

Electronic Supplementary Information for:

Mechanistic Insights into the Formation of Oxenium Ion and Radical Intermediates through the Photolysis of Phenylhydroxylamine and its Substitutes

Yumei Yang, Weihai Fang and Xuebo Chen *

Key Laboratory of Theoretical and Computational Photochemistry of Ministry of Education, †
Department of Chemistry, Beijing Normal University, Xin-wai-da-jie No. 19, Beijing, 100875, People's
Republic of China

Email: xuebochen@bnu.edu.cn

Contents

Section 1. Molecular orbitals of **1**, **2** and **3** (Figure S-1.1 to S-1.3)

Section 2. Schematic structures with selective parameters

Section 3. MEPs for the photolysis of **1** and **2** leading to produce HBD

Section 4. Charge Translocation Calculations and Solvent effects

Section 5. Tables (S5-1 to S5-6)

Section 6. Cartesian Coordinates

Section 1. Molecular orbitals

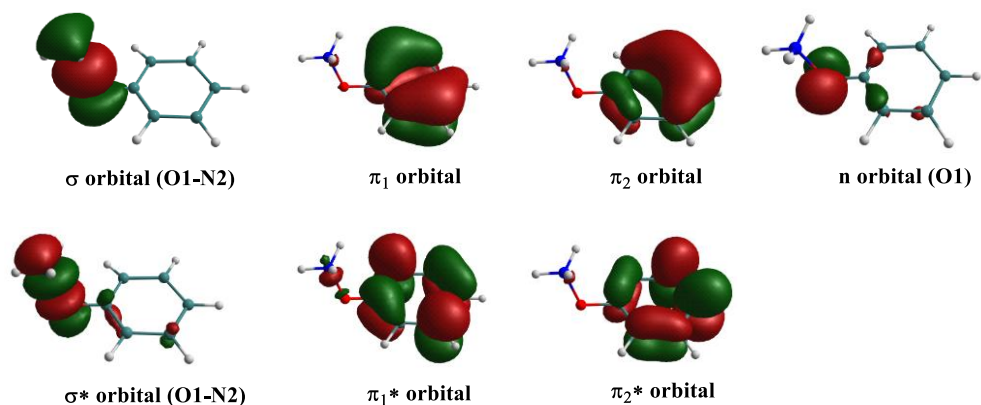


Figure S-1.1 Molecular orbitals of phenylhydroxylamine (1) used in defining the active space for the CASSCF(8e/7o)/CASPT2 calculations.

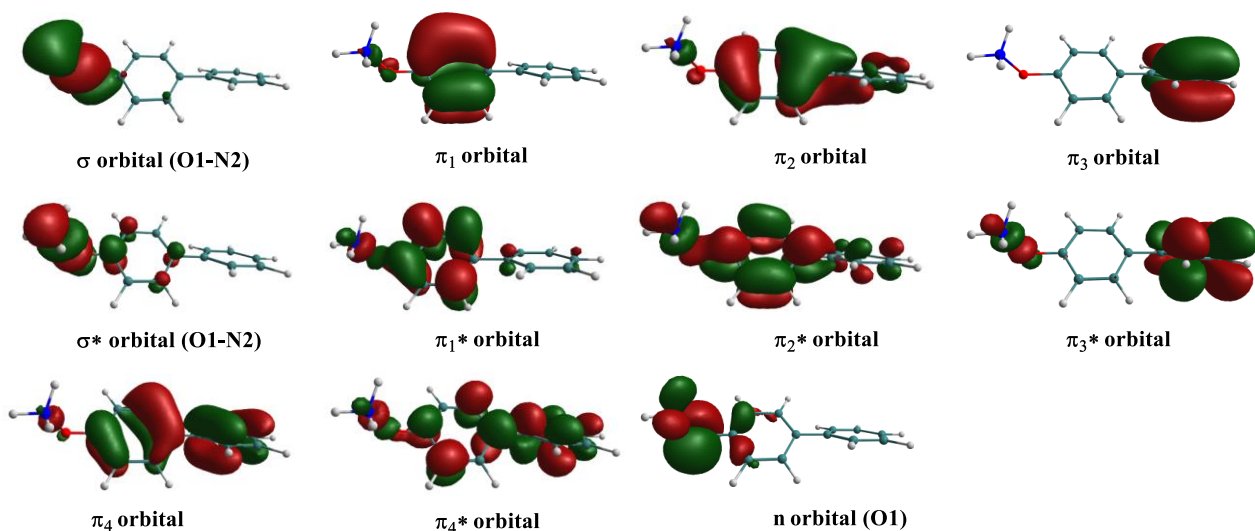


Figure S-1.2 Molecular orbitals of para-biphenyl-hydroxylamine (2) used in defining the active space for the CASSCF(12e/11o)/CASPT2 calculations.

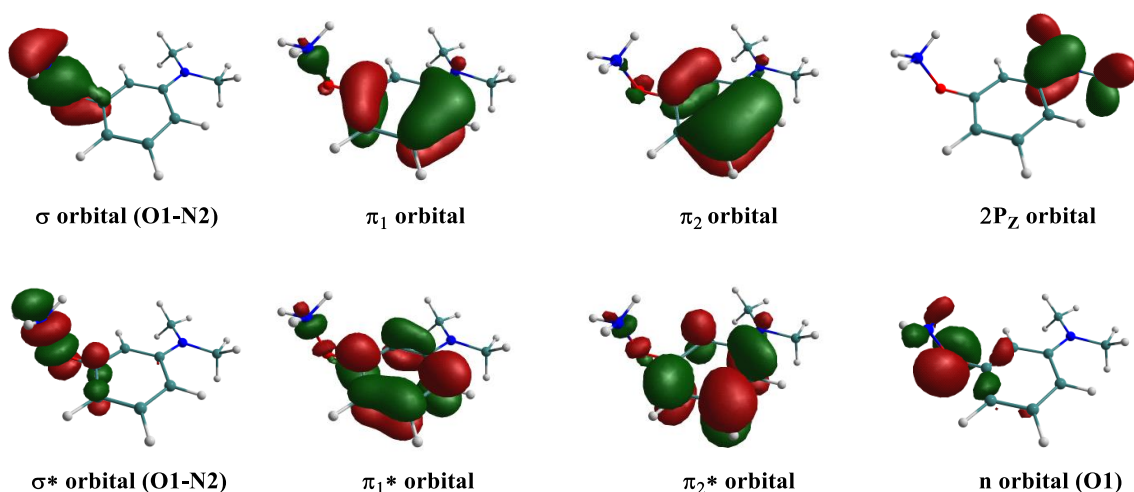


Figure S-1.3 Molecular orbitals of m-dimethylamino phenylhydroxylamine (3) used in defining the active space for the CASSCF(10e/8o)/CASPT2 calculation.

Section 2. Schematic structures with selective parameters

Figure S-2.1 The schematic structures of 1, 2 and 3.

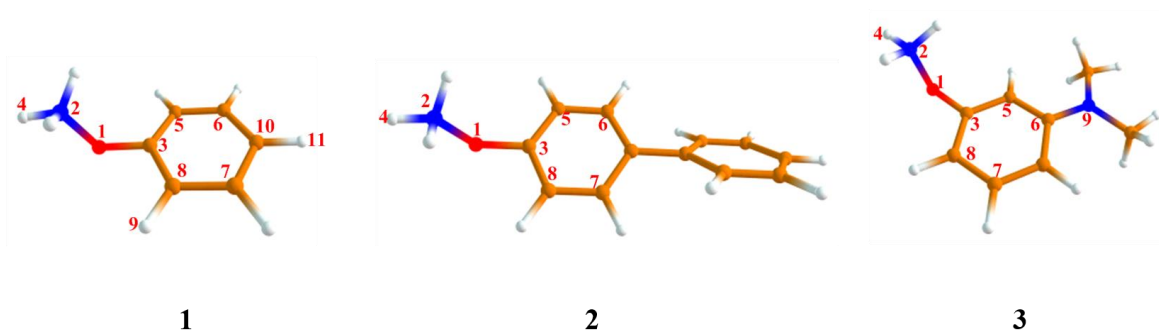


Figure S-2.2.1 Schematically critical points with the key bond lengths/distances (\AA) for 1 to produce oxenium ion from the CASSCF(8e/7o) calculations.

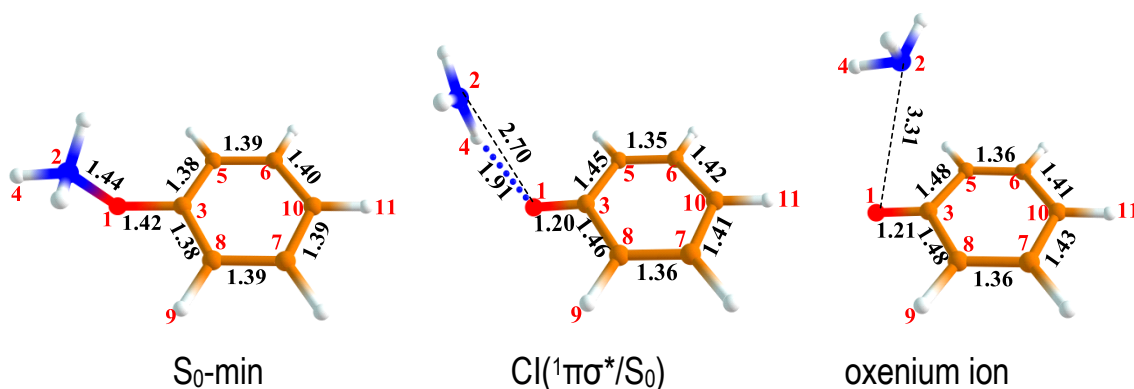


Figure S-2.2.2 Schematically critical points with the key bond lengths/distances (\AA) and angle ($^\circ$) for 1 to produce HBD from the CASSCF(8e/7o) calculations.

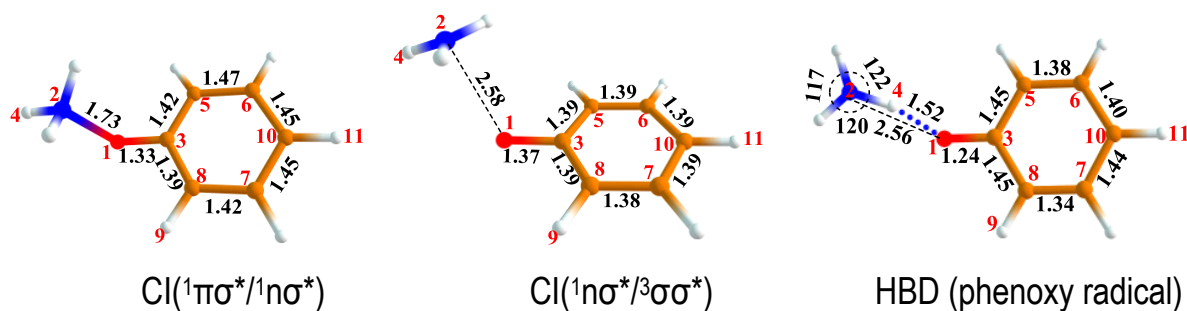
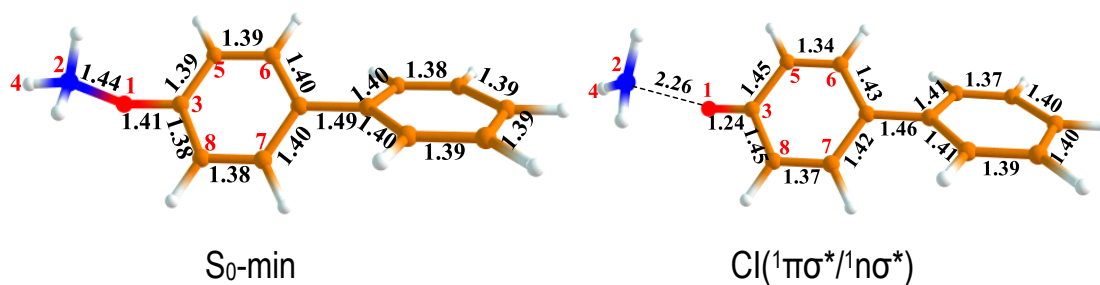


Figure S-2.3.1 Schematically critical points with the key bond lengths/distances (\AA) and angle ($^\circ$) for 2 to produce oxenium ion (closed-shell singlet ground state) obtained from the CASSCF(12e/11o) calculation.



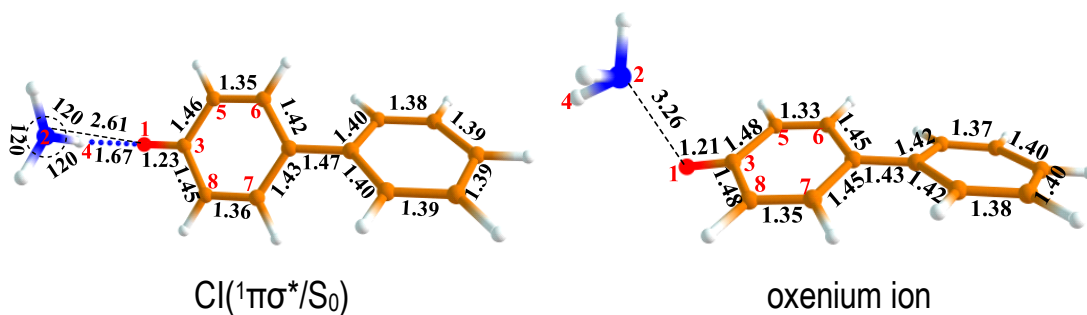


Figure S-2.3.2 Schematically critical points with the key bond lengths/distances (Å) and angle (°) for **2** to produce HBD obtained from the CASSCF(12e/11o) calculation.

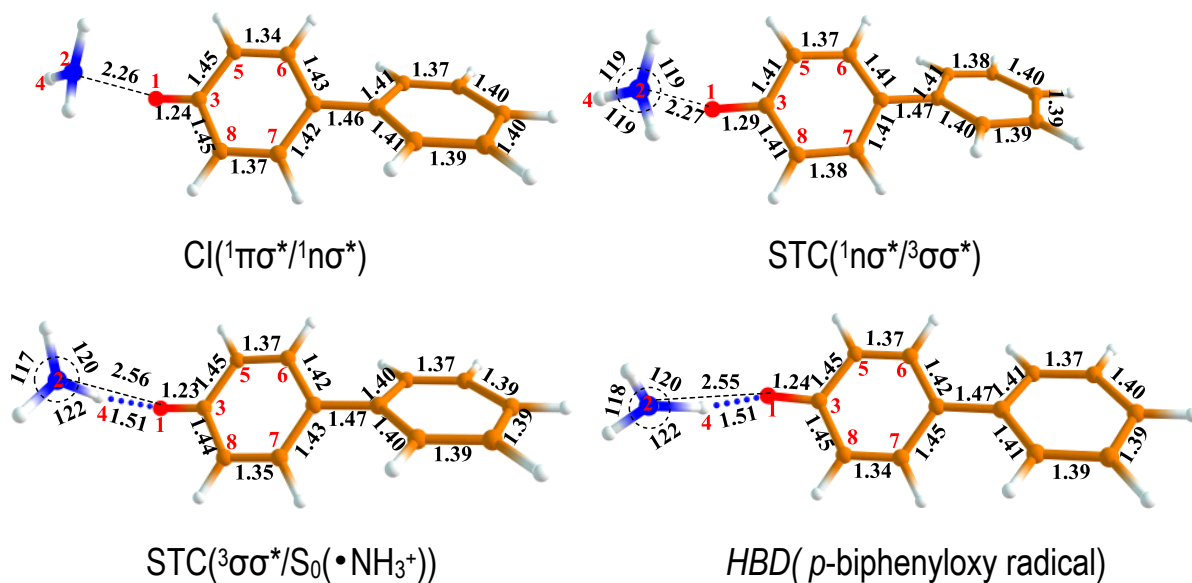


Figure S-2.3.3 Schematically critical points with the key bond lengths/distances (Å) for **2** to yield triplet state oxenium ion obtained from the CASSCF(12e/11o) calculation.

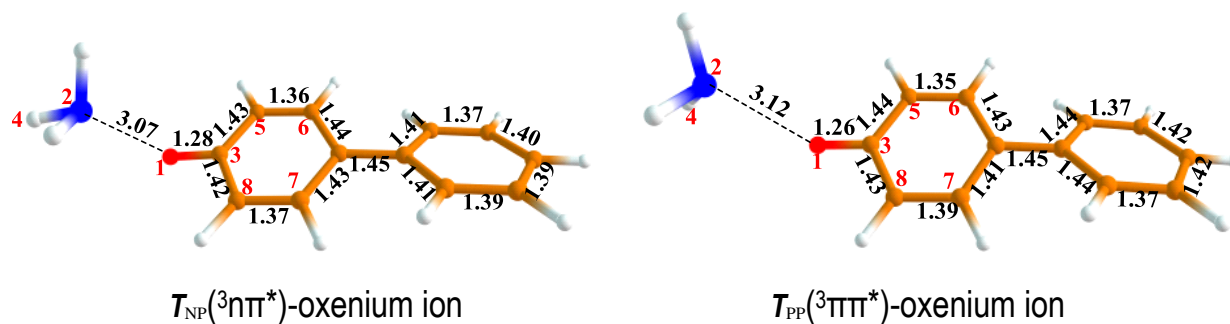


Figure S-2.4 Schematically critical points with the key bond lengths/distances (Å) for **3** to yield oxenium ion (closed-shell singlet ground state) obtained from the CASSCF(10e/8o) calculation.

