Identifying cysteine residues susceptible to oxidation by photoactivatable atomic oxygen precursors using a proteome-wide analysis.

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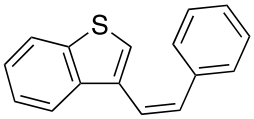
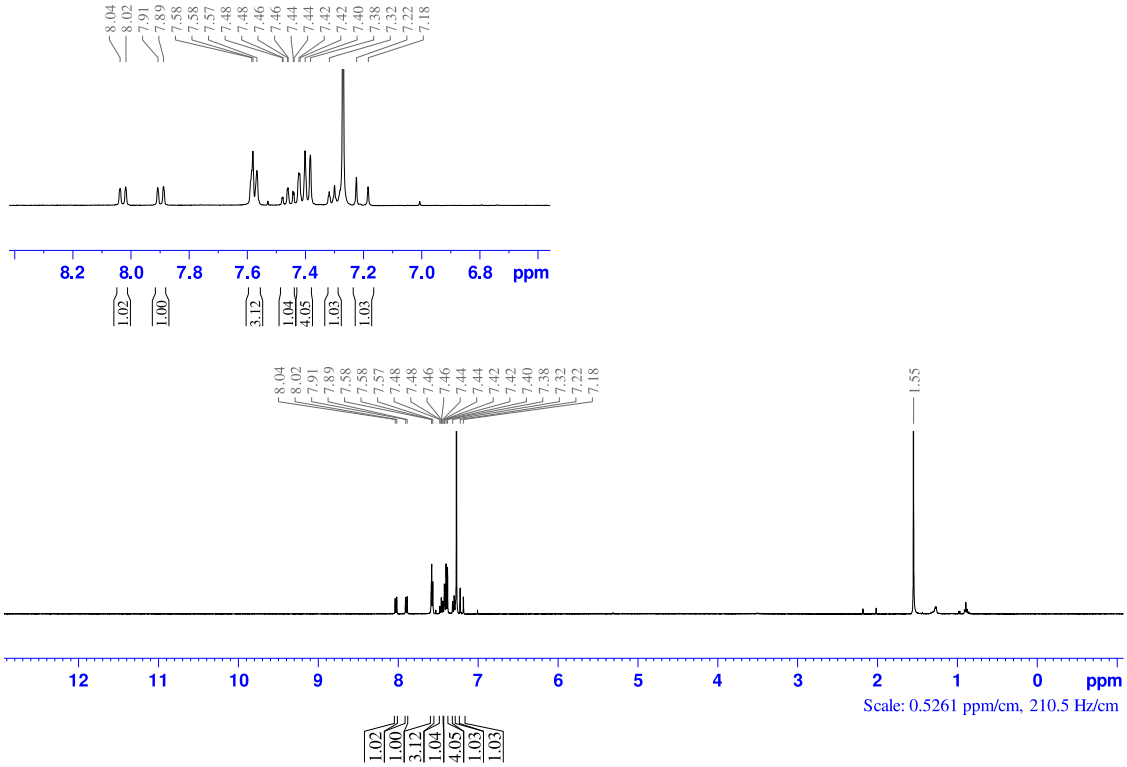
1. Spectral Data (^{1}H-NMR, ^{13}C-NMR, HRMS, HPLC Analysis for purity)

3-styrylbenzo[b]thiophene

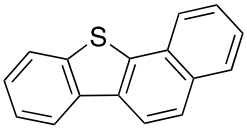


^{1}H-NMR (in $CDCl_3$)

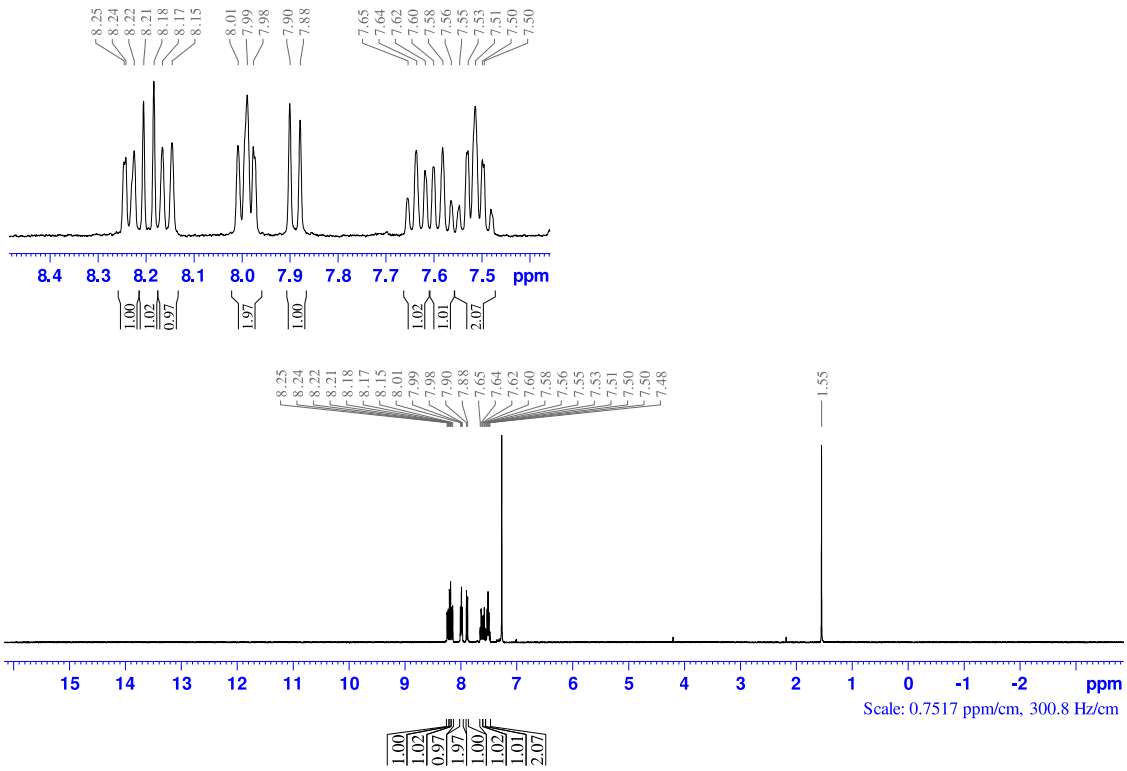


Impurities: Solvent Peak Chloroform (7.27 ppm), Water (1.55 ppm)

Benzo[b]naphtho-[1,2-d]-thiophene

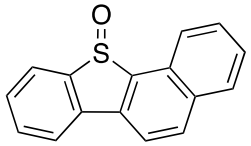


^{1}H-NMR (in $CDCl_3$)

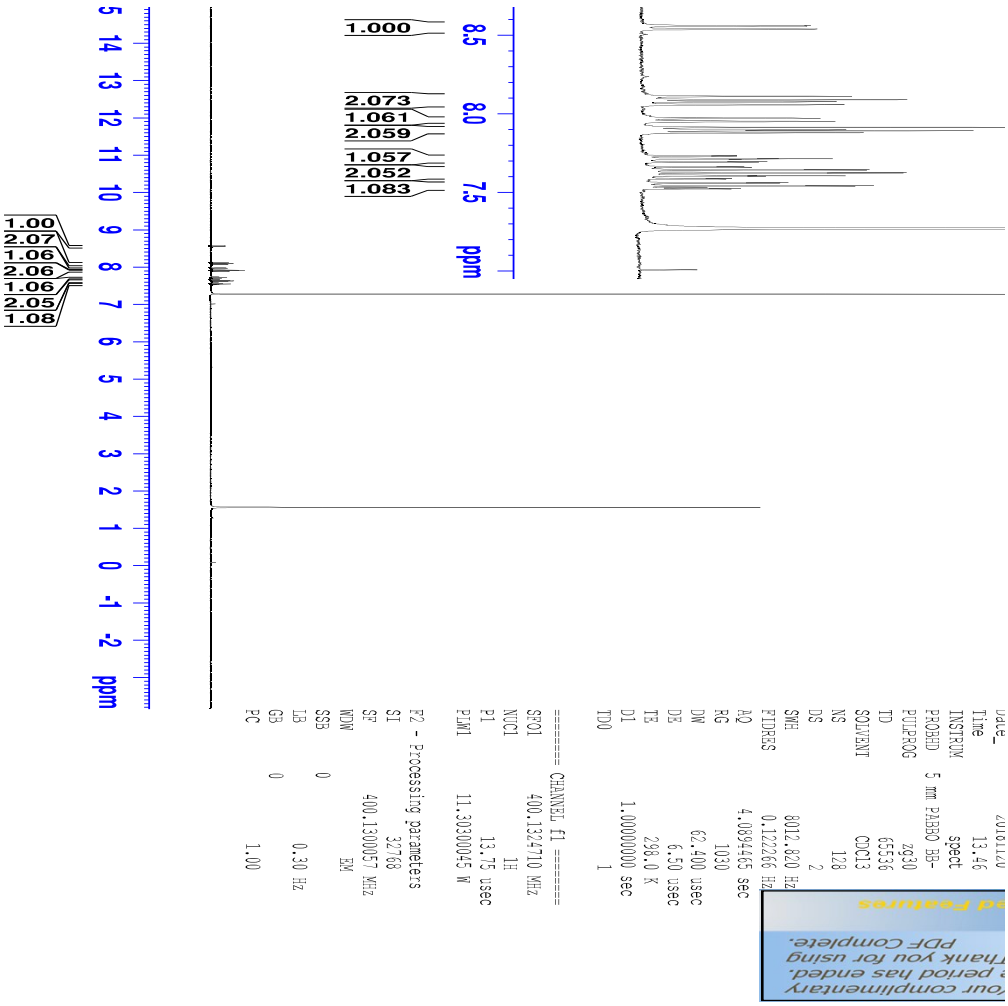


Impurities: Solvent Peak Chloroform (7.27 ppm), Water (1.56 ppm)

Benzo[b]naphtho-[1,2-d]thiophene-S-oxide

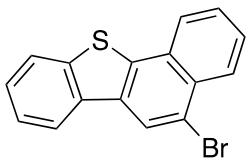


^{1}H-NMR in $CDCl_3$

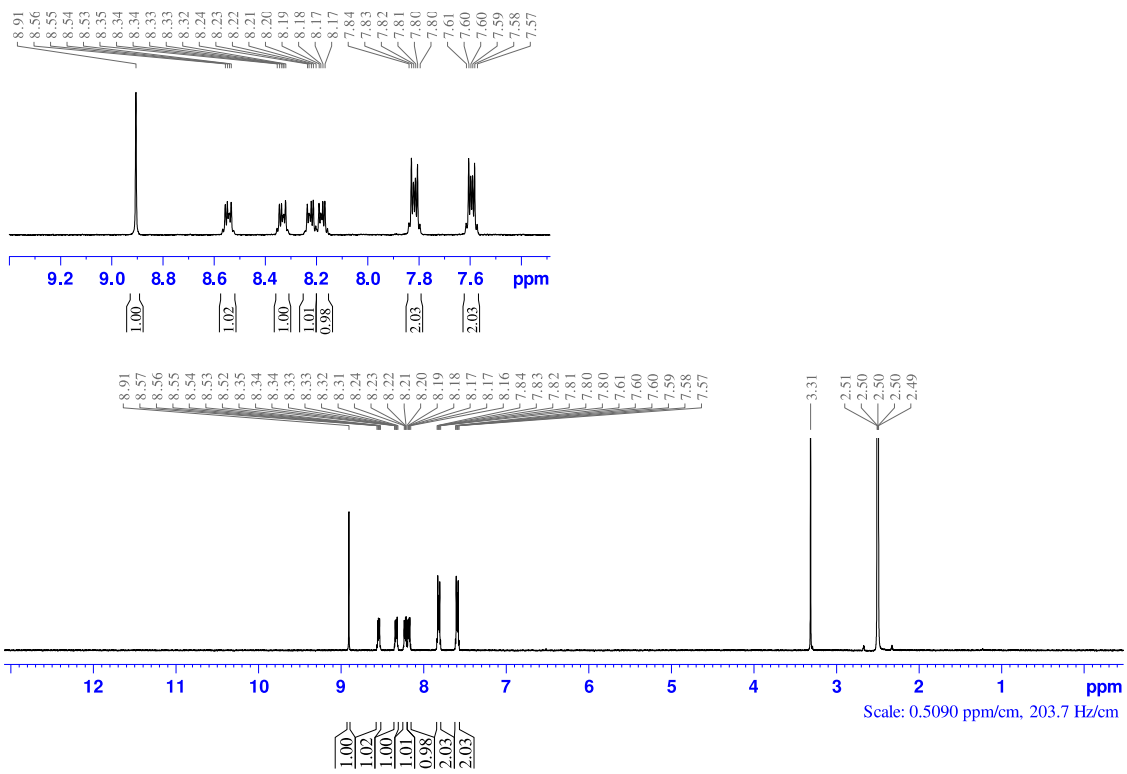


Impurities: Solvent Peak Chloroform (7.27 ppm), Water (1.55 ppm)

5-Bromobenzo[b]naphtho-[1,2-d]thiophene

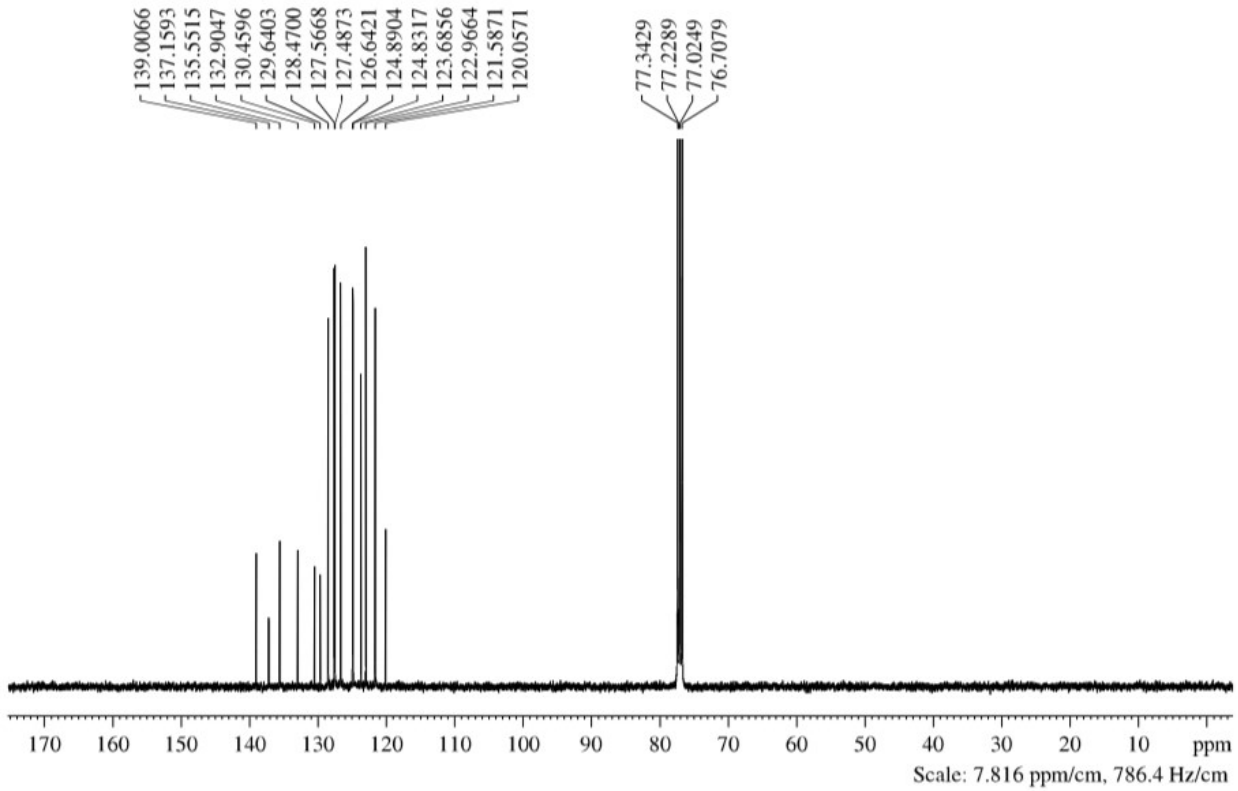


[1]H-NMR (in DMSO)



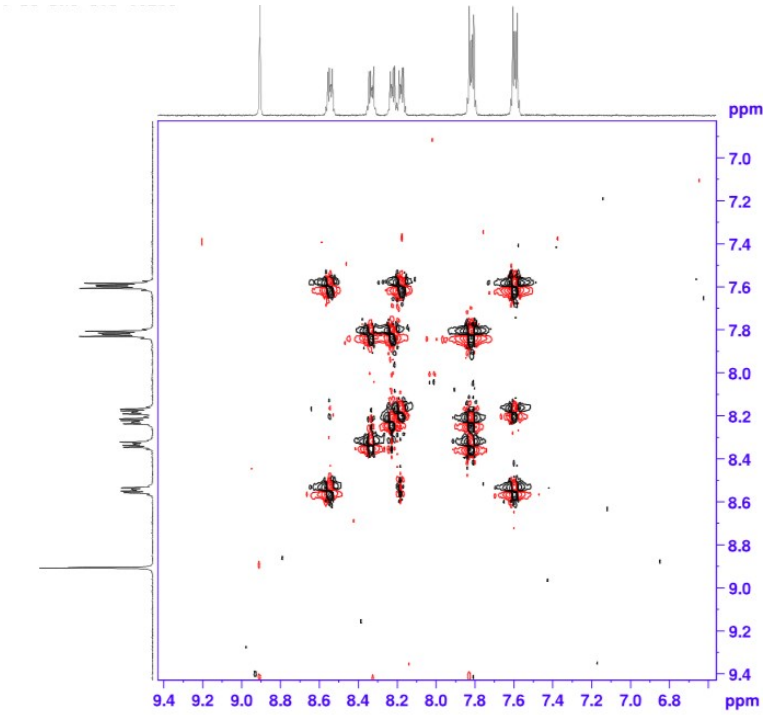
Impurities: Solvent Peak DMSO (2.50 ppm), water (3.31 ppm)

^{13}C-NMR (in $CDCl_3$)

