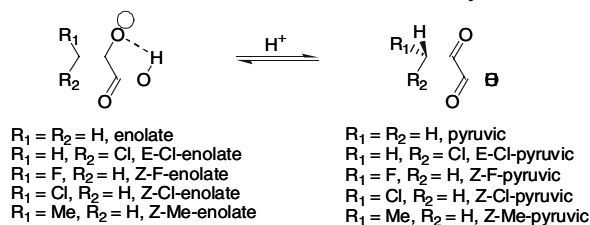


Supporting Information for World Wide Web Edition

Figure SM1: Cartesian coordinates for all the optimized structures, energies in atomic units (PM3) and thermochemical analysis (STO-3G)

Semiempiric PM3							
<u>Pyruvoyl Enolate (PM3)</u>			<u>Pyruvic (PM3)</u>				
E (a.u.) = -0.2371951 hartrees			E (a.u.) = -0.2052225 hartrees				
C	-0.685915	0.243625	-0.000275	C	-0.730431	-0.212278	0.000124
O	-1.322303	1.284511	-0.000891	O	-1.099261	-1.366577	-0.001650
O	-1.475287	-0.854599	0.001377	O	-1.774714	0.637204	0.001513
C	0.806728	-0.085814	-0.000866	C	0.724513	0.279068	-0.000303
C	1.736107	0.903307	0.000677	C	1.781852	-0.778006	0.001238
O	0.976208	-1.357593	-0.000899	O	0.957610	1.470465	-0.001520
H	-0.831641	-1.587518	0.001031	H	-1.480780	1.540524	0.001837
H	2.796218	0.692367	0.002484	H	1.681239	-1.417889	0.888815
H	1.464964	1.949902	0.002573	H	1.677425	-1.423266	-0.882028
				H	2.797427	-0.360803	-0.001727

<u>Z-3-Me-pyruvoyl enolate (PM3)</u>			<u>Z-3-Me-pyruvic (PM3)</u>				
E (a.u.) = -0.2458915 hartrees			E (a.u.) = -0.212163 hartrees				
C	1.136531	-0.302770	0.000026	C	1.217074	-0.238067	-0.000603
O	1.528227	-1.476418	-0.001867	O	1.530659	-1.408705	-0.005766
O	2.175469	0.595829	0.002185	O	2.301560	0.559256	0.006654
C	-0.261651	0.282996	-0.000271	C	-0.214180	0.326809	-0.001700
C	-1.297202	-0.611979	0.001156	C	-1.315242	-0.697057	0.003538
O	-0.288214	1.562325	-0.002213	O	-0.376040	1.529284	-0.006567
C	-2.702665	-0.199208	0.000609	C	-2.707917	-0.112340	0.001930
H	1.791503	1.490674	0.002699	H	2.052875	1.476101	0.009241
H	-1.088693	-1.686682	0.001984	H	-1.171275	-1.357356	-0.876709
H	-3.240917	-0.593503	-0.901414	H	-1.169972	-1.349533	0.889371
H	-2.794064	0.915720	0.001027	H	-3.462300	-0.909632	0.006004
H	-3.241765	-0.594331	0.901748	H	-2.889199	0.508897	-0.884923
				H	-2.887974	0.516779	0.883458

<u>Z-3-F-pyruvoyl enolate (PM3)</u>			<u>Z-3-F-pyruvic (PM3)</u>				
E (a.u.) = -0.3158069 hartrees			E (a.u.) = -0.2659561 hartrees				
C	1.115570	-0.312662	0.000267	C	1.174320	-0.239224	-0.005710
O	1.576907	-1.441475	-0.000327	O	1.456810	-1.416756	-0.047332
O	2.063759	0.650925	0.000140	O	2.272417	0.534698	0.054793
C	-0.302102	0.244766	0.000059	C	-0.240919	0.351565	-0.015306
C	-1.365470	-0.616955	0.000287	C	-1.369167	-0.666846	0.027107
O	-0.292364	1.521629	-0.000221	O	-0.410507	1.549322	-0.053066
F	-2.635129	-0.168116	-0.000097	F	-2.597364	-0.094731	0.017734
H	1.543351	1.475146	0.000098	H	2.043653	1.456646	0.072932
H	-1.301593	-1.701621	0.000368	H	-1.308060	-1.337444	-0.848041
				H	-1.294483	-1.277709	0.943797

