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

Diyne-steered switchable regioselectivity in cobalt(II)-catalysed C(sp^2)-H activation of amides with unsymmetrical 1,3-diynes

Prakriti Dhillon, Prasad Anaspure, Jesper G. Wiklander, Subban Kathiravan and Ian A. Nicholls*

Bioorganic & Biophysical Chemistry Laboratory, Centre for Biomaterials Chemistry, Department of Chemistry & Biomedical Sciences, Linnaeus University, Kalmar, 39130, Sweden.

E-mail: ian.nicholls@lnu.se

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General information

All solvents were used as received. $Co(acac)_2$, $Mn(OAc)_2$, and $NaOPiv \cdot H_2O$ were purchased from Aldrich and Chemtronica. Terminal alkynes, 8-aminoquinoline and benzoyl chlorides were purchased from commercial sources (Aldrich/Chemtronica). Silica gel (60 Å) from Chemtronica was used for column chromatography. Preparative TLC plates were purchased from Merck (PLC Silica gel 60 F_{254} 0.5 mm with concentrating zone 20 x 20 cm). Thin layer chromatography was performed on aluminum sheets precoated with silica gel with fluorescence indicator (254 nm).

Analytical information

Melting points (uncorrected) were recorded using a Stuart Scientific Melting Point SMP1. IR spectra were recorded using an Agilent Cary 630 FTIR spectrometer. NMR spectra were recorded using a Bruker Avance Neo 400 MHz NMR spectrometer. Chemical shifts (δ) are reported parts in per million (ppm), relative to the signals for residual undeuterated solvent, unless otherwise stated. Mass spectra (HRMS) were obtained at the Lund University Kemicentrum Mass Spectrometry facility using a Waters XEVO-G2 QTOF ESI+ mass spectrometer. The capillary voltage, cone voltage, source temperature, and desolvation temperature was 3.0 kV, 35 V, 120°C and 300°C, respectively. Cone gas flow and desolvation gas flow was 50 and 400 l h^{-1}, respectively. Analyses were performed in continuum resolution mode with a mass range of m/z 100-1200, using manual lock mass correction with leucine-enkephalin (m/z 556.2771) as reference. HPLC chromatograms were recorded using Merck-Hitachi (Model D-7000IF) using a silica column (Material: Ultrasphere 5 SI, Batch: S806073, Dimensions: 250 x 4.6mm).

General procedures

Synthesis of benzamides[1]

To a solution of 8-aminoquinoline (1.0 equiv., 17 mmol) and *N*,*N*-dimethyl-4-aminopyridine (1.7 mmol, 10 mol%) in anhydrous CH_2Cl_2 (20 mL) under nitrogen was added Et_3N (1.1 equiv., 19 mmol) and the resulting solution was cooled to 0 °C. Benzoyl chlorides (1.2 equiv., 20.4 mmol) was added dropwise, and the reaction mixture was stirred at room temperature for 48 h. The mixture was quenched with water (20 mL) and extracted with CH_2Cl_2 (4x10 mL). The combined organic phase was dried over $MgSO_4$ and filtered. Concentration under reduced pressure followed by flash column chromatography on silica gel using petroleum

ether: acetone (8:2) as eluent afforded the *N*-(quinolin-8-yl)benzamides in 85-95% yield. Data is consistent with literature.

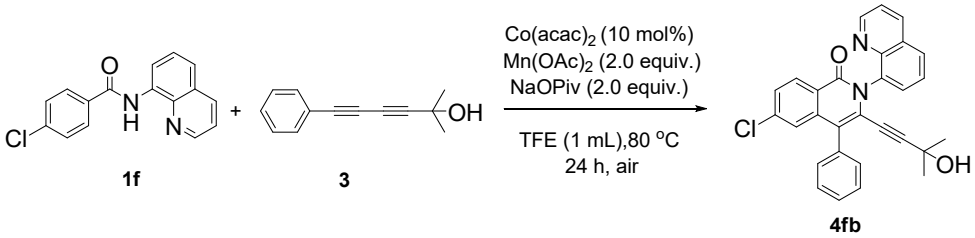
Synthesis of unsymmetrical 1,3-diynes (2-5)

Bromination of terminal alkynes[2]

Br_2 (0.73 equiv.) was added dropwise using a syringe to a stirring solution of KOH (5.23 eq) and water (25 mL) cooled to 0 °C. After 15 mins., the terminal alkyne (1.0 equiv.) was added dropwise, and the mixture was left to stir for 1.5 h at 0 °C after which it was warmed to room temperature and extracted using Et_2O, dried over $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure which gave the bromoalkynes as a colorless oily liquid with pungent smell in more than 95 % yield.

Cross-coupling reaction[3]

A 30% solution of $BuNH_2/H_2O$ (20 mL) was prepared in a round-bottom flask equipped with a magnetic stirrer to which was added CuCl (20 mol %, 0.2 equiv.). The resulting blue color was quenched by adding enough $NH_2OH{\cdot}HCl$, then phenylacetylene (1.0 equiv.) was added resulting in a cloudy yellow solution which was left to stir at 0 °C for 15 min. Then, the bromo-alkyne (1.0 equiv.) in Et_2O (2 mL) was added to the above solution along with a spatula of $NH_2OH{\cdot}HCl$. The reaction mixture was stirred at 0 °C for 1-1.5 h after which it was warmed to room temperature and extracted with Et_2O (10 mL x 3) and dried over $MgSO_4$, filtered, concentrated *in vacuo,* and purified through flash chromatography using petroleum ether:acetone (4:1) which afforded the unsymmetrical 1,3-diynes in 50 - 80 % yield.



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Processed: 21-05-26 15:34

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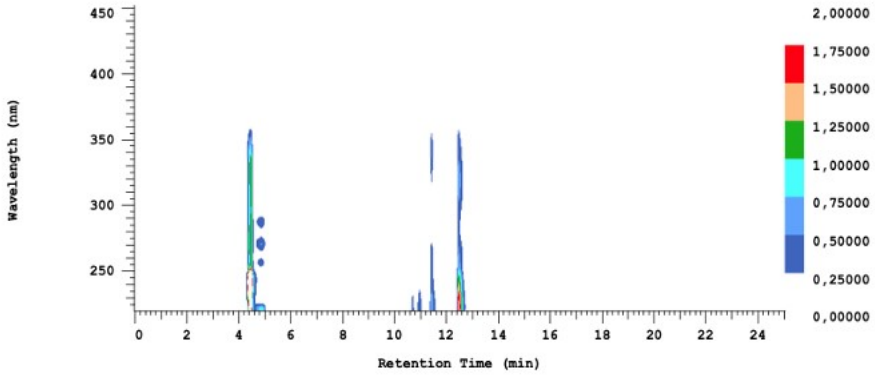

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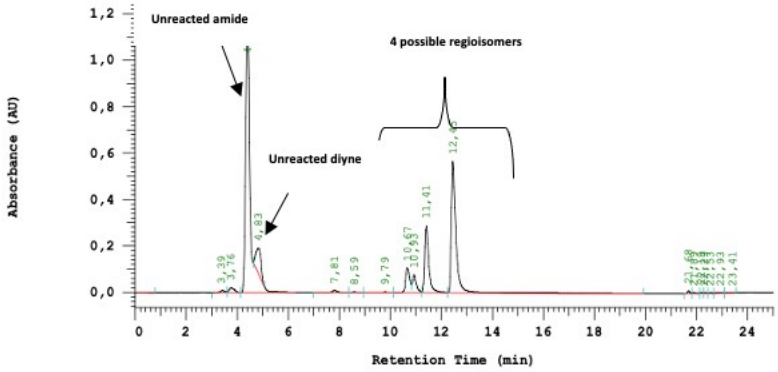

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Solvent A: Solvent B: IPA
Solvent C: Pet Ether
Method Description:

Chrom Type: Best Chromatogram

HPLC trace of reaction between 4-chlorobenzamide (1f) and diyne 3

HPLC of the major regioisomer 4fb from the reaction between 4-chlorobenzamide (1f) and diyne 3 after purification

D-7000 HSM: kleomenis Series: 1124 Report: original System: Sys 1

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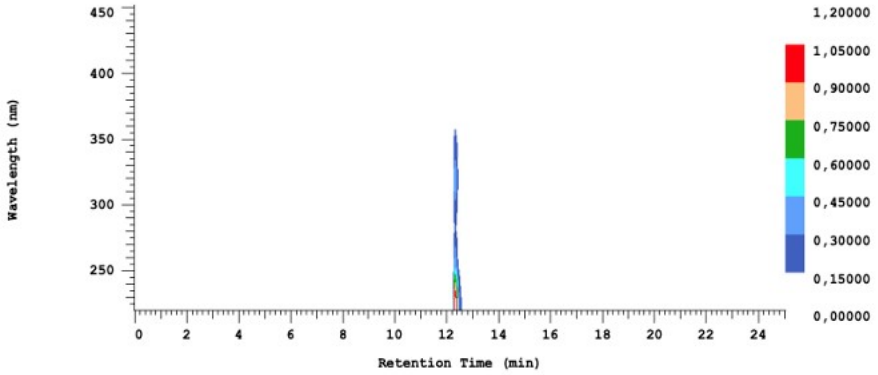
Spectral Bandwidth: AUTO Spectral Interval: 1600 ms



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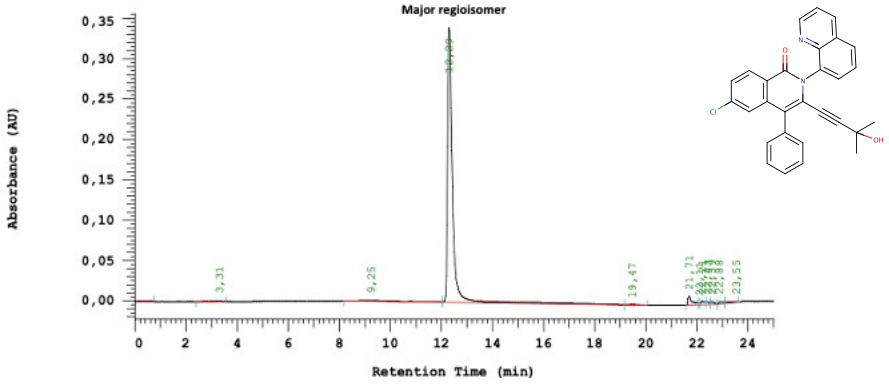

Acquisition Method: Prasad gradient update
Column Type: Developed by: Prasad
Pump A Type: L-7100
Solvent A: Solvent B: IPA
Solvent C: Pet Ether
Method Description:

Chrom Type: Fixed WL Chromatogram, 330 nm
Peak Quantitation: AREA

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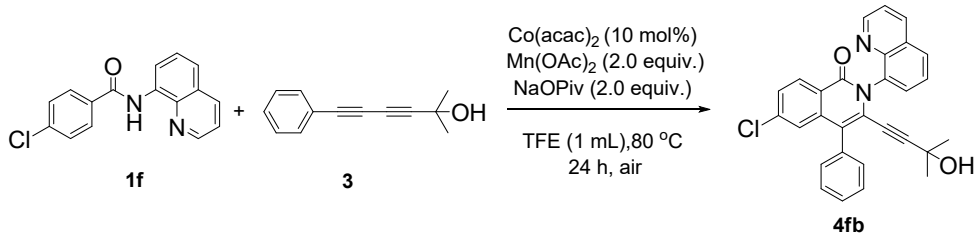
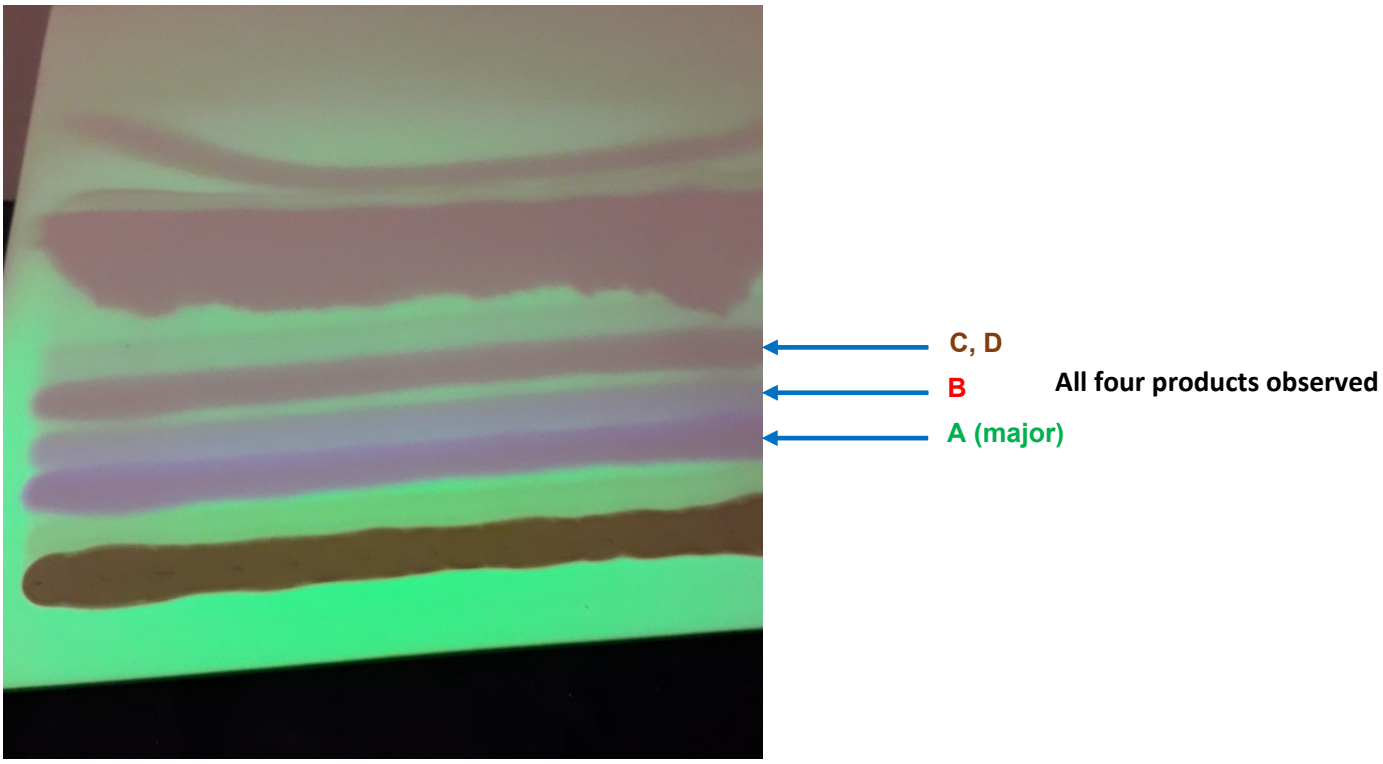
Preparative TLC chromatography example



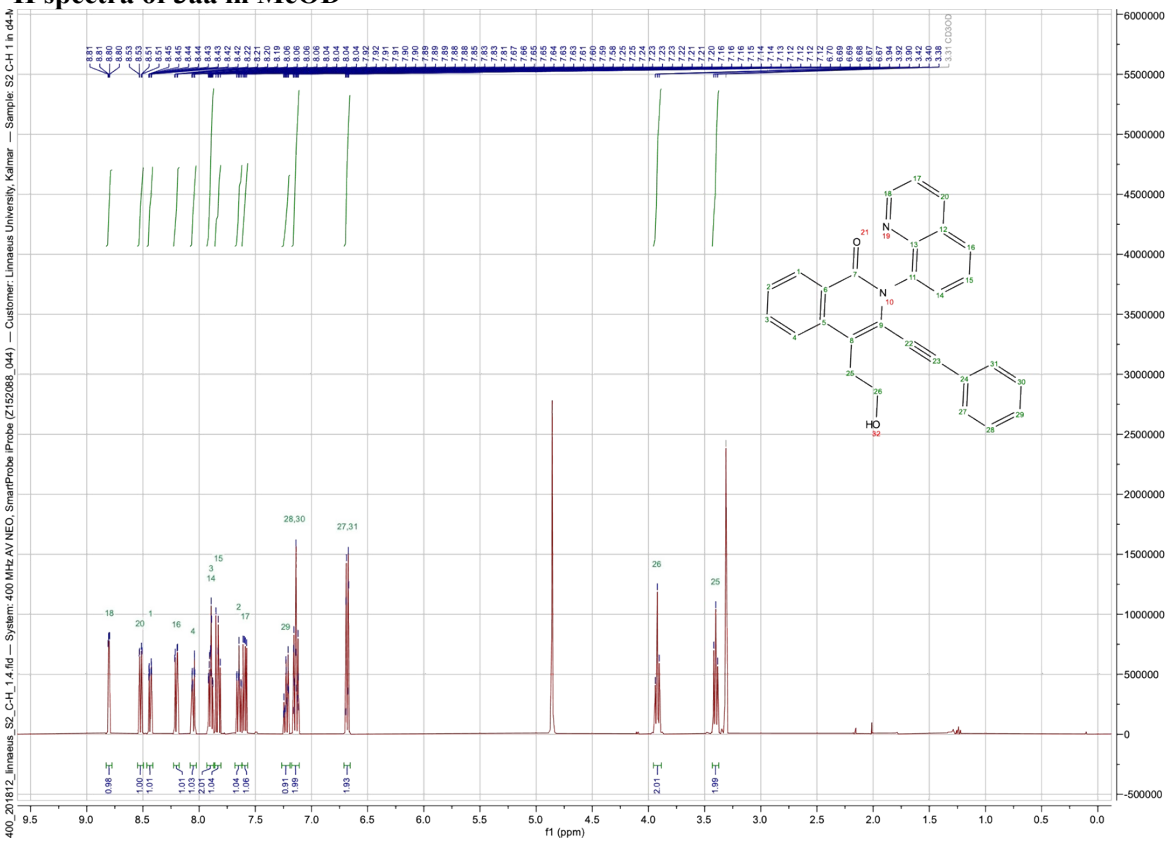


TLC condition: Petroleum ether/2-propanol (90:10)

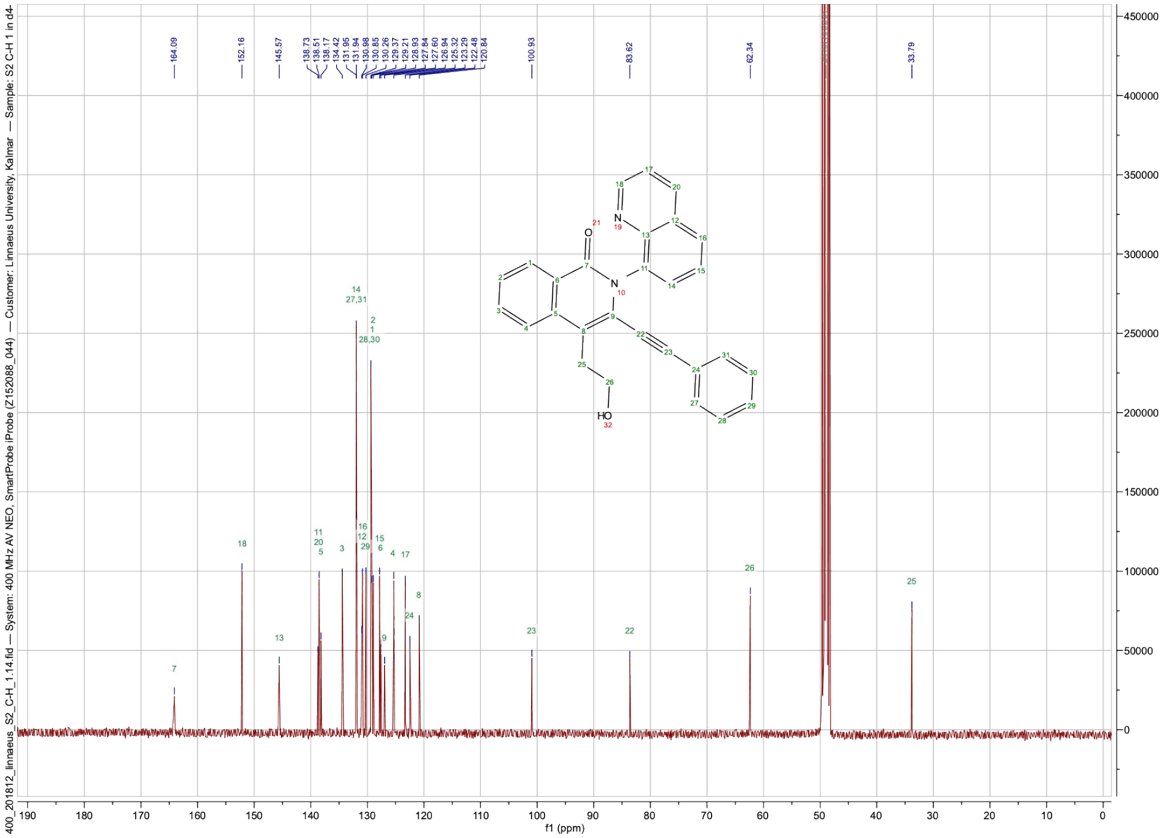
NMR & HRMS spectra

3aa

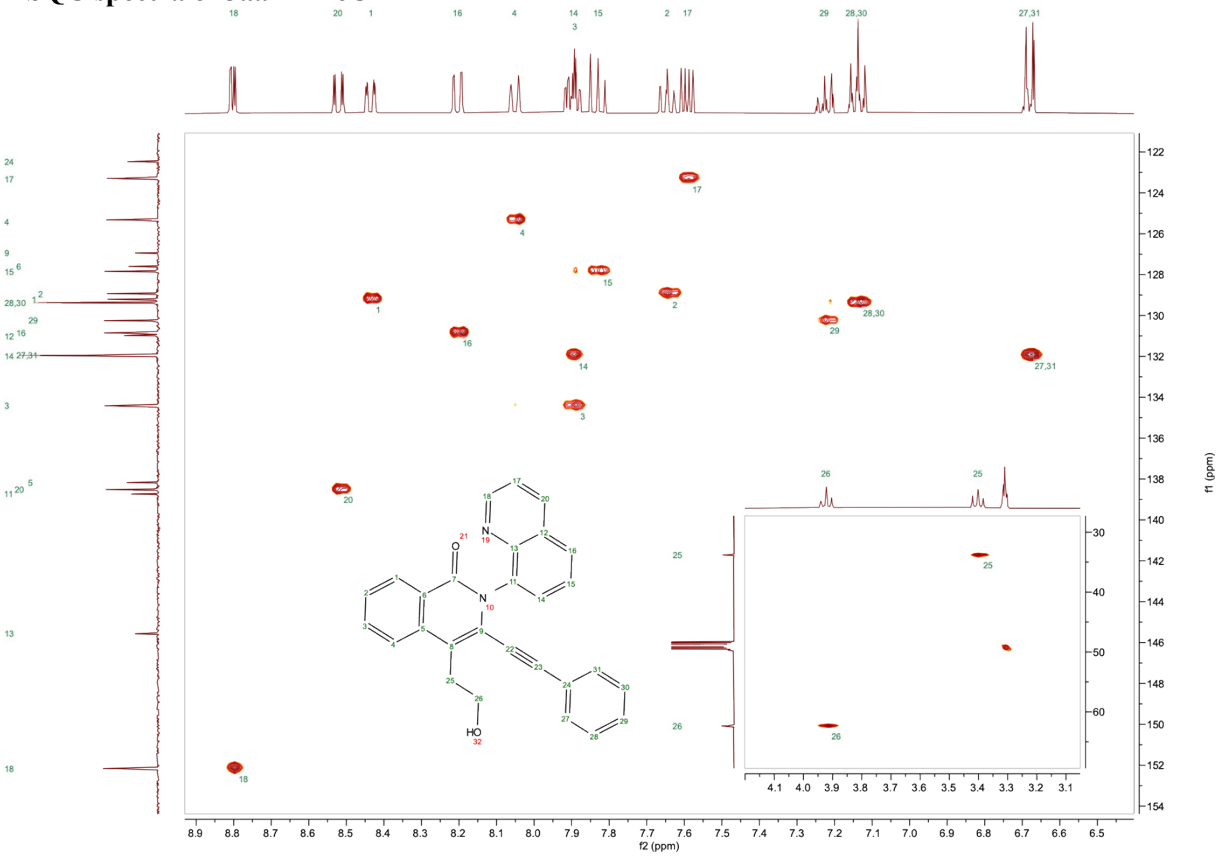
^{1}H spectra of 3aa in MeOD



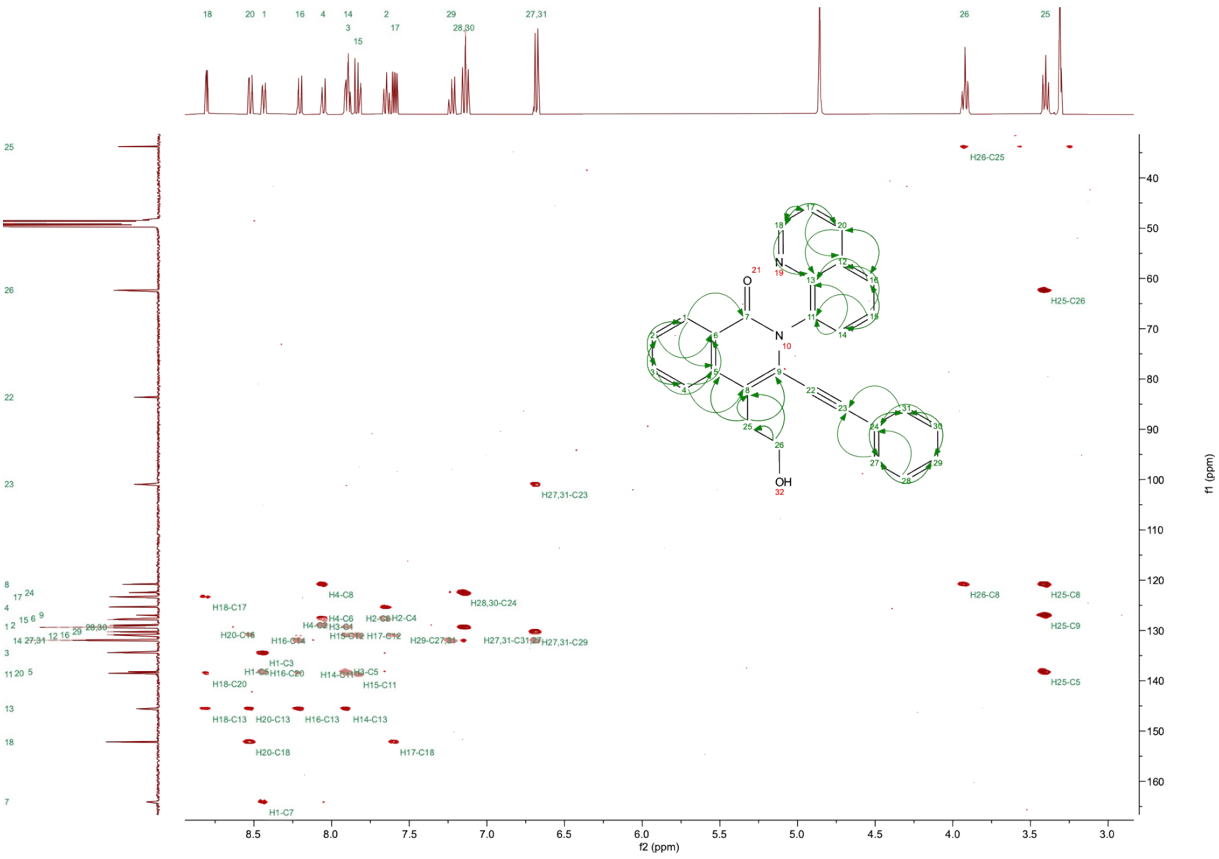
^{13}C spectra of 3aa in MeOD



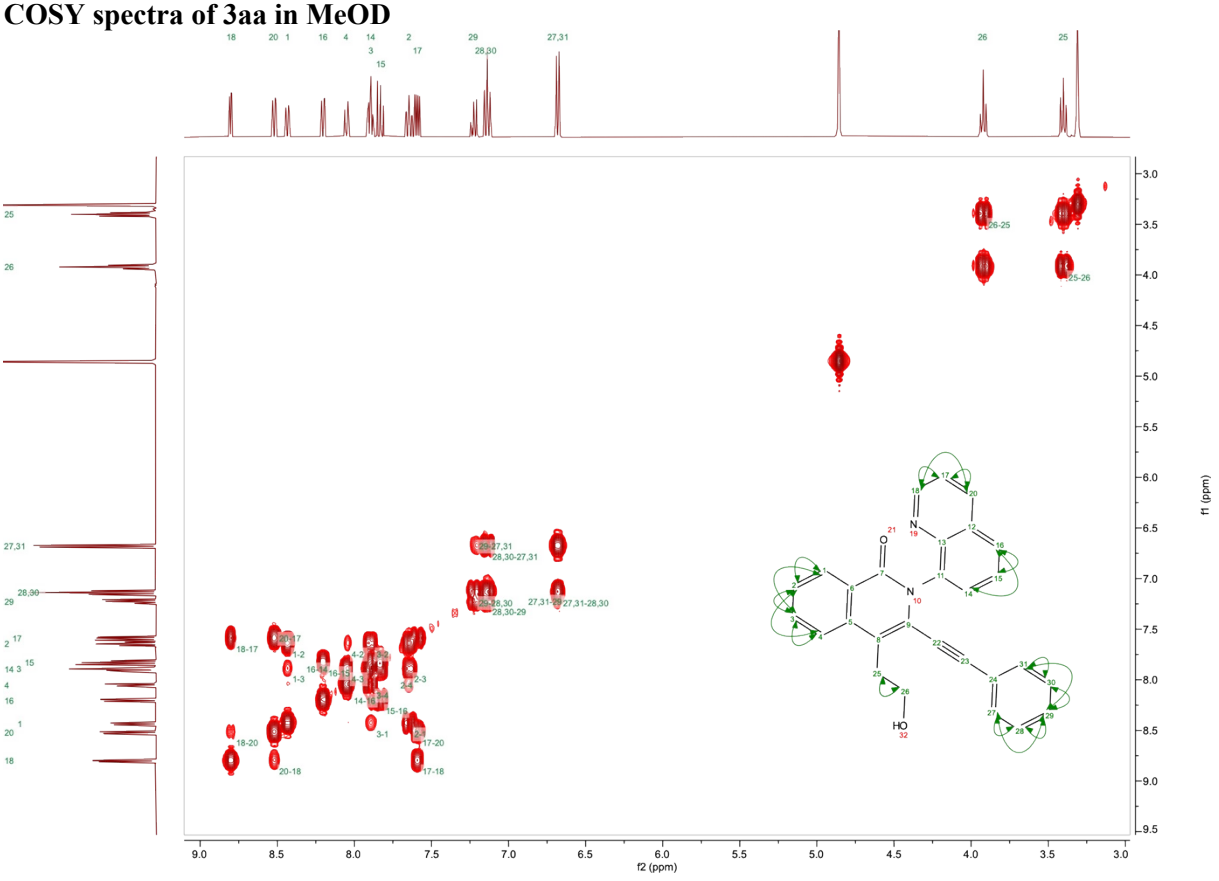
HSQC spectra of 3aa in MeOD



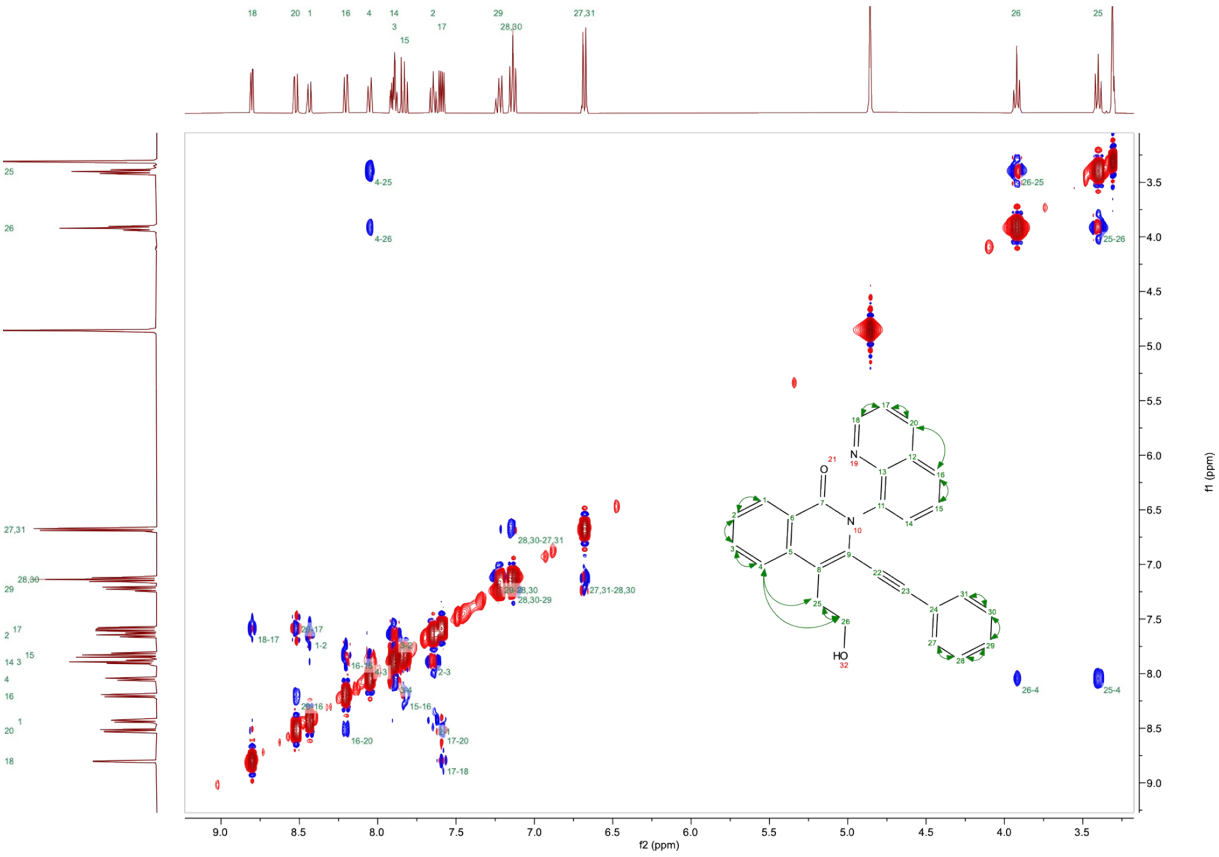
HMBC spectra of 3aa in MeOD



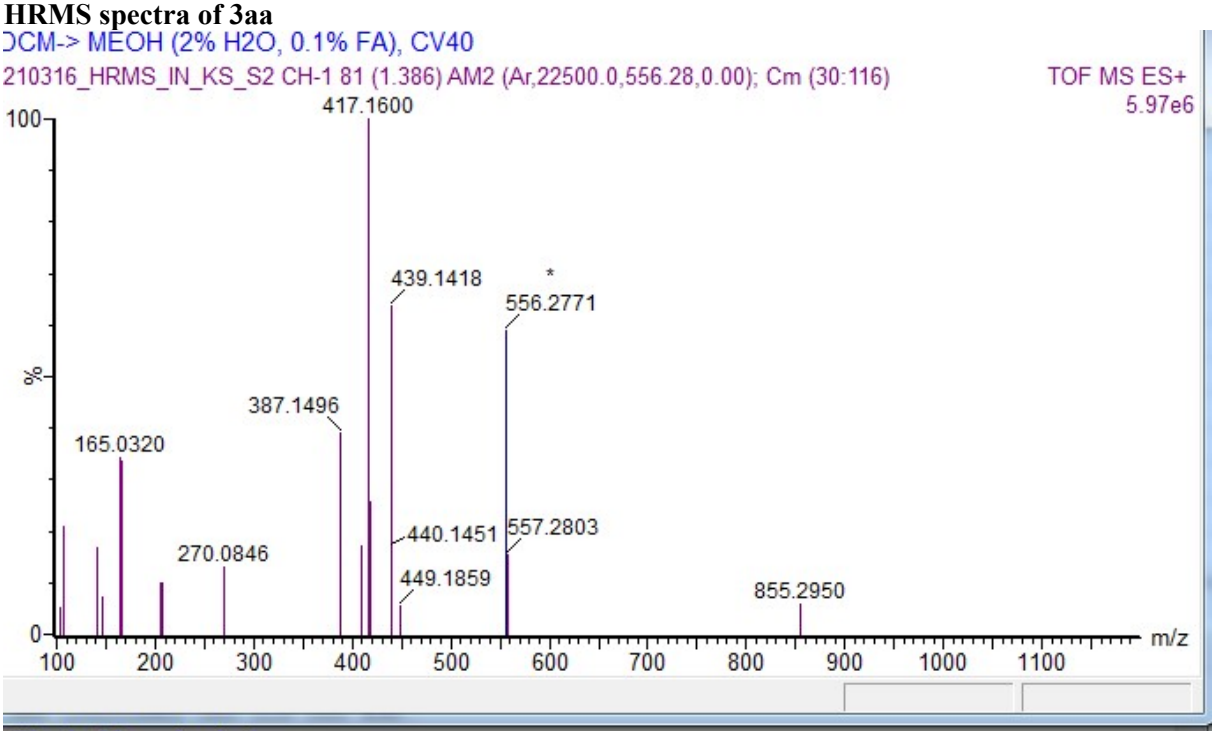
COSY spectra of 3aa in MeOD



NOESY spectra of 3aa in MeOD



HRMS spectra of 3aa



Single Mass Analysis

Tolerance = 2.0 mDa / DBE: min = -0.5, max = 100.0

Element prediction: Off

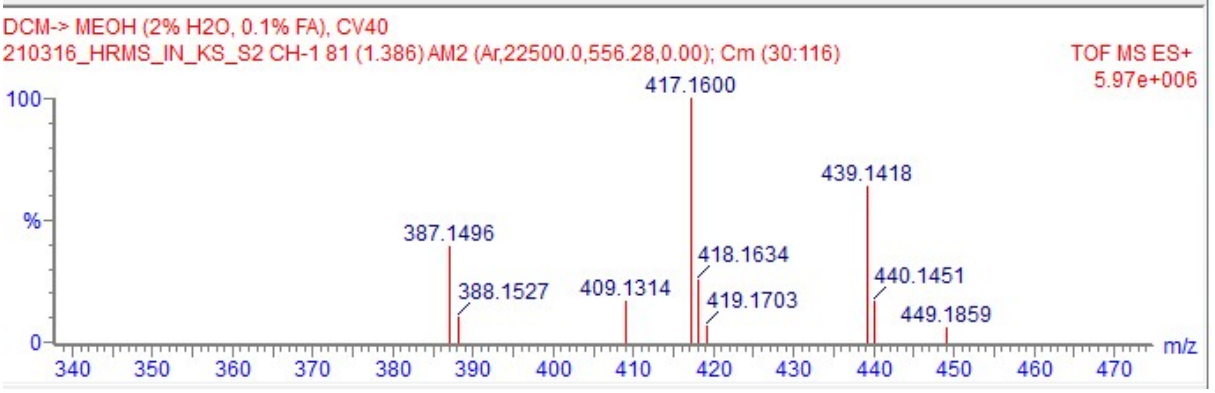
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

163 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

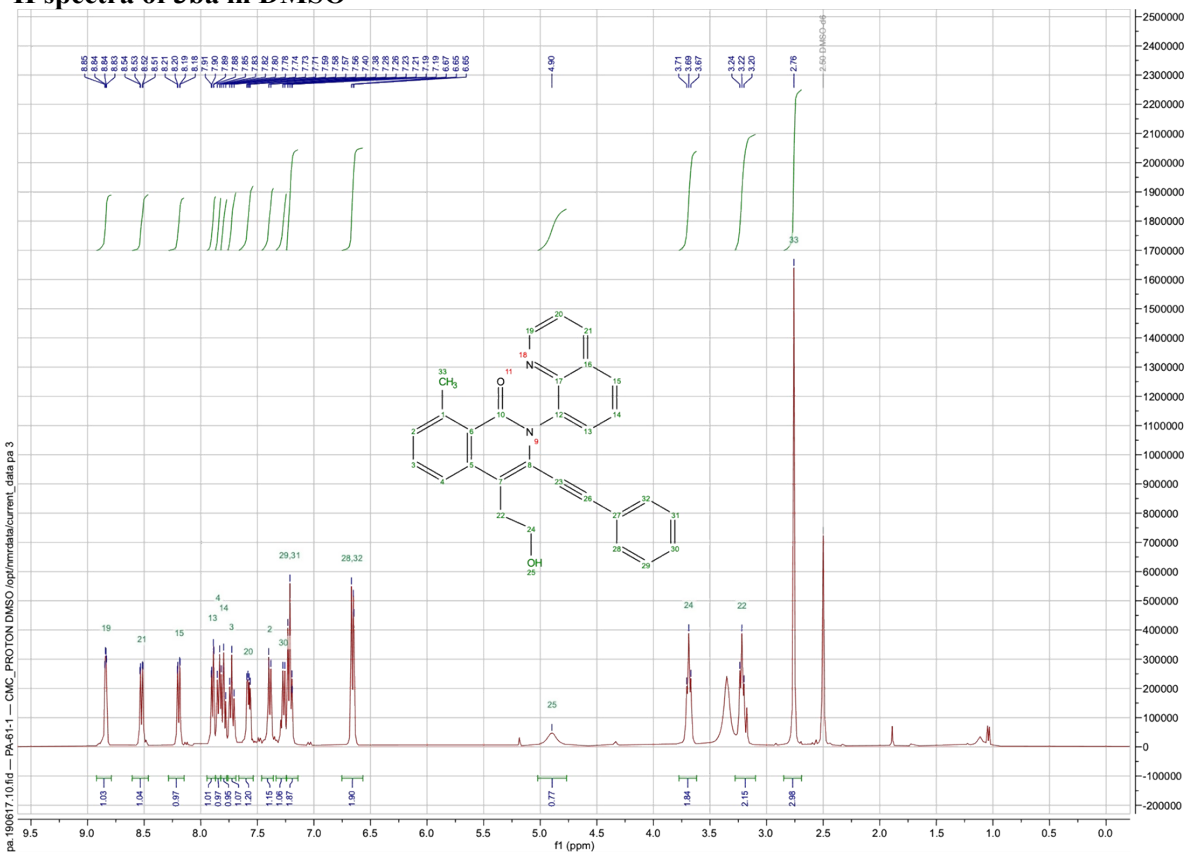
Elements Used:

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT Norm	Fit Conf %	C	H	N	O	Na
417.1600	417.1603	-0.3	-0.7	19.5	C28 H21 N2 O2	1.501	60.57	28	21	2	2	
	417.1619	-1.9	-4.6	20.5	C31 H22 Na	1.931	39.43	31	22			1

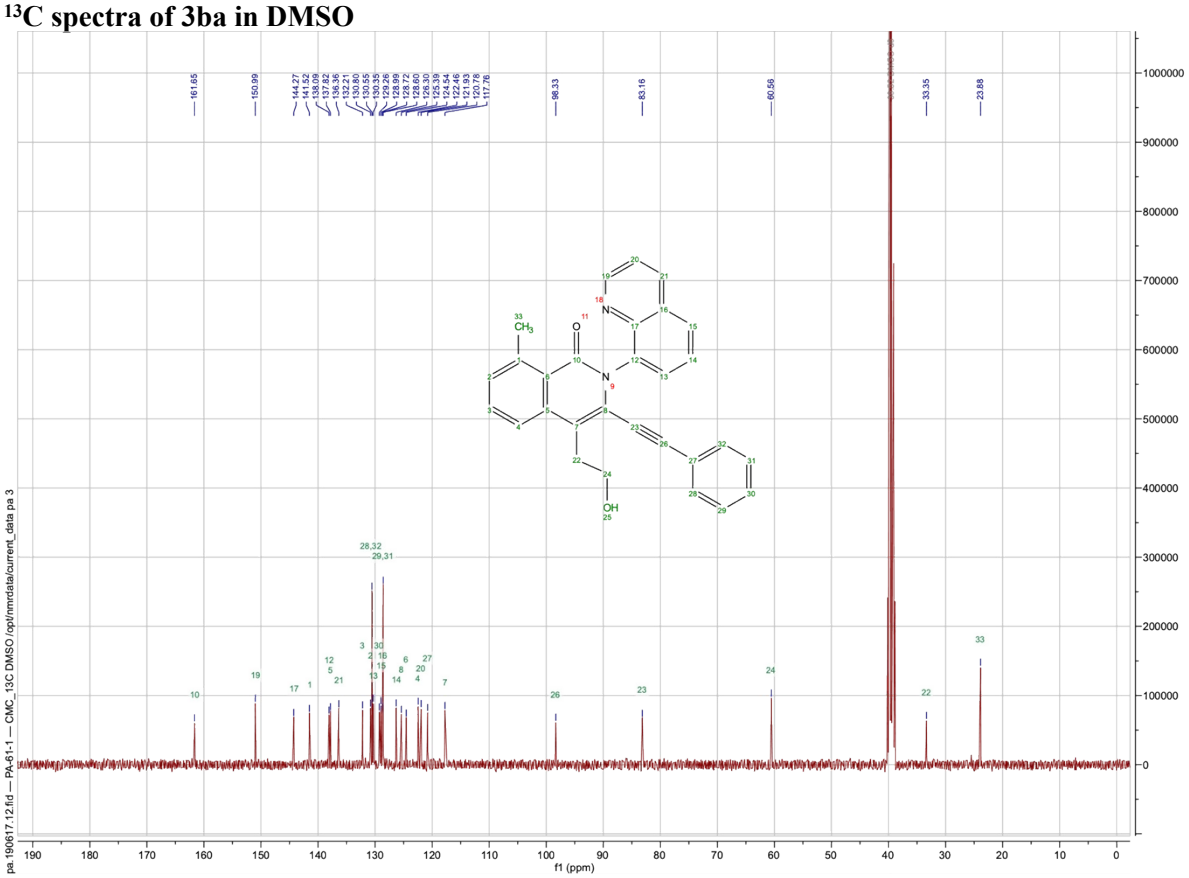


3ba

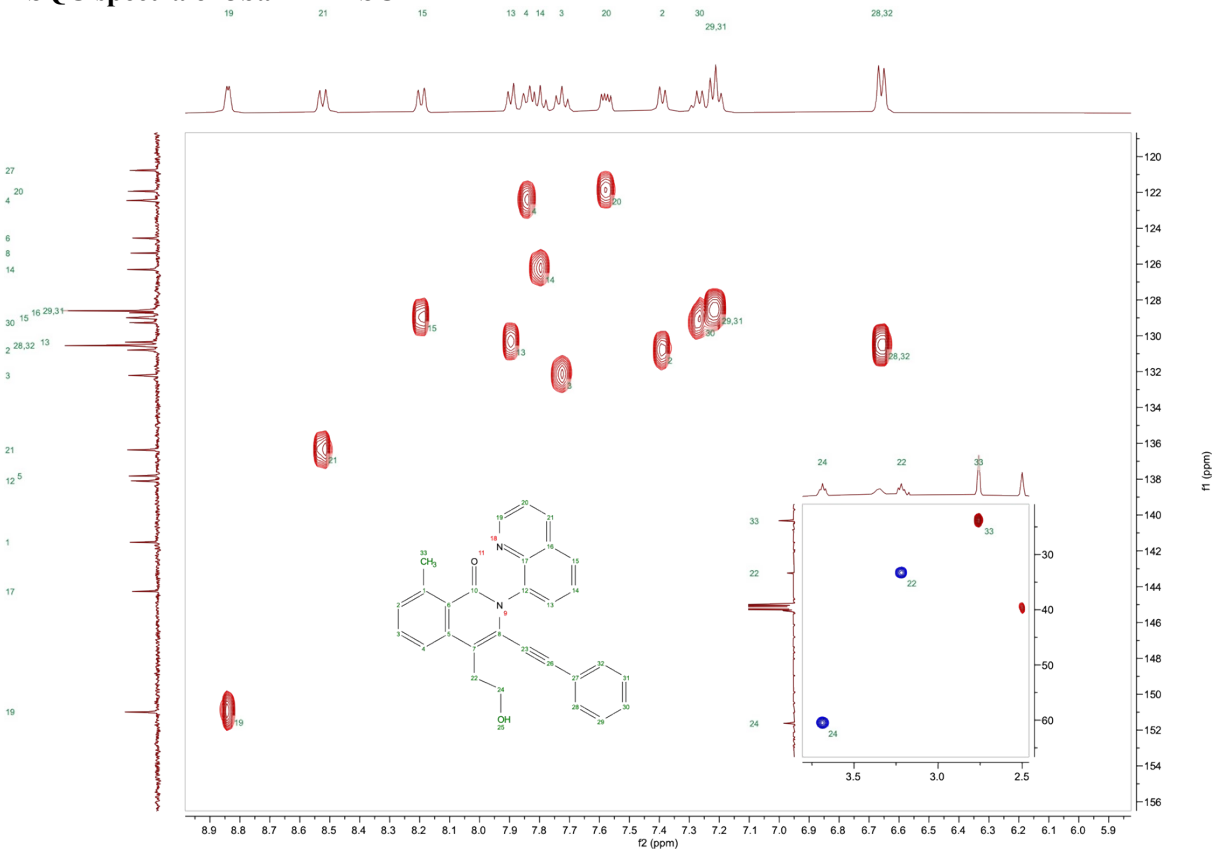
^{1}H spectra of 3ba in DMSO



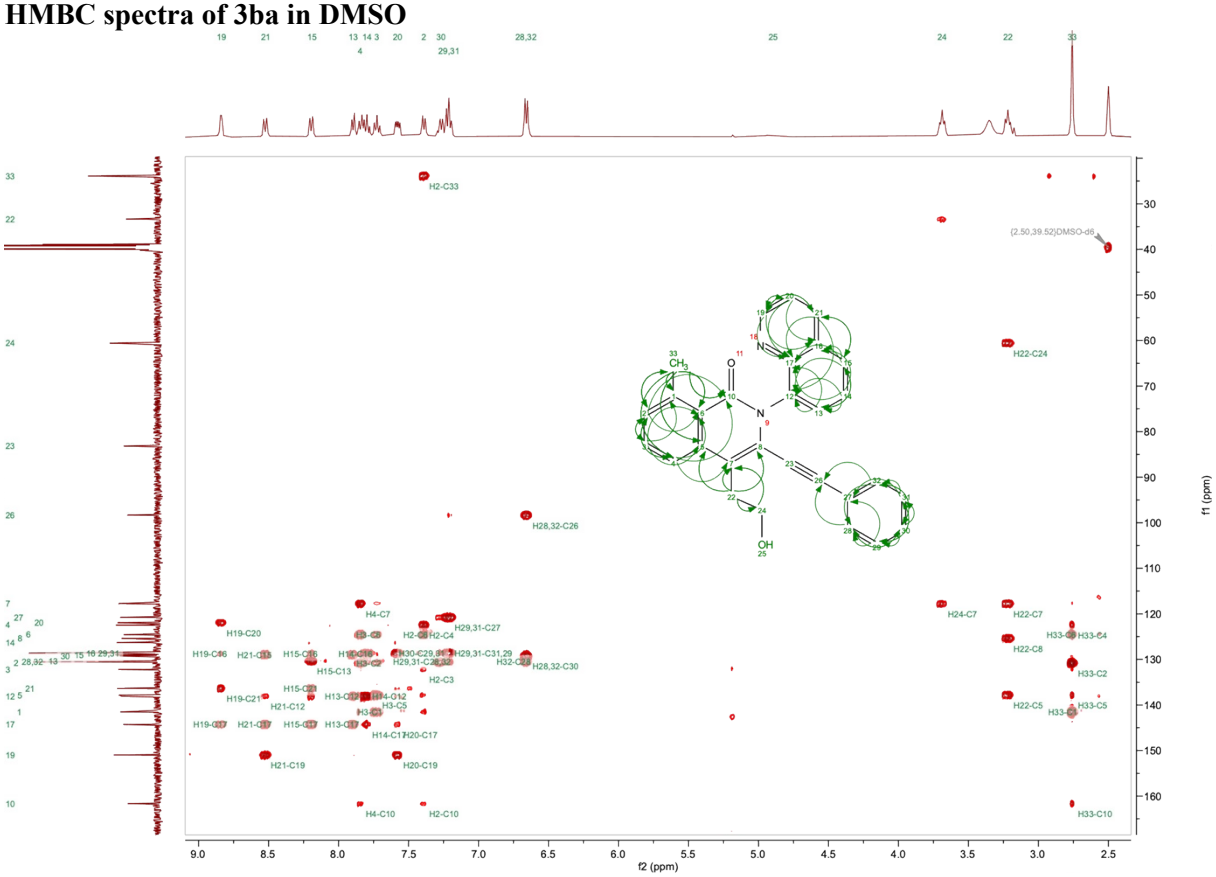
^{13}C spectra of 3ba in DMSO



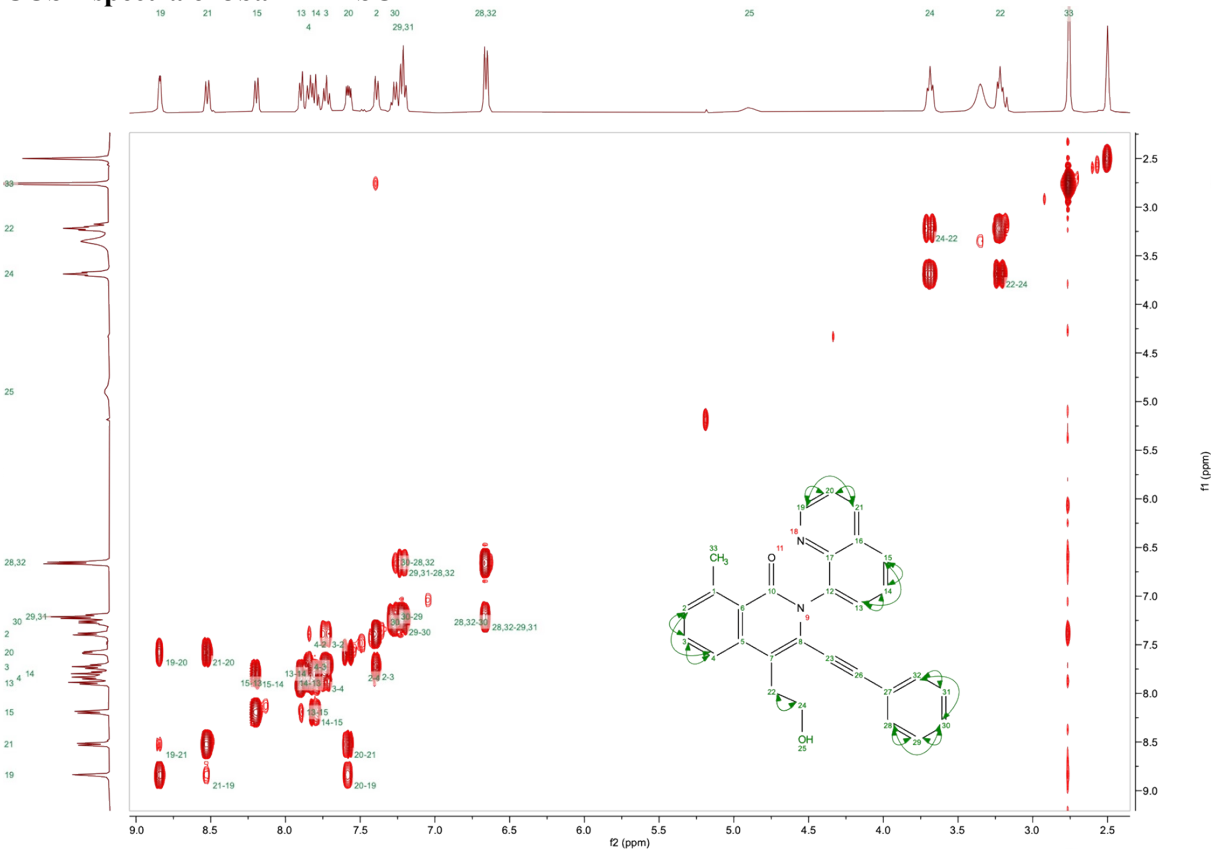
HSQC spectra of 3ba in DMSO



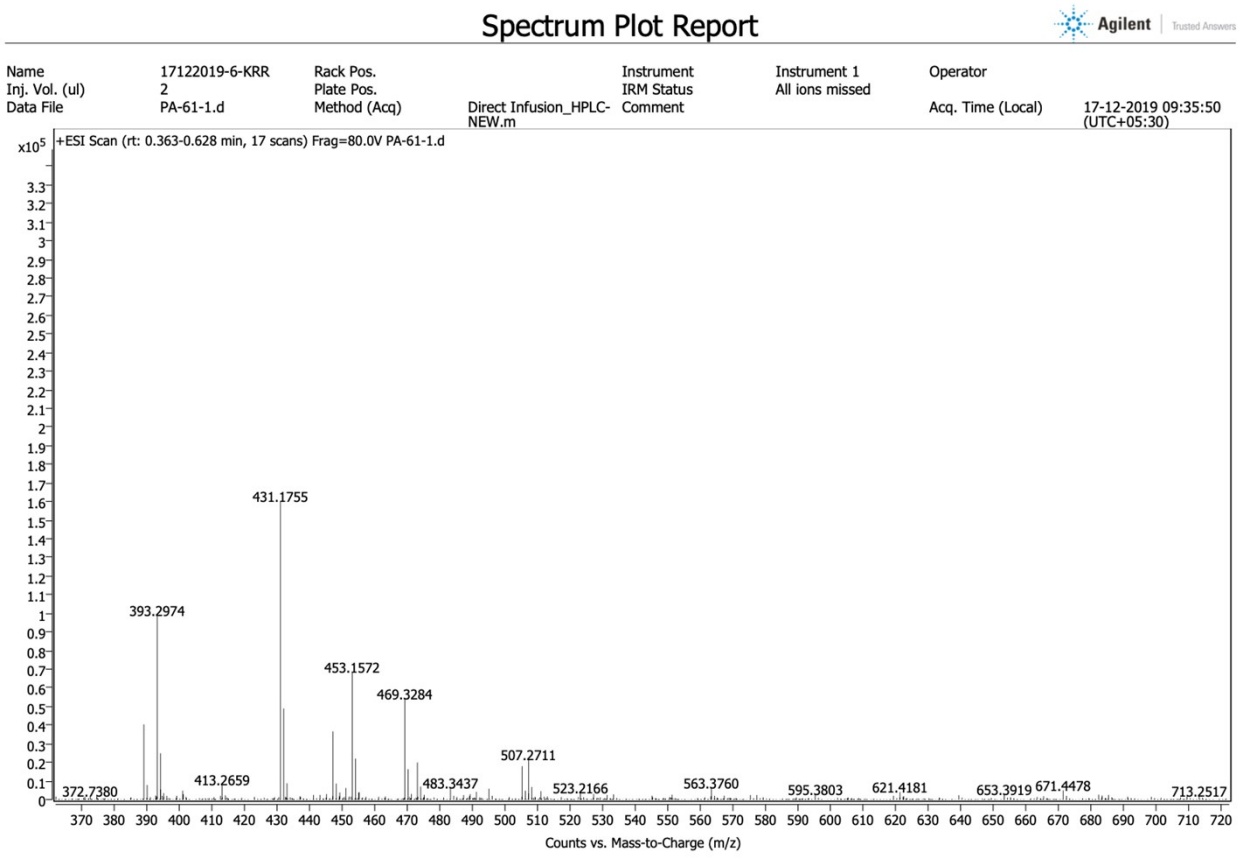
HMBC spectra of 3ba in DMSO



COSY spectra of 3ba in DMSO



HRMS spectra of 3ba



3ca

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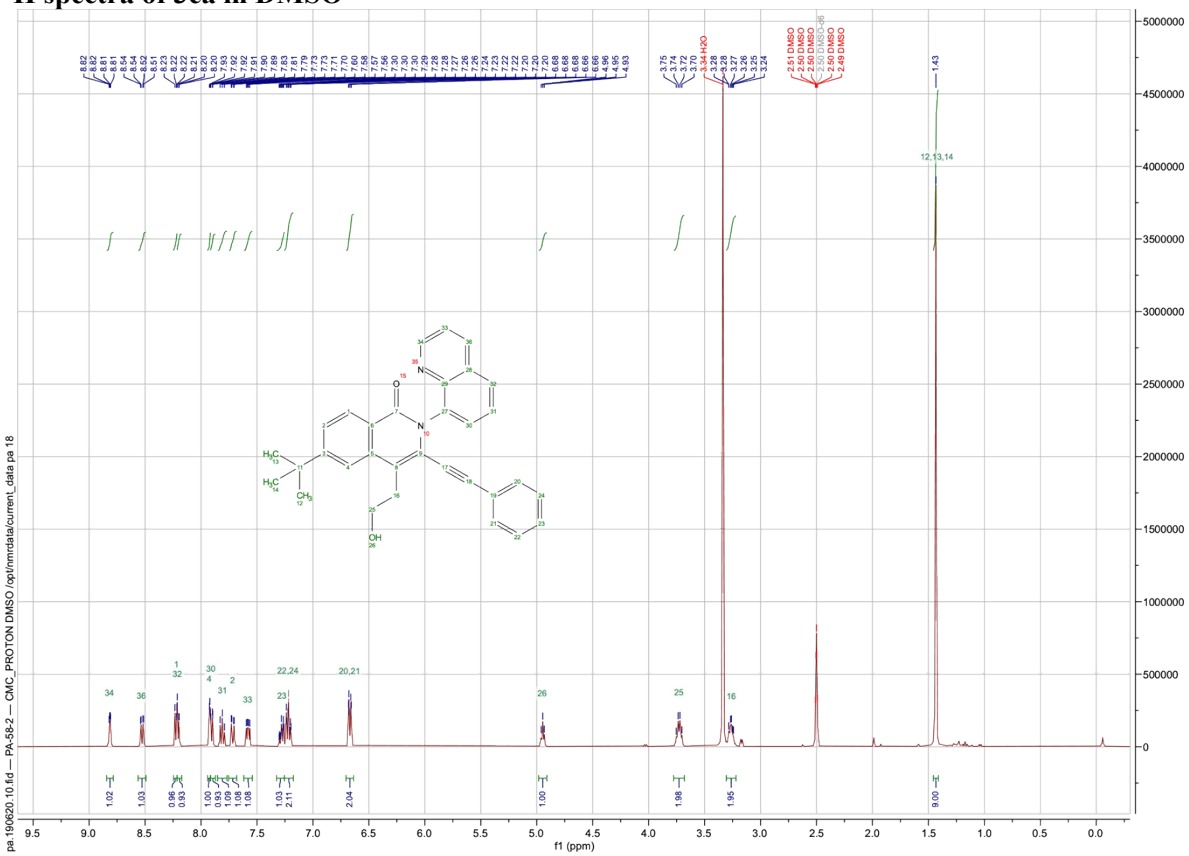
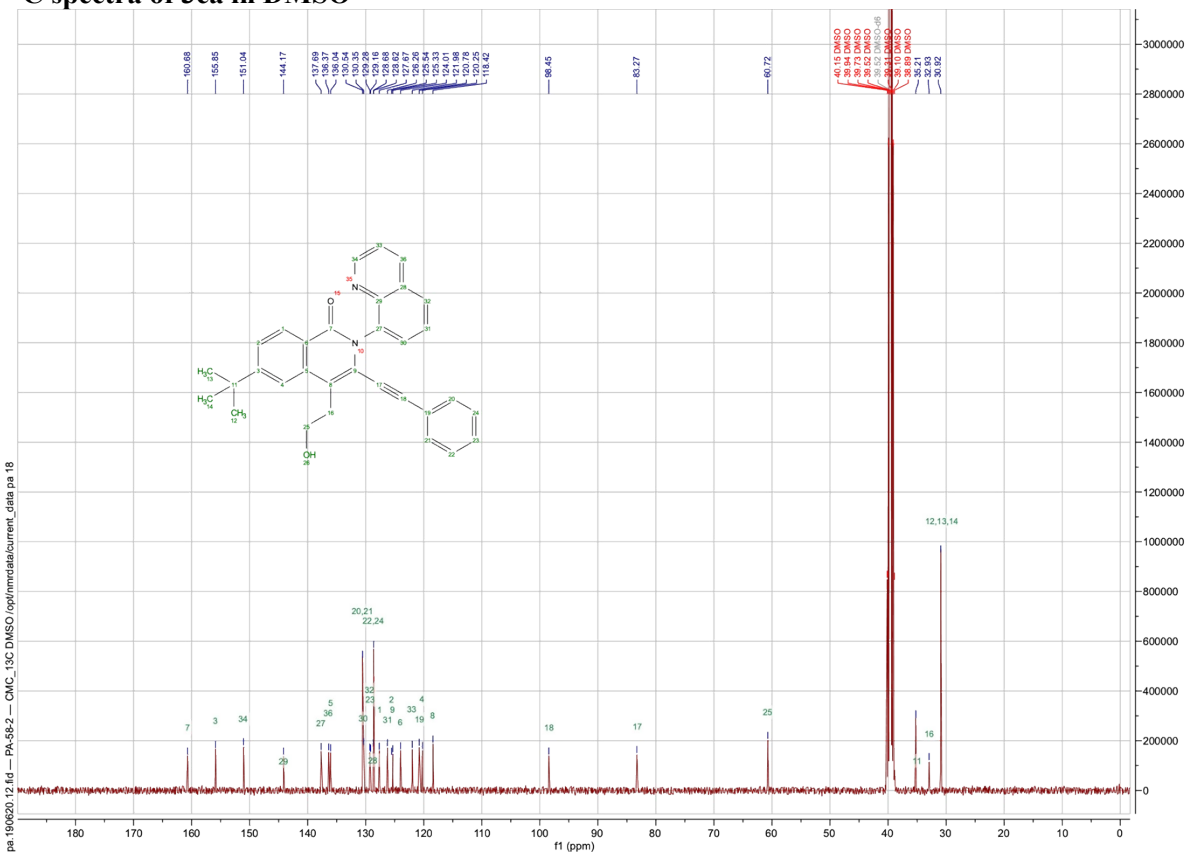
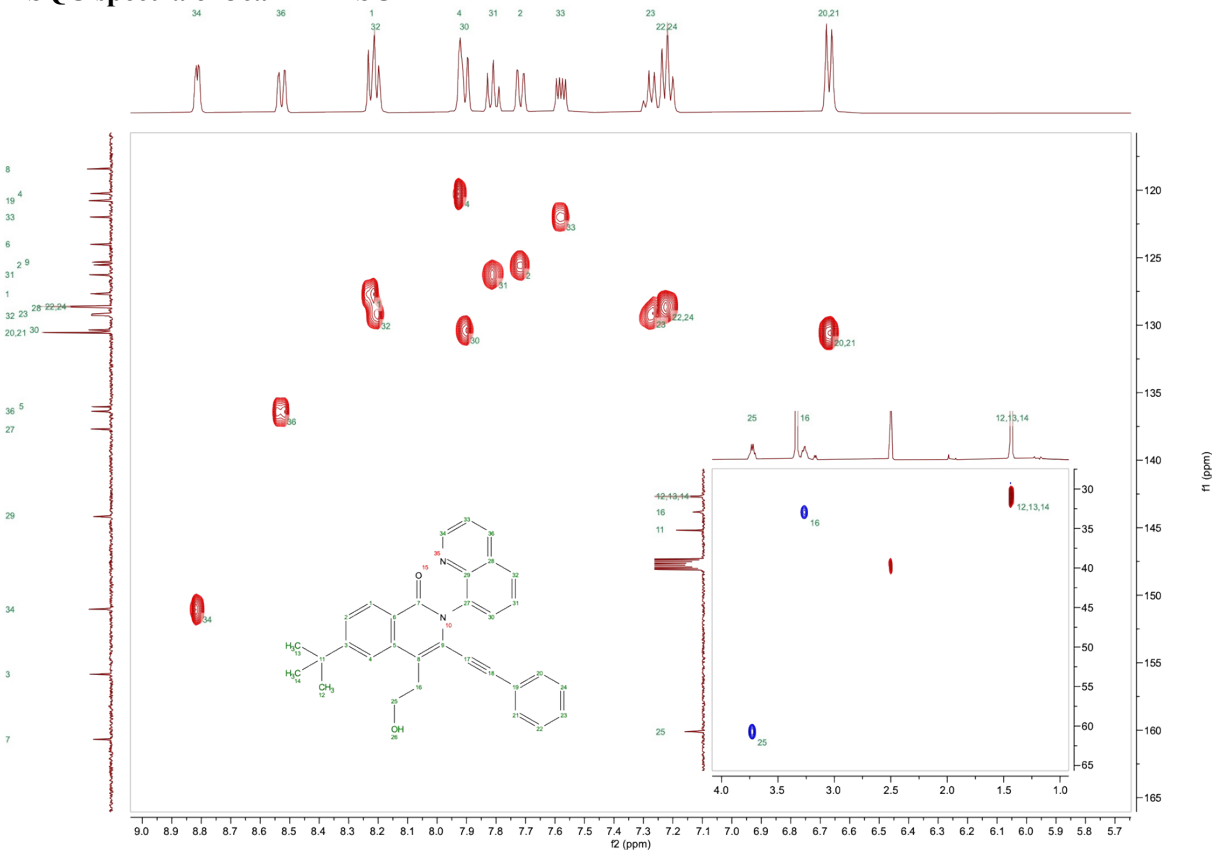