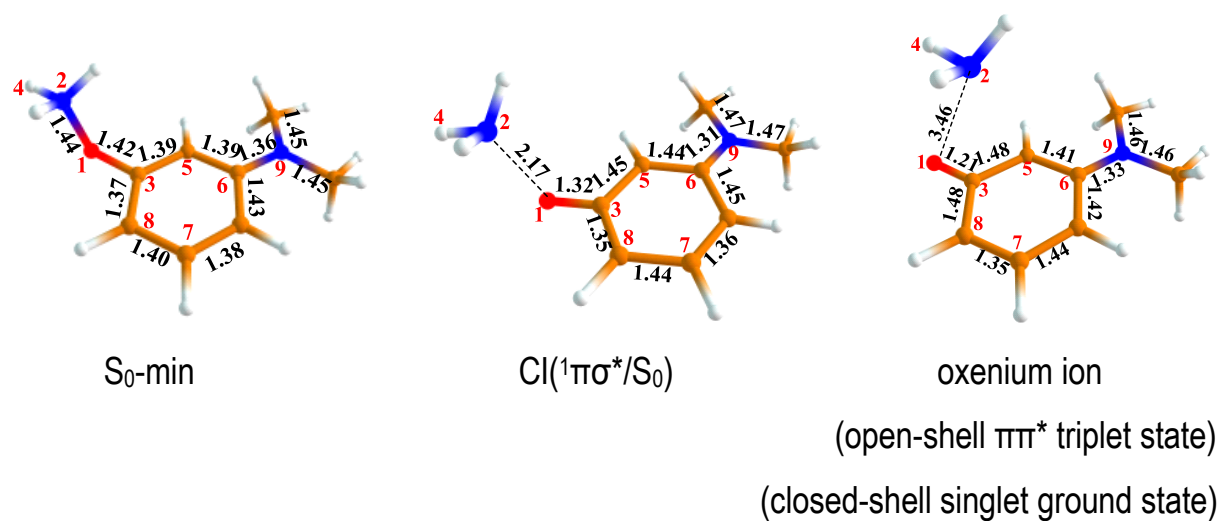
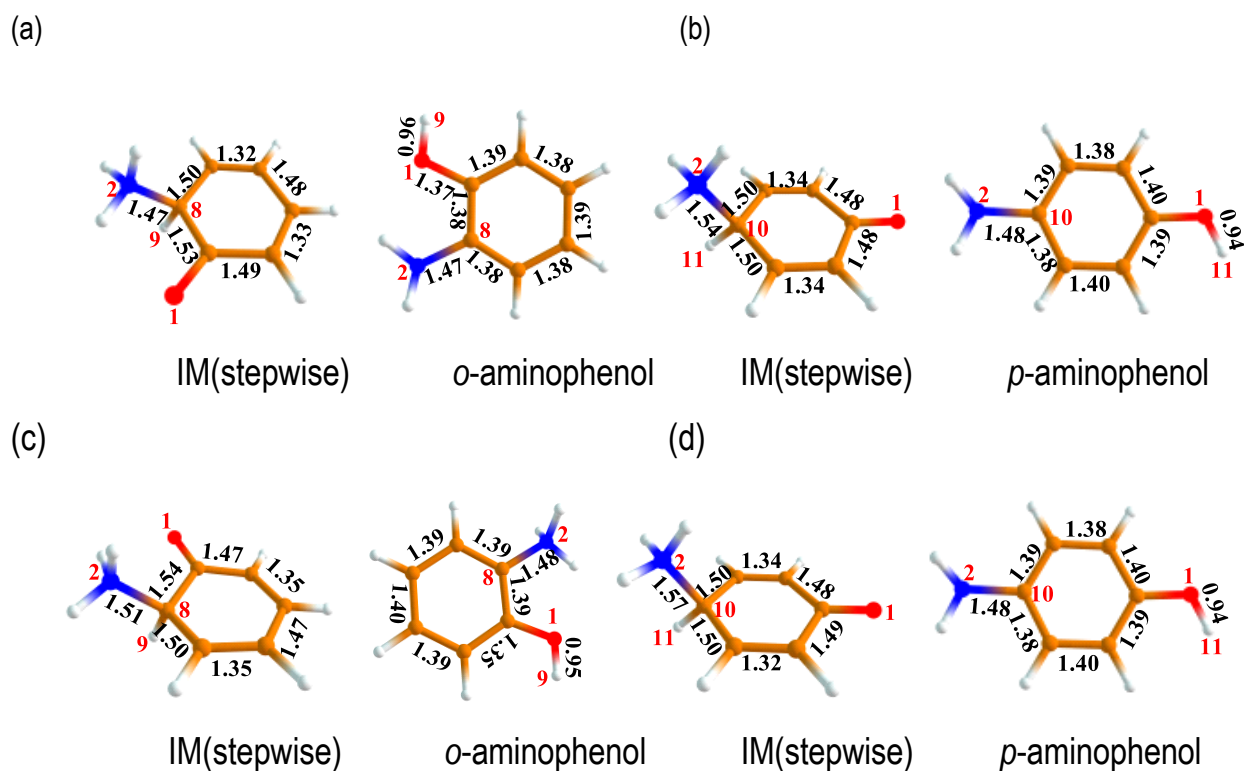


Figure S-2.5 Schematically critical points with the key bond lengths/distances (Å) for the *para*, *ortho* nucleophilic (a, b) and radical (c, d) addition reactions for parent molecule **1** respectively along the predefined reaction coordinates on the full three-dimensional PESs computed at CASPT2//CASSCF(8,7)/6-31G** level of theory.



Section 3. MEPs for the photolysis of 1 and 2 leading to the hydrogen-bonded-diradical (HBD)

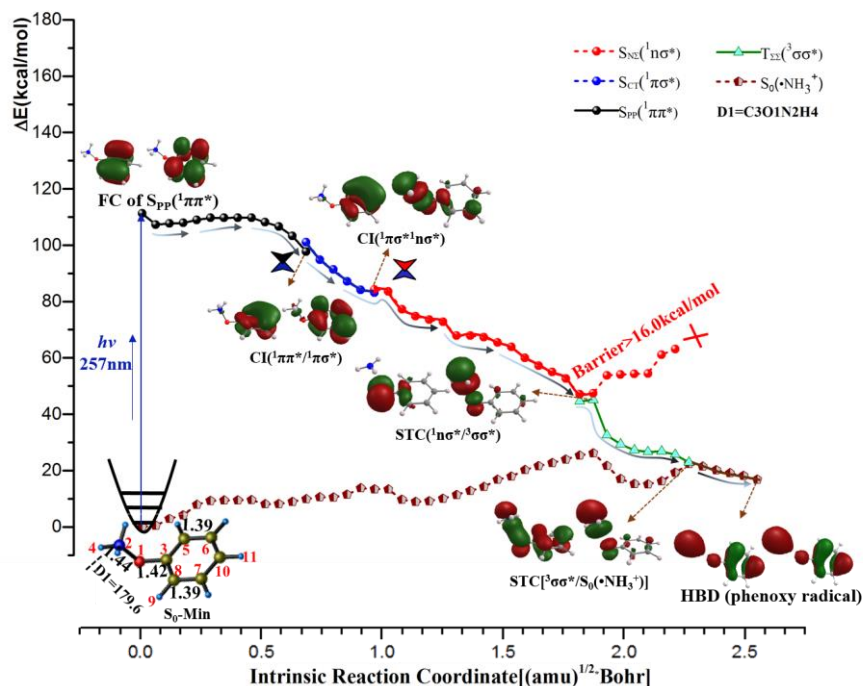


Figure S-3.1 The MEPs with the evolution of singly occupied orbitals for the photolysis of **1** leading to the HBD along the reaction channels of singlet, triplet and ground states calculated at the CASPT2//IRC/CASSCF/6-31G** level of theory.

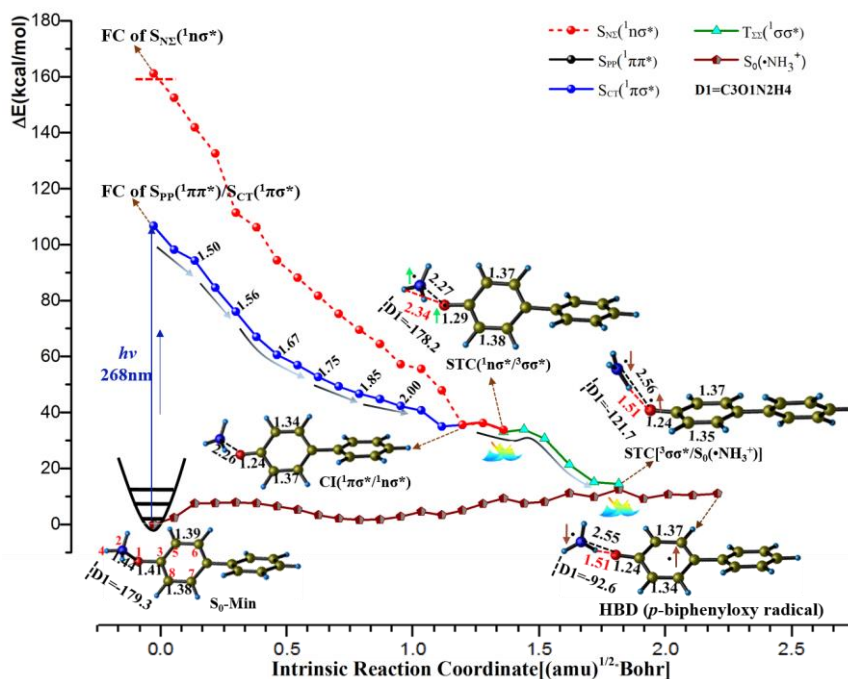


Figure S-3.2 MEPs for the photolysis of **2** leading to the HBD along the reaction channels of singlet, triplet and ground states calculated at the CASPT2//IRC/CASSCF/6-31G** level of theory. Selected stationary structures are given with

their key bond lengths and the C3O1N2H4 (D1) dihedral angles in degree. The structural evolution of O1-N2 distance (Å) are provided along the relaxation paths.

Section 4. Charge Translocation Calculations and Solvent Effects

To further explore the properties of **1-3** in the excited state, a charge translocation calculation was performed based on Mulliken charge population and an appropriate fragment partition strategy. As shown in Figure S4-1, the phenyl ring is defined as part 1, while the rest moiety of the NH_3 group is defined as part 2. The charge distributions were obtained using a full Mulliken population analysis at the CASPT2//CASSCF level of theory. Table S4-1 present the Mulliken charge distributions of parts 1 and 2 in the ground (S_0) and $S_{CT}(^1\pi\sigma^*)$ state upon the photo-excitation of **1-3**. {Charge translocation: oxenium ion(part2-part1)- S_0 (part2-part1)}/2

Figure S4-1. The scheme of fragment partition for charge translocation calculation is shown in which the phenyl ring is defined as part 1, while the rest moiety of the NH_3 group is defined as part 2.

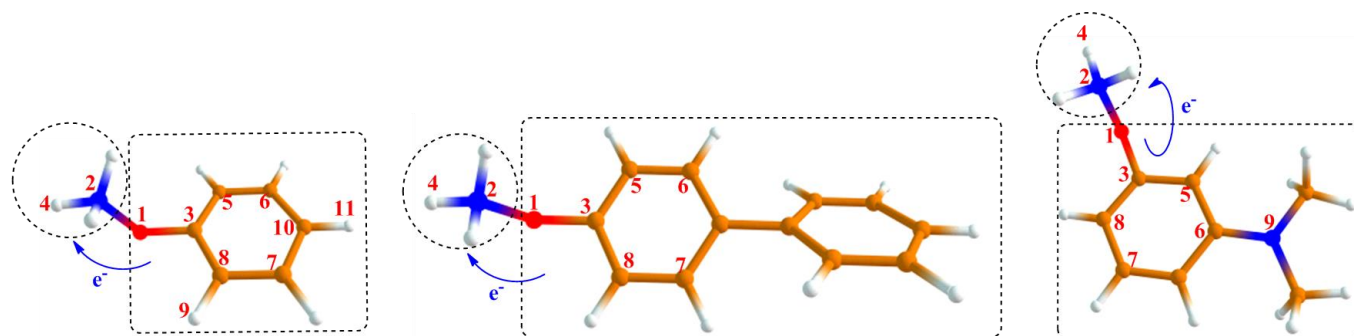


Table S4-1. Mulliken charge distribution for **1**, **2** and **3** in parts 1 and 2 in the ground (S_0) and the products of oxenium ion upon the photo-excitation. (unit: e)

		S_0	Oxenium ion	Charge translocation
1	Part 1	0.059	0.975	-0.916
	Part 2	0.941	0.025	
2	Part 1	0.063	0.989	-0.926
	Part 2	0.937	0.011	
3	Part 1	0.066	0.981	-0.915
	Part 2	0.934	0.019	

Table S4-2. Vertical excitation energy (ΔE , kcal/mol), oscillator strength (f), dipole moment (D.M., Debye), and the character of singly occupied orbital for different transition of phenylhydroxylamine (1), para-biphenyl-hydroxylamine (2) and *m*-dimethylamino phenylhydroxylamine (3) calculated at the CASPT2/CASSCF/PCM level of theory in water ($\epsilon=78.3$), acetonitrile ($\epsilon=36.6$) and methanol ($\epsilon=32.6$) matrix at a temperature of 298.15 K.

Species	Transition	Water	Acetonitrile	Methanol	Singly occupied orbitals	
1	$S_0 \rightarrow S_{PP}(^1\pi\pi^*)$	102.1	102.1	102.1	π	π^*
	$S_0 \rightarrow S_{P\Sigma}(^1\pi\sigma^*)$	114.6	114.5	114.5	π	σ^*
	$S_0 \rightarrow S_{N\Sigma}(^1n\sigma^*)$	158.5	158.5	158.5	n	σ^*
2	$S_0 \rightarrow S_{PP}(^1\pi\pi^*)$	103.7	105.3	106.2	π	π^*
	$S_0 \rightarrow S_{P\Sigma}(^1\pi\sigma^*)$	99.4	99.2	99.7	π	σ^*
	$S_0 \rightarrow S_{N\Sigma}(^1n\sigma^*)$	163.7	164.0	164.3	n	σ^*
3	$S_0 \rightarrow S_{PP}(^1\pi\pi^*)$	109.4	109.3	109.3	π	π^*
	$S_0 \rightarrow S_{P\Sigma}(^1\pi\sigma^*)$	75.6	75.5	75.5	π	σ^*
	$S_0 \rightarrow S_{N\Sigma}(^1n\sigma^*)$	163.4	163.5	163.5	n	σ^*

Section 5. Tables

Table S5-1 The absolute energies (A.E.) in Hartree and relative energies (R.E.) in kcal/mol for the optimized structures of **1** along the reaction pathway leading to oxenium ion at the CAS(8,7)/6-31G**/CASPT2 level of theory. The corresponding energy profiles are plotted in Figure 1 of the main article.

