Supporting Information

Photoinduced solid state keto-enol tautomerization of 2-(2-(3-nitrophenyl)-4, 5-diphenyl-1H-imidazol-1-yloxy)-1-phenylethanone

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General experimental:

^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra were recorded on Bruker Avance 500 spectrometer. The chemical shifts (δ ppm) and coupling constants (Hz) are reported in the standard fashion with reference to either internal tetramethylsilane or residual $CHCl_3$ or DMSO. In the ^{13}C NMR spectra, the nature of the carbons (C, CH, CH_2 or CH_3) was determined by recording the DEPT-135 experiment. CP-MAS solid state NMR was recorded on Bruker Avance 400 spectrometer. All the commercial reagents were used as such without further purification.

The absorption, transmittance, and DRS spectra were collected using Cary 5E UV-vis spectrophotometer.

All computational works were carried out using Gaussian 09 program package. Optimization of ground state geometries of the keto and enol forms were performed without any symmetry constrains at the DFT level with B3LYP hybrid functional using 6-311+g** basis set. Vibrational analyses were carried out on the optimized geometry to ascertain the absence of any imaginary frequencies. The excitation energies and oscillator strengths for the first three singlet vertical transitions were achieved by TD-DFT calculations using the same basis set as for the ground state and using the same level of theory.

Synthesis and spectral data:

Synthesis of 2-(2-(3-nitrophenyl)-4,5-diphenyl-1H-imidazol-1-yloxy)-1-phenylethanone:

To a solution of 1-hydroxy imidazole (I) (0.001mol, in acetone, 10mL) was added a pinch of K_2CO_3 and stirred for 10minutes. Then the solution became red and phenacyl bromide (0.001mol) was added to it. The stirring was continued for 4hrs. The precipitate thus formed was filtered and recrystallized from ethanol to afford the desired product in 85% yield.

^{1}H NMR (500MHz, $CDCl_3$, TMS standard) δ 4.89 (s,2H, CH_2), 7.28 (m,3H, ArH), 7.30 (s, 1H, ArH), 7.36 (t, 2H, ArH), 7.4(m, 3H, ArH), 7.5(m, 3H, ArH), 7.6(m, 5H, ArH), 8.2(dd,

1H, ArH), 8.56 (d, 1H, ArH), 9.0(s, 1H, ArH); (500MHz, DMSO-d_6, TMS standard) δ 5.69 (s,1H, -CH), 7.28 (m, 2H, ArH), 7.36 (t, 4H, ArH), 7.5 (m, 6H, ArH), 7.6 (m, 1H, ArH), 7.73 (t,1H, ArH), 8.06 (d, 1H, ArH), 8.07 (d, 1H, ArH), 8.15 (d, 1H, ArH), 8.5 (d,1H, ArH), 8.93 (s, 1H, ArH); **^{13}C NMR** (125 MHz, $CDCl_3$, TMS standard) δ 79.3, 122, 123, 127, 128, 129, 130, 132, 133, 134, 135, 138, 149, 190; (125 MHz, DMSO-d_6, TMS standard) δ 89, 119, 122, 126, 127, 128, 129, 130, 131, 132, 133, 134, 148, 196. DEPT ^{13}C NMR: in DMSO the peak at 89ppm is in the normal phase corresponding to the –CH proton after enolization and the $CDCl_3$ spectra reveals the phase change at 79 ppm emphasizing the existence of a methylenic proton (-CH_2) corresponding to the keto form.

