Supporting Information

Tuning Optoelectronic Properties of core-Substituted Naphthalene Diimides by the Selective Conversion of Imides to Monothioimides

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NMR(^{1}H, ^{13}C, and gHMBC), MALDI-TOF of RF2, RF2-1S, and RF2-2S

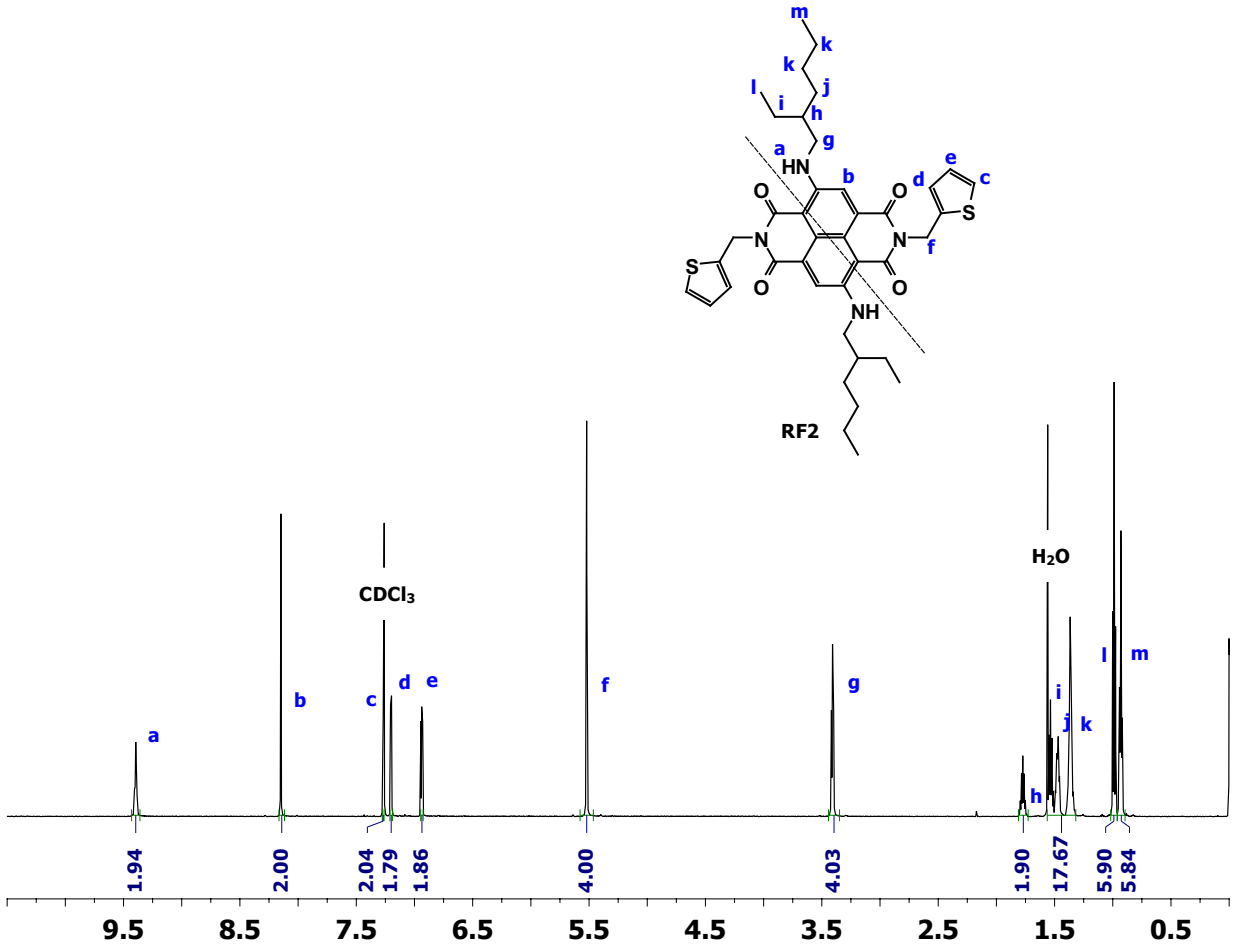

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Figure 1: ^{1}H NMR of RF2

