Supplementary Material (ESI) for Dalton Transactions

Supporting Information

Reactivity of CO_2 towards $Mo[N(R)Ph]_3$

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2 General Basis Set (GBS) 2

This basis set is LANL2TZ+(3f) for Molybdenum.
It was obtained in the same way as described in Yates, B.F. for platinum.[1]
a) The triple-zeta split was obtained by uncontracting the LANL2DZ basis set of Hay and Wadt to give: [341/321/31] -> [3311/3111/211]
b) The f-function exponent (1.043) was taken from Frenking and co-workers and then split according to the even scaling rule to give three exponents (4.172, 1.043, 0.26075). [2]
c) Diffuse s, p and d functions were added using an even tempered extension of the two outermost exponents. This gave exponents of s=0.0106044, p=0.0078217 and d=0. 037293.

```
-C -H -N 0
6-311+G(2d,p)
****
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 S   3 1.00       0.000000000000
      0.2361000000D+01 -0.9121761947D+00
      0.1309000000D+01  0.1147745245D+01
      0.4500000000D+00  0.6097110301D+00
 S   3 1.00       0.000000000000
      0.2361000000D+01  0.8139263079D+00
      0.1309000000D+01 -0.1136008569D+01
      0.4500000000D+00 -0.1161159582D+01
 S   1 1.00
      0.1681000000D+00  0.1006479504D+01
 S   1 1.00       0.000000000000
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 S   1 1.00
      0.1064420000D-01  0.1000000000D+01
 P   3 1.00       0.000000000000
      0.4895000000D+01 -0.9082579957D-01
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      0.3877000000D+00  0.3973178981D+00
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      0.4995000000D+00 -0.1081945315D+00
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 P   1 1.00       0.000000000000
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 D   1 1.00
      0.3729300000D-01  0.1000000000D+01
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      1.0430000000D+00  0.1000000000D+01
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      0.2607500000D+00  0.1000000000D+01
****
```

Mo 0
lanl2dz

3 CO_2 and CS_2 Bending Energies

Table S1

CO_2			CS_2		
O-C-O Angle	Model-Opt Energy	Energy Relative to 180° (kJ mol^{-1})	O-C-O Angle	Model-Opt Energy	Energy Relative to 180° (kJ mol^{-1})
140.0	-188.5364058	116.92	140.0	-834.4536598	92.45
141.0	-188.5387805	110.69	141.0	-834.4555088	87.59
142.0	-188.5410782	104.66	142.0	-834.4572982	82.90
143.0	-188.5433005	98.82	143.0	-834.4590292	78.35
144.0	-188.5454484	93.18	144.0	-834.460703	73.96
145.0	-188.5475232	87.74	145.0	-834.4623208	69.71
146.0	-188.5495261	82.48	146.0	-834.4638834	65.61
147.0	-188.5514581	77.41	147.0	-834.465392	61.65
148.0	-188.5533203	72.52	148.0	-834.4668475	57.82
149.0	-188.5551138	67.81	149.0	-834.4682507	54.14
150.0	-188.5568394	63.28	150.0	-834.4696024	50.59
151.0	-188.5584983	58.92	151.0	-834.4709035	47.18
152.0	-188.5600912	54.74	152.0	-834.4721547	43.89
153.0	-188.5616191	50.73	153.0	-834.4733567	40.73
154.0	-188.563083	46.88	154.0	-834.4745101	37.71
155.0	-188.5644835	43.21	155.0	-834.4756157	34.80
156.0	-188.5658215	39.69	156.0	-834.476674	32.02
157.0	-188.5670979	36.34	157.0	-834.4776855	29.37
158.0	-188.5683133	33.15	158.0	-834.4786509	26.83
159.0	-188.5694686	30.12	159.0	-834.4795706	24.42
160.0	-188.5705645	27.24	160.0	-834.4804451	22.12
161.0	-188.5716016	24.52	161.0	-834.4812748	19.95
162.0	-188.5725808	21.95	162.0	-834.4820602	17.88
163.0	-188.5735026	19.53	163.0	-834.4828015	15.94
164.0	-188.5743678	17.26	164.0	-834.4834991	14.11
165.0	-188.5751769	15.13	165.0	-834.4841533	12.39
166.0	-188.5759306	13.15	166.0	-834.4847642	10.78
167.0	-188.5766295	11.32	167.0	-834.4853322	9.29
168.0	-188.5772742	9.62	168.0	-834.4858573	7.91
169.0	-188.5778652	8.07	169.0	-834.4863398	6.65
170.0	-188.5784029	6.66	170.0	-834.4867799	5.49
171.0	-188.578888	5.39	171.0	-834.4871774	4.45
172.0	-188.5793207	4.25	172.0	-834.4875329	3.51
173.0	-188.5797016	3.25	173.0	-834.4878463	2.69
174.0	-188.5800309	2.39	174.0	-834.4881176	1.98
175.0	-188.5803091	1.66	175.0	-834.488347	1.38
176.0	-188.5805363	1.06	176.0	-834.4885346	0.88
177.0	-188.5807128	0.60	177.0	-834.4886804	0.50

178.0	-188.5808388	0.27	178.0	-834.4887845	0.23
179.0	-188.5809143	0.07	179.0	-834.4888469	0.06
180.0	-188.5809402	0.00	180.0	-834.4888716	0.00

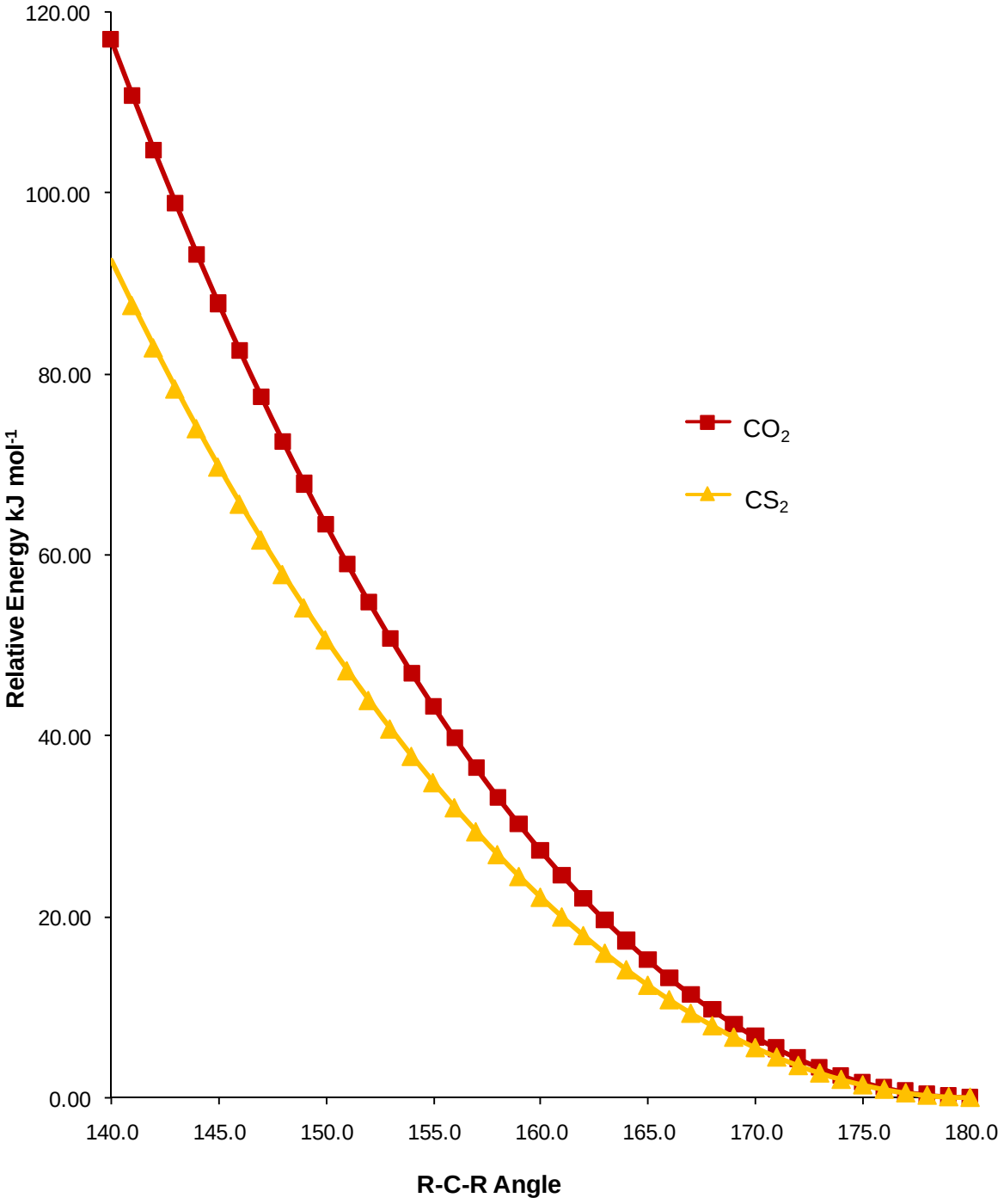


Figure S1. CO_2 and CS_2 bending energies relative to 180°

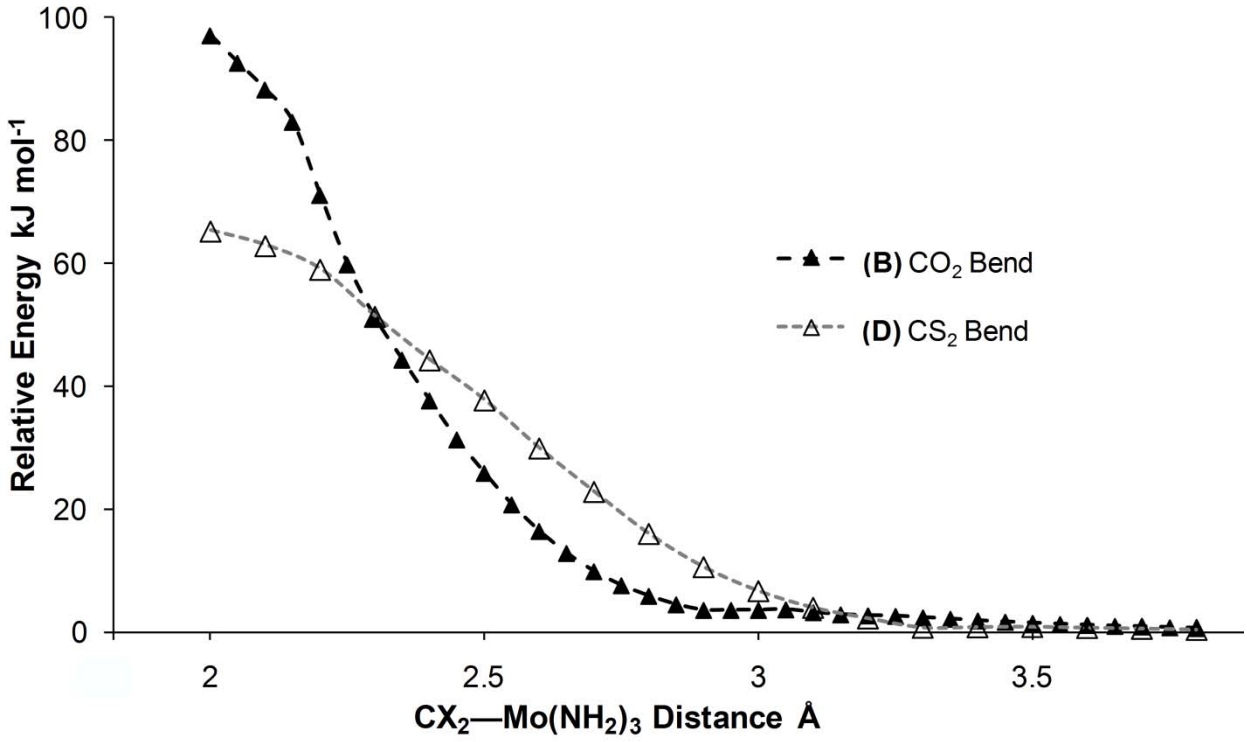


Figure S2. Destabilisation energy due to CO_2 and CS_2 bending during the CX_2 + $Mo(NH_2)_3$ interaction.

