Electronic Supporting Information

How chlorination affects prototropic tautomerism: the 2-hydroxypyridine/2-pyridone equilibrium explored by X-ray photoemission spectroscopy

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Theoretical results (TD)-B3LYP/aug-cc-pVTZ

Figure S01.
Optimized geometries of 2-pyridone in the S_0, D_0 and D_1 states.

2PO S_0	2PO D_0	2PO D_1
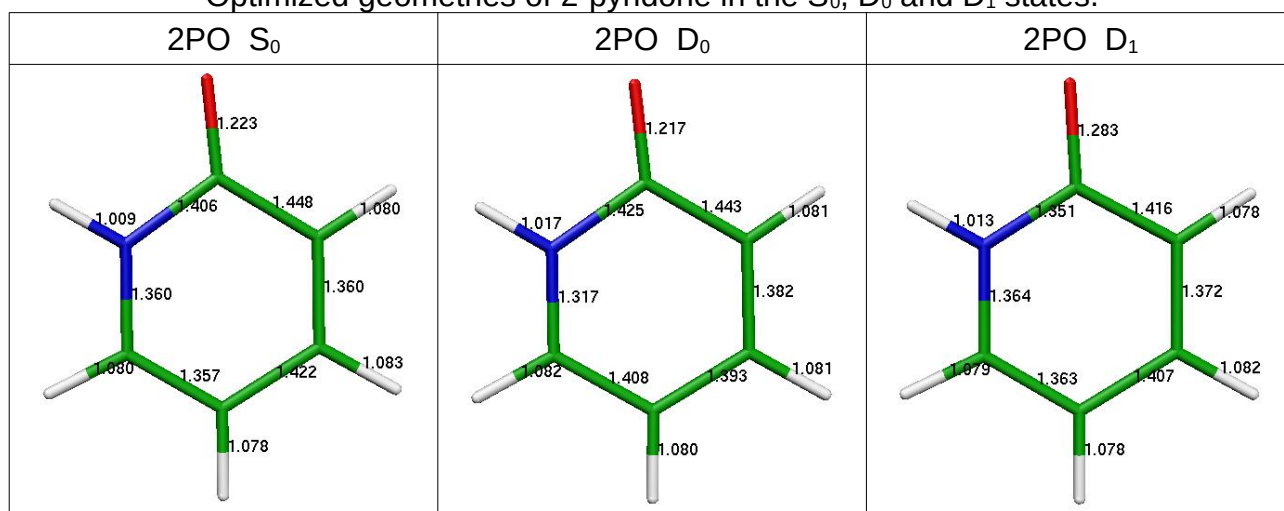
Figure S02.
Optimized geometries of 2-hydroxypyridine in the S_0 and D_0 states.

2HP S_0	2HP D_0	
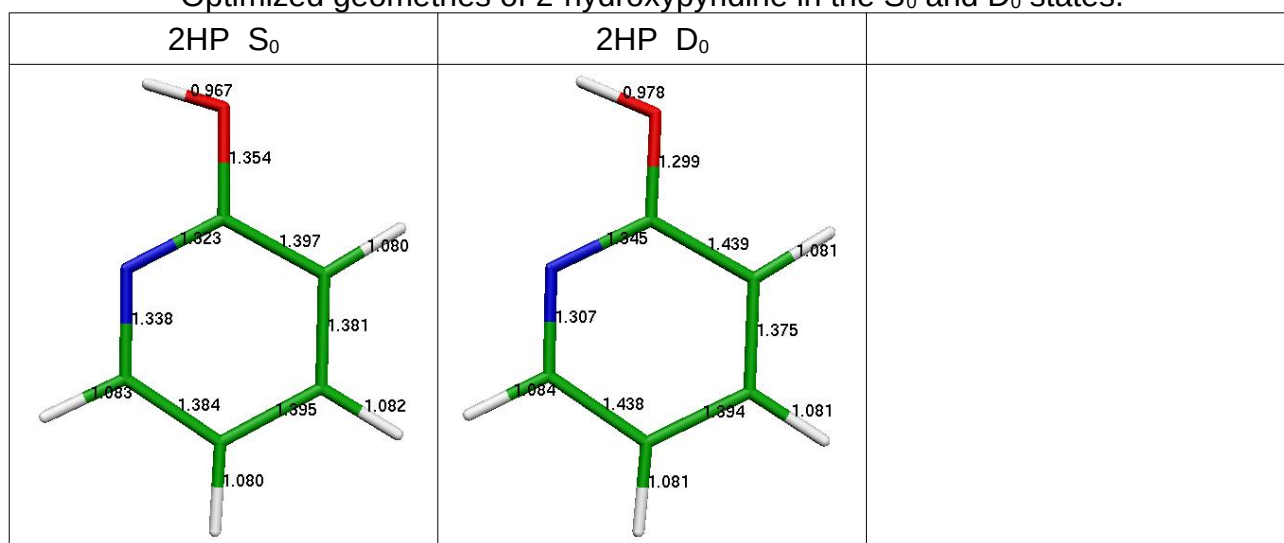
Figure S03.

Optimized geometries of 3-chloro-2-pyridone in the S_0, D_0 and D_1 states.

