Supporting Information

Probing the Aromaticity and Stability of Metallatricycles by DFT Calculations: Toward Clar Structure in Organometallic Chemistry

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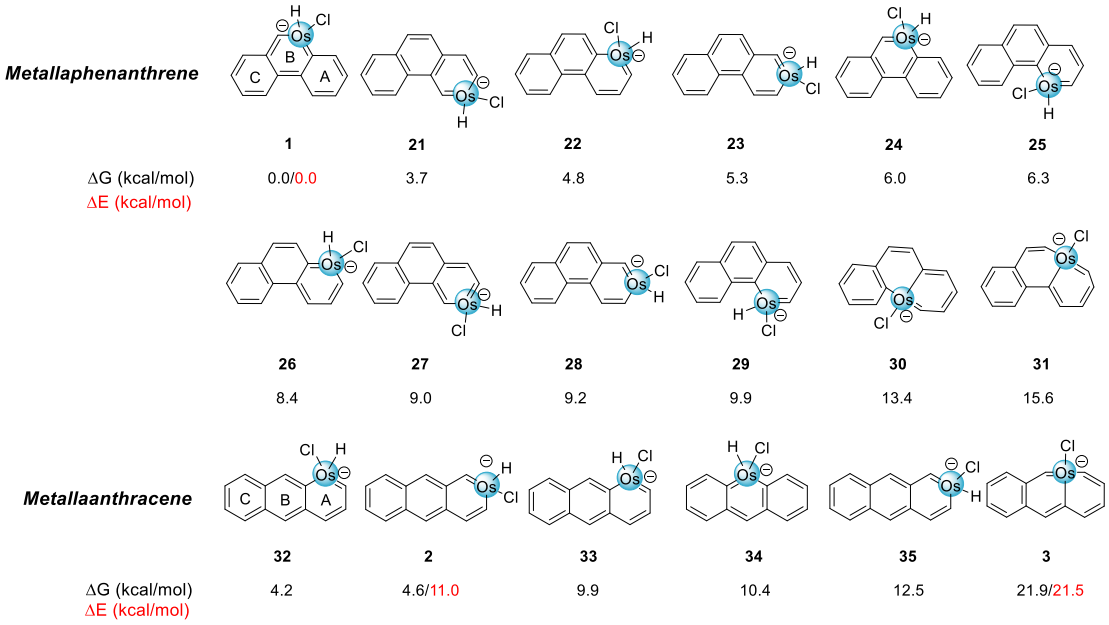

Figure S1. The relative Gibbs free energy (black, M06/6-311++G(d,p)-LANL2TZ(f)//M06/6-31G(d)-LANL2DZ) and electronic energy (red, CCSD(T)/6-311++G(d,p)-LANL2TZ(f)//M06/6-31G(d)-LANL2DZ) of metallaphenanthrenes and metallaanthracenes.

