Electronic Supplementary Information for

Theoretical Studies on the Photophysical Properties of Luminescent Pincer Type Gold(III) Arylacetylide Complexes: The Role of $\pi$-Conjugation at the Tridentate C-deprotonated Cyclometalated [C$^\text{N}$$^\text{C}$] Ligand.

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Experimental Section.

Synthesis and characterization of complex 3-endo. Complex 3-endo was synthesized according to Scheme S1. It followed the same procedure as reported in our previous paper.\textsuperscript{[1]} Except that in the procedure of (e), the mercurated product was isolated by column chromatography on SiO$_2$ using hexane: CH$_2$Cl$_2$ = 2:1 ($R_f$ = 0.40) as the eluent. The final product was isolated as yellow powder. Yield: 54 mg (81.7%). X-ray crystal structure has been determined.\textsuperscript{[2]}
Scheme S1. Synthetic scheme for complex 3-endo. (a) n-bromohexane, KOrBu, THF, reflux. (b) AlCl₃, acetic anhydride, CS₂, 40°C. (c) 3,5-di-tert-butylbenzaldehyde, NaOH, MeOH, 60°C. (d) 1-(2-oxo-2-phenylethyl)pyridinium iodide, NH₄OAc, acetic acid, methanol, reflux. (e) Hg(OAc)₂, ethanol, reflux 48 hrs; LiCl, reflux 2 hrs. (f) KAuCl₄, acetonitrile, reflux 48 hrs. (g) Cul, 1-ethynyl-4-methoxybenzene, CH₂Cl₂/NEt₃, under N₂ stir 3h.

3-endo: MS (+FAB) m/z (%): 1002.8 (100) [M⁺], 868.6 (26), 784.5 (21). ¹H NMR (400 MHz, [d₆]DMSO): δ 8.25 (d, 1H, J = 8.21 Hz, H₄), 8.21 (s, 1H, H₅), 8.20 (d, 1H, J = 8.01 Hz, H₆), 8.14 (d, 1H, J = 8.10 Hz, H₇), 8.13 (s, 1H, H₈), 7.82–7.84 (m, 2H, H¹⁰ and H¹¹), 7.76 (s, 2H, H⁶ and H⁶'), 7.60 (s, 1H, H⁷), 7.51 (d, 2H, J = 8.68 Hz, H¹⁵), 7.47 (t, 1H, J = 7.88 Hz, H³), 7.39–7.41 (m, 1H, H¹⁴), 7.37 (t, 1H, J = 8.20 Hz, H²), 7.30–7.33 (m, 2H, H¹² and H¹³), 7.01 (d, 2H, J = 8.74 Hz, H¹⁶), 3.80 (s, 3H), 3.49–3.51 (m, 2H), 1.91–1.95 (m, 2H), 1.40 (s, 18H), 0.96–0.99 (m, 12H), 0.62 (t, 6H, J = 6.47 Hz), 0.42–0.47 (m, 4H). Calcd for C₅₉H₆₆AuNO: C, 70.71; H, 6.64; N, 1.40; found: C, 70.31; H, 6.51; N, 1.45.
### Table S1. Crystal data of 3-endo

| Complex | 3-endo |
|---------|--------|
| Empirical formula | C_{65}H_{80}AuNO |
| Formula weight | 1088.26 |
| Temperature/K | 100 |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 11.6132(9) |
| b/Å | 14.7425(11) |
| c/Å | 16.9669(13) |
| α/° | 87.393(3) |
| β/° | 71.112(3) |
| γ/° | 80.062(3) |
| Volume/Å³ | 2707.0(4) |
| Z | 2 |
| ρ calc/g/cm³ | 1.335 |
| μ/mm⁻¹ | 5.414 |
| F(000) | 1128 |
| Crystal size/mm³ | 0.06 × 0.06 × 0.02 |
| Radiation | CuKα (λ = 1.54178) |
| 2θ range for data collection/° | 5.506 to 133.47 |
| Index ranges | -13 ≤ h ≤ 13, -10 ≤ k ≤ 17, -19 ≤ l ≤ 20 |
| Reflections collected | 86638 |
| Independent reflections | 9371 [R_{int} = 0.0774, R_{eins} = 0.0428] |
| Data/restraints/parameters | 9371/70/650 |
| Goodness-of-fit on F^2 | 1.046 |
| Final R indexes [I>2σ(I)] | R_f = 0.0398, wR^2 = 0.1010 |
| Final R indexes [all data] | R_f = 0.0423, wR^2 = 0.1043 |
| Largest diff. peak/hole / e Å⁻³ | 1.58/-2.79 |
Figure S1. ORTEP diagram of 3-endo with atomic numbering. All hydrogen atoms and solvent molecules are omitted for clarity. Thermal ellipsoids are drawn at 50 % probability level.

Table S2. Selected bond lengths and angles of 3-endo

| Bond lengths (Å) | Bond angles (deg) |
|------------------|-------------------|
| Au1-C1           | 2.063(6)          |
| Au1-C30          | 2.130(5)          |
| Au1-C31          | 1.947(5)          |
| Au1-N1           | 1.987(3)          |
| C31-C32          | 1.221(6)          |
| C32-C33          | 1.443(6)          |
| C1-Au1-N1        | 81.1(2)           |
| C30-Au1-N1       | 80.9(1)           |
| C30-Au1-C1       | 162.0(2)          |
| C31-Au1-N1       | 172.8(2)          |
| Au1-C31-C32      | 174.2(4)          |
| C31-C32-C33      | 174.0(5)          |
Table S3. Photophysical data of complex 3-endo.

| Complex | Medium [Temp]       | UV/Vis absorption $\lambda_{\text{max}}$ [nm] ($\epsilon$ [mol$^{-1}$dm$^3$ cm$^{-1}$]) | Emission |
|---------|---------------------|-------------------------------------------------------------------------------------------------|----------|
|         |                     | $\lambda_{\text{max}}$ [nm]                                                                 | $\tau$ [μs] | $\phi_{\text{em}}$ |
| 3-endo  | DCM (298 K)         | 270 (56500), 305 (38500), 323 (42100), 337 (39700), 387 (8670), 409 (12100), 430 (12200)    | 536, 574 | 14.5 | 0.02 |
|         | EtOH : MeOH = 4 : 1 (77 K) | -                                                                                           | 530, 576, 614 (sh) | 406.5 | - |

Figure S2. Electronic absorption spectrum of 3-endo in dichloromethane (DCM) at room temperature at $2 \times 10^{-5}$ mol dm$^{-3}$. 
Figure S3. Emission spectra of 3-endo in dichloromethane (DCM) at room temperature (top) and in a glassy medium at 77K (bottom); $\lambda_{exc} = 430$ nm.
Computational Details.

In this work, the hybrid density functional, PBE0,[3] was employed for all calculations using the program package G09.[4] The 6-31G* basis set[5] is used for all atoms except Au, which is described by the Stuttgart relativistic pseudopotential and its accompanying basis set (ECP60MWB).[6] Solvent effect was also included by means of the polarizable continuum model (PCM).[7] Geometry optimizations of the singlet ground state (S₀) and the lowest triplet excited state (T₁) were respectively carried out using restricted and unrestricted density functional theory (i.e. RDFT and UDFT) formalism without symmetry constraints. Frequency calculations were performed on the optimized structures to ensure that they are minimum energy structures by the absence of imaginary frequency (i.e. NImag = 0). Stability calculations were also performed for all the optimized structures to ensure that all the wavefunctions obtained are stable.

(a) **SS-PCM energy calculations.** Vertical transition energies were computed using the linear response approximation for optical absorption calculations, but the state specific approach for emissions. [8] In an absorption process, the solvent is in equilibrium solvation with the ground state electron density but non-equilibrium solvation with the excited state electron density. Thus, LR-TDDFT should give reasonable estimate of the absorption energies. However, as mentioned in the main text, SS-TDDFT is more adequate for calculations involving an emission process.

Within the state-specific (SS) approach, the equilibrium solvation of the T₁ excited state at its equilibrium geometry is written out via “NonEq=write”:

```
%oldchk=cncauccphome_pbe0_t1.chk          chk file of optimized T₁ that is confirmed to be stable
%chk=cncauccphome_pbe0_t1ss.chk
#p pbe1pbe/chkbas geom=check guess=read scrf=(solvent=dichloromethane,read)
nosymm pop=full

Save solvent reaction field in equilibrium with T₁ density at its optimized geometry to the checkpoint file, cncauccphome_pbe0_t1ss.chk

0 3
NonEq=write
```

The ground state and the singlet excited state energy could then be computed with non-equilibrium solvation using “NonEq = read”; for example, for the singlet excited state energy calculation,

```
%oldchk=cncauccphome_pbe0_t1ss.chk
%chk=cncauccphome_pbe0_td-t1ss.chk
#p rpbe1pbe/chkbas geom=check guess=read td=(singlets,nstates=3,root=1) scrf=(solvent=dichloromethane,read,externaliteration) nosymm pop=full

S₁ energy and density with non-eqm solvation, i.e. fast polarization is solved self-consistently in a state-specific way for S₁ and the slow polarization is frozen at that in eqm with T₁ density
```
The energy that should be extracted would appear near the end of the output file:

After PCM corrections, the energy is $-1265.80793189$ a.u.

That is, this is the $S_1$ energy at the $T_1$ optimized geometry, with non-equilibrium solvation done in an SS approach.

Similarly, for the ground state energy calculation with non-equilibrium solvation at the $T_1$ excited state geometry,

And the energy of the ground state from a non-equilibrium solvation in solution is:

SCF Done: $E(RPBE1PBE) = -1265.92332980$ A.U. after 13 cycles

(b) **Radiative decay rate calculations.** The spin wavefunctions of the triplet sub-states $T_1^\alpha$ are expressed along the three Cartesian coordinates, $x$, $y$, and $z$ as:

$$
\sigma_{T}^x = \frac{1}{\sqrt{2}} (\beta \beta - \alpha \alpha) \\
\sigma_{T}^y = \frac{i}{\sqrt{2}} (\beta \beta + \alpha \alpha) \\
\sigma_{T}^z = \frac{1}{\sqrt{2}} (\alpha \beta + \beta \alpha)
$$

and the singlet spin wavefunction as:

$$
\sigma_{S} = \frac{1}{\sqrt{2}} (\alpha \beta - \beta \alpha)
$$
Table S4. SOC matrix elements between the $^3(d_{x^2\pi^*})$ and $^1(d_{y^2\pi^*})$ states; $\langle S_m|H_{SOC}|T_1\rangle$

| $\langle S_m|H_{SOC}|T_1\rangle$ | $^3(d_{x^2\pi^*})$ | $^3(d_{y^2\pi^*})$ | $^3(d_{x\pi^*})$ | $^3(d_{y\pi^*})$ | $^3(d_{x\pi^*})$ |
|------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $^1(d_{x^2\pi^*})$     | 0               | 0               | 0               | $-\frac{i\sqrt{3}}{2} \xi_{x^2\pi^*} c_{YZ}$ | $-\frac{i\sqrt{3}}{2} \xi_{x^2\pi^*} c_{YZ}$ |
| $^1(d_{y^2\pi^*})$     | 0               | 0               | $i \xi_{x^2\pi^*} c_{YZ} y_z$ | $-\frac{i}{2} \xi_{x^2\pi^*} c_{YZ} x_z$ | $-\frac{i}{2} \xi_{x^2\pi^*} c_{YZ} y_z$ |
| $^1(d_{x\pi^*})$      | 0               | $-\frac{i}{2} \xi_{x^2\pi^*} c_{YZ} y_z$ | 0               | $\frac{i}{2} \xi_{x^2\pi^*} c_{YZ} x_z$ | $-\frac{i}{2} \xi_{x^2\pi^*} c_{YZ} y_z$ |
| $^1(d_{y\pi^*})$      | $-\frac{i\sqrt{3}}{2} \xi_{x^2\pi^*} c_{YZ} y_z$ | $\frac{i}{2} \xi_{x^2\pi^*} c_{YZ} x_z$ | $-\frac{i}{2} \xi_{x^2\pi^*} c_{YZ} x_z$ | 0               | $\frac{i}{2} \xi_{x^2\pi^*} c_{YZ} y_z$ |

Phosphorescence, being a spin-forbidden process, borrows its emission intensity by first-order perturbative interactions with the singlet excited states via spin-orbit coupling (SOC). Therefore, the singlet excited state energies should also be evaluated at non-equilibrium solvation with the emitting triplet excited state electronic density. Therefore, in principle, the SS approach is more appropriate than the LR approach for calculating the energy difference between the singlet and triplet excited states in eq.(9) of the main text. If the singlet excited state energies are computed within the LR-TDDFT, the singlet excited state energies are obtained either through non-equilibrium solvation with ground state electronic density or equilibrium solvation with the singlet excited state of interest (by specifying the “root” in the LR-TDDFT calculation). In either case, the energies obtained are not the solvent response to the emitting triplet excited state electronic density.

To calculate the radiative decay rate constant using the SS-TDDFT results, the metal coefficients ($c_m$), the CI coefficients ($a_i$), and the transition dipole moments ($M_{cm}$, $M_{cm}$, $M_{cm}$) of each singlet excited state ($S_m$) of interest, could be extracted from the output files of the SS-TDDFT calculations at the $T_1$ optimized geometry at the last step of the iterative procedure for each $S_m$ excited state considered. For the singlet-triplet energy gap, $(E(S_m) - E(T_1))$, it should be emphasized that this is not the energy difference for the transitions, $S_m \rightarrow S_0$ and $T_1 \rightarrow S_0$, from TDDFT calculations (i.e., the section where the CI coefficients are extracted), but those with PCM corrections added, i.e., the energies mentioned in the previous section (“After PCM corrections…”).

In addition, the singlet excited state energies may shift, depending on the electron density of the emitting $T_1$ state. This is particularly important if there is a large difference in dipole moments between the emitting $T_1$ and $S_m$ excited states in a polar medium. This means that one has to do a SS-TDDFT calculation for each singlet excited state $S_m$. For example, if one wants to include the first ten singlet excited states in estimating the radiative decay rate constant through eq. (9), then one has to do a SS-TDDFT calculation for each singlet excited state, i.e. a total of ten SS-TDDFT jobs (with root = 1, 2, …, 10 in the “NonEq=read” step). This could be quite a lengthy task; hence, for simplicity, only the closest-lying singlet excited state(s) that could have effective SOC perturbative interactions with the singlet excited states via spin-orbit coupling (SOC). Therefore, in principle, the SS approach is more appropriate than the LR approach for calculating the energy difference between the singlet and triplet excited states in eq.(9) of the main text. If the singlet excited state energies are computed within the LR-TDDFT, the singlet excited state energies are obtained either through non-equilibrium solvation with ground state electronic density or equilibrium solvation with the singlet excited state of interest (by specifying the “root” in the LR-TDDFT calculation). In either case, the energies obtained are not the solvent response to the emitting triplet excited state electronic density.

