Supporting Information

Computational Design of Rhenium(I) Carbonyl Complexes for Anticancer Photodynamic Therapy

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Figure S7. PCM-TD-M06/6-31+G(d)-LANL2DZ//B3LYP-D3/6-31+G(d)-LANL2DZ electronic absorption spectra of Re(I) complexes bearing the phosphine ligands DAPTA (1k), PMe3 (1p and 1q), and CAP (1r and 1s).

Figure S8. Contour maps of the frontier Kohn-Sham orbitals involved in the main orbital transition of the lowest-lying absorption band found for Re(I) complexes containing the phosphine ligands DAPTA (1k), PMe3 (1p and 1q) CAP (1r and 1s).

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Table S18. B3LYP-D3/6-31+G(d)-LANL2DZ cartesian coordinates of the optimized structures in the triplet excited state of Re(I) complexes 1-3 and 1a-1s.

References related to Discussion 1.

References related to Discussion 2.
Discussion 1. Validating the computational protocol for geometry optimizations.

The geometry of all the Re(I) carbonyl complexes investigated in this work was optimized in the gas phase at the B3LYP-D3/6-31+G(d)-LANL2DZ level of theory. Although this computational level was chosen on the basis of numerous theoretical investigations on the photophysical and spectroscopic properties of Re(I) carbonyl complexes,\textsuperscript{1-39} we checked its performance for geometry optimizations by comparing the X-ray structure of a \(N\)-benzylated derivative of the Re(I) tricarbonyl complex containing pyridyl and pyridocarbazol ligands (\(1^{\text{ref}}\) in Scheme S1)\textsuperscript{40} with its B3LYP-D3/6-31+G(d)-LANL2DZ optimized structure. Complex \(1^{\text{ref}}\) is closely related to the Re(I) carbonyl indolato complexes studied in the present investigation and furthermore its X-ray structure is available.\textsuperscript{40} Cartesian coordinates of both structures are collected in Table S1.

![Scheme S1](image.png)

\textbf{Scheme S1.} \(N\)-benzylated derivative of the Re(I) tricarbonyl complex containing a pyridine ligand and another pyrido[2,3-\(a\)]pyrrolo[3,4-\(c\)]carbazole-5,7(6\(H\))-dione ligand considered in the validation calculations of the B3LYP-D3/6-31+G(d)-LANL2DZ level for geometry optimizations. Atom numbering of the non-hydrogen atoms, the most relevant ones, is included.

Figure S1 shows that the main difference between X-ray (in blue colour) and B3LYP-D3/6-31+G(d)-LANL2DZ (in red colour) structures lies in the orientation of the benzyl...
group attached to the nitrogen atom N32 of the pyridocarbazol ligand (Scheme S1), which can be ascribed to the crystal packing of $1^{\text{ref}}$. Specifically, as collected in Table S2, we note that the absolute difference between X-ray and B3LYP-D3 bond distances involving non-hydrogen atoms in $1^{\text{ref}}$ varies from 0.0002 Å (C27-C28 bond distance) to 0.048 Å (Re1-N8 bond distance). The mean absolute deviation (MAD) and the root mean square deviation (RMSD) between all those X-ray and B3LYP-D3 bond distances are 0.011 and 0.014 Å, respectively. When comparing X-ray and B3LYP-D3 bond angles involving non-hydrogen atoms in $1^{\text{ref}}$ (see Table S3), the absolute discrepancy between them ranges from 0.020º (Re1-N21-C20 bond angle) to 3.9º (C2-Re1-N8 bond angle). MAD of all the differences in those bond angles is 0.65º, whereas the RMSD value is about 1.0º. The relatively small RMSD value obtained for both bond distances (less than 0.02 Å) and bond angles (less than 2º) confirms the adequacy of using the B3LYP-D3/6-31+G(d)-LANL2DZ optimized geometries to carry out Time-Dependent Density Functional Theory (TD-DFT) calculations.
Discussion 2. Validating the computational protocol for TD-DFT calculations.

Electronic excitation energies and oscillator strengths of the Re(I) carbonyl complexes were computed by performing TD-DFT calculations on the B3LYP-D3/6-31+G(d)-LANL2DZ optimized geometries. To predict a reliable level of theory for studying the excited-state properties of the Re(I) complexes investigated in this work, different density functionals (B3LYP-D3,\textsuperscript{1-4} CAM-B3LYP,\textsuperscript{5} M05,\textsuperscript{6} M06,\textsuperscript{7} MN15,\textsuperscript{8} PBE,\textsuperscript{9,10} PBE0,\textsuperscript{11} TPSS,\textsuperscript{12} TPSSh,\textsuperscript{12,13} wB97x,\textsuperscript{14} wB97xD)\textsuperscript{15} were employed along with the same basis set (6-31+G(d)-LANL2DZ) as the one used for geometry optimizations in gas phase. Bulk solvent effects (dimethyl sulfoxide, DMSO, $\varepsilon = 46.826$) were taken into account with the polarizable continuum model (PCM) developed by Tomasi and coworkers\textsuperscript{16-22} using the integral equation formalism variant (IEF)\textsuperscript{20} and the universal force field (UFF) radii.\textsuperscript{23} In these PCM-TD-DFT computations, the solute-solvent electrostatic interaction energy and the non-electrostatic terms due to the solute cavitation energy\textsuperscript{24} as well as to the solute-solvent dispersion\textsuperscript{25,26} and repulsion\textsuperscript{25,26} interaction energies were considered.

Among the TD-DFT computational levels mentioned above, the most reliable was chosen by comparing the theoretical electronic spectra obtained for complexes 1-3 (see Scheme S2) with those measured experimentally in DMSO for the same complexes.\textsuperscript{27} Tables S4-S6 collect excitation energies (both in eV, $E$, and in nm, $\lambda$) and oscillator strengths ($f$) of the first ten lowest-lying singlet-singlet electron transitions for complexes 1-3, respectively. Figures S2-S4 display the corresponding simulated absorption spectra obtained through TD-DFT calculations and, for comparison purposes, the respective experimental spectra reported are also included.\textsuperscript{27}

Scheme S2. Rhenium(I) tricarbonyl complexes used for validating the computational protocol employed in the TD-DFT computations.
As seen in Figure S2, B3LYP-D3, PBE, TPSS, and TPSSh provide UV/Vis absorbance spectra for 1 in Scheme S2 that differ greatly from the experimental one. The B3LYP-D3 spectrum shows three absorption bands as in the experimental one, but the sequence of the first and third intensities is erroneously predicted. Specifically, the most red-shifted absorption band is more intense than the least one, while the reverse trend was found experimentally. For PBE, TPSS, and TPSSh, the simulated UV/Vis spectra do not clearly show the presence of three absorption bands, nor at least the two most intense ones. However, the general shape of the UV/Vis spectrum of 1 is acceptably well-reproduced with the remaining functionals (CAM-B3LYP, M05, M06, MN15, PBE0, wB97x, wB97xD), although we note that the intermediate absorption band, the experimentally less intense, does not reproduce sharply. For complexes 2 and 3 in Scheme S2 (see Figures S3 and S4, respectively), the UV/Vis spectra predicted by all the functionals fit reasonably well the main features of those reported experimentally.

