# Carboxamide substituted cyclopentadienyl iridium(III) complexes: synthesis, characterisation and enantioselective imine reduction

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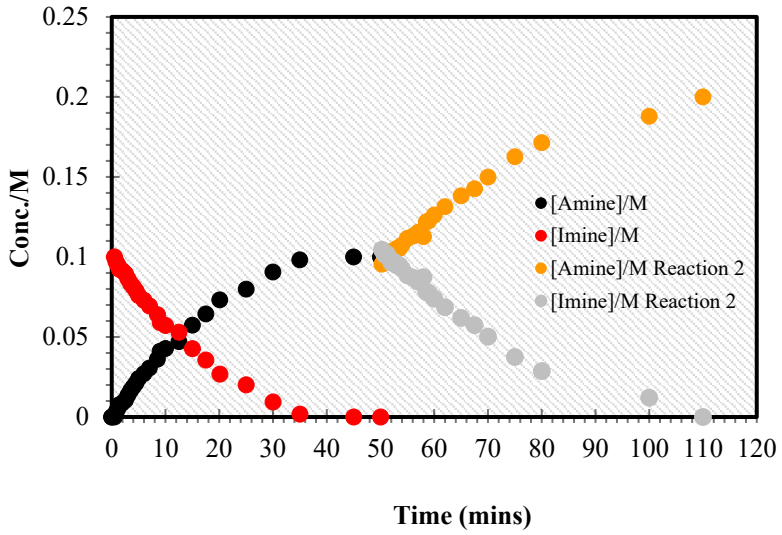
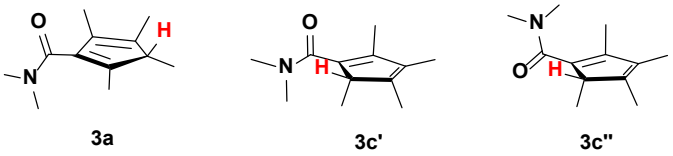
**Page**

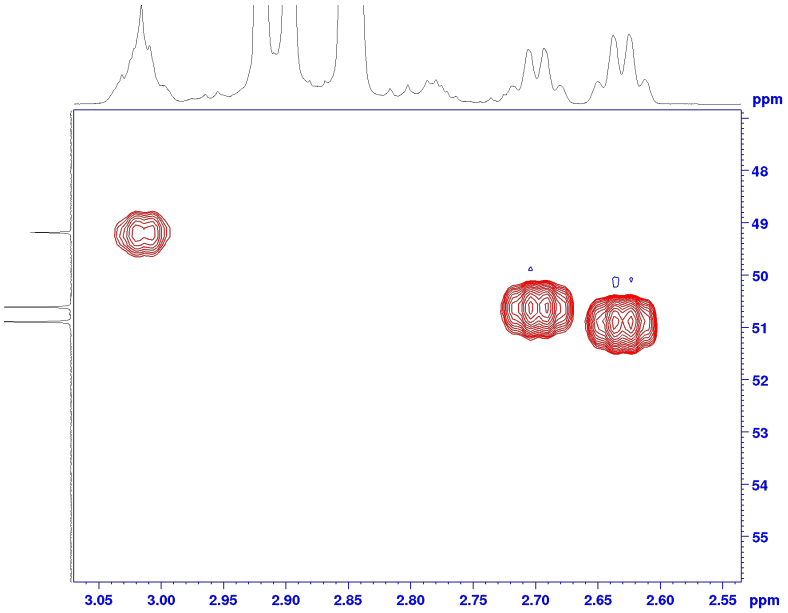
**SUPPLEMENTARY INFORMATION**

**S1.** ATH of 1-methyl-3,4-dihydroisoquinoline [0.1M] with IrCp*I-(*R,R*)TsDPEN [1.00 x $10^{-3}$M] in acetonitrile at 28 °C with a 5:2 azeotropic mixture, followed by a further introduction of imine substrate.

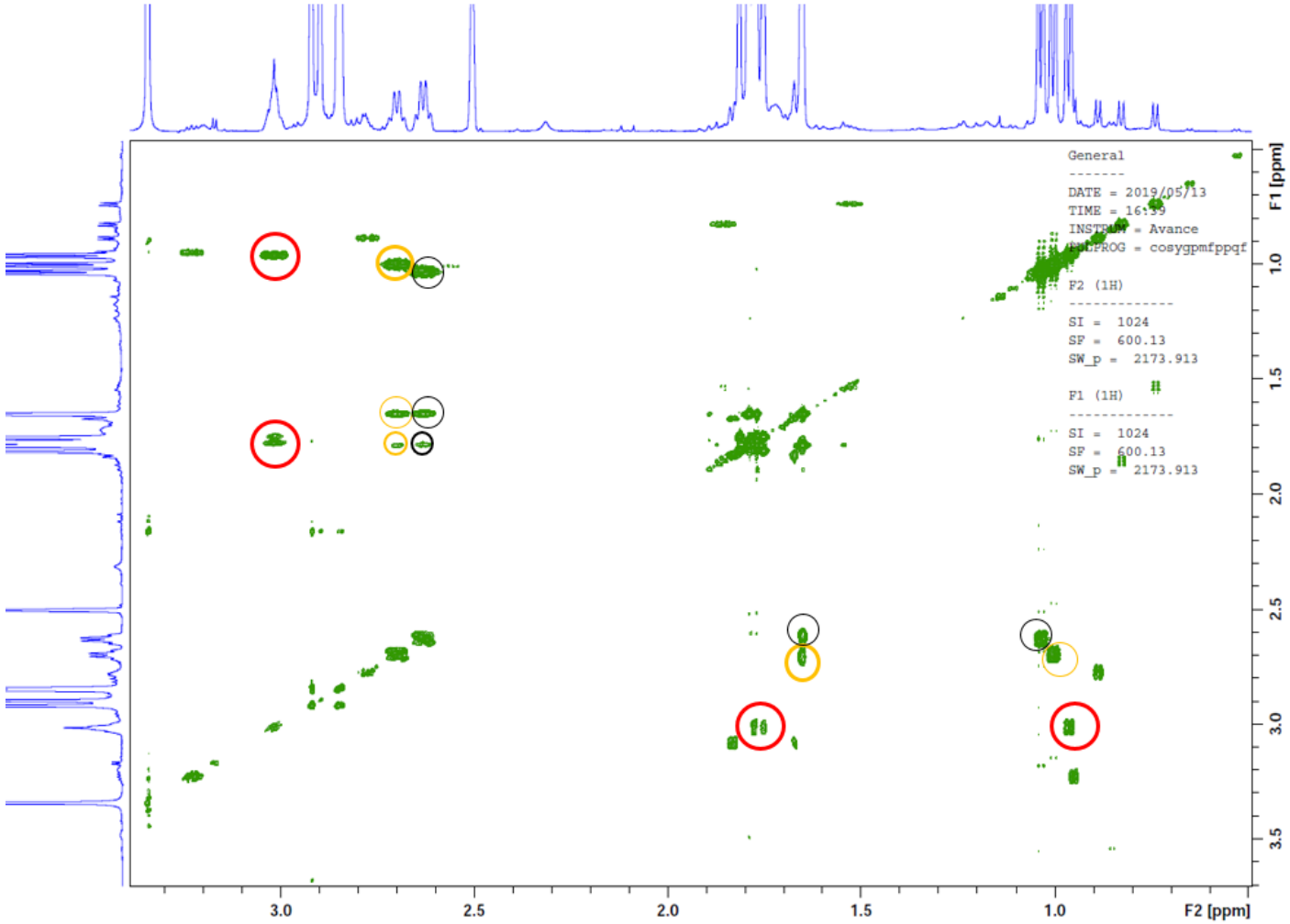



**S2.** HSQC of Cp*CONMe$_2$ in DMSO-d$_6$ showing the 3 *Me*-C-**H** signals. Structure 1(**3.01 ppm**), structure 2 (**2.70 ppm**) and structure 3 (**2.63 ppm**)