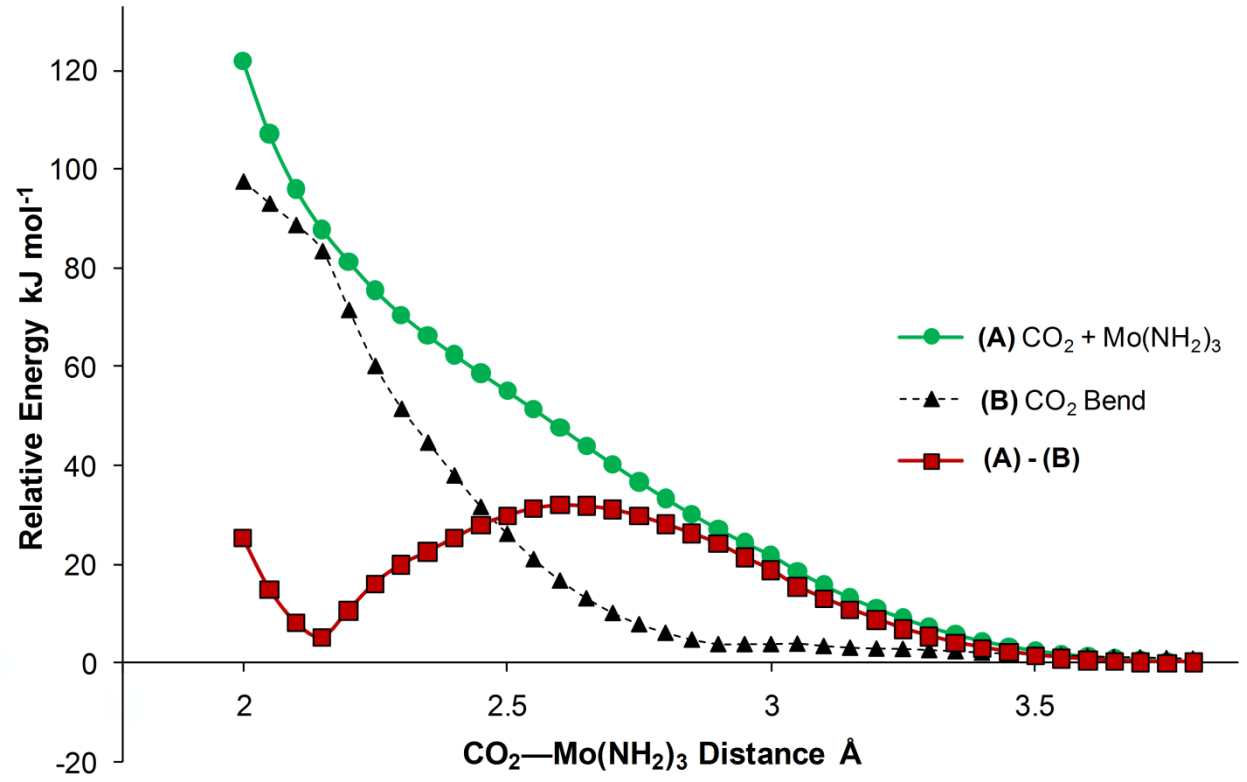


Figure S3. Graph displaying the initial CO_2 + $Mo(NH_2)_3$ interaction on the quartet surface (A), the bending energy (B) associated with each point of the initial interaction and the difference (A) – (B).

4 ONIOM-opt linear transit

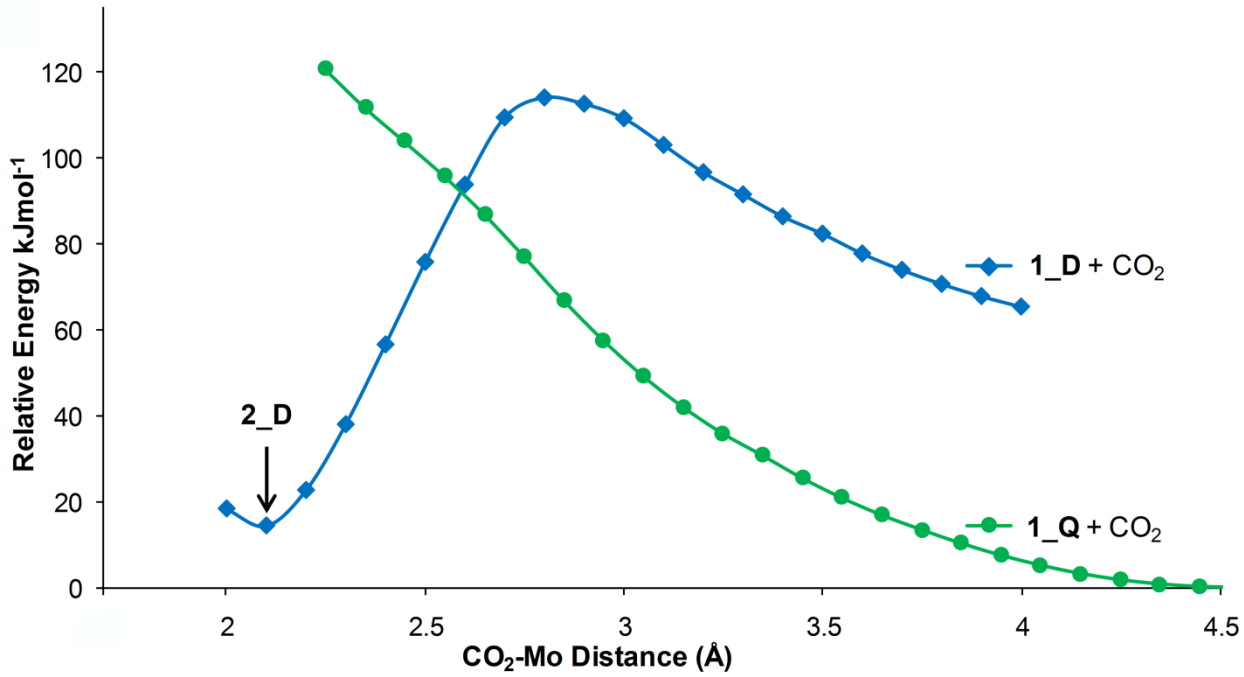


Figure S4. Linear transit, at Oniom-opt level of theory, where the Mo-C distance is altered from 2.0 Å to 3.8 Å for the doublet and quartet CO_2-Mo[N(^{t}Bu)Ph]$_3$species.

5 Slower CS_2 Bonding Onset

The apparent slower onset of bonding in CO_2 is a slight distortion of the linear transit data due to the measurement method. The transits consider the interaction based on Mo-C distances, when in fact the initial interactions of CO_2 and CS_2 differ due to the orbitals involved. Figure III highlights the initial interaction where CO_2 bonding is via the carbon centred π* orbital, while CS_2 is via the sulfur bound π non-bonding orbital giving an apparent 'early-onset' based on Mo-C bonding distance.

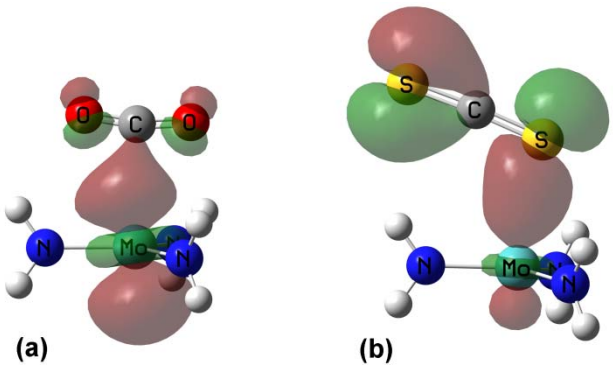


Figure S5. Molecular orbital diagrams of the attractive component of the initial interaction of a) π* of CO_2 with d_{z^2} of $Mo(NH_2)_3$ b) π non-bonding CS_2 with d_{z^2} $Mo(NH_2)_3$

6 Diagrams and Measurements of 1_Q, 4_D and 6_T

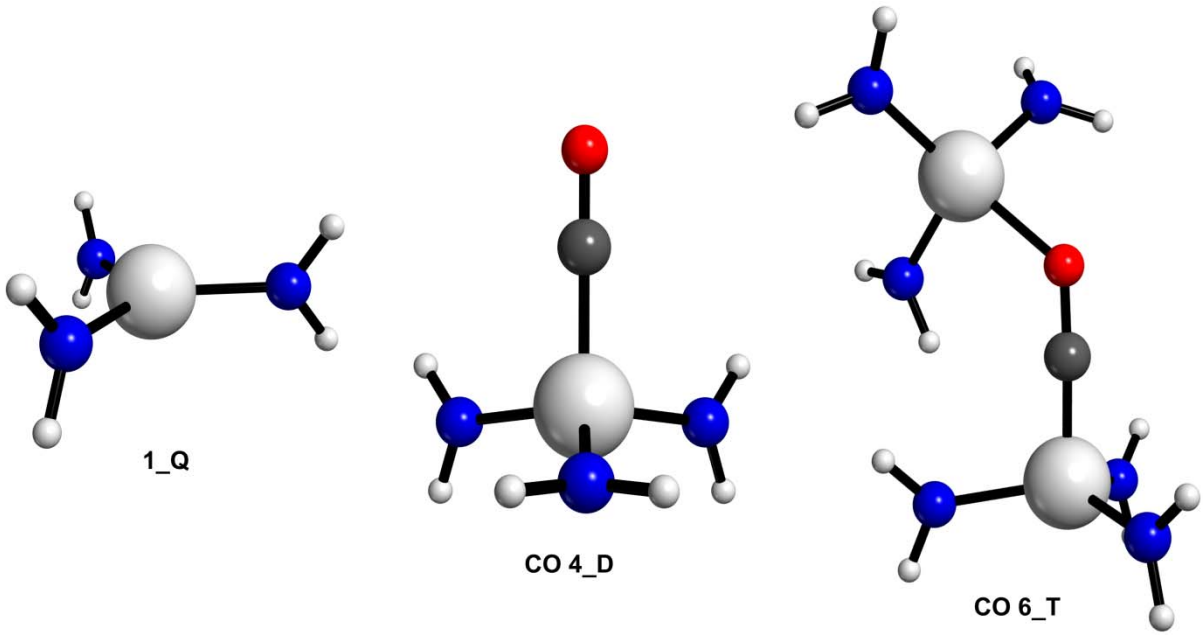


Figure S6. Pictorial representation of CO 1_Q, 4_D and 6_T.

