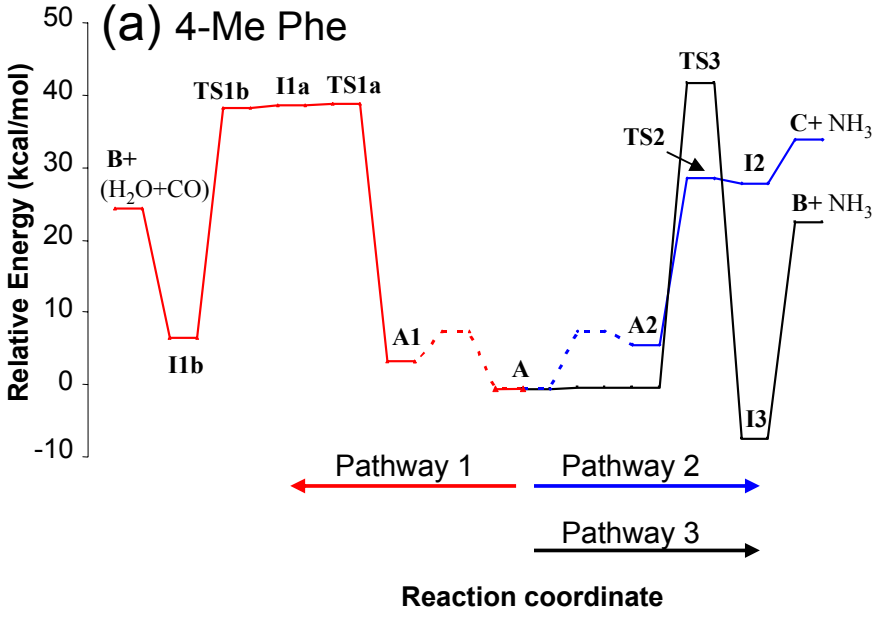
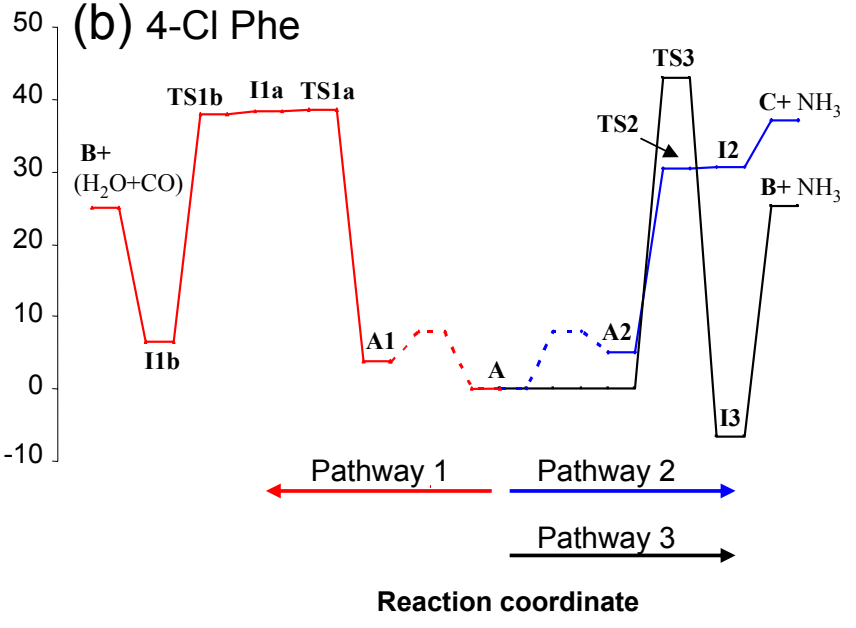
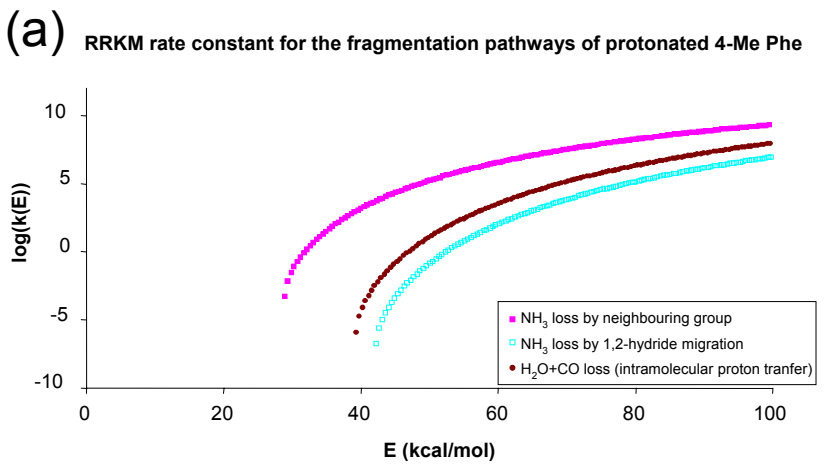
SUPPLEMENTARY MATERIALS for OBC Manuscript "Neighbouring Group Processes in the Deamination of Protonated Phenylalanine Derivatives" By Hadi Lioe and Richard A. J. O'Hair*

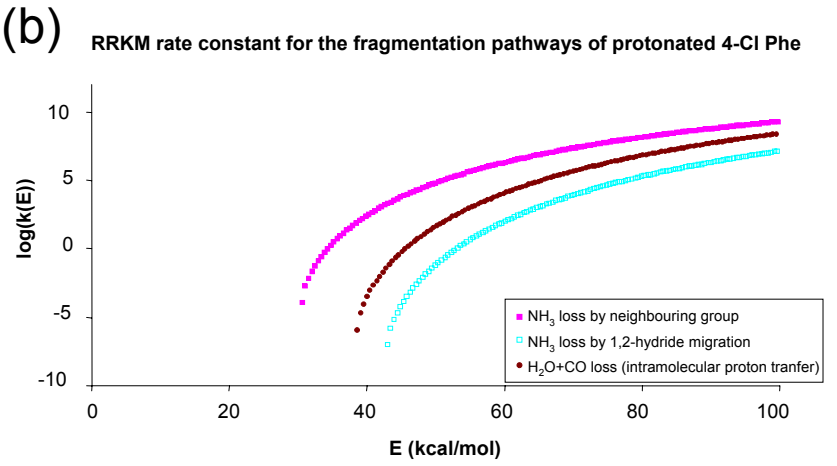
Supplementary Figure S1. The full potential energy surface for the competing fragmentation pathways 1-3 shown in scheme 2 for protonated (a) 4-Me Phe, and (b) 4-Cl Phe. All energies are relative to global minimum **A**. The combined H_2O+CO loss (pathway 1 in scheme 2) is represented by the red PES, NH_3 loss by neighbouring group mechanism (pathway 2 in scheme 2) is represented by the blue PES, and NH_3 loss by 1,2-hydride migration process (pathway 3 in scheme 2) is represented by the black PES.





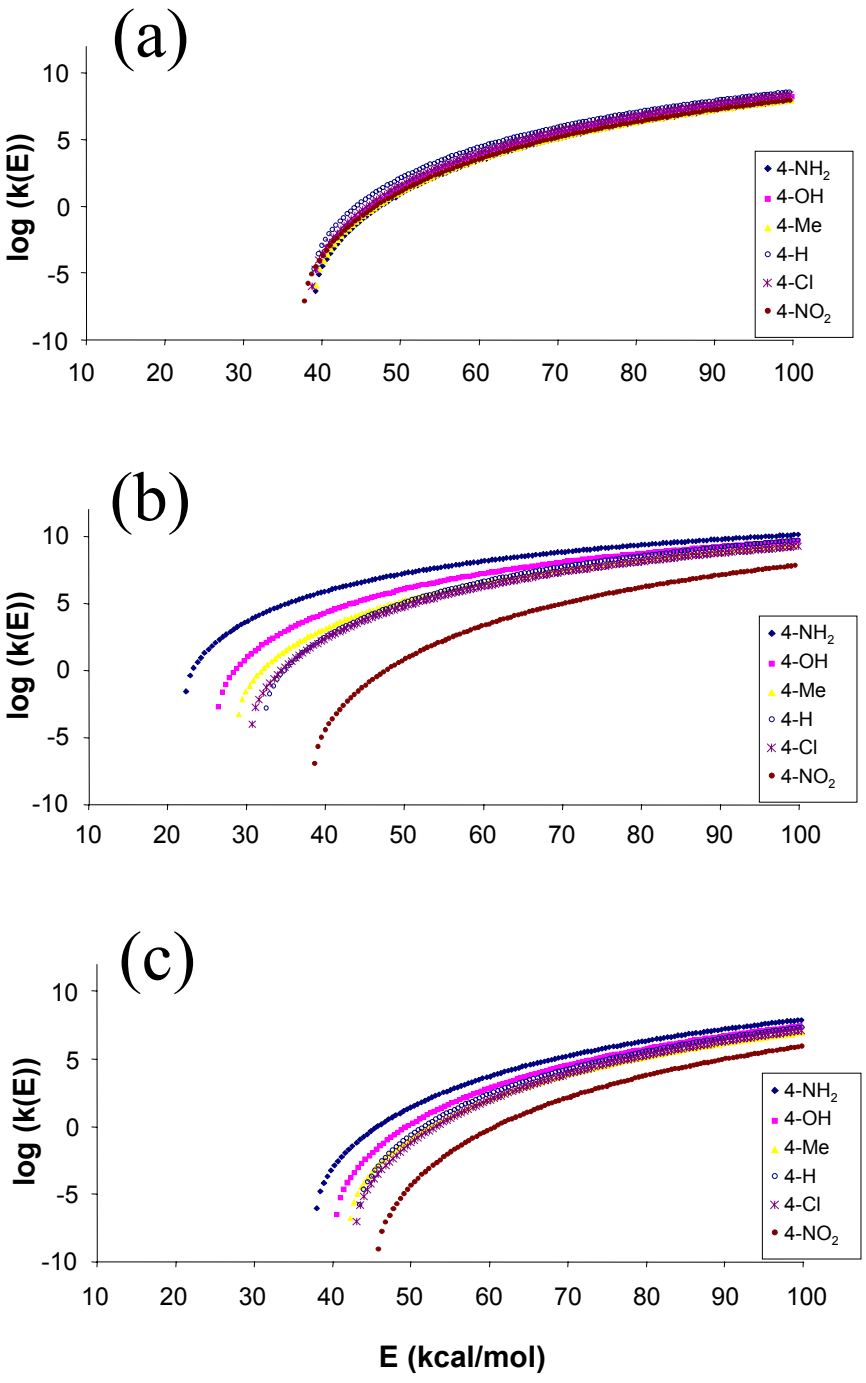
Supplementary figure S2. RRKM unimolecular rate constant for the competitive fragmentation reactions 1-3 shown in scheme 2 for protonated (a) 4-Me Phe and (b) 4-Cl Phe, (c) Phe



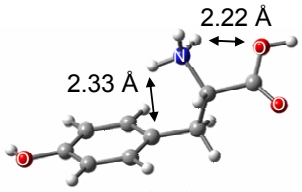


Supplementary Figure S3

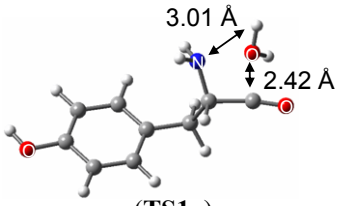
RRKM unimolecular rate constant for (a) initial intramolecular proton tranfer for combined H_2O+CO loss (Pathway 1 of Scheme 2), (b) NH_3 loss by neighbouring group (Pathway 2 of Scheme 2), (c) NH_3 loss by 1,2-hydride migration (Pathway 3 of Scheme 2) from B3LYP/6-31+G(d,p) calculated data



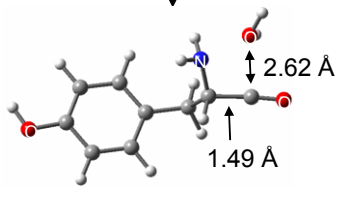
Pathway 1



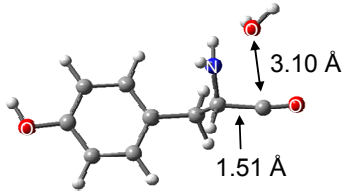
(A1)
+3.8 kcal/mol



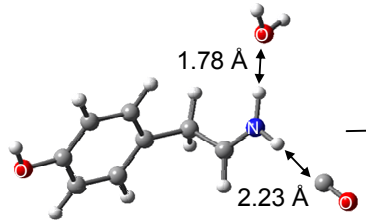
(TS1a)
+39.1 kcal/mol



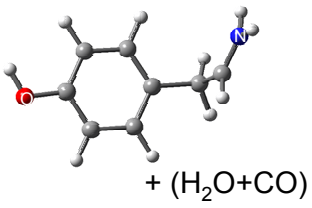
(I1a)
+38.9 kcal/mol



(TS1b)
+38.5 kcal/mol

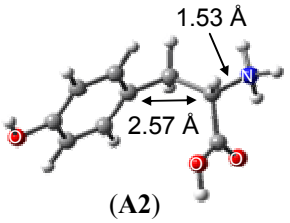


(I1b)
+6.7 kcal/mol

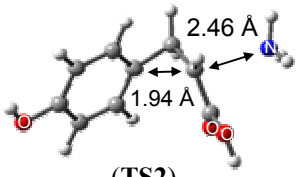


(B+H_2O+CO)
+24.4 kcal/mol

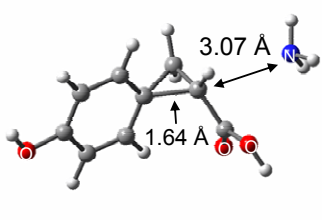
Pathway 2



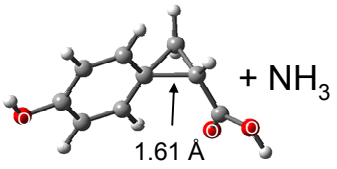
(A2)
+5.7 kcal/mol



(TS2)
+26.5 kcal/mol

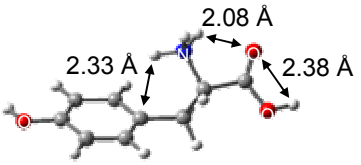


(I2)
+24.4 kcal/mol

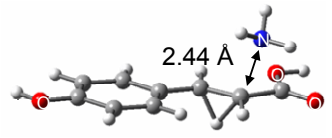


(C+NH_3)
+30.1 kcal/mol

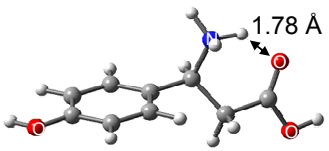
Pathway 3



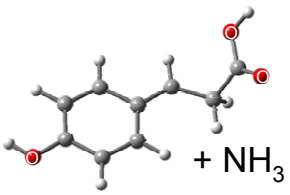
(A)
0.0 kcal/mol



(TS3)
+40.8 kcal/mol



(I3)
-7.3 kcal/mol

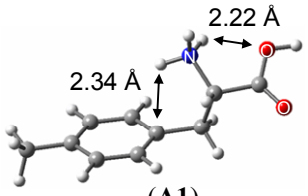


(D+NH_3)
+18.4 kcal/mol

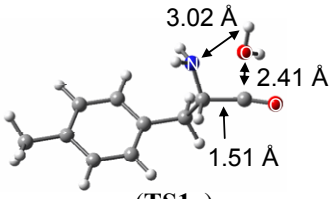
B3LYP/6-31+G(d,p) optimized structures and relative energies for all related species in the competing pathways 1-3 in scheme 2 for protonated 4-OH Phe . All energy values are relative to the global minimum **A**.

Supplementary Figure S4

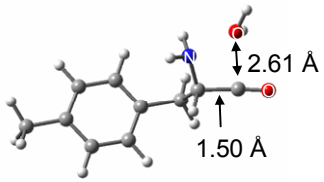
Pathway 1



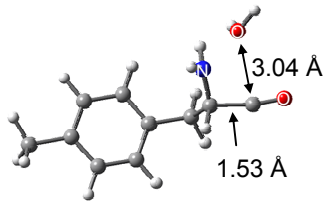
(A1)
+3.8 kcal/mol



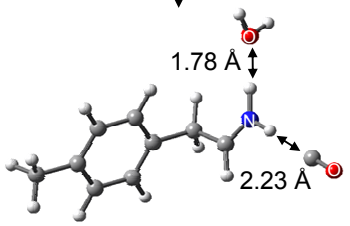
(TS1a)
+39.3 kcal/mol



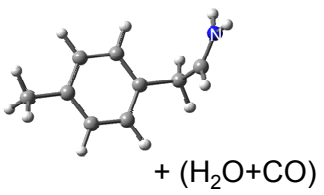
(I1a)
+39.2 kcal/mol



(TS1b)
+38.8 kcal/mol

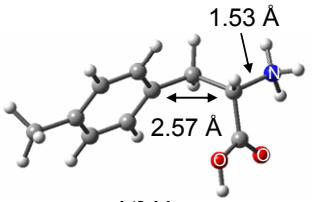


(I1b)
+6.9 kcal/mol

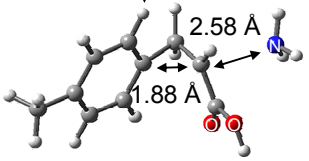


(B+H_2O+CO)
+24.9 kcal/mol

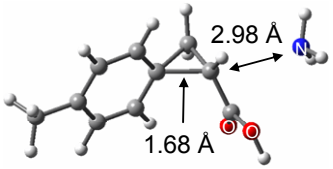
Pathway 2



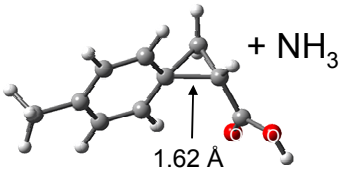
(A2)
+5.9 kcal/mol



(TS2)
+29.0 kcal/mol

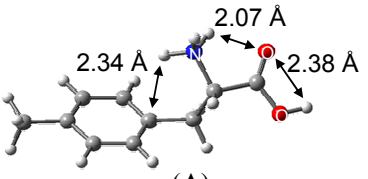


(I2)
+28.4 kcal/mol

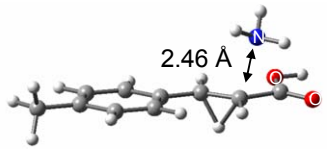


(C+NH_3)
+34.4 kcal/mol

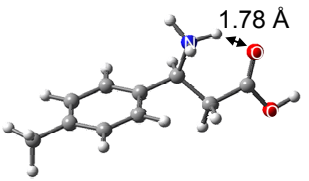
Pathway 3



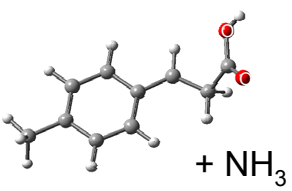
(A)
0.0 kcal/mol



(TS3)
+42.2 kcal/mol



(I3)
-7.0 kcal/mol

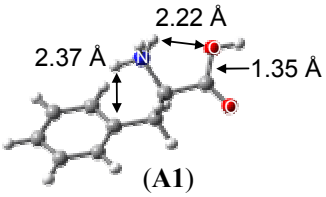


(D+NH_3)
+22.9 kcal/mol

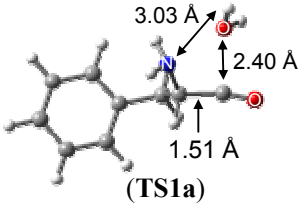
B3LYP/6-31+G(d,p) optimized structures and relative energies for all related species in the competing pathways 1-3 in scheme 2 for protonated 4-Me Phe . All energy values are relative to the global minimum **A**.