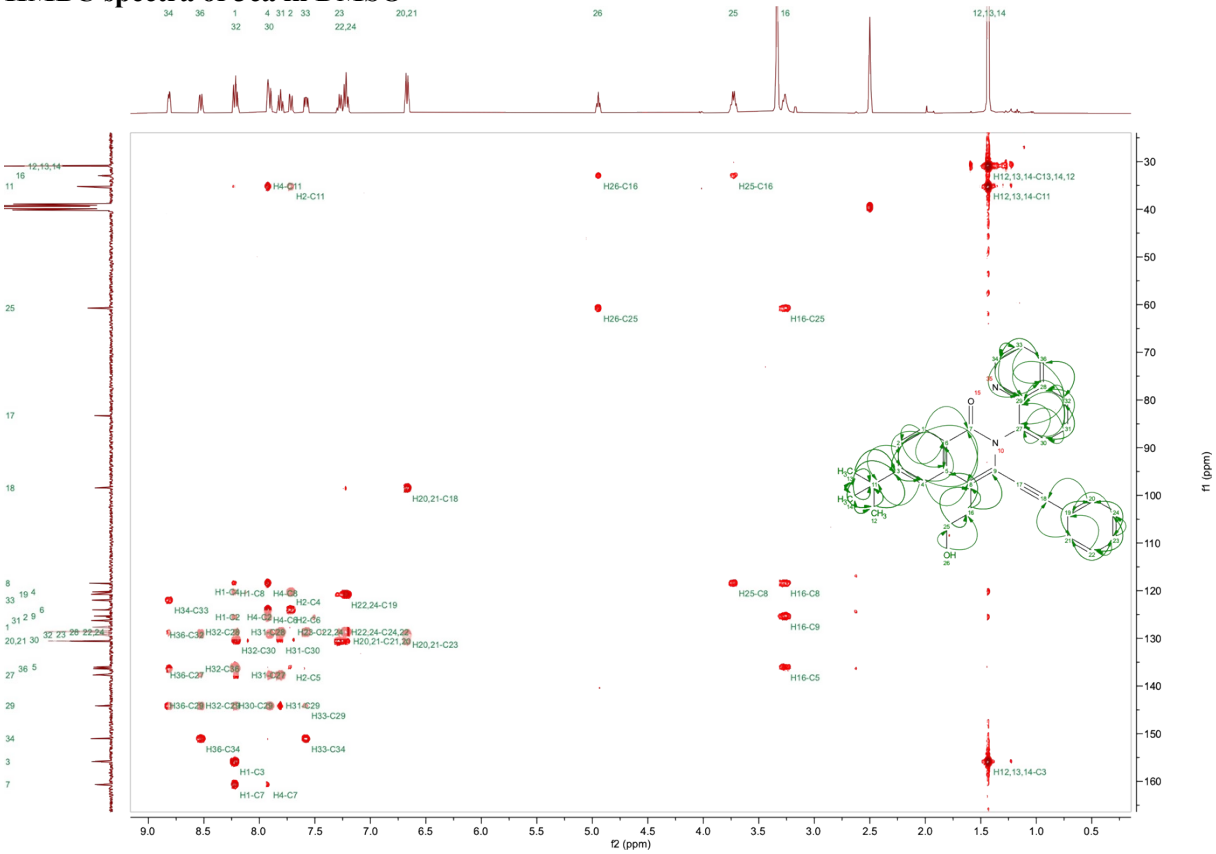
^{13}C spectra of 3ca in DMSO



HSQC spectra of 3ca in DMSO



HMBC spectra of 3ca in DMSO



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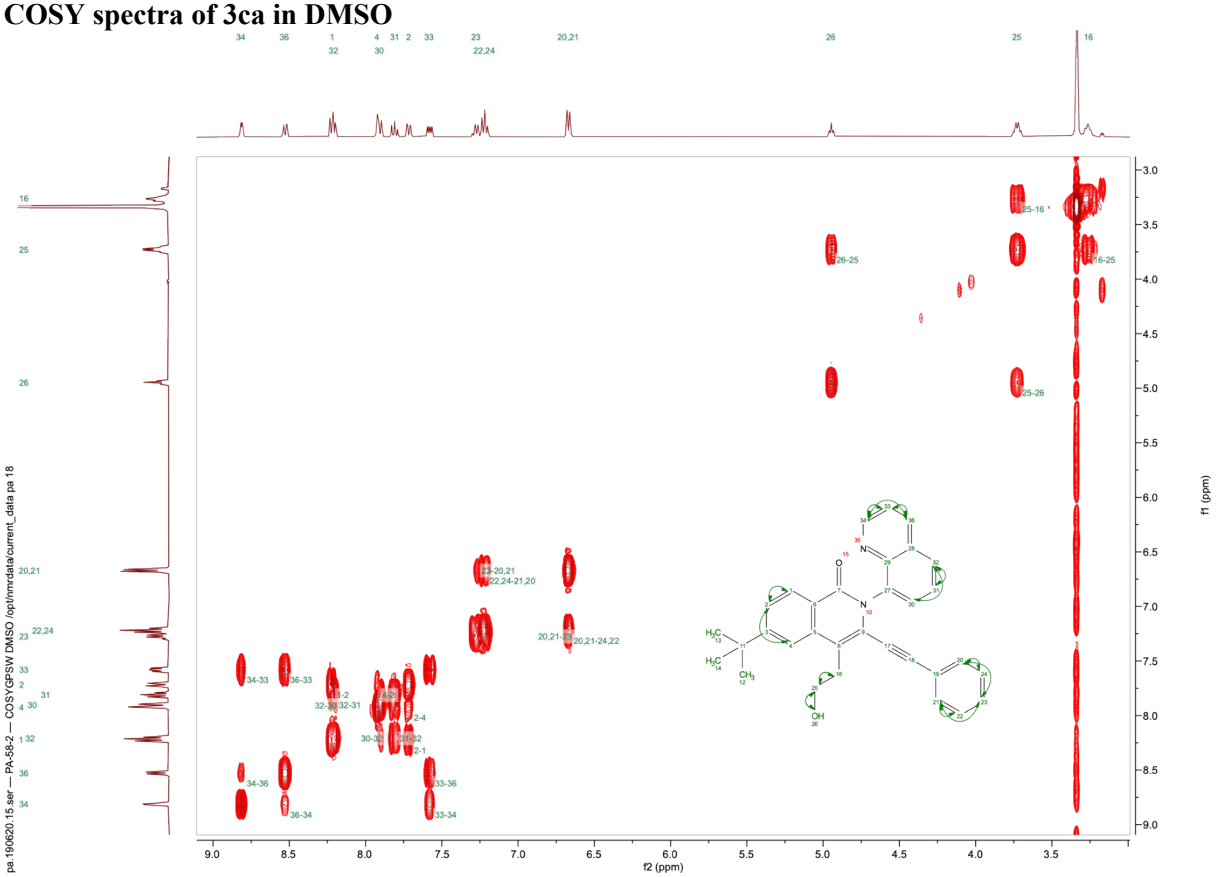
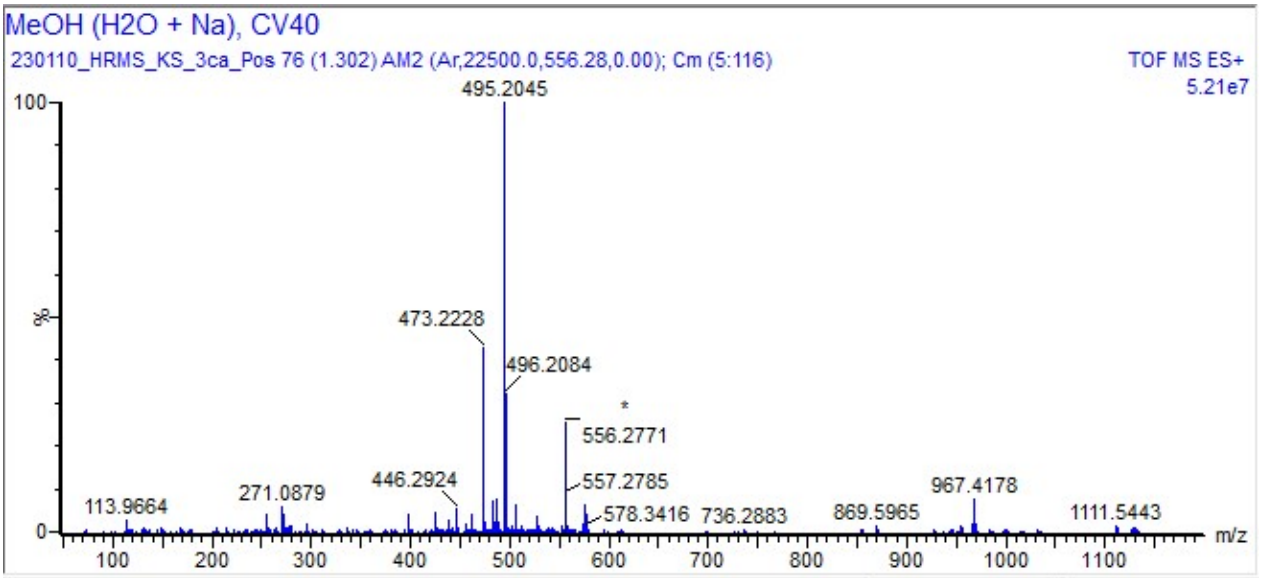


HRMS spectra of 3ca



Single Mass Analysis

Tolerance = 2.0 mDa / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

104 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 1-40 H: 1-40 N: 1-4 O: 1-4 Na: 0-1

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i..	Fit Conf %	C	H	N	O	Na
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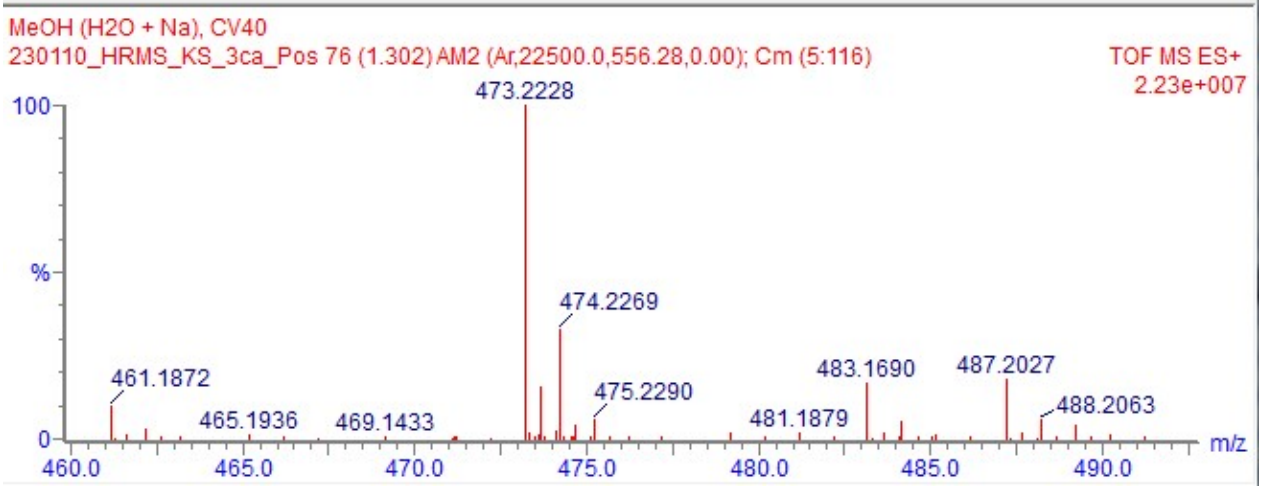
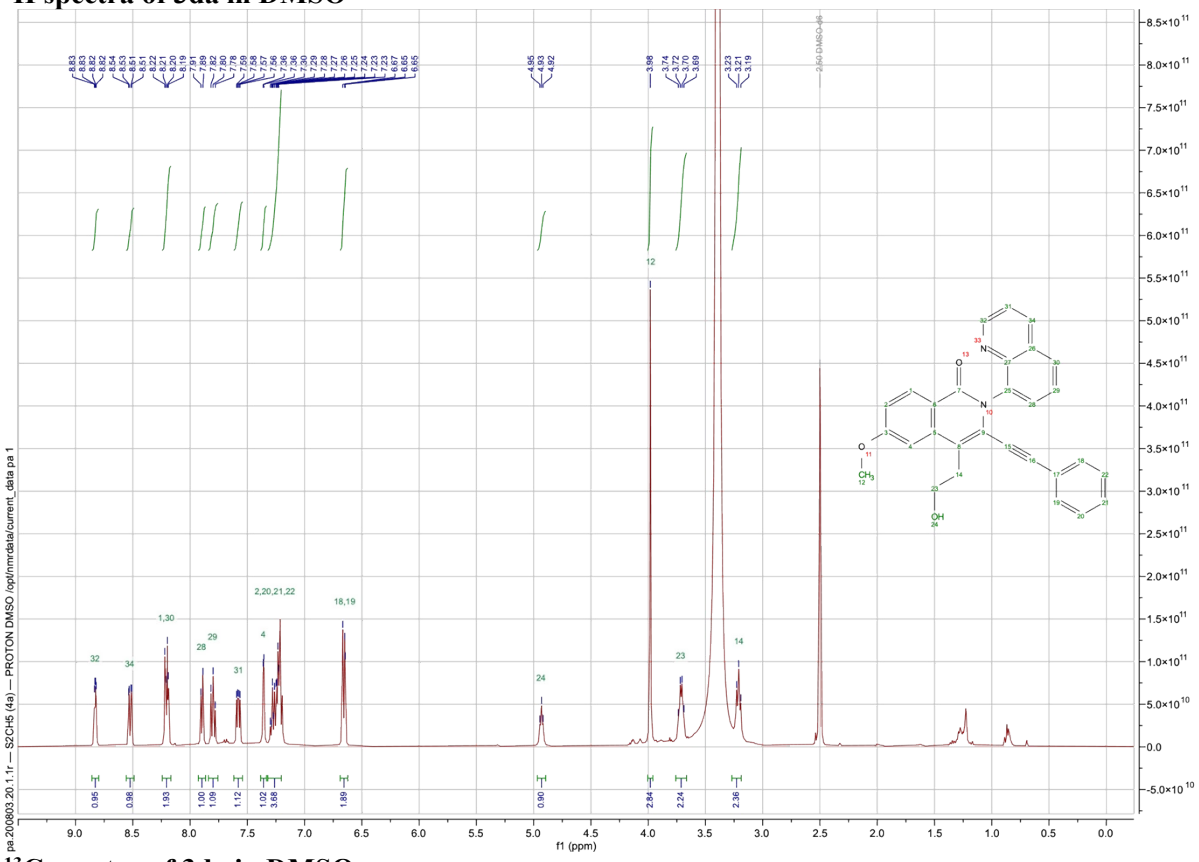
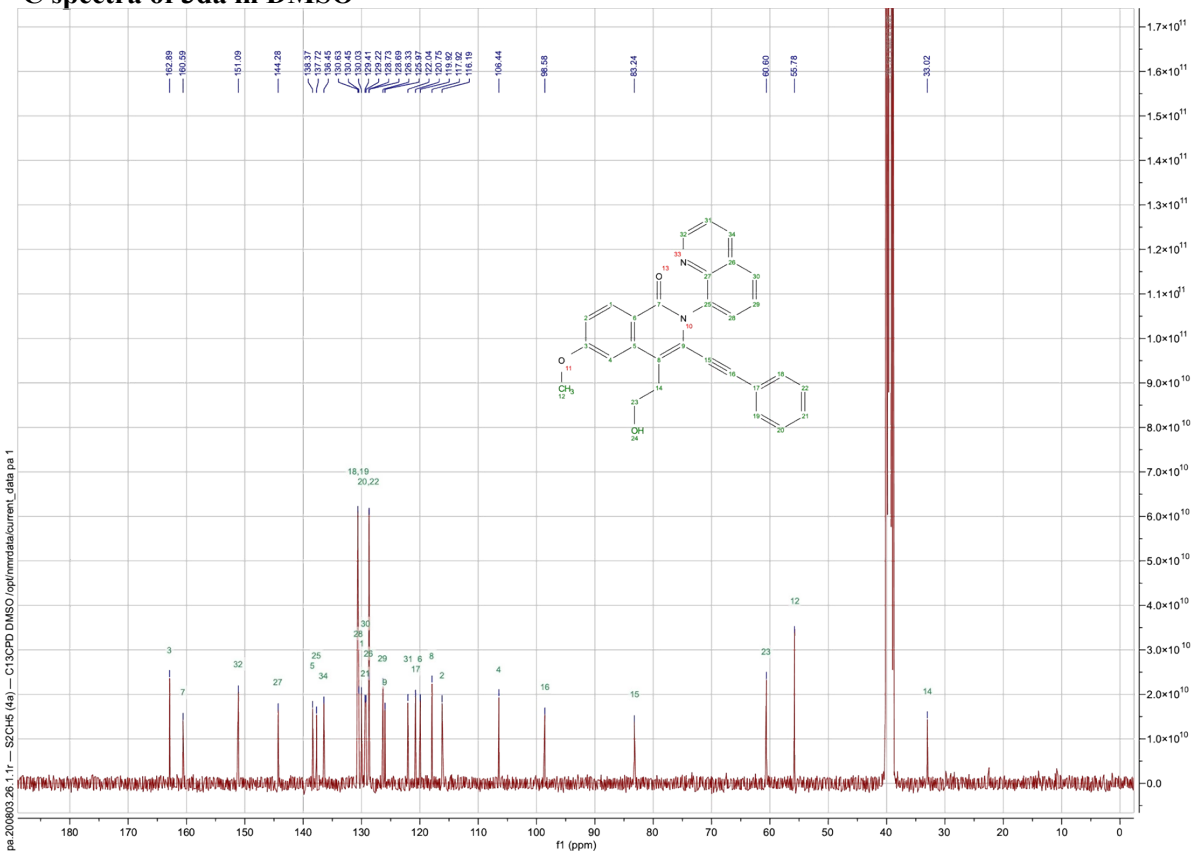


3da

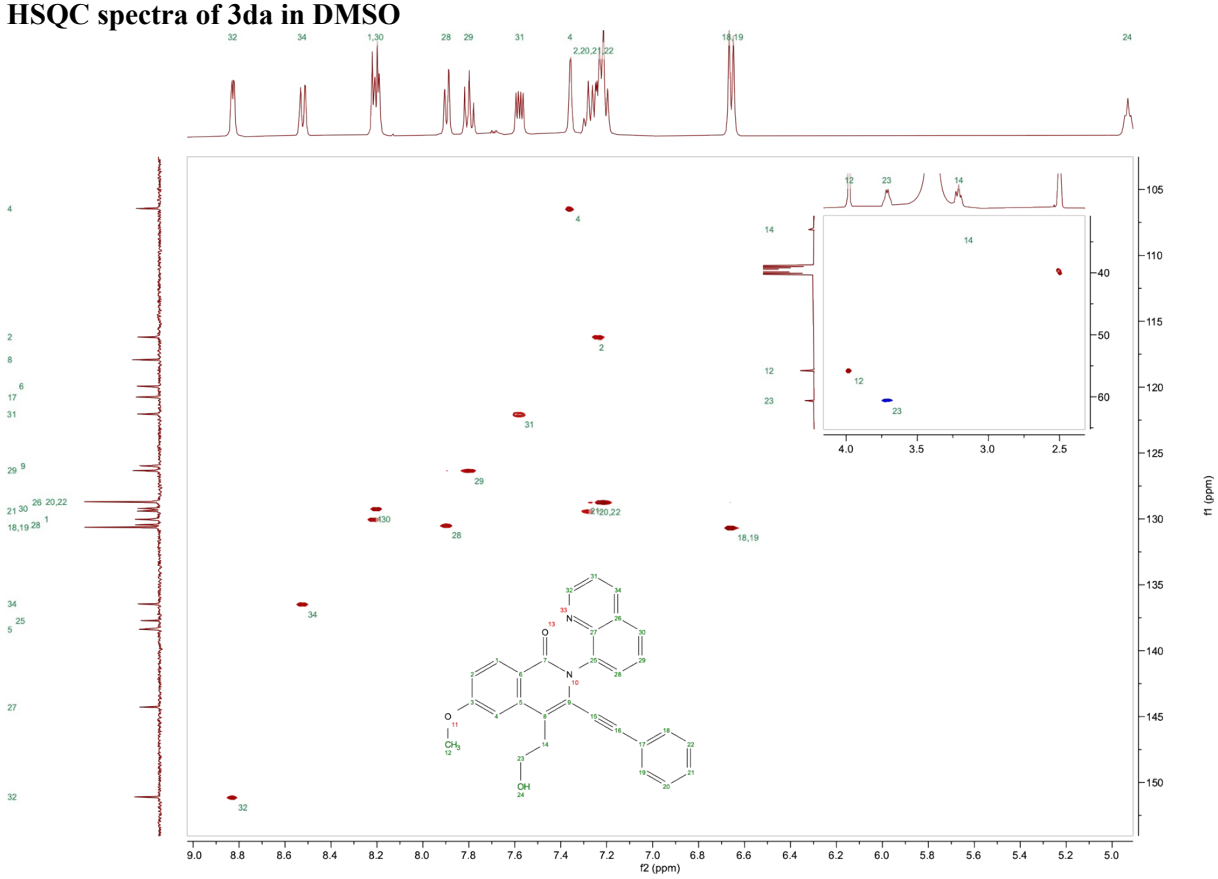
^{1}H spectra of 3da in DMSO



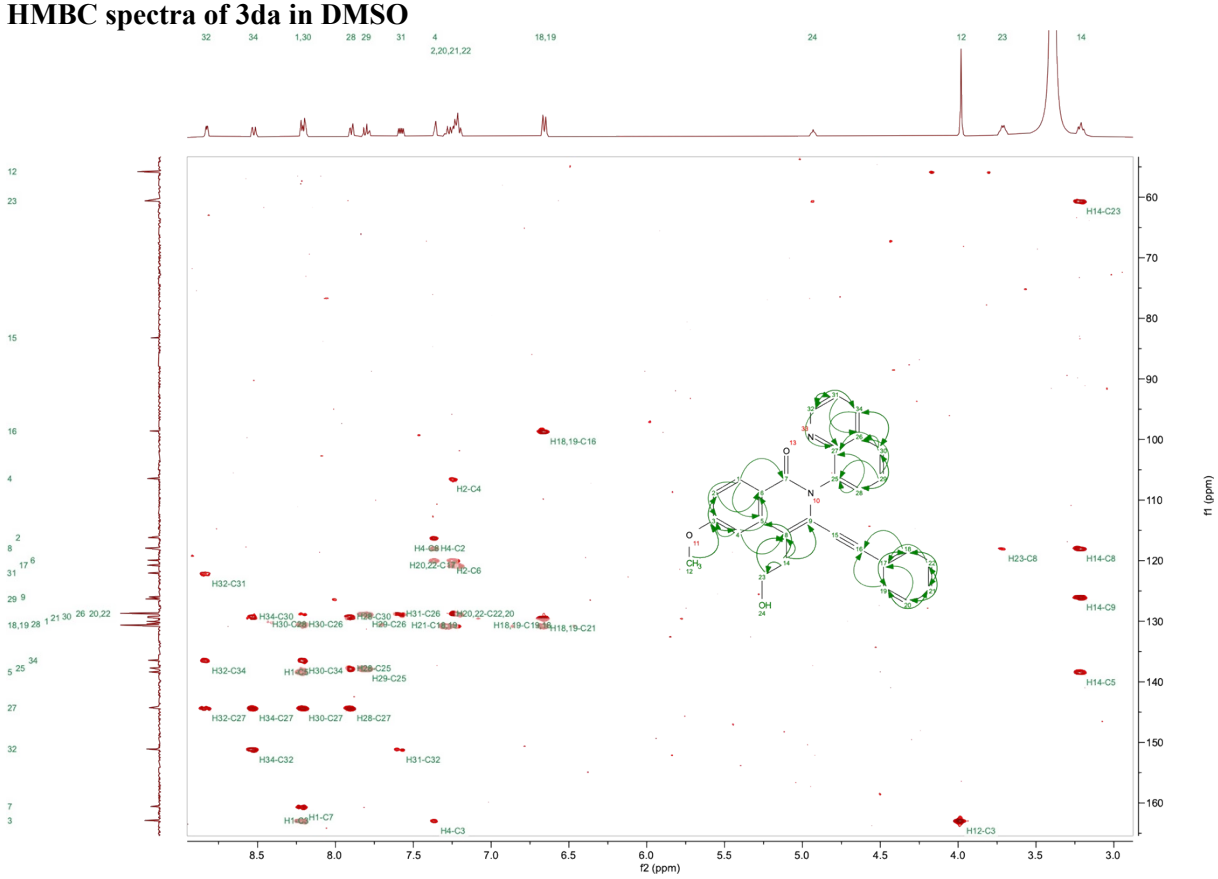
^{13}C spectra of 3da in DMSO



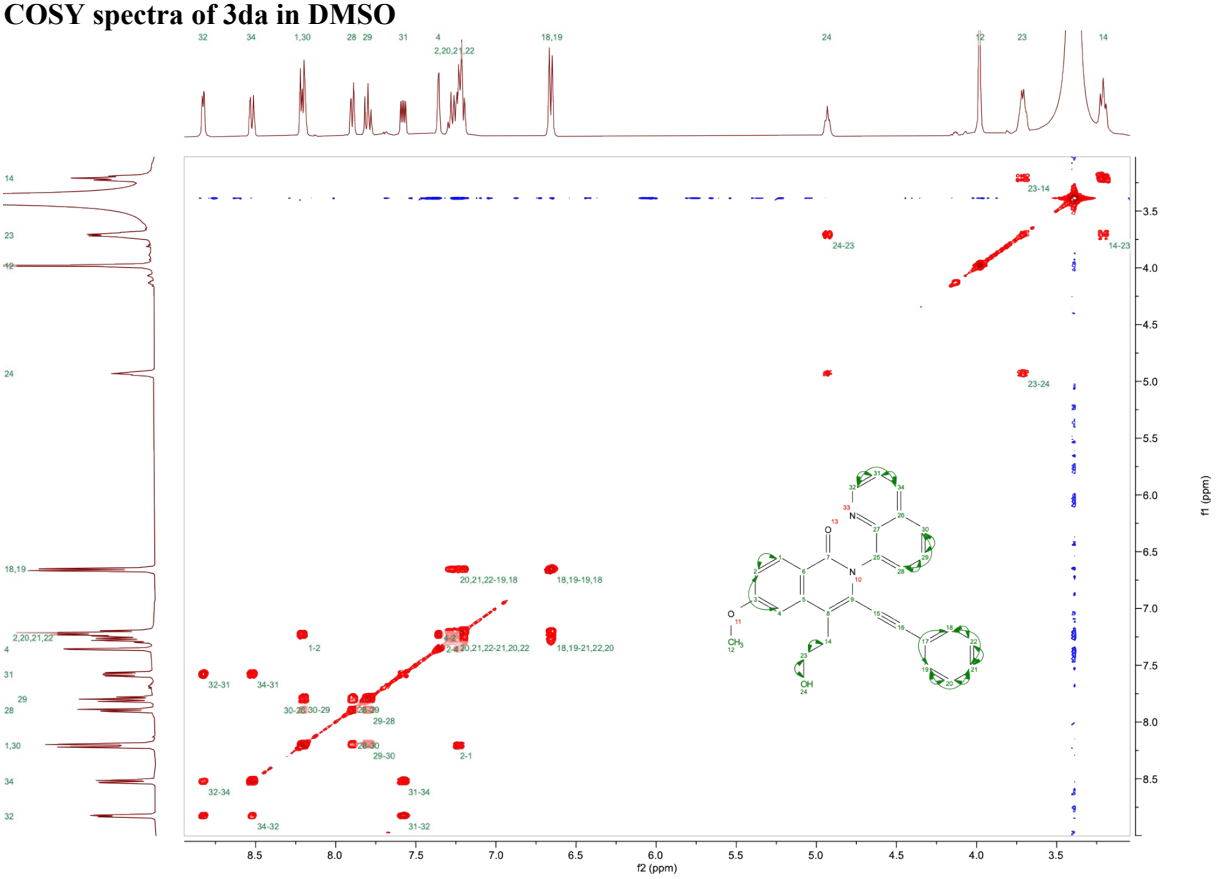
HSQC spectra of 3da in DMSO



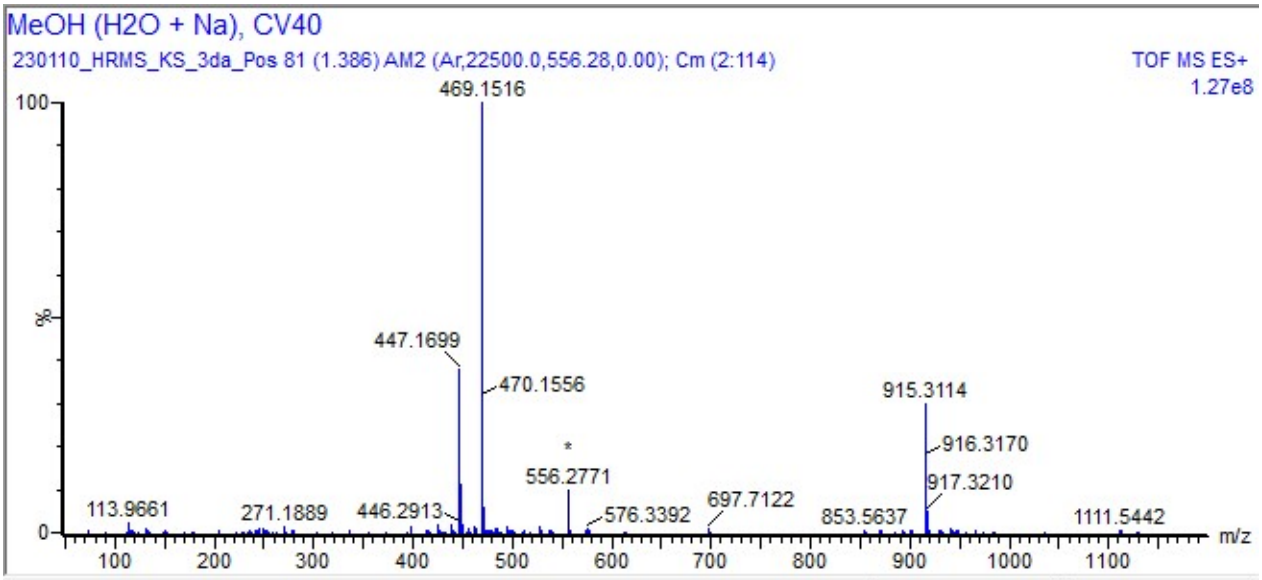
HMBC spectra of 3da in DMSO



COSY spectra of 3da in DMSO



HRMS spectra of 3da



Single Mass Analysis

Tolerance = 2.0 mDa / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

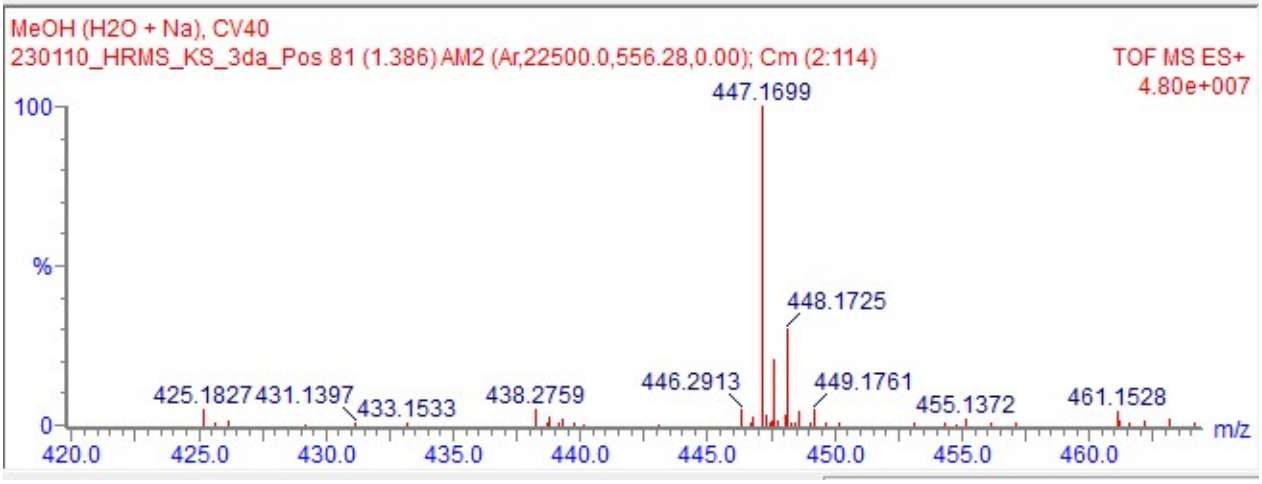
Monoisotopic Mass, Even Electron Ions

106 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

Elements Used:

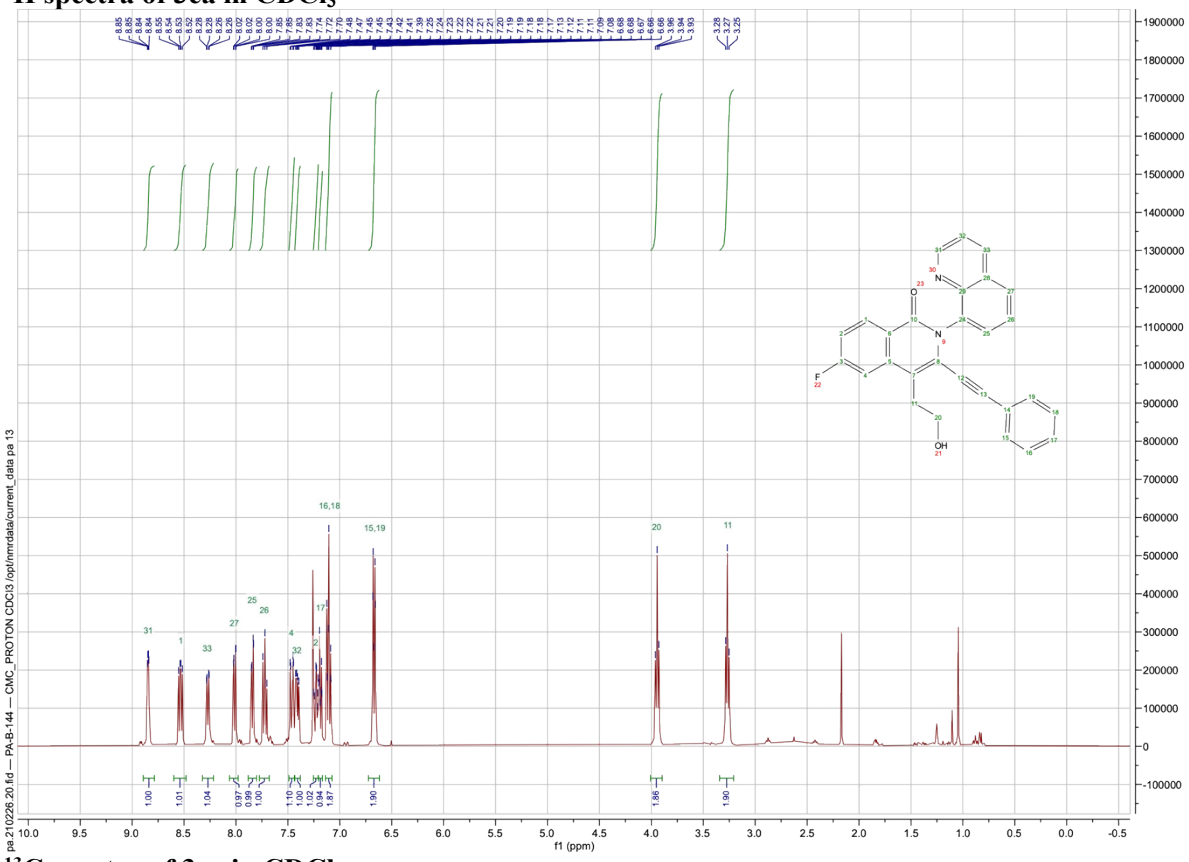
C: 1-40 H: 1-40 N: 1-4 O: 1-4 Na: 0-1

Mass	Calc. Mass	mDa	PPM	DBE	Formula	Fit Conf %	C	H	N	O	N
447.1699	447.1709	-1.0	-2.2	19.5	C29 H23 N2 O3	2.50.31	29	23	2	3	
	447.1685	1.4	3.1	16.5	C27 H24 N2 O3 Na	2.099.69	27	24	2	3	1

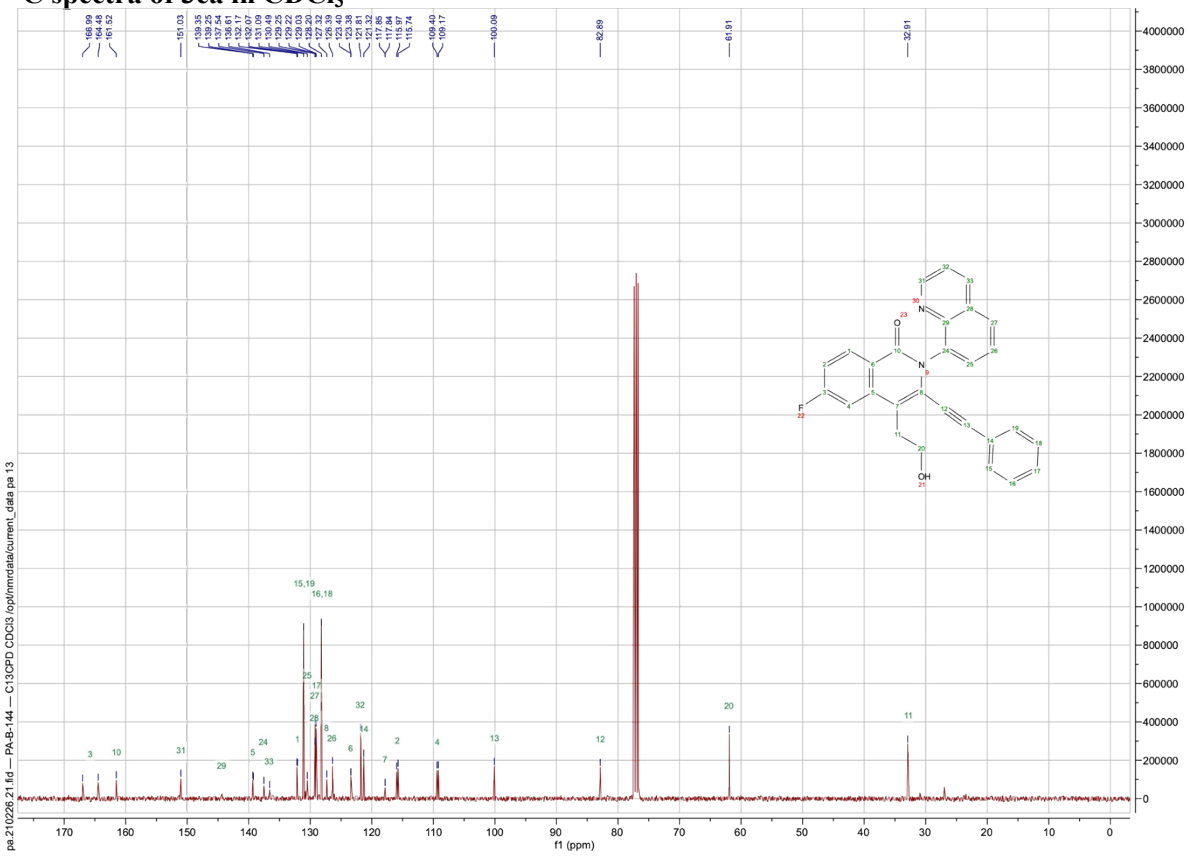


3ea

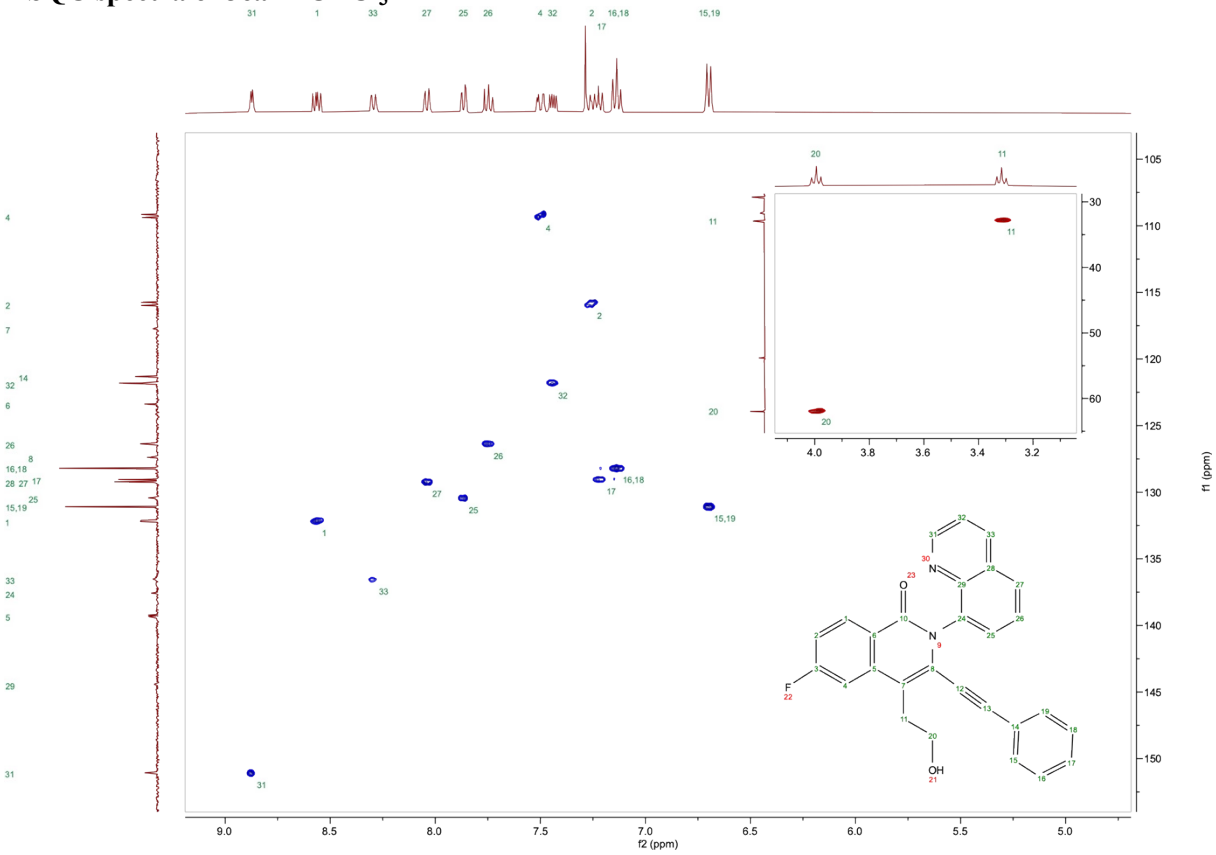
^{1}H spectra of 3ea in $CDCl_3$



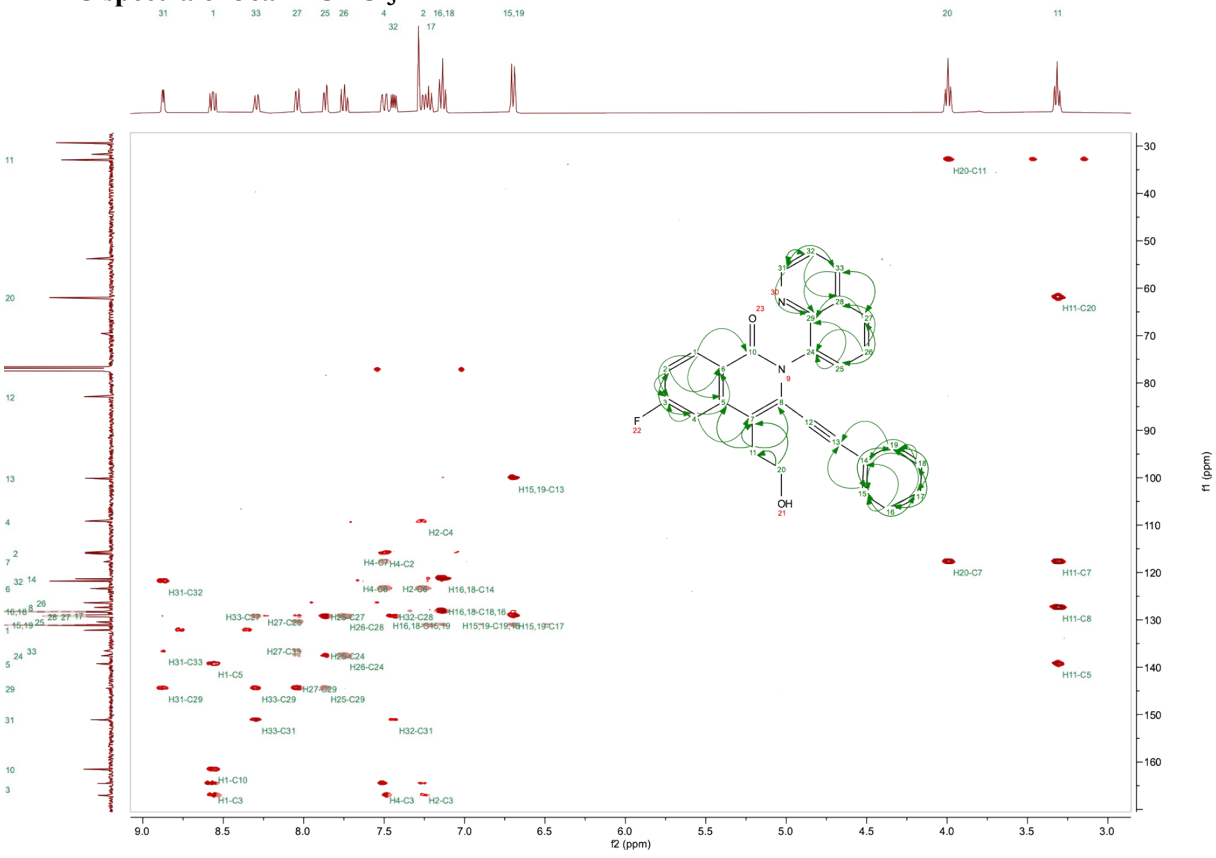
^{13}C spectra of 3ea in $CDCl_3$



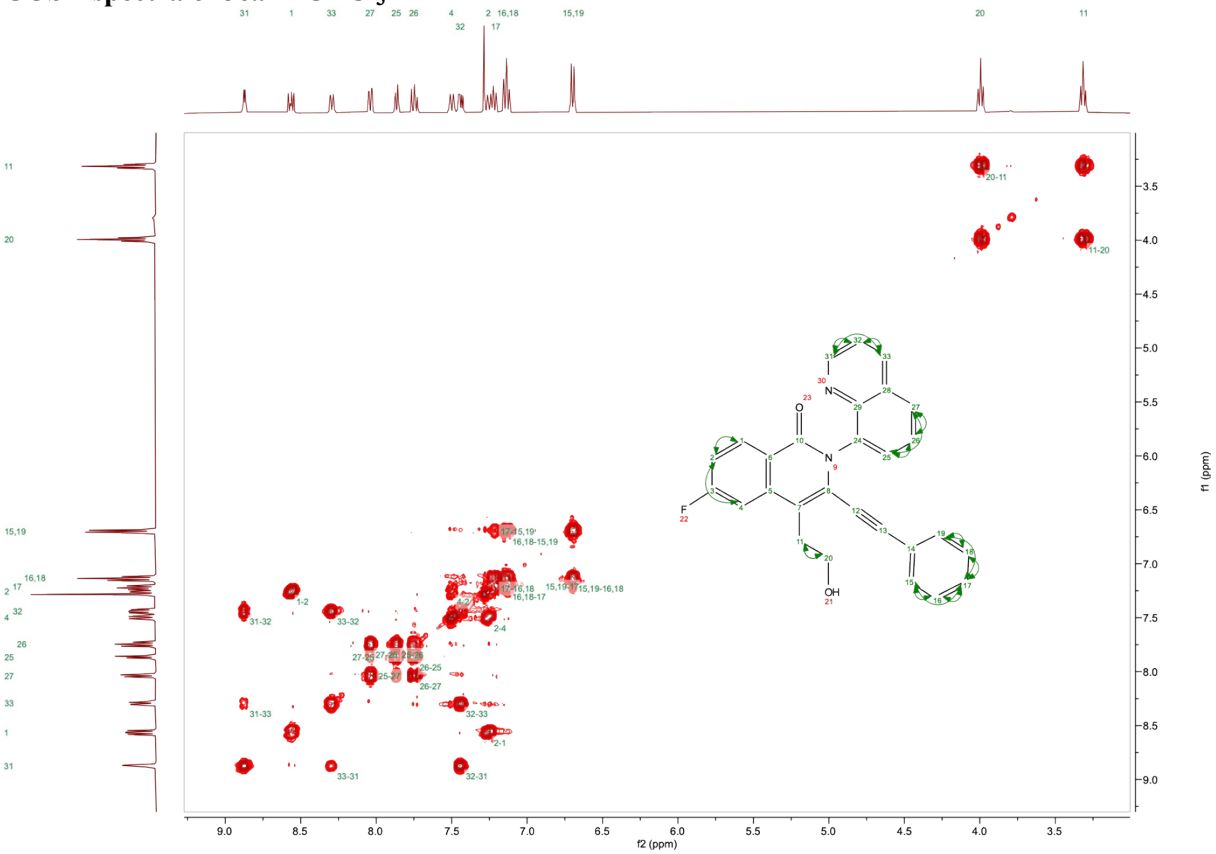
HSQC spectra of 3ea in $CDCl_3$



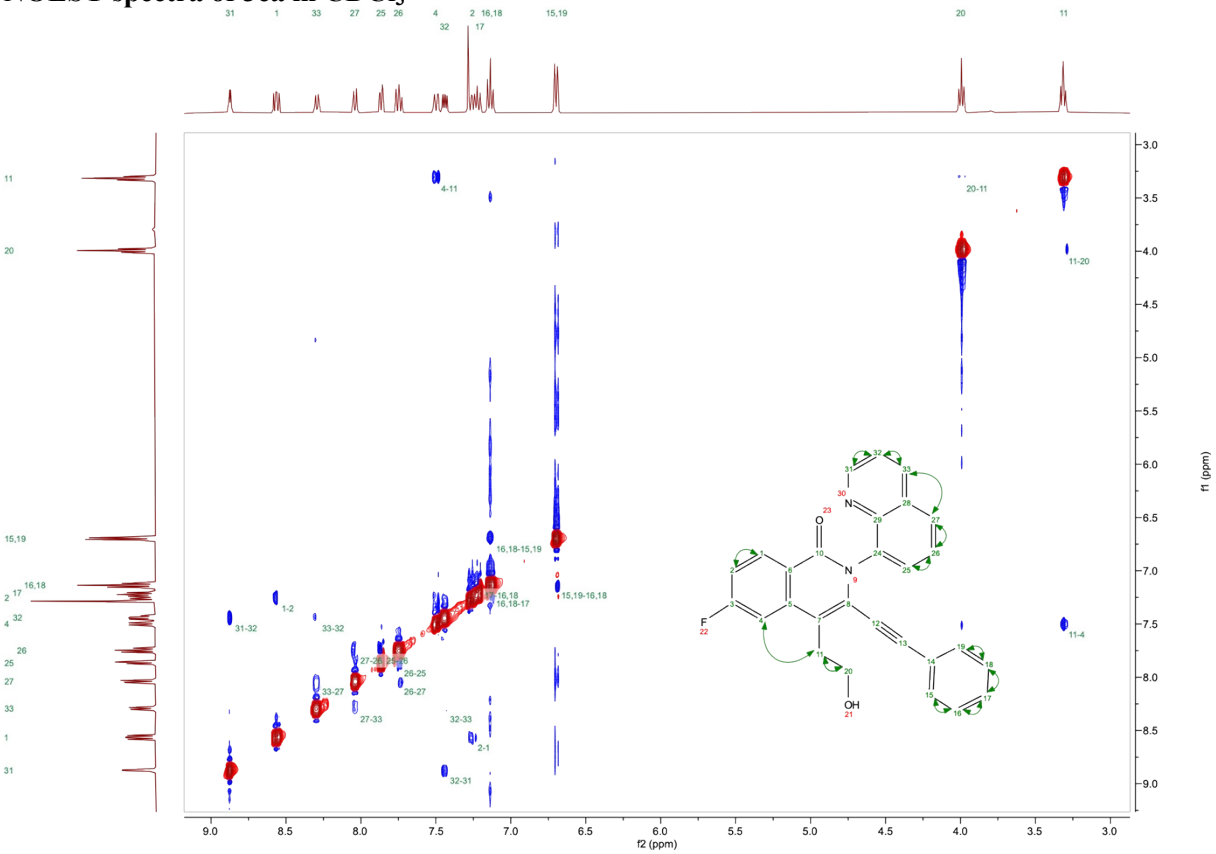
HMBC spectra of 3ea in $CDCl_3$



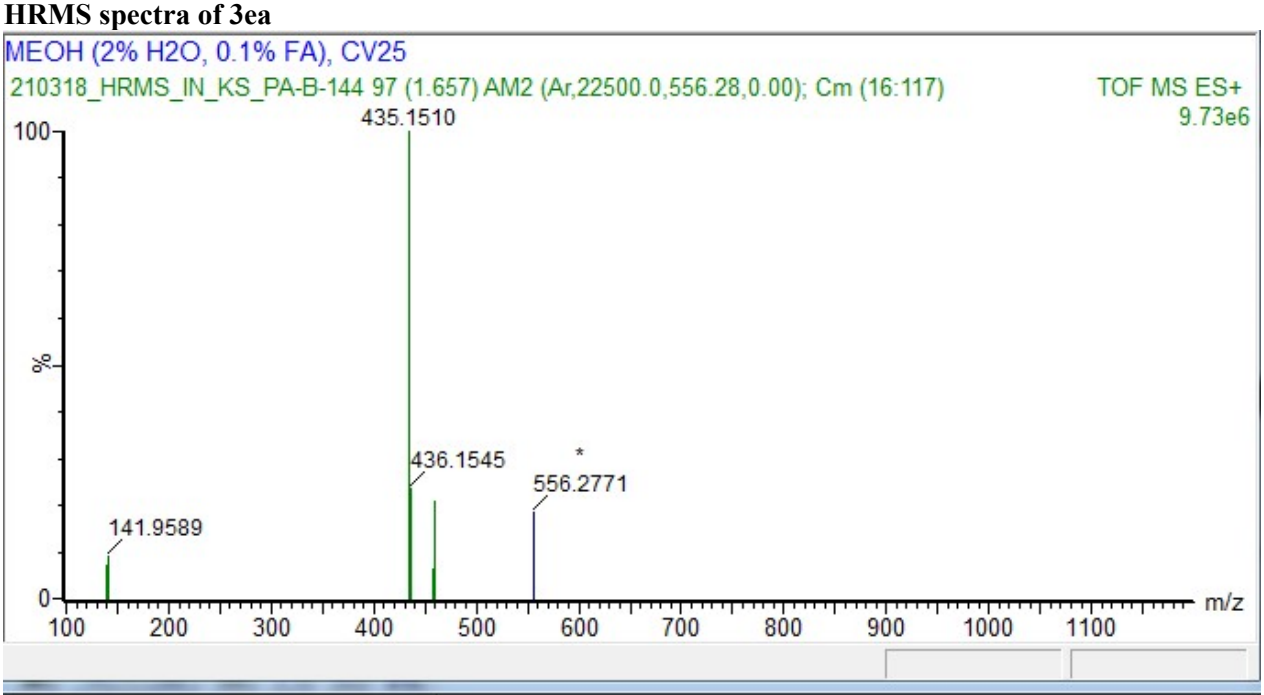
COSY spectra of 3ea in $CDCl_3$



NOESY spectra of 3ea in $CDCl_3$



HRMS spectra of 3ea



Single Mass Analysis

Tolerance = 2.0 mDa / DBE: min = -0.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

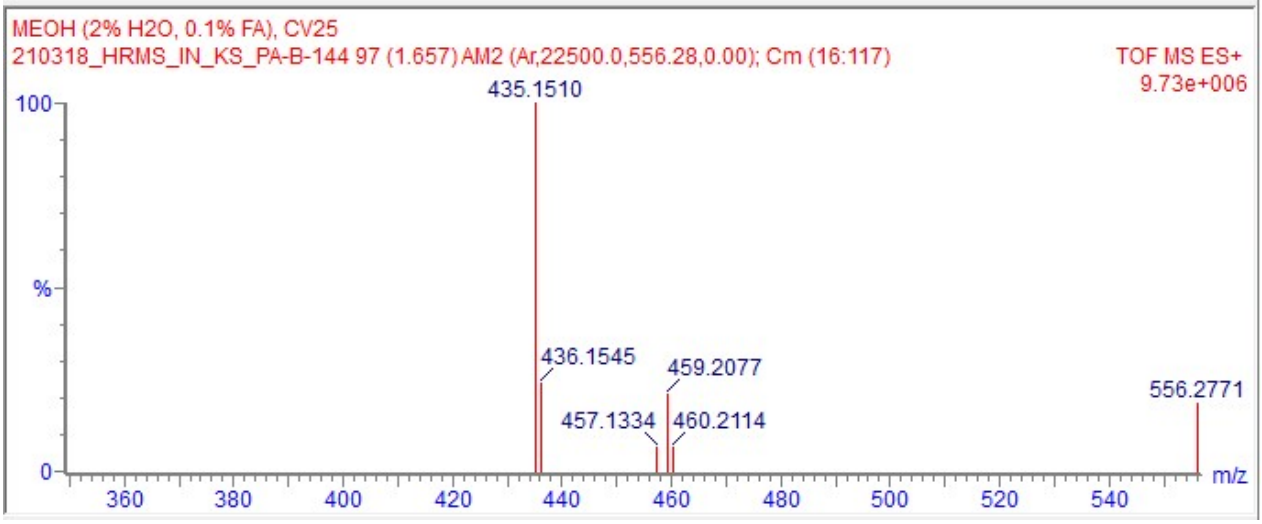
Monoisotopic Mass, Even Electron Ions

329 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)

Elements Used:

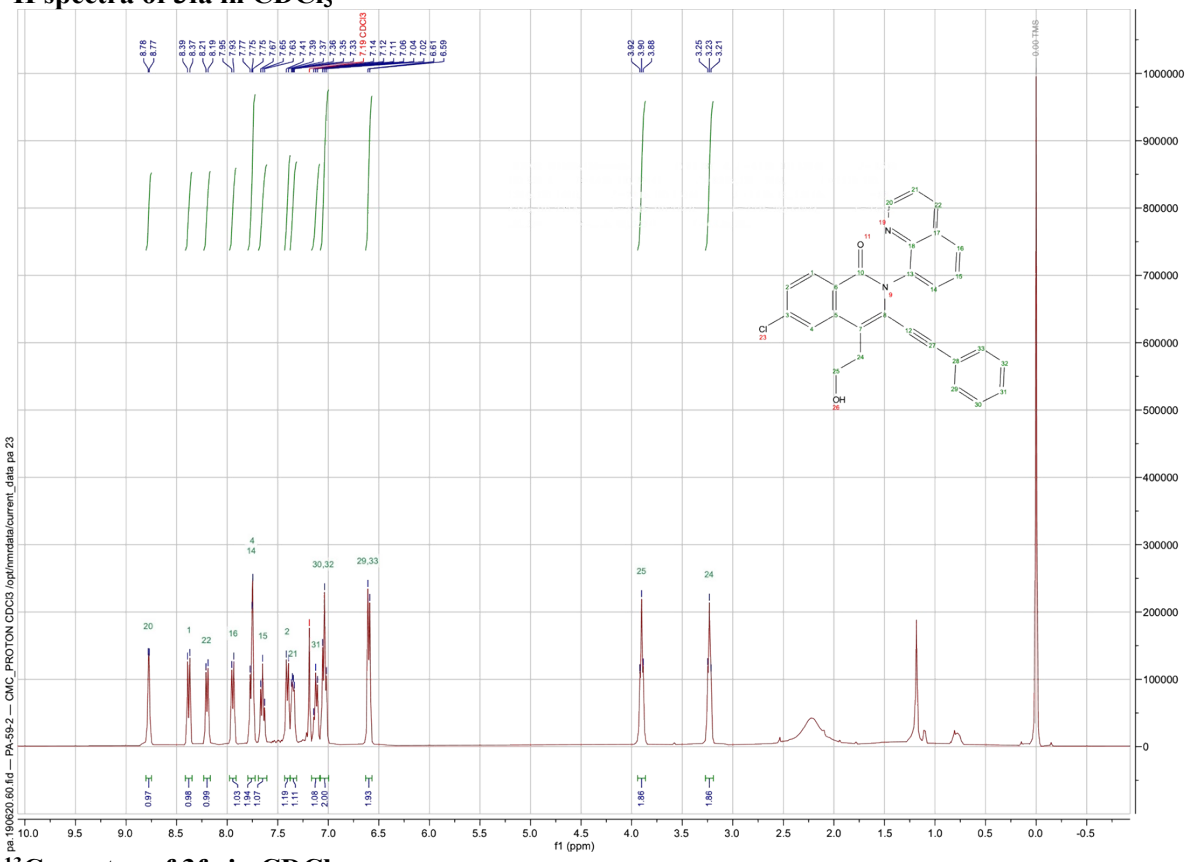
C: 0-50 H: 1-100 N: 0-3 O: 0-3 Na: 0-1 F: 0-1

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i..	Fit Conf %	C	H	N	O	Na	F
435.1510	435.1509	0.1	0.2	19.5	C28 H20 N2 O2 F	40...	70.65	28	20	2	2		1
	435.1497	1.3	3.0	23.5	C31 H19 N2 O	41...	14.26	31	19	2	1		
	435.1525	-1.5	-3.4	20.5	C31 H21 Na F	41...	15.09	31	21			1	1