In addition to the aforementioned and since we are interested in Re(I) carbonyl complexes that absorb in the red region of Vis spectrum, let us turn our attention to the excitation energy of the most red-shifted absorption band. Table S7 collects the excitation energy of the most red-shifted absorption band found for complexes 1-3 at the levels of theory PCM-TD-DFT/6-31+G(d)-LANL2DZ//B3LYP-D3/6-31+G(d)-LANL2DZ (DFT = B3LYP-D3, CAM-B3LYP, M05, M06, MN15, PBE, PBE0, TPSS, TPSSh, wB97x, wB97xD). For each computational level and each complex, the choice of that excitation energy is based on the position and intensity of the most red-shifted absorption wavelength that fits better the one found experimentally. In addition, we also show in Table S7 the absolute error obtained when comparing the computed excitation energies with the respective experimental value for each complex. For 1 (sixth column in Table S7), the excitation energy obtained with M05, PBE, PBE0, M06, and TPSS only differs, in absolute value, 0.01, 0.03, 0.03, 0.04, and 0.04 eV from the experimental one, respectively. B3LYP-D3 and MN15 give similar absolute errors (0.15 and 0.17 eV, respectively) and clearly larger than the previous functionals. The remaining DFT methods provide discrepancies larger than 0.25 eV, thus preventing their use to predict reliable UV/Vis spectra. In the case of 2 (seventh column in Table S7), we found that M06, PBE0, and M05 with absolute discrepancies of 0.003, 0.04, and 0.06 eV are the most adequate to fit the excitation energy of the experimental most red-shifted absorption band. We note, however, that M06 behaves better than PBE0 and M05. It
then follows B3LYP-D3 that only differs by 0.09 eV (in absolute value) from the experimental excitation energy. All the others functionals investigated present absolute errors larger than 0.23 eV. Concerning 3 (eighth column in Table S7), the absolute error in the excitation energy predicted by M06 (0.003 eV), MN15 (0.01 eV), B3LYP-D3 (0.02 eV), M05 (0.07 eV), PBE0 (0.09 eV), and TPSSh (0.09 eV) is very small. Yet again, M06 presents the best behavior. The remaining functionals provide absolute errors larger than 0.20 eV. Therefore, looking at the Re(I) complexes 1-3, M06 is the best functional in predicting the shortest excitation energy (longest maximum absorption wavelength) by far. In fact, M06 shows a total absolute error of 0.04 eV (tenth column in Table S7). M05 and PBE0 are the following functionals in level of accuracy with total absolute errors of 0.14 and 0.16 eV, respectively. By contrast, wB97xD and wB97x present the largest total absolute errors, 1.18 and 1.80 eV, respectively. In addition, M06 is also one of the best functionals in reproducing the general shape of the UV/Vis absorption spectrum for complexes 1-3. So, we conclude that M06 presents the best performance in order to investigate the spectroscopic properties of the Re(I) pyridocarbazole complexes investigated in the present work.
Table S1. Cartesian coordinates in Å of the X-ray and B3LYP-D3-6/31+G(d)-LANL2DZ structures of the Re(I) complex 1
ref in Scheme S1.

| X-ray | B3LYP-D3-6/31+G(d)-LANL2DZ |
|-------|-----------------------------|
| Re    | 3.040103 -0.242807 -0.178800 |
| C     | 3.699845 0.001476 -1.987624 |
| O     | 4.025991 0.146154 -3.081539 |
| C     | 4.316517 -1.657436 0.135955 |
| O     | 5.048850 -2.507994 0.310089 |
| C     | 4.275556 1.802073 0.473025 |
| C     | 4.979725 1.851145 0.888496 |
| C     | 2.099165 -0.514888 1.857485 |
| C     | 1.927124 -1.740486 2.392311 |
| C     | 1.281818 -1.945750 3.610858 |
| C     | 0.804432 -0.840493 4.317730 |
| C     | 0.991635 0.430061 3.772191 |
| C     | 1.638909 0.551652 2.545791 |
| C     | 1.385682 -1.640745 0.790725 |
| C     | 1.408909 -2.960677 -0.987918 |
| C     | 0.249393 -3.698935 -2.184159 |
| N     | -0.984563 -3.662745 -1.373311 |
| N     | -1.048278 -1.662671 -1.179767 |
| N     | 0.181435 -0.998904 -0.894885 |
| N     | 0.197913 0.398307 -0.706764 |
| N     | 1.330822 0.189506 -0.443334 |
| N     | 0.941905 2.415625 -0.329574 |
| N     | 1.740037 3.534037 -0.054229 |
| N     | 1.134164 4.776614 0.031234 |
| N     | -0.279204 4.917168 -0.153690 |
| N     | -1.028637 3.813327 -0.429946 |
| N     | -0.477051 2.549981 -0.513697 |
| N     | -0.963162 1.216903 -0.772528 |
| N     | -2.163334 0.543719 -0.103772 |
| N     | -3.559937 1.669740 -1.158649 |
| N     | -3.966111 2.217935 -1.476725 |
| N     | -4.361547 -0.034274 -1.448507 |
| N     | -0.639548 -1.226615 -1.485731 |
| N     | -4.095950 -2.334434 -1.692132 |
| N     | -2.208880 -0.838652 -1.234787 |
| N     | -0.581957 0.014248 -1.544490 |
| N     | -6.487940 -0.149211 -0.927977 |
| N     | -6.810970 -1.426076 0.280706 |
| N     | -7.395947 -1.580027 1.547138 |
| N     | -7.660734 -0.457987 3.239045 |
| N     | -7.306015 -1.818145 -1.907028 |
| N     | -6.751433 0.971553 0.606950 |
| N     | -2.302890 -2.573579 1.813327 |
| N     | -1.163166 -2.559512 3.895003 |
| N     | -0.298927 -0.967138 5.270833 |
| N     | 0.639605 1.323007 4.278496 |
| N     | 1.788111 1.520371 2.084648 |
| N     | 2.378521 -3.442779 -0.913017 |
| N     | 0.328466 -4.770239 1.434252 |
| N     | -1.894517 -3.618886 -1.582809 |
| N     | -2.154101 3.902928 -1.755034 |
| N     | -0.728402 5.039351 -0.081770 |
| N     | 1.714187 5.658776 0.240095 |
| N     | 2.812288 3.92183 0.078584 |
| N     | -6.117710 -0.785548 -2.227302 |
| N     | -6.591474 -2.967393 -3.326124 |
| N     | -7.646496 -2.574406 -1.908711 |
| N     | -8.118903 -0.577141 3.318155 |
| N     | -7.538917 1.693922 2.478711 |
| N     | -6.485796 1.960781 -0.242434 |
| N     | -6.076038 0.977394 -1.936788 |
Figure S1. Two comparative views for the X-ray and B3LYP-D3/6-31+G(d)-LANL2DZ structures (blue and red colours, respectively) of the N-benzylated derivative of the Re(I) tricarbonyl complex containing pyridine and pyridocarbazole ligands (1_{\text{ref}} in Scheme S1).
Table S2. X-Ray and B3LYP-D3/6-31+G(d)-LANL2DZ bond distances ($r_{X\text{-Ray}}$ and $r_{B3LYP-D3}$, respectively) of the Re(I) tricarbonyl complex 1$^{\text{ref}}$ in Scheme S1. Absolute difference and square of the absolute difference of the X-Ray and B3LYP-D3/6-31+G(d)-LANL2DZ distances are also given for each bond. Only bond distances involving non-hydrogen atoms (the most relevant ones) are considered.

