

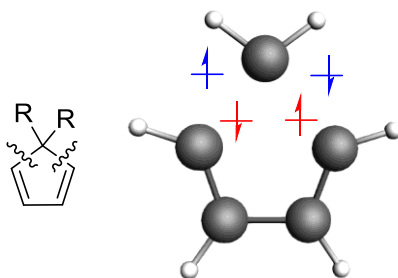
Supporting Information

Probing the Strongest Aromatic Cyclopentadiene Ring by Hyperconjugation

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Table S1. The EDA results for electropositive substituted cyclopentadienes at the TPSS-D3/TZ2P level. Energies are given in kcal mol⁻¹.



	1	3	4	5
Symmetry	C _{2v}	C _{2v}	C _{2v}	C ₂
ΔE_{int}	-293.0	-285.7	-288.0	-269.6
ΔE_{σ}	-236.5	-286.8	-316.7	-523.4
ΔE_{π}	-189.9	-207.2	-218.2	-274.8
ΔE_{meta}	5.6	4.7	2.0	11.6
ΔE_{orb}	-420.8	-489.2	-532.9	-786.6
ΔE_{Pauli}	395.4	514.7	542.8	995.0
ΔE_{elstat}	-266.3	-308.0	-293.5	-466.4
ΔE_{disp}	-1.2	-3.1	-4.5	-11.6

Table S2. The EDA results for the complexes **5** to **11** at the TPSS-D3/TZ2P level. Energies are given in kcal mol⁻¹.

	6	7	8	5	9	10	11
ΔE_{int}	-268.5	-268.7	-269.0	-269.6	-273.1	-272.7	-275.6
ΔE_{π}	-513.6	-519.7	-519.0	-523.4	-801.7	-520.1	-814.6
ΔE_{σ}	-264.2	-268.9	-271.0	-274.8	/	-278.4	/
ΔE_{meta}	11.2	11.2	11.3	11.6	11.7	11.8	11.6
ΔE_{orb}	-766.5	-777.4	-778.7	-786.6	-790.1	-786.6	-803.0
ΔE_{Pauli}	967.6	983.4	982.1	995.0	994.0	988.4	1014.0
ΔE_{elstat}	-458.4	-463.0	-461.2	-466.4	-465.5	-463.1	-475.1
ΔE_{disp}	-11.2	-11.7	-11.2	-11.6	-11.5	-11.4	-11.5

In EDA, bond formation between the interacting fragments can be divided into four terms: electrostatic interactions (ΔE_{elstat}), Pauli repulsive orbital interactions (ΔE_{Pauli}), and attractive orbital interactions (ΔE_{orb}), and dispersion interactions (ΔE_{disp}), the total bonding energy can be described in this equation [Eq. (1)], in which the ΔE_{elstat} and ΔE_{Pauli} can be combined into a steric interaction term, $\Delta E_{\text{steric}} = \Delta E_{\text{Pauli}} + \Delta E_{\text{elstat}}$. The term ΔE_{elstat} corresponds to quasi-classical electrostatic attraction, which is calculated with the frozen geometry of the entire molecule, are superimposed without electronic relaxation. The Pauli repulsion ΔE_{Pauli} refers to the product wave function becomes antisymmetrized and renormalized. The stabilizing orbital interaction ΔE_{orb} represents the molecular orbitals relax to their final form. The orbital interaction energy can be further divided into contributions of orbitals having different symmetry ($\Delta E_{\text{orb}} = \Delta E_{\pi} + \Delta E_{\sigma}$). In addition, the ΔE_{meta} refers the MetaGGA correction in the total orbital interactions. This orbital interaction ΔE_{orb} is crucial for the present study.

$$\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}} + \Delta E_{\text{disp}} \quad (1).$$

