Supplementary Information

Direct Spectroscopic Detection and EPR Investigation of a Ground State Triplet Phenyl Oxenium Ion

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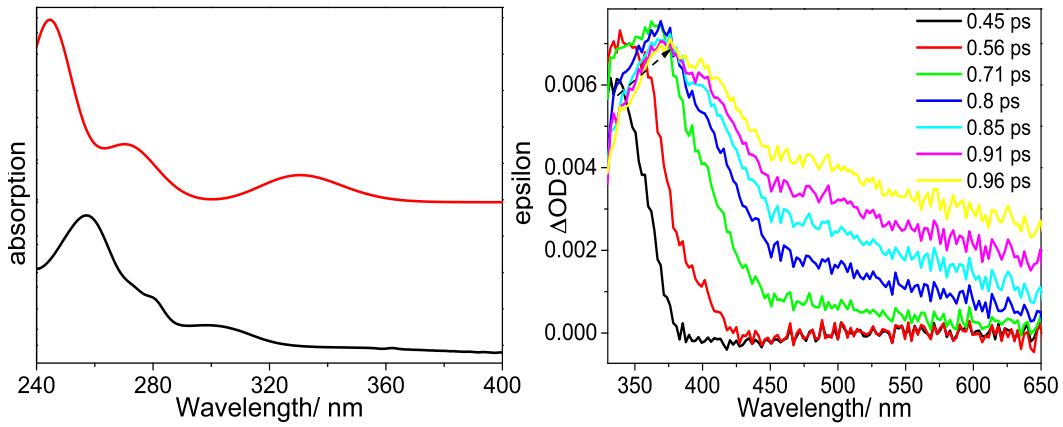


Figure 1S. Left bottom is the experimental UV-vis spectrum of precursor recorded in aqueous solution and left top is the computed spectrum of the precursor. Right shows the fs-TA spectra recorded from 0.45 ps to 0.96 ps.

Table 1S. Excited state energies and oscillator strength from TD-DFT (B3LYP/6-311G**) calculations for precursor.

Excited state	Transition Energy (nm)	Oscillator Strength
1	330	0.0441
2	272	0.0748
3	266	0.0210
4	244	0.2523
5	241	0.0480

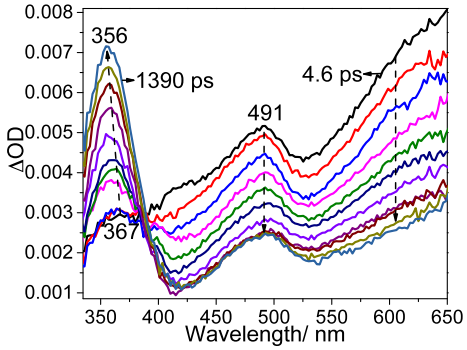


Figure 2S. The fs-TA spectra of species produced in MeCN:H_2O 1:9 solution acquired after 266 nm irradiation of the precursor m-dimethylamino phenyloxenium (Top left) LFP from 4.6 ps to 1390 ps.

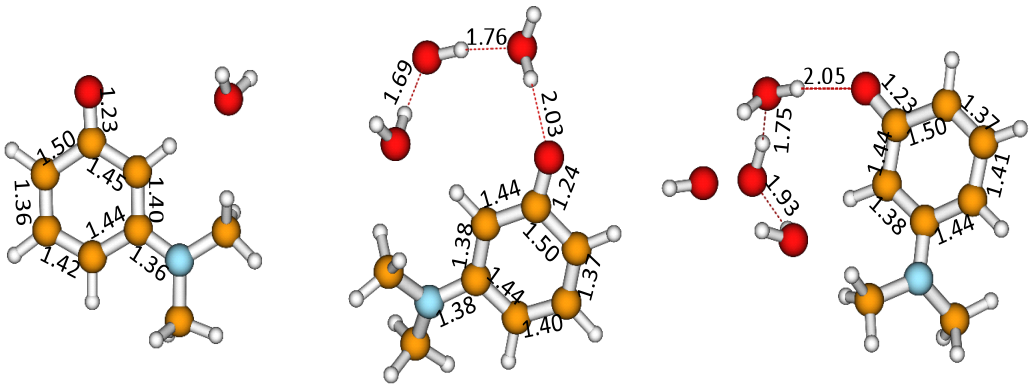
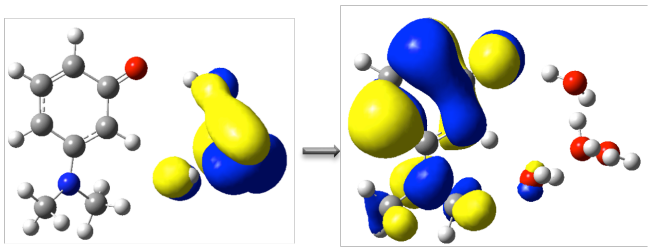
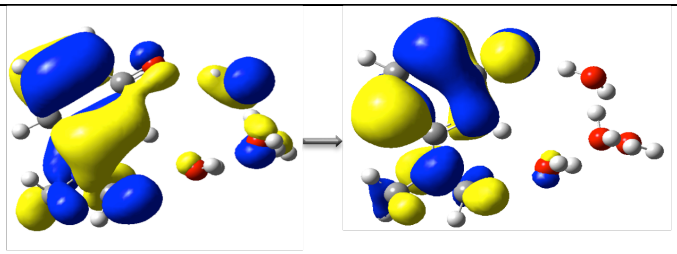
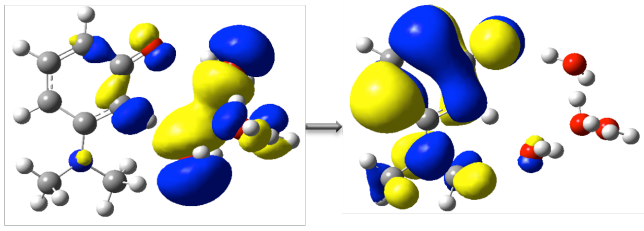
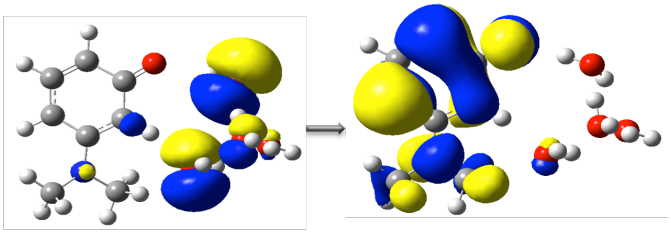


Figure 3S. Shown are the optimized structure of the adducts of closed-shell singlet *m*-dimethylamino phenyloxenium ion with one water (left), three water molecules (middle) and four water molecules (right) from B3LYP/6-311G(d,p) calculations.

Table 2S. Shown are the transition energy and its corresponding molecular orbital with weight coefficient.

Transition Energy (nm)	Molecular Orbital	percent
332		2.3%
		93.4%
588		88.4%

		10.8%

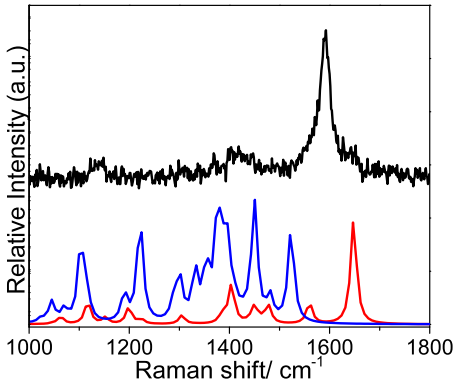


Figure 4S. (Top) Ns-TR[3] spectrum (black) obtained at 20 ns in MeCN:H_2O 1:1 solution. (Bottom) Shown is the calculated normal Raman spectrum of the singlet m-dimethylamino phenyloxenium ion (red) and m-dimethylamino phenyloxy radical (blue) using MP2/6-311G(d,p) calculation.