Supplementary Figure S5

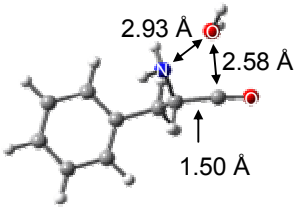
Pathway 1



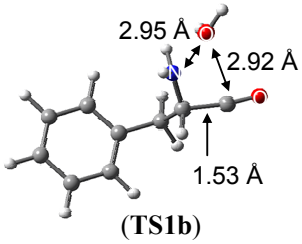
(A1)
+3.8 kcal/mol



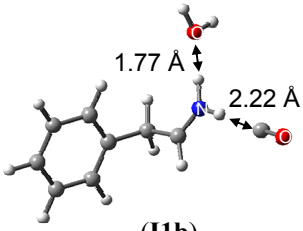
(TS1a)
+39.1 kcal/mol



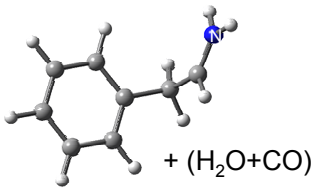
(I1a)
+39.0 kcal/mol



(TS1b)
+38.6 kcal/mol

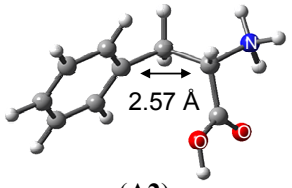


(I1b)
+6.8 kcal/mol

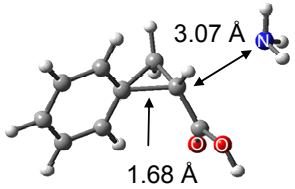


(**B**+H_2O+CO)
+25.3 kcal/mol

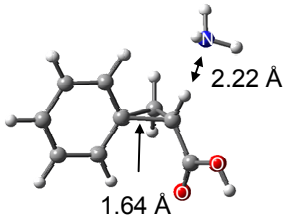
Pathway 2



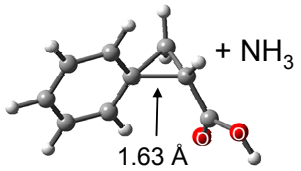
(A2)
+5.6 kcal/mol



(TS2)
+32.5 kcal/mol

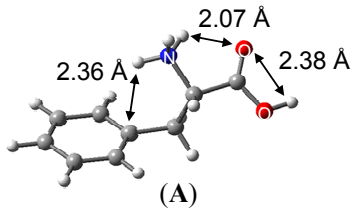


(I2)
+30.2 kcal/mol

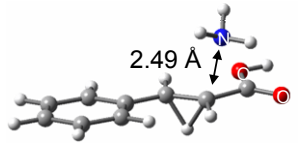


(**C**+NH_3)
+39.1 kcal/mol

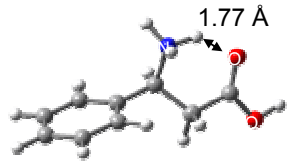
Pathway 3



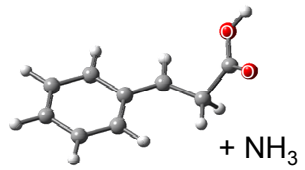
(A)
0.0 kcal/mol



(TS3)
+43.6 kcal/mol



(I3)
-6.7 kcal/mol

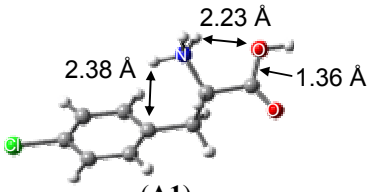


(**D**+NH_3)
+27.6 kcal/mol

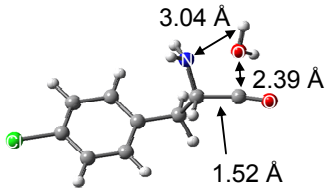
B3LYP/6-31+G(d,p) optimized structures and relative energies for all related species in the competing pathways 1-3 in scheme 2 for protonated Phe . All energy values are relative to the global minimum **A**.

Supplementary Figure S6

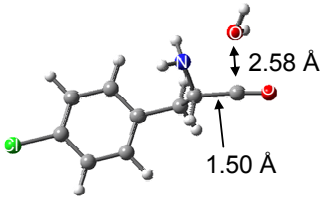
Pathway 1



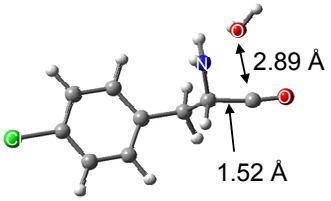
(**A1**)
+3.8 kcal/mol



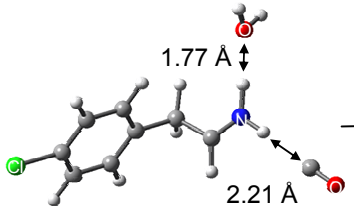
(**TS1a**)
+38.7 kcal/mol



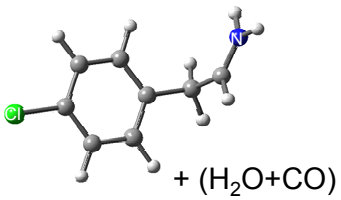
(**I1a**)
+38.6 kcal/mol



(**TS1b**)
+38.1 kcal/mol

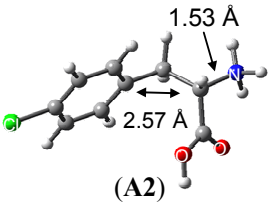


(**I1b**)
+6.4 kcal/mol

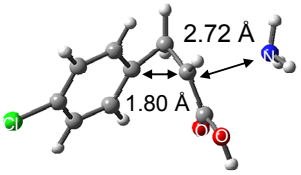


(**B**+H_2O+CO)
+25.1 kcal/mol

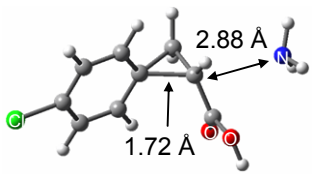
Pathway 2



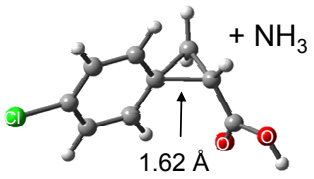
(**A2**)
+5.1 kcal/mol



(**TS2**)
+30.7 kcal/mol

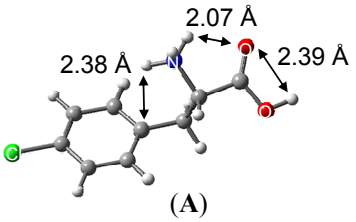


(**I2**)
+30.7 kcal/mol

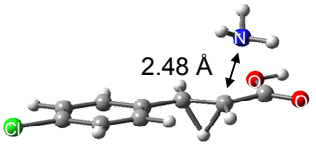


(**C**+NH_3)
+37.2 kcal/mol

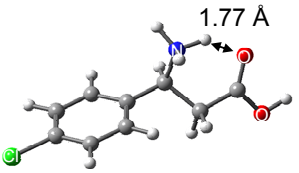
Pathway 3



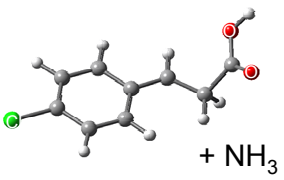
(**A**)
0.0 kcal/mol



(**TS3**)
+43.1 kcal/mol



(**I3**)
-6.7 kcal/mol

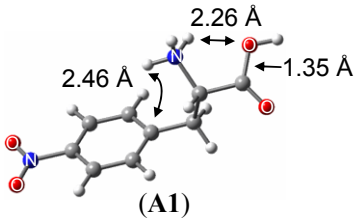


(**D**+NH_3)
+25.3 kcal/mol

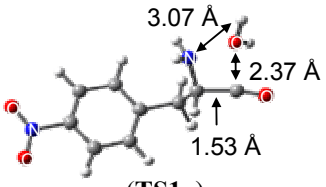
B3LYP/6-31+G(d,p) optimized structures and relative energies for all related species in the competing pathways 1-3 in scheme 2 for protonated 4-Cl Phe . All energy values are relative to the global minimum **A**.

Supplementary Figure S7

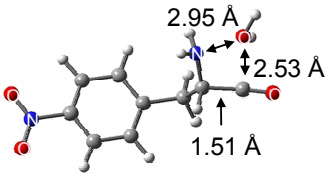
Pathway 1



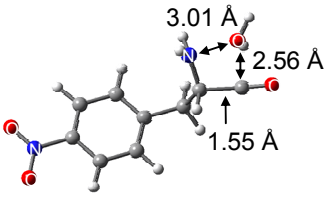
(A1)
3.8 kcal/mol



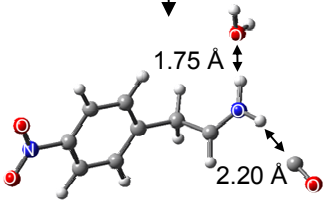
(TS1a)
+37.8 kcal/mol



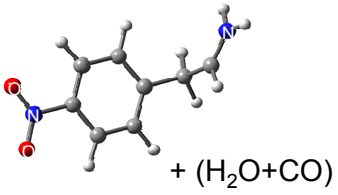
(I1a)
+37.8 kcal/mol



(TS1b)
+37.2 kcal/mol

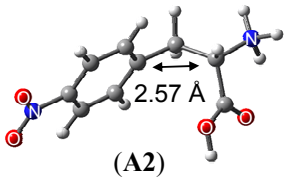


(I1b)
+5.8 kcal/mol

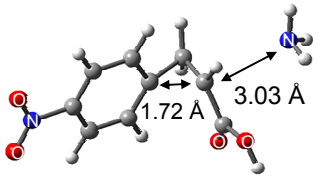


(B+H_2O+CO)
+25.8 kcal/mol

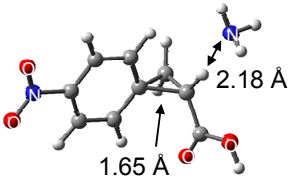
Pathway 2



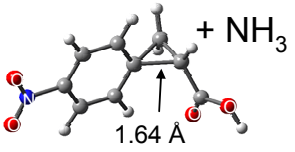
(A2)
+4.0 kcal/mol



(TS2)
+38.7 kcal/mol

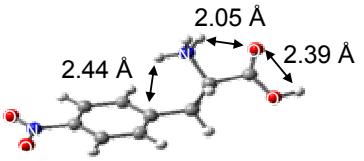


(I2)
+36.3 kcal/mol

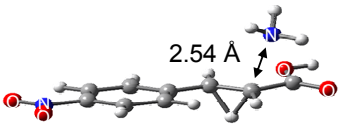


(C+NH_3)
+46.4 kcal/mol

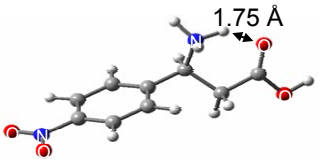
Pathway 3



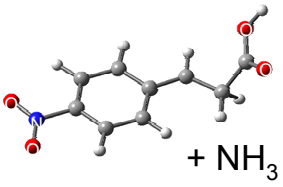
(A)
0.0 kcal/mol



(TS3)
+45.9 kcal/mol



(I3)
-6.1 kcal/mol



(D+NH_3)
+34.3 kcal/mol

B3LYP/6-31+G(d,p) optimized structures and relative energies for all related species in the competing pathways 1-3 in scheme 2 for protonated 4-NO_2 Phe . All energy values are relative to the global minimum **A**.

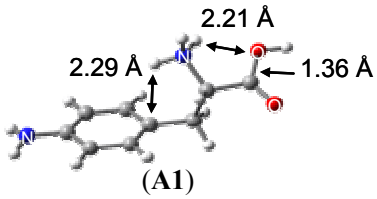
Supplementary Figure S8

Key species on the potential energy surface for fragmentation pathways 1, 2, and 3 optimized at the B3LYP/6-31+G(d,p) level of theory

PES of 4-NH_2 Phe (figure 3a)

Pathway 1

A1

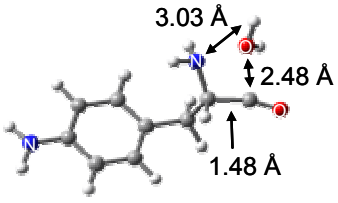


(**A1**)
+3.7 kcal/mol

N	-1.068378	1.079322	-1.400225
C	0.225753	0.392108	-1.803332
C	0.232903	0.060523	-3.290413
C	0.408859	-0.873853	-0.918164
O	1.234685	-0.234717	-3.883529
C	0.266447	-0.551377	0.552349
O	-1.015472	0.090331	-3.818189
C	-0.912768	-0.862429	1.255323
C	1.302040	0.083725	1.264683
C	-1.061719	-0.549761	2.604555
C	1.167027	0.399727	2.609297
C	-0.022249	0.091335	3.310569
N	-0.168736	0.435391	4.630766
H	-1.159686	0.984969	-0.370823
H	-1.088157	2.070433	-1.656593
H	-1.870808	0.626965	-1.854058
H	1.030751	1.101599	-1.601982
H	1.398854	-1.272199	-1.159929
H	-0.322727	-1.632643	-1.220434
H	-0.977493	-0.174397	-4.755952
H	-1.715821	-1.402167	0.755581
H	2.241906	0.312991	0.766979
H	-1.977911	-0.819735	3.121721
H	1.989134	0.877713	3.134388
H	0.643573	0.704394	5.165068
H	-0.923274	0.034187	5.166788

Zero point vibrational energy	138.02922 kcal/mol
Electronic energy	-610.5701472 Hartree

TS1a



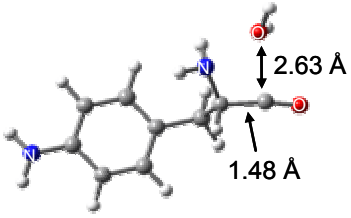
(**TS1a**)
+39.2 kcal/mol

N	0.769394	1.400854	1.676488
C	-0.391510	0.554400	1.675093
C	-0.816998	0.268703	3.065674
C	-0.337411	-0.823259	0.879479
O	-1.396436	-0.037731	3.990275
C	-0.193317	-0.528987	-0.584710
O	1.465127	-0.435524	3.732565
C	1.071056	-0.483715	-1.200063
C	-1.323461	-0.269284	-1.383200
C	1.207272	-0.201513	-2.552199
C	-1.203143	0.018686	-2.734198
C	0.070188	0.060281	-3.349459
N	0.197024	0.365791	-4.677473
H	1.627863	0.859209	1.678135
H	0.758116	2.035087	0.885347
H	1.974268	0.240640	4.203253

H	-1.259151	1.124643	1.305277
H	-1.252632	-1.389534	1.086936
H	0.513934	-1.387053	1.270564
H	1.616623	-1.261918	4.214040
H	1.963934	-0.704837	-0.620261
H	-2.319436	-0.316494	-0.947286
H	2.194227	-0.193448	-3.005589
H	-2.093030	0.199753	-3.330023
H	-0.617461	0.398334	-5.270670
H	1.082224	0.243277	-5.144065

1 Imaginary Frequency -43.96 cm^{-1}
Zero point vibrational energy 133.15433 kcal/mol
Electronic energy -610.5057824 Hartree

I1a

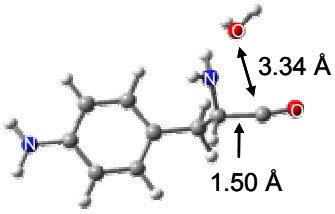


(**I1a**)
+39.1 kcal/mol

N	0.612116	1.458328	1.684431
C	-0.491531	0.535844	1.669195
C	-0.873548	0.269653	3.068969
C	-0.347481	-0.838509	0.881853
O	-1.314589	-0.017154	4.070835
C	-0.194851	-0.540611	-0.581491
O	1.588700	-0.461178	3.632458
C	1.075896	-0.417167	-1.172102
C	-1.322934	-0.350998	-1.401807
C	1.220808	-0.126094	-2.521765
C	-1.194068	-0.055661	-2.750695
C	0.085788	0.065483	-3.341086
N	0.218960	0.381539	-4.666494
H	1.501868	0.977223	1.770966
H	0.600926	2.059628	0.868110
H	2.061707	0.126042	4.239904
H	-1.390686	1.046992	1.288698
H	-1.234268	-1.451951	1.078435
H	0.527787	-1.352786	1.286655
H	1.860082	-1.356882	3.879348
H	1.969181	-0.580236	-0.574027
H	-2.322658	-0.459671	-0.985784
H	2.214136	-0.055379	-2.955440
H	-2.081747	0.070508	-3.363733
H	-0.584016	0.359653	-5.275661
H	1.118794	0.312802	-5.115806

Zero point vibrational energy 133.07931 kcal/mol
Electronic energy -610.5058134 Hartree

TS1b



(**TS1b**)
+38.8 kcal/mol

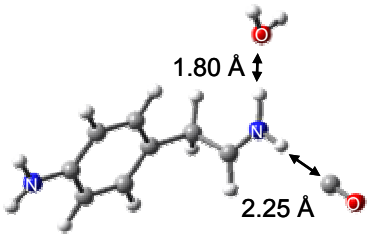
N	0.259116	1.453400	1.832378
C	-0.786173	0.502389	1.689461
C	-1.102886	0.169196	3.118495
C	-0.500133	-0.847144	0.902967
O	-1.127236	-0.158805	4.203269
C	-0.279391	-0.536736	-0.547287
C	1.014176	-0.345971	-1.064170
C	-1.367268	-0.403335	-1.430075
C	1.220903	-0.046872	-2.403750
C	-1.177459	-0.101452	-2.770207
C	0.126145	0.084964	-3.286995

N	0.318252	0.408353	-4.603701
O	2.194280	-0.358799	3.097989
H	1.195766	1.068593	1.909620
H	0.162282	2.318753	1.321564
H	-1.695848	0.953347	1.279216
H	-1.363685	-1.505812	1.052928
H	0.374943	-1.315939	1.359296
H	1.878074	-0.453832	-0.413006
H	-2.382213	-0.562674	-1.071072
H	2.232034	0.079648	-2.779805
H	-2.034109	-0.020809	-3.433104
H	-0.446072	0.341856	-5.257734
H	1.244602	0.383857	-5.000680
H	2.814049	-1.064765	2.866735
H	2.554762	0.036105	3.904603

1 Imaginary Frequency	-56.71 cm^{-1}
Zero point vibrational energy	132.42256 kcal/mol
Electronic energy	-610.5052054 Hartree

I1b

N	0.460262	0.261841	-2.284433
C	0.287213	1.072356	-1.288675
C	-2.026615	-0.213551	-4.361844
C	1.276383	1.297848	-0.208151
O	-2.869425	-0.395216	-5.095617
C	0.612303	0.681517	1.020347
C	0.665005	-0.705650	1.243161
C	-0.093918	1.476607	1.940001
C	0.064057	-1.278656	2.354665
C	-0.702218	0.915985	3.053343
C	-0.635901	-0.477346	3.285422
N	-1.256422	-1.038065	4.368922
O	2.963848	-1.003164	-2.684954
H	1.359730	-0.224683	-2.439175
H	-0.297998	0.085319	-2.946617
H	-0.683099	1.560596	-1.212882
H	1.424432	2.373504	-0.064215
H	2.239540	0.836609	-0.443901
H	1.205434	-1.347890	0.551611
H	-0.147321	2.553506	1.799548
H	0.134601	-2.350531	2.515382
H	-1.225567	1.553428	3.760061
H	-1.625586	-0.452266	5.101544
H	-1.079070	-1.999364	4.614856
H	3.167499	-1.941707	-2.571737
H	3.667282	-0.640564	-3.240942

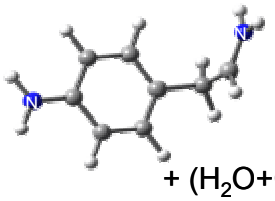


(**I1b**)
+6.5 kcal/mol

Zero point vibrational energy	132.26854 kcal/mol
Electronic energy	-610.5564106 Hartree