| bond distance | $r_{X\text{-Ray}}$ (Å) | $r_{B3LYP-D3}$ (Å) | $|r_{X\text{-Ray}} - r_{B3LYP-D3}|$ (Å) | $|r_{X\text{-Ray}} - r_{B3LYP-D3}|^2$ (Å$^2$) |
|---------------|------------------------|---------------------|--------------------------------------|-------------------------------------|
| Re(1) - C(2)  | 1.92656                | 1.93083             | 0.00427                              | 0.000182                           |
| C(2) - O(3)   | 1.14216                | 1.15949             | 0.01733                              | 0.003003                           |
| Re(1) - C(4)  | 1.91904                | 1.92845             | 0.00941                              | 0.000885                           |
| C(4) - O(5)   | 1.15512                | 1.16557             | 0.01045                              | 0.001092                           |
| Re(1) - C(6)  | 1.91364                | 1.92400             | 0.01036                              | 0.001073                           |
| C(6) - O(7)   | 1.15496                | 1.16273             | 0.00777                              | 0.000604                           |
| Re(1) - N(8)  | 2.21128                | 2.25961             | 0.04833                              | 0.0023358                          |
| N(8) - C(9)   | 1.34431                | 1.34898             | 0.00467                              | 0.000218                           |
| C(9) - C(10)  | 1.38195                | 1.39139             | 0.00944                              | 0.000891                           |
| C(10) - C(11)| 1.38781                | 1.39612             | 0.00831                              | 0.000691                           |
| C(11) - C(12)| 1.37191                | 1.39534             | 0.02343                              | 0.0005490                          |
| C(12) - C(13)| 1.39173                | 1.39205             | 0.00032                              | 0.000001                           |
| N(8) - C(13) | 1.33803                | 1.35002             | 0.01199                              | 0.001438                           |
| Re(1) - N(14)| 2.21866                | 2.25154             | 0.03288                              | 0.0010811                          |
| Re(1) - N(21)| 2.17397                | 2.18049             | 0.00652                              | 0.000425                           |
| N(14) - C(15)| 1.32074                | 1.33489             | 0.01415                              | 0.000202                           |
| C(15) - C(16)| 1.40748                | 1.40920             | 0.00172                              | 0.000030                           |
| C(16) - C(17)| 1.36647                | 1.38737             | 0.02090                              | 0.0004368                          |
| C(17) - C(18)| 1.40526                | 1.41480             | 0.00954                              | 0.000910                           |
| C(18) - C(19)| 1.41332                | 1.42617             | 0.01285                              | 0.001651                           |
| C(19)-N(14)  | 1.37225                | 1.36760             | 0.00465                              | 0.000216                           |
| C(19) - C(20)| 1.40722                | 1.40979             | 0.00257                              | 0.000066                           |
| C(20) - N(21)| 1.35023                | 1.35091             | 0.00068                              | 0.000005                           |
| N(21) - C(22)| 1.38875                | 1.39092             | 0.00217                              | 0.000047                           |
| C(22) - C(23)| 1.39289                | 1.40131             | 0.00842                              | 0.0000709                          |
| C(23) - C(24)| 1.38801                | 1.39392             | 0.00591                              | 0.000349                           |
| C(24) - C(25)| 1.40238                | 1.41242             | 0.01004                              | 0.000108                           |
| C(25) - C(26)| 1.37808                | 1.39301             | 0.01493                              | 0.000229                           |
| C(26) - C(27)| 1.40214                | 1.40385             | 0.00171                              | 0.000029                           |
| C(27) - C(28)| 1.44159                | 1.44140             | 0.00019                              | 0.000000                           |
| C(28) - C(29)| 1.40589                | 1.42211             | 0.01622                              | 0.0002631                          |
| C(28) - C(29)| 1.41251                | 1.40140             | 0.01111                              | 0.001234                           |
| C(29) - C(30)| 1.48885                | 1.49727             | 0.00842                              | 0.0000709                          |
| C(30) - O(31)| 1.20486                | 1.22049             | 0.01563                              | 0.0002443                          |
| C(30) - N(32)| 1.38975                | 1.39479             | 0.00504                              | 0.000254                           |
| N(32) - C(33)| 1.40075                | 1.41033             | 0.00958                              | 0.000918                           |
| C(33) - O(34)| 1.21731                | 1.22344             | 0.00613                              | 0.000376                           |
| C(33) - C(35)| 1.47742                | 1.47497             | 0.00245                              | 0.000060                           |
| C(18) - C(35)| 1.42273                | 1.42443             | 0.00170                              | 0.000029                           |
| C(29)-C(35)  | 1.38885                | 1.39713             | 0.00828                              | 0.0000686                          |
| N(32) - C(36)| 1.45464                | 1.46194             | 0.00730                              | 0.000533                           |
| Bond         | Ethylene (Å) | B3LYP-D3 (Å) | Δ (Å)  | Δ (Å^2)  |
|--------------|--------------|--------------|--------|----------|
| C(36) - C(37)| 1.50855      | 1.51676      | 0.00821| 0.0000674|
| C(37) - C(38)| 1.38933      | 1.40177      | 0.01244| 0.0001548|
| C(38) - C(39)| 1.38889      | 1.39780      | 0.00891| 0.0000794|
| C(39) - C(40)| 1.37658      | 1.39885      | 0.02227| 0.0004960|
| C(40) - C(41)| 1.36538      | 1.39885      | 0.03347| 0.0011202|
| C(41) - C(42)| 1.39352      | 1.39776      | 0.00424| 0.0000180|
| C(37) - C(42)| 1.38647      | 1.40183      | 0.01536| 0.0002359|