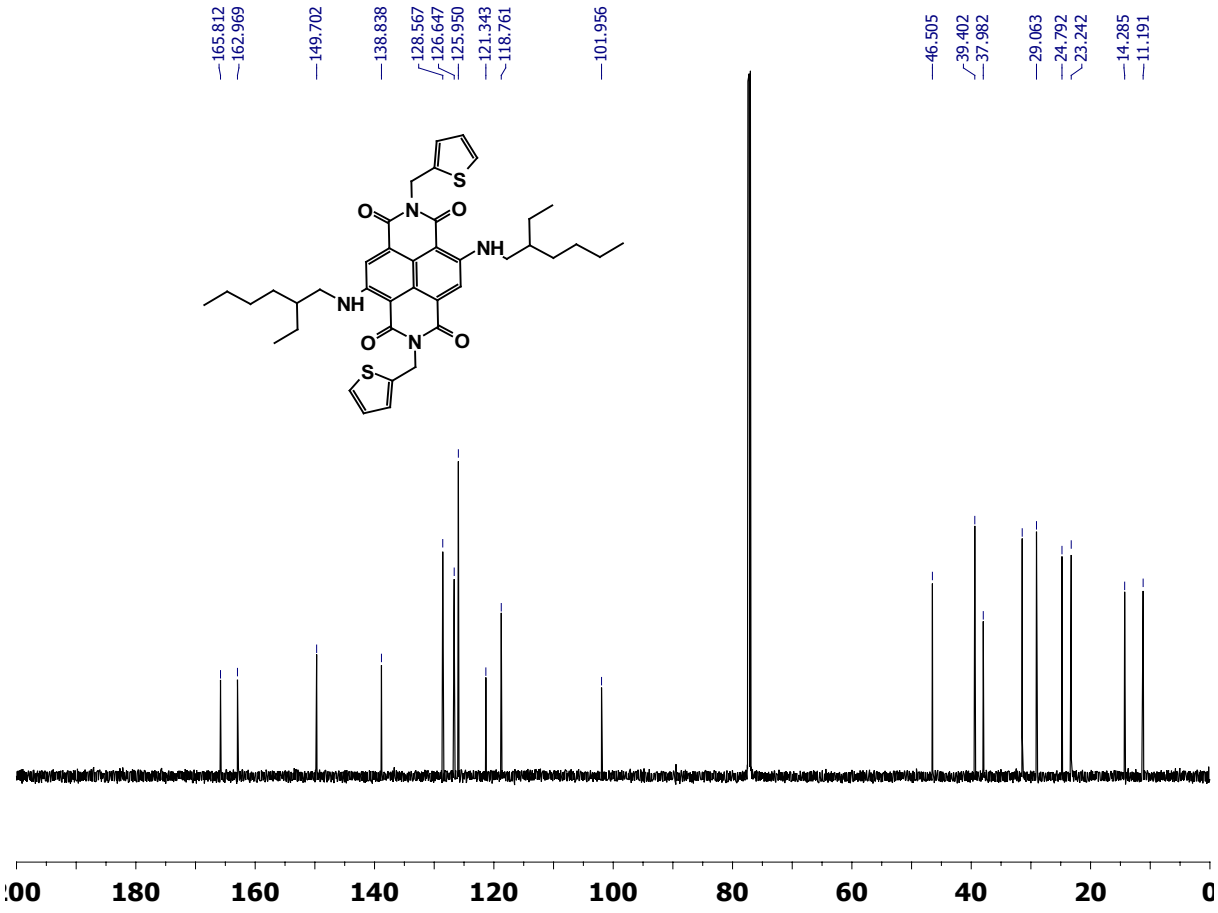

Figure 2: ^{13}C NMR of RF2

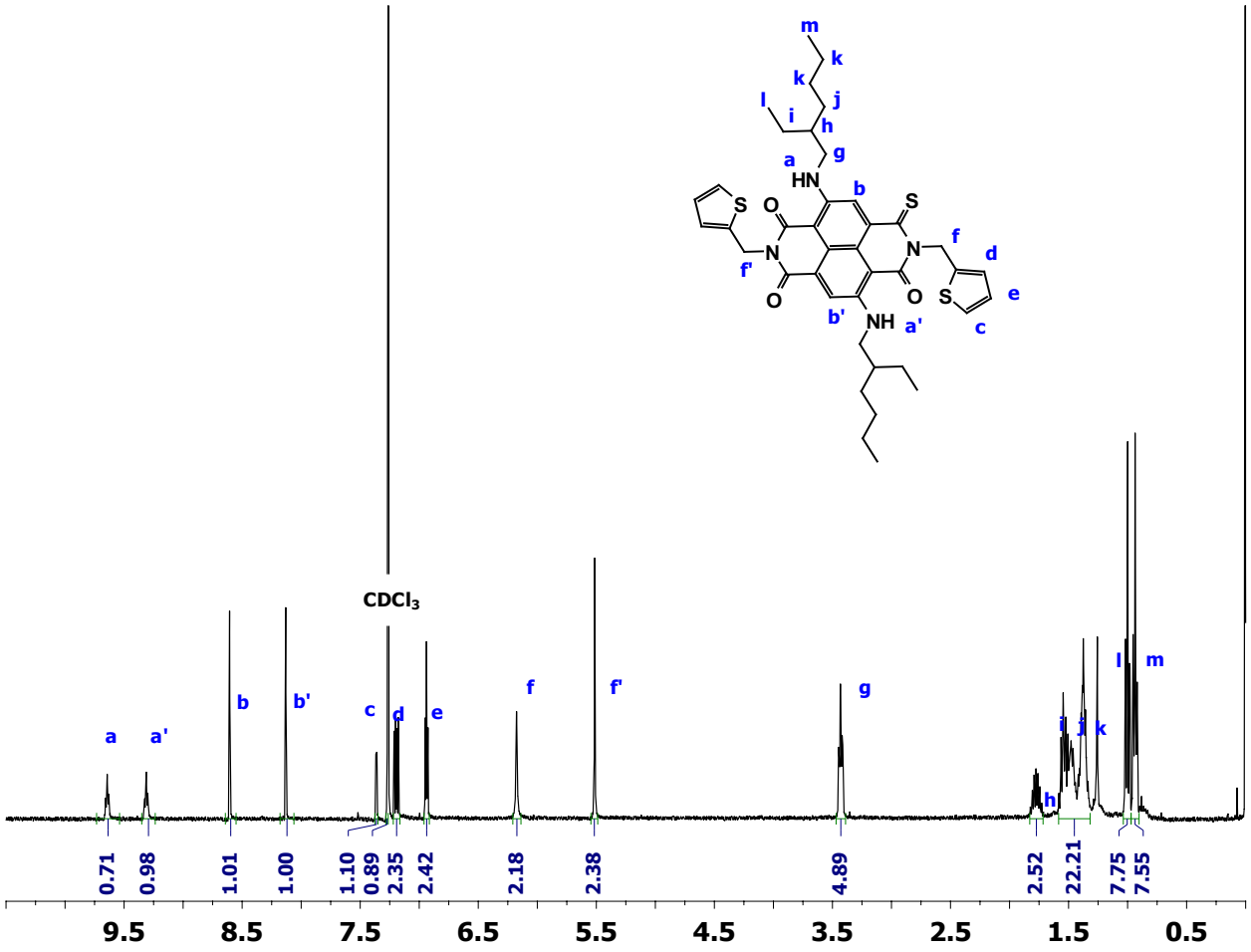

Figure 3: ^{1}H NMR of RF2-1S

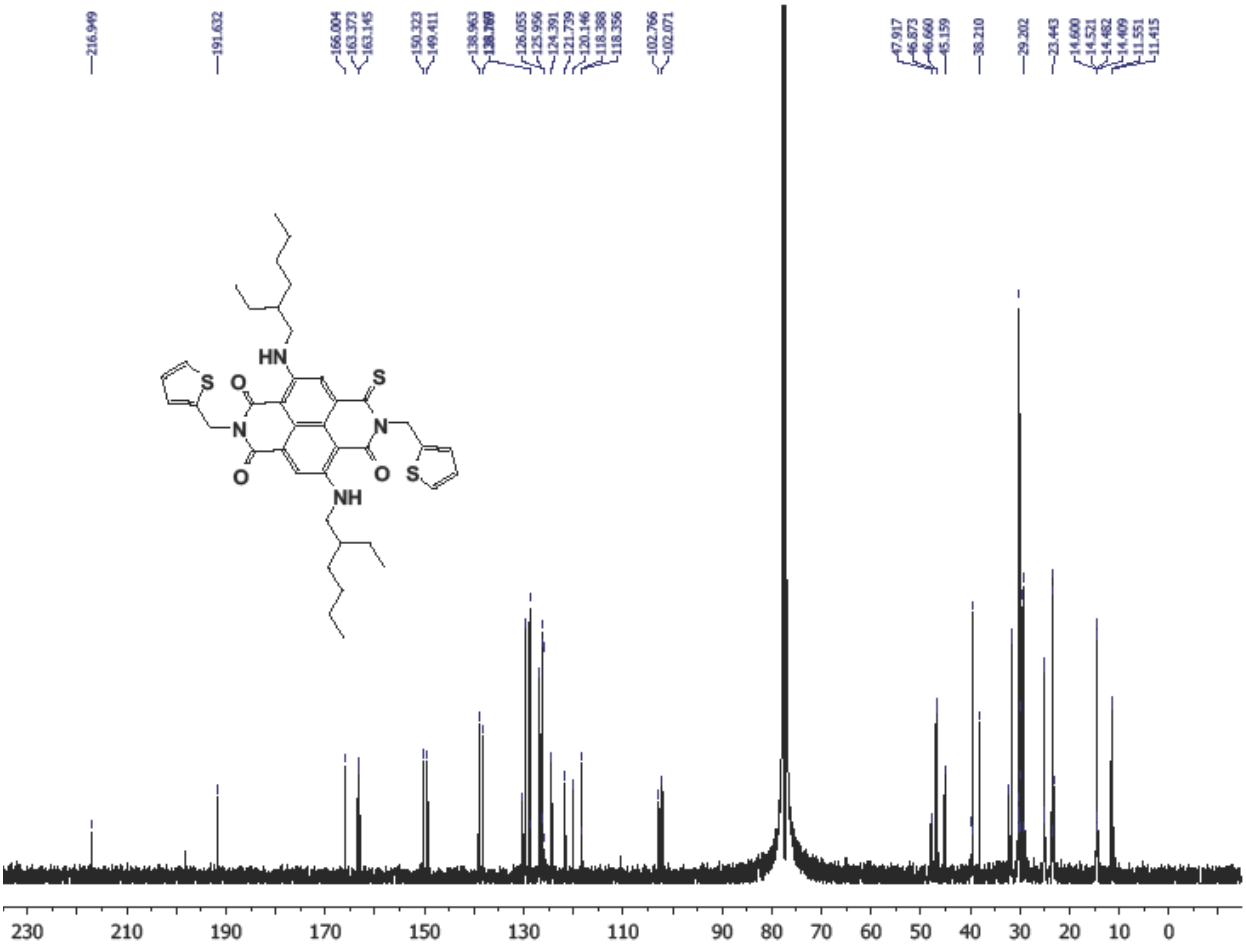

Figure 4: ^{13}C NMR of RF2-1S

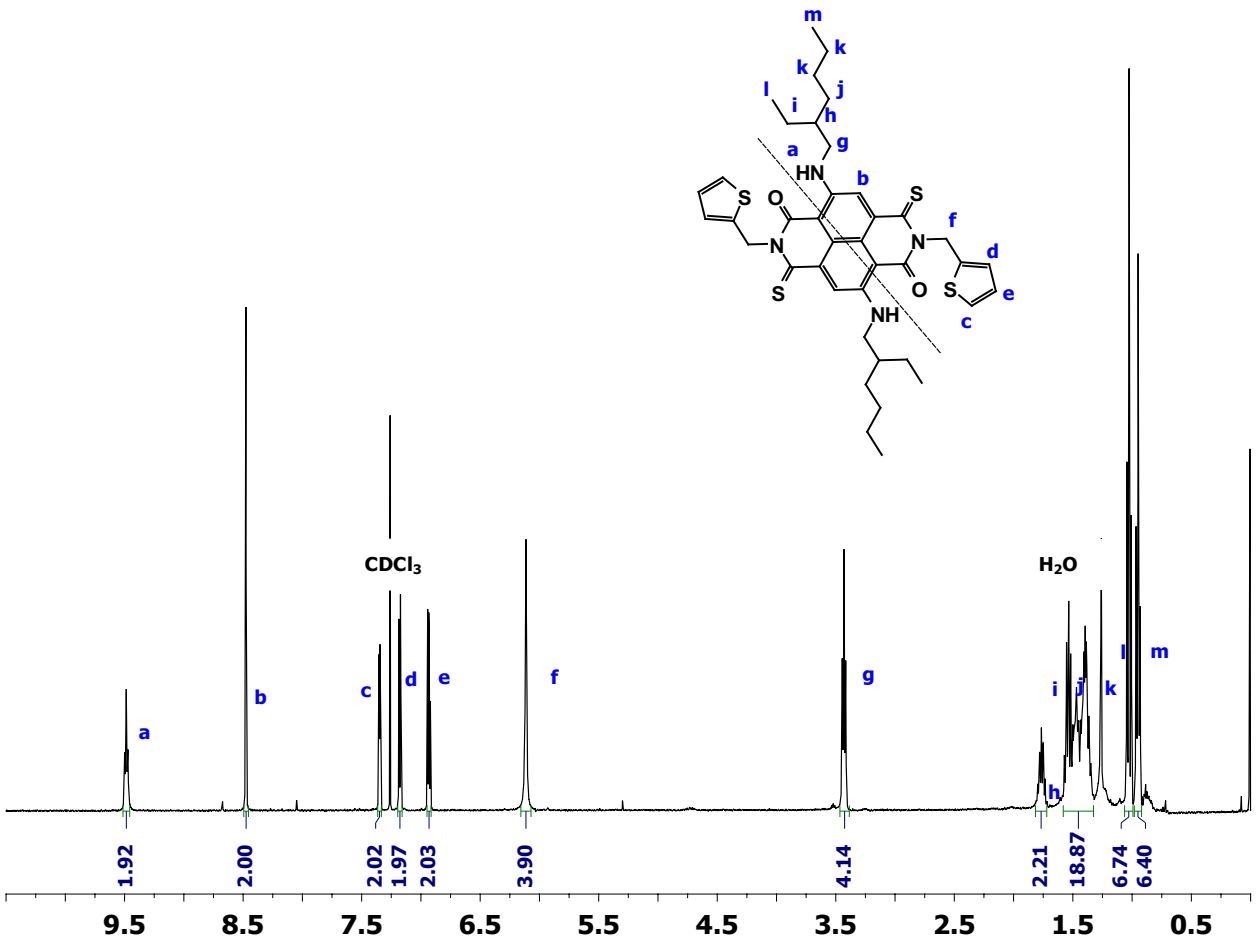

Figure 5: ^{1}H NMR of RF2-2S

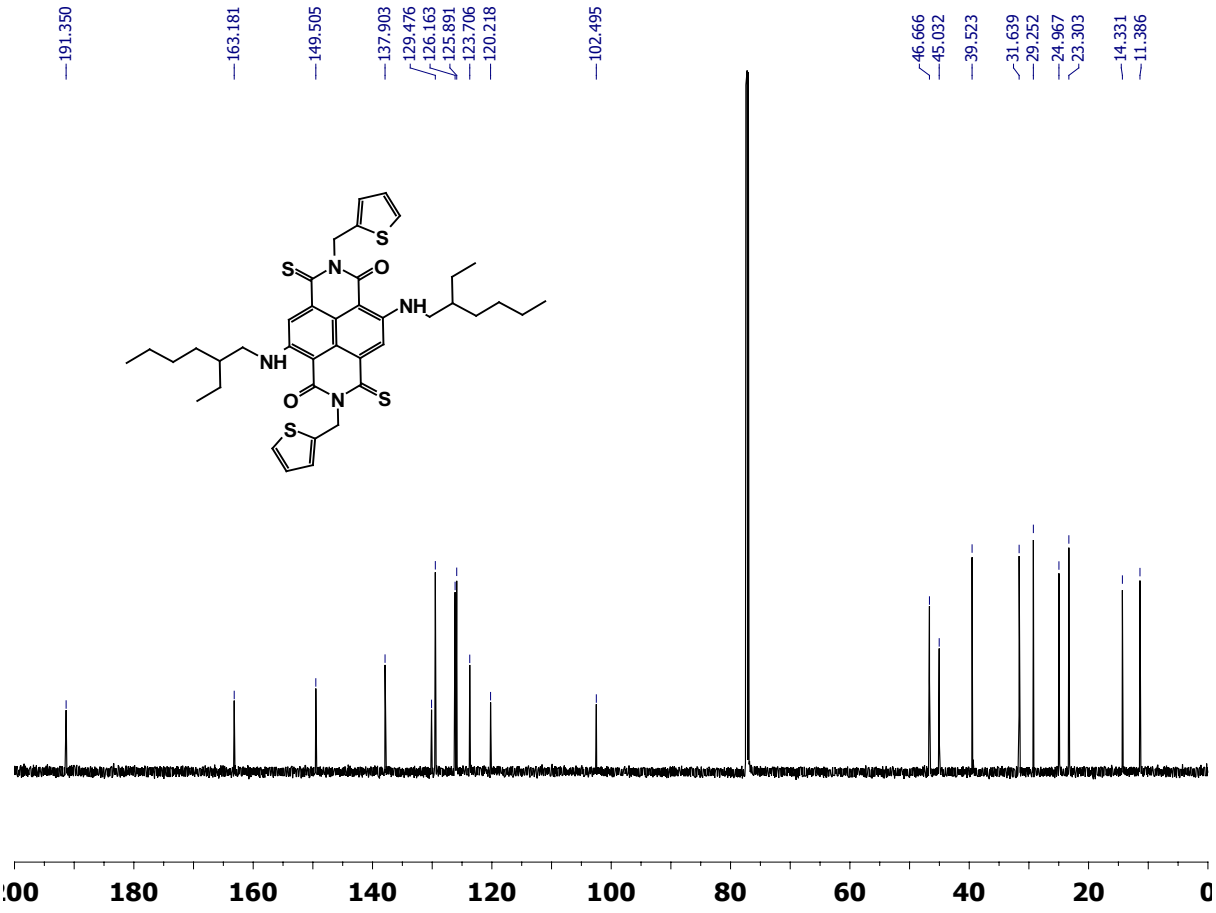

Figure 6: ^{13}C NMR of RF2-2S

