Synthesis, C-H bond functionalisation and cycloadditions of 6-styryl-1,2-oxathiine 2,2-dioxides

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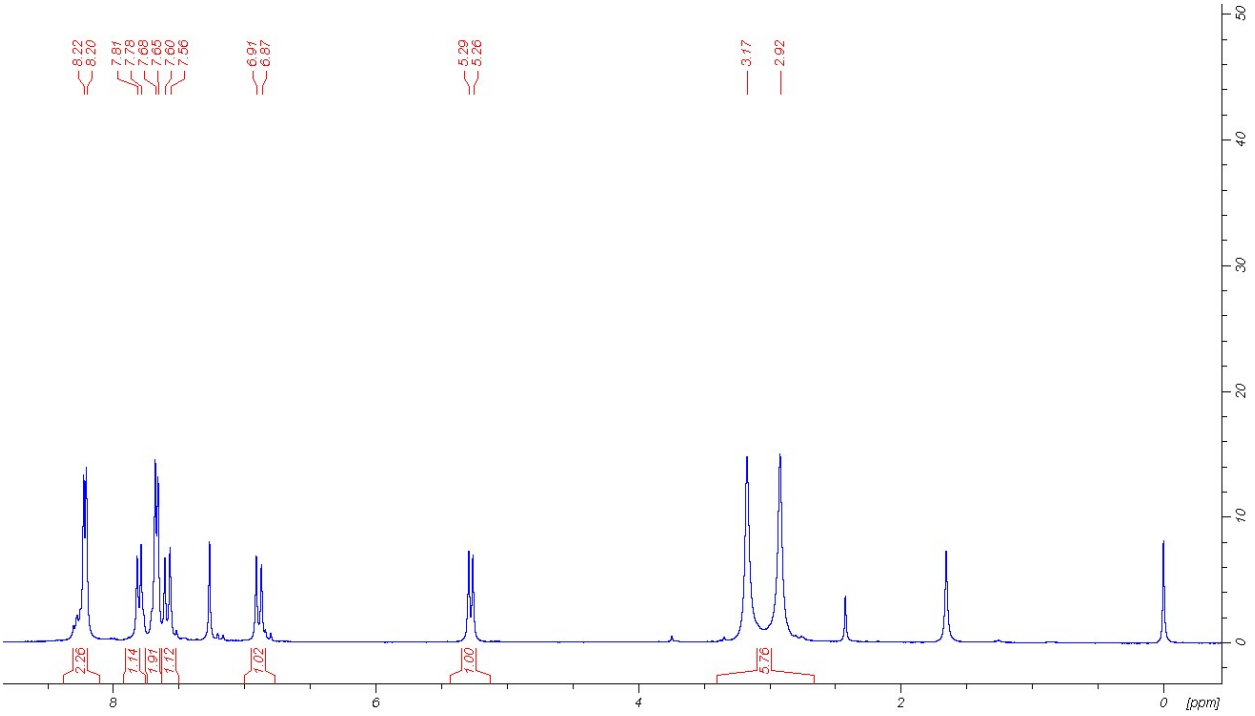
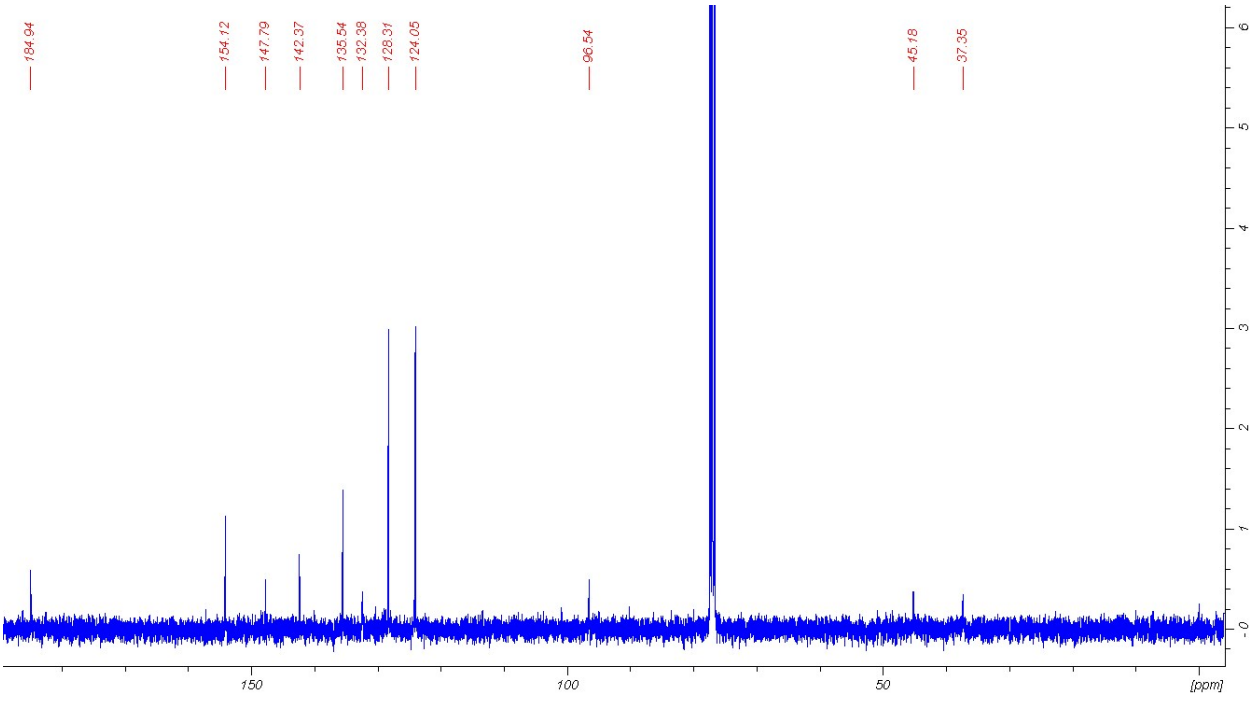
Electronic Supplementary Information

^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra, assorted 2D NMR spectra, DEPT spectra and mass spectra for new compounds and intermediates.

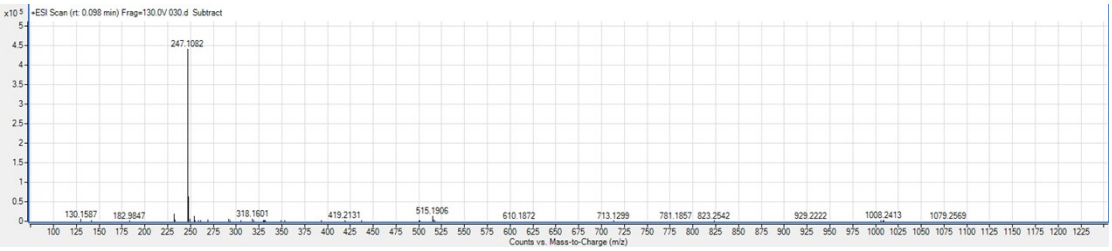
(1*E*,4*E*)-1-(Dimethylamino)-5-(4-nitrophenyl)penta-1,4-dien-3-one 2d ^{1}H-NMR



2d ^{13}C-NMR

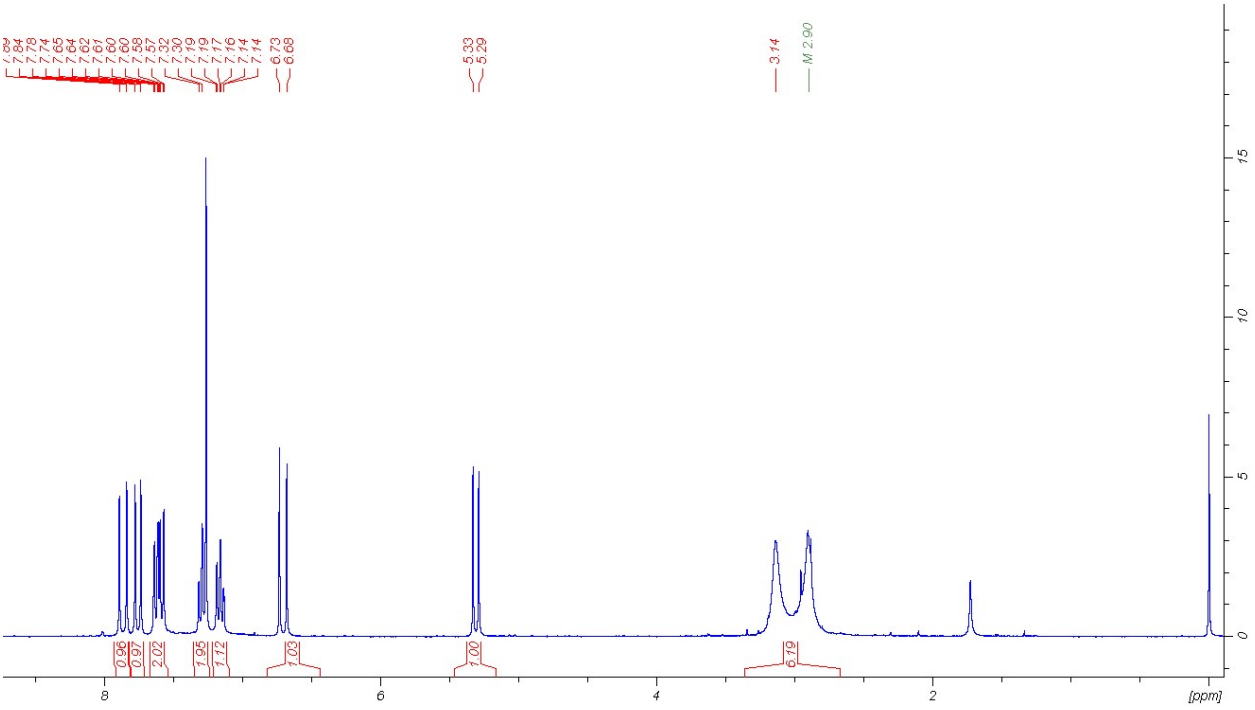


2d HRMS

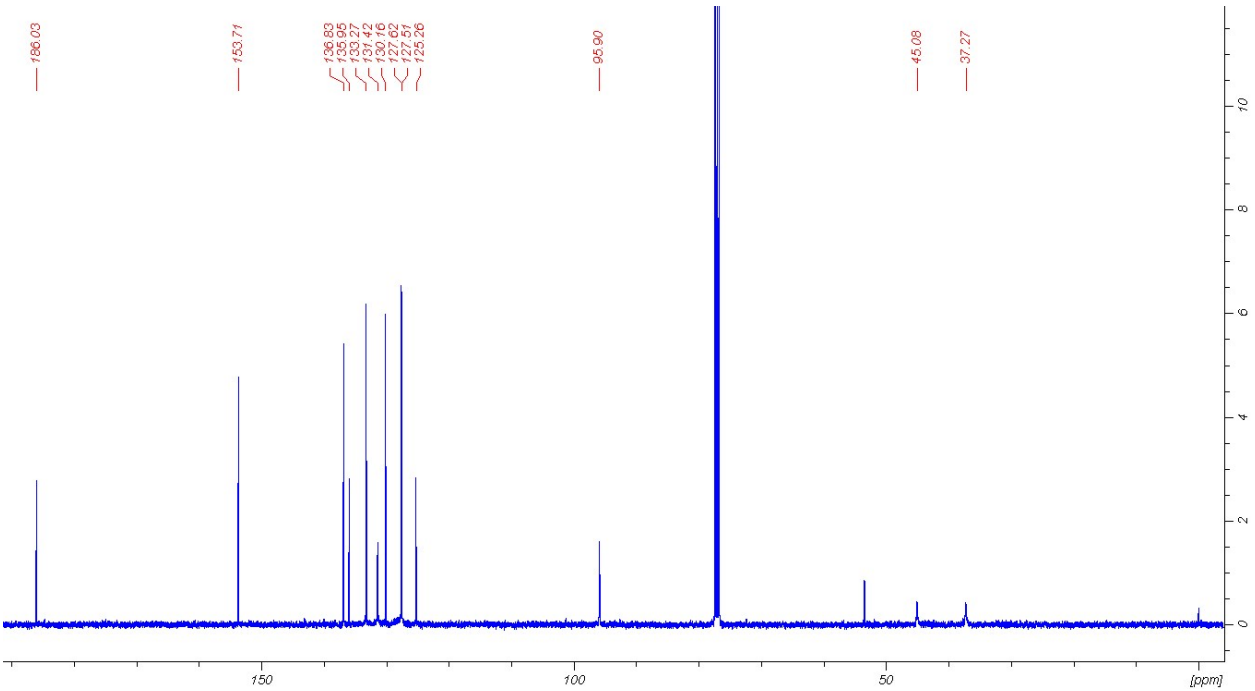


Formula	Observed m/z	Proposed adduct	Charge	Observed neutral mass	Theoretical neutral mass	Mass error (ppm)
C13H14N2O3	247.1082	H+	1+	246.1009	246.1004	1.69

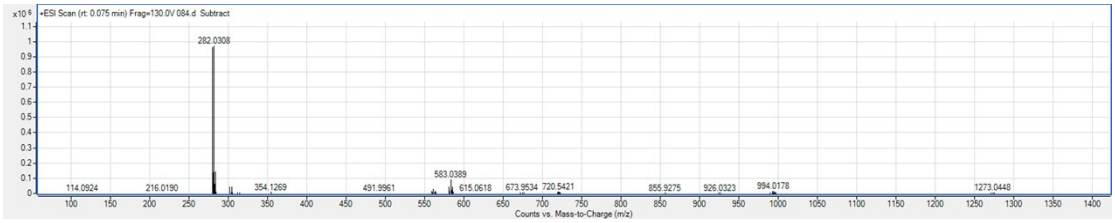
(1*E*,4*E*)-1-(2-Bromophenyl)-5-(dimethylamino)penta-1,4-dien-3-one 2e ^{1}H-NMR

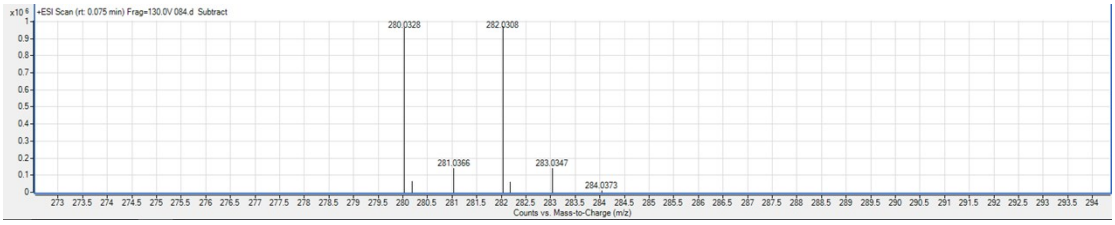


2e ^{13}C-NMR



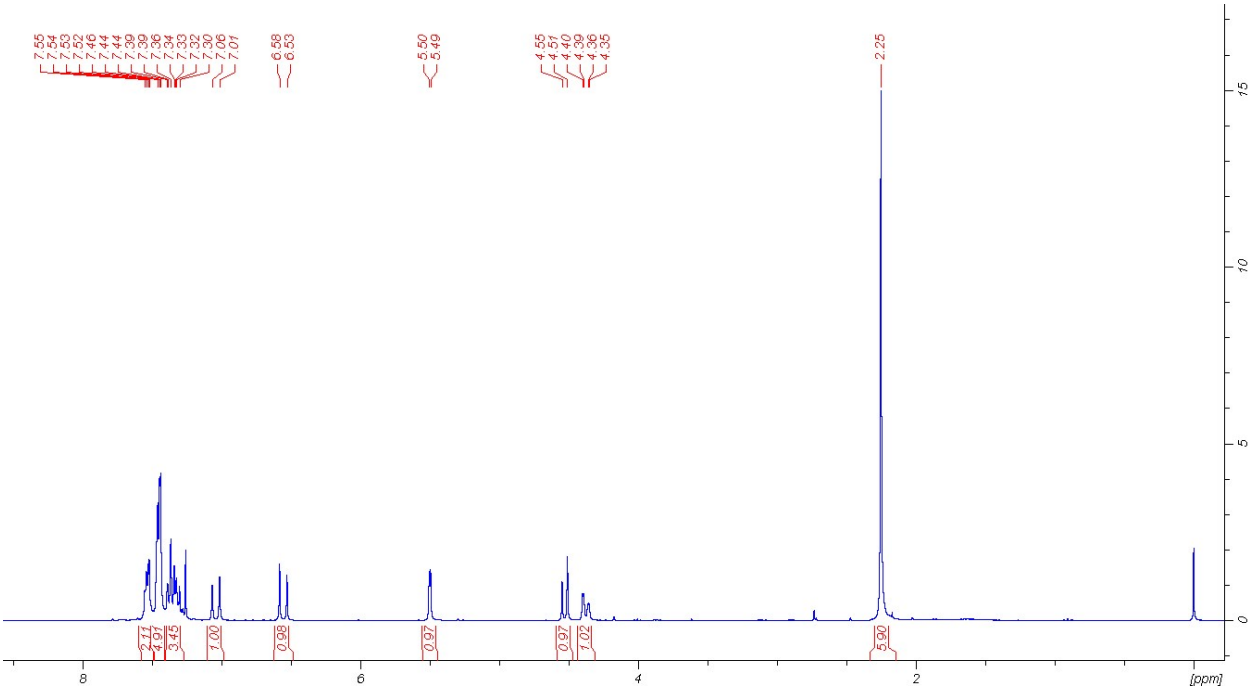
2e HRMS



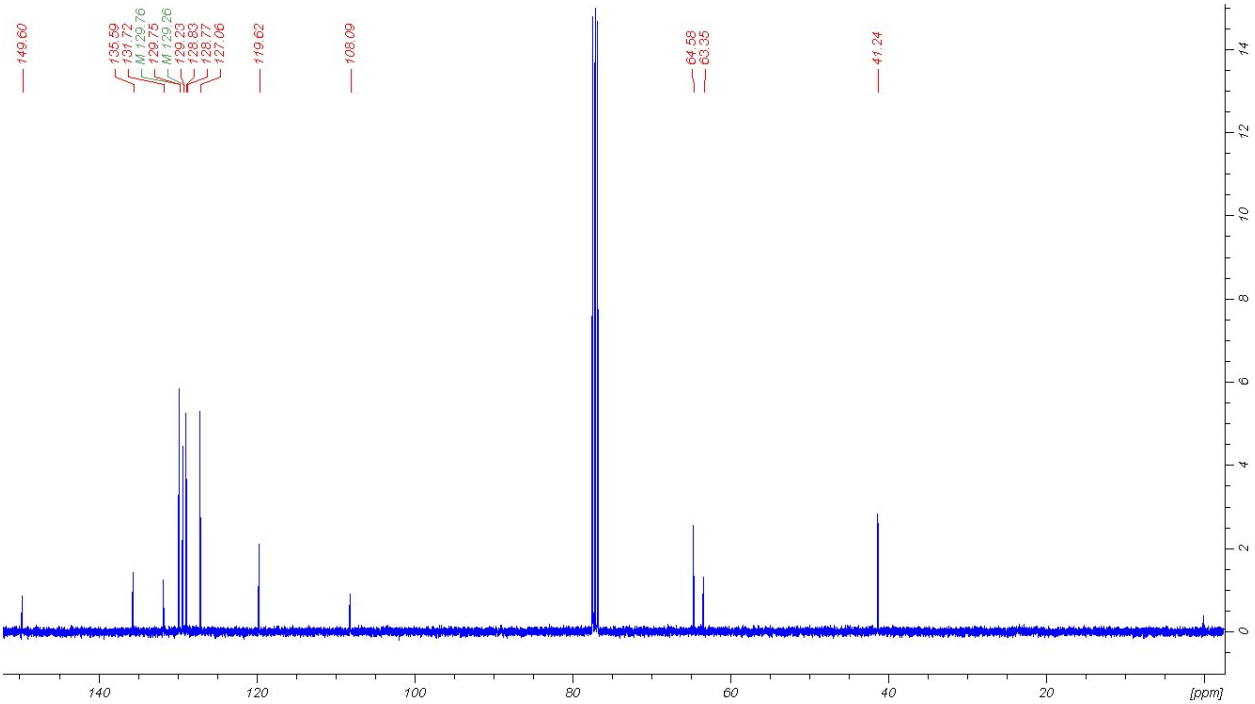


Formula	Observed m/z	Proposed adduct	Charge	Observed neutral mass	Theoretical neutral mass	Mass error (ppm)
C13H14BrNO	282.0308	H+	1+	279.0256	279.0259	1.09

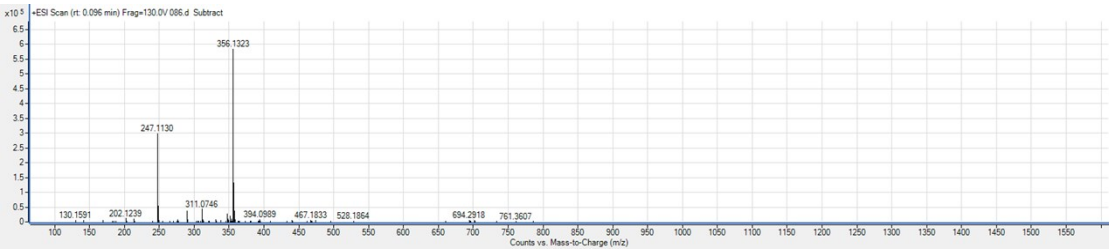
(*E*)-4-(Dimethylamino)-3-phenyl-6-styryl-3,4-dihydro-1,2-oxathiine 2,2-oxide 3a ^{1}H-NMR



3a ^{13}C-NMR

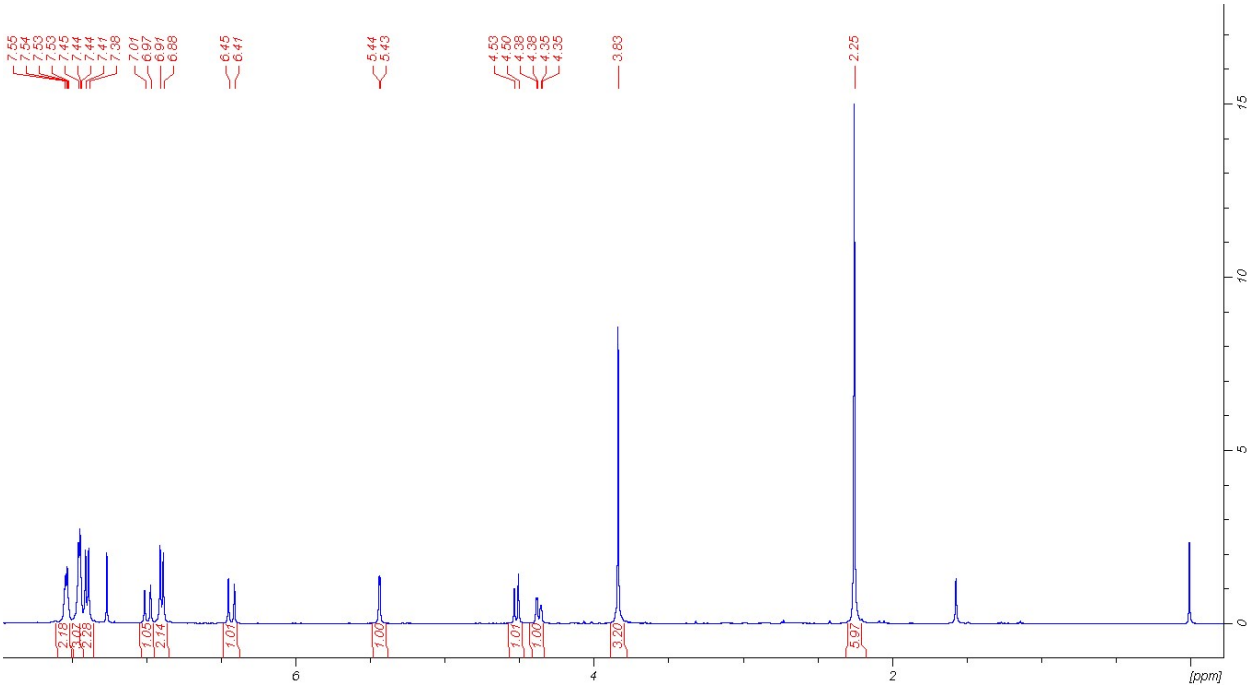


3a HRMS

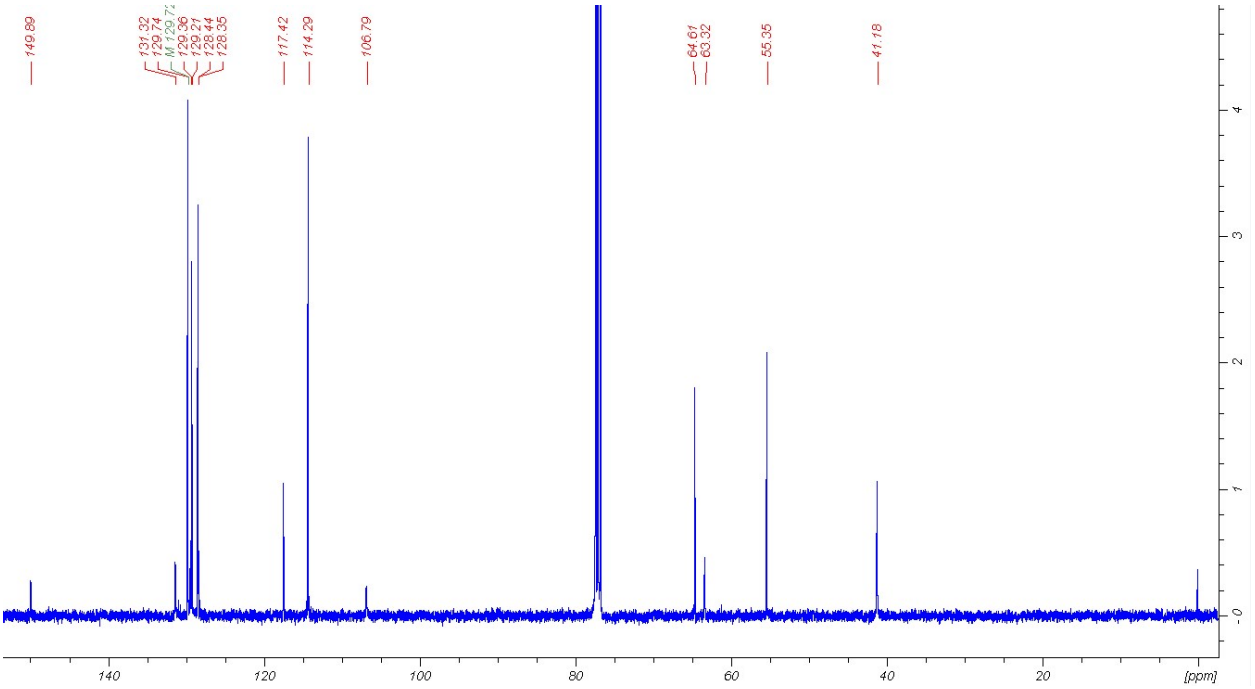


Formula	Observed m/z	Proposed adduct	Charge	Observed neutral mass	Theoretical neutral mass	Mass error (ppm)
C20H21NO3S	356.1323	H+	1+	355.1250	355.1242	2.17

(*E*)-4-(Dimethylamino)-6-(4-methoxystyryl)-3-phenyl-3,4-dihydro-1,2-oxathiine 2,2-dioxide 3b ^{1}H-NMR



3b ^{13}C-NMR



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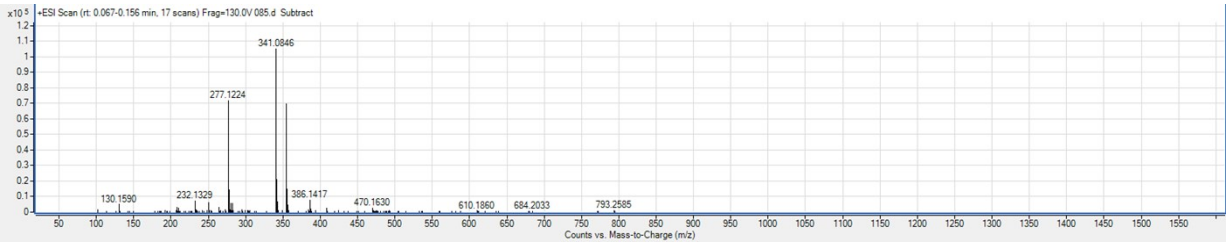
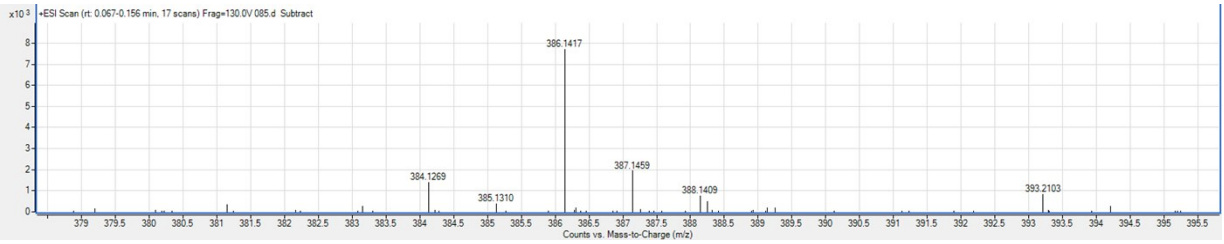
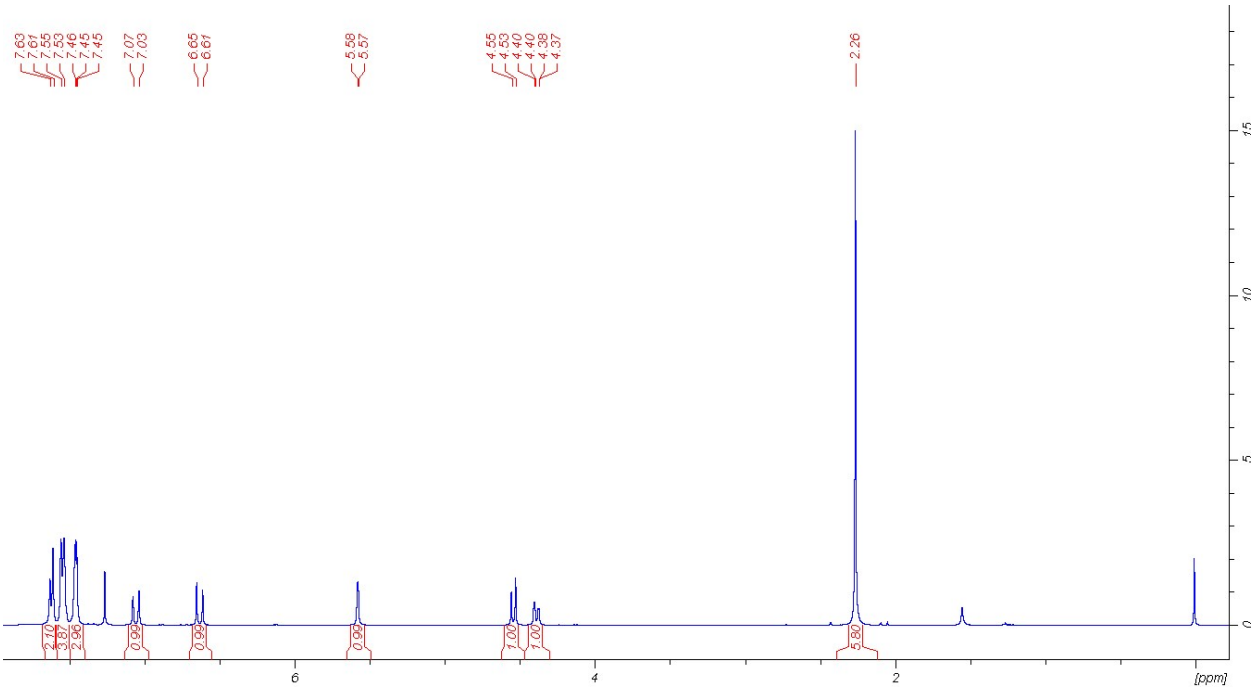




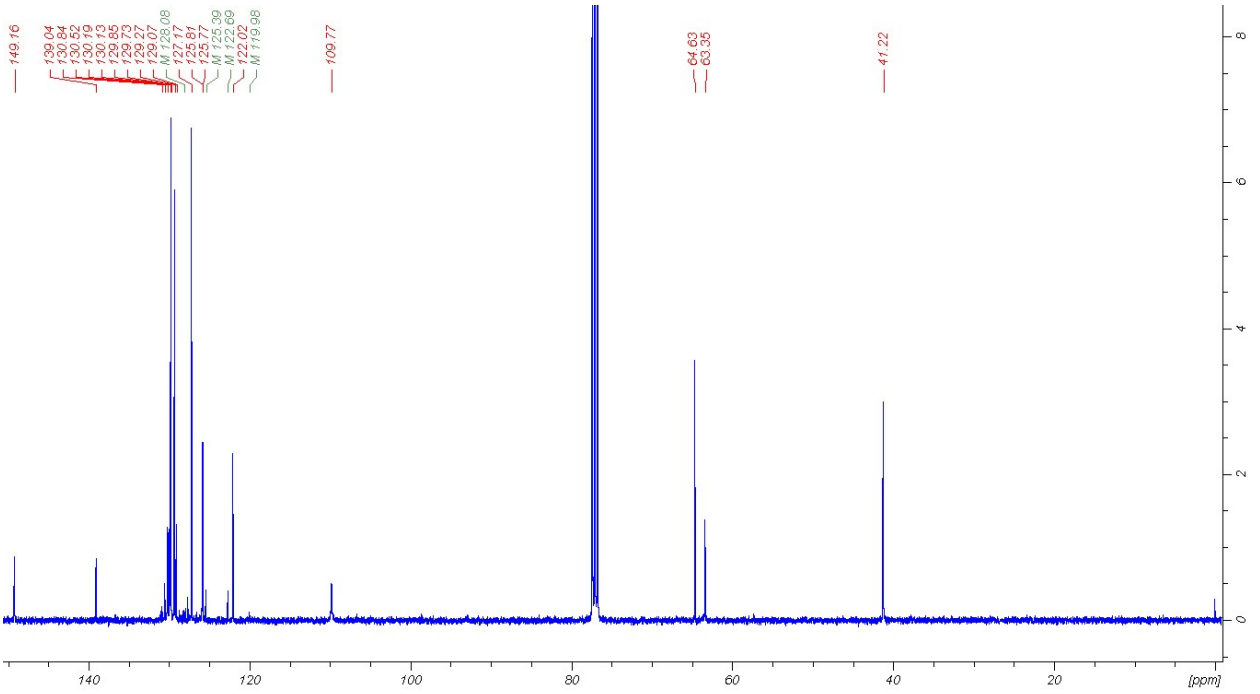
Formula	Observed m/z	Proposed adduct	Charge	Observed neutral mass	Theoretical neutral mass	Mass error (ppm)
C21H23NO4S	386.1417	H+	1+	385.1346	385.1348	0.55

(*E*)-4-(Dimethylamino)-3-phenyl-6-(4-(trifluoromethyl)styryl)-3,4-dihydro-1,2-oxathiine 2,2-dioxide 3c

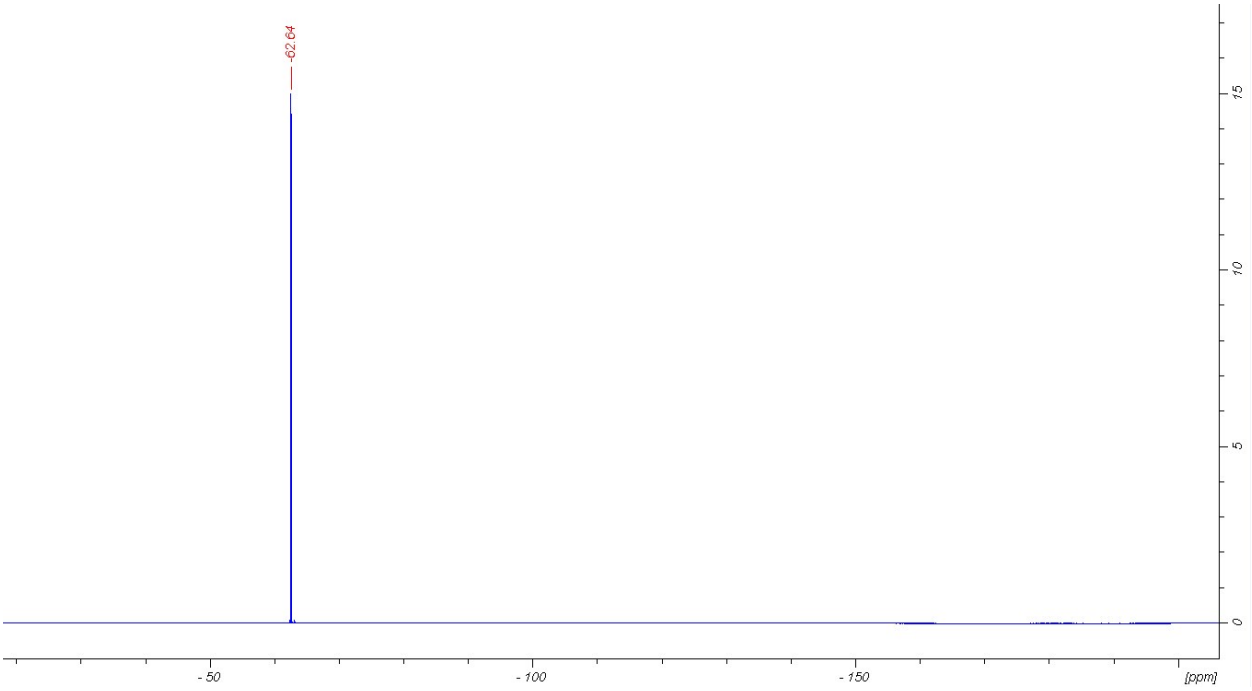
^{1}H-NMR



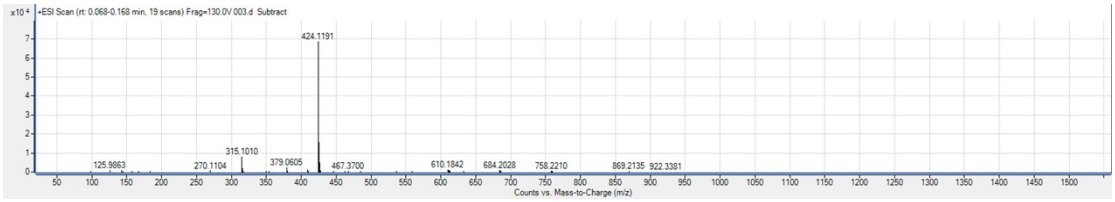
3c ^{13}C-NMR



3c ^{19}F-NMR

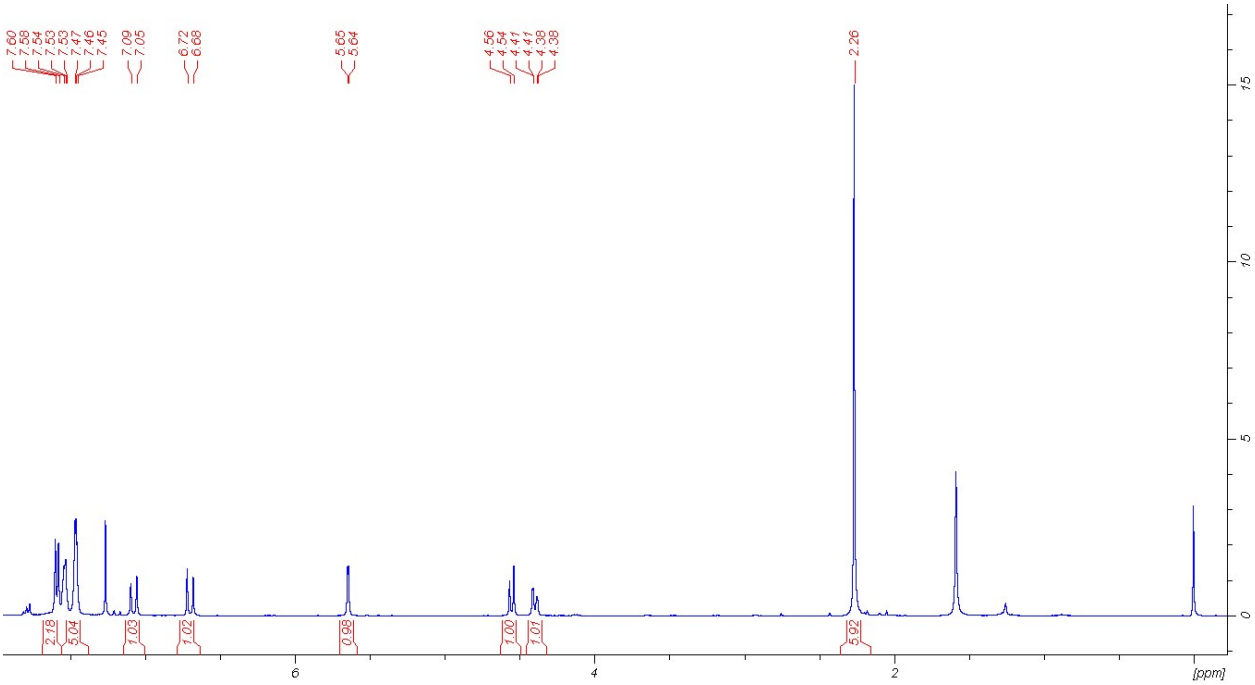


3c HRMS

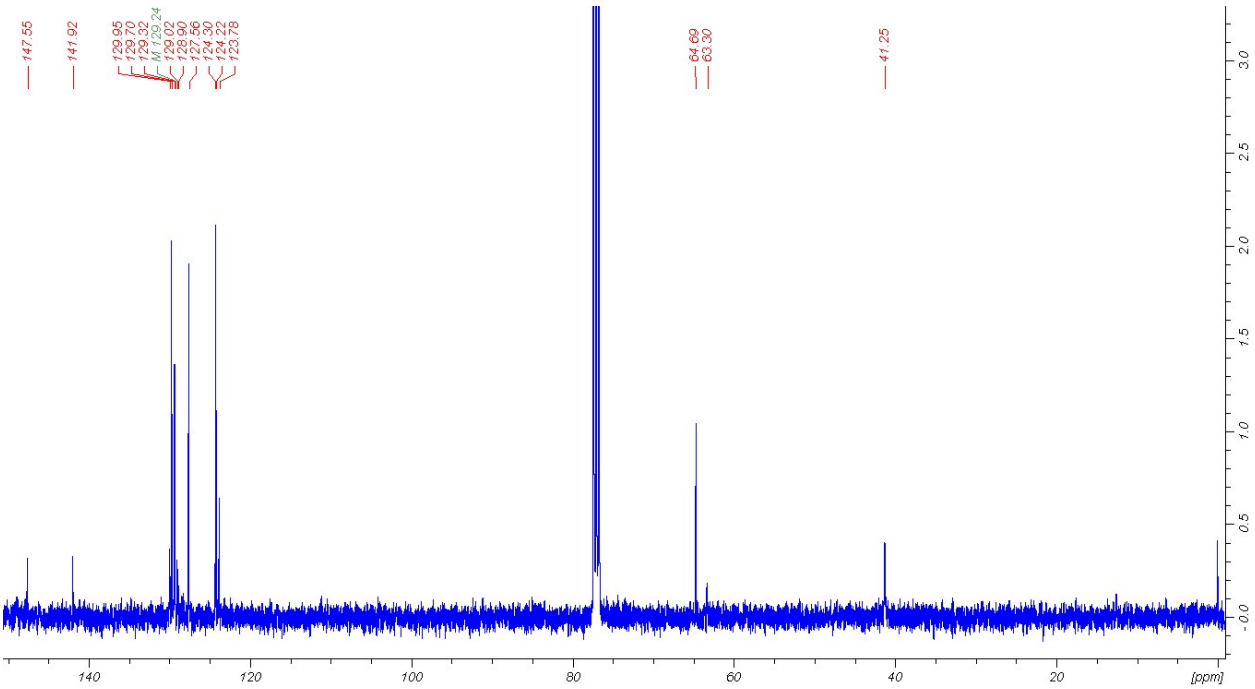


Formula	Observed m/z	Proposed adduct	Charge	Observed neutral mass	Theoretical neutral mass	Mass error (ppm)
C21H20F3NO3S	424.1191	H+	1+	423.1118	423.1116	0.42

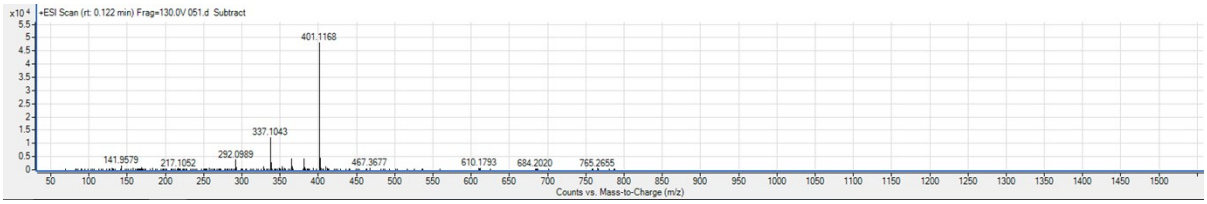
(*E*)-4-(Dimethylamino)-6-(4-nitrostyryl)-3-phenyl-3,4-dihydro-1,2-oxathiine 2,2-dioxide 3d ^{1}H-NMR



