

Supporting Information

Multicomponent Construction of C3-Unsubstituted Iminocoumarins using CaC₂ as Stable Surrogate for Gaseous Acetylene: Scope and Mechanistic Investigations

Manpreet Kaur^a, Divya Bharti^a, Kamlesh K. Gurjar^b, Praveen Kumar Verma^c Vinod Kumar^a, and Rakesh Kumar^{a*}

^aLaboratory of Organic Synthesis and Catalysis, Department of Chemistry, Central University of Punjab, Bathinda-151401, India.

^bChemical Department, VGEC, Ahmedabad, Gujarat-382424, India.

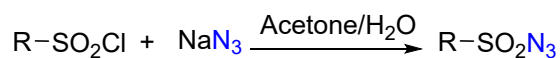
^cSchool of Advanced Chemical Sciences Shoolini University, Solan, Himachal Pradesh, 173229, India

*Corresponding author: Dr. Rakesh Kumar, Email: rakesh.kumar@cup.edu.in
Laboratory of Organic Synthesis and Catalysis, Department of Chemistry, Central University of Punjab, Bathinda-151401, India*

Table of Contents

1. Procedure for the synthesis of sulfonyl azides	S2
2. Table S1: Optimization of reaction conditions	S2
3. Zwitterionic resonance form of iminocoumarin 3a	S3
4. ¹H, ¹³C NMR spectra, and MS of synthesized compounds	S4-S60
5. Cartesian coordinates	S61-S74
6. References	S75

- 1. Procedure for the synthesis of sulfonyl azides:** The starting material, azides, were synthesized following the procedure outlined in the Scheme S1.



Scheme S1: Synthesis of sulfonyl azides

Sulfonylchloride (190 mmol) was dissolved in acetone and water (200 mL). Then NaN₃ (1.1 equiv.) was added in the portions at 0 °C and mixture was stirred for 2.5 h. The reaction mixture was concentrated under reduced pressure to half of its volume. The aqueous phase was extracted with diethyl ether and combined organic phases were dried over Na₂SO₄. After evaporation of the solvent, the desired sulfonyl azides were obtained (Alassad *et al.*, 2022).

2. Table S1: Optimization of reaction conditions^a

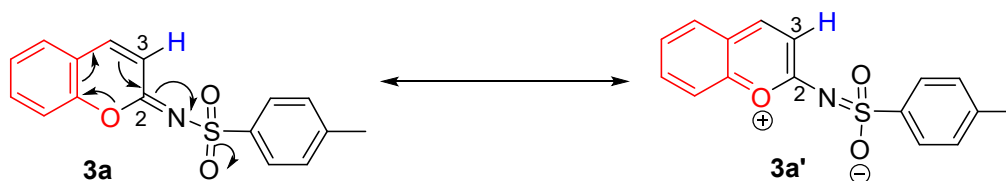
Entry	Catalyst (mol%)	Base (equiv.)	Additive/Ligand	Temp. (°C)	Time (h)	Yield ^b 4a (%)
1	CuI (10)	Et ₃ N (2)	-	rt	14	71
2	CuI (20)	Et ₃ N (2)	-	70	6	60
3	CuI (20)	Et ₃ N (4)	-	rt	14	75
4	CuI (20)	Et ₃ N (2)	TBAF	rt	14	69
5	CuI (20)	Et ₃ N (1)	-	rt	14	70

^aGeneral conditions: **1a** (0.5 mmol), **2a** (0.65 mmol), CaC₂ (1.0 mmol). ^bYield of isolated product after column chromatography.

3. Zwitterionic Resonance form of iminocoumarin **3a**

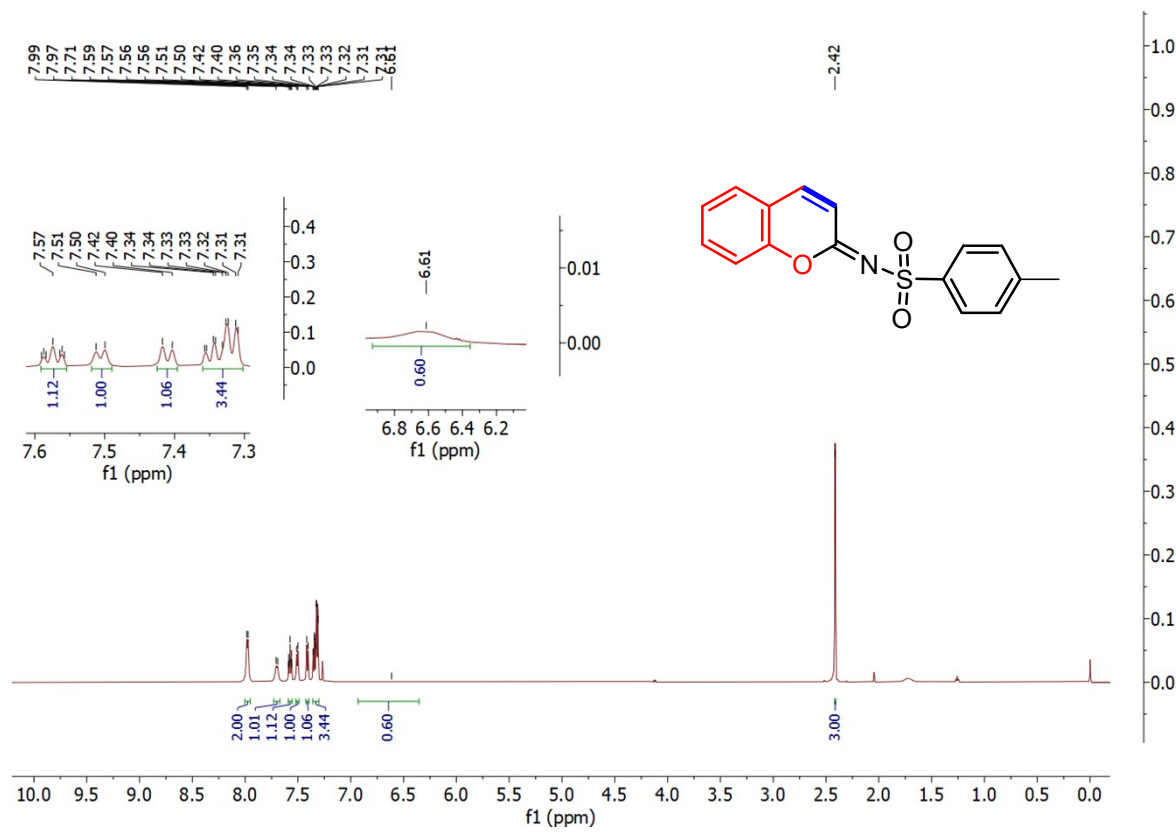
In the ^1H NMR spectra of all the synthesised iminocoumarins, the proton at C-3 position appeared as a broad signal, probably due to resonance influence of nearby sulfonyl group as also observed by the research group of Banwell (Zhao *et al.*, 2021). For instance, iminocoumarin **3a** can exist in its zwitterionic form (**3a'**), which allows free rotation of the C-N bond that would otherwise be restricted in C=N bond of **3a** (Figure S1).