The SOC matrix elements are listed in Table S4.
\[
\begin{array}{cccc}
1(d_{yz}^\pi) & \frac{\sqrt{3}}{2} \sigma_y^2 \sigma_z^2 & \frac{\sqrt{3}}{2} \sigma_y^2 \sigma_z^2 & \frac{\sqrt{3}}{2} \sigma_y^2 \sigma_z^2 & \frac{\sqrt{3}}{2} \sigma_y^2 \sigma_z^2 & 0 \\
\end{array}
\]

**x-component: magenta**

**y-component: brown**

**z-component: green**

(c) **Non-radiative decay rates.** To calculate the Huang-Rhys factor, \( S_j \), and to simulate the emission spectrum for \( (\tilde{\nu})_{fc} \), a Franck-Condon calculation is done using the keyword “freq=fc”. One could request the printing of the “shift vector” (which relates to \( [\tilde{\mu}]_j \Delta Q_j \)) for the computation of \( S_j \). For a more detailed theoretical background for the Franck-Condon calculation implemented in the G09 program, please consult the references cited in G09 and its document titled “Vibrationally-resolved electronic spectra in Gaussian 09”.

Following our previous work,\[^9\] we have grouped the normal modes into 5 sets:

\[ \omega_{\text{lf1}} \leq 200 \text{ cm}^{-1}, 200 < \omega_{\text{lf2}} \leq 1000 \text{ cm}^{-1}, 1000 < \omega_m \leq 1800 \text{ cm}^{-1}, \omega_{\text{C=C}} \text{, and } \omega_{\text{hf}} \geq 3000 \text{ cm}^{-1} \]

For the non-radiative decay rate calculations, \( k_B T \) is assumed to be \(~200 \text{ cm}^{-1} \).

For \(^3\text{IL} \rightarrow S_0 \) transition, the single-mode expression (eq.(11) of the main text) is used; however, for \(^3\text{LLCT} \rightarrow S_0 \) transition, as both aromatic CC/CN stretching and C=C stretching normal modes could act as effective accepting modes, the two-mode expression is used instead:\[^{10}\]

\[
k_{nr}(T_1 \rightarrow S_0) = \frac{2\pi(\frac{T_1}{H_{SOC}} | S_0 \rangle | S_0 \rangle^2}{\hbar} \exp\left(-S_C - S_M \coth\left(\frac{\hbar \omega_M}{2k_B T}\right)\right) \times \sum_{n_C} \sum_{n_M} \exp\left(-\frac{(\Delta E - n_M \hbar \omega_M - n_C \hbar \omega_C - \lambda_s)^2}{4\lambda_s k_B T}\right) \\
\quad \times \frac{S_C^{n_C}}{n_C!} \exp\left(\frac{n_M \hbar \omega_M}{2k_B T}\right) I_n\left(\frac{\hbar \omega_M}{2k_B T}\right) I_{nM}\left(\frac{\hbar \omega_M}{2k_B T}\right) \right]
\]

Here, \( S_C \) and \( n_C \) are respectively the Huang-Rhys factor and change in the vibrational quantum number of the C=C stretching normal mode (\( \hbar \omega_C = \hbar \omega_{\text{C=C}} \sim 2200–2300 \text{ cm}^{-1} \)) and \( I_{nM} \) is the modified Bessel function of order \( n_M \).

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Table S5. Calculated low-lying singlet and triplet excited state energies ($\lambda$ / nm), the associated oscillator strengths ($f$) and the nature of the transitions at the optimized ground state ($S_0$) geometries of complex 1 in dichloromethane (DCM) by LR-PCM TD-PBE0 method. The values in the parentheses are the % contributions of that particular configuration state function (CSF).

|   | E (cm$^{-1}$) | $\lambda$ (nm) | $f$ | Major contribs | Minor contribs  |
|---|--------------|----------------|-----|---------------|----------------|
| T1 | 22041        | 454            | 0.0000 | H-4$\rightarrow$LUMO (13%), H-1$\rightarrow$L+1 (46%), HOMO$\rightarrow$LUMO (17%) | H-10$\rightarrow$L+10 (2%), H-9$\rightarrow$LUMO (2%), H-3$\rightarrow$L+1 (4%), HOMO$\rightarrow$L+2 (3%), HOMO$\rightarrow$L+4 (2%) |
| T2 | 22108        | 452            | 0.0000 | H-1$\rightarrow$LUMO (83%) | H-6$\rightarrow$L+1 (2%), H-4$\rightarrow$L+1 (4%), H-4$\rightarrow$L+7 (2%), H-3$\rightarrow$L+4 (2%) |
| T3 | 22670        | 441            | 0.0000 | H-1$\rightarrow$L+1 (15%), HOMO$\rightarrow$LUMO (44%), HOMO$\rightarrow$L+2 (20%) | H-5$\rightarrow$L+5 (2%), H-4$\rightarrow$LUMO (5%), HOMO$\rightarrow$L+4 (6%) |
| S1 | 25484        | 392            | 0.2510 | HOMO$\rightarrow$LUMO (98%) | |
| T4 | 26853        | 372            | 0.0000 | H-2$\rightarrow$LUMO (83%) | H-7$\rightarrow$LUMO (3%), HOMO$\rightarrow$LUMO (4%), HOMO$\rightarrow$L+2 (4%), HOMO$\rightarrow$L+4 (2%) |
| T5 | 27190        | 368            | 0.0000 | H-2$\rightarrow$LUMO (11%), HOMO$\rightarrow$LUMO (31%), HOMO$\rightarrow$L+2 (27%), HOMO$\rightarrow$L+4 (13%) | H-5$\rightarrow$L+5 (7%), HOMO$\rightarrow$L+6 (3%) |
| S2 | 27220        | 367            | 0.0519 | H-1$\rightarrow$LUMO (97%) | |
| S3 | 28076        | 356            | 0.0029 | H-2$\rightarrow$LUMO (97%) | |

Figure S4. Frontier MOs of complex 1 at the optimized $S_0$ geometry from the LR-PCM TD-PBE0 calculation. The orbital energy and the Au character (in %) is also displayed.

MO102 (H-2) -6.6eV 11%
MO103 (H-1) -6.47eV 4%
MO104 (HOMO) -5.84eV 4%
MO105 (LUMO) -2.12eV 9%
MO106 (L+1) -1.55eV
Table S6. Calculated low-lying singlet and triplet excited state energies ($\lambda$ / nm), the associated oscillator strengths ($f$) and the nature of the transitions at the optimized ground state ($S_0$) geometries of complex 2 in dichloromethane (DCM) by LR-PCM TD-PBE0 method. The values in the parentheses are the % contributions of that particular configuration state function (CSF).

| No. | E (cm$^{-1}$) | $\lambda$ (nm) | $f$ | Major contribs | Minor contribs |
|-----|--------------|----------------|-----|----------------|----------------|
| T1  | 19149        | 522            | 0   | H-1->LUMO (11%), H-1->L+1 (47%), H-1->L+2 (12%) | H-6->LUMO (2%), H-2->LUMO (3%), H-2->L+1 (3%), H-2->L+2 (3%), H-1->L+3 (2%), HOMO->LUMO (2%), HOMO->L+1 (3%) |
| T2  | 22044        | 454            | 0   | H-2->LUMO (24%), H-2->L+1 (19%) | H-7->L+8 (2%), H-6->LUMO (5%), H-6->L+1 (4%), H-5->LUMO (6%), H-1->LUMO (9%), H-1->L+2 (2%), HOMO->LUMO (9%), HOMO->L+5 (2%) |
| T3  | 22522        | 444            | 0   | HOMO->LUMO (49%), HOMO->L+5 (11%) | H-8->L+7 (3%), H-6->LUMO (2%), H-2->LUMO (6%), H-2->L+1 (3%), H-1->L+1 (2%), HOMO->L+2 (5%), HOMO->L+3 (8%) |
| T4  | 24715        | 405            | 0   | H-5->LUMO (15%), H-2->LUMO (24%), H-2->L+1 (15%), H-1->L+2 (10%) | H-12->LUMO (2%), H-5->L+3 (3%), H-4->L+6 (3%), H-1->LUMO (6%), H-1->L+1 (4%), HOMO->L+3 (3%), HOMO->L+5 (4%) |
| S1  | 24954        | 401            | 0.2737 | HOMO->LUMO (97%) | |
| T5  | 25090        | 399            | 0   | H-2->LUMO (15%), H-1->LUMO (55%) | H-5->LUMO (4%), H-5->L+3 (2%), H-4->L+6 (2%), H-2->L+2 (2%), H-1->L+2 (6%) |
| T6  | 26062        | 384            | 0   | H-5->LUMO (18%), H-2->LUMO (11%), H-2->L+1 (21%) | H-8->L+7 (2%), H-6->LUMO (3%), H-5->L+3 (5%), H-4->L+6 (8%), HOMO->LUMO (7%), HOMO->L+2 (2%), HOMO->L+3 (3%), HOMO->L+5 (6%) |
| T7  | 27003        | 370            | 0   | H-3->LUMO (10%), HOMO->LUMO (25%), HOMO->L+5 (16%) | H-8->L+7 (5%), H-5->LUMO (8%), H-5->L+3 (2%), H-4->L+6 (4%), H-1->LUMO (6%), HOMO->L+2 (4%), HOMO->L+3 (6%), HOMO->L+8 (2%) |
| S2  | 27050        | 370            | 0.2623 | H-2->LUMO (27%), H-1->LUMO (68%) | |
| T8  | 27257        | 367            | 0   | H-3->LUMO (81%) | H-9->LUMO (2%), H-5->LUMO (2%), H-3->L+1 (2%), H-3->L+3 (2%), HOMO->LUMO (3%), HOMO->L+5 (2%) |
| S3  | 27609        | 362            | 0.028 | H-2->LUMO (68%), H-1->LUMO (26%) | HOMO->L+1 (2%) |
| S4  | 28139        | 355            | 0.0021 | H-3->LUMO (96%) | |
| MO Number | Name   | Energy (eV) | Character (%) |
|-----------|--------|-------------|---------------|
| MO166     | H-3    | -6.59       | 11            |
| MO167     | H-2    | -6.50       | 5             |
| MO168     | H-1    | -6.23       | 1             |
| MO169     | HOMO   | -5.81       | 4             |
| MO170     | LUMO   | -2.19       | 7             |
| MO171     | L+1    | -1.74       | 1             |

Figure S5. Frontier MOs of complex 2 at the optimized $S_0$ geometry from the LR-PCM TD-PBE0 calculation. The orbital energy and the Au character (in %) is also displayed.
**Table S7.** Calculated low-lying singlet and triplet excited state energies ($\lambda$ / nm) with $\lambda > 300$ nm, the associated oscillator strengths ($f$) and the nature of the transitions at the optimized ground state ($S_0$) geometries of complex 3-exo in dichloromethane (DCM) by LR-PCM TD-PBE0 method. The values in the parentheses are the % contributions of that particular configuration state function (CSF).

|   | E (cm⁻¹) | $\lambda$ (nm) | $f$     | Major contribs                              | Minor contribs                           |
|---|----------|-----------------|---------|---------------------------------------------|------------------------------------------|
| T1| 19235    | 520             | 0       | H-1->LUMO (55%), H-1->L+1 (27%)             | H-5->LUMO (7%), H-5->L+1 (7%), H-3->L+1 (9%), HOMO->LUMO (8%) |
| T2| 21713    | 461             | 0       | H-3->LUMO (14%), H-1->LUMO (18%), H-1->L+1 (20%) | H-9->L+8 (2%), H-3->LUMO (2%), H-1->L+1 (5%), HOMO->L+2 (9%), HOMO->L+3 (8%), HOMO->L+5 (7%), HOMO->L+8 (2%) |
| T3| 22427    | 446             | 0       | HOMO->LUMO (54%)                            | H-5->L+1 (2%), H-1->LUMO (2%), H-1->L+1 (5%), HOMO->L+2 (9%), HOMO->L+3 (8%), HOMO->L+5 (7%), HOMO->L+8 (2%) |
| S1| 24447    | 409             | 0.1645  | H-1->LUMO (84%), HOMO->LUMO (11%)           | H-3->LUMO (3%)                           |
| S2| 24932    | 401             | 0.3078  | H-1->LUMO (10%), HOMO->LUMO (87%)           |                                          |
| T4| 25514    | 392             | 0       | H-6->LUMO (34%), H-4->L+6 (10%)             | H-6->L+2 (9%), H-5->LUMO (2%), H-4->L+4 (2%), H-3->LUMO (3%), H-1->L+1 (4%), H-1->L+3 (2%), HOMO->L+2 (4%), HOMO->L+3 (2%), HOMO->L+5 (3%) |
| T5| 26681    | 375             | 0       | H-2->LUMO (92%)                             | H-10->LUMO (2%), H-2->L+2 (2%)            |
| T6| 26759    | 374             | 0       | HOMO->LUMO (20%), HOMO->L+5 (10%)           | H-12->LUMO (2%), H-9->L+7 (2%), H-9->L+8 (2%), H-8->LUMO (2%), H-3->L+1 (9%), H-1->LUMO (5%), H-1->L+1 (2%), H-1->L+2 (3%), H-1->L+3 (4%), HOMO->L+1 (2%), HOMO->L+2 (6%), HOMO->L+3 (8%), HOMO->L+5 (3%), HOMO->L+8 (2%) |
| T7| 26981    | 371             | 0       | HOMO->LUMO (11%)                            | H-12->LUMO (2%), H-11->LUMO (2%), H-3->LUMO (2%), H-9->L+8 (2%), H-6->L+2 (4%), H-6->L+4 (2%), H-5->L+1 (3%), H-4->L+6 (7%), H-3->LUMO (2%), H-3->L+1 (6%), H-1->LUMO (6%), H-1->L+1 (4%), H-1->L+2 (3%), H-1->L+3 (4%), HOMO->L+2 (3%), HOMO->L+3 (3%), HOMO->L+5 (4%) |
| T8| 27314    | 366             | 0       | H-3->LUMO (40%), H-1->L+1 (18%)             | H-12->L+1 (4%), H-5->LUMO (8%), H-3->L+1 (2%), H-1->LUMO (5%), H-1->L+3 (2%), H-1->L+10 (2%) |
| S3| 27705    | 361             | 0.0001  | H-2->LUMO (97%)                             |                                          |
Figure S6. Frontier MOs of complex 3-exo at the optimized $S_0$ geometry from the LR-PCM TD-PBE0 calculation. The orbital energy and the Au character (in %) is also displayed.
Table S8. Calculated low-lying singlet and triplet excited state energies (\(\lambda / \text{nm}\)) with \(\lambda > 300 \text{ nm}\), the associated oscillator strengths (\(f\)) and the nature of the transitions at the optimized ground state (\(S_0\)) geometries of complex 3-endo in dichloromethane (DCM) by LR-PCM TD-PBE0 method. The values in the parentheses are the % contributions of that particular configuration state function (CSF).