**Mean Absolute Deviation (MAD):**

\[
\left( \frac{1}{48} \sum |r_{X-Ray} - r_{B3LYP-D3}| \right) = 0.01068
\]

\[
\sum |r_{X-Ray} - r_{B3LYP-D3}|^2 = 0.00954
\]

**Root Mean Square Deviation (RMSD):**

\[
\sqrt{\left( \frac{1}{48} \sum |r_{X-Ray} - r_{B3LYP-D3}|^2 \right)} = 0.01429
\]
Table S3. X-Ray and B3LYP-D3/6-31+G(d)-LANL2DZ bond angles in degrees (θ\text{X-Ray} and θ\text{B3LYP-D3}, respectively) of the Re(I) tricarbonyl complex 1ref in Scheme S1. Absolute difference and square of the absolute difference of the X-Ray and B3LYP-D3/6-31+G(d)-LANL2DZ angles are also given for each bond angle (in degrees and degrees squared, respectively). Only bond angles involving non-hydrogen atoms (the most relevant ones) are considered.

| bond angle       | θ\text{X-Ray} | θ\text{B3LYP-D3} | |θ\text{X-Ray} − θ\text{B3LYP-D3}| |θ\text{X-Ray} − θ\text{B3LYP-D3}|² |
|------------------|---------------|------------------|-----------------|-------------------------------|-------------------------------|
| Re(1) - C(2) - C(3)          | 178.131       | 178.843          | 0.712           | 0.507                         |
| Re(1) - C(4) - C(5)          | 178.311       | 177.246          | 1.065           | 1.134                         |
| Re(1) - C(6) - C(7)          | 177.580       | 178.307          | 0.727           | 0.529                         |
| Re(1) - N(8) - C(9)          | 120.921       | 121.438          | 0.517           | 0.267                         |
| Re(1) - N(8) - C(13)         | 121.462       | 120.413          | 1.049           | 1.100                         |
| Re(1) - N(14) - C(15)        | 129.562       | 129.845          | 0.283           | 0.080                         |
| Re(1) - N(14) - C(19)        | 112.325       | 112.095          | 0.230           | 0.053                         |
| Re(1) - N(21) - C(20)        | 111.792       | 111.812          | 0.020           | 0.000                         |
| Re(1) - N(21) - C(22)        | 142.704       | 142.353          | 0.351           | 0.123                         |
| C(2) - Re(1) - N(14)         | 96.584        | 93.655           | 2.929           | 8.579                         |
| C(2) - Re(1) - N(21)         | 95.264        | 93.725           | 1.539           | 2.369                         |
| C(2) - Re(1) - C(4)          | 88.684        | 91.255           | 2.571           | 6.610                         |
| C(2) - Re(1) - C(6)          | 88.064        | 91.200           | 3.136           | 9.834                         |
| C(2) - Re(1) - N(8)          | 178.354       | 174.427          | 3.927           | 15.421                        |
| C(4) - Re(1) - N(14)         | 95.222        | 94.198           | 1.024           | 1.049                         |
| C(4) - Re(1) - N(21)         | 171.686       | 169.811          | 1.875           | 3.516                         |
| C(4) - Re(1) - C(6)          | 90.710        | 91.552           | 0.842           | 0.709                         |
| C(4) - Re(1) - N(8)          | 91.344        | 92.741           | 1.397           | 1.952                         |
| C(6) - Re(1) - N(14)         | 172.534       | 173.878          | 0.147           | 0.022                         |
| C(6) - Re(1) - N(21)         | 96.722        | 97.220           | 0.498           | 0.248                         |
| C(6) - Re(1) - N(8)          | 93.582        | 92.573           | 1.009           | 1.018                         |
| N(8) - Re(1) - N(14)         | 81.774        | 82.183           | 0.409           | 0.167                         |
| N(8) - Re(1) - N(21)         | 84.500        | 81.736           | 2.764           | 7.640                         |
| N(8) - C(9) - C(10)          | 123.322       | 122.809          | 0.513           | 0.263                         |
| C(9) - C(10) - C(11)         | 118.326       | 118.933          | 0.607           | 0.368                         |
| C(10) - C(11) - C(12)        | 119.031       | 118.492          | 0.539           | 0.291                         |
| C(11) - C(12) - C(13)        | 119.174       | 119.102          | 0.072           | 0.005                         |
| C(12) - C(13) - N(8)         | 122.517       | 122.590          | 0.073           | 0.005                         |
| C(13) - N(8) - C(9)          | 117.617       | 118.073          | 0.456           | 0.208                         |
| N(14) - C(15) - C(16)        | 121.782       | 122.255          | 0.473           | 0.224                         |
| C(15) - C(16) - C(17)        | 120.825       | 120.369          | 0.456           | 0.208                         |
| C(16) - C(17) - C(18)        | 119.127       | 118.990          | 0.137           | 0.019                         |
| C(17) - C(18) - C(19)        | 116.781       | 116.682          | 0.099           | 0.010                         |
| C(17) - C(18) - C(35)        | 127.214       | 127.148          | 0.066           | 0.004                         |
| C(18) - C(19) - N(14)        | 123.388       | 123.734          | 0.346           | 0.120                         |
| C(18) - C(19) - C(20)        | 120.036       | 119.859          | 0.177           | 0.031                         |
| C(19) - N(14) - C(15)        | 118.087       | 117.962          | 0.125           | 0.016                         |
| C(19) - C(20) - C(28)        | 123.947       | 123.703          | 0.244           | 0.060                         |
| C(20) - C(28) - C(29)        | 115.524       | 115.552          | 0.028           | 0.001                         |
| C(28) - C(29) - C(35)        | 121.297       | 121.999          | 0.702           | 0.493                         |
| Bond                  | Distance (Å) | Angle (°) | MAD (Å) | RMSD (Å) |
|----------------------|--------------|-----------|---------|----------|
| C(29) - C(35) - C(18)| 123.153      | 122.709   | 0.444   | 0.197    |
| C(35) - C(18) - C(19)| 115.951      | 116.170   | 0.219   | 0.048    |
| C(19) - N(21) - C(22)| 105.462      | 105.534   | 0.072   | 0.005    |
| N(21) - C(22) - C(27)| 110.520      | 110.764   | 0.244   | 0.060    |
| C(22) - C(23) - C(24)| 118.214      | 117.890   | 0.324   | 0.105    |
| C(23) - C(24) - C(25)| 121.313      | 121.572   | 0.259   | 0.067    |
| C(24) - C(25) - C(26)| 121.358      | 121.071   | 0.287   | 0.082    |
| C(25) - C(26) - C(27)| 118.631      | 118.482   | 0.149   | 0.022    |
| C(26) - C(27) - C(22)| 119.824      | 120.093   | 0.269   | 0.072    |
| C(27) - C(22) - C(23)| 120.655      | 120.892   | 0.237   | 0.056    |
| C(26) - C(27) - C(28)| 134.490      | 134.265   | 0.225   | 0.051    |
| C(27) - C(28) - C(20)| 104.504      | 104.416   | 0.088   | 0.008    |
| C(27) - C(28) - C(29)| 139.923      | 140.030   | 0.107   | 0.011    |
| C(28) - C(20) - N(21)| 113.882      | 113.641   | 0.241   | 0.058    |
| C(28) - C(29) - C(30)| 130.634      | 130.192   | 0.442   | 0.195    |
| C(29) - C(30) - O(31)| 129.120      | 128.707   | 0.413   | 0.171    |
| O(31) - C(30) - N(32)| 125.040      | 125.343   | 0.303   | 0.092    |
| C(29) - C(30) - N(32)| 105.840      | 105.949   | 0.109   | 0.012    |
| C(30) - N(32) - C(33)| 111.887      | 111.613   | 0.274   | 0.075    |
| C(30) - N(32) - C(36)| 123.225      | 124.092   | 0.867   | 0.752    |
| N(32) - C(33) - O(34)| 124.303      | 124.198   | 0.105   | 0.011    |
| N(32) - C(33) - C(35)| 105.999      | 106.221   | 0.222   | 0.049    |
| C(33) - C(35) - C(29)| 108.194      | 108.380   | 0.186   | 0.035    |
| C(33) - C(35) - C(18)| 128.611      | 128.910   | 0.299   | 0.089    |
| C(33) - N(32) - C(36)| 124.809      | 123.924   | 0.885   | 0.783    |
| O(34) - C(33) - C(35)| 129.698      | 129.581   | 0.117   | 0.014    |
| C(35) - C(29) - C(30)| 108.065      | 107.808   | 0.257   | 0.066    |
| N(32) - C(36) - C(37)| 114.309      | 112.173   | 2.136   | 4.562    |
| C(36) - C(37) - C(42)| 122.620      | 120.337   | 2.283   | 5.212    |
| C(36) - C(37) - C(38)| 118.826      | 120.315   | 1.489   | 2.217    |
| C(37) - C(38) - C(39)| 120.256      | 120.354   | 0.098   | 0.010    |
| C(38) - C(39) - C(40)| 120.600      | 120.097   | 0.503   | 0.253    |
| C(39) - C(40) - C(41)| 119.638      | 119.778   | 0.140   | 0.020    |
| C(40) - C(41) - C(42)| 120.398      | 120.102   | 0.296   | 0.088    |
| C(41) - C(42) - C(37)| 120.575      | 120.349   | 0.226   | 0.051    |
| C(42) - C(37) - C(38)| 118.521      | 119.319   | 0.798   | 0.637    |