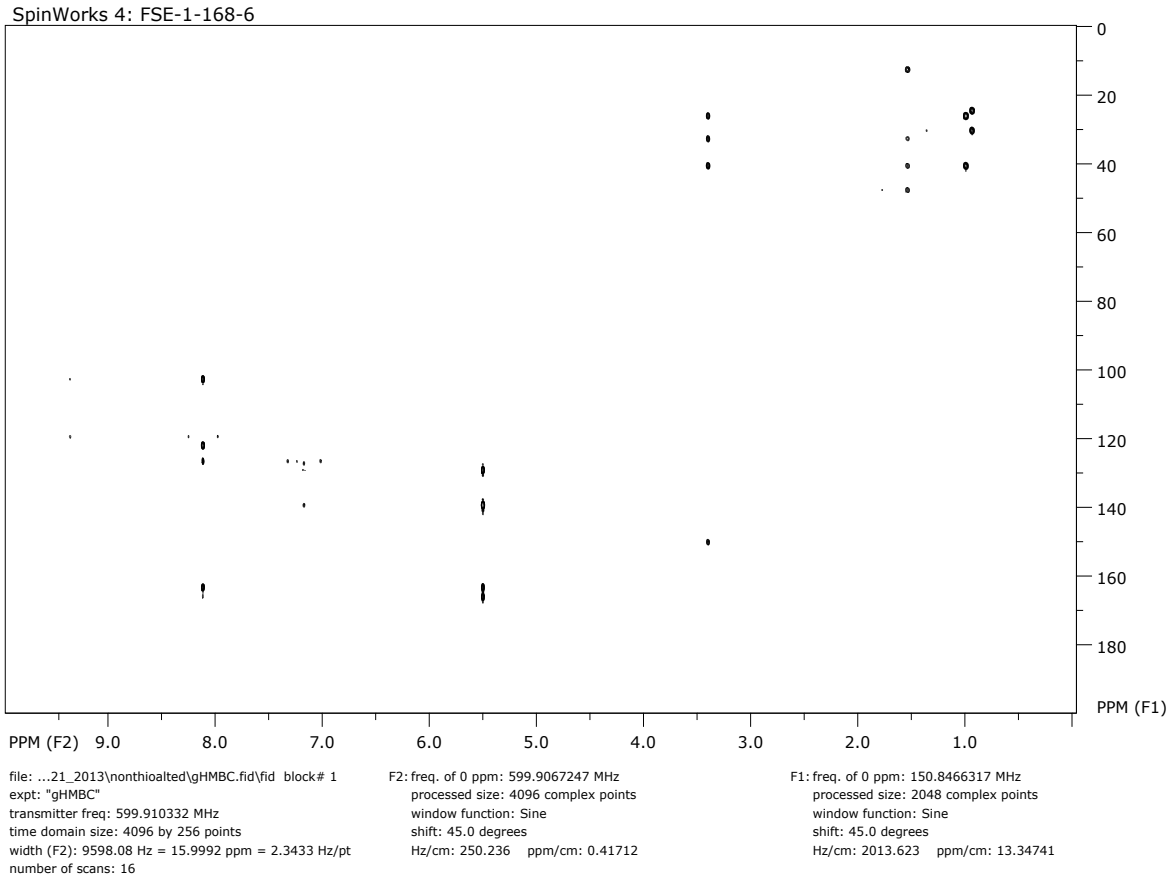

Figure 7: gHMBC of RF2

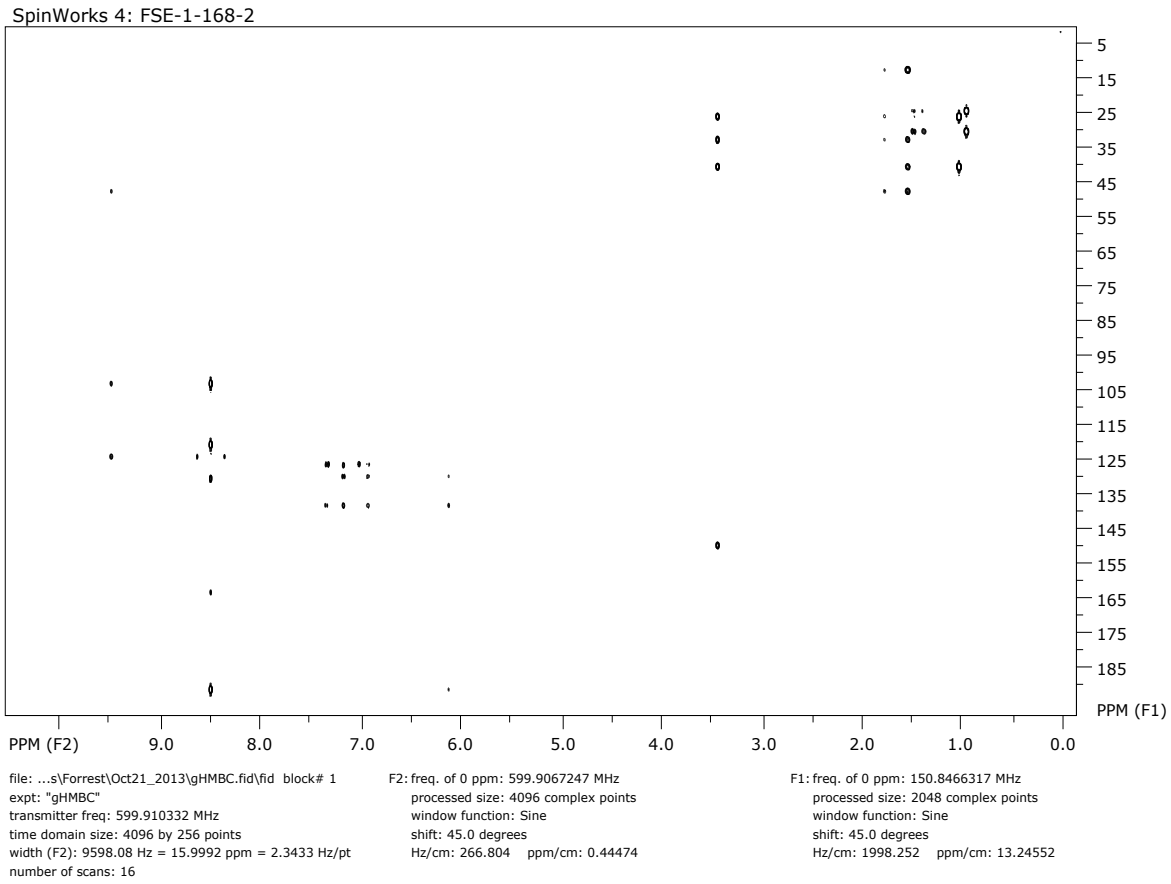

Figure 8: gHMBC of RF2-2S

MALDI-TOF MS of The reaction thionated-RF2 reaction mixture

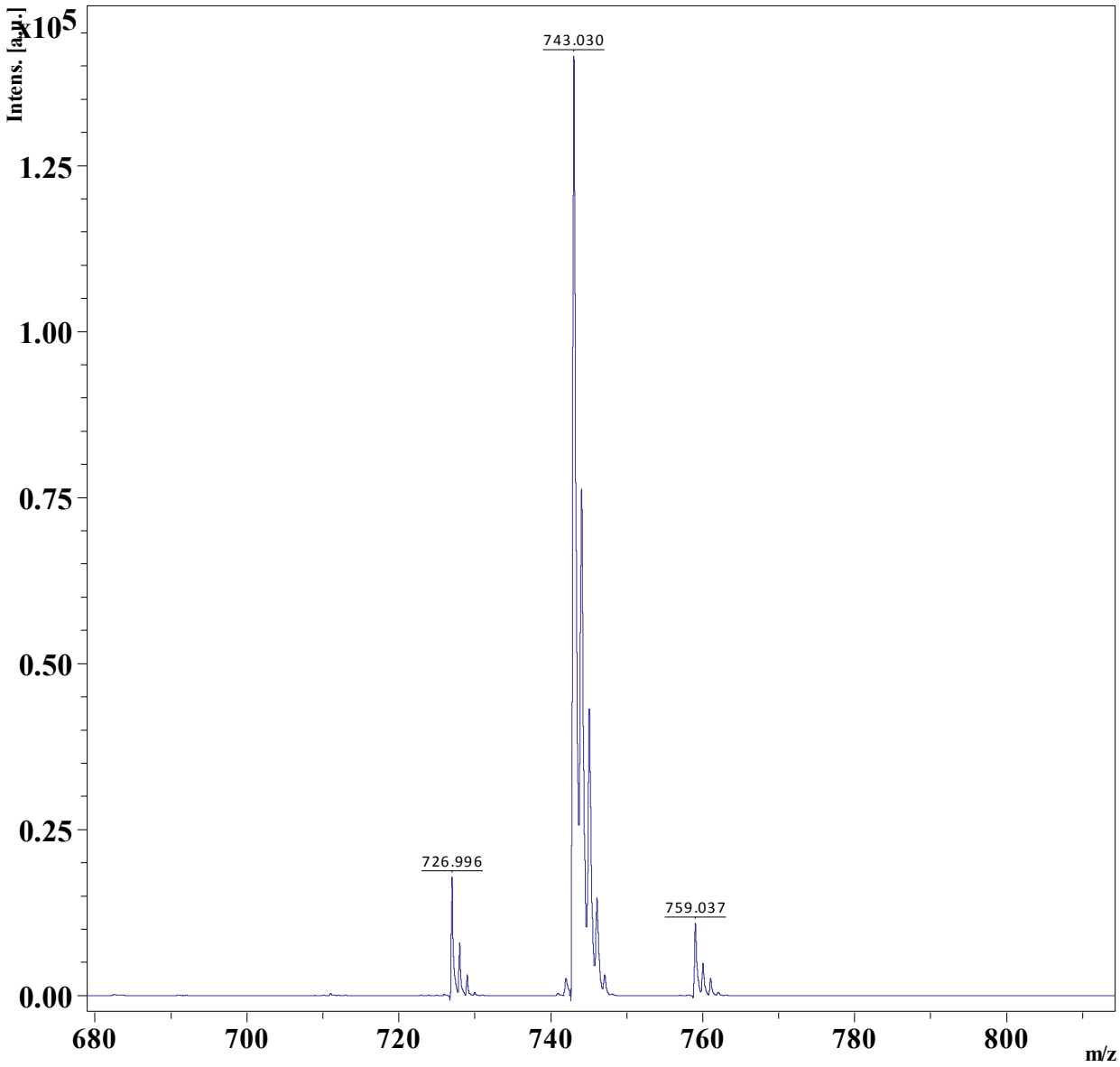

Figure 9: MALDI-TOF MS of thionated-RF2 reaction mixture before purification showing mono-, di- and tri-thioRF2 derivatives at 726, 743, and 759 m/z respectively.