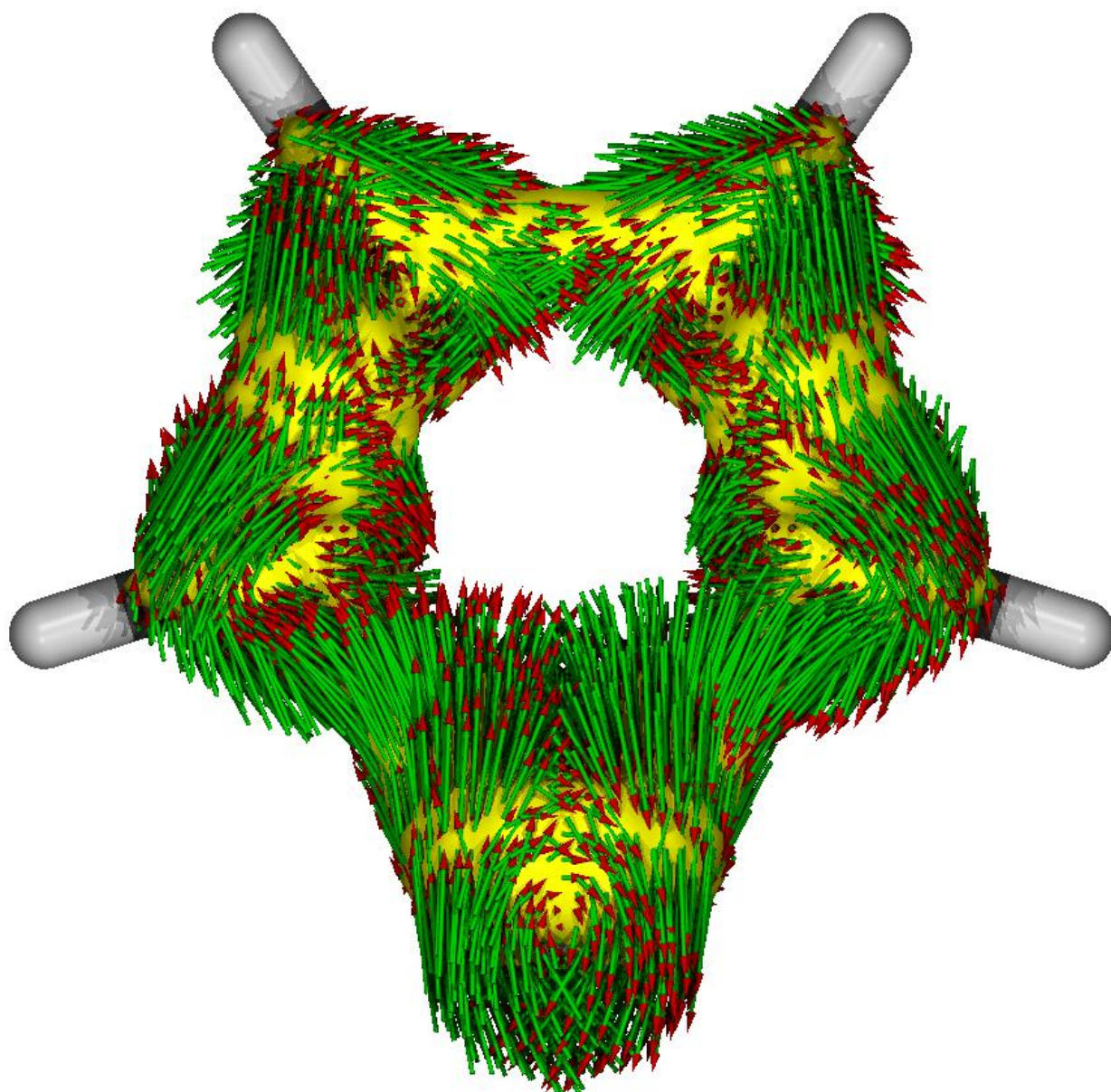


Figure S1. ACID isosurfaces of **1**. Current density vectors are plotted onto the ACID by the π contribution with an isosurface of 0.030 to indicate dia- and paratropic ring currents. The magnetic field vector is orthogonal with respect to the ring plane and points upward (clockwise currents are diatropic).

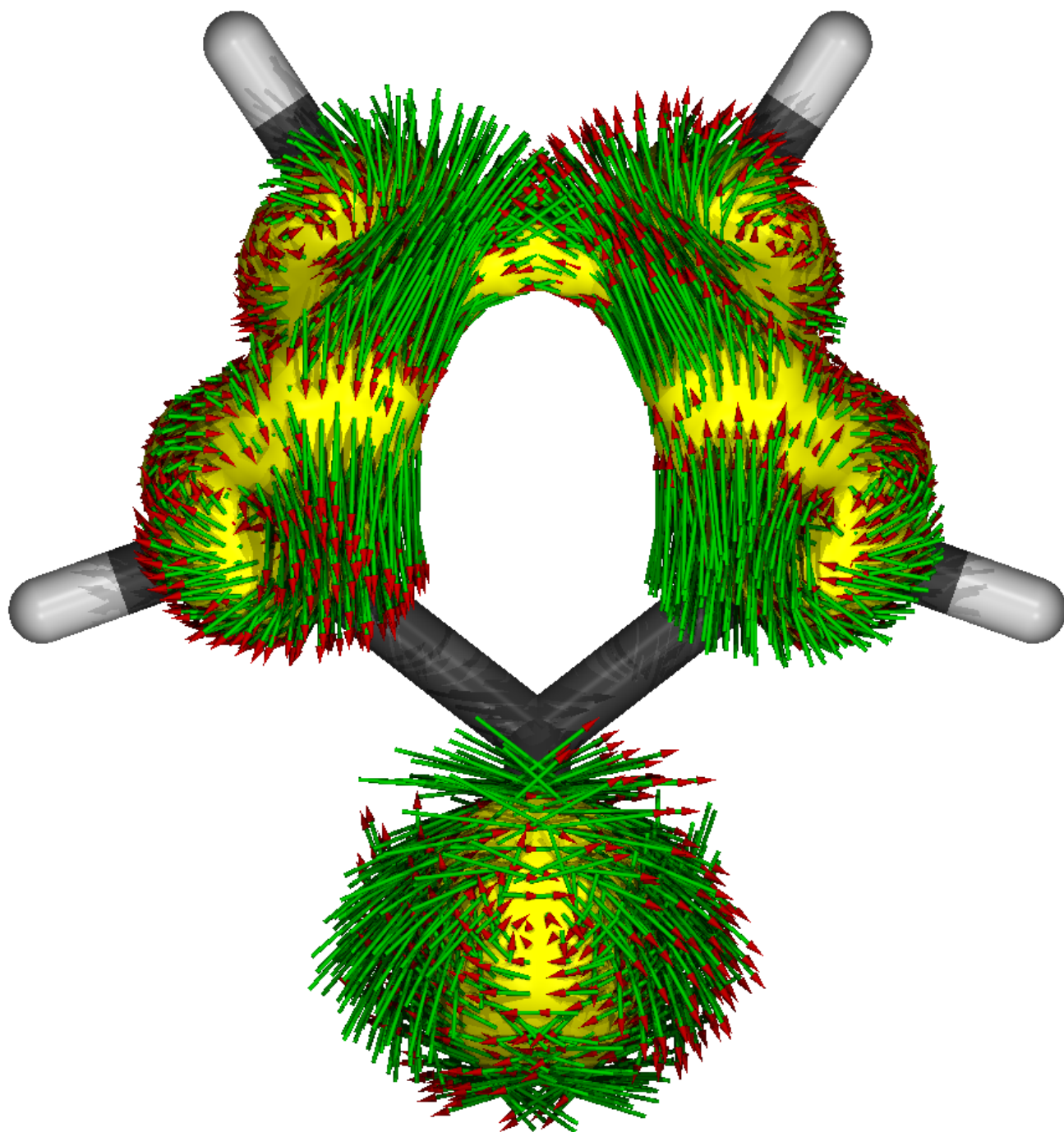


Figure S2. ACID isosurfaces of **2**. Current density vectors are plotted onto the ACID by the π contribution with an isosurface of 0.030 to indicate dia- and paratropic ring currents. The magnetic field vector is orthogonal with respect to the ring plane and points upward (clockwise currents are diatropic).