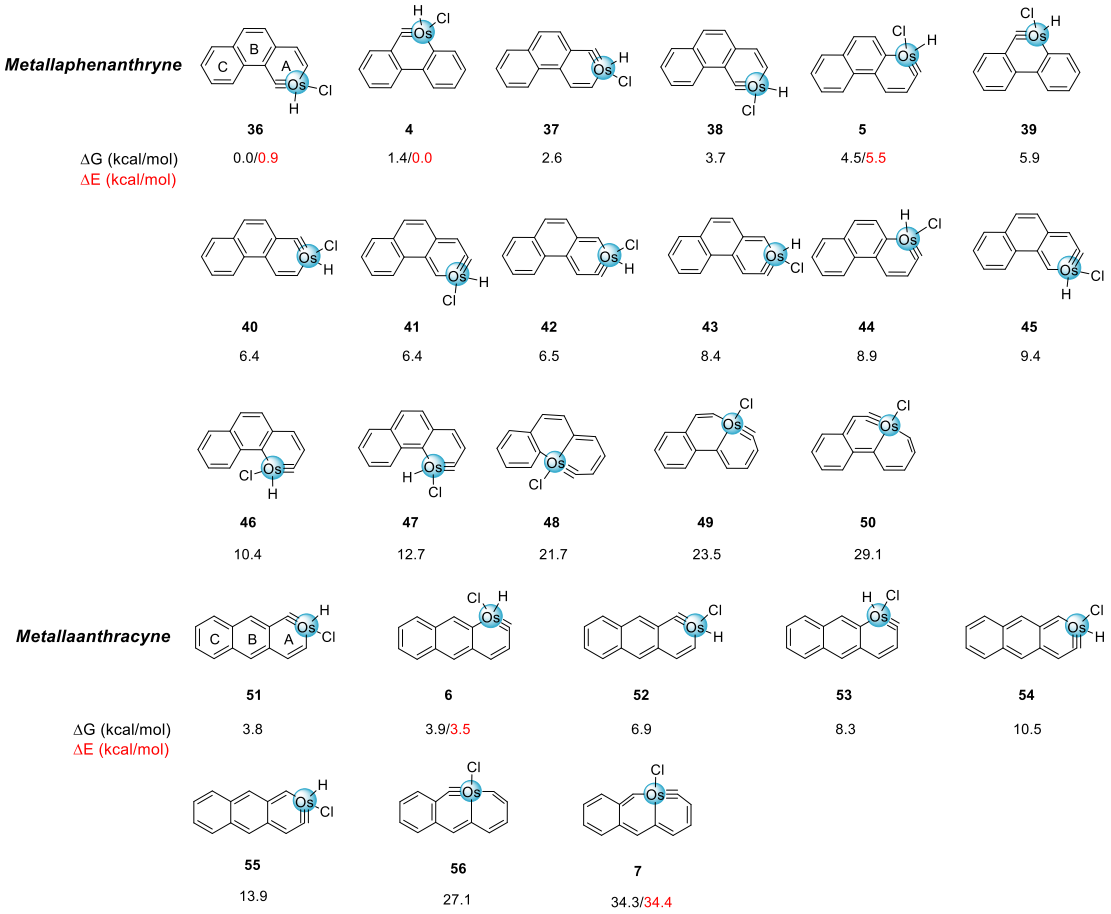

Figure S2. The relative Gibbs free energy (black, M06/6-311++G(d,p)-LANL2TZ(f)//M06/6-31G(d)-LANL2DZ) and electronic energy (red, CCSD(T)/6-311++G(d,p)-LANL2TZ(f)//M06/6-31G(d)-LANL2DZ) of metallaphenanthrynes and metallaanthracynes.

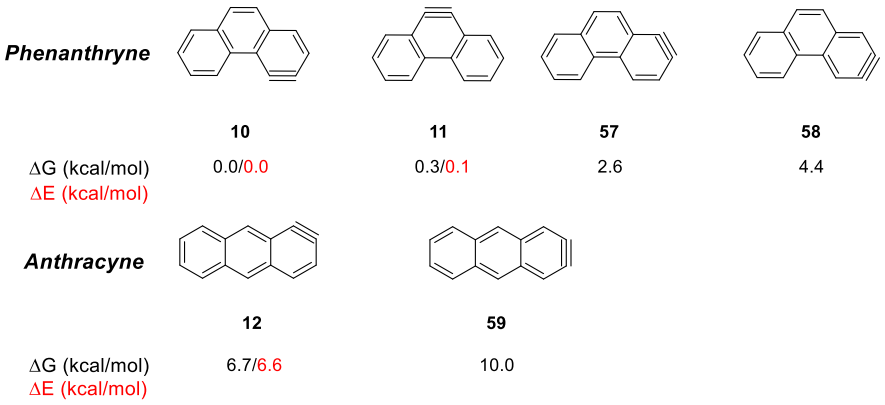

Figure S3. The relative Gibbs free energy (black, M06/6-311++G(d,p)-LANL2TZ(f)//M06/6-31G(d)-LANL2DZ) and electronic energy (red, CCSD(T)/6-311++G(d,p)-LANL2TZ(f)//M06/6-31G(d)-LANL2DZ) of organic system.

Table S1. The $NICS(1)_{zz}$ values (ppm) and the normalized multi-centered indices ($MCI^{1/6}$, 6 is the number of centers) of 1-7.

Species	$NICS(1)_{zz}$			$MCI^{1/6}$		
	A	B	C	A	B	C
1	-18.5	-5.6	-23.6	0.640	0.410	0.639
2	-8.1	-25.7	-24.6	0.454	0.582	0.602
3	4.8	-1.4	-14.2	0.473	0.514	0.608
4	-24.4	-1.3	-22.5	0.641	0.429	0.627
5	-6.5	-21.6	-28.1	0.519	0.569	0.619
6	-2.8	-26.4	-26.2	0.462	0.580	0.602
7	42.3	39.5	4.5	0.446	0.492	0.589