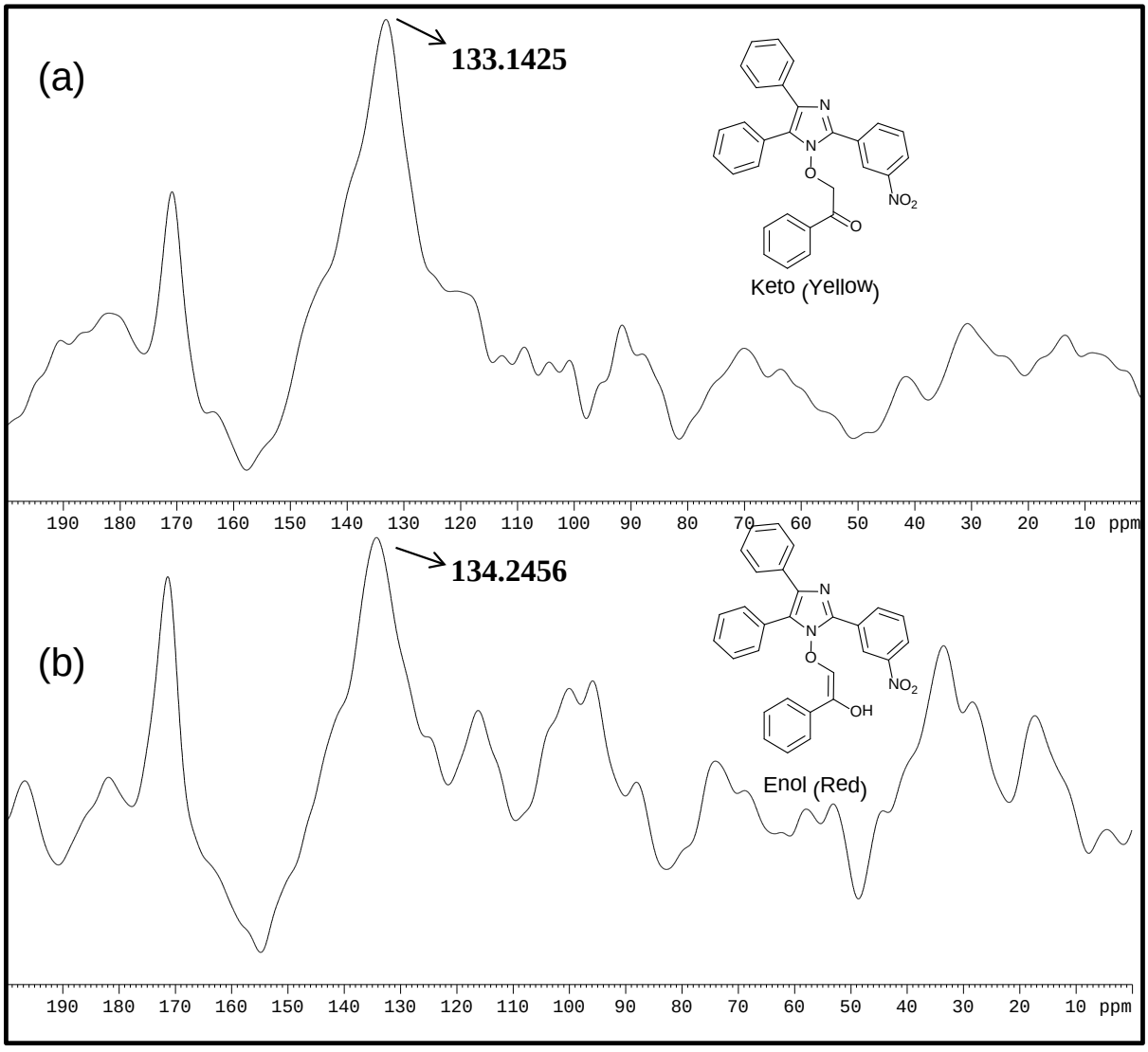

Figure 1. CP-MAS Solid state NMR spectra of (a) keto form, and (b) enol form

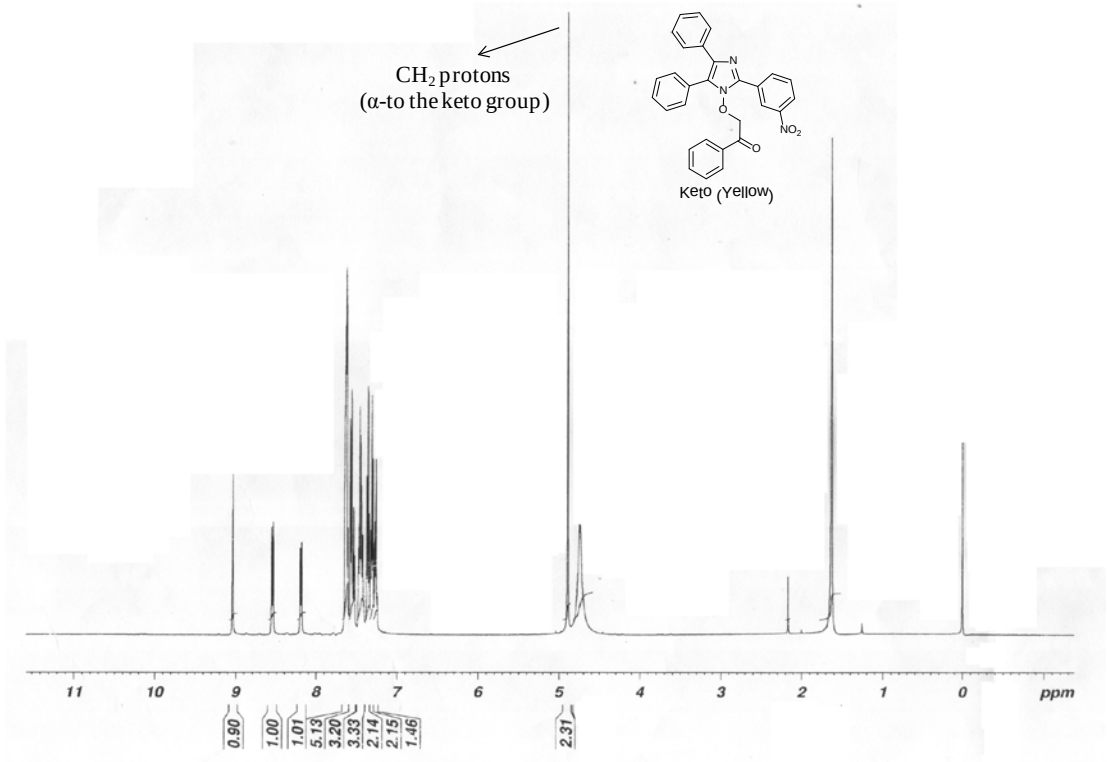

Figure 2. ^{1}H NMR spectrum of keto form in $CDCl_3$

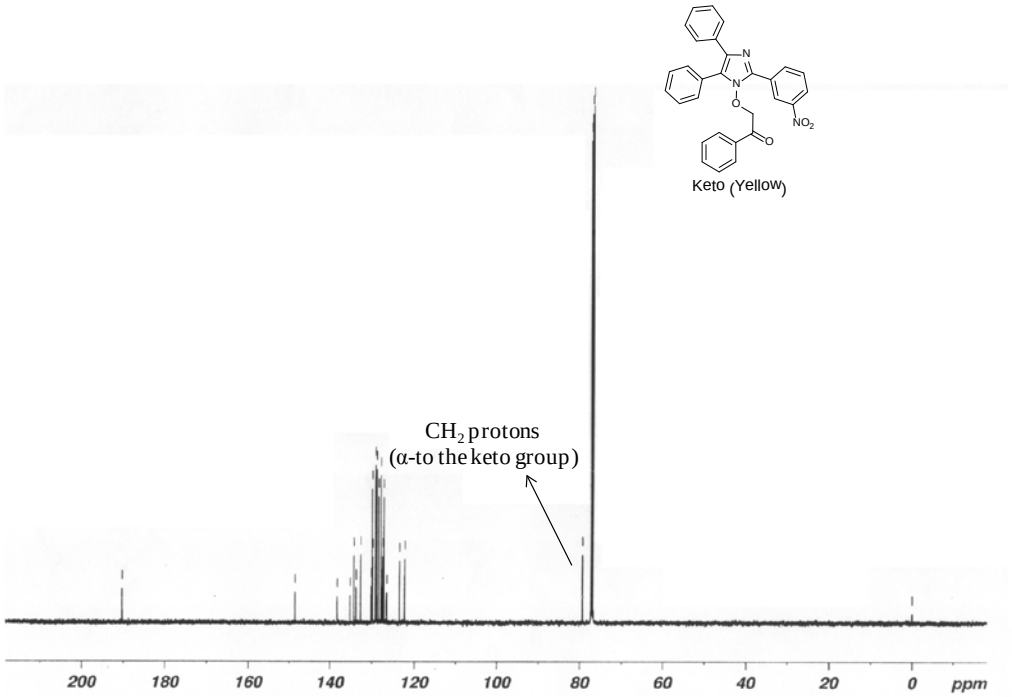

Figure 3. ^{13}C NMR spectrum of keto form in $CDCl_3$

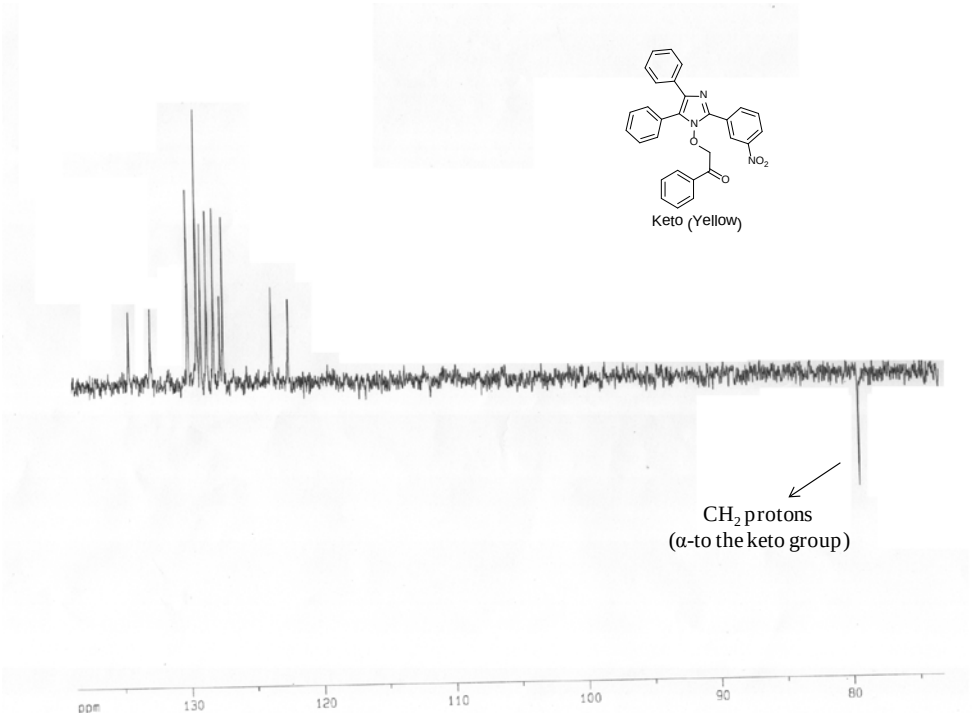

Figure 4. ^{13}C-DEPT NMR spectrum of keto form in $CDCl_3$

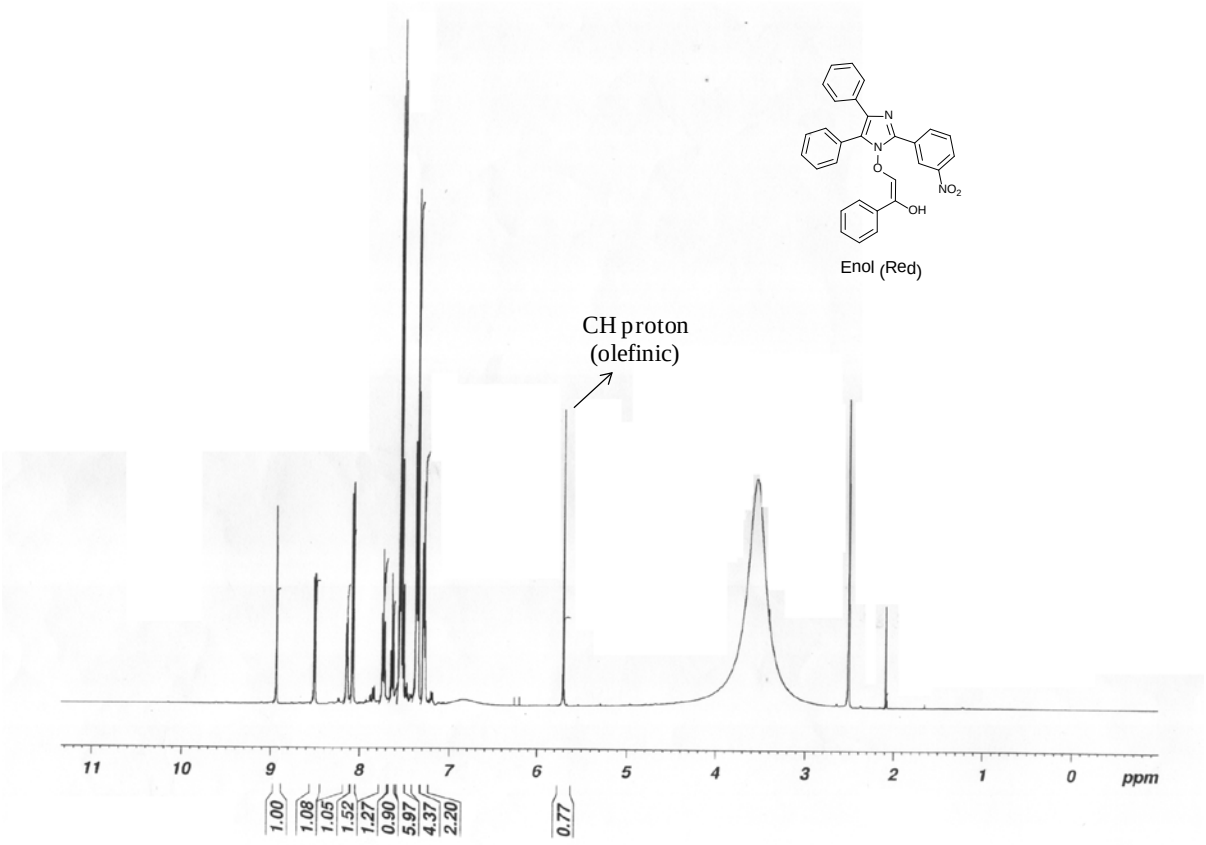

Figure 5. ^{1}H NMR spectrum of enol form in DMSO-D6

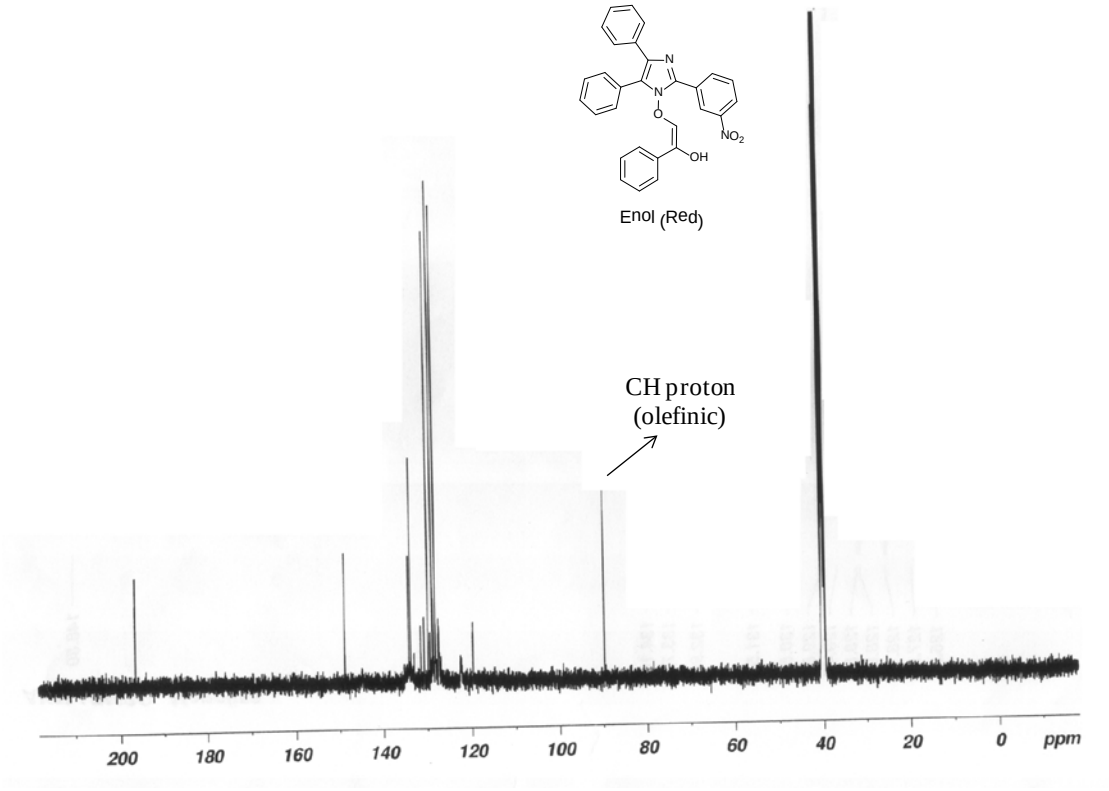

Figure 6. ^{13}C NMR spectrum of enol form in DMSO-D6

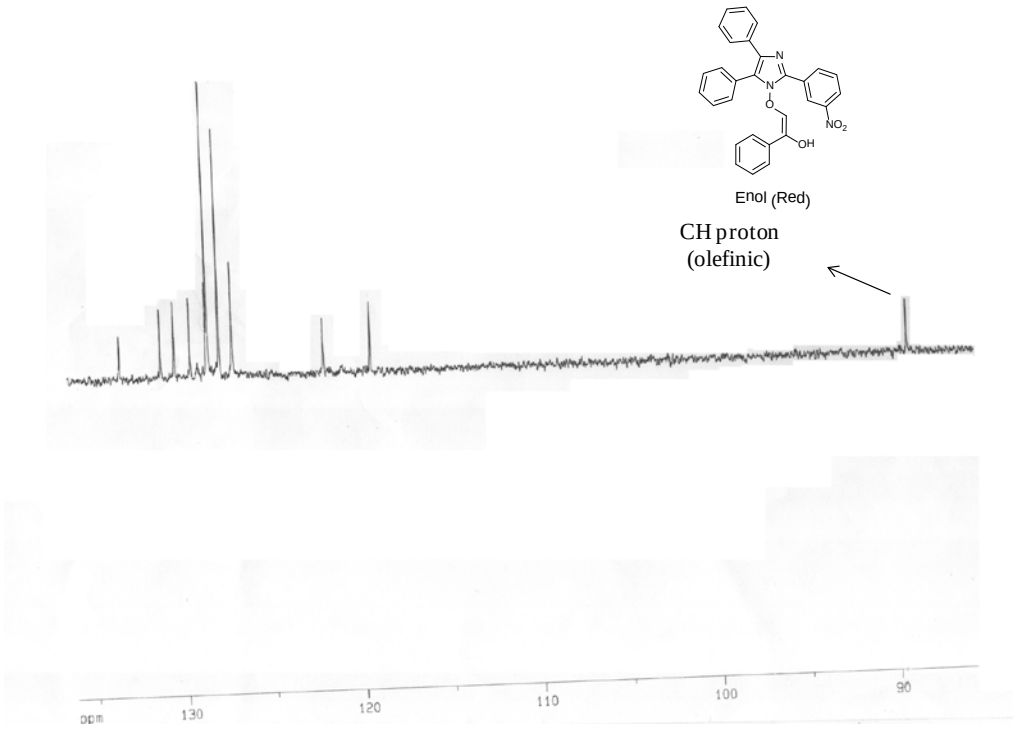

Figure 7. ^{13}C-DEPT NMR spectrum of enol form in DMSO-D6