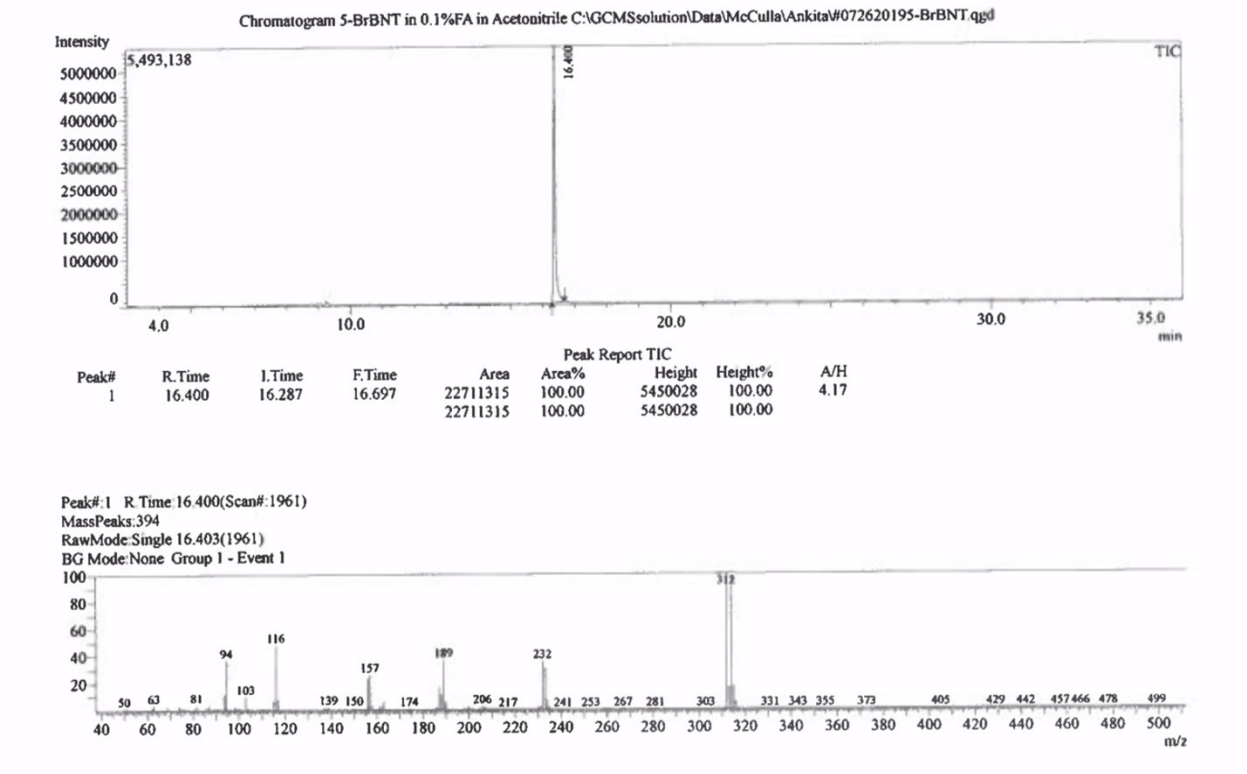


Impurities: Solvent Peak Chloroform (77.23 ppm)

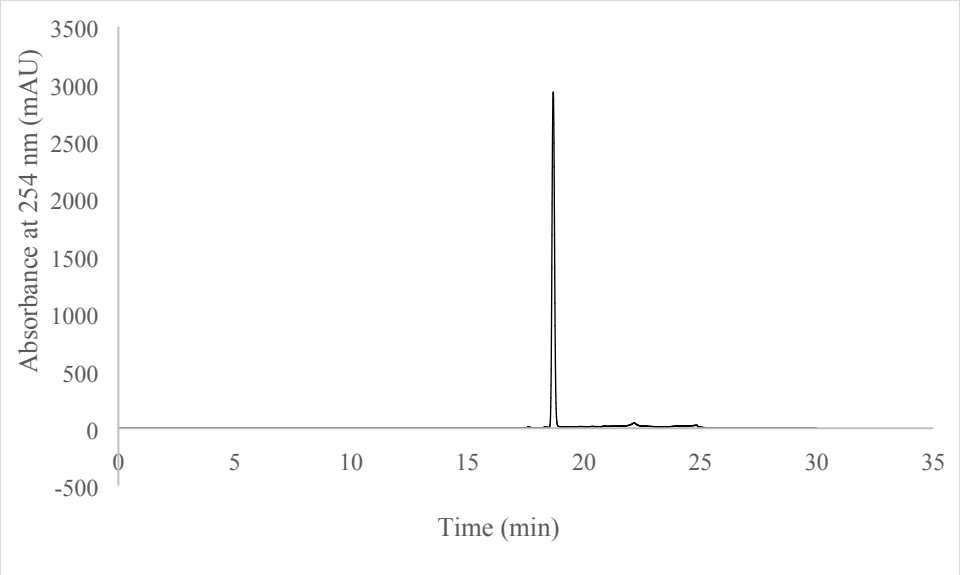
COSY ^{1}H-NMR (in $CDCl_3$)



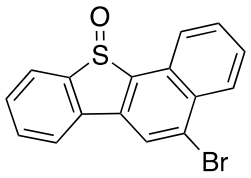
GCMS



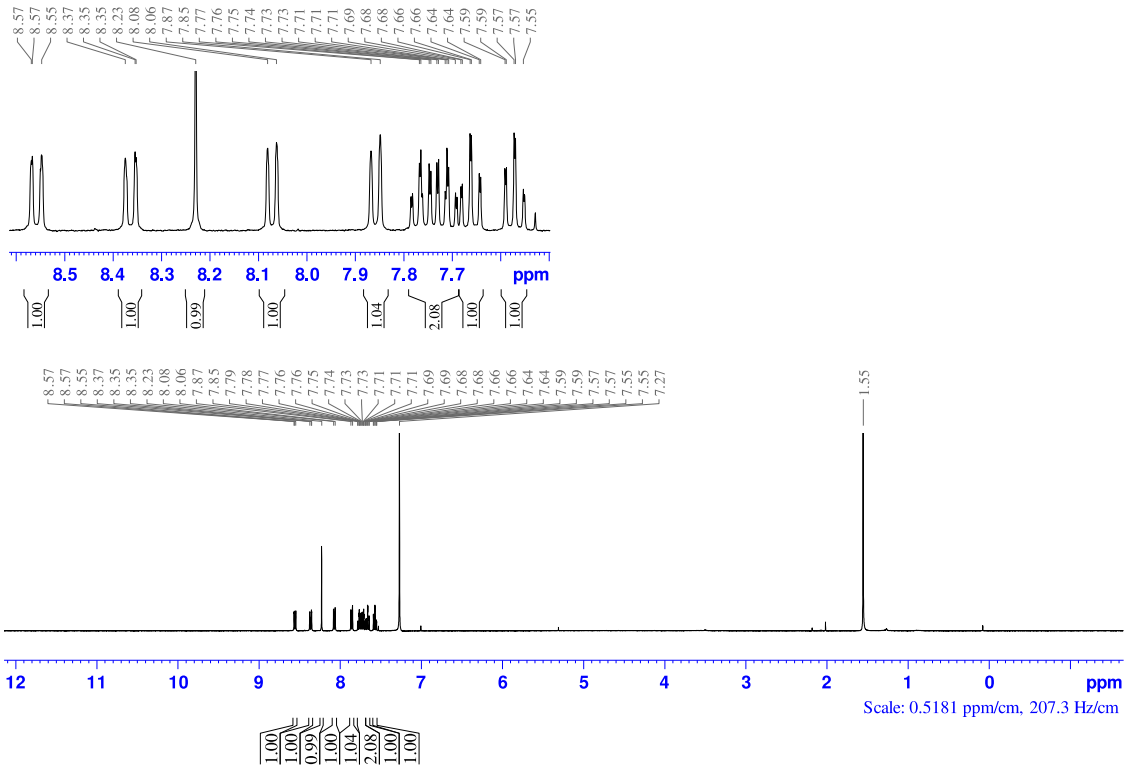
HPLC trace for purity



5-Bromobenzo[b]naphtho-[1,2-d]thiophene-S-oxide

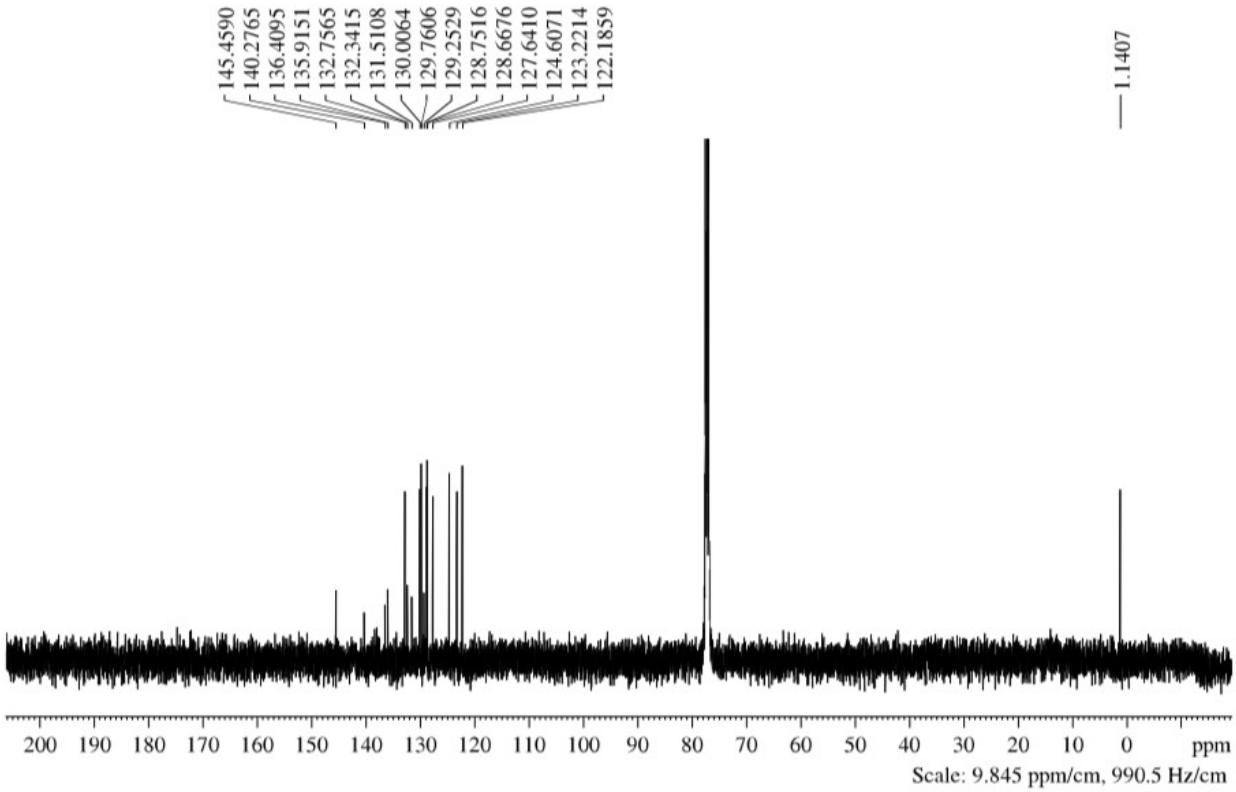


^{1}H-NMR in $CDCl_3$



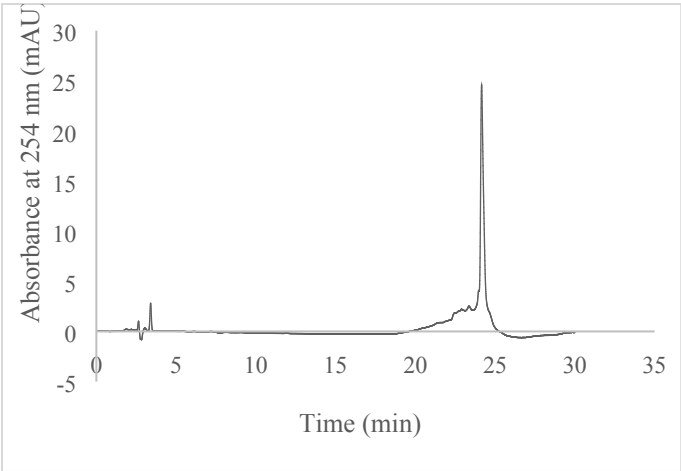
Impurities: Solvent Peak Chloroform (7.27 ppm), Water (1.55 ppm)

^{13}C-NMR (in $CDCl_3$)

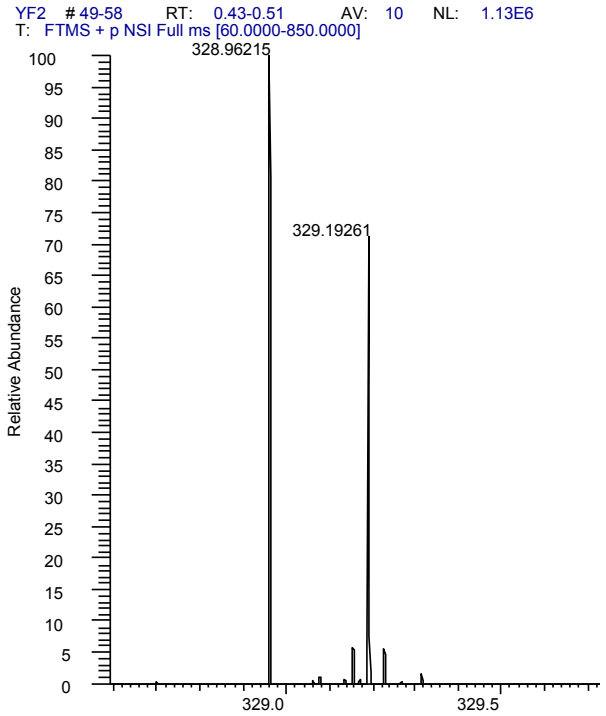


Impurities: Solvent Chloroform Peak (77.23 ppm), Silicone Grease (1.14 ppm)

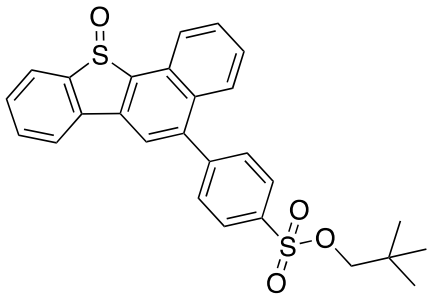
HPLC Analysis for Purity



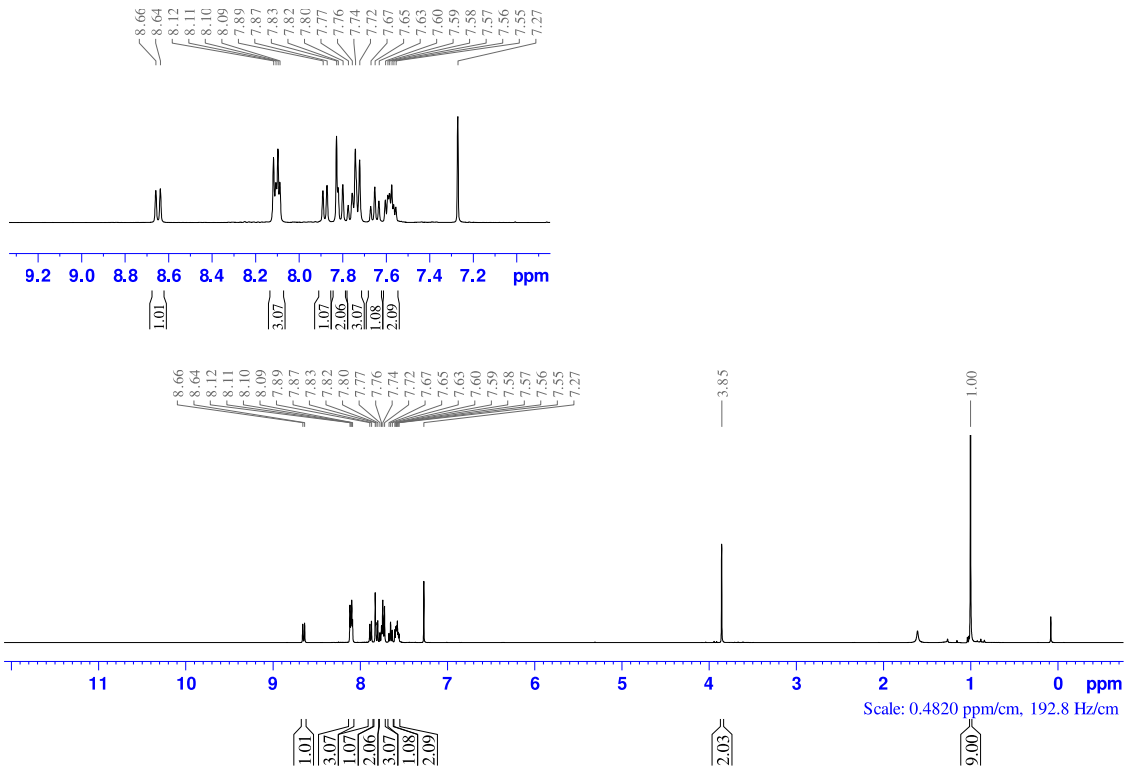
HRMS



5-neopentylsulfonatephenylbenzo[b]naphtho-[1,2-d]thiophene-S-oxide

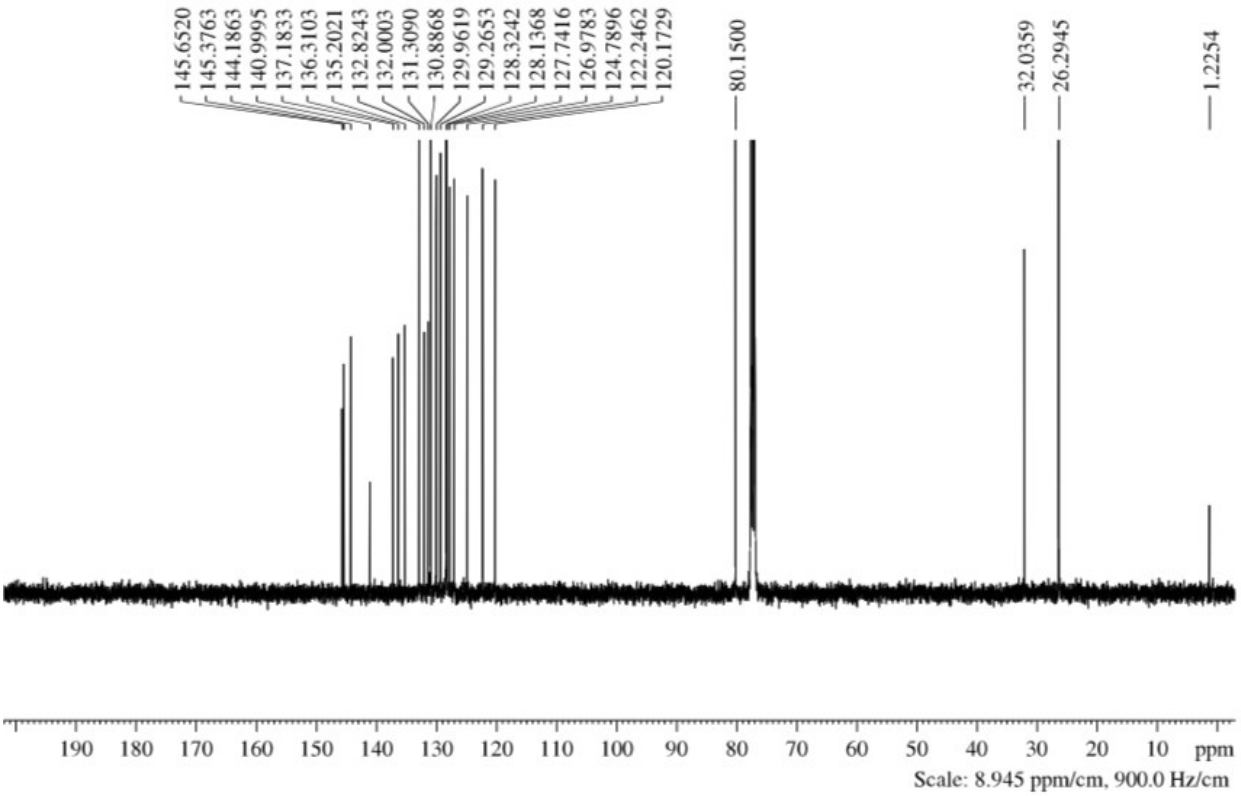


^{1}H-NMR (in $CDCl_3$)