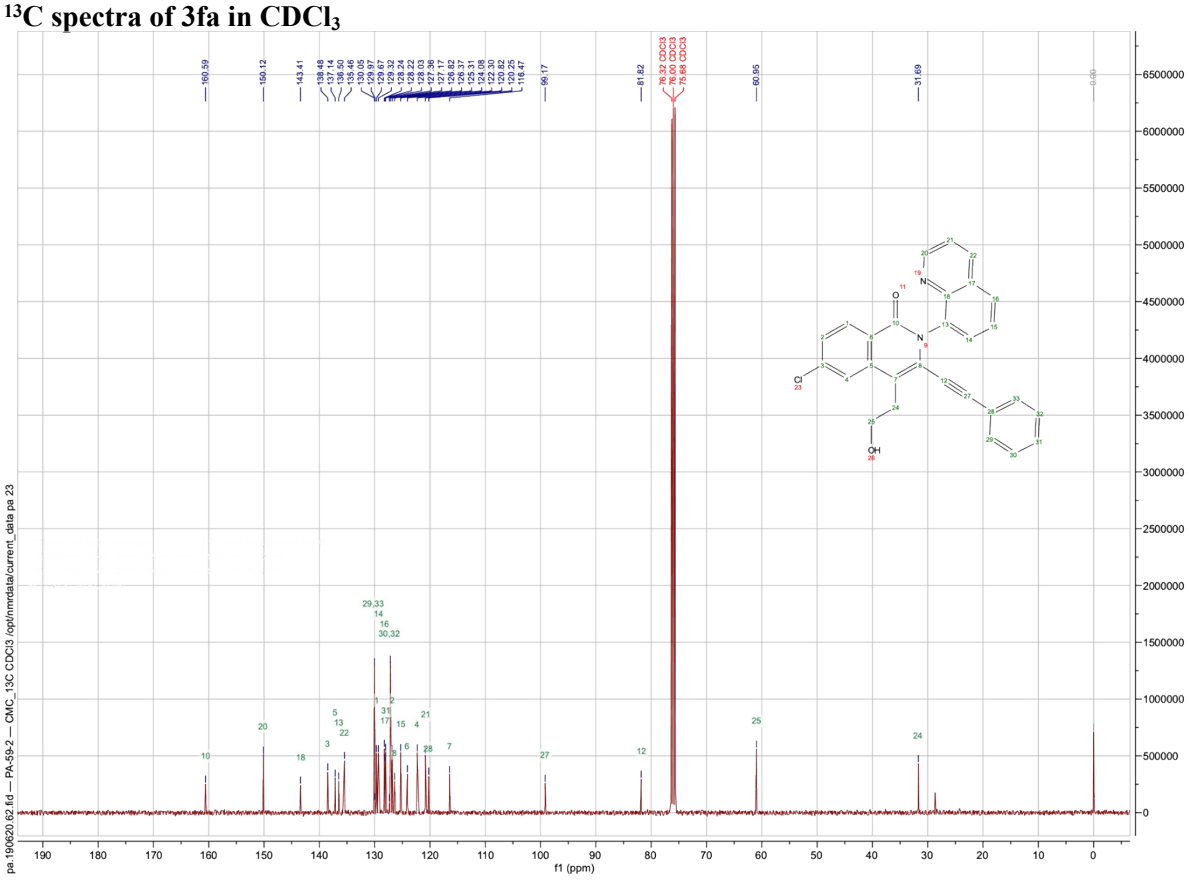


3fa

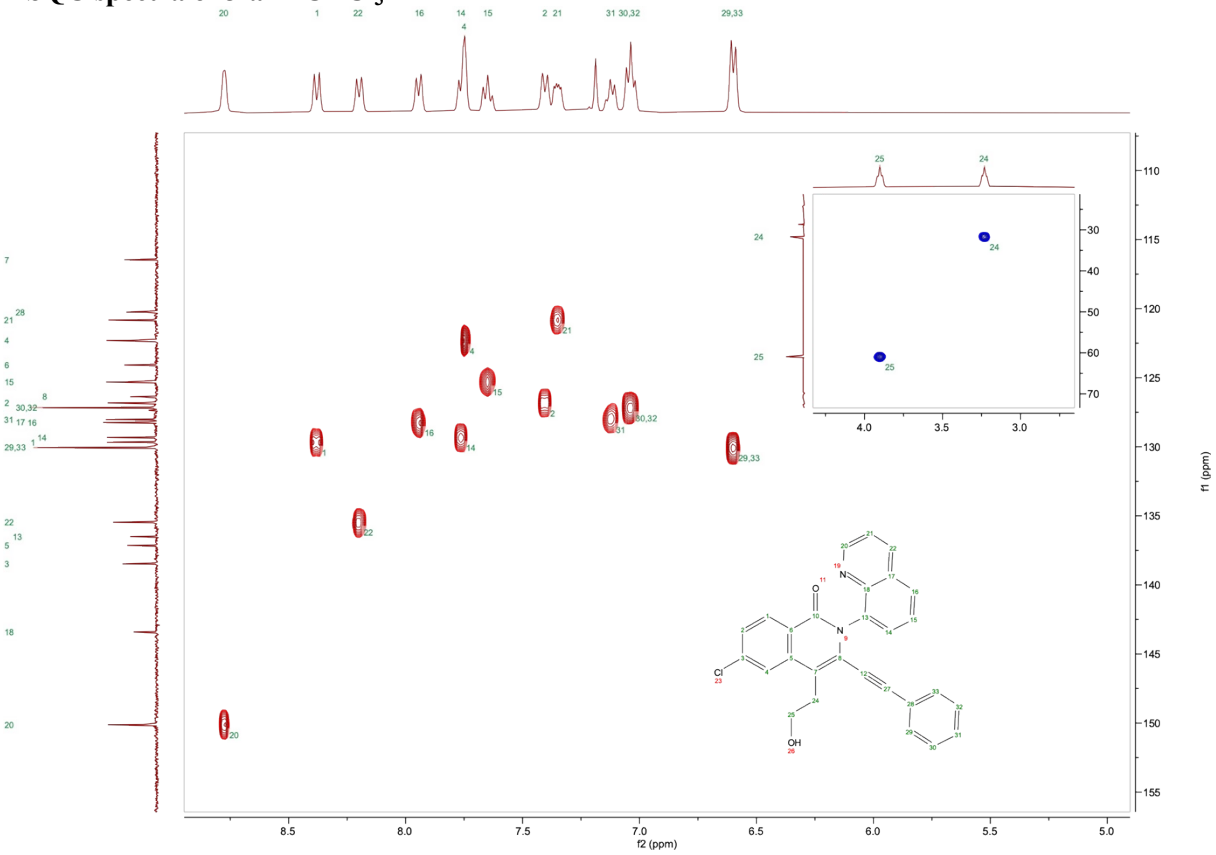
^{1}H spectra of 3fa in $CDCl_3$



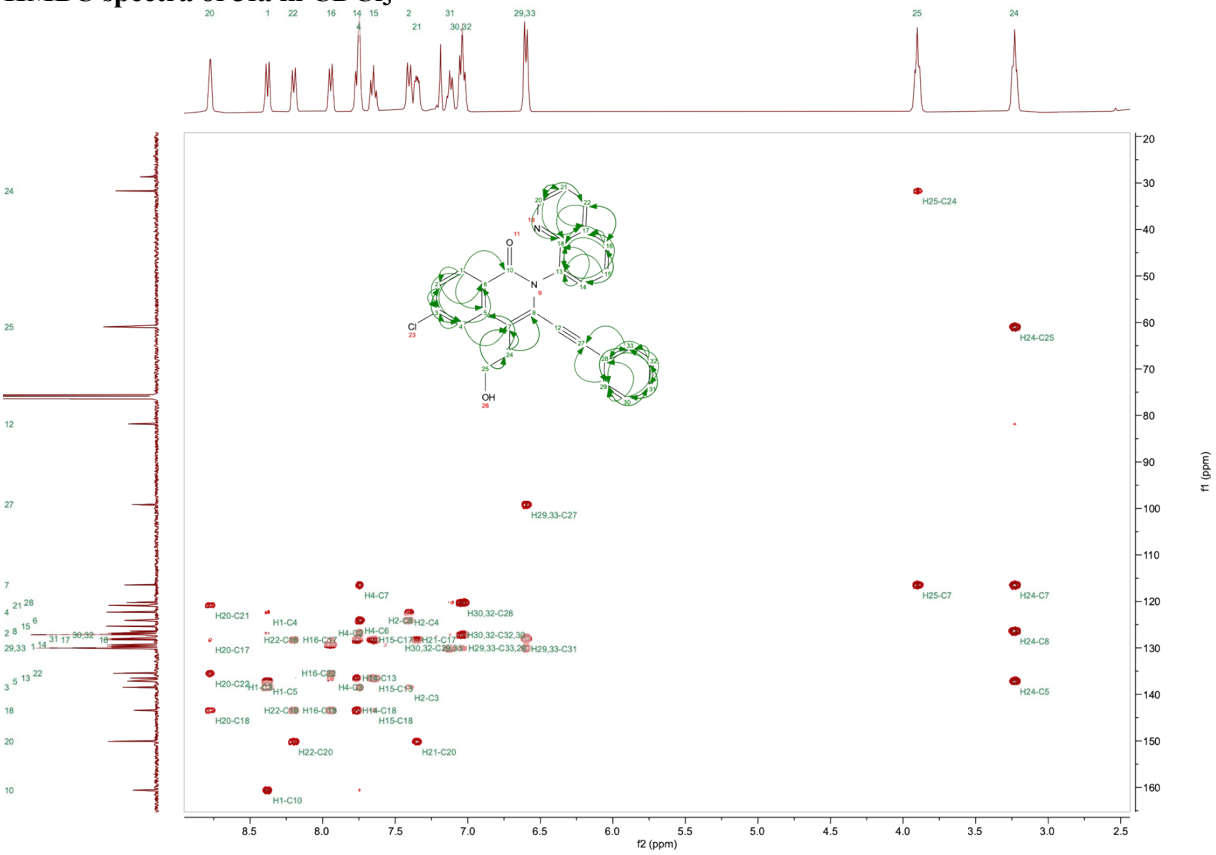
^{13}C spectra of 3fa in $CDCl_3$



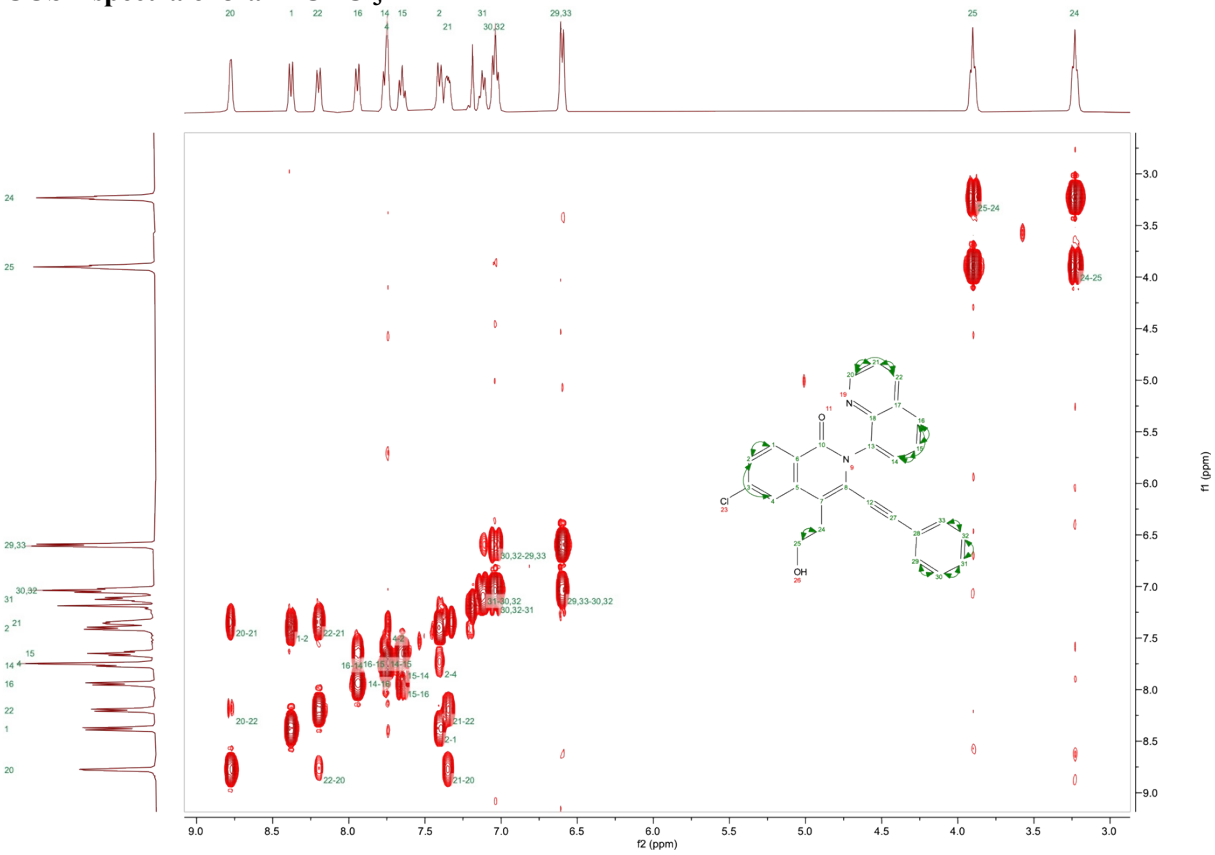
HSQC spectra of 3fa in $CDCl_3$



HMBC spectra of 3fa in $CDCl_3$



COSY spectra of 3fa in $CDCl_3$



HRMS spectra of 3fa

HRMS DST-FIST Funded, Department of Chemistry, IIT Madras

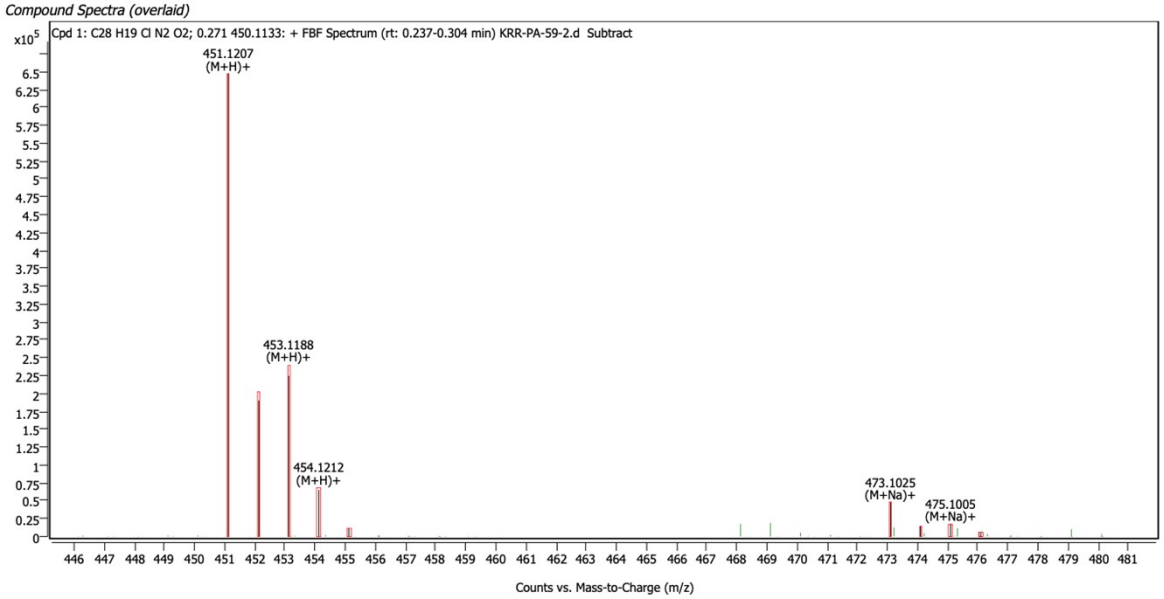
ESI Mass Report

Name	011119-2-KRR-PA-59-2	**Data File Path**	D:\MassHunter\Data\2019\NOV-2019\KRR\KRR-PA-59-2.d
Sample ID		**Acq. Time (Local)**	01-11-2019 09:28:03 (UTC+05:30)
Instrument	Instrument 1	**Method Path (Acq)**	D:\MassHunter\Methods\Direct Infusion_HPLC.m
MS Type	QTOF	**Version (Acq SW)**	6200 series TOF/6500 series Q-TOF B.08.00 (B8058.0)
Inj. Vol. (ul)	5	**IRM Status**	Success
Position	P2-D2	**Method Path (DA)**	D:\MassHunter\Methods\10.0\IIT-Target Screening_1.m
Plate Pos.		**Target Source Path**	
Operator		**Result Summary**	1 qualified (1 targets)

Compound Details

Cpd. 1: C28 H19 Cl N2 O2

Compound Spectra (overlaid)

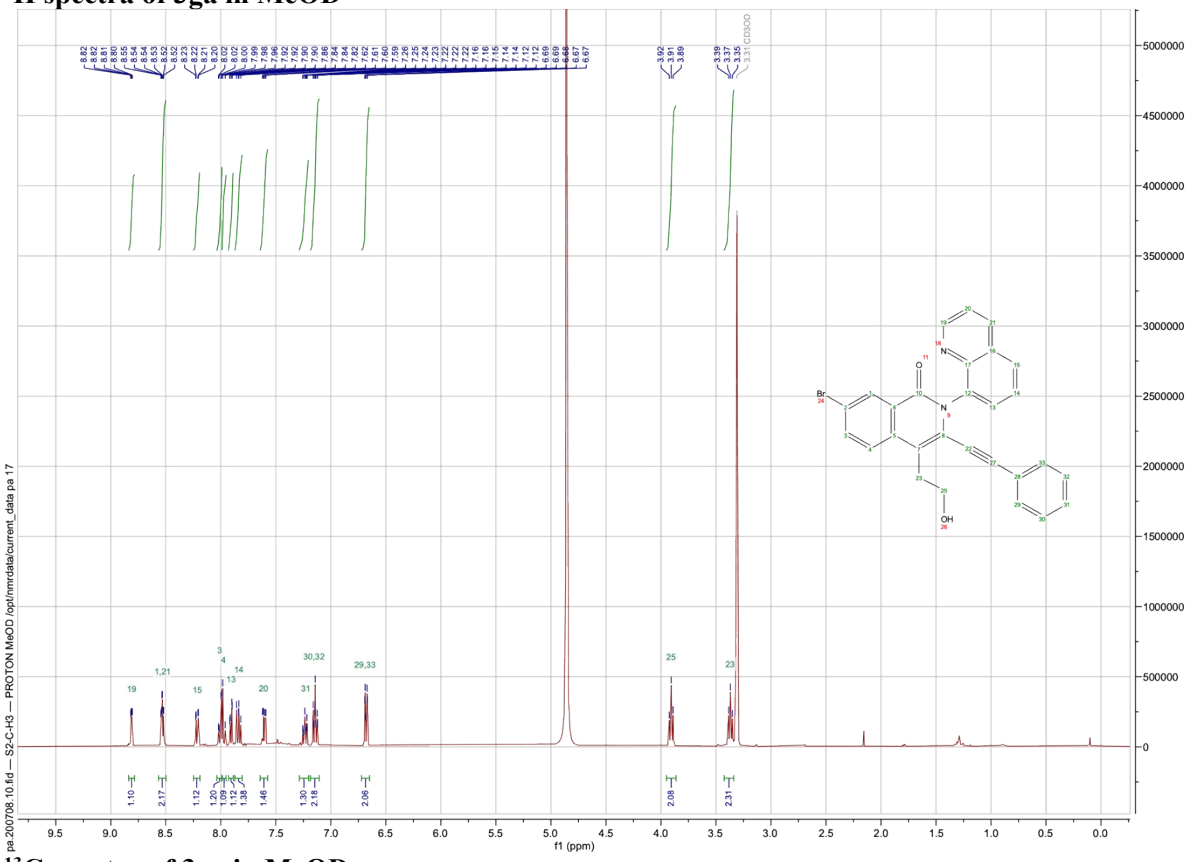


Compound ID Table

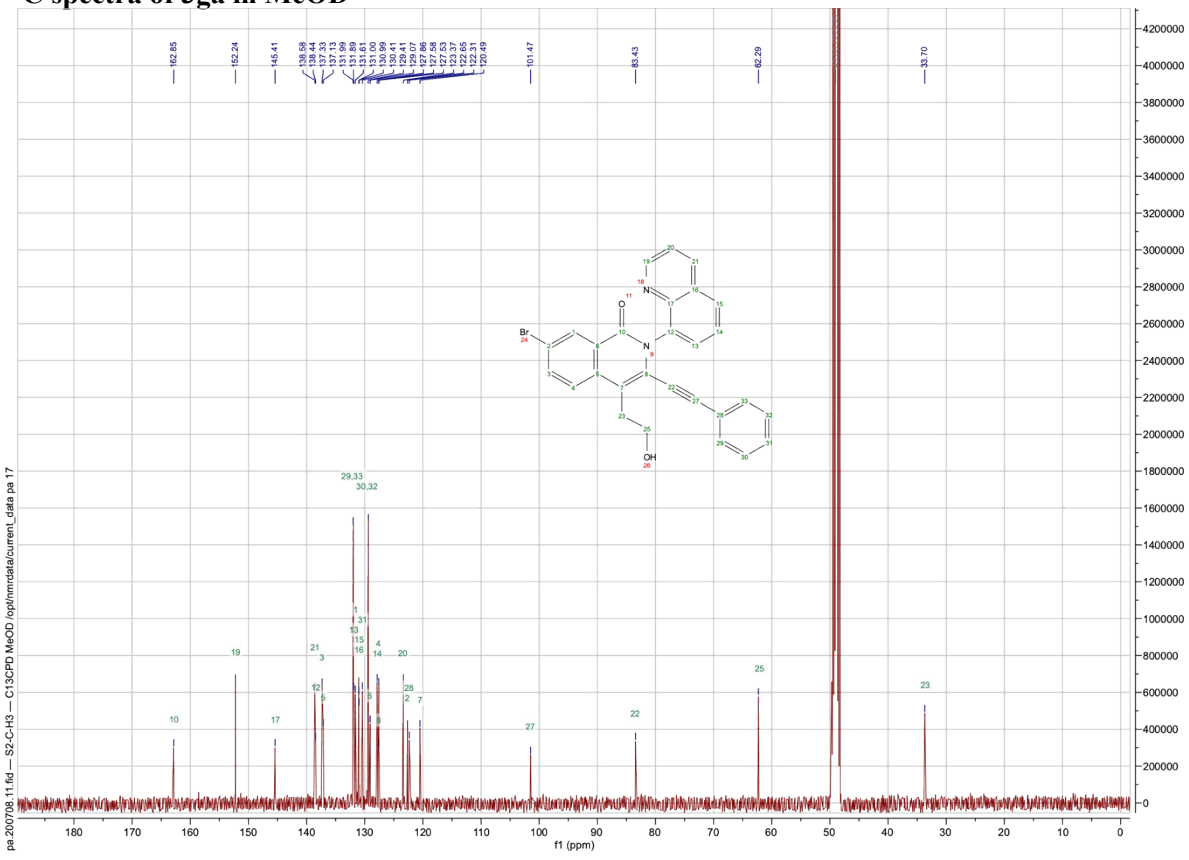
Cpd	Formula	Mass (Tgt)	Calc. Mass	Mass	Species	Diff(Tgt.ppm)	mDa
1	C28 H19 Cl N2 O2	450.1135	450.1133	451.1207 473.1025	(M+H)+ (M+Na)+	-0.45	-0.20

3ga

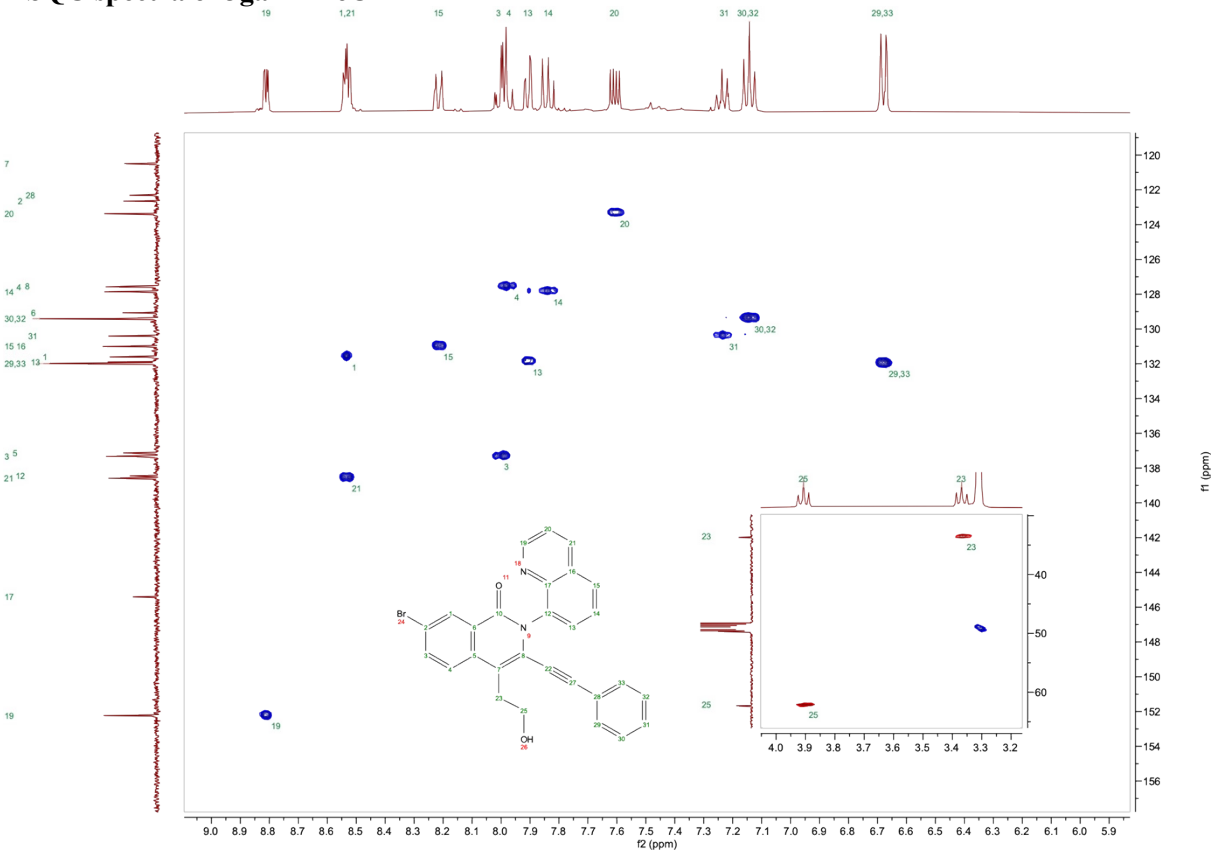
^{1}H spectra of 3ga in MeOD



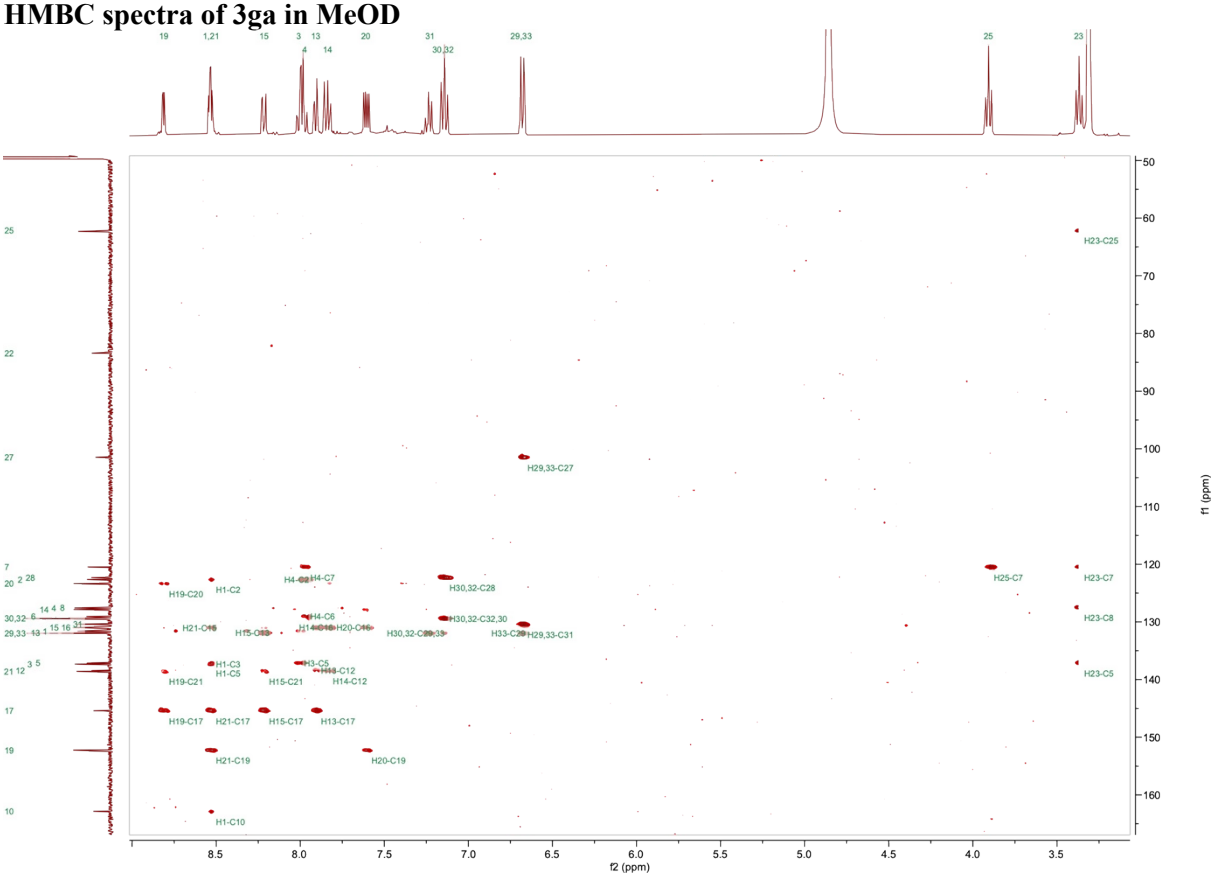
^{13}C spectra of 3ga in MeOD



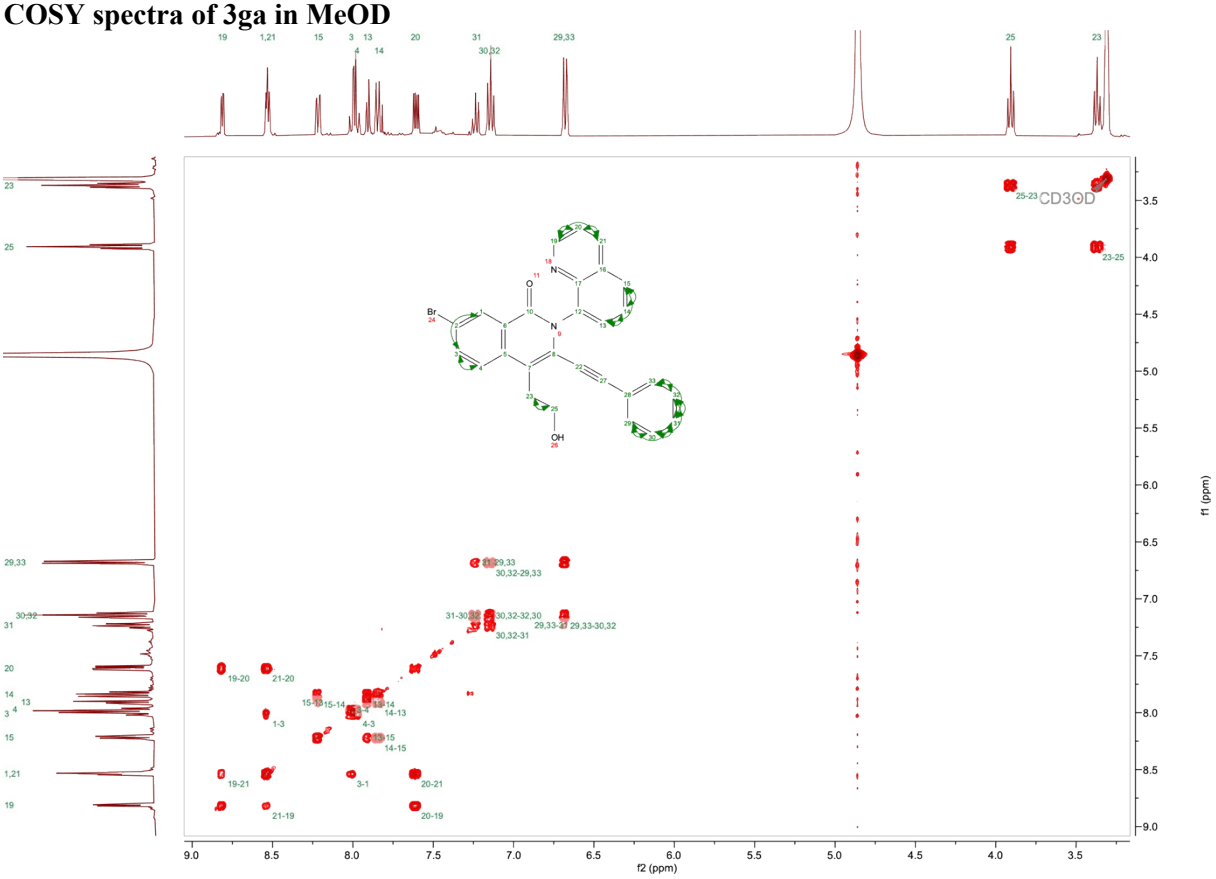
HSQC spectra of 3ga in MeOD



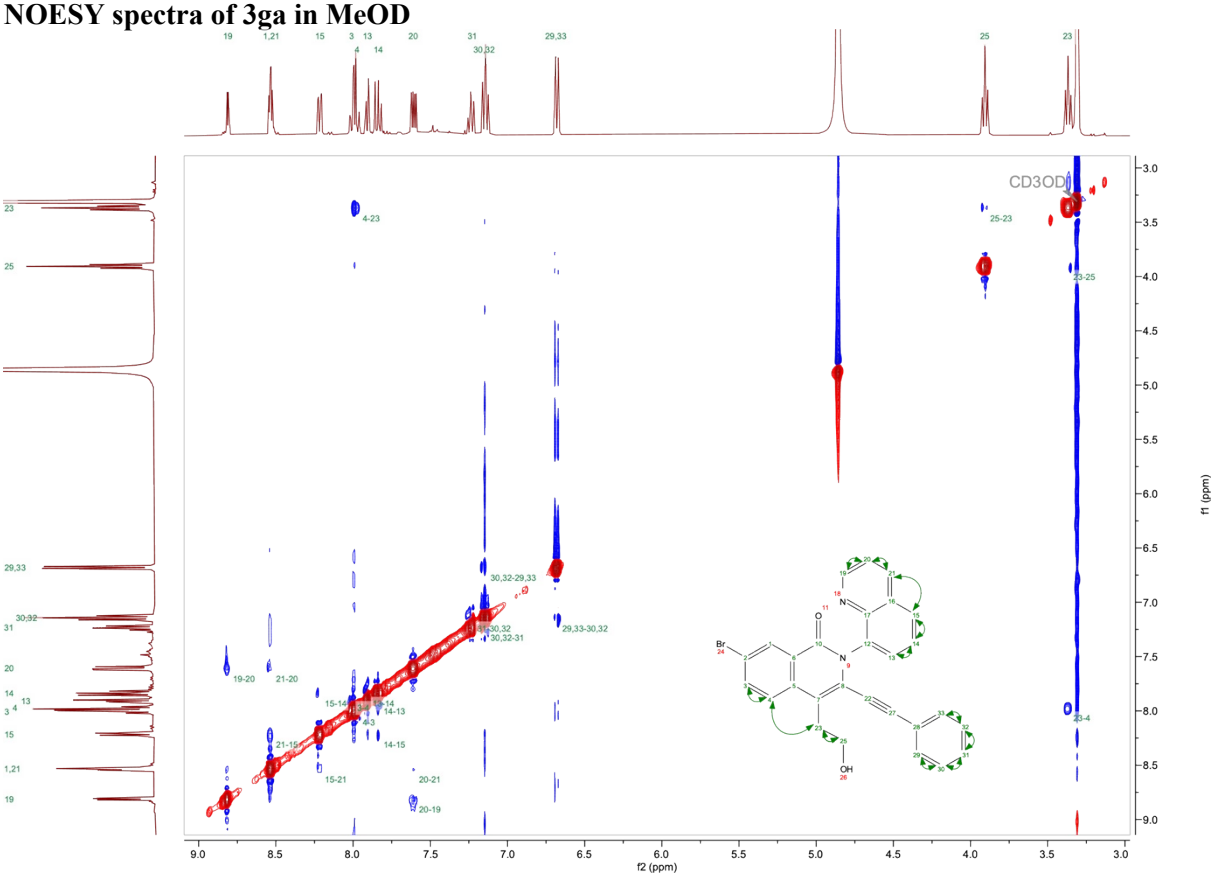
HMBC spectra of 3ga in MeOD



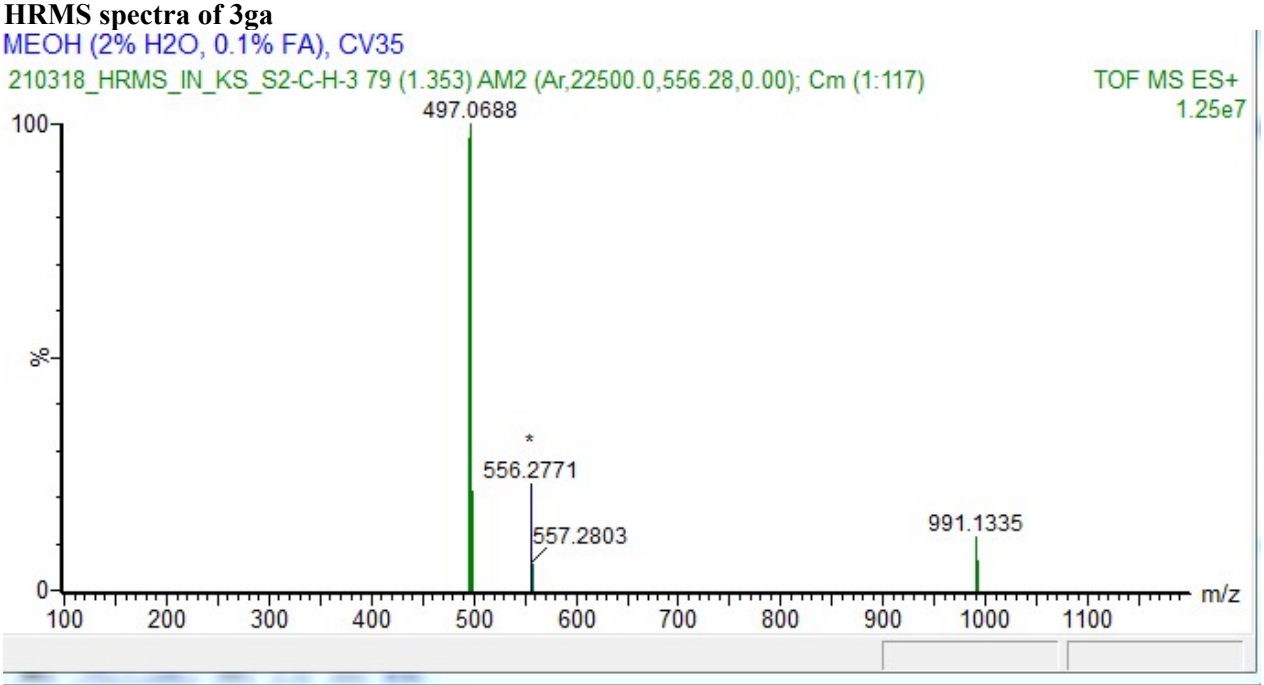
COSY spectra of 3ga in MeOD



NOESY spectra of 3ga in MeOD



HRMS spectra of 3ga



Single Mass Analysis

Tolerance = 2.0 mDa / DBE: min = -0.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

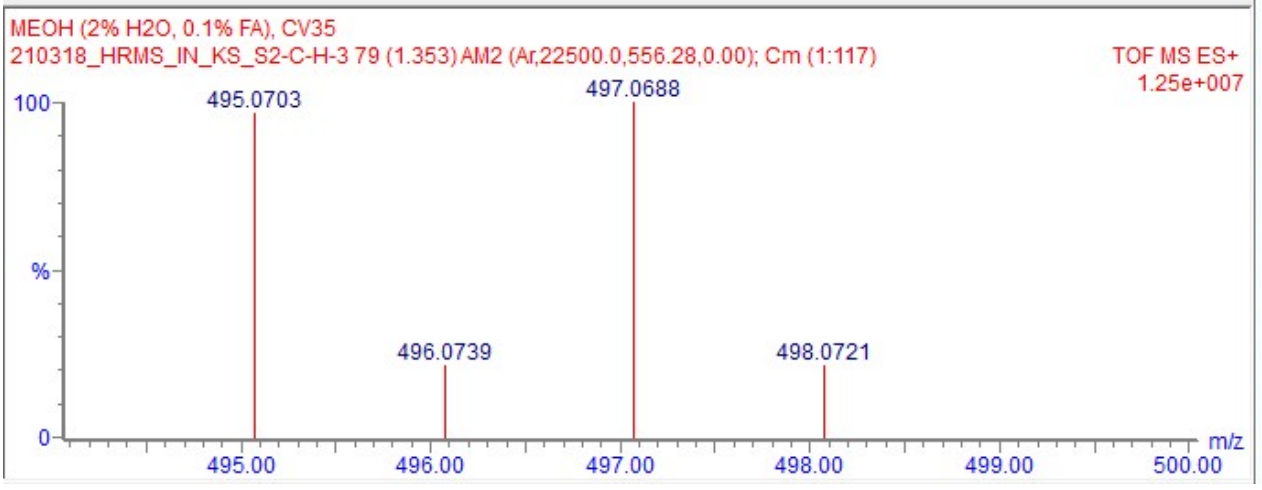
Monoisotopic Mass, Even Electron Ions

353 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

Elements Used:

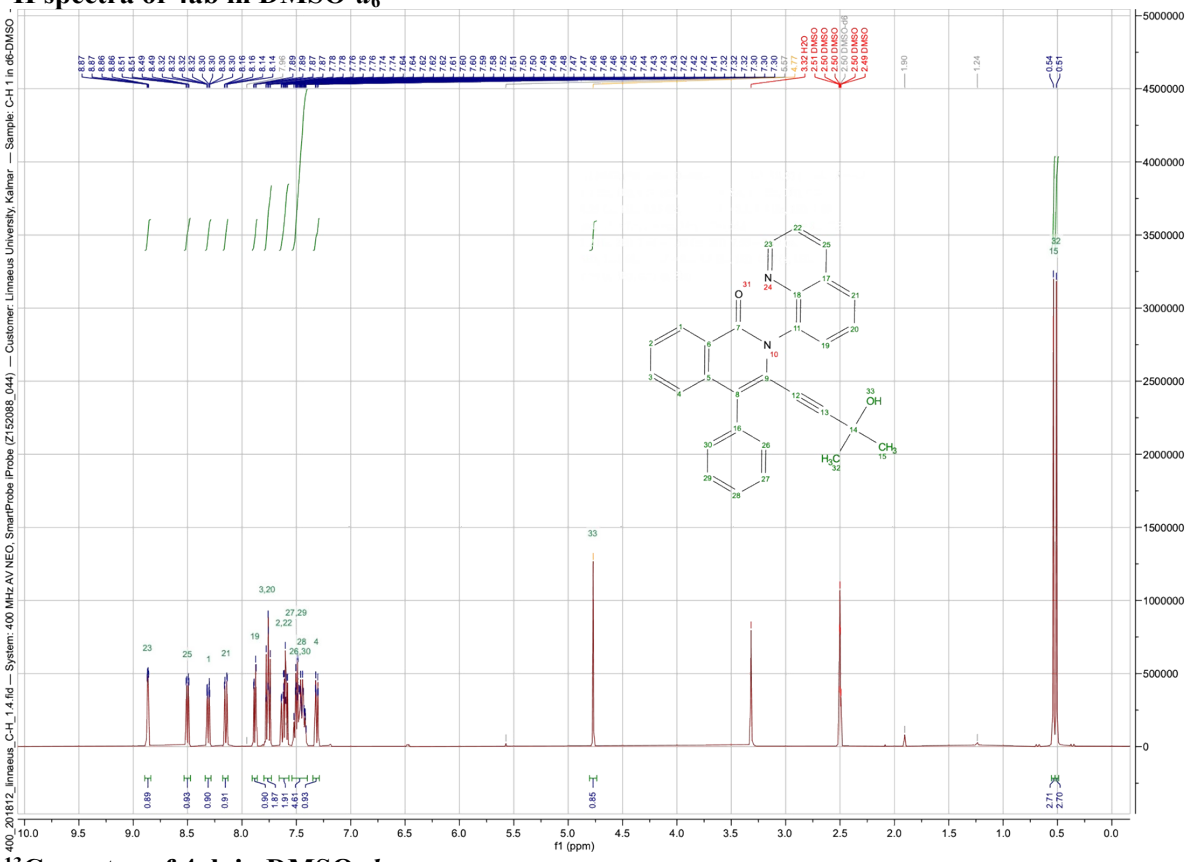
C: 0-50 H: 1-100 N: 0-3 O: 0-3 Na: 0-1 Br: 0-1

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i..	Fit Conf %	C	H	N	O	Na	Br
495.0703	495.0708	-0.5	-1.0	19.5	C28 H20 N2 O2 Br	3...	89.40	28	20	2	2		1
	495.0684	1.9	3.8	16.5	C26 H21 N2 O2 Na Br	2...	10.60	26	21	2	2	1	1

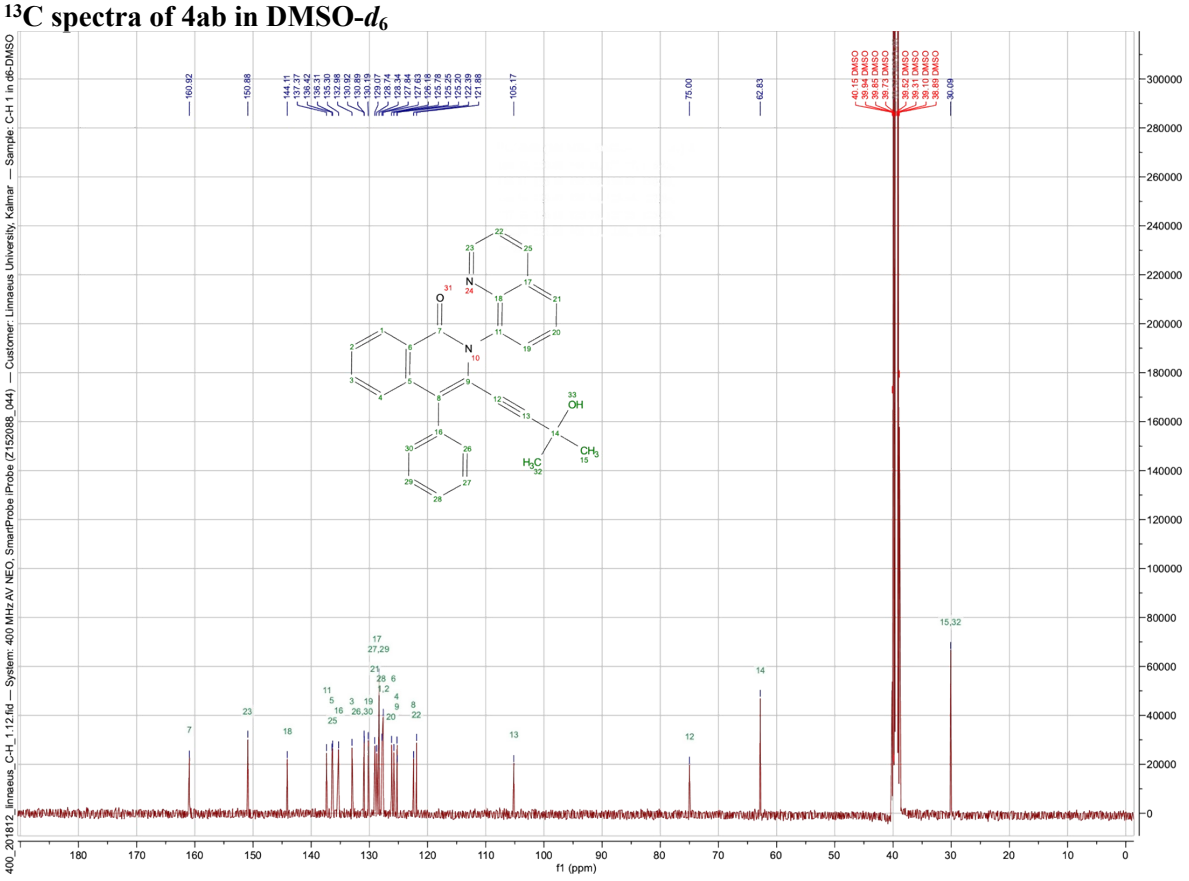


4ab

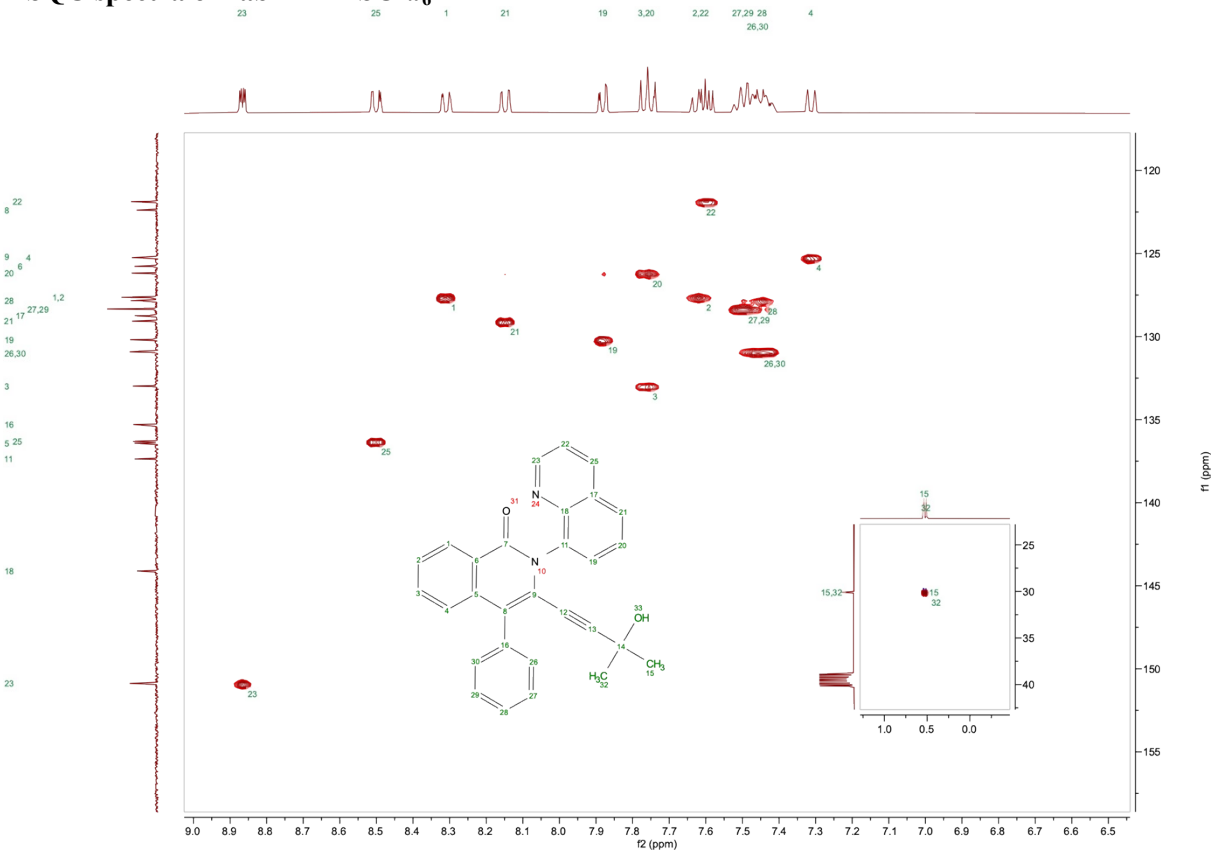
^{1}H spectra of 4ab in DMSO-d_6



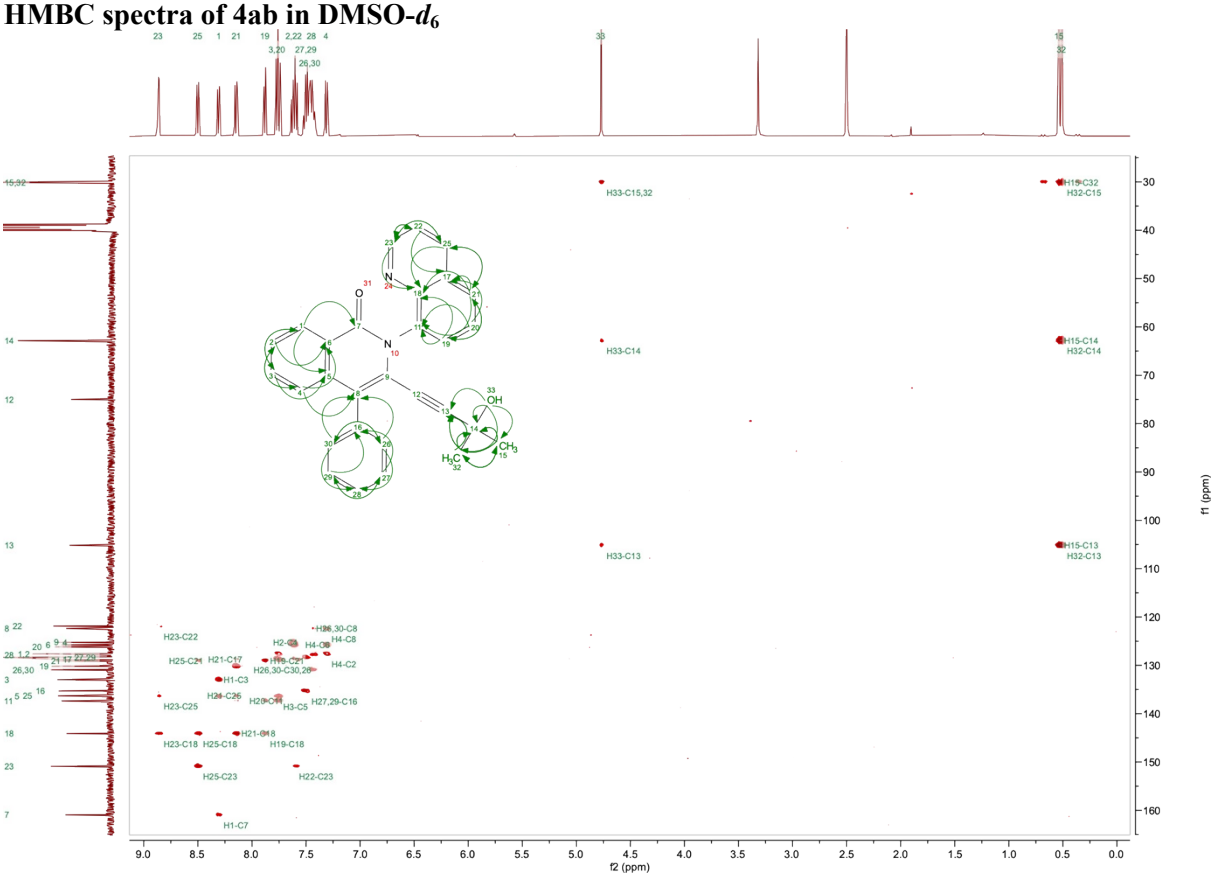
^{13}C spectra of 4ab in DMSO-d_6



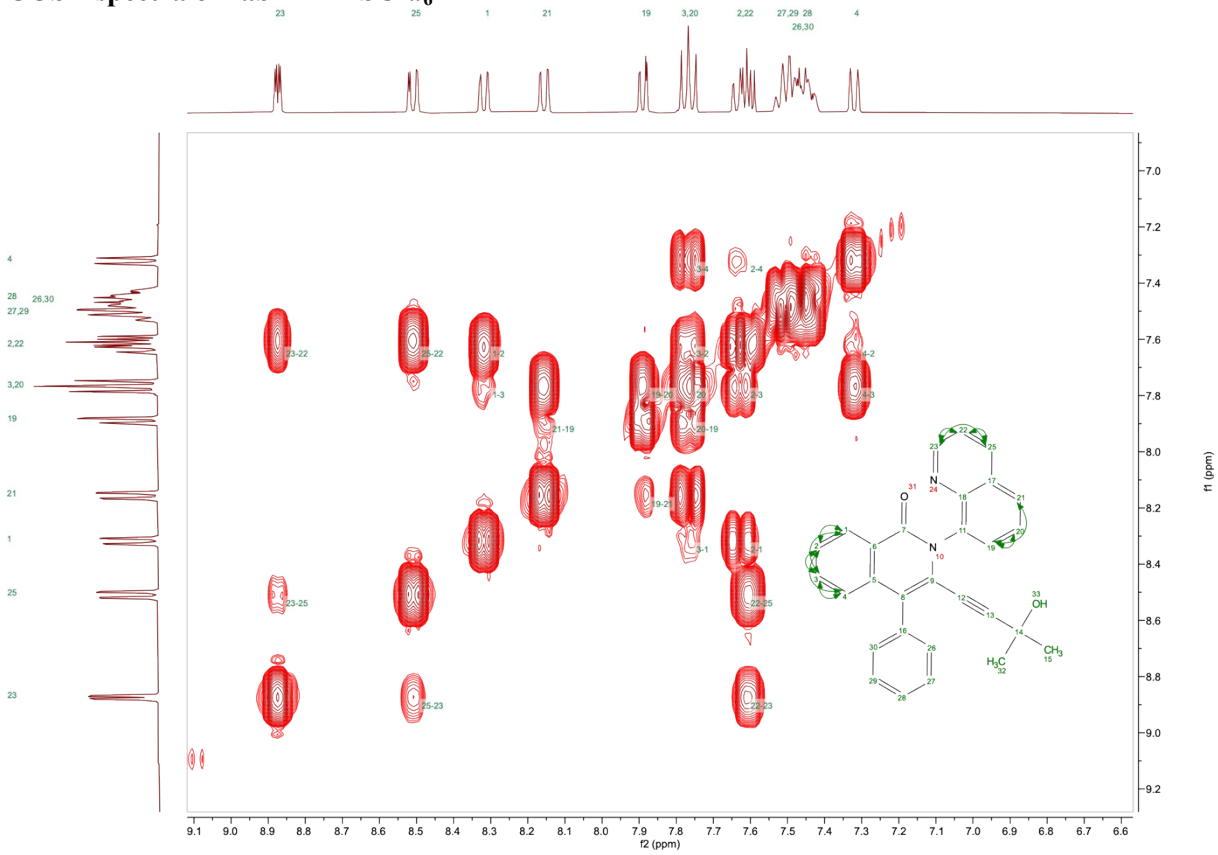
HSQC spectra of 4ab in DMSO-d_6



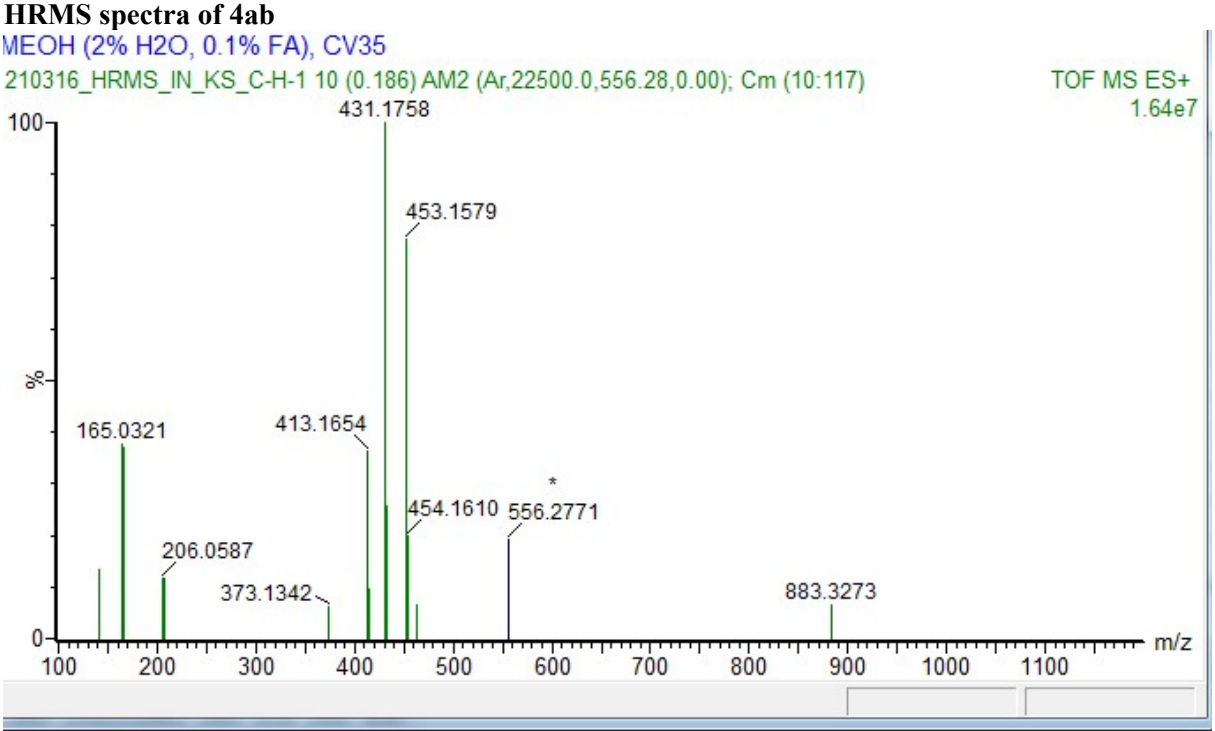
HMBC spectra of 4ab in DMSO-d_6



COSY spectra of 4ab in DMSO-d_6



HRMS spectra of 4ab



Single Mass Analysis

Tolerance = 2.0 mDa / DBE: min = -0.5, max = 100.0

Element prediction: Off

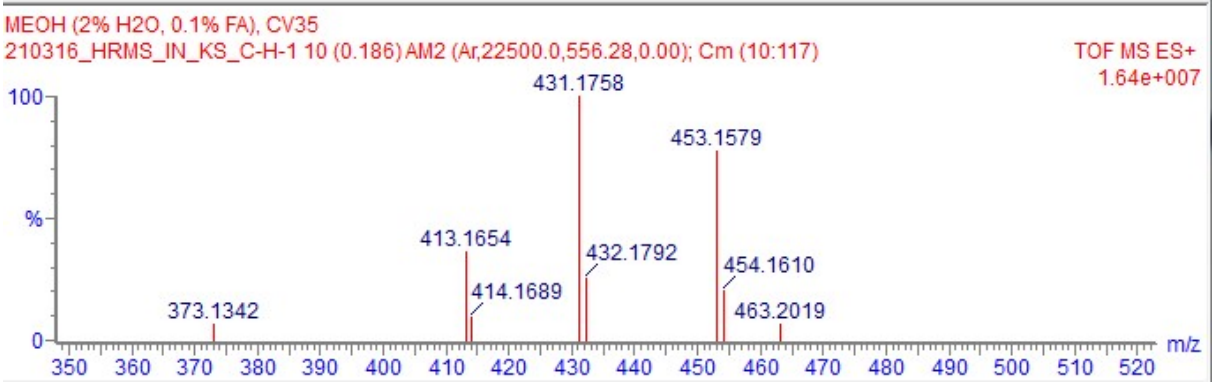
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

167 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

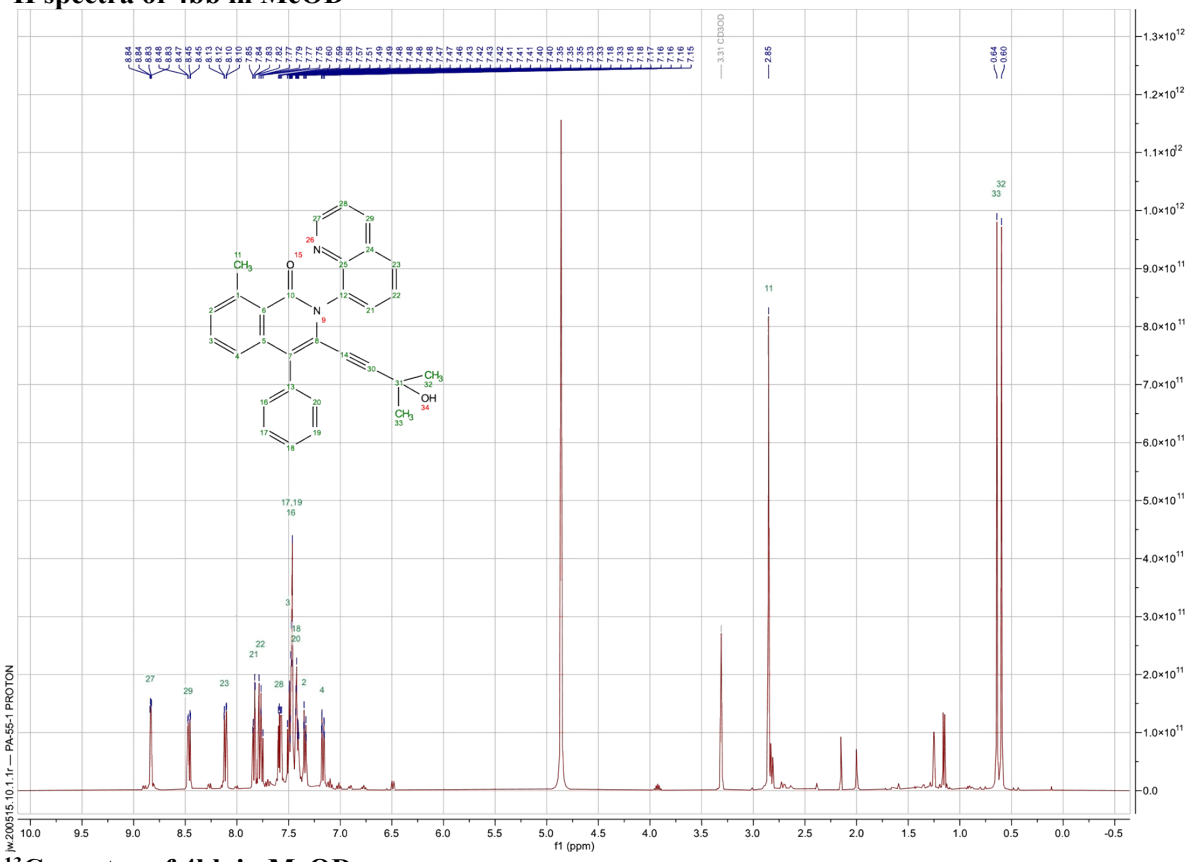
Elements Used:

Mass	Calc. Mass	mDa	PPM	DBE	Formula	Fit Conf %	C	H	N	O	Na
431.1758	431.1760	-0.2	-0.5	19.5	C29 H23 N2 O2	40.90.32	29	23	2	2	
	431.1776	-1.8	-4.2	20.5	C32 H24 Na	52.9.68	32	24			1