Cartesian co-ordinates of the optimized geometry of the keto and enol form in gas phase, $CHCl_3$, and DMSO

Keto form in gas phase

6	1.156726000	-0.645516000	-0.324938000
6	1.928502000	1.383862000	-0.164799000
6	0.546419000	1.518248000	-0.135697000
7	0.083963000	0.213214000	-0.259760000
8	-1.239046000	-0.164564000	-0.144614000
6	-1.626867000	-0.303219000	1.252679000
1	-0.838468000	-0.817480000	1.801299000
1	-1.792956000	0.691035000	1.682182000
6	-2.893687000	-1.159757000	1.363795000
6	-4.086381000	-0.858256000	0.525276000
6	-4.214040000	0.332523000	-0.202110000
6	-5.132079000	-1.794377000	0.504862000
6	-5.372454000	0.583190000	-0.933196000
1	-3.418170000	1.065662000	-0.199246000
6	-6.279626000	-1.546690000	-0.235957000
1	-5.023149000	-2.705635000	1.080000000
6	-6.402387000	-0.355185000	-0.954881000
1	-5.470502000	1.510148000	-1.486276000
1	-7.081329000	-2.275962000	-0.252778000
1	-7.300777000	-0.159873000	-1.529729000
8	-2.892530000	-2.058880000	2.181984000
6	-0.365407000	2.666246000	-0.013536000
6	-0.244276000	3.560960000	1.059952000
6	-1.363938000	2.893216000	-0.973193000

6	-1.097581000	4.655605000	1.167879000
1	0.524274000	3.395349000	1.805767000
6	-2.217390000	3.988013000	-0.860455000
1	-1.455263000	2.219328000	-1.817037000
6	-2.087491000	4.872181000	0.209838000
1	-0.990785000	5.338392000	2.003129000
1	-2.976346000	4.157688000	-1.616184000
1	-2.749932000	5.726010000	0.294750000
6	2.978032000	2.417895000	-0.135377000
6	2.764721000	3.715431000	-0.622551000
6	4.245772000	2.090394000	0.368682000
6	3.784769000	4.662607000	-0.588350000
1	1.804629000	3.982950000	-1.045592000
6	5.263041000	3.038867000	0.401341000
1	4.422952000	1.084055000	0.727000000
6	5.036801000	4.330587000	-0.073251000
1	3.603173000	5.659246000	-0.975274000
1	6.235776000	2.768126000	0.796744000
1	5.830626000	5.068626000	-0.049303000
6	1.091104000	-2.103887000	-0.457765000
6	2.217944000	-2.844020000	-0.073004000
6	-0.020036000	-2.781411000	-0.984692000
6	2.199444000	-4.222313000	-0.215249000
1	3.090995000	-2.345880000	0.323015000
6	-0.009156000	-4.168702000	-1.113167000
1	-0.889077000	-2.222805000	-1.303482000
6	1.102192000	-4.909296000	-0.727862000