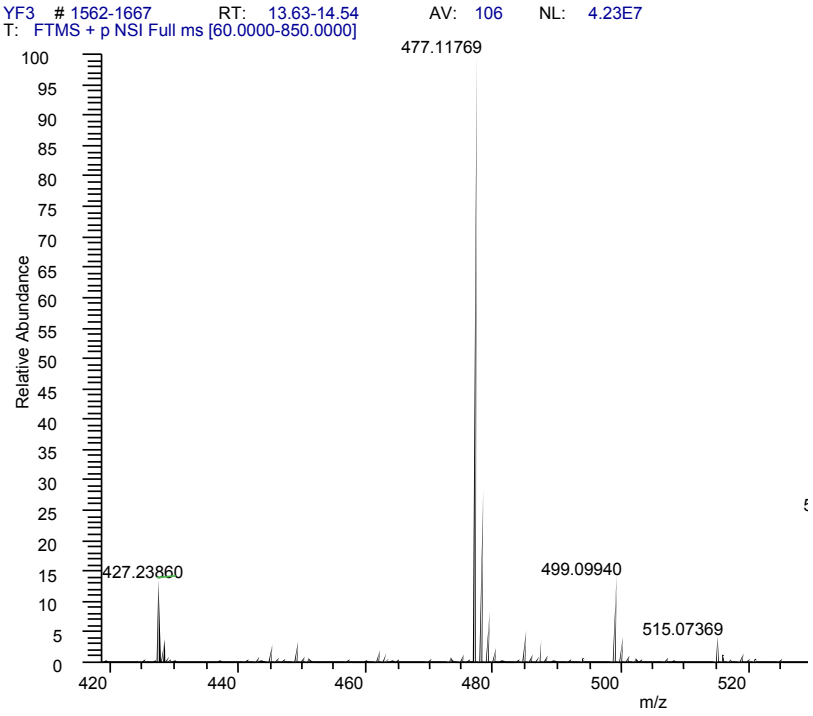
Impurities: Solvent Peak Chloroform (7.27 ppm)

^{13}C-NMR (in $CDCl_3$)

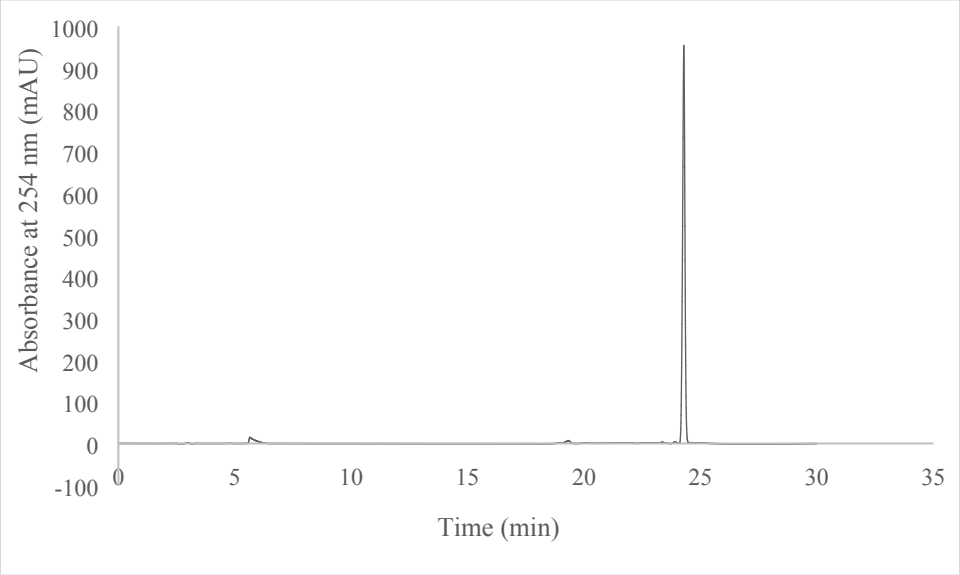


Impurities: Solvent Peak Chloroform (77.23 ppm), Silicone Grease (1.22 ppm)

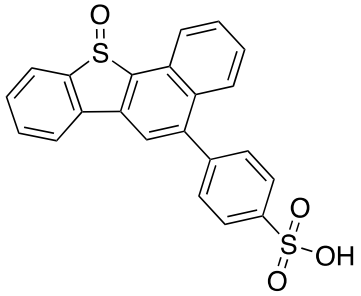
HRMS



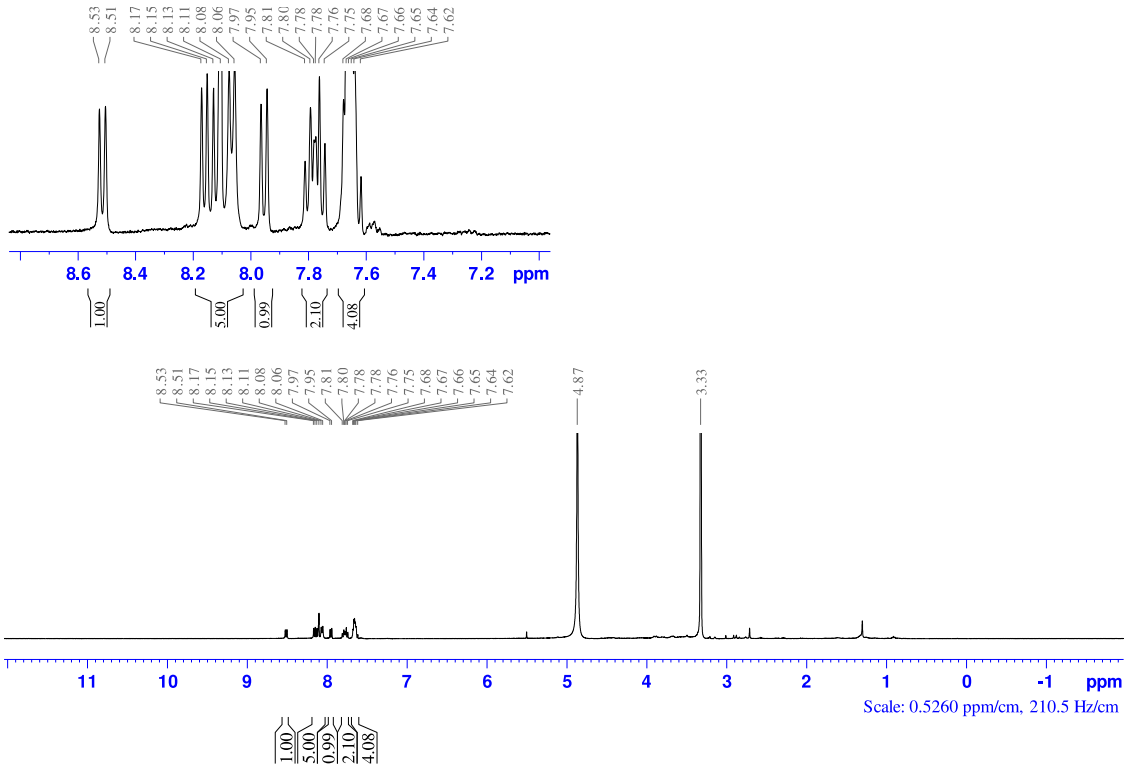
HPLC Analysis for purity



5-phenylbenzo[b]naphtho-[1,2-d]thiophene-S-oxide sulfonic acid

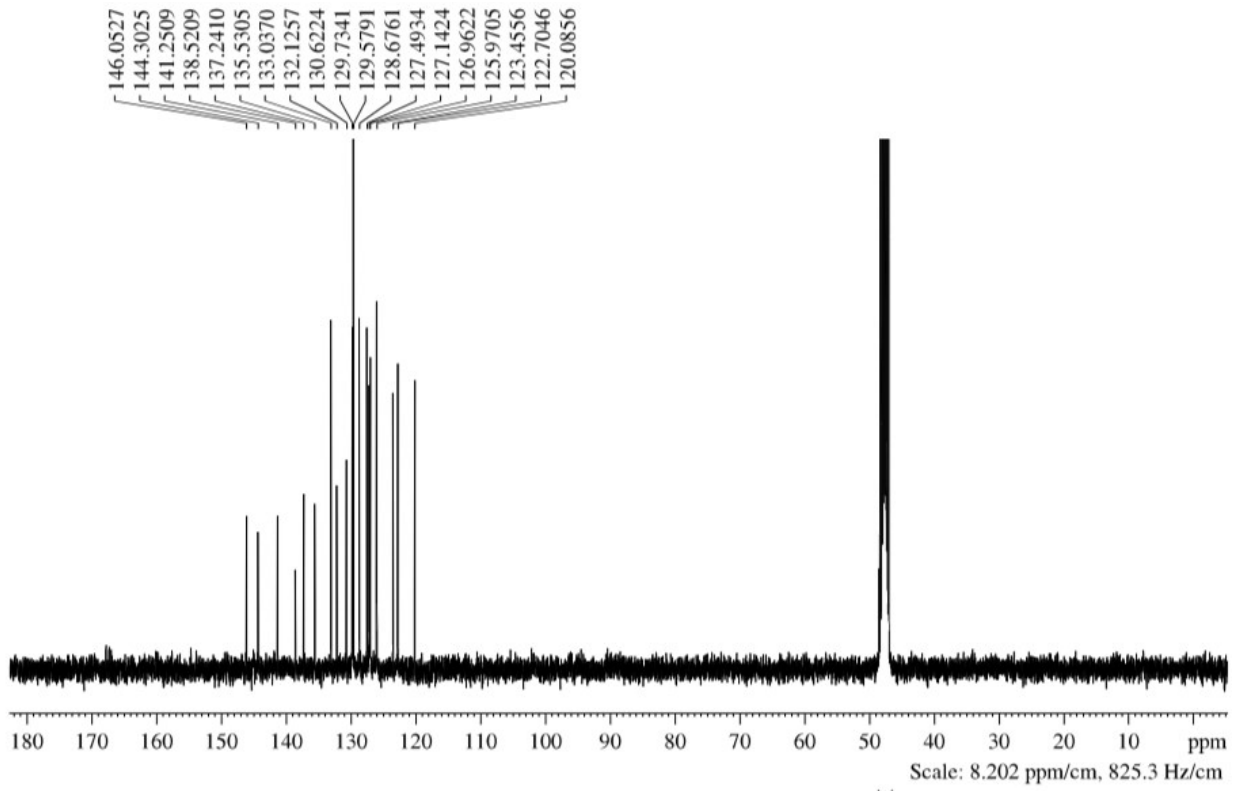


^{1}H-NMR (in Methanol-D_4)

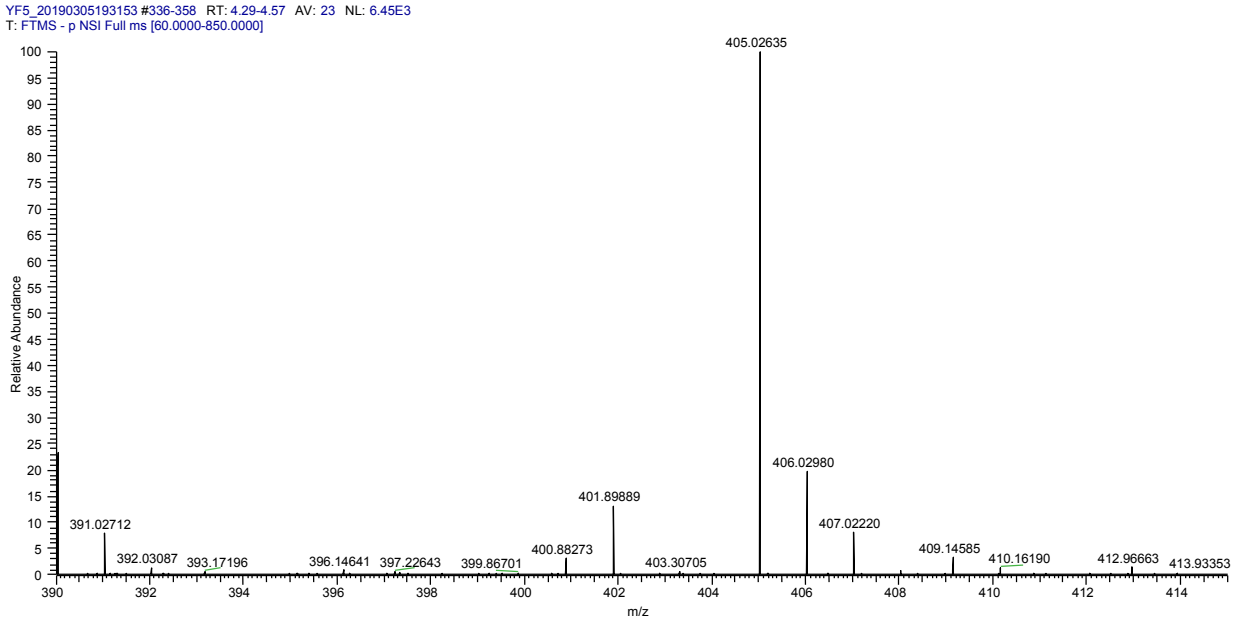


Impurities: Solvent Peak Methanol (3.31 ppm), Water (4.87 ppm)

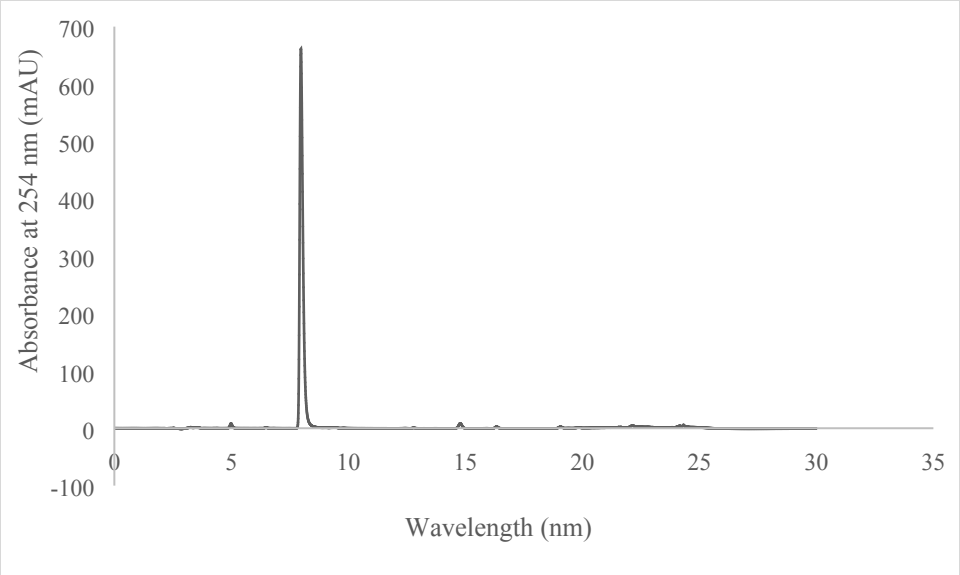
^{13}C-NMR (in Methanol-D$_4$)