| HOMO in 227 E (cm\(^{-1}\)) | \(\lambda\) (nm) | \(f\) | Major contribs | Minor contribs |
|-------------------------------|-----------------|------|----------------|----------------|
|                               |                 |      |                | H-12->LUMO (2%), H-1->L+2 (2%), H-1->L+4 (2%) |
| T1 19337                      | 517             | 0    | H-1->LUMO (54%), H-1->L+1 (28%) | |
| T2 21609                      | 463             | 0    | H-2->LUMO (11%), H-1->LUMO (18%), H-1->L+1 (22%) | H-7->L+1 (3%), H-6->LUMO (4%), H-4->LUMO (5%), H-4->L+1 (4%), H-3->LUMO (3%), H-3->L+1 (3%), H-2->L+1 (7%), HOMO->LUMO (5%) |
| T3 22314                      | 448             | 0    | HOMO->LUMO (69%) | H-9->L+8 (2%), H-2->LUMO (2%), H-1->L+1 (2%), HOMO->L+2 (4%), HOMO->L+3 (3%), HOMO->L+4 (4%), HOMO->L+5 (4%), HOMO->L+6 (2%) |
| S1 23499                      | 426             | 0.0671 | HOMO->LUMO (96%) | |
| S2 24564                      | 407             | 0.2505 | H-1->LUMO (93%) | H-2->LUMO (3%) |
| T4 25235                      | 396             | 0    | HOMO->LUMO (17%), HOMO->L+3 (11%), HOMO->L+5 (16%) | H-9->L+8 (7%), H-6->LUMO (3%), HOMO->L+2 (6%), HOMO->L+4 (9%), HOMO->L+6 (8%), HOMO->L+7 (8%), HOMO->L+8 (2%) |
| T5 25640                      | 390             | 0    | H-6->LUMO (27%), H-6->L+2 (10%), H-3->LUMO (15%) | H-7->LUMO (4%), H-5->L+5 (5%), H-5->L+6 (8%), H-4->LUMO (3%), H-2->LUMO (2%), H-1->L+1 (2%), HOMO->LUMO (2%) |
| T6 26691                      | 375             | 0    | H-2->LUMO (35%), H-1->LUMO (17%), H-1->L+1 (17%) | H-12->L+1 (2%), H-3->LUMO (6%), H-2->L+2 (2%) |
| T7 26978                      | 371             | 0    | H-2->LUMO (11%), H-2->L+1 (15%) | H-12->LUMO (4%), H-10->LUMO (2%), H-7->L+1 (3%), H-6->LUMO (4%), H-6->L+2 (2%), H-5->L+5 (2%), H-5->L+6 (3%), H-4->L+9 (2%), H-3->L+1 (3%), H-1->LUMO (3%), H-1->L+2 (7%), H-1->L+4 (6%), H-1->L+9 (4%) |
| T8 28155                      | 355             | 0    | H-7->LUMO (20%), H-4->LUMO (20%), HOMO->L+1 (11%) | H-7->L+1 (2%), H-6->LUMO (4%), H-4->L+1 (3%), H-3->LUMO (7%), H-2->LUMO (7%), H-1->L+1 (5%), H-1->L+2 (3%) |
| T9 28425                      | 352             | 0    | H-3->LUMO (16%), HOMO->L+1 (64%) | H-6->LUMO (3%), H-2->LUMO (6%) |
| S3 28623                      | 349             | 0.0053 | HOMO->L+1 (97%) | |
| T10 28716                     | 348             | 0    | H-4->LUMO (13%), H-3->LUMO (33%), HOMO->L+1 (19%) | H-7->LUMO (9%), H-2->LUMO (5%), H-1->L+1 (2%), HOMO->LUMO (2%) |
| S4 29756                      | 336             | 0.0356 | H-2->LUMO (87%) | H-3->LUMO (2%), H-1->LUMO (2%) |
**Figure S7.** Frontier MOs of complex 3-endo at the optimized $S_0$ geometry from the LR-PCM TD-PBE0 calculation. The orbital energy and the Au character (in %) is also displayed.

**Table S9.** CI coefficients of the HOMO $\rightarrow$ LUMO and H−1 $\rightarrow$ LUMO transitions from the LR-PCM TD-PBE0 calculation of the first singlet excited state at the optimized ground state geometries of complexes depicted in Chart 1 of the main text.

| CI coefficients of $S_1$ | 1     | 2     | 3-exo | 3-endo |
|-------------------------|-------|-------|-------|--------|
| HOMO $\rightarrow$ LUMO | 0.70139 | 0.69767 | 0.23644 | 0.68544 |
| H−1 $\rightarrow$ LUMO  | 0     | 0.07379 | 0.64616 | 0.09113 |
Radiative decay rate calculation results. For the $^3$IL excited state, the singlet excited state that could have appreciable SOC is $^1$LLCT as the HOMO and H–1 are orthogonal. For complexes 1 and 2, the lowest-lying $^1$LLCT excited state is $S_1$ and $k_r$ is calculated for $m = 1$ for these two complexes using eq.(9) of the main text. On the other hand, for complexes 3-exo and 3-end, the closest-lying $^1$LLCT excited state is $S_2$; hence, for these two complexes, both $S_1$ and $S_2$ are included in the $k_r$ calculations.

Similarly, for the $^3$LLCT excited state of complexes 1 and 3-end, the singlet excited state that could have appreciable SOC is $^1$IL/$^1$MLCT. For complex 1, $S_3$ is of the character $^1$IL/$^1$MLCT from the NonEq SS-TDDFT calculation, and it is found to be mainly of “H–4” $\rightarrow$ L transition (“H–4” in the NEQ SS-TDDFT calculation of the $S_1$ excited state; this orbital becomes H–1 in the NonEq SS-TDDFT calculation of the $S_3$ excited state). But $S_4$, though also a $^1$LLCT and is derived from a “H–2” $\rightarrow$ L transition (“H–2” in the NEQ SS-TDDFT calculation of the $S_1$ excited state; this orbital becomes H–1 in the NonEq SS-TDDFT calculation of the $S_4$ excited state), could also has significant SOC with the $^3$LLCT excited state of complex 1 because this H-2 has the Au(d) orbital orthogonal to the HOMO, see Figure S8. Therefore, in estimating the $k_r$ of $^3$LLCT $\rightarrow$ $S_0$ of complex 1 using eq.(9) of the main text, both $m = 3$ and 4 are considered to be the main states that contribute to the radiative decay rate.

Likewise, for the $^3$LLCT excited state of complex 3-end, both the $^1$IL/$^1$MLCT and $^1$LLCT singlet excited states were considered to be the two major $S_m$ excited states contributing to the radiative decay rates. Therefore, NonEq SS-TDDFT calculations were also performed for the $S_3$ (mainly of $^1$IL/$^1$MLCT character and is derived from H–1 $\rightarrow$ L and H–5 $\rightarrow$ L transitions) and $S_4$ (mainly of $^1$LLCT character and is derived from “H–3” $\rightarrow$ L transition; “H–3” in the NEQ SS-TDDFT calculation of the $S_1$ excited state and becomes H–2 in the NonEq SS-TDDFT calculation of the $S_4$ excited state)

Figure S8. MO surfaces relevant to the SOC calculation of the $^3$LLCT excited state of complex 1. The relative MO orders are those obtained from a NEQ SS-TDDFT calculation of the $S_1$ excited state.

Figure S9. MO surfaces relevant to the SOC calculation of the $^3$LLCT excited state of complex 3-end. The relative MO orders are those obtained from a NEQ SS-TDDFT calculation of the $S_1$ excited state.
Non-radiative decay rate calculations. Basically, the FCF’s were calculated using eq.(11) of the main text. For complex 3-endo, as the Huang-Rhys factor for the low-frequency modes, i.e., \( \omega_{lf1} \leq 200 \text{ cm}^{-1} \) \( (\text{vide infra}) \), eq.(S1) would be used:

\[
k_{nr}(T_1\rightarrow S_0) = \frac{2\pi}{\hbar} \left| \left. H_{SOC} \right|_{S_0} \right|^2 \sum_{n_M}^{\infty} \exp \left( - \frac{(\Delta E - n_M \hbar \omega_M - \lambda_s)^2}{4\lambda k_B T} \right) \exp \left( - S_M \right) S_M^{n_M} \]

(S1)

where \( \lambda \) includes contributions from both solvent modes and the low-frequency normal modes \( (\omega_{lf1} \leq 200 \text{ cm}^{-1}) \), i.e.,

\[
\lambda = \lambda_s + \lambda_{lf1}
\]

(S2a)

\[
\lambda_{lf1} = \sum_{j \in lf1} S_j \hbar \omega_j
\]

(S2b)

**Table S10.** Average normal mode \( \omega_A \) (cm\(^{-1}\)) and the corresponding Huang-Rhys factor \( S_A \) and reorganization energy \( \lambda_A \) (cm\(^{-1}\)) of \( ^3\text{IL} \rightarrow S_0 \) transition of complex 1.

| \( \omega_{lf1} \) (cm\(^{-1}\)) | \( \omega_A \) | \( S_A \) | \( \lambda_A \) |
|-------------------------------|-----------|-------|---------|
| \( \omega_{lf1} \leq 200 \text{ cm}^{-1} \) | 76        | 0.21  | 15.9    |
| 200 < \( \omega_{lf2} \leq 1000 \text{ cm}^{-1} \) | 579       | 0.56  | 327     |
| 1000 < \( \omega_M \leq 1800 \text{ cm}^{-1} \) | 1467      | 1.75  | 2570    |
| \( \omega_{hf} \geq 3000 \text{ cm}^{-1} \) | 3182      | 0.00  | 6.43    |

**Table S11.** Average normal mode \( \omega_A \) (cm\(^{-1}\)) and the corresponding Huang-Rhys factor \( S_A \) and reorganization energy \( \lambda_A \) (cm\(^{-1}\)) of \( ^3\text{IL} \rightarrow S_0 \) transition of complex 2.

| \( \omega_{lf1} \) (cm\(^{-1}\)) | \( \omega_A \) | \( S_A \) | \( \lambda_A \) |
|-------------------------------|-----------|-------|---------|
| \( \omega_{lf1} \leq 200 \text{ cm}^{-1} \) | 18        | 0.90  | 16.2    |
| 200 < \( \omega_{lf2} \leq 1000 \text{ cm}^{-1} \) | 373       | 0.99  | 368     |
| 1000 < \( \omega_M \leq 1800 \text{ cm}^{-1} \) | 1508      | 1.47  | 2223    |
| \( \omega_{hf} \geq 3000 \text{ cm}^{-1} \) | 3114      | 0.00  | 10.3    |

**Table S12.** Average normal mode \( \omega_A \) (cm\(^{-1}\)) and the corresponding Huang-Rhys factor \( S_A \) and reorganization energy \( \lambda_A \) (cm\(^{-1}\)) of \( ^3\text{IL} \rightarrow S_0 \) transition of complex 3-exo.

| \( \omega_{lf1} \) (cm\(^{-1}\)) | \( \omega_A \) | \( S_A \) | \( \lambda_A \) |
|-------------------------------|-----------|-------|---------|
| \( \omega_{lf1} \leq 200 \text{ cm}^{-1} \) | 72        | 0.76  | 54.4    |
| 200 < \( \omega_{lf2} \leq 1000 \text{ cm}^{-1} \) | 619       | 0.70  | 435     |
| 1000 < \( \omega_M \leq 1800 \text{ cm}^{-1} \) | 1483      | 1.29  | 1917    |
| \( \omega_{hf} \geq 3000 \text{ cm}^{-1} \) | 3147      | 0.00  | 2.13    |
Is PBE0 calculation reliable in predicting the relative energies of the \(3^{\text{LLCT}}\) and \(3^{\text{IL}}\) excited states?

Global hybrid functionals are known to fail in zero-overlap charge transfer transition.\(^{[11]}\) However, it has also been shown that TD-PBE0 can also provide accurate descriptions with partial charge transfer character, without resorting to range-separated hybrid density functionals.\(^{[12]}\) To confirm that our present calculation results using the PBE0 functional are valid, we have also done SS-TDDFT calculation using the same basis set but a long-range corrected density functional, CAM-B3LYP\(^{[13]}\) for complex 1. It was found that with the CAM-B3LYP functional at the PBE0 optimized triplet excited state geometries, the \(3^{\text{LLCT}}\) excited state is only ~0.04 eV above the \(3^{\text{IL}}\) excited state using the unrestricted formalism (UDFT); when SS-TDDFT was employed, the \(3^{\text{LLCT}}\) excited state was found to be ~0.05 eV below the \(3^{\text{IL}}\) excited state. That is, even with a long-range corrected functional, the TD-CAMB3LYP results also showed that the \(3^{\text{LLCT}}\) excited state is slightly lower-lying than the \(3^{\text{IL}}\) excited state. Therefore, the \(3^{\text{LLCT}}\) excited state is a thermally accessible excited state that contributes to the fast non-radiative decay rate of complex 1.

Table S13. Average normal mode \(\omega_A\) (cm\(^{-1}\)) and the corresponding Huang-Rhys factor \(S_A\) and reorganization energy \(\lambda_A\) (cm\(^{-1}\)) of \(3^{\text{IL}} \rightarrow S_0\) transition of complex \(3\text{-endo}\).

| \(\omega_l\) | \(\omega_A\) | \(S_A\) | \(\lambda_A\) |
|------------|------------|--------|------------|
| \(\omega_{lf} \leq 200\) cm\(^{-1}\) | 53 | 1.33 | 69.9 |
| \(200 < \omega_{lf} \leq 1000\) cm\(^{-1}\) | 625 | 0.74 | 462 |
| \(1000 < \omega_M \leq 1800\) cm\(^{-1}\) | 1501 | 1.27 | 1906 |
| \(\omega_{hf} \geq 3000\) cm\(^{-1}\) | 3137 | 0.00 | 1.16 |

Table S14. Optimized \(S_0\) structures of complex 1.