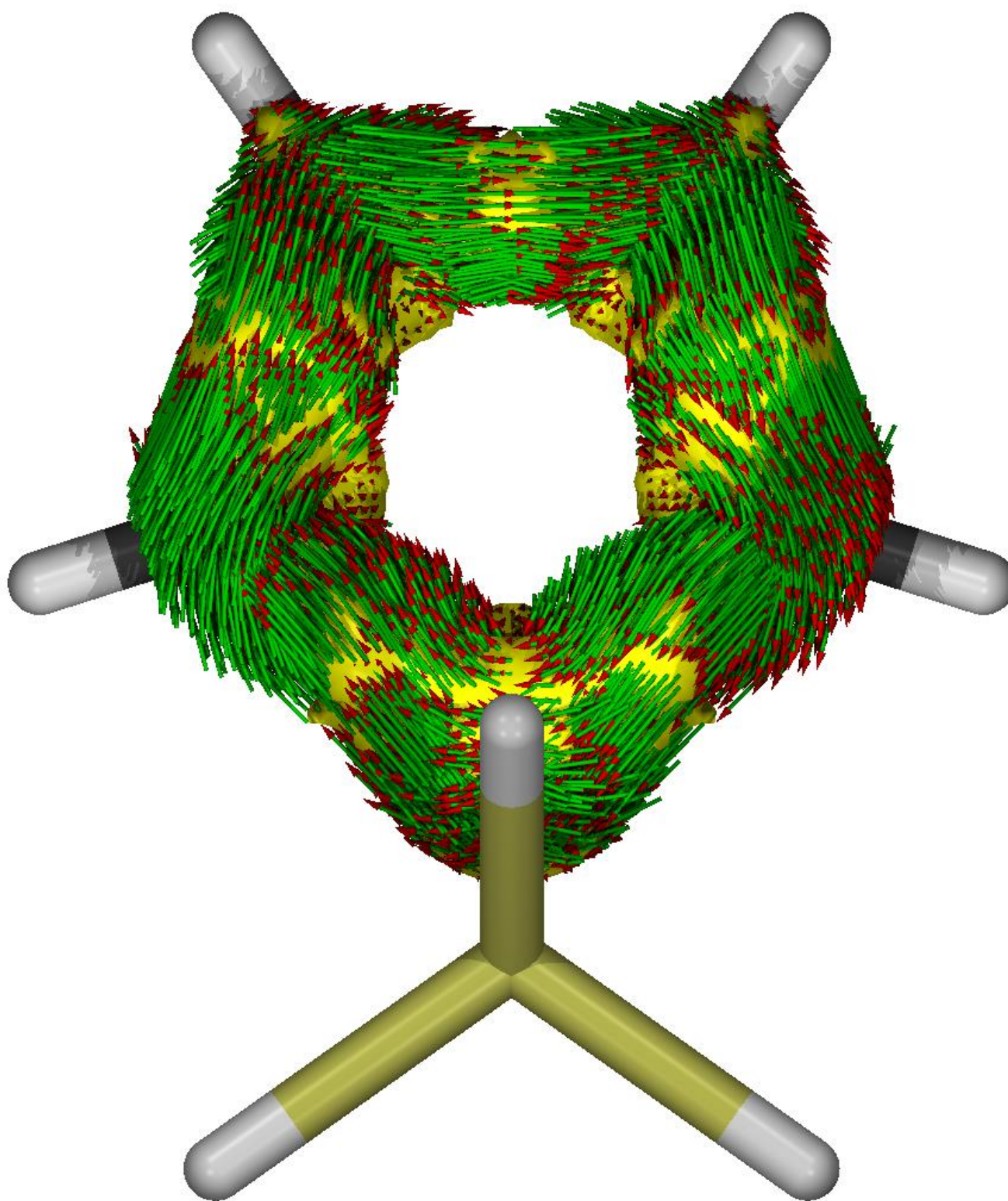


Figure S3. ACID isosurfaces of **3**. Current density vectors are plotted onto the ACID by the π contribution with an isosurface of 0.030 to indicate dia- and paratropic ring currents. The magnetic field vector is orthogonal with respect to the ring plane and points upward (clockwise currents are diatropic).

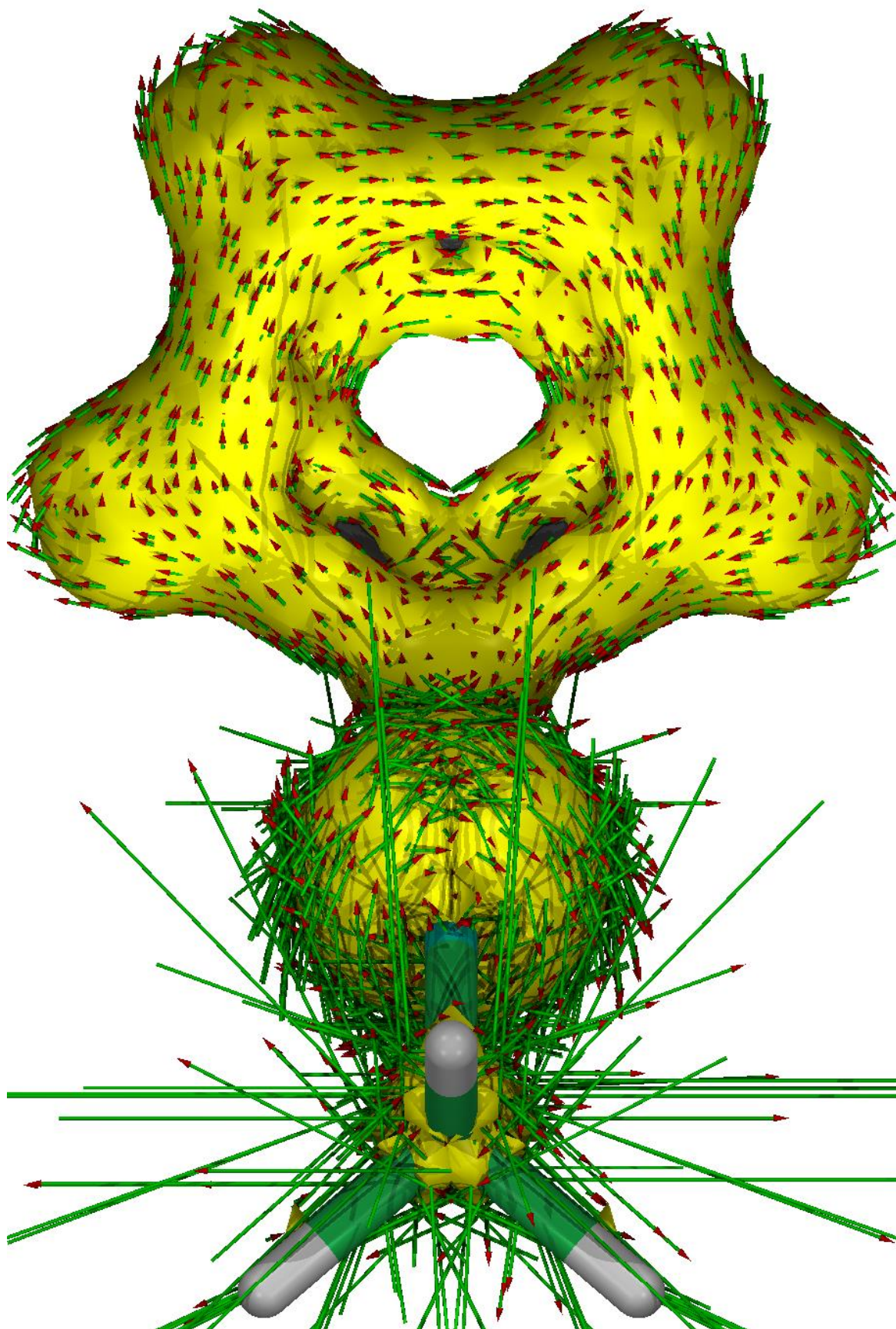


Figure S4. ACID isosurfaces of **4**. Current density vectors are plotted onto the ACID isosurface of 0.030 to indicate dia- and paratropic ring currents. The magnetic field vector is orthogonal with respect to the ring plane and points upward (clockwise currents are

diatropic).