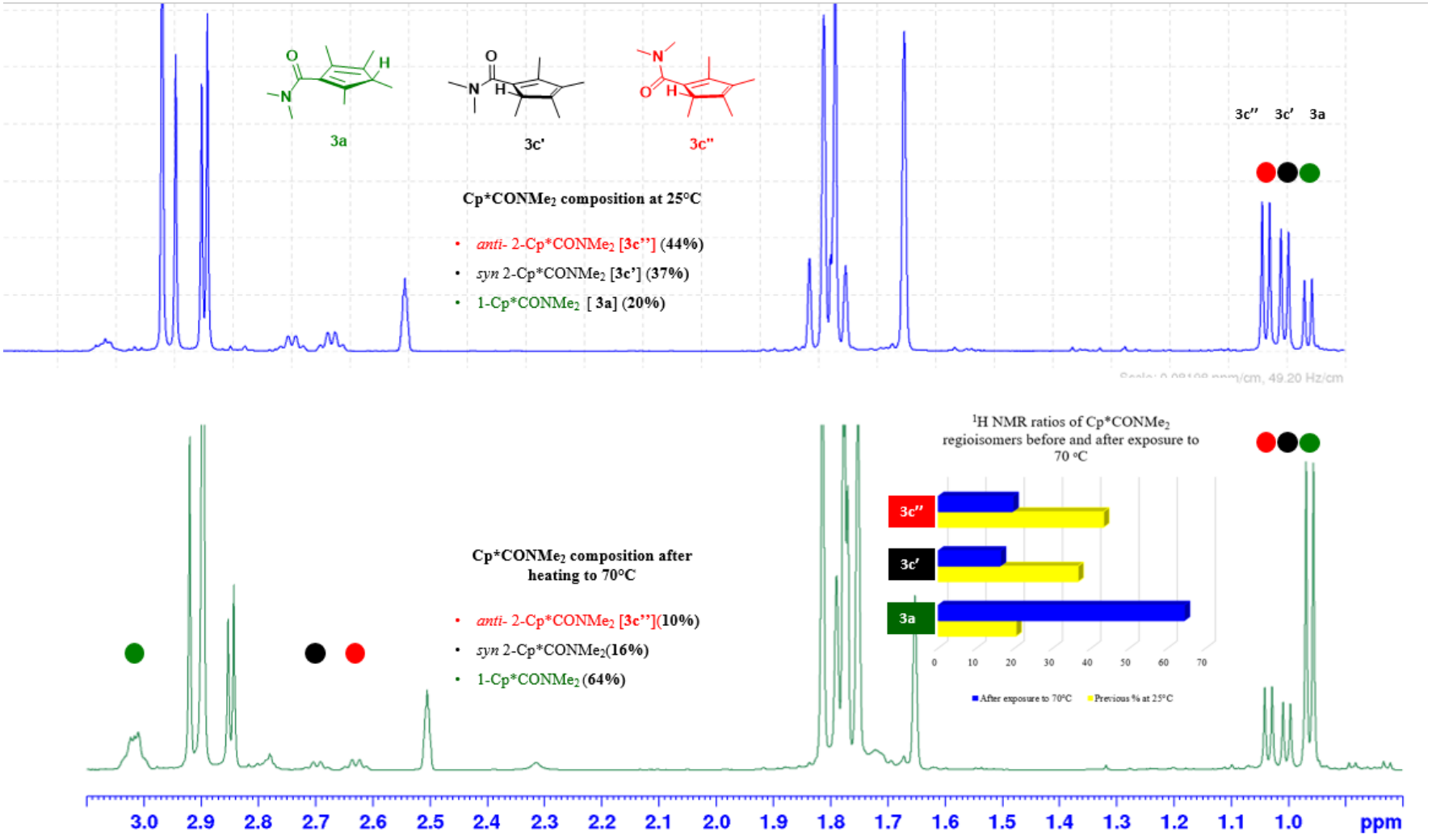


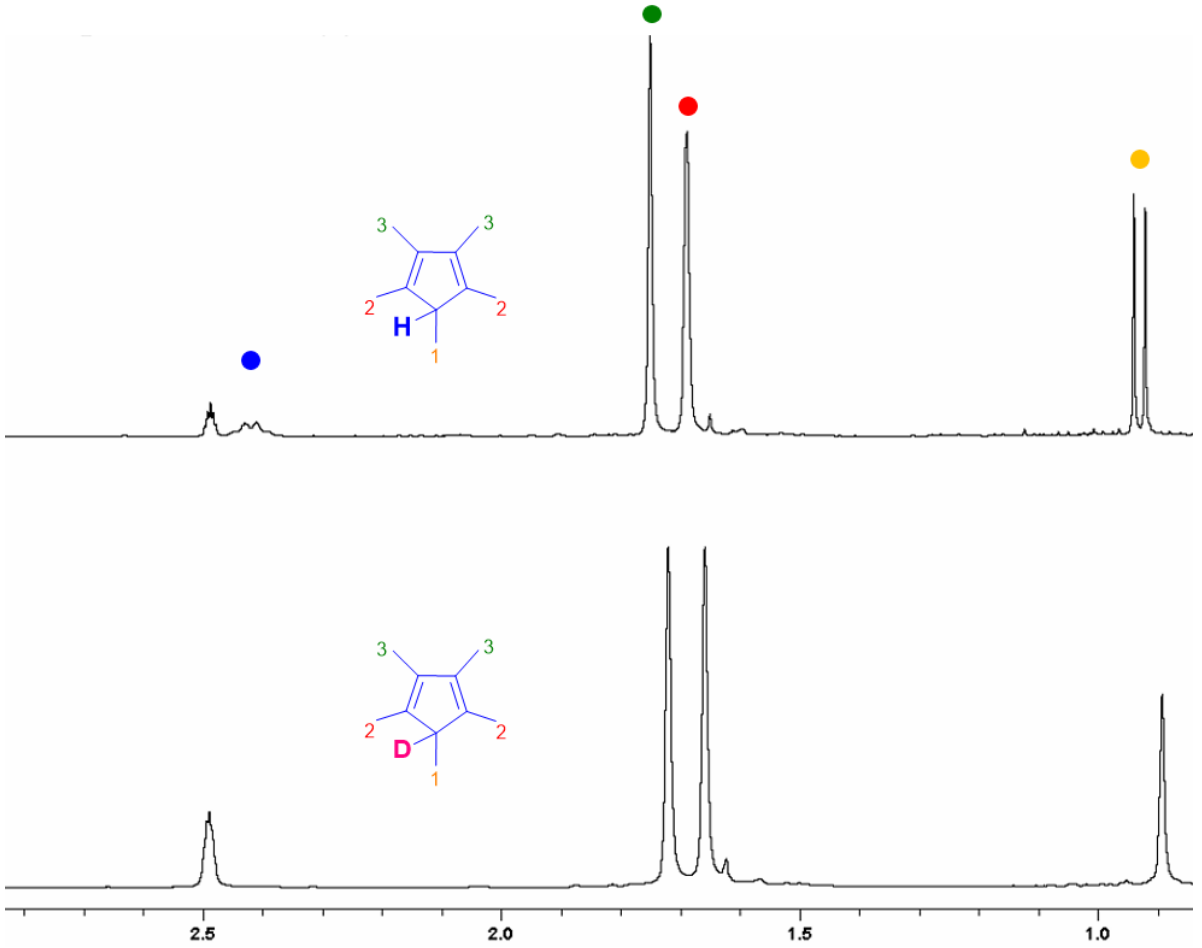
**S3.** COSY of Cp*CONMe$_2$ (**3**) in DMSO-d$_6$ (structure **3a**-**red**, structure **3c´**-**yellow** and structure **3c´´- black**).



**S4.** Structural ratios before and after heating to 70 °C -$^{1}$H NMR of 0.1M of Cp*CONMe$_2$ (**3**) in DMSO-d$_6$ was run at room temperature and the sample was progressively heated to 70 °C and allowed to cool to room temperature after which the second scan was taken.



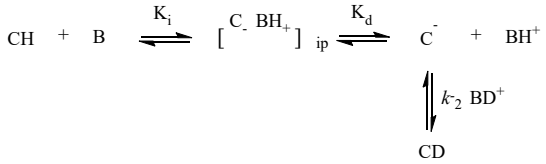
**S5.** $^{1}H$ NMR signal identification of Cp* in DMSO-$d_6$ (upper spectrum) and the spectrum of the deuterated species upon H/D exchange with [0.05M] NaOD (lower spectrum).



The effect of the basicity of the Cp* ligand on the catalytic activity of **i** is of interest. A common method of estimating the acidity of weak carbon acids is to determine their p$K_a$ from their rates of H/D exchange.[1] Solubility studies indicated that 90%/10% v/v DMSO/water was a suitable solvent system for both Cp* and Cp*CONMe$_2$. The p$K_a$ of $H_2O$ in DMSO is 32[2] reflecting the poor ability of DMSO, like all aprotic solvents, to solvate anions. Consequently, the basicity of hydroxide ion in water–DMSO mixtures increases strongly with increasing DMSO content of the mixtures, and this fact has been used to determine the ionization of weakly acidic substrates. The p$K_a$ of DMSO in water is 35[3] which presumably increases in water-DMSO mixtures and so it is unlikely that there are any significant amounts of the DMSO anion in low concentrations of NaOD in these mixtures.

The acidity of the cyclopentadiene derivatives were estimated by determining the rates of base catalysed H/D exchange by $^1$H NMR. A solution of 0.1 M cyclopentadiene was dissolved in 90/10% v/v d$_6$DMSO/D$_2$O containing various concentrations of NaOD at 25$^o$C. For example, the loss of the quartet C-*H* signal at 2.45 ppm of Cp* coupled with the transformation of the *Me*-CH doublet at 0.9 ppm into a singlet which indicated the exchange of the acidic proton. The loss of the C-*H* signal was normalised against the integration of the methyl signal as a constant and changed exponentially with reaction time giving pseudo first-order rate constants for D-exchange which in turn showed a first-order dependence on the concentration of NaOD. The corresponding second-order rate constant $k_{OD^-}$ for H/D exchange of Cp* by OD$^-$ is 8.70 ± 0.40 x 10$^{-2}$ M$^{-1}$s$^{-1}$ in 90%/10% v/v DMSO-d$_6$/D$_2$O. The mechanism of D-exchange presumably occurs through the formation of the intermediate carbanion (**Scheme**). The relatively high dielectric constant of the solvent mixture of 58[4] may mean that the ionization of these carbon acids may not give rise to substantial ion-pairs in equilibrium with the dissociated species where the product $K_iK_d$ corresponds to the normal ionization constant $K_a$. However, it is unlikely that exchange can occur from the ion-pair and so if isotopic exchange occurs with the dissociated carbanion, then the rate of protonation of the carbanion $k_{-2}$ can be assumed to be diffusion-controlled,[5,6] which is approximately ~ 10$^9$ M$^{-1}$s$^{-1}$.

From this the p$K_a$ of the carbon acids could be evaluated if p$K_w$ in 90%/10% v/v DMSO-d$_6$/D$_2$O was known, which it is not although there are some uncertain estimates based on H- functions.[7] For the purpose of this study it is the relative difference in p$K_a$ that is of interest. As the objective is to estimate the relative basicities of the anions of Cp* and Cp*CONMe$_2$ then their relative rates of H/D exchange are directly related to their relative p$K_a$'s.

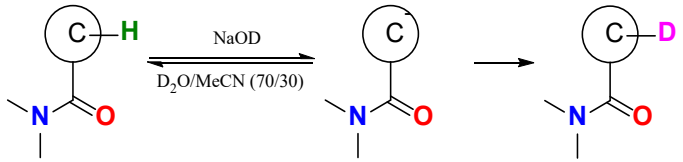


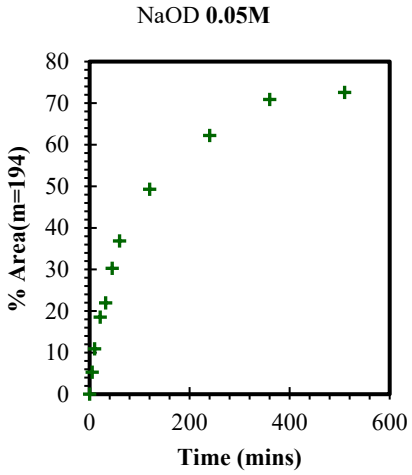

The p$K_a$ of cyclopentadiene and pentamethylcyclopentadiene in DMSO are 18.0 and 26.1, respectively,[8] i.e. a difference of 8.1 The p$K_a$ of cyclopentadiene in DMSO is 3 units higher than in water,[10] and and so a crude estimation can be made that Cp* would have a p$K_a$ ~23 in water. Extrapolating the Brönsted plot for the base catalysed ionisation of strongly acidic cyclopentadienes against their p$K_a$ in water ($\beta$ = -0.3)[9] gives a predicted $k_{OD^-}$ = 2.34 x 10$^{-2}$ M$^{-1}$s$^{-1}$ for Cp* in water. Conversely the observed $k_{OD^-}$ = 8.70 x 10$^{-2}$ M$^{-1}$s$^{-1}$ for H/D exchange gives, ignoring solvent isotope effects, a predicted p$K_a$ ~21 in water and estimated ~24 in DMSO in reasonable agreement with the experimental value of 26.1 in pure DMSO.

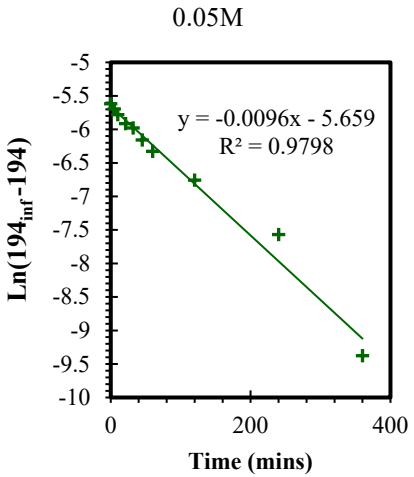
The rates of H/D exchange of Cp*CONMe$_2$ in 90%/10% v/v DMSO/D$_2$O with NaOD were determined by $^1$H NMR and also follow an exponential decay and the corresponding observed pseudo first-order rate constants show a first-order dependence on base concentration. The second-order rate constant for *syn* 2-Cp*CONMe$_2$ **3c´** $k_{OD^-}$ = 0.492 M$^{-1}$s$^{-1}$ and that for *anti* 2-Cp*CONMe$_2$ **3c´´** $k_{OD^-}$ = 0.569 M$^{-1}$s$^{-1}$.The rates of exchange of the two conformers of 2-Cp*CONMe$_2$ **3** are very similar, which would not be expected for significantly different regioisomers and is compatible with distinguishable rotamers of the same regioisomer. The rate of H/D exchange of Cp*CONMe$_2$ **3** is 6-fold faster than that of Cp*, corresponding to a difference of only 0.8 in p$K_a$. Using the extrapolated Brönsted plot of log $k_{OH^-}$ for CH ionisation as a function of the p$K_a$ of substituted cyclopentadienes in water gives a crude estimate of the p$K_a$ of ~18.4 for 2-Cp*CONMe$_2$ **3c** in water

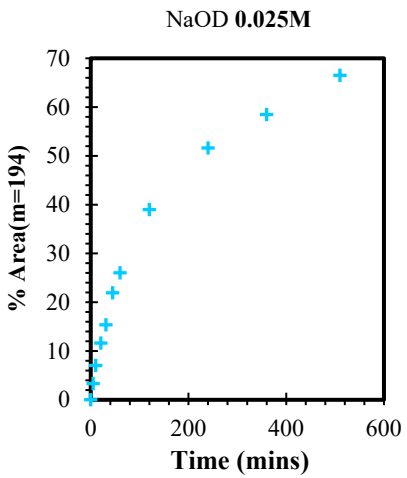
As an indication of the importance of solvent on the rates of H/D exchange of 2-Cp*CONMe$_2$ **3c´** and **3c´´** were determined in D$_2$O/ acetonitrile (70/30, v/v %) with NaOD monitored by GC-MS using the rate of disappearance of the molecular mass (m) 193.1 and the appearance of mass plus one (m+1) 194.1. The exponential growths of m+1 give observed pseudo-first order rate constants for H/D exchange reaction and the corresponding rate constants are first order in [NaOD]. The corresponding second-order rate constant $k_{OD^-}$ in 70/30% v/v D$_2$O/ACN is 3.54 x 10$^{-3}$ M$^{-1}$ s$^{-1}$, more than 2-orders of magnitude less than that in in 90%/10% v/v DMSO/D$_2$O. This probably reflects the increased basicity of hydroxide-ion in DMSO which is very poor at stabilising anions.