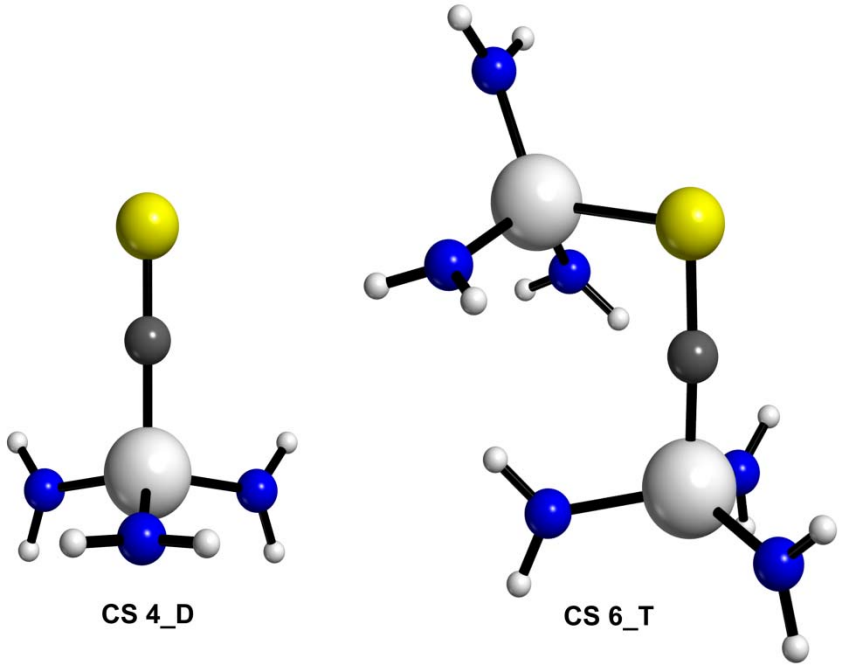


Figure S7. Pictorial representation of CS 1_Q, 4_D and 6_T.

Table S2 Dimensions from Figures S3 and S4. All measurements in Å

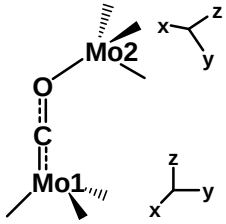
	Dimension	**4_D**	**6_T**
CO	Mo1-C	1.936	1.777
	C-O	1.170	1.268
	O-Mo2		2.054
	C-O-Mo		129.9°
CS	Mo1-C	1.861	1.756
	C-S	1.594	1.700
	S-Mo2		2.436
	C-S-Mo		96.8°

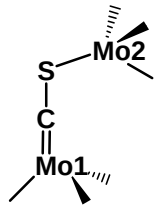
7 Reaction of 4_D + 1_Q.

The second section of this analysis is concerned with the potential for further reaction within the profile described in Figure 1 of the manuscript, that being **4_D** + **1_Q**. This may appear hypothetical since **4_D** can not be produced in our proposed reaction mechanism, but it should be remembered that **4_D** has been synthesised by an alternate route[3] and found to be unreactive towards additional reactant **1_Q** ($Mo[N(^tBu)Ar]_3$). This contrasts to the analogous CS reaction where **4_D(CS)** does react with additional **1_Q** to form a diamagnetic Mo-CS-Mo **6_S(CS)** product.

Firstly consider the Model-opt reaction analysis. Our calculations without Gibbs free energy correction, in reasonable agreement with those of Christian,[4] indicate that the reaction **4_D** + **1_Q** → **6_T** is exothermic by -76.0 kJ mol^{-1}. Should the reaction proceed to the singlet **6_S** it would have a similar value of -72.9 kJ mol^{-1}. Compare this with our previous calculations on the CS equivalent,[5] where the reaction **4_D(CS)** + **1_Q** → **6_S(CS)** is exothermic by -156.5 kJ mol^{-1}. This -82.6 kJ mol^{-1} difference in exothermicity between the CO and CS reaction analogues is rather surprising since the Model-opt structures of **1_Q**, **4_D**, **6_S** (and **6_T)** for both the CO and CS analogues appear remarkably similar in geometry, even to the rotation of one amide at one end of the **6_T** and **6_S** moiety (see supporting information). Both analogues show some activation of the C=O (and C=S) bond when the second MoL_3 coordinates, along with the corresponding shortening of the M-C bond length. Certainly from a structural perspective it would appear there should be little difference in reaction thermodynamics. The electronic properties of CO and CS are however, quite different. We have mentioned previously that the CO_2 orbital energies are significantly different (lower) to those of CS_2 and it similarly follows for CO versus CS. The carbonyl group has lower lying orbital energies than CS, and its π bonding is far stronger. It follows that the stability afforded by the bonding interaction with the second reactant will be less significant for CO when compared with the analogous CS complex. Indeed, when comparing natural bond orbital electron populations in **6_T(CO)** to that in **6_T(CS)** we find a series of subtle differences, as outlined in Table S3.

Table S3. Natural Bond Orbital population analysis of **6_T**, **6_S** and **4_D** for the CO and CS analogues.

		6_T		**6_S**		**4_D**
	Charge on CO (or CS)	Mo1	Mo2	Mo1	Mo2	Mo
	-0.395	Total d 4.88 d_{xz} = 1.30 d_{yz} = 1.34 d_{z^2} = 0.80	Total d 4.25 d_{xz} = 1.01 d_{yz} = 1.06 d_{z^2} = 0.63	Total d 4.84 d_{xz} = 1.25 d_{yz} = 1.31 d_{z^2} = 0.81	Total d 4.43 d_{xz} = 0.68 d_{yz} = 1.14 d_{z^2} = 0.57	Total d 4.76 d_{xz} = 1.02 d_{yz} = 1.61 d_{z^2} = 0.74

	-0.309	Total d = 4.76 d_{xz} = 1.17 d_{yz} = 1.22 d_{z^2} = 0.89	Total d = 4.48 d_{xz} = 1.06 d_{yz} = 1.11 d_{z^2} = 0.79	Total d = 4.75 d_{xz} = 1.16 d_{yz} = 1.19 d_{z^2} = 0.90	Total d = 4.70 d_{xz} = 0.73 d_{yz} = 1.63 d_{z^2} = 0.75	Total d 4.66 d_{xz} = 0.95 d_{yz} = 1.44 d_{z^2} = 0.84

Firstly, Mo1 receives less σ donation from CO as seen by its lower electron density d_{z^2} orbital (0.80 versus 0.89) and donates less density to the CO π orbitals as seen from higher density d_{xz} and d_{yz} orbitals (1.30 and 1.34 versus 1.17 and 1.22) . Similarly Mo2 receives less σ donation from O since its d_{z^2} orbital is less populated (0.63 versus 0.79). This pattern is reciprocated for the **6_S** structure. The bonding in Mo-CO (**4_D**) has been investigated by our group in the past where it was found that M-CO π back donation dominates the interaction.[6, 7]

We have established a significant reduction in exothermicity which is related to CO energetics when compared to CS, but it should be remembered the overall **4_D** + **1_Q** → **6_T** reaction is still exothermic by -76.0 kJ mol^{-1} and, according to the uncorrected Model-opt calculations, the reaction should still proceed. However, two corrections yet to be considered are due to entropy and geometric distortion due to steric bulk. Both of these will have destabilising effects and both are likely to be very similar for both the CS and CO species since their reaction geometries are so similar. Essentially the same destabilisation correction due to entropy and steric bulk would be expected for both reactions. Given that the CS reaction analogue proceeds while the CO does not, one might expect this overall correction to be greater than the **6_T(CO)** formation energy but less than the **6_S(CS)** formation energy, ie greater than +76.0 kJ mol^{-1} but less than +156.5 kJ mol^{-1}.

In regard to an entropy correction, a relatively simple calculation of Gibbs free energy at the Model-opt level of theory provides us with a correction of +67.0 and +64.7 kJ mol^{-1} for the **6_T** CO and CS

formation respectively, and +71.8 and +75.0 kJ mol^{-1} for the **6_S** CO and CS formation. Steric corrections are unfortunately quite a challenge for systems of this size, particularly given the array of potential conformers presented by ligand rotation. However, a moderately accurate approximation can be made based on the known **6_S(CS)** x-ray crystal structure.[8] Using this structure as the starting point for our Oniom-opt calculations removes errors associated with conformer choice and vastly reduces computational time. If we assume the corrections on the singlet surface are of similar magnitude to the triplet surface a moderately accurate general correction can be made.

The Oniom-opt structures obtained are displayed in Figure S8 and as expected the CS analogue is in close agreement with its crystal structure (see above for exact coordinates and comparison). The figure indicates that the CS analogue has maintained a bent arrangement as found in the smaller Model-opt calculation due to its longer Mo-S and C-S bond distances, while the CO analogue shows greater distortion from the Model-opt geometry and a near linear central axis. The approximate steric correction, calculated as ΔE(Oniom-opt) – ΔE(Model-opt), for the **6_S(CO)** formation was found to be +116 kJ mol^{-1}, while for the **6_S(CS)** an unexpectedly large correction of +134 kJ mol^{-1} was obtained. From the geometries one might expect the CS analogue to show a low level of destabilisation due to steric inclusion but unfortunately the calculated figures do not match this finding.

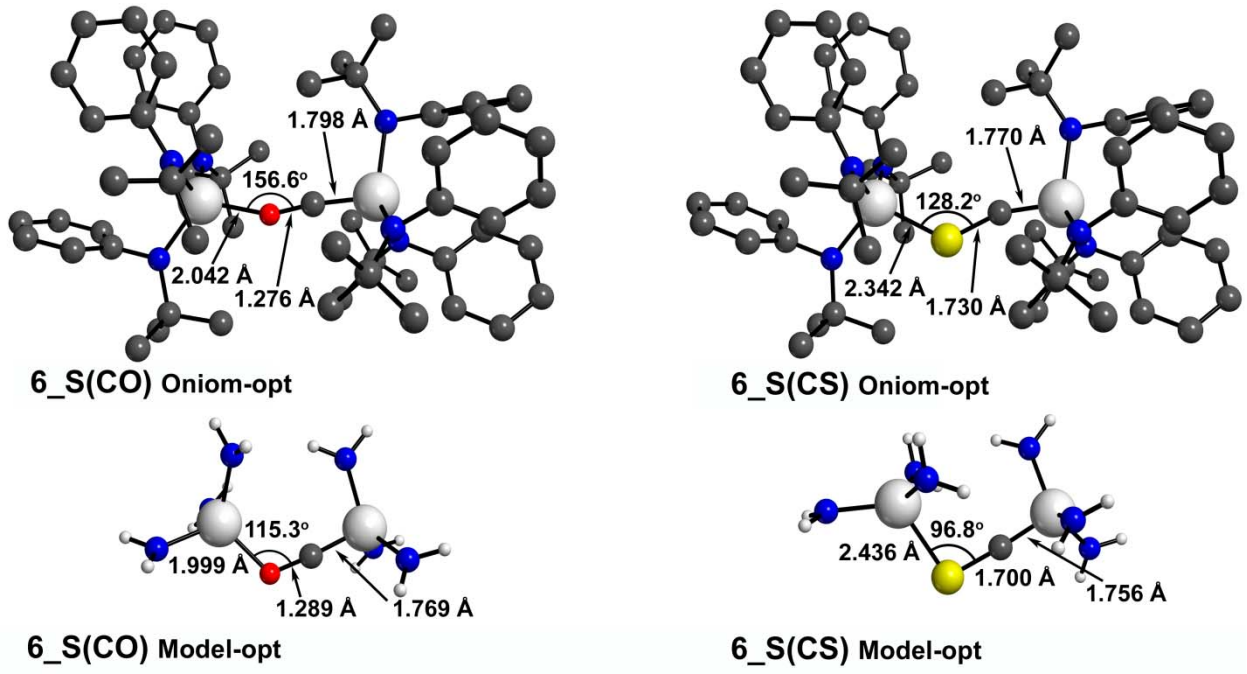


Figure S8. Model-opt and Oniom-opt structures of CO and CS analogues of **6_S**.