3d ^{13}C-NMR

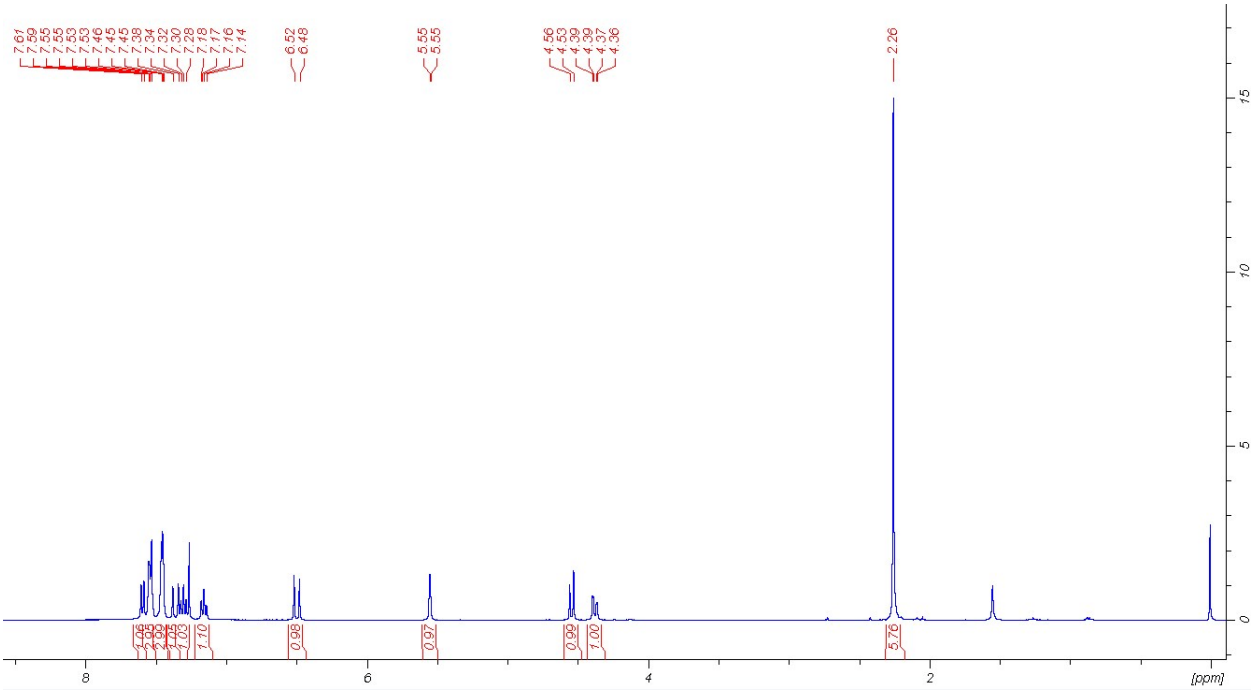


3d HRMS

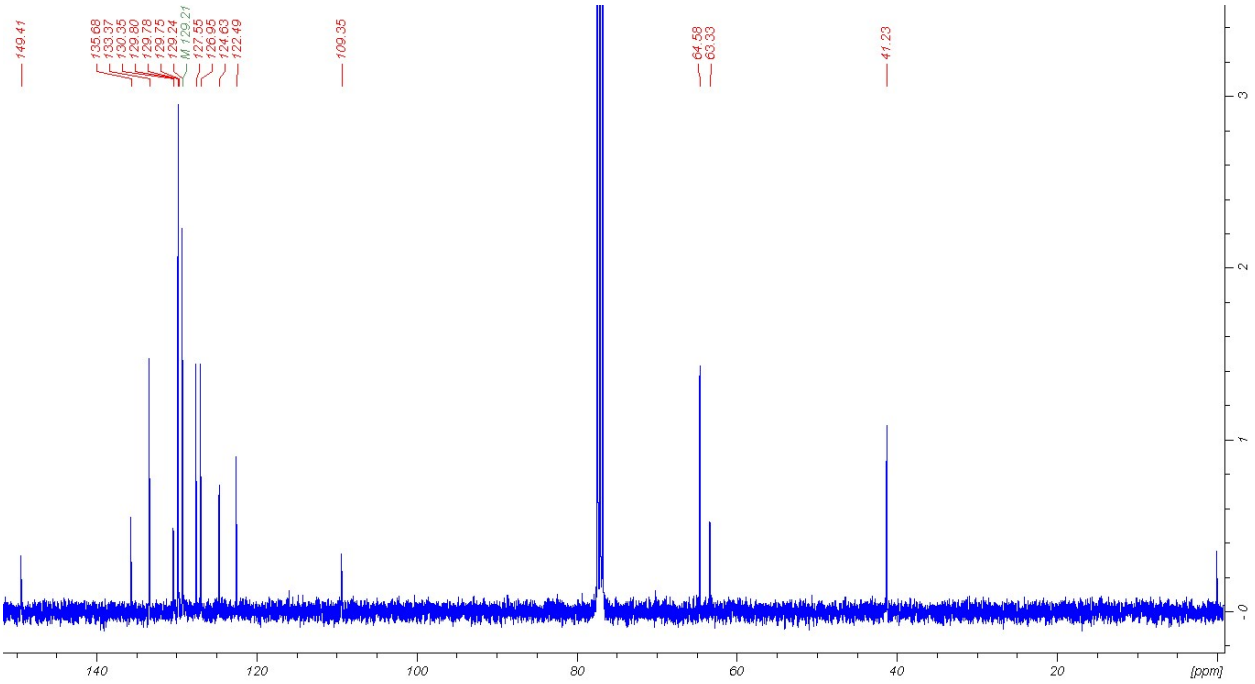


Formula	Observed m/z	Proposed adduct	Charge	Observed neutral mass	Theoretical neutral mass	Mass error (ppm)
C20H20N2O5S	401.1168	H+	1+	400.1095	400.1093	0.64

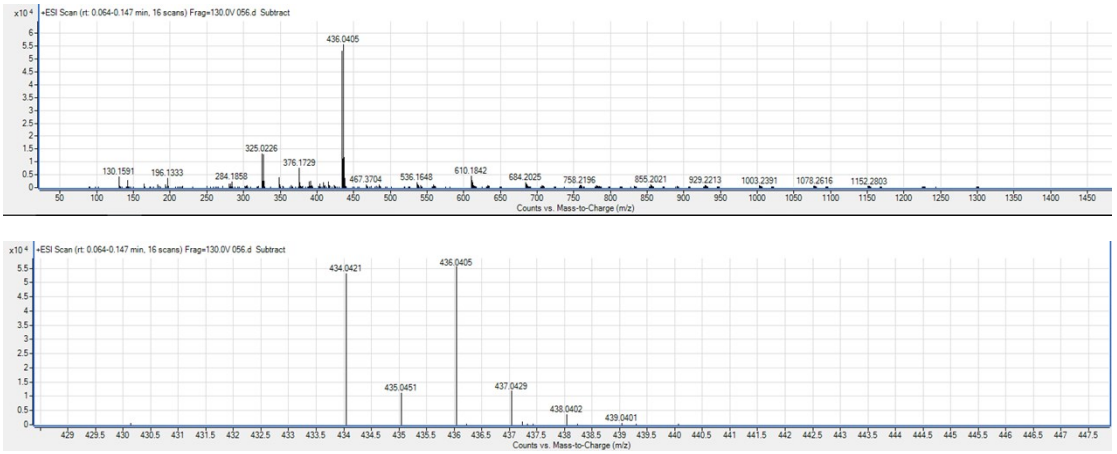
(*E*)-6-(2-Bromostyryl)-4-(dimethylamino)-3-phenyl-3,4-dihydro-1,2-oxathiine 2,2-dioxide 3e ^{1}H-NMR



3e ^{13}C-NMR

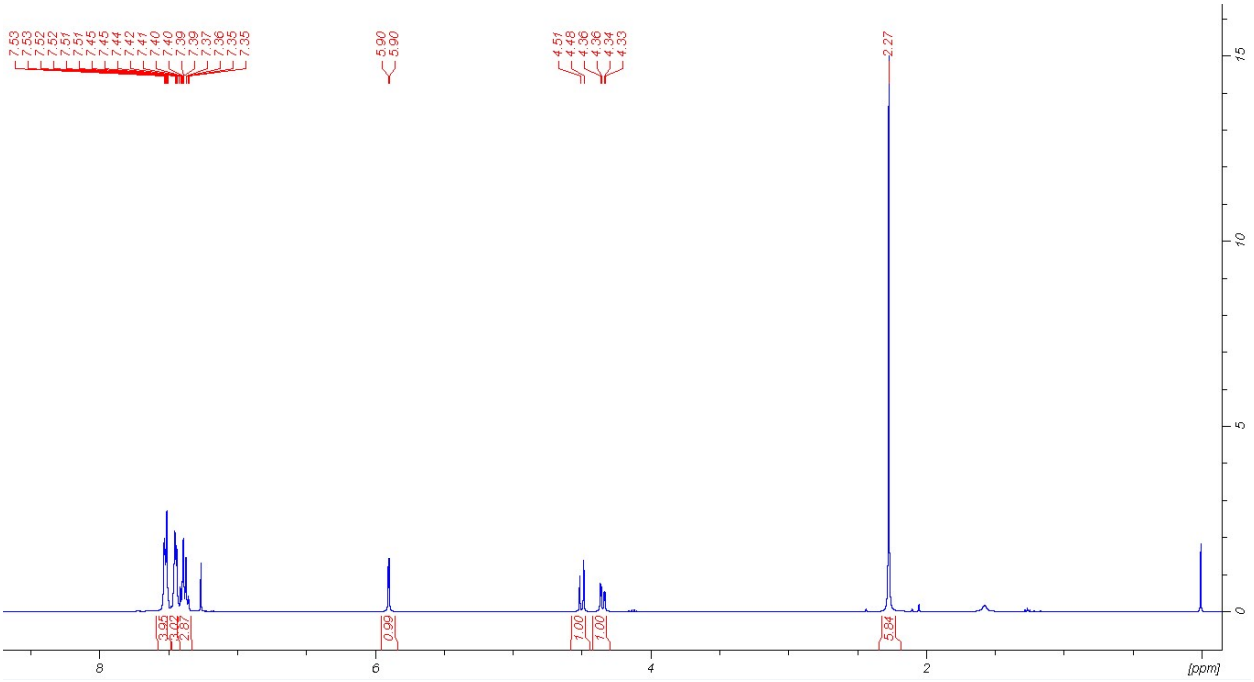


3e HRMS

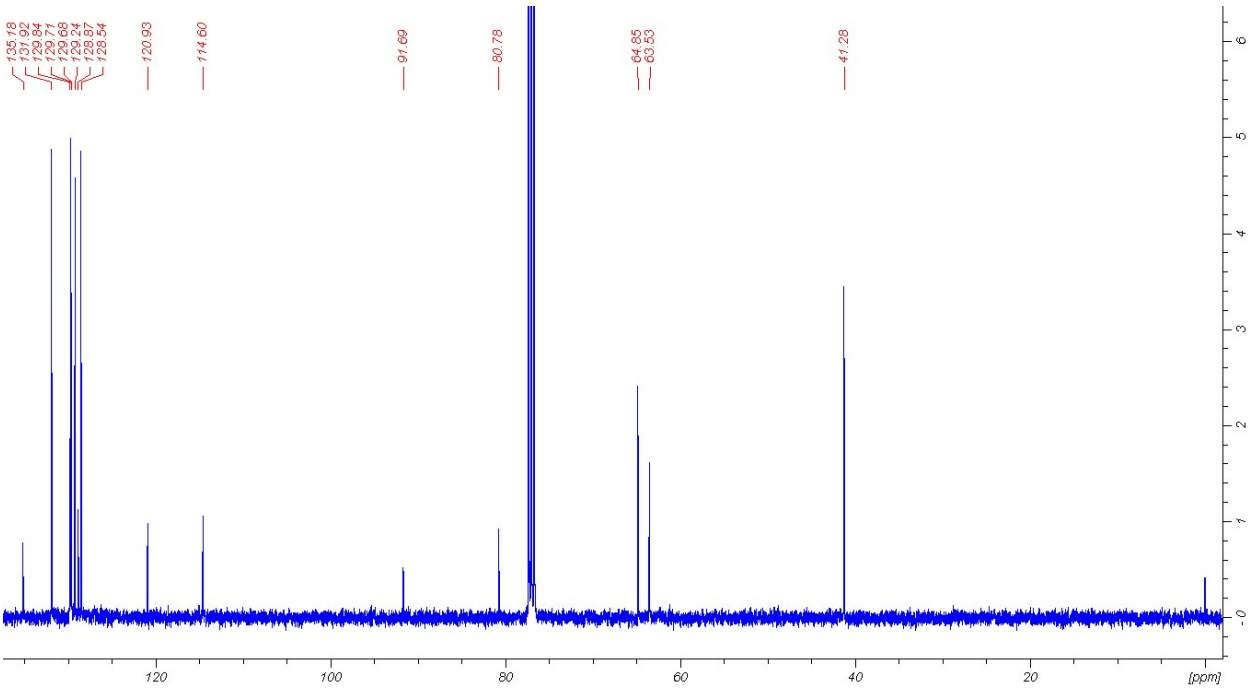


Formula	Observed m/z	Proposed adduct	Charge	Observed neutral mass	Theoretical neutral mass	Mass error (ppm)
C20H20BrNO3S	436.0404	H+	1+	433.0349	433.0347	0.38

4-(Dimethylamino)-3-phenyl-6-(phenylethynyl)-3,4-dihydro-1,2-oxathiine 2,2-dioxide 3f ^{1}H-NMR



3f ^{13}C-NMR



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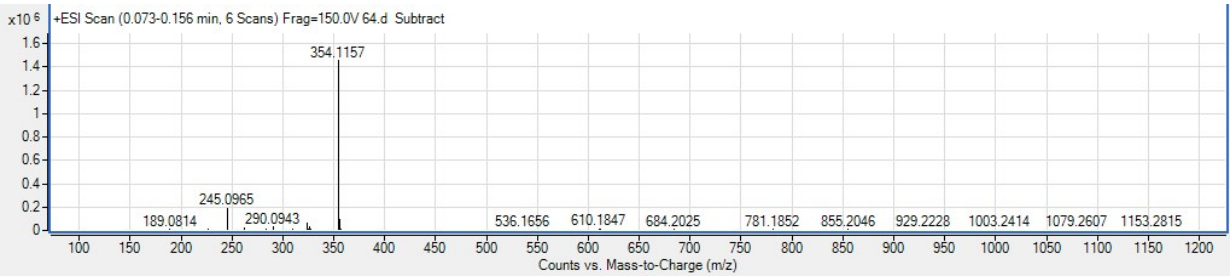
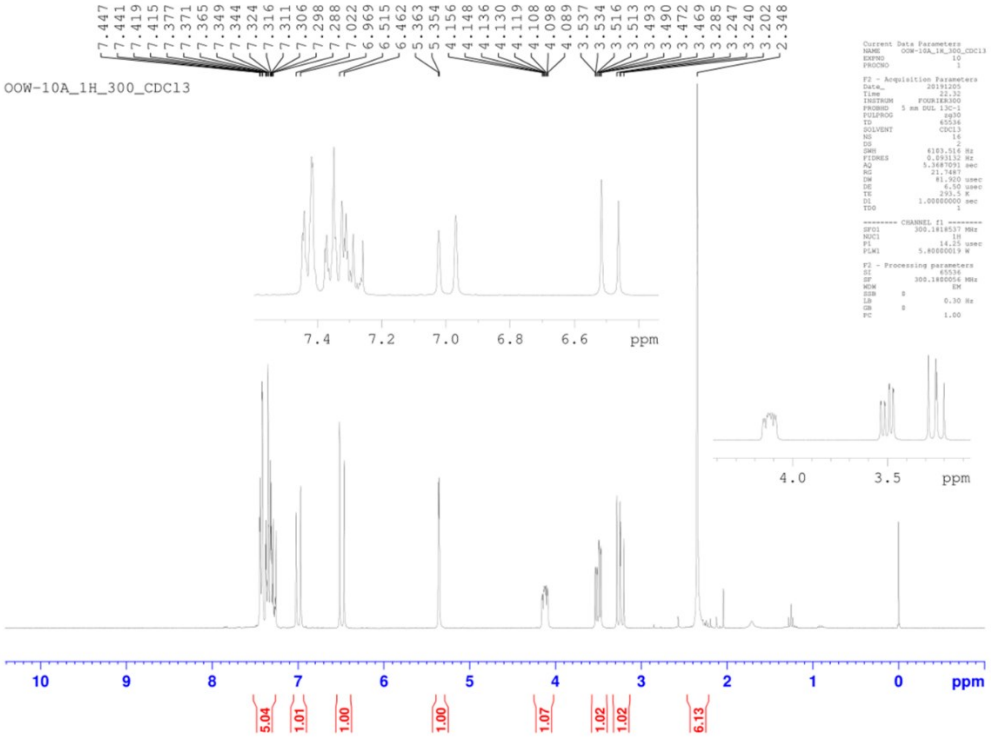


Formula	Observed m/z	Proposed adduct	Charge	Observed neutral mass	Theoretical neutral mass	Mass error (ppm)
C20H19NO3S	354.1157	H+	1+	353.1085	353.1086	0.28

(*E*)-4-(Dimethylamino)-6-styryl-3,4-dihydro-1,2-oxathiine 2,2-dioxide 3g ^{1}H-NMR



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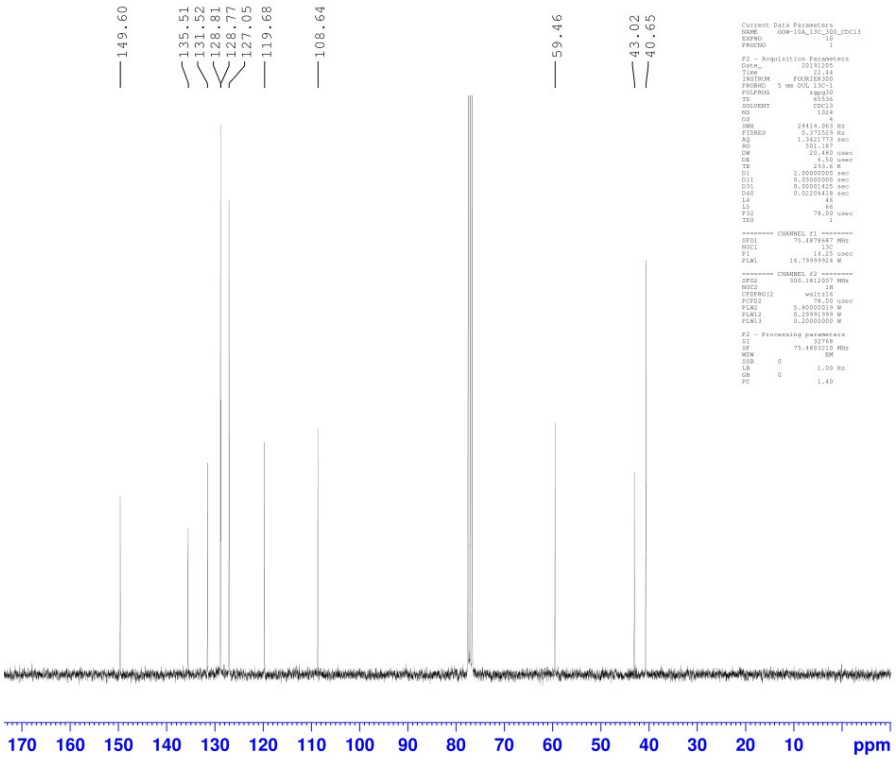

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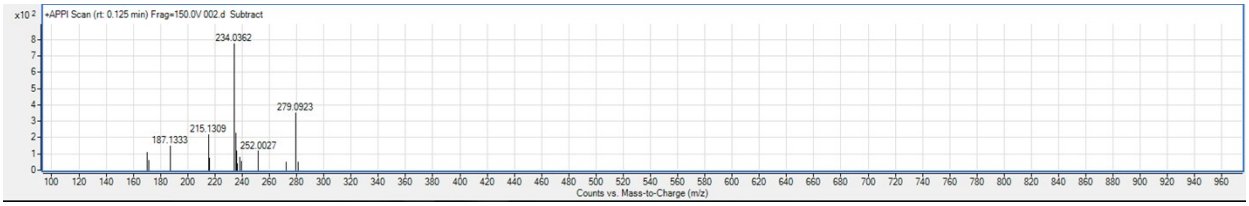
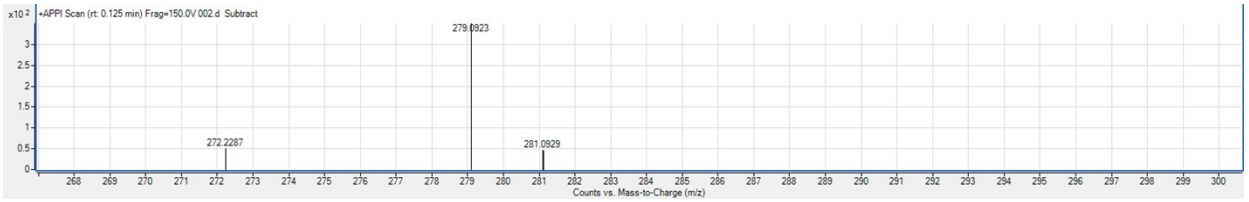
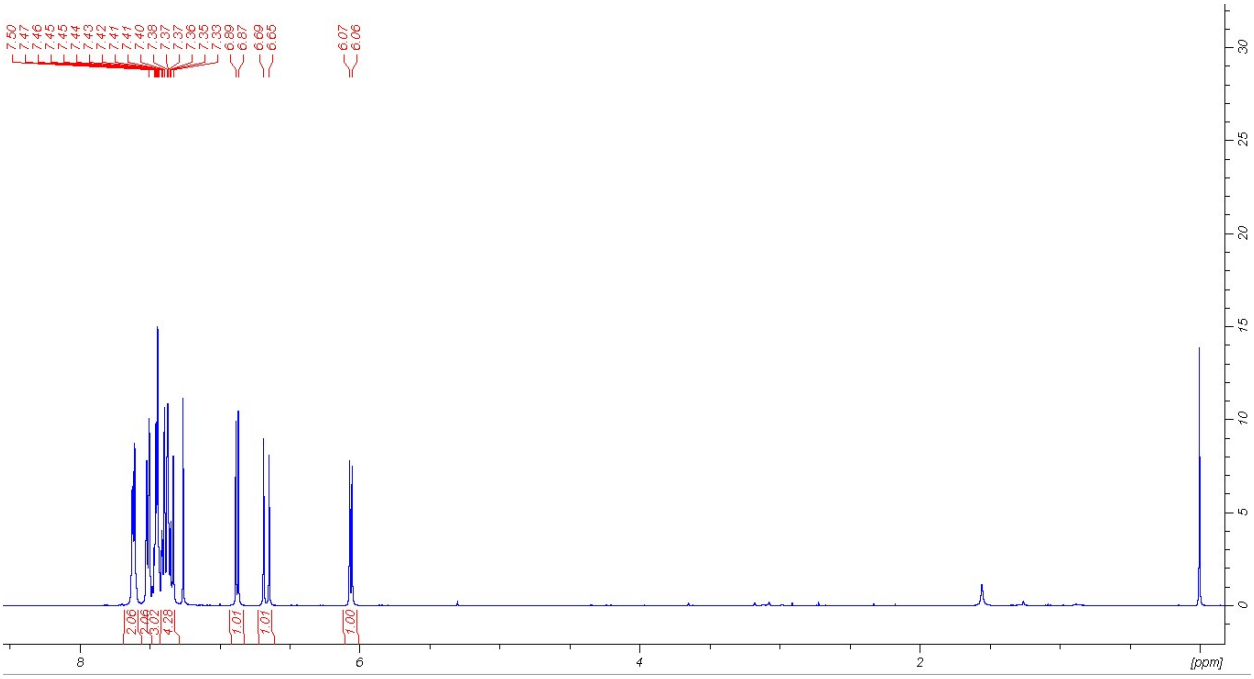


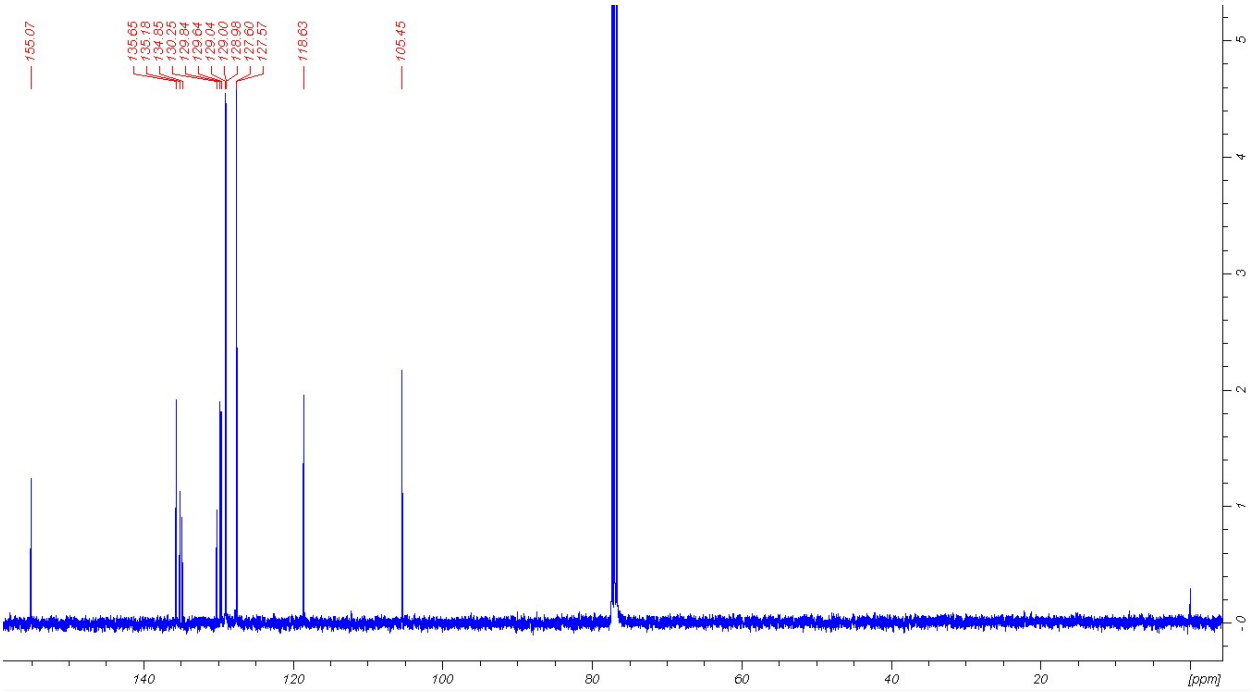


Formula	Observed m/z	Proposed adduct	Charge	Observed neutral mass	Theoretical neutral mass	Mass error (ppm)
C14H17NO3S	279.0923	radical	1+	279.0928	279.0929	0.36

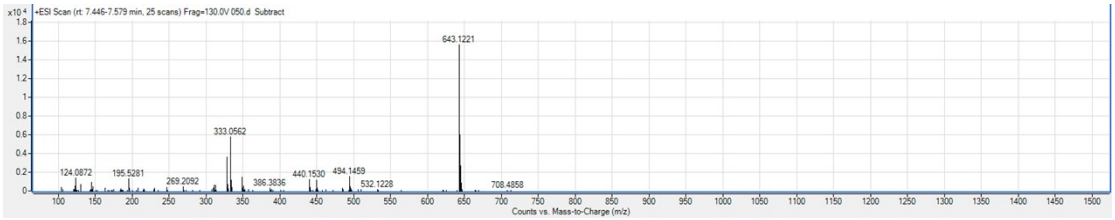
(*E*)-3-Phenyl-6-styryl-1,2-oxathiine 2,2-dioxide 4a ^{1}H-NMR

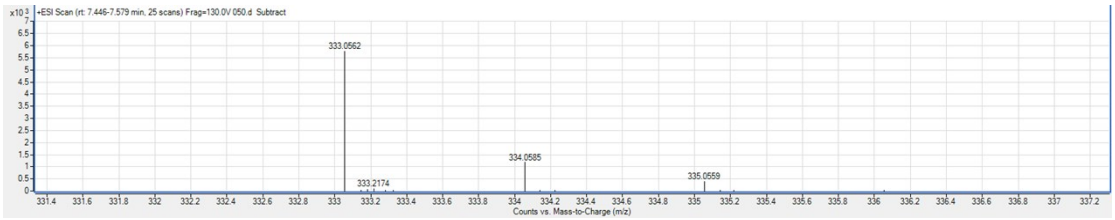


4a ^{13}C-NMR



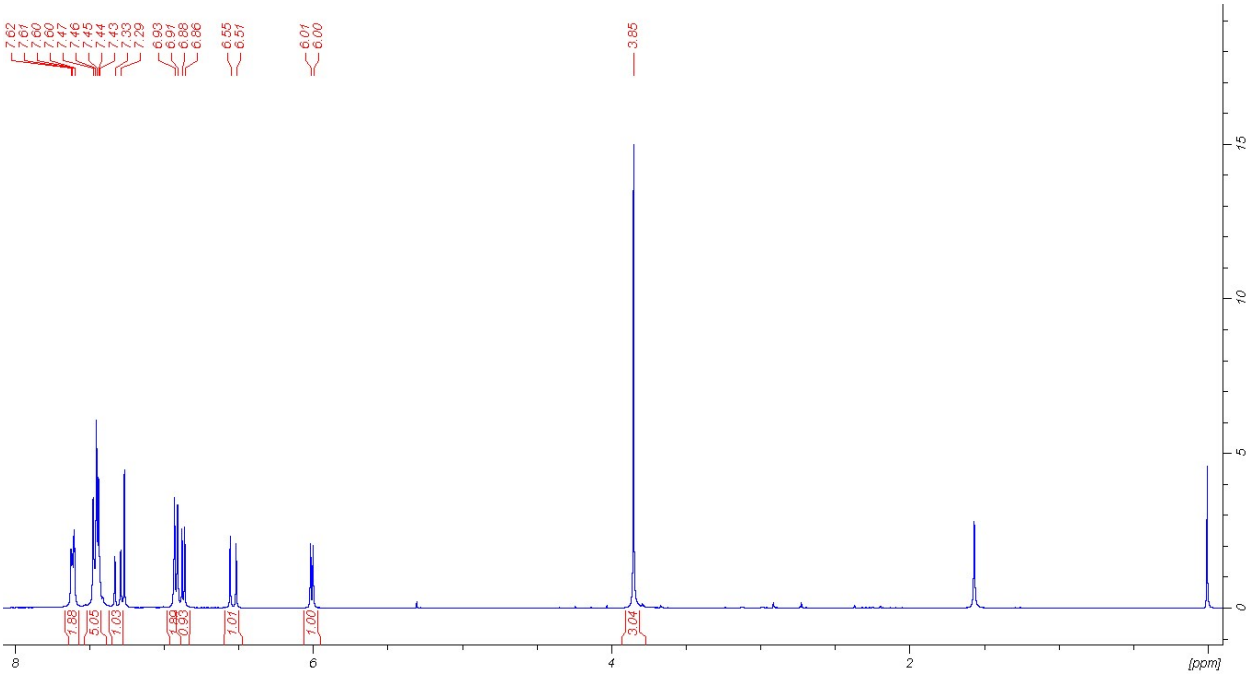
4a HRMS



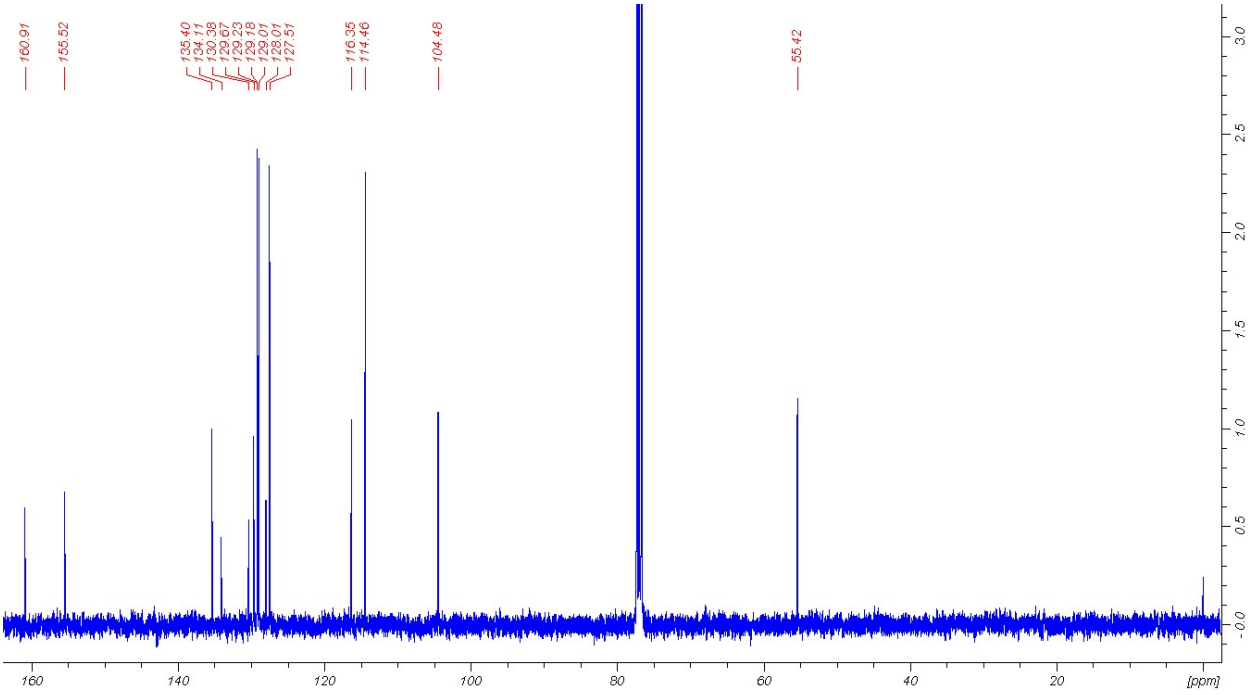


Formula	Observed m/z	Proposed adduct	Charge	Observed neutral mass	Theoretical neutral mass	Mass error (ppm)
C18H14O3S	333.0562	Na+	1+	310.0669	310.0664	1.57

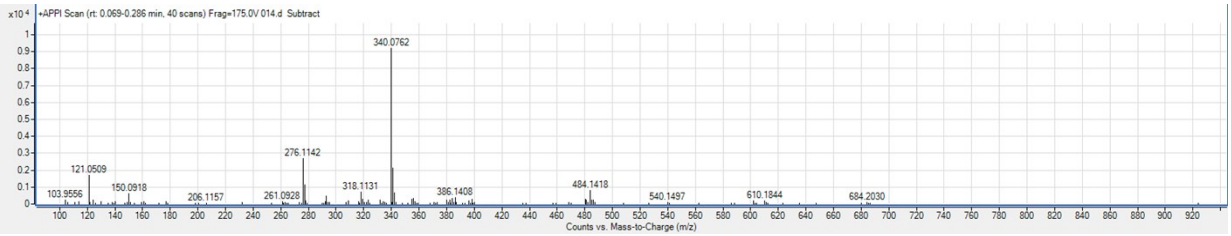
(*E*)-6-(4-Methoxystyryl)-3-phenyl-1,2-oxathiine 2,2-dioxide 4b ^{1}H-NMR



4b ^{13}C-NMR

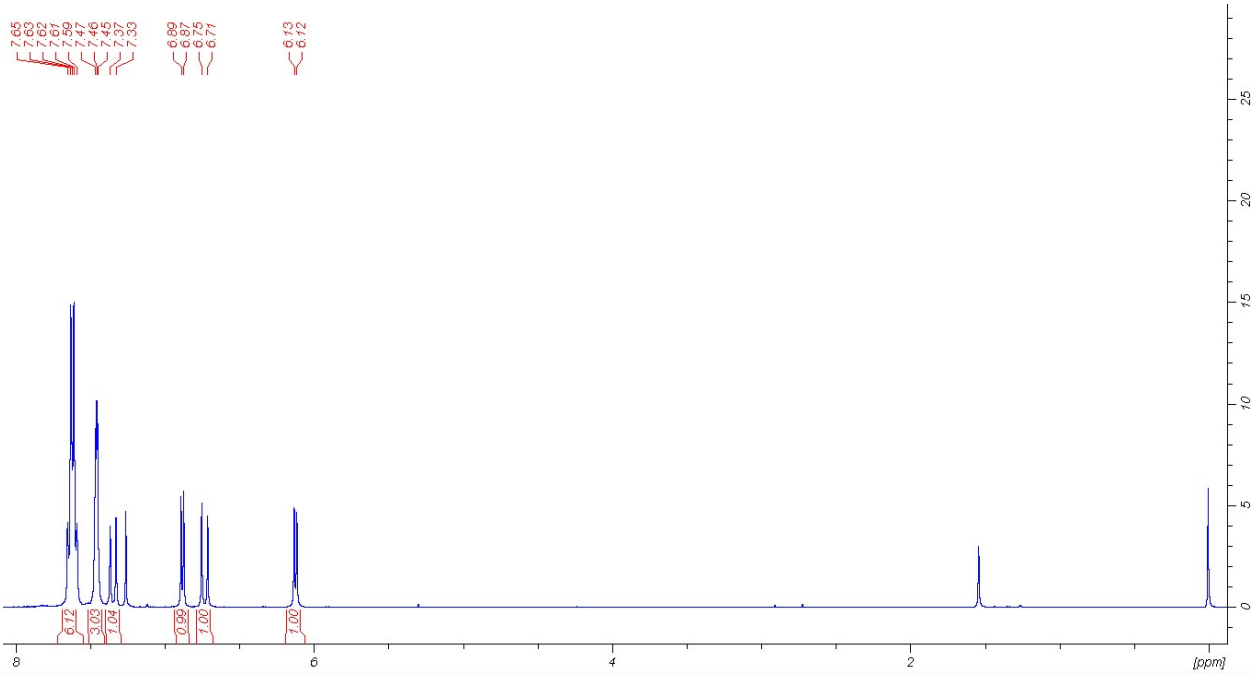


4b HRMS

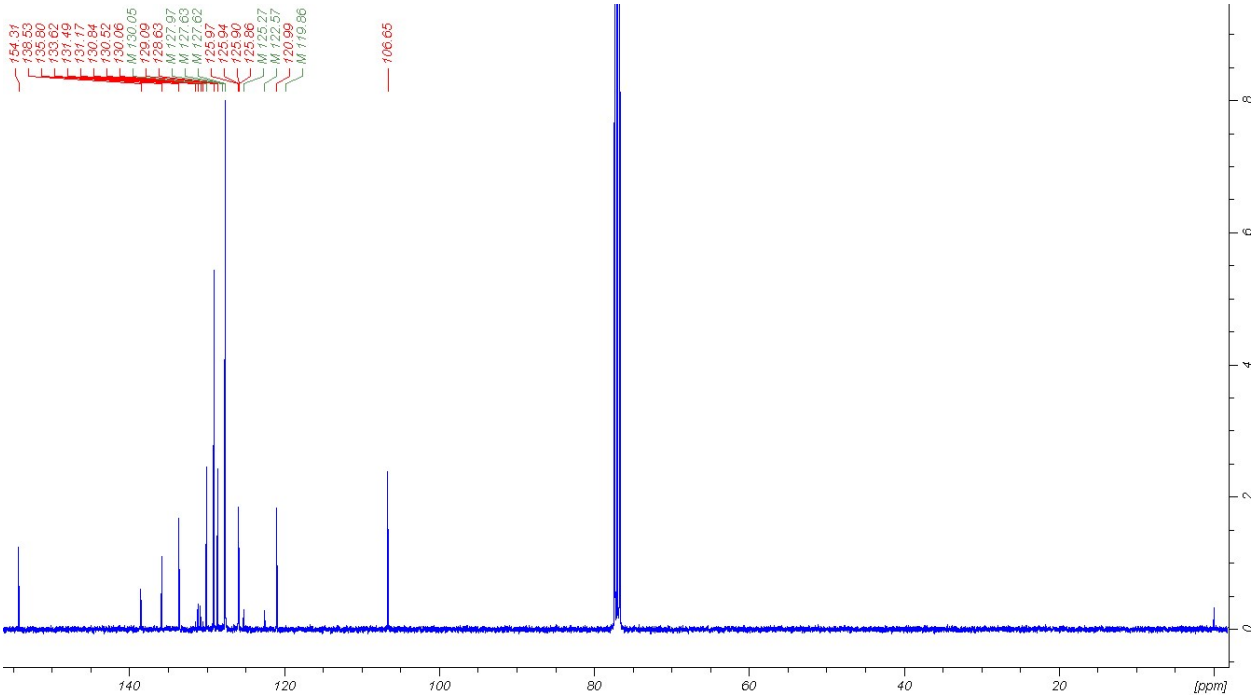


Formula	Observed m/z	Proposed adduct	Charge	Observed neutral mass	Theoretical neutral mass	Mass error (ppm)
C19H16O4S	340.0761	radical	1+	340.0767	340.0769	0.75

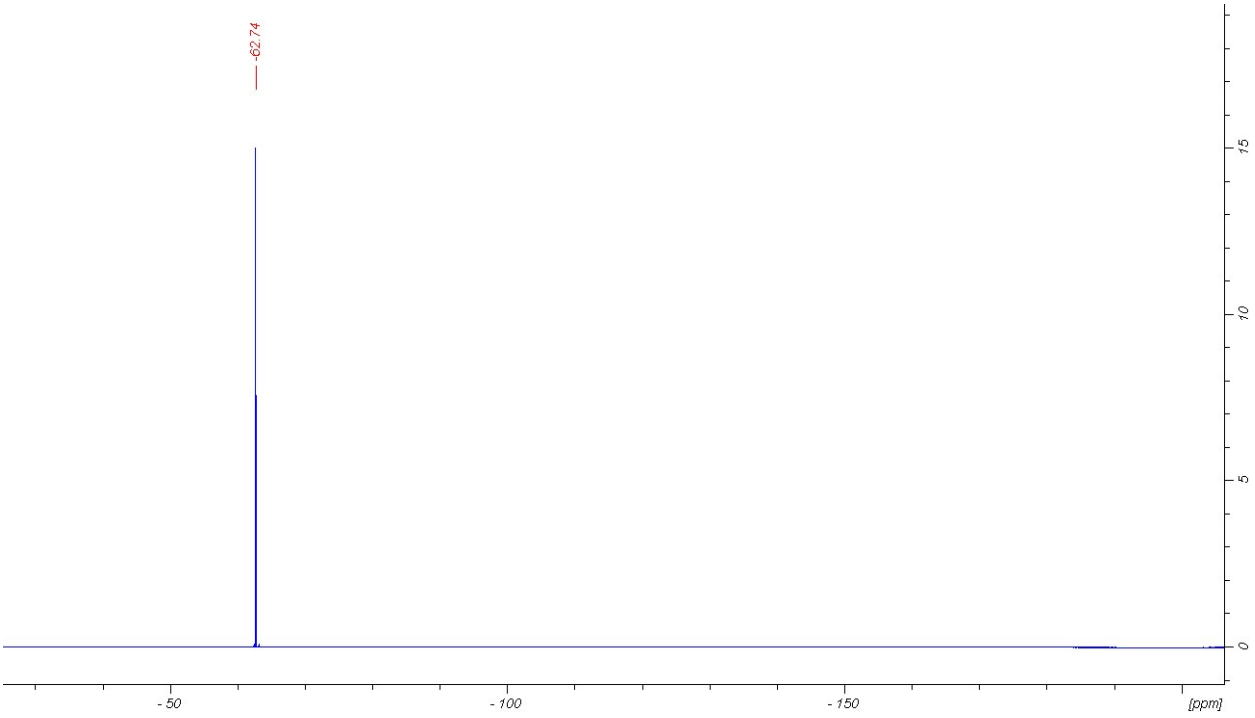
(*E*)-3-Phenyl-6-(4-(trifluoromethyl)styryl)-1,2-oxathiine 2,2-dioxide 4c ^{1}H-NMR