B

N	-0.826831	-0.704762	3.301480
C	0.265296	-0.494833	2.615159
C	0.635422	0.799530	2.010856
C	0.359819	0.476048	0.544041
C	-0.940114	0.590161	0.012817
C	1.392738	0.030557	-0.305708



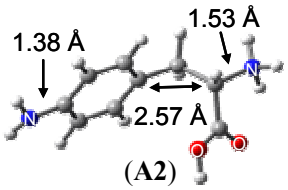
(**B**+H_2O+CO)
+22.9 kcal/mol

C	-1.196606	0.315744	-1.319252
C	1.149164	-0.251433	-1.638314
C	-0.153974	-0.112488	-2.178169
N	-0.398937	-0.391654	-3.486926
H	-1.448821	0.056145	3.556690
H	-1.104104	-1.637002	3.590459
H	0.889793	-1.363835	2.422875
H	1.692954	1.021480	2.178349
H	0.031203	1.629903	2.387646
H	-1.760246	0.929112	0.641646
H	2.406777	-0.065292	0.074516
H	-2.201047	0.437517	-1.713431
H	1.965109	-0.568043	-2.281112
H	0.346935	-0.646051	-4.115254
H	-1.308646	-0.238737	-3.892843

Zero point vibrational energy 113.21129 kcal/mol
Electronic energy -420.7749205 Hartree

Pathway 2

A2

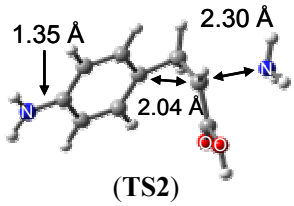


(**A2**)
+6.5 kcal/mol

N	-1.097033	0.047941	3.455878
C	-0.598550	-0.329636	2.063943
C	0.923706	-0.368389	2.225206
C	-1.086623	0.742426	1.049070
O	1.471776	0.265460	3.109002
C	-0.672125	0.470790	-0.376487
C	-1.331818	-0.498869	-1.148348
C	-0.951130	-0.760615	-2.458171
C	0.112552	-0.047945	-3.053064
C	0.767210	0.936637	-2.283778
C	0.377584	1.185158	-0.972612
H	-0.349065	0.629123	3.881026
H	-0.994005	-1.315271	1.811869
H	-0.709494	1.720489	1.373358
H	-2.183194	0.768828	1.126574
H	-2.169995	-1.053561	-0.730477
H	-1.481363	-1.513675	-3.034137
N	0.520450	-0.330501	-4.336859
H	1.578362	1.510574	-2.722757
H	0.894093	1.961557	-0.412179
O	1.516257	-1.127937	1.321637
H	2.484941	-1.076875	1.427514
H	-1.975124	0.574536	3.415692
H	-1.234772	-0.766565	4.062468
H	1.115588	0.328147	-4.816137
H	-0.089002	-0.866919	-4.935622

Zero point vibrational energy 138.03199 kcal/mol
Electronic energy -610.5656962 Hartree

TS2



(**TS2**)
+22.4 kcal/mol

N	1.046344	0.210622	3.798927
C	0.542452	0.153780	1.560501
C	-0.913426	0.227101	1.912475
C	1.113200	-1.077753	1.023112
O	-1.627699	-0.741827	2.053455

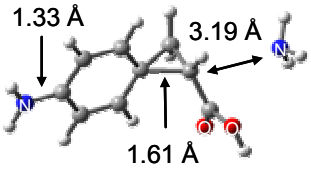
C	0.643548	-0.578144	-0.340293
C	1.479459	0.262205	-1.129387
C	1.131592	0.616687	-2.411308
C	-0.092053	0.156514	-2.975022
C	-0.942722	-0.669238	-2.187069
C	-0.587775	-1.016124	-0.904805
H	0.585659	-0.560697	4.278691
H	1.075581	1.089808	1.461268
H	0.604052	-1.985508	1.343496
H	2.196120	-1.163935	1.103688
H	2.427569	0.607126	-0.724850
H	1.793118	1.241235	-3.003788
N	-0.441135	0.500036	-4.233027
H	-1.876265	-1.029969	-2.608248
H	-1.248072	-1.646817	-0.318689
O	-1.303995	1.501344	2.093254
H	-2.247195	1.505416	2.336294
H	2.051316	0.110690	3.925900
H	0.754266	1.082454	4.236740
H	-1.299559	0.170582	-4.648829
H	0.154854	1.078704	-4.805865

1 Imaginary Frequency	-257.25 cm^{-1}
Zero point vibrational energy	135.02947 kcal/mol
Electronic energy	-610.5355874 Hartree

I2

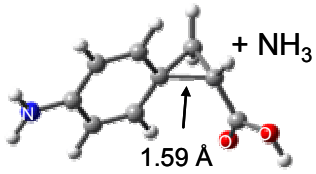
N	1.042933	-0.112756	4.336060
C	0.487499	0.166198	1.212272
C	-0.846814	0.287339	1.894032
C	1.016750	-1.147292	0.887013
O	-1.646691	-0.618416	1.997863
C	0.466979	-0.311284	-0.325900
C	1.431499	0.339934	-1.191552
C	1.187374	0.540320	-2.514750
C	-0.052925	0.101856	-3.088426
C	-1.026407	-0.543979	-2.258076
C	-0.780717	-0.735549	-0.932601
H	0.356654	-0.705566	4.799514
H	1.169995	0.988683	1.389633
H	0.409088	-2.009477	1.141575
H	2.089920	-1.301878	0.888811
H	2.374714	0.669239	-0.764218
H	1.923408	1.027817	-3.146484
N	-0.296886	0.294833	-4.385836
H	-1.961562	-0.876958	-2.697820
H	-1.522487	-1.217922	-0.304045
O	-1.053912	1.538799	2.330349
H	-1.924199	1.571494	2.765919
H	1.955408	-0.504476	4.561061
H	1.000329	0.794074	4.797083
H	-1.163539	-0.006847	-4.810861
H	0.375343	0.748960	-4.989503

Zero point vibrational energy	134.86286 kcal/mol
Electronic energy	-610.5442677 Hartree



(**I2**)
+16.8 kcal/mol

C



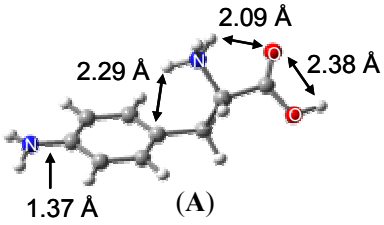
(**C**+NH_3)
+21.6 kcal/mol

C	0.833868	-0.025728	-1.594165
C	-0.342255	-0.267797	-2.502137
C	1.142856	1.340603	-1.163289
C	0.541653	0.379267	-0.081931
O	-1.299780	0.469440	-2.597995
C	1.458388	-0.177403	0.901376
C	-0.823766	0.624278	0.356464
O	-0.173429	-1.399513	-3.199279
C	1.068256	-0.443727	2.175026
C	-1.214643	0.364934	1.633057
C	-0.284599	-0.178240	2.580695
N	-0.670497	-0.435468	3.829082
H	1.642004	-0.742255	-1.693736
H	0.470463	2.131281	-1.480288
H	2.177557	1.626721	-1.009678
H	2.483808	-0.376229	0.601606
H	-1.530623	1.026464	-0.361687
H	-0.928372	-1.510988	-3.805495
H	1.769098	-0.854572	2.895084
H	-2.234321	0.566069	1.947012
H	-1.617185	-0.255802	4.137667
H	-0.031819	-0.818941	4.513561

Zero point vibrational energy 112.23504 kcal/mol
Electronic energy -553.9679504 Hartree

Pathway 3

A



(**A**)
0.0 kcal/mol

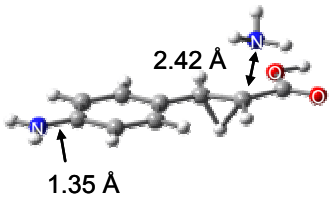
N	-1.093487	1.081417	-1.373138
C	0.197093	0.423983	-1.807934
C	0.008213	0.081698	-3.283006
C	0.454923	-0.837024	-0.928630
O	-1.087273	0.087455	-3.808479
C	0.304262	-0.536847	0.545083
O	1.155783	-0.249908	-3.862725
C	-0.862293	-0.903788	1.242184
C	1.308279	0.139751	1.263428
C	-1.029169	-0.604761	2.592671
C	1.155302	0.441909	2.609437
C	-0.021744	0.078531	3.305075
N	-0.187847	0.410144	4.626300
H	-1.852943	0.714557	-1.971445
H	-1.258403	0.855751	-0.375112
H	-1.077949	2.098425	-1.487193
H	1.003377	1.147871	-1.674473
H	1.461524	-1.186130	-1.177314
H	-0.241896	-1.627590	-1.230267
H	0.996684	-0.504826	-4.790762
H	-1.638775	-1.476337	0.737032
H	2.237924	0.414590	0.769597
H	-1.934264	-0.917582	3.105205
H	1.953620	0.953222	3.139864
H	0.610008	0.711215	5.165178
H	-0.926838	-0.025180	5.157332

Zero point vibrational energy 138.1381 kcal/mol

Electronic energy -610.5761837 Hartree

TS3

N	1.766320	1.318959	-2.241238
C	0.157448	-0.443761	-1.823816
C	-0.246203	-0.363930	-3.270145
C	-0.697394	-0.066274	-0.750451
O	0.470047	-0.756899	-4.159738
C	-0.382283	-0.067560	0.665682
O	-1.462259	0.188241	-3.434251
C	-1.362422	0.406823	1.571647
C	0.842868	-0.537567	1.199493
C	-1.137088	0.426549	2.932102
C	1.079589	-0.526975	2.557113
C	0.091918	-0.044944	3.460294
N	0.326132	-0.033347	4.794373
H	2.357387	0.997072	-3.005844
H	1.325498	2.188329	-2.535727
H	2.364356	1.534655	-1.446469
H	1.047115	-1.031935	-1.638383
H	-0.904360	-1.212137	-1.203603
H	-1.594536	0.475685	-1.046445
H	-1.680593	0.187984	-4.383540
H	-2.313522	0.767982	1.189644
H	1.624450	-0.911445	0.544655
H	-1.901961	0.802015	3.604823
H	2.027788	-0.886311	2.945478
H	1.190722	-0.380504	5.180142
H	-0.369090	0.296414	5.446318

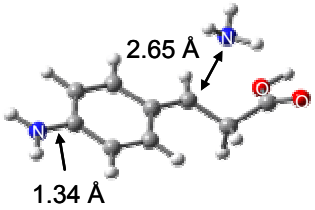


(**TS3**)
+37.9 kcal/mol

1 Imaginary Frequency -795.39 cm^{-1}
Zero point vibrational energy 132.45147 kcal/mol
Electronic energy -610.5066451 Hartree

I3

N	1.365349	1.657156	1.750419
C	-0.925086	-0.417660	1.807059
C	-0.444247	-0.210254	3.235413
C	0.176974	-0.510911	0.806100
O	-0.781476	0.712110	3.939025
C	0.056552	-0.301349	-0.560922
O	0.389874	-1.196679	3.624134
C	1.168272	-0.620230	-1.414836
C	-1.134220	0.201909	-1.188364
C	1.100645	-0.470887	-2.772216
C	-1.213786	0.354370	-2.544457
C	-0.098013	0.019282	-3.376269
N	-0.178704	0.166804	-4.706250
H	0.782681	2.168158	2.412197
H	2.264544	1.502099	2.202538
H	1.532238	2.267151	0.953176
H	-1.648483	0.365379	1.577908
H	-1.459203	-1.382461	1.784669
H	1.102656	-0.950338	1.163823
H	0.639506	-1.042097	4.552555
H	2.081419	-0.997314	-0.963401
H	-1.994097	0.465500	-0.582283
H	1.948651	-0.726153	-3.400142

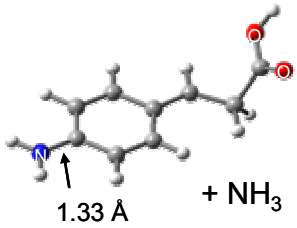


(**I3**)
+4.1 kcal/mol

H	-2.122719	0.731143	-3.003454
H	-1.019961	0.508026	-5.149908
H	0.596524	-0.065883	-5.311173

Zero point vibrational energy 134.97098 kcal/mol
Electronic energy -610.5645625 Hartree

D



(**D**+NH_3)
+10.1 kcal/mol

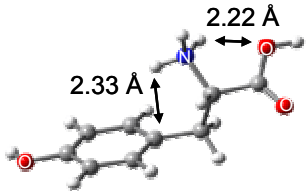
C	-0.307021	0.872724	-2.133017
C	-0.251306	-0.185743	-3.249429
C	0.636301	0.582181	-1.024350
O	-1.231059	-0.673534	-3.749172
C	0.335878	0.339413	0.296315
O	1.019421	-0.468585	-3.596522
C	1.417925	0.082678	1.222135
C	-1.009110	0.321784	0.827579
C	1.190452	-0.162067	2.542765
C	-1.245602	0.074997	2.145884
C	-0.152570	-0.172907	3.044261
N	-0.388704	-0.412478	4.334920
H	-1.347376	0.969596	-1.828505
H	0.003389	1.817160	-2.606312
H	1.686291	0.546585	-1.309495
H	1.006987	-1.110616	-4.329392
H	2.435957	0.087936	0.843993
H	-1.850692	0.501576	0.168569
H	2.014788	-0.351694	3.223155
H	-2.260354	0.061342	2.531614
H	-1.328890	-0.425139	4.708074
H	0.364249	-0.590811	4.986560

Zero point vibrational energy 111.97181 kcal/mol
Electronic energy -553.9858092 Hartree

PES of 4-OH Phe (figure 3b)

Pathway 1

A1

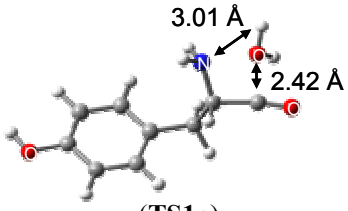


(**A1**)
+3.8 kcal/mol

N	-1.090475	1.076289	-1.415581
C	0.211705	0.385764	-1.791256
C	0.243646	0.046715	-3.277978
C	0.384802	-0.873816	-0.900668
O	1.252003	-0.273282	-3.845575
C	0.251435	-0.543649	0.571094
C	-0.912687	-0.875350	1.283512
C	1.287338	0.116503	1.261249
C	-1.048512	-0.559131	2.638382
C	1.164890	0.436914	2.606892
C	-0.008015	0.100214	3.304475
O	-0.056282	0.439897	4.614473
H	-1.196677	1.013223	-0.387430
H	-1.111736	2.060142	-1.699751
H	1.011548	1.099288	-1.582263
H	1.371664	-1.281387	-1.140006
H	-0.351987	-1.630165	-1.195917
H	-1.711566	-1.429902	0.794642
H	2.214378	0.359969	0.747012
H	-1.950286	-0.843754	3.173886
H	1.968803	0.930174	3.142666
H	-0.871897	0.132253	5.034230
O	-0.990793	0.108008	-3.833263
H	-1.886764	0.610292	-1.866539
H	-0.939180	-0.156122	-4.770766

Zero point vibrational energy	130.37057 kcal/mol
Electronic energy	-630.4271902 Hartree

TS1a



(**TS1a**)
+39.1 kcal/mol

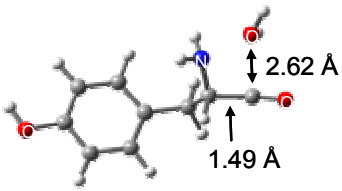
N	0.533414	1.488657	1.702566
C	-0.466334	0.463170	1.668336
C	-0.802521	0.152095	3.100892
C	-0.176151	-0.848405	0.868095
O	-1.297385	-0.003342	4.105731
C	-0.101096	-0.535435	-0.607430
C	1.135572	-0.391996	-1.251231
C	-1.273522	-0.372395	-1.367077
C	1.208461	-0.092825	-2.611805
C	-1.216674	-0.069320	-2.721479
C	0.030125	0.074316	-3.351095
O	0.016499	0.366561	-4.675054
H	1.458932	1.145885	1.471694
H	0.293284	2.302461	1.149945
H	-1.428468	0.876521	1.324370
H	-0.971531	-1.573852	1.078727
H	0.764756	-1.262582	1.238813
H	2.059733	-0.540041	-0.697733
H	-2.248643	-0.506420	-0.902851
H	2.176909	-0.000477	-3.096310
H	-2.119174	0.043773	-3.312266
H	0.912731	0.423692	-5.034559
O	1.487792	-0.441353	3.613167

H	1.990848	0.268039	4.039597
H	1.694326	-1.247755	4.108627

1 Imaginary Frequency -83.8396 cm^{-1}
Zero point vibrational energy 125.53162 kcal/mol
Electronic energy -630.3632597 Hartree

I1a

N	0.424018	1.503678	1.746204
C	-0.548525	0.452694	1.658815
C	-0.887338	0.171994	3.084759
C	-0.216595	-0.853143	0.862718
O	-1.247884	0.020615	4.144108
C	-0.117345	-0.534790	-0.609712
C	1.126814	-0.323810	-1.219538
C	-1.276127	-0.434152	-1.400564
C	1.220189	-0.021855	-2.578197
C	-1.198970	-0.129283	-2.753553
C	0.055034	0.079827	-3.349669
O	0.061661	0.368601	-4.674399
H	1.379641	1.165640	1.731462
H	0.264730	2.261996	1.094660
H	-1.502513	0.854653	1.281509
H	-1.004442	-1.591479	1.056143
H	0.724615	-1.249997	1.249904
H	2.041421	-0.417095	-0.639351
H	-2.254817	-0.619616	-0.962275
H	2.194893	0.123627	-3.036395
H	-2.089933	-0.065141	-3.368688
H	0.962953	0.473498	-5.009685
O	1.608596	-0.470707	3.562499
H	2.056767	0.106448	4.197891
H	1.936751	-1.361242	3.753391

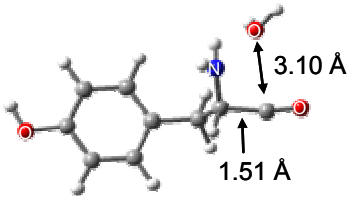


(**I1a**)
+38.9 kcal/mol

Zero point vibrational energy 125.49888 kcal/mol
Electronic energy -630.3633948 Hartree

TS1b

N	0.294080	1.449556	1.824716
C	-0.713378	0.478604	1.650885
C	-1.074510	0.128433	3.084938
C	-0.379350	-0.835011	0.860593
O	-1.172724	-0.085675	4.191329
C	-0.202547	-0.520298	-0.603254
C	1.070505	-0.304818	-1.148123
C	-1.319755	-0.426494	-1.452506
C	1.232396	-0.007153	-2.500655
C	-1.174397	-0.126135	-2.800770
C	0.107876	0.086401	-3.331663
O	0.182522	0.371111	-4.655240
O	1.966424	-0.407171	3.361321
H	1.239651	1.123269	1.985002
H	0.150795	2.380881	1.466003
H	-1.629522	0.916098	1.236261
H	-1.203280	-1.541662	1.018892
H	0.525685	-1.267989	1.293027
H	1.953240	-0.384978	-0.519127
H	-2.318713	-0.613003	-1.063430

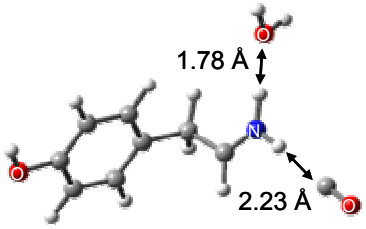


(**TS1b**)
+38.5 kcal/mol

H	2.228401	0.143694	-2.908587
H	-2.032692	-0.067657	-3.461213
H	1.099669	0.481385	-4.942247
H	2.530354	-1.179589	3.213314
H	2.307032	-0.004637	4.173143