Figure SM1: Continuation page 2

Semiempiric PM3	
<u>Z-3-Cl-pyruvoyl enolate (PM3)</u> E (a.u.) = -0.256956 hartrees C 1.555201 -0.308813 0.000204 O 2.033429 -1.429891 -0.000189 O 2.490561 0.667445 0.000048 C 0.123683 0.228035 -0.000009 C -0.924477 -0.644881 0.000172 O 0.121841 1.502199 -0.000089 Cl -2.520562 -0.077764 -0.000033 H 1.961061 1.484750 0.000004 H -0.804590 -1.726835 0.000194	<u>Z-3-Cl-pyruvic (PM3)</u> E (a.u.) = -0.2050668 hartrees C 1.612892 -0.221855 -0.000949 O 1.948322 -1.386153 -0.008754 O 2.675899 0.601754 0.009635 C 0.170008 0.305405 -0.002153 C -0.902731 -0.744046 0.006006 O -0.041511 1.498219 -0.009566 Cl -2.515669 -0.027663 0.001015 H 2.405087 1.512440 0.012967 H -0.790929 -1.401654 -0.877463 H -0.790469 -1.388106 0.899307
<u>E-3-Cl-pyruvoyl enolate (PM3)</u> E (a.u.) = -0.2539846 hartrees C 0.988529 -0.587747 0.000027 O 0.564445 -1.728610 -0.001745 O 2.341464 -0.534079 0.001748 C 0.335164 0.791608 -0.000180 C -1.015992 0.985577 0.000547 O 1.230797 1.704615 -0.001261 Cl -2.118617 -0.298472 0.000373 H 2.533201 0.420196 0.001629 H -1.456572 1.981792 -0.000274	<u>E-3-Cl-pyruvic (PM3)</u> E (a.u.) = -0.203941 hartrees C 1.312927 -0.302761 0.099233 O 1.539968 -1.268996 0.792673 O 2.180409 -0.203072 -0.925084 C 0.193626 0.720997 0.315782 C -1.106396 0.189804 0.857278 O 0.376331 1.890625 0.057547 Cl -2.033590 -0.468104 -0.503929 H 2.032424 0.593446 -1.420311 H -0.931719 -0.609787 1.600957 H -1.704277 0.977423 1.351301
Ab initio (STO-3G)	
<u>Pyruvoyl enolate (STO-3G)</u> C 0.803626 0.206786 -0.000037 O 1.372873 1.305661 0.000130 O 1.306292 -1.007563 -0.000038 C -0.773478 0.003288 -0.000162 C -1.682737 0.965543 -0.000051 O -0.942533 -1.335568 0.000080 H 0.150914 -1.523915 -0.000097 H -2.742053 0.770309 0.000875 H -1.386385 1.999660 -0.000645 Zero-point correction (Hartree/Particle)= 0.067682 Thermal correction to Energy= 0.072496 Thermal correction to Enthalpy= 0.073441 Thermal correction to Gibbs Free Energy= 0.039170 Sum of electronic and zero-point Energies= -335.230434 Sum of electronic and thermal Energies= -335.225619 Sum of electronic and thermal Enthalpies= -335.224675 Sum of electronic and thermal Free Energies= -335.258945	<u>Pyruvic (STO-3G)</u> C 0.762194 0.304462 -0.000003 O 1.015666 1.493305 -0.000372 O 1.746457 -0.670752 0.000400 C -0.682307 -0.294250 -0.000105 C -1.855176 0.695732 0.000250 O -0.782848 -1.511779 -0.000382 H 1.234607 -1.519664 0.000342 H -2.466896 0.549027 0.886455 H -1.472785 1.711065 -0.008214 H -2.477395 0.537716 -0.876605 Zero-point correction (Hartree/Particle)= 0.082359 Thermal correction to Energy= 0.087748 Thermal correction to Enthalpy= 0.088692 Thermal correction to Gibbs Free Energy= 0.053083 Sum of electronic and zero-point Energies= -335.949620 Sum of electronic and thermal Energies= -335.944231 Sum of electronic and thermal Enthalpies= -335.943287 Sum of electronic and thermal Free Energies= -335.978896
<u>Z-3-Me-pyruvoyl enolate (STO-3G)</u> C 1.278036 -0.318767 -0.000010 O 1.657079 -1.496604 -0.000027 O 1.975330 0.796222 -0.000207 C -0.240792 0.145172 -0.000190 C -1.298369 -0.655674 0.000145 O -0.186830 1.493506 0.000389 C -2.737377 -0.171000 -0.000266 H 0.926299 1.495407 -0.000077 H -1.150437 -1.723937 0.001898 H -3.292021 -0.516497 -0.873950 H -2.766039 0.914898 -0.002260 H -3.291421 -0.513254 0.875090 Zero-point correction (Hartree/Particle) = 0.101510 Thermal correction to Energy= 0.107918 Thermal correction to Enthalpy= 0.108863 Thermal correction to Gibbs Free Energy= 0.070686 Sum of electronic and zero-point Energies= -373.781325 Sum of electronic and thermal Energies= -373.774917 Sum of electronic and thermal Enthalpies= -373.773972 Sum of electronic and thermal Free Energies= -373.812149	<u>Z-3-Me-pyruvic (STO-3G)</u> C 1.267281 0.299760 0.000011 O 1.539787 1.484347 0.000239 O 2.239578 -0.688629 -0.000204 C -0.184212 -0.281936 -0.000017 C -1.343101 0.730244 -0.000267 O -0.301363 -1.497338 0.000177 C -2.721939 0.046537 0.000077 H 1.717222 -1.531068 -0.000001 H -1.230599 1.369589 0.874648 H -1.230726 1.368976 -0.875654 H -3.508741 0.794810 -0.000784 H -2.839858 -0.577659 0.880636 H -2.839494 -0.579316 -0.879355 Zero-point correction (Hartree/Particle) = 0.116819 Thermal correction to Energy= 0.124173 Thermal correction to Enthalpy= 0.125118 Thermal correction to Gibbs Free Energy= 0.084334 Sum of electronic and zero-point Energies= -374.496397 Sum of electronic and thermal Energies= -374.489043 Sum of electronic and thermal Enthalpies= -374.488099 Sum of electronic and thermal Free Energies= -374.528883

