Supporting Information for –

Computational and Synthetic Studies on the Cyclometallation Reaction of Dimethylbenzylamine with $[IrCl_2Cp^*]_2$: Role of the Chelating Base.†

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Contents:

Experimental Details of Cyclometalation Reactions.

Reaction with CH_3CO_2Na

A mixture of $[IrCl_2Cp^*]_2$ (20 mg, 0.025 mmol), DMBA-H (8.5 mg, 0.063 mmol) and NaOAc (5.2 mg, 0.063 mmol) in dichloromethane (10 ml) was stirred for 18 hours. After this time the mixture was filtered through celite and evaporated to dryness. The sample was dissolved in 0.5 ml of a $CDCl_3$ solution containing mesitylene (0.05 mmol/litre) and the amount of product was determined by integration of the ^1H NMR spectrum. The yield was 65%.

Reaction with CF_3CO_2Na

This was done using $[IrCl_2Cp^*]_2$ (20 mg, 0.025 mmol), DMBA-H (8.5 mg, 0.063 mmol) and $NaCF_3CO_2$ (8.6 mg, 0.063 mmol). The yield was 55%.

Reaction with $PhCO_2Na$

This was done using $[IrCl_2Cp^*]_2$ (20 mg, 0.025 mmol), DMBA-H (8.5 mg, 0.063 mmol) and $NaPhCO_2$ (9.1 mg, 0.063 mmol). The yield was 29%.

Reaction with $NaHCO_3$

This was done using $[IrCl_2Cp^*]_2$ (20 mg, 0.025 mmol), DMBA-H (8.5 mg, 0.063 mmol) and $NaHCO_3$ (10.8 mg, 0.063 mmol). This reaction failed, only starting material was observed.

Reaction with CF_3SO_2Na

This was done using $[IrCl_2Cp^*]_2$ (20 mg, 0.025 mmol), DMBA-H (8.5 mg, 0.063 mmol) and NaOTf (10.8 mg, 0.063 mmol). Only traces of product were observed after 18 hours. If the reaction is left for 4 days a 50% yield is obtained.

Reaction with CCl_3CO_2Na :

This was prepared from $[IrCl_2Cp^*]_2$ (20 mg, 0.025 mmol), DMBA-H (8.5 mg, 0.063 mmol) and $NaCCl_3CO_2$ (10.8 mg, 0.063 mmol). In this case the NMR sample was made up in $CDCl_3$ and a known amount of mesitylene was added. The yield was 28%.

Computed Energies and Cartesian Coordinates.

1. ACETATE

(i) Pathway I

1_{Me}

BP86 Energy = -931.889670429
Enthalpy 0K= -931.556776
Enthalpy 298K= -931.536124
Free Energy 298K= -931.606812
PCM (CH_2Cl_2)= -931.947777

Ir	-0.77813	-0.43582	0.12366
N	0.09013	1.35892	1.12481
C	-0.93441	2.40950	1.44617
C	0.69584	0.94270	2.43123
C	1.15394	2.03892	0.25204
H	0.61241	2.43026	-0.62237
H	1.52493	2.89882	0.84322
C	2.30770	1.17221	-0.19701
C	2.30014	0.60447	-1.49013
H	1.44892	0.79455	-2.15349
C	3.37967	-0.17542	-1.93480
H	3.37212	-0.59099	-2.94779
C	4.48135	-0.40060	-1.09100
H	5.32588	-1.00325	-1.43926
C	4.51109	0.17905	0.18852
H	5.38114	0.03555	0.83672
C	3.43686	0.97091	0.62648
H	3.49180	1.45806	1.60663
C	-1.45481	-2.40994	0.75183
H	-2.43470	-2.55583	1.20968
C	-1.17647	-2.44074	-0.66745
H	-1.88688	-2.66328	-1.46267
C	0.23105	-2.11843	-0.82913
H	0.75668	-2.00955	-1.77798
C	0.81295	-1.90217	0.46954
H	1.85533	-1.64517	0.65803
C	-0.24019	-2.07936	1.46006
H	-0.13424	-2.01151	2.54182
O	-1.18208	0.91084	-1.53478
O	-2.68297	0.59201	0.02178
C	-2.37683	1.15431	-1.09984
C	-3.34452	2.00616	-1.85906
H	-3.97422	1.35502	-2.49086
H	-4.00862	2.54601	-1.16799
H	-2.80992	2.70712	-2.51620
H	-0.45695	3.21602	2.03117
H	-1.33356	2.84184	0.51952
H	-1.75425	1.96488	2.02604
H	1.48422	0.19871	2.26320
H	1.13640	1.82395	2.93382
H	-0.09125	0.52226	3.07287

TS (1-2)$_{Me}$

BP86 Energy = -931.867068252
Enthalpy 0K= -931.535443
Enthalpy 298K= -931.514884
Free Energy 298K= -931.588286
PCM (CH_2Cl_2)= -931.927577489
Frequency= -112.9998cm-1

Ir	-0.71621	-0.37714	-0.02549
N	0.45476	-0.10986	1.81890
C	-0.44212	0.22400	2.97763
C	1.21591	-1.35181	2.16403
C	1.43142	1.04300	1.61690
H	0.81232	1.93897	1.44597
H	1.98060	1.17973	2.56787
C	2.37652	0.79195	0.46510
C	1.91360	0.96077	-0.85998
H	0.93256	1.42330	-1.05279
C	2.74919	0.64975	-1.95006
H	2.38958	0.80634	-2.97216
C	4.05885	0.19814	-1.72392
H	4.71822	-0.02075	-2.56947
C	4.53372	0.05768	-0.40772
H	5.56080	-0.27480	-0.22834
C	3.69481	0.34822	0.68144
H	4.07309	0.23752	1.70409
C	-2.28300	-1.81146	-0.21108
H	-3.13852	-1.86136	0.46403
C	-2.22027	-1.07570	-1.46627
H	-2.99171	-0.42381	-1.87398
C	-0.90977	-1.27408	-2.00834
H	-0.51525	-0.77458	-2.89376
C	-0.16435	-2.19485	-1.15192
H	0.85006	-2.55129	-1.32642
C	-1.01760	-2.53101	-0.05008
H	-0.77392	-3.20223	0.77346
O	-1.05881	1.97565	-1.43843
O	-1.66341	1.38131	0.63458
C	-1.65967	2.24041	-0.37067
C	-2.39255	3.54296	-0.14112
H	-3.05406	3.74095	-0.99917
H	-2.97668	3.53010	0.78904
H	-1.66030	4.36688	-0.10278
H	0.17246	0.38324	3.88191
H	-1.01887	1.12696	2.74302
H	-1.13202	-0.61482	3.15176
H	1.84757	-1.64862	1.31707
H	1.85309	-1.16391	3.04759
H	0.50552	-2.15272	2.41024

2_{Me}

BP86 Energy = -931.875253486
Enthalpy 0K= -931.543083
Enthalpy 298K= -931.522022
Free Energy 298K= -931.593482
PCM (CH_2Cl_2)= -931.936099348

Ir	-0.24661	-0.02361	0.43296
N	0.32452	2.07785	-0.06110

C	-0.82162	3.02490	-0.22773
C	1.25768	2.63972	0.96096
C	1.05173	1.87844	-1.37102
H	0.29179	1.86828	-2.16725
H	1.74678	2.71919	-1.55139
C	1.75632	0.53535	-1.29989
C	1.02007	-0.64475	-1.63271
C	1.65320	-1.91740	-1.55626
H	1.09602	-2.80759	-1.86419
C	2.98592	-2.01606	-1.15305
H	3.48040	-2.99169	-1.11845
C	3.71747	-0.84568	-0.84562
H	4.77494	-0.92340	-0.57338
C	3.11041	0.41457	-0.90927
H	3.69759	1.31459	-0.69772
C	0.47312	-0.22954	2.51218
H	1.18493	0.43453	3.00154
C	-0.97762	-0.06341	2.47284
H	-1.55203	0.73219	2.94852
C	-1.53200	-1.20024	1.75848
H	-2.58146	-1.36064	1.51630
C	-0.44813	-2.02664	1.30938
H	-0.54958	-2.92880	0.70969
C	0.79387	-1.41695	1.77986
H	1.79861	-1.79205	1.58427
O	-2.59019	-1.68538	-0.91581
O	-1.64937	0.39421	-1.04156
C	-2.56308	-0.54187	-1.37399
C	-3.56622	-0.01959	-2.39349
H	-3.05401	0.44459	-3.25133
H	-4.20155	-0.84595	-2.73841
H	-4.19914	0.75619	-1.93033
H	-0.45275	3.98930	-0.62192
H	-1.55479	2.57997	-0.91133
H	-1.28912	3.18947	0.75435
H	2.12432	1.97570	1.08416
H	1.60258	3.64132	0.64320
H	0.72920	2.73394	1.92031
H	0.07430	-0.55234	-2.17241

TS (2-3)$_{Me}$

BP86 Energy = -931.873090772
Enthalpy 0K= -931.541640
Enthalpy 298K= -931.521434
Free Energy 298K= -931.590747
PCM (CH_2Cl_2)= -931.933886181
Frequency= -42.7748cm-1

Ir	-0.49094	-0.42802	-0.05019
N	0.44577	-0.16467	1.93856
C	-0.56286	0.05182	3.02501
C	1.29626	-1.33988	2.30548
C	1.32036	1.06700	1.80415
H	0.63641	1.92921	1.75980
H	1.95835	1.15876	2.70232
C	2.12580	0.95095	0.53172
C	1.42019	0.96851	-0.70594
C	2.11742	0.74266	-1.92046
H	1.57530	0.81558	-2.86838
C	3.49773	0.51074	-1.90695
H	4.04172	0.36382	-2.84475
C	4.19132	0.50446	-0.68185
H	5.27322	0.33894	-0.66975
C	3.50753	0.71035	0.53134
H	4.05882	0.68967	1.47763
C	-0.64155	-2.62618	-0.19405
H	-0.21311	-3.32676	0.52265
C	-1.96088	-2.00847	-0.09782
H	-2.71288	-2.20125	0.66751
C	-2.13265	-1.17413	-1.28163
H	-2.99985	-0.55372	-1.50808
C	-0.92729	-1.23054	-2.04933
H	-0.73562	-0.67041	-2.96368
C	0.00411	-2.13641	-1.37125
H	1.00875	-2.39107	-1.70794
O	-1.44616	2.11315	-1.55751
O	-1.45573	1.31858	0.57222
C	-1.81313	2.19656	-0.37713
C	-2.71701	3.30050	0.14568
H	-2.42950	3.61044	1.16164
H	-2.68660	4.15751	-0.54070
H	-3.75406	2.92585	0.19457
H	-0.04414	0.28515	3.97257
H	-1.22586	0.87709	2.73636
H	-1.15024	-0.86908	3.15396
H	2.05280	-1.51208	1.52731
H	1.79959	-1.15024	3.27163
H	0.65749	-2.22754	2.40901
H	0.43429	1.47908	-0.81856

3$_{Me}$

BP86 Energy = -931.898549998
Enthalpy 0K= -931.565927
Enthalpy 298K= -931.545255
Free Energy 298K= -931.615081
PCM (CH_2Cl_2)= -931.95507909

Ir	-0.69442	-0.11850	-0.15246
N	-0.01087	-1.00476	1.73776
C	-0.82782	-0.53997	2.90036
C	-0.07770	-2.49917	1.65773
C	1.43286	-0.59400	1.92759
H	1.41396	0.43427	2.32908
H	1.90415	-1.24135	2.69103
C	2.12869	-0.64647	0.59160
C	1.30848	-0.39505	-0.54692
C	1.93463	-0.39669	-1.81829
H	1.35210	-0.20185	-2.72541
C	3.31718	-0.63281	-1.94686
H	3.77546	-0.62221	-2.94101
C	4.10079	-0.88947	-0.81268
H	5.17217	-1.08525	-0.91518
C	3.50263	-0.90055	0.45893
H	4.11085	-1.10576	1.34754
C	-2.86526	-0.92746	-0.28836
H	-3.42057	-1.36869	0.54015

C	-2.91038	0.42507	-0.68572
H	-3.48723	1.21617	-0.20581
C	-1.97986	0.60803	-1.80285
H	-1.81624	1.53459	-2.35298
C	-1.41936	-0.67702	-2.12277
H	-0.73630	-0.89949	-2.94175
C	-1.89508	-1.62922	-1.13718
H	-1.69176	-2.69989	-1.13547
O	1.22426	2.58404	-0.65375
O	-0.23239	1.75726	0.88976
C	0.45288	2.70506	0.41083
C	0.43483	4.06995	1.03334
H	-0.26987	4.10209	1.87330
H	1.44927	4.33263	1.37685
H	0.15249	4.81601	0.27194
H	-0.41483	-0.94982	3.84082
H	-0.81646	0.55780	2.93737
H	-1.86171	-0.89169	2.77611
H	0.55303	-2.84478	0.82709
H	0.28275	-2.93918	2.60595
H	-1.11785	-2.81088	1.48997
H	1.25258	1.61300	-0.91526

(ii) Pathway II

2′$_{Me}$

BP86 Energy = -931.875185609
Enthalpy 0K= -931.542795
Enthalpy 298K= -931.521739
Free Energy 298K= -931.593569

Ir	0.29511	-0.29838	-0.28331
N	-0.29127	1.68602	-1.11777
C	0.86423	2.57594	-1.44947
C	-1.13196	1.51719	-2.34131
C	-1.11768	2.28708	-0.00143
H	-0.41111	2.72490	0.72019
H	-1.75992	3.09099	-0.40643
C	-1.91589	1.17665	0.65497
C	-1.29355	0.38957	1.66944
H	-0.35507	0.73137	2.11539
C	-2.01053	-0.67126	2.28274
H	-1.54424	-1.23137	3.09952
C	-3.32012	-0.95600	1.88600
H	-3.88223	-1.75842	2.37362
C	-3.93916	-0.16940	0.89051
H	-4.97773	-0.36926	0.60833
C	-3.24464	0.88327	0.27777
H	-3.74868	1.50595	-0.46930
C	0.72607	-1.44218	-2.07657
H	0.98269	-0.99359	-3.03722
C	1.67897	-1.77905	-1.02794
H	2.75287	-1.60273	-1.04424
C	0.94160	-2.36295	0.07325
H	1.36984	-2.70599	1.01263
C	-0.45614	-2.36009	-0.30402
H	-1.28316	-2.67285	0.33460
C	-0.59808	-1.82110	-1.63510
H	-1.52758	-1.71835	-2.19325
O	3.11163	-0.64533	1.19593
O	1.48066	0.92681	0.87661
C	2.65133	0.47831	1.38814
C	3.33676	1.53850	2.23802
H	4.26584	1.12919	2.65561
H	3.56827	2.42793	1.62860
H	2.67480	1.86737	3.05586
H	0.49508	3.57683	-1.73812
H	1.51989	2.64420	-0.57267
H	1.42094	2.13720	-2.29082
H	-1.99971	0.88403	-2.11209
H	-1.47803	2.50442	-2.70005
H	-0.53287	1.04272	-3.13143

TS (2′-3′)$_{Me}$

BP86 Energy = -931.851440113
Enthalpy 0K= -931.525221
Enthalpy 298K= -931.504684
Free Energy 298K= -931.574127
Frequency= -1057.3294cm-1

Ir	-0.55616	-0.31757	-0.15509
N	0.42953	-1.00132	1.69678
C	-0.43544	-0.75513	2.89391
C	0.72935	-2.46621	1.59844
C	1.73950	-0.25964	1.87000
H	1.49649	0.70971	2.33826
H	2.38932	-0.81982	2.56671
C	2.37485	-0.02445	0.52509
C	1.46707	0.31895	-0.52846
H	0.68390	1.31463	0.02788
C	2.00730	0.64184	-1.80383
H	1.33861	0.93898	-2.61899
C	3.39153	0.61748	-2.02029
H	3.79851	0.87792	-3.00215
C	4.26044	0.25966	-0.97279
H	5.34062	0.23417	-1.14754
C	3.75653	-0.05805	0.30238
H	4.44409	-0.32423	1.11261
C	-2.27629	-1.75479	-0.29241
H	-2.64263	-2.36095	0.53684
C	-2.75832	-0.46522	-0.65409
H	-3.52360	0.11173	-0.13692
C	-1.98896	0.00578	-1.80075
H	-2.12679	0.96095	-2.30345
C	-1.05567	-1.03091	-2.15520
H	-0.33585	-0.99639	-2.97341
C	-1.18741	-2.11295	-1.20002
H	-0.64788	-3.05927	-1.22617
O	-2.17869	2.51794	-0.06715
O	-0.25529	1.65645	0.81197
C	-1.11391	2.70212	0.49738
C	-0.58568	4.03912	0.96938
H	-1.30338	4.82968	0.71446
H	-0.42214	4.02062	2.05933
H	0.38877	4.25246	0.49851
H	0.10200	-1.04255	3.81665

H -0.69804 0.31100 2.93134
H -1.35113 -1.35709 2.80850
H 1.39689 -2.64305 0.74333
H 1.21802 -2.81155 2.52828
H -0.20583 -3.02535 1.45929

3'$_{Me}$

BP86 Energy = -931.875253038
Enthalpy 0K= -931.543078
Enthalpy 298K= -931.522020
Free Energy 298K= -931.593446

Ir -0.24659 -0.02249 0.43329
N 0.32444 2.07791 -0.06511
C -0.82172 3.02467 -0.23330
C 1.25806 2.64196 0.95533
C 1.05112 1.87576 -1.37491
H 0.29087 1.86394 -2.17082
H 1.74615 2.71610 -1.55727
C 1.75563 0.53275 -1.30123
C 1.01930 -0.64789 -1.63193
H 0.07345 -0.55636 -2.17164
C 1.65227 -1.92046 -1.55312
H 1.09497 -2.81114 -1.85940
C 2.98494 -2.01854 -1.14962
H 3.47927 -2.99417 -1.11312
C 3.71663 -0.84767 -0.84435
H 4.77407 -0.92501 -0.57191
C 3.10973 0.41252 -0.91039
H 3.69703 1.31286 -0.70054
C -0.97816 -0.05942 2.47302
H -1.55331 0.73645 2.94735
C -1.53140 -1.19793 1.76043
H -2.58068 -1.35957 1.51825
C -0.44676 -2.02416 1.31301
H -0.54737 -2.92729 0.71464
C 0.79465 -1.41274 1.78286
H 1.79975 -1.78736 1.58817
C 0.47271 -0.22439 2.51308
H 1.18383 0.44123 3.00138
O -2.58730 -1.68834 -0.91436
O -1.64990 0.39267 -1.04137
C -2.56224 -0.54500 -1.37309
C -3.56634 -0.02489 -2.39274
H -4.20252 -0.85182 -2.73472
H -4.19812 0.75275 -1.93120
H -3.05468 0.43641 -3.25248
H -0.45305 3.98806 -0.63013
H -1.55540 2.57810 -0.91530
H -1.28850 3.19169 0.74871
H 2.12438 1.97783 1.08009
H 1.60340 3.64256 0.63489
H 0.72984 2.73896 1.91453