1	CASSCF	RASSCF	CASPT2	
	A.E.	A.E.	A.E.	R.E.
S₀				
Root1	-360.9570	-360.9450	-362.0198	0
Root2($S_{PP}(^1\pi\pi^*)$)		-360.7083	-361.8425	111.2687
Root3($S_{N\Sigma}(^1n\sigma^*)$)		-360.6596	-361.7623	161.5757
Root4($S_{CT}(^1\pi\sigma^*)$)		-360.6464	-361.8170	127.2372
Root5		-360.6061	-361.7880	145.4835
Path-$S_{PP}(^1\pi\pi^*)$-4				
Root1		-360.9378	-362.0132	4.1715
Root2	-360.7399	-360.7227	-361.8478	107.9447
Root3		-360.6568	-361.7630	161.1181
Root4		-360.6515	-361.8176	126.8931
Root5		-360.6042	-361.7857	146.9208
Path-$S_{PP}(^1\pi\pi^*)$-7				
Root1		-360.9285	-362.0048	9.4429
Root2	-360.7425	-360.7268	-361.8450	109.7161
Root3		-360.6468	-361.7745	153.9611
Root4		-360.6420	-361.8081	132.8583

Root5		-360.5987	-361.7818	149.3506
Path-S_{PP}(1ππ*)-Min				
Root1		-360.9282	-362.0046	9.5527
Root2	-360.7427	-360.7273	-361.8448	109.7986
Root3		-360.6489	-361.7862	146.5720
Root4		-360.6413	-361.8065	133.8275
Root5		-360.5985	-361.7989	138.6260
CI(1ππ*/1πσ*)				
Root1		-360.9141	-362.0040	9.9186
Root2	-360.7406	-360.7319	-361.8640	97.7841
Root3		-360.7251	-361.8587	101.1042
Root4		-360.6993	-361.8442	110.2164
Root5		-360.6555	-361.8200	125.3554
Path-S_{CT}(1πσ*)-16				
Root1		-360.9153	-362.0014	11.5333
Root2	-360.7744	-360.7603	-361.8814	86.8242
Root3		-360.7523	-361.8809	87.1410
Root4(S _{NΣ} (1πσ*))		-360.7280	-361.8642	97.6545
Root5		-360.6605	-361.8213	124.5493
CI(1πσ*/1πσ*)				
Root1		-360.9094	-361.9984	13.4372
Root2	-360.8104	-360.7814	-361.8873	83.1353
Root3		-360.7649	-361.8921	80.1297
Root4(S _{NΣ} (1πσ*))		-360.7520	-361.8854	84.3203
Root5		-360.6780	-361.8161	127.8229
Path-S_{CT}(1πσ*)-21				
Root1		-360.9153	-362.0083	7.2429
Root2	-360.8044	-360.8208	-361.9223	61.1822
Root3		-360.7959	-361.9132	66.9101
Root4		-360.7753	-361.8966	77.2873
Root5		-360.7517	-361.8701	93.9530
STC(1πσ*/3ππ*/3ηπ*)				
Root1		-360.9085	-362.0011	11.7435
Root2	-360.8423	-360.8364	-361.9458	46.4179
Root3		-360.8220	-361.9358	52.7227
Root4		-360.8123	-361.9289	57.0061
Root5		-360.8019	-361.9060	71.3913
CI(1πσ*/S₀)				
Root1	-360.9439	-360.9066	-361.9708	30.7572
Root2(S _{CT} (1πσ*))		-360.8464	-361.9631	35.5600
Root3		-360.8369	-361.9445	47.2698
Root4		-360.7878	-361.8758	90.3509
Root5		-360.7849	-361.8688	94.7790

Path-S₀-33				
Root1	-360.9614	-360.9248	-361.9896	18.9753
Root2		-360.8599	-361.9451	46.8403
Root3		-360.8245	-361.9481	45.0020
Root4		-360.8036	-361.8925	79.9105
Root5		-360.8005	-361.8851	84.5105
Oxenium Ion				
Root1	-360.9740	-360.9387	-362.0052	9.1608
Root2		-360.8696	-361.9564	39.8193
Root3		-360.8215	-361.9266	58.4570
Root4		-360.8126	-361.8996	75.4402
Root5		-360.7825	-361.9156	65.4103

Table S5-2 The absolute energies (A. E.) in Hartree and relative energies (R.E.) in kcal/mol for the optimized structures of **2** along the reaction pathway leading to oxenium ion at the CAS(12,11)/6-31G**/CASPT2 level of theory. The corresponding energy profiles are plotted in Figure 2a of the main article.

2	CASSCF	RASSCF	CASPT2	
	A.E.	A.E.	A.E.	R.E.
S₀				
Root1	-590.5582	-590.5467	-592.3596	0
Root2		-590.3300	-592.1976	101.6506
Root3(S _{PP} (¹ ππ*))		-590.3250	-592.1897	106.6020
Root4(S _{CT} (¹ πσ*))		-590.3099	-592.1896	106.7167
Root5		-590.2608	-592.1538	129.1595
Root6		-590.2581	-592.1532	129.5505
Root7		-590.2539	-592.1742	116.3744
Root8(S _{N₂} (¹ nσ*))		-590.2497	-592.1028	161.1740
Path-S_{CT}(¹πσ*)-4				
Root1		-590.5233	-592.3475	7.6051
Root2	-590.3546	-590.3346	-592.2249	84.5573
Root3		-590.3118	-592.1929	104.6009
Root4		-590.3076	-592.2055	96.7248
Root5		-590.2984	-592.1484	132.5526
Root6		-590.2754	-592.1829	110.8503
Root7		-590.2605	-592.1699	119.0128
Root8		-590.2519	-592.1857	109.1201
Path-S_{CT}(¹πσ*)-8				
Root1		-590.5118	-592.3511	5.3153
Root2	-590.3977	-590.3916	-592.2689	56.8982
Root3		-590.3622	-592.2192	88.1219
Root4		-590.3499	-592.2338	78.9464
Root5		-590.3439	-592.2278	82.7087

Root6		-590.3341	-592.2289	81.9882
Root7		-590.3007	-592.2066	96.0253
Root8		-590.2809	-592.1859	108.9876
Path-S_{CT}(1πσ*)-11				
Root1		-590.5097	-592.3569	1.6482
Root2	-590.4249	-590.4211	-592.2852	46.6753
Root3		-590.3909	-592.2489	69.5026
Root4		-590.3801	-592.2520	67.4854
Root5		-590.3758	-592.2467	70.8300
Root6		-590.3688	-592.2491	69.3443
Root7		-590.3424	-592.2094	94.2679
Root8		-590.3247	-592.2278	82.7259
Path-S_{CT}(1πσ*)-14				
Root1		-590.5113	-592.3523	4.5669
Root2	-590.4448	-590.4377	-592.2947	40.7280
Root3		-590.4307	-592.2712	55.4747
Root4		-590.4092	-592.2691	56.8096
Root5		-590.4043	-592.2676	57.7639
Root6		-590.4022	-592.2647	59.5724
Root7		-590.3947	-592.2569	64.4372
Root8		-590.3638	-592.21505	90.7203
STC(1πσ*/³ππ*/³ηπ*)				
Root1		-590.5221	-592.3516	5.0091
Root2(S _{CT} (1πσ*))	-590.4612	-590.4445	-592.3029	35.5923
Root3(S _{NΣ} (1πσ*))		-590.4422	-592.3029	35.5394
Root4		-590.4129	-592.2711	55.5261
Root5		-590.4064	-592.2591	63.0700
Root6		-590.3912	-592.2575	64.1136
Root7		-590.3829	-592.2578	63.9204
Root8		-590.3719	-592.2293	81.7582
CI(1πσ*/S₀)				
Root1		-590.5221	-592.3298	18.7293
Root2(S _{CT} (1πσ*))	-590.4919	-590.4445	-592.3265	20.8126
Root3		-590.4422	-592.2779	51.2921
Root4		-590.4129	-592.2540	66.2659
Root5		-590.4064	-592.2492	69.2912
Root6		-590.3912	-592.2589	63.1553
Root7		-590.3829	-592.2157	90.2969
Root8		-590.3719	-592.2234	85.4599
Path-S₀-22				
Root1	-590.5510	-590.5333	-592.3451	9.1116
Root2		-590.4555	-592.2869	45.5758
Root3		-590.4369	-592.3243	22.1481
Root4		-590.4305	-592.2622	61.0862
Root5		-590.4184	-592.2583	63.5539

Root6		-590.3851	-592.2206	87.2257
Root7		-590.3829	-592.2302	81.2231
Root8		-590.3766	-592.2367	77.1277
Path-S₀-25				
Root1	-590.5745	-590.5698	-592.3676	-5.01130
Root2		-590.4947	-592.3071	32.9460
Root3		-590.4746	-592.2884	44.6919
Root4		-590.4449	-592.2732	54.2616
Root5		-590.4315	-592.2455	71.6378
Root6		-590.4176	-592.2481	69.9941
Root7		-590.4119	-592.2589	63.1448
Root8		-590.3900	-592.2194	88.0034
Oxenium Ion				
Root1	-590.5832	-590.5829	-592.3743	-9.2308
Root2		-590.5033	-592.3129	29.2839
Root3		-590.4797	-592.2877	45.1484
Root4		-590.4393	-592.2658	58.8550
Root5		-590.4349	-592.2473	70.4922
Root6		-590.4196	-592.2472	70.5511
Root7		-590.4157	-592.2712	55.5105
Root8		-590.3914	-592.2567	64.5686

Table S5-3 The absolute energies (A. E.) in Hartree and relative energies (R.E.) in kcal/mol for the optimized structures of **3** along the reaction pathway leading to oxenium ion at the CAS(10,8)/6-31G**/CASPT2 level of theory. The corresponding energy profiles are plotted in Figure 2b of the main article.

3	CASSCF	RASSCF	CASPT2	
	A.E.	A.E.	A.E.	R.E.
S₀				
Root1	-494.0494	-494.0422	-495.5764	0
Root2(S _{CT} (¹ πσ*))		-493.8456	-495.4403	85.3932
Root3(S _{PP} (¹ ππ*))		-493.8044	-495.4043	108.0050
Root4		-493.7589	-495.3743	126.8480
Root5(S _{NΣ} (¹ nσ*))		-493.7547	-495.3217	159.8430
Path-S_{CT}(¹πσ*)-4				
Root1		-494.0404	-495.5751	0.8511
Root2(S _{CT} (¹ πσ*))	-493.8618	-493.8547	-495.4464	81.5867
Root3		-493.8106	-495.4088	105.1586
Root4		-493.7689	-495.3787	124.0853
Root5		-493.7604	-495.3275	156.2053
Path-S_{CT}(¹πσ*)-7				
Root1		-494.0255	-495.5715	3.08738
Root2	-493.8735	-493.8722	-495.4728	65.0094

Root3		-493.8317	-495.4269	93.8083
Root4		-493.7999	-495.3786	124.1577
Root5		-493.7932	-495.4159	100.7171
Path-S_{CT}(1πσ*)-10				
Root1		-494.0107	-495.5672	5.7838
Root2	-493.9329	-493.9298	-495.5077	43.1405
Root3		-493.8752	-495.4546	76.4720
Root4		-493.8525	-495.4264	94.1586
Root5		-493.8260	-495.4172	99.9120
Path-S_{CT}(1πσ*)-13				
Root1		-590.5113	-495.5662	6.3973
Root2	-493.9693	-590.4377	-495.5304	28.8738
Root3		-590.4307	-495.4712	66.0552
Root4		-590.4092	-495.4579	74.3938
Root5		-590.4043	-495.4368	87.6314
Path-S_{CT}(1πσ*)-16				
Root1		-493.9996	-495.5504	16.2990
Root2	-493.9922	-493.9872	-495.5285	30.0813
Root3		-493.9328	-495.4617	71.9653
Root4		-493.9002	-495.4754	63.3982
Root5		-493.8922	-495.4463	81.6266
Path-S_{CT}(1πσ*)-18				
Root1		-494.0048	-495.5399	22.8633
Root2	-494.0050	-494.0021	-495.5305	28.8305
Root3		-493.9693	-495.4892	54.7512
Root4		-493.9222	-495.4580	74.2802
Root5		-493.9062	-495.4496	79.5608
CI(1πσ*/S₀)				
Root1(S ₀)	-494.0100	-494.0093	-495.5366	24.9628
Root2(S _{CT} (1πσ*))		-494.0074	-495.5339	26.6710
Root3		-493.9863	-495.5061	44.1156
Root4		-493.9359	-495.4676	68.3011
Root5		-493.9141	-495.4534	77.1643
Path-S₀-23				
Root1	-494.0547	-494.0467	-495.5614	9.4371
Root2		-494.0022	-495.5257	31.8036
Root3		-493.9787	-495.5211	34.7111
Root4		-493.9455	-495.4810	59.86968
Root5		-493.9191	-495.4525	77.77422
Path-S₀-25				
Root1	-494.0677	-494.0592	-495.5680	5.25346
Root2		-494.0029	-495.5302	29.0007
Root3		-493.9803	-495.5298	29.2501

Root4		-493.9569	-495.4934	52.1153
Root5		-493.9347	-495.4641	70.4715
Oxenium Ion				
Root1	-494.0785	-494.0703	-495.5784	-1.2273
Root2		-494.0042	-495.5333	27.0853
Root3		-493.9851	-495.5368	24.8626
Root4		-493.9693	-495.5057	44.4047
Root5		-493.9465	-495.4782	61.6409

Table S5-4 The absolute energies (A. E.) in Hartree and relative energies (R.E.) in kcal/mol for the optimized structures of **1** along the reaction pathway leading to HBD at the CAS(8,7)/6-31G**/CASPT2 level of theory. The corresponding energy profiles are plotted in Figure 3 of the main article.

1 Lead to HBD	CASSCF	RASSCF	CASPT2	
	A.E.	A.E.	A.E.	R.E.
S₀				
Root1	-360.9570	-360.9450	-362.0198	0
Root2(S _{PP} (¹ ππ*))		-360.7083	-361.8425	111.2687
Root3(S _{NΣ} (¹ nσ*))		-360.6596	-361.7623	161.5757
Root4(S _{CT} (¹ πσ*))		-360.6464	-361.8170	127.2372
Root5		-360.6061	-361.7880	145.4835
Path-S_{PP}(¹ππ*)-4				
Root1		-360.9378	-362.0132	4.1715
Root2	-360.7399	-360.7227	-361.8478	107.9447
Root3		-360.6568	-361.7630	161.1181
Root4		-360.6515	-361.8176	126.8931
Root5		-360.6042	-361.7857	146.9208
Path-S_{PP}(¹ππ*)-7				
Root1		-360.9285	-362.0048	9.4429
Root2	-360.7425	-360.7268	-361.8450	109.7161
Root3		-360.6468	-361.7745	153.9611
Root4		-360.6420	-361.8081	132.8583
Root5		-360.5987	-361.7818	149.3506
Path-S_{PP}(¹ππ*)-Min				
Root1		-360.9282	-362.0046	9.5527
Root2	-360.7427	-360.7273	-361.8448	109.7986
Root3		-360.6489	-361.7862	146.5720
Root4		-360.6413	-361.8065	133.8275
Root5		-360.5985	-361.7989	138.6260
CI(¹ππ*/¹πσ*)				
Root1		-360.9141	-362.0040	9.9186
Root2	-360.7406	-360.7319	-361.8640	97.7841

Root3		-360.7251	-361.8587	101.1042
Root4		-360.6993	-361.8442	110.2164
Root5		-360.6555	-361.8200	125.3554
Path-S_{CT}(1πσ*)-16				
Root1		-360.9153	-362.0014	11.5333
Root2	--360.7744	-360.7603	-361.8814	86.8242
Root3		-360.7523	-361.8809	87.1410
Root4(S _{NΣ} (1πσ*))		-360.7280	-361.8642	97.6545
Root5		-360.6605	-361.8213	124.5493
CI(1πσ*/1πσ*)				
Root1		-360.9094	-361.9984	13.4372
Root2(S _{CT} (1πσ*))	-360.8104	-360.7814	-361.8873	83.1353
Root3		-360.7649	-361.8921	80.1297
Root4(S _{NΣ} (1πσ*))		-360.7520	-361.8854	84.3203
Root5		-360.6780	-361.8161	127.8229
Path-S_{NΣ}(1πσ*)-21				
Root1		-360.9127	-362.0056	8.9342
Root2		-360.8122	-361.9122	67.4960
Root3		-360.7857	-361.9072	70.6711
Root4	-360.8291	-360.7769	-361.9006	74.8330
Root5		-360.7201	-361.8436	110.5545
Path-S_{NΣ}(1πσ*)-24				
Root1		-360.9055	-362.0017	11.3917
Root2		-360.8271	-361.9243	59.9476
Root3	-360.8532	-360.7977	-361.9116	67.9224
Root4		-360.7893	-361.9046	72.2865
Root5		-360.7573	-361.8663	96.2912
Path-S_{NΣ}(1πσ*)-27				
Root1		-360.8951	-361.9930	16.8065
Root2		-360.8345	-361.9303	56.1634
Root3	-360.8681	-360.8144	-361.9156	65.4138
Root4		-360.7988	-361.9101	68.8477
Root5		-360.7907	-361.8931	79.5002
Path-S_{NΣ}(1πσ*)-30				
Root1		-360.8881	-361.9853	21.6493
Root2		-360.8380	-361.9358	52.6950
Root3	-360.8753	-360.8303	-361.9286	57.2058
Root4		-360.8126	-361.9086	69.8080
Root5		-360.8032	-361.9038	72.7682
CI(1πσ*/³σσ*)				
Root1		-360.8840	-361.9794	25.3417
Root2	-360.8772	-360.8407	-361.9448	47.0804
Root3		-360.8364	-361.9361	52.5007

Root4		-360.8217	-361.9151	65.6823
Root5		-360.8053	-361.8985	76.1233
Path-T_{ΣΣ}(³σσ*)-37				
Root1	-360.9186	-360.8984	-361.9764	27.2381
Root2		-360.8394	-361.9244	59.8742
Root3		-360.7950	-361.8890	82.1297
Root4		-360.7803	-361.8872	83.2376
Root5		-360.7547	-361.8536	104.2738
CI(³σσ*/S₀(-NH₃⁺))				
Root1	-360.9272	-360.9057	-361.9832	22.9225
Root2		-360.8218	-361.9180	63.9045
Root3		-360.8088	-361.9080	70.1256
Root4		-360.7711	-361.8718	92.8633
Root5		-360.7643	-361.8686	94.9036
Path-S₀-43				
Root1	-360.9309	-360.9099	-361.9876	20.2017
Root2		-360.8636	-361.9515	42.8705
Root3		-360.8170	-361.9093	69.3735
Root4		-360.7753	-361.8806	87.3831
Root5		-360.7692	-361.8762	90.1401
HBD(Radical)				
Root1	-360.9363	-360.9156	-361.9929	16.8809
Root2		-360.8579	-361.9455	46.6498
Root3		-360.8219	-361.9137	66.5570
Root4		-360.7760	-361.8755	90.5228
Root5		-360.7689	-361.8725	92.4498

Table S5-5 The absolute energies (A. E.) in Hartree and relative energies (R.E.) in kcal/mol for the optimized structures of **2** along the reaction pathway leading to HBD at the CAS(12,11)/6-31G**/CASPT2 level of theory. The corresponding energy profiles are plotted in Figure S-3.2 of the SI.

