

# Hyperconjugative $\pi \rightarrow \sigma^*_{CF}$ Interactions Stabilize the Enol Form of Perfluorinated Cyclic Keto–Enol Systems

Brian J. Levandowski,<sup>†,‡</sup> Ronald T. Raines,<sup>\*,‡</sup> K. N. Houk<sup>\*,†</sup>

<sup>†</sup>Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095, United States; and <sup>‡</sup>Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

[rtraines@mit.edu](mailto:rtraines@mit.edu)

[houk@chem.ucla.edu](mailto:houk@chem.ucla.edu)

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**Table S1. M06-2X/6-31G(d) optimized cartesian coordinates of Keto(K) and Enol(E) systems 1–10.**

**1E**

C	1.56343700	-0.40146500	-0.00362100
C	-0.64351800	0.80612600	-0.00896800
C	0.68776400	0.83536800	-0.00831300
F	1.68074600	-0.90766300	1.22517100
F	2.77852700	-0.09697300	-0.44762700
O	1.39617200	1.97814600	0.01260800
F	1.05214700	-1.34833600	-0.79552300
C	-1.56187600	-0.38528100	0.00190900
F	-2.73244600	-0.02983100	0.53238700
F	-1.79460300	-0.85841800	-1.22501700
F	-1.05126900	-1.37790400	0.73455100
F	-1.29079200	1.98824200	-0.02786600
H	0.77499700	2.72428900	0.04841600

**1K**

C	1.51042982	-0.71639664	0.22340456
C	3.71870831	-1.35295129	-1.13051725
C	2.40790988	-1.77633207	-0.44192725
F	1.87504215	-0.56415490	1.51428810
F	0.22226635	-1.11586694	0.16375265
O	2.07016973	-2.98841332	-0.42292199
H	4.54412955	-1.84392447	-0.65879157
F	1.64722896	0.45999609	-0.42458165
C	3.89209688	0.17254649	-1.01054664
F	4.84998558	0.58535248	-1.86759999
F	2.72605983	0.78297929	-1.31092870
F	4.25224168	0.48659412	0.25205774
F	3.67436908	-1.69964067	-2.43448831

**2E**

C	1.50786600	0.11855500	0.09802200
C	-0.60088000	1.42608100	-0.02841100
C	0.73139000	1.40634400	0.02182300
C	-1.49385800	0.23197700	-0.09537300
C	-0.73870500	-1.04268800	0.31389400
C	0.65467000	-1.09142700	-0.31518700
F	-2.54388500	0.39820500	0.73350300
F	-1.98350800	0.06054900	-1.34320900
F	1.95213300	-0.07755000	1.35630900
F	2.57580200	0.18350700	-0.71666900
O	1.50921200	2.49749400	0.05761000
H	0.94583400	3.28858400	0.02919100

F	-1.23560700	2.60831100	-0.06767800
F	-0.59887800	-1.04381800	1.65300700
F	-1.43753100	-2.12153100	-0.06031600
F	1.27326100	-2.22152400	0.04845700
F	0.51127700	-1.07076800	-1.65436900

### 2K

C	1.53184746	-0.69696287	0.14450343
C	3.65438855	-1.35415222	-1.07161341
C	2.51842344	-1.73619967	-0.42628459
C	3.86592093	0.10388244	-1.52826781
C	3.07250414	1.08304156	-0.64475559
C	1.60997062	0.62862880	-0.63367401
F	5.17855691	0.41552455	-1.47962648
F	3.41864533	0.21360910	-2.79728499
F	1.87144699	-0.45974597	1.42937708
F	0.27205943	-1.17888659	0.08807966
O	2.24228623	-3.12929119	-0.25911926
F	3.54560353	1.08934611	0.61961667
F	3.18072380	2.32327961	-1.16686484
F	0.83335568	1.54203021	-0.01313625
F	1.18362697	0.47167237	-1.90493156
F	3.75900178	-2.12860649	-2.17242068
H	4.47412068	-1.60052103	-0.42955295

### 3E

C	1.24936900	-0.03820100	0.08283100
C	-0.80268900	1.13708000	-0.02583400
C	0.52530500	1.25933900	-0.02392300
C	-1.20481900	-0.30503600	0.08516100
F	-1.68886800	-0.58987900	1.31074600
F	-2.14018100	-0.63988300	-0.81848200
F	1.80435400	-0.22700500	1.29955900
F	2.23064700	-0.15921400	-0.83096300
C	0.12021300	-1.07495000	-0.15534300
O	-1.76007400	2.06567500	-0.08257900
H	-1.35489000	2.94742600	-0.11601300
F	1.18433300	2.41512300	-0.07411600
F	0.23502500	-2.12992700	0.65652000
F	0.16482500	-1.48501600	-1.43223100

### 3K

C	-0.00880000	-1.21501800	0.07482000
C	-0.02433500	0.66329400	-1.32579100
C	-0.02406500	-0.66329400	-1.32579100
C	-0.00880000	1.21501800	0.07482000

F	1.11022800	1.96144600	0.28193300
F	-1.06163200	2.05399000	0.27794700
F	1.11003200	-1.96159000	0.28234700
F	-1.06182800	-2.05384600	0.27753300
C	-0.06380000	0.00000000	1.00681700
O	-0.02725587	1.53401225	-2.46013715
F	1.06849996	-1.10390111	-1.98508395
H	-0.90098425	-1.01287066	-1.82948613
F	0.98612692	-0.00009513	1.85543555
F	-1.22088111	0.00009501	1.70227606

#### 4E

C	0.09387900	-0.92876100	-0.00009200
C	-0.50513500	1.04516300	0.00003800
C	-1.17208700	-0.11887900	0.00016600
C	0.85397500	0.42508900	0.00006700
O	-2.42620000	-0.56145000	0.00010000
H	-3.04331800	0.18702400	0.00019900
F	-0.88832200	2.31065600	-0.00014700
F	1.62094700	0.62834900	1.08656600
F	1.62113000	0.62852900	-1.08632300
F	0.31370900	-1.68559300	1.08826400
F	0.31355100	-1.68539700	-1.08859100

#### 4K

C	2.13366640	-0.44678784	-0.21748689
C	3.75644200	-1.50163772	-0.99838153
C	2.50715357	-1.90832759	-0.51658950
C	3.23788730	-0.06317100	-1.16260092
O	1.84975976	-3.16831516	-0.35795566
F	4.07318273	-2.07880426	-2.17696292
F	2.81600351	0.10739578	-2.43359307
F	3.98409209	1.02301651	-0.86955638
F	0.89930659	0.05400474	-0.43671884
F	2.42024500	-0.17748076	1.07396439
H	4.52855675	-1.58052421	-0.26182485

#### 5E

C	-0.61549300	0.68015200	0.00162300
C	-0.65620200	-0.62879200	0.00054400
C	0.66604400	0.01913900	0.00005400
F	1.48757000	-0.01754400	-1.07982700
F	1.48913000	-0.01999900	1.07871200
O	-1.37586600	-1.74749400	-0.00155500
F	-1.26342100	1.82282400	0.00052100
H	-0.77867900	-2.51056800	0.00446600

**5K**

C	2.21410354	-0.81285227	-1.14755206
C	3.63232024	-1.24780663	-0.93598046
C	3.30781547	0.22881878	-1.03126954
F	3.69392554	0.96268812	-2.09656519
F	3.39267098	1.03683701	0.04687984
O	4.58984909	-2.29441972	-0.75531631
F	1.72113593	-1.00782105	-2.38911161
H	1.56909624	-0.90499133	-0.29880240