If we assume these steric bulk corrections can be similarly applied to **6_T**, our overall correction for entropy and steric bulk is between +183 and +209 kJ mol^{-1} , a value which is outside the expected +76.0 to +156.5 range by some +26 kJ mol^{-1}. These final reaction energies and corrections are illustrated in Table S4 along with the final corrected energies.

Table S4. Reaction energies and corrections of the **4_D** + **1_Q** → **6_T** (or **6_S**) reactions. All values in kJ mol^{-1}.

CO Reaction	**4_D + 1_Q → 6_T**		**4_D + 1_Q → 6_S**	
ΔE uncorrected	-76.0		-72.0	
Model-opt Gibbs Free Energy Correction	+67.0	+183	+71.8	+188
Oniom-opt Steric Bulk Correction	+115.9*		+115.9	
CO Corrected Energy	+107		+116	
CS Reaction				
ΔE uncorrected	-143.9		-156.5	
Model-opt Gibbs Free Energy Correction	+64.7	+199	+75.0	+209
Oniom-opt Steric Bulk Correction	+134.0*		+134.0	
CS Corrected Energy	+56		+52	

* Singlet **6_S** steric correction applied to triplet **6_T**

Even though we have not taken into account a full exploration of conformational space, our calculations suggest that large corrections due to entropy and steric bulk destabilisation exist, and although they may be overestimated it is clear that the true entropy and steric bulk correction is at the high end of the previously established +76.0 to +156.5 kJ mol^{-1} range. Our figures from Table S4 would suggest the corrections are overestimated by around +52 kJ mol^{-1} , since the calculated (corrected) gibbs free energy of the CS **4_D** + **1_Q** → **6_S** reaction should be negative, as it is known to proceed experimentally. If our calculated (corrected) CO **4_D** + **1_Q** → **6_T** reaction was endothermic by +107 kJ mol^{-1} and our corrections are overestimated by some +52 kJ mol^{-1}, it still places the CO **4_D** + **1_Q** → **6_T** reaction endothermic by around +55 kJ mol^{-1} (ie 107 – 52). This reaction will thermodynamically not proceed.

8 Geometric and energetic details of Model structures

CO_2
B3LYP/GBS(1) = -188.577570 a.u.
B3LYP/GBS(2)//B3LYP/GBS(1) = -188.650304 a.u.
CCSD(T)/GBS(1)//B3LYP/GBS(1) = -188.114308a.u.
Enthalpy Correction = 0.015204
Gibbs Free Energy Correction = -0.009752

Atomic No	x-coord	y-coord	z-coord
8	0.000000	0.000000	1.169591
6	0.000000	0.000000	0.000000
8	0.000000	0.000000	-1.169591

Structure 1_Q
B3LYP/GBS(1) = -235.389457 a.u.
B3LYP/GBS(2)//B3LYP/GBS(1) = -235.494256 a.u.
CCSD(T)/GBS(1)//B3LYP/GBS(1) = -234.428708 a.u.
Enthalpy Correction = 0.082433

Gibbs Free Energy Correction = 0.039541

Atomic No	x-coord	y-coord	z-coord
42	0.000000	0.000079	0.000000
7	0.000000	1.981422	0.000000
1	0.090038	2.566539	0.826505
7	-1.715834	-0.990670	-0.000032
1	-2.177712	-1.360784	-0.826632
7	1.715834	-0.990670	0.000032
1	2.177712	-1.360784	0.826632
1	2.267327	-1.205835	-0.826491
1	-0.090038	2.566539	-0.826505
1	-2.267327	-1.205835	0.826491

Structure 1_D
B3LYP/GBS(1) = -235.3666549 a.u.
B3LYP/GBS(2)//B3LYP/GBS(1) = -235.470088 a.u.
CCSD(T)/GBS(1)//B3LYP/GBS(1) = -234.4003381 a.u.
Enthalpy Correction = 0.082743
Gibbs Free Energy Correction = 0.042062

Atomic No	x-coord	y-coord	z-coord
42	0.332737	0.054316	0.000000
7	0.065478	-0.902700	1.676069
1	-0.827787	-1.145830	2.094445
7	-0.081101	1.953243	0.000000
1	-0.299110	2.492351	-0.834357
7	0.065478	-0.902700	-1.676069
1	-0.827786	-1.145830	-2.094445
1	0.809075	-1.490121	-2.057949
1	0.809075	-1.490121	2.057949
1	-0.299110	2.492351	0.834357

Structure 2_Q
B3LYP/GBS(1) = -423.972047 a.u.
B3LYP/GBS(2)//B3LYP/GBS(1) = -424.146998 a.u.
CCSD(T)/GBS(1)//B3LYP/GBS(1) = -422.551043 a.u.
Enthalpy Correction = 0.099216
Gibbs Free Energy Correction = 0.041774

Atomic No	x-coord	y-coord	z-coord
42	0.553115	-0.222847	2.733487
7	-0.353906	-1.372256	1.393893
7	0.609685	1.728186	2.374161
7	1.373287	-0.989462	4.361338
1	-0.001606	2.413922	2.810555
1	0.882945	-1.166776	5.234447
1	-1.340975	-1.616004	1.413175
1	1.353790	2.201762	1.867820

1	0.124490	-1.922248	0.684716
1	2.344503	-1.277676	4.448738
8	0.020814	1.199781	-0.927747
6	-1.000769	1.232633	-0.358819
8	-2.048320	1.288683	0.159249

Structure 2_Q to 2_D MECP/GBS1
B3LYP/GBS(1) = -423.948453884 a.u.

Atomic No	x-coord	y-coord	z-coord
42	0.740134	-0.208005	1.993692
7	1.167847	-1.612245	0.705816
7	1.646693	1.498556	1.715431
7	0.341497	-0.822775	3.805262
1	1.120333	2.372234	1.766431
1	-0.454310	-0.444949	4.320297
1	1.023475	-2.604082	0.877465
1	2.639003	1.677722	1.843033
1	1.719249	-1.475640	-0.137062
1	1.016208	-1.224821	4.450685
8	-3.204362	1.015041	1.209340
6	-2.410526	1.444061	1.949547
8	-1.648161	1.911199	2.712090

Structure 2_Q to 2_D MECP/GBS2
B3LYP/GBS(2) = -424.122903 a.u.

Atomic No	x-coord	y-coord	z-coord
42	-0.7630025	0.0094296	0.0004968
7	-1.8403008	1.5532297	-0.4574072
7	-0.7422406	-1.4296883	-1.3012930
7	-0.6653741	-0.4207257	1.8919804
1	0.1409180	-1.8550160	-1.5748259
1	0.2278154	-0.6346572	2.3293323
1	-2.1941856	2.2201277	0.2187195
1	-1.5164493	-2.0320496	-1.5522457
1	-2.2806247	1.7015394	-1.3579706
1	-1.4277041	-0.7576689	2.4670539
8	3.2531444	1.1914295	-0.2680107
6	2.7904052	0.1484578	-0.0714322
8	2.3756846	-0.9214309	0.1322205

Structure 2_D
B3LYP/GBS(1) = -423.985609 a.u.
B3LYP/GBS(2)//B3LYP/GBS(1) = -424.161869 a.u.
CCSD(T)/GBS(1)//B3LYP/GBS(1) = -422.553281 a.u.
Enthalpy Correction = 0.099871
Gibbs Free Energy Correction = 0.052922

Atomic No	x-coord	y-coord	z-coord

42	-0.304412	-1.684353	1.355381
7	-2.037318	-2.323323	0.758097
7	-0.448142	-1.071567	3.213116
7	1.294693	-2.767366	1.162801
1	0.356121	-0.842980	3.795831
1	1.511439	-3.588996	1.722978
1	-2.584630	-3.041803	1.227325
1	-1.278136	-0.621151	3.596369
1	-2.286776	-2.250677	-0.227365
1	1.782784	-2.787623	0.268383
8	0.223054	1.135439	-0.001836
6	0.063717	-0.053372	0.067744
8	0.031569	-1.073607	-0.704911

Structure 3_T

B3LYP/GBS(1) = -659.4235013 a.u.

B3LYP/GBS(2)//B3LYP/GBS(1) = -659.701137 a.u.

CCSD(T)/GBS(1)//B3LYP/GBS(1) = -657.031063 a.u.

Enthalpy Correction = 0.185042

Gibbs Free Energy Correction = 0.116251

Atomic No	x-coord	y-coord	z-coord
42	-0.208568	2.555056	2.998987
7	-1.926100	1.658737	3.151711
7	-0.179103	4.275421	3.887951
7	1.298662	1.424619	3.478977
1	0.669564	4.760335	4.175783
1	1.548074	1.179731	4.436673
1	-2.392973	1.458002	4.035490
1	-0.993346	4.877250	4.002207
1	-2.248660	1.019143	2.424663
1	1.656678	0.725173	2.827831
8	0.120408	3.583853	0.040486
6	-0.010339	2.726041	1.004012
8	-0.057880	1.466632	0.708119
1	-1.903853	1.581665	-3.065495
7	-1.435310	1.306632	-2.207203
42	0.161758	2.199095	-1.533695
1	-1.860960	0.485867	-1.784338
7	0.317718	3.538788	-3.013819
7	1.831896	1.219823	-1.787206
1	0.649655	4.474429	-2.787015
1	0.576889	3.307008	-3.970608
1	2.094176	0.426353	-1.206995
1	2.409958	1.279591	-2.620466

Structure 3_S

B3LYP/GBS(1) = -659.423658 a.u.

B3LYP/GBS(2)//B3LYP/GBS(1) = -659.697617 a.u.

CCSD(T)/GBS(1)//B3LYP/GBS(1) = -657.027338 a.u.

Enthalpy Correction = 0.186027

Gibbs Free Energy Correction = 0.120436

Atomic No	x-coord	y-coord	z-coord

42	-0.064415	2.342873	2.976791
7	-1.980532	2.668505	2.979619
7	0.986418	3.977506	3.027912
7	0.481401	1.061330	4.319967
1	1.112998	4.552173	3.860508
1	1.429696	0.978031	4.683406
1	-2.513757	2.954049	3.800335
1	1.126426	4.536539	2.185440
1	-2.463046	2.951597	2.125802
1	-0.104349	0.301297	4.662748
8	-0.200798	2.736430	0.481073
6	0.274594	1.635525	1.111742
8	0.694658	0.695741	0.406043
1	-1.444730	0.635490	-3.079958
7	-1.029049	0.647403	-2.149157
42	0.104454	2.068880	-1.457551
1	-0.974451	-0.297956	-1.770967
7	-0.542625	3.557879	-2.516753
7	1.927301	1.939487	-2.123430
1	0.006347	4.383762	-2.763821
1	-1.518818	3.709286	-2.778965
1	2.232105	2.235542	-3.050101
1	2.578518	1.257875	-1.734637

Structure 4_D

B3LYP/GBS(1) = -348.747844 a.u.

B3LYP/GBS(2)//B3LYP/GBS(1) = -348.893196 a.u.

CCSD(T)/GBS(1)//B3LYP/GBS(1) = -347.492091 a.u.

Enthalpy Correction = 0.094406

Gibbs Free Energy Correction = 0.049417

Atomic No	x-coord	y-coord	z-coord
42	-0.299222	-0.105416	1.290147
7	-1.999078	-1.027619	1.727568
7	-0.260733	1.797691	1.770696
7	1.311508	-1.190545	1.576164
1	-0.215482	2.093359	2.746467
1	1.632667	-1.416959	2.518077
1	-2.902638	-0.558955	1.713640
1	0.003639	2.572070	1.167743
1	-2.127009	-2.031583	1.618102
1	2.065790	-1.346105	0.912868
8	-0.074984	0.215872	-1.790305
6	-0.121531	0.113335	-0.625338

Structure 5_D

B3LYP/GBS(1) = -310.673746 a.u.