MALDI-TOF and NMR of Supporting structures and their thionated-derivatives

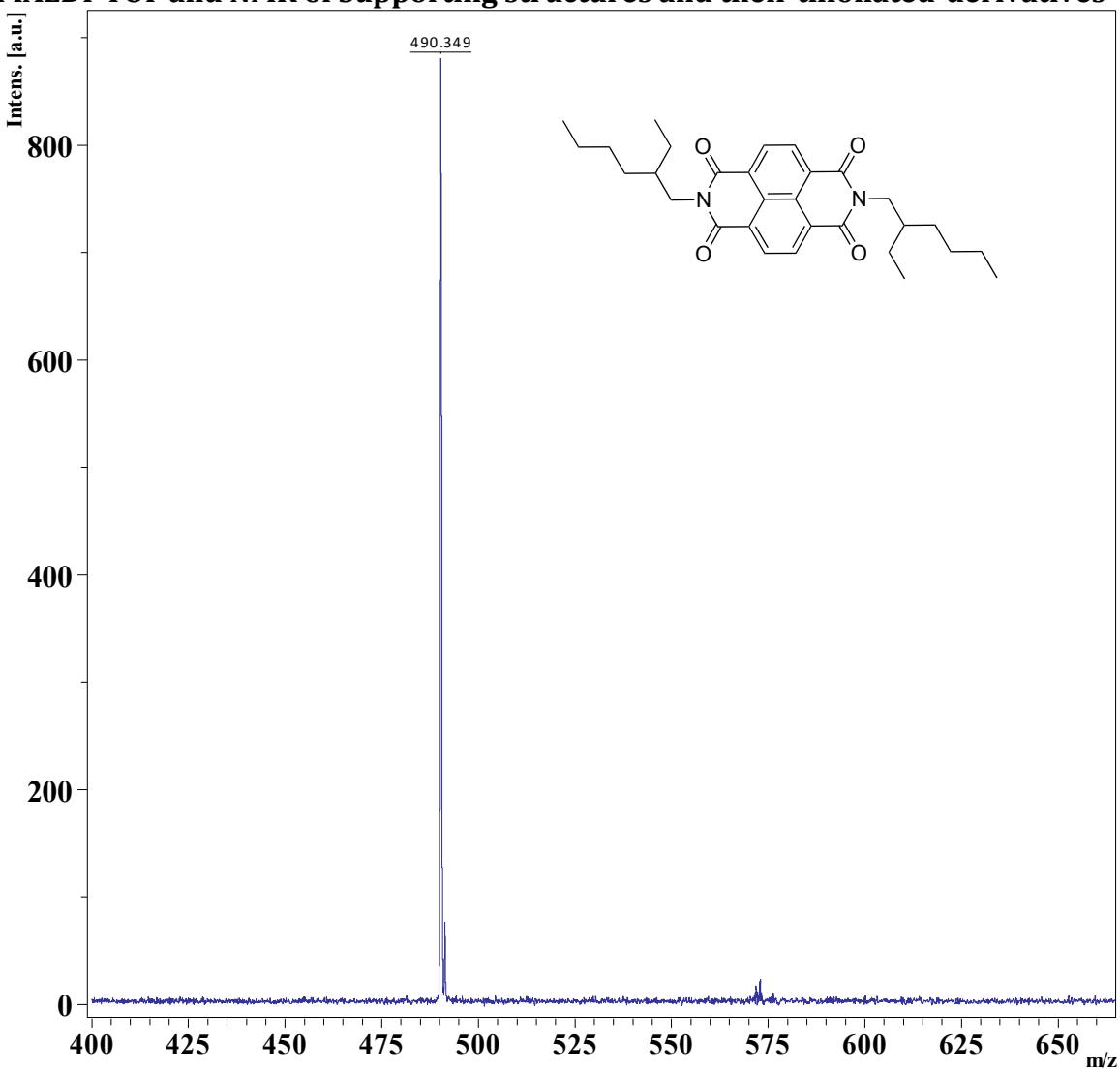

Figure 10: MALDI-TOF MS of Compound 1 in an isovanillan matrix

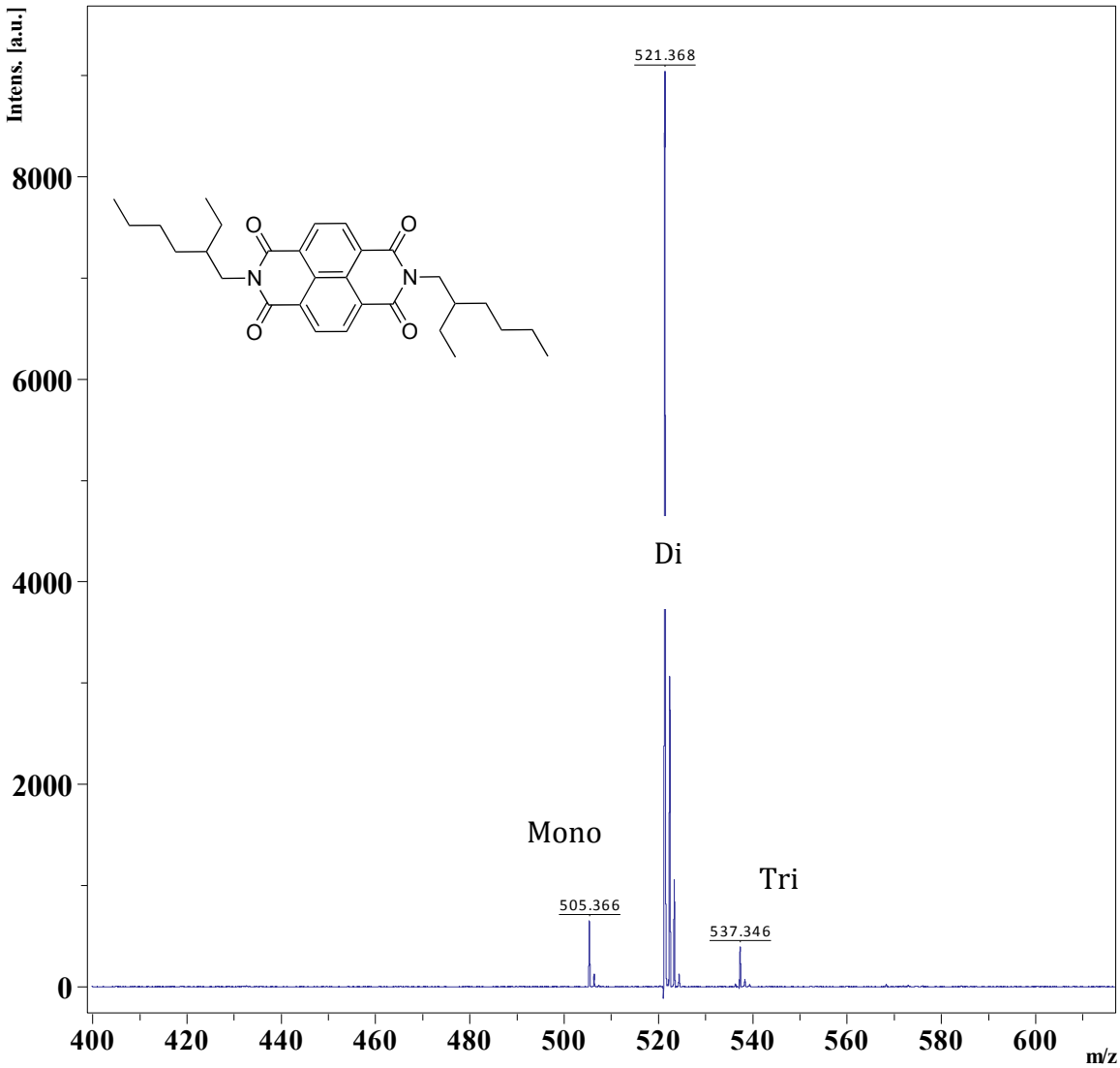

Figure 11: MALDI-TOF MS of the thio-derivative of compound 1 in an isovanillan matrix showing mono-, di- and tri-thio derivatives.

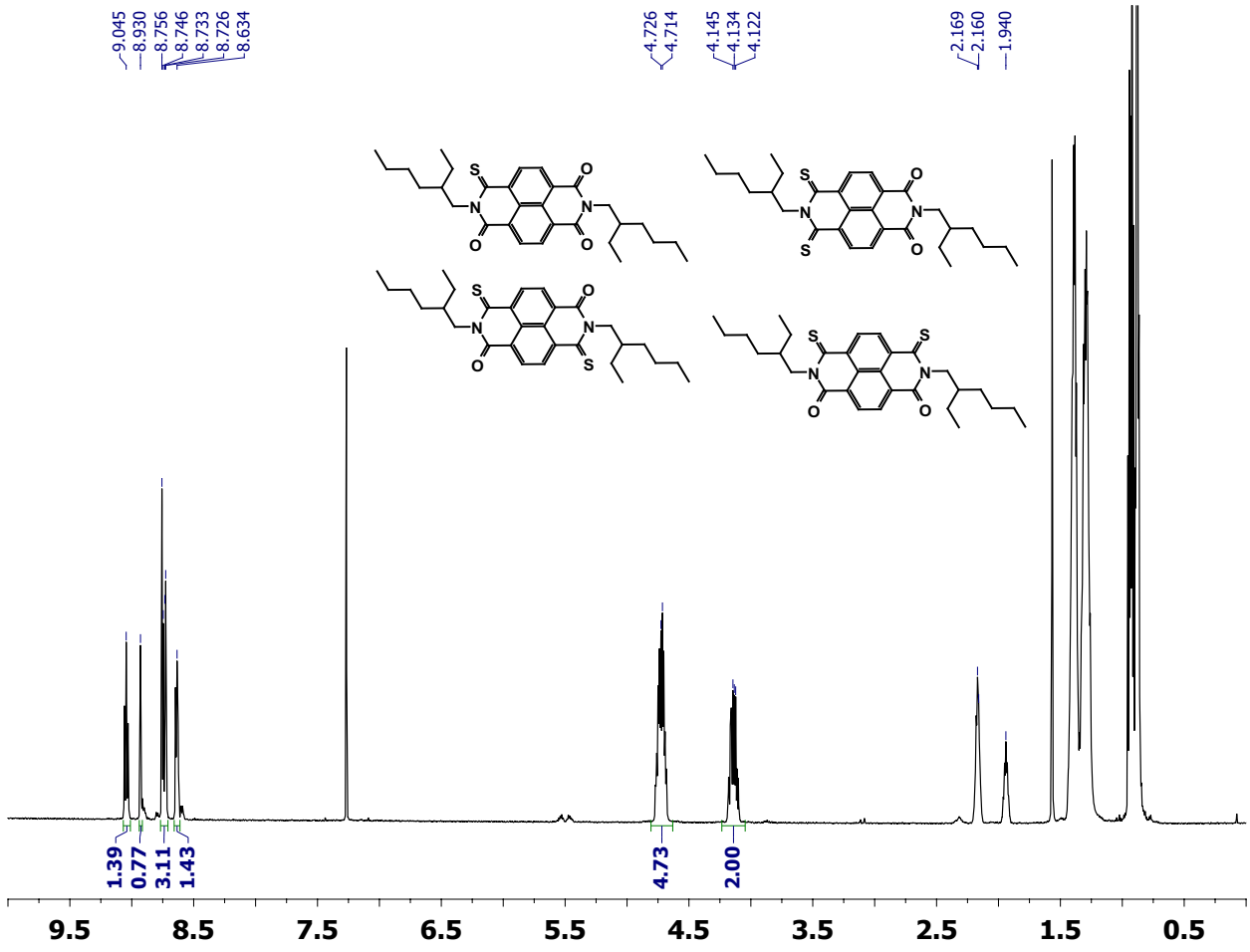

Figure 12: 600 mHz ^{1}H NMR of the thioderivatives of compound 1 in $CDCl_3$. The peaks shown are primarily a mixture of dithioderives with minor mono- and tri-thio peaks.

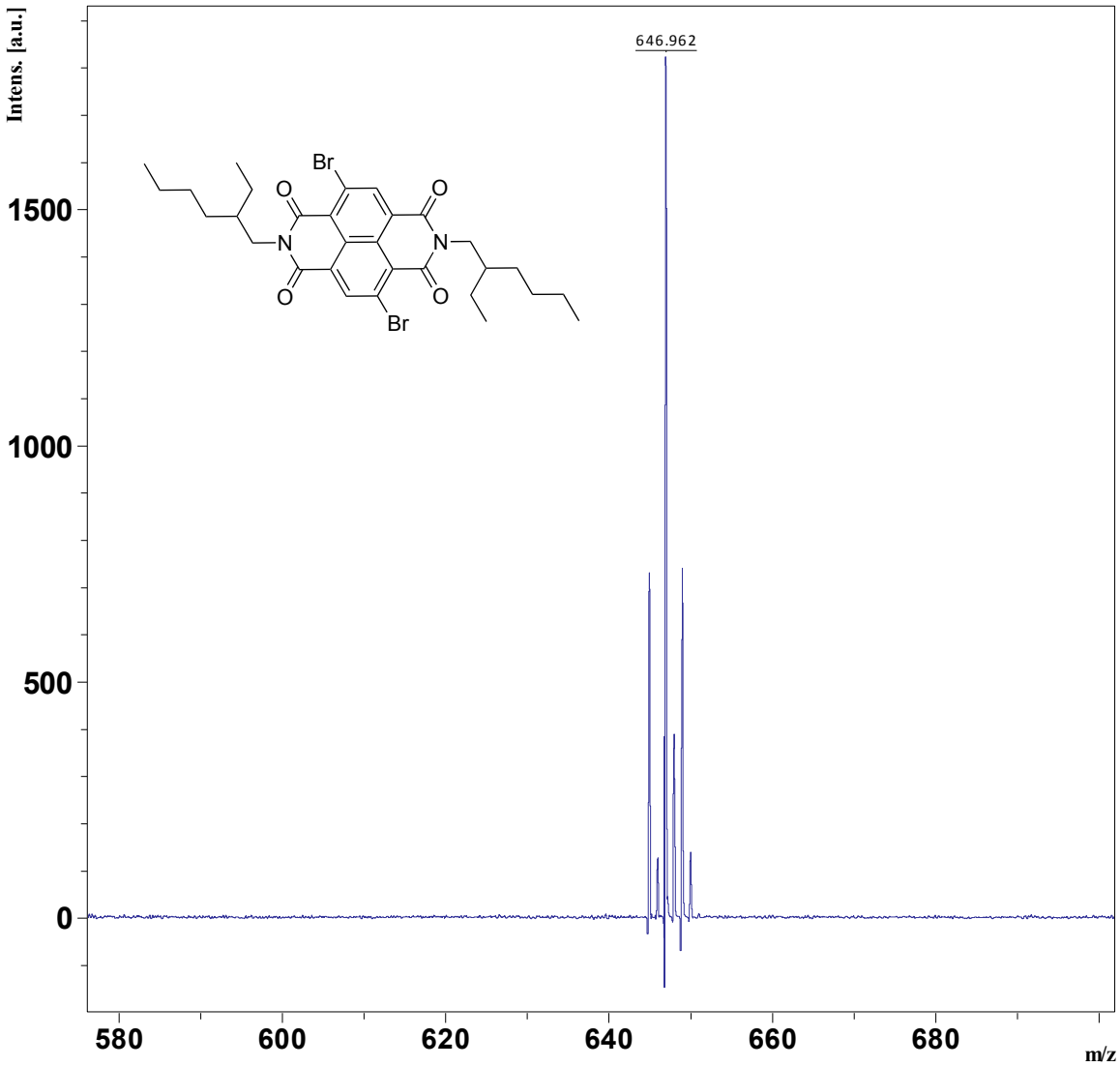

Figure 13: MALDI-TOF MS of Compound 2 in terthiophene matrix.

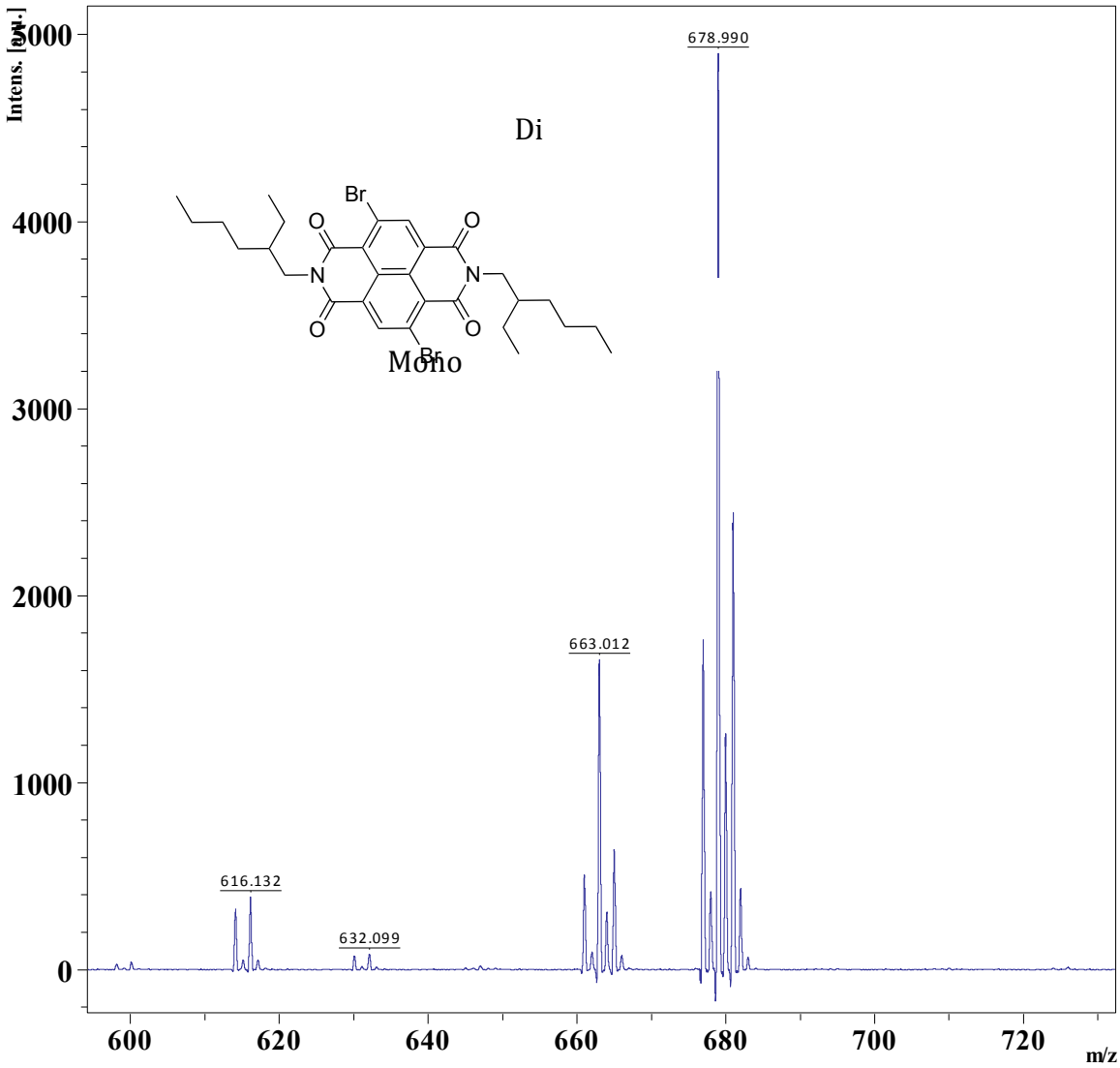

Figure 14: MALDI-TOF MS of the thio-derivative of compound 2 in terthiophene matrix showing the mono- and di-thio derivatives.