(iii) Pathway III

2''$_{Me}$

BP86 Energy = -931.867617791
Enthalpy 0K= -931.535655
Enthalpy 298K= -931.515290
Free Energy 298K= -931.585151

Ir -0.44842 -0.34650 -0.13114
N -0.09490 -0.39601 2.04982
C -1.09037 0.43535 2.80105
C -0.12776 -1.78082 2.61714
C 1.29801 0.20127 2.17728
H 1.18394 1.25760 2.45778
H 1.83890 -0.31382 2.99250
C 2.03929 0.12382 0.85130
C 2.16598 -1.09896 0.13445
C 2.91830 -1.14951 -1.06563
H 3.04399 -2.10641 -1.58228
C 3.54554 0.00055 -1.54912
H 4.14364 -0.04322 -2.46447
C 3.43181 1.21548 -0.83813
H 3.93313 2.11389 -1.21066
C 2.68563 1.27681 0.34008
H 2.59212 2.22340 0.88015
C -2.37982 -0.65030 -1.00679
H -3.26011 -0.06516 -0.74609
C -1.45090 -0.34433 -2.08752
H -1.49139 0.53991 -2.71914
C -0.44184 -1.36059 -2.08593
H 0.43994 -1.37360 -2.72725
C -0.75484 -2.34845 -1.05971
H -0.19194 -3.25660 -0.84622
C -1.95052 -1.90850 -0.40219
H -2.45390 -2.41649 0.42132
O -2.05216 2.24493 -1.08462
O -0.27355 1.67646 0.23967
C -1.10093 2.55346 -0.36598
C -0.71351 3.99691 -0.07548
H -1.57427 4.65221 -0.26599
H -0.35550 4.12534 0.95717
H 0.10613 4.29262 -0.75296
H -0.80971 0.48540 3.86873
H -1.11149 1.43969 2.36080
H -2.08345 -0.02836 2.70682
H 0.59175 -2.42912 2.09972
H 0.12633 -1.75029 3.69237
H -1.13780 -2.19900 2.50412
H 1.82396 -2.03983 0.57343

TS (2''-3'')$_{Me}$

BP86 Energy = -931.848066543
Enthalpy 0K= -931.519772
Enthalpy 298K= -931.499365
Free Energy 298K= -931.568232
Frequency= -480.0643cm-1

Ir -0.45952 -0.47349 0.02569
N 0.24059 0.65388 1.78581
C -0.77757 1.63557 2.28394
C 0.58625 -0.27155 2.91816

C	1.50277	1.37645	1.34933
H	1.17610	2.27522	0.80375
H	2.05904	1.69422	2.25035
C	2.31715	0.49006	0.43676
C	1.62674	-0.48120	-0.32297
C	2.31048	-1.29719	-1.23805
H	1.78189	-2.06186	-1.81492
C	3.69222	-1.11287	-1.42432
H	4.22602	-1.73591	-2.14847
C	4.38418	-0.14415	-0.67997
H	5.46146	-0.01421	-0.81837
C	3.70010	0.65359	0.25193
H	4.24265	1.40893	0.83137
C	-2.74178	-1.03180	0.41722
H	-3.36381	-0.58564	1.19273
C	-2.61538	-0.55392	-0.91350
H	-3.11271	0.33035	-1.30961
C	-1.64708	-1.38372	-1.62471
H	-1.35945	-1.28204	-2.67065
C	-1.20137	-2.39727	-0.71097
H	-0.51486	-3.21438	-0.93578
C	-1.83941	-2.14553	0.58072
H	-1.73078	-2.76330	1.47226
O	-2.20092	2.26571	-0.54883
O	-0.14281	1.35677	-1.00212
C	-1.08683	2.30213	-1.08630
C	-0.61662	3.48968	-1.92131
H	-0.31689	4.30482	-1.24032
H	0.23434	3.23401	-2.56656
H	-1.46246	3.85689	-2.52145
H	-0.31220	2.28987	3.04307
H	-1.17463	2.22445	1.44795
H	-1.60439	1.08024	2.74998
H	1.42925	-0.91610	2.62900
H	0.87780	0.32721	3.79948
H	-0.28859	-0.88701	3.16969
H	0.63761	-1.43367	0.66929

3''$_{Me}$

BP86 Energy = -931.849730578
Enthalpy 0K= -931.520065
Enthalpy 298K= -931.500176
Free Energy 298K= -931.567454

Ir	-0.42734	-0.49190	0.08202
N	0.27764	0.74994	1.75506
C	-0.75835	1.72225	2.23505
C	0.70094	-0.09116	2.92865
C	1.50156	1.48383	1.23178
H	1.12875	2.33830	0.64573
H	2.07551	1.87133	2.09330
C	2.30513	0.55644	0.35321
C	1.60178	-0.45224	-0.34144
C	2.27579	-1.31652	-1.21616
H	1.74453	-2.10909	-1.75215
C	3.65769	-1.14929	-1.42330
H	4.18228	-1.81386	-2.11687
C	4.36169	-0.14433	-0.74070
H	5.43832	-0.02779	-0.89534
C	3.68821	0.70631	0.14968
H	4.23708	1.49045	0.68331
C	-2.79233	-1.04122	0.37920
H	-3.46018	-0.58297	1.10782
C	-2.58889	-0.59595	-0.95087
H	-3.08370	0.26180	-1.40395
C	-1.56781	-1.43116	-1.58486
H	-1.22582	-1.35174	-2.61633
C	-1.16802	-2.41905	-0.62951
H	-0.48285	-3.25064	-0.79524
C	-1.89116	-2.13245	0.61822
H	-1.82170	-2.72141	1.53343
O	-2.28614	2.20424	-0.59022
O	-0.22526	1.30141	-1.04766
C	-1.18114	2.23372	-1.14568
C	-0.73424	3.39324	-2.03277
H	-0.19451	4.13045	-1.41339
H	-0.05641	3.05700	-2.82959
H	-1.62244	3.88475	-2.45395
H	-0.29426	2.42113	2.95428
H	-1.19063	2.26781	1.38756
H	-1.55845	1.16494	2.74374
H	1.55285	-0.72389	2.63979
H	1.00734	0.57336	3.75577
H	-0.14182	-0.71557	3.25741
H	0.35358	-1.51732	0.99400

2. BICARBONATE

(i) Pathway I

1$_{OH}$

BP86 Energy = -967.806366628
Enthalpy 0K= -967.495206
Enthalpy 298K= -967.475433
Free Energy 298K= -967.543893
PCM (CH_2Cl_2)= -967.868848135

Ir	-0.78220	-0.42283	0.12101
N	0.06209	1.42834	1.03723
C	-0.96259	2.50318	1.27010
C	0.62787	1.08513	2.38211
C	1.15372	2.05237	0.15709
H	0.63694	2.40598	-0.74795
H	1.52069	2.93711	0.71294
C	2.30662	1.15270	-0.22413
C	2.32251	0.53059	-1.49202
C	3.40034	-0.28260	-1.87703
H	3.41104	-0.73998	-2.87184
C	4.47772	-0.48724	-0.99745
H	5.32124	-1.11581	-1.29913
C	4.48500	0.14604	0.25678
H	5.33705	0.01805	0.93156
C	3.41267	0.97111	0.63450
H	3.45274	1.49903	1.59400
C	-0.26149	-1.98935	1.53700
H	-0.17046	-1.86632	2.61546

C	-1.46619	-2.36301	0.82976
H	-2.45282	-2.48604	1.28003
C	-1.16797	-2.46398	-0.58085
H	-1.86853	-2.72343	-1.37383
C	0.24094	-2.14472	-0.74042
H	0.77853	-2.08225	-1.68675
C	0.80657	-1.86333	0.55292
H	1.84629	-1.59536	0.74204
O	-1.19900	0.86051	-1.61229
O	-2.69452	0.59720	-0.00051
C	-2.37993	1.09766	-1.14085
H	-0.48991	3.33940	1.81563
H	-1.33916	2.88409	0.31165
H	-1.79871	2.10204	1.85772
H	1.41500	0.32825	2.27954
H	1.05978	1.99139	2.84616
H	-0.17952	0.70498	3.02397
H	1.49084	0.70366	-2.18438
O	-3.26519	1.85105	-1.78501
H	-2.88165	2.11712	-2.64776

TS (1-2)$_{OH}$

BP86 Energy = -967.787116741
Enthalpy 0K= -967.477076
Enthalpy 298K= -967.457501
Free Energy 298K= -967.526199
PCM (CH_2Cl_2)= -967.851521177
Frequency= -115.3855cm-1

Ir	-0.75509	-0.35129	-0.04607
N	0.42378	-0.22272	1.80042
C	-0.45960	0.07206	2.98204
C	1.14472	-1.50607	2.07284
C	1.43417	0.91406	1.66393
H	0.83905	1.83265	1.53199
H	1.96844	0.98763	2.63048
C	2.39834	0.70920	0.51833
C	2.01555	1.07304	-0.79253
C	2.87975	0.83363	-1.87751
H	2.58197	1.13835	-2.88601
C	4.13953	0.25456	-1.65861
H	4.82140	0.08835	-2.49832
C	4.53811	-0.08156	-0.35245
H	5.52910	-0.51052	-0.17489
C	3.67129	0.14310	0.72954
H	3.99343	-0.11142	1.74571
C	-1.01475	-2.49279	-0.25504
H	-0.76477	-3.22440	0.51352
C	-2.29499	-1.79042	-0.37366
H	-3.15463	-1.90934	0.28758
C	-2.23514	-0.95190	-1.56149
H	-3.01755	-0.28465	-1.92123
C	-0.91450	-1.07613	-2.10178
H	-0.52024	-0.49371	-2.93529
C	-0.15668	-2.04717	-1.31447
H	0.86613	-2.36779	-1.50729
O	-0.99440	2.12091	-1.27248
O	-1.69576	1.35303	0.73633
C	-1.62821	2.27060	-0.20069
H	0.16413	0.15245	3.89021
H	-1.00381	1.00860	2.80878
H	-1.17887	-0.75052	3.10763
H	1.77014	-1.77331	1.21116
H	1.78407	-1.39107	2.96702
H	0.40635	-2.29530	2.26990
H	1.06969	1.60572	-0.96266
O	-2.29986	3.39370	0.11400
H	-2.16363	4.02019	-0.62732

2$_{OH}$

BP86 Energy = -967.794189738
Enthalpy 0K= -967.485613
Enthalpy 298K= -967.465703
Free Energy 298K= -967.534647

Ir	-0.59064	-0.34377	-0.09750
N	0.29910	-0.21270	1.91996
C	-0.70227	0.19912	2.95593
C	0.90240	-1.52200	2.32620
C	1.39641	0.82685	1.82714
H	0.89728	1.80777	1.76136
H	2.00317	0.80277	2.75086
C	2.20636	0.54435	0.58806
C	1.47694	0.46016	-0.64144
C	2.18233	0.10817	-1.82743
H	1.65651	0.12536	-2.78738
C	3.55487	-0.16211	-1.79141
H	4.09105	-0.41062	-2.71216
C	4.24979	-0.08445	-0.57077
H	5.32402	-0.29199	-0.54138
C	3.57611	0.26181	0.61737
H	4.12756	0.30827	1.56261
C	-1.75358	-2.19363	0.13015
H	-1.94969	-2.67713	1.08791
C	-2.59257	-1.19486	-0.47957
H	-3.50427	-0.77437	-0.05423
C	-1.98232	-0.80990	-1.74367
H	-2.36292	-0.06799	-2.44505
C	-0.78109	-1.58756	-1.89587
H	-0.08868	-1.51973	-2.73481
C	-0.61694	-2.44755	-0.73960
H	0.16725	-3.18860	-0.59256
O	-0.24785	2.62076	-1.30787
O	-1.28310	1.57695	0.44623
C	-1.05841	2.59293	-0.35464
H	-0.19218	0.35207	3.92437
H	-1.19519	1.12477	2.63187
H	-1.45012	-0.59960	3.06816
H	1.66824	-1.82002	1.59726
H	1.36405	-1.42400	3.32596
H	0.11670	-2.28826	2.37379
H	0.65596	1.26920	-0.88362
O	-1.81156	3.66466	-0.01809
H	-1.55087	4.38426	-0.63031

TS (2-3)$_{OH}$

BP86 Energy = -967.793965793
Enthalpy 0K= -967.486380
Enthalpy 298K= -967.467290
Free Energy 298K= -967.533315
PCM (CH_2Cl_2)= -967.874969501
Frequency= -54.4074cm-1

Ir	-0.61159	-0.32134	-0.09919
N	0.28363	-0.24213	1.91843
C	-0.70102	0.20577	2.95487
C	0.83269	-1.57771	2.31532
C	1.42447	0.74971	1.83272
H	0.96743	1.75152	1.77278
H	2.02844	0.69568	2.75701
C	2.22094	0.43957	0.59229
C	1.47157	0.35159	-0.62713
C	2.16343	-0.02745	-1.81470
H	1.62960	-0.02482	-2.77061
C	3.53412	-0.30891	-1.79046
H	4.05637	-0.57755	-2.71363
C	4.24496	-0.21998	-0.58000
H	5.31762	-0.43672	-0.56078
C	3.58815	0.14719	0.61142
H	4.15049	0.20042	1.54992
C	-1.85900	-2.13030	0.11293
H	-2.05187	-2.63042	1.06296
C	-2.66778	-1.08485	-0.44989
H	-3.55493	-0.64175	0.00317
C	-2.06432	-0.68875	-1.71525
H	-2.42805	0.08834	-2.38699
C	-0.90219	-1.51086	-1.91802
H	-0.23130	-1.45443	-2.77475
C	-0.74692	-2.40283	-0.78320
H	0.00827	-3.17917	-0.67009
O	-0.00948	2.62352	-1.24598
O	-1.20358	1.64248	0.43958
C	-0.87679	2.64297	-0.33674
H	-0.18848	0.32879	3.92636
H	-1.15087	1.15543	2.63727
H	-1.48471	-0.55893	3.05805
H	1.57895	-1.90415	1.57832
H	1.30642	-1.50382	3.31165
H	0.01573	-2.31015	2.36703
H	0.71850	1.25211	-0.88551
O	-1.57676	3.76087	-0.04809
H	-1.23614	4.46190	-0.64269

3_{OH}

BP86 Energy = -967.814994978
Enthalpy 0K= -967.504579
Enthalpy 298K= -967.484691
Free Energy 298K= -967.552598

Ir	-0.70794	-0.06577	-0.16340
N	-0.07442	-1.26798	1.56073
C	-0.87648	-0.94845	2.78289
C	-0.20764	-2.72822	1.25364
C	1.38463	-0.95734	1.81399
H	1.40701	-0.01145	2.38262
H	1.82466	-1.74400	2.45525
C	2.08665	-0.80863	0.48811
C	1.28347	-0.34050	-0.59489
C	1.92545	-0.13445	-1.84282
H	1.35727	0.22837	-2.70648
C	3.30353	-0.38332	-2.00230
H	3.77316	-0.21081	-2.97601
C	4.06614	-0.86011	-0.92683
H	5.13253	-1.06727	-1.05565
C	3.45381	-1.07592	0.32011
H	4.04686	-1.44986	1.16277
C	-2.90786	-0.74129	-0.41115
H	-3.47918	-1.29028	0.33811
C	-2.89376	0.65918	-0.57632
H	-3.43145	1.38375	0.03596
C	-1.95800	0.98616	-1.65644
H	-1.75807	1.98418	-2.04638
C	-1.45390	-0.24867	-2.19153
H	-0.78421	-0.35931	-3.04367
C	-1.96729	-1.33197	-1.37157
H	-1.81212	-2.39572	-1.55120
O	1.41909	2.59017	-0.22549
O	-0.12829	1.60134	1.16622
C	0.60438	2.55953	0.81854
H	-0.47246	-1.49836	3.65303
H	-0.83335	0.13254	2.97375
H	-1.92001	-1.25288	2.61950
H	0.42529	-2.97508	0.38996
H	0.11230	-3.32292	2.12914
H	-1.25706	-2.96056	1.02545
H	1.45385	1.66693	-0.62846
O	0.57847	3.67089	1.54560
H	1.23413	4.30760	1.18762

(ii) Pathway II

$2'_{OH}$

BP86 Energy = -967.790847220
Enthalpy 0K= -967.480469
Enthalpy 298K= -967.460124
Free Energy 298K= -967.531322

Ir	-0.61485	-0.41097	0.02766
N	0.47158	-0.00702	1.89971
C	-0.48051	0.39970	2.98893
C	1.20944	-1.22199	2.36872
C	1.45834	1.13422	1.66440
H	0.84792	2.04378	1.56180
H	2.07339	1.22697	2.57964
C	2.31783	0.93639	0.43300
C	1.88274	1.44645	-0.81395
H	0.96152	2.03600	-0.86303
C	2.65609	1.25978	-1.97376
H	2.32001	1.68335	-2.92557
C	3.87569	0.56731	-1.89945
H	4.48693	0.43338	-2.79728

```
C   4.33024  0.08125 -0.66049
H   5.29688 -0.42737 -0.59309
C   3.55900  0.26900  0.49828
H   3.94147 -0.08036  1.46406
C  -1.40811 -2.42010 -0.06679
H  -1.85982 -2.93578  0.78185
C  -2.12632 -1.56774 -1.02158
H  -3.17868 -1.28925 -0.97358
C  -1.18238 -1.08507 -1.97835
H  -1.39589 -0.38333 -2.78304
C   0.12802 -1.62113 -1.61037
H   1.06962 -1.38667 -2.10996
C  -0.02749 -2.49324 -0.47503
H   0.76634 -3.05199  0.01799
O  -2.91549  1.31169 -1.30396
O  -1.29067  1.44594  0.33866
C  -2.32149  1.92804 -0.43867
H   0.08583  0.63405  3.90841
H  -1.05015  1.27882  2.66352
H  -1.17214 -0.43166  3.19063
H   1.96145 -1.51223  1.62283
H   1.71490 -1.00331  3.32745
H   0.49450 -2.04297  2.52152
O  -2.60981  3.20858 -0.12394
H  -2.02051  3.49525  0.60301
```