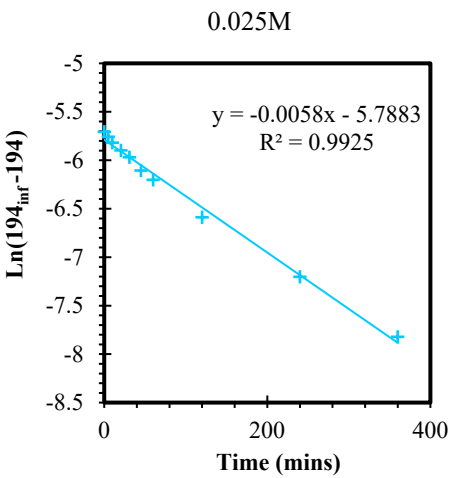
**S6.** Rate of H/D exchange of Cp*CONMe$_2$ (**3**) (5mM) in $D_2O$/MeCN (70/30 %) with NaOD at 2 different concentrations ([0.05M] and [0.025M]) using GC-MS.



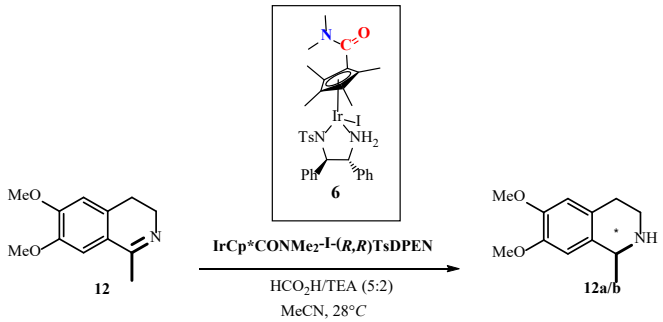



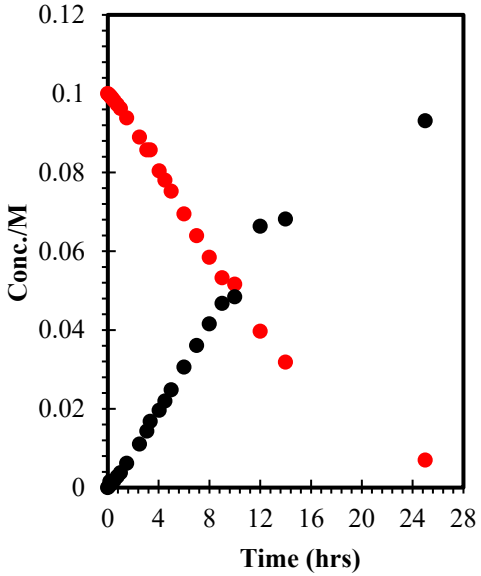



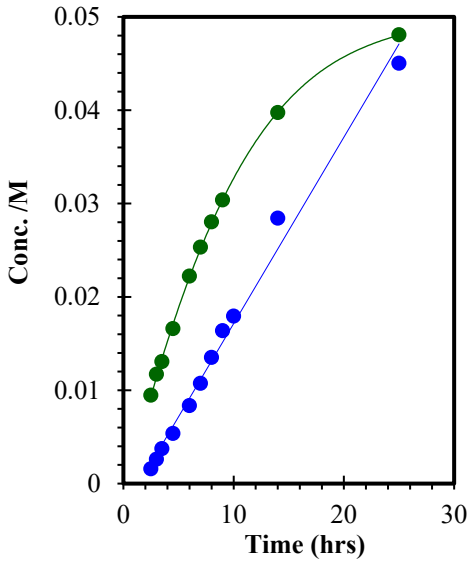



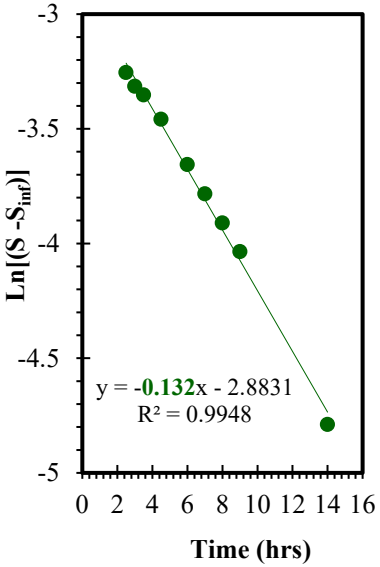



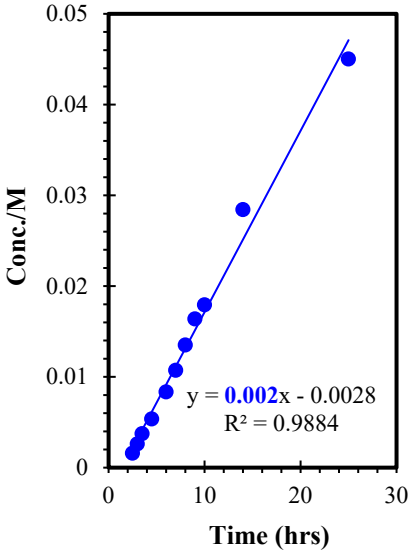
**S7a.** A plot of ATH of 6,7-Dimethoxy-1-methyl-3,4-DHIQ (●) **12** [0.1M] in acetonitrile at 28°C with IrCp*CONMe$_2$-I-*(R,R)* TsDPEN - [1.0 x $10^{-3}$ M]-*Cat.* and $HCO_2H/Et_3N$ (5:2) indicating the formation of *(S●)*-6,7-dimethoxy-1-methyl-1,2,3,4-tetrahydroisoquinoline **12a** *via* first-order kinetics and *(R●)*-enantiomer **12b** *via* zero-order kinetics with IrCp*CONMe$_2$ catalyst.



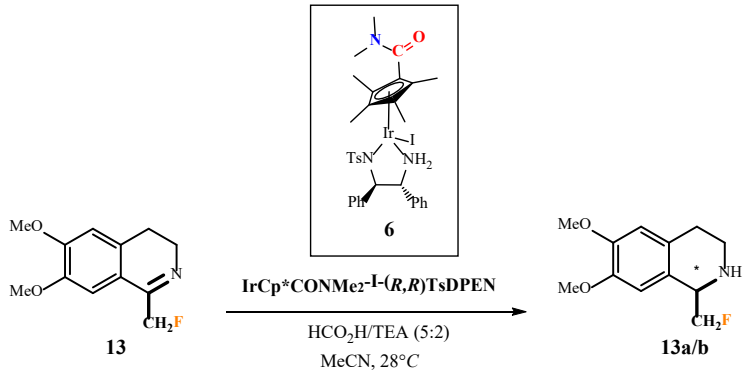



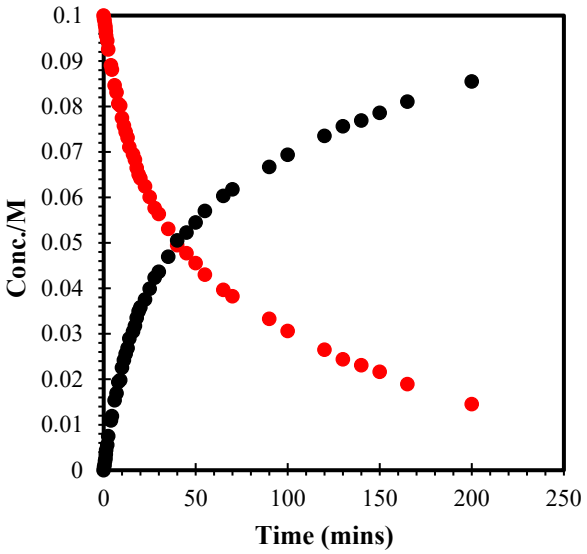



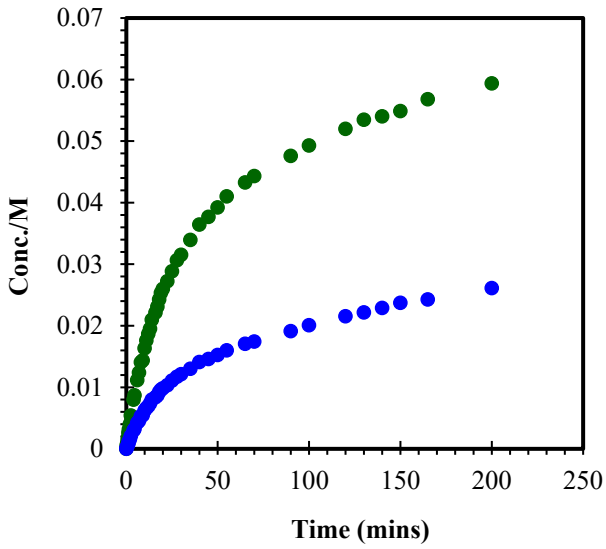



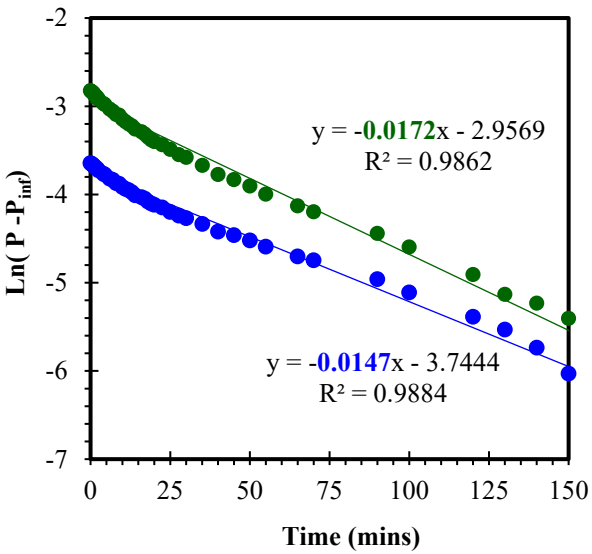



**S7b** A plot of the ATH of 1-monofluoromethyl-6,7-Dimethoxy-3,4-dihydroisoquinoline (●) **13** [0.1M] with IrCp*CONMe$_2$-I-(*R,R*)TsDPEN [5.0x10$^{-4}$M] in acetonitrile at 28 °C with a $HCO_2H$ [0.6 M] and $Et_3N$ [0.24M] azeotropic mixture (*left*) with formation of *(S●)* **13a** and *(R●)* -1-(monofluoromethyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline **13b** enantiomers.