2 Lead to HBD	CASSCF	RASSCF	CASPT2	
	A.E.	A.E.	A.E.	R.E.
S₀				
Root1	-590.5582	-590.5467	-592.3596	0
Root2		-590.3300	-592.1976	101.6506
Root3(S _{PP} (¹ ππ*))		-590.3250	-592.1897	106.6020
Root4(S _{CT} (¹ πσ*))		-590.3099	-592.1896	106.7167
Root5		-590.2608	-592.1538	129.1595
Root6		-590.2581	-592.1532	129.5505
Root7		-590.2539	-592.1742	116.3744
Root8(S _{NΣ} (¹ nσ*))		-590.2497	-592.1028	161.1740

Path-S_{CT}(1πσ*)-4				
Root1		-590.5233	-592.3475	7.6051
Root2	-590.3546	-590.3346	-592.2249	84.5573
Root3		-590.3118	-592.1929	104.6009
Root4		-590.3076	-592.2055	96.7248
Root5		-590.2984	-592.1484	132.5526
Root6		-590.2754	-592.1829	110.8503
Root7		-590.2605	-592.1699	119.0128
Root8		-590.2519	-592.1857	109.1201
Path-S_{CT}(1πσ*)-8				
Root1		-590.5118	-592.3511	5.3153
Root2	-590.3977	-590.3916	-592.2689	56.8982
Root3		-590.3622	-592.2192	88.1219
Root4		-590.3499	-592.2338	78.9464
Root5		-590.3439	-592.2278	82.7087
Root6		-590.3341	-592.2289	81.9882
Root7		-590.3007	-592.2066	96.0253
Root8		-590.2809	-592.1859	108.9876
Path-S_{CT}(1πσ*)-11				
Root1		-590.5097	-592.3569	1.6482
Root2	-590.4249	-590.4211	-592.2852	46.6753
Root3		-590.3909	-592.2489	69.5026
Root4		-590.3801	-592.2520	67.4854
Root5		-590.3758	-592.2467	70.8300
Root6		-590.3688	-592.2491	69.3443
Root7		-590.3424	-592.2094	94.2679
Root8		-590.3247	-592.2278	82.7259
Path-S_{CT}(1πσ*)-14				
Root1		-590.5113	-592.3523	4.5669
Root2	-590.4448	-590.4377	-592.2947	40.7280
Root3		-590.4307	-592.2712	55.4747
Root4		-590.4092	-592.2691	56.8096
Root5		-590.4043	-592.2676	57.7639
Root6		-590.4022	-592.2647	59.5724
Root7		-590.3947	-592.2569	64.4372
Root8		-590.3638	-592.21505	90.7203
CI(1πσ*/1πσ*)				
Root1		-590.5221	-592.3516	5.0091
Root2(S _{CT} (1πσ*))	-590.4612	-590.4445	-592.3029	35.5923
Root3(S _{N₂} (1πσ*))		-590.4422	-592.3029	35.5394
Root4		-590.4129	-592.3039	34.9811
Root5		-590.4064	-592.2591	63.0700
Root6		-590.3912	-592.2575	64.1136
Root7		-590.3829	-592.2578	63.9204
Root8		-590.3719	-592.2293	81.7582

STC($1n\sigma^*/3\sigma\sigma^*$)				
Root3($S_{N_2}(1n\sigma^*)$)		-590.4799	-592.3034	35.2981
Root2		-590.4764	-592.2873	45.4037
Root3($S_{N_2}(3\sigma\sigma^*)$)	-590.5222	-590.4531	-592.3070	33.0142
Root4		-590.4486	-592.2750	53.0806
Root5		-590.3995	-592.2315	80.3672
Root6		-590.3737	-592.2113	93.0497
Root7		-590.3713	-592.1971	102.0105
Root8		-590.3689	-592.1922	105.0378
Path-$T_{\Sigma\Sigma}(3\sigma\sigma^*)$-20				
Root1		-590.4808	-592.3132	29.1238
Root2		-590.4764	-592.2834	47.8286
Root3 ($T_{\Sigma\Sigma}(3\sigma\sigma^*)$)	-590.5290	-590.4561	-592.3107	30.6856
Root4		-590.4494	-592.2709	55.6625
Root5		-590.3994	-592.2322	79.9640
Root6		-590.3757	-592.2253	84.3132
Root7		-590.3717	-592.1907	105.9891
Root8		-590.3695	-592.1936	104.1777
Path-$T_{\Sigma\Sigma}(3\sigma\sigma^*)$-22				
Root1($T_{\Sigma\Sigma}(3\sigma\sigma^*)$)	-590.5350	-590.5045	-592.3356	15.0709
Root2		-590.4475	-592.2764	52.2118
Root3		-590.4431	-592.2773	51.6483
Root4		-590.4245	-592.2684	57.2320
Root5		-590.4051	-592.2510	68.1543
Root6		-590.3888	-592.2596	62.7741
Root7		-590.3734	-592.2363	77.3761
Root8		-590.3715	-592.2421	73.7512
STC($3\sigma\sigma^*/S_0(\cdot NH_3^+)$)				
Root1($T_{\Sigma\Sigma}(3\sigma\sigma^*)$)	-590.5287	-590.5072	-592.3449	9.1958
Root2		-590.5003	-592.3283	19.6795
Root3		-590.4061	-592.2569	64.4775
Root4		-590.3970	-592.2777	51.4285
Root5		-590.3883	-592.2571	64.3208
Root6		-590.3782	-592.2318	80.2383
Root7		-590.3753	-592.2825	48.3761
Root8		-590.3535	-592.2529	66.9764
Path-S_0-25				
Root1	-590.5361	-590.5075	-592.3425	10.7651
Root2		-590.5067	-592.3334	16.4433
Root3		-590.4088	-592.2568	64.4774
Root4		-590.4080	-592.2777	51.4285
Root5		-590.3928	-592.2571	64.3208
Root6		-590.3861	-592.2317	80.2383
Root7		-590.3817	-592.2825	48.3761
Root8		-590.3622	-592.2529	66.9764

HBD(Radical)				
Root1	-590.5369	-590.5080	-592.3421	11.0234
Root2		-590.5002	-592.3282	19.7055
Root3		-590.4099	-592.2634	60.3953
Root4		-590.4041	-592.2531	66.8433
Root5		-590.3879	-592.2821	48.6472
Root6		-590.3875	-592.2483	69.8319
Root7		-590.3765	-592.2418	73.9132
Root8		-590.3644	-592.2320	80.0620

Table S5-6 The absolute energies (A. E.) in Hartree and relative energies (R.E.) in kcal/mol for the three-dimensional PESs of para, ortho nucleophilic (a, b) and radical (c, d) addition reactions for parent molecule **1** respectively were computed along the concerted (red line) and stepwise (black line) pathways at the CASPT2//CASSCF(8,7)/6-31G** level of theory. The corresponding energy profiles are plotted in Figure 4 of the main article.

	CASSCF	RASSCF	CASPT2	
	A.E.	A.E.	A.E.	R.E.
(a)oxenium ion				
Root1	-360.9454	-360.9646	-362.0065	0
Root2		-360.8906	-361.9593	29.6233
TS(stepwise)				
Root1	-360.9734	-360.9595	-362.0197	-8.2760
Root2		-360.7798	-361.8857	75.7803
IM(concerted)				
Root1	-360.9830	-360.9728	-362.0236	-10.7790
Root2		-360.8717	-361.9405	41.3743
IM(stepwise)				
Root1	-361.0265	-361.0169	-362.0703	-39.9550
Root2		-360.8748	-361.9368	43.6916
o-aminophenol				
Root1	-361.0164	-361.0421	-362.1113	-65.762
Root2		-360.8559	-361.9362	44.1254
(b)oxenium ion				
Root1	-360.9454	-360.9646	-362.0065	0
Root2		-360.8906	-361.9593	29.6233
TS(stepwise)				
Root1	-360.9503	-360.9429	-362.0009	5.3012
Root2		-360.6472	-361.7011	193.48
TS(concerted)				

Root1	-360.9514	-360.9291	-361.9798	18.5822
Root2		-360.8384	-361.9197	56.2749
IM(concerted)				
Root1	-360.9569	-360.9456	-361.9871	14.0053
Root2		-360.8482	-361.9259	52.3742
IM(stepwise)				
Root1	-361.0246	-361.0169	-362.0653	-35.0600
Root2		-360.8748	-361.8476	101.510
p-aminophenol				
Root1	-361.0397	-361.0421	-362.1044	-59.6510
Root2		-360.8559	-361.9327	48.1402
(c)HBD				
Root1	-360.9399	-360.9350	-361.9986	0
Root2		-360.8504	-361.9219	48.1385
TS(stepwise)				
Root1	-360.9260	-360.9157	-361.9834	9.5411
Root2		-360.7840	-361.8655	83.5073
TS(concerted)				
Root1	-360.9156	-360.9104	-361.9788	12.3804
Root2		-360.8203	-361.8979	63.178
IM(concerted)				
Root1	-360.9746	-360.9628	-362.0077	-5.7224
Root2		-360.8512	-361.9164	51.5982
IM(stepwise)				
Root1	-361.0315	-361.0247	-362.0775	-49.5250
Root2		-360.8018	-361.8743	77.9951
o-aminophenol				
Root1	-361.0486	-361.0459	-362.1123	-71.3600
Root2		-360.8637	-361.9408	36.2537
(d)HBD				
Root1	-360.9399	-360.9350	-361.9986	0
Root2		-360.8504	-361.9219	48.1385
TS(stepwise)				
Root1	-360.9527	-360.9432	-362.0035	-3.3141
Root2		-360.7998	-361.8655	83.2464

TS(concerted)				
Root1	-360.9325	-360.9096	-361.9659	20.2910
Root2		-360.8267	-361.9111	54.6583
IM(concerted)				
Root1	-360.9716	-360.9597	-362.0057	-4.7067
Root2		-360.8419	-361.9088	56.0833
IM(stepwise)				
Root1	-361.0155	-361.0054	-362.0613	-39.5802
Root2		-360.8763	-361.9453	33.1945
p-aminophenol				
Root1	-361.0397	-361.0295	-362.1051	-67.0718
Root2		-360.8135	-361.9367	38.5962

Section 6. Cartesian Coordinates

Cartesian coordinates for 1 to produce oxenium ion

1 S₀-min

C	2.279745686	0.001790568	0.236324391
C	1.605209818	-1.209660328	0.092503135
C	0.241618801	-1.216080741	-0.189901613
C	-0.398596568	-0.002739729	-0.314550880
C	0.239122166	1.215045437	-0.192323385
C	1.602320076	1.212089220	0.090279529
H	3.332654633	0.003084955	0.449090765
H	2.133801194	-2.139648697	0.186969367
H	-0.294307504	-2.136689872	-0.338450158
H	-0.299055516	2.133828208	-0.343967161
H	2.129204480	2.143265365	0.182638559
O	-1.778141895	-0.004950009	-0.628653899
N	-2.563361397	0.002808162	0.579221182
H	-2.367184283	-0.828127871	1.120282280
H	-3.524761156	0.007159600	0.268187090
H	-2.358206770	0.834404670	1.115945128

1 Path-S_{PP}(¹ππ*)-4

C	2.321034243	-0.002391129	0.245308677
C	1.600402946	-1.243164874	0.091312582
C	0.229188377	-1.216117778	-0.193193696

C	-0.405467514	-0.021638338	-0.316541726
C	0.209497759	1.235686779	-0.195557878
C	1.623651100	1.251116566	0.094645046
H	3.367104643	-0.007120841	0.456107392
H	2.123559778	-2.171951894	0.181746145
H	-0.307671730	-2.136318426	-0.341381342
H	-0.328565988	2.144244004	-0.368125588
H	2.146531711	2.176552074	0.184252945
O	-1.768322148	-0.008261801	-0.630561800
N	-2.564048592	0.003582986	0.580409830
H	-2.367531741	-0.827572378	1.119984253
H	-3.523492332	0.008962581	0.264190902
H	-2.357366812	0.836276042	1.114544920

1 Path-S_{PP}(1ππ*)-7

C	2.352717218	-0.004760003	0.254518761
C	1.604015121	-1.259671854	0.087486612
C	0.221980548	-1.215684271	-0.201535292
C	-0.412877650	-0.021426648	-0.321612364
C	0.200642091	1.252857332	-0.189955240
C	1.645142835	1.276442931	0.104640654
H	3.400726078	-0.023912789	0.464347623
H	2.106857314	-2.201856394	0.167397297
H	-0.326505755	-2.129109513	-0.353705758
H	-0.337575304	2.149479784	-0.424714137
H	2.165671110	2.206086790	0.184471827
O	-1.787519069	-0.037452732	-0.633518403
N	-2.572581702	0.012545914	0.582660823
H	-2.385009852	-0.811574503	1.136362268
H	-3.534864827	0.027455812	0.275621763
H	-2.345714197	0.851020561	1.098959036

1 S_{PP}(1ππ*)-min

C	2.352106674	0.000358718	0.258632387
C	1.614626744	-1.258502156	0.075448074
C	0.232545497	-1.223909627	-0.208499772

C	-0.412534870	-0.034396152	-0.321531184
C	0.192296738	1.245819714	-0.185448661
C	1.635632112	1.277276459	0.118484394
H	3.399235307	-0.012040574	0.474600373
H	2.126936024	-2.196376901	0.146320945
H	-0.309776154	-2.140448591	-0.362127132
H	-0.345604200	2.139363365	-0.433053758
H	2.148576325	2.210613420	0.207833547
O	-1.786792890	-0.064395402	-0.632297866
N	-2.574495683	0.046454700	0.579074917
H	-2.403045800	-0.758974284	1.164237828
H	-3.535117308	0.068086717	0.266533216
H	-2.335592386	0.901120131	1.063729367

1 CI($1\pi\pi^*/1\pi\sigma^*$)

C	2.349438086	0.068630304	0.255835120
C	1.660810741	-1.216637340	0.128351776
C	0.288686135	-1.252948525	-0.141585705
C	-0.410030551	-0.095122969	-0.329949763
C	0.150571135	1.218591422	-0.253458345
C	1.588567522	1.312186177	0.066743908
H	3.395105306	0.102865069	0.476592381
H	2.211190059	-2.130222156	0.236703088
H	-0.218658719	-2.197212662	-0.235527517
H	-0.403446351	2.074859341	-0.584960199
H	2.069223821	2.265143008	0.128420688
O	-1.758683132	-0.203962389	-0.652157206
N	-2.624895826	0.114011005	0.617720642
H	-2.460376276	-0.618754786	1.289927966
H	-3.570033534	0.108137866	0.266947281
H	-2.347526857	1.020611952	0.959487519

1 Path- $S_{CT}(1\pi\sigma^*)-16$

C	2.327854978	0.001544295	0.255124772
C	1.624814507	-1.235912960	0.062961664
C	0.267486647	-1.254525161	-0.192540311

C	-0.453585065	-0.046737689	-0.327953245
C	0.166248693	1.230092259	-0.163904656
C	1.603680930	1.265914526	0.148438332
H	3.379171694	0.005086541	0.469737546
H	2.158650934	-2.169870899	0.111883269
H	-0.269305944	-2.175628374	-0.350317427
H	-0.375515073	2.121254925	-0.426365025
H	2.107384739	2.209439758	0.263669983
O	-1.731515770	-0.124182512	-0.641584191
N	-2.648025306	0.140325597	0.688261345
H	-2.492284235	-0.632513871	1.296381346
H	-3.574231730	0.169679627	0.321539752
H	-2.346176042	1.012611094	1.060715660

1 Cl(1πσ*/1nσ*)

C	2.348848969	0.076822054	0.280402716
C	1.684760356	-1.206672916	0.147112372
C	0.303131469	-1.256301874	-0.157309928
C	-0.415310772	-0.087845839	-0.360453018
C	0.176172614	1.204228393	-0.272706264
C	1.603164976	1.298376603	0.073256548
H	3.395160901	0.113421765	0.519515895
H	2.229012759	-2.129540888	0.271171689
H	-0.213670971	-2.195658410	-0.271662071
H	-0.394926665	2.066054218	-0.588819102
H	2.076619062	2.264992076	0.140234233
O	-1.696156120	-0.199155340	-0.703144402
N	-2.700154801	0.115222031	0.665825531
H	-2.545048626	-0.609327192	1.324022861
H	-3.618913288	0.091320486	0.291862785
H	-2.462305762	1.010965442	1.015790978

