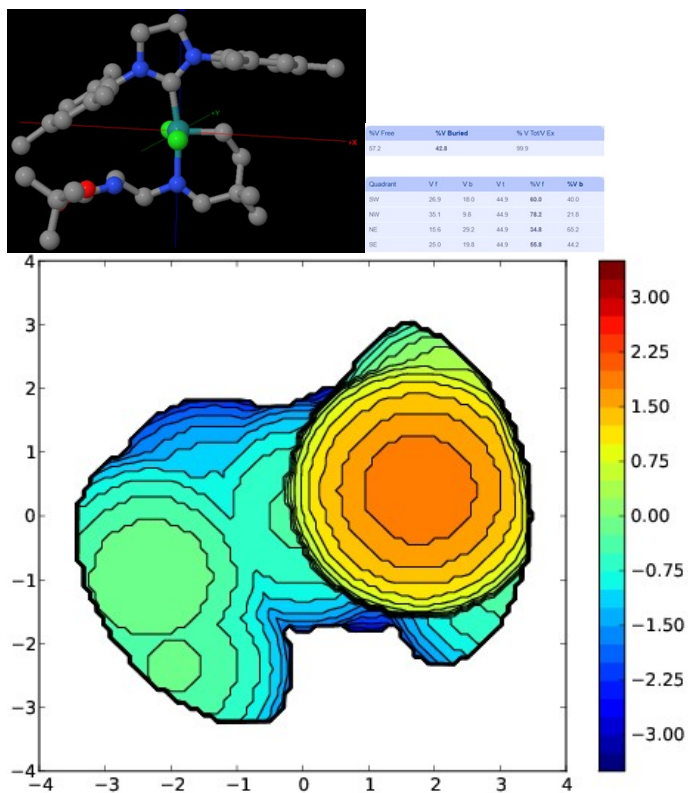
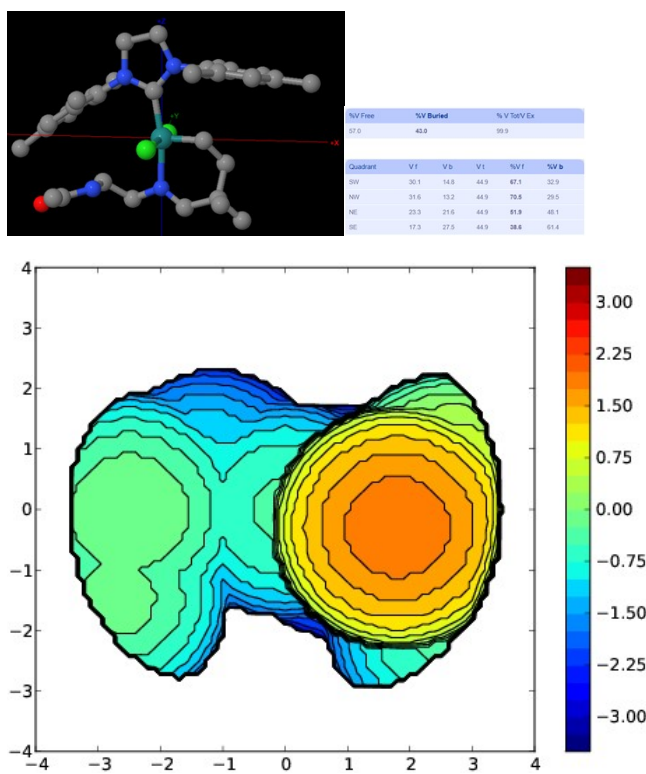


### Steric maps:

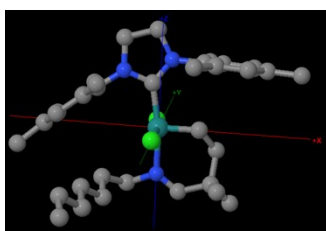
#### 1A:



