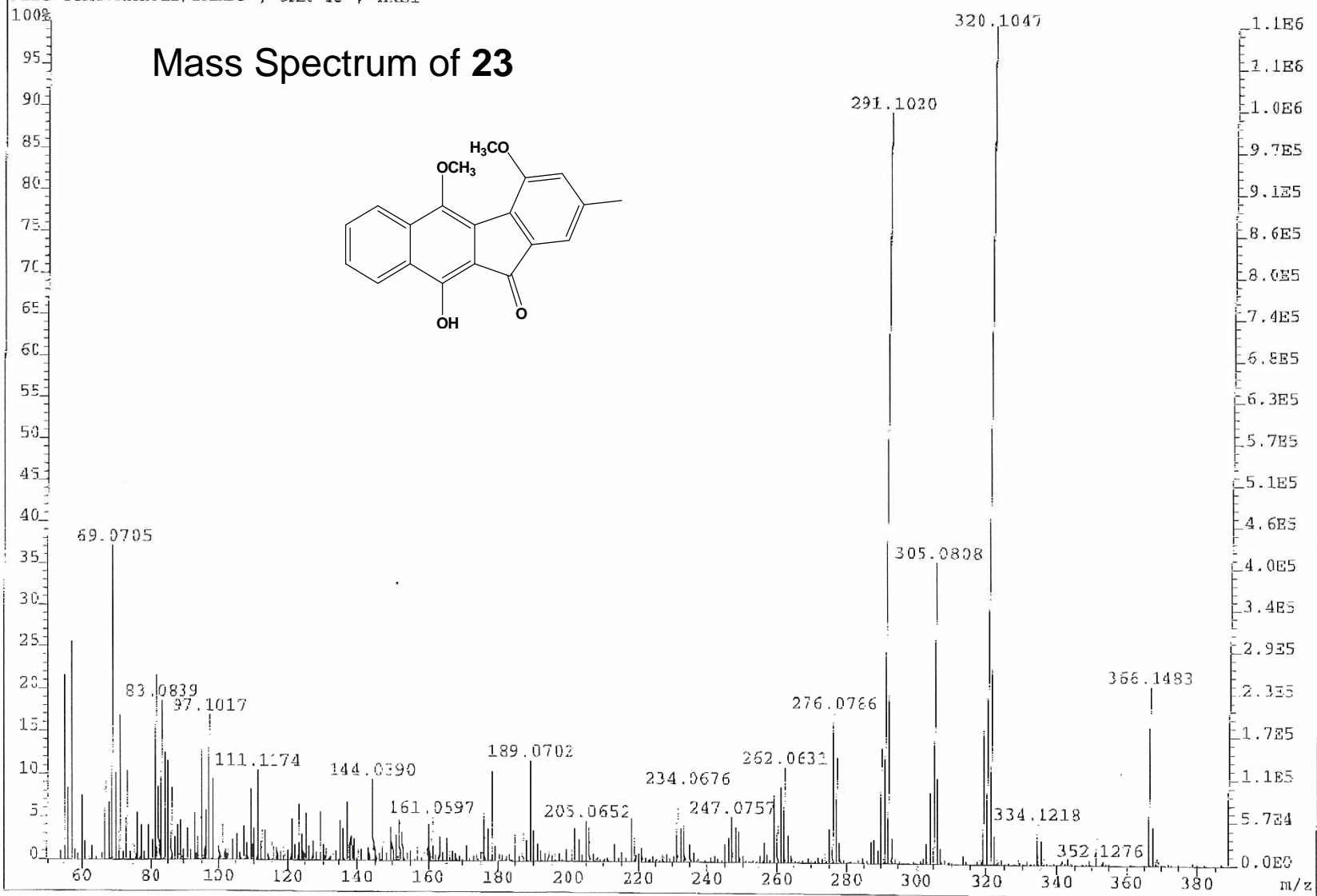
H-NMR of 23



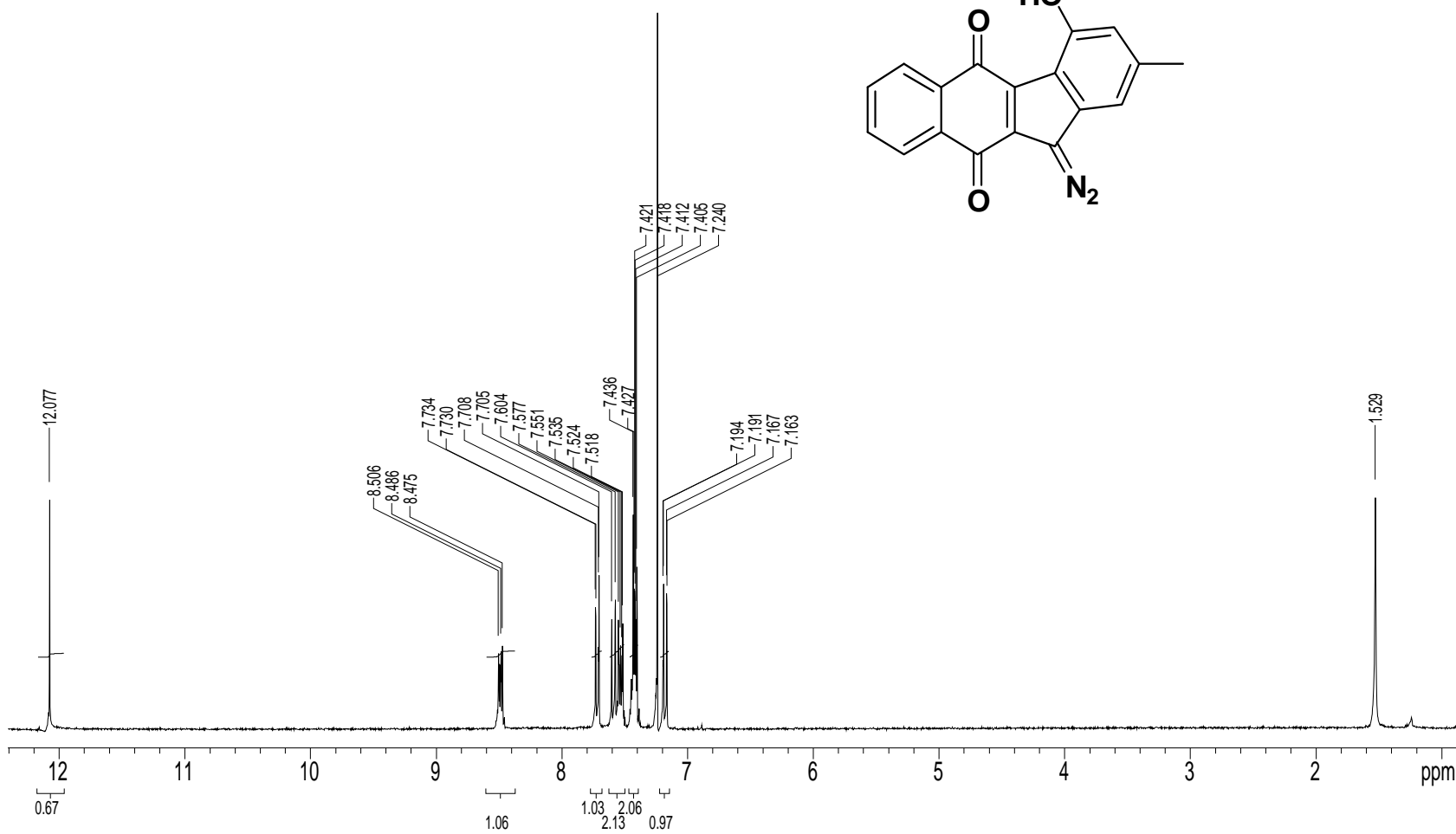
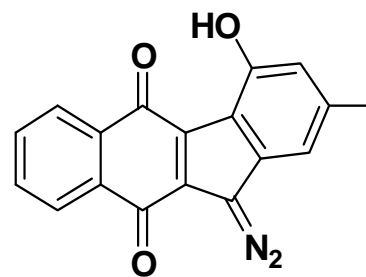
¹³C-NMR of 23



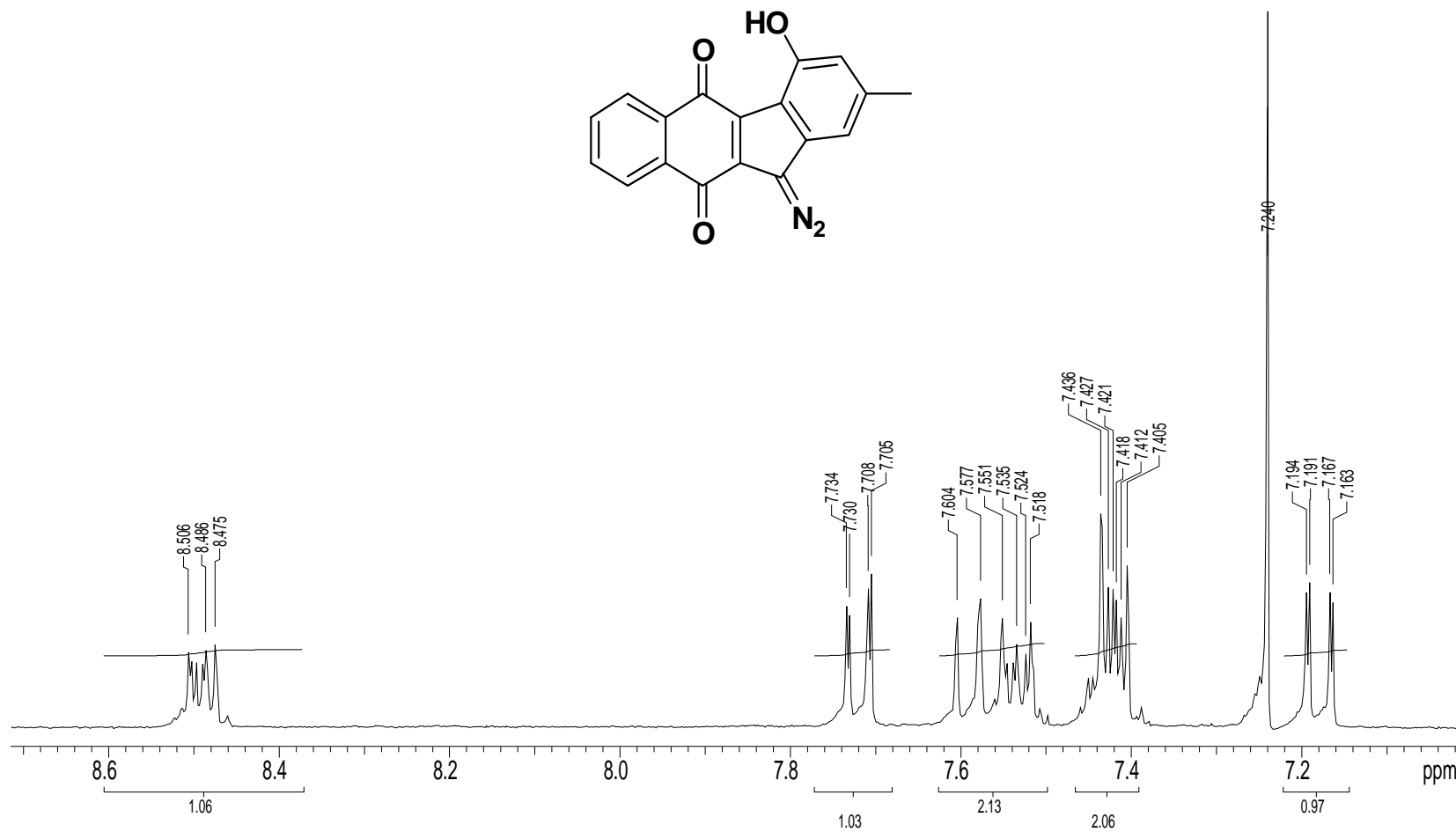
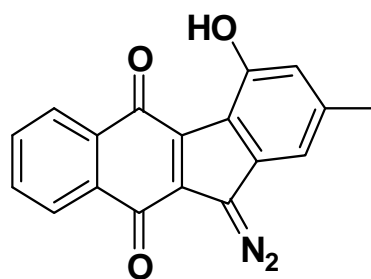
File:54345 Ident:14_24-1_10 Win 100PPM Acq: 9-NOV-2006 17:14:55 +4:10 Cal:54345
AutoSpec3TOFFPD EI+ Magnet BpM:320 SpI:1140096 TIC:18667116 Flags:ACC
File Tex::Khdour/Skibo ; OMK-4c ; HRBI



H-NMR of 4

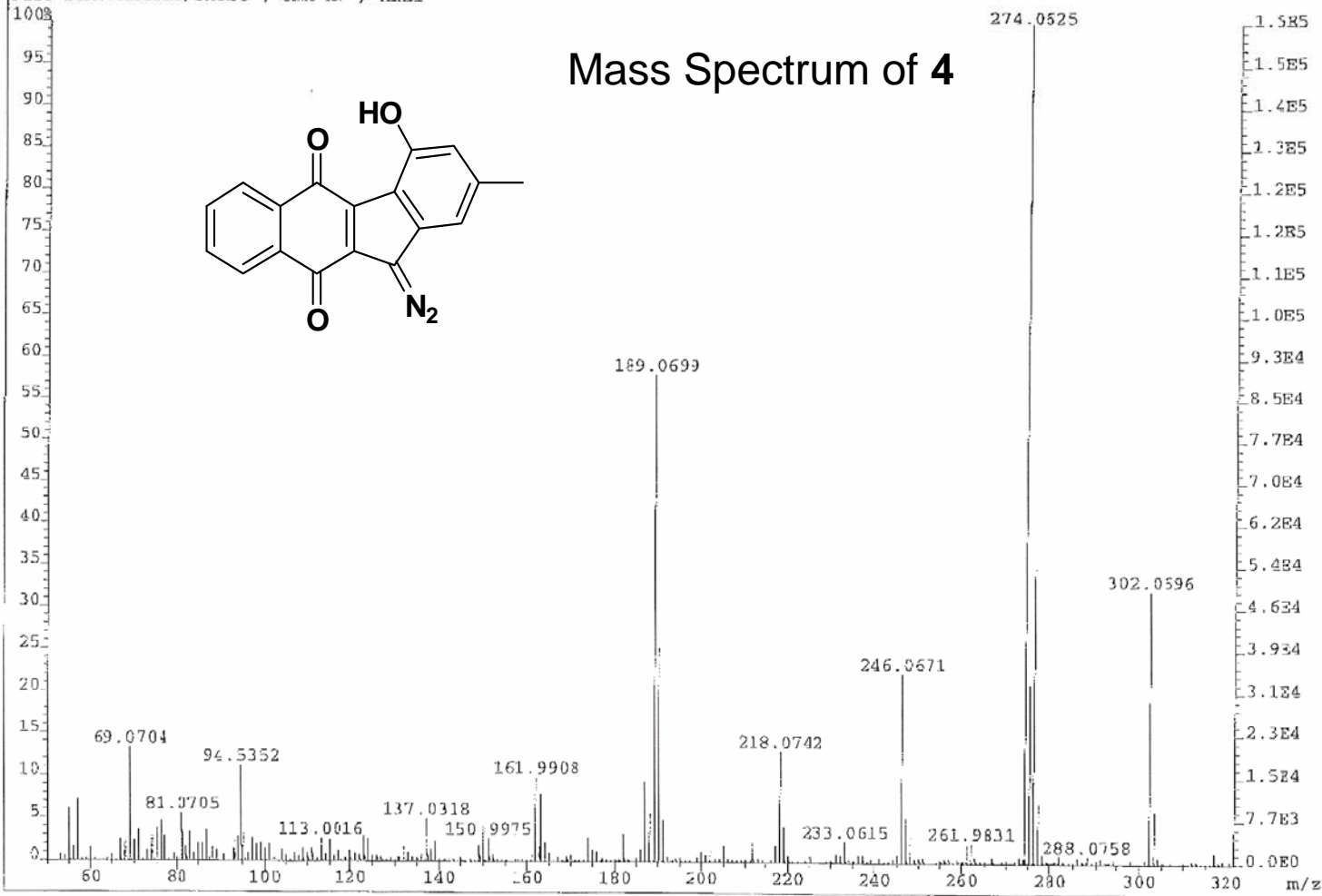
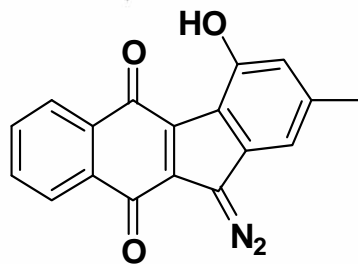


H-NMR of 4

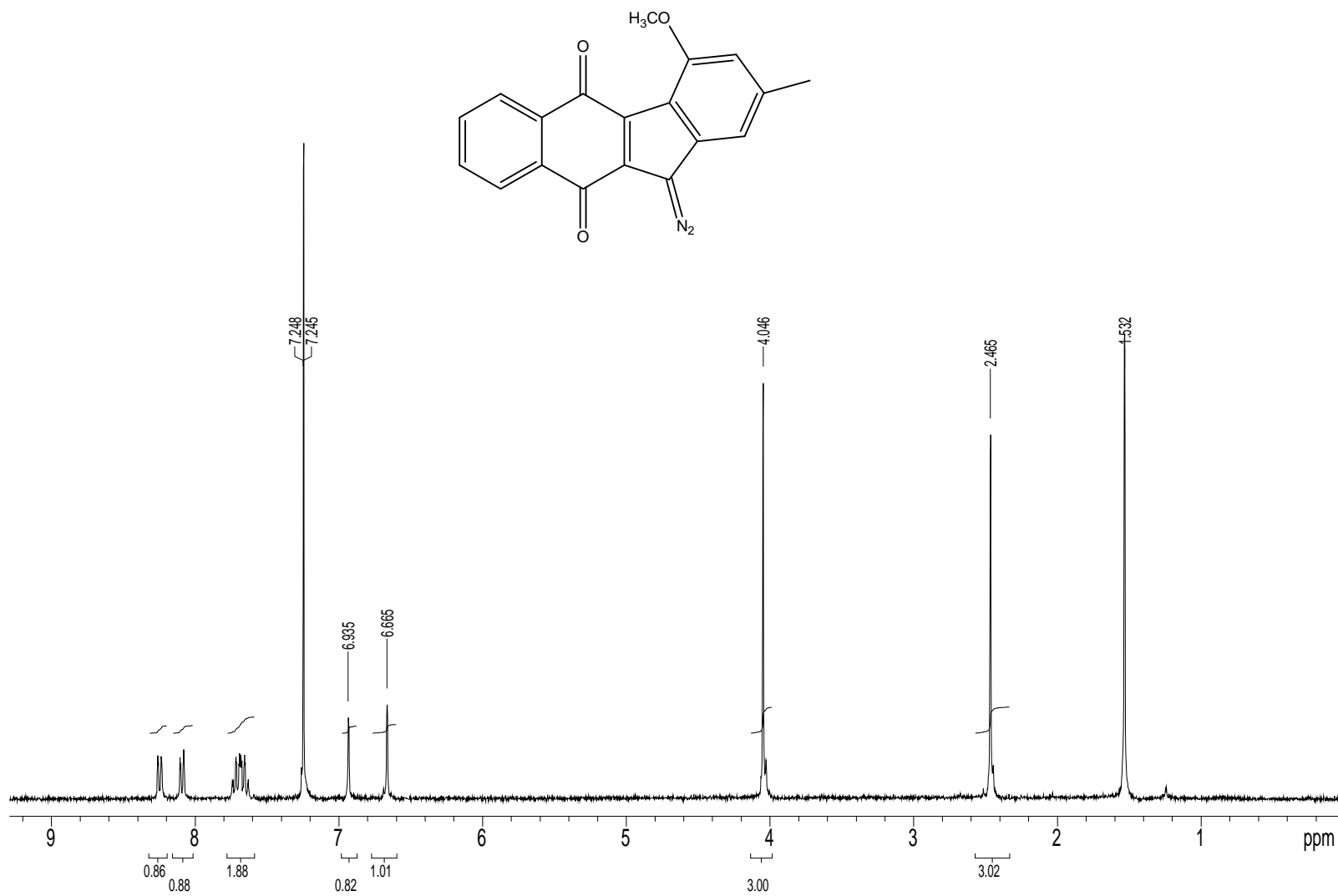


File:53934 Ident:17_27-1_11 Win 100PEM Acq:18-MAY-2006 13:47:15 +4:49 Cal:53934
AutoSpecETOPFFD EI+ Magnet BpM:274 BpI:154963 TIC:1419441 Flags:ACC
File Text:Khfour/Skibo ; omk-k7 ; HREI