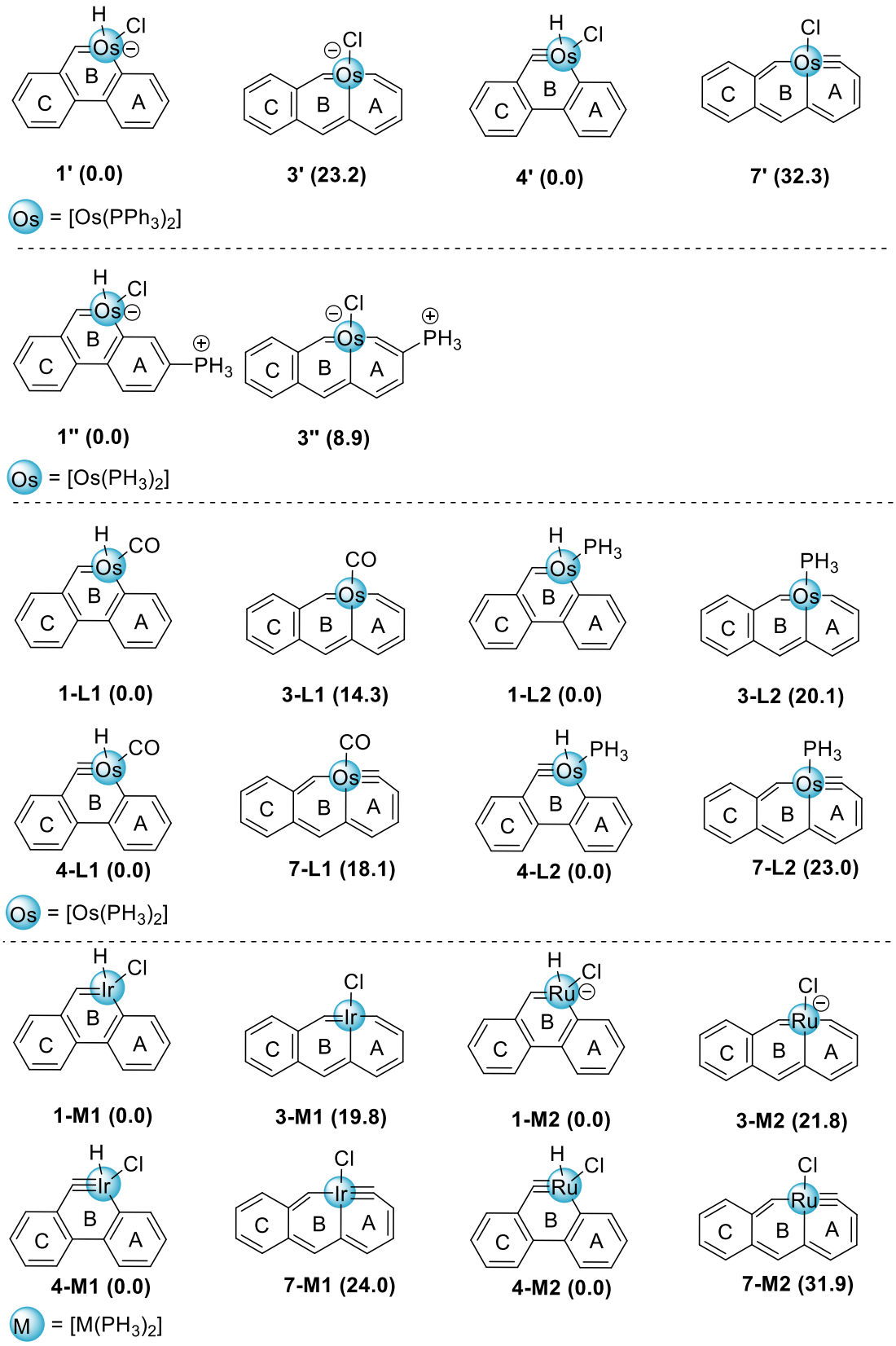

Figure S4. The relative Gibbs free energies (in kcal mol^{-1}) of metallatricycles with different metal centers and ligands computed at the M06 level (M06/6-311++G(d,p)-LANL2TZ(f)//M06/6-31G(d)-LANL2DZ).

Table S2. The NICS(1)$_{zz}$ values (the center of the rings, ppm)

Species	NICS(1)$_{zz}$		
	A	B	C
1'	-25.2	-5.7	-25.4
3'	9.4	2.5	-12.3
4'	-28.7	-3.7	-24.6
7'	38.2	38.1	4.8
1"	-16.7	-6.2	-23.7
3"	4.8	-4.2	-17.8
1-L1	-18.8	-8.2	-23.4
3-L1	26.8	20.5	-11.2
1-L2	-19.0	-9.1	-23.9
3-L2	20.9	15.1	-12.4
1-M1	-20.0	-1.4	-21.8
3-M1	21.5	16.6	-8.5
1-M2	-19.5	-7.4	-23.1
3-M2	11.6	6.3	-11.0
4-L1	-24.0	-3.3	-18.8
7-L1	38.1	40.2	1.7
4-L2	-23.6	-1.9	-19.6
7-L2	44.0	45.6	4.5
4-M1	-23.7	0.5	-17.4
7-M1	24.2	24.3	-2.4
4-M2	-24.5	-1.0	-21.7
7-M2	31.0	28.7	-0.7