1 Imaginary Frequency	-242.03 cm^{-1}
Zero point vibrational energy	124.67248 kcal/mol
Electronic energy	-630.3627193 Hartree

I1b

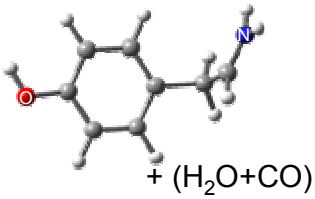


(**I1b**)
+6.7 kcal/mol

N	0.449638	0.251106	-2.319678
C	0.225480	1.009421	-1.298027
C	-1.974148	-0.234849	-4.438179
C	1.196636	1.254891	-0.203786
O	-2.801206	-0.421061	-5.188091
C	0.562329	0.654697	1.050184
C	0.645344	-0.723764	1.294653
C	-0.137468	1.463116	1.962260
C	0.066197	-1.284162	2.431194
C	-0.722544	0.915474	3.096727
C	-0.623161	-0.464291	3.336482
O	-1.213059	-0.933693	4.462072
O	2.998566	-0.887997	-2.708346
H	1.373752	-0.190964	-2.477922
H	-0.289593	0.073689	-3.005088
H	-0.768903	1.447134	-1.216416
H	1.323557	2.336767	-0.079802
H	2.170523	0.813255	-0.433129
H	1.185764	-1.370403	0.607683
H	-0.207202	2.535544	1.798786
H	0.154501	-2.351319	2.616819
H	-1.248205	1.536433	3.813833
H	-1.080231	-1.886678	4.562058
H	3.233428	-1.822700	-2.626887
H	3.698746	-0.479682	-3.236315

Zero point vibrational energy	124.73575 kcal/mol
Electronic energy	-630.4135601 Hartree

B



(**B**+H_2O+CO)
+24.4 kcal/mol

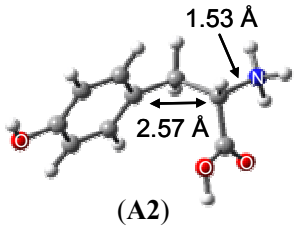
N	-0.785080	-0.666677	3.382001
C	0.264727	-0.484723	2.635433
C	0.613605	0.790662	1.977443
C	0.345734	0.467632	0.505514
C	-0.953506	0.567357	-0.018457
C	1.390078	0.041112	-0.337182
C	-1.204205	0.286970	-1.357683
C	1.150163	-0.246925	-1.672178
C	-0.151087	-0.124349	-2.191147
O	-0.312602	-0.416217	-3.498923
H	-1.396155	0.104091	3.638785
H	-1.039282	-1.586009	3.731516
H	0.874762	-1.363707	2.436422
H	1.671707	1.019601	2.138630
H	0.010490	1.626441	2.344377
H	-1.777727	0.895931	0.610114
H	2.404158	-0.037728	0.046085

H	-2.209211	0.393155	-1.756503
H	1.952036	-0.553798	-2.334673
H	-1.227468	-0.287916	-3.787829

Zero point vibrational energy 105.67398 kcal/mol
Electronic energy -440.6298909 Hartree

Pathway 2

A2

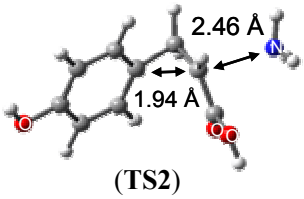


(**A2**)
+5.7 kcal/mol

N	-1.100822	0.049040	3.443345
C	-0.603700	-0.332885	2.052641
C	0.920274	-0.364765	2.211554
C	-1.098123	0.731415	1.034931
O	1.466320	0.275700	3.091004
C	-0.672520	0.461658	-0.390534
C	-1.332033	-0.501267	-1.166256
C	-0.939054	-0.758445	-2.478294
C	0.127383	-0.040952	-3.038422
C	0.788045	0.934490	-2.278616
C	0.386720	1.177984	-0.969565
H	-0.356645	0.638850	3.863515
H	-0.994498	-1.322066	1.806885
H	-0.732446	1.714210	1.357278
H	-2.194802	0.748099	1.102943
H	-2.174666	-1.054287	-0.756415
H	-1.466419	-1.504071	-3.067454
O	0.565291	-0.232399	-4.308798
H	1.598641	1.494623	-2.731972
H	0.898833	1.948818	-0.398236
O	1.513079	-1.127875	1.311077
H	2.482106	-1.075466	1.414830
H	-1.984077	0.567115	3.405826
H	-1.228280	-0.763727	4.054835
H	0.038543	-0.902164	-4.766356

Zero point vibrational energy 130.38911 kcal/mol
Electronic energy -630.4241548 Hartree

TS2



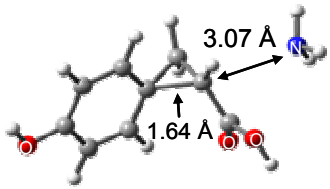
(**TS2**)
+26.5 kcal/mol

N	1.030376	0.239499	3.867128
C	0.545482	0.124243	1.463195
C	-0.893697	0.218911	1.885491
C	1.107342	-1.126398	0.995895
O	-1.609409	-0.742552	2.058249
C	0.616952	-0.567167	-0.349894
C	1.475644	0.248906	-1.140840
C	1.129626	0.604940	-2.426736
C	-0.101520	0.162062	-2.962212
C	-0.976329	-0.636788	-2.191002
C	-0.628494	-0.985487	-0.906085
H	0.531683	-0.495440	4.365706
H	1.115168	1.042320	1.422220
H	0.572424	-2.021674	1.305417
H	2.188624	-1.227314	1.056360
H	2.430022	0.575092	-0.736453
H	1.798563	1.214676	-3.027296
O	-0.505872	0.465628	-4.198016

H	-1.910767	-0.963393	-2.633711
H	-1.299423	-1.596706	-0.311632
O	-1.262765	1.498245	2.054009
H	-2.195799	1.520617	2.333366
H	2.025850	0.102811	4.030408
H	0.768485	1.131683	4.282298
H	0.136864	1.010933	-4.677379

1 Imaginary Frequency -230.53 cm^{-1}
Zero point vibrational energy 126.93086 kcal/mol
Electronic energy -630.3854935 Hartree

I2

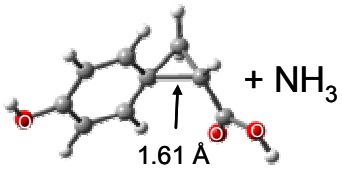


(**I2**)
+24.4 kcal/mol

N	1.060013	0.002702	4.251709
C	0.502393	0.108990	1.233025
C	-0.845097	0.257359	1.891388
C	1.001058	-1.199980	0.889356
O	-1.635032	-0.650945	2.028918
C	0.464469	-0.353645	-0.340142
C	1.434944	0.297052	-1.183924
C	1.180495	0.533998	-2.507693
C	-0.065129	0.125632	-3.057864
C	-1.044945	-0.518667	-2.259073
C	-0.791231	-0.746662	-0.933906
H	0.393811	-0.590364	4.743763
H	1.192784	0.926937	1.398161
H	0.376015	-2.055676	1.123767
H	2.070501	-1.377633	0.872764
H	2.387024	0.599081	-0.756342
H	1.917957	1.024366	-3.136604
O	-0.380283	0.319223	-4.329196
H	-1.979132	-0.815967	-2.722436
H	-1.534792	-1.232233	-0.309891
O	-1.063860	1.528125	2.254685
H	-1.940991	1.584438	2.674451
H	1.983894	-0.362339	4.475901
H	1.003969	0.921845	4.686557
H	0.320519	0.762942	-4.834318

Zero point vibrational energy 126.79966 kcal/mol
Electronic energy -630.3885949 Hartree

C



(**C**+NH_3)
+30.1 kcal/mol

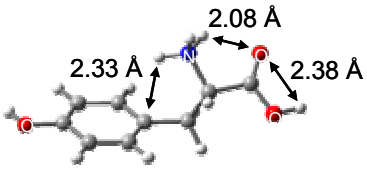
C	0.845096	-0.010826	-1.586907
C	-0.330665	-0.263497	-2.499852
C	1.136096	1.346649	-1.149857
C	0.526993	0.368070	-0.059710
O	-1.286843	0.472831	-2.599789
C	1.445970	-0.177844	0.915661
C	-0.837763	0.609967	0.360622
O	-0.149144	-1.395805	-3.188353
C	1.048213	-0.444452	2.195006
C	-1.233827	0.349931	1.642506
C	-0.299792	-0.180780	2.571496
O	-0.754424	-0.410358	3.789962
H	1.656509	-0.725256	-1.675761
H	0.452966	2.134404	-1.450909
H	2.162832	1.643719	-0.967467

H	2.473450	-0.371372	0.619664
H	-1.541838	1.007341	-0.362999
H	-0.896998	-1.519422	-3.801579
H	1.745977	-0.850386	2.921739
H	-2.248275	0.536983	1.976943
H	-0.083251	-0.772664	4.392009

Zero point vibrational energy 104.08058 kcal/mol
Electronic energy -573.8107346 Hartree

Pathway 3

A

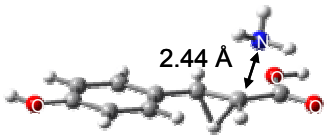


(A)
0.0 kcal/mol

N	-1.108690	1.086333	-1.389128
C	0.186906	0.417323	-1.795178
C	0.021241	0.071925	-3.274023
C	0.422374	-0.840968	-0.911814
O	-1.064927	0.090706	-3.817629
C	0.283538	-0.531409	0.563195
O	1.175097	-0.272826	-3.830916
C	-0.870172	-0.908357	1.270051
C	1.293544	0.160852	1.259334
C	-1.020673	-0.604673	2.626549
C	1.156391	0.468436	2.606536
C	-0.006286	0.087656	3.298858
O	-0.069761	0.418868	4.610489
H	-1.856666	0.723380	-2.004941
H	-1.302879	0.871695	-0.395951
H	-1.081997	2.102796	-1.508820
H	0.994604	1.137830	-1.651220
H	1.422614	-1.209527	-1.158238
H	-0.287859	-1.621922	-1.206728
H	1.033131	-0.526225	-4.762306
H	-1.647103	-1.488949	0.775999
H	2.211972	0.441518	0.748626
H	-1.913367	-0.923965	3.157689
H	1.940681	0.986933	3.147577
H	-0.876748	0.083421	5.025614

Zero point vibrational energy 130.46032 kcal/mol
Electronic energy -630.4333484 Hartree

TS3



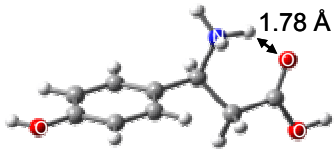
(TS3)
+40.8 kcal/mol

N	1.791496	1.287546	-2.260119
H	2.379443	0.943193	-3.017668
H	1.373272	2.162622	-2.571178
H	2.395013	1.506603	-1.470011
C	0.138421	-0.454938	-1.805452
C	-0.263312	-0.358408	-3.257057
C	-0.699200	-0.052783	-0.734289
O	0.436992	-0.780528	-4.143586
C	-0.380398	-0.066908	0.683951
O	-1.459371	0.234070	-3.414188
C	-1.362324	0.397064	1.587365
C	0.854846	-0.525486	1.202515
C	-1.127564	0.413543	2.952875
C	1.097378	-0.516971	2.561565
C	0.104987	-0.047600	3.448637

O	0.413329	-0.067591	4.755620
H	1.028225	-1.044126	-1.622882
H	-0.900649	-1.212505	-1.211117
H	-1.599808	0.484827	-1.027729
H	-1.685689	0.243574	-4.361883
H	-2.317928	0.750519	1.210090
H	1.635562	-0.885838	0.539746
H	-1.890586	0.778432	3.634462
H	2.040793	-0.861379	2.970470
H	-0.310268	0.265064	5.307225

1 Imaginary Frequency	-790.40 cm^{-1}
Zero point vibrational energy	124.72552 kcal/mol
Electronic energy	-630.3595618 Hartree

I3

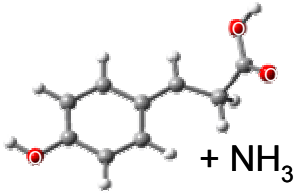


(**I3**)
-7.3 kcal/mol

N	1.420620	1.052554	1.314160
C	0.542781	-0.150216	0.899556
C	-0.695017	-0.185682	1.813097
C	0.253848	-0.102758	-0.577056
C	-0.358836	-0.176003	3.294104
C	0.871199	-1.021836	-1.437872
C	-0.620610	0.853345	-1.129231
O	0.667885	0.311981	3.755234
O	-1.306094	-0.727582	4.039800
C	0.629853	-0.994633	-2.809864
C	-0.862949	0.896484	-2.495167
C	-0.238137	-0.032431	-3.344485
O	-0.523669	0.061429	-4.662456
H	1.501204	1.023563	2.357883
H	2.341289	0.998990	0.870552
H	0.993810	1.938039	1.026828
H	1.171905	-1.015640	1.125353
H	-1.363772	0.663183	1.620430
H	-1.274433	-1.081273	1.574525
H	1.542006	-1.778508	-1.038184
H	-1.135333	1.573351	-0.496353
H	-1.063037	-0.661745	4.982468
H	1.111524	-1.720118	-3.459656
H	-1.537355	1.628994	-2.924854
H	-0.069915	-0.620952	-5.177230

Zero point vibrational energy	130.62451 kcal/mol
Electronic energy	-630.4453111 Hartree

D



(**D**+NH_3)
+18.4 kcal/mol

C	-0.335803	0.855847	-2.117131
C	-0.230280	-0.183520	-3.254045
C	0.606896	0.586075	-1.010154
O	-1.190326	-0.649015	-3.806356
C	0.309001	0.335465	0.316049
O	1.053496	-0.465031	-3.544057
C	1.400532	0.103974	1.230284
C	-1.034092	0.292552	0.842239
C	1.178477	-0.144012	2.558513
C	-1.261274	0.042144	2.166484
C	-0.158165	-0.177026	3.039272
O	-0.458215	-0.410915	4.305395

H	-1.381902	0.916206	-1.823432
H	-0.049570	1.814081	-2.579733
H	1.658480	0.572358	-1.292373
H	1.077992	-1.087987	-4.293432
H	2.417003	0.129444	0.848820
H	-1.879374	0.455072	0.183584
H	2.006118	-0.316019	3.240564
H	-2.262431	0.003055	2.581299
H	0.322299	-0.555528	4.865787

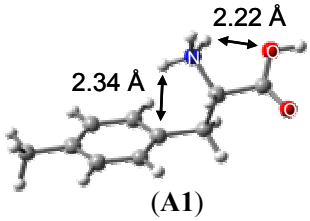
Zero point vibrational energy	103.83859 kcal/mol
Electronic energy	-573.8289978 Hartree

PES of 4-Me Phe (supplementary figure S1a)

Pathway 1

A1

N	-1.159333	0.998716	-1.424548
C	0.185253	0.394719	-1.802907
C	0.244806	0.081942	-3.295094
C	0.433269	-0.865665	-0.932735
O	1.273792	-0.166748	-3.861435
C	0.288809	-0.557232	0.543108
C	-0.892608	-0.878647	1.231283
C	1.314666	0.095141	1.248406
C	-1.042691	-0.556357	2.585280
C	1.158907	0.410619	2.596249
C	-0.021893	0.092136	3.292138
C	-0.160764	0.411211	4.759999
H	-1.273887	0.908782	-0.398602
H	-1.236097	1.985123	-1.689522
H	0.938982	1.152430	-1.578389
H	1.440647	-1.213370	-1.179545
H	-0.262571	-1.657472	-1.234262
H	-1.684119	-1.432001	0.727713
H	2.250101	0.337235	0.748705
H	-1.959382	-0.832266	3.098644
H	1.972203	0.902085	3.123403
H	0.465106	-0.258541	5.361302
H	-1.192551	0.296534	5.100815
H	0.160446	1.434860	4.976692
O	-0.987797	0.077952	-3.857077
H	-0.915467	-0.167465	-4.798268
H	-1.922554	0.496216	-1.893103

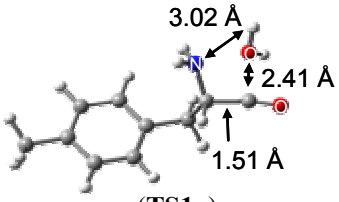


(**A1**)
+3.8 kcal/mol

Zero point vibrational energy	144.93149 kcal/mol
Electronic energy	-594.5238125 Hartree

TS1a

N	0.512801	1.492690	1.724051
C	-0.472015	0.454170	1.689788
C	-0.799991	0.148452	3.129490
C	-0.163866	-0.851912	0.896649
O	-1.288691	0.023740	4.141447
C	-0.094362	-0.541858	-0.582336
C	1.141209	-0.381627	-1.223347
C	-1.267083	-0.395385	-1.338879
C	1.201089	-0.080800	-2.585454
C	-1.201445	-0.092041	-2.697637
C	0.033693	0.069942	-3.347806
C	0.098658	0.359798	-4.826999
H	1.440764	1.168624	1.476698
H	0.253748	2.314456	1.192274
H	-1.441027	0.852835	1.347549
H	-0.949293	-1.587998	1.107899
H	0.783198	-1.252969	1.265928
H	2.066277	-0.513954	-0.666653
H	-2.241040	-0.538861	-0.874234
H	2.170554	0.030591	-3.063041



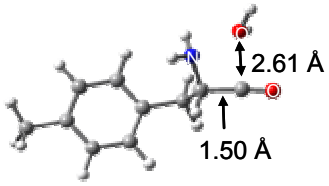
(**TS1a**)
+39.3 kcal/mol

H	-2.122124	0.008410	-3.265787
H	0.044478	-0.570647	-5.405251
H	1.032487	0.860021	-5.096973
H	-0.734480	0.991752	-5.147705
O	1.484509	-0.443431	3.633222
H	1.693220	-1.250805	4.126195
H	1.991764	0.264808	4.056570

1 Imaginary Frequency -81.976 cm^{-1}
Zero point vibrational energy 140.04807 kcal/mol
Electronic energy -594.4593674 Hartree

I1a

N	0.431377	1.501766	1.769215
C	-0.539641	0.450312	1.679728
C	-0.881404	0.178461	3.109760
C	-0.207199	-0.854400	0.891148
O	-1.250749	0.057415	4.169837
C	-0.113142	-0.540243	-0.585113
C	1.128926	-0.314971	-1.193015
C	-1.271875	-0.454456	-1.372202
C	1.208897	-0.012601	-2.553770
C	-1.186136	-0.149472	-2.729383
C	0.055856	0.075356	-3.347124
C	0.144283	0.365619	-4.825037
H	1.387810	1.166530	1.748258
H	0.268457	2.265900	1.125304
H	-1.493680	0.851688	1.301259
H	-0.993088	-1.594234	1.086879
H	0.736215	-1.248700	1.275591
H	2.043703	-0.394348	-0.610364
H	-2.248868	-0.647584	-0.932649
H	2.183370	0.149695	-3.005836
H	-2.095392	-0.097840	-3.321933
H	1.067533	0.894683	-5.075404
H	-0.701131	0.970757	-5.164987
H	0.131548	-0.566634	-5.402739
O	1.589640	-0.486170	3.595719
H	1.906413	-1.380625	3.787800
H	2.044964	0.086761	4.229925

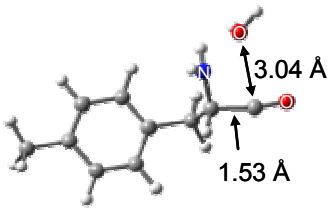


(**I1a**)
+39.2 kcal/mol

Zero point vibrational energy 140.03452 kcal/mol
Electronic energy -594.4595048 Hartree