B3LYP/GBS(2)//B3LYP/GBS(1) = -310.817551 a.u.

CCSD(T)/GBS(1)//B3LYP/GBS(1) = -309.533073 a.u.

Enthalpy Correction = 0.088036

Gibbs Free Energy Correction = 0.044663

Atomic No	x-coord	y-coord	z-coord
42	0.058984	-0.123576	1.866068
7	-1.667669	-0.743308	2.570793
7	0.036031	1.718734	2.560406
7	1.634743	-0.940297	2.712319
1	0.856617	2.314277	2.464536
1	2.216619	-1.636537	2.255328
1	-2.087351	-0.418112	3.437720
1	-0.806890	2.284686	2.477153
1	-2.227390	-1.475863	2.144483
1	1.924569	-0.797561	3.675985
8	0.114082	-0.154799	0.147979

Structure 6_T

B3LYP/GBS(1) = -584.169893 a.u.

B3LYP/GBS(2)//B3LYP/GBS(1) = -584.416394 a.u.

CCSD(T)/GBS(1)//B3LYP/GBS(1) = -581.964367 a.u.

Enthalpy Correction = 0.179974

Gibbs Free Energy Correction = 0.114452

Atomic No	x-coord	y-coord	z-coord
42	-0.978678	-2.445060	-0.920603
7	-2.194596	-3.403455	-2.187067
7	-1.738356	-1.741367	0.770256
7	0.904333	-3.078703	-0.887310
1	-2.020230	-2.359061	1.530111
1	1.174089	-3.898838	-0.345468
1	-2.731714	-3.020820	-2.957134
1	-1.885414	-0.775394	1.039054
1	-2.514232	-4.350962	-1.988984
1	1.734054	-2.612030	-1.235093
8	-0.617650	0.103314	-2.547098
6	-0.769294	-0.936558	-1.836813
42	-0.903563	0.374203	-4.562533
7	0.787085	1.348434	-4.712487
7	-1.018833	-1.551296	-4.829140
7	-2.292171	1.272956	-5.626152
1	1.382057	1.438383	-3.890043
1	1.339219	1.427996	-5.563466
1	-0.916927	-2.189298	-4.032323
1	-0.809581	-2.026579	-5.704981
1	-3.184818	0.841305	-5.857122
1	-2.363349	2.284245	-5.721731

Structure 6_S

B3LYP/GBS(1) = -584.168566 a.u.

B3LYP/GBS(2)//B3LYP/GBS(1) = -584.414886 a.u.

CCSD(T)/GBS(1)//B3LYP/GBS(1) = -581.957903 a.u.

Enthalpy Correction = 0.180523

Gibbs Free Energy Correction = 0.116302

Atomic No	x-coord	y-coord	z-coord

42	-0.151033	-0.168857	-0.090000
7	-1.848854	-1.045705	-0.618689
7	-0.289327	1.652976	0.686781
7	1.305743	-1.335260	0.587541
1	-0.565583	1.796683	1.656989
1	1.251255	-1.782380	1.501336
1	-2.177250	-1.202759	-1.568358
1	-0.028324	2.538044	0.268563
1	-2.532694	-1.369245	0.063343
1	2.185765	-1.566281	0.141976
8	0.805762	0.451080	-2.925489
6	0.447846	0.211267	-1.710429
42	-0.562070	0.025043	-4.319107
7	0.187351	-0.141692	-6.104895
7	-1.813347	-1.437900	-3.970189
7	-1.734692	1.538514	-4.449688
1	0.926669	-0.805570	-6.339581
1	-0.302537	0.135009	-6.956071
1	-1.505675	-2.374298	-3.705056
1	-2.746558	-1.490325	-4.380067
1	-1.520660	2.392970	-4.966683
1	-2.527862	1.688868	-3.823022

Structure 7_D
B3LYP/GBS(1) = -273.412894 a.u.
B3LYP/GBS(2)//B3LYP/GBS(1) = -273.529349 a.u.
CCSD(T)/GBS(1)//B3LYP/GBS(1) = -272.345912 a.u.
Enthalpy Correction = 0.088698
Gibbs Free Energy Correction = 0.047172

Atomic No	x-coord	y-coord	z-coord
42	0.077951	0.031079	2.079294
7	-1.624961	-0.918103	2.559785
7	0.019775	1.922225	2.602998
7	1.656580	-1.039775	2.543886
1	0.076559	2.206572	3.579224
1	1.942332	-1.174930	3.511953
1	-2.537308	-0.467829	2.575609
1	0.190214	2.712735	1.991059
1	-1.737227	-1.929127	2.535948
1	2.406622	-1.296601	1.911528
6	0.205078	0.136112	0.335158

9 Full-Opt Structures

Structure 1_Q (rx4tbuphqmc)
B3LYP/GBS(1) = -1400.264476a.u.
B3LYP/GBS(2)//B3LYP/GBS(1) = -1400.680278 a.u.
Enthalpy Correction = 0.69558
Gibbs Free Energy Correction = 0.582432

Atomic No	x-coord	y-coord	z-coord
42	0.033910	-0.003613	-0.703881
7	-0.597324	1.905579	-0.653458
7	-1.314236	-1.496188	-0.696383
7	2.001078	-0.407982	-0.581877
6	2.922624	-1.032289	-1.576066
6	-0.435340	2.997351	-1.658092
6	-2.262783	-1.950184	-1.755007
6	-3.721154	-1.773879	-1.279882
1	-4.420778	-2.086894	-2.064281
1	-3.926235	-2.374013	-0.387774
1	-3.923515	-0.724437	-1.037861
6	-2.025970	-3.430056	-2.126388
1	-2.200737	-4.091256	-1.272160
1	-2.708068	-3.735039	-2.929240
1	-0.998218	-3.583165	-2.475088
6	-1.800896	3.535304	-2.137632
1	-2.368187	3.982841	-1.316159
1	-1.657029	4.307668	-2.902909
1	-2.403399	2.730527	-2.574703
6	0.385418	4.157307	-1.055150
1	0.530420	4.952522	-1.796305
1	-0.119781	4.593746	-0.187749
1	1.370883	3.803243	-0.731909
6	4.098024	-0.094827	-1.926441
1	4.715250	0.120845	-1.049304
1	4.742541	-0.560723	-2.681677
1	3.730262	0.855057	-2.331424
6	3.481866	-2.362179	-1.025666
1	4.136397	-2.839187	-1.765158
1	4.066112	-2.203609	-0.113607
1	2.666180	-3.055367	-0.790821
6	-1.238579	2.228695	0.586144
6	-0.479183	2.512931	1.737135
6	-2.642737	2.215592	0.706635
6	-1.100318	2.776170	2.959337
1	0.604228	2.512445	1.661568
6	-3.261056	2.488002	1.927209
1	-3.240650	1.973108	-0.166485
6	-2.492791	2.770079	3.059995
1	-0.491055	2.985411	3.834931
1	-4.346166	2.471776	1.994934
1	-2.975223	2.977076	4.011475
6	2.531189	-0.088922	0.710671
6	3.210608	1.124062	0.943750
6	2.335730	-0.956402	1.802045
6	3.683459	1.448848	2.215497
1	3.350499	1.814073	0.117280
6	2.800837	-0.624175	3.075638
1	1.799190	-1.886273	1.639884
6	3.480624	0.576538	3.288280
1	4.204344	2.390705	2.370159
1	2.628217	-1.307448	3.903281
1	3.843910	0.833718	4.279645
6	-1.377398	-2.144644	0.579973
6	-0.661751	-3.332762	0.828888
6	-2.108838	-1.578541	1.641401
6	-0.687688	-3.936626	2.086366
1	-0.072713	-3.765098	0.025892
6	-2.126042	-2.179968	2.900996

1	-2.648732	-0.652435	1.468711
6	-1.421053	-3.363451	3.128674
1	-0.126658	-4.852789	2.254252
1	-2.691043	-1.718008	3.706603
1	-1.436365	-3.831120	4.109490
6	0.323025	2.434984	-2.871111
1	1.312802	2.065483	-2.579850
1	-0.231647	1.614295	-3.341099
1	0.463616	3.217755	-3.625700
6	-2.046826	-1.087112	-3.008828
1	-2.216803	-0.026249	-2.791308
1	-1.031033	-1.203700	-3.404046
1	-2.747437	-1.385248	-3.797600
6	2.130110	-1.325074	-2.860137
1	2.782534	-1.788213	-3.609643
1	1.301014	-2.014415	-2.664000
1	1.723551	-0.404358	-3.294625

Structure 1_D (rx2tbuphqm3f)

B3LYP/GBS(1) = -1400.239242 a.u.

B3LYP/GBS(2)//B3LYP/GBS(1) = -1400.657254 a.u.

Enthalpy Correction = 0.695472

Gibbs Free Energy Correction = 0.588733

Atomic No	x-coord	y-coord	z-coord
42	0.518185	0.007330	-0.270196
7	-0.878695	-1.252288	-0.975821
7	2.287873	-0.731435	0.177822
7	0.059015	1.947251	-0.555835
6	0.931299	3.082810	-0.988330
6	-1.106078	-1.452990	-2.446427
6	3.514372	-1.432098	-0.233498
6	3.517330	-2.846480	0.383573
1	4.420234	-3.398346	0.095308
1	3.486777	-2.792569	1.477624
1	2.643329	-3.413808	0.045207
6	4.774669	-0.668867	0.226678
1	4.830382	-0.616306	1.318772
1	5.678422	-1.178565	-0.128112
1	4.779885	0.351788	-0.171923
6	-0.769276	-2.894929	-2.883981
1	-1.423072	-3.624507	-2.397910
1	-0.897106	-3.002758	-3.968075
1	0.268961	-3.144201	-2.635867
6	-2.572935	-1.143991	-2.815696
1	-2.720064	-1.239024	-3.898497
1	-3.263354	-1.833603	-2.320733
1	-2.840657	-0.124647	-2.518252
6	0.245863	3.922104	-2.087724
1	-0.679506	4.382690	-1.730210
1	0.915492	4.727094	-2.413113
1	0.009629	3.303947	-2.961427
6	1.259822	3.991811	0.215877
1	1.918422	4.813026	-0.091539
1	0.352455	4.430899	0.642637
1	1.764060	3.418584	1.001519
6	-1.709970	-2.027661	-0.107040

6	-2.867697	-1.465647	0.461364
6	-1.381960	-3.351955	0.239768
6	-3.664114	-2.199452	1.341325
1	-3.127018	-0.441550	0.211275
6	-2.178922	-4.084536	1.122498
1	-0.482337	-3.795576	-0.176710
6	-3.325839	-3.513344	1.676741
1	-4.552526	-1.740182	1.768220
1	-1.897698	-5.102978	1.379706
1	-3.945857	-4.082662	2.364113
6	-1.242931	2.275610	-0.050395
6	-2.340067	2.436874	-0.919021
6	-1.470104	2.393756	1.332482
6	-3.612798	2.716848	-0.421861
1	-2.184341	2.328691	-1.987644
6	-2.746109	2.667880	1.828116
1	-0.637986	2.254581	2.014971
6	-3.822693	2.833778	0.955238
1	-4.444329	2.836239	-1.111985
1	-2.896807	2.748784	2.901739
1	-4.815611	3.047059	1.341891
6	1.861731	-0.412884	1.479362
6	2.442985	0.613280	2.312070
6	0.637475	-1.034203	1.921214
6	1.825355	0.997864	3.475634
1	3.377405	1.071665	2.003926
6	0.009363	-0.568113	3.114912
1	0.373547	-2.019972	1.555665
6	0.580757	0.424402	3.874594
1	2.283994	1.760471	4.100815
1	-0.910716	-1.050120	3.434983
1	0.107867	0.756348	4.794766
6	-0.194663	-0.485298	-3.223013
1	-0.432498	0.559123	-2.996173
1	0.865550	-0.661552	-2.997370
1	-0.322598	-0.630640	-4.302298
6	3.510244	-1.533276	-1.765071
1	2.639775	-2.098386	-2.115019
1	3.483562	-0.538929	-2.224076
1	4.412667	-2.047740	-2.113979
6	2.243093	2.521094	-1.559748
1	2.888291	3.346135	-1.884186
1	2.788707	1.935893	-0.813485
1	2.054335	1.878740	-2.427350

Structure 2_Q (ecqco2tbu5qmf)

B3LYP/GBS(1) = -1588.843768 a.u.