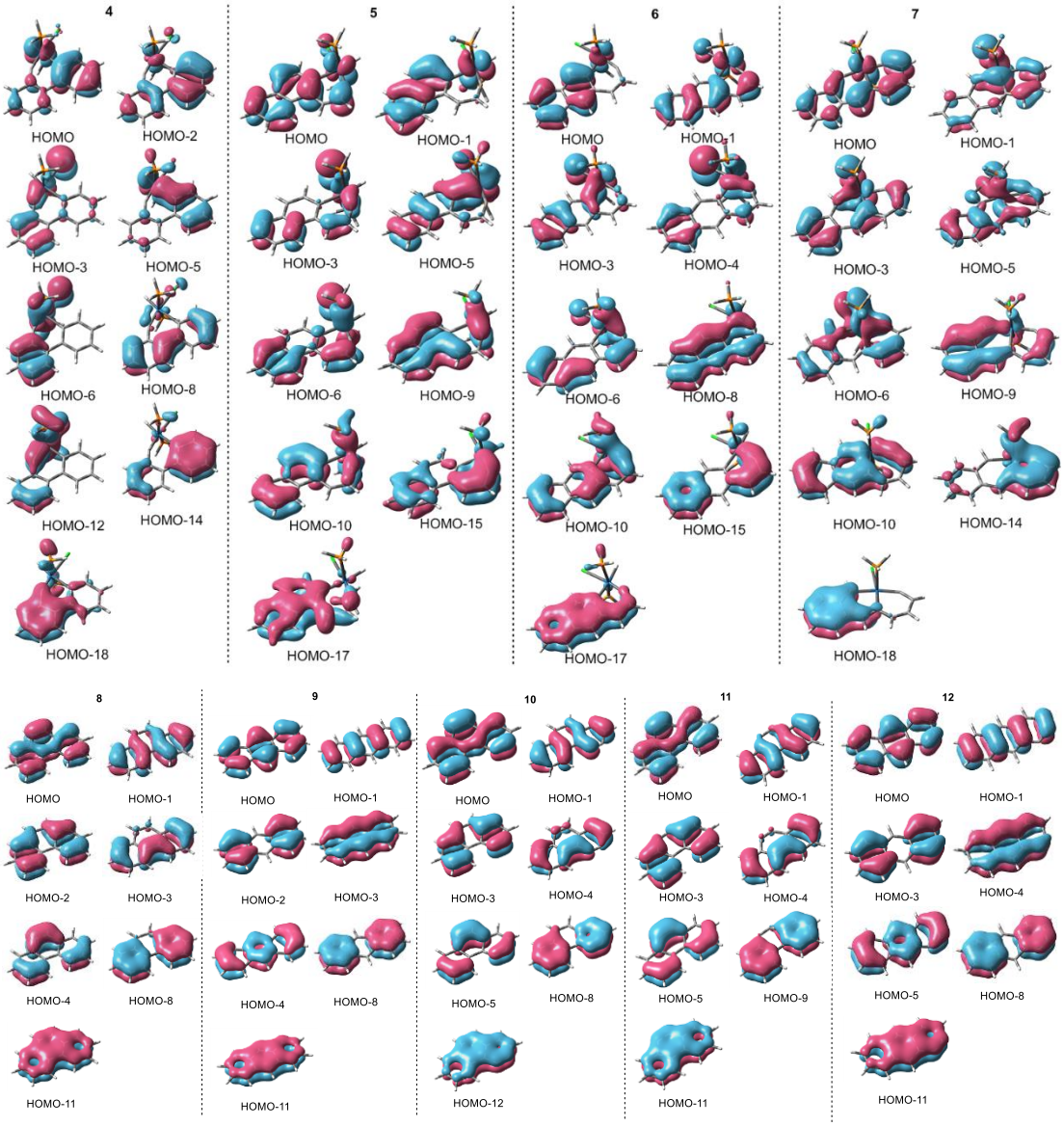

Figure S5. Key π molecular orbitals of compounds **4-12**. The isovalue is 0.030 a.u.

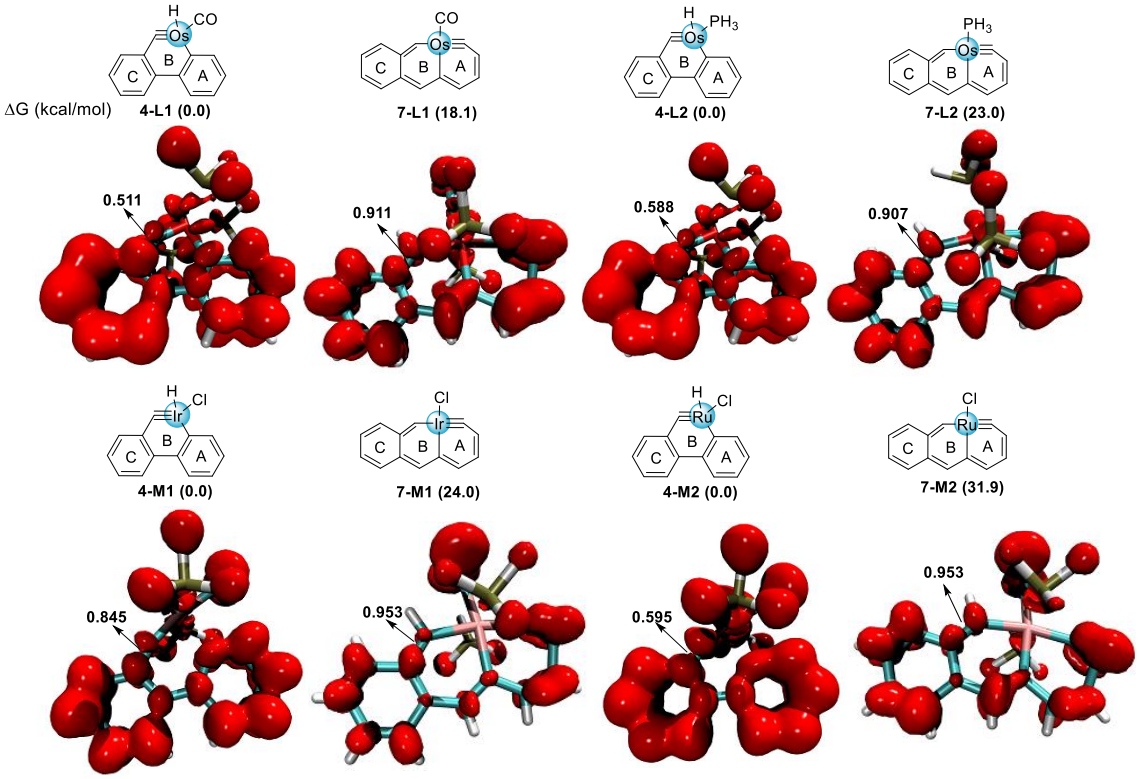

Figure S6. The Clar structure and BV(ELF_{π}) values in some metallatricycles.