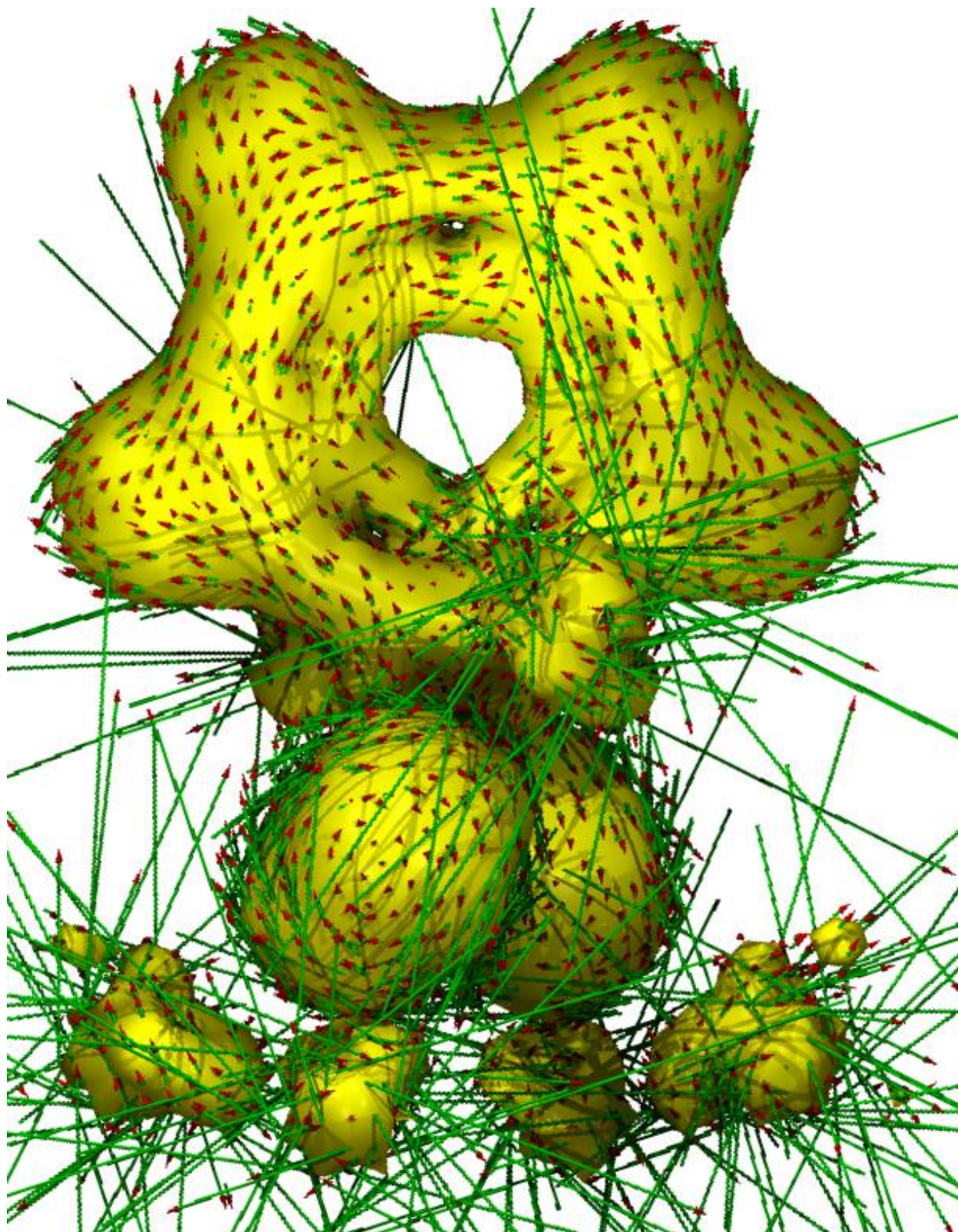


Figure S5. ACID isosurfaces of **5**. Current density vectors are plotted onto the ACID isosurface of 0.030 to indicate dia- and paratropic ring currents. The magnetic field vector is orthogonal with respect to the ring plane and points upward (clockwise currents are diatropic).