TS(2'-3')$_{OH}$

```
BP86 Energy = -967.766364950
Enthalpy 0K= -967.462166
Enthalpy 298K= -967.442374
Free Energy 298K= -967.510424
Frequency= -1038.1403cm-1

Ir -0.55871 -0.29207 -0.16951
N   0.43963 -1.18408  1.58344
C  -0.41420 -1.05815  2.80744
C   0.72027 -2.63357  1.32419
C   1.76219 -0.48200  1.81851
H   1.54315  0.42298  2.41095
H   2.41813 -1.13050  2.42730
C   2.37725 -0.09163  0.49915
C   1.45747  0.35919 -0.50192
H   0.66227  1.30000  0.16663
C   1.98099  0.82203 -1.74006
H   1.30163  1.20188 -2.51070
C   3.36287  0.82846 -1.97318
H   3.75692  1.19681 -2.92524
C   4.24474  0.36190 -0.98116
H   5.32279  0.35883 -1.17003
C   3.75640 -0.09485  0.25744
H   4.45460 -0.44611  1.02504
C  -2.32220 -1.66098 -0.41435
H  -2.70135 -2.32694  0.36108
C  -2.76695 -0.33268 -0.66244
H  -3.50950  0.22189 -0.08961
C  -1.99456  0.21510 -1.77287
H  -2.10922  1.21704 -2.18200
C  -1.08924 -0.80792 -2.22008
H  -0.37158 -0.72218 -3.03638
C  -1.24239 -1.96302 -1.35515
H  -0.72416 -2.91531 -1.46514
O  -2.05502  2.60323  0.03778
O  -0.21835  1.60131  1.01955
C  -1.05915  2.66895  0.72827
H   0.13234 -1.43335  3.69248
H  -0.68002 -0.00166  2.95087
H  -1.32948 -1.65176  2.67179
H   1.39869 -2.72328  0.46377
H   1.19201 -3.08734  2.21530
H  -0.22045 -3.15912  1.11059
O  -0.65032  3.80238  1.33186
H   0.15531  3.61591  1.85546
```

3'$_{OH}$

```
BP86 Energy = -967.780577269
Enthalpy 0K= -967.471568
Enthalpy 298K= -967.451027
Free Energy 298K= -967.521015

Ir -0.52560 -0.32340 -0.18787
N   0.36949 -1.12116  1.64606
C  -0.51660 -0.90607  2.83258
C   0.61971 -2.59110  1.48153
C   1.70070 -0.43562  1.87395
H   1.48511  0.49285  2.43213
H   2.33234 -1.06520  2.52836
C   2.34249 -0.14195  0.53898
C   1.46313 -0.01991 -0.57959
H   0.78813  1.91648  0.41177
C   2.03569  0.32182 -1.82983
H   1.39813  0.44800 -2.71068
C   3.42052  0.51760 -1.96422
H   3.83764  0.78243 -2.94114
C   4.26970  0.36880 -0.85434
H   5.34950  0.50612 -0.96499
C   3.73001  0.04186  0.39905
H   4.38984 -0.07348  1.26682
C  -2.43395 -1.60710 -0.35335
H  -2.81410 -2.25734  0.43533
C  -2.82950 -0.27701 -0.59128
H  -3.54570  0.30392 -0.01161
C  -2.03245  0.24497 -1.70773
H  -2.12225  1.24576 -2.12928
C  -1.19206 -0.80761 -2.19324
H  -0.52502 -0.76582 -3.05348
C  -1.35243 -1.94487 -1.29191
H  -0.88703 -2.92338 -1.41320
O  -2.17699  2.65775  0.50296
O  -0.09824  1.76437  0.83037
C  -0.99919  2.85071  0.64538
H  -0.00814 -1.24851  3.75305
H  -0.75758  0.16275  2.91993
H  -1.44547 -1.47873  2.70053
H   1.32497 -2.74578  0.65303
H   1.04693 -3.00228  2.41481
H  -0.32768 -3.10250  1.26279
```

```
O  -0.41190  4.05732  0.66143
H   0.50755  4.03221  0.99550
```

(iii) Pathway III

2''$_{OH}$

```
BP86 Energy = -967.784228830
Enthalpy 0K= -967.474185
Enthalpy 298K= -967.453858
Free Energy 298K= -967.524177

Ir -0.42524 -0.34754 -0.10913
N  -0.11309 -0.00118  2.06325
C  -1.02731  1.06558  2.58750
C  -0.32887 -1.23695  2.88072
C   1.33736  0.45164  2.16663
H   1.34622  1.54111  2.31409
H   1.79802 -0.01277  3.05779
C   2.07787  0.11300  0.88797
C   1.93197 -1.16937  0.28163
C   2.62197 -1.45649 -0.93352
H   2.55216 -2.46067 -1.36391
C   3.43128 -0.49174 -1.53002
H   3.97100 -0.71988 -2.45387
C   3.58667  0.77106 -0.91480
H   4.23986  1.52098 -1.37148
C   2.90949  1.07143  0.27012
H   3.02108  2.05837  0.73012
C  -2.47341 -0.64735 -0.70445
H  -3.29637 -0.01677 -0.37216
C  -1.68026 -0.42643 -1.90690
H  -1.78070  0.43523 -2.56512
C  -0.69958 -1.46329 -1.99083
H   0.07229 -1.55032 -2.75541
C  -0.90065 -2.37763 -0.86487
H  -0.32632 -3.28194 -0.66317
C  -1.99898 -1.88359 -0.09239
H  -2.40413 -2.34701  0.80745
O  -2.09553  2.25110 -0.91587
O   0.02102  1.67789 -0.19027
C  -0.92277  2.51260 -0.67615
H  -0.78802  1.27725  3.64530
H  -0.90301  1.97061  1.98186
H  -2.06725  0.71633  2.51179
H   0.32126 -2.05085  2.53104
H  -0.10162 -1.02856  3.94205
H  -1.37914 -1.54885  2.79908
H   1.53396 -2.01063  0.85702
O  -0.42496  3.76419 -0.86501
H   0.53307  3.73706 -0.66712
```

TS(2''-3'')$_{OH}$

```
BP86 Energy = -967.765759710
Enthalpy 0K= -967.459287
Enthalpy 298K= -967.439743
Free Energy 298K= -967.506539
Frequency= -431.9193cm-1

Ir -0.45646 -0.45970  0.05759
N   0.23658  0.82959  1.71197
C  -0.78172  1.85091  2.12526
C   0.58925  0.00823  2.92048
C   1.49462  1.51469  1.21166
H   1.16577  2.36241  0.59044
H   2.05012  1.91352  2.08018
C   2.31325  0.55071  0.38547
C   1.63187 -0.49715 -0.27370
C   2.32157 -1.39689 -1.10194
H   1.79901 -2.21918 -1.59971
C   3.70241 -1.22272 -1.30459
H   4.24211 -1.91210 -1.96103
C   4.38604 -0.17857 -0.66114
H   5.46273 -0.05589 -0.81055
C   3.69543  0.70447  0.18503
H   4.23231  1.51765  0.68612
C  -2.72654 -0.98506  0.51554
H  -3.33857 -0.47490  1.25921
C  -2.61338 -0.62037 -0.85010
H  -3.10324  0.23891 -1.30854
C  -1.65385 -1.50952 -1.50193
H  -1.37515 -1.49277 -2.55510
C  -1.19578 -2.44180 -0.51331
H  -0.50797 -3.27262 -0.67533
C  -1.81613 -2.07960  0.76174
H  -1.69688 -2.62067  1.70057
O  -2.18494  2.24951 -0.69270
O  -0.14633  1.25537 -1.14214
C  -1.10557  2.18651 -1.27861
H  -0.31884  2.55452  2.84040
H  -1.16585  2.38407  1.24613
H  -1.61852  1.33663  2.61974
H   1.43176 -0.65843  2.68442
H   0.88482  0.68383  3.74266
H  -0.28295 -0.58274  3.23218
H   0.62557 -1.35750  0.80656
O  -0.73984  3.12955 -2.18426
H   0.12514  2.86692 -2.56314
```

3''$_{OH}$

```
BP86 Energy = -967.767176837
Enthalpy 0K= -967.459226
Enthalpy 298K= -967.439400
Free Energy 298K= -967.506794

Ir -0.43007 -0.47004  0.11475
N   0.26726  0.93014  1.66846
C  -0.76785  1.94623  2.04949
C   0.68321  0.20176  2.91761
C   1.49562  1.60742  1.08417
H   1.13040  2.40796  0.42175
H   2.06806  2.07105  1.90816
C   2.30125  0.59734  0.30300
C   1.60450 -0.48254 -0.28315
C   2.28212 -1.43526 -1.05744
H   1.75243 -2.28232 -1.50335
```

C	3.66375	-1.28757	-1.27874
H	4.19234	-2.02192	-1.89447
C	4.36199	-0.21136	-0.70766
H	5.43863	-0.10860	-0.87178
C	3.68442	0.72832	0.08524
H	4.23095	1.56584	0.53321
C	-2.78236	-0.99559	0.48289
H	-3.43961	-0.48349	1.18505
C	-2.59759	-0.65539	-0.87754
H	-3.08176	0.18076	-1.38224
C	-1.58713	-1.54217	-1.46138
H	-1.25473	-1.53664	-2.49907
C	-1.17212	-2.45309	-0.44131
H	-0.48594	-3.29317	-0.54991
C	-1.87067	-2.06471	0.79275
H	-1.78834	-2.58121	1.74977
O	-2.24055	2.19623	-0.75495
O	-0.21080	1.18125	-1.19816
C	-1.16430	2.11718	-1.34453
H	-0.30501	2.70252	2.70869
H	-1.19015	2.41806	1.15329
H	-1.57536	1.43885	2.59731
H	1.53135	-0.46107	2.69211
H	0.99169	0.94047	3.67811
H	-0.16505	-0.38111	3.30332
H	0.33389	-1.40431	1.13480
O	-0.80025	3.03761	-2.27344
H	0.06423	2.76621	-2.64759

3. **TRIFLUOROACETATE**

(i) Pathway I

1_{CF3}

BP86 Energy = -1229.59092764
Enthalpy 0K= -1229.280830
Enthalpy 298K= -1229.258285
Free Energy 298K= -1229.333614
PCM (CH_2Cl_2)= -1229.64543

Ir	0.78398	-0.58000	-0.14437
N	1.04217	0.19426	1.89051
C	0.54866	-0.77155	2.92169
C	2.48811	0.49297	2.15138
C	0.25728	1.48495	1.98201
H	-0.79588	1.19816	2.14977
H	0.58957	2.05873	2.86736
C	0.41873	2.24239	0.68837
C	0.63166	1.44702	-0.47702
C	0.73859	2.12122	-1.72019
H	0.89616	1.55947	-2.64732
C	0.63418	3.52445	-1.79636
H	0.71452	4.01852	-2.76984
C	0.44015	4.28465	-0.63435
H	0.37318	5.37486	-0.69358
C	0.33650	3.64115	0.61113
H	0.18754	4.23303	1.52153
C	2.11746	-2.47125	-0.08337
H	2.51247	-2.92553	0.82605
C	0.92633	-2.84180	-0.74065
H	0.22754	-3.61492	-0.41973
C	0.74066	-1.94992	-1.88913
H	-0.07205	-2.00471	-2.61363
C	1.87615	-1.07347	-1.95797
H	2.07495	-0.33125	-2.73032
C	2.70251	-1.32413	-0.78941
H	3.66525	-0.85927	-0.57733
O	-2.13989	0.78140	-1.21790
O	-1.34713	-0.60662	0.42301
C	-2.26625	-0.08948	-0.25043
C	-3.73014	-0.47862	0.09229
F	-3.79936	-1.81085	0.28492
F	-4.06701	0.15437	1.24067
F	-4.57233	-0.11775	-0.88486
H	0.62644	-0.32051	3.92815
H	-0.49903	-1.02762	2.71273
H	1.16263	-1.68253	2.88672
H	2.84112	1.23124	1.41824
H	2.60478	0.89932	3.17291
H	3.07664	-0.43121	2.06458
H	-1.16668	1.06252	-1.26869

TS (1-2)$_{CF3}$

BP86 Energy = -1229.57548936
Enthalpy 0K= -1229.269951
Enthalpy 298K= -1229.247977
Free Energy 298K= -1229.322177
PCM (CH_2Cl_2)= -1229.63679
Frequency= -193.9661cm-1

Ir	0.40615	-0.77946	-0.11596
N	0.83326	-0.02941	1.91652
C	-0.09878	-0.60159	2.93969
C	2.24228	-0.35722	2.30443
C	0.68203	1.47555	1.86845
H	-0.40113	1.68710	1.84597
H	1.09432	1.91820	2.79386
C	1.35499	1.98249	0.62119
C	1.03311	1.27063	-0.58421
C	1.67574	1.68610	-1.78884
H	1.39760	1.21426	-2.73712
C	2.58288	2.75264	-1.79372
H	3.04626	3.07276	-2.73183
C	2.88261	3.42488	-0.59575
H	3.59164	4.25849	-0.60053
C	2.27209	3.03700	0.61352
H	2.51698	3.56321	1.54249
C	1.05458	-2.90205	0.10614
H	1.20972	-3.40110	1.06343
C	-0.16774	-2.89304	-0.63407
H	-1.11051	-3.34227	-0.31987
C	0.03783	-2.10681	-1.84323
H	-0.70137	-1.91905	-2.62159
C	1.41290	-1.67335	-1.84682
H	1.88798	-1.07122	-2.62089
C	2.05191	-2.13160	-0.63316
H	3.10140	-2.00266	-0.37124

O	-1.61534	1.55642	-1.05258
O	-1.59202	-0.21443	0.37568
C	-2.16972	0.73244	-0.28578
C	-3.71219	0.78065	-0.08139
F	-4.25794	-0.32198	-0.65143
F	-3.99701	0.77230	1.24290
F	-4.24249	1.87651	-0.64119
H	0.09362	-0.13489	3.92280
H	-1.13589	-0.41806	2.63086
H	0.07473	-1.68460	3.01638
H	2.93470	0.10197	1.58549
H	2.45019	0.03160	3.31815
H	2.37504	-1.44747	2.30500
H	-0.20299	1.26048	-0.84447

2_{CF3}

BP86 Energy = -1229.57690853
Enthalpy 0K= -1229.268141
Enthalpy 298K= -1229.246090
Free Energy 298K= -1229.321148

Ir	0.33655	-0.76930	-0.06136
N	0.71607	0.12876	1.93002
C	-0.32804	-0.24649	2.93895
C	2.05652	-0.28055	2.45598
C	0.69802	1.62850	1.71254
H	-0.35608	1.91067	1.55664
H	1.06818	2.13458	2.62273
C	1.53047	1.94402	0.49423
C	1.11735	1.36733	-0.74468
C	1.91735	1.54843	-1.90515
H	1.55604	1.17041	-2.86700
C	3.10921	2.27753	-1.83369
H	3.71344	2.43670	-2.73168
C	3.51064	2.83717	-0.60587
H	4.43740	3.41682	-0.55002
C	2.73084	2.66357	0.55447
H	3.06306	3.09718	1.50372
C	0.72589	-2.87642	0.30985
H	0.70273	-3.34617	1.29402
C	-0.40398	-2.75615	-0.58697
H	-1.42678	-3.06532	-0.36630
C	0.04334	-2.09596	-1.79654
H	-0.56985	-1.84239	-2.66043
C	1.45679	-1.82808	-1.63454
H	2.08737	-1.31029	-2.35770
C	1.89488	-2.31182	-0.35064
H	2.91367	-2.28560	0.03353
O	-1.80259	1.05012	-1.68568
O	-1.57081	0.01445	0.34205
C	-2.22770	0.66852	-0.59306
C	-3.69219	0.94561	-0.13552
F	-4.35191	-0.22977	0.02611
F	-3.68159	1.59742	1.05916
F	-4.34560	1.69481	-1.03393
H	-0.14114	0.29660	3.88295
H	-1.32062	0.00390	2.54429
H	-0.26772	-1.32831	3.12821
H	2.84276	0.02840	1.75350
H	2.23270	0.19573	3.43805
H	2.07715	-1.37163	2.58284
H	0.02356	1.20384	-0.98164

TS(2-3)$_{CF3}$

BP86 Energy = -1229.57548936
Enthalpy 0K= -1229.269951
Enthalpy 298K= -1229.247977
Free Energy 298K= -1229.322177
PCM (CH_2Cl_2)= -1229.64846
Frequency= -193.9661cm-1

Ir	0.40615	-0.77946	-0.11596
N	0.83326	-0.02941	1.91652
C	-0.09878	-0.60159	2.93969
C	2.24228	-0.35722	2.30443
C	0.68203	1.47555	1.86845
H	-0.40113	1.68710	1.84597
H	1.09432	1.91820	2.79386
C	1.35499	1.98249	0.62119
C	1.03311	1.27063	-0.58421
C	1.67574	1.68610	-1.78884
H	1.39760	1.21426	-2.73712
C	2.58288	2.75264	-1.79372
H	3.04626	3.07276	-2.73183
C	2.88261	3.42488	-0.59575
H	3.59164	4.25849	-0.60053
C	2.27209	3.03700	0.61352
H	2.51698	3.56321	1.54249
C	1.05458	-2.90205	0.10614
H	1.20972	-3.40110	1.06343
C	-0.16774	-2.89304	-0.63407
H	-1.11051	-3.34227	-0.31987
C	0.03783	-2.10681	-1.84323
H	-0.70137	-1.91905	-2.62159
C	1.41290	-1.67335	-1.84682
H	1.88798	-1.07122	-2.62089
C	2.05191	-2.13160	-0.63316
H	3.10140	-2.00266	-0.37124
O	-1.61534	1.55642	-1.05258
O	-1.59202	-0.21443	0.37568
C	-2.16972	0.73244	-0.28578
C	-3.71219	0.78065	-0.08139
F	-4.25794	-0.32198	-0.65143
F	-3.99701	0.77230	1.24290
F	-4.24249	1.87651	-0.64119
H	0.09362	-0.13489	3.92280
H	-1.13589	-0.41806	2.63086
H	0.07473	-1.68460	3.01638
H	2.93470	0.10197	1.58549
H	2.45019	0.03160	3.31815
H	2.37504	-1.44747	2.30500
H	-0.20299	1.26048	-0.84447

3_{CF3}

BP86 Energy = -1229.59092764

Enthalpy 0K= -1229.280830
Enthalpy 298K= -1229.258285
Free Energy 298K= -1229.333614