**Mean Absolute Deviation (MAD):** \[ \left( \frac{1}{78} \right) \sum \left| \theta_{\text{X-Ray}} - \theta_{B3LYP-D3} \right| = 0.6519 \]

\[ \sum \left| \theta_{\text{X-Ray}} - \theta_{B3LYP-D3} \right|^2 = 82.112 \]

**Root Mean Square Deviation (RMSD):** \[ \sqrt{\left( \frac{1}{78} \right) \sum \left| \theta_{\text{X-Ray}} - \theta_{B3LYP-D3} \right|^2} = 1.026 \]
Table S4. Excitation energies, $E$, in eV (in parentheses absorption wavelengths, $\lambda$, in nm) and oscillator strengths ($f$) of the first ten lowest-lying singlet-singlet electron transitions calculated at the PCM-TD-DFT/6-31+G(d)-LANL2DZ//B3LYP-D3/6-31+G(d)-LANL2DZ level for Re(I) complex 1.

| B3LYP-D3 | CAM-B3LYP | M05 | M06 | MN15 | PBE | PBE0 | TPSS | TPSSh | wB97x | wB97xD |
|----------|------------|-----|-----|------|-----|------|------|-------|-------|--------|
| $E (\lambda)$ | $f$ | $E (\lambda)$ | $f$ | $E (\lambda)$ | $f$ | $E (\lambda)$ | $f$ | $E (\lambda)$ | $f$ | $E (\lambda)$ | $f$ |
| 2.27 (547) | 0.1344 | 2.81 (441) | 0.0699 | 3.08 (403) | 0.0382 | 3.25 (381) | 0.0116 | 3.27 (379) | 0.0044 | 3.36 (369) | 0.0027 | 3.40 (350) | 0.0151 |
| 2.73 (454) | 0.2056 | 3.36 (369) | 0.0206 | 3.67 (338) | 0.1676 | 4.03 (308) | 0.0146 | 4.11 (302) | 0.0046 | 4.14 (299) | 0.0158 | 4.15 (299) | 0.0073 |
| 2.41 (514) | 0.1514 | 2.94 (421) | 0.0573 | 3.24 (383) | 0.0668 | 3.40 (365) | 0.0049 | 3.49 (355) | 0.0056 | 3.52 (352) | 0.0049 | 3.54 (350) | 0.0150 |
| 2.38 (521) | 0.1459 | 2.89 (428) | 0.0577 | 3.18 (390) | 0.0606 | 3.36 (369) | 0.0062 | 3.44 (361) | 0.0056 | 3.45 (359) | 0.0056 | 3.49 (356) | 0.0025 |
| 2.59 (479) | 0.1802 | 3.19 (389) | 0.0343 | 3.45 (359) | 0.1206 | 3.78 (328) | 0.0005 | 3.82 (324) | 0.0002 | 3.84 (323) | 0.0002 | 3.88 (319) | 0.0012 |
| 1.88 (660) | 0.0896 | 2.39 (519) | 0.0723 | 2.56 (485) | 0.0025 | 2.58 (480) | 0.0080 | 2.62 (474) | 0.0005 | 2.67 (473) | 0.0005 | 2.71 (457) | 0.0012 |
| 2.39 (519) | 0.1466 | 2.95 (420) | 0.0629 | 3.21 (386) | 0.0561 | 3.44 (360) | 0.0109 | 3.48 (357) | 0.0089 | 3.55 (349) | 0.0031 | 3.58 (346) | 0.0060 |
| 1.94 (640) | 0.0960 | 2.46 (504) | 0.0766 | 2.66 (467) | 0.0020 | 2.69 (462) | 0.0001 | 2.70 (458) | 0.0001 | 2.73 (454) | 0.0001 | 2.82 (440) | 0.0001 |
| 2.14 (579) | 0.1142 | 2.68 (462) | 0.0750 | 2.93 (424) | 0.0198 | 3.02 (411) | 0.0090 | 3.04 (408) | 0.0090 | 3.10 (399) | 0.0040 | 3.16 (393) | 0.0040 |
| 2.97 (418) | 0.2331 | 3.62 (342) | 0.0021 | 4.04 (307) | 0.2763 | 4.25 (292) | 0.0113 | 4.27 (290) | 0.0173 | 4.31 (288) | 0.0028 | 4.44 (279) | 0.1233 |
| 2.79 (445) | 0.2080 | 3.43 (362) | 0.0116 | 4.09 (303) | 0.1949 | 4.27 (290) | 0.0005 | 4.31 (288) | 0.0005 | 4.41 (279) | 0.0005 | 4.44 (279) | 0.0005 |