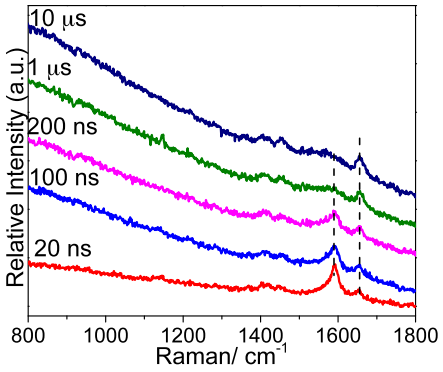


Figure 5S. Ns-TR[3] spectra obtained with various delay times indicated next to the spectra after 266 nm photo-excitation of m-dimethylamino phenyloxenium and using 355 nm as probe wavelength in MeCN:H_2O 1:9 solution.

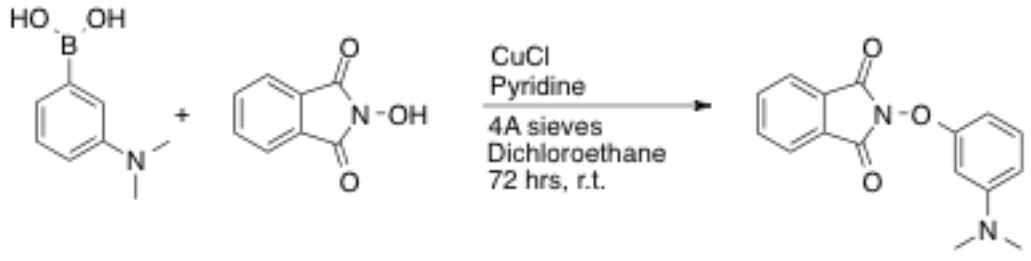


Figure 6S. Synthetic route for the formation of N-m-dimethylaminophenoxyphthalimide.

Synthesis of *N*-*m*-dimethylaminophenoxyphthalimide.

326 mg (2 mmol, 1eq) of N-hydroxyphthalimide, 200 mg (2 mmol, 1 eq) of CuCl, 660 mg (4 mmol, 2 eq) of 3-(*N*,*N*-dimethylamino)phenylboronic acid, and ~500 mg of 4Å molecular sieves were combined in a 50 mL round bottom flask. 15 mL of 1,2-dichloroethane solvent was added followed by 180 μL (2.2 mmol, 1.1 eq) of pyridine, resulting in a light brown suspension. The reaction was stirred for 72 hours under ambient temperature and atmosphere. Progress of the reaction was monitored by TLC (72:25 Hexanes:Ethyl Acetate). The reaction mixture turned a teal bluish-green as the reaction proceeded. After 72 hours, the solvent was evaporated under reduced pressure. The crude product was then purified by column chromatography (70:30 Hexanes: Ethyl Acetate). A white solid was collected and dried under high vacuum, to give 277.6 mg (60% yield), of the desired product.

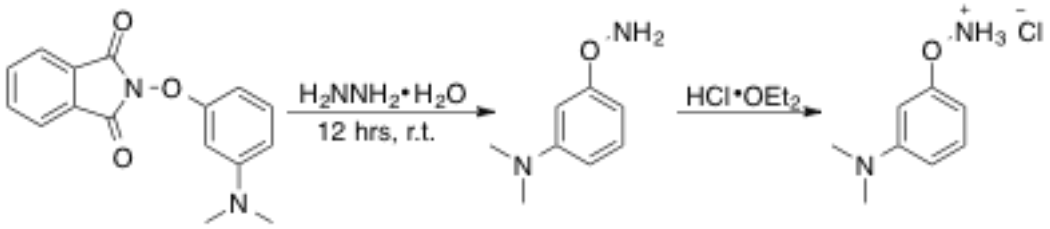
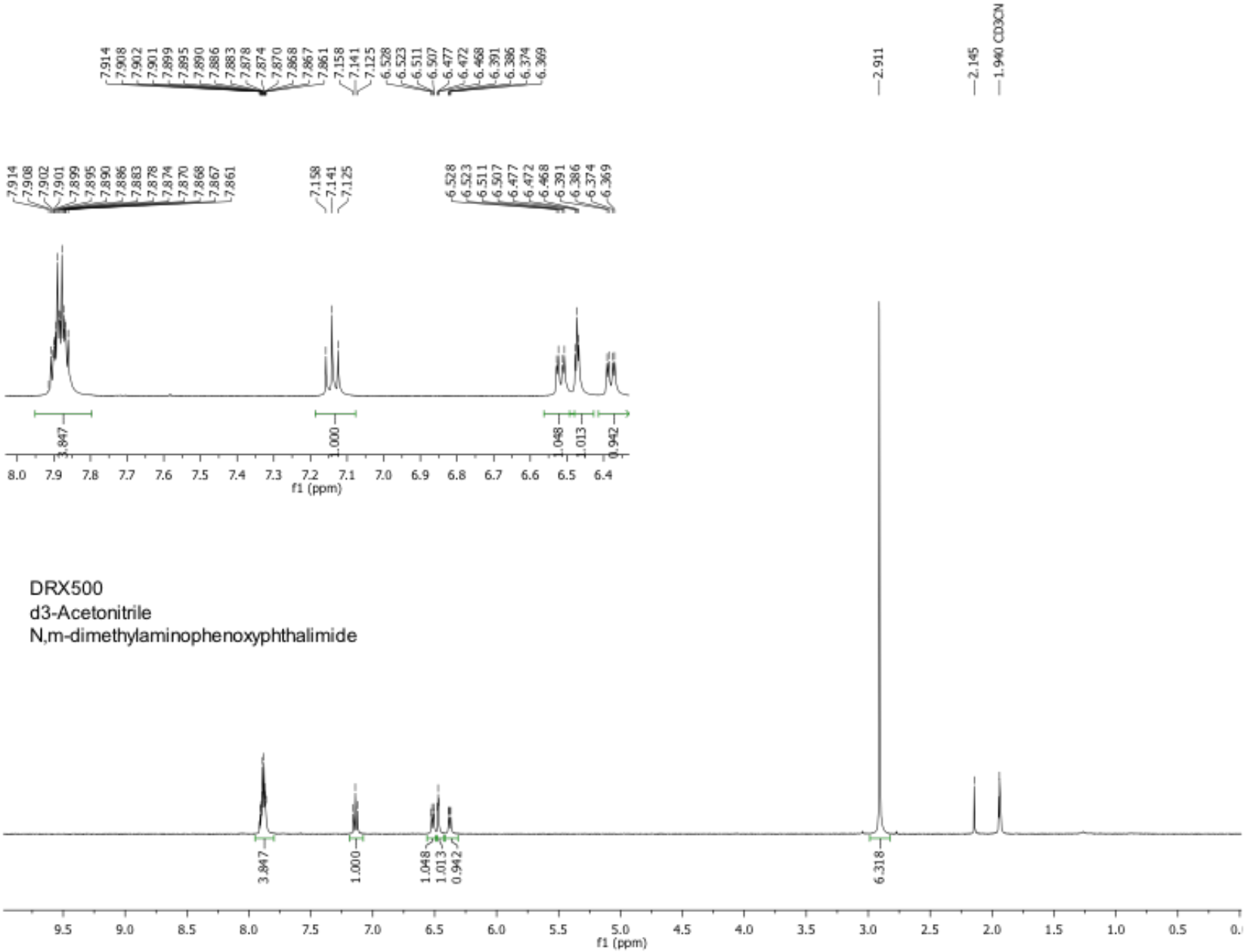
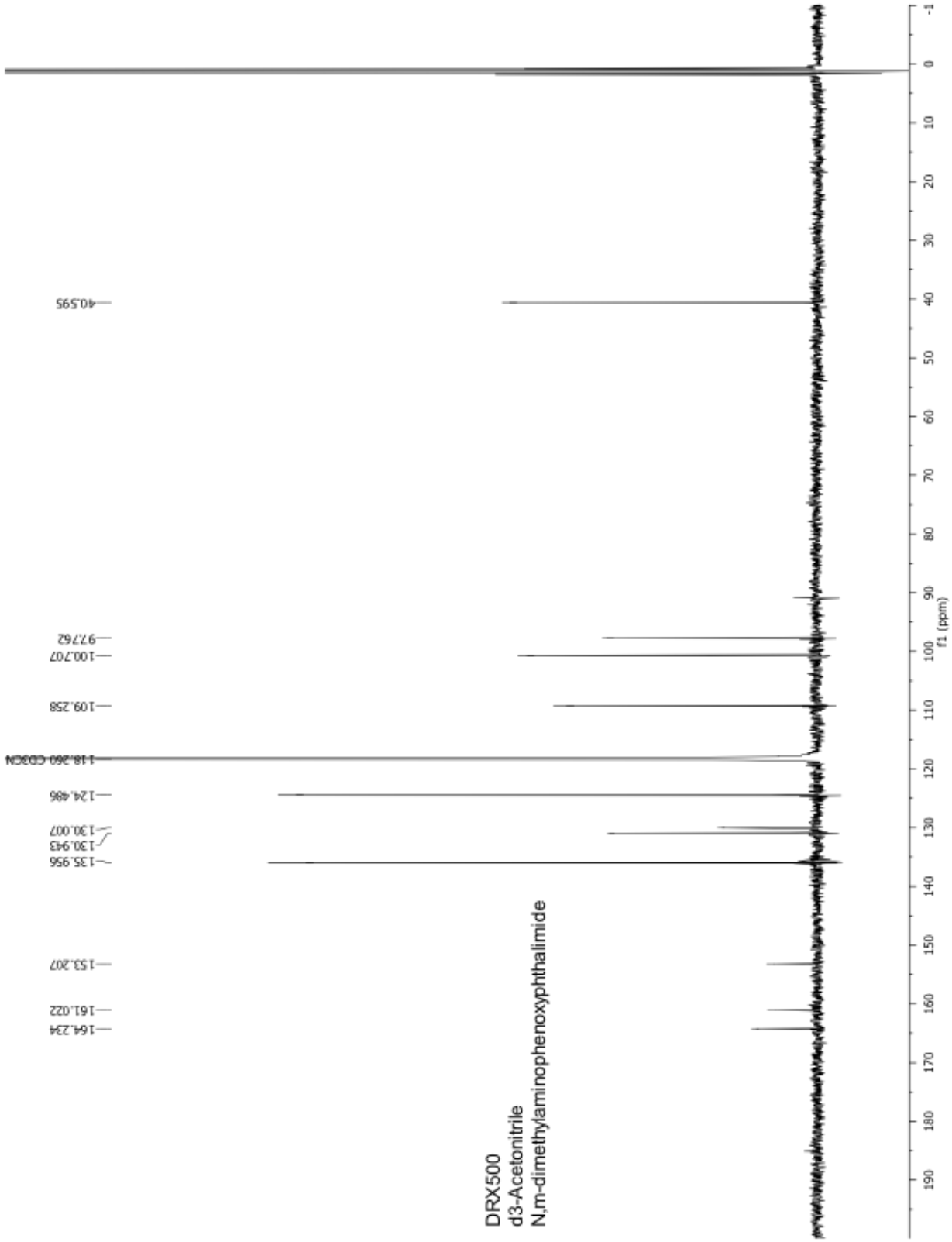