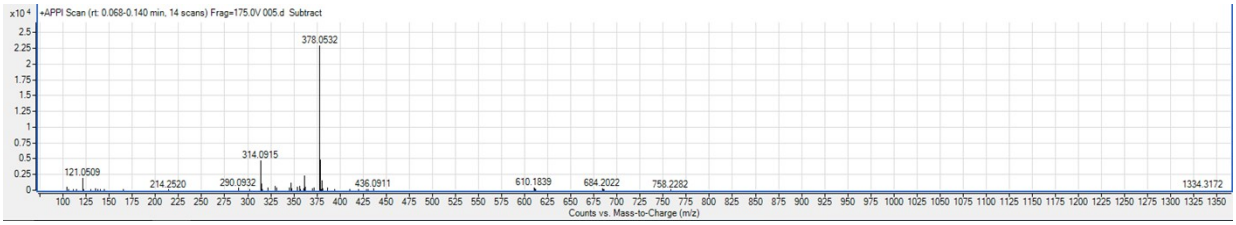
4c ^{13}C-NMR



4c ^{19}F-NMR

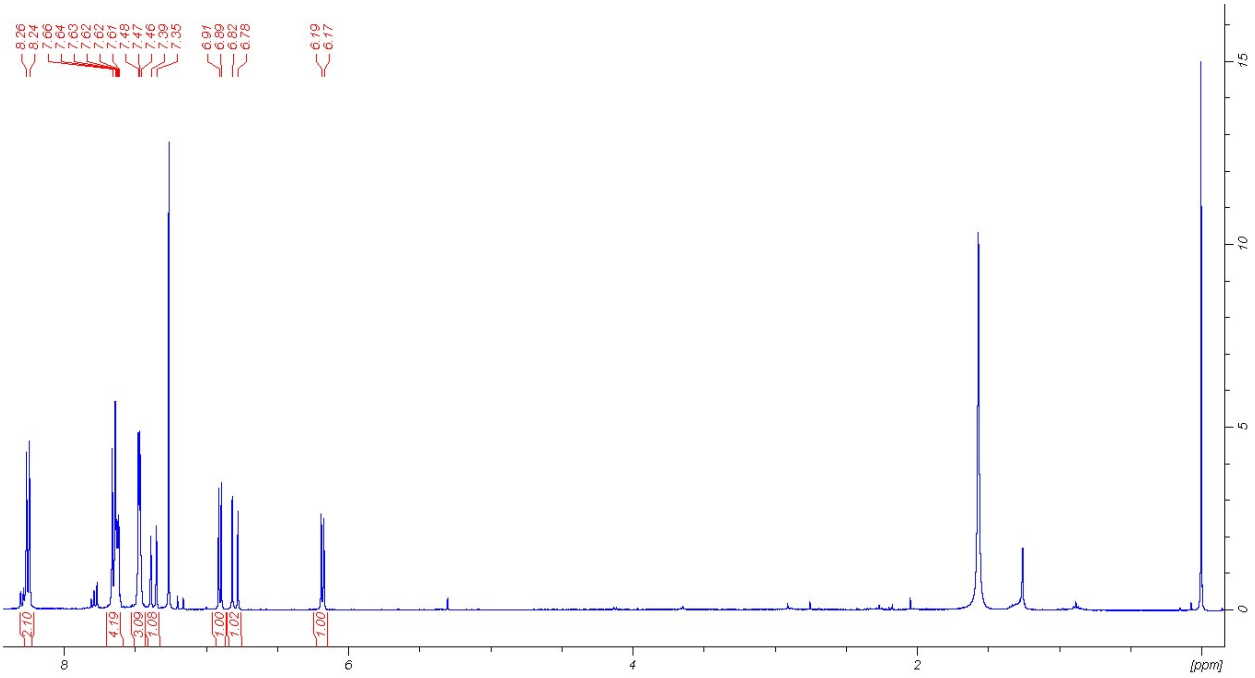


4c HRMS

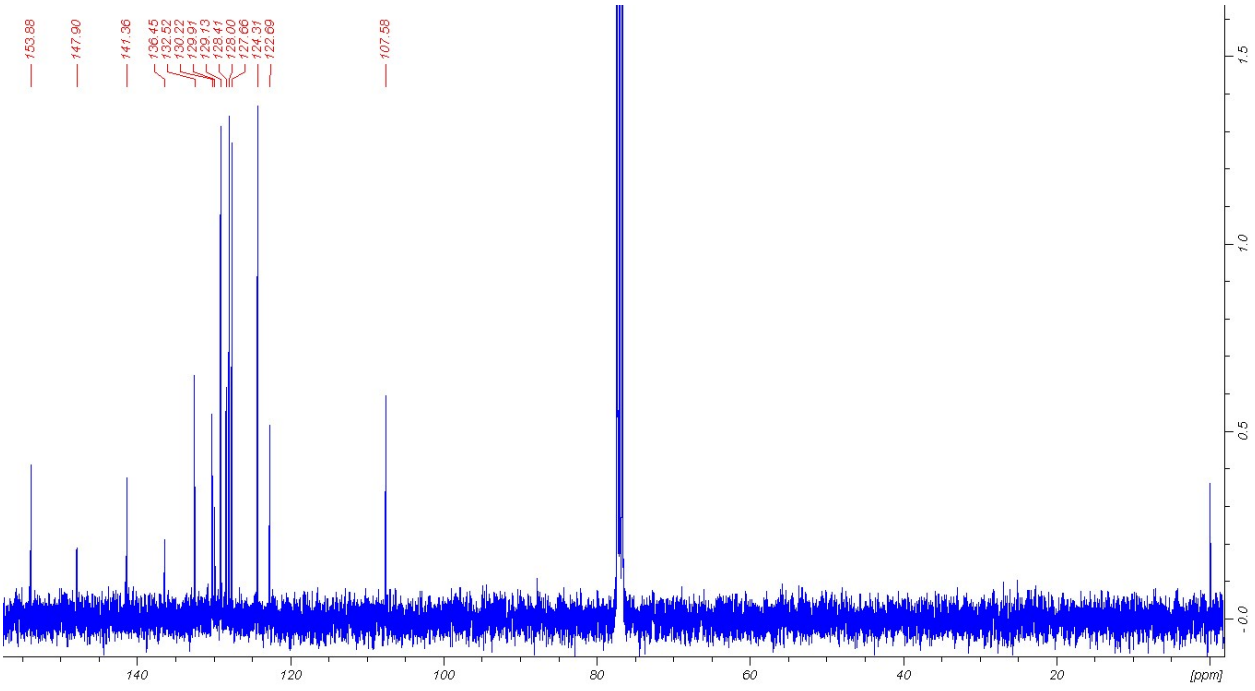


Formula	Observed m/z	Proposed adduct	Charge	Observed neutral mass	Theoretical neutral mass	Mass error (ppm)
C19H13F3O3S	378.0532	radical	1+	378.0538	378.0537	0.17

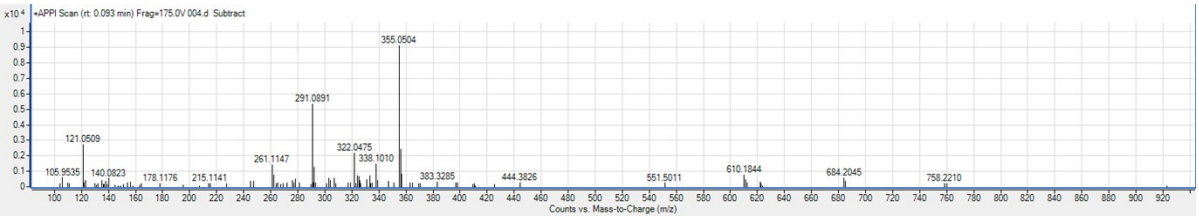
(*E*)-6-(4-Nitrostyryl)-3-phenyl-1,2-oxathiine 2,2-dioxide 4d ^{1}H-NMR



4d ^{13}C-NMR

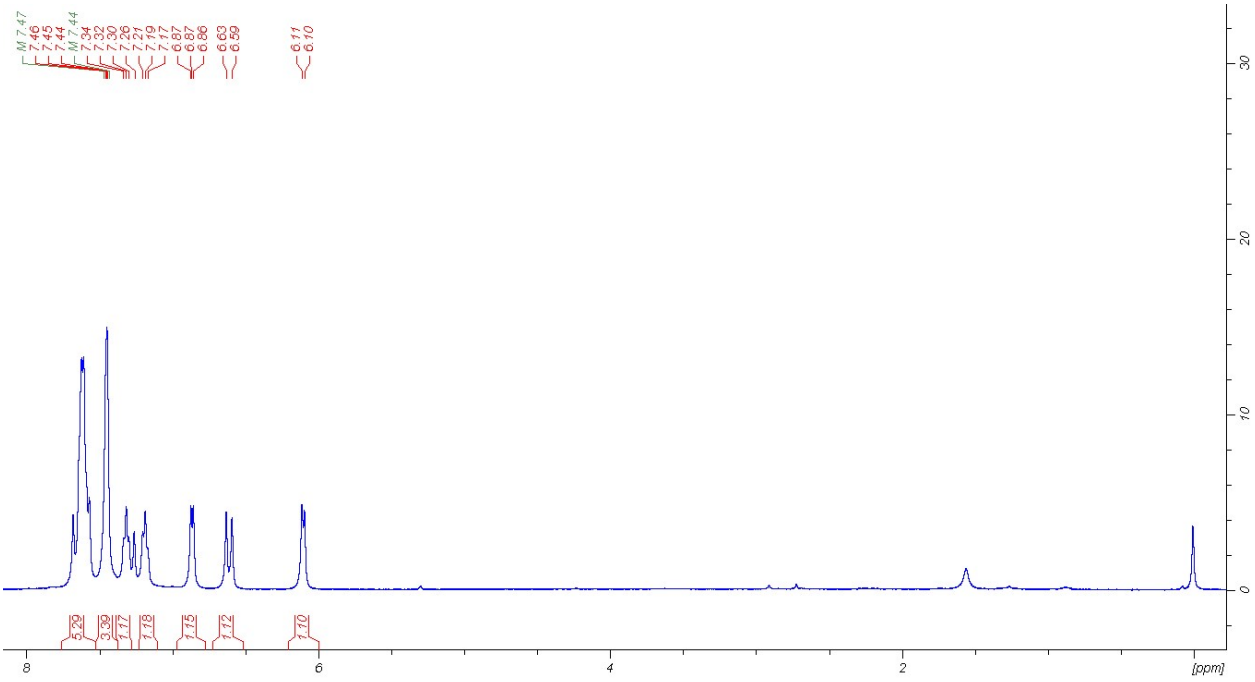


4d HRMS

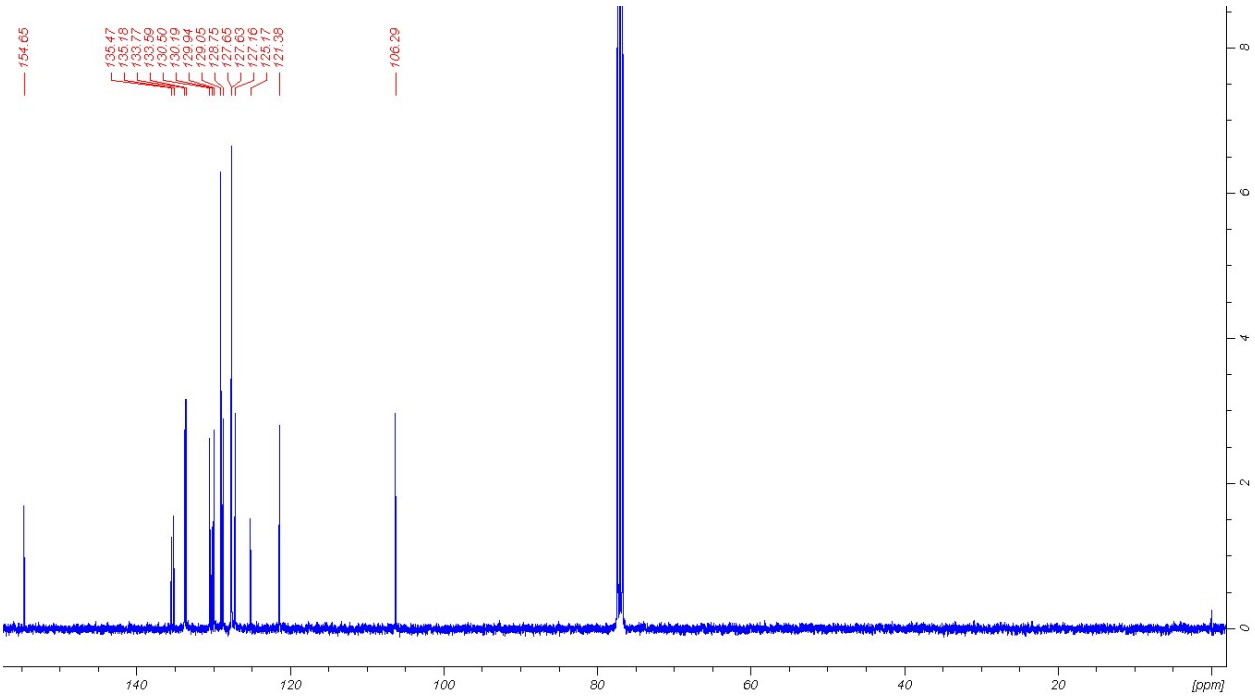


Formula	Observed m/z	Proposed adduct	Charge	Observed neutral mass	Theoretical neutral mass	Mass error (ppm)
C18H13NO5S	355.0504	radical	1+	355.0508	355.0514	1.69

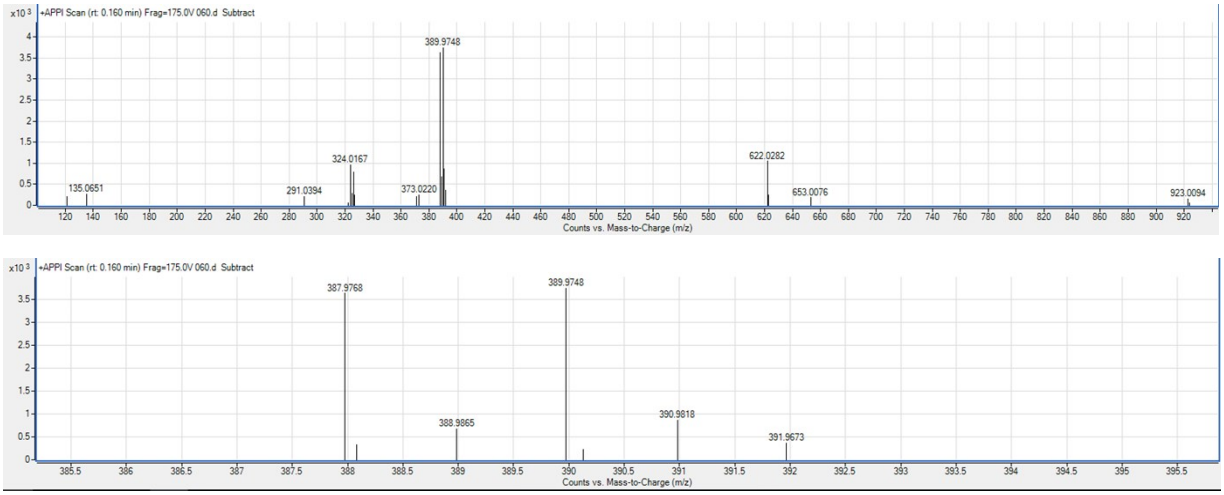
(*E*)-6-(2-Bromostyryl)-3-phenyl-1,2-oxathiine 2,2-dioxide 4e ^{1}H-NMR



4e ^{13}C-NMR

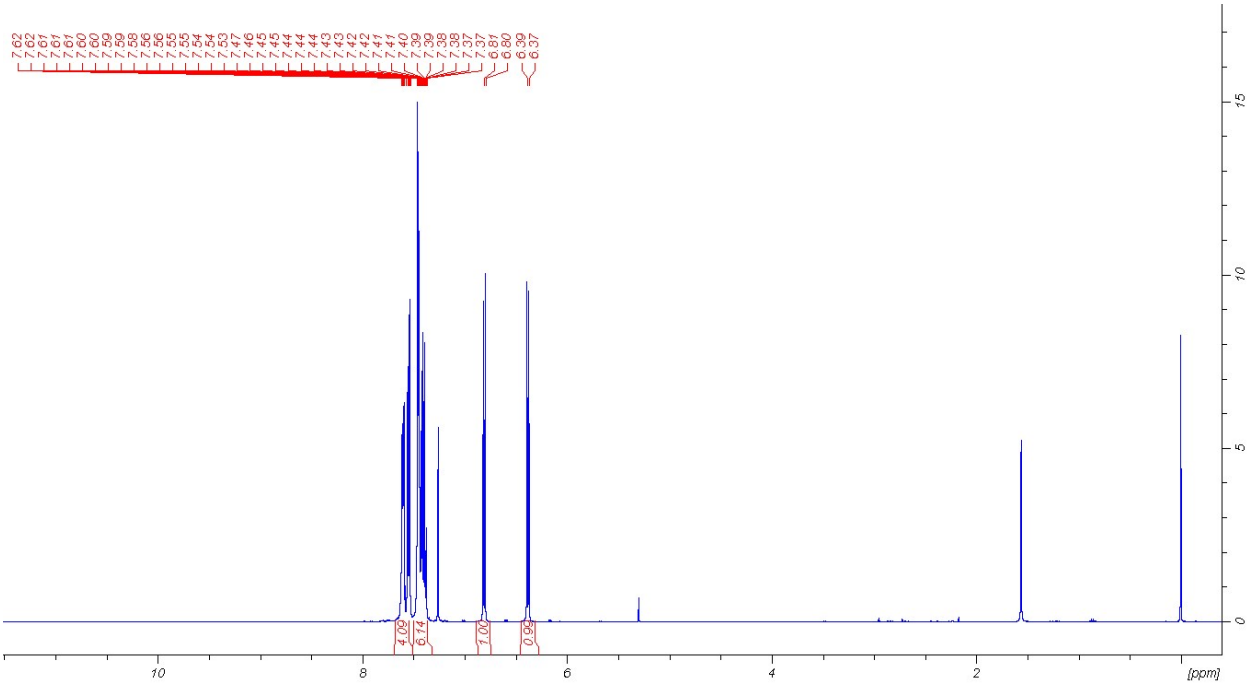


4e HRMS

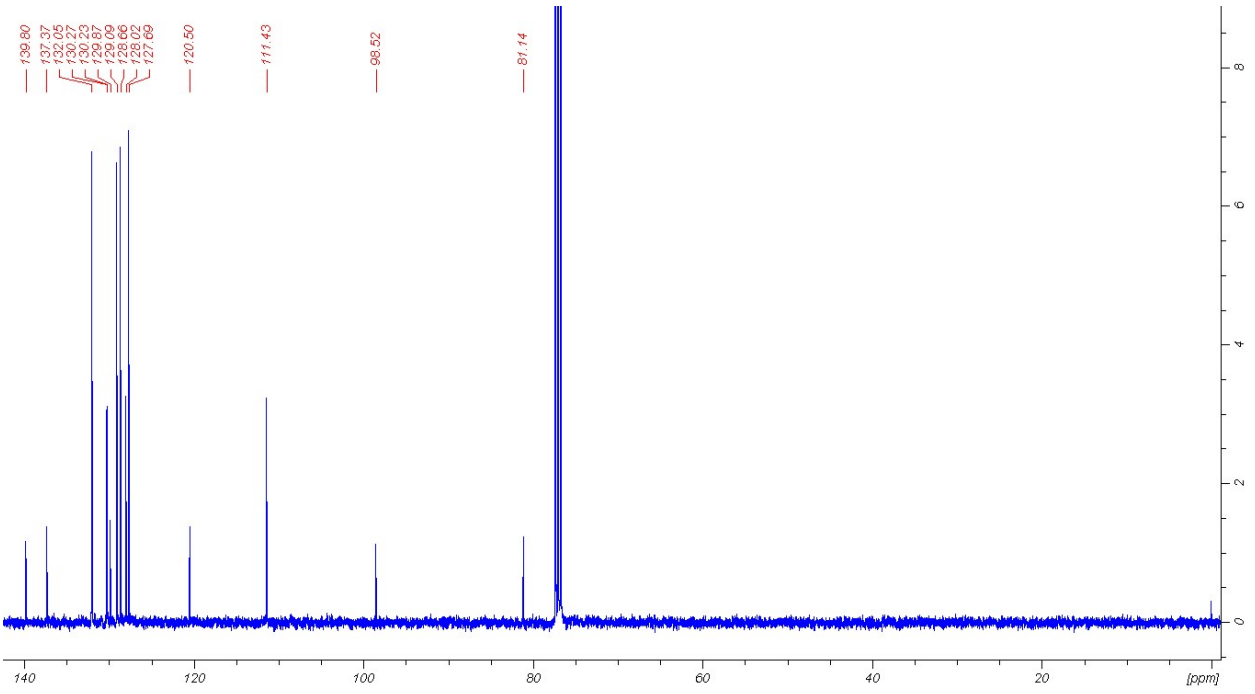


Formula	Observed m/z	Proposed adduct	Charge	Observed neutral mass	Theoretical neutral mass	Mass error (ppm)
C18H13BrO3S	389.9748	radical	1+	387.9772	387.9769	0.87

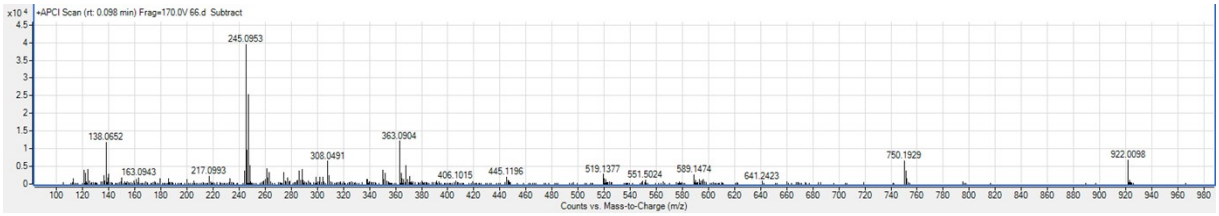
3-Phenyl-6-(phenylethynyl)-1,2-oxathiine 2,2-dioxide 4f ^{1}H-NMR

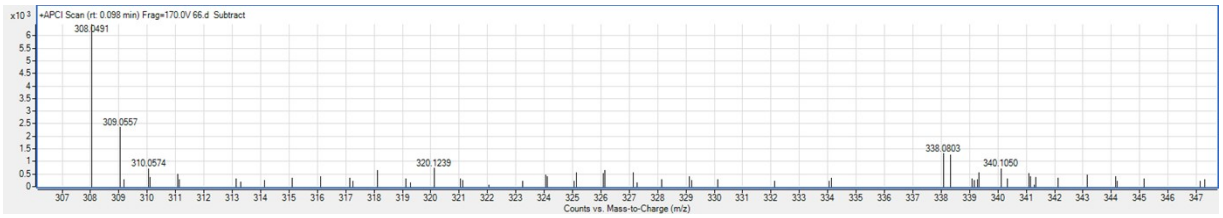


4f ^{13}C-NMR



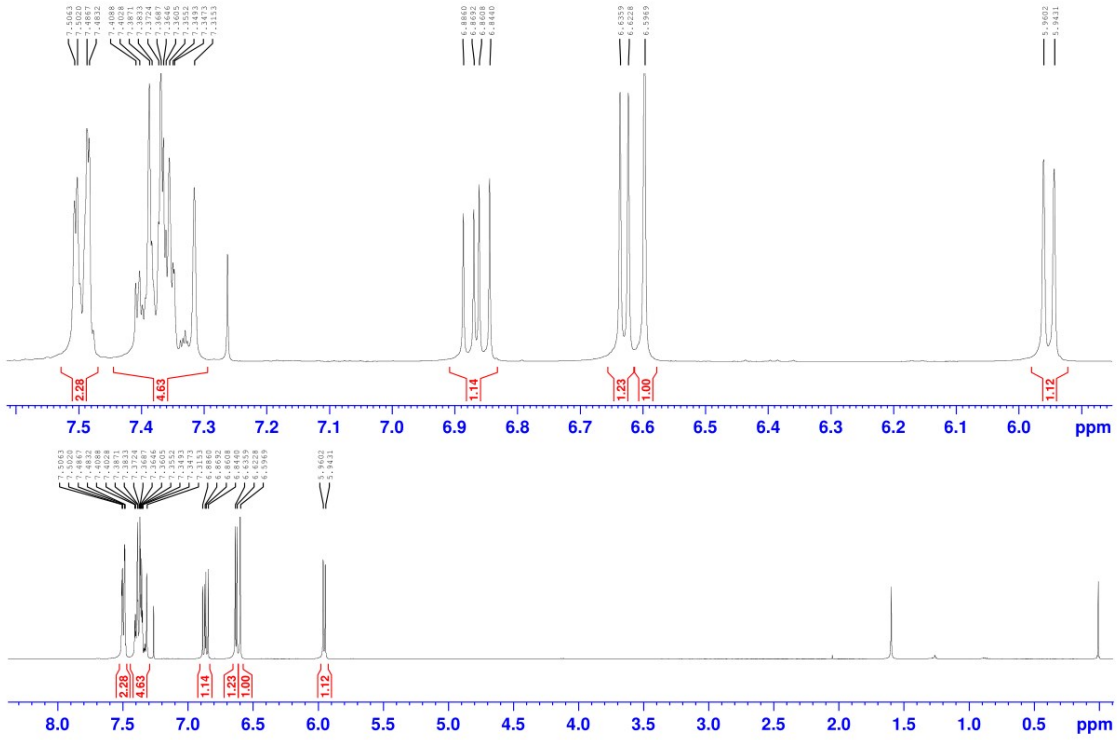
4f HRMS



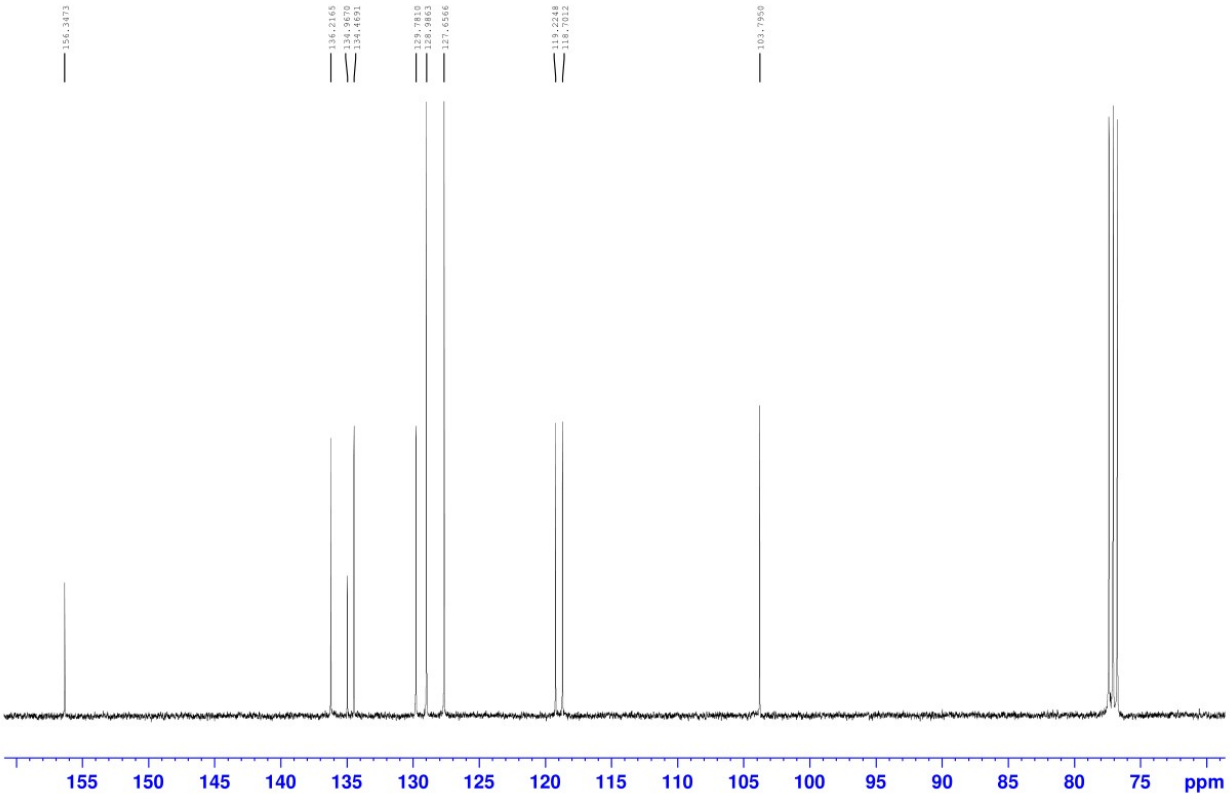


Formula	Observed m/z	Proposed adduct	Charge	Observed neutral mass	Theoretical neutral mass	Mass error (ppm)
C18H12O3S	308.0491	radical	1+	308.0496	308.0507	3.57

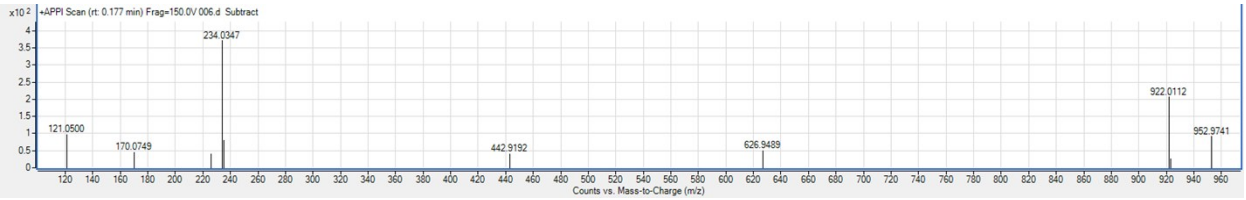
(*E*)-6-styryl-1,2-oxathiine 2,2-dioxide 4g ^{1}H-NMR

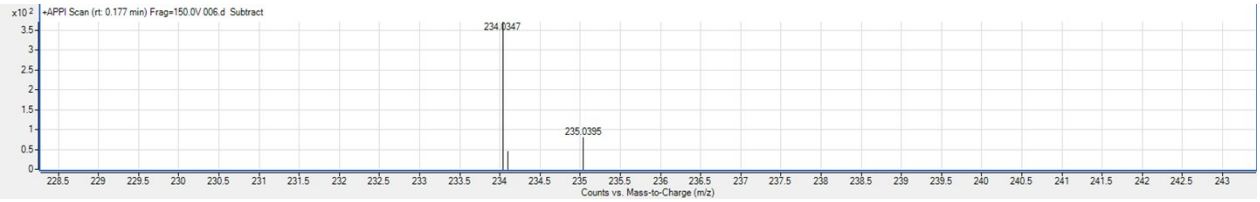


4g ^{13}C-NMR



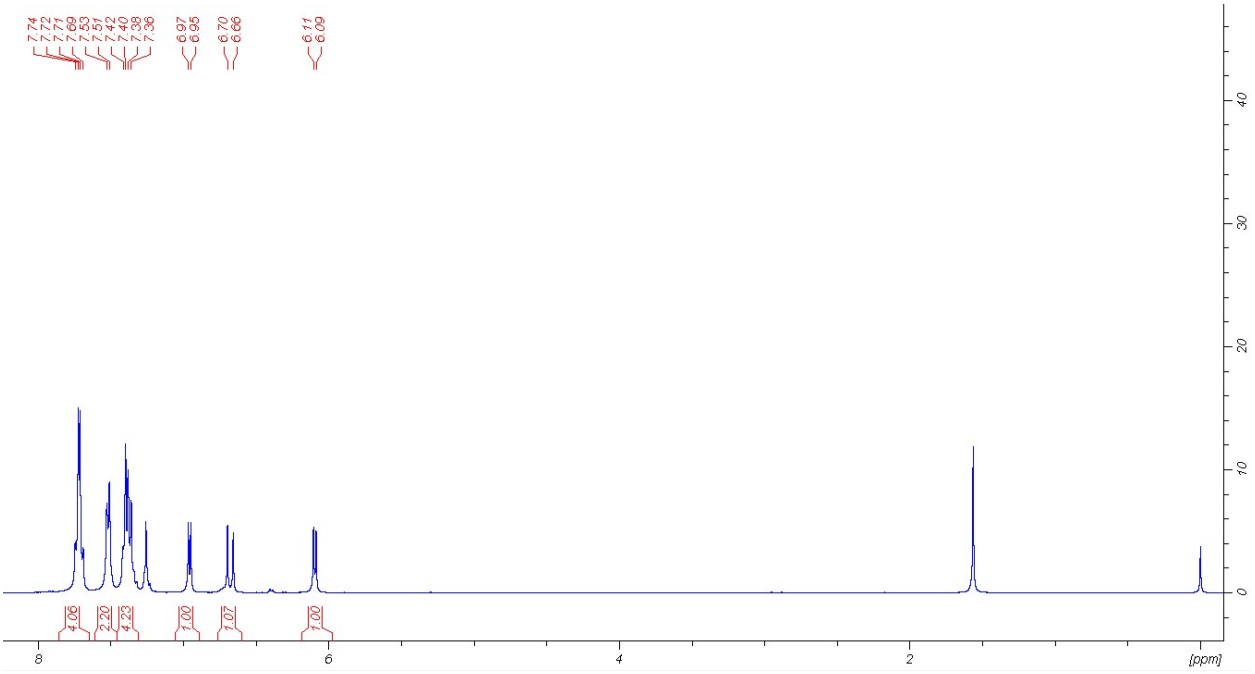
4g HRMS



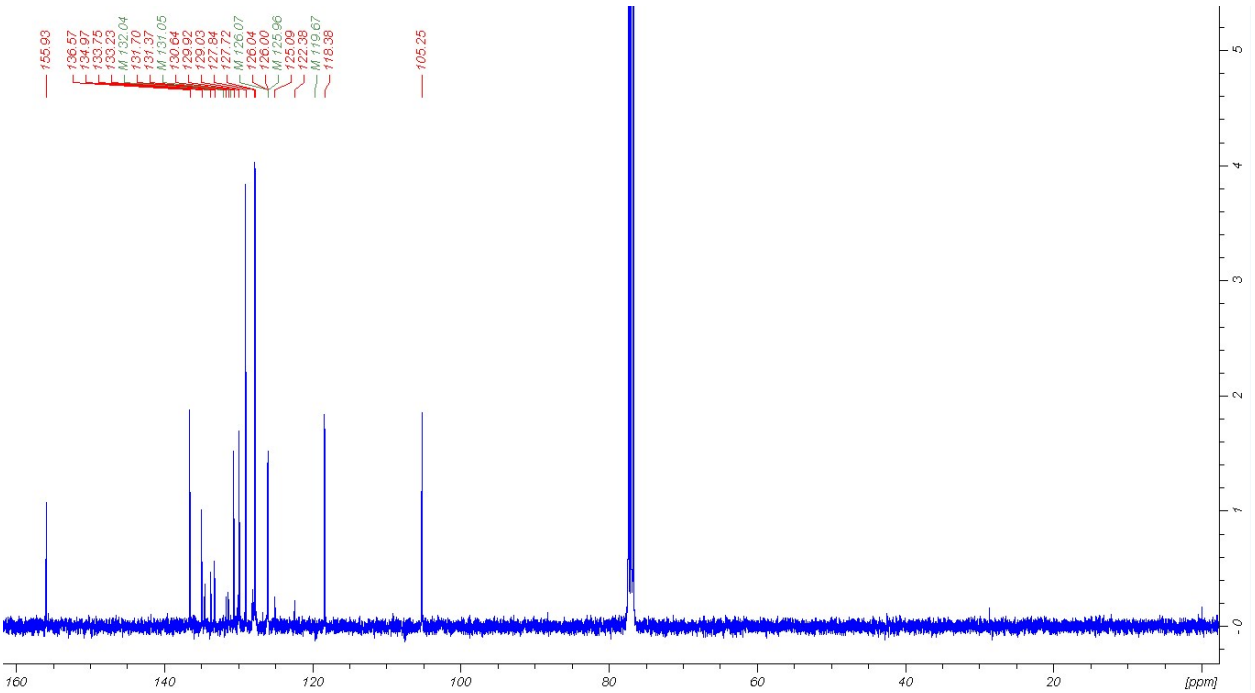


Formula	Observed m/z	Proposed adduct	Charge	Observed neutral mass	Theoretical neutral mass	Mass error (ppm)
C12H10O3S	234.0347	radical	1+	234.0352	234.0351	0.43

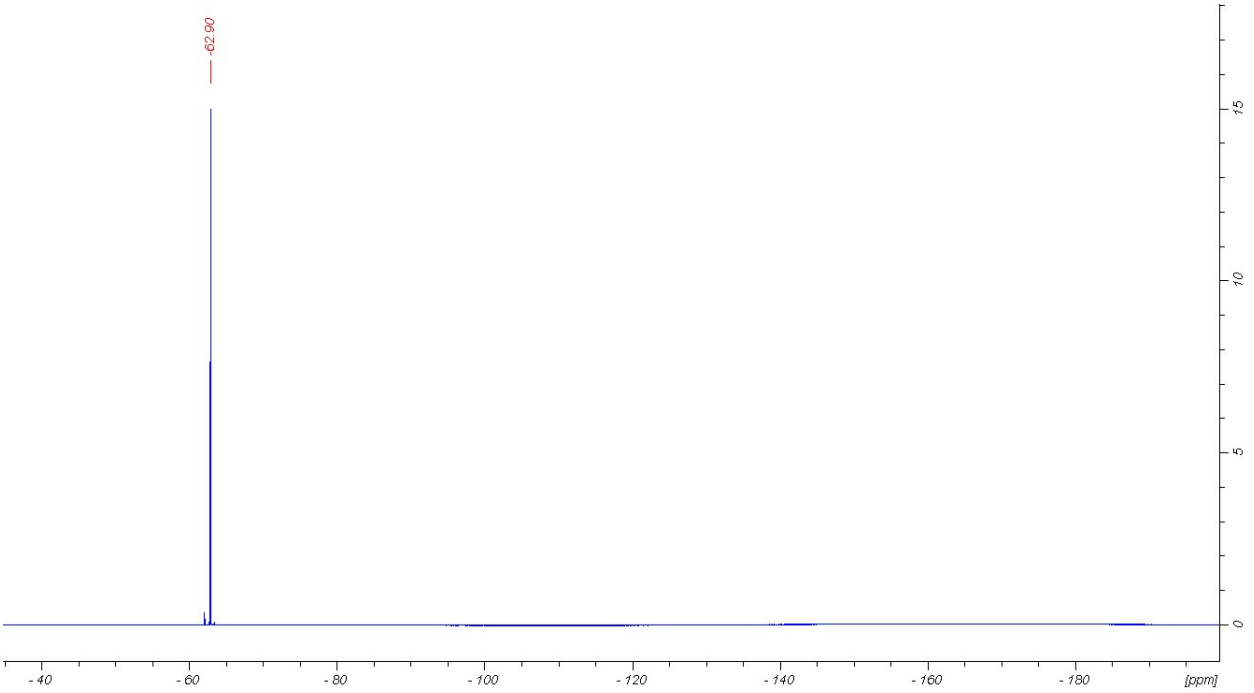
(*E*)-6-Styryl-3-(4-(trifluoromethyl)phenyl)-1,2-oxathiine 2,2-dioxide 4h ^{1}H-NMR



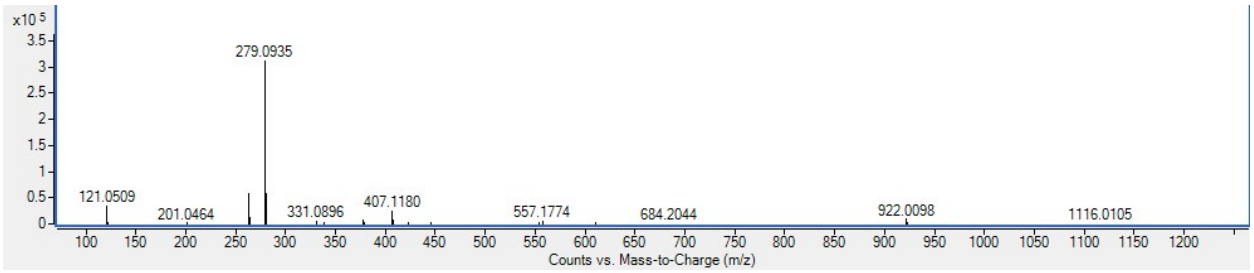
4h ^{13}C-NMR

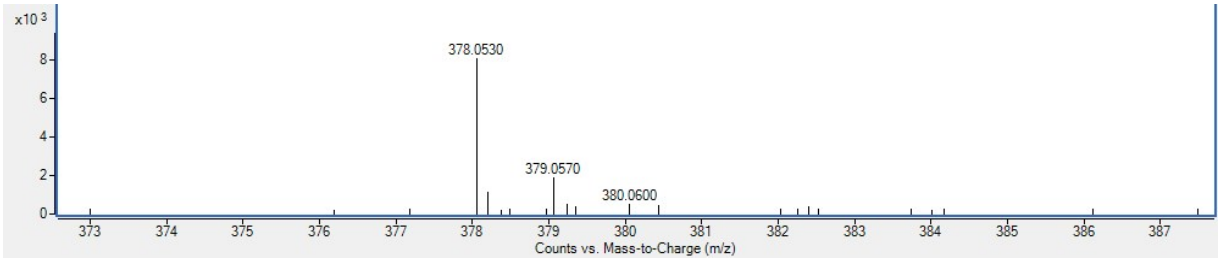


4h ^{19}F-NMR



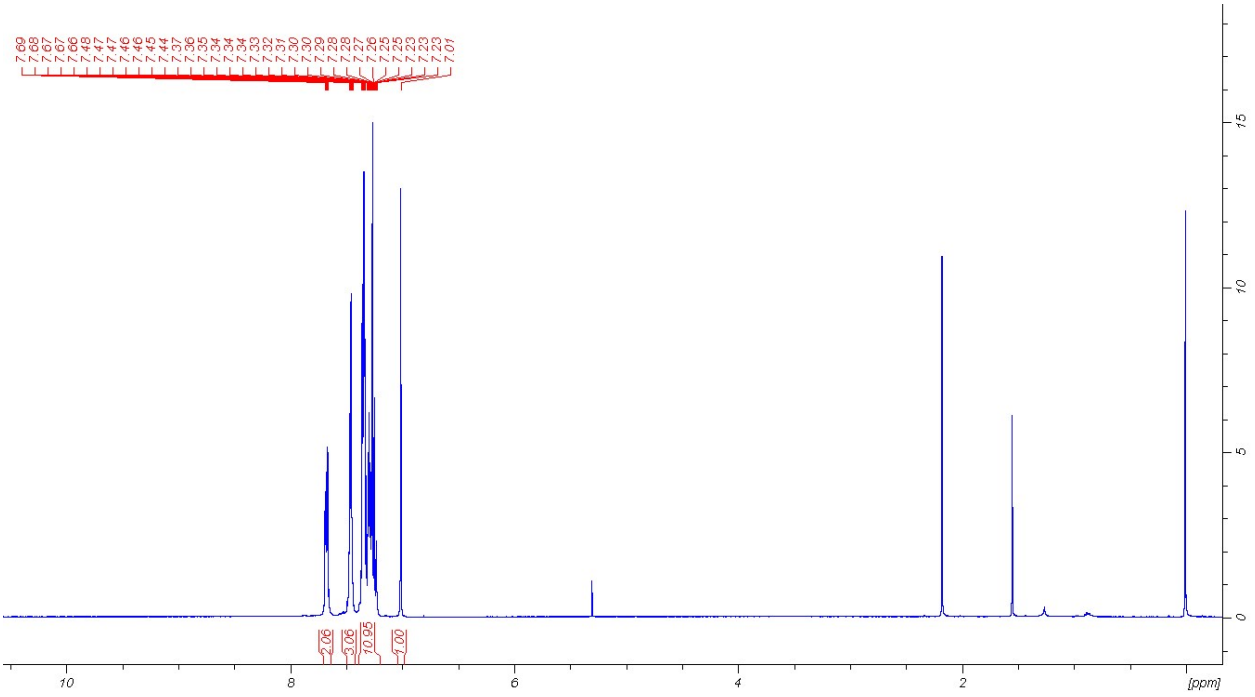
4h HRMS



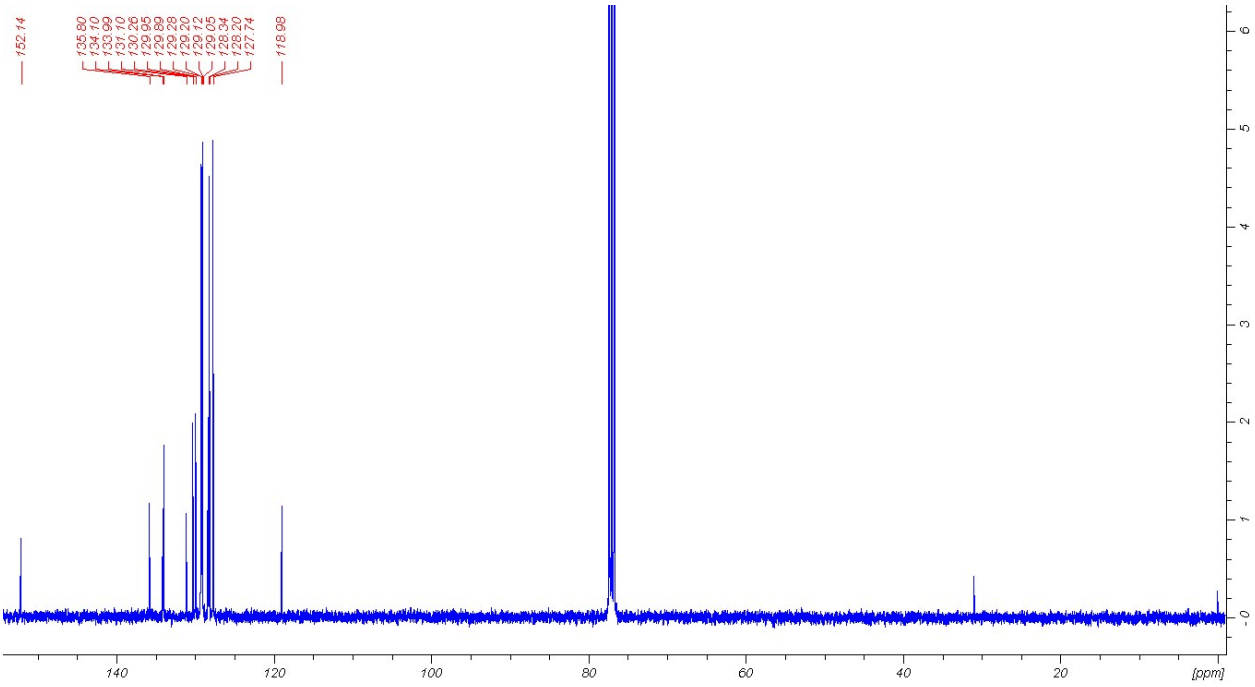


Formula	Observed m/z	Proposed adduct	Charge	Observed neutral mass	Theoretical neutral mass	Mass error (ppm)
C19H13F3O3S	378.0530	radical	1+	378.0535	378.0537	0.53