Figure S1: Zwitterionic resonance forms of **3a**

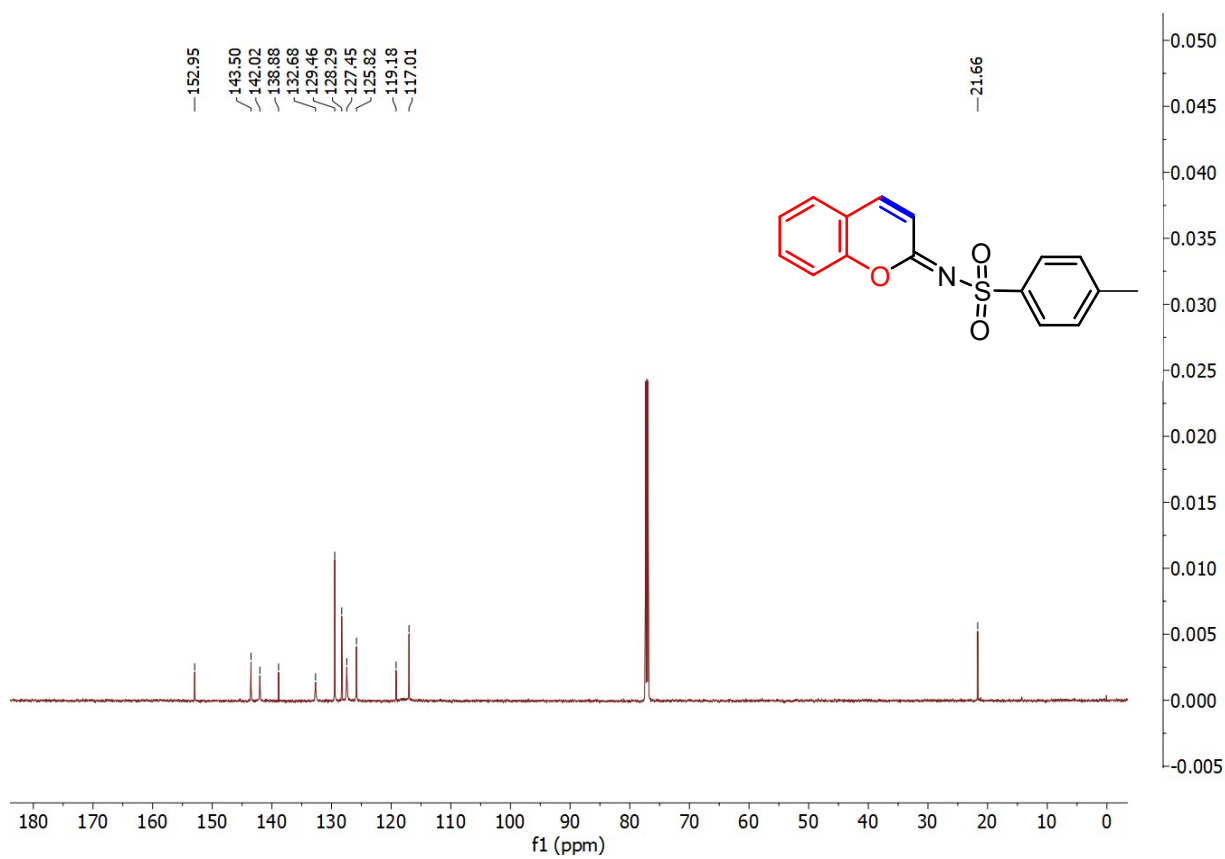


^1H , ^{13}C NMR spectra, MS of synthesized compounds

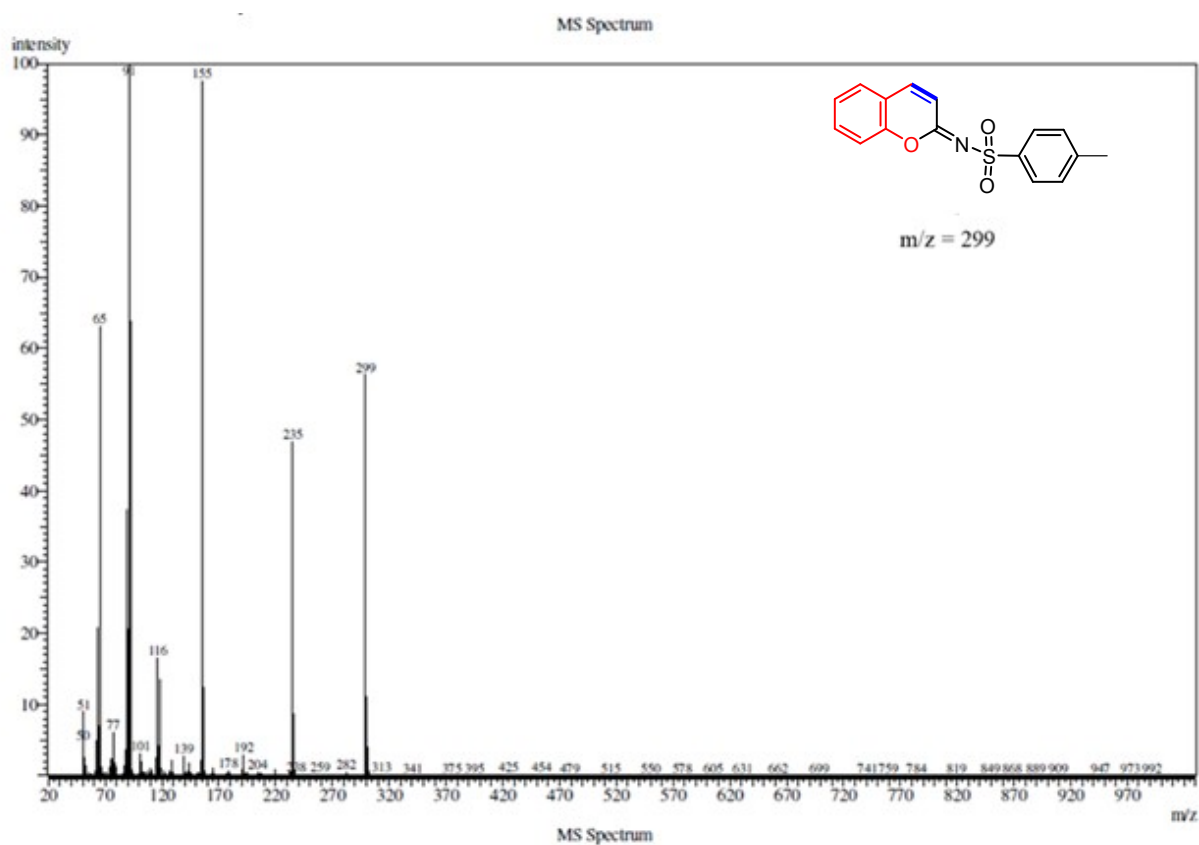
^1H -NMR of 3a



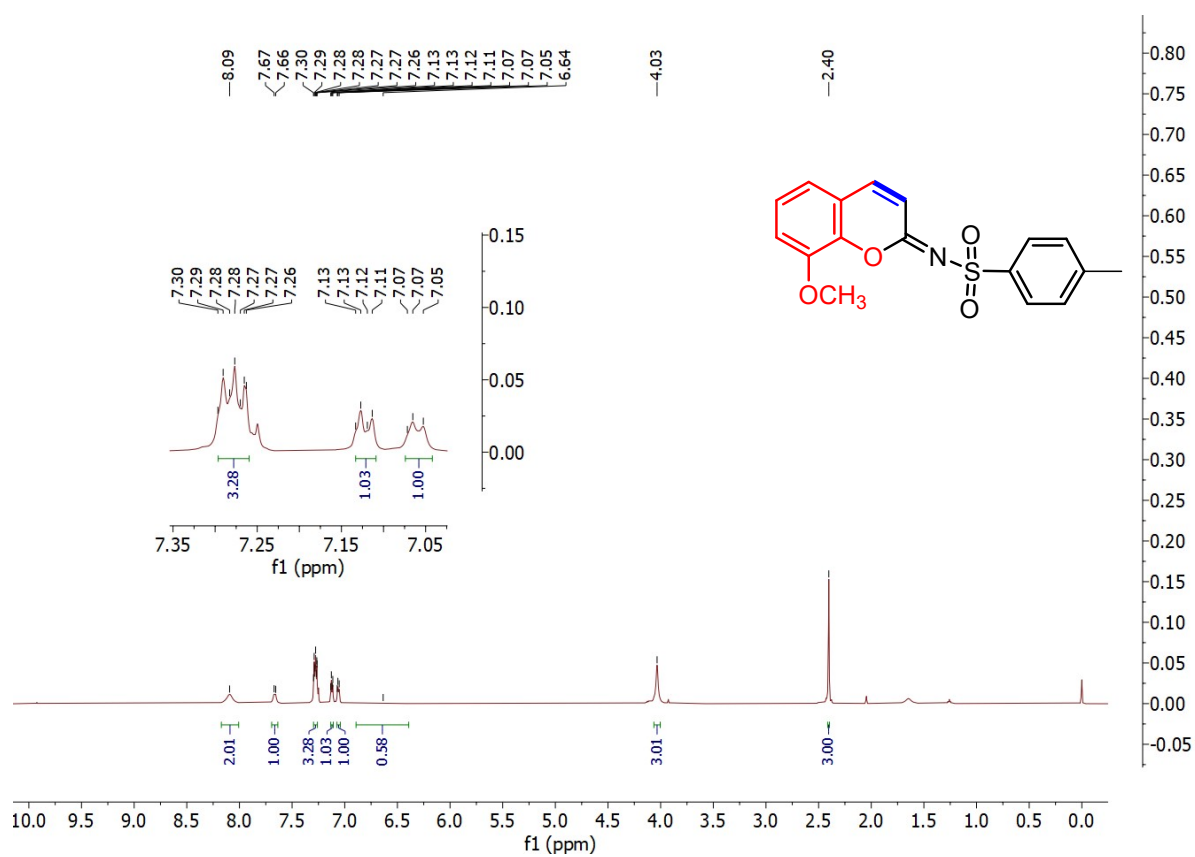
¹³C-NMR of 3a



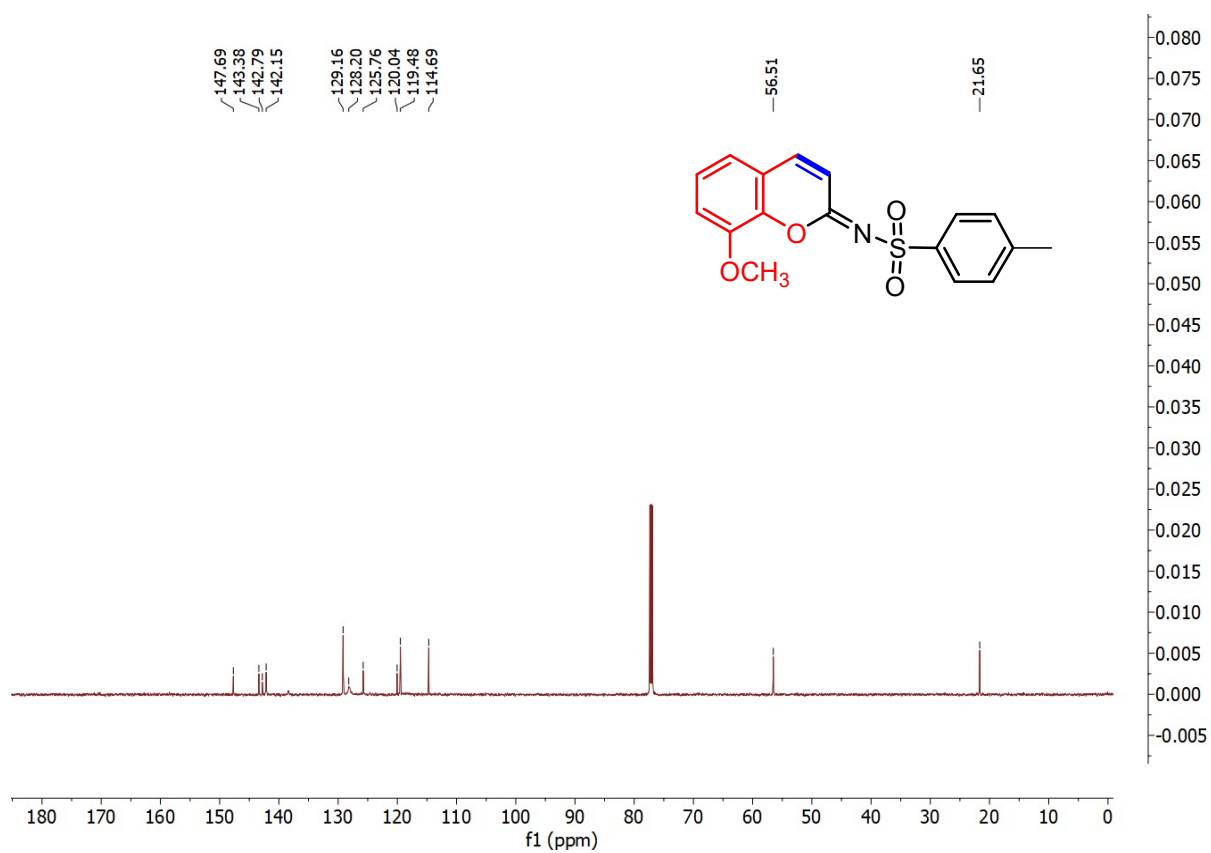
Mass Spectrum of 3a



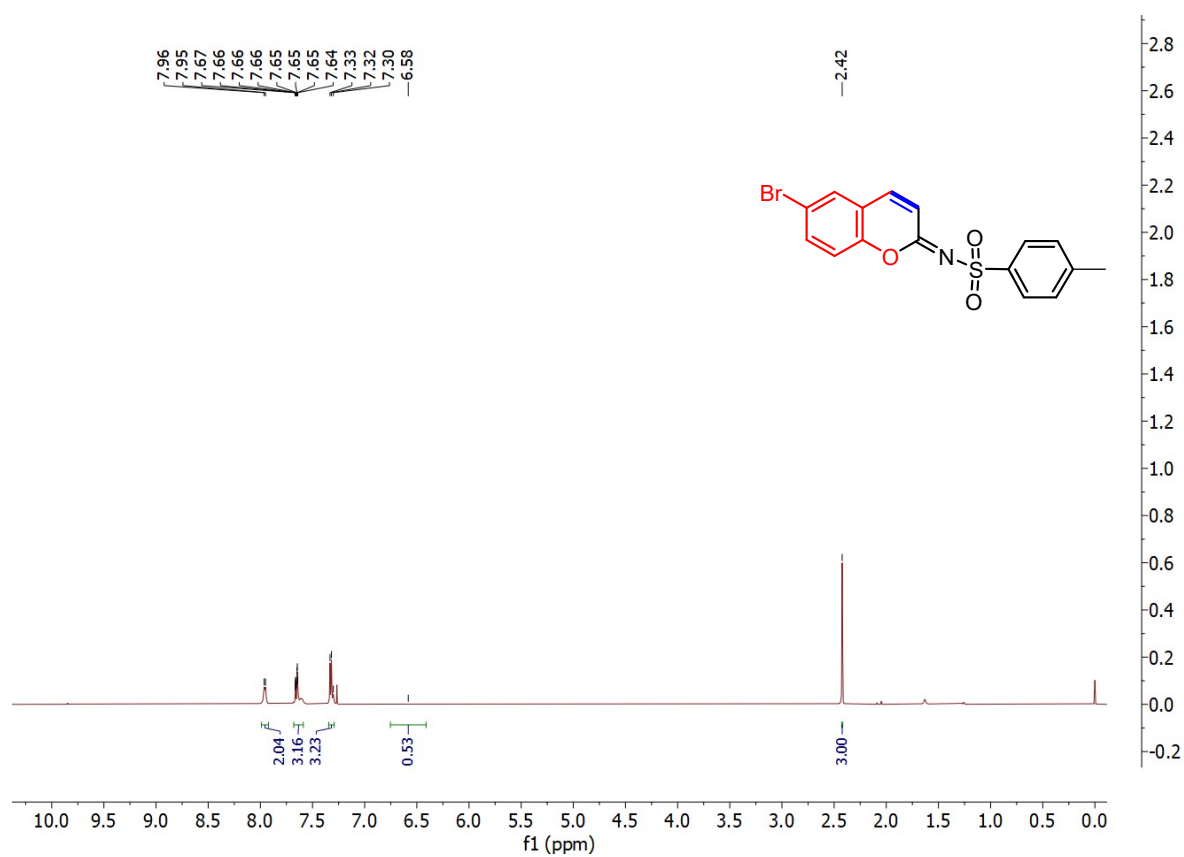
¹H-NMR of 3b



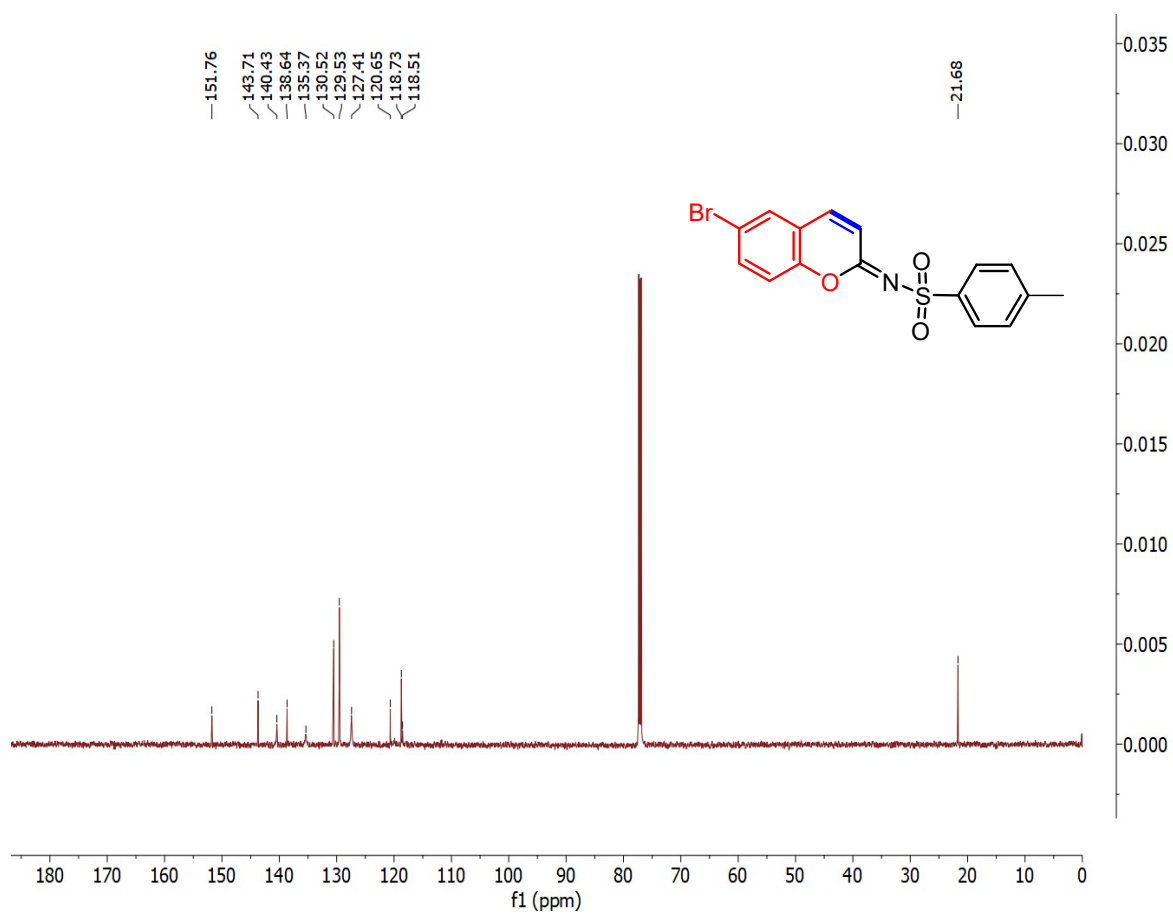
¹³C-NMR of 3b



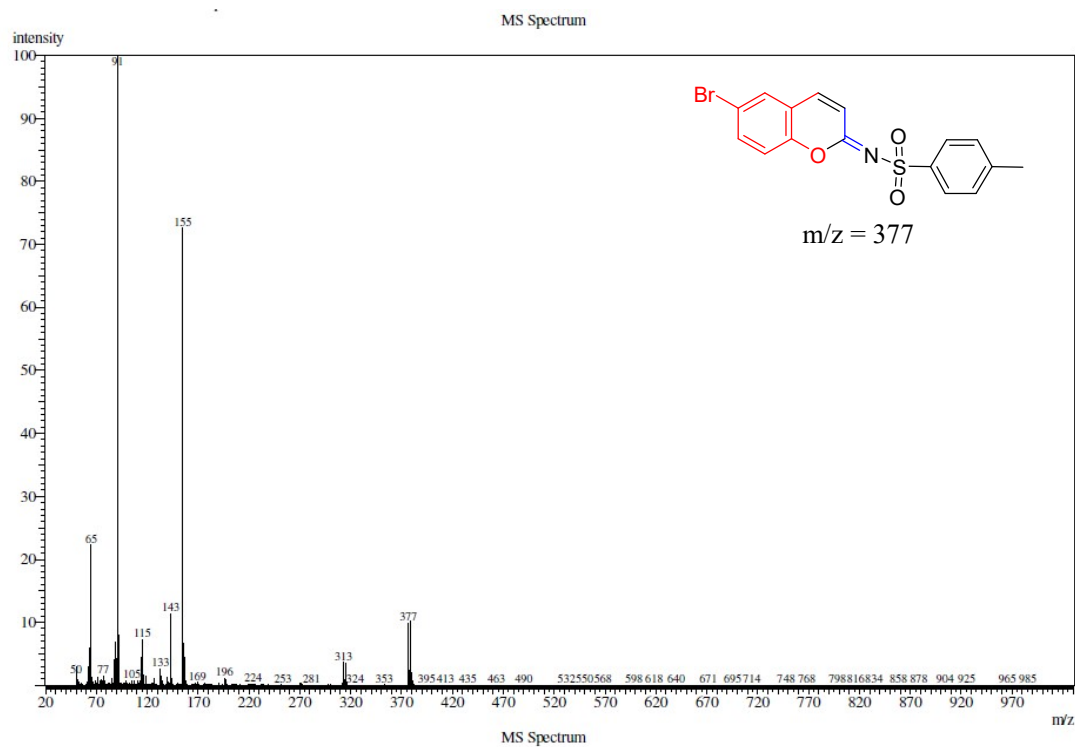
¹H-NMR of 3c



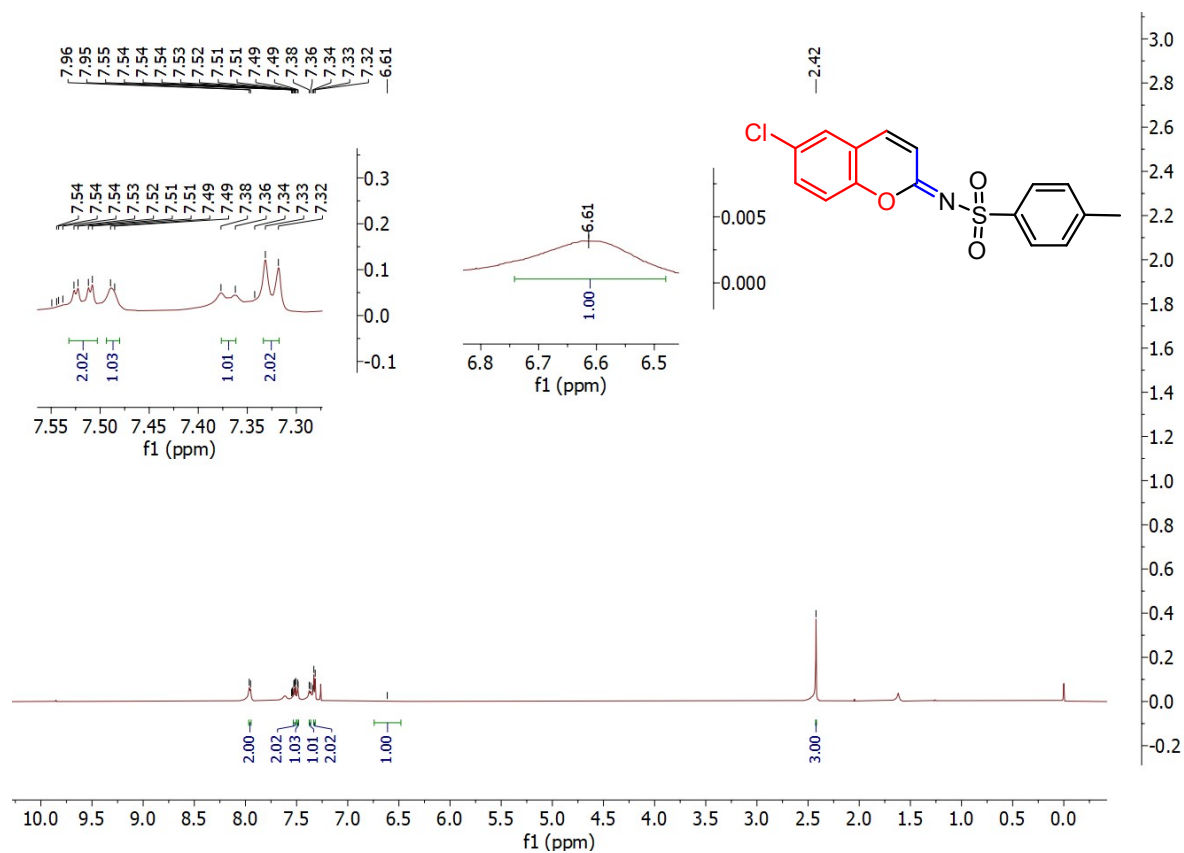
¹³C-NMR of 3c



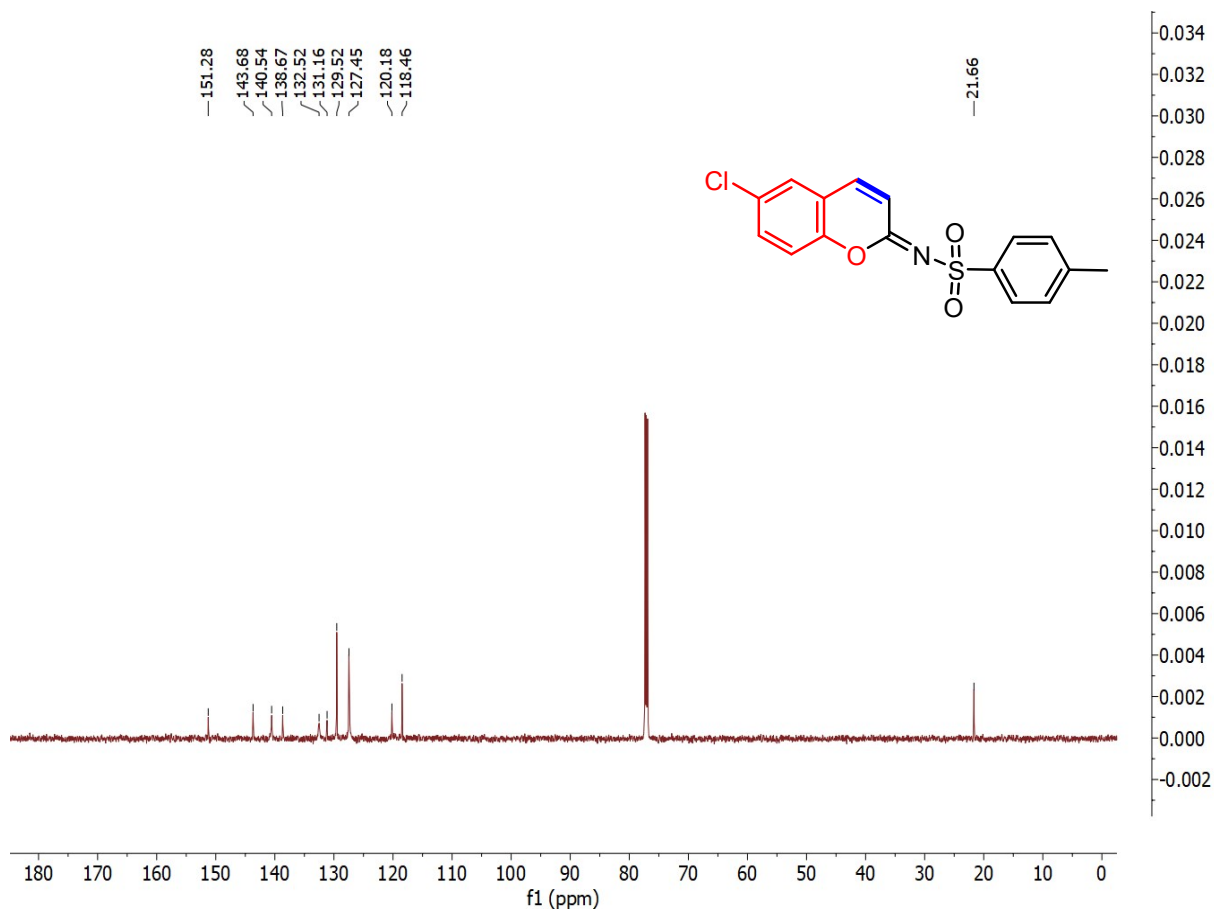
Mass Spectrum of 3c



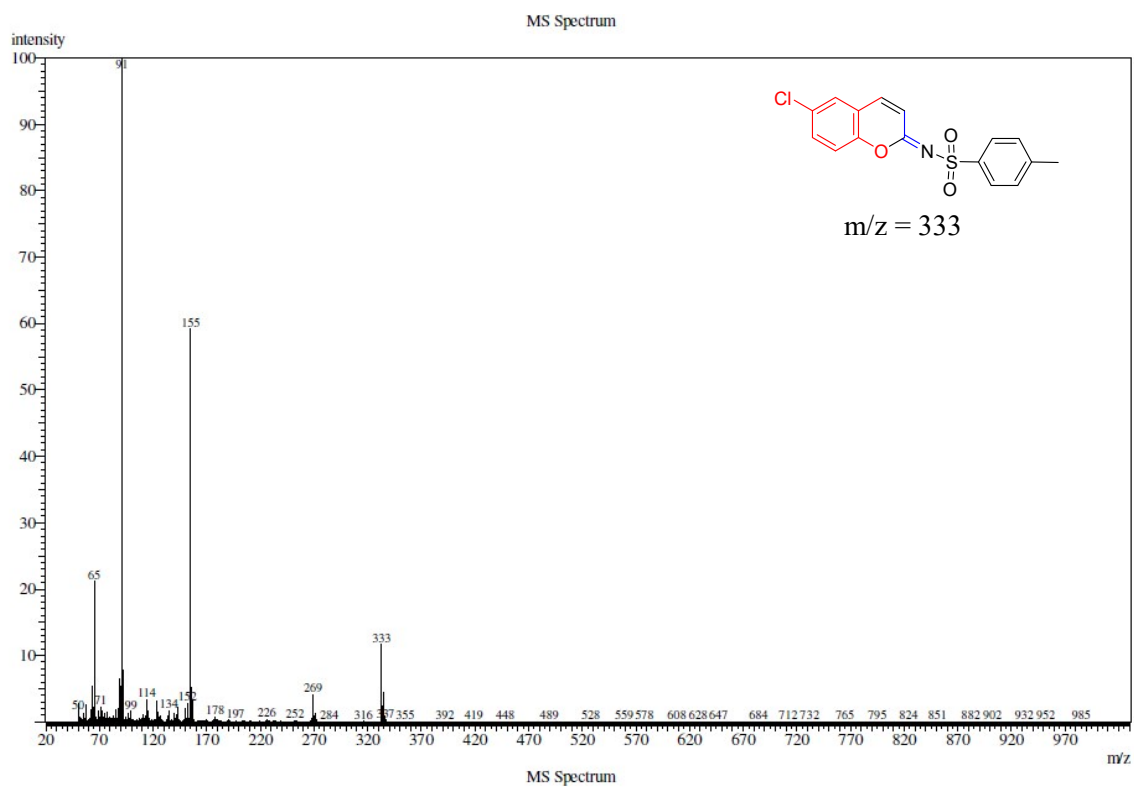
¹H-NMR of 3d



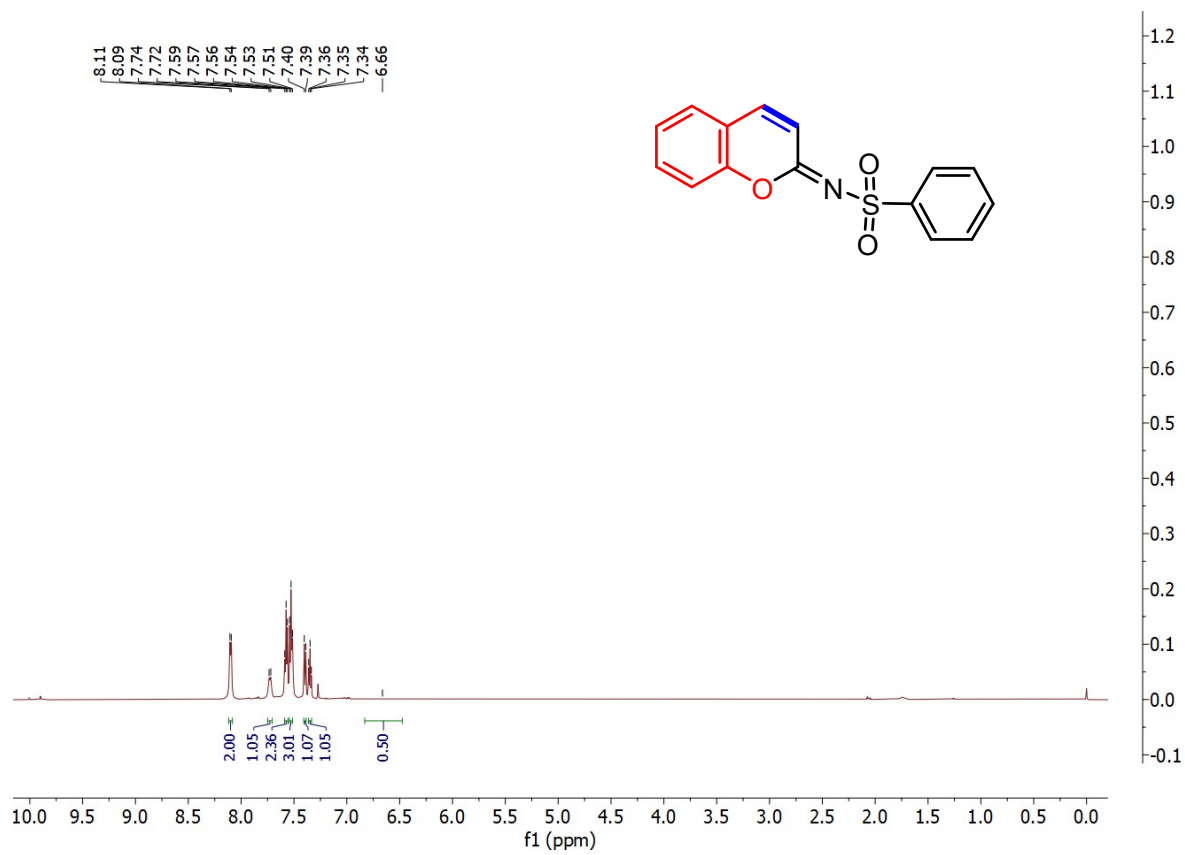
¹³C-NMR of 3d



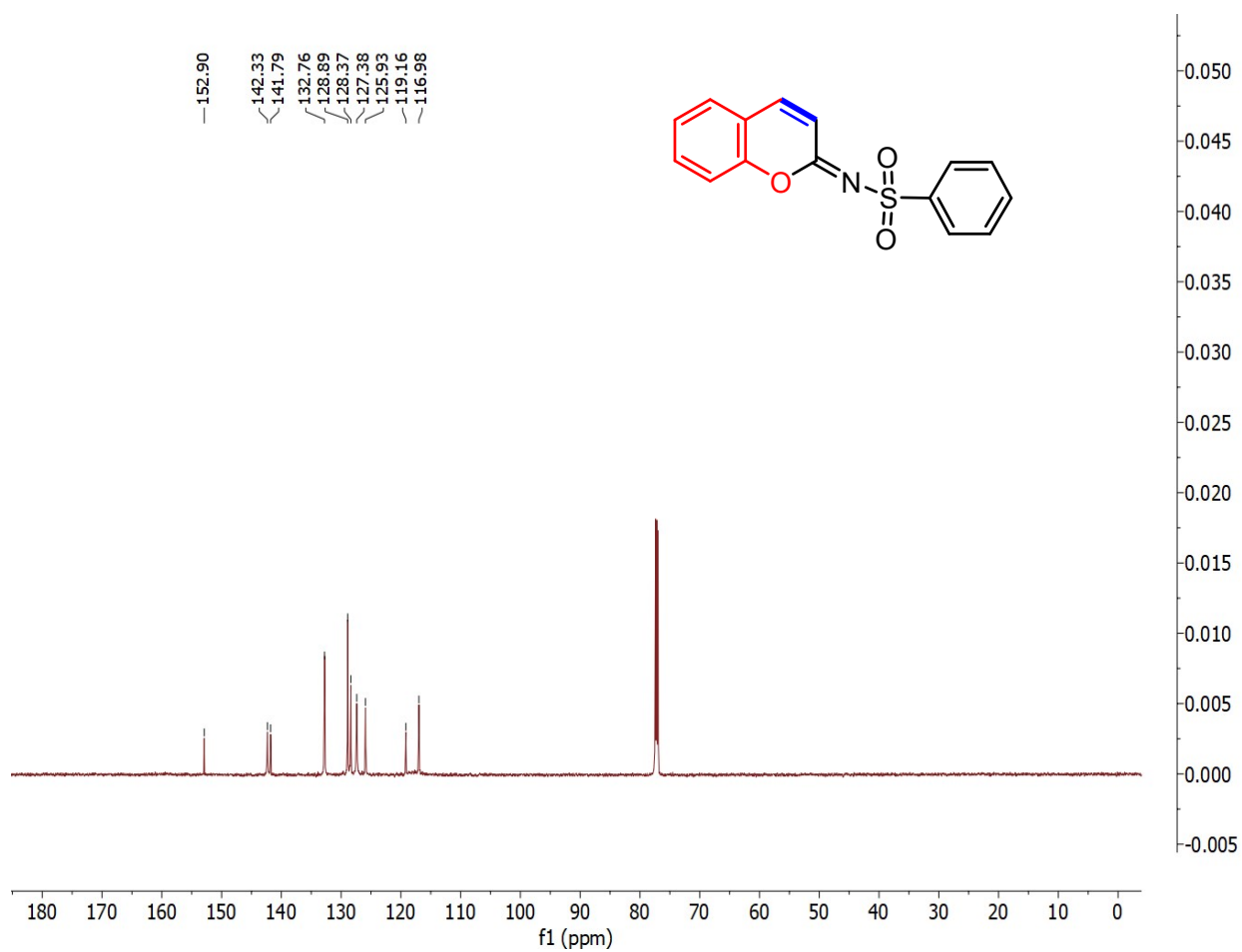
Mass Spectrum of 3d



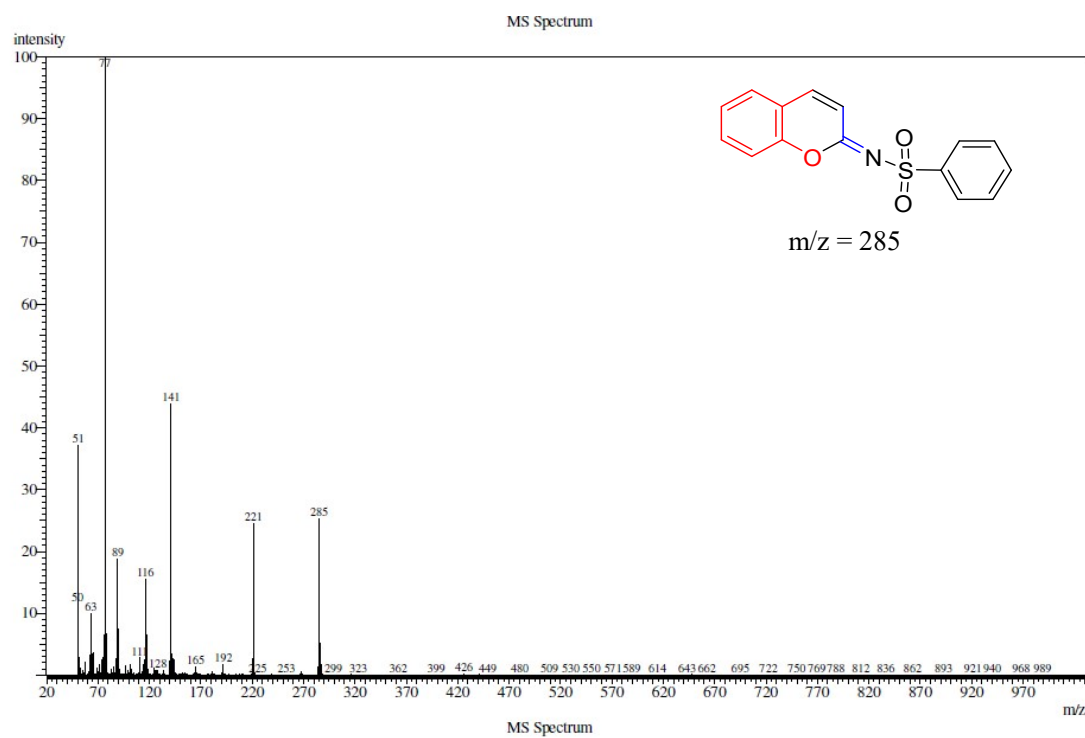
¹H-NMR of 3e



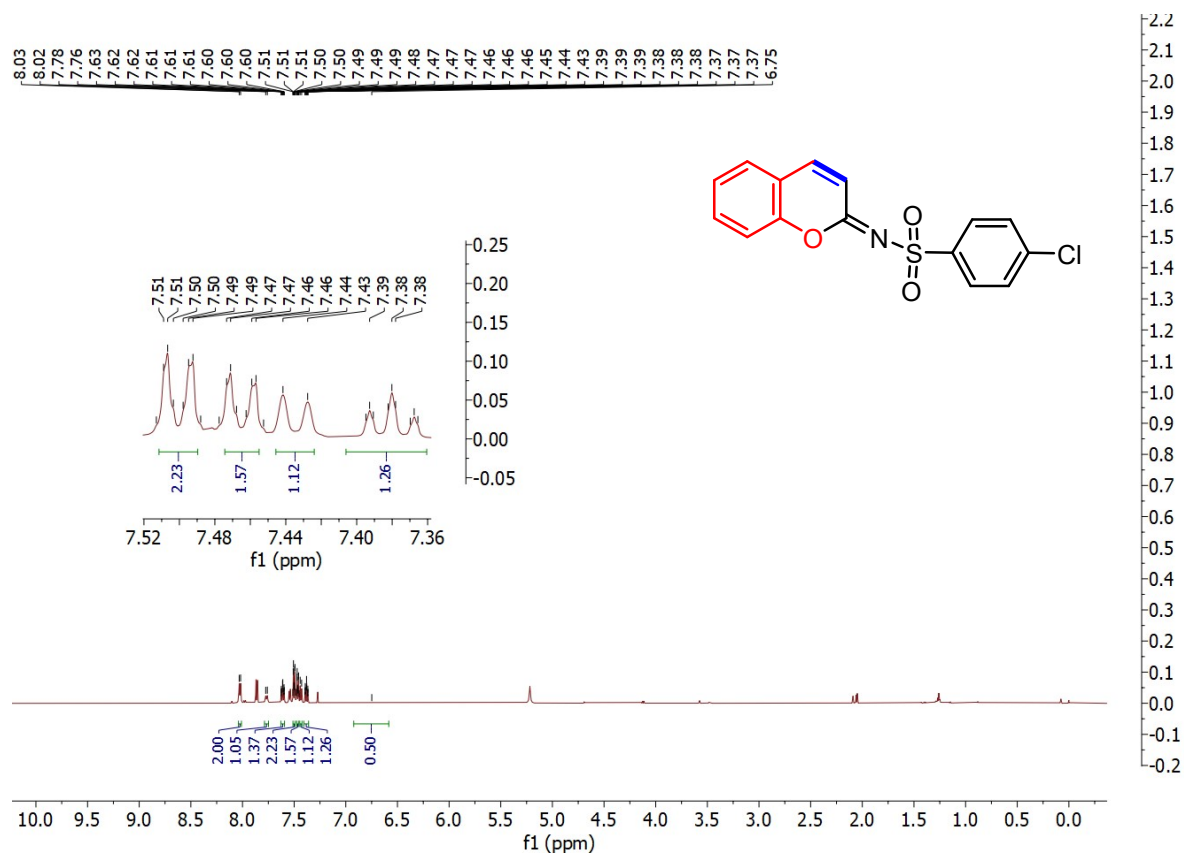
^{13}C -NMR of 3e



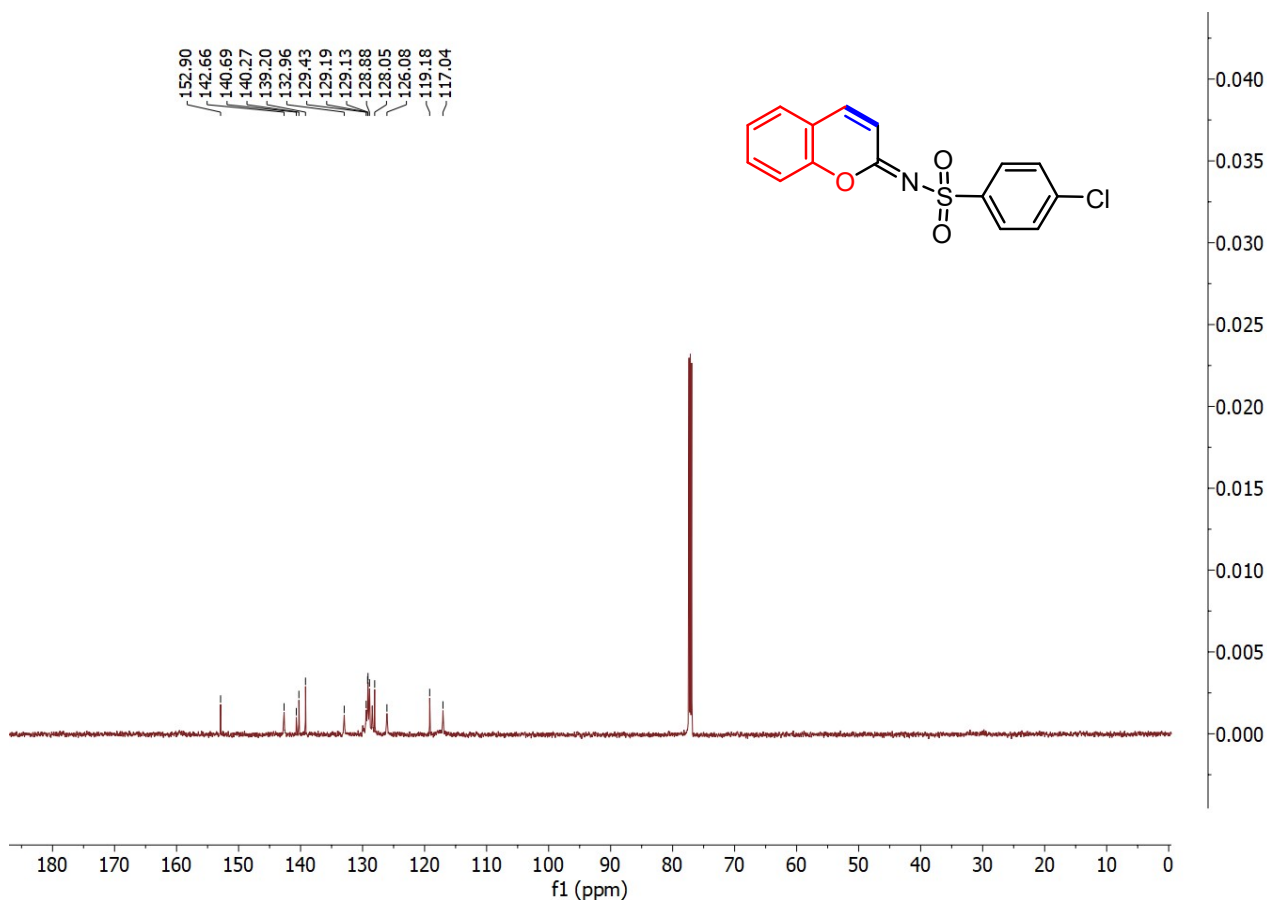
Mass Spectrum of 3e



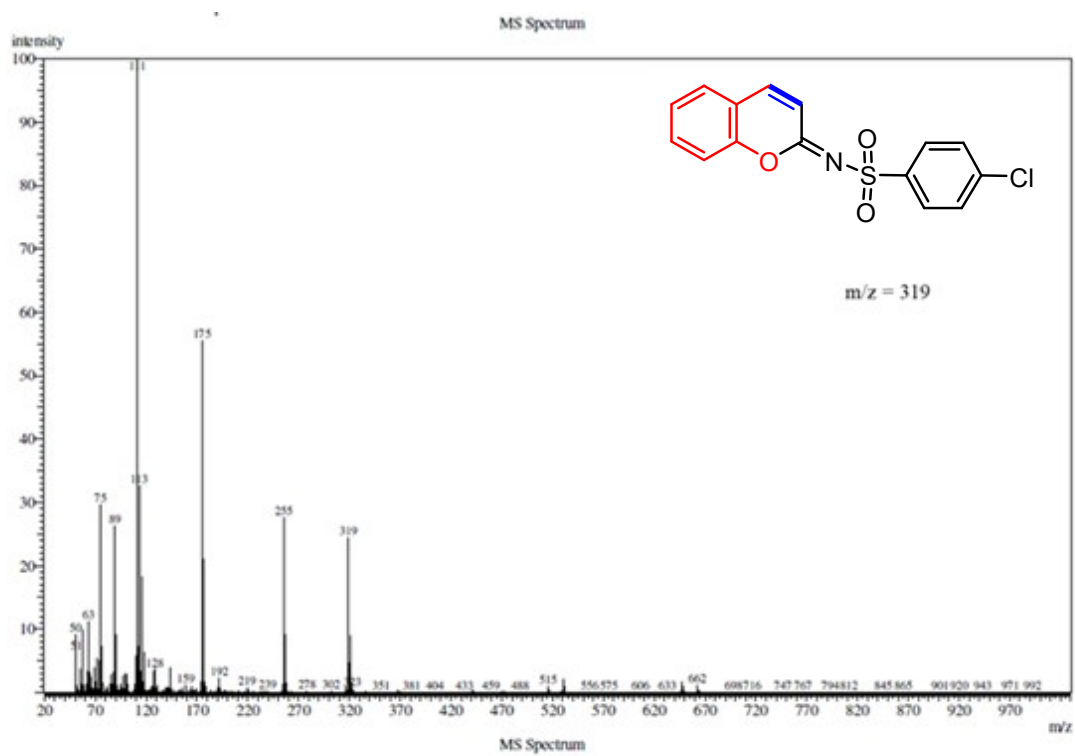
¹H-NMR of 3f



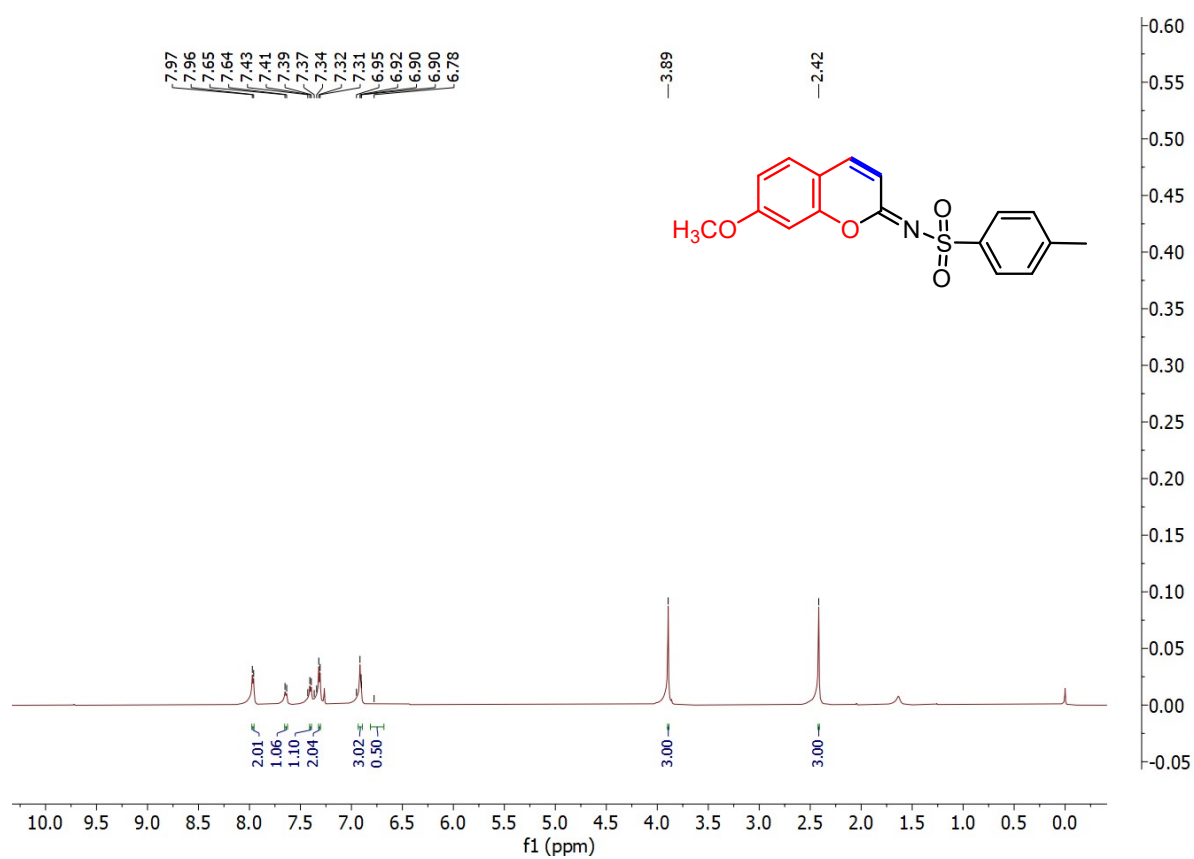
^{13}C -NMR of 3f



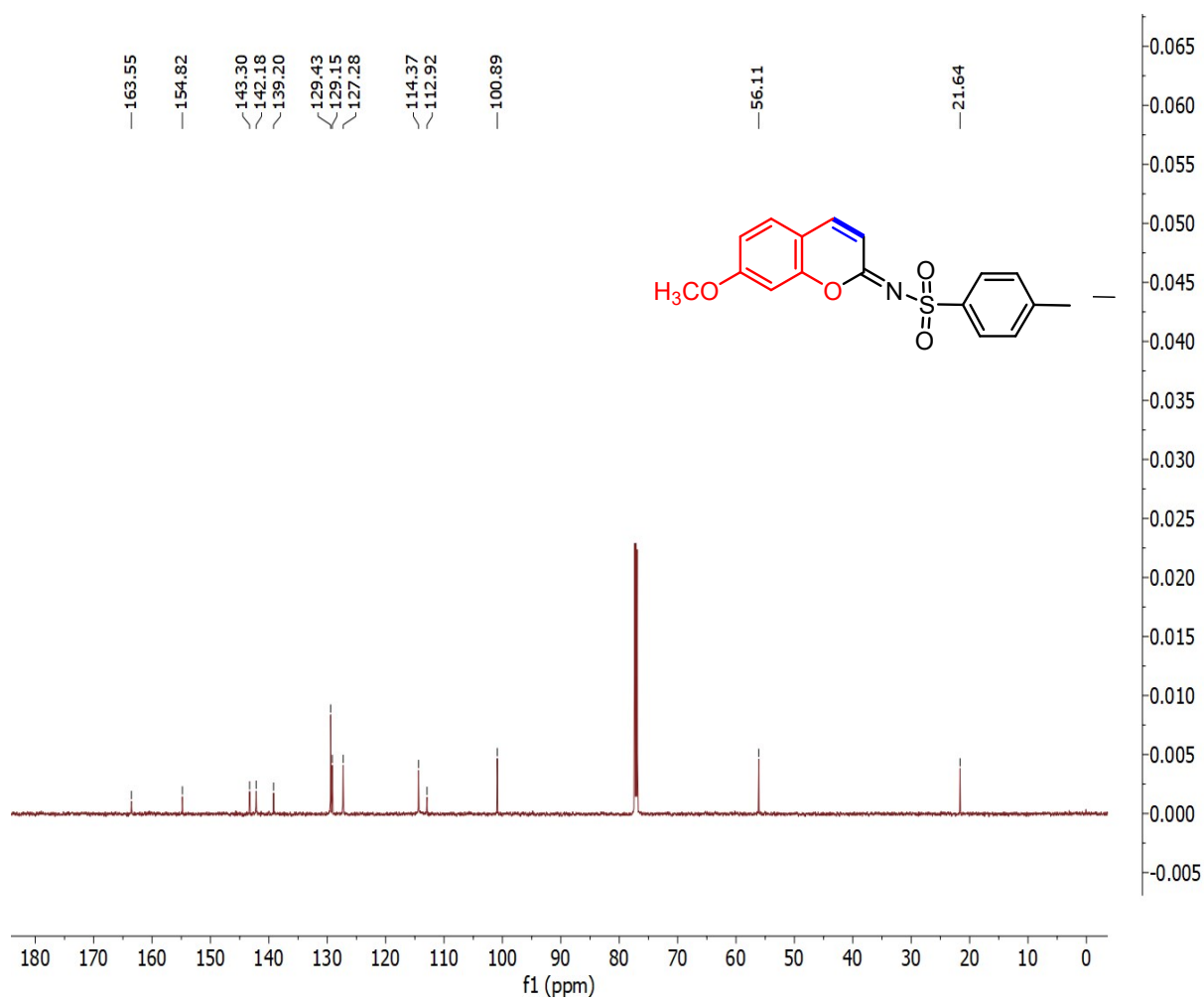
Mass Spectrum of 3f



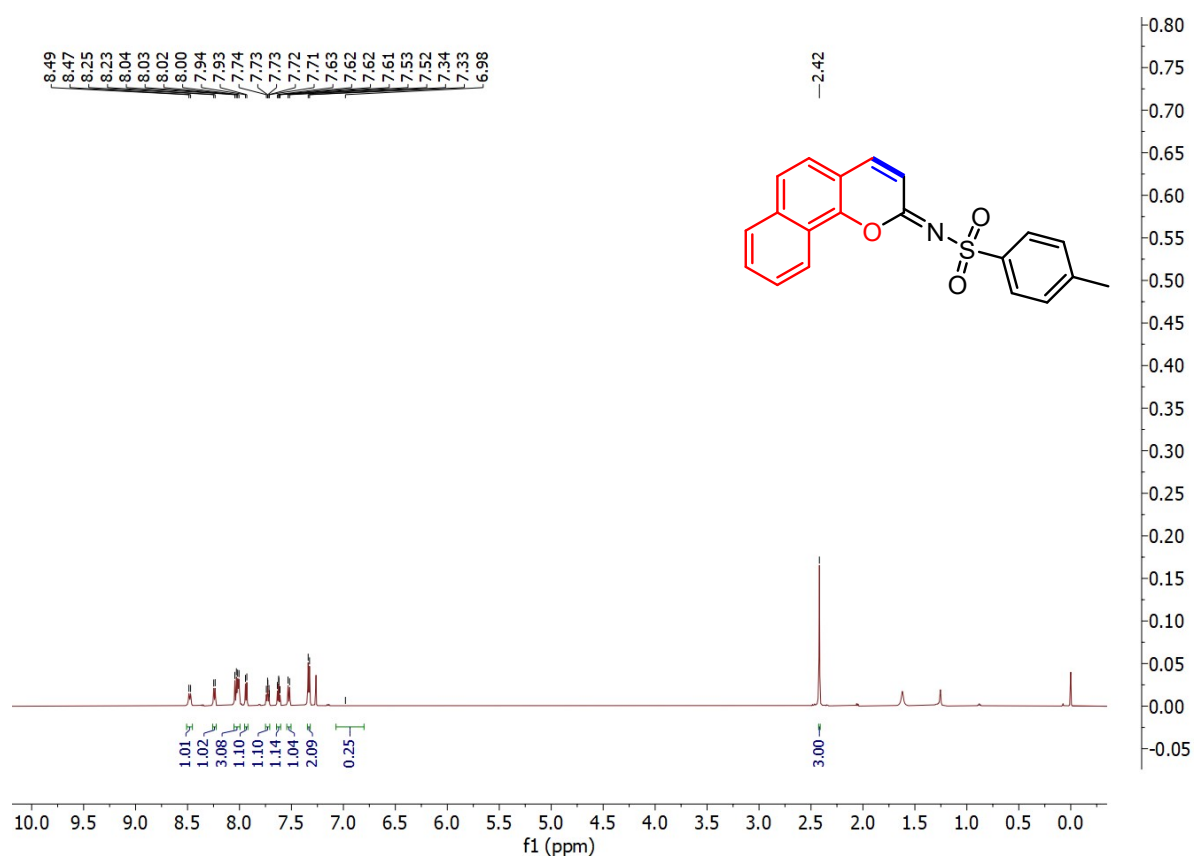
¹H-NMR of 3g



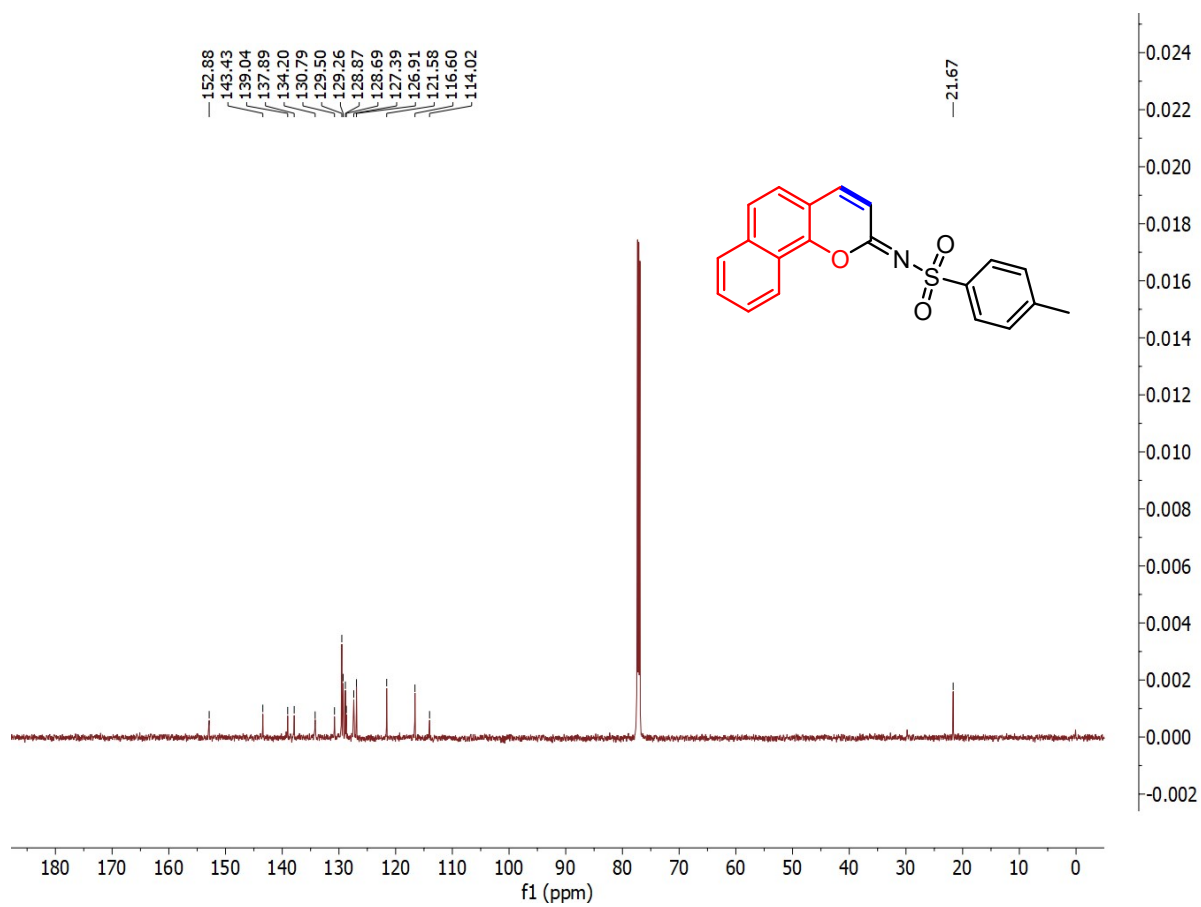
¹³C-NMR of 3g



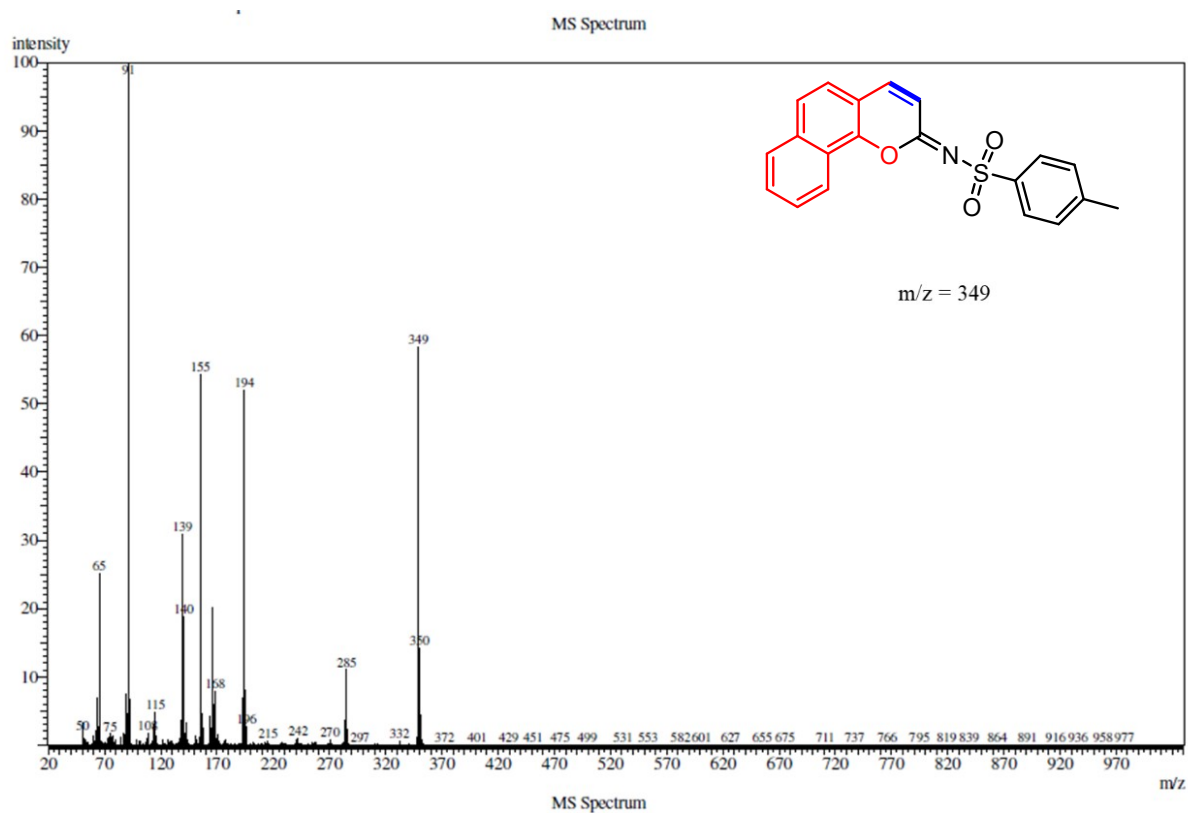
¹H-NMR of 3h



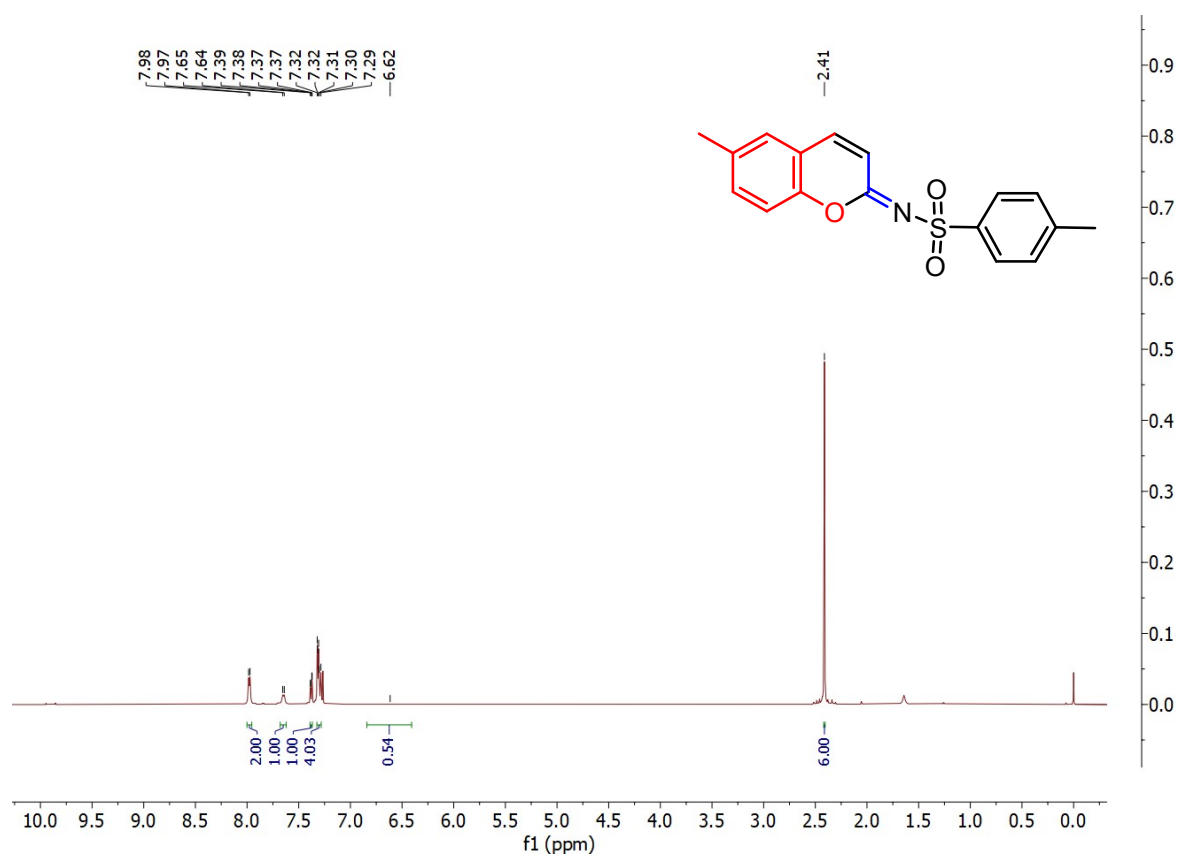