1 Path-S_{CT}(1πσ*)-21

C	2.363586000	0.104916999	0.280291002
C	1.754338999	-1.165054999	0.160818998
C	0.424527998	-1.272872001	-0.159095002

C	-0.335012999	-0.112075000	-0.328009999
C	0.238929000	1.163129000	-0.236678001
C	1.582955999	1.280609001	0.069369999
H	3.412969001	0.178232999	0.516007001
H	2.332302999	-2.049118001	0.334520001
H	-0.039730998	-2.229486997	-0.276692998
H	-0.353134001	2.028552998	-0.448968001
H	2.039858002	2.246122002	0.132302001
O	-1.590096002	-0.262114001	-0.679157998
N	-2.940983002	0.150978000	0.582905001
H	-2.830519997	-0.567998999	1.272998998
H	-3.662238998	-0.026507002	-0.093223002
H	-2.879134998	1.096079999	0.911202000

1 STC(${}^1\pi\sigma^*/{}^3n\pi^*/{}^3\pi\pi^*$)

C	2.375852000	0.122894002	0.287155002
C	1.804649997	-1.157736002	0.180688000
C	0.466088002	-1.295296998	-0.139226000
C	-0.332216001	-0.119846000	-0.380049999
C	0.239735000	1.161142998	-0.238324002
C	1.629583002	1.259828999	0.088810003
H	3.419246001	0.211394997	0.515738999
H	2.417838003	-2.026097002	0.324351998
H	0.003680999	-2.256352998	-0.273079998
H	-0.351620999	2.032581000	-0.445516998
H	2.093608001	2.226848001	0.161925000
O	-1.518258000	-0.283005998	-0.807038999
N	-3.056919000	0.191984998	0.699805997
H	-2.950876002	-0.544467000	1.363923000
H	-3.628999999	-0.001650001	-0.094042999
H	-3.068991999	1.127067000	1.046943002

1 CI (${}^1\pi\sigma^*/S_0$)

C	2.297230406	0.316637583	0.426197761
C	1.859123350	-1.027130516	0.405075671
C	0.608286512	-1.319863501	-0.042411005

C	-0.268843020	-0.253188494	-0.502790593
C	0.200855050	1.119185455	-0.433910280
C	1.450859250	1.375584194	0.012393171
H	3.298990630	0.543226445	0.753731561
H	2.527476284	-1.801317339	0.728306605
H	0.238242835	-2.326163495	-0.105703017
H	-0.447217198	1.898041505	-0.786665707
H	1.822389267	2.380684352	0.043388873
O	-1.348688934	-0.524581019	-0.946204016
N	-3.284928867	0.229391778	0.778349998
H	-3.147686350	-0.493195406	1.434329520
H	-2.933022795	0.148633602	-0.128210104
H	-3.902549885	0.964222936	1.002721713

1 Path-S₀-33

C	2.290711244	0.317087927	0.424323448
C	1.868235549	-1.039748536	0.409150965
C	0.620202716	-1.333164996	-0.036660310
C	-0.269878846	-0.258185964	-0.503580079
C	0.203724265	1.133747577	-0.436044675
C	1.459828629	1.393150957	0.013471010
H	3.289669866	0.540730638	0.761158199
H	2.544562264	-1.804518899	0.739724457
H	0.243479444	-2.337802394	-0.089554196
H	-0.467516150	1.904843756	-0.763935983
H	1.842890240	2.394542086	0.059435447
O	-1.355164286	-0.532244085	-0.964895202
N	-3.258632536	0.255140318	0.797884010
H	-3.315939511	-0.568610077	1.356904311
H	-3.221956483	0.039158900	-0.172931401
H	-4.016326439	0.871634147	0.996997793

1 T_{PP}(1 $\pi\pi^*$)-min

C	2.048857079	0.296968109	0.723310050
C	1.753456850	-1.027572125	0.397075950
C	0.589154045	-1.371603018	-0.360063415

C	-0.315667947	-0.342573466	-0.815237674
C	0.006804547	1.010524199	-0.445433011
C	1.186047990	1.297365684	0.313193593
H	2.931671636	0.525513047	1.288917761
H	2.411842504	-1.816862159	0.716773558
H	0.377699444	-2.397374676	-0.598893452
H	-0.656777727	1.796899085	-0.744410628
H	1.399559622	2.319798546	0.566430830
O	-1.312167126	-0.633206442	-1.490327639
N	-2.626892010	0.616045266	1.290556427
H	-2.787160330	-0.113191392	1.960628563
H	-3.298021199	0.475107606	0.558096854
H	-2.882316618	1.472107738	1.746007082

1 T_{NP}(1nπ*)-min

C	2.157905821	0.395187933	0.579251159
C	1.897376049	-1.000851876	0.350363905
C	0.754393282	-1.426306934	-0.218854655
C	-0.211360925	-0.427739205	-0.585798887
C	0.011948348	0.986555052	-0.351586858
C	1.206430162	1.363298386	0.221443464
H	3.086562864	0.687339211	1.030443901
H	2.640153954	-1.720435296	0.643173951
H	0.536131141	-2.459042241	-0.407303348
H	-0.765754802	1.671399171	-0.619434726
H	1.401400741	2.403607792	0.399309072
O	-1.270784481	-0.780275378	-1.148603244
N	-3.020564867	0.692082634	0.784487253
H	-3.075616928	0.101226850	1.593462808
H	-3.799952005	0.443138740	0.203806178
H	-3.201951826	1.623799979	1.109053631

1 oxenium ion

C	1.893096042	0.431851420	0.728375118
C	1.723580683	-0.975652725	0.533266016
C	0.667632883	-1.415351790	-0.196794548

C	-0.277968310	-0.440819332	-0.789550045
C	-0.070033959	1.000810139	-0.503088266
C	1.010621424	1.406077577	0.221642375
H	2.746470134	0.763018739	1.297028170
H	2.440369523	-1.649495625	0.962736434
H	0.490788310	-2.456729816	-0.392159173
H	-0.777337074	1.688938317	-0.921918950
H	1.199780505	2.443415965	0.422584919
O	-1.175280603	-0.806049670	-1.518166659
N	-2.511312391	0.626315337	1.148481549
H	-2.624514432	-0.069792245	1.862098411
H	-3.235095705	0.454483946	0.474533130
H	-2.730854532	1.504979339	1.580109988

Cartesian coordinates for 2 to produce oxenium ion

2 S₀-Min

C	-0.550195047	-0.993438531	-0.693601024
C	-1.924331407	-0.953882722	-0.789153057
C	-2.587140823	0.154664233	-0.291077331
C	-1.925892279	1.225593083	0.286098364
C	-0.537814358	1.165345332	0.376382854
C	0.170065593	0.057145324	-0.107459640
H	-0.020273729	-1.833504456	-1.102124262
H	-2.469134900	-1.744221977	-1.275066462
H	-2.469257394	2.086412736	0.633450404
O	-3.993048948	0.211551504	-0.410880240
N	-4.616259099	-0.370938700	0.753187493
H	-5.609762931	-0.300806277	0.583485408
H	-4.335917313	-1.337887305	0.842138151
H	-4.356821910	0.153279064	1.577405618
C	1.655040921	0.001164789	-0.012996717
C	2.297120189	-1.162270045	0.419868264
C	2.431186388	1.113321097	-0.356962530
C	3.686316340	-1.208114432	0.509864326
H	1.718812436	-2.022686767	0.707873818

C	3.805875616	1.064071538	-0.271274647
H	1.955148118	2.009258831	-0.714850882
C	4.442824336	-0.093359783	0.163359682
H	4.170187338	-2.104832994	0.852364877
H	4.387564769	1.924584645	-0.548983533
H	5.515069573	-0.126447045	0.229578674
H	-0.005741576	1.979571172	0.831166423

2 Path-S_{CT}(¹πσ*)-4

C	-0.515473811	-1.062212348	-0.675558138
C	-1.973505906	-1.025383559	-0.796293012
C	-2.612797670	0.180618497	-0.315173545
C	-1.904335651	1.239584794	0.281979542
C	-0.546341171	1.207536237	0.361714275
C	0.207924523	0.064331870	-0.094570737
H	0.028131957	-1.893092084	-1.077613454
H	-2.504844321	-1.717209384	-1.418760940
H	-2.453942010	2.096864309	0.628139877
O	-3.971440370	0.269267076	-0.409457106
N	-4.641713483	-0.397467313	0.789392853
H	-5.626669562	-0.330038790	0.596215100
H	-4.330371064	-1.352719349	0.828583641
H	-4.384690998	0.118731504	1.612909749
C	1.655436581	0.010059788	-0.005118950
C	2.306696011	-1.173906981	0.401966224
C	2.443268949	1.133827191	-0.331179122
C	3.690628034	-1.215892735	0.504463968
H	1.726711169	-2.037620816	0.673756586
C	3.811606044	1.071451815	-0.267324636
H	1.966655749	2.034803656	-0.674605079
C	4.448642830	-0.095729131	0.162117297
H	4.176086220	-2.113195577	0.843370584
H	4.398729117	1.927204157	-0.548947671
H	5.521353605	-0.130491830	0.225151609
H	-0.022427697	2.034168516	0.802159953

2 Path-S_{CT}(¹πσ*)-8

C	-0.527014737	-1.051034320	-0.666188282
C	-1.963048284	-1.006442099	-0.792909421
C	-2.628362228	0.170859180	-0.339519698
C	-1.894219110	1.239424855	0.281940579
C	-0.541112757	1.199006101	0.355828121
C	0.202068845	0.061528404	-0.094171477
H	0.015899875	-1.894932912	-1.056989078
H	-2.501101032	-1.737355363	-1.369623096
H	-2.446943513	2.096451668	0.622869891
O	-3.922018295	0.301780329	-0.466586589
N	-4.685280217	-0.438746491	0.861551579
H	-5.634345225	-0.330270104	0.595934314
H	-4.360030586	-1.373978860	0.857218337
H	-4.413568989	0.101721750	1.645910555
C	1.648573470	0.011523496	-0.006770323
C	2.309616255	-1.178579002	0.400167223
C	2.445761369	1.138735660	-0.328675587
C	3.689289993	-1.219092019	0.503593902
H	1.728089183	-2.041575024	0.672394314
C	3.808730580	1.075948128	-0.266654635
H	1.967743891	2.038991004	-0.671153441
C	4.450930220	-0.096815844	0.162409973
H	4.175663719	-2.116132918	0.842249776
H	4.397963467	1.930692789	-0.548256475
H	5.524926081	-0.131185555	0.224836759
H	-0.015566873	2.027589737	0.795053944

2 Path-S_{CT}(¹πσ*)-11

C	-0.533376038	-1.036821905	-0.655603610
C	-1.948633136	-0.981868949	-0.790634700
C	-2.608595907	0.165361612	-0.340622239
C	-1.888522067	1.230410178	0.274995512
C	-0.534682195	1.192456676	0.352371800
C	0.193684618	0.054994533	-0.096341866

H	-0.003747024	-1.892809144	-1.034417435
H	-2.494174763	-1.749948717	-1.306895785
H	-2.445261524	2.083391425	0.616357756
O	-3.906022156	0.332544295	-0.533499029
N	-4.717067339	-0.474133842	0.926119819
H	-5.644186705	-0.332984404	0.603649893
H	-4.401463974	-1.413052758	0.918032503
H	-4.449993343	0.073472739	1.707360188
C	1.643746759	0.011147752	-0.010164698
C	2.311017696	-1.184017018	0.398904626
C	2.444411861	1.143880263	-0.327725352
C	3.688886538	-1.223844009	0.503800294
H	1.728342500	-2.046398167	0.671009627
C	3.805100932	1.080816913	-0.266679445
H	1.966225745	2.044222566	-0.669226686
C	4.451979679	-0.098559979	0.163008732
H	4.175255433	-2.120624818	0.843372616
H	4.395021501	1.935453850	-0.548665593
H	5.526309350	-0.131829310	0.225179044
H	-0.007913197	2.018878278	0.792411836

2 Path-Scr($^1\pi\sigma^*$)-14

C	-0.528069555	-1.028906752	-0.638275849
C	-1.927275177	-0.956342814	-0.790062125
C	-2.594439807	0.187234245	-0.361616641
C	-1.877841968	1.236581141	0.262595912
C	-0.526719577	1.184958747	0.354413815
C	0.189974034	0.047951651	-0.097022183
H	-0.007641914	-1.895234903	-0.996992353
H	-2.474099292	-1.742101908	-1.274903565
H	-2.426656916	2.094500453	0.599312073
O	-3.881037677	0.367939639	-0.643456849
N	-4.771620936	-0.531662265	1.041089164
H	-5.677418877	-0.354227475	0.655628857
H	-4.480748294	-1.488036973	1.048355456
H	-4.524633842	0.012188280	1.843355450

C	1.650939056	0.005118192	-0.013583378
C	2.310602763	-1.187337759	0.394740567
C	2.435361459	1.142002424	-0.326693334
C	3.690777601	-1.227911334	0.500134700
H	1.726612810	-2.049021003	0.662876130
C	3.799490452	1.082273257	-0.261581187
H	1.952994393	2.042151367	-0.661354343
C	4.446071648	-0.098473446	0.162862688
H	4.179267755	-2.124299477	0.837138384
H	4.388122029	1.939623507	-0.535384916
H	5.519191281	-0.128049291	0.225450387
H	0.007427586	2.003445136	0.797867426

2 STC($1\pi\sigma^*/3n\pi^*/3\pi\pi^*$)

C	-0.543242420	-1.040265553	-0.638187910
C	-1.906811041	-0.971822963	-0.794262401
C	-2.633812849	0.215109345	-0.400235432
C	-1.869369655	1.258093885	0.264322138
C	-0.530919867	1.191290649	0.358542881
C	0.196099531	0.047911287	-0.094553242
H	-0.010030944	-1.899331412	-0.995587128
H	-2.450714981	-1.746793027	-1.297006849
H	-2.410101458	2.121702529	0.598831892
O	-3.827896374	0.381109952	-0.681688720
N	-4.812433138	-0.569409971	1.114201812
H	-5.646981766	-0.322167091	0.601060628
H	-4.479666185	-1.519456322	1.068034399
H	-4.522528680	0.017349878	1.880820294
C	1.653985614	0.000765453	-0.010929112
C	2.306961102	-1.184034941	0.390257929
C	2.431519637	1.135638983	-0.322618253
C	3.691456339	-1.222471879	0.496540518
H	1.728672321	-2.049061342	0.657103394
C	3.802122839	1.076428600	-0.257827778
H	1.951795743	2.037832349	-0.655453980
C	4.441613991	-0.094804538	0.161591848

H	4.179591770	-2.118792324	0.830917784
H	4.386766092	1.936093615	-0.529239882
H	5.513127757	-0.124850811	0.224805002
H	0.012731962	1.999746118	0.807826462

2 Cl ($1\pi\sigma^*/S_0$)

C	-0.539603792	-1.037018018	-0.630138198
C	-1.876568863	-0.929531250	-0.868457088
C	-2.588653609	0.283969504	-0.523380087
C	-1.826616097	1.351116704	0.103834097
C	-0.501650446	1.219926494	0.305929678
C	0.199053702	0.048991512	-0.073197093
H	-0.008590187	-1.915926834	-0.936853497
H	-2.414191792	-1.700718718	-1.378743324
H	-2.349425608	2.243517174	0.377309944
O	-3.806497939	0.384904917	-0.687075935
N	-4.981597775	-0.719384598	1.360990893
H	-4.701431485	-0.287969458	0.429841891
H	-5.142375381	-1.734526942	1.450448375
H	-5.073435439	-0.128088344	2.201976866
C	1.660196128	-0.012899197	0.025488468
C	2.316950328	-1.197705770	0.384977443
C	2.426453416	1.122206967	-0.271797543
C	3.704573775	-1.229307510	0.465835856
H	1.749494001	-2.072324016	0.635557513
C	3.800613101	1.074593143	-0.223338627
H	1.939734931	2.025385629	-0.585467987
C	4.448449538	-0.096359007	0.155677032
H	4.200106115	-2.132612968	0.764752731
H	4.371875388	1.946267497	-0.481406033
H	5.518004019	-0.125852134	0.204199869
H	0.047739419	2.014463903	0.770225212