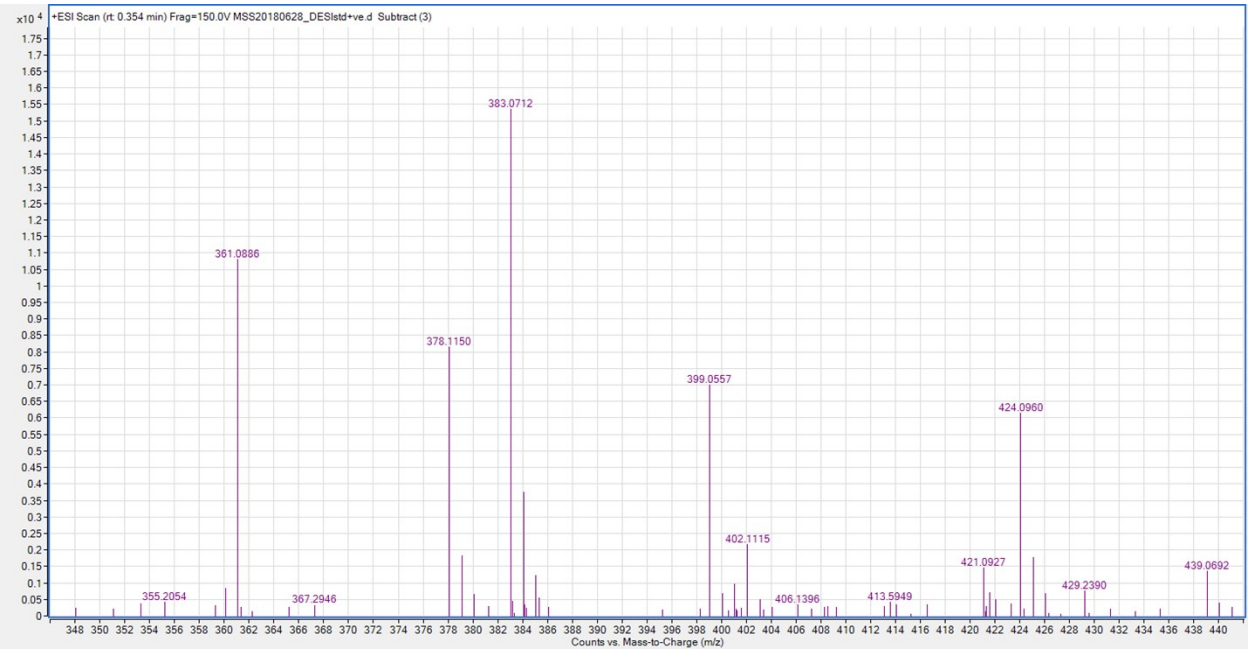
3,5,6-(Triphenyl)-1,2-oxathiine 2,2-dioxide 6a ^{1}H-NMR



6a ^{13}C-NMR

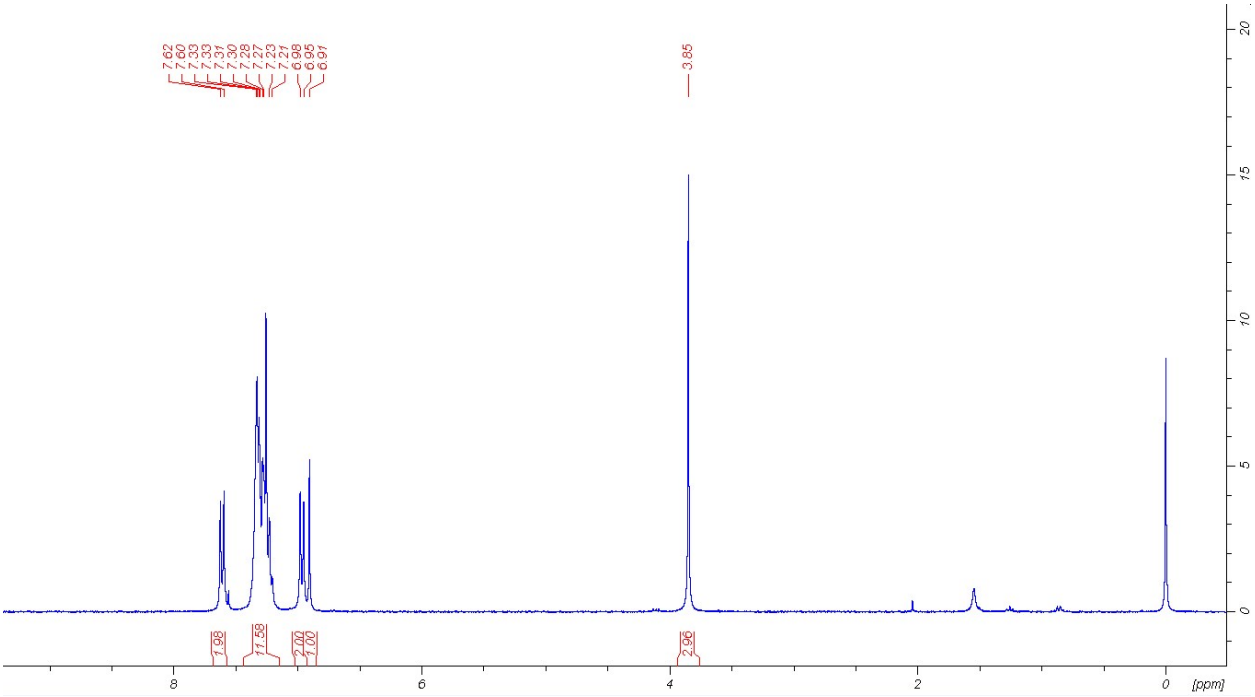


6a HRMS

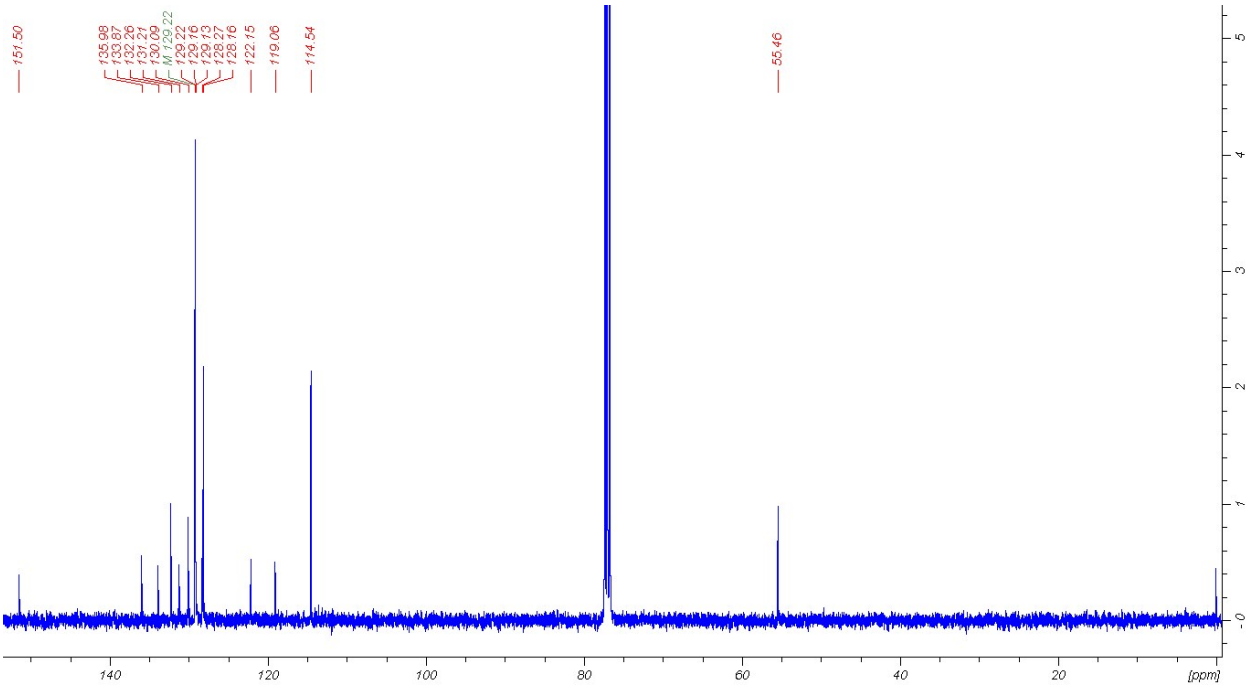


Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
C20 H18 O3 S	(M+Na)+	361.0886	338.0983	338.0977	75.3	-1.97
C17 H22 O4 S	(M+K)+	361.0886	322.1244	322.1239	67.68	-1.7
C22 H16 O3 S	(M+H)+	361.0886	360.0803	360.082	64.31	4.87
C25 H12 O3	(M+H)+	361.0886	360.0801	360.0786	59.8	-3.99
C25 H11 S	(M+NH4)+	361.0886	343.0537	343.0581	33.76	12.92

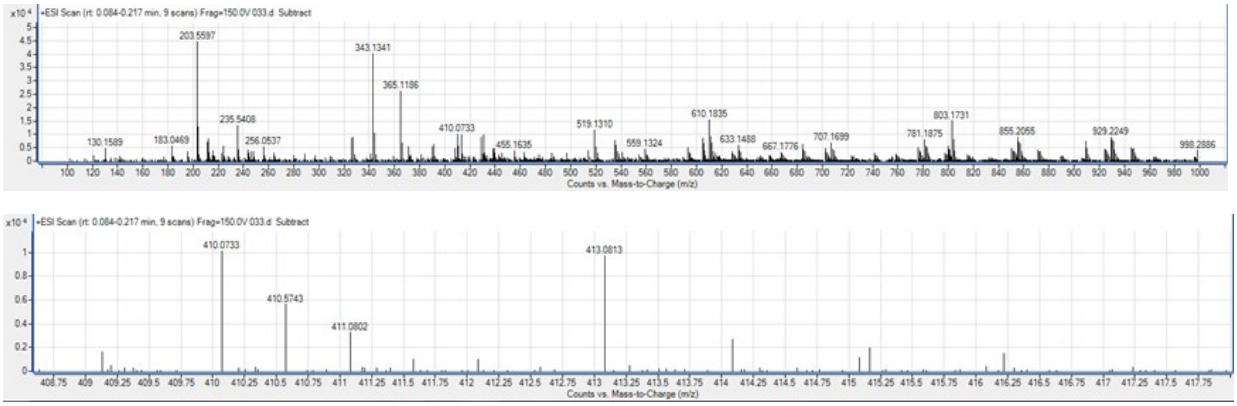
3-(4-Methoxyphenyl)-5,6-diphenyl-1,2-oxathiine 2,2-dioxide 6b ^{1}H-NMR



6b ^{13}C-NMR

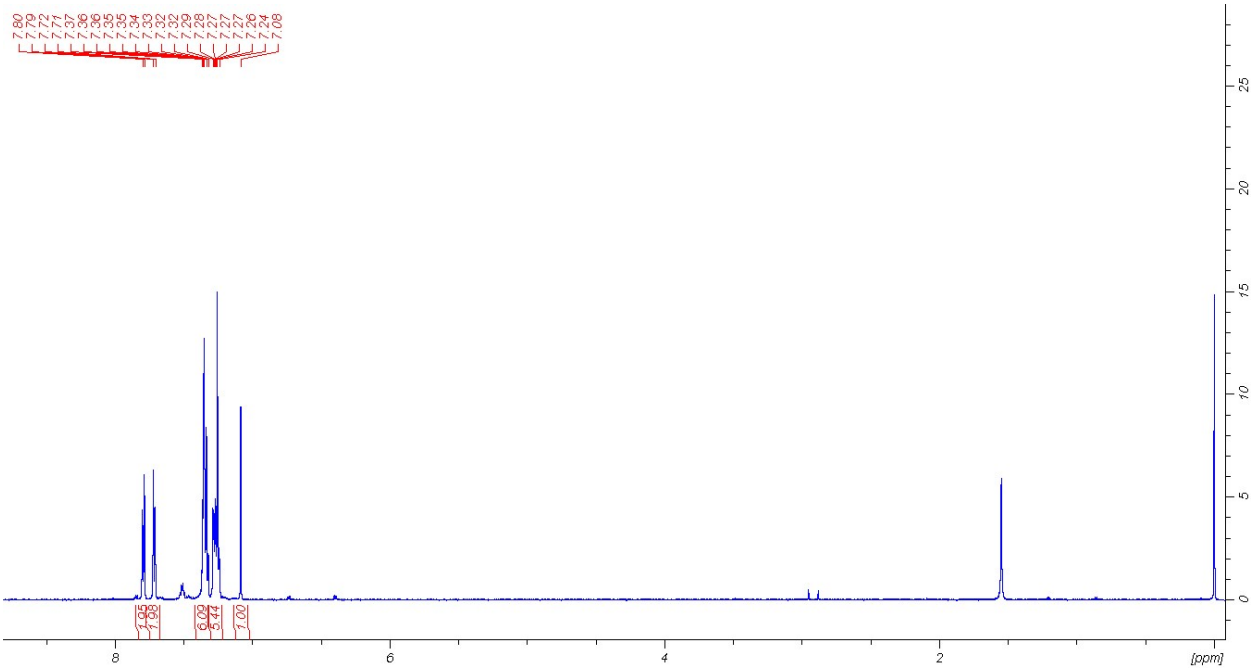


6b HRMS

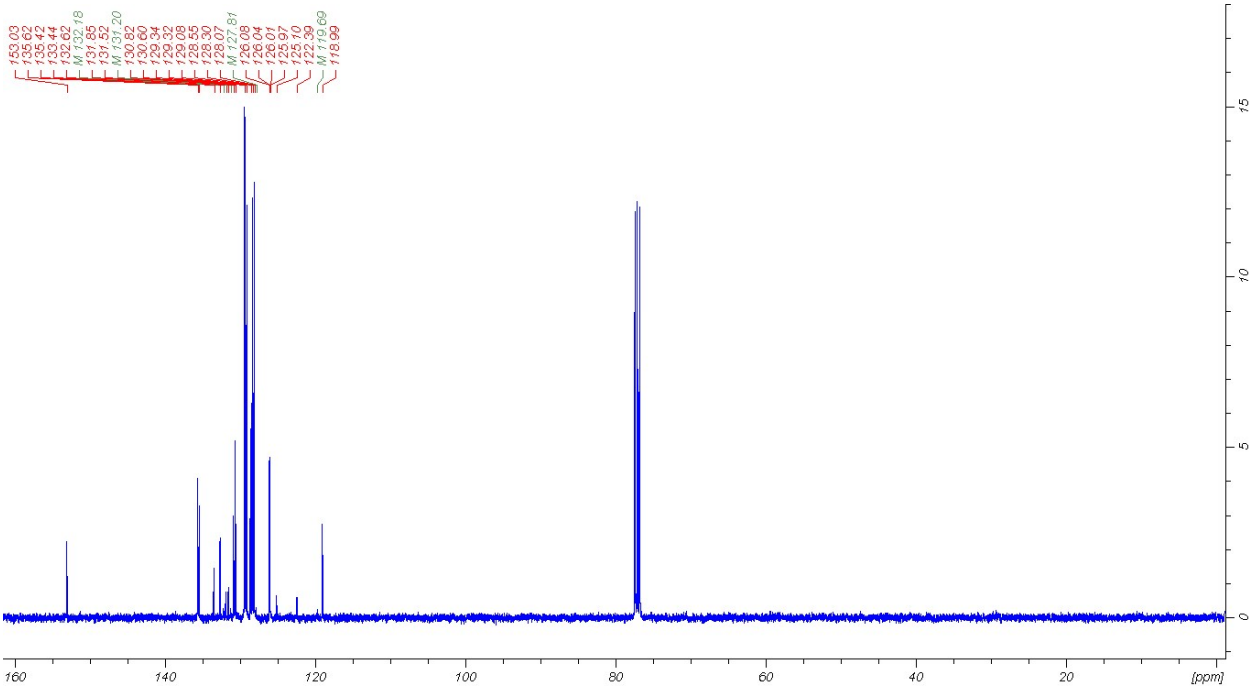


Formula	Observed m/z	Proposed adduct	Charge	Observed neutral mass	Theoretical neutral mass	Mass error (ppm)
C23H18O4S	413.0813	**Na+**	1+	390.0923	390.0926	0.76

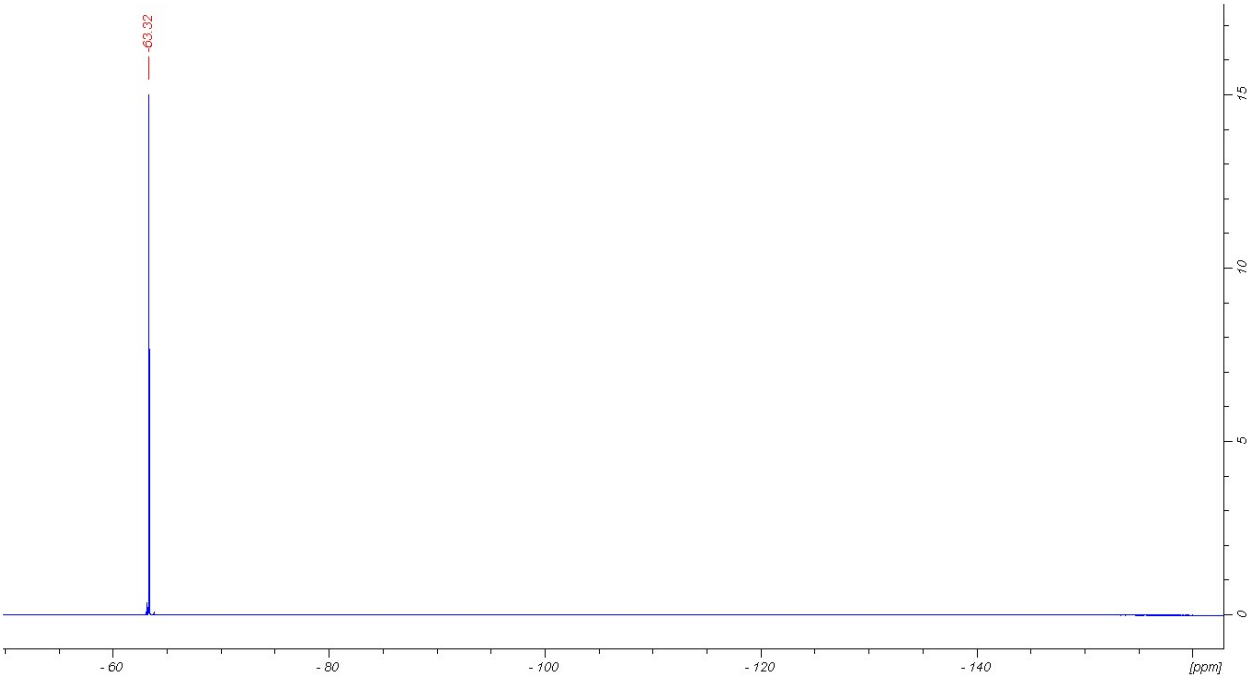
5,6-Diphenyl-3-((4-trifluoromethy)phenyl)-1,2-oxathiine 2,2 dioxide 6c ^{1}H-NMR



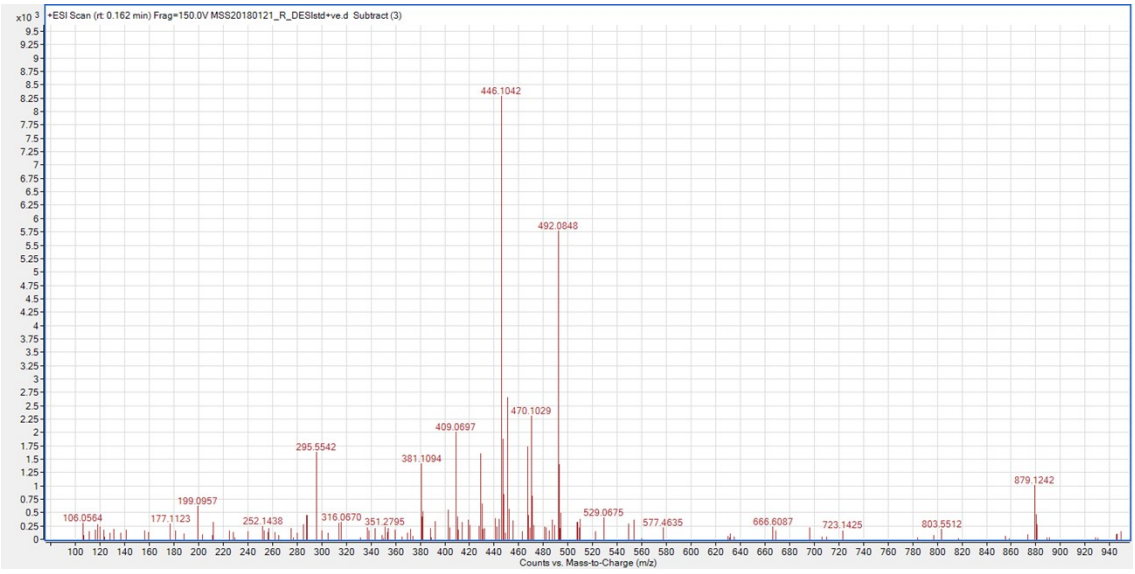
6c ^{13}C-NMR



6c ^{19}F-NMR

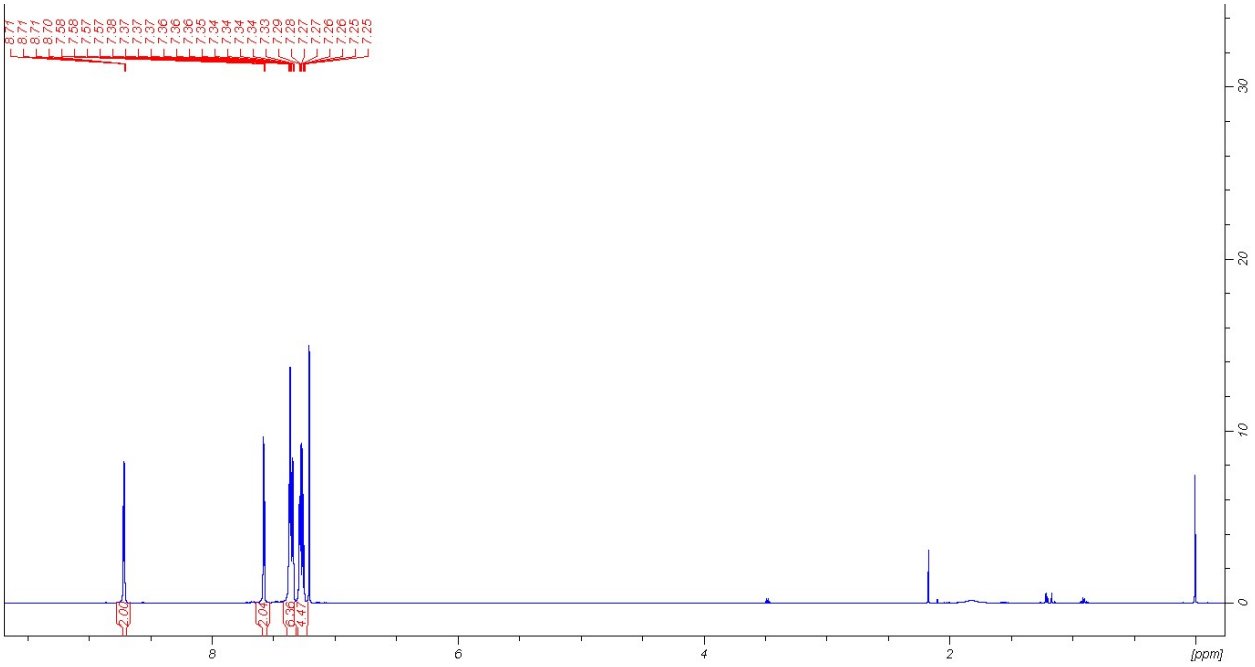


6c HRMS

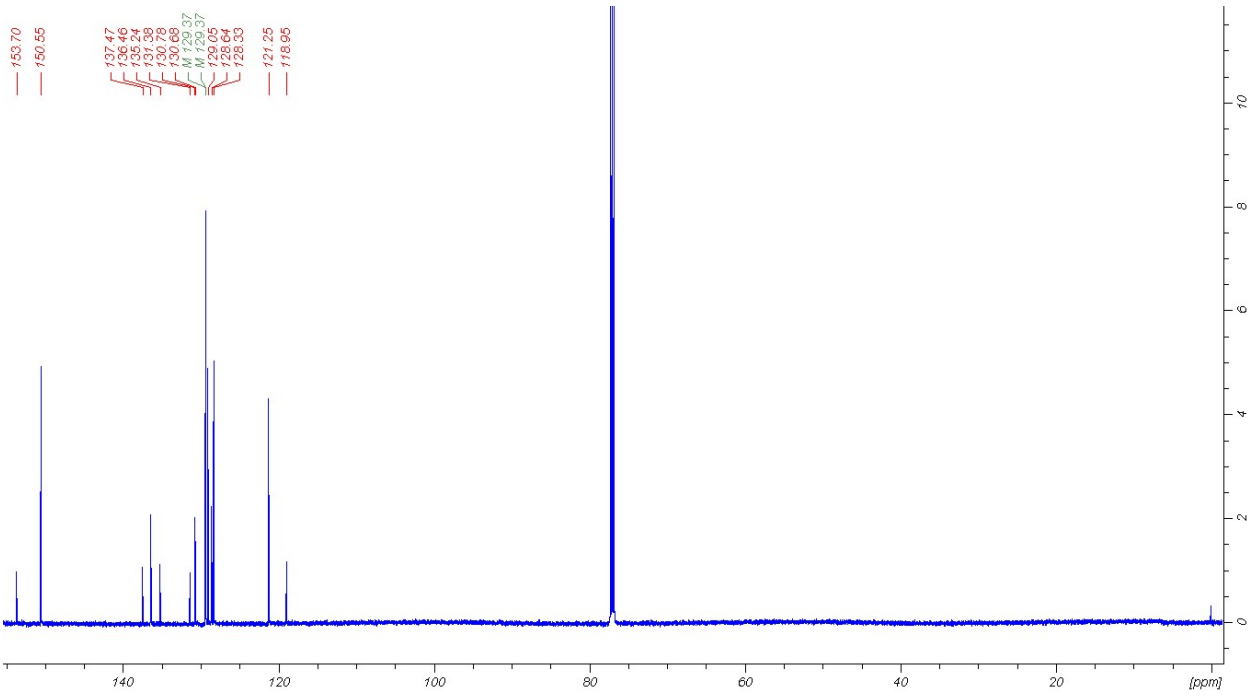


Best	Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
●	C23 H15 F3 O3 S	(M+NH4)+	446.1042	428.0707	428.0694	90.21	-3.04
○	C23 H18 F2 O2 S2	(M+NH4)+	446.1042	428.0708	428.0716	90.17	1.82
○	C25 H16 O5 S	(M+NH4)+	446.1042	428.0707	428.0718	88.76	2.77
○	C26 H17 F O S2	(M+NH4)+	446.1042	428.0708	428.0705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

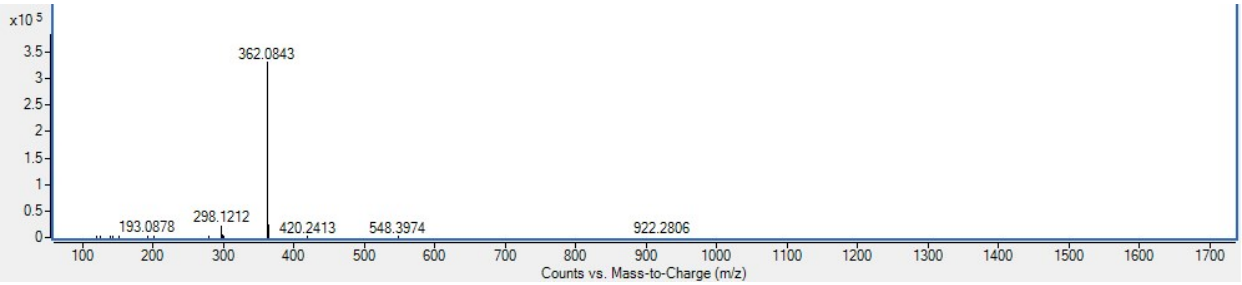
5,6-Diphenyl-3-(pyridin-4-yl)-1,2-oxathiine 2,2-dioxide 6d ^{1}H-NMR



6d ^{13}C-NMR

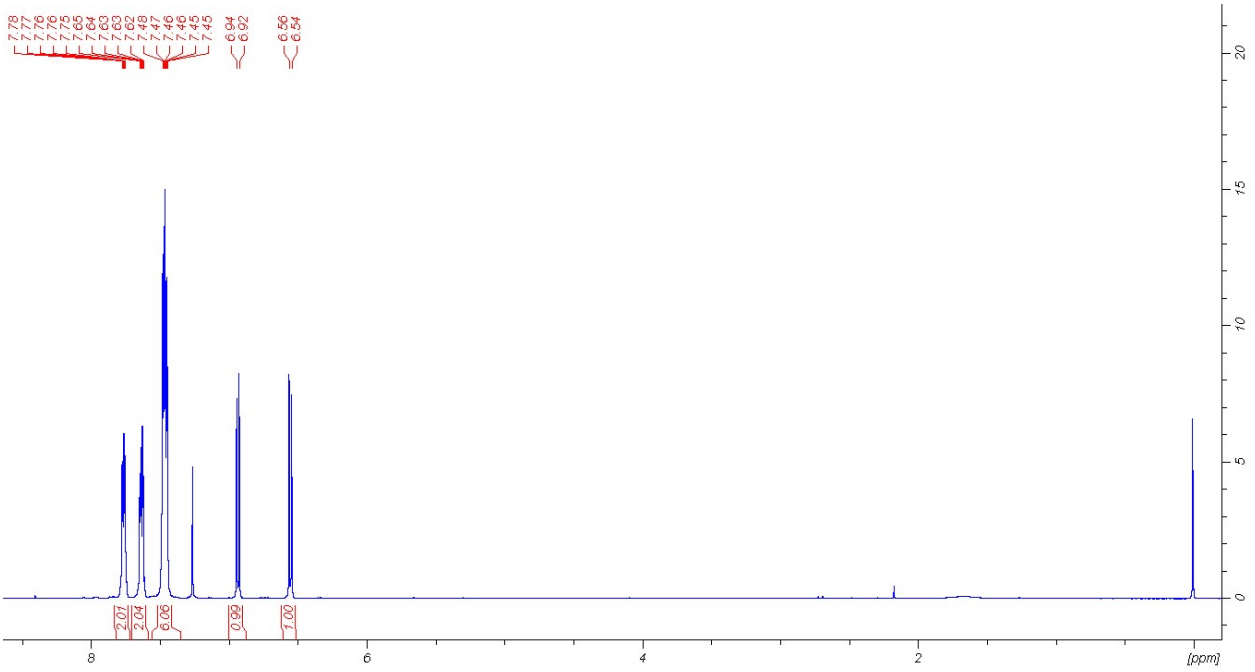


6d HRMS

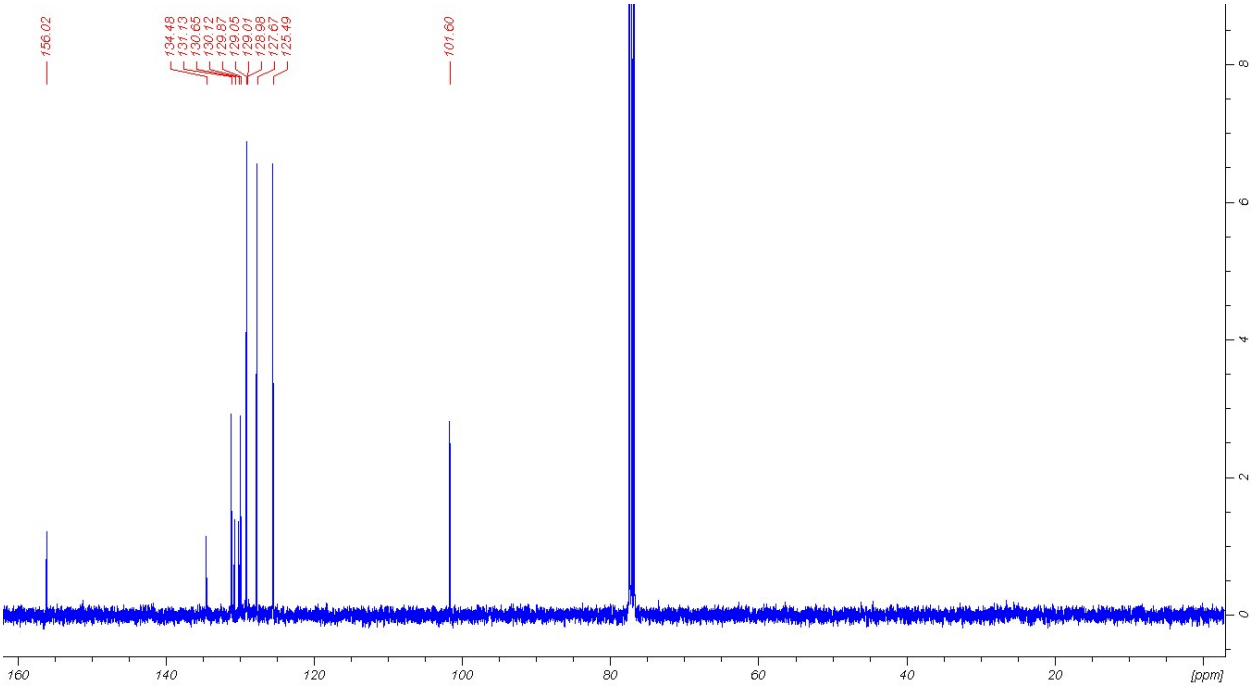


Formula	Observed m/z	Proposed adduct	Charge	Observed neutral mass	Theoretical neutral mass	Mass error (ppm)
C21H15NO3S	362.0843	H+	1+	361.0771	361.0773	0.55

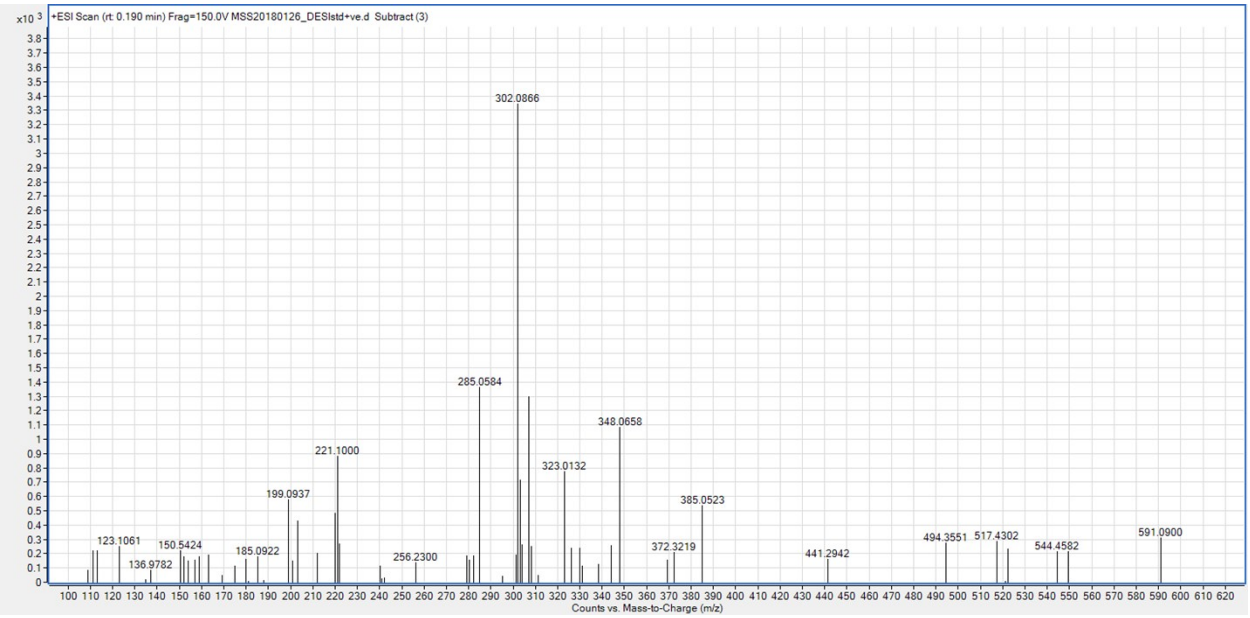
3,6-Diphenyl-1,2-oxathiine 2,2-dioxide 6e ^{1}H-NMR



6e ^{13}C-NMR

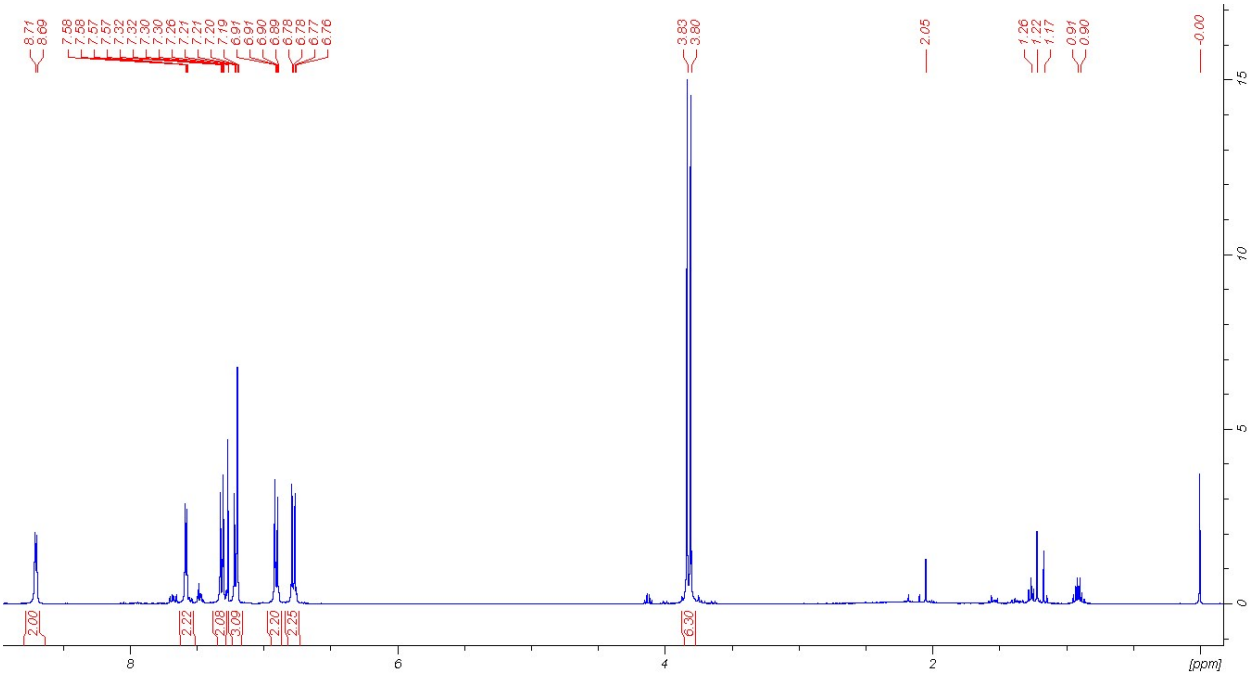


6e HRMS

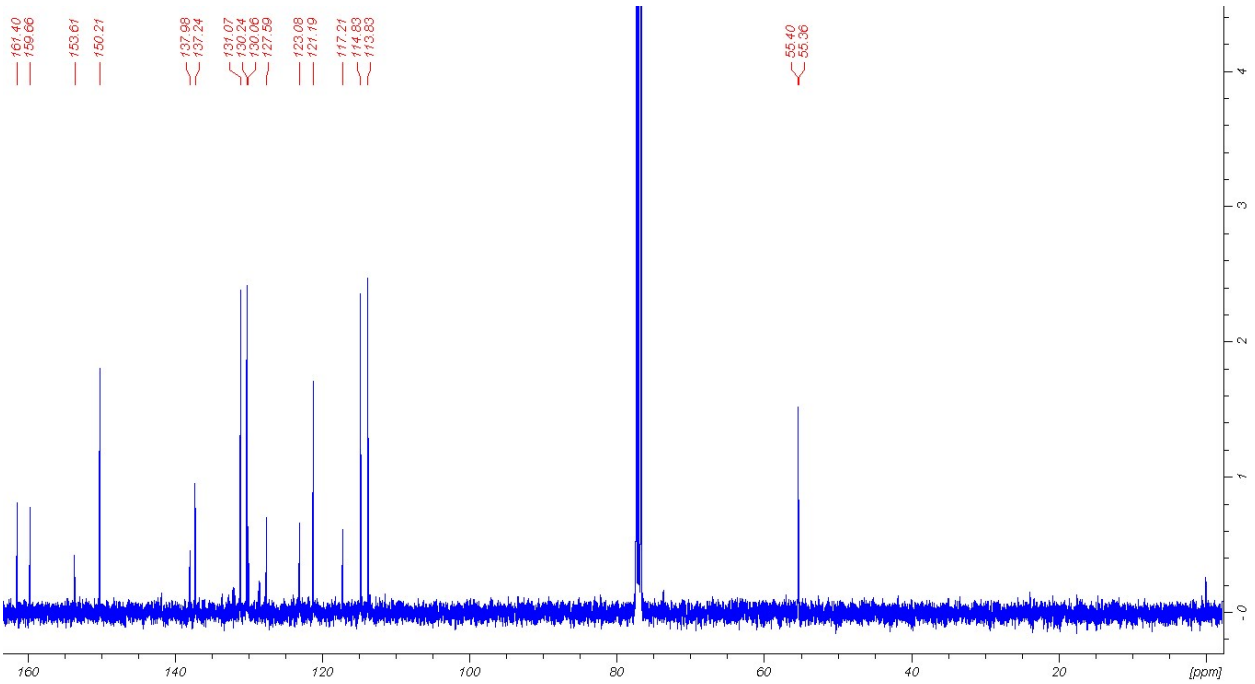


Best	Formula	Species	m/z	Mass	Mass (MFG)	Score	Diff (ppm)
○	C19 H10 N S	(M+NH4)+	302.0866	284.0526	284.0534	95.2	2.7
○	C13 H16 O3 S2	(M+NH4)+	302.0866	284.0528	284.0541	85.34	4.63
▶ ○	C16 H12 O3 S	(M+NH4)+	302.0866	284.0526	284.0507	85.19	-6.74
○	C22 H6 N	(M+NH4)+	302.0866	284.0522	284.05	67.47	-7.57
○	C8 H16 N2 O5 S2	(M+NH4)+	302.0866	284.0529	284.0501	60.54	-9.92
○	C15 H10 N O5	(M+NH4)+	302.0866	284.0522	284.0559	52.29	12.87

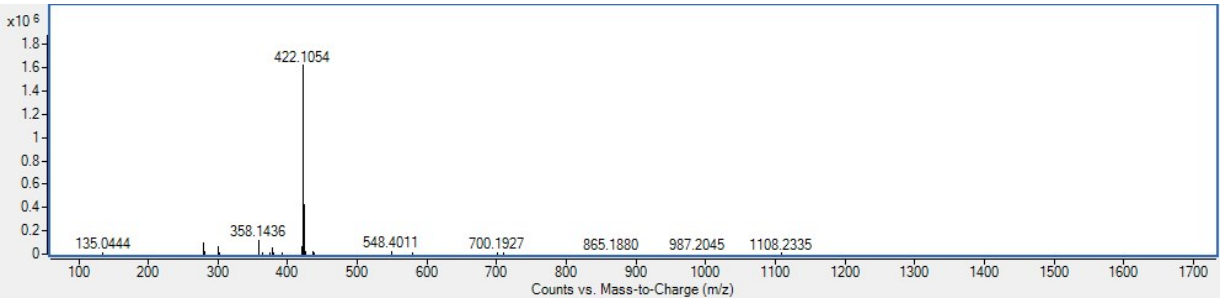
5,6-Bis(4-methoxyphenyl)-3-(pyridin-4-yl)-1,2-oxathiine 2,2-dioxide 6f ^{1}H-NMR



6f ^{13}C-NMR

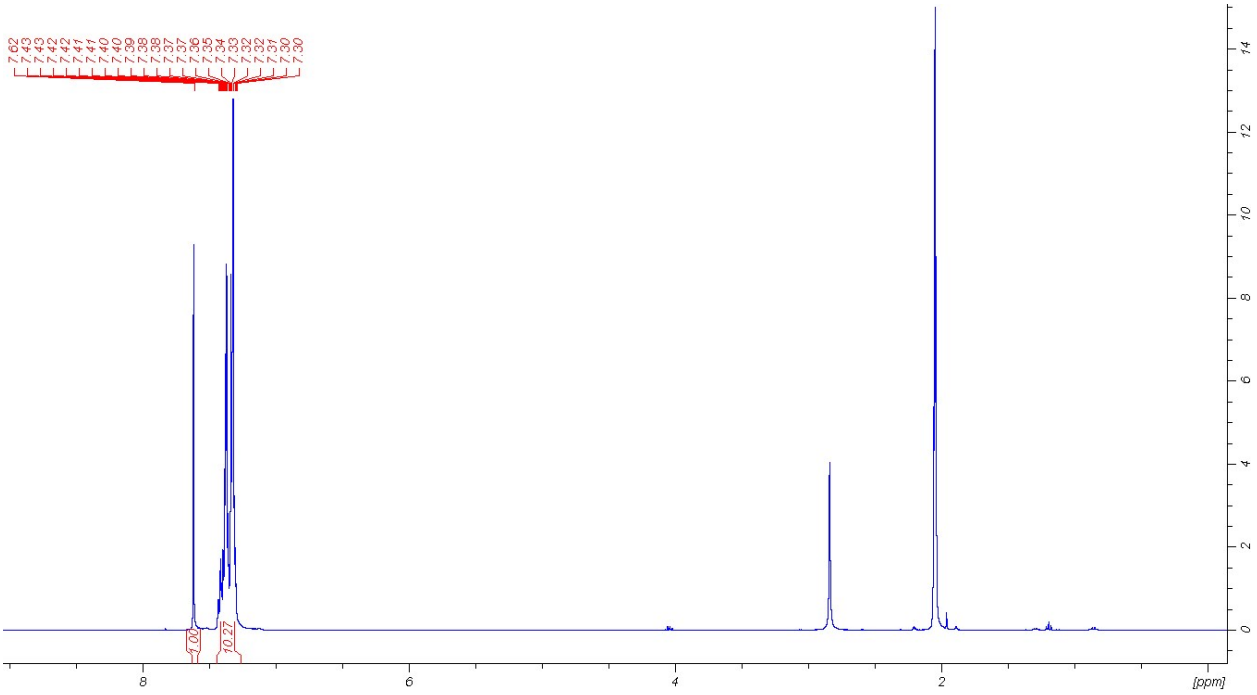


6f HRMS

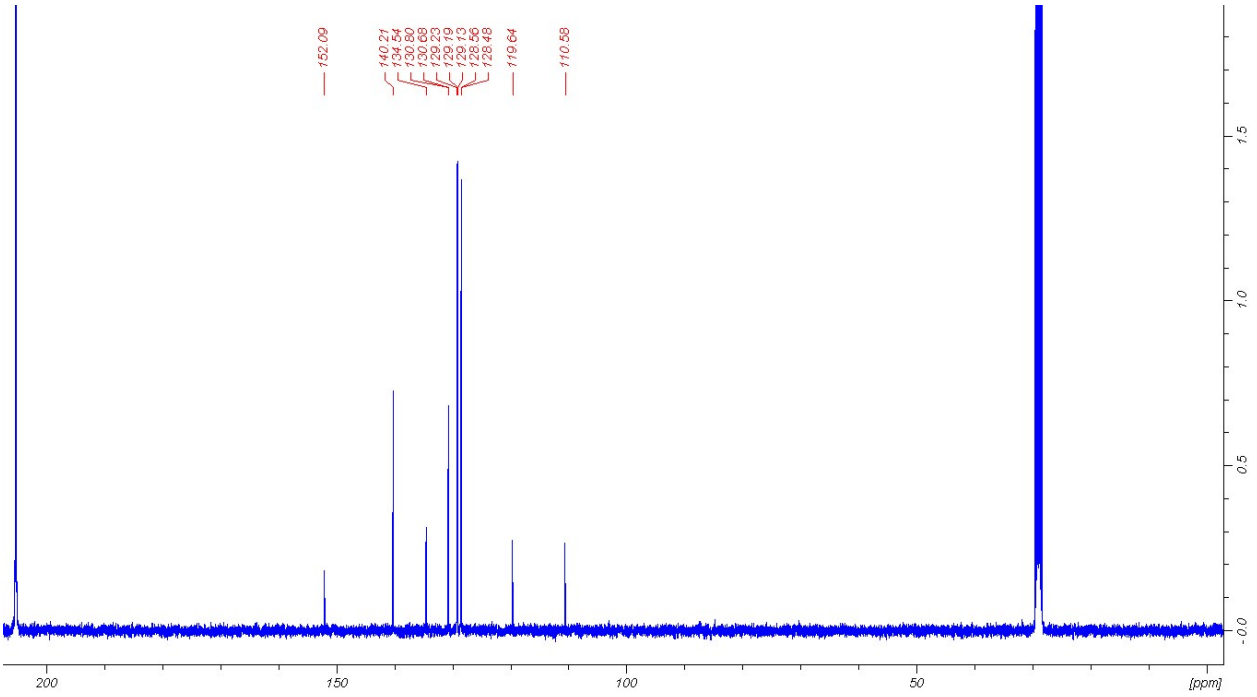


Formula	Observed m/z	Proposed adduct	Charge	Observed neutral mass	Theoretical neutral mass	Mass error (ppm)
C23H19NO5S	422.1054	H+	1+	421.0983	421.0984	0.24