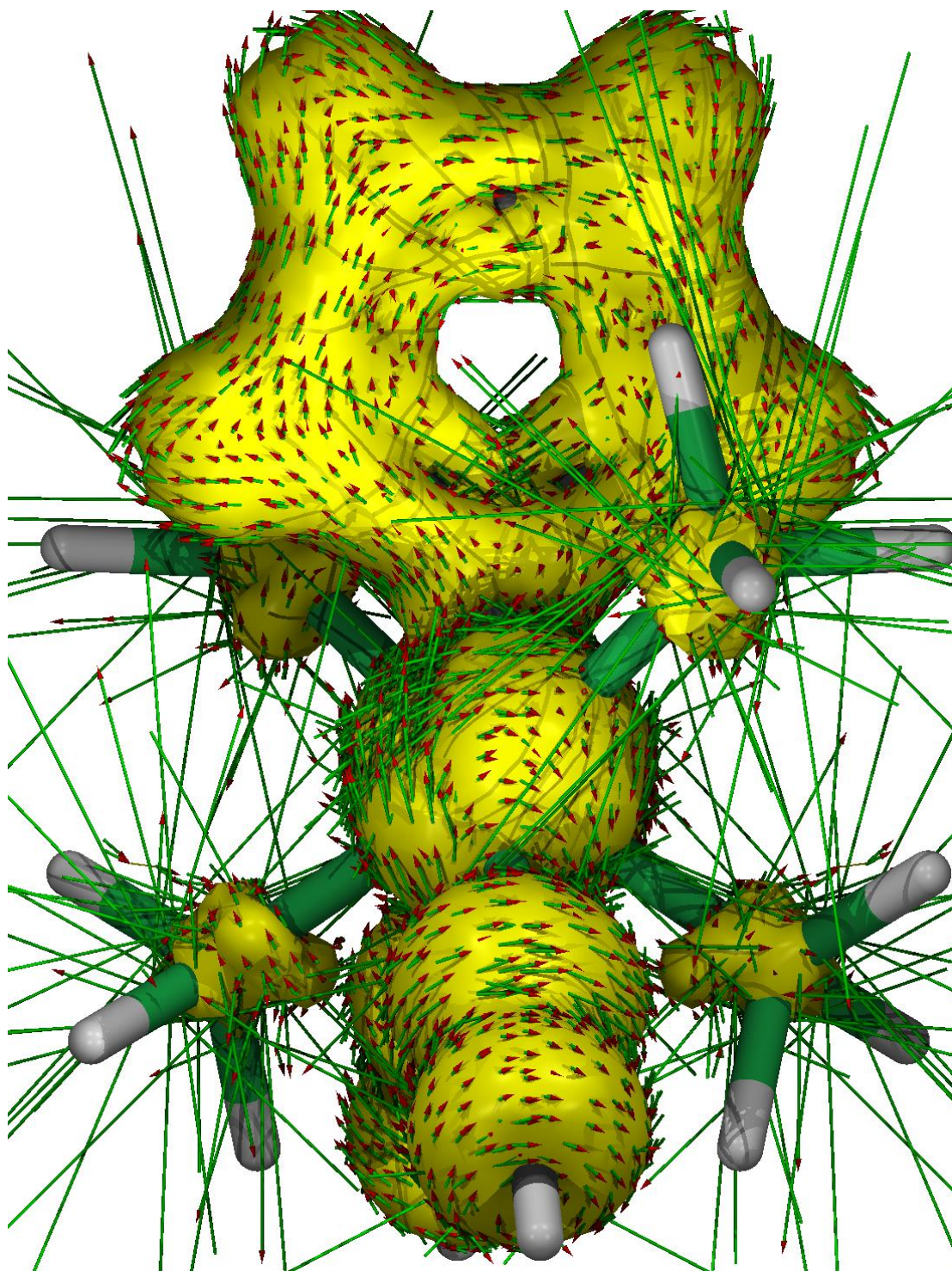


Figure S6. ACID isosurfaces of **6**. Current density vectors are plotted onto the ACID isosurface of 0.030 to indicate dia- and paratropic ring currents. The magnetic field vector is orthogonal with respect to the ring plane and points upward (clockwise currents are diatropic).

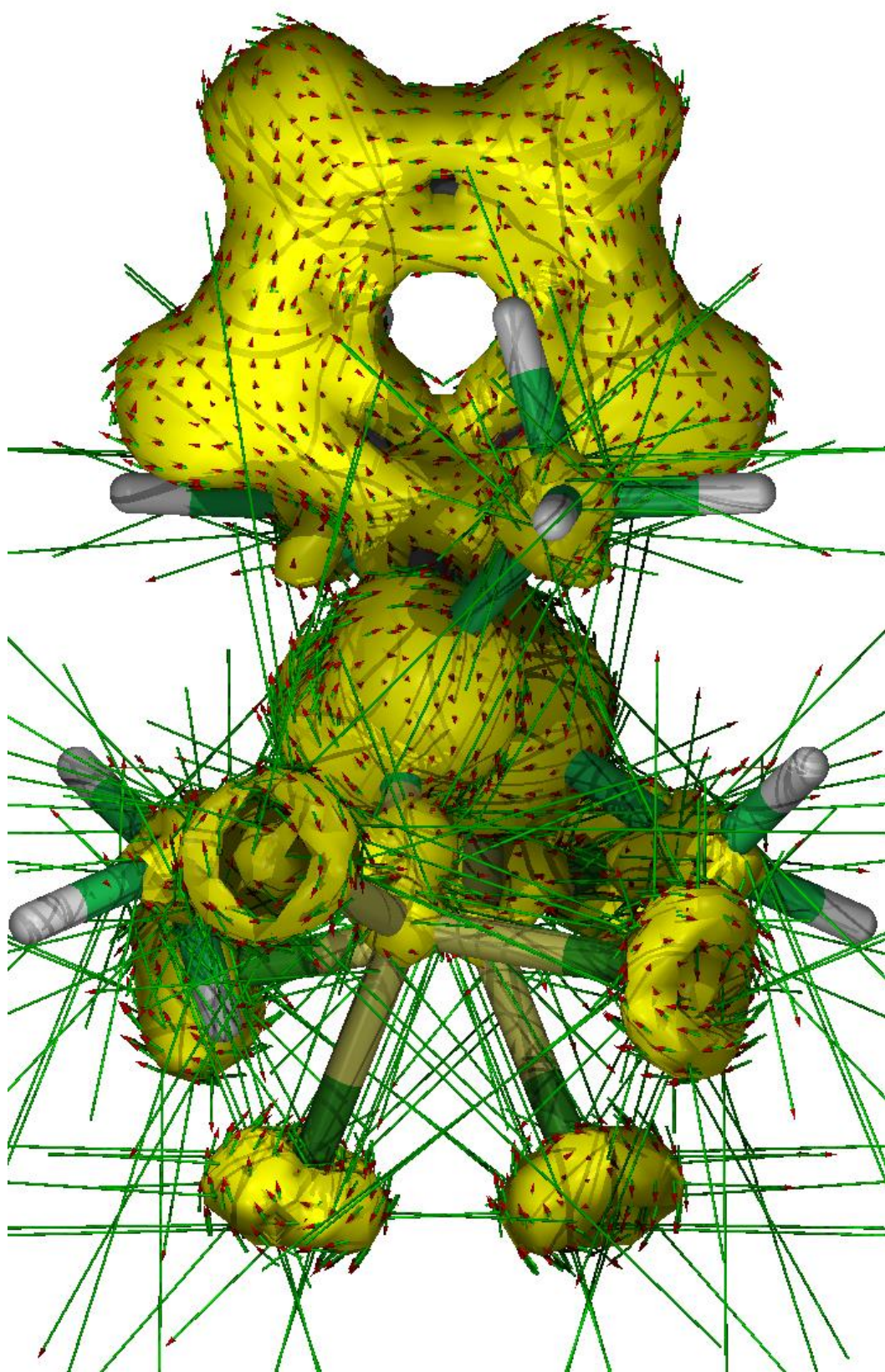


Figure S7. ACID isosurfaces of **7**. Current density vectors are plotted onto the ACID isosurface of 0.030 to indicate dia- and paratropic ring currents. The magnetic field vector is orthogonal with respect to the ring plane and points upward (clockwise currents are diatropic).