**6E**

C	-0.81202200	1.36970800	-0.00000900
C	0.74113000	-0.64706100	-0.00004200
C	-0.47290300	-0.08803200	-0.00000800
H	0.78749500	-1.73747200	-0.00012000
O	-1.62825600	-0.82510300	0.00001700
H	-1.39589600	-1.76525600	0.00009300
H	-1.41576900	1.60616900	0.88179100
H	-1.41664300	1.60588600	-0.88128400
H	0.07478400	2.00206700	-0.00055400
C	2.06422100	0.05976800	0.00002000
H	2.65732600	-0.21154900	0.88085500
H	2.65745500	-0.21157000	-0.88071300
H	1.95474000	1.14624800	0.00002100

**6K**

C	-1.88928900	-0.48752500	0.00000000
C	0.67723600	-0.76749300	0.00000000
C	-0.52202500	0.16669200	0.00000000
O	-0.39086800	1.36953800	0.00000000
H	-2.00299500	-1.12788900	-0.88108100
H	-2.66403900	0.27948800	0.00000100
H	-2.00299400	-1.12789100	0.88107900
H	0.58945400	-1.42798000	-0.87318800
C	2.00281200	-0.02027100	0.00000000
H	2.84373200	-0.71804000	-0.00000100
H	2.08096200	0.62278600	-0.87963800
H	2.08096400	0.62278500	0.87963800
H	0.58945400	-1.42798000	0.87318900

**7E**

C	0.36759400	-1.27889000	0.07662800
C	0.35354200	1.22419200	-0.09465300
C	1.02029100	0.07122800	0.00635700

H	0.91095000	2.15812300	-0.16484400
C	-1.15227200	1.29767900	-0.10987100
C	-1.78280700	-0.01440500	0.36216300
C	-1.10809400	-1.20585700	-0.31721800
H	-1.65843000	-0.10552100	1.44910800
H	-1.18752700	-1.08952700	-1.40574600
H	-1.61182800	-2.14204100	-0.05635000
H	-2.85853700	-0.01076800	0.15820400
O	2.38146600	-0.03227100	0.06278500
H	2.76067200	0.85898900	0.05301200
H	-1.48897400	2.12333600	0.52860200
H	-1.50904500	1.53441400	-1.12296200
H	0.48003000	-1.67119100	1.09629500
H	0.92144100	-1.96132300	-0.57803200

### 7K

C	-0.38806300	1.28160800	0.36087900
C	-0.38804300	-1.28177000	0.36074900
C	-1.15093900	-0.00023000	0.07145000
H	-0.99079900	-2.12869400	0.02453800
C	1.00430000	-1.25902500	-0.29037300
C	1.77795800	0.00013600	0.10368000
C	1.00404500	1.25926800	-0.29041300
H	1.94586900	0.00018200	1.18991500
H	0.89102100	1.28601500	-1.38202100
H	1.55835900	2.15985800	-0.00746400
H	2.76522300	-0.00002400	-0.37039400
O	-2.28083700	0.00006200	-0.36111700
H	-0.26825100	-1.35868400	1.45122500
H	1.55851100	-2.15959900	-0.00704800
H	0.89138500	-1.28603600	-1.38195500
H	-0.26828400	1.35868200	1.45138400
H	-0.99189000	2.12787900	0.02491900

### 8E

C	1.42961100	0.82400900	0.10253500
C	-0.78094400	0.05883100	-0.00174200
C	-0.03508800	1.16623600	-0.02884200
H	-0.41814100	2.18079900	-0.07980800
C	0.03237500	-1.19833200	0.13864200
C	1.45518600	-0.69857100	-0.17683700
H	2.22702700	-1.22213400	0.39225900
H	1.65989200	-0.86061900	-1.23944200
O	-2.12933700	-0.08281500	-0.04151400
H	-2.53340800	0.79635700	-0.07985500
H	1.80035700	1.05204700	1.11163700

H	2.06600300	1.37557400	-0.59780400
H	-0.06084400	-1.58688100	1.16116900
H	-0.31302300	-1.98566300	-0.53857900

**8K**

C	-1.37245900	-0.73247700	0.23821000
C	0.92184600	0.00000100	0.00000400
C	0.02779900	-1.23470900	-0.12710500
H	0.40970000	-2.05626900	0.48300500
C	0.02779400	1.23470900	0.12710500
C	-1.37246500	0.73247200	-0.23821000
H	-2.17392000	1.32292200	0.21172800
H	-1.50732800	0.76438500	-1.32570300
O	2.12657400	0.00000300	-0.00000100
H	0.06770100	-1.55758700	-1.17599600
H	-1.50731700	-0.76438400	1.32570400
H	-2.17391400	-1.32293100	-0.21172300
H	0.40969500	2.05626000	-0.48301700
H	0.06769300	1.55760400	1.17598800

**9E**

C	0.52481100	-1.04325500	0.00016100
C	0.34239600	1.06676700	-0.00004400
C	-0.51495800	0.03854900	-0.00004300
H	0.24147500	2.14599200	0.00092200
C	1.54637200	0.14223700	-0.00004100
O	-1.85067400	-0.13971700	-0.00015100
H	-2.27975800	0.72885100	0.00052300
H	2.17913000	0.18239400	-0.89227800
H	0.54606700	-1.67441500	-0.89264200
H	2.18086600	0.18256300	0.89069100
H	0.54588600	-1.67342900	0.89380000

**9K**

C	0.38638600	1.10559200	0.08086200
C	0.38641900	-1.10561200	0.08082400
C	-0.67376200	-0.00002500	0.03249200
H	0.29447000	-1.88444100	-0.68013200
C	1.45715300	0.00002400	-0.12798200
O	-1.86622800	-0.00000200	-0.07710400
H	0.42865900	-1.57860700	1.06745500
H	0.29431600	1.88417100	-0.68035300
H	0.42866800	1.57894200	1.06730200
H	1.86496500	0.00008300	-1.14041200
H	2.28157200	-0.00000700	0.58579800

**10E**

C	-0.80306600	0.84806300	0.00003900
C	0.21271700	0.04753200	0.00001900
C	-1.08355800	-0.65441900	-0.00002100
O	1.52338300	-0.20466200	0.00003100
H	1.99660600	0.64191800	-0.00023700
H	-1.44081700	-1.13743600	-0.91388000
H	-1.44102300	-1.13738900	0.91378000
H	-1.25839300	1.82314600	-0.00013200

**10K**

C	0.85913900	0.78104900	0.00023800
C	-0.38471000	-0.00006700	-0.00082600
C	0.85935400	-0.78100800	0.00025000
O	-1.58119200	-0.00004000	0.00018900
H	1.16082600	1.28339300	0.91524100
H	1.16116200	-1.28332200	0.91518600
H	1.16242300	-1.28187600	-0.91507200
H	1.16243100	1.28228200	-0.91484300

**Table S2. Coordinates of the endocyclic and exocyclic structures from Isodesmic Equations 1-5****(1)-Endocyclic**

C	-0.62285900	1.45250700	-0.00001800
C	0.73135100	-0.67586700	-0.00001400
C	-0.44590000	-0.04273800	0.00005800
H	0.70789000	-1.76614600	0.00024700
H	-1.19862100	1.76745800	0.87890100
H	-1.19675000	1.76800000	-0.87996100
H	0.32032200	2.00032600	0.00141000
C	2.10706300	-0.07660000	-0.00000400
H	2.67279600	-0.40506000	0.87953800
H	2.67243000	-0.40504400	-0.87976600
H	2.09670000	1.01486000	-0.00016800
C	-1.73942000	-0.81582100	-0.00004200
H	-2.34443200	-0.56417300	-0.88000700
H	-1.56710700	-1.89515000	0.00019800
H	-2.34464100	-0.56395500	0.87973100