TS1b

N	0.319299	1.448303	1.843712
C	-0.687172	0.479197	1.670581
C	-1.059364	0.135539	3.109390
C	-0.355885	-0.831283	0.885949
O	-1.183649	-0.038638	4.219715
C	-0.191172	-0.521117	-0.583594
C	1.076034	-0.288363	-1.132703
C	-1.312473	-0.450065	-1.424730
C	1.217733	0.006381	-2.489890
C	-1.165276	-0.152603	-2.777962
C	0.102882	0.079626	-3.337276
C	0.256466	0.366112	-4.810624
O	1.913859	-0.437862	3.431313



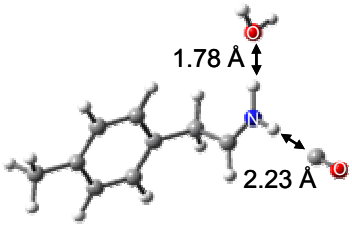
(**TS1b**)
+38.8 kcal/mol

H	1.264153	1.126147	2.013414
H	0.171083	2.388052	1.510102
H	-1.603263	0.918901	1.256629
H	-1.175848	-1.541332	1.049741
H	0.554181	-1.261160	1.310781
H	1.961714	-0.349455	-0.505128
H	-2.307198	-0.648157	-1.029686
H	2.210729	0.176245	-2.896446
H	-2.045820	-0.112350	-3.413308
H	0.201530	-0.561701	-5.392832
H	1.218296	0.836667	-5.029915
H	-0.538174	1.024707	-5.173882
H	2.459641	-1.224448	3.289619
H	2.261569	-0.038779	4.241856

1 Imaginary Frequency	-262.21 cm^{-1}
Zero point vibrational energy	139.19992 kcal/mol
Electronic energy	-594.4587513 Hartree

I1b

N	0.435032	0.233710	-2.361836
C	0.216234	0.984565	-1.335043
C	-1.986196	-0.224474	-4.485778
C	1.194743	1.227355	-0.247283
O	-2.811217	-0.400732	-5.240310
C	0.573794	0.652607	1.027076
C	0.620452	-0.726780	1.271798
C	-0.073481	1.485469	1.950522
C	0.049150	-1.257357	2.428654
C	-0.643895	0.946864	3.102397
C	-0.592058	-0.432405	3.365323
C	-1.183038	-1.000313	4.631561
O	2.970576	-0.919420	-2.761203
H	1.357052	-0.212813	-2.524083
H	-0.306162	0.065020	-3.047796
H	-0.777133	1.423759	-1.246421
H	1.332134	2.310057	-0.138897
H	2.162569	0.774166	-0.480210
H	1.119698	-1.391566	0.570532
H	-0.116566	2.558903	1.783098
H	0.105270	-2.327332	2.607769
H	-1.130071	1.608984	3.813511
H	-0.491699	-0.868493	5.472823
H	-1.385329	-2.070201	4.535934
H	-2.117042	-0.496381	4.896900
H	3.205664	-1.850388	-2.644733
H	3.667303	-0.531655	-3.308827

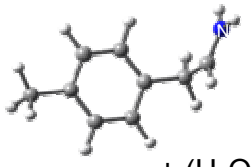


(**I1b**)
+6.9 kcal/mol

Zero point vibrational energy	139.24833 kcal/mol
Electronic energy	-594.5096743 Hartree

B

N	-0.800854	0.639816	-3.443553
C	0.242915	0.499060	-2.683537
C	0.626398	-0.758944	-2.012979
C	0.358180	-0.453095	-0.534541
C	-0.941229	-0.563409	-0.017306
C	1.398972	-0.034065	0.309440



+ (H_2O+CO)

(**B**+H_2O+CO)
+24.9 kcal/mol

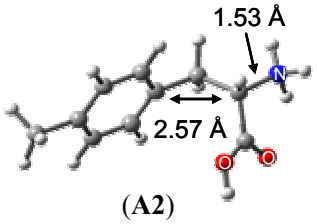
C	-1.185827	-0.294756	1.328356
C	1.143011	0.236456	1.650716
C	-0.151088	0.109467	2.187371
C	-0.408212	0.373588	3.648480
H	-1.388092	-0.152057	-3.693290
H	-1.077038	1.546327	-3.810532
H	0.822171	1.399253	-2.485345
H	1.691272	-0.954305	-2.176587
H	0.048472	-1.613956	-2.376418
H	-1.763107	-0.885971	-0.652700
H	2.413109	0.055288	-0.071929
H	-2.193545	-0.404285	1.718121
H	1.961719	0.542128	2.295957
H	-1.468276	0.551188	3.845205
H	0.158894	1.239298	4.003026
H	-0.098314	-0.487431	4.253359

Zero point vibrational energy 120.11259 kcal/mol
Electronic energy -404.7255517 Hartree

Pathway 2

A2

N	-1.093780	0.022830	3.468419
C	-0.590061	-0.336355	2.074207
C	0.934146	-0.354667	2.236132
C	-1.090914	0.733965	1.068642
O	1.471499	0.277741	3.126645
C	-0.675880	0.465549	-0.362084
O	1.536783	-1.097764	1.325668
C	-1.315776	-0.529296	-1.116089
C	0.346662	1.209506	-0.960951
C	-0.929634	-0.779438	-2.430830
C	0.727257	0.956958	-2.280851
C	0.099416	-0.040562	-3.039210
C	0.490078	-0.299170	-4.473770
H	-0.357804	0.616594	3.897230
H	-1.983758	0.529433	3.435991
H	-1.211312	-0.799171	4.069555
H	-0.970279	-1.326328	1.815374
H	-0.722403	1.715516	1.390877
H	-2.187341	0.750413	1.141330
H	2.504844	-1.037190	1.433253
H	-2.131444	-1.106283	-0.684206
H	0.845035	2.000169	-0.404344
H	-1.441168	-1.552110	-2.998375
H	1.518509	1.551433	-2.728752
H	1.424784	0.204649	-4.732134
H	0.615284	-1.369764	-4.664992
H	-0.284517	0.064060	-5.159426

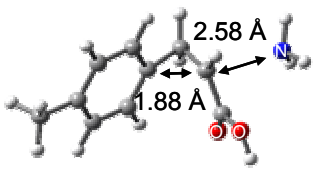


(**A2**)
+5.9 kcal/mol

Zero point vibrational energy 144.91738 kcal/mol
Electronic energy -594.5203459 Hartree

TS2

N	0.996445	0.290180	3.965136
C	0.536316	0.106113	1.436921
C	-0.892495	0.202768	1.899984



(**TS2**)
+29.0 kcal/mol

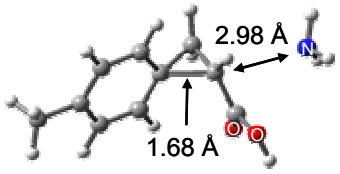
C	1.104590	-1.151141	1.023062
O	-1.601507	-0.758626	2.096683
C	0.609742	-0.552740	-0.318700
O	-1.261197	1.482620	2.056565
C	1.488801	0.243371	-1.108223
C	-0.633241	-0.963280	-0.880326
C	1.150349	0.582896	-2.403230
C	-0.952131	-0.619671	-2.180088
C	-0.073265	0.157035	-2.967912
C	-0.421877	0.503715	-4.384581
H	0.476904	-0.417997	4.480868
H	1.984793	0.139506	4.157355
H	0.747104	1.197208	4.355012
H	1.120038	1.016174	1.434477
H	0.556874	-2.042516	1.318611
H	2.185297	-1.252824	1.073689
H	-2.186580	1.506757	2.359969
H	2.439628	0.566953	-0.693181
H	-1.320699	-1.554499	-0.284125
H	1.832660	1.182076	-2.998034
H	-1.895520	-0.949925	-2.603877
H	-1.502758	0.578148	-4.527943
H	0.046400	1.439380	-4.699811
H	-0.058361	-0.286051	-5.056392

1 Imaginary Frequency	-171.65 cm^{-1}
Zero point vibrational energy	140.95997 kcal/mol
Electronic energy	-594.4772906 Hartree

I2

N	1.030490	0.129159	4.226220
C	0.511915	0.074857	1.294133
C	-0.855350	0.228282	1.911885
C	1.012577	-1.223870	0.946417
O	-1.625547	-0.690702	2.081744
C	0.491779	-0.405651	-0.314422
O	-1.109369	1.511585	2.199622
C	1.456529	0.266019	-1.135674
C	-0.758223	-0.787237	-0.904167
C	1.185304	0.531645	-2.458052
C	-1.007693	-0.520235	-2.232318
C	-0.048977	0.142533	-3.035561
C	-0.323591	0.406146	-4.482675
H	0.393339	-0.478297	4.738833
H	1.971343	-0.185249	4.456560
H	0.932452	1.059037	4.629719
H	1.189488	0.907158	1.435457
H	0.389701	-2.082648	1.175979
H	2.082796	-1.397983	0.932266
H	-1.997153	1.571973	2.595763
H	2.408618	0.561601	-0.703307
H	-1.500977	-1.288686	-0.291703
H	1.921727	1.043062	-3.069751
H	-1.954462	-0.818073	-2.671787
H	-1.392981	0.512033	-4.680154
H	0.201782	1.295011	-4.840414
H	0.034607	-0.445062	-5.079320

Zero point vibrational energy	140.85029 kcal/mol

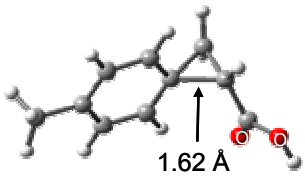


(**I2**)
+28.4 kcal/mol

Electronic energy -594.4780771 Hartree

C

C	0.837216	-0.018466	-1.636405
C	-0.356833	-0.260800	-2.531238
C	1.146272	1.328314	-1.205644
O	-1.296483	0.495675	-2.631117
C	0.534644	0.348268	-0.091706
O	-0.205962	-1.407181	-3.202341
C	1.460079	-0.199807	0.866969
C	-0.812739	0.614592	0.338035
C	1.064135	-0.447784	2.157479
C	-1.185458	0.365006	1.638888
C	-0.265093	-0.169291	2.573308
C	-0.674595	-0.413811	3.989247
H	1.636125	-0.746768	-1.725987
H	0.464446	2.124491	-1.486463
H	2.174832	1.613695	-1.016024
H	-0.961983	-1.526250	-3.806484
H	2.479949	-0.411900	0.557223
H	-1.523193	1.015794	-0.377370
H	1.769513	-0.861068	2.871411
H	-2.201427	0.576777	1.956434
H	-1.755892	-0.527996	4.089694
H	-0.173007	-1.290449	4.408298
H	-0.375581	0.448400	4.603328



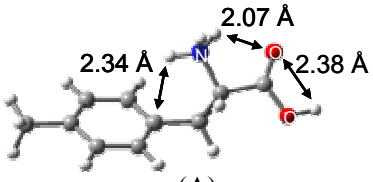
(**C**+NH_3)
+34.4 kcal/mol

Zero point vibrational energy 118.02053 kcal/mol
Electronic energy -537.8995317 Hartree

Pathway 3

A

N	-1.184396	1.000886	-1.398606
C	0.154924	0.423846	-1.805411
C	0.021978	0.095120	-3.291847
C	0.469218	-0.831316	-0.943582
O	-1.058544	0.059532	-3.845531
C	0.321051	-0.543349	0.535246
O	1.199061	-0.169907	-3.843937
C	-0.849467	-0.910829	1.219402
C	1.321948	0.140604	1.245218
C	-1.013716	-0.599536	2.574452
C	1.152666	0.443572	2.594465
C	-0.017952	0.081723	3.286184
C	-0.171246	0.388547	4.755249
H	-1.901585	0.605556	-2.030961
H	-1.378057	0.754563	-0.412077
H	-1.219855	2.019309	-1.497254
H	0.913514	1.192264	-1.642845
H	1.488418	-1.136215	-1.197835
H	-0.196451	-1.648409	-1.244717
H	1.080082	-0.414155	-4.780959
H	-1.619080	-1.491119	0.712045
H	2.248421	0.419585	0.748065
H	-1.921506	-0.909135	3.084490
H	1.946895	0.961110	3.125712
H	0.158526	1.406149	4.986107

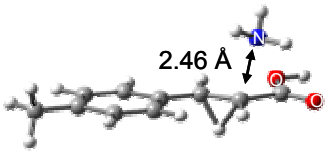


(**A**)
0.0 kcal/mol

H	-1.208347	0.281629	5.082446
H	0.439233	-0.294622	5.357509

Zero point vibrational energy 145.03677 kcal/mol
Electronic energy -594.5299566 Hartree

TS3

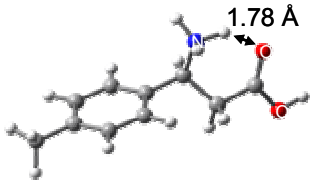


(**TS3**)
+42.2 kcal/mol

N	1.807970	1.281226	-2.297157
C	0.132919	-0.462443	-1.825494
C	-0.256017	-0.362817	-3.282496
C	-0.701174	-0.042576	-0.762154
O	0.441448	-0.804627	-4.160889
C	-0.391555	-0.063964	0.661032
O	-1.439191	0.251221	-3.448559
C	-1.377091	0.404187	1.554391
C	0.838934	-0.522643	1.183024
C	-1.139260	0.417553	2.923988
C	1.063098	-0.508215	2.549877
C	0.080130	-0.040012	3.449441
C	0.346154	-0.036352	4.929757
H	2.410310	0.925274	-3.037859
H	1.398640	2.152473	-2.630214
H	2.397478	1.512723	-1.499993
H	1.023780	-1.047999	-1.635827
H	-0.896173	-1.213425	-1.247897
H	-1.601751	0.492687	-1.060279
H	-1.661021	0.262105	-4.397370
H	-2.329585	0.759534	1.170391
H	1.623629	-0.883817	0.525016
H	-1.908241	0.784942	3.596276
H	2.014374	-0.860331	2.938244
H	-0.498528	0.366240	5.492306
H	1.232206	0.564310	5.164531
H	0.544203	-1.052364	5.290157

1 Imaginary Frequency -773.2613 cm^{-1}
Zero point vibrational energy 139.08818 kcal/mol
Electronic energy -594.4531778 Hartree

I3



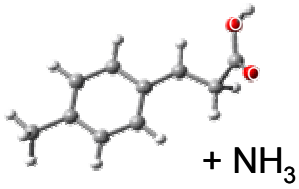
(**I3**)
-7.0 kcal/mol

N	1.424784	1.039469	1.338090
C	-0.702486	-0.178413	1.837257
C	-0.370827	-0.167910	3.319154
C	0.539661	-0.157381	0.930021
O	0.655695	0.318663	3.781828
C	0.257148	-0.111192	-0.550716
O	-1.321398	-0.714955	4.063684
C	0.886990	-1.025179	-1.405361
C	-0.613838	0.842903	-1.105270
C	0.652547	-0.986783	-2.780970
C	-0.836904	0.879080	-2.479157
C	-0.211353	-0.037054	-3.343683
C	-0.483957	-0.003356	-4.826422
H	1.008381	1.926171	1.040147
H	1.500021	1.017738	2.382727
H	2.347325	0.972805	0.899754
H	-1.361122	0.677075	1.638948
H	-1.289386	-1.069054	1.598204

H	1.160715	-1.027352	1.160745
H	-1.080364	-0.647833	5.006788
H	1.558164	-1.778955	-1.000039
H	-1.135907	1.560858	-0.475488
H	1.148188	-1.708013	-3.423997
H	-1.513663	1.623961	-2.888388
H	0.216169	-0.634971	-5.377956
H	-0.410647	1.015187	-5.220303
H	-1.497639	-0.361854	-5.040985

Zero point vibrational energy 145.08936 kcal/mol
Electronic energy -594.5412248 Hartree

D



(**D**+NH_3)
+22.9 kcal/mol

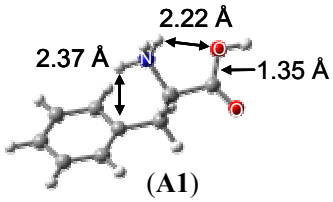
C	-0.337730	0.854141	-2.146883
C	-0.247133	-0.191290	-3.283027
C	0.609864	0.580487	-1.049340
O	-1.215970	-0.647370	-3.826417
C	0.320856	0.338169	0.285472
O	1.031758	-0.484330	-3.578120
C	1.416917	0.103593	1.186627
C	-1.014580	0.309906	0.819739
C	1.192072	-0.135261	2.523242
C	-1.220065	0.066319	2.155176
C	-0.127053	-0.160280	3.037258
C	-0.384670	-0.425882	4.484539
H	-1.381036	0.926076	-1.846644
H	-0.042242	1.806082	-2.617815
H	1.659255	0.554016	-1.339909
H	1.049288	-1.109869	-4.325732
H	2.430581	0.118727	0.796538
H	-1.865466	0.476021	0.168894
H	2.027465	-0.308596	3.193653
H	-2.230394	0.043989	2.552016
H	0.536737	-0.538733	5.057243
H	-0.982856	-1.339494	4.598730
H	-0.978513	0.385972	4.922494

Zero point vibrational energy 117.80198 kcal/mol
Electronic energy -537.9174995 Hartree

PES of Phe (figure 3c)

Pathway 1

A1

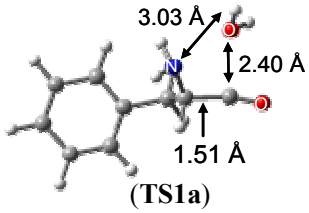


(**A1**)
+3.8 kcal/mol

N	-1.152855	1.020429	-1.042377
C	0.190974	0.381584	-1.365120
C	0.278339	0.011622	-2.843647
C	0.403158	-0.847911	-0.444989
O	1.314582	-0.280530	-3.374410
C	0.245921	-0.481738	1.017401
O	-0.940281	0.016047	-3.434510
C	-0.953028	-0.762312	1.696155
C	1.278306	0.178001	1.704934
C	-1.116991	-0.388805	3.035666
C	1.113667	0.548386	3.040478
C	-0.085182	0.269611	3.706510
H	-1.291643	0.987341	-0.017120
H	-1.210601	1.992838	-1.359510
H	0.950358	1.137542	-1.153465
H	1.407641	-1.222111	-0.663221
H	-0.302054	-1.638989	-0.725779
H	-0.852905	-0.263626	-4.364882
H	-1.742229	-1.323124	1.197811
H	2.222384	0.380523	1.204315
H	-2.040249	-0.629232	3.553366
H	1.924484	1.043623	3.565400
H	-0.206464	0.552000	4.747367
H	-1.914132	0.505444	-1.500612

Zero point vibrational energy	127.88317 kcal/mol
Electronic energy	-555.200553 Hartree

TS1a



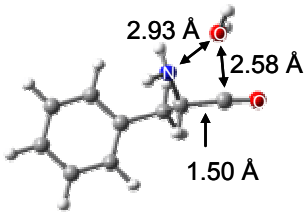
(**TS1a**)
+39.1 kcal/mol

N	0.460063	1.504148	1.326587
C	-0.484463	0.433659	1.245393
C	-0.810794	0.069308	2.676658
C	-0.122372	-0.829493	0.413477
O	-1.304715	-0.078097	3.682970
C	-0.056584	-0.470348	-1.056652
O	1.472016	-0.481724	3.172625
C	1.181273	-0.276022	-1.685018
C	-1.234867	-0.320136	-1.804099
C	1.241069	0.067437	-3.038415
C	-1.175422	0.026292	-3.154758
C	0.063547	0.223324	-3.772971
H	1.401544	1.232134	1.068633
H	0.168732	2.346569	0.846658
H	-1.465565	0.809111	0.911558
H	-0.880150	-1.601954	0.594039
H	0.836974	-1.207943	0.774421
H	1.690606	-1.300945	3.641414
H	2.103785	-0.416945	-1.126648
H	-2.203809	-0.497505	-1.341090
H	2.205370	0.204817	-3.517417
H	-2.092357	0.129333	-3.726397
H	0.109534	0.486613	-4.824908
H	1.958160	0.222121	3.627170