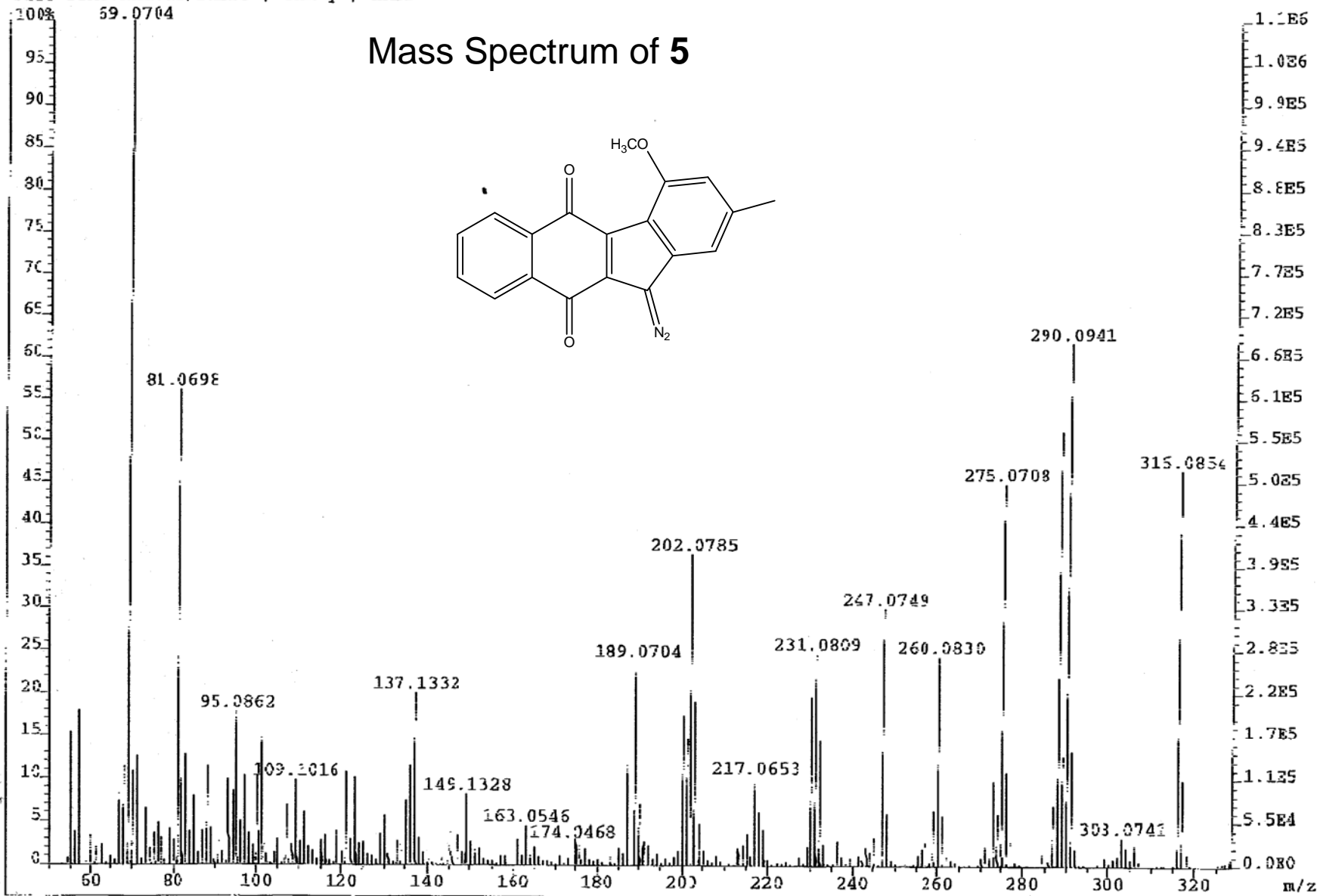
Mass Spectrum of 4



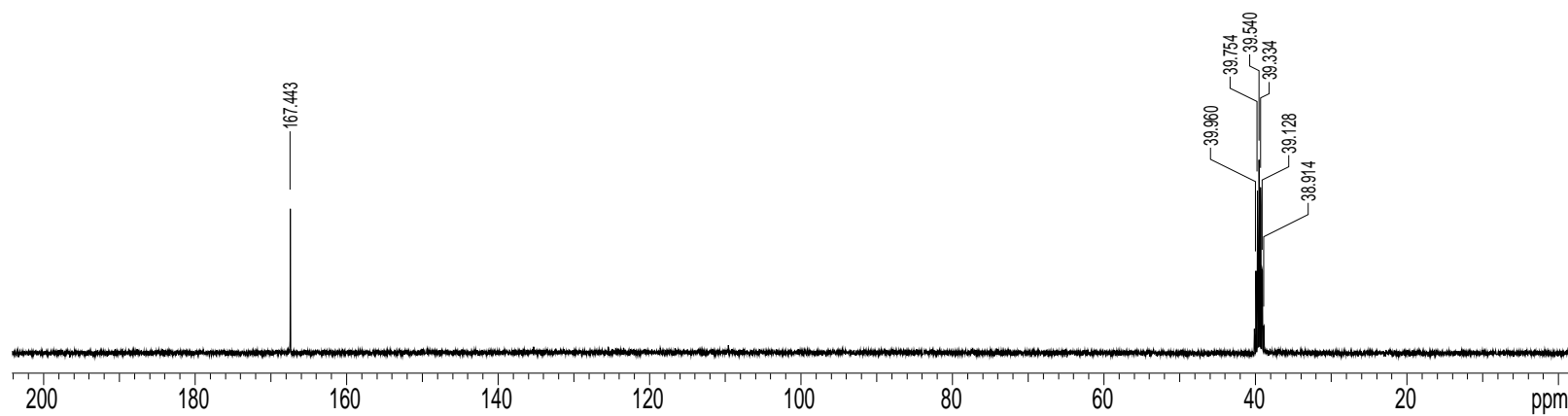
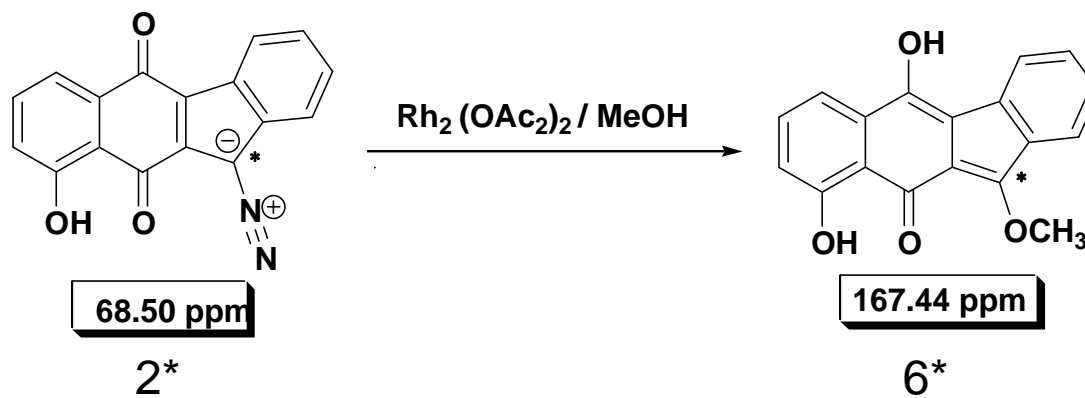
H-NMR of 5



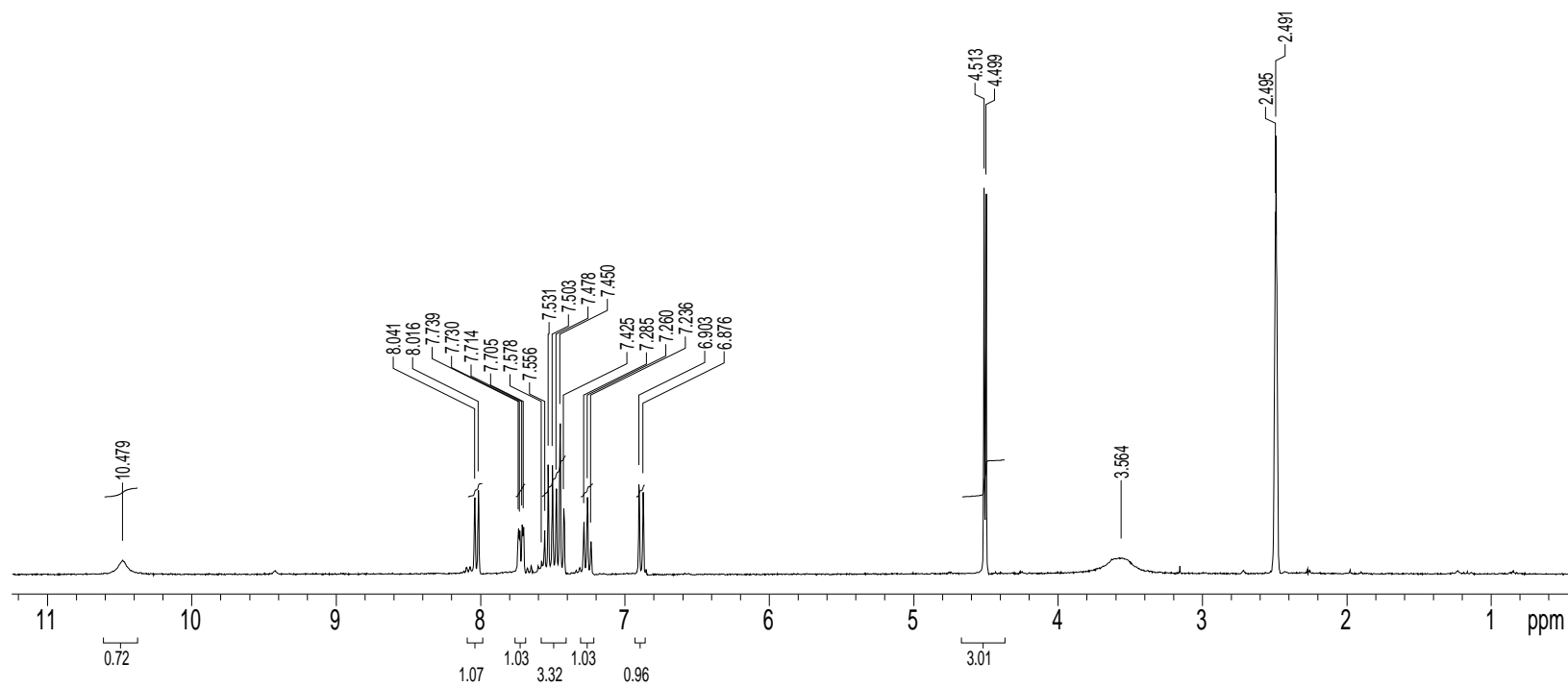
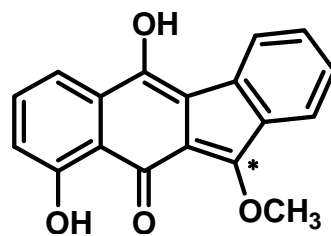
File:54519 Ident:15_25-1_8 Win 100PPM Acq:3C-JAN-2007 15:32:34 +4:21 Cal:54519
AutoSpecTOFFPD EI+ Magnet BpX:69 BpI:1100199 TIC:17542212 Flags:ACC
File Text:Khdour/Skibo ; OMK-y ; HREI



^{13}C -NMR of 6*

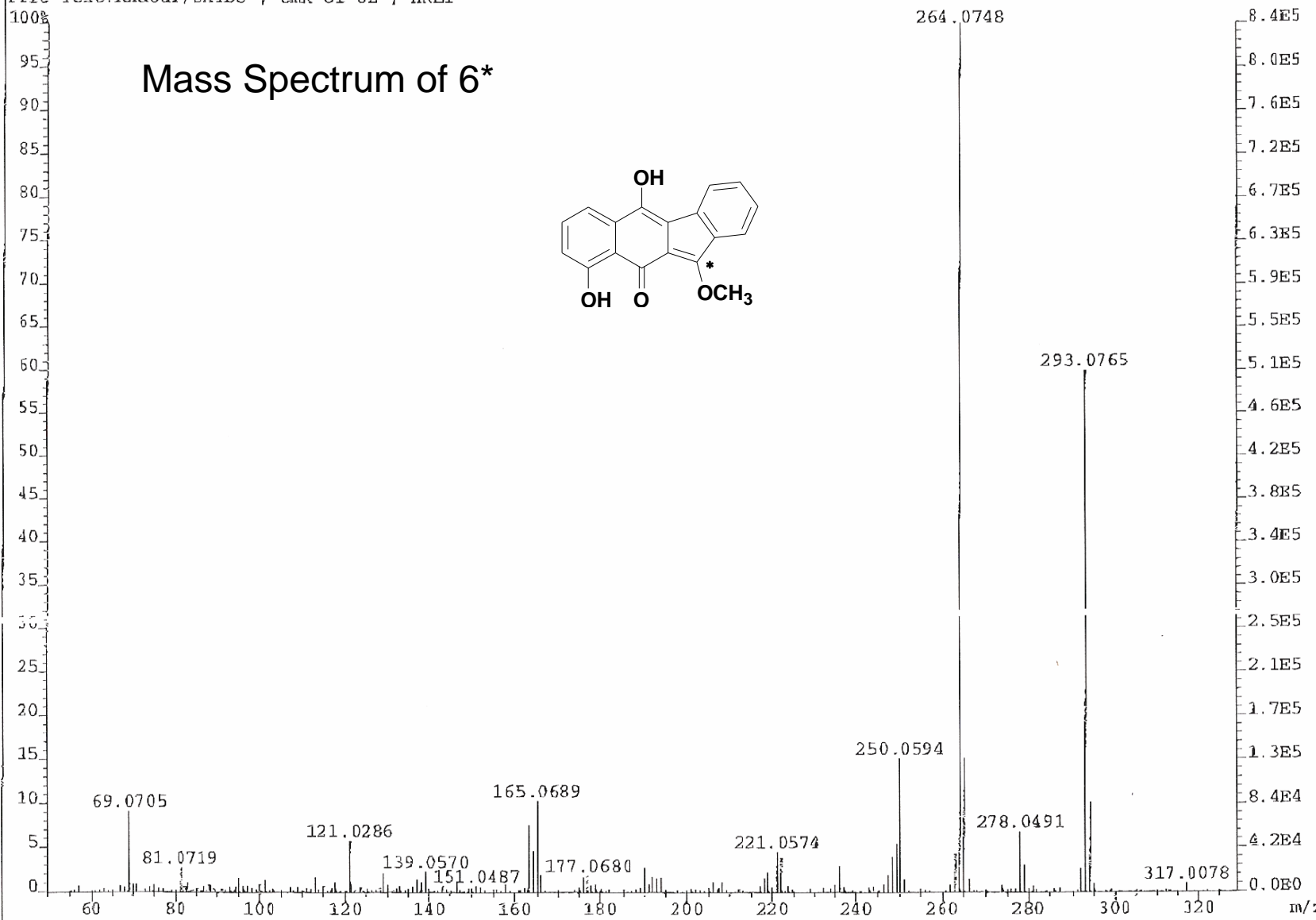
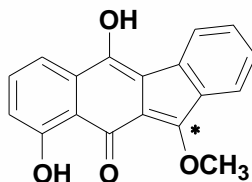


H-NMR of 6*

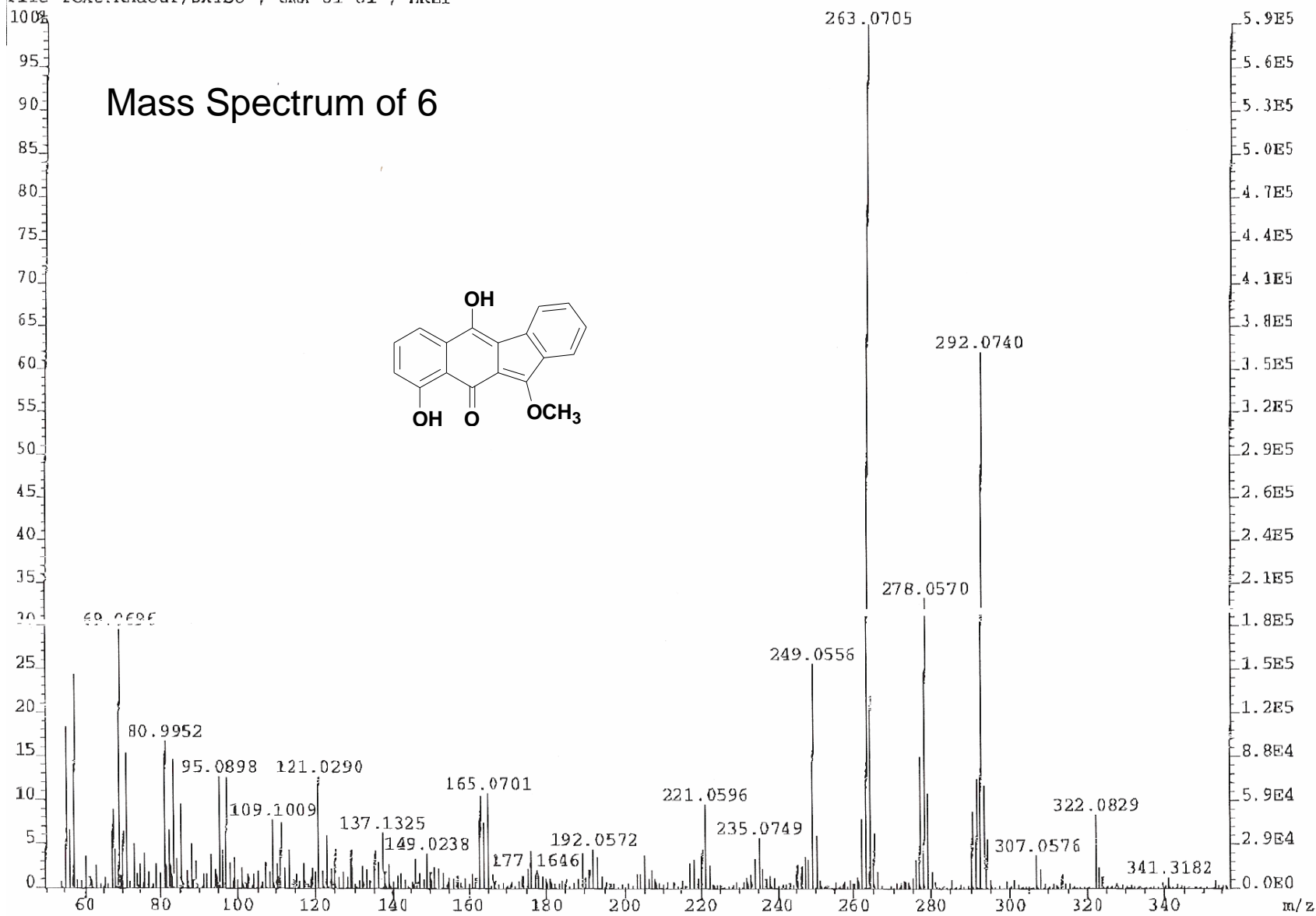


AutoSpecETOFPPD EI+ Magnet BpM:264 BpI:843020 TIC:5477927 Flags:ACC
File Text:Khfour/Skibo ; cmk-81-82 ; HREI