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
| 1 79 0 | 0.011802 | 0.025754 | 0.050905 |
| 2 6 0 | 0.033738 | -0.242844 | 2.099473 |
| 3 7 0 | 1.998046 | -0.022517 | 0.334485 |
| 4 8 0 | -8.679474 | 0.249951 | -1.075167 |
| 5 6 0 | -1.918426 | 0.077301 | -0.225173 |
| 6 6 0 | -3.129049 | 0.112220 | -0.399538 |
| 7 6 0 | -4.540640 | 0.152312 | -0.598238 |
| 8 6 0 | -5.430142 | -0.067671 | 0.471986 |
| 9 1 0 | -5.029683 | -0.270935 | 1.461025 |
|   |   |   |     |     |     |
|---|---|---|-----|-----|-----|
| 10| 6 | 0 | -6.799179 | -0.028823 | 0.280546 |
| 11| 1 | 0 | -7.484991 | -0.198882 | 1.105240 |
| 12| 6 | 0 | -7.329502 | 0.232917  | -0.990429 |
| 13| 6 | 0 | -6.463536 | 0.454401  | -2.065754 |
| 14| 1 | 0 | -6.846662 | 0.658823  | -3.059449 |
| 15| 6 | 0 | -5.087967 | 0.412221  | -1.863146 |
| 16| 1 | 0 | -4.421111 | 0.584999  | -2.703099 |
| 17| 6 | 0 | -1.012383 | -0.356589 | 3.011030 |
| 18| 1 | 0 | -2.038678 | -0.305470 | 2.655946 |
| 19| 6 | 0 | -0.760610 | -0.536252 | 4.373795 |
| 20| 1 | 0 | -1.590954 | -0.623305 | 5.070352 |
| 21| 6 | 0 | 0.549083  | -0.604145 | 4.845197 |
| 22| 1 | 0 | 0.743074  | -0.743197 | 5.904909 |
| 23| 6 | 0 | 1.613420  | -0.493561 | 3.956000 |
| 24| 1 | 0 | 2.631689  | -0.546497 | 4.332694 |
| 25| 6 | 0 | 1.365785  | -0.314747 | 2.591340 |
| 26| 6 | 0 | 2.443496  | -0.192015 | 1.597493 |
| 27| 6 | 0 | 3.820954  | -0.230589 | 1.809461 |
| 28| 1 | 0 | 4.222809  | -0.366266 | 2.806660 |
| 29| 6 | 0 | 4.671148  | -0.091767 | 0.715878 |
| 30| 1 | 0 | 5.745844  | -0.119882 | 0.869039 |
| 31| 6 | 0 | 4.168465  | 0.082529  | -0.570647 |
| 32| 1 | 0 | 4.839638  | 0.189803  | -1.414635 |
| 33| 6 | 0 | 2.786604  | 0.115559  | -0.752513 |
| 34| 6 | 0 | 2.036971  | 0.284407  | -2.007085 |
| 35| 6 | 0 | 2.664103  | 0.444002  | -3.246782 |
| 36| 1 | 0 | 3.748364  | 0.449082  | -3.323670 |
| 37| 6 | 0 | 1.897016  | 0.598370  | -4.397287 |
| 38| 1 | 0 | 2.385888  | 0.722570  | -5.359352 |
| 39| 6 | 0 | 0.506071  | 0.592944  | -4.311609 |
Table S15. Optimized $S_0$ structures of complex 2.

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
| 1             | 79            | 0           | -0.084471 0.321506 0.044532 |
| 2             | 7             | 0           | -0.054457 0.273884 2.048074  |
| 3             | 6             | 0           | 1.922044 -0.080445 0.318458 |
| 4             | 6             | 0           | 2.934288 -0.253487 -0.591986 |
| 5             | 1             | 0           | 2.721484 -0.188753 -1.657421 |
| 6             | 6             | 0           | 4.272848 -0.517500 -0.188052 |
| 7             | 6             | 0           | 5.320497 -0.693836 -1.124292 |
| 8             | 1             | 0           | 5.090903 -0.626145 -2.185144 |
| 9             | 6             | 0           | 6.605769 -0.945688 -0.702927 |
| 10            | 1             | 0           | 7.400528 -1.078614 -1.431915 |
| 11            | 6             | 0           | 6.902571 -1.033054 0.676255 |
| 12            | 1             | 0           | 7.921781 -1.232120 0.995444 |
| 13            | 6             | 0           | 5.907198 -0.867048 1.609831 |
| 14            | 1             | 0           | 6.129771 -0.933063 2.672369 |
| 15            | 6             | 0           | 4.573692 -0.606155 1.205067 |
| 16            | 6             | 0           | 3.528790 -0.428332 2.142560 |
|   |   |   |    |    |    |
|---|---|---|----|----|----|
| 17| 1 | 0 | 3.772115 | -0.497161 | 3.200614 |
| 18| 6 | 0 | 2.240030 | -0.172662 | 1.724024 |
| 19| 6 | 0 | 1.122763 | 0.026866 | 2.659678 |
| 20| 6 | 0 | 1.152017 | -0.016684 | 4.049639 |
| 21| 1 | 0 | 2.077105 | -0.245813 | 4.565689 |
| 22| 6 | 0 | -0.023007 | 0.202744 | 4.781191 |
| 23| 6 | 0 | -1.215154 | 0.459868 | 4.088009 |
| 24| 1 | 0 | -2.127929 | 0.660442 | 4.636871 |
| 25| 6 | 0 | -1.218299 | 0.489108 | 2.698485 |
| 26| 6 | 0 | -2.356109 | 0.737994 | 1.799000 |
| 27| 6 | 0 | -3.650721 | 0.985855 | 2.266228 |
| 28| 1 | 0 | -3.861685 | 1.004725 | 3.332429 |
| 29| 6 | 0 | -4.683547 | 1.210904 | 1.361913 |
| 30| 1 | 0 | -5.688401 | 1.403300 | 1.726976 |
| 31| 1 | 0 | -5.234483 | 1.364295 | -0.712794 |
| 32| 6 | 0 | -4.425745 | 1.188511 | -0.007581 |
| 33| 6 | 0 | -3.133948 | 0.940878 | -0.478736 |
| 34| 1 | 0 | -2.945564 | 0.926048 | -1.549401 |
| 35| 6 | 0 | -2.081477 | 0.712992 | 0.404157 |
| 36| 6 | 0 | -0.116728 | 0.366438 | -1.905781 |
| 37| 6 | 0 | -0.139156 | 0.393530 | -3.128904 |
| 38| 6 | 0 | -0.163855 | 0.423475 | -4.554562 |
| 39| 6 | 0 | -1.345118 | 0.713848 | -5.252708 |
| 40| 1 | 0 | -2.253463 | 0.919111 | -4.693365 |
| 41| 6 | 0 | -1.379790 | 0.745191 | -6.643016 |
| 42| 1 | 0 | -2.313464 | 0.974402 | -7.144710 |
| 43| 6 | 0 | -0.215605 | 0.481899 | -7.371297 |
| 44| 6 | 0 | 0.973795 | 0.189759 | -6.689433 |
| 45| 1 | 0 | 1.869524 | -0.012357 | -7.269315 |
| 46| 6 | 0 | 0.998167 | 0.161534 | -5.306964 |
|   |   |   |   |   |   |
|---|---|---|---|---|---|
| 47 | 1 | 0 | 1.925334 | -0.066024 | -4.788808 |
| 48 | 8 | 0 | -0.136490 | 0.485228 | -8.721830 |
| 49 | 6 | 0 | -1.311430 | 0.774964 | -9.453352 |
| 50 | 1 | 0 | -1.030106 | 0.724876 | -10.506007 |
| 51 | 1 | 0 | -2.099739 | 0.038978 | -9.253212 |
| 52 | 1 | 0 | -1.687339 | 1.780013 | -9.225932 |
| 53 | 6 | 0 | -0.007600 | 0.164229 | 6.258458 |
| 54 | 6 | 0 | -1.097733 | -0.355817 | 6.962974 |
| 55 | 6 | 0 | 1.096247 | 0.648421 | 6.967270 |
| 56 | 6 | 0 | -1.102573 | -0.402385 | 8.358387 |
| 57 | 1 | 0 | -1.940304 | -0.756997 | 6.406096 |
| 58 | 6 | 0 | 1.127127 | 0.625914 | 8.363038 |
| 59 | 1 | 0 | 1.928548 | 1.076454 | 6.414866 |
| 60 | 6 | 0 | 0.018412 | 0.095396 | 9.032472 |
| 61 | 1 | 0 | 0.028180 | 0.068936 | 10.114758 |
| 62 | 6 | 0 | -2.311734 | -0.990652 | 9.092033 |
| 63 | 6 | 0 | -3.568977 | -0.184663 | 8.725230 |
| 64 | 6 | 0 | -2.503954 | -2.455564 | 8.665995 |
| 65 | 6 | 0 | -2.147142 | -0.953190 | 10.613738 |
| 66 | 1 | 0 | -3.463204 | 0.864070 | 9.025655 |
| 67 | 1 | 0 | -3.769691 | -0.208995 | 7.648729 |
| 68 | 1 | 0 | -4.445317 | -0.599535 | 9.237500 |
| 69 | 1 | 0 | -1.624353 | -3.057041 | 8.922495 |
| 70 | 1 | 0 | -3.372480 | -2.885522 | 9.179210 |
| 71 | 1 | 0 | -2.673530 | -2.549185 | 7.588008 |
| 72 | 1 | 0 | -2.038733 | -1.379598 | 11.086749 |
| 73 | 1 | 0 | -1.283585 | -1.540862 | 10.945997 |
| 74 | 1 | 0 | -2.032356 | 0.070896 | 10.987390 |
| 75 | 6 | 0 | 2.350588 | 1.176380 | 9.102489 |
| 76 | 6 | 0 | 3.597568 | 0.382135 | 8.679752 |
Table S16. Optimized $S_0$ structures of complex 3-exo.

| Center Number | Atomic Number | Atomic Type | X     | Y     | Z     |
|---------------|---------------|-------------|-------|-------|-------|
| 1             | 79            | 0           | 0.018801 | 0.099452 | 0.041414 |
| 2             | 7             | 0           | 0.017803 | 0.101186 | 2.043292 |
| 3             | 6             | 0           | 2.060191 | 0.059409 | 0.360590 |
| 4             | 6             | 0           | 0.025914 | 0.092290 | -1.910309 |
| 5             | 6             | 0           | -3.081496 | 0.169336 | -0.542610 |
| 6             | 1             | 0           | -2.872661 | 0.163059 | -1.609646 |
| 7             | 6             | 0           | -4.405377 | 0.200218 | -0.096847 |
| 8             | 1             | 0           | -5.219037 | 0.218013 | -0.817915 |
| 9             | 1             | 0           | -5.718255 | 0.232535 | 1.613110 |
| 10            | 6             | 0           | -4.688594 | 0.208524 | 1.267742 |
| 11            | 6             | 0           | -3.649424 | 0.185937 | 2.192753 |
| 12            | 1             | 0           | -3.879786 | 0.193151 | 3.255088 |
| 13            | 6             | 0           | -2.323226 | 0.154517 | 1.750978 |
| 14 | 6  | 0  | -1.175607 | 0.129606 | 2.672861 |
|---|----|----|-----------|---------|---------|
| 15 | 6  | 0  | -1.191101 | 0.123554 | 4.063071 |
| 16 | 1  | 0  | -2.133958 | 0.117859 | 4.597882 |
| 17 | 6  | 0  | 0.017757  | 0.085714 | 4.773367 |
| 18 | 6  | 0  | 1.225420  | 0.058447 | 4.063254 |
| 19 | 1  | 0  | 2.167549  | 0.056827 | 4.599311 |
| 20 | 6  | 0  | 1.212780  | 0.067861 | 2.671365 |
| 21 | 6  | 0  | 2.360290  | 0.053598 | 1.754272 |
| 22 | 6  | 0  | 3.687549  | 0.039373 | 2.208291 |
| 23 | 1  | 0  | 3.910386  | 0.038055 | 3.273324 |
| 24 | 6  | 0  | 4.716050  | 0.030815 | 1.281608 |
| 25 | 6  | 0  | 4.428719  | 0.032708 | -0.095087 |
| 26 | 6  | 0  | 3.108680  | 0.046765 | -0.553739 |
| 27 | 1  | 0  | 2.892645  | 0.050654 | -1.619722 |
| 28 | 6  | 0  | 5.695214  | 0.022159 | -0.827493 |
| 29 | 6  | 0  | 5.956654  | 0.018142 | -2.197442 |
| 30 | 1  | 0  | 5.145045  | 0.022590 | -2.920848 |
| 31 | 6  | 0  | 7.282384  | 0.008261 | -2.625791 |
| 32 | 1  | 0  | 7.505385  | 0.004959 | -3.689321 |
| 33 | 6  | 0  | 8.328388  | 0.002552 | -1.699530 |
| 34 | 1  | 0  | 9.356929  | -0.005157| -2.050420 |
| 35 | 6  | 0  | 8.065498  | 0.006773 | -0.327422 |
| 36 | 1  | 0  | 8.887796  | 0.002532 | 0.384700 |
| 37 | 6  | 0  | 6.746585  | 0.016638 | 0.106196 |
| 38 | 6  | 0  | 0.062996  | 0.072480 | -4.559810 |
| 39 | 6  | 0  | 1.282688  | 0.037757 | -5.264245 |
| 40 | 6  | 0  | 1.307695  | 0.025566 | -6.646862 |
| 41 | 1  | 0  | 2.247929  | -0.001391| -7.189654 |
| 42 | 6  | 0  | 0.111429  | 0.047663 | -7.377155 |
| 43 | 6  | 0  | -1.109762 | 0.082537 | -6.697150 |
44 1 0 -2.050031 0.100361 -7.237178
45 6 0 -1.124236 0.094617 -5.306123
46 1 0 -2.076696 0.121598 -4.784447
47 1 0 2.215829 0.020166 -4.708316
48 6 0 0.039543 0.083689 -3.133929
49 6 0 6.214792 0.024987 1.529014
50 6 0 6.504532 -7.636690 2.205237
51 1 0 6.858242 -8.465106 2.205237
52 1 0 6.939400 -7.762353 1.206122
53 1 0 6.856590 -7.734540 2.105865
54 6 0 6.881305 -6.285761 2.801592
55 1 0 7.972460 -6.227563 2.921354
56 1 0 6.459502 -6.199695 3.813119
57 6 0 6.405982 -5.106362 1.958203
58 1 0 6.830435 -5.189616 0.946595
59 1 0 5.314311 -5.165414 1.834758
60 6 0 6.773819 -3.749362 2.550376
61 1 0 7.865506 -3.691174 2.674811
62 1 0 6.348082 -3.668023 3.561850
63 6 0 6.297140 -2.571854 1.704363
64 1 0 6.730524 -2.648560 0.697980
65 1 0 5.207697 -2.634302 1.576963
66 6 0 6.664964 -1.225411 2.319027
67 1 0 7.755623 -1.169707 2.446277
68 1 0 6.237906 -1.158604 3.330255
69 6 0 6.671396 1.283036 2.304637
70 1 0 6.235154 1.234854 3.312927
71 1 0 7.760449 1.218878 2.441498
72 6 0 6.321300 2.623537 1.666934
73 1 0 6.774508 2.686032 0.668318
|   |   |   |   |   |
|---|---|---|---|---|
| 74| 1 | 0 | 5.234745 | 2.688659 | 1.517420 |
| 75| 6 | 0 | 6.784238 | 3.810942 | 2.507276 |
| 76| 1 | 0 | 6.334751 | 3.739407 | 3.507614 |
| 77| 1 | 0 | 7.873157 | 3.751840 | 2.656267 |
| 78| 6 | 0 | 6.939271 | 6.373164 | 2.652723 |
| 79| 1 | 0 | 8.030820 | 6.304294 | 2.764926 |
| 80| 1 | 0 | 6.751805 | 7.274954 | 2.054764 |
| 81| 6 | 0 | 6.437189 | 5.156357 | 1.874270 |
| 82| 1 | 0 | 5.345734 | 5.229012 | 1.754518 |
| 83| 1 | 0 | 6.856833 | 5.185792 | 0.858726 |
| 84| 6 | 0 | 6.296151 | 6.547059 | 4.024976 |
| 85| 1 | 0 | 6.645051 | 7.465096 | 4.511091 |
| 86| 1 | 0 | 6.529892 | 5.712115 | 4.694949 |
| 87| 1 | 0 | 5.203940 | 6.608966 | 3.940680 |
| 88| 6 | 0 | -2.022652 | 0.145831 | 0.361181 |
| 89| 8 | 0 | 0.241044 | 0.032949 | -8.723733 |
| 90| 6 | 0 | -0.939204 | 0.051974 | -9.502409 |
| 91| 1 | 0 | -1.524403 | 0.961653 | -9.320421 |
| 92| 1 | 0 | -0.613115 | 0.035019 | -10.543126 |
| 93| 1 | 0 | -1.564089 | -0.827292 | -9.303637 |
| 94| 6 | 0 | 0.018097 | 0.073485 | 6.251255 |
| 95| 6 | 0 | 0.934373 | -0.717929 | 6.949956 |
| 96| 6 | 0 | -0.897818 | 0.852355 | 6.964277 |
| 97| 6 | 0 | 0.947483 | -0.748209 | 8.345959 |
| 98| 1 | 0 | 1.623754 | -1.341942 | 6.387354 |
| 99| 6 | 0 | -0.909526 | 0.858437 | 8.360673 |
|100| 1 | 0 | -1.588578 | 1.485166 | 6.413311 |
|101| 6 | 0 | 0.019391 | 0.049448 | 9.025462 |
|102| 1 | 0 | 0.019913 | 0.040030 | 10.108238 |
|103| 6 | 0 | -1.912125 | 1.745366 | 9.105251 |
Table S17. Optimized S₀ structures of complex 3-endo.