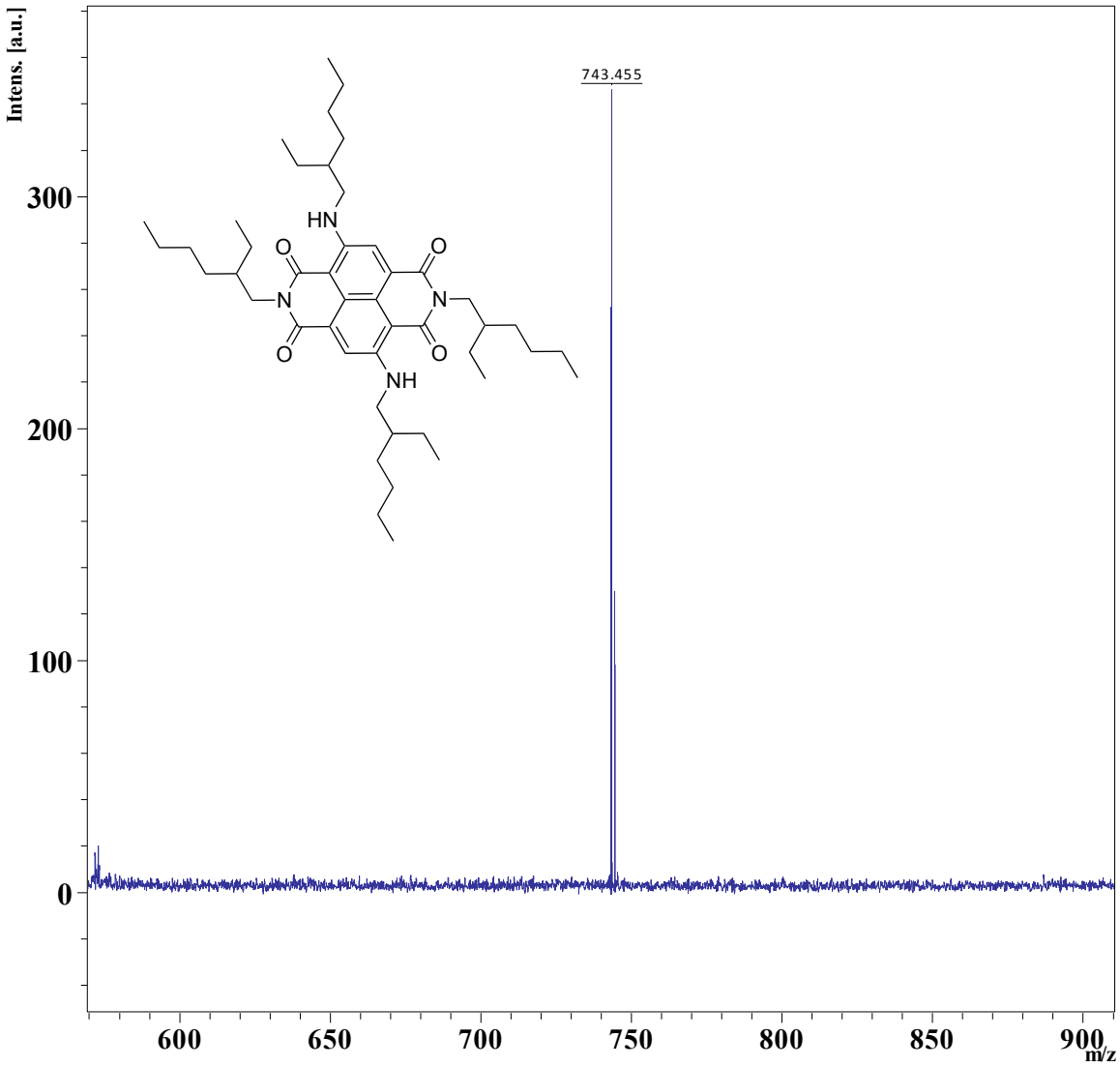

Figure 15: MALDI-TOF MS of Compound 3 in terthiophene matrix.

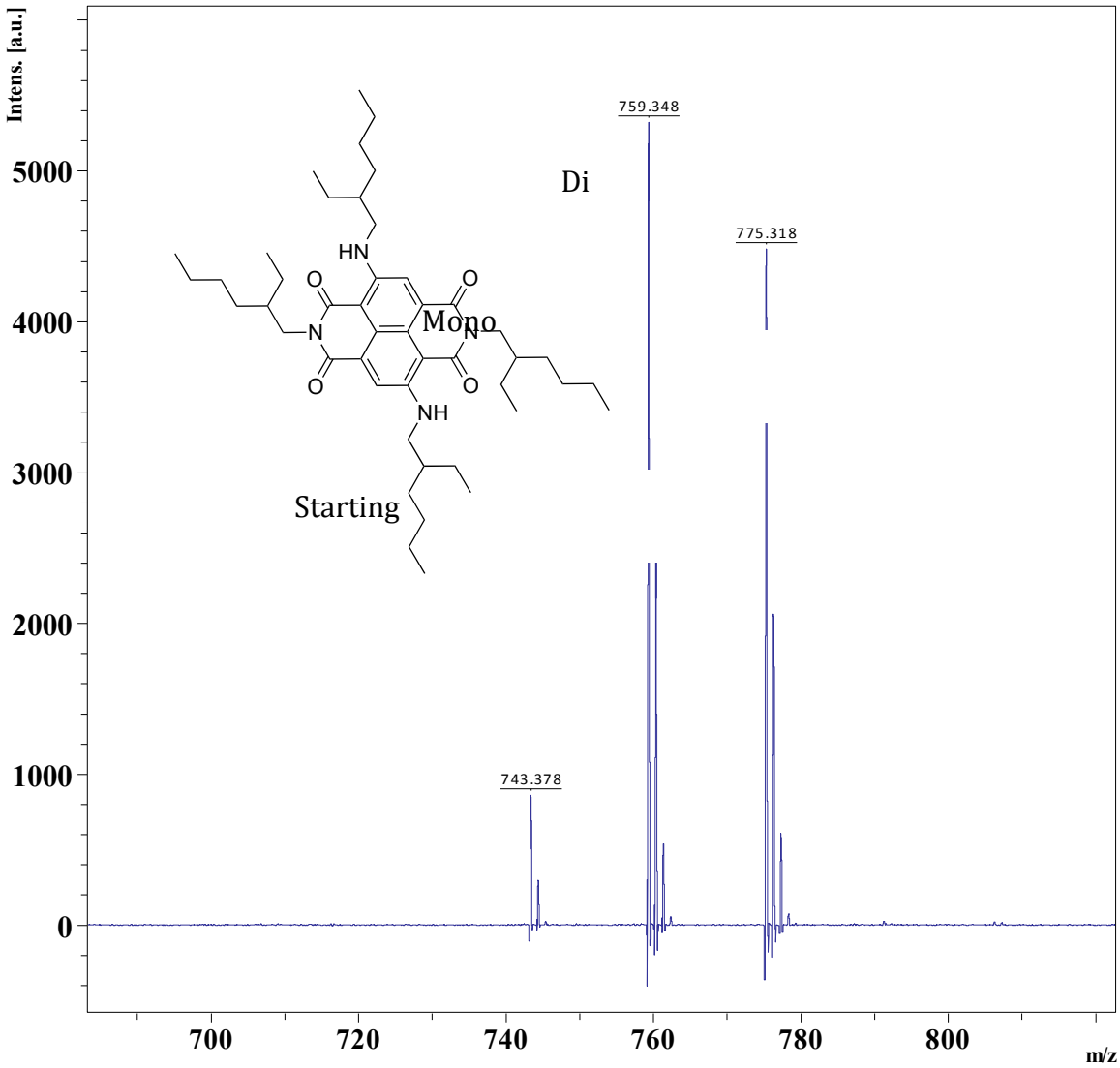

Figure 16: MALDI-TOF MS of the thio-derivative of compound 3 in terthiophene matrix showing the starting material, mono- and di-thio derivatives.

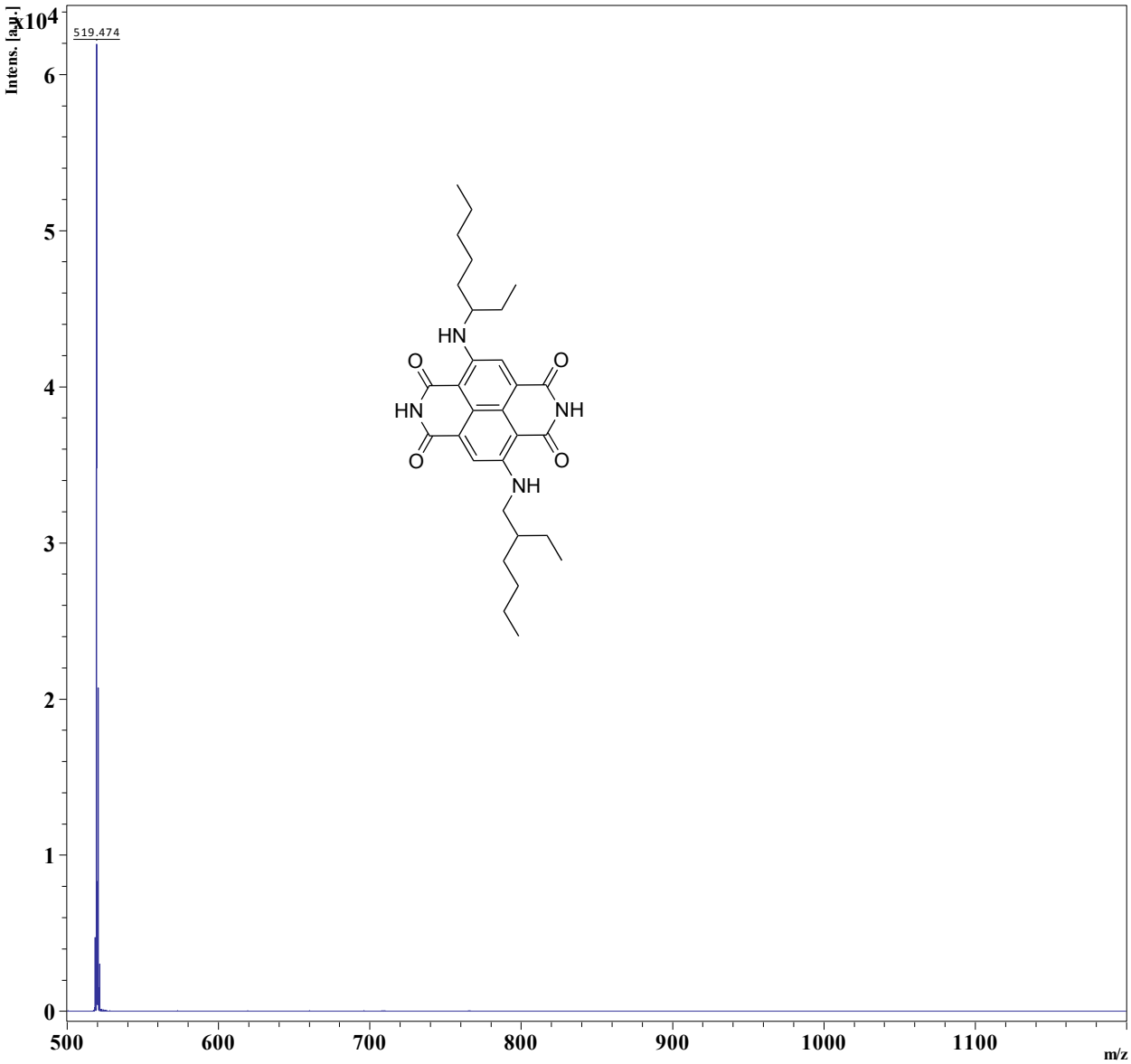

Figure 17: MALDI-TOF MS of Compound 4 in terthiophene matrix.