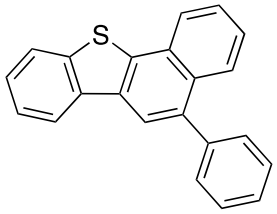
HRMS



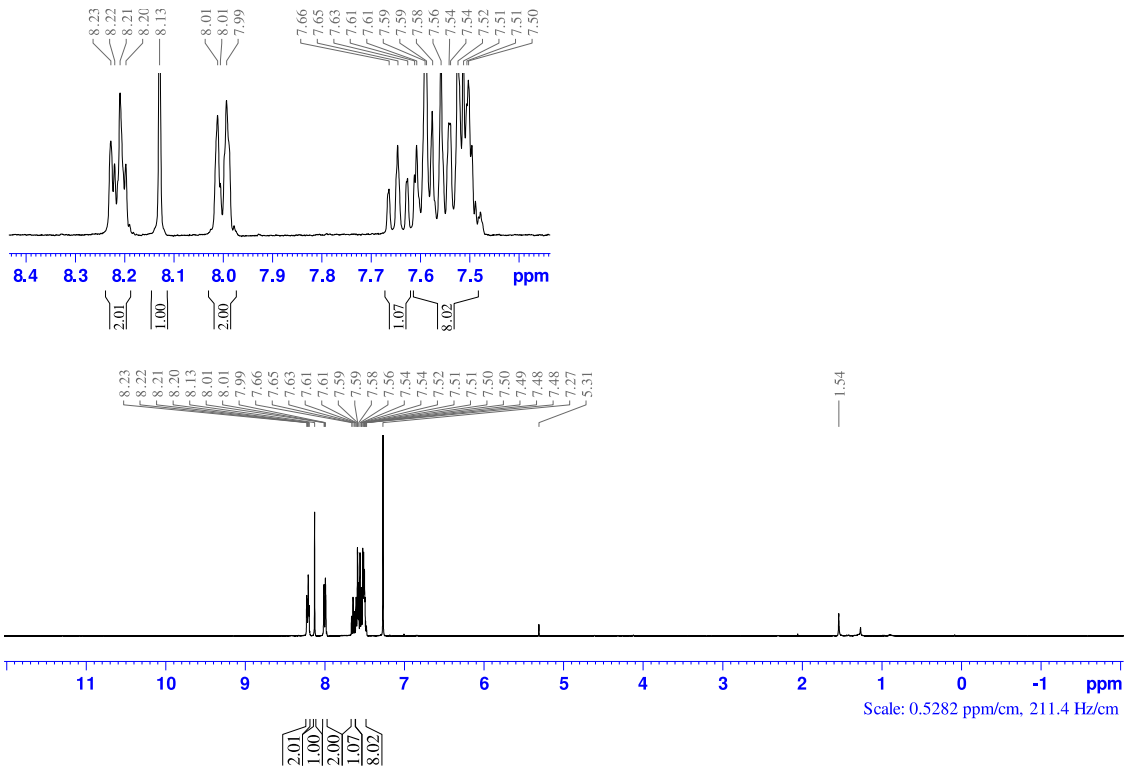
HPLC Analysis for purity



5-phenylbenzo[b]naphtho-[1,2-d]thiophene

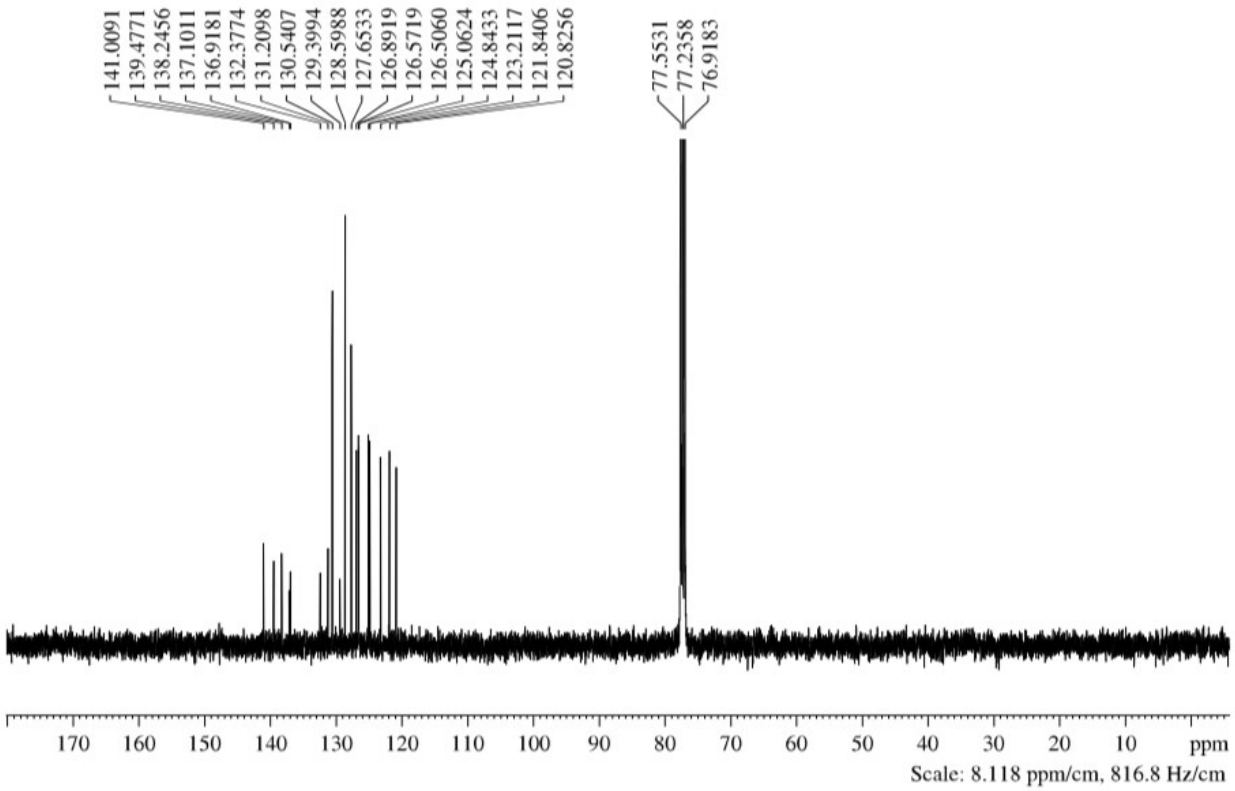


^{1}H-NMR (in $CDCl_3$)

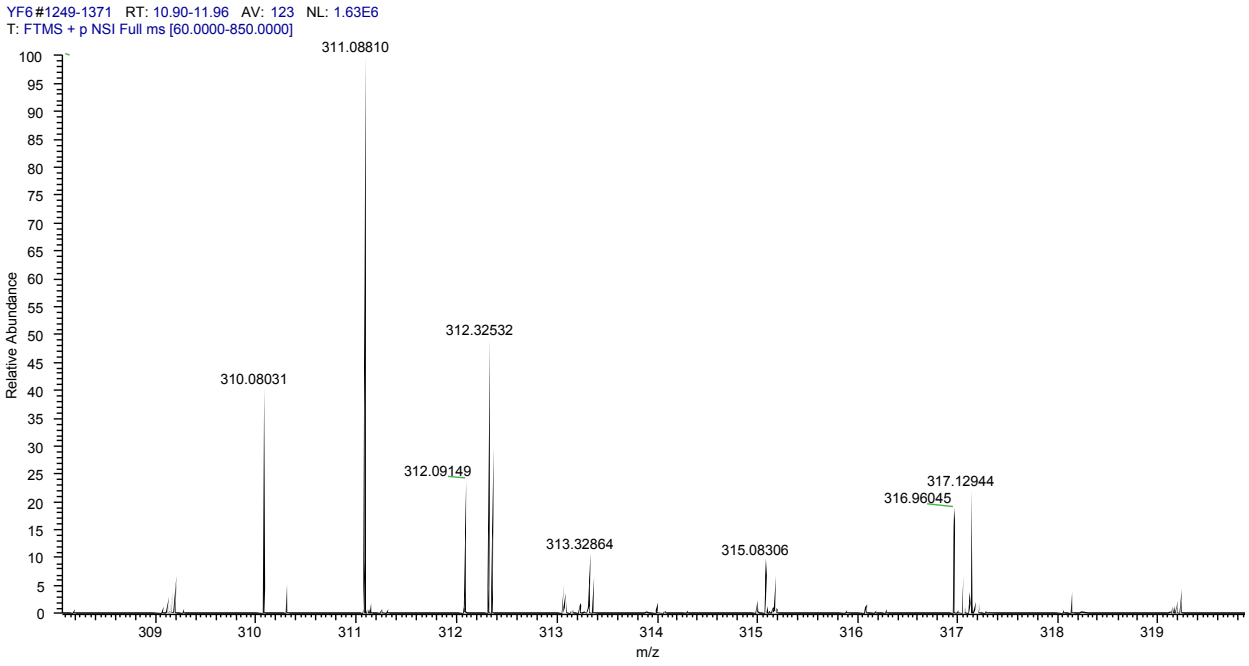


Impurities: Solvent Peak Chloroform (7.27 ppm), Dichloromethane (5.31 ppm), Water (1.54 ppm)

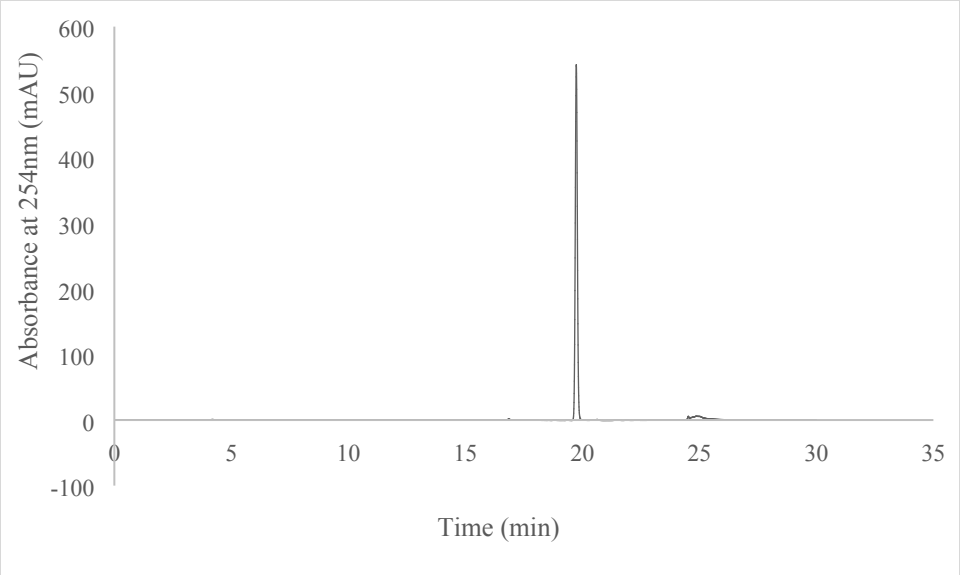
^{13}C-NMR (in $CDCl_3$)



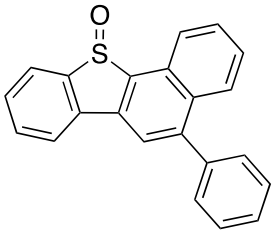
HRMS



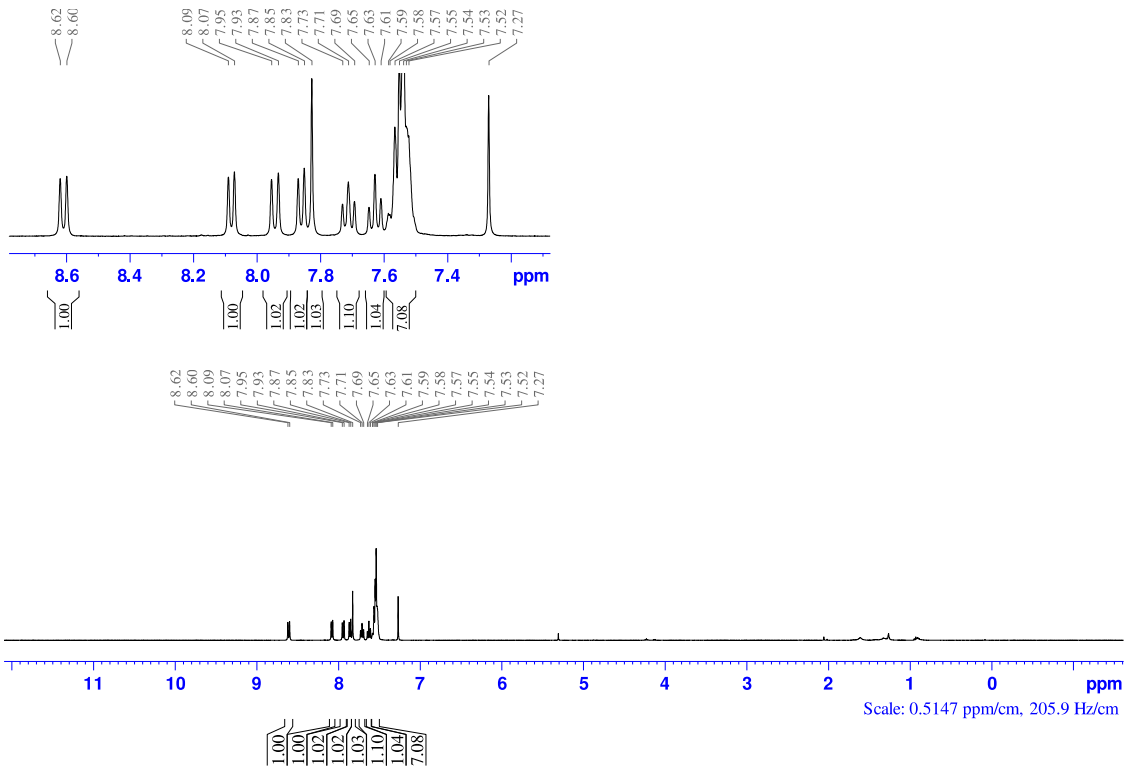
HPLC Signal for purity



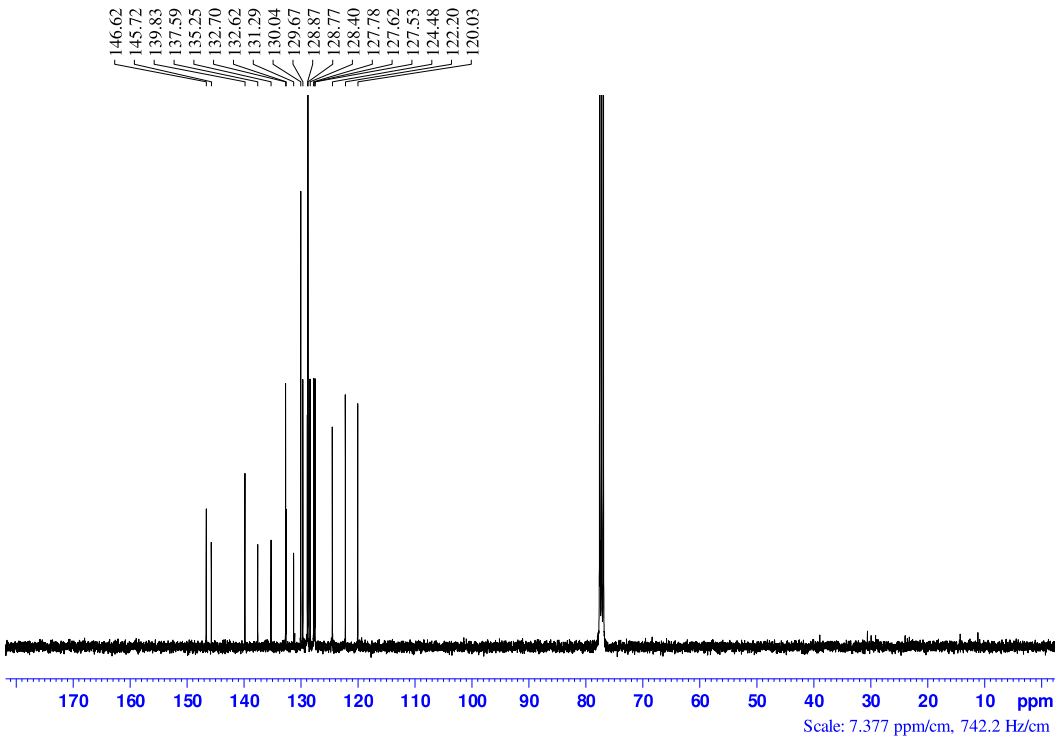
5-phenylbenzo[b]naphtho-[1,2-d]thiophene-S-oxide



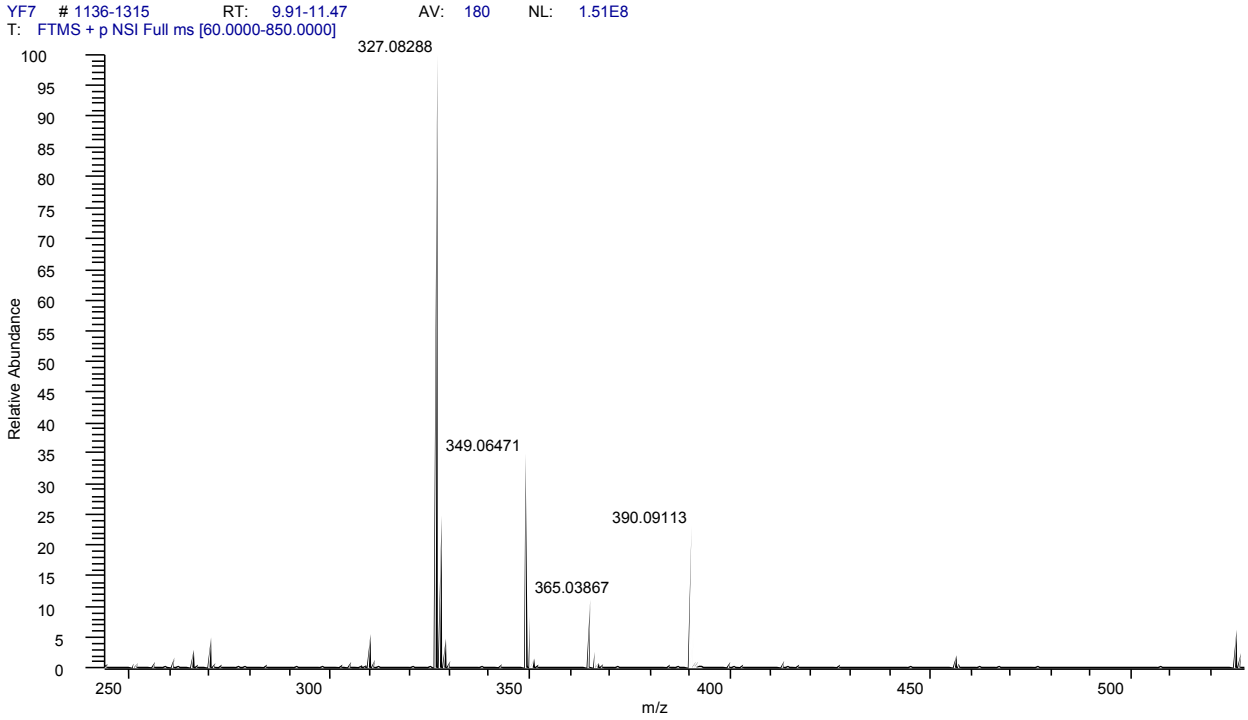
^{1}H-NMR (in $CDCl_3$)