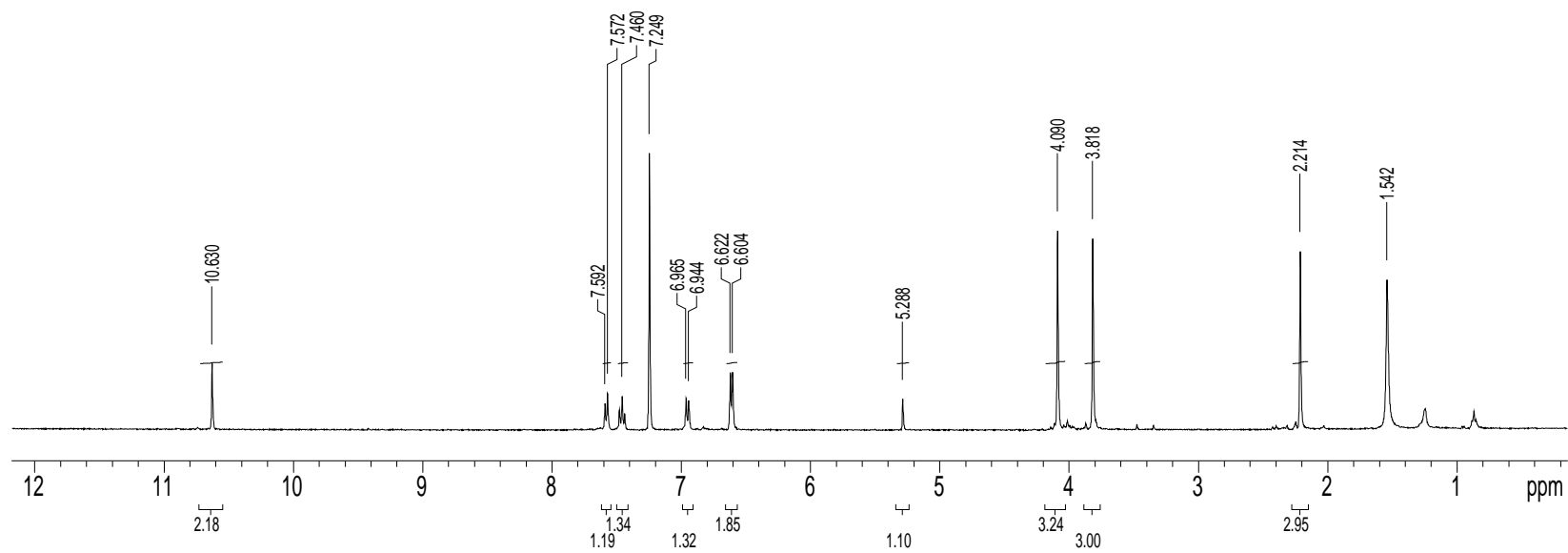
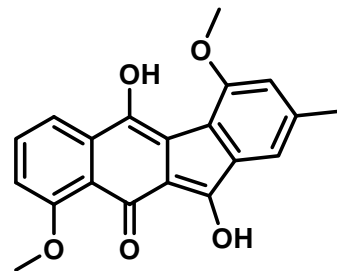
Mass Spectrum of 6*



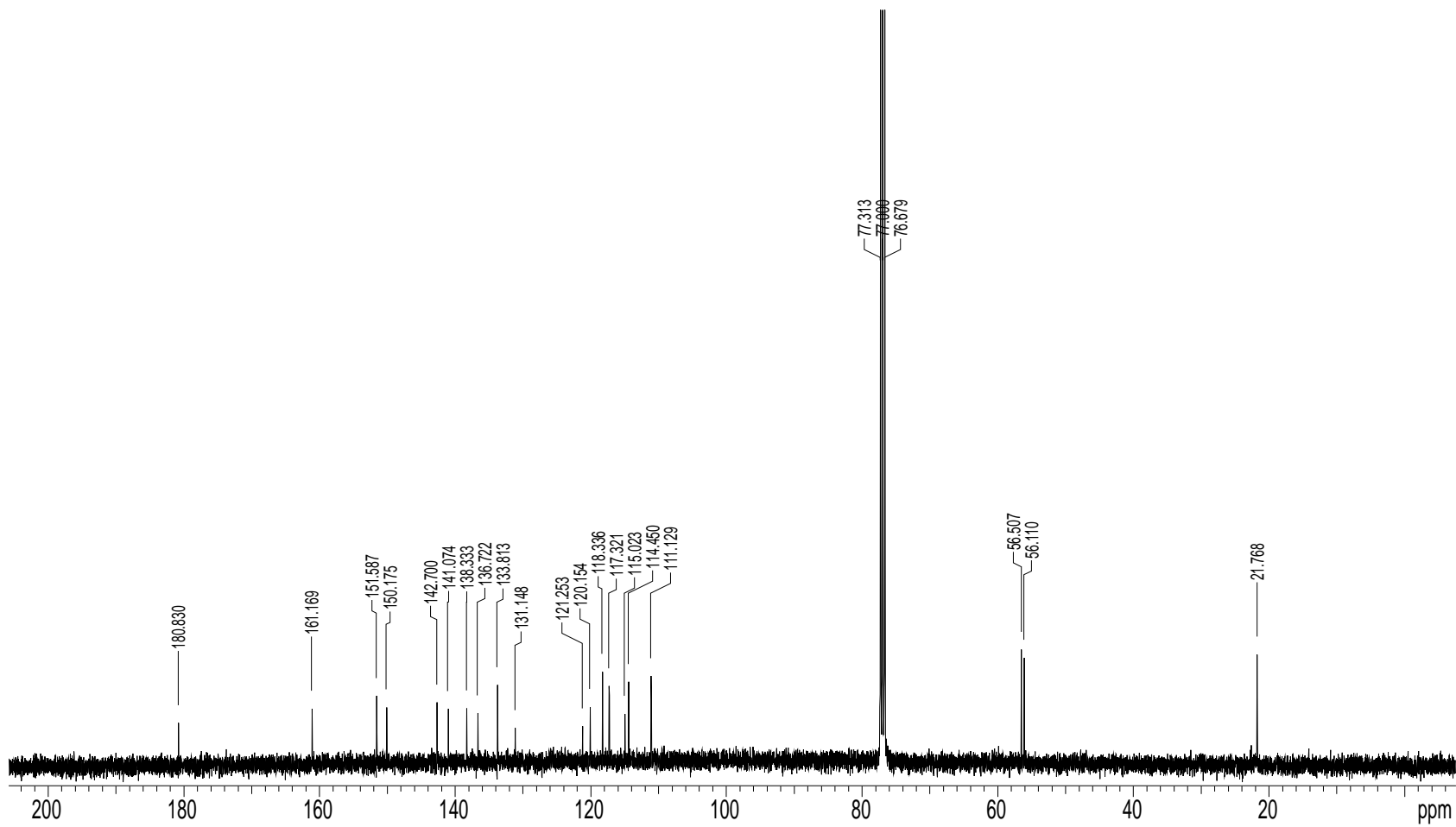
File: 54125B Ident: 21_31-1_8 Win 100PPM Acq: 19-SEP-2006 10:15:40 +5:37 Cal: 54125B
AutoSpecEIOPFPD EI+ Magnet EpM: 263 EpI: 588812 TIC: 8342453 Flags: ACC
File Text: Khmour/Skibo ; amk-81-81 ; HREI



H-NMR of 24

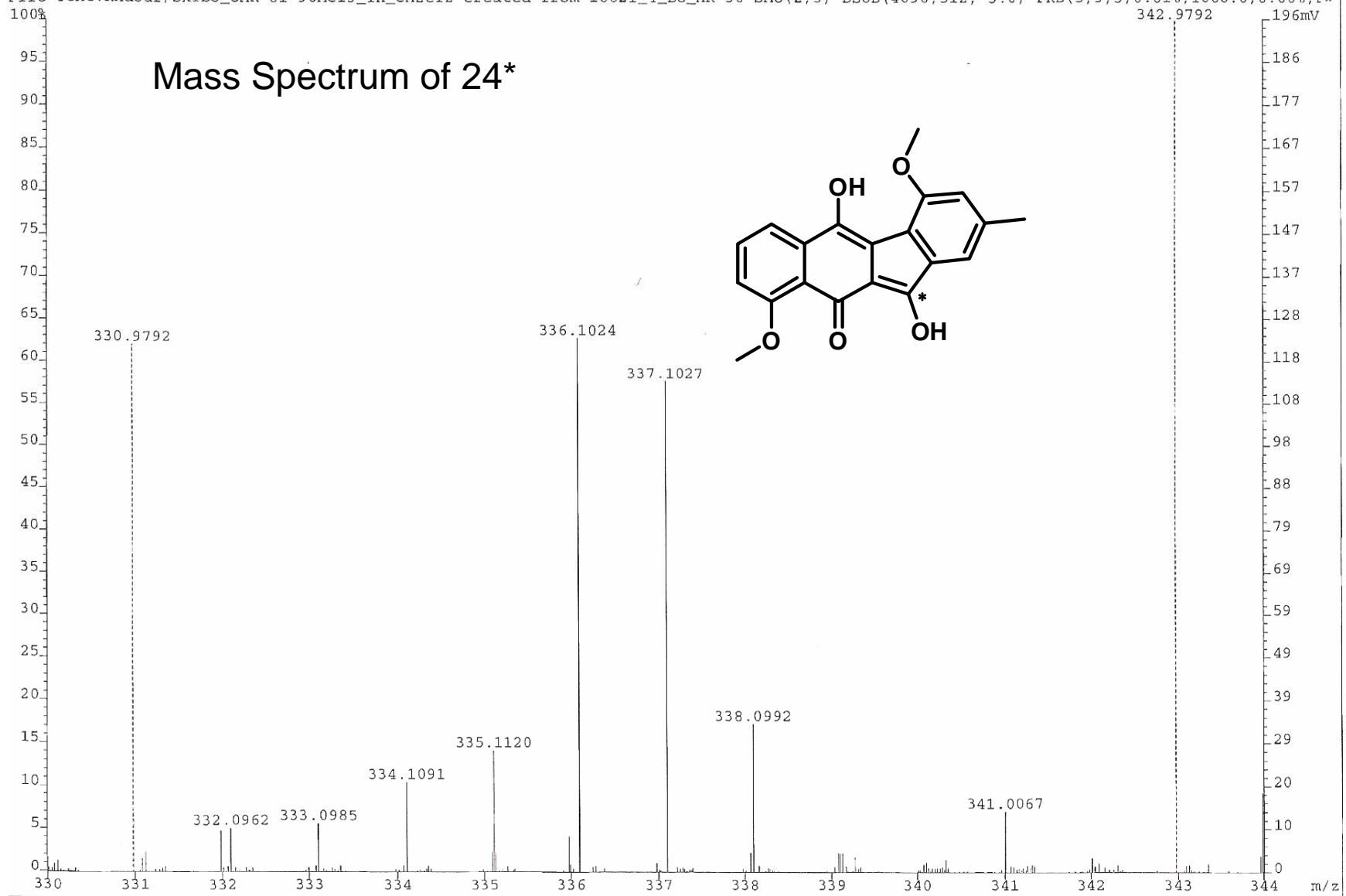


^{13}C -NMR of **24**

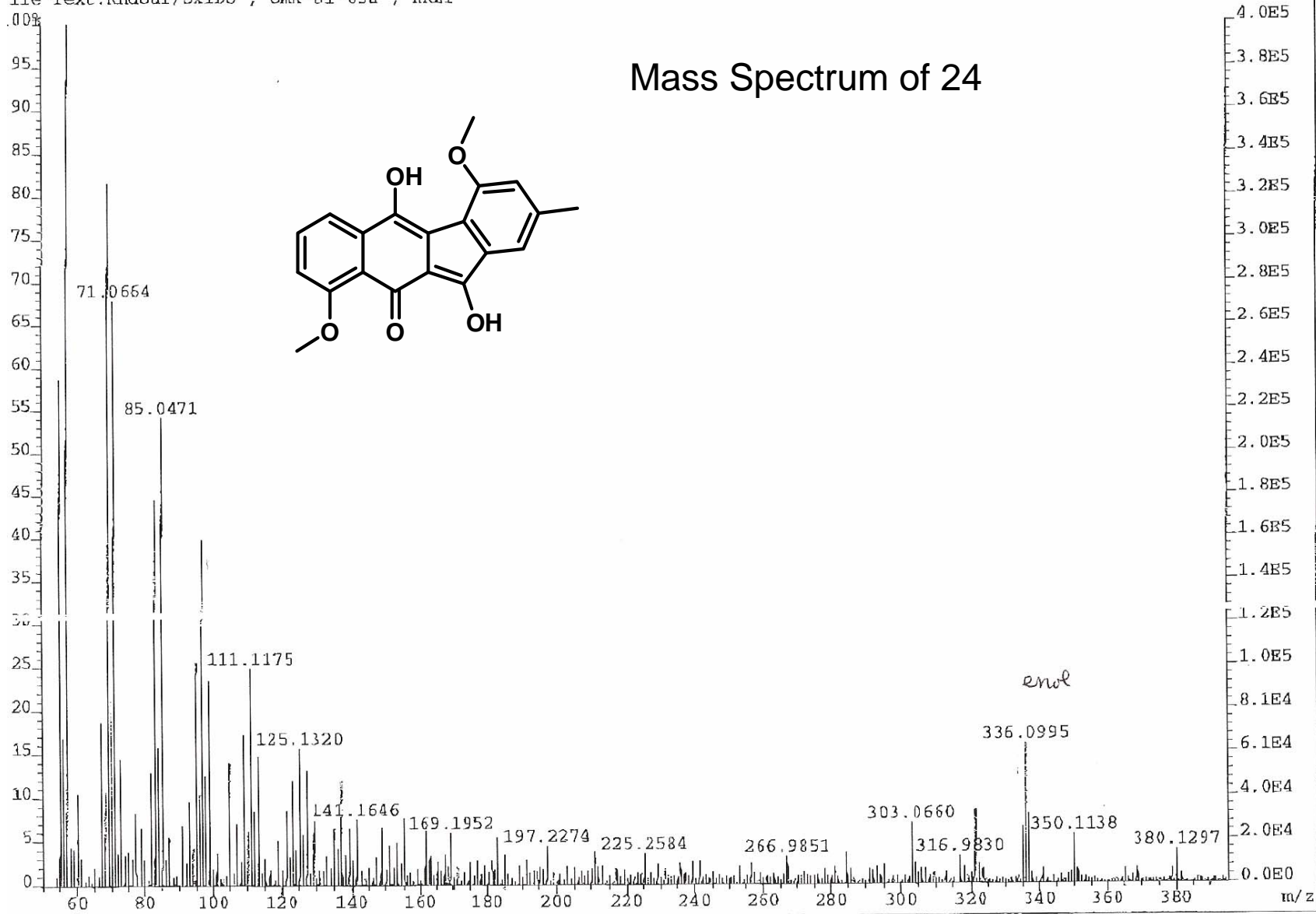


File:18821_4B_BG_HRS Ident:1_5 Win 100PPM Acq:20-OCT-2006 11:37:24 +6:02 Cal:18821_4B_BG_HRS
ZAB-SET EI+ Voltage BpM:343 BpI:6348800 TIC:33933152 Flags:ACC
File Text:Khdour/Skibo_OMK-81-90AC13_in_CH2Cl2 Created from 18821_4_BG_HR 36 SMO(2,5) BSUB(4096,512,-3.0) PKD(5,3,5,0.01%,1068.0,0.00%,F>>

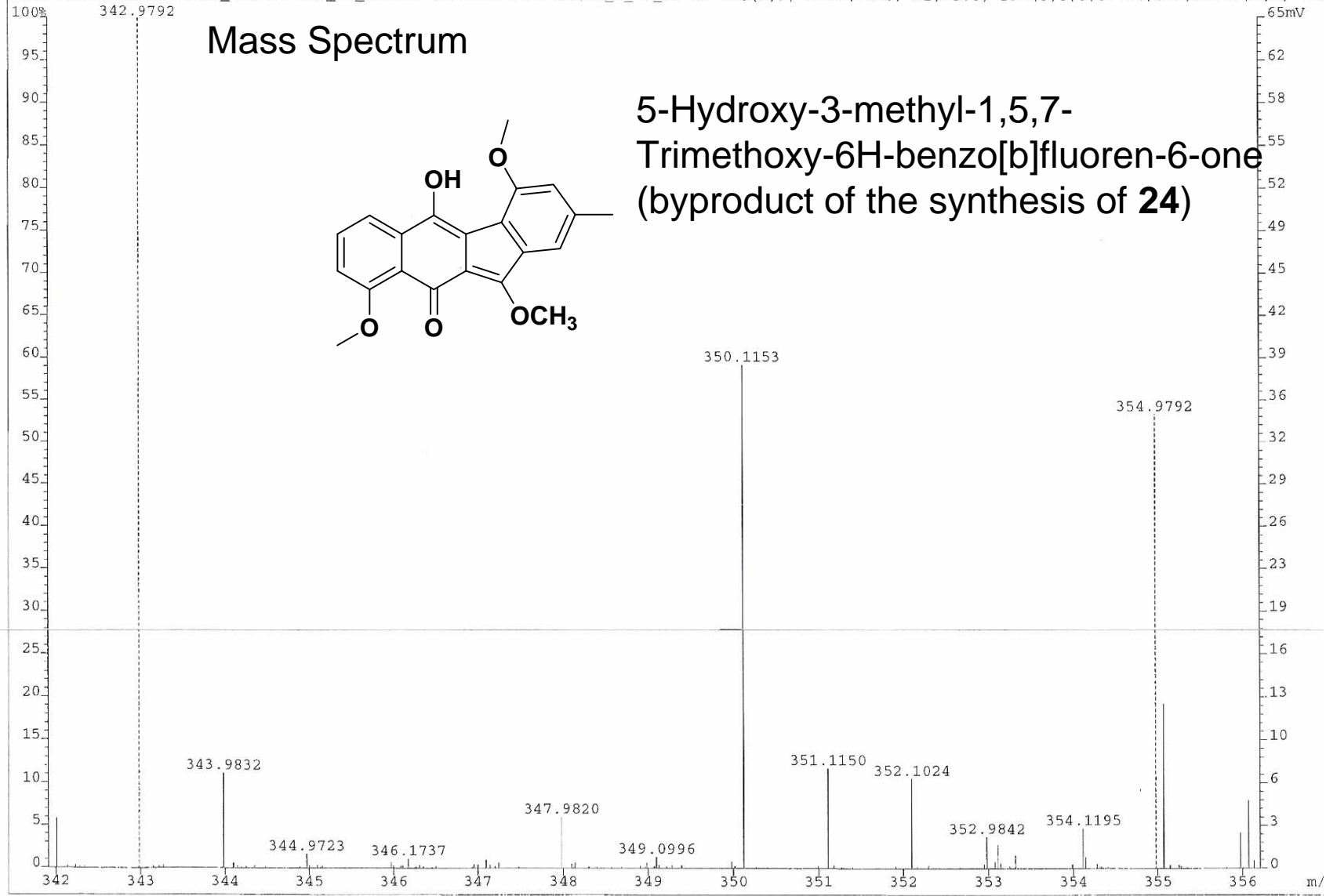
Mass Spectrum of 24*



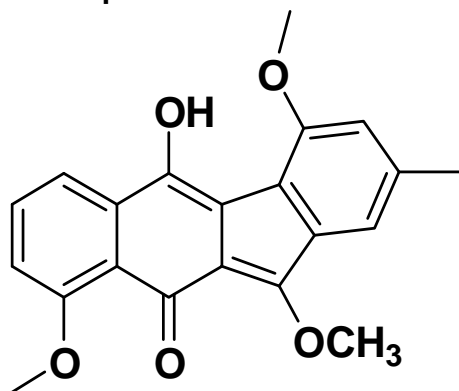
file:54130A Ident:20_30-1_13 Win 100PPM Acq:19-SEP-2006 14:36:37 +5:23 Cal:54130A
AutoSpecETOFPPD EI+ Magnet BpM:57 EpI:404468 TIC:8293047 Flags:ACC
file Text:Khdour/Skibo ; omk-81-83a ; HRRI