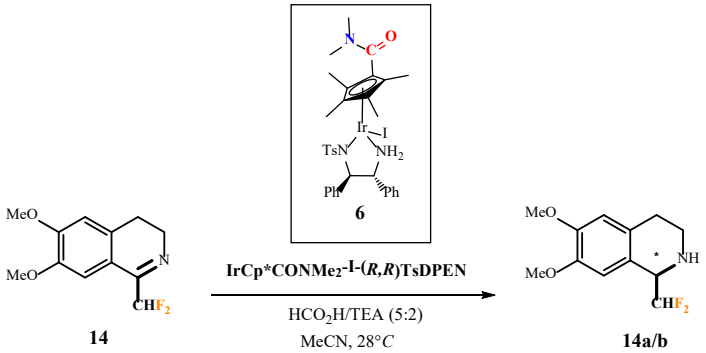


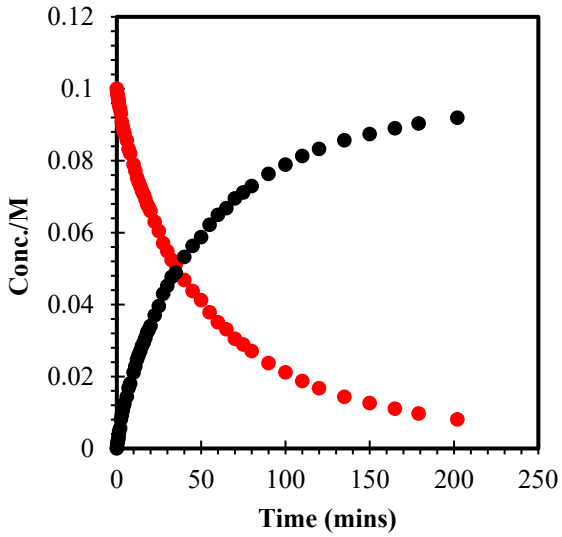



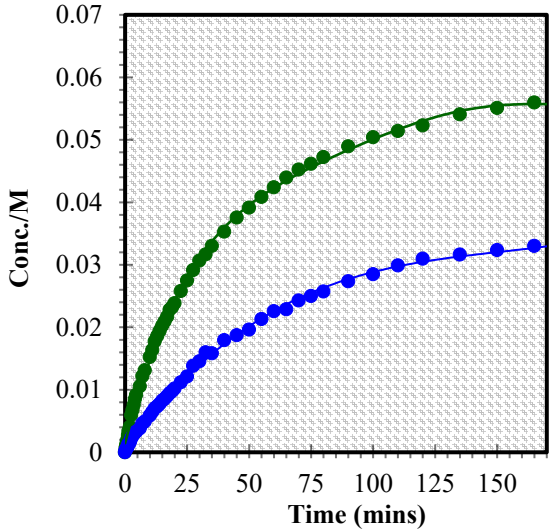



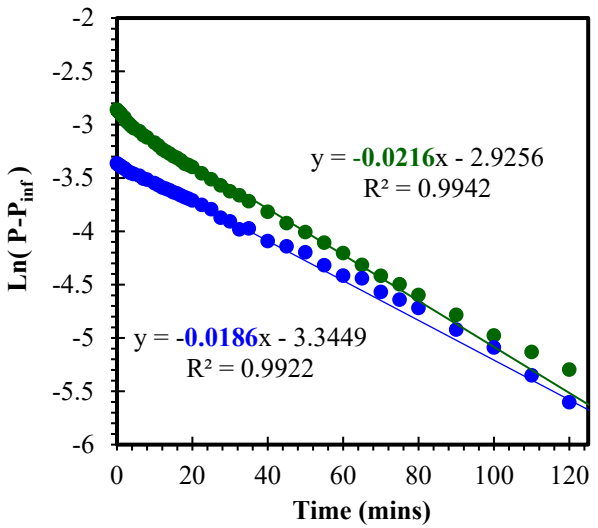



**S7c** A plot of the ATH of 1-difluoromethyl-6,7-Dimethoxy-3,4-dihydroisoquinoline (●) **14** [0.1M] with IrCp*CONMe$_2$-I-(*R,R*)TsDPEN [5.0x10$^{-4}$M] in acetonitrile at 28 °C with a $HCO_2H$ [0.6 M] and $Et_3N$ [0.24M] azeotropic mixture (*left*) with formation of *(S●)* **14a** and *(R●)* -1-(difluoromethyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline **14b** enantiomers using the IrCp*CONMe$_2$ catalyst (*right*).

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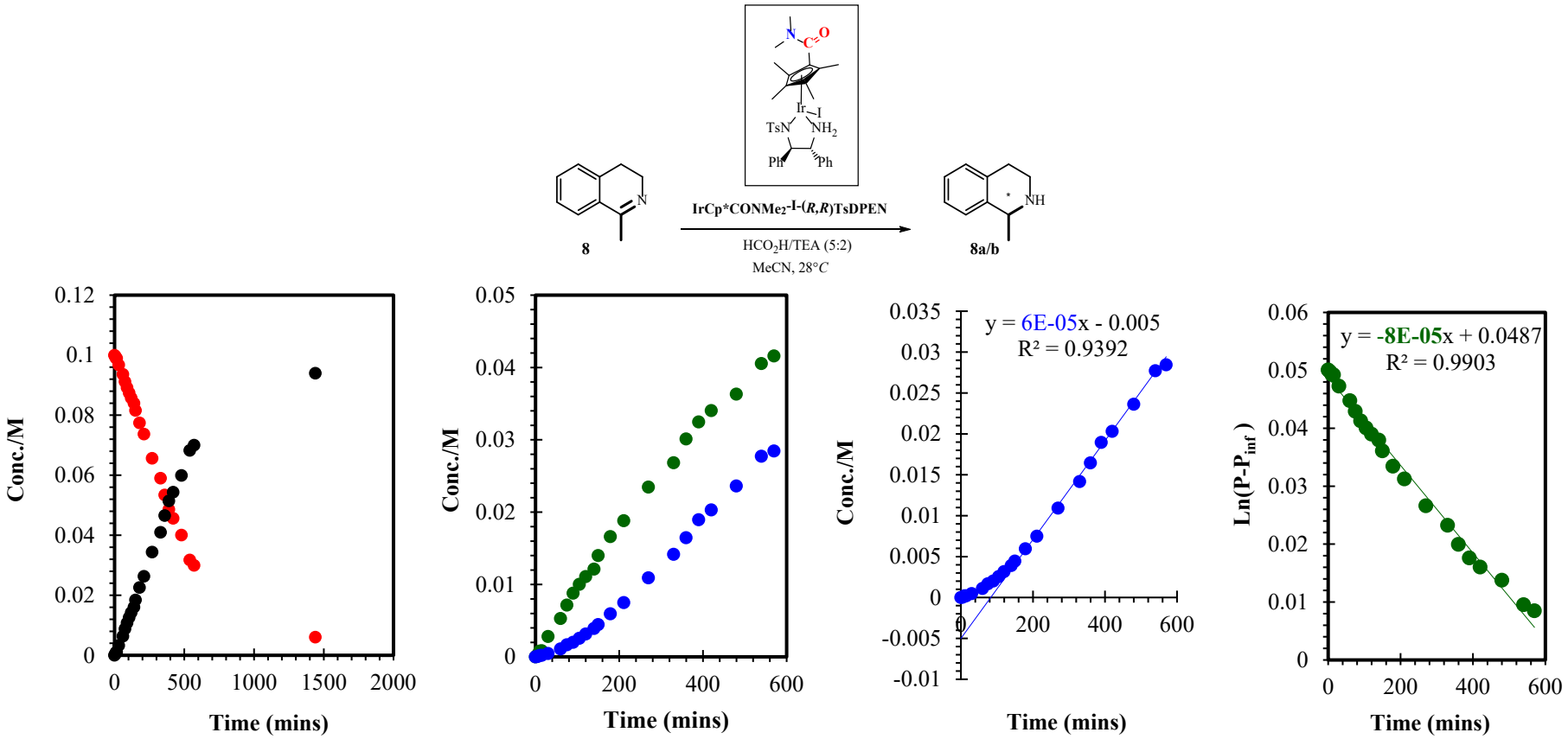
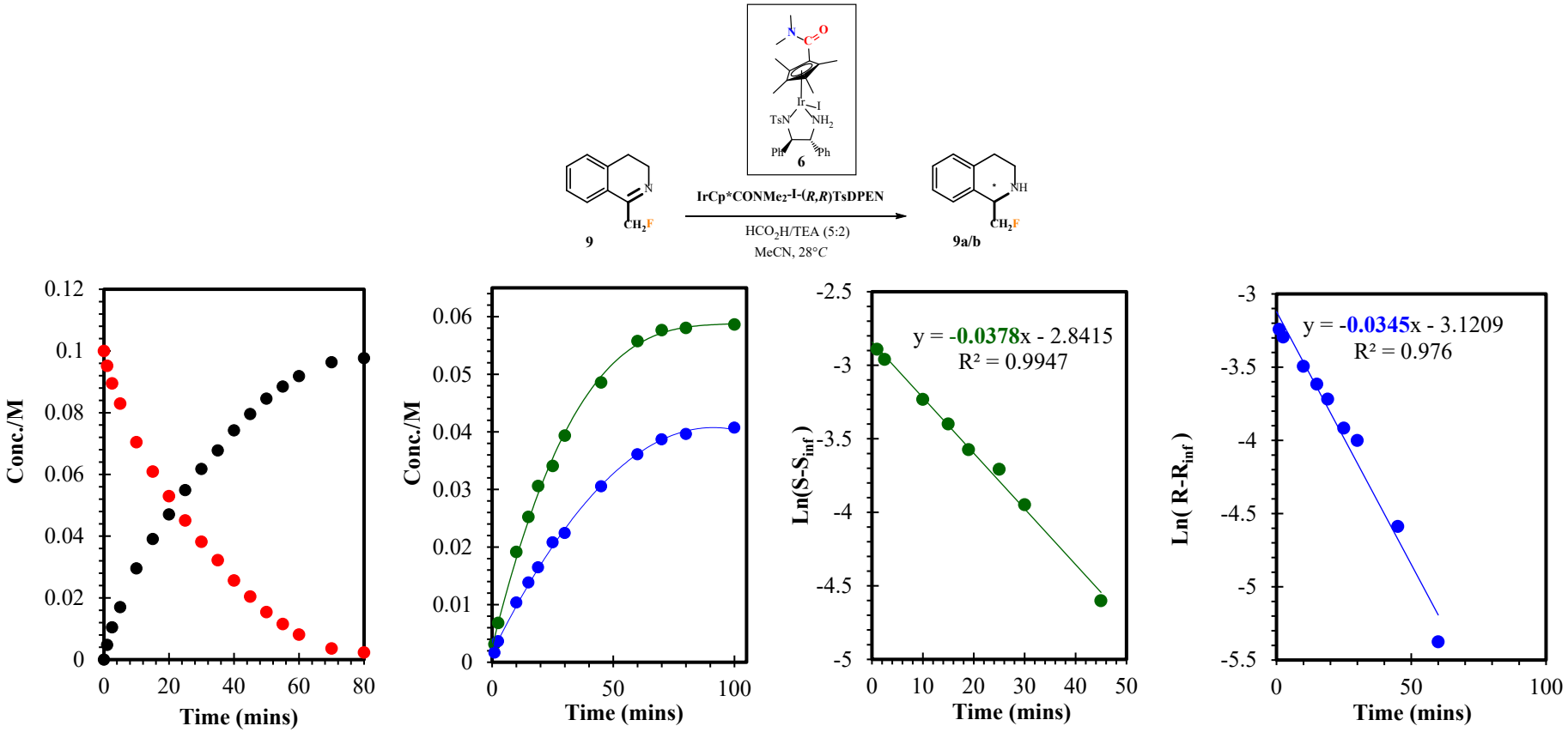
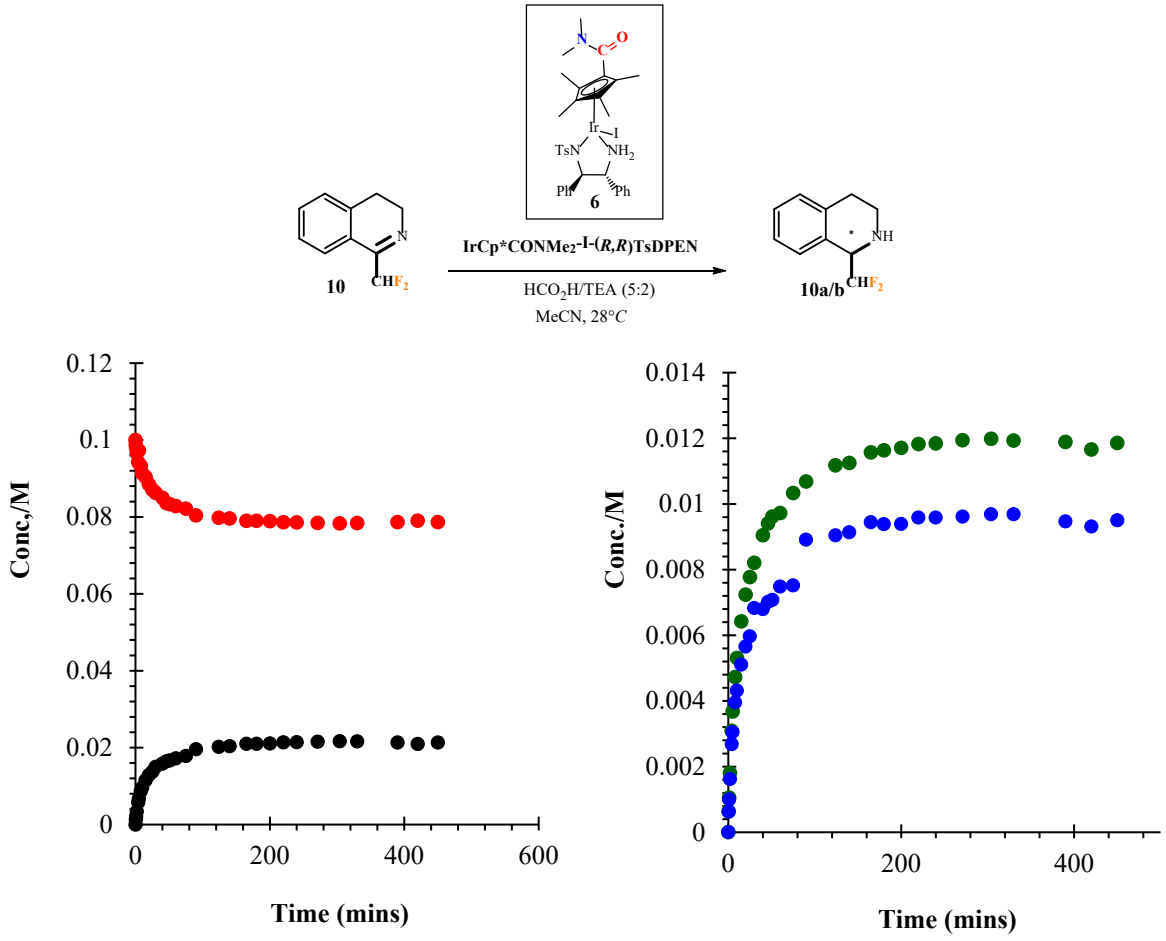
**S7d.** A plot of ATH 1-methyl-3,4-DHIQ (●) **8** [0.1M] in acetonitrile at 28°C with IrCp*CONMe$_2$-I-*(R,R)* TsDPEN - [1.0 x $10^{-3}$ M] and $HCO_2H/Et_3N$ (5:2) indicating the formation of *(S●)* -1-methyl-1,2,3,4-tetrahydroisoquinoline **8a** *via* first order kinetics and *(R●)*-enantiomer **8b** *via* zero order kinetics with IrCp*CONMe$_2$ catalyst