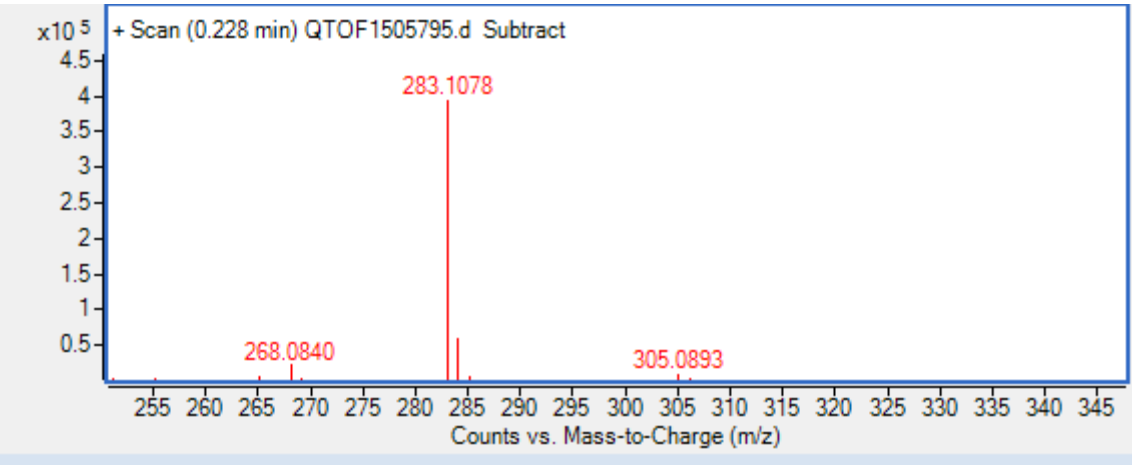
Figure 7S. Synthetic route for the formation of m-Dimethylaminophenylhydroxylamine hydrochloride.

Synthesis of *m*-Dimethylaminophenylhydroxylamine hydrochloride.

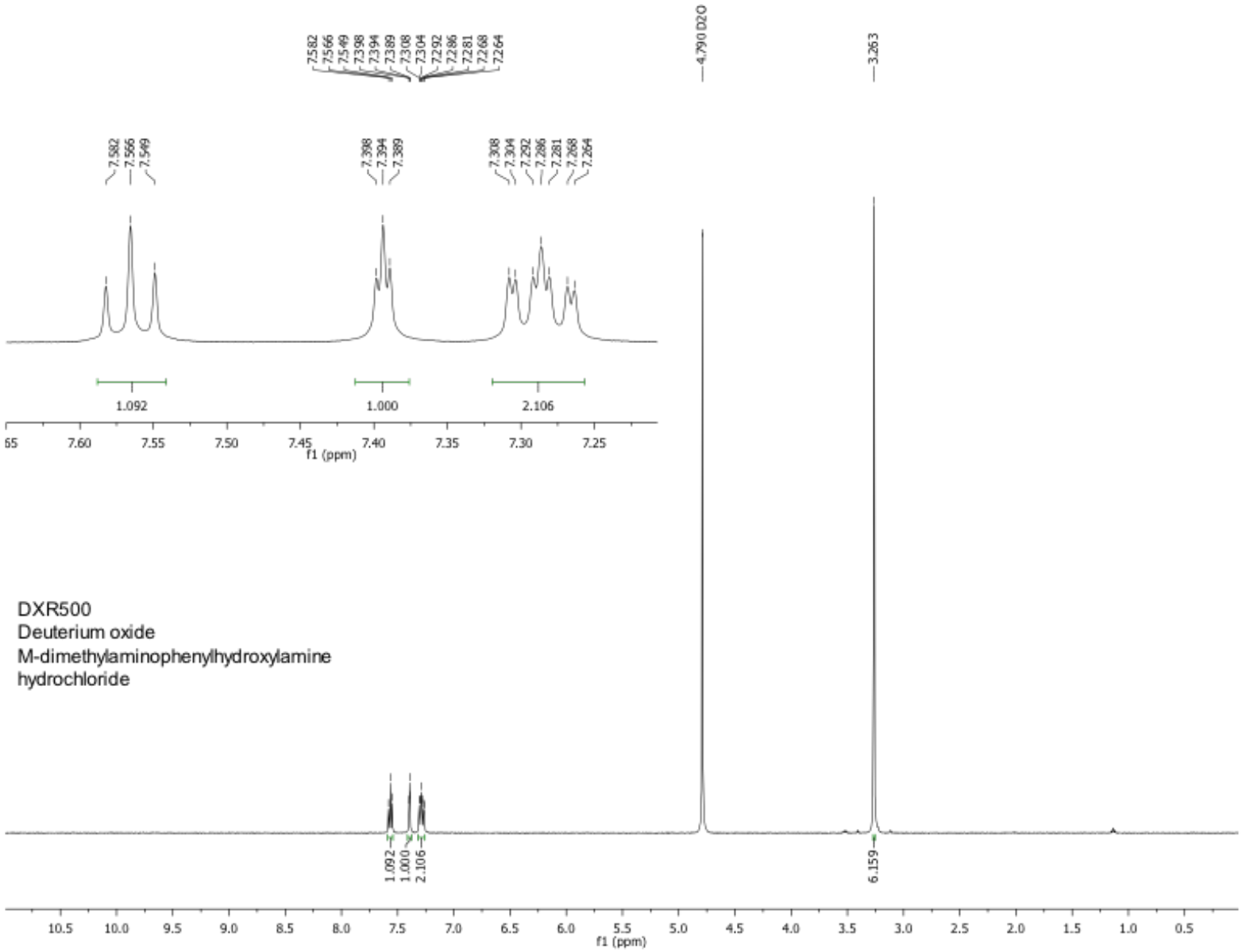
277.6 mg (0.98 mmol, 1 eq) of N-m-dimethylaminophenoxyphthalimide was added to a flask containing 100 mL of 10% MeOH in $CHCl_3$ and 0.48 mL (9.8 mmol, 10 eq) of hydrazine monohydrate. A colorless solution was formed, which yielded a white precipitate (phthalazine) over time. The reaction was allowed to stir overnight (12 hours) at room temperature. The white precipitate was filtered off and the filtrate was then purified by column chromatography (75:25 Hexanes:Ethyl Acetate). The resulting clear oil was dissolved in ether (5-10 mL) and then HCl*OEt_2 (~ 0.3 mL) was added until white precipitate no longer formed upon addition. The white solid was collected and dried under high vacuum to yield 162 mg of the desired salt (87% yield). The product was reasonably stable stored in the freezer in the dark.