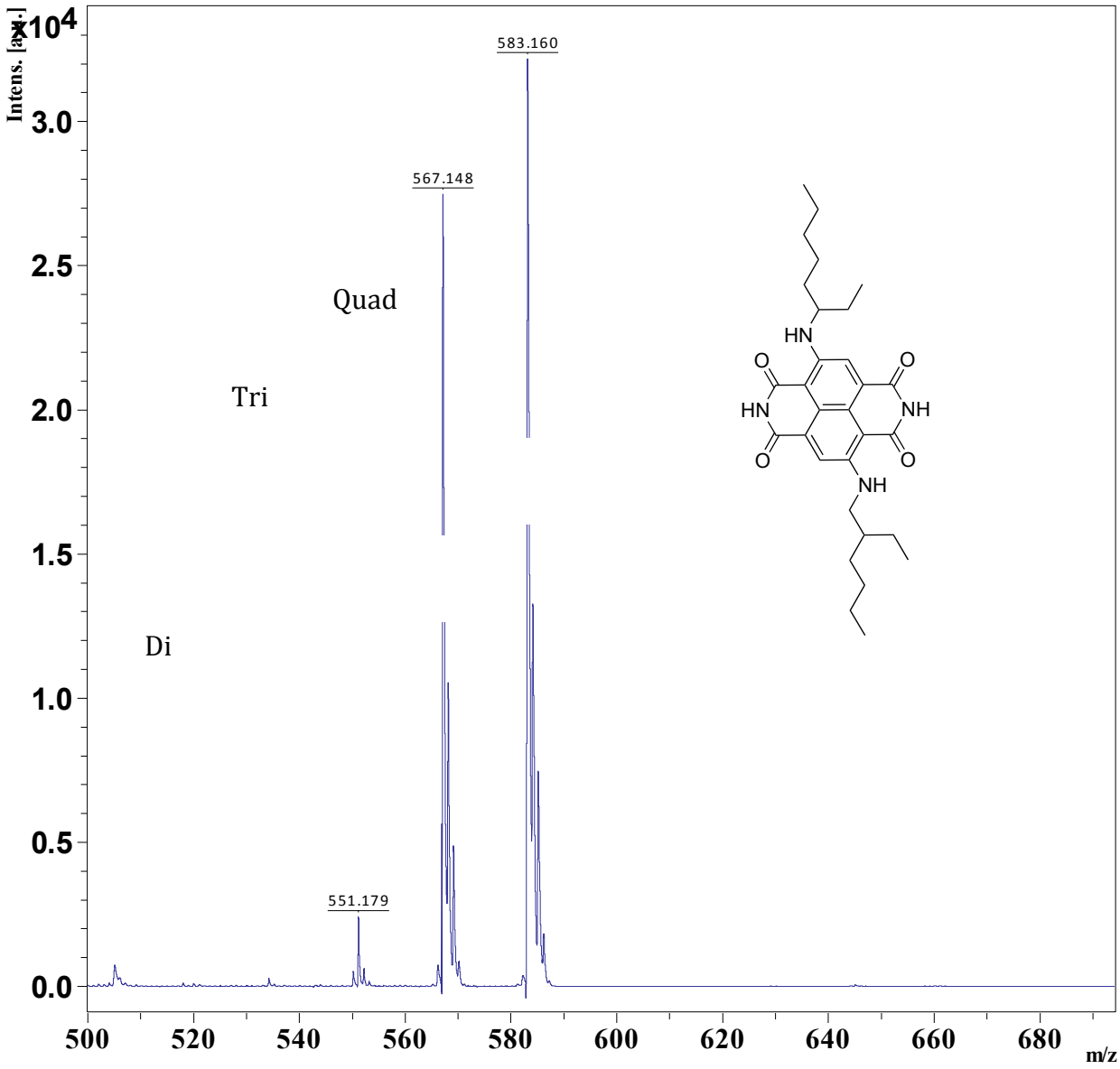

Figure 18: MALDI-TOF MS of the thio-derivative of compound 4 in terthiophene matrix showing the Di, Tri, and Quad-thio derivatives.

Computational Data

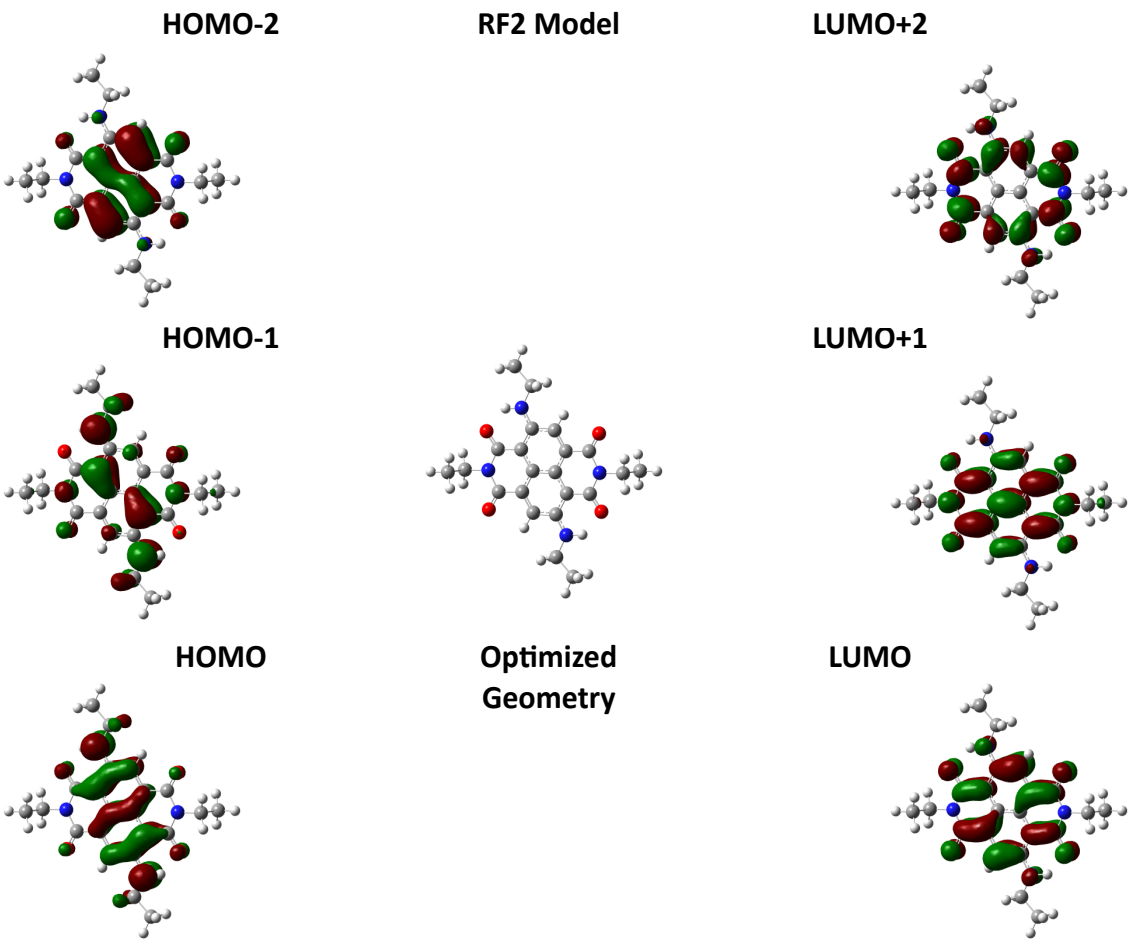

Figure 19**:** Kohn-Sham frontier molecular orbitals of RF2 at the B3LYP/6-31G(d,p) level of theory.

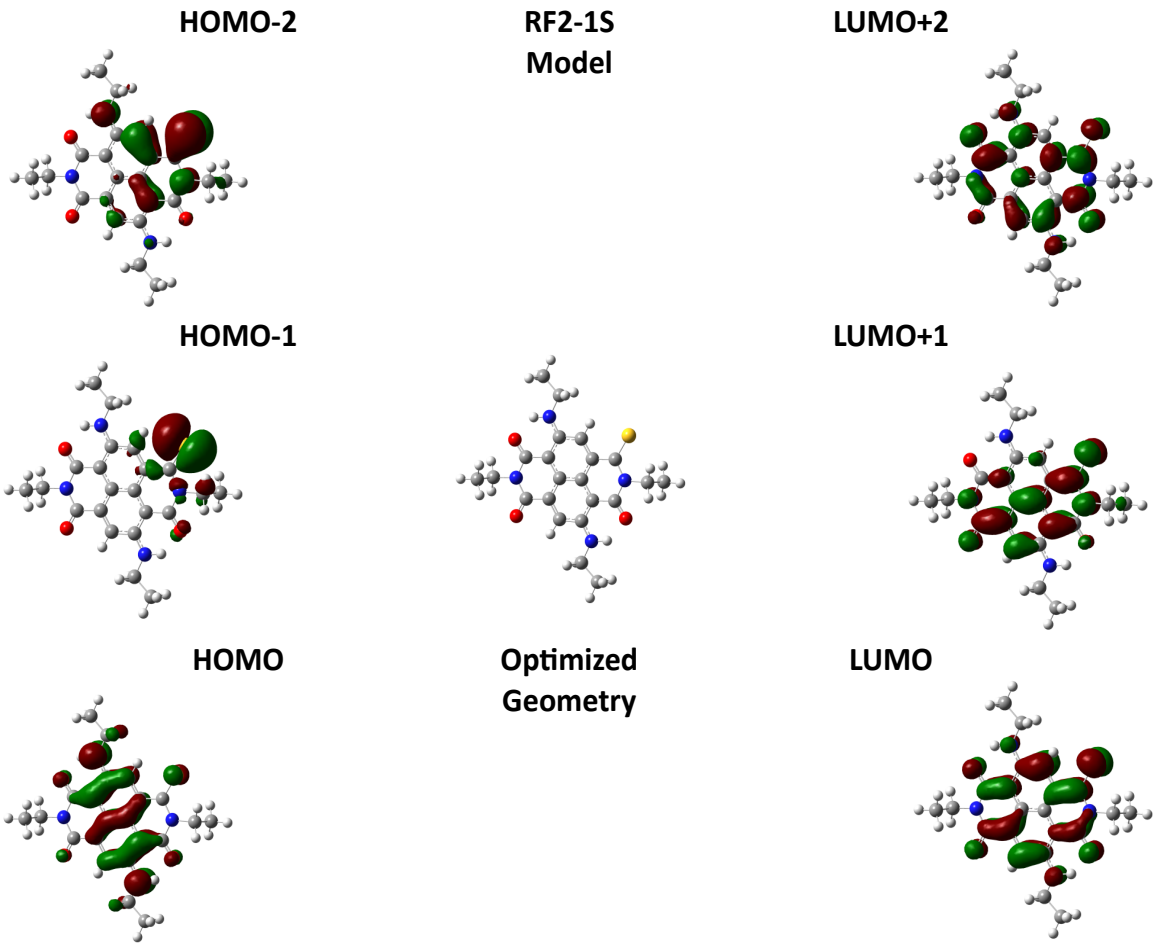

Figure 20: Kohn-Sham frontier molecular orbitals of RF2-1S model at the B3LYP/6-31G(d,p) level of theory.