2 Path-S₀-22

C	-0.541267002	-1.045640999	-0.631514001
C	-1.869535002	-0.936164000	-0.872240002

C	-2.587858001	0.282839001	-0.521885001
C	-1.819025002	1.357464000	0.106138002
C	-0.504093999	1.231890001	0.307451003
C	0.209563001	0.047488001	-0.074972002
H	-0.009607001	-1.925800001	-0.933840001
H	-2.421059999	-1.710717998	-1.370004998
H	-2.355091001	2.244551001	0.388368999
O	-3.779632001	0.390773998	-0.696856998
N	-4.976831999	-0.724170000	1.369594997
H	-4.837939000	-0.326271001	0.491501998
H	-5.165669001	-1.690466999	1.447032002
H	-5.100403999	-0.151132001	2.164380997
C	1.651779998	-0.012275002	0.024950998
C	2.318021002	-1.202631002	0.383570001
C	2.427881999	1.127076001	-0.270135000
C	3.702339002	-1.232247000	0.467042003
H	1.752472999	-2.080022000	0.636275998
C	3.798016000	1.077242998	-0.224532002
H	1.944155000	2.033565000	-0.582126000
C	4.448228998	-0.096491000	0.155644999
H	4.198468999	-2.135510002	0.767727998
H	4.371132000	1.947641998	-0.483544998
H	5.520993998	-0.126219003	0.204766999
H	0.047335000	2.021673001	0.776573000

2 Path-S₀-25

C	-0.531036000	-1.067092998	-0.622504002
C	-1.857841000	-0.953549002	-0.870538999
C	-2.583287000	0.280828000	-0.519743998
C	-1.807278003	1.367291002	0.116543002
C	-0.488039999	1.258336999	0.297412002
C	0.217102999	0.052312002	-0.085783998
H	0.002344001	-1.954135003	-0.903987001
H	-2.420520000	-1.740217000	-1.337272999
H	-2.354958998	2.241161002	0.419801000
O	-3.766405999	0.416119001	-0.745830998

N	-4.947751000	-0.746171000	1.403872999
H	-5.372522001	-0.368961000	0.579670998
H	-5.330966998	-1.665217999	1.524642000
H	-5.286155998	-0.198789000	2.173326998
C	1.648055998	-0.011533000	0.022790997
C	2.311750998	-1.213940002	0.367023999
C	2.423805000	1.140968999	-0.252934998
C	3.694104998	-1.239200997	0.468639001
H	1.746655002	-2.094605998	0.610454001
C	3.791832998	1.082390999	-0.224105999
H	1.941833997	2.054002000	-0.548629000
C	4.436731997	-0.097988000	0.155167999
H	4.192492000	-2.139799000	0.774522999
H	4.370153001	1.949310002	-0.484051998
H	5.509780001	-0.128092999	0.204754003
H	0.066763002	2.045369002	0.769464001

2 oxenium ion

C	-0.667636693	-1.042572808	-0.478969817
C	-1.985827428	-0.919419863	-0.753853330
C	-2.646980472	0.396989989	-0.703757327
C	-1.831976795	1.533347701	-0.217405572
C	-0.530496726	1.395427642	0.036069002
C	0.137339351	0.112529542	-0.126702586
H	-0.197820061	-1.998314085	-0.581361375
H	-2.583135094	-1.757837829	-1.055482981
H	-2.335738021	2.474869345	-0.095409970
O	-3.786676721	0.563976575	-1.079632075
N	-4.136346225	-1.048793810	1.731403383
H	-4.985645113	-0.957423992	1.205719905
H	-4.119676131	-1.984951312	2.089774250
H	-4.227354240	-0.443605605	2.525749500
C	1.550462875	-0.000580518	0.038806706
C	2.171505094	-1.262692387	0.242874847
C	2.383207495	1.150025677	-0.026264787
C	3.542429268	-1.357055438	0.387661812

H	1.584033965	-2.153688310	0.336004423
C	3.741716303	1.041617167	0.085050616
H	1.960410246	2.116281595	-0.214435258
C	4.330453520	-0.206219956	0.299319501
H	3.999777532	-2.312081533	0.564496385
H	4.357668175	1.917672896	0.005567177
H	5.398000483	-0.282165892	0.397130227
H	0.030981090	2.232271216	0.396362427

Cartesian coordinates for 3 to produce oxenium ion

3 S₀-Min

C	0.422748516	2.187366213	0.032205640
C	1.603750014	1.464729996	-0.206160021
C	1.455907326	0.105781328	-0.335421331
C	0.246168765	-0.578156477	-0.240170800
C	-0.923793058	0.137092764	-0.001677328
C	-0.796922336	1.551927929	0.138186210
H	0.465785841	3.256460882	0.128135074
H	2.557103019	1.946057107	-0.322156443
H	0.238125522	-1.636089464	-0.414428065
H	-1.667267132	2.150037553	0.314351048
O	2.611811686	-0.674659669	-0.577892634
N	3.158034930	-1.119243659	0.679152013
H	3.946754008	-1.701970058	0.437832622
H	3.454687325	-0.317796095	1.218511887
H	2.458421924	-1.647448640	1.182357481
N	-2.138745889	-0.472368490	0.094916687
C	-3.353202225	0.318331869	0.214018548
H	-4.198890526	-0.348087989	0.277081850
H	-3.345354326	0.920273490	1.115888390
H	-3.502682537	0.970775991	-0.641826073
C	-2.249325323	-1.893215377	-0.167651711
H	-1.649331215	-2.469507885	0.530797648
H	-3.275433919	-2.200281705	-0.041800071
H	-1.943424879	-2.147010214	-1.180060423

3 Path-S_{CT}(¹πσ*)-4

C	0.429157495	2.201160324	0.032862964
C	1.608413325	1.477031462	-0.205275070
C	1.470888143	0.087273099	-0.347961094
C	0.249972254	-0.596303219	-0.238146788
C	-0.934781365	0.150923069	0.002308158
C	-0.815366741	1.545808597	0.139849774
H	0.468410091	3.265225523	0.122218964
H	2.563466264	1.952951725	-0.328365769
H	0.234273143	-1.643582238	-0.433025045
H	-1.674061932	2.147453776	0.316733777
O	2.628375209	-0.667689198	-0.580498250
N	3.164114579	-1.122426194	0.687041893
H	3.950330585	-1.705585116	0.450240967
H	3.459115274	-0.321939362	1.223404131
H	2.453632018	-1.644824392	1.176932091
N	-2.128937933	-0.467640495	0.092454319
C	-3.355814678	0.319211663	0.215572462
H	-4.198438979	-0.350604701	0.278240324
H	-3.336337690	0.920680718	1.115777850
H	-3.492396294	0.968053634	-0.642962931
C	-2.249842261	-1.897134612	-0.166471906
H	-1.648928193	-2.466348030	0.532761176
H	-3.277233164	-2.197949642	-0.038764304
H	-1.946373174	-2.142578588	-1.178884470

3 Path-S_{CT}(¹πσ*)-7

C	0.426110147	2.207891231	0.036180223
C	1.607197238	1.485809147	-0.201909564
C	1.484757836	0.068192357	-0.376320680
C	0.255041722	-0.612661326	-0.231730496
C	-0.938513203	0.158416421	0.005848536
C	-0.825280083	1.553368831	0.142346906
H	0.465471303	3.276535973	0.116421066
H	2.561716677	1.964109338	-0.336271056

H	0.220710269	-1.653295699	-0.467869765
H	-1.688821765	2.149917382	0.322757132
O	2.609300279	-0.652495413	-0.597972652
N	3.180469939	-1.136404464	0.718142661
H	3.955041326	-1.716561200	0.461875948
H	3.471796080	-0.332631534	1.239624069
H	2.454580684	-1.648288640	1.182165025
N	-2.122392397	-0.463017439	0.087359608
C	-3.356973910	0.318941572	0.217118730
H	-4.197244732	-0.353481169	0.279842416
H	-3.332947908	0.919711884	1.117480890
H	-3.490563203	0.966837320	-0.642343714
C	-2.249873847	-1.900216725	-0.165860952
H	-1.647949406	-2.467554724	0.533139247
H	-3.278964997	-2.192429831	-0.033422727
H	-1.952434846	-2.144953848	-1.179734381

3 Path-S_{CT}(¹πσ*)-10

C	0.415378001	2.202236798	0.037831214
C	1.599756821	1.479851024	-0.201374187
C	1.496685925	0.059190019	-0.387165106
C	0.263873344	-0.606504380	-0.234741750
C	-0.943005907	0.153536653	0.007218838
C	-0.818958722	1.567563968	0.143604255
H	0.458761858	3.274471890	0.122527514
H	2.553483954	1.960655647	-0.337163006
H	0.228684610	-1.658105423	-0.455642576
H	-1.689840860	2.158607356	0.322371529
O	2.574764130	-0.627769786	-0.652521999
N	3.209790206	-1.160401843	0.784564338
H	3.956735757	-1.717738868	0.457311910
H	3.491690303	-0.346002159	1.264809541
H	2.479078024	-1.665800110	1.210904382
N	-2.118169790	-0.459615273	0.084567107
C	-3.357420414	0.319542314	0.218004839
H	-4.195250358	-0.355294904	0.280595654

H	-3.335557741	0.917894796	1.119524800
H	-3.494493318	0.965586054	-0.641743135
C	-2.249459411	-1.901348905	-0.165396473
H	-1.648509857	-2.468883345	0.533934489
H	-3.279032763	-2.189533554	-0.030609322
H	-1.955226219	-2.146718543	-1.179831443

3 Path-S_{CT}(¹πσ*)-13

C	0.400186498	2.195949839	0.040843948
C	1.591686693	1.458743668	-0.203495114
C	1.505349573	0.082359075	-0.386410045
C	0.265555817	-0.597288796	-0.242368958
C	-0.946988987	0.154153999	0.008609570
C	-0.818104762	1.579215557	0.145925555
H	0.451061229	3.267212679	0.132139206
H	2.538165659	1.947730381	-0.335141019
H	0.246224574	-1.659172139	-0.429011129
H	-1.687313679	2.171034459	0.321146134
O	2.551606206	-0.617826122	-0.724564851
N	3.240214352	-1.183257421	0.855887711
H	3.974684640	-1.724424901	0.468480724
H	3.529337005	-0.362258535	1.328312023
H	2.521699971	-1.705002894	1.291601928
N	-2.116040613	-0.457631440	0.080733503
C	-3.357186639	0.320238991	0.219306843
H	-4.191474165	-0.358378078	0.282009998
H	-3.336671897	0.916294976	1.122235886
H	-3.499204398	0.966210832	-0.639471710
C	-2.248380387	-1.901790806	-0.164586153
H	-1.649688319	-2.470026357	0.535919687
H	-3.278621730	-2.185153427	-0.026467290
H	-1.958789323	-2.150429170	-1.179380806

3 Path-S_{CT}(¹πσ*)-16

C	0.391433382	2.186801798	0.046207628
C	1.592001834	1.451306590	-0.207351088

C	1.522827080	0.113389255	-0.398769907
C	0.250746372	-0.584936433	-0.248645062
C	-0.956503218	0.157944315	0.008382371
C	-0.828705320	1.580189810	0.149458340
H	0.446884365	3.257107076	0.142896063
H	2.530251591	1.950838827	-0.329902123
H	0.249018497	-1.651428683	-0.405946880
H	-1.693592748	2.177891866	0.323763004
O	2.532351483	-0.614072636	-0.797847777
N	3.271814743	-1.206332603	0.923276576
H	4.021165400	-1.744986612	0.550532049
H	3.599072411	-0.419801162	1.438852049
H	2.631377750	-1.765128447	1.440687188
N	-2.119908809	-0.456807373	0.075740424
C	-3.357246865	0.320145301	0.221663081
H	-4.190965049	-0.358201183	0.285246018
H	-3.333965267	0.912356405	1.126909104
H	-3.503705278	0.969027055	-0.633977184
C	-2.247172635	-1.901390853	-0.163030146
H	-1.648308384	-2.465964366	0.539732446
H	-3.276891993	-2.183273176	-0.021251507
H	-1.960696975	-2.154466777	-1.177262446

3 Path-S_{CT}(¹πσ*)-18

C	0.382753981	2.185682006	0.053548829
C	1.594070060	1.452873626	-0.212257858
C	1.513432089	0.121163160	-0.410782702
C	0.237112556	-0.574631611	-0.247309912
C	-0.970985519	0.158741140	0.009005643
C	-0.837500415	1.586073054	0.152497623
H	0.438428425	3.254762176	0.156580661
H	2.531065694	1.957024803	-0.330671327
H	0.240474375	-1.639897958	-0.393453242
H	-1.699593824	2.187824719	0.328125719
O	2.504127132	-0.616284825	-0.862462262
N	3.293821352	-1.222557426	0.979050964

H	4.046963060	-1.746639661	0.583006302
H	3.671134832	-0.468785086	1.517081422
H	2.759451286	-1.819432400	1.576712411
N	-2.128885185	-0.454569249	0.072846087
C	-3.365552614	0.321243829	0.224541260
H	-4.198977316	-0.357180390	0.288201161
H	-3.338525706	0.909842586	1.131711768
H	-3.513113155	0.971574250	-0.629367780
C	-2.249213249	-1.902005292	-0.161337262
H	-1.647704407	-2.458865120	0.544693028
H	-3.278013615	-2.187156278	-0.020817821
H	-1.958350143	-2.153814450	-1.174197579

3 Cl ($1\pi\sigma^*/S_0$)

C	0.377507155	2.187816289	0.050015837
C	1.590839205	1.454239825	-0.227987035
C	1.498421817	0.124928725	-0.424847083
C	0.236160653	-0.567791535	-0.267381509
C	-0.973940212	0.158945902	-0.005419424
C	-0.840626895	1.590315796	0.147449090
H	0.434736027	3.255490398	0.163481823
H	2.529410110	1.957090976	-0.342746245
H	0.244349882	-1.631779771	-0.416174300
H	-1.701865000	2.190827546	0.331316623
O	2.479947933	-0.618145894	-0.894681928
N	3.304650927	-1.232850452	1.018995326
H	4.055135626	-1.750196187	0.606929241
H	3.697398920	-0.486941245	1.558719633
H	2.803608096	-1.840344860	1.636106636
N	-2.131826796	-0.451736442	0.062896967
C	-3.370301313	0.320838397	0.237000255
H	-4.200241727	-0.361168768	0.307134381
H	-3.332072627	0.902641992	1.148048708
H	-3.531120110	0.976019487	-0.610552327
C	-2.253840644	-1.900759804	-0.167801852
H	-1.642742751	-2.454232803	0.532524126

H	-3.280561985	-2.187335283	-0.015866538
H	-1.972442625	-2.152202999	-1.183284975

3 Path-S₀-23

C	0.432833446	2.219576412	0.126596414
C	1.543172459	1.564279159	-0.208433941
C	1.433113195	0.114551550	-0.509767362
C	0.222781700	-0.587212261	-0.362627991
C	-0.960669182	0.101430908	-0.013011142
C	-0.809851608	1.508586212	0.217844047
H	0.443745896	3.275854996	0.316555644
H	2.495217041	2.046032051	-0.315954288
H	0.232747809	-1.634937170	-0.572224262
H	-1.686057227	2.072040213	0.470804172
O	2.419877970	-0.455540893	-0.987749293
N	3.421207751	-1.267540101	0.992632647
H	4.145889339	-1.720941814	0.479454757
H	3.825595342	-0.529072353	1.527324209
H	3.005942398	-1.929784652	1.619275275
N	-2.148369078	-0.484181311	0.083322565
C	-3.364631665	0.282564386	0.369363612
H	-4.193942930	-0.400668227	0.436304700
H	-3.285287956	0.799944039	1.317478177
H	-3.574746884	0.995937010	-0.419735287
C	-2.280436638	-1.910845811	-0.221210452
H	-1.636606058	-2.501210640	0.418514803
H	-3.297720859	-2.212919685	-0.040486643
H	-2.041540638	-2.111480143	-1.259522531

3 Path-S₀-25

C	0.377321999	2.237510415	0.175984318
C	1.513748378	1.627642202	-0.231917134
C	1.452533593	0.180706102	-0.623960970
C	0.182598963	-0.538854128	-0.479031418
C	-0.994349525	0.106716861	-0.040370022
C	-0.852503892	1.486627118	0.261714615

H	0.339045881	3.274008278	0.449423878
H	2.466240279	2.116145380	-0.309072800
H	0.204640211	-1.574297643	-0.749814935
H	-1.720085568	2.031786626	0.580386911
O	2.421543461	-0.387469064	-1.084259031
N	3.563130412	-1.333353113	1.121553497
H	4.239796388	-1.777500183	0.532249128
H	4.032066086	-0.613323300	1.632323627
H	3.234940910	-2.014394697	1.777690295
N	-2.170244197	-0.515618350	0.078769825
C	-3.366885272	0.214830033	0.489903643
H	-4.189752328	-0.477405233	0.551178232
H	-3.237963962	0.659377924	1.470337989
H	-3.628736453	0.985929712	-0.226967298
C	-2.289647211	-1.929273319	-0.276990233
H	-1.618557970	-2.538167834	0.317253714
H	-3.296247190	-2.255358648	-0.074926457
H	-2.084839619	-2.089679358	-1.330250076