¹³C-NMR of 3h



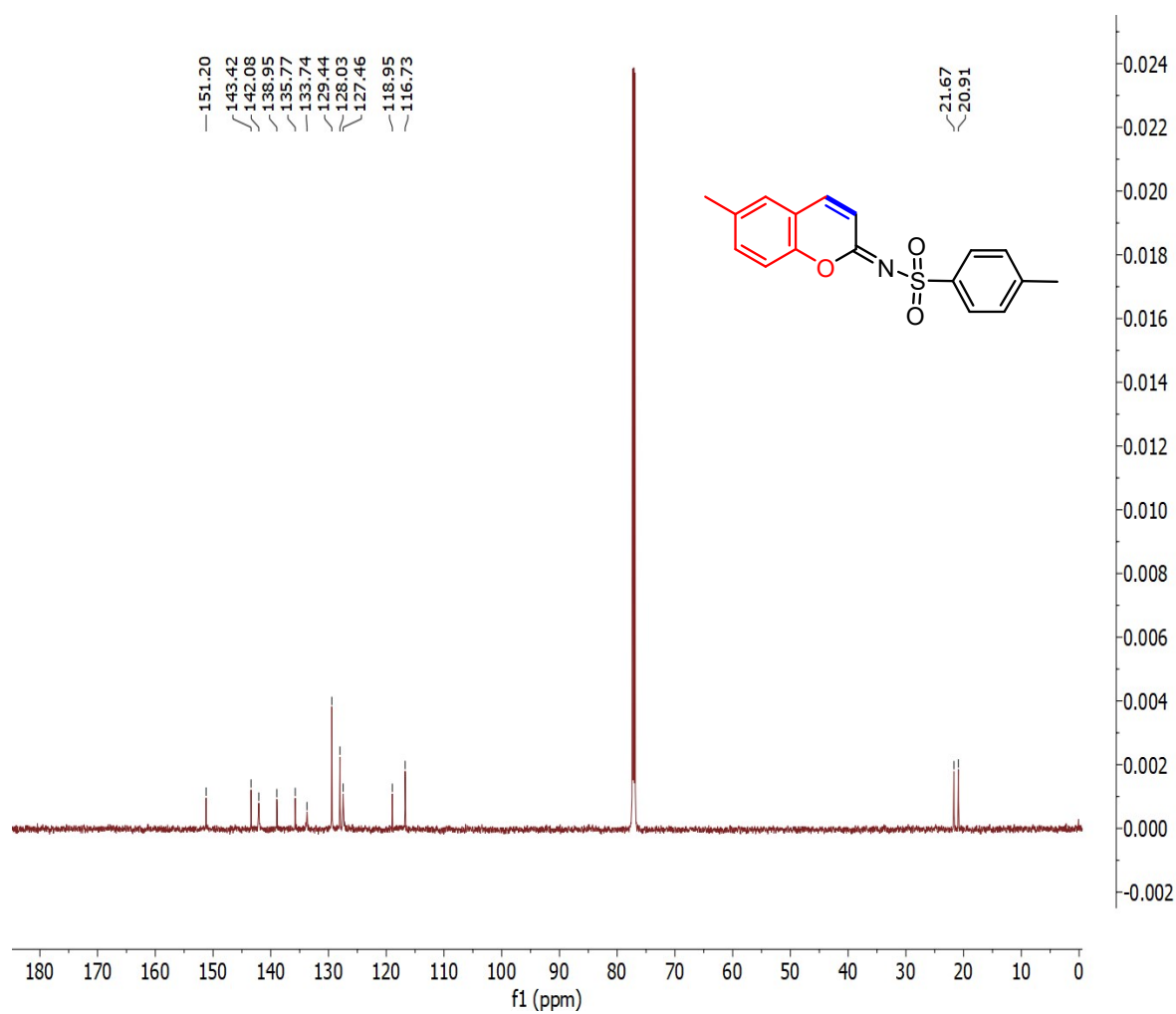
Mass Spectrum of 3h



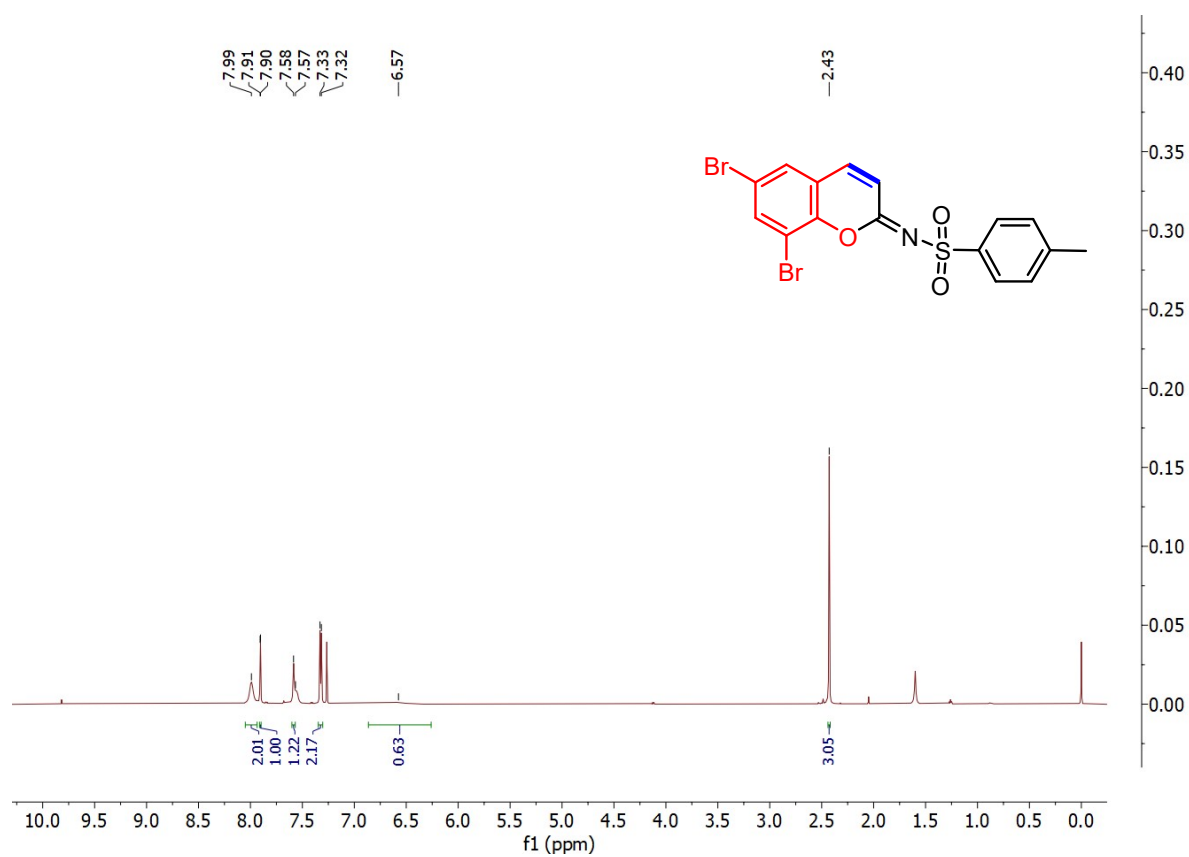
¹H-NMR of 3i



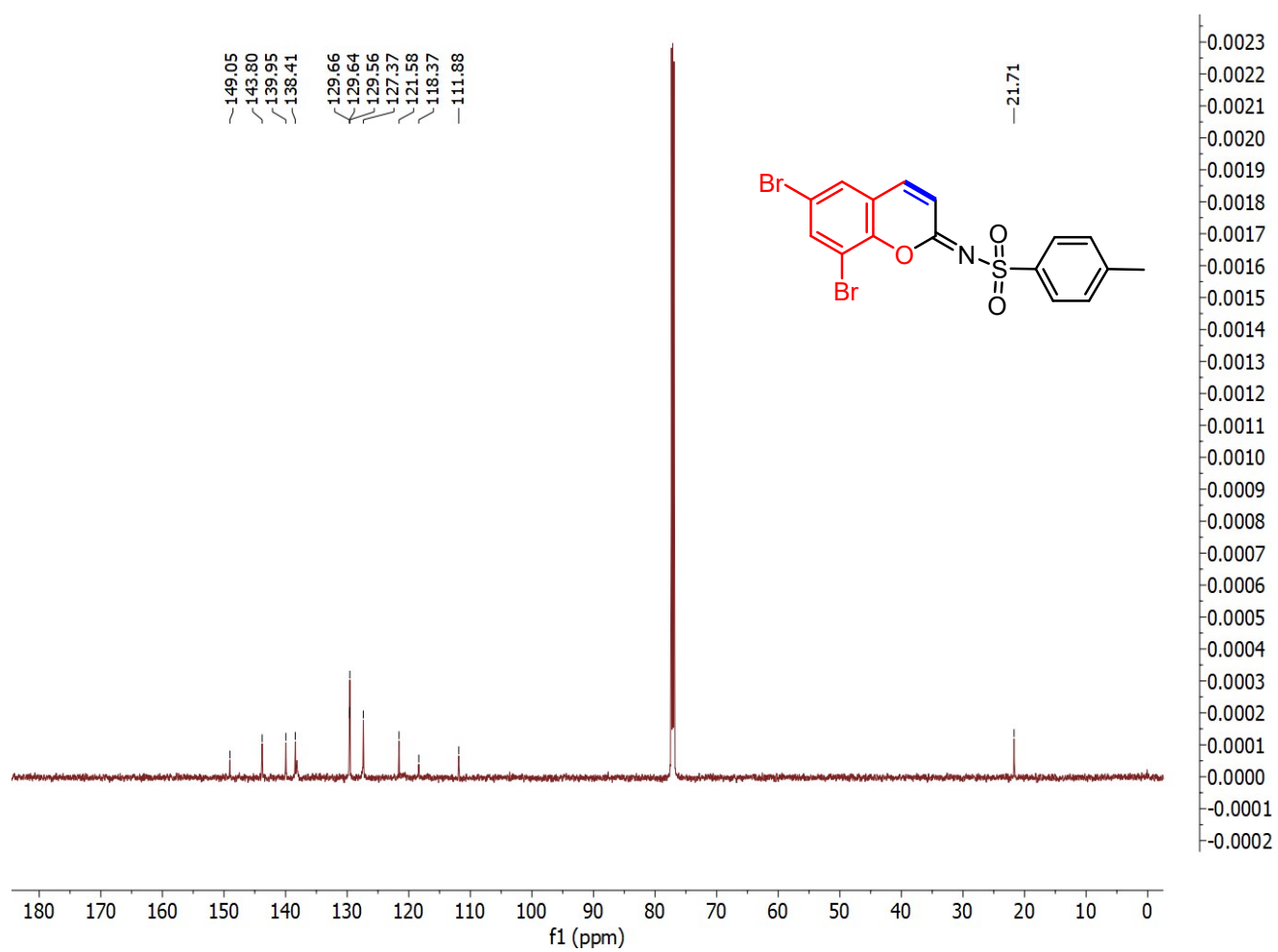
¹³C-NMR of 3i



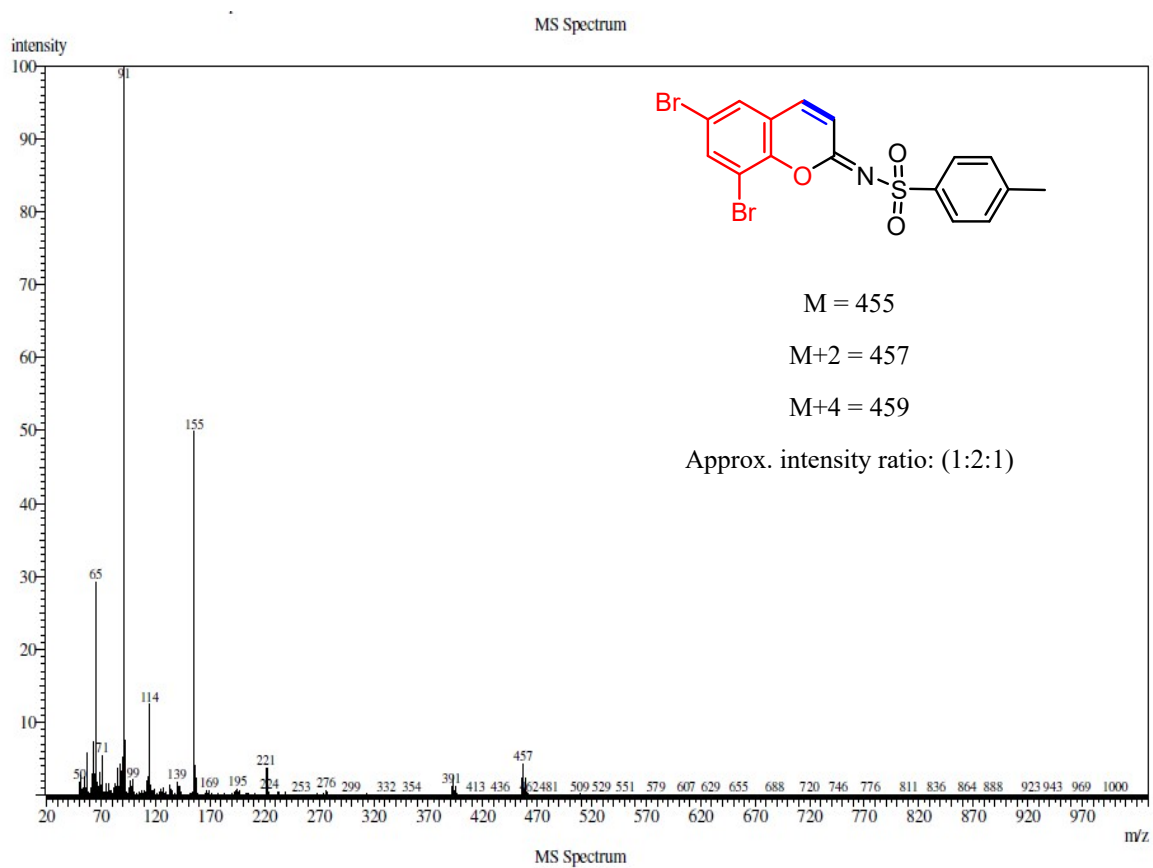
¹H-NMR of 3j



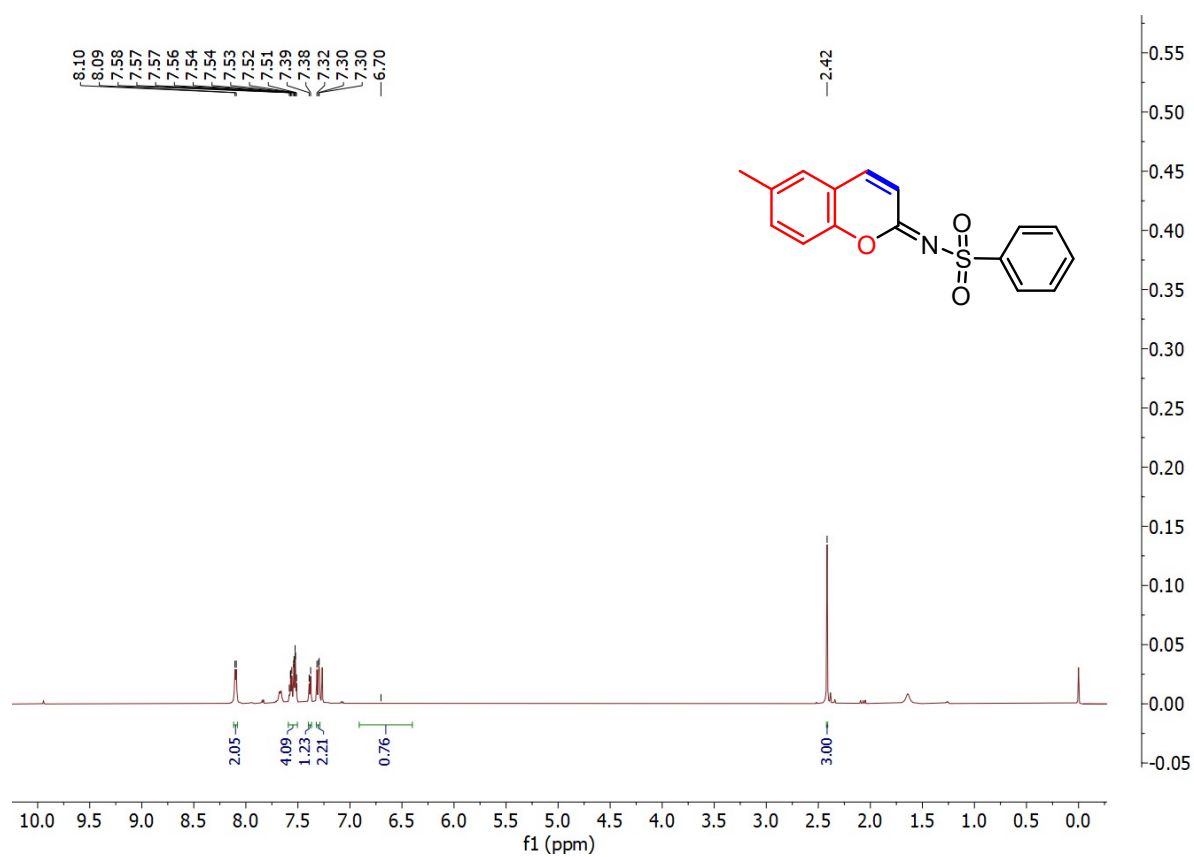
¹³C-NMR of 3j



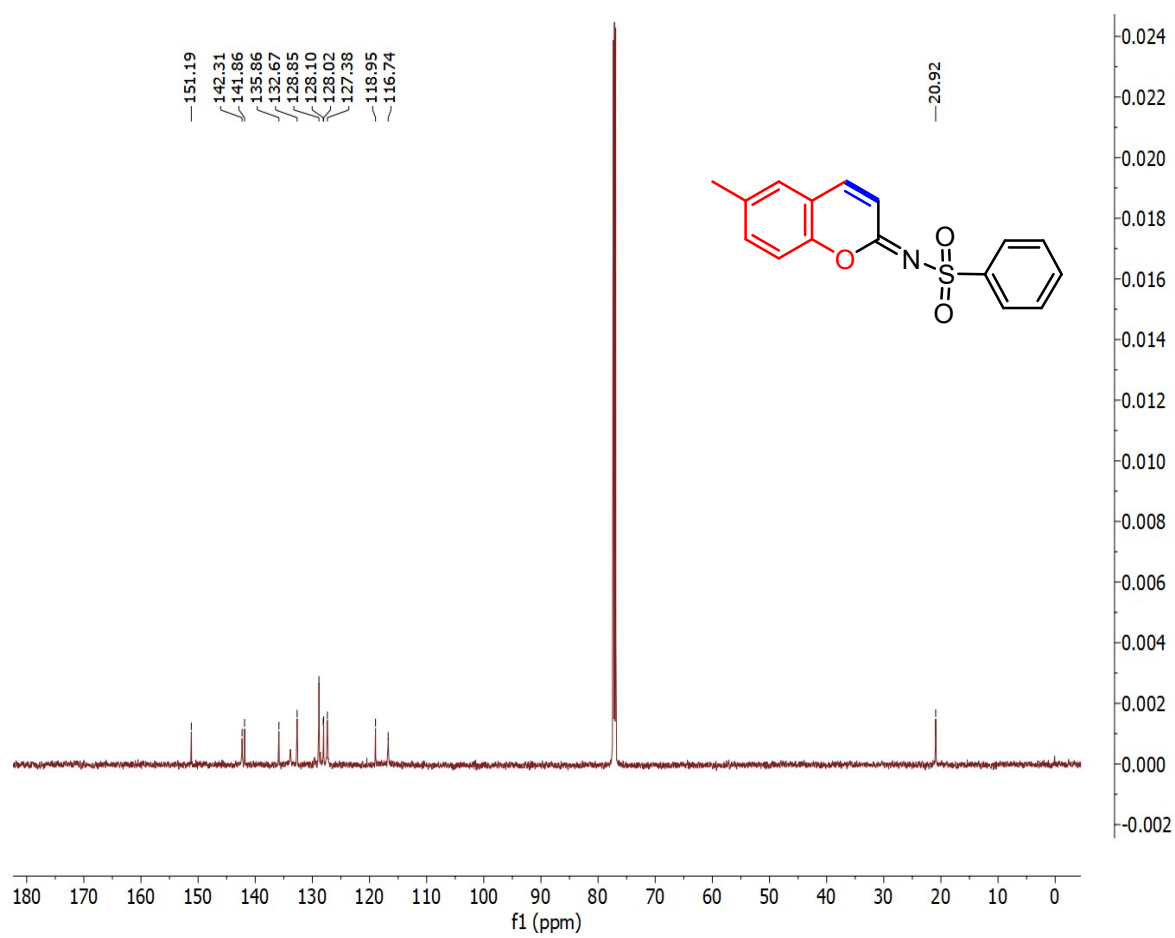
Mass Spectrum of 3j



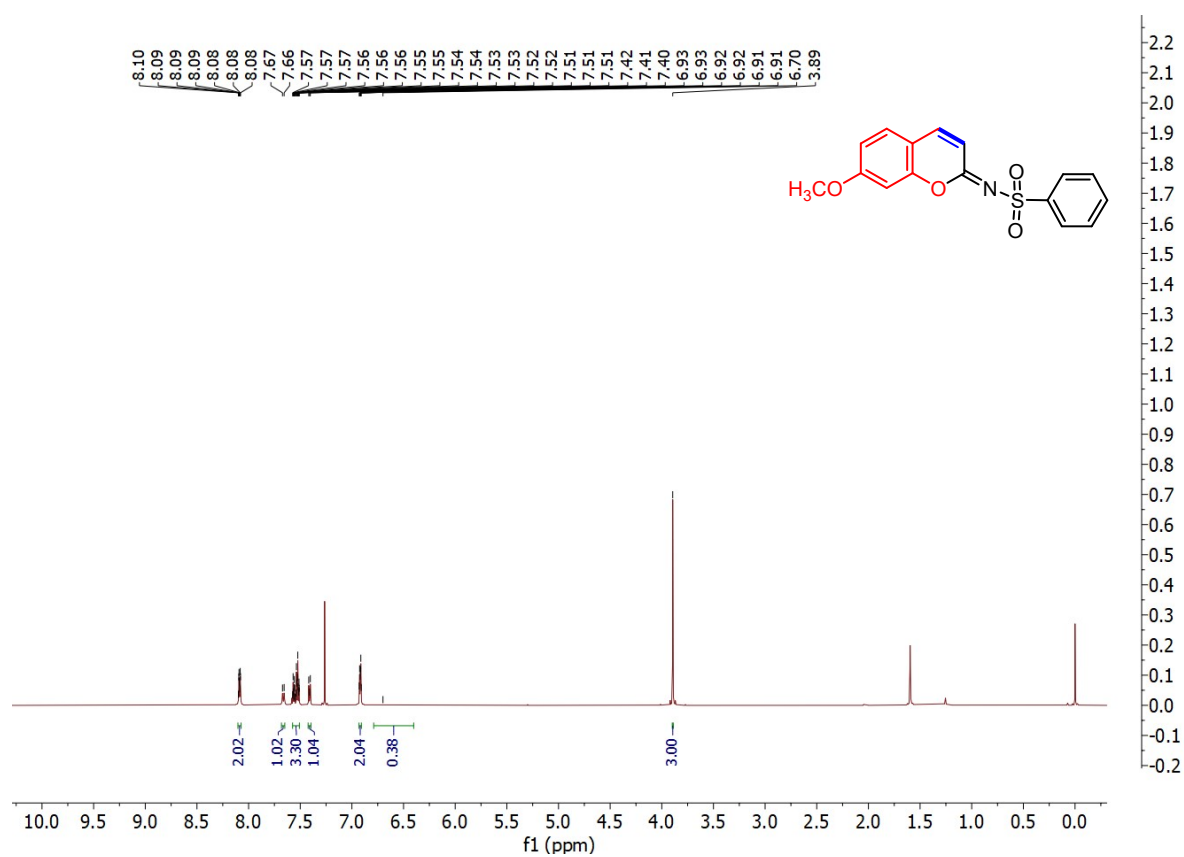
¹H-NMR of 3k



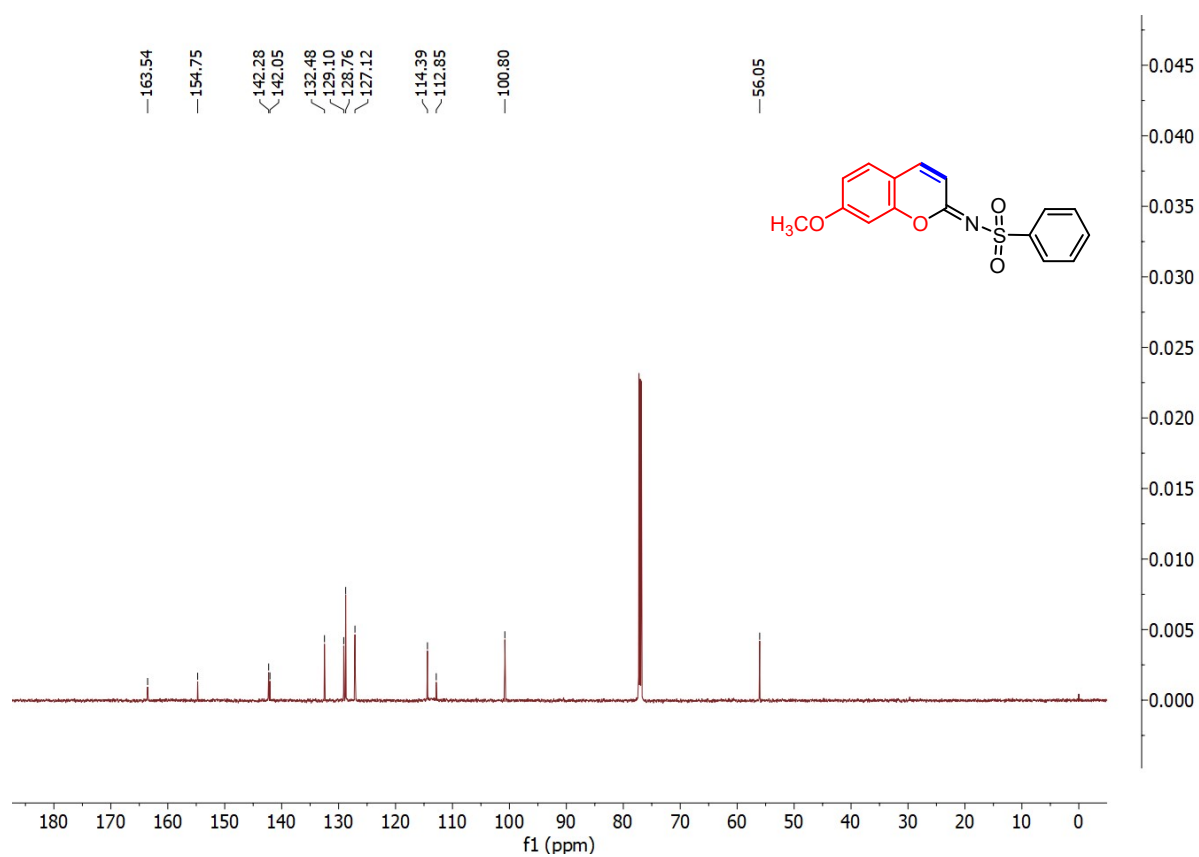
¹³C-NMR of 3k



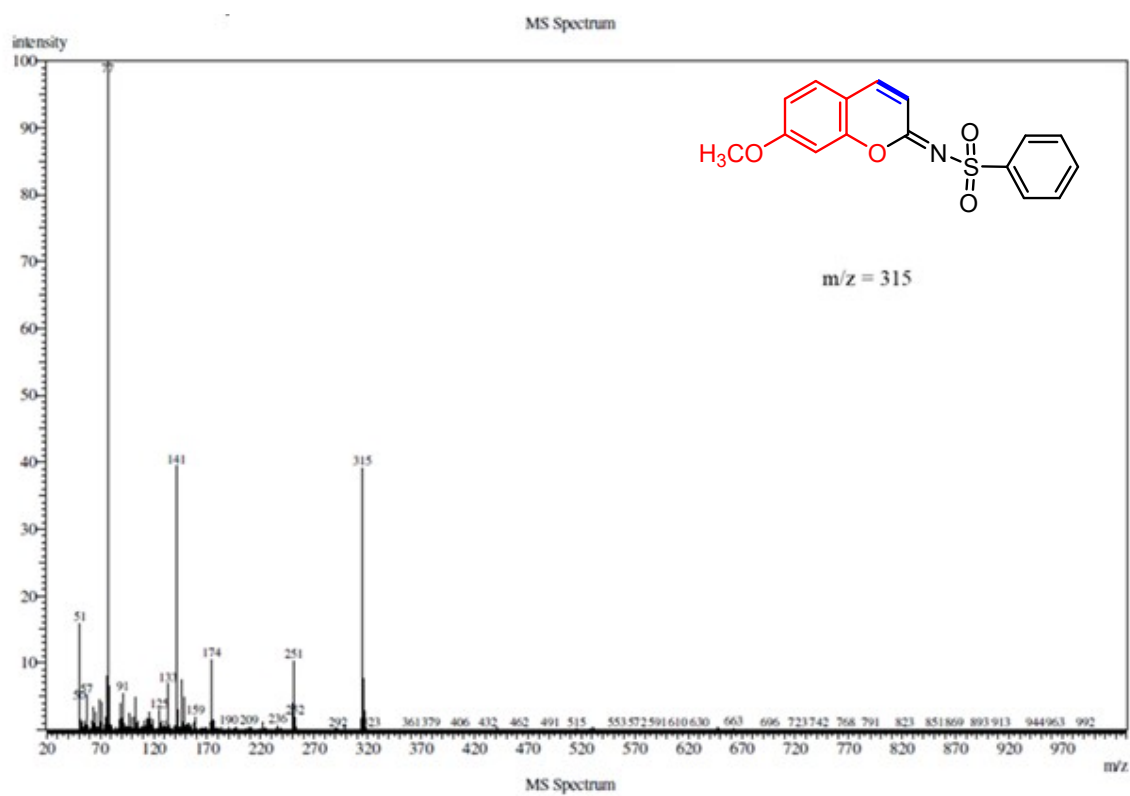
¹H-NMR of 3l



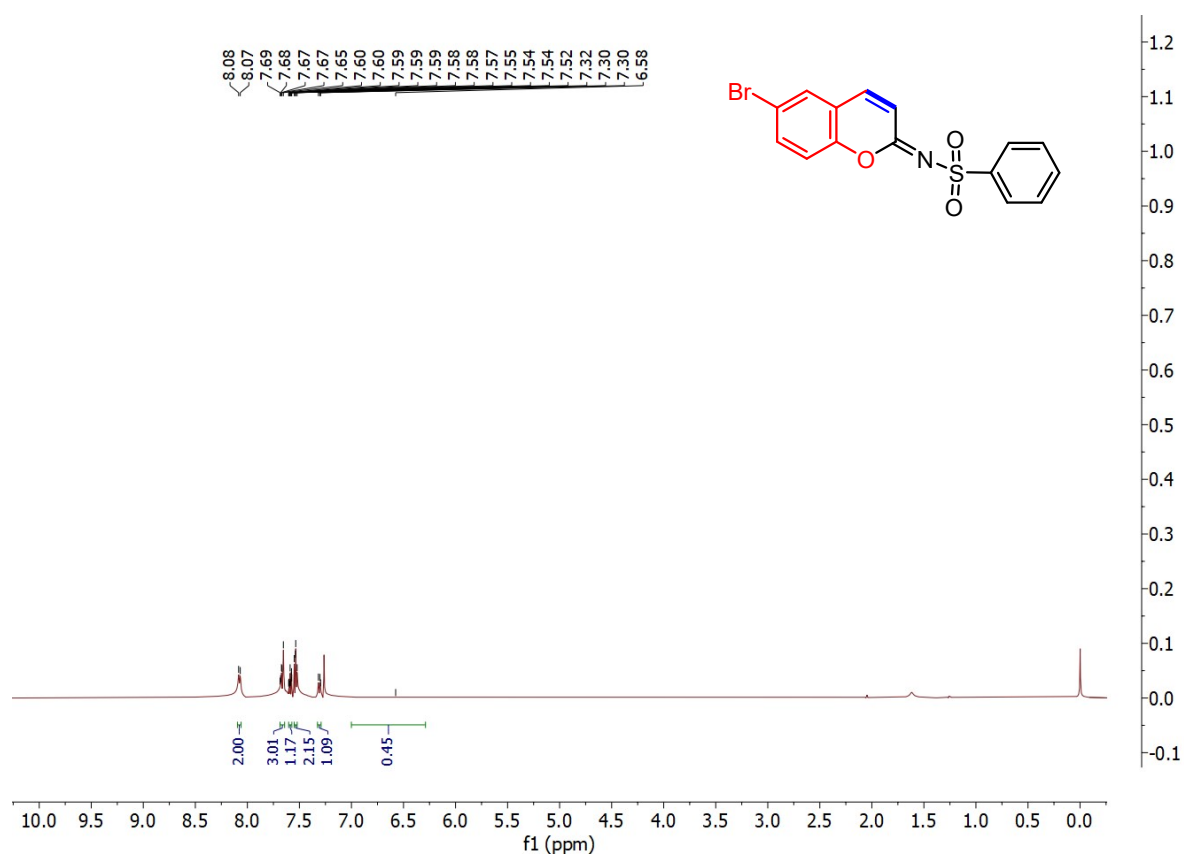
¹³C-NMR of 3l



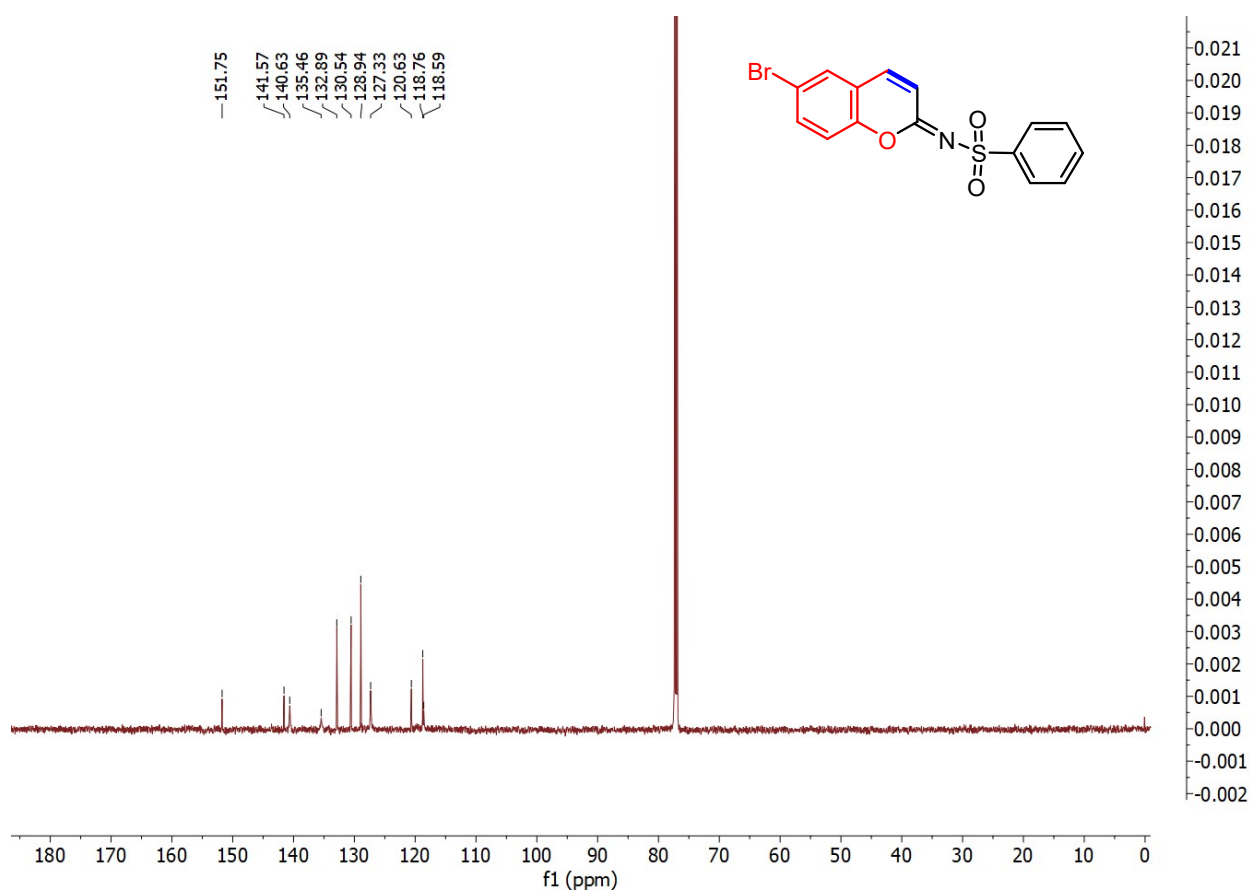
Mass Spectrum of 3l



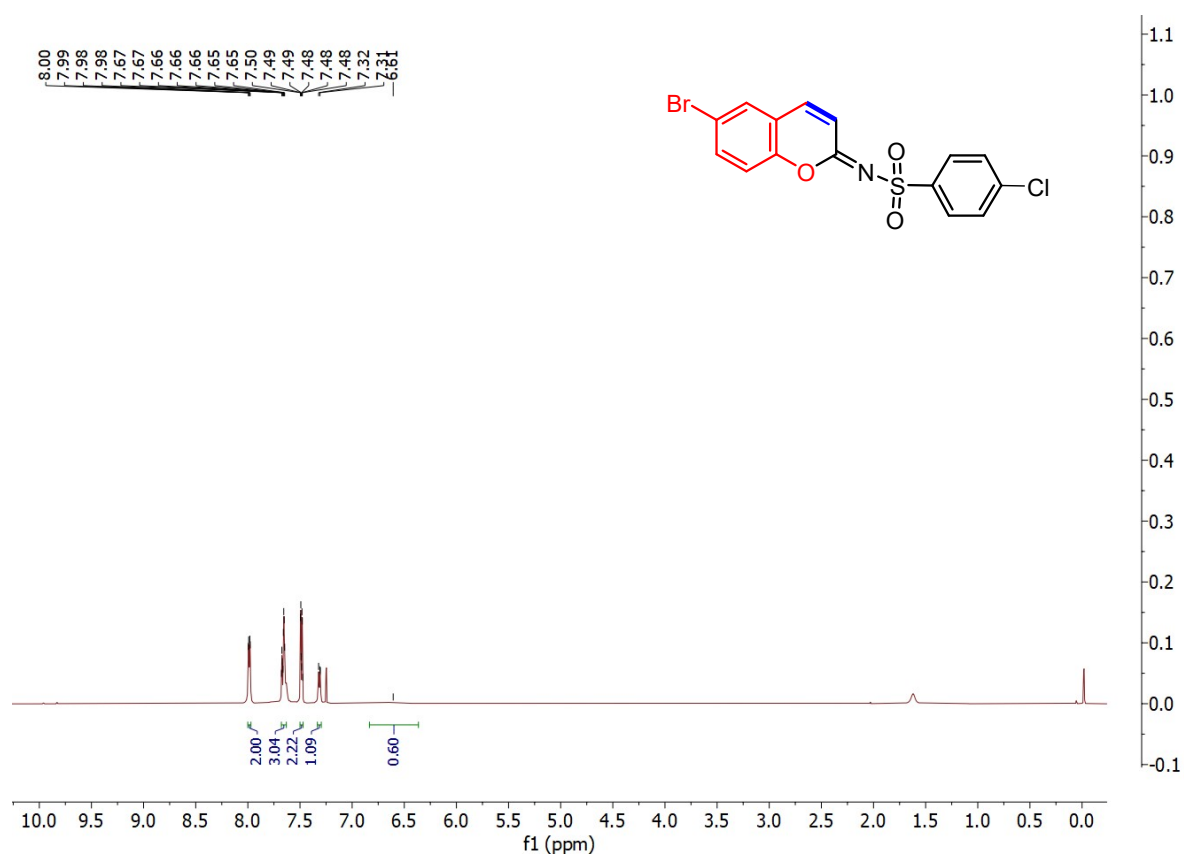
¹H-NMR of 3m



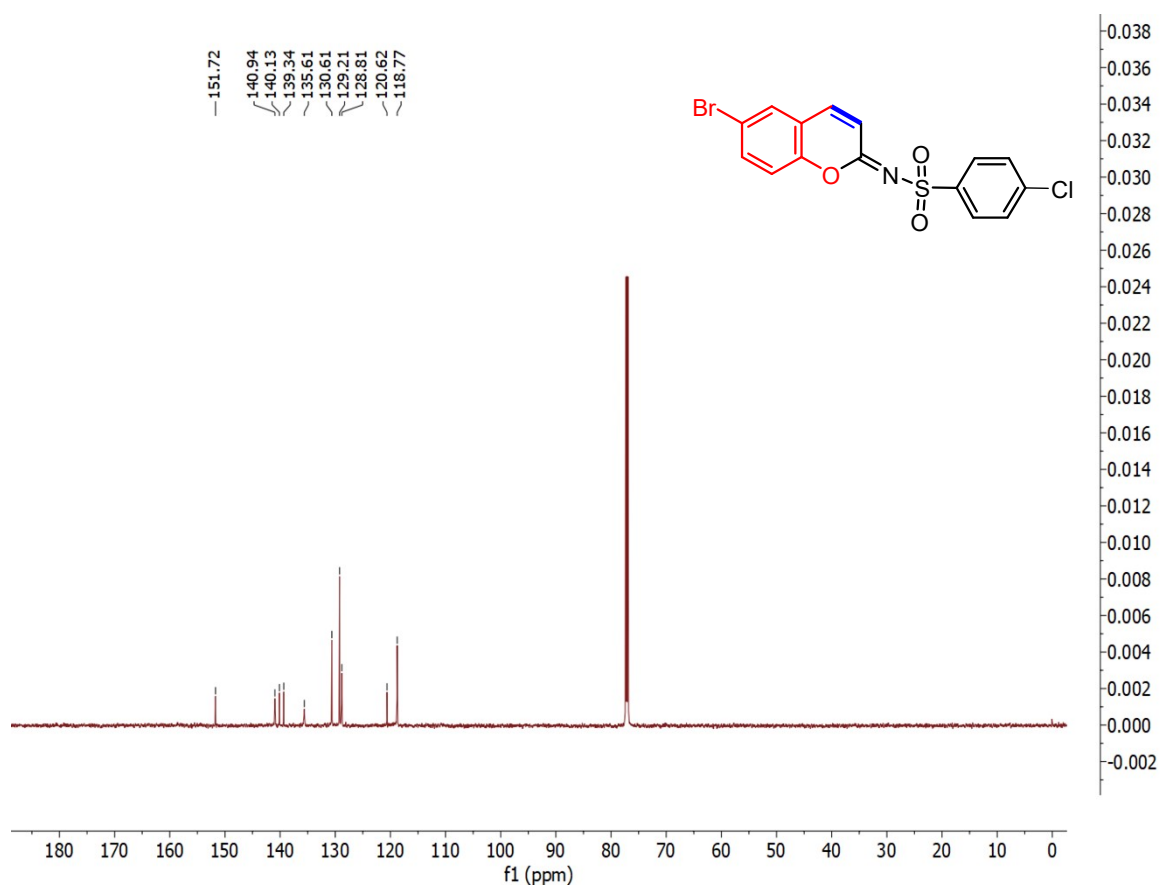
¹³C-NMR of 3m



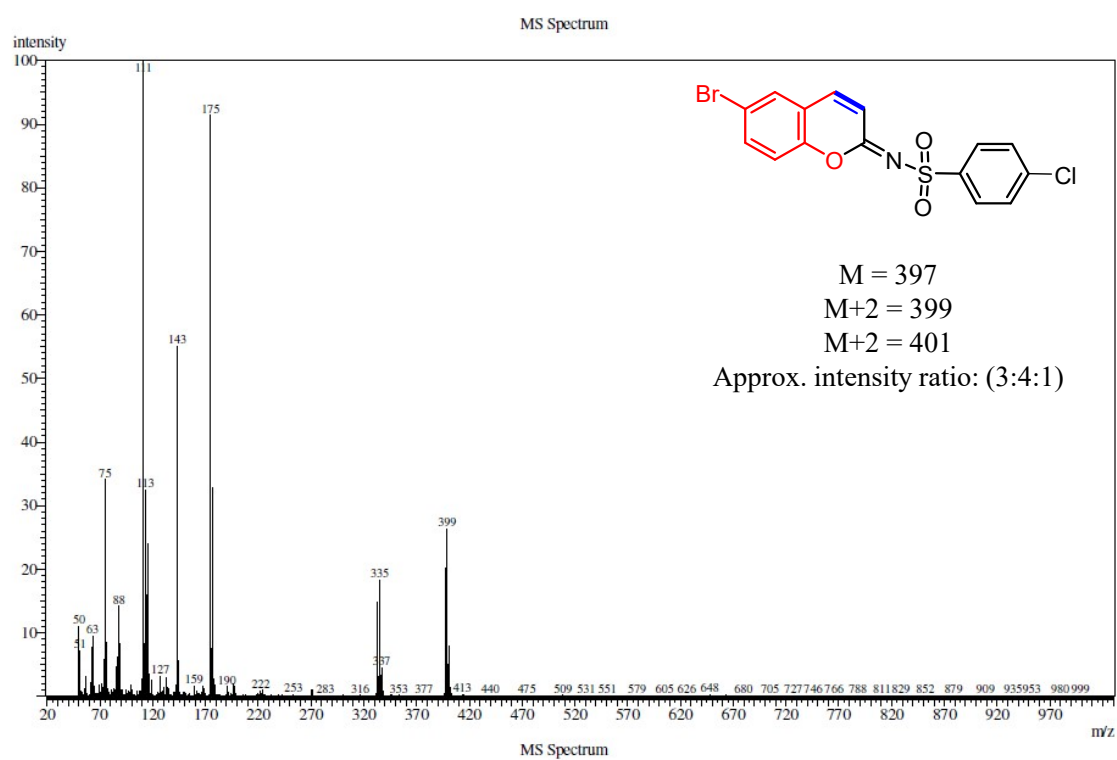
¹H-NMR of 3n



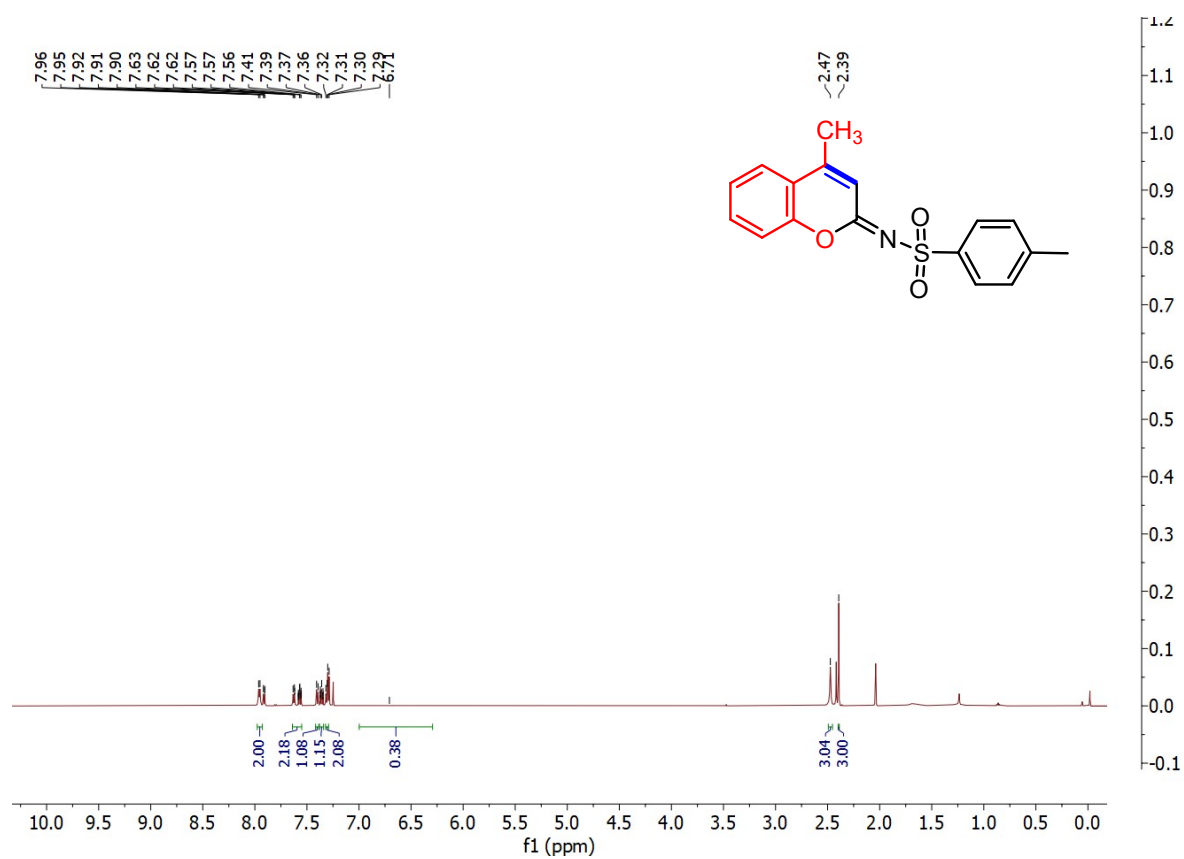
¹³C-NMR of 3n



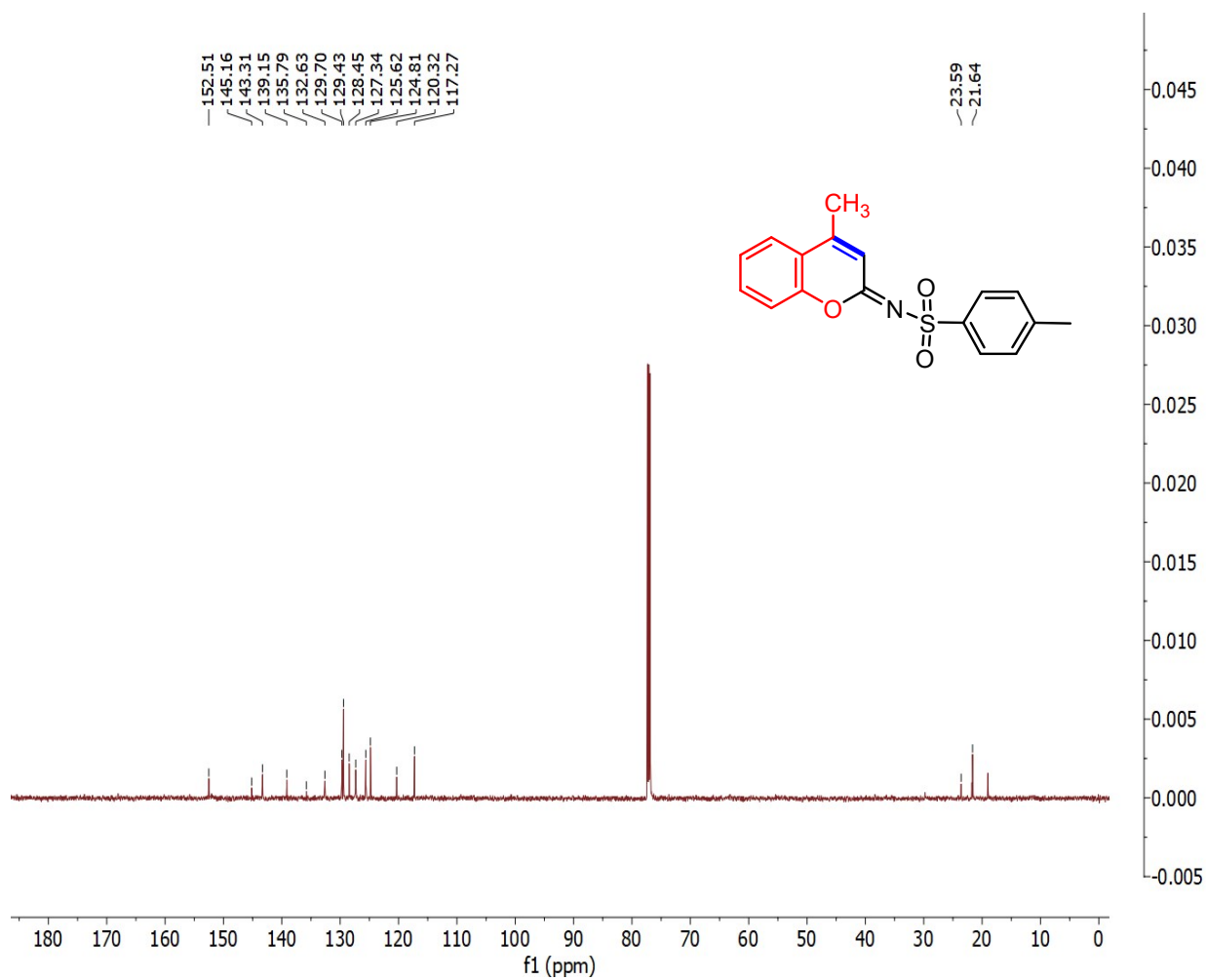
Mass Spectrum of 3n



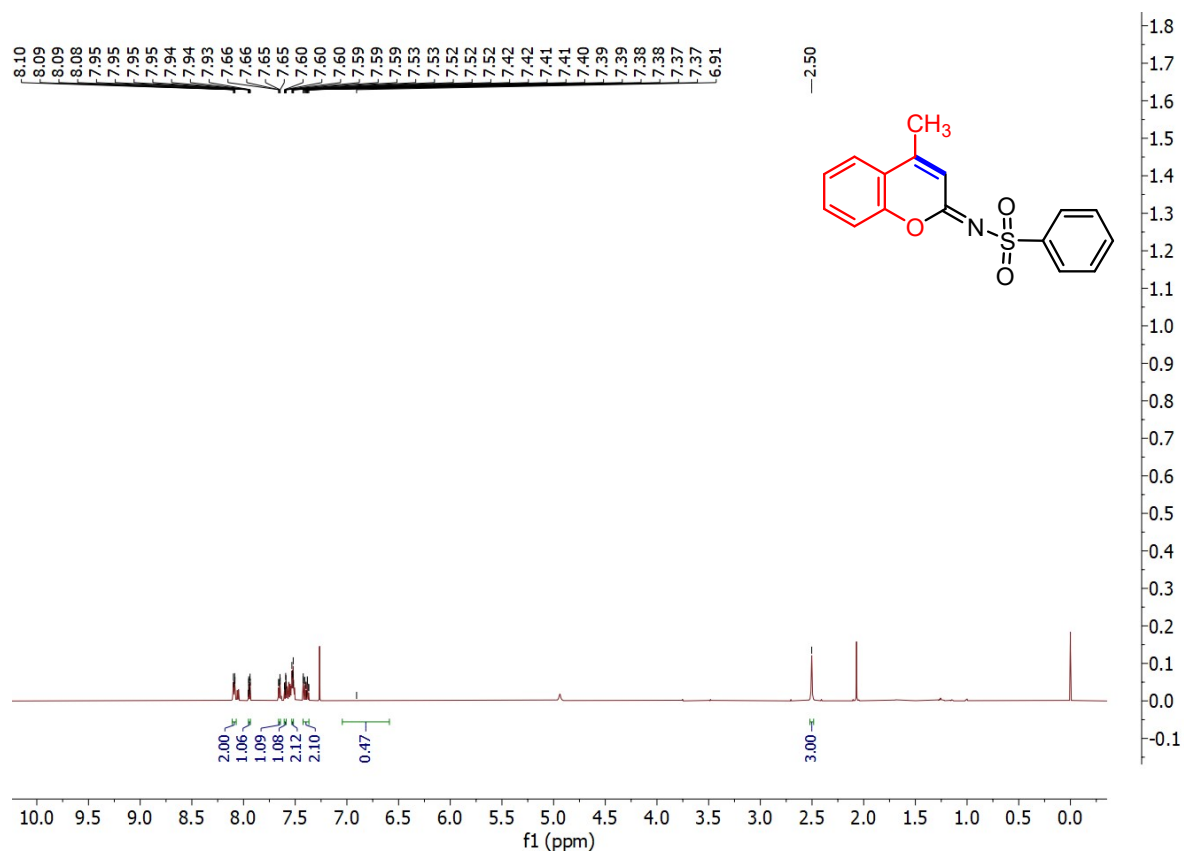
¹H-NMR of 3o



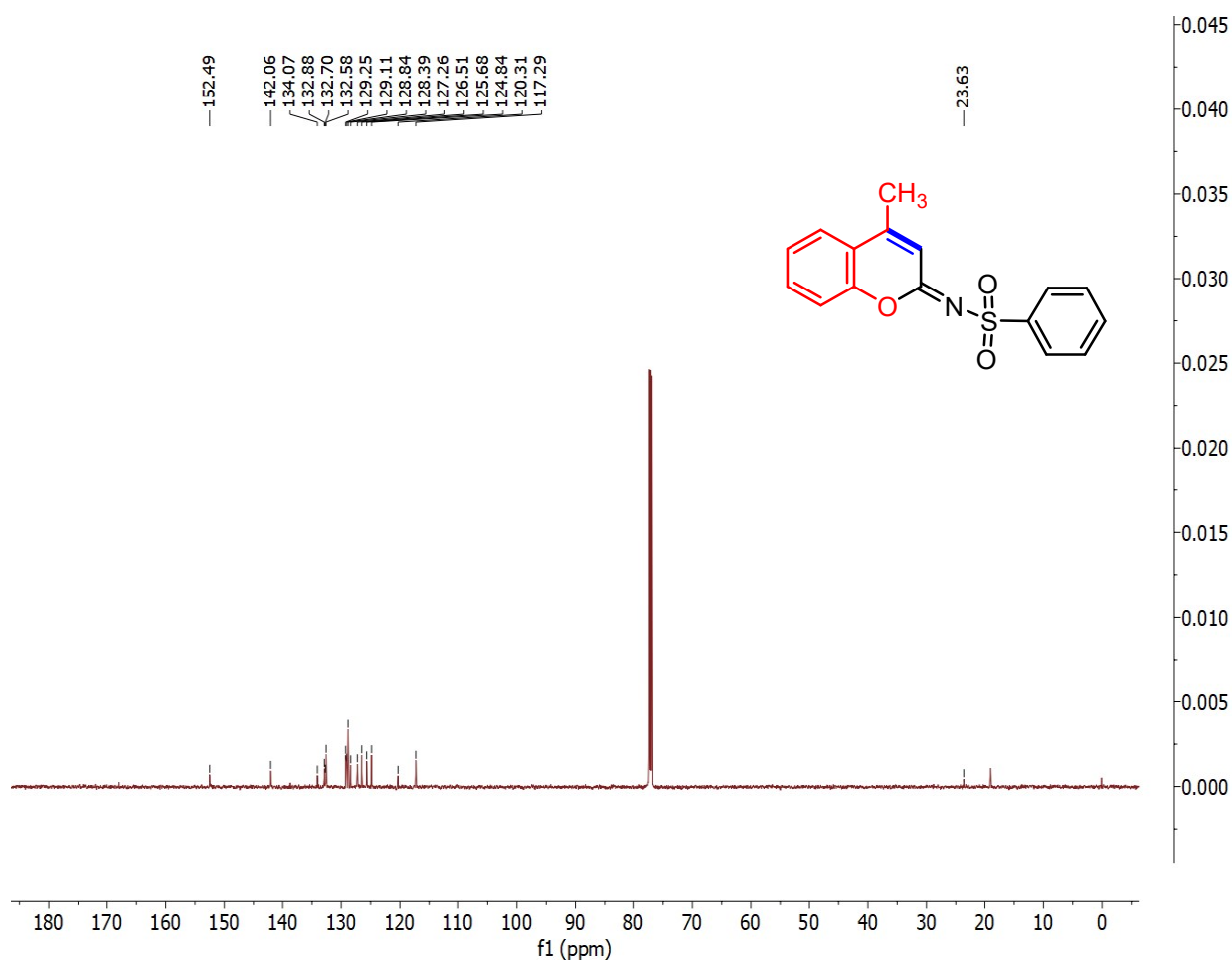
¹³C-NMR of 3o



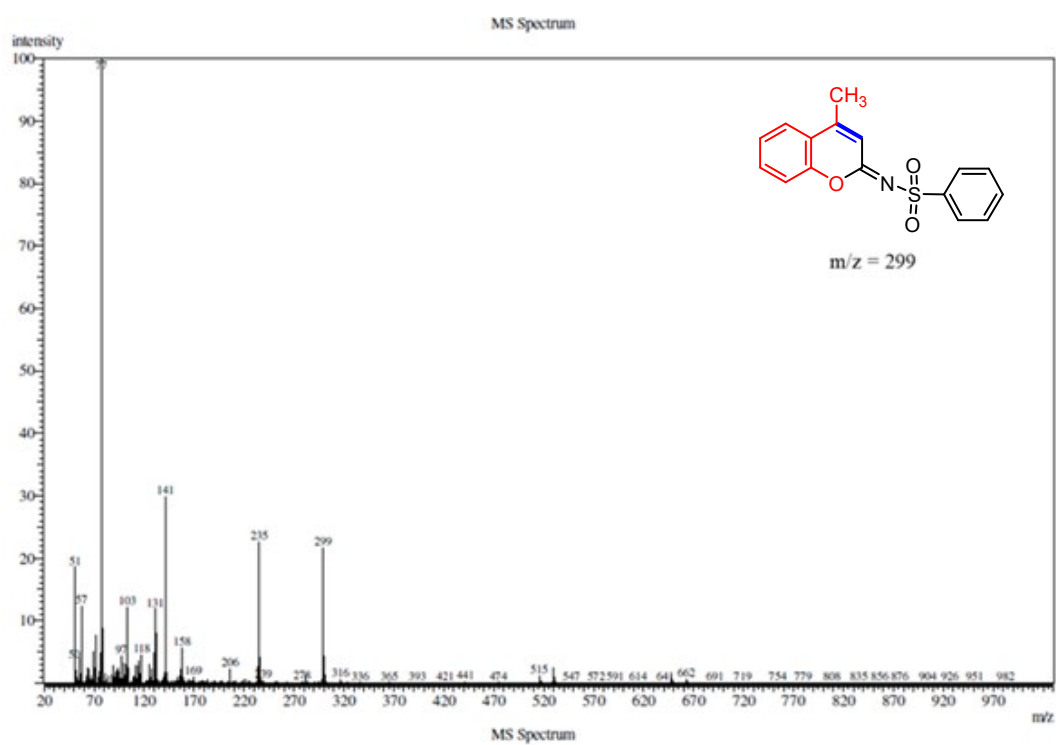
¹H-NMR of 3p



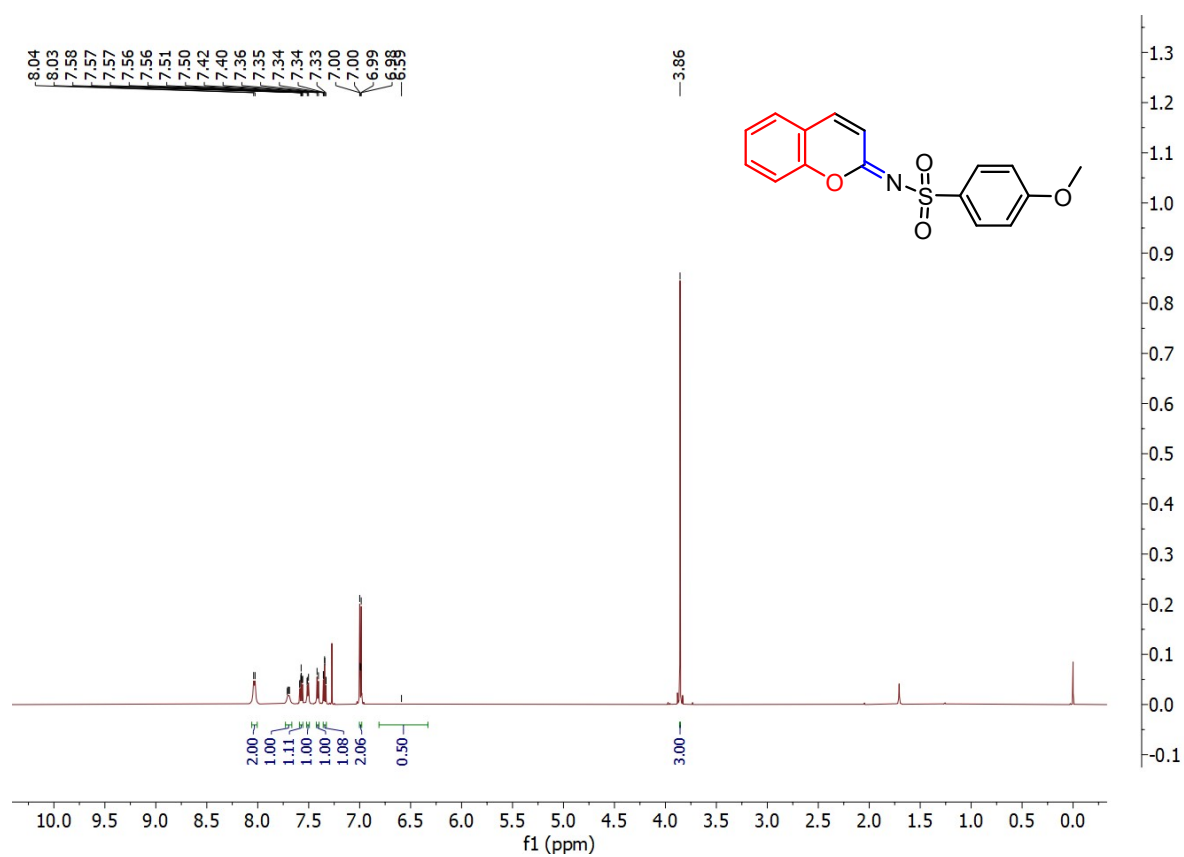
¹³C-NMR of 3p



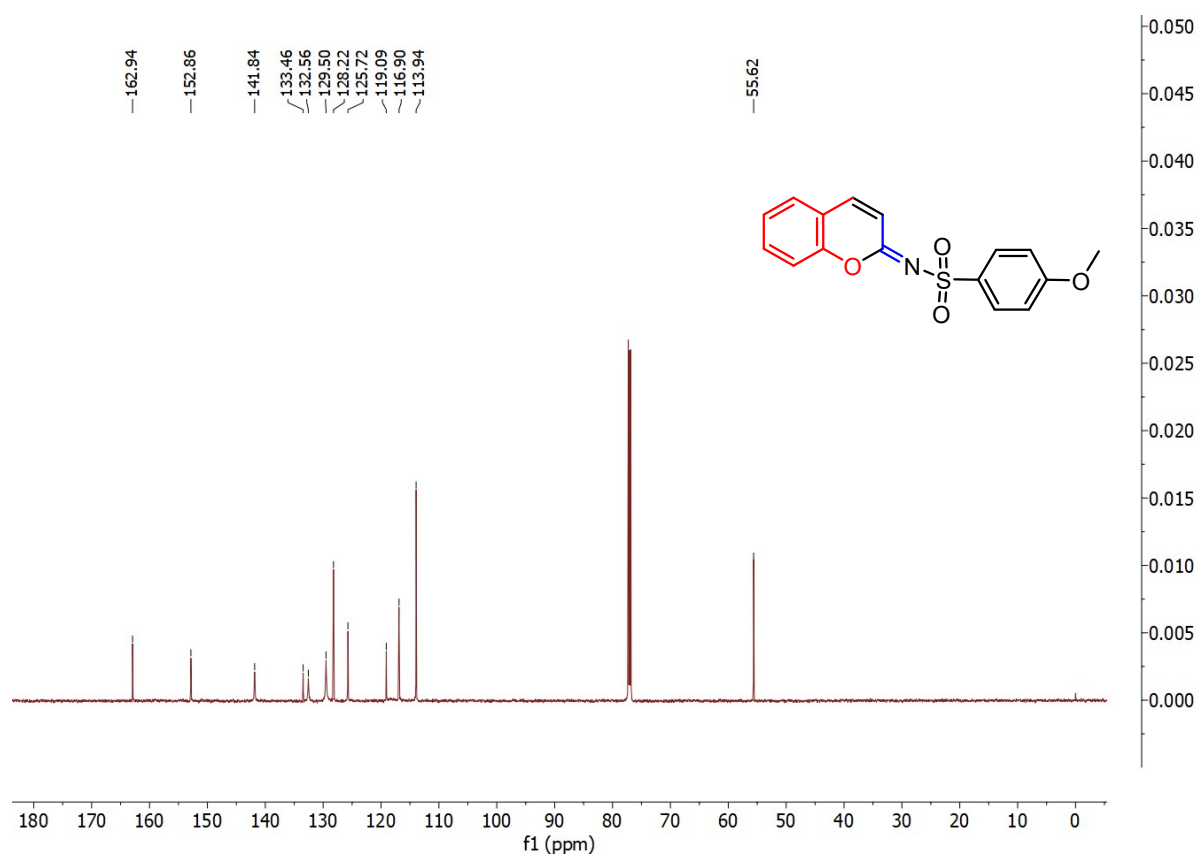
Mass Spectrum of 3p



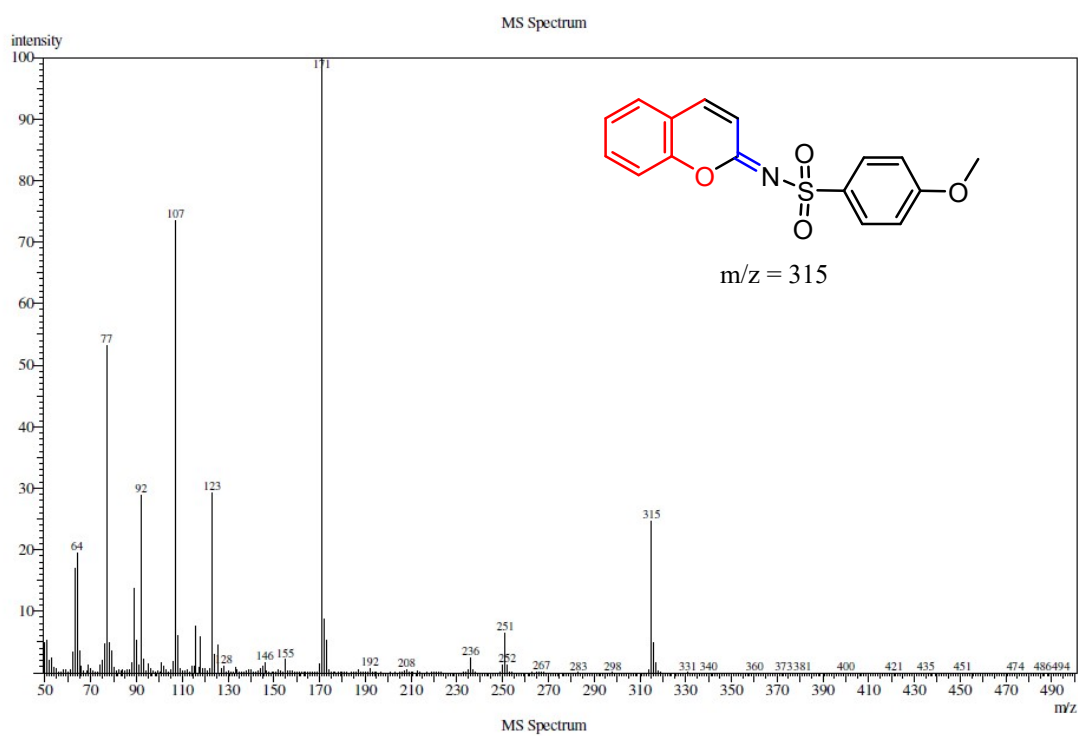
¹H-NMR of 3s



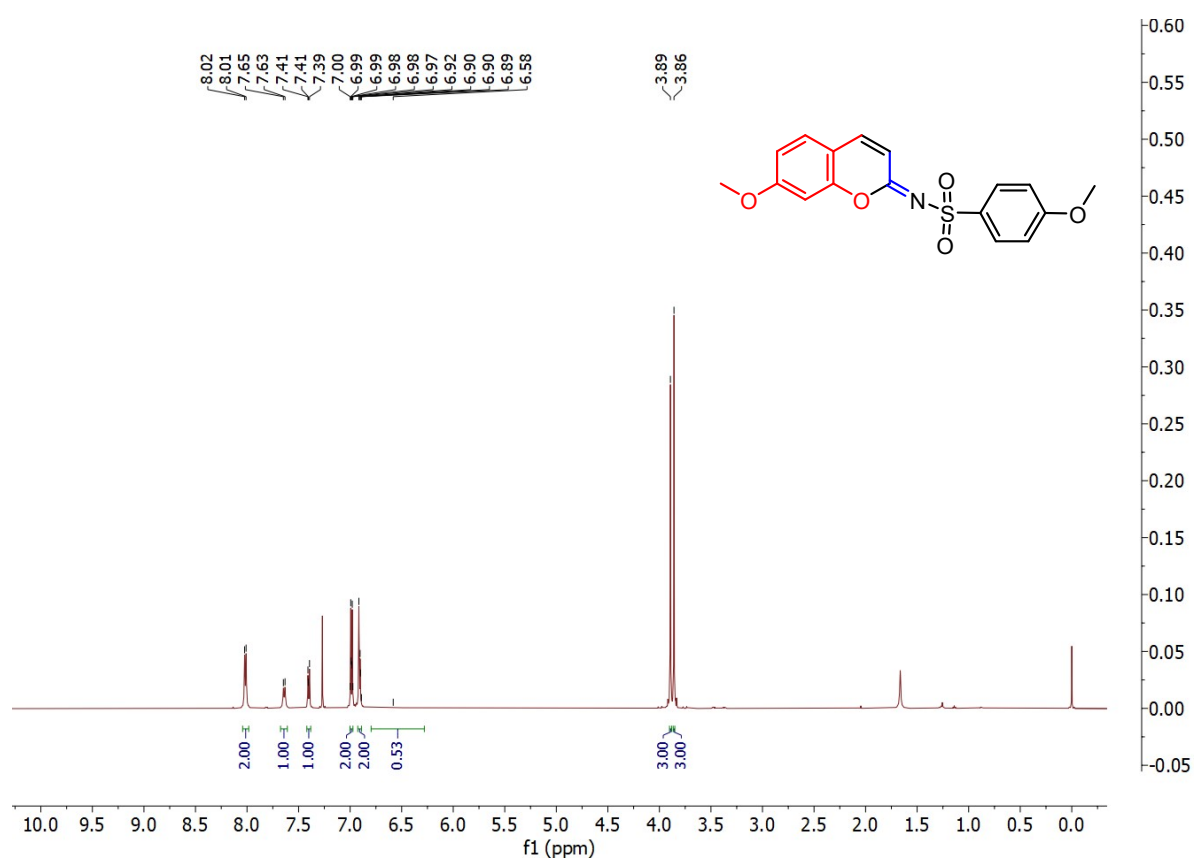
¹³C-NMR of 3s