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Table S5. Excitation energies, \( E \), in eV (in parentheses absorption wavelengths, \( \lambda \), in nm) and oscillator strengths (\( f \)) of the first ten lowest-lying singlet-singlet electron transitions calculated at the PCM-TD-DFT/6-31+G(d)-LANL2DZ//B3LYP-D3/6-31+G(d)-LANL2DZ level for Re(I) complex 2.

|          | B3LYP-D3 | CAM-B3LYP | M05    | M06    | MN15    | PBE    | PBE0    | TPSS    | TPSSh   | wB97x   | wB97xD  |
|----------|----------|-----------|--------|--------|---------|--------|--------|---------|---------|---------|---------|
| **E (\( \lambda \))** |          |           |        |        |         |        |        |         |         |         |         |
| 2.69 (462) | 3.25 (381) | 2.84 (436) | 2.78 (446) | 3.06 (405) | 2.23 (556) | 2.82 (440) | 2.31 (537) | 2.54 (488) | 3.56 (348) | 3.32 (374) |
| **f**     | 0.0638   | 0.1007    | 0.0712 | 0.0676 | 0.0877  | 0.0371 | 0.0706 | 0.0439  | 0.0557  | 0.1240  | 0.1053  |
| 2.97 (417) | 3.67 (338) | 3.24 (382) | 3.16 (392) | 3.51 (353) | 2.30 (539) | 3.19 (389) | 2.40 (517) | 2.74 (452) | 3.87 (321) | 3.73 (333) |
| **f**     | 0.0061   | 0.0099    | 0.0067 | 0.0066 | 0.0021  | 0.0143 | 0.0067 | 0.0101  | 0.0058  | 0.0009  | 0.0010  |
| 3.25 (382) | 3.95 (314) | 3.36 (369) | 3.29 (376) | 3.63 (341) | 2.84 (437) | 3.37 (368) | 2.91 (426) | 3.13 (396) | 4.19 (296) | 4.06 (306) |
| **f**     | 0.0095   | 0.0248    | 0.0088 | 0.0122 | 0.0155  | 0.0115 | 0.0071 | 0.0148  | 0.0121  | 0.0006  | 0.0043  |
| 3.50 (354) | 4.05 (306) | 3.67 (338) | 3.57 (347) | 3.81 (325) | 2.89 (430) | 3.66 (339) | 3.01 (412) | 3.34 (371) | 4.28 (289) | 4.13 (301) |
| **f**     | 0.0307   | 0.1339    | 0.1321 | 0.0443 | 0.0352  | 0.0044 | 0.1175 | 0.0035  | 0.0085  | 0.0884  | 0.2089  |
| 3.55 (350) | 4.11 (302) | 3.73 (333) | 3.63 (341) | 3.90 (318) | 2.92 (425) | 3.72 (333) | 3.02 (410) | 3.38 (367) | 4.44 (280) | 4.20 (295) |
| **f**     | 0.1018   | 0.0640    | 0.0487 | 0.1115 | 0.1473  | 0.0022 | 0.0493 | 0.0021  | 0.0320  | 0.4352  | 0.0123  |
| 3.65 (340) | 4.30 (288) | 3.90 (318) | 3.79 (327) | 4.11 (302) | 3.05 (407) | 3.88 (320) | 3.14 (394) | 3.43 (361) | 4.52 (274) | 4.38 (283) |
| **f**     | 0.0115   | 0.2694    | 0.0071 | 0.0222 | 0.1596  | 0.0121 | 0.0020 | 0.0109  | 0.0682  | 0.0175  | 0.3124  |
| 3.73 (333) | 4.40 (282) | 3.96 (313) | 3.85 (322) | 4.16 (298) | 3.10 (400) | 3.95 (314) | 3.20 (388) | 3.51 (353) | 4.62 (268) | 4.43 (280) |
| **f**     | 0.0088   | 0.0086    | 0.0753 | 0.0832 | 0.0054  | 0.0809 | 0.0095 | 0.0894  | 0.0221  | 0.0665  | 0.0087  |
| 3.76 (330) | 4.47 (277) | 3.98 (311) | 3.90 (318) | 4.26 (291) | 3.19 (389) | 3.97 (313) | 3.28 (379) | 3.59 (345) | 4.67 (266) | 4.52 (274) |
| **f**     | 0.0709   | 0.0855    | 0.0257 | 0.0078 | 0.0223  | 0.0153 | 0.0853 | 0.0216  | 0.0373  | 0.1414  | 0.0078  |
| 3.90 (318) | 4.49 (276) | 4.01 (309) | 3.92 (316) | 4.33 (287) | 3.28 (378) | 4.05 (306) | 3.41 (363) | 3.71 (334) | 4.69 (265) | 4.54 (273) |
| **f**     | 0.0224   | 0.1854    | 0.0129 | 0.0103 | 0.2907  | 0.0062 | 0.0237 | 0.0115  | 0.0249  | 0.1638  | 0.2382  |
| 3.92 (316) | 4.61 (269) | 4.02 (308) | 3.95 (314) | 4.38 (283) | 3.31 (374) | 4.08 (304) | 3.43 (361) | 3.74 (332) | 4.75 (261) | 4.64 (267) |
| **f**     | 0.0075   | 0.0849    | 0.0199 | 0.0220 | 0.0060  | 0.0349 | 0.0056 | 0.0295  | 0.0154  | 0.0800  | 0.0955  |
|          | B3LYP-D3 | CAM-B3LYP | M05 | M06 | MN15 | PBE | PBE0 | TPSS | TPSSh | wB97x | wB97xD |
|----------|----------|-----------|-----|-----|------|-----|------|------|-------|-------|--------|
| **E (λ)** | 2.94 (422) | 3.53 (351) | 3.11 (399) | 3.05 (407) | 3.33 (372) | 2.32 (533) | 3.08 (403) | 2.44 (509) | 2.77 (448) | 3.79 (327) | 3.59 (346) |
| **f**    | 0.0944   | 0.3091    | 0.1413 | 0.1335 | 0.1911 | 0.0049 | 0.1128 | 0.0059 | 0.0676 | 0.5748 | 0.3361 |