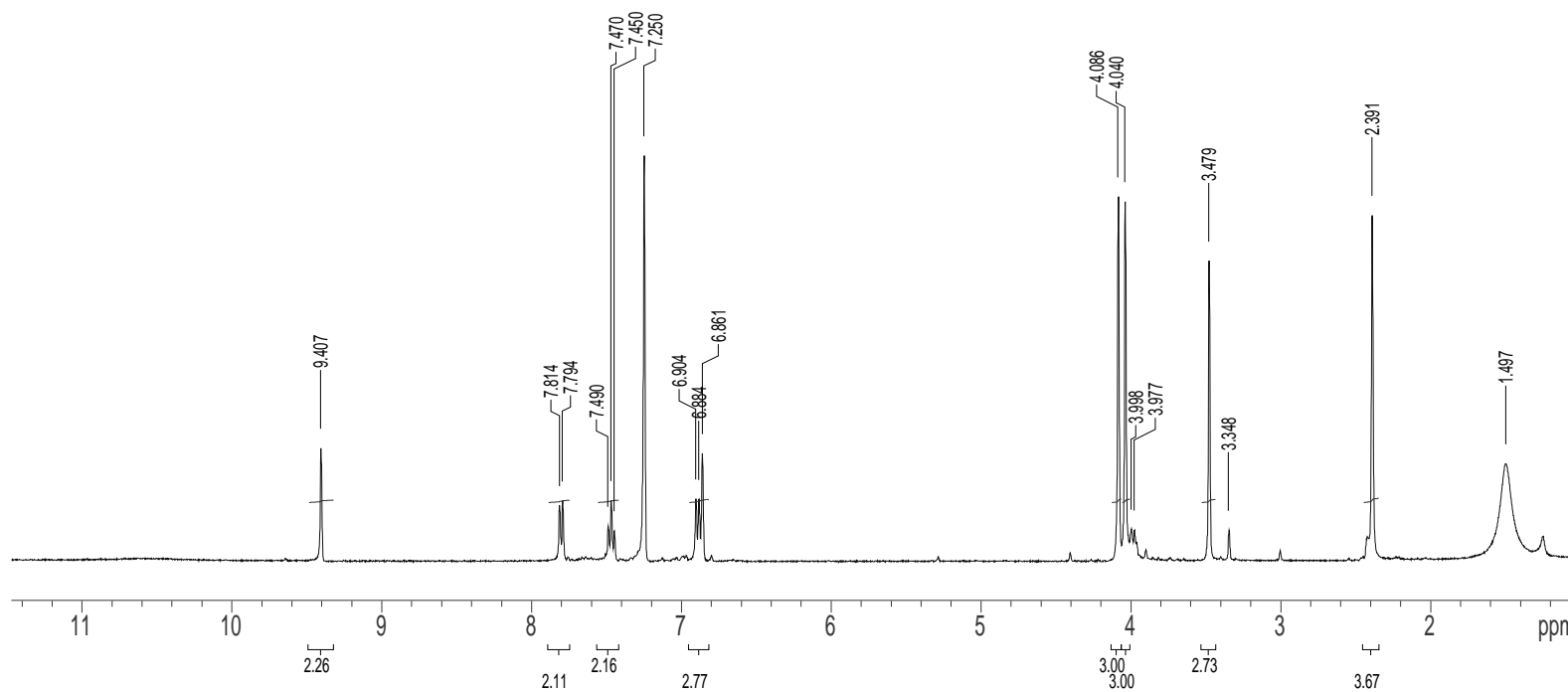
File:18819_1B_BG_HRS Ident:1_6 Win 100PPM Acq:19-OCT-2006 12:18:21 +4:47 Cal:18819_1B_BG_HRS
ZAB-SET EI+ Voltage BpM:336 BpI:16485035 TIC:30486864 Flags:ACC
File Text:Khdour/Skibo_OMK-81-90C_in_CH2Cl2 Created from 18819_1_BG_HR 24 SMO(2,9) BSUB(4096,512,-3.0) PKD(5,3,5,0.01%,4.0,0.00%,F,F) SP:



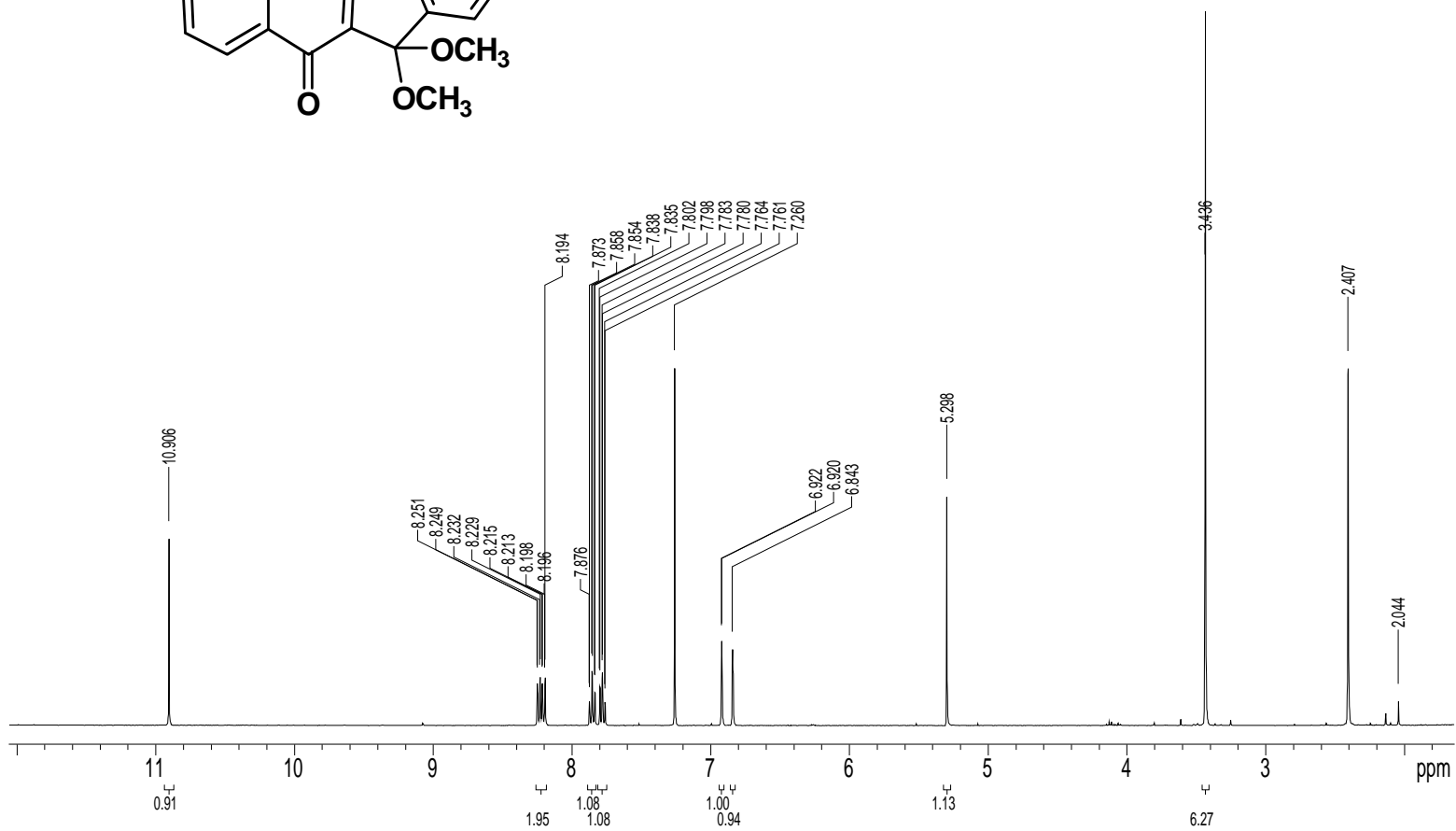
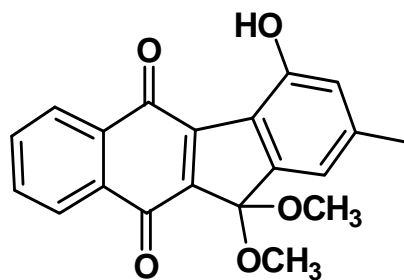
H-NMR Spectrum



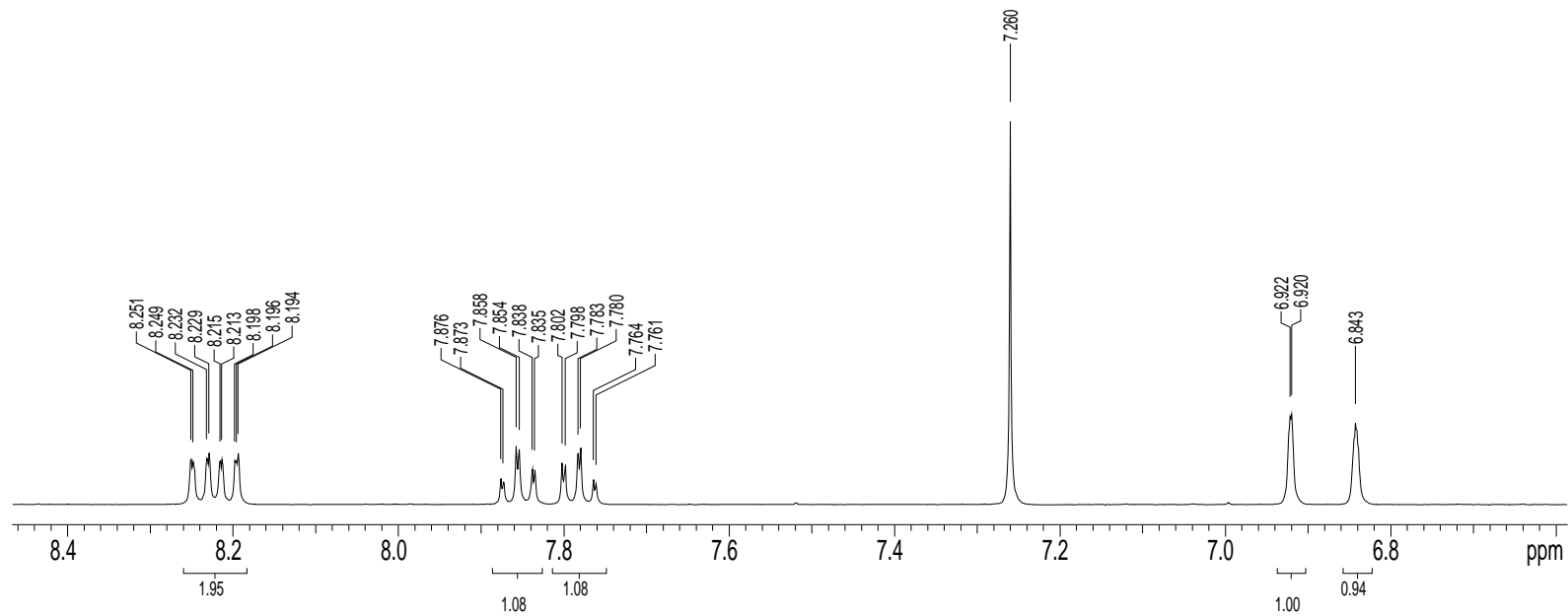
5-Hydroxy-3-methyl-1,5,7-Trimethoxy-6H-benzo[b]fluoren-6-one
(byproduct of the synthesis of **24**)



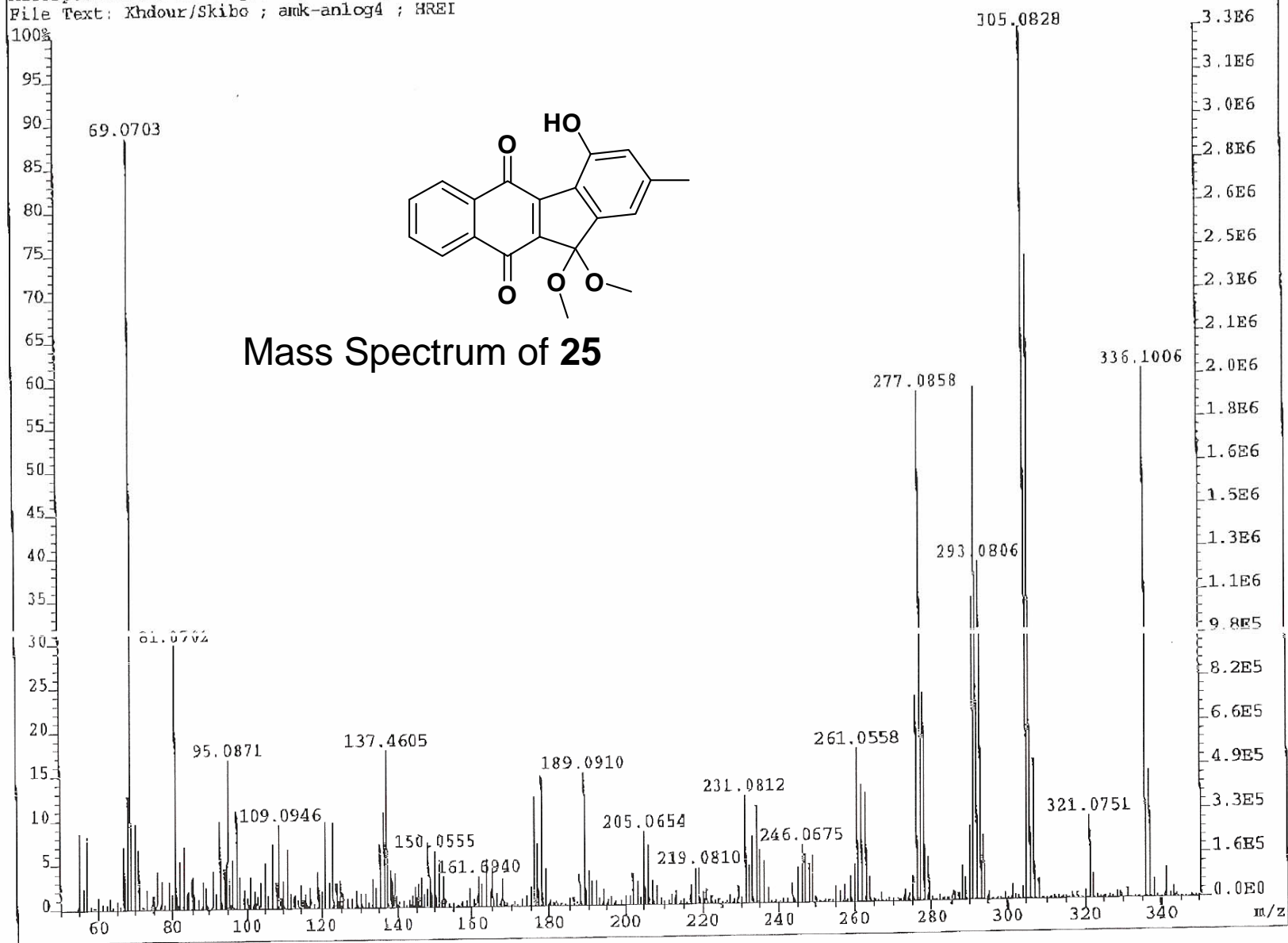
H-NMR of 25



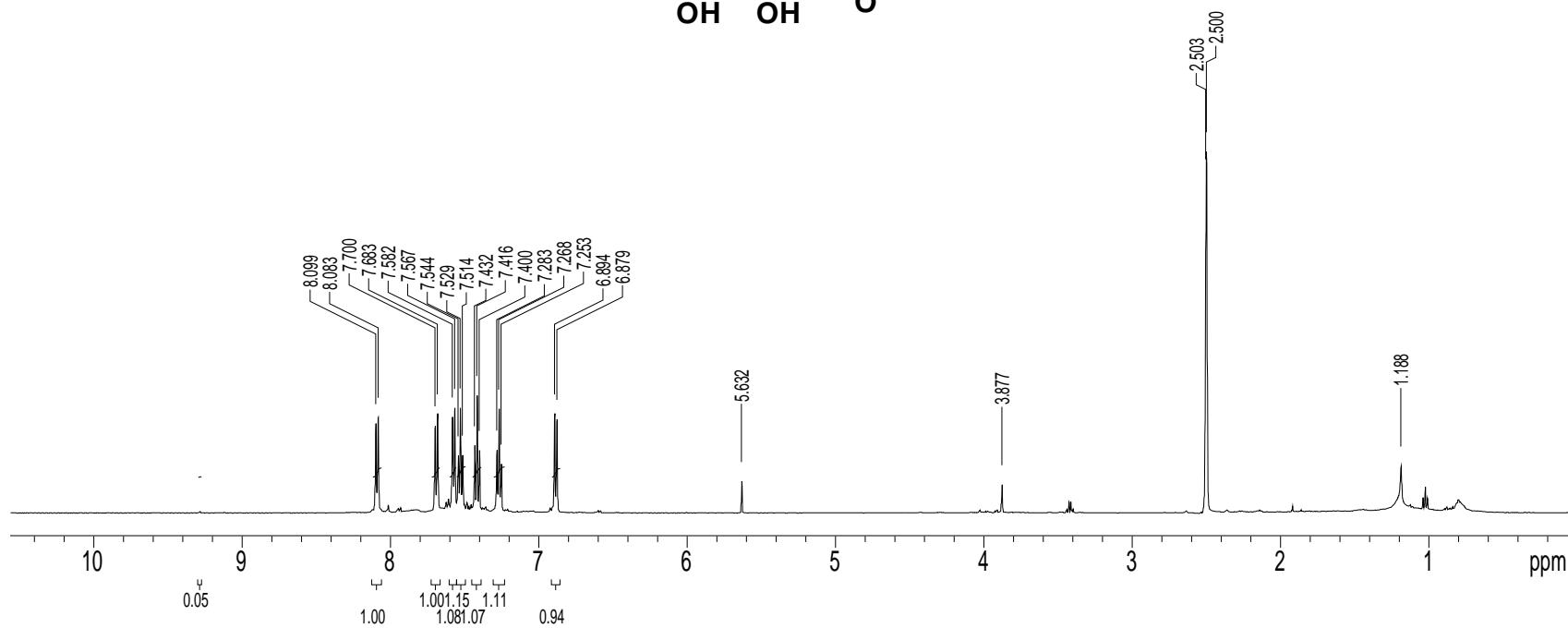
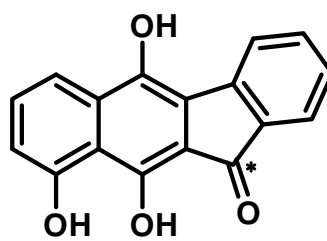
H-NMR of 25