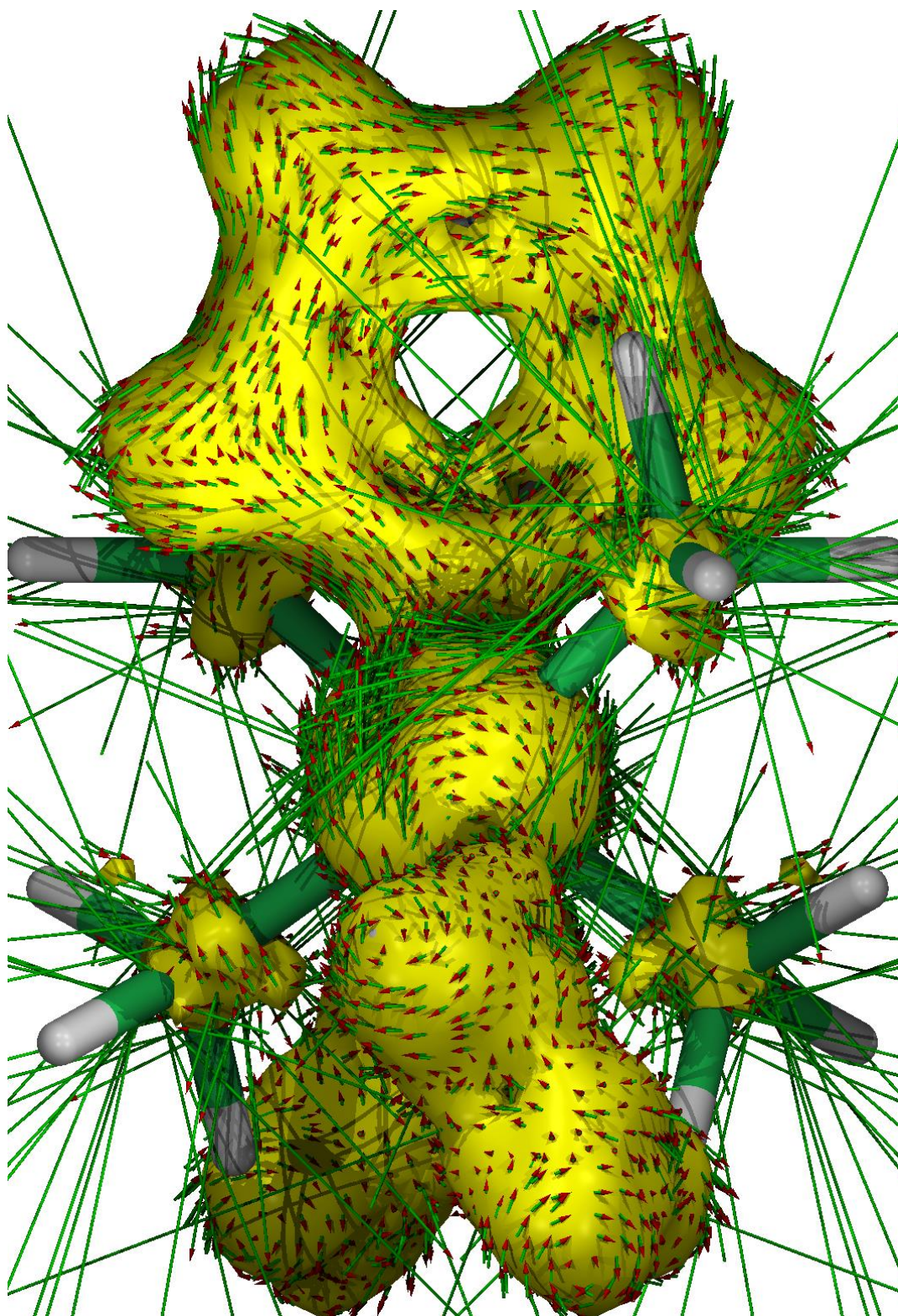


Figure S8. ACID isosurfaces of **8**. Current density vectors are plotted onto the ACID isosurface of 0.030 to indicate dia- and paratropic ring currents. The magnetic field vector is orthogonal with respect to the ring plane and points upward (clockwise currents are diatropic).