3Cl-2PO S_0	3Cl-2PO D_0	3Cl-2PO D_1
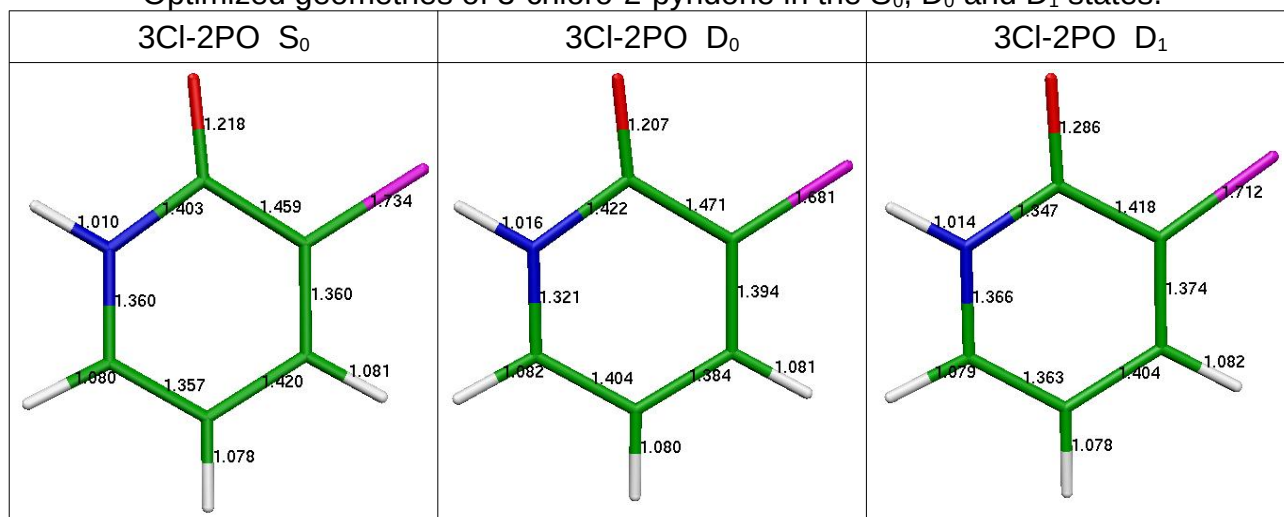
Figure S04.

Optimized geometries of 3-chloro-2-hydroxypyridine in the S_0, D_0 and D_1 states.

3Cl-2HP S_0	3Cl-2HP D_0	3Cl-2HP D_1

Figure S05.
Optimized geometries of 4-chloro-2-pyridone in the S_0, D_0 and D_1 states.

4Cl-2PO S_0	4Cl-2PO D_0	4Cl-2PO D_1

Figure S06.
Optimized geometries of 4-chloro-2-hydroxypyridine in the S_0 and D_0 states.

4Cl-2HP S_0	4Cl-2HP D_0	
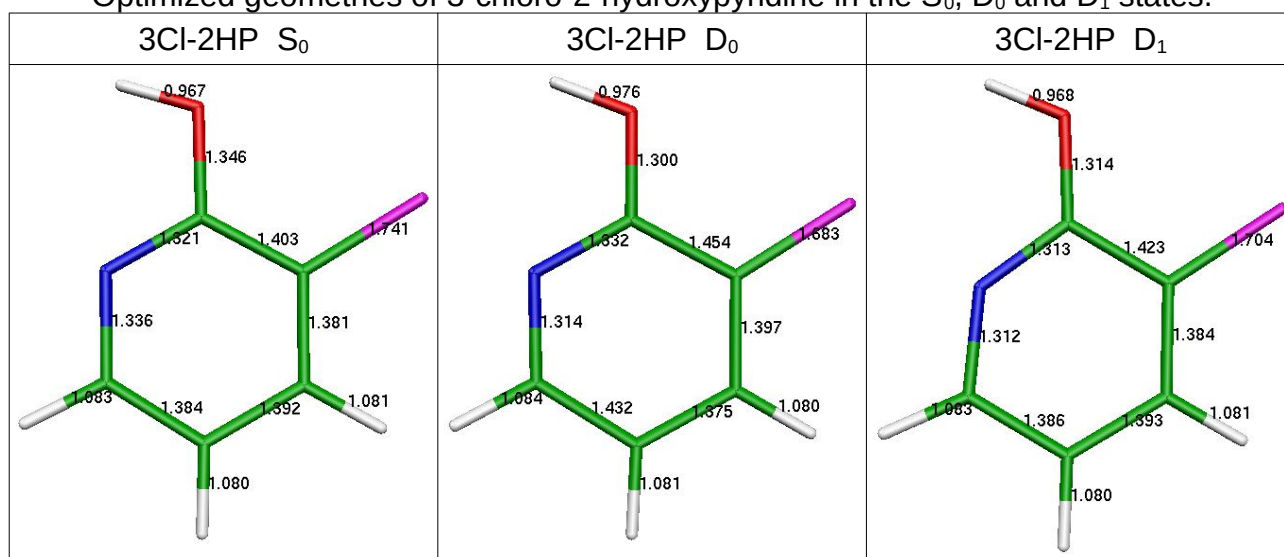
Figure S07.
Optimized geometries of 5-chloro-2-pyridone in the S_0, D_0 and D_1 states.