1 Imaginary Frequency	-80.8901 cm^{-1}
Zero point vibrational energy	122.98088 kcal/mol
Electronic energy	-555.1364663 Hartree

I1a

N	0.402800	1.502676	1.373904
C	-0.541940	0.435270	1.231542
C	-0.900711	0.109533	2.649798
C	-0.170157	-0.832326	0.406677
O	-1.290327	-0.032246	3.699885
C	-0.069997	-0.469530	-1.060052
O	1.554890	-0.536702	3.149587
C	1.177132	-0.207353	-1.643973
C	-1.228027	-0.380272	-1.847977
C	1.265909	0.140415	-2.994561
C	-1.139573	-0.029836	-3.196035
C	0.108219	0.233056	-3.770389
H	1.368385	1.195274	1.354898
H	0.226586	2.295718	0.769893
H	-1.499274	0.830123	0.854230
H	-0.939218	-1.597533	0.569022
H	0.778837	-1.216984	0.786885
H	1.875892	-1.434650	3.317069
H	2.084618	-0.295840	-1.051756
H	-2.201638	-0.608486	-1.418348
H	2.237544	0.330632	-3.439430
H	-2.040011	0.024736	-3.799669
H	0.177136	0.498933	-4.820427
H	1.989907	0.017166	3.814351

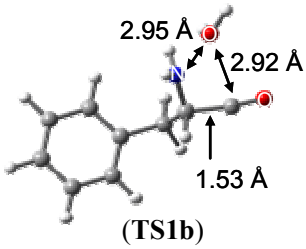


(**I1a**)
+39.0 kcal/mol

Zero point vibrational energy	122.99466 kcal/mol
Electronic energy	-555.136606 Hartree

TS1b

N	0.323361	1.454296	1.427731
C	-0.650275	0.463279	1.211459
C	-1.060513	0.073616	2.633313
C	-0.269710	-0.807375	0.394641
O	-1.265571	-0.088716	3.732804
C	-0.105246	-0.450569	-1.067011
C	1.161728	-0.164170	-1.593345
C	-1.226323	-0.395070	-1.909148
C	1.306268	0.175275	-2.940778
C	-1.082256	-0.053245	-3.254728
C	0.184808	0.234448	-3.771484
H	1.273857	1.160522	1.609828
H	0.145191	2.407224	1.151330
H	-1.571043	0.892661	0.794333
H	-1.064055	-1.551924	0.528842
H	0.652273	-1.218116	0.812330
H	2.041076	-0.221402	-0.956894
H	-2.213538	-0.641575	-1.523139
H	2.292979	0.386585	-3.340678
H	-1.954130	-0.024531	-3.900605
H	0.297488	0.494161	-4.819300
O	1.756858	-0.519040	3.085416
H	2.266171	-1.335654	2.982417

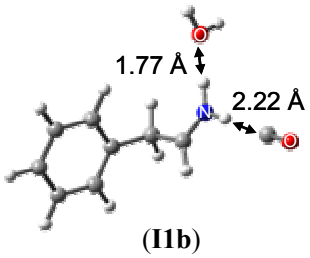


(**TS1b**)
+38.6 kcal/mol

H	2.089018	-0.123101	3.904147

1 Imaginary Frequency -282.023 cm^{-1}
Zero point vibrational energy 122.15639 kcal/mol
Electronic energy -555.1359064 Hartree

I1b

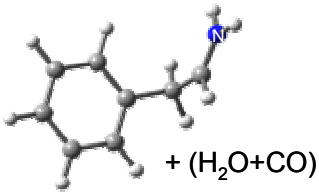


(**I1b**)
+6.8 kcal/mol

N	0.467452	-0.318612	1.888357
C	0.051162	-0.931709	0.832893
C	-1.654388	0.251175	4.278563
C	0.885263	-1.208883	-0.362553
O	-2.373071	0.463548	5.126632
C	0.239783	-0.477101	-1.541618
C	0.451627	0.899579	-1.706706
C	-0.580590	-1.165360	-2.445815
C	-0.138010	1.576846	-2.775898
C	-1.170749	-0.485095	-3.512774
C	-0.951502	0.885690	-3.677990
H	1.455344	-0.016360	1.990069
H	-0.176511	-0.120109	2.659980
H	-0.999098	-1.222377	0.811401
H	0.871023	-2.290579	-0.545732
H	1.921089	-0.898362	-0.198132
H	1.093563	1.441537	-1.016230
H	-0.742730	-2.234293	-2.332536
H	0.041062	2.639405	-2.906316
H	-1.792846	-1.026894	-4.218064
H	-1.408125	1.411955	-4.510168
O	3.162007	0.439408	2.112977
H	3.517849	1.335872	2.039354
H	3.840157	-0.084008	2.562394

Zero point vibrational energy 122.1367 kcal/mol
Electronic energy -555.186582 Hartree

B



(**B**+H_2O+CO)
+25.3 kcal/mol

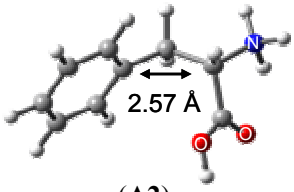
N	0.570950	-0.535739	-3.100488
C	-0.377767	-0.402303	-2.226498
C	-0.624263	0.821922	-1.437897
C	-0.274469	0.415615	0.000358
C	1.065547	0.417406	0.417637
C	-1.284115	0.019806	0.890399
C	1.389298	0.053552	1.725475
C	-0.954633	-0.346834	2.195522
C	0.380366	-0.331943	2.613031
H	1.176232	0.242214	-3.352767
H	0.751380	-1.422776	-3.563433
H	-0.983951	-1.285789	-2.031591
H	-1.684419	1.089069	-1.508778
H	-0.023508	1.665405	-1.791473
H	1.855063	0.729247	-0.262303
H	-2.324914	0.023710	0.577044
H	2.424317	0.075131	2.050859
H	-1.739377	-0.634105	2.887853
H	0.632748	-0.615253	3.629839

Zero point vibrational energy 103.04783 kcal/mol
Electronic energy -365.4016557 Hartree

Pathway 2

A2

N	-1.228917	0.153565	2.973021
C	-0.659238	-0.280333	1.626477
C	0.850312	-0.361539	1.883310
C	-1.046651	0.771791	0.554816
C	-0.555315	0.430936	-0.837497
O	1.361834	0.276469	2.784680
C	-1.188376	-0.572294	-1.585372
C	0.527696	1.122399	-1.395430
O	1.470135	-1.162048	1.035313
C	-0.735047	-0.889352	-2.866502
C	0.979237	0.807707	-2.679621
C	0.351505	-0.200796	-3.414303
H	-0.494306	0.731237	3.425476
H	-2.092106	0.695656	2.868925
H	-1.418109	-0.639591	3.594309
H	-1.069194	-1.261580	1.380001
H	-0.653714	1.747586	0.864843
H	-2.143237	0.839612	0.554474
H	-2.048901	-1.099690	-1.178452
H	1.012686	1.918994	-0.835898
H	2.431899	-1.143978	1.200406
H	-1.235204	-1.663453	-3.439848
H	1.813005	1.355934	-3.106804
H	0.699115	-0.442167	-4.413792

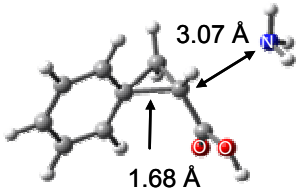


(**A2**)
+5.6 kcal/mol

Zero point vibrational energy	127.85259 kcal/mol
Electronic energy	-555.1976111 Hartree

TS2

N	1.603736	-0.068489	-3.700729
C	0.320032	0.119470	-0.908554
C	-1.038516	-0.196503	-1.491109
C	0.608842	1.441113	-0.441580
C	0.316779	0.392010	0.744739
O	-1.968248	0.578969	-1.483636
C	1.444084	-0.165317	1.429124
C	-0.936236	0.498580	1.427448
O	-1.064353	-1.432079	-2.002150
C	1.321142	-0.586705	2.738460
C	-1.039946	0.080009	2.741577
C	0.081335	-0.462299	3.391358
H	1.146981	0.610693	-4.307012
H	2.604980	0.071558	-3.824171
H	1.393364	-0.986067	-4.089420
H	1.125116	-0.542131	-1.201067
H	-0.167279	2.195964	-0.520107
H	1.632931	1.796920	-0.441161
H	2.395246	-0.247100	0.910664
H	-1.792562	0.912206	0.904410
H	-1.947219	-1.596314	-2.381146
H	2.172801	-1.007648	3.261636
H	-1.983968	0.168179	3.268293
H	-0.010838	-0.794091	4.421700

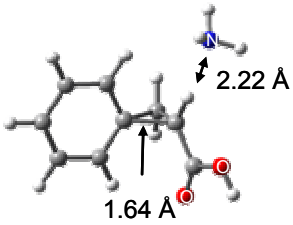


(**TS2**)
+32.5 kcal/mol

1 Imaginary Frequency	-44.84 cm^{-1}
Zero point vibrational energy	123.59332 kcal/mol
Electronic energy	-555.147953 Hartree

I2

N	3.116640	-0.224186	-1.989118
C	0.009757	0.422287	-1.072106
C	-1.192773	-0.198921	-1.744397
C	-0.117042	1.715742	-0.457172
C	-0.027645	0.458107	0.565009
O	-2.339618	0.128209	-1.535069
C	1.243037	0.225394	1.187491
C	-1.229886	0.129904	1.271610
O	-0.803695	-1.134958	-2.618651
C	1.300796	-0.299051	2.463146
C	-1.151125	-0.386721	2.551669
C	0.105900	-0.600522	3.142111
H	3.875730	0.449758	-1.901890
H	3.500886	-1.124334	-1.706151
H	2.929587	-0.304035	-2.987924
H	0.996327	0.097544	-1.413660
H	-1.091724	2.192890	-0.434980
H	0.747476	2.366251	-0.387479
H	2.147651	0.457157	0.632935
H	-2.188892	0.295598	0.792019
H	-1.591227	-1.490739	-3.070186
H	2.257970	-0.477592	2.940904
H	-2.056482	-0.627049	3.098408
H	0.156610	-1.009457	4.147421

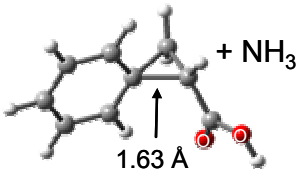


(**I2**)
+30.2 kcal/mol

Zero point vibrational energy	123.99907 kcal/mol
Electronic energy	-555.1522779 Hartree

C

C	-0.889059	0.112456	1.127212
C	0.174423	-0.207379	2.156897
C	-0.984603	1.446959	0.593747
C	-0.379423	0.320199	-0.405012
O	1.178128	0.448408	2.318290
C	-1.269876	-0.175354	-1.417775
C	1.024600	0.409572	-0.688329
O	-0.178148	-1.286581	2.859931
C	-0.777487	-0.550409	-2.649859
C	1.497763	0.035850	-1.932037
C	0.603618	-0.443953	-2.904093
H	-1.772575	-0.516202	1.162675
H	-0.237448	2.175629	0.891777
H	-1.940362	1.835604	0.260909
H	-2.333074	-0.245308	-1.204754
H	1.697010	0.774664	0.081003
H	0.490151	-1.454988	3.550024
H	-1.445968	-0.922754	-3.418418
H	2.556214	0.110776	-2.156506
H	0.986478	-0.739690	-3.876986



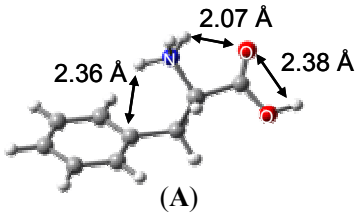
(**C**+NH_3)
+39.1 kcal/mol

Zero point vibrational energy	100.98724 kcal/mol
Electronic energy	-498.5687606 Hartree

Pathway 3

A

N	-1.167945	1.035679	-1.017583
C	0.166420	0.410832	-1.369865
C	0.057813	0.030268	-2.846740
C	0.431692	-0.817868	-0.457935
O	-1.011163	0.001629	-3.422463
C	0.271166	-0.472115	1.008472
O	1.239535	-0.282901	-3.361471
C	-0.917499	-0.797906	1.685185
C	1.281553	0.215916	1.700100
C	-1.093169	-0.439257	3.027522
C	1.105508	0.570401	3.038487
C	-0.083592	0.248261	3.702657
H	-1.879373	0.633601	-1.652613
H	-1.394926	0.836272	-0.028502
H	-1.175086	2.049989	-1.157865
H	0.939319	1.167448	-1.219337
H	1.445906	-1.159761	-0.683528
H	-0.251445	-1.627681	-0.738602
H	1.136304	-0.557110	-4.292137
H	-1.687203	-1.382429	1.183470
H	2.217741	0.454383	1.200504
H	-2.007920	-0.713489	3.543505
H	1.899690	1.088303	3.567013
H	-0.213715	0.519701	4.745348

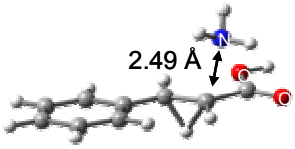


(**A**)
0.0 kcal/mol

Zero point vibrational energy 127.93612 kcal/mol
Electronic energy -555.2066902 Hartree

TS3

N	1.797560	1.269168	-1.911133
H	2.372193	0.901029	-2.667870
H	1.385659	2.140505	-2.241137
H	2.417658	1.507055	-1.139296
C	0.109856	-0.472047	-1.363683
C	-0.326504	-0.357695	-2.808243
C	-0.675715	-0.038248	-0.272815
O	0.331092	-0.811463	-3.710048
C	-0.316645	-0.068228	1.141075
O	-1.502301	0.279414	-2.928949
C	-1.277890	0.394156	2.065002
C	0.935255	-0.524130	1.608517
C	-0.993574	0.402577	3.427520
C	1.210427	-0.516916	2.970135
C	0.247604	-0.055279	3.879998
H	1.007631	-1.057287	-1.208053
H	-0.887770	-1.216518	-0.764638
H	-1.586589	0.497403	-0.537384
H	-1.759293	0.299454	-3.868830
H	-2.242762	0.746153	1.710452
H	1.694299	-0.875823	0.916615
H	-1.734708	0.761622	4.133615
H	2.173316	-0.865040	3.328990
H	0.470241	-0.051487	4.942421

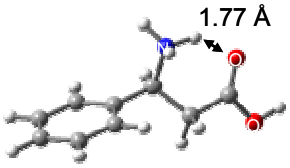


(**TS3**)
+43.6 kcal/mol

1 Imaginary Frequency -760.5438 cm^{-1}

Zero point vibrational energy 121.98779 kcal/mol
Electronic energy -555.1277784 Hartree

I3

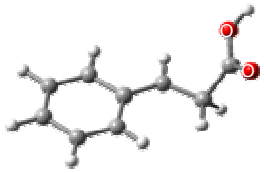


(**I3**)
-6.7 kcal/mol

N	1.446818	0.996932	0.825078
H	1.555804	0.973736	1.867504
H	2.352008	0.899413	0.357305
H	1.050509	1.897698	0.541073
C	-0.695971	-0.150082	1.411444
C	-0.299619	-0.158438	2.877607
C	0.508896	-0.168046	0.454866
O	0.754362	0.309610	3.296627
C	0.164467	-0.111678	-1.014842
O	-1.223030	-0.699218	3.658912
C	0.702188	-1.071587	-1.884031
C	-0.674317	0.891249	-1.529557
C	0.406812	-1.031005	-3.248701
C	-0.961924	0.934217	-2.894126
C	-0.422521	-0.027711	-3.754249
H	-1.327118	0.732318	1.244843
H	-1.325960	-1.016080	1.193471
H	1.109702	-1.058596	0.658722
H	-0.940428	-0.643397	4.591265
H	1.344576	-1.858883	-1.496936
H	-1.122590	1.638526	-0.877603
H	0.822449	-1.782439	-3.912140
H	-1.612309	1.710782	-3.283542
H	-0.653101	0.003753	-4.814292

Zero point vibrational energy 128.11625 kcal/mol
Electronic energy -555.2175942 Hartree

D



(**D**+NH_3)
+27.6 kcal/mol

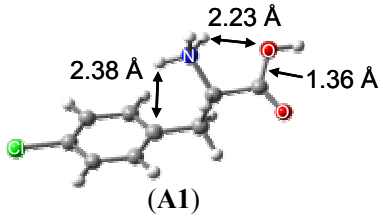
C	0.353364	0.859783	1.652251
C	0.164616	-0.137808	2.824316
C	-0.557899	0.583223	0.530168
O	1.089056	-0.602436	3.431609
C	-0.228446	0.270752	-0.786095
O	-1.136994	-0.371741	3.060702
C	-1.304934	0.045576	-1.711513
C	1.124693	0.168116	-1.256493
C	-1.040606	-0.259430	-3.031974
C	1.372351	-0.140547	-2.577744
C	0.294889	-0.352124	-3.462283
H	1.410971	0.876979	1.397962
H	0.075954	1.838459	2.078180
H	-1.618483	0.613411	0.777301
H	-1.220741	-0.964261	3.830767
H	-2.328929	0.119652	-1.357138
H	1.953374	0.327930	-0.576258
H	-1.851198	-0.428304	-3.732367
H	2.391480	-0.221901	-2.939854
H	0.502901	-0.593794	-4.500872

Zero point vibrational energy 100.77965 kcal/mol
Electronic energy -498.5868028 Hartree

PES of 4-Cl Phe (supplementary figure S1b)

Pathway 1

A1

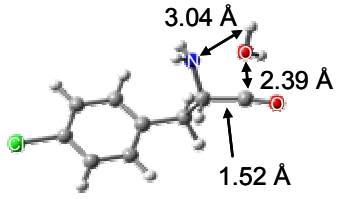


(**A1**)
+3.8 kcal/mol

N	-1.185647	-0.988891	1.798747
C	0.167149	-0.403073	2.179627
C	0.234799	-0.113853	3.677476
C	0.430292	0.867812	1.331558
O	1.265996	0.138261	4.237477
C	0.302966	0.590287	-0.152471
O	-0.992614	-0.138156	4.248462
C	-0.856076	0.963590	-0.853995
C	1.327333	-0.070723	-0.851400
C	-0.998075	0.680103	-2.215752
C	1.198482	-0.357663	-2.209110
C	0.030522	0.014609	-2.885376
Cl	-0.133821	-0.344066	-4.581705
H	-1.297805	-0.914048	0.773501
H	-1.279291	-1.970626	2.076831
H	-1.944205	-0.470589	2.257844
H	0.910660	-1.167398	1.942668
H	1.436842	1.205524	1.595509
H	-0.262588	1.659921	1.638719
H	-0.917668	0.088118	5.194424
H	-1.641268	1.526530	-0.352580
H	2.247767	-0.345212	-0.341438
H	-1.888305	0.987364	-2.753342
H	1.998942	-0.855596	-2.745238

Zero point vibrational energy	121.73661 kcal/mol
Electronic energy	-1014.789987 Hartree