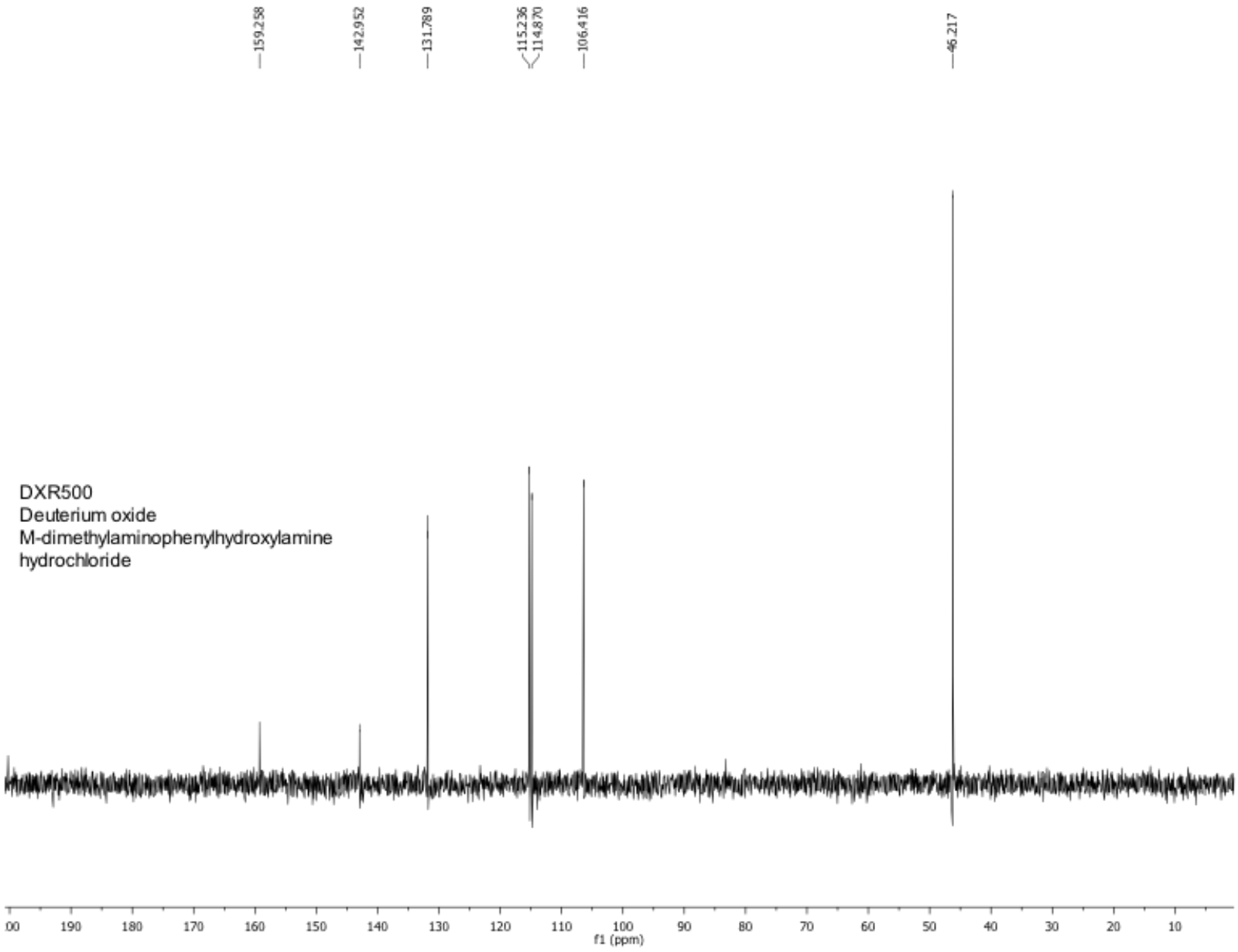

7.914
7.908
7.902
7.901
7.899
7.895
7.890
7.886
7.883
7.878
7.874
7.870
7.868
7.867
7.861
7.158
7.141
7.125
6.528
6.523
6.511
6.507
6.477
6.472
6.468
6.391
6.386
6.374
6.369
2.911
2.145
1.940 CD3CN
3.847
1.000
1.048
1.013
0.942
6.318
f1 (ppm)
DRX500
d3-Acetonitrile
N,m-dimethylaminophenoxyphthalimide

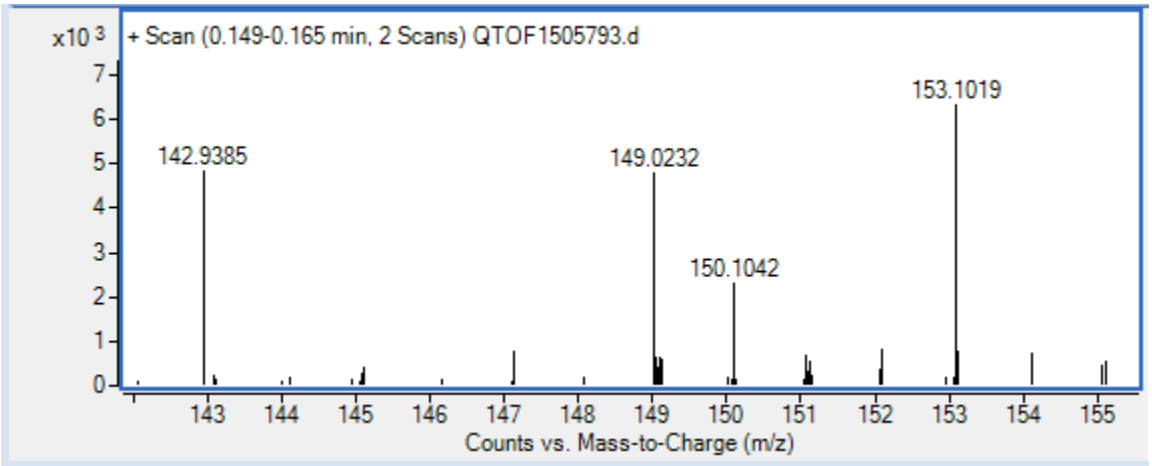

DRX500
d3-Acetonitrile
N,m-dimethylaminophenoxyphthalimide
40.595
97.762
100.707
109.258
118.260 CD3CN
124.486
130.007
130.943
135.956
153.207
161.022
164.234
f1 (ppm)