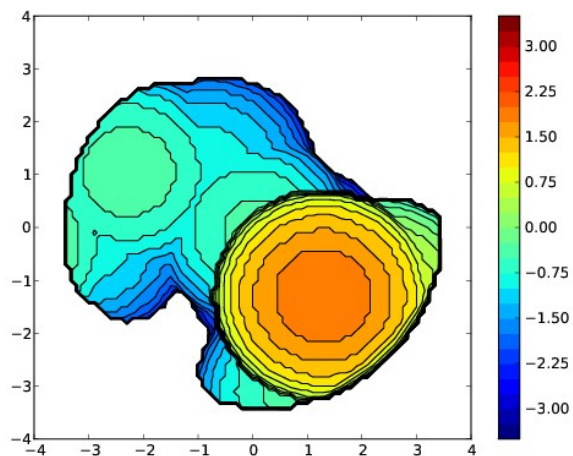
#### 2A:



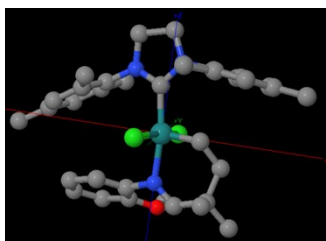
### 3A:



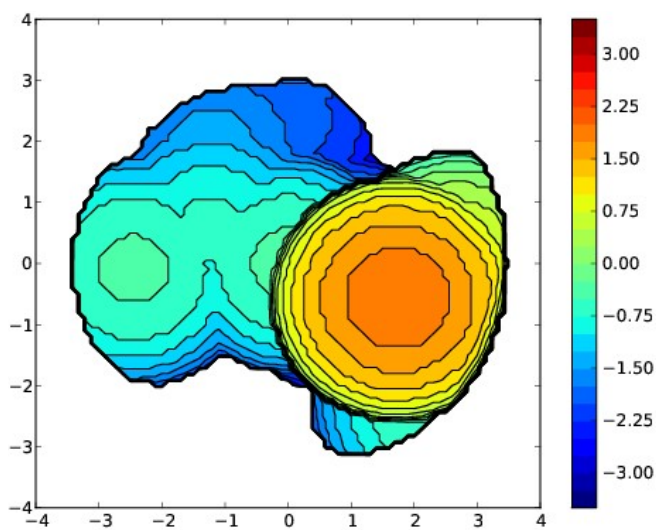
%V Free	%V Buried	%V TotV Ex			
35.1	41.5	93.5			
Quadrant	V1	V2	V3	%V1	%V2
SW	29.3	15.6	44.9	68.2	24.7
SW	24.5	10.2	44.5	71.2	23.5
NE	15.8	25.1	44.9	44.1	55.9
NE	20.5	24.3	44.9	45.8	54.2



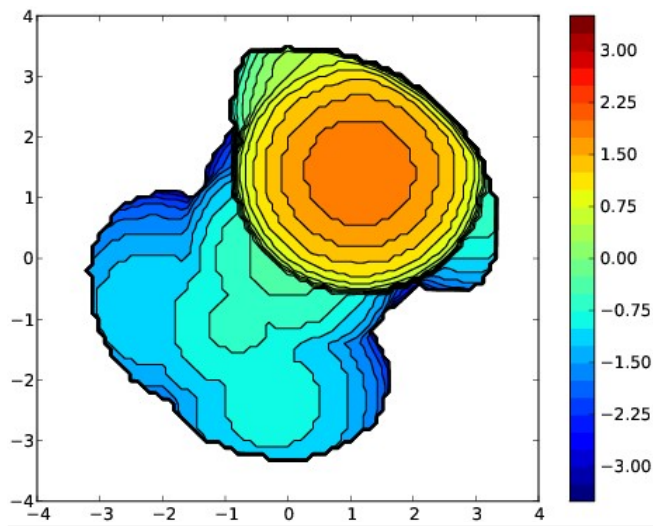
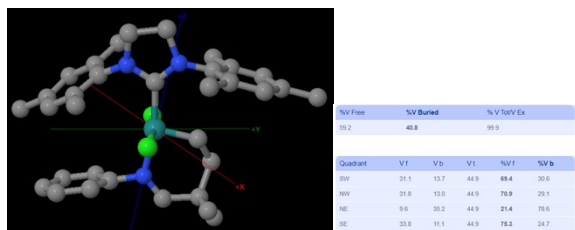
### 4A:



%V Free	%V Buried	%V TotV Ex			
34.5	41.5	93.5			
Quadrant	V1	V2	V3	%V1	%V2
SW	35.5	11.3	44.9	74.7	25.3
SW	31.5	13.4	44.9	70.2	29.8
SE	25.5	19.3	44.9	56.9	43.1
SE	14.5	30.3	44.9	32.4	67.6



### 5A:



**Figure S1.** Orientation, % $V_{Bur}$  values and steric maps of precatalyst **A** for systems 1-5.

### **NBO Analysis:**

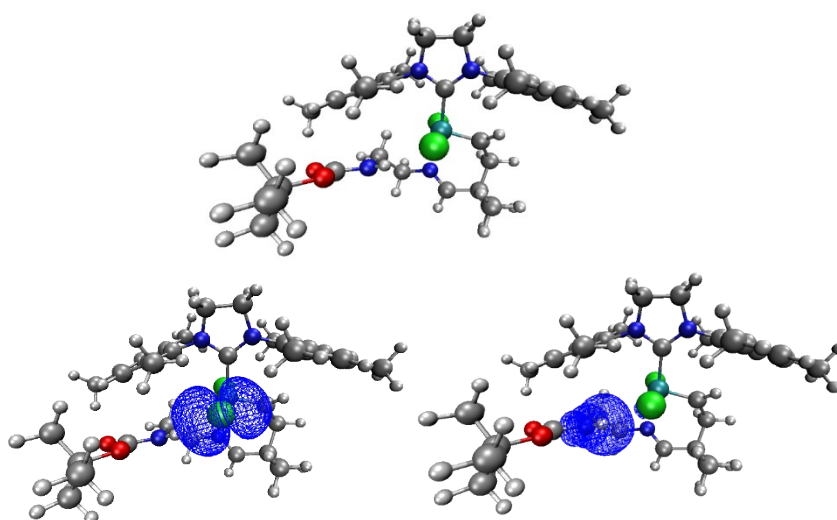
Occupancies:

Total Lewis	369.25723 ( 98.207% of 376)
Total non-Lewis	6.74277 ( 1.793% of 376)