TS1a



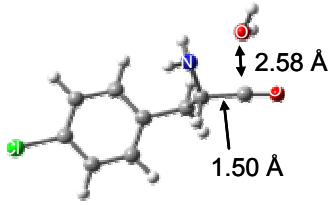
(**TS1a**)
+38.7 kcal/mol

N	0.516427	1.501455	2.094631
C	-0.461166	0.460230	2.071304
C	-0.787160	0.171799	3.522042
C	-0.146141	-0.852283	1.297000
O	-1.281873	0.089843	4.535467
C	-0.091696	-0.573169	-0.189694
O	1.473294	-0.430293	4.026662
C	1.138884	-0.422705	-0.843730
C	-1.273271	-0.455766	-0.937590
C	1.195566	-0.154313	-2.212142
C	-1.232274	-0.184942	-2.304272
C	0.006697	-0.031591	-2.934699
Cl	0.066442	0.304479	-4.644688
H	1.449109	1.191568	1.849076
H	0.247962	2.336446	1.589479
H	1.982657	0.275537	4.451999
H	-1.433130	0.850814	1.728494
H	-0.921214	-1.593728	1.526964
H	0.807430	-1.239069	1.664521
H	1.664272	-1.235698	4.530415
H	2.069185	-0.538918	-0.293236
H	-2.241564	-0.598308	-0.462201
H	2.150622	-0.049350	-2.714809

H	-2.147829	-0.105583	-2.879774

1 Imaginary Frequency	-76.293 cm^{-1}
Zero point vibrational energy	116.89889 kcal/mol
Electronic energy	-1014.726669 Hartree

I1a

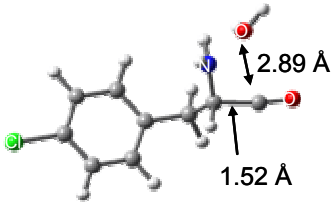


(**I1a**)
+38.6 kcal/mol

N	0.443800	1.508368	2.135968
C	-0.525246	0.458184	2.062542
C	-0.863228	0.205581	3.503307
C	-0.194009	-0.855221	1.293005
O	-1.237058	0.128031	4.565769
C	-0.117058	-0.573132	-0.191612
O	1.579289	-0.476024	3.985317
C	1.119729	-0.361962	-0.816626
C	-1.285521	-0.512427	-0.966511
C	1.194859	-0.091297	-2.183616
C	-1.225927	-0.240326	-2.332272
C	0.018531	-0.027597	-2.933941
Cl	0.101786	0.309359	-4.642717
H	1.403439	1.185049	2.103806
H	0.262945	2.292717	1.522536
H	2.043470	0.105202	4.605652
H	-1.481957	0.854525	1.685704
H	-0.972496	-1.596868	1.510192
H	0.755249	-1.238434	1.673903
H	1.873037	-1.371466	4.207861
H	2.040819	-0.428968	-0.243370
H	-2.256429	-0.701291	-0.513154
H	2.154957	0.060815	-2.664094
H	-2.130631	-0.205836	-2.928950

Zero point vibrational energy	116.86426 kcal/mol
Electronic energy	-1014.726776 Hartree

TS1b



(**TS1b**)
+38.1 kcal/mol

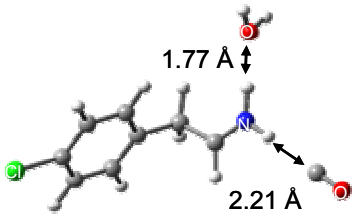
N	0.380349	1.464028	2.183634
C	-0.622725	0.486350	2.052326
C	-0.991954	0.180853	3.504007
C	-0.302701	-0.832103	1.284985
O	-1.174467	0.082527	4.614815
C	-0.180156	-0.554852	-0.196670
C	1.072189	-0.325452	-0.782309
C	-1.324040	-0.518413	-1.008418
C	1.186657	-0.061651	-2.147487
C	-1.225231	-0.253043	-2.373353
C	0.034096	-0.023043	-2.935674
Cl	0.167151	0.305234	-4.643428
O	1.794111	-0.474873	3.896305
H	1.330032	1.157067	2.346867
H	0.215269	2.403684	1.857782
H	-1.547870	0.918894	1.647853
H	-1.109177	-1.548584	1.483616
H	0.623014	-1.245821	1.691016
H	1.974115	-0.366721	-0.177565
H	-2.305552	-0.720062	-0.584566
H	2.158690	0.105935	-2.597754
H	-2.110761	-0.237006	-2.998810

H	2.266718	-1.317376	3.834137
H	2.167555	-0.040283	4.676859

1 Imaginary Frequency -276.9799 cm^{-1}
Zero point vibrational energy 116.06216 kcal/mol
Electronic energy -1014.726206 Hartree

I1b

N	-0.385043	0.174686	2.789280
C	-0.256333	0.951623	1.768247
C	2.145445	-0.191730	4.781958
C	-1.306034	1.168978	0.740386
O	3.011899	-0.340060	5.494634
C	-0.737924	0.697706	-0.598201
C	-0.705330	-0.670897	-0.903187
C	-0.226141	1.616939	-1.524234
C	-0.185356	-1.117391	-2.117262
C	0.298030	1.182137	-2.740884
C	0.317385	-0.185635	-3.030004
Cl	0.970016	-0.735569	-4.549400
O	-2.830983	-1.115794	3.269072
H	-1.274577	-0.323196	2.987404
H	0.396765	0.036682	3.437341
H	0.707674	1.443390	1.638475
H	-1.519713	2.244225	0.694396
H	-2.228604	0.645065	1.007051
H	-1.105765	-1.399847	-0.203037
H	-0.251672	2.682509	-1.311707
H	-0.172972	-2.174561	-2.357835
H	0.680135	1.895548	-3.462523
H	-3.009012	-2.061424	3.169390
H	-3.526991	-0.770071	3.845323

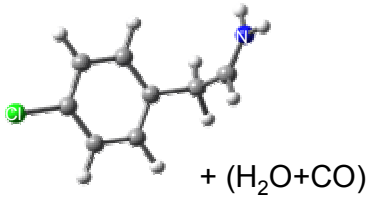


(**I1b**)
+6.4 kcal/mol

Zero point vibrational energy 116.10666 kcal/mol
Electronic energy -1014.7767994 Hartree

B

N	-0.866264	0.672390	-3.829542
C	0.181133	0.544927	-3.074998
C	0.600210	-0.717468	-2.429726
C	0.378368	-0.461970	-0.934980
C	-0.901454	-0.615328	-0.379203
C	1.441606	-0.052979	-0.115334
C	-1.114676	-0.393547	0.979398
C	1.237149	0.175624	1.243118
C	-0.042438	0.005322	1.784930
Cl	-0.300898	0.287234	3.480330
H	-1.436705	-0.128836	-4.090129
H	-1.160265	1.577109	-4.188564
H	0.739860	1.455569	-2.864353
H	1.662513	-0.891887	-2.633043
H	0.027498	-1.574892	-2.796094
H	-1.737428	-0.938288	-0.994926
H	2.441118	0.063060	-0.525985
H	-2.098326	-0.532272	1.413615
H	2.061458	0.473238	1.881440



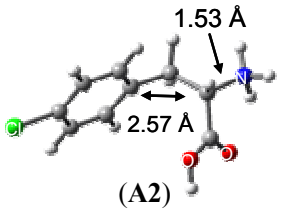
(**B**+H_2O+CO)
+25.1 kcal/mol

Zero point vibrational energy 96.94229 kcal/mol

Electronic energy -824.9913795 Hartree

Pathway 2

A2

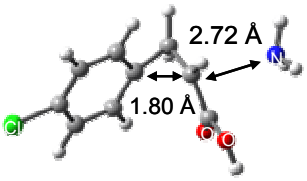


(**A2**)
+5.1 kcal/mol

N	-1.014875	-0.034309	3.862478
C	-0.551803	-0.363035	2.447334
C	0.978058	-0.352721	2.557343
C	-1.108878	0.710094	1.474626
C	-0.733489	0.475286	0.026521
O	1.532297	0.274337	3.440634
C	-1.377439	-0.519089	-0.723546
C	0.252794	1.256313	-0.589232
O	1.562197	-1.066849	1.612296
C	-1.034968	-0.744535	-2.055615
C	0.603158	1.044816	-1.923165
C	-0.040576	0.039472	-2.647963
Cl	0.391417	-0.233605	-4.316036
H	-0.276360	0.566881	4.276769
H	-1.915426	0.454556	3.870466
H	-1.095723	-0.867987	4.453793
H	-0.919703	-1.357617	2.187993
H	-0.753799	1.695017	1.800951
H	-2.202372	0.700575	1.579987
H	-2.167390	-1.120193	-0.278462
H	0.748786	2.049344	-0.034835
H	2.532632	-0.995363	1.689467
H	-1.538632	-1.511073	-2.633816
H	1.360909	1.657793	-2.398312

Zero point vibrational energy 121.77444 kcal/mol
Electronic energy -1014.787963 Hartree

TS2



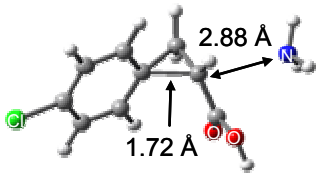
(**TS2**)
+30.7 kcal/mol

N	0.911982	-0.375414	-4.418767
C	0.521856	-0.104039	-1.741977
C	-0.903890	-0.200033	-2.219849
C	1.112837	1.163940	-1.414972
C	0.624166	0.546271	-0.067019
O	-1.611659	0.762953	-2.413813
C	1.535402	-0.211255	0.730897
C	-0.598844	0.992545	0.520930
O	-1.274895	-1.478543	-2.369534
C	1.250672	-0.495281	2.049624
C	-0.880713	0.715551	1.842839
C	0.041168	-0.029597	2.605024
Cl	-0.317504	-0.382518	4.247470
H	0.357470	0.294835	-4.948819
H	1.886344	-0.210276	-4.664085
H	0.672771	-1.302255	-4.766260
H	1.115058	-1.007536	-1.783553
H	0.555279	2.051074	-1.702560
H	2.192676	1.259474	-1.476684
H	2.470970	-0.554519	0.298092
H	-1.304229	1.558862	-0.078609
H	-2.198347	-1.503237	-2.678983
H	1.942725	-1.063338	2.660691
H	-1.800517	1.063717	2.298930

1 Imaginary Frequency	-85.8718 cm^{-1}
Zero point vibrational energy	117.72879 kcal/mol
Electronic energy	-1014.740763 Hartree

I2

N	0.936557	0.297270	4.526322
C	0.516835	0.084940	1.689253
C	-0.884108	0.213441	2.233035
C	1.070166	-1.201814	1.380207
C	0.567515	-0.485680	0.065975
O	-1.622196	-0.729096	2.414848
C	1.516660	0.217860	-0.743639
C	-0.662655	-0.911796	-0.531070
O	-1.201647	1.497539	2.440775
C	1.258321	0.475888	-2.071046
C	-0.917598	-0.661434	-1.861992
C	0.039571	0.034005	-2.629867
Cl	-0.284922	0.353320	-4.283647
H	0.335433	-0.335577	5.051653
H	1.893824	0.066119	4.785743
H	0.758410	1.234133	4.883635
H	1.152477	0.954989	1.790052
H	0.478258	-2.075062	1.637632
H	2.146468	-1.335105	1.410558
H	2.455701	0.543907	-0.305123
H	-1.393262	-1.438416	0.074754
H	-2.109971	1.543022	2.789935
H	1.974852	1.005498	-2.688393
H	-1.841915	-0.990837	-2.322832

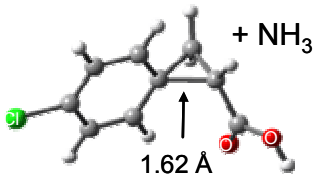


(**I2**)
+30.7 kcal/mol

Zero point vibrational energy	117.76232 kcal/mol
Electronic energy	-1014.740812 Hartree

C

C	0.805830	-0.075170	-2.030274
C	-0.444646	-0.281337	-2.856311
C	1.202644	1.264965	-1.657142
C	0.597503	0.351444	-0.481924
O	-1.351771	0.517102	-2.923311
C	1.541193	-0.217289	0.446211
C	-0.714071	0.697303	0.000155
O	-0.380464	-1.446750	-3.505954
C	1.204802	-0.414638	1.762309
C	-1.045447	0.505211	1.321303
C	-0.091187	-0.051838	2.201053
Cl	-0.509112	-0.293850	3.840839
H	1.560991	-0.847192	-2.133680
H	0.548473	2.087351	-1.928751
H	2.252090	1.502762	-1.523902
H	2.534351	-0.486735	0.097233
H	-1.436988	1.115206	-0.692940
H	-1.170772	-1.545766	-4.068719
H	1.912561	-0.839221	2.465123
H	-2.027633	0.774328	1.693208

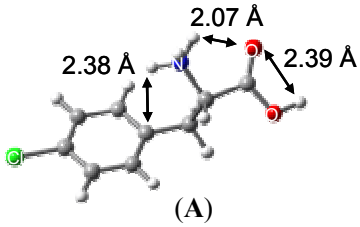


(**C**+NH_3)
+37.2 kcal/mol

Zero point vibrational energy	94.94054 kcal/mol
Electronic energy	-958.161466 Hartree

Pathway 3

A

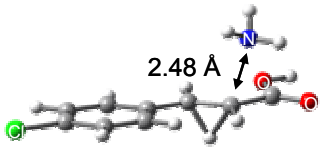


(**A**)
0.0 kcal/mol

N	-1.203228	-1.000198	1.772761
C	0.140774	-0.433300	2.181412
C	0.012018	-0.126081	3.674144
C	0.460197	0.834280	1.341700
C	0.331676	0.574982	-0.144735
O	-1.068082	-0.096499	4.228498
O	1.190740	0.126684	4.226671
C	-0.819627	0.981508	-0.840771
C	1.337598	-0.106661	-0.849626
C	-0.972424	0.708404	-2.203778
C	1.198263	-0.382186	-2.208612
C	0.037466	0.021242	-2.879566
Cl	-0.140094	-0.325410	-4.577129
H	-1.915437	-0.608699	2.413986
H	-1.405262	-0.748286	0.791500
H	-1.242497	-2.019602	1.863441
H	0.895176	-1.203255	2.006710
H	1.475826	1.137559	1.612075
H	-0.209274	1.645997	1.648507
H	1.076926	0.356084	5.168258
H	-1.588075	1.563287	-0.334682
H	2.251531	-0.408075	-0.343268
H	-1.856376	1.040260	-2.737097
H	1.984755	-0.896508	-2.749933

Zero point vibrational energy	121.82567 kcal/mol
Electronic energy	-1014.796154 Hartree

TS3

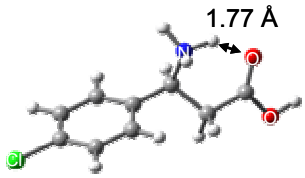


(**TS3**)
+43.1 kcal/mol

N	1.837524	1.271237	-2.676342
C	0.132048	-0.470233	-2.214821
C	-0.233417	-0.363183	-3.678588
C	-0.711802	-0.038807	-1.165117
O	0.475186	-0.807605	-4.545995
C	-0.424652	-0.060715	0.263007
O	-1.410223	0.258049	-3.859030
C	-1.428211	0.402754	1.140886
C	0.800766	-0.513412	0.799924
C	-1.220266	0.419945	2.513693
C	1.014391	-0.503323	2.169393
C	0.001442	-0.036546	3.024411
Cl	0.273601	-0.023078	4.733418
H	2.438546	0.902767	-3.412174
H	1.437266	2.142396	-3.020883
H	2.429846	1.509417	-1.883074
H	1.020704	-1.055240	-2.013229
H	-0.898777	-1.215320	-1.660621
H	-1.607779	0.495843	-1.477749
H	-1.619999	0.274263	-4.810648
H	-2.376404	0.753529	0.743174
H	1.596957	-0.868741	0.153367
H	-1.990513	0.779297	3.186421
H	1.954759	-0.846981	2.585165

1 Imaginary Frequency	-778.1234 cm^{-1}
Zero point vibrational energy	115.91224 kcal/mol
Electronic energy	-1014.718107 Hartree

I3

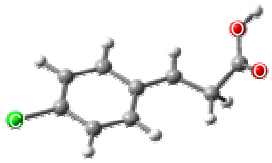


(**I3**)
-6.7 kcal/mol

N	1.414344	1.055240	1.757875
C	-0.710084	-0.185152	2.209210
C	-0.406548	-0.172576	3.697773
C	0.550944	-0.147836	1.328558
O	0.607590	0.323167	4.178476
C	0.298107	-0.104972	-0.158953
O	-1.365789	-0.728716	4.422513
C	0.957796	-1.014995	-0.997823
C	-0.575442	0.836014	-0.729772
C	0.756664	-0.990743	-2.377551
C	-0.778696	0.874615	-2.107321
C	-0.110020	-0.042094	-2.926565
Cl	-0.366470	-0.001160	-4.646420
H	1.464751	1.027079	2.804945
H	2.348442	1.002234	1.342624
H	0.995369	1.940707	1.458652
H	-1.373966	0.663631	2.000679
H	-1.282485	-1.081856	1.958073
H	1.175326	-1.012291	1.570254
H	-1.145536	-0.661202	5.370806
H	1.628796	-1.759998	-0.577430
H	-1.120832	1.546176	-0.112140
H	1.263983	-1.700927	-3.020788
H	-1.455002	1.600308	-2.544918

Zero point vibrational energy	121.94154 kcal/mol
Electronic energy	-1014.807042 Hartree

D



(**D**+NH_3)
+25.3 kcal/mol

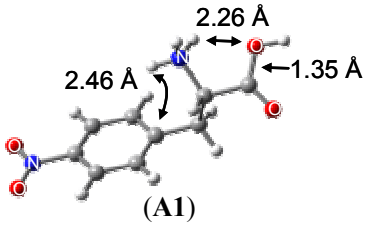
C	-0.329420	0.857042	-2.555814
C	-0.285377	-0.222141	-3.665915
C	0.631470	0.587031	-1.471118
O	-1.276032	-0.666873	-4.177266
C	0.361922	0.372115	-0.125490
O	0.979999	-0.553764	-3.974402
C	1.469872	0.133944	0.760300
C	-0.964935	0.376737	0.427771
C	1.272342	-0.078625	2.104612
C	-1.164051	0.160664	1.770027
C	-0.046605	-0.065378	2.610478
Cl	-0.303712	-0.330831	4.279754
H	-1.365156	0.963437	-2.239958
H	-0.018625	1.787004	-3.059706
H	1.674974	0.535931	-1.778918
H	0.971206	-1.198624	-4.705799
H	2.477260	0.124106	0.354657
H	-1.823442	0.545898	-0.212023
H	2.105227	-0.256714	2.775162
H	-2.161379	0.159862	2.195015

Zero point vibrational energy	94.75608 kcal/mol
Electronic energy	-958.1800595 Hartree

PES of 4-NO_2 Phe (figure 3d)

Pathway 1

A1

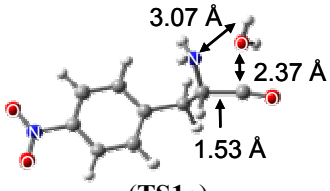


(**A1**)
3.8 kcal/mol

N	-1.138592	1.082059	-2.099276
C	0.173384	0.386323	-2.442054
C	0.263029	0.104526	-3.942515
C	0.312850	-0.907429	-1.604559
O	1.274796	-0.277932	-4.461538
C	0.229175	-0.634876	-0.115206
C	-0.956387	-0.901263	0.591469
C	1.327648	-0.090506	0.572034
C	-1.052947	-0.623942	1.957846
C	1.246337	0.189515	1.934962
C	0.051410	-0.076499	2.602408
N	-0.043951	0.226790	4.052172
O	0.953844	0.694272	4.592748
O	-1.116221	-0.006932	4.602930
O	-0.922475	0.308234	-4.561205
H	-1.277507	1.059984	-1.077133
H	-1.154465	2.056872	-2.416314
H	-1.928706	0.608126	-2.553166
H	0.968273	1.088344	-2.178165
H	1.280311	-1.339885	-1.876661
H	-0.454932	-1.627424	-1.911306
H	-1.797878	-1.374494	0.089947
H	2.262607	0.094579	0.049438
H	-1.954439	-0.836196	2.520324
H	2.087374	0.598220	2.482493
H	-0.839374	0.093708	-5.509520