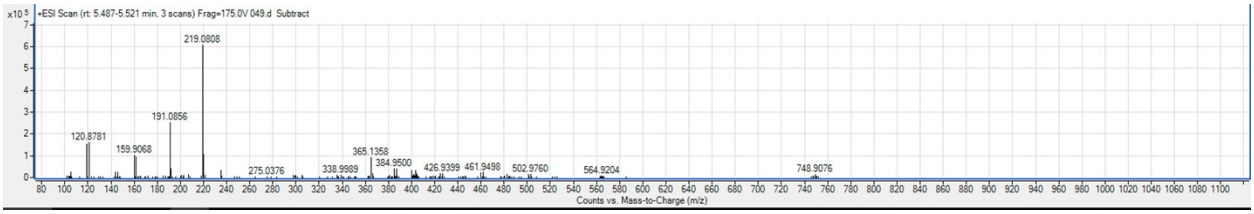
3-Bromo-3,6-diphenyl-1,2-oxathiine 2,2-dioxide 7 ^{1}H-NMR

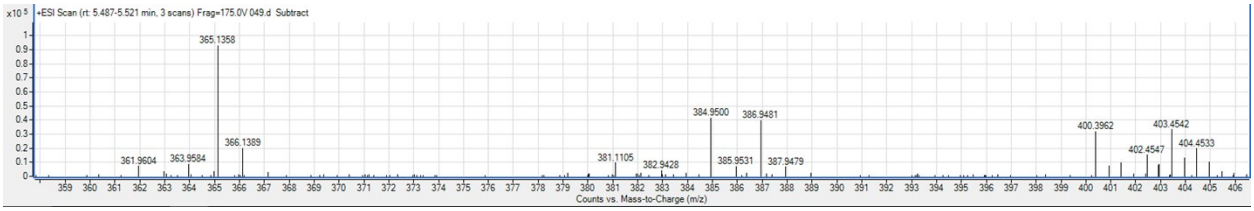


7 ^{13}C-NMR



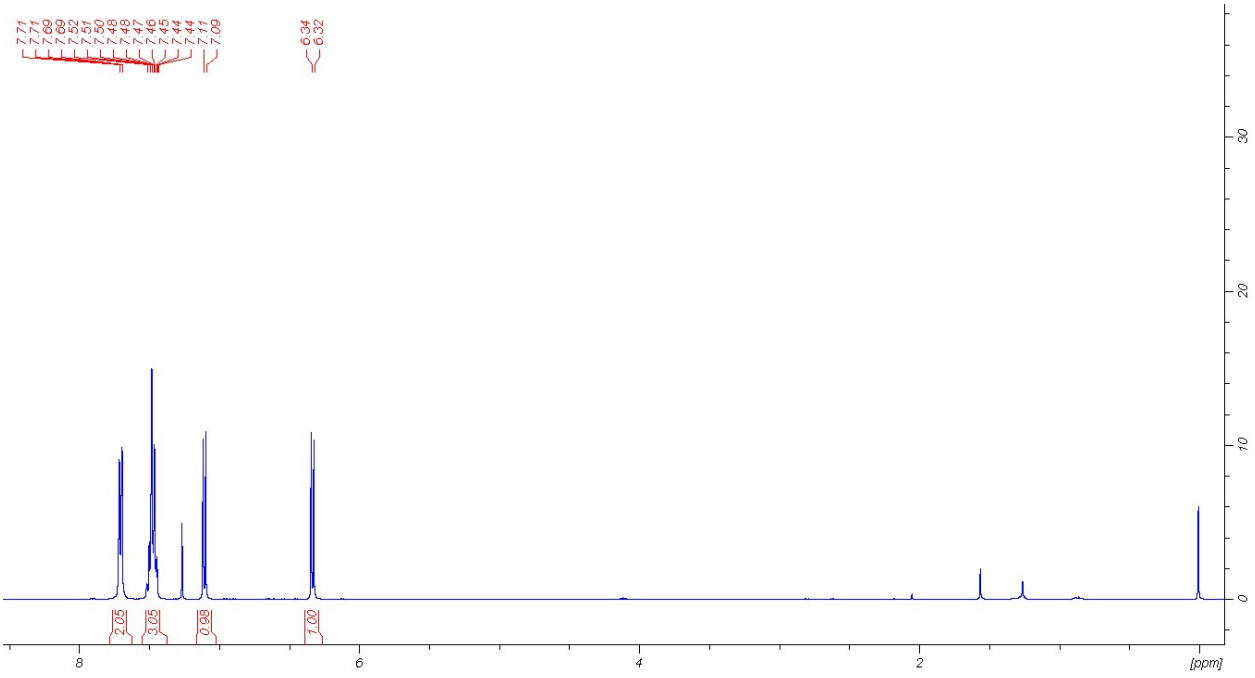
7 HRMS



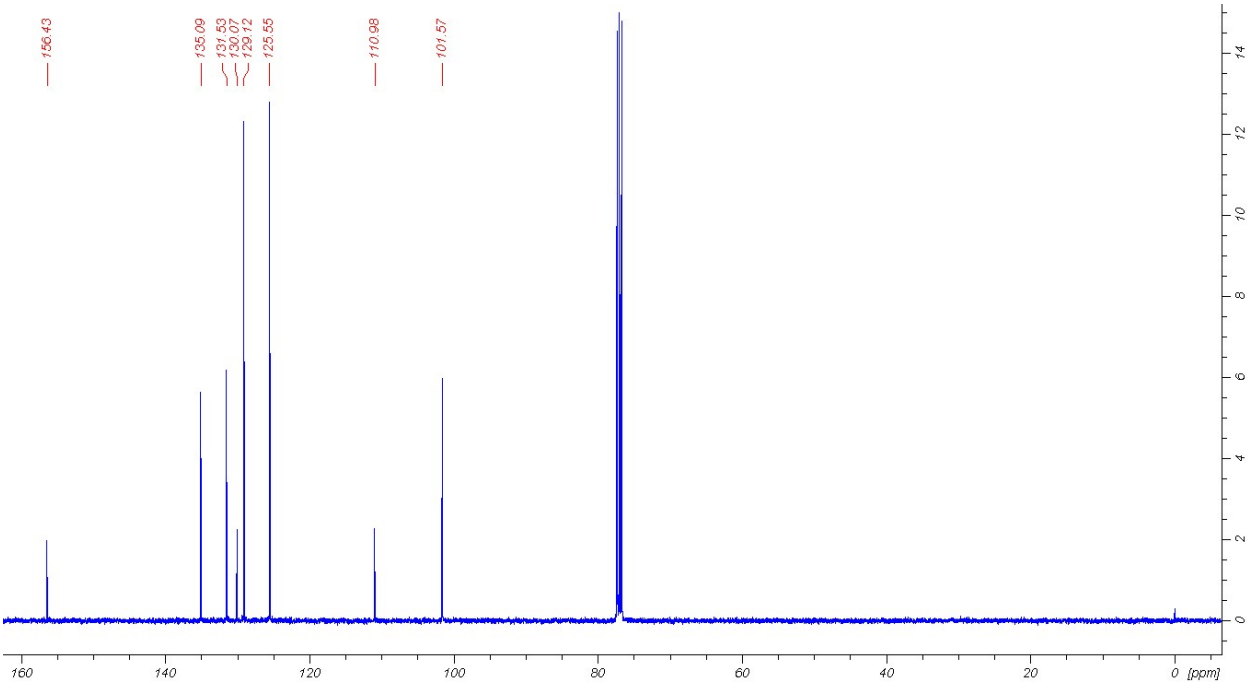


Species	Calc m/z
(M+H)+	362.9685
(M+Na)+	384.9504

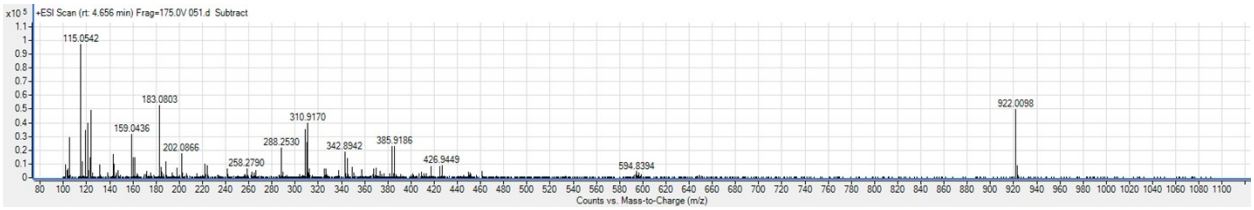
3-Bromo-6-phenyl-1,2-oxathiine 2,2-dioxide 8 ^{1}H-NMR

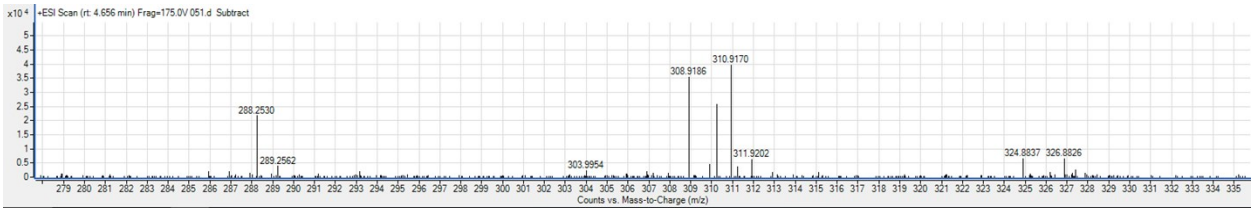


8 ^{13}C-NMR



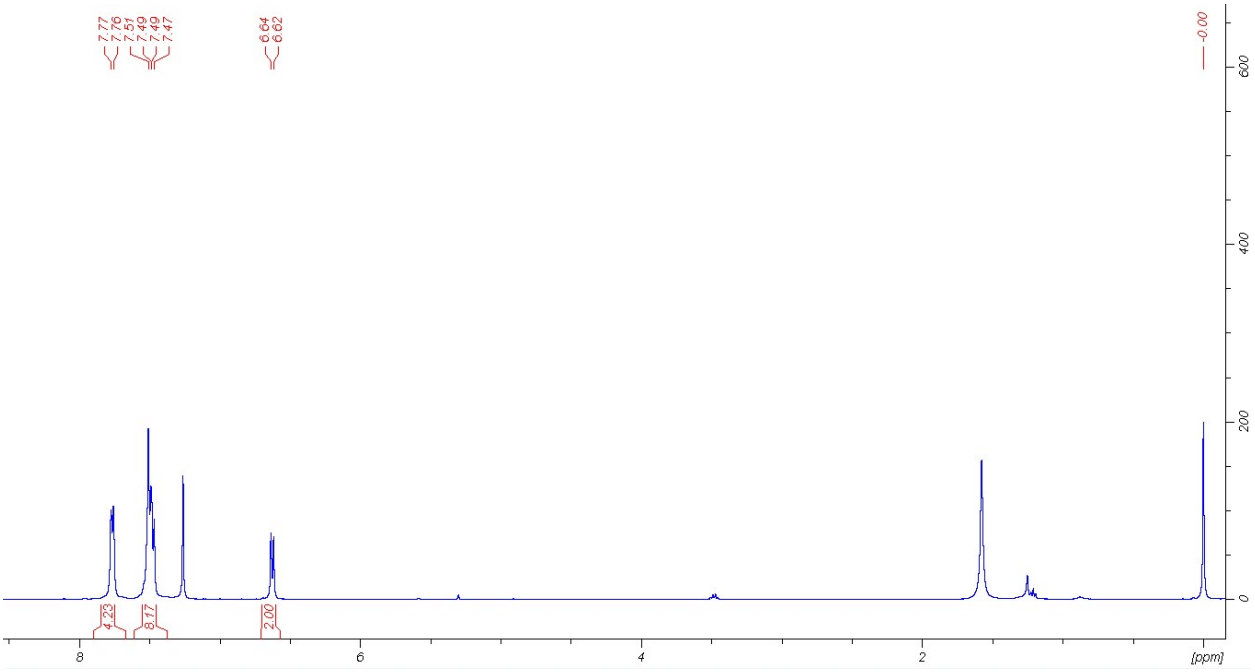
8 HRMS



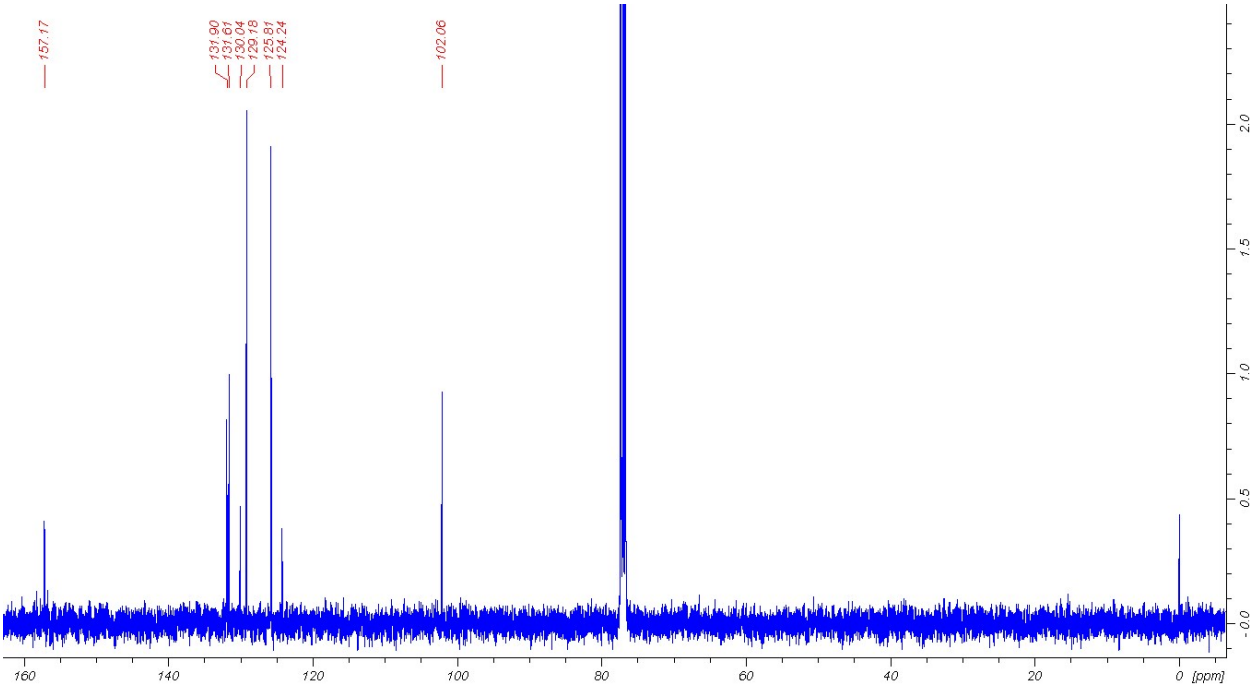


Species	Calc m/z
(M+H)+	286.9372
(M+Na)+	308.9191

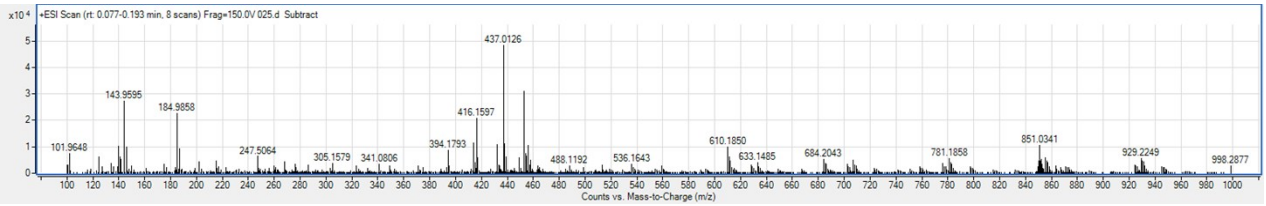
6,6'-Diphenyl-[3,3'-bi(1,2-oxathiine)] 2,2,2',2'-tetraoxide 9 ^{1}H-NMR



9 ^{13}C-NMR

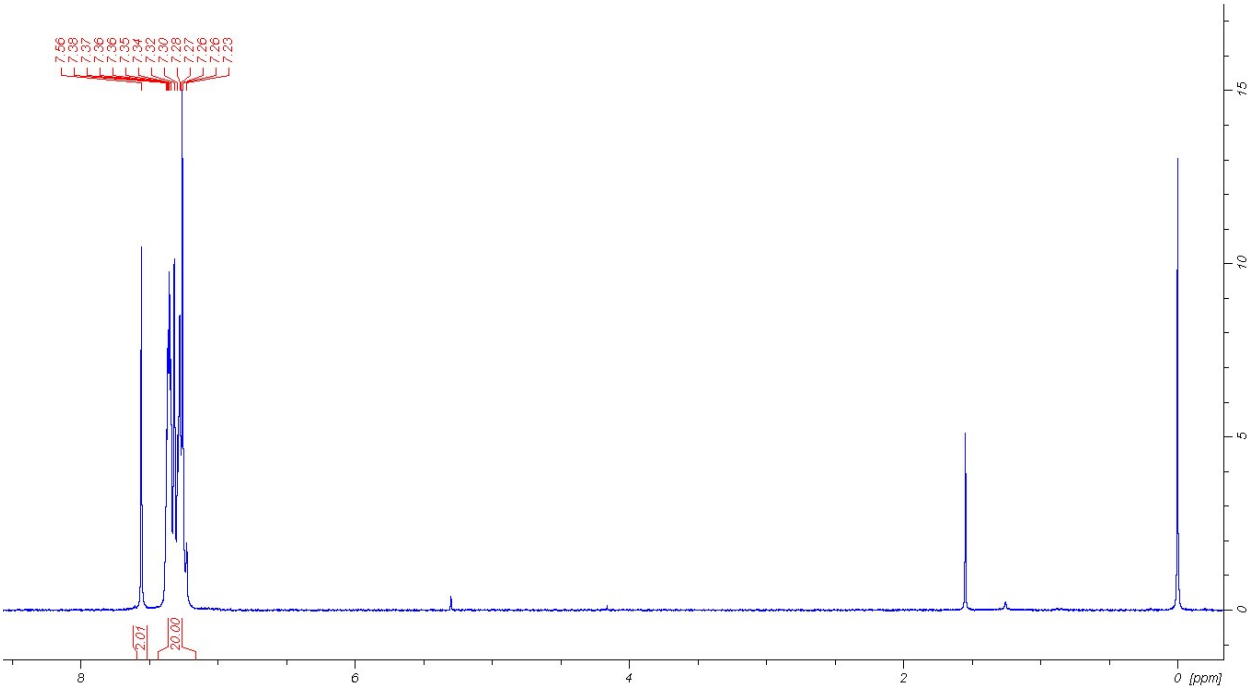


9 HRMS

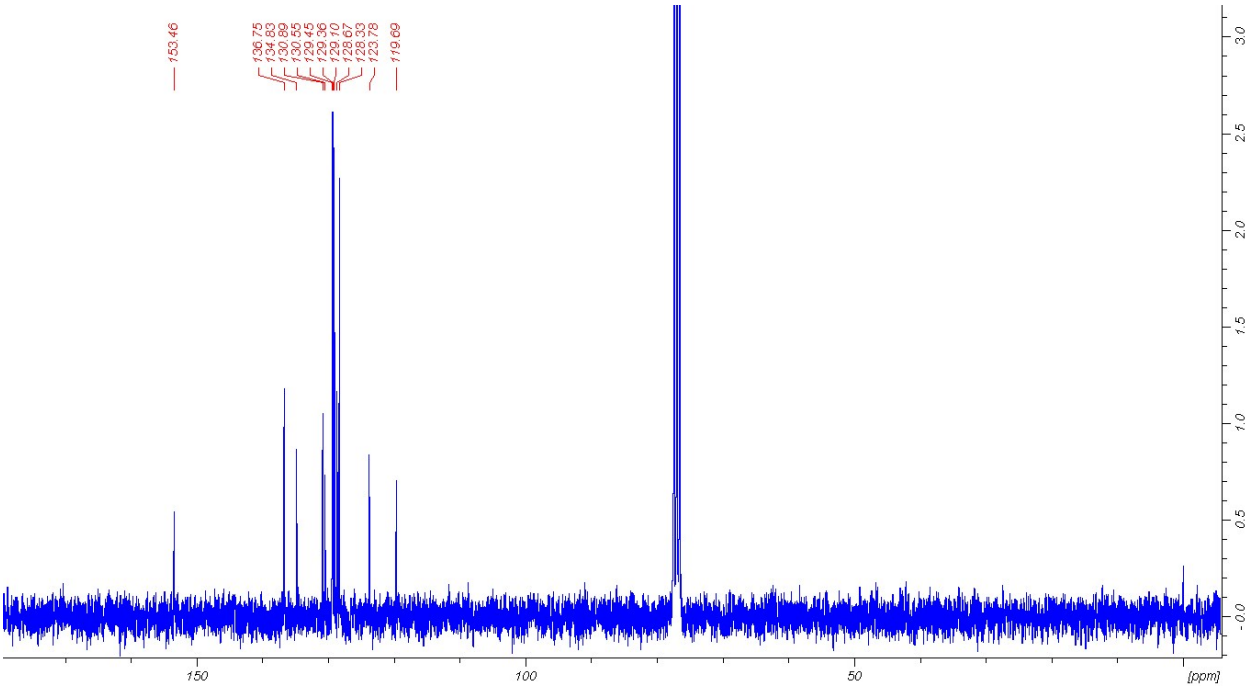


Formula	Observed m/z	Proposed adduct	Charge	Observed neutral mass	Theoretical neutral mass	Mass error (ppm)
C20H14O6S2	437.0126	**Na+**	1+	414.0231	414.0232	0.09

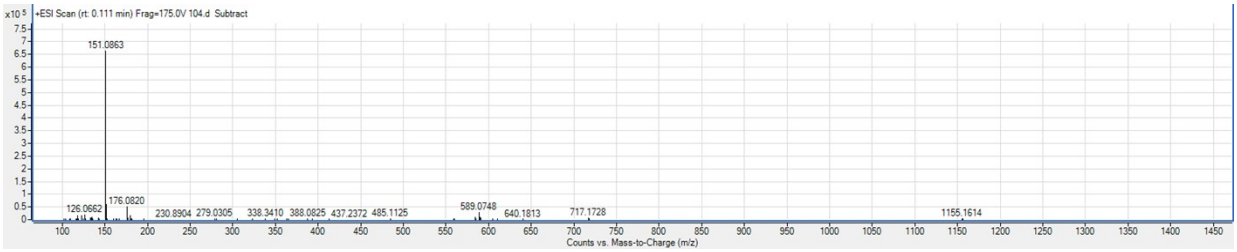
5,5',6,6'-Tetraphenyl-[3,3'-bi(1,2-oxathiine)] 2,2,2',2'-tetraoxide 10 ^{1}H-NMR

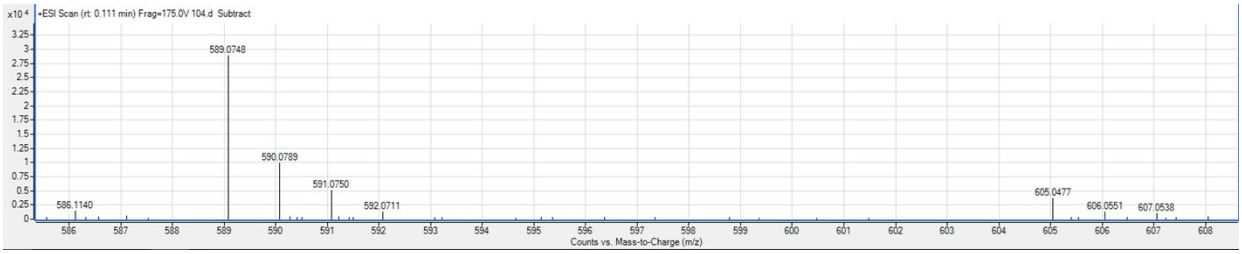


10 ^{13}C-NMR



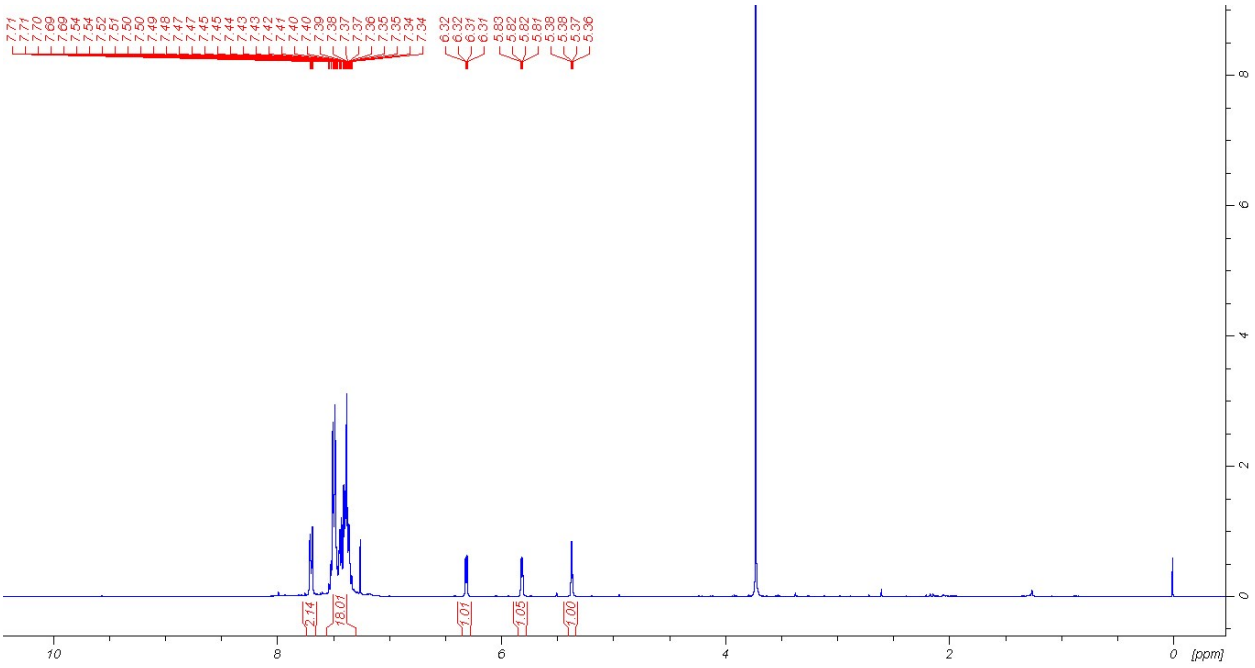
10 HRMS



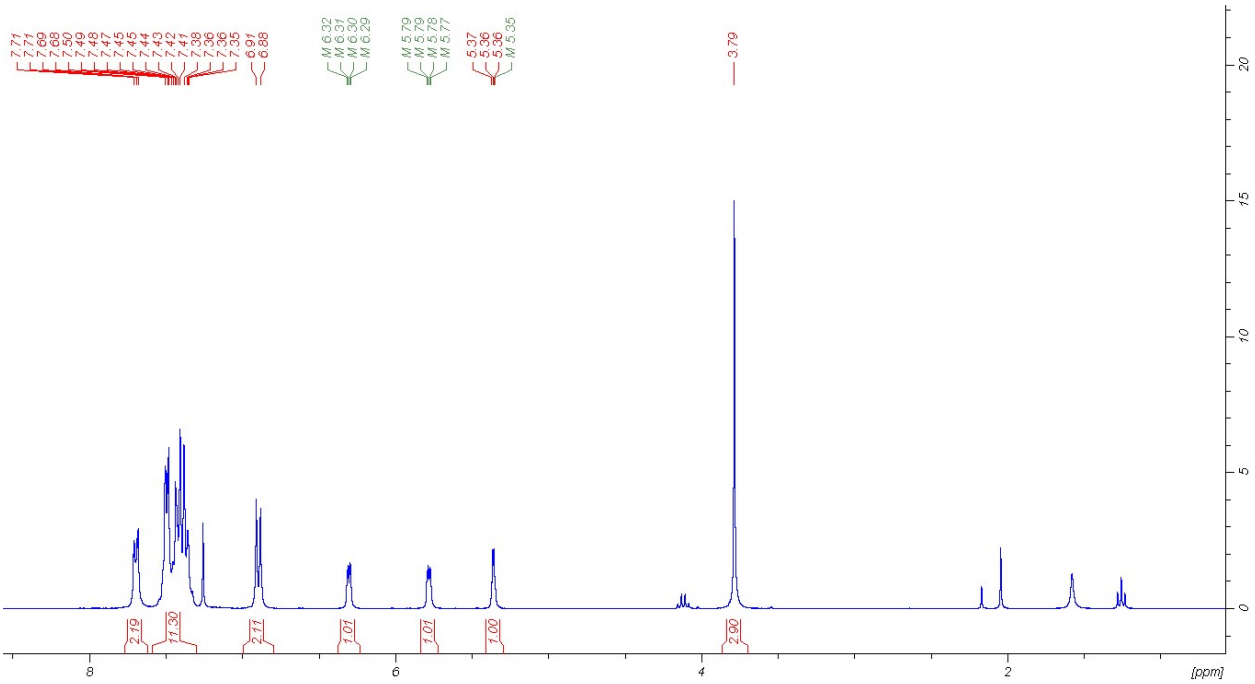


Formula	Observed m/z	Proposed adduct	Charge	Observed neutral mass	Theoretical neutral mass	Mass error (ppm)
C32H22O6S2	589.0749	**Na+**	1+	566.0856	566.0858	0.25
	605.0489	K+	1+	566.0861		0.61

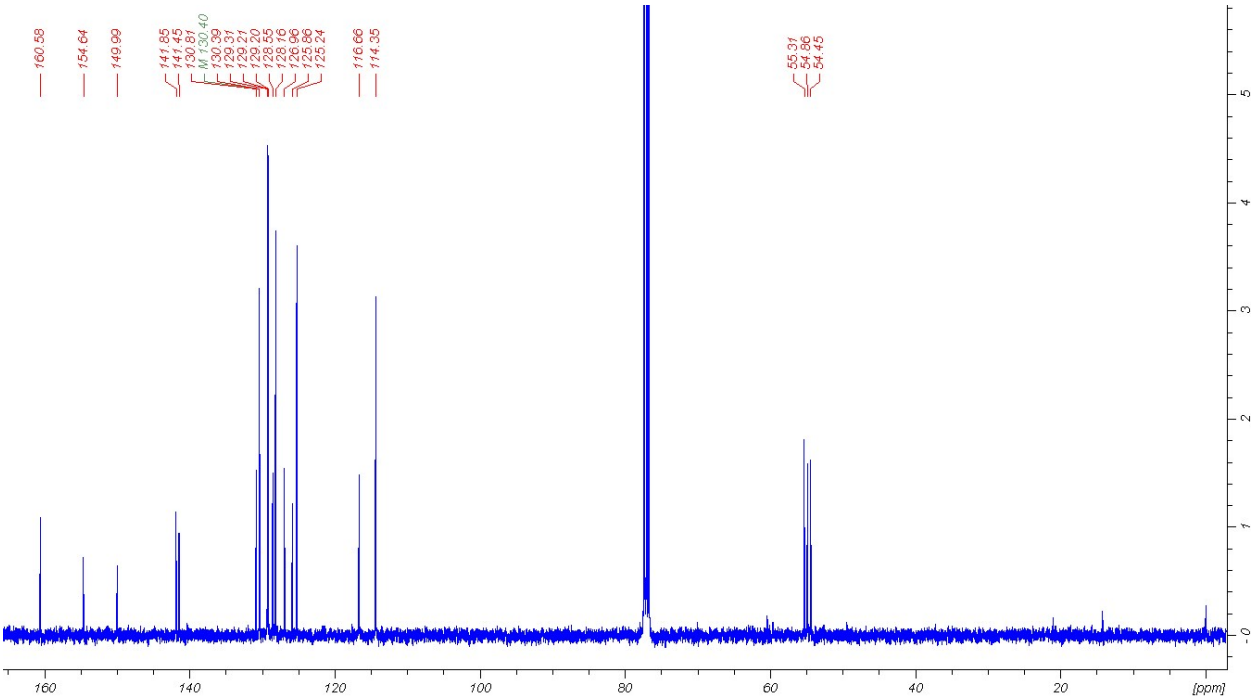
2,5,9-Triphenyl-5,10a-dihydro-1*H*-[1,2]oxathiino[5,6-*c*][1,2,4] triazolo[1,2-*a*]pyridazine-1,3(2*H*)-dione 8,8-dioxide 11a (crude intermediate) ^{1}H-NMR



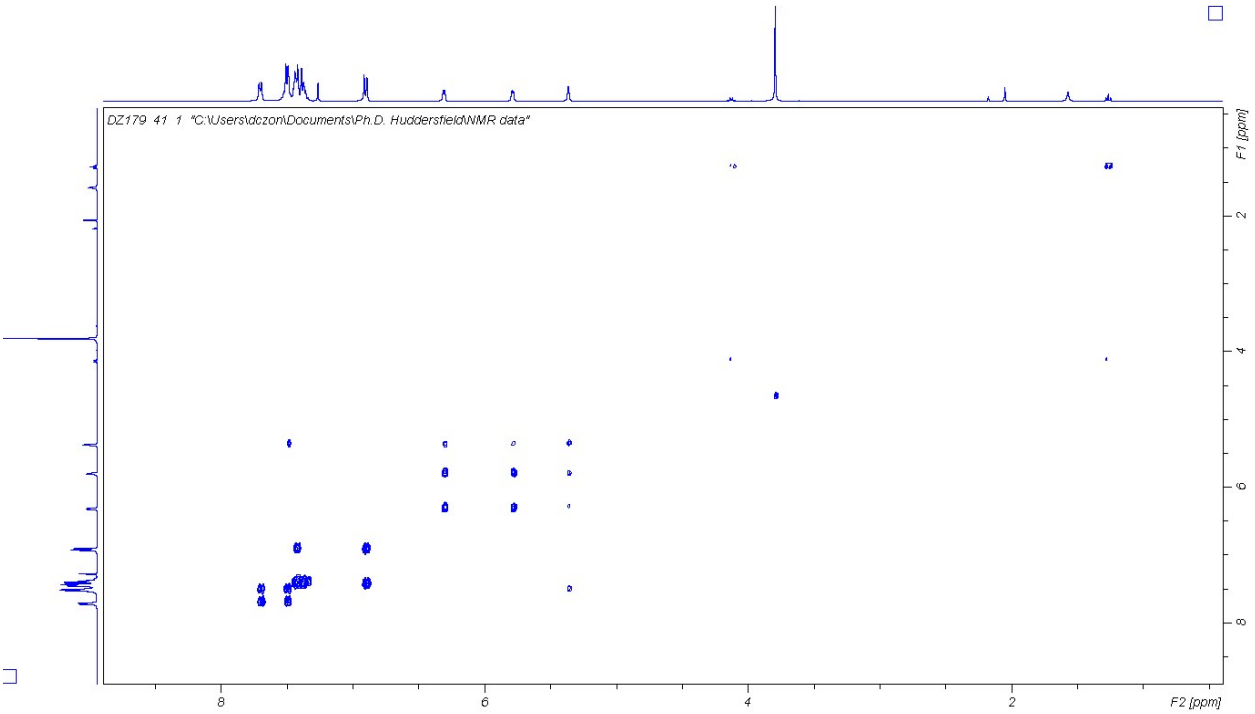
5-(4-Methoxyphenyl)-2,9-diphenyl-5,10a-dihydro-1*H*-[1,2]oxathiino[5,6-*c*][1,2,4] triazolo[1,2-*a*]pyridazine-1,3(2*H*)-dione 8,8-dioxide 11b (crude intermediate) ^{1}H-NMR



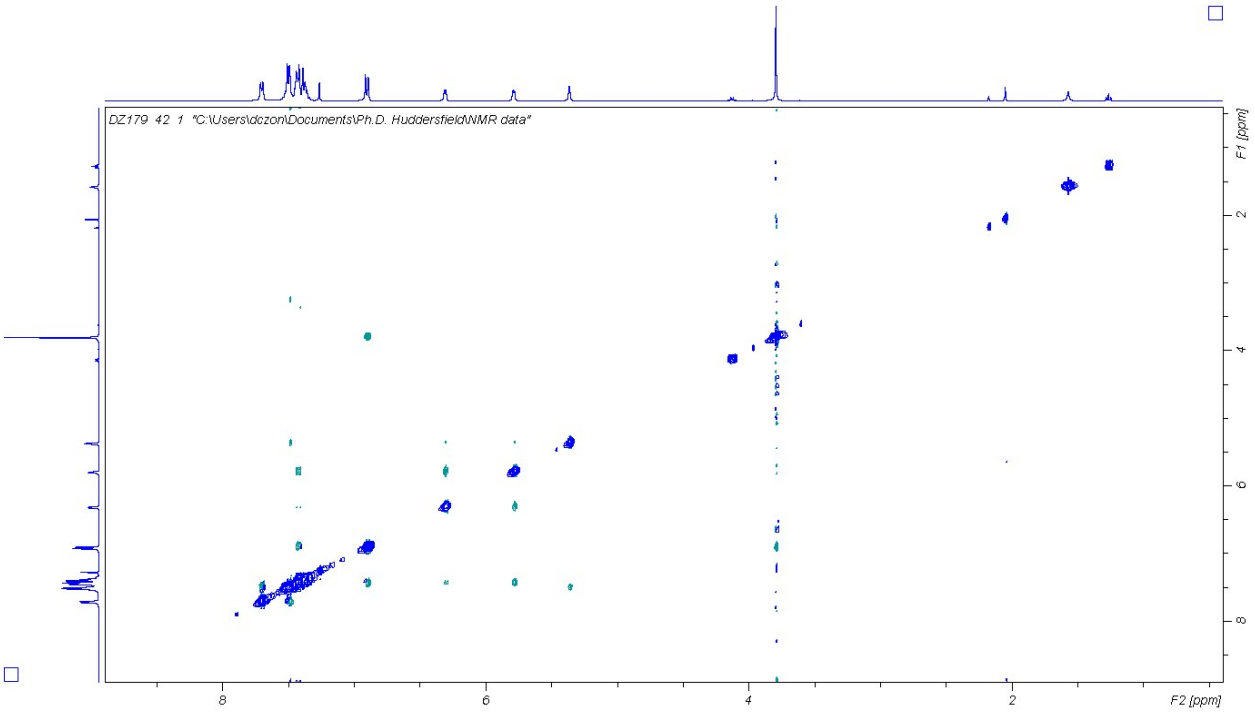
11b (intermediate) ^{13}C-NMR



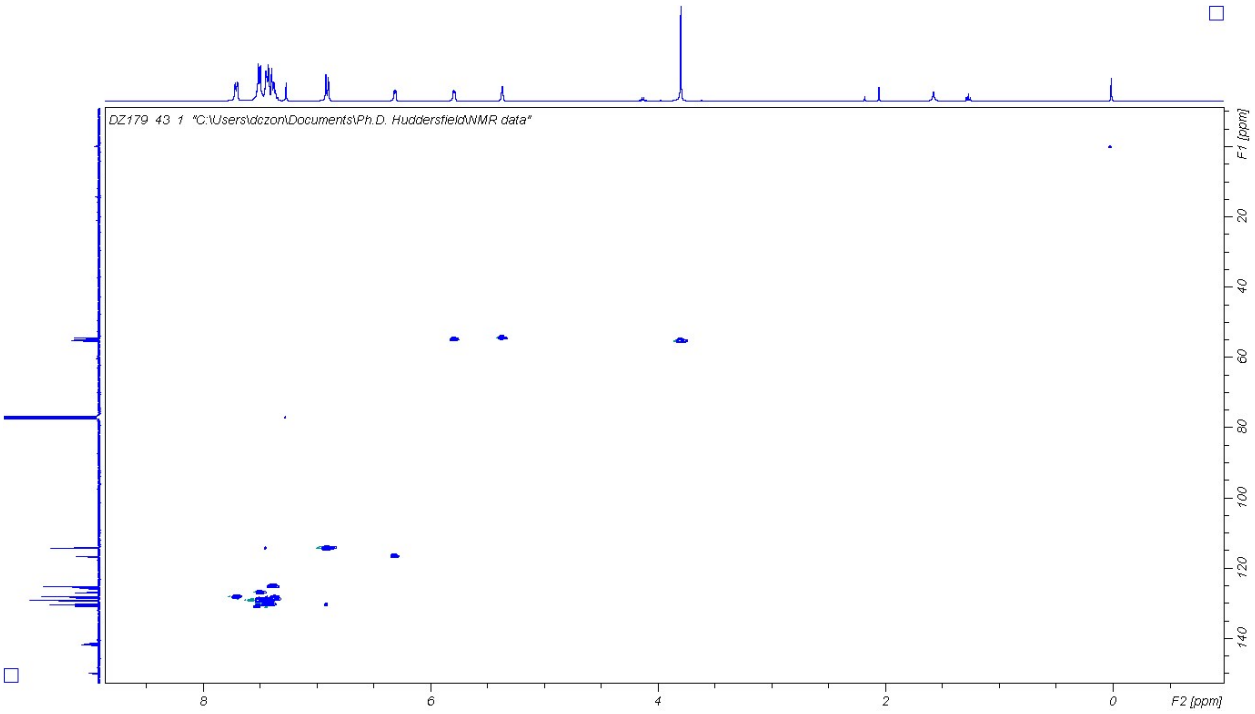
11b COSY-NMR



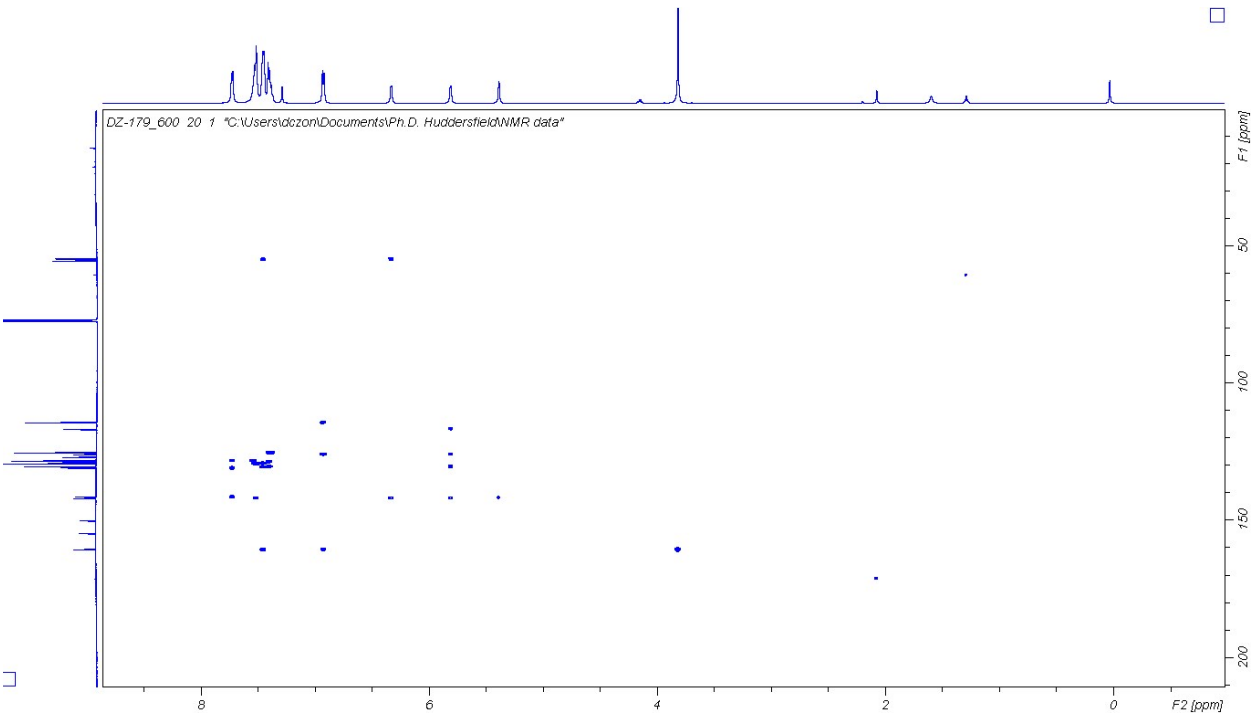
11b NOESY-NMR



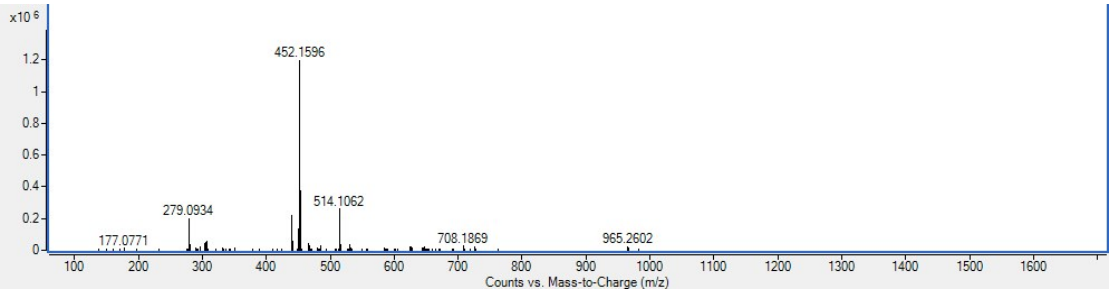
11b HSQC-NMR

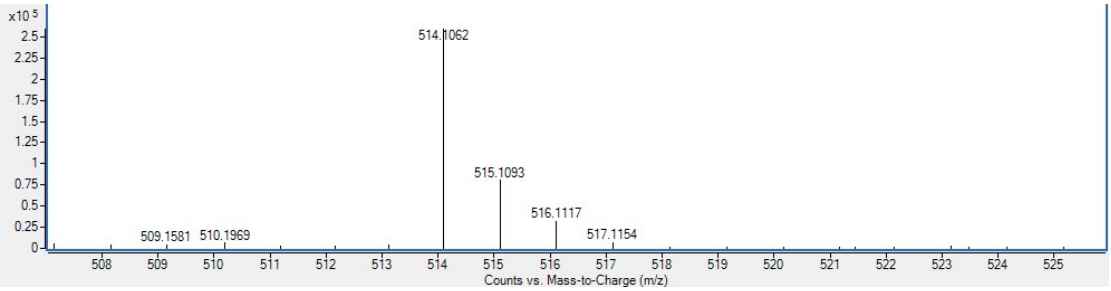


11b HMBC-NMR



11b HRMS





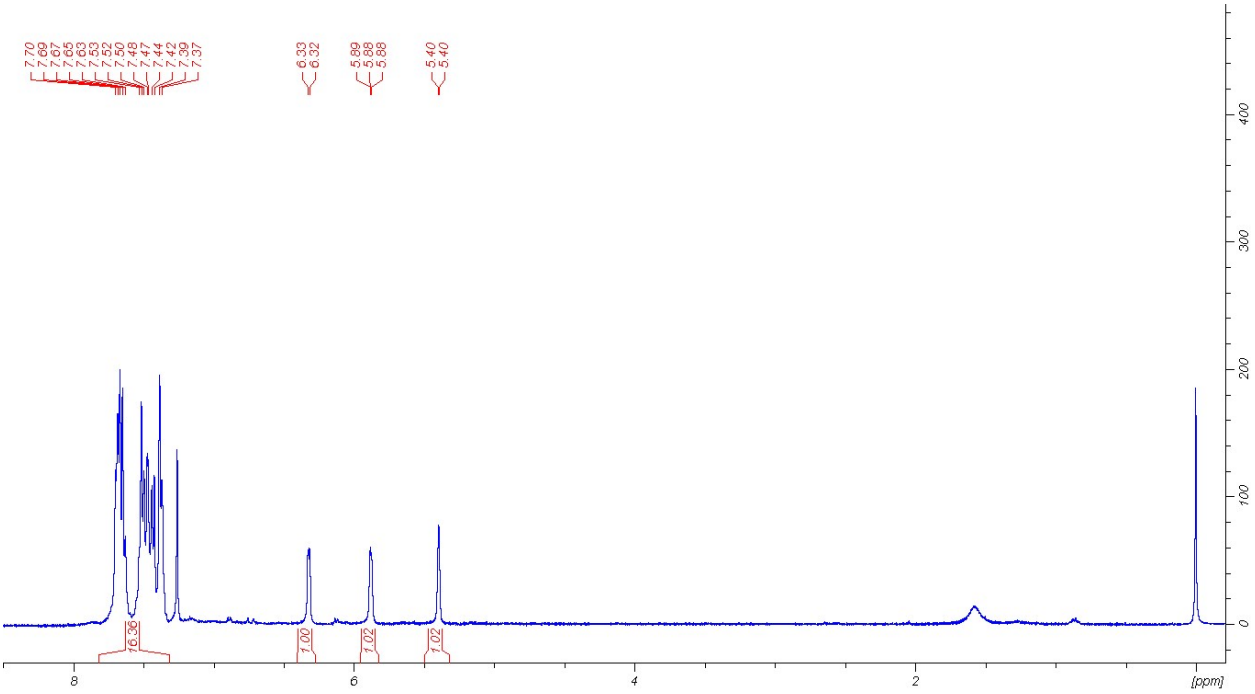
Base formula (M)