Ir	0.78398	-0.58000	-0.14437
N	1.04217	0.19426	1.89051
C	0.54866	-0.77155	2.92169
C	2.48811	0.49297	2.15138
C	0.25728	1.48495	1.98201
H	-0.79588	1.19816	2.14977
H	0.58957	2.05873	2.86736
C	0.41873	2.24239	0.68837
C	0.63166	1.44702	-0.47702
C	0.73859	2.12122	-1.72019
H	0.89616	1.55947	-2.64732
C	0.63418	3.52445	-1.79636
H	0.71452	4.01852	-2.76984
C	0.44015	4.28465	-0.63435
H	0.37318	5.37486	-0.69358
C	0.33650	3.64115	0.61113
H	0.18754	4.23303	1.52153
C	2.11746	-2.47125	-0.08337
H	2.51247	-2.92553	0.82605
C	0.92633	-2.84180	-0.74065
H	0.22754	-3.61492	-0.41973
C	0.74066	-1.94992	-1.88913
H	-0.07205	-2.00471	-2.61363
C	1.87615	-1.07347	-1.95797
H	2.07495	-0.33125	-2.73032
C	2.70251	-1.32413	-0.78941
H	3.66525	-0.85927	-0.57733
O	-2.13989	0.78140	-1.21790
O	-1.34713	-0.60662	0.42301
C	-2.26625	-0.08948	-0.25043
C	-3.73014	-0.47862	0.09229
F	-3.79936	-1.81085	0.28492
F	-4.06701	0.15437	1.24067
F	-4.57233	-0.11775	-0.88486
H	0.62644	-0.32051	3.92815
H	-0.49903	-1.02762	2.71273
H	1.16263	-1.68253	2.88672
H	2.84112	1.23124	1.41824
H	2.60478	0.89932	3.17291
H	3.07664	-0.43121	2.06458
H	-1.16668	1.06252	-1.26869

(ii) Pathway II

2'$_{CF3}$

BP86 Energy = -1229.58165240
Enthalpy 0K= -1229.271691
Enthalpy 298K= -1229.248672
Free Energy 298K= -1229.326352

Ir	0.43271	-0.59660	0.02307
N	0.58222	0.34439	2.04043
C	-0.59885	0.13590	2.93742
C	1.80882	-0.12218	2.75419
C	0.72372	1.80104	1.66196
H	-0.29080	2.21192	1.54878
H	1.24299	2.35350	2.46611
C	1.46566	1.85463	0.33680
C	0.72164	1.73747	-0.88106
H	-0.36606	1.84657	-0.85914
C	1.39908	1.79957	-2.13187
H	0.81339	1.76701	-3.05588
C	2.78330	1.96852	-2.17455
H	3.29976	2.04561	-3.13629
C	3.51473	2.10206	-0.97080
H	4.59404	2.28049	-1.00982
C	2.86848	2.03971	0.26874
H	3.44202	2.18576	1.19020
C	0.78236	-2.72001	0.34938
H	0.53520	-3.25856	1.26515
C	-0.09341	-2.55969	-0.79549
H	-1.13079	-2.88426	-0.86500
C	0.60801	-1.80583	-1.80371
H	0.20711	-1.51233	-2.77219
C	1.93417	-1.51366	-1.27761
H	2.69894	-0.92173	-1.78163
C	2.05647	-2.08767	0.03377
H	2.94241	-2.05990	0.66684
O	-2.47647	-0.97841	-1.46895
O	-1.45937	0.23505	0.20096
C	-2.46435	-0.13826	-0.57775
C	-3.72031	0.71559	-0.22407
F	-3.99681	0.61780	1.10585
F	-3.46814	2.02490	-0.50644
F	-4.79290	0.31938	-0.92006
H	-0.47916	0.74721	3.85023
H	-1.51640	0.41674	2.40681
H	-0.64661	-0.92668	3.21825
H	2.69594	0.06144	2.13286
H	1.91272	0.41841	3.71313
H	1.72178	-1.19872	2.96020

TS(2'-3')$_{CF3}$

BP86 Energy = -1229.55192403
Enthalpy 0K= -1229.248108
Enthalpy 298K= -1229.225623
Free Energy 298K= -1229.300794
Frequency= -1027.0671cm-1

Ir	0.82382	-0.52866	-0.13941
N	1.28630	0.49427	1.75649
C	0.99835	-0.39041	2.93072
C	2.73314	0.88635	1.77274
C	0.45350	1.75504	1.86509
H	-0.53456	1.45690	2.25728
H	0.91488	2.43695	2.60215
C	0.29428	2.37605	0.50247
C	0.13887	1.44880	-0.58124
H	-0.92681	0.66485	-0.09803
C	-0.10706	1.97364	-1.88177
H	-0.26308	1.29054	-2.72341
C	-0.19302	3.35550	-2.09180

H	-0.39590	3.74715	-3.09315
C	-0.02267	4.24238	-1.01204
H	-0.08484	5.32199	-1.18098
C	0.21577	3.75718	0.28675
H	0.33268	4.45781	1.12061
C	2.37815	-2.16159	-0.12684
H	2.95887	-2.45097	0.74965
C	1.14959	-2.74617	-0.53575
H	0.60418	-3.53774	-0.02288
C	0.69163	-2.05074	-1.73670
H	-0.21922	-2.27788	-2.28889
C	1.67540	-1.05978	-2.07425
H	1.64264	-0.38277	-2.92791
C	2.70519	-1.07394	-1.04900
H	3.61376	-0.47227	-1.04604
O	-2.08564	-2.30790	-0.11996
O	-1.26275	-0.29896	0.60648
C	-2.24730	-1.15092	0.20686
C	-3.63005	-0.44043	0.22583
F	-3.89945	0.04019	1.46205
F	-3.58036	0.61209	-0.64266
F	-4.60325	-1.27481	-0.15257
H	1.18101	0.15886	3.87280
H	-0.05049	-0.71559	2.88945
H	1.65716	-1.26937	2.89250
H	2.92633	1.58441	0.94593
H	2.97738	1.37427	2.73437
H	3.35955	-0.00847	1.65537

3'$_{CF3}$

BP86 Energy = -1229.56982061
Enthalpy 0K= -1229.260649
Enthalpy 298K= -1229.237396
Free Energy 298K= -1229.315961

Ir	0.70576	-0.64128	-0.18473
N	1.33014	0.01916	1.80423
C	0.70489	-0.80385	2.88672
C	2.82328	-0.07137	1.92276
C	0.92758	1.47087	1.96700
H	-0.12481	1.46919	2.30262
H	1.52710	1.93112	2.77454
C	1.07966	2.17165	0.63955
C	0.98212	1.35293	-0.52431
H	-1.53388	1.11905	0.00553
C	1.06131	1.98886	-1.78700
H	0.97500	1.40290	-2.70751
C	1.23329	3.37941	-1.88650
H	1.28665	3.84925	-2.87385
C	1.34269	4.16551	-0.72691
H	1.49191	5.24638	-0.80728
C	1.26403	3.56128	0.53776
H	1.34812	4.17282	1.44348
C	1.42345	-2.84148	-0.22412
H	1.77476	-3.39799	0.64529
C	0.11020	-2.83997	-0.73071
H	-0.74343	-3.37095	-0.30991
C	0.05765	-1.91740	-1.87282
H	-0.82038	-1.71653	-2.48702
C	1.37434	-1.40245	-2.09736
H	1.68868	-0.74220	-2.90486
C	2.22031	-1.88532	-1.00838
H	3.29268	-1.71230	-0.91263
O	-2.68382	-1.61461	0.81100
O	-1.42791	0.24069	0.45003
C	-2.61820	-0.46443	0.45975
C	-3.84157	0.39185	0.00999
F	-4.54889	0.76848	1.08733
F	-3.39756	1.51859	-0.63860
F	-4.61067	-0.31428	-0.82419
H	0.97537	-0.39405	3.87754
H	-0.38795	-0.79742	2.77079
H	1.07067	-1.83761	2.81205
H	3.28329	0.58227	1.16872
H	3.13527	0.25062	2.93340
H	3.14432	-1.11001	1.76203

(iii) Pathway III

2''$_{CF3}$

BP86 Energy = -1229.56875887
Enthalpy 0K= -1229.259111
Enthalpy 298K= -1229.236130
Free Energy 298K= -1229.312559

Ir	0.17001	-0.38655	0.43622
C	0.79217	0.54440	2.31523
C	-0.66081	0.53834	2.24745
C	-1.07450	-0.84179	2.15725
C	0.11138	-1.67983	2.17575
C	1.27051	-0.81134	2.30068
H	1.41996	1.43575	2.34613
H	-1.31672	1.40602	2.25406
H	-2.10060	-1.19381	2.05351
H	0.11761	-2.76954	2.13446
H	2.31123	-1.12527	2.36677
H	-0.10170	1.41250	-1.44076
C	0.89038	1.55640	-1.00348
C	1.15040	2.75754	-0.28672
C	2.46415	3.12785	0.01141
C	3.53634	2.31899	-0.42445
C	3.29759	1.13000	-1.13137
C	1.97873	0.73541	-1.43218
H	0.31308	3.40886	-0.01820
H	2.66773	4.06355	0.54100
H	4.56654	2.62961	-0.22300
H	4.14101	0.52521	-1.48137
C	1.65956	-0.56747	-2.13590
N	1.31707	-1.59275	-1.07836
H	2.49733	-0.93595	-2.75575
H	0.76765	-0.45384	-2.77088
C	2.57147	-2.14339	-0.48037
C	0.54327	-2.72555	-1.68232
O	-1.20386	-0.53110	-1.10389
C	-2.51710	-0.33258	-1.20772
O	-3.24153	-0.99752	-1.92900

C	-3.12254	0.87430	-0.42408
F	-2.25750	1.94030	-0.38407
F	-4.26649	1.28488	-0.97394
F	-3.37613	0.52183	0.87926
H	3.16021	-2.66144	-1.25975
H	3.17152	-1.32994	-0.04980
H	2.31436	-2.86833	0.30523
H	1.13443	-3.18016	-2.49777
H	0.35869	-3.48239	-0.90531
H	-0.41454	-2.34914	-2.06257

TS(2''-3'')$_{CF3}$

BP86 Energy = -1229.54623113
Enthalpy 0K= -1229.240746
Enthalpy 298K= -1229.218272
Free Energy 298K= -1229.292745
Frequency= -327.4676cm-1

Ir	-0.07512	-0.69887	-0.17485
C	-0.15402	-1.61681	-2.15350
C	1.21530	-1.72429	-1.67886
C	1.22990	-2.66178	-0.57573
C	-0.10553	-3.06782	-0.32551
C	-0.98617	-2.41351	-1.28713
H	-0.48765	-1.05435	-3.02509
H	2.08702	-1.24154	-2.11754
H	2.10743	-2.93819	0.01026
H	-0.42088	-3.74901	0.46660
H	-2.05820	-2.57226	-1.39942
H	0.39677	0.65564	-0.85107
C	-1.32190	0.96937	-0.58116
C	-1.59917	1.51163	-1.84886
C	-2.49931	2.58715	-1.96768
C	-3.11536	3.12511	-0.82930
C	-2.83975	2.58440	0.43723
C	-1.93497	1.51804	0.57113
H	-1.10455	1.13223	-2.74774
H	-2.70540	3.00494	-2.95782
H	-3.81284	3.96211	-0.92475
H	-3.32963	2.99339	1.32760
C	-1.59589	0.87347	1.88545
N	-1.38517	-0.60666	1.63532
H	-2.38901	0.99616	2.64589
H	-0.64916	1.25738	2.29928
C	-2.71126	-1.25140	1.36329
C	-0.76614	-1.23952	2.84391
O	1.16664	0.15829	1.27076
C	2.16947	1.03607	1.25837
O	2.60923	1.51178	2.29220
C	2.83335	1.40836	-0.10230
F	1.91726	1.95052	-0.98268
F	3.81272	2.29340	0.06411
F	3.34936	0.29189	-0.70412
H	-3.36387	-1.12182	2.24499
H	-3.17882	-0.77628	0.49038
H	-2.57050	-2.32612	1.18325
H	-1.40116	-1.02999	3.72304
H	-0.70713	-2.32741	2.69646
H	0.23583	-0.81870	2.99581

3''$_{CF3}$

BP86 Energy = -1229.55358330
Enthalpy 0K= -1229.246175
Enthalpy 298K= -1229.223536
Free Energy 298K= -1229.298370

Ir	0.78628	-0.63614	-0.06412
N	0.48681	0.19684	1.94655
C	-0.48223	-0.59929	2.76849
C	1.78335	0.27098	2.70791
C	-0.02514	1.61481	1.73780
H	-1.10464	1.54137	1.53212
H	0.11491	2.18024	2.67704
C	0.69152	2.23340	0.56325
C	1.15239	1.36682	-0.45254
C	1.78037	1.87638	-1.59830
H	2.15078	1.21263	-2.38527
C	1.91464	3.26880	-1.74754
H	2.38866	3.67048	-2.64841
C	1.44926	4.13774	-0.74722
H	1.56626	5.21909	-0.86355
C	0.84149	3.62271	0.40819
H	0.47766	4.30104	1.18796
C	0.77754	-3.08060	0.03692
H	0.50911	-3.68093	0.90584
C	-0.10272	-2.66914	-0.99158
H	-1.16563	-2.90276	-1.04075
C	0.63449	-1.82932	-1.94268
H	0.22853	-1.38953	-2.85357
C	1.99116	-1.76396	-1.50084
H	2.82687	-1.29031	-2.01651
C	2.06221	-2.48936	-0.22298
H	2.97075	-2.64569	0.35997
O	-2.45783	-1.64813	0.30962
O	-1.17464	0.12817	-0.41175
C	-2.29065	-0.51179	-0.13046
C	-3.50873	0.44211	-0.38318
F	-3.49923	1.40220	0.58979
F	-3.42197	1.04905	-1.58524
F	-4.66421	-0.23247	-0.31036
H	-0.67083	-0.06937	3.71936
H	-1.42409	-0.74181	2.22627
H	-0.04004	-1.58230	2.98610
H	2.47537	0.94977	2.18876
H	1.58334	0.66209	3.72081
H	2.22234	-0.73362	2.78741
H	2.25454	-0.24629	0.36590

4. TRICLHOROACETATE

(i) Pathway I

1$_{CCl3}$

BP86 Energy = -975.121089545
Enthalpy 0K= -974.816056
Enthalpy 298K= -974.792071

Free Energy 298K= -974.872586
PCM (CH_2Cl_2)= -975.181349

Ir	0.36205	-0.93438	0.08855
N	0.81049	0.51844	1.71553
C	-0.37735	0.82434	2.58505
C	1.85773	-0.07068	2.61124
C	1.29775	1.86500	1.15603
H	0.42674	2.30747	0.64944
H	1.53573	2.48829	2.03976
C	2.47396	1.81086	0.20875
C	2.25483	1.88521	-1.18484
C	3.33569	1.86411	-2.08111
H	3.15302	1.94552	-3.15763
C	4.65163	1.76808	-1.59613
H	5.49484	1.75830	-2.29369
C	4.88390	1.72364	-0.21091
H	5.90803	1.68843	0.17331
C	3.80264	1.75881	0.68528
H	3.99903	1.77608	1.76320
C	1.77825	-2.55130	0.43429
H	2.15738	-2.86412	1.40642
C	0.60079	-3.07739	-0.22079
H	-0.09716	-3.79506	0.21439
C	0.45593	-2.43868	-1.50921
H	-0.33678	-2.61737	-2.23497
C	1.55591	-1.50040	-1.64248
H	1.71195	-0.81266	-2.47398
C	2.37719	-1.56901	-0.45926
H	3.27561	-0.97741	-0.28131
O	-0.94655	0.64006	-0.69559
O	-1.75251	-0.88329	0.66945
C	-1.95197	0.13419	-0.08003
C	-3.36650	0.70930	-0.28609
H	-0.05555	1.47105	3.42060
H	-1.14143	1.36189	2.00823
H	-0.80256	-0.10785	2.98045
H	2.76895	-0.28009	2.03780
H	2.09877	0.64345	3.42023
H	1.46852	-0.99738	3.05610
H	1.23152	1.98456	-1.56389
Cl	-3.27175	2.49892	-0.43991
Cl	-3.97351	-0.02270	-1.82867
Cl	-4.43340	0.25756	1.07791

TS(1-2)$_{CCl3}$

BP86 Energy = -975.104794298
Enthalpy 0K= -974.800878
Enthalpy 298K= -974.777087
Free Energy 298K= -974.858067
PCM (CH_2Cl_2)= -975.169537
Frequency= -108.3175cm-1

Ir	0.59301	-0.98115	-0.04061
N	1.16815	0.05154	1.80978
C	0.22904	-0.27793	2.93820
C	2.55025	-0.34067	2.23324
C	1.11606	1.55870	1.56674
H	0.06312	1.79780	1.34084
H	1.37817	2.04897	2.52375
C	2.03426	2.00225	0.45151
C	1.60944	1.88460	-0.89212
C	2.47531	2.23555	-1.94598
H	2.12644	2.16692	-2.98153
C	3.75826	2.73058	-1.66519
H	4.42356	3.02749	-2.48176
C	4.17449	2.87954	-0.32984
H	5.16460	3.28893	-0.10709
C	3.31777	2.51559	0.72243
H	3.64623	2.64618	1.75980
C	1.76639	-2.78553	0.03461
H	2.21937	-3.19443	0.93841
C	0.41083	-3.07938	-0.43895
H	-0.31801	-3.71279	0.06953
C	0.21388	-2.38971	-1.69601
H	-0.69391	-2.38090	-2.29776
C	1.41321	-1.63363	-1.95347
H	1.54582	-0.93115	-2.77762
C	2.39268	-1.89773	-0.91349
H	3.40292	-1.49381	-0.86624
O	-1.26883	0.57876	-1.40829
O	-1.37116	-0.49245	0.56636
C	-1.88738	0.23129	-0.38715
C	-3.35137	0.69807	-0.12030
H	0.55408	0.25953	3.84667
H	-0.79262	0.01588	2.66876
H	0.25845	-1.36114	3.12706
H	3.26278	-0.11904	1.42831
H	2.83492	0.22493	3.13882
H	2.56170	-1.41309	2.47097
H	0.57302	1.60019	-1.11953
Cl	-3.22506	2.01629	1.13828
Cl	-4.09122	1.35263	-1.60494
Cl	-4.34654	-0.66084	0.51883

2$_{CCl3}$

BP86 Energy = -975.118371692
Enthalpy 0K= -974.813956
Enthalpy 298K= -974.789590
Free Energy 298K= -974.870378
PCM (CH_2Cl_2)= -975.183621