3 oxenium ion

C	1.053120337	1.976950067	0.196522929
C	2.049928494	1.187742145	-0.270333626
C	1.700957287	-0.158246964	-0.762280970
C	0.291521798	-0.603516492	-0.693798132
C	-0.734086639	0.227114037	-0.186739269
C	-0.309100168	1.518674214	0.235237291
H	1.247286662	2.970656478	0.552919903
H	3.075868192	1.496552970	-0.322722644
H	0.103385353	-1.595302096	-1.050208195
H	-1.039251141	2.202904540	0.619482886
O	2.524654828	-0.908210561	-1.241726824
N	1.561109980	-1.378192953	2.048844194
H	2.182852485	-2.102864656	1.740303218
H	2.102062793	-0.783819717	2.649082682
H	0.880503036	-1.822135278	2.636966777
N	-2.003158110	-0.160349777	-0.118919065

C	-3.037743575	0.737334036	0.396834174
H	-3.985347963	0.226799303	0.367720275
H	-2.838469271	1.015008198	1.425593777
H	-3.120632656	1.631219816	-0.211050285
C	-2.385300280	-1.499637618	-0.571024295
H	-1.874178861	-2.263569208	0.003152098
H	-3.445234060	-1.625839925	-0.428858774
H	-2.167529761	-1.632607383	-1.624551664

Cartesian coordinates for 1 to produce HBD

1 Path-S_{NE}(1nσ*)-21

C	2.325318489	0.077425488	0.275098665
C	1.676652530	-1.186540516	0.146754928
C	0.322198479	-1.258493726	-0.155992293
C	-0.381101937	-0.073890950	-0.361518287
C	0.196851568	1.196671583	-0.267120235
C	1.587798135	1.273869992	0.069306001
H	3.372911887	0.117971727	0.513556868
H	2.229102788	-2.100831419	0.278903923
H	-0.183414195	-2.201101490	-0.272164007
H	-0.368336834	2.068821926	-0.549537672
H	2.065855507	2.236318385	0.135684049
O	-1.656610852	-0.212278040	-0.743212417
N	-2.743690747	0.130471264	0.715482804
H	-2.508819844	-0.636992690	1.314824951
H	-3.633273354	0.084985102	0.259020788
H	-2.431421988	1.034130044	1.012617544

1 Path-S_{NE}(1nσ*)-24

C	2.304007648	0.078344809	0.270424630
C	1.677155741	-1.170839970	0.151355704
C	0.341699276	-1.256842989	-0.158323475
C	-0.352403694	-0.071379899	-0.374933849
C	0.214219719	1.189236140	-0.262716907
C	1.578240453	1.252913483	0.067297602
H	3.349084300	0.127032590	0.507086241

H	2.242749238	-2.072718581	0.294765096
H	-0.150947191	-2.203954423	-0.282381252
H	-0.344073338	2.074235103	-0.508409243
H	2.061126451	2.209808885	0.136981709
O	-1.632802834	-0.226022029	-0.795740139
N	-2.804112608	0.150932260	0.784511648
H	-2.494606852	-0.647723684	1.306894865
H	-3.655697208	0.090541327	0.258279536
H	-2.422152390	1.049680759	1.013288874

1 Path-S_{NE}(1nσ*)-27

C	2.305819016	0.081225713	0.275305867
C	1.693594219	-1.166347986	0.164996198
C	0.367453952	-1.260750497	-0.173455198
C	-0.329652690	-0.082812554	-0.413569334
C	0.222845087	1.178701025	-0.267702927
C	1.577575134	1.246499791	0.071471978
H	3.348868602	0.140619665	0.516559340
H	2.265572795	-2.060901688	0.327775320
H	-0.112879008	-2.212118569	-0.309436660
H	-0.337752369	2.066709821	-0.496417524
H	2.057127390	2.203999276	0.153613665
O	-1.609688679	-0.236090290	-0.863020083
N	-2.892126622	0.180462818	0.883117632
H	-2.520455356	-0.642296935	1.325228967
H	-3.708338194	0.113515968	0.299135317
H	-2.443815843	1.067099570	1.038108187

1 Path-S_{NE}(1nσ*)-30

C	2.317540504	0.090527955	0.309453359
C	1.721321705	-1.161642372	0.175272926
C	0.407144061	-1.273757404	-0.214932463
C	-0.305485172	-0.106572919	-0.473671933
C	0.237908369	1.156742593	-0.305860069
C	1.578340647	1.244132855	0.081140428
H	3.349894132	0.163509570	0.590008158

H	2.294943910	-2.050958040	0.360570597
H	-0.051735806	-2.234609147	-0.361092171
H	-0.326764155	2.040250064	-0.541912191
H	2.037068905	2.209617640	0.183979120
O	-1.598464269	-0.236623778	-0.914273318
N	-2.994195404	0.215427020	0.994636556
H	-2.610402788	-0.626279528	1.392297193
H	-3.801697946	0.162360782	0.394692308
H	-2.512776455	1.090805647	1.124757813

1 Cl ($1\sigma^*/3\sigma^*$)

C	2.317898402	0.098856441	0.351893051
C	1.744948956	-1.158053397	0.172666019
C	0.446118493	-1.284127913	-0.265655937
C	-0.280387893	-0.124521066	-0.524836806
C	0.256377531	1.141705863	-0.354918819
C	1.578501231	1.244372287	0.085696835
H	3.333637934	0.182549688	0.685830961
H	2.323524372	-2.041436342	0.370791038
H	0.005274709	-2.250406453	-0.427987126
H	-0.312003932	2.019379372	-0.603123208
H	2.022482335	2.214701388	0.208211796
O	-1.588137576	-0.246922969	-0.927875920
N	-3.085410247	0.245687056	1.080554658
H	-2.730721370	-0.622711482	1.448932425
H	-3.890339163	0.242463562	0.473761847
H	-2.567523900	1.094993582	1.233718541

1 Path- $T_{\Sigma\Sigma}(3\sigma^*)$ -37

C	2.291620873	0.245813728	0.458570632
C	1.765774366	-1.091617844	0.360197623
C	0.539016321	-1.324894612	-0.127758940
C	-0.307923632	-0.212240919	-0.538554169
C	0.258175033	1.128675063	-0.487682916
C	1.527417873	1.335725399	0.018029587
H	3.278105306	0.398067156	0.852867987

H	2.382281234	-1.910587075	0.684655716
H	0.137446673	-2.317246879	-0.217163394
H	-0.341430008	1.939470321	-0.862356881
H	1.934173373	2.328588466	0.065725868
O	-1.489530348	-0.384575237	-0.868050093
N	-3.180222977	0.213529698	0.830470121
H	-2.893350953	-0.620555598	1.314933665
H	-3.705858655	0.128299431	-0.025296636
H	-2.797473656	1.105708099	1.093927867

1 Cl ($^3\sigma\sigma^*/S_0$)

C	2.343365454	0.238886475	0.403534647
C	1.808376797	-1.096384763	0.322838382
C	0.566908846	-1.324060549	-0.128162295
C	-0.281357077	-0.206298364	-0.506353078
C	0.284049038	1.133960004	-0.468427632
C	1.570682119	1.334080213	-0.009917104
H	3.342481010	0.386060130	0.766859708
H	2.429629215	-1.917204326	0.632505134
H	0.151059789	-2.311668219	-0.200736420
H	-0.327558283	1.948609757	-0.811083130
H	1.982685168	2.324967459	0.027592360
O	-1.469673115	-0.385035780	-0.808673040
N	-3.356887257	0.218904477	0.821126703
H	-3.634463325	-0.625072057	1.295953130
H	-2.708599856	0.149126806	-0.000508852
H	-3.662968976	1.097931506	1.203185040

1 Path-S₀-43

C	2.420076999	0.235511001	0.324935998
C	1.890839001	-1.102245999	0.239269001
C	0.627367998	-1.329181000	-0.145835000
C	-0.253625998	-0.207562002	-0.426662000
C	0.310487999	1.133699998	-0.414084002
C	1.620527002	1.333564001	-0.027668001
H	3.434961999	0.381124001	0.640928001

H	2.533793999	-1.926077999	0.491475000
H	0.211590999	-2.316730000	-0.217257000
H	-0.328826001	1.949624000	-0.699288002
H	2.027907000	2.326589001	0.003607999
O	-1.463007000	-0.388206002	-0.622455000
N	-3.583497000	0.237544000	0.707910998
H	-4.070232000	-0.571335001	1.056626999
H	-2.758734997	0.118148002	0.062093002
H	-3.893408999	1.141204002	1.025977000

1 HBD

C	2.540433782	0.239446133	-0.028162930
C	2.019936564	-1.103994909	-0.048742194
C	0.702028949	-1.340745058	-0.090856040
C	-0.236128673	-0.229562695	-0.101645800
C	0.299626662	1.122965527	-0.098556511
C	1.663556055	1.333399231	-0.059865081
H	3.601771734	0.394974327	0.005548561
H	2.714647854	-1.923911875	-0.029619395
H	0.294792284	-2.334090380	-0.106628872
H	-0.393747609	1.943554527	-0.125813822
H	2.054122742	2.333844249	-0.053760233
O	-1.456140957	-0.440712090	-0.105640242
N	-3.878801627	0.315798361	0.241381371
H	-4.532081938	-0.448504347	0.186794738
H	-2.842387120	0.144123445	0.076236487
H	-4.251391270	1.222414072	0.468394638

Cartesian coordinates for 2 to produce HBD

2 CI ($1\pi\sigma^*/1n\sigma^*$)

C	-0.535240498	-1.034604145	-0.637266137
C	-1.915724455	-0.962178909	-0.793009552
C	-2.614913860	0.203615769	-0.383950131
C	-1.872600674	1.249007049	0.261743895
C	-0.529083907	1.188024853	0.357205153
C	0.193559814	0.047083540	-0.095554986

H	-0.007389442	-1.896894154	-0.994589915
H	-2.462238165	-1.740991371	-1.287671829
H	-2.417130980	2.110374136	0.596242951
O	-3.850820581	0.375627247	-0.669170476
N	-4.797384158	-0.554777241	1.087230129
H	-5.668747249	-0.339570151	0.632207795
H	-4.481761404	-1.507972461	1.063088481
H	-4.526313847	0.013236258	1.870466063
C	1.653720920	0.001761282	-0.011814919
C	2.308228635	-1.185033583	0.391999102
C	2.432624866	1.137687846	-0.324501009
C	3.691567456	-1.224751056	0.497747237
H	1.728024565	-2.048881406	0.659500191
C	3.801292724	1.078538731	-0.258931820
H	1.951791499	2.039308891	-0.658045747
C	4.442854753	-0.095924336	0.161996005
H	4.179831165	-2.121080238	0.832837776
H	4.387059680	1.937590223	-0.530753377
H	5.514926218	-0.125734959	0.225072864
H	0.010907116	1.999808683	0.804465229

2 STC($1\sigma^*/3\sigma^*$)

C	-0.542134000	-1.033294997	-0.635844999
C	-1.910363001	-0.965018998	-0.793361000
C	-2.582720003	0.211950998	-0.391663000
C	-1.885511001	1.253552999	0.257448002
C	-0.519053998	1.183600000	0.357941000
C	0.188122999	0.047612998	-0.095104000
H	-0.014846999	-1.898653001	-0.992869999
H	-2.446441001	-1.749998000	-1.298097002
H	-2.410325998	2.128757002	0.592584997
O	-3.828530001	0.384844001	-0.688419997
N	-4.819041001	-0.572464001	1.119547999
H	-5.647745998	-0.322625002	0.603321998
H	-4.461647001	-1.514015999	1.057273003
H	-4.505447002	0.024374999	1.870305997

C	1.659117999	-0.000297001	-0.009971001
C	2.305731998	-1.181127001	0.390104002
C	2.430315002	1.132634997	-0.322644999
C	3.692408001	-1.220866001	0.495477998
H	1.727786002	-2.047724000	0.657424001
C	3.803302999	1.074898997	-0.256743000
H	1.950779998	2.035927999	-0.655506998
C	4.441279001	-0.094439999	0.161474998
H	4.180665000	-2.118297999	0.829334999
H	4.387546999	1.935951001	-0.527391001
H	5.513228999	-0.124586999	0.224730999
H	0.014218998	1.998132001	0.810474000

2 STC($^3\sigma\sigma^*/S_0(\bullet\text{NH}_3^+)$)

C	-0.503668260	-0.978498778	-0.729590987
C	-1.843464339	-0.929623597	-0.863419707
C	-2.574923412	0.239537691	-0.436667784
C	-1.814789774	1.375969022	0.045926018
C	-0.454632563	1.299122754	0.169619729
C	0.250903455	0.118020439	-0.196933821
H	0.029491916	-1.851122931	-1.058316434
H	-2.393635769	-1.750528458	-1.284136914
H	-2.365568668	2.252989690	0.332393248
O	-3.818018344	0.271689845	-0.435390313
N	-5.328059814	-0.754374708	1.354559410
H	-4.765027207	-0.406786309	0.523759850
H	-5.528790662	-1.729903399	1.497994025
H	-5.676675648	-0.104542728	2.039532574
C	1.710235383	0.024657686	-0.048591172
C	2.317126111	-1.179209125	0.335591781
C	2.524562984	1.142365461	-0.288969778
C	3.698683482	-1.257340268	0.483104538
H	1.714850819	-2.044616433	0.546012949
C	3.890211689	1.056570536	-0.160719947
H	2.085848315	2.069539739	-0.610350578

C	4.489065791	-0.139916920	0.230216625
H	4.150378821	-2.182317836	0.791927729
H	4.497617592	1.919750060	-0.365767325
H	5.556894313	-0.198808707	0.335774183
H	0.087384097	2.130873007	0.579190124

2 Path- $T_{\Sigma}(3\sigma^*)$ -22

C	-0.509312057	-0.978312137	-0.732947797
C	-1.848992505	-0.929440380	-0.872395638
C	-2.585665176	0.236185771	-0.442028831
C	-1.828441240	1.361611316	0.072234631
C	-0.467112436	1.287241751	0.193564116
C	0.242591213	0.114333946	-0.187494770
H	0.024951432	-1.848958003	-1.066316472
H	-2.401463258	-1.740210390	-1.311936670
H	-2.374340427	2.237501334	0.371496822
O	-3.827289456	0.277917541	-0.476583079
N	-5.262334159	-0.735135447	1.351649851
H	-4.897831070	-0.390456809	0.428700470
H	-5.289971324	-1.715848715	1.574473552
H	-5.440705564	-0.079147459	2.092410833
C	1.704016005	0.023073250	-0.042202087
C	2.312764484	-1.177966506	0.347577646
C	2.516872742	1.139357935	-0.292503243
C	3.695009426	-1.254359296	0.489740494
H	1.712527922	-2.042323958	0.568762089
C	3.883419440	1.054876724	-0.169262809
H	2.073377507	2.063236471	-0.618284194
C	4.484247611	-0.138761297	0.226352637
H	4.146876657	-2.177438033	0.804500493
H	4.489549226	1.915808081	-0.385266247
H	5.552759852	-0.196796293	0.325611990
H	0.073352291	2.114550762	0.612449703

2 Path-S₀-25

C	-0.504907000	-0.867214998	-0.817585999
C	-1.836225998	-0.762566001	-0.924024002
C	-2.518884002	0.400288002	-0.391175998
C	-1.711886998	1.493801999	0.115703002
C	-0.354613999	1.357689001	0.212909000
C	0.298513998	0.167995001	-0.210782998
H	-0.010302002	-1.733929998	-1.216283998
H	-2.431793000	-1.520121000	-1.398442000
H	-2.229144000	2.370045000	0.459755999
O	-3.754906999	0.463491001	-0.321702000
N	-5.575627998	-0.870955001	0.978804002
H	-4.889543000	-0.400751000	0.325426000
H	-6.401371999	-1.346046001	0.652686002
H	-5.412335001	-0.852873999	1.972306002
C	1.740572998	-0.005344002	-0.035528998
C	2.291900998	-1.279094998	0.164750002
C	2.601754000	1.104383002	-0.046410998
C	3.661256998	-1.433514000	0.352338002
H	1.658171999	-2.145970000	0.208495000
C	3.953699999	0.946621997	0.125216000
H	2.210475998	2.088680001	-0.225600999
C	4.496995999	-0.321791997	0.329237002
H	4.068714002	-2.414018999	0.518283998
H	4.596834998	1.807252999	0.094048000
H	5.556185999	-0.438478999	0.465710000
H	0.222928003	2.145150998	0.661108001

2 HBD

C	-0.505557618	-0.859957899	-0.813494670
C	-1.842026802	-0.767890810	-0.904536917
C	-2.529082475	0.392414897	-0.373094932
C	-1.715506444	1.492804643	0.111176584
C	-0.356401777	1.362931084	0.204061209
C	0.305025334	0.175842261	-0.216223681