**S7e.** A plot of ATH 1-monofluoromethyl-3,4-DHIQ (●) [0.1M] in acetonitrile at 28°C with IrCp*CONMe$_2$-I-*(R,R)* TsDPEN - [1.0 x $10^{-3}$ M] and $HCO_2H/Et_3N$ (5:2) indicating the formation of *(S●)* -1-monofluoro-methyl-1,2,3,4-tetrahydroisoquinoline **9a** *via* first order kinetics and *(R●)*-enantiomer **9b** *via* zero order kinetics with IrCp*CONMe$_2$ catalyst

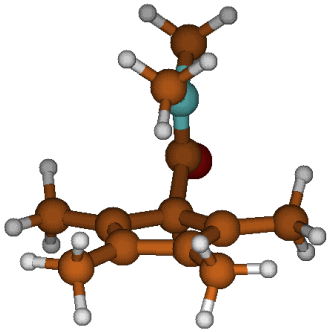


**S7f.** A plot of ATH 1-difluoromethyl-3,4-DHIQ (●) **10** [0.1M] in acetonitrile at 28°C with IrCp*CONMe$_2$-I-*(R,R)* TsDPEN - [1.0 x $10^{-3}$ M] and $HCO_2H/Et_3N$ (5:2) indicating the formation of *(S●)* -1-difluoromethyl-1,2,3,4-tetrahydroisoquinoline **10a** *via* first order kinetics and *(R●)*-enantiomer **10b** *via* zero order kinetics with IrCp*CONMe$_2$ catalyst

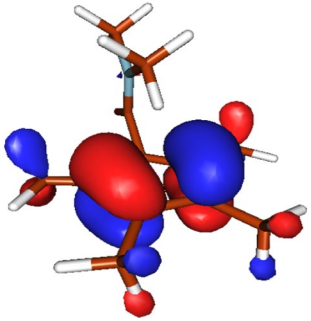


**Scheme 8.** DFT calculations of the neutral and anionic form of the Cp*CONMe$_2$ ligand.

**Neutral form:**

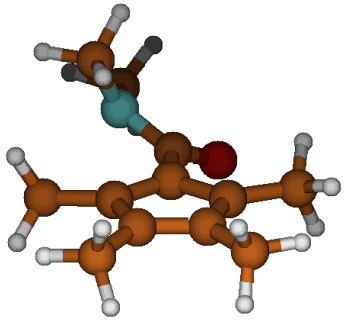


**Geometry: dihedral angle 90°**

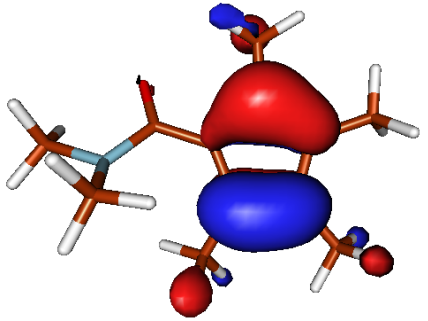


**HOMO**

**Anion:**



**Geometry: dihedral angle 30°**



**HOMO**

**S9.** Calculated coordinates

33
**3a´** scf done:  -598.916893 Sum of electronic and thermal Free Energies -598.674556 imaginary frequencies: 0

| | | | |
|---|---|---|---|
| C | -0.030757 | 0.209038 | 0.178122 |
| C | 0.157121 | 0.273469 | 1.513205 |
| C | 1.605990 | 0.290998 | 1.826122 |
| C | 2.297384 | 0.261912 | 0.666171 |
| C | 1.324890 | 0.202539 | -0.494354 |
| C | -0.888337 | 0.163849 | 2.572915 |
| O | -0.857176 | -0.772232 | 3.367236 |
| C | 2.124578 | 0.341495 | 3.228612 |
| C | 3.776746 | 0.277922 | 0.456746 |
| C | 1.498038 | 1.347430 | -1.506120 |
| C | -1.313786 | 0.130193 | -0.581401 |
| N | -1.873967 | 1.118096 | 2.608302 |
| C | -1.844865 | 2.368251 | 1.867237 |
| C | -2.949971 | 0.985958 | 3.578916 |
| H | 3.214822 | 0.347190 | 3.257477 |
| H | 1.769838 | 1.240595 | 3.744994 |
| H | 1.759085 | -0.513504 | 3.802696 |
| H | 4.103399 | -0.583669 | -0.136767 |
| H | 4.097839 | 1.174817 | -0.086427 |
| H | 4.320442 | 0.254232 | 1.402129 |
| H | 0.763295 | 1.277720 | -2.312077 |
| H | 1.372925 | 2.313114 | -1.008584 |
| H | 2.492274 | 1.323919 | -1.958235 |
| H | -1.305557 | -0.711107 | -1.282407 |
| H | -2.167622 | 0.003463 | 0.085716 |
| H | -1.483161 | 1.035343 | -1.177886 |
| H | -1.897900 | 3.213341 | 2.562749 |
| H | -0.925285 | 2.444475 | 1.293979 |
| H | -2.696888 | 2.437201 | 1.181858 |
| H | -2.842974 | 1.722660 | 4.383716 |
| H | -3.913987 | 1.148060 | 3.086931 |
| H | -2.917215 | -0.012341 | 4.007399 |
| H | 1.453821 | -0.753045 | -1.024962 |

33
**3a´DMSO** scf done:  -598.930660 Sum of electronic and thermal Free Energies -598.688999 imaginary frequencies: 0