**(1)-Exocyclic**

C	-0.89799600	1.35871400	0.04898000
C	0.80318700	-0.49725600	0.53209600
C	-0.59046000	-0.11516600	0.09444200
H	0.88389300	-1.58887700	0.56836700
H	-0.64583100	1.83934600	1.00216200



H	-1.95522800	1.53923200	-0.15984500
H	-0.30987100	1.86297300	-0.72649800
H	0.96950900	-0.13183700	1.55516500
C	1.89739800	0.06969400	-0.37895800
H	1.91337800	1.16349000	-0.35347400
H	2.88424900	-0.28292200	-0.06618600
H	1.73538000	-0.24191700	-1.41558200
C	-1.49688500	-1.03379800	-0.23768300
H	-1.26650200	-2.09527100	-0.20808400
H	-2.50044400	-0.75734300	-0.54929200

**(2)-Endocyclic**

C	-0.32837200	-1.26447200	-0.07899500
C	-0.30321400	1.21952200	0.09467300
C	-1.00317500	0.08624900	-0.00401000
H	-0.84134400	2.16444400	0.16592900
C	1.20243200	1.28936800	0.10591300
C	1.83406400	-0.02303600	-0.36077600
C	1.14756700	-1.20780900	0.31734400
H	1.71475000	-0.11568200	-1.44826700
H	1.22514600	-1.08979400	1.40617100
H	1.64520600	-2.14877600	0.06015700
H	2.90916100	-0.02295500	-0.15282300
H	1.53573900	2.11862300	-0.52986700
H	1.55182300	1.53110400	1.12057100
H	-0.42951900	-1.65710200	-1.10219100
H	-0.86844500	-1.97261400	0.56376400
C	-2.50599000	0.07134000	-0.05372100
H	-2.92100000	-0.48842900	0.79352900
H	-2.92178300	1.08227400	-0.03490800
H	-2.85959700	-0.42807100	-0.96462400

**(2)-Exocyclic**

C	-0.33889200	1.26648300	0.42874700
C	-0.33873000	-1.26639600	0.42886600
C	-1.10677100	-0.00001800	0.14099700
H	-0.93082400	-2.14558600	0.15490900
C	1.00885700	-1.26188100	-0.30958000
C	1.80969400	0.00001200	0.01997600
C	1.00888400	1.26190300	-0.30948600
H	2.05820900	-0.00007400	1.09082100
H	0.82110500	1.29833700	-1.39059900
H	1.58202000	2.15889100	-0.05066600
H	2.75946900	-0.00001100	-0.52607000
H	-0.14207900	-1.32894900	1.50987600
H	1.58193500	-2.15889700	-0.05072000

H	0.82114200	-1.29826300	-1.39068900
H	-0.14243200	1.32918300	1.50977200
H	-0.93105100	2.14552900	0.15453900
C	-2.33555500	-0.00008800	-0.37202100
H	-2.86109800	-0.92649200	-0.58819200
H	-2.86131900	0.92623600	-0.58797400

**(3)-Endocyclic**

C	1.49259100	0.81062300	0.09688100
C	-0.75382500	0.07587900	-0.00120600
C	0.02814500	1.15641700	-0.02567900
H	-0.33765400	2.17832000	-0.07975200
C	0.07309900	-1.18516300	0.14113800
C	1.50467800	-0.70929100	-0.17739700
H	2.27078400	-1.24086400	0.39260400
H	1.70744300	-0.87754900	-1.23980100
H	1.85898700	1.04242900	1.10681700
H	2.12789400	1.36564200	-0.60166600
H	-0.01254200	-1.57404700	1.16619800
H	-0.26410100	-1.98763800	-0.52573900
C	-2.24860600	0.03023900	-0.04356600
H	-2.59759400	-0.56915200	-0.89290900
H	-2.65012000	-0.44056900	0.86205900
H	-2.67958500	1.03120300	-0.12883300

**(3)-Exocyclic**

C	-1.41485700	-0.72377700	0.25389200
C	0.87479400	-0.00000200	0.00000000
C	-0.01462700	-1.22716000	-0.12867100
H	0.33380400	-2.06538500	0.48147500
C	-0.01462300	1.22715600	0.12867500
C	-1.41485300	0.72378100	-0.25389500
H	-2.22030400	1.33090900	0.16779800
H	-1.52748200	0.72895300	-1.34480000
H	-0.01785500	-1.56443500	-1.17368200
H	-1.52749100	-0.72894700	1.34479700
H	-2.22031000	-1.33090000	-0.16780300
H	0.33381400	2.06538700	-0.48146200
H	-0.01785500	1.56442200	1.17368900
C	2.20393100	-0.00000100	-0.00000100
H	2.77254200	0.92289200	0.07627900
H	2.77254800	-0.92288900	-0.07628500

**(4)-Endocyclic**

C	0.57184200	-1.03661900	0.00013700
C	0.42477300	1.04694500	0.00015300

C	-0.47791700	0.05898800	-0.00014800
H	0.33990500	2.13033700	0.00034000
C	1.62048600	0.11996800	-0.00019300
H	2.25658100	0.15852600	-0.89043400
H	0.58979900	-1.67506800	-0.88989000
H	2.25710700	0.15856000	0.88970600
H	0.58971900	-1.67409400	0.89085400
C	-1.96604600	-0.01658400	-0.00012000
H	-2.41315600	0.98129300	0.00033600
H	-2.32985100	-0.55781900	-0.88111500
H	-2.32892900	-0.55791500	0.88122800

**(4)-Exocyclic**

C	0.44384300	1.08810500	0.14089300
C	0.44408300	-1.08808100	0.14088900
C	-0.61355800	-0.00010400	0.09503600
H	0.31970900	-1.94078500	-0.53195500
C	1.48233900	0.00010400	-0.24413400
H	0.60519000	-1.46080000	1.15868300
H	0.31931200	1.94092000	-0.53176100
H	0.60491800	1.46051400	1.15881700
H	1.68312300	0.00007600	-1.31777500
H	2.42946000	0.00023800	0.29909200
C	-1.92312100	-0.00005500	-0.10726700
H	-2.48172100	-0.92777900	-0.19379400
H	-2.48150000	0.92780300	-0.19380400

**(5)-Endocyclic**

C	-1.13880000	-0.67535400	-0.00006300
C	-0.92038600	0.80976900	-0.00005500
C	0.15496100	0.09081800	0.00044000
H	-1.40407300	1.77400100	-0.00038800
C	1.62521200	-0.06731100	-0.00008500
H	2.13242100	0.90043100	0.00010900
H	1.94508900	-0.63417100	0.88045600
H	1.94443800	-0.63351500	-0.88129500
H	-1.47216700	-1.17713200	0.91251200
H	-1.47163200	-1.17714200	-0.91282100

**(5)-Exocyclic**

C	-0.93299200	-0.76482200	0.00029200
C	-0.93212500	0.76542500	0.00025000
C	0.31774200	-0.00074600	-0.00095200
H	-1.23450800	1.26993000	-0.91357800
H	-1.23264000	1.27141000	0.91383600
C	1.63660700	-0.00014500	0.00009200