| Center Number | Atomic Number | Atomic Type | Coordinates (Å) |
|---------------|---------------|-------------|-----------------|
|               |               |             | X    | Y    | Z    |
| 104           | 6             | 0           | -1.645288     | 3.217426 | 8.749333 |
| 105           | 6             | 0           | -3.341673     | 1.370648 | 8.681083 |
| 106           | 6             | 0           | -1.810232     | 1.593162 | 10.625325 |
| 107           | 1             | 0           | -0.634105     | 3.515963 | 9.048776 |
| 108           | 1             | 0           | -1.746493     | 3.400810 | 7.674218 |
| 109           | 1             | 0           | -2.360350     | 3.866818 | 9.268621 |
| 110           | 1             | 0           | -3.562706     | 0.325807 | 8.927485 |
| 111           | 1             | 0           | -4.067674     | 2.005149 | 9.203403 |
| 112           | 1             | 0           | -3.497000     | 1.504356 | 7.605238 |
| 113           | 1             | 0           | -2.551688     | 2.240949 | 11.106107 |
| 114           | 1             | 0           | -2.010546     | 0.564430 | 10.946670 |
| 115           | 1             | 0           | -0.822950     | 1.885827 | 11.000842 |
| 116           | 6             | 0           | 1.949764      | -1.649150 | 9.074040 |
| 117           | 6             | 0           | 1.678117      | -3.114653 | 8.695216 |
| 118           | 6             | 0           | 3.379356      | -1.271794 | 8.652408 |
| 119           | 6             | 0           | 1.851964      | -1.520661 | 10.596521 |
| 120           | 1             | 0           | 0.667021      | -3.415357 | 8.992751 |
| 121           | 1             | 0           | 1.775551      | -3.280592 | 7.616929 |
| 122           | 1             | 0           | 2.392956      | -3.774363 | 9.201703 |
| 123           | 1             | 0           | 3.603709      | -0.231310 | 8.913771 |
| 124           | 1             | 0           | 4.104803      | -1.915861 | 9.163676 |
| 125           | 1             | 0           | 3.532043      | -1.390139 | 7.574370 |
| 126           | 1             | 0           | 2.593558      | -2.177115 | 11.065161 |
| 127           | 1             | 0           | 2.054737      | -0.497304 | 10.933130 |
| 128           | 1             | 0           | 0.865175      | -1.817485 | 10.970028 |
| 1 | 79 | 0  | -0.008708  | -0.097263  | 0.000965  |
|---|----|----|-------------|-------------|------------|
| 2 | 7  | 0  | -0.009251  | -0.119995  | 2.009559  |
| 3 | 6  | 0  | 2.100433   | -0.068407  | 0.338541  |
| 4 | 6  | 0  | -0.272270  | -0.055309  | -1.934969 |
| 5 | 8  | 0  | -1.846117  | 0.279886   | -8.558806 |
| 6 | 6  | 0  | -2.048085  | -0.148422  | 0.333096  |
| 7 | 6  | 0  | -3.103660  | -0.161868  | -0.574312 |
| 8 | 1  | 0  | -2.892441  | -0.140405  | -1.639370 |
| 9 | 6  | 0  | -4.427488  | -0.201325  | -0.130253 |
| 10| 1  | 0  | -5.238243  | -0.210965  | -0.854635 |
| 11| 6  | 0  | -4.714848  | -0.227913  | 1.232836  |
| 12| 1  | 0  | -5.744977  | -0.258405  | 1.576125  |
| 13| 6  | 0  | -3.677017  | -0.214784  | 2.158150  |
| 14| 1  | 0  | -3.907205  | -0.235753  | 3.220072  |
| 15| 6  | 0  | -2.349960  | -0.174930  | 1.718770  |
| 16| 6  | 0  | -1.205976  | -0.155916  | 2.637328  |
| 17| 6  | 0  | -1.235688  | -0.159506  | 4.025144  |
| 18| 1  | 0  | -2.184078  | -0.161603  | 4.549747  |
| 19| 6  | 0  | -0.034059  | -0.120492  | 4.746564  |
| 20| 6  | 0  | 1.174197   | -0.080202  | 4.043620  |
| 21| 1  | 0  | 2.109400   | -0.077310  | 4.589937  |
| 22| 6  | 0  | 1.173592   | -0.081214  | 2.648877  |
| 23| 6  | 0  | -0.044941  | -0.121907  | 6.224281  |
| 24| 6  | 0  | -0.964962  | -0.909821  | 6.921941  |
| 25| 1  | 0  | -1.650317  | -1.537993  | 6.359013  |
| 26| 6  | 0  | -0.987525  | -0.930726  | 8.318028  |
| 27| 6  | 0  | -0.065301  | -0.127106  | 8.998481  |
| 28| 1  | 0  | -0.073379  | -0.129129  | 10.081270 |
| 29| 6  | 0  | 0.866489   | 0.679366   | 8.334635  |
|   |   |   |          |          |          |
|---|---|---|----------|----------|----------|
| 30 | 6 | 0 | 0.864127 | 0.664028 | 6.938309 |
| 31 | 1 | 0 | 1.556609 | 1.295346 | 6.387835 |
| 32 | 6 | 0 | 2.335242 | -0.059157 | 1.754522 |
| 33 | 6 | 0 | 3.622251 | -0.041499 | 2.307621 |
| 34 | 1 | 0 | 3.756570 | -0.030881 | 1.354522 |
| 35 | 6 | 0 | 4.738371 | -0.042988 | 1.491178 |
| 36 | 1 | 0 | 5.737613 | -0.032922 | 1.917766 |
| 37 | 6 | 0 | 4.542895 | -0.063586 | 0.115201 |
| 38 | 6 | 0 | 5.555802 | -0.083968 | -0.933354 |
| 39 | 6 | 0 | 6.949393 | -0.084646 | -0.855867 |
| 40 | 1 | 0 | 7.458221 | -0.072612 | 0.104886 |
| 41 | 6 | 0 | 7.682668 | -0.114764 | -2.039170 |
| 42 | 1 | 0 | 8.768740 | -0.119115 | -2.001805 |
| 43 | 6 | 0 | 7.031745 | -0.136242 | -3.276493 |
| 44 | 1 | 0 | 7.618274 | -0.157223 | -4.191325 |
| 45 | 6 | 0 | 5.637452 | -0.131330 | -3.348827 |
| 46 | 1 | 0 | 5.141702 | -0.148175 | -4.316999 |
| 47 | 6 | 0 | 4.901666 | -0.105143 | -2.170164 |
| 48 | 6 | 0 | 3.395862 | -0.090841 | -1.992247 |
| 49 | 6 | 0 | 3.247662 | -0.072016 | -0.464557 |
| 50 | 6 | 0 | -0.602485 | -0.014305 | -3.112177 |
| 51 | 6 | 0 | -0.934224 | 0.039564 | -4.498223 |
| 52 | 6 | 0 | -1.827268 | -0.881252 | -5.064821 |
| 53 | 1 | 0 | -2.270154 | -1.646900 | -4.434103 |
| 54 | 6 | 0 | -2.155791 | -0.838327 | -6.416285 |
| 55 | 1 | 0 | -2.848098 | -1.571096 | -6.816098 |
| 56 | 6 | 0 | -1.593839 | 0.144968 | -7.235710 |
| 57 | 6 | 0 | -0.701983 | 1.074869 | -6.684029 |
| 58 | 1 | 0 | -0.273766 | 1.833101 | -7.333052 |
| 59 | 6 | 0 | -0.376092 | 1.021233 | -5.340711 |
| index | x   | y  | z   | v1  | v2  | v3  |
|-------|-----|----|-----|-----|-----|-----|
| 60    | 1   | 0  | 0.318229 | 1.746015 | -4.925257 |
| 61    | 6   | 0  | -2.742173 | -0.635641 | -9.156833 |
| 62    | 1   | 0  | -3.739923 | -0.572682 | -8.705295 |
| 63    | 1   | 0  | -2.373779 | -1.665962 | -9.079160 |
| 64    | 1   | 0  | -2.803752 | -0.353086 | -10.208588 |
| 65    | 6   | 0  | -1.994277 | -1.827279 | 9.045300  |
| 66    | 6   | 0  | 1.861842  | 1.573823  | 9.079965  |
| 67    | 6   | 0  | 3.295191  | 1.201613  | 8.666542  |
| 68    | 1   | 0  | 3.518148  | 0.158791  | 8.919647  |
| 69    | 1   | 0  | 4.015841  | 1.841183  | 9.190092  |
| 70    | 1   | 0  | 3.456840  | 1.330426  | 7.591021  |
| 71    | 6   | 0  | 1.751443  | 1.430025  | 10.600266 |
| 72    | 1   | 0  | 0.761153  | 1.721890  | 10.968377 |
| 73    | 1   | 0  | 2.488191  | 2.082740  | 11.081622 |
| 74    | 1   | 0  | 1.952881  | 0.403700  | 10.928562 |
| 75    | 6   | 0  | 1.592159  | 3.042873  | 8.713822  |
| 76    | 1   | 0  | 1.698775  | 3.220093  | 7.638204  |
| 77    | 1   | 0  | 2.302102  | 3.697797  | 9.233210  |
| 78    | 1   | 0  | 0.578297  | 3.339742  | 9.005783  |
| 79    | 6   | 0  | -3.421139 | -1.450483 | 8.614008  |
| 80    | 1   | 0  | -3.645912 | -0.408627 | 8.869488  |
| 81    | 1   | 0  | -4.150109 | -2.091582 | 9.124004  |
| 82    | 1   | 0  | -3.567822 | -1.573289 | 7.535653  |
| 83    | 6   | 0  | -1.904378 | -1.691221 | 10.567601 |
| 84    | 1   | 0  | -0.919559 | -1.986413 | 10.947606 |
| 85    | 1   | 0  | -2.648561 | -2.345142 | 11.035681 |
| 86    | 1   | 0  | -2.108618 | -0.666194 | 10.898152 |
| 87    | 6   | 0  | -1.722204 | -3.294978 | 8.675476  |
| 88    | 1   | 0  | -1.814570 | -3.466605 | 7.597634  |
| 89    | 1   | 0  | -2.440282 | -3.951221 | 9.181864  |
|   |   |   |     |     |     |
|---|---|---|-----|-----|-----|
| 90| 1 | 0 | -0.712920 | -3.595181 | 8.979605 |
| 91| 6 | 0 | 2.776632 | -1.354342 | -2.631587 |
| 92| 1 | 0 | 1.690654 | -1.303744 | -2.507122 |
| 93| 1 | 0 | 2.963858 | -1.303477 | -3.714617 |
| 94| 6 | 0 | 3.289872 | -2.688022 | -2.097237 |
| 95| 1 | 0 | 4.378032 | -2.756515 | -2.234717 |
| 96| 1 | 0 | 3.111257 | -2.744775 | -1.014335 |
| 97| 6 | 0 | 2.620617 | -3.879474 | -2.777190 |
| 98| 1 | 0 | 2.789031 | -3.821649 | -3.863164 |
| 99| 1 | 0 | 1.531298 | -3.814008 | -2.635156 |
|100| 6 | 0 | 3.114435 | -5.228353 | -2.263381 |
|101| 1 | 0 | 4.203197 | -5.296655 | -2.407853 |
|102| 1 | 0 | 2.948037 | -5.287080 | -1.177175 |
|103| 6 | 0 | 2.441816 | -6.419329 | -2.939627 |
|104| 1 | 0 | 2.607180 | -6.359047 | -4.024735 |
|105| 1 | 0 | 1.354462 | -6.350202 | -2.793732 |
|106| 6 | 0 | 2.942111 | -7.762212 | -2.420782 |
|107| 1 | 0 | 4.021446 | -7.870591 | -2.583654 |
|108| 1 | 0 | 2.443476 | -8.599436 | -2.922110 |
|109| 1 | 0 | 2.759525 | -7.861528 | -1.343745 |
|110| 6 | 0 | 2.805471 | 1.174781 | -2.655929 |
|111| 1 | 0 | 2.988124 | 1.095746 | -3.738265 |
|112| 1 | 0 | 1.719575 | 1.152425 | -2.526128 |
|113| 6 | 0 | 3.350935 | 2.507808 | -2.152887 |
|114| 1 | 0 | 3.169940 | 2.596051 | -1.072557 |
|115| 1 | 0 | 4.440804 | 2.546243 | -2.287791 |
|116| 6 | 0 | 2.713427 | 3.698074 | -2.864928 |
|117| 1 | 0 | 1.621656 | 3.659557 | -2.731178 |
|118| 1 | 0 | 2.890657 | 3.613004 | -3.947935 |
|119| 6 | 0 | 3.232064 | 5.047011 | -2.376088 |
Table S18. Optimized $^3$IL state of complex 1.