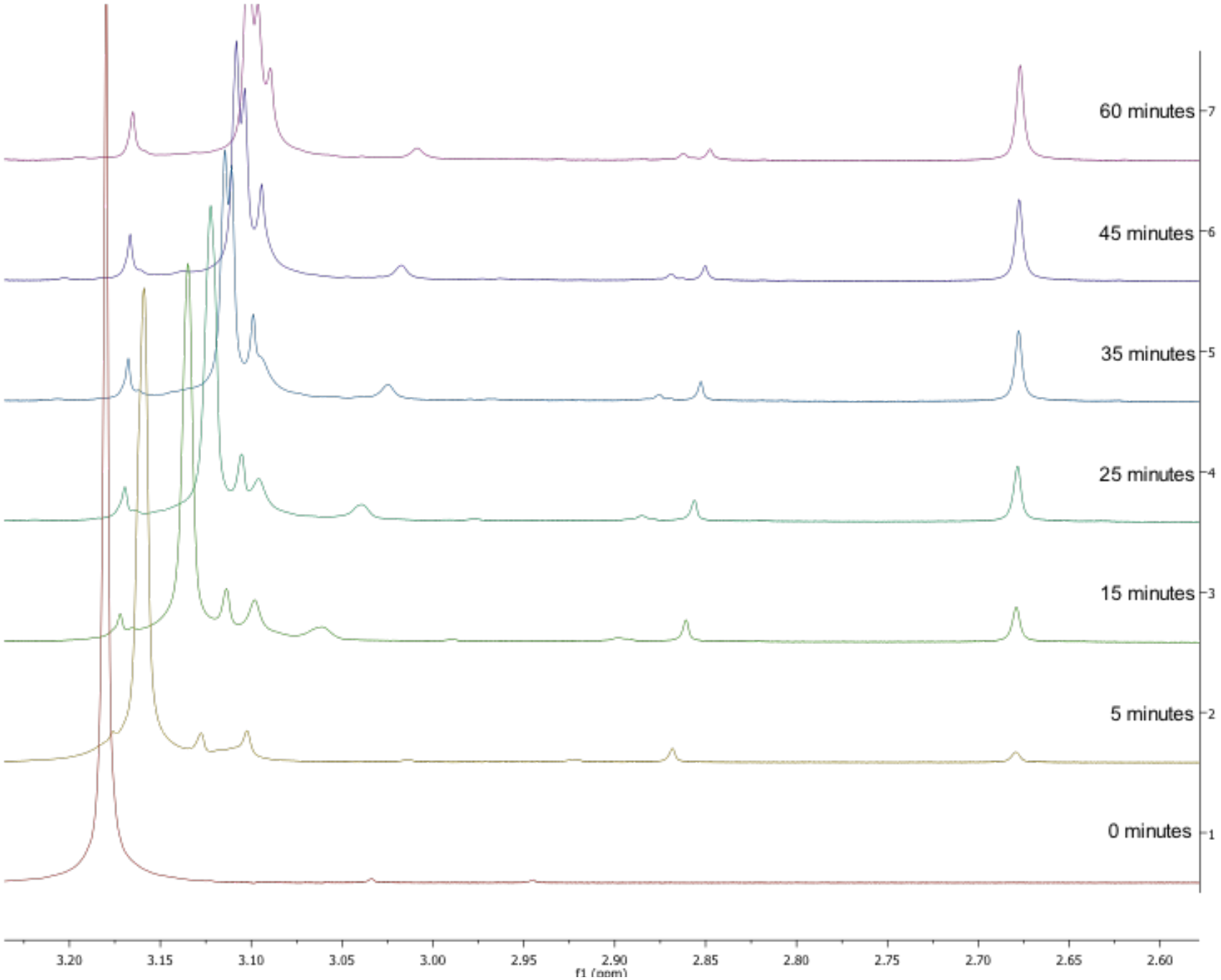
Formula (M)	Score (MFG	Mass	Mass (MFG)	m/z (Calc)	Diff (ppm)	DBE	m/z
C16 H14 N2 O3	99.98	282.10052	282.10044	283.1077	-0.29	11	283.1078


7.582
7.566
7.549
7.398
7.394
7.389
7.308
7.304
7.292
7.286
7.281
7.268
7.264
4.790 D2O
3.263
1.092
1.000
2.106
6.159
f1 (ppm)
DXR500
Deuterium oxide
M-dimethylaminophenylhydroxylamine
hydrochloride


159.258
142.952
131.789
115.236
114.870
106.416
46.217
DXR500
Deuterium oxide
M-dimethylaminophenylhydroxylamine
hydrochloride
f1 (ppm)