H	2.20028000	0.92826600	0.00055500
H	2.20162700	-0.92774300	0.00014600
H	-1.23388600	-1.27044100	0.91401500
H	-1.23626600	-1.26970000	-0.91307000

**Table S3. Coordinates of the fluorinated(F) and hydrocarbon(H) alkane structures from Isodesmic Equations 6–10**

**(6)-F**

C	1.60658800	-0.10372700	-0.00397300
C	-0.68901200	0.82842200	-0.68593800
C	0.72404200	0.45185200	-1.10127700
H	-1.25404300	1.12285300	-1.57707400
C	-1.48365000	-0.28188000	-0.01002100
H	1.20543700	1.35655600	-1.48127700
H	0.69338500	-0.28523700	-1.90738300
F	1.26812300	-1.35913200	0.31803900
F	2.88170800	-0.12964700	-0.41856200
F	1.55114100	0.63531500	1.10650000
F	-1.38998200	-1.40882000	-0.72841300
F	-1.05255600	-0.52024500	1.22529000
F	-2.77437600	0.05621800	0.06377200
F	-0.66101200	1.88607100	0.18592800

**(6)-H**

C	-1.54687500	-0.56648600	-0.12374600
C	0.70398700	0.63519600	-0.30026900
C	-0.70394500	0.63520600	0.30025900
H	1.21759600	1.55803800	-0.00553100
H	-1.59589700	-0.64154300	-1.21605300
H	-2.57059900	-0.48403900	0.25273800
H	-1.13127500	-1.50471400	0.25594700
H	0.62712900	0.66013100	-1.39532300
C	1.54683200	-0.56652600	0.12374600
H	1.13103600	-1.50473300	-0.25575000
H	2.57052100	-0.48427600	-0.25290500
H	1.59604900	-0.64137300	1.21605900
H	-1.21751200	1.55808300	0.00557200
H	-0.62704500	0.66008700	1.39530700

**(7)-F**

C	-0.11690800	1.77905400	0.26277500
C	-1.10672400	-0.55131500	0.28664500
C	-1.30701200	0.91941700	-0.10621500
C	0.21769400	-1.10701500	-0.25624300
C	1.40669700	-0.19771500	0.08004300

C	1.15842900	1.23683200	-0.37133900
H	-0.00261500	1.78292400	1.35049100
H	-0.30524200	2.79905100	-0.08026400
F	-2.42791100	1.36726200	0.49158600
F	-1.49943600	0.95486300	-1.44938300
F	-2.12050100	-1.29640200	-0.17459400
F	-1.07626000	-0.62313600	1.63301400
F	0.12342000	-1.17808500	-1.60134100
F	0.42472200	-2.33426800	0.23890400
F	2.50891300	-0.69562800	-0.50791500
F	1.58636200	-0.22118800	1.41930600
F	2.22391700	1.99192400	0.04159200
H	1.10576000	1.25440100	-1.46473300

**(7)-H**

C	0.89152900	-1.15338500	0.23377600
C	0.55343600	1.34841800	0.23375900
C	1.44515700	0.19510100	-0.23391700
H	0.94595400	2.30538100	-0.12791600
C	-0.89150800	1.15328300	-0.23386600
C	-1.44504000	-0.19505800	0.23398900
C	-0.55348200	-1.34834500	-0.23373500
H	-1.49371400	-0.20157900	1.33217200
H	-0.57188100	-1.39261200	-1.33201300
H	-0.94617500	-2.30520000	0.12812700
H	-2.46941200	-0.33354500	-0.12940500
H	0.57163400	1.39258600	1.33208600
H	-1.52388900	1.97160900	0.12830000
H	-0.92125400	1.19108400	-1.33210100
H	0.92123000	-1.19129400	1.33205700
H	1.52375400	-1.97176900	-0.12843500
H	1.49363800	0.20162200	-1.33207700
H	2.46956300	0.33362800	0.12916700

**(8)-F**

C	-1.20647300	0.57112500	0.09825900
C	0.94845700	-0.49789900	0.22698800
C	-0.47646000	-0.70713800	-0.32702000
C	1.13206200	1.03865400	0.36943400
C	-0.18167400	1.66609100	-0.11766500
H	-0.45490500	2.58604300	0.39980900
H	-0.09464000	1.85541700	-1.19128400
H	1.33646100	1.25864100	1.42066300
F	-2.35645300	0.75185200	-0.56815500
F	-1.48427400	0.45138400	1.42228500
F	-0.41910300	-0.73108400	-1.67458900

F	-1.05493800	-1.82424000	0.12060000
F	1.86825200	-1.03260500	-0.58470000
F	1.02810500	-1.08708500	1.43813700
F	2.18703400	1.45787800	-0.39015100

**(8)-H**

C	-0.34048300	-0.68553600	-1.02392200
C	0.00000000	0.00000000	1.30165800
C	0.00000000	-1.23716800	0.36744800
H	-0.69353800	-2.01531200	0.69775100
C	0.00000000	1.23716800	0.36744800
C	0.34048300	0.68553600	-1.02392200
H	0.00945600	1.33869800	-1.83658800
H	1.42556200	0.55417400	-1.12330100
H	0.99925300	-1.68609300	0.34159100
H	-1.42556200	-0.55417400	-1.12330100
H	-0.00945600	-1.33869800	-1.83658800
H	0.69353800	2.01531200	0.69775100
H	-0.99925300	1.68609300	0.34159100
H	0.87743100	-0.00576500	1.95441700
H	-0.87743100	0.00576500	1.95441700

**(9)-F**

C	-1.17718800	-0.18422100	-0.71228700
C	0.82774000	-0.42155500	0.04149400
C	0.02107700	-1.08825800	-1.08107500
C	-0.19742900	0.73168700	0.04764100
H	-1.75618800	0.27642400	-1.51474700
H	0.44001100	-0.84845200	-2.05977600
H	-0.15328200	-2.15845500	-0.96879200
F	-0.58833000	1.21276400	1.22684700
F	0.23004700	1.73713400	-0.74562100
F	-2.00732400	-0.80724100	0.17848300
F	0.77982400	-1.11117000	1.19752300
F	2.09959000	-0.08653600	-0.21626700

**(9)-H**

C	0.00428400	-1.07484600	0.14000800
C	-0.00410000	1.07484700	0.14000900
C	1.07490900	0.00419200	-0.13995100
H	-0.00753300	1.97764500	-0.47570700
C	-1.07495800	-0.00419300	-0.14000400
H	-0.00556700	1.36558800	1.19487600
H	0.00788700	-1.97764600	-0.47570400
H	0.00508000	-1.36558600	1.19487600
H	-1.36561800	-0.00532100	-1.19489100

H	-1.97772100	-0.00771100	0.47578200
H	1.36477400	0.00532000	-1.19505700
H	1.97789000	0.00771000	0.47545200

**(10)-F**

C	0.18112500	-0.89401000	0.95151400
C	0.78618400	-0.49069500	-0.38690800
C	-0.53075500	0.02973100	0.03375000
H	0.63299700	-0.43513000	1.82470400
H	-0.18471600	-1.90840900	1.06206800
H	0.84469700	-1.22301500	-1.18608700
F	-1.63506700	-0.39169900	-0.60288000
F	-0.63338800	1.32136800	0.36830500
F	1.83375500	0.36993100	-0.35329400