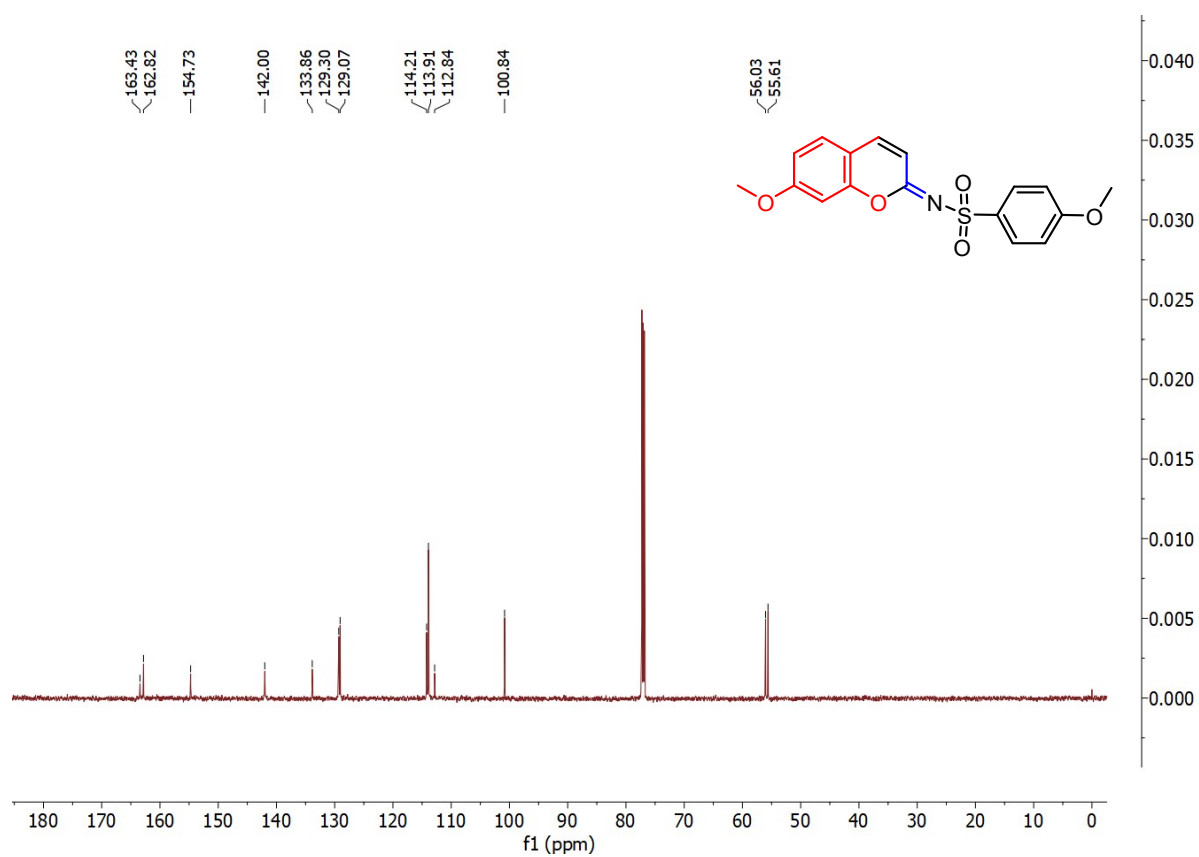
Mass Spectrum of 3s



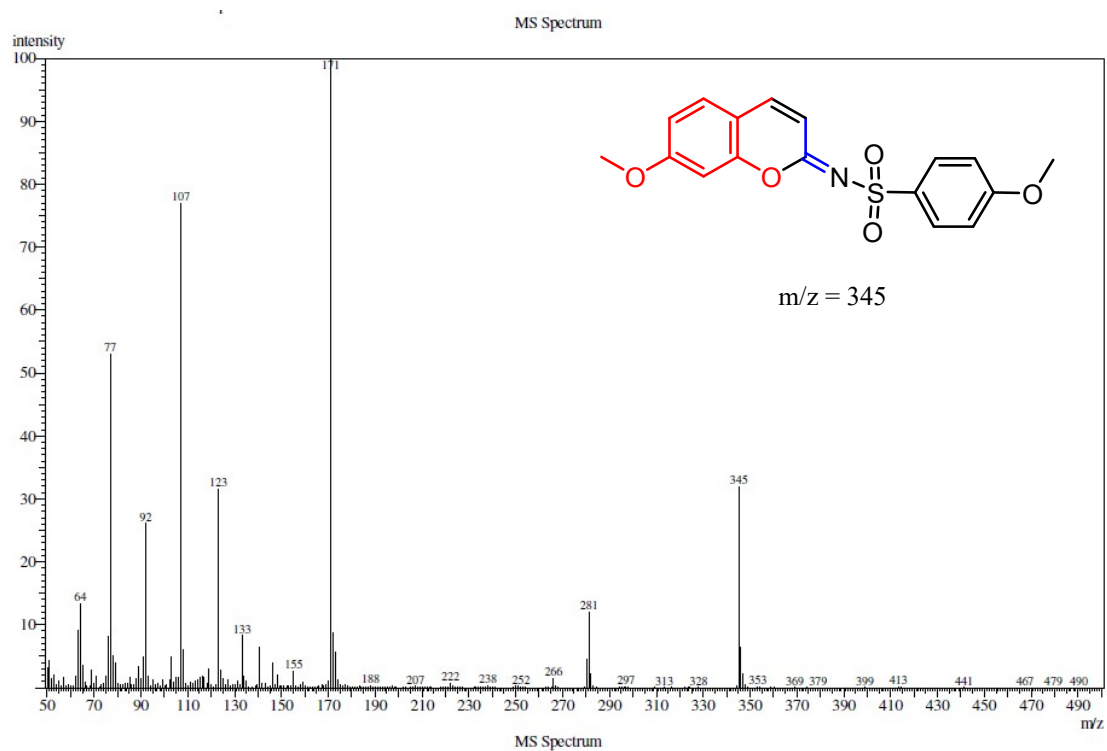
¹H-NMR of 3t



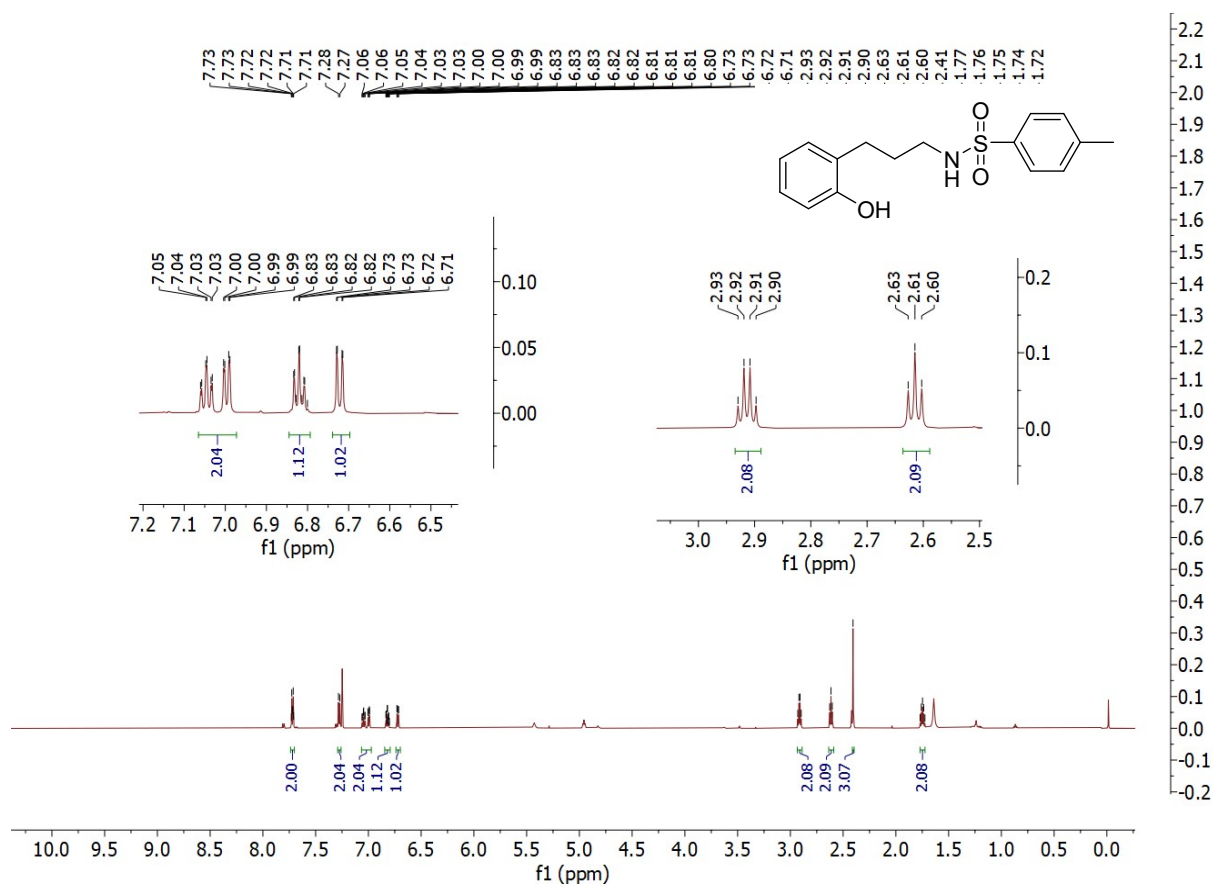
¹³C-NMR of 3t



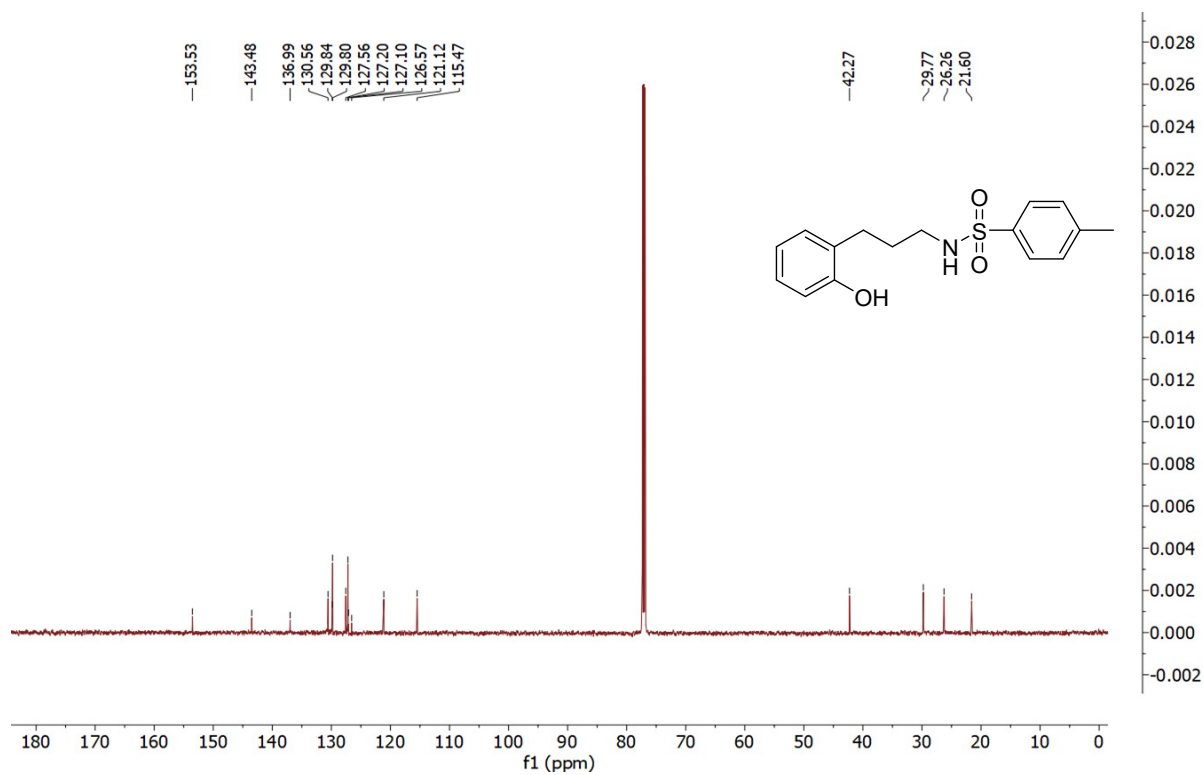
Mass Spectrum of 3t



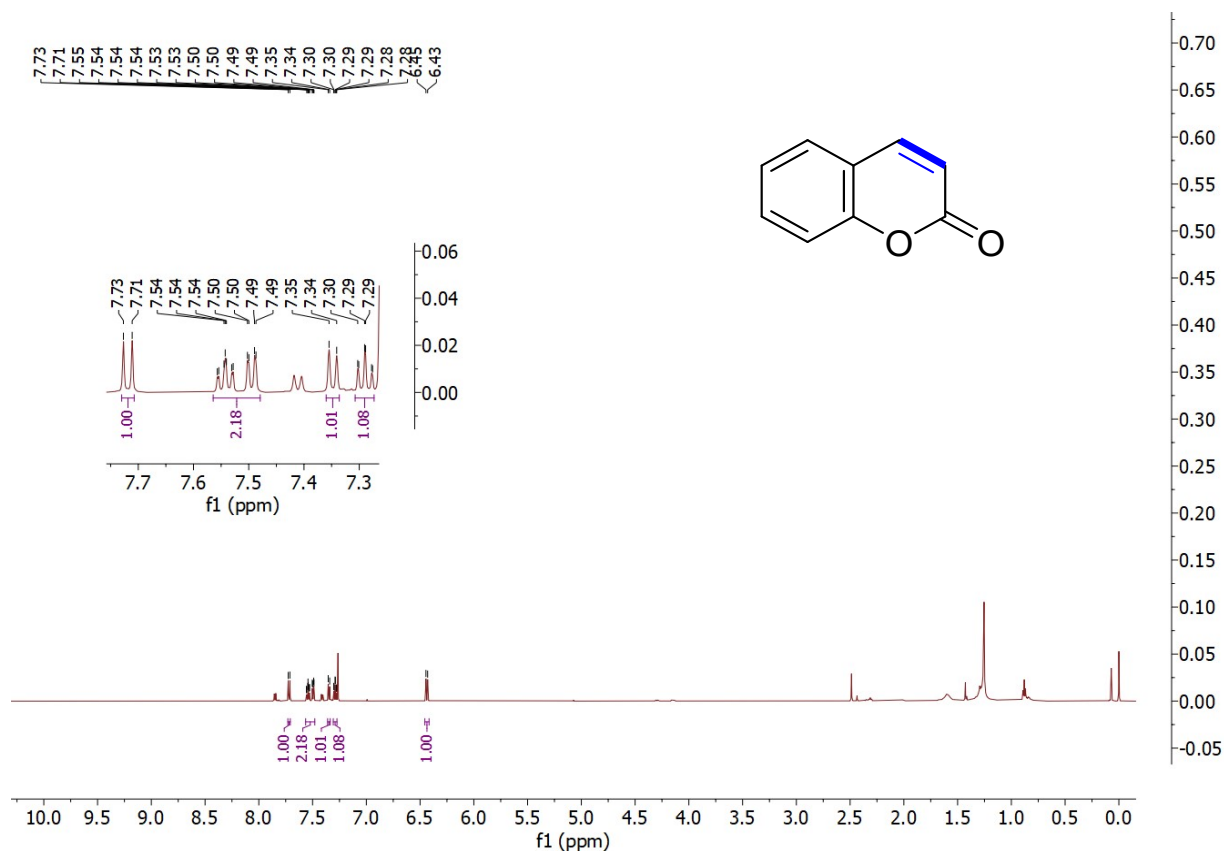
¹H-NMR of 4



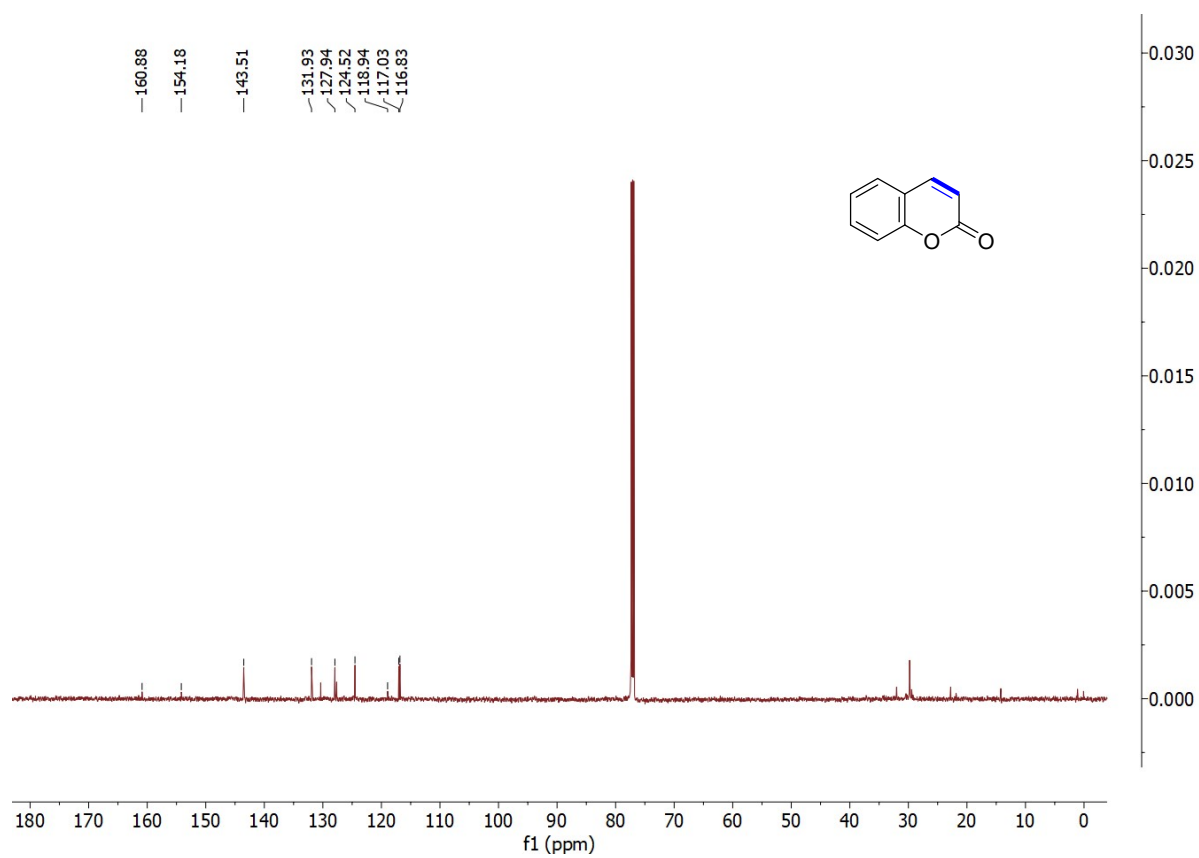
¹³C-NMR of 4



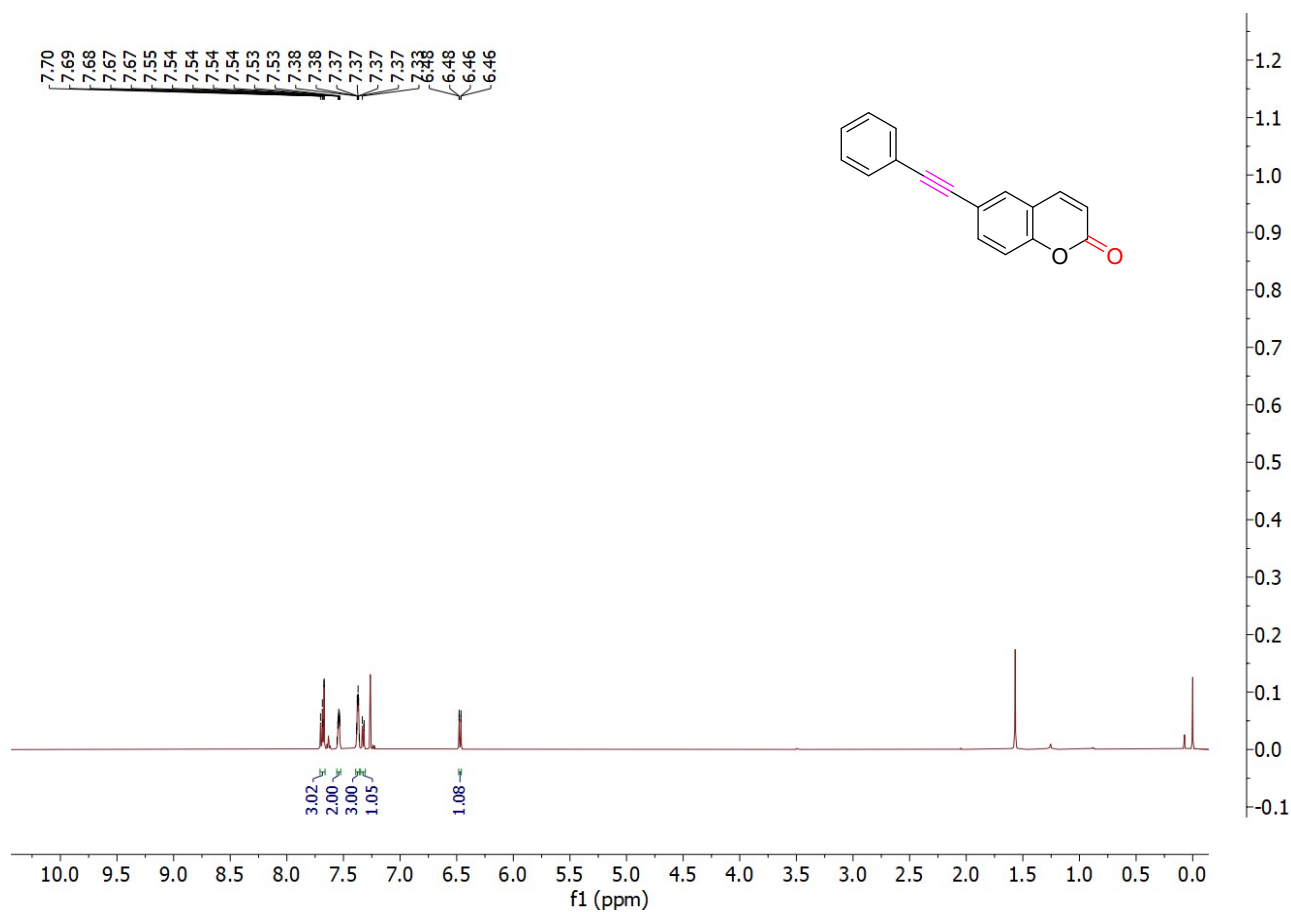
¹H-NMR of 5



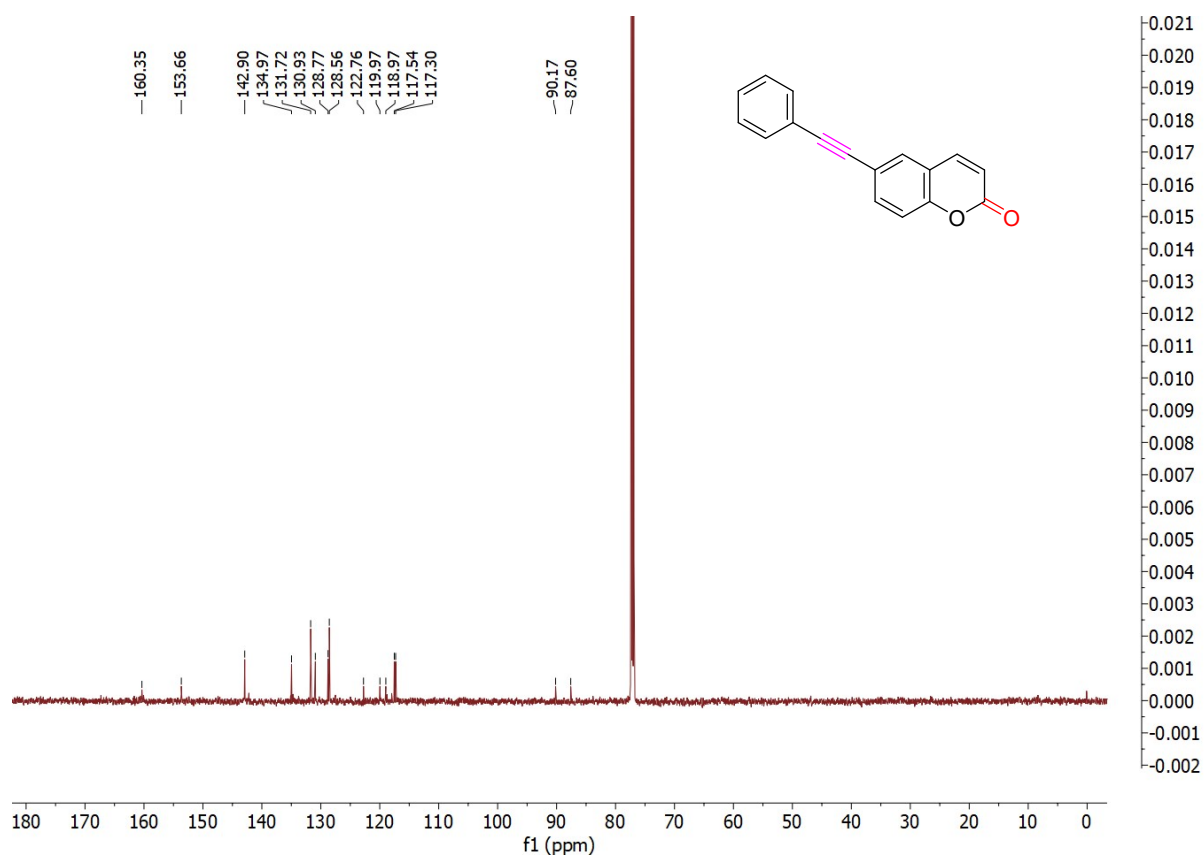
¹³C-NMR of 5



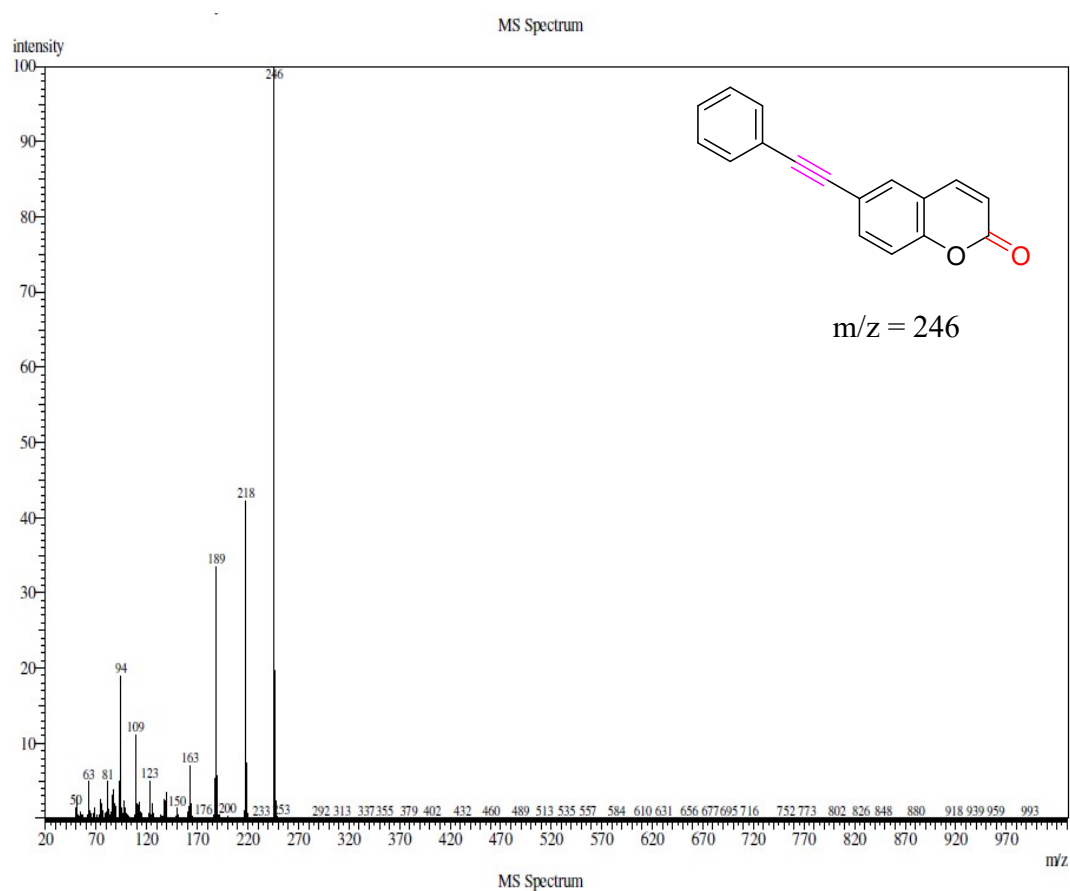
¹H-NMR of 6



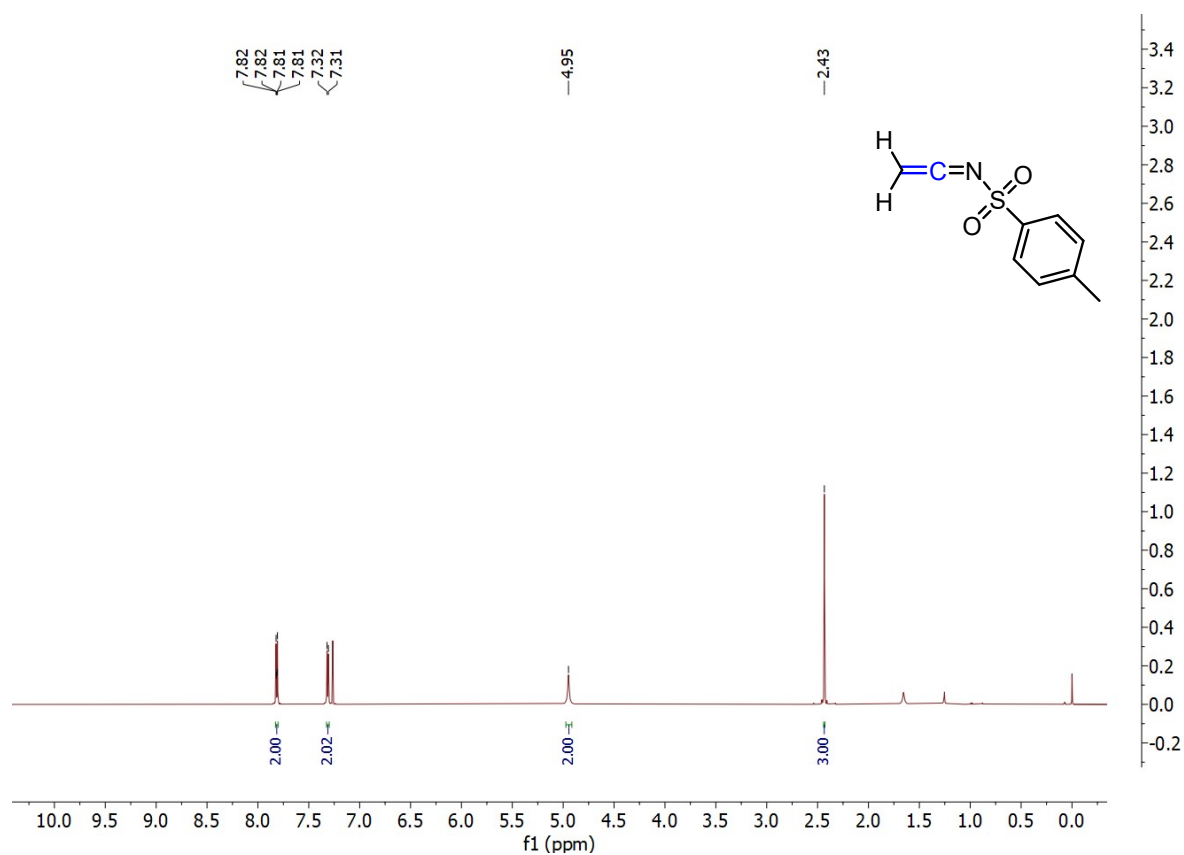
¹³C-NMR of 6



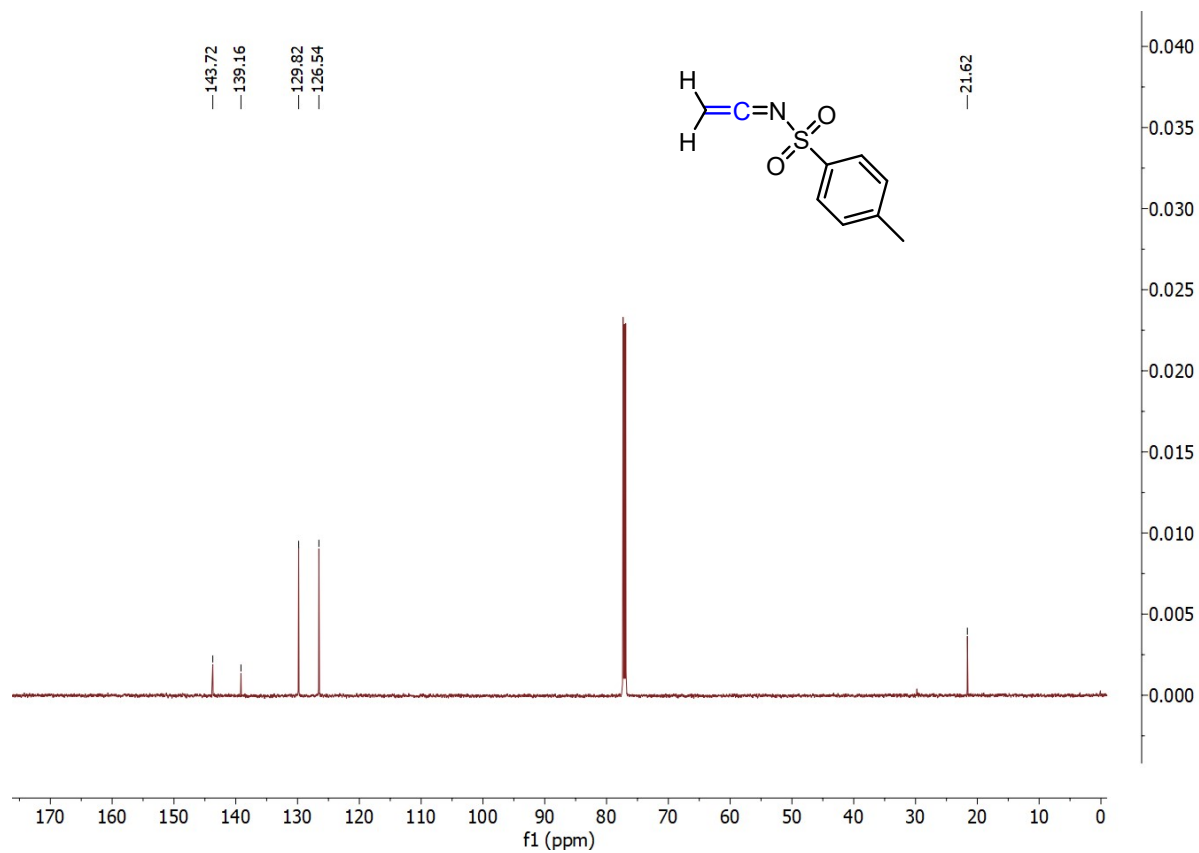
Mass Spectrum of 6



**¹H-NMR of 4-Methyl-*N*-vinylidenebenzenesulfonamide
(Ethenimine intermediate G)**



**^{13}C -NMR of 4-Methyl-*N*-vinylidenebenzenesulfonamide
(Ethenimine intermediate G)**

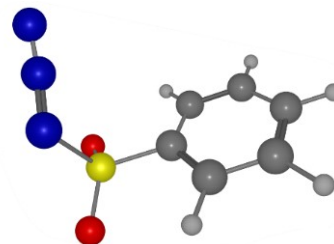


2. Cartesian coordinates

List of Cartesian coordinates of all the optimized structures

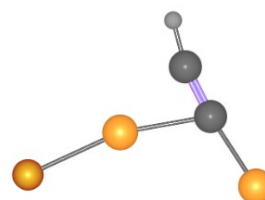
RN₃ (PhSO₂N₃)

N	1.850309000	0.044311000	-1.015185000
S	1.042185000	-0.773508000	0.327557000
O	1.190389000	-2.182301000	-0.035122000
O	1.589179000	-0.244958000	1.583181000
C	-0.660221000	-0.270261000	0.158490000
C	-1.468823000	-0.944281000	-0.762422000
C	-2.790654000	-0.524822000	-0.912605000
C	-3.278618000	0.547127000	-0.155707000
C	-2.451603000	1.206947000	0.759156000