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
| 1             | 79            | 0           | -0.008307 0.009540 -0.001996 |
| 2             | 6             | 0           | -0.006560 -0.012111 2.061108 |
| 3             | 7             | 0           | 1.952548 -0.003598 0.314321 |
| 4             | 8             | 0           | -8.695390 0.088496 -1.236058 |
| 5             | 6             | 0           | -1.940565 0.023746 -0.307881 |
| 6             | 6             | 0           | -3.150029 0.034213 -0.496730 |
| 7             | 6             | 0           | -4.559625 0.047220 -0.712028 |
| 8             | 6             | 0           | -5.459652 0.044541 0.372173 |
| 9             | 1             | 0           | -5.068777 0.031641 1.385575 |
| 10            | 6             | 0           | -6.826906 0.058347 0.164432 |
| 11            | 1             | 0           | -7.520047 0.056502 1.000512 |
| 12            | 6             | 0           | -7.345812 0.075408 -1.137594 |
| 13            | 6             | 0           | -6.469898 0.077893 -2.227301 |
| 14            | 1             | 0           | -6.843966 0.090641 -3.245076 |
|   |   |   |       |       |       |
|---|---|---|-------|-------|-------|
|15 | 6 | 0 | -5.096165 | 0.063965 | -2.008010 |
|16 | 1 | 0 | -4.421785 | 0.066211 | -2.859695 |
|17 | 6 | 0 | -1.058691 | -0.016764 | 2.974647 |
|18 | 1 | 0 | -2.082996 | -0.008436 | 2.610601 |
|19 | 6 | 0 | -0.813782 | -0.032160 | 4.348939 |
|20 | 1 | 0 | -1.648492 | -0.035536 | 5.045783 |
|21 | 6 | 0 | 0.494325  | -0.043380 | 4.838743 |
|22 | 1 | 0 | 0.676485  | -0.055366 | 5.909382 |
|23 | 6 | 0 | 1.564458  | -0.039224 | 3.954230 |
|24 | 1 | 0 | 2.579787  | -0.048045 | 4.341360 |
|25 | 6 | 0 | 1.325490  | -0.023712 | 2.573568 |
|26 | 6 | 0 | 2.394885  | -0.018485 | 1.574993 |
|27 | 6 | 0 | 3.781795  | -0.027364 | 1.813463 |
|28 | 1 | 0 | 4.161267  | -0.038940 | 2.827966 |
|29 | 6 | 0 | 4.678155  | -0.021064 | 0.710594 |
|30 | 1 | 0 | 5.747247  | -0.028650 | 0.894442 |
|31 | 6 | 0 | 4.199576  | -0.005618 | -0.573205 |
|32 | 1 | 0 | 4.882200  | -0.001241 | -1.416127 |
|33 | 6 | 0 | 2.783860  | 0.004439  | -0.812610 |
|34 | 6 | 0 | 2.098244  | 0.021405  | -2.024581 |
|35 | 6 | 0 | 2.737215  | 0.033081  | -3.317571 |
|36 | 1 | 0 | 3.821033  | 0.029553  | -3.387259 |
|37 | 6 | 0 | 1.977331  | 0.048871  | -4.450418 |
|38 | 1 | 0 | 2.459817  | 0.057646  | -5.423878 |
|39 | 6 | 0 | 0.551800  | 0.054256  | -4.381179 |
|40 | 1 | 0 | -0.027437 | 0.066815  | -5.299713 |
|41 | 6 | 0 | -0.096264 | 0.043664  | -3.137461 |
|42 | 1 | 0 | -1.182936 | 0.048219  | -3.102285 |
|43 | 6 | 0 | 0.615588  | 0.027596  | -1.952816 |
|44 | 6 | 0 | -9.264285 | 0.107296  | -2.530324 |
Table S19. Optimized \(^3\)IL state of complex 2.

| Center Number | Atomic Number | Atomic Type | X     | Y     | Z     |
|---------------|---------------|-------------|-------|-------|-------|
| 1             | 79            | 0           | -0.064775 | 0.018658 | 0.006848 |
| 2             | 7             | 0           | -0.062408 | 0.020342 | 1.998853 |
| 3             | 6             | 0           | 1.979370  | -0.013737| 0.332691 |
| 4             | 6             | 0           | 3.025655  | -0.036032| -0.568605|
| 5             | 1             | 0           | 2.813286  | -0.036340| -1.636018|
| 6             | 6             | 0           | 4.413647  | -0.060133| -0.158471|
| 7             | 6             | 0           | 5.445391  | -0.084657| -1.077850|
| 8             | 1             | 0           | 5.210420  | -0.086362| -2.139674|
| 9             | 6             | 0           | 6.805033  | -0.107543| -0.662688|
| 10            | 1             | 0           | 7.594392  | -0.126653| -1.407406|
| 11            | 6             | 0           | 7.104919  | -0.104985| 0.686265 |
| 12            | 1             | 0           | 8.139229  | -0.122200| 1.017613 |
| 13            | 6             | 0           | 6.075727  | -0.080262| 1.639633 |
| 14            | 1             | 0           | 6.317763  | -0.078747| 2.699376 |
| 15            | 6             | 0           | 4.714987  | -0.057790| 1.247281 |
| 16            | 6             | 0           | 3.666413  | -0.033602| 2.173272 |
| 17            | 1             | 0           | 3.898742  | -0.029659| 3.234232 |
| 18            | 6             | 0           | 2.266880  | -0.013551| 1.729360 |
| 19            | 6             | 0           | 1.160692  | 0.006469 | 2.621378 |
| 20            | 6             | 0           | 1.170635  | 0.004295 | 4.031829 |
| 21            | 1             | 0           | 2.114733  | -0.038485| 4.563363 |
|   |   |   |   |   |   |
|---|---|---|---|---|---|
| 22 | 6 | 0 | -0.026093 | 0.016682 | 4.742282 |
| 23 | 6 | 0 | -1.250571 | 0.030596 | 4.034584 |
| 24 | 1 | 0 | -2.189058 | 0.072487 | 4.574577 |
| 25 | 6 | 0 | -1.241559 | 0.032250 | 2.642470 |
| 26 | 6 | 0 | -2.397292 | 0.052916 | 1.728619 |
| 27 | 6 | 0 | -3.721424 | 0.073098 | 2.174824 |
| 28 | 1 | 0 | -3.946413 | 0.074258 | 3.238338 |
| 29 | 6 | 0 | -4.765064 | 0.092278 | 1.253707 |
| 30 | 1 | 0 | -5.793482 | 0.108441 | 1.603362 |
| 31 | 1 | 0 | -5.304174 | 0.105753 | -0.829553 |
| 32 | 6 | 0 | -4.487662 | 0.090810 | -0.111625 |
| 33 | 6 | 0 | -3.164869 | 0.069986 | -0.563205 |
| 34 | 1 | 0 | -2.960416 | 0.068667 | -1.631084 |
| 35 | 6 | 0 | -2.103387 | 0.050949 | 0.336825 |
| 36 | 6 | 0 | -0.056558 | 0.016415 | -1.947883 |
| 37 | 6 | 0 | -0.035049 | 0.013899 | -3.172092 |
| 38 | 6 | 0 | -0.005027 | 0.010990 | -4.597414 |
| 39 | 6 | 0 | -1.188992 | 0.037225 | -5.349266 |
| 40 | 1 | 0 | -2.143803 | 0.060167 | -4.831762 |
| 41 | 6 | 0 | -1.168016 | 0.034537 | -6.740119 |
| 42 | 1 | 0 | -2.105764 | 0.055417 | -7.284397 |
| 43 | 6 | 0 | 0.056436 | 0.005045 | -7.414750 |
| 44 | 6 | 0 | 1.249427 | -0.021392 | -6.679063 |
| 45 | 1 | 0 | 2.192116 | -0.044183 | -7.217774 |
| 46 | 6 | 0 | 1.218027 | -0.018424 | -5.296641 |
| 47 | 1 | 0 | 2.148505 | -0.039117 | -4.736512 |
| 48 | 8 | 0 | 0.192315 | -0.000319 | -8.760567 |
| 49 | 6 | 0 | -0.984233 | 0.023718 | -9.544889 |
| 50 | 1 | 0 | -0.653000 | 0.013879 | -10.584060 |
| 51 | 1 | 0 | -1.609755 | -0.857018 | -9.355047 |
52  1  0  -1.570437  0.932034  -9.359535
53  6  0  -0.022297  0.008481   6.220767
54  6  0  -0.979460  -0.727506   6.925988
55  6  0   0.937773   0.734617   6.932292
56  6  0  -0.989761  -0.755520   8.322250
57  1  0  -1.707230  -1.310257   6.367402
58  6  0   0.959256   0.736086   8.328528
59  1  0   1.658784   1.330182   6.378402
60  6  0  -0.012541  -0.016260   8.998571
61  1  0  -0.009042  -0.025474  10.081324
62  6  0  -2.043986  -1.591834   9.054244
63  6  0  -3.448363  -1.129433  10.576445
64  6  0  -1.862263  -3.072510   8.681073
65  6  0  -1.938328  -1.463979  10.576445
66  1  0  -3.606742  -0.075275   8.887189
67  1  0  -3.609939  -1.244831   7.555377
68  1  0  -4.211797  -1.723493   9.149032
69  1  0  -0.871730  -3.432998   8.981590
70  1  0  -2.616844  -3.685566   9.188629
71  1  0  -1.967541  -3.235793   7.603139
72  1  0  -2.718316  -2.072590  11.047538
73  1  0  -0.971398  -1.818355  10.951758
74  1  0  -2.079161  -0.428954  10.909066
75  6  0  2.017735  1.560346   9.068014
76  6  0  3.419463  1.107754   8.627196
77  6  0  1.831640  3.047493   8.724111
78  6  0  1.923574  1.404170  10.588347
79  1  0  3.581568  0.049657   8.862642
80  1  0  3.572062  1.241677   7.550981
81  1  0  4.186090  1.694257   9.147686
Table S20. Optimized $^3$I state of complex 3-exo.