**(10)-H**

C	0.42377100	-0.75623600	-0.00001500
C	-0.86727200	0.01151500	0.00001700
C	0.44370400	0.74472500	-0.00002200
H	0.70966100	-1.26899600	-0.91179200
H	0.74315300	1.24971700	-0.91178200
H	0.74317700	1.24945300	0.91188300
H	0.70975700	-1.26878900	0.91185300
H	-1.45354100	0.01931500	0.91217400
H	-1.45342600	0.01927600	-0.91221800

**Table S4. Coordinates of the endocyclic and exocyclic fluorinated alkene structures from Isodesmic Equations 11–15**

**(11)-endocyclic**

C	-1.28000800	-0.72440400	0.00028700
C	0.73921000	0.75108000	-0.00000300
C	-0.58527200	0.60989100	-0.00009600
H	1.17218400	1.75003400	-0.00021000
H	-0.62636000	-1.59850000	0.00077700
C	1.77568200	-0.32543200	0.00018000
H	1.39756000	-1.35007500	0.00053500
C	-1.53359900	1.77516900	-0.00051300
H	-2.18027500	1.73310300	0.88095700
H	-0.99380600	2.72348500	-0.00075400
H	-2.18005600	1.73254100	-0.88212700
F	2.57000800	-0.17187800	-1.09221300
F	2.57047300	-0.17124000	1.09209300
F	-2.08629000	-0.80066700	1.09277200
F	-2.08589400	-0.80159300	-1.09246400

**(11)-exocyclic**

C	-1.32106500	-0.53112900	0.26637400
C	0.72524400	0.54872700	-0.79454700
C	-0.66244900	0.72436200	-0.23461800
H	1.21557200	1.52048100	-0.90019300
H	-0.90860500	-0.86929100	1.22425600
H	0.67727700	0.08035400	-1.78428700
C	1.61322000	-0.31817000	0.07406500
H	1.31290500	-1.37032400	0.09538800
C	-1.29147600	1.89154800	-0.16241900
H	-0.81403000	2.80793700	-0.49513600
H	-2.30110300	1.96203300	0.22630200
F	2.88861100	-0.24855100	-0.38144600
F	1.60101900	0.14856100	1.35319600
F	-2.65474300	-0.36730100	0.41680900
F	-1.11964900	-1.53528800	-0.63960900

**(12)-endocyclic**

C	-1.22294400	-0.50454500	0.01586600
C	0.56103600	1.19930800	-0.00917700
C	-0.74321500	0.93010900	0.01943900
H	0.92758200	2.22295300	-0.01415100
C	1.61828200	0.13265500	-0.01386000
C	1.10693800	-1.23366000	-0.41356400
C	-0.16902200	-1.52995700	0.36777100
H	0.90116600	-1.22349100	-1.48804200
H	0.02397200	-1.46670800	1.44285700
H	-0.56889300	-2.52218800	0.14383600
H	1.88977800	-1.96986900	-0.21498900
C	-1.82533500	1.96718100	0.00865300
H	-2.41191300	1.91759800	0.93055000
H	-1.40760600	2.97017500	-0.09575800
H	-2.51212700	1.77914500	-0.82320100
F	2.62974800	0.51183800	-0.84517600
F	2.17113400	0.05477000	1.23843800
F	-2.28065500	-0.62148800	0.86965700
F	-1.71982600	-0.77558200	-1.23312600

**(12)-exocyclic**

C	-1.32132100	-0.37524900	-0.03011600
C	0.65752000	0.96011800	-0.80783900
C	-0.72399100	0.99816700	-0.21028900
H	1.11898000	1.95106100	-0.81355300
C	1.54427300	0.01527700	-0.00983300
C	0.95987500	-1.37334200	0.16586000



C	-0.43232600	-1.28948300	0.79419100
H	0.90470600	-1.84931100	-0.81777800
H	-0.37129300	-0.88068800	1.80702900
H	-0.90572500	-2.27405300	0.84301800
H	1.64304900	-1.95467800	0.79075500
C	-1.36333500	2.09478200	0.17605900
F	2.76504500	-0.07104700	-0.60579400
F	1.75018400	0.55933600	1.22879100
F	-2.55751500	-0.30980800	0.52561800
F	-1.47595000	-0.94241900	-1.27271800
H	0.61659800	0.58595000	-1.83726900
H	-0.91139300	3.07566000	0.06553200
H	-2.35496700	2.03988400	0.61099200

**(13)-endocyclic**

C	1.43294500	0.07229000	-0.00308900
C	-0.77451100	0.88036000	-0.00159500
C	0.50283600	1.25084000	0.00005200
C	-0.88516900	-0.62611300	-0.00450000
C	0.54060400	-1.17218300	-0.03168300
C	-2.01875400	1.70179000	0.00369000
H	-2.62080300	1.45668600	0.88445700
F	2.23981300	0.08422300	1.09438500
F	2.27037800	0.11203800	-1.07636700
F	-1.61307300	-1.04401600	-1.07784500
F	-1.57240300	-1.04769900	1.09417400
H	0.71292000	-1.73993700	-0.94703100
H	0.73003400	-1.80131900	0.83892400
H	0.88588000	2.26570200	0.00643700
H	-1.79577000	2.76994400	0.00933200
H	-2.62239900	1.46609900	-0.87849000

**(13)-exocyclic**

C	1.35833100	0.04800400	-0.07363300
C	-0.86483500	0.95513100	0.05279800
C	0.59195300	1.36819300	0.04939000
H	0.90103800	1.90072600	0.95224400
C	-0.93195100	-0.55328500	-0.10494100
C	0.40403000	-0.95321000	-0.70873400
H	0.82552600	1.99116600	-0.81978100
C	-1.94555800	1.71869200	0.12316700
H	-2.93604300	1.27792300	0.06549500
H	-1.88093000	2.79686100	0.23493800
F	1.71266700	-0.39382200	1.16453300
F	2.50446900	0.18850700	-0.78402500
F	-1.99075600	-0.95170000	-0.85040700

F	-1.07417500	-1.14270200	1.11656600
H	0.37255800	-0.78315500	-1.78854900
H	0.67619300	-1.98721600	-0.49263400

**(14)-endocyclic**

C	-0.09796800	-1.45977900	-0.00080600
C	-0.19419000	0.61741100	-0.00004900
C	-1.11255100	-0.58119700	-0.00067900
C	0.97071500	-0.40146300	-0.00023400
C	-2.59630700	-0.63674200	-0.00020400
H	-2.98915200	-0.12108700	-0.88241200
F	-0.25611700	1.40897900	1.08966600
F	-0.25561500	1.41044400	-1.08869200
H	-2.95899100	-1.66614900	0.00068000
F	1.76519000	-0.34145500	-1.08746700
F	1.76433200	-0.34245400	1.08793500
H	-2.98843500	-0.11969200	0.88154600
H	-0.04171300	-2.54206700	-0.00095800

**(14)-exocyclic**

C	-0.01022400	-1.46695300	-0.49135300
C	-0.26635000	0.64081200	-0.01339200
C	-1.18629100	-0.55239600	-0.17016900
C	0.91635100	-0.35677300	0.03285600
H	0.05200800	-2.41369400	0.04810900
H	0.13454000	-1.62439700	-1.56408300
C	-2.48062300	-0.70054500	0.05519900
H	-3.08949100	0.14677000	0.35545900
F	-0.43613100	1.43296700	1.05391800
F	-0.19652700	1.41776700	-1.11804700
H	-2.97174200	-1.66365300	-0.04371800
F	1.98499000	-0.04051600	-0.71315500
F	1.31850200	-0.56909500	1.30232700