C	-1.125306000	0.802827000	0.924640000
N	2.080340000	1.249418000	-0.792035000
N	2.336710000	2.349412000	-0.684797000
H	-1.075861000	-1.774765000	-1.337975000
H	-3.438075000	-1.036248000	-1.617194000
H	-4.308439000	0.867305000	-0.278382000
H	-2.836094000	2.033543000	1.347354000
H	-0.473201000	1.297161000	1.635621000



Species A2

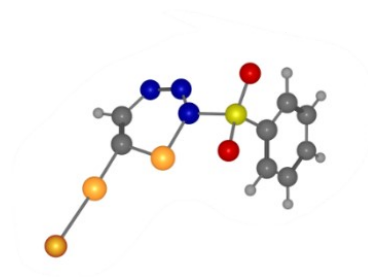
C	1.107072000	1.974954000	-0.000229000
C	1.664705000	0.862691000	0.000326000
Cu	2.672111000	-0.702831000	-0.000044000
Cu	-0.354415000	0.518047000	0.000086000
Br	-2.419529000	-0.419464000	-0.000036000
H	0.839659000	3.014079000	-0.000561000



Species B

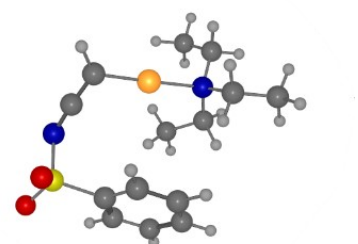
C	-0.682380000	2.131280000	-1.528981000
C	-1.247581000	1.172012000	-0.813739000
N	1.111196000	1.128316000	0.122050000
N	1.497873000	2.089560000	-0.685572000
N	0.682765000	2.609673000	-1.491265000
Cu	-0.465172000	0.109304000	0.485984000
S	2.215548000	0.385443000	1.192579000

C	3.397115000	-0.510149000	0.211990000
O	2.904526000	1.346293000	2.055242000
O	1.226951000	-0.578042000	1.784015000
C	3.014496000	-1.731929000	-0.352294000
C	3.938075000	-2.408670000	-1.148291000
C	5.208029000	-1.862972000	-1.371120000
C	5.567584000	-0.638464000	-0.798250000
C	4.658615000	0.054649000	0.002944000
H	2.029919000	-2.144711000	-0.165417000
H	3.666720000	-3.361462000	-1.590446000
H	5.920712000	-2.396192000	-1.992248000