| | | | |
|---|---|---|---|
| C | 0.000687 | -0.024020 | 0.004840 |
| C | -0.002855 | -0.035263 | 1.517631 |
| C | 1.278123 | -0.032333 | 1.946540 |
| C | 2.205686 | -0.030506 | 0.788636 |

```
 C     1.473925    -0.016208    -0.349045
 C    -1.258008    -0.035448     2.323903
 C     1.744537    -0.160844     3.357960
 N     1.412552     0.821702     4.235763
 C     1.772696     0.682731     5.640324
 C     3.694264    -0.012849     0.943827
 C     1.943852     0.013591    -1.766796
 C    -0.784293     1.157330    -0.587543
 O     2.395182    -1.158491     3.699664
 C     0.851176     2.114520     3.864241
 H     4.200074     0.073439    -0.019194
 H     4.010815     0.830219     1.568523
 H     4.050762    -0.920748     1.439726
 H     1.519248    -0.817840    -2.341663
 H     1.630871     0.934624    -2.273356
 H     3.031170    -0.051540    -1.838677
 H    -1.834517     1.118150    -0.287773
 H    -0.364150     2.107360    -0.244223
 H    -0.745681     1.140438    -1.679500
 H    -1.951075    -0.807605     1.973140
 H    -1.060603    -0.210155     3.383321
 H    -1.784014     0.922973     2.234539
 H     1.503713     2.912276     4.233091
 H     0.771185     2.200335     2.784672
 H    -0.139639     2.246127     4.309403
 H     2.693144     1.233189     5.866646
 H     0.966446     1.086592     6.257217
 H     1.922343    -0.367455     5.878663
 H    -0.455882    -0.955706    -0.360936

33
3a´´scf done:  -598.916124 Sum of electronic and thermal Free Energies -598.674512 imaginary frequencies: 0
 C     0.061230     0.082927     0.153144
 C     0.228819     0.161077     1.487468
 C     1.669851     0.263498     1.819888
 C     2.380751     0.235220     0.671221
 C     1.426112     0.122879    -0.501459
 C    -0.868556     0.207031     2.503408
 O    -1.592308     1.191524     2.610921
 C     2.162089     0.417354     3.225530
 C     3.860381     0.324714     0.483161
 C     1.570840     1.270210    -1.515460
 C    -1.216674    -0.021341    -0.610292
 N    -0.995590    -0.888500     3.319303
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 C    -0.298070    -2.145370     3.109640
 C    -2.003702    -0.886618     4.367126
 H     3.241793     0.565368     3.262739
 H     1.685473     1.277526     3.706638
 H     1.921677    -0.458567     3.836599
 H     4.241617    -0.530892    -0.086083
 H     4.140674     1.224922    -0.076178
 H     4.391294     0.351184     1.435968
 H     0.851729     1.165855    -2.331300
 H     1.395388     2.230346    -1.023741
 H     2.572013     1.284538    -1.952723
 H    -1.238904    -0.922036    -1.234729
 H    -2.077178    -0.040821     0.059692
 H    -1.344293     0.834279    -1.282745
 H    -1.013925    -2.944733     2.884220
 H     0.395900    -2.060333     2.277339
 H     0.258050    -2.430888     4.009375
 H    -2.822956    -1.572663     4.121919
 H    -1.556957    -1.205093     5.314207
 H    -2.402674     0.119571     4.467836
 H     1.601303    -0.828792    -1.026196

33
3a´´ DMSO scf done:  -598.930074 Sum of electronic and thermal Free Energies -598.689863 imaginary frequencies: 0
 C     0.012176     0.005092     0.002827
 C     0.014687     0.003960     1.516314
 C     1.295395     0.019290     1.938367
 C     2.220007     0.036754     0.777480
 C     1.484104     0.030179    -0.357706
 C    -1.232283    -0.032517     2.334315
 C     1.753282     0.067303     3.362108
 N     2.319439    -1.059862     3.866187
 C     2.838893    -1.068944     5.226115
 C     3.708691     0.068396     0.932766
 C     1.950348     0.054966    -1.776605
 C    -0.793788     1.164302    -0.603472
 O     1.646933     1.108162     4.023156
 C     2.309224    -2.351705     3.193127
 H     4.213425     0.149647    -0.031127
 H     4.020154     0.919149     1.549105
 H     4.078788    -0.833987     1.431141
 H     1.536921    -0.787478    -2.343467
 H     1.622565     0.967109    -2.289755
 H     3.038440     0.005720    -1.849743
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 H    -1.842044     1.111720    -0.298730
 H    -0.388542     2.125895    -0.274634
 H    -0.759171     1.133216    -1.695318
 H    -1.871840    -0.873113     2.042079
 H    -1.011995    -0.125927     3.399746
 H    -1.826802     0.877974     2.193420
 H     1.714389    -3.068312     3.769659
 H     1.878083    -2.264176     2.199638
 H     3.328712    -2.738515     3.107924
 H     2.131973    -1.550275     5.911571
 H     3.778202    -1.626759     5.248392
 H     3.012512    -0.048077     5.557328
 H    -0.428756    -0.939287    -0.349968

 33
3b´´  scf done:  -598.912892 Sum of electronic and thermal Free Energies -598.671236 imaginary frequencies: 0
 C     0.038241     0.004884     0.009133
 C     0.002880     0.003481     1.491917
 C     1.262281     0.022056     1.971612
 C     2.225348     0.066837     0.806456
 C     1.318047     0.037154    -0.417313
 C    -1.278321    -0.032859     2.265485
 C     1.746310    -0.027257     3.381716
 C     3.201723    -1.115962     0.803643
 O     2.867771    -2.192793     1.278198
 C     1.845758     0.029165    -1.815592
 C    -1.207958    -0.027597    -0.819980
 N     4.441492    -0.936471     0.236667
 C     4.939874     0.267278    -0.405783
 C     5.357650    -2.068544     0.184439
 H     1.039111    -0.043852    -2.546243
 H     2.413490     0.938817    -2.044744
 H     2.520256    -0.818075    -1.983892
 H    -1.803070    -0.919411    -0.596857
 H    -1.844866     0.838548    -0.610371
 H    -0.990361    -0.030473    -1.888531
 H    -1.102952    -0.000871     3.341299
 H    -1.926080     0.811154     2.005105
 H    -1.843051    -0.945849     2.047757
 H     0.927981     0.066621     4.097291
 H     2.256690    -0.977818     3.571538
 H     2.464259     0.774848     3.588543
 H     5.146228     0.076995    -1.465336
 H     4.226030     1.081043    -0.345222
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 H     5.873594     0.588319     0.069216
 H     5.541151    -2.366676    -0.854111
 H     6.315181    -1.796096     0.640120
 H     4.918089    -2.901673     0.725287
 H     2.763847     1.019893     0.848876

33
3b´´ DMSO scf done:  -598.928439 Sum of electronic and thermal Free Energies -598.687202 imaginary frequencies: 0
 C    -0.026635    -0.018668     0.014111
 C    -0.016359    -0.009666     1.365567
 C     1.386914    -0.022559     1.854262
 C     2.229704    -0.053385     0.799530
 C     1.415310    -0.028712    -0.474763
 C    -1.186704     0.023768     2.298619
 C     1.729315     0.000615     3.311477
 C     3.720958    -0.092344     0.772633
 C     1.687853    -1.230407    -1.385729
 N     1.658802    -1.045244    -2.733821
 C     1.890724    -2.194604    -3.602634
 C    -1.188207    -0.015618    -0.925771
 O     1.921782    -2.338421    -0.895043
 C     1.209119     0.151092    -3.436360
 H    -2.139301    -0.040074    -0.390795
 H    -1.186652     0.875859    -1.563466
 H    -1.162903    -0.881176    -1.598466
 H    -1.172748    -0.835542     2.978153
 H    -1.164699     0.921105     2.927196
 H    -2.137352     0.013071     1.763263
 H     2.808366     0.002523     3.474763
 H     1.311724     0.886003     3.803632
 H     1.313001    -0.871451     3.828191
 H     4.150220    -0.007012     1.772820
 H     4.078597    -1.030344     0.331592
 H     4.129305     0.720383     0.160454
 H     0.299132    -0.071398    -4.003308
 H     0.990344     0.965356    -2.755118
 H     1.980801     0.478718    -4.139023
 H     0.945470    -2.675802    -3.879876
 H     2.387186    -1.854133    -4.513532
 H     2.519349    -2.921710    -3.094978
 H     1.633690     0.906877    -0.998143

33
3b´ scf done:  -598.917910 Sum of electronic and thermal Free Energies -598.676912 imaginary frequencies: 0
```

| | | | |
|---|---|---|---|
| C | -0.010490 | -0.063225 | -0.004138 |
| C | -0.010988 | -0.048007 | 1.347588 |
| C | 1.383610 | 0.035235 | 1.842456 |
| C | 2.235598 | 0.068649 | 0.792174 |
| C | 1.417611 | 0.093185 | -0.482678 |
| C | -1.189483 | -0.113377 | 2.269178 |
| C | 1.719275 | 0.064001 | 3.301648 |
| C | 3.727107 | 0.135749 | 0.768443 |
| C | 1.870518 | -0.805169 | -1.640962 |
| O | 2.223193 | -0.291887 | -2.697402 |
| C | -1.151928 | -0.159916 | -0.961745 |
| N | 1.864125 | -2.161356 | -1.462376 |
| C | 1.407810 | -2.845420 | -0.264227 |
| C | 2.210580 | -3.024475 | -2.582748 |
| H | 1.512796 | 1.099022 | -0.910634 |
| H | -2.112589 | -0.216614 | -0.447645 |
| H | -1.179663 | 0.702621 | -1.636229 |
| H | -1.059512 | -1.047781 | -1.598704 |
| H | -1.124235 | -0.979949 | 2.936245 |
| H | -1.242155 | 0.774020 | 2.908963 |
| H | -2.129666 | -0.184173 | 1.721237 |
| H | 2.794978 | 0.124278 | 3.470117 |
| H | 1.254453 | 0.922809 | 3.797474 |
| H | 1.349992 | -0.832462 | 3.811898 |
| H | 4.150455 | 0.169270 | 1.773443 |
| H | 4.152641 | -0.732956 | 0.252694 |
| H | 4.075439 | 1.020477 | 0.224861 |
| H | 2.098264 | -3.662838 | -0.035168 |
| H | 1.386318 | -2.170339 | 0.584183 |
| H | 0.408093 | -3.272761 | -0.408169 |
| H | 2.531492 | -2.407271 | -3.417358 |
| H | 3.018308 | -3.705628 | -2.296632 |
| H | 1.344171 | -3.623482 | -2.886054 |

33

**3b´ DMSO** scf done: -598.930403 Sum of electronic and thermal Free Energies -598.690078 imaginary frequencies: 0

| | | | |
|---|---|---|---|
| C | 0.000766 | 0.006850 | -0.003498 |
| C | -0.002346 | 0.003316 | 1.512096 |
| C | 1.280791 | 0.009293 | 1.940494 |
| C | 2.193531 | -0.068151 | 0.774032 |
| C | 1.467331 | -0.123847 | -0.366832 |
| C | -1.273960 | 0.027348 | 2.293312 |
| C | 1.783763 | 0.059021 | 3.349413 |
| C | 3.682533 | -0.099860 | 0.922600 |

```
 C     1.916070    -0.248096    -1.784981
 C    -0.994232    -0.922358    -0.707172
 N    -0.905378    -2.259663    -0.494859
 C    -1.893171    -3.157648    -1.078916
 O    -1.857578    -0.431403    -1.443968
 C     0.068879    -2.904791     0.373840
 H    -0.322200     1.004253    -0.327415
 H    -1.091700     0.083027     3.367982
 H    -1.899486     0.882626     2.012102
 H    -1.871324    -0.872927     2.101794
 H     2.376519    -0.831576     3.587154
 H     2.438797     0.923159     3.505658
 H     0.967642     0.121634     4.071039
 H     4.187745    -0.153520    -0.043032
 H     4.046716     0.791844     1.444541
 H     3.999880    -0.963713     1.517627
 H     3.004127    -0.262696    -1.869369
 H     1.533195    -1.170805    -2.238809
 H     1.540906     0.580652    -2.396571
 H     0.423223    -3.817079    -0.113236
 H     0.923988    -2.260990     0.548317
 H    -0.382736    -3.179940     1.333086
 H    -2.618356    -2.581409    -1.646384
 H    -1.402301    -3.877922    -1.740752
 H    -2.407635    -3.710618    -0.286259

33
3c´ scf done:  -598.919365 Sum of electronic and thermal Free Energies -598.676338 imaginary frequencies: 0
 C    -0.072363    -0.218159    -0.171464
 C    -0.101861     0.183462     1.283216
 C     1.147285     0.530198     1.677548
 C     2.063842     0.432802     0.521130
 C     1.369813     0.007736    -0.560308
 C    -1.325784    -0.027160     2.088056
 O    -1.983061    -1.058269     1.950499
 C     1.617791     0.895907     3.050649
 C     3.522068     0.762052     0.620083
 C     1.856209    -0.222416    -1.953429
 C    -1.089388     0.535796    -1.042447
 N    -1.690434     0.939737     2.999722
 C    -1.292584     2.336041     2.910094
 C    -2.838034     0.676665     3.855693
 H     2.485039     0.291700     3.333288
 H     1.936406     1.943809     3.094708
```

| | | | |
|---|---|---|---|
| H | 0.838451 | 0.743718 | 3.796585 |
| H | 4.031877 | 0.102976 | 1.331147 |
| H | 4.025982 | 0.662879 | -0.341881 |
| H | 3.674763 | 1.787566 | 0.972891 |
| H | 1.634971 | -1.242716 | -2.285481 |
| H | 1.363217 | 0.452436 | -2.662719 |
| H | 2.932389 | -0.068084 | -2.043334 |
| H | -1.032999 | 0.209873 | -2.083864 |
| H | -2.104770 | 0.349796 | -0.686777 |
| H | -0.898223 | 1.612219 | -1.010257 |
| H | -0.858253 | 2.680814 | 3.854165 |
| H | -0.563193 | 2.469544 | 2.116137 |
| H | -2.166784 | 2.960646 | 2.689180 |
| H | -2.674143 | 1.143340 | 4.830746 |
| H | -3.761132 | 1.083977 | 3.424216 |
| H | -2.958505 | -0.397146 | 3.973518 |
| H | -0.300002 | -1.291532 | -0.225296 |

33

**3c´ DMSO** scf done: -598.933072 Sum of electronic and thermal Free Energies -598.690286 imaginary frequencies: 0

| | | | |
|---|---|---|---|
| C | 0.002353 | -0.002129 | 0.004008 |
| C | -0.001112 | -0.015384 | 1.516193 |
| C | 1.469658 | -0.060080 | 1.859929 |
| C | 2.198269 | -0.099790 | 0.718070 |
| C | 1.280041 | -0.059040 | -0.442657 |
| C | -0.738404 | 1.177729 | 2.144489 |
| C | 1.925516 | -0.197931 | 3.261514 |
| N | 2.928429 | 0.612570 | 3.706309 |
| C | 3.458634 | 0.408349 | 5.047333 |
| C | 3.681979 | -0.203458 | 0.567313 |
| C | 1.773754 | -0.081912 | -1.856163 |
| C | -1.263278 | 0.081866 | -0.783377 |
| O | 1.408342 | -1.051273 | 3.999952 |
| C | 3.327488 | 1.862209 | 3.070434 |
| H | 3.943941 | -1.017199 | -0.116230 |
| H | 4.095863 | 0.715336 | 0.136459 |
| H | 4.176826 | -0.384497 | 1.521835 |
| H | 2.334749 | -0.999524 | -2.065141 |
| H | 0.953030 | -0.020778 | -2.572569 |
| H | 2.454105 | 0.754418 | -2.050848 |
| H | -1.958092 | -0.717119 | -0.500494 |
| H | -1.784138 | 1.028685 | -0.596395 |
| H | -1.083336 | 0.007864 | -1.857355 |
| H | -1.795660 | 1.173439 | 1.867528 |