**(15)-endocyclic**

C	-0.59102800	-0.04223900	0.04904200
C	0.14760000	-0.84633100	0.99206000
C	0.85262600	-0.12480400	0.14282200
C	2.16694600	0.31951000	-0.37604300
F	-1.28019400	1.06983700	0.41909600
F	-1.28492100	-0.58290200	-0.98690900
H	2.98707200	-0.16350000	0.15841700
H	2.24636000	0.08542600	-1.44137800
H	2.26081900	1.40416100	-0.27011100
H	0.13491600	-1.54532600	1.81610200

**(15)-exocyclic**

C	-0.52232600	-0.00282700	0.00035900
C	0.16069800	1.33161900	0.02400900
C	0.92945700	0.04986600	-0.00087000
H	0.12231700	1.92546300	-0.88657600
C	2.10036200	-0.55600300	-0.01055600
F	-1.19371300	-0.37446900	-1.10418000
F	-1.19042600	-0.41721300	1.09137100
H	0.12634800	1.89372600	0.95457100
H	3.02778600	0.00923800	-0.00030400
H	2.17164900	-1.63922100	-0.03005900

**Table S5. Energetics**

Energetic values are reported in Hartree-Fock (HF)

**E**-Electronic Energy (M06-2X/6-311++G(d,p)-SMD(CCl<sub>4</sub>)/M06-2X/6-31G(d))

**H**-Sum of Electronic Energy (M06-2X/6-311++G(d,p)-SMD(CCl<sub>4</sub>)/M06-2X/6-31G(d)) and Enthalpy (M06-2X/6-31G(d))

**G**-Sum of Electronic (M06-2X/6-311++G(d,p)-SMD(CCl<sub>4</sub>)/M06-2X/6-31G(d)) and Thermal Free Energies (M06-2X/6-31G(d))

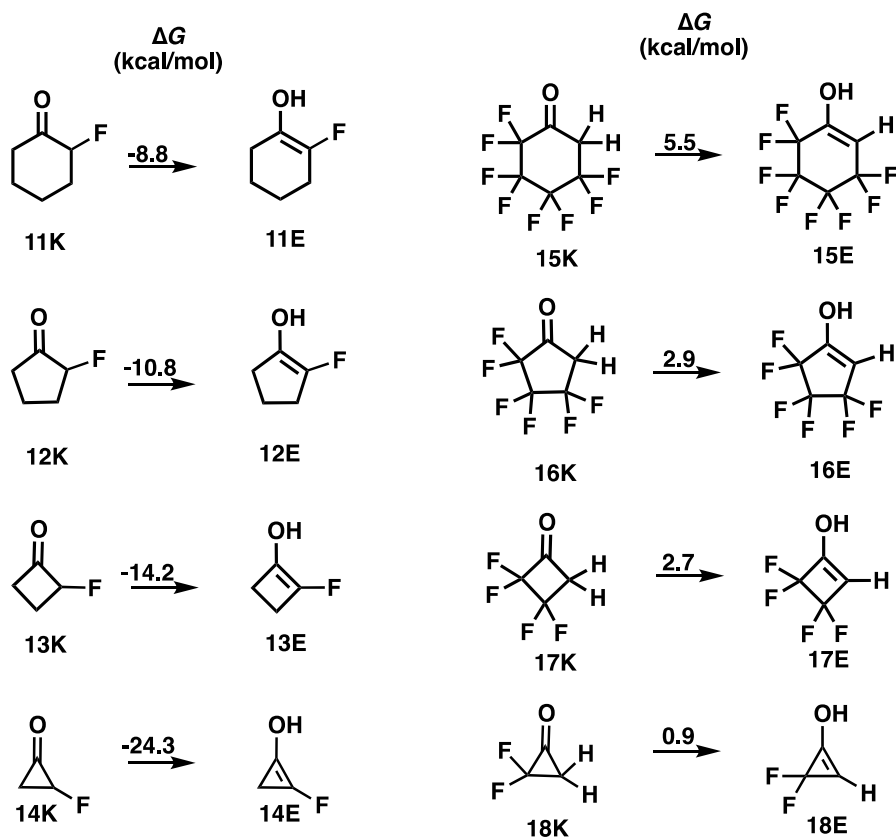
	<b>E</b>	<b>G</b>	<b>H</b>
<b>1E</b>	<b>-927.11136</b>	<b>-927.08619</b>	<b>-927.03839</b>
<b>1K</b>	<b>-927.12432</b>	<b>-927.09909</b>	<b>-927.05117</b>
<b>2E</b>	<b>-1202.98833</b>	<b>-1202.94617</b>	<b>-1202.89272</b>
<b>2K</b>	<b>-1202.99210</b>	<b>-1202.95007</b>	<b>-1202.89668</b>
<b>3E</b>	<b>-965.19806</b>	<b>-965.16619</b>	<b>-965.11822</b>
<b>3k</b>	<b>-965.19566</b>	<b>-965.16427</b>	<b>-965.11610</b>
<b>4E</b>	<b>-727.38193</b>	<b>-727.36140</b>	<b>-727.31838</b>
<b>4K</b>	<b>-727.37925</b>	<b>-727.35926</b>	<b>-727.31611</b>
<b>5E</b>	<b>-489.55000</b>	<b>-489.54067</b>	<b>-489.50293</b>
<b>5K</b>	<b>-489.54579</b>	<b>-489.53759</b>	<b>-489.49943</b>
<b>6E</b>	<b>-232.41216</b>	<b>-232.32667</b>	<b>-232.29017</b>
<b>6K</b>	<b>-232.43187</b>	<b>-232.34722</b>	<b>-232.31017</b>
<b>7E</b>	<b>-309.82867</b>	<b>-309.70545</b>	<b>-309.66803</b>
<b>7K</b>	<b>-309.84508</b>	<b>-309.72216</b>	<b>-309.68451</b>
<b>8E</b>	<b>-270.51424</b>	<b>-270.41960</b>	<b>-270.38427</b>
<b>8K</b>	<b>-270.53465</b>	<b>-270.44064</b>	<b>-270.40518</b>
<b>9E</b>	<b>-231.17303</b>	<b>-231.10707</b>	<b>-231.07418</b>
<b>9K</b>	<b>-231.19739</b>	<b>-231.13281</b>	<b>-231.09927</b>
<b>10E</b>	<b>-191.82705</b>	<b>-191.79051</b>	<b>-191.75950</b>
<b>10K</b>	<b>-191.86217</b>	<b>-191.82607</b>	<b>-191.79532</b>
<b>(1)-Endocyclic</b>	<b>-196.49182</b>	<b>-196.38335</b>	<b>-196.34585</b>
<b>(1)-Exocyclic</b>	<b>-196.48889</b>	<b>-196.37996</b>	<b>-196.34293</b>
<b>(2)-Endocyclic</b>	<b>-273.90829</b>	<b>-273.76254</b>	<b>-273.72393</b>