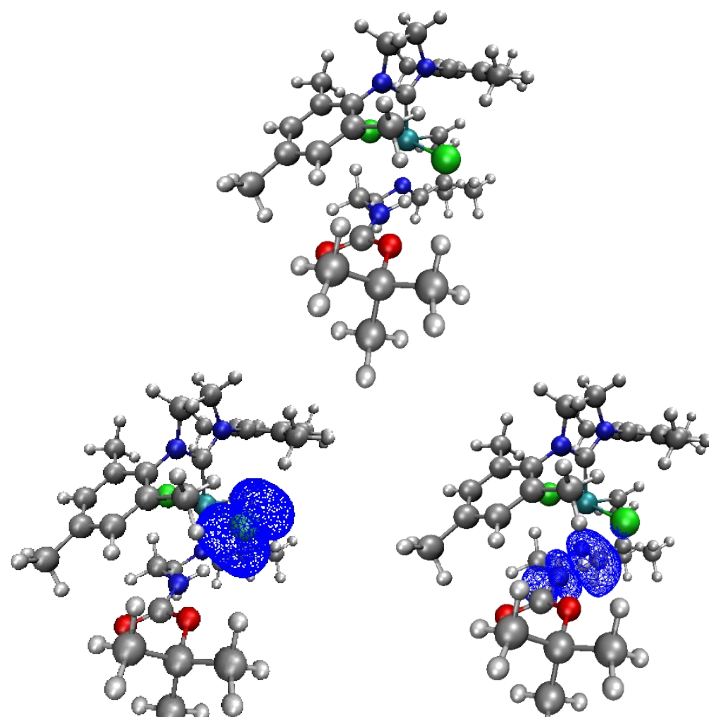
CR	BD	nC	LP
54	103	0	17

### SECOND ORDER PERTURBATION THEORY ANALYSIS

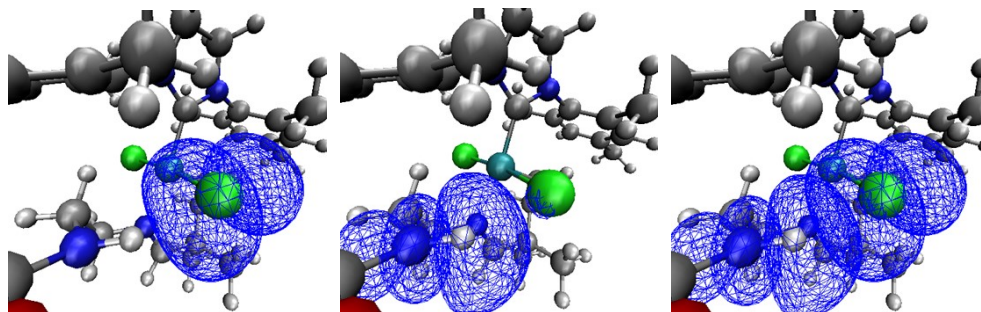
59. LP (3)Cl2	197. BD* (1) N11-H81	E=-11.60
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*Figure S2. Frontal view: (left) 59. LP (3)Cl2 (right)197. BD\* (1) N11-H81*



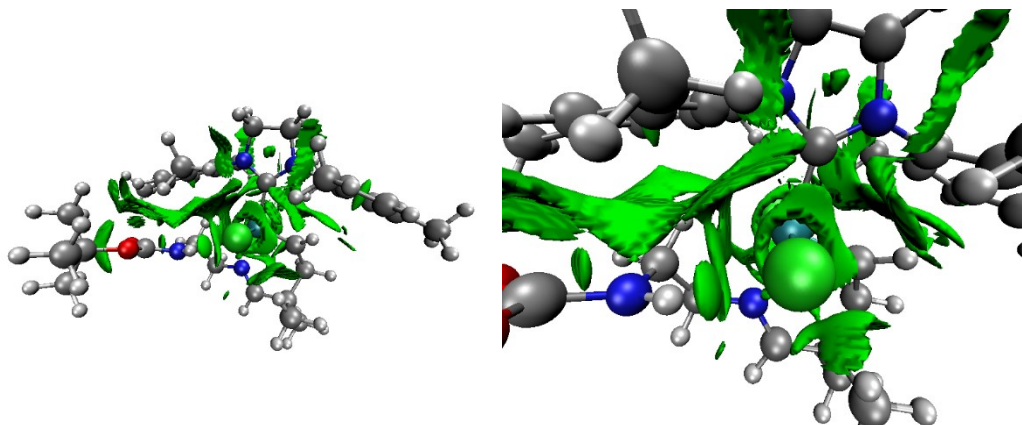
*Figure S3. Lateral view: (left) 59. LP (3)Cl2 (right)197. BD\* (1) N11-H81*