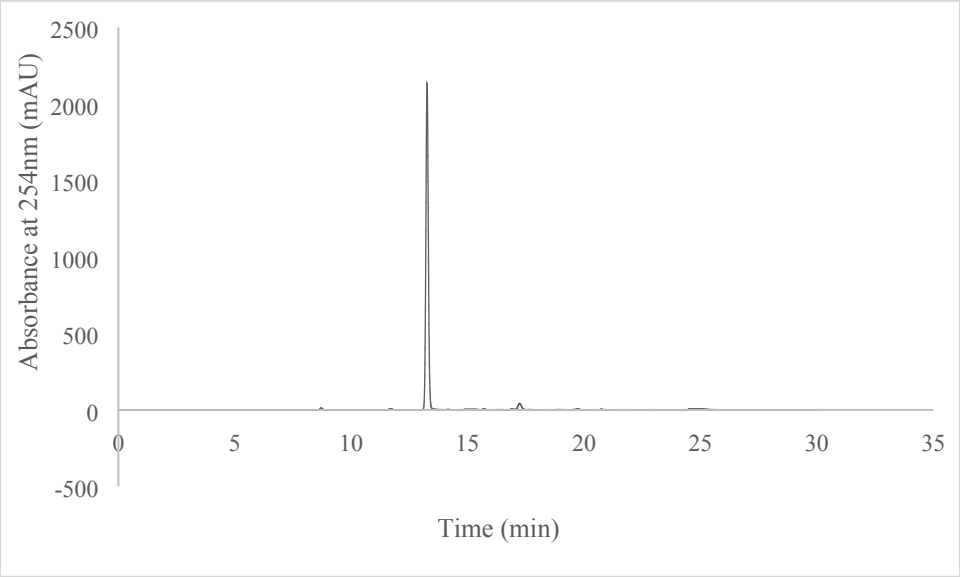
^{13}C-NMR (in $CDCl_3$)



HRMS

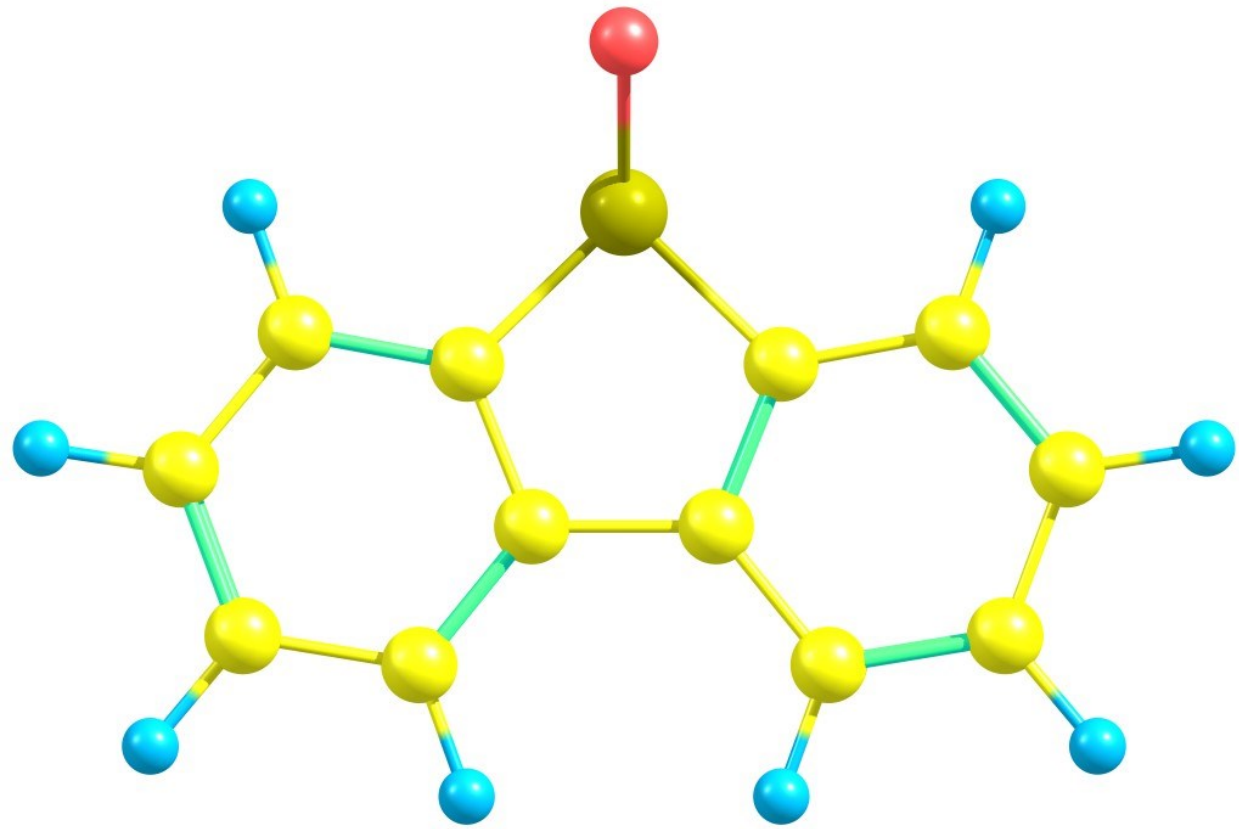


HPLC signal (for purity)



2. Optimized geometry using HSEH1PBE with 6-311G(d,p) basis set[1]

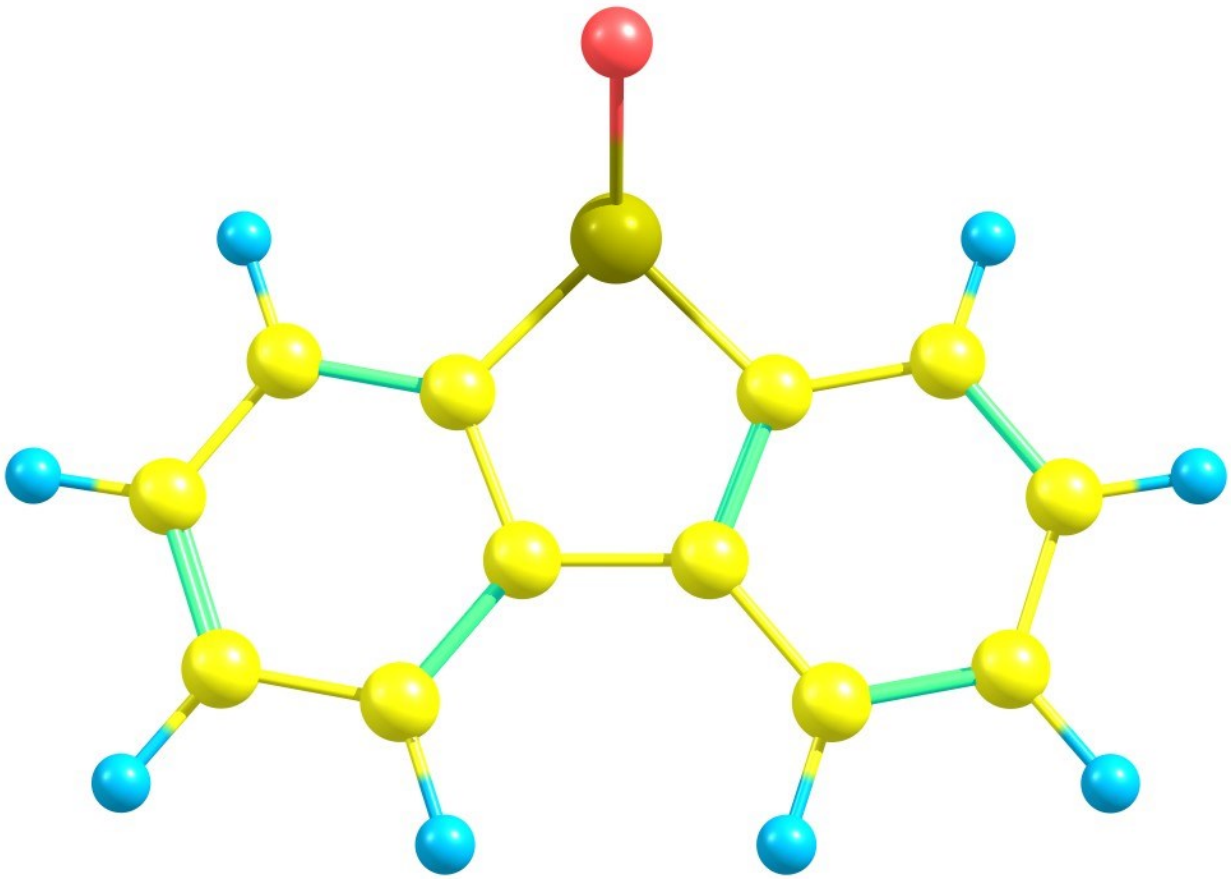
A1) DBTO (Charge = 0, Multiplicity = 1)



Coordinates

C	-0.731700000000	-0.816666000000	-0.048182000000
C	-1.606430000000	-1.895278000000	0.047422000000
C	-1.258377000000	0.476146000000	-0.118410000000
C	-2.975070000000	-1.657584000000	0.098028000000
C	-2.617291000000	0.725185000000	-0.071982000000
C	-3.480052000000	-0.360068000000	0.049740000000
H	-1.227675000000	-2.910790000000	0.094535000000
H	-3.659545000000	-2.494586000000	0.182810000000
H	-2.996259000000	1.740632000000	-0.114454000000
H	-4.550129000000	-0.194346000000	0.105347000000
C	0.731907000000	-0.816534000000	-0.048055000000
C	1.258406000000	0.476386000000	-0.117681000000
C	1.606747000000	-1.895113000000	0.046871000000
C	2.617295000000	0.725525000000	-0.071374000000
C	2.975375000000	-1.657296000000	0.097514000000
C	3.480179000000	-0.359693000000	0.049885000000
H	1.228091000000	-2.910690000000	0.093336000000
H	2.996170000000	1.741026000000	-0.113392000000
H	3.659958000000	-2.494265000000	0.181731000000
H	4.550233000000	-0.193823000000	0.105507000000
S	-0.000111000000	1.745336000000	-0.367871000000
O	-0.000625000000	2.765177000000	0.733481000000

A2) DBTO (Charge = 0, Multiplicity = 3)



Coordinates

C	-0.719779000000	-0.827922000000	-0.005504000000
C	-1.621251000000	-1.874356000000	0.186266000000
C	-1.250351000000	0.472154000000	-0.239358000000
C	-2.985398000000	-1.637048000000	0.122962000000
C	-2.626946000000	0.721998000000	-0.280527000000
C	-3.486456000000	-0.344780000000	-0.116612000000
H	-1.252544000000	-2.876599000000	0.379947000000
H	-3.677884000000	-2.459304000000	0.263373000000
H	-3.003864000000	1.725137000000	-0.446566000000
H	-4.557185000000	-0.183843000000	-0.168966000000
C	0.718323000000	-0.828526000000	-0.005784000000
C	1.250051000000	0.471216000000	-0.238137000000
C	1.618941000000	-1.875996000000	0.184551000000
C	2.626724000000	0.719943000000	-0.279417000000
C	2.983269000000	-1.639813000000	0.121274000000
C	3.485419000000	-0.347780000000	-0.116822000000
H	1.249369000000	-2.878131000000	0.377090000000
H	3.004451000000	1.722952000000	-0.444340000000
H	3.675045000000	-2.462869000000	0.260509000000
H	4.556273000000	-0.187663000000	-0.169031000000
S	0.000393000000	1.680161000000	-0.192722000000

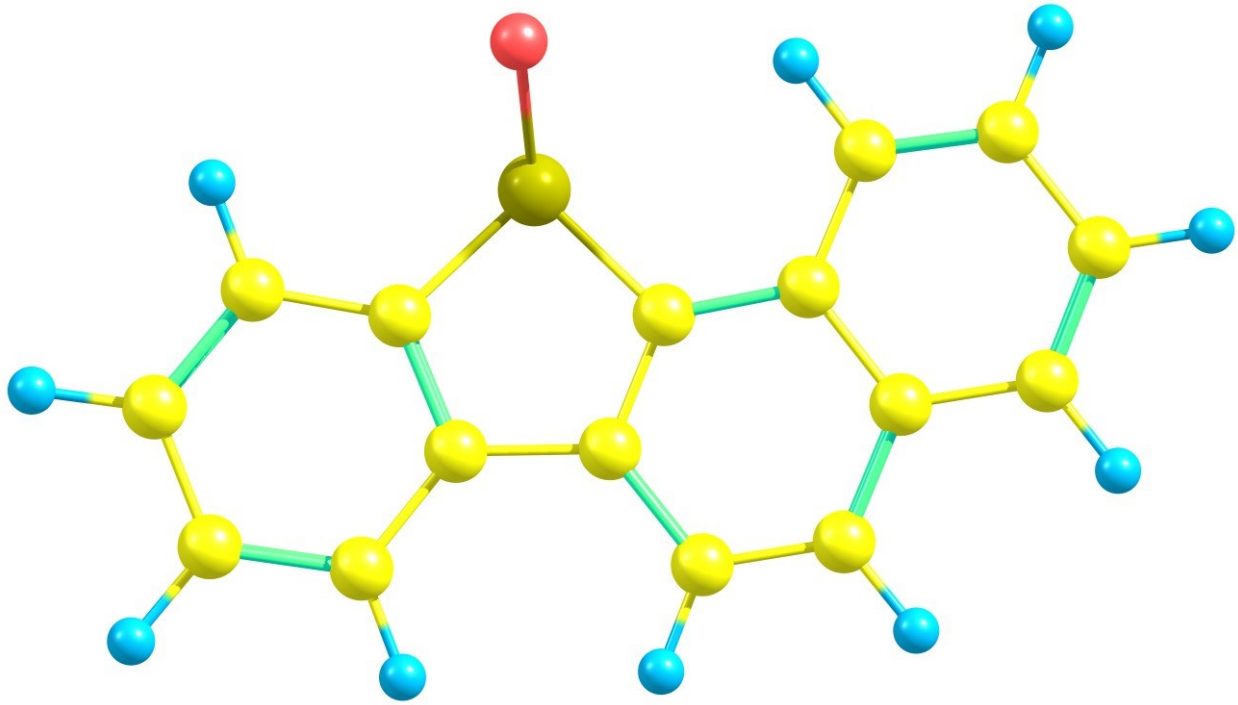
O 0.005597000000 2.832902000000 0.879273000000

A3) Energy calculations for DBTO

Charge	Multiplicity	Sum of electronic and thermal free energies (hartree/particle)
0	1	-934.761157
0	3	-934.664716
Difference		0.096441

In kcal/mol = 0.096441* 627.5 = 60.5 kcal/mol

B1) Benzonaphtho(1,2-d)thiophene (1) (Charge = 0, Multiplicity = 1)

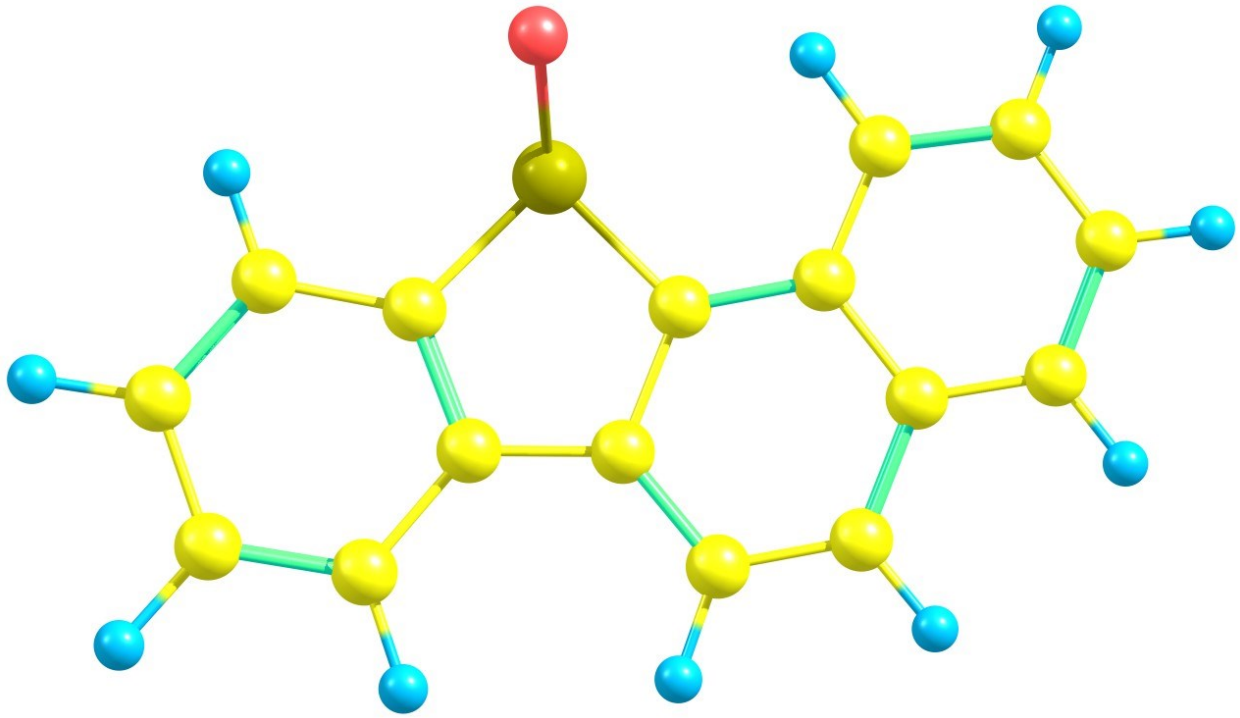


Coordinates

C 4.449124000000 -0.139866000000 0.079334000000
C 3.414694000000 -1.063889000000 -0.045211000000
C 4.172974000000 1.224903000000 0.115541000000
H 3.613451000000 -2.129556000000 -0.079739000000
H 4.989911000000 1.933052000000 0.201479000000
C 2.120539000000 -0.584657000000 -0.101733000000
C 2.865174000000 1.693474000000 0.052566000000
H 2.665767000000 2.759090000000 0.090638000000
C 1.820284000000 0.778864000000 -0.041231000000
H 5.474553000000 -0.485661000000 0.146398000000
C -0.360257000000 -0.143294000000 -0.080319000000