(2)-Exocyclic	-273.90453	-273.75734	-273.71968
(3)-Endocyclic	-234.59591	-234.47874	-234.44221
(3)-Exocyclic	-234.59030	-234.47249	-234.43667
(4)-Endocyclic	-195.25274	-195.16468	-195.13028
(4)-Exocyclic	-195.25177	-195.16344	-195.12947
(5)-Endocyclic	-155.91607	-155.85690	-155.82453
(5)-Exocyclic	-155.93300	-155.87270	-155.84146
(6)-F	-853.14364	-853.09822	-853.051585
(6)-H	-158.40900	-158.30306	-158.26837
(7)-F	-1129.01030	-1128.94749	-1128.895962
(7)-H	-235.82412	-235.68028	-235.64494
(8)-F	-891.21079	-891.15855	-891.112465
(8)-H	-196.50897	-196.39336	-196.36013
(9)-F	-653.39408	-653.35341	-653.312432
(9)-H	-157.17359	-157.08674	-157.05572
(10)-F	-415.58314	-415.55297	-415.517942
(10)-H	-117.87114	-117.81295	-117.78439
(11)-Endocyclic	-593.46805	-593.39323	-593.34832
(11)-Exocyclic	-593.46992	-593.39391	-593.35000
(12)-Endocyclic	-670.90663	-670.79621	-670.75080
(12)-Exocyclic	-670.90582	-670.79443	-670.74978
(13)-Endocyclic	-631.59127	-631.50998	-631.46631
(13)-Exocyclic	-631.58231	-631.50047	-631.45748
(14)-Endocyclic	-592.23924	-592.18757	-592.14507
(14)-Exocyclic	-592.23129	-592.17845	-592.13718
(15)-Endocyclic	-354.41741	-354.37634	-354.33981
(15)-Exocyclic	-354.40992	-354.36812	-354.33256

**Table S6. Coordinates for DIFO**

C	0.76421000	-1.45607000	-0.06583800
C	-0.41007300	-1.17844900	-0.07556400
C	-1.50511000	-0.20219900	-0.01632800
C	-0.97269000	1.16196900	-0.44475600
C	0.32913700	1.58008400	0.26618400
H	-1.77587500	1.87715400	-0.23516200
H	-0.83308800	1.13067200	-1.53039100
C	1.67407000	1.18138500	-0.40914000
H	0.30736800	2.67085700	0.35024200
H	0.29691300	1.20343500	1.29578800
C	2.53904500	0.12258900	0.31006700
H	2.28268300	2.08755300	-0.49270900
H	1.48791400	0.85199400	-1.43990300
C	2.21850500	-1.34048000	-0.08322500

H	3.59806700	0.30326400	0.09554300
H	2.41345300	0.22960100	1.39356600
H	2.59052900	-1.55078000	-1.09275400
H	2.70443200	-2.04455500	0.59890800
F	-2.56347600	-0.54496200	-0.79701600
F	-1.98040900	-0.11861200	1.26018000



**Figure S1.** Effect of incorporating an alpha fluorine on the cyclic hydrocarbon keto-enol systems (11-14) and removal of the alpha fluorine from the cyclic perfluorinated keto-enol systems (15-18).

**Table S7.** M06-2X/6-31G(d) optimized cartesian coordinates of keto(K) and enol(E) systems 11–18.....S21

11K			
C	-0.86689200	1.35501300	-0.39292800
C	0.80892300	-0.56954000	-0.40493400
C	0.54654000	0.89811600	-0.08300900
C	-0.21893000	-1.45341000	0.29740400
C	-1.64288800	-1.03184500	-0.07136900
C	-1.89122400	0.43435500	0.29203000

H	-1.80062600	-1.17288400	-1.14961200
H	-1.81148400	0.55659000	1.37958900
H	-2.90470100	0.73635400	0.01050200
H	-2.36439000	-1.67695800	0.43941900
O	1.39213200	1.60612000	0.40452300
H	0.73216800	-0.70415400	-1.49510800
H	-0.02581200	-2.49825900	0.03563900
H	-0.06355000	-1.35244800	1.37905500
H	-1.01534800	1.30997000	-1.48109100
H	-0.96590300	2.39627700	-0.07768900
F	2.07438000	-0.91550900	-0.01111700

11E

C	-0.57163000	-1.51827200	0.06314900
C	0.59647600	0.66802900	-0.03790100
C	0.65583300	-0.66043900	0.03480600
C	-0.64007300	1.49996100	-0.06005000
C	-1.84334500	0.64305400	0.35052600
C	-1.80906700	-0.71709100	-0.35133500
H	-1.81770600	0.48673300	1.43620600
H	-1.79027000	-0.55993500	-1.43713000
H	-2.71475000	-1.28789700	-0.12448100
H	-2.77308900	1.17292200	0.12213200
O	1.83202800	-1.34704100	0.08642500
H	2.54889500	-0.69305800	0.08020500
H	-0.51364400	2.34461300	0.62768800
H	-0.79336400	1.92933000	-1.05977200
H	-0.69581400	-1.93592300	1.07102300
H	-0.41148000	-2.36885600	-0.60902700
F	1.77509300	1.35521600	-0.08815700

12K

C	1.33854000	0.21896200	0.69874600
C	-0.94605700	-0.24686300	0.11900300
C	0.02055100	0.91624200	0.42539800
H	-0.35309200	1.58634800	1.20283400
C	-0.10955400	-1.46207300	-0.27773400
C	1.33689300	-0.94746700	-0.30950900
H	2.07028700	-1.71767700	-0.06317100
H	1.57520600	-0.55996600	-1.30416300
O	-2.14481300	-0.18577500	0.18569000
H	1.33573100	-0.16535600	1.72619000
H	2.18760400	0.89711000	0.58608900
H	-0.47071300	-1.88576500	-1.21773800
H	-0.24971400	-2.22459600	0.49854200
F	0.13566200	1.63147700	-0.76105800

## 12E

C	1.04937200	1.19488400	0.10798800
C	-0.44625400	-0.64633600	0.00062900
C	-0.34932200	0.68083100	-0.00333300
C	0.90344800	-1.28810100	0.10866300
C	1.86004400	-0.09890900	-0.16147200
H	2.76929700	-0.15116200	0.44047500
H	2.15779800	-0.11591300	-1.21315000
O	-1.56466600	-1.41163100	-0.02843600
H	-2.33154900	-0.81773700	-0.04371300
H	1.24491200	1.60961400	1.10555800
H	1.27052300	1.98248700	-0.61970000
H	1.03974400	-1.71824400	1.10876300
H	1.02954600	-2.10072300	-0.61345300
F	-1.41851800	1.50561200	-0.02801500

## 13K

C	1.21688100	0.95323700	0.00215800
C	-0.73017600	0.05050400	0.40180600
C	0.68153500	-0.48070700	0.11177300
H	-0.90293500	0.12445400	1.48326500
C	-0.25841500	1.39271400	-0.19775200
O	1.12971000	-1.56454800	-0.11849400
H	1.64379900	1.30166100	0.94746500
H	1.92528100	1.13814000	-0.80658000
H	-0.58952200	2.30092400	0.30553000
H	-0.52119200	1.43347100	-1.25729200
F	-1.78356200	-0.58630600	-0.18137100

## 13E

C	-0.53243900	1.42799100	-0.00004200
C	0.62815400	-0.27872600	-0.00019900
C	-0.68827500	-0.06889800	-0.00010700
C	1.01593100	1.16853500	0.00014100
O	-1.83186500	-0.78236900	-0.00000100
H	-1.60954100	-1.72542000	0.00083000
H	1.53058900	1.53125800	0.89479400
H	-0.90190900	1.93576900	0.89509700
H	1.53109800	1.53174700	-0.89402000
H	-0.90162400	1.93559800	-0.89538600
F	1.38512000	-1.38260100	-0.00000700