B3LYP/GBS(2)//B3LYP/GBS(1) = -1589.329873 a.u.

Enthalpy Correction = 0.712582

Gibbs Free Energy Correction = 0.588394

Atomic No	x-coord	y-coord	z-coord
Mo	-0.19113	0.02056	-0.62167
N	-2.11532	-0.07768	-1.20215
N	0.81865	-1.67621	-0.23077
N	0.65495	1.80894	-0.25419
C	1.74018	2.53555	-0.97545

C	-2.76229	0.3453	-2.47928
C	1.26306	-2.7648	-1.14997
C	0.54023	-4.08461	-0.8038
H	0.84761	-4.88225	-1.49086
H	0.77118	-4.41062	0.21521
H	-0.54563	-3.9613	-0.88406
C	2.78841	-2.98923	-1.07071
H	3.09745	-3.2934	-0.0662
H	3.09235	-3.78001	-1.76717
H	3.32975	-2.07566	-1.34185
C	-3.48606	-0.83159	-3.16847
H	-4.30232	-1.21795	-2.55099
H	-3.91609	-0.50485	-4.12298
H	-2.78873	-1.65239	-3.37195
C	-3.77839	1.47622	-2.21128
H	-4.24515	1.80318	-3.14832
H	-4.57384	1.14457	-1.5365
H	-3.28196	2.33966	-1.75446
C	1.24226	3.88689	-1.53261
H	0.92959	4.56096	-0.72951
H	2.04201	4.385	-2.09393
H	0.3921	3.73914	-2.20852
C	2.93529	2.79041	-0.03181
H	3.74366	3.30257	-0.568
H	2.64689	3.41814	0.81723
H	3.32626	1.8473	0.36623
C	-2.96262	-0.57438	-0.15838
C	-3.36136	0.26054	0.90257
C	-3.37088	-1.92326	-0.12744
C	-4.13739	-0.23374	1.95252
H	-3.04008	1.29762	0.89989
C	-4.15507	-2.41206	0.91773
H	-3.05177	-2.58609	-0.92565
C	-4.54226	-1.56972	1.9636
H	-4.4236	0.42993	2.76444
H	-4.45636	-3.45681	0.91943
H	-5.14784	-1.95328	2.78031
C	0.10889	2.42237	0.92054
C	-0.92995	3.37066	0.83184
C	0.55544	2.0483	2.20207
C	-1.48977	3.9315	1.98019
H	-1.30184	3.64678	-0.15013
C	-0.0131	2.60365	3.34958
H	1.34182	1.30425	2.28501
C	-1.03367	3.55079	3.24511
H	-2.29082	4.66077	1.88645
H	0.34326	2.29144	4.3279
H	-1.47436	3.98343	4.13926
C	1.00957	-1.86693	1.17693
C	2.2329	-1.55185	1.80197
C	-0.0486	-2.31904	1.98891
C	2.39103	-1.69268	3.18118
H	3.05871	-1.18522	1.20081
C	0.10974	-2.4498	3.36962
H	-1.00104	-2.55408	1.52349
C	1.33037	-2.14125	3.97251
H	3.34509	-1.44236	3.63858
H	-0.72664	-2.7927	3.97335
H	1.45386	-2.24444	5.04724
C	-1.67364	0.87458	-3.42643

H	-1.14665	1.72659	-2.98194
H	-0.93976	0.09612	-3.66607
H	-2.12273	1.21057	-4.36847
C	0.90045	-2.36815	-2.59015
H	-0.18088	-2.22682	-2.69971
H	1.405	-1.44159	-2.88782
H	1.20981	-3.15495	-3.28808
C	2.21265	1.6639	-2.1497
H	3.02929	2.1596	-2.68721
H	2.5821	0.69426	-1.79798
H	1.40199	1.48591	-2.86572
O	5.49642	-0.15163	-1.81129
C	5.56381	-0.08515	-0.64572
O	5.63014	-0.02012	0.52062

Structure 2_D to 2_Q MECP
B3LYP/GBS(1) = -1588.797681 a.u.

Atomic No	x-coord	y-coord	z-coord
42	1.0559042	-0.6830092	-1.4247995
7	2.1710628	0.6313398	-0.4020881
7	2.1654472	-2.0409262	-2.4116145
7	-0.6153188	-1.3159514	-0.5067868
6	-2.0204130	-0.7620433	-0.3814755
6	2.0275107	-2.6817904	-3.7822399
6	2.9182028	1.8634827	-0.8554986
6	3.2875793	-2.4605431	-1.6196892
6	3.1330501	-3.4399729	-0.6239544
6	4.5726213	-1.9249276	-1.8353055
6	4.2250184	-3.8596367	0.1406540
1	2.1532954	-3.8750315	-0.4595414
6	5.6609838	-2.3488163	-1.0750111
1	4.7078165	-1.1767399	-2.6096114
6	5.4914587	-3.3170605	-0.0790715
1	4.0795011	-4.6167814	0.9067083
1	6.6450121	-1.9256570	-1.2614233
1	6.3413328	-3.6471259	0.5120053
6	-0.3933274	-2.5963315	0.1085725
6	-0.7673594	-3.7924622	-0.5341560
6	0.1917962	-2.6794462	1.3845360
6	-0.5618709	-5.0277276	0.0802419
1	-1.2099235	-3.7422253	-1.5225613
6	0.4027779	-3.9180240	1.9934946
1	0.4750562	-1.7654041	1.8943697
6	0.0264266	-5.0965381	1.3469961
1	-0.8600812	-5.9391591	-0.4315407
1	0.8600430	-3.9578725	2.9787325
1	0.1845444	-6.0598154	1.8243157
6	2.1924676	0.3675178	1.0095603
6	3.1134211	-0.5459899	1.5529290
6	1.2988033	1.0123044	1.8860445
6	3.1336728	-0.8085616	2.9242051
1	3.8123207	-1.0474812	0.8935195
6	1.3243913	0.7509861	3.2561007

1	0.5774595	1.7123724	1.4796368
6	2.2414930	-0.1630618	3.7823700
1	3.8527476	-1.5205893	3.3203866
1	0.6249587	1.2609934	3.9136854
1	2.2601258	-0.3669207	4.8496706
6	2.3636743	-1.6457178	-4.8737428
1	3.3881689	-1.2753571	-4.7557280
1	2.2829738	-2.1016345	-5.8683869
1	1.6795144	-0.7961127	-4.8413011
6	2.0656798	3.1296336	-0.6304320
1	1.8677586	3.2860076	0.4345678
1	2.6001249	4.0139690	-0.9986627
1	1.1144761	3.0541030	-1.1622084
6	-2.6968389	-1.2628754	0.9130900
1	-3.6766582	-0.7812072	1.0070013
1	-2.8558569	-2.3446984	0.9090897
1	-2.1063669	-1.0051767	1.7982910
6	-1.9640615	0.7727942	-0.2982515
1	-1.4187938	1.0856983	0.5978683
1	-1.4859570	1.2248523	-1.1676494
1	-2.9815778	1.1753896	-0.2329647
6	-2.8786816	-1.1964180	-1.5875513
1	-2.9733134	-2.2866177	-1.6287633
1	-3.8899741	-0.7796961	-1.5030551
1	-2.4441782	-0.8552393	-2.5298409
6	0.5893623	-3.2046795	-3.9525125
1	0.3932601	-4.0059721	-3.2327112
1	-0.1485023	-2.4135560	-3.8166108
1	0.4564974	-3.6130193	-4.9619549
6	2.9769702	-3.8864159	-3.9487213
1	2.7820259	-4.3493585	-4.9224744
1	4.0314068	-3.5978589	-3.9202749
1	2.8098762	-4.6427112	-3.1756606
6	4.2435237	2.0017550	-0.0749488
1	4.8044726	2.8554468	-0.4717711
1	4.0798974	2.1780343	0.9920100
1	4.8626404	1.1052184	-0.1845381
6	3.2711896	1.7349282	-2.3471151
1	3.9113618	0.8650510	-2.5185648
1	2.3818734	1.6548713	-2.9734612
1	3.8204218	2.6266947	-2.6700820
8	0.1146644	1.5094871	-2.7571882
6	-0.0970871	0.3974565	-3.2200890
8	-0.6266431	-0.2307770	-4.1005514

Structure 2_D (ecdtbuqm2f)

B3LYP/GBS(1) = -1588.831399 a.u.

B3LYP/GBS(2)//B3LYP/GBS(1) = -1589.317823 a.u.

Enthalpy Correction = 0.713345

Gibbs Free Energy Correction = 0.601548

Atomic No	x-coord	y-coord	z-coord
42	0.276368	0.079076	-0.834336
7	-1.623587	-0.484690	-1.041211

7	0.514995	1.902195	-0.029062
7	1.600531	-1.228762	-0.097556
6	2.470215	-2.299840	-0.743279
6	1.470856	3.053321	-0.253661
6	-2.551346	-0.351159	-2.230912
6	-0.576316	2.172052	0.870872
6	-0.484873	1.788462	2.220550
6	-1.736161	2.850457	0.445833
6	-1.514135	2.081603	3.118093
1	0.404568	1.269749	2.559692
6	-2.761718	3.141067	1.343753
1	-1.826933	3.139359	-0.595605
6	-2.654221	2.760180	2.686176
1	-1.419850	1.776317	4.156862
1	-3.647523	3.666394	0.995951
1	-3.453965	2.990657	3.384864
6	1.694716	-1.092245	1.330606
6	2.750548	-0.368915	1.919491
6	0.745254	-1.687501	2.177010
6	2.844172	-0.237070	3.303143
1	3.497952	0.084032	1.276907
6	0.836381	-1.547621	3.565093
1	-0.060059	-2.267414	1.741754
6	1.882393	-0.822387	4.134736
1	3.669016	0.324306	3.734687
1	0.085522	-2.014592	4.196848
1	1.954741	-0.716345	5.213779
6	-2.087417	-1.345284	0.013921
6	-2.690856	-0.801244	1.158801
6	-1.957152	-2.744217	-0.077193
6	-3.148042	-1.630719	2.184455
1	-2.803122	0.273462	1.232687
6	-2.422078	-3.570550	0.946090
1	-1.472258	-3.173709	-0.946378
6	-3.018812	-3.017003	2.082871
1	-3.608978	-1.187965	3.063439
1	-2.311265	-4.648278	0.858016
1	-3.378595	-3.661593	2.880312
6	0.930236	3.996068	-1.348256
1	-0.023477	4.444947	-1.051759
1	1.639820	4.815481	-1.517232
1	0.803239	3.456665	-2.289772
6	-2.488890	-1.592903	-3.143640
1	-2.848743	-2.489142	-2.629167
1	-3.128553	-1.438827	-4.021339
1	-1.466338	-1.764769	-3.489668
6	3.235258	-3.120401	0.317850
1	3.793785	-3.910402	-0.195869
1	3.952989	-2.514893	0.878187
1	2.559990	-3.597818	1.034465
6	1.577606	-3.282603	-1.526113
1	0.878386	-3.783239	-0.847205
1	1.011451	-2.772805	-2.306083
1	2.197365	-4.053021	-2.001210
6	3.507585	-1.646900	-1.677869
1	4.118786	-0.921325	-1.129824
1	4.177768	-2.412522	-2.087838
1	3.030027	-1.136675	-2.515332
6	2.847464	2.512835	-0.674524
1	3.245922	1.838490	0.088422