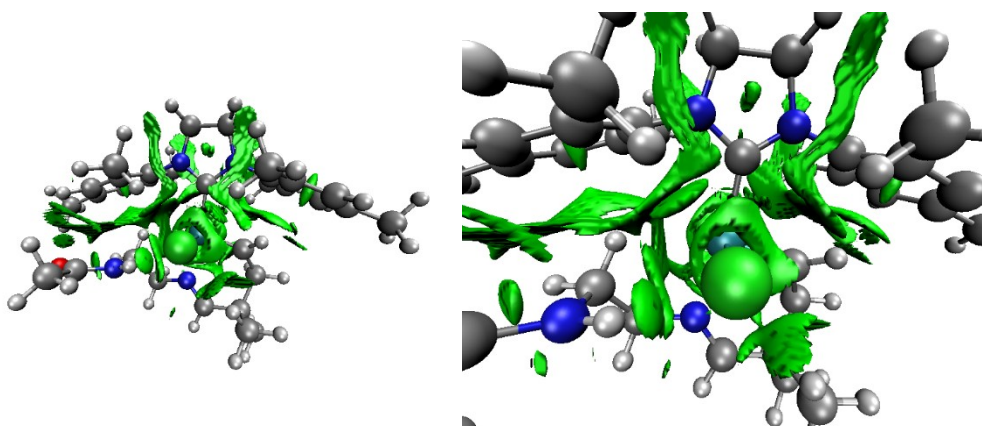
*Figure S4. Frontal close-up: (a) 59. LP (3)Cl2 (b)197. BD\* (1) N11-H81 (c) Overlap of the two orbitals.*