C	-1.770376000000	-0.157411000000	-0.044344000000
C	0.378530000000	1.023337000000	-0.046404000000
C	-2.429565000000	1.108109000000	0.019307000000
C	-0.287619000000	2.266607000000	0.005474000000
H	0.281452000000	3.189665000000	0.025512000000
C	-1.656321000000	2.296855000000	0.034499000000
H	-2.176879000000	3.248512000000	0.075940000000
S	0.660114000000	-1.597359000000	-0.380926000000
C	-2.542267000000	-1.343258000000	-0.039728000000
C	-3.910854000000	-1.273984000000	0.003270000000
C	-4.567128000000	-0.027082000000	0.052915000000
C	-3.841789000000	1.136420000000	0.065218000000
H	-2.036537000000	-2.302574000000	-0.041494000000
H	-4.495542000000	-2.187391000000	0.008826000000
H	-5.650556000000	0.007728000000	0.088105000000
H	-4.343689000000	2.097880000000	0.112141000000
O	0.498171000000	-2.667973000000	0.661510000000

B2) Benzonaphtho(1,2-d)thiophene (1) (Charge = 0, Multiplicity = 3)



Coordinates

C	4.435600000000	-0.193406000000	-0.015848000000
C	3.377998000000	-1.086275000000	-0.149364000000
C	4.189729000000	1.184191000000	0.107719000000
H	3.557277000000	-2.152494000000	-0.237755000000
H	5.027162000000	1.865381000000	0.212641000000

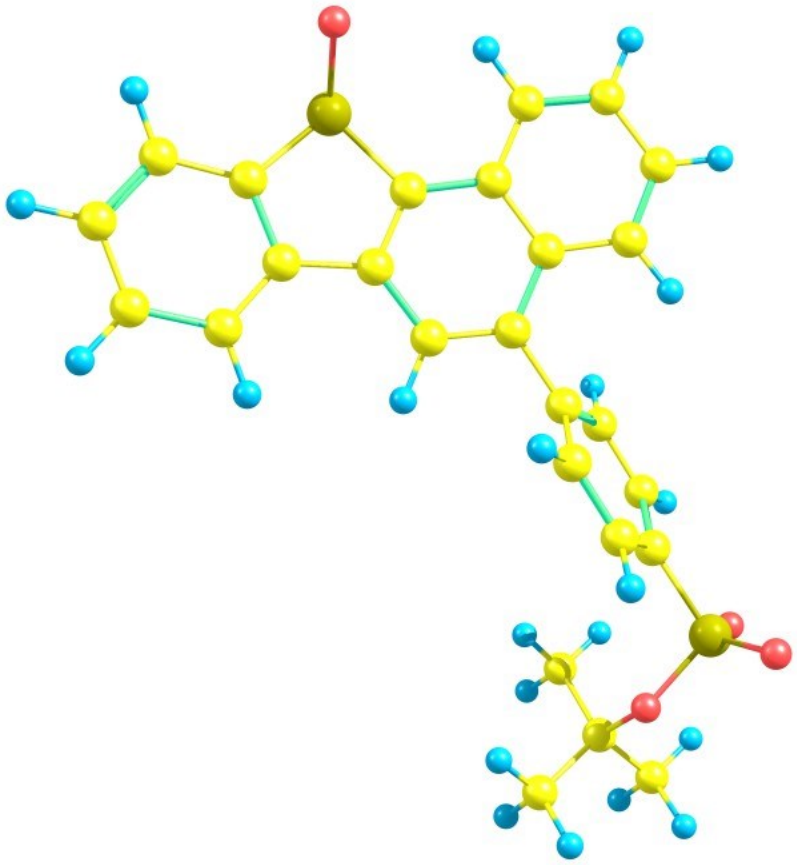
C	2.088948000000	-0.587301000000	-0.159666000000
C	2.904244000000	1.681366000000	0.106485000000
H	2.728523000000	2.745672000000	0.220586000000
C	1.815803000000	0.794440000000	-0.022329000000
H	5.455311000000	-0.561239000000	-0.008044000000
C	-0.364166000000	-0.164391000000	-0.143513000000
C	-1.768213000000	-0.164300000000	-0.065490000000
C	0.426769000000	1.077282000000	-0.026909000000
C	-2.425733000000	1.110529000000	0.007370000000
C	-0.245085000000	2.288557000000	0.053790000000
H	0.311623000000	3.217916000000	0.115505000000
C	-1.628638000000	2.316160000000	0.055896000000
H	-2.150385000000	3.265090000000	0.117709000000
S	0.628847000000	-1.633159000000	-0.337110000000
C	-2.548308000000	-1.335147000000	-0.057861000000
C	-3.947847000000	-1.263918000000	-0.033793000000
C	-4.576363000000	-0.040239000000	0.007333000000
C	-3.806384000000	1.147702000000	0.035602000000
H	-2.052267000000	-2.299056000000	-0.039037000000
H	-4.528115000000	-2.179638000000	-0.034881000000
H	-5.658307000000	0.023051000000	0.030146000000
H	-4.309115000000	2.108870000000	0.080286000000
O	0.498326000000	-2.561813000000	0.842510000000

B3) Energy calculations for 1

Charge	Multiplicity	Sum of electronic and thermal free energies (hartree/particle)
0	1	-1088.226958
0	3	-1088.146953
Difference		0.080005

in kcal/mol = 0.080005 * 627.5 = 50.2 kcal/mol

C1) 5-neopentylsulfonatephenylbenzonaphtho(1,2-d)thiophene (2) (Charge = 0, Multiplicity = 1)

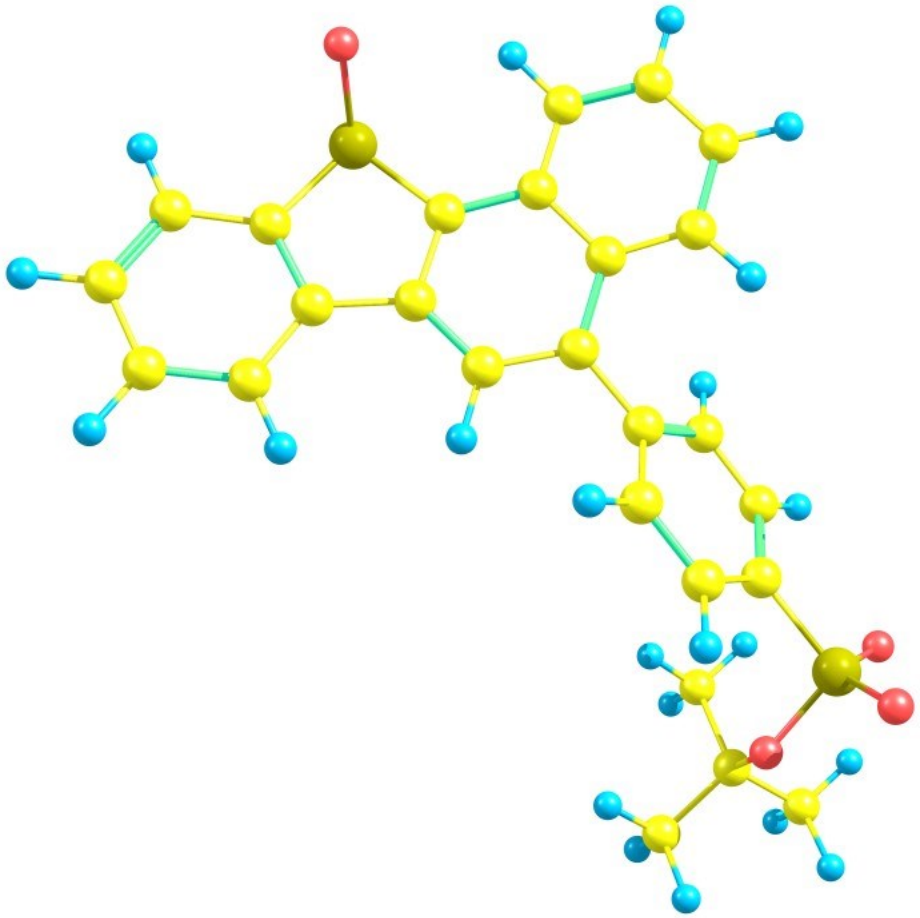


Coordinates

C	5.750362000000	3.846545000000	0.208670000000
C	6.136166000000	2.537916000000	-0.070331000000
C	4.405831000000	4.160240000000	0.392965000000
H	7.178540000000	2.278839000000	-0.220821000000
H	4.120139000000	5.185900000000	0.599155000000
C	5.151719000000	1.570811000000	-0.128501000000
C	3.424671000000	3.176902000000	0.326313000000
H	2.382682000000	3.435769000000	0.481446000000
C	3.800311000000	1.860069000000	0.077788000000
H	6.501401000000	4.625148000000	0.280912000000
C	3.709387000000	-0.493978000000	-0.162660000000
C	3.125008000000	-1.776787000000	-0.179918000000
C	2.972826000000	0.655012000000	0.037164000000
C	1.707172000000	-1.863463000000	-0.006990000000
C	1.575890000000	0.562579000000	0.181898000000
H	0.982195000000	1.463763000000	0.294467000000
C	0.943017000000	-0.660366000000	0.140770000000
S	5.426011000000	-0.146878000000	-0.587508000000
C	3.888510000000	-2.960519000000	-0.314538000000
C	3.277178000000	-4.186332000000	-0.281734000000

C	1.885464000000	-4.281511000000	-0.091945000000
C	1.121588000000	-3.150376000000	0.047729000000
H	4.966370000000	-2.882707000000	-0.404671000000
H	3.870511000000	-5.088658000000	-0.379972000000
H	1.415372000000	-5.257476000000	-0.040880000000
H	0.055531000000	-3.239181000000	0.219584000000
O	6.415996000000	-0.827377000000	0.314821000000
C	-0.535389000000	-0.691133000000	0.243254000000
C	-1.313603000000	-1.259194000000	-0.769122000000
C	-2.699318000000	-1.240017000000	-0.695028000000
C	-3.308838000000	-0.652481000000	0.404633000000
C	-2.559194000000	-0.092055000000	1.432493000000
C	-1.176695000000	-0.107711000000	1.341696000000
H	-0.827813000000	-1.705644000000	-1.629840000000
H	-3.310412000000	-1.676223000000	-1.476580000000
H	-3.053949000000	0.338129000000	2.295496000000
H	-0.579349000000	0.315689000000	2.141986000000
S	-5.082084000000	-0.667338000000	0.533177000000
O	-5.433945000000	-1.129435000000	1.852877000000
O	-5.617034000000	-1.305228000000	-0.654259000000
O	-5.440071000000	0.900394000000	0.547929000000
C	-5.837533000000	1.698858000000	-0.634441000000
C	-7.239950000000	1.292170000000	-1.054485000000
H	-7.257628000000	0.267688000000	-1.426689000000
H	-7.924818000000	1.372654000000	-0.207214000000
H	-7.590287000000	1.960208000000	-1.846486000000
C	-5.815667000000	3.110075000000	-0.073714000000
H	-6.130293000000	3.818445000000	-0.844383000000
H	-6.496119000000	3.192397000000	0.776117000000
H	-4.809717000000	3.376219000000	0.258261000000
C	-4.829764000000	1.543108000000	-1.761457000000
H	-5.084698000000	2.239603000000	-2.564545000000
H	-3.819487000000	1.776561000000	-1.416401000000
H	-4.845474000000	0.533323000000	-2.173652000000

C2) 5-neopentylsulfonatephenylbenzonaphtho(1,2-d)thiophene (2) (Charge = 0, Multiplicity = 3)



Coordinates

C	5.811281000000	-3.773514000000	-0.180725000000
C	6.113189000000	-2.484979000000	0.244148000000
C	4.515811000000	-4.094013000000	-0.604728000000
H	7.114652000000	-2.223397000000	0.568344000000
H	4.297662000000	-5.104225000000	-0.933193000000
C	5.105463000000	-1.537588000000	0.234321000000
C	3.515288000000	-3.140057000000	-0.621056000000
H	2.521405000000	-3.396718000000	-0.971876000000
C	3.802126000000	-1.832504000000	-0.202952000000
H	6.582809000000	-4.535143000000	-0.182854000000
C	3.670929000000	0.502063000000	0.283766000000
C	3.080026000000	1.783370000000	0.260196000000
C	2.942219000000	-0.683794000000	-0.171794000000
C	1.686627000000	1.878358000000	-0.072554000000
C	1.611189000000	-0.577786000000	-0.461891000000
H	1.042866000000	-1.467286000000	-0.712293000000
C	0.922786000000	0.654094000000	-0.330950000000
S	5.342872000000	0.163308000000	0.792374000000
C	3.817819000000	2.955822000000	0.490966000000

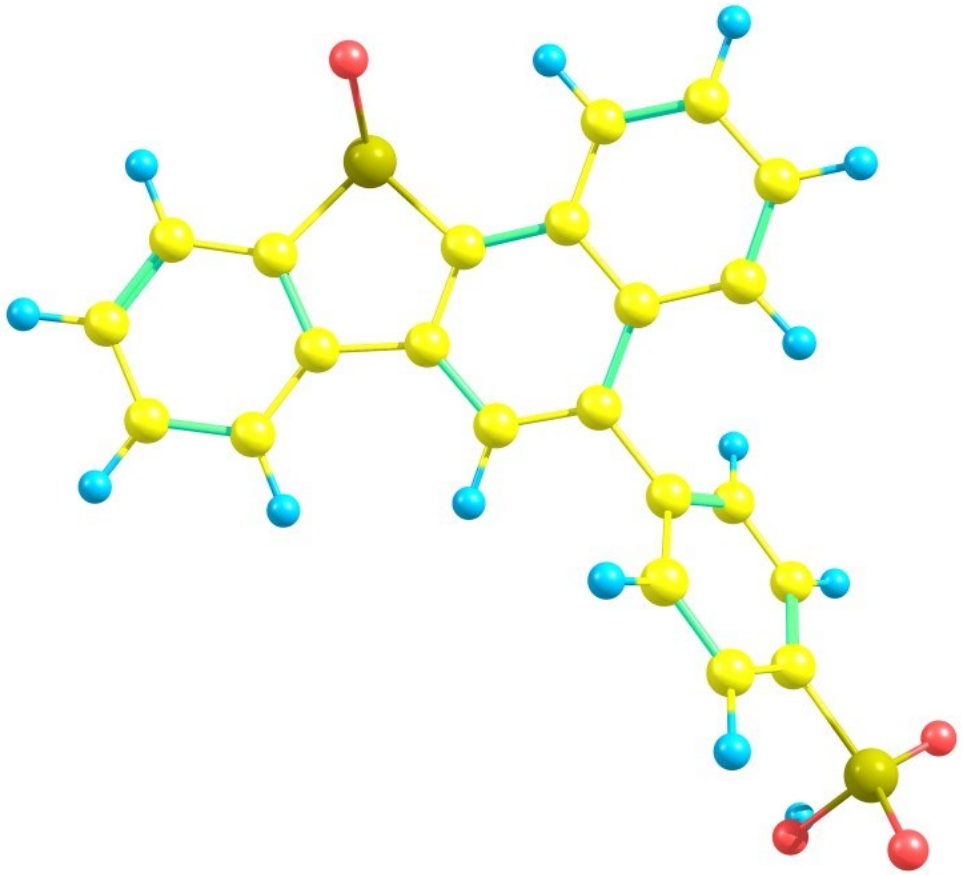
C	3.215630000000	4.215169000000	0.400945000000
C	1.890647000000	4.312019000000	0.042104000000
C	1.138891000000	3.143677000000	-0.210517000000
H	4.879127000000	2.875795000000	0.698106000000
H	3.804375000000	5.105722000000	0.588741000000
H	1.415506000000	5.280800000000	-0.061943000000
H	0.110603000000	3.248415000000	-0.534815000000
O	6.369319000000	0.864464000000	-0.057589000000
C	-0.528845000000	0.651111000000	-0.434183000000
C	-1.334942000000	1.422689000000	0.425044000000
C	-2.716221000000	1.365373000000	0.356882000000
C	-3.319657000000	0.542343000000	-0.586812000000
C	-2.553792000000	-0.224396000000	-1.463022000000
C	-1.177066000000	-0.177279000000	-1.374488000000
H	-0.866821000000	2.040037000000	1.182618000000
H	-3.334648000000	1.947603000000	1.030079000000
H	-3.038877000000	-0.836527000000	-2.214550000000
H	-0.582809000000	-0.754085000000	-2.074368000000
S	-5.087899000000	0.495485000000	-0.712808000000
O	-5.446079000000	0.622675000000	-2.104084000000
O	-5.638975000000	1.386112000000	0.290578000000
O	-5.423534000000	-1.037883000000	-0.356441000000
C	-5.782947000000	-1.542612000000	0.987647000000
C	-7.193366000000	-1.085948000000	1.321477000000
H	-7.238460000000	-0.002743000000	1.436338000000
H	-7.883227000000	-1.386745000000	0.529621000000
H	-7.515597000000	-1.552922000000	2.256578000000
C	-5.723797000000	-3.045939000000	0.779161000000
H	-6.013817000000	-3.557696000000	1.700435000000
H	-6.406869000000	-3.346069000000	-0.017942000000
H	-4.712671000000	-3.357190000000	0.507621000000
C	-4.771168000000	-1.095630000000	2.030205000000
H	-4.989895000000	-1.599469000000	2.975327000000
H	-3.755427000000	-1.362619000000	1.728399000000
H	-4.824031000000	-0.019465000000	2.201705000000

C3) Energy calculations for 2

Charge	Multiplicity	Sum of electronic and thermal free energies (hartree/particle)
0	1	-2099.540992
0	3	-2099.464567
Difference		0.076425

in kcal/mol = 0.076425 * 627.5 = 47.9 kcal/mol

D1) 5-phenylsulfonicacidbenzonaphtho(1,2-d)thiophene (3) (Charge = 0, Multiplicity = 1)