| Center Number | Atomic Number | Atomic Type | X     | Y     | Z     |
|--------------|---------------|-------------|-------|-------|-------|
| 1            | 79            | 0           | 0.014062 | -0.018325 | -0.011838 |
| 2            | 7             | 0           | 0.013628 | -0.026455 | 1.975212  |
| 3            | 6             | 0           | 2.045165 | -0.016403 | 0.292460  |
| 4            | 6             | 0           | 0.013952 | -0.009457 | -1.968938 |
| 5            | 6             | 0           | -3.084980 | -0.015835 | -0.591285 |
| 6            | 1             | 0           | -2.876826 | -0.014137 | -1.658516 |
| 7            | 6             | 0           | -4.407593 | -0.015531 | -0.144027 |
| 8            | 1             | 0           | -5.222484 | -0.013804 | -0.864068 |
| 9            | 1             | 0           | -5.720356 | -0.016834 | 1.567556  |
| 10           | 6             | 0           | -4.690364 | -0.017112 | 1.222113  |
| 11           | 6             | 0           | -3.651107 | -0.019134 | 2.145870  |
| 12           | 1             | 0           | -3.880127 | -0.020000 | 3.208572  |
| 13           | 6             | 0           | -2.323842 | -0.020176 | 1.703565  |
| 14           | 6             | 0           | -1.171281 | -0.021812 | 2.616193  |
| 15           | 6             | 0           | -1.187898 | -0.025331 | 4.006480  |
| 16           | 1             | 0           | -2.132732 | -0.052103 | 4.536819  |
| 17           | 6             | 0           | 0.032231  | -0.037359 | 4.736316  |
| 18           | 6             | 0           | 1.228259  | -0.040628 | 4.033652  |
| 19 | 1  | 0  | 2.169853 | -0.019808 | 4.571721 |
| 20 | 6  | 0  | 1.235983 | -0.033639 | 2.620183 |
| 21 | 6  | 0  | 2.349068 | -0.022688 | 1.751758 |
| 22 | 6  | 0  | 3.714058 | -0.014225 | 2.203255 |
| 23 | 1  | 0  | 3.937899 | -0.015101 | 3.267108 |
| 24 | 6  | 0  | 4.712874 | -0.000388 | 1.283823 |
| 25 | 6  | 0  | 4.423098 | 0.000749  | -0.142294|
| 26 | 6  | 0  | 3.079378 | -0.006908 | -0.601807|
| 27 | 1  | 0  | 2.869829 | -0.003005 | -1.669095|
| 28 | 6  | 0  | 5.653743 | 0.013537  | -0.849079|
| 29 | 6  | 0  | 5.915022 | 0.016946  | -2.236987|
| 30 | 1  | 0  | 5.098155 | 0.009025  | -2.953192|
| 31 | 6  | 0  | 7.231006 | 0.030030  | -2.665893|
| 32 | 1  | 0  | 7.452404 | 0.032603  | -3.729414|
| 33 | 6  | 0  | 8.288378 | 0.039992  | -1.741185|
| 34 | 1  | 0  | 9.313303 | 0.050233  | -2.100776|
| 35 | 6  | 0  | 8.037663 | 0.037028  | -0.361710|
| 36 | 1  | 0  | 8.867772 | 0.045399  | 0.340519 |
| 37 | 6  | 0  | 6.729849 | 0.023797  | 0.083815 |
| 38 | 6  | 0  | 0.032940 | 0.008743  | -4.619222|
| 39 | 6  | 0  | 1.246388 | 0.037874  | -5.334809|
| 40 | 6  | 0  | 1.259976 | 0.048630  | -6.717822|
| 41 | 1  | 0  | 2.195929 | 0.071333  | -7.268270|
| 42 | 6  | 0  | 0.057962 | 0.030386  | -7.438338|
| 43 | 6  | 0  | -1.157253| 0.001059  | -6.747821|
| 44 | 1  | 0  | -2.102236| -0.013764 | -7.279742|
| 45 | 6  | 0  | -1.160186| -0.009342 | -5.356524|
| 46 | 1  | 0  | -2.108569| -0.031957 | -4.827224|
| 47 | 1  | 0  | 2.184482 | 0.052307  | -4.787083|
| 48 | 6  | 0  | 0.020723 | -0.001363 | -3.193093|
| Index | Type | Mass | Xcoordinate | Ycoordinate | Zcoordinate |
|-------|------|------|-------------|-------------|-------------|
| 49    | 6    | 0    | 6.214609    | 0.020132    | 1.513762    |
| 50    | 6    | 0    | 6.631569    | -7.636955   | 2.113423    |
| 51    | 1    | 0    | 6.996763    | -8.466050   | 2.729849    |
| 52    | 1    | 0    | 7.072790    | -7.744029   | 1.114948    |
| 53    | 1    | 0    | 5.545903    | -7.752242   | 2.008259    |
| 54    | 6    | 0    | 6.982659    | -6.286598   | 2.726524    |
| 55    | 1    | 0    | 8.072150    | -6.210939   | 2.851528    |
| 56    | 1    | 0    | 6.555220    | -6.219151   | 3.737048    |
| 57    | 6    | 0    | 6.490370    | -5.106334   | 1.894151    |
| 58    | 1    | 0    | 6.918763    | -5.171931   | 0.882927    |
| 59    | 1    | 0    | 5.400132    | -5.181655   | 1.767383    |
| 60    | 6    | 0    | 6.835213    | -3.750115   | 2.501761    |
| 61    | 1    | 0    | 7.925693    | -3.674478   | 2.626983    |
| 62    | 1    | 0    | 6.407803    | -3.686530   | 3.513633    |
| 63    | 6    | 0    | 6.338956    | -2.571848   | 1.668483    |
| 64    | 1    | 0    | 6.768645    | -2.634036   | 0.659176    |
| 65    | 1    | 0    | 5.249377    | -2.647894   | 1.546370    |
| 66    | 6    | 0    | 6.691402    | -1.226064   | 2.293416    |
| 67    | 1    | 0    | 7.781916    | -1.152562   | 2.412149    |
| 68    | 1    | 0    | 6.269339    | -1.171982   | 3.307078    |
| 69    | 6    | 0    | 6.652075    | 1.287151    | 2.284179    |
| 70    | 1    | 0    | 6.227118    | 1.228817    | 3.296373    |
| 71    | 1    | 0    | 7.743745    | 1.247078    | 2.407293    |
| 72    | 6    | 0    | 6.261728    | 2.616124    | 1.646014    |
| 73    | 1    | 0    | 6.697279    | 2.684600    | 0.639624    |
| 74    | 1    | 0    | 5.171335    | 2.655585    | 1.514243    |
| 75    | 6    | 0    | 6.710178    | 3.817854    | 2.473363    |
| 76    | 1    | 0    | 6.278745    | 3.740011    | 3.481041    |
| 77    | 1    | 0    | 7.802415    | 3.784671    | 2.604530    |
| 78    | 6    | 0    | 6.806351    | 6.383148    | 2.605270    |
|    |   |   | 1st Column | 2nd Column | 3rd Column |
|----|---|---|------------|------------|------------|
| 79 | 1 | 0 | 7.900738   | 6.340107   | 2.701433   |
| 80 | 1 | 0 | 6.589163   | 7.277297   | 2.005951   |
| 81 | 6 | 0 | 6.321038   | 5.151386   | 1.839861   |
| 82 | 1 | 0 | 5.226451   | 5.197480   | 1.737311   |
| 83 | 1 | 0 | 6.723875   | 5.186069   | 0.817690   |
| 84 | 6 | 0 | 6.179603   | 6.548793   | 3.986068   |
| 85 | 1 | 0 | 6.514981   | 7.476598   | 4.463007   |
| 86 | 1 | 0 | 6.441741   | 5.722420   | 4.656191   |
| 87 | 1 | 0 | 5.085205   | 6.585958   | 3.917547   |
| 88 | 6 | 0 | -2.023639  | -0.018355  | 0.311913   |
| 89 | 8 | 0 | 0.176467   | 0.043003   | -8.786652  |
| 90 | 6 | 0 | -1.010534  | 0.027314   | -9.554605  |
| 91 | 1 | 0 | -1.630744  | 0.908973   | -9.351487  |
| 92 | 1 | 0 | -0.693904  | 0.041858   | -10.598329 |
| 93 | 1 | 0 | -1.597594  | -0.879979  | -9.366421  |
| 94 | 6 | 0 | 0.018723   | -0.037998  | 6.213300   |
| 95 | 6 | 0 | 0.963263   | -0.777376  | 6.933009   |
| 96 | 6 | 0 | -0.938730  | 0.703216   | 6.913633   |
| 97 | 6 | 0 | 0.971577   | -0.784035  | 8.329211   |
| 98 | 1 | 0 | 1.682423   | -1.380277  | 6.384517   |
| 99 | 6 | 0 | -0.963251  | 0.724674   | 8.309876   |
|100 | 1 | 0 | -1.655630  | 1.296257   | 6.351578   |
|101 | 6 | 0 | 0.000293   | -0.025761  | 8.993498   |
|102 | 1 | 0 | -0.007496  | -0.021693  | 10.076229  |
|103 | 6 | 0 | -2.016754  | 1.568195   | 9.034843   |
|104 | 6 | 0 | -1.815867  | 3.048792   | 8.671149   |
|105 | 6 | 0 | -3.421366  | 1.122798   | 8.596122   |
|106 | 6 | 0 | -1.928508  | 1.432115   | 10.557429  |
|107 | 1 | 0 | -0.824553  | 3.397379   | 8.982955   |
|108 | 1 | 0 | -1.908882  | 3.218524   | 7.593077   |
| Center | Atomic Number | Atomic Number | Type | X     | Y     | Z     |
|--------|---------------|---------------|------|-------|-------|-------|
| 109    | 1             | 0             | 0    | -2.568819 | 3.667372 | 9.174461 |
| 110    | 1             | 0             | 0    | -3.594043 | 0.069571 | 8.845448 |
| 111    | 1             | 0             | 0    | -4.183927 | 1.723467 | 9.106360 |
| 112    | 1             | 0             | 0    | -3.569800 | 1.243440 | 7.517788 |
| 113    | 1             | 0             | 0    | -2.707483 | 2.045907 | 11.023484 |
| 114    | 1             | 0             | 0    | -2.082378 | 0.396869 | 10.883495 |
| 115    | 1             | 0             | 0    | -0.962154 | 1.775319 | 10.944478 |
| 116    | 6             | 0             | 0    | 2.013400 | -1.623574 | 9.075442 |
| 117    | 6             | 0             | 0    | 1.809737 | -3.107496 | 8.727360 |
| 118    | 6             | 0             | 0    | 3.424805 | -1.189831 | 8.646884 |
| 119    | 6             | 0             | 0    | 1.909542 | -1.468955 | 10.595322 |
| 120    | 1             | 0             | 0    | 0.813392 | -3.447795 | 9.032085 |
| 121    | 1             | 0             | 0    | 1.913951 | -3.290700 | 7.652503 |
| 122    | 1             | 0             | 0    | 2.554083 | -3.723316 | 9.246624 |
| 123    | 1             | 0             | 0    | 3.599813 | -0.134552 | 8.885785 |
| 124    | 1             | 0             | 0    | 4.178979 | -1.787999 | 9.172328 |
| 125    | 1             | 0             | 0    | 3.584195 | -1.323776 | 7.571653 |
| 126    | 1             | 0             | 0    | 2.681639 | -2.079478 | 11.076909 |
| 127    | 1             | 0             | 0    | 2.063040 | -0.430356 | 10.910810 |
| 128    | 1             | 0             | 0    | 0.938163 | -1.804767 | 10.976094 |

Table S21. Optimized $^3$IL state of complex 3-endo.
|   |   |   | x   | y   | z   |
|---|---|---|-----|-----|-----|
| 5 | 8 | 0 | -2.052723 | 0.257162 | -8.541897 |
| 6 | 6 | 0 | -2.043829 | -0.039108 | 0.326712  |
| 7 | 6 | 0 | -3.106802 | -0.072070 | -0.573417 |
| 8 | 1 | 0 | -2.902911 | -0.059343 | -1.640149 |
| 9 | 6 | 0 | -4.426372 | -0.120947 | -0.120262 |
| 10| 1 | 0 | -5.241891 | -0.145087 | -0.839135 |
| 11| 6 | 0 | -4.705661 | -0.139694 | 1.245928  |
| 12| 1 | 0 | -5.733571 | -0.178158 | 1.595233  |
| 13| 6 | 0 | -3.662806 | -0.109838 | 2.163985  |
| 14| 1 | 0 | -3.885361 | -0.127151 | 3.227651  |
| 15| 6 | 0 | -2.338103 | -0.059512 | 1.715950  |
| 16| 6 | 0 | -1.184659 | -0.026932 | 2.619052  |
| 17| 6 | 0 | -1.208282 | -0.027195 | 4.008199  |
| 18| 1 | 0 | -2.156747 | -0.031489 | 4.532435  |
| 19| 6 | 0 | 0.005158  | 0.022745  | 4.742909  |
| 20| 6 | 0 | 1.199416  | 0.072125  | 4.040030  |
| 21| 1 | 0 | 2.136541  | 0.079940  | 4.584453  |
| 22| 6 | 0 | 1.210516  | 0.069856  | 2.625731  |
| 23| 6 | 0 | -0.011695 | 0.013165  | 6.219394  |
| 24| 6 | 0 | -0.946156 | -0.764351 | 6.911449  |
| 25| 1 | 0 | -1.640592 | -1.377396 | 6.342695  |
| 26| 6 | 0 | -0.975038 | -0.795753 | 8.307348  |
| 27| 6 | 0 | -0.040548 | -0.016817 | 8.999472  |
| 28| 1 | 0 | -0.052596 | -0.027707 | 10.082134 |
| 29| 6 | 0 | 0.906819  | 0.778245  | 8.343631  |
| 30| 6 | 0 | 0.904715  | 0.779341  | 6.947380  |
| 31| 1 | 0 | 1.605618  | 1.409208  | 6.405606  |
| 32| 6 | 0 | 2.330038  | 0.104064  | 1.768057  |
| 33| 6 | 0 | 3.665221  | 0.172635  | 2.321501  |
| 34| 1 | 0 | 3.795528  | 0.240255  | 3.396422  |
|   |   |   |        |        |        |
|---|---|---|--------|--------|--------|
| 35| 6 | 0 | 4.749037| 0.146728| 1.513792|
| 36| 1 | 0 | 5.754369| 0.191458| 1.922638|
| 37| 6 | 0 | 4.546733| 0.060590| 0.099241|
| 38| 6 | 0 | 5.533317| 0.002452| -0.911047|
| 39| 6 | 0 | 6.944410| -0.002480| -0.824383|
| 40| 1 | 0 | 7.443648| 0.043859| 0.139353|
| 41| 6 | 0 | 7.677551| -0.070219| -1.995830|
| 42| 1 | 0 | 8.763151| -0.076224| -1.954939|
| 43| 6 | 0 | 7.033555| -0.132401| -3.243763|
| 44| 1 | 0 | 7.630017| -0.185161| -4.150173|
| 45| 6 | 0 | 5.634140| -0.127162| -3.33956|
| 46| 1 | 0 | 5.152610| -0.174788| -4.307693|
| 47| 6 | 0 | 4.887520| -0.060248| -2.173163|
| 48| 6 | 0 | 3.380937| -0.033036| -2.008489|
| 49| 6 | 0 | 3.218689| 0.032351 | -0.482292|
| 50| 6 | 0 | -0.616071| 0.081337| -3.136420|
| 51| 6 | 0 | -0.959047| 0.112044| -4.520556|
| 52| 6 | 0 | -0.196007| -0.578572| -5.473586|
| 53| 1 | 0 | 0.671675| -1.144705| -5.147207|
| 54| 6 | 0 | -0.527524| -0.558371| -6.824884|
| 55| 1 | 0 | 0.086921| -1.108437| -7.529218|
| 56| 6 | 0 | -1.641747| 0.168201| -7.254978|
| 57| 6 | 0 | -2.413076| 0.866918| -6.316423|
| 58| 1 | 0 | -3.275429| 1.427241| -6.665636|
| 59| 6 | 0 | -2.078811| 0.836743| -4.974427|
| 60| 1 | 0 | -2.685095| 1.381282| -4.256053|
| 61| 6 | 0 | -1.308344| -0.436853| -9.522943|
| 62| 1 | 0 | -1.308999| -1.517838| -9.336229|
| 63| 1 | 0 | -0.272817| -0.077797| -9.569433|
| 64| 1 | 0 | -1.802517| -0.235198| -10.474266|
|   |   |   |         |         |         |
|---|---|---|---------|---------|---------|
| 65| 6 | 0 |-2.001156| -1.680209|  9.022828|
| 66| 6 | 0 | 1.915815 |  1.648932|  9.099260|
| 67| 6 | 0 | 3.343510 |  1.262064|  8.679950|
| 68| 1 | 0 | 3.551695 |  0.213000|  8.919680|
| 69| 1 | 0 | 4.074002 |  1.884590|  9.210562|
| 70| 1 | 0 | 3.505534 |  1.401630|  7.605844|
| 71| 6 | 0 | 1.805638 |  1.487518| 10.617929|
| 72| 1 | 0 | 0.820685 |  1.790274| 10.991493|
| 73| 1 | 0 | 2.553437 |  2.122091| 11.106682|
| 74| 1 | 0 | 1.990769 |  0.453863| 10.932630|
| 75| 6 | 0 | 1.667198 |  3.126473|  8.753128|
| 76| 1 | 0 | 1.775021 |  3.316151|  7.679755|
| 77| 1 | 0 | 2.386655 |  3.764630|  9.280444|
| 78| 1 | 0 | 0.657775 |  3.433654|  9.049865|
| 79| 6 | 0 | -3.419171|  -1.279387|  8.584313|
| 80| 1 | 0 | -3.629099|  -0.235284|  8.843324|
| 81| 1 | 0 | -4.161704|  -1.911239|  9.086392|
| 82| 1 | 0 | -3.560479|  -1.394490|  7.504430|
| 83| 6 | 0 | -1.920444|  -1.554019| 10.546562|
| 84| 1 | 0 | -0.943589|  -1.867583| 10.932416|
| 85| 1 | 0 | -2.679042|  -2.197648| 11.005882|
| 86| 1 | 0 | -2.109491|  -0.527252| 10.880788|
| 87| 6 | 0 | -1.749645|  -3.150130|  8.647208|
| 88| 1 | 0 | -1.836017|  -3.313921|  7.567668|
| 89| 1 | 0 | -2.481525|  -3.798293|  9.144385|
| 90| 1 | 0 | -0.747347|  -3.467517|  8.957151|
| 91| 6 | 0 |  2.762719|  -1.313610| -2.610965|
| 92| 1 | 0 |  1.676550|  -1.255263| -2.492119|
| 93| 1 | 0 |  2.958125|  -1.297230| -3.694011|
| 94| 6 | 0 |  3.273253|  -2.628401| -2.029478|
|    |    |    |          |          |          |
|----|----|----|----------|----------|----------|
| 95 | 1  | 0  | 4.362317 | -2.701284| -2.159884|
| 96 | 1  | 0  | 3.088793 | -2.647115| -0.946141|
| 97 | 6  | 0  | 2.607625 | -3.842712| -2.671196|
| 98 | 1  | 0  | 2.775155 | -3.818052| -3.758702|
| 99 | 1  | 0  | 1.518451 | -3.776799| -2.529646|
|100 | 6  | 0  | 3.108055 | -5.172627| -2.116065|
|101 | 1  | 0  | 4.197057 | -5.240088| -2.259279|
|102 | 1  | 0  | 2.942395 | -5.198282| -1.028593|
|103 | 6  | 0  | 2.440734 | -6.387198| -2.754559|
|104 | 1  | 0  | 2.603528 | -6.358840| -3.841381|
|105 | 1  | 0  | 1.353404 | -6.319933| -2.608245|
|106 | 6  | 0  | 2.950040 | -7.710759| -2.196396|
|107 | 1  | 0  | 4.029721 | -7.817722| -2.357958|
|108 | 1  | 0  | 2.455425 | -8.565502| -2.671371|
|109 | 1  | 0  | 2.769715 | -7.778751| -1.116585|
|110 | 6  | 0  | 2.805851 | 1.218453 | -2.709676|
|111 | 1  | 0  | 3.000326 | 1.113465 | -3.787566|
|112 | 1  | 0  | 1.718732 | 1.204206 | -2.588573|
|113 | 6  | 0  | 3.357621 | 2.556292 | -2.226727|
|114 | 1  | 0  | 3.162217 | 2.666658 | -1.150743|
|115 | 1  | 0  | 4.449976 | 2.582491 | -2.347781|
|116 | 6  | 0  | 2.741182 | 3.738792 | -2.969150|
|117 | 1  | 0  | 1.647619 | 3.710807 | -2.851361|
|118 | 1  | 0  | 2.933399 | 3.633315 | -4.047483|
|119 | 6  | 0  | 3.264091 | 5.091091 | -2.494549|
|120 | 1  | 0  | 3.072972 | 5.196151 | -1.415985|
|121 | 1  | 0  | 4.357660 | 5.121649 | -2.613685|
|122 | 6  | 0  | 2.644845 | 6.274880 | -3.231638|
|123 | 1  | 0  | 1.552545 | 6.241671 | -3.113394|
|124 | 1  | 0  | 2.837199 | 6.170635 | -4.308903|
Table S22. Optimized $^3$LLCT state of complex 1.