**NCI PLOTS:**

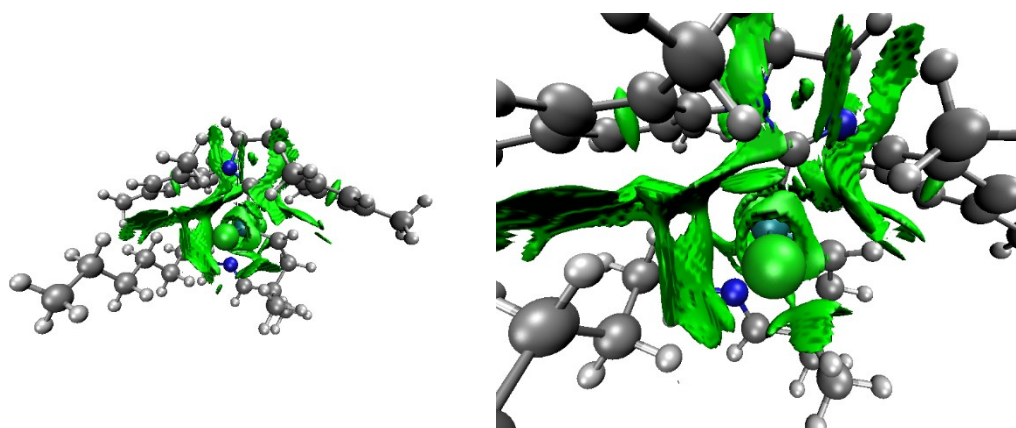
1A



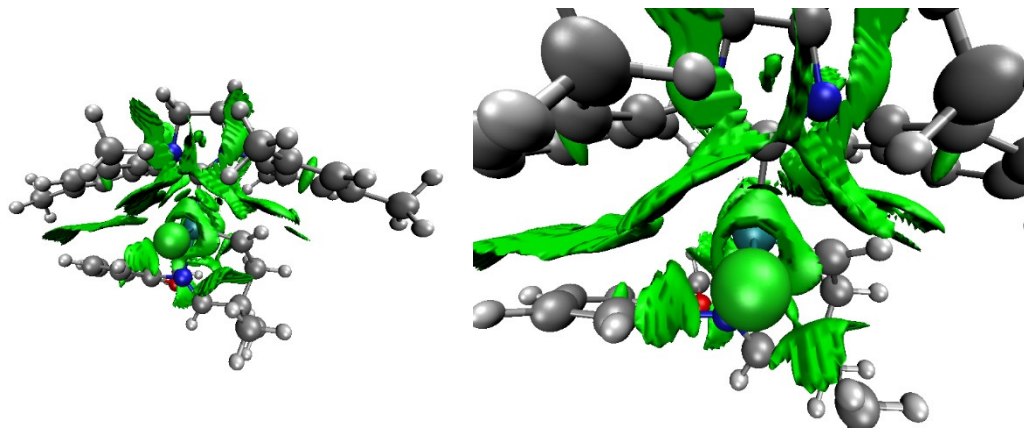
2A



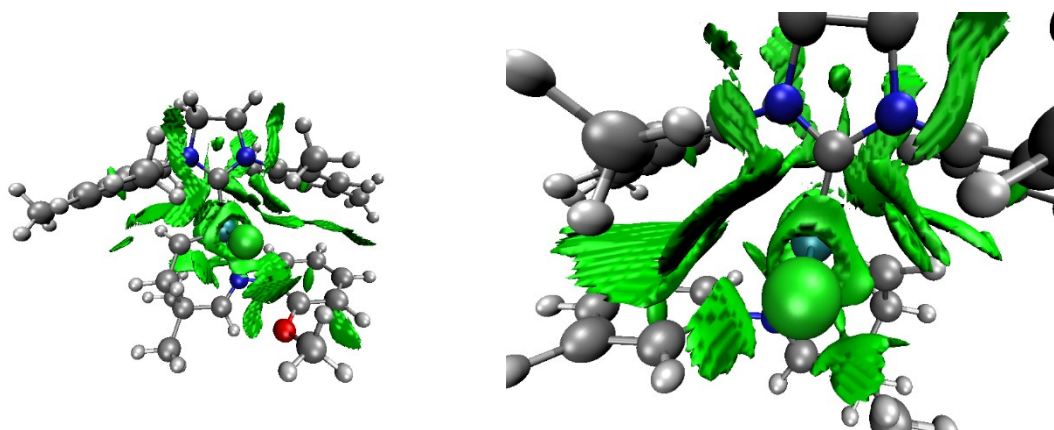
3A



4A

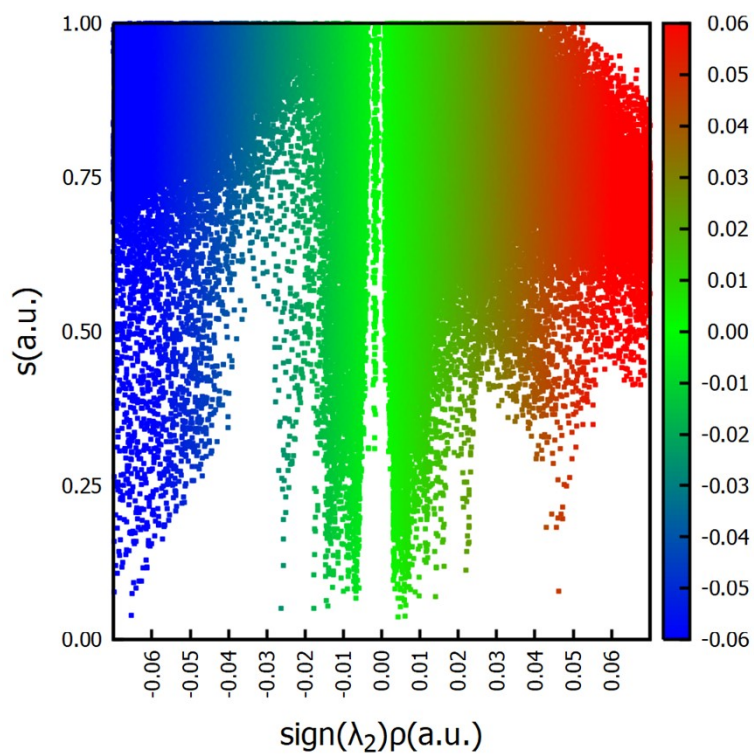


5A