Ir	0.89789	-0.60552	-0.12357
N	1.06374	-0.18343	2.05766
C	-0.03651	-0.73889	2.90817
C	2.37039	-0.66023	2.60462
C	1.02379	1.32788	2.04091
H	-0.03511	1.62855	2.05335
H	1.52210	1.73320	2.94030
C	1.68124	1.77782	0.74626
C	0.88494	1.87002	-0.44053
C	1.48249	2.30835	-1.65810
H	0.85293	2.43017	-2.54508
C	2.83576	2.64338	-1.69694
H	3.28620	3.00992	-2.62452
C	3.61637	2.56739	-0.51847

H	4.66681	2.87442	-0.54394
C	3.05183	2.13334	0.68530
H	3.65732	2.11781	1.59771
C	2.64222	-1.88639	-0.52459
H	3.54959	-1.93239	0.07622
C	1.44658	-2.70172	-0.35279
H	1.28938	-3.47229	0.40295
C	0.51131	-2.34414	-1.40054
H	-0.49689	-2.73729	-1.52483
C	1.09644	-1.29848	-2.20170
H	0.62377	-0.80990	-3.05131
C	2.41292	-1.01904	-1.64730
H	3.10082	-0.25143	-2.00372
O	-1.93357	-0.75036	-1.72095
O	-1.08218	-0.08558	0.30086
C	-2.02754	-0.26156	-0.60254
C	-3.39818	0.31585	-0.07665
H	0.07204	-0.36067	3.94092
H	-1.00700	-0.44195	2.49308
H	0.03929	-1.83630	2.91469
H	3.20111	-0.24249	2.01954
H	2.46907	-0.34625	3.66011
H	2.40455	-1.75808	2.55638
H	-0.20602	1.86138	-0.35646
Cl	-3.19470	2.12561	0.08538
Cl	-4.72491	-0.03200	-1.20737
Cl	-3.78698	-0.39194	1.54998

TS(2-3)$_{CCl3}$

BP86 Energy = -975.111697227
Enthalpy 0K= -974.811885
Enthalpy 298K= -974.788537
Free Energy 298K= -974.866251
PCM (CH_2Cl_2)= -975.173246
Frequency= -250.6717cm-1

Ir	0.96314	-0.75417	-0.12166
N	1.17162	0.08324	1.90505
C	0.34125	-0.65782	2.90815
C	2.60362	0.05401	2.34668
C	0.71803	1.52565	1.82980
H	-0.38443	1.51214	1.77090
H	1.00255	2.05051	2.76019
C	1.31815	2.14780	0.59674
C	1.20702	1.36871	-0.60573
C	1.80454	1.89367	-1.79087
H	1.67600	1.36199	-2.73957
C	2.46399	3.12884	-1.78336
H	2.89129	3.52684	-2.70865
C	2.55951	3.86542	-0.58971
H	3.07528	4.83063	-0.58368
C	1.99168	3.37232	0.60206
H	2.08006	3.95033	1.52835
C	1.94938	-2.73853	0.14780
H	2.14184	-3.20761	1.11328
C	0.78090	-2.93316	-0.65139
H	-0.08656	-3.53641	-0.38073
C	0.90967	-2.12392	-1.85589
H	0.18700	-2.06005	-2.66876
C	2.18813	-1.46060	-1.79357
H	2.59323	-0.78531	-2.54688
C	2.83403	-1.80543	-0.54657
H	3.83097	-1.49717	-0.23361
O	-1.40776	1.11838	-1.22022
O	-1.12580	-0.53425	0.30691
C	-1.83953	0.27372	-0.39836
C	-3.37601	0.21417	-0.11127
H	0.41666	-0.16294	3.89350
H	-0.70438	-0.67506	2.57468
H	0.71710	-1.68773	2.99196
H	3.21776	0.63140	1.64157
H	2.68969	0.49573	3.35645
H	2.95618	-0.98610	2.38391
H	0.01104	1.10593	-0.93549
Cl	-3.61382	1.24732	1.37626
Cl	-4.31366	0.88296	-1.47208
Cl	-3.90380	-1.47151	0.23080

3$_{CCl3}$

BP86 Energy = -975.127198289
Enthalpy 0K= -974.822943
Enthalpy 298K= -974.799868
Free Energy 298K= -974.876316
PCM (CH_2Cl_2)= -975.184442

Ir	1.17525	-0.59951	-0.14872
N	1.38934	0.16136	1.89848
C	0.81701	-0.78318	2.90842
C	2.83507	0.40151	2.21392
C	0.65426	1.48344	1.96382
H	-0.41524	1.24071	2.09443
H	0.97944	2.04321	2.86078
C	0.88862	2.23375	0.67739
C	1.10879	1.43038	-0.48063
C	1.28015	2.09800	-1.72020
H	1.44562	1.52844	-2.64119
C	1.23034	3.50368	-1.80039
H	1.35929	3.99316	-2.77096
C	1.02944	4.27198	-0.64463
H	1.00650	5.36390	-0.70597
C	0.86221	3.63462	0.59722
H	0.70813	4.23320	1.50239
C	2.40017	-2.56563	-0.05743
H	2.72042	-3.06137	0.85953
C	1.22872	-2.85331	-0.78690
H	0.47172	-3.59208	-0.52160
C	1.15390	-1.93033	-1.92340
H	0.38099	-1.92693	-2.69205
C	2.33730	-1.11646	-1.90936
H	2.61804	-0.36776	-2.64949
C	3.08217	-1.43667	-0.70365
H	4.05433	-1.02779	-0.42822
O	-1.66037	0.85789	-1.31164
O	-0.97972	-0.53826	0.36103
C	-1.86263	0.01780	-0.32822
C	-3.36014	-0.23021	-0.00004

```
H   0.86699 -0.33159  3.91644
H  -0.22893 -1.00257  2.65324
H   1.39982 -1.71509  2.90213
H   3.24502  1.12344  1.49409
H   2.92957  0.80471  3.23901
H   3.38895 -0.54565  2.14949
H  -0.67531  1.09343 -1.32604
Cl -3.82983  1.17646  1.05181
Cl -4.34475 -0.25468 -1.49280
Cl -3.55875 -1.76496  0.89953
```

TS(2′-3′)$_{cc13}$

```
BP86 Energy =    -975.088807048
Enthalpy 0K=             -974.791023
Enthalpy 298K=           -974.766990
Free Energy 298K=        -974.847157
Frequency= -1061.9642cm-1

Ir  1.18355 -0.60546 -0.12911
N   1.55265  0.33324  1.82937
C   1.05051 -0.53380  2.94343
C   3.02264  0.56729  2.01009
C   0.85108  1.67643  1.88502
H  -0.19654  1.48468  2.17613
H   1.31116  2.29644  2.67556
C   0.89029  2.32550  0.52659
C   0.74813  1.43238 -0.58615
H  -0.44681  0.74685 -0.21688
C   0.68807  1.99289 -1.89323
H   0.54745  1.33798 -2.75962
C   0.77175  3.37792 -2.08280
H   0.71543  3.79856 -3.09141
C   0.92781  4.23066 -0.97329
H   1.00234  5.31201 -1.12548
C   0.98111  3.70940  0.33237
H   1.09034  4.38483  1.18779
C   2.52019 -2.42191 -0.01665
H   2.95442 -2.81314  0.90392
C   1.28795 -2.83010 -0.59290
H   0.58962 -3.55902 -0.18284
C   1.06283 -2.04249 -1.80297
H   0.20309 -2.13470 -2.46484
C   2.19068 -1.16902 -1.97404
H   2.33917 -0.46005 -2.78873
C   3.08018 -1.34820 -0.83902
H   4.04553 -0.86150 -0.70161
O  -1.83735 -2.06001 -0.45847
O  -0.94180 -0.16566  0.44399
C  -1.95884 -0.93148 -0.03117
C  -3.33521 -0.19448  0.07484
Cl -3.23266  1.29580 -0.96818
Cl -4.66210 -1.23312 -0.48504
Cl -3.60737  0.28317  1.80248
H   1.18932 -0.02233  3.91389
H  -0.01631 -0.74327  2.78458
H   1.61435 -1.47734  2.94920
H   3.38130  1.24540  1.22282
H   3.20854  1.02089  3.00113
H   3.56031 -0.38889  1.95048
```

3′$_{cc13}$

```
BP86 Energy = -975.107817339
Enthalpy 0K= -974.804510
Enthalpy 298K= -974.779869
Free Energy 298K= -974.862463

Ir  1.19599 -0.62663 -0.16115
N   1.45609  0.10835  1.88363
C   0.74199 -0.74296  2.88588
C   2.91764  0.13195  2.22439
C   0.93140  1.52827  1.94546
H  -0.15736  1.45481  2.11596
H   1.36475  2.04376  2.82320
C   1.23723  2.21853  0.63984
C   1.37123  1.38028 -0.50572
H  -1.24884  0.92396 -0.36840
C   1.59495  2.00468 -1.75643
H   1.68765  1.40426 -2.66719
C   1.68534  3.40301 -1.86076
H   1.85519  3.86313 -2.83956
C   1.56824  4.20949 -0.71604
H   1.65769  5.29695 -0.79694
C   1.34197  3.61617  0.53598
H   1.24999  4.24235  1.43096
C   2.08975 -2.75266 -0.01595
H   2.34061 -3.25963  0.91616
C   0.88028 -2.87655 -0.72612
H   0.01662 -3.47176 -0.42975
C   0.93582 -1.98369 -1.89121
H   0.15522 -1.87477 -2.64464
C   2.22403 -1.35962 -1.91910
H   2.60849 -0.68945 -2.68702
C   2.92124 -1.74645 -0.69497
H   3.94682 -1.47992 -0.43793
O  -2.11017 -1.87988  0.53684
O  -1.06262  0.07411  0.11188
C  -2.18156 -0.72375  0.20420
C  -3.52600  0.03431 -0.05600
Cl -3.26661  1.36053 -1.29262
Cl -4.77376 -1.08658 -0.61865
Cl -3.97751  0.77856  1.53019
H   0.86200 -0.31527  3.89861
H  -0.32669 -0.79798  2.63624
H   1.16765 -1.75593  2.86769
H   3.44036  0.79810  1.52418
H   3.05072  0.50107  3.25793
H   3.33067 -0.88383  2.15143
```

TS(2′′-3′′)$_{cc13}$

```
BP86 Energy = -975.088410939
Enthalpy 0K= -974.787997
Enthalpy 298K= -974.764286
Free Energy 298K= -974.842499
Frequency= -434.9096cm-1
```

Ir	1.18939	-0.60476	-0.12169
N	1.07523	0.16268	1.94053
C	0.24282	-0.70783	2.83380
C	2.44487	0.27868	2.54857
C	0.46476	1.55149	1.84460
H	-0.62658	1.41602	1.77121
H	0.68676	2.10004	2.77835
C	0.97708	2.25835	0.61278
C	1.38197	1.46582	-0.48413
C	1.80881	2.05423	-1.68487
H	2.13679	1.44284	-2.53061
C	1.78978	3.45528	-1.80435
H	2.10501	3.91987	-2.74360
C	1.37850	4.25237	-0.72391
H	1.37855	5.34219	-0.81766
C	0.97595	3.65762	0.48290
H	0.65432	4.28290	1.32310
C	1.52415	-2.96669	0.03339
H	1.41983	-3.55342	0.94612
C	0.49994	-2.72248	-0.91440
H	-0.52730	-3.07742	-0.83655
C	1.02514	-1.84890	-1.96585
H	0.47995	-1.50420	-2.84431
C	2.39925	-1.58739	-1.65996
H	3.10413	-1.01850	-2.26713
C	2.69473	-2.22570	-0.37401
H	3.66858	-2.24051	0.11603
O	-1.84915	-1.87395	0.54975
O	-0.84380	0.03848	-0.22915
C	-1.85662	-0.73473	0.09022
C	-3.22250	0.02553	-0.15732
Cl	-3.35571	1.28915	1.15910
Cl	-3.23033	0.82820	-1.77111
Cl	-4.60279	-1.09618	-0.03733
H	0.12715	-0.21467	3.81564
H	-0.74142	-0.88753	2.38535
H	0.75609	-1.67007	2.97212
H	3.03843	1.01600	1.98840
H	2.34815	0.61639	3.59557
H	2.94192	-0.70100	2.52724
H	2.52218	0.24893	0.01621

$3''_{CCl3}$

BP86 Energy = -975.089568647
Enthalpy 0K= -974.787518
Enthalpy 298K= -974.763568
Free Energy 298K= -974.842191

Ir	1.20557	-0.60799	-0.09594
N	1.07340	0.18257	1.94696
C	0.23856	-0.67851	2.84718
C	2.43601	0.32071	2.57070
C	0.46325	1.56989	1.81801
H	-0.62722	1.43428	1.73383
H	0.67437	2.13469	2.74442
C	1.00338	2.24256	0.58002
C	1.39581	1.41538	-0.49590
C	1.85771	1.97152	-1.69788
H	2.17565	1.33867	-2.53181
C	1.88924	3.37053	-1.84023
H	2.23325	3.80833	-2.78239
C	1.49057	4.20055	-0.77945
H	1.53052	5.28798	-0.89105
C	1.05081	3.63967	0.42988
H	0.74034	4.28830	1.25657
C	1.39501	-3.04624	-0.02052
H	1.27680	-3.66431	0.86927
C	0.37257	-2.70115	-0.93429
H	-0.66941	-3.01083	-0.85865
C	0.92786	-1.80756	-1.95870
H	0.38392	-1.39580	-2.80873
C	2.31700	-1.63805	-1.67751
H	3.04933	-1.10090	-2.28021
C	2.59102	-2.35466	-0.42197
H	3.57032	-2.43994	0.05079
O	-1.89055	-1.83388	0.61205
O	-0.84211	0.02185	-0.24336
C	-1.87140	-0.71231	0.11064
C	-3.22291	0.06884	-0.16027
Cl	-3.34867	1.33691	1.15137
Cl	-3.20266	0.86689	-1.77532
Cl	-4.62073	-1.03259	-0.05232
H	0.12148	-0.17420	3.82314
H	-0.74507	-0.86348	2.39964
H	0.75265	-1.63876	2.99686
H	3.02918	1.04832	1.99780
H	2.32164	0.68295	3.60740
H	2.93789	-0.65715	2.58132
H	2.68058	-0.12238	0.17875

5. BENZOATE

(i) Pathway I

1_{Ph}

BP86 Energy = -1123.62972873
Enthalpy 0K= -1123.244222
Enthalpy 298K= -1123.220747
Free Energy 298K= -1123.297909
PCM (CH_2Cl_2)= -1123.68454

Ir	0.29422	-0.94806	-0.04909
N	0.60767	0.40819	1.69932
C	-0.61627	0.55554	2.55687
C	1.67638	-0.17080	2.57414
C	1.00134	1.82187	1.25585
H	0.12349	2.21621	0.72240
H	1.13337	2.40613	2.18778
C	2.23232	1.94082	0.38568
C	2.09399	2.07704	-1.01324
H	1.09107	2.08517	-1.45467
C	3.22417	2.22627	-1.83282
H	3.10152	2.35208	-2.91362
C	4.50988	2.24226	-1.26487
H	5.39067	2.36570	-1.90259
C	4.65888	2.13419	0.12785

H	5.65480	2.18114	0.57920
C	3.52659	1.99699	0.94752
H	3.65242	1.96185	2.03559
C	0.68625	-3.03850	-0.51971
H	0.01881	-3.82981	-0.17447
C	0.54375	-2.29775	-1.75380
H	-0.20843	-2.46121	-2.52454
C	1.59271	-1.29160	-1.76613
H	1.74070	-0.53204	-2.53386
C	2.37452	-1.41871	-0.56513
H	3.22840	-0.79488	-0.30207
C	1.80666	-2.50578	0.22066
H	2.17323	-2.87848	1.17617
O	-1.07491	0.57612	-0.74070
O	-1.78646	-1.08834	0.48912
C	-2.08855	-0.01146	-0.17217
H	-0.36163	1.14847	3.45388
H	-1.40533	1.08064	2.00290
H	-0.97775	-0.43716	2.85589
H	2.60800	-0.28468	2.00685
H	1.85829	0.50046	3.43425
H	1.34101	-1.14838	2.94871
C	-3.45342	0.51945	-0.23906
C	-3.71988	1.68745	-0.99141
C	-5.02577	2.18512	-1.05493
C	-6.06485	1.52314	-0.37575
C	-5.80196	0.35950	0.36991
C	-4.49985	-0.14694	0.44105
H	-2.90290	2.18541	-1.52132
H	-5.23800	3.08682	-1.63688
H	-7.08560	1.91434	-0.43050
H	-6.61525	-0.15234	0.89277
H	-4.27970	-1.05319	1.01239

TS(1-2)$_{Ph}$

BP86 Energy = -1123.61015815
Enthalpy 0K= -1123.226672
Enthalpy 298K= -1123.203466
Free Energy 298K= -1123.280492
PCM (CH_2Cl_2)= -1123.67014
Frequency= -26.4791cm-1

Ir	0.71463	-0.71459	-0.11728
N	1.04463	-0.06326	1.97647
C	0.06248	-0.66563	2.93282
C	2.42685	-0.39547	2.44025
C	0.86382	1.44207	1.93943
H	-0.21653	1.62127	1.82357
H	1.20250	1.87333	2.89955
C	1.63049	1.98707	0.75659
C	1.13896	1.69815	-0.54994
H	0.07198	1.46644	-0.73950
C	1.89546	2.08164	-1.68823
H	1.48054	1.90521	-2.68562
C	3.11668	2.74652	-1.53262
H	3.68757	3.06634	-2.40952
C	3.58989	3.04111	-0.23897
H	4.53474	3.57965	-0.11462
C	2.85812	2.65267	0.89828
H	3.24342	2.88015	1.89814
C	0.73576	-2.85203	-0.37875
H	0.24804	-3.57496	0.27563
C	0.15622	-2.24277	-1.57066
H	-0.87453	-2.34794	-1.90914
C	1.14134	-1.39244	-2.16286
H	0.98393	-0.76053	-3.03582
C	2.36836	-1.48677	-1.36616
H	3.30171	-0.95994	-1.56303
C	2.12186	-2.39752	-0.29196
H	2.83996	-2.68729	0.47510
O	-1.59071	0.55334	-1.75090
O	-1.22745	-0.15089	0.38078
C	-2.02307	0.27234	-0.61842
H	0.20797	-0.23169	3.93884
H	-0.95373	-0.46466	2.57124
H	0.23197	-1.75148	2.97920
H	3.16593	0.02940	1.74713
H	2.59135	0.01567	3.45359
H	2.54001	-1.48764	2.48055
C	-3.46472	0.41152	-0.24476
C	-4.32438	1.05510	-1.16171
C	-5.68377	1.20468	-0.86194
C	-6.19630	0.70849	0.34946
C	-5.34646	0.06018	1.26240
C	-3.98419	-0.08702	0.96969
H	-3.90475	1.42755	-2.10035
H	-6.34668	1.70673	-1.57340
H	-7.25998	0.82354	0.58113
H	-5.74862	-0.33272	2.20151
H	-3.32067	-0.60108	1.67056