1	-0.874612000	-4.675161000	-1.523203000
1	1.134234000	-5.985879000	-0.817523000
7	2.270974000	0.056350000	-0.274486000
7	3.393910000	-4.995898000	0.200521000
8	3.365363000	-6.209980000	0.040345000
8	4.335805000	-4.378672000	0.678807000

Keto form in $CHCl_3$

6	-0.920095000	0.937791000	-0.339615000
6	-2.248680000	-0.780316000	-0.193289000
6	-0.965623000	-1.306718000	-0.128506000
7	-0.145252000	-0.192343000	-0.240126000
8	1.228009000	-0.210239000	-0.118922000
6	1.635835000	-0.180613000	1.280417000
1	1.025907000	0.540952000	1.822420000
1	1.508354000	-1.176468000	1.718026000
6	3.095346000	0.268879000	1.394905000
6	4.140416000	-0.313490000	0.513385000
6	3.929263000	-1.486417000	-0.225399000
6	5.393032000	0.319367000	0.459218000
6	4.956948000	-2.018923000	-0.999602000
1	2.972422000	-1.990266000	-0.193832000
6	6.410420000	-0.206352000	-0.325942000
1	5.549126000	1.221590000	1.037510000
6	6.194237000	-1.378856000	-1.054930000
1	4.791803000	-2.931548000	-1.560113000
1	7.372115000	0.291253000	-0.370582000
1	6.990316000	-1.791662000	-1.664137000

8	3.361072000	1.089358000	2.256421000
6	-0.434219000	-2.669676000	0.032343000
6	-0.839077000	-3.462801000	1.116042000
6	0.471671000	-3.202126000	-0.897604000
6	-0.352880000	-4.759336000	1.262681000
1	-1.535157000	-3.059275000	1.841939000
6	0.958790000	-4.498435000	-0.745382000
1	0.778685000	-2.605480000	-1.748598000
6	0.547775000	-5.280771000	0.333768000
1	-0.674725000	-5.360887000	2.105087000
1	1.651854000	-4.900583000	-1.475699000
1	0.925110000	-6.290389000	0.448948000
6	-3.549023000	-1.474101000	-0.183598000
6	-3.709054000	-2.765192000	-0.708726000
6	-4.674402000	-0.819481000	0.340656000
6	-4.954936000	-3.388001000	-0.694249000
1	-2.861382000	-3.279835000	-1.143601000
6	-5.918751000	-1.443489000	0.353071000
1	-4.563620000	0.182485000	0.736632000
6	-6.064589000	-2.732398000	-0.160952000
1	-5.060141000	-4.384225000	-1.109410000
1	-6.775904000	-0.922712000	0.765355000
1	-7.033713000	-3.218253000	-0.151878000
6	-0.427866000	2.312297000	-0.472446000
6	-1.269537000	3.351222000	-0.054681000
6	0.819848000	2.631487000	-1.032669000
6	-0.843342000	4.663480000	-0.198507000

1	-2.238012000	3.133270000	0.370779000
6	1.221859000	3.959457000	-1.161435000
1	1.472986000	1.842485000	-1.378708000
6	0.394854000	4.995587000	-0.743684000
1	2.186277000	4.187304000	-1.598287000
1	0.689588000	6.031031000	-0.835721000
7	-2.192771000	0.589703000	-0.316272000
7	-1.736863000	5.749353000	0.251385000
8	-1.352880000	6.905522000	0.106909000
8	-2.815830000	5.443080000	0.746509000

Keto form in DMSO

6	-0.954752000	0.915695000	-0.342990000
6	-2.220500000	-0.849259000	-0.196433000
6	-0.919720000	-1.327399000	-0.121481000
7	-0.141066000	-0.184369000	-0.230923000
8	1.231316000	-0.151292000	-0.112649000
6	1.641736000	-0.090058000	1.285537000
1	1.015766000	0.624445000	1.818194000
1	1.541056000	-1.081431000	1.739018000
6	3.090169000	0.395491000	1.380825000
6	4.140541000	-0.185358000	0.506866000
6	3.956884000	-1.396703000	-0.175716000
6	5.368995000	0.487371000	0.399645000
6	4.988226000	-1.928206000	-0.945711000
1	3.019757000	-1.932287000	-0.102872000
6	6.389610000	-0.037863000	-0.381978000
1	5.505000000	1.421243000	0.930868000

6	6.201235000	-1.249056000	-1.053809000
1	4.844155000	-2.869911000	-1.462013000
1	7.331612000	0.490693000	-0.469311000
1	6.999672000	-1.660924000	-1.660440000
8	3.343186000	1.244945000	2.219746000
6	-0.342257000	-2.670716000	0.048471000
6	-0.716956000	-3.466832000	1.140739000
6	0.576466000	-3.180240000	-0.881525000
6	-0.188563000	-4.746047000	1.295379000
1	-1.419613000	-3.078731000	1.868726000
6	1.105847000	-4.459011000	-0.721222000
1	0.862341000	-2.580663000	-1.737733000
6	0.724283000	-5.245504000	0.365958000
1	-0.485720000	-5.350414000	2.144813000
1	1.810595000	-4.842958000	-1.449959000
1	1.135229000	-6.241131000	0.487807000
6	-3.492690000	-1.593535000	-0.191656000
6	-3.602301000	-2.880810000	-0.739549000
6	-4.641991000	-0.995764000	0.349313000
6	-4.821849000	-3.554454000	-0.732904000
1	-2.735477000	-3.352273000	-1.185709000
6	-5.860409000	-1.670157000	0.353405000
1	-4.571369000	0.000540000	0.768624000
6	-5.955801000	-2.954302000	-0.184657000
1	-4.887601000	-4.546617000	-1.165429000
1	-6.736117000	-1.193391000	0.779731000
1	-6.904218000	-3.479406000	-0.181274000