| Center Number | Atomic Number | Atomic Type | X     | Y     | Z     |
|---------------|---------------|-------------|-------|-------|-------|
| 1             | 79            | 0           | -0.018347 | -0.024757 | -0.022465 |
| 2             | 6             | 0           | -0.017241  | 0.153699  | 2.044697  |
| 3             | 7             | 0           | 1.933000   | 0.002689   | 0.308858   |
| 4             | 8             | 0           | -8.558832  | -0.334461  | -1.525588  |
| 5             | 6             | 0           | -1.911320  | -0.059789  | -0.345502  |
| 6             | 6             | 0           | -3.137214  | -0.086833  | -0.559892  |
| 7             | 6             | 0           | -4.503741  | -0.125340  | -0.802177  |
| 8             | 6             | 0           | -5.211719  | -1.363174  | -0.793789  |
| 9             | 1             | 0           | -4.665691  | -2.278736  | -0.592238  |
| 10            | 6             | 0           | -6.558113  | -1.394942  | -1.036750  |
| 11            | 1             | 0           | -7.114942  | -2.326064  | -1.035140  |
| 12            | 6             | 0           | -7.260936  | -0.193639  | -1.300969  |
| 13            | 6             | 0           | -6.579968  | 1.043535   | -1.313127  |
| 14            | 1             | 0           | -7.109737  | 1.967286   | -1.513366  |
| 15            | 6             | 0           | -5.227524  | 1.070790   | -1.067178  |
| 16            | 1             | 0           | -4.691992  | 2.014463   | -1.073533  |
| 17            | 6             | 0           | -1.107025  | 0.229838   | 2.915633   |
| 18            | 1             | 0           | -2.119864  | 0.197420   | 2.523453   |
| 19            | 6             | 0           | -0.909598  | 0.348175   | 4.290446   |
|   |   |   |   |   |   |
|---|---|---|---|---|---|
| 20 | 1 | 0 | -1.766781 | 0.406598 | 4.956811 |
| 21 | 6 | 0 | 0.389219  | 0.391640 | 4.810660 |
| 22 | 1 | 0 | 0.543447  | 0.483795 | 5.882606 |
| 23 | 6 | 0 | 1.483453  | 0.317327 | 3.963186 |
| 24 | 1 | 0 | 2.487802  | 0.351521 | 4.379046 |
| 25 | 6 | 0 | 1.304388  | 0.197942 | 2.573482 |
| 26 | 6 | 0 | 2.385680  | 0.115089 | 1.612742 |
| 27 | 6 | 0 | 3.749608  | 0.135043 | 1.843809 |
| 28 | 1 | 0 | 4.120718  | 0.221844 | 2.860305 |
| 29 | 6 | 0 | 4.647257  | 0.043411 | 0.769603 |
| 30 | 1 | 0 | 5.717015  | 0.059193 | 0.951119 |
| 31 | 6 | 0 | 4.157222  | -0.068291 | -0.540171 |
| 32 | 1 | 0 | 4.845555  | -0.138995 | -1.376718 |
| 33 | 6 | 0 | 2.793470  | -0.088606 | -0.772340 |
| 34 | 6 | 0 | 2.092538  | -0.195680 | -2.035757 |
| 35 | 6 | 0 | 2.723390  | -0.301875 | -3.288097 |
| 36 | 1 | 0 | 3.809236  | -0.308806 | -3.349127 |
| 37 | 6 | 0 | 1.972754  | -0.397775 | -4.449325 |
| 38 | 1 | 0 | 2.474835  | -0.479191 | -5.409870 |
| 39 | 6 | 0 | 0.574386  | -0.389985 | -4.387581 |
| 40 | 1 | 0 | -0.012818 | -0.465108 | -5.299584 |
| 41 | 6 | 0 | -0.068827 | -0.286252 | -3.155319 |
| 42 | 1 | 0 | -1.154806 | -0.281528 | -3.119530 |
| 43 | 6 | 0 | 0.669768  | -0.188790 | -1.973466 |
| 44 | 6 | 0 | -9.356093 | 0.814839  | -1.805453 |
| 45 | 1 | 0 | -10.367345 | 0.437724  | -1.949755 |
| 46 | 1 | 0 | -9.011497 | 1.310829  | -2.717709 |
| 47 | 1 | 0 | -9.337305 | 1.512715  | -0.963078 |

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**Table S23.** Optimized $^3$LLCT state of complex 3-endo.
| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
| 1             | 79            | 0           | 0.015212 -0.018864 -0.007959 |
| 2             | 7             | 0           | 0.009539 -0.014986 1.969964 |
| 3             | 6             | 0           | 2.114780 -0.000814 0.357798 |
| 4             | 6             | 0           | -0.248915 -0.017403 -1.913068 |
| 5             | 8             | 0           | -2.147165 0.023195 -8.395920 |
| 6             | 6             | 0           | -2.038704 -0.048332 0.338203 |
| 7             | 6             | 0           | -3.091132 -0.055468 -0.580920 |
| 8             | 6             | 0           | -2.886553 -0.048639 -1.647016 |
| 9             | 6             | 0           | -4.415563 -0.070693 -0.147857 |
| 10            | 1             | 0           | -5.221017 -0.076062 -0.878117 |
| 11            | 6             | 0           | -4.706750 -0.078180 1.219433 |
| 12            | 1             | 0           | -5.739116 -0.088392 1.558672 |
| 13            | 6             | 0           | -3.676985 -0.071403 2.147165 |
| 14            | 1             | 0           | -3.912069 -0.076177 3.208661 |
| 15            | 6             | 0           | -2.336293 -0.057251 1.728045 |
| 16            | 6             | 0           | -1.202159 -0.054626 2.632652 |
| 17            | 6             | 0           | -1.220980 -0.084195 4.009368 |
| 18            | 6             | 0           | -2.176521 -0.087394 4.523297 |
| 19            | 6             | 0           | -0.020198 -0.066562 4.757531 |
| 20            | 6             | 0           | 1.191439 -0.021386 4.033551 |
| 21            | 1             | 0           | 2.133148 -0.044560 4.570874 |
| 22            | 6             | 0           | 1.205001 -0.002828 2.651924 |
| 23            | 6             | 0           | -0.034027 -0.106266 6.225792 |
| 24            | 6             | 0           | -1.067137 -0.755133 6.919803 |
| 25            | 1             | 0           | -1.844696 -1.255184 6.348371 |
| 26            | 6             | 0           | -1.097381 -0.811653 8.313660 |
|   |   |   | x-coordinate | y-coordinate | z-coordinate |
|---|---|---|--------------|--------------|--------------|
| 27 | 6 | 0 | -0.056696    | -0.198500    | 9.021850     |
| 28 | 1 | 0 | -0.064404    | -0.236052    | 10.103768    |
| 29 | 6 | 0 | 0.993921     | 0.461511     | 8.372311     |
| 30 | 6 | 0 | 0.985828     | 0.498019     | 6.977330     |
| 31 | 1 | 0 | 1.771600     | 1.034867     | 6.452382     |
| 32 | 6 | 0 | 2.356231     | 0.012791     | 1.773303     |
| 33 | 6 | 0 | 3.663742     | 0.038402     | 2.291012     |
| 34 | 1 | 0 | 3.816461     | 0.055128     | 3.366527     |
| 35 | 6 | 0 | 4.758090     | 0.041762     | 1.452318     |
| 36 | 1 | 0 | 5.766423     | 0.059184     | 1.857913     |
| 37 | 6 | 0 | 4.540684     | 0.020513     | 0.073812     |
| 38 | 6 | 0 | 5.533518     | 0.012477     | -0.991999    |
| 39 | 6 | 0 | 6.928874     | 0.023326     | -0.943191    |
| 40 | 1 | 0 | 7.455824     | 0.041975     | 0.007788     |
| 41 | 6 | 0 | 7.641103     | 0.009455     | -2.140817    |
| 42 | 1 | 0 | 8.727886     | 0.017457     | -2.121351    |
| 43 | 6 | 0 | 6.971151     | -0.014661    | -3.366647    |
| 44 | 1 | 0 | 7.540820     | -0.025242    | -4.292237    |
| 45 | 6 | 0 | 5.574047     | -0.025231    | -3.411197    |
| 46 | 1 | 0 | 5.060231     | -0.043524    | -4.370215    |
| 47 | 6 | 0 | 4.861210     | -0.011657    | -2.220015    |
| 48 | 6 | 0 | 3.357458     | -0.016812    | -2.012733    |
| 49 | 6 | 0 | 3.237898     | 0.001869     | -0.479810    |
| 50 | 6 | 0 | -0.601958    | -0.025022    | -3.108270    |
| 51 | 6 | 0 | -0.982802    | -0.034151    | -4.441329    |
| 52 | 6 | 0 | -1.179393    | -1.265559    | -5.128350    |
| 53 | 1 | 0 | -1.018944    | -2.194524    | -4.590982    |
| 54 | 6 | 0 | -1.566394    | -1.289118    | -6.446812    |
| 55 | 1 | 0 | -1.710882    | -2.238155    | -6.949310    |
| 56 | 6 | 0 | -1.772163    | -0.069582    | -7.129687    |
|   |   |   |    |    |    |
|---|---|---|----|----|----|
| 57|  6|  0| -1.578286|  1.166124| -6.463574|
| 58|  1|  0| -1.744472|  2.081573| -7.021597|
| 59|  6|  0| -1.193277|  1.185424| -5.150915|
| 60|  1|  0| -1.044068|  2.127013| -4.632997|
| 61|  6|  0| -2.370021| -1.163087| -9.157023|
| 62|  1|  0| -3.170068| -1.762250| -8.712544|
| 63|  1|  0| -1.450934| -1.751663| -9.232096|
| 64|  1|  0| -2.670746| -0.820109| -10.145714|
| 65|  6|  0| -2.245002| -1.548111|  9.013770|
| 66|  6|  0|  2.127236|  1.152095|  9.139275|
| 67|  6|  0|  3.477352|  0.556384|  8.707789|
| 68|  1|  0|  3.520418| -0.516442|  8.928444|
| 69|  1|  0|  4.297386|  1.048407|  9.245164|
| 70|  1|  0|  3.655881|  0.686897|  7.635140|
| 71|  6|  0|  1.960821|  0.982680| 10.655823|
| 72|  1|  0|  1.070750|  1.427028| 11.038502|
| 73|  1|  0|  2.834503|  1.485352| 11.152695|
| 74|  1|  0|  2.020269| -0.072605| 10.951895|
| 75|  6|  0|  2.112999|  2.656741|  8.823180|
| 76|  1|  0|  2.248486|  2.848048|  7.753361|
| 77|  1|  0|  2.923178|  3.165069|  9.360517|
| 78|  1|  0|  1.163547|  3.110931|  9.129505|
| 79|  6|  0| -3.582231| -0.895579|  8.626616|
| 80|  1|  0| -3.611071|  0.153574|  8.943104|
| 81|  1|  0| -4.414788| -1.420911|  9.110639|
| 82|  1|  0| -3.751285| -0.925474|  7.544920|
| 83|  6|  0| -2.121982| -1.510906| 10.539650|
| 84|  1|  0| -1.201966| -1.995513| 10.886384|
| 85|  1|  0| -2.967052| -2.046673| 10.986948|
| 86|  1|  0| -2.138053| -0.485073| 10.925554|
|   |   |   |   |   |   |
|---|---|---|---|---|---|
| 117 | 1 | 0 | 1.536566 | 3.716112 | -2.732272 |
| 118 | 1 | 0 | 2.788591 | 3.677602 | -3.967404 |
| 119 | 6 | 0 | 3.140675 | 5.115839 | -2.401564 |
| 120 | 1 | 0 | 2.978381 | 5.201539 | -1.316764 |
| 121 | 1 | 0 | 4.229727 | 5.165040 | -2.550686 |
| 122 | 6 | 0 | 2.482821 | 6.300226 | -3.103339 |
| 123 | 1 | 0 | 1.394902 | 6.249038 | -2.954013 |
| 124 | 1 | 0 | 2.645741 | 6.214135 | -4.187184 |
| 125 | 6 | 0 | 3.001986 | 7.647284 | -2.614751 |
| 126 | 1 | 0 | 2.822985 | 7.772011 | -1.539861 |
| 127 | 1 | 0 | 2.513391 | 8.479979 | -3.133186 |
| 128 | 1 | 0 | 4.082296 | 7.737684 | -2.781886 |