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 H    -0.676310     1.140509     3.235078
 H    -0.299180     2.121263     1.807591
 H     4.390293     1.844420     2.812863
 H     2.744681     2.035348     2.170645
 H     3.154856     2.692961     3.763161
 H     4.510605     0.701948     5.060110
 H     2.919530     1.013266     5.786506
 H     3.371614    -0.639900     5.324189
 H    -0.479279    -0.939717     1.867439

33
3c´´ scf done:  -598.917395 Sum of electronic and thermal Free Energies -598.674741 imaginary frequencies: 0
 C    -0.036998    -0.133999    -0.048611
 C     0.096387    -0.089388     1.459641
 C     1.386009     0.164211     1.784684
 C     2.192806     0.256576     0.548646
 C     1.388124     0.060080    -0.519700
 C    -1.070628    -0.196736     2.371198
 O    -2.070466     0.500333     2.206696
 C     1.973446     0.355956     3.148099
 C     3.665611     0.529962     0.567446
 C     1.742119     0.048127    -1.970310
 C    -0.998613     0.918876    -0.631950
 N    -0.984824    -1.081336     3.424393
 C    -0.054708    -2.196603     3.492707
 C    -2.080727    -1.127819     4.380892
 H     2.687484    -0.440753     3.386818
 H     2.525828     1.299022     3.200555
 H     1.204254     0.367678     3.919937
 H     4.090734     0.527908    -0.436751
 H     3.881346     1.505346     1.016832
 H     4.203169    -0.217686     1.160363
 H     1.400314    -0.874127    -2.453150
 H     1.262052     0.877408    -2.502574
 H     2.818185     0.129656    -2.130720
 H    -1.030231     0.841221    -1.722049
 H    -2.002376     0.787436    -0.232744
 H    -0.659500     1.921992    -0.362876
 H    -0.605348    -3.144751     3.471208
 H     0.626998    -2.170859     2.647410
 H     0.527895    -2.162950     4.419558
 H    -2.772020    -1.949163     4.154542
 H    -1.678378    -1.280208     5.386437
 H    -2.630806    -0.191380     4.339144
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 H    -0.390945    -1.129521    -0.357222

33
3c´´ DMSO scf done:  -598.930492 Sum of electronic and thermal Free Energies -598.688165 imaginary frequencies: 0

 C     0.016815     0.008535     0.002766
 C     0.018798     0.005936     1.517713
 C     1.495856     0.052303     1.852703
 C     2.214005     0.107859     0.706285
 C     1.289767     0.086298    -0.450024
 C    -0.824147     1.143162     2.116860
 C     2.016590     0.091644     3.242727
 N     2.916629    -0.862949     3.615083
 C     3.529810    -0.784951     4.933865
 C     3.699598     0.171755     0.549721
 C     1.775083     0.138931    -1.865484
 C    -1.253936    -0.052023    -0.778683
 O     1.660502     0.982424     4.029058
 C     3.164436    -2.103871     2.892025
 H     4.080512    -0.738526     0.072927
 H     3.985417     1.008206    -0.096053
 H     4.205527     0.290997     1.508539
 H     0.951532     0.075857    -2.578453
 H     2.318305     1.069920    -2.062293
 H     2.469352    -0.681443    -2.077755
 H    -1.861236    -0.913467    -0.478064
 H    -1.869928     0.838947    -0.607123
 H    -1.070431    -0.127256    -1.852028
 H    -1.868763     1.043399     1.809925
 H    -0.777198     1.128698     3.205533
 H    -0.455189     2.113847     1.773433
 H     2.949077    -2.954532     3.547115
 H     2.526055    -2.169816     2.015839
 H     4.210876    -2.167558     2.578972
 H     2.969980    -1.375717     5.668820
 H     4.547148    -1.178442     4.875755
 H     3.559090     0.250039     5.266617
 H    -0.399723    -0.948049     1.872722

33
TS 3c´ - 3c´´scf done:  -598.897829 Sum of electronic and thermal Free Energies -598.652502 imaginary frequencies: 1 (-103.59)
 C    -0.009499     0.094197     0.007049
 C     0.180238     0.183304     1.490398
 C     1.679116    -0.007345     1.690500
```

| | | | |
|---|---|---|---|
| C | 2.254465 | -0.110619 | 0.450957 |
| C | 1.195221 | -0.058698 | -0.584235 |
| C | -0.335898 | 1.531072 | 2.038512 |
| C | 2.057098 | -0.100860 | 3.138944 |
| N | 3.330728 | 0.033456 | 3.647548 |
| C | 3.445117 | 0.099889 | 5.103231 |
| C | 3.677633 | -0.280440 | -0.014658 |
| C | 1.469839 | -0.169238 | -2.055291 |
| C | -1.357372 | 0.215105 | -0.624083 |
| O | 1.127670 | -0.236451 | 3.942083 |
| C | 4.581370 | -0.162633 | 2.935221 |
| H | 4.047835 | -1.293926 | 0.165132 |
| H | 3.742118 | -0.111356 | -1.088557 |
| H | 4.359738 | 0.419400 | 0.459637 |
| H | 0.543019 | -0.162316 | -2.629370 |
| H | 2.083527 | 0.662554 | -2.417719 |
| H | 2.002694 | -1.093591 | -2.300898 |
| H | -1.765839 | 1.223937 | -0.494729 |
| H | -1.334151 | 0.003447 | -1.693646 |
| H | -2.070099 | -0.473730 | -0.158595 |
| H | -1.405009 | 1.640535 | 1.839997 |
| H | -0.178951 | 1.582871 | 3.114282 |
| H | 0.188552 | 2.359928 | 1.554358 |
| H | 5.338687 | -0.478771 | 3.653606 |
| H | 4.496893 | -0.951210 | 2.194136 |
| H | 4.939595 | 0.753745 | 2.455412 |
| H | 4.336615 | 0.676684 | 5.357713 |
| H | 2.564995 | 0.582507 | 5.518860 |
| H | 3.526651 | -0.898575 | 5.550395 |
| H | -0.358040 | -0.621238 | 2.002429 |

33

**TS 3c´ - 3c´´DMSO** scf done: -598.911091 Sum of electronic and thermal Free Energies -598.665430 imaginary frequencies: 1 (-100.90)

| | | | |
|---|---|---|---|
| C | -0.001797 | 0.002409 | -0.002494 |
| C | -0.001489 | -0.001718 | 1.480812 |
| C | 1.271771 | -0.001495 | 1.935738 |
| C | 2.209775 | 0.028012 | 0.767383 |
| C | 1.295771 | -0.021319 | -0.453259 |
| C | -1.253350 | -0.004089 | 2.306328 |
| C | 1.766039 | 0.028635 | 3.343997 |
| C | 3.101726 | 1.285562 | 0.811052 |
| C | 2.048948 | -0.157851 | -1.741556 |
| N | 1.543485 | 0.068928 | -2.993780 |

```
 C     2.502059     0.073729    -4.097548
 C    -1.337958     0.009448    -0.693784
 O     3.258829    -0.435294    -1.646496
 C     0.141298     0.034868    -3.390500
 H    -1.594171    -0.977467    -1.090307
 H    -2.121165     0.276022     0.014848
 H    -1.387353     0.725091    -1.508911
 H    -1.022021    -0.063628     3.370833
 H    -1.843660     0.905028     2.148635
 H    -1.901565    -0.851065     2.058425
 H     2.177707     1.013360     3.597004
 H     0.975211    -0.192214     4.062458
 H     2.574138    -0.695347     3.492631
 H     3.708691     1.293723     1.720278
 H     3.770333     1.308162    -0.048880
 H     2.485854     2.190291     0.807041
 H     0.094571    -0.239352    -4.444433
 H    -0.404740    -0.722473    -2.837669
 H    -0.345151     1.006794    -3.274839
 H     2.074748     0.642680    -4.923966
 H     3.434922     0.538844    -3.786462
 H     2.725330    -0.941819    -4.447419
 H     2.861822    -0.851608     0.778221

71
[i] scf done: -1926.996521 Sum of electronic and thermal Free Energies -1926.476354 imaginary frequencies: 0
 C     3.707982     0.985414     0.290386
 C     3.506085     0.678049    -1.116136
 C     3.229658    -0.706495    -1.265455
 C     3.204712    -1.282113     0.074619
 C     3.565777    -0.260176     1.020226
Ir     1.642191     0.291832     0.156830
 N     0.218933     1.685498    -0.656465
 C    -1.006167     1.687982     0.192948
 C    -2.138614     2.472669    -0.430403
 C    -2.644738     3.606137     0.217753
 C    -3.696472     4.338895    -0.340161
 C    -4.248950     3.946533    -1.561324
 C    -3.745251     2.818468    -2.218380
 C    -2.700761     2.083215    -1.657342
 C     3.598686     1.677664    -2.228885
 C     3.102419    -1.455018    -2.555740
 C     3.002587    -2.734132     0.381571
 C     3.838726    -0.458959     2.480917
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| | | | |
|---|---|---|---|
| C | 4.211181 | 2.285075 | 0.844397 |
| N | -0.269637 | -0.719753 | 0.092977 |
| S | -0.566384 | -1.447911 | -1.347347 |
| O | -0.706749 | -0.473463 | -2.474926 |
| C | -1.359994 | 0.185174 | 0.496114 |
| C | -1.730614 | -0.010169 | 1.957739 |
| C | -0.978293 | -0.831374 | 2.803094 |
| C | -1.348565 | -0.997693 | 4.140104 |
| C | -2.476757 | -0.347394 | 4.647739 |
| C | -3.237659 | 0.468399 | 3.805044 |
| C | -2.866386 | 0.633206 | 2.468736 |
| C | -2.190548 | -2.196039 | -1.128118 |
| C | -3.177296 | -2.003267 | -2.094035 |
| C | -4.423996 | -2.610701 | -1.920403 |
| C | -4.670999 | -3.393120 | -0.789242 |
| C | -3.670728 | -3.576261 | 0.172391 |
| C | -2.421471 | -2.979663 | 0.005225 |
| O | 0.400391 | -2.542820 | -1.538101 |
| H | -0.709525 | 2.165899 | 1.127959 |
| H | -2.263611 | -0.042301 | -0.078234 |
| H | -2.219891 | 3.908754 | 1.172283 |
| H | -4.081832 | 5.212642 | 0.178652 |
| H | -5.066204 | 4.513694 | -1.998596 |
| H | -4.170524 | 2.507632 | -3.169082 |
| H | -2.317458 | 1.204410 | -2.169542 |
| H | -0.108322 | -1.333705 | 2.396470 |
| H | -0.753889 | -1.638407 | 4.786740 |
| H | -2.764996 | -0.480102 | 5.687304 |
| H | -4.125199 | 0.968782 | 4.184120 |
| H | -3.472031 | 1.256818 | 1.815713 |
| H | -2.963361 | -1.384878 | -2.959085 |
| H | -5.201454 | -2.468131 | -2.665880 |
| H | -5.643566 | -3.858365 | -0.653767 |
| H | -3.865601 | -4.178565 | 1.055211 |
| H | -1.639068 | -3.098795 | 0.746903 |
| H | 0.566167 | 2.637547 | -0.756950 |
| H | -0.015172 | 1.329787 | -1.590090 |
| H | 2.720362 | -2.880896 | 1.427953 |
| H | 2.213011 | -3.153374 | -0.244597 |
| H | 3.931137 | -3.294057 | 0.200845 |
| H | 1.074239 | 0.794202 | 1.569866 |
| H | 4.633555 | 1.759722 | -2.588341 |
| H | 2.973418 | 1.389779 | -3.078846 |
| H | 3.290224 | 2.674822 | -1.898374 |

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 H     2.438934    -2.313176    -2.451003
 H     2.687295    -0.822817    -3.346821
 H     4.088772    -1.807998    -2.891562
 H     4.896628    -0.709461     2.642618
 H     3.612989     0.443774     3.054769
 H     3.233672    -1.271618     2.891357
 H     3.818270     3.139488     0.283932
 H     3.912059     2.412102     1.888600
 H     5.308860     2.336511     0.799422

71
[i] AN scf done: -1927.040342 Sum of electronic and thermal Free Energies -1926.522003 imaginary frequencies: 0
 C    -2.480382    -3.021810    -0.364328
 C    -2.257536    -2.038710    -1.333477
 C    -3.277310    -1.611875    -2.184496
 C    -4.547709    -2.184084    -2.062757
 C    -4.785090    -3.166817    -1.097116
 C    -3.751756    -3.585364    -0.249277
 S    -0.605286    -1.330269    -1.475055
 O     0.325464    -2.453553    -1.734290
 N    -0.290376    -0.719465     0.005348
 C    -1.366903     0.153538     0.509020
 C    -1.765106    -0.223360     1.930259
 C    -1.117508    -1.243866     2.635476
 C    -1.523417    -1.584639     3.930264
 C    -2.588099    -0.911084     4.536933
 C    -3.246184     0.105740     3.835283
 C    -2.836872     0.444762     2.542861
Ir     1.664022     0.241193     0.215901
 N     0.273274     1.770704    -0.388130
 C    -0.984062     1.675484     0.400649
 C    -2.082822     2.543384    -0.175934
 C    -2.571657     3.632743     0.556627
 C    -3.587625     4.443651     0.039180
 C    -4.121995     4.174863    -1.224395
 C    -3.634284     3.091688    -1.966011
 C    -2.624352     2.280368    -1.445062
 C     3.731330     0.931936     0.390813
 C     3.487602     0.814152    -1.037950
 C     3.216957    -0.543047    -1.356810
 C     3.249149    -1.294219    -0.105021
 C     3.629166    -0.401489     0.953952
 C     4.238810     2.156652     1.091245
 C     3.527849     1.960609    -2.000029
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 C     3.055035    -1.127847    -2.724375
 C     3.100876    -2.779564     0.006263
 C     3.963470    -0.787590     2.362986
 O    -0.683817    -0.296174    -2.553091
 H    -0.729974     2.043868     1.395111
 H    -2.268666     0.016395    -0.094724
 H    -2.159270     3.840789     1.541151
 H    -3.959783     5.281919     0.622678
 H    -4.911777     4.802433    -1.629111
 H    -4.044214     2.876171    -2.949626
 H    -2.254980     1.439272    -2.025935
 H    -0.298822    -1.770503     2.158784
 H    -1.007326    -2.379836     4.463046
 H    -2.906069    -1.178222     5.541559
 H    -4.082238     0.630889     4.290698
 H    -3.362578     1.228664     2.004203
 H    -3.079630    -0.841867    -2.922132
 H    -5.349395    -1.857715    -2.719458
 H    -5.774276    -3.606417    -1.002589
 H    -3.936307    -4.347600     0.502592
 H    -1.675816    -3.333616     0.293612
 H     0.653290     2.713964    -0.308654
 H     0.078340     1.608527    -1.379436
 H     2.845865    -3.078676     1.027438
 H     2.316935    -3.140498    -0.662943
 H     4.044163    -3.276248    -0.263534
 H     1.086833     0.538923     1.697111
 H     4.559882     2.145349    -2.329262
 H     2.922721     1.761419    -2.889202
 H     3.162712     2.882137    -1.535583
 H     2.347074    -1.958265    -2.716081
 H     2.691487    -0.382354    -3.438782
 H     4.021368    -1.499371    -3.096918
 H     5.032257    -1.032197     2.443245
 H     3.754418     0.027056     3.062261
 H     3.394440    -1.664738     2.684205
 H     3.796918     3.067473     0.674577
 H     4.005733     2.129270     2.159892
 H     5.330644     2.240001     0.988226

71
16 scf done: -1926.992632 Sum of electronic and thermal Free Energies -1926.472477 imaginary frequencies: 0
 C     2.606887     0.042518     1.590177
 C     3.221323     1.045673     0.788546
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| | | | |
|---|---|---|---|
| C | 3.811223 | 0.435471 | -0.389475 |
| C | 3.550989 | -0.990302 | -0.304272 |
| C | 2.761134 | -1.216722 | 0.876207 |
| Ir | 1.653571 | 0.052514 | -0.550839 |
| N | 0.302202 | 1.618569 | -1.095961 |
| C | -0.704333 | 1.738008 | -0.001704 |
| C | -1.792858 | 2.732464 | -0.347514 |
| C | -1.909422 | 3.930505 | 0.367833 |
| C | -2.896740 | 4.865147 | 0.043165 |
| C | -3.774673 | 4.612227 | -1.012980 |
| C | -3.656466 | 3.423970 | -1.742059 |
| C | -2.674548 | 2.489047 | -1.412946 |
| C | 3.282527 | 2.507856 | 1.112355 |
| C | 4.715889 | 1.113383 | -1.374997 |
| C | 4.075691 | -2.047665 | -1.228462 |
| C | 2.277461 | -2.552232 | 1.352643 |
| C | 1.997626 | 0.229948 | 2.946320 |
| N | -0.328532 | -0.725599 | -0.300476 |
| S | -0.964756 | -1.388494 | -1.673259 |
| O | -1.378209 | -0.337017 | -2.651975 |
| C | -1.212033 | 0.288537 | 0.310604 |
| C | -1.365040 | 0.024675 | 1.805677 |
| C | -1.206519 | -1.275828 | 2.298408 |
| C | -1.385593 | -1.556502 | 3.653740 |
| C | -1.727202 | -0.536086 | 4.545571 |
| C | -1.903365 | 0.762383 | 4.061936 |
| C | -1.730356 | 1.037414 | 2.702543 |
| C | -2.490648 | -2.158634 | -1.102107 |
| C | -3.725105 | -1.565996 | -1.365605 |
| C | -4.888849 | -2.167597 | -0.878065 |
| C | -4.809614 | -3.352570 | -0.142683 |
| C | -3.565771 | -3.946319 | 0.101073 |
| C | -2.400178 | -3.350376 | -0.378548 |
| O | -0.083560 | -2.470211 | -2.134285 |
| H | -0.142818 | 2.105345 | 0.861401 |
| H | -2.220039 | 0.211251 | -0.111341 |
| H | -1.224914 | 4.132841 | 1.189426 |
| H | -2.977512 | 5.787121 | 0.612756 |
| H | -4.543514 | 5.335988 | -1.269186 |
| H | -4.330891 | 3.224801 | -2.570654 |
| H | -2.578846 | 1.572381 | -1.989360 |
| H | -0.924016 | -2.055718 | 1.603270 |
| H | -1.252672 | -2.573660 | 4.014245 |
| H | -1.860330 | -0.750518 | 5.602582 |

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 H    -2.180521     1.564767     4.740981
 H    -1.896447     2.049396     2.348389
 H    -3.766949    -0.657234    -1.955908
 H    -5.854757    -1.711640    -1.077025
 H    -5.715657    -3.818045     0.235535
 H    -3.505665    -4.874347     0.662990
 H    -1.427832    -3.801912    -0.210549
 H     0.725346     2.527038    -1.279223
 H    -0.164592     1.309809    -1.956193
 H     3.370746    -2.878203    -1.317688
 H     4.239510    -1.649477    -2.233274
 H     5.031847    -2.444606    -0.858834
 H     1.539264    -0.304664    -2.102517
 H     4.202875     2.745361     1.663244
 H     3.280382     3.118548     0.203755
 H     2.437310     2.817588     1.734942
 H     4.694995     0.605566    -2.343105
 H     4.417983     2.152998    -1.544117
 H     5.756735     1.118983    -1.019433
 H     3.054724    -3.058068     1.942122
 H     1.390967    -2.445861     1.981681
 H     2.012474    -3.194600     0.508622
 H     1.531093     1.214399     3.050276
 H     1.222631    -0.511358     3.147607
 H     2.760086     0.140720     3.734188

71
16 AN scf done: -1927.043092 Sum of electronic and thermal Free Energies -1926.524747 imaginary frequencies: 0
 C    -2.627551    -3.198805    -0.291278
 C    -2.613080    -2.070579    -1.116748
 C    -3.797001    -1.439062    -1.501777
 C    -5.018262    -1.944072    -1.044846
 C    -5.045840    -3.069629    -0.216052
 C    -3.851279    -3.698024     0.157034
 S    -1.022984    -1.425934    -1.670881
 O    -0.208788    -2.588816    -2.095399
 N    -0.353236    -0.772045    -0.328032
 C    -1.210641     0.242391     0.323859
 C    -1.347096    -0.057481     1.814472
 C    -1.114729    -1.349462     2.301257
 C    -1.280969    -1.648250     3.656433
 C    -1.685775    -0.654561     4.552596
 C    -1.928335     0.637903     4.075615
 C    -1.763800     0.931264     2.718682
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| | | | |
|---|---|---|---|
| Ir | 1.669681 | 0.005179 | -0.575002 |
| N | 0.325096 | 1.592373 | -1.050573 |
| C | -0.678433 | 1.689721 | 0.047321 |
| C | -1.753325 | 2.708709 | -0.274589 |
| C | -1.827089 | 3.903767 | 0.452856 |
| C | -2.797160 | 4.865358 | 0.151545 |
| C | -3.702019 | 4.642738 | -0.890714 |
| C | -3.628855 | 3.455533 | -1.629454 |
| C | -2.662349 | 2.495111 | -1.323301 |
| C | 2.656434 | 0.126320 | 1.558313 |
| C | 3.213659 | 1.102508 | 0.678044 |
| C | 3.821909 | 0.434290 | -0.455571 |
| C | 3.616305 | -0.993049 | -0.272238 |
| C | 2.855385 | -1.168167 | 0.933906 |
| C | 2.053317 | 0.380552 | 2.905599 |
| C | 3.203504 | 2.583411 | 0.898755 |
| C | 4.702820 | 1.075328 | -1.485710 |
| C | 4.213596 | -2.083377 | -1.109117 |
| C | 2.454773 | -2.482739 | 1.528160 |
| O | -1.340998 | -0.419892 | -2.732048 |
| H | -0.114720 | 2.032819 | 0.916854 |
| H | -2.225724 | 0.192654 | -0.083714 |
| H | -1.123880 | 4.078513 | 1.263885 |
| H | -2.844140 | 5.784843 | 0.729374 |
| H | -4.457459 | 5.387441 | -1.127292 |
| H | -4.326315 | 3.276787 | -2.443897 |
| H | -2.610785 | 1.578627 | -1.905302 |
| H | -0.783852 | -2.113441 | 1.609543 |
| H | -1.086618 | -2.657657 | 4.011213 |
| H | -1.811447 | -0.882733 | 5.607957 |
| H | -2.246943 | 1.421477 | 4.758704 |
| H | -1.965813 | 1.939721 | 2.373045 |
| H | -3.761010 | -0.567979 | -2.146727 |
| H | -5.944237 | -1.456786 | -1.337530 |
| H | -5.996342 | -3.459411 | 0.137891 |
| H | -3.872218 | -4.575023 | 0.798053 |
| H | -1.697280 | -3.678865 | -0.006071 |
| H | 0.783092 | 2.496624 | -1.170136 |
| H | -0.145140 | 1.370623 | -1.931872 |
| H | 3.593549 | -2.984730 | -1.094206 |
| H | 4.329268 | -1.769671 | -2.150743 |
| H | 5.208970 | -2.354948 | -0.728595 |
| H | 1.521884 | -0.332065 | -2.146725 |
| H | 4.098674 | 2.892412 | 1.456172 |

| | | | |
|---|---|---|---|
| H | 3.200944 | 3.128146 | -0.050250 |
| H | 2.327864 | 2.895900 | 1.476145 |
| H | 4.714181 | 0.497592 | -2.414828 |
| H | 4.368714 | 2.089917 | -1.724530 |
| H | 5.738514 | 1.143156 | -1.121469 |
| H | 3.251478 | -2.860337 | 2.184776 |
| H | 1.545667 | -2.389485 | 2.127363 |
| H | 2.276633 | -3.233201 | 0.752451 |
| H | 1.578369 | 1.365023 | 2.955262 |
| H | 1.298614 | -0.367709 | 3.158032 |
| H | 2.826431 | 0.349391 | 3.687880 |

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