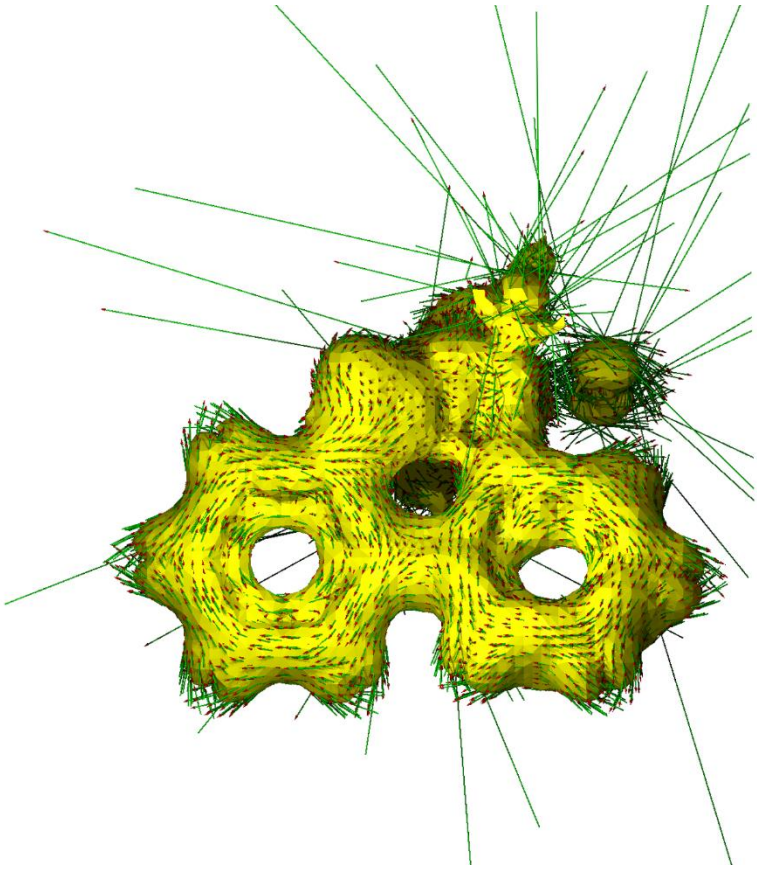

Figure S7. Computed ACID plot of **1** from the total contribution with isosurfacevalue of 0.030 a.u.

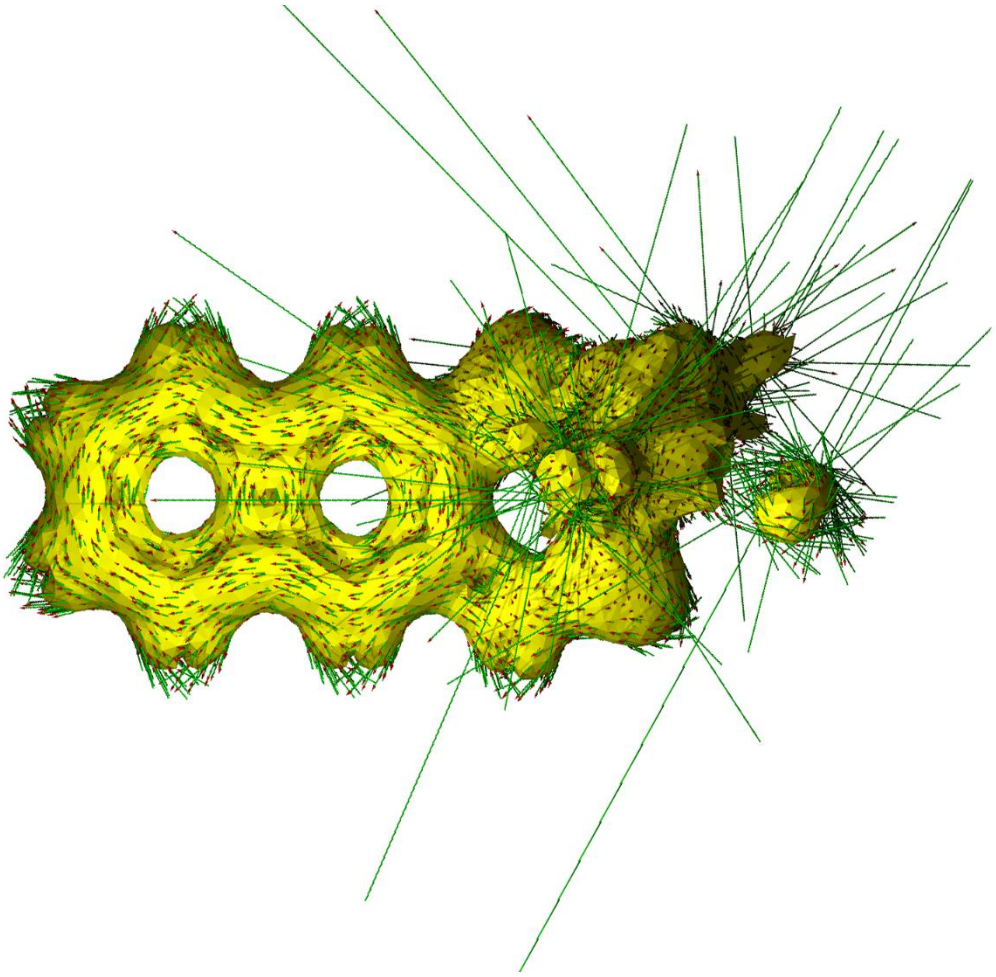

Figure S8. Computed ACID plot of **2** from the total contribution with isosurfacevalue of 0.030 a.u.