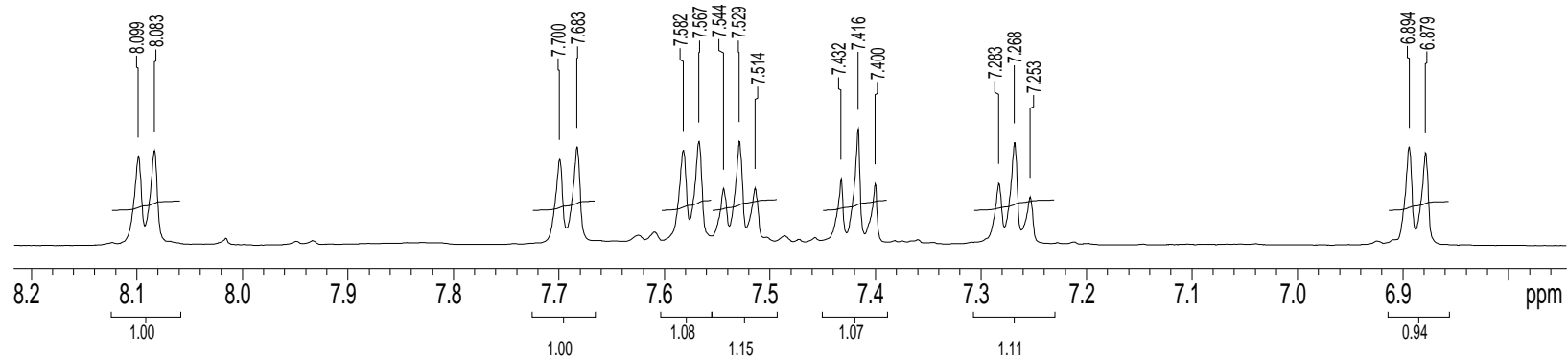
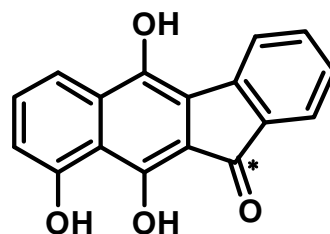
File: 54248 Ident: 41_51-1_9 Win 100PPM Acq: 16-OCT-2006 13:33:58 49:44 Cal: 54248
AutoSpecETOFPPD EI+ Magnet BpM: 305 BpI: 3280788 TIC: 67064164 Flags: ACC
File Text: Khmour/Skibo ; amk-anlog4 ; HREI



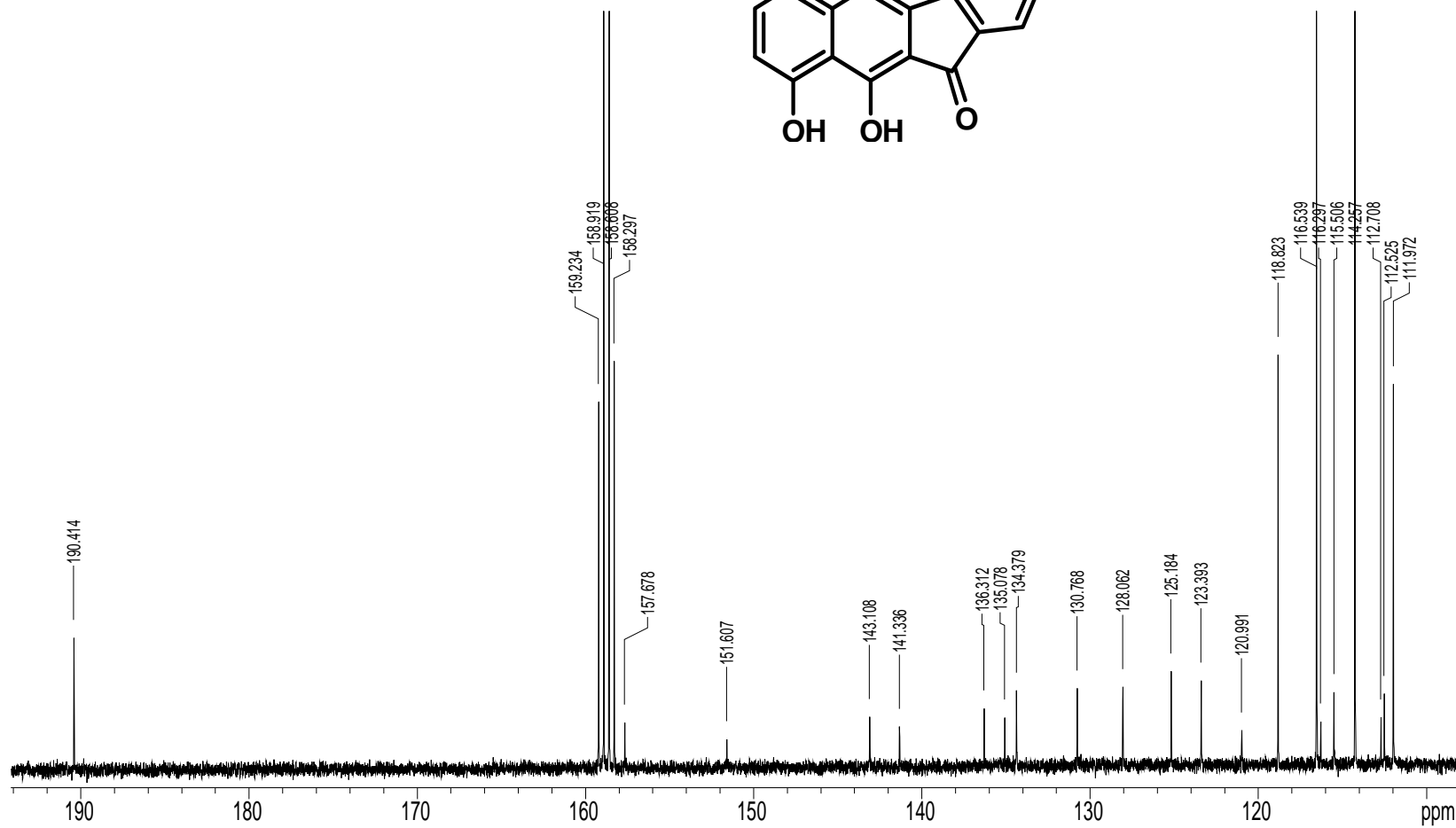
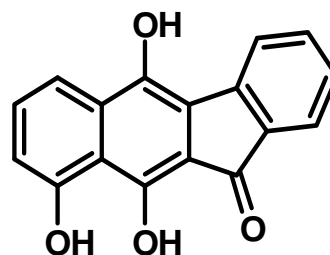
H-NMR of 28*



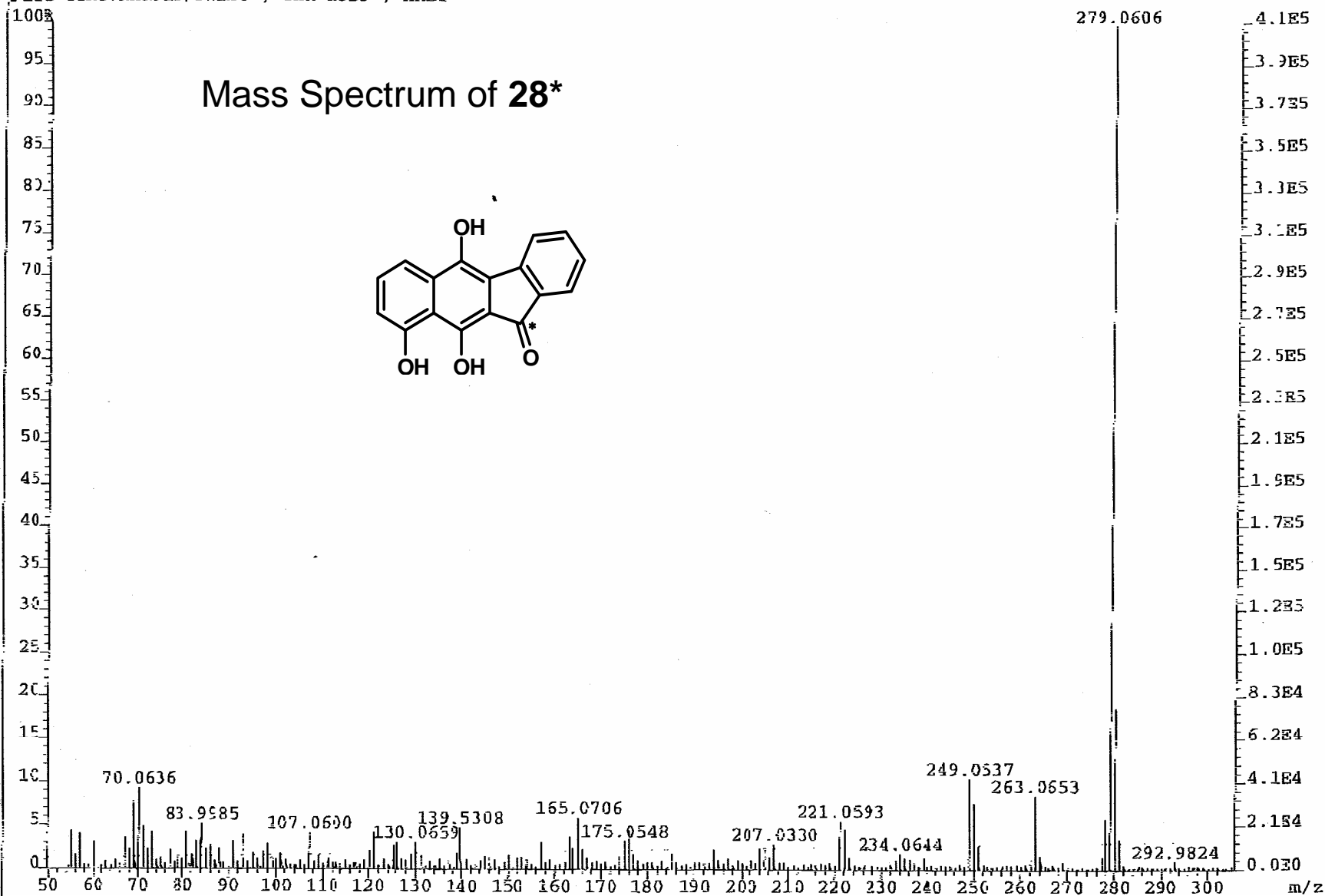
H-NMR of 28*



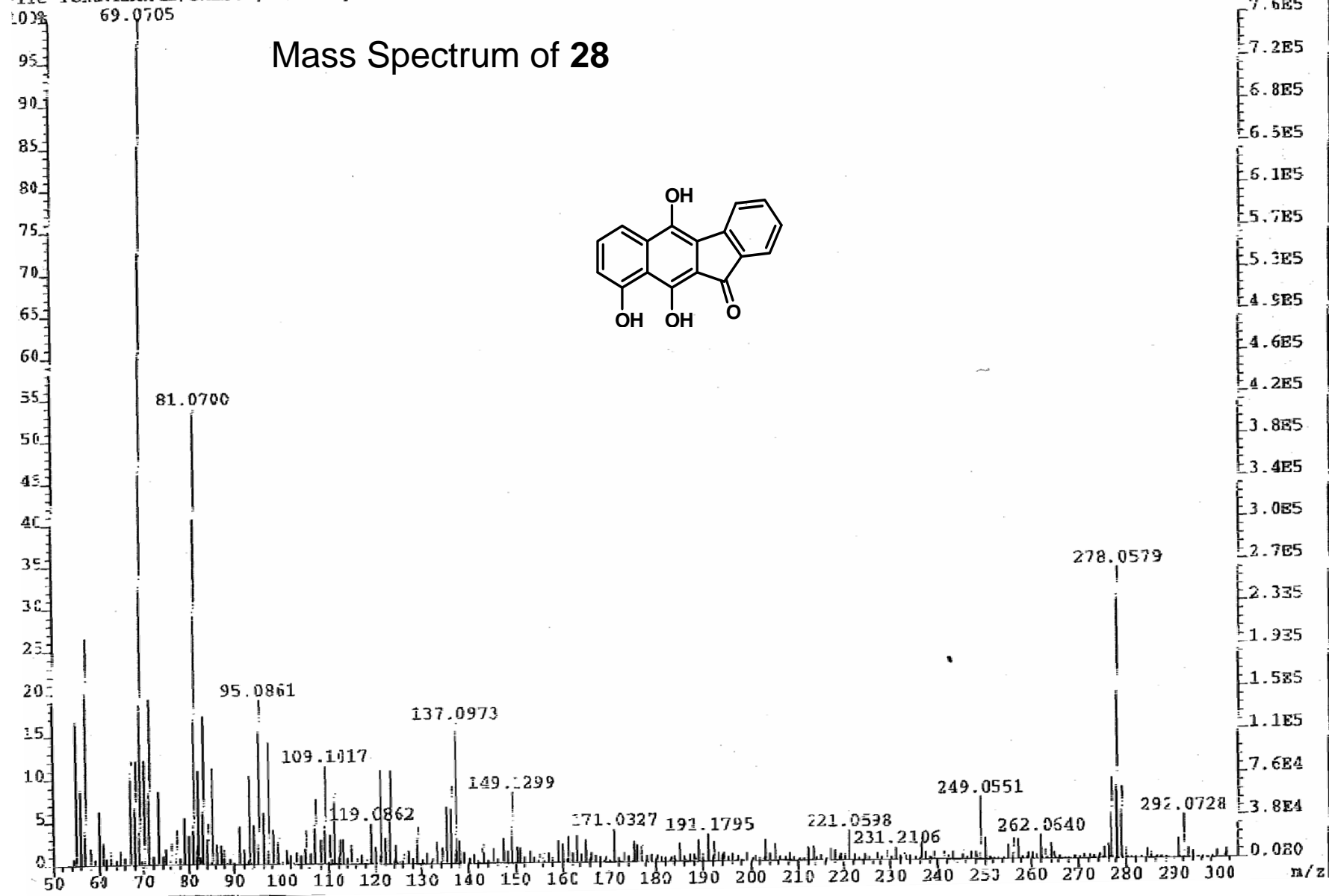
¹³C-NMR of 28



File:54516A Ident:64_74-1_9 Win 10CPM Acq:30-JAN-2007 14:36:11 +14:30 Cal:54516A
AutoSpecRTOFFPD EI+ Magnet BpM:279 BpI:414325 TIC:4483296 Flags:ACC
File Text:Khdour/Skibo ; OMK-EC13 ; HREI

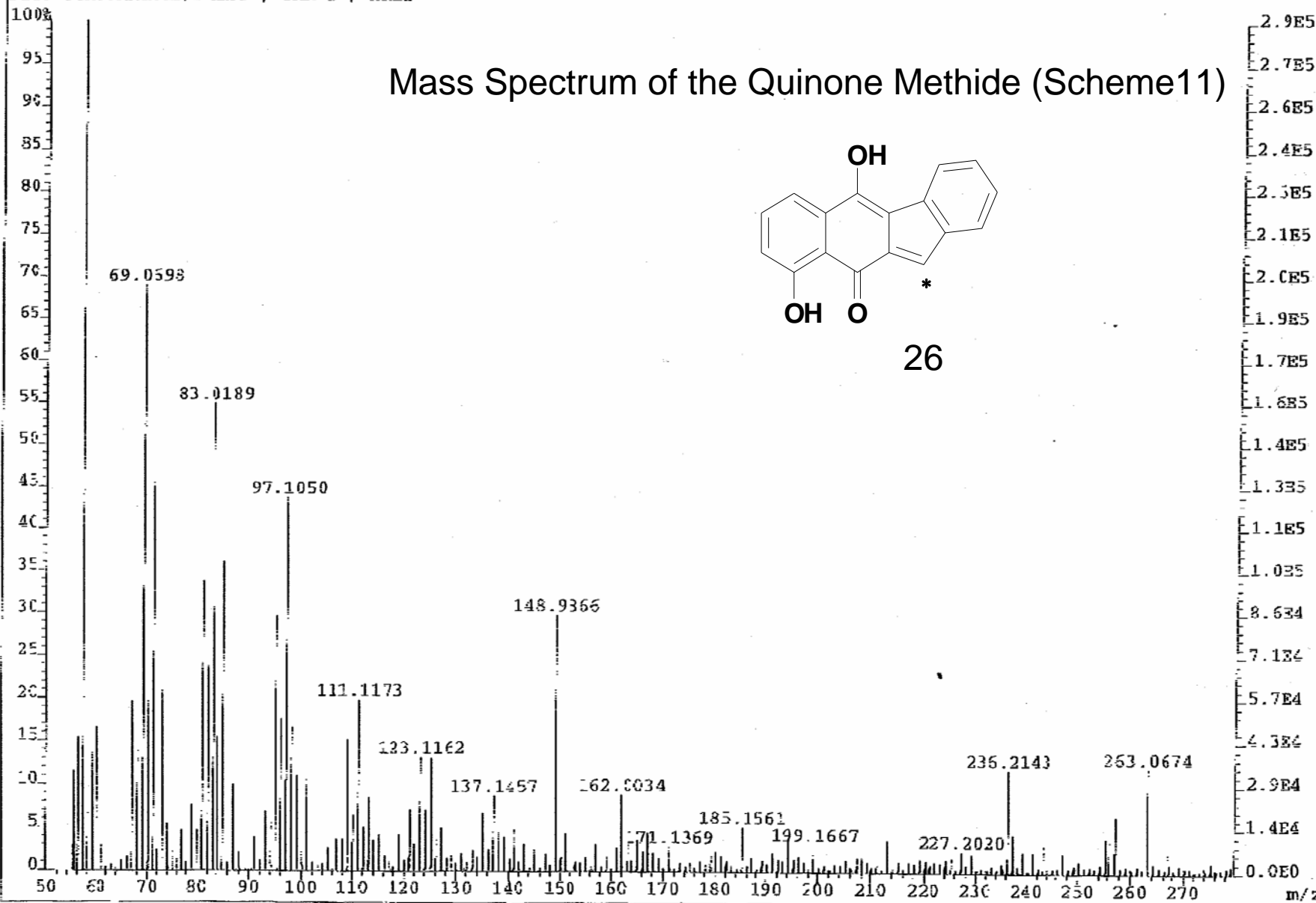
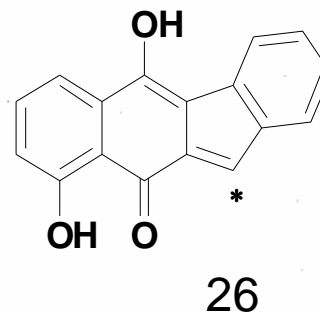


AutoSpecETOFFPD EI+ Magnet SpM:69 RpI:760092 TIC:8521565 Flags:ACC
File Text:Khdour/Skibo ; OMK-R ; HRBI