Formula (M)	Score (MFG	Mass	Mass (MFG)	m/z (Calc)	Diff (ppm)
C8 H13 N2 O	99.33	153.10245	153.10279	153.1022	2.22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7
45 minutes
6
35 minutes
5
25 minutes
4
15 minutes
3
5 minutes
2
0 minutes
1
3.20
3.15
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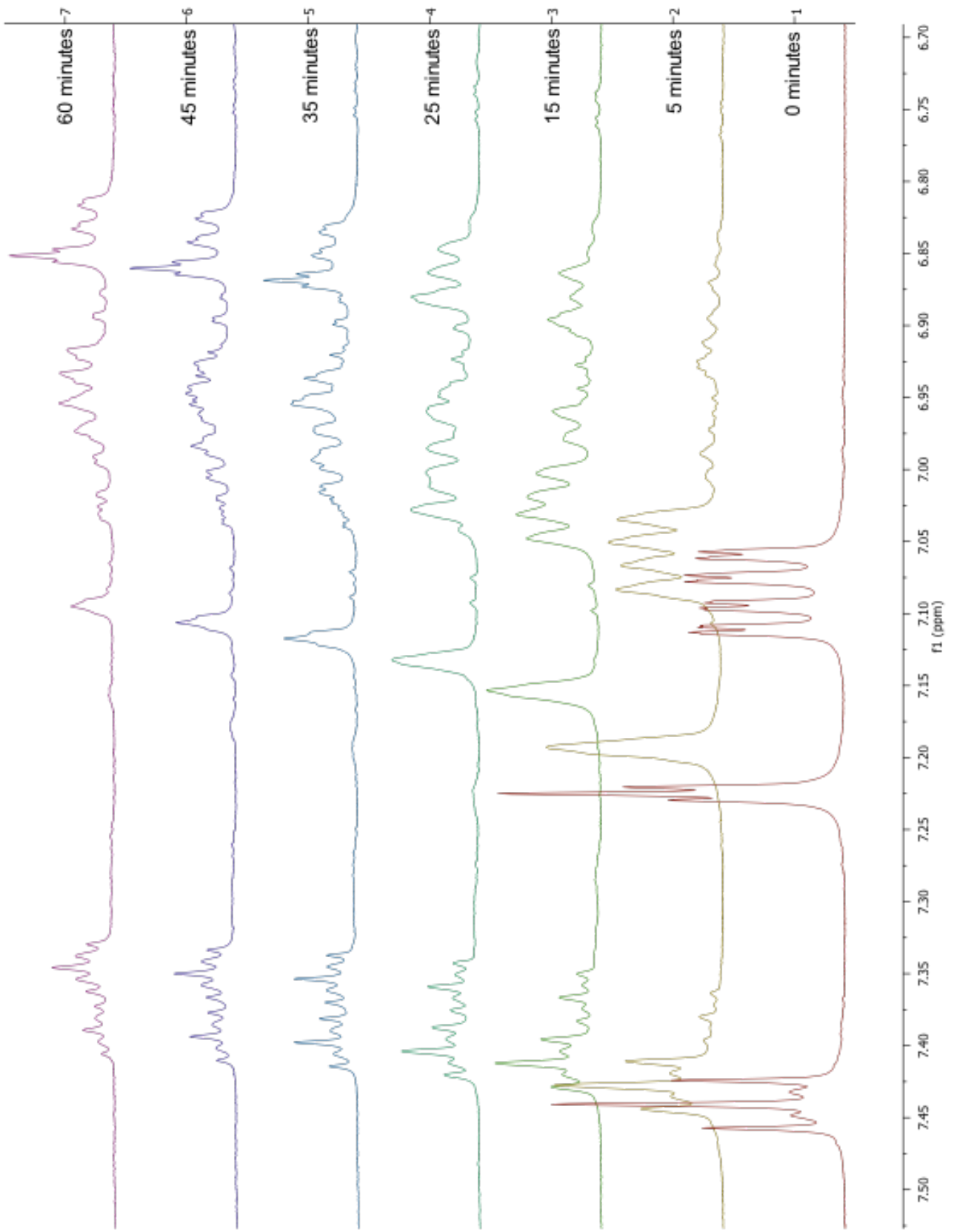
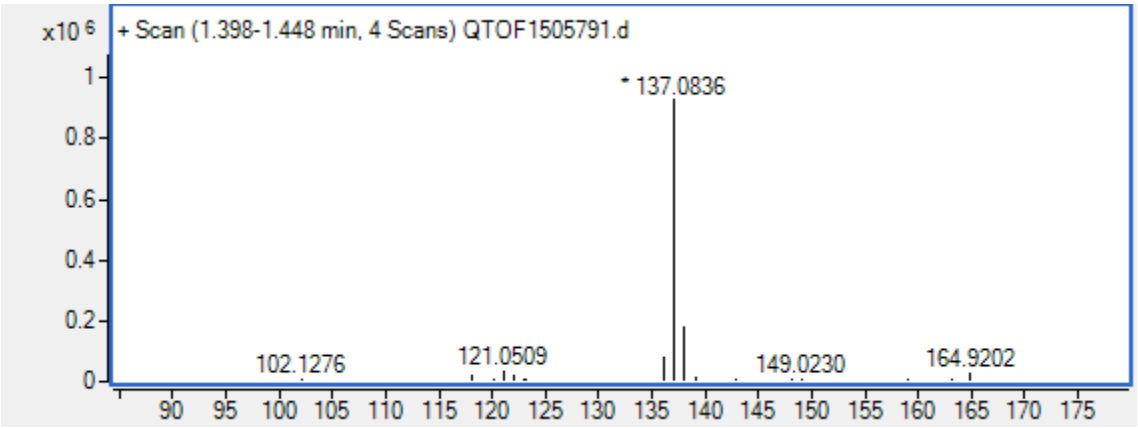
2.90
2.85
2.80
2.75
2.70
2.65
2.60
f1 (ppm)


60 minutes
45 minutes
35 minutes
25 minutes
15 minutes
5 minutes
0 minutes
7.50
7.45
7.40
7.35
7.30
7.25
7.20
7.15
7.10
7.05
7.00
6.95
6.90
6.85
6.80
6.75
6.70
f1 (ppm)



Formula (M)	Score (MFG	Mass	Mass (MFG)	m/z (Calc)	Diff (ppm)
C8 H11 N O	99.96	137.08415	137.08406	137.0835	-0.62

Quantitative Product Studies. Photolysis studies were performed as follows: addition of 10 mg of *m*-Dimethylaminophenylhydroxylamine hydrochloride and 5-10 mg of sodium acetate trihydrate (internal standard) to 0.8 mL of deuterium oxide and placed in a quartz NMR tube. An initial ^{1}H NMR was taken with a 90° angle and a relaxation delay of 60 seconds. The solution was then degassed for 30 minutes (under argon) and photolyzed for 1 hour in a Rayonet photoreactor fitted with 254 nm bulbs. After photolysis was complete, an NMR spectrum was taken with the previous parameters.

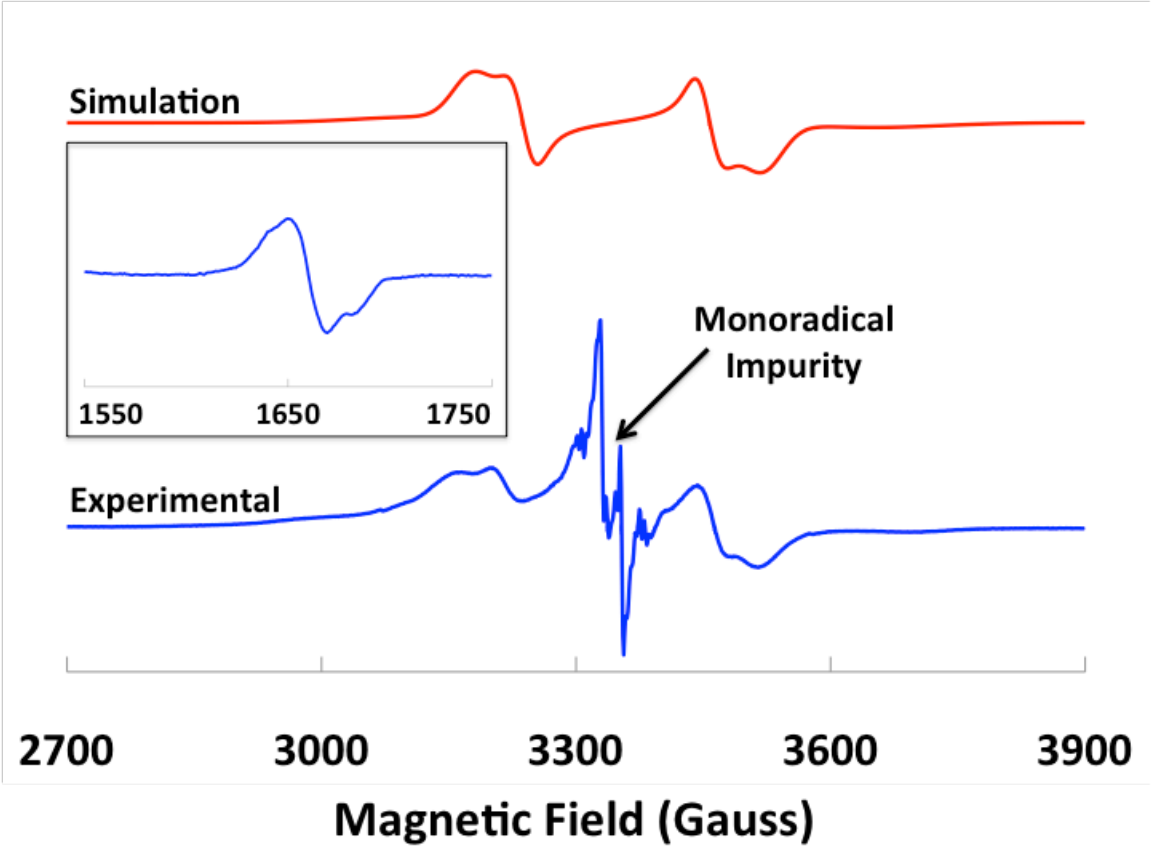
Thermolysis studies were performed as follows: addition of 10 mg of *m*-Dimethylaminophenylhydroxylamine hydrochloride and 5-10 mg of sodium acetate trihydrate (internal standard) in 0.8 mL of deuterium oxide. An initial ^{1}H NMR was taken with a 90° angle and a relaxation delay of 60 seconds. The solution was degassed for 30 minutes (under argon). The NMR tube was then heated at 80°C for 1 hour in a water bath. After thermolysis was complete, an NMR spectrum was taken with the previous parameters.