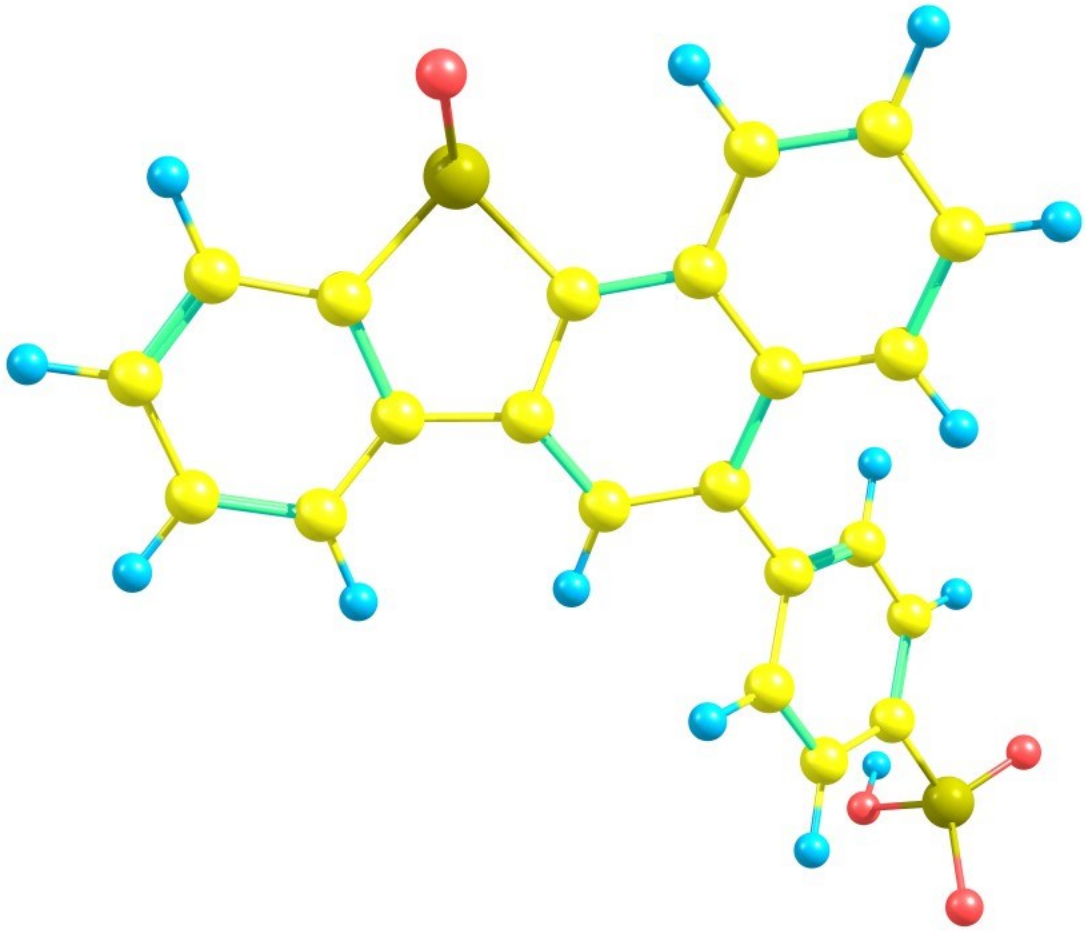


Coordinates

C	-5.415741000000	-3.348146000000	-0.013607000000
C	-5.606061000000	-1.974196000000	-0.136391000000
C	-4.129140000000	-3.878096000000	0.050442000000
H	-6.601292000000	-1.546818000000	-0.191964000000
H	-3.997100000000	-4.951176000000	0.134851000000
C	-4.486876000000	-1.165255000000	-0.162725000000
C	-3.011005000000	-3.051825000000	0.017360000000
H	-2.015786000000	-3.479342000000	0.077106000000
C	-3.188553000000	-1.674561000000	-0.074597000000
H	-6.274476000000	-4.008540000000	0.030359000000
C	-2.744490000000	0.651446000000	-0.085671000000
C	-1.970294000000	1.827094000000	-0.011688000000
C	-2.186654000000	-0.609557000000	-0.048775000000
C	-0.549660000000	1.683095000000	0.077950000000
C	-0.786906000000	-0.742225000000	0.015382000000
H	-0.334860000000	-1.728492000000	-0.000839000000
C	0.024407000000	0.370486000000	0.056354000000
S	-4.512325000000	0.613145000000	-0.432834000000
C	-2.547692000000	3.118497000000	0.022377000000

C	-1.753702000000	4.229185000000	0.137872000000
C	-0.356451000000	4.095641000000	0.246071000000
C	0.229530000000	2.855202000000	0.223060000000
H	-3.627805000000	3.210972000000	-0.004680000000
H	-2.204739000000	5.214801000000	0.168978000000
H	0.260441000000	4.979730000000	0.363906000000
H	1.303489000000	2.766171000000	0.335241000000
O	-5.339914000000	1.335845000000	0.591900000000
C	1.492525000000	0.167660000000	0.067081000000
C	2.301942000000	0.724089000000	-0.928932000000
C	3.668065000000	0.489129000000	-0.946409000000
C	4.227544000000	-0.305773000000	0.046495000000
C	3.450577000000	-0.862347000000	1.054266000000
C	2.084907000000	-0.623534000000	1.056288000000
H	1.852078000000	1.335290000000	-1.703509000000
H	4.301336000000	0.927542000000	-1.709011000000
H	3.917506000000	-1.453707000000	1.833095000000
H	1.467805000000	-1.036631000000	1.846686000000
S	5.970372000000	-0.624640000000	0.024500000000
O	6.407328000000	-0.887967000000	1.369539000000
O	6.612646000000	0.350910000000	-0.831259000000
O	6.051862000000	-2.051902000000	-0.749228000000
H	6.291642000000	-1.877039000000	-1.667696000000

D2) 5-neopentylsulfonatephenylbenzonaphtho(1,2-d)thiophene (3) (Charge = 0, Multiplicity = 3)



Coordinates

C	5.423909000000	-3.322629000000	0.063777000000
C	5.568074000000	-1.960933000000	0.303720000000
C	4.161104000000	-3.865412000000	-0.201493000000
H	6.542007000000	-1.527942000000	0.504410000000
H	4.066906000000	-4.929859000000	-0.385909000000
C	4.436734000000	-1.166302000000	0.269806000000
C	3.035529000000	-3.063217000000	-0.243379000000
H	2.066412000000	-3.493538000000	-0.472102000000
C	3.161971000000	-1.686251000000	-0.012400000000
H	6.294420000000	-3.968527000000	0.083935000000
C	2.734619000000	0.655431000000	0.185825000000
C	1.971095000000	1.833555000000	0.039057000000
C	2.151296000000	-0.666017000000	-0.050205000000
C	0.560847000000	1.698705000000	-0.190779000000
C	0.803361000000	-0.777259000000	-0.237877000000
H	0.351543000000	-1.759967000000	-0.319742000000
C	-0.041980000000	0.362210000000	-0.209663000000
S	4.462855000000	0.607957000000	0.607276000000

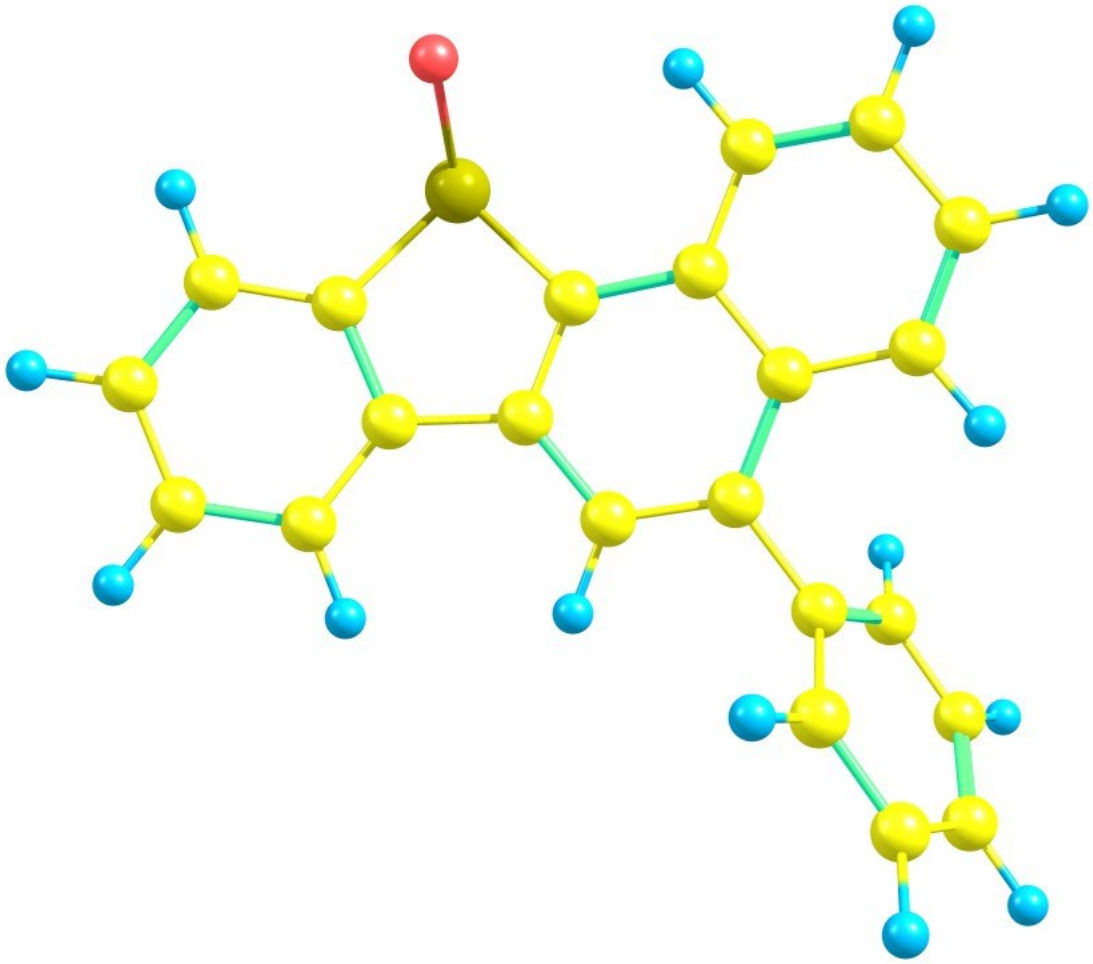
C	2.552417000000	3.111805000000	0.046615000000
C	1.777926000000	4.255913000000	-0.171423000000
C	0.433911000000	4.127550000000	-0.438605000000
C	-0.162785000000	2.848459000000	-0.464708000000
H	3.625074000000	3.199171000000	0.178680000000
H	2.247889000000	5.232550000000	-0.155684000000
H	-0.175092000000	5.000956000000	-0.641938000000
H	-1.212744000000	2.771404000000	-0.720275000000
O	5.333316000000	1.329950000000	-0.386637000000
C	-1.480594000000	0.158414000000	-0.172438000000
C	-2.322116000000	0.957013000000	0.629045000000
C	-3.681770000000	0.718546000000	0.701698000000
C	-4.232703000000	-0.320013000000	-0.043888000000
C	-3.434938000000	-1.124266000000	-0.854247000000
C	-2.075502000000	-0.889042000000	-0.907124000000
H	-1.890130000000	1.746094000000	1.232774000000
H	-4.322417000000	1.334888000000	1.321865000000
H	-3.889641000000	-1.905170000000	-1.452472000000
H	-1.461831000000	-1.494551000000	-1.564412000000
S	-5.968121000000	-0.635599000000	0.047692000000
O	-6.393937000000	-1.241341000000	-1.186343000000
O	-6.623078000000	0.522518000000	0.620044000000
O	-6.056878000000	-1.819575000000	1.159936000000
H	-6.275962000000	-1.413201000000	2.007507000000

D3) Energy calculations for 3

Charge	Multiplicity	Sum of electronic and thermal free energies (hartree/particle)
0	1	-1942.539267
0	3	-1942.462598
Difference		0.076669

in kcal/mol = 0.076669 * 627.5 = 48.1 kcal/mol

E1) 5-phenylbenzonaptho(1,2-d)thiophene (Charge = 0, Multiplicity = 1)

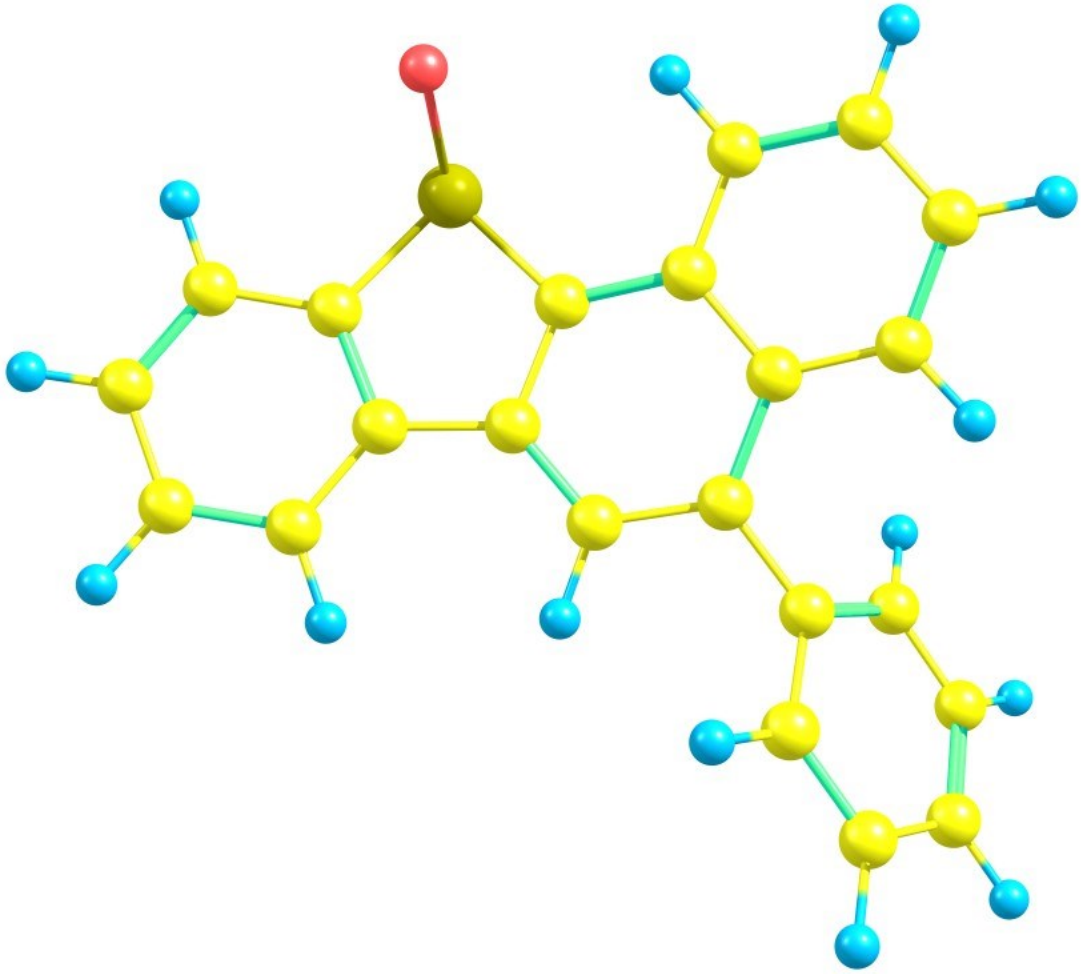


Coordinates

C	4.761393000000	-2.339283000000	0.007195000000
C	4.576375000000	-0.962362000000	0.103801000000
C	3.663876000000	-3.196446000000	-0.020698000000
H	5.420412000000	-0.281754000000	0.131222000000
H	3.823876000000	-4.267208000000	-0.084841000000
C	3.281453000000	-0.483395000000	0.141994000000
C	2.365355000000	-2.700250000000	0.022974000000
H	1.520665000000	-3.380201000000	-0.008699000000
C	2.166768000000	-1.324350000000	0.089029000000
H	5.765491000000	-2.745183000000	-0.044180000000
C	1.112754000000	0.795231000000	0.074938000000
C	0.046829000000	1.715269000000	0.007950000000
C	0.914260000000	-0.569710000000	0.068296000000
C	-1.282564000000	1.188516000000	-0.046850000000
C	-0.397815000000	-1.078094000000	0.036648000000
H	-0.565585000000	-2.149476000000	0.071679000000
C	-1.482947000000	-0.230051000000	-0.001791000000
S	2.831376000000	1.242569000000	0.378173000000

C	0.250111000000	3.114368000000	-0.051104000000
C	-0.818350000000	3.965707000000	-0.155841000000
C	-2.128699000000	3.455573000000	-0.227482000000
C	-2.353977000000	2.102983000000	-0.180806000000
H	1.264744000000	3.497255000000	-0.050075000000
H	-0.653224000000	5.036401000000	-0.205372000000
H	-2.965402000000	4.137328000000	-0.335132000000
H	-3.364035000000	1.719624000000	-0.261385000000
O	3.415953000000	2.132514000000	-0.683028000000
C	-2.843586000000	-0.819952000000	0.002924000000
C	-3.761319000000	-0.511174000000	1.011723000000
C	-5.016166000000	-1.104946000000	1.031382000000
C	-5.376762000000	-2.012703000000	0.041754000000
C	-4.472721000000	-2.326932000000	-0.965386000000
C	-3.215044000000	-1.737109000000	-0.983194000000
H	-3.478081000000	0.185715000000	1.793675000000
H	-5.713114000000	-0.862004000000	1.826422000000
H	-6.358478000000	-2.473584000000	0.056683000000
H	-4.747985000000	-3.030648000000	-1.743721000000
H	-2.514253000000	-1.972836000000	-1.777553000000

E2) 5-phenylbenzonaptho(1,2-d)thiophene (Charge = 0, Multiplicity = 3)