5Cl-2PO S_0	5Cl-2PO D_0	5Cl-2PO D_1
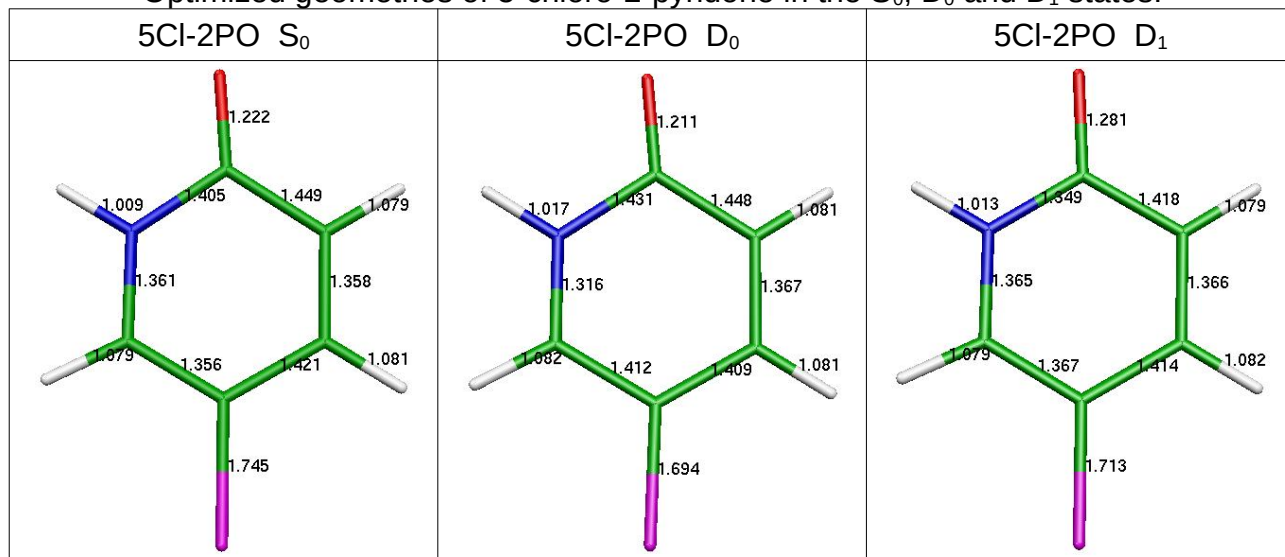
Figure S08.
Optimized geometries of 5-chloro-2-hydroxypyridine in the S_0, D_0 and D_1 states.

5Cl-2HP S_0	5Cl-2HP D_0	5Cl-2HP D_1
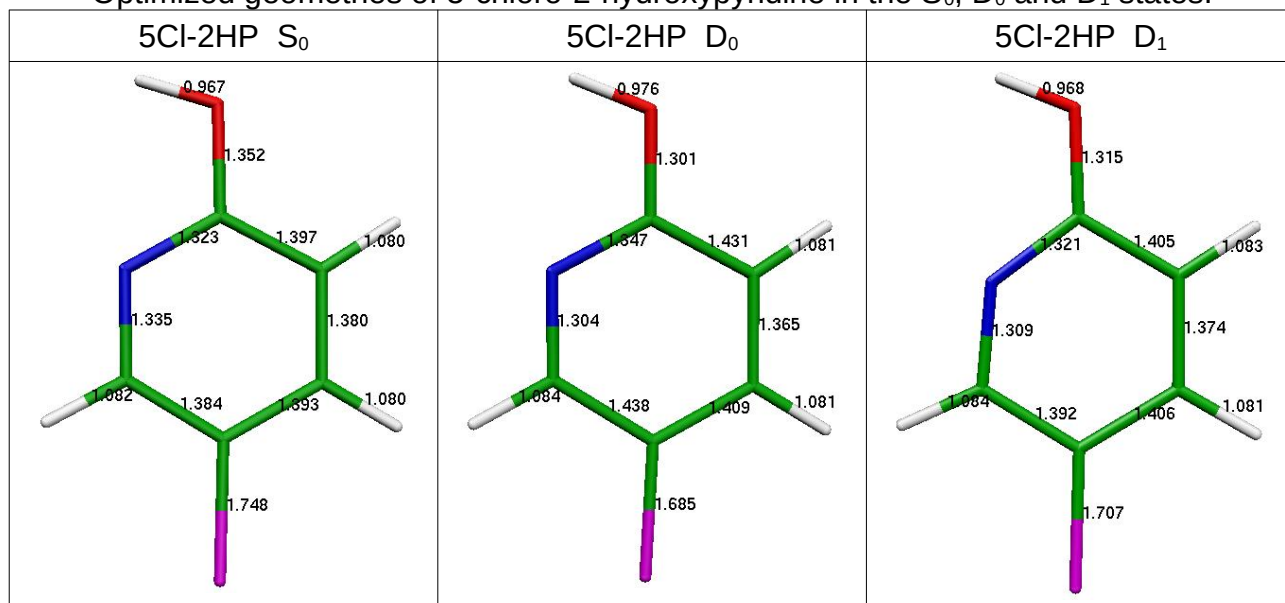
Figure S09.
Optimized geometries of 6-chloro-2-pyridone in the S_0, D_0 and D_1 states.

6Cl-2PO S_0	6Cl-2PO D_0	6Cl-2PO D_1
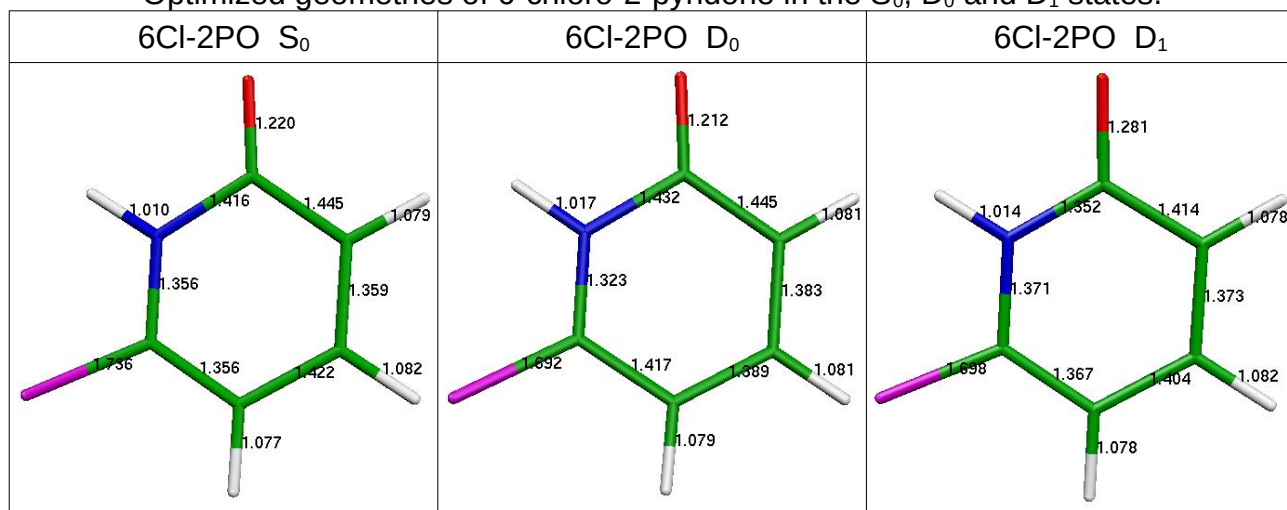
Figure S10.
Optimized geometries of 6-chloro-2-hydroxypyridine in the S_0, D_0 and D_1 states.