Photolysis Results

46% conversion of starting material to product resulted in a 89% mass balance of 3-dimethylaminophenol and 11% was unaccounted for asan insoluble precipitate.

Thermolysis Results

Thermolysis studies yielded an insoluble black tar that was not investigated further.



Simulated Values

Gxx 2.00 G
Gyy 2.00 G
Gzz 1.98 G
D 280.00 G
E/D 0.075 G

Linewidths

X 15
Y 26
Z 90

Experimental Parameters

Centerfield	2500 G
Sweepwidth	4000 G
Power	1.984 mW
ConvTime	327.68 ms
Gain	50 dB
ModAmp	1.000 G
ModFreq	100.00 KHz
Resolution	4096
SweepTime	1342.18 s
TimeConstant	1.28 ms

CASSCF Computations

CASSCF and MRMP2 calculations were performed using the GAMESS software package using the 6-31G(d) basis set and a (8,8) pi active space.

m-Dimethylaminophenylhydroxylamine hydrochloride Singlet
CASMRMP/6-31G(d)//CASSCF/6-31G(d) (8,8) active space
CASMRMP Energy = -439.1083353290 a.u.

MCSCF Energy = -437.869215811 a.u.

Atomic	Atomic	Coordinates (Angstroms)		
Number	Type	X	Y	Z
6	C	1.712234139	-1.906748501	0.207353310
6	C	0.666777466	-2.716956289	-0.112506262
6	C	-0.636530067	-2.091825338	-0.421707101
6	C	-0.762140395	-0.625577952	-0.366094688
6	C	0.348372065	0.213256496	-0.010802191
6	C	1.577692618	-0.484646812	0.256412043
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1	H	0.737564023	-3.785715696	-0.154840530
1	H	-1.726850145	-0.230609801	-0.607536294
1	H	2.451261098	0.080893261	0.508443158
7	N	0.251291150	1.523466971	0.060926812
6	C	1.410542887	2.352991403	0.426081835
1	H	2.201876493	2.240389636	-0.302902503
1	H	1.105290725	3.384606414	0.442779456
1	H	1.771333174	2.086240356	1.410261226
6	C	-1.028410323	2.192158550	-0.225805392
1	H	-0.899706720	3.253664717	-0.105867356
1	H	-1.337336960	1.994131603	-1.243344622
1	H	-1.790958477	1.856526631	0.464099861
8	O	-1.614995401	-2.749263658	-0.723253146

State 2 Energy= -437.8692158107 S= 0.00 SZ= 0.00 Space Sym – A

ALPHA	BETA	COEFFICIENT
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11101000	11101000	-0.3854871
11010100	11010100	-0.0834304
11110000	11101000	0.0811186
11101000	11110000	0.0811186
11011000	11100100	-0.0718789
11100100	11011000	-0.0718789
11011000	11011000	-0.0598459
11100100	01111000	-0.0594789
01111000	11100100	-0.0594789
10110010	10110010	-0.0580697
01111000	11101000	0.0560245
11101000	01111000	0.0560245
11101000	10111000	0.0557696
10111000	11101000	0.0557696
11001100	11001100	0.0534981
11011000	10111000	-0.0512943
10111000	11011000	-0.0512943

m-Dimethylaminophenylhydroxylamine hydrochloride Triplet

CASMRMP/6-31G(d)//CASSCF/6-31G(d) (8,8) active space

CASMRMP Energy = -439.1224630390 a.u.

=MRPT2,

MCSCF Energy = -437.882934687 a.u.

Atomic	Atomic	Coordinates (Angstroms)		
Number	Type	X	Y	Z
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6	C	-0.649876446	-2.091414716	-0.396891815
6	C	-0.766973311	-0.649347886	-0.335240770
6	C	0.365386559	0.170301723	-0.011312359
6	C	1.628433365	-0.487885934	0.245388238
1	H	2.691120129	-2.320877269	0.357553978
1	H	0.729371328	-3.753668176	-0.186226114
1	H	-1.741515045	-0.242142238	-0.504776709
1	H	2.503179189	0.089121568	0.459774901
7	N	0.250642967	1.490245963	0.056182911
6	C	1.355048276	2.347943755	0.533682555
1	H	2.071154419	2.485145277	-0.265237729
1	H	0.941688166	3.301281530	0.816485567
1	H	1.825122945	1.901664212	1.393566304
6	C	-0.985804563	2.201784917	-0.330424208
1	H	-0.721106607	3.213986028	-0.586781980
1	H	-1.436333184	1.733201308	-1.187666996
1	H	-1.669922829	2.205590964	0.507456606
8	O	-1.650857172	-2.765242773	-0.668173879

State 1 Energy= -437.8829346870 S= 1.00 SZ= 1.00 Space Sym – A

ALPHA	BETA	COEFFICIENT
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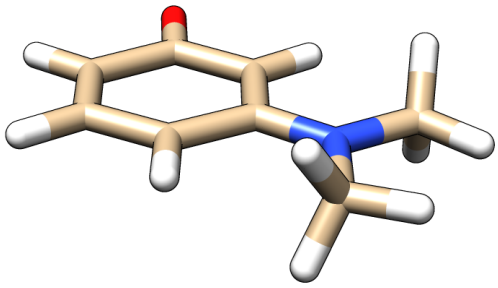
11011100	11000100	-0.1006318
11111000	10100010	0.0905974
11111000	11010000	-0.0904207
11110010	10101000	0.0812807
11101100	11100000	-0.0764740
11011100	11100000	-0.0739879
10111010	10100010	-0.0715486
11101010	10110000	-0.0701862
10111010	11100000	-0.0608695
11101100	01110000	0.0577019
11110010	11001000	0.0560866
11111000	10101000	0.0540606
11111000	01100001	0.0537654
11101001	01110000	-0.0518671

DFT Computations

Density functional theory (DFT) computations were performed using the Gaussian09 software suite employing the B3LYP functional that consists of Becke's three-parameter gradient-corrected exchange functional and the LYP correlational functional along with the 6-31G(d,p) polarized double-ζ basis set. Energies, geometries, and analytical frequencies were calculated at this level of theory. In all cases, optimized geometries were found to have zero imaginary frequencies and corrections for the zero point vibrational energy were added unscaled.

m-Dimethylaminophenylhydroxylamine hydrochloride Singlet



Sum of electronic and zero-point energies= -440.345772

Atomic	Atomic	Coordinates (Angstroms)		
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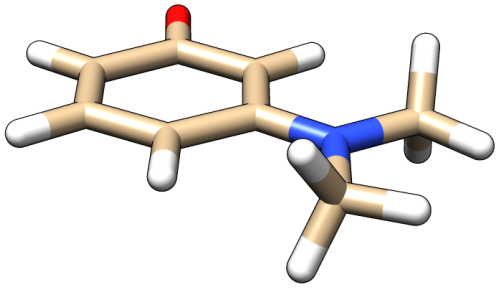
6	C	-0.652915	-2.065024	-0.42352
6	C	-0.783918	-0.624496	-0.358031
6	C	0.307543	0.179894	-0.017687
6	C	1.546299	-0.504855	0.25533
1	H	2.713017	-2.314801	0.433474
1	H	0.725821	-3.783563	-0.182833
1	H	-1.764159	-0.227696	-0.585234
1	H	2.413184	0.093821	0.519636
7	N	0.258963	1.537485	0.064225
6	C	1.424994	2.351667	0.431921
1	H	2.236352	2.251208	-0.298013
1	H	1.122081	3.397306	0.446232
1	H	1.794175	2.101111	1.43267
6	C	-1.013284	2.194036	-0.230107
1	H	-0.896798	3.271887	-0.133329
1	H	-1.340017	1.966735	-1.253352
1	H	-1.793367	1.861051	0.467245
8	O	-1.589268	-2.809121	-0.718146