6	-0.509373000	2.305834000	-0.480177000
6	-1.374786000	3.317374000	-0.046192000
6	0.718490000	2.663812000	-1.061043000
6	-0.991681000	4.643015000	-0.195485000
1	-2.326764000	3.069607000	0.399329000
6	1.077957000	4.003584000	-1.193997000
1	1.389736000	1.895994000	-1.419648000
6	0.227026000	5.013482000	-0.760312000
1	2.026946000	4.261339000	-1.647243000
1	0.490506000	6.056856000	-0.856625000
7	-2.215147000	0.521979000	-0.326197000
7	-1.909840000	5.697550000	0.269902000
8	-1.554931000	6.866456000	0.149959000
8	-2.985338000	5.359513000	0.754927000

Enol form in gas phase

6	-0.203458000	1.025696000	-0.292372000
6	-2.357707000	0.710914000	-0.199374000
6	-1.806164000	-0.564393000	-0.175553000
7	-0.438907000	-0.329215000	-0.255837000
8	0.511708000	-1.333398000	-0.173074000
6	0.913005000	-1.558068000	1.149426000
1	0.179480000	-1.325771000	1.908616000
6	2.128343000	-2.037278000	1.441894000
6	3.191253000	-2.422316000	0.493234000
6	2.898727000	-3.022739000	-0.741438000
6	4.536648000	-2.210644000	0.838628000
6	3.924129000	-3.386662000	-1.609417000

1	1.869200000	-3.216003000	-1.012774000
6	5.558138000	-2.577392000	-0.032601000
1	4.777182000	-1.734577000	1.782154000
6	5.255953000	-3.165433000	-1.260147000
1	3.682471000	-3.854925000	-2.556922000
1	6.590725000	-2.399536000	0.245827000
1	6.051974000	-3.453736000	-1.937114000
6	-2.369358000	-1.917128000	-0.055042000
6	-3.306484000	-2.201376000	0.949543000
6	-1.987551000	-2.943509000	-0.932194000
6	-3.852413000	-3.475814000	1.067604000
1	-3.604569000	-1.417970000	1.636042000
6	-2.532675000	-4.218472000	-0.808289000
1	-1.270870000	-2.736077000	-1.717579000
6	-3.467141000	-4.488993000	0.190380000
1	-4.575015000	-3.679076000	1.849804000
1	-2.232531000	-4.999918000	-1.497431000
1	-3.891683000	-5.482022000	0.284493000
6	-3.771072000	1.128235000	-0.201588000
6	-4.783001000	0.338722000	-0.766381000
6	-4.117826000	2.371180000	0.348806000
6	-6.106029000	0.772492000	-0.762543000
1	-4.534751000	-0.610733000	-1.224179000
6	-5.440734000	2.802186000	0.350875000
1	-3.337882000	2.994744000	0.767743000
6	-6.441950000	2.003407000	-0.200719000
1	-6.874438000	0.151193000	-1.209239000

1	-5.690230000	3.764855000	0.783213000
1	-7.472538000	2.340120000	-0.199743000
6	1.101036000	1.687078000	-0.380677000
6	1.167616000	3.039102000	-0.014542000
6	2.262721000	1.051252000	-0.844625000
6	2.378154000	3.705621000	-0.114408000
1	0.285124000	3.555017000	0.334870000
6	3.465904000	1.748401000	-0.933578000
1	2.228086000	0.013858000	-1.145682000
6	3.540762000	3.087054000	-0.567635000
1	4.351254000	1.239999000	-1.295855000
1	4.462151000	3.648850000	-0.627278000
7	-1.361138000	1.655441000	-0.261528000
7	2.438710000	5.132211000	0.283139000
8	3.516032000	5.705352000	0.172149000
8	1.413197000	5.653881000	0.699224000
8	2.422667000	-2.123501000	2.789423000
1	2.954426000	-2.912745000	2.945229000

Enol form in $CHCl_3$

6	-0.197497000	1.030339000	-0.304077000
6	-2.355790000	0.745582000	-0.209819000
6	-1.819749000	-0.535201000	-0.165605000
7	-0.451218000	-0.318412000	-0.243743000
8	0.486524000	-1.331702000	-0.157144000
6	0.899533000	-1.544267000	1.166524000
1	0.173237000	-1.297733000	1.928121000
6	2.114131000	-2.032161000	1.449310000