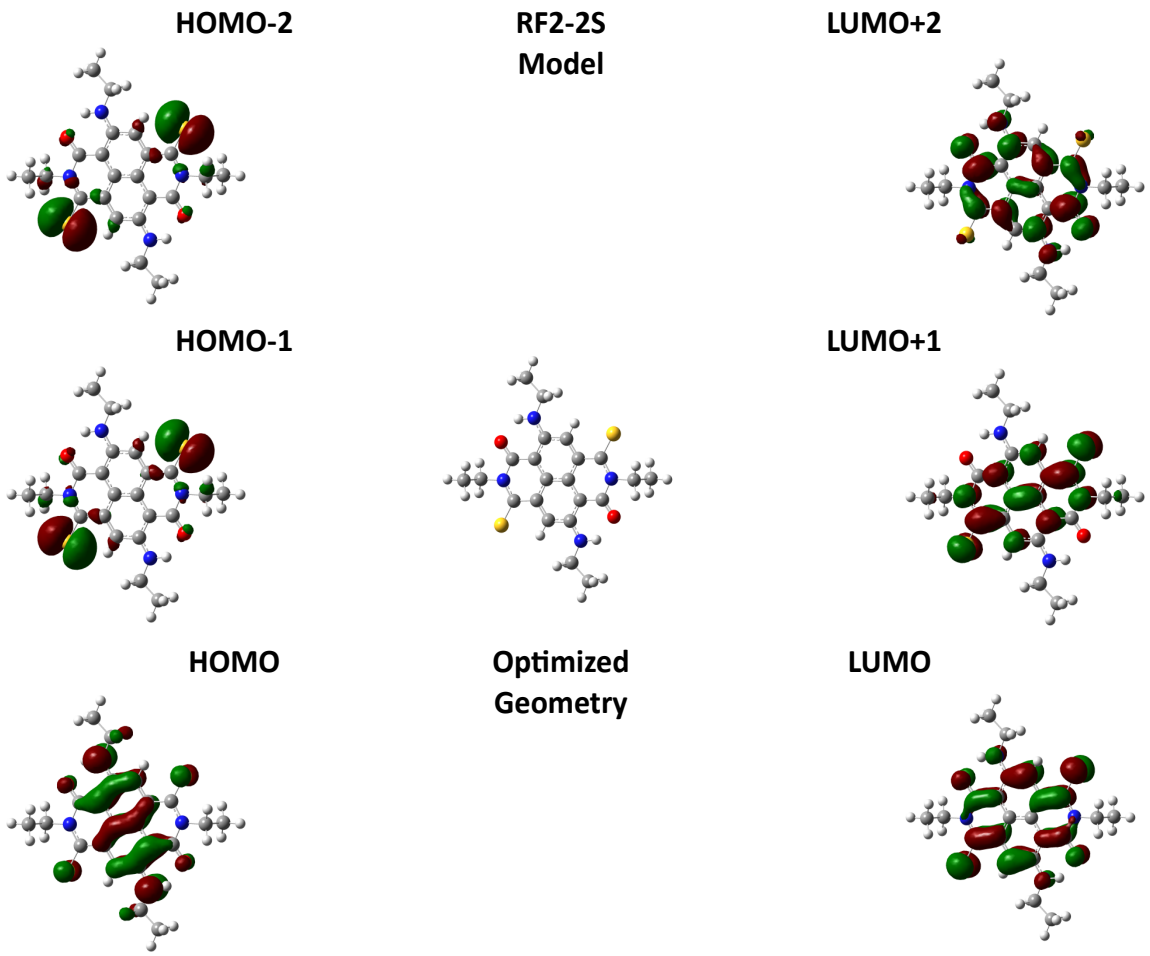

Figure 21: Kohn-Sham frontier molecular orbitals of RF2-2S model at the B3LYP/6-31G(d,p) level of theory.

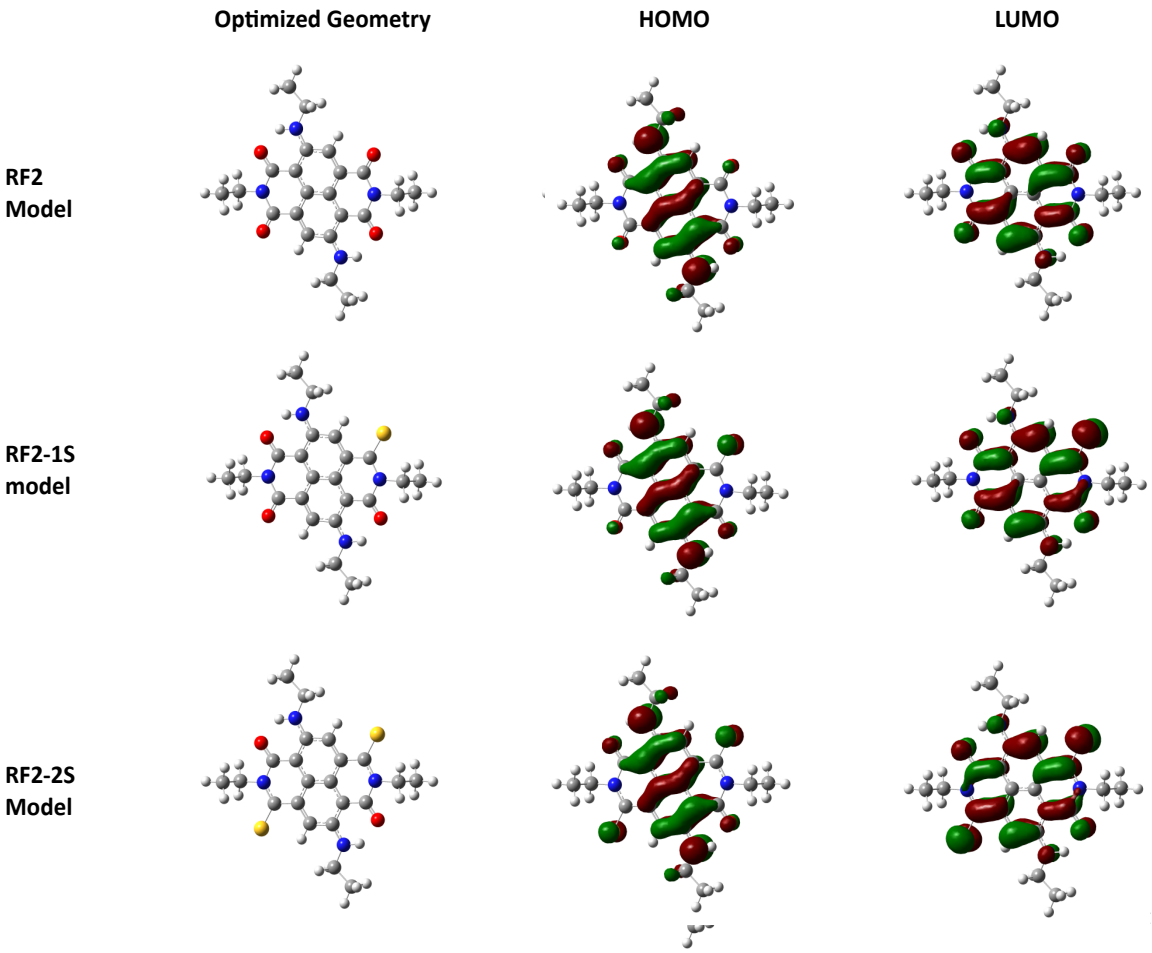

Figure 22: Kohn-Sham frontier molecular orbitals comparing RF2, RF2-1S, and RF2-2S models at the B3LYP/6-31G(d,p) level of theory.

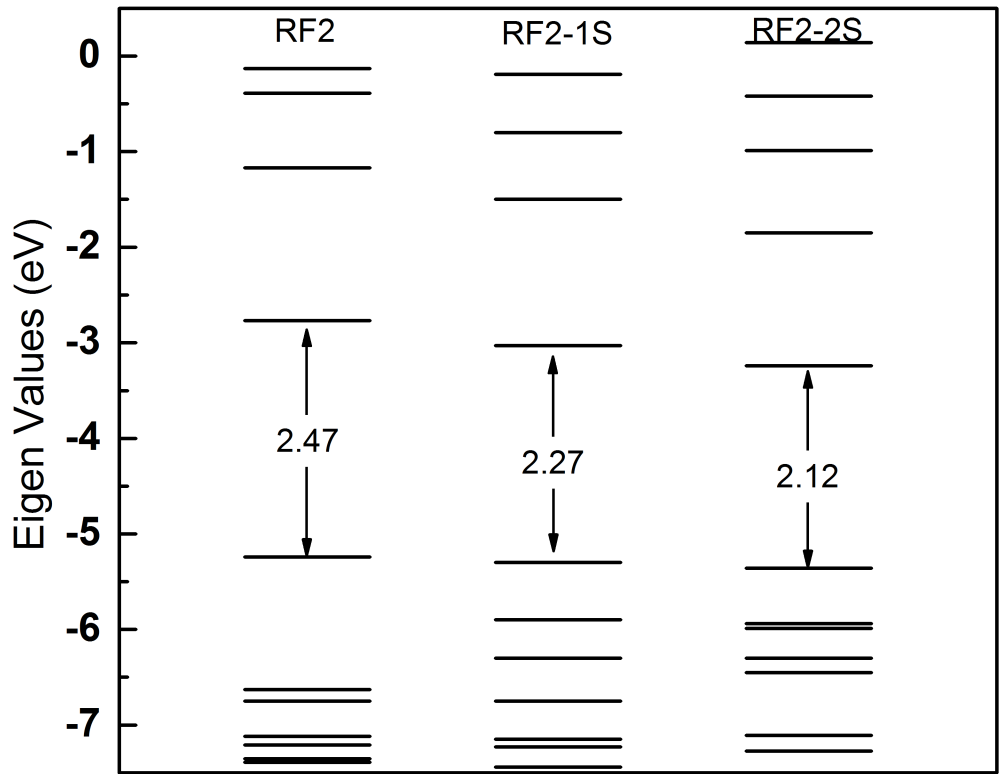

Figure 23: Comparison of eigen values for RF2, RF2-1S and RF2-2S.

Cartesian coordinates, frequencies and energies of optimized geometries in gas phase

Note: All molecules are neutral and were optimized using B3LYP/6-31G(d,p) level of theory at normal optimization criteria in Gaussian 09 software package.

RF2 Model

Cartesian coordinates

C	-3.04508100	-0.71953100	-0.17544500
C	-1.88155800	0.16338300	-0.07786200
C	-0.58114000	-0.40356900	-0.04787500
C	-0.39578200	-1.81084500	-0.11068100
C	-1.56574200	-2.71790500	-0.20612400
C	-2.04132900	1.57775400	-0.00929600
C	0.58114000	0.40356900	0.04787500
C	0.39578200	1.81084500	0.11068100
C	-0.86117200	2.37227000	0.08176700
C	1.56574200	2.71790500	0.20612400
C	3.04508100	0.71953100	0.17544500
C	1.88155800	-0.16338300	0.07786200
C	2.04132900	-1.57775400	0.00929600
C	0.86117200	-2.37227000	-0.08176700
H	0.92539500	-3.45186500	-0.13190300
H	-0.92539500	3.45186500	0.13190300
O	1.45822100	3.93831400	0.24152000
O	4.21457300	0.30810900	0.19039800
O	-4.21457300	-0.30810900	-0.19039800
O	-1.45822100	-3.93831400	-0.24152000
N	2.82013600	2.10316500	0.25974000
N	-2.82013600	-2.10316500	-0.25974000
N	-3.26215900	2.16467200	-0.03173800
H	-4.04359200	1.51621200	-0.09526700
N	3.26215900	-2.16467200	0.03173800
H	4.04359200	-1.51621200	0.09526700
C	-3.50478600	3.59670200	0.03003800
H	-3.08600000	4.01435100	0.95684400
H	-2.99715400	4.10452800	-0.80234400
C	3.50478600	-3.59670200	-0.03003800
H	3.08600000	-4.01435100	-0.95684400
H	2.99715400	-4.10452800	0.80234400
C	4.00188700	2.98357600	0.36249600
H	3.68315600	3.86260600	0.92240500
C	-4.00188700	-2.98357600	-0.36249600
H	-3.68315600	-3.86260600	-0.92240500

H	-4.75367100	-2.43786200	-0.93179300
H	4.75367100	2.43786200	0.93179300
C	5.00311200	-3.87952000	0.03149600
H	5.43613500	-3.50073100	0.96267800
H	5.18691500	-4.95601800	-0.01532900
H	5.52650200	-3.40866900	-0.80666900
C	-5.00311200	3.87952000	-0.03149600
H	-5.18691500	4.95601800	0.01532900
H	-5.43613500	3.50073100	-0.96267800
H	-5.52650200	3.40866900	0.80666900
C	-4.54811900	-3.38654800	1.00672900
H	-3.79350600	-3.93218000	1.57958400
H	-4.86137400	-2.50589700	1.57361900
H	-5.41815700	-4.03907400	0.88137600
C	4.54811900	3.38654800	-1.00672900
H	4.86137400	2.50589700	-1.57361900
H	3.79350600	3.93218000	-1.57958400
H	5.41815700	4.03907400	-0.88137600

Frequencies

25.8929	40.6583	44.1492
44.1980	54.5806	64.9904
69.4772	75.5478	81.0382
96.6212	102.8538	112.0872
113.8406	136.5740	159.7818
180.5811	192.9075	206.0273
224.3065	237.2299	247.8160
255.7811	260.9151	266.5801
276.4400	300.4371	316.0198
320.8387	334.9249	360.9985
376.7621	398.4926	408.7953
421.4560	423.1187	445.9729
462.5131	481.3543	481.4621
494.2279	525.7736	543.4431
575.3121	575.8534	612.3758
622.2683	627.2515	633.6550
653.8453	665.8989	689.5500
720.2055	730.5981	742.5752
758.4659	761.0408	763.1135
770.3274	782.4017	808.6929
825.8558	825.8566	845.0525
881.8937	903.4192	917.7907
920.9060	927.3450	929.7790
974.7921	995.9343	1046.5891
1048.5220	1058.7179	1086.4147
1091.0853	1110.0461	1115.3851