m-Dimethylaminophenylhydroxylamine hydrochloride Triplet



Sum of electronic and zero-point energies= -440.365686

Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
6	C	1.744412	-1.877985	0.15051
6	C	0.653054	-2.69361	-0.142163
6	C	-0.651519	-2.11111	-0.389553
6	C	-0.766206	-0.66906	-0.323316
6	C	0.364134	0.149465	-0.020029
6	C	1.626166	-0.4922	0.219446
1	H	2.718322	-2.325079	0.324539
1	H	0.741932	-3.773681	-0.196809
1	H	-1.758358	-0.264879	-0.480375
1	H	2.508743	0.099961	0.424069
7	N	0.24159	1.498768	0.059826
6	C	1.32777	2.344338	0.580848
1	H	2.070133	2.526095	-0.20568
1	H	0.902882	3.298729	0.89206
1	H	1.804789	1.870978	1.43957
6	C	-0.967753	2.224485	-0.357902
1	H	-0.658468	3.182343	-0.781253
1	H	-1.520813	1.671271	-1.113392
1	H	-1.604335	2.413434	0.514807
8	O	-1.661522	-2.801771	-0.659265

Cartesian coordinates, total energies and vibrational zero-point energies for the optimized geometries obtained from B3LYP/6-311G** calculations for the water adducts are given.

One water adduct

C	-0.40029200	-0.54076100	0.10487700
C	0.35315800	0.63259200	-0.00080400

C	-0.38793700	1.85925000	-0.09449600
C	-1.79877600	1.96948900	-0.10547000
C	-2.54525700	0.83733600	-0.01829700
C	-1.84845700	-0.48850300	0.08542000
H	0.03368100	-1.53428700	0.17199600
H	0.16927300	2.78684200	-0.16222700
H	-2.24745500	2.95206800	-0.18198400
H	-3.62907400	0.82533500	-0.02196400
N	1.71182400	0.66947200	-0.01396700
C	2.46514500	1.92881000	-0.03601300
H	3.52192600	1.69089100	-0.12060700
H	2.20208400	2.54047300	-0.90247600
H	2.32481500	2.51008600	0.88131000
C	2.44425600	-0.58064100	0.19160200
H	2.32824900	-0.93408700	1.22436500
H	2.08096200	-1.36910400	-0.47015600
H	3.49947200	-0.41029400	-0.00475600
O	-2.54785400	-1.49283700	0.14894000
O	0.86277100	-3.43476500	-0.22444500
H	1.07962300	-4.08407000	0.45325500
H	0.44330300	-3.94477700	-0.92584200

Sum of electronic and thermal Free Energies= -516.937520
Zero-point correction= 0.187687 (Hartree/Particle)

Three water adduct

C	0.17531100	1.64691900	-0.40017700
C	-0.27872300	0.28482100	-0.38782000
C	-1.57447900	0.00240300	0.00917200
C	-2.45273300	1.08585800	0.35540300
C	-2.07049000	2.43757900	0.33030000
C	-0.79330700	2.73500900	-0.05461200
N	-2.14937100	-1.25031400	-0.06762200
C	-1.49627600	-2.26401000	-0.88446800
O	1.33826600	2.00020700	-0.62097600
C	-3.10895700	-1.74488700	0.91697500
O	3.98260200	1.05410300	0.31604700
O	3.71426900	-1.61188900	0.85991500
O	1.56713600	-2.20567900	-0.59951900
H	0.43715000	-0.49773600	-0.63899800
H	-3.48573200	0.85859400	0.59346000
H	-2.78657500	3.20600100	0.59307000
H	-0.41653600	3.75076300	-0.11150900
H	-2.59885200	-2.40599400	1.62831200

H	-3.55809200	-0.93621100	1.48989200
H	-3.89171100	-2.31458500	0.41354000
H	-0.53625700	-2.58491900	-0.45109200
H	-2.16760900	-3.11441800	-0.99034000
H	-1.27134200	-1.84097800	-1.86808100
H	3.90942100	-0.66510100	0.70128000
H	3.92073300	-1.78590300	1.78202700
H	2.30894600	-2.06865100	0.03997900
H	1.98316600	-2.63353700	-1.35497000
H	4.75959700	1.40982500	-0.12588700
H	3.21901600	1.37896400	-0.17969900

Sum of electronic and thermal Free Energies= -669.829693
Zero-point correction= 0.238203(Hartree/Particle)

Four water adduct

C	-0.66404800	1.78420400	-0.18764800
C	-0.74569900	0.34947200	-0.17487800
C	-1.97600700	-0.26282900	-0.01053800
C	-3.14957500	0.55323400	0.12440200
C	-3.12892400	1.95922900	0.11153000
C	-1.92391000	2.58180100	-0.05130600
N	-2.18613800	-1.62096900	-0.14692600
C	-1.16422300	-2.41923000	-0.81184300
O	0.38777000	2.42628300	-0.25943300
C	-3.14218000	-2.36007100	0.67377300
O	3.27768700	1.64457600	0.04560200
O	3.77037500	-0.49717200	1.56532800
O	1.67941300	-1.56725300	0.06235200
H	0.18353700	-0.21754000	-0.23759700
H	-4.11542000	0.06397900	0.18255500
H	-4.05414300	2.51272000	0.21128800
H	-1.81683200	3.66083700	-0.08538500
H	-2.61430300	-2.86833800	1.49009600
H	-3.88353200	-1.70326900	1.12511800
H	-3.64487900	-3.11260800	0.06410600
H	-0.24967500	-2.50986300	-0.20749600
H	-1.57506500	-3.40485500	-1.02446700
H	-0.87657400	-1.92613600	-1.74510900
H	3.58337800	0.42294400	1.26433700
H	4.27112700	-0.44441700	2.38440500
H	2.20992300	-1.39014000	0.85941500
H	2.35507100	-1.53394200	-0.63630700
H	3.52700100	1.09984500	-0.71741000
H	2.38493600	1.96737500	-0.13155700

O	4.10540000	-0.80249600	-1.14851200
H	4.40125600	-0.89224200	-0.22355000
H	4.81941100	-1.12391400	-1.70760100

Sum of electronic and thermal Free Energies= -746.276458
Zero-point correction= 0.265800 (Hartree/Particle)

m-dimethylamino phenol radical cation

C	0.49889700	-0.86162800	-0.03215100
C	-0.50925600	0.13514800	0.00104800
C	-0.12389600	1.51934100	0.05398000
C	1.21267800	1.85683800	0.07304300
C	2.19937900	0.86991400	0.03072800
C	1.83262600	-0.50092700	-0.02452000
H	0.26245200	-1.91286100	-0.09898900
H	-0.86846600	2.29809200	0.11793700
H	1.50220900	2.89855200	0.12701400
H	3.24796900	1.14824600	0.04109400
N	-1.82084200	-0.21167500	-0.00054300
C	-2.91226800	0.75809200	-0.15826900
H	-3.71429900	0.27953900	-0.71966300
H	-3.29923500	1.05140800	0.82265400
H	-2.58562600	1.63574400	-0.70692500
C	-2.24400300	-1.61024200	0.14980500
H	-3.28508400	-1.62467900	0.46446800
H	-2.15693200	-2.13740300	-0.80557600
H	-1.64033600	-2.11429300	0.90222700
O	2.73950700	-1.48675200	-0.07764300
H	3.64223800	-1.14581400	-0.08127800

Sum of electronic and thermal Free Energies= -441.158380
Zero-point correction= 0.177088 (Hartree/Particle)