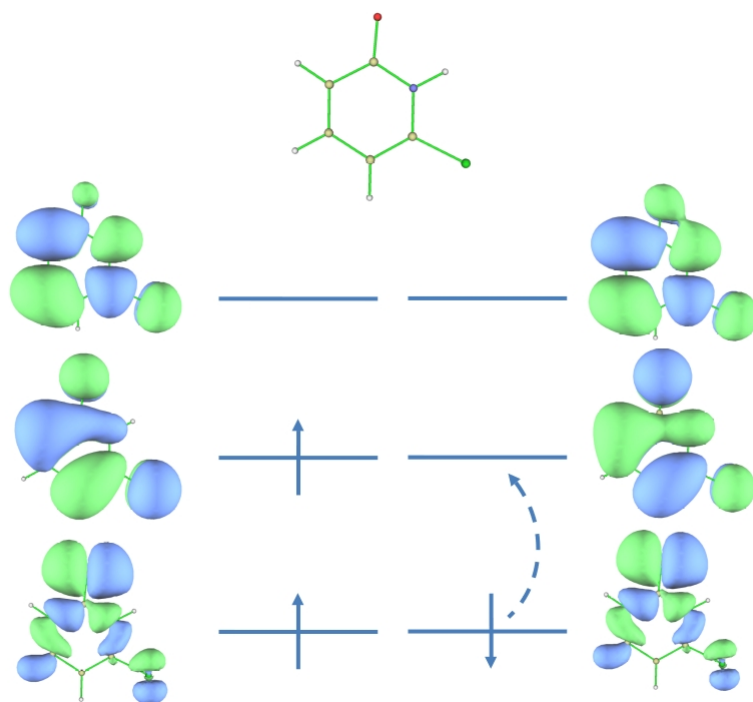| 6Cl-2HP S_0	6Cl-2HP D_0	6Cl-2HP D_1
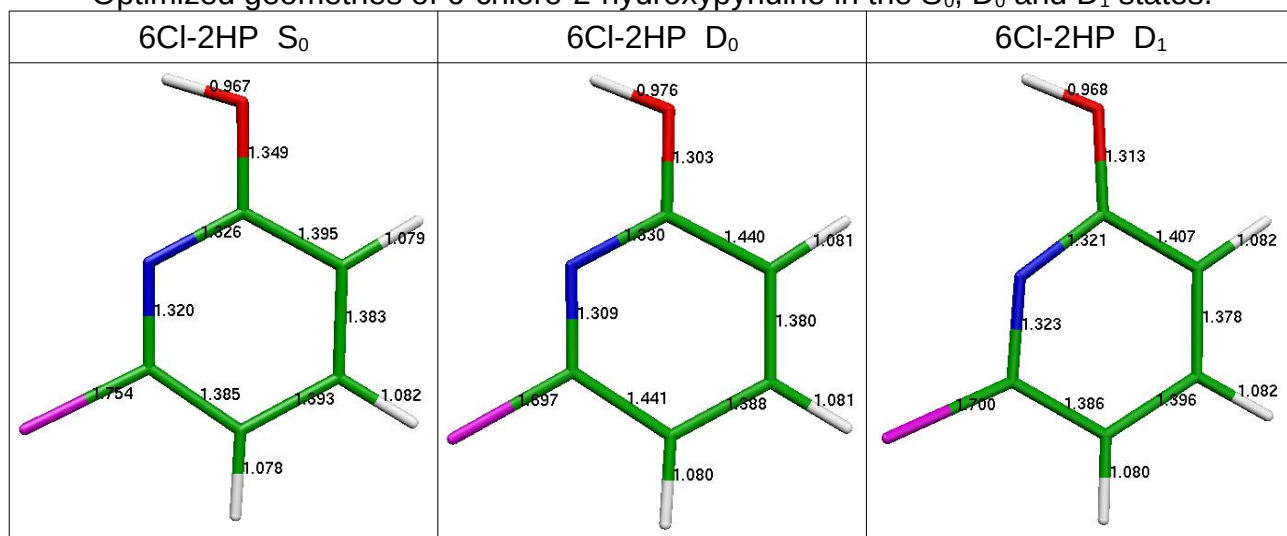
Figure S11.
Frontier molecular orbitals of 2-pyridone at D_1 geometry.
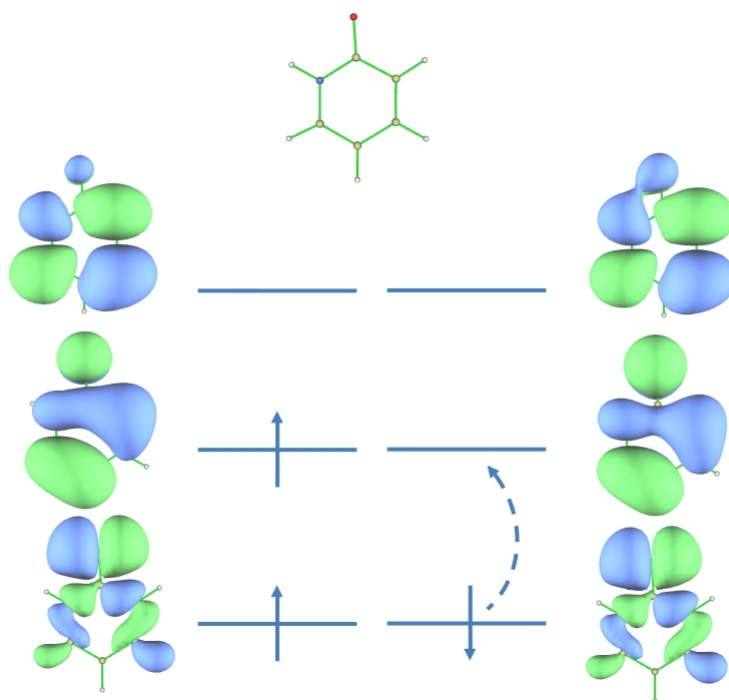
Figure S12.
Frontier molecular orbitals of 2-hydroxypyridine at D_1 geometry.
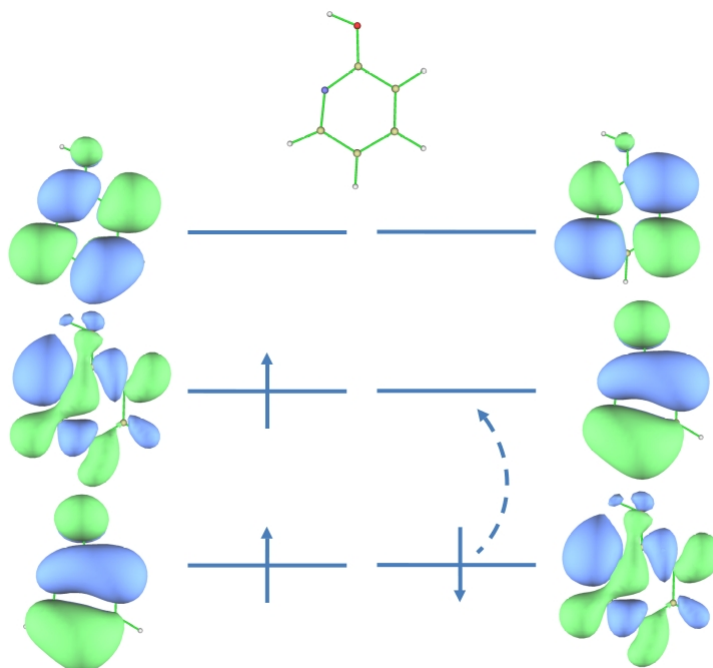
Figure S13.
Frontier molecular orbitals of 3-chloro-2-pyridone at D_1 geometry.
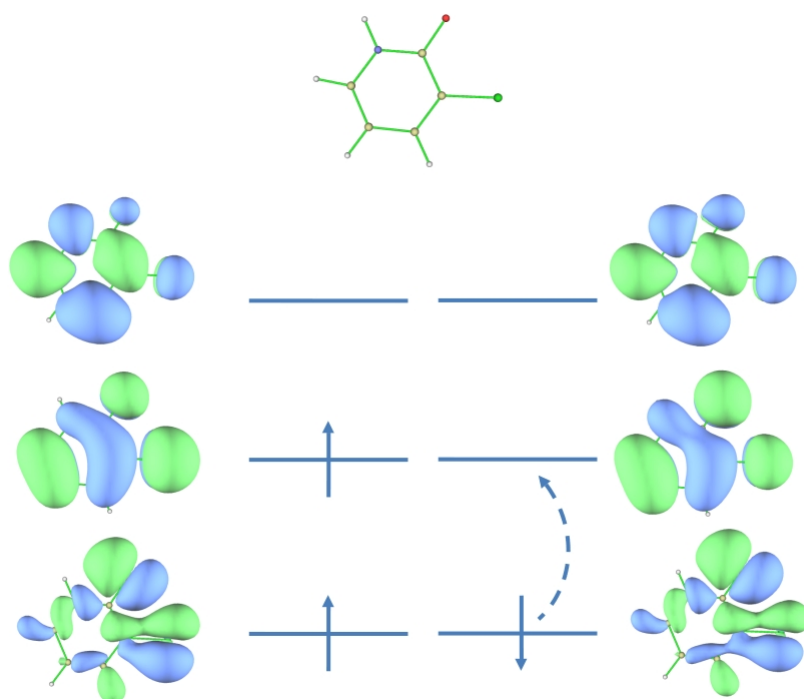
Figure S14.
Frontier molecular orbitals of 3-chloro-2-hydroxypyridine at D_1 geometry.
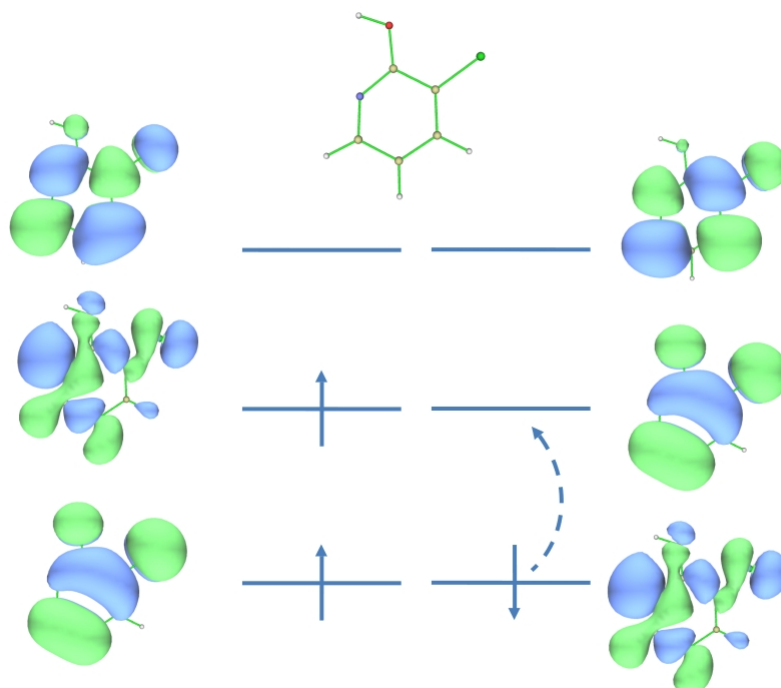
Figure S15.
Frontier molecular orbitals of 5-chloro-2-pyridone at D_1 geometry.
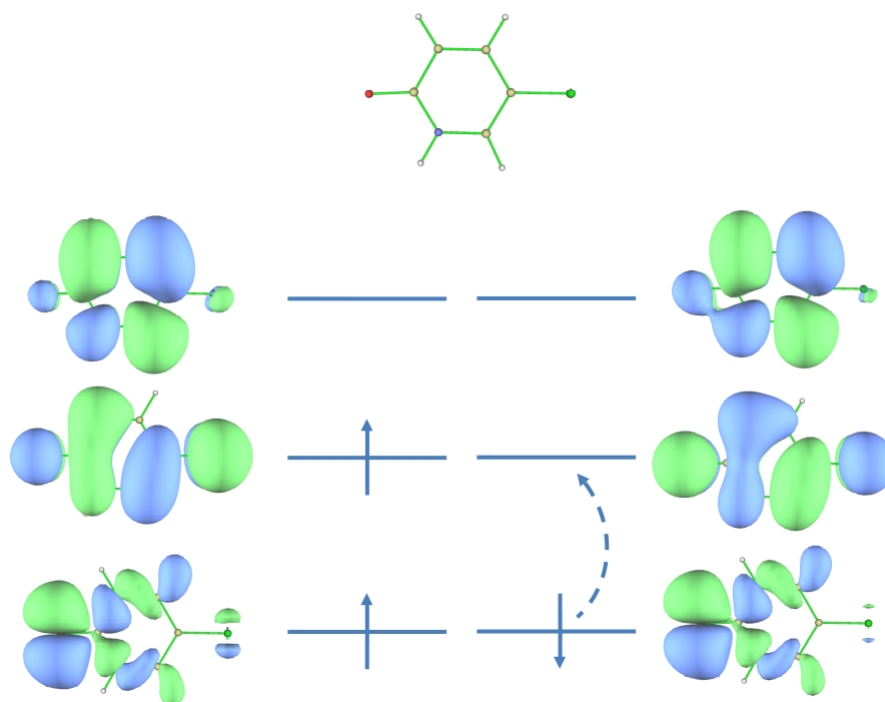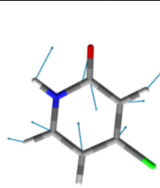