Coordinates

C	4.767703000000	-2.302470000000	0.071133000000
C	4.545712000000	-0.940606000000	0.236967000000
C	3.688406000000	-3.178069000000	-0.108467000000
H	5.373181000000	-0.251686000000	0.368666000000
H	3.878777000000	-4.238064000000	-0.236845000000
C	3.241810000000	-0.478735000000	0.219761000000
C	2.388377000000	-2.711066000000	-0.134273000000
H	1.563868000000	-3.397902000000	-0.293512000000
C	2.143292000000	-1.337687000000	0.024763000000
H	5.780316000000	-2.689604000000	0.081541000000
C	1.108696000000	0.809750000000	0.160108000000
C	0.046870000000	1.729454000000	0.033899000000
C	0.897770000000	-0.632943000000	-0.001692000000
C	-1.284716000000	1.208574000000	-0.105316000000
C	-0.382008000000	-1.107514000000	-0.112571000000
H	-0.559218000000	-2.177622000000	-0.145104000000
C	-1.496822000000	-0.241302000000	-0.082025000000
S	2.808424000000	1.258893000000	0.444629000000

C	0.254891000000	3.117876000000	-0.011577000000
C	-0.816304000000	4.001663000000	-0.183323000000
C	-2.088323000000	3.504768000000	-0.349726000000
C	-2.312699000000	2.109890000000	-0.328088000000
H	1.268763000000	3.497979000000	0.044075000000
H	-0.631650000000	5.069581000000	-0.208939000000
H	-2.926006000000	4.174070000000	-0.510259000000
H	-3.315918000000	1.740513000000	-0.502904000000
O	3.385910000000	2.097608000000	-0.666488000000
C	-2.833751000000	-0.826850000000	-0.012858000000
C	-3.815770000000	-0.322361000000	0.858602000000
C	-5.060830000000	-0.922892000000	0.954462000000
C	-5.368215000000	-2.035614000000	0.177291000000
C	-4.409559000000	-2.548941000000	-0.690702000000
C	-3.159072000000	-1.958912000000	-0.780249000000
H	-3.577314000000	0.524062000000	1.492928000000
H	-5.794259000000	-0.526163000000	1.648473000000
H	-6.345321000000	-2.500338000000	0.249615000000
H	-4.641182000000	-3.410758000000	-1.307584000000
H	-2.428811000000	-2.353307000000	-1.479031000000

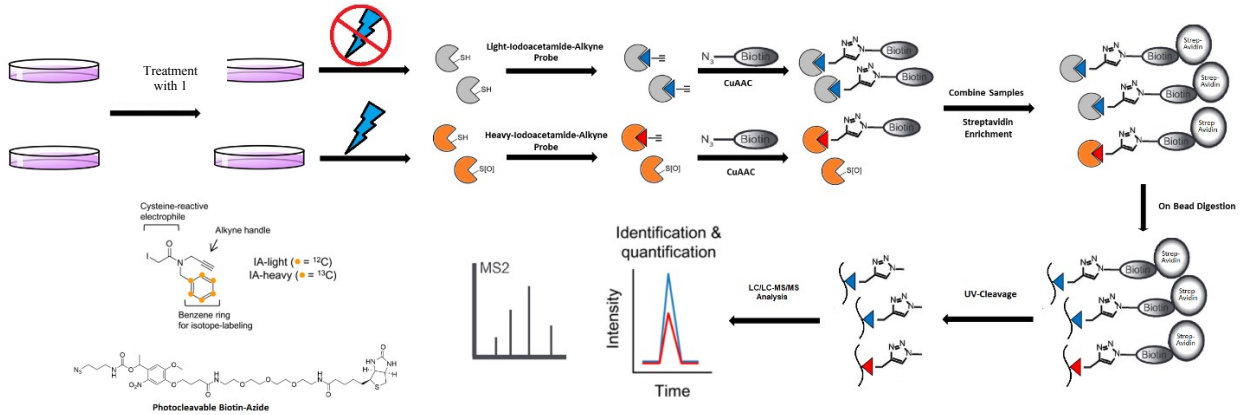
E3) Energy calculations for 6

Charge	Multiplicity	Sum of electronic and thermal free energies (hartree/particle)
0	1	-1319.002595
0	3	-1318.925184
Difference		0.077411

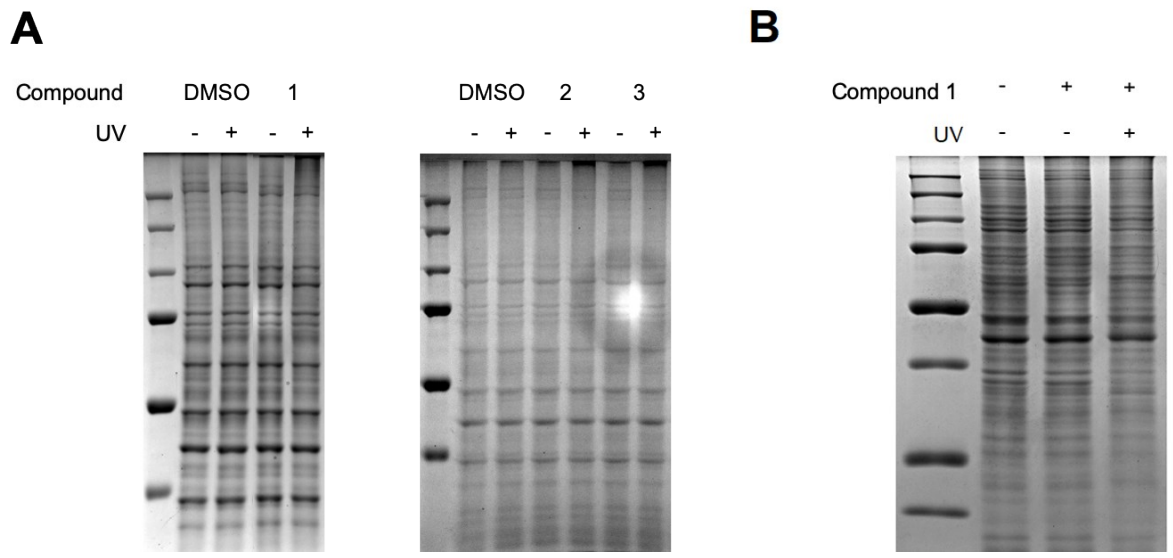
in kcal/mol = 0.077411 * 627.5 = 48.6 kcal/mol

3. Figures

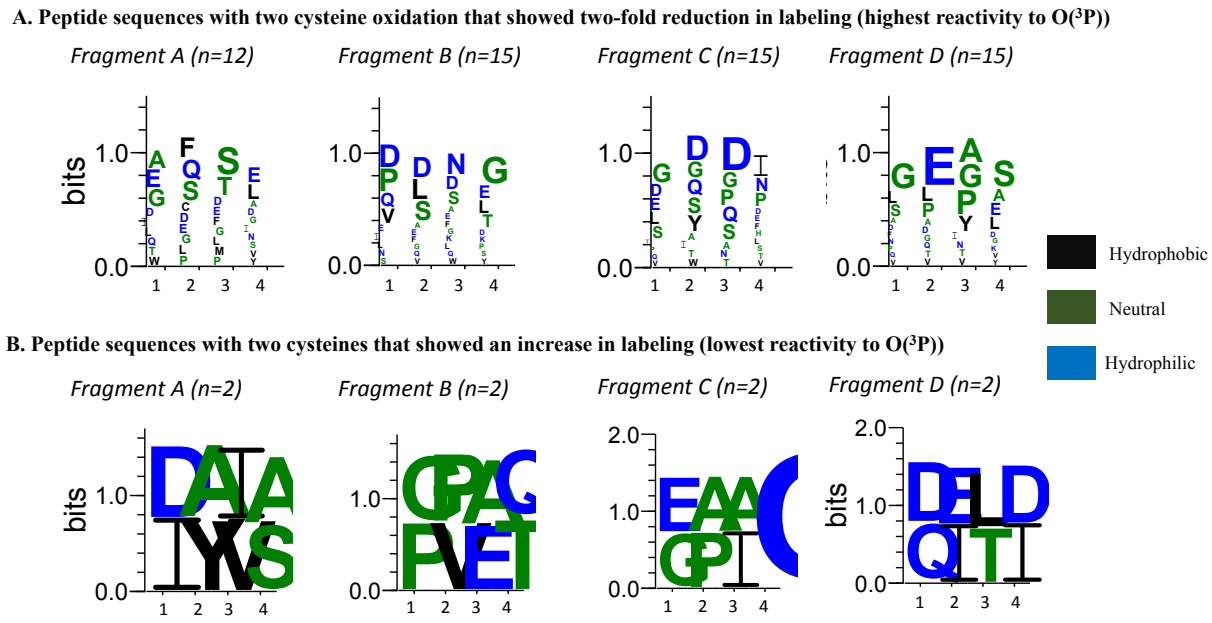
S1. isoTOP-ABPP workflow scheme



S2. (A) Coomassie staining in lysate treated with 1-3 -/+ UV irradiation (B) Coomassie staining in lysates from live HeLa cells -/+ treatment with 1 -/+ UV irradiation



S3. (Generated using WebLogo) [2,3]: A) Sequence Logos for peptides with two modified cysteines exhibiting two-fold reduction in labeling segmented by "C" in the sequence B) Sequence Logos for peptides with two modified cysteines that showed an increase in labeling segmented by "C" in the sequence



4. Tables

Table S1 – Distribution of peptide sequences based on cysteine reactivity and amino acid length

Cysteine reactivity	Sequence criteria	Single cysteine		Two cysteines			
		Fragment A	Fragment B	Fragment A	Fragment B	Fragment C	Fragment D
Two-fold reduction in labeling (n=461)	Sequence number less than 4	176	131	15	12	12	12
	Sequences	258	303	12	15	15	15
Increase in labeling (n=200)	Sequence number less than 4	58	61	2	2	2	2
	Sequences	138	135	2	2	2	2
No difference in labeling (n=80)	Sequences number less than 4	27	27	x	x	x	x
	Sequences	53	53	x	x	x	x

Table S2 - Summary of ten peptides with the highest reduction in labelling as a result of treatment with 1 and irradiation

Protein	**Peptide Sequence**	**$Log_2 (R_{L:H})$**
TK1 Thymidine kinase, cytosolic	YHSVC*R	4.32
DCAFDDB1- and CUL4-associated factor 7	VPC*TPVAR	4.32
ILF3 Interleukin enhancer-binding factor 3	VLEC *LASGIVMPDGSGIYDPC*EK	4.32
PKM Pyruvate kinase isozymes M1/M2	PVIC*ATQMLESMIK	4.32
LRPPRC Leucine-rich PPR motif containing protein, mitochondrial	AILQENGC*LSDSDMFSQAGLR	4.32
ANKHD1 Ankyrin repeat and KH domain-containing protein 1	DTVSLHQQC*SHR	4.32
TUBB Tubulin beta chain	VSDTVVEPYNATLSVHQLVENTDETYC*IDNEALYDIC*FR	3.22
LRRC40 Leucine-rich repeat-containing protein 40	NLSEVPQC*VWR	2.92
TUBB Tubulin beta chain	LTTPTYGDLNHLVSATMSGVTTC*LR	2.80
RRP8 Ribosomal RNA-processing protein 8	NPVHC*FDLASLDPR	2.75

Table S3- Summary of ten peptides with the least difference in labeling as a result of treatment with 1 and irradiation

Protein	**Peptide sequence**	**$Log_2 (R_{L:H})$**
HSPA4 Heat shock 70 kDa protein 4	FDEVLVNHFC*EEFGK	-0.0097
EIF3CL Eukaryotic translation initiation factor 3 subunit	C*LEEFELLGK	-0.0048
SEC13 Protein SEC13 homolog	FASGGC*DNLIK	-0.0048

SF3A1 Splicing factor 3A subunit 1	EVLDQVC*YR	-0.0048
SMU1 WD40 repeat-containing protein SMU1	NPEHFVVC*NR	0.0000
HNRNPL Heterogeneous nuclear ribonucleoprotein L	ASLNGADIYSGC*CTLK	0.0000
ILVBL Acetolactate synthase-like protein	EQVPSLGSNVAC*GLAYTDYHK	0.0048
FLNB Filamin-B	C*LATGPGIASTVK	0.0048
IARS Isoleucine--tRNA ligase, cytoplasmic	NNDLC*YWVPELVR	0.0048
ANLN Actin-binding protein anillin	SC*EGQNPELLPK	0.0072

Table S4 - Summary of ten peptides with the lowest reduction in labelling (increase in labeling) as a result of treatment with 1 and irradiation

Protein	**Peptide sequence**	**Log_2 ($R_{L:H}$)**
LRRC47 Leucine-rich repeat-containing protein 47	MVSGC*QTR	-6.06
RAP1B Ras-related protein Rap-1b	C*DLEDER	-2.60
RAP1B Ras-related protein Rap-1b	QVEVDAQQC*MLEILDTAGTEQFTAMR	-2.51
CDC42 Cell division control protein 42 homolog	YVEC*SALTQK	-2.35
SDHA Succinate dehydrogenase	TLNEADC*ATVPPAIR	-2.25
ECHS1 Enoyl-CoA hydratase, mitochondrial	IC*PVETLVEEAIQC*AEK	-2.08
RAB8A Ras-related protein Rab-8A	C*DVNDK	-1.94
RAB10 Ras-related protein Rab-10	C*DMDDK	-1.94
RAB21 Ras-related protein Rab-21	GIEELFLDLC*K	-1.91
MDH2 Malate dehydrogenase, mitochondrial	SQETEC*TYFSTPLLLGK	-1.84

Table S5 - Solvent accessible surface area of sulfur atoms in cysteines within peptides with highest reduction in labeling

ID	**Description**	**Cysteine position**	**PDB file ID**	**Chain**	**Cysteine**	**Solvent accessibility for Sulfur ($Å^2$)**
Q12906	ILF3 Interleukin enhancer-binding factor 3	278|295	4ATB [4](Q9Z1X4)	B	278	10.29
				D		10.42
				B	295	2.83
				D		1.54
P04183	TK1 Thymidine kinase, cytosolic	185	1XBT[5]	A	185	2.7
				B		5.28
				C		3.73
				D		3.35
				E		4.5

				F		4.25
				G		4.5
				H		4.25
P14618	PKM Pyruvate kinase isozymes M1/M2	326	3BJT[6]	A|B|C|D	326	0
			1ZJH[7]	A	325	0
P07437	TUBB Tubulin beta chain	201|211	5N5N[8]	A|B|E|F	203	3.09
				C|D		2.7
				A|B	213	0.39
				C|D		0.26
				E|F		0.52
		239		A|B|C|D|E|F	241	0
O43159	RRP8 Ribosomal RNA-processing protein 8		2ZFU[9]	A	332	0.16
				B		0

Table S6 – Solvent accessible surface area of sulfur atoms in cysteines within peptides that exhibited least reactivity with O(^{3}P)

ID	Description	Cysteine position	PDB file ID	Chain	Cysteine	Solvent accessibility for Sulfur (Å^2)
B5ME19	EIF3CL Eukaryotic translation initiation factor 3 subunit	79	6ZP4 (Q99613)[10]	C	79	0.77
P55735	SEC13 Protein SEC13 homolog	187	3BG1[11]	A	187	3.35
				D		2.83
				E		2.96
				H		2.57
Q15459	SF3A1 Splicing factor 3A subunit 1	244	6FF7[12]	p	244	65.11
Q2TAY7	SMU1 WD40 repeat-containing protein SMU1	416	5O9Z[13]	L	416	0
P14866	HNRNPL Heterogeneous nuclear ribonucleoprotein L	260	2MQP (F1LQ48) [14]	A	257	40.79
O75369	FLNB Filamin-B	1617	2DMB[15]	A	14	1.03

Table S7 - Solvent accessible surface area of sulfur atoms in cysteines within peptides that exhibited an increase in labeling

ID	Description	Cysteine position	PDB file ID	Chain	Cysteine	Solvent accessibility for Sulfur (Å²)
P61224	RAP1B Ras-related protein Rap-1b	118	4HDO[16]	B	118	7.08
P61224	RAP1B Ras-related protein Rap-1b	51	4HDO[16]	B	51	0.77
P60953	CDC42 Cell division control protein 42 homolog	157	2NGR[17]	A	157	0.13
P31040	SDHA Succinate dehydrogenase	654	6VAX[18]	A,C	654	0.64
P30084	ECHS1 Enoyl-CoA hydratase, mitochondrial	213	2HW5[19]	A|B|C|D|E	213	0
				F		0.39
		225		A	225	13.12
				B		11.32
				C		14.03
				D		14.8
				E		16.6
				F		13.51
P61006	RAB8A Ras-related protein Rab-8A	123	6RIR[20]	A	123	6.18
				B		5.53
P61026	RAB10 Ras-related protein Rab-10	124	5LPN[21]	A	124	1.42
				C		10.42
Q9UL25	RAB21 Ras-related protein Rab-21	177	1Z0I[22]	A	177	0
P40926	MDH2 Malate dehydrogenase, mitochondrial	285	4WLE[23]	A|B|C|D	285	0

Appendix

Supporting Information excel workbook with protein analysis

Sheet 1 - CysAnn_L-UV_H+UV_LHratios – $Log_2(R_{L:H})$ for 1 treatment of HeLa cells in UV
Sheet 2 - Control_L&H_noUV_LHratios - $Log_2(R_{L:H})$ for 1 treatment of HeLa cells in No-UV
Sheet 3 – Seq (two-fold red in label) – peptides with $Log_2(R_{L:H}) > 1$in Sheet 1
Sheet 4 – 200 seq (increase in label) – top 200 peptides with highest increase in labeling ($Log_2(R_{L:H}) \leq 0$)
Sheet 5 - Seq (no reactivity) - peptides with $-0.05 < Log_2(R_{L:H}) < 0.05$
Sheet 6 - Segmentation for 461 peptides – Location and sub-cellular location of peptides in Sheet 3
Sheet 7 – Mem count increase label – Location and sub-cellular location of peptides in Sheet 4
Sheet 8 – Segmentation of no reactive seq - Location and sub-cellular location of peptides in Sheet 5

Sheet 9 – 2.9% increase in label mem loc – Peptides with highest increase in labeling segmented by location
Sheet 10 - WebLogo (oxidized) - Fragments for peptides in Sheet 3
Sheet 11 - WebLogo (Not Oxidized) – Fragments for peptides in Sheet 4
Sheet 12 – WebLogo (No reactivity) – Fragments for peptides in Sheet 5
Sheet 13 – Cysteine SA structure – Details on crystal structures used to determine Cys solvent accessibility

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