2$_{Ph}$

BP86 Energy = -1123.61231092
Enthalpy 0K= -1123.228168
Enthalpy 298K= -1123.204110
Free Energy 298K= -1123.283737
PCM (CH_2Cl_2)= -1123.67255

Ir	0.75492	-0.58991	-0.01474
N	0.78741	0.44327	1.96149
C	-0.41265	0.18739	2.81888
C	2.01025	0.08886	2.74314
C	0.84011	1.89736	1.54784
H	-0.19368	2.20616	1.33129
H	1.23022	2.50965	2.38163
C	1.69069	1.99873	0.29636
C	1.07914	1.76593	-0.97277
H	-0.01260	1.74929	-1.05406
C	1.86550	1.83013	-2.15449
H	1.37820	1.70873	-3.12730
C	3.23199	2.10979	-2.07853
H	3.83168	2.18097	-2.99112
C	3.83004	2.35907	-0.82347
H	4.89169	2.62043	-0.76996
C	3.07028	2.30046	0.35185
H	3.53842	2.52666	1.31593

C	2.10321	-2.26838	0.37873
H	2.63811	-2.42234	1.31565
C	0.74864	-2.73390	0.08076
H	0.09436	-3.31521	0.72871
C	0.45437	-2.35762	-1.29574
H	-0.49274	-2.53874	-1.80001
C	1.56603	-1.61036	-1.79490
H	1.62801	-1.14125	-2.77641
C	2.59831	-1.55665	-0.75987
H	3.56592	-1.06295	-0.84660
O	-2.13647	-1.86909	-0.21783
O	-1.15926	0.18615	-0.01186
C	-2.22219	-0.63587	-0.15852
H	-0.35396	0.80641	3.73262
H	-1.31747	0.43293	2.25071
H	-0.43191	-0.87596	3.09869
H	2.90880	0.25109	2.13174
H	2.06566	0.71309	3.65424
H	1.95299	-0.96681	3.04316
C	-3.53440	0.08582	-0.21646
C	-4.70752	-0.69421	-0.31476
C	-5.96116	-0.07386	-0.37335
C	-6.05558	1.32834	-0.33553
C	-4.89181	2.11058	-0.23956
C	-3.63491	1.49395	-0.17963
H	-4.60950	-1.78292	-0.34421
H	-6.86730	-0.68286	-0.44914
H	-7.03643	1.81214	-0.38201
H	-4.96602	3.20232	-0.21310
H	-2.72697	2.09927	-0.10866

TS(2-3)$_{Ph}$

BP86 Energy = -1123.60438150
Enthalpy 0K= -1123.221020
Enthalpy 298K= -1123.197428
Free Energy 298K= -1123.277161
PCM (CH_2Cl_2)= -1123.66393
Frequency= -148.1170cm-1

Ir	0.51802	-0.82463	-0.09999
N	0.98107	0.02722	1.86026
C	-0.13910	-0.24131	2.82707
C	2.23530	-0.55946	2.42653
C	1.13151	1.54047	1.71257
H	0.12046	1.92259	1.50518
H	1.46009	1.92840	2.69550
C	2.08103	1.94295	0.60514
C	1.57423	2.16818	-0.69743
H	0.49350	2.11463	-0.87198
C	2.44070	2.52248	-1.74680
H	2.03508	2.72140	-2.74418
C	3.81749	2.66316	-1.50594
H	4.49019	2.95480	-2.31848
C	4.32503	2.46727	-0.20946
H	5.39197	2.60889	-0.01116
C	3.46083	2.11424	0.84023
H	3.86089	1.99749	1.85382
C	1.96554	-2.45682	-0.34846
H	2.63136	-2.82959	0.42865
C	0.59686	-2.89315	-0.58645
H	0.04799	-3.63992	-0.01137
C	0.07775	-2.18726	-1.75595
H	-0.92344	-2.29648	-2.16997
C	1.07638	-1.24685	-2.15585
H	0.97849	-0.50312	-2.94727
C	2.24570	-1.40172	-1.27838
H	3.16110	-0.81258	-1.33936
O	-2.16825	-1.54181	0.29055
O	-1.13650	0.43242	-0.04508
C	-2.24331	-0.31157	0.06550
H	0.12092	0.17999	3.81513
H	-1.05848	0.22810	2.45621
H	-0.29191	-1.32618	2.91683
H	3.07199	-0.38480	1.73685
H	2.45985	-0.08895	3.40149
H	2.09094	-1.63850	2.57773
C	-3.53773	0.41075	-0.06156
C	-4.73041	-0.30998	0.17176
C	-5.96874	0.33202	0.05776
C	-6.02585	1.69370	-0.28867
C	-4.84178	2.41479	-0.52312
C	-3.59913	1.77849	-0.41058
H	-4.66213	-1.36806	0.43967
H	-6.89168	-0.22719	0.23924
H	-6.99538	2.19422	-0.37675
H	-4.88981	3.47371	-0.79520
H	-2.67306	2.33005	-0.59481

3$_{Ph}$

BP86 Energy = -1123.63819926
Enthalpy 0K= -1123.253366
Enthalpy 298K= -1123.229824
Free Energy 298K= -1123.306730
PCM (CH_2Cl_2)= -1123.69175

Ir	0.94912	-0.66249	-0.19013
N	1.30133	-0.14400	1.91354
C	0.59108	-1.07251	2.84522
C	2.76785	-0.17496	2.21292
C	0.78946	1.26618	2.11361
H	-0.30635	1.18501	2.21962
H	1.19153	1.67491	3.06002
C	1.16020	2.08652	0.90501
C	1.24399	1.37350	-0.32636
H	-0.59989	1.28345	-1.20188
C	1.55399	2.11495	-1.49293
H	1.62104	1.61712	-2.46635
C	1.76575	3.50599	-1.43449
H	1.99808	4.05458	-2.35300
C	1.68887	4.18379	-0.20930
H	1.86531	5.26247	-0.16348
C	1.38939	3.46986	0.96353
H	1.33255	3.99495	1.92413
C	0.64197	-2.82624	-1.04333
H	-0.22208	-3.45754	-0.83450
C	0.70838	-1.79036	-2.07761

H	-0.05517	-1.58828	-2.82855
C	2.01192	-1.18562	-2.00930
H	2.40731	-0.42356	-2.67980
C	2.70376	-1.74367	-0.86301
H	3.73172	-1.52880	-0.57192
C	1.84794	-2.80102	-0.31265
H	2.08725	-3.42883	0.54648
O	-1.59814	1.19322	-1.25156
O	-1.13414	-0.32691	0.38074
C	-1.97321	0.33491	-0.31136
H	0.69859	-0.71683	3.88687
H	-0.47238	-1.11124	2.57335
H	1.03072	-2.07694	2.76247
H	3.28167	0.55583	1.57317
H	2.93725	0.07874	3.27587
H	3.15578	-1.18319	2.01257
C	-3.42136	0.17860	-0.11099
C	-4.33230	1.01319	-0.80200
C	-5.70741	0.84746	-0.60516
C	-6.17972	-0.14228	0.27525
C	-5.27626	-0.97274	0.96377
C	-3.90006	-0.81631	0.77406
H	-3.95547	1.78180	-1.48139
H	-6.41390	1.49084	-1.13757
H	-7.25659	-0.26817	0.42501
H	-5.64933	-1.74297	1.64514
H	-3.18654	-1.45929	1.29637

6 TRIFLATE

(i) Pathway I

4

BP86 Energy = -1276.84000415
Enthalpy 0K= -1276.530403
Enthalpy 298K= -1276.505891
Free Energy 298K= -1276.586204
PCM (CH_2Cl_2)= -1276.90129

Ir	-0.10874	0.94425	0.14888
N	-0.64099	-0.59189	1.65296
C	0.50972	-0.91221	2.56487
C	-1.74392	-0.07568	2.52730
C	-1.08046	-1.90558	0.98800
H	-0.20208	-2.26472	0.43186
H	-1.27841	-2.61059	1.81859
C	-2.28559	-1.81175	0.07780
C	-2.11384	-1.65689	-1.31607
C	-3.22683	-1.59191	-2.17002
H	-3.07921	-1.49556	-3.25071
C	-4.52666	-1.68449	-1.64347
H	-5.39359	-1.64388	-2.31015
C	-4.70897	-1.86532	-0.26228
H	-5.71716	-1.97210	0.14978
C	-3.59546	-1.93788	0.59022
H	-3.74811	-2.12053	1.66010
C	-0.14607	3.12004	0.10661
H	0.62396	3.70945	0.60803
C	-0.08217	2.64272	-1.25581
H	0.72017	2.82754	-1.96986
C	-1.25789	1.82332	-1.47126
H	-1.48219	1.25651	-2.37573
C	-2.05231	1.80788	-0.26384
H	-2.99922	1.28315	-0.14077
C	-1.35558	2.61898	0.72697
H	-1.69356	2.84648	1.73720
O	0.95898	-0.64083	-1.01094
O	2.05042	0.70818	0.69766
S	2.37098	-0.05360	-0.63692
H	0.16237	-1.60292	3.35404
H	1.31844	-1.38659	2.00084
H	0.88332	0.01358	3.02405
H	-2.62866	0.16186	1.92417
H	-2.01466	-0.84695	3.27118
H	-1.38979	0.81895	3.05800
H	-1.10117	-1.61502	-1.73120
O	3.09737	0.69492	-1.68581
C	3.47366	-1.56534	-0.18046
F	3.83878	-2.15377	-1.31759
F	4.53085	-1.11002	0.49157
F	2.76861	-2.42489	0.57914

TS(4-5)

BP86 Energy = -1276.82826185
Enthalpy 0K= -1276.519299
Enthalpy 298K= -1276.495151
Free Energy 298K= -1276.575799
PCM (CH_2Cl_2)= -1276.89343
Frequency= -124.8206cm-1

Ir	-0.25827	0.89888	0.17101
N	-0.81435	-0.41153	1.83243
C	0.27899	-0.56341	2.85658
C	-2.02056	0.12138	2.54347
C	-1.11021	-1.80391	1.26090
H	-0.15227	-2.17987	0.86588
H	-1.39459	-2.43586	2.12452
C	-2.17582	-1.83269	0.18677
C	-1.79940	-1.77684	-1.17485
C	-2.77751	-1.79797	-2.18505
H	-2.47252	-1.78242	-3.23659
C	-4.13818	-1.88403	-1.84753
H	-4.89878	-1.91605	-2.63376
C	-4.51916	-1.97023	-0.49661
H	-5.57555	-2.07337	-0.23011
C	-3.54327	-1.95335	0.51358
H	-3.84936	-2.06158	1.56028
C	-0.21236	3.02438	-0.06628
H	0.47152	3.65825	0.50113
C	0.04198	2.45415	-1.36989
H	0.96597	2.53624	-1.94354
C	-1.09711	1.63384	-1.69731
H	-1.17176	0.98189	-2.56879
C	-2.10391	1.74881	-0.65124
H	-3.07526	1.25545	-0.64471
C	-1.55091	2.60331	0.36606

H	-2.03345	2.89956	1.29788
O	1.31680	-0.85499	-1.47611
O	1.73327	0.39263	0.65688
S	2.39062	-0.09360	-0.72766
H	-0.08744	-1.20615	3.67617
H	1.16398	-1.01058	2.39134
H	0.54247	0.42634	3.25628
H	-2.85122	0.24725	1.83698
H	-2.32462	-0.58524	3.33706
H	-1.76444	1.08438	3.00842
H	-0.73722	-1.75574	-1.44132
O	3.15050	0.96861	-1.43672
C	3.63754	-1.36785	-0.03247
F	4.22749	-1.97253	-1.06575
F	4.53609	-0.73425	0.72492
F	2.96050	-2.26896	0.70763

5

BP86 Energy = -1276.84475905
Enthalpy 0K= -1276.535066
Enthalpy 298K= -1276.510388
Free Energy 298K= -1276.591499
PCM (CH_2Cl_2)= -1276.91017

Ir	0.61603	-0.62308	0.04121
N	0.96855	0.28527	2.03944
C	-0.13591	0.04689	3.02278
C	2.25018	-0.20617	2.63208
C	1.08678	1.75881	1.71006
H	0.06415	2.16005	1.64501
H	1.62250	2.27981	2.52436
C	1.79201	1.88253	0.37218
C	1.02806	1.74024	-0.82797
C	1.67526	1.82116	-2.09190
H	1.06763	1.76960	-3.00099
C	3.05454	2.02738	-2.16421
H	3.55000	2.11531	-3.13600
C	3.80449	2.18162	-0.97691
H	4.87864	2.38407	-1.03641
C	3.18344	2.10439	0.27763
H	3.77403	2.25612	1.18756
C	0.07541	-2.67977	-0.35346
H	-0.86153	-3.11015	0.00101
C	0.26390	-2.00994	-1.63180
H	-0.50210	-1.84452	-2.38944
C	1.62549	-1.54799	-1.67525
H	2.06468	-0.95037	-2.47416
C	2.30856	-1.94406	-0.45736
H	3.35578	-1.76301	-0.21830
C	1.34401	-2.64967	0.35507
H	1.52514	-3.08591	1.33819
O	-2.15344	0.30853	-2.03423
O	-1.23255	0.30750	0.35752
S	-2.42570	-0.16292	-0.64388
H	0.05887	0.62401	3.94471
H	-1.09166	0.34653	2.57615
H	-0.16898	-1.02553	3.26503
H	3.07778	-0.03151	1.93095
H	2.45097	0.32502	3.58064
H	2.16478	-1.28140	2.84162
H	-0.06320	1.80822	-0.79648
O	-2.80871	-1.58525	-0.40653
C	-3.77934	0.95361	0.12057
F	-4.92101	0.71841	-0.53074
F	-3.91311	0.65244	1.42223
F	-3.41859	2.23915	-0.01750

TS(5-6)

BP86 Energy = -1276.83308162
Enthalpy 0K= -1276.529064
Enthalpy 298K= -1276.505258
Free Energy 298K= -1276.582691
PCM (CH_2Cl_2)= -1276.89372
Frequency= -677.1824cm-1

Ir	0.84516	-0.69909	-0.03543
N	1.07411	0.29625	1.91284
C	0.44754	-0.49212	3.02144
C	2.52362	0.50903	2.22666
C	0.39823	1.64618	1.79597
H	-0.68845	1.45966	1.81254
H	0.66076	2.26753	2.67189
C	0.82140	2.26168	0.48903
C	0.80120	1.37399	-0.64521
C	1.28140	1.89684	-1.88720
H	1.23146	1.27545	-2.78711
C	1.71653	3.22272	-2.00230
H	2.05135	3.60627	-2.97081
C	1.70845	4.06346	-0.87603
H	2.04875	5.09980	-0.96565
C	1.26711	3.58087	0.37211
H	1.28176	4.23926	1.24758
C	2.24756	-2.41366	0.26296
H	2.71994	-2.65359	1.21657
C	1.01846	-2.95841	-0.20960
H	0.37799	-3.66597	0.31700
C	0.73082	-2.35024	-1.50555
H	-0.15397	-2.53816	-2.11486
C	1.81742	-1.47279	-1.83545
H	1.91012	-0.89541	-2.75443
C	2.75290	-1.45799	-0.72010
H	3.70761	-0.93422	-0.68411
O	-1.69862	0.88340	-1.41931
O	-1.25787	-0.59836	0.57484
S	-2.23731	-0.33651	-0.62794
H	0.50823	0.07854	3.96615
H	-0.60232	-0.69679	2.77488
H	0.99020	-1.44102	3.14001
H	2.98051	1.13167	1.44505
H	2.62276	1.01338	3.20533
H	3.03319	-0.46274	2.27013
H	-0.43033	1.04999	-0.99328
O	-2.62409	-1.52262	-1.42809
C	-3.77588	0.32389	0.30961
F	-4.70404	0.64862	-0.58935
F	-4.21436	-0.64018	1.12402

F -3.40881 1.40342 1.01990

6

BP86 Energy = -1276.84538074
Enthalpy 0K= -1276.537402
Enthalpy 298K= -1276.512794
Free Energy 298K= -1276.592586
PCM (CH_2Cl_2)= -1276.90203

Ir	1.07945	-0.48444	-0.07843
N	1.31680	0.51469	1.85750
C	1.00958	-0.40057	3.00098
C	2.72053	1.02167	2.00014
C	0.37239	1.69745	1.88379
H	-0.62304	1.30097	2.14587
H	0.68020	2.39685	2.68353
C	0.35209	2.32867	0.51547
C	0.62340	1.45652	-0.58224
C	0.55705	2.01203	-1.88692
H	0.75763	1.38952	-2.76531
C	0.23445	3.37028	-2.08625
H	0.18560	3.76852	-3.10465
C	-0.01297	4.20715	-0.98904
H	-0.25127	5.26352	-1.14374
C	0.05026	3.68437	0.31429
H	-0.14137	4.33649	1.17425
C	2.68574	-2.12390	0.08559
H	3.22026	-2.37623	1.00227
C	1.52299	-2.76098	-0.39468
H	0.98698	-3.57878	0.08713
C	1.10480	-2.07727	-1.62258
H	0.24053	-2.34391	-2.23121
C	2.07174	-1.06270	-1.92319
H	2.08717	-0.42488	-2.80585
C	3.01795	-1.01166	-0.81642
H	3.90835	-0.38492	-0.76478
O	-2.07239	0.44948	-1.48770
O	-1.07539	-0.59501	0.65388
S	-2.14683	-0.78415	-0.42726
H	1.07301	0.15551	3.95470
H	-0.00278	-0.81049	2.88077
H	1.73988	-1.22232	3.01513
H	2.92744	1.74188	1.19634
H	2.83860	1.51699	2.98144
H	3.42346	0.17985	1.93491
H	-1.20599	0.95682	-1.33130
O	-2.27021	-2.07804	-1.12661
C	-3.79128	-0.36860	0.49347
F	-4.77583	-0.38224	-0.39892
F	-3.96437	-1.30750	1.42427
F	-3.65971	0.83795	1.05154