1118.0177 1147.4216 1172.2963
1172.3618 1173.4218 1179.8768
1207.4529 1213.0755 1229.9936
1261.8435 1274.8927 1284.0677
1308.5185 1308.5922 1335.4533
1350.7924 1365.1812 1380.9968
1385.1367 1388.9410 1396.2834
1401.5422 1407.8806 1410.6459
1421.1437 1426.3155 1428.2307
1433.7191 1442.1104 1450.6058
1471.5631 1472.8161 1482.8988
1486.2011 1507.7570 1507.7573
1508.2303 1508.2321 1516.2756
1516.6415 1517.8640 1517.9689
1526.5859 1538.7622 1539.4833
1551.2804 1584.1614 1621.8089
1644.4770 1669.5400 1696.4137
1707.0389 1756.8679 1758.7368
3005.4909 3005.7705 3032.7505
3032.7894 3053.1939 3053.2262
3055.1765 3055.2253 3111.8452
3111.8573 3124.9156 3124.9306
3130.6094 3130.6561 3136.3672
3136.3814 3137.9845 3137.9882
3173.8420 3173.8508 3239.7876
3240.0181 3480.7000 3483.4005

Energies

SCF Done: E(RB3LYP) = -1372.86517000 A.U. after 15 cycles
Zero-point correction= 0.439962 (Hartree/Particle)
Thermal correction to Energy= 0.467936
Thermal correction to Enthalpy= 0.468880
Thermal correction to Gibbs Free Energy= 0.380961
Sum of electronic and zero-point Energies= -1372.438268
Sum of electronic and thermal Energies= -1372.410295
Sum of electronic and thermal Enthalpies= -1372.409351
Sum of electronic and thermal Free Energies= -1372.497270

RF2-1S Model

Cartesian coordinates

C	3.19143100	0.47752200	-0.19598200
C	1.92303700	-0.24711700	-0.09697300
C	0.70454900	0.47439600	-0.06173900
C	0.70519400	1.89525100	-0.12084700

C	1.98271700	2.64555100	-0.21895000
C	1.89601100	-1.66935400	-0.03201400
C	-0.55252300	-0.18014400	0.03583700
C	-0.56594400	-1.60700500	0.09148300
C	0.62768700	-2.30527400	0.05728900
C	-1.84906000	-2.33935400	0.18705200
C	-3.02134500	-0.15200900	0.18139900
C	-1.75947000	0.56050000	0.07220000
C	-1.73461600	1.98664200	0.00716400
C	-0.46341100	2.62019000	-0.08727900
H	-0.38378600	3.69867300	-0.13564000
H	0.57173100	-3.38462800	0.10198100
O	-4.12556000	0.41114400	0.20757700
O	4.29687400	-0.08256400	-0.21403000
O	2.02933500	3.86988400	-0.25133400
N	-2.99188100	-1.56542900	0.26467600
N	3.14760000	1.87811400	-0.27870300
N	3.02957700	-2.41122800	-0.05720200
H	3.88950300	-1.87207500	-0.12025900
N	-2.86731800	2.72669300	0.03712700
H	-3.72676100	2.18635200	0.10549900
C	3.08359900	-3.86349600	-0.00318600
H	2.61408900	-4.22789000	0.92148600
H	2.51418800	-4.29634000	-0.83767000
C	-2.92172100	4.17934900	-0.01457700
H	-2.45606100	4.54365800	-0.94113700
H	-2.34817700	4.60975700	0.81827900
C	-4.32232500	-2.20723500	0.40512900
H	-4.16521800	-3.13239100	0.95695300
C	4.43159100	2.60043500	-0.38753700
H	4.22582600	3.51077000	-0.95036300
H	5.10585300	1.96115400	-0.95659100
H	-4.93238900	-1.52418800	0.99387500
C	-4.37057400	4.65332000	0.05693500
H	-4.84452700	4.32713000	0.98804400
H	-4.41361200	5.74481600	0.01820900
H	-4.95420100	4.26033500	-0.78153200
C	4.53303300	-4.33696700	-0.06756800
H	4.57657600	-5.42841900	-0.02716600
H	5.01112600	-4.01168700	-0.99695800
H	5.11286600	-3.94242400	0.77289500
C	5.02857400	2.93566700	0.97875000
H	4.35076900	3.57450100	1.55125400
H	5.22979500	2.02466700	1.54856300
H	5.97370300	3.47245700	0.84844400
C	-4.98217200	-2.48386400	-0.94471300

H	-5.14753700	-1.55314700	-1.49319000
H	-4.36984000	-3.15689900	-1.54974300
H	-5.95369500	-2.96148000	-0.78243400
S	-1.91855200	-4.01434500	0.19981100

Frequencies

22.0506	35.6013	41.8126
44.7114	57.0970	67.0502
75.7225	77.9436	89.9656
98.0524	101.2974	110.7332
116.9574	134.9613	162.1600
184.7154	190.7230	201.2315
221.3382	230.5993	246.1889
249.2267	260.1650	266.1203
273.7666	282.5287	307.7914
324.6592	325.2430	345.6781
365.2955	381.9484	404.5592
421.7421	427.9405	447.1257
461.5286	475.0929	476.1014
497.2770	503.3308	537.1313
561.5821	576.5864	604.4158
612.6661	621.8537	631.9471
648.9071	657.8221	683.8525
700.1565	720.0119	734.5387
735.4281	749.3726	759.1237
763.1878	773.2080	803.0865
825.2788	825.4140	832.0383
869.7927	901.6589	919.4462
921.9887	925.4095	928.6799
957.7646	989.5970	1022.1460
1041.2297	1048.3668	1072.0964
1090.7414	1098.1434	1112.7474
1116.3232	1133.2120	1156.2116
1171.4087	1171.7120	1174.2439
1181.9549	1211.5245	1220.5227
1231.2661	1269.6142	1278.3760
1289.6533	1306.5442	1307.1146
1326.4581	1351.4107	1366.3070
1382.3908	1383.6592	1389.3076
1397.1458	1404.0982	1406.6325
1411.9039	1422.5190	1427.3548
1428.9635	1432.8907	1441.9553
1450.7915	1467.8374	1468.8771
1480.5154	1484.4281	1507.7548
1507.8373	1508.1207	1508.7633
1516.1672	1516.5478	1518.1751

1518.3470	1526.6964	1537.0446
1539.2228	1552.7058	1581.4479
1618.1362	1642.6278	1669.1706
1700.1381	1708.2982	1757.5017
3008.5688	3009.2497	3036.5621
3037.5169	3052.8888	3053.7051
3055.8054	3058.5765	3112.3174
3117.4834	3124.6007	3125.7995
3131.0689	3134.4599	3136.4734
3137.1906	3138.5965	3144.7204
3174.3362	3179.4061	3238.7345
3241.3318	3481.3584	3492.4447

Energies

SCF Done: E(RB3LYP) = -1695.81844749 A.U. after 16 cycles
Zero-point correction= 0.437792 (Hartree/Particle)
Thermal correction to Energy= 0.465986
Thermal correction to Enthalpy= 0.466930
Thermal correction to Gibbs Free Energy= 0.378417
Sum of electronic and zero-point Energies= -1695.390849
Sum of electronic and thermal Energies= -1695.362655
Sum of electronic and thermal Enthalpies= -1695.361710
Sum of electronic and thermal Free Energies= -1695.450224

RF2-2S Model

Cartesian coordinates

C	-3.02772000	-0.74280200	-0.16566300
C	-1.87728300	0.13999300	-0.06826100
C	-0.57667200	-0.41476400	-0.04312400
C	-0.39176100	-1.83120000	-0.09784200
C	-1.55993400	-2.73931000	-0.17886600
C	-2.05046000	1.55467500	-0.00224700
C	0.57667200	0.41476400	0.04312400
C	0.39176100	1.83120000	0.09784200
C	-0.88459700	2.36058200	0.07586900
C	1.55993400	2.73931000	0.17886600
C	3.02772000	0.74280200	0.16566300
C	1.87728300	-0.13999300	0.06826100
C	2.05046000	-1.55467500	0.00224700
C	0.88459700	-2.36058200	-0.07586900
H	0.97678700	-3.43733200	-0.11915200
H	-0.97678700	3.43733200	0.11915200
O	4.19973000	0.34025600	0.18170200

O	-4.19973000	-0.34025600	-0.18170200
N	2.80098600	2.13748100	0.24752700
N	-2.80098600	-2.13748100	-0.24752700
N	-3.27546800	2.13030400	-0.01665800
H	-4.05256900	1.47720400	-0.07829100
N	3.27546800	-2.13030400	0.01665800
H	4.05256900	-1.47720400	0.07829100
C	-3.53018400	3.56176800	0.03868100
H	-3.10276600	3.98712700	0.95744500
H	-3.03628800	4.06739800	-0.80279400
C	3.53018400	-3.56176800	-0.03868100
H	3.10276600	-3.98712700	-0.95744500
H	3.03628800	-4.06739800	0.80279400
C	4.02932700	2.96108700	0.37054700
H	3.74878100	3.85955300	0.91755100
C	-4.02932700	-2.96108700	-0.37054700
H	-3.74878100	-3.85955300	-0.91755100
H	-4.73429700	-2.37501700	-0.95791300
H	4.73429700	2.37501700	0.95791300
C	5.03164800	-3.83029100	0.00569500
H	5.47337300	-3.44238600	0.92904700
H	5.22372200	-4.90547600	-0.03650100
H	5.54043400	-3.36096200	-0.84227800
C	-5.03164800	3.83029100	-0.00569500
H	-5.22372200	4.90547600	0.03650100
H	-5.47337300	3.44238600	-0.92904700
H	-5.54043400	3.36096200	0.84227800
C	-4.63135600	-3.31499600	0.98824400
H	-3.92622000	-3.89196800	1.59151900
H	-4.91799400	-2.41109500	1.53136000
H	-5.52921300	-3.92327000	0.83971400
C	4.63135600	3.31499600	-0.98824400
H	4.91799400	2.41109500	-1.53136000
H	3.92622000	3.89196800	-1.59151900
H	5.52921300	3.92327000	-0.83971400
S	1.39032800	4.40742500	0.18494000
S	-1.39032800	-4.40742500	-0.18494000

Frequencies

21.1531	35.6995	36.0079
44.5534	58.9596	69.0192
77.5367	88.3964	88.9559
96.7259	102.5767	105.8256
115.5177	135.1297	165.5136
180.1772	195.8843	198.5516
220.4225	225.1858	238.0576

241.3954	259.9927	262.7840
267.1002	281.0233	297.9603
314.3310	326.6999	329.1259
356.8816	370.5670	391.0485
422.5258	428.2273	451.0162
454.4350	468.2464	472.3466
489.8461	501.5062	520.6926
537.0359	576.2501	595.3297
604.6795	621.4411	626.7539
648.3210	656.9645	679.1557
680.6683	702.9333	706.8870
729.9865	744.7822	749.6808
752.3301	766.0202	799.5850
807.5790	824.8714	824.9365
857.6312	894.1901	921.3609
923.2959	924.3399	926.9492
950.7016	970.0706	1020.8717
1025.2299	1034.6166	1047.1278
1086.0056	1092.3045	1111.4456
1114.5781	1129.5166	1140.5065
1159.4696	1170.9059	1170.9394
1175.4870	1182.7189	1216.9346
1221.7579	1235.7806	1274.4556
1282.1002	1293.7858	1309.9692
1310.0511	1322.3930	1351.0781
1354.5258	1381.6614	1384.6893
1389.2143	1398.4454	1405.2308
1409.1756	1412.4821	1421.9804
1425.0346	1428.6906	1433.3036
1442.4267	1449.2250	1461.9157
1465.9089	1481.5225	1483.0000
1507.9926	1507.9941	1508.2616
1508.2701	1515.3395	1516.1397
1517.7388	1517.9940	1522.5137
1535.3914	1537.6658	1552.7091
1575.9742	1613.4719	1640.2359
1666.9447	1704.0611	1706.9752
3010.8613	3011.0457	3039.2993
3039.3348	3053.2000	3053.2311
3058.8905	3058.9349	3117.3970
3117.4054	3124.8174	3124.8323
3134.8823	3134.9154	3137.0334
3137.0432	3144.8200	3144.8231
3179.1109	3179.1240	3239.8847
3240.2201	3487.0488	3490.0501

Energies

SCF Done: E(RB3LYP) = -2018.75863212 A.U. after 15 cycles
Zero-point correction= 0.435437 (Hartree/Particle)
Thermal correction to Energy= 0.463888
Thermal correction to Enthalpy= 0.464833
Thermal correction to Gibbs Free Energy= 0.375683
Sum of electronic and zero-point Energies= -2018.343444
Sum of electronic and thermal Energies= -2018.314993
Sum of electronic and thermal Enthalpies= -2018.314048
Sum of electronic and thermal Free Energies= -2018.403198