Figure S16.
Frontier molecular orbitals of 5-chloro-2-hydroxypyridine at D_1 geometry.
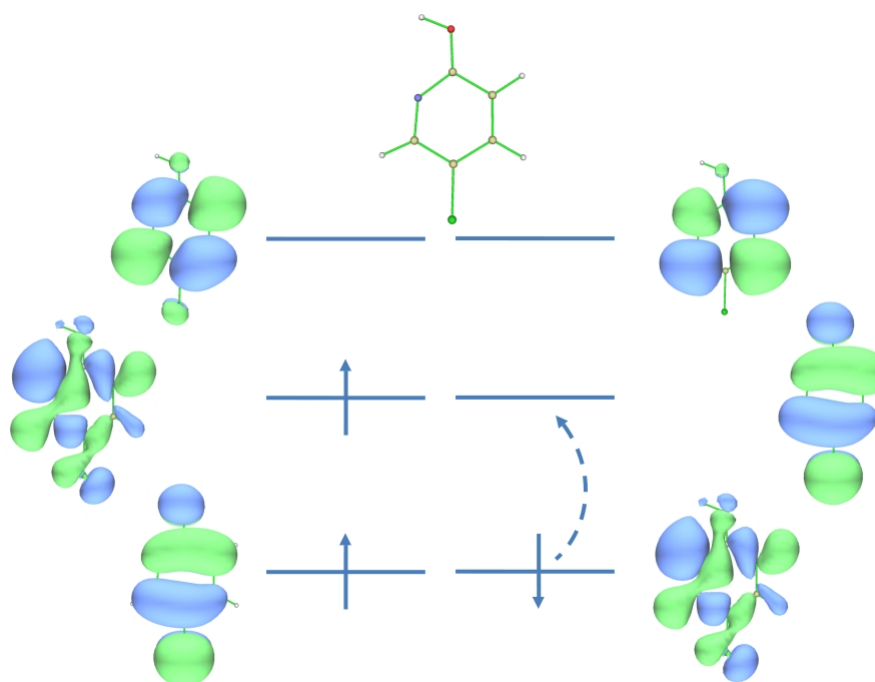
Figure S17.
Frontier molecular orbitals of 6-chloro-2-pyridone at D_1 geometry.