H	6.554240000	-0.221858000	-0.971081000
H	4.921155000	1.002029000	0.459564000
Cu	-2.771315000	0.164306000	-0.371923000
Br	-4.646697000	-0.966437000	0.074154000
H	-1.267368000	2.672349000	-2.268894000



Species C

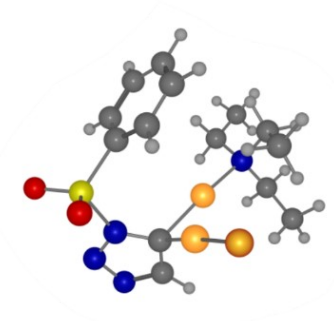
C	0.253898000	-2.533738000	0.610154000
C	1.331397000	-2.180770000	0.004671000
N	2.305849000	-1.756836000	-0.688228000
S	3.307319000	-0.604412000	0.089438000
C	2.327421000	0.899043000	0.077053000
O	3.551117000	-0.978820000	1.499846000
O	4.463973000	-0.422880000	-0.806762000
C	2.434545000	1.773995000	-1.007237000
C	1.641009000	2.922788000	-1.023930000
C	0.756892000	3.181639000	0.028984000
C	0.659822000	2.293089000	1.104249000
C	1.442592000	1.136501000	1.134516000
H	3.128130000	1.560445000	-1.812778000
H	1.714590000	3.613900000	-1.857366000
H	0.142371000	4.076286000	0.011275000
H	-0.019907000	2.501347000	1.923991000
H	1.382855000	0.443563000	1.965195000
Cu	-1.151152000	-1.265160000	0.316680000
H	0.178792000	-3.403793000	1.255380000
N	-2.645368000	0.024485000	0.035173000
C	-2.278042000	1.102707000	-0.953466000
H	-3.179697000	1.406545000	-1.497527000
H	-1.939167000	1.969525000	-0.383168000
C	-1.166374000	0.705381000	-1.923142000



H	-1.386531000	-0.224292000	-2.451245000
H	-0.214951000	0.584758000	-1.396419000
H	-1.031201000	1.498475000	-2.665956000
C	-2.891566000	0.619288000	1.399178000
H	-3.076147000	-0.217537000	2.079874000