(ii) Pathway II

5'

BP86 Energy = -1276.84510198
Enthalpy 0K= -1276.535511
Enthalpy 298K= -1276.510814
Free Energy 298K= -1276.591785

Ir	0.63791	-0.61962	0.05730
N	0.94763	0.31341	2.05478
C	-0.14553	0.05040	3.04558
C	2.24485	-0.11505	2.66020
C	1.00514	1.78415	1.69629
H	-0.03256	2.14463	1.63308
H	1.52872	2.34197	2.49393
C	1.69242	1.90367	0.34832
C	0.92028	1.72881	-0.84318
H	-0.17167	1.77297	-0.80600
C	1.55669	1.80102	-2.11333
H	0.94255	1.72606	-3.01604
C	2.93039	2.03575	-2.20133
H	3.41469	2.11898	-3.17911
C	3.68709	2.22684	-1.02326
H	4.75557	2.45381	-1.09539
C	3.07876	2.15424	0.23723
H	3.67305	2.33407	1.13956
C	0.75368	-2.77837	0.16816
H	0.33228	-3.39247	0.96431
C	0.08817	-2.43247	-1.07855
H	-0.95329	-2.65842	-1.31641
C	0.98371	-1.64174	-1.86770
H	0.75439	-1.19787	-2.83560
C	2.23952	-1.51235	-1.12820
H	3.11876	-0.95718	-1.45538
C	2.10693	-2.23416	0.10508
H	2.88078	-2.34556	0.86386
O	-2.10450	0.23927	-2.01082
O	-1.25427	0.20585	0.40278
S	-2.42989	-0.23064	-0.63114
C	-3.77345	0.92003	0.10078
F	-4.90622	0.70989	-0.57381
F	-3.94135	0.62943	1.40029
F	-3.37885	2.19680	-0.03555
H	0.03079	0.65277	3.95498
H	-1.11339	0.30490	2.59808
H	-0.13664	-1.01724	3.30934
H	3.06773	0.07667	1.95751
H	2.42240	0.44383	3.59747
H	2.19680	-1.18824	2.89261
O	-2.86115	-1.64218	-0.41107

TS(5'-6')

BP86 Energy = -1276.82854615
Enthalpy 0K= -1276.521538
Enthalpy 298K= -1276.497639
Free Energy 298K= -1276.577371
Frequency= -70.5824cm-1

Ir	0.35612	-0.98308	0.00244
N	1.25620	-0.06844	1.78884
C	0.46278	-0.43852	3.01215
C	2.67260	-0.51281	1.99460
C	1.22860	1.44810	1.64080

```
H   0.16694  1.73508  1.60123
H   1.67413  1.87708  2.55747
C   1.96980  1.91579  0.41230
C   1.52126  1.55815 -0.87477
C   2.21430  1.93222 -2.03595
H   1.83936  1.64499 -3.02258
C   3.36291  2.73329 -1.91494
H   3.89645  3.05970 -2.81271
C   3.81441  3.12302 -0.64335
H   4.70775  3.74742 -0.54769
C   3.12734  2.71113  0.51156
H   3.49044  3.01645  1.49915
C   1.51904 -2.82155 -0.18578
H   2.33397 -3.10337  0.48051
C   0.10105 -3.10051  0.02873
H  -0.33141 -3.65913  0.85983
C  -0.62950 -2.59522 -1.13297
H  -1.71228 -2.62622 -1.26540
C   0.30733 -1.94173 -1.98642
H   0.05466 -1.38666 -2.88977
C   1.64487 -2.07467 -1.39998
H   2.56883 -1.67722 -1.82027
O  -1.82526  0.32716 -1.72523
O  -1.23684  0.13381  0.70531
S  -2.45118  0.11497 -0.38424
C  -3.30856  1.73670  0.16701
F  -2.42235  2.74304  0.09356
F  -4.33088  1.95541 -0.66298
F  -3.74179  1.59324  1.42480
H   0.89602  0.06363  3.89573
H  -0.58077 -0.12788  2.87673
H   0.50932 -1.52745  3.15763
H   3.26935 -0.28909  1.10015
H   3.10320  0.01943  2.86214
H   2.68890 -1.59110  2.20374
H   0.44631  0.96549 -1.05041
O  -3.38932 -1.01969 -0.16803
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6’

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BP86 Energy = -1276.84508601
Enthalpy 0K= -1276.535451
Enthalpy 298K= -1276.510767
Free Energy 298K= -1276.591584

Ir  0.64104 -0.61966  0.05291
N   0.95050  0.29599  2.05811
C  -0.13845  0.01817  3.04950
C   2.25179 -0.12960  2.65669
C   0.99799  1.76978  1.71096
H  -0.04208  2.12416  1.65289
H   1.52046  2.32495  2.51118
C   1.68075  1.90271  0.36179
C   0.90659  1.73215 -0.82928
H  -0.18552  1.77177 -0.79089
C   1.53987  1.81767 -2.10043
H   0.92364  1.74595 -3.00197
C   2.91180  2.06107 -2.19004
H   3.39324  2.15460 -3.16830
C   3.67025  2.24769 -1.01224
H   4.73721  2.48148 -1.08519
C   3.06551  2.16200  0.24901
H   3.66089  2.33865  1.15125
C   0.76604 -2.77909  0.14892
H   0.35145 -3.40061  0.94285
C   0.09308 -2.42766 -1.09200
H  -0.94878 -2.65567 -1.32645
C   0.98154 -1.62827 -1.88065
H   0.74579 -1.17979 -2.84487
C   2.24031 -1.49856 -1.14647
H   3.11585 -0.93786 -1.47421
C   2.11657 -2.22863  0.08287
H   2.89490 -2.34219  0.83675
O  -2.09436  0.26717 -2.00332
O  -1.25579  0.19167  0.41277
S  -2.42681 -0.22624 -0.63341
C  -3.77313  0.91309  0.11110
F  -4.90365  0.71271 -0.57021
F  -3.94521  0.60365  1.40560
F  -3.37819  2.19180 -0.00552
H   0.03571  0.61539  3.96271
H  -1.10915  0.26888  2.60598
H  -0.12124 -1.05117  3.30594
H   3.07213  0.07443  1.95453
H   2.42742  0.42134  3.59903
H   2.21142 -1.20532  2.87857
O  -2.86075 -1.64085 -0.43990
```

(iii) Pathway III

TS(5’’-6’’)

```
BP86 Energy = -1276.81693727
Enthalpy 0K= -1276.511504
Enthalpy 298K= -1276.487397
Free Energy 298K= -1276.566323
Frequency= -352.4316cm-1

C  -1.61771  1.90436  0.74240
C  -1.33454  1.24508 -0.47816
C  -1.64149  1.86956 -1.70056
C  -2.24332  3.14219 -1.70365
C  -2.53338  3.79216 -0.49617
C  -2.22974  3.16848  0.72512
Ir -0.52400 -0.70490 -0.22525
O   1.09082 -0.09603  0.97949
S   2.65005 -0.27676  0.54571
C   2.98064  1.42161 -0.27246
C  -1.27207  1.16615  2.00376
N  -1.48092 -0.31535  1.74953
C  -0.86408 -1.10635  2.86415
C  -1.13238 -1.55102 -2.14544
C   0.22595 -1.99711 -1.88439
C   0.18610 -2.91823 -0.76841
C  -1.15010 -2.98280 -0.29884
C  -1.98457 -2.11836 -1.13075
C  -2.95165 -0.60186  1.69363
O   3.42797 -0.32261  1.80656
```

H	-1.45387	-0.91301	-2.96847
H	1.11857	-1.73785	-2.45241
H	1.06085	-3.39103	-0.32103
H	-1.49420	-3.57111	0.55355
H	-3.06611	-2.00170	-1.06848
H	0.16792	0.47690	-1.02564
H	-1.39688	1.39638	-2.65599
H	-2.47445	3.62217	-2.65942
H	-3.00004	4.78129	-0.50170
H	-2.46936	3.66641	1.67102
H	-1.89122	1.46783	2.86851
H	-0.20947	1.28998	2.26671
F	2.65864	2.40240	0.58050
F	4.26664	1.49976	-0.61460
F	2.20657	1.52651	-1.38609
H	-3.40903	-0.33400	2.66261
H	-3.41112	-0.00487	0.89443
H	-3.11076	-1.67295	1.51024
H	-1.28852	-0.76266	3.82422
H	-1.09879	-2.17228	2.73196
H	0.22257	-0.95168	2.85905
O	2.81930	-1.29838	-0.52885

6''

BP86 Energy = -1276.81749454
Enthalpy 0K= -1276.510796
Enthalpy 298K= -1276.486389
Free Energy 298K= -1276.565619

C	-1.79895	1.81990	0.76119
C	-1.46994	1.19001	-0.46121
C	-1.81037	1.80480	-1.67802
C	-2.49416	3.03566	-1.67359
C	-2.83360	3.65432	-0.46220
C	-2.49172	3.04283	0.75421
Ir	-0.50829	-0.66280	-0.26247
O	1.04983	0.15732	0.87120
S	2.62019	-0.17848	0.58803
C	3.13232	1.43362	-0.30616
C	-1.37207	1.11586	2.01710
N	-1.43824	-0.37926	1.76565
C	-0.69558	-1.10455	2.84643
C	-1.15320	-1.61148	-2.11626
C	0.23620	-2.00238	-1.89327
C	0.28012	-2.90386	-0.76386
C	-1.02866	-2.99562	-0.23662
C	-1.93235	-2.17985	-1.05186
C	-2.87611	-0.80536	1.77355
O	3.29439	-0.20557	1.90885
H	-1.53291	-1.01885	-2.94828
H	1.09167	-1.72882	-2.51044
H	1.18968	-3.33503	-0.34637
H	-1.31702	-3.57300	0.64371
H	-3.01368	-2.10096	-0.94474
H	0.22103	0.33302	-1.24198
H	-1.53610	1.35583	-2.63750
H	-2.75171	3.50810	-2.62652
H	-3.36549	4.60998	-0.46201
H	-2.75983	3.51861	1.70399
H	-2.00789	1.35218	2.88993
H	-0.32477	1.34516	2.26985
F	2.87724	2.48356	0.48147
F	4.43204	1.37004	-0.60062
F	2.40855	1.53642	-1.44792
H	-3.31154	-0.57874	2.76293
H	-3.42698	-0.25267	1.00008
H	-2.94800	-1.88748	1.59747
H	-1.10943	-0.80707	3.82638
H	-0.82477	-2.18872	2.71819
H	0.36811	-0.83817	2.79625
O	2.78461	-1.28185	-0.40528

[IrCpCl$_2$]$_2$ Iridium dimer

BP86 Energy = --656.363170040
Enthalpy 0K= -656.193582
Enthalpy 298K= -656.175619
Free Energy 298K= -656.243061
PCM (CH_2Cl_2)= -656.355871

Ir	1.25821	0.35872	1.36485
Cl	1.10276	0.35136	-1.11862
Cl	1.87915	-1.94714	1.24594
C	1.56420	2.51940	1.61682
C	0.78853	2.00370	2.70896
C	1.56981	0.98243	3.40499
C	2.85025	0.88624	2.72399
C	2.84314	1.80804	1.61213
H	1.23115	3.25561	0.88581
H	-0.24175	2.27965	2.93598
H	1.26114	0.41468	4.28182
H	3.64563	0.17879	2.96002
H	3.64790	1.94110	0.88925
Cl	-1.10276	-0.35136	1.11862
Ir	-1.25821	-0.35872	-1.36485
Cl	-1.87915	1.94714	-1.24594
C	-1.56420	-2.51940	-1.61682
C	-0.78853	-2.00370	-2.70896
C	-1.56981	-0.98243	-3.40499
C	-2.85025	-0.88624	-2.72399
C	-2.84314	-1.80804	-1.61213
H	-1.23115	-3.25561	-0.88581
H	0.24175	-2.27965	-2.93598
H	-1.26114	-0.41468	-4.28182
H	-3.64563	-0.17879	-2.96002
H	-3.64790	-1.94110	-0.88925

DMBA-H

BP86 Energy = -405.518206127
Enthalpy 0K= -405.322133
Enthalpy 298K= -405.312185
Free Energy 298K= -405.357698
PCM (CH_2Cl_2)= -405.518206

N	2.03910	-0.28821	-0.01171
C	2.05472	-0.18435	1.44904
H	2.40199	0.81416	1.81174
H	1.04134	-0.35879	1.84489
H	2.72713	-0.95253	1.86765
C	3.38027	-0.09838	-0.56286
C	1.08017	0.65010	-0.60973
C	-0.36958	0.29680	-0.31123
H	1.27388	1.70810	-0.29955
H	1.23797	0.61897	-1.70612
H	3.35841	-0.23371	-1.65807
H	3.81116	0.91044	-0.34880
H	4.06425	-0.85288	-0.13754
C	-1.30940	1.30175	-0.01439
C	-2.65910	0.98091	0.20563

```
C  -3.08309 -0.35560  0.14136
C  -2.14987 -1.36705 -0.14470
C  -0.80434 -1.04300 -0.37211
H  -0.97848  2.34587  0.04484
H  -3.37733  1.77535  0.43567
H  -4.13388 -0.60907  0.31775
H  -2.47325 -2.41275 -0.19206
H  -0.06550 -1.82287 -0.58453
```

$CH_3CO_2^-$

```
BP86 Energy = -228.501362318
Enthalpy 0K= -228.454938
Enthalpy 298K= -228.450370
Free Energy 298K= -228.482867
PCM (CH2Cl2)= -228.501360

O  -1.17106  0.71143  0.00000
O   1.12728  0.80361  0.00000
C   0.00000  0.22378  0.00000
C   0.04308 -1.36353  0.00000
H   1.07606 -1.76004  0.00000
H  -0.49216 -1.76090  0.88516
H  -0.49216 -1.76090 -0.88516
```

CH_3CO_2H

```
BP86 Energy = -229.088334758
Enthalpy 0K= -229.028311
Enthalpy 298K= -229.024485
Free Energy 298K= -229.054397
PCM (CH2Cl2)= -229.088335

C  -1.03207 -0.95831  0.00000
H  -0.57189 -1.95565  0.00000
H  -1.67648 -0.84461  0.88640
H  -1.67648 -0.84461 -0.88640
C   0.00000  0.15046  0.00000
O  -0.24387  1.34801  0.00000
O   1.27691 -0.34318  0.00000
H   1.85293  0.45341  0.00000
```

$HOCO_2^-$

```
BP86 Energy = -264.436226957
Enthalpy 0K= -264.410964
Enthalpy 298K= -264.407356
Free Energy 298K= -264.436812
PCM (CH2Cl2)= -264.436227

O  -1.00628  0.92147  0.00000
O   1.24662  0.40715  0.00000
C   0.00000  0.17901  0.00000
O  -0.31544 -1.26214  0.00000
H   0.60076 -1.60587  0.00000
```

$HOCO_2H$

```
BP86 Energy = -265.006249032
Enthalpy 0K= -264.968103
Enthalpy 298K= -264.964273
Free Energy 298K= -264.994088
PCM (CH2Cl2)= -265.006249

C   0.00000  0.14945  0.00000
O  -0.91487 -0.87642  0.00000
O  -0.26965  1.33216  0.00000
H  -1.79088 -0.44005  0.00000
O   1.25849 -0.34730  0.00000
H   1.19920 -1.32420  0.00000
```

$CF_3SO_3^-$

```
BP86 Energy = -573.538118132
Enthalpy 0K= -573.512682
Enthalpy 298K= -573.505152
Free Energy 298K= -573.545666
PCM (CH2Cl2)= -573.533316

O  -1.26140  1.40403 -0.46180
O  -1.26249 -1.10169 -0.98482
S  -0.94356  0.00005 -0.00005
C   0.96179 -0.00018  0.00021
F   1.46801 -1.20324  0.39517
F   1.46721  0.25929 -1.23928
F   1.46778  0.94357  0.84445
O  -1.26371 -0.30188  1.44617
```

CF_3SO_3H

```
BP86 Energy = -574.047272559
Enthalpy 0K= -574.010780
Enthalpy 298K= -574.002498
Free Energy 298K= -574.044527
PCM (CH2Cl2)= -574.047273

C  -1.03504  0.00742 -0.00078
F  -1.44373 -0.19041 -1.25906
F  -1.56886 -0.91607  0.81028
F  -1.38459  1.23762  0.41081
S   0.86933 -0.15143  0.08598
O   1.28852  0.24523  1.45513
O   1.25964  1.09335 -0.96715
H   1.51062  1.84126 -0.38028
O   1.24746 -1.41899 -0.56909
```

$CF_3CO_2^-$

```
BP86 Energy = -526.240029439
Enthalpy 0K= -526.215325
Enthalpy 298K= -526.209059
Free Energy 298K= -526.247272
PCM (CH2Cl2)= -526.235296

O  -1.54554 -1.15936  0.00004
O  -1.60583  1.15180  0.00003
C  -1.07638  0.01026 -0.00130
C   0.51382  0.01318 -0.00010
F   1.09229  1.26187  0.00044
F   1.04120 -0.63551  1.09971
F   1.04277 -0.63527 -1.09928
```

CF_3CO_2H

```
BP86 Energy = -526.789395124
Enthalpy 0K= -526.751670
Enthalpy 298K= -526.746197
Free Energy 298K= -526.781277
PCM (CH2Cl2)= -526.789424

C   0.12522  0.59048  0.00000
F  -1.03327  1.28407  0.00000
F   0.83675  0.93563  1.09917
F   0.83675  0.93563 -1.09917
```

```
C  -0.08938 -0.94828  0.00000
O   0.83675 -1.73505  0.00000
O  -1.40399 -1.26531  0.00000
H  -1.43915 -2.24824  0.00000
```

$CCl_3CO_2^-$

```
BP86 Energy = -271.807878231
Enthalpy 0K= -271.789429
Enthalpy 298K= -271.781447
Free Energy 298K= -271.824540
PCM (CH2Cl2)= -271.805960

O  -2.13195 -0.88679 -0.00001
O  -1.90269  1.41502 -0.00002
C  -1.56558  0.21990 -0.00001
C   0.10565  0.01231 -0.00000
Cl  1.10683  1.57598 -0.00005
Cl  0.65354 -0.95321  1.49523
Cl  0.65355 -0.95330 -1.49517
```