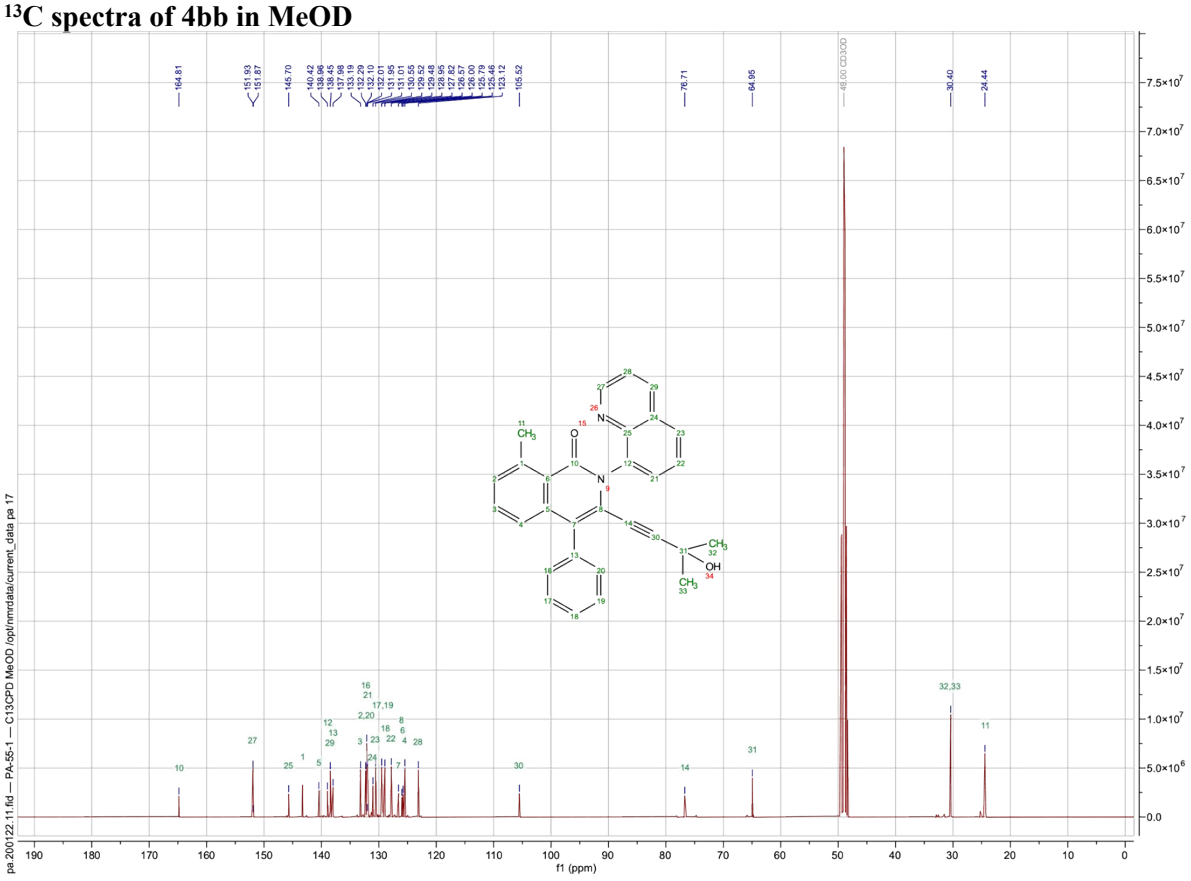


4bb

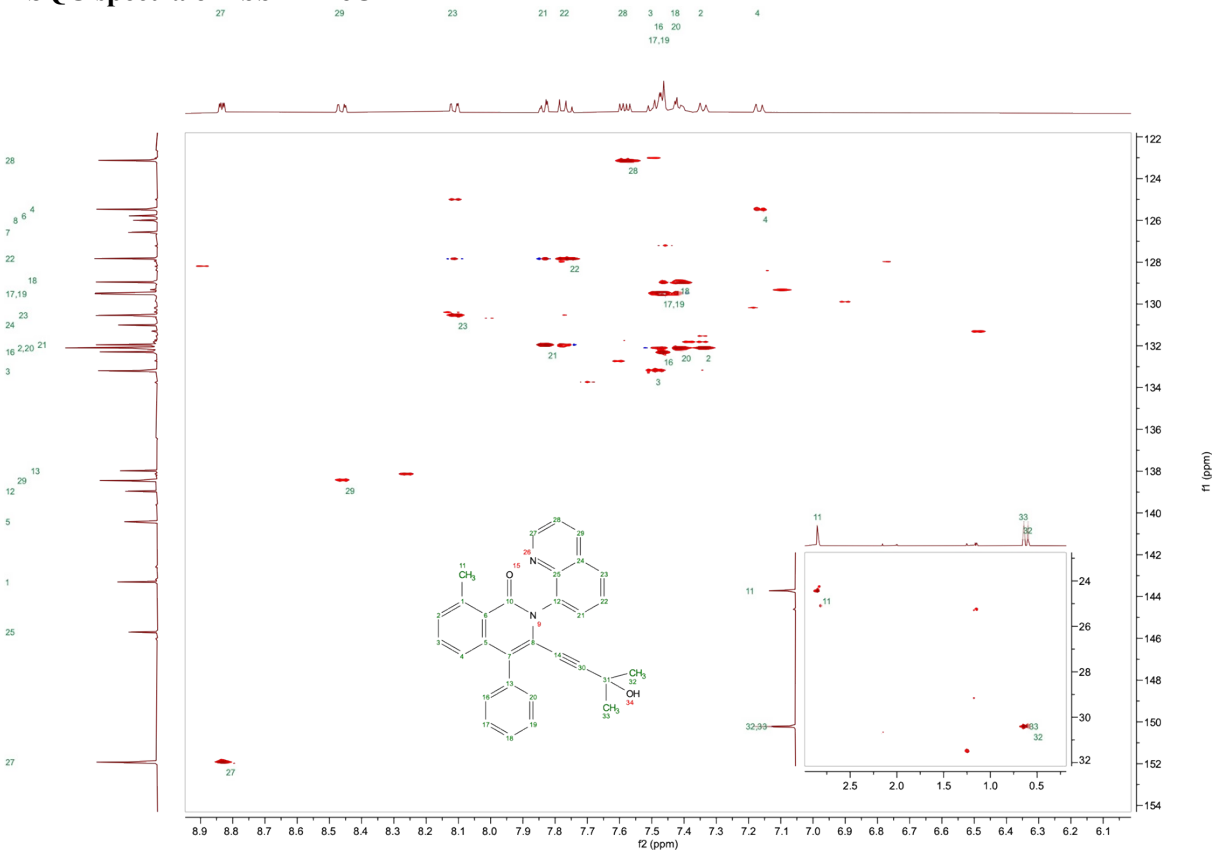
^{1}H spectra of 4bb in MeOD



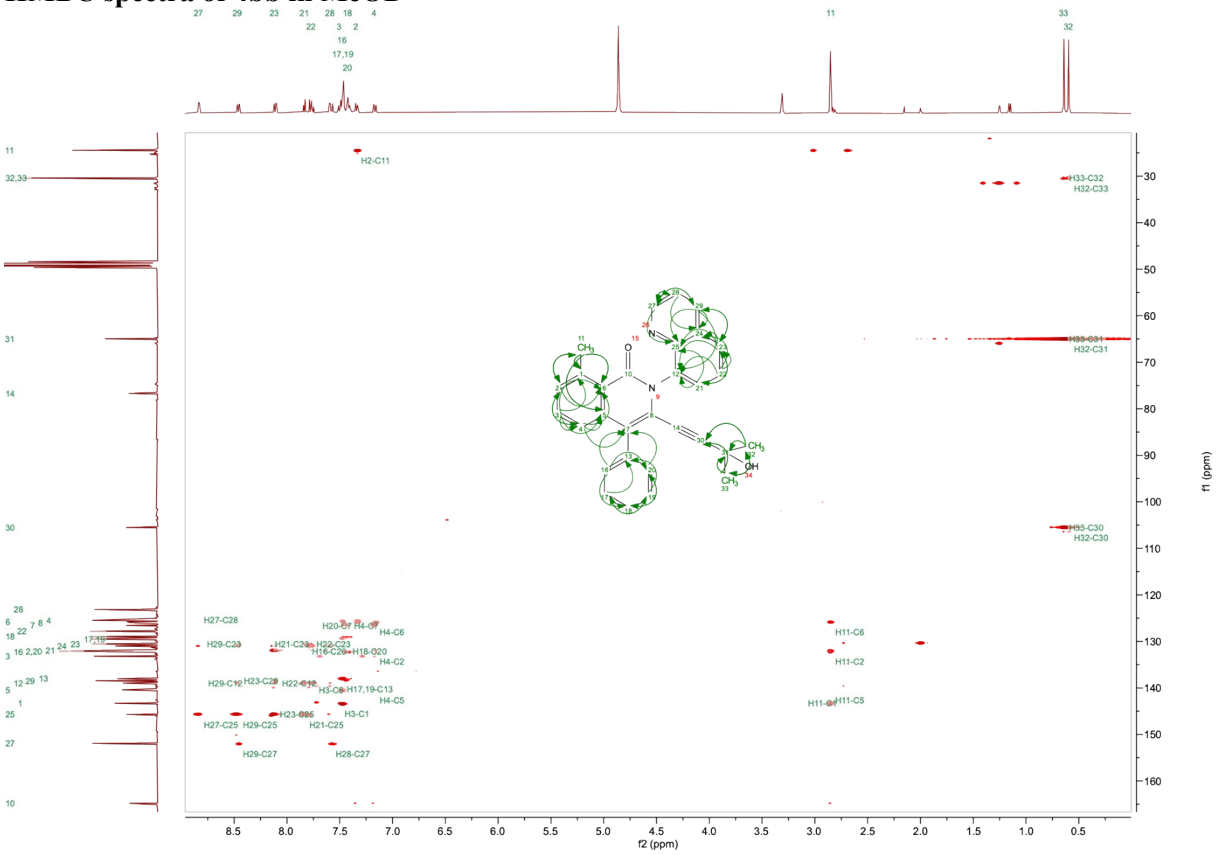
^{13}C spectra of 4bb in MeOD



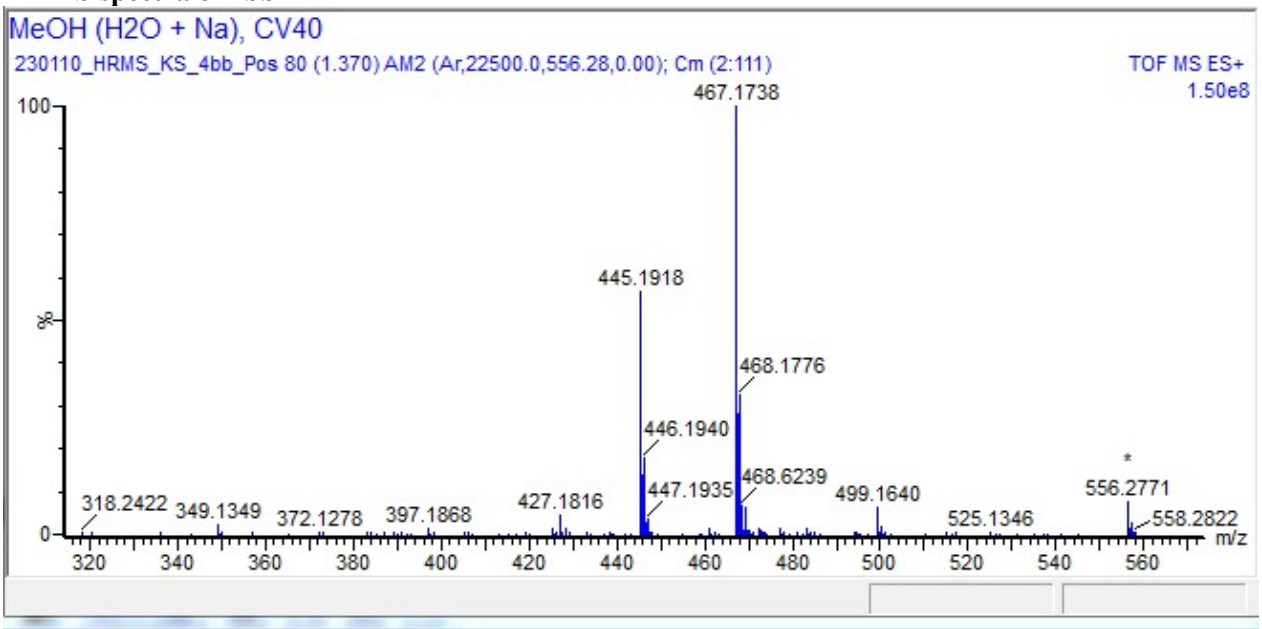
HSQC spectra of 4bb in MeOD



HMBC spectra of 4bb in MeOD



HRMS spectra of 4bb



Single Mass Analysis

Tolerance = 2.0 mDa / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

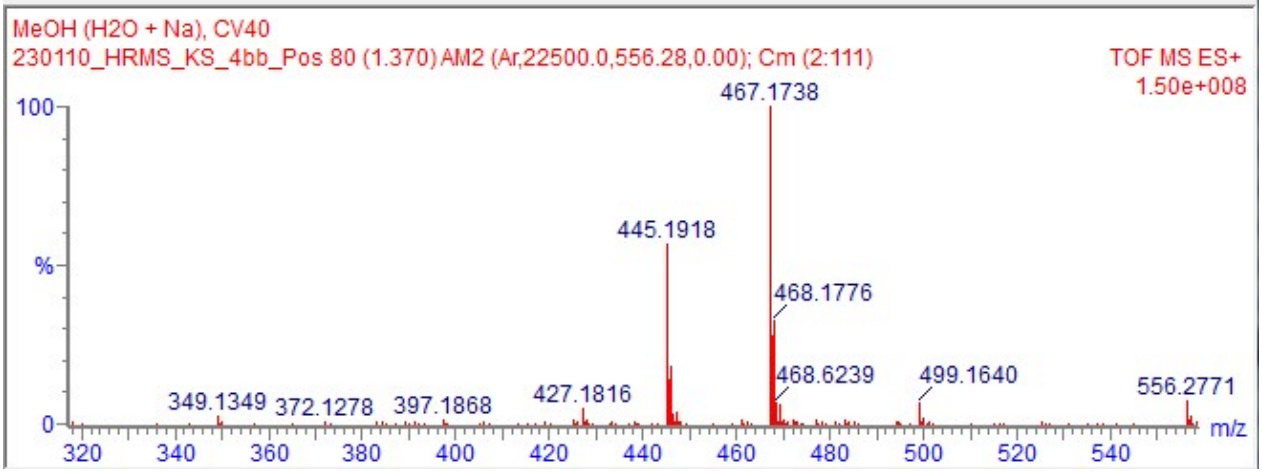
Monoisotopic Mass, Even Electron Ions

108 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

Elements Used:

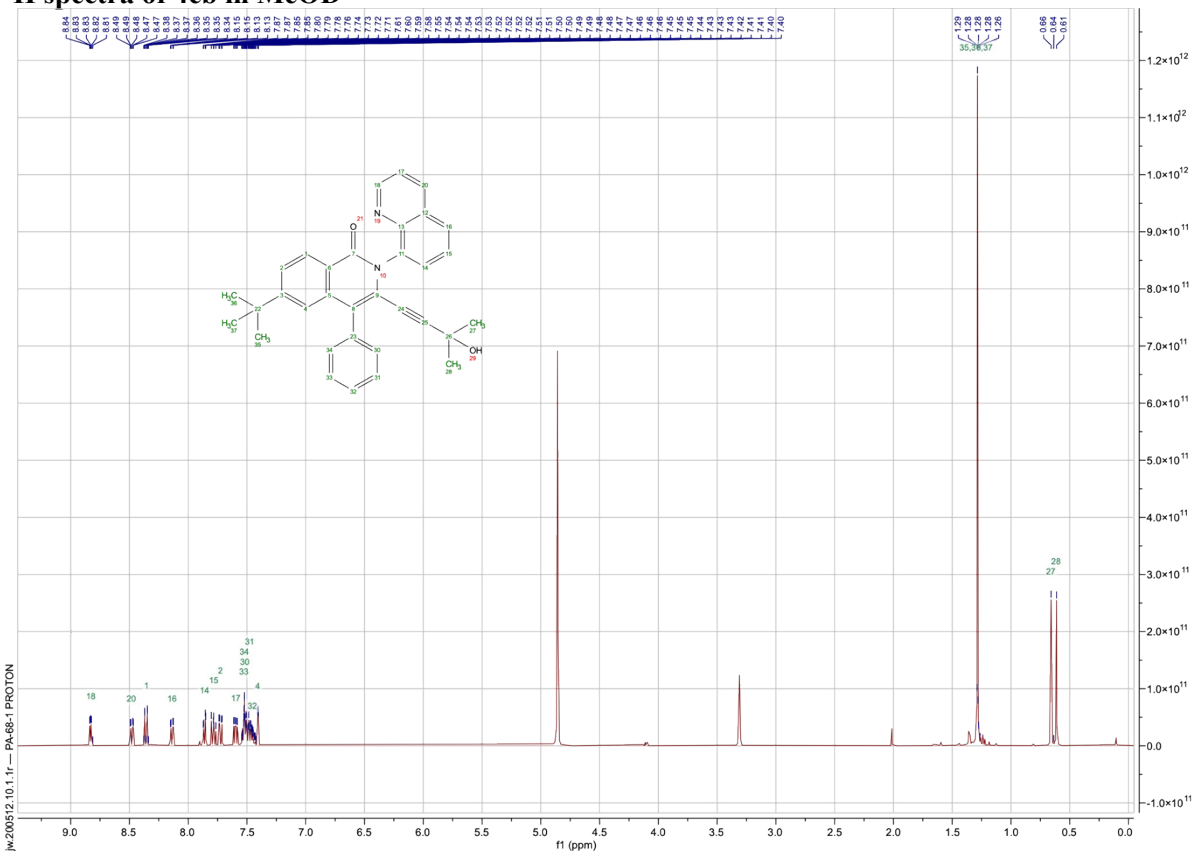
C: 1-40 H: 1-40 N: 1-4 O: 1-4 Na: 0-1

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i.	Fit Conf %	C	H	N	O	Na
445.1918	445.1916	0.2	0.4	19.5	C30 H25 N2 O2		3.n..n/a	30	25	2	2	

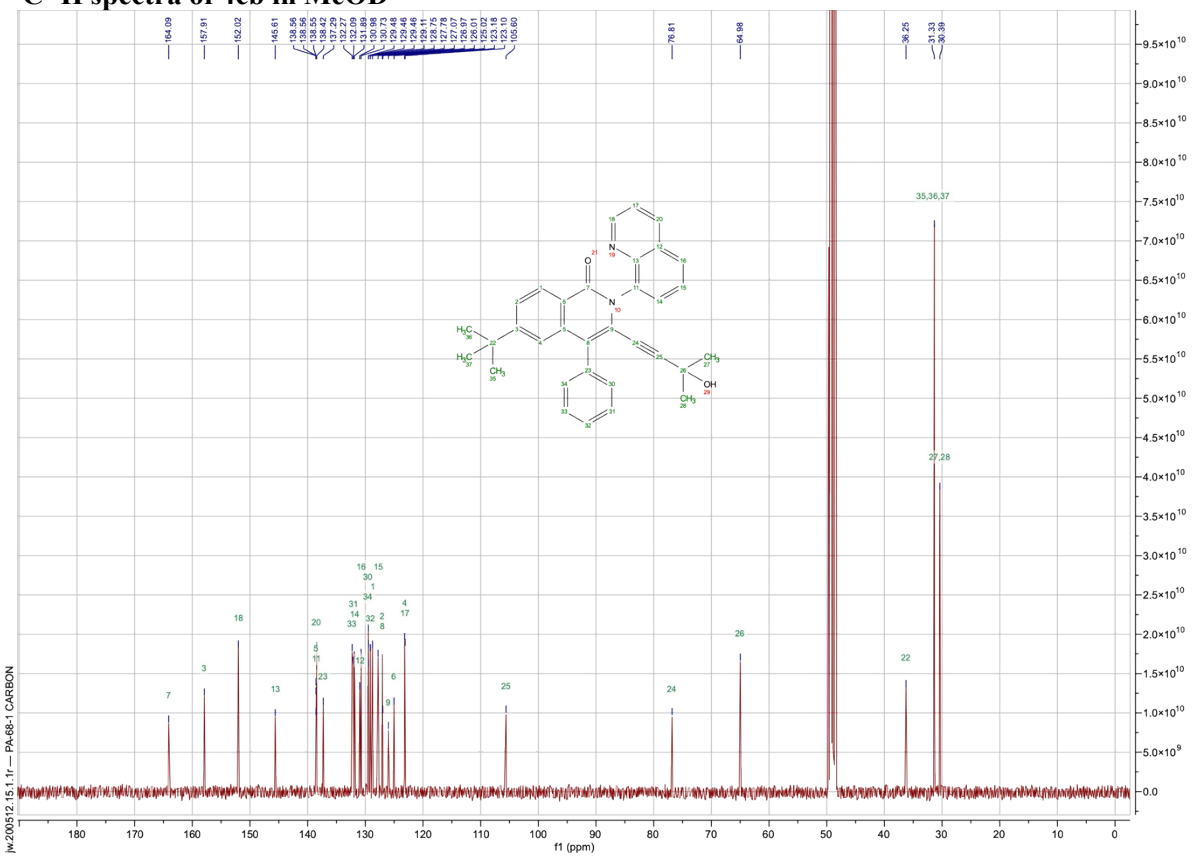


4cb

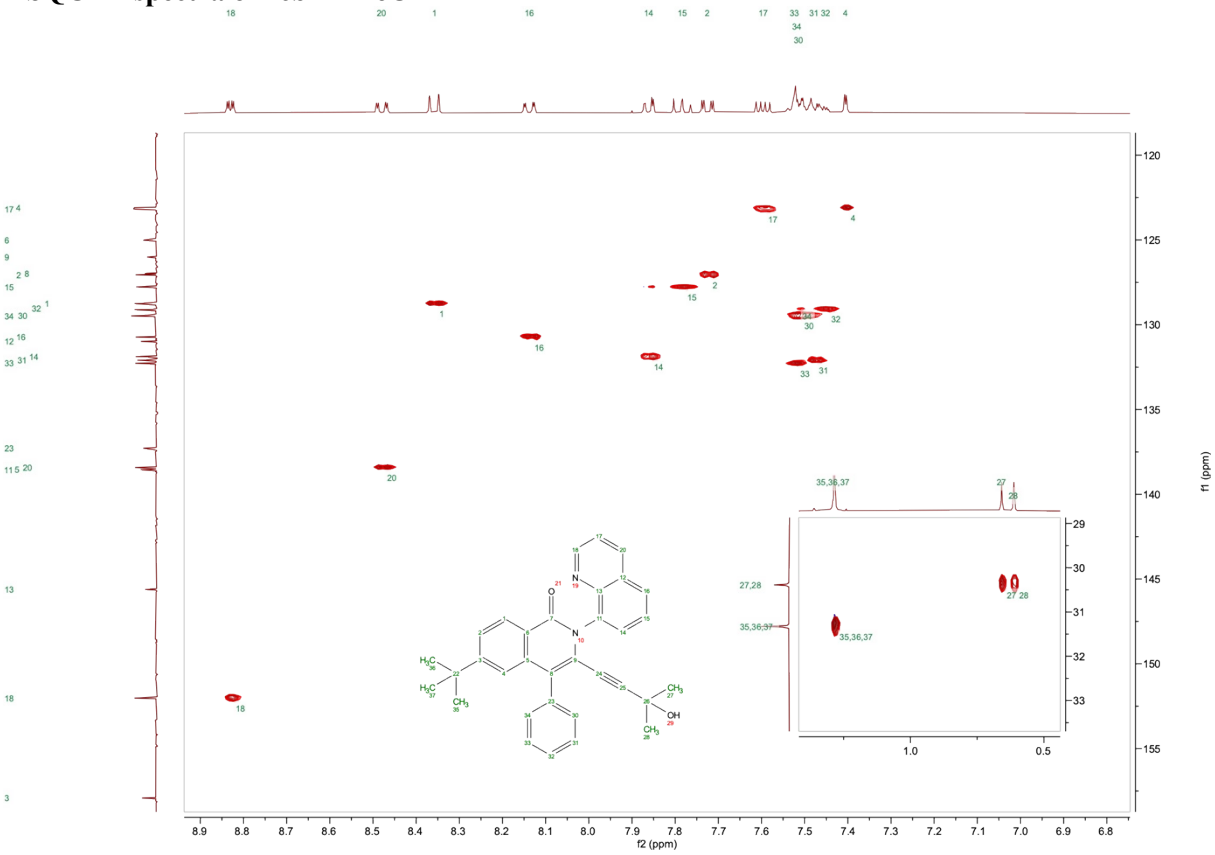
^{1}H spectra of 4cb in MeOD



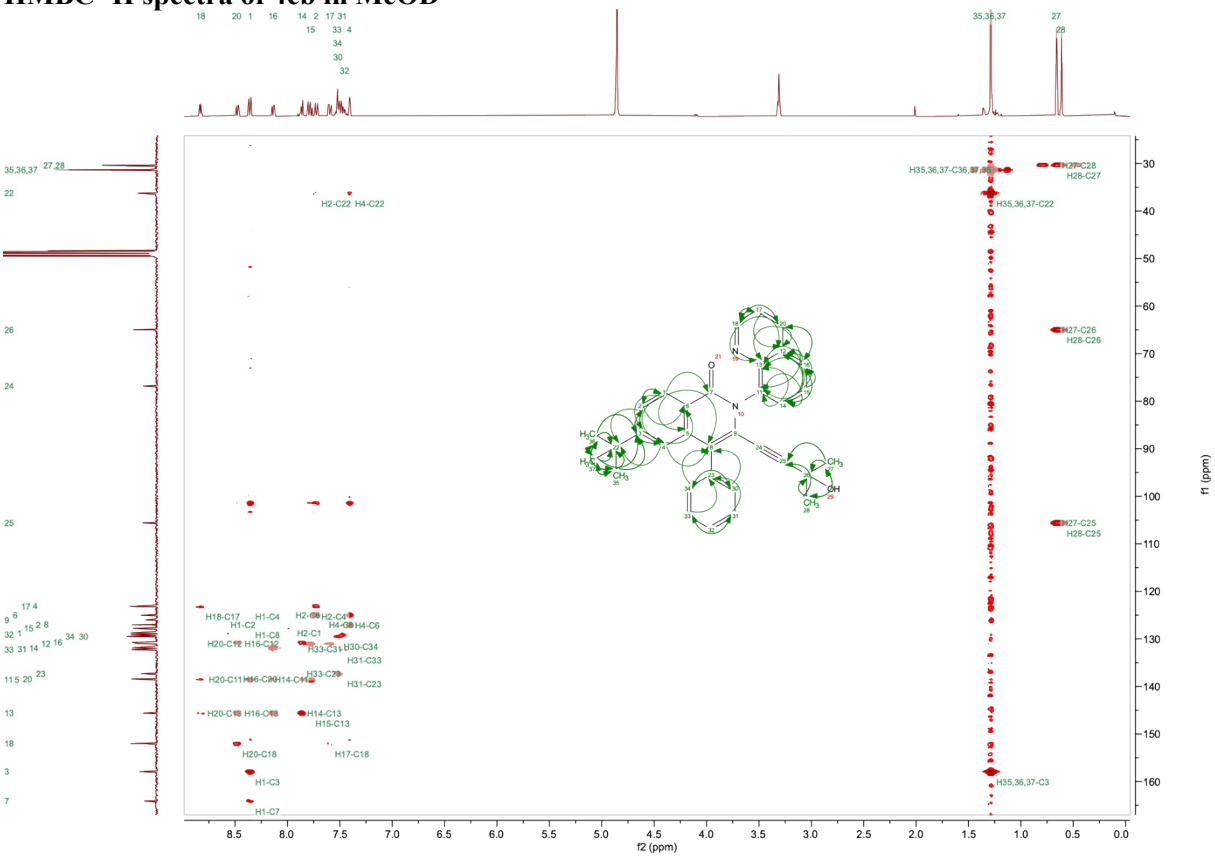
^{13}C ^{1}H spectra of 4cb in MeOD



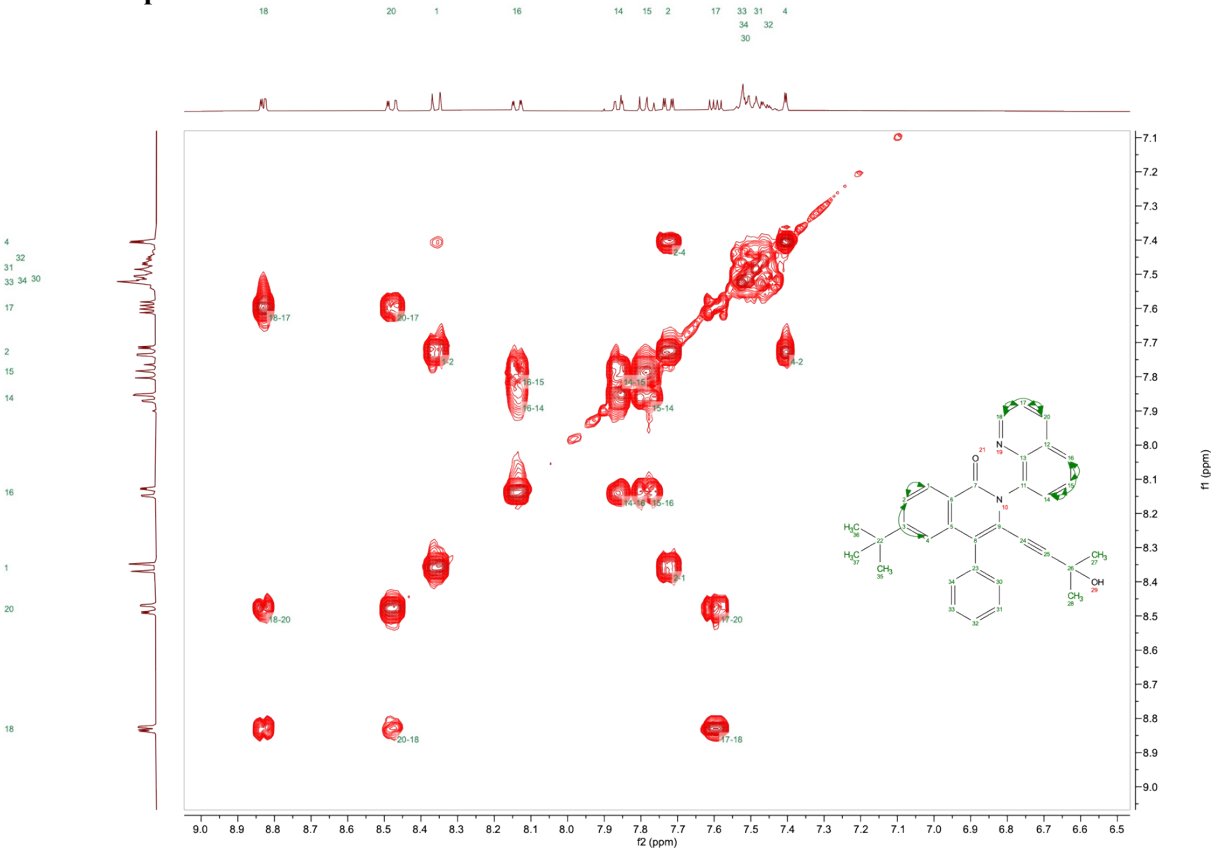
HSQC ^{1}H spectra of 4cb in MeOD



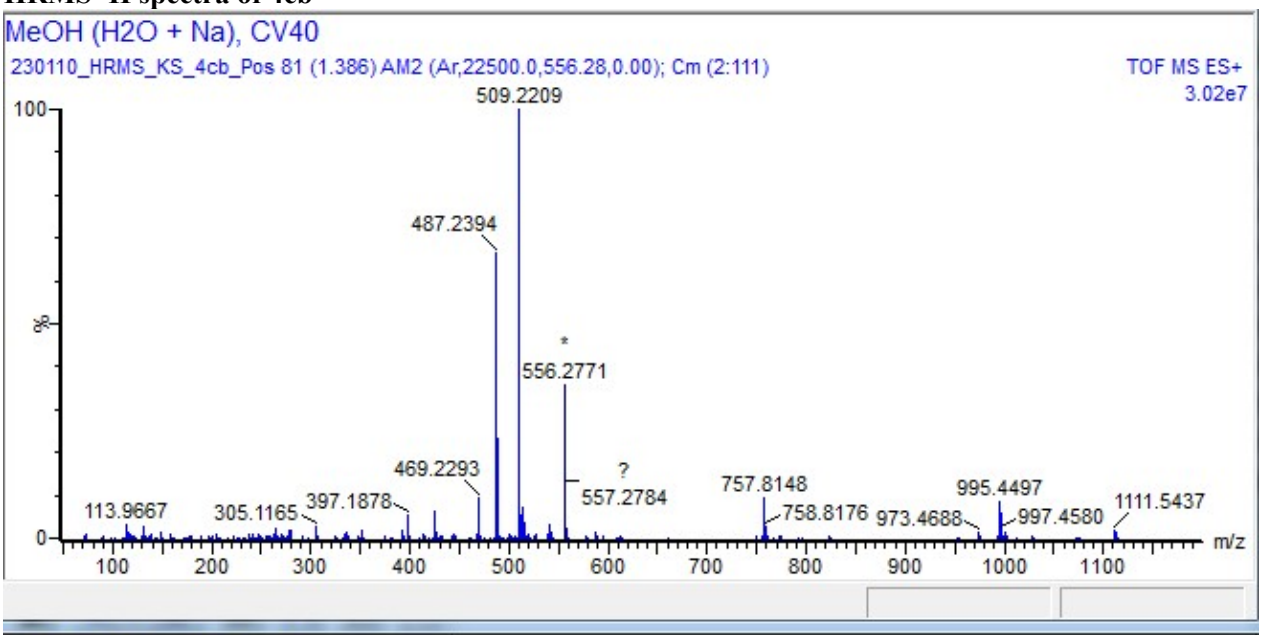
HMBC ^{1}H spectra of 4cb in MeOD



COSY ^{1}H spectra of 4cb in MeOD



HRMS ^{1}H spectra of 4cb



Single Mass Analysis

Tolerance = 2.0 mDa / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

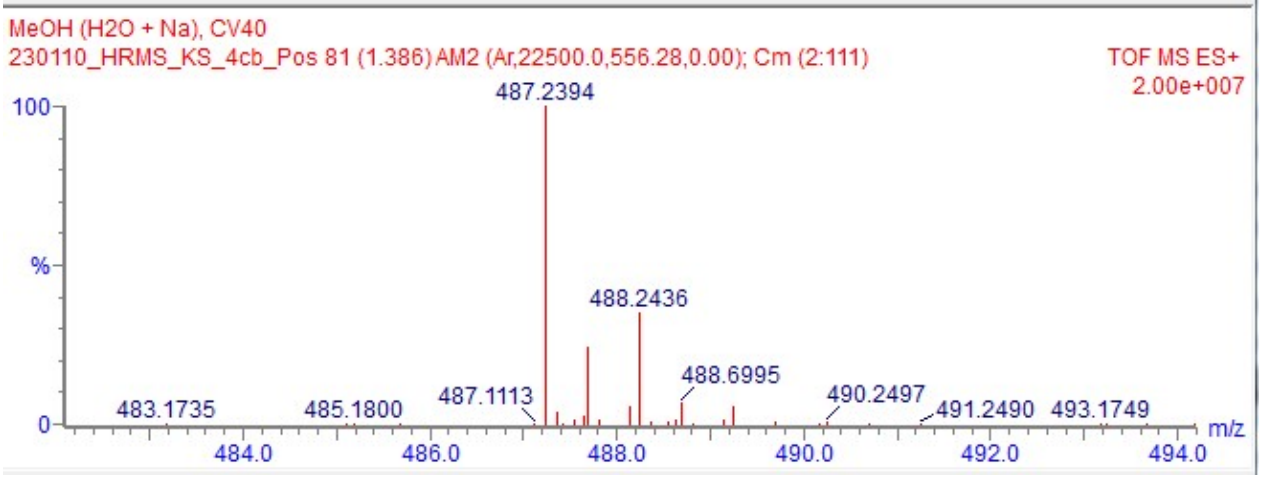
Monoisotopic Mass, Even Electron Ions

106 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

Elements Used:

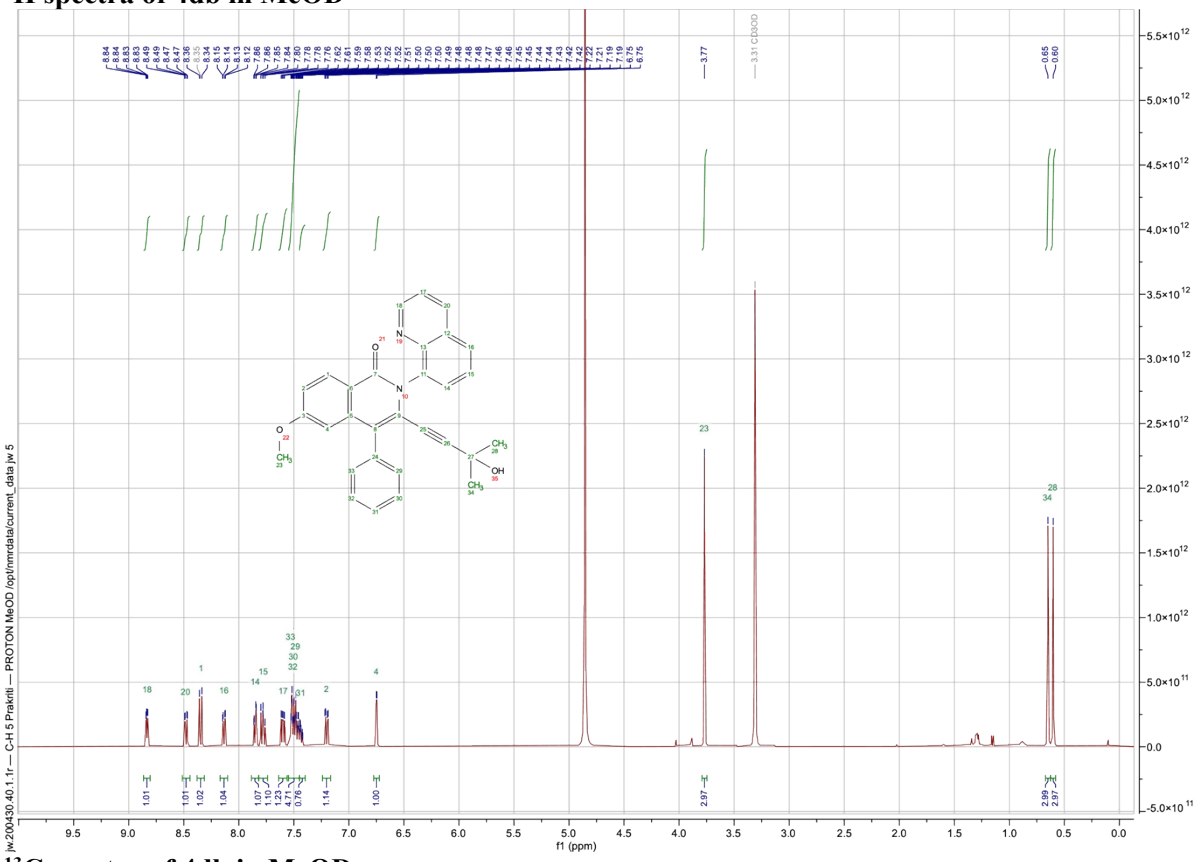
C: 1-40 H: 1-40 N: 1-4 O: 1-4 Na: 0-1

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i.	i...	Fit Conf %	C	H	N	O	Na
487.2394	487.2386	0.8	1.6	19.5	C33 H31 N2 O2	3...	n...	n/a	33	31	2	2	

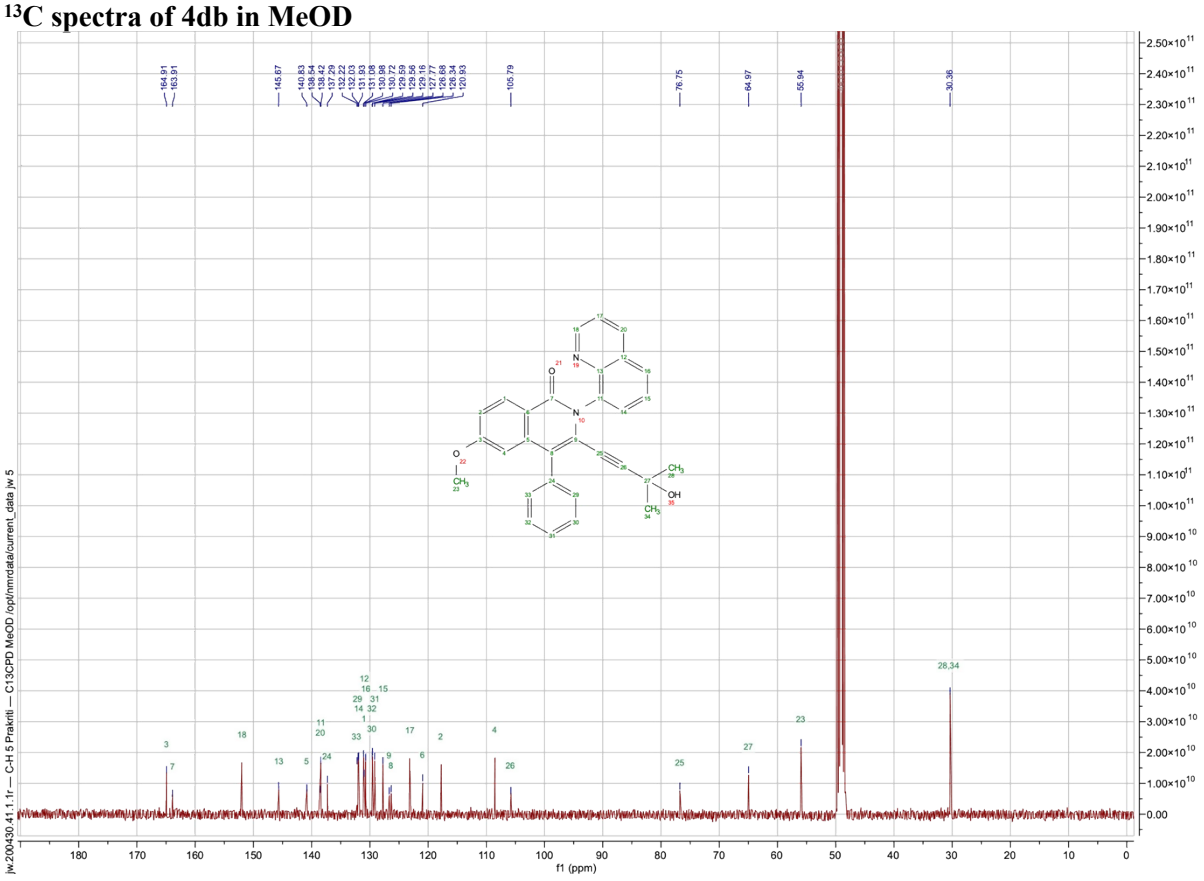


4db

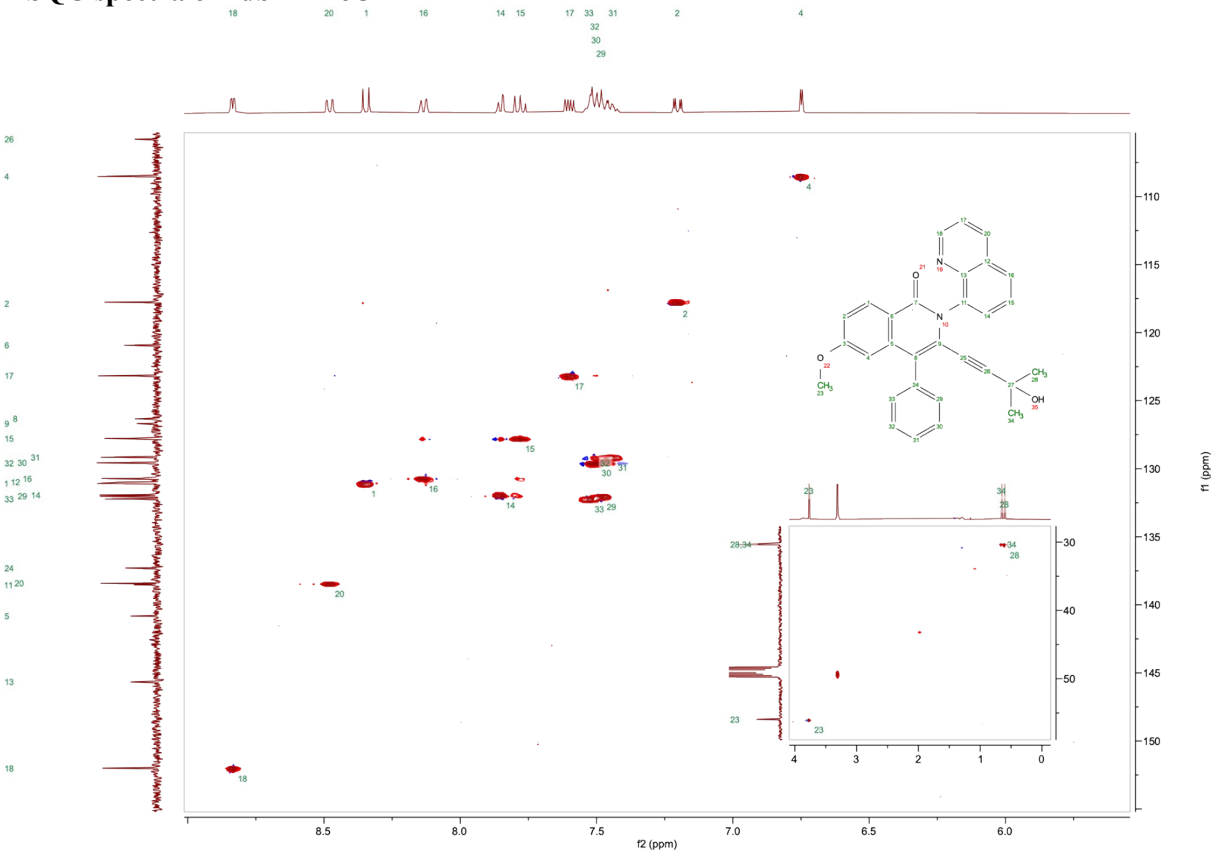
^{1}H spectra of 4db in MeOD



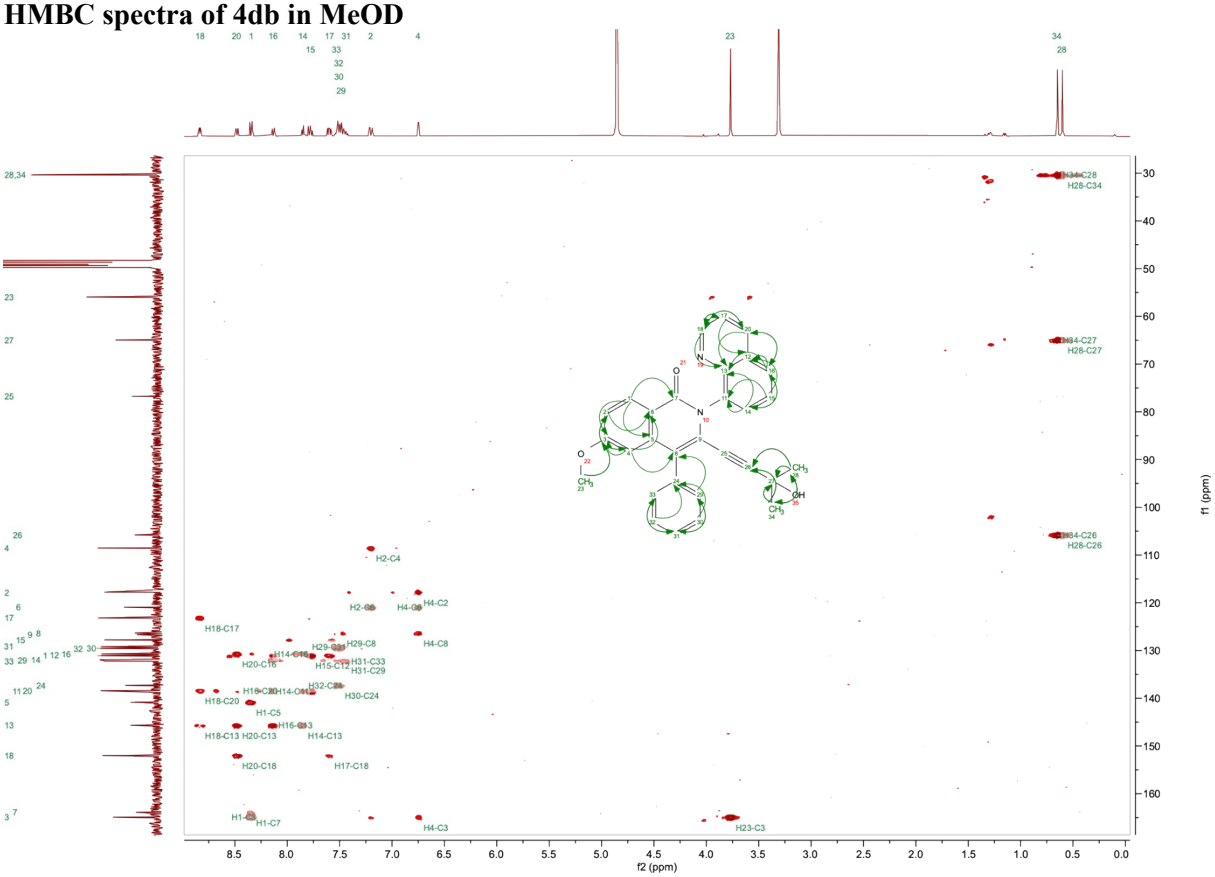
^{13}C spectra of 4db in MeOD



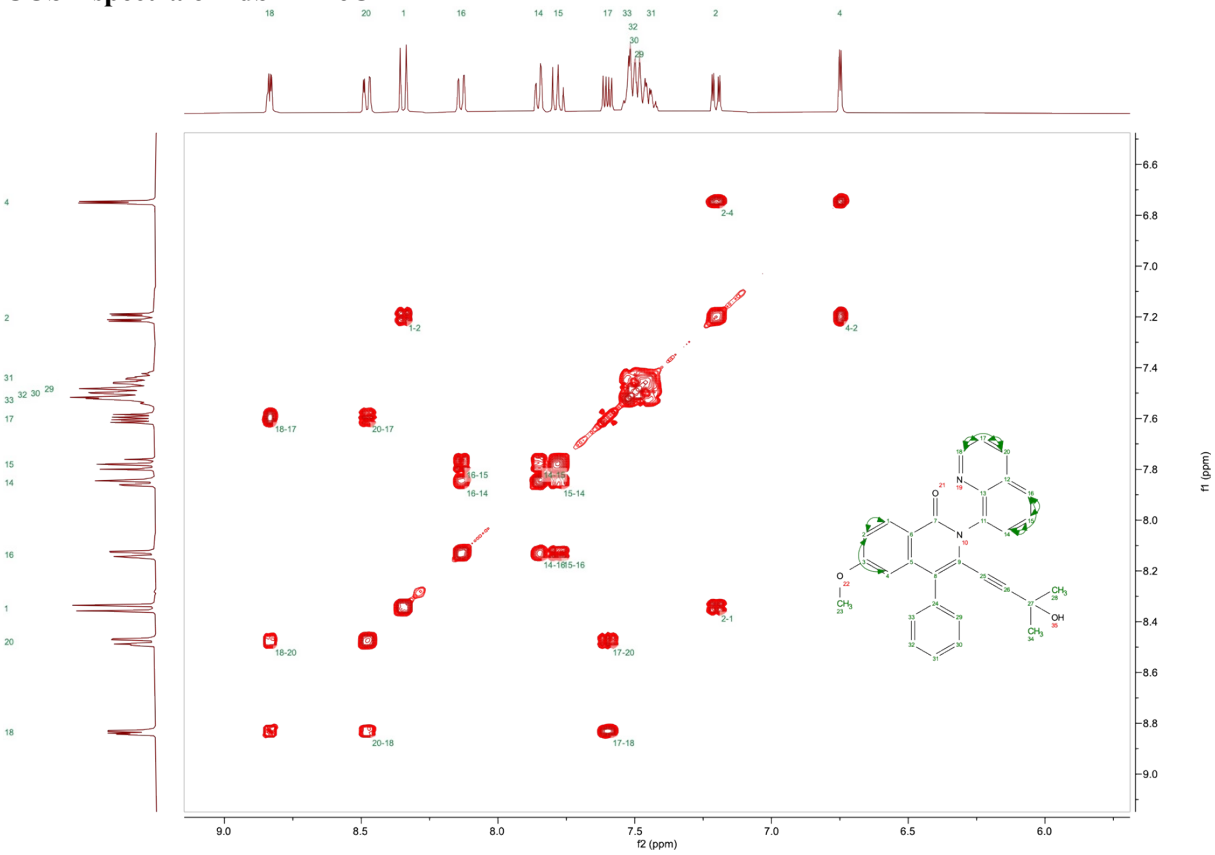
HSQC spectra of 4db in MeOD



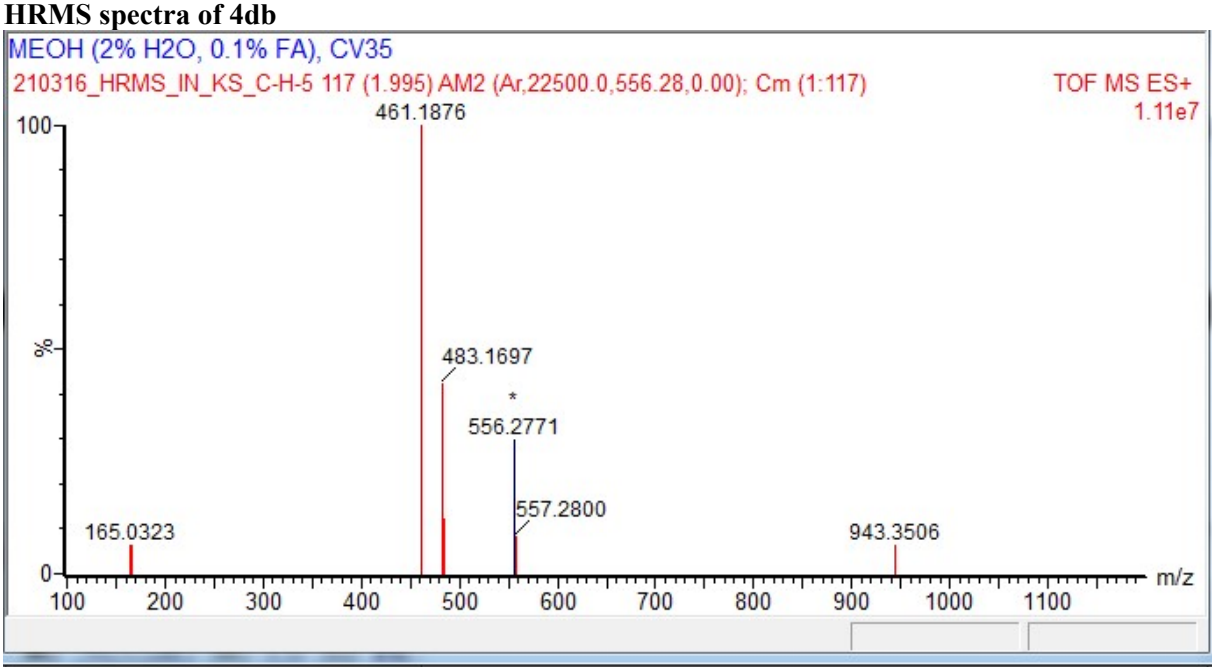
HMBC spectra of 4db in MeOD



COSY spectra of 4db in MeOD



HRMS spectra of 4db



Single Mass Analysis

Tolerance = 2.0 mDa / DBE: min = -0.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

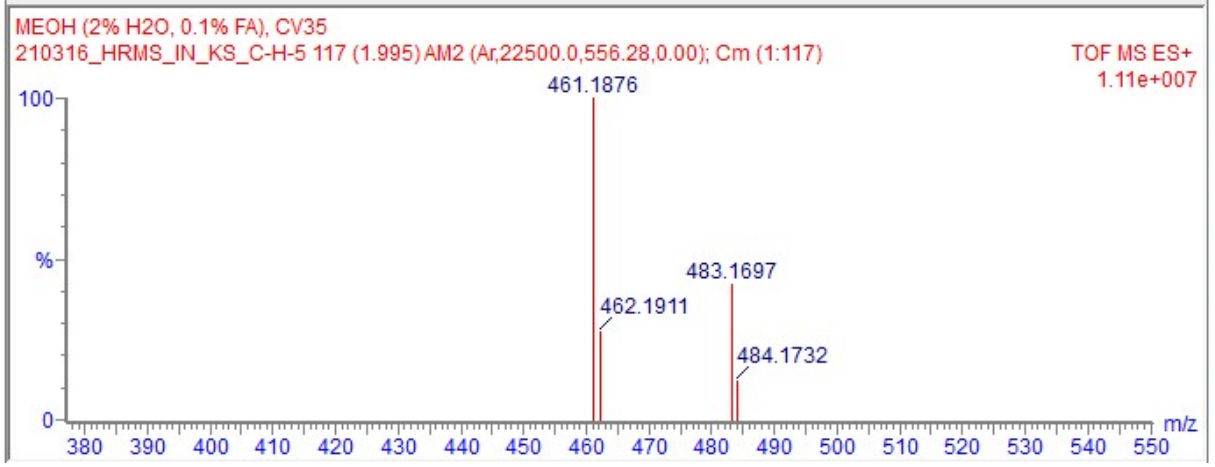
Monoisotopic Mass, Even Electron Ions

179 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

Elements Used:

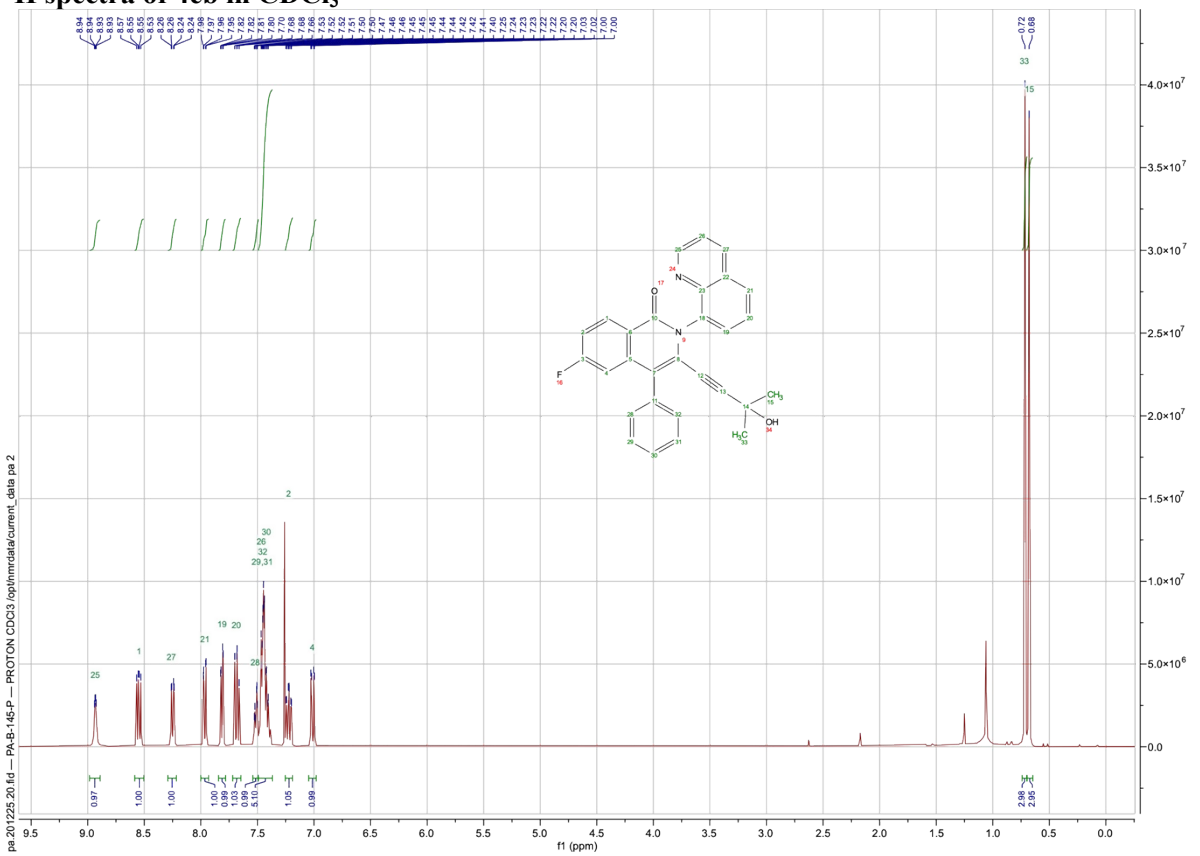
C: 0-50 H: 1-100 N: 0-3 O: 0-3 Na: 0-1

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	Fit Conf %	C	H	N	O	Na
461.1876	461.1881	-0.5	-1.1	20.5	C33 H26 O Na	47.7	0..73.87	33	26		1	1
	461.1865	1.1	2.4	19.5	C30 H25 N2 O3	48.8	1..26.13	30	25	2	3	

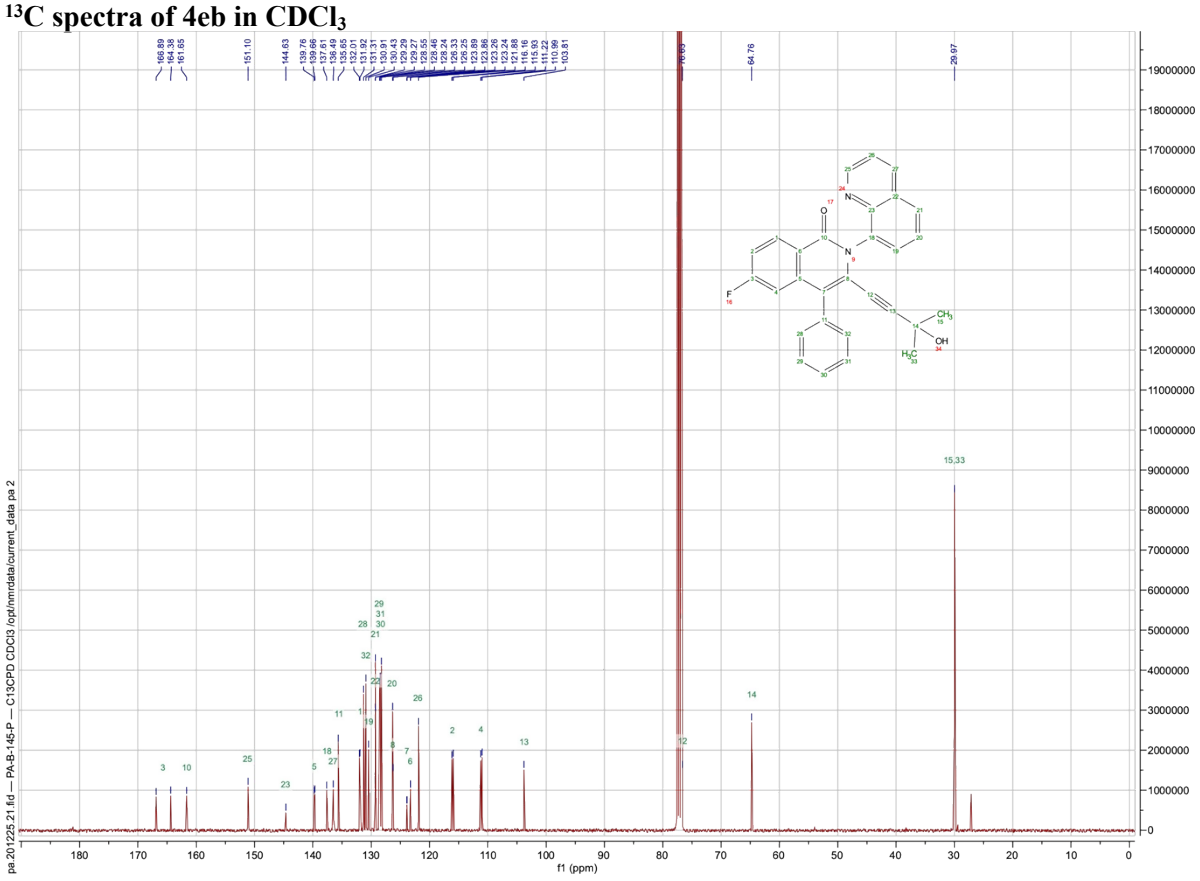


4eb

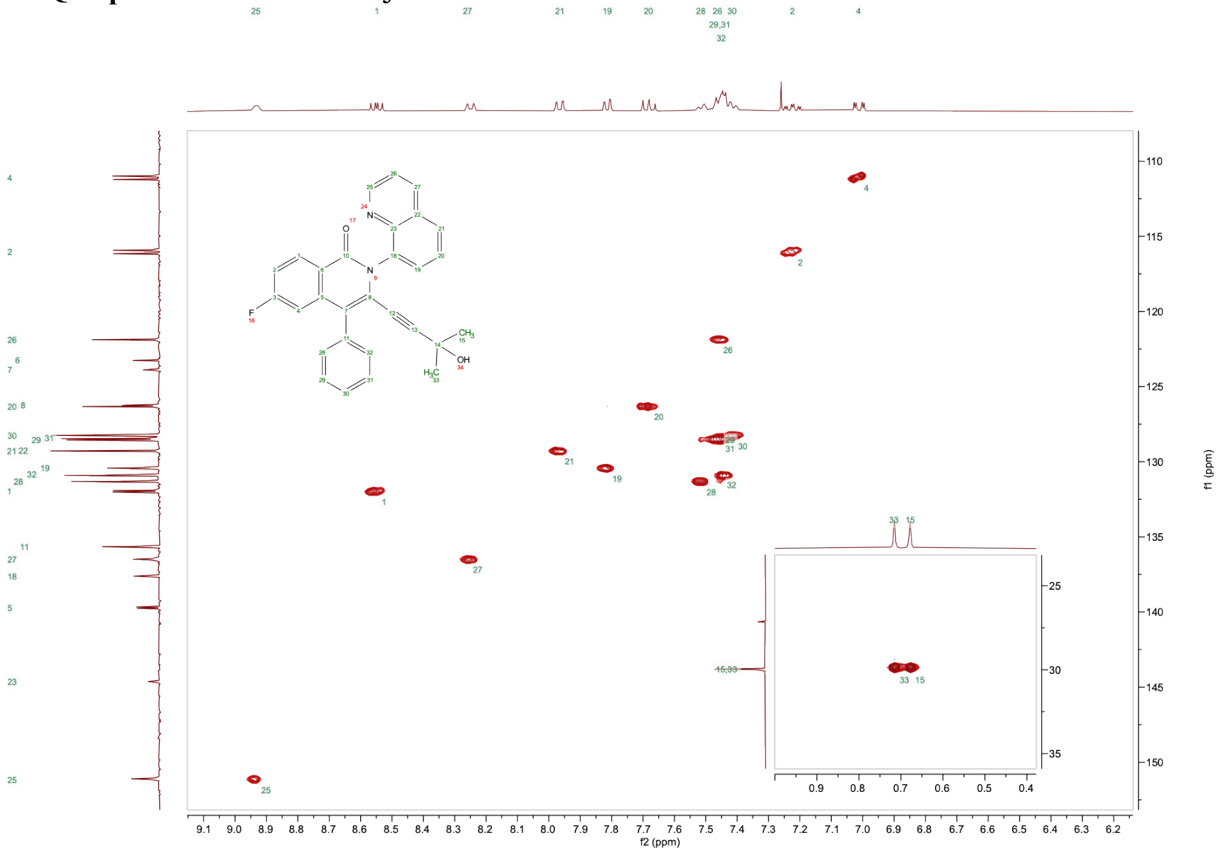
^{1}H spectra of 4eb in $CDCl_3$



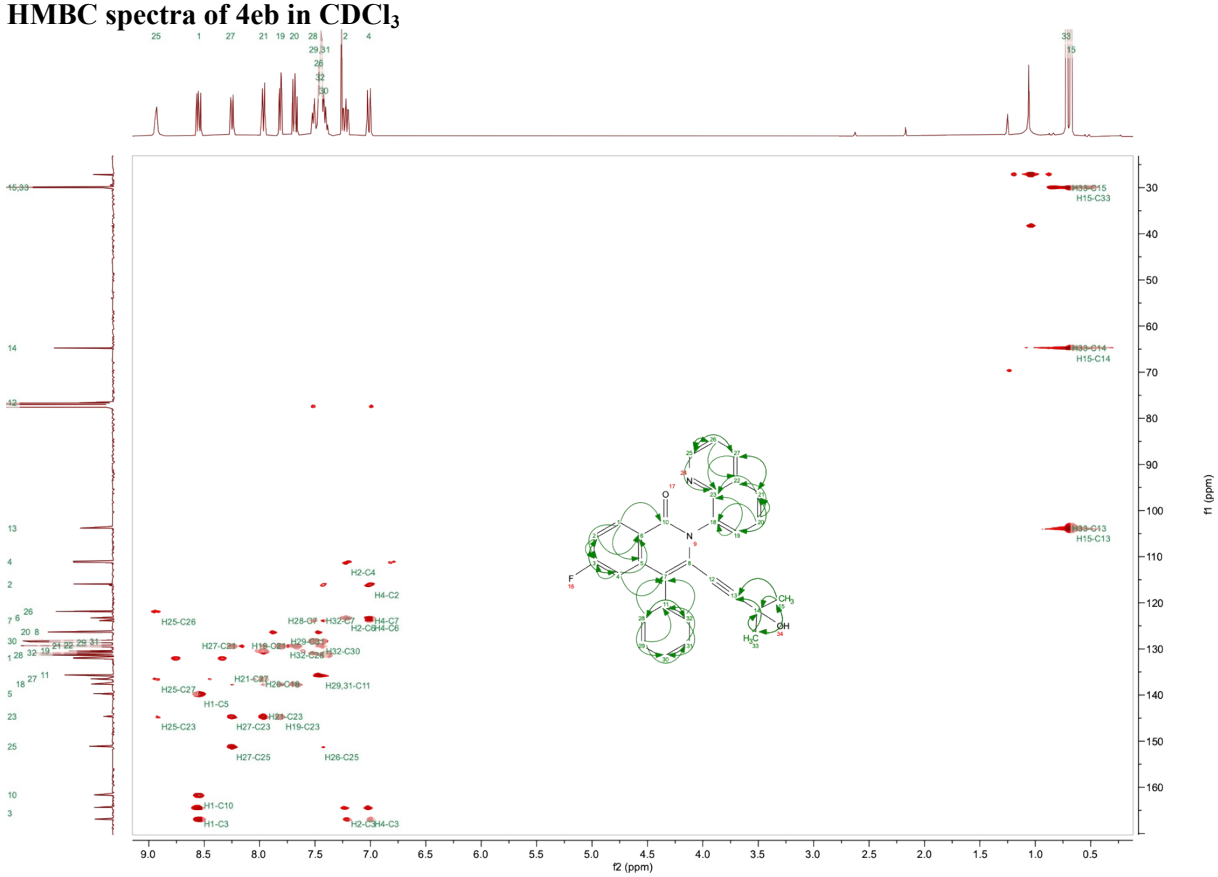
^{13}C spectra of 4eb in $CDCl_3$



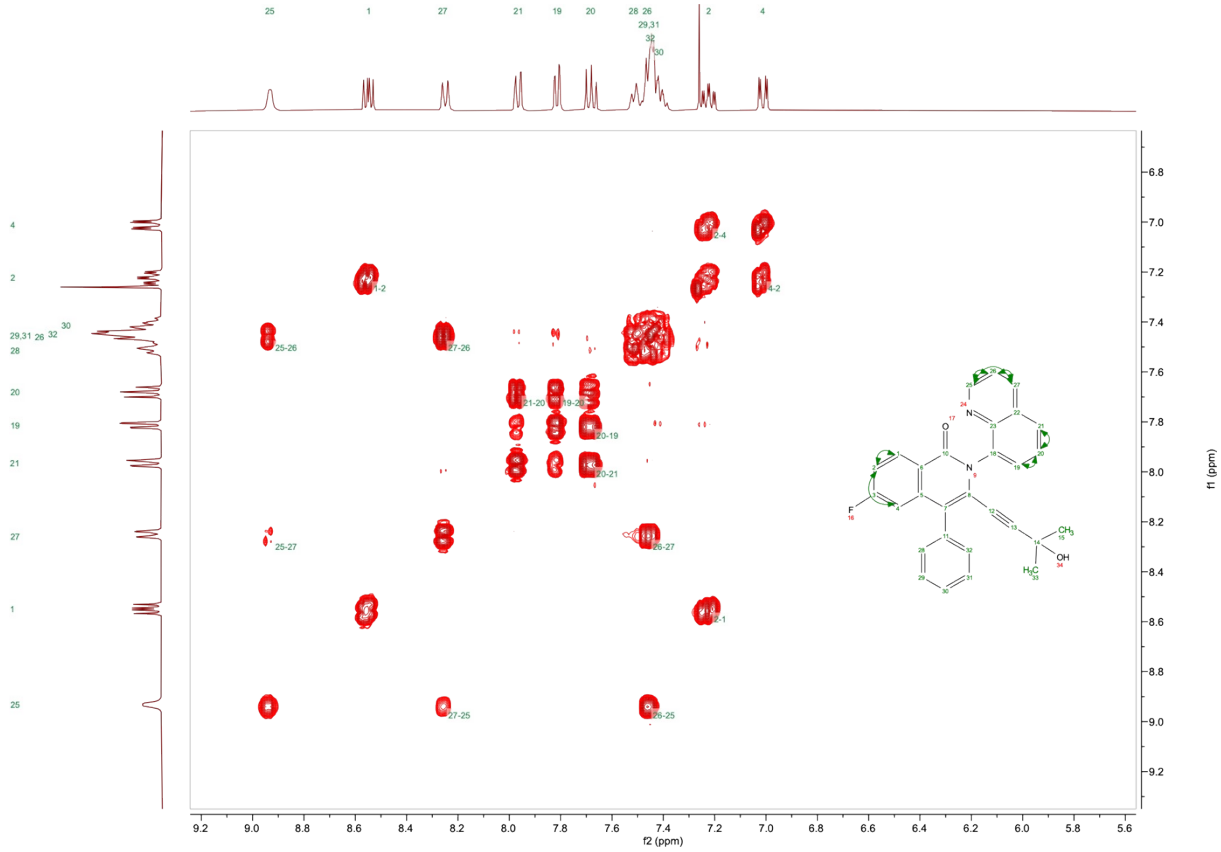
HSQC spectra of 4eb in $CDCl_3$



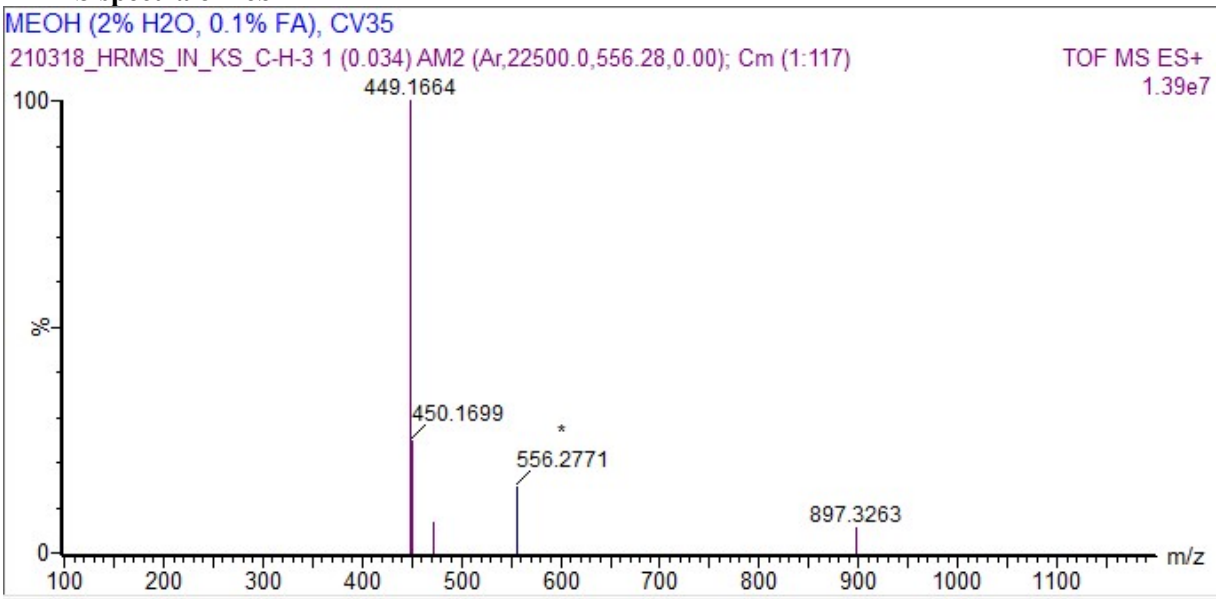
HMBC spectra of 4eb in $CDCl_3$



COSY spectra of 4eb in $CDCl_3$



HRMS spectra of 4eb



Single Mass Analysis

Tolerance = 2.0 mDa / DBE: min = -0.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