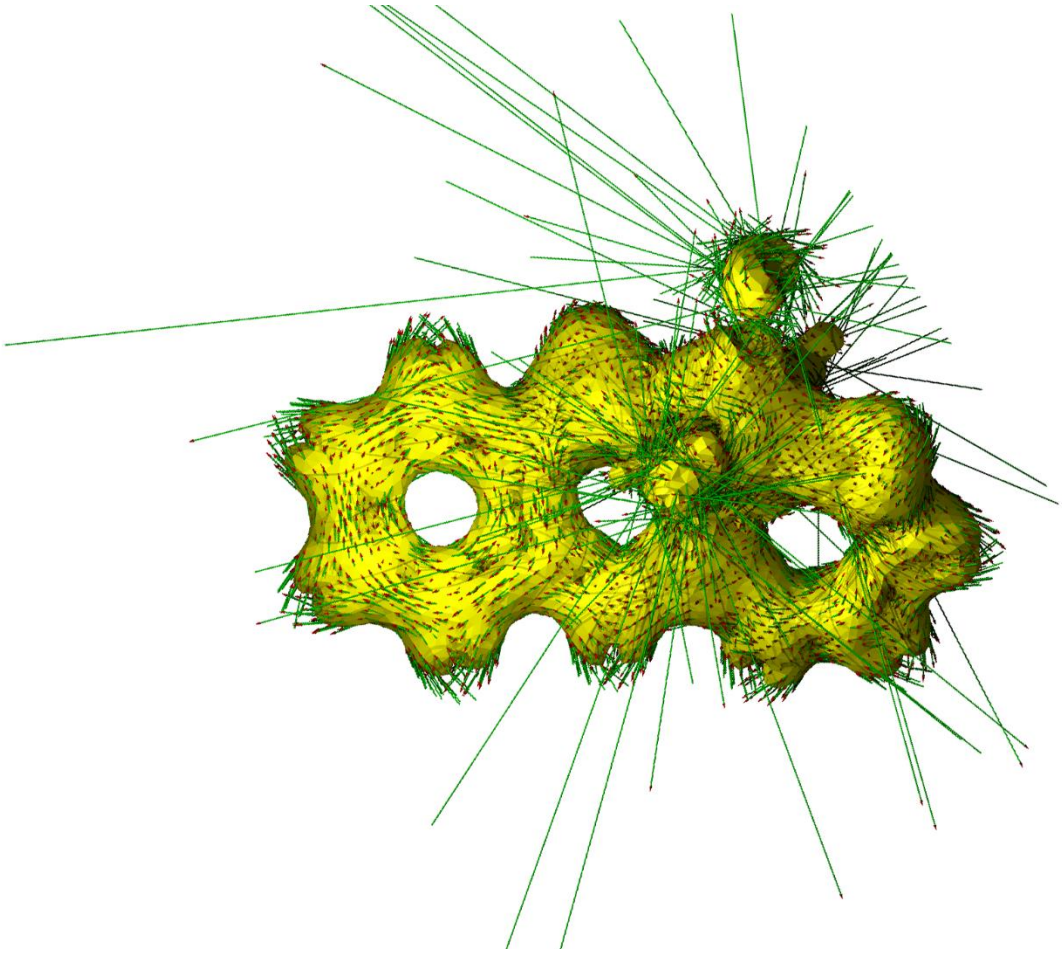

Figure S9. Computed ACID plot of **3** from the total contribution with isosurfacevalue of 0.030 a.u.

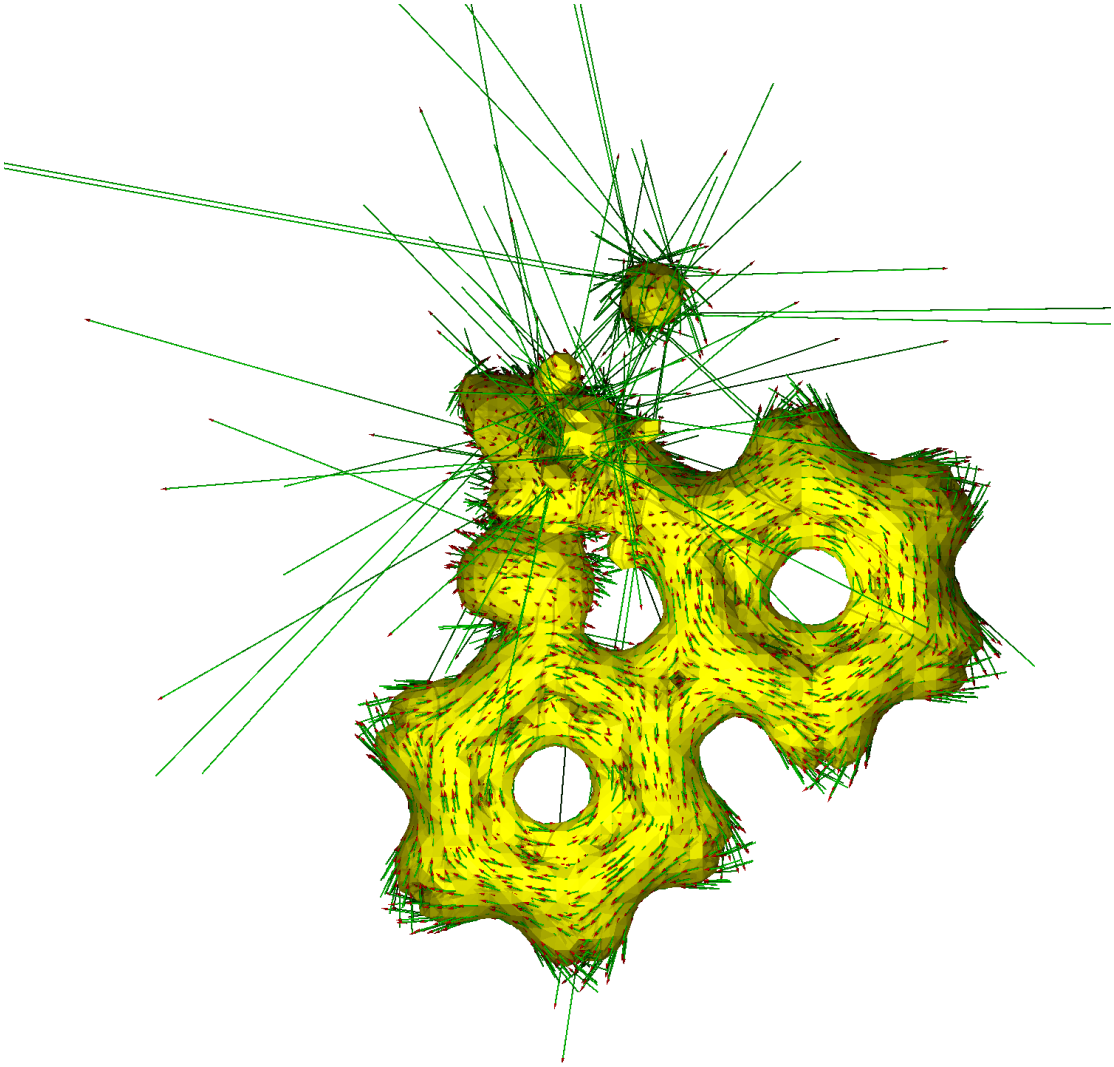

Figure S10. Computed ACID plot of **4** from the total contribution with isosurfacevalue of 0.030 a.u.

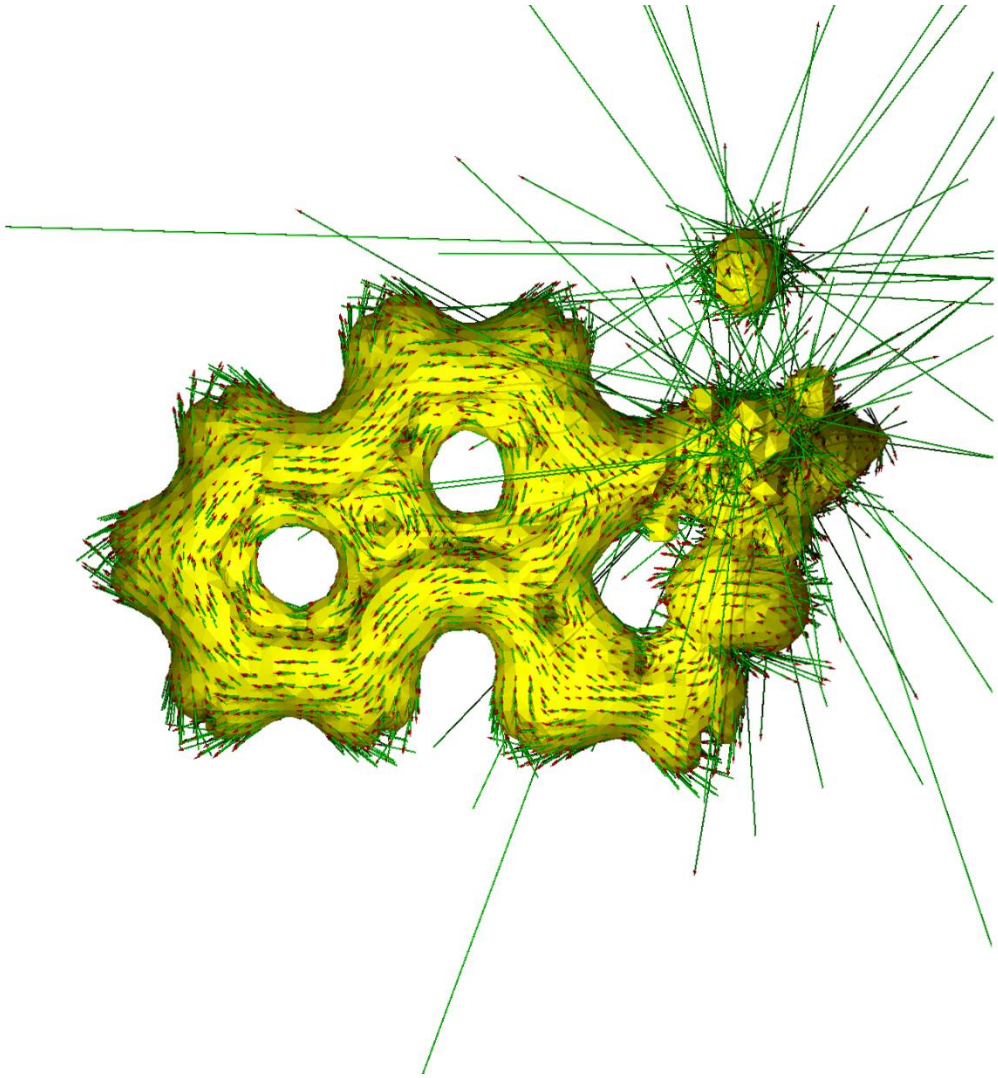

Figure S11. Computed ACID plot of **5** from the total contribution with isosurfacevalue of 0.030 a.u.

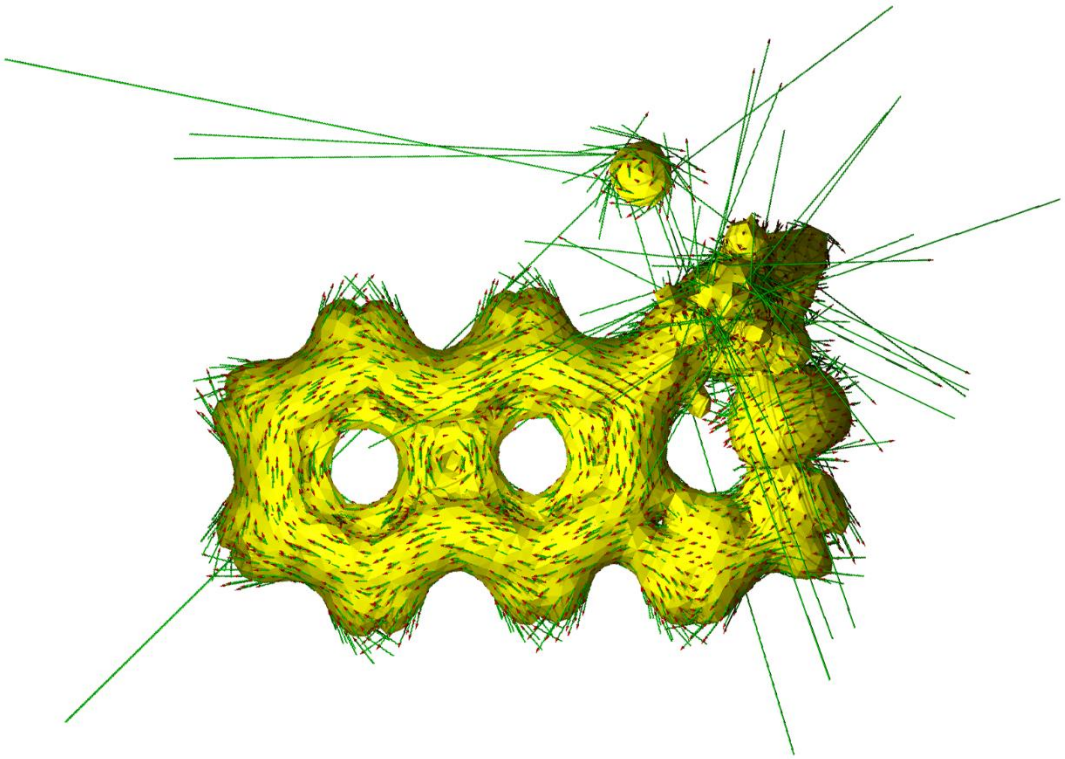

Figure S12. Computed ACID plot of **6** from the total contribution with isosurfacevalue of 0.030 a.u.

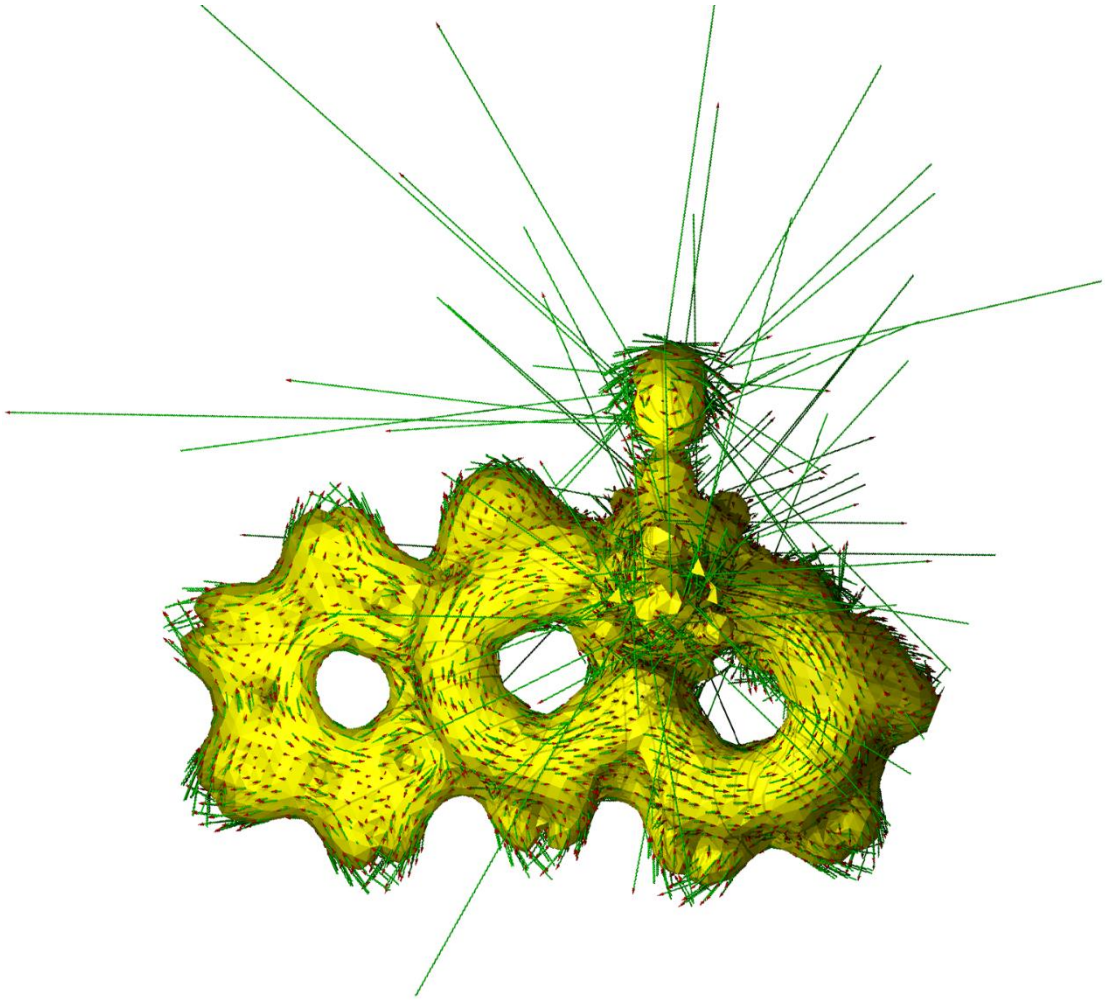

Figure S13. Computed ACID plot of **7** from the total contribution with isosurfacevalue of 0.030 a.u.