## 14K

C	0.64914900	0.01818100	0.46900500
C	-0.04817100	1.23949400	-0.17033200

H	0.19645000	1.43338500	-1.21382400
F	1.59010900	-0.63907500	-0.25881700
C	-0.77030300	-0.02810400	0.06630500
O	-1.77438800	-0.65969500	-0.07631300
H	-0.20030100	2.12635800	0.43969700
H	0.90392000	0.09206600	1.52411300

14E

C	-0.02633200	1.32410900	0.00001900
C	-0.66001500	-0.02552400	-0.00005200
C	0.62362800	-0.05141600	-0.00005400
O	1.79516600	-0.69741200	0.00002000
H	2.50447000	-0.03922300	0.00000400
F	-1.82913700	-0.63582200	0.00002900
H	-0.01372000	1.92899600	-0.91374900
H	-0.01353000	1.92890500	0.91384600

15K

C	1.46105700	0.00072000	0.24502200
C	-0.38554700	1.73180500	0.61259600
C	1.00511200	1.46496300	0.06758200
C	-1.38108300	0.77374700	-0.01958100
C	-0.98463000	-0.70000200	0.15439100
C	0.44073200	-0.98151400	-0.34615500
F	-2.60601500	0.94132300	0.51424800
F	-1.45690800	1.01638900	-1.34938000
F	1.53775600	-0.23869900	1.57903000
F	2.65282200	-0.20396400	-0.31577200
O	1.72057600	2.27993100	-0.43966100
H	-0.68099700	2.75804300	0.38804900
F	-1.03607200	-0.99090300	1.47067200
F	-1.84627100	-1.48411500	-0.50632100
F	0.78062700	-2.23701800	-0.02452800
F	0.45979300	-0.83682200	-1.68460200
H	-0.38905900	1.56847500	1.69596500

15E

C	-1.41142100	-0.14963000	-0.11279800
C	0.16162500	1.78709800	0.04696300
C	-1.08666400	1.32097900	-0.00086900
C	1.35854500	0.89865000	0.10367500
C	1.06135500	-0.55265400	-0.30339000
C	-0.24715600	-1.04568900	0.31381000
F	2.33274000	1.36218200	-0.71282900
F	1.87273400	0.87341000	1.35855500
F	-1.76557100	-0.45415900	-1.37786900



F	-2.48914100	-0.41335200	0.67307600
O	-2.15764600	2.13302400	-0.02320600
H	-2.96133400	1.61429900	0.14283800
F	0.93075200	-0.60731700	-1.64380400
F	2.06397900	-1.35638500	0.07519900
F	-0.48503200	-2.30877100	-0.06515700
F	-0.14277100	-0.99400100	1.65483400
H	0.34559100	2.85451000	0.10042500

16K

C	1.18425400	0.55129800	0.09106400
C	-1.16225400	1.07836900	-0.14768200
C	0.23427400	1.67992000	-0.28455200
C	-1.01975700	-0.43669800	0.15733000
F	-1.15443200	-0.62874900	1.48641700
F	-1.91450000	-1.17998700	-0.49738300
F	1.42108800	0.55222500	1.42316100
F	2.36159200	0.60716700	-0.55402100
C	0.42668400	-0.74567000	-0.24513500
O	-2.21206000	1.63882500	-0.26352900
H	0.39459800	1.96528900	-1.32949600
F	0.93595600	-1.82114400	0.35741300
F	0.45647500	-0.90704900	-1.58653400
H	0.36707000	2.55862300	0.35009300

16E

C	1.20182900	0.63364900	0.06213800
C	-1.08595900	1.04065800	-0.06200800
C	0.10783800	1.63833100	-0.08969500
C	-0.97376000	-0.44881400	0.12202400
F	-1.28835200	-0.82383300	1.37956300
F	-1.81795100	-1.09872100	-0.71317300
F	1.75422400	0.64058100	1.29872600
F	2.20584500	0.81503300	-0.82130000
C	0.50921600	-0.73338600	-0.17374400
O	-2.29044900	1.61156000	-0.15425500
H	-2.96620600	0.92312300	-0.26514300
F	1.00149800	-1.70441100	0.60225300
F	0.63789900	-1.08391500	-1.46452900
H	0.29634300	2.69915700	-0.18697100

17K

C	0.29518800	0.65808400	0.00392300
C	0.02425900	-1.49123100	-0.42022100
C	1.22626900	-0.58971600	-0.08892800
C	-0.89462800	-0.34111500	0.01610500

O	2.38991700	-0.76540700	0.09328800
F	-1.35850000	-0.50121000	1.27129200
F	-1.91093100	-0.03029800	-0.79768100
F	0.41424300	1.46761000	1.05446900
F	0.30949700	1.37603200	-1.13513000
H	-0.05082500	-1.68330700	-1.49516100
H	-0.06382200	-2.41877700	0.14704400

17E

C	0.25230000	0.60531000	0.00000300
C	0.05104600	-1.48741400	-0.00003100
C	1.09664300	-0.64441800	-0.00001600
C	-0.94748100	-0.37096800	0.00005400
O	2.41636200	-0.81528600	0.00017000
F	-1.74009600	-0.25916600	1.08617800
F	-1.74008900	-0.25926200	-1.08617300
F	0.35979500	1.39378600	-1.08761800
H	-0.05941000	-2.56254000	-0.00004700
F	0.35973600	1.39388000	1.08753300
H	2.85935500	0.04662400	-0.00065400

18K

C	-0.49832700	-0.00011200	0.01631000
C	0.29695800	0.01065900	-1.28760800
C	0.98467200	0.00012000	0.04037700
O	2.01434500	-0.00483100	0.64117300
F	-1.18825400	-1.10605700	0.32413500
F	-1.19028100	1.09966100	0.34130100
H	0.29608700	0.93834000	-1.85772300
H	0.29615100	-0.90613300	-1.87506400

18E

C	0.25230000	0.60531000	0.00000300
C	0.05104600	-1.48741400	-0.00003100
C	1.09664300	-0.64441800	-0.00001600
C	-0.94748100	-0.37096800	0.00005400
O	2.41636200	-0.81528600	0.00017000
F	-1.74009600	-0.25916600	1.08617800
F	-1.74008900	-0.25926200	-1.08617300
F	0.35979500	1.39378600	-1.08761800
H	-0.05941000	-2.56254000	-0.00004700
F	0.35973600	1.39388000	1.08753300
H	2.85935500	0.04662400	-0.00065400

**Table S8. Energetics of keto(K) and enol(E) systems 11–18**

	<b>E</b>	<b>G</b>	<b>H</b>
<b>11K</b>	-409.084693	-408.970702	-408.931139
<b>11E</b>	-409.071128	-408.956686	-408.917232
<b>12K</b>	-369.769502	-369.684223	-369.646753
<b>12E</b>	-369.752509	-369.666978	-369.629214
<b>13K</b>	-330.433955	-330.377895	-330.342397
<b>13E</b>	-330.411710	-330.355279	-330.319814
<b>14K</b>	-291.089550	-291.062889	-291.029565
<b>14E</b>	-291.051658	-291.024112	-290.990331
<b>15K</b>	-1103.770566	-1103.719752	-1103.668229
<b>15E</b>	-1103.762172	-1103.710968	-1103.659636
<b>16K</b>	-865.975738	-865.935833	-865.889534
<b>16E</b>	-865.972051	-865.931210	-865.885374
<b>17K</b>	-628.157267	-628.128570	-628.087602
<b>17E</b>	-628.153486	-628.124190	-628.083173
<b>18K</b>	-390.327629	-390.310077	-390.274798
<b>18E</b>	-390.327282	-390.308606	-390.273638