Figure S18.
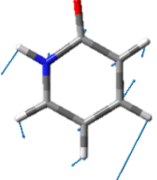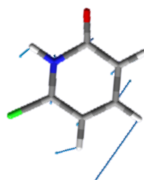Frontier molecular orbitals of 6-chloro-2-hydroxypyridine at D_1 geometry.
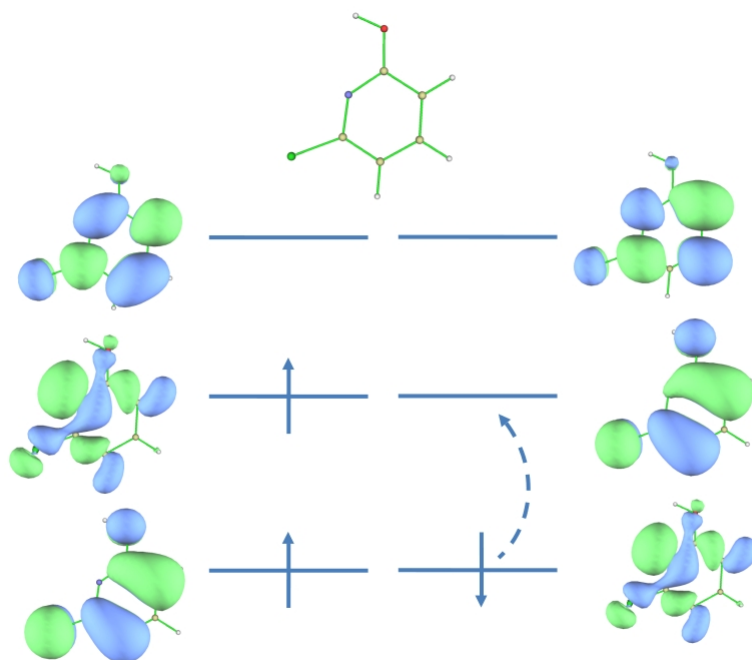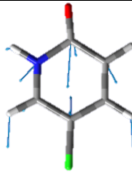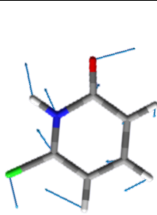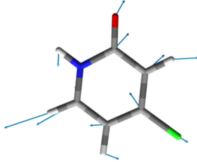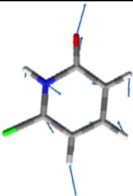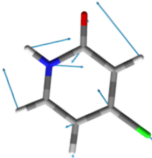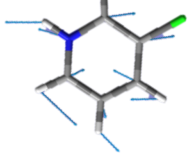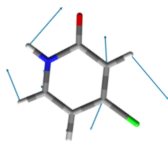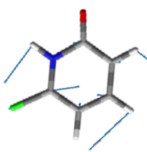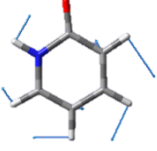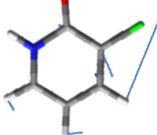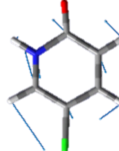
Figure S19.
The most active vibrational normal modes in the D_0 state of 2-pyridone and its chlorinated analogues. Only modes with Huang Rhys factors greater than 0.1 are reported. The modes are collected in two groups: below and above 1000 cm^{-1}.