C27 H19 N3 O6 S

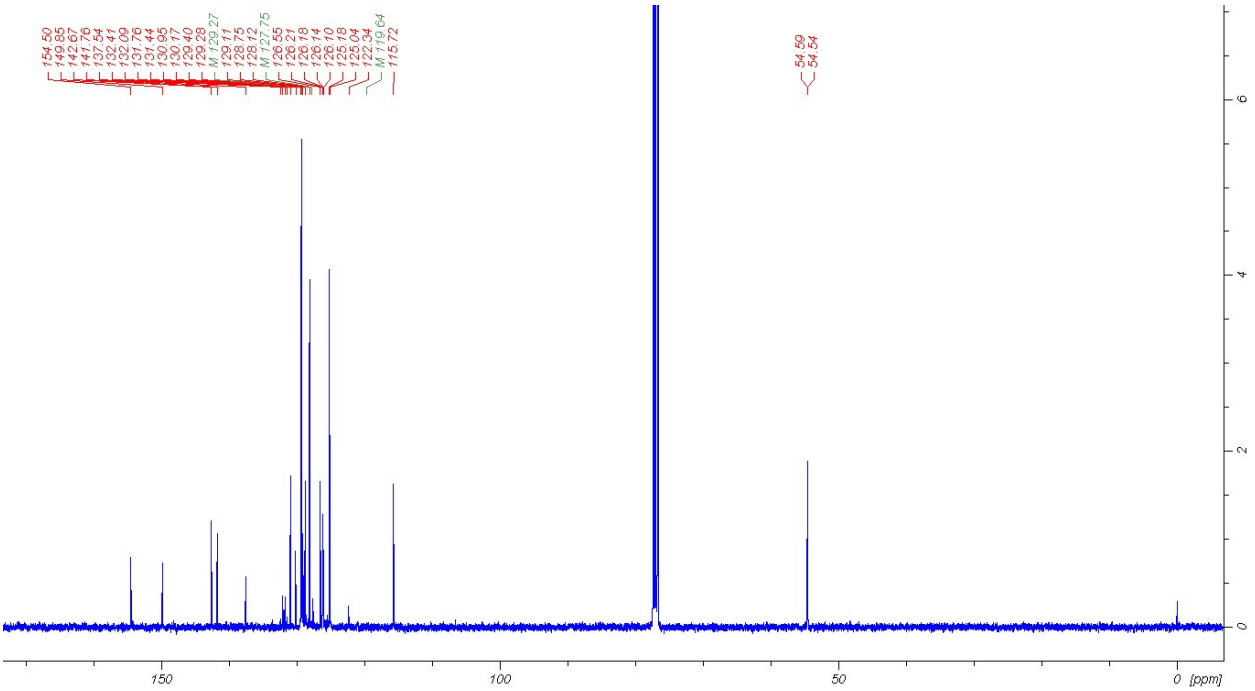
Species to calculate

Species	Calc m/z	Mono m/z
M+	513.0989	513.0989
M	513.0995	513.0995
(M+H)+	514.1067	514.1067

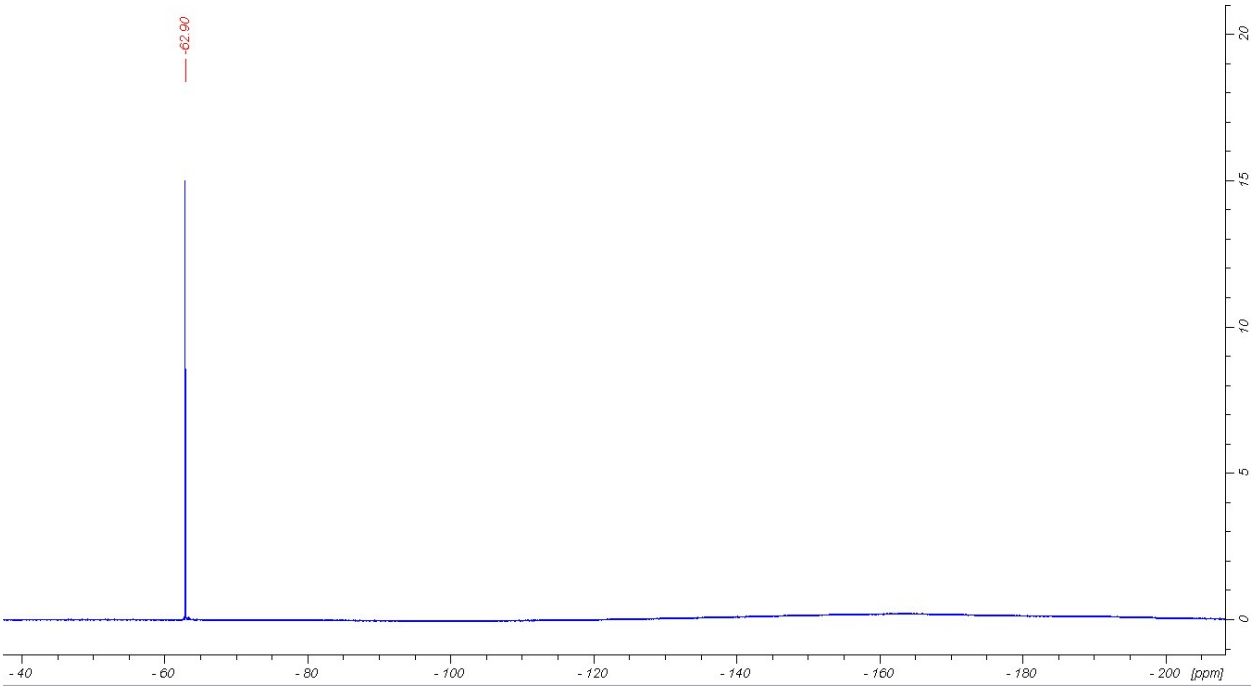
2,9-Diphenyl-5-(4-(trifluoromethyl)phenyl)-5,10a-dihydro-1*H*-[1,2]oxathiino [5,6-*c*][1,2,4]triazolo [1,2-*a*]pyridazine-1,3(2*H*)-dione 8,8-dioxide 11c (crude intermediate) ^{1}H-NMR



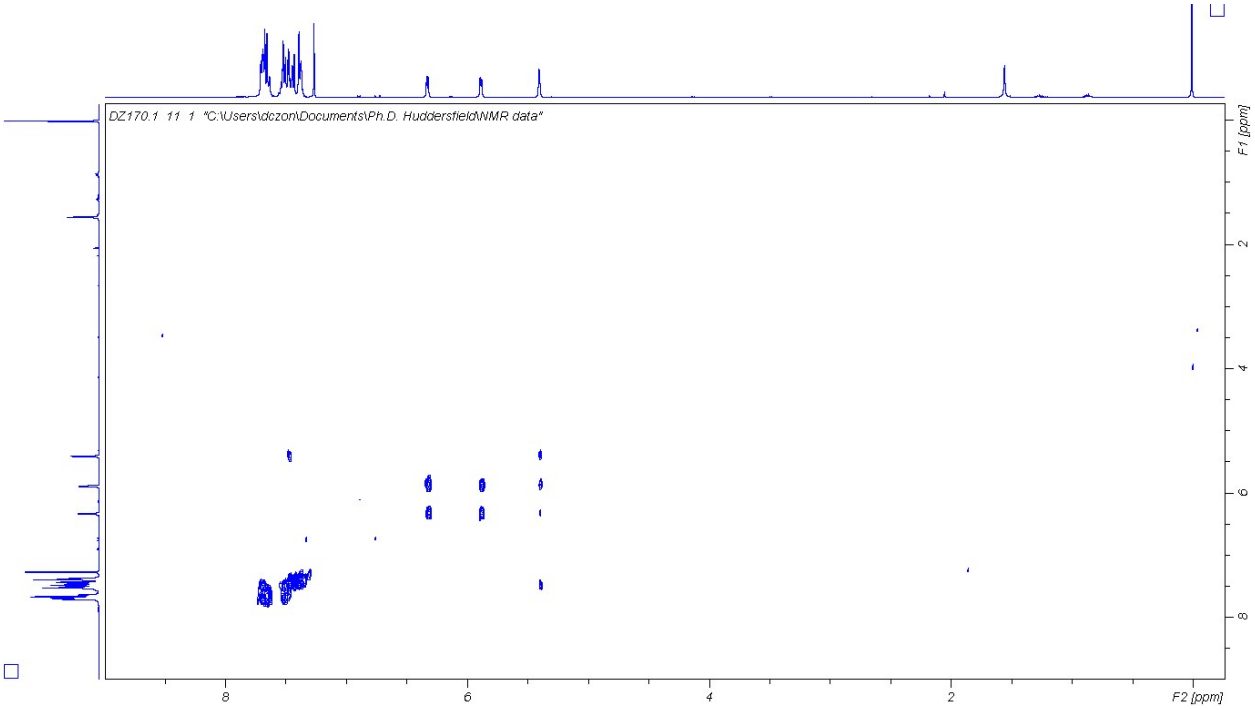
11c ^{13}C-NMR (intermediate)



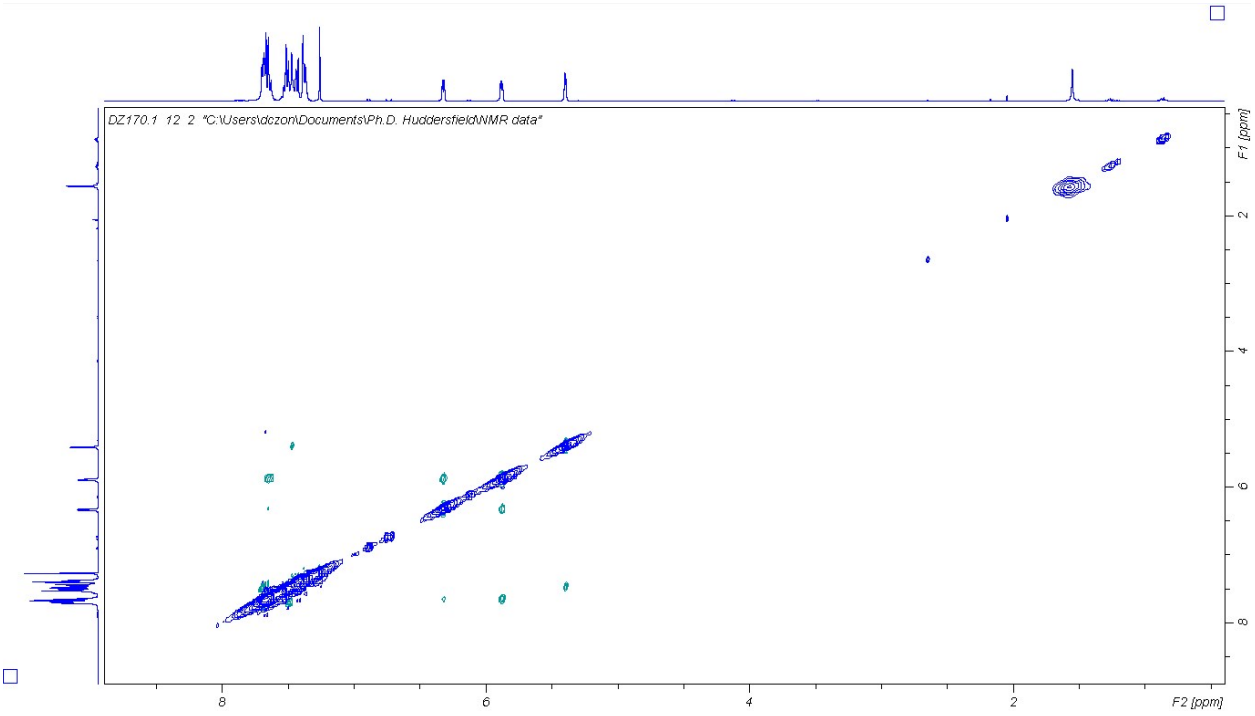
11c ^{19}F-NMR



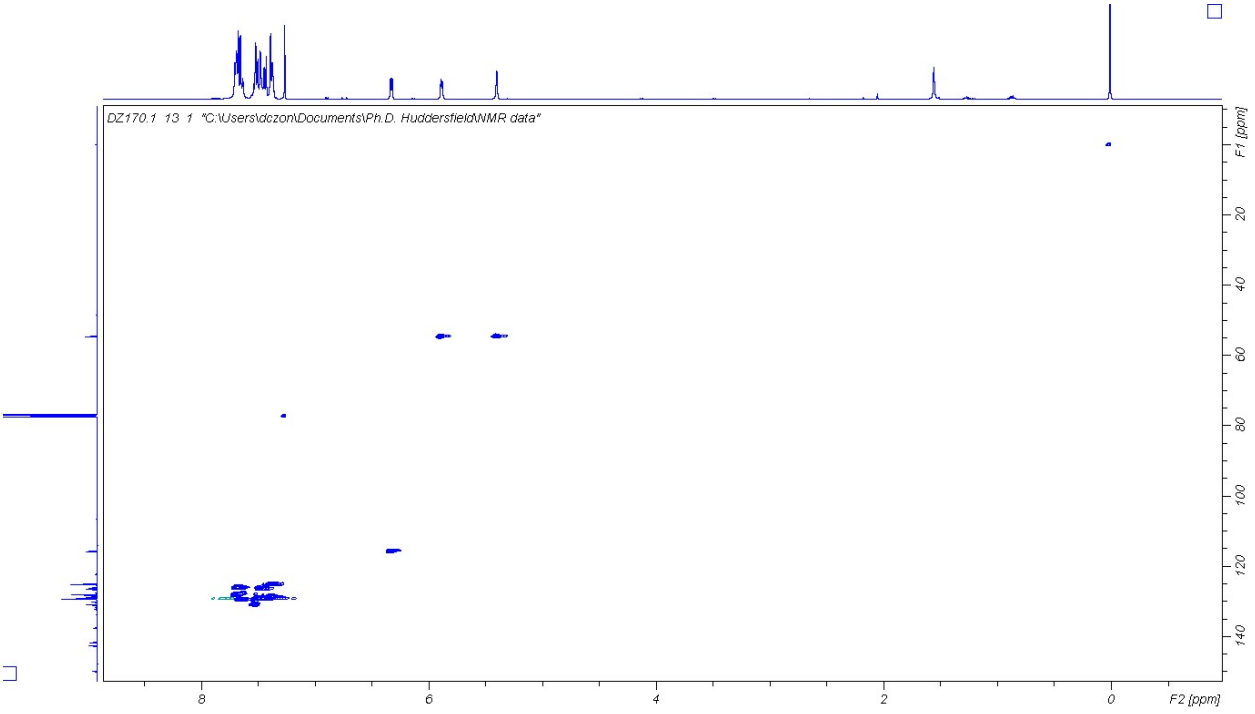
11c COSY-NMR



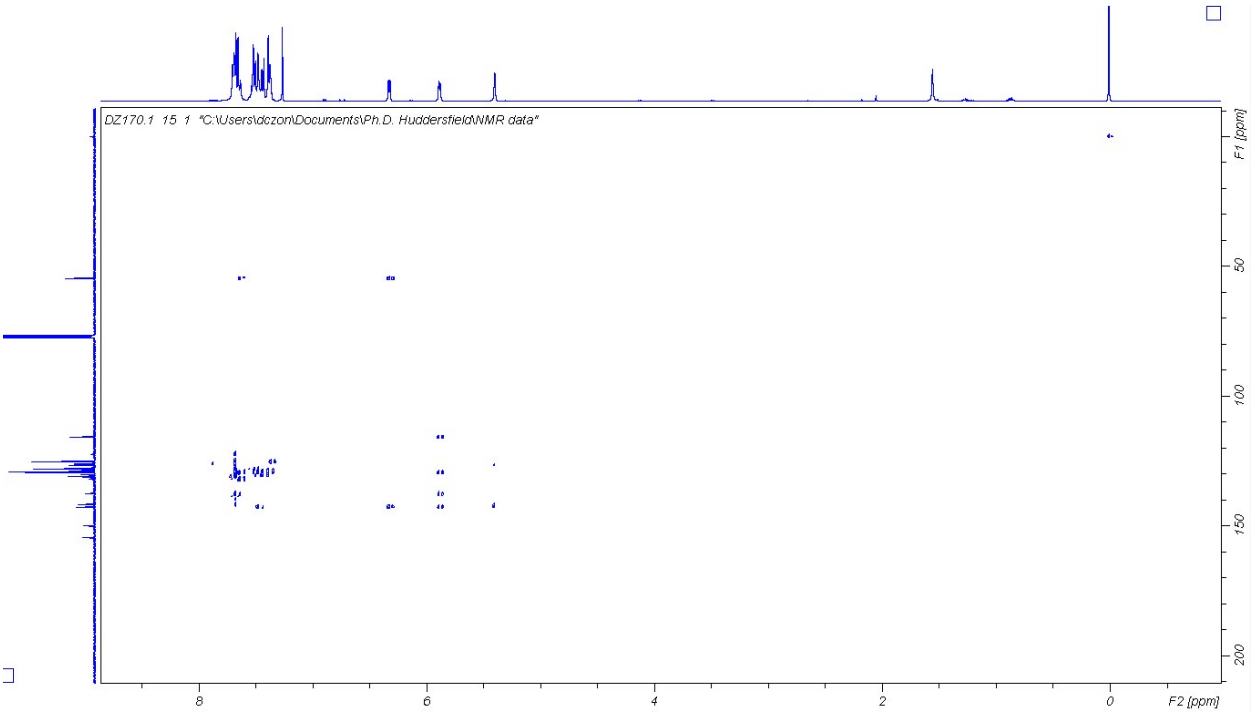
11c NOESY-NMR



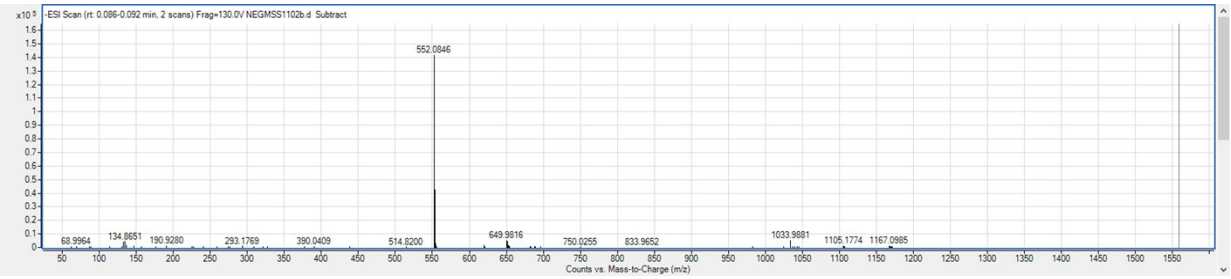
11c HSQC-NMR



11c HMBC-NMR

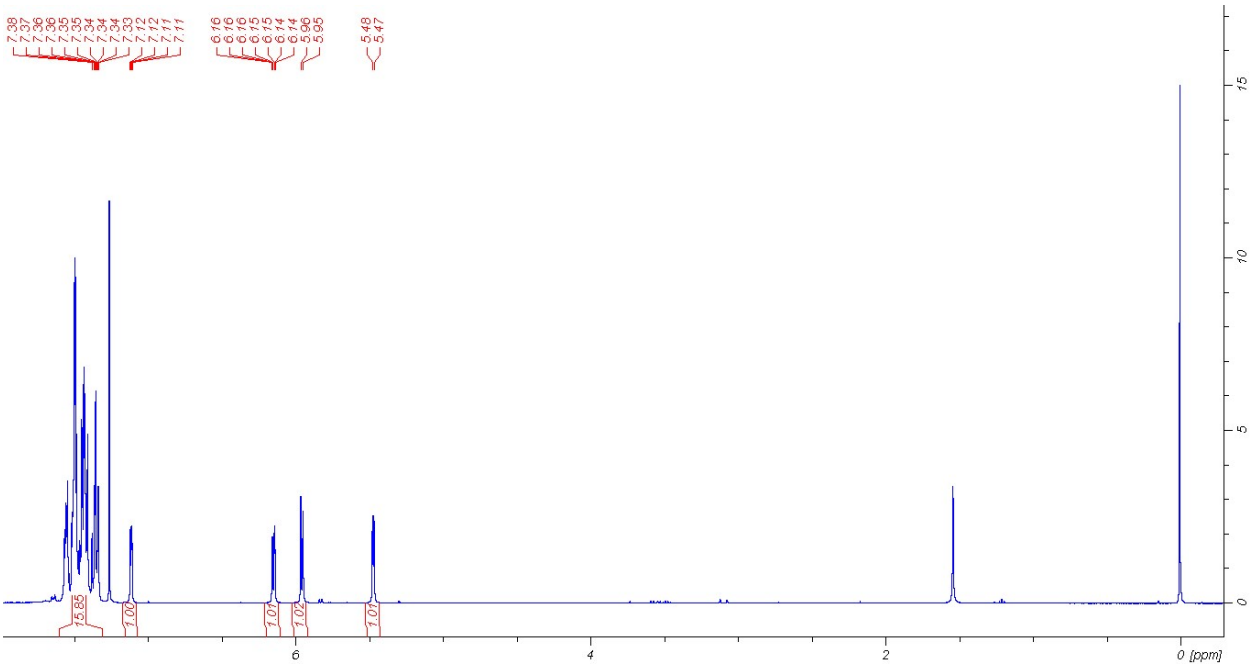


11c HRMS

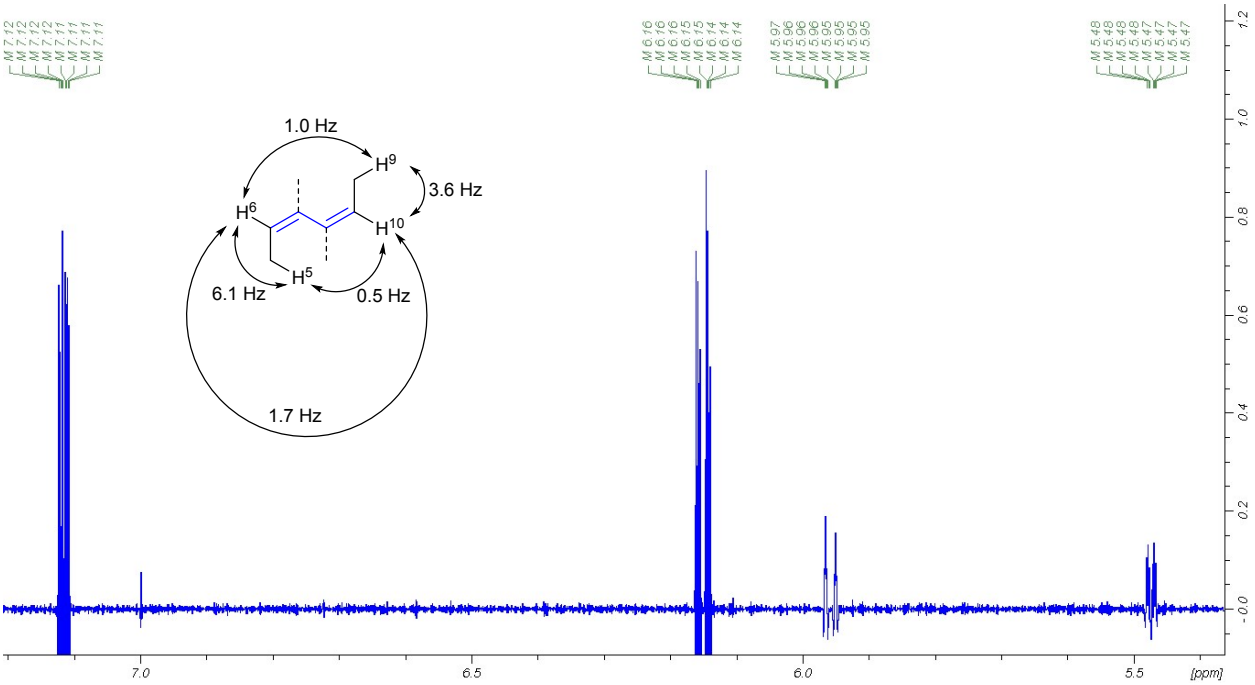


Formula	Observed m/z	Proposed adduct	Charge	Observed neutral mass	Theoretical neutral mass	Mass error (ppm)
$C_{27}H_{18}F_3N_3O_5S$	552.0846	(M-H)-	1	553.0918.1394	553.0919	0.48

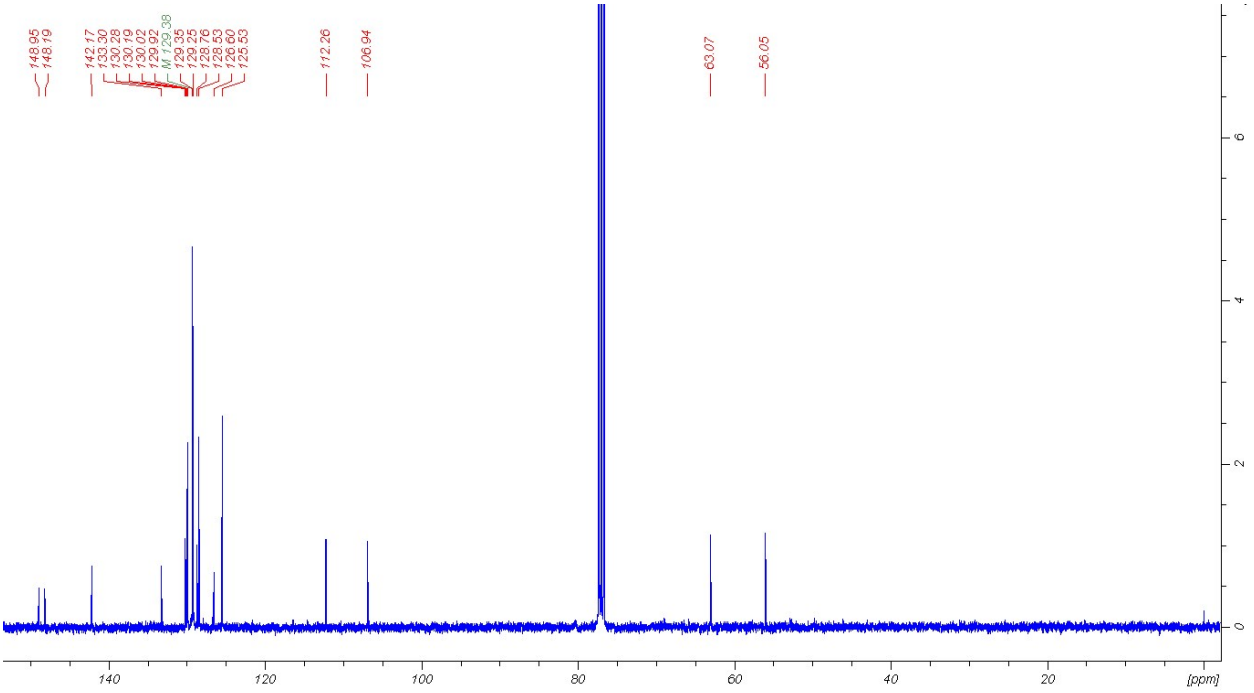
2,5,9-Triphenyl-5,9-dihydro-1*H*-[1,2]oxathiino[5,6-*c*][1,2,4]triazolo[1,2-*a*]pyridazine-1,3(2*H*)-dione 8,8-dioxide 12a ^{1}H-NMR



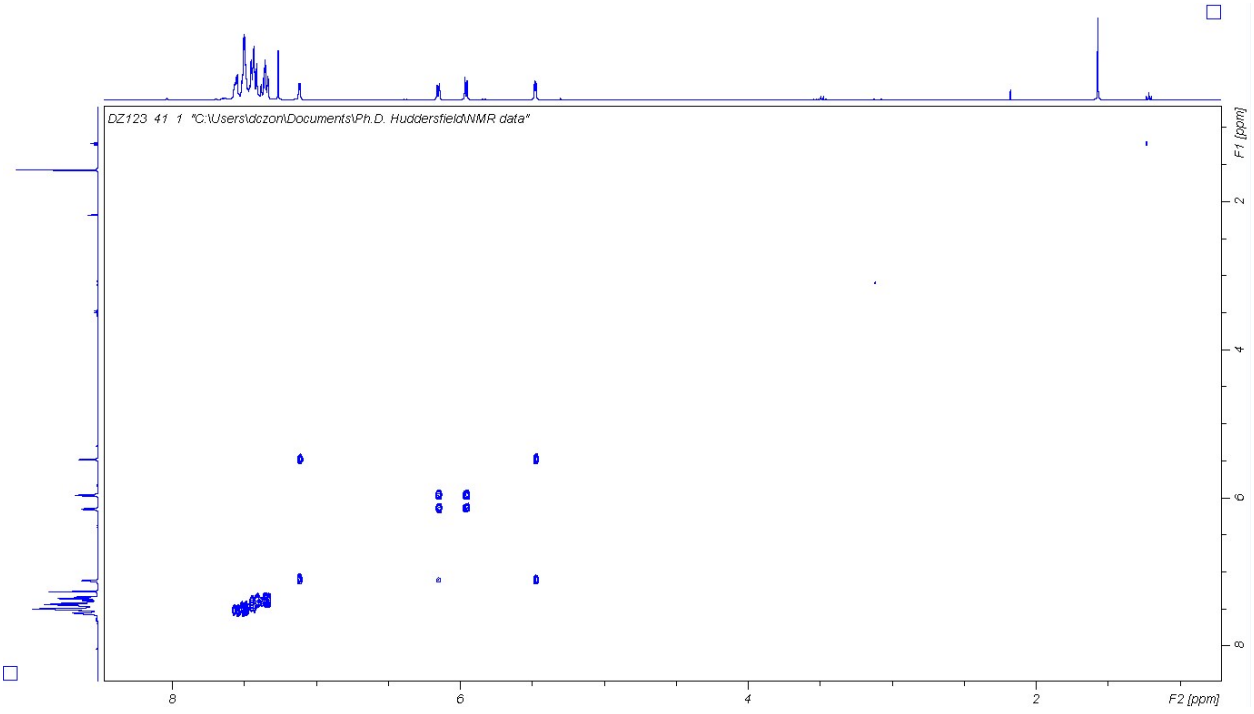
12a ^{1}H-NMR expansion (inset showing coupling constants for protons appended to butadiene unit)