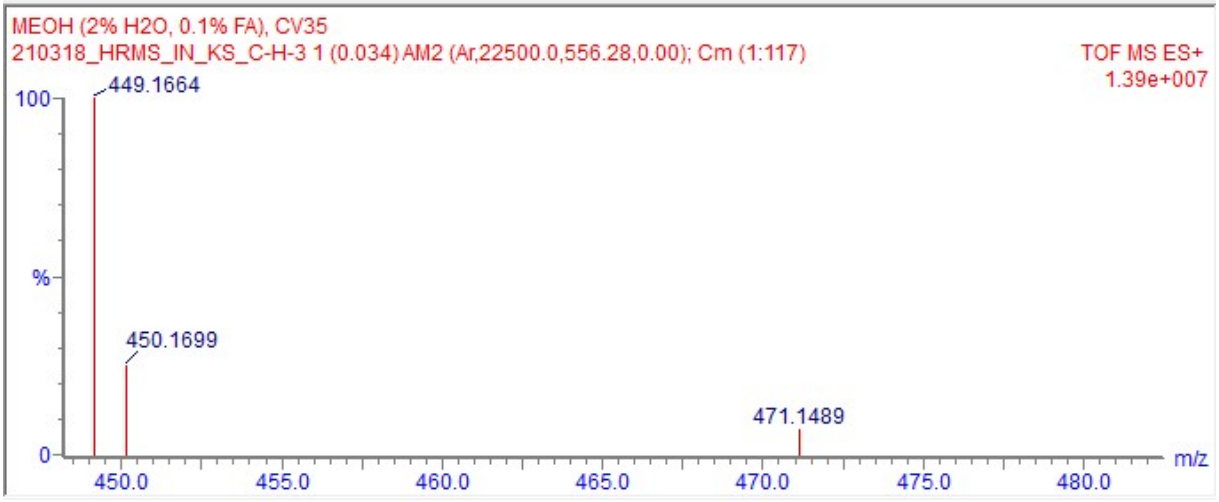
Monoisotopic Mass, Even Electron Ions

339 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)

Elements Used:

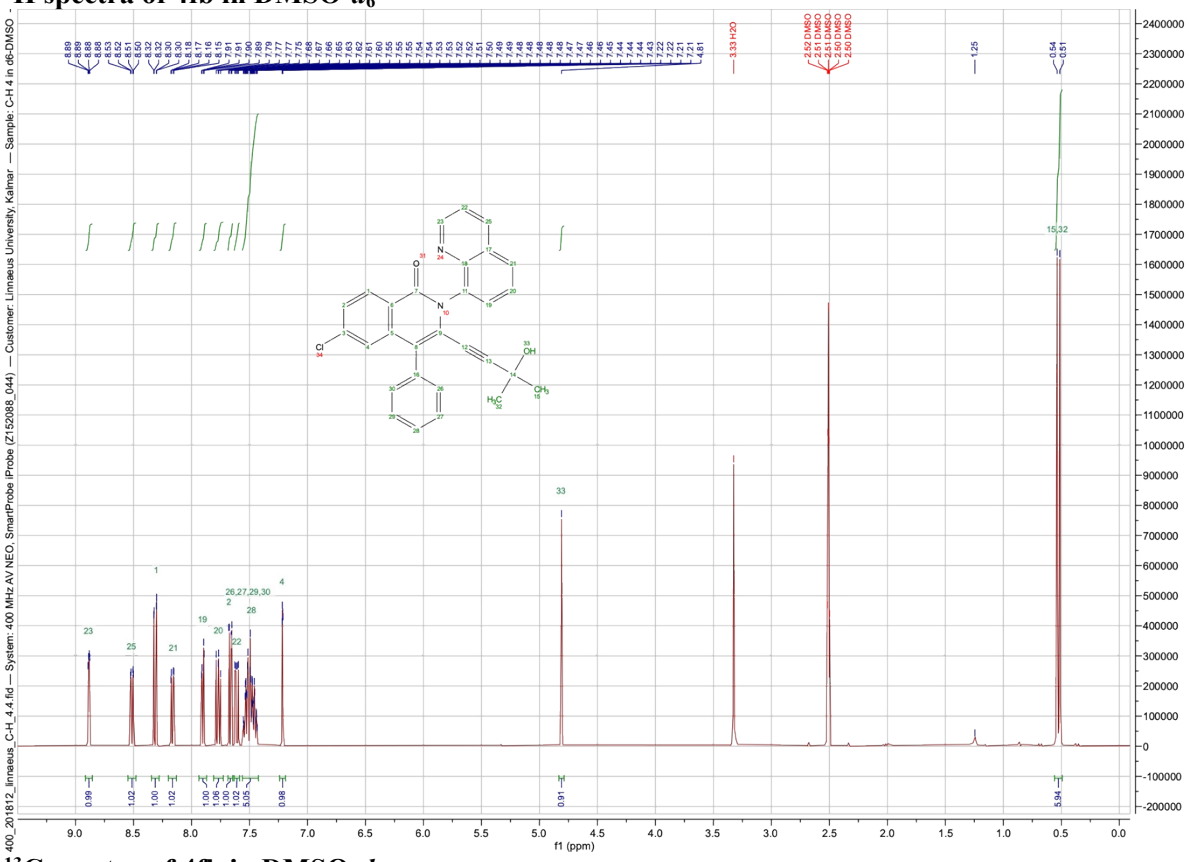
C: 0-50 H: 1-100 N: 0-3 O: 0-3 Na: 0-1 F: 0-1

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i.	Fit Conf %	C	H	N	O	Na	F
449.1664	449.1665	-0.1	-0.2	19.5	C29 H22 N2 O2 F	40	70.55	29	22	2	2		1
	449.1654	1.0	2.2	23.5	C32 H21 N2 O	41	20.55	32	21	2	1		
	449.1681	-1.7	-3.8	20.5	C32 H23 Na F	52	8.90	32	23			1	1

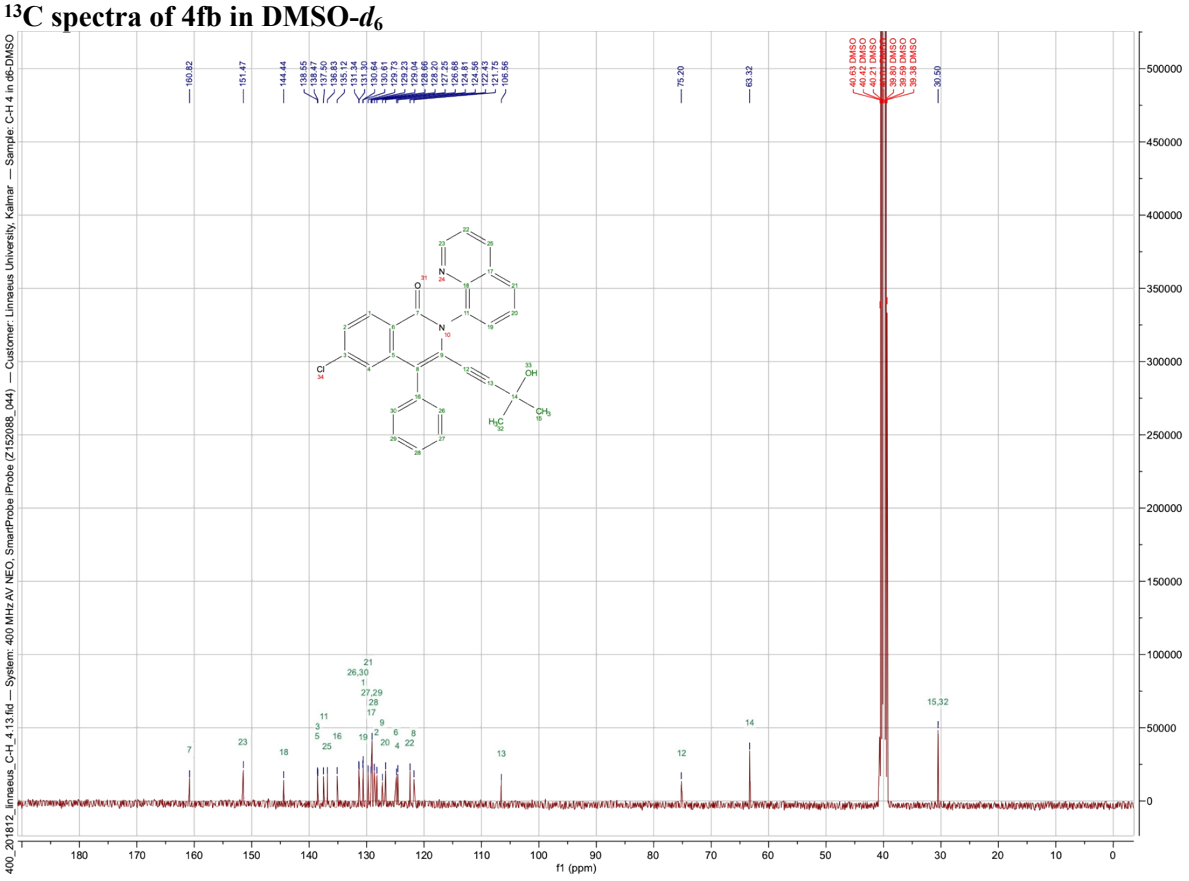


4fb

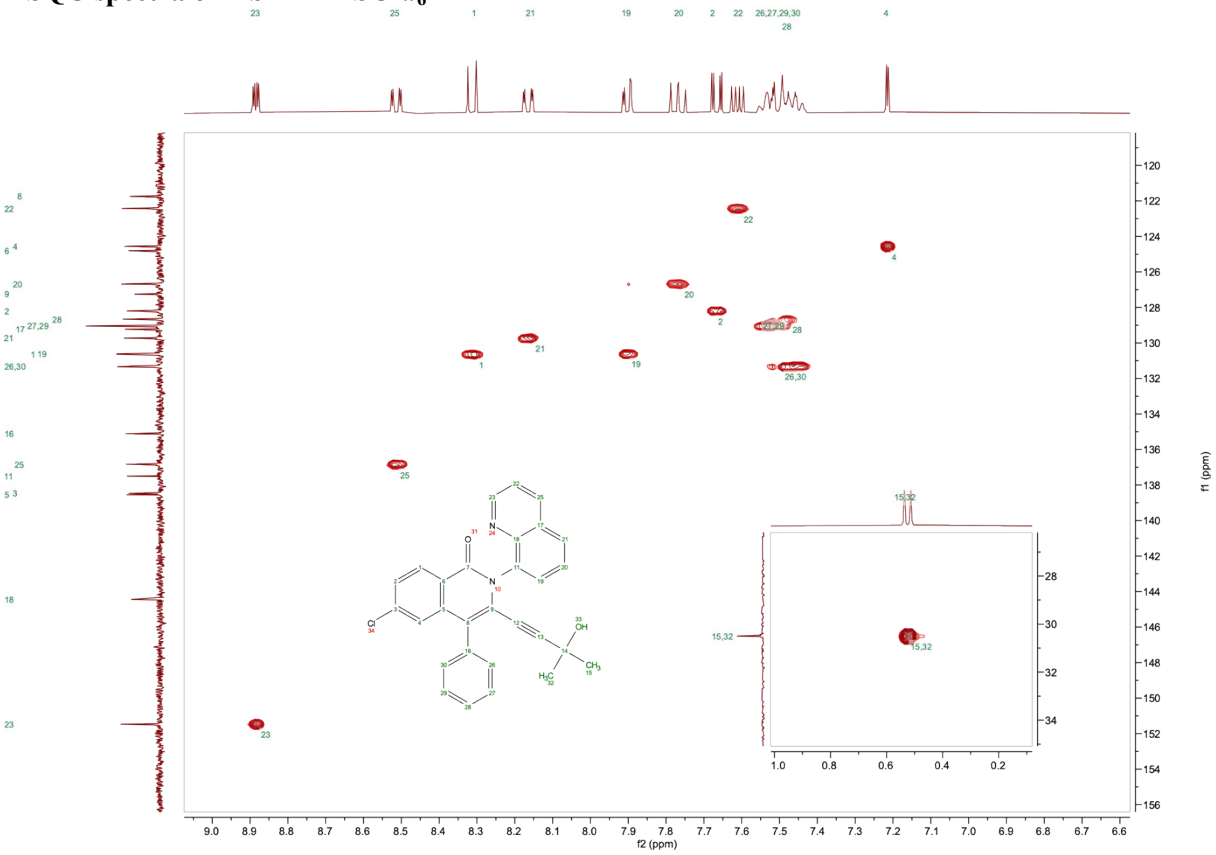
^{1}H spectra of 4fb in DMSO-d_6



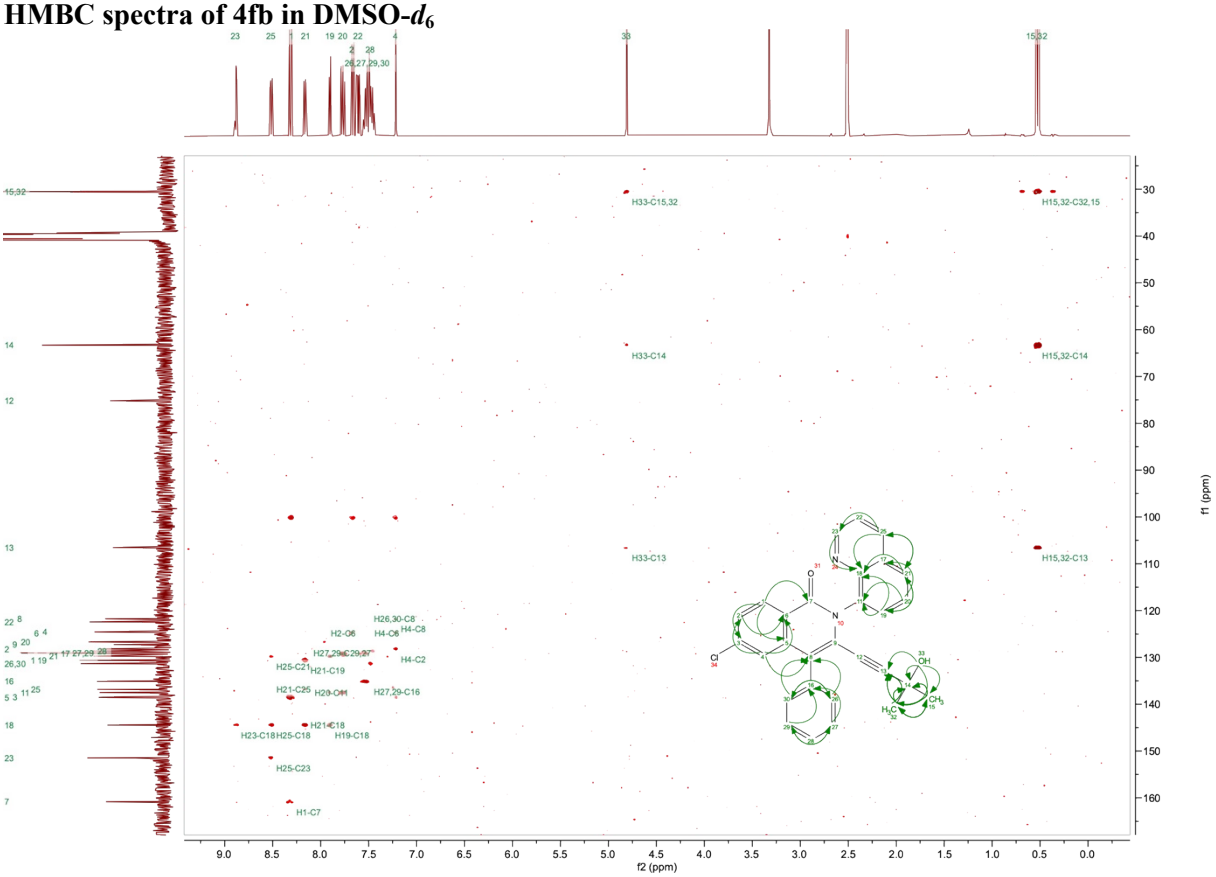
^{13}C spectra of 4fb in DMSO-d_6



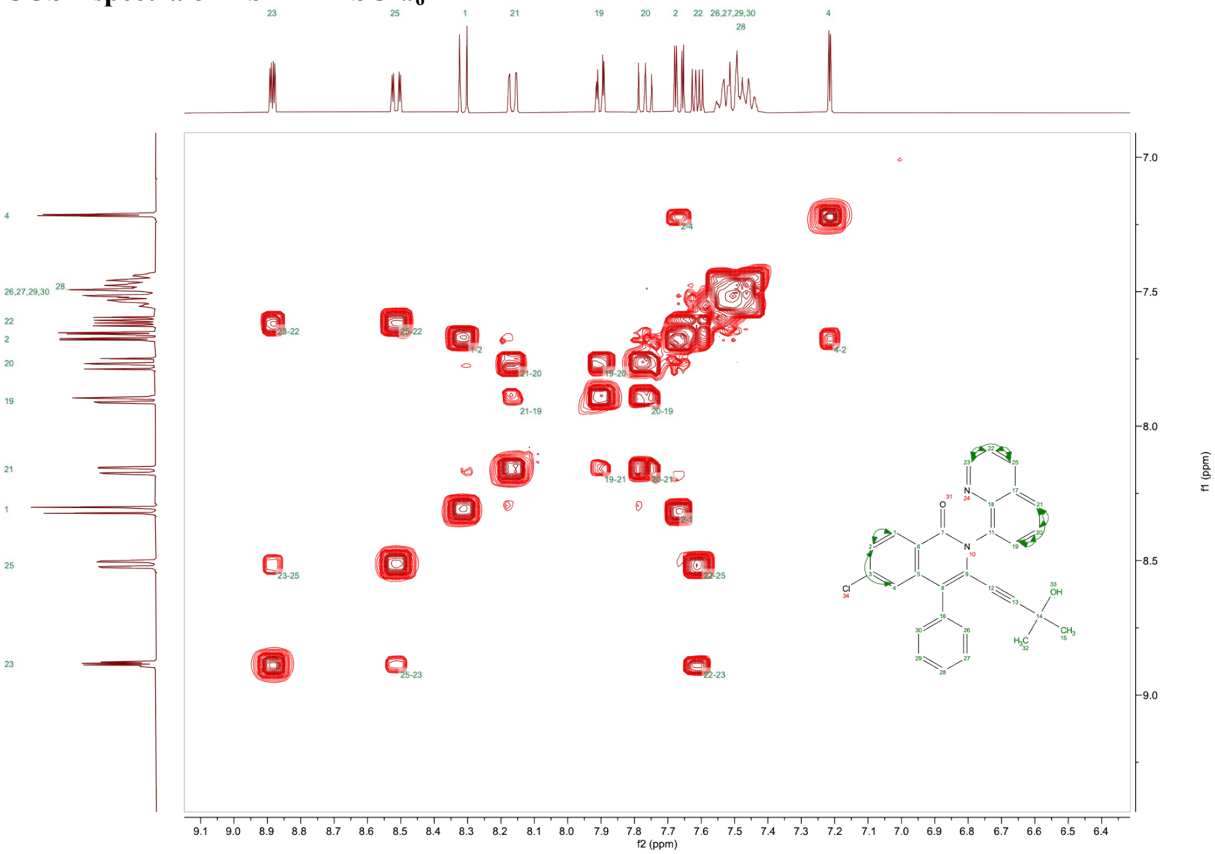
HSQC spectra of 4fb in DMSO-d_6



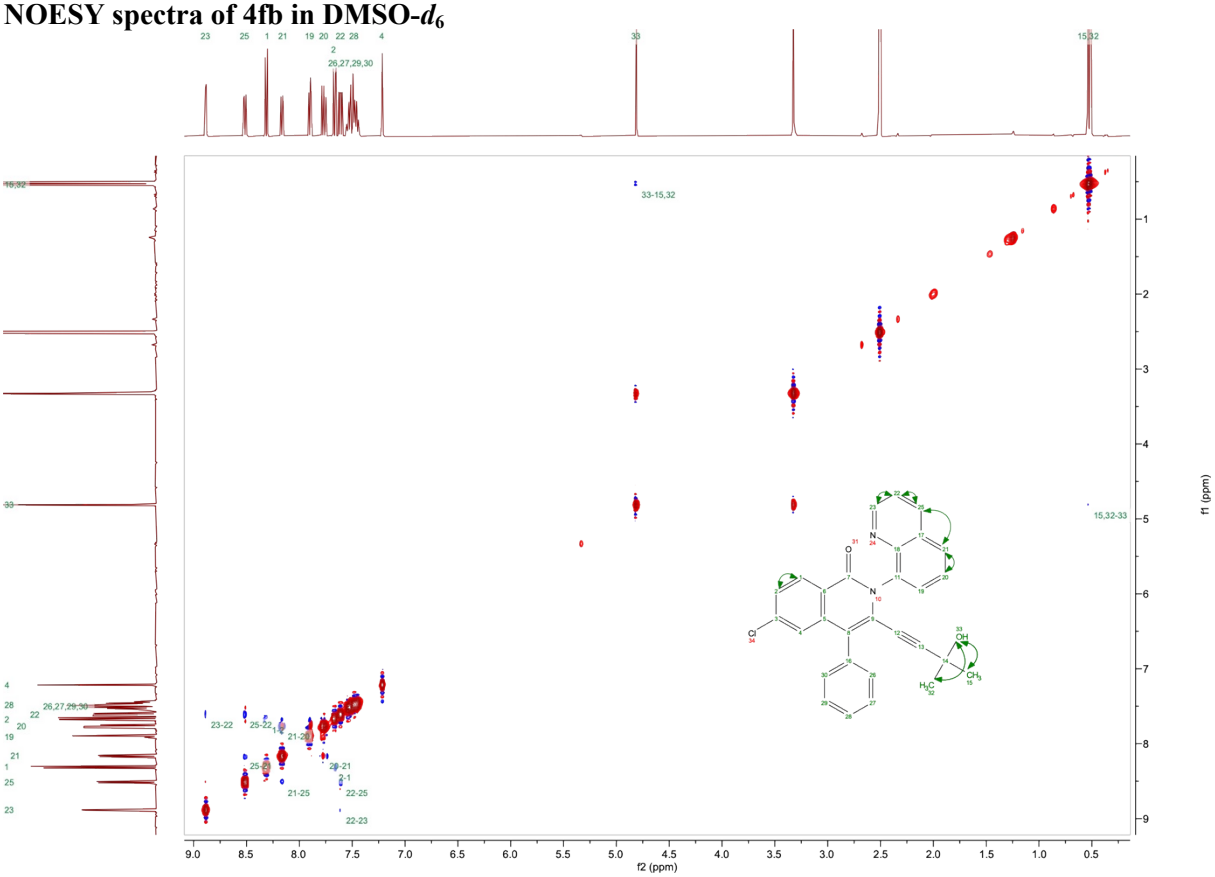
HMBC spectra of 4fb in DMSO-d_6



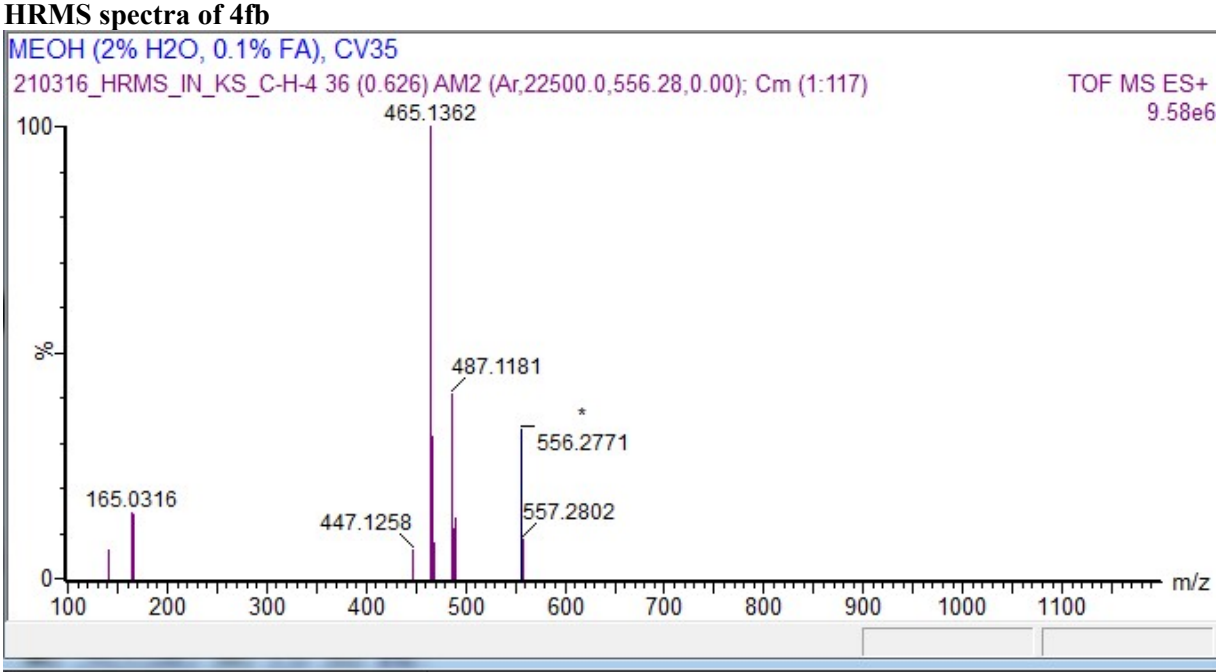
COSY spectra of 4fb in DMSO-d_6



NOESY spectra of 4fb in DMSO-d_6



HRMS spectra of 4fb



Single Mass Analysis

Tolerance = 2.0 mDa / DBE: min = -0.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

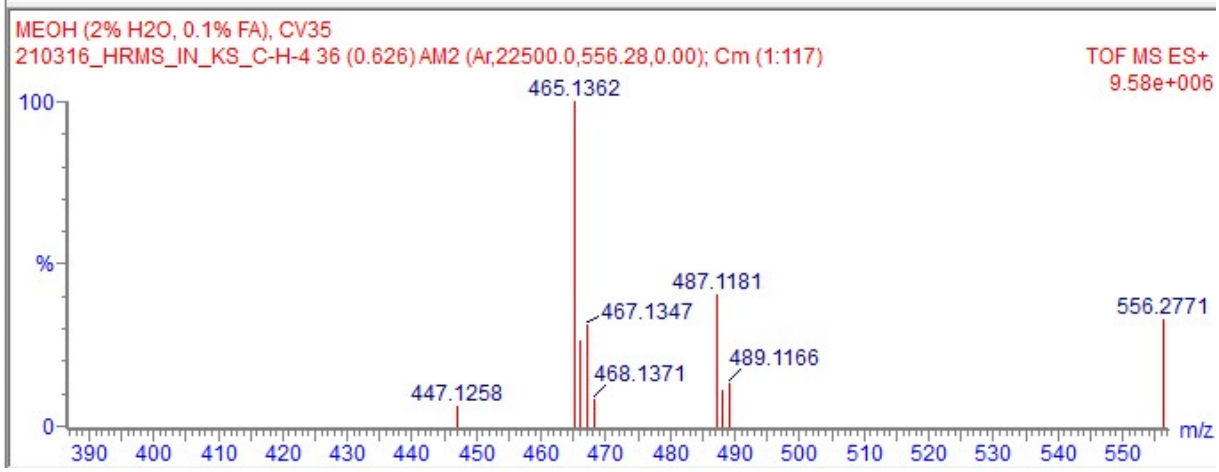
Monoisotopic Mass, Even Electron Ions

426 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)

Elements Used:

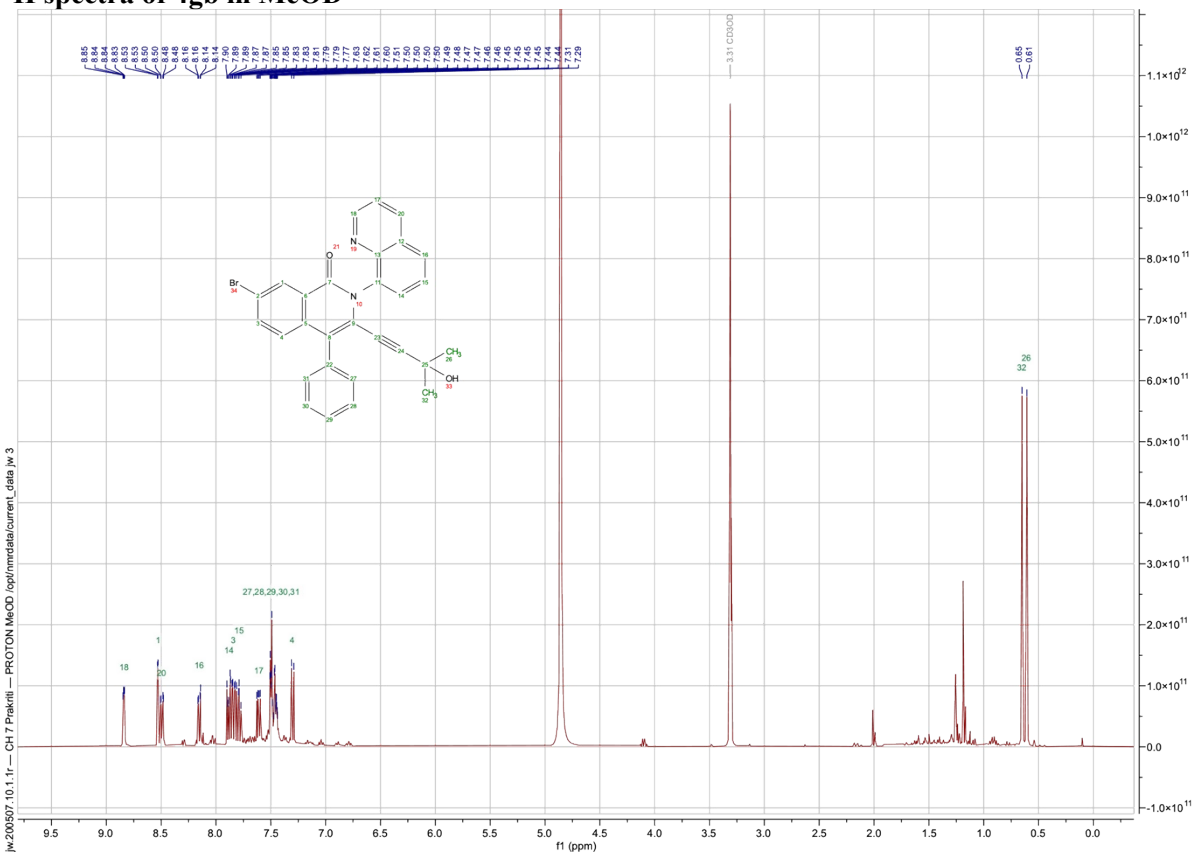
C: 0-50 H: 1-100 N: 0-3 O: 0-4 Na: 0-1 Cl: 0-1

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i.	Fit Conf %	C	H	N	O	Na	Cl
465.1362	465.1368	-0.6	-1.3	25.5	C33 H18 N2 Na	4	0.00	33	18	2		1	
	465.1370	-0.8	-1.7	19.5	C29 H22 N2 O2 Cl	3	76.64	29	22	2	2		1
	465.1346	1.6	3.4	16.5	C27 H23 N2 O2 Na Cl	3	23.36	27	23	2	2	1	1

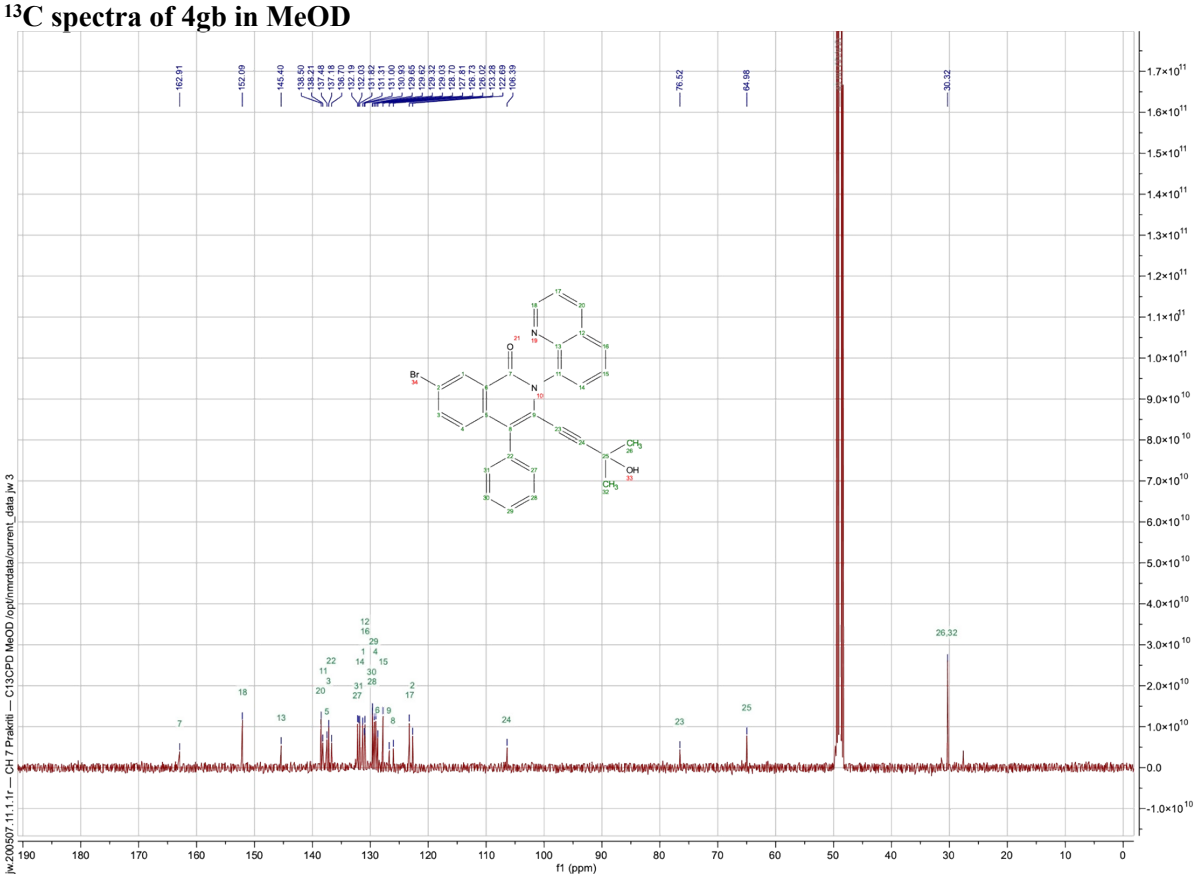


4gb

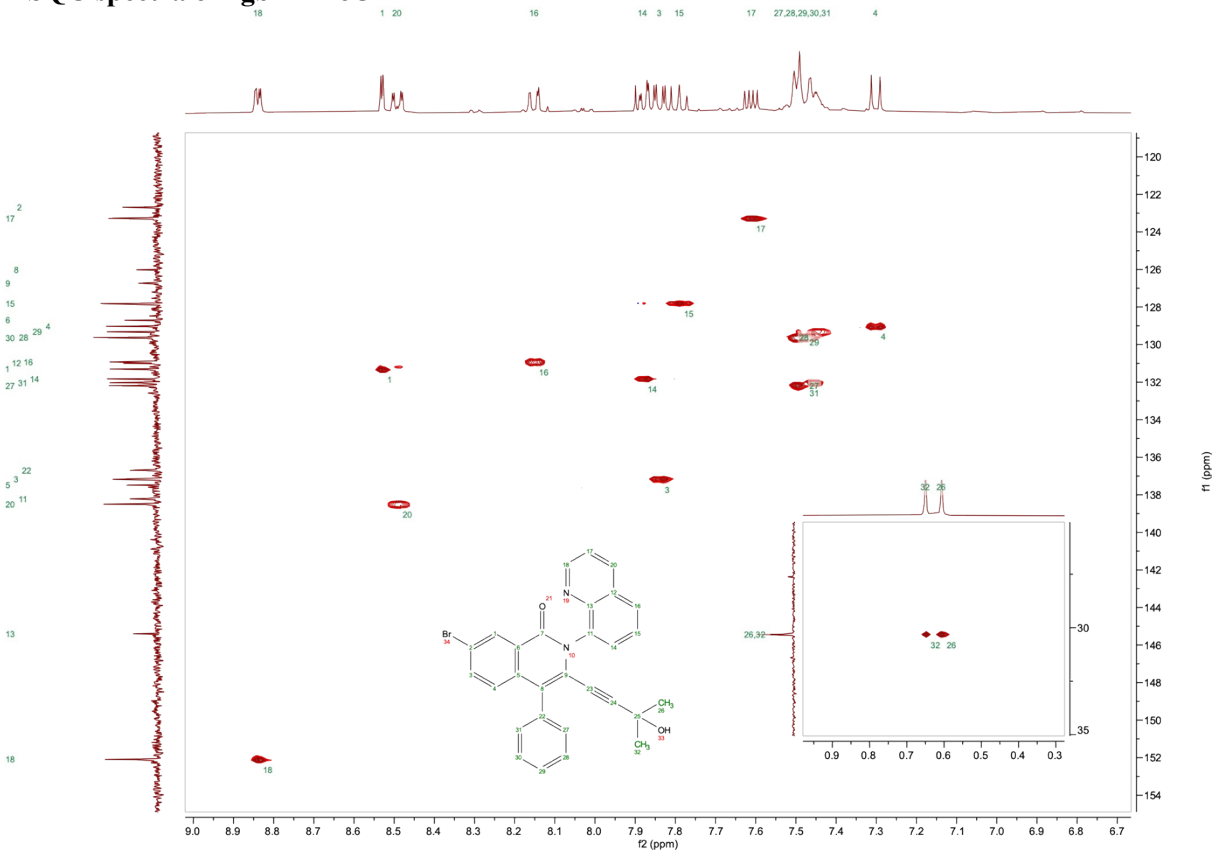
^{1}H spectra of 4gb in MeOD



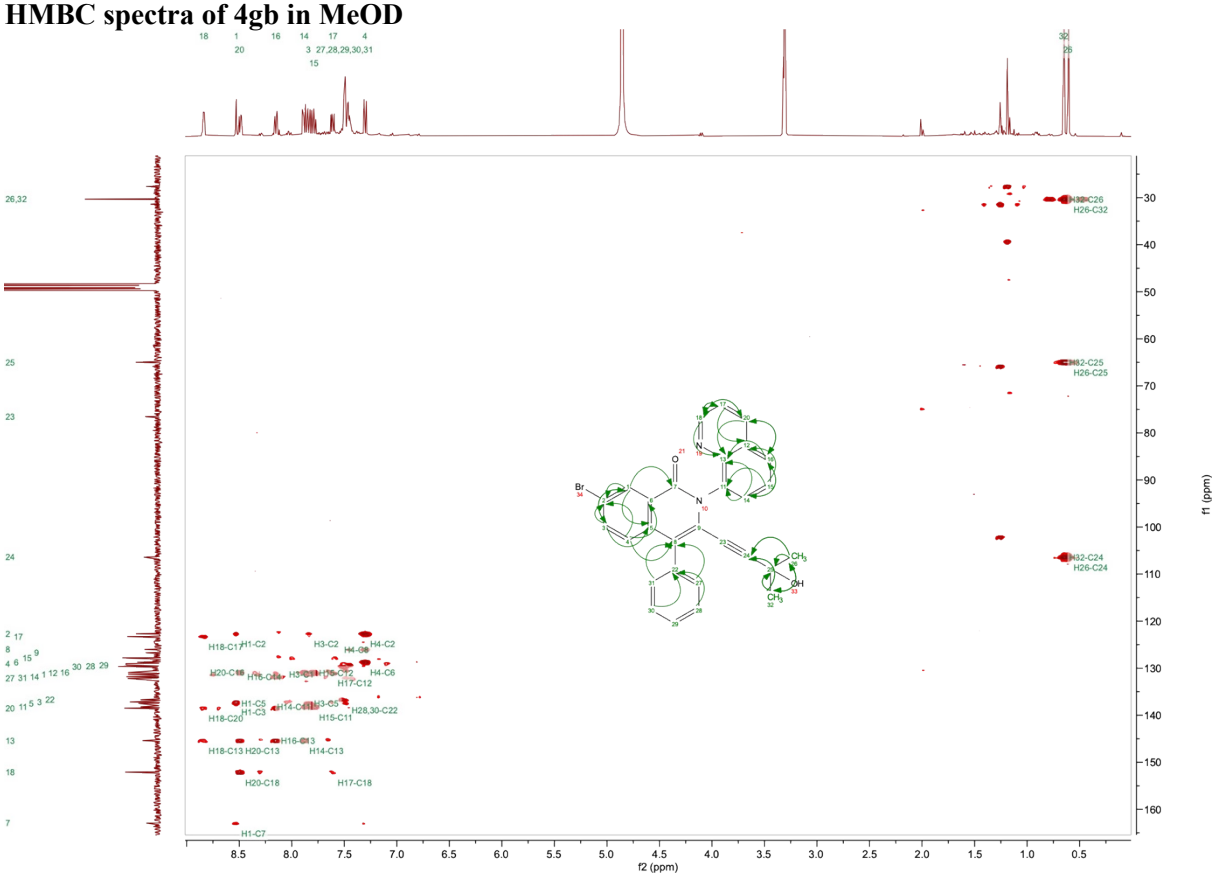
^{13}C spectra of 4gb in MeOD



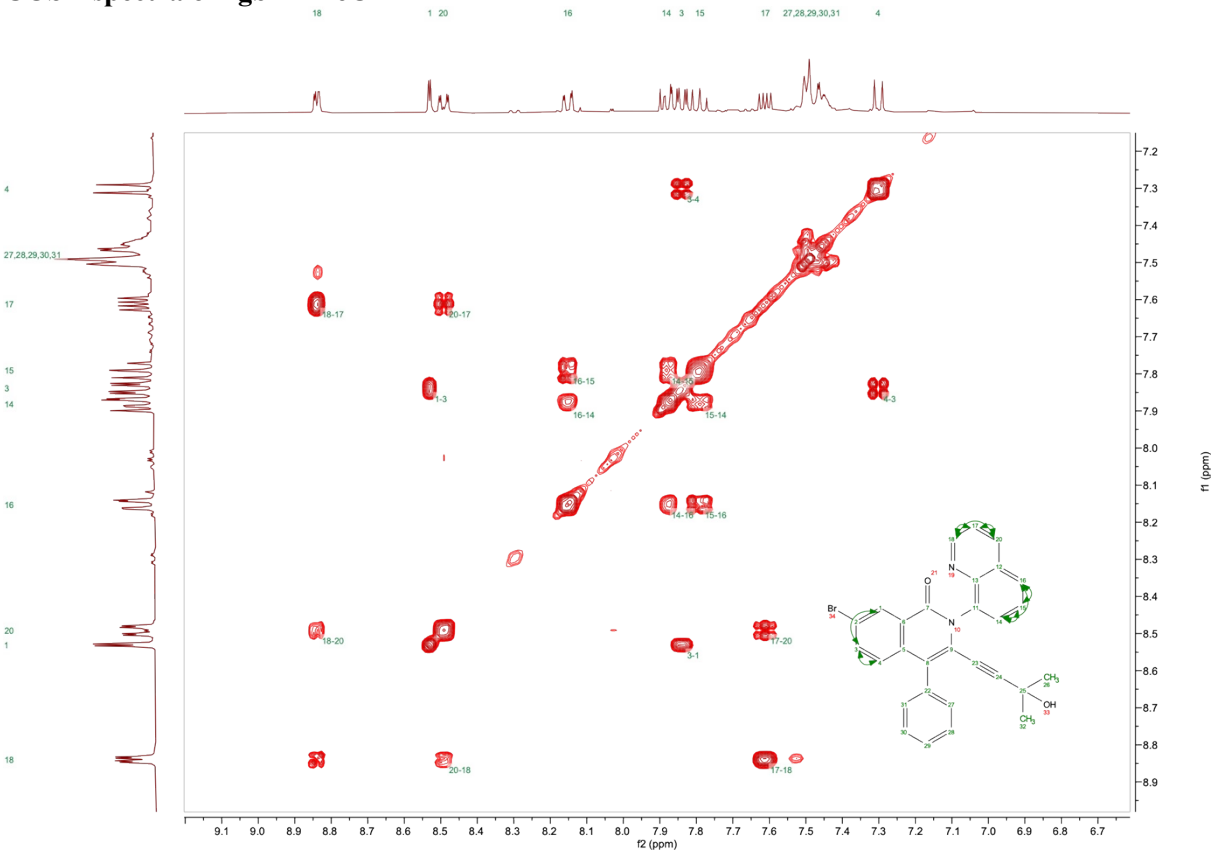
HSQC spectra of 4gb in MeOD



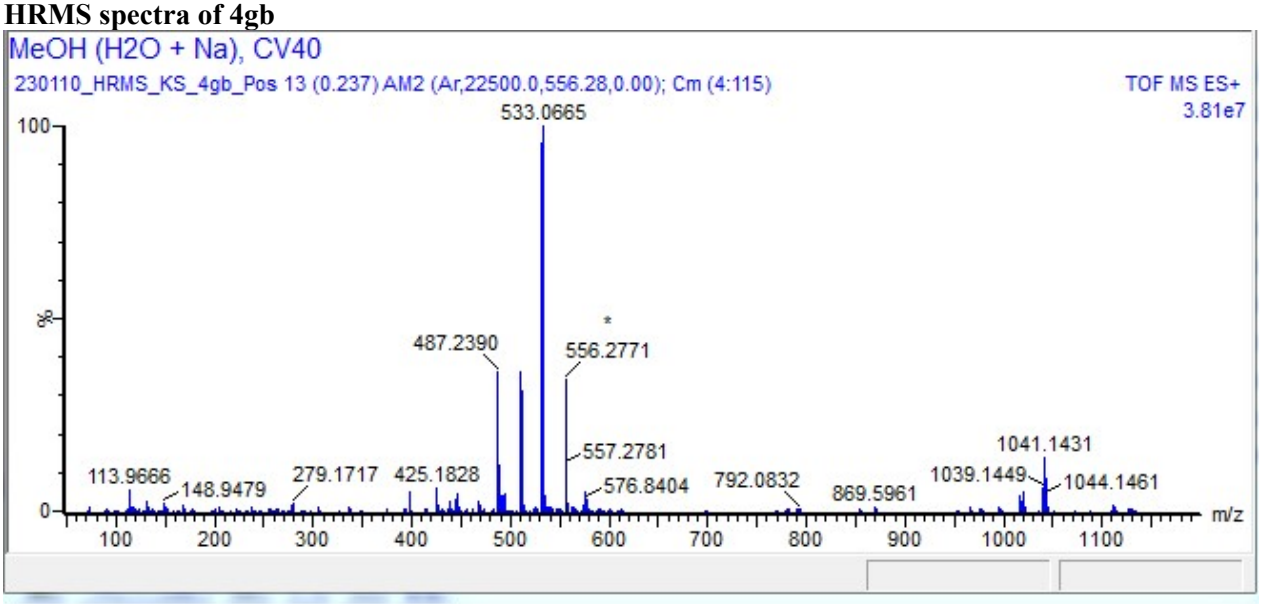
HMBC spectra of 4gb in MeOD



COSY spectra of 4gb in MeOD



HRMS spectra of 4gb



Single Mass Analysis

Tolerance = 2.0 mDa / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

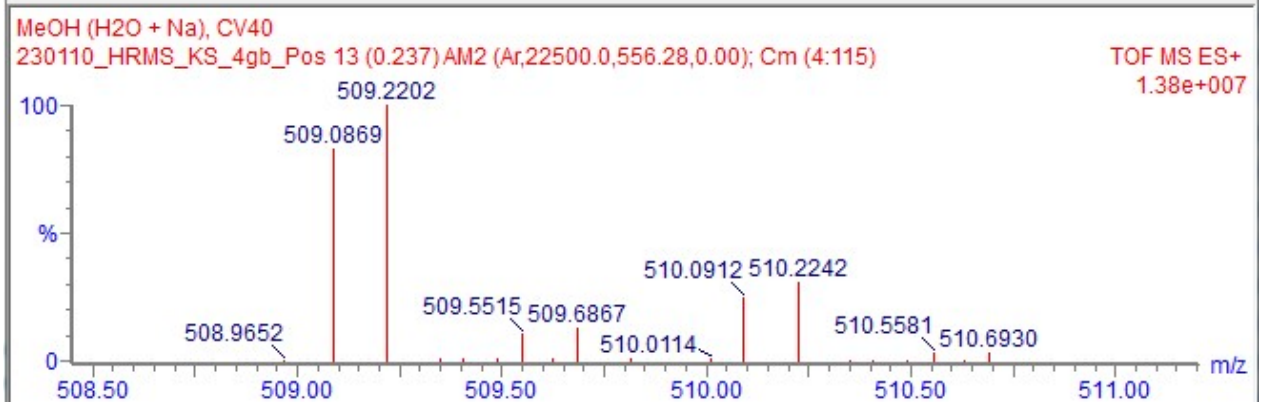
Monoisotopic Mass, Even Electron Ions

108 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

Elements Used:

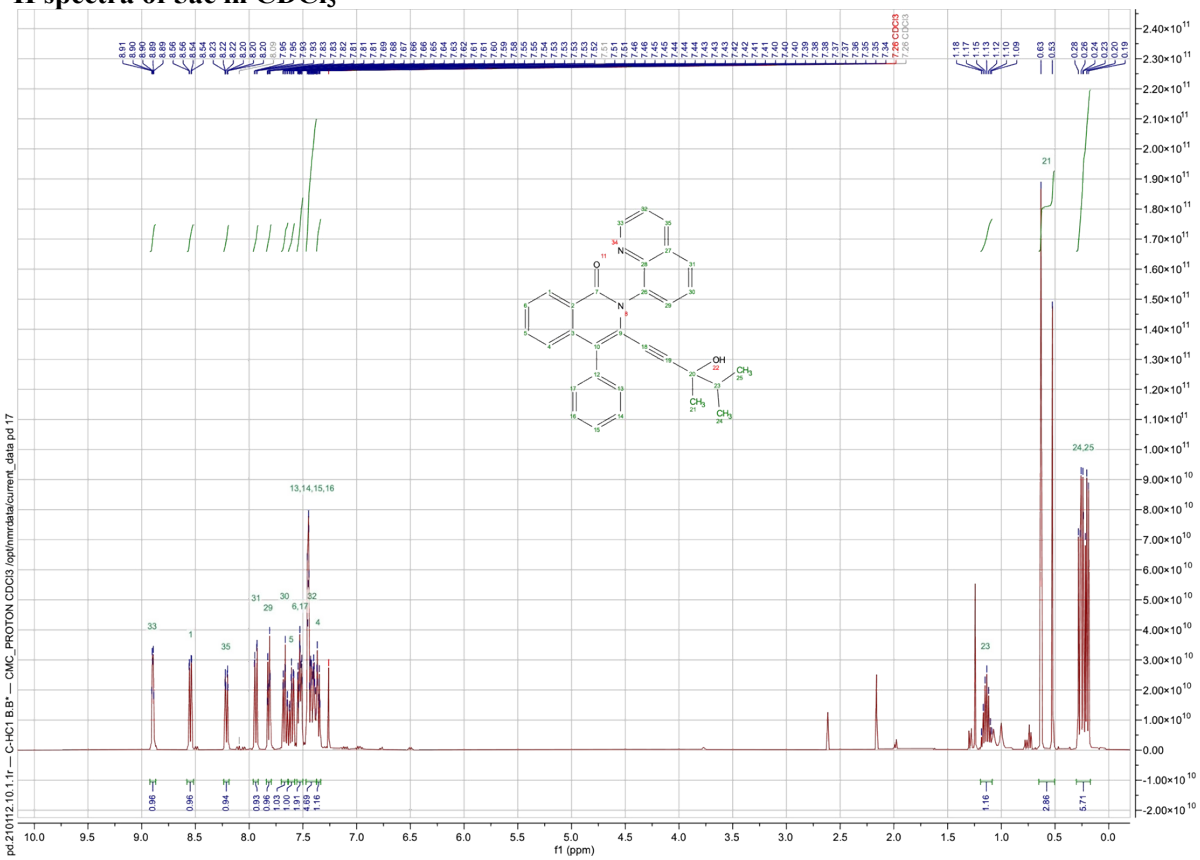
C: 1-40 H: 1-40 N: 1-4 O: 1-4 Na: 0-1 Br: 1-1

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i..	i...	Fit Conf %	C	H	N	O	Na	Br
509.0869	509.0865	0.4	0.8	19.5	C29 H22 N2 O2 Br	3...	n...	n/a	29	22	2	2		1