2PO	3Cl-2PO	4Cl-2PO	5Cl-2PO	6Cl-2PO
539 cm^{-1}	567 cm^{-1}	538 cm^{-1}	388 cm^{-1}	260 cm^{-1}
		698 cm^{-1}		536 cm^{-1}
		852 cm^{-1}		
1256 cm^{-1}	1066 cm^{-1}	1403cm^{-1}	1328 cm^{-1}	1118 cm^{-1}
1386 cm^{-1}	1302 cm^{-1}		1600 cm^{-1}	1430 cm^{-1}
1474 cm^{-1}	1490 cm^{-1}			1472 cm^{-1}

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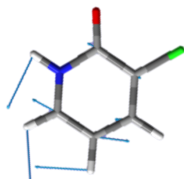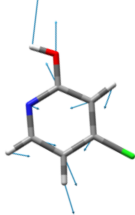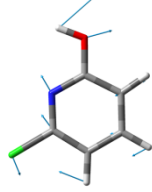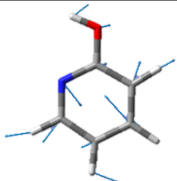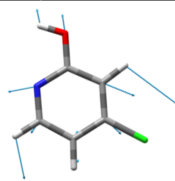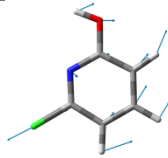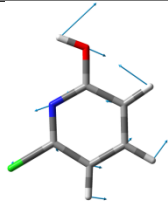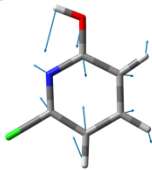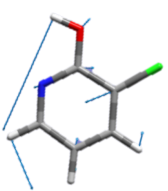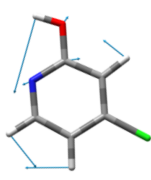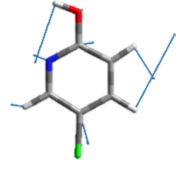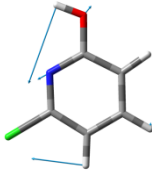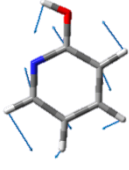
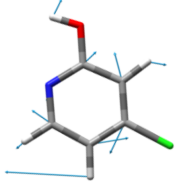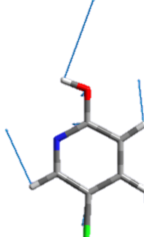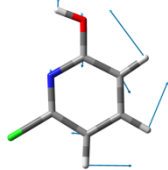|				
		12		
	1569 cm⁻¹			1532 cm⁻¹

Figure S20.
The most active vibrational normal modes in the D_0 state of 2-hydroxypyridine and its chlorinated analogues. Only modes with Huang Rhys factors greater than 0.1 are reported. The modes are collected in two groups: below and above 1000 cm^{-1}.