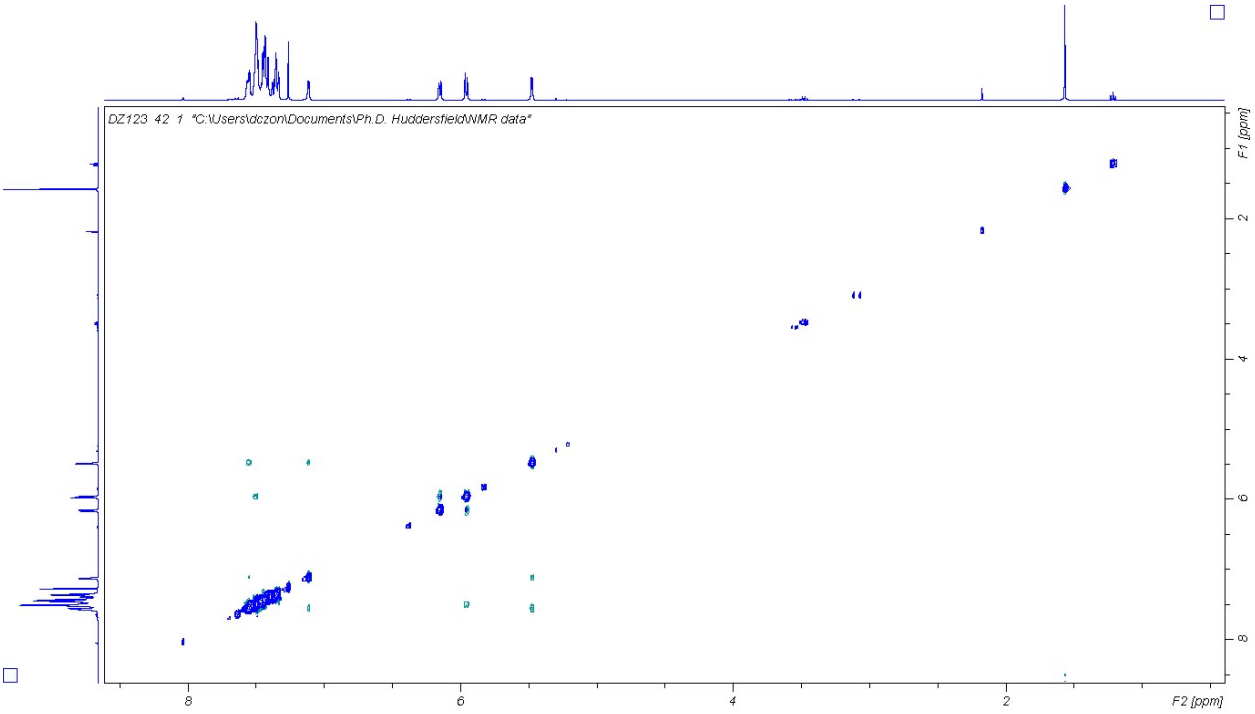
12a ^{13}C-NMR



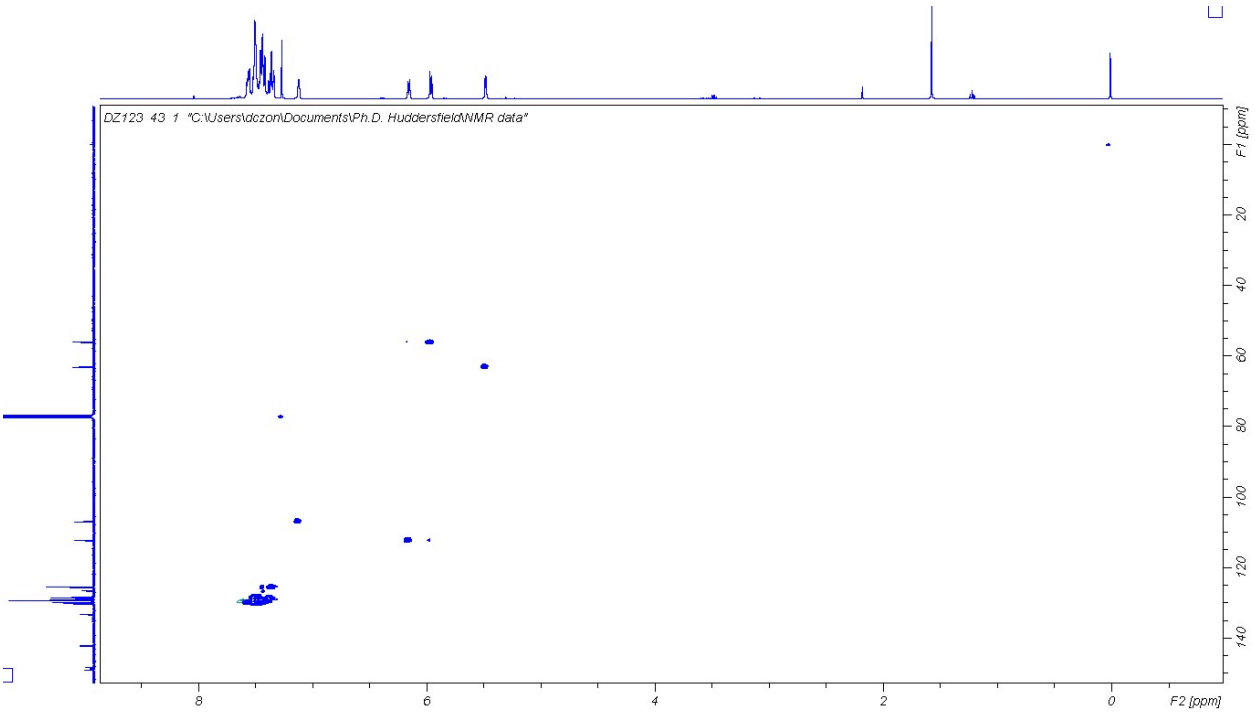
12a COSY-NMR



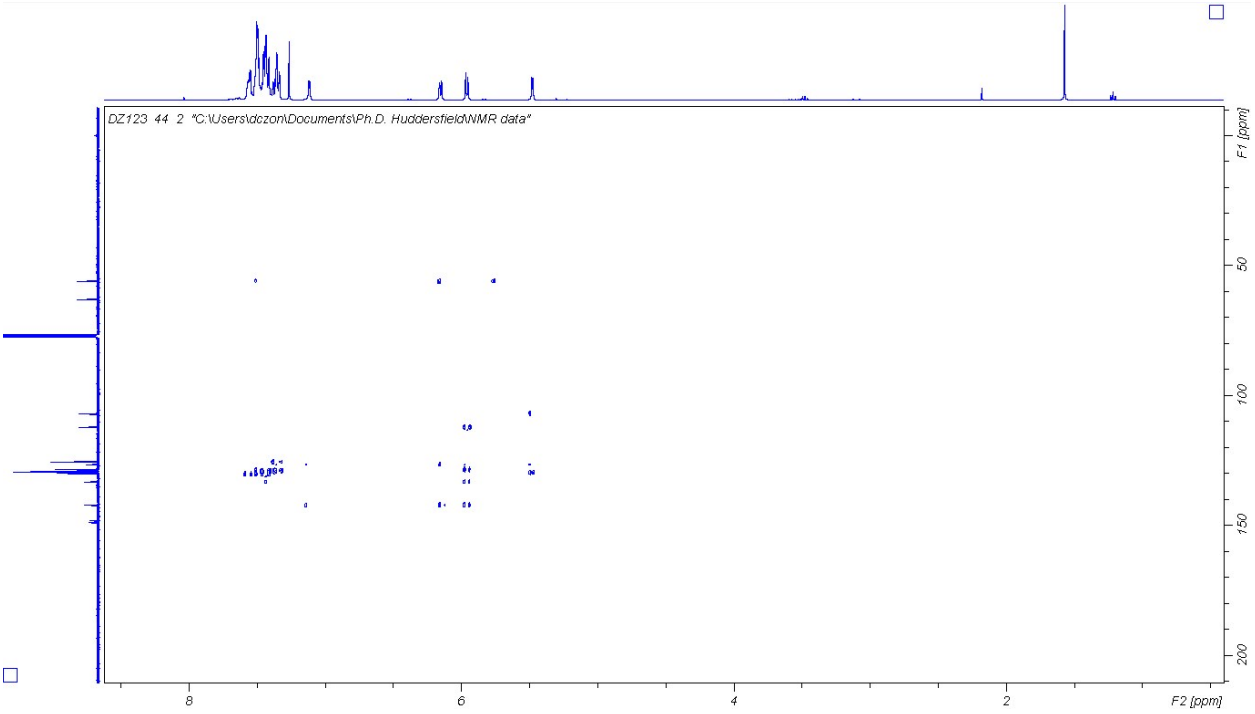
12a NOESY-NMR



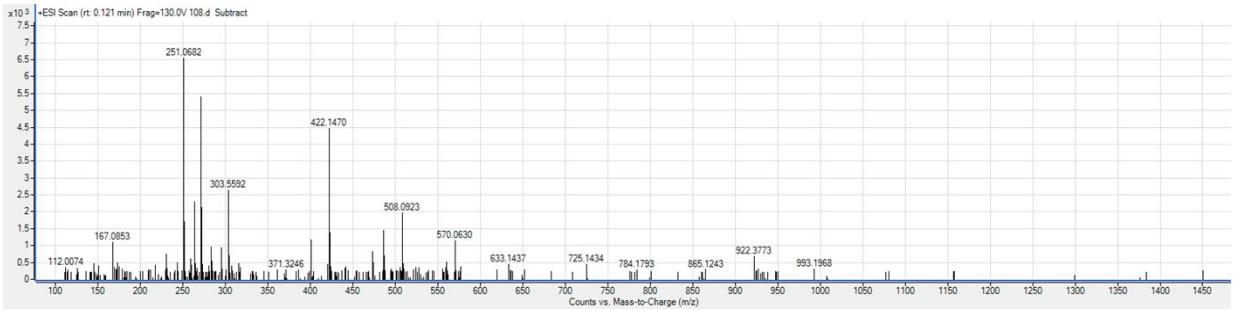
12a HSQC-NMR

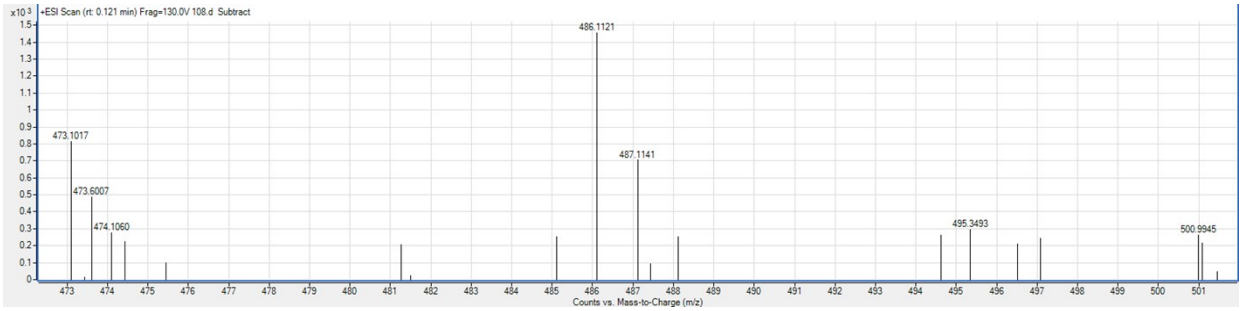


12a HMBC-NMR



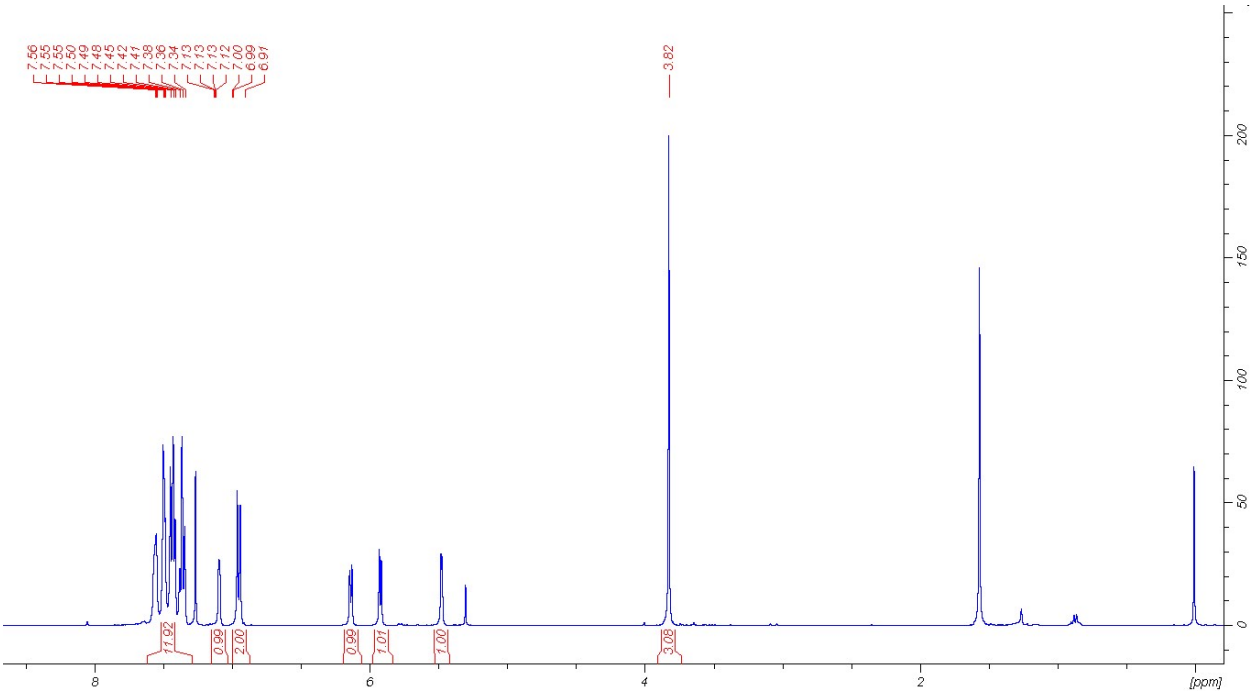
12a HRMS



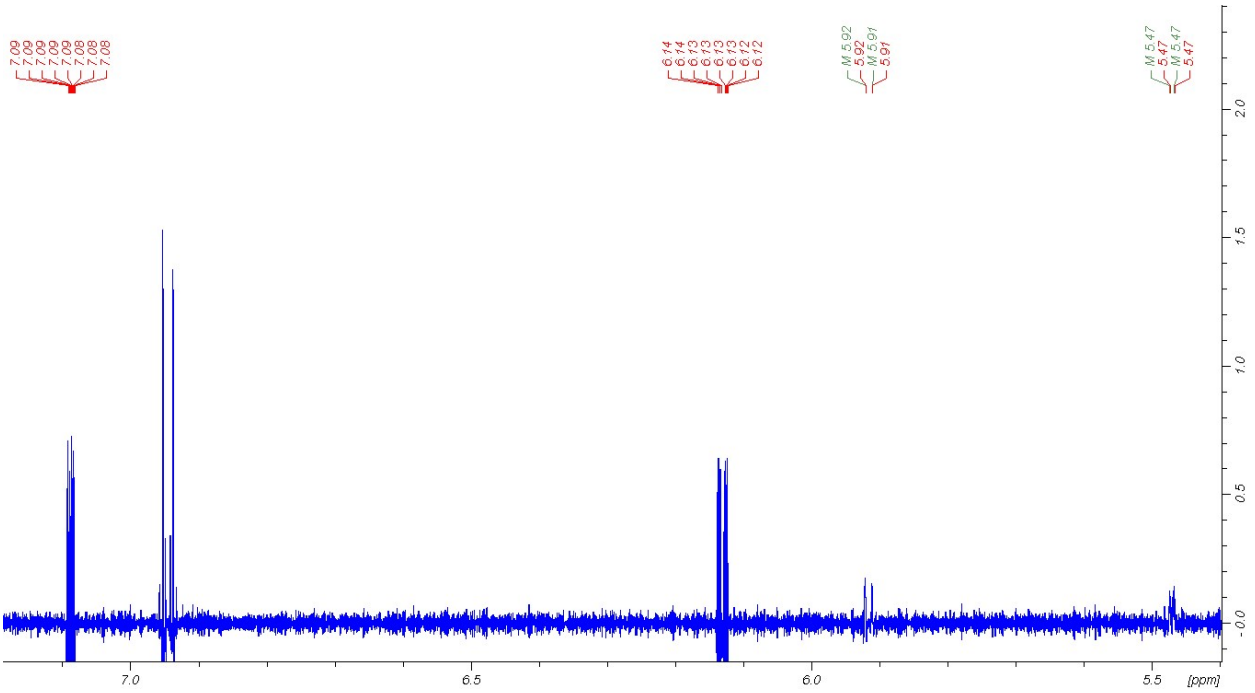


Formula	Observed m/z	Proposed adduct	Charge	Observed neutral mass	Theoretical neutral mass	Mass error (ppm)
C26H19N3O5S	486.1121	H+	1+	485.1048	485.1045	0.62

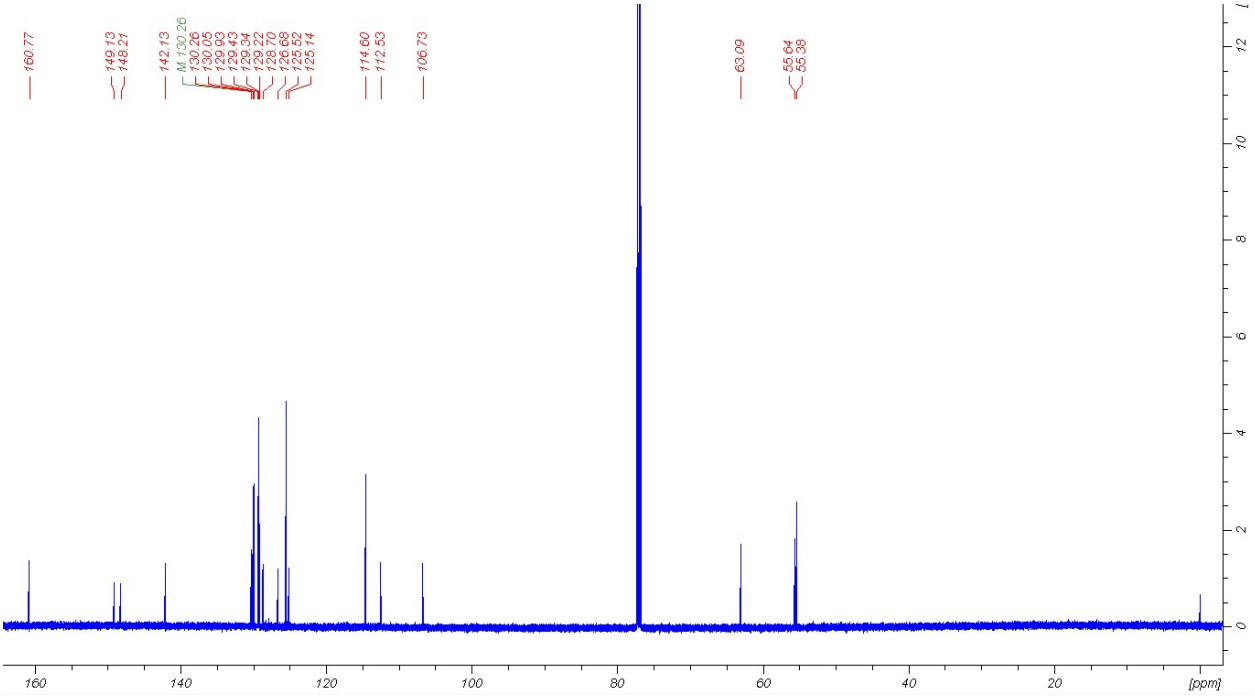
5-(4-Methoxyphenyl)-2,9-diphenyl-5,9-dihydro-1*H*-[1,2]oxathiino[5,6-*c*][1,2,4]triazolo[1,2-*a*] pyridazine-1,3(2*H*)-dione 8,8-dioxide 12b ^{1}H-NMR



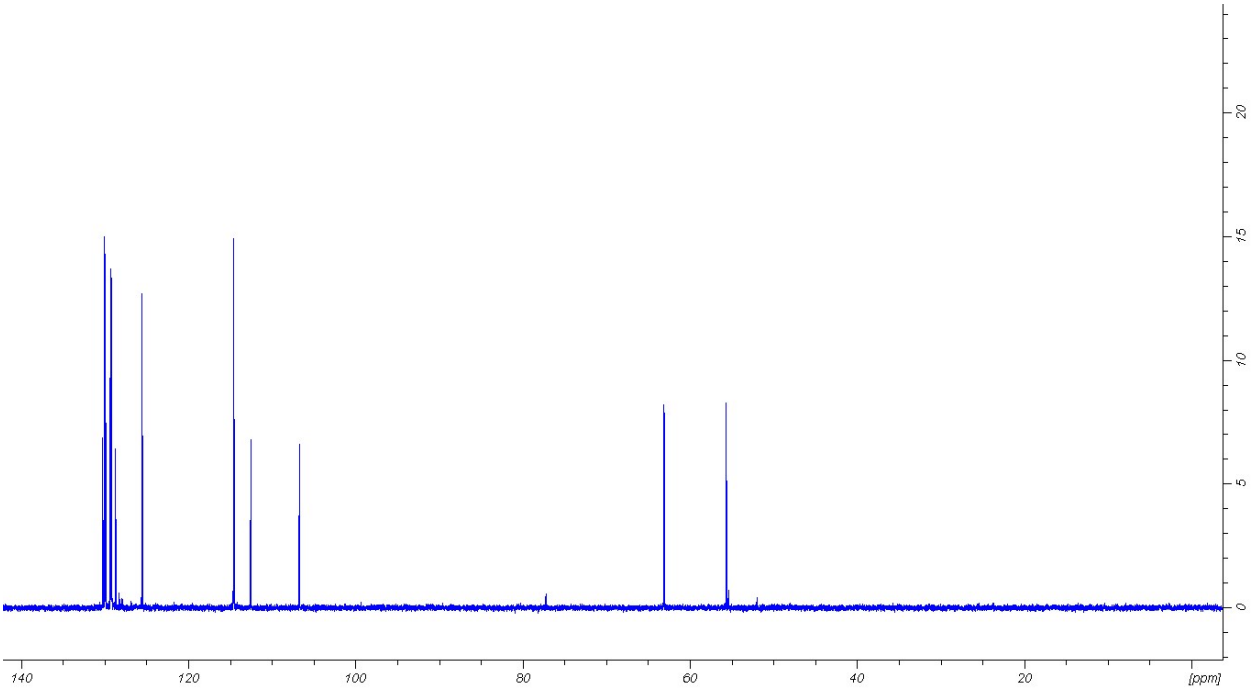
12b ^{1}H-NMR expansion



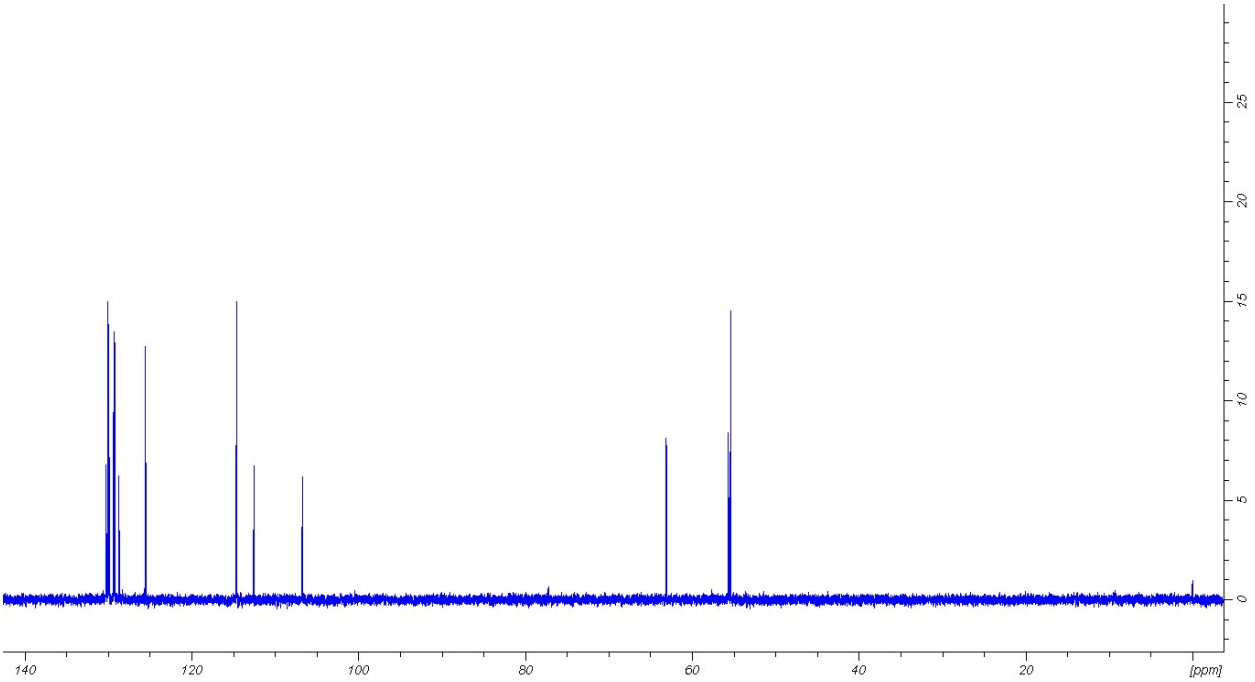
12b ^{13}C-NMR



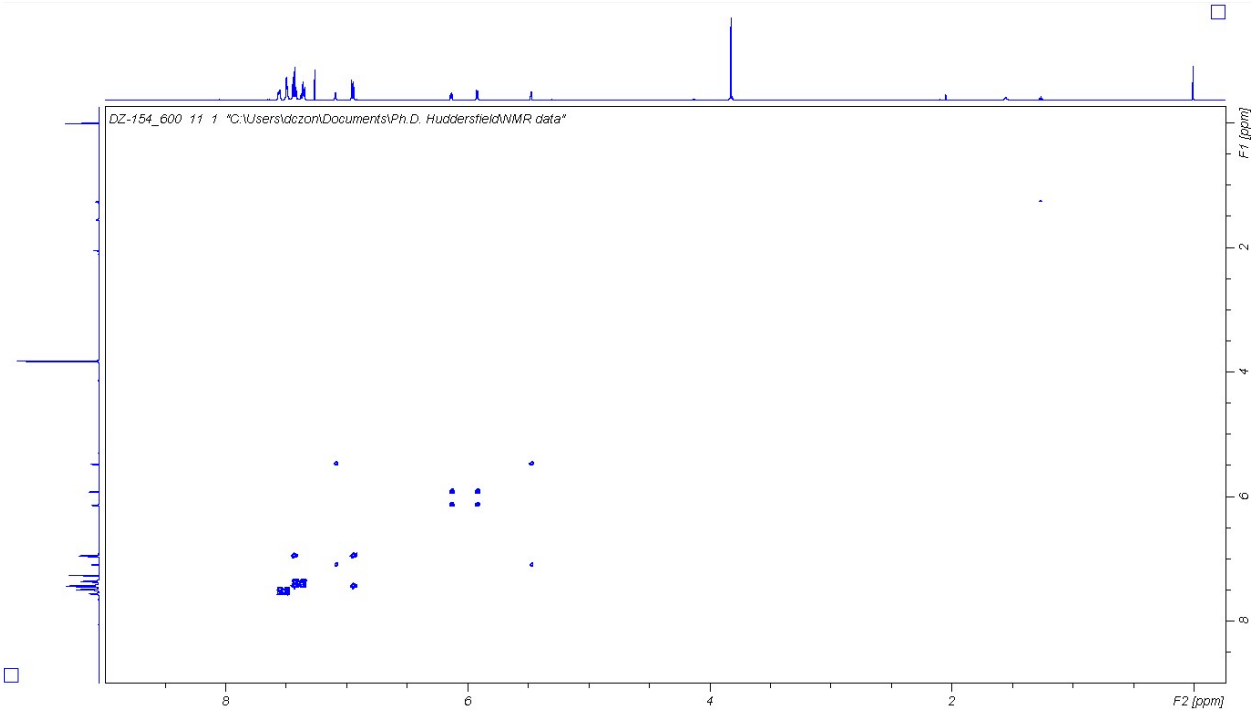
12b DEPT90 ^{13}C-NMR



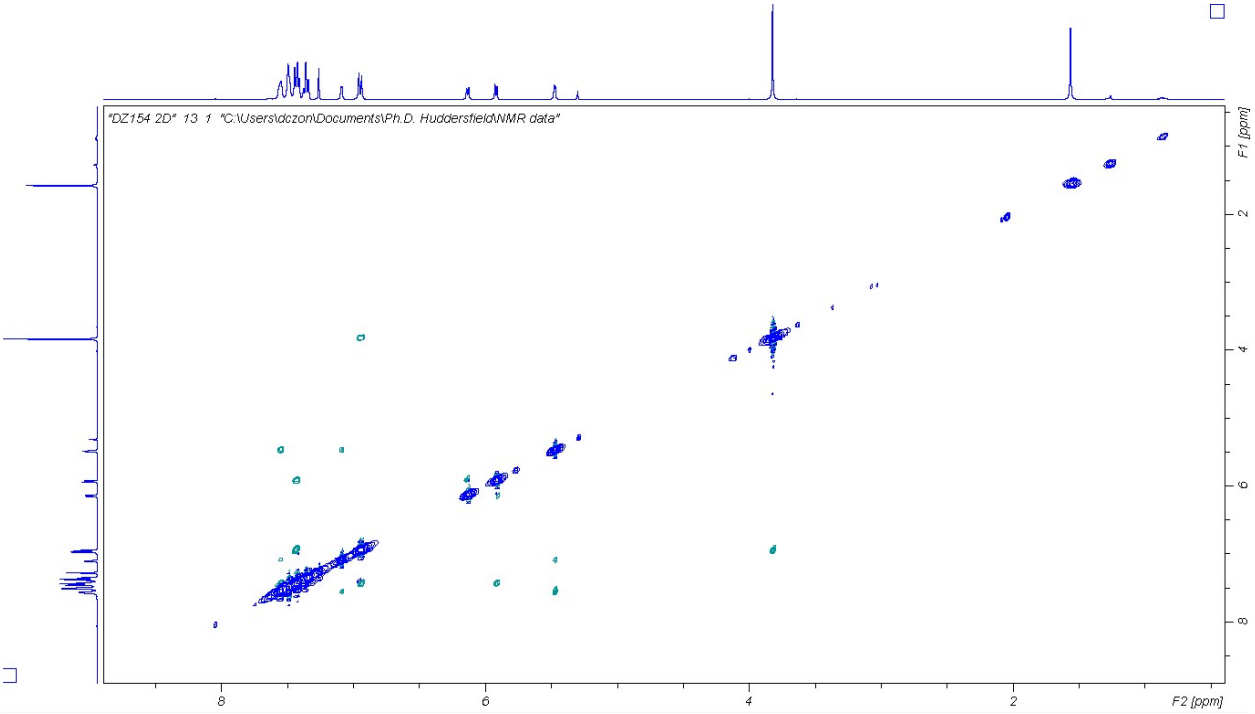
12b DEPT135 ^{13}C-NMR



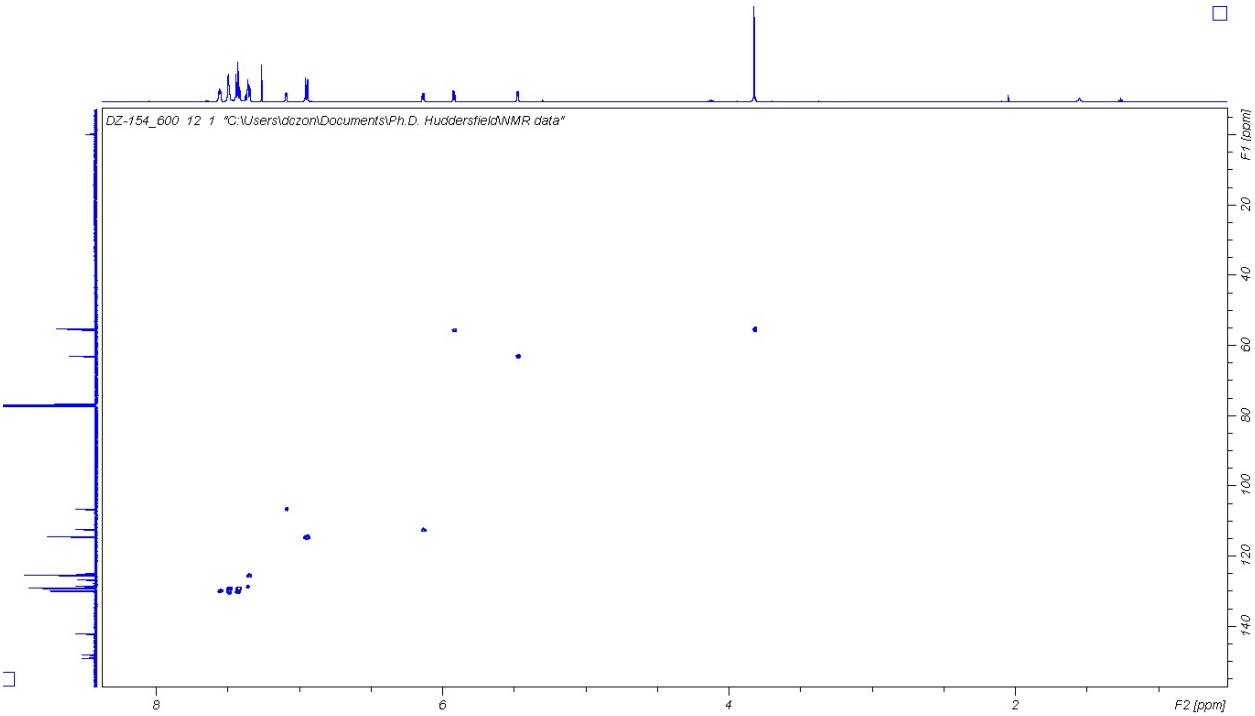
12b COSY-NMR



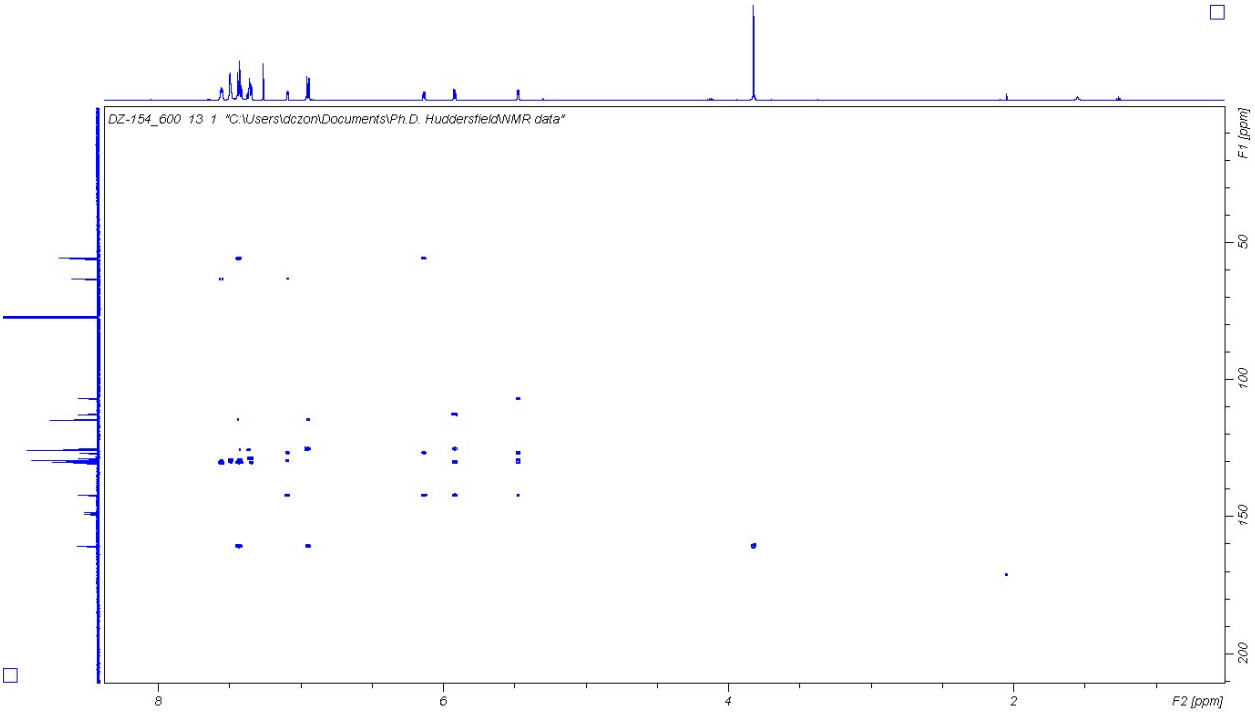
12b NOESY-NMR



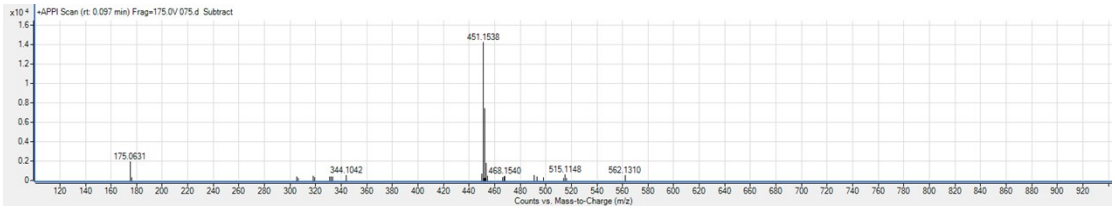
12b HSQC-NMR

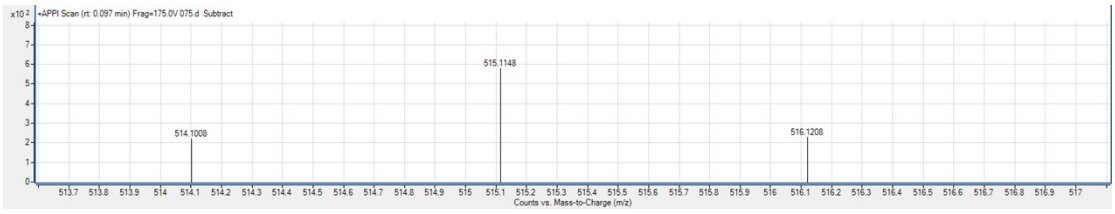


12b HMBC-NMR



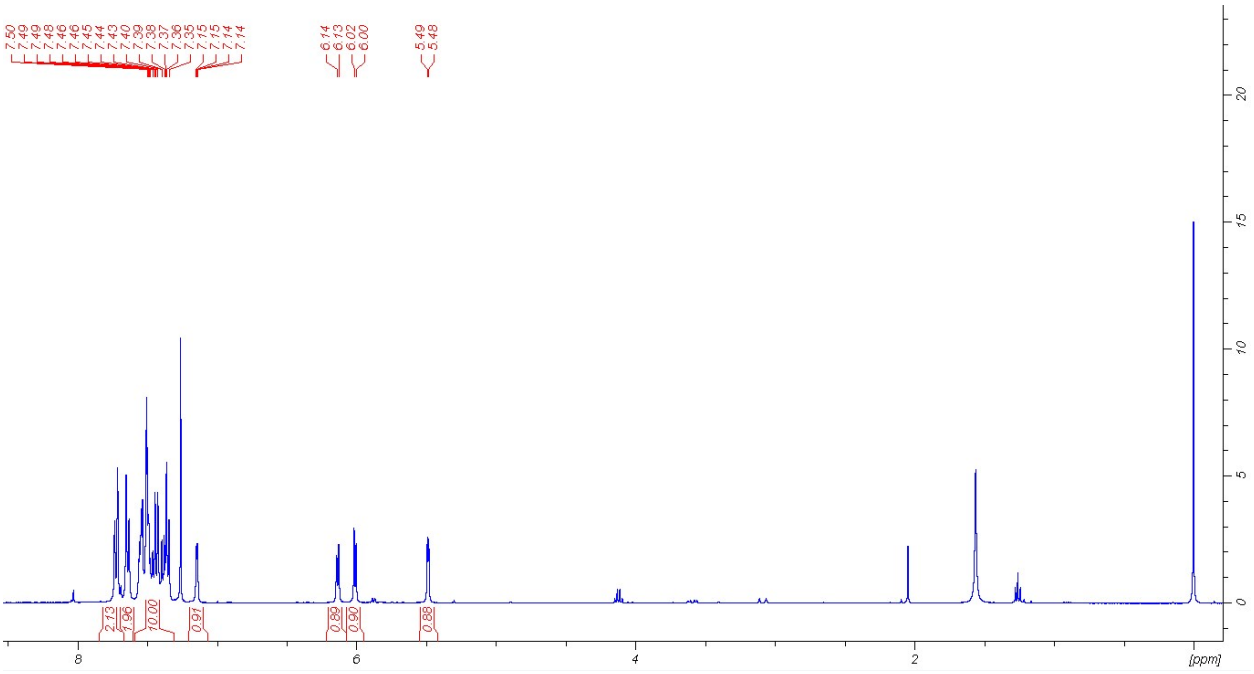
12b HRMS



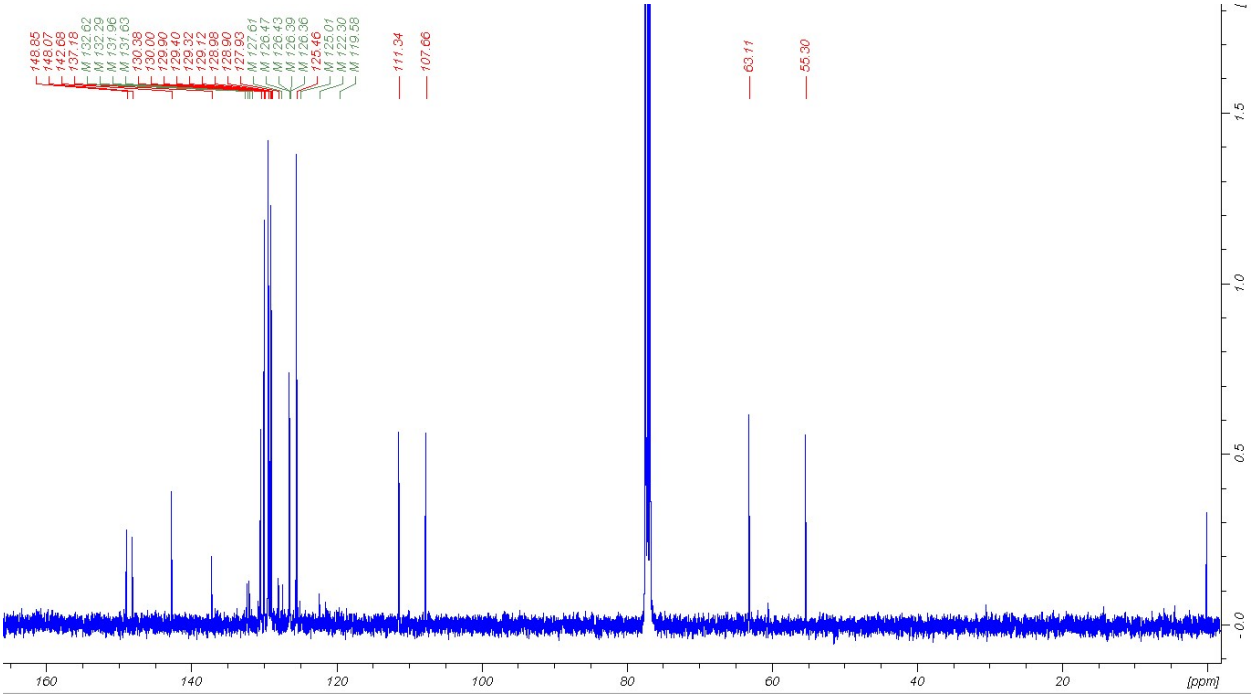


Formula	Observed m/z	Proposed adduct	Charge	Observed neutral mass	Theoretical neutral mass	Mass error (ppm)
C27H21N3O6S	515.1148	radical	1+	515.1149	515.1151	0.39

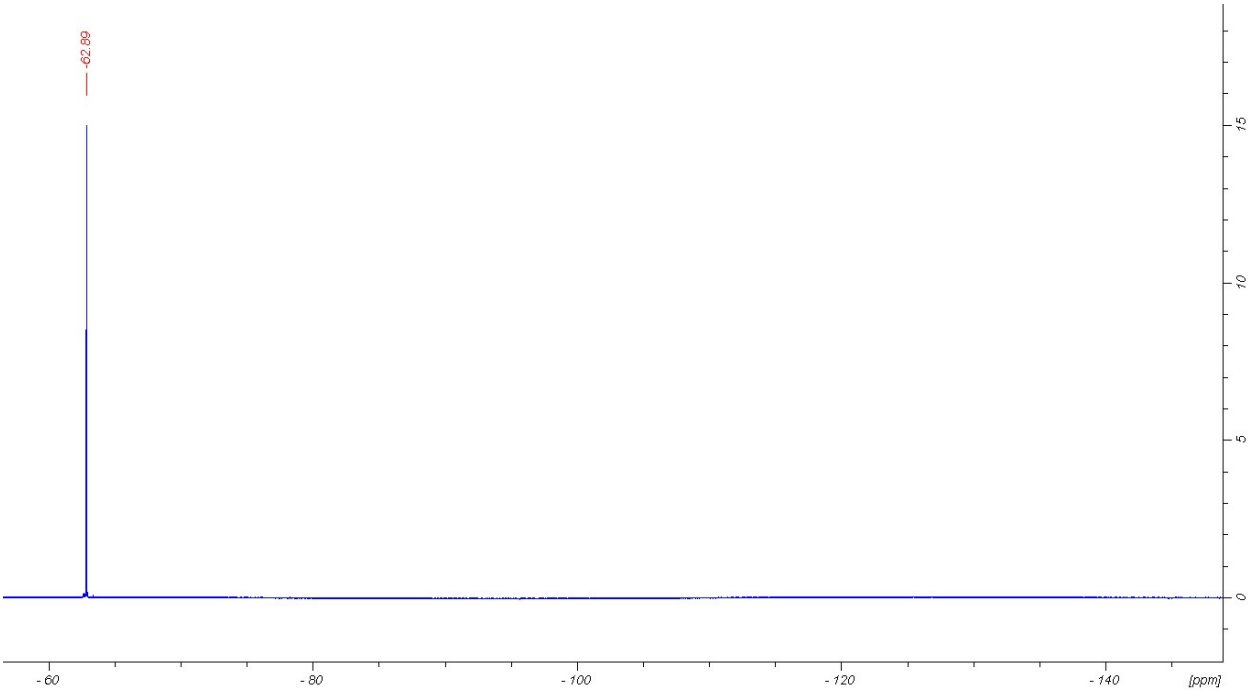
2,9-diphenyl-5-(4-(trifluoromethyl)phenyl)-5,9-dihydro-1*H*-[1,2]oxathiino[5,6-*c*][1,2,4]triazolo[1,2-*a*]pyridazine-1,3(2*H*)-dione 8,8-dioxide 12c ^{1}H-NMR



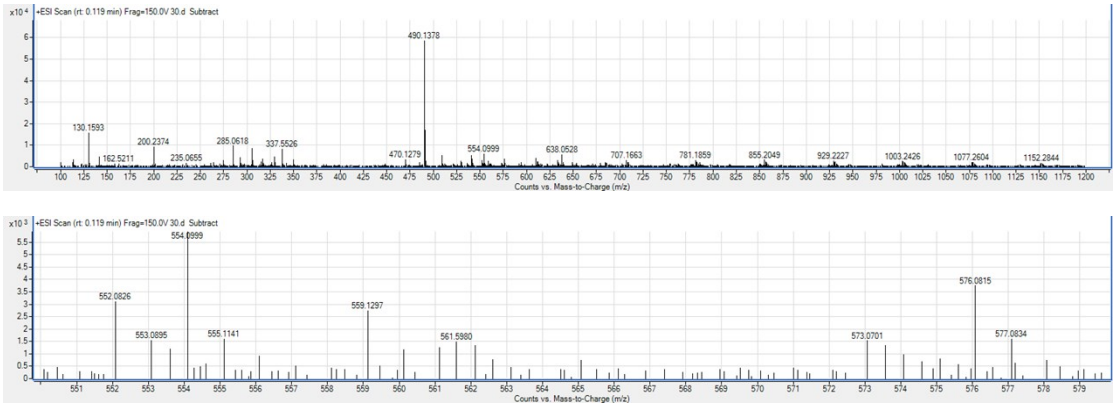
12c ^{13}C-NMR



12c ^{19}F-NMR

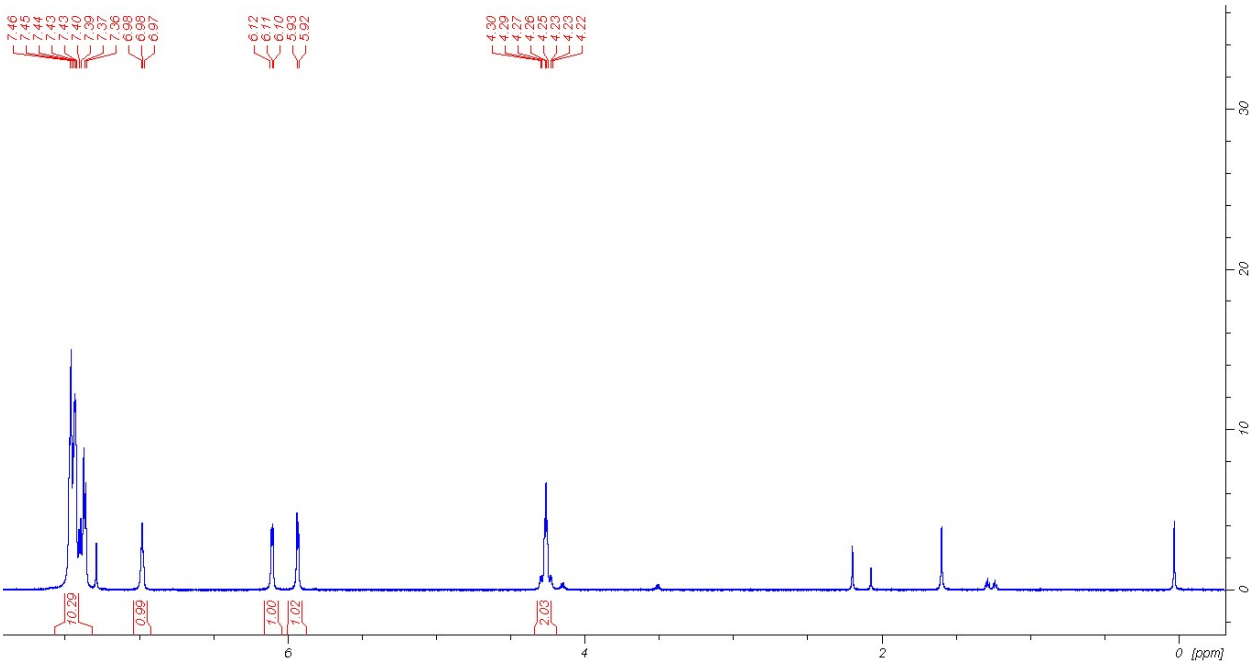


12c HRMS

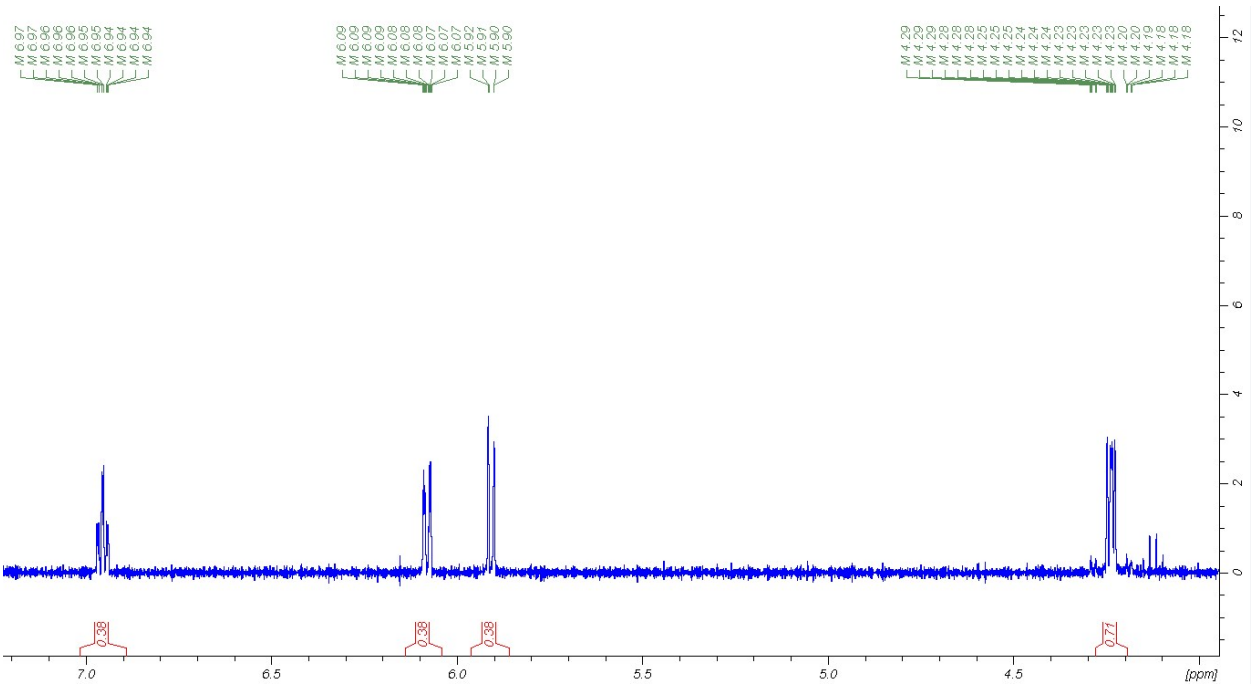


Formula	Observed m/z	Proposed adduct	Charge	Observed neutral mass	Theoretical neutral mass	Mass error (ppm)
C27H18F3N3O5S	554.0999	H+	1+	553.0926	553.0919	1.27
	576.0815	**Na+**	1+	553.0915		0.72