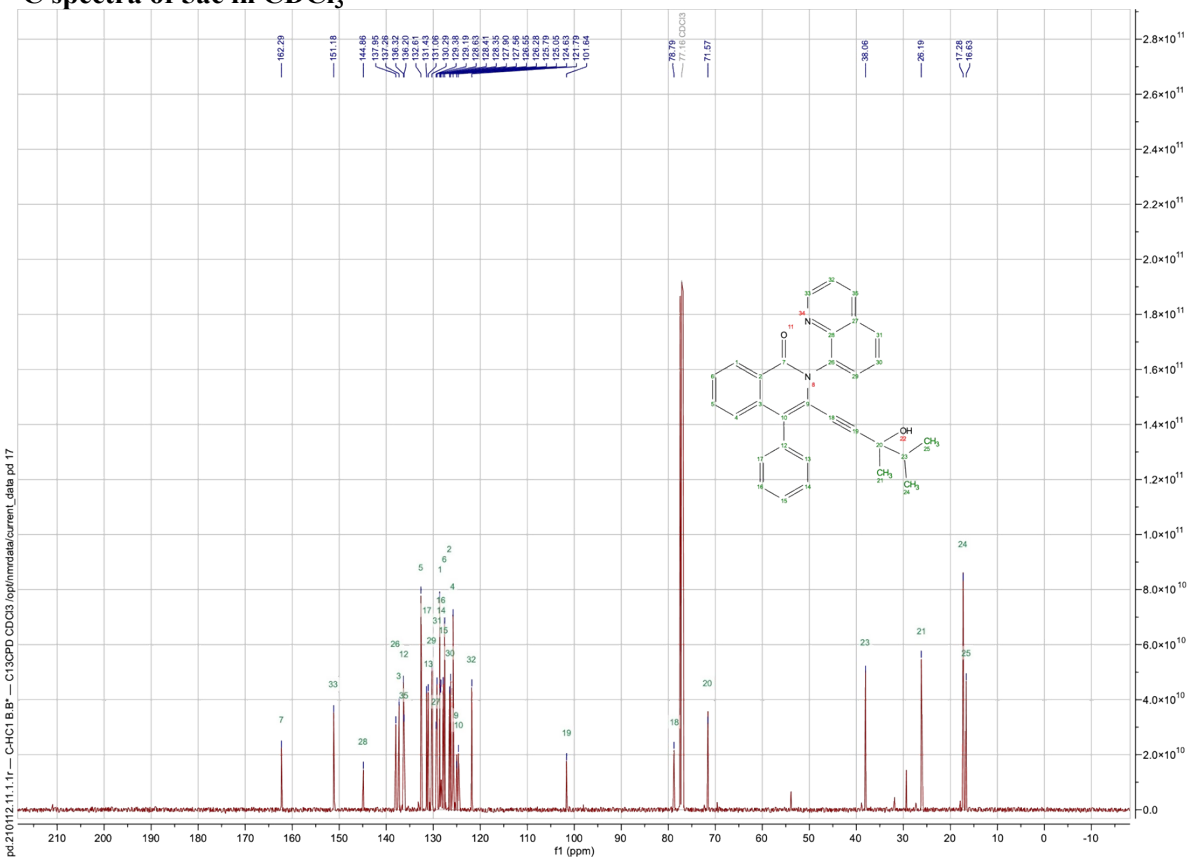


5ac

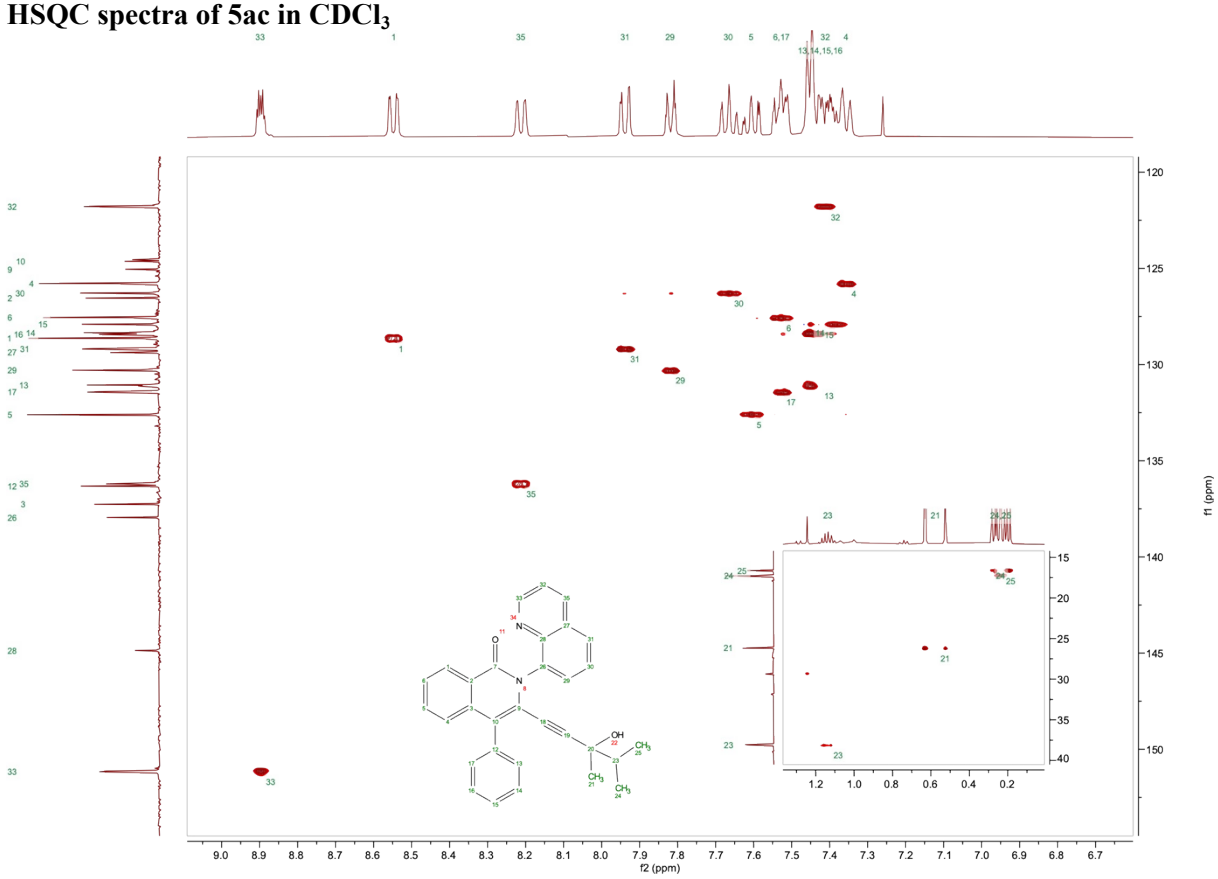
^{1}H spectra of 5ac in $CDCl_3$



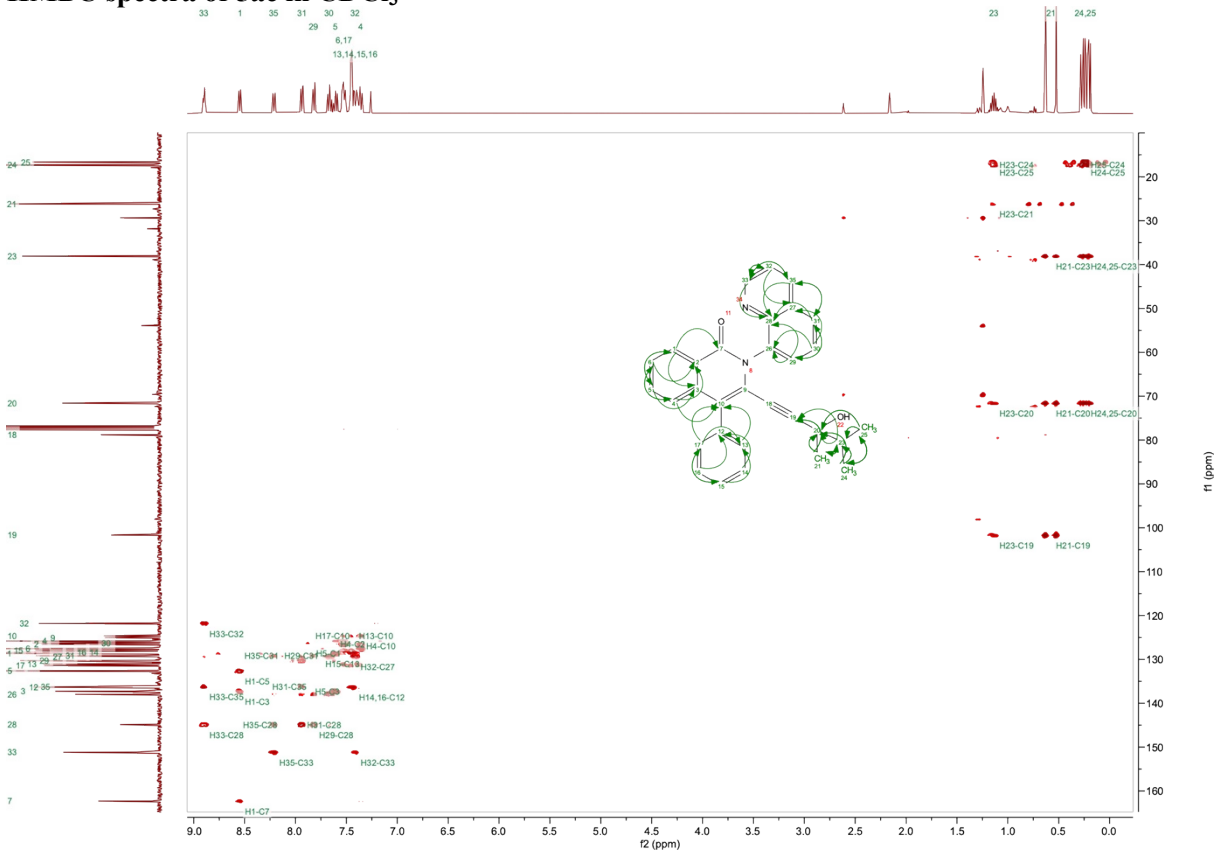
^{13}C spectra of 5ac in $CDCl_3$



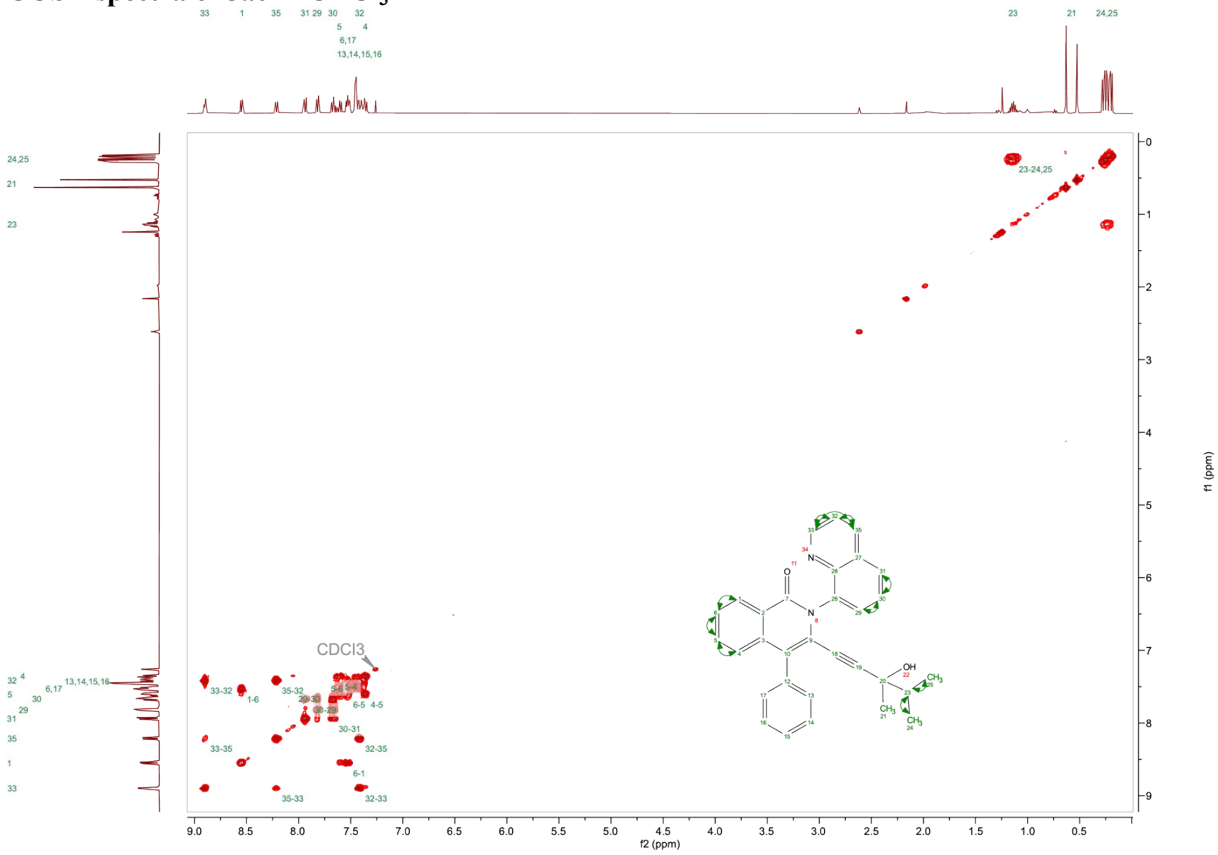
HSQC spectra of 5ac in $CDCl_3$



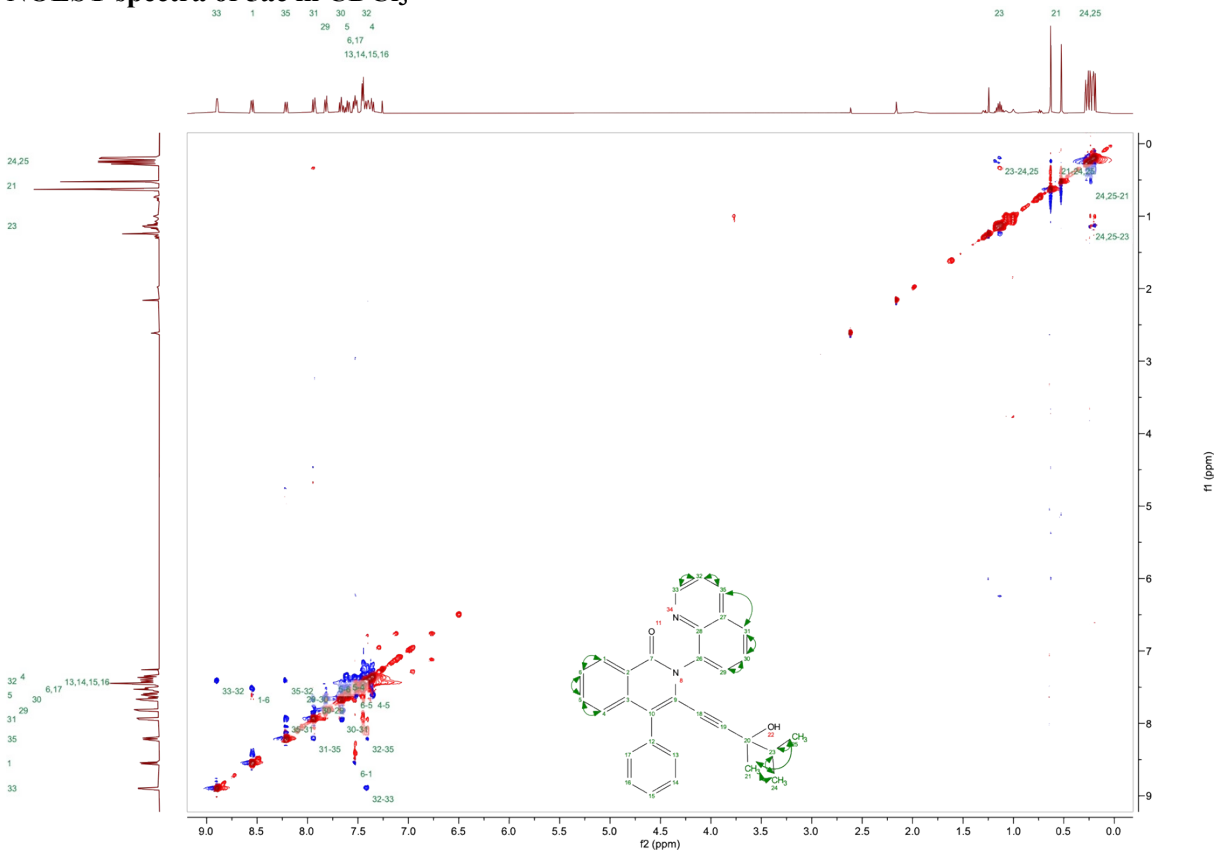
HMBC spectra of 5ac in $CDCl_3$



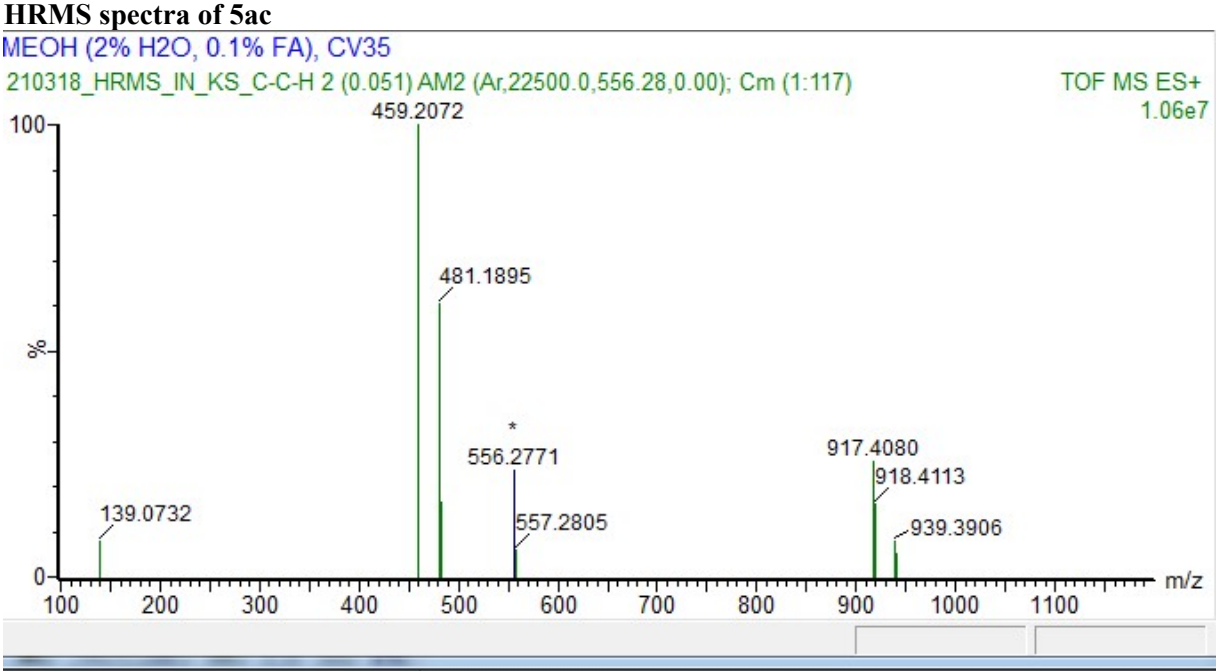
COSY spectra of 5ac in $CDCl_3$



NOESY spectra of 5ac in $CDCl_3$



HRMS spectra of 5ac



Single Mass Analysis

Tolerance = 2.0 mDa / DBE: min = -0.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

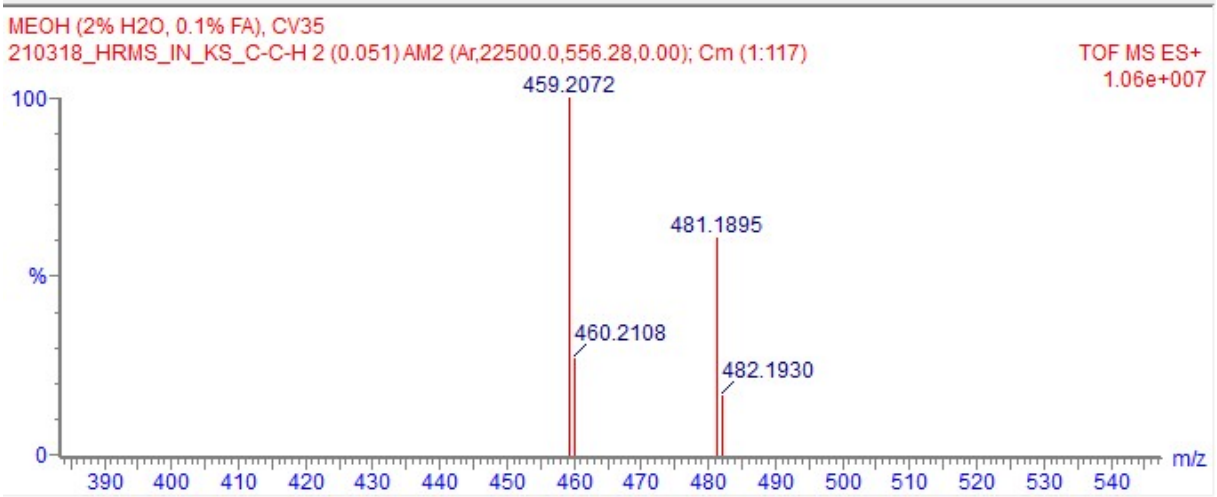
Monoisotopic Mass, Even Electron Ions

179 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

Elements Used:

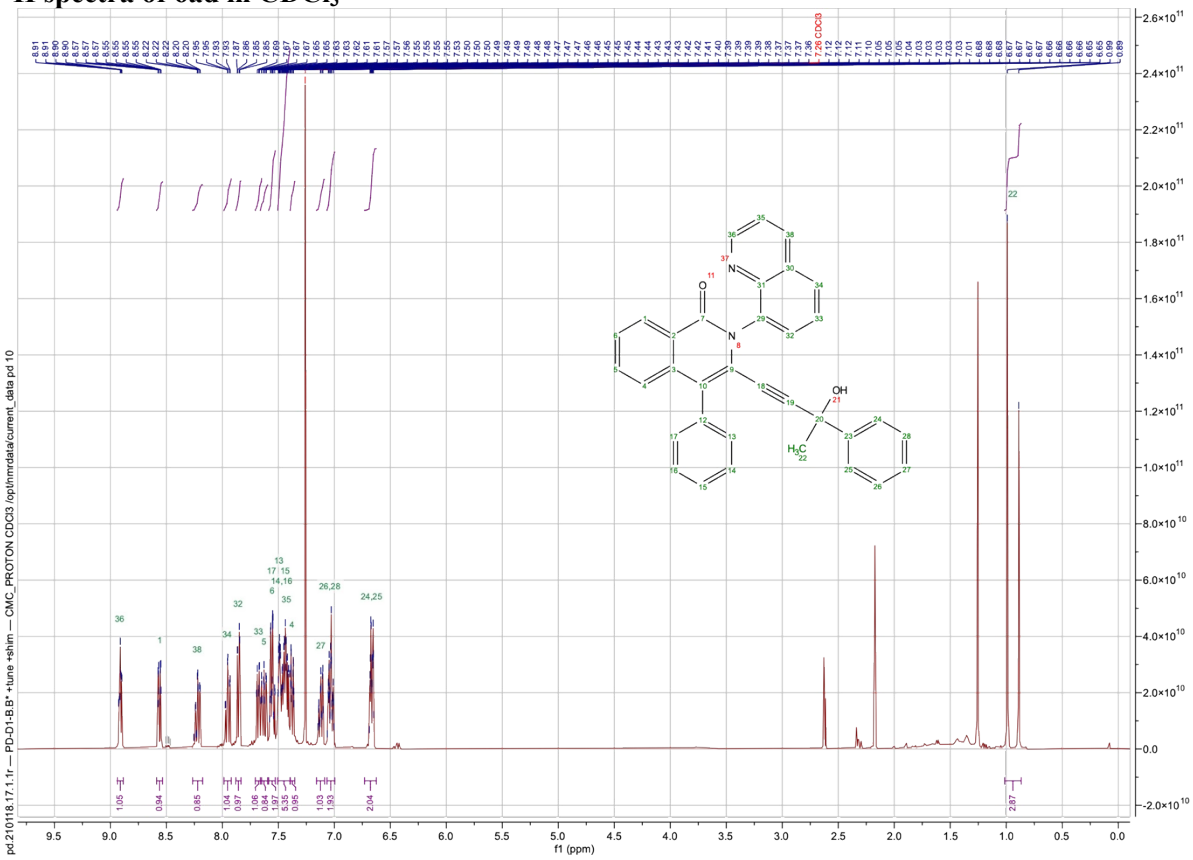
C: 0-50 H: 1-100 N: 0-3 O: 0-3 Na: 0-1

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i..	Fit Conf %	C	H	N	O	Na
459.2072	459.2073	-0.1	-0.2	19.5	C31 H27 N2 O2	40...	85.67	31	27	2	2	
	459.2089	-1.7	-3.7	20.5	C34 H28 Na	41...	14.33	34	28			1

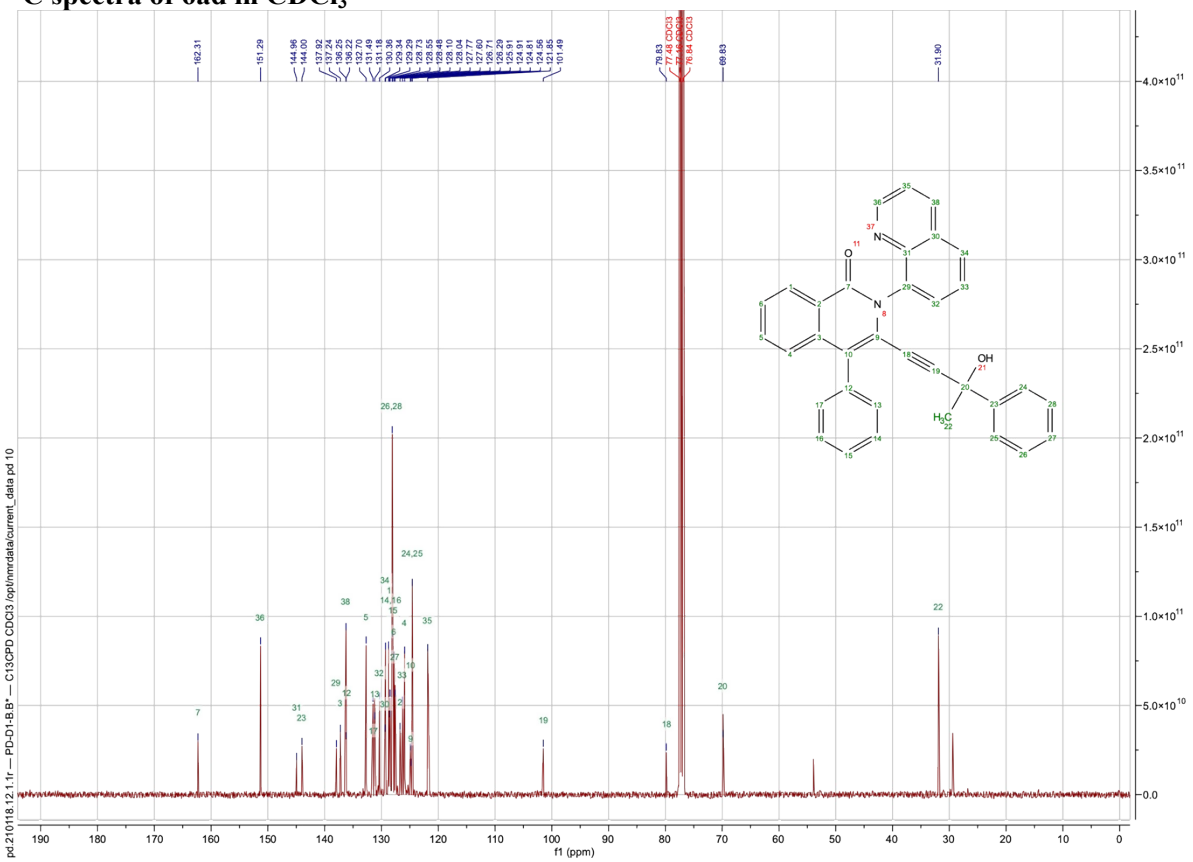


6ad

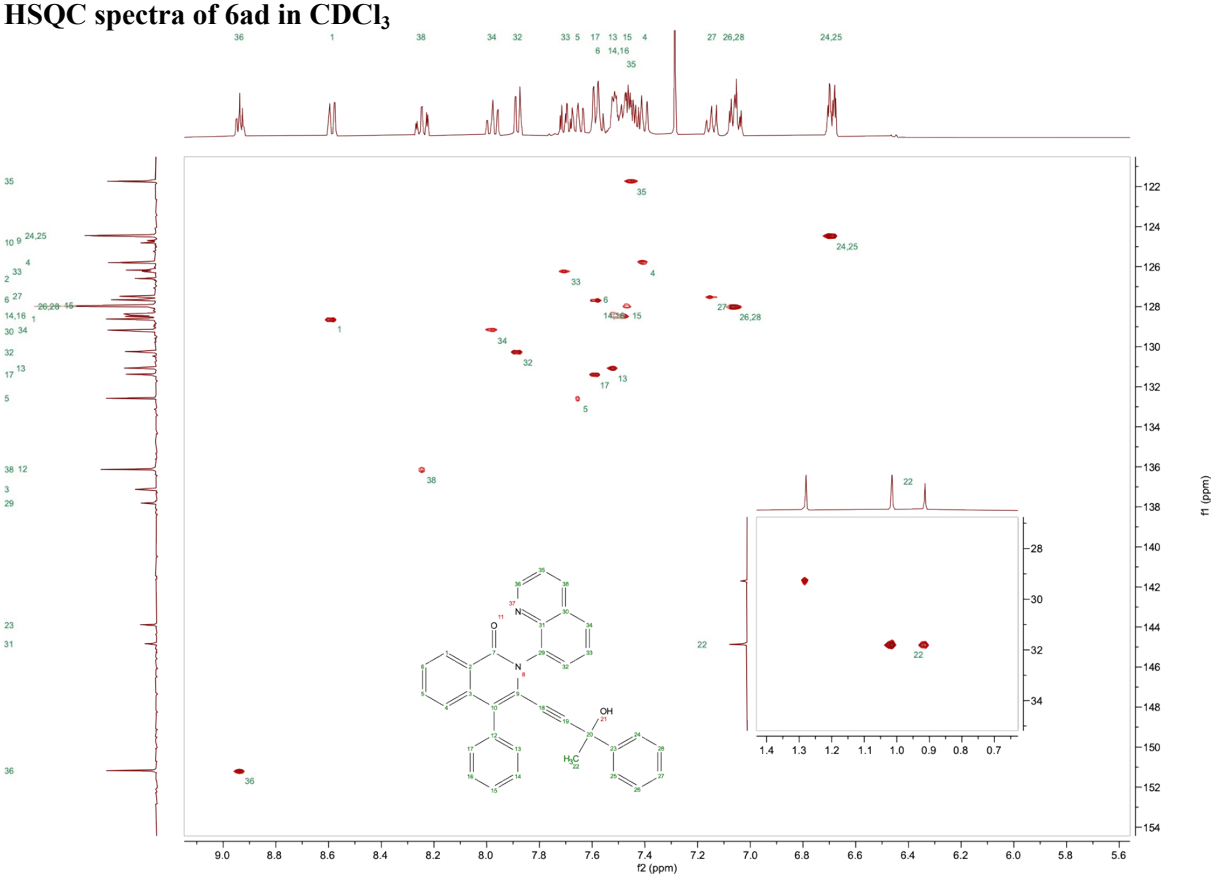
^{1}H spectra of 6ad in $CDCl_3$



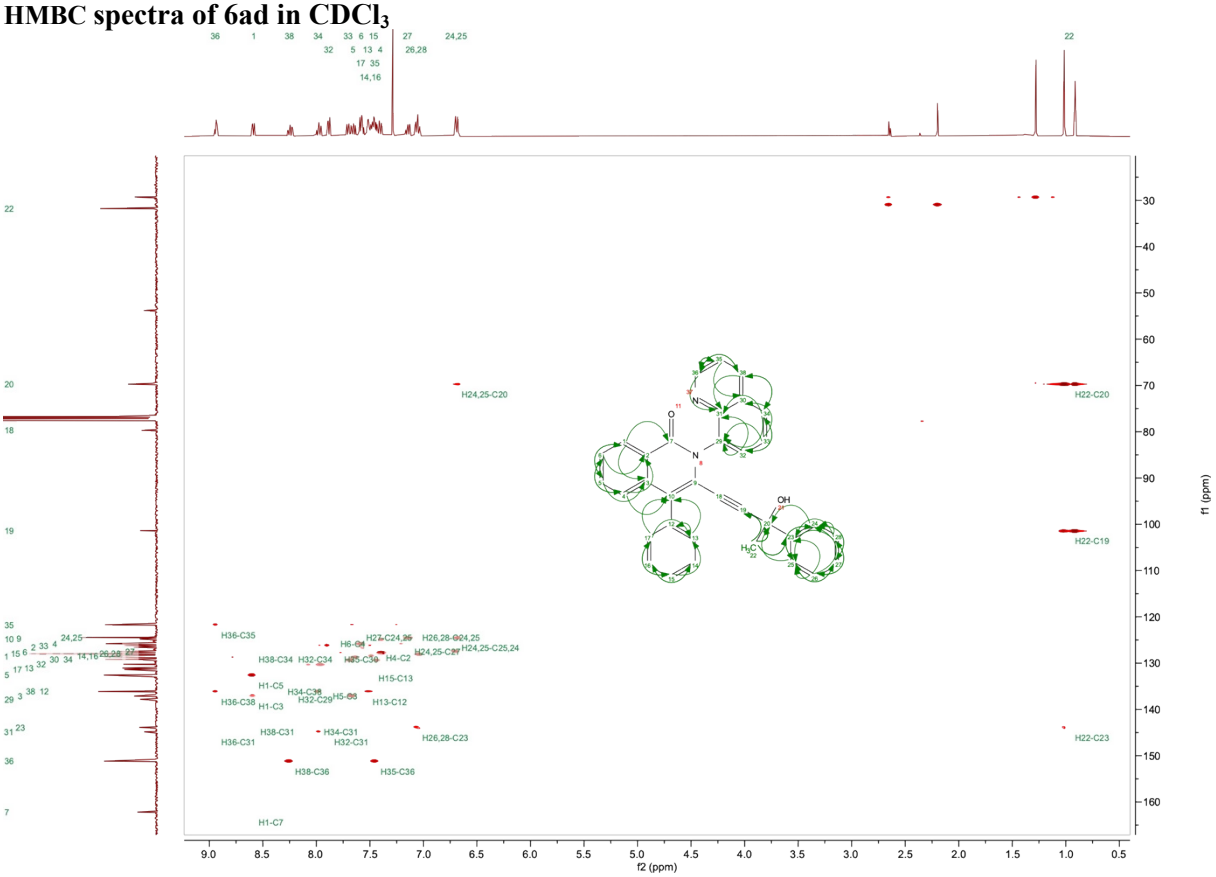
^{13}C spectra of 6ad in $CDCl_3$



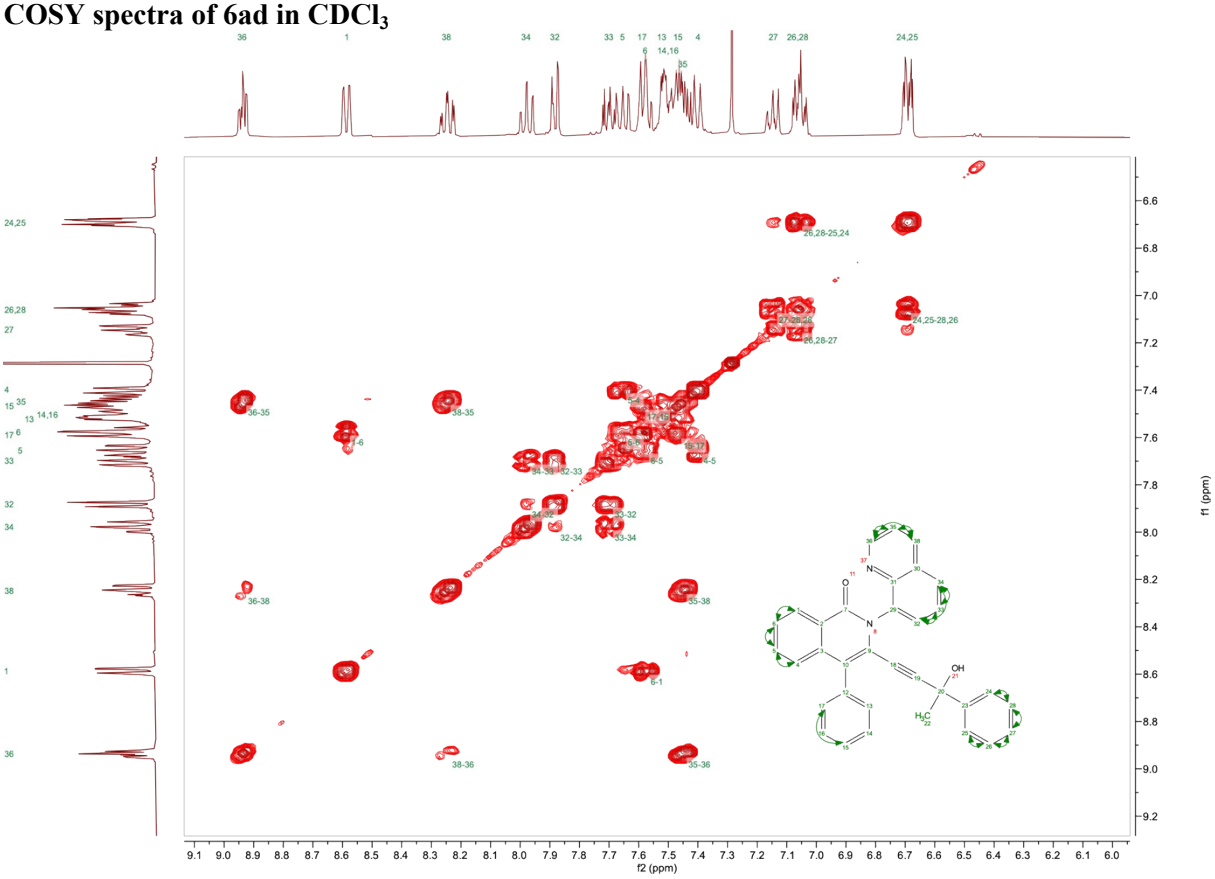
HSQC spectra of 6ad in $CDCl_3$



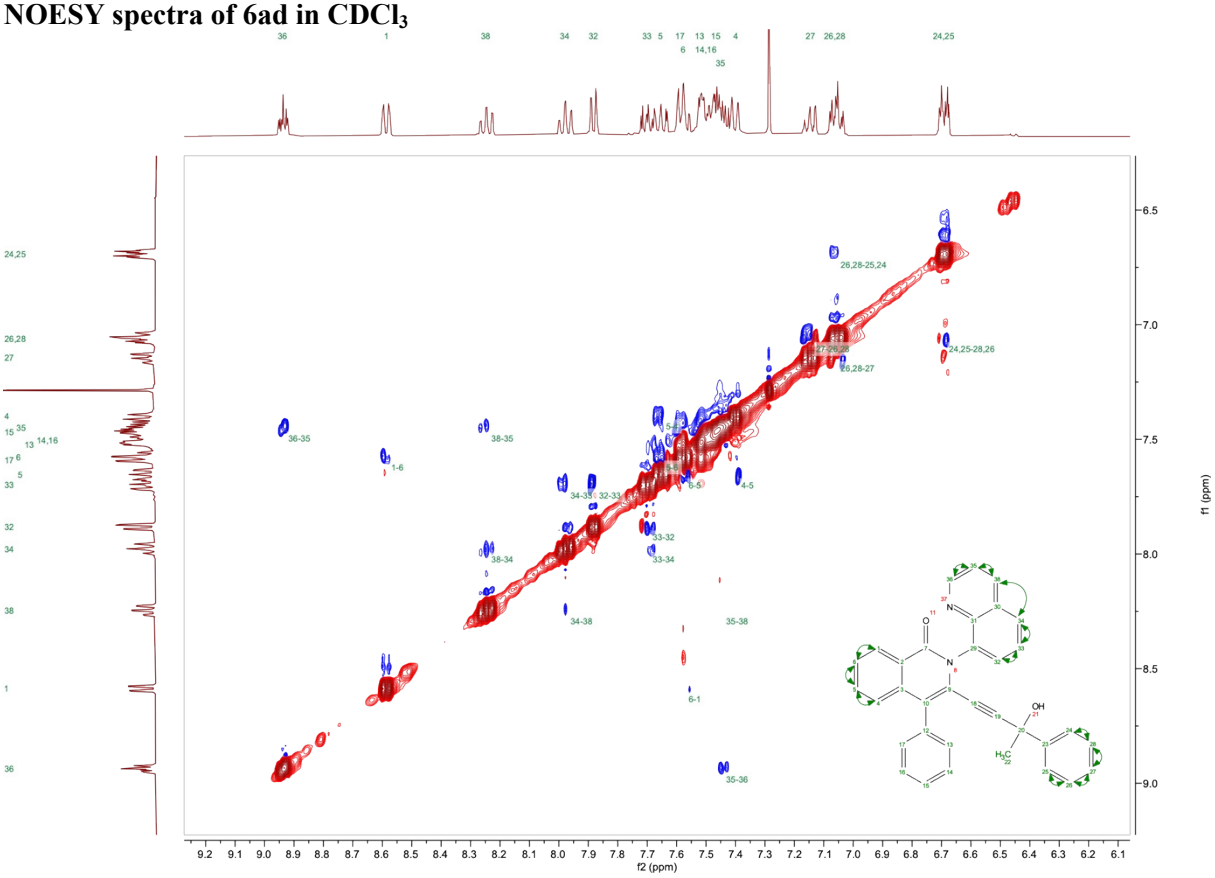
HMBC spectra of 6ad in $CDCl_3$



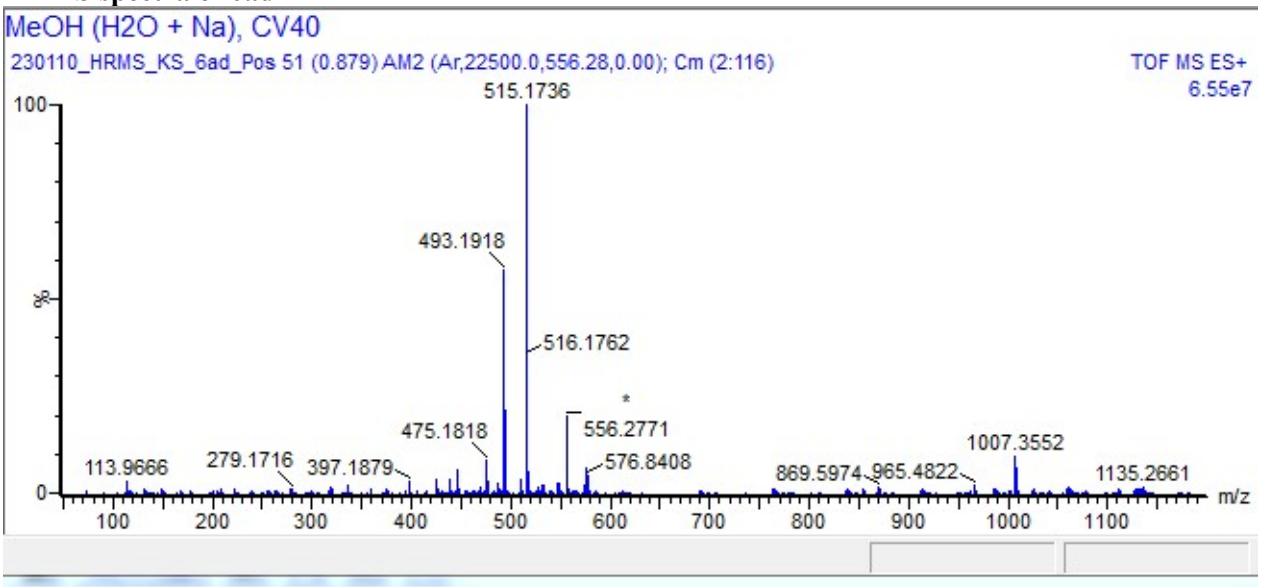
COSY spectra of 6ad in $CDCl_3$



NOESY spectra of 6ad in $CDCl_3$



HRMS spectra of 6ad



Single Mass Analysis

Tolerance = 2.0 mDa / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

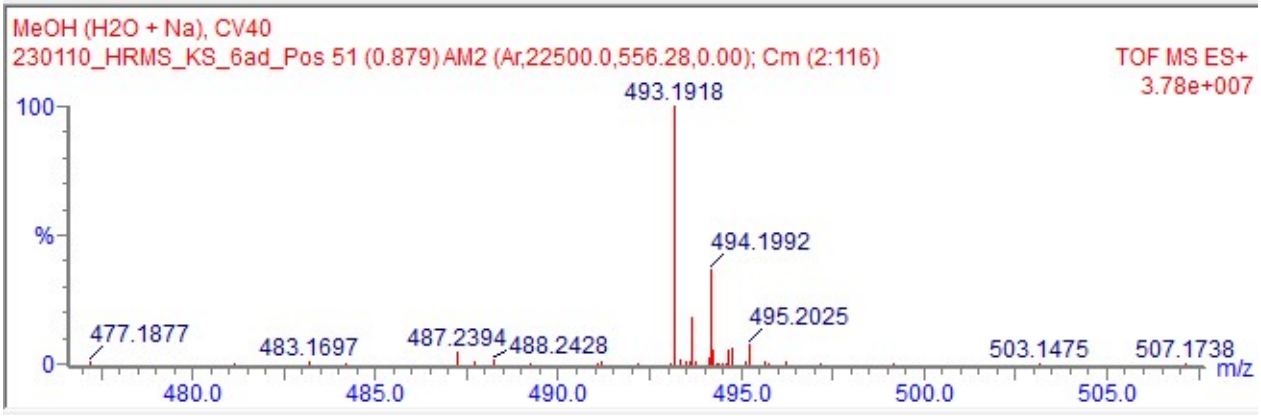
Monoisotopic Mass, Even Electron Ions

108 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 1-40 H: 1-40 N: 1-4 O: 1-4 Na: 0-1

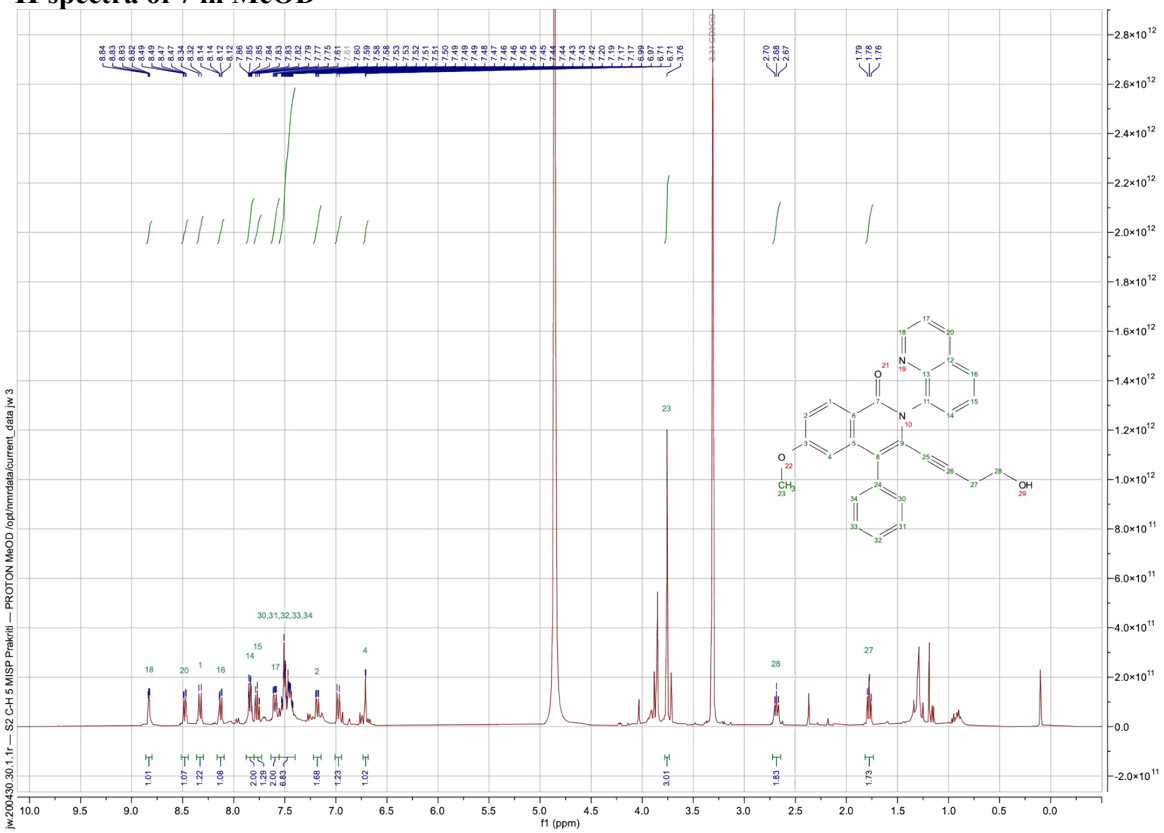
Mass	Calc. Mass	mDa	PPM	DBE	Formula	i...	i..	Fit Conf %	C	H	N	O	Na
493.1918	493.1916	0.2	0.4	23.5	C34 H25 N2 O2	3...	n...	n/a	34	25	2	2	



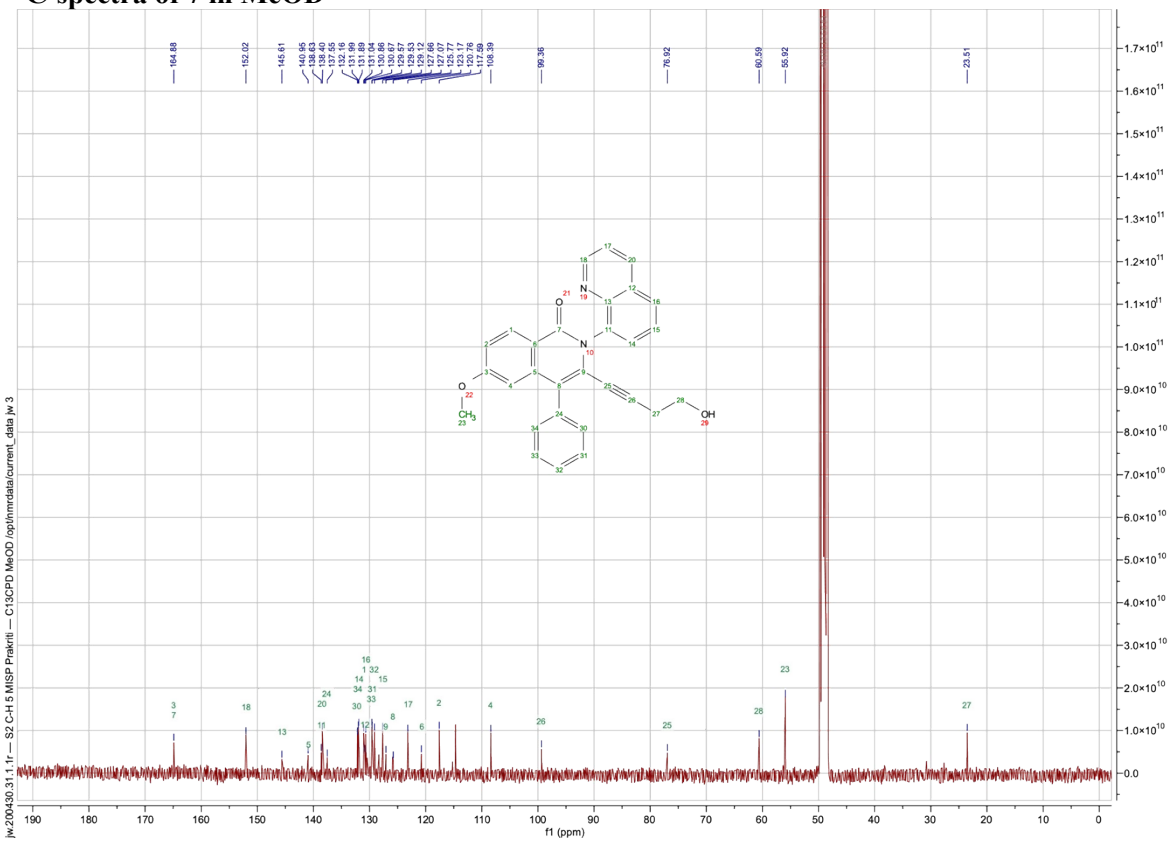
Minor isomers

7

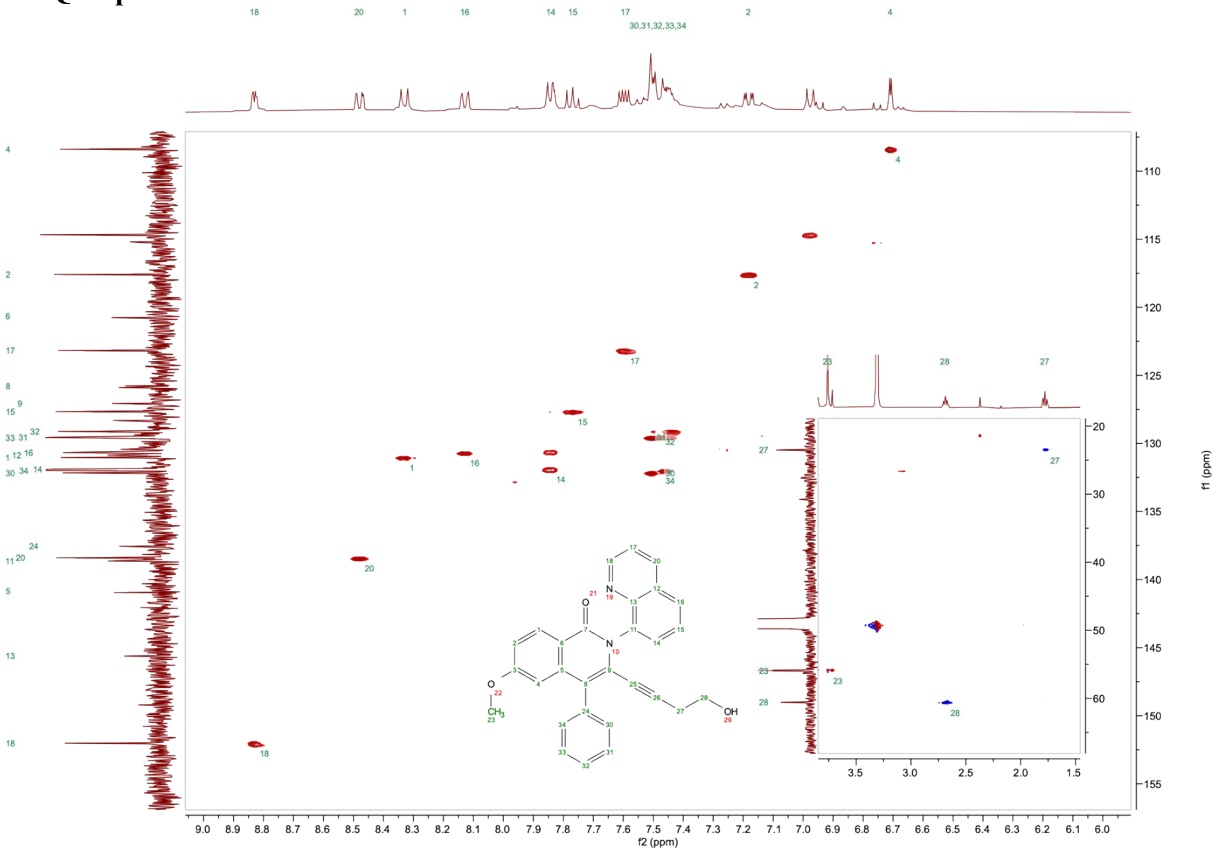
^{1}H spectra of 7 in MeOD



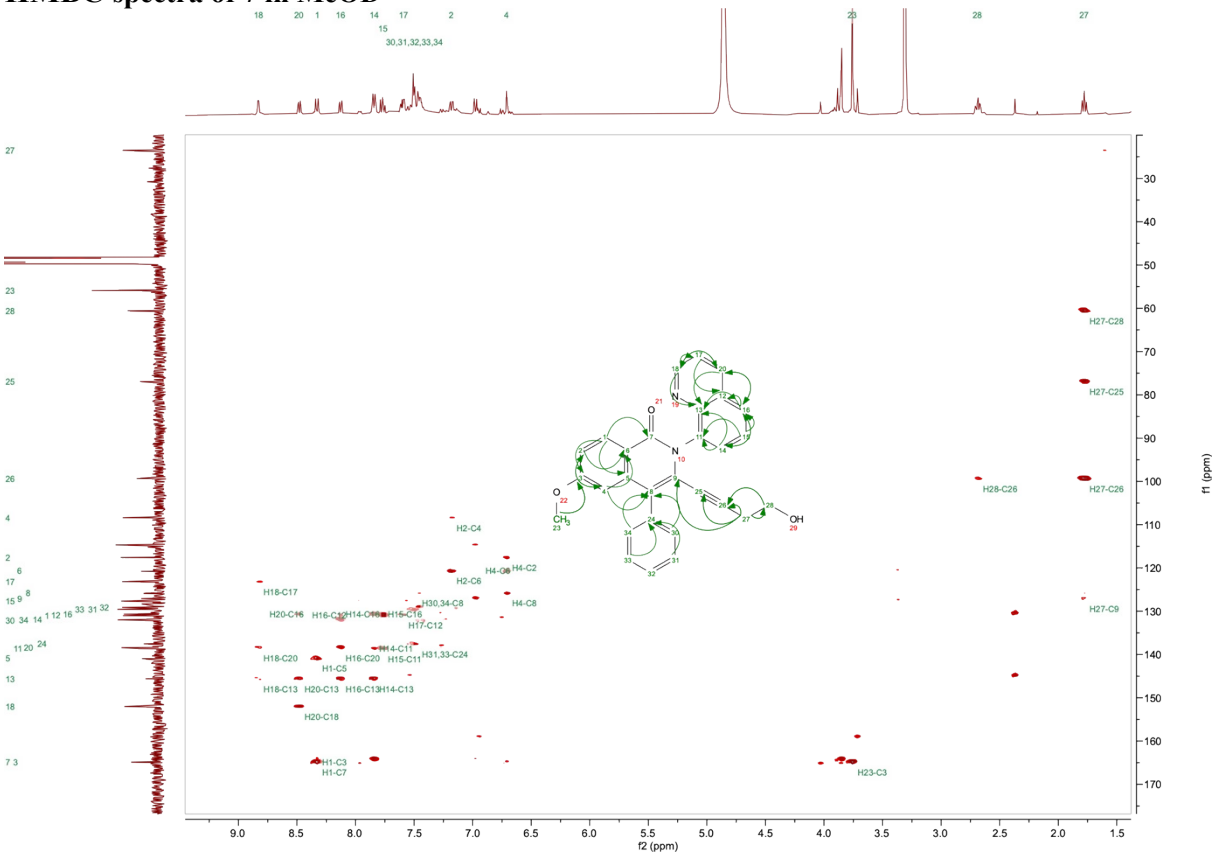
^{13}C spectra of 7 in MeOD



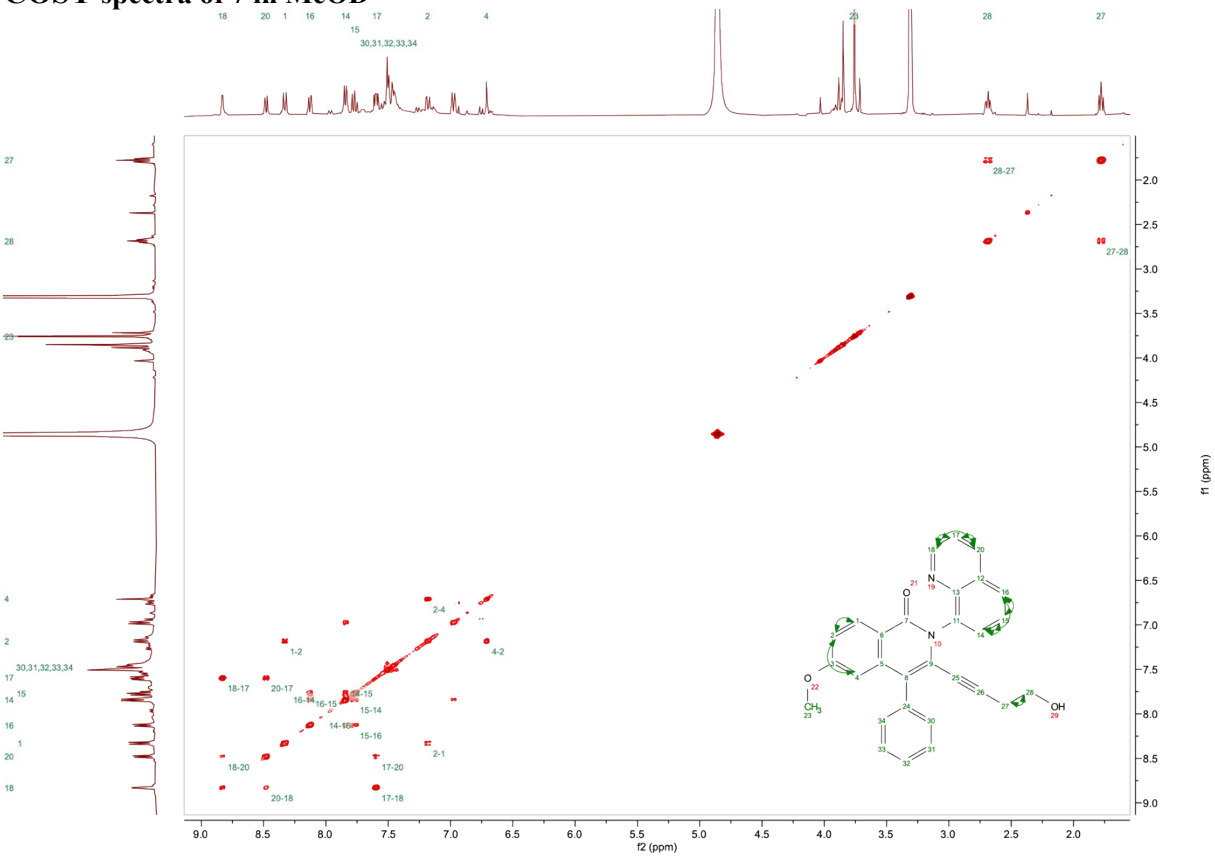
HSQC spectra of 7 in MeOD



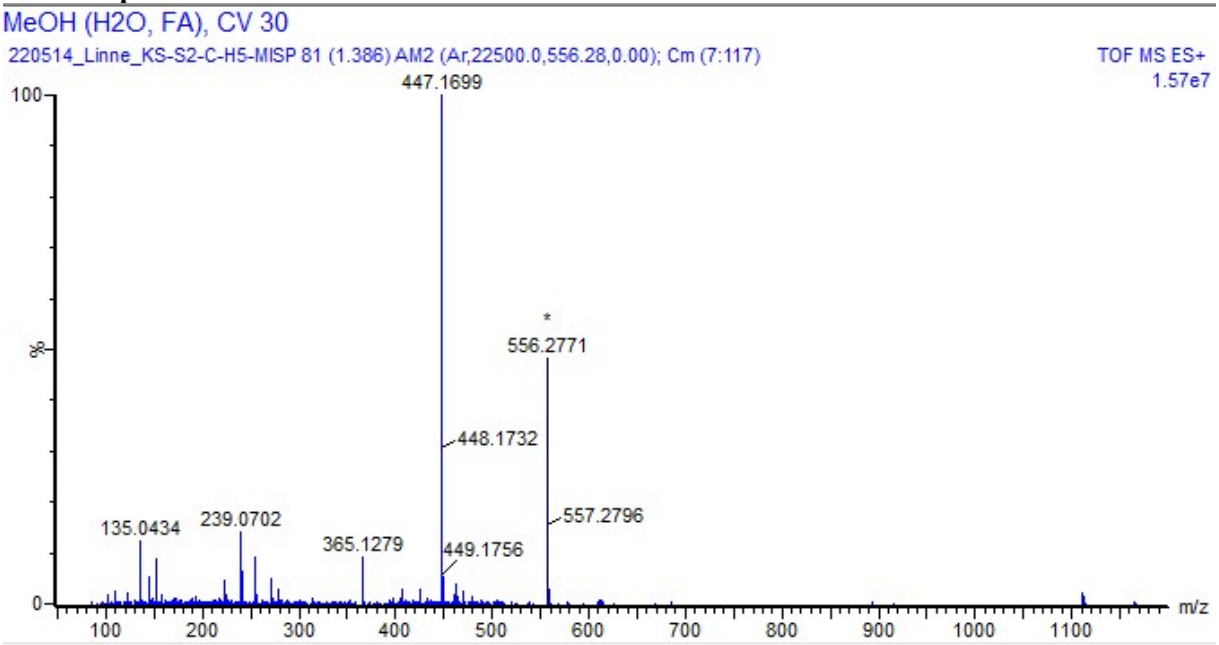
HMBC spectra of 7 in MeOD



COSY spectra of 7 in MeOD



HRMS spectra of 7



Single Mass Analysis

Tolerance = 2.0 mDa / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

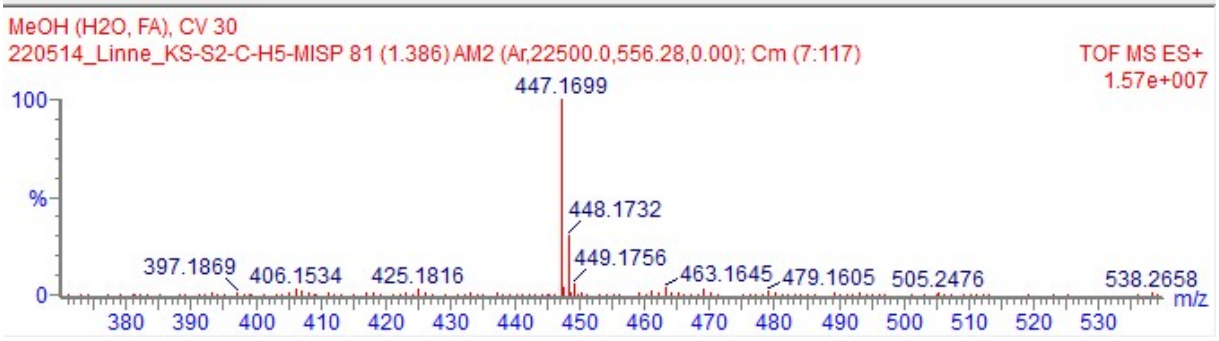
Monoisotopic Mass, Even Electron Ions

662 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-70 H: 0-120 N: 0-5 O: 0-5 S: 0-1 I: 0-1

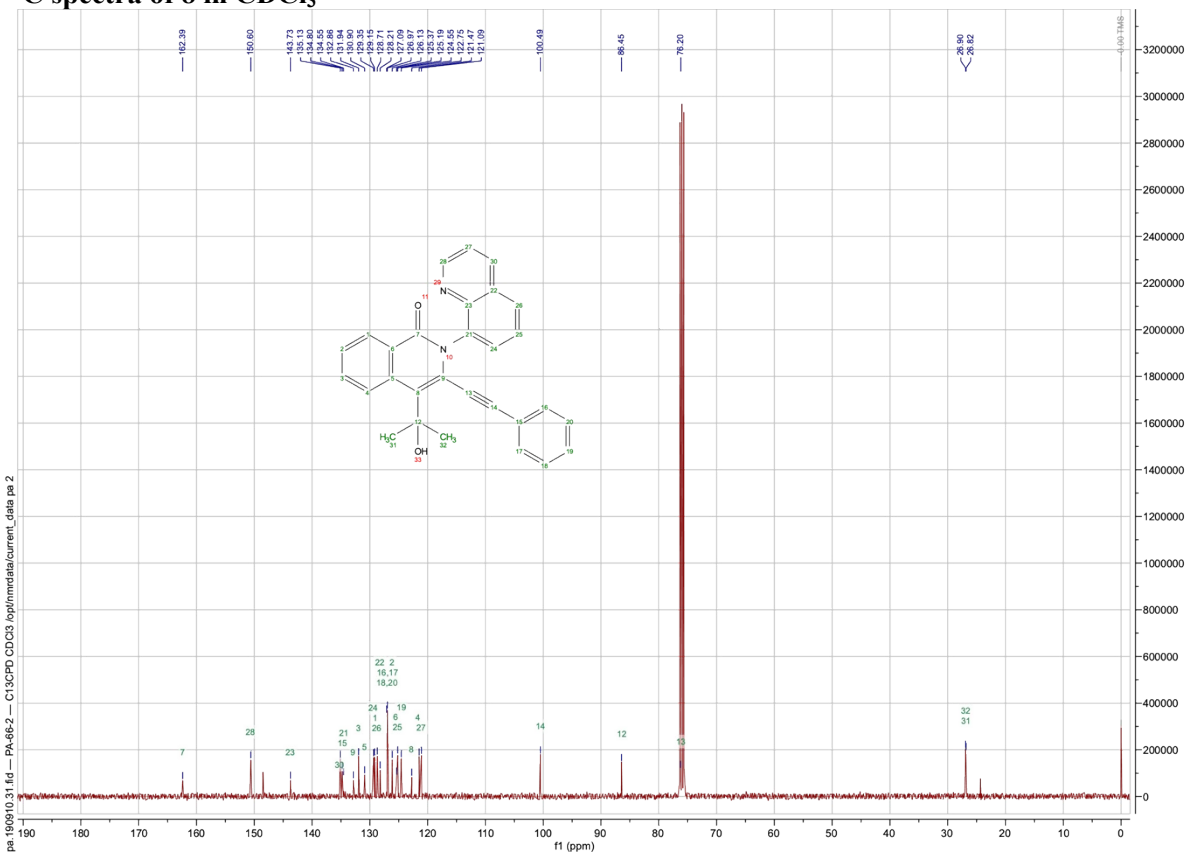
Mass	Calc. Ma...	mDa	PPM	DBE	Formula	i...	Fit Conf %	C	H	N	O	S	I
447.1699	447.1702	-0.3	-0.7	10.5	C21 H27 N4 O5 S	11...	22.88	21	27	4	5	1	
	447.1709	-1.0	-2.2	19.5	C29 H23 N2 O3	10...	77.12	29	23	2	3		