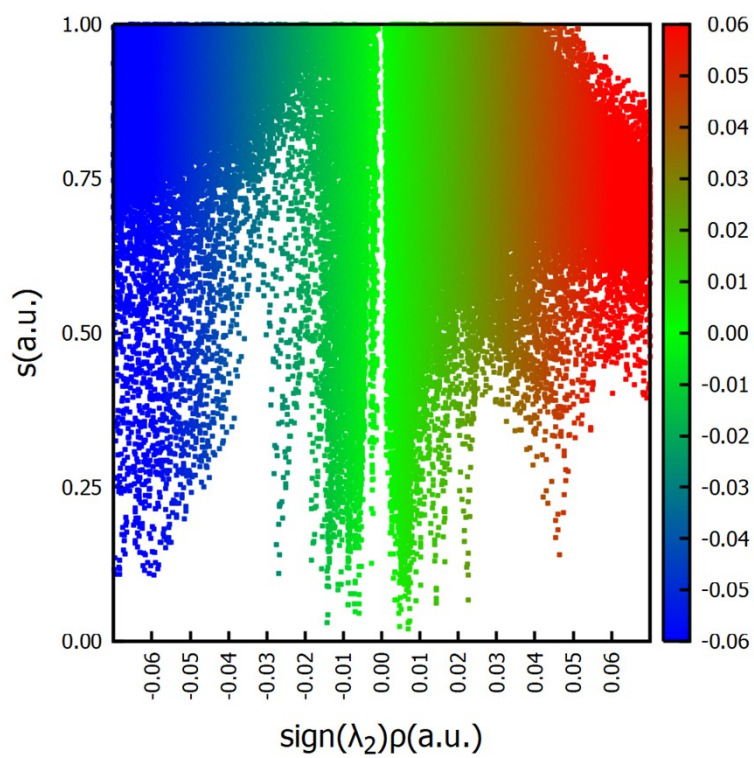


**Figure S5.** NCI plots of the initial intermediate **A** for systems **1-5** (the whole picture is truncated on the right for the sake of clarity of the metal centre).