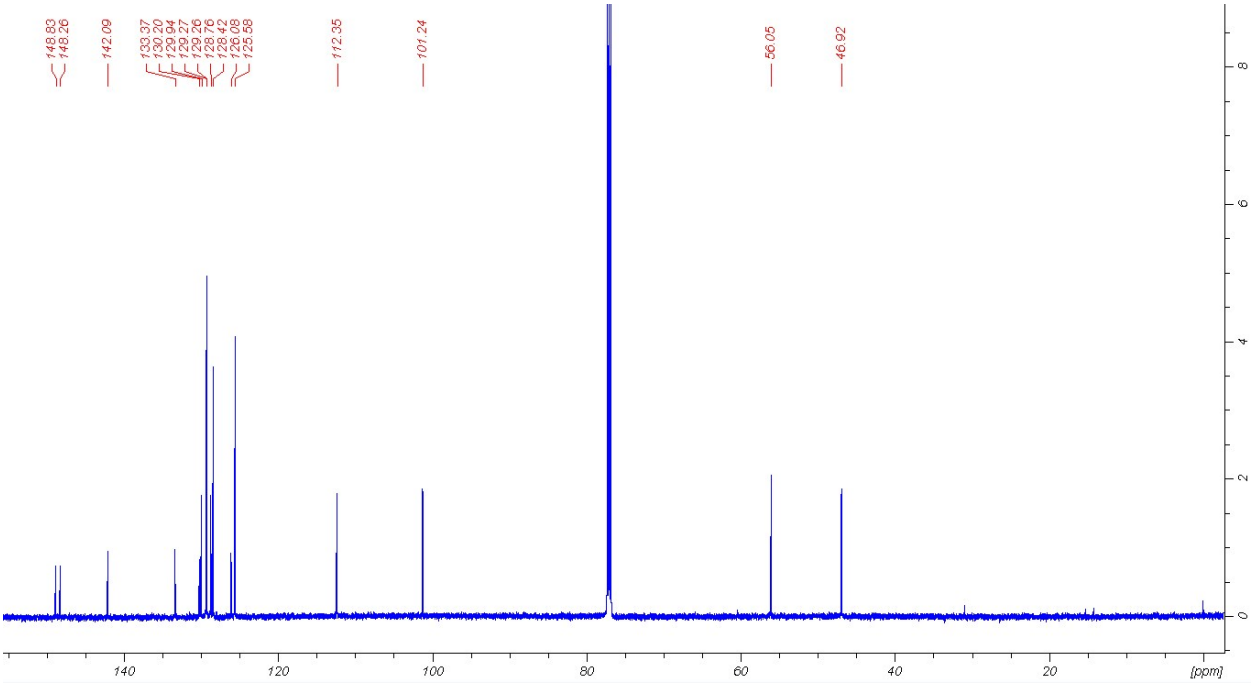
2,5-Diphenyl-5,9-dihydro-1*H*-[1,2]oxathiino[5,6-*c*][1,2,4]triazolo[1,2-*a*]pyridazine-1,3(2*H*)-dione 8,8-dioxide 12e ^{1}H-NMR



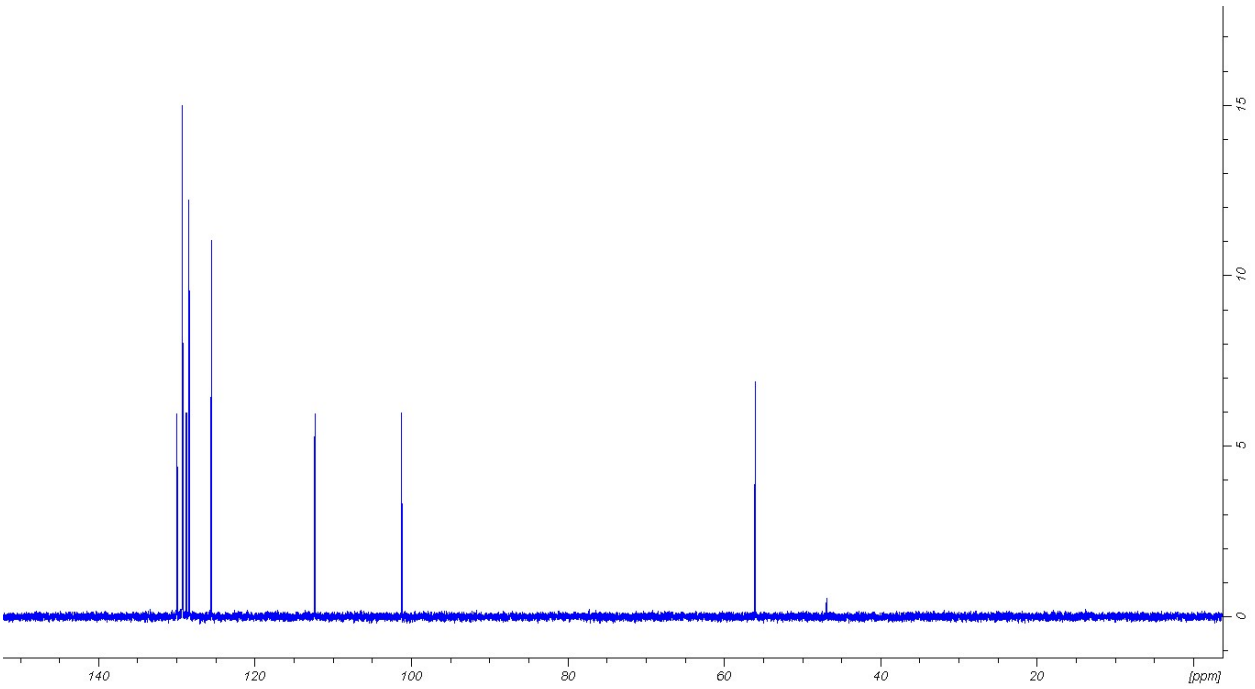
12e ^{1}H-NMR expansion



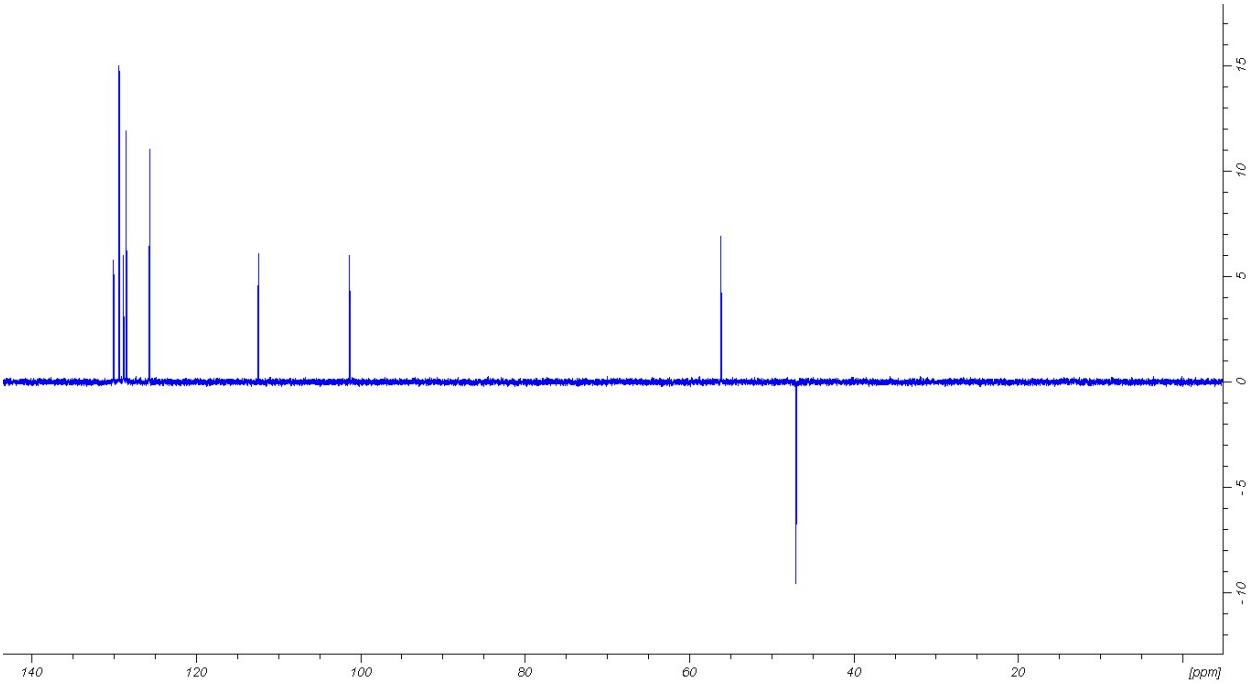
12e ^{13}C-NMR



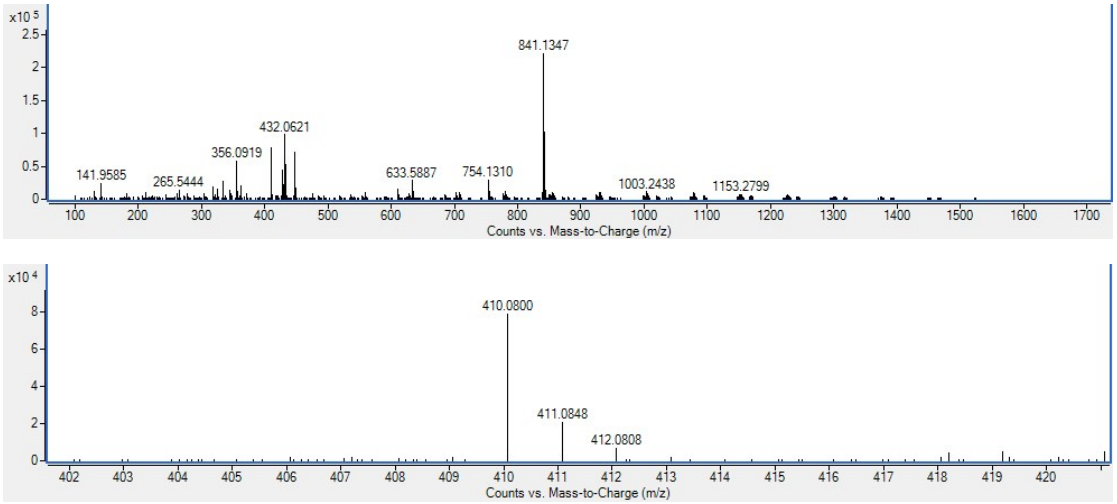
12e DEPT90 ^{13}C-NMR



12e DEPT135 ^{13}C-NMR

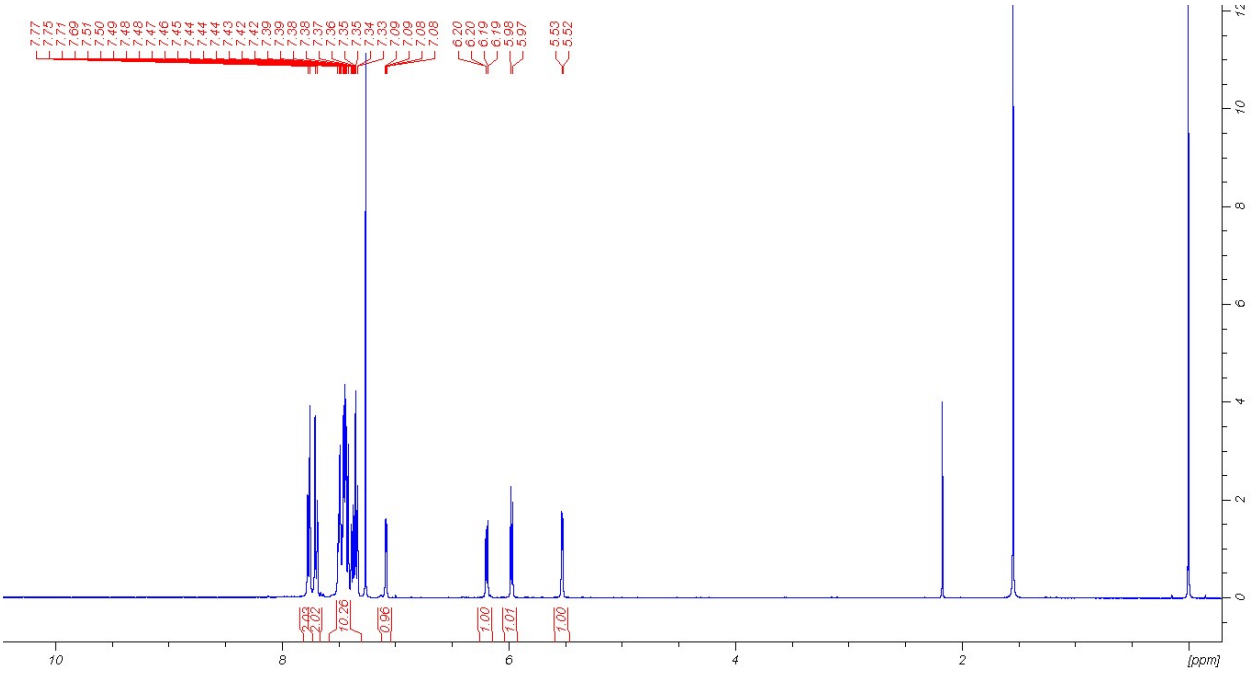


12e HRMS

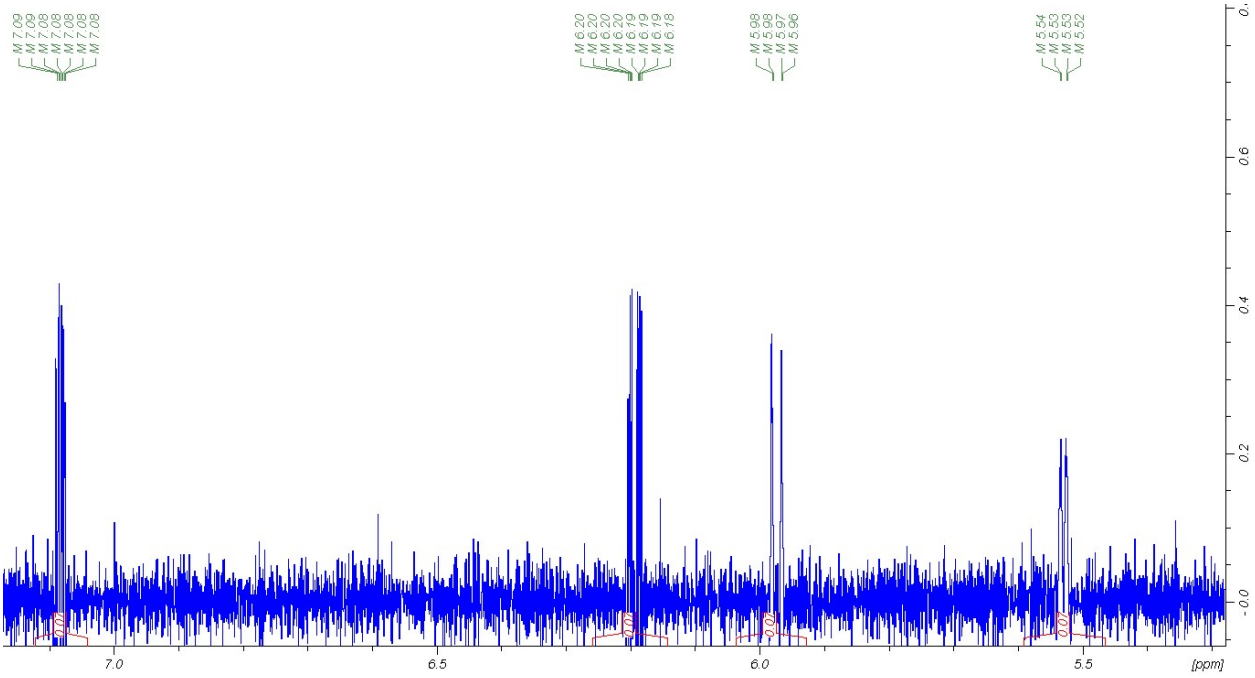


Formula	Observed m/z	Proposed adduct	Charge	Observed neutral mass	Theoretical neutral mass	Mass error (ppm)
C20H15N3O5S	410.0800	H+	1+	409.0730	409.0732	0.49

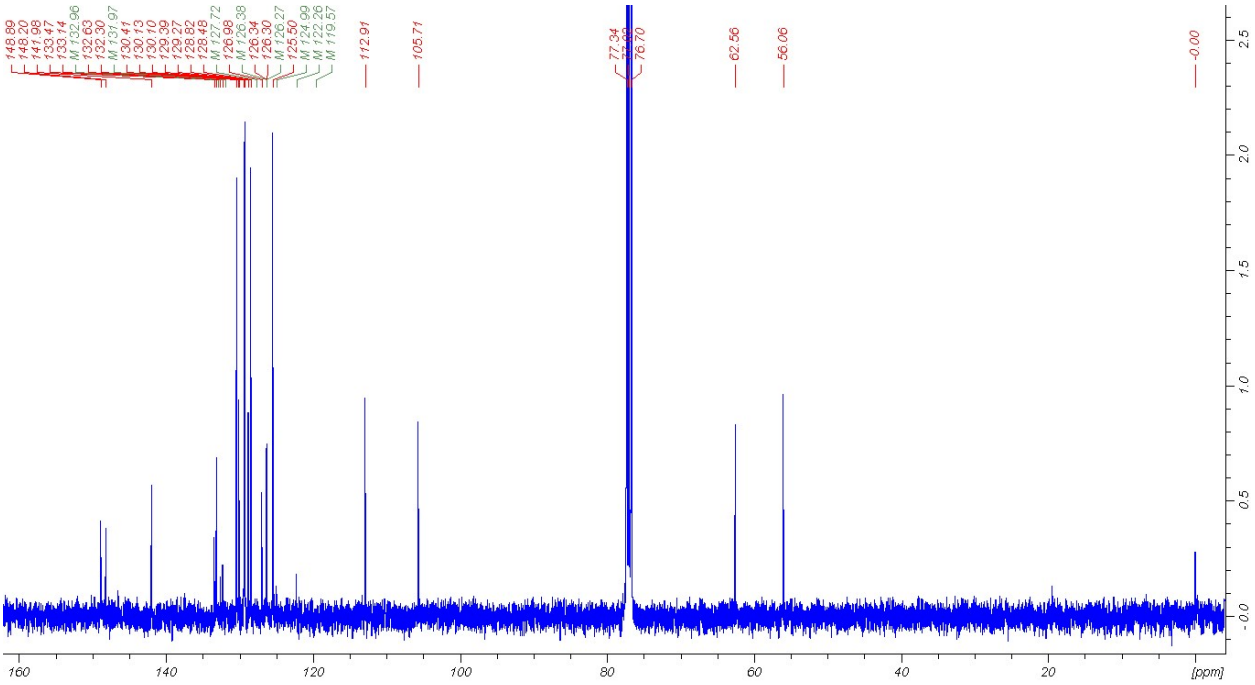
2,5-Diphenyl-9-(4-(trifluoromethyl)phenyl)-5,9-dihydro-1*H*-[1,2]oxathiino[5,6-*c*][1,2,4]triazolo[1,2-*a*]pyridazine-1,3(2*H*)-dione 8,8-dioxide 12f ^{1}H-NMR



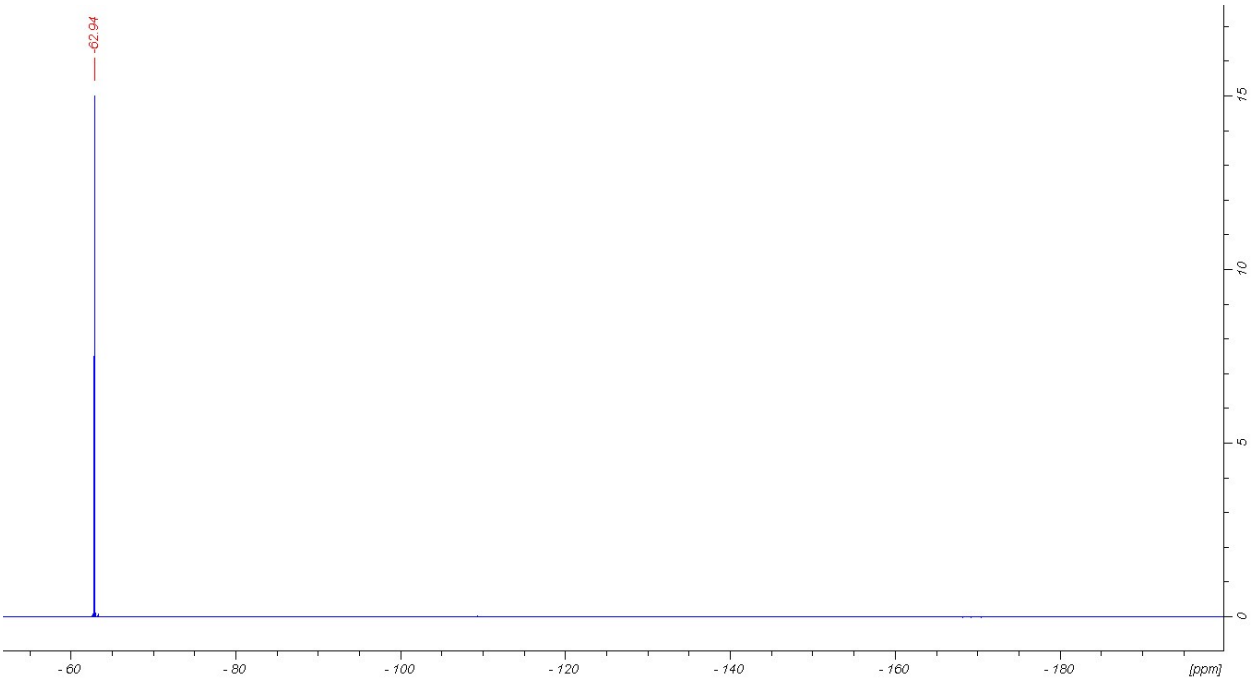
12f ^{1}H-NMR expansion



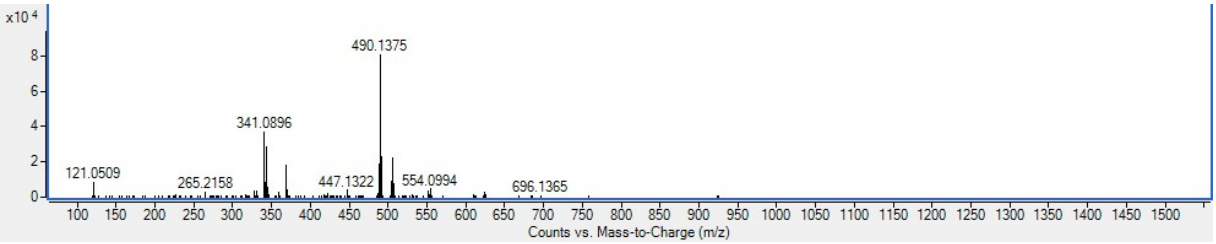
12f ^{13}C-NMR

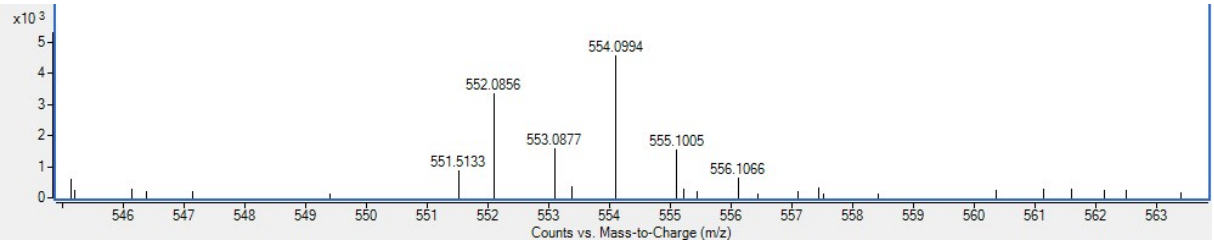


12f ^{19}F-NMR



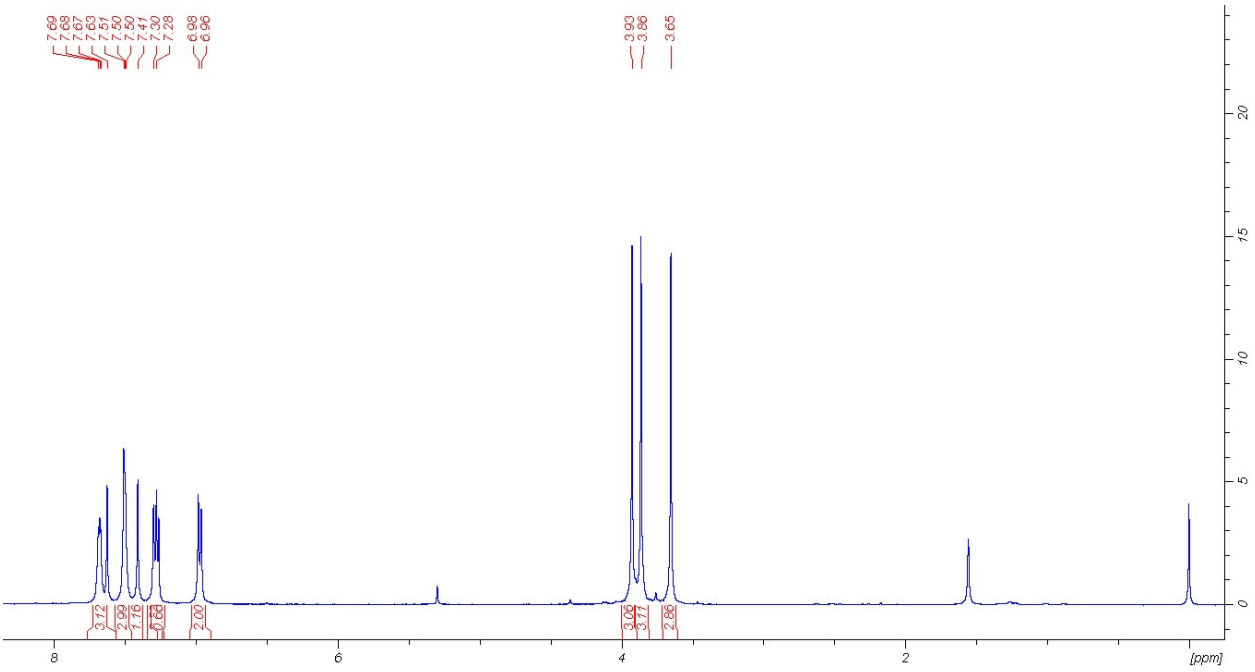
12f HRMS



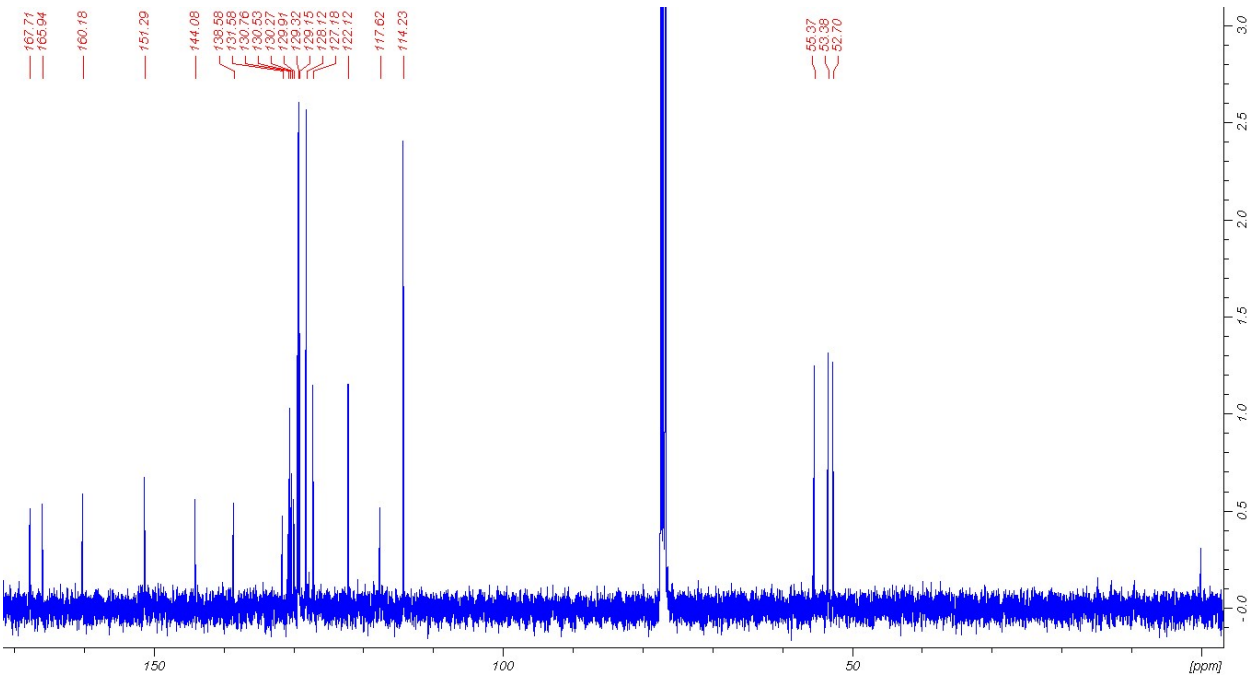


Formula	Observed m/z	Proposed adduct	Charge	Observed neutral mass	Theoretical neutral mass	Mass error (ppm)
C27H18F3N3O5S	554.0994	H+	1+	553.0917	553.0919	0.36

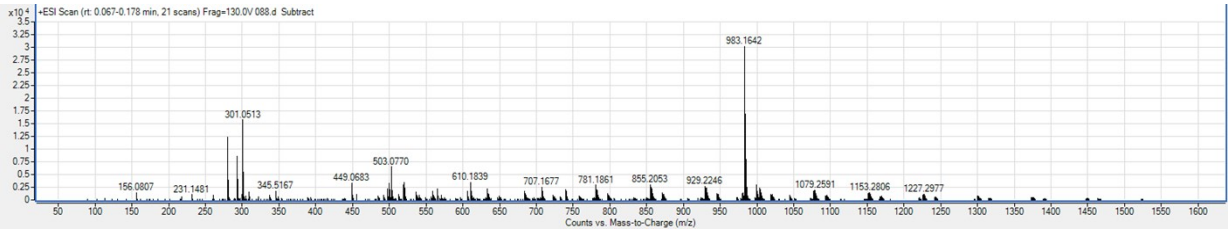
Dimethyl 7-(4-methoxyphenyl)-3-phenylbenzo[*e*][1,2]oxathiine-5,6-dicarboxylate 2,2-dioxide 13 ^{1}H-NMR



13 ^{13}C-NMR

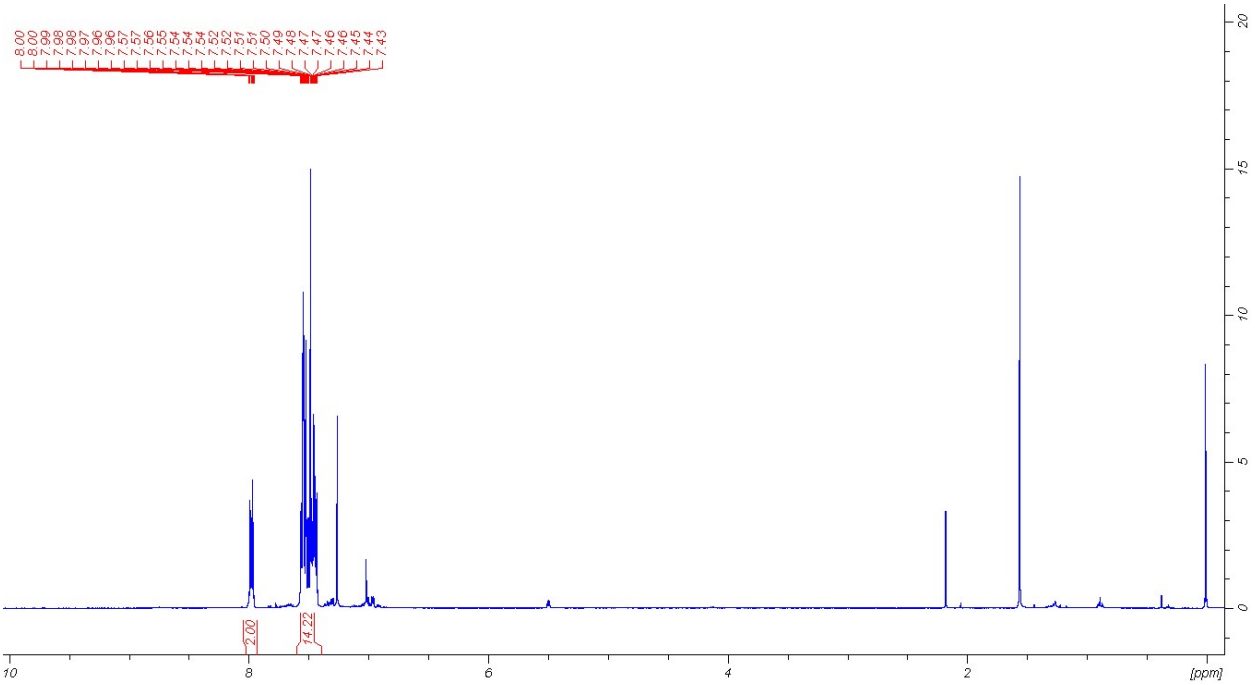


13 HRMS

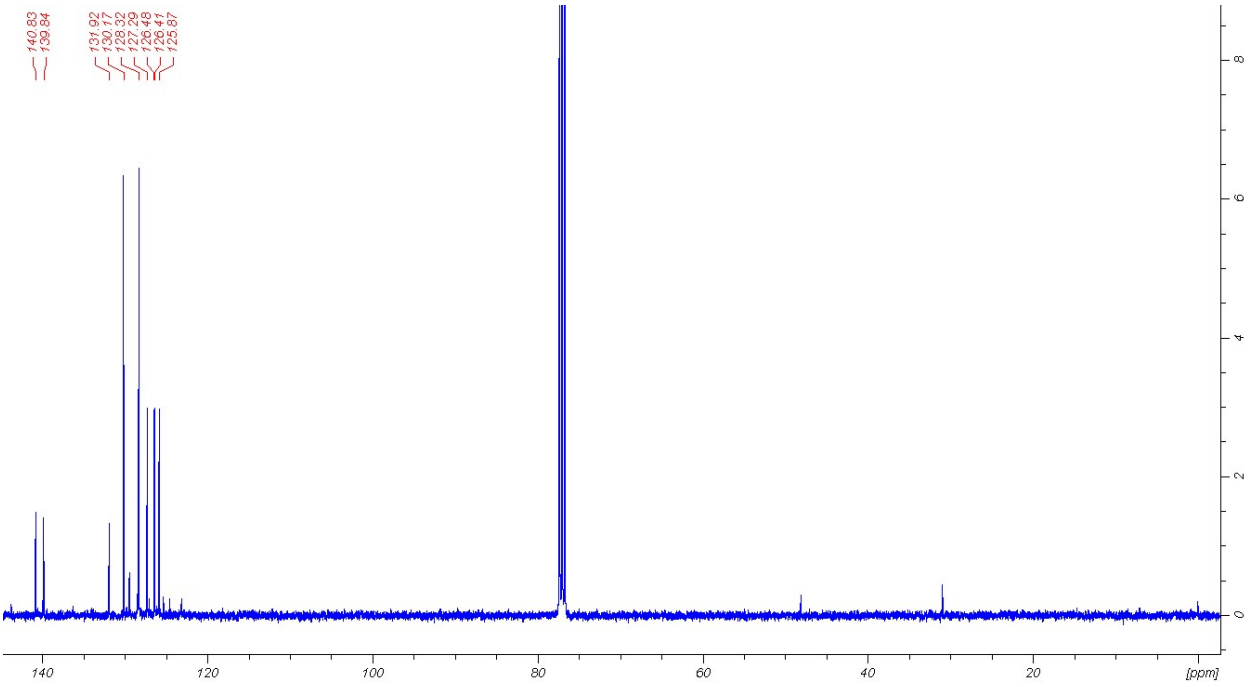


Formula	Observed m/z	Proposed adduct	Charge	Observed neutral mass	Theoretical neutral mass	Mass error (ppm)
C25H20O8S	503.0770	Na+	1+	480.0879	480.0879	0.1

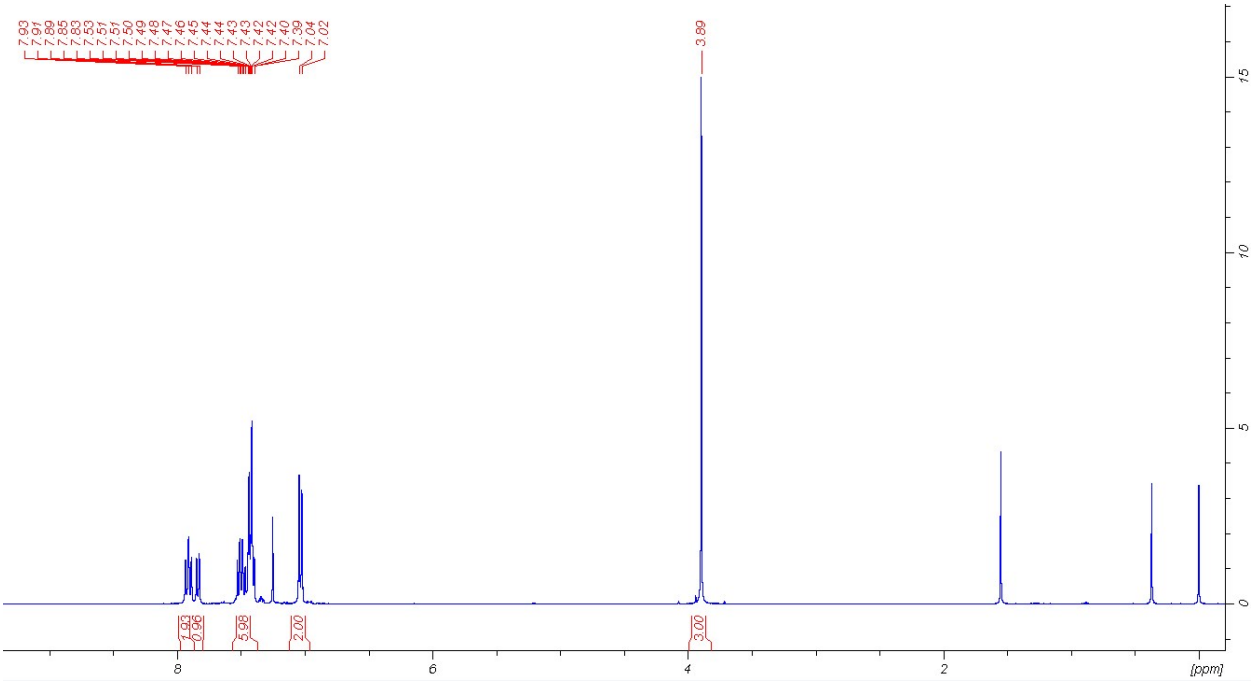
1,4-Diphenylnaphthalene 16 ^{1}H-NMR



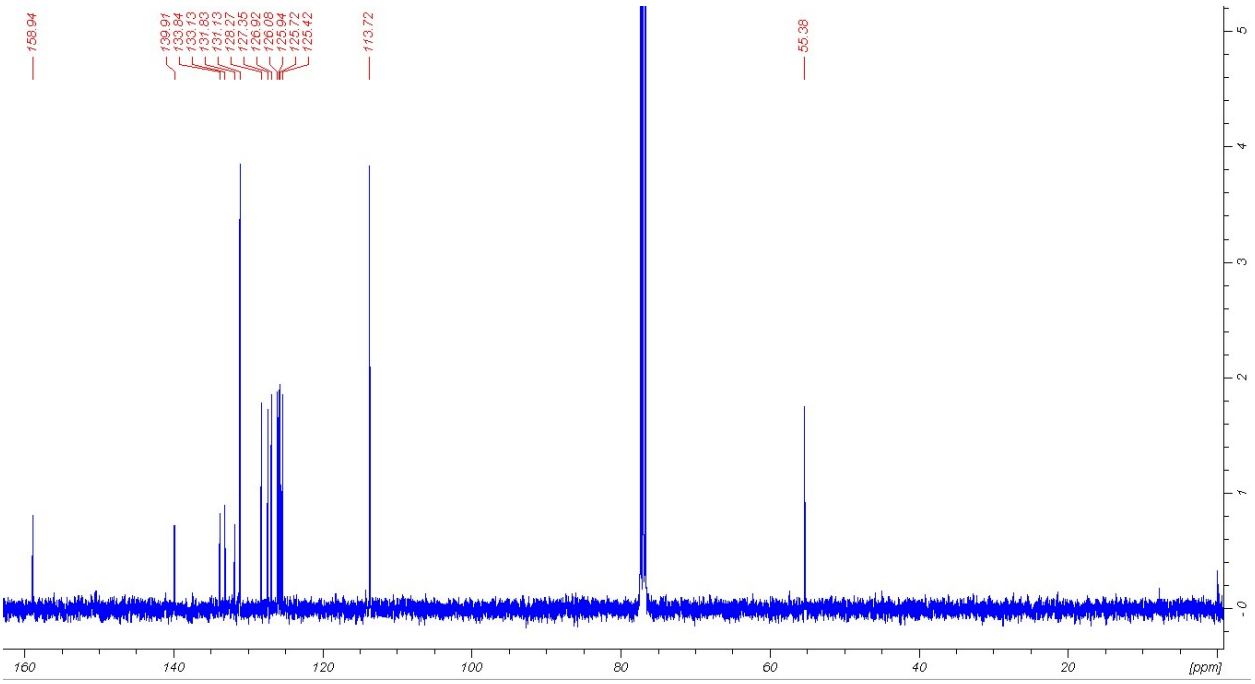
16 ^{13}C-NMR



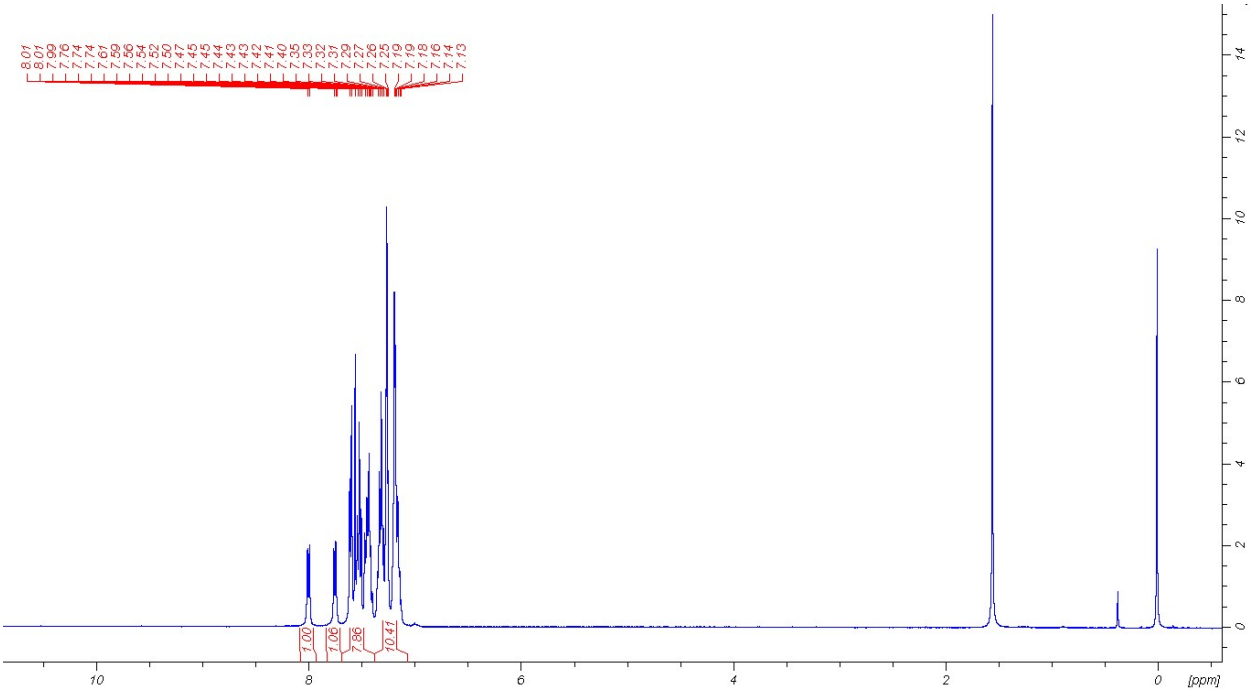
1-(4-Methoxyphenyl)naphthalene 17 ^{1}H-NMR



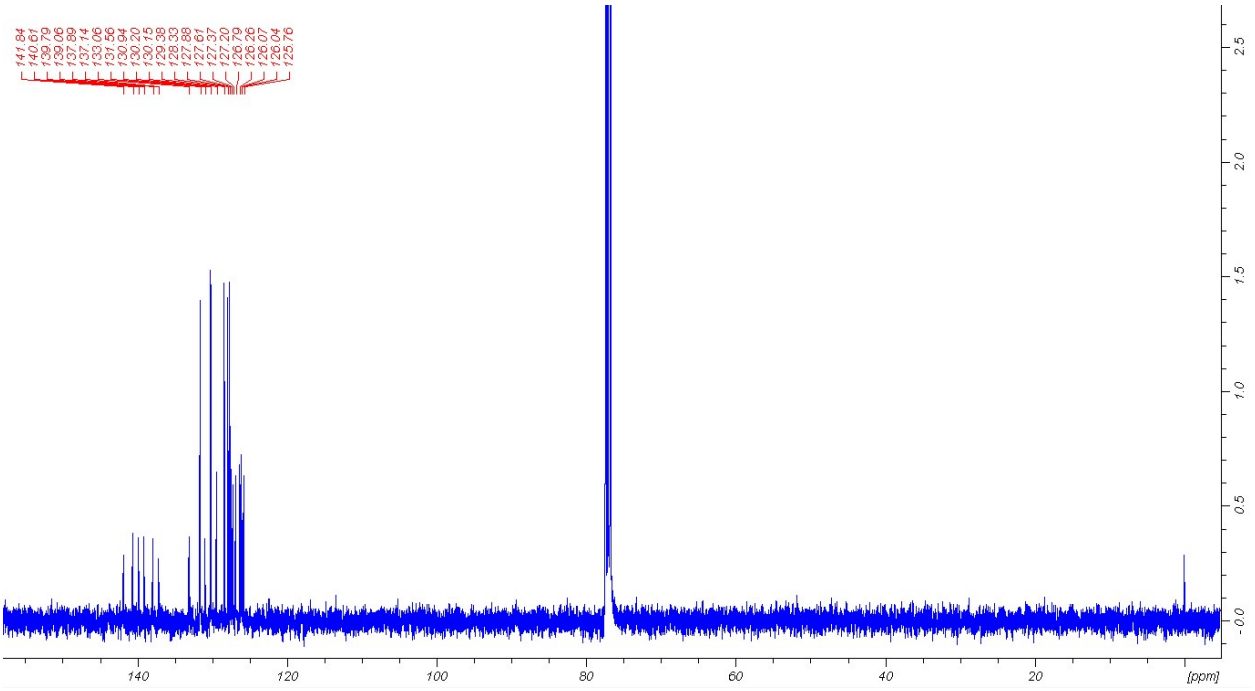
17 ^{13}C-NMR



1,2,4-Triphenylnaphthalene 18 ^{1}H-NMR



18 ^{13}C-NMR



END