H	-1.950123000	1.081035000	1.705955000
C	-4.030279000	1.638516000	1.506250000
H	-5.009414000	1.189219000	1.321328000
H	-3.897627000	2.477296000	0.816854000
H	-4.038158000	2.042493000	2.523437000
C	-3.858467000	-0.741966000	-0.405866000
H	-4.097450000	-1.433374000	0.407526000
H	-4.702457000	-0.050029000	-0.514621000
C	-3.679170000	-1.521785000	-1.704950000
H	-2.820789000	-2.200822000	-1.650579000
H	-3.545967000	-0.861330000	-2.565459000
H	-4.577002000	-2.121554000	-1.882489000

Species D

C	-0.866225000	-0.034427000	2.998491000
C	-0.892268000	-0.151126000	1.590939000
N	-1.655379000	-1.316929000	1.444904000
N	-2.089867000	-1.863633000	2.649869000
N	-1.580369000	-1.066006000	3.600389000
Cu	-1.166286000	1.379492000	0.335624000
S	-2.297602000	-1.991658000	-0.161917000
C	-0.786536000	-2.035590000	-1.246459000
O	-2.831310000	-3.480548000	0.172053000
O	-3.324287000	-0.867584000	-0.723590000
C	-0.607639000	-0.974358000	-2.142774000
C	0.510523000	-1.036140000	-2.994804000
C	1.389773000	-2.135697000	-2.929926000
C	1.165893000	-3.186470000	-2.015459000
C	0.057669000	-3.147784000	-1.149251000
H	-1.306461000	-0.144587000	-2.184223000
H	0.687759000	-0.231234000	-3.700459000
H	2.249304000	-2.175094000	-3.592247000
H	1.847261000	-4.030026000	-1.973947000
H	-0.134933000	-3.949217000	-0.442843000
Cu	0.910133000	0.072401000	0.784439000
Br	-1.762392000	3.136101000	-1.118662000