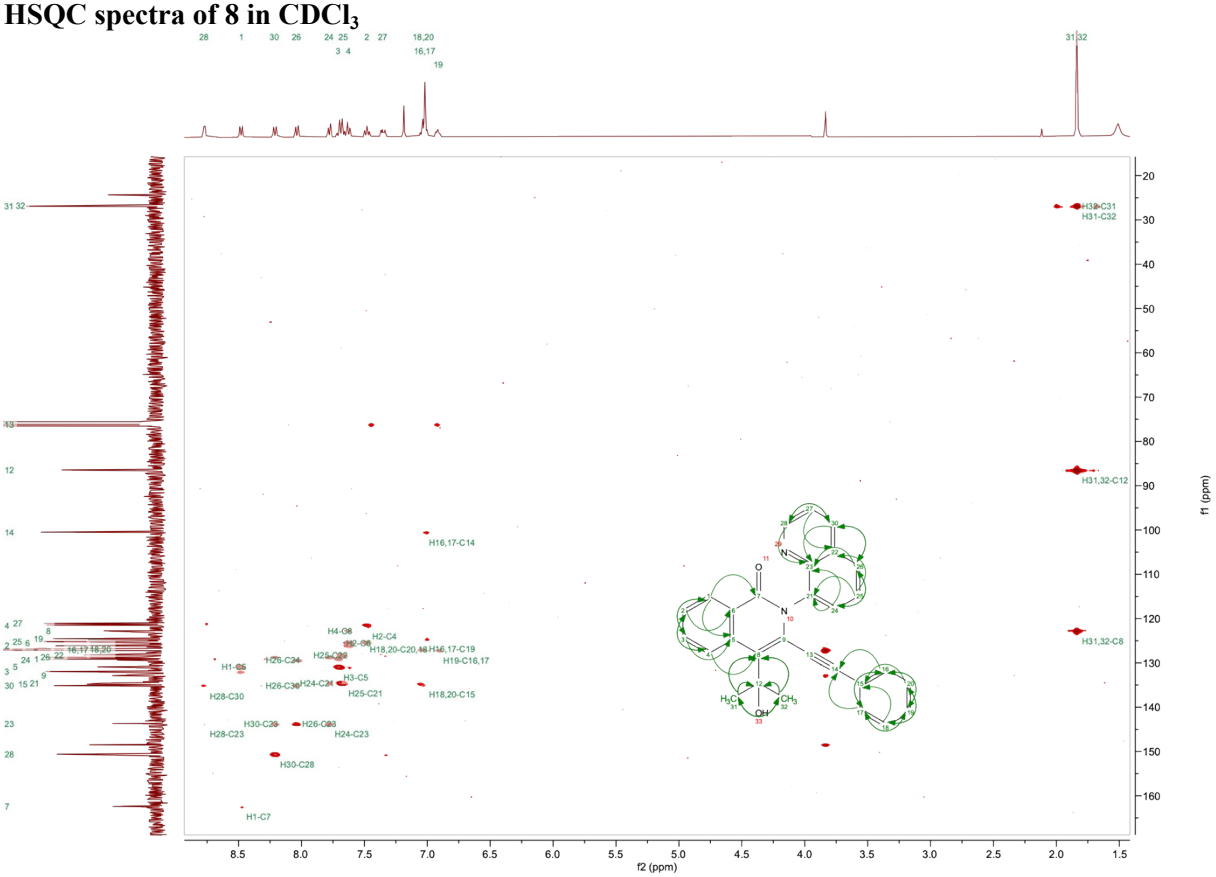
8

^{1}H spectra of 8 in $CDCl_3$

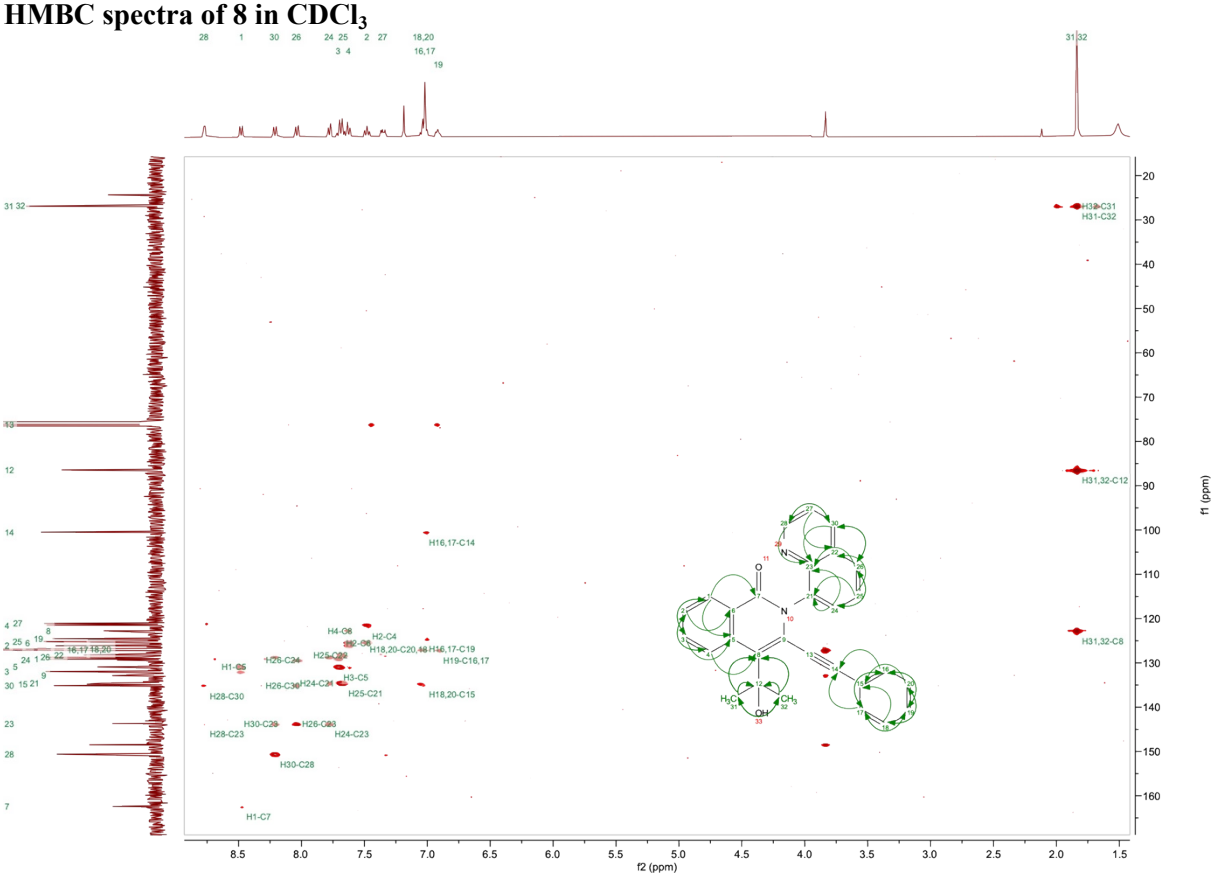
^{13}C spectra of 8 in $CDCl_3$



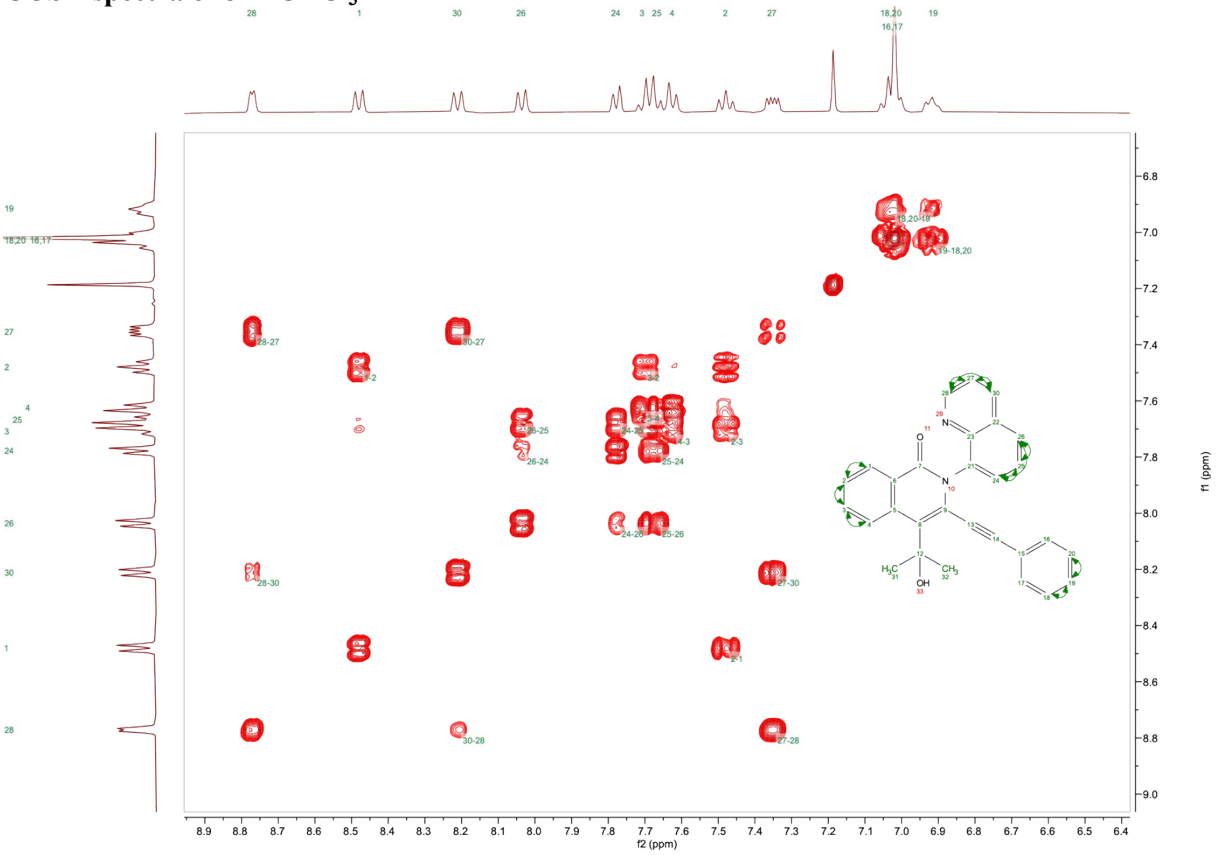
HSQC spectra of 8 in $CDCl_3$



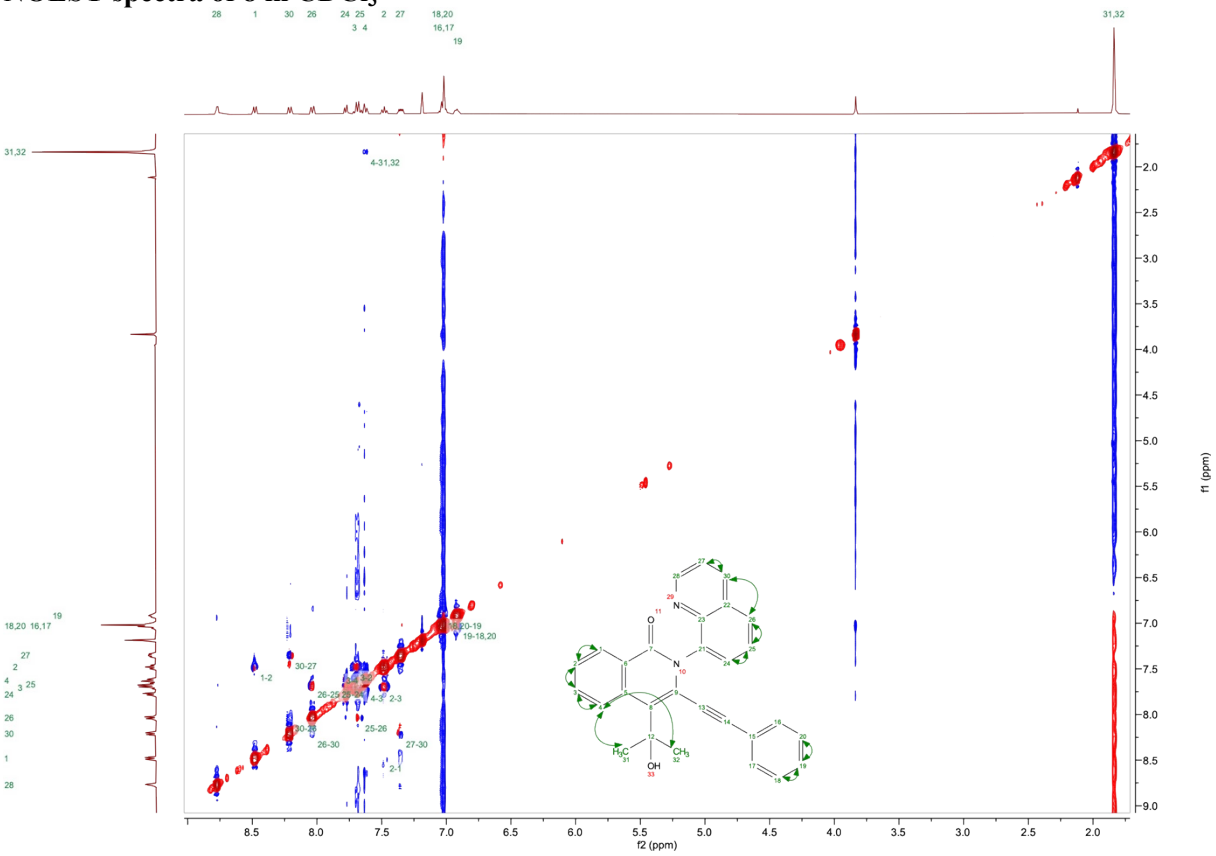
HMBC spectra of 8 in $CDCl_3$



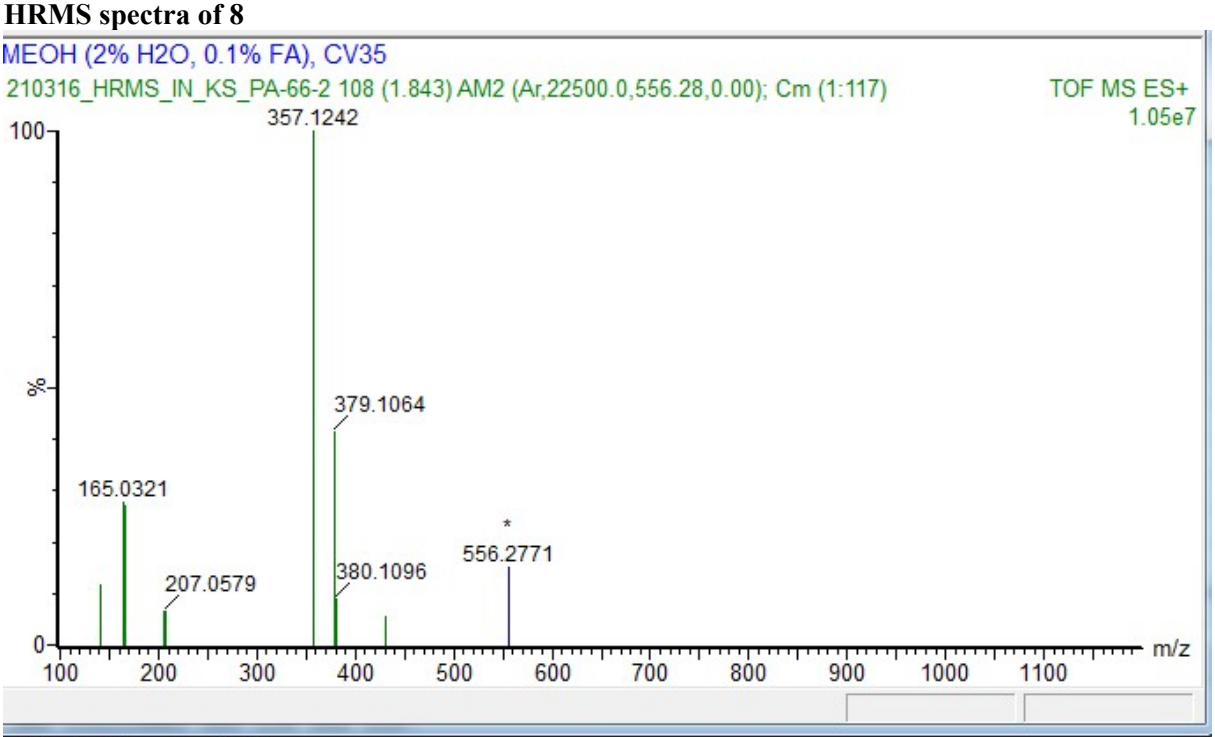
COSY spectra of 8 in $CDCl_3$



NOESY spectra of 8 in $CDCl_3$



HRMS spectra of 8



Single Mass Analysis

Tolerance = 2.0 mDa / DBE: min = -0.5, max = 100.0

Element prediction: Off

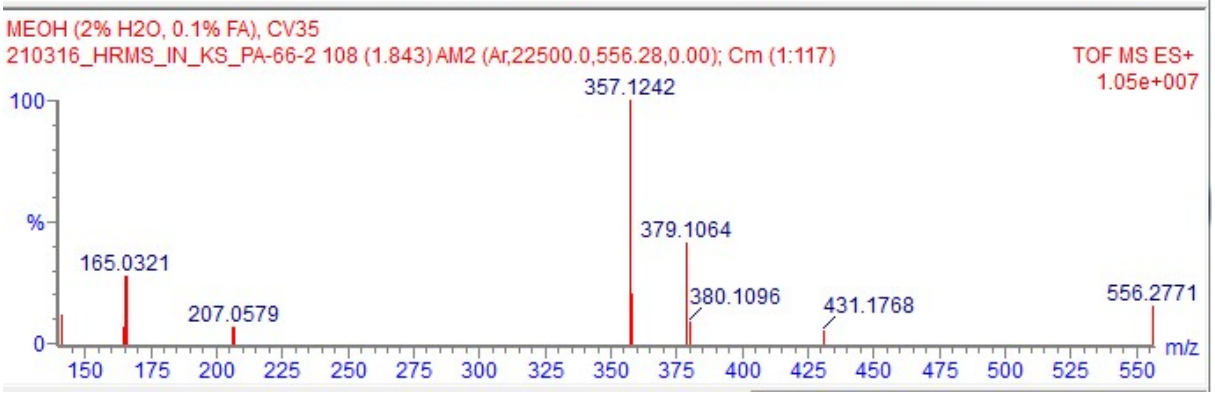
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

266 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)

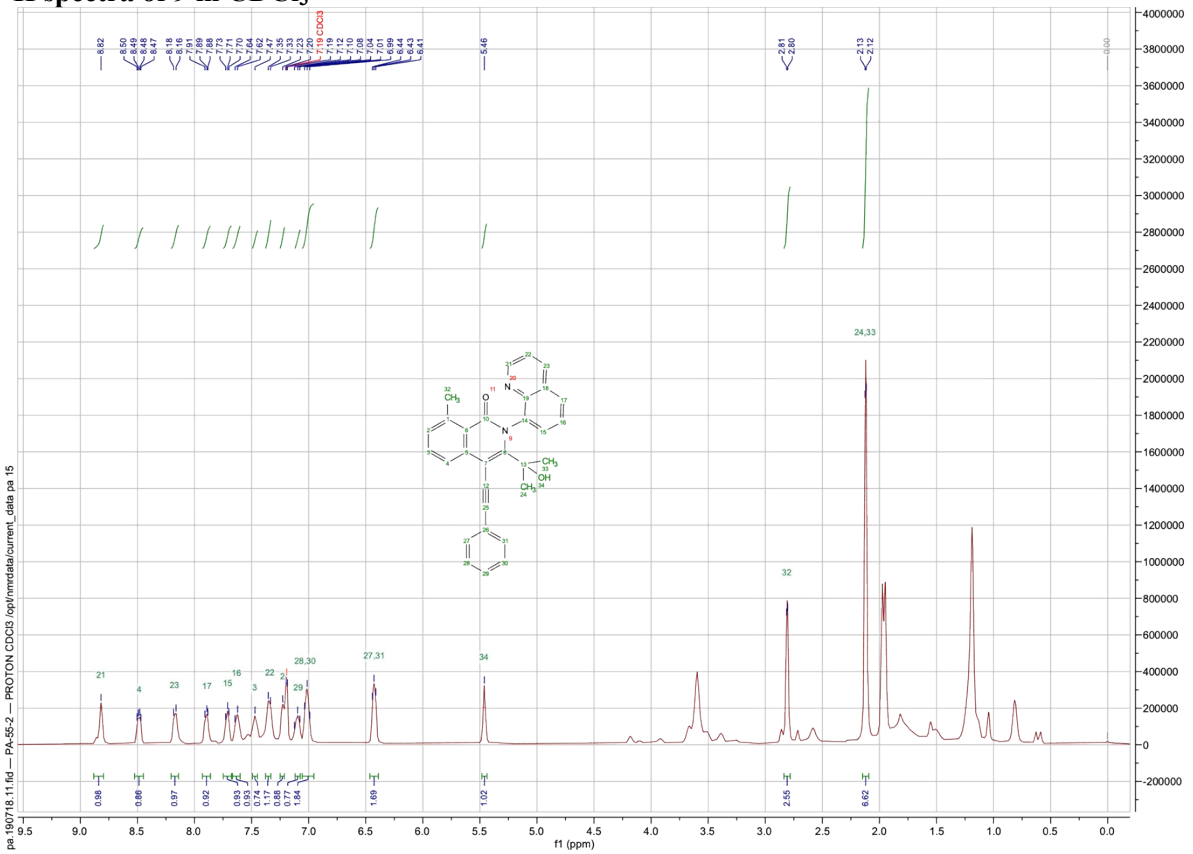
Elements Used:

Mass	Calc. Mass	mDa	PPM	DBE	Formula	Fit Conf %	C	H	N	O	Na	S
357.1242	357.1239	0.3	0.8	15.5	C22 H17 N2 O3	0..63.30	22	17	2	3		
	357.1249	-0.7	-2.0	7.5	C17 H22 N2 O3 Na S	1..22.77	17	22	2	3	1	1
	357.1255	-1.3	-3.6	16.5	C25 H18 O Na	1..13.93	25	18		1	1	

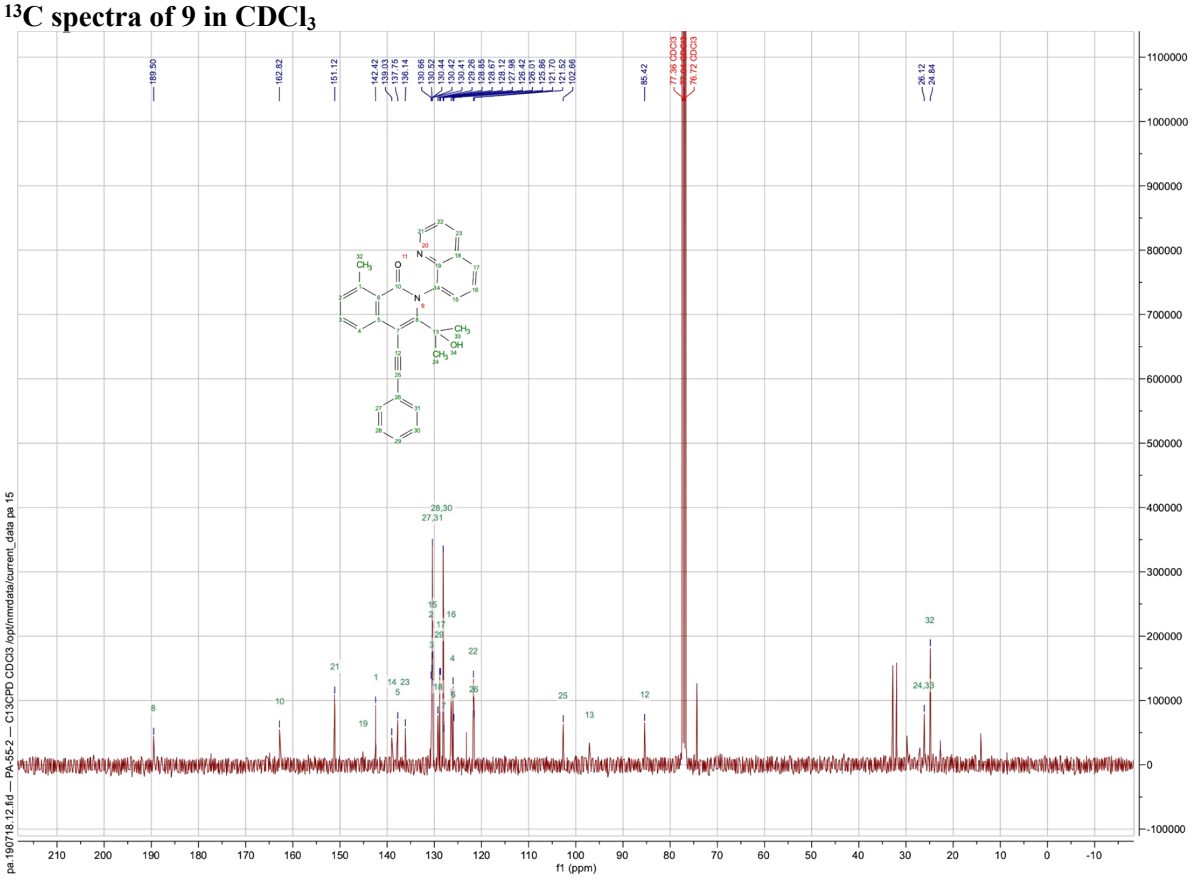


9

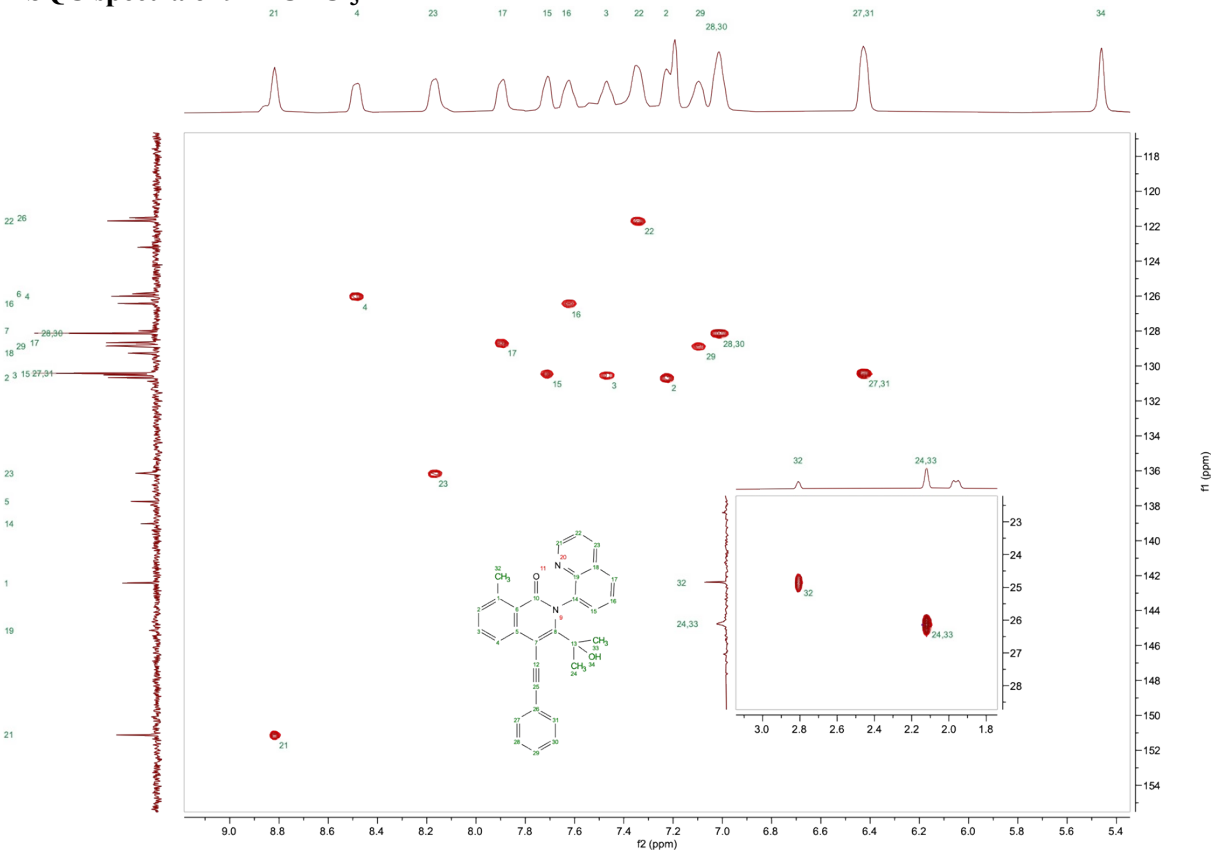
^{1}H spectra of 9 in $CDCl_3$



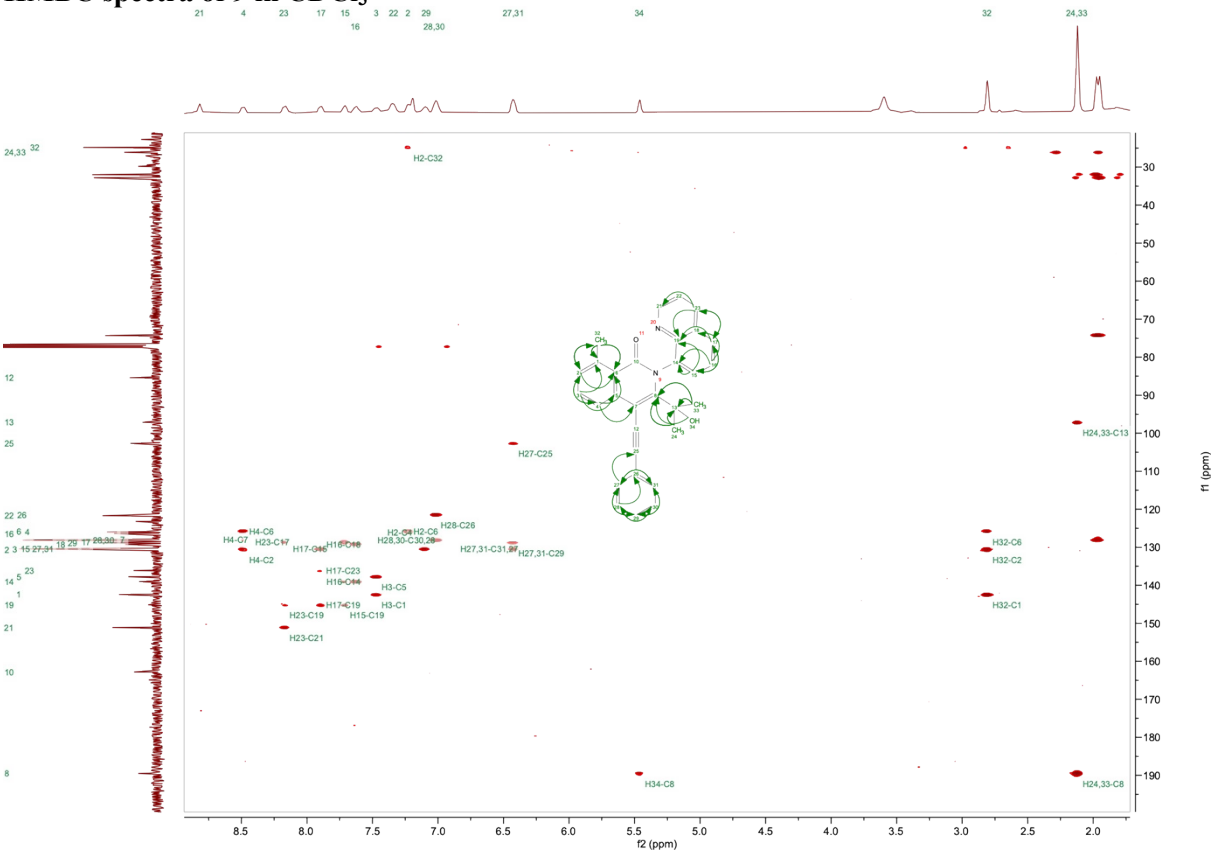
^{13}C spectra of 9 in $CDCl_3$



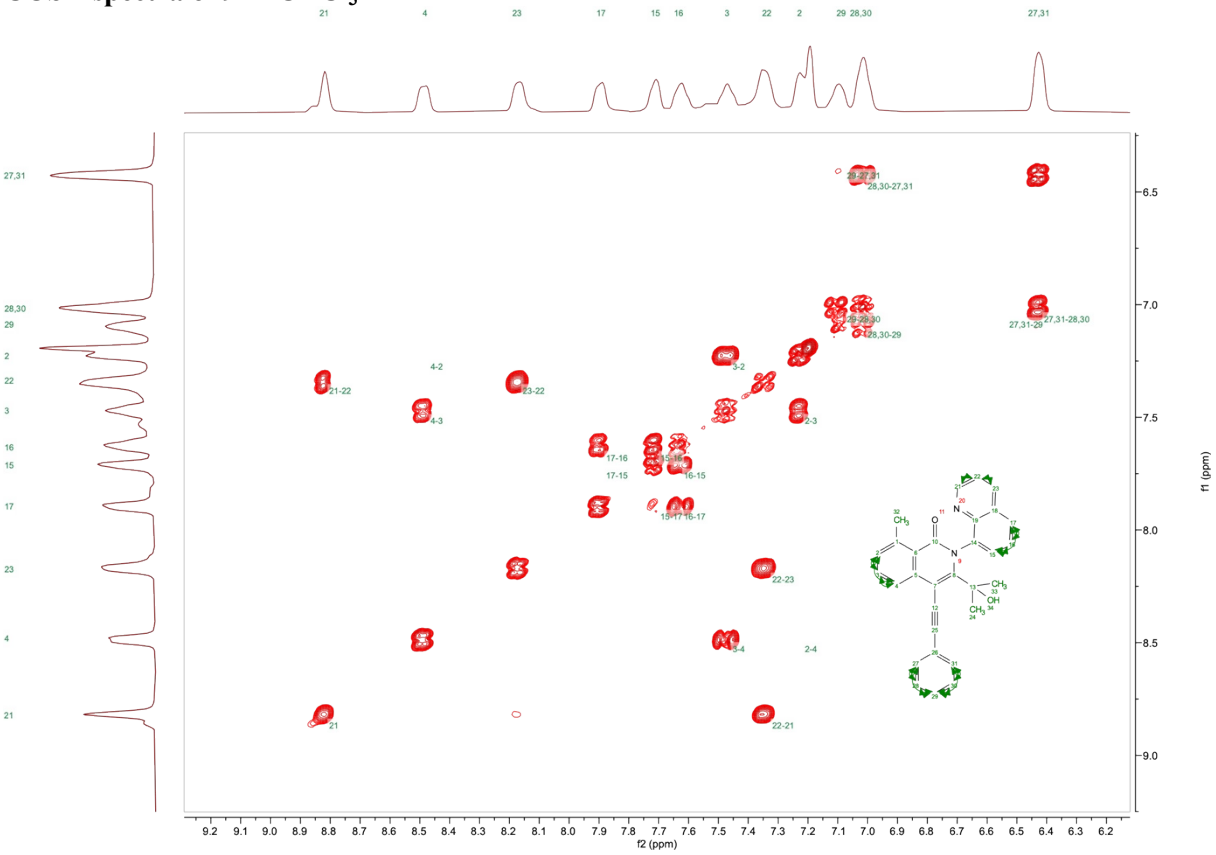
HSQC spectra of 9 in $CDCl_3$



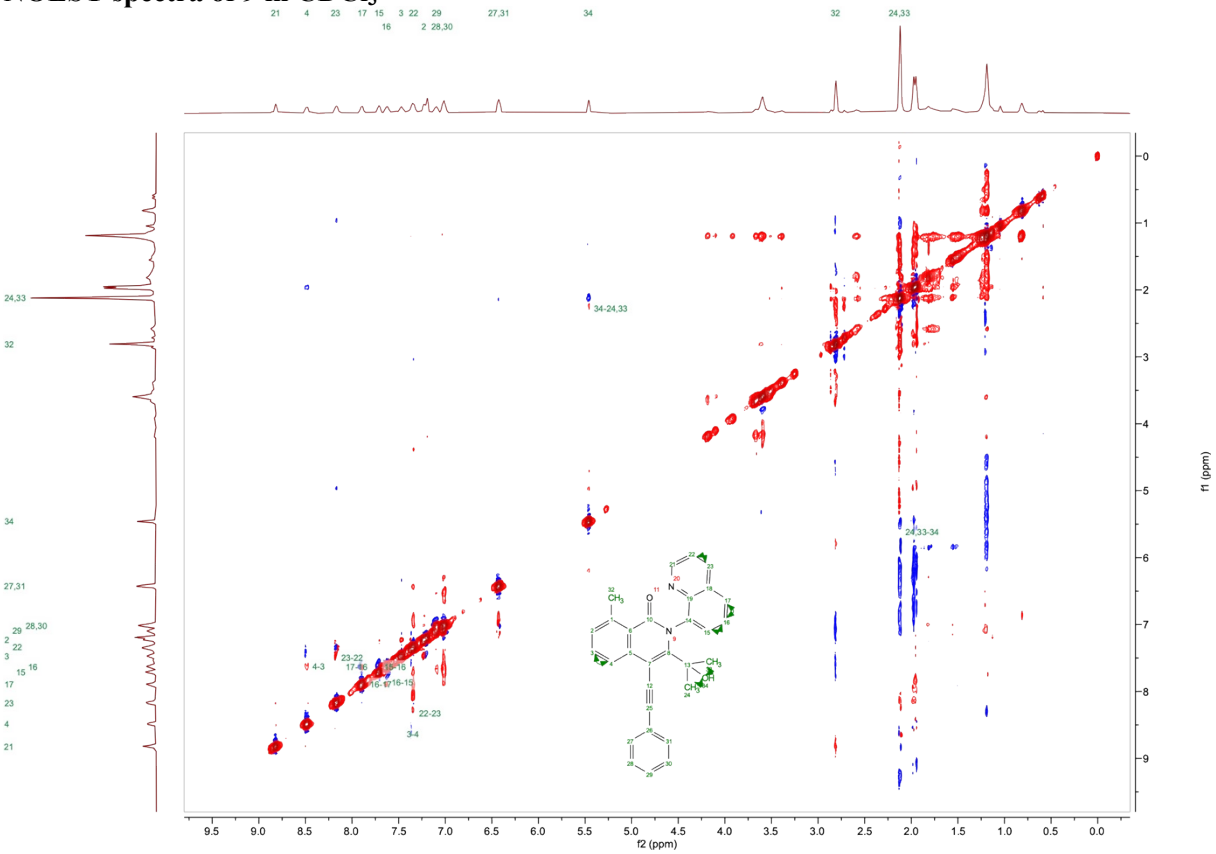
HMBC spectra of 9 in $CDCl_3$



COSY spectra of 9 in $CDCl_3$



NOESY spectra of 9 in $CDCl_3$



HRMS spectra of 9

HRMS DST-FIST Funded, Department of Chemistry, IIT Madras

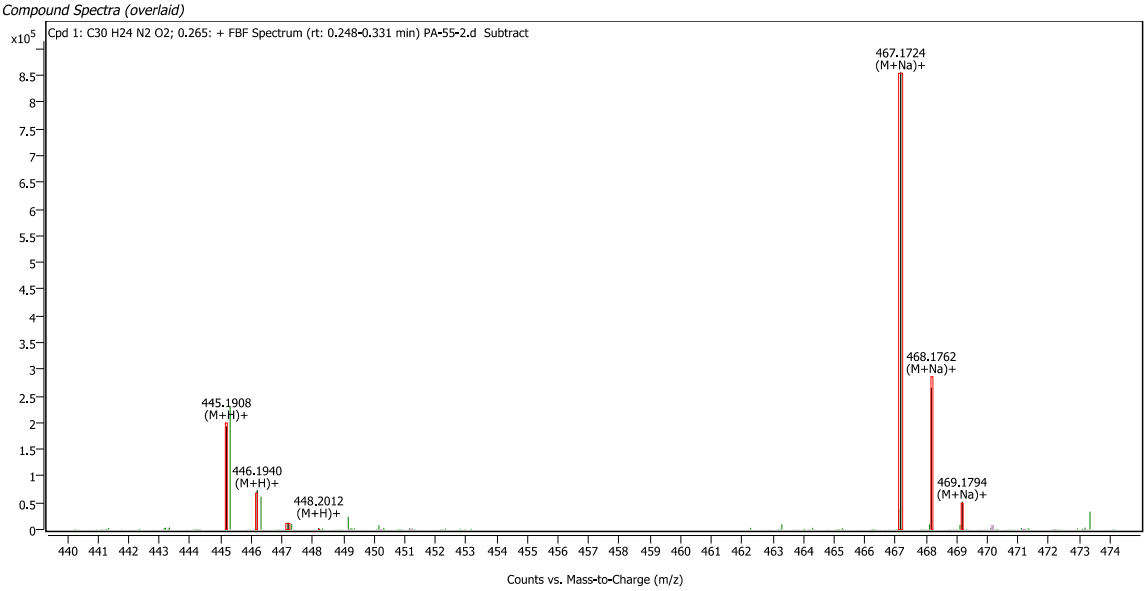
ESI Mass Report

Name	071119-24-KRR-PA-55-2	**Data File Path**	D:\MassHunter\Data\2019\NOV-2019\KRR\PA-55-2.d
Sample ID		**Acq. Time (Local)**	27-11-2019 13:58:16 (UTC+05:30)
Instrument	Instrument 1	**Method Path (Acq)**	D:\MassHunter\Methods\Direct Infusion_HPLC.m
MS Type	QTOF	**Version (Acq SW)**	6200 series TOF/6500 series Q-TOF B.08.00 (B8058.0)
Inj. Vol (ul)	5	**IRM Status**	Success
Position	P1-C2	**Method Path (DA)**	D:\MassHunter\Methods\10.0\Default.m
Plate Pos.		**Target Source Path**	
Operator		**Result Summary**	1 qualified (1 targets)

Compound Details

Cpd. 1: C30 H24 N2 O2

Compound Spectra (overlaid)

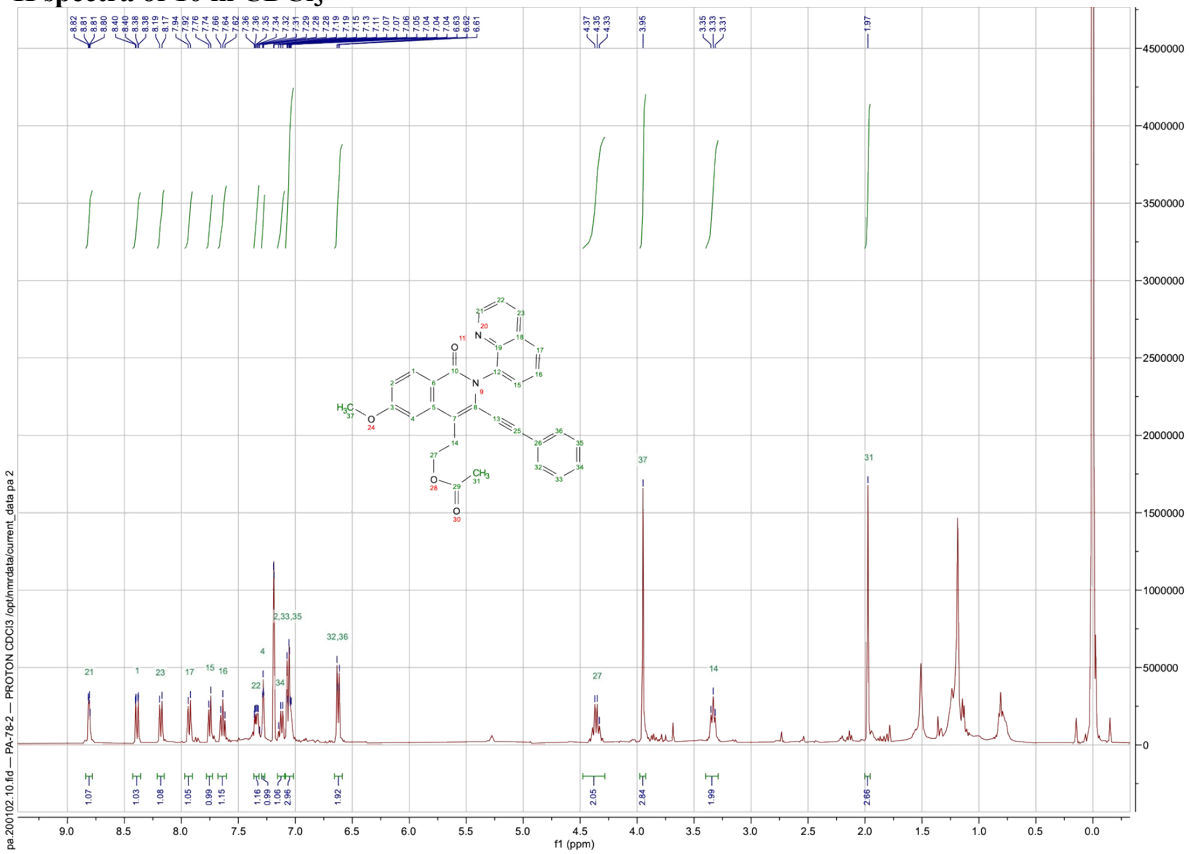


Compound ID Table

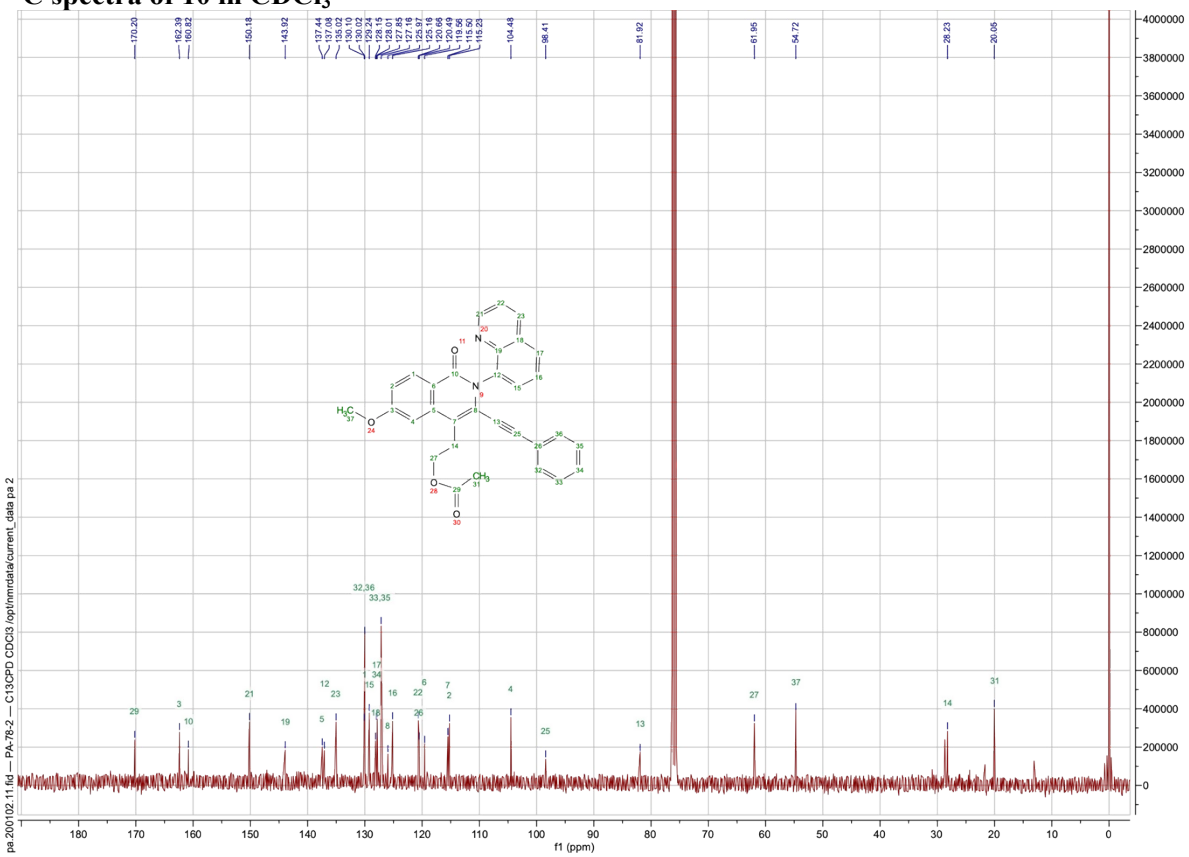
Cpd	Formula	Mass (Tgt)	Calc. Mass	Mass	Species	Diff(Tgt.ppm)	mDa
1	C30 H24 N2 O2	444.1838	444.1834	445.1908 467.1724	(M+H)+ (M+Na)+	-0.88	-0.39

Acylated side product

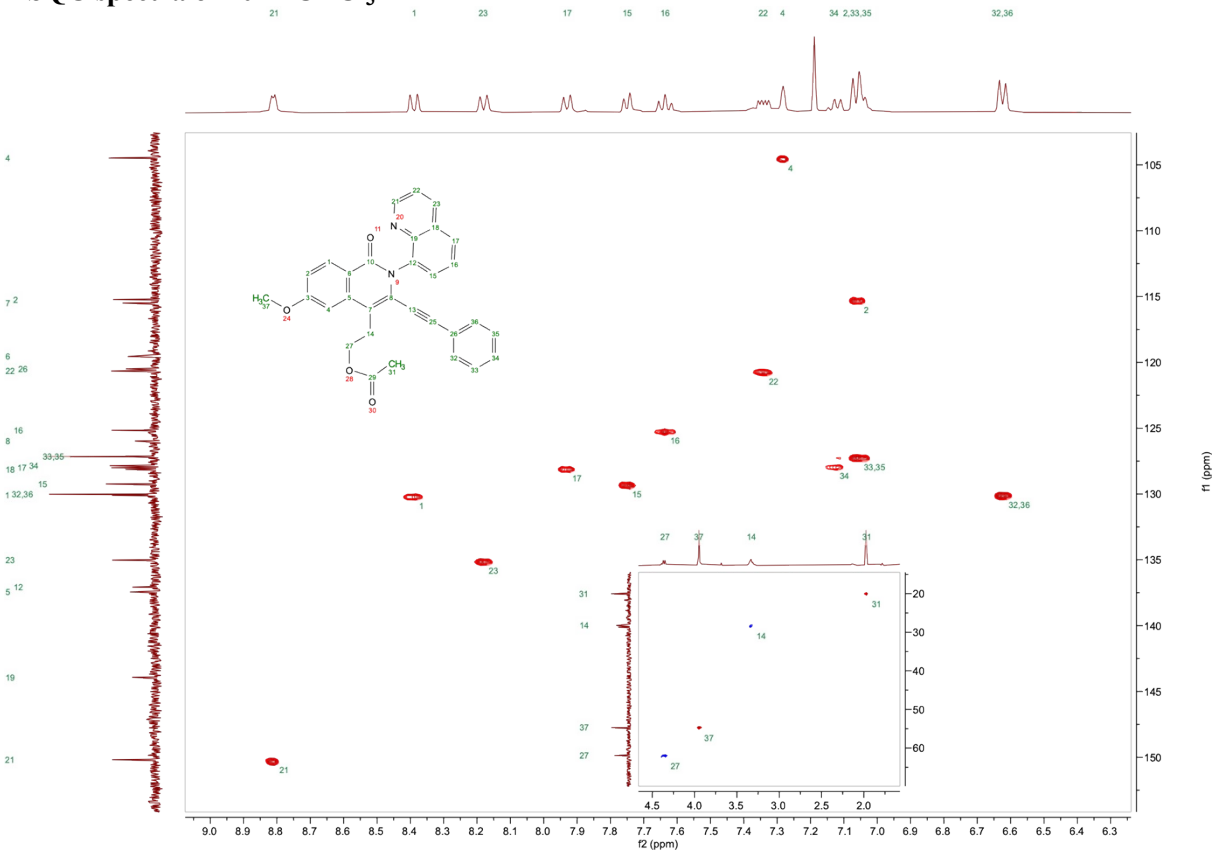
^{1}H spectra of 10 in $CDCl_3$



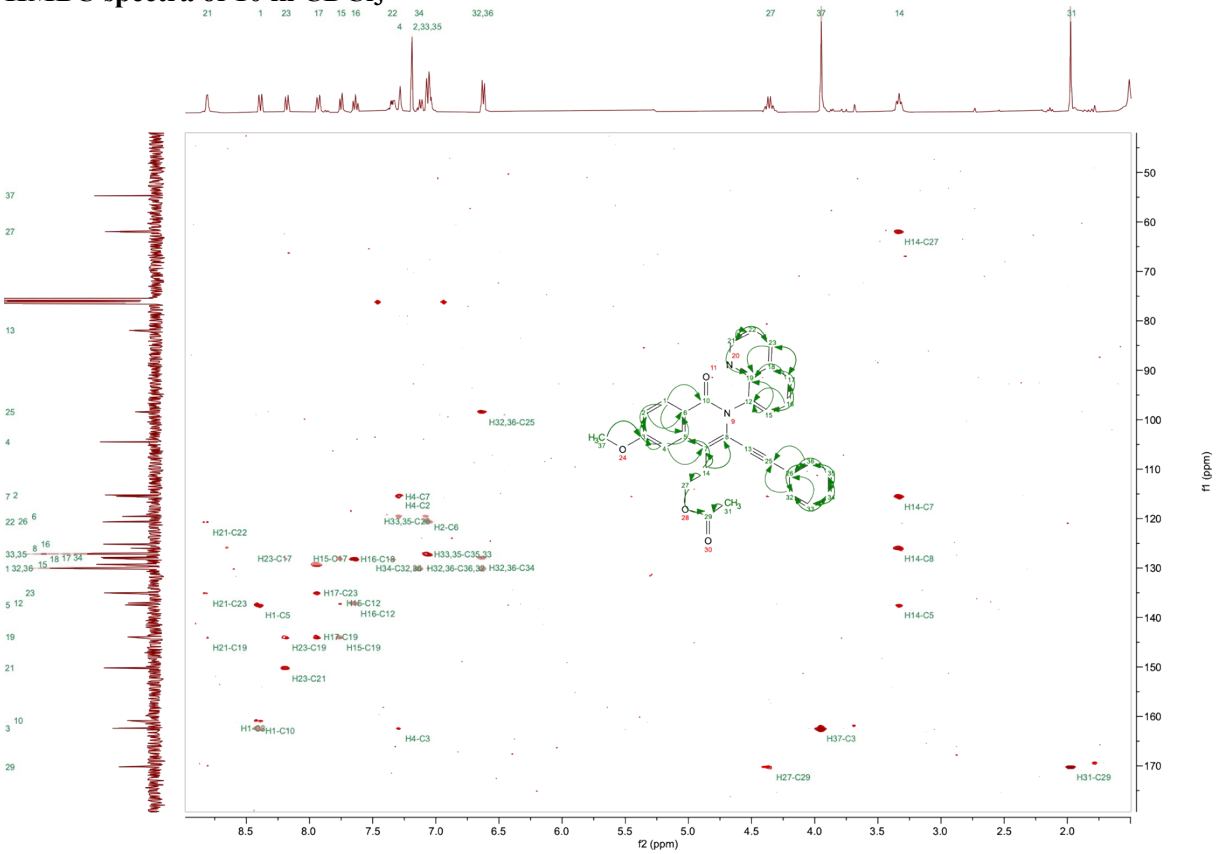
^{13}C spectra of 10 in $CDCl_3$



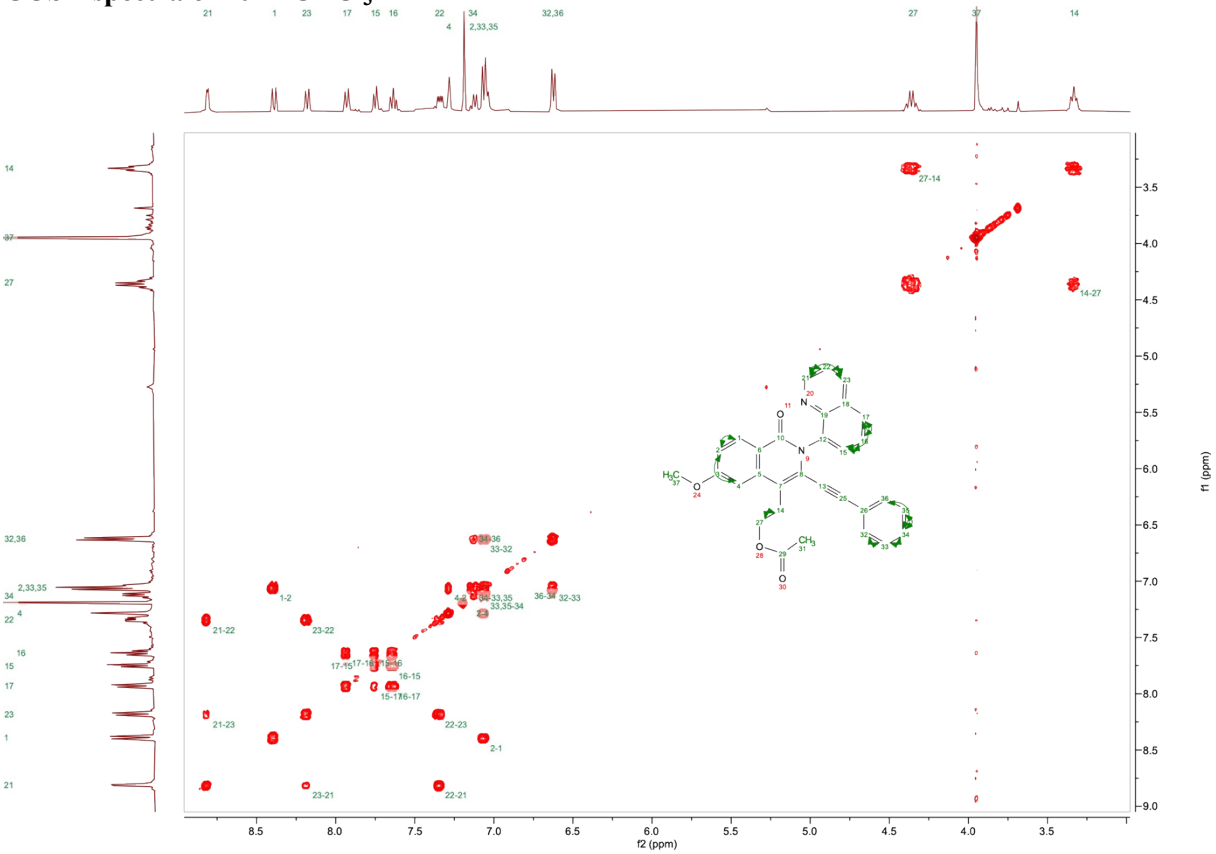
HSQC spectra of 10 in $CDCl_3$



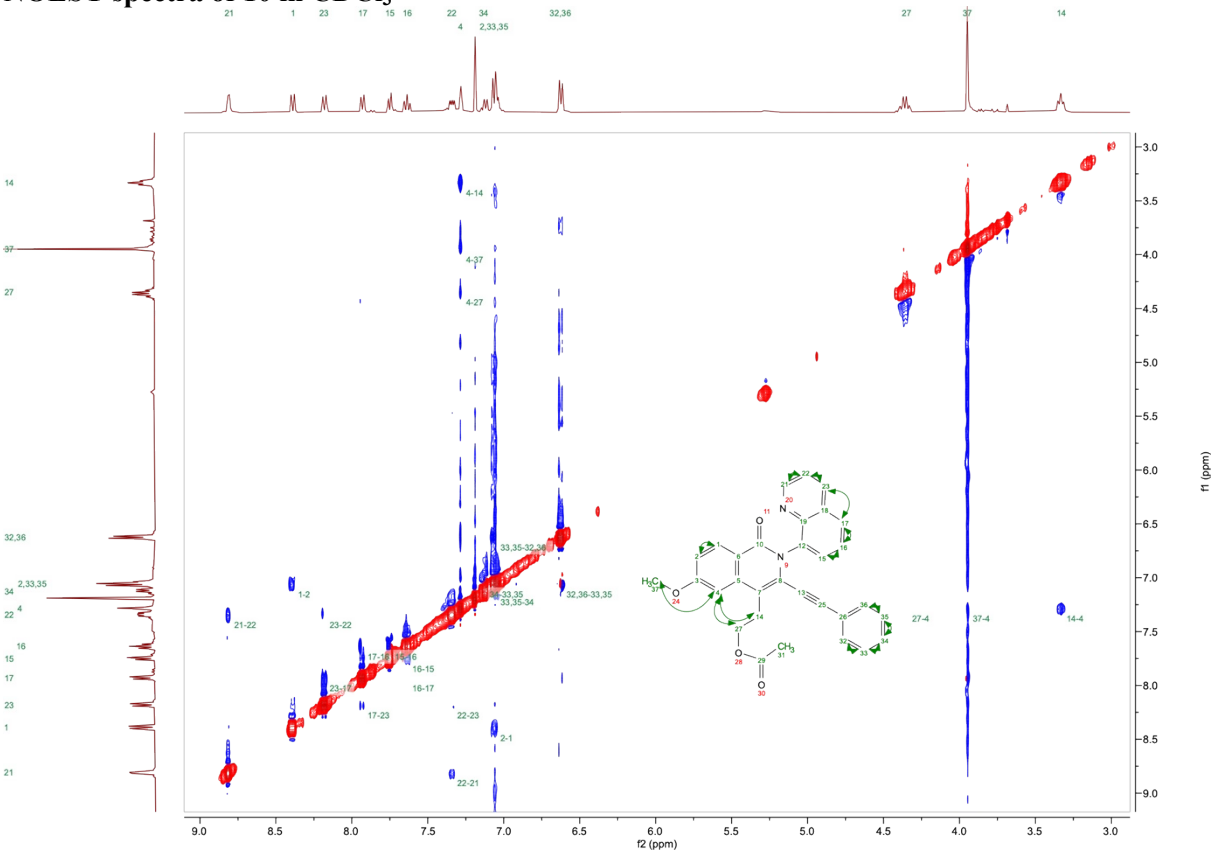
HMBC spectra of 10 in $CDCl_3$



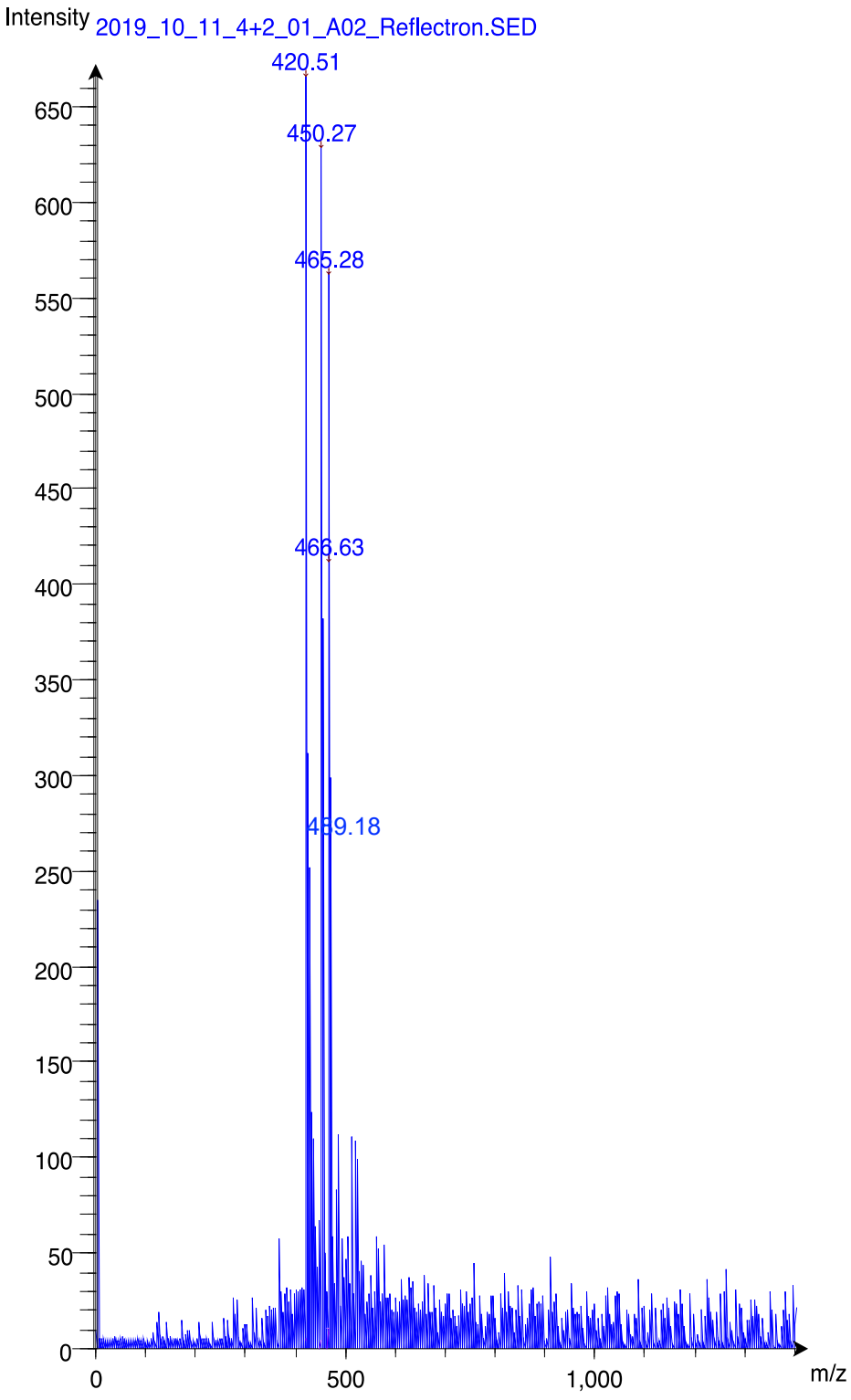
COSY spectra of 10 in $CDCl_3$



NOESY spectra of 10 in $CDCl_3$

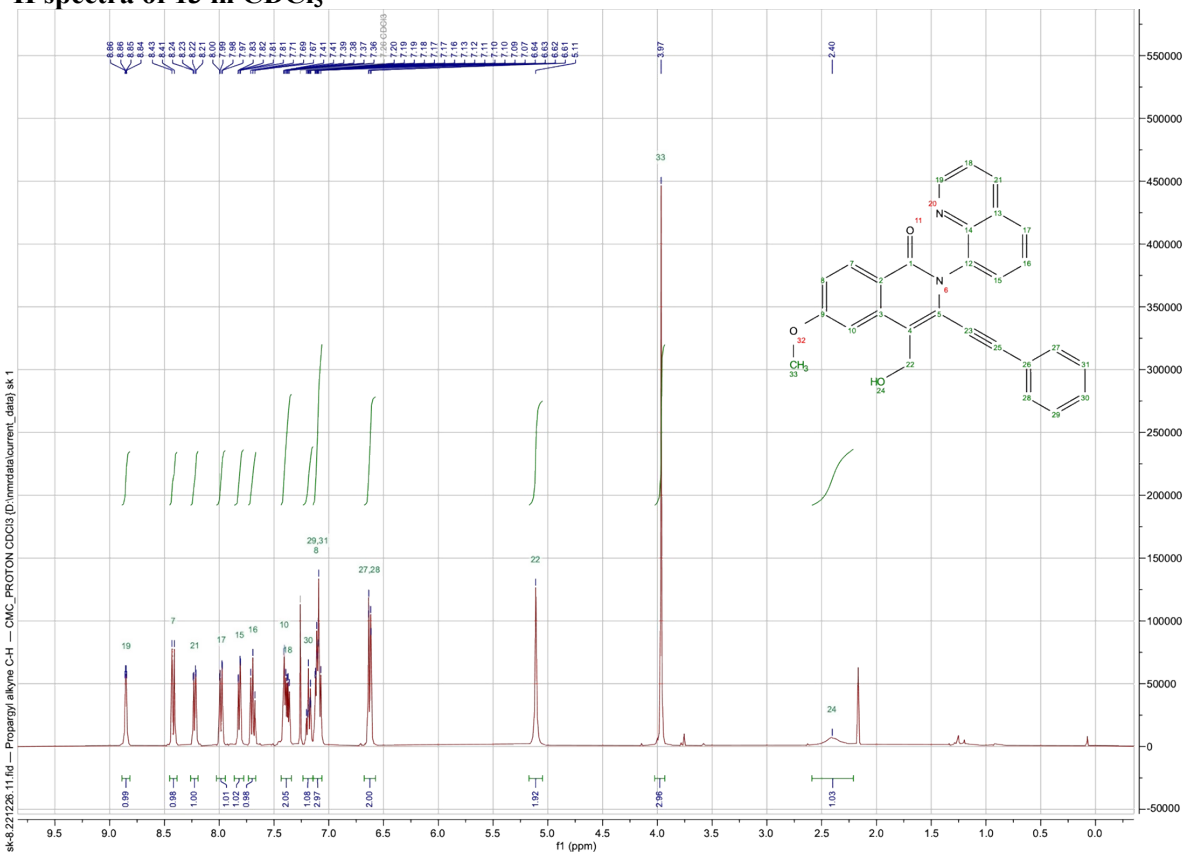


MALDI spectra of 10 in $CDCl_3$

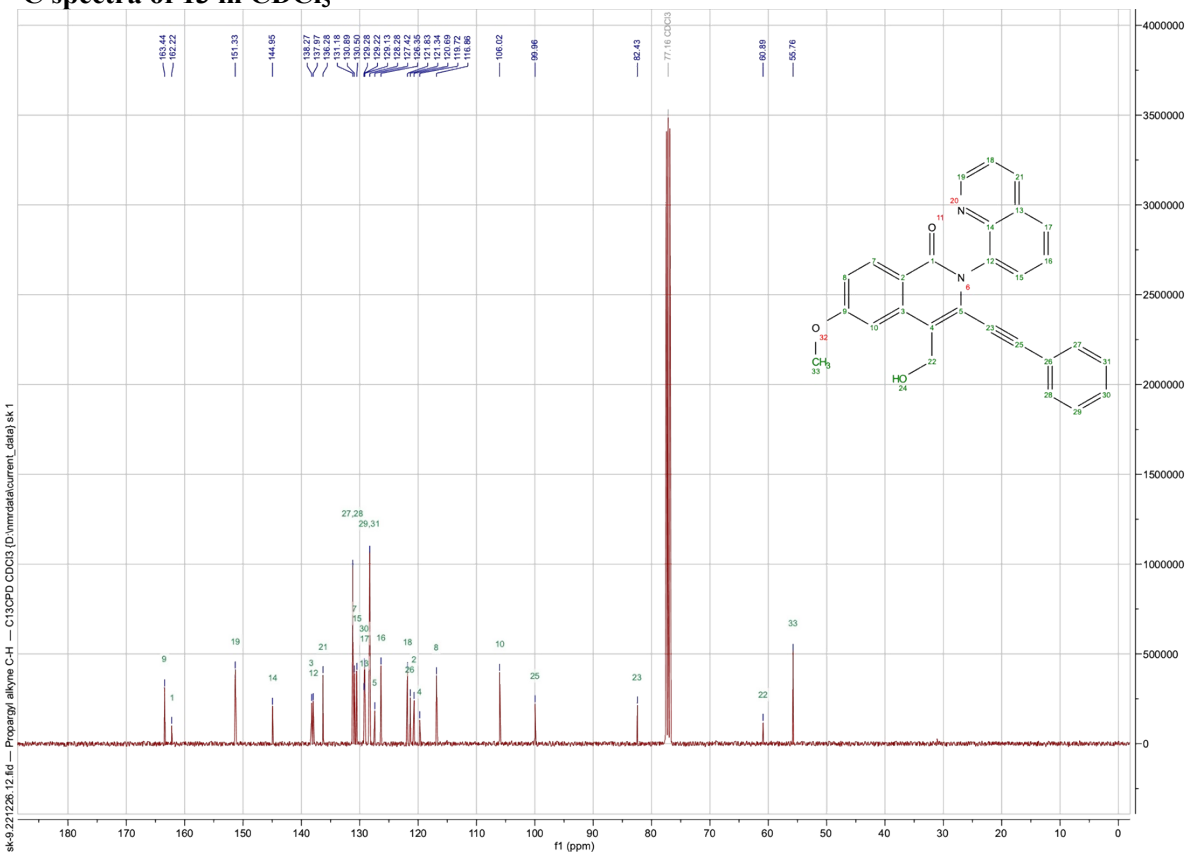


13

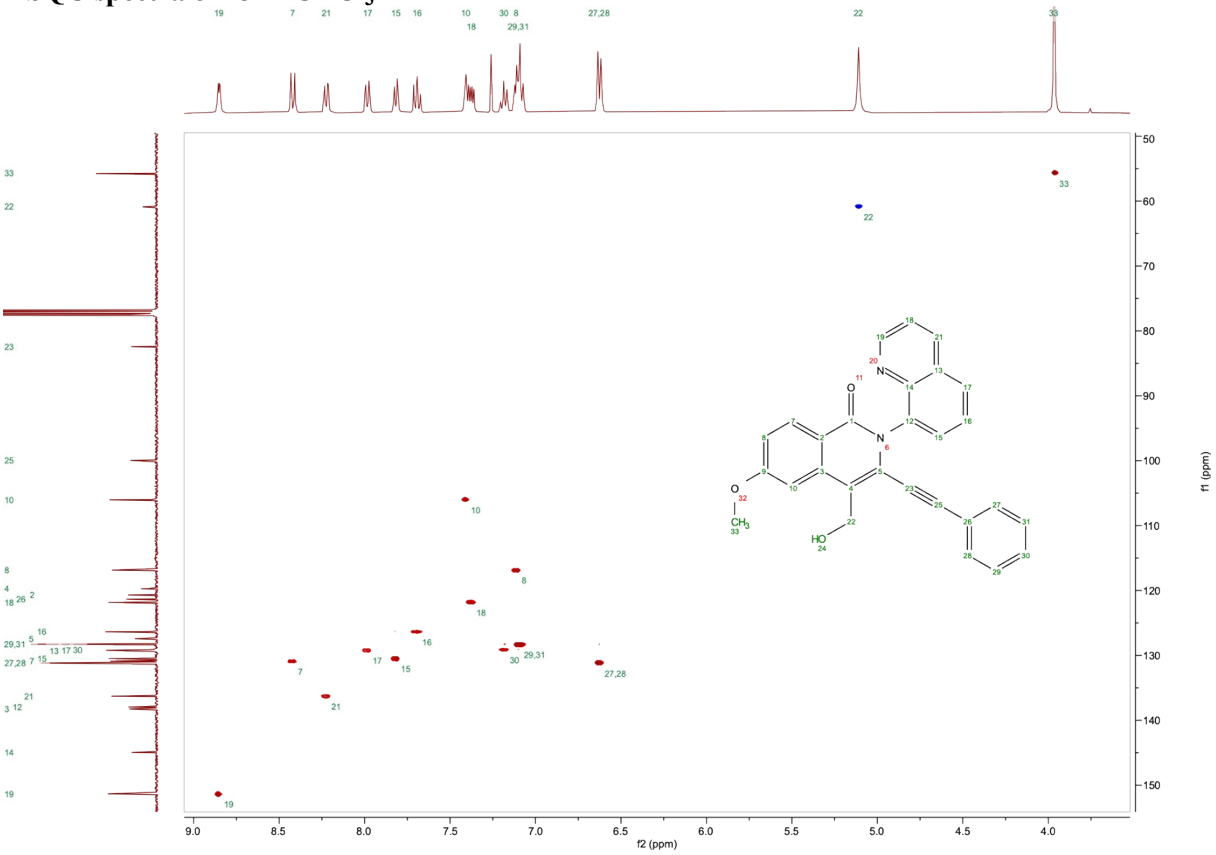
^{1}H spectra of 13 in $CDCl_3$



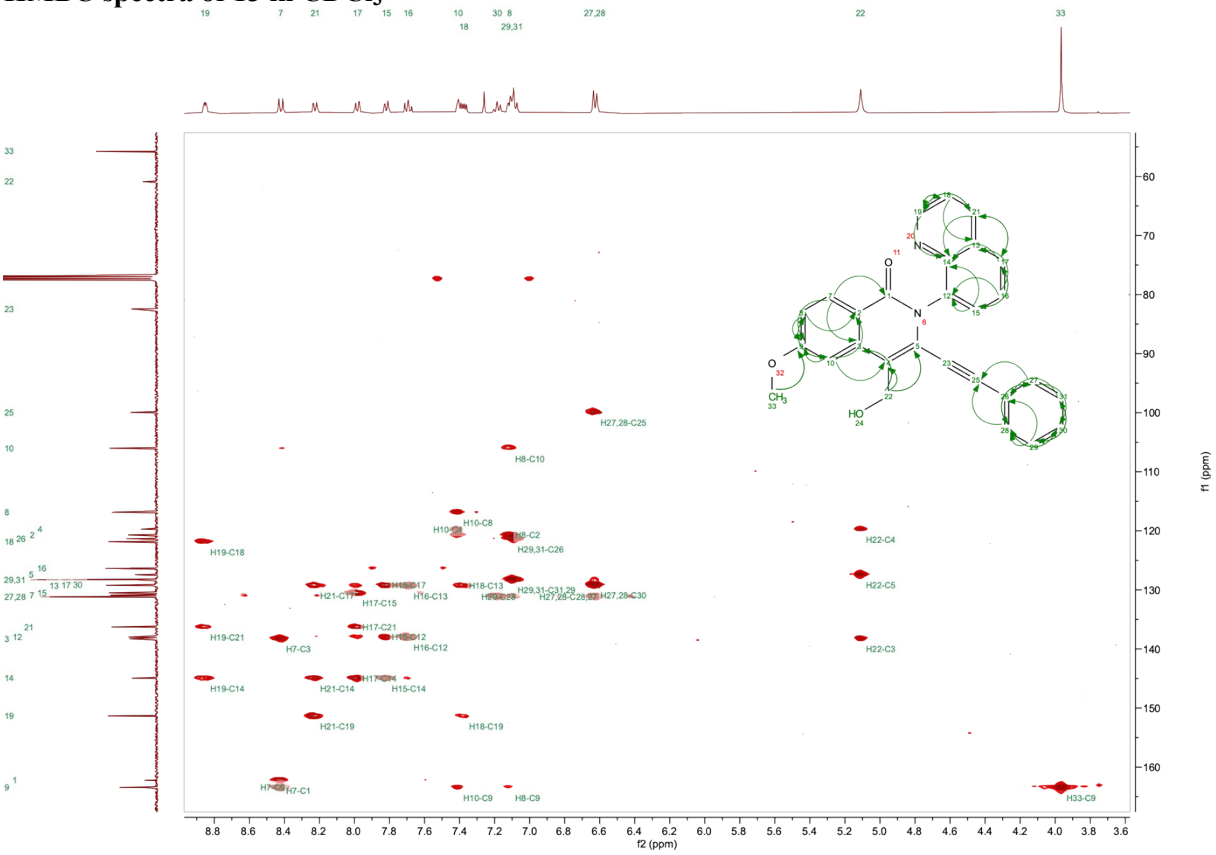
^{13}C spectra of 13 in $CDCl_3$



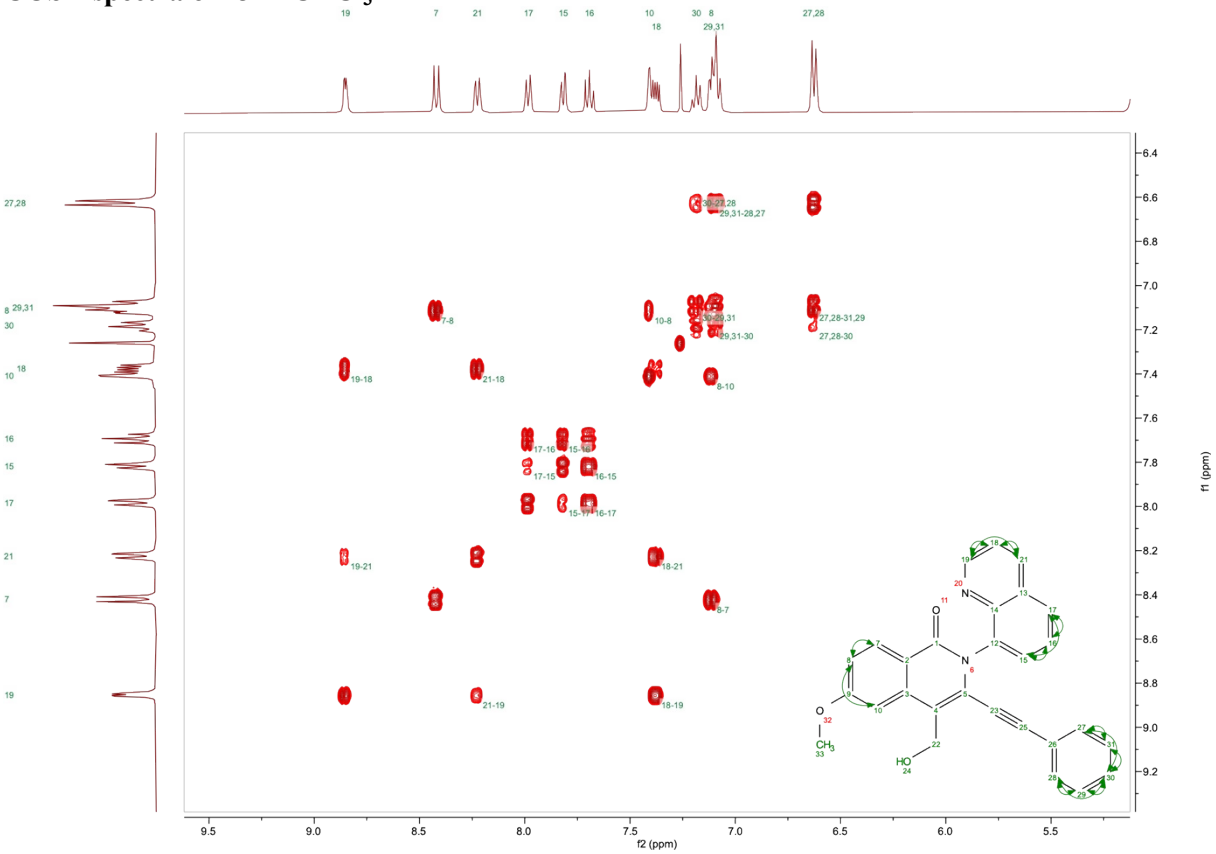
HSQC spectra of 13 in $CDCl_3$



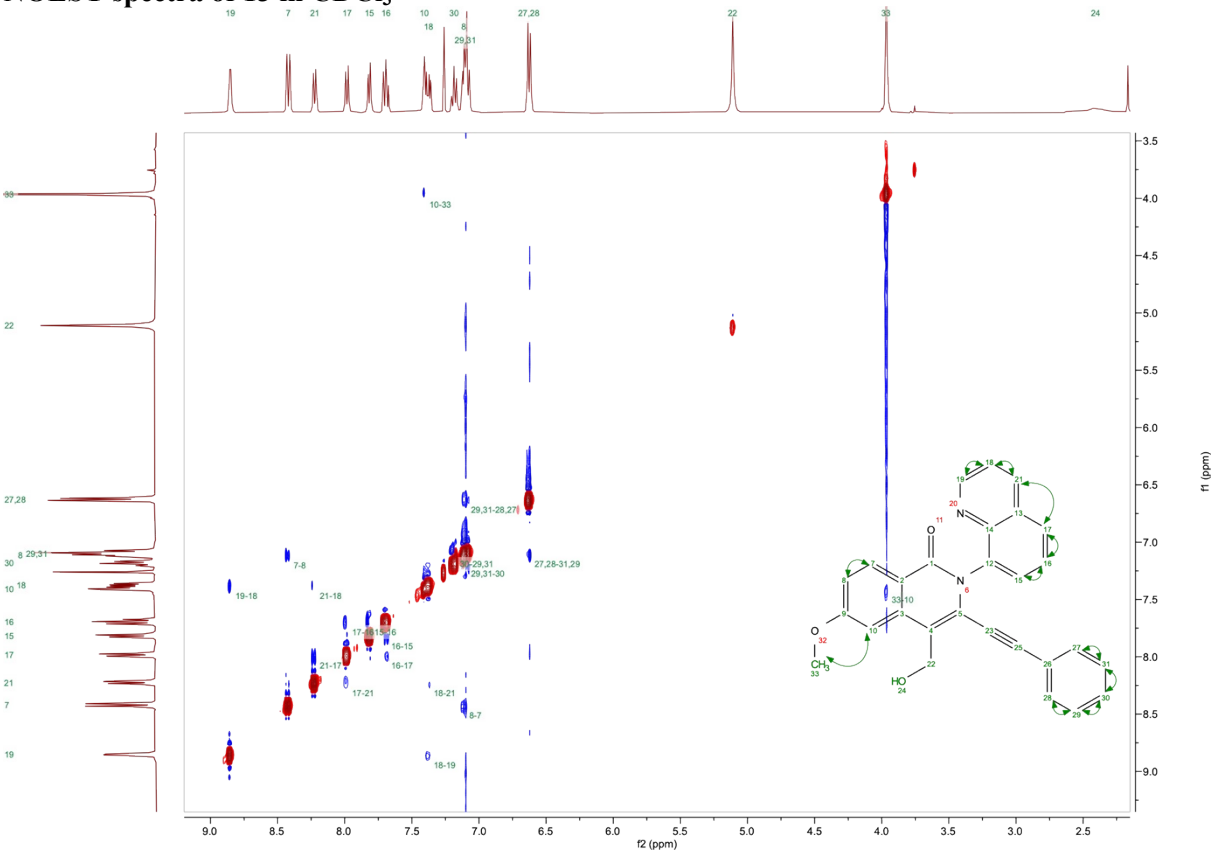
HMBC spectra of 13 in $CDCl_3$



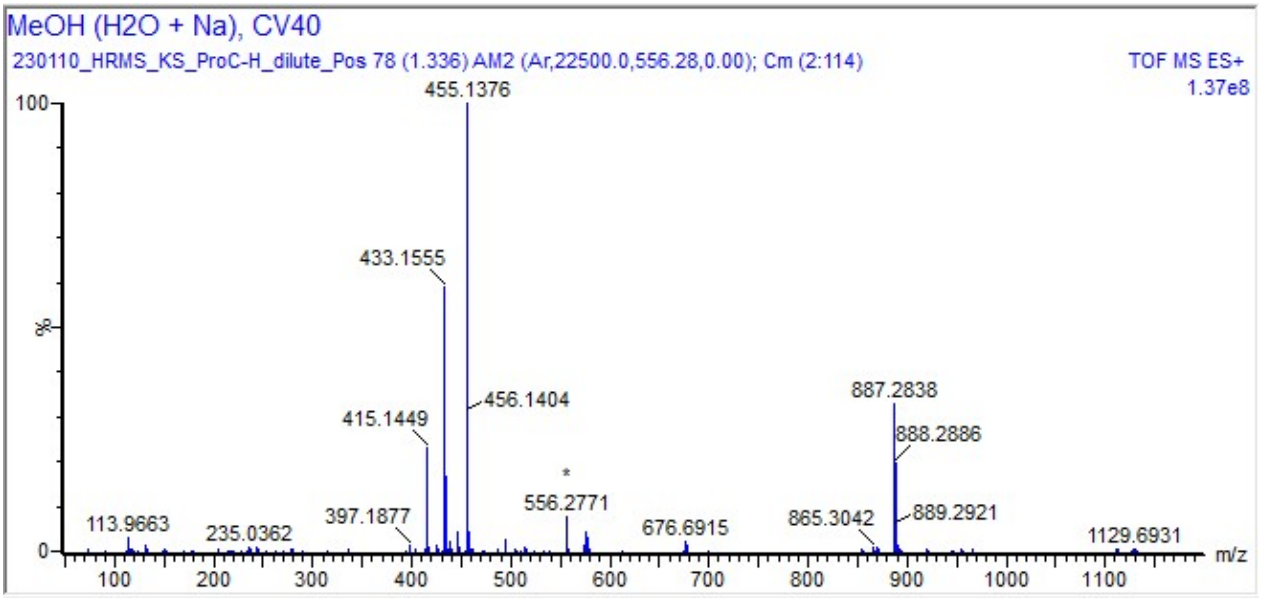
COSY spectra of 13 in $CDCl_3$



NOESY spectra of 13 in $CDCl_3$



HRMS spectra of 13



Single Mass Analysis

Tolerance = 2.0 mDa / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

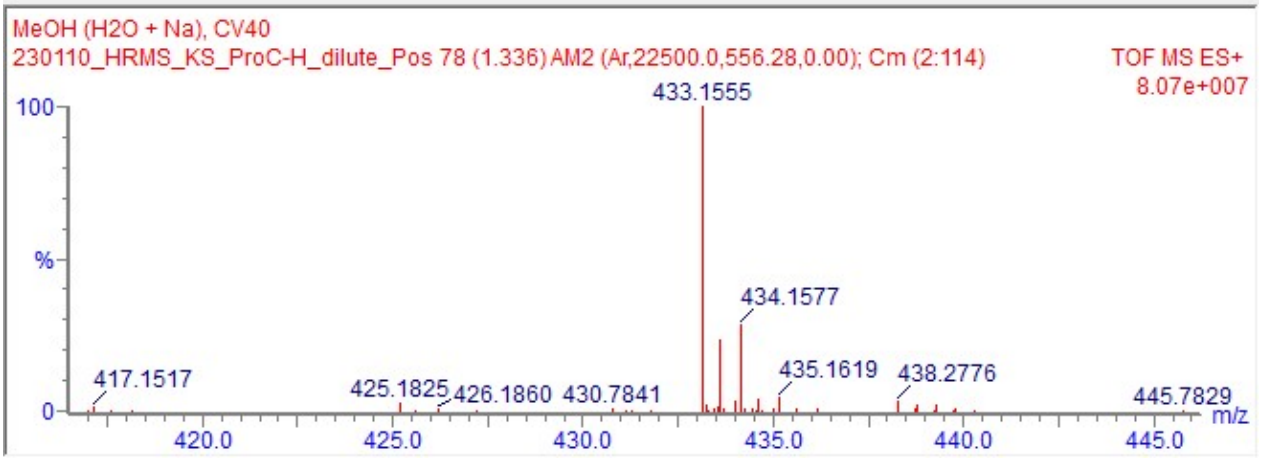
Monoisotopic Mass, Even Electron Ions

79 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

Elements Used:

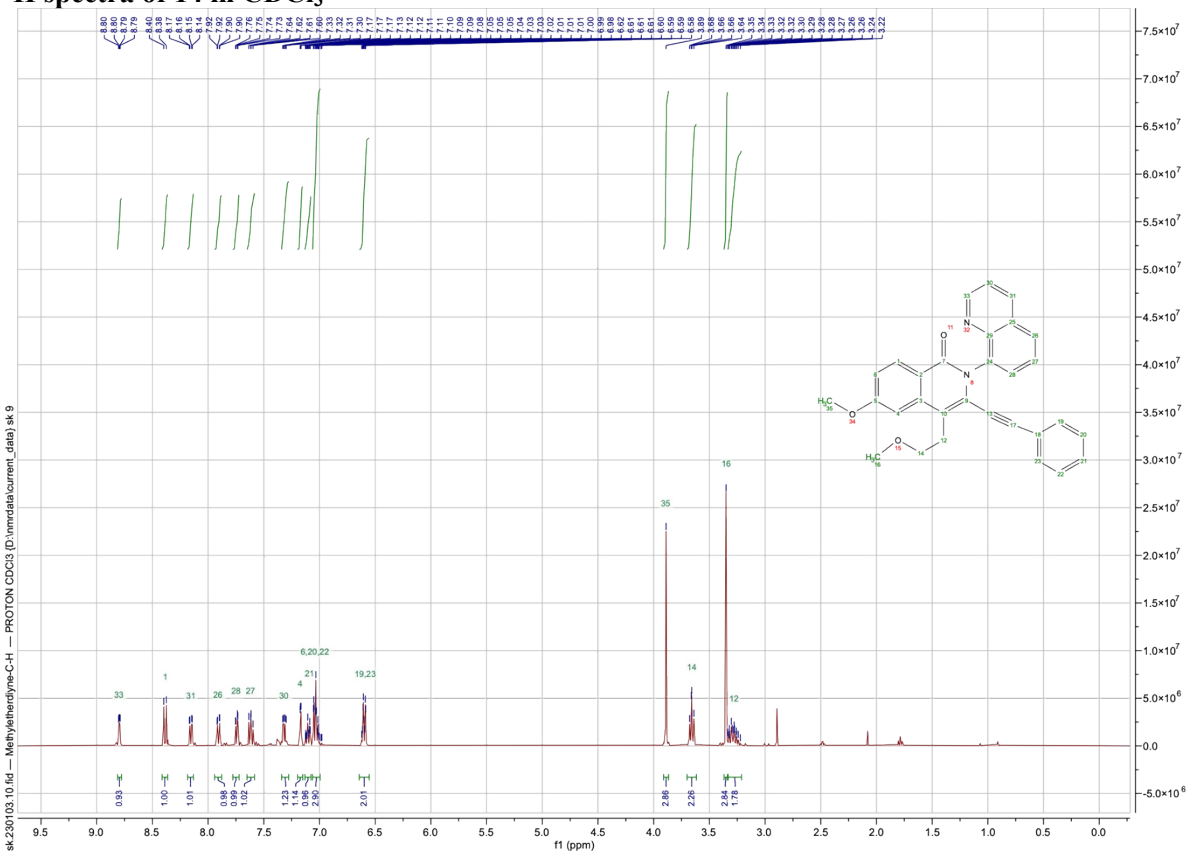
C: 1-30 H: 1-22 N: 1-4 O: 1-6 Na: 0-1

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i..	i...	Fit Conf %	C	H	N	O	Na
433.1555	433.1552	0.3	0.7	19.5	C28 H21 N2 O3	3...	n...	n/a	28	21	2	3	

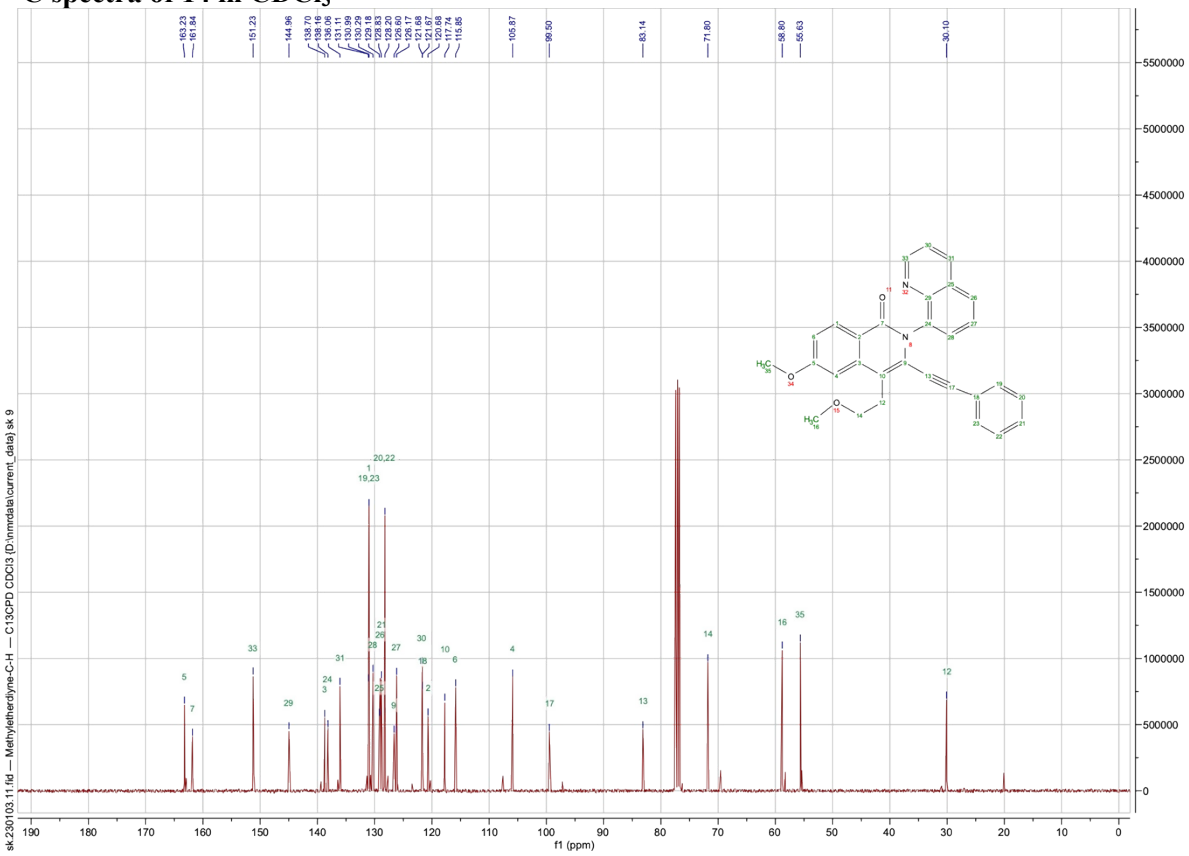


14

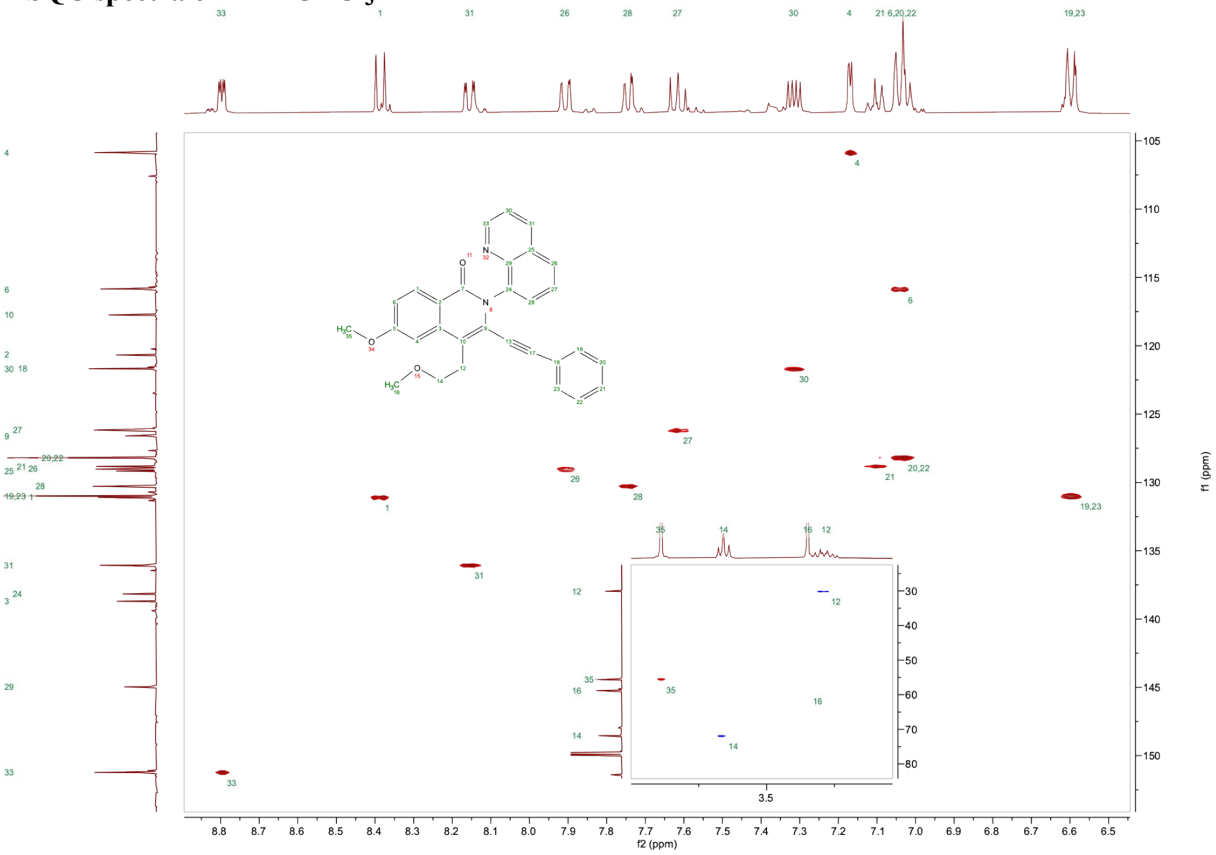
^{1}H spectra of 14 in $CDCl_3$



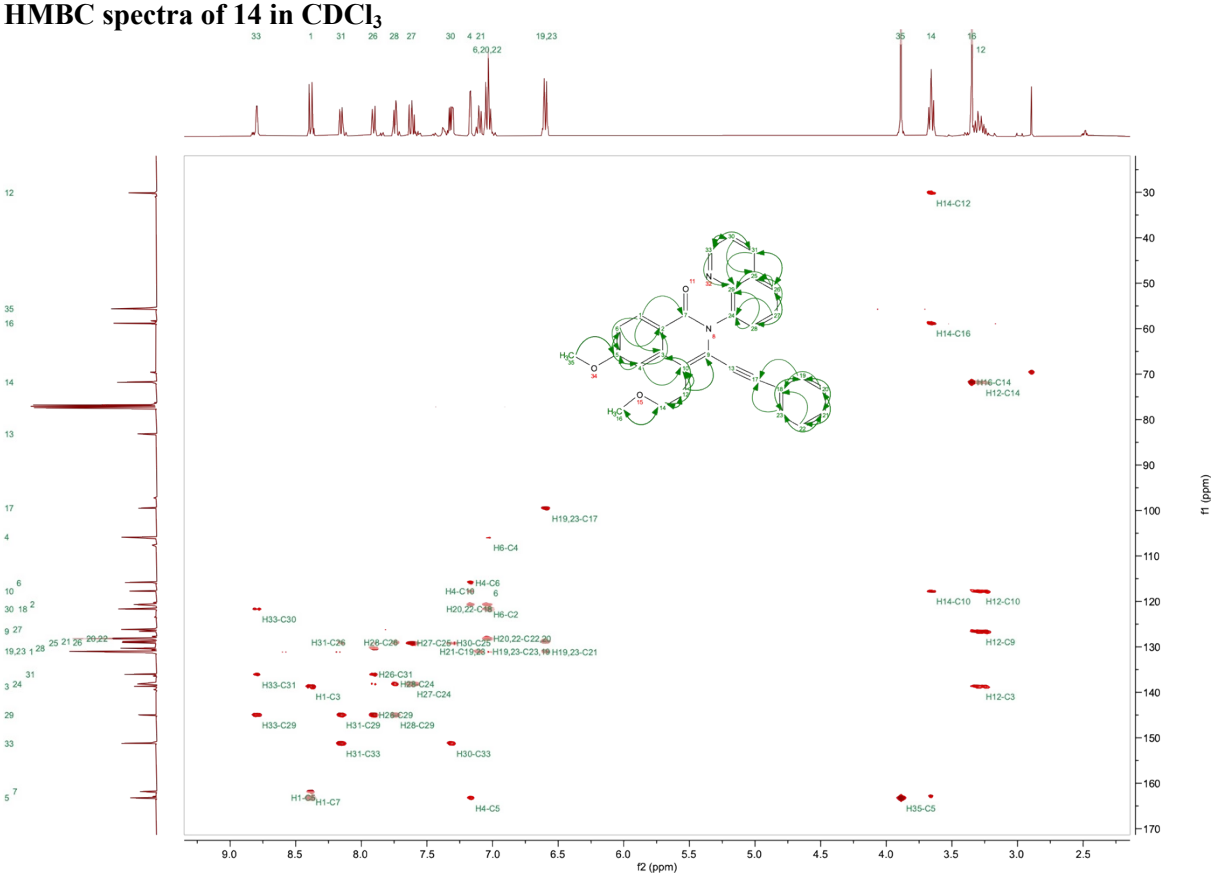
^{13}C spectra of 14 in $CDCl_3$



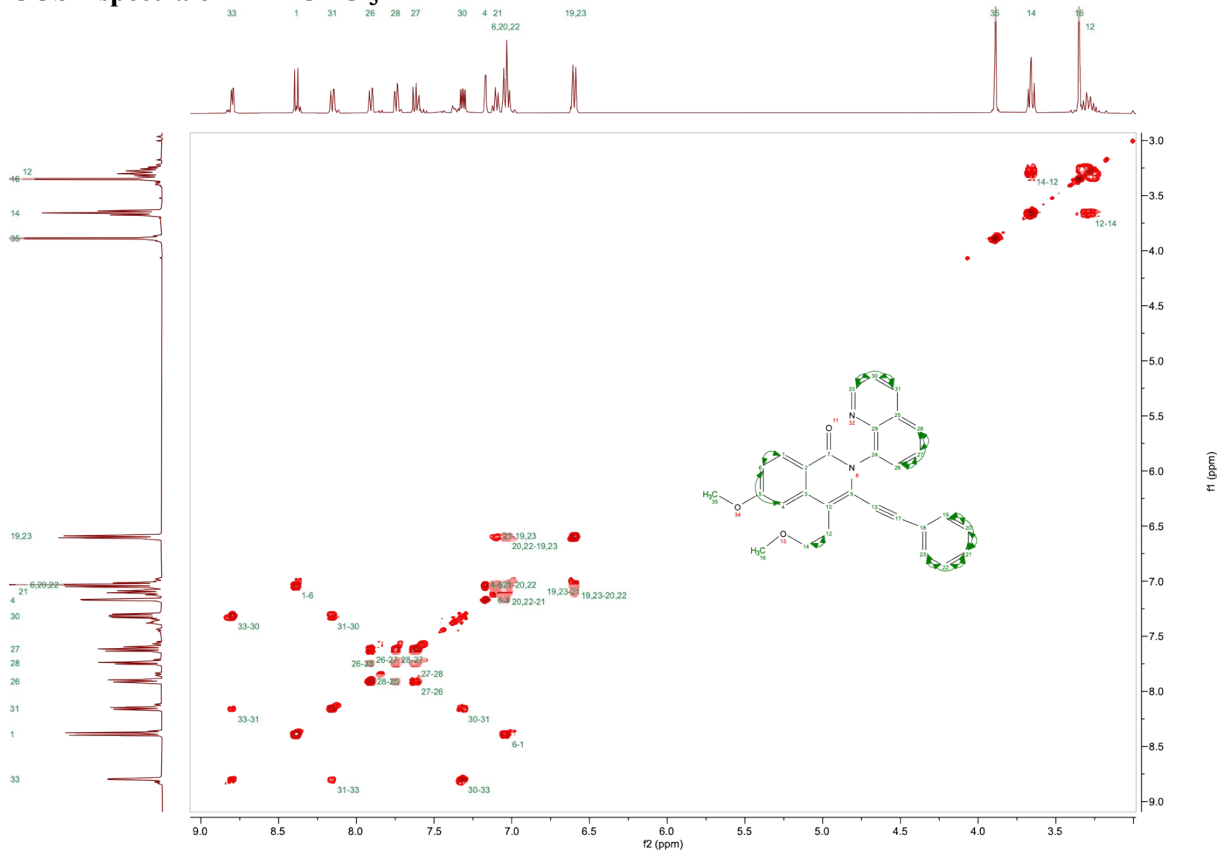
HSQC spectra of 14 in $CDCl_3$



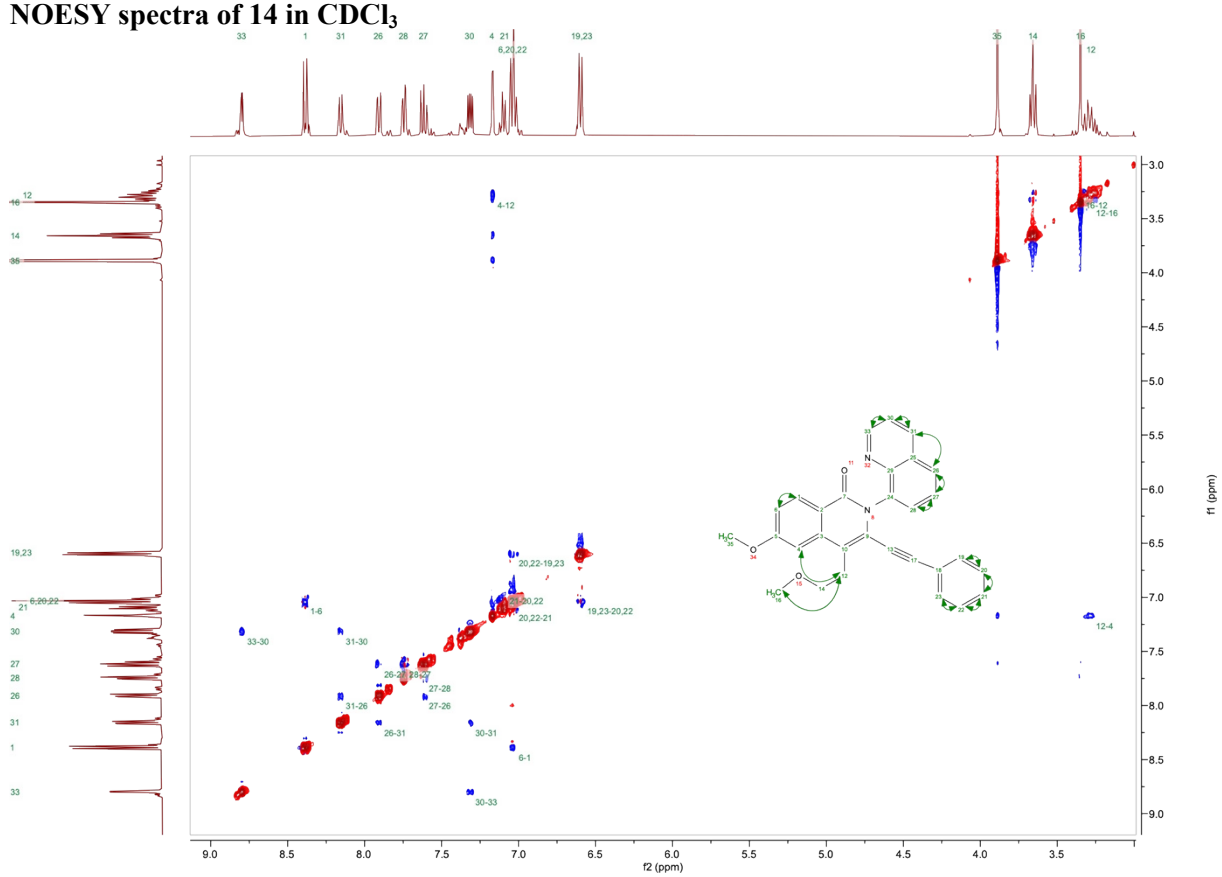
HMBC spectra of 14 in $CDCl_3$



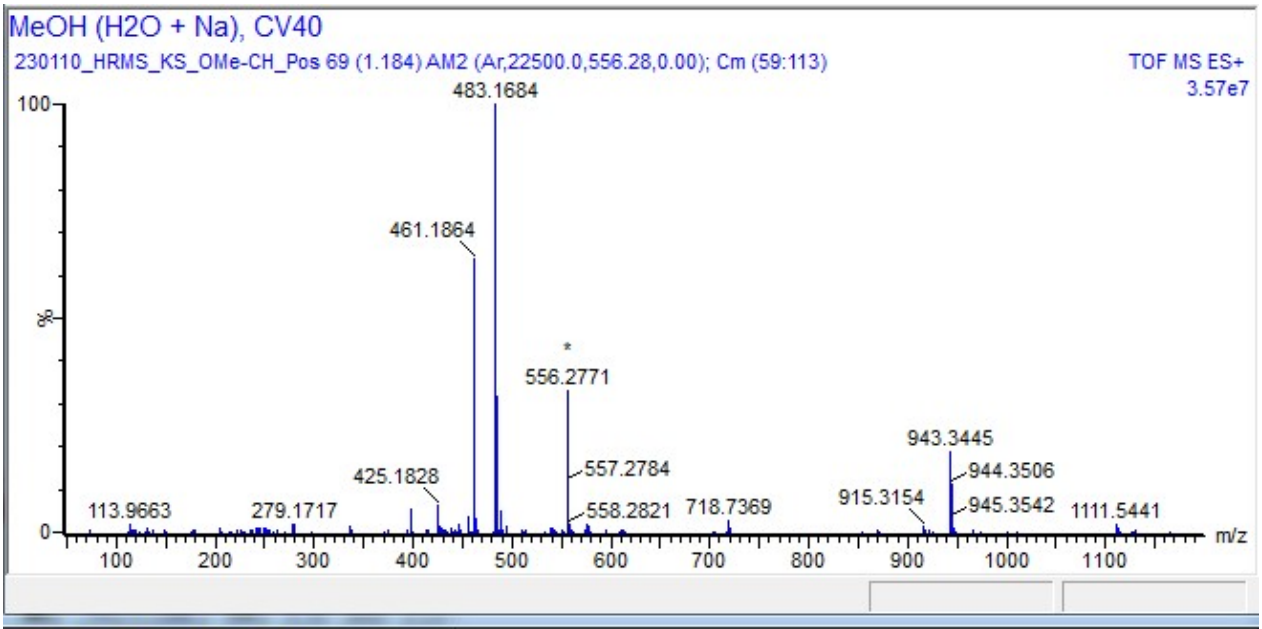
COSY spectra of 14 in $CDCl_3$



NOESY spectra of 14 in $CDCl_3$



HRMS spectra of 14



Single Mass Analysis

Tolerance = 2.0 mDa / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

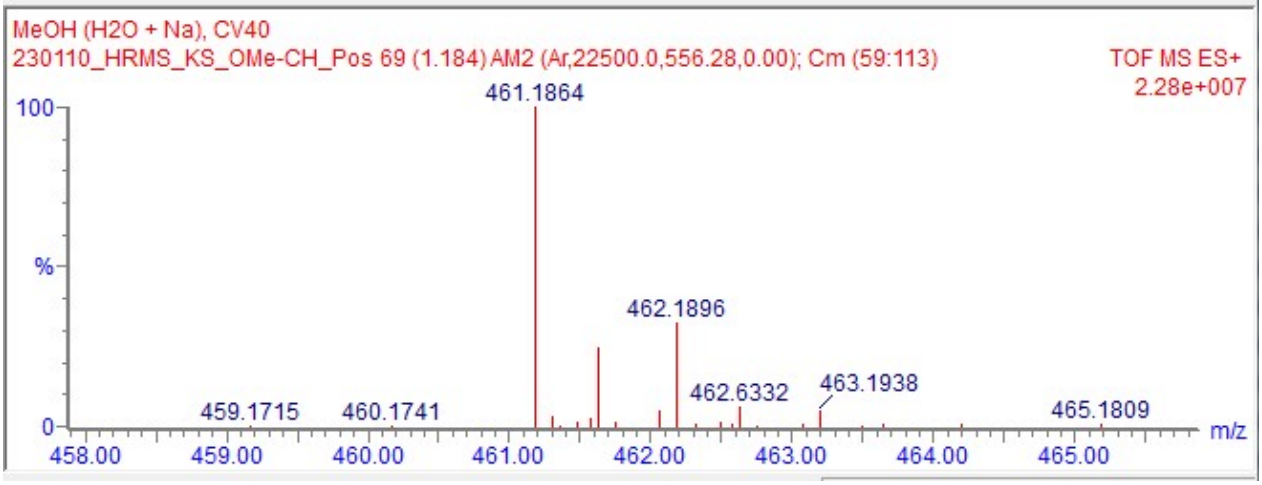
Monoisotopic Mass, Even Electron Ions

89 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 1-30 H: 1-30 N: 1-4 O: 1-6 Na: 0-1

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i..	i...	Fit Conf %	C	H	N	O	Na
461.1864	461.1865	-0.1	-0.2	19.5	C30 H25 N2 O3	3...	n...	n/a	30	25	2	3	



XRD

3aa

Bond precision: C-C = 0.0067 A Wavelength=0.71073

Cell: a=7.0317(4) b=18.8318(12) c=8.3435(6)
alpha=90 beta=99.423(2) gamma=90
Temperature: 296 K

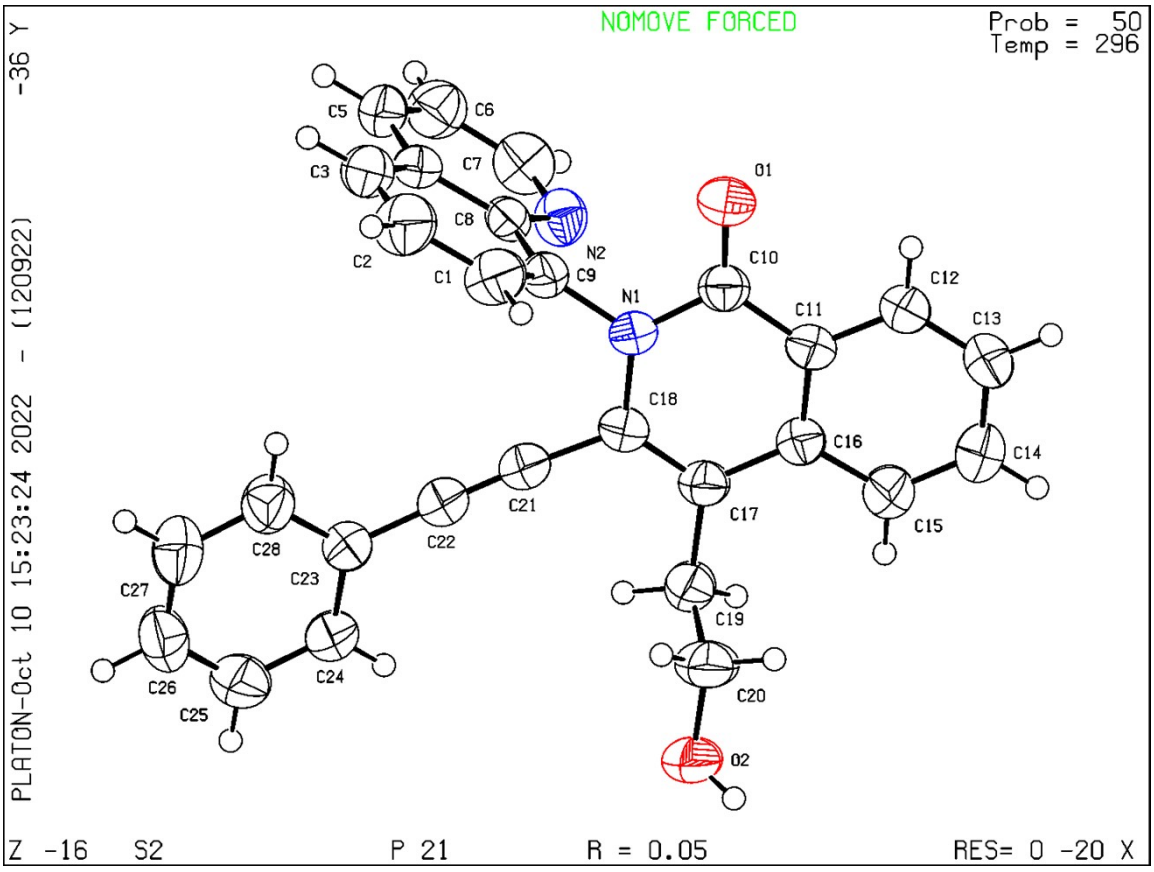
	Calculated	Reported
Volume	1089.94(12)	1089.93(12)
Space group	P 21	P 21
Hall group	P 2yb	P 2yb
Moiety formula	C28 H20 N2 O2	C28 H20 N2 O2
Sum formula	C28 H20 N2 O2	C28 H20 N2 O2
Mr	416.46	416.46
Dx,g cm-3	1.269	1.269
Z	2	2
Mu (mm-1)	0.080	0.080
F000	436.0	436.0
F000'	436.18	
h,k,lmax	9,24,10	9,24,10
Nref	4781[2464]	4777
Tmin,Tmax	0.981,0.988	0.704,
Tmin'	0.980	

Correction method= # Reported T Limits: Tmin=0.704 Tmax=*****
AbsCorr = MULTI-SCAN

Data completeness= 1.94/1.00 Theta(max)= 27.071

R(reflections)= 0.0510(2644) wR^2(reflections)= 0.1502(4777)

S = 0.968 Npar= 290



3da

Bond precision: C-C = 0.0076 A Wavelength=0.71073

Cell:	a=18.7888(12)	b=10.0222(4)	c=12.1293(8)
	alpha=90	beta=90	gamma=90
Temperature:	296 K		

	Calculated	Reported
Volume	2284.0(2)	2284.0(2)
Space group	P n a 21	P n a 21
Hall group	P 2c -2n	P 2c -2n
Moiety formula	C29 H22 N2 O3	C29 H22 N2 O3
Sum formula	C29 H22 N2 O3	C29 H22 N2 O3
Mr	446.49	446.48

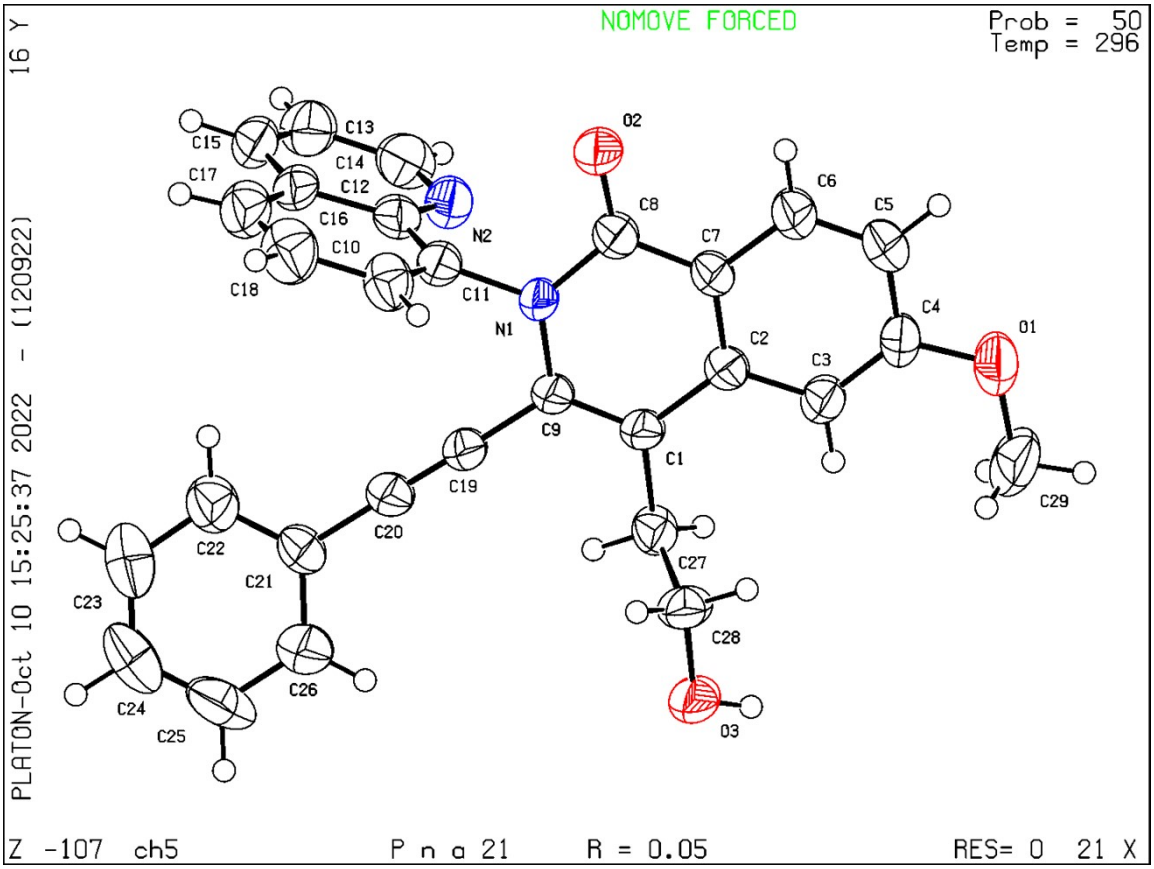
Dx,g cm-3	1.298	1.298
Z	4	4
Mu (mm-1)	0.085	0.085
F000	936.0	936.0
F000'	936.41	
h,k,lmax	22,11,14	22,11,14
Nref	4029[2119]	3300
Tmin,Tmax	0.979,0.992	0.979,0.992
Tmin'	0.979	

Correction method= # Reported T Limits: Tmin=0.979 Tmax=0.992
AbsCorr = MULTI-SCAN

Data completeness= 1.56/0.82 Theta(max)= 24.998

R(reflections)= 0.0541(2636) wR^2 (reflections)= 0.1438(3300)

S = 1.033 Npar= 309



3ga

Bond precision: C-C = 0.0037 A Wavelength=0.71073

Cell:	a=11.3549(3)	b=10.5712(4)	c=18.7259(6)
	alpha=90	beta=93.0039(14)	gamma=90
Temperature:	296 K		

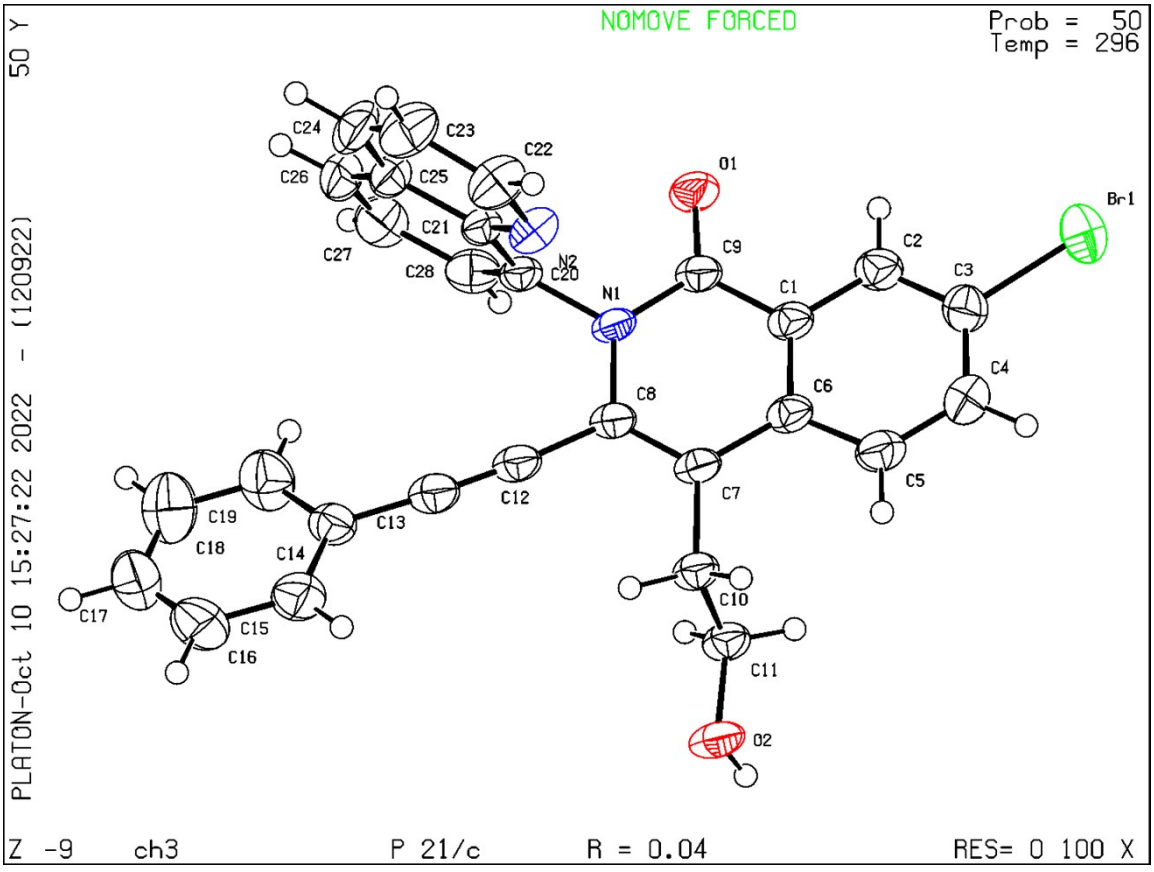
	Calculated	Reported
Volume	2244.67(13)	2244.67(13)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C28 H19 Br N2 O2	C28 H19 Br N2 O2
Sum formula	C28 H19 Br N2 O2	C28 H19 Br N2 O2
Mr	495.35	495.36
Dx,g cm-3	1.466	1.466
Z	4	4
Mu (mm-1)	1.860	1.860
F000	1008.0	1008.0
F000'	1007.22	
h,k,lmax	13,12,22	13,12,22
Nref	3966	3966
Tmin,Tmax	0.578,0.743	
Tmin'	0.567	

Correction method= Not given

Data completeness= 1.000 Theta(max)= 24.999

R(reflections)= 0.0350(3207) wR^2(reflections)= 0.0879(3966)

S = 1.026 Npar= 302



4ab

Bond precision: C-C = 0.0049 A Wavelength=0.71073

Cell: a=9.1585(3) b=10.7347(4) c=11.6344(5)
alpha=93.7241(17) beta=98.7149(18) gamma=99.1029(17)
Temperature: 296 K

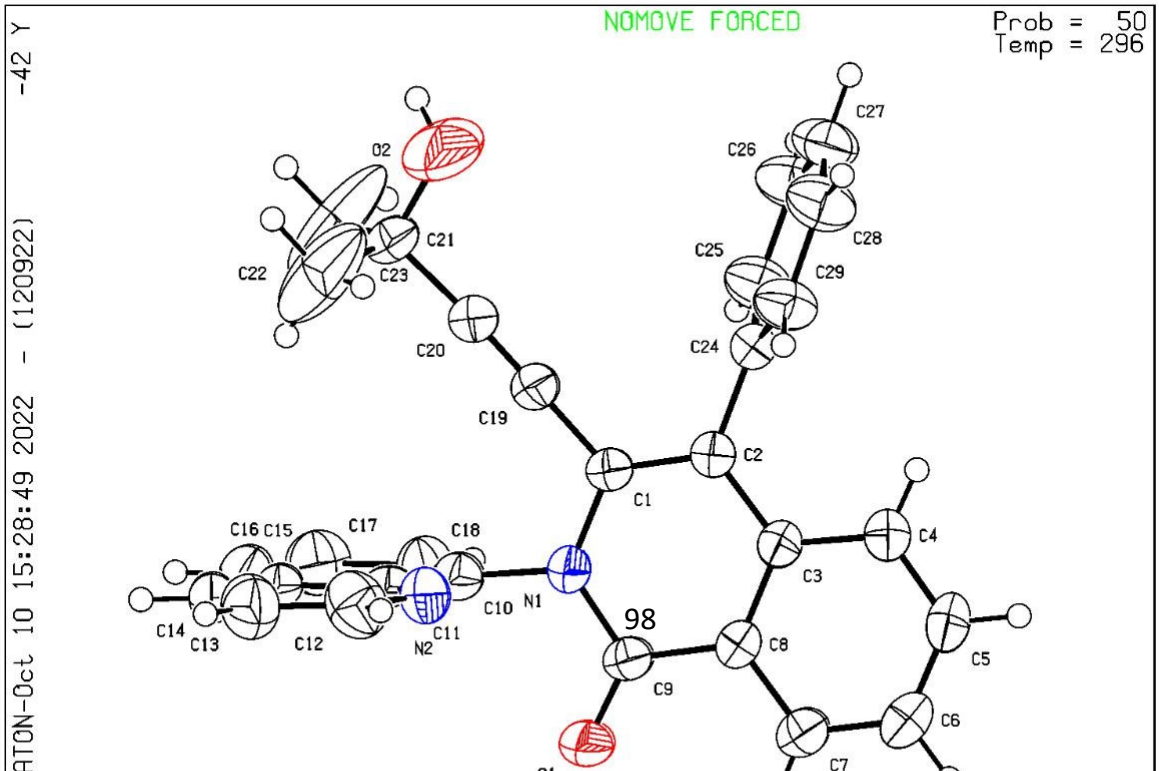
	Calculated	Reported
Volume	1111.73(7)	1111.73(7)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C29 H22 N2 O2	C29 H22 N2 O2
Sum formula	C29 H22 N2 O2	C29 H22 N2 O2
Mr	430.49	430.48
Dx,g cm-3	1.286	1.286
Z	2	2
Mu (mm-1)	0.081	0.081
F000	452.0	452.0
F000'	452.19	
h,k,lmax	10,12,13	10,12,13
Nref	3909	3903
Tmin,Tmax	0.980,0.987	0.980,0.987
Tmin'	0.980	

Correction method= # Reported T Limits: Tmin=0.980
Tmax=0.987 AbsCorr = MULTI-SCAN

Data completeness= 0.998 Theta(max)= 24.998

R(reflections)= 0.0654(2286) wR2(reflections)= 0.2109(3903)

S = 1.057 Npar= 302



4db

Bond precision: C-C = 0.0033 A Wavelength=0.71073

Cell:	a=12.6907(7)	b=16.3431(9)	c=13.3615(9)
	alpha=90	beta=118.292(2)	gamma=90
Temperature:	296 K		

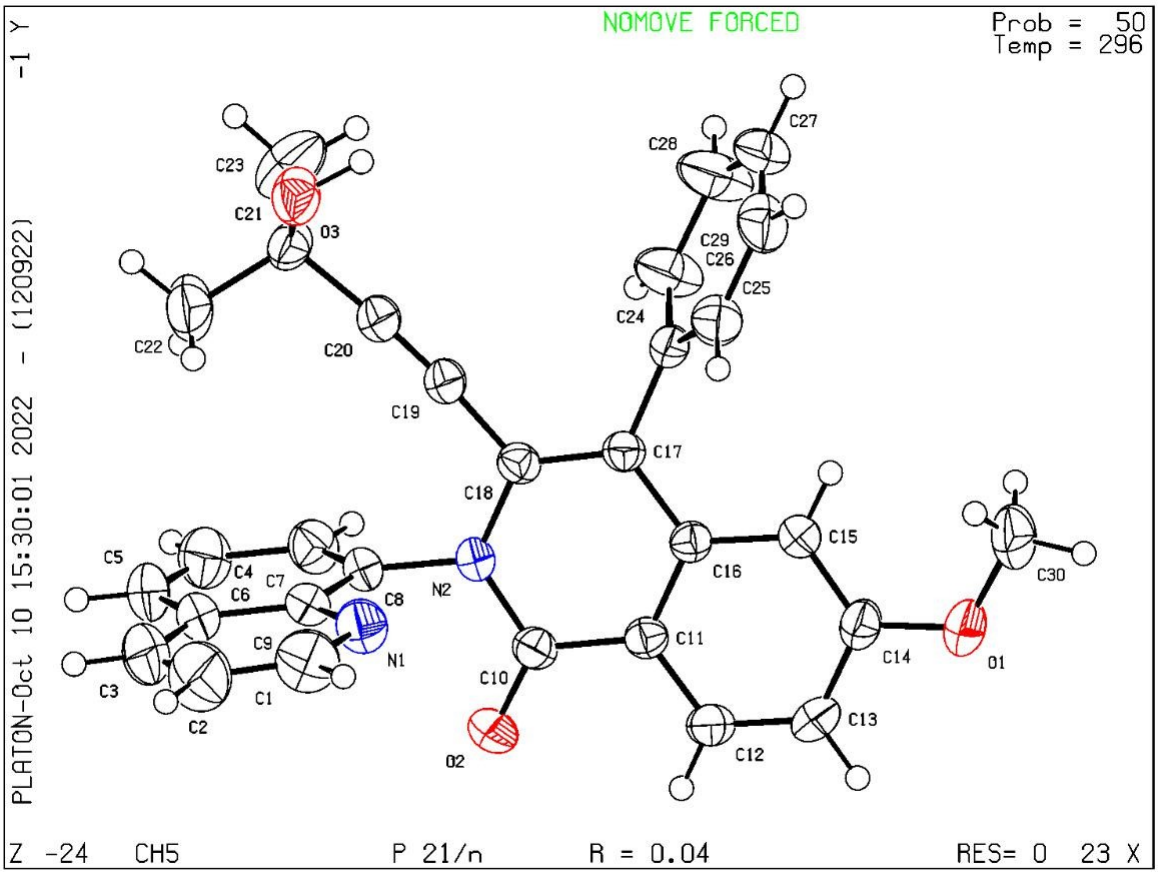
	Calculated	Reported
Volume	2440.2(3)	2440.2(3)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C30 H24 N2 O3	C30 H24 N2 O3
Sum formula	C30 H24 N2 O3	C30 H24 N2 O3
Mr	460.51	460.51
Dx,g cm-3	1.253	1.253
Z	4	4
Mu (mm-1)	0.081	0.081
F000	968.0	968.0
F000’	968.42	
h,k,lmax	15,19,16	15,19,16
Nref	4403	4393
Tmin,Tmax	0.992,0.996	0.686,0.745
Tmin’	0.992	

Correction method= # Reported T Limits: Tmin=0.686
Tmax=0.745 AbsCorr = MULTI-SCAN

Data completeness= 0.998 Theta(max)= 25.233

R(reflections)=
0.0441(2922) wR^2(reflections)=
0.1210(4393)

S = 1.006 Npar= 323



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