1A

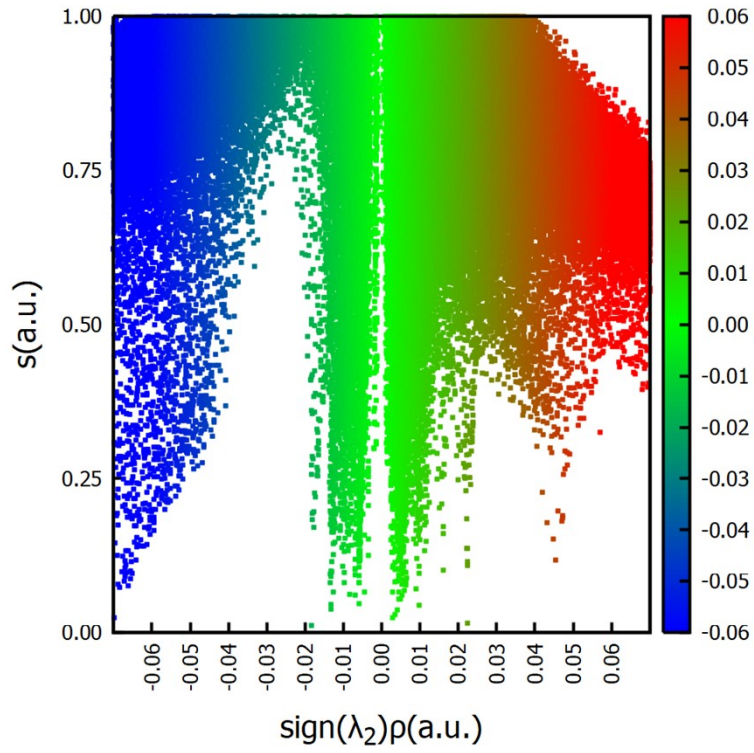


2A

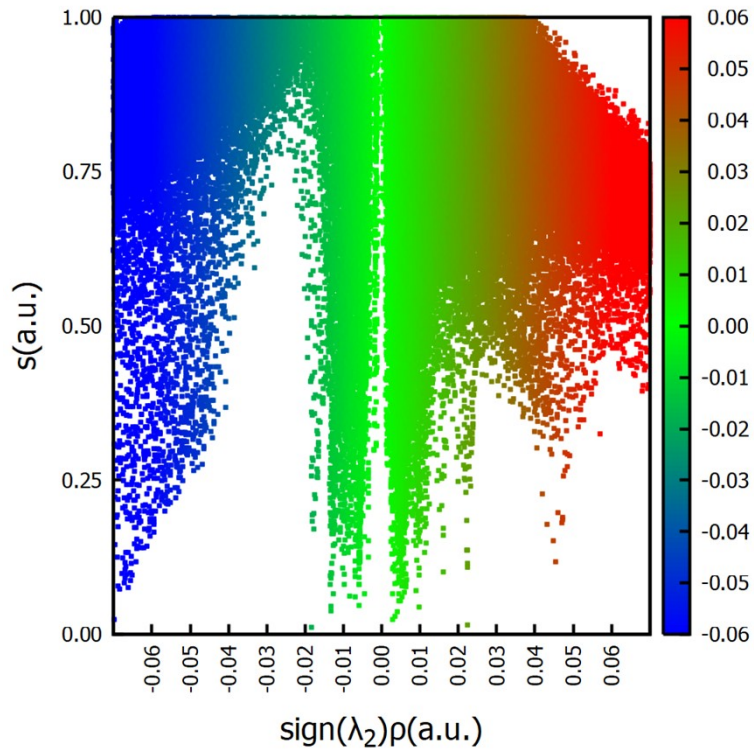




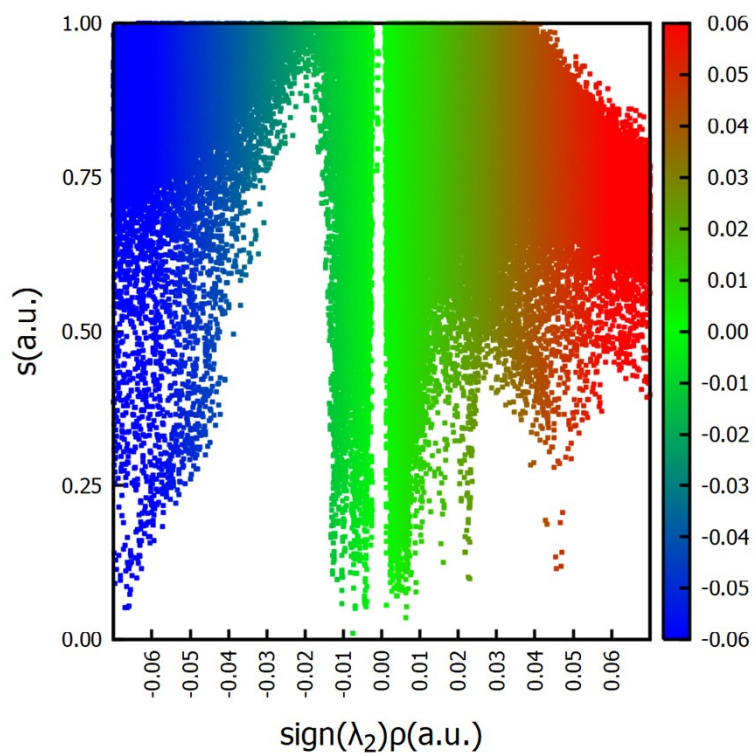
3A



4A



5A



**Figure S6.** 2D-NCI plots of reduced density gradient ( $S$ ) vs  $\text{sign}(\lambda_2)\rho$ , in a.u. for the initial intermediate **A** for systems 1-5.