Zero point vibrational energy	129.23178 kcal/mol
Electronic energy	-759.6958448 Hartree

TS1a



(**TS1a**)
+37.8 kcal/mol

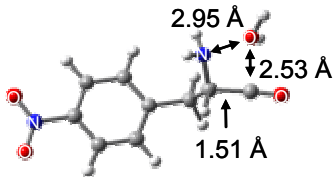
N	0.487016	1.520038	2.367888
C	-0.457675	0.456575	2.338981
C	-0.782683	0.162354	3.801092
C	-0.100592	-0.844504	1.574658
O	-1.287448	0.125887	4.812379
C	-0.065131	-0.583630	0.081391
C	1.160261	-0.432138	-0.582802
C	-1.259759	-0.491350	-0.650216
C	1.200018	-0.182735	-1.955089
C	-1.237423	-0.239970	-2.020668
C	-0.002852	-0.085423	-2.648355
N	0.030202	0.184822	-4.105804
O	-1.049040	0.262430	-4.687063
O	1.134226	0.315744	-4.627864
H	1.433869	1.255487	2.126607
H	0.189631	2.377230	1.920515
H	-1.440162	0.820198	1.997145
H	-0.847357	-1.612115	1.812623
H	0.867681	-1.197254	1.937434
H	2.094784	-0.530236	-0.037180
H	-2.218863	-0.637919	-0.158957

H	2.137549	-0.069565	-2.485995
H	-2.148676	-0.172981	-2.602629
O	1.452979	-0.424346	4.309395
H	1.628574	-1.235451	4.810247
H	1.951727	0.275786	4.756875

1 Imaginary Frequency -63.906 cm^{-1}
Zero point vibrational energy 124.42491 kcal/mol
Electronic energy -759.6338959 Hartree

I1a

N	0.467307	1.518443	2.411747
C	-0.493203	0.469455	2.331177
C	-0.848870	0.210533	3.780163
C	-0.147182	-0.839057	1.571434
O	-1.258860	0.185994	4.831895
C	-0.091935	-0.578141	0.079197
C	1.139272	-0.383846	-0.562822
C	-1.275938	-0.527926	-0.673587
C	1.194714	-0.135212	-1.934638
C	-1.237774	-0.278262	-2.044047
C	0.001798	-0.082212	-2.649728
N	0.051744	0.185071	-4.107290
O	-1.018895	0.223794	-4.707977
O	1.159860	0.352274	-4.609965
H	1.433435	1.221077	2.358108
H	0.258446	2.349229	1.874143
H	-1.451245	0.860981	1.952770
H	-0.909448	-1.593727	1.801369
H	0.812076	-1.204299	1.944449
H	2.066197	-0.445481	0.000445
H	-2.237839	-0.706770	-0.198780
H	2.136936	0.010567	-2.449012
H	-2.140201	-0.244503	-2.642396
O	1.518124	-0.508071	4.285553
H	1.760106	-1.408331	4.548727
H	1.991062	0.072725	4.900050

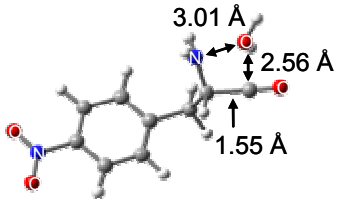


(**I1a**)
+37.8 kcal/mol

Zero point vibrational energy 124.36791 kcal/mol
Electronic energy -759.6339554 Hartree

TS1b

N	0.482346	1.508779	2.417059
C	-0.477335	0.493571	2.318713
C	-0.884465	0.192417	3.790619
C	-0.115443	-0.806660	1.564704
O	-1.275547	0.238268	4.849752
C	-0.069580	-0.556864	0.069765
C	1.152788	-0.326433	-0.576415
C	-1.255756	-0.553610	-0.680776
C	1.197274	-0.087388	-1.950001
C	-1.229028	-0.313487	-2.053343
C	0.001850	-0.080679	-2.663225
N	0.040186	0.176286	-4.122662
O	1.493539	-0.596695	4.321425
O	-1.032335	0.176633	-4.721498
O	1.141366	0.373981	-4.629807
H	1.458143	1.255205	2.470879



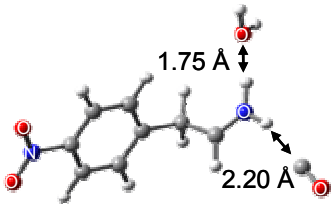
(**TS1b**)
+37.2 kcal/mol

H	0.249975	2.454484	2.154784
H	-1.428186	0.890620	1.932340
H	-0.866824	-1.569819	1.802562
H	0.849233	-1.160269	1.935228
H	2.081762	-0.348327	-0.013829
H	-2.210054	-0.760585	-0.202117
H	2.132964	0.086678	-2.467400
H	-2.133363	-0.314616	-2.649722
H	1.734106	-1.523624	4.466426
H	1.936498	-0.107900	5.030837

1 Imaginary Frequency	-260.3274 cm^{-1}
Zero point vibrational energy	123.64199 kcal/mol
Electronic energy	-759.633703 Hartree

I1b

N	-0.337502	0.153796	3.118400
C	-0.206050	0.890395	2.070785
C	2.203859	-0.213811	5.070659
C	-1.280099	1.122729	1.068642
O	3.077417	-0.364338	5.773733
C	-0.773731	0.704143	-0.311294
C	-0.744061	-0.655300	-0.656822
C	-0.326216	1.664721	-1.228575
C	-0.279068	-1.056577	-1.908234
C	0.141923	1.276944	-2.483701
C	0.159303	-0.079550	-2.798773
N	0.658642	-0.499355	-4.130609
O	-2.801345	-1.053504	3.650623
O	1.032163	0.386042	-4.894953
O	0.665708	-1.703609	-4.372978
H	-1.237621	-0.315331	3.347473
H	0.452230	0.019726	3.759842
H	0.769059	1.349641	1.906041
H	-1.499439	2.198973	1.068086
H	-2.193457	0.590041	1.349914
H	-1.101325	-1.408098	0.040686
H	-0.356714	2.721131	-0.977155
H	-0.255027	-2.099635	-2.199583
H	0.482711	2.002934	-3.212019
H	-2.995390	-1.999094	3.583546
H	-3.479707	-0.680268	4.231099

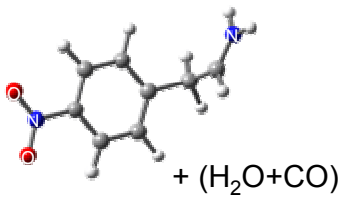


(**I1b**)
+5.8 kcal/mol

Zero point vibrational energy	123.64989 kcal/mol
Electronic energy	-759.6837137 Hartree

B

N	-0.796061	0.695848	-4.212024
C	0.179129	0.564014	-3.372537
C	0.537806	-0.702926	-2.695595
C	0.353212	-0.470233	-1.191555
C	-0.930824	-0.547971	-0.630900
C	1.456302	-0.166779	-0.380773
C	-1.114751	-0.340730	0.735499
C	1.283184	0.045256	0.986142
C	-0.001661	-0.043195	1.517455
N	-0.191650	0.184832	2.972629
O	0.809925	0.443066	3.633034



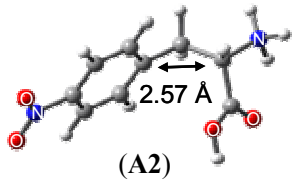
(**B**+H_2O+CO)
+25.8 kcal/mol

O	-1.337072	0.101257	3.406079
H	-1.362837	-0.098812	-4.502937
H	-1.033643	1.597736	-4.619669
H	0.735593	1.468818	-3.129413
H	1.591899	-0.917948	-2.912606
H	-0.065776	-1.540050	-3.060460
H	-1.791204	-0.795861	-1.246962
H	2.455733	-0.116716	-0.803509
H	-2.093409	-0.408689	1.195097
H	2.120417	0.267568	1.636910

Zero point vibrational energy 104.44201 kcal/mol
Electronic energy -569.8962009 Hartree

Pathway 2

A2

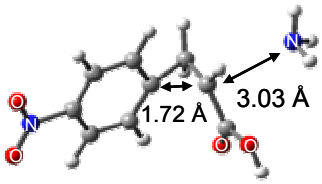


(**A2**)
+4.0 kcal/mol

N	-0.976965	0.086298	4.128880
C	-0.585223	-0.285666	2.703754
C	0.930934	-0.511990	2.794073
C	-0.982500	0.873017	1.752435
C	-0.669582	0.598682	0.294142
O	1.580553	-0.005940	3.689014
C	-1.458512	-0.297548	-0.442496
C	0.400585	1.250846	-0.332956
O	1.389823	-1.275320	1.818839
C	-1.176350	-0.556518	-1.781990
C	0.693787	1.005480	-1.674360
C	-0.098410	0.099198	-2.373239
N	0.209863	-0.171820	-3.797665
O	1.169984	0.417783	-4.286907
O	-0.514394	-0.969790	-4.387306
H	-1.183464	-0.736353	4.705314
H	-0.147459	0.552348	4.546002
H	-1.788094	0.711712	4.159983
H	-1.102576	-1.209167	2.436345
H	-0.474304	1.787885	2.079233
H	-2.062573	1.033075	1.869990
H	-2.310592	-0.790853	0.018835
H	1.006069	1.965025	0.218512
H	2.359690	-1.364147	1.888258
H	-1.775929	-1.242250	-2.368245
H	1.512836	1.504511	-2.178044

Zero point vibrational energy 129.22375 kcal/mol
Electronic energy -759.6954823 Hartree

TS2



(**TS2**)
+38.7 kcal/mol

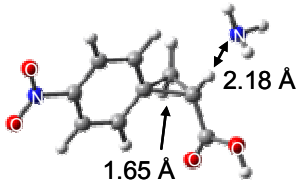
N	1.738440	-0.409331	-4.588911
C	0.273264	0.180244	-2.000791
C	-1.069710	-0.327123	-2.483958
C	0.446255	1.559491	-1.677943
C	0.266091	0.673998	-0.348556
O	-2.062781	0.362387	-2.531507
C	1.440529	0.272305	0.355334
C	-0.985160	0.725942	0.333088
O	-0.989923	-1.610383	-2.844711
C	1.370553	-0.053630	1.698112

C	-1.051224	0.407889	1.680285
C	0.124669	0.023024	2.329072
N	0.048062	-0.329931	3.781764
O	-1.055221	-0.253520	4.307128
O	1.095990	-0.665061	4.319938
H	1.542833	-1.373471	-4.852949
H	1.322694	0.176041	-5.311470
H	2.746439	-0.288012	-4.671887
H	1.129951	-0.448575	-2.209201
H	-0.392413	2.232250	-1.831746
H	1.435503	1.999931	-1.741224
H	2.393459	0.231259	-0.163903
H	-1.879972	1.018972	-0.206321
H	-1.860750	-1.903869	-3.171134
H	2.243421	-0.358563	2.262939
H	-1.982802	0.448659	2.232272

1 Imaginary Frequency	-57.6731 cm^{-1}
Zero point vibrational energy	124.69268 kcal/mol
Electronic energy	-759.6330417 Hartree

I2

N	3.147749	-0.436174	-2.771634
C	0.042361	0.379920	-2.135974
C	-1.118906	-0.384507	-2.737408
C	-0.148676	1.740815	-1.736101
C	-0.065328	0.655597	-0.508682
O	-2.279693	-0.066919	-2.611365
C	1.183259	0.567604	0.181119
C	-1.284361	0.401000	0.190099
O	-0.667572	-1.426698	-3.441738
C	1.211731	0.245308	1.525626
C	-1.250837	0.088239	1.539352
C	-0.007455	0.016202	2.172510
N	0.023166	-0.327234	3.630403
O	-1.059176	-0.497977	4.176246
O	1.129046	-0.408161	4.150548
H	3.104167	-1.445808	-2.905501
H	3.297069	-0.038076	-3.698086
H	4.007632	-0.260318	-2.253796
H	1.053668	0.030722	-2.372659
H	-1.138701	2.179864	-1.814086
H	0.692254	2.425350	-1.717280
H	2.104458	0.742474	-0.366134
H	-2.228827	0.457398	-0.340865
H	-1.422867	-1.879285	-3.861521
H	2.138893	0.167970	2.080738
H	-2.155720	-0.099453	2.105036

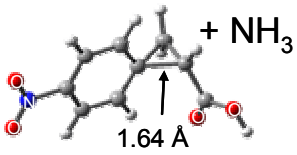


(**I2**)
+36.3 kcal/mol

Zero point vibrational energy	125.0117 kcal/mol
Electronic energy	-759.6372632 Hartree

C

C	0.807364	0.002400	2.321237
C	-0.443532	0.348506	3.108762
C	1.075866	-1.363946	1.979053
C	0.575821	-0.401305	0.747186
O	-1.415950	-0.367078	3.171417



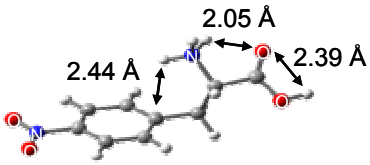
(**C**+NH_3)
+46.4 kcal/mol

C	1.592339	0.053389	-0.153706
C	-0.746601	-0.642718	0.258259
O	-0.282867	1.520925	3.722440
C	1.300391	0.253512	-1.488952
C	-1.031667	-0.448255	-1.083109
C	-0.006473	-0.002961	-1.921296
N	-0.322271	0.212766	-3.371094
O	0.598877	0.601575	-4.077435
O	-1.472352	-0.018505	-3.719375
H	1.628482	0.705816	2.415107
H	0.332676	-2.116434	2.224331
H	2.094922	-1.706778	1.838348
H	2.597522	0.237233	0.214993
H	-1.517561	-0.978869	0.943794
H	-1.068763	1.716285	4.266785
H	2.045688	0.596024	-2.197117
H	-2.019769	-0.629715	-1.489561

Zero point vibrational energy 102.00012 kcal/mol
Electronic energy -703.0519218 Hartree

Pathway 3

A

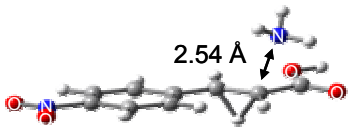


(**A**)
0.0 kcal/mol

N	-1.113900	1.137006	-2.071781
C	0.168592	0.418375	-2.444308
C	0.045841	0.138568	-3.945233
C	0.319506	-0.883283	-1.615263
C	0.240193	-0.624581	-0.123720
O	-1.014516	0.246854	-4.526454
C	-0.945719	-0.899508	0.579280
C	1.335880	-0.081096	0.567904
O	1.200128	-0.250115	-4.466939
C	-1.045048	-0.630268	1.947417
C	1.251885	0.189815	1.932314
C	0.056553	-0.083211	2.596563
N	-0.041039	0.211393	4.047928
O	0.954981	0.678973	4.591941
O	-1.112840	-0.028924	4.596500
H	-1.843131	0.837280	-2.744094
H	-1.386962	0.912803	-1.103318
H	-1.028782	2.154652	-2.156064
H	1.001133	1.096057	-2.243448
H	1.285604	-1.315820	-1.891727
H	-0.451501	-1.599149	-1.922284
H	-1.784206	-1.374545	0.074170
H	2.270515	0.111861	0.047652
H	1.089974	-0.454513	-5.414946
H	-1.946831	-0.848551	2.507159
H	2.090634	0.597963	2.483753

Zero point vibrational energy 129.32452 kcal/mol
Electronic energy -759.7020173 Hartree

TS3



(**TS3**)
+45.9 kcal/mol

N	1.790708	1.381062	-2.983486
H	2.408546	1.022739	-3.710656
H	1.352374	2.223073	-3.353932

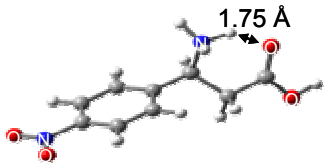
H	2.376726	1.674897	-2.203991
C	0.141348	-0.480476	-2.485627
C	-0.215330	-0.376111	-3.956142
C	-0.718263	-0.075795	-1.444424
O	0.517067	-0.790594	-4.816625
C	-0.440156	-0.089552	-0.010426
O	-1.414444	0.197796	-4.137617
C	-1.483968	0.300464	0.854485
C	0.814635	-0.452907	0.524459
C	-1.285066	0.329604	2.231563
C	1.019494	-0.429059	1.897625
C	-0.036093	-0.038381	2.724460
N	0.187428	-0.010022	4.196514
O	1.301913	-0.332862	4.594362
O	-0.759738	0.333656	4.894892
H	1.073575	-0.992545	-2.281490
H	-0.808776	-1.284904	-1.966336
H	-1.650881	0.389802	-1.761311
H	-1.623337	0.214098	-5.089728
H	-2.450952	0.582433	0.448483
H	1.635957	-0.744947	-0.121382
H	-2.070280	0.626799	2.916195
H	1.972116	-0.699410	2.337025

1 Imaginary Frequency	-751.1807 cm^{-1}
Zero point vibrational energy	123.225 kcal/mol
Electronic energy	-759.619106 Hartree

I3

N	0.857873	1.540005	2.052223
H	0.117956	2.182232	1.752886
H	0.897113	1.518078	3.102448
H	1.739524	1.881435	1.659258
C	-0.569769	-0.471719	2.468308
C	-0.317927	-0.340345	3.961489
C	0.573545	0.095773	1.608657
O	0.396368	0.528728	4.452025
C	0.338958	0.040578	0.114326
O	-0.972470	-1.243211	4.673475
C	1.304163	-0.557477	-0.708638
C	-0.822224	0.583467	-0.461392
C	1.121090	-0.614369	-2.090765
C	-1.013824	0.540192	-1.840862
C	-0.035087	-0.060039	-2.630321
N	-0.235614	-0.110313	-4.101546
O	-1.263804	0.395376	-4.541712
O	0.641904	-0.651949	-4.766289
H	-1.525666	0.021137	2.248927
H	-0.709566	-1.524859	2.210398
H	1.496089	-0.437425	1.853665
H	-0.815081	-1.095787	5.625452
H	2.201657	-0.990970	-0.275864
H	-1.598617	1.034827	0.151872
H	1.852683	-1.076530	-2.742710
H	-1.901435	0.952103	-2.305868

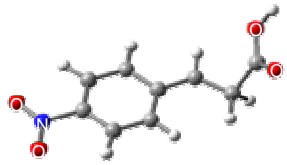
Zero point vibrational energy	129.42474 kcal/mol
Electronic energy	-759.7119592 Hartree



(**I3**)
-6.1 kcal/mol

D

C	-0.349439	0.849281	-2.848491
C	-0.289608	-0.259694	-3.941207
C	0.621051	0.614861	-1.775046
O	-1.278637	-0.720120	-4.436438
C	0.366849	0.404143	-0.415132
O	0.978605	-0.578559	-4.237783
C	1.491724	0.203657	0.451255
C	-0.954049	0.385022	0.140576
C	1.309658	-0.000580	1.807180
C	-1.134289	0.177923	1.494323
C	0.000054	-0.008721	2.296653
N	-0.203957	-0.230982	3.763384
O	-1.359515	-0.192385	4.166535
O	0.802558	-0.431597	4.430896
H	-1.385190	0.948231	-2.531307
H	-0.049000	1.765165	-3.384939
H	1.663827	0.582093	-2.089439
H	0.987750	-1.236577	-4.958217
H	2.494242	0.214079	0.034231
H	-1.821098	0.527422	-0.493868
H	2.139865	-0.154534	2.486290
H	-2.118492	0.156934	1.947207



(**D**+NH_3)
+34.3 kcal/mol

Zero point vibrational energy	101.79959 kcal/mol
Electronic energy	-703.0708092 Hartree