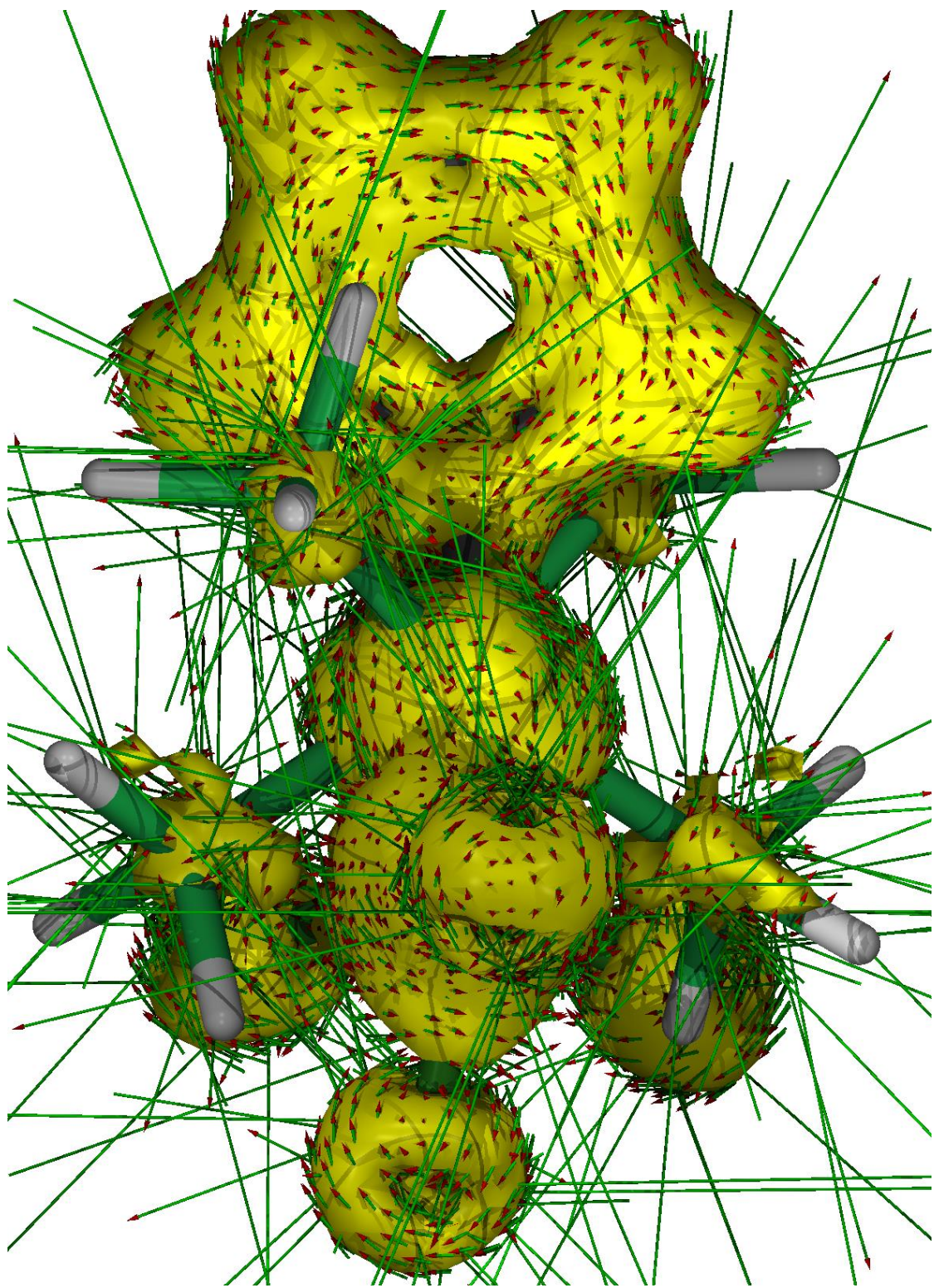


Figure S9. ACID isosurfaces of **9**. Current density vectors are plotted onto the ACID isosurface of 0.030 to indicate dia- and paratropic ring currents. The magnetic field vector is orthogonal with respect to the ring plane and points upward (clockwise currents are diatropic).

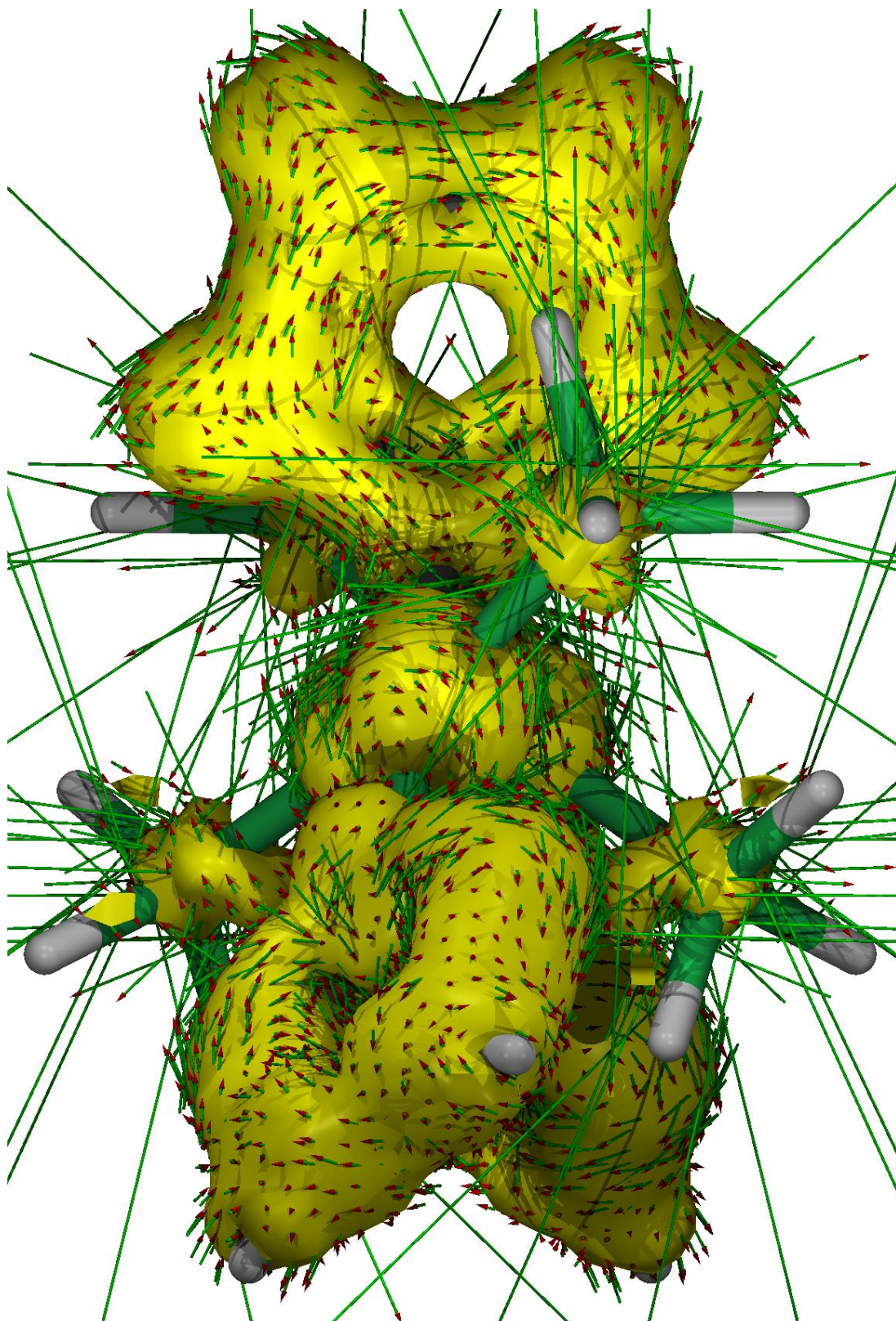


Figure S10. ACID isosurfaces of **10**. Current density vectors are plotted onto the ACID isosurface of 0.030 to indicate dia- and paratropic ring currents. The magnetic field vector is orthogonal with respect to the ring plane and points upward (clockwise currents are diatropic).