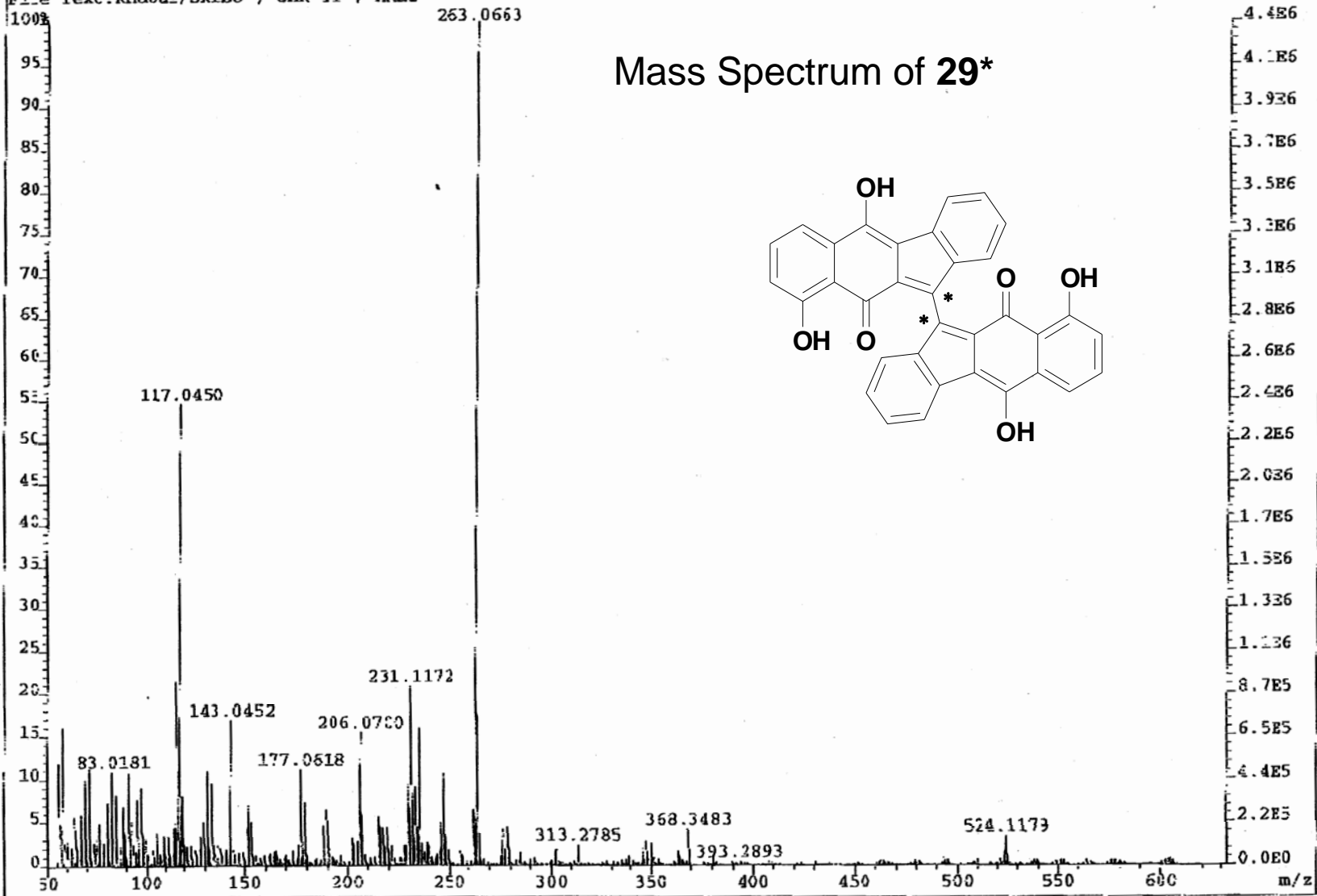


File: 54524C Ident: 37_40-19 Win 100PPM Acq: 1-FEB-2007 16:28:49 +8:11 Cal: 54524C
AutoSpecE TOF/MS EI+ Magnet BpM: 57 BpI: 285662 TIC: 6533805 Flags: ACC
File Text: Khmour/Skibo ; OMK-i ; HREI

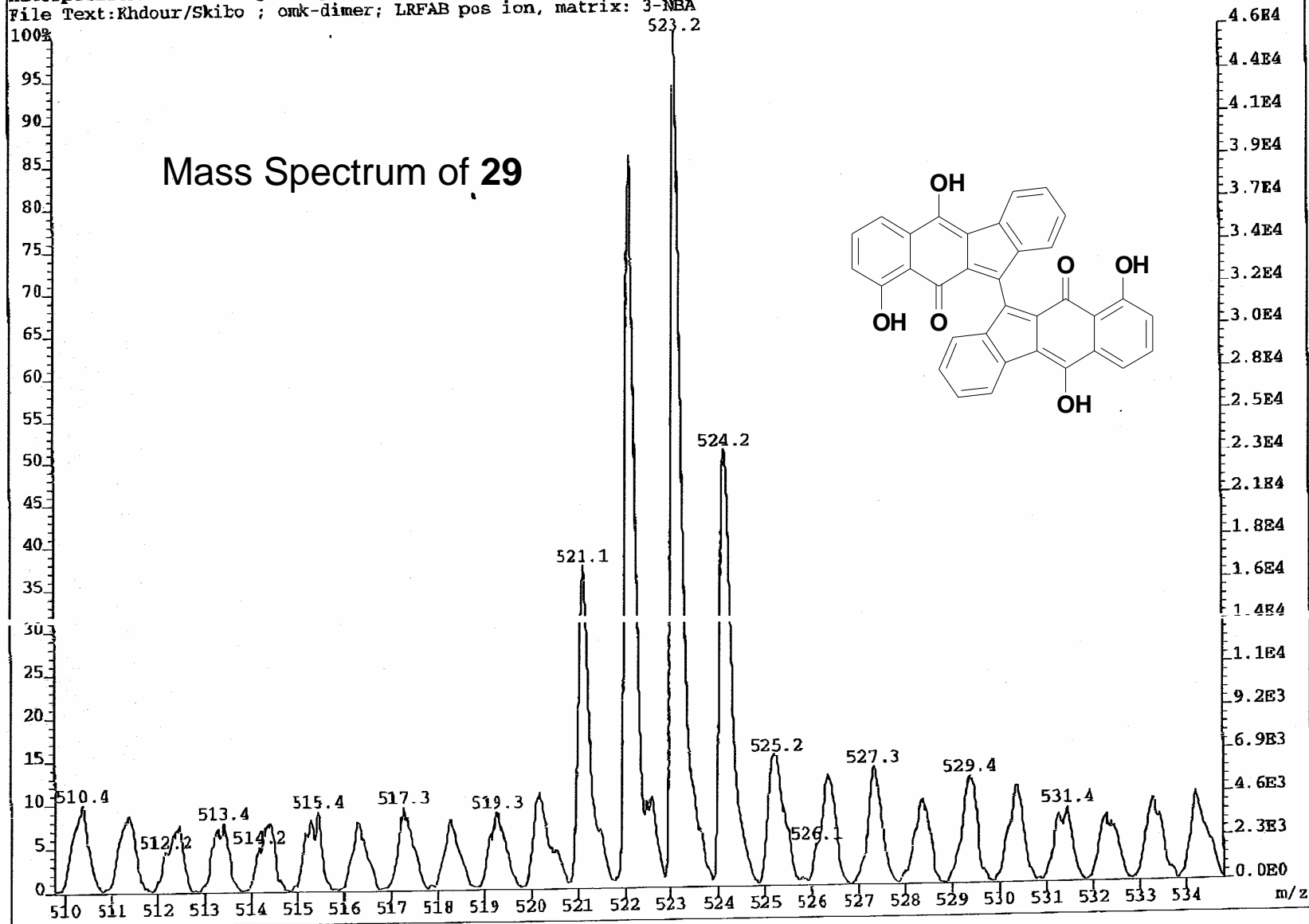
Mass Spectrum of the Quinone Methide (Scheme 11)



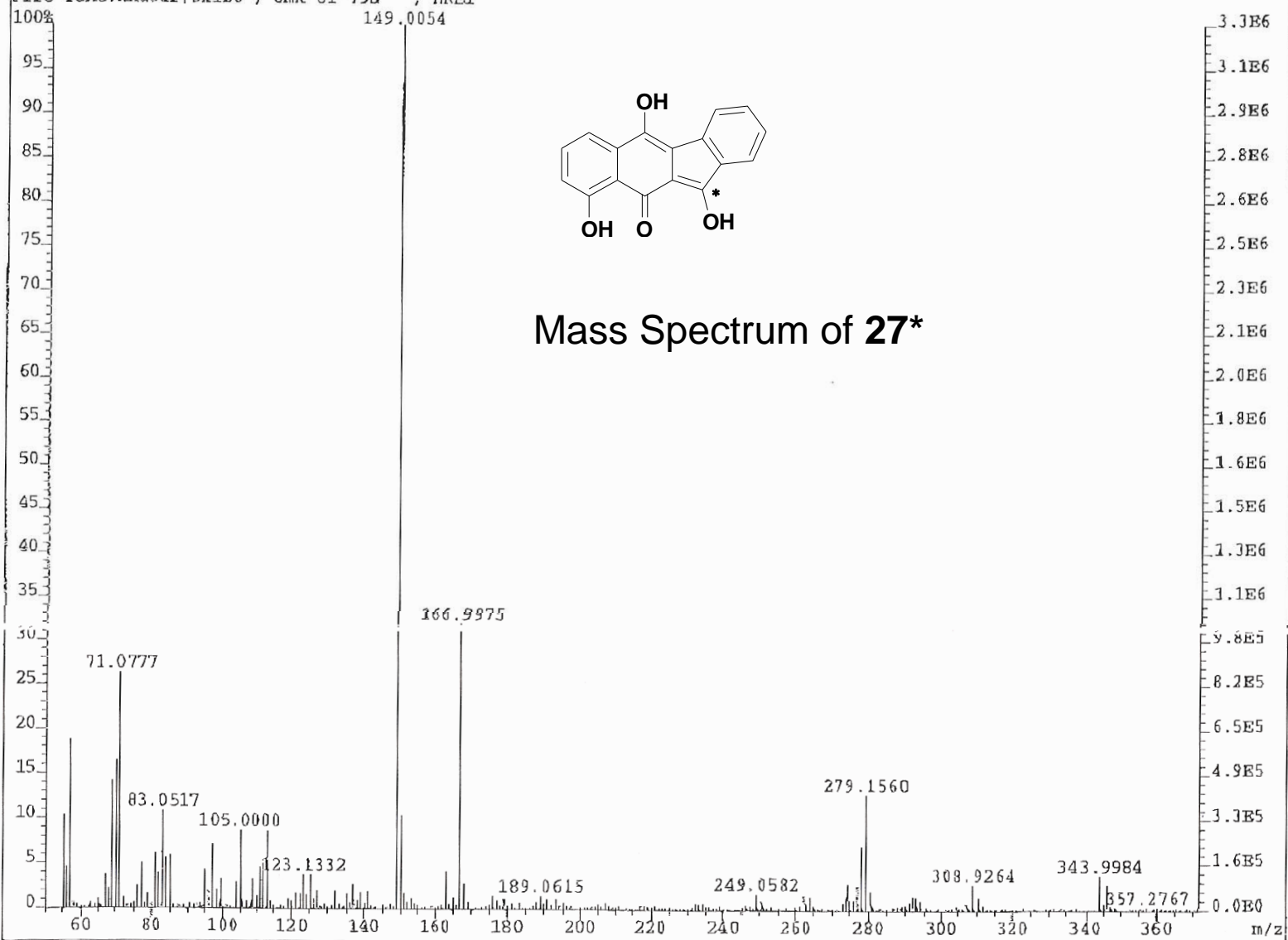
File:54525A Ident:73_75-1_11 Win 100PPM Acq: 1-FEB-2007 12:13:49 +15:32 Cal:54525A
AutoSpecETOFFPD EI+ Magnet BpM:263 BpI:4360991 TIC:72542344 Flags:ACC
File Text:Khdour/Skibo ; OMK-ii ; HREI



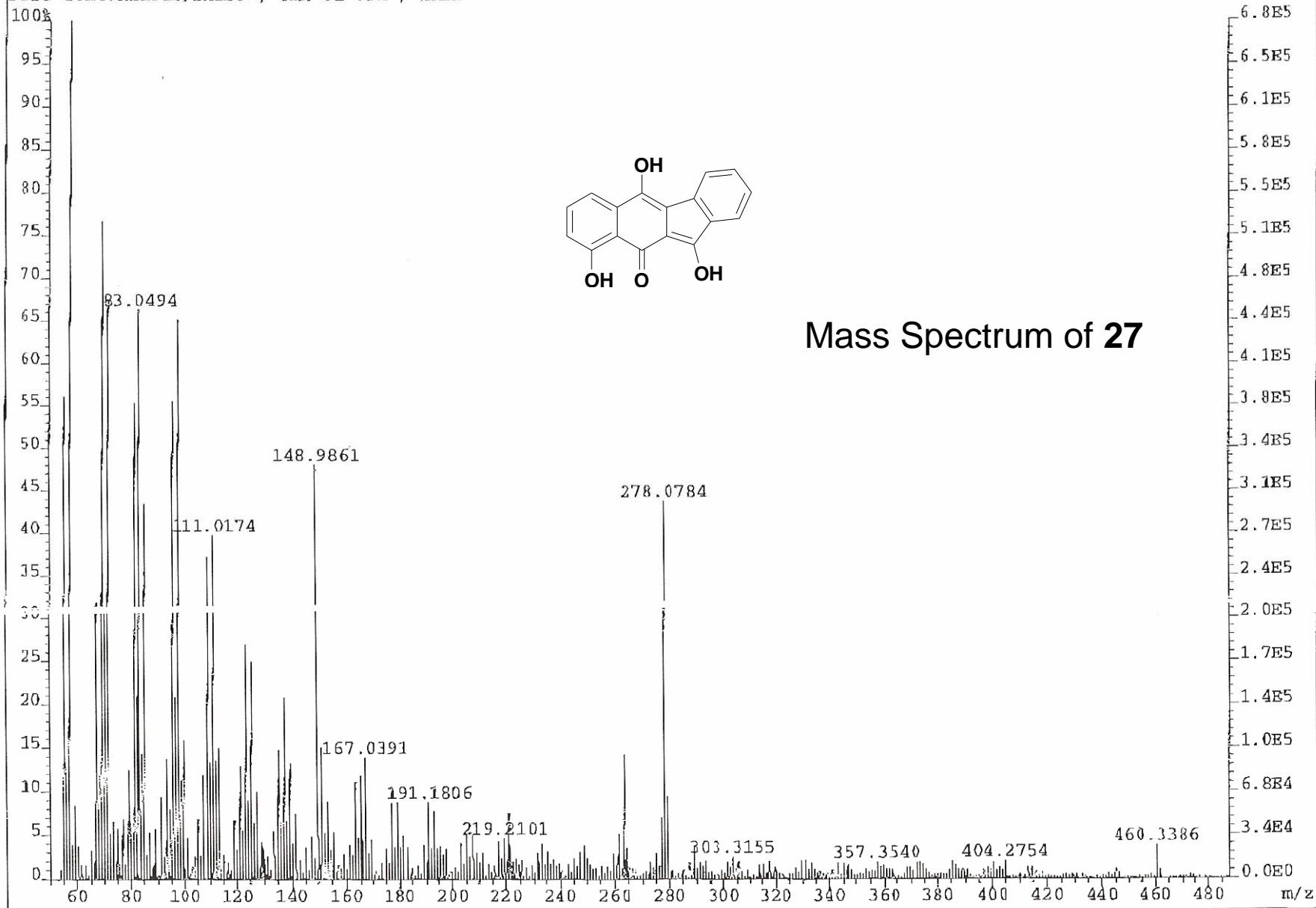
File:54249B Ident:39_49 SMO(1,7) Acq:25-OCT-2006 14:04:50 +9:51 Cal:SERCAL02506
AutoSpecTTOFFPD FAB+ Magnet BpI:3477248 TIC:488030496
File Text:Rhdour/Skibo ; onk-dimer; LRFAB pos ion, matrix: 3-NBA



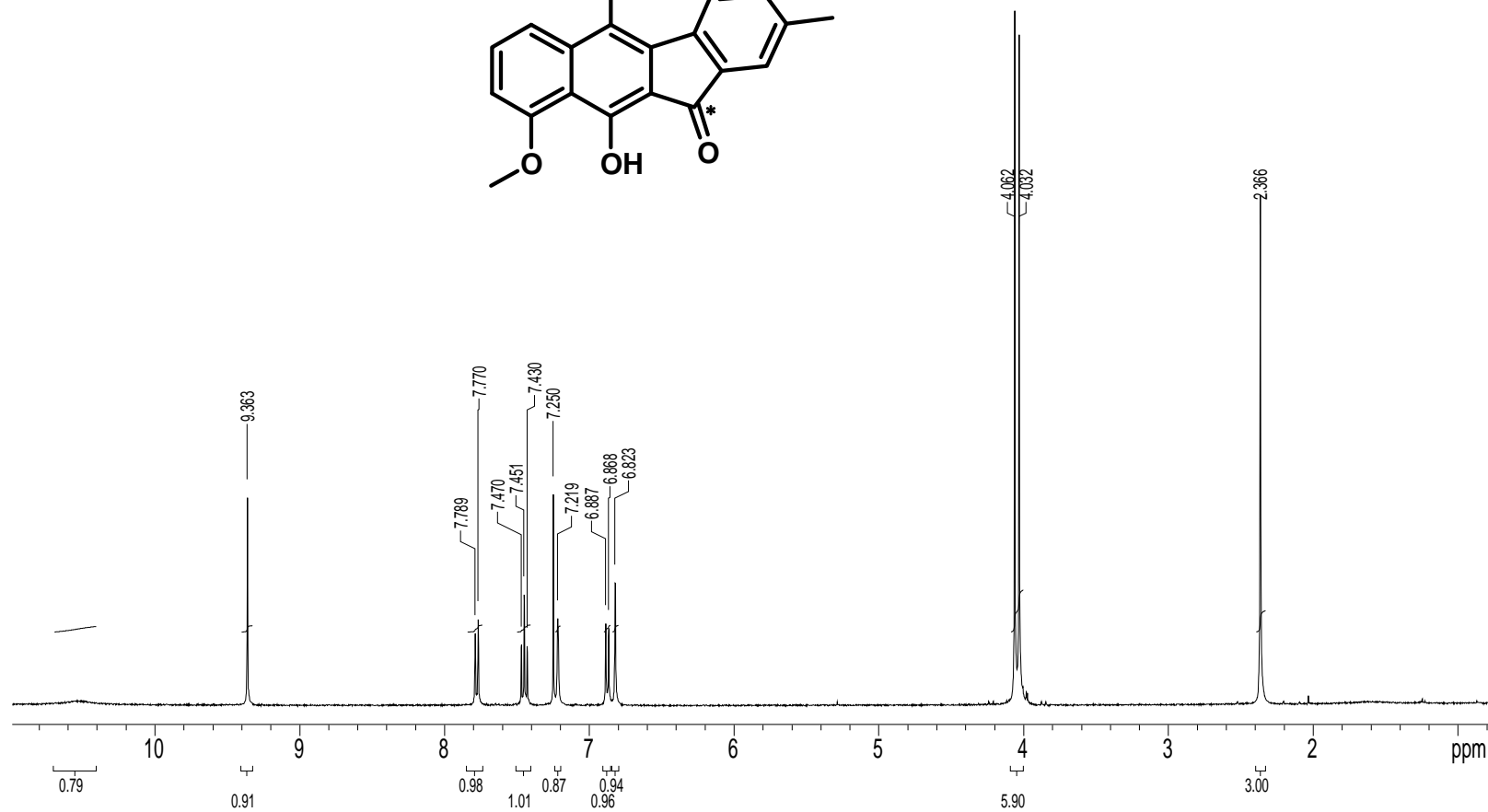
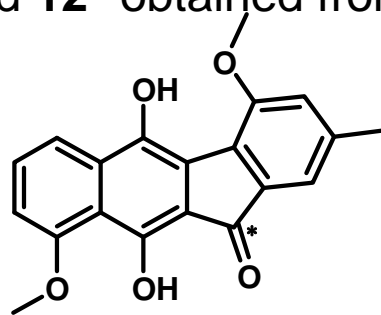
File:541318 Ident:30_32-1_0 Win 100PPM Acq:19-SRP-2006 17:05:37 +6:38 Cal:54131B
AutoSpecETOFFPD EI+ Magnet BpM:149 BpI:3272672 TIC:26906838 Flags:ACC
File Text:Khdour/Skibo ; omk-81-79a ; HREI