H	-0.009268391	-1.723488103	-1.215710444
H	-2.428307425	-1.540230016	-1.368596482
H	-2.224664991	2.374462063	0.452705331
O	-3.763896974	0.452906869	-0.286581199
N	-5.577805176	-0.863320159	0.938082876
H	-4.845986029	-0.405886327	0.313291373
H	-6.406941786	-1.294914715	0.565829965
H	-5.475149658	-0.844689611	1.939528578
C	1.752096352	-0.002194138	-0.043582350
C	2.302837425	-1.278099976	0.160713432
C	2.619147548	1.104466543	-0.055596425
C	3.672765725	-1.435155814	0.352107059
H	1.667825637	-2.144906529	0.204838930
C	3.970904483	0.942679294	0.124210876
H	2.232518209	2.090343269	-0.239700408
C	4.511692855	-0.325725837	0.332818628
H	4.076913614	-2.416479943	0.519691249
H	4.615454099	1.801692066	0.095890331
H	5.570308957	-0.444050659	0.475670412
H	0.215166348	2.157233369	0.643196414

Cartesian coordinates for reaction of 1

(a)

IM(stepwise)

C	-1.662079121	-1.038210075	0.038010003
C	-1.962989144	0.403117031	0.161247012
C	-1.021940076	1.337978096	0.101122010
C	0.395608027	0.922111068	-0.073221007
C	0.694084051	-0.540319039	-0.387919029
C	-0.442487030	-1.498359110	-0.193135017
H	-2.482504177	-1.726003124	0.130599008
H	-2.989463215	0.682476051	0.312987022
H	-1.217355090	2.387579171	0.210626013
H	1.032661075	-0.503784038	-1.414320100
H	-0.254298016	-2.550905184	-0.316804025

O	1.373546099	1.657013117	-0.016754000
N	1.880948133	-0.908858067	0.398701031
H	2.322465165	-1.751713127	0.061112003
H	1.654650118	-1.052970077	1.373388097
H	2.551946181	-0.148814009	0.347191023

TS(stepwise)/ts(concerted)

C	1.578558113	0.472042034	0.885850065
C	1.496753110	-0.972891071	0.565007041
C	0.538134040	-1.492529106	-0.237664017
C	-0.413783032	-0.525334036	-0.780551058
C	-0.537262040	0.834255061	-0.187723015
C	0.632039045	1.369940100	0.529154039
H	2.454479177	0.807980056	1.409873101
H	2.269049162	-1.606334113	0.960103068
H	0.507201036	-2.521934179	-0.538921037
H	-1.021371073	1.142260081	-1.103862080
H	0.713933051	2.416803175	0.753503052
O	-1.073586077	-0.515341037	-1.792854128
N	-1.894712134	0.776338056	0.947922070
H	-1.659491121	0.226728014	1.758551129
H	-2.705836196	0.381541030	0.497506038
H	-2.114610152	1.713609121	1.244032089

IM(concerted)

C	1.638218117	0.461958033	0.862786060
C	1.540371111	-0.975782072	0.566086039
C	0.577232041	-1.468171104	-0.243381015
C	-0.380525026	-0.529660039	-0.841029059
C	-0.357233024	0.894114062	-0.375702025
C	0.727857054	1.373180099	0.428227031
H	2.483568178	0.796830058	1.436002101
H	2.278019166	-1.625756119	0.997386072
H	0.500879035	-2.505828183	-0.506637034
H	-0.943628066	1.507340110	-1.027198076
H	0.816298061	2.420183173	0.646338044

O	-1.185649085	-0.776971058	-1.707965123
N	-2.025947144	0.745186053	1.004717071
H	-1.820691132	0.144089012	1.782664127
H	-2.834438206	0.388583030	0.525958036
H	-2.244835159	1.657837120	1.361673097

o-aminophenol

C	-1.838038134	-1.042492077	0.228382015
C	-2.000854147	0.308382021	-0.056399002
C	-0.913999067	1.142821083	-0.243054016
C	0.365393027	0.620334047	-0.142232012
C	0.515446036	-0.726531052	0.139021012
C	-0.565362040	-1.567295115	0.327868026
H	-2.692897193	-1.676269120	0.365983028
H	-2.990850215	0.717987051	-0.136575012
H	-1.055582075	2.185584156	-0.463287035
H	1.337126188	2.227671524	-0.552939315
H	-0.420114030	-2.611371188	0.546461041
O	1.532671111	1.327366097	-0.298260019
N	1.892431136	-1.233154089	0.241410015
H	1.997379145	-2.130672153	-0.208586013
H	2.192971158	-1.328023097	1.202355084
H	2.525256179	-0.581676040	-0.206661015

(b)

IM(stepwise)

C	0.282939359	0.373464012	1.342117119
C	0.315085988	-0.992746388	0.713945656
C	0.108930385	-1.178049105	-0.598931341
C	-0.156059700	-0.042332370	-1.515978617
C	-0.218791175	1.311008974	-0.910419453
C	-0.014058118	1.508386870	0.400767823
H	-0.394734392	0.390258225	2.187878452
H	0.474251498	-1.831272079	1.370987405
H	0.112431829	-2.160631126	-1.033469335
H	-0.452155008	2.126677092	-1.569691774

H	-0.095615301	2.493221826	0.829276180
O	-0.313322293	-0.211144919	-2.701873182
N	1.662535663	0.633271690	1.967386517
H	1.905471133	-0.078435319	2.641800139
H	1.694371438	1.524957014	2.440943792
H	2.378357686	0.638237595	1.254004334

TS(stepwise)

C	0.456183894	0.362751888	0.949373968
C	0.941899969	-0.949751806	0.346878354
C	0.300097540	-1.216400560	-0.800182820
C	-0.694470679	-0.106247779	-1.037619227
C	-0.044742635	1.248351028	-1.182268526
C	0.596928812	1.516723407	-0.035562865
H	-0.620347604	0.236763225	1.107504380
H	1.665038889	-1.582641826	0.828237437
H	0.412873700	-2.092612233	-1.407002151
H	-0.145412283	1.901061705	-2.026377715
H	1.103853248	2.433355856	0.205306855
O	-1.766572667	-0.169837792	-0.480212055
N	1.157115896	0.678423119	2.352601100
H	0.997898241	-0.076446215	3.003246785
H	0.776437964	1.522429271	2.754174500
H	2.152856713	0.798950699	2.240645673

TS(concerted)

C	0.014835939	-0.016976509	0.773973353
C	0.939457530	-0.908660277	0.141662501
C	0.820449229	-0.980207390	-1.201525985
C	-0.275830111	-0.163518479	-1.790874439
C	-0.592412660	1.148628940	-1.163035071
C	-0.457888792	1.196788198	0.179734994
H	-0.477579266	-0.359557557	1.646026058
H	1.513355400	-1.592018117	0.737475744
H	1.280267734	-1.746087655	-1.797801772
H	-1.129257793	1.884471025	-1.732142803

H	-0.854577182	1.975759170	0.801964840
O	-1.090965221	-0.691764091	-2.495640161
N	1.733620604	1.082996960	2.973027446
H	2.111142469	0.367611894	3.566304486
H	1.238715790	1.715864824	3.573706099
H	2.516305310	1.591541074	2.605888457

IM(concerted)

C	0.661627997	0.722484370	0.288359521
C	1.542331940	0.066059186	-0.621770017
C	0.949559561	-0.571834280	-1.657172478
C	-0.534729567	-0.558276431	-1.656601449
C	-1.248076088	0.610829214	-1.084237589
C	-0.625181813	1.232383797	-0.056608773
H	0.937999816	0.737256125	1.319750363
H	2.580571426	-0.041067224	-0.370436378
H	1.460250093	-1.260060180	-2.304862216
H	-2.284153182	0.754965396	-1.328641197
H	-1.104914952	1.941891508	0.590739370
O	-1.126960513	-1.595185137	-1.787605330
N	1.455277652	0.626758327	3.593046850
H	0.874244192	-0.017623322	4.096348485
H	1.349179815	1.516660377	4.043529944
H	2.402612605	0.339630292	3.754904681

p-aminophenol

C	1.082172020	0.470038114	1.120010199
C	0.697570218	-0.828787454	0.837691004
C	-0.218853973	-1.045667770	-0.193516559
C	-0.729755667	0.034909162	-0.910933479
C	-0.324394073	1.342940667	-0.602828906
C	0.584793444	1.567507743	0.418066241
H	-1.844546485	-0.994086101	-2.078148956
H	1.088709105	-1.666510150	1.388513751
H	-0.523440020	-2.049947783	-0.426291645
H	-0.728092897	2.158871929	-1.170948129

H	0.896221892	2.570737022	0.652294157
O	-1.604776041	-0.096256590	-1.911385784
N	2.046868728	0.716329731	2.218635080
H	2.420265291	-0.149697253	2.579068796
H	1.615573209	1.203051952	2.992724175
H	2.831324246	1.271438777	1.905793762

(c)

IM(stepwise)

C	1.406963129	0.892050371	-0.320882426
C	1.632888280	-0.563863024	-0.317671267
C	0.634672184	-1.440754742	-0.081401548
C	-0.727733586	-0.943563067	0.144745340
C	-0.883005335	0.540136303	0.507514971
C	0.221646007	1.431224414	0.013989568
H	2.224793809	1.531612508	-0.595906691
H	2.621761927	-0.920823247	-0.537002839
H	0.765766015	-2.504985002	-0.130645470
H	-0.966404606	0.607807083	1.588582286
H	0.082528388	2.497089725	0.065278236
O	-1.730150540	-1.612146660	0.065344722
N	-2.230678636	0.960093728	-0.023198818
H	-2.565710986	1.810554890	0.403604107
H	-2.893075093	0.213385233	0.156411221
H	-2.203103304	1.102475112	-1.023111875

TS(stepwise)

C	1.353284939	0.823191187	-0.226919317
C	1.363237319	-0.605650955	-0.623359777
C	0.385935577	-1.475289977	-0.269840788
C	-0.642465986	-0.874941066	0.569246889
C	-0.906866826	0.599153225	0.620461764
C	0.304270293	1.426088442	0.378025457
H	2.245304941	1.387954738	-0.426586788
H	2.217568772	-0.956483618	-1.172367827
H	0.411592482	-2.527971901	-0.474863676

H	-1.378372910	0.135295208	1.569126751
H	0.328503595	2.464544917	0.654326615
O	-1.249488902	-1.258671270	1.553417743
N	-2.063483517	1.033811035	-0.396057187
H	-2.338755199	1.983347413	-0.194141543
H	-2.880555669	0.450950871	-0.287266420
H	-1.758551234	0.994965361	-1.357552378

TS(concerted)

C	2.094476561	0.489205655	-0.204045186
C	1.917563288	-0.925389448	-0.410729860
C	0.754611784	-1.552499689	-0.145260462
C	-0.334555165	-0.739821185	0.333086285
C	-0.140913218	0.659890475	0.566634039
C	1.055946556	1.286915534	0.306727162
H	3.051605352	0.925937644	-0.417424132
H	2.753099397	-1.485717108	-0.789317038
H	0.610147866	-2.605393840	-0.295729441
H	-1.015295922	0.977668858	1.081598810
H	1.213967926	2.329651916	0.507529518
O	-1.490752658	-1.110207751	0.576907730
N	-3.029388697	0.761634887	-0.237330376
H	-3.729389537	1.284552774	0.263090640
H	-2.503358708	-0.051022143	0.204733015
H	-2.907527500	0.983592040	-1.211406000

IM(concerted)

C	2.191483387	0.408893937	-0.019563683
C	2.304836837	-1.016677265	-0.132518742
C	1.178787953	-1.776331929	-0.165070884
C	-0.129101431	-1.095053660	-0.081811776
C	-0.181304905	0.367911345	0.032687342
C	0.964221671	1.102804419	0.062748214
H	3.104288212	0.981381783	0.003393952
H	3.284968047	-1.450594492	-0.188998983
H	1.198499218	-2.847043377	-0.248348926

H	-1.200379544	0.716050760	0.083408807
H	0.962023670	2.173024166	0.145652651
O	-1.193212346	-1.676752762	-0.102173459
N	-3.415446255	1.405048820	0.189777011
H	-3.676727315	1.858882664	1.044652326
H	-3.968347605	0.571149223	0.125124389
H	-3.710175969	2.005339564	-0.557101768

o-aminophenol

C	1.534461302	0.929754684	-0.524010114
C	1.625206648	-0.424619450	-0.186708180
C	0.505687171	-1.138134863	0.236785139
C	-0.724868943	-0.489065513	0.327971195
C	-0.796402801	0.856146150	-0.012700042
C	0.309345875	1.584612340	-0.438687839
H	2.404525898	1.467087841	-0.849515427
H	2.571427466	-0.927734212	-0.254895431
H	0.583265249	-2.180008533	0.490859270
H	-1.790756094	-1.975397498	0.944168076
H	0.220637178	2.625576708	-0.695935203
O	-1.885566485	-1.064102326	0.711309459
N	-2.123662322	1.491106222	0.092868009
H	-2.123237001	2.262563899	0.744773347
H	-2.789311748	0.802039274	0.424374610
H	-2.450770396	1.834534843	-0.798933956

(d)

IM(stepwise)

C	0.254592228	0.393497128	1.332912615
C	0.309476466	-0.985675802	0.739064303
C	0.134752806	-1.203181400	-0.552192358
C	-0.120612963	-0.093454639	-1.511195987
C	-0.212640326	1.275177224	-0.945616963
C	-0.037781435	1.505182755	0.364484303
H	-0.422225833	0.426326904	2.179074779
H	0.462177620	-1.806397309	1.420160175

H	0.156383133	-2.195889925	-0.963925183
H	-0.441188656	2.069659445	-1.631715237
H	-0.138366642	2.498237728	0.769060673
O	-0.245982181	-0.303078549	-2.693264135
N	1.657064214	0.682942510	1.972634076
H	1.891685060	-0.014955364	2.663532391
H	1.674604662	1.587643456	2.420857483
H	2.367700856	0.668837841	1.254872804

TS(stepwise)

C	0.431626630	0.360295098	0.948232490
C	0.897986364	-0.955830301	0.357174788
C	0.299926203	-1.214614317	-0.787965276
C	-0.676541259	-0.114492207	-1.120460021
C	-0.045618984	1.252375410	-1.182254016
C	0.560173060	1.522291521	-0.018274792
H	-0.624540334	0.254996329	1.197097835
H	1.586959003	-1.606323604	0.864898223
H	0.421558059	-2.104028893	-1.375545077
H	-0.166500631	1.931751477	-2.002946736
H	1.000649751	2.462933789	0.257118531
O	-1.837108460	-0.231202557	-0.816180478
N	1.241147867	0.688176708	2.406714385
H	1.095249397	-0.073901143	3.050497408
H	0.876737601	1.536673559	2.811224062
H	2.227934751	0.795771117	2.229412420

TS(concerted)

C	1.004147364	0.376284157	-0.086184754
C	1.940377320	-0.602812104	0.379233748
C	1.805031899	-1.805830248	-0.224111116
C	0.769604286	-1.815981063	-1.297816242
C	-0.512112997	-1.098591469	-1.044251263
C	-0.349760613	0.102394946	-0.435709714
H	1.383129261	1.332937884	-0.347168867
H	2.788822762	-0.309014981	0.968586928

H	2.548395354	-2.580182905	-0.184821414
H	-1.396600838	-1.372725398	-1.588712283
H	-1.065642565	0.911732373	-0.415443358
O	1.134864733	-1.952978661	-2.433102533
N	-1.878619928	2.994258117	-0.300347280
H	-1.312086967	3.808038696	-0.148114373
H	-2.570341414	2.993915078	0.426436380
H	-2.372987760	3.153700095	-1.158760653

IM(concerted)

C	2.016790526	0.330377702	0.641563707
C	2.378612453	-0.974151481	0.197843482
C	1.472841564	-1.648876958	-0.542630877
C	0.202596436	-0.971975118	-0.874192423
C	-0.183299855	0.297572121	-0.219394755
C	0.746884294	0.928295907	0.541048049
H	2.788975593	0.918010257	1.052835645
H	3.360963202	-1.347810945	0.414419659
H	1.654635661	-2.611498619	-0.982684702
H	-1.140770050	0.730930303	-0.480772856
H	0.575993232	1.888538456	0.989045233
O	-0.474323804	-1.395773861	-1.776875087
N	-2.668003663	1.875714104	-1.554940133
H	-2.352731818	2.723367748	-1.988480511
H	-3.476708581	2.115010993	-1.012573231
H	-2.986235292	1.277413881	-2.294497983

p-aminophenol

C	1.054228990	0.461969090	1.139954000
C	0.898209180	-0.877896570	0.781319320
C	0.036316370	-1.185890980	-0.252335610
C	-0.660733440	-0.164457310	-0.918767340
C	-0.488854730	1.152816550	-0.544964130
C	0.378895680	1.478986250	0.497916460
H	-1.915945170	0.167898270	-2.319805480
H	1.430663650	-1.663025020	1.289634710

H	-0.115998920	-2.201613890	-0.563248200
H	-1.020838580	1.937007830	-1.052827930
H	0.503965220	2.510169800	0.779513730
O	-1.469338710	-0.551759630	-1.901634250
N	1.996396580	0.797152650	2.268722080
H	1.709851100	0.347996890	3.126948050
H	2.013919210	1.792698680	2.432873670
H	2.938902070	0.502819070	2.055444180