H	-0.375629000	0.720262000	3.592967000
N	2.853276000	0.199894000	0.394990000
C	3.500928000	0.956234000	1.544095000
H	3.341372000	0.346961000	2.441343000
H	4.583024000	1.017760000	1.366800000
C	2.945842000	2.368580000	1.778032000
H	1.851808000	2.363076000	1.873734000
H	3.221599000	3.056377000	0.972783000
H	3.364798000	2.762198000	2.711930000
C	3.137531000	0.845018000	-0.954485000
H	4.126604000	1.320652000	-0.916879000
H	3.189799000	0.037988000	-1.692532000
C	2.074635000	1.854097000	-1.414284000
H	1.939564000	2.676750000	-0.709307000
H	1.100925000	1.370035000	-1.551084000
H	2.373171000	2.276208000	-2.382344000
C	3.336705000	-1.249464000	0.404096000
H	3.042226000	-1.679378000	1.369256000
H	2.772067000	-1.771376000	-0.373419000
C	4.845639000	-1.453422000	0.178022000
H	5.446461000	-1.043045000	0.996325000
H	5.180301000	-1.001295000	-0.762196000
H	5.049076000	-2.529879000	0.122171000

Species E

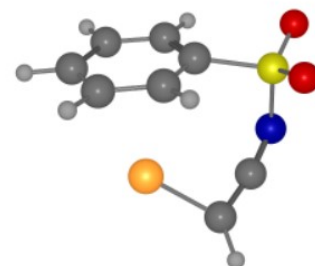
C	-2.247875000	-1.996426000	-0.516617000
C	-1.113393000	-1.296601000	-0.124115000
N	-1.605000000	-0.002914000	-0.164855000
N	-2.925902000	0.075513000	-0.525841000
N	-3.302160000	-1.151123000	-0.745391000
S	-0.835554000	1.484221000	0.378722000
C	0.869993000	1.080917000	0.057168000
O	-1.300699000	2.541112000	-0.520180000
O	-1.054214000	1.583813000	1.825325000
C	1.554055000	0.321256000	1.033570000
C	2.786156000	-0.255887000	0.682715000
C	3.317449000	-0.041696000	-0.606326000
C	2.647622000	0.763365000	-1.526930000
C	1.399455000	1.318169000	-1.205973000
H	1.167910000	0.259736000	2.047011000



H	3.345342000	-0.818838000	1.422039000
H	4.265435000	-0.496420000	-0.872665000
H	3.075821000	0.943005000	-2.506799000
H	0.839910000	1.892769000	-1.935596000
Cu	0.738637000	-1.630130000	0.320440000
H	-2.356073000	-3.062336000	-0.655804000

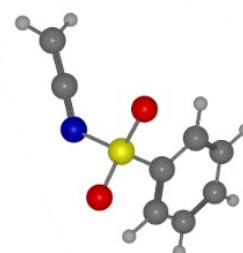
Species F

C	-0.228116000	-2.513763000	-0.527799000
C	0.803560000	-1.787360000	-0.763395000
N	1.675531000	-0.906865000	-1.052632000
S	1.964168000	0.249906000	0.182039000
C	0.346197000	1.023991000	0.262670000
O	2.241779000	-0.383655000	1.487698000
O	2.939618000	1.197558000	-0.380256000
C	-0.020749000	1.935782000	-0.724516000
C	-1.365819000	2.306824000	-0.852261000
C	-2.334112000	1.746934000	-0.016720000
C	-1.964611000	0.843093000	1.000837000
C	-0.606110000	0.476208000	1.151536000
H	0.729007000	2.332149000	-1.400735000
H	-1.654232000	3.019898000	-1.616894000
H	-3.377360000	2.020279000	-0.132091000
H	-2.699179000	0.508840000	1.728250000
H	-0.275673000	-0.130932000	1.988380000
Cu	-1.546476000	-1.122826000	-0.067794000
H	-0.262793000	-3.540213000	-0.186756000



Species G

C	3.468084000	-1.704982000	-0.661876000
C	2.533587000	-0.802139000	-0.812349000
N	1.659786000	0.043188000	-1.036498000
S	0.864076000	0.756765000	0.375078000
C	-0.807085000	0.175571000	0.140521000
O	1.411883000	0.194551000	1.620500000
O	0.924904000	2.205336000	0.135086000
C	-1.658723000	0.900365000	-0.697870000
C	-2.957681000	0.427835000	-0.893451000
C	-3.380996000	-0.745842000	-0.259798000
C	-2.511485000	-1.456274000	0.575389000



C	-1.208622000	-0.999525000	0.782020000
H	-1.316349000	1.811340000	-1.175762000
H	-3.636946000	0.977381000	-1.536886000
H	-4.392675000	-1.107055000	-0.415736000
H	-2.845712000	-2.363504000	1.067911000
H	-0.522788000	-1.534820000	1.429017000
H	4.505084000	-1.404484000	-0.553961000
H	3.208903000	-2.758562000	-0.640528000

Substrate 1a

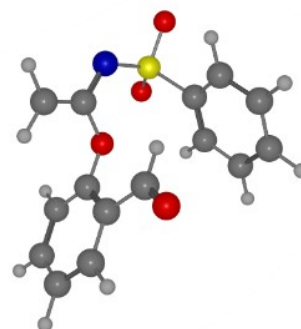
C	1.265906000	1.289108000	0.000100000
C	2.305942000	0.363516000	0.000126000
C	2.054023000	-1.020973000	0.000068000
C	0.741256000	-1.468536000	-0.000017000
C	-0.334486000	-0.553955000	-0.000050000
C	-0.062079000	0.841661000	0.000016000
C	-1.701934000	-1.041860000	-0.000159000
H	-1.832912000	-2.137707000	-0.000082000
O	-2.702380000	-0.306430000	-0.000126000
O	-1.054699000	1.756377000	0.000026000
H	1.459736000	2.356595000	0.000154000
H	3.331075000	0.721977000	0.000196000
H	2.877373000	-1.726936000	0.000089000
H	0.522079000	-2.533124000	-0.000069000
H	-1.912492000	1.265863000	0.000004000

Deprotonated 1a (1a')

C	1.770338000	0.751644000	0.000044000
C	2.221020000	-0.552285000	-0.000032000
C	1.317746000	-1.648988000	-0.000121000
C	-0.038676000	-1.384922000	-0.000116000
C	-0.545299000	-0.060330000	-0.000038000
C	0.360112000	1.083501000	-0.000085000
C	-1.970732000	0.165153000	0.000132000
H	-2.271635000	1.227929000	0.000036000
O	-2.854728000	-0.714020000	-0.000038000
O	-0.034115000	2.299119000	0.000205000
H	2.472788000	1.582054000	0.000171000
H	3.292221000	-0.745771000	0.000025000
H	1.690400000	-2.668837000	-0.000135000
H	-0.760082000	-2.198808000	-0.000129000

Species H

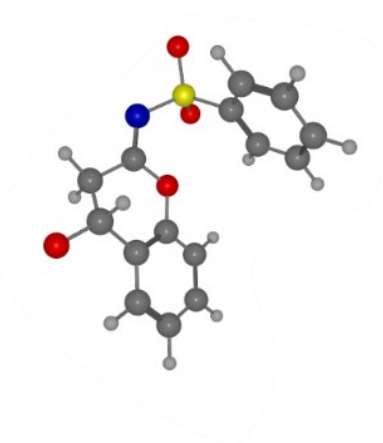
C	2.264446000	0.584560000	0.268150000
C	1.873340000	-0.671121000	-0.237174000
C	2.788980000	-1.497378000	-0.887538000
C	4.110749000	-1.074132000	-1.042181000
C	4.520460000	0.170916000	-0.543598000
C	3.601599000	0.989599000	0.106351000
C	1.294843000	1.463011000	0.952759000
O	0.558534000	-1.078634000	-0.166942000
O	1.597909000	2.532894000	1.474584000
C	0.048404000	-1.634504000	1.017922000
N	-1.301413000	-1.851513000	1.007673000
C	0.855748000	-1.916590000	2.070959000
S	-2.251447000	-1.345320000	-0.182323000
C	-2.045349000	0.447977000	-0.356909000
O	-1.952895000	-1.929257000	-1.524135000
O	-3.651613000	-1.554141000	0.286932000
C	-1.355192000	0.974121000	-1.450330000
C	-1.144063000	2.353892000	-1.525524000
C	-1.617543000	3.194085000	-0.512285000
C	-2.309761000	2.656040000	0.578684000
C	-2.525722000	1.278156000	0.661064000
H	2.452803000	-2.457586000	-1.264092000
H	4.822152000	-1.716132000	-1.552684000
H	5.548587000	0.495590000	-0.667400000
H	3.895051000	1.959355000	0.495602000
H	0.251791000	1.114712000	0.971453000
H	1.925571000	-1.767318000	2.025417000
H	-0.979986000	0.306404000	-2.216779000
H	-0.603501000	2.769529000	-2.370575000
H	-1.443717000	4.264350000	-0.569329000
H	-2.677498000	3.306558000	1.366399000
H	-3.057425000	0.850848000	1.504854000
H	0.418110000	-2.319282000	2.974965000



Species I

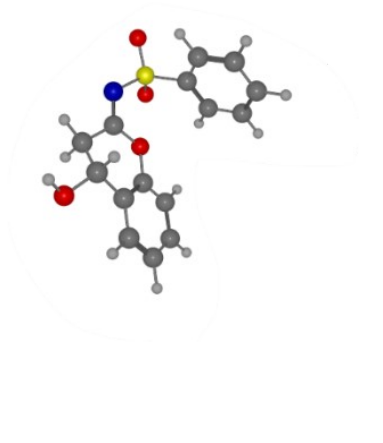
C	2.673940000	-0.121886000	0.382506000
C	1.774959000	0.268462000	-0.611787000
C	2.029694000	1.293235000	-1.516290000
C	3.253402000	1.966087000	-1.430319000

C	4.186818000	1.593369000	-0.456529000
C	3.894595000	0.554234000	0.435521000
C	2.304230000	-1.259178000	1.351919000
O	0.513404000	-0.347942000	-0.724419000
O	3.341106000	-1.868202000	1.962491000
C	0.276569000	-1.530131000	-0.132098000
N	-0.928355000	-2.007478000	-0.067975000
C	1.431230000	-2.242658000	0.484671000
S	-2.234748000	-1.159967000	-0.727710000
C	-2.288215000	0.438373000	0.095886000
O	-2.050359000	-0.945373000	-2.179301000
O	-3.418751000	-1.925403000	-0.289009000
C	-1.817974000	1.571458000	-0.570281000
C	-1.853044000	2.801393000	0.089783000
C	-2.342443000	2.882672000	1.398102000
C	-2.808300000	1.736139000	2.051705000
C	-2.787196000	0.501161000	1.400197000
H	1.287105000	1.550573000	-2.264489000
H	3.473876000	2.770042000	-2.125838000
H	5.141285000	2.108409000	-0.395608000
H	4.609205000	0.237709000	1.189130000
H	1.579763000	-0.791884000	2.073162000
H	2.076093000	-2.636688000	-0.312379000
H	-1.430695000	1.485381000	-1.578305000
H	-1.493911000	3.692009000	-0.416117000
H	-2.362329000	3.840534000	1.908827000
H	-3.191420000	1.802217000	3.065049000
H	-3.153684000	-0.393858000	1.890945000
H	1.066370000	-3.073634000	1.088798000



Species J

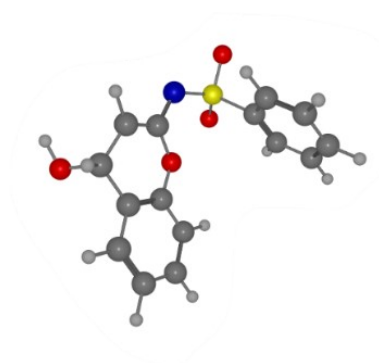
C	2.708410000	-0.044485000	0.341807000
C	1.748656000	0.372307000	-0.582999000
C	1.940720000	1.456734000	-1.430917000
C	3.148170000	2.155417000	-1.357008000
C	4.132545000	1.759649000	-0.445179000
C	3.910883000	0.666400000	0.397693000
C	2.389160000	-1.224575000	1.228549000
O	0.500598000	-0.262469000	-0.676864000
O	3.600446000	-1.865189000	1.612300000
C	0.290815000	-1.465322000	-0.120049000
N	-0.884692000	-1.994200000	-0.078475000
C	1.475603000	-2.188456000	0.450169000



S	-2.224926000	-1.196279000	-0.758072000
C	-2.365090000	0.374232000	0.102014000
O	-2.001464000	-0.946165000	-2.195913000
O	-3.371309000	-2.033343000	-0.361569000
C	-1.948766000	1.544658000	-0.535065000
C	-2.054461000	2.755446000	0.152156000
C	-2.559898000	2.780754000	1.456523000
C	-2.971469000	1.597138000	2.079815000
C	-2.879934000	0.379971000	1.401793000
H	1.158910000	1.737251000	-2.127985000
H	3.316352000	3.003788000	-2.012520000
H	5.071828000	2.300585000	-0.389981000
H	4.669782000	0.348617000	1.103801000
H	1.857607000	-0.867438000	2.123278000
H	2.052351000	-2.603746000	-0.386845000
H	-1.551663000	1.503270000	-1.542142000
H	-1.738810000	3.674923000	-0.330343000
H	-2.635272000	3.724431000	1.987904000
H	-3.367640000	1.620446000	3.089915000
H	-3.205091000	-0.543242000	1.868786000
H	3.419178000	-2.449307000	2.361690000
H	1.125885000	-3.011598000	1.073479000

Intermediate (Int)

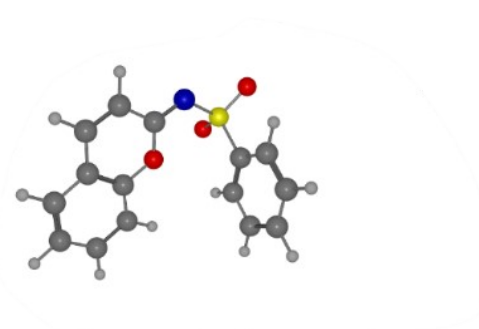
C	2.834574000	0.088826000	0.356287000
C	1.794115000	0.410650000	-0.522636000
C	1.813059000	1.586617000	-1.280980000
C	2.887978000	2.464145000	-1.151309000
C	3.932901000	2.174855000	-0.261909000
C	3.898577000	0.994697000	0.480672000
C	2.798400000	-1.222059000	1.092619000
O	0.694799000	-0.403049000	-0.680508000
O	3.728188000	-2.123830000	0.379089000
C	0.457870000	-1.417697000	0.240425000
N	-0.756808000	-2.035650000	0.154404000
C	1.410236000	-1.755891000	1.153418000
S	-2.014204000	-1.404264000	-0.615870000
C	-2.366802000	0.231950000	0.088626000
O	-1.831701000	-1.193104000	-2.082163000
O	-3.184471000	-2.263419000	-0.269760000
C	-2.609653000	1.320238000	-0.752039000
C	-2.916829000	2.564461000	-0.191167000
C	-2.976483000	2.714412000	1.197607000



C	-2.728510000	1.617846000	2.031670000
C	-2.423100000	0.371612000	1.479852000
H	0.986450000	1.798999000	-1.951329000
H	2.905880000	3.378936000	-1.736245000
H	4.765327000	2.863336000	-0.153768000
H	4.708608000	0.758271000	1.165874000
H	3.212076000	-1.095342000	2.101430000
H	-2.554200000	1.191202000	-1.827204000
H	-3.106851000	3.414031000	-0.840418000
H	-3.213428000	3.681936000	1.630009000
H	-2.771633000	1.732154000	3.110671000
H	-2.228150000	-0.481102000	2.122348000
H	3.568161000	-3.017379000	0.718386000
H	1.160157000	-2.508019000	1.893265000

Substrate 3

C	2.993295000	-0.540074000	0.483659000
C	1.986604000	0.088863000	-0.269503000
C	2.208734000	1.264388000	-0.981338000
C	3.481882000	1.829559000	-0.939198000
C	4.512689000	1.226596000	-0.196440000
C	4.271713000	0.053606000	0.508355000
C	2.646345000	-1.749997000	1.181890000
O	0.719628000	-0.449840000	-0.329691000
C	0.375123000	-1.572390000	0.344831000
N	-0.850850000	-2.021901000	0.302937000
C	1.385090000	-2.249573000	1.117118000
S	-2.029477000	-1.261040000	-0.611812000
C	-2.143514000	0.431040000	-0.011921000
O	-1.650461000	-1.228764000	-2.041234000
O	-3.281249000	-1.952068000	-0.245089000
C	-1.685295000	1.476007000	-0.815616000
C	-1.768416000	2.783277000	-0.331044000
C	-2.294759000	3.027766000	0.941686000
C	-2.749421000	1.967619000	1.734854000
C	-2.680026000	0.656757000	1.259178000
H	1.398914000	1.713476000	-1.544586000
H	3.674949000	2.746227000	-1.486958000
H	5.498056000	1.679847000	-0.173929000
H	5.059980000	-0.419097000	1.086272000
H	3.408149000	-2.257707000	1.765561000
H	-1.272638000	1.263964000	-1.795032000
H	-1.418460000	3.606561000	-0.945706000

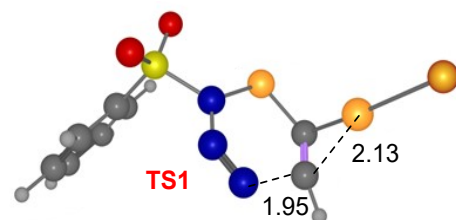


H	-2.352747000	4.045177000	1.316036000
H	-3.161293000	2.160252000	2.720357000
H	-3.036834000	-0.172156000	1.861009000
H	1.085879000	-3.151890000	1.634465000

TS1

Img. Frequency -320.2505

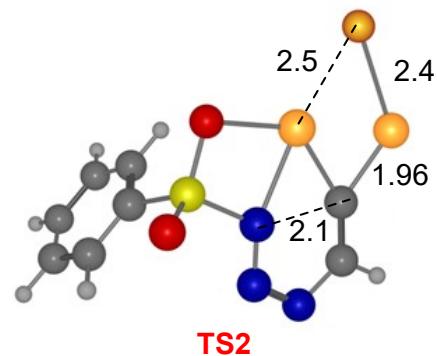
C	1.345497000	-1.451676000	1.409156000
C	1.278709000	-1.682513000	0.143407000
N	-0.823571000	0.263058000	-0.075981000
N	-0.633707000	0.371024000	1.201555000
N	0.083018000	-0.102915000	2.015818000
Cu	0.121774000	-1.085722000	-1.185262000
S	-2.135681000	1.204085000	-0.719255000
C	-3.603077000	0.430249000	-0.064069000
O	-2.043941000	2.584175000	-0.230229000
O	-2.004756000	0.896420000	-2.152165000
C	-4.063208000	-0.743998000	-0.668944000
C	-5.188975000	-1.368046000	-0.130968000
C	-5.828202000	-0.821762000	0.988558000
C	-5.349921000	0.353321000	1.577625000
C	-4.224638000	0.992948000	1.053261000
H	-3.556783000	-1.151379000	-1.536958000
H	-5.566765000	-2.277470000	-0.586598000
H	-6.703321000	-1.313603000	1.401456000
H	-5.851067000	0.775124000	2.442605000
H	-3.841846000	1.906716000	1.493386000
Cu	2.848894000	-0.458854000	0.279359000
Br	4.791042000	0.674038000	0.097612000
H	1.667126000	-1.817448000	2.370213000



TS2

Img. Frequency -208.9230

C	-0.558919000	2.779435000	-0.849752000
C	-1.125950000	1.621769000	-0.515244000
N	0.736175000	1.203105000	0.398603000
N	1.400639000	2.304428000	0.108999000
N	0.762068000	3.183619000	-0.549701000
Cu	-0.972619000	-0.199063000	0.270323000
S	1.673302000	0.033693000	1.255541000
C	2.950351000	-0.506393000	0.140687000
O	2.268588000	0.599443000	2.467802000

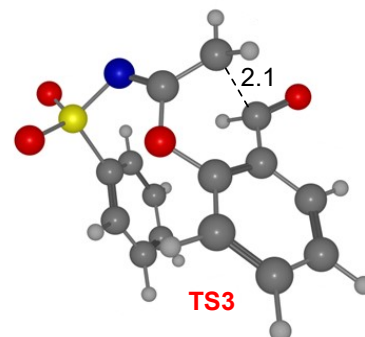


O	0.649335000	-1.050342000	1.376545000
C	2.620452000	-1.428529000	-0.858180000
C	3.617399000	-1.818207000	-1.752025000
C	4.907300000	-1.284849000	-1.642627000
C	5.213199000	-0.362025000	-0.636735000
C	4.229426000	0.040691000	0.268422000
H	1.617835000	-1.835472000	-0.926882000
H	3.387034000	-2.537645000	-2.530744000
H	5.677210000	-1.592140000	-2.343268000
H	6.215427000	0.045084000	-0.553823000
H	4.447865000	0.752003000	1.056579000
Cu	-2.868302000	0.744852000	-0.704367000
Br	-3.152604000	-1.491019000	0.109070000
H	-1.145441000	3.504616000	-1.408033000

TS3

Img. Frequency -320.1916

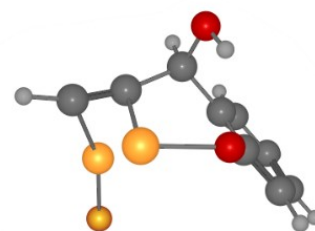
C	2.178505000	-0.339458000	0.456112000
C	1.579223000	-0.464691000	-0.806413000
C	2.172239000	0.040991000	-1.958443000
C	3.401506000	0.703342000	-1.862094000
C	4.026074000	0.837485000	-0.619809000
C	3.413821000	0.311522000	0.524563000
C	1.532297000	-0.883514000	1.720172000
O	0.327167000	-1.054091000	-0.976356000
O	2.261568000	-1.208456000	2.706678000
C	-0.170538000	-1.895571000	-0.003749000
N	-1.481941000	-1.904988000	0.196169000
C	0.743633000	-2.567842000	0.819452000
S	-2.456577000	-0.755776000	-0.488548000
C	-1.812660000	0.856490000	0.008831000
O	-2.463290000	-0.808155000	-1.972022000
O	-3.769500000	-0.921522000	0.180436000
C	-1.060241000	1.612564000	-0.891253000
C	-0.521566000	2.830147000	-0.468246000
C	-0.732879000	3.274803000	0.840831000
C	-1.493185000	2.507581000	1.731602000
C	-2.039047000	1.290690000	1.318653000
H	1.668205000	-0.083794000	-2.911338000
H	3.865848000	1.103384000	-2.758336000
H	4.984133000	1.342213000	-0.539999000
H	3.887186000	0.398132000	1.497743000
H	0.546465000	-0.424225000	1.926169000
H	1.675131000	-2.914939000	0.385654000



H	-0.891943000	1.244111000	-1.895802000
H	0.069080000	3.423793000	-1.159086000
H	-0.306711000	4.218536000	1.167494000
H	-1.661068000	2.855292000	2.746216000
H	-2.630594000	0.687504000	1.998868000
H	0.322440000	-3.172136000	1.614862000

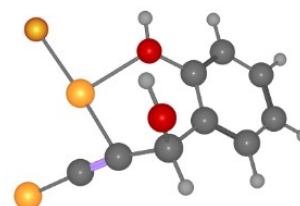
**Coordinate of Route2
Species K**

C	0.218610000	-2.439737000	0.706594000
C	0.772374000	-1.337508000	0.983486000
Cu	1.461284000	-1.615846000	-0.992930000
Cu	-1.252447000	-0.905712000	0.330686000
Br	-3.194146000	0.270451000	-0.238354000
H	-0.143247000	-3.451783000	0.720256000
C	0.659684000	2.223058000	1.334649000
C	1.302544000	1.106297000	0.769468000
C	0.468016000	3.394763000	0.579795000
H	-0.032747000	4.253188000	1.017958000
C	1.773052000	1.145981000	-0.582875000
C	0.934042000	3.441073000	-0.753321000
H	0.792902000	4.343451000	-1.344027000
C	1.577682000	2.331934000	-1.329718000
H	1.934636000	2.361777000	-2.355961000
H	0.305077000	2.174068000	2.362473000
O	2.413820000	0.059002000	-1.133005000
H	3.327856000	-0.443057000	0.737555000
C	1.535283000	-0.162417000	1.571332000
H	1.195725000	-0.047511000	2.604671000
O	2.950043000	-0.527931000	1.649016000



Species L

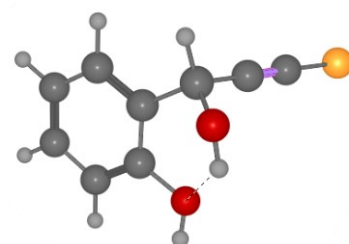
C	-0.905316000	-1.849521000	0.061279000
C	0.212553000	-1.530599000	0.543052000
Cu	-2.552426000	-2.375831000	-0.660535000
Cu	-0.827455000	0.306945000	0.205266000
Br	-2.120849000	2.321239000	-0.076657000
H	1.081346000	2.247839000	0.510693000



C	3.678816000	-1.252676000	-0.312316000
C	2.542285000	-0.653795000	0.259793000
C	4.573539000	-0.501073000	-1.100330000
H	5.446226000	-0.978526000	-1.535913000
C	2.326897000	0.721687000	0.025800000
C	4.333702000	0.869703000	-1.317810000
H	5.019533000	1.456911000	-1.921857000
C	3.200989000	1.490275000	-0.753665000
H	3.008146000	2.547598000	-0.918350000
H	3.864839000	-2.310200000	-0.140830000
O	1.160450000	1.275676000	0.611132000
H	1.184803000	0.037652000	2.448561000
C	1.576964000	-1.444038000	1.135952000
H	1.959935000	-2.458693000	1.277751000
O	1.519408000	-0.886677000	2.503268000

Species M

C	2.051720000	0.073231000	-0.314398000
C	0.948516000	0.542811000	-0.639714000
Cu	3.696642000	-0.627101000	0.204747000
H	-1.521952000	1.171285000	2.571852000
C	-2.221910000	-0.634063000	-1.403193000
C	-1.523303000	0.228503000	-0.538760000
C	-3.275607000	-1.443716000	-0.932133000
H	-3.801191000	-2.105176000	-1.614816000
C	-1.913755000	0.273296000	0.819271000
C	-3.643687000	-1.386421000	0.426051000
H	-4.455388000	-2.003662000	0.801410000
C	-2.963666000	-0.523003000	1.307696000
H	-3.247700000	-0.470901000	2.356628000
H	-1.937232000	-0.674522000	-2.452348000
O	-1.199160000	1.159645000	1.648010000
H	-0.583661000	2.509635000	0.352427000
C	-0.367009000	1.091227000	-1.047346000
H	-0.416646000	1.134222000	-2.140795000
O	-0.524171000	2.502090000	-0.632620000



References:

- Alassad, Z.; AboRaed, A.; Mizrachi, M. S.; Pérez-Temprano, M. H. and Milo, A. Metal-free multicomponent strategy for amidine synthesis. *J. Am. Chem. Soc.* 2022, *144*(45): 20672-20679.
- Zhao, Y.; Zhou, Z.; Liu, L.; Chen, M.; Yang, W.; Chen, Q.; Gardiner M. G.; Banwell, M. G. The Copper-catalyzed Reaction of 2-(1-hydroxyprop-2-yn-1-yl)Phenols with Sulfonyl Azides Leading to C₃-unsubstituted *N*-sulfonyl-2-iminocoumarins. *J. Org. Chem.* 2021, *86*, 9155-9162.