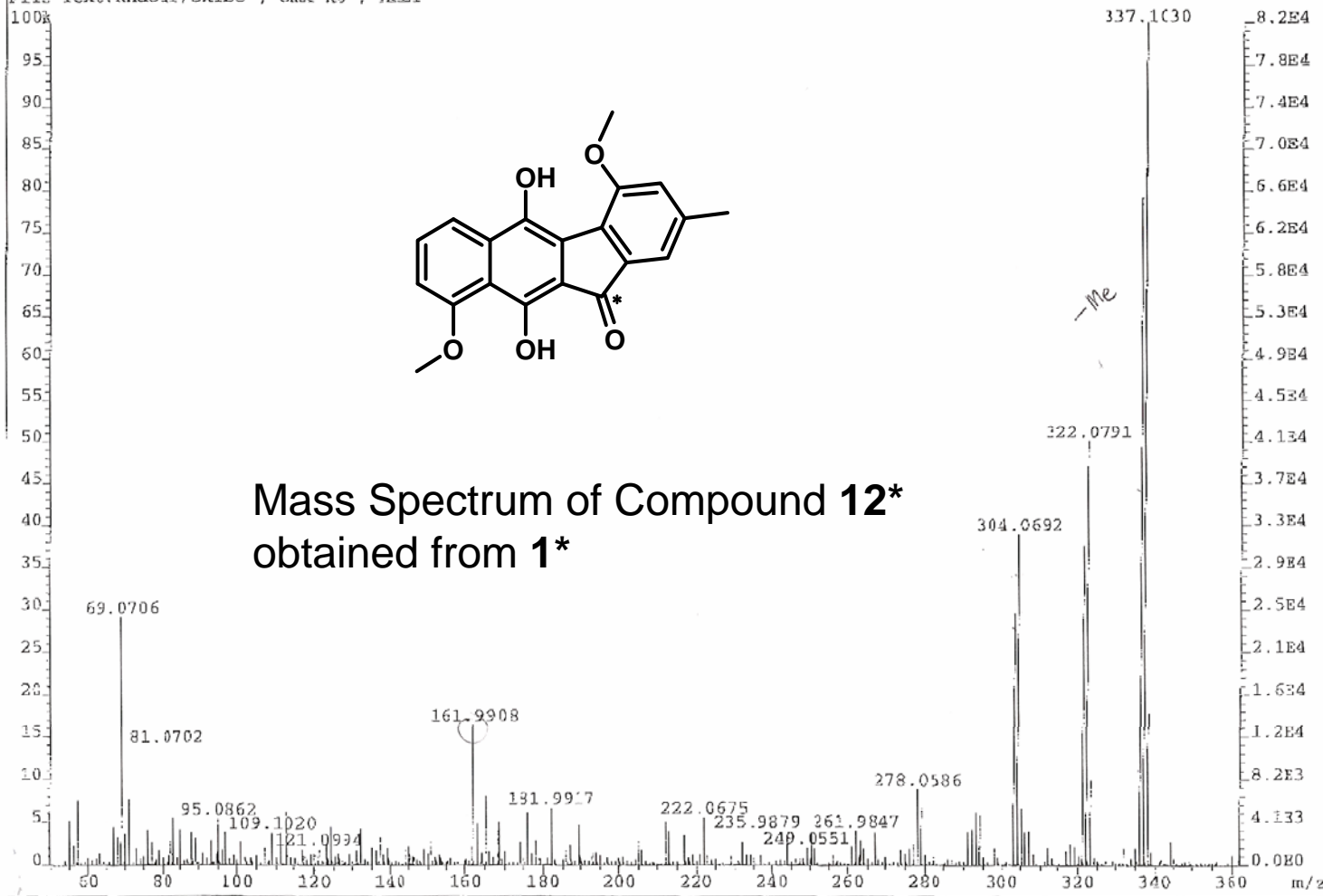
File:54126A Ident:26_36-1_11 Win 100PPM Acq:19-SEP-2006 09:04:21 +6:39 Cal:54126A
AutoSpecEToFPPD RI+ Magnet EpM:57 BpL:682915 TIC:19668568 Flags:ACC
File Text:Khdour/Skibo ; cmk-81-79x ; HREI



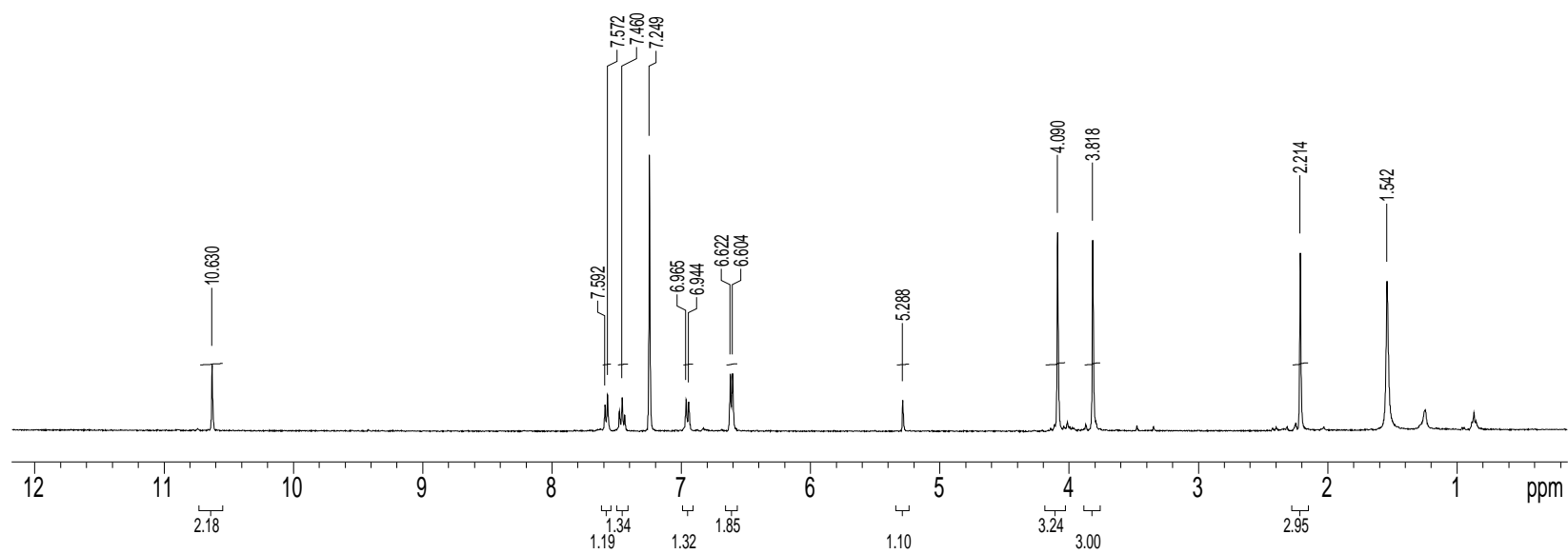
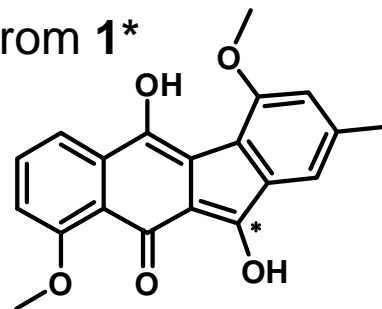
H-NMR of Compound **12*** obtained from **1***



File:53933A Ident:30_40-1_10 Win 10UPPM Acq:18-MAY-2006 13:31:11 +7:33 Cal:53933A
AutoSpecTTOFPPD EI+ Magnet BpM:337 BpI:82207 TIC:1144341 Flags:ACC
File Text:Khdor/Skibo ; omk-k5 ; HFEI

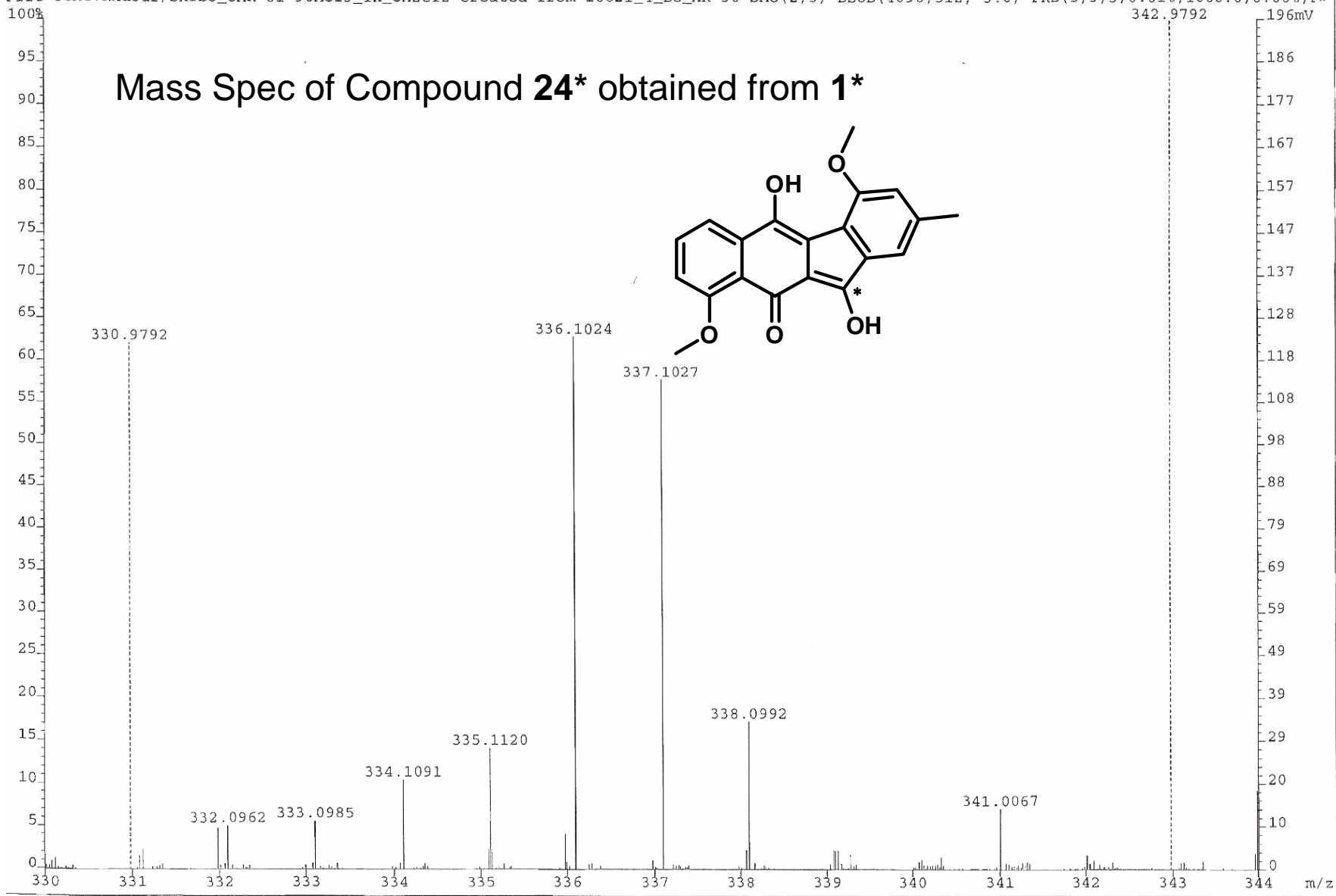
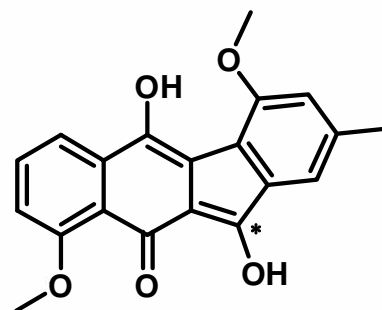


H-NMR of Compound **24*** obtained from **1***



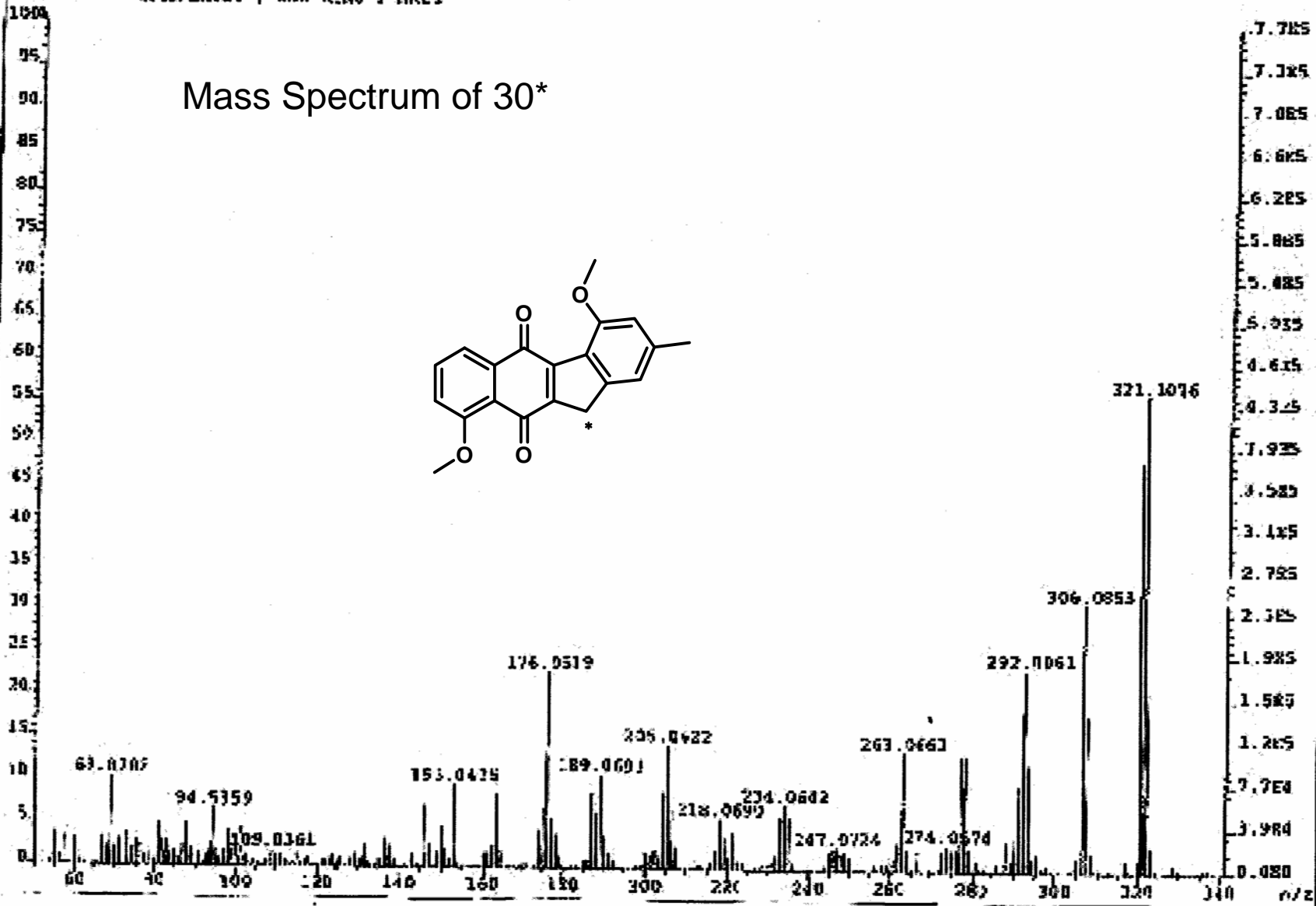
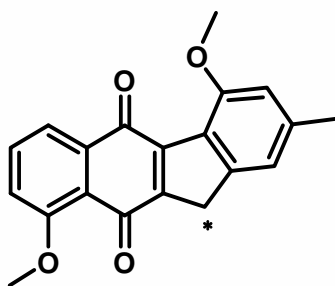
File:18821_4B_BG_HRS Ident:1_5 Win 100PPM Acq:20-OCT-2006 11:37:24 +6:02 Cal:18821_4B_BG_HRS
ZAB-SET EI+ Voltage BpM:343 BpI:6348800 TIC:33933152 Flags:ACC
File Text:Khdour/Skibo_OMK-81-90AC13_in_CH2Cl2 Created from 18821_4_BG_HR 36 SMO(2,5) BSUB(4096,512,-3.0) PKD(5,3,5,0.01%,1068.0,0.00%,F>>

Mass Spec of Compound 24* obtained from 1*

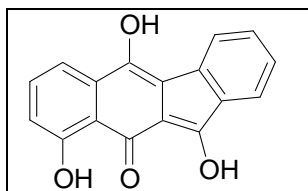


File:hd16 Ident:13_23-1.8 Nam:JUDITH Acq:17-AUG-2006 09:18:23 P3:56 P01134116
AutoSpock2008P1 M1+ Magnet OpM.12L Exp:770399 TIC:BSR9326 Flags:ACC
File Text:Khadoyy/Skilo ; unk kin6 ; HRFI

Mass Spectrum of 30*



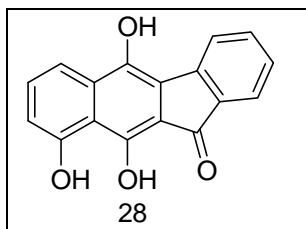
Prekinamycin Quinone Methide 27



C	3.371766	-0.620746	0.054317
C	2.683161	2.080986	-0.058504
C	2.031178	-0.241016	0.027342
C	4.361402	0.355701	0.027699
C	4.015247	1.682292	-0.027738
C	1.687839	1.128814	-0.029548
H	5.381557	0.037476	0.050494
H	4.785139	2.427645	-0.048641
H	2.422210	3.114931	-0.102599
C	0.991330	-1.265343	0.052103
C	0.274200	1.549093	-0.059128
C	-0.686438	0.628459	-0.016433
C	-0.335731	-0.778282	0.028106
O	1.233040	-2.498139	0.092615
O	0.105145	2.902753	-0.134465
H	-0.790383	3.177780	-0.354202
O	3.758107	-1.913980	0.105262
H	2.985767	-2.517072	0.116691
C	-1.451257	-1.544757	0.041231
O	-1.514027	-2.869444	0.076007
H	-0.614115	-3.257033	0.094842
C	-2.622099	-0.669891	0.015431
C	-4.444648	1.370841	0.005151
C	-3.960328	-0.983983	0.028368
C	-2.165631	0.663777	-0.009427
C	-3.091198	1.687029	-0.005779
C	-4.879319	0.054920	0.018600
H	-4.276155	-2.007370	0.048671
H	-2.798420	2.717499	0.007506
H	-5.928806	-0.158428	0.027814
H	-5.166064	2.163567	0.008006

Energy = -943.7702652 Hartrees

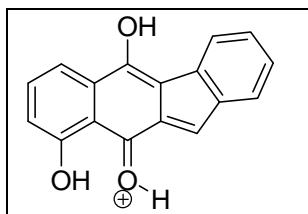
Compound **28** in Scheme 15.



C	3.465461	-0.831021	-0.003063
C	2.746909	1.873052	0.081491
C	2.099322	-0.469146	0.001468
C	4.424040	0.149493	0.030302
C	4.062639	1.491532	0.078691
C	1.741075	0.902849	0.032348
H	5.449660	-0.151485	0.027394
H	4.831947	2.236737	0.121156
H	2.471938	2.903584	0.149137
C	1.051317	-1.442137	-0.014612
C	0.352679	1.293743	0.023252
C	-0.589462	0.343819	0.019504
C	-0.225818	-1.028039	0.003459
O	1.371930	-2.769367	-0.045941
O	0.022970	2.645827	0.031287
H	0.185170	3.059194	-0.831077
O	3.882761	-2.122456	-0.038148
H	3.146293	-2.755770	-0.050388
C	-1.423493	-1.868993	-0.014273
O	-1.429373	-3.091434	-0.041632
C	-2.565015	-0.912612	0.004348
C	-4.297661	1.208833	0.075610
C	-3.913278	-1.167502	0.008750
C	-2.068362	0.395494	0.030686
C	-2.930005	1.466668	0.071329
C	-4.787311	-0.086478	0.042348
H	-4.276488	-2.175672	-0.010612
H	-2.545698	2.463353	0.112321
H	-5.845221	-0.255267	0.047192
H	-4.985738	2.030226	0.109047
H	0.576812	-3.337026	-0.051374

Energy = -943.7837005 Hartrees

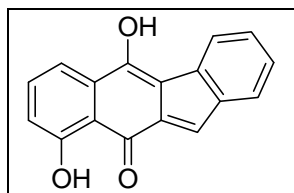
Protonated Prekinamycin Quinone Methide **26H⁺**.