Figure SM1: Continuation page 3

Ab initio (STO-3G)							
<u>Z-3-F-pyruvoyl enolate (STO-3G)</u>				<u>Z-3-F-pyruvic (STO-3G)</u>			
C	1.222598	-0.332276	-0.000146	C	1.219203	-0.306332	-0.000082
O	1.554066	-1.524770	0.000106	O	1.451460	-1.499438	-0.000104
O	1.954253	0.756340	-0.000063	O	2.221116	0.650937	-0.000687
C	-0.279454	0.183354	-0.000207	C	-0.214820	0.313413	0.000562
C	-1.345858	-0.602787	0.000017	C	-1.401465	-0.687011	0.001047
O	-0.186107	1.534855	0.000222	O	-0.322756	1.528685	0.000747
F	-2.647553	-0.159918	-0.000071	F	-2.613871	-0.023444	-0.001449
H	0.917604	1.501636	-0.000078	H	1.730628	1.512165	-0.000434
H	-1.251043	-1.683515	0.000615	H	-1.309938	-1.333145	-0.884002
Zero-point correction (Hartree/Particle)=			0.058782	H	-1.311909	-1.329926	0.888660
Thermal correction to Energy=			0.064419	Zero-point correction (Hartree/Particle) =			0.073293
Thermal correction to Enthalpy=			0.065364	Thermal correction to Energy=			0.080080
Thermal correction to Gibbs Free Energy=			0.028650	Thermal correction to Enthalpy=			0.081024
Sum of electronic and zero-point Energies=			-432.698358	Thermal correction to Gibbs Free Energy=			0.041227
Sum of electronic and thermal Energies=			-432.692721	Sum of electronic and zero-point Energies=			-433.401048
Sum of electronic and thermal Enthalpies=			-432.691777	Sum of electronic and thermal Energies=			-433.394262
Sum of electronic and thermal Free Energies=			-432.728491	Sum of electronic and thermal Enthalpies=			-433.393318
				Sum of electronic and thermal Free Energies=			-433.433115
<u>Z-3-Cl-pyruvoyl enolate (STO-3G)</u>				<u>Z-3-Cl-pyruvic (STO-3G)</u>			
C	1.676484	0.336381	-0.000012	C	-1.667408	0.284980	-0.000193
O	2.032749	1.514416	-0.000278	O	-1.931985	1.471106	-0.000539
O	2.398520	-0.773774	-0.000271	O	-2.638921	-0.701888	-0.000236
C	0.168470	-0.186867	0.000436	C	-0.213140	-0.287610	0.000364
C	-0.871561	0.642306	0.000813	C	0.913188	0.767752	0.001319
O	0.262233	-1.509237	0.000195	O	-0.054655	-1.495405	0.000312
Cl	-2.589411	0.067409	-0.000321	Cl	2.545665	-0.001751	-0.000597
H	1.436397	-1.463407	-0.000092	H	-2.126644	-1.550119	0.000324
H	-0.804788	1.715303	0.000965	H	0.829020	1.400633	-0.884282
Zero-point correction (Hartree/Particle) =			0.055941	H	0.829958	1.398025	0.888879
Thermal correction to Energy=			0.061937	Zero-point correction (Hartree/Particle) =			0.071726
Thermal correction to Enthalpy=			0.062881	Thermal correction to Energy=			0.078707
Thermal correction to Gibbs Free Energy=			0.024827	Thermal correction to Enthalpy=			0.079651
Sum of electronic and zero-point Energies=			-789.269233	Thermal correction to Gibbs Free Energy=			0.038695
Sum of electronic and thermal Energies=			-789.263237	Sum of electronic and zero-point Energies=			-789.953289
Sum of electronic and thermal Enthalpies=			-789.262293	Sum of electronic and thermal Energies=			-789.946309
Sum of electronic and thermal Free Energies=			-789.300346	Sum of electronic and thermal Enthalpies=			-789.945365
				Sum of electronic and thermal Free Energies=			-789.986321
<u>E-3-Cl-pyruvoyl enolate (STO-3G)</u>				<u>E-3-Cl-pyruvic (STO-3G)</u>			
C	1.063924	0.716297	0.000017	C	1.300040	-0.497690	0.061994
O	0.501991	1.808325	0.000287	O	1.078180	-1.643408	0.399765
O	2.368986	0.448522	-0.000197	O	2.487505	-0.108440	-0.536909
C	0.378659	-0.722648	-0.000025	C	0.299771	0.682159	0.272268
C	-0.921549	-1.025130	0.000191	C	-1.083597	0.326419	0.852720
O	1.391184	-1.583896	-0.000010	O	0.644053	1.812976	-0.031663
Cl	-2.240802	0.207157	-0.000151	Cl	-2.153272	-0.304252	-0.469173
H	2.193353	-0.692852	-0.000269	H	2.383623	0.866587	-0.678284
H	-1.323220	-2.023541	0.001103	H	-0.992026	-0.458125	1.604476
Zero-point correction (Hartree/Particle)=			0.056121	H	-1.561169	1.209471	1.278319
Thermal correction to Energy=			0.062060	Zero-point correction (Hartree/Particle)=			0.071866
Thermal correction to Enthalpy=			0.063004	Thermal correction to Energy=			0.078799
Thermal correction to Gibbs Free Energy=			0.025068	Thermal correction to Enthalpy=			0.079743
Sum of electronic and zero-point Energies=			-789.263080	Thermal correction to Gibbs Free Energy=			0.038876
Sum of electronic and thermal Energies=			-789.257141	Sum of electronic and zero-point Energies=			-789.952885
Sum of electronic and thermal Enthalpies=			-789.256197	Sum of electronic and thermal Energies=			-789.945952
Sum of electronic and thermal Free Energies=			-789.294134	Sum of electronic and thermal Enthalpies=			-789.945008
				Sum of electronic and thermal Free Energies=			-789.985875