| **E (λ)** | 3.06 (405) | 3.68 (337) | 3.34 (372) | 3.26 (381) | 3.53 (351) | 2.42 (512) | 3.28 (378) | 2.51 (494) | 2.81 (441) | 3.92 (316) | 3.74 (332) |
| **f**    | 0.0046   | 0.3310    | 0.0072 | 0.0060 | 0.3852 | 0.0438 | 0.0051 | 0.0496 | 0.0074 | 0.1262 | 0.3172 |
| **E (λ)** | 3.30 (376) | 4.05 (306) | 3.39 (365) | 3.33 (373) | 3.72 (333) | 2.74 (453) | 3.41 (364) | 2.84 (436) | 3.19 (389) | 4.24 (293) | 4.13 (300) |
| **f**    | 0.3312   | 0.0029    | 0.3704 | 0.3587 | 0.0056 | 0.0002 | 0.3714 | 0.0008 | 0.1273 | 0.0012 | 0.0019 |
| **E (λ)** | 3.45 (359) | 4.17 (298) | 3.71 (334) | 3.62 (343) | 3.89 (319) | 2.86 (433) | 3.68 (337) | 2.98 (416) | 3.23 (383) | 4.39 (282) | 4.29 (289) |
| **f**    | 0.0198   | 0.0088    | 0.0108 | 0.0089 | 0.0045 | 0.0083 | 0.0137 | 0.0256 | 0.1486 | 0.0357 | 0.0219 |
| **E (λ)** | 3.53 (351) | 4.27 (290) | 3.76 (330) | 3.67 (338) | 4.06 (305) | 2.94 (422) | 3.72 (333) | 3.04 (408) | 3.33 (373) | 4.51 (275) | 4.32 (287) |
| **f**    | 0.0173   | 0.0220    | 0.0035 | 0.0016 | 0.0026 | 0.0206 | 0.0084 | 0.2049 | 0.0378 | 0.0032 | 0.0224 |
| **E (λ)** | 3.62 (343) | 4.39 (282) | 3.82 (325) | 3.70 (335) | 4.14 (299) | 2.96 (419) | 3.81 (326) | 3.07 (403) | 3.43 (361) | 4.62 (268) | 4.42 (280) |
| **f**    | 0.0049   | 0.0086    | 0.0083 | 0.0129 | 0.0082 | 0.1897 | 0.0071 | 0.0085 | 0.0025 | 0.0222 | 0.0097 |
| **E (λ)** | 3.82 (325) | 4.40 (282) | 4.00 (310) | 3.92 (316) | 4.17 (297) | 3.14 (395) | 4.04 (307) | 3.23 (384) | 3.59 (346) | 4.69 (265) | 4.51 (275) |
| **f**    | 0.0109   | 0.0551    | 0.0248 | 0.0361 | 0.0542 | 0.0114 | 0.0019 | 0.0129 | 0.0122 | 0.0148 | 0.0229 |
| **E (λ)** | 3.86 (321) | 4.47 (277) | 4.03 (308) | 3.94 (315) | 4.19 (296) | 3.26 (380) | 4.05 (306) | 3.36 (369) | 3.69 (336) | 4.76 (261) | 4.52 (274) |
| **f**    | 0.0133   | 0.0361    | 0.0442 | 0.0203 | 0.0375 | 0.002 | 0.0175 | 0.0032 | 0.0026 | 0.0293 | 0.0588 |
| **E (λ)** | 3.89 (319) | 4.53 (274) | 4.05 (306) | 3.97 (312) | 4.27 (291) | 3.32 (374) | 4.06 (305) | 3.44 (361) | 3.72 (333) | 4.83 (257) | 4.64 (267) |
| **f**    | 0.0223   | 0.0220    | 0.0204 | 0.0048 | 0.0490 | 0.0188 | 0.0466 | 0.0241 | 0.0262 | 0.0545 | 0.0328 |
| **E (λ)** | 3.97 (312) | 4.64 (267) | 4.10 (303) | 3.99 (311) | 4.45 (279) | 3.36 (369) | 4.12 (301) | 3.49 (355) | 3.80 (326) | 5.04 (246) | 4.72 (263) |
| **f**    | 0.0078   | 0.0206    | 0.0110 | 0.0076 | 0.0395 | 0.0075 | 0.0086 | 0.0066 | 0.0017 | 0.0805 | 0.0206 |
Figure S2. Simulated electronic spectra obtained at the PCM-TD-DFT/6-31+G(d)-LANL2DZ//B3LYP-D3/6-31+G(d)-LANL2DZ (DFT = B3LYP-D3, CAM-B3LYP, M05, M06, MN15, PBE, PBE0, TPSS, TPSSh, wB97x, wB97xD) levels for complex 1. Experimental UV/Vis absorbance spectrum measured in DMSO for the same complex is also provided for comparison purposes.
Figure S3. Simulated electronic spectra obtained at the PCM-TD-DFT/6-31+G(d)-LANL2DZ/B3LYP-D3/6-31+G(d)-LANL2DZ (DFT = B3LYP-D3, CAM-B3LYP, M05, M06, MN15, PBE, PBE0, TPSS, TPSSh, wB97x, wB97xD) levels for complex 2. Experimental UV/Vis absorbance spectrum measured in DMSO for the same complex is also provided for comparison purposes.
TPSS

TPSSh

wB97x

wB97xD
Figure S4. Simulated electronic spectra obtained at the PCM-TD-DFT/6-31+G(d)-LANL2DZ//B3LYP-D3/6-31+G(d)-LANL2DZ (DFT = B3LYP-D3, CAM-B3LYP, M05, M06, MN15, PBE, PBE0, TPSS, TPSSh, wB97x, wB97xD) levels for complex 3. Experimental UV/Vis absorbance spectrum measured in DMSO for the same complex is also provided for comparison purposes.
**Table S7.** Excitation energy, $E$ (in parenthesis the corresponding absorption wavelength, $\lambda$), of the most red-shifted absorption band found for complexes 1-3 at the PCM-TD-DFT/6-31+G(d)-LANL2DZ//B3LYP-D3/6-31+G(d)-LANL2DZ levels along with the difference in absolute value between the computed excitation energies and the respective experimental value, $\Delta E$, for each level of theory and complex and the total error, $\Delta E_{\text{total}}$, obtained for each level of theory, $\Delta E_{\text{total}}$.