CCl_3CO_2H

```
BP86 Energy = -272.329024474
Enthalpy 0K= -272.296778
Enthalpy 298K= -272.290026
Free Energy 298K= -272.328937
PCM (CH2Cl2)= -272.329077

C   0.01578  0.20053  0.00000
Cl -1.58771  1.01920  0.00000
Cl  0.93367  0.68704  1.48092
Cl  0.93367  0.68704 -1.48092
C  -0.06218 -1.36314  0.00000
O   0.93367 -2.05682  0.00000
O  -1.33463 -1.80829  0.00000
H  -1.26764 -2.78924  0.00000
```

$PhCO_2^-$

```
BP86 Energy = -420.255572485
Enthalpy 0K= -420.156934
Enthalpy 298K= -420.149796
Free Energy 298K= -420.188999
PCM (CH2Cl2)= -420.255572

O   2.37763 -1.15116 -0.00000
O   2.37810  1.15102 -0.00000
C   1.84350 -0.00000  0.00000
C   0.28211  0.00006  0.00000
C  -0.43809  1.21021  0.00000
C  -1.84277  1.21596  0.00000
C  -2.55219 -0.00001 -0.00000
C  -1.84271 -1.21593  0.00000
C  -0.43803 -1.21010  0.00000
H   0.16041  2.12938  0.00000
H  -2.39378  2.16706 -0.00000
H  -3.65026 -0.00003 -0.00000
H  -2.39365 -2.16708 -0.00000
H   0.16052 -2.12926  0.00000
```

$PhCO_2H$

```
BP86 Energy = -420.825105495
Enthalpy 0K= -420.712755
Enthalpy 298K= -420.705447
Free Energy 298K= -420.744901
PCM (CH2Cl2)= -420.825088

C  -1.71086  0.12137  0.00000
O  -2.32323 -1.10471  0.00000
O  -2.35032  1.16898  0.00000
H  -3.28309 -0.89924  0.00000
C  -0.22291  0.02561  0.00000
C   0.51176  1.22914  0.00000
C   1.91146  1.19583  0.00000
C   2.58443 -0.03868  0.00000
C   1.85497 -1.24001  0.00000
C   0.45352 -1.21227  0.00000
H  -0.03979  2.17393  0.00000
H   2.48022  2.13130  0.00000
H   3.67929 -0.06474  0.00000
H   2.38052 -2.20049  0.00000
H  -0.12302 -2.14101  0.00000
```

$[IrCpCl_2(\eta^1\text{-}CH_3CO_2)]^-$

```
BP86 Energy = -556.756905088
Enthalpy 0K= -556.624004
Enthalpy 298K= -556.609649
Free Energy 298K= -556.668298
PCM (CH2Cl2)= -556.756902

Ir -0.34939 -0.02473 -0.00006
Cl -0.48290 -1.73846  1.74333
Cl -0.50380 -1.75214 -1.72891
C  -0.36284  2.02455  0.73370
C  -1.55688  1.33384  1.16298
C  -2.31549  0.91572 -0.00600
C  -1.54825  1.33723 -1.16908
C  -0.35786  2.02622 -0.72857
H   0.42590  2.42880  1.36404
H  -1.81238  1.09360  2.19575
H  -3.25520  0.36578 -0.01020
H  -1.79663  1.10072 -2.20441
H   0.43677  2.43036 -1.35157
O   1.69007 -0.53634 -0.01058
C   2.62841  0.37843 -0.00614
C   4.02590 -0.26852 -0.00918
H   4.14580 -0.90507  0.88353
H   4.80424  0.50943 -0.02015
H   4.13602 -0.92297 -0.88990
O   2.49923  1.61875  0.00135
```

$[IrCpCl_2(\eta^1\text{-}OHCO_2)]^-$

```
BP86 Energy = -592.683534252
Enthalpy 0K= -592.572321
Enthalpy 298K= -592.558831
Free Energy 298K= -592.615335
PCM (CH2Cl2)= -592.683534

Ir -0.33990 -0.01991 -0.00003
Cl -0.50718 -1.73158  1.73942
Cl -0.53161 -1.74603 -1.72343
C  -0.30007  2.02654  0.73690
C  -1.51151  1.36667  1.16342
C  -2.27495  0.96465 -0.00926
C  -1.49731  1.37343 -1.17146
C  -0.29171  2.03006 -0.72586
H   0.50238  2.40349  1.36745
H  -1.77545  1.13163  2.19518
H  -3.22709  0.43667 -0.01650
H  -1.74931  1.14517 -2.20766
```

```
H   0.52045  2.40714 -1.34384
O   1.69076 -0.56936 -0.01213
C   2.64141  0.33623 -0.00648
O   3.89052 -0.27907 -0.01050
H   3.67113 -1.23419 -0.01438
O   2.58050  1.57053  0.00093
```

[IrCpCl$_2$(η^1-CF$_3$SO$_3$)]$^-$

```
BP86 Energy = -901.746304707
Enthalpy 0K= -901.635919
Enthalpy 298K= -901.618020
Free Energy 298K= -901.685965
PCM (CH2Cl2)= -901.746305

Ir  1.14849  0.06193 -0.00013
Cl  1.24749  1.77757  1.70630
Cl  1.24661  1.78012 -1.70404
C   1.16020 -1.99858  0.73159
C   2.33938 -1.29974  1.17179
C   3.08247 -0.84420 -0.00081
C   2.33942 -1.29808 -1.17406
C   1.16025 -1.99758 -0.73491
H   0.36285 -2.39123  1.36269
H   2.58830 -1.06380  2.20682
H   4.01950 -0.28907 -0.00037
H   2.58844 -1.06078 -2.20875
H   0.36285 -2.38925 -1.36654
O  -0.99198  0.52290  0.00049
S  -1.98141 -0.68627  0.00128
C  -3.58976  0.32549 -0.00079
F  -3.67447  1.10563  1.09537
F  -4.64297 -0.53269  0.00132
F  -3.67462  1.10040 -1.10068
O  -2.00819 -1.47899 -1.27669
O  -2.00932 -1.47632  1.28077
```

[IrCpCl$_2$(η^1-CF$_3$CO$_2$)]$^-$

```
BP86 Energy = -854.477012636
Enthalpy 0K= -854.366360
Enthalpy 298K= -854.350125
Free Energy 298K= -854.414605
PCM (CH2Cl2)= -854.477013

Ir -0.89806 -0.02954 -0.00005
Cl -0.90741 -1.76045  1.71149
Cl -0.96779 -1.73690 -1.73361
C  -1.00203  2.02040  0.74265
C  -2.14106  1.26386  1.20126
C  -2.89717  0.79572  0.04675
C  -2.19238  1.27526 -1.13465
C  -1.03438  2.02803 -0.71977
H  -0.22334  2.46851  1.35611
H  -2.35699  1.00858  2.23931
H  -3.80588  0.19596  0.06383
H  -2.45353  1.02956 -2.16463
H  -0.28205  2.48069 -1.36187
O   1.18528 -0.42971 -0.03447
C   2.04339  0.53720 -0.05772
C   3.51017  0.00580 -0.00526
F   4.01491  0.16744  1.25803
F   4.31328  0.71978 -0.84814
F   3.64842 -1.30231 -0.33175
O   1.89500  1.77029 -0.07746
```

[IrCpCl$_2$(η^1-CCl$_3$CO$_2$)]$^-$

```
BP86 Energy = -600.019422060
Enthalpy 0K= -599.914589
Enthalpy 298K= -599.896843
Free Energy 298K= -599.965669
PCM (CH2Cl2)= -600.019422

Ir -1.37431  0.01714 -0.00001
Cl -1.41330  1.73385 -1.71493
Cl -1.41147  1.72980  1.71889
C  -1.49041 -2.04031 -0.73114
C  -2.63572 -1.28592 -1.17222
C  -3.36285 -0.80253 -0.00360
C  -2.64022 -1.28506  1.16794
C  -1.49320 -2.04001  0.73204
H  -0.72416 -2.49188 -1.35791
H  -2.87246 -1.03710 -2.20724
H  -4.27124 -0.20192 -0.00554
H  -2.88083 -1.03531  2.20185
H  -0.72961 -2.49148  1.36209
O   0.73669  0.40944 -0.00086
C   1.58014 -0.55823  0.00164
C   3.08717 -0.02974 -0.00006
Cl  3.93551 -0.69605 -1.48311
Cl  3.93918 -0.69434  1.48101
Cl  3.27877  1.76308 -0.00130
O   1.44373 -1.78808  0.00464
```

[IrCpCl$_2$(η^1-PhCO$_2$)]$^-$

```
BP86 Energy = -748.496863638
Enthalpy 0K= -748.312185
Enthalpy 298K= -748.294836
Free Energy 298K= -748.361999
PCM (CH2Cl2)= -748.496864

Ir -1.23621 -0.04639 -0.00022
Cl -1.14482 -1.76640  1.73222
Cl -1.14737 -1.77860 -1.72128
C  -1.52919  1.98264  0.73929
C  -2.62175  1.13603  1.15668
C  -3.30296  0.61888 -0.02112
C  -2.59401  1.15045 -1.17733
C  -1.51218  1.99072 -0.72304
H  -0.80629  2.48462  1.37831
H  -2.85176  0.86018  2.18653
H  -4.16038 -0.05222 -0.03516
H  -2.80027  0.88801 -2.21562
H  -0.77126  2.49673 -1.33776
O   0.85679 -0.27686 -0.00101
C   1.67271  0.74519  0.00275
C   3.13439  0.31864  0.00063
O   1.38867  1.96290  0.00743
C   4.12914  1.31588 -0.00071
C   5.48742  0.96666 -0.00289
C   5.86424 -0.38783 -0.00341
C   4.87500 -1.38716 -0.00188
C   3.51529 -1.03862 -0.00004
H   3.79817  2.35937  0.00010
H   6.25536  1.74980 -0.00415
H   6.92565 -0.66382 -0.00500
H   5.16572 -2.44436 -0.00219
H   2.72798 -1.79788  0.00092
```

[IrCpCl(η^2-CH$_3$CO$_2$)]

```
BP86 Energy = -541.622669298
```

Enthalpy 0K= -541.489194
Enthalpy 298K= -541.477326
Free Energy 298K= -541.529407
PCM (CH_2Cl_2)= -541.622669

Ir	-0.22545	0.00322	-0.00118
C	-2.17288	0.30094	-0.88098
H	-2.37844	1.03641	-1.65722
C	-1.75696	-1.07519	-1.08558
H	-1.56030	-1.53673	-2.05422
C	-1.58996	-1.71557	0.19925
H	-1.28693	-2.74655	0.37651
C	-1.87005	-0.70899	1.21292
H	-1.77820	-0.84883	2.29045
C	-2.24963	0.51904	0.55717
H	-2.48664	1.46143	1.04979
O	1.59318	-0.49642	1.09852
O	1.58776	-0.50021	-1.09228
C	2.25863	-0.61398	0.00263
C	3.74428	-0.82964	-0.00182
H	4.04924	-1.38295	-0.90215
H	4.24281	0.15489	-0.01385
H	4.05681	-1.36555	0.90629
Cl	0.63961	2.21724	0.00140

[IrCpCl(η^2-$OHCO_2$)]

BP86 Energy = -577.540564044
Enthalpy 0K= -577.429022
Enthalpy 298K= -577.417984
Free Energy 298K= -577.467783
PCM (CH_2Cl_2)= -577.540564

Ir	0.21124	0.00924	0.00026
C	2.15618	0.33419	0.85860
H	2.36436	1.09759	1.60679
C	1.74443	-1.03407	1.11420
H	1.55293	-1.46007	2.10001
C	1.57179	-1.72204	-0.14593
H	1.26772	-2.75871	-0.28373
C	1.84032	-0.75276	-1.19586
H	1.73695	-0.93100	-2.26677
C	2.21936	0.50270	-0.58850
H	2.45637	1.42569	-1.11654
O	-1.60116	-0.50030	-1.13090
O	-1.62795	-0.49806	1.08720
C	-2.24879	-0.62368	-0.03495
Cl	-0.65501	2.21781	-0.00081
O	-3.56280	-0.89106	-0.07455
H	-3.87320	-0.89846	0.85438

[IrCpCl(η^2-CF_3SO_3)]

BP86 Energy = -886.584640171
Enthalpy 0K= -886.474208
Enthalpy 298K= -886.458408
Free Energy 298K= -886.521689
PCM (CH_2Cl_2)= -886.581913

Ir	-1.13277	0.17109	0.00003
Cl	-1.33754	2.47586	-0.00002
O	0.84982	0.59492	-0.00003
C	-3.04132	-0.54954	0.71656
H	-3.68577	0.04837	1.36042
C	-3.03990	-0.55044	-0.71893
H	-3.68317	0.04670	-1.36469
C	-1.96319	-1.43926	-1.16042
H	-1.66853	-1.61670	-2.19522
C	-1.34544	-2.03315	0.00135
H	-0.49960	-2.71922	0.00260
C	-1.96536	-1.43763	1.16119
H	-1.67257	-1.61361	2.19678
S	1.84425	-0.69515	-0.00005
O	1.77115	-1.44390	-1.28958
O	1.77113	-1.44402	1.28943
C	3.46636	0.30974	0.00003
F	4.48818	-0.56604	-0.00025
F	3.52596	1.07495	1.09939
F	3.52577	1.07545	-1.09899

[IrCpCl(η^2-CF_3CO_2)]

BP86 Energy = -839.324411658
Enthalpy 0K= -839.213549
Enthalpy 298K= -839.200548
Free Energy 298K= -839.256014
PCM (CH_2Cl_2)= -839.324412

Ir	-0.79533	0.01873	-0.00207
C	-2.71117	-0.05446	-0.96856
H	-2.98687	0.56159	-1.82328
C	-2.10420	-1.37944	-1.01642
H	-1.80293	-1.90280	-1.92483
C	-1.91017	-1.85516	0.32924
H	-1.46741	-2.80610	0.62310
C	-2.36900	-0.80243	1.22744
H	-2.30991	-0.82268	2.31599
C	-2.88886	0.28592	0.43442
H	-3.27131	1.23101	0.81927
O	1.10291	-0.23626	1.11031
O	1.09763	-0.23998	-1.09727
C	1.74150	-0.26560	0.00632
C	3.28145	-0.27009	0.00001
F	3.75013	-0.92690	-1.08606
F	3.73954	1.00378	-0.03347
F	3.76023	-0.87307	1.11184
Cl	-0.23598	2.31295	0.00230

[IrCpCl(η^2-CCl_3CO_2)]

BP86 Energy = -584.860960814
Enthalpy 0K= -584.755692
Enthalpy 298K= -584.741334
Free Energy 298K= -584.799764
PCM (CH_2Cl_2)= -584.860961

Ir	-1.26383	0.01789	-0.00116
C	-3.18818	-0.11137	-0.93866
H	-3.50420	0.52181	-1.76651
C	-2.52439	-1.40436	-1.04289
H	-2.21323	-1.87973	-1.97406
C	-2.28707	-1.91927	0.28212
H	-1.79657	-2.85863	0.53424
C	-2.77542	-0.92084	1.22332
H	-2.69411	-0.97595	2.30932
C	-3.35484	0.17313	0.47922
H	-3.77577	1.08395	0.90428
O	0.65014	-0.16315	1.11035
O	0.64365	-0.16858	-1.09644
C	1.28688	-0.18170	0.00637
C	2.83307	-0.16333	0.00018
Cl	3.46039	-0.99770	-1.47162
Cl	3.35403	1.56700	-0.00740
Cl	3.47116	-0.98800	1.47249

```
Cl -0.81449  2.33349  0.00140
```

[IrCpCl(η^2-PhCO$_2$)]

```
BP86 Energy = -733.357899887
Enthalpy 0K= -733.172571
Enthalpy 298K= -733.157679
Free Energy 298K= -733.217432
PCM (CH2Cl2)= -733.357900

C  -5.67622 -0.19733 -0.00008
C  -4.97571 -0.18448  1.21887
C  -3.57526 -0.16808  1.22330
C  -2.87112 -0.16428  0.00048
C  -3.57466 -0.17586 -1.22263
C  -4.97510 -0.19229 -1.21874
C  -1.39345 -0.15328  0.00086
O  -0.70849 -0.14833  1.09748
O  -0.70855 -0.15290 -1.09584
Ir  1.16042  0.00463  0.00009
Cl  0.73607  2.34153 -0.00463
C   2.90965 -0.49156  1.17415
C   3.31444  0.24047 -0.00398
C   2.90643 -0.50130 -1.17475
C   2.26866 -1.73405 -0.71334
C   2.27057 -1.72796  0.72450
H   3.05258 -0.19860 -2.21078
H   3.75919  1.23582 -0.00874
H   3.05926 -0.18066  2.20724
H   1.83722 -2.49287  1.36900
H   1.83414 -2.50459 -1.35029
H  -3.01102 -0.16658 -2.15986
H  -5.52265 -0.19875 -2.16669
H  -6.77130 -0.20895 -0.00032
H  -5.52372 -0.18474  2.16659
H  -3.01205 -0.15274  2.16072
```

[IrCpDMBACl]

```
BP86 Energy = -718.057534215
Enthalpy 0K= -717.786697
Enthalpy 298K= -717.769795
Free Energy 298K= -717.830856
PCM (CH2Cl2)= -718.057534

Ir  0.62185 -0.14689  0.04711
N  -0.22446  1.82599 -0.50119
C  -1.37773 -0.56920  0.01182
C   1.25154 -1.94043 -0.98644
H   0.51695 -2.65630 -1.35577
C   1.85120 -1.93105  0.33058
H   1.68231 -2.65217  1.12899
C   2.82472 -0.83759  0.35452
H   3.40534 -0.53870  1.22746
C   2.78416 -0.16384 -0.88501
H   3.35948  0.72369 -1.14947
C   1.76934 -0.80915 -1.72207
H   1.54186 -0.56834 -2.76071
C   0.60709  2.95976 -0.00661
C  -0.35135  1.91929 -1.98397
H   1.58793  2.92665 -0.50427
H   0.74255  2.84664  1.07858
H   0.11197  3.92394 -0.23612
H   0.64331  1.81371 -2.43942
H  -0.78296  2.90007 -2.26654
H  -1.00783  1.11186 -2.33758
C  -1.60161  1.89311  0.11551
H  -1.44248  2.12001  1.18359
H  -2.17543  2.72074 -0.34748
C  -2.25823  0.54608 -0.02717
C  -3.64937  0.38172 -0.12437
H  -4.30199  1.26313 -0.16246
C  -4.20432 -0.90787 -0.15833
H  -5.28872 -1.03942 -0.23267
C  -3.35454 -2.02316 -0.09089
H  -3.77662 -3.03471 -0.09987
C  -1.95992 -1.85575 -0.01031
H  -1.32754 -2.74783  0.05973
Cl  0.36556  0.55555  2.36417
```