1	2.806648	1.993690	-1.631187
1	3.546127	3.350566	-0.783968
6	1.666757	3.850131	1.054863
1	2.406661	4.638960	0.879754
1	0.744530	4.328659	1.396245
1	2.039583	3.208122	1.860289
6	-3.997537	-0.156580	-1.725548
1	-4.658246	-0.002362	-2.585948
1	-4.363994	-1.026119	-1.173456
1	-4.073058	0.721326	-1.074723
6	-2.177044	0.897319	-3.051215
1	-2.111581	1.783826	-2.412472
1	-1.235969	0.778472	-3.588636
1	-2.954335	1.082041	-3.801376
8	0.685001	-0.621195	-2.804279
6	1.034621	0.613485	-2.710177
8	1.486493	1.438758	-3.468399

10 Oniom-Opt Structures

Structure 1_Q (rxtbuphb3b3)
B3LYP/GBS(1) = -1393.954182 a.u.
B3LYP/GBS(2)//B3LYP/GBS(1) = -1400.67907835 a.u.
Enthalpy Correction = 0.699853
Gibbs Free Energy Correction = 0.58663

Atomic No	x-coord	y-coord	z-coord
42	-0.383790	-0.093129	0.753555
7	-1.671539	1.441552	0.649599
7	1.589199	0.268339	0.823538
7	-1.058195	-1.980444	0.663621
6	-1.035540	-3.083139	1.682015
6	-2.714143	1.922331	1.616197
6	2.445304	0.896363	1.883862
6	3.040180	2.228152	1.364271
1	3.650012	2.698094	2.144091
1	3.667181	2.052254	0.484875
1	2.229998	2.910184	1.084643
6	3.593976	-0.050372	2.310660
1	4.257789	-0.258794	1.466647
1	4.181051	0.414044	3.110999
1	3.179690	-0.995982	2.677120
6	-2.453827	3.389797	2.036800
1	-2.510076	4.056664	1.171693
1	-3.203748	3.705870	2.770814
1	-1.458630	3.475436	2.487132
6	-4.120248	1.807564	0.979065
1	-4.884502	2.142702	1.689318
1	-4.184426	2.422426	0.076263
1	-4.318039	0.765207	0.706766
6	-2.463550	-3.605080	1.973185

1	-2.913100	-4.024293	1.068589
1	-2.425430	-4.387252	2.739884
1	-3.092958	-2.784452	2.334674
6	-0.150679	-4.251145	1.181056
1	-0.117843	-5.048183	1.932490
1	-0.547969	-4.663533	0.248619
1	0.867346	-3.890458	0.998384
6	-1.578797	2.111585	-0.622225
6	-2.185276	1.563773	-1.768003
6	-0.810708	3.283742	-0.769274
6	-2.033702	2.171755	-3.015574
1	-2.756803	0.648551	-1.669155
6	-0.668199	3.893800	-2.015968
1	-0.316462	3.694187	0.102804
6	-1.280306	3.340624	-3.144656
1	-2.501452	1.728009	-3.887347
1	-0.072977	4.795792	-2.108804
1	-1.164646	3.811938	-4.113809
6	-1.556583	-2.297341	-0.650592
6	-2.934753	-2.235976	-0.938444
6	-0.669421	-2.599439	-1.700799
6	-3.407721	-2.481112	-2.228094
1	-3.622569	-1.980478	-0.141664
6	-1.144996	-2.834548	-2.992035
1	0.393884	-2.624596	-1.495100
6	-2.514487	-2.781529	-3.260692
1	-4.472253	-2.429570	-2.429606
1	-0.443202	-3.054196	-3.788865
1	-2.882186	-2.965183	-4.263623
6	2.215991	-0.064198	-0.430343
6	2.880072	-1.294883	-0.604064
6	2.107596	0.797162	-1.538337
6	3.427547	-1.644271	-1.838916
1	2.944113	-1.974670	0.236832
6	2.648545	0.440488	-2.775002
1	1.575984	1.734014	-1.421773
6	3.314678	-0.777280	-2.929805
1	3.934620	-2.596304	-1.952911
1	2.543842	1.113601	-3.618594
1	3.734634	-1.052016	-3.890518
6	-2.655784	1.025597	2.870254
1	-2.847801	-0.019491	2.602933
1	-1.672032	1.096864	3.347831
1	-3.415829	1.347173	3.591570
6	1.555701	1.188737	3.109851
1	0.736964	1.863797	2.836196
1	1.134096	0.259683	3.509612
1	2.153398	1.665138	3.895546
6	-0.431909	-2.520479	2.985462
1	-0.399261	-3.306757	3.748362
1	0.588089	-2.160065	2.811319
1	-1.042219	-1.693253	3.364657

Structure 1_D (rx2tbuphfb3)

B3LYP/GBS(1) = -1393.931567 a.u.

B3LYP/GBS(2)//B3LYP/GBS(1) = -1400.653951 a.u.

Enthalpy Correction = 0.699419

Gibbs Free Energy Correction = 0.593532

Atomic No	x-coord	y-coord	z-coord
42	-0.494229	-0.250002	-0.271782
7	0.296597	1.445610	-0.998438
7	-2.417803	-0.262564	0.190775
7	0.615030	-1.892148	-0.577739
6	0.177438	-3.292277	-0.920795
6	0.458402	1.685776	-2.484274
6	-3.759982	0.266850	-0.167251
6	-3.835131	1.781062	0.139080
1	-4.821380	2.175629	-0.130566
1	-3.663574	1.960302	1.205737
1	-3.068390	2.312328	-0.434968
6	-4.839197	-0.486454	0.645179
1	-4.686644	-0.328083	1.717827
1	-5.836216	-0.121736	0.373993
1	-4.782379	-1.559266	0.433548
6	-0.301288	2.957953	-2.932685
1	0.106779	3.847034	-2.444406
1	-0.207818	3.081472	-4.017812
1	-1.362977	2.867825	-2.677191
6	1.956685	1.825559	-2.848129
1	2.066253	1.970284	-3.929142
1	2.398999	2.682459	-2.331965
1	2.497404	0.922074	-2.549757
6	1.111683	-3.911382	-1.988625
1	2.135296	-3.993382	-1.612739
1	0.752650	-4.913395	-2.248602
1	1.112432	-3.291710	-2.891902
6	0.188406	-4.177871	0.348968
1	-0.139714	-5.193041	0.098794
1	1.196429	-4.228660	0.771841
1	-0.486686	-3.757051	1.100922
6	0.839206	2.471095	-0.148979
6	2.121628	2.330356	0.411031
6	0.086720	3.610478	0.192627
6	2.632274	3.295730	1.279737
1	2.705303	1.451263	0.166659
6	0.598045	4.574042	1.065207
1	-0.908795	3.722888	-0.219885
6	1.874101	4.422593	1.611621
1	3.623355	3.165837	1.700767
1	-0.002902	5.440017	1.320977
1	2.271200	5.169695	2.289062
6	1.956366	-1.724084	-0.075798
6	3.039169	-1.552859	-0.959833
6	2.200609	-1.645213	1.306457
6	4.326879	-1.325332	-0.474613
1	2.852749	-1.586152	-2.025871
6	3.490112	-1.410704	1.788555
1	1.370875	-1.743513	1.995110
6	4.558138	-1.253631	0.903007
1	5.148543	-1.194581	-1.170147
1	3.656470	-1.345096	2.858173
1	5.558255	-1.071537	1.278972
6	-1.847826	-0.290281	1.498520
6	-1.970351	-1.416776	2.386540
6	-0.927386	0.775613	1.848723
6	-1.189216	-1.506741	3.509539

1	-2.699829	-2.181847	2.143431
6	-0.104505	0.610671	3.006533
1	-1.072959	1.778113	1.464668
6	-0.218136	-0.498765	3.807959
1	-1.299114	-2.350738	4.182366
1	0.588548	1.406369	3.258320
1	0.399536	-0.602081	4.693029
6	-0.128265	0.472962	-3.239882
1	0.378084	-0.453053	-2.944791
1	-1.203329	0.376559	-3.046042
1	0.007534	0.610254	-4.319173
6	-3.971810	0.017558	-1.672282
1	-3.206782	0.541060	-2.254556
1	-3.900984	-1.053333	-1.887206
1	-4.958065	0.381871	-1.979532
6	-1.255930	-3.233016	-1.489931
1	-1.601466	-4.249602	-1.710029
1	-1.941684	-2.769152	-0.774934
1	-1.275159	-2.649983	-2.417555

Structure 4_D (ecdcomoqmqm2)

B3LYP/GBS(1) = -1507.30782567 a.u.

B3LYP/GBS(2)//B3LYP/GBS(1) = -1514.063647 a.u.

Enthalpy Correction = 0.711781

Gibbs Free Energy Correction = 0.600136

Atomic No	x-coord	y-coord	z-coord
42	0.142025	-0.309750	-0.688811
7	0.755836	-1.988591	0.224890
7	1.306093	1.334040	-0.729131
7	-1.835328	-0.037019	-0.786439
6	-2.817426	-0.038079	-1.948039
6	1.007761	-3.404590	-0.226406
6	2.709342	1.591431	-1.227041
6	3.606720	2.079944	-0.062642
1	4.624762	2.241147	-0.433935
1	3.233779	3.019593	0.353658
1	3.630345	1.325436	0.730259
6	2.685432	2.655131	-2.351327
1	2.311327	3.611909	-1.976031
1	3.699872	2.803997	-2.738289
1	2.040809	2.313348	-3.167947
6	2.258585	-3.501697	-1.134379
1	3.163992	-3.229153	-0.583538
1	2.375377	-4.527422	-1.503101
1	2.149041	-2.829337	-1.989271
6	1.166919	-4.340544	0.996095
1	1.260754	-5.375509	0.649584
1	2.053668	-4.086296	1.582999
1	0.288554	-4.263517	1.645527
6	-2.951954	-1.456442	-2.550686
1	-3.299367	-2.161985	-1.789149
1	-3.674884	-1.446929	-3.375064
1	-1.989550	-1.799273	-2.937318