6	3.160775000	-2.437901000	0.490425000
6	2.843928000	-3.051961000	-0.731699000
6	4.512756000	-2.232115000	0.813007000
6	3.853037000	-3.434031000	-1.611604000
1	1.809631000	-3.243932000	-0.985282000
6	5.517972000	-2.616641000	-0.069942000
1	4.774508000	-1.752183000	1.748710000
6	5.192051000	-3.217108000	-1.285948000
1	3.592919000	-3.912804000	-2.548814000
1	6.555905000	-2.443812000	0.190747000
1	5.975294000	-3.518994000	-1.971777000
6	-2.402915000	-1.878432000	-0.027410000
6	-3.328530000	-2.140177000	0.993708000
6	-2.050663000	-2.914743000	-0.905244000
6	-3.894528000	-3.404981000	1.127183000
1	-3.599757000	-1.350163000	1.683834000
6	-2.616001000	-4.179862000	-0.766132000
1	-1.341586000	-2.725229000	-1.701996000
6	-3.540122000	-4.428868000	0.248554000
1	-4.607189000	-3.592401000	1.922265000
1	-2.338698000	-4.969962000	-1.454763000
1	-3.979813000	-5.414037000	0.354568000
6	-3.765722000	1.174745000	-0.221426000
6	-4.776002000	0.397269000	-0.807031000
6	-4.113238000	2.413176000	0.340055000
6	-6.096877000	0.839273000	-0.815685000
1	-4.527817000	-0.549862000	-1.269813000

6	-5.433970000	2.853468000	0.329155000
1	-3.338179000	3.026338000	0.783237000
6	-6.432980000	2.067228000	-0.245580000
1	-6.863216000	0.226791000	-1.277721000
1	-5.683569000	3.811828000	0.770929000
1	-7.461397000	2.410236000	-0.254339000
6	1.119105000	1.666531000	-0.401223000
6	1.229023000	3.002558000	0.005960000
6	2.251978000	1.017684000	-0.917147000
6	2.453600000	3.643690000	-0.109173000
1	0.370943000	3.526116000	0.400847000
6	3.469738000	1.687373000	-1.018728000
1	2.182470000	-0.008519000	-1.249454000
6	3.587911000	3.011846000	-0.614649000
1	4.332050000	1.170930000	-1.421669000
1	4.523685000	3.547363000	-0.685729000
7	-1.347205000	1.678517000	-0.285734000
7	2.557951000	5.049645000	0.328272000
8	3.642556000	5.610194000	0.205592000
8	1.558567000	5.587421000	0.792190000
8	2.422495000	-2.107603000	2.794180000
1	2.967022000	-2.888595000	2.953462000

Enol form in DMSO

6	-0.195917000	1.033030000	-0.313879000
6	-2.355837000	0.762653000	-0.215948000
6	-1.827461000	-0.520512000	-0.163209000
7	-0.458387000	-0.312323000	-0.242466000

8	0.473993000	-1.328967000	-0.151988000
6	0.892095000	-1.533311000	1.172253000
1	0.169253000	-1.278498000	1.934441000
6	2.106017000	-2.025104000	1.452567000
6	3.146518000	-2.442134000	0.491761000
6	2.820363000	-3.057060000	-0.727662000
6	4.501151000	-2.245456000	0.809146000
6	3.823436000	-3.448421000	-1.610573000
1	1.784144000	-3.242663000	-0.977976000
6	5.500276000	-2.639118000	-0.076880000
1	4.771549000	-1.767558000	1.743387000
6	5.165352000	-3.239921000	-1.290483000
1	3.556090000	-3.927163000	-2.545696000
1	6.540298000	-2.473243000	0.179705000
1	5.943829000	-3.548378000	-1.978787000
6	-2.420712000	-1.858181000	-0.014732000
6	-3.351581000	-2.102984000	1.005977000
6	-2.072841000	-2.904944000	-0.882060000
6	-3.928234000	-3.362191000	1.148955000
1	-3.616830000	-1.305663000	1.690014000
6	-2.648755000	-4.164443000	-0.733136000
1	-1.358682000	-2.729456000	-1.677420000
6	-3.578786000	-4.396812000	0.280491000
1	-4.644315000	-3.537154000	1.943781000
1	-2.374390000	-4.963065000	-1.412924000
1	-4.026292000	-5.377578000	0.394055000
6	-3.764271000	1.196914000	-0.230588000

6	-4.769610000	0.434882000	-0.844970000
6	-4.116239000	2.422535000	0.356255000
6	-6.089759000	0.879855000	-0.858658000
1	-4.517516000	-0.502262000	-1.325858000
6	-5.436248000	2.866353000	0.340122000
1	-3.347096000	3.022833000	0.826979000
6	-6.430055000	2.095721000	-0.264671000
1	-6.852040000	0.279513000	-1.342697000
1	-5.689610000	3.813828000	0.802699000
1	-7.457664000	2.440851000	-0.276972000
6	1.126623000	1.656020000	-0.417792000
6	1.261894000	2.980508000	0.015977000
6	2.241017000	1.003061000	-0.968471000
6	2.493232000	3.608350000	-0.108973000
1	0.419676000	3.505942000	0.441001000
6	3.465767000	1.658436000	-1.078841000
1	2.150795000	-0.014677000	-1.321519000
6	3.609328000	2.972386000	-0.649086000
1	4.313286000	1.140468000	-1.509755000
1	4.551780000	3.494804000	-0.727822000
7	-1.341656000	1.690123000	-0.299542000
7	2.623163000	5.000958000	0.355054000
8	3.715275000	5.549058000	0.238217000
8	1.635571000	5.548245000	0.836101000
8	2.419000000	-2.092637000	2.796858000
1	2.970619000	-2.868469000	2.959175000