	X	Y	Z
H	-2.163589	-3.077974	0.000000
C	-2.480750	-2.059260	0.000000
C	-3.309659	0.587608	0.000000
C	-1.532438	-1.056275	0.000000
C	-3.826973	-1.736033	0.000000
C	-4.246106	-0.419026	0.000000
C	-1.941541	0.296438	0.000000
H	-4.557464	-2.518905	0.000000
H	-5.290935	-0.183685	0.000000
C	-0.102605	-1.406903	0.000000
O	0.111388	-2.740773	0.000000
H	1.030499	-3.026976	0.000000
C	0.805928	-0.430370	0.000000
C	0.385890	0.963131	0.000000
C	-0.950353	1.340549	0.000000
O	-1.249620	2.613867	0.000000
H	-2.215992	2.800001	0.000000
O	-3.656082	1.918448	0.000000
H	-4.604151	2.106849	0.000000
C	1.488512	1.781367	0.000000
H	1.464185	2.850461	0.000000
C	2.280732	-0.396697	0.000000
C	4.965183	0.345687	0.000000
C	3.249145	-1.375118	0.000000
C	2.669451	0.966382	0.000000
C	4.005210	1.338761	0.000000
C	4.586248	-0.990854	0.000000
H	3.014173	-2.419400	0.000000
H	4.285626	2.373116	0.000000
H	5.344080	-1.748210	0.000000
H	6.004036	0.602264	0.000000

Energy = -869.6815298 Hartrees

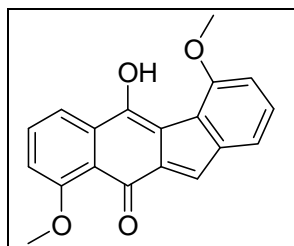
Prekinamycin Quinone Methide **26**.



	X	Y	Z
H	-2.160903	-3.036927	0.000000
C	-2.487627	-2.021006	0.000000
C	-3.339392	0.631934	0.000000
C	-1.560034	-1.007300	0.000000
C	-3.845938	-1.708378	0.000000
C	-4.269166	-0.407636	0.000000
C	-1.979407	0.338855	0.000000
H	-4.566842	-2.501226	0.000000
H	-5.306059	-0.148103	0.000000
C	-0.121709	-1.338795	0.000000
O	0.120244	-2.675464	0.000000
H	1.051393	-2.915325	0.000000
C	0.793474	-0.369938	0.000000
C	-1.004008	1.439321	0.000000
O	-1.347341	2.624999	0.000000
O	-3.822383	1.892828	0.000000
H	-3.100777	2.553232	0.000000
C	0.390423	1.035495	0.000000
C	2.266668	-0.360061	0.000000
C	4.956338	0.331840	0.000000
C	3.226860	-1.354122	0.000000
C	2.669084	0.992935	0.000000
C	4.004891	1.338837	0.000000
C	4.568128	-0.999042	0.000000
H	2.973747	-2.395749	0.000000
H	4.301460	2.369102	0.000000
H	5.314934	-1.767843	0.000000
H	5.998332	0.580914	0.000000
C	1.468601	1.831464	0.000000
H	1.455549	2.899487	0.000000

Energy = -869.3069255 Hartrees

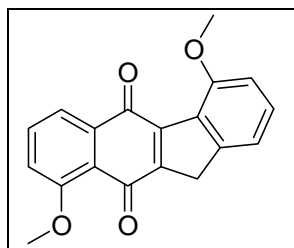
Quinone Methide **31** in Scheme 16.



	X	Y	Z
H	-1.946575	-3.219056	-0.019679
C	-2.479865	-2.295131	-0.012677
C	-3.826640	0.138155	0.005533
C	-1.767555	-1.108769	-0.005396
C	-3.858241	-2.263089	-0.010829
C	-4.527623	-1.060742	-0.001922
C	-2.428063	0.131281	0.004022
H	-4.413909	-3.179527	-0.016425
H	-5.595982	-1.054558	-0.000747
C	-0.290029	-1.201788	-0.008180
O	0.188920	-2.456298	-0.017848
H	1.173385	-2.479910	-0.019793
C	0.446550	-0.088556	-0.001429
C	-1.642307	1.404599	0.012207
O	-2.122364	2.522206	0.020892
C	-0.184720	1.220160	0.008996
C	0.745796	2.185741	0.014839
H	0.557654	3.236486	0.022783
C	1.887676	0.165929	-0.001896
C	4.439431	1.282137	0.002302
C	2.997439	-0.660955	-0.009703
C	2.069904	1.557017	0.008165
C	3.338145	2.115743	0.010497
C	4.258880	-0.102589	-0.007574
H	3.463414	3.180370	0.018485
H	5.125556	-0.730495	-0.013424
O	2.774580	-2.030898	-0.019306
O	-4.460915	1.336369	0.014168
C	3.873074	-2.968003	-0.027137
H	4.478642	-2.837382	-0.912864
H	3.419749	-3.945382	-0.033300
H	4.480758	-2.849690	0.858840
C	-5.893286	1.447953	0.015475
H	-6.324980	1.002069	-0.871863
H	-6.088478	2.506707	0.022616
H	-6.324330	0.990415	0.897131
C	5.849693	1.841945	0.001071
H	6.378984	1.544172	-0.897565
H	6.407449	1.480617	0.858615
H	5.836280	2.923795	0.039966

Energy = -1060.1888746 Hartrees

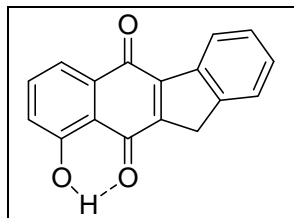
Keto form **30** in Scheme 16



	X	Y	Z
H	-2.099592	-3.253551	0.025004
C	-2.601820	-2.310679	0.021130
C	-3.852841	0.170945	0.011177
C	-1.846144	-1.154692	0.016161
C	-3.977847	-2.227346	0.021000
C	-4.599615	-0.997996	0.016108
C	-2.455832	0.099525	0.011019
H	-4.569526	-3.120798	0.024728
H	-5.667052	-0.949918	0.016125
C	-0.348070	-1.347599	0.016734
C	-1.609619	1.318636	0.005430
O	0.103055	-2.471961	0.022142
O	-2.014304	2.465469	0.000740
O	-4.429422	1.397687	0.006310
C	-5.856292	1.574716	0.007086
H	-6.307545	1.139267	-0.875597
H	-6.003522	2.641163	0.003319
H	-6.305774	1.145922	0.893875
C	0.454147	-0.106583	0.010631
C	-0.159915	1.076298	0.005470
C	1.921458	0.110887	0.008792
C	4.499882	1.164379	0.000484
C	3.012626	-0.754419	0.011333
C	2.145080	1.486738	0.002014
C	3.414657	2.023415	-0.002564
C	4.285583	-0.208479	0.006928
H	3.560085	3.085584	-0.008669
H	5.136633	-0.857376	0.008015
C	0.820072	2.216760	-0.000585
H	0.695185	2.834476	-0.883360
H	0.696252	2.842844	0.876441
O	2.777050	-2.089869	0.017340
C	3.839581	-3.055070	0.016789
H	4.455216	-2.963394	-0.869598
H	3.345916	-4.011925	0.021140
H	4.460898	-2.958378	0.898629
C	5.920122	1.695953	0.006489
H	6.495257	1.262725	-0.804680
H	6.413244	1.448342	0.940816
H	5.932668	2.772306	-0.106864

Energy = -1060.1765447 Hartrees

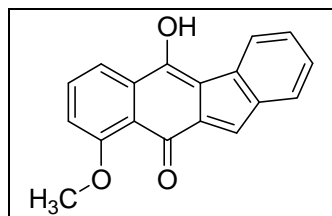
Keto form **32** in Scheme 16.



	X	Y	Z
H	-2.208783	-3.058068	0.000000
C	-2.535168	-2.039685	0.000000
C	-3.353036	0.623044	0.000000
C	-1.602760	-1.037446	0.000000
C	-3.892329	-1.715137	0.000000
C	-4.294680	-0.408225	0.000000
C	-1.999640	0.310368	0.000000
H	-4.624102	-2.497522	0.000000
H	-5.327982	-0.134274	0.000000
C	-0.158425	-1.415566	0.000000
C	-1.003644	1.393678	0.000000
O	0.207489	-2.575344	0.000000
O	-1.318700	2.583130	0.000000
C	0.788837	-0.289397	0.000000
C	0.396258	0.982514	0.000000
C	2.253391	-0.362474	0.000000
C	4.960506	0.089642	0.000000
C	3.105416	-1.449199	0.000000
C	2.742779	0.947034	0.000000
C	4.098988	1.179670	0.000000
C	4.470120	-1.207726	0.000000
H	2.708041	-2.441548	0.000000
H	4.488673	2.178509	0.000000
H	5.154242	-2.032464	0.000000
H	6.019691	0.254148	0.000000
C	1.577224	1.925390	0.000000
H	1.572696	2.557878	-0.881335
H	1.572696	2.557878	0.881335
O	-3.826819	1.888538	0.000000
H	-3.107082	2.547191	0.000000

Energy = -869.3227535 Hartrees

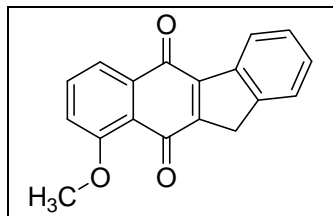
Quinone methide form **33** in Scheme 16



	X	Y	Z
H	-1.516542	-3.304958	-0.013585
C	-1.965875	-2.337642	-0.005857
C	-3.106033	0.199676	0.013446
C	-1.156682	-1.214192	-0.011059
C	-3.336507	-2.190255	0.011370
C	-3.903937	-0.936771	0.021528
C	-1.712471	0.076864	-0.003741
H	-3.965931	-3.057561	0.017022
H	-4.967925	-0.842110	0.035086
C	0.306863	-1.420172	-0.021340
O	0.667591	-2.733369	-0.055045
H	1.604730	-2.880705	-0.214775
C	1.136665	-0.382896	-0.001995
C	-0.825688	1.280903	-0.020318
O	-1.211453	2.434515	-0.036832
C	0.610429	0.977787	-0.016158
C	1.614441	1.862330	-0.032767
H	1.508065	2.924640	-0.051384
O	-3.637408	1.445633	0.022622
C	-5.055743	1.678241	0.039150
H	-5.533249	1.265980	-0.840780
H	-5.159982	2.749656	0.042020
H	-5.513119	1.263124	0.928386
C	2.604050	-0.250893	0.012354
C	5.222264	0.663159	0.024347
C	3.641721	-1.160535	0.063744
C	2.887296	1.131247	-0.016886
C	4.188564	1.587262	-0.013133
C	4.949797	-0.694524	0.066071
H	3.472490	-2.217701	0.121815
H	4.398520	2.638360	-0.035347
H	5.758593	-1.396710	0.105904
H	6.239313	1.000553	0.027731

Energy = -908.0936127 Hartrees

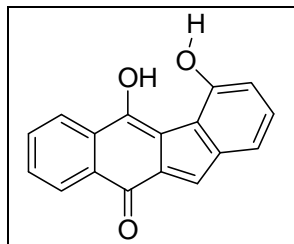
Keto form **34** in Scheme 16.



	X	Y	Z
H	-1.568284	-3.329068	0.000000
C	-2.016227	-2.358519	0.000000
C	-3.118369	0.195248	0.000000
C	-1.198073	-1.248383	0.000000
C	-3.386365	-2.194950	0.000000
C	-3.931554	-0.931344	0.000000
C	-1.728460	0.046561	0.000000
H	-4.030206	-3.051315	0.000000
H	-4.994145	-0.819652	0.000000
C	0.277640	-1.507283	0.000000
C	-0.817736	1.229812	0.000000
O	0.726863	-2.638456	0.000000
O	-1.168266	2.393002	0.000000
C	1.125300	-0.317207	0.000000
C	0.619498	0.910464	0.000000
C	2.592312	-0.261742	0.000000
C	5.249303	0.430009	0.000000
C	3.537362	-1.267224	0.000000
C	2.962938	1.086041	0.000000
C	4.292775	1.438495	0.000000
C	4.876109	-0.905088	0.000000
H	3.229575	-2.291112	0.000000
H	4.591575	2.468342	0.000000
H	5.630772	-1.666070	0.000000
H	6.289588	0.688707	0.000000
C	1.712747	1.954342	0.000000
H	1.648364	2.584410	-0.880573
H	1.648364	2.584410	0.880573
O	-3.627135	1.450457	0.000000
C	-5.042274	1.708726	0.000000
H	-5.515940	1.303011	-0.884821
H	-5.127596	2.781702	0.000000
H	-5.515940	1.303011	0.884821

Energy = -908.1125796 Hartrees

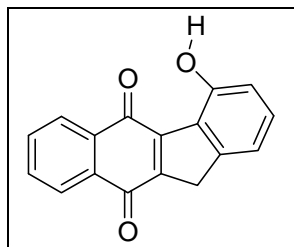
Quinone Methide form **35** in Scheme 16.



	X	Y	Z
H	2.800091	-2.416260	-0.153524
C	3.012732	-1.369795	-0.082655
C	3.573289	1.335868	-0.004520
C	1.968755	-0.459300	-0.009023
C	4.324059	-0.930719	-0.102138
C	4.609344	0.422081	-0.055513
C	2.259302	0.909578	0.013662
H	5.119977	-1.646043	-0.161409
H	5.625370	0.760824	-0.069629
H	3.763356	2.389333	0.015806
C	0.573411	-0.921883	0.024377
C	-0.433818	-0.061946	0.001024
C	-0.175119	1.386065	0.004761
C	1.176847	1.933346	0.032883
O	1.419627	3.128181	0.062785
O	0.351587	-2.301446	0.068191
H	0.737455	-2.711284	0.857893
C	-1.332473	2.055040	0.026445
H	-1.437909	3.118082	0.054686
C	-1.900221	-0.207690	-0.010829
C	-4.633715	0.187491	-0.023794
C	-2.730001	-1.306882	-0.064886
C	-2.447801	1.093142	0.013800
C	-3.801667	1.307343	0.010934
C	-4.110934	-1.082740	-0.063752
H	-4.209962	2.297448	0.029988
H	-4.747189	-1.941736	-0.101447
H	-5.697539	0.317350	-0.027041
O	-2.313450	-2.596759	-0.126868
H	-1.343404	-2.686686	-0.160209

Energy = -869.3031735 Hartrees

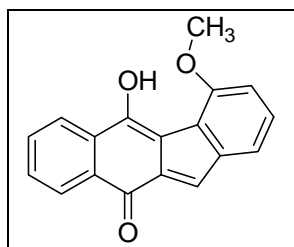
Keto form **36** in Scheme 16.



	X	Y	Z
H	2.919267	-2.560710	-0.000612
C	3.136140	-1.512725	-0.000648
C	3.646754	1.209422	-0.000585
C	2.086910	-0.612888	0.000720
C	4.441497	-1.053233	-0.002134
C	4.696231	0.306317	-0.002100
C	2.344132	0.754647	0.000745
H	5.252636	-1.752903	-0.003371
H	5.706328	0.663449	-0.003295
H	3.823668	2.265115	-0.000497
C	0.698368	-1.138449	0.001941
C	1.231988	1.743203	0.001984
O	0.481432	-2.342623	0.002793
O	1.430564	2.943588	0.002579
C	-0.381019	-0.134859	0.001725
C	-0.114691	1.172271	0.001911
C	-1.378253	1.990687	0.001710
H	-1.435930	2.620852	0.883153
H	-1.434906	2.622466	-0.878597
C	-1.839987	-0.353951	0.000886
C	-4.585652	-0.100468	-0.002213
C	-2.618075	-1.503982	0.000143
C	-2.448236	0.913188	0.000472
C	-3.810226	1.056935	-0.000968
C	-4.002975	-1.345960	-0.001690
H	-4.267982	2.025608	-0.001221
H	-4.596177	-2.235736	-0.002611
H	-5.654790	-0.022321	-0.003617
O	-2.150188	-2.775080	0.001235
H	-1.176828	-2.841861	0.002162

Energy = -869.3222170 Hartrees

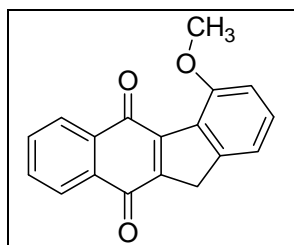
Quinone Methide form **37** in Scheme 16.



	X	Y	Z
H	2.636923	-2.647655	0.000000
C	3.085632	-1.677989	0.000000
C	4.214249	0.848759	0.000000
C	2.266478	-0.560880	0.000000
C	4.461100	-1.530863	0.000000
C	5.028338	-0.269171	0.000000
C	2.839842	0.713266	0.000000
H	5.086626	-2.401116	0.000000
H	6.093834	-0.156478	0.000000
H	4.627353	1.836321	0.000000
C	0.800251	-0.732673	0.000000
C	0.007347	0.348429	0.000000
C	0.561105	1.697704	0.000000
C	2.000122	1.945631	0.000000
O	2.493983	3.060294	0.000000
C	-0.424842	2.607765	0.000000
H	-0.300381	3.668431	0.000000
O	0.390116	-2.007580	0.000000
H	-0.592351	-2.087863	0.000000
C	-1.445381	0.522444	0.000000
C	-4.042998	1.481938	0.000000
C	-2.503988	-0.371205	0.000000
C	-1.707231	1.904341	0.000000
C	-3.005283	2.389311	0.000000
C	-3.797134	0.111994	0.000000
H	-3.196249	3.443587	0.000000
H	-4.627498	-0.561490	0.000000
H	-5.057627	1.826331	0.000000
O	-2.201222	-1.726281	0.000000
C	-3.244017	-2.726253	0.000000
H	-3.856400	-2.636853	0.886049
H	-2.734297	-3.675343	0.000000
H	-3.856400	-2.636853	-0.886049

Energy = -908.1263857 Hartrees

Quinone Methide form **38** in Scheme 16.



	X	Y	Z
H	2.834687	-2.583180	-0.249271
C	3.181382	-1.573814	-0.171534
C	4.031486	1.050520	0.048801
C	2.250484	-0.556156	-0.071379
C	4.532934	-1.281135	-0.170857
C	4.959186	0.031450	-0.060433
C	2.680497	0.759717	0.040284
H	5.249439	-2.073484	-0.254207
H	6.006261	0.258735	-0.057429
H	4.336999	2.072358	0.141647
C	0.799449	-0.922339	-0.063774
C	1.701563	1.866429	0.163171
O	0.463626	-2.087914	-0.025615
O	2.038921	3.027854	0.304033
C	-0.146329	0.220537	-0.063947
C	0.294587	1.472079	0.082938
C	-0.833890	2.463841	0.148575
H	-0.834875	2.987980	1.098825
H	-0.762296	3.196111	-0.648717
C	-1.625146	0.232600	-0.156938
C	-4.306647	0.915211	-0.272174
C	-2.566653	-0.755493	-0.397077
C	-2.041449	1.565076	-0.015910
C	-3.368475	1.915672	-0.061407
C	-3.905944	-0.394571	-0.442201
H	-3.672224	2.937426	0.050825
H	-4.626248	-1.161151	-0.641181
H	-5.348827	1.161022	-0.319254
O	-2.223072	-2.064790	-0.636648
C	-2.271338	-2.992449	0.483492
H	-1.615549	-2.669244	1.274992
H	-1.927305	-3.933738	0.091157
H	-3.285234	-3.085162	0.851215

Energy = -908.1135495 Hartrees