| DFT      | $E$ (eV) | $\Delta E$/eV | $\Delta E_{\text{total}}$/eV |
|----------|----------|----------------|-------------------------------|
|          | $\lambda$/nm | 1 | 2 | 3 | 1 | 2 | 3 |                          |
| B3LYP-D3 |          | 2.27 (547) | 2.69 (462) | 3.30 (376) | 0.15 | 0.09 | 0.02 | 0.26 |
| CAM-B3LYP|          | 2.73 (454) | 3.25 (381) | 3.53 (351) | 0.31 | 0.47 | 0.21 | 0.99 |
| M05      |          | 2.41 (514) | 2.84 (436) | 3.39 (365) | 0.01 | 0.06 | 0.07 | 0.14 |
| M06      |          | 2.38 (521) | 2.78 (446) | 3.33 (373) | 0.04 | 0.00 | 0.00 | 0.04 |
| MN15     |          | 2.59 (479) | 3.06 (405) | 3.33 (372) | 0.17 | 0.28 | 0.01 | 0.46 |
| PBE      |          | 2.39 (519) | 3.10 (400) | 2.96 (419) | 0.03 | 0.32 | 0.36 | 0.71 |
| PBE0     |          | 2.39 (519) | 2.82 (440) | 3.41 (364) | 0.03 | 0.04 | 0.09 | 0.16 |
| TPSS     |          | 2.46 (504) | 3.20 (388) | 3.04 (408) | 0.04 | 0.42 | 0.28 | 0.74 |
| TPSSh    |          | 2.68 (462) | 2.54 (488) | 3.23 (383) | 0.26 | 0.24 | 0.09 | 0.59 |
| wB97x    |          | 2.97 (418) | 3.56 (348) | 3.79 (327) | 0.55 | 0.78 | 0.47 | 1.80 |
| wB97xD   |          | 2.79 (445) | 3.32 (374) | 3.59 (346) | 0.37 | 0.54 | 0.27 | 1.18 |
| exp.     |          | 2.42 (512) | 2.78 (446) | 3.32 (373) |           |           |       |       |
Table S8. B3LYP-D3/6-31+G(d)-LANL2DZ relevant optimized geometry data for Re(I) complexes 1-3 and 1a-1s in their singlet ground states. Bond distances, bond angles, and dihedral angles are given in Å, degrees, and degrees, respectively. The atom numbering used is collected for complex 1.a

|   | Re-C1 | Re-C2 | Re-L3 | Re-N4 | Re-N5 | Re-N6 | N4-Re-N7 | L3-Re-N7 | C8-N4-Re-N7 | C9-N5-N6-C10 |
|---|-------|-------|-------|-------|-------|-------|----------|----------|-------------|-------------|
| 1 | 1.928 | 1.924 | 1.931 | 2.259 | 2.251 | 2.181 | 75.7     | 98.3     | -80.4       | 1.3         |
| 2 | 1.928 | 1.923 | 1.929 | 2.261 | 2.254 | 2.178 |          |          |             | 1.1         |
| 3 | 1.929 | 1.927 | 1.928 | 2.265 | 2.224 | 2.158 |          |          |             | 2.1         |
| 1a| 1.931 | 1.923 | 1.931 | 2.258 | 2.254 | 2.183 | 76.5     | 98.1     | -79.1       | 0.7         |
| 1b| 1.929 | 1.924 | 1.932 | 2.258 | 2.254 | 2.181 | 76.0     | 98.2     | -79.4       | 1.0         |
| 1c| 1.929 | 1.924 | 1.931 | 2.260 | 2.251 | 2.178 | 75.4     | 98.7     | -79.3       | 1.3         |
| 1d| 1.929 | 1.924 | 1.931 | 2.260 | 2.251 | 2.177 | 75.4     | 98.6     | -79.8       | 1.2         |
| 1e| 1.931 | 1.922 | 1.931 | 2.259 | 2.254 | 2.180 | 76.2     | 98.3     | -78.4       | 0.5         |
| 1f| 1.931 | 1.926 | 1.931 | 2.258 | 2.254 | 2.179 | 76.2     | 98.3     | -78.5       | 0.6         |
| 1g| 1.930 | 1.923 | 1.932 | 2.257 | 2.254 | 2.185 | 77.0     | 97.6     | -80.1       | 1.0         |
| 1h| 1.930 | 1.923 | 1.932 | 2.259 | 2.254 | 2.178 | 75.8     | 98.8     | -78.6       | 0.7         |
| 1i| 1.902 | 1.900 | 2.381 | 2.225 | 2.258 | 2.194 | 81.6     | 90.1     | -76.8       | -2.0        |
| 1j| 1.901 | 1.900 | 2.382 | 2.226 | 2.260 | 2.199 | 82.7     | 88.3     | -77.0       | -1.9        |
| 1k| 1.906 | 1.903 | 2.359 | 2.217 | 2.263 | 2.197 | 87.9     | 82.0     | -76.0       | -5.9        |
| 1l| 1.905 | 1.899 | 2.380 | 2.224 | 2.259 | 2.196 | 81.9     | 89.9     | -76.7       | -2.1        |
| 1m| 1.905 | 1.899 | 2.380 | 2.224 | 2.259 | 2.193 | 81.6     | 90.1     | -76.0       | -1.9        |
| 1n| 1.904 | 1.899 | 2.383 | 2.225 | 2.261 | 2.200 | 83.1     | 88.0     | -76.7       | -1.9        |
| 1o| 1.904 | 1.898 | 2.382 | 2.226 | 2.261 | 2.198 | 82.5     | 88.5     | -76.0       | -2.0        |
| 1p| 1.903 | 1.900 | 2.382 | 2.226 | 2.257 | 2.194 | 81.6     | 90.3     | -76.2       | -2.0        |
| 1q| 1.904 | 1.900 | 2.382 | 2.226 | 2.258 | 2.191 | 81.5     | 90.2     | -75.5       | -2.3        |
| 1r| 1.902 | 1.900 | 2.385 | 2.227 | 2.259 | 2.199 | 82.3     | 88.7     | -76.4       | -1.8        |
| 1s| 1.902 | 1.899 | 2.384 | 2.227 | 2.260 | 2.196 | 82.7     | 88.3     | -75.3       | -2.0        |

*a* L3 is the carbon atom of the carbonyl ligand in trans disposition to the pyridine ligand for complexes 1-3 and 1a-1h or the phosphorus atom of the phosphine ligand in trans disposition to the pyridine ligand for complexes 1i-1s.
**Table S9.** Excitation energies in eV ($E$) and nm ($\lambda$), and oscillator strengths ($f$) of the first ten lowest-lying singlet-singlet electron transitions calculated at the PCM-TD-M06/6-31+G(d)-LANL2DZ//B3LYP-D3/6-31+G(d)-LