Supplementary Information

Expedient Synthesis of highly Substituted 3,4-Dihydro-1,2-oxathiine 2,2-dioxides and 1,2-Oxathiine 2,2-dioxides: Revisiting sulfene additions to enaminoketones

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Equipment and materials

Unless otherwise stated, reagents and solvents were purchased from major chemical catalogue companies and were used as supplied. Routine ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Avance DPX400 instrument in $CDCl_3$. Variable Temperature ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Bruker Avance I 500MHz NMR instrument in $CDCl_3$. Chemical shifts are provided in parts per million (ppm) using either the residual solvent peak or TMS as the internal reference. Coupling constants (*J*) are provided in Hz and where applicable, in order to resolve close signals and extract valuable coupling information, the raw FID data was processed using a Gaussian multiplication in place of the more usual exponential multiplication. All FT-IR spectra were recorded on a Nicolet 380 FTIR spectrophotometer equipped with a diamond ATR attachment (neat sample). Flash column chromatography was performed on chromatography silica gel (Fluorochem, 40-63 micron particle size distribution). All final compounds were homogeneous by TLC using a range of eluent systems of differing polarity (Merck TLC aluminium sheets silica gel 60 F254 (cat. No 105554)). High resolution mass spectra were recorded on an Agilent 6210 1200 SL TOF spectrometer within the IPOS centre at the University of Huddersfield. Single crystal X-ray diffraction data was collected on a Bruker Venture diffractometer equipped with a graphite monochromated Cu(Kα) radiation source and a cold stream of N_2 gas.

The following enamino-carbonyl compounds [(*E*)-3-(dimethylamino)-1,2-diphenylprop-2-en-1-one[1], (*E*)-3-(dimethylamino)-1,2-bis(4-methoxyphenyl)prop-2-en-1-one[2], (*E*)-3-(dimethylamino)-1-(4-methoxyphenyl)prop-2-en-1-one[3], (*E*)-3-(dimethylamino)-1-(2-nitrophenyl)prop-2-en-1-one[4], (*E*)-3-(dimethylamino)-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one[5], 2-((dimethylamino)methylene)-1,3-diphenylpropane-1,3-dione[6], ethyl 2-benzoyl-3-(dimethylamino)acrylate[7], 1-((dimethylamino)methylene)-3,4-dihydronaphthalen-2(1*H*)-one[8], 3-(dimethylamino)-2-phenylacrylaldehyde[9], (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one[10]] and (*E*)-*N*-((dimethylamino)methylene)-4-methylbenzamide[11] were obtained by refluxing the requisite α-methylene carbonyl compound in neat *N*,*N*-dimethylformamide dimethylacetal (DMFDMA) (2.5 equivalents) until TLC examination of the reaction mixture indicated that no starting α-methylene carbonyl compound remained. (*Z*)-3-(Hydroxymethylene)-2,2-dimethylchroman-4-one[12] and (*Z*)-3-(hydroxymethylene)-2,2,6-trimethylthiochroman-4-one[13] and isothiochromanone[14] were prepared according to previously reported procedures. 4-(Dimethylamino)-3-(2-fluorophenyl)but-3-en-2-one was prepared according to the procedure described by Kozmin *et al*., for the preparation of 4-(dimethylamino)-3-phenylbut-3-en-2-one.[15] (*E*)-4-(Dimethylamino)-1,3-diphenylbut-3-en-2-one[16] was prepared by heating 1,3-diphenylacetone in toluene containing DMFDMA. 3-(Dimethylamino)-1-(4-pyridyl)-2-propen-1-one was obtained by heating 4-acetylpyridine in DMFDMA containing 10 mol% L-proline.[10]

References to reactants

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Sartin, M. B. Coppock, K. E. Krumpe, B. S. Burnham, H. Holt, K. X. Du, K. M. Keertikar, A. Diebes, S. Ghassemi, J. A. Sikorski, *Tetrahedron*, **2006**, *62*, 8243-8255.

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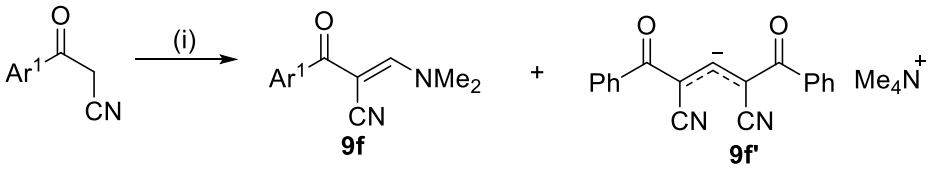
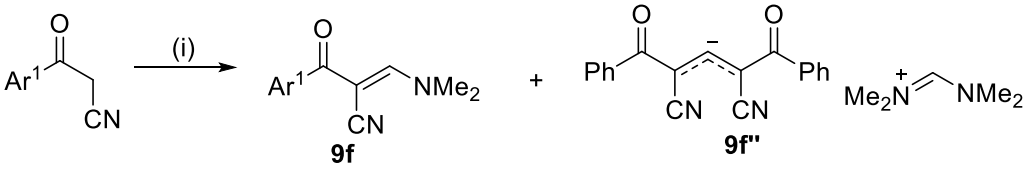
Observations on the Synthesis of Enaminoketones

All of the enaminoketones **9** were present as single geometrical isomers as indicated by ^{1}H NMR spectroscopy, NOESY experiments and in the case of **9f** by X-ray crystallography (CCDC 1913658), (ESI Figure 1). Of note was the influence of the reaction conditions on the outcome of the reaction of 3-oxo-3-phenylpropanenitrile (benzoylacetonitrile) with DMFDMA to afford **9f** (ESI Scheme 1).



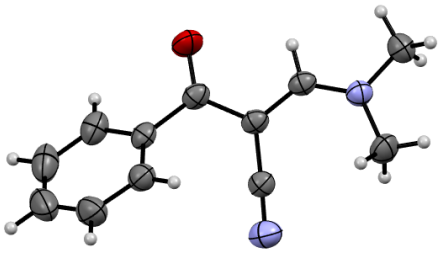
Reagents and conditions: (i) DMFDMA, reflux overnight



Reagents and conditions: (i) DMFDMA, PhMe, RT overnight

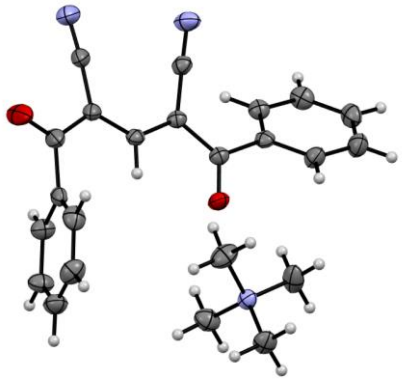
ESI Scheme 1: synthesis of enaminoketone **9f**

Whilst the synthesis of **9f** has been described in the literature using either neat DMFDMA at reflux[1] or using a solution of DMFDMA in PhMe at room temperature (rt),[2] in our hands the former approach gave a moderate yield of **9f** (57 %) accompanied by the novel, extensively delocalised carbanion as the tetramethylammonium salt **9f′** (14 %). The ^{1}H NMR spectrum (d_6-DMSO) of **9f′** displayed a singlet at δ 3.09 accounting for the equivalent 12H of the Me_4N^+ unit and a low field singlet at δ 8.02 assigned to 3-H. Whilst the ^{13}C NMR spectrum of **9f′** displayed a triplet at δ 54.4 (J = 4.0 Hz) as a consequence of $^{14}N^+$ coupling.[3] The structure of **9f′** was established by crystallography (CCDC 1913654), (ESI Figure 2). An improved yield of **9f** (85 %) was noted using DMFDMA in toluene at rt. However, the same delocalised carbanion was isolated, but under these milder conditions it was present with the *N*-((dimethylamino)methylene)-*N*-methylmethanaminium counterion, **9f′′** (3.5 %) as shown by crystallography (CCDC 1913653), (ESI Figure 3). The ^{1}H NMR spectrum of **9f′′** ($CDCl_3$) displayed a similar low field singlet for 3-H (δ 8.04) but an additional singlet was present at δ 8.16 assigned to the central proton of the counterion.

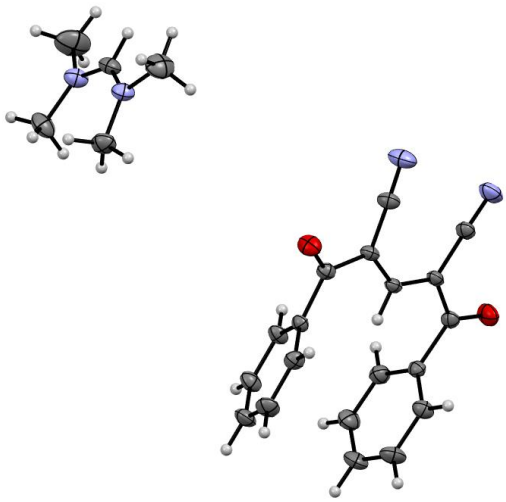


ESI Figure 1: Crystal structure of **9f** (thermal ellipsoids shown at 50 % probability level)

The X-ray data for **9f** and that of the by-products (**9f′**, **9f′′**) merits some comment. The C=O bond length is ca. 1.23 Å for the series which indicates that the carbonyl functions in **9f′**, **9f′′** do not play an appreciable role in delocalisation of the -ve charge. The C-2 – C-3 and C-3 – C-4 bondlengths, 1.38 – 1.40 Å, are similar in **9f′**, **9f′′** and compare favourably with the C-2 – C-3 double bond length of 1.39 Å of **9f** and indicate that the -ve charge is delocalised between the two nitrile substituents. The C-NMe_2 bondlengths in the *N*-((dimethylamino)methylene)-*N*-methylmethanaminium cation are 1.317 Å and 1.311 Å indicating delocalisation of the +ve charge over the N-C-N unit. The ^{1}H NMR spectrum of the foregoing cation displayed two signals for the NMe groups (δ 3.29 and δ 3.32 ($CDCl_3$)) which is in agreement with the bent structure; $^{<}$NCN = 131 $^{\circ}$.



ESI Figure 2: Crystal structure of **9f′** (thermal ellipsoids shown at 50 % probability level)



ESI Figure 3: Crystal structure of **9f″** (thermal ellipsoids shown at 50 % probability level)

References to Observations on the Synthesis of Enaminoketones

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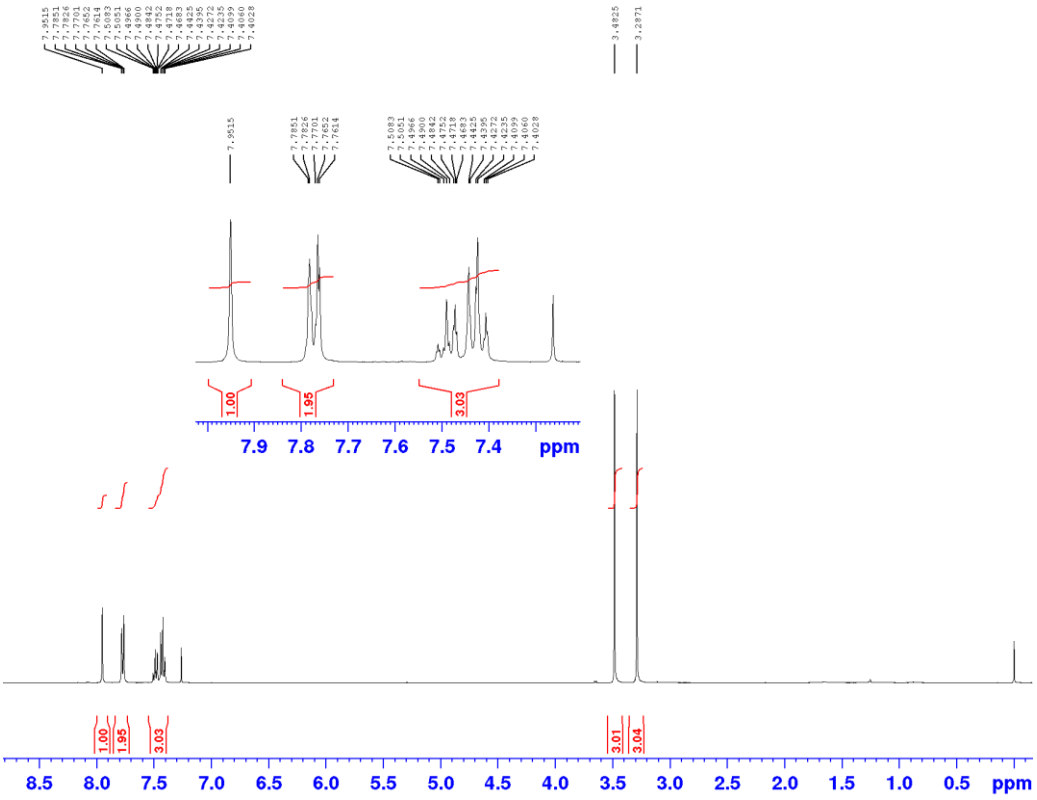
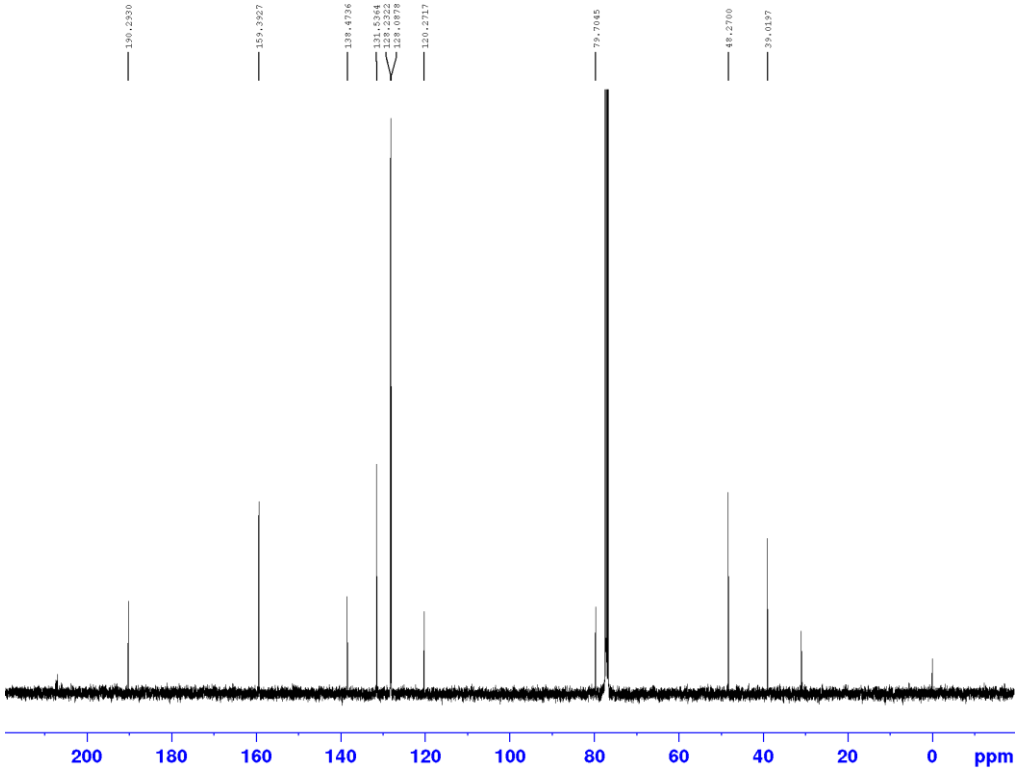
^{1}H NMR, ^{13}C NMR and mass spectra for novel compounds.

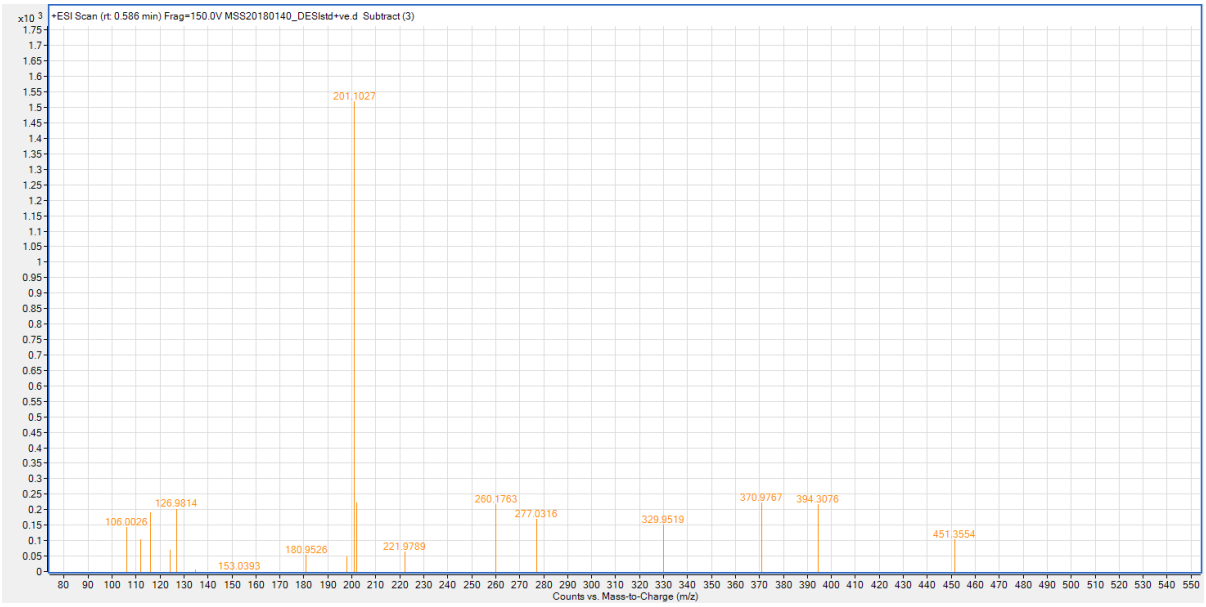
Compound 9f ^{1}H NMR $CDCl_3$



Compound 9f ^{13}C NMR $CDCl_3$

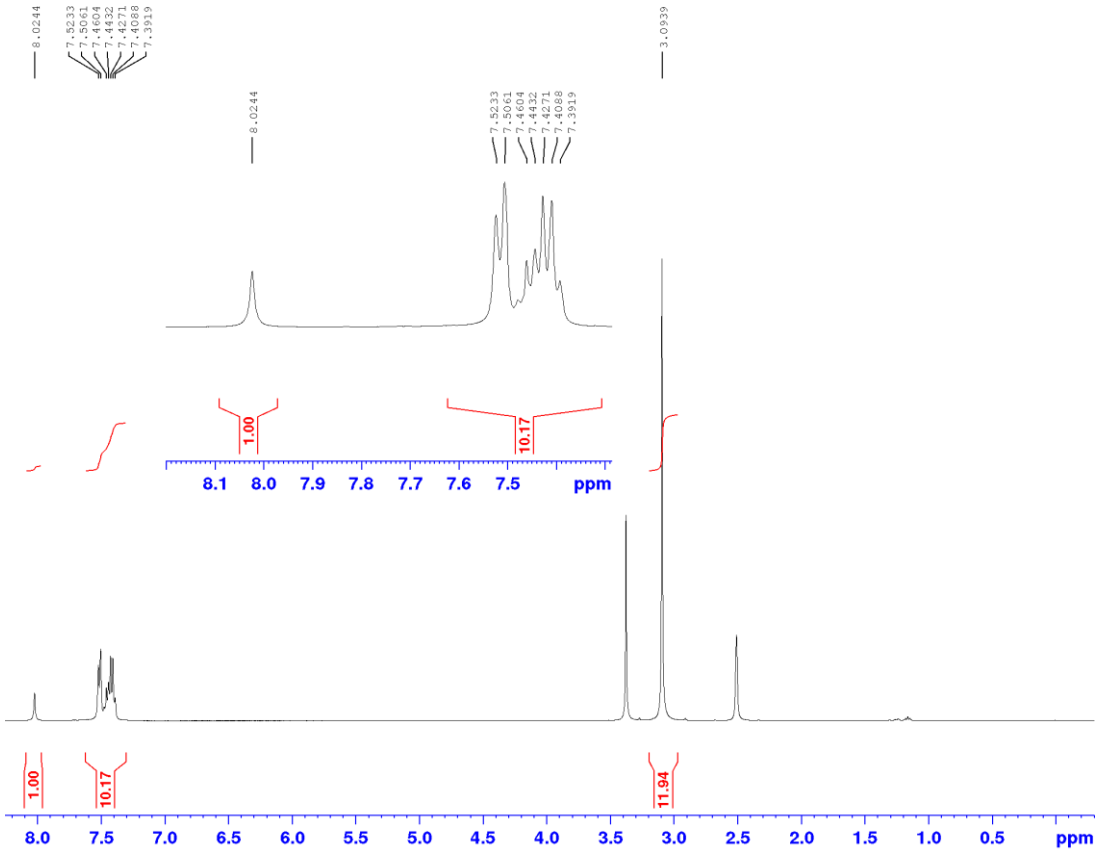


Compound 9f MS

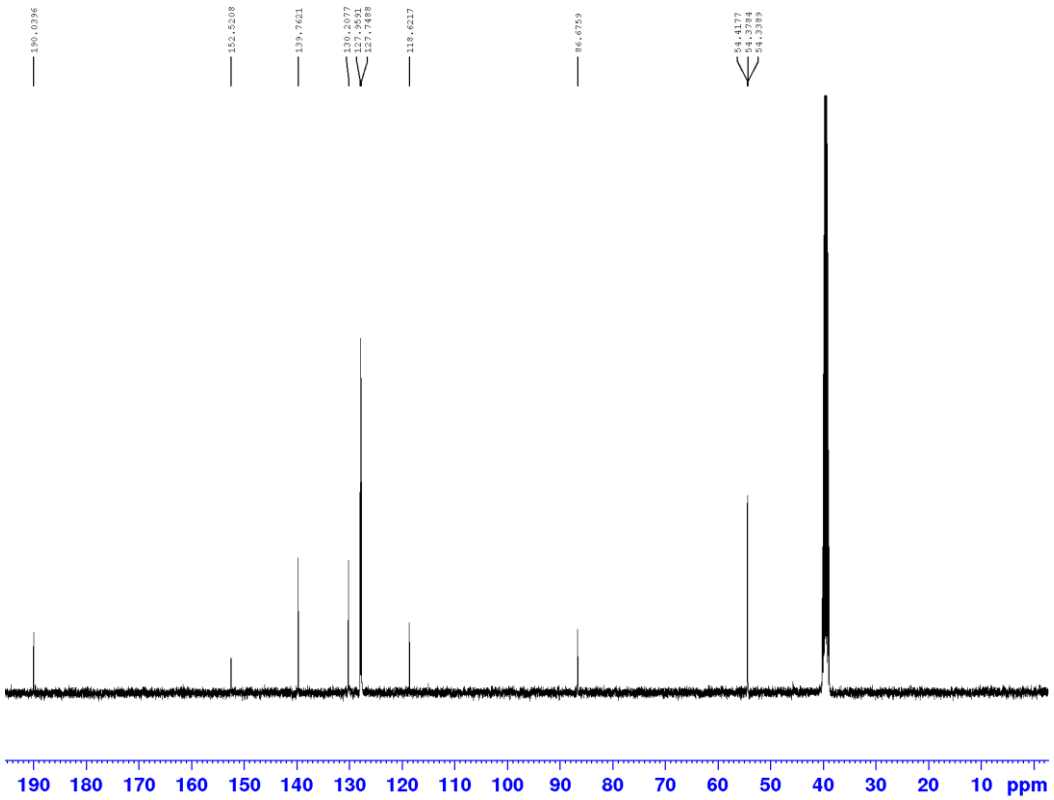


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C12 H12 N2 O	(M+H)+	201.1027	200.0958	200.095	75.14	-4.33
C10 H10 N5	(M+H)+	201.1027	200.0959	200.0936	57.94	-11.41
C9 H14 N O4	(M+H)+	201.1027	200.0958	200.0923	39.4	-17.64

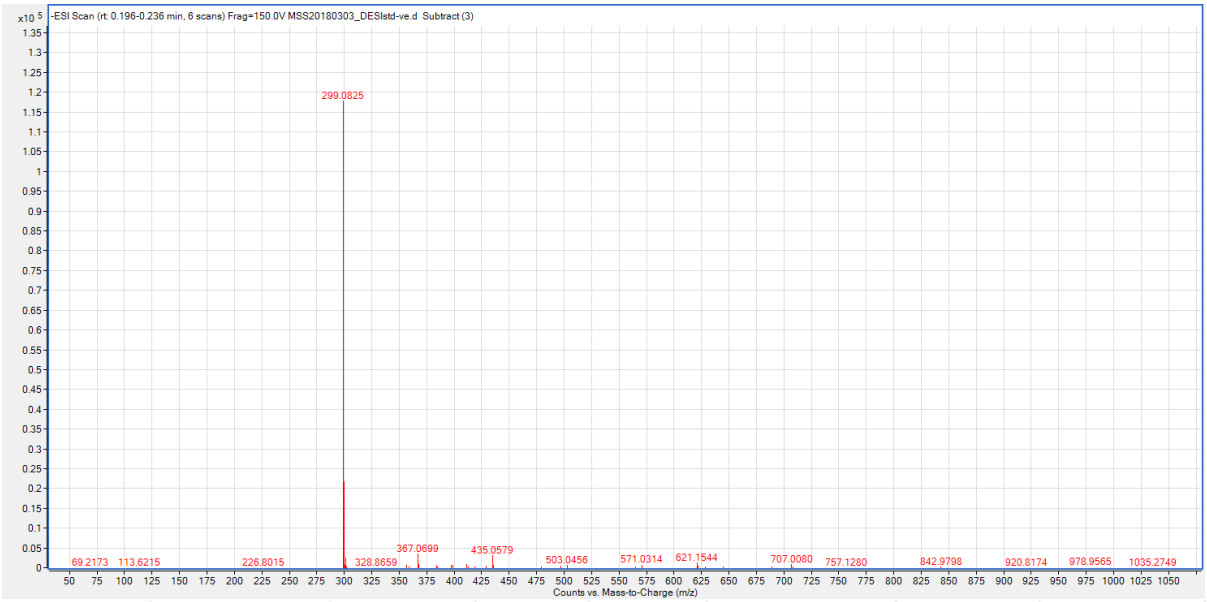
Compound 9f' ^{1}H NMR d$_6$-DMSO



Compound 9f' ^{13}C NMR d$_6$-DMSO

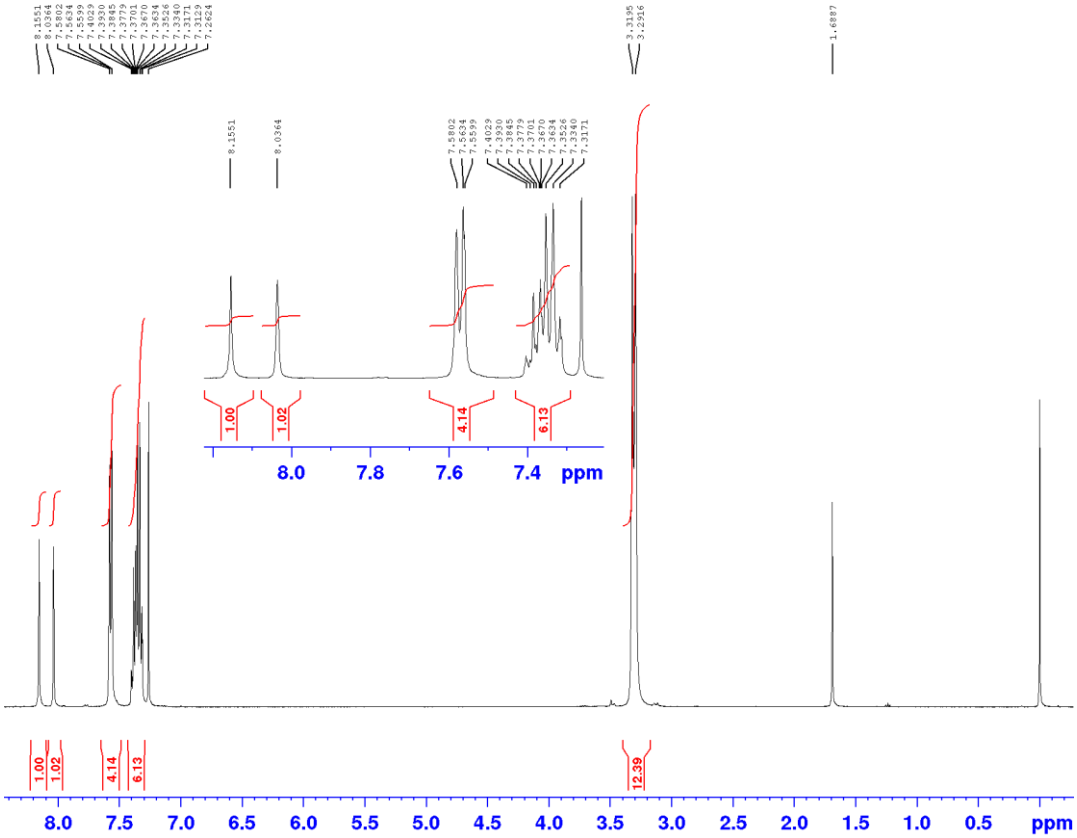


Compound 9f' MS

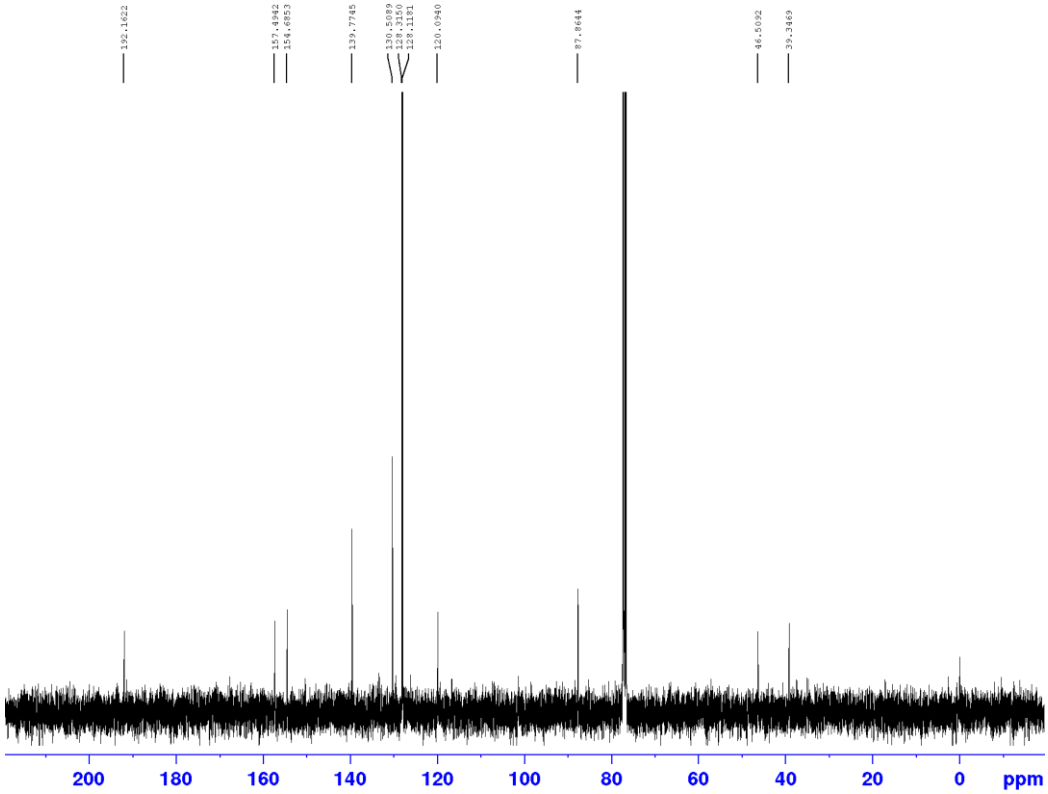


Best	Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
◉	C19 H11 N2 O2	M-	299.0825	299.082	299.0821	98.07	0.33
○	C19 H12 N2 O2	(M-H)-	299.0825	300.0898	300.0899	98.07	0.33
○	C17 H9 N5 O	M-	299.0825	299.082	299.0807	93.35	-4.37
○	C17 H10 N5 O	(M-H)-	299.0825	300.0898	300.0885	93.35	-4.36
○	C16 H13 N O5	M-	299.0825	299.0819	299.0794	81.35	-8.6
○	C16 H14 N O5	(M-H)-	299.0825	300.0898	300.0872	81.35	-8.57

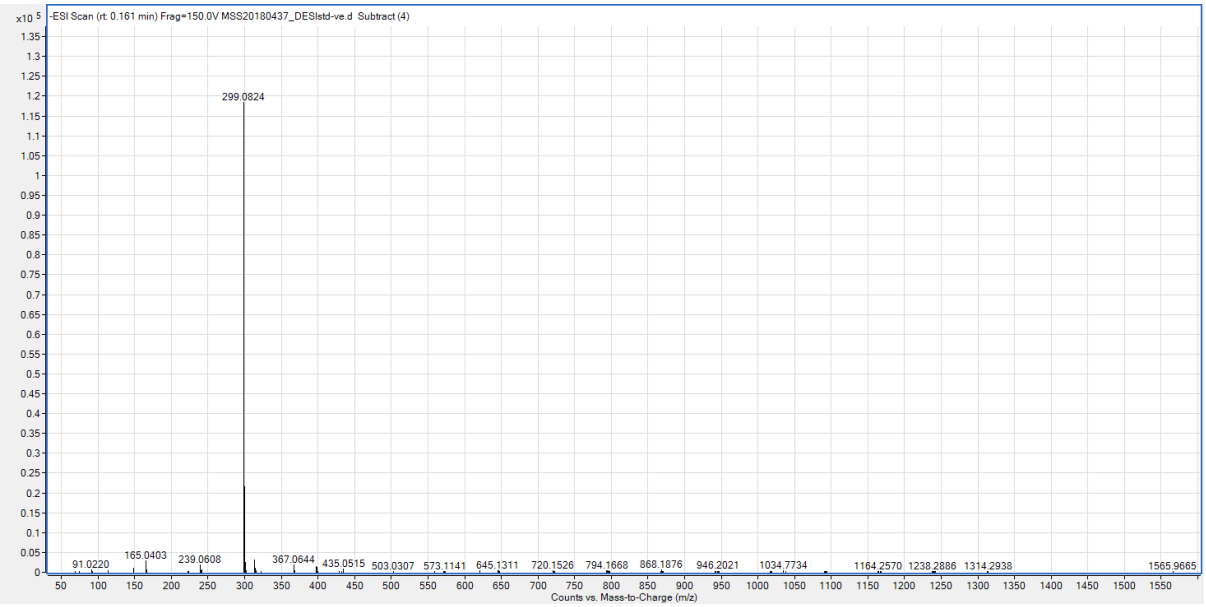
Compound 9f'' ^{1}H NMR $CDCl_3$



Compound 9f'' ^{13}C NMR $CDCl_3$

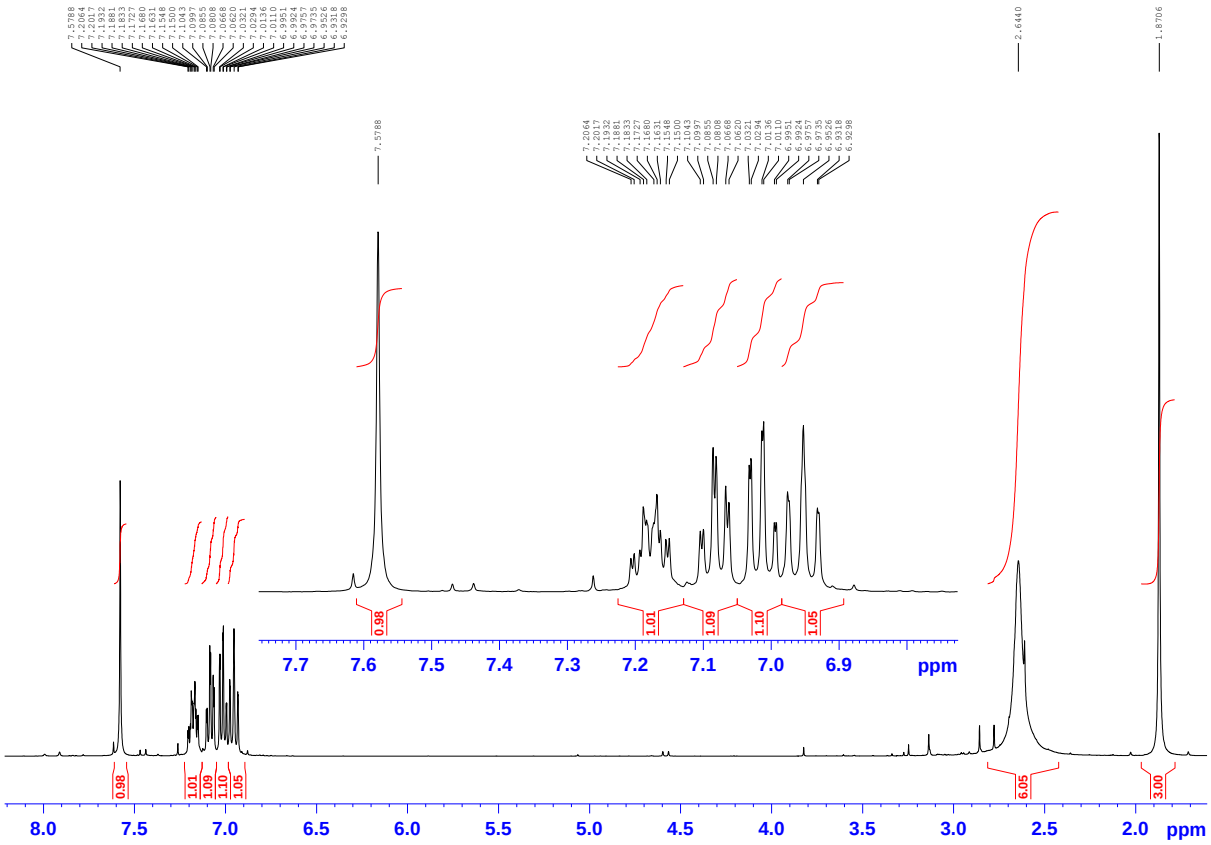


Compound 9f'' MS

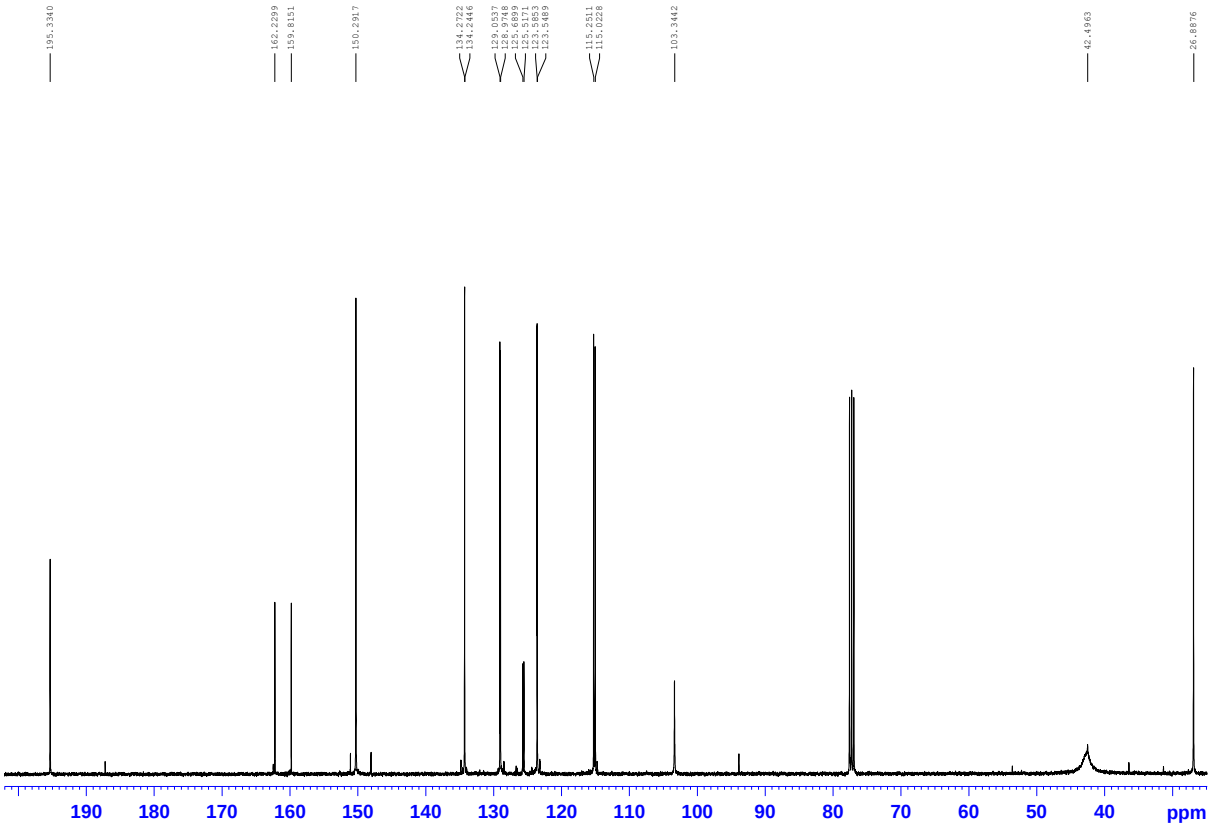


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C19 H11 N2 O2	M-	299.0824	299.0819	299.0821	97.45	0.36
C19 H12 N2 O2	(M-H)-	299.0824	300.0898	300.0899	97.45	0.36
C17 H9 N5 O	M-	299.0824	299.082	299.0807	92.54	-4.34
C17 H10 N5 O	(M-H)-	299.0824	300.0898	300.0885	92.54	-4.32
C16 H13 N O5	M-	299.0824	299.0819	299.0794	81.35	-8.57
C16 H14 N O5	(M-H)-	299.0824	300.0898	300.0872	81.35	-8.54

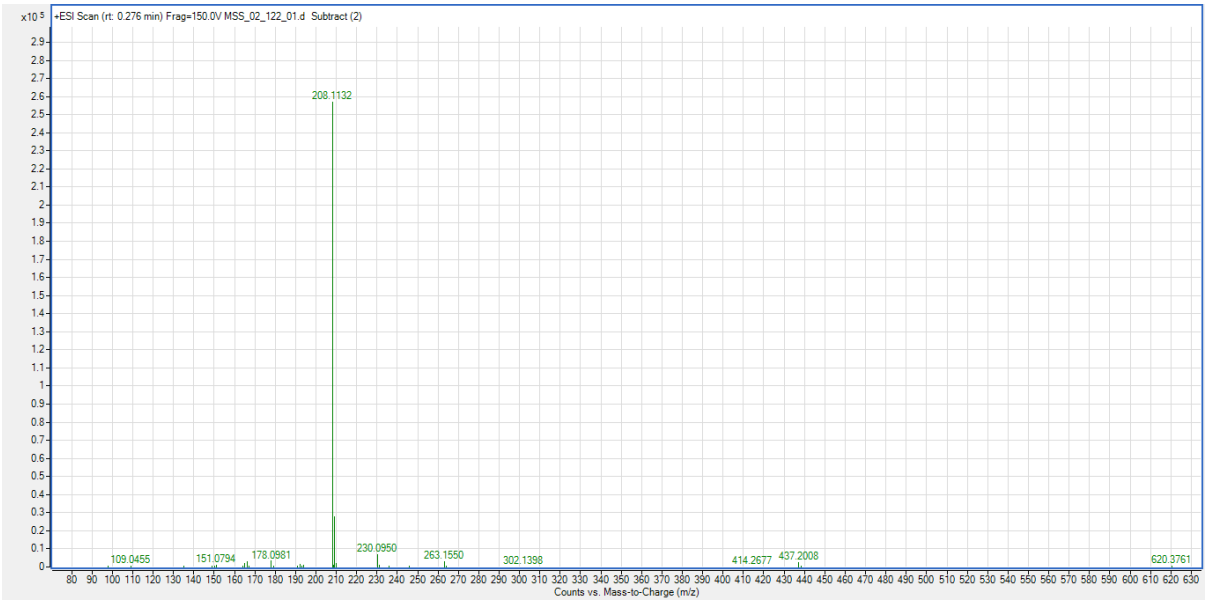
Compound 15 (crude – used directly) ^{1}H NMR $CDCl_3$



Compound 15 (crude – used directly) ^{13}C NMR $CDCl_3$

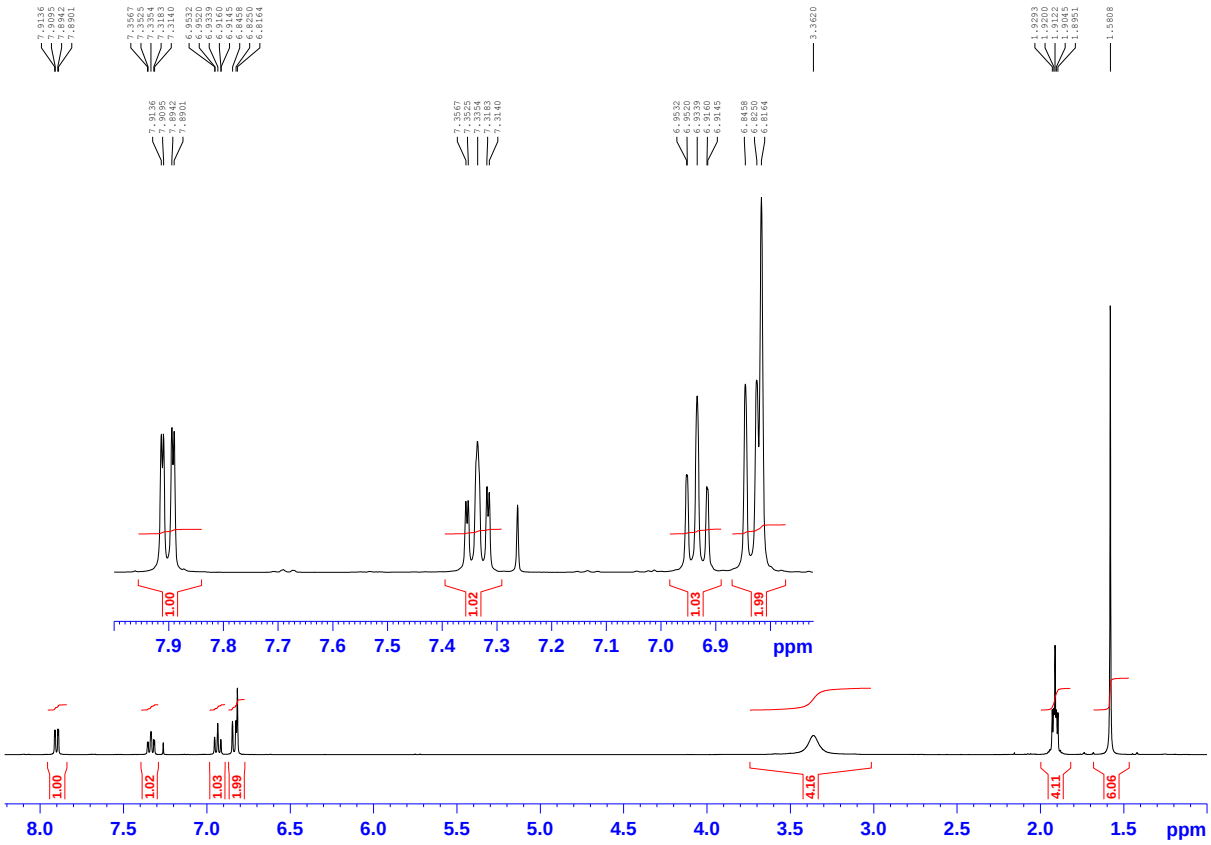


Compound 15 (crude – used directly in next step) MS

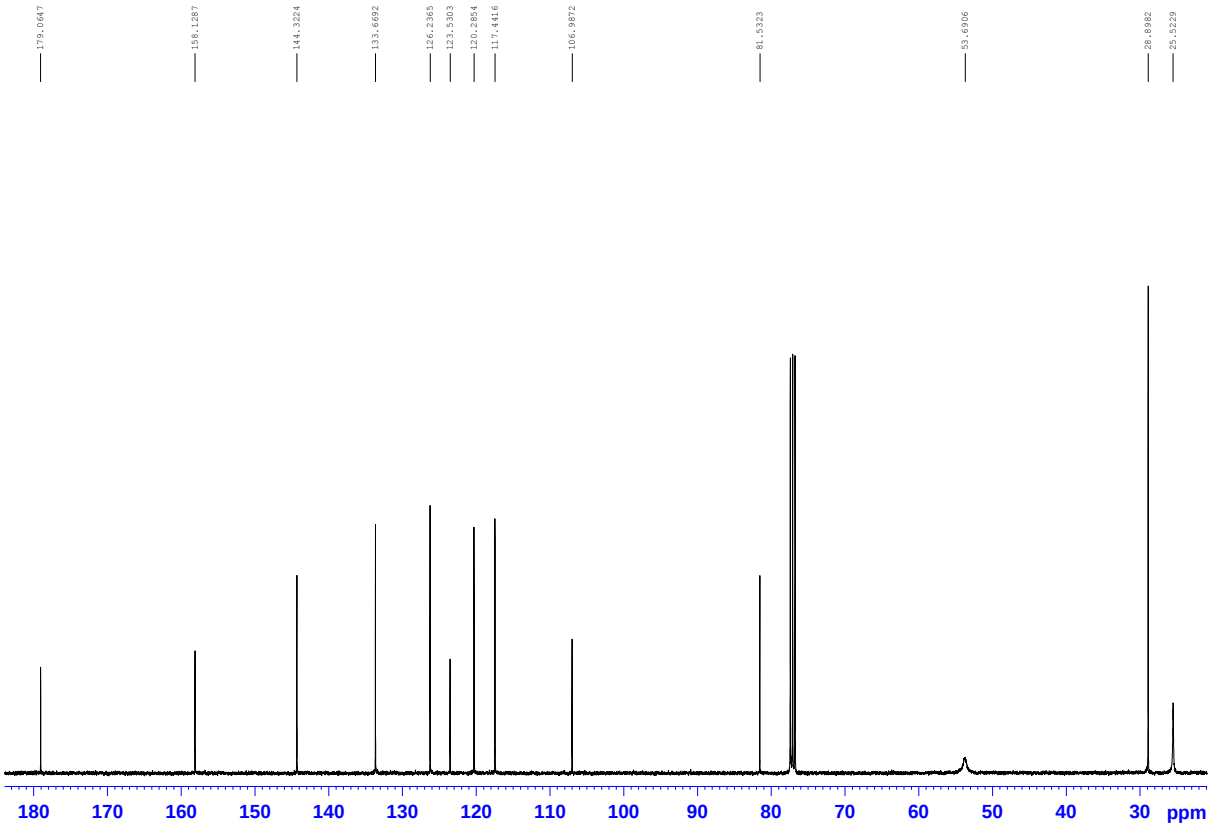


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C12 H14 F N O	(M+H)+	208.1132	207.1059	207.1059	85.02	0.32
C12 H11 F O	(M+NH4)+	208.1132	190.0793	190.0794	85.02	0.35
C9 H15 F2 N O2	(M+H)+	208.1132	207.1059	207.1071	80.69	5.83
C9 H12 F2 O2	(M+NH4)+	208.1132	190.0793	190.0805	80.69	6.35

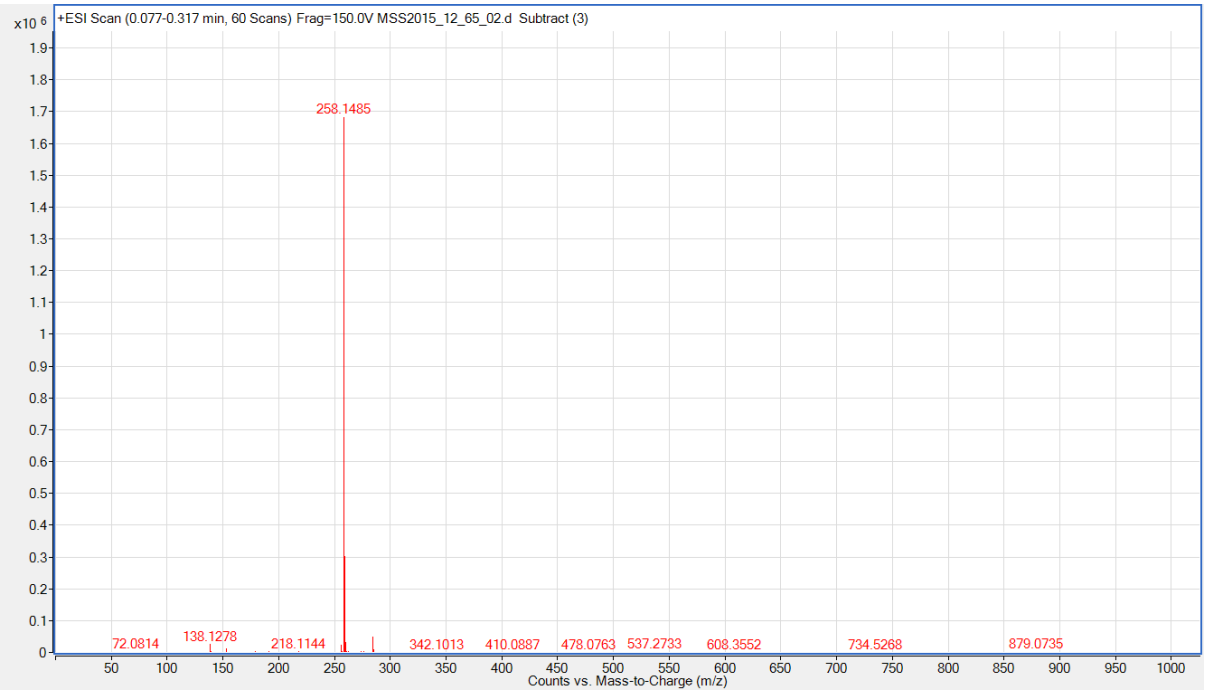
Compound 26 ^{1}H NMR $CDCl_3$



Compound 26 ^{13}C NMR $CDCl_3$

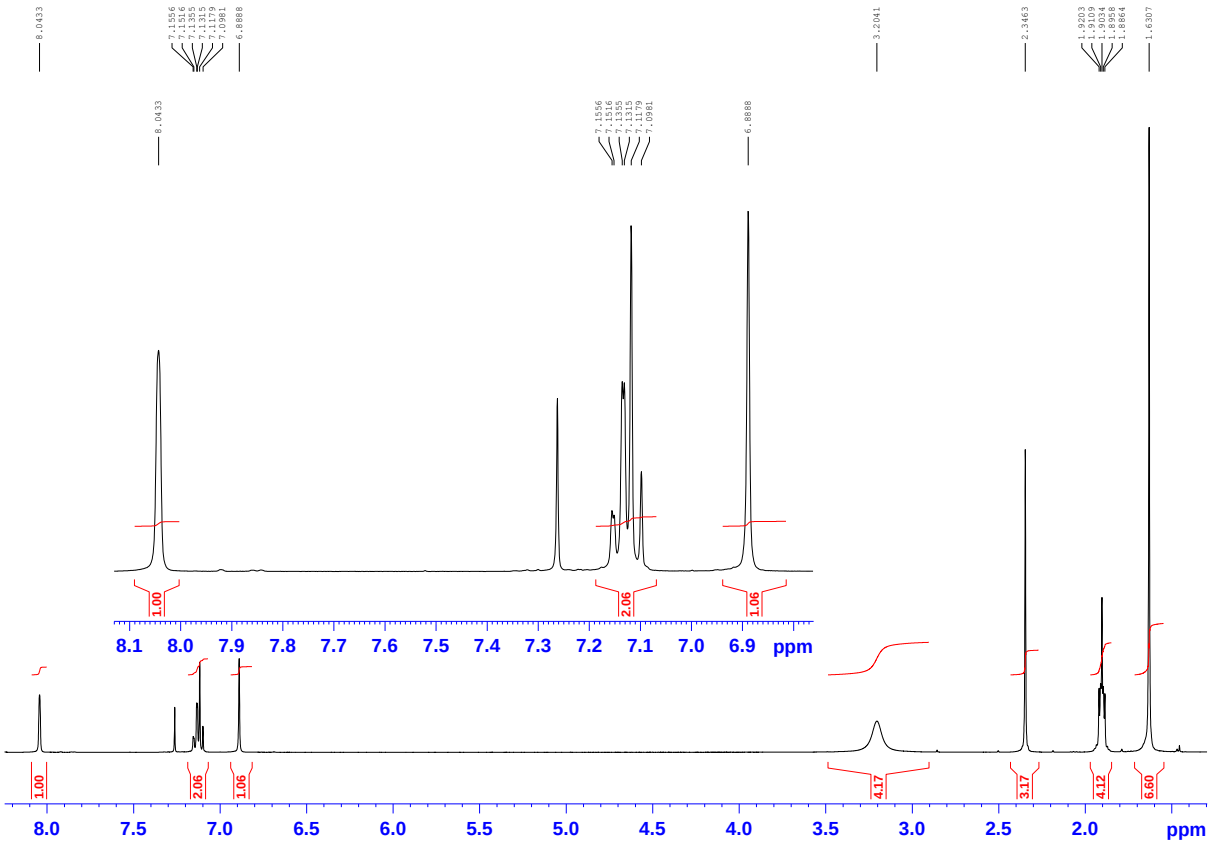


Compound 26 MS

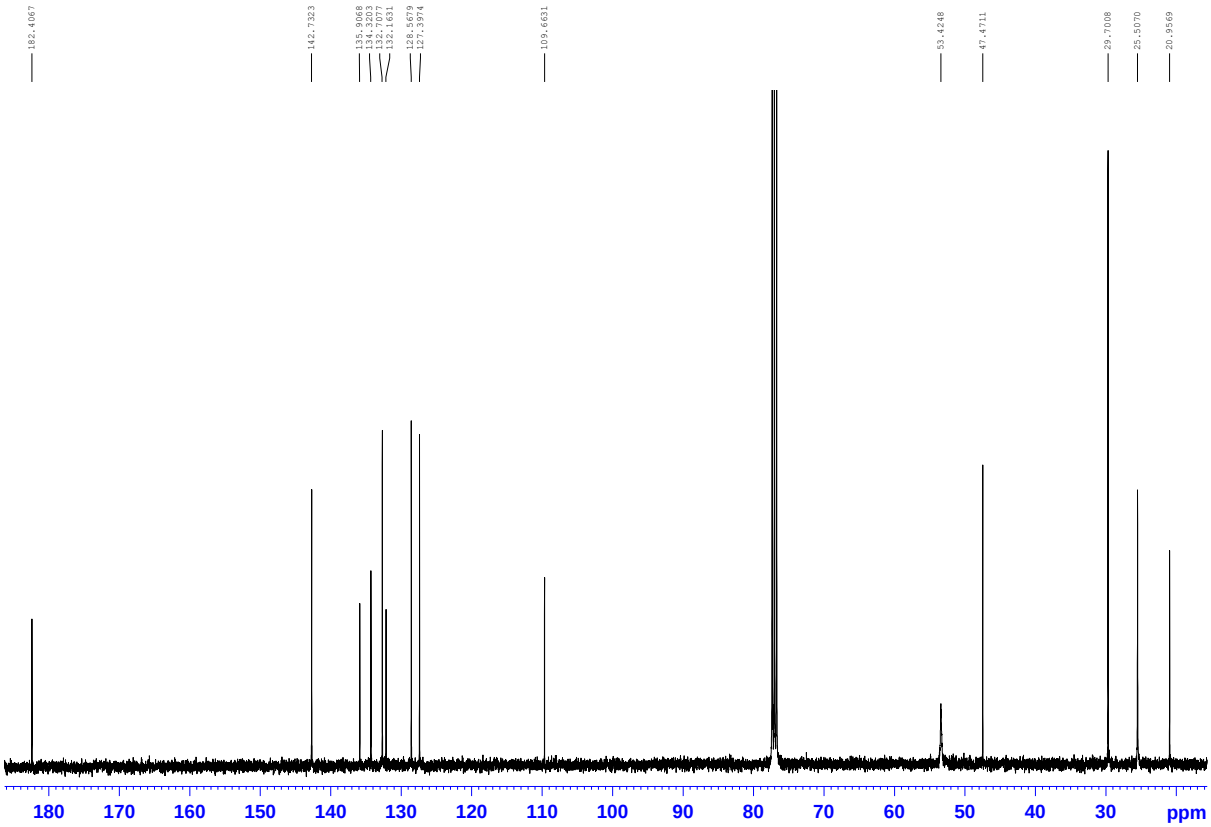


Best	Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
●	C16 H19 N O2	(M+H)+	258.1485	257.1413	257.1416	99.39	1.07
○	C16 H16 O2	(M+NH4)+	258.1485	240.1148	240.115	99.39	1.14
○	C14 H23 N2	(M+K)+	258.1485	219.1856	219.1861	84.55	2.58

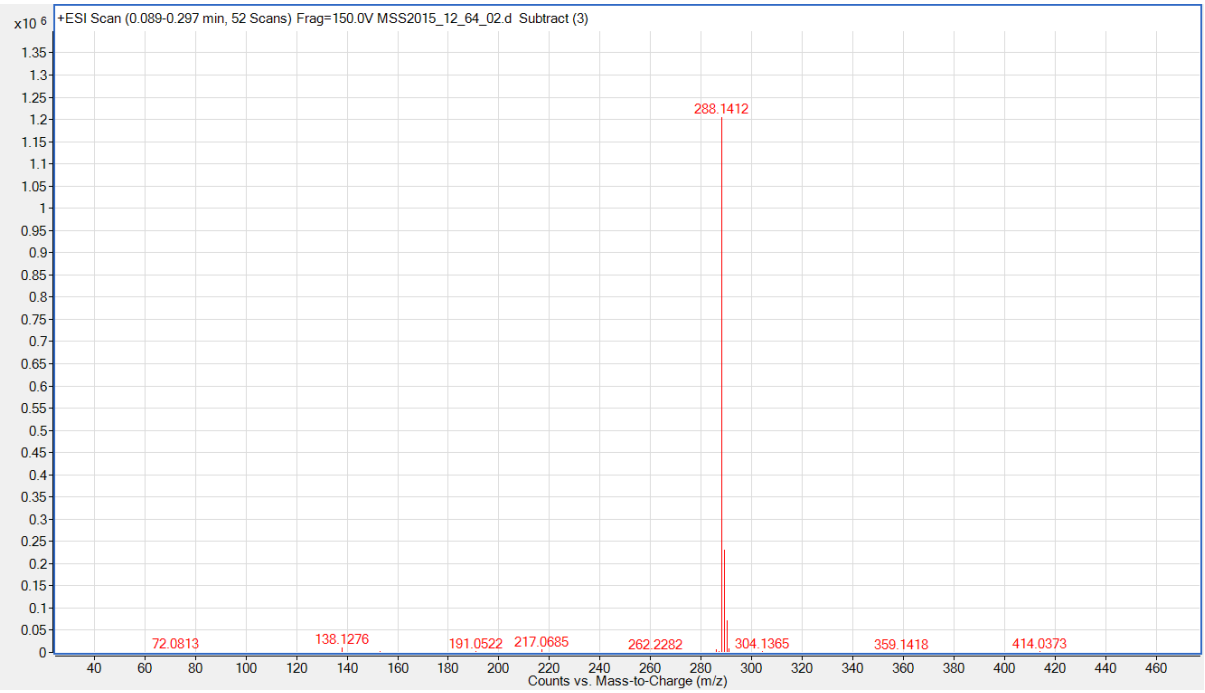
Compound 27 ^{1}H NMR $CDCl_3$



Compound 27 ^{13}C NMR $CDCl_3$

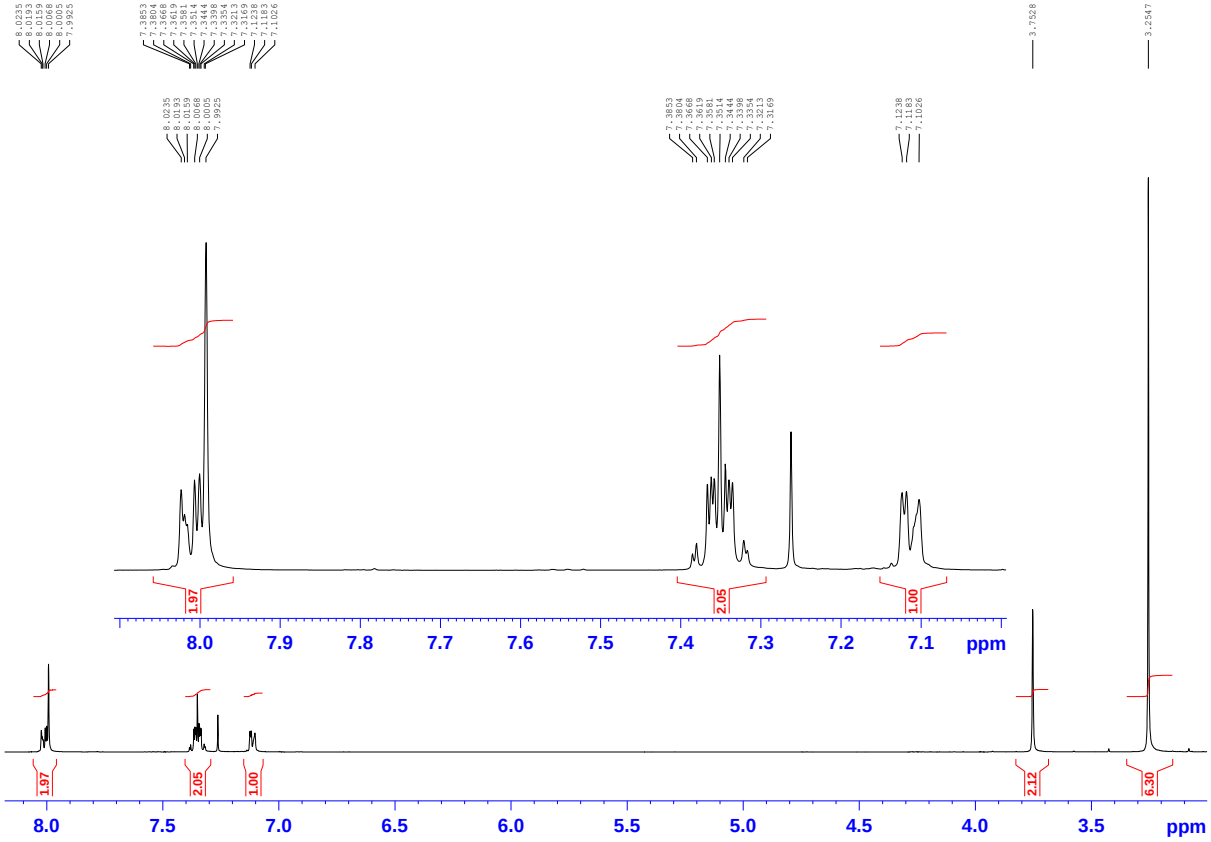


Compound 27 MS

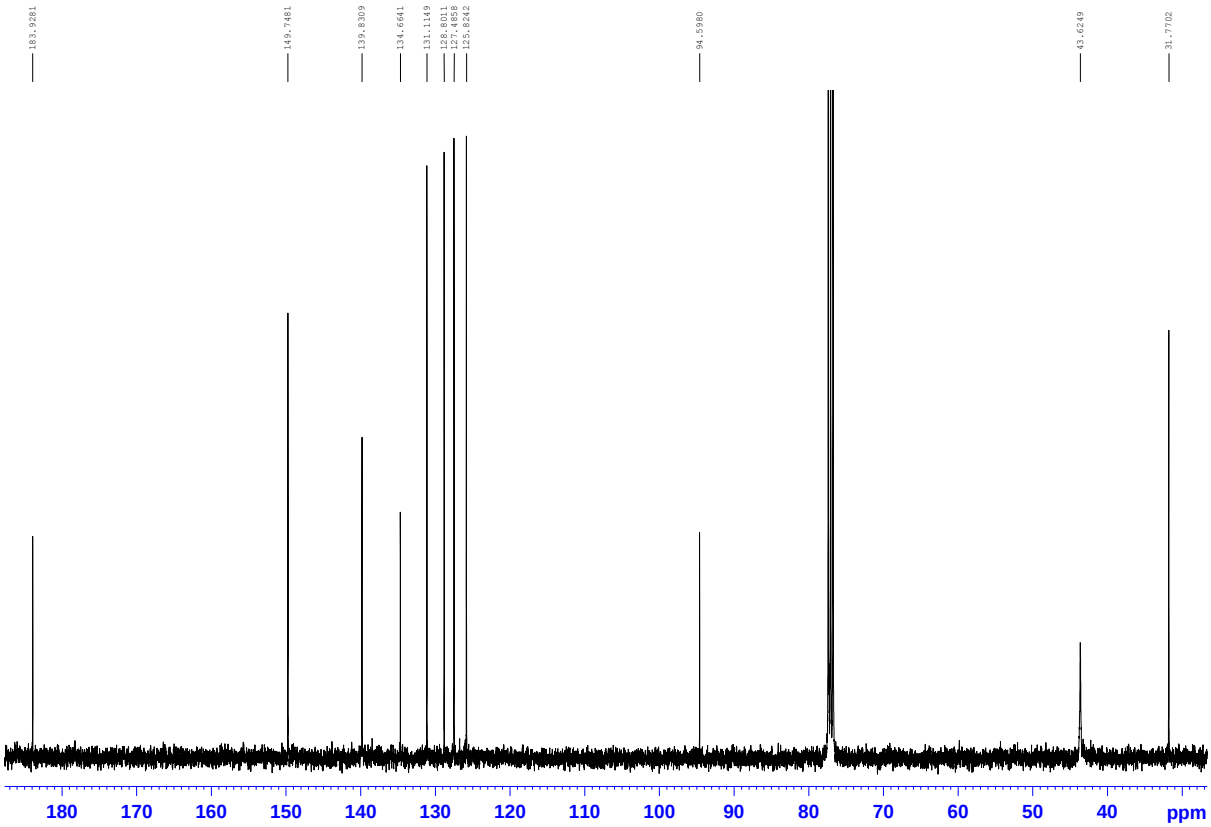


Best	Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
◉	C17 H21 N O S	(M+H)+	288.1412	287.1341	287.1344	98.63	1.06
○	C17 H18 O S	(M+NH4)+	288.1412	270.1075	270.1078	98.63	1.13
○	C15 H23 N O S	(M+Na)+	288.1412	265.1522	265.15	84.22	-8.02
○	C12 H27 N O S2	(M+Na)+	288.1412	265.1523	265.1534	83.11	4.26

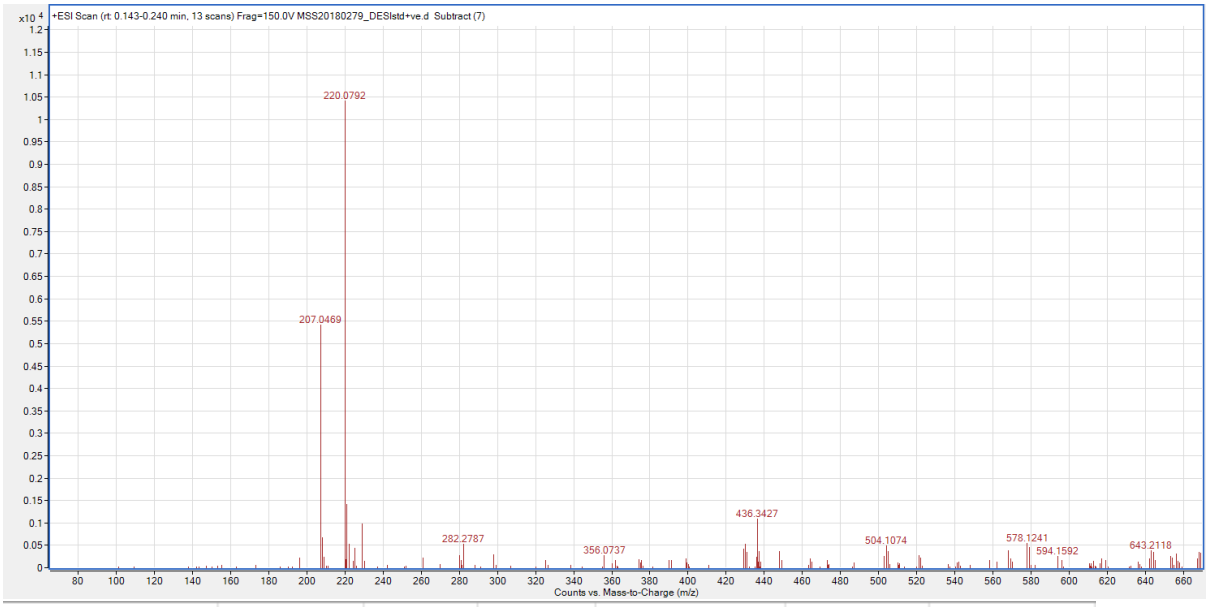
Compound 33 ^{1}H NMR $CDCl_3$



Compound 33 ^{13}C NMR $CDCl_3$

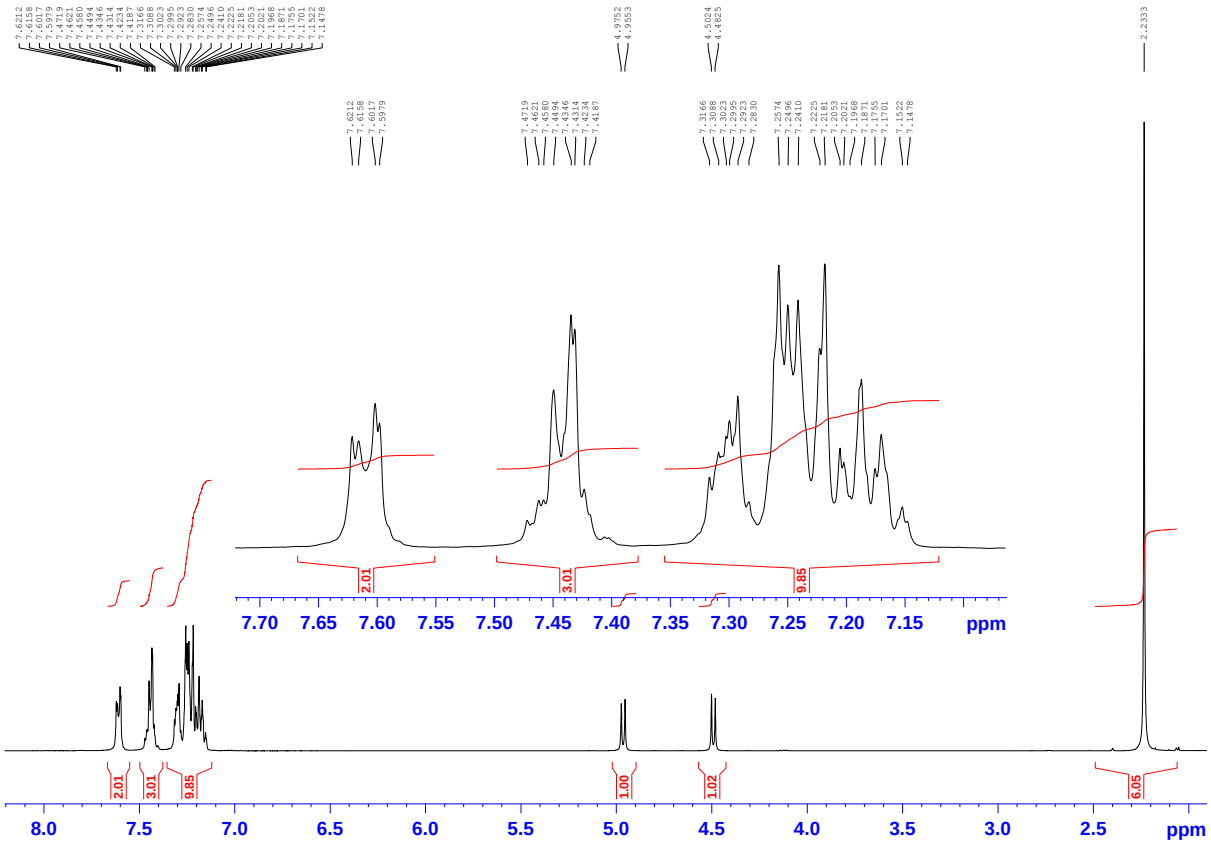


Compound 33 MS

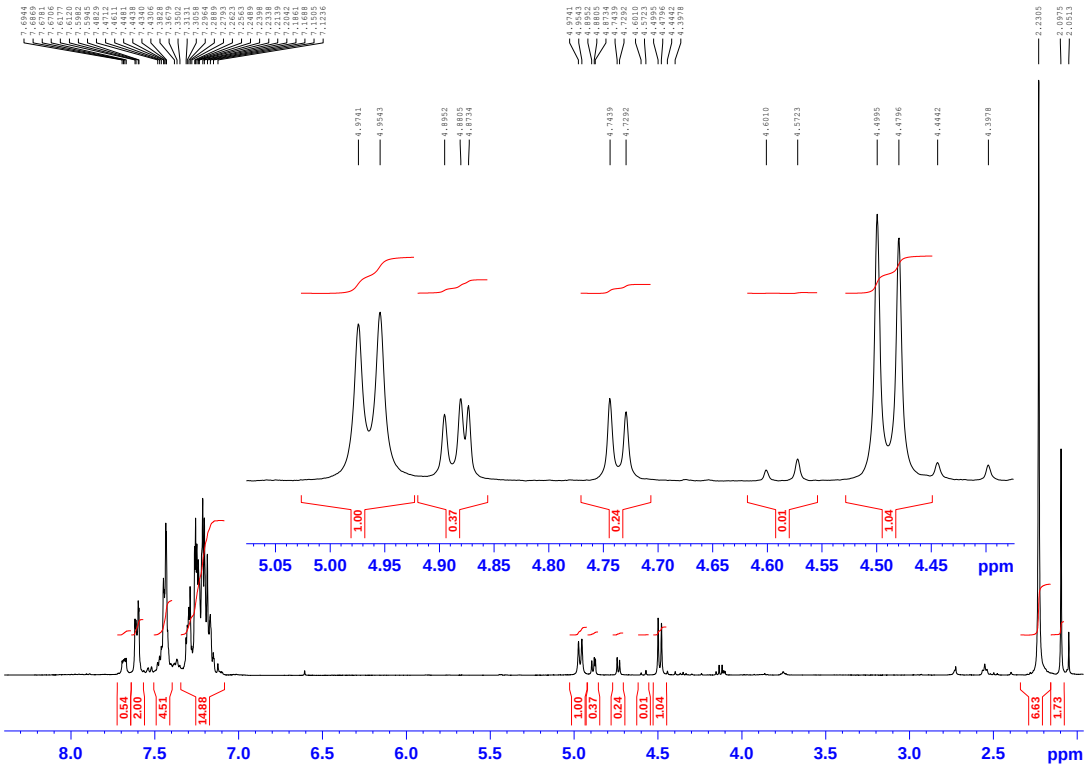


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C12 H13 N O S	(M+H)+	220.0792	219.0719	219.0718	61.71	-0.72
C10 H11 N4 S	(M+H)+	220.0792	219.072	219.0704	53.11	-6.99
C9 H15 O4 S	(M+H)+	220.0792	219.0719	219.0691	40.16	-12.93

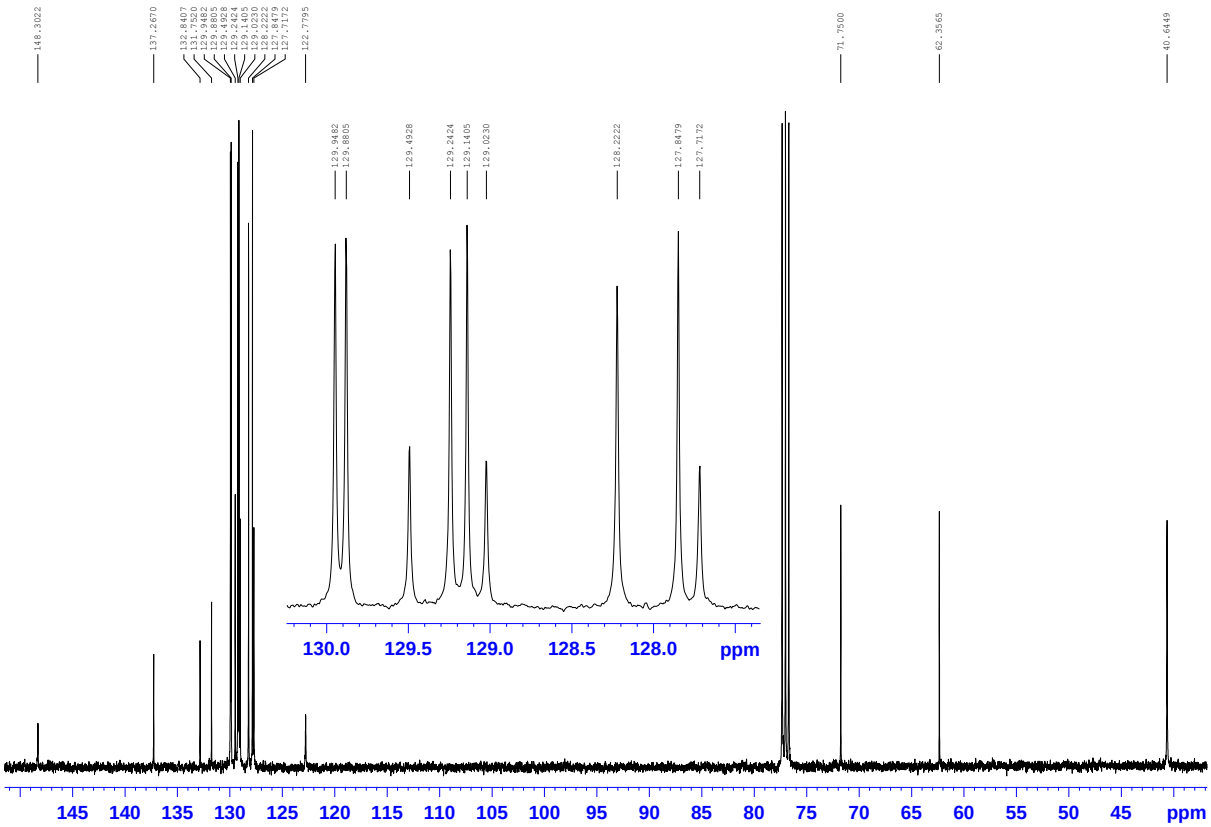
Compound 10a ^{1}H NMR $CDCl_3$



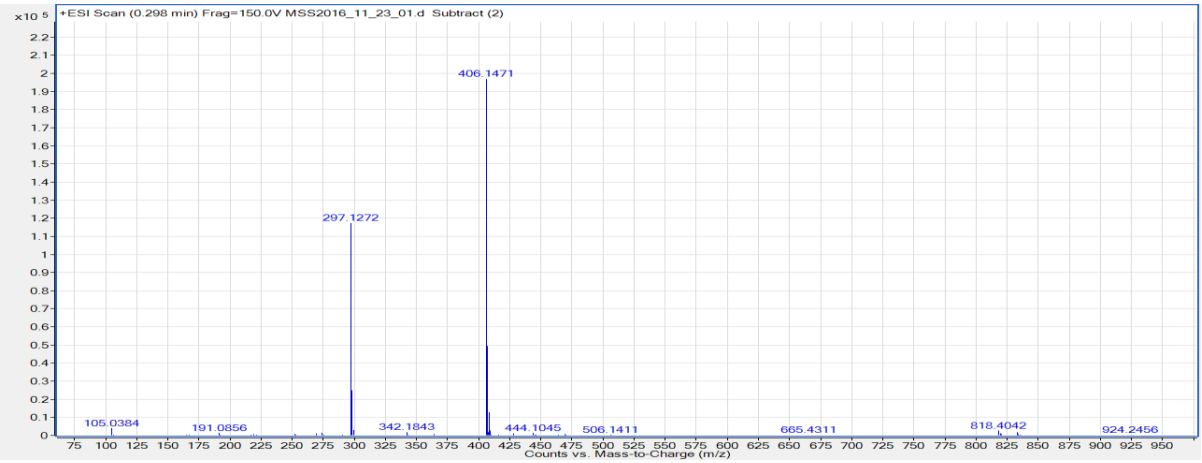
Compound 10a (crude) ^{1}H NMR $CDCl_3$



Compound 10a ^{13}C NMR $CDCl_3$

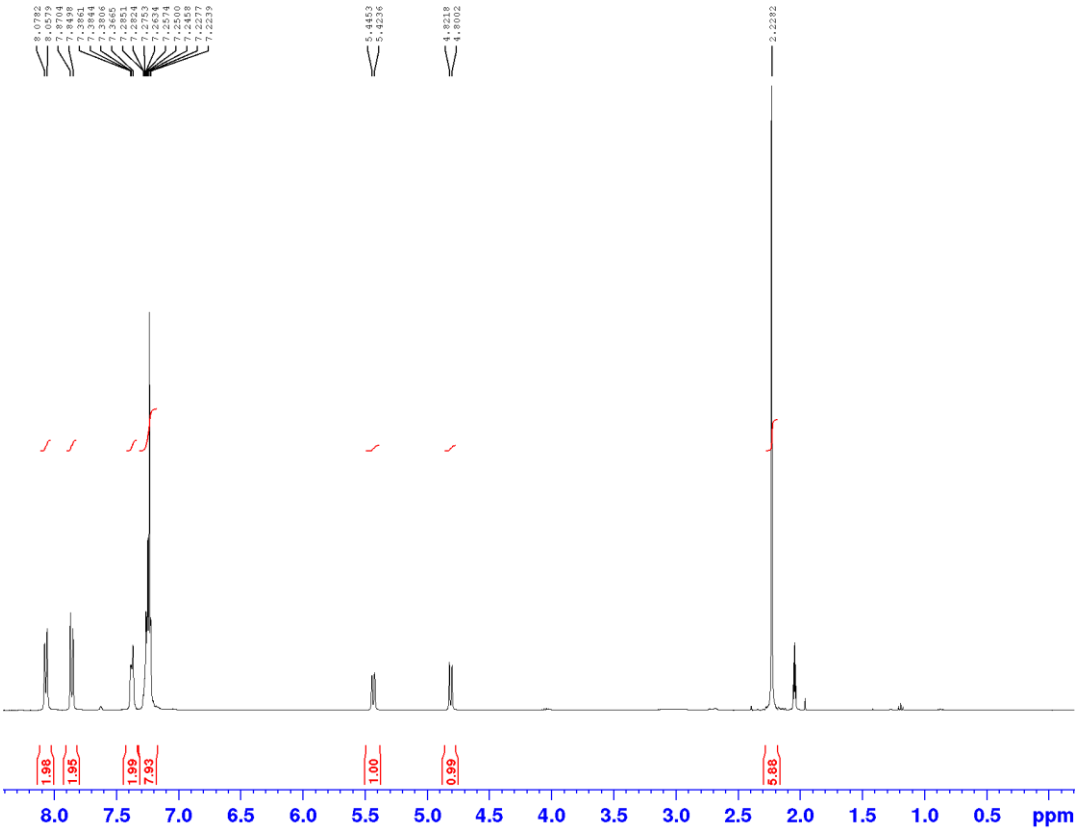


Compound 10a MS

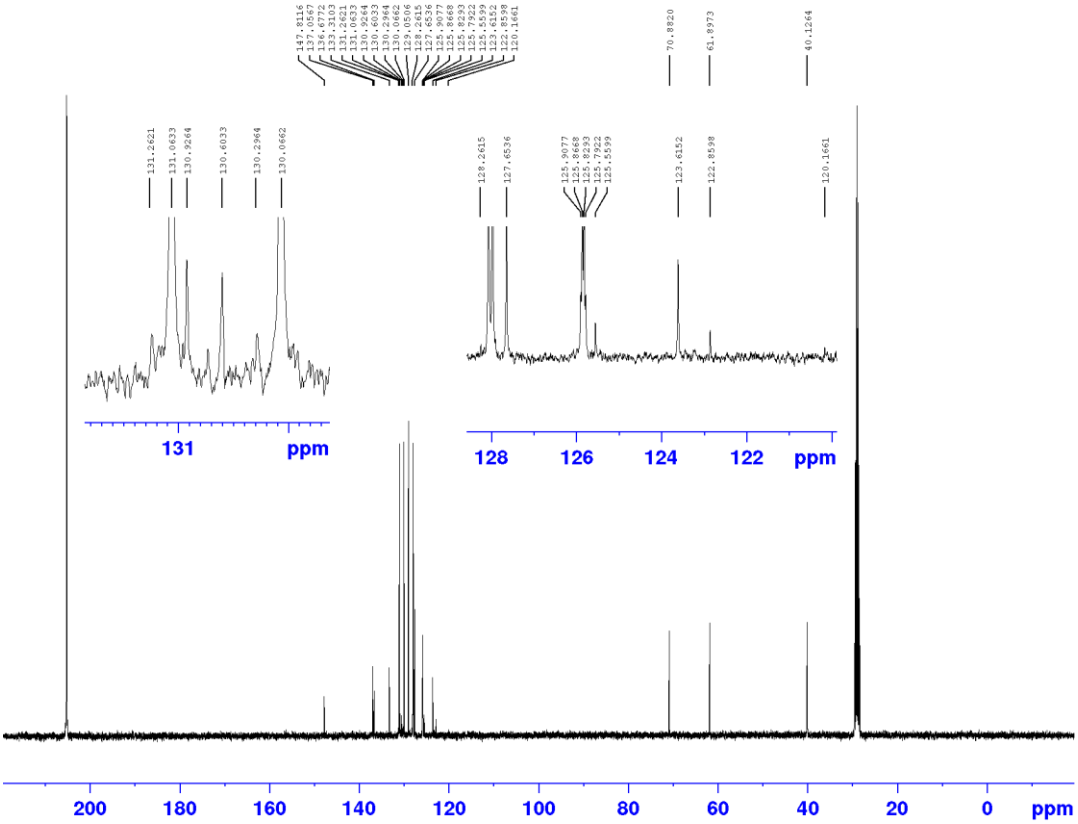


Best	Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
●	C24 H23 N O3 S	(M+H)+	406.1471	405.1398	405.1399	98.37	0.12
○	C24 H20 O3 S	(M+NH4)+	406.1471	388.1133	388.1133	98.37	0.12
○	C13 H14 N10 O5	(M+NH4)+	408.1478	390.114	390.1149	96.91	2.24
○	C12 H21 N7 O9	(M+H)+	408.1478	407.1405	407.1401	94.75	-0.95

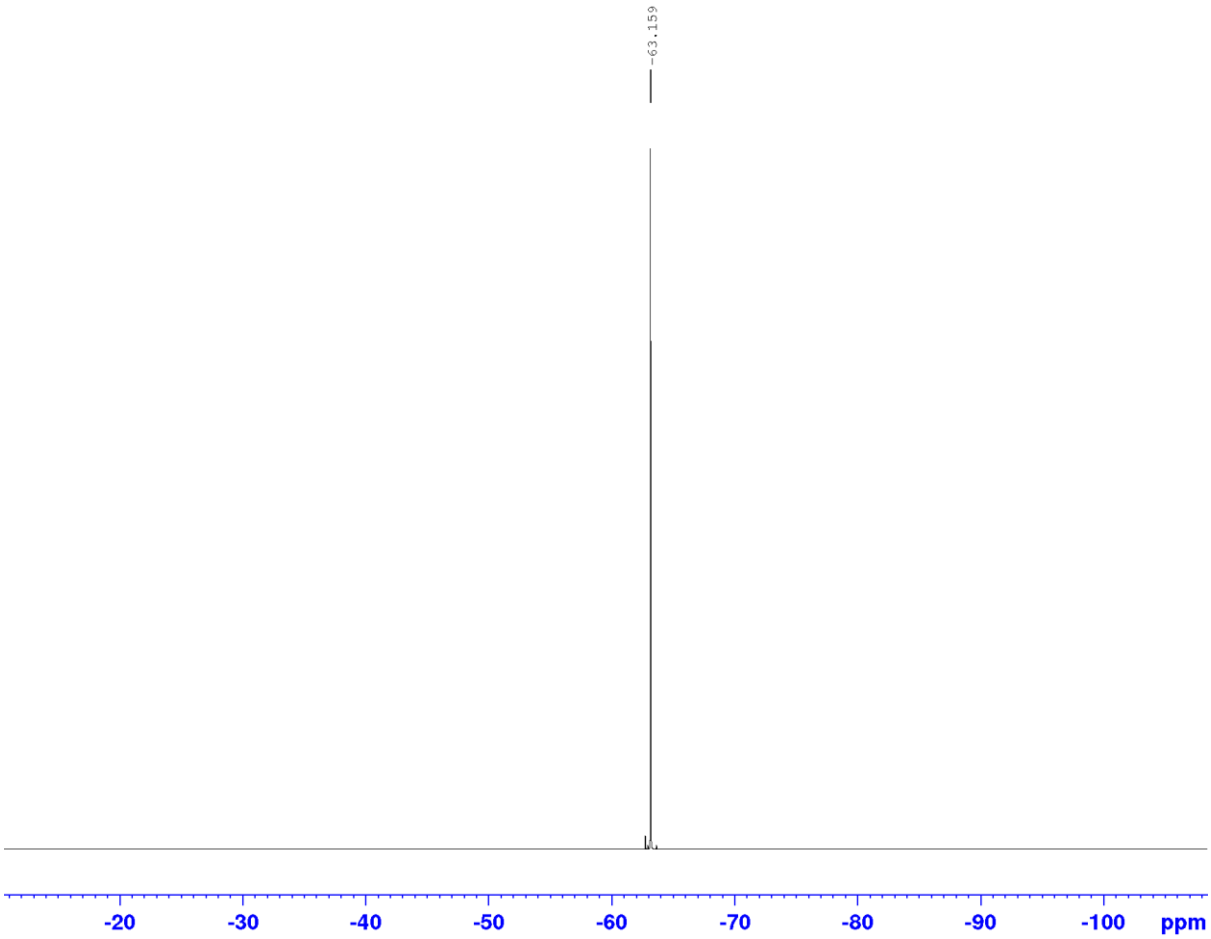
Compound 10b ^{1}H NMR $CDCl_3$



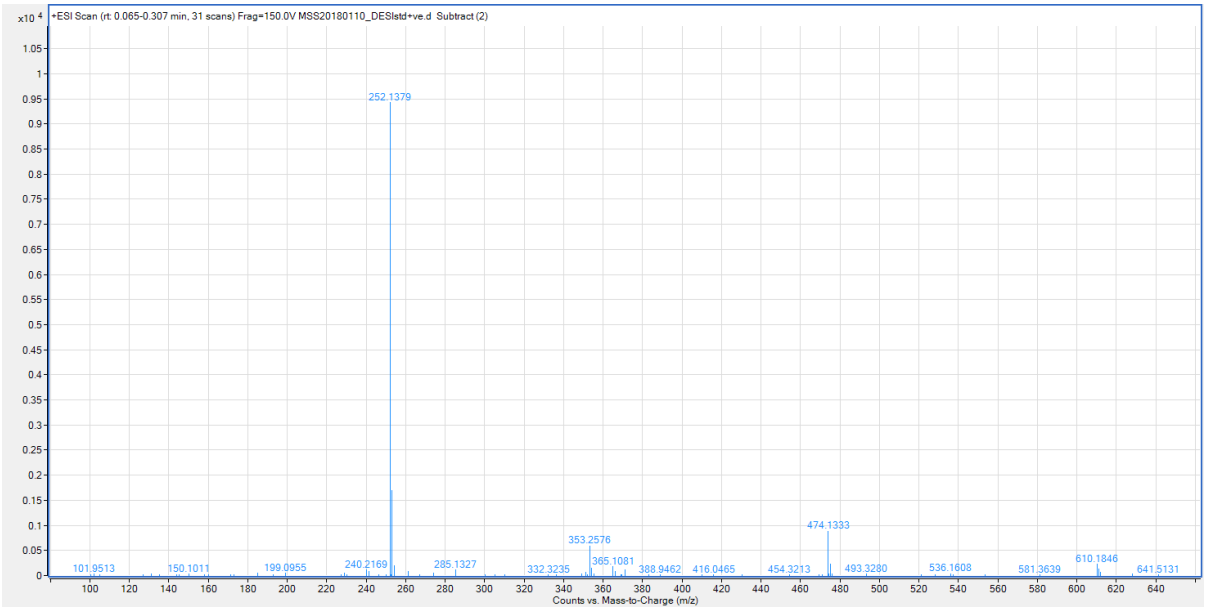
Compound 10b ^{13}C NMR $CDCl_3$



Compound 10b ^{19}F NMR $CDCl_3$

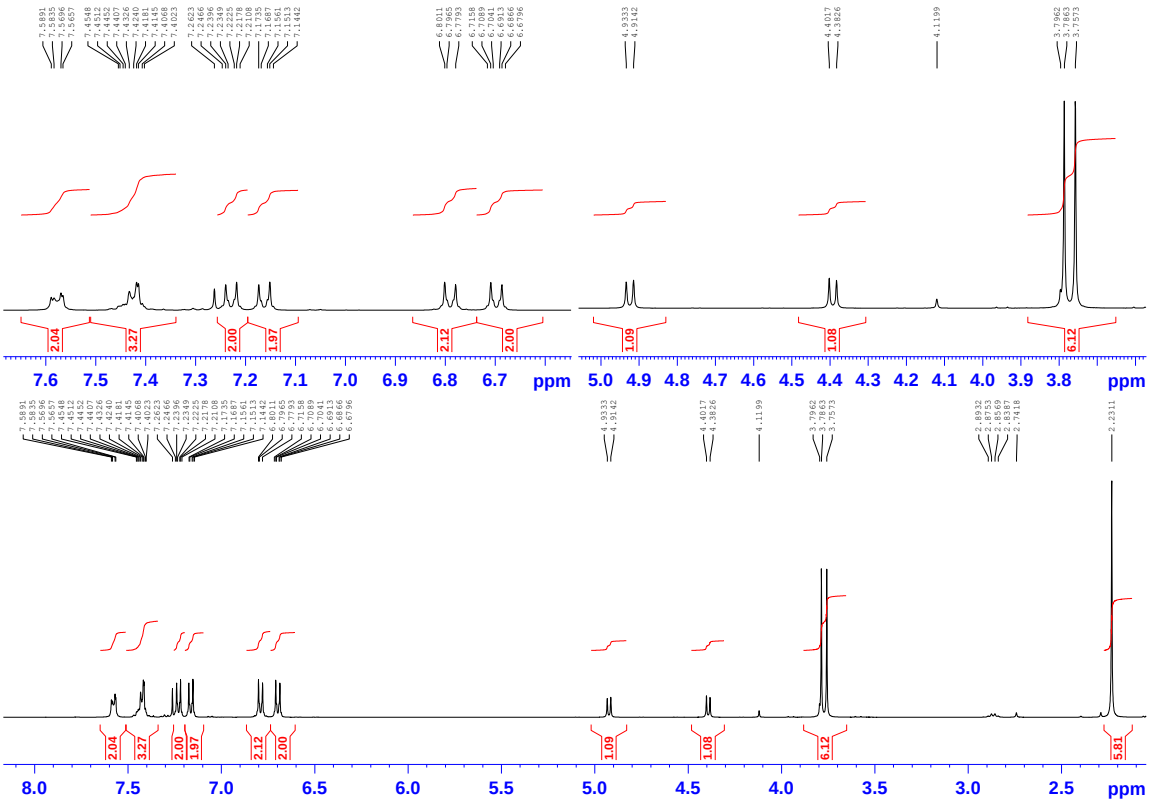


Compound 10b MS

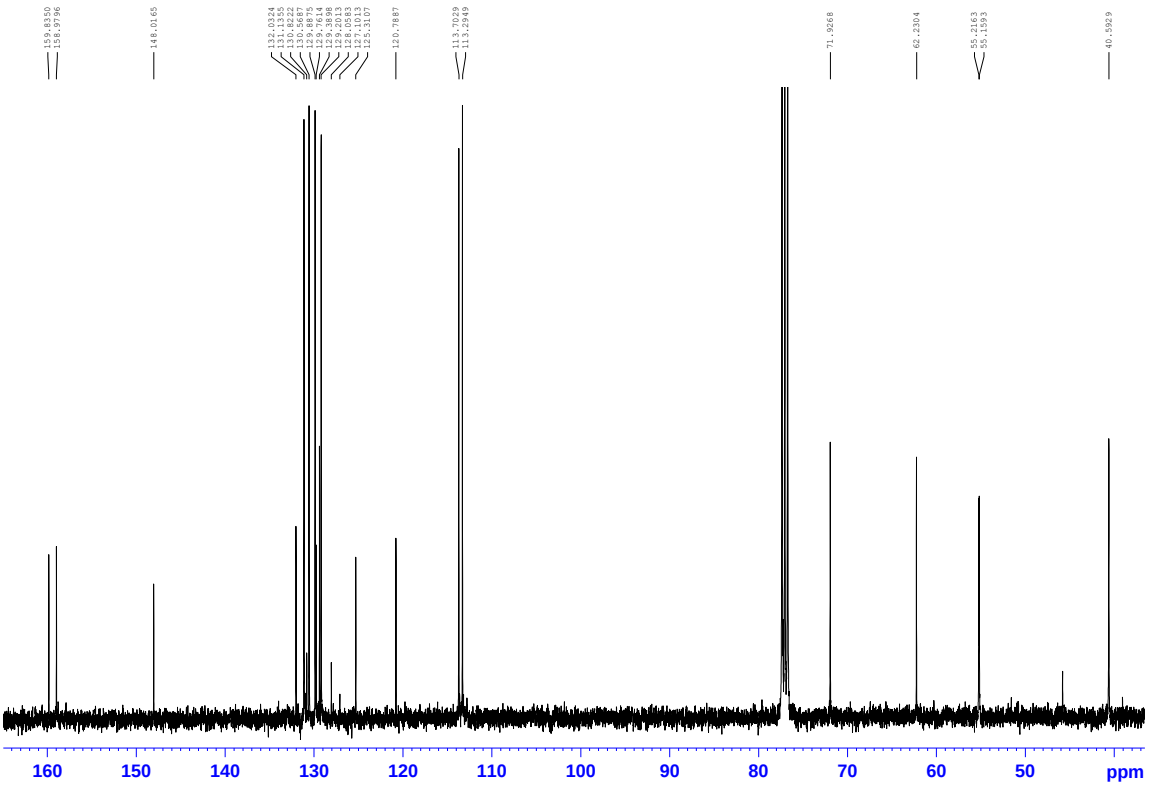


Best	Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
◉	C25 H22 F3 N O3 S	(M+H)+	474.1333	473.126	473.1272	90.27	2.59
○	C28 H21 F2 N O2 S	(M+H)+	474.1333	473.126	473.1261	90.16	0.21
○	C22 H24 F3 O6 S	(M+H)+	474.1333	473.126	473.1246	89.43	-3.06
○	C27 H20 F N O6	(M+H)+	474.1333	473.1258	473.1275	89.18	3.42
○	C30 H19 N O5	(M+H)+	474.1333	473.1258	473.1263	89.12	1.02

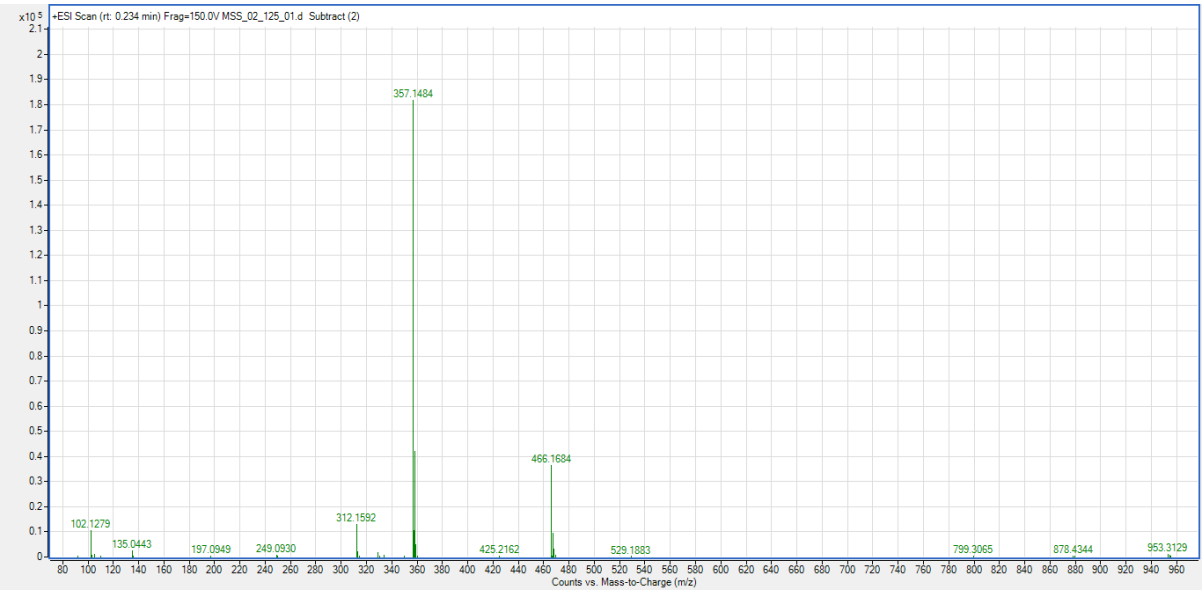
Compound 10c ^{1}H NMR $CDCl_3$



Compound 10c ^{13}C NMR $CDCl_3$

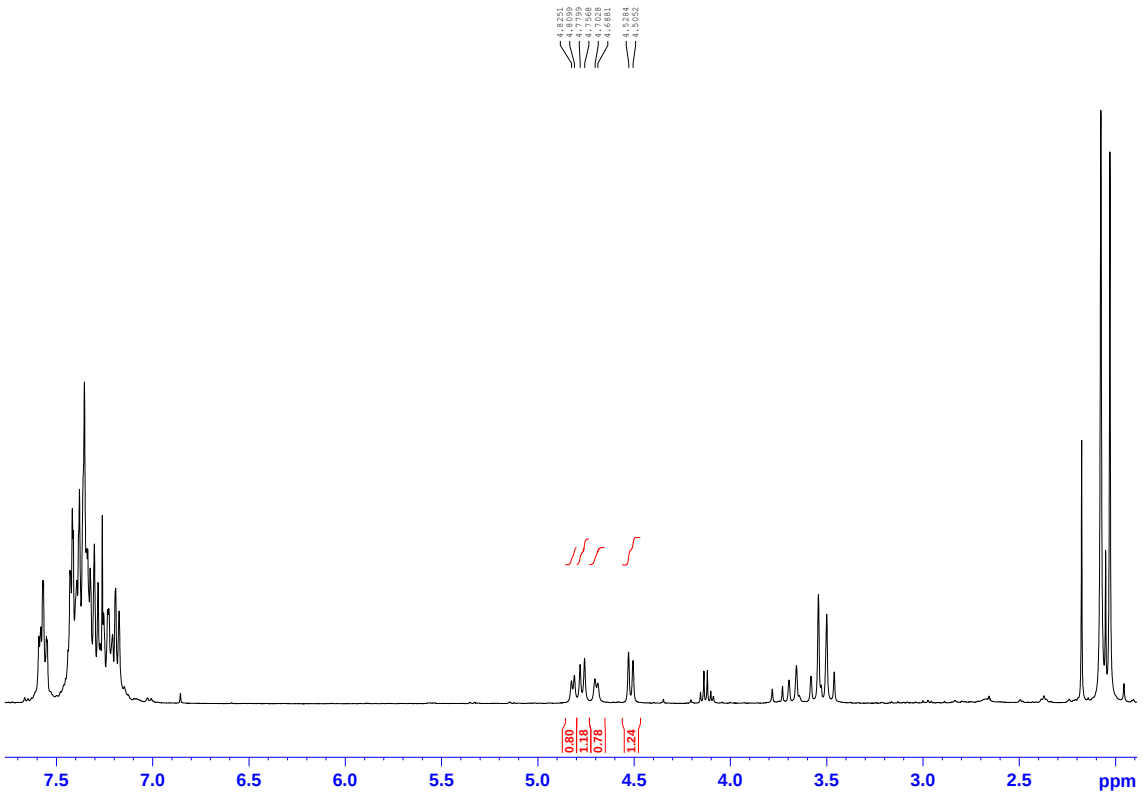


Compound 10c MS

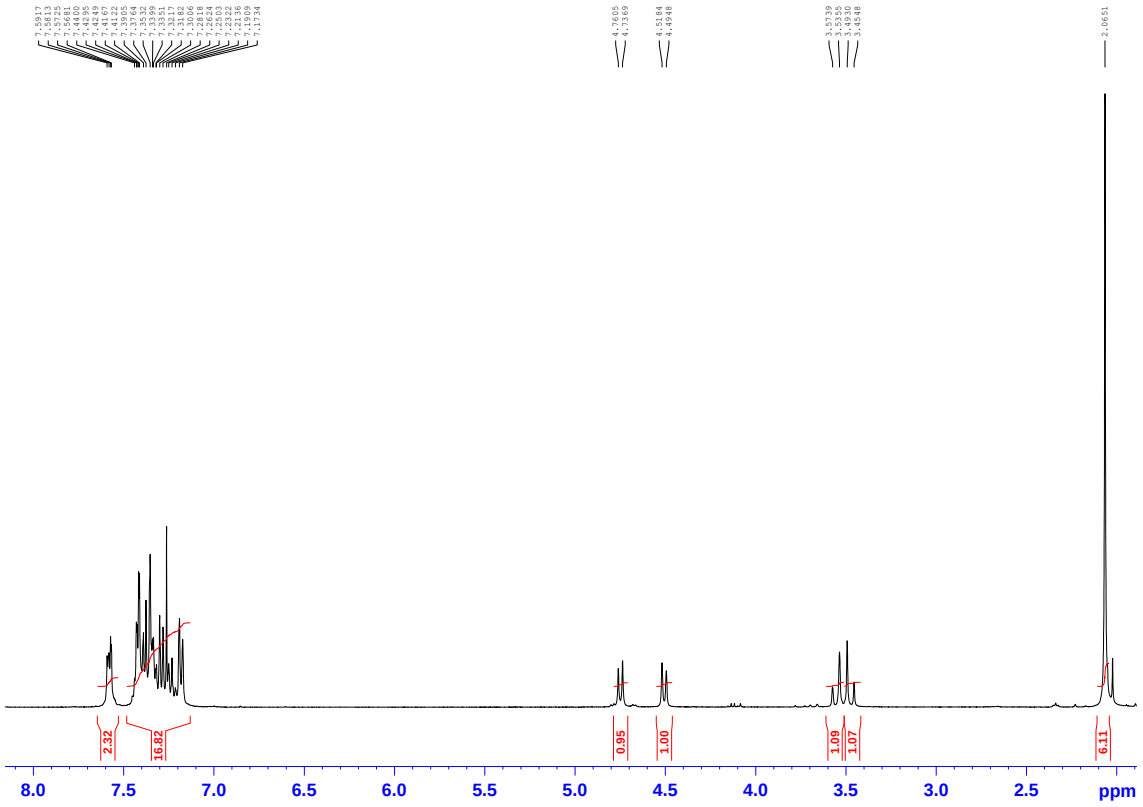


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C26 H27 N O5 S	(M+H)+	466.1684	465.161	465.161	97.68	-0.06
C26 H24 O5 S	(M+NH4)+	466.1684	448.1345	448.1344	97.68	-0.06
C27 H27 N2 O2 S	(M+Na)+	466.1684	443.1791	443.1793	96.05	0.51
C25 H25 N5 O S	(M+Na)+	466.1684	443.1792	443.178	94.19	-2.71

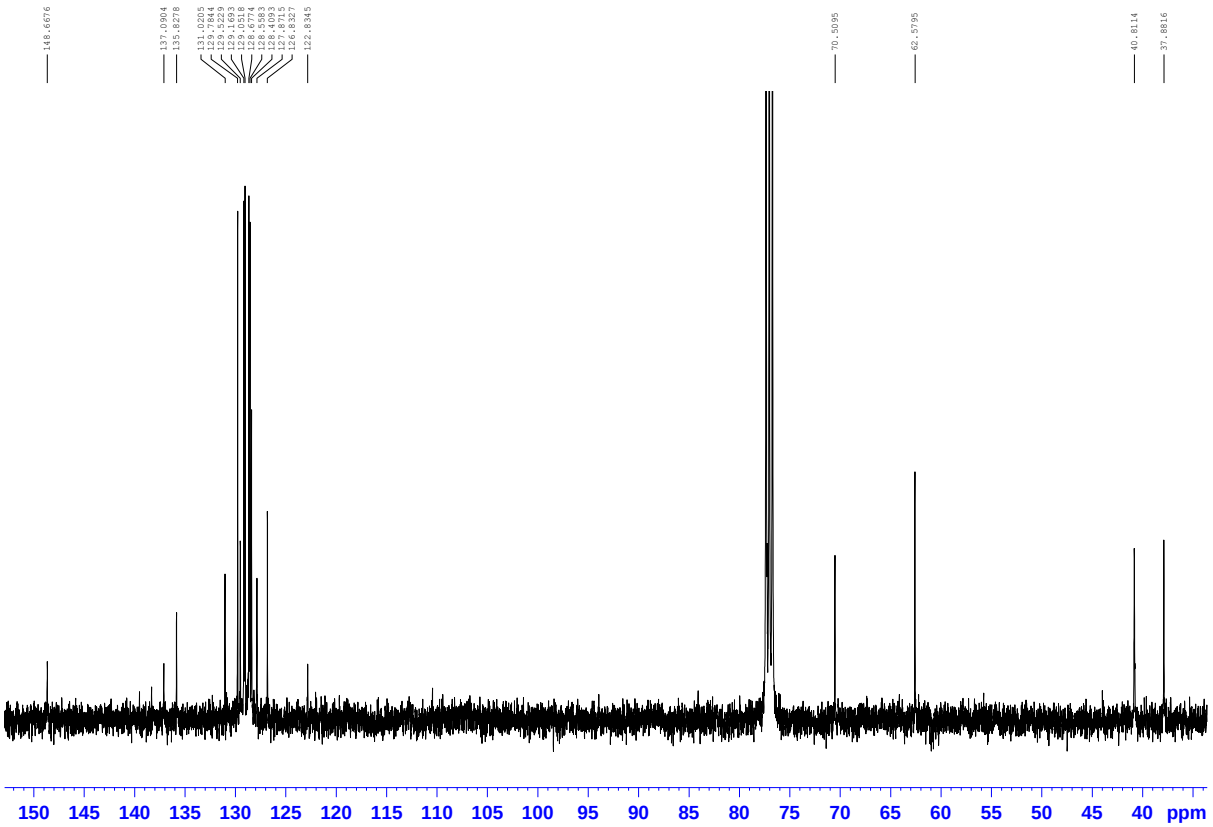
Compound 10d ^{1}H NMR $CDCl_3$ (crude mixture)



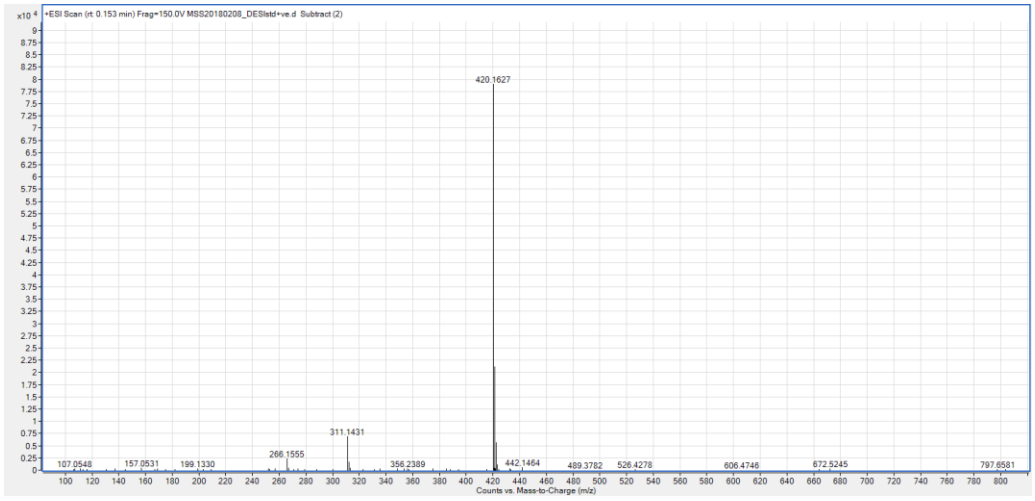
Compound 10d1 ^{1}H NMR $CDCl_3$



Compound 10d1 ^{13}C NMR $CDCl_3$

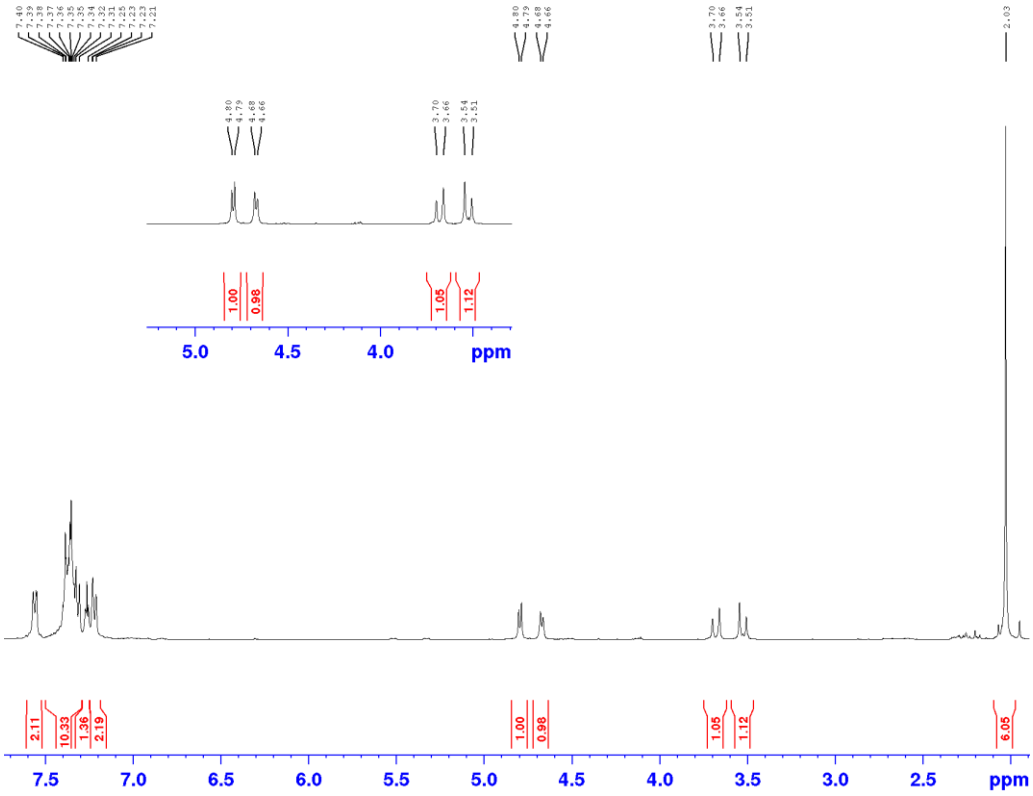


Compound 10d1 MS

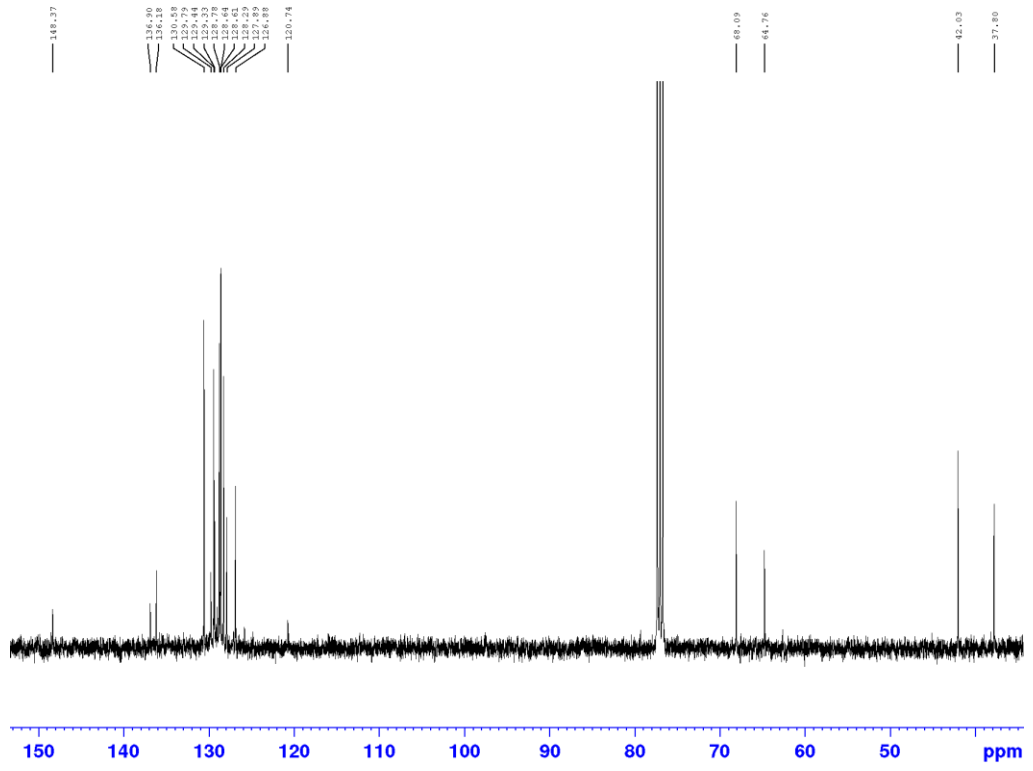


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C25 H25 N O3 S	(M+H)+	420.1627	419.1554	419.1555	47.58	0.29
C17 H29 N3 O5 S2	(M+H)+	420.1627	419.1554	419.1549	46.92	-1.27
C11 H27 N6 O9 S	(M+H)+	420.1627	419.1554	419.156	46.63	1.5
C18 H25 N7 O S2	(M+H)+	420.1627	419.1554	419.1562	46.01	1.92
C23 H23 N4 O2 S	(M+H)+	420.1627	419.1554	419.1542	44.01	-2.91
C15 H27 N6 O4 S2	(M+H)+	420.1627	419.1554	419.1535	39.57	-4.47
C12 H23 N10 O5 S	(M+H)+	420.1627	419.1554	419.1574	38.83	4.69
C13 H29 N3 O10 S	(M+H)+	420.1627	419.1554	419.1574	38.79	4.7

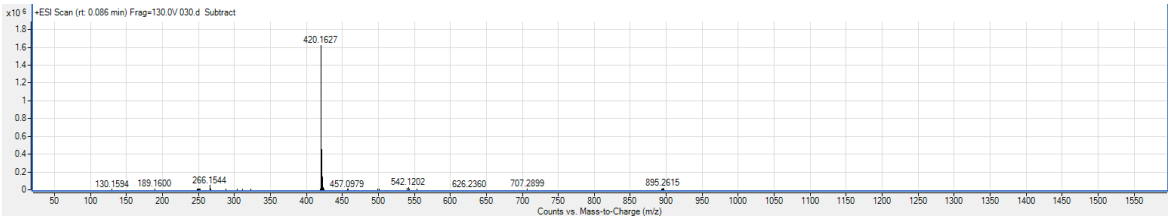
Compound 10d2 ^{1}H NMR $CDCl_3$



Compound 10d2 ^{13}C NMR $CDCl_3$

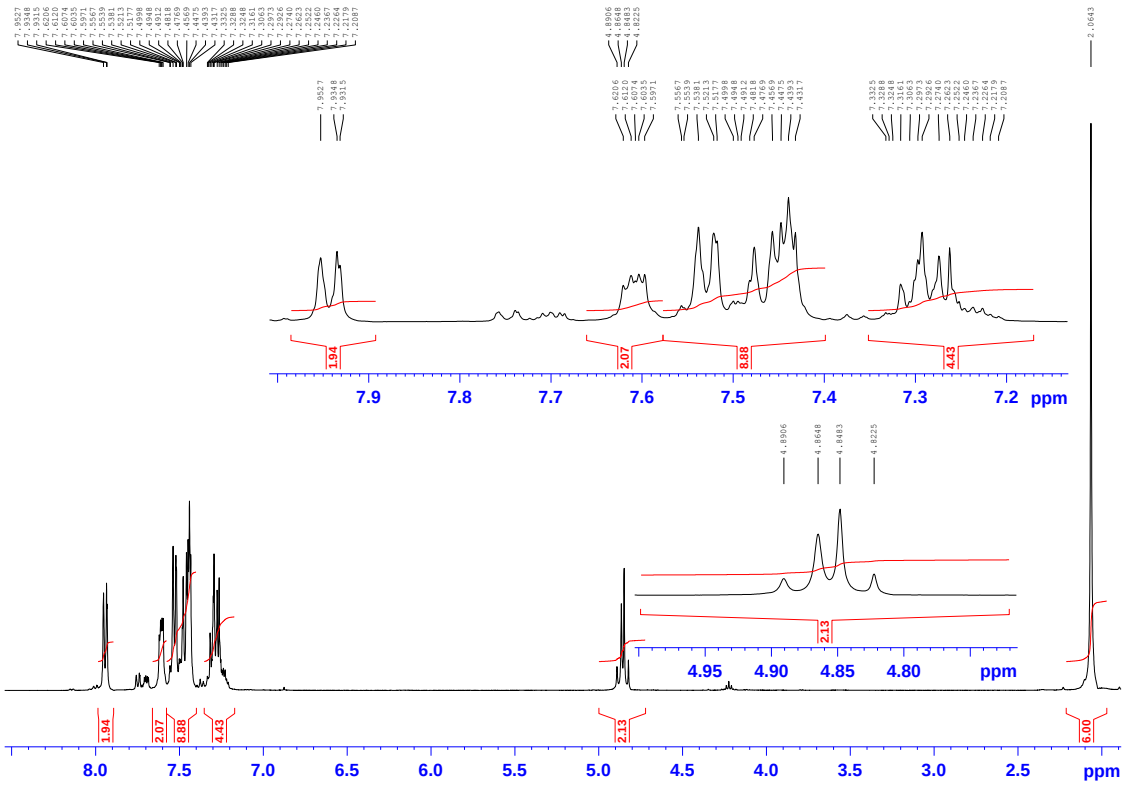


Compound 10d2 MS

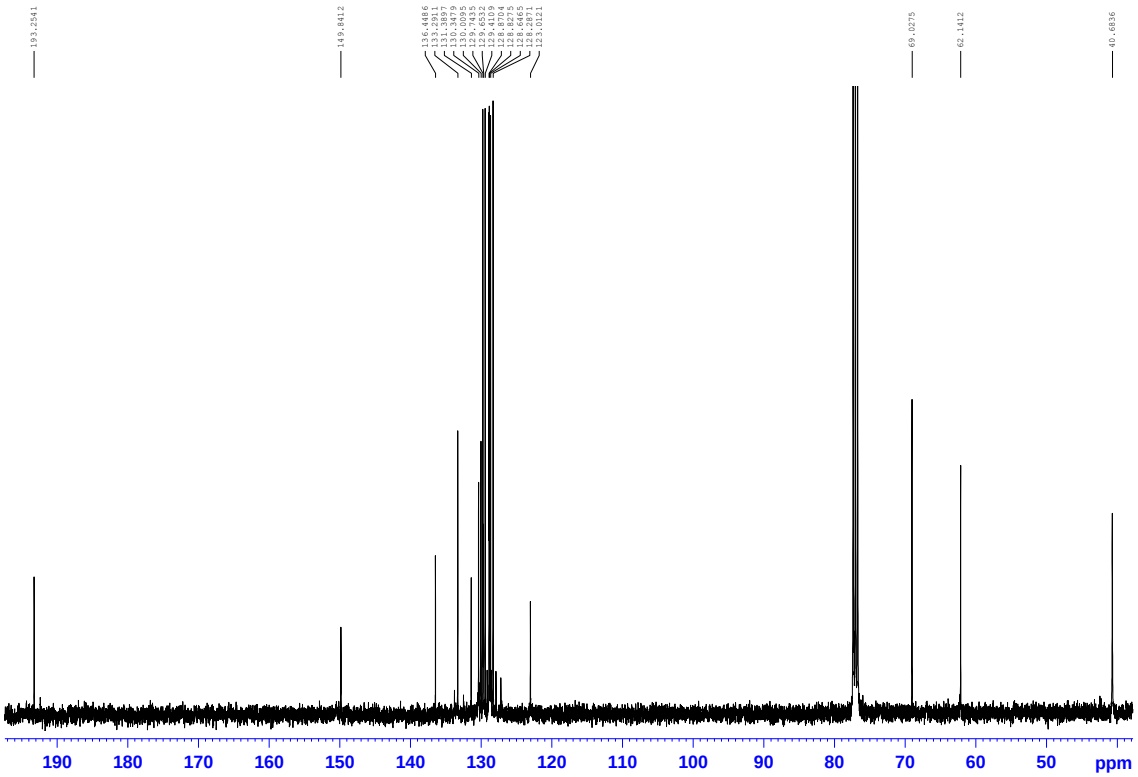


Formula	Observed m/z	Proposed adduct	Charge	Observed neutral mass	Theoretical neutral mass	Mass error (ppm)
C25H25NO3S	420.1627	H+	1+	419.1557	419.1555	0.43

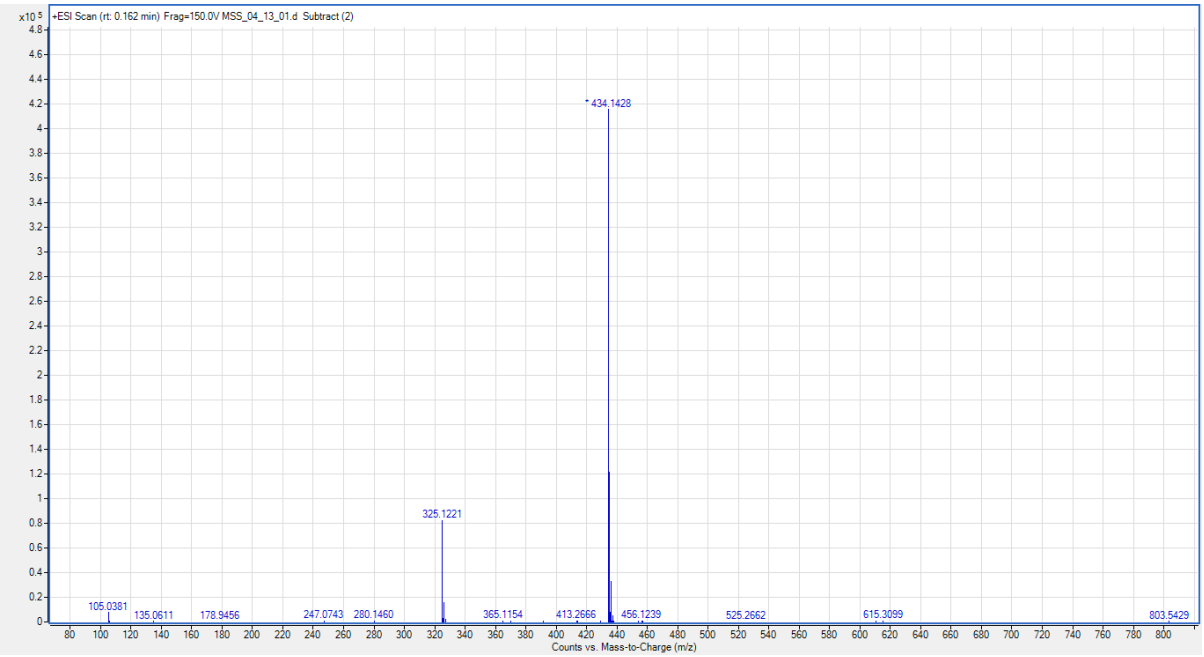
Compound 10e ^{1}H NMR $CDCl_3$



Compound 10e ^{13}C NMR $CDCl_3$

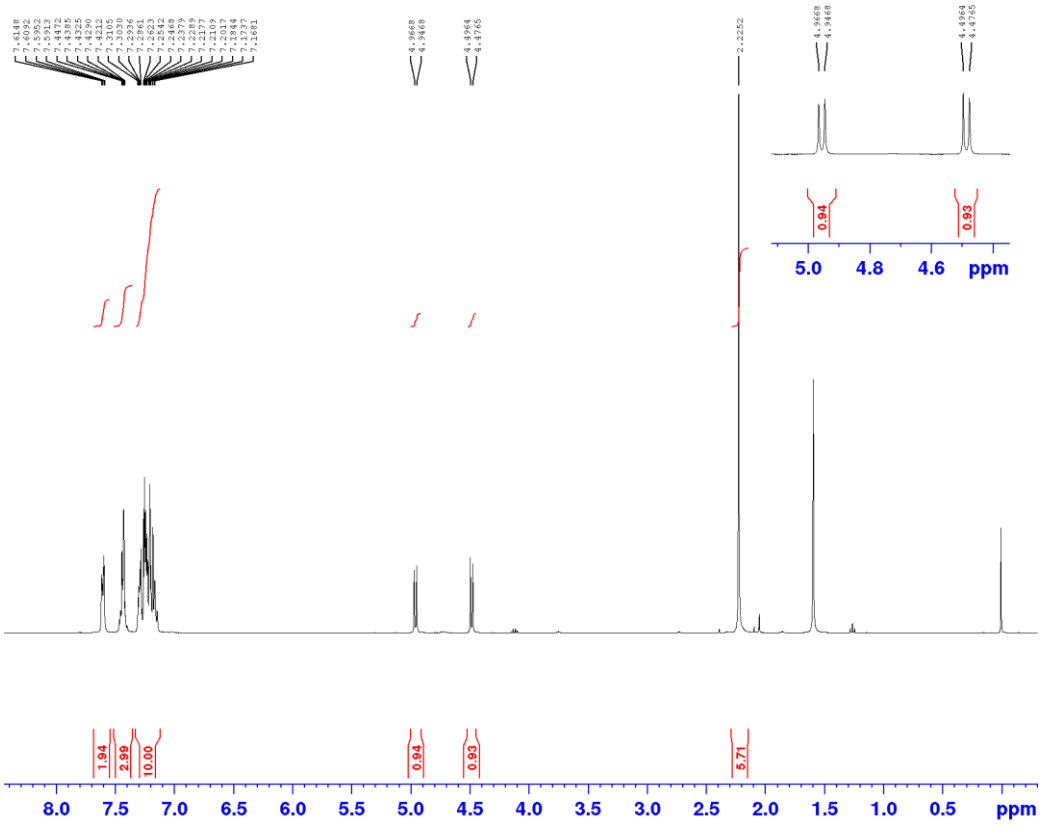


Compound 10e MS

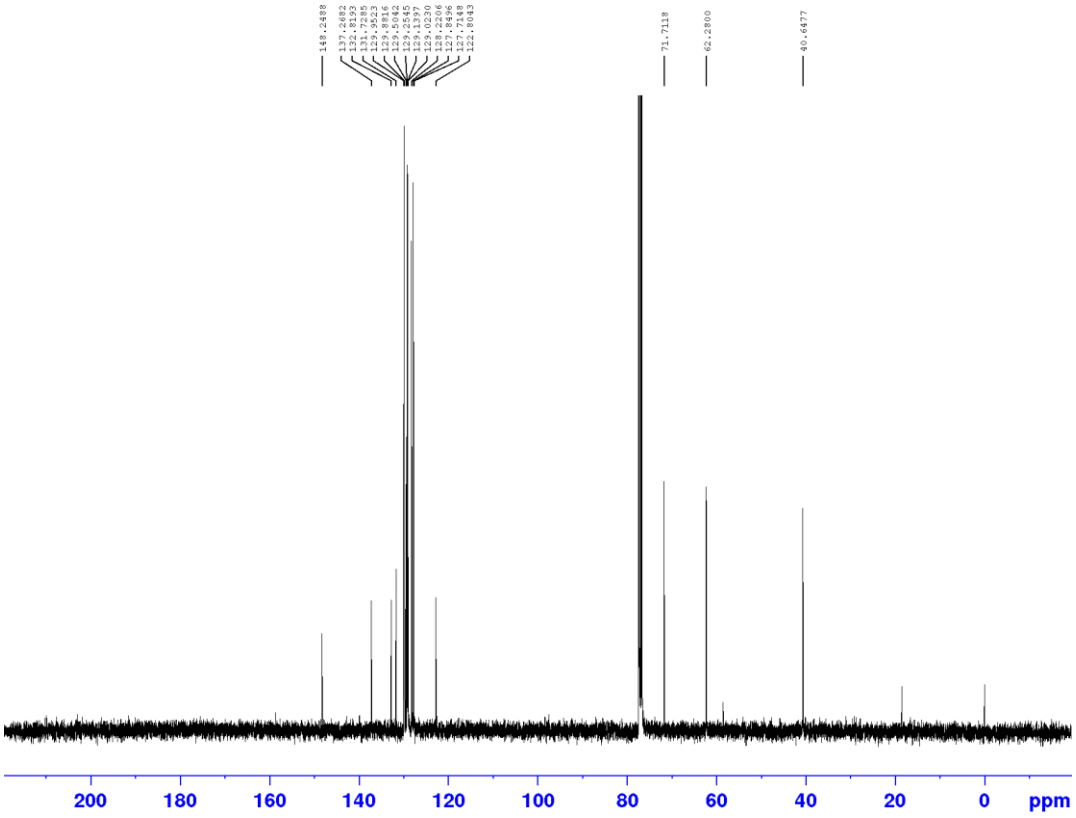


Best	Formula	Species	m/z	Mass	Mass (MFG)	Score (MFG)	Diff (ppm)
○	C25 H23 N O4 S	(M+H)+	434.1428	433.1353	433.1348	97.94	-1.12
○	C25 H20 O4 S	(M+NH4)+	434.1428	416.1087	416.1082	97.94	-1.17
○	C26 H19 N5 S	(M+H)+	434.1428	433.1353	433.1361	97.71	1.78
○	C26 H16 N4 S	(M+NH4)+	434.1428	416.1088	416.1096	97.71	1.85

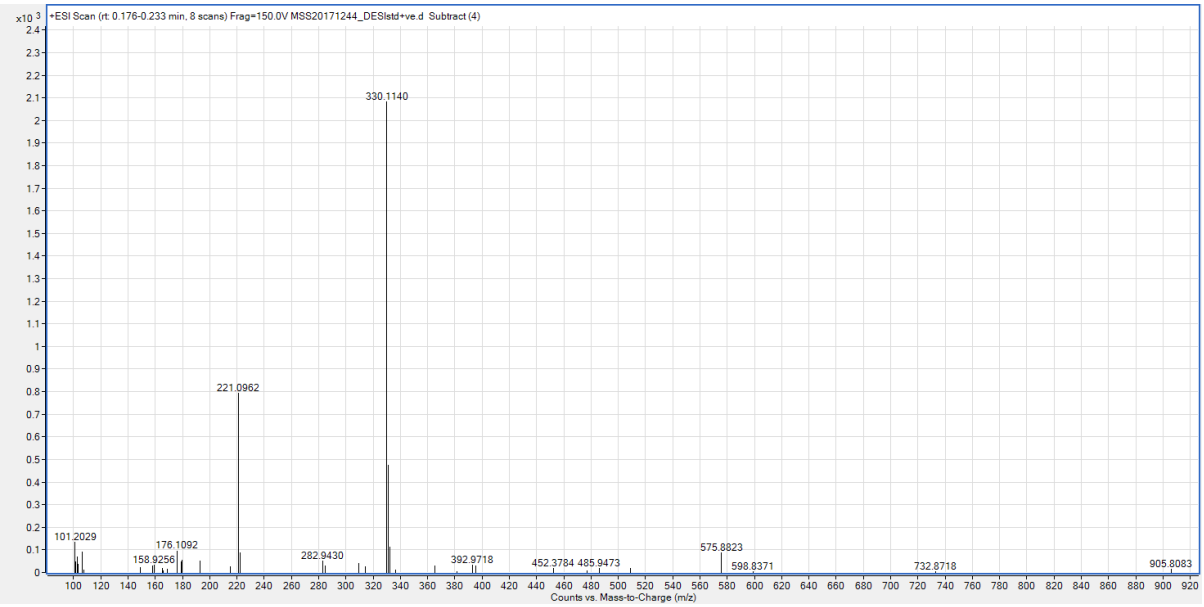
Compound 10f ^{1}H NMR $CDCl_3$



Compound 10f ^{13}C NMR $CDCl_3$

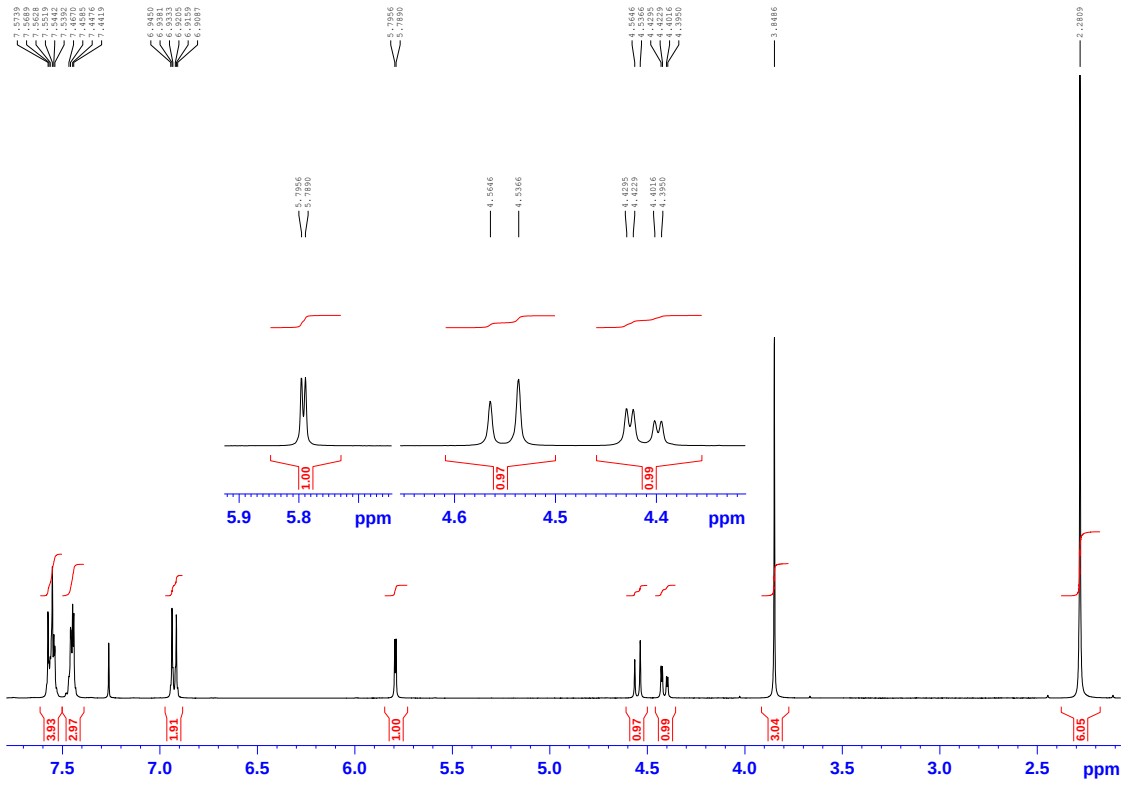


Compound 10f MS

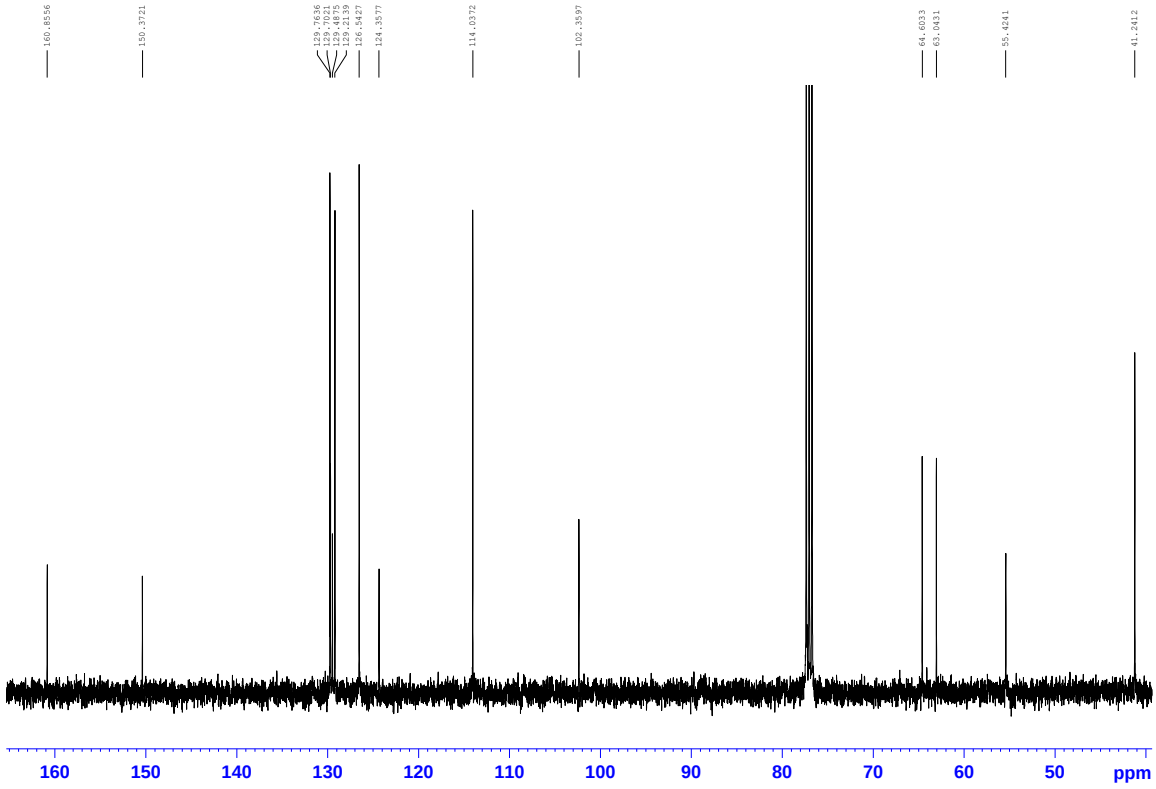


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C24 H13 N2	(M+H)+	330.1140	329.1069	329.1079	91.81	3.09
C21 H15 N O3	(M+H)+	330.1140	329.1069	329.1052	90.06	-5.04
C16 H17 N4 O2 S	(M+H)+	330.1140	329.1072	329.1072	89.6	-0.08
C18 H19 N O3 S	(M+H)+	330.1140	329.1072	329.1086	85.7	4.27
C19 H13 N4 O2	(M+H)+	330.1140	329.1069	329.1039	74.7	-9.35
C10 H23 N3 O5 S2	(M+H)+	330.1140	329.1074	329.1079	70.23	1.65

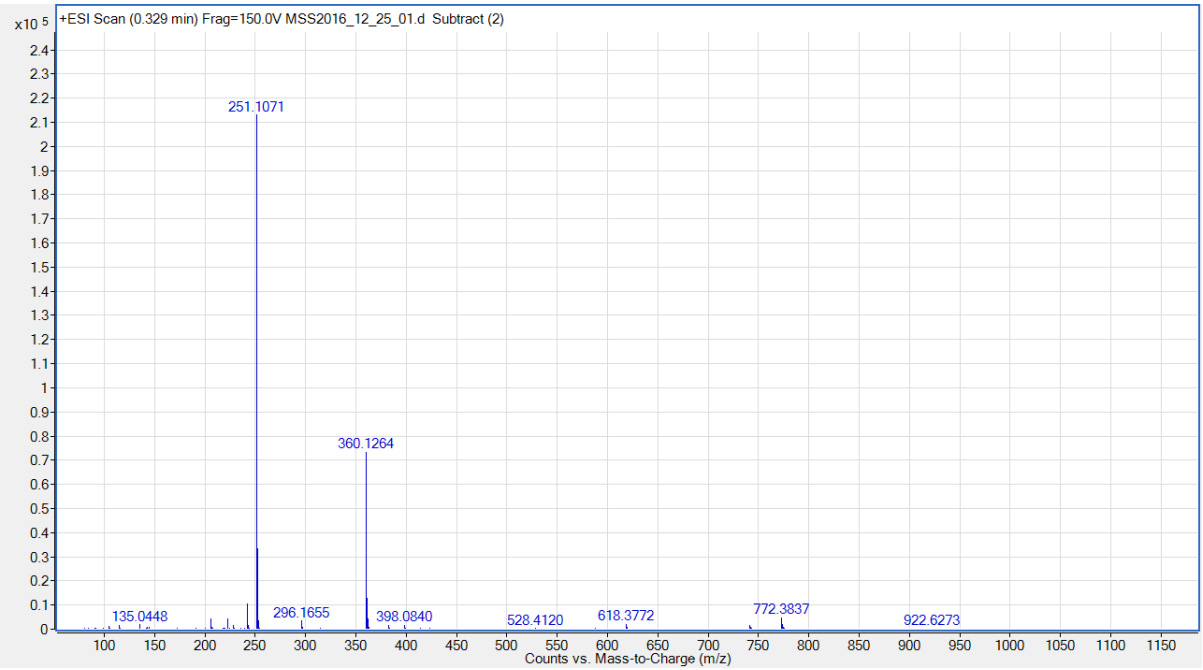
Compound 10g ^{1}H NMR $CDCl_3$



Compound 10g ^{13}C NMR $CDCl_3$

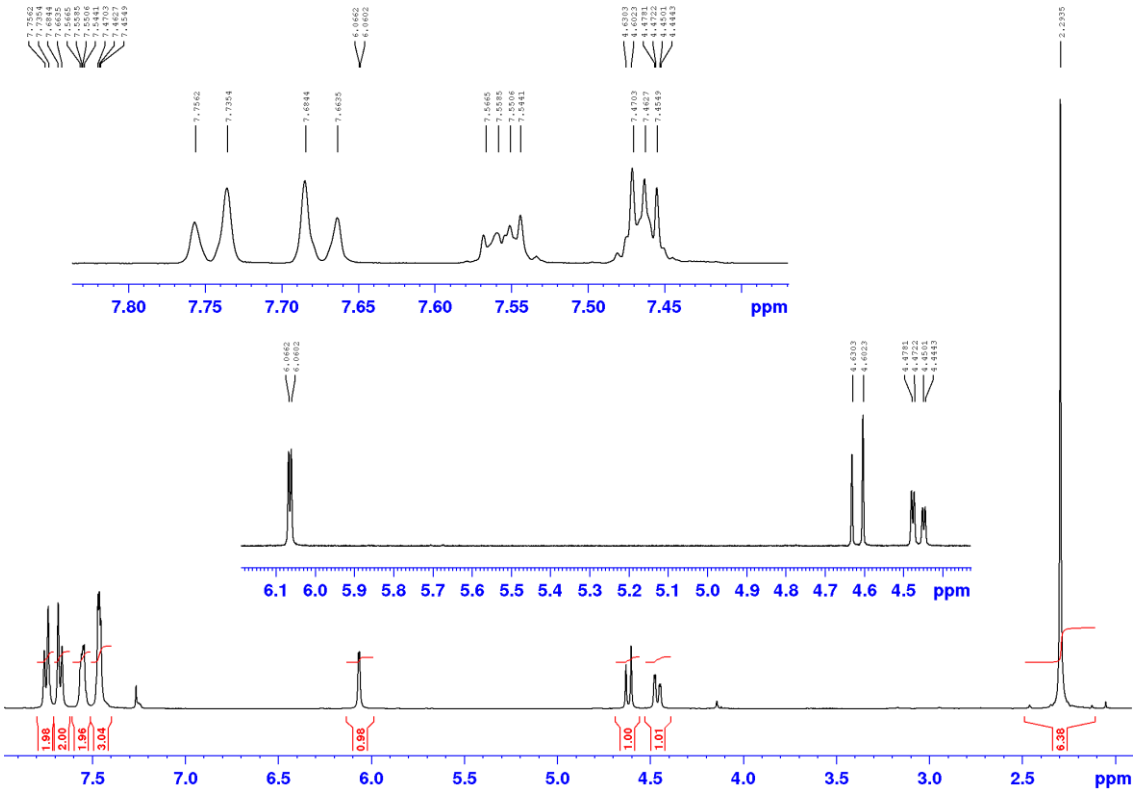


Compound 10g MS

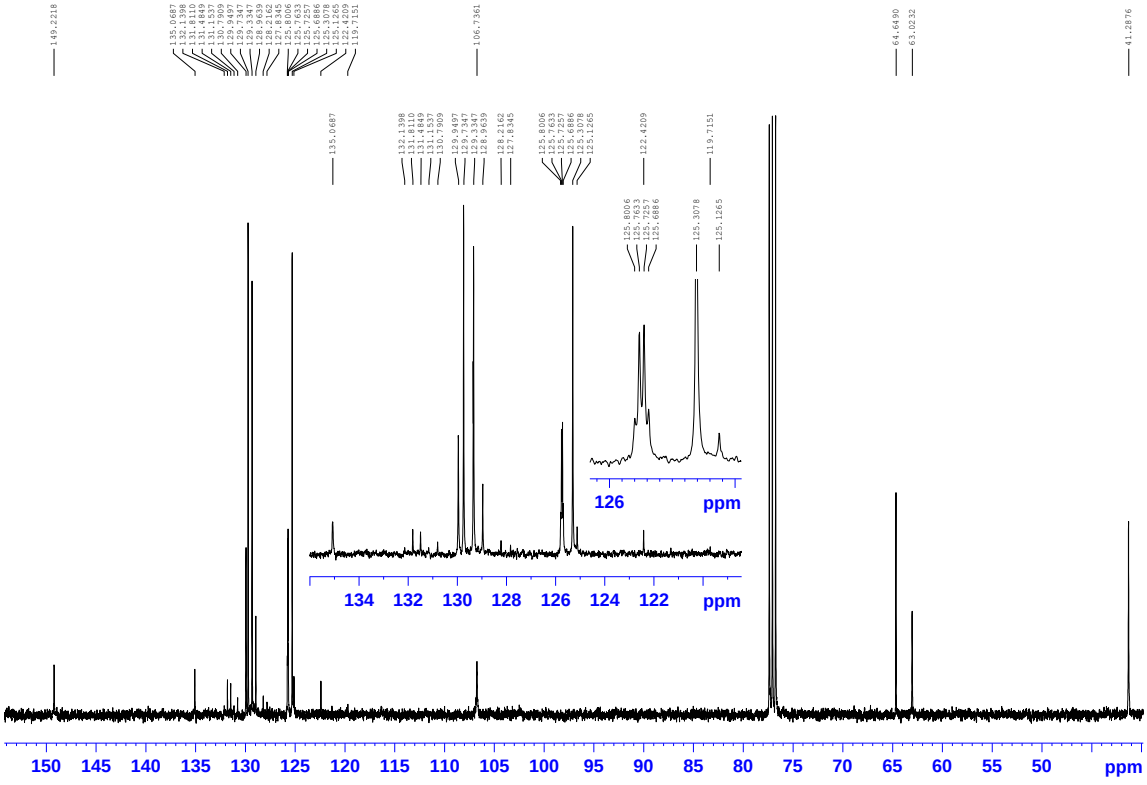


Best	Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
▶	C19 H21 N O4 S	(M+H)+	360.1264	359.1192	359.1191	95.43	-0.19
	C19 H18 O4 S	(M+NH4)+	360.1264	342.0926	342.0926	95.43	-0.2
	C13 H23 N O9	(M+Na)+	360.1264	337.1369	337.1373	93.44	0.99

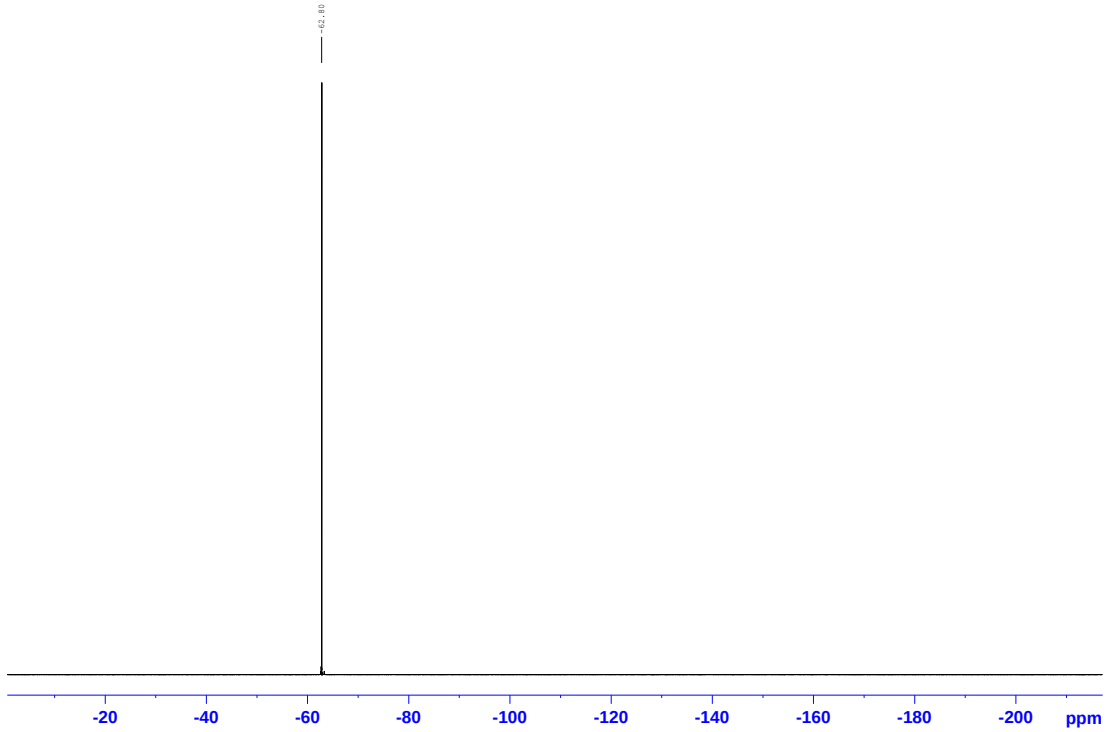
Compound 10h ^{1}H NMR $CDCl_3$ (inserts use Guassian multiplication to improve resolution of the signals)



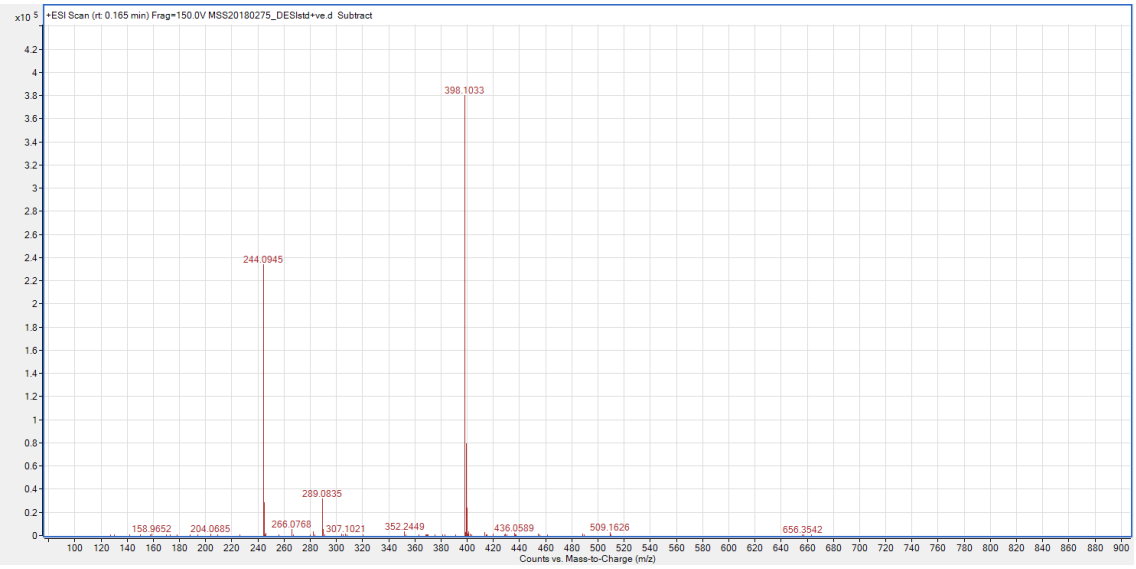
Compound 10h ^{13}C NMR $CDCl_3$



Compound 10h ^{19}F NMR $CDCl_3$

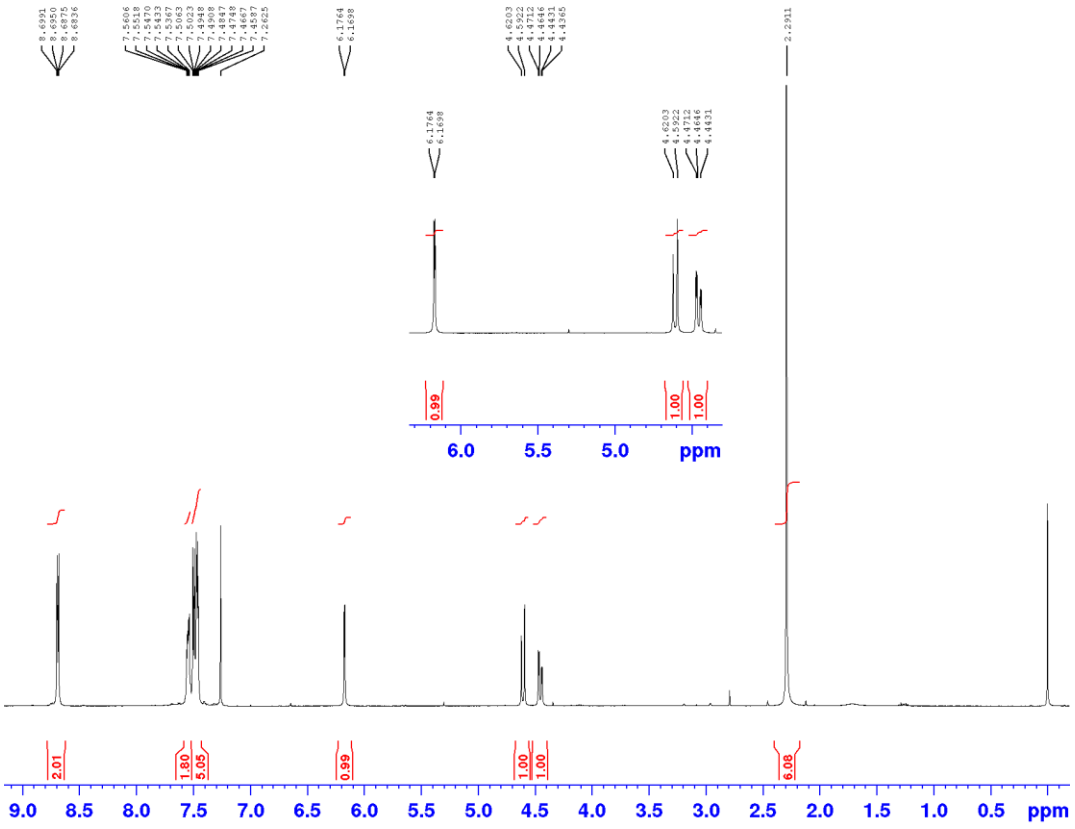


Compound 10h MS

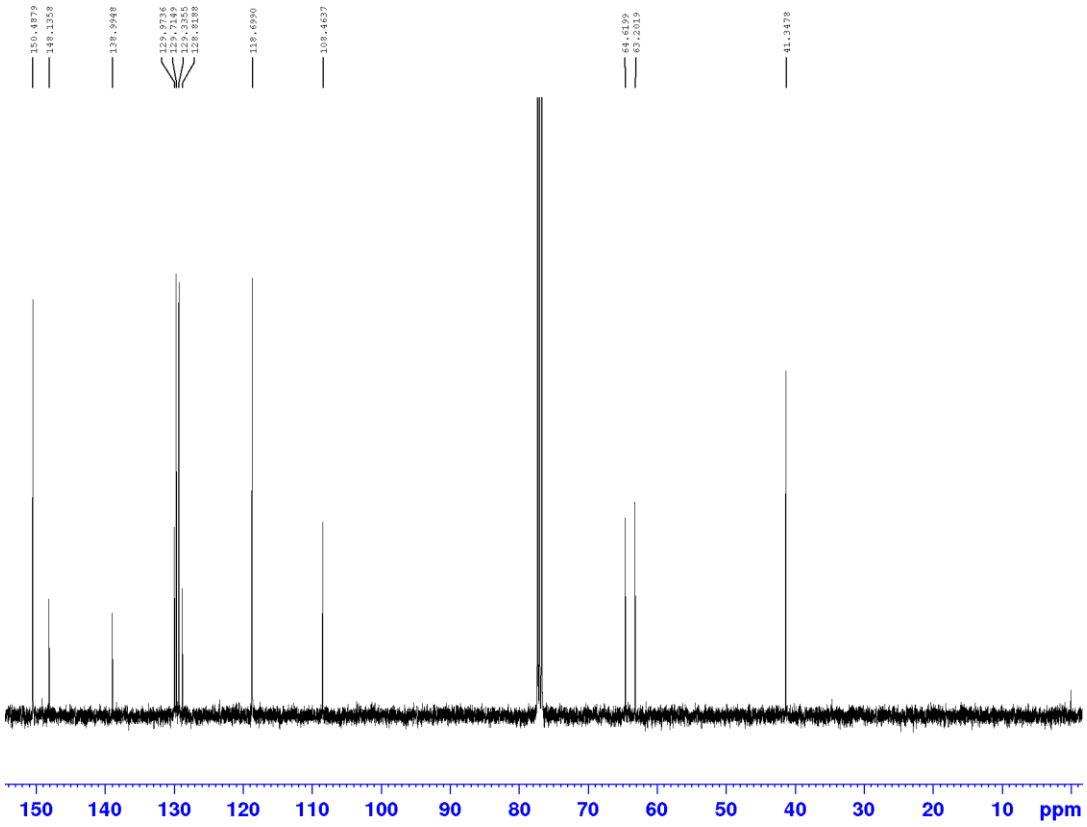


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C16 H15 F2 N4 O6	(M+H)+	398.1033	397.0961	397.096	47.6	-0.23
C19 H18 F3 N O3 S	(M+H)+	398.1033	397.0961	397.0959	47.59	-0.27
C21 H16 F N O6	(M+H)+	398.1033	397.0961	397.0962	47.59	0.28
C25 H19 N S2	(M+H)+	398.1033	397.0961	397.0959	47.55	-0.41
C20 H18 F N4 S2	(M+H)+	398.1033	397.0961	397.0957	47.27	-0.92

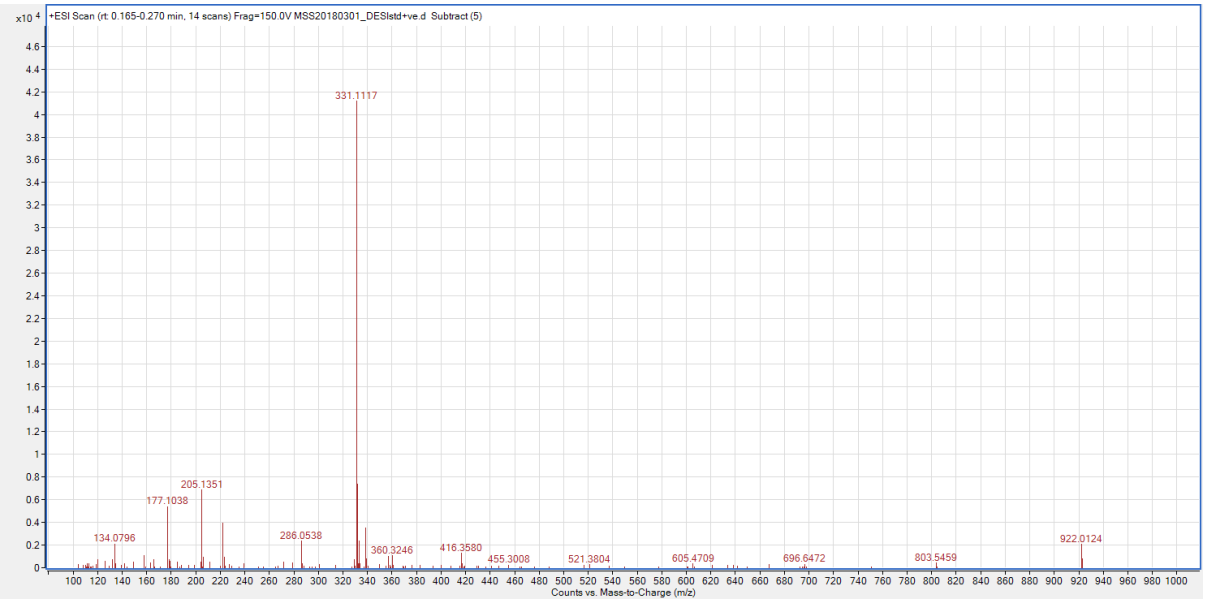
Compound 10i ^{1}H NMR $CDCl_3$



Compound 10i ^{13}C NMR $CDCl_3$

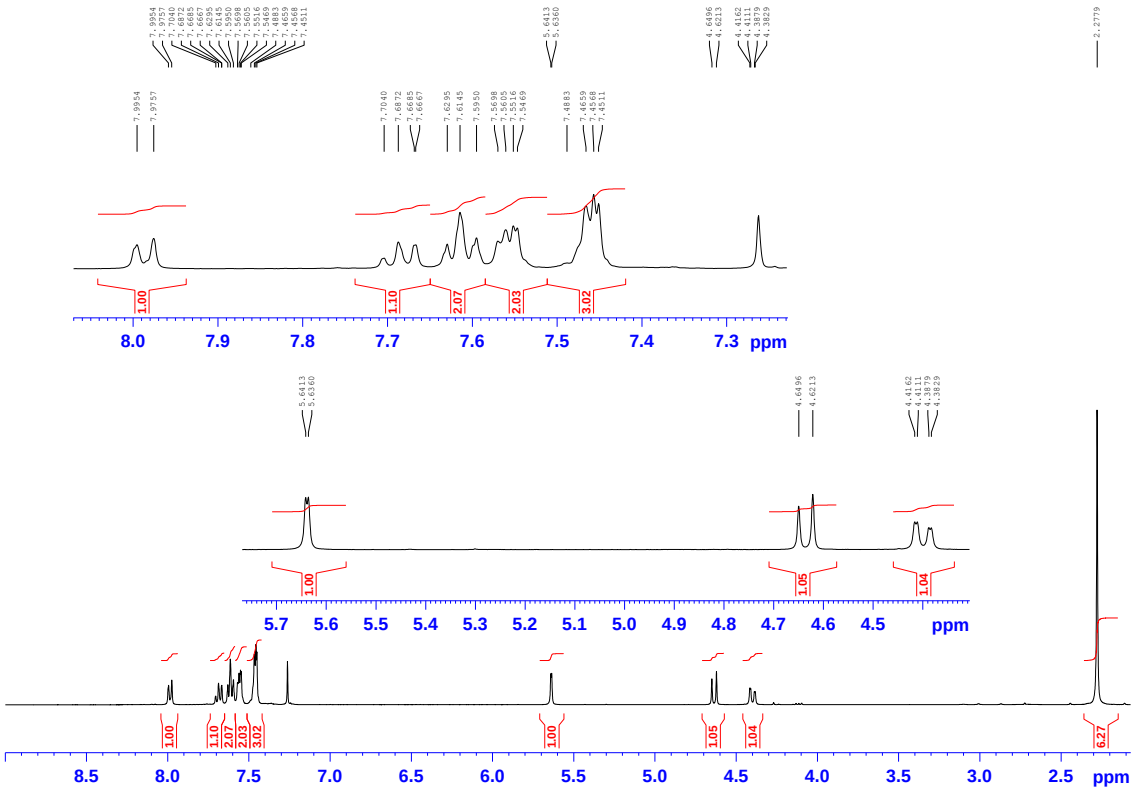


Compound 10i MS

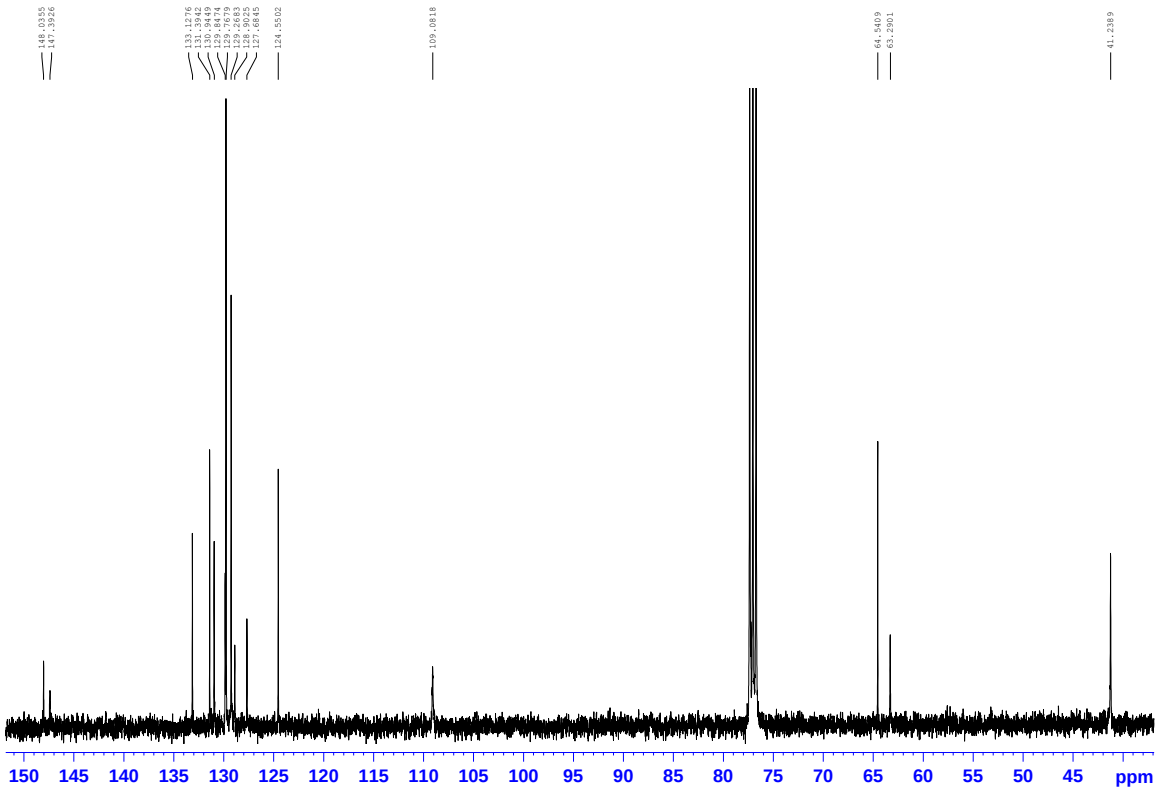


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C17 H18 N2 O3 S	(M+H)+	331.1117	330.1045	330.1038	96.76	-2.12
C20 H16 N3 S	(M+H)+	331.1117	330.1045	330.1065	82.77	6.01
C25 H14 O	(M+H)+	331.1117	330.1041	330.1045	79.2	1.04
C23 H12 N3	(M+H)+	331.1117	330.1042	330.1031	77.99	-3.21
C14 H22 N2 O3 S2	(M+H)+	331.1117	330.1046	330.1072	74.06	7.75
C22 H18 O S	(M+H)+	331.1117	330.1044	330.1078	66.32	10.29

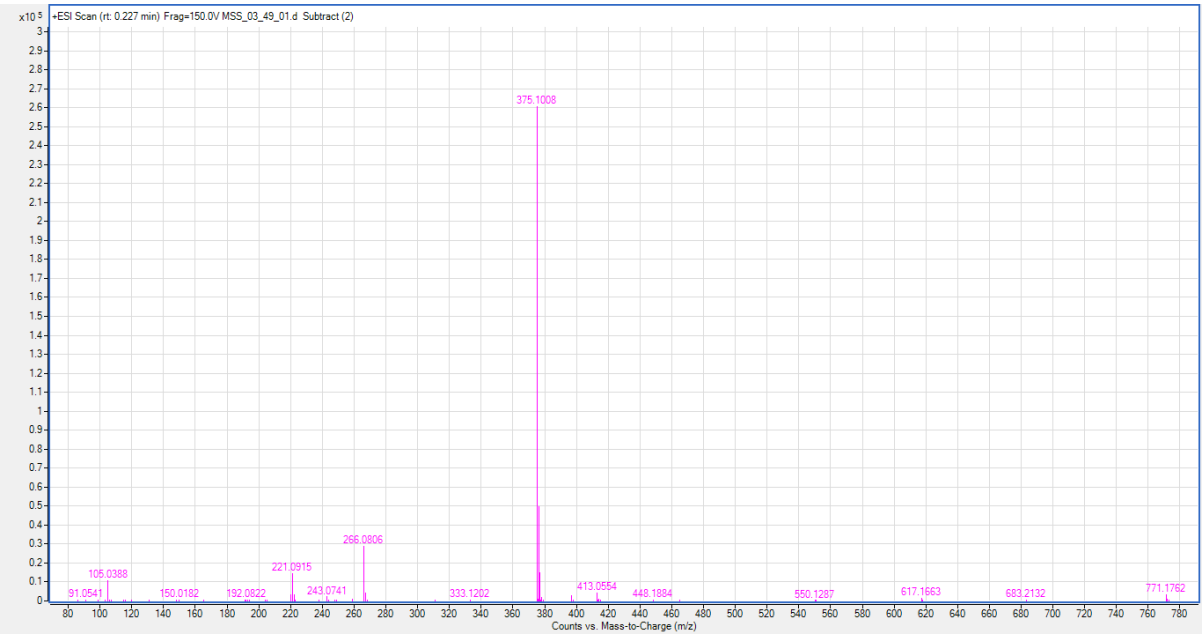
Compound 10j ^{1}H NMR $CDCl_3$



Compound 10j ^{13}C NMR $CDCl_3$

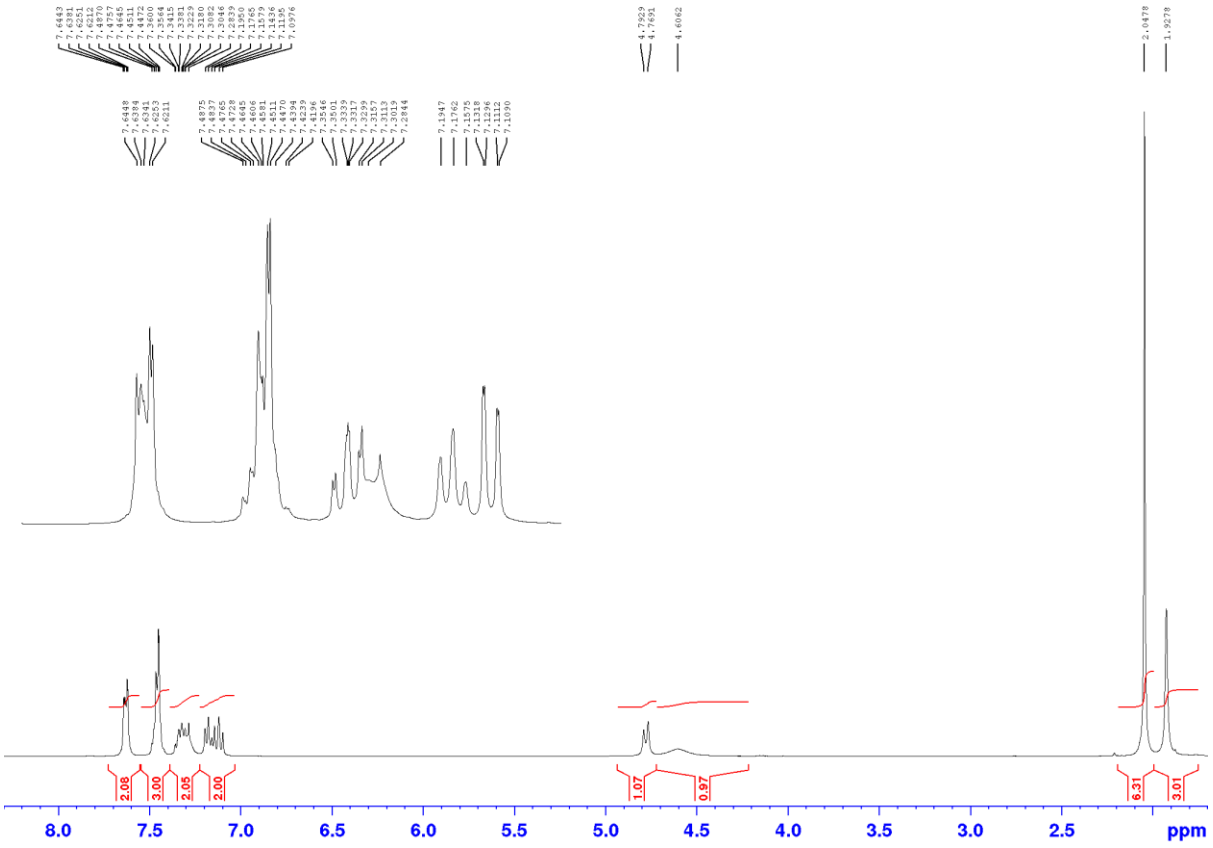


Compound 10j MS

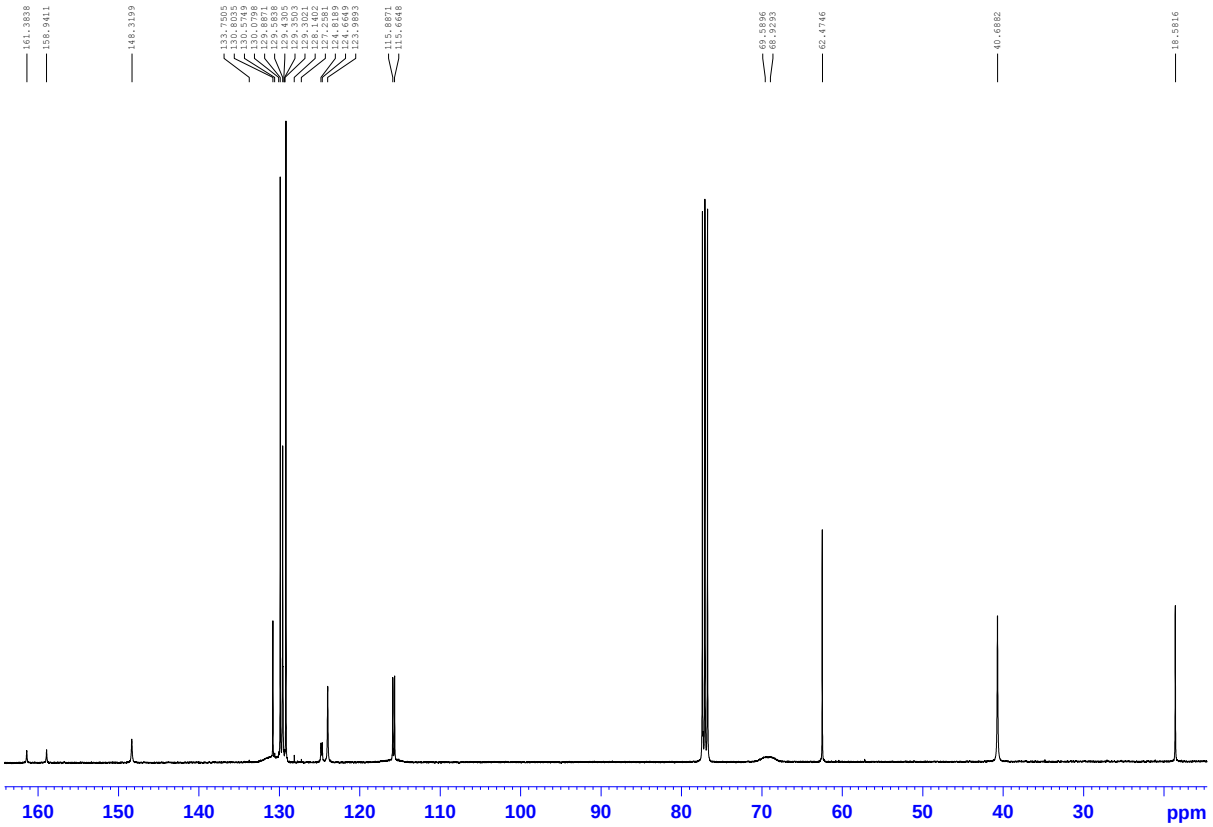


Best	Formula	Species	m/z	Mass	Mass (MFG)	Score (MFG)	Diff (ppm)
▶ ○	C18 H18 N2 O5	(M+H)+	375.1008	374.0935	374.0936	98.2	0.39
○	C18 H15 N O5 S	(M+NH4)+	375.1008	357.0669	357.0671	98.2	0.41
○	C21 H20 O4	(M+K)+	375.1008	336.1375	336.1362	87.91	-4.03

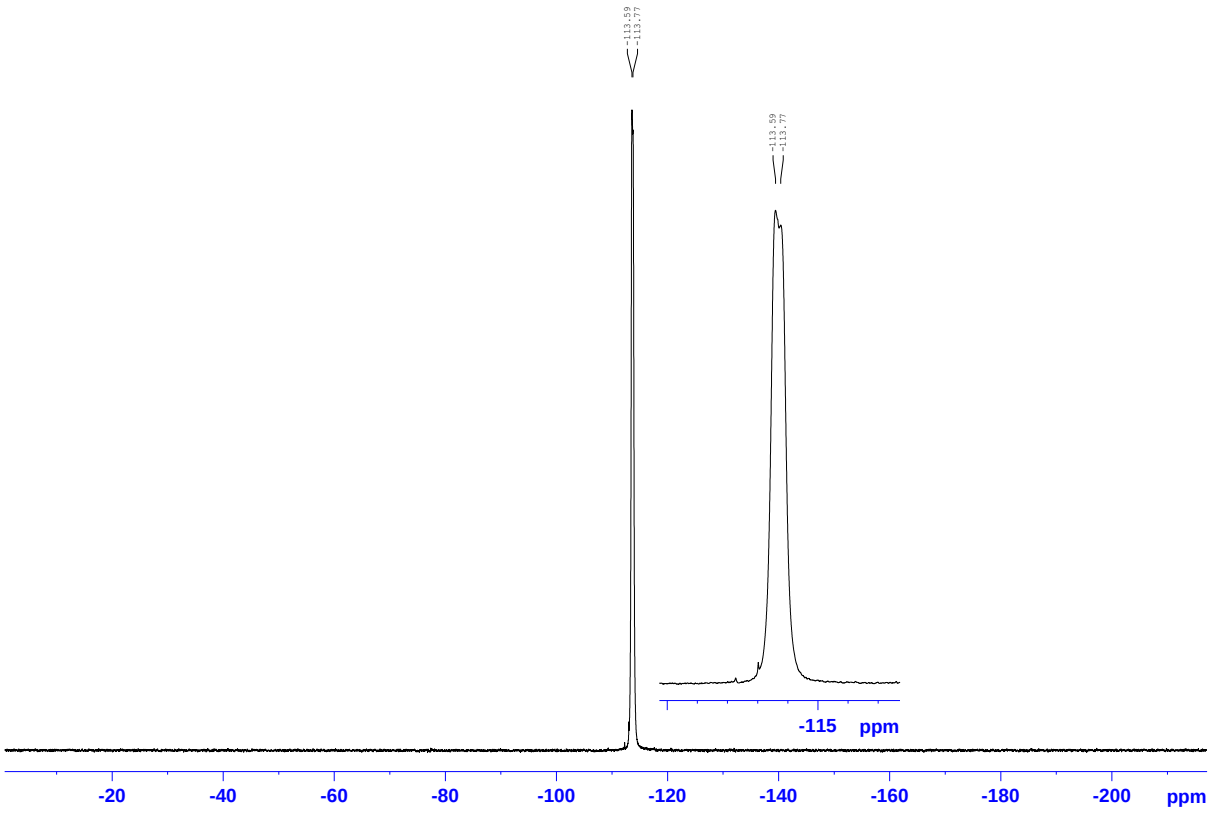
Compound 16 ^{1}H NMR $CDCl_3$ (400MHz, 295K, ^{19}F decoupled as insert)



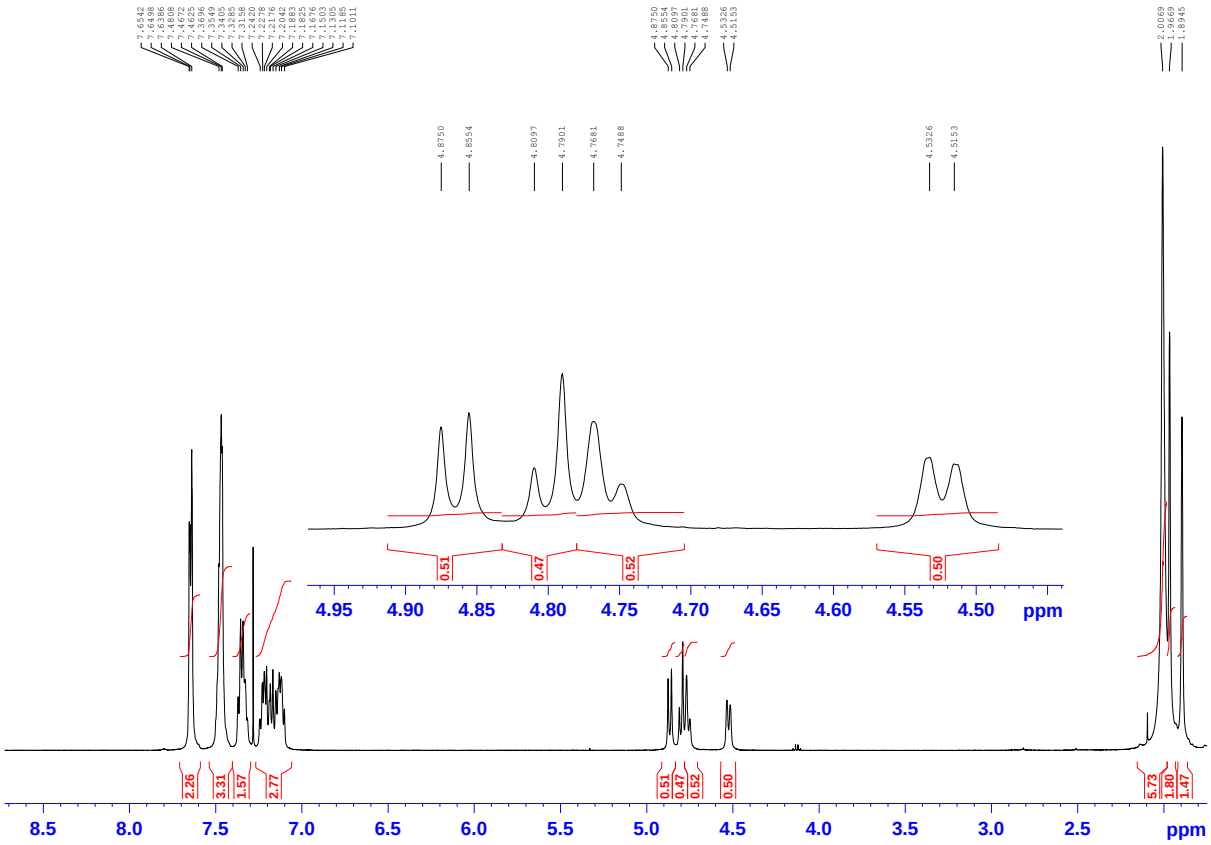
Compound 16 ^{13}C NMR $CDCl_3$ (400MHz, 295K)



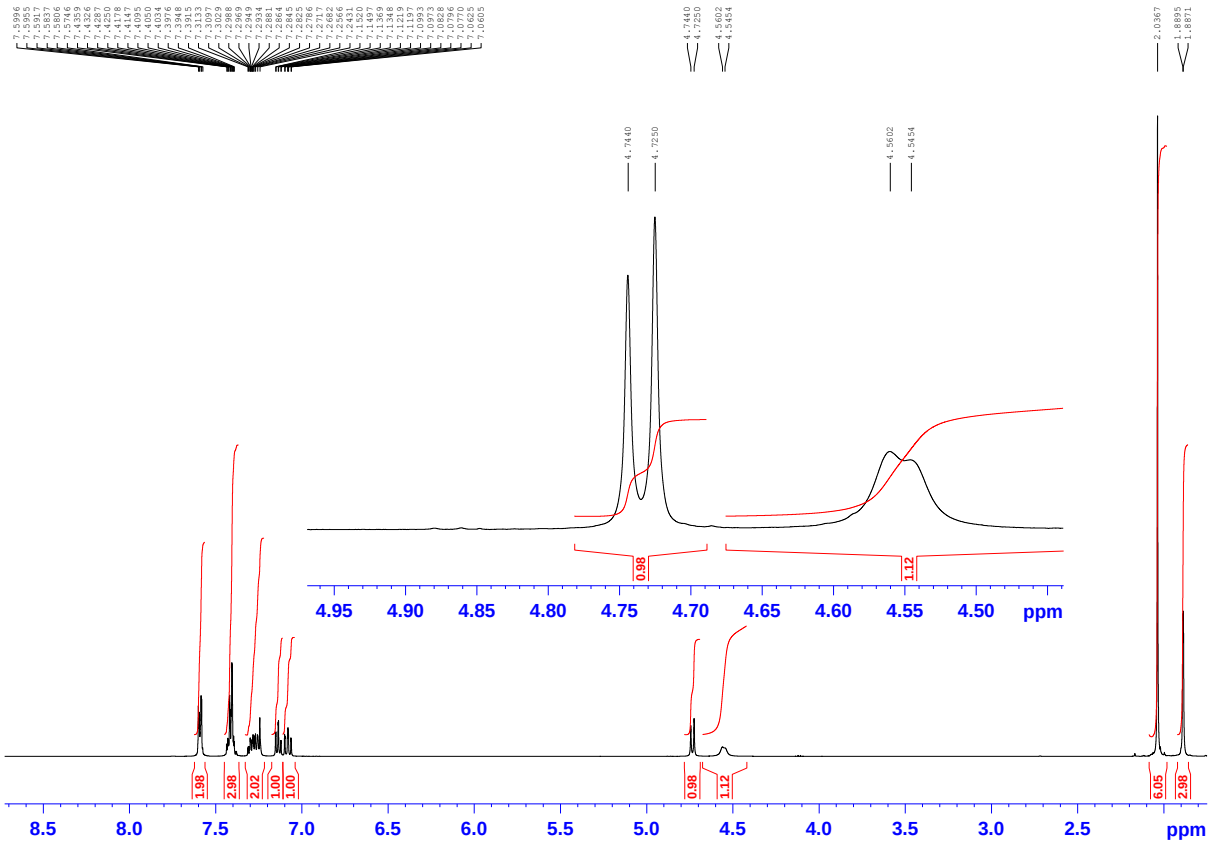
Compound 16 ^{19}F NMR $CDCl_3$ (400MHz, 295K)



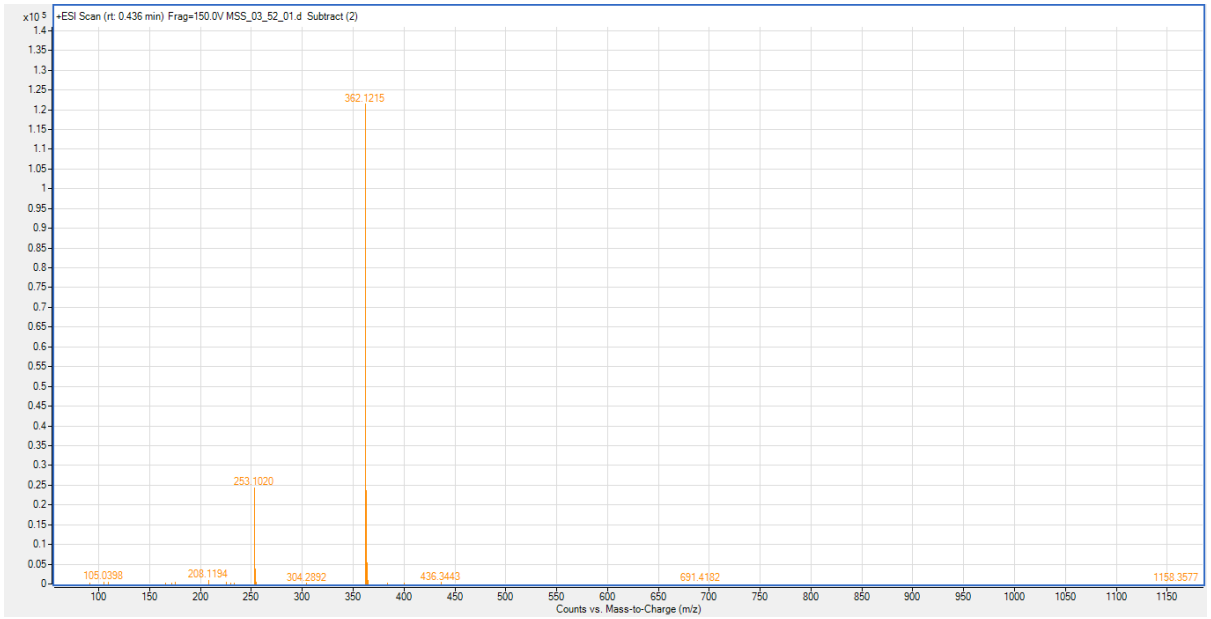
Compound 16 ^{1}H NMR $CDCl_3$ (500MHz, 233K)



Compound 16 ^{1}H NMR $CDCl_3$ (500MHz, 323K)

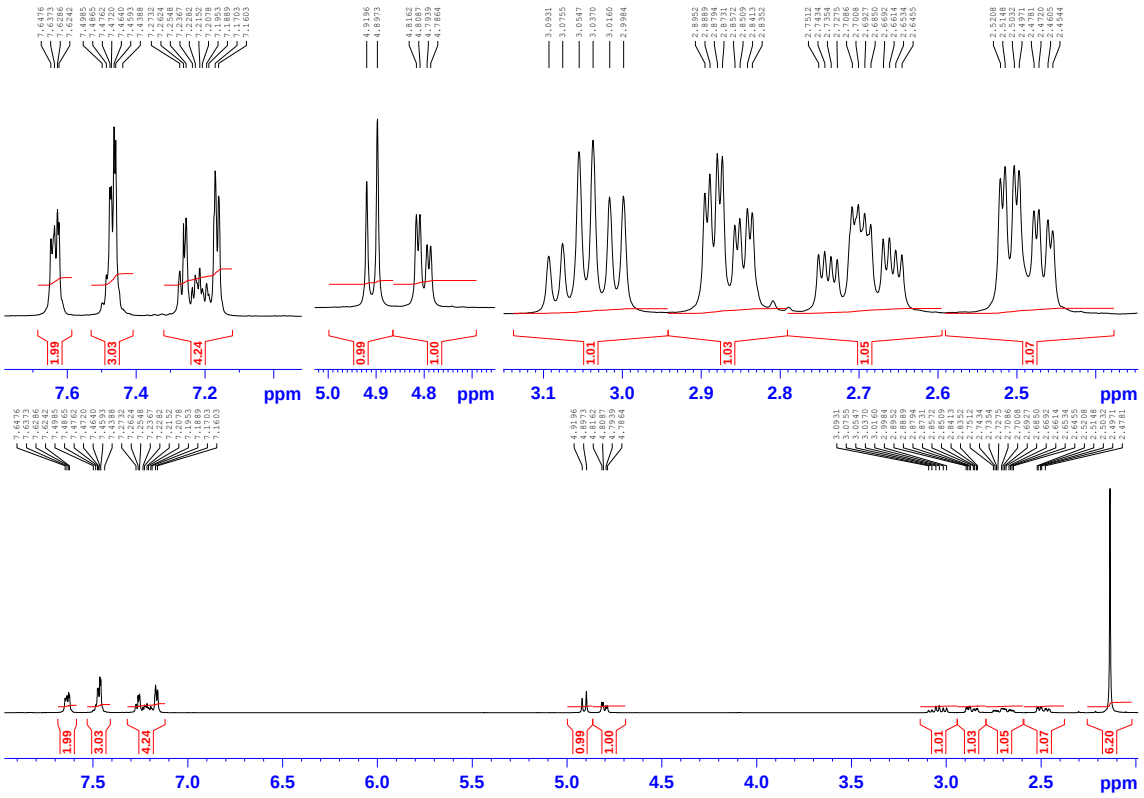


Compound 16 MS

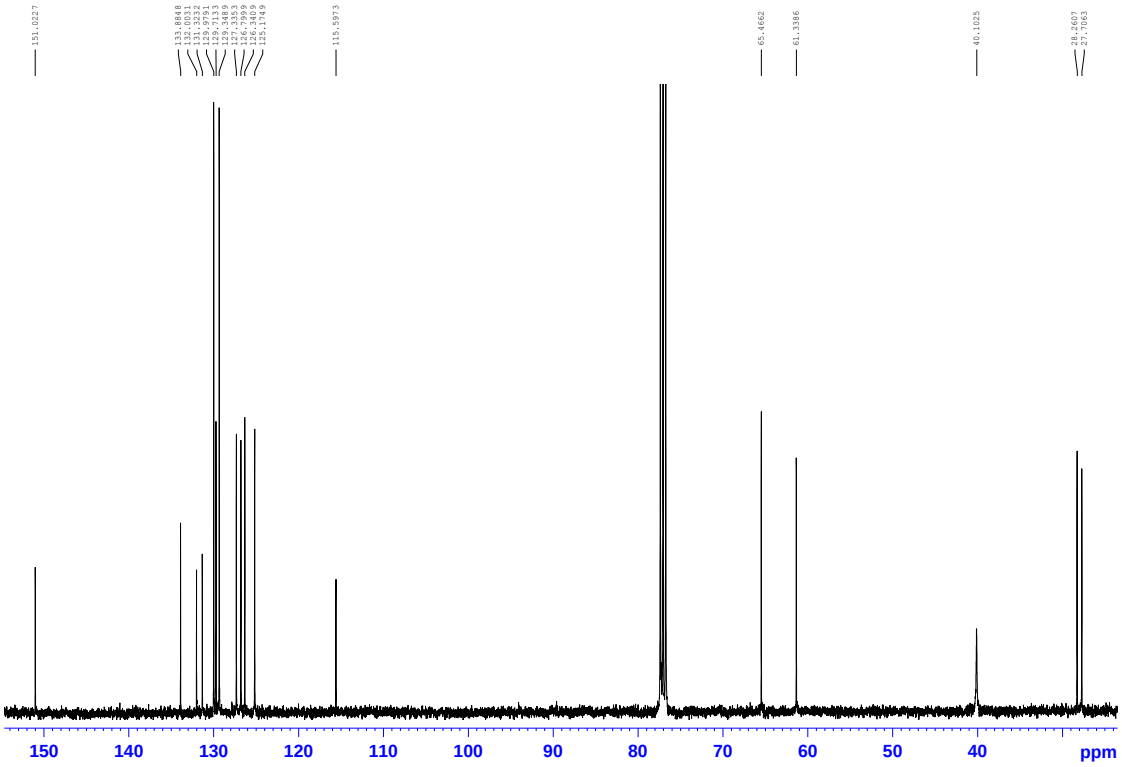


Best	Formula	Species	m/z	Mass	Mass (MFG)	Score (MFG)	Diff (ppm)
▶	C19 H20 F N O3 S	(M+H)+	362.1215	361.1143	361.1148	95.88	1.24
	C19 H17 F O3 S	(M+NH4)+	362.1215	344.0878	344.0882	95.88	1.3
	C20 H20 F N2 S	(M+Na)+	362.1215	339.1324	339.1331	94.15	2.06
	C14 H23 F2 N O4	(M+Na)+	362.1215	339.1324	339.1316	93.19	-2.53

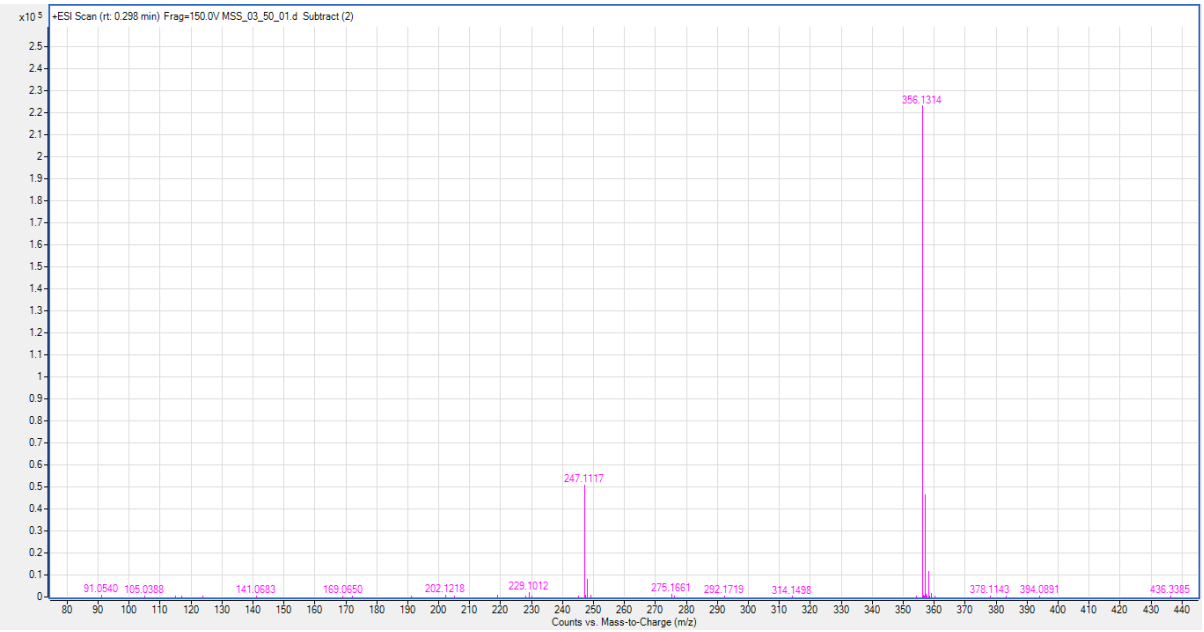
Compound 19 ^{1}H NMR $CDCl_3$



Compound 19 ^{13}C NMR $CDCl_3$

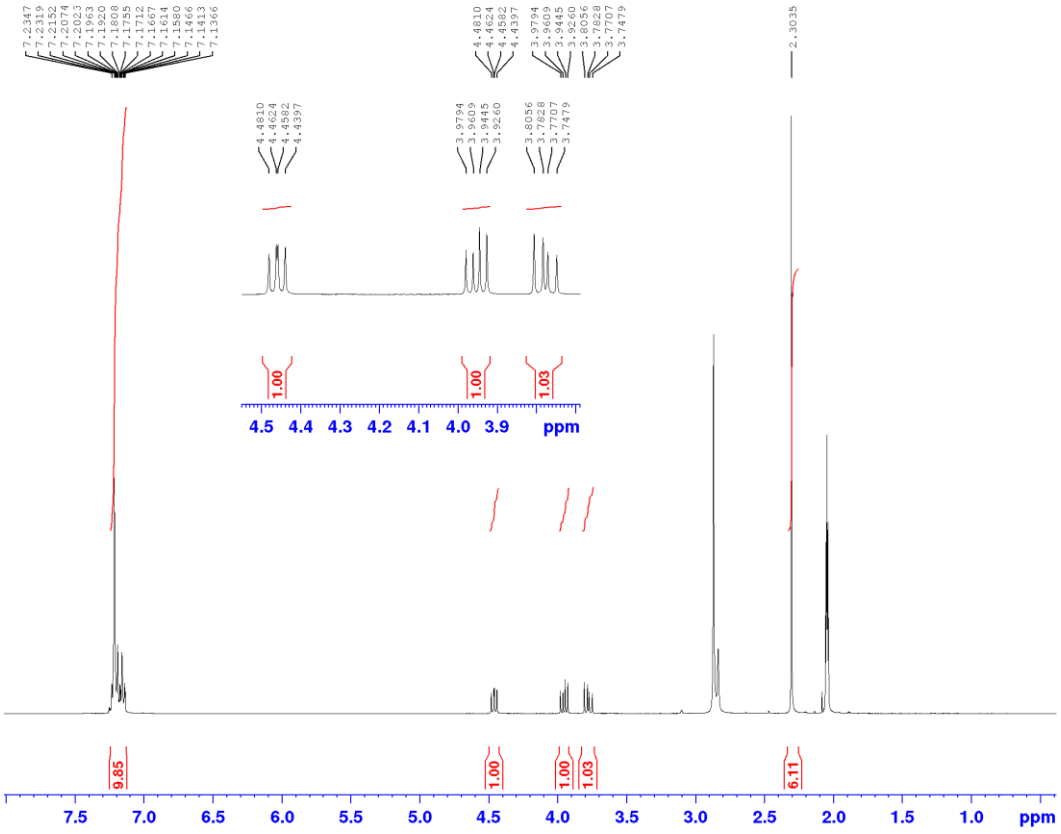


Compound 19 MS

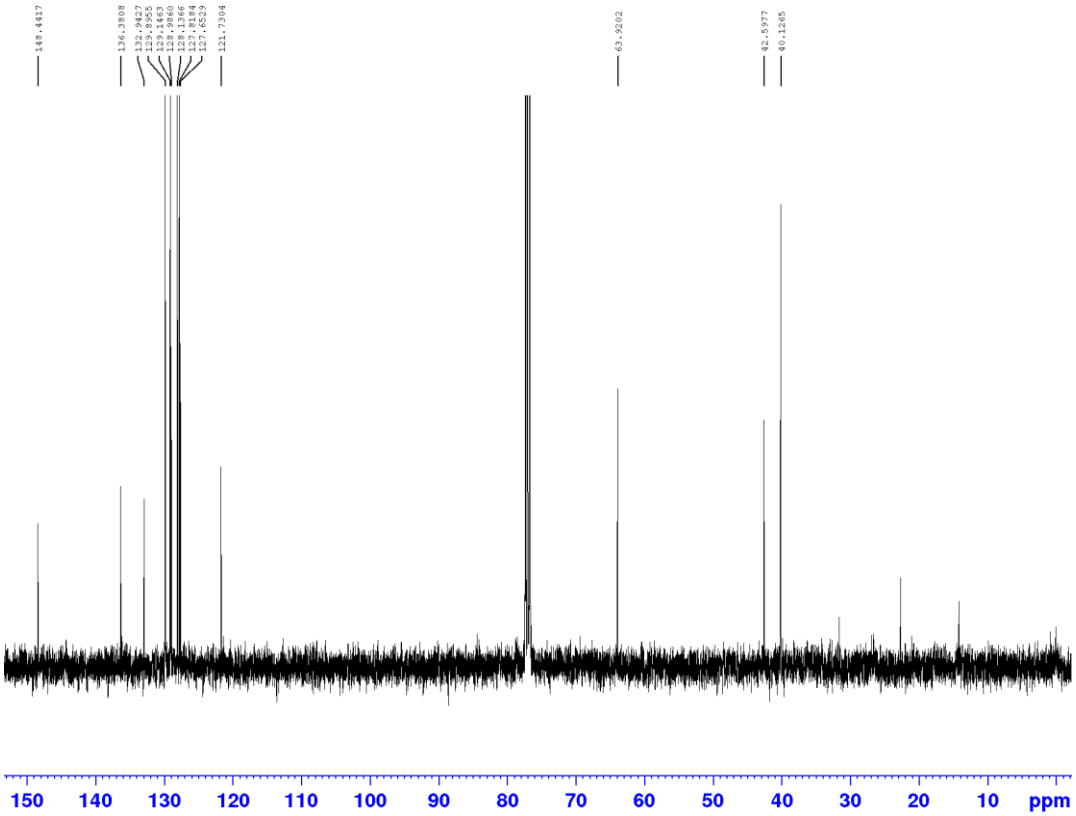


Best	Formula	Species	m/z	Mass	Mass (MFG)	Score (MFG)	Diff (ppm)
●	C20 H21 N O3 S	(M+H)+	356.1314	355.1241	355.1242	97.93	0.23
○	C20 H18 O3 S	(M+NH4)+	356.1314	338.0976	338.0977	97.93	0.25
○	C21 H21 N2 S	(M+Na)+	356.1314	333.1422	333.1425	96.78	1

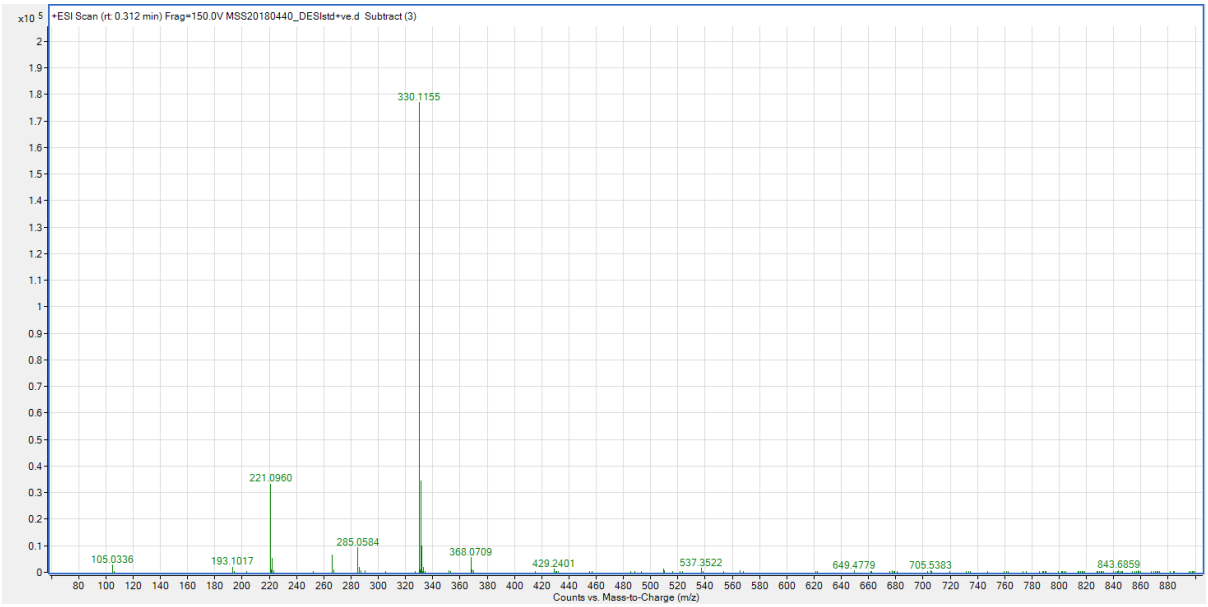
Compound 12a ^{1}H NMR d$_6$-AcMe



Compound 12a ^{13}C NMR $CDCl_3$

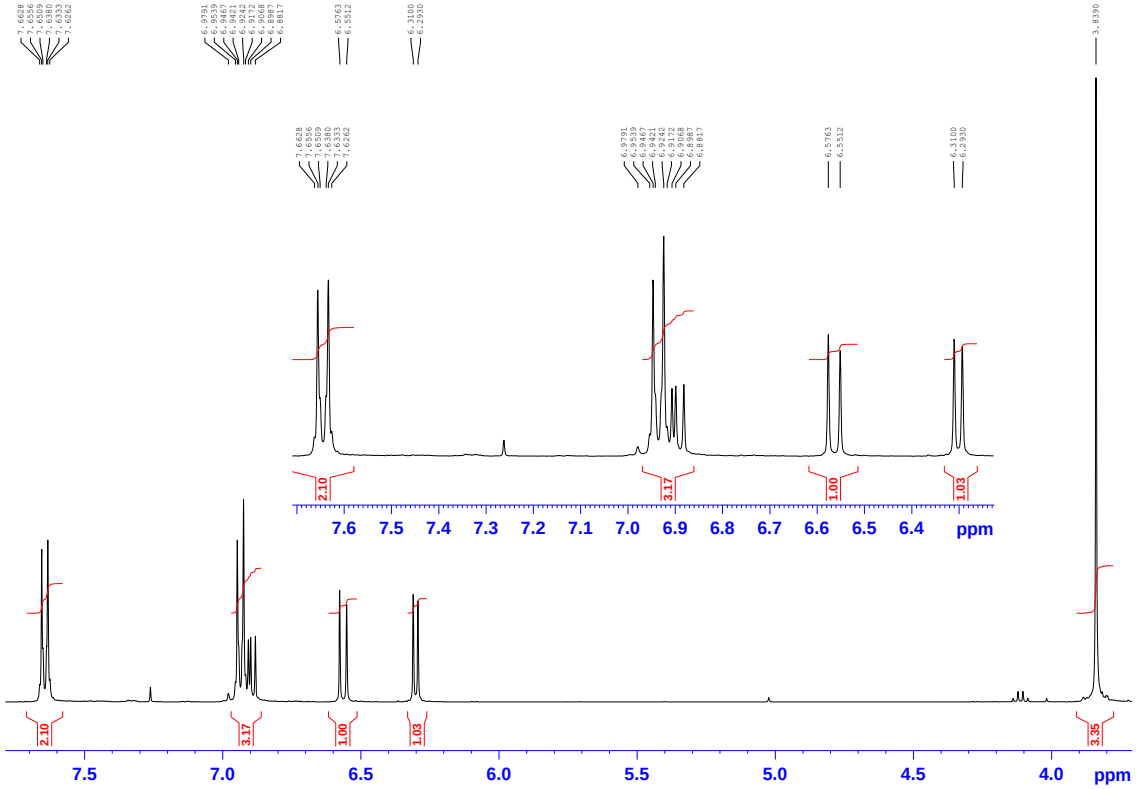


Compound 12a MS

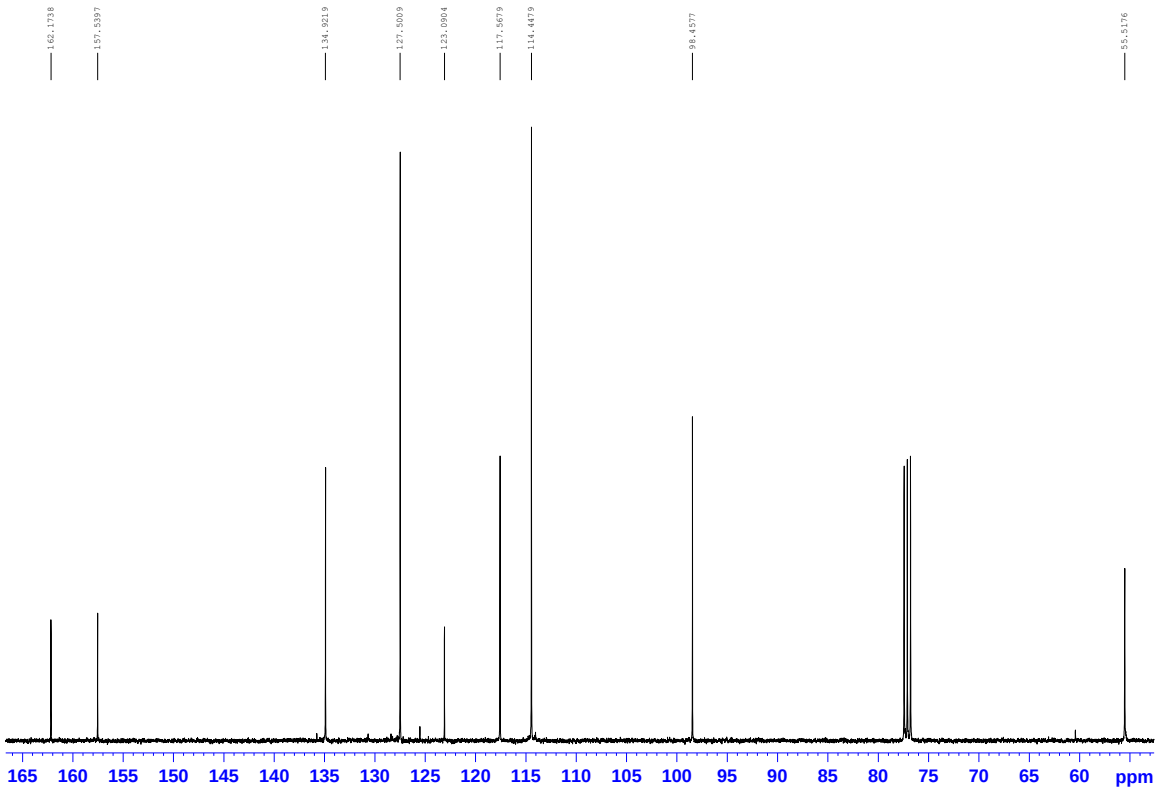


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C10 H15 N7 O6	(M+H)+	330.1155	329.1082	329.1084	47.54	0.49
C18 H19 N O3 S	(M+H)+	330.1155	329.1082	329.1086	47.24	1.04
C24 H13 N2	(M+H)+	330.1155	329.1082	329.1079	47.23	-1.06
C16 H17 N4 O2 S	(M+H)+	330.1155	329.1082	329.1072	44.51	-3.04
C9 H19 N3 O10	(M+H)+	330.1155	329.1082	329.107	43.37	-3.58
C12 H17 N4 O7	(M+H)+	330.1155	329.1082	329.1097	40.88	4.57
C15 H21 O6 S	(M+H)+	330.1155	329.1082	329.1059	32.94	-7.1
C14 H15 N7 O S	(M+H)+	330.1155	329.1082	329.1059	32.88	-7.12
C13 H13 N8 O3	(M+H)+	330.1155	329.1082	329.1111	27.62	8.63
C14 H19 N O8	(M+H)+	330.1155	329.1082	329.1111	27.57	8.65
C21 H17 N2 S	(M+H)+	330.1155	329.1082	329.1112	25.69	9.19
C21 H15 N O3	(M+H)+	330.1155	329.1082	329.1052	25.65	-9.2
C13 H19 N3 O5 S	(M+H)+	330.1155	329.1082	329.1045	19.09	-11.18
C12 H13 N10 S	(M+H)+	330.1155	329.1082	329.1045	19.04	-11.2

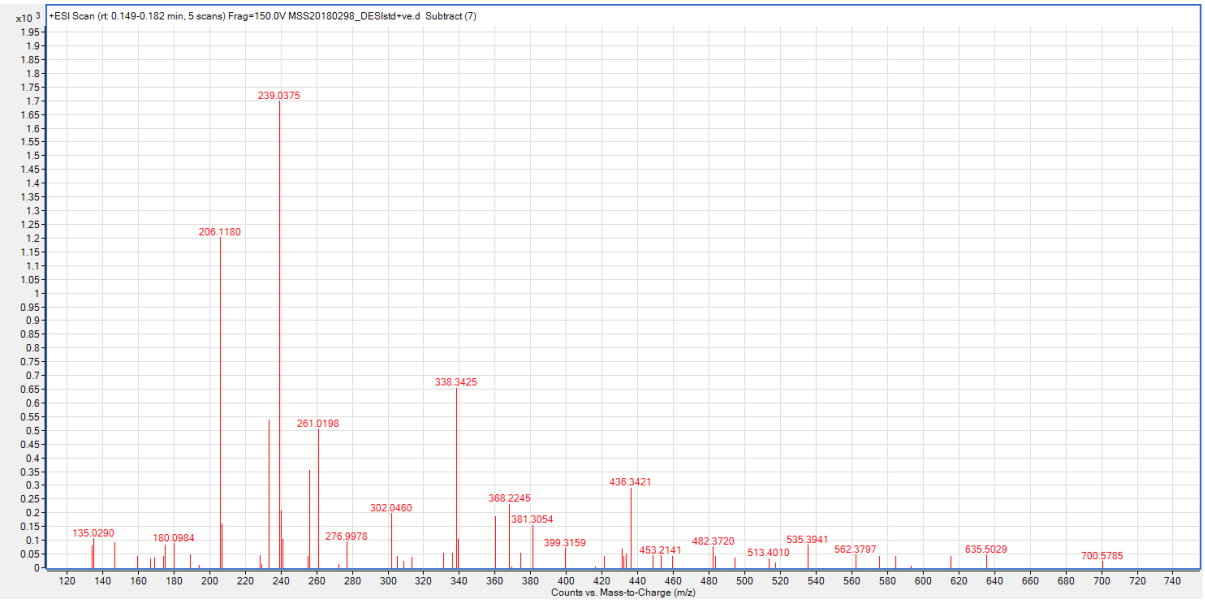
Compound 13b ^{1}H NMR $CDCl_3$



Compound 13b ^{13}C NMR $CDCl_3$

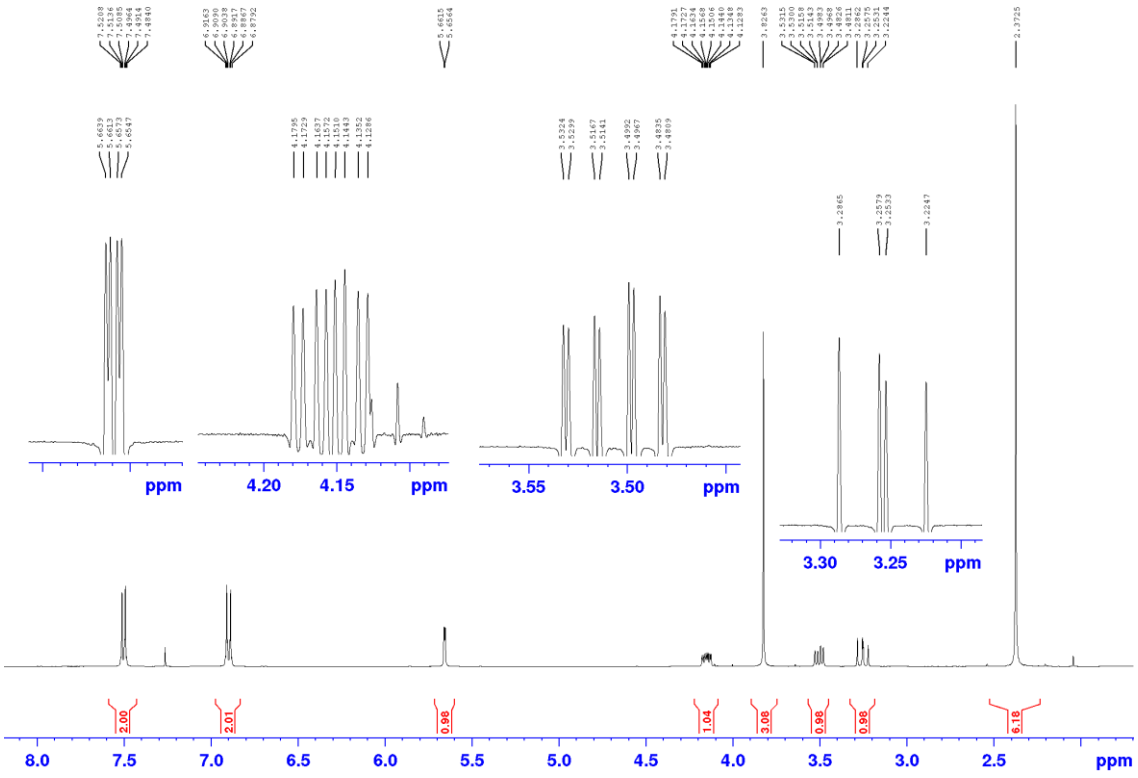


Compound 13b MS

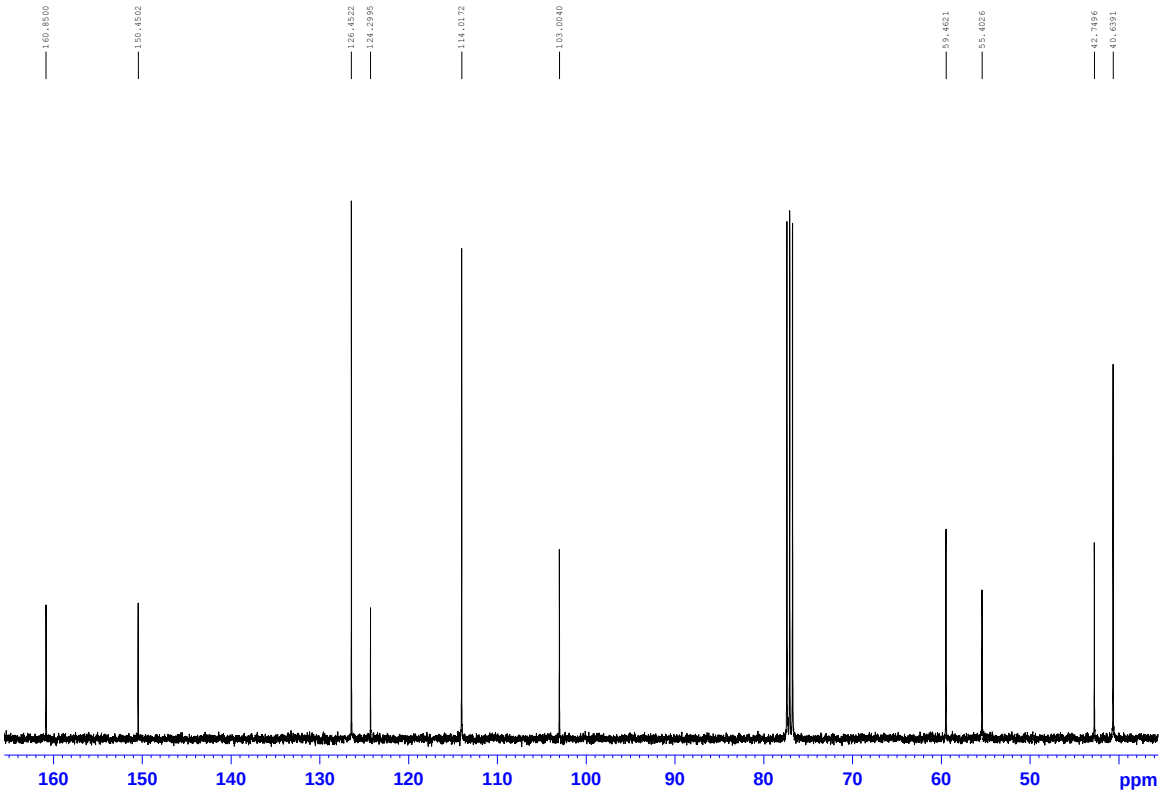


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C11 H10 O4 S	(M+H)+	239.0375	238.03	238.03	94.52	0.1
C17 H4 N O	(M+H)+	239.0375	238.0295	238.0293	73.91	-1.04
C14 H8 N O S	(M+H)+	239.0375	238.03	238.0327	67.92	11.32
C8 H14 O4 S2	(M+H)+	239.0375	238.0301	238.0334	61.33	13.84

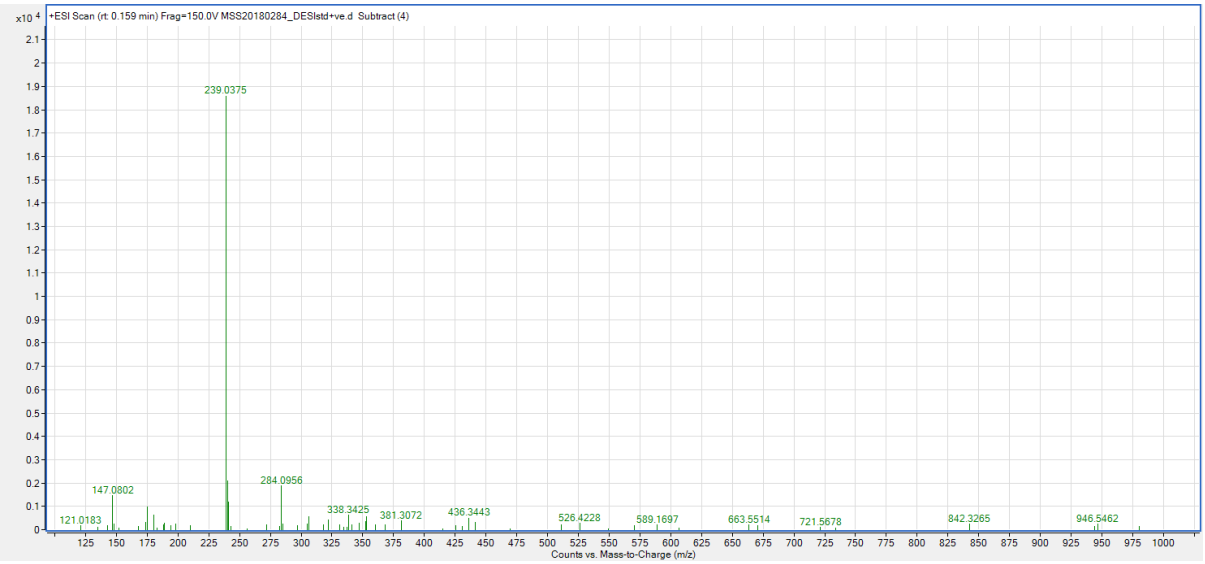
Compound 12b ^{1}H NMR $CDCl_3$



Compound 12b ^{13}C NMR $CDCl_3$

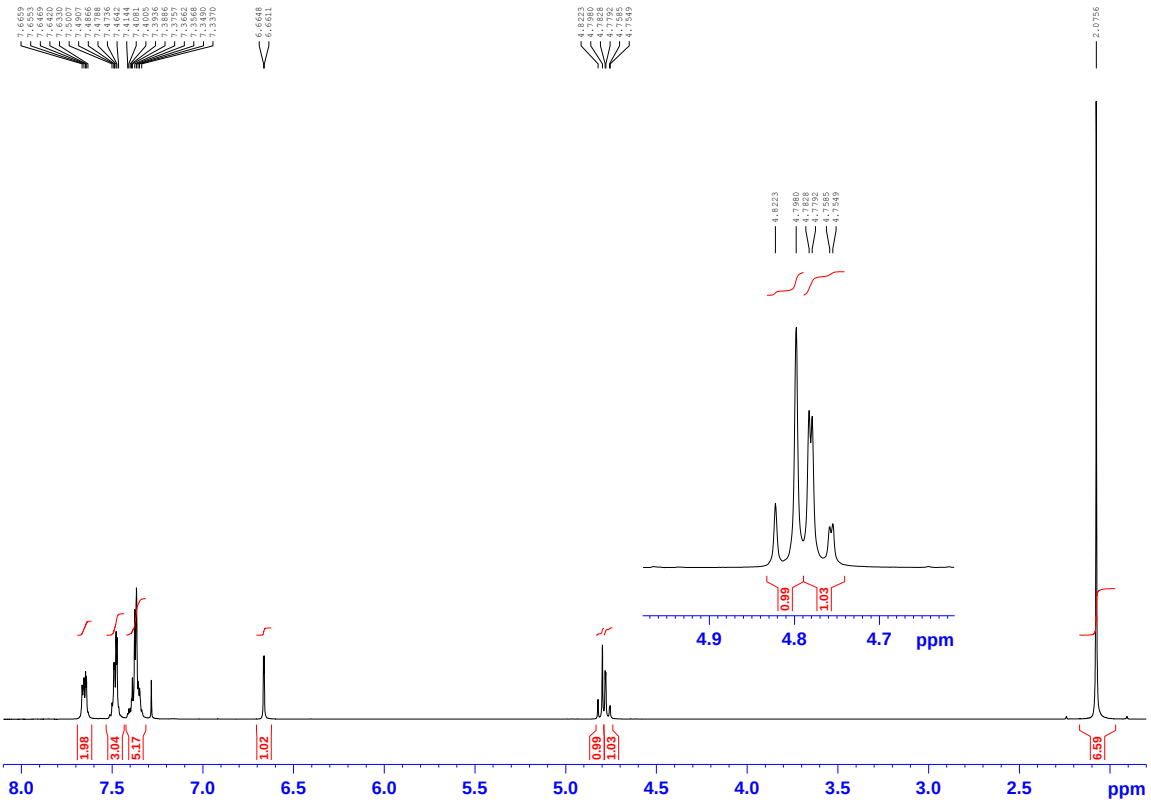


Compound 12b MS

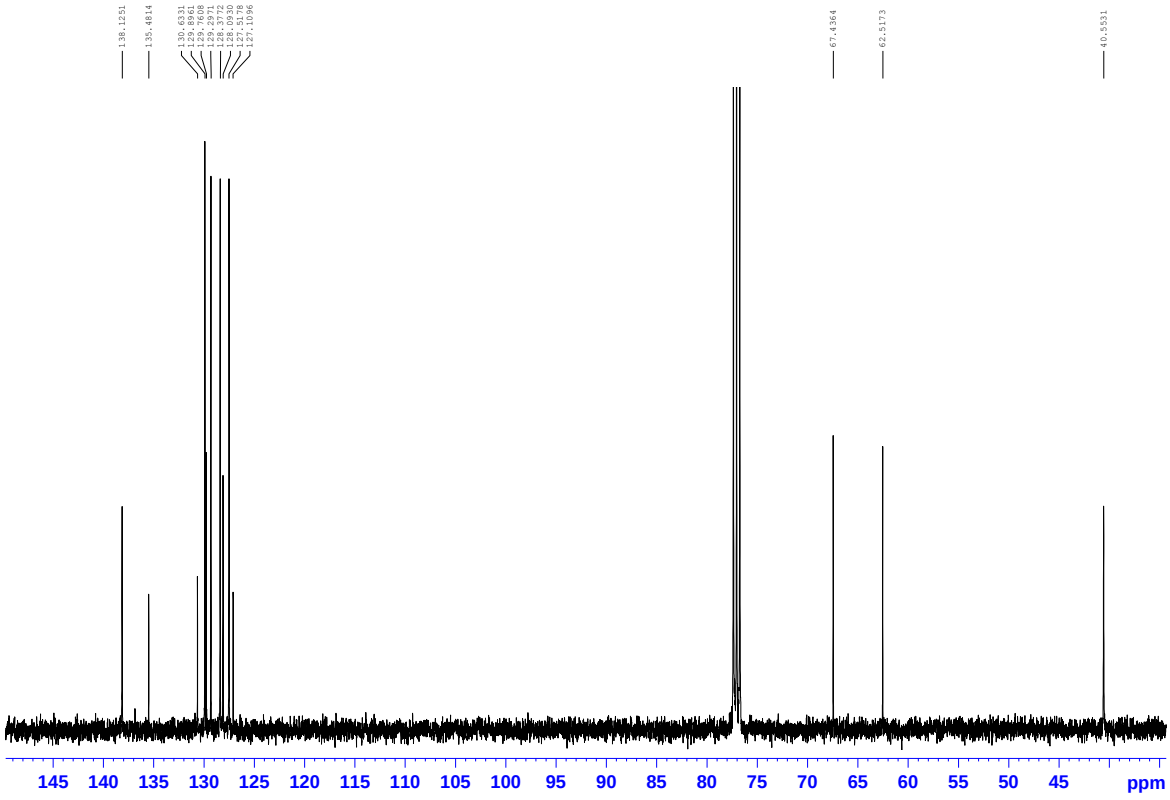


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C13 H17 N O4 S	(M+H)+	284.0956	283.0882	283.0878	73.91	-1.45
C19 H11 N2 O	(M+H)+	284.0956	283.0882	283.0871	66.44	-3.85
C16 H15 N2 O S	(M+H)+	284.0956	283.0882	283.0905	55.68	7.99
C10 H19 O7 S	(M+H)+	284.0956	283.0882	283.0851	49.5	-10.87
C10 H21 N O4 S2	(M+H)+	284.0956	283.0883	283.0912	43.47	10.35

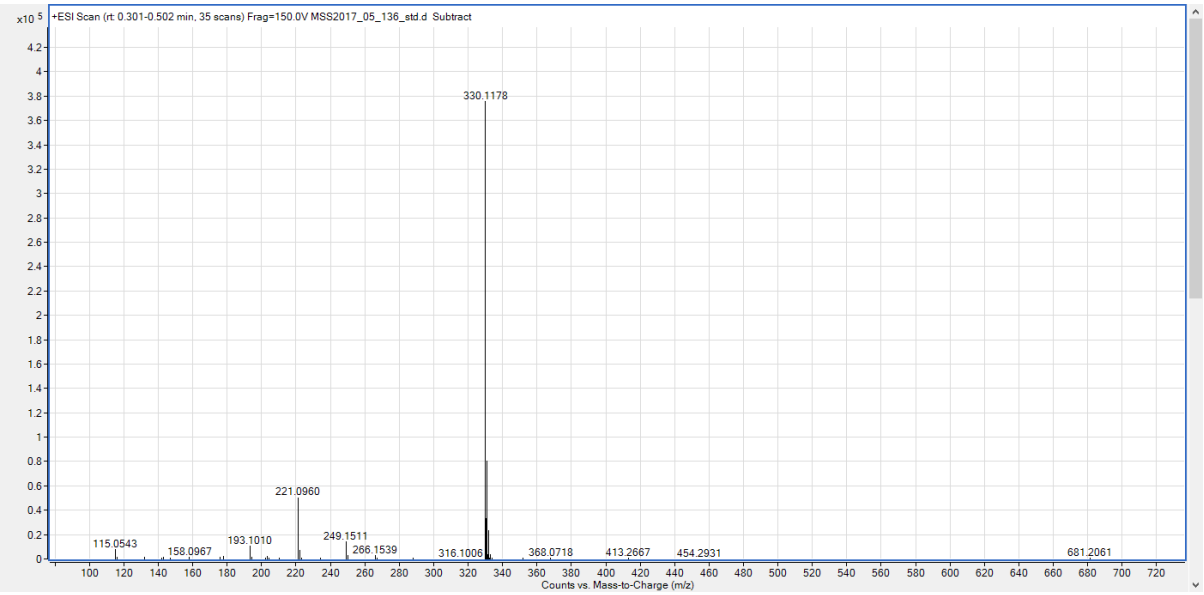
Compound 22 ^{1}H NMR $CDCl_3$



Compound 22 ^{13}C NMR $CDCl_3$

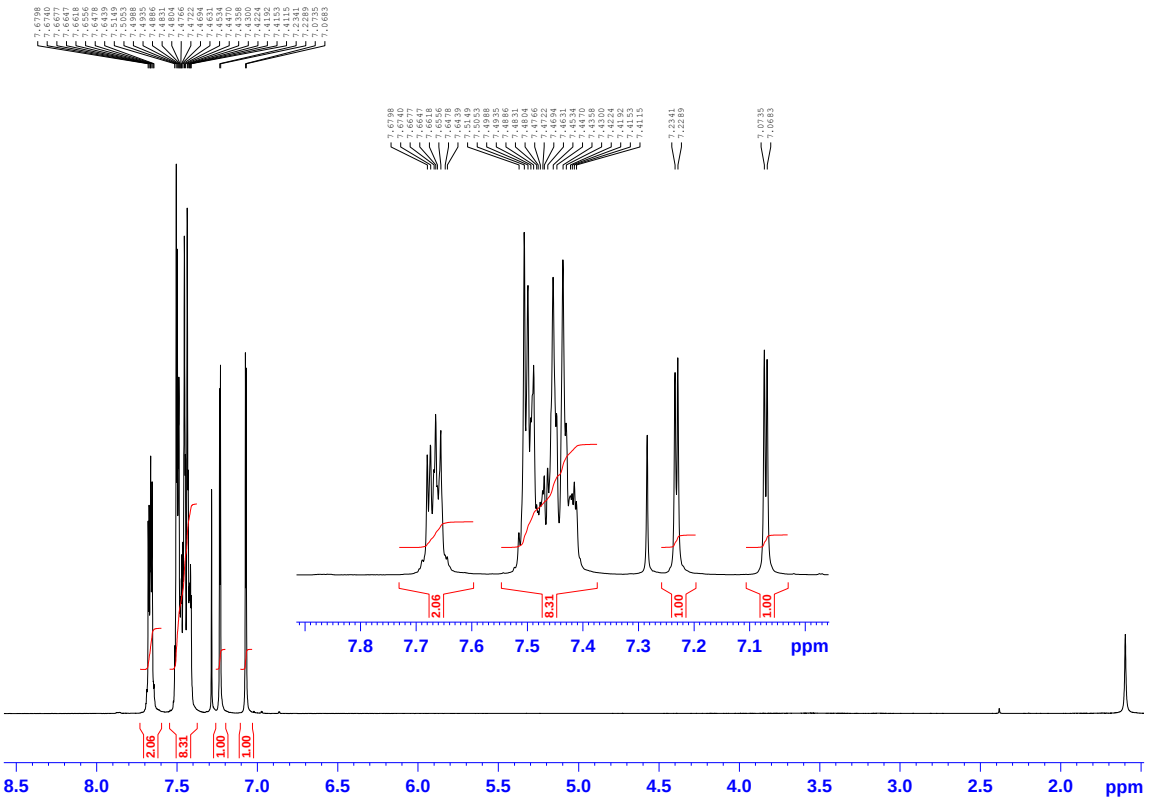


Compound 22 MS

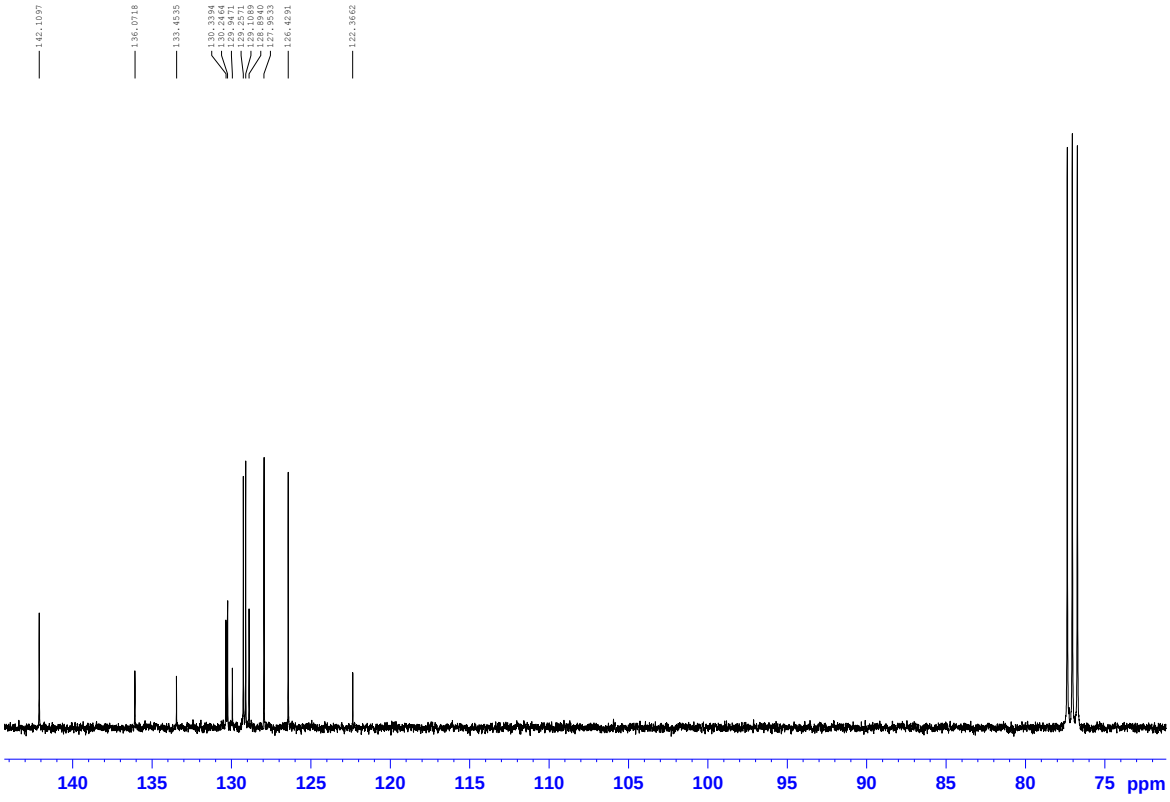


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C21 H17 N2 S	(M+H)+	330.1178	329.1101	329.1112	88.3	3.53
C18 H19 N O3 S	(M+H)+	330.1178	329.1101	329.1086	86.83	-4.61
C12 H25 O6 S2	(M+H)+	330.1178	329.1102	329.1093	78.16	-2.85
C15 H23 N O3 S2	(M+H)+	330.1178	329.1102	329.1119	77.92	5.26
C24 H13 N2	(M+H)+	330.1178	329.1097	329.1079	68.79	-5.68
C17 H17 N2 O5	(M+H)+	330.1178	329.1098	329.1137	53.45	12.03

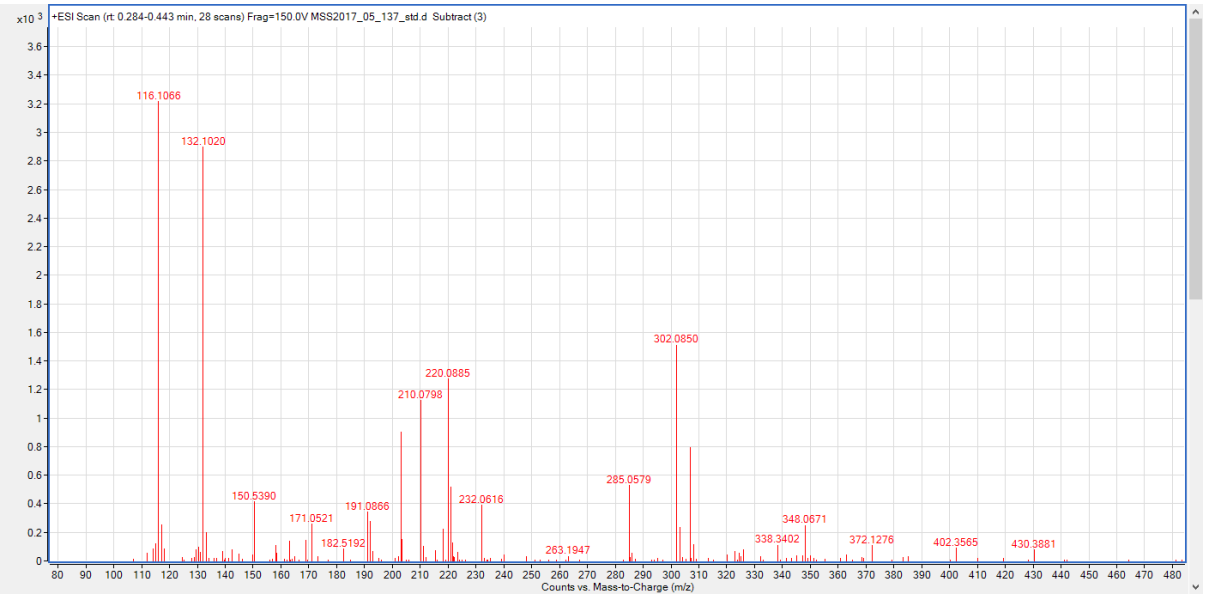
Compound 23 ^{1}H NMR $CDCl_3$



Compound 23 ^{13}C NMR $CDCl_3$

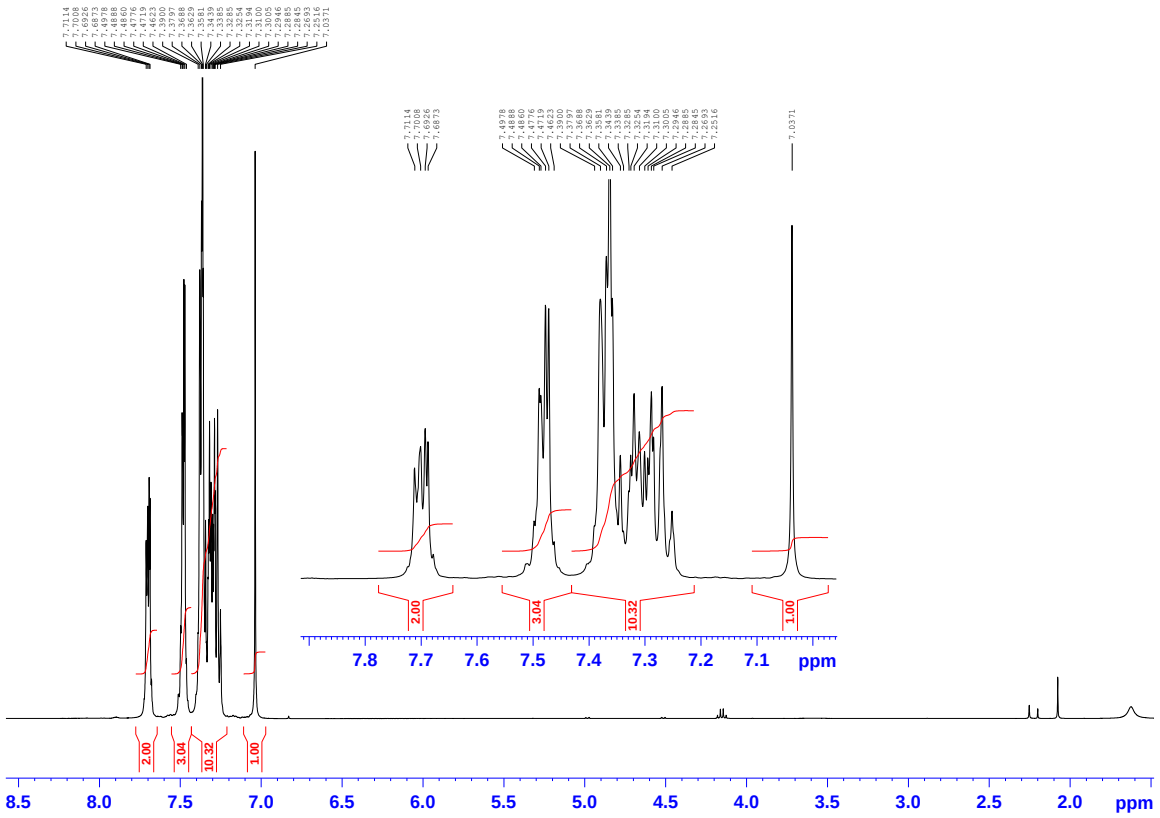


Compound 23 MS

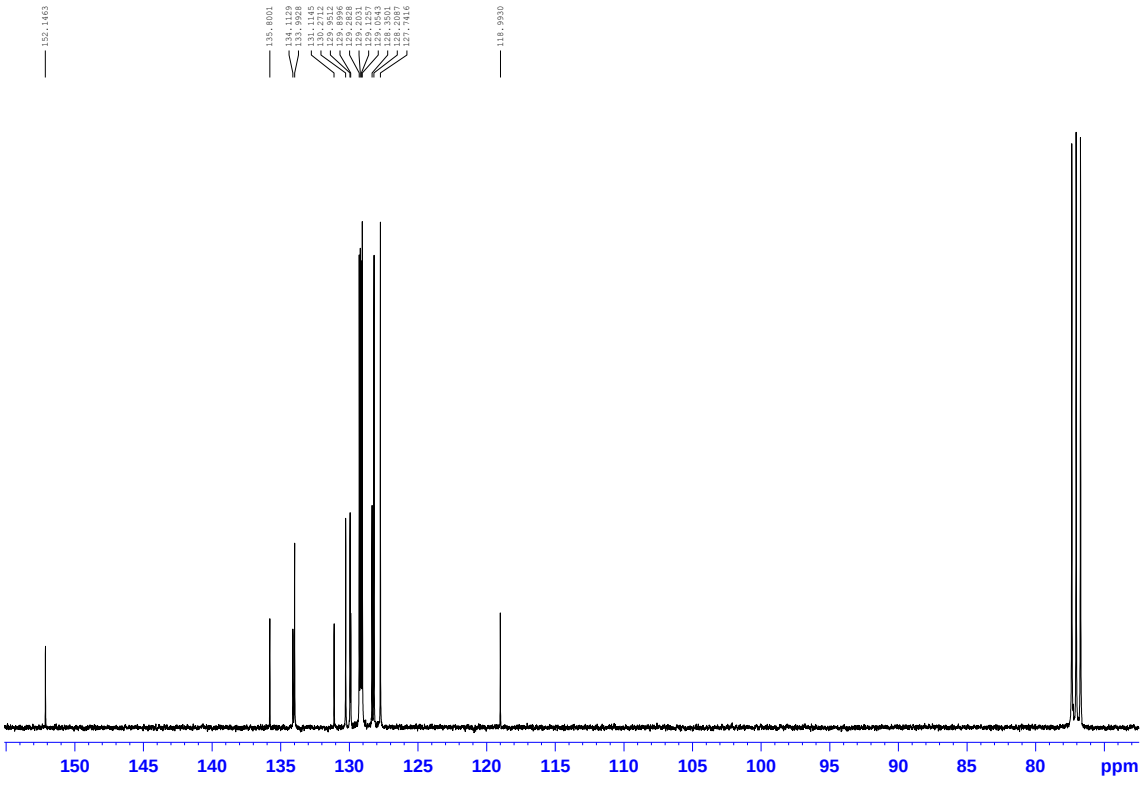


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C16 H12 O3 S	(M+NH4)+	302.0850	284.0511	284.0507	91.06	-1.33
C13 H16 O3 S2	(M+NH4)+	302.0850	284.0511	284.0541	60.46	10.35

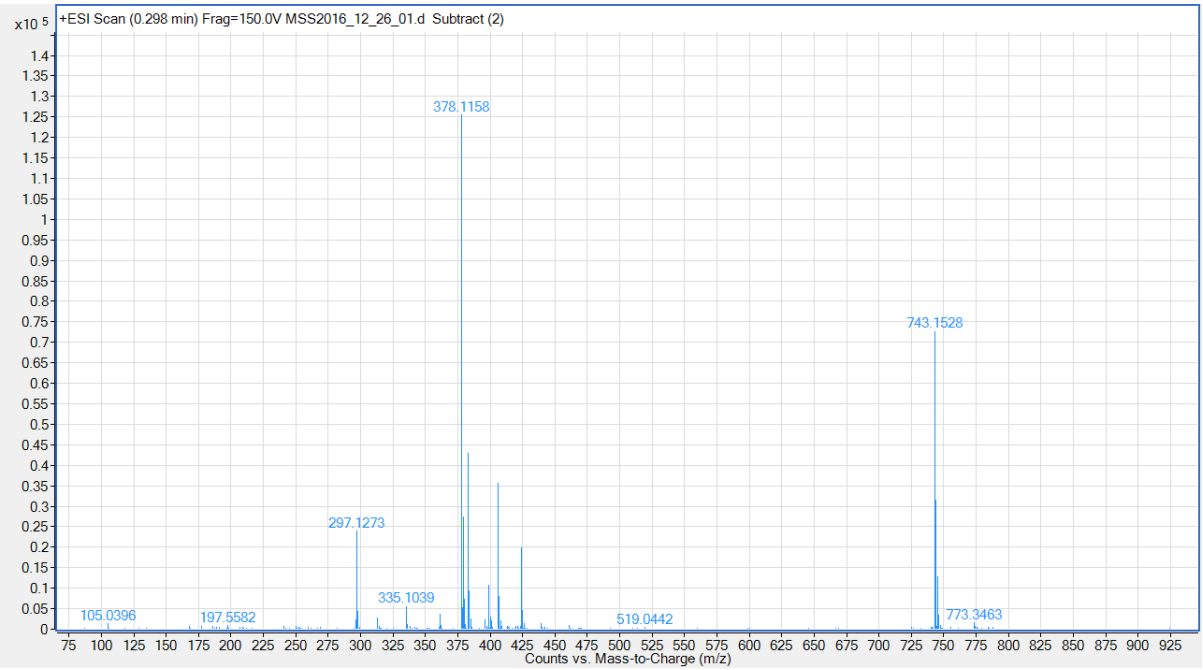
Compound 11a ^{1}H NMR $CDCl_3$



Compound 11a ^{13}C NMR $CDCl_3$

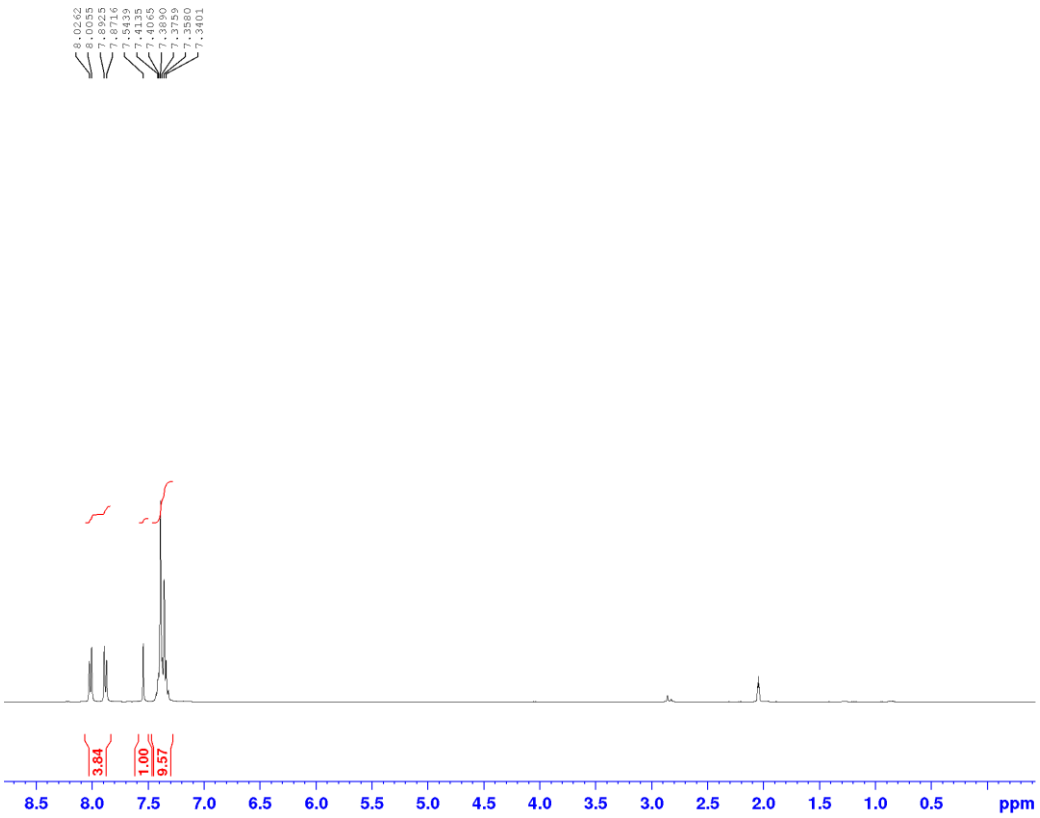


Compound 11a MS

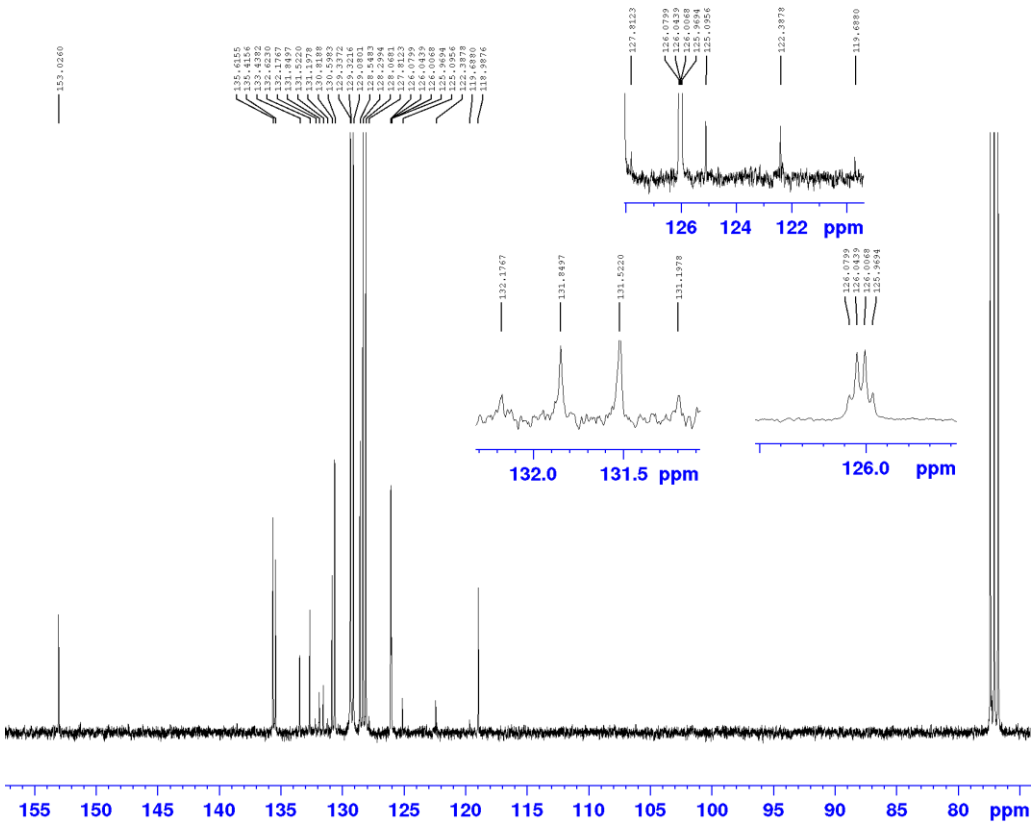


Best	Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
▶	C22 H16 O3 S	(M+NH4)+	378.1158	360.082	360.082	97.29	0
	C16 H25 O6 S2	(M+H)+	378.1158	377.1087	377.1093	87.11	1.51
	C19 H21 O6 S	(M+H)+	378.1158	377.1086	377.1059	82.16	-7.09
	C18 H16 O8	(M+NH4)+	378.1158	360.0817	360.0845	77.92	7.78

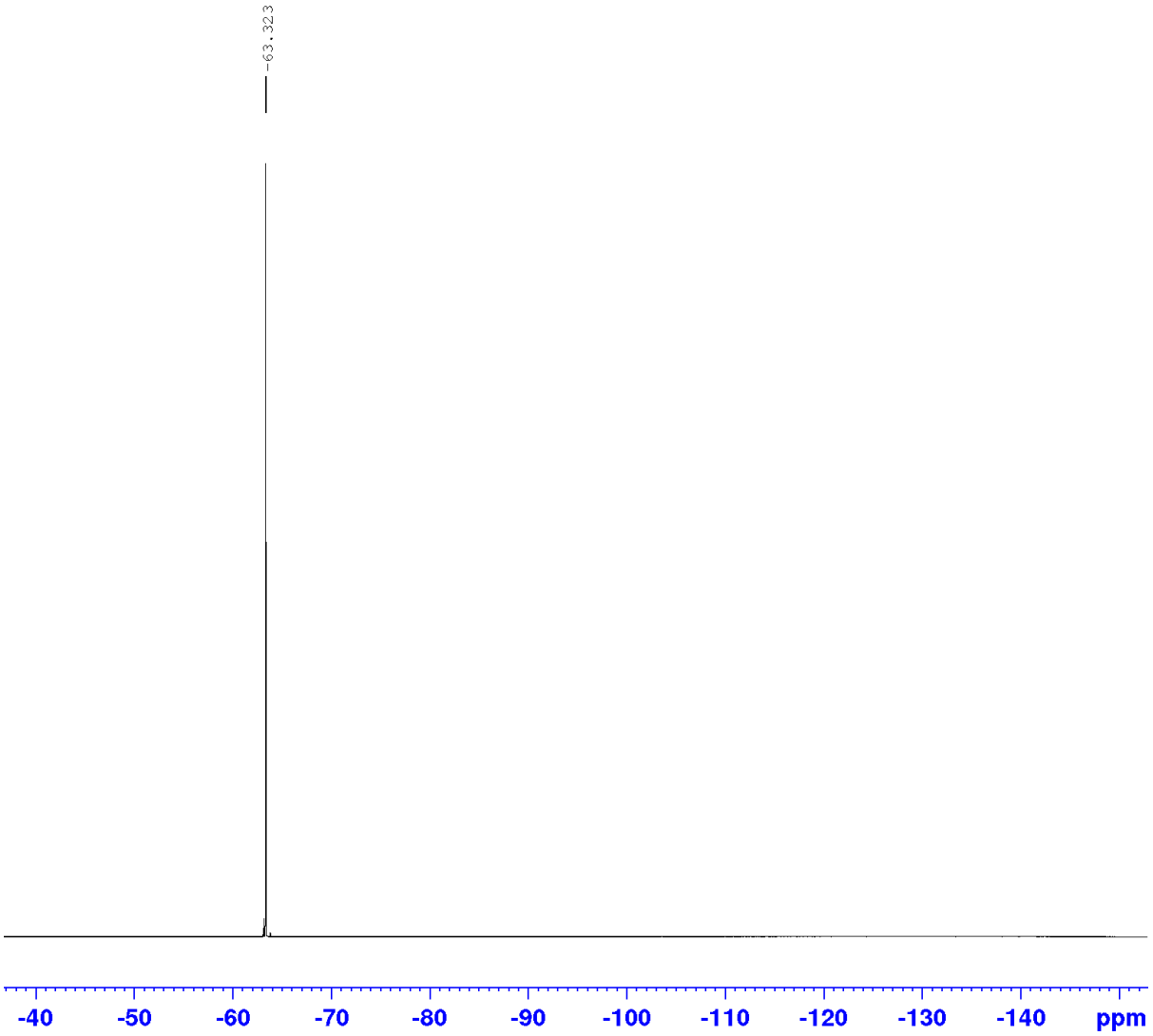
Compound 11b ^{1}H NMR $CDCl_3$



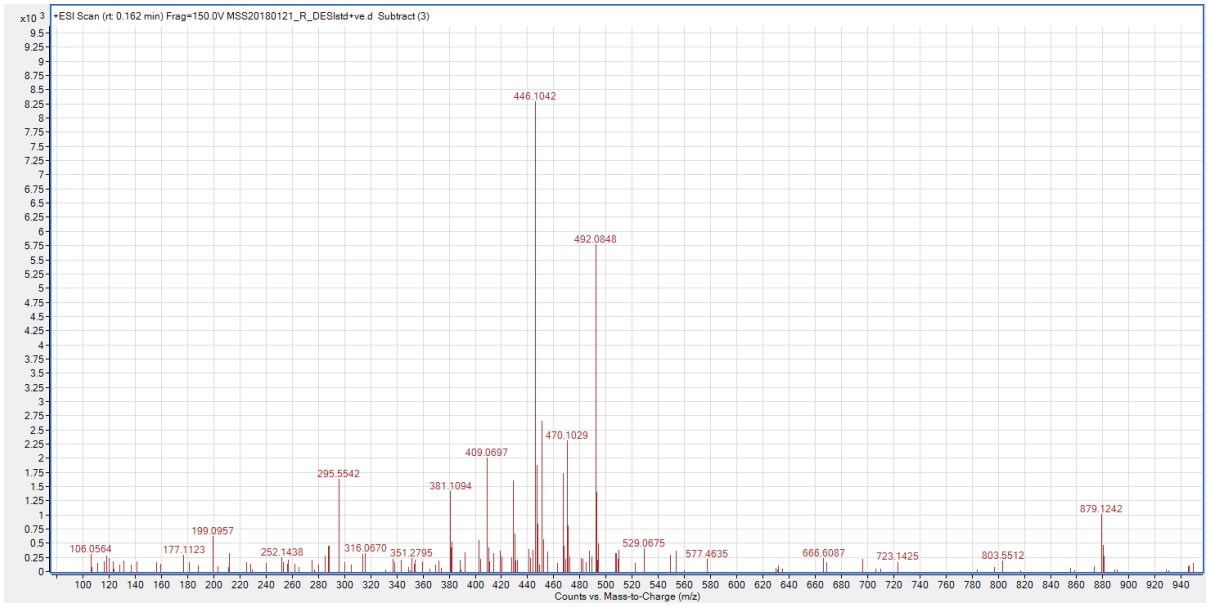
Compound 11b ^{13}C NMR $CDCl_3$



Compound 11b ^{19}F NMR $CDCl_3$

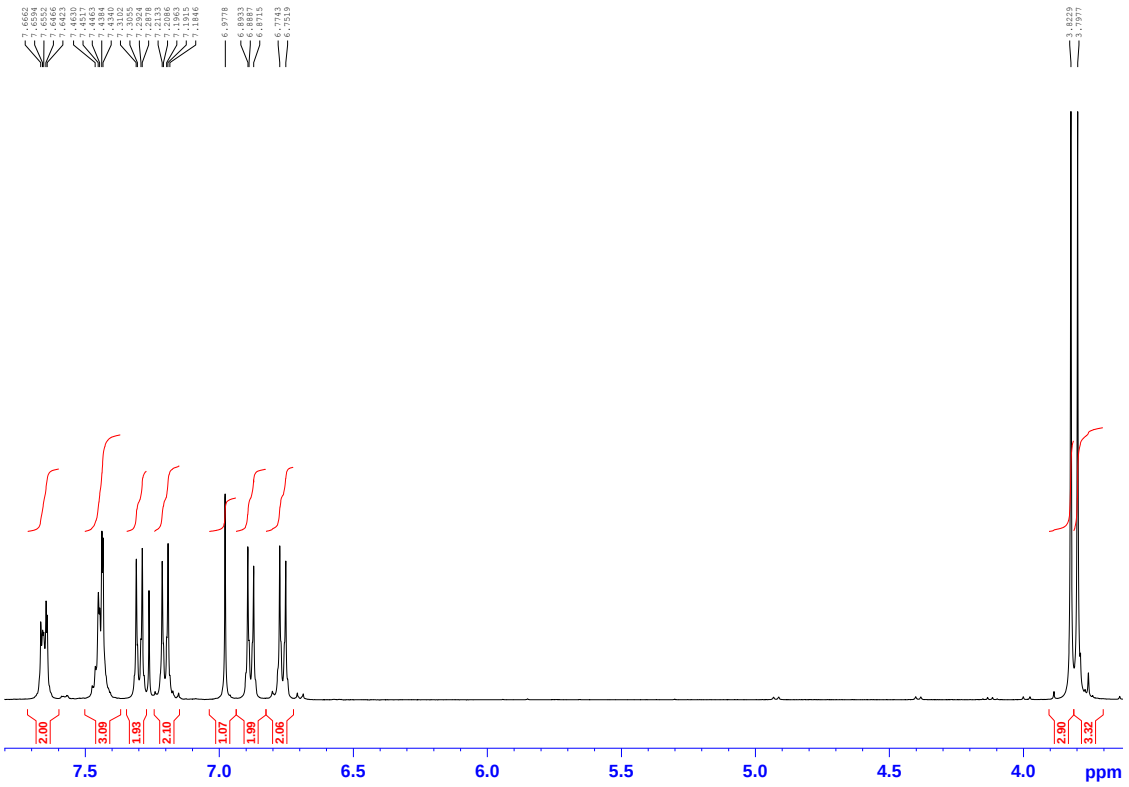


Compound 11b MS

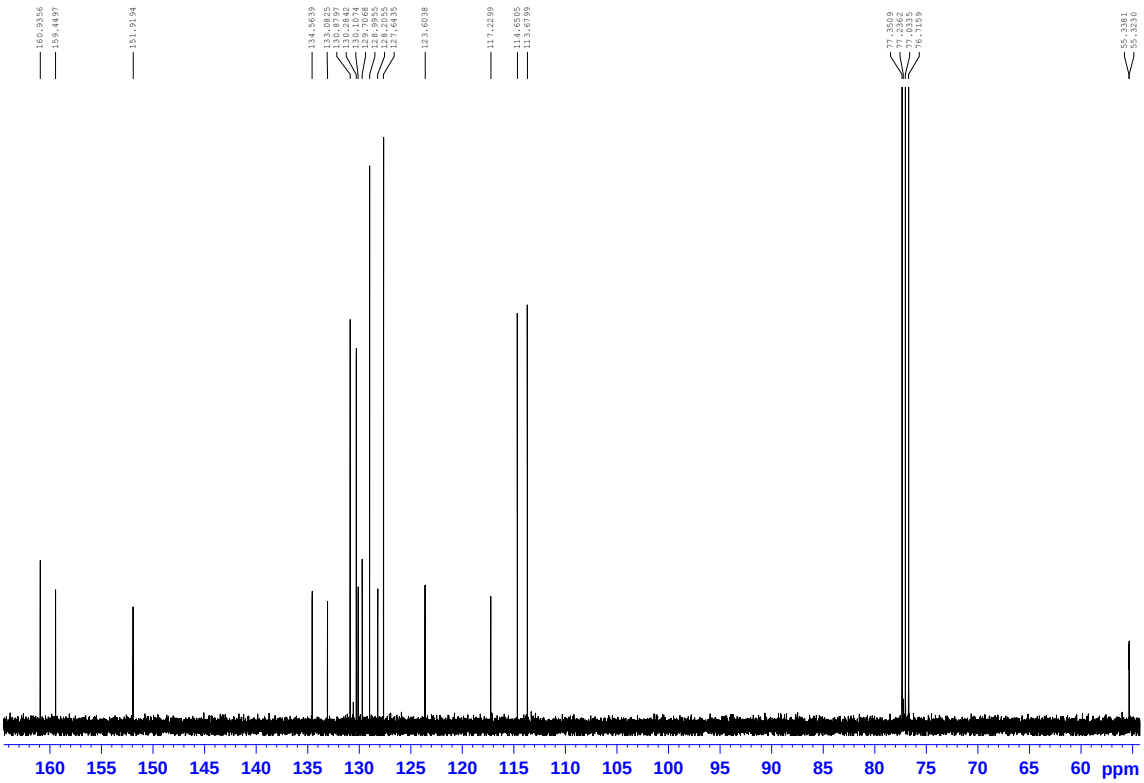


Best	Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
▶	C23 H15 F3 O3 S	(M+NH4)+	446.1042	428.0707	428.0694	90.21	-3.04
	C23 H18 F2 O2 S2	(M+NH4)+	446.1042	428.0708	428.0716	90.17	1.82
	C25 H16 O5 S	(M+NH4)+	446.1042	428.0707	428.0718	88.76	2.77
	C26 H17 F O S2	(M+NH4)+	446.1042	428.0708	428.0705	87.95	-0.76
	C20 H19 F3 O3 S2	(M+NH4)+	446.1042	428.0709	428.0728	85.35	4.4

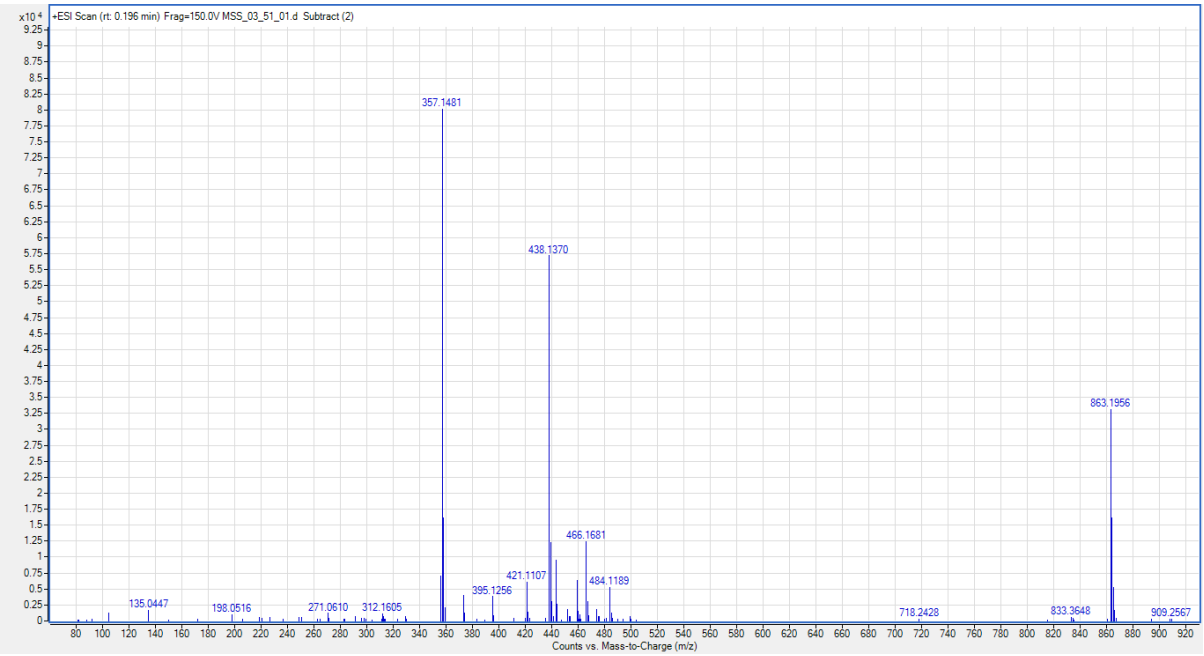
Compound 11c ^{1}H NMR $CDCl_3$



Compound 11c ^{13}C NMR $CDCl_3$

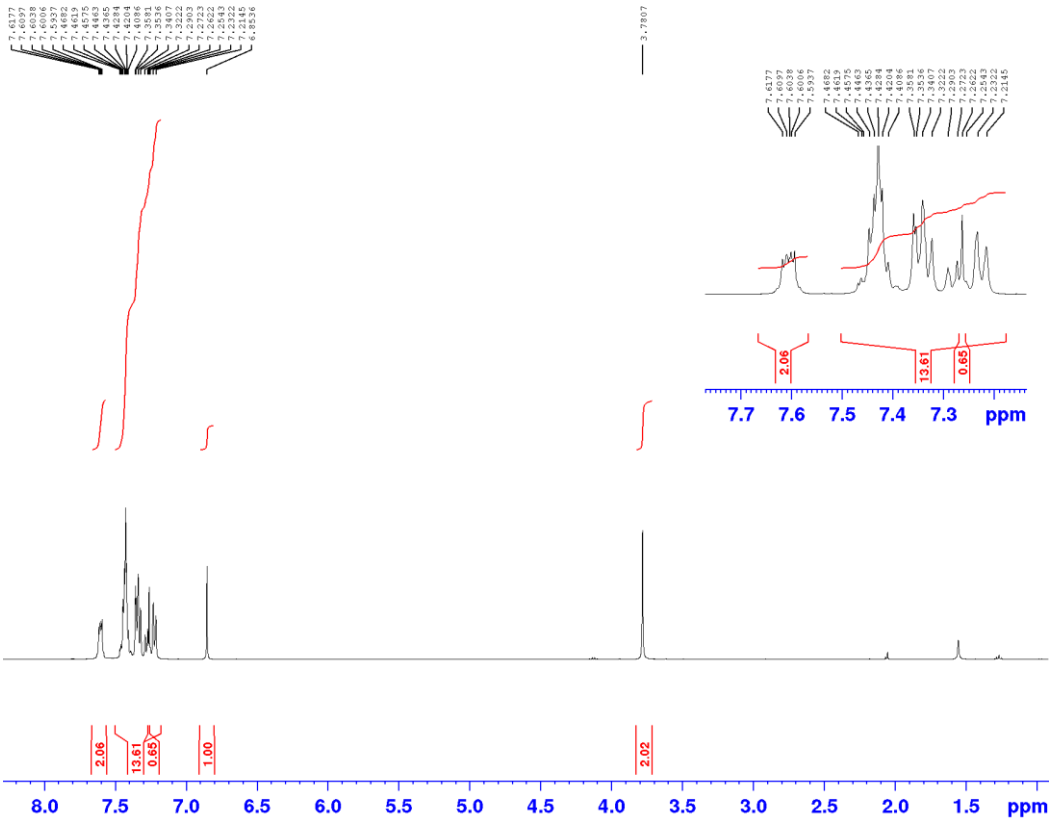


Compound 11c MS

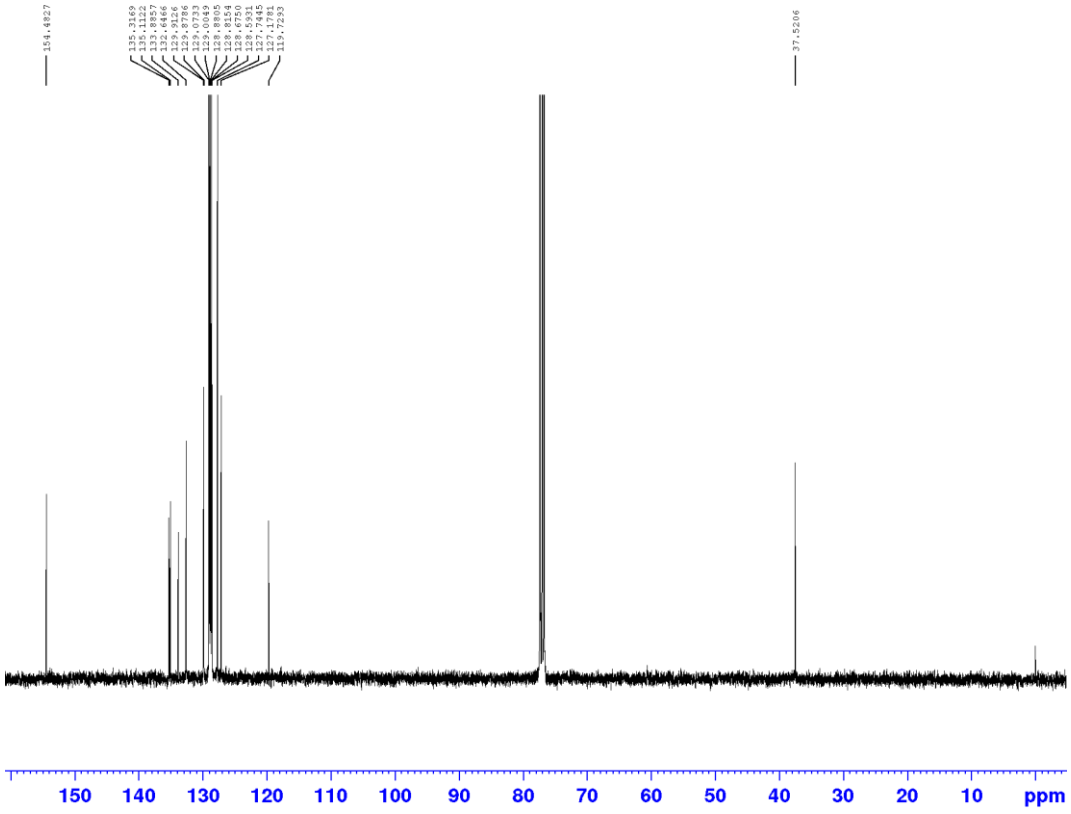


Best	Formula	Species	m/z	Mass	Mass (MFG)	Score (MFG)	Diff (ppm)
●	C24 H20 O5 S	(M+NH4)+	438.1370	420.1032	420.1031	92.46	-0.14
○	C30 H23 O	(M+K)+	438.1370	399.1738	399.1749	80.11	2.72
○	C25 H24 S3	(M+NH4)+	438.1370	420.1033	420.104	77.61	1.59

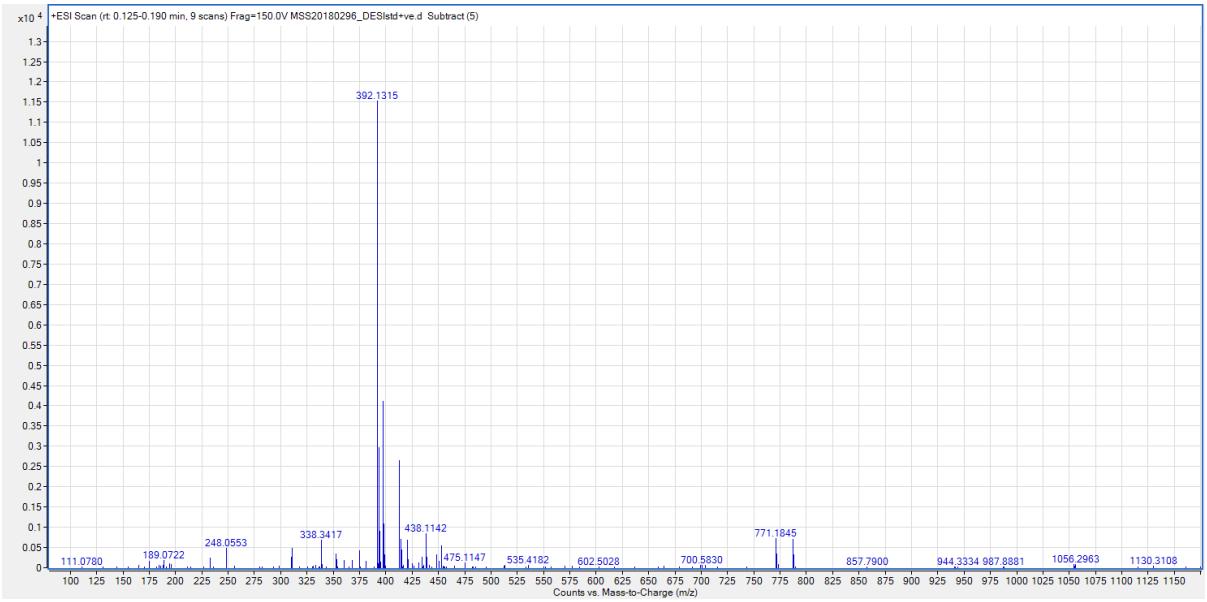
Compound 11d ^{1}H NMR $CDCl_3$



Compound 11d ^{13}C NMR $CDCl_3$

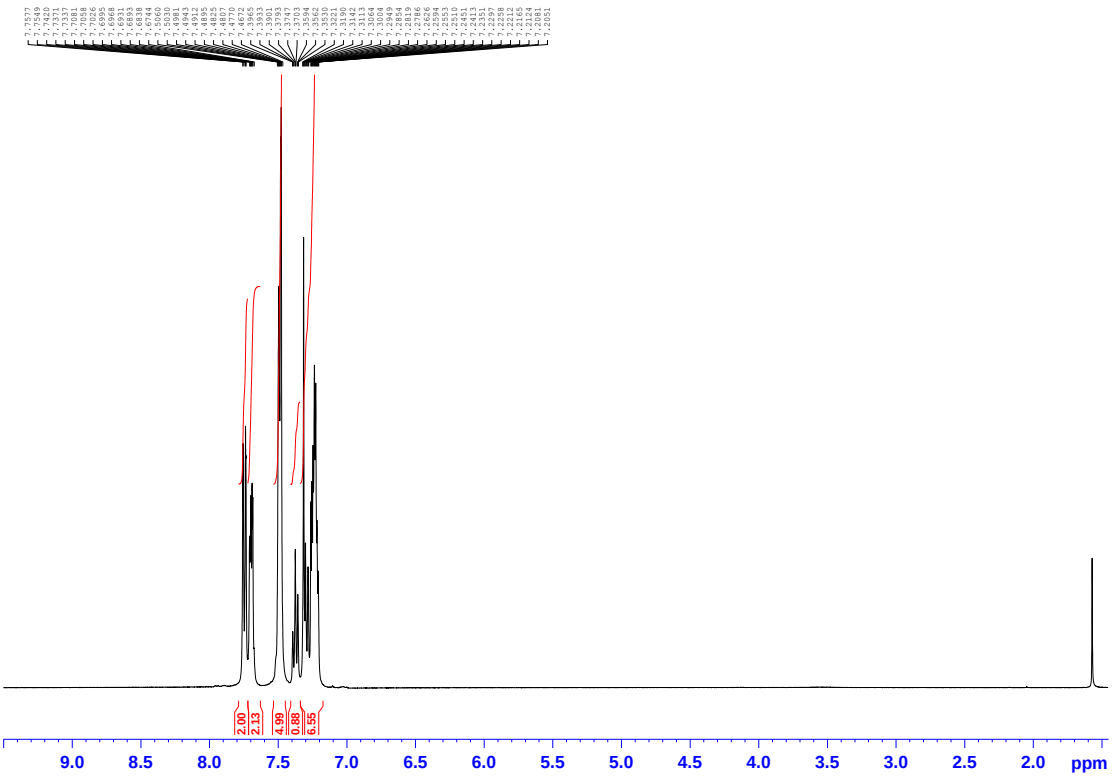


Compound 11d MS

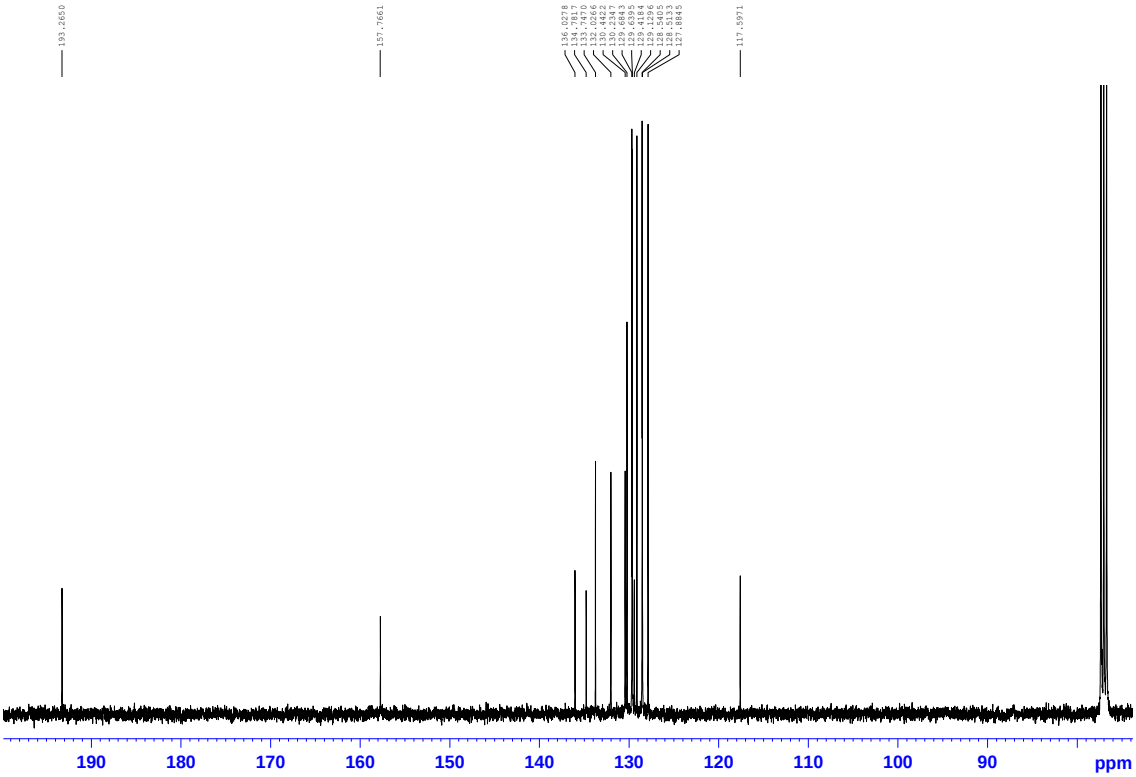


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C23 H18 O3 S	(M+K)+	413.0609	374.0977	374.0977	97.48	-0.02
C19 H18 O8	(M+K)+	413.0609	374.0975	374.1002	74.51	7.15
C20 H22 O3 S2	(M+K)+	413.0609	374.0978	374.101	73.11	8.58
C26 H14 O3	(M+K)+	413.0609	374.0974	374.0943	71.05	-8.38

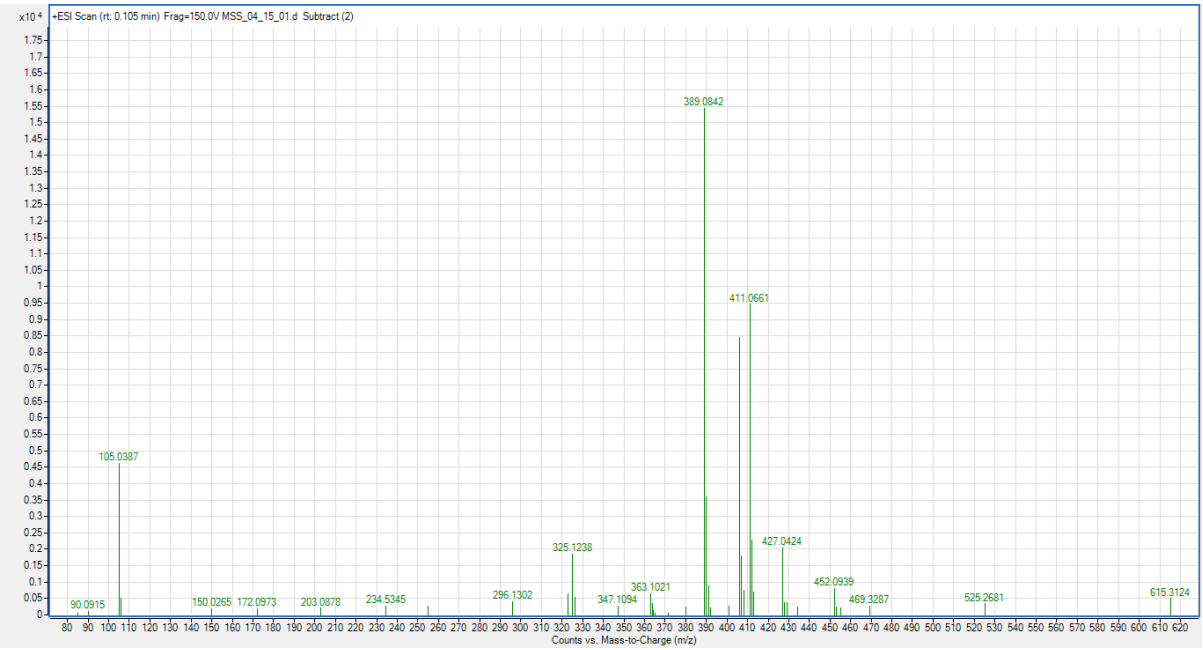
Compound 11e ^{1}H NMR $CDCl_3$



Compound 11e ^{13}C NMR $CDCl_3$

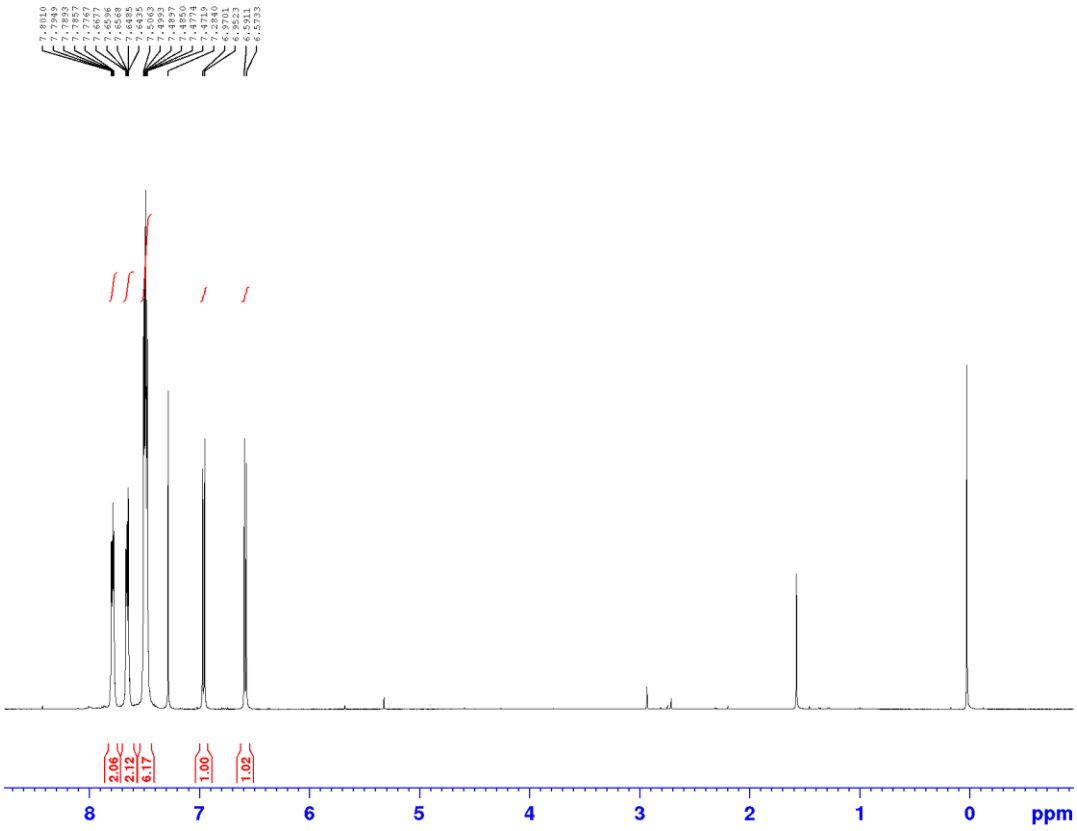


Compound 11e MS

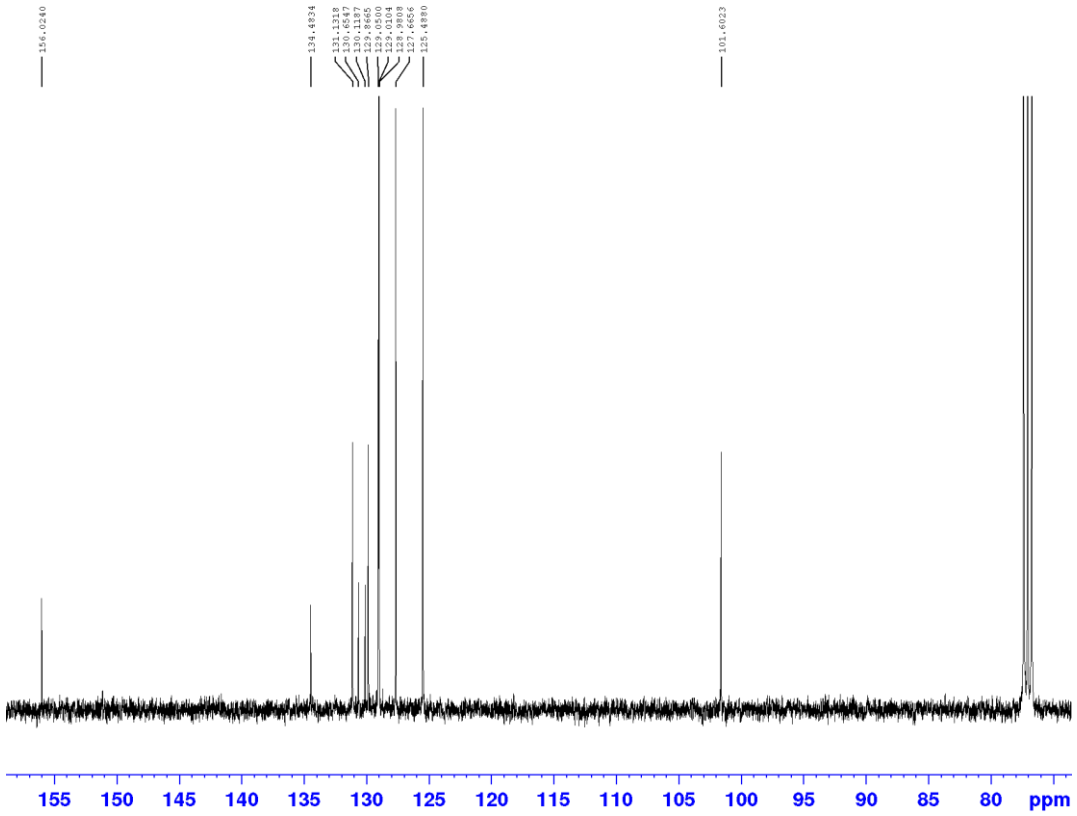


Best	Formula	Species	m/z	Mass	Mass (MFG)	Score (MFG)	Diff (ppm)
●	C23 H16 O4 S	(M+Na)+	411.0661	388.0772	388.0769	96.42	-0.61
○	C28 H10 O4	(M+H)+	411.0661	410.0588	410.0579	86.15	-2.1
○	C25 H14 O4 S	(M+H)+	411.0661	410.0591	410.0613	84.23	5.34
○	C20 H20 O5 S	(M+K)+	411.0661	372.1033	372.1031	82.71	-0.46

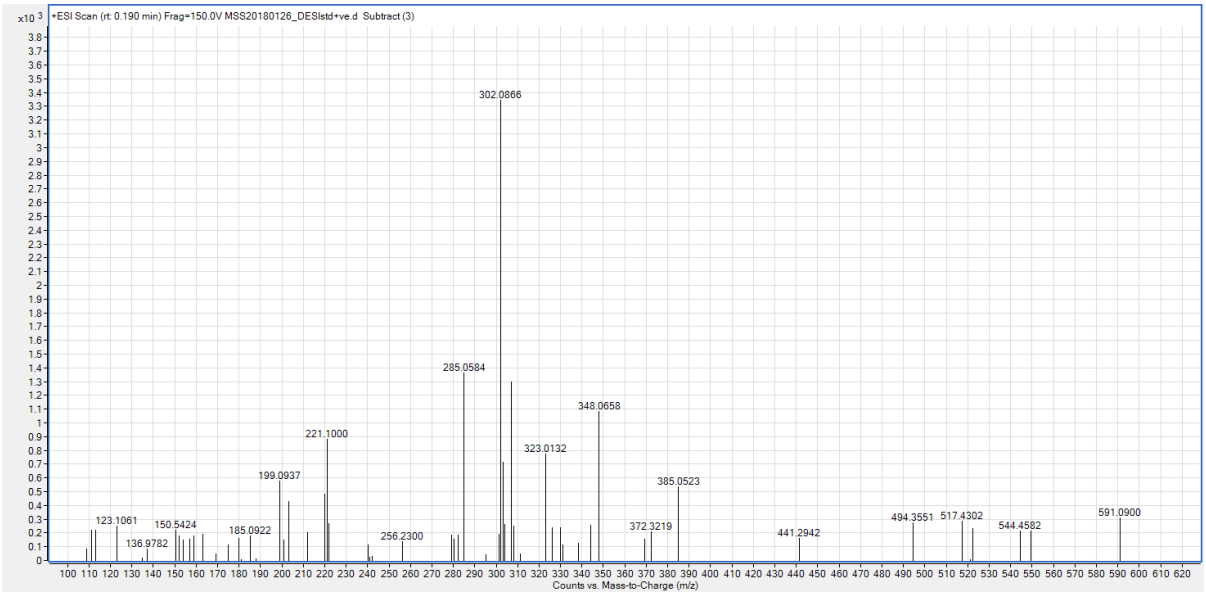
Compound 11f ^{1}H NMR $CDCl_3$



Compound 11f ^{13}C NMR $CDCl_3$

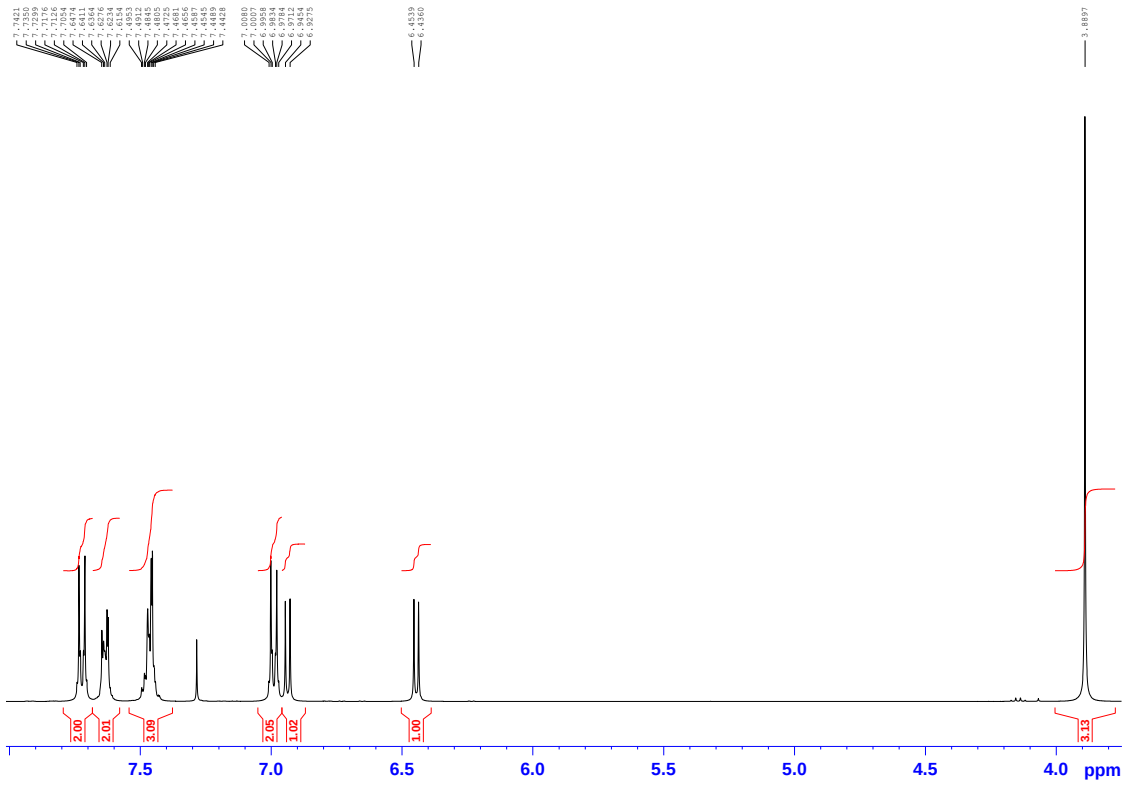


Compound 11f MS

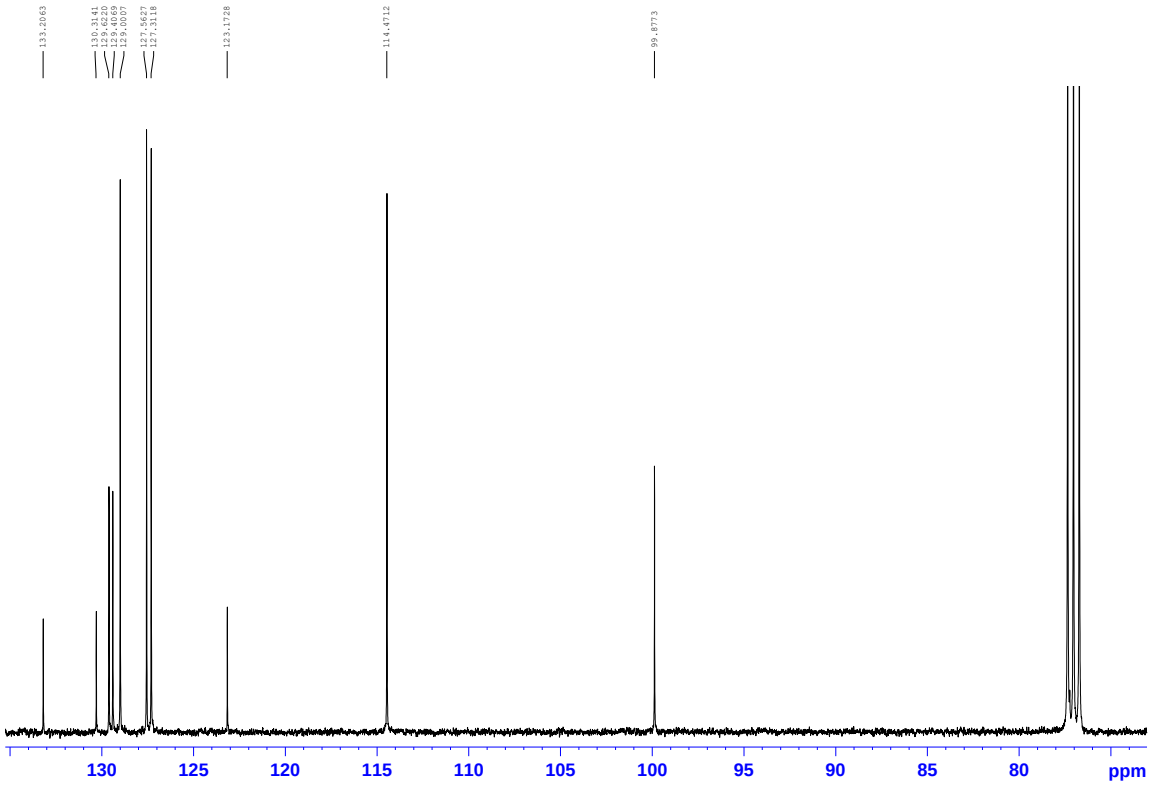


Best	Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
○	C16 H12 O3 S	(M+H)+	285.0584	284.0511	284.0507	46.95	-1.51
○	C8 H16 N2 O5 S2	(M+H)+	285.0584	284.0511	284.0501	43.52	-3.8
○	C22 H6 N	(M+H)+	285.0584	284.0511	284.05	43.23	-3.94
○	C19 H10 N S	(M+H)+	285.0584	284.0511	284.0534	32.17	7.93
○	C13 H16 O3 S2	(M+H)+	285.0584	284.0511	284.0541	24.37	10.36

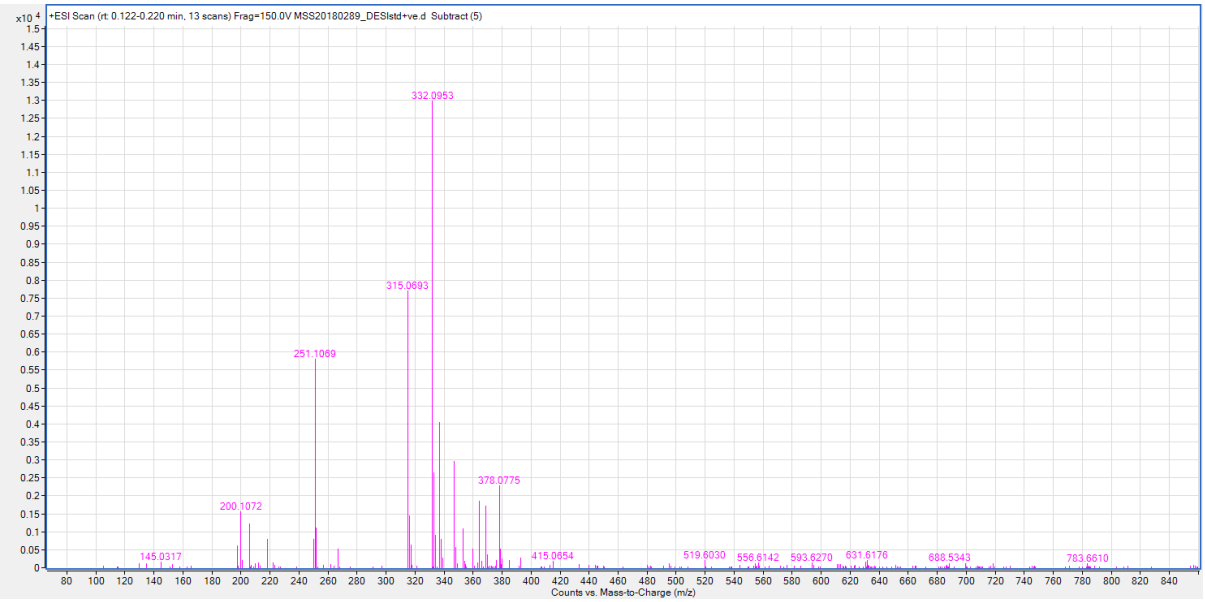
Compound 11g ^{1}H NMR $CDCl_3$



Compound 11g ^{13}C NMR $CDCl_3$

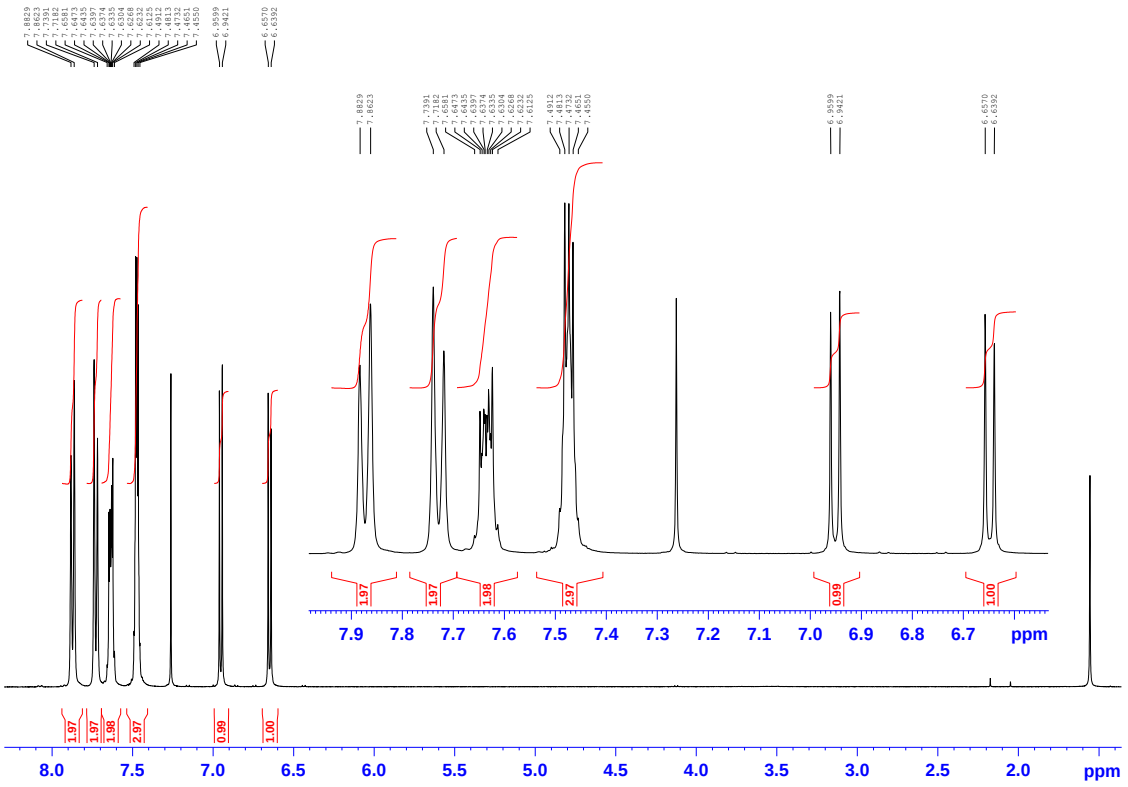


Compound 11g MS

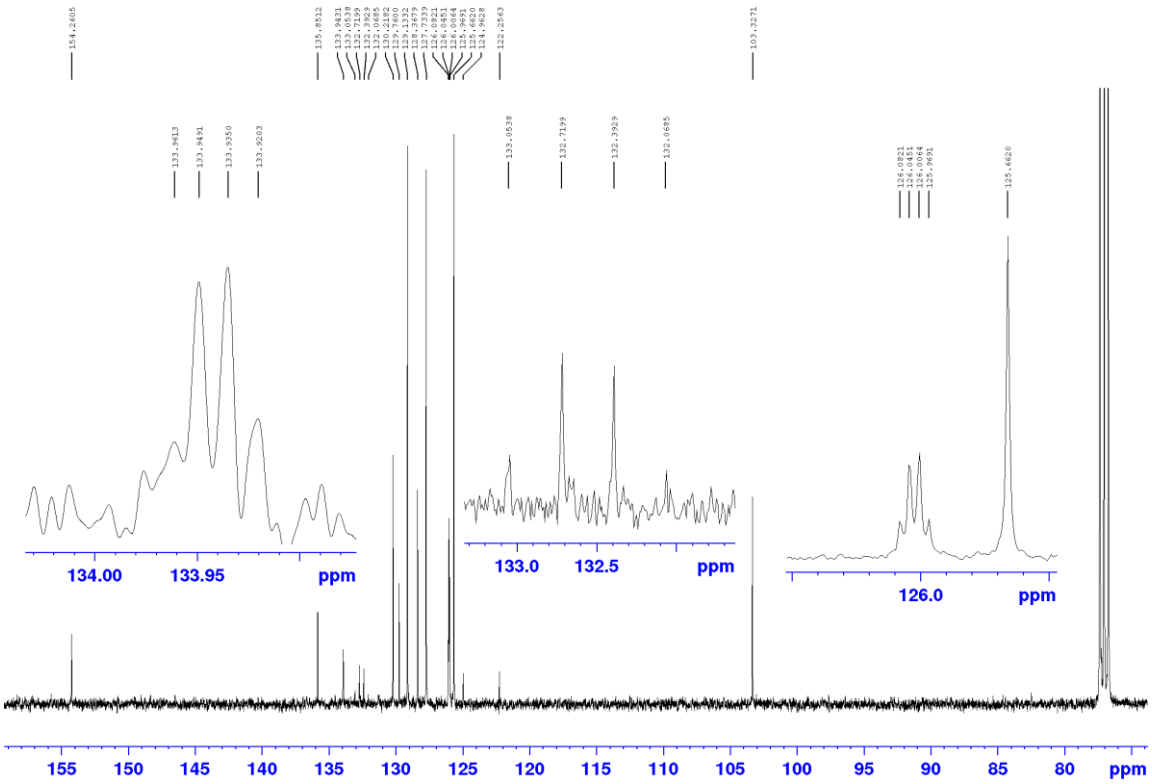


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C17 H14 O4 S	(M+NH4)+	332.0953	314.0612	314.0613	98.07	0.17
C14 H18 O4 S2	(M+NH4)+	332.0953	314.0614	314.0647	67.25	10.48
C20 H10 O4	(M+NH4)+	332.0953	314.0608	314.0579	64.93	-9.33

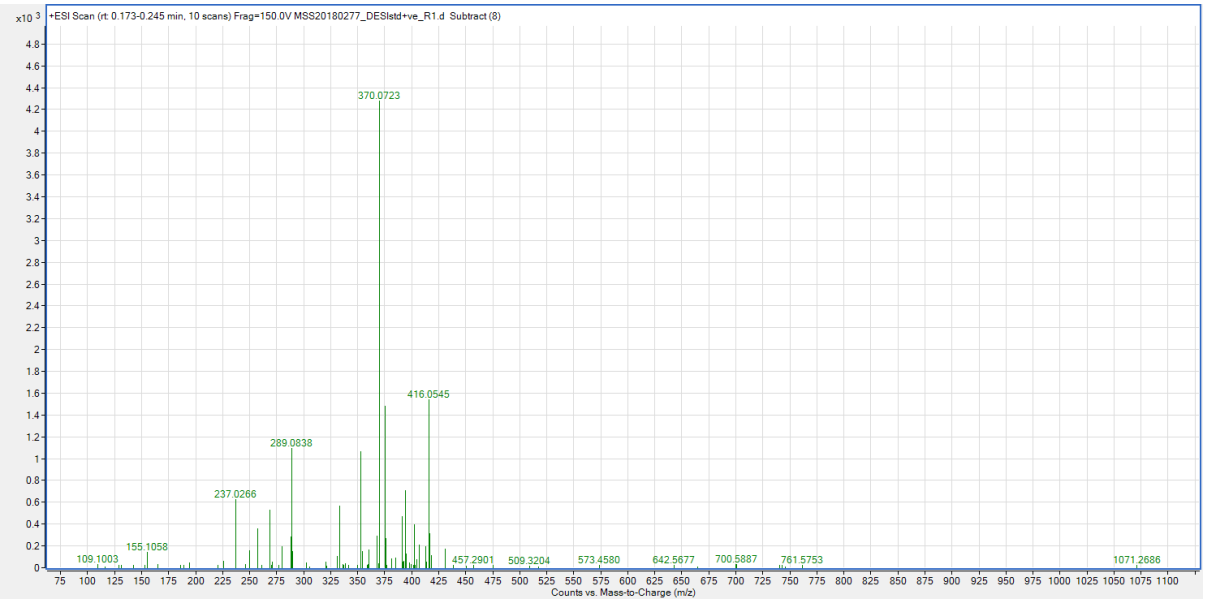
Compound 11h ^{1}H NMR $CDCl_3$



Compound 11h ^{13}C NMR $CDCl_3$

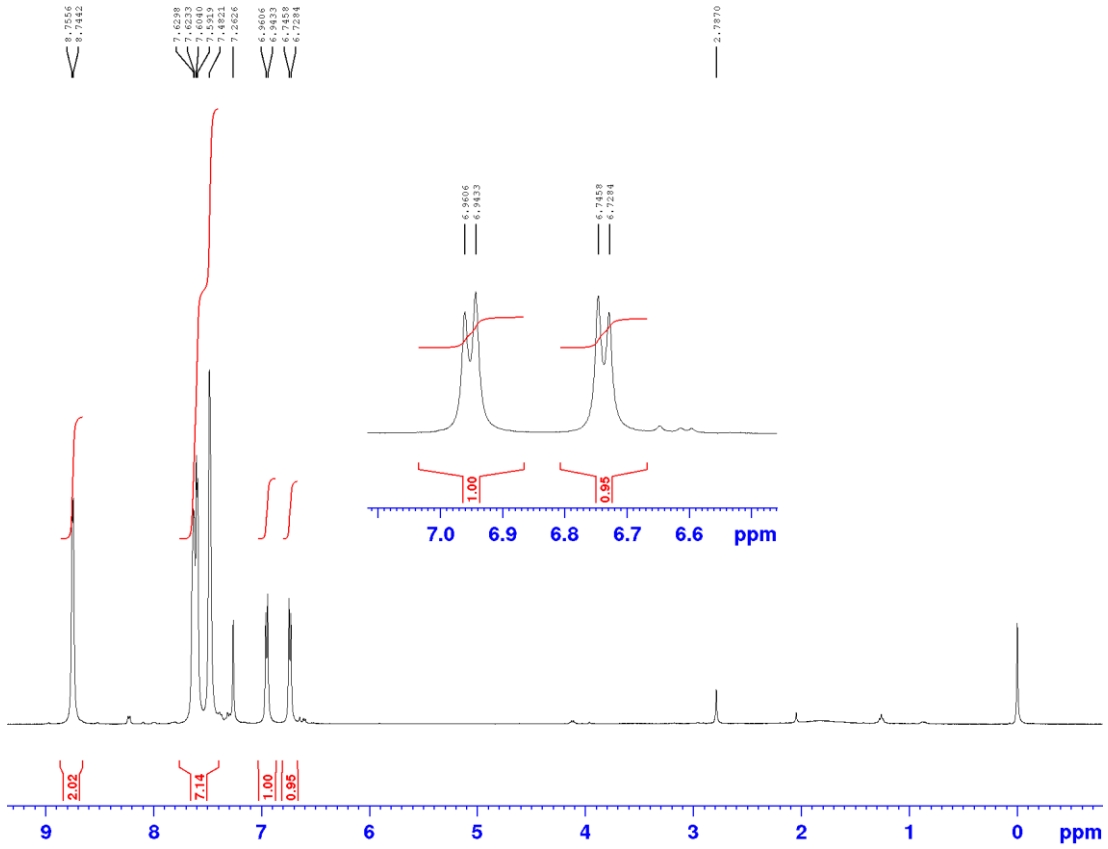


Compound 11h MS

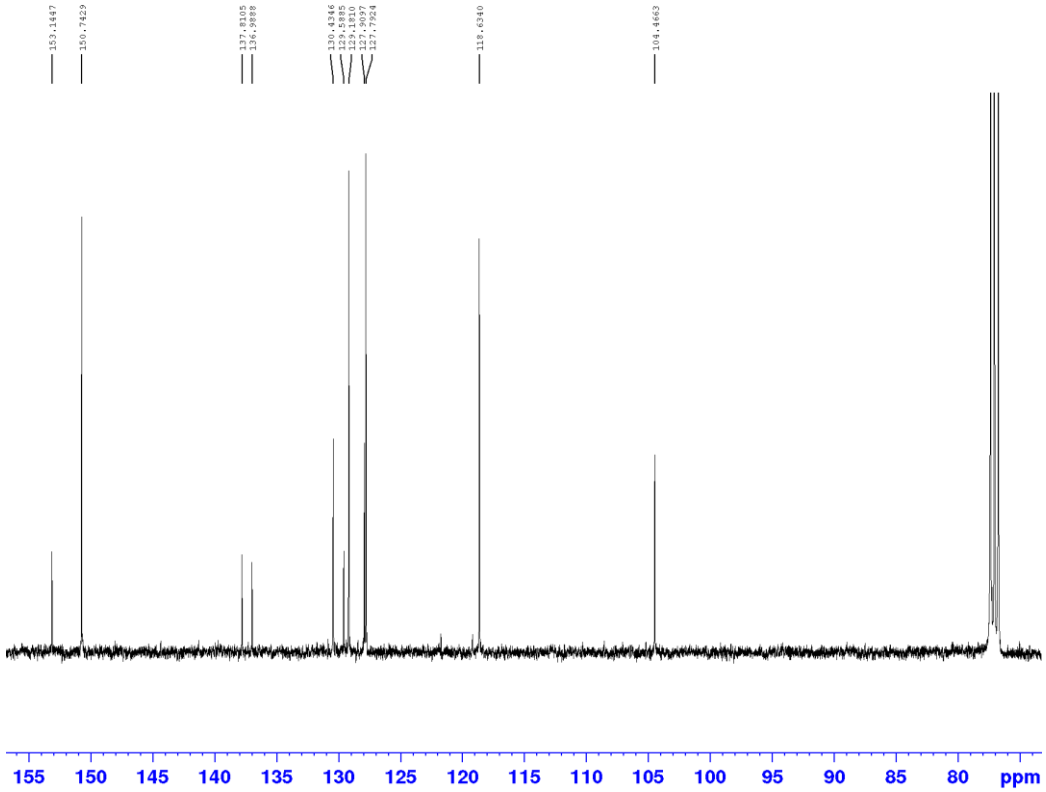


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C16 H10 F2 O7	(M+H)+	353.0453	352.0382	352.0395	76.04	3.43
C19 H9 F O6	(M+H)+	353.0453	352.0383	352.0383	74.38	0.19
C17 H11 F3 O3 S	(M+H)+	353.0453	352.0383	352.0381	70.63	-0.49
C13 H11 F3 O8	(M+H)+	353.0453	352.0382	352.0406	69.11	6.69
C22 H8 O5	(M+H)+	353.0453	352.0383	352.0372	64.92	-3.06
C20 H10 F2 O2 S	(M+H)+	353.0453	352.0383	352.037	61.81	-3.73
C23 H12 S2	(M+H)+	353.0453	352.0383	352.038	59.14	-0.68

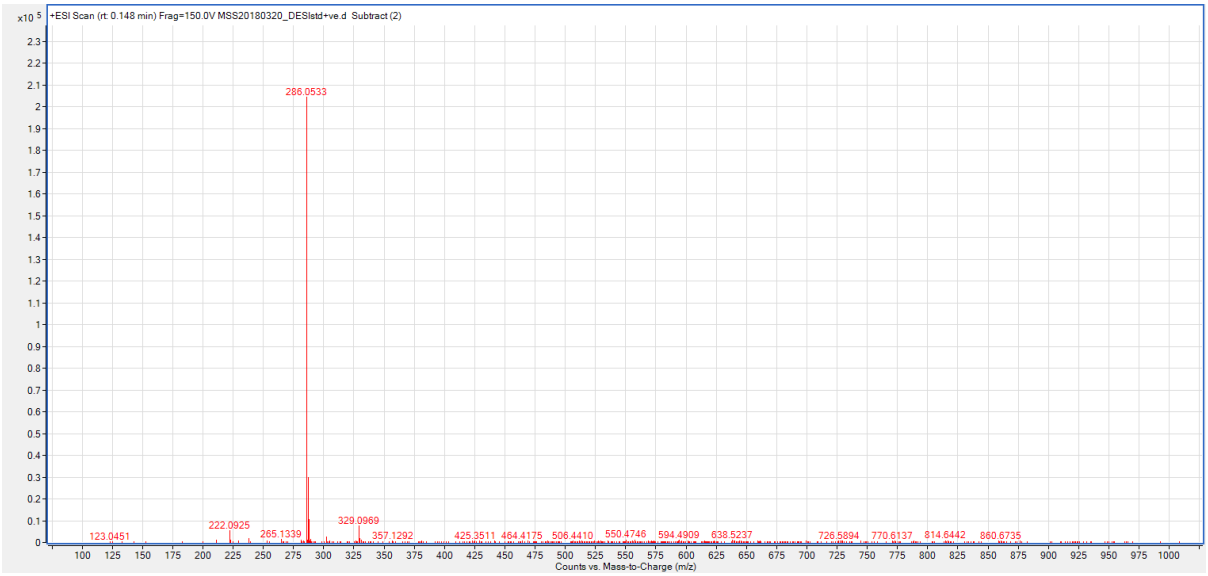
Compound 11i ^{1}H NMR $CDCl_3$



Compound 11i ^{13}C NMR $CDCl_3$

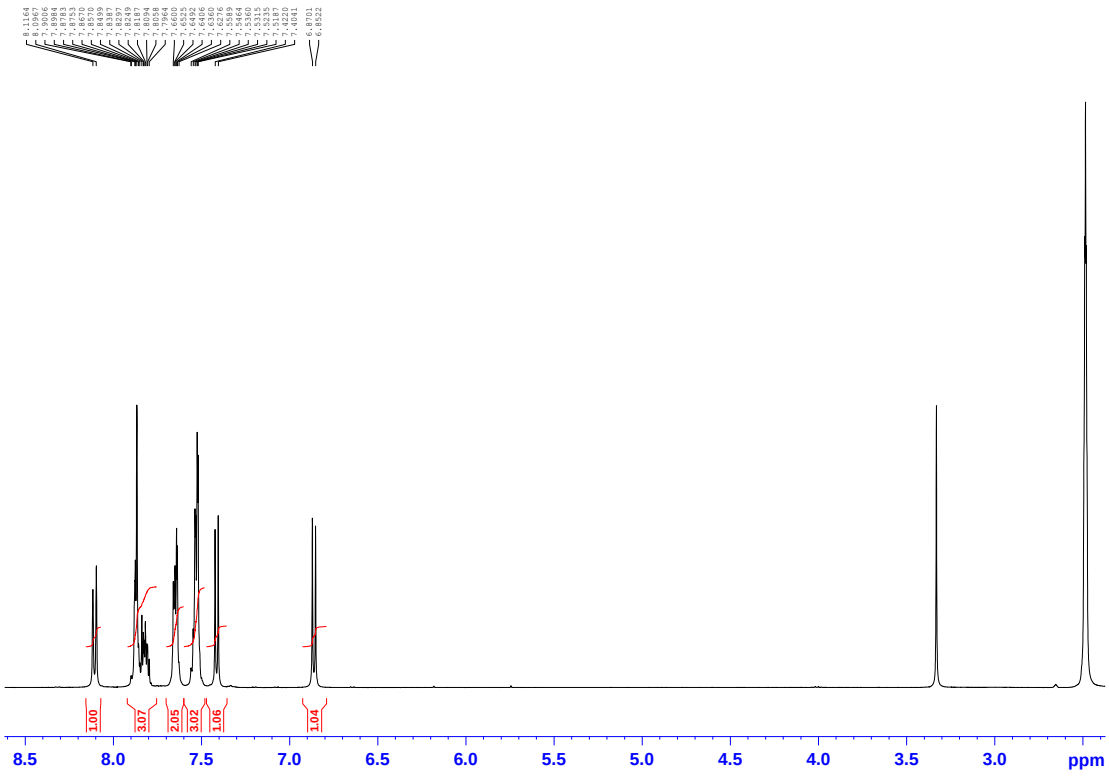


Compound 11i MS

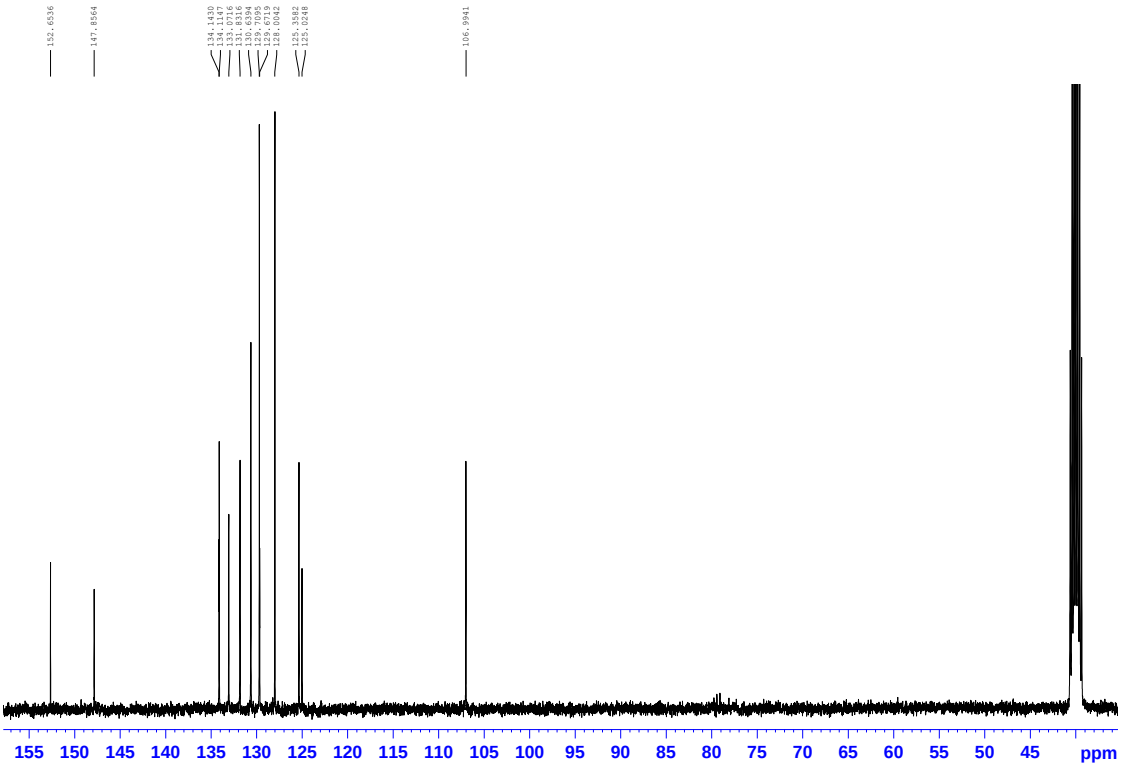


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C15 H11 N O3 S	(M+H)+	286.0533	285.046	285.046	47.62	-0.05
C15 H8 O3 S	(M+NH4)+	286.0533	268.0194	268.0194	47.62	-0.06
C9 H13 N O8	(M+Na)+	286.0533	263.064	263.0641	47.59	0.31
C16 H11 N2 S	(M+Na)+	286.0533	263.064	263.0643	47.37	0.99
C13 H15 N2 O S	(M+K)+	286.0533	247.0901	247.0905	47	1.67
C7 H12 N2 O5 S2	(M+NH4)+	286.0533	268.0194	268.0188	46.01	-2.49
C9 H17 O6 S2	(M+H)+	286.0533	285.046	285.0467	45.97	2.37
C21 H5 N2	(M+H)+	286.0533	285.046	285.0453	45.83	-2.48

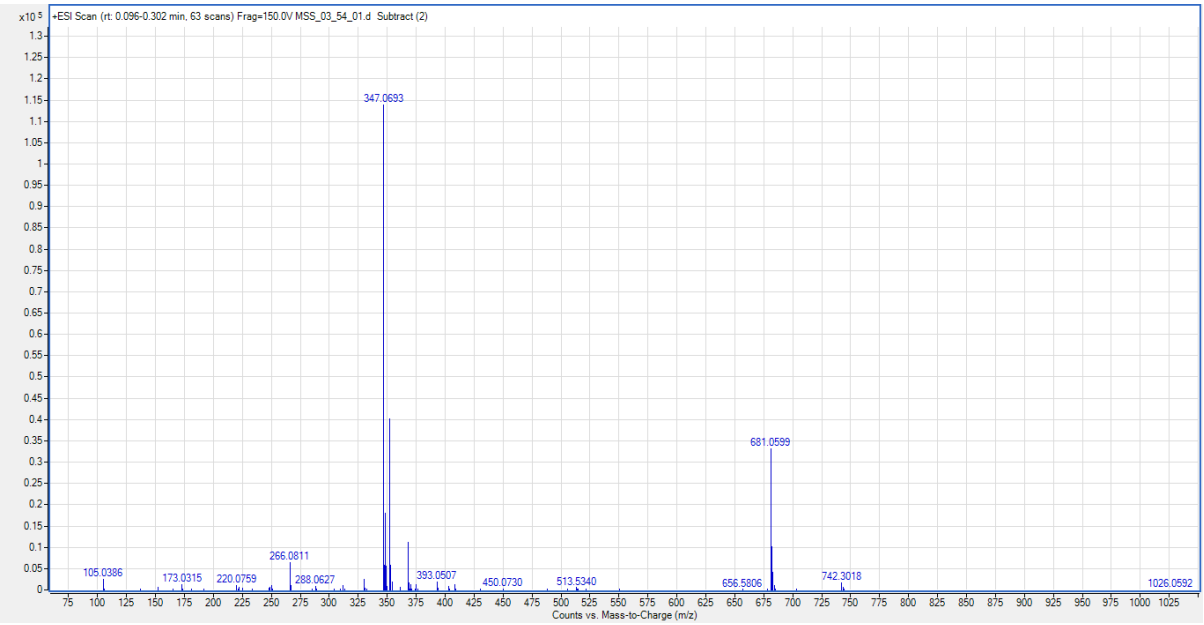
Compound 11j ^{1}H NMR $CDCl_3$ (d_6-DMSO)



Compound 11j ^{13}C NMR $CDCl_3$ (d_6-DMSO)

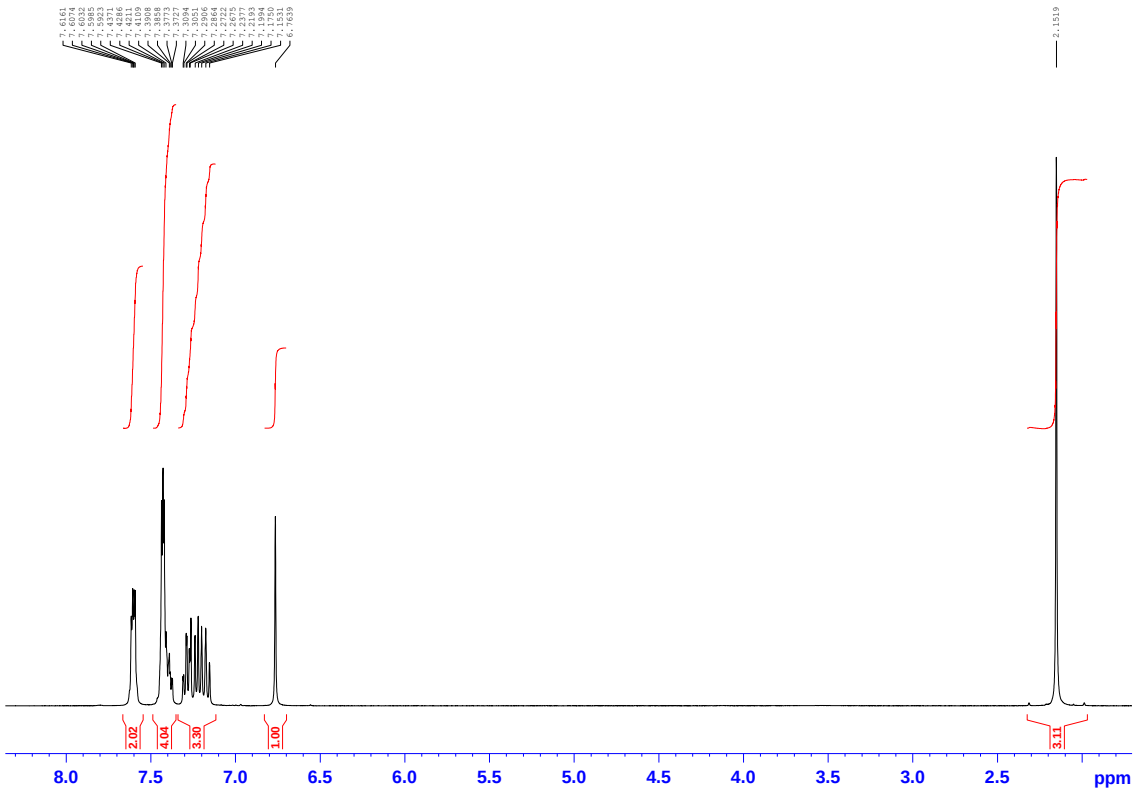


Compound 11j MS

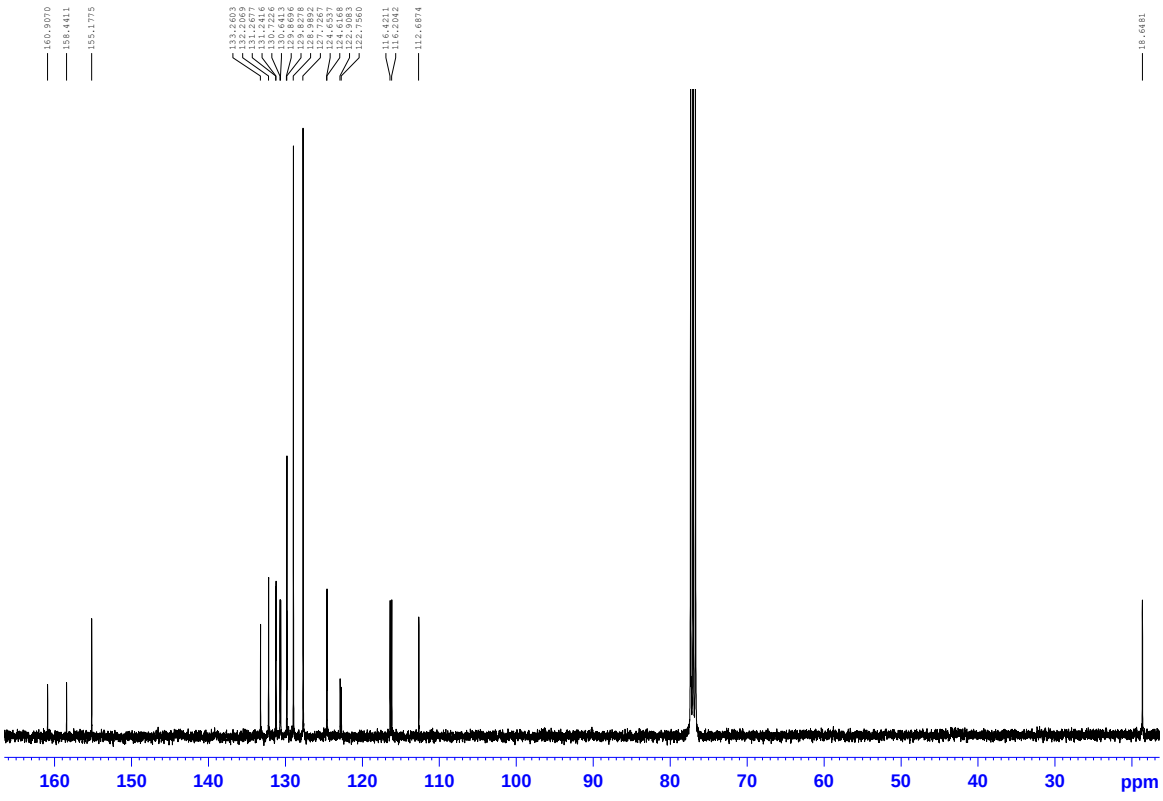


Best	Formula	Species	m/z	Mass	Mass (MFG)	Score (MFG)	Diff (ppm)
●	C16 H11 N O5 S	(M+Na)+	352.0246	329.0355	329.0358	94.67	1.01
○	C13 H6 N2 O7 S	(M+NH4)+	352.0246	333.9909	333.9896	92.21	-3.99
○	C19 H9 N2 O3	(M+K)+	352.0246	313.0615	313.0613	87.92	-0.52

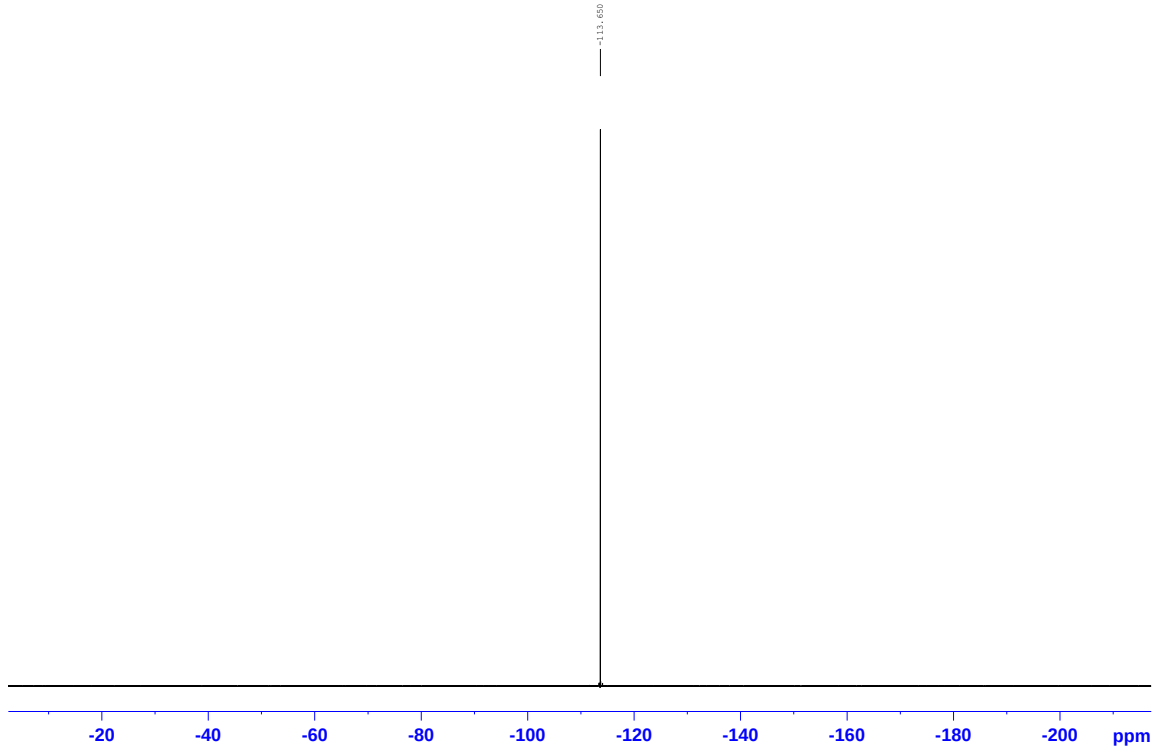
Compound 17 ^{1}H NMR $CDCl_3$



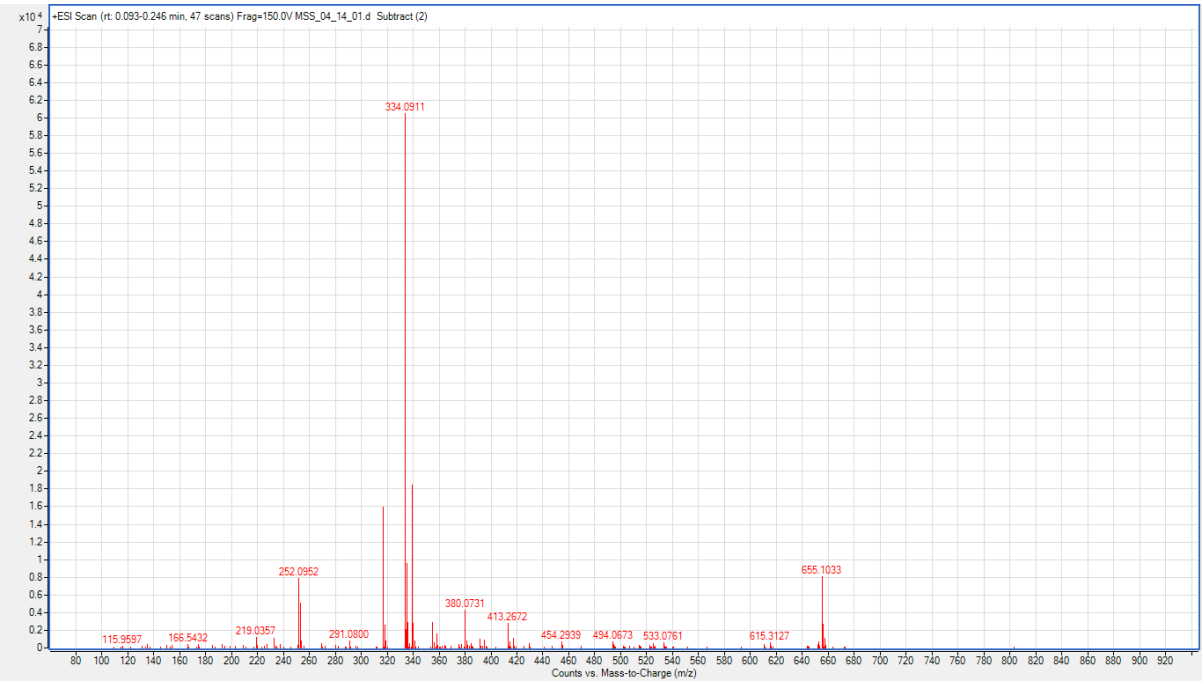
Compound 17 ^{13}C NMR $CDCl_3$



Compound 17 ^{19}F NMR $CDCl_3$

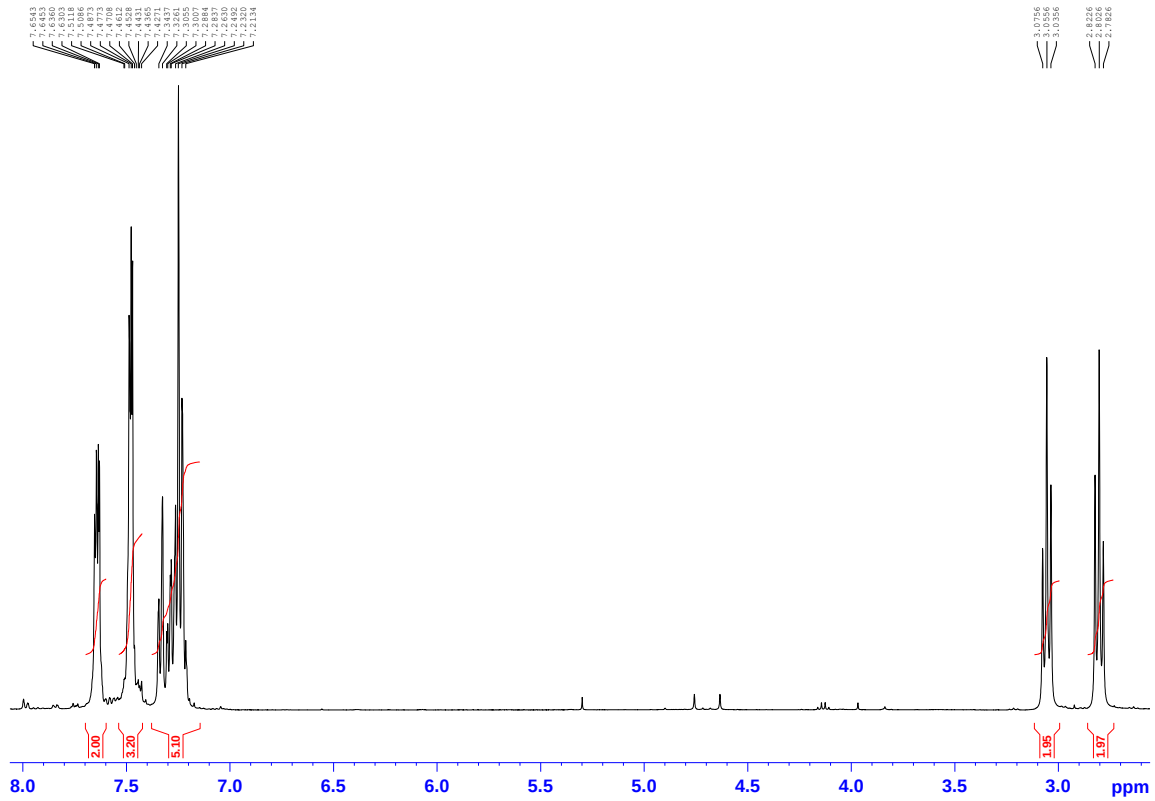


Compound 17 MS

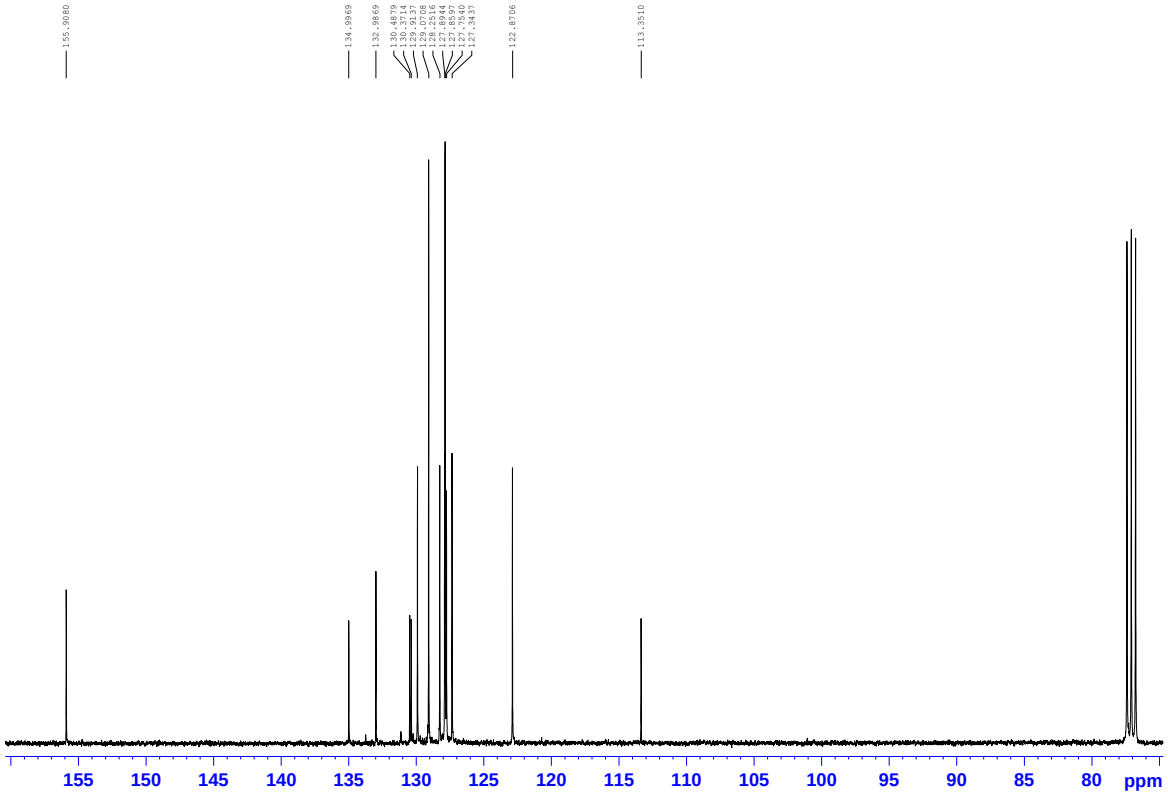


Best	Formula	Species	m/z	Mass	Mass (MFG)	Score (MFG)	Diff (ppm)
▶	C17 H13 F O3 S	(M+NH4)+	334.0911	316.0572	316.0569	95.59	-0.9
	C14 H21 O5 S2	(M+H)+	334.0911	333.0838	333.083	87.83	-2.43
	C20 H12 O2 S	(M+NH4)+	334.0911	316.0572	316.0558	84.38	-4.44
	C20 H17 F2	(M+K)+	334.0911	295.1278	295.1298	78.91	6.79

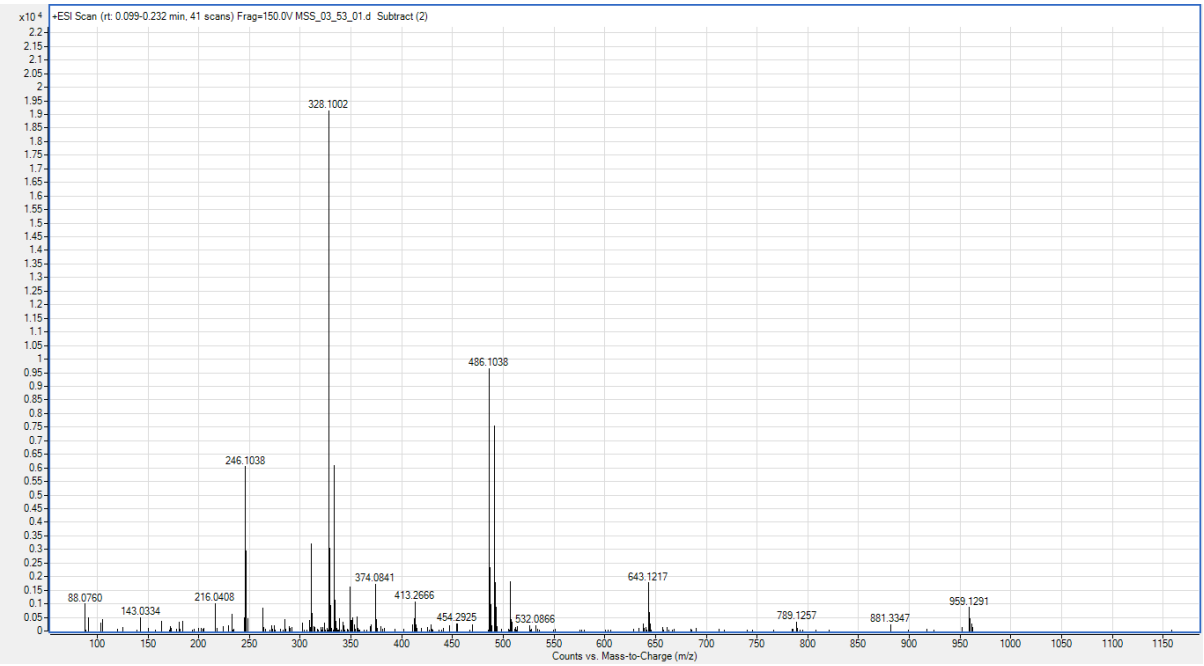
Compound 20 ^{1}H NMR $CDCl_3$



Compound 20 ^{13}C NMR $CDCl_3$

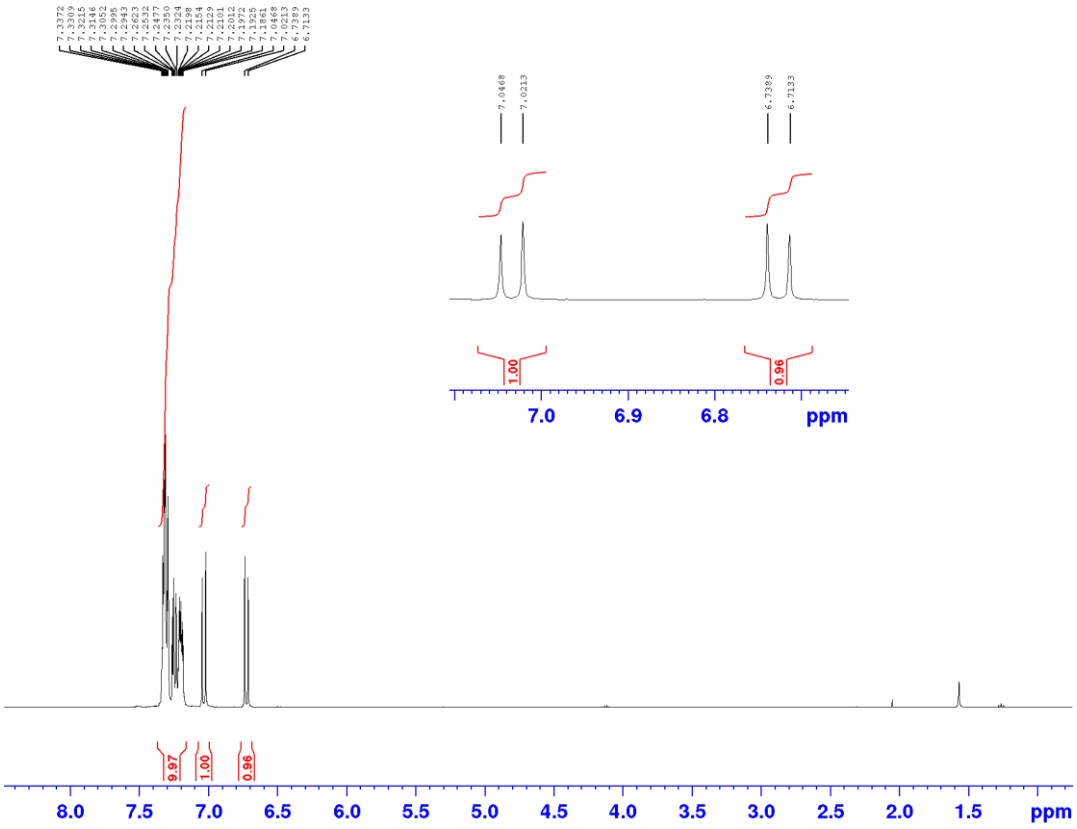


Compound 20 MS

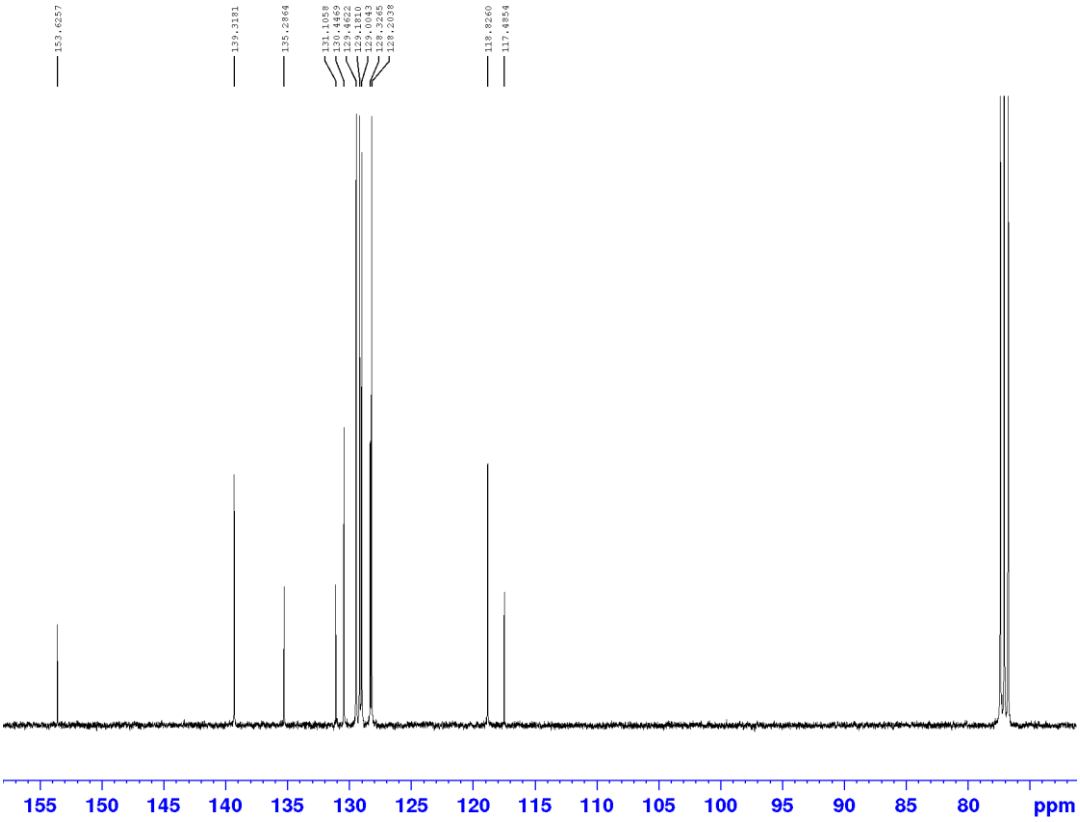


Best	Formula	Species	m/z	Mass	Mass (MFG)	Score (MFG)	Diff (ppm)
▶	C18 H14 O3 S	(M+NH4)+	328.1002	310.0662	310.0664	94.06	0.44
	C12 H23 O6 S2	(M+H)+	328.1002	327.0929	327.0936	88.1	2.24
	C15 H19 O6 S	(M+H)+	328.1002	327.0928	327.0902	81.09	-7.75
	C14 H14 O8	(M+NH4)+	328.1002	310.066	310.0689	73.11	9.15

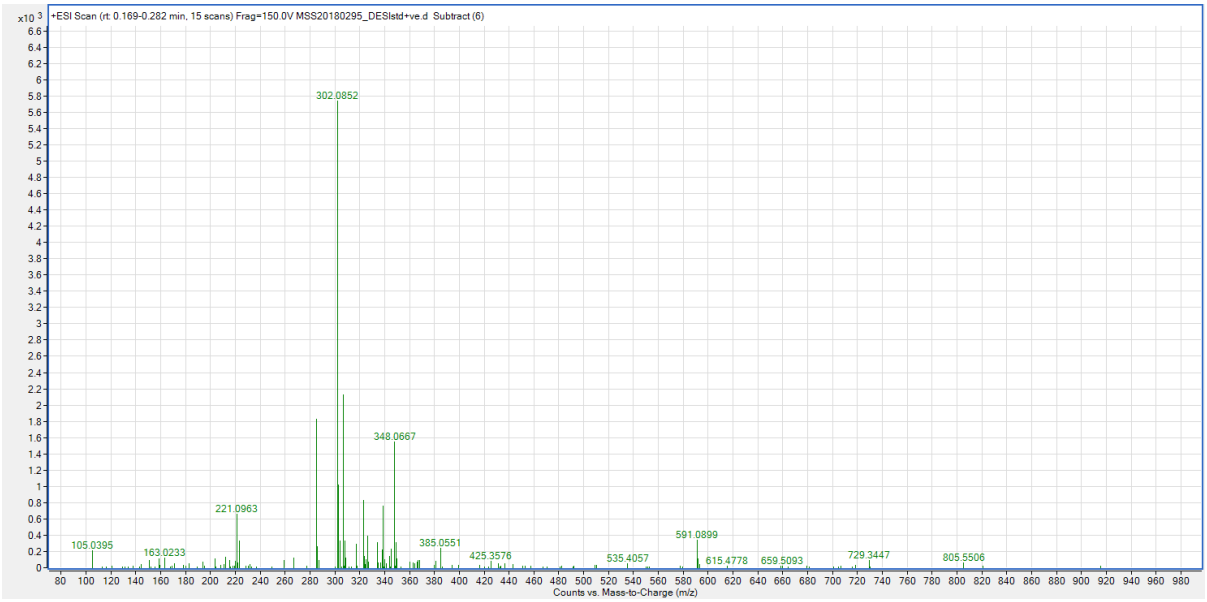
Compound 13a ^{1}H NMR $CDCl_3$



Compound 13a ^{13}C NMR $CDCl_3$

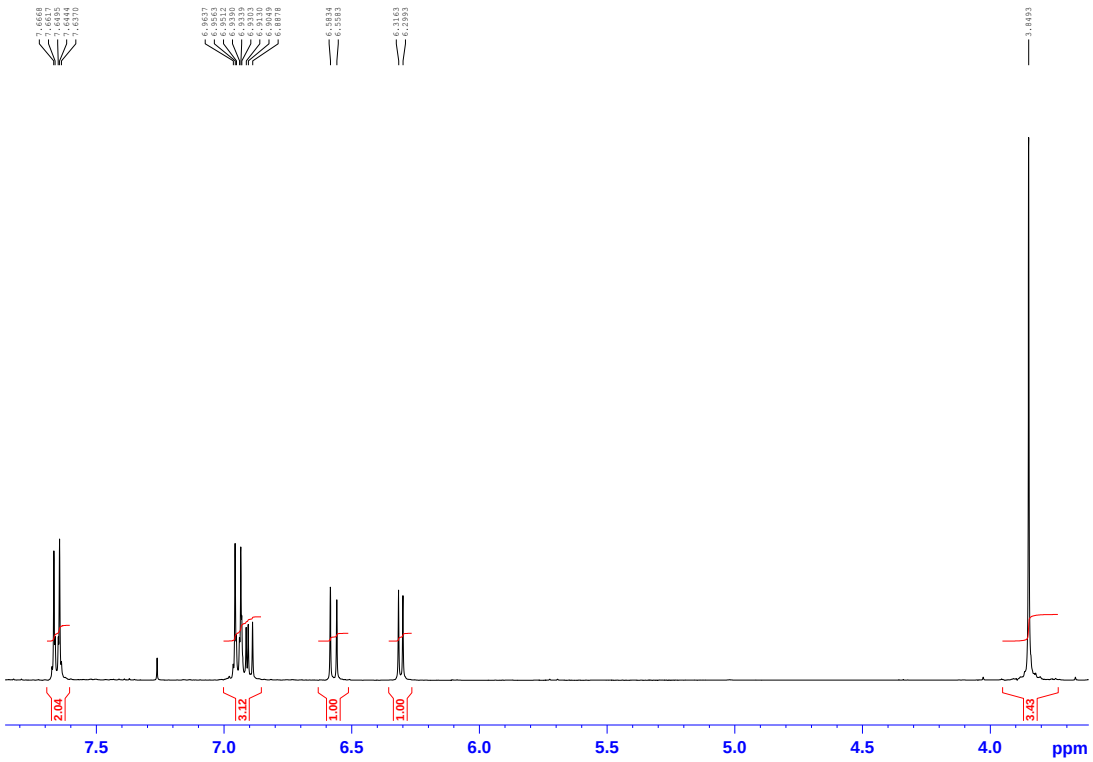


Compound 13a MS

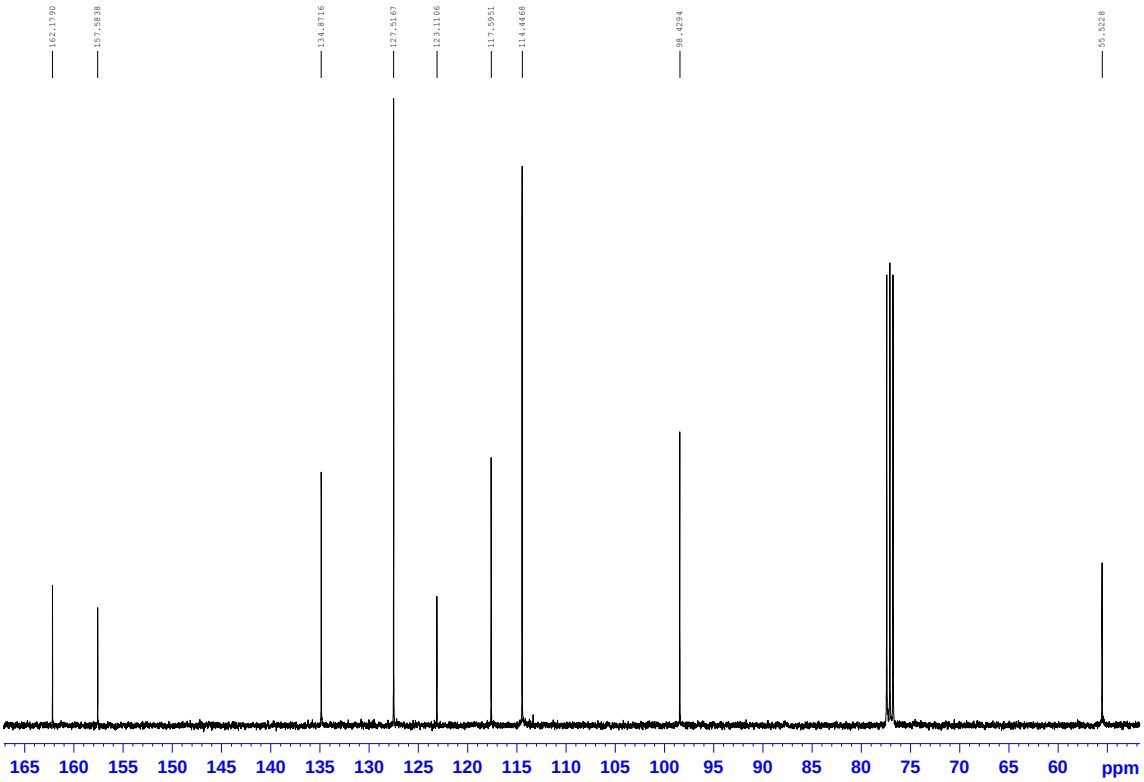


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C17 H16 O4 S	(M+Na)+	339.0661	316.0769	316.0769	89.7	0.11
C14 H20 O4 S2	(M+Na)+	339.0661	316.077	316.0803	67.94	10.39
C20 H12 O4	(M+Na)+	339.0661	316.0765	316.0736	52.83	-9.3

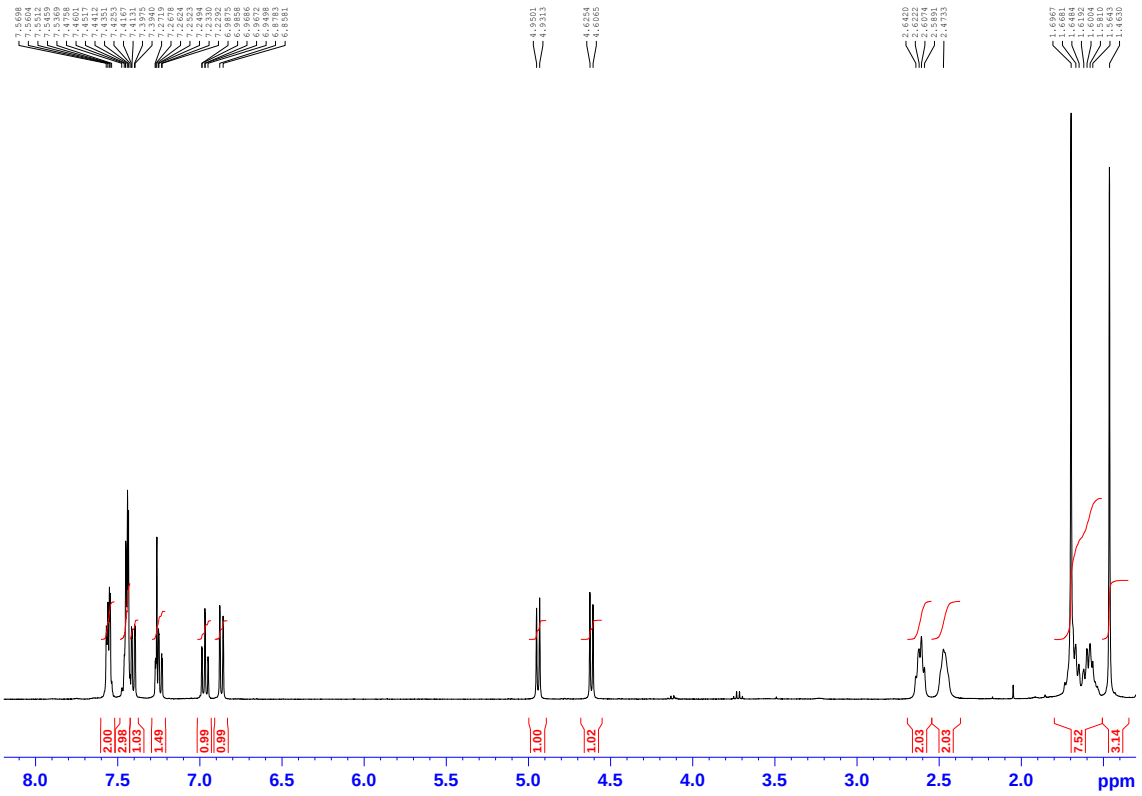
Compound 13b ^{1}H NMR $CDCl_3$



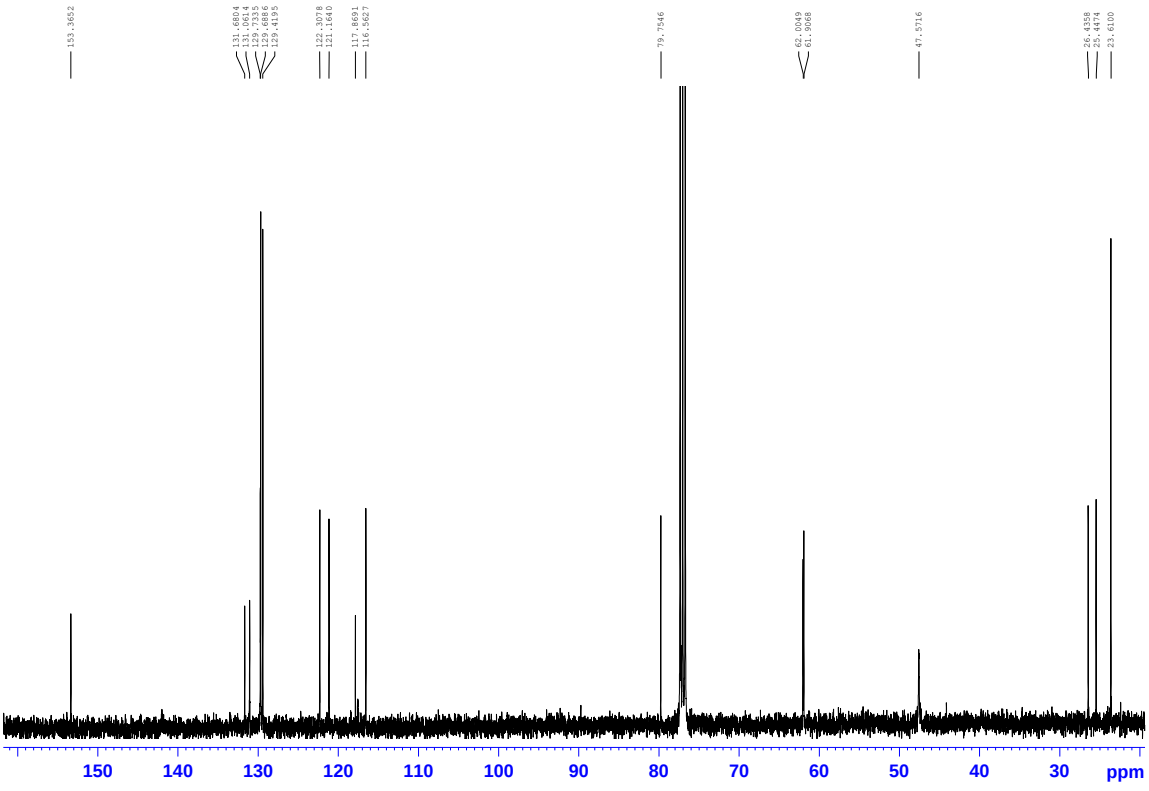
Compound 13b ^{13}C NMR $CDCl_3$



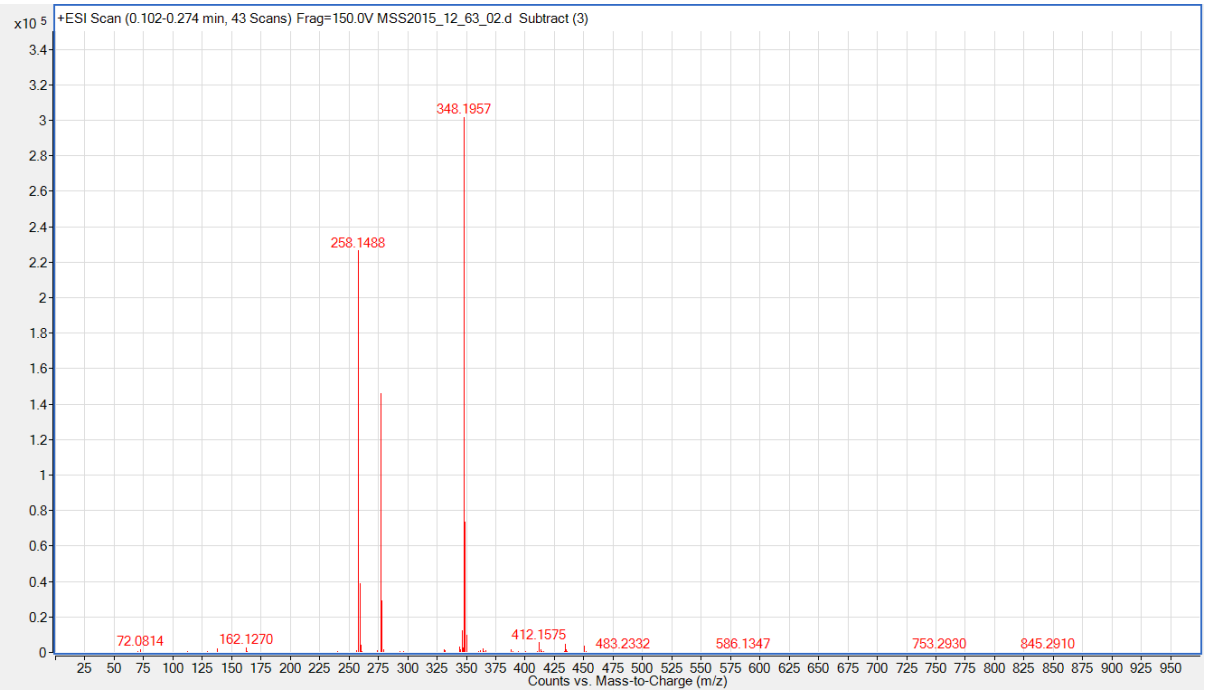
Compound 28 ^{1}H NMR $CDCl_3$



Compound 28 ^{13}C NMR $CDCl_3$

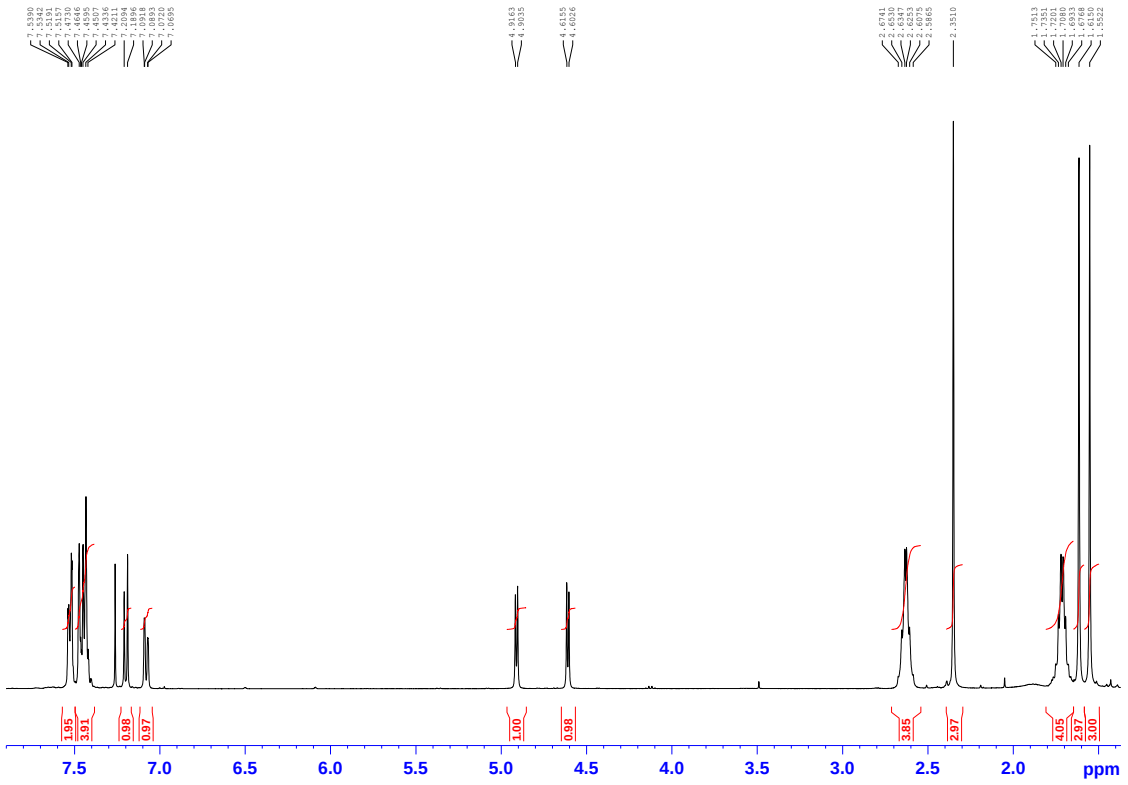


Compound 28 MS

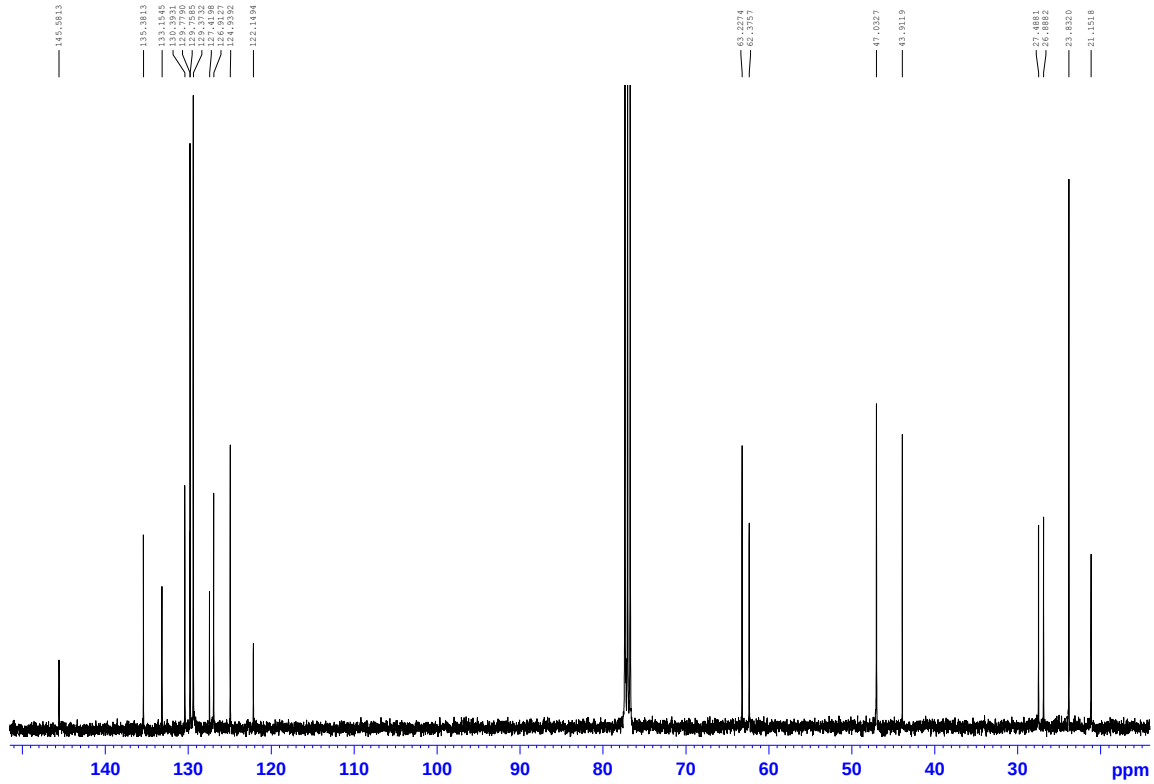


Best	Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
●	C23 H25 N O4 S	(M+H)+	412.1575	411.1503	411.1504	98.79	0.3
○	C23 H22 O4 S	(M+NH4)+	412.1575	394.1238	394.1239	98.79	0.31
○	C24 H25 N2 O S	(M+Na)+	412.1575	389.1684	389.1688	97.47	0.95

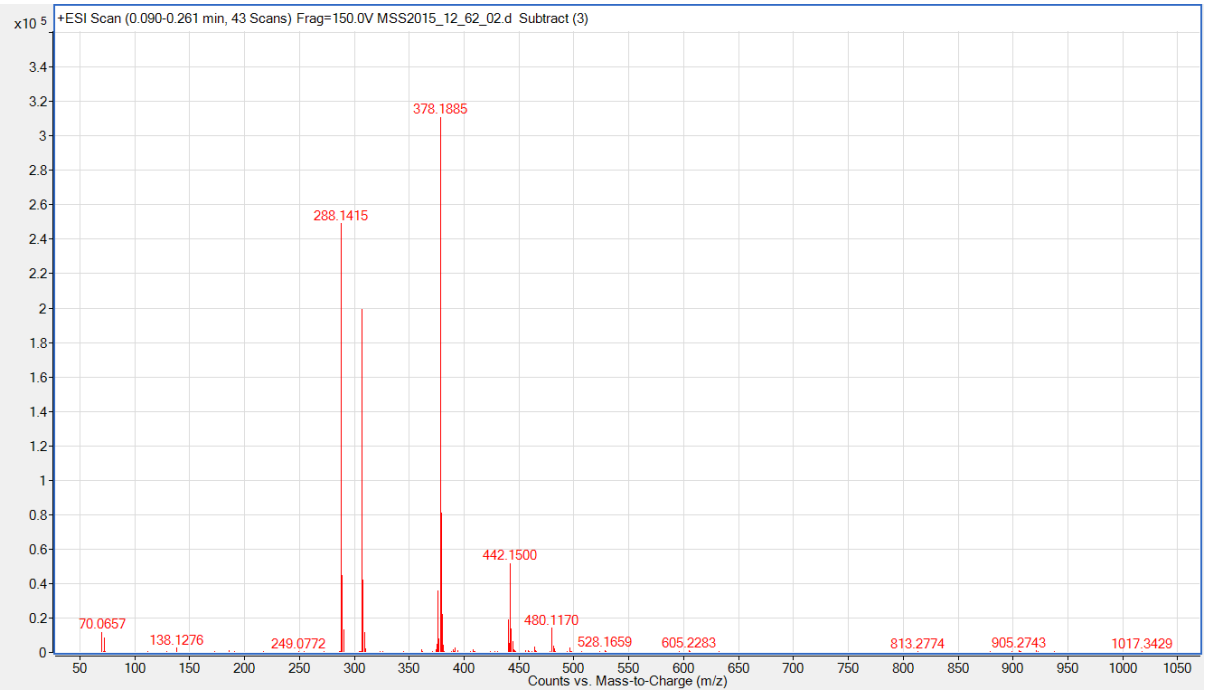
Compound 29 ^{1}H NMR $CDCl_3$



Compound 29 ^{13}C NMR $CDCl_3$

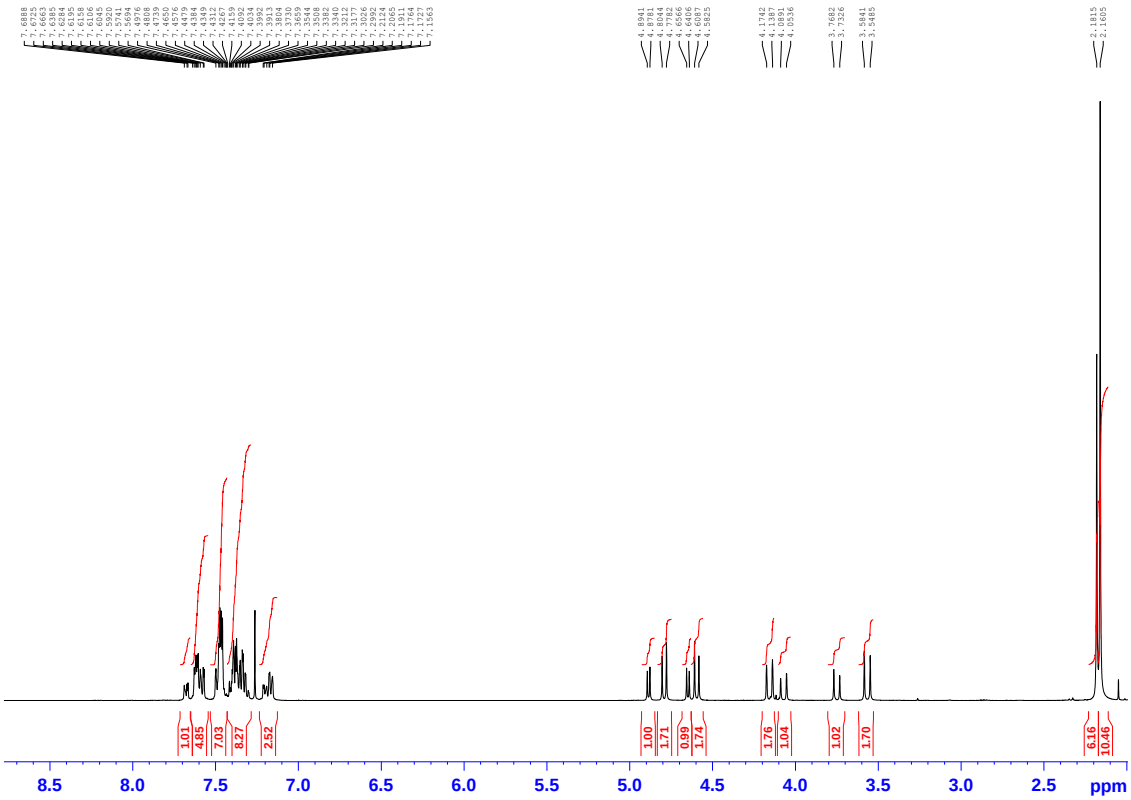


Compound 29 MS

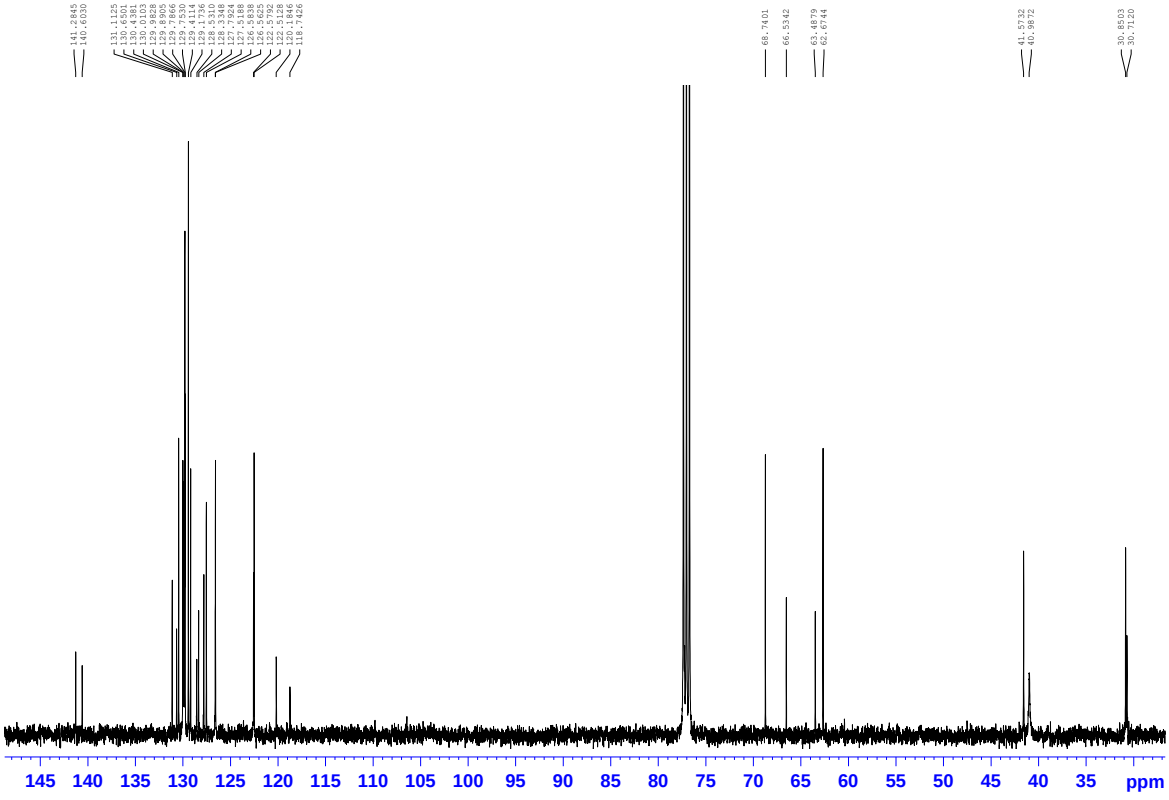


Best	Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
▶	C24 H27 N O3 S2	(M+H)+	442.1500	441.1427	441.1432	98.24	1.17
	C24 H24 O3 S2	(M+NH4)+	442.1500	424.1162	424.1167	98.24	1.22
	C21 H27 N2 O6	(M+K)+	442.1500	403.1866	403.1869	97.22	0.69

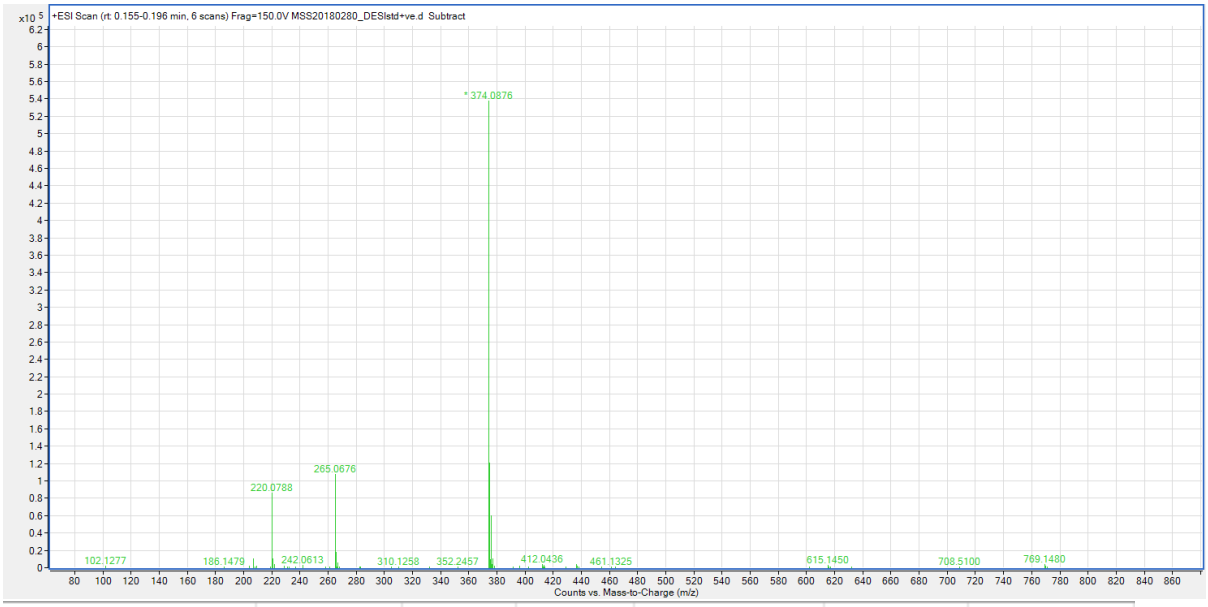
Compound 34 ^{1}H NMR $CDCl_3$



Compound 34 ^{13}C NMR $CDCl_3$

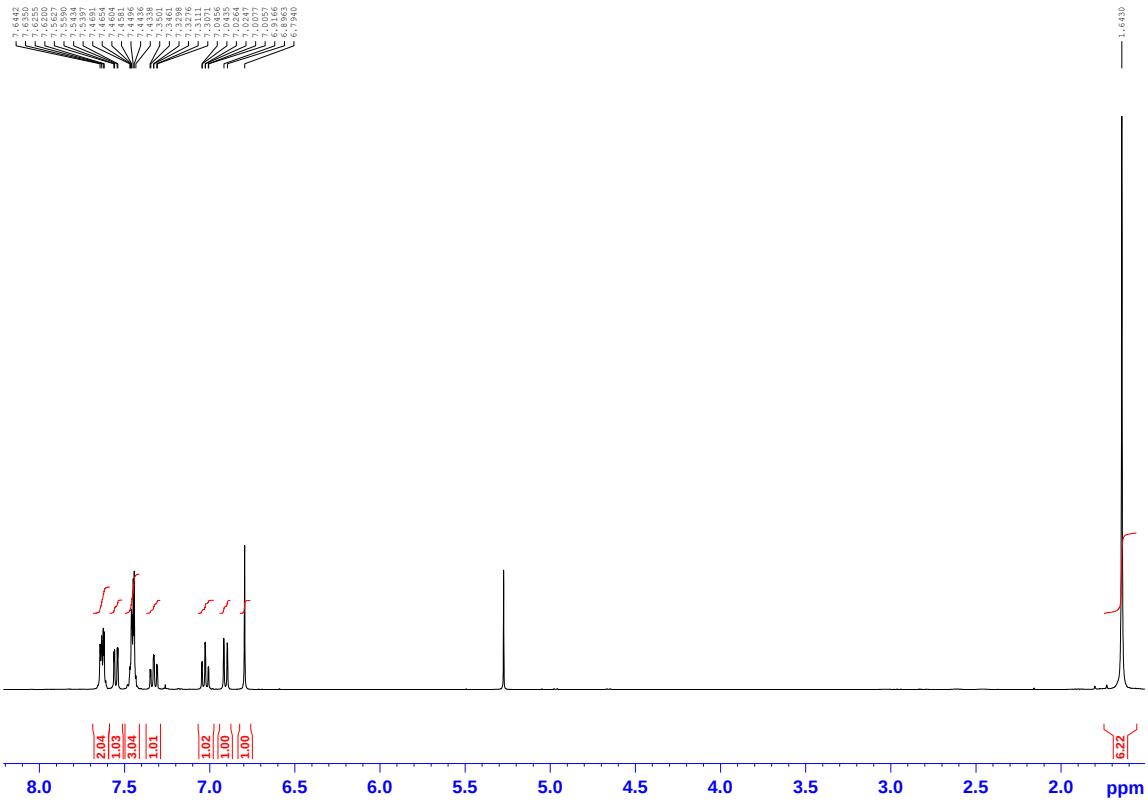


Compound 34 MS

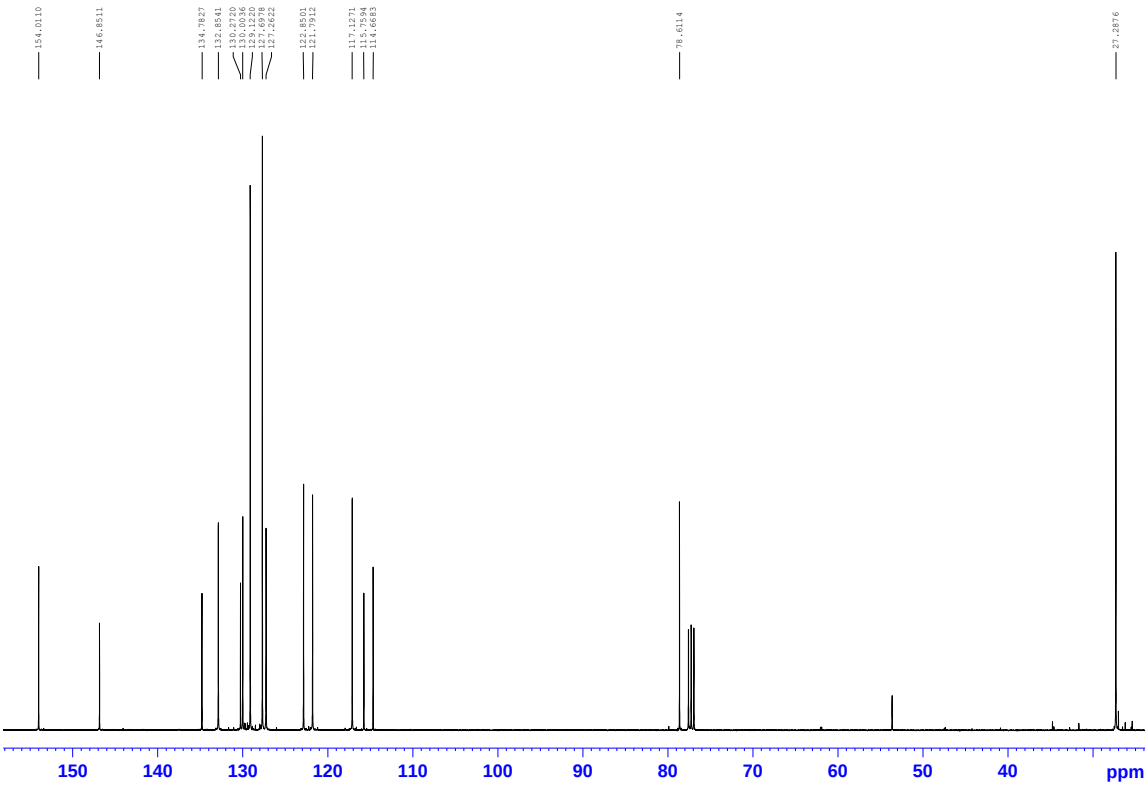


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C19 H19 N O3 S2	(M+H)+	374.0876	373.0802	373.0806	97.71	1.08
C17 H17 N4 O2 S2	(M+H)+	374.0876	373.0803	373.0793	95.53	-2.76
C25 H13 N2 S	(M+H)+	374.0876	373.08	373.0799	87.27	-0.2
C14 H21 N4 O2 S3	(M+H)+	374.0876	373.0804	373.0827	78.74	5.97
C22 H17 N2 S2	(M+H)+	374.0876	373.0802	373.0833	75.7	8.29
C22 H15 N O3 S	(M+H)+	374.0876	373.08	373.0773	74.6	-7.42
C16 H23 N O3 S3	(M+H)+	374.0876	373.0803	373.084	65.46	9.81
C28 H9 N2	(M+H)+	374.0876	373.0795	373.0766	52.09	-7.89

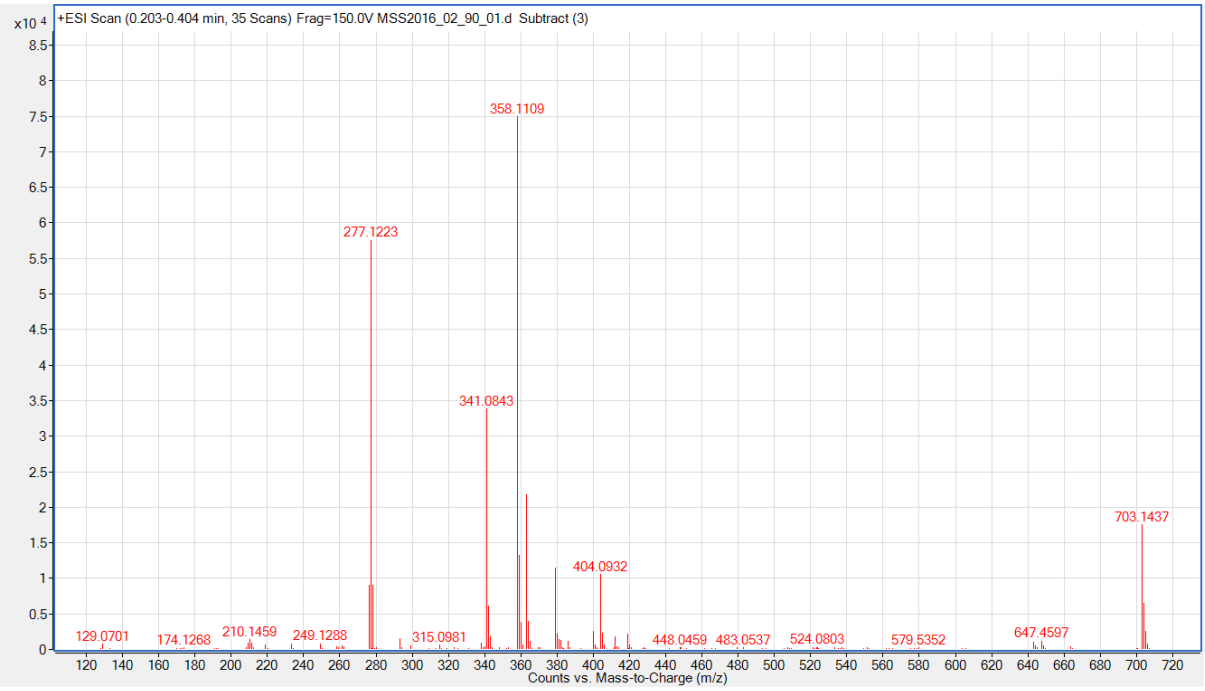
Compound 30 ^{1}H NMR $CDCl_3$



Compound 30 ^{13}C NMR $CDCl_3$

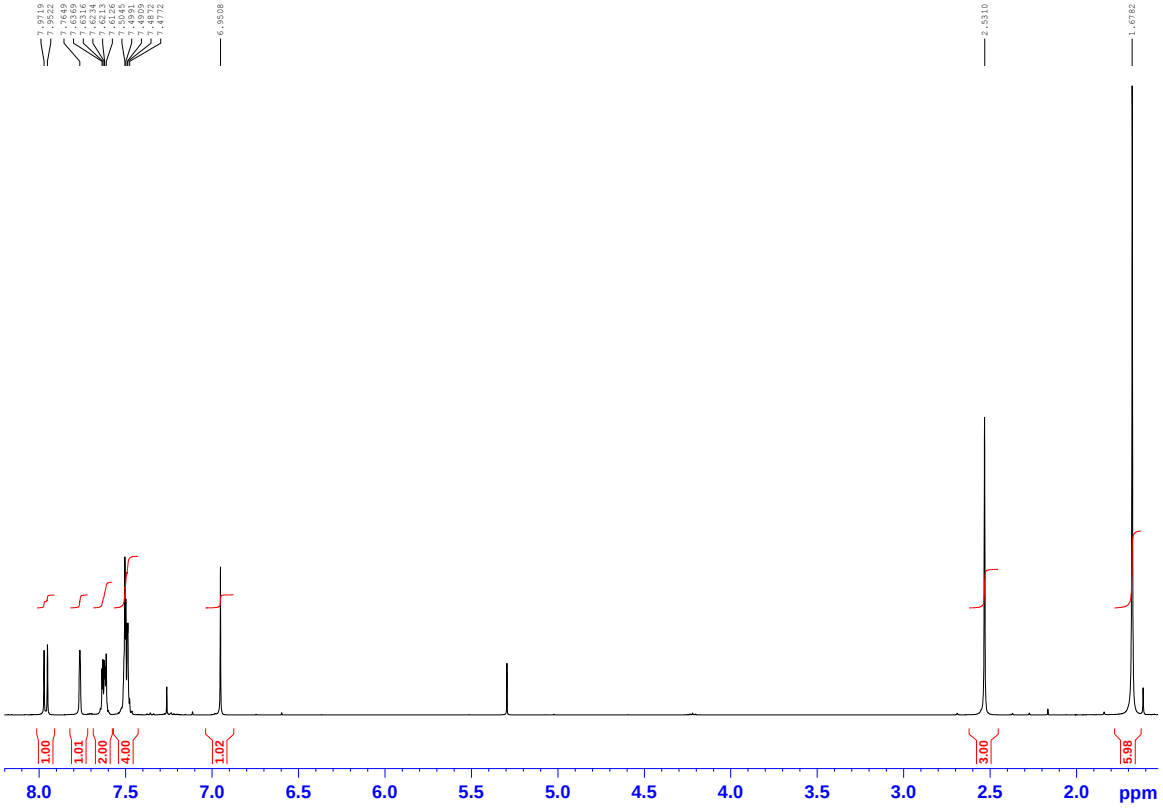


Compound 30 MS

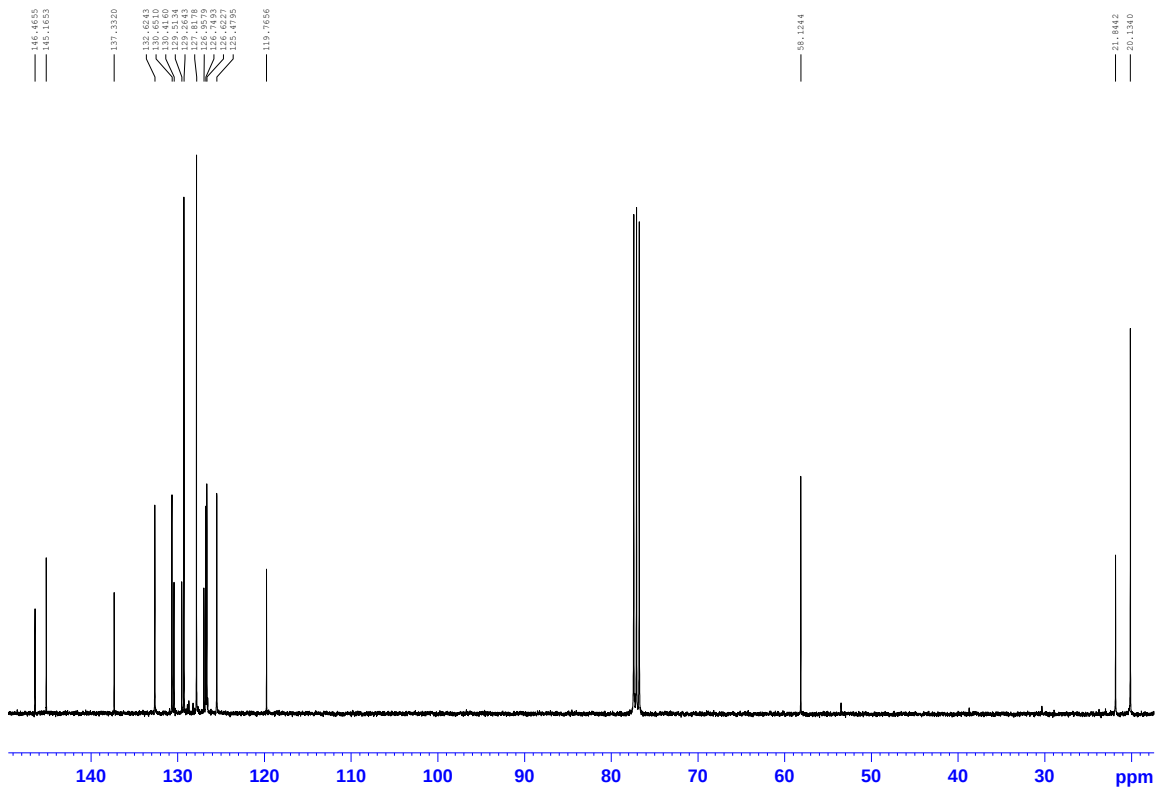


Best	Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
●	C19 H16 O4 S	(M+H)+	341.0843	340.0771	340.0769	96.49	-0.56
○	C17 H18 O4 S	(M+Na)+	341.0843	318.0952	318.0926	81.51	-8.22
○	C25 H7 O	(M+NH4)+	341.0843	323.0502	323.0497	78.79	-1.66
○	C22 H11 O S	(M+NH4)+	341.0843	323.0506	323.0531	75.23	7.7

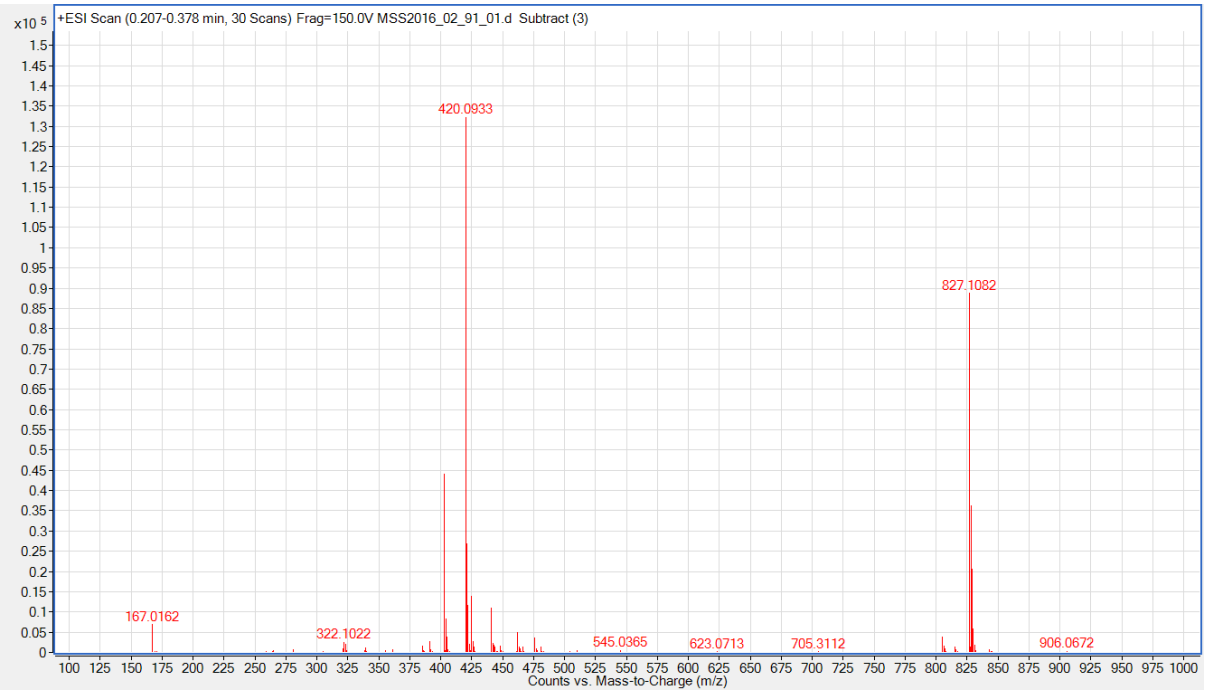
Compound 31a ^{1}H NMR $CDCl_3$



Compound 31a ^{13}C NMR $CDCl_3$

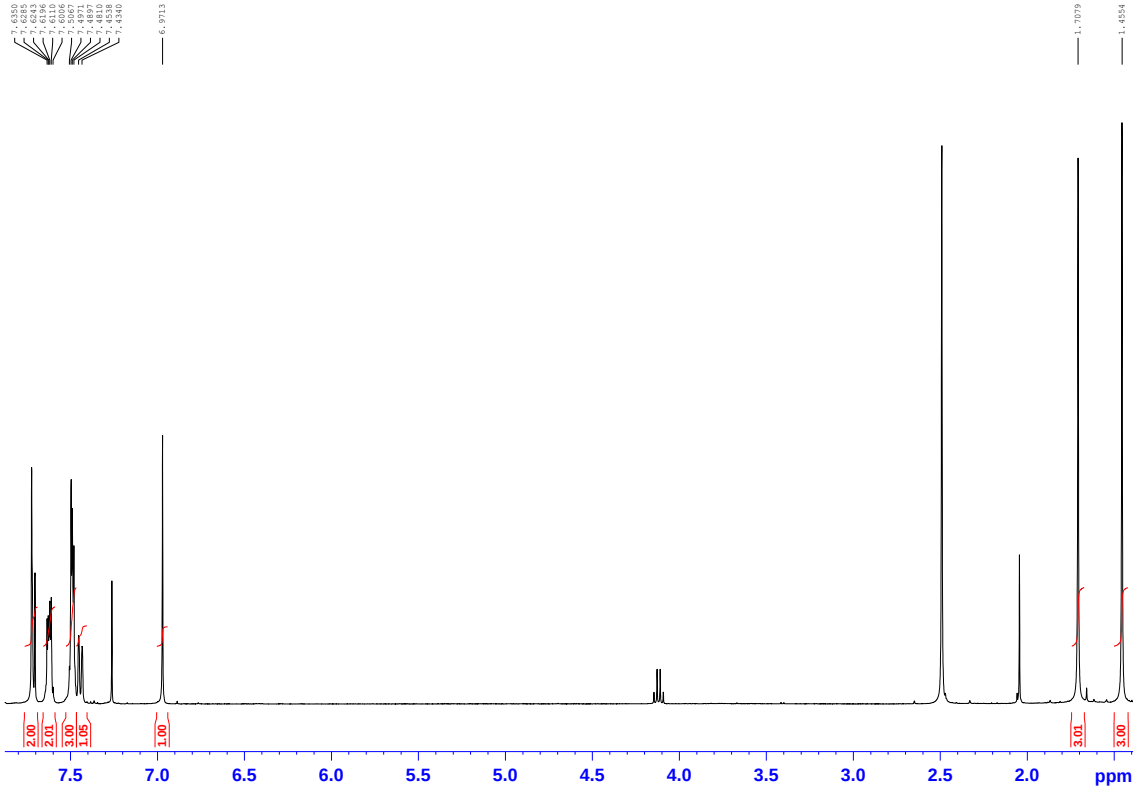


Compound 31a MS

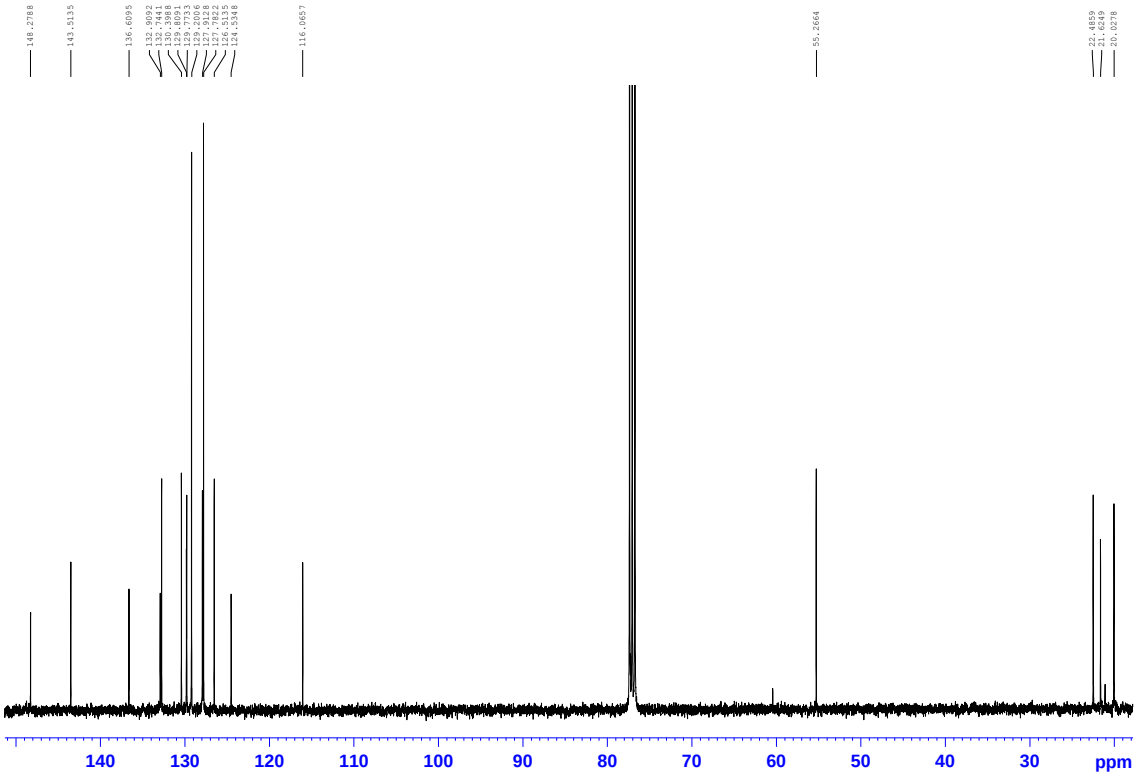


Best	Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
●	C20 H18 O5 S2	(M+H)+	403.0669	402.0596	402.0596	94.42	-0.02
○	C18 H20 O5 S2	(M+Na)+	403.0669	380.0777	380.0752	83.26	-6.42
○	C26 H9 O2 S	(M+NH4)+	403.0669	385.0328	385.0323	82.86	-1.32
○	C23 H13 O2 S2	(M+NH4)+	403.0669	385.033	385.0357	74.2	6.94

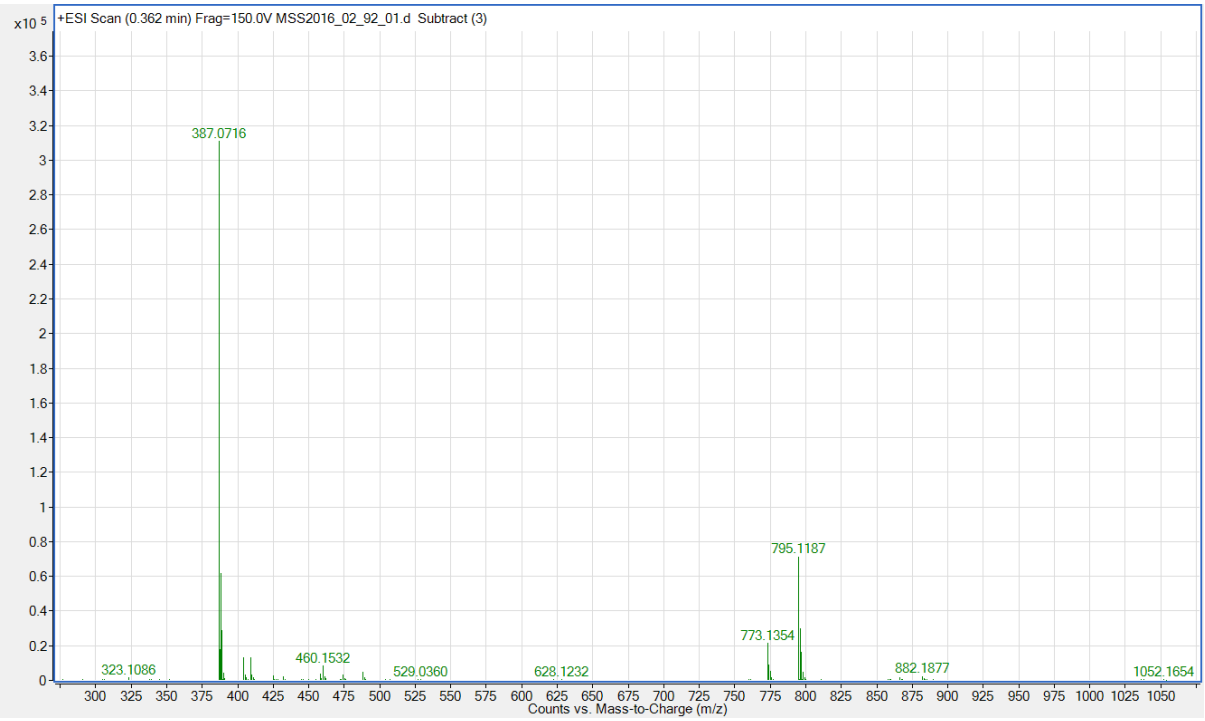
Compound 31b ^{1}H NMR $CDCl_3$



Compound 31b ^{13}C NMR $CDCl_3$

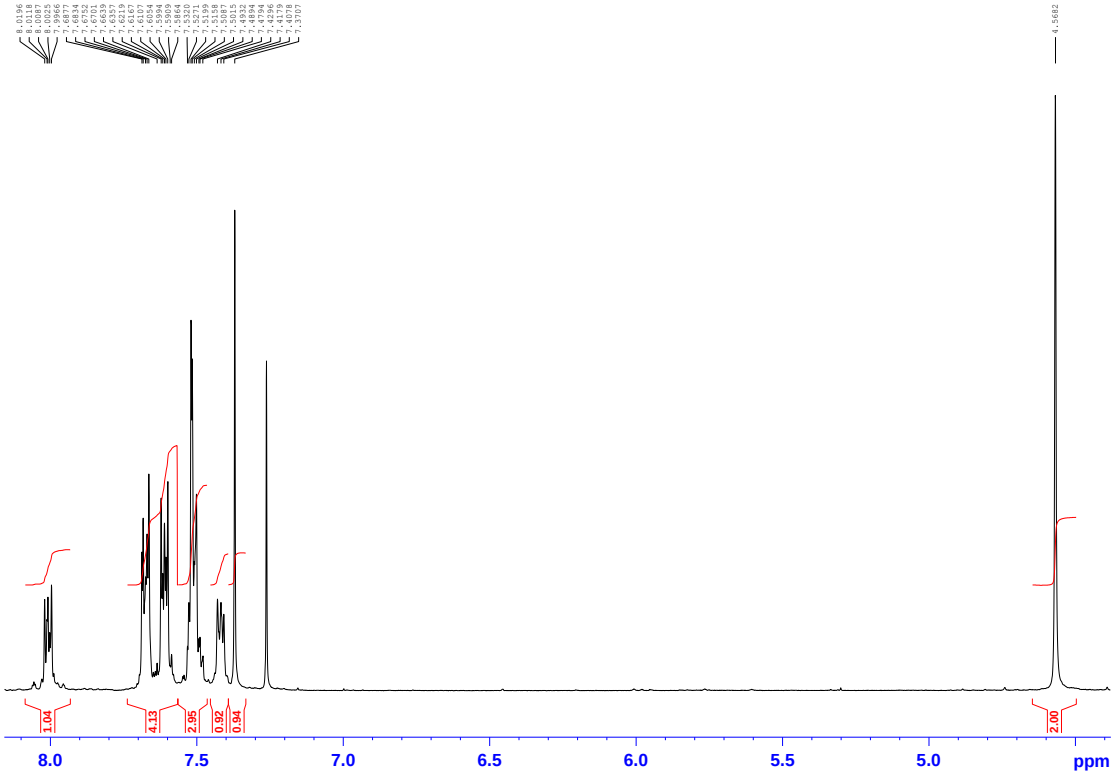


Compound 31b MS

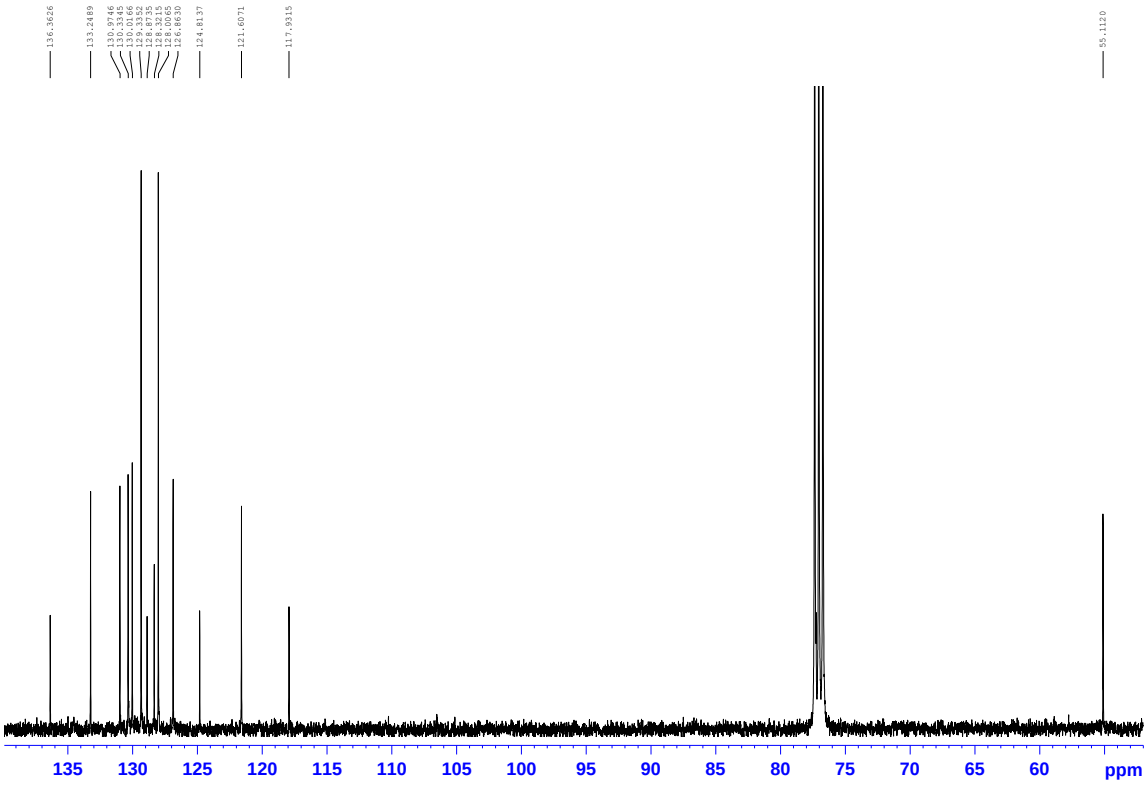


Best	Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
●	C20 H18 O4 S2	(M+H)+	387.0716	386.0642	386.0647	96.17	1.05
○	C18 H20 O4 S2	(M+Na)+	387.0716	364.0823	364.0803	88.2	-5.57
○	C26 H9 O S	(M+NH4)+	387.0716	369.0375	369.0374	84.72	-0.22
○	C15 H24 O5 S2	(M+K)+	387.0716	348.1084	348.1065	75.15	-5.45
○	C23 H14 O4 S	(M+H)+	387.0716	386.064	386.0613	74.32	-7.17

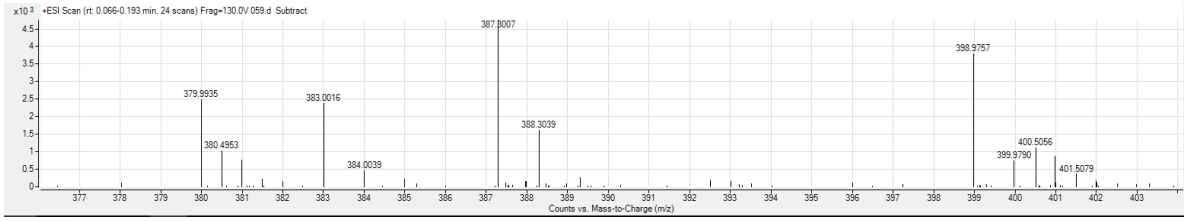
Compound 35 ^{1}H NMR $CDCl_3$



Compound 35 ^{13}C NMR $CDCl_3$

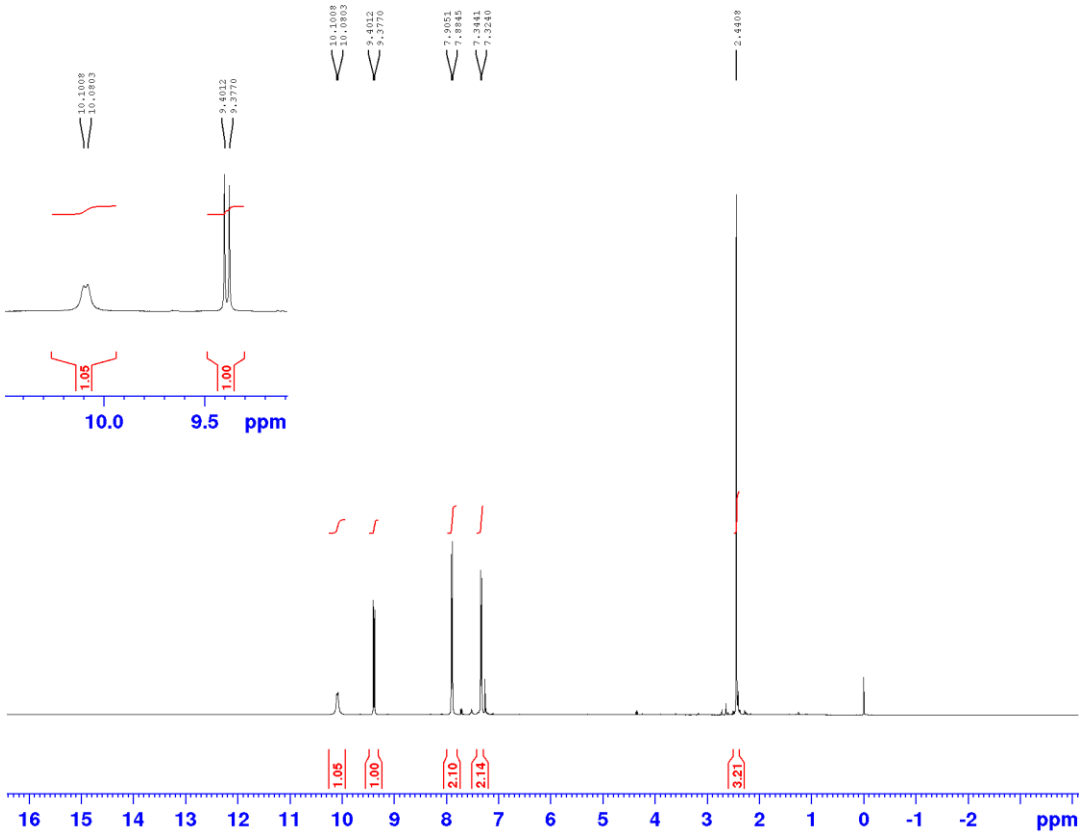


Compound 35 MS

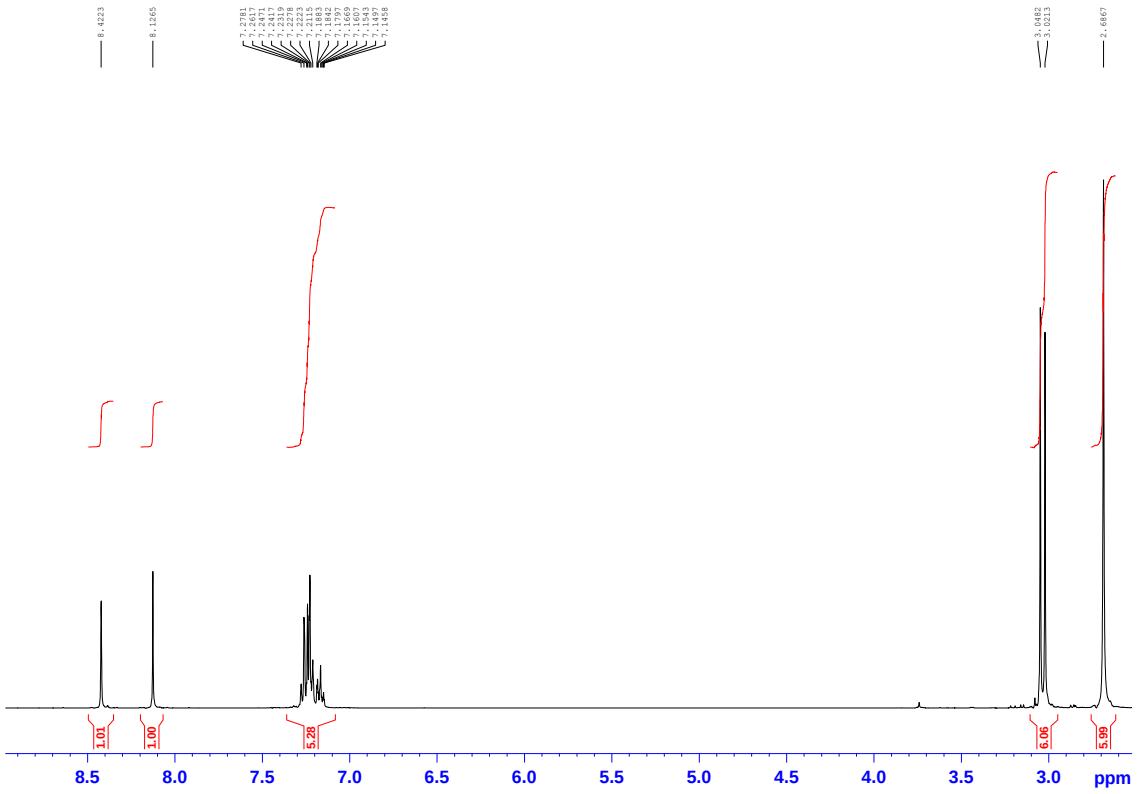


Formula	Observed m/z	Proposed adduct	Charge	Observed neutral mass	Theoretical neutral mass	Mass error (ppm)
C17H12O5S2	383.0017	Na+	1+	360.0137	360.0126	3.07
	398.9756	K+	1+	360.0143		4.72

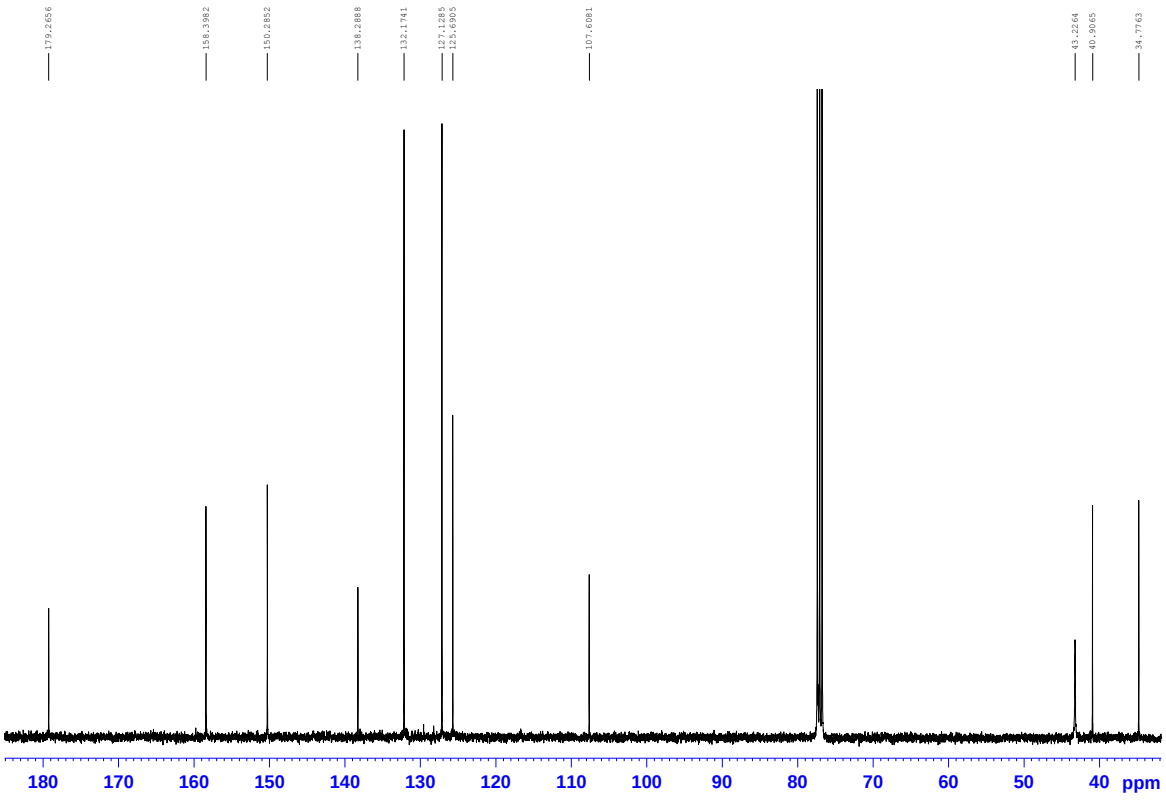
Compound 38 ^{1}H NMR $CDCl_3$



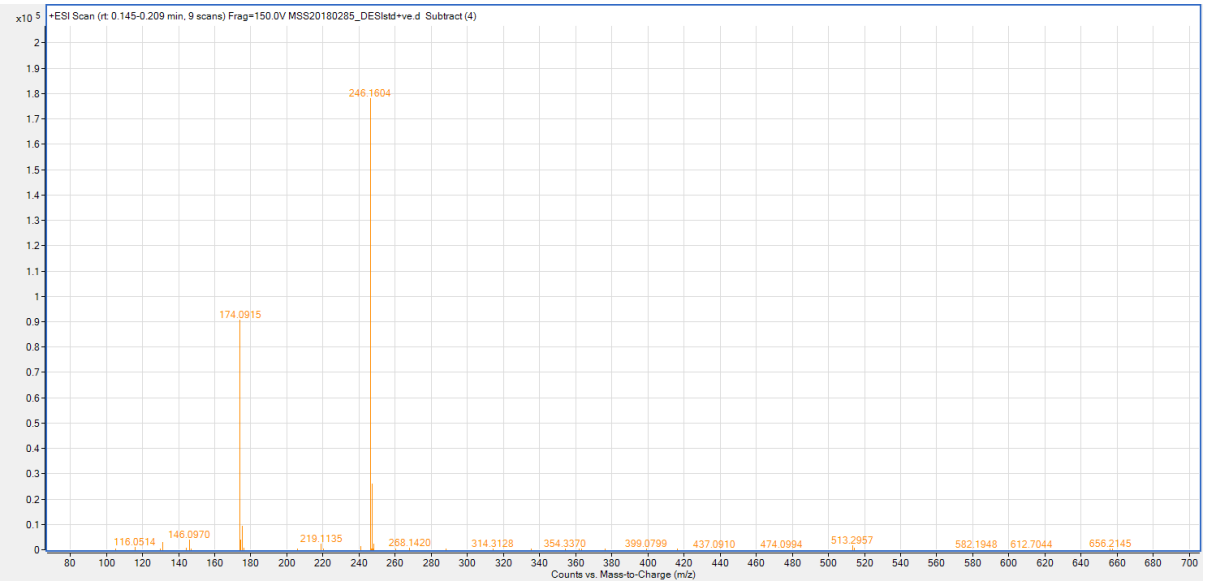
Compound 39 ^{1}H NMR $CDCl_3$



Compound 39 ^{13}C NMR $CDCl_3$

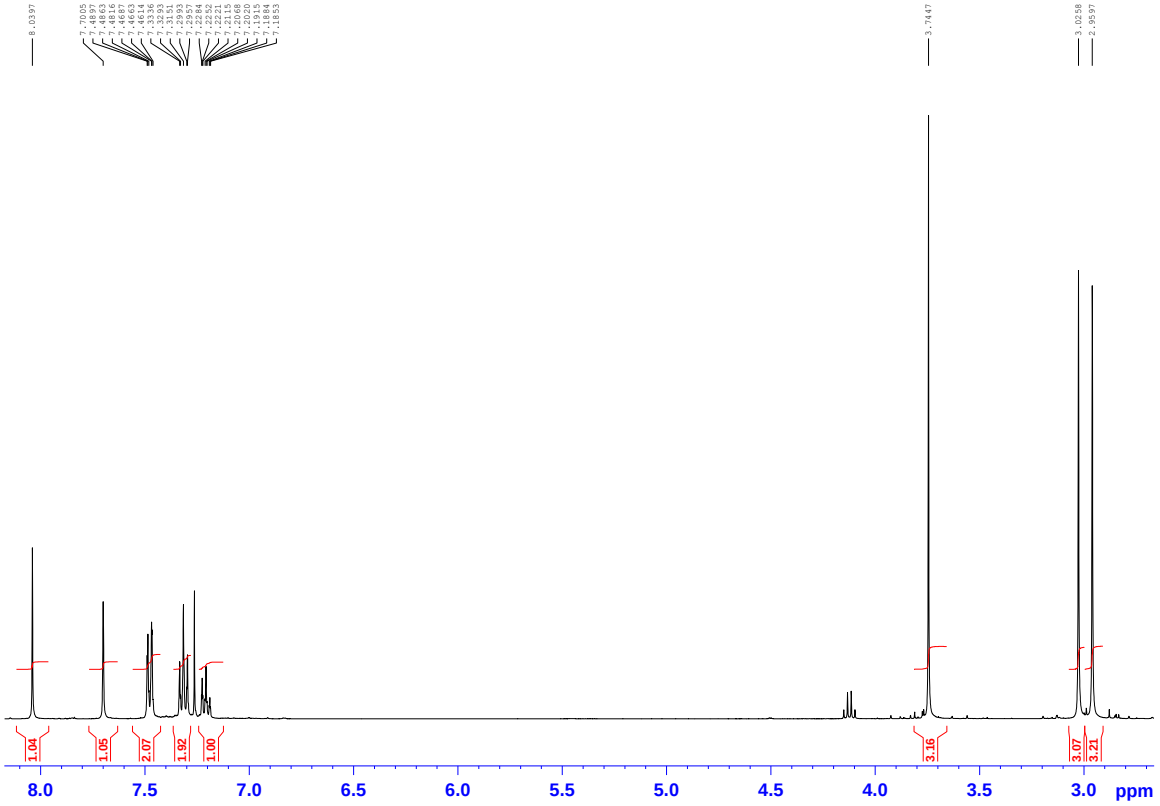


Compound 39 MS

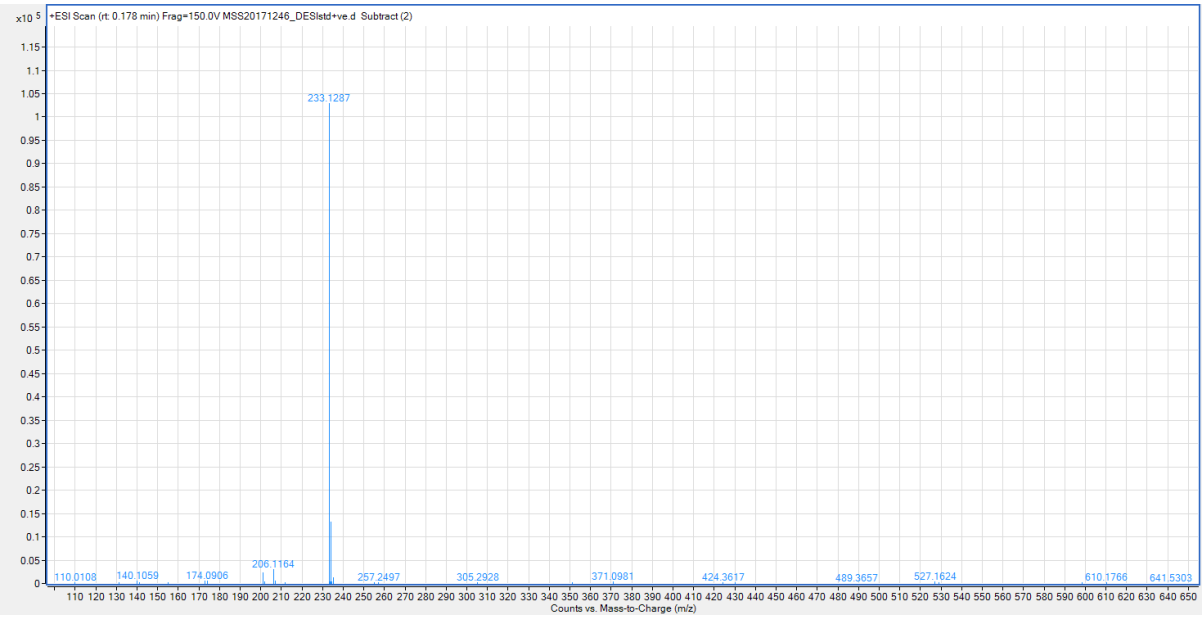


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C14 H19 N3 O	(M+H)+	246.1604	245.1531	245.1528	98.66	-1.09
C16 H21 O2	(M+H)+	246.1604	245.153	245.1542	92.22	4.63
C11 H21 N2 O4	(M+H)+	246.1604	245.1531	245.1501	73.92	-12
C11 H23 N3 O S	(M+H)+	246.1604	245.1532	245.1562	67.05	12.18

Compound 41 ^{1}H NMR $CDCl_3$

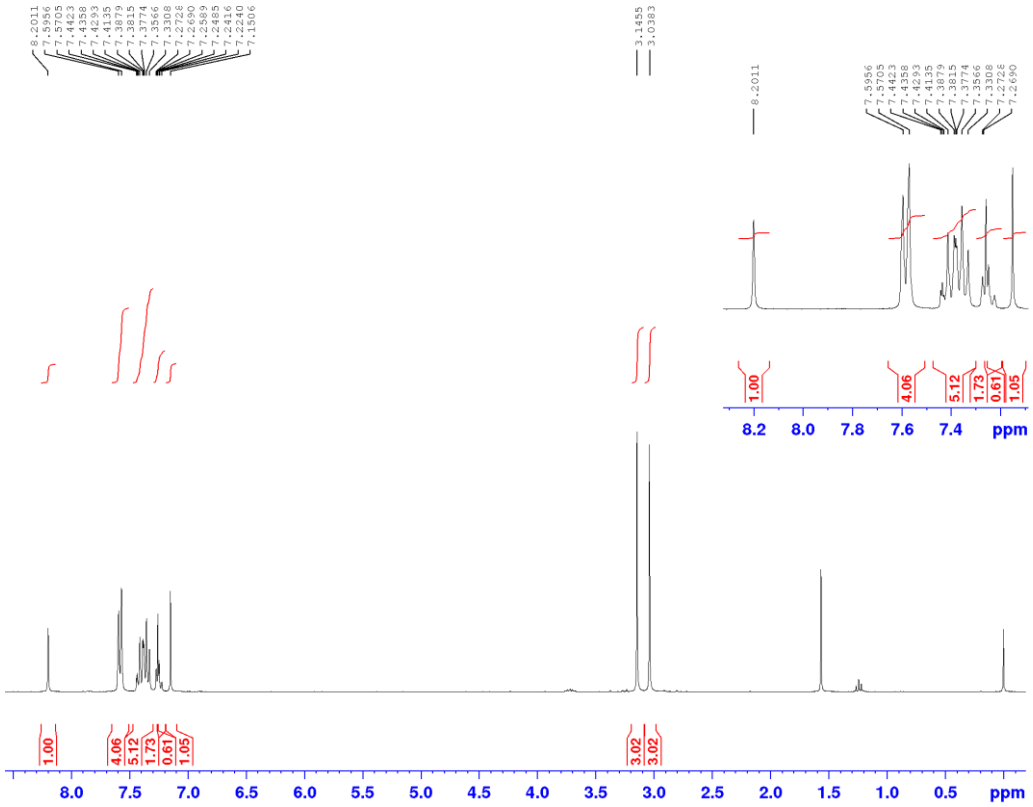


Compound 41 MS

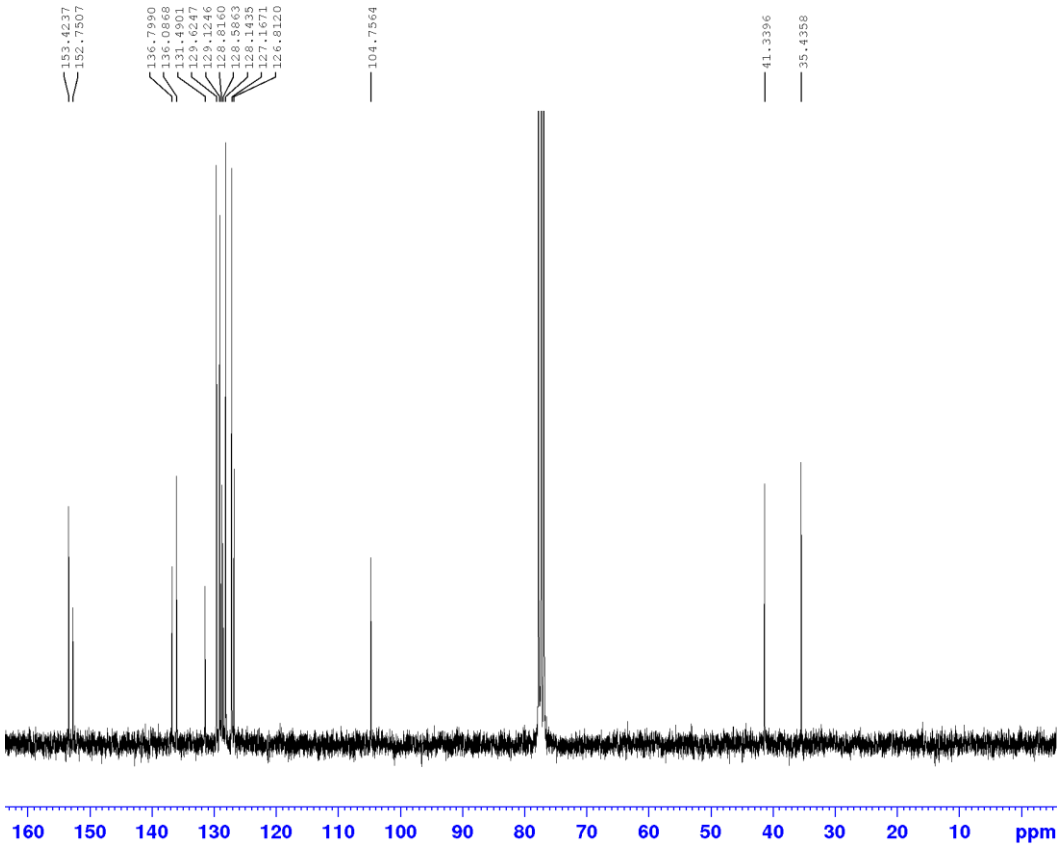


Best	Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
○	C13 H16 N2 O2	(M+H)+	233.1287	232.1215	232.1212	97.41	-1.24
○	C13 H13 N O2	(M+NH4)+	233.1287	215.0949	215.0946	97.41	-1.34
○	C16 H18	(M+Na)+	233.1287	210.1395	210.1409	86.62	6.55
○	C11 H14 N5 O	(M+H)+	233.1287	232.1215	232.1198	86.23	-7.31
○	C11 H11 N4 O	(M+NH4)+	233.1287	215.095	215.0933	86.23	-7.89
○	C11 H20 N3	(M+K)+	233.1287	194.1657	194.1657	86.17	0.21
○	C13 H22 O	(M+K)+	233.1287	194.1656	194.1671	78.38	7.45
○	C11 H18 N2 O2	(M+Na)+	233.1287	210.1395	210.1368	75.85	-12.85
○	C10 H18 N O5	(M+H)+	233.1287	232.1215	232.1185	72.55	-12.75
○	C10 H15 O5	(M+NH4)+	233.1287	215.0949	215.0919	72.55	-13.76

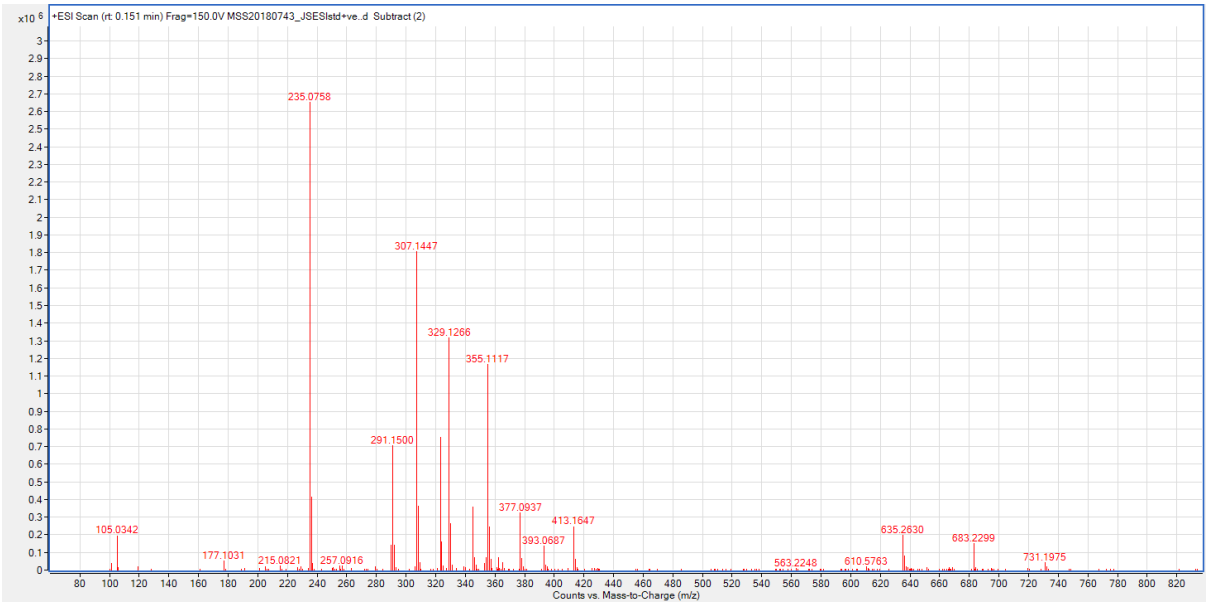
Compound 42 ^{1}H NMR $CDCl_3$



Compound 42 ^{13}C NMR $CDCl_3$



Compound 42 MS



Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C19 H18 N2 O3 S	(M+H)+	355.1117	354.1044	354.1038	97.12	-1.75
C13 H16 N5 O7	(M+H)+	355.1117	354.1043	354.105	90.44	1.96
C11 H14 N8 O6	(M+H)+	355.1117	354.1044	354.1036	87.67	-2.13
C17 H16 N5 O2 S	(M+H)+	355.1117	354.1045	354.1025	87.6	-5.77
C12 H18 N8 O S2	(M+H)+	355.1117	354.1047	354.1045	86.75	-0.62
C13 H24 N O6 S2	(M+H)+	355.1117	354.1045	354.1045	85.05	-0.09

checkCIF/PLATON report for compound 9f (CCDC 1913658)

Structure factors have been supplied for datablock(s) DZ_017_0ma_a

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: DZ_017_0ma_a

```
Bond precision: C-C = 0.0021 A          Wavelength=0.71073
Cell:             a=11.8439(7)     b=7.4115(5)    c=23.3606(17)
                  alpha=90         beta=90         gamma=90
Temperature:      202 K
                Calculated                Reported
Volume          2050.6(2)                 2050.6(2)
Space group     P b c a                   P b c a
Hall group      -P 2ac 2ab                -P 2ac 2ab
Moiety formula C12 H12 N2 O               ?
Sum formula     C12 H12 N2 O              C12 H12 N2 O
Mr              200.24                    200.24
Dx,g cm-3       1.297                     1.297
Z               8                         8
Mu (mm-1)       0.085                     0.085
F000            848.0                     848.0
F000'           848.33
h,k,lmax        16,10,33                  16,10,33
Nref            3124                      3116
Tmin,Tmax       0.9830,0.992              0.780,0.960
Tmin'           0.983
Correction method= # Reported T Limits: Tmin=0.780 Tmax=0.960
AbsCorr = MULTI-SCAN

Data completeness= 0.997          Theta(max)= 30.508

R(reflections)= 0.0669( 2491)     wR2(reflections)= 0.1925( 3116)
```

S = 1.042 Npar= 138

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level. Click on the
hyperlinks for more details of the test.

Alert level C

PLAT147_ALERT_1_C	s.u. on Symmetry Constrained Cell Angle(s)	Please Check
PLAT906_ALERT_3_C	Large K Value in the Analysis of Variance	6.163 Check
PLAT906_ALERT_3_C	Large K Value in the Analysis of Variance	2.045 Check
PLAT934_ALERT_3_C	Number of (Iobs-Icalc)/SigmaW > 10 Outliers	1 Check
PLAT978_ALERT_2_C	Number C-C Bonds with Positive Residual Density.	0 Info

---

Alert level G

PLAT910_ALERT_3_G	Missing # of FCF Reflection(s) Below Theta(Min).	1 Note
PLAT912_ALERT_4_G	Missing # of FCF Reflections Above STh/L= 0.600	10 Note

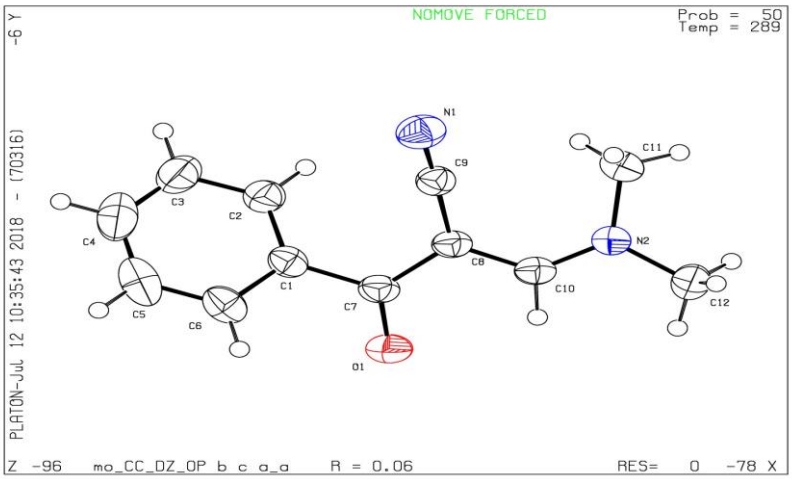
---

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
5 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
2 **ALERT level G** = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
1 ALERT type 2 Indicator that the structure model may be wrong or deficient
4 ALERT type 3 Indicator that the structure quality may be low
1 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

PLATON version of 23/04/2018; check.def file version of 23/04/2018

Datablock DZ_017_0ma_a - ellipsoid plot



CheckCIF/PLATON report for compound 9f′ (CCDC 1913654)

Structure factors have been supplied for datablock(s) cu_ColourChem_ID0176_0m_a

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: cu_ColourChem_ID0176_0m_a

```
Bond precision: C-C = 0.0025 A            Wavelength=1.54178

Cell:           a=38.3150(15)      b=38.3150(15)     c=5.5470(8)
                alpha=90           beta=90           gamma=90
Temperature:    150 K

                Calculated         Reported
Volume          8143.2(13)         8143.4(16)
Space group     I 41/a             I 41/a
Hall group      -I 4ad             -I 4ad
Moiety formula C19 H11 N2 O2, C4 H12 N
Sum formula     C23 H23 N3 O2              C23 H23 N3 O2
Mr              373.44                     373.44
Dx,g cm-3       1.218                      1.218
Z               16                         16
Mu (mm-1)       0.631                      0.631
F000            3168.0                     3168.0
F000'           3177.14
h,k,lmax        47,47,6                    46,47,6
Nref            4139                       4122
Tmin,Tmax       0.963,0.969                0.690,0.890
Tmin'           0.881
Correction method= # Reported T Limits: Tmin=0.690 Tmax=0.890
AbsCorr = MULTI-SCAN

Data completeness= 0.996          Theta(max)= 74.521

R(reflections)= 0.0502( 3134)     wR2(reflections)= 0.1205( 4122)

S = 1.055                 Npar= 257
```

The following ALERTS were generated. Each ALERT has the format **test-name_ALERT_alert-type_alert-level.**
Click on the hyperlinks for more details of the test.

Alert level C

PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ..... 5.263 Check

```
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600         15
Report
```

Alert level G

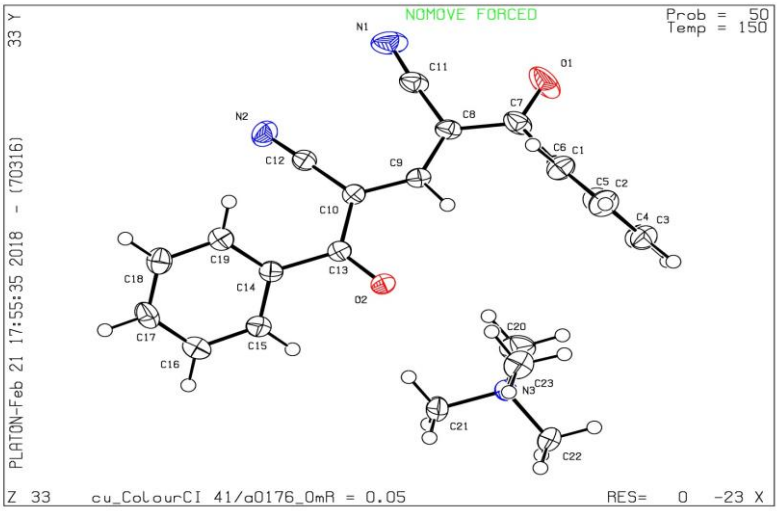
```
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT  Unusually Large       5.93 Why ?
PLAT152_ALERT_1_G The Supplied and Calc. Volume s.u. Differ by ...        -3 Units
PLAT180_ALERT_4_G Check Cell Rounding: # of Values Ending with 0 =         3 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600        6 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.        1 Info
```

```
0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   2 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   5 ALERT level G = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
2 ALERT type 2 Indicator that the structure model may be wrong or deficient
   2 ALERT type 3 Indicator that the structure quality may be low
   2 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

PLATON version of 30/01/2018; check.def file version of 30/01/2018

Datablock cu_ColourChem_ID0176_0m_a - ellipsoid plot



checkCIF/PLATON report for compound 9f″ (CCDC 1913653)

Structure factors have been supplied for datablock(s) mo_ColourChem_DZ025b_0m_a

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: mo_ColourChem_DZ025b_0m_a

```
Bond precision: C-C = 0.0026 A           Wavelength=0.71073

Cell:          a=9.145(6)         b=11.501(7)      c=11.649(8)
alpha=117.55(2) beta=94.48(3) gamma=91.05(2) Temperature: 150 K

                Calculated                Reported
Volume          1080.9(12)                1080.9(12)

Space group     P -1                      P -1

Hall group      -P 1                      -P 1

Moiety formula C19 H11 N2 O2, C5 H13 N2 ?
Sum formula     C24 H24 N4 O2             C24 H24 N4 O2

Mr              400.47                    400.47

Dx,g cm-3       1.230                     1.230

Z               2                         2

Mu (mm-1)       0.080                     0.080

F000            424.0                     424.0

F000'           424.16

h,k,lmax        12,16,16                  12,16,16

Nref            6292                      6260

Tmin,Tmax       0.980,0.985               0.580,0.890

Tmin'           0.978

Correction method= # Reported T Limits: Tmin=0.580 Tmax=0.890
AbsCorr = MULTI-SCAN

Data completeness= 0.995          Theta(max)= 29.984

R(reflections)= 0.0610( 4483)     wR2(reflections)= 0.1621( 6260)

S = 1.024                 Npar= 275
```

The following ALERTS were generated. Each ALERT has the format **test-name_ALERT_alert-type_alert-level.**
Click on the hyperlinks for more details of the test.

Alert level C

PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ..... 5.974 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.600 2 Report
PLAT918_ALERT_3_C Reflection(s) with I(obs) much Smaller I(calc) . 1 Check

Alert level G

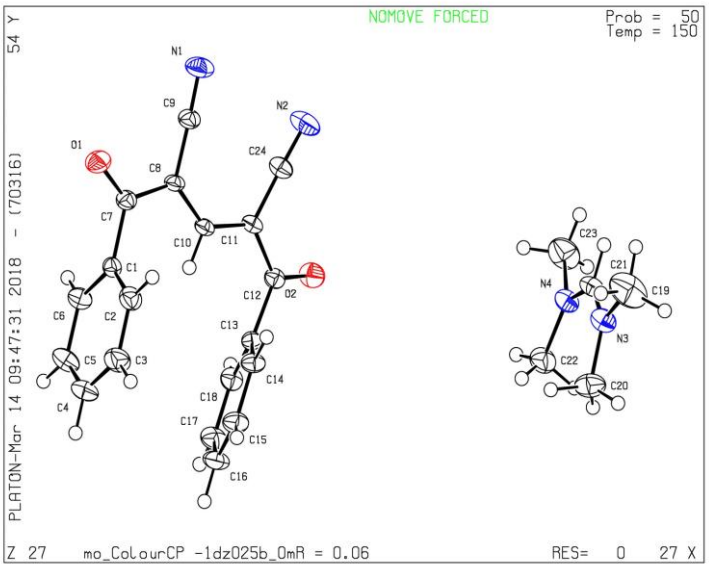
PLAT230_ALERT_2_G Hirshfeld Test Diff for C8 --C9 . 5.5 s.u.
PLAT230_ALERT_2_G Hirshfeld Test Diff for C11 --C24 . 5.6 s.u.
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety ..... C19 Check
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 32 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 11 Info

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
3 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
5 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
3 ALERT type 2 Indicator that the structure model may be wrong or deficient
3 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

PLATON version of 30/01/2018; check.def file version of 30/01/2018

Datablock mo_ColourChem_DZ025b_0m_a - ellipsoid plot



checkCIF/PLATON report for compound 10a (CCDC 1913655)

Structure factors have been supplied for datablock(s) mo_CC_KAA4R_0m

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: mo_CC_KAA4R_0m

```
Bond precision: C-C = 0.0018 A           Wavelength=0.71073

Cell:           a=9.6018(7)    b=12.4113(10)       c=16.8115(14)
           alpha=90            beta=96.978(3)     gamma=90
Temperature:    150 K

Calculated                     Reported
Volume          1988.6(3)      1988.6(3)
Space group     P 21/n                  P 1 21/n 1
Hall group      -P 2yn                  -P 2ybc (x-
Moiety formula C24 H23 N O3 S          C24 H23 N O3 S
Sum formula      C24 H23 N O3 S        C24 H23 N O3 S
Mr              405.49         405.52
Dx,g cm-3       1.354          1.354
Z               4              4
Mu (mm-1)       0.189          0.189
F000            856.0          856.9
F000'           856.86
h,k,lmax        13,17,24       13,17,24
Nref            6069           6044
Tmin,Tmax       0.963,0.972
Tmin'           0.963

Correction method= Not given

Data completeness= 0.996       Theta(max)= 30.510

R(reflections)= 0.0396( 5031)     wR2(reflections)= 0.1086( 6044)
S = 1.052                 Npar= 263
```

The following ALERTS were generated. Each ALERT has the format **test-name_ALERT_alert-type_alert-level.**

Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT126_ALERT_1_C Error in or Uninterpretable Hall Symbol  .......    -P 2YBC (X-
Z,Y
PLAT761_ALERT_1_C CIF Contains no X-H Bonds .....................     Please Check
```

```
PLAT762_ALERT_1_C CIF Contains no X-Y-H or H-Y-H Angles ..........     Please Check
```

Alert level G

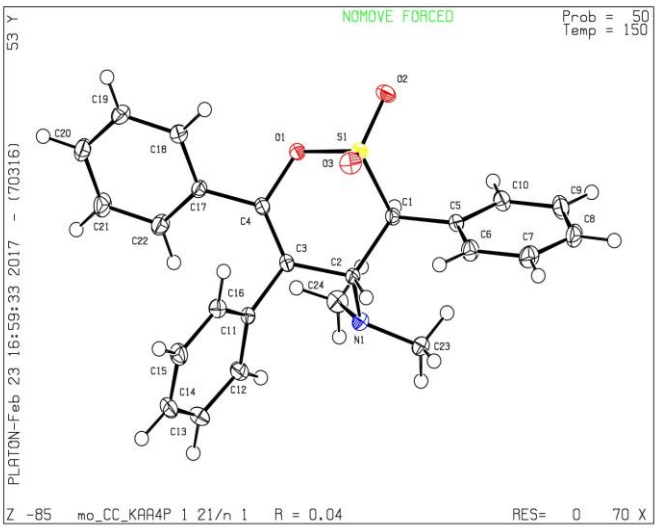
```
PLAT073_ALERT_1_G H-atoms ref, but _hydrogen_treatment reported as     constr Check
PLAT395_ALERT_2_G Deviating  X-O-Y   Angle from 120 Deg for  O1          116.2
Degre
PLAT793_ALERT_4_G The Model has Chirality at C1      (Centro SPGR)          S
Verify
PLAT793_ALERT_4_G The Model has Chirality at C2      (Centro SPGR)          R
Verify
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min)           1 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600         27 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...          1 Note
PLAT960_ALERT_3_G Number of Intensities with I  <   - 2*sig(I) ...          8 Check
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.         23 Note
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   3 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   9 ALERT level G = General information/check it is not something unexpected

   4 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   3 ALERT type 2 Indicator that the structure model may be wrong or deficient
  2    ALERT type 3 Indicator that the structure quality may be low
  3    ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

PLATON version of 24/11/2016; check.def file version of 23/11/2016

Datablock mo_CC_KAA4R_0m - ellipsoid plot



checkCIF/PLATON report for compound 11a (CCDC 1913656)

Structure factors have been supplied for datablock(s) mo_CC_KAA9R_0m_a

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: mo_CC_KAA9R_0m_a

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

Cell:            a=8.8058(9)     b=20.394(2)          c=9.6437(10)
            alpha=90             beta=99.794(4)      gamma=90
Temperature:     150 K

Calculated                       Reported
Volume           1706.6(3)       1706.7(3)
Space group      P 21/n                    P 1 21/n 1
Hall group       -P 2yn                    -P 2ybc (x-
Moiety formula C22 H16 O3 S                C22 H16 O3 S
Sum formula      C22 H16 O3 S              C22 H16 O3 S
Mr               360.41          360.44
Dx,g cm-3        1.403           1.403
Z                4               4
Mu (mm-1)        0.209           0.209
F000             752.0           752.9
F000'            752.83
h,k,lmax         12,29,13        12,29,13
Nref             5220            5218
Tmin,Tmax        0.959,0.975
Tmin'            0.959

Correction method= Not given

Data completeness= 1.000         Theta(max)= 30.510

R(reflections)= 0.0686( 3595)      wR2(reflections)= 0.1417( 5218)
S = 1.056                  Npar= 235
```

The following ALERTS were generated. Each ALERT has the format **test-name_ALERT_alert-type_alert-level.**
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT126_ALERT_1_C Error in or Uninterpretable Hall Symbol  .......    -P 2YBC (X-
Z,Y
PLAT906_ALERT_3_C Large K value in the Analysis of Variance ......      7.438 Check
```

```
PLAT906_ALERT_3_C Large K value in the Analysis of Variance ......      2.097 Check
```

Alert level G

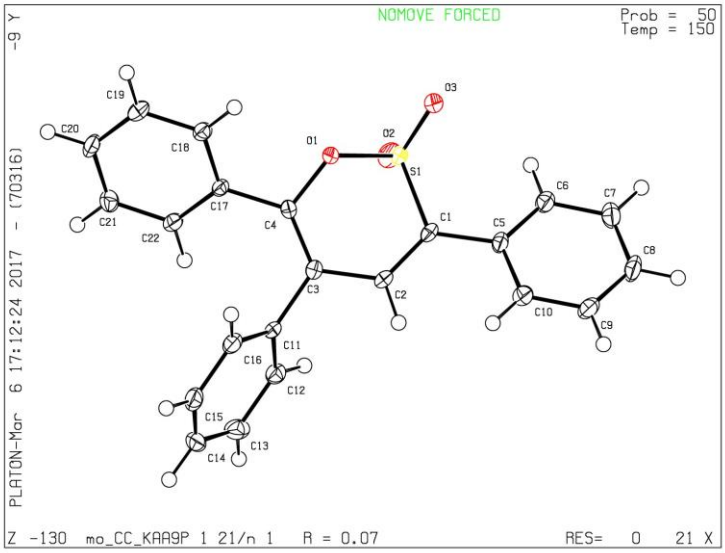
```
PLAT073_ALERT_1_G H-atoms ref, but _hydrogen_treatment reported as     constr Check
PLAT395_ALERT_2_G Deviating  X-O-Y  Angle from 120 Deg for  O1          120.2
Degree
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min)           1 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...          1 Note
PLAT960_ALERT_3_G Number of Intensities with I  <   - 2*sig(I) ...          8 Check
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.         11 Note
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   3 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   6 ALERT level G = General information/check it is not something unexpected

  2    ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  3    ALERT type 2 Indicator that the structure model may be wrong or deficient
  4    ALERT type 3 Indicator that the structure quality may be low
   0 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

PLATON version of 26/02/2017; check.def file version of 21/02/2017

Datablock mo_CC_KAA9R_0m_a - ellipsoid plot



checkCIF/PLATON report for compound 28 (CCDC 1913658)

Structure factors have been supplied for datablock(s) mo_Ross_SO2_0m

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: mo_Ross_SO2_0m

```
Bond precision: C-C = 0.0027 A           Wavelength=0.71073

Cell: a=11.6856(9)     b=14.0485(11)    c=13.2869(10) alpha=90
      beta=96.0216(18) gamma=90 Temperature: 296 K
```

	Calculated	Reported
Volume	2169.2(3)	2169.2(3)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C23 H25 N O4 S	
Sum formula	C23 H25 N O4 S	C23 H25 N O4 S
Mr	411.50	411.50
Dx,g cm-3	1.260	1.260
Z	4	4
Mu (mm-1)	0.177	0.177
F000	872.0	872.0
F000'	872.89	
h,k,lmax	16,20,19	16,20,18
Nref	6639	6623
Tmin,Tmax	0.958,0.982	0.770,0.880
Tmin'	0.957	

```
Correction method= # Reported T Limits: Tmin=0.770 Tmax=0.880
AbsCorr = MULTI-SCAN

Data completeness= 0.998          Theta(max)= 30.568

R(reflections)= 0.0480( 4378)     wR2(reflections)= 0.1333( 6623)

S = 1.008                 Npar= 264
```

The following ALERTS were generated. Each ALERT has the format **test-name_ALERT_alert-type_alert-level.**
Click on the hyperlinks for more details of the test.

Alert level B

```
PLAT601_ALERT_2_B Structure Contains Solvent Accessible VOIDS of .        129 Ang3
```

Author Response: Voids are present from evaporation of solvent. However, the structure refined well and gives the overall molecular connectivity.

Alert level C

```
PLAT220_ALERT_2_C Large Non-Solvent  C     Ueq(max)/Ueq(min) Range         3.4 Ratio
PLAT241_ALERT_2_C High   'MainMol' Ueq as Compared to Neighbors of        C21 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of        C20 Check
```

Alert level G

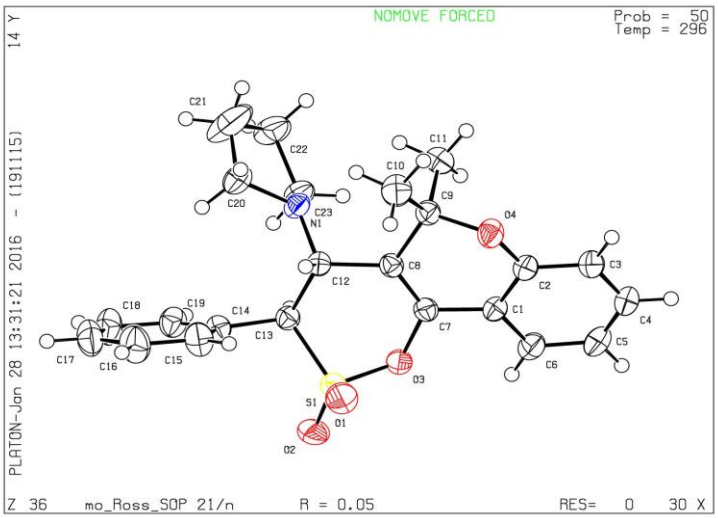
```
PLAT793_ALERT_4_G The Model has Chirality at C12     (Centro SPGR)          R
Verify
PLAT793_ALERT_4_G The Model has Chirality at C13     (Centro SPGR)          S
Verify
```

```
0 ALERT level A = Most likely a serious problem - resolve or explain
1 ALERT level B = A potentially serious problem, consider carefully
   3 ALERT level C = Check. Ensure it is not caused by an omission or oversight
2 ALERT level G = General information/check it is not something unexpected

   0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   4 ALERT type 2 Indicator that the structure model may be wrong or deficient
   0 ALERT type 3 Indicator that the structure quality may be low
   2 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

PLATON version of 19/11/2015; check.def file version of 17/11/2015

Datablock mo_Ross_SO2_0m - ellipsoid plot



checkCIF/PLATON report for compound 35 (CCDC 1913657)

Structure factors have been supplied for datablock(s) mo_ColourChem_OrlandoX_0m

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: mo_ColourChem_OrlandoX_0m

```
Bond precision: C-C = 0.0019 A           Wavelength=0.71073

Cell:           a=8.7498(5)     b=18.5113(11)         c=9.4511(6)
                alpha=90        beta=99.3488(19)      gamma=90
Temperature:    150 K

                Calculated      Reported
Volume          1510.46(16)               1510.46(16)
Space group     P 21/c          P 21/c
Hall group      -P 2ybc         -P 2ybc
Moiety formula C17 H12 O5 S2              ?
Sum formula     C17 H12 O5 S2             C17 H12 O5 S2
Mr              360.39                   360.39
Dx,g cm-3       1.585                     1.585
Z               4                          4
Mu (mm-1)       0.379                     0.379
F000            744.0                     744.0
F000'           745.36
h,k,lmax        13,28,14                 13,28,14
Nref            5796                       5781
Tmin,Tmax       0.913,0.934                0.690,0.750
Tmin'           0.910
Correction method= # Reported T Limits: Tmin=0.690 Tmax=0.750
AbsCorr = MULTI-SCAN

Data completeness= 0.997          Theta(max)= 33.186

R(reflections)= 0.0412( 4611)     wR2(reflections)= 0.1090( 5781)

S = 1.034                 Npar= 217
```

The following ALERTS were generated. Each ALERT has the format **test-name_ALERT_alert-type_alert-level.**
Click on the hyperlinks for more details of the test.

Alert level C

PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ..... 2.257 Check

Alert level G

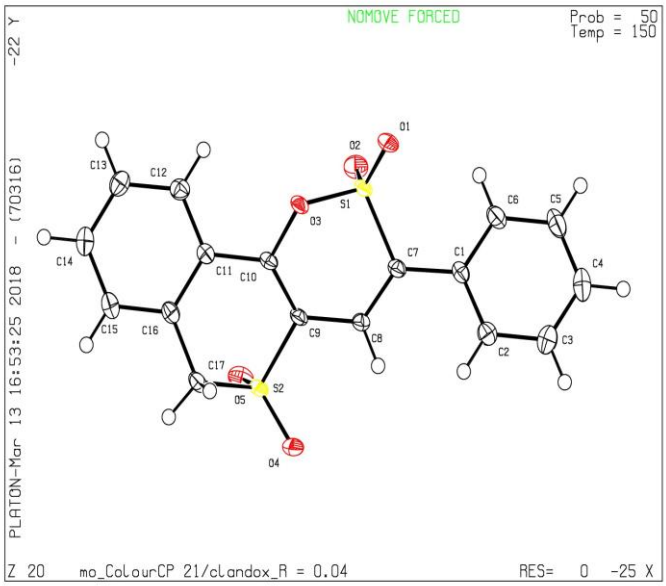
```
PLAT395_ALERT_2_G Deviating  X-O-Y    Angle From 120 for O3             120.0
Degree
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600         14 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...          1 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.         16 Info
```

```
0 ALERT level A = Most likely a serious problem - resolve or explain
0 ALERT level B = A potentially serious problem, consider carefully
1 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   4 ALERT level G = General information/check it is not something unexpected

   0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   3 ALERT type 2 Indicator that the structure model may be wrong or deficient
1 ALERT type 3 Indicator that the structure quality may be low
   1 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

PLATON version of 30/01/2018; check.def file version of 30/01/2018

Datablock mo_ColourChem_OrlandoX_0m - ellipsoid plot



It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals
Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.