2HP	3Cl-2HP	4Cl-2HP	5Cl-2HP	6Cl-2HP
545 cm^{-1}	575 cm^{-1}	547 cm^{-1}	393 cm^{-1}	268 cm^{-1}
610 cm^{-1}		921 cm^{-1}		413 cm^{-1}
984 cm^{-1}				474 cm^{-1}
				545 cm^{-1}
1384 cm^{-1}	1154 cm^{-1}	1144 cm^{-1}	1107 cm^{-1}	1218 cm^{-1}
1603 cm^{-1}	1557 cm^{-1}	1386 cm^{-1}	1147 cm^{-1}	1373 cm^{-1}

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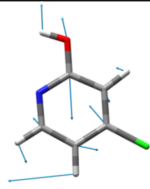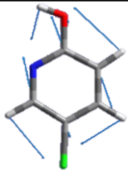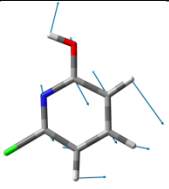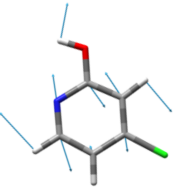
		1477 cm^{-1}	1627 cm^{-1}	1572 cm^{-1}
		1601 cm^{-1}		

Figure S21.
The most active vibrational normal modes in the D_1 state of 2-pyridone and its chlorinated analogues. Only modes with Huang Rhys factors greater than 0.1 are reported. The modes are collected in two groups: below and above 1000 cm^{-1}.
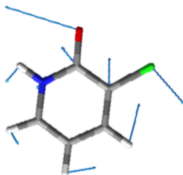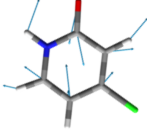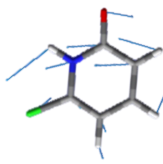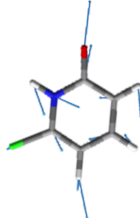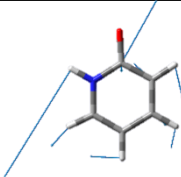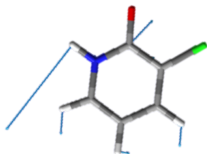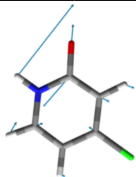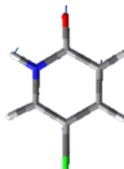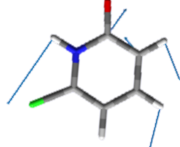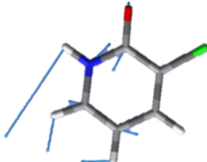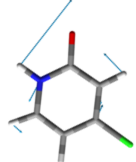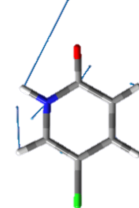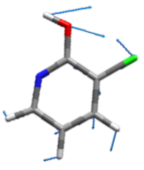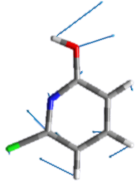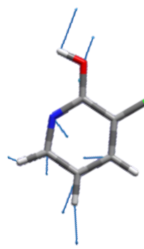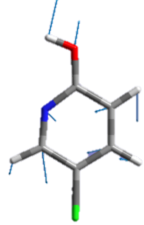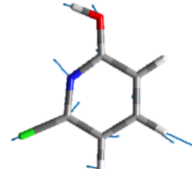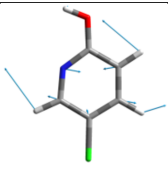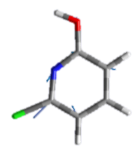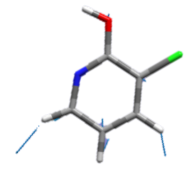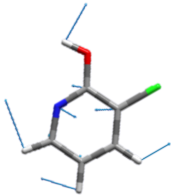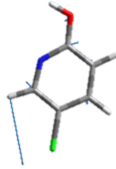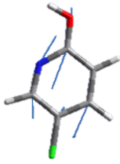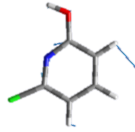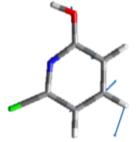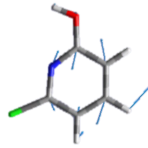
2PO	3Cl-2PO	4Cl-2PO	5Cl-2PO	6Cl-2PO
542 cm^{-1}	179 cm^{-1}	544 cm^{-1}	390 cm^{-1}	456 cm^{-1}
				546 cm^{-1}
1435 cm^{-1}	1445 cm^{-1}	1424 cm^{-1}	1439 cm^{-1}	1444 cm^{-1}
1616 cm^{-1}	1629 cm^{-1}	1601 cm^{-1}	1615 cm^{-1}	1609 cm^{-1}
			1648 cm^{-1}	

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Figure S22.
The most active vibrational normal modes in the D_1 state of 2-hydroxypyridine and its chlorinated analogues. Only modes with Huang Rhys factors greater than 0.1 are reported. The modes are collected in two groups: below and above 1000 cm^{-1}.

2HP	3Cl-2HP	4Cl-2HP	5Cl-2HP	6Cl-2HP
	238 cm^{-1}		388 cm^{-1}	208 cm^{-1}
	486 cm^{-1}		648 cm^{-1}	553 cm^{-1}
	582 cm^{-1}		678 cm^{-1}	703 cm^{-1}
	694 cm^{-1}		991 cm^{-1}	942 cm^{-1}
	856 cm^{-1}			980 cm^{-1}

	1058 cm^{-1}		1292 cm^{-1}	1245 cm^{-1}
	1543 cm^{-1}		1648 cm^{-1}	1424 cm^{-1}
				1554 cm^{-1}
				1623 cm^{-1}