6	-4.215459	0.442874	-1.484348
1	-4.875626	0.494410	-2.357016
1	-4.652880	-0.242849	-0.754070
1	-4.151272	1.437194	-1.032096
6	1.261726	-1.549416	1.494921
6	0.364453	-1.062528	2.466372
6	2.645416	-1.492766	1.783135
6	0.833434	-0.500423	3.658518
1	-0.698962	-1.146263	2.287176
6	3.103982	-0.957068	2.983076
1	3.353004	-1.855464	1.048815
6	2.200854	-0.444862	3.924478
1	0.118747	-0.124406	4.381874
1	4.169584	-0.924918	3.183525
1	2.564009	-0.020160	4.853064
6	-2.413321	-0.002637	0.536270
6	-2.911112	-1.173947	1.139911
6	-2.444709	1.194466	1.268744
6	-3.421086	-1.146986	2.437382
1	-2.871285	-2.103650	0.584801
6	-2.944733	1.217015	2.573293
1	-2.070024	2.100070	0.810444
6	-3.434996	0.050088	3.162443
1	-3.796674	-2.058878	2.888640
1	-2.949696	2.149804	3.125851
1	-3.824673	0.069444	4.173713
6	0.661313	2.448380	-0.075024
6	-0.100005	3.375390	-0.809225
6	0.749905	2.601962	1.319816
6	-0.751088	4.428394	-0.166193
1	-0.188374	3.245699	-1.880233
6	0.103089	3.661792	1.959362
1	1.316883	1.879849	1.894020
6	-0.648862	4.578022	1.220974
1	-1.339694	5.130762	-0.745790
1	0.181167	3.764689	3.035899
1	-1.153069	5.398302	1.718645
6	-0.231020	-3.863165	-1.028037
1	-1.123983	-3.795770	-0.398915
1	-0.374474	-3.230179	-1.906443
1	-0.100683	-4.899160	-1.360532
6	3.303130	0.283467	-1.786905
1	3.255584	-0.510246	-1.035929
1	2.768559	-0.041353	-2.681554
1	4.352427	0.452765	-2.053766
6	-2.312889	0.945955	-3.028155
1	-3.030656	0.989134	-3.855657
1	-2.208520	1.943742	-2.590990
1	-1.345811	0.630028	-3.422173
6	0.402798	-0.829788	-2.503899
8	0.583754	-1.158777	-3.618445

Structure 6_T (imtmocomoqmqm4)
B3LYP/GBS(1) = -2901.265416 a.u.
B3LYP/GBS(2)//B3LYP/GBS(1) = -2914.730754 a.u.

Enthalpy Correction = 1.415787
Gibbs Free Energy Correction = 1.226409

Atomic No	x-coord	y-coord	z-coord
42	-2.513270	-0.019785	0.005384
42	2.565254	-0.007315	0.002117
7	-3.036047	1.830813	-0.560493
7	-3.068462	-0.459189	1.883865
7	-3.102500	-1.405317	-1.316459
7	2.976688	1.698180	-1.009425
7	3.003273	0.019499	1.979466
7	3.035579	-1.724704	-0.959857
6	-4.200459	0.279481	2.396057
6	-4.013912	1.368469	3.267128
6	-5.513373	-0.077345	2.044157
6	-5.105981	2.076242	3.770556
1	-3.005891	1.655938	3.536681
6	-6.605336	0.636406	2.545043
1	-5.668597	-0.913690	1.375543
6	-6.407012	1.714501	3.409982
1	-4.941150	2.913280	4.439966
1	-7.610853	0.343893	2.262187
1	-7.254347	2.265847	3.800628
6	-4.262738	-2.188944	-0.957838
6	-4.122480	-3.489956	-0.441022
6	-5.559594	-1.675204	-1.129279
6	-5.242969	-4.253246	-0.110543
1	-3.128035	-3.890573	-0.294246
6	-6.679966	-2.438689	-0.791480
1	-5.681421	-0.676775	-1.527607
6	-6.527535	-3.730174	-0.282909
1	-5.112922	-5.253935	0.286392
1	-7.672172	-2.023897	-0.933357
1	-7.397266	-4.323173	-0.025048
6	-4.177862	1.935845	-1.441332
6	-4.006305	2.147628	-2.821441
6	-5.486147	1.843605	-0.937156
6	-5.108586	2.262851	-3.669184
1	-3.002661	2.215164	-3.220144
6	-6.588568	1.954520	-1.788677
1	-5.630840	1.683882	0.123134
6	-6.405371	2.164597	-3.156684
1	-4.955146	2.425633	-4.730227
1	-7.590242	1.881900	-1.378808
1	-7.260623	2.253530	-3.816348
6	4.299922	-0.588944	2.192198
6	5.482580	0.165759	2.116639
6	4.407294	-1.970721	2.447820
6	6.728915	-0.439163	2.300058
1	5.417440	1.224414	1.907361
6	5.651072	-2.572192	2.638381
1	3.502094	-2.564262	2.468040
6	6.820040	-1.806012	2.567176
1	7.627684	0.163511	2.229708
1	5.711096	-3.637942	2.832375
1	7.787727	-2.272813	2.712919
6	4.251047	2.222491	-0.565847
6	4.311010	3.146620	0.496292
6	5.458188	1.804971	-1.151013

6	5.532551	3.647518	0.945573
1	3.386474	3.444156	0.975078
6	6.682388	2.301604	-0.695132
1	5.429511	1.086994	-1.958586
6	6.726311	3.227211	0.348321
1	5.556060	4.356964	1.766007
1	7.600776	1.957553	-1.157888
1	7.676773	3.614321	0.698114
6	4.315365	-1.568868	-1.619973
6	5.519494	-1.827193	-0.944406
6	4.384340	-1.117086	-2.953191
6	6.749755	-1.647458	-1.582351
1	5.483536	-2.163783	0.081998
6	5.612499	-0.945728	-3.591746
1	3.462281	-0.882109	-3.469933
6	6.803635	-1.212322	-2.907243
1	7.665049	-1.846655	-1.035944
1	5.642231	-0.595151	-4.617994
1	7.759020	-1.077047	-3.401657
6	2.372143	-3.054938	-1.215971
6	2.309207	0.436523	3.251079
6	2.293727	2.549131	-2.048141
6	-2.586200	-1.573375	2.801400
6	-2.581215	-1.666355	-2.721370
6	-2.516066	3.166844	-0.054313
6	1.865309	3.918448	-1.464987
1	1.205426	3.763791	-0.606267
1	2.740289	4.489801	-1.141564
1	1.331451	4.501011	-2.224911
6	1.886542	-3.172320	-2.681794
1	1.201784	-2.350049	-2.909597
1	2.733270	-3.134013	-3.373369
1	1.361412	-4.123387	-2.829013
6	1.878813	-0.791977	4.090887
1	1.225950	-1.434969	3.493073
1	2.752325	-1.367980	4.410388
1	1.335094	-0.464725	4.984751
6	-3.635204	3.934005	0.690117
1	-4.462744	4.166894	0.014222
1	-4.015338	3.337797	1.522520
1	-3.227729	4.874019	1.079513
6	-3.704954	-1.430973	-3.760005
1	-4.531911	-2.129779	-3.606856
1	-4.084582	-0.409419	-3.680027
1	-3.300306	-1.584966	-4.766885
6	-3.743941	-2.553552	3.111643
1	-4.550340	-2.049006	3.651203
1	-4.145060	-2.972414	2.185693
1	-3.363102	-3.369181	3.736879
6	-2.065728	-3.119771	-2.847195
1	-2.880809	-3.836610	-2.714619
1	-1.635026	-3.265846	-3.844198
1	-1.290968	-3.309999	-2.099158
6	-2.050696	-0.986451	4.129280
1	-2.848899	-0.486287	4.684822
1	-1.653350	-1.798179	4.749065
1	-1.247266	-0.273180	3.928210
6	-2.005927	4.033371	-1.230731
1	-2.823801	4.296294	-1.907369
1	-1.572786	4.959053	-0.835490

1	-1.234004	3.497149	-1.788505
6	3.247384	2.791096	-3.248725
1	3.575413	1.831638	-3.660721
1	2.719372	3.353980	-4.026952
1	4.130132	3.359129	-2.943135
6	3.251311	1.326716	4.104215
1	3.568853	2.195832	3.519056
1	2.718026	1.671698	4.997360
1	4.140705	0.774102	4.418370
6	3.365236	-4.210263	-0.920141
1	3.728263	-4.132484	0.109658
1	2.853310	-5.170874	-1.047058
1	4.224002	-4.178437	-1.595966
6	-1.419963	-0.698218	-3.013664
1	-0.573616	-0.880490	-2.350404
1	-1.088290	-0.839865	-4.048387
1	-1.742108	0.340769	-2.896255
6	-1.349994	2.903315	0.915238
1	-0.516276	2.412102	0.409509
1	-0.994977	3.858121	1.319221
1	-1.674628	2.278153	1.752655
6	-1.451589	-2.343670	2.101171
1	-0.591074	-1.700161	1.914768
1	-1.135576	-3.174819	2.741530
1	-1.794894	-2.756134	1.147587
6	1.170466	-3.214755	-0.267385
1	0.410917	-2.458111	-0.462523
1	0.728918	-4.209093	-0.406973
1	1.498175	-3.114358	0.772351
6	1.065580	1.269953	2.898094
1	1.350951	2.132035	2.287145
1	0.344791	0.674996	2.337059
1	0.593361	1.627119	3.821295
6	1.054475	1.804581	-2.572661
1	1.343401	0.824186	-2.964374
1	0.324318	1.650101	-1.777712
1	0.591280	2.389828	-3.376271
6	0.769562	-0.057888	0.003752
8	-0.491166	-0.160072	0.007054

11 Model CS_2 (or CS) Structures

Geometries taken from
A. Ariafard, N. J. Brookes, R. Stranger and B. F. Yates, *J. Am. Chem. Soc.*, 2008, **130**, 11928-11938.

Structure 4_D
B3LYP/GBS(1) = -671.694251 a.u.
B3LYP/GBS(2)//B3LYP/GBS(1) = -671.841335 a.u.
Enthalpy Correction = 0.092339
Gibbs Free Energy Correction = 0.045905

Atomic No	x-coord	y-coord	z-coord
7	-1.310762	-0.001955	1.831040
7	-0.891314	-1.682360	-0.969636
7	-0.892524	1.683781	-0.966686
1	-1.827643	1.977182	-1.249028
1	-0.190136	2.209712	-1.479325
1	-1.300013	-0.835567	2.415211
1	-1.304135	0.831904	2.414922
1	-0.188648	-2.207005	-1.483195
1	-1.826305	-1.976671	-1.251417
6	1.265434	0.000370	0.024121
16	2.856470	0.000174	0.116195
42	-0.595168	-0.000019	-0.015096

Structure 6_T

B3LYP/GBS(1) = -907.137037 a.u.

B3LYP/GBS(2)//B3LYP/GBS(1) = -907.390388 a.u.

Enthalpy Correction = 0.178055

Gibbs Free Energy Correction = 0.110073

Atomic No	x-coord	y-coord	z-coord
7	-1.536207	0.810085	1.794366
7	-3.588143	-1.314495	0.158483
7	-2.381224	1.443759	-1.393638
1	-3.106212	2.159012	-1.398160
1	-1.920550	1.414072	-2.296487
1	-2.122595	1.305930	2.462508
1	-0.588088	0.711965	2.143476
1	-3.474716	-2.289522	-0.092891
1	-4.555611	-1.124764	0.412825
6	-0.805732	-0.757956	-0.492289
16	0.637908	-1.466189	-1.042357
42	-2.222137	0.111997	0.073948
42	2.164958	0.079388	0.059996
7	1.753263	-0.487375	1.892390
7	1.442821	1.743318	-0.668782
7	4.099030	-0.018810	-0.307868
1	1.040701	-1.186006	2.092823
1	2.029692	0.010662	2.735540
1	0.486175	1.763904	-1.026234
1	1.683705	2.652037	-0.274283
1	4.515861	0.328995	-1.169402
1	4.706118	-0.717824	0.115654

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