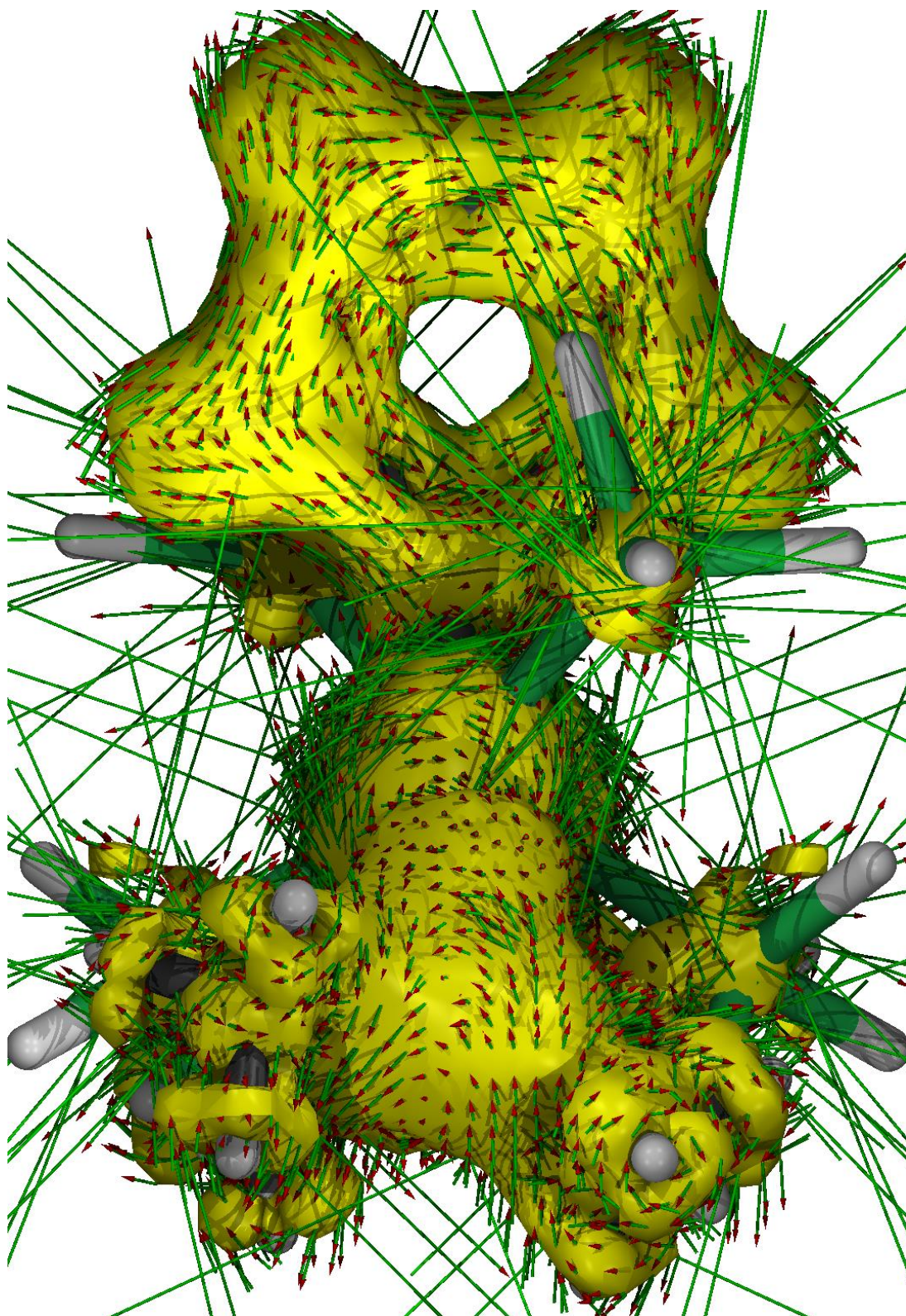


Figure S11. ACID isosurfaces of **11**. Current density vectors are plotted onto the ACID isosurface of 0.030 to indicate dia- and paratropic ring currents. The magnetic field vector is orthogonal with respect to the ring plane and points upward (clockwise currents are diatropic).

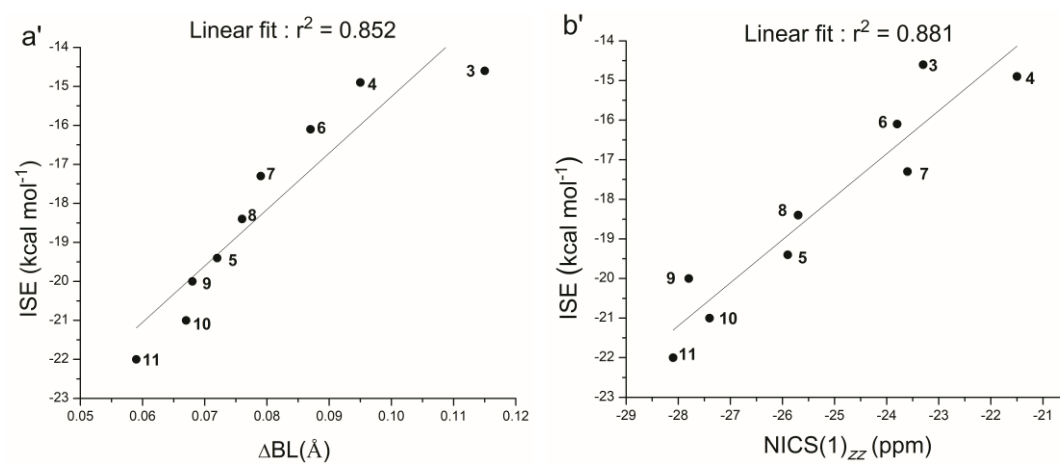
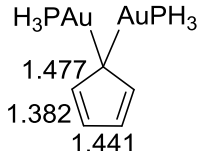


Figure S12. Correlation between the ISE values against ΔBL (a') or NICS values (b') for the substituted cyclopentadienes without **1** and **2**.

PH_3

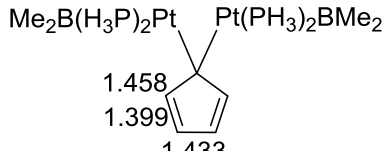


4

ΔBL 0.095

ISE -14.9

NICS(1)_{zz} -21.5



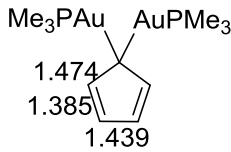
11

0.059

-22.0

-28.1

PMe_3

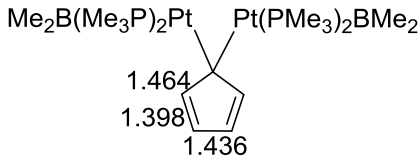


4'

ΔBL 0.089

ISE -16.0

NICS(1)_{zz} -22.8



11'

0.066

-23.1

-30.4

Figure S13. The C-C bond lengths (Å), ΔBL values (Å), ISE values (kcal mol⁻¹) and NICS values (ppm) of substituted cyclopentadienes **4**, **4'**, **11** and **11'**.

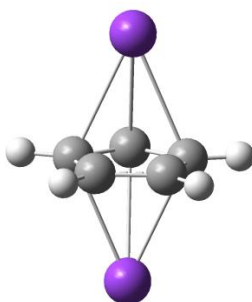


Figure S14. Optimizing the geometry of complex **12** (potassium substituted cyclopentadiene) leads to a η^5 copper complex (Similar Cp complexes have been previously reported). So in our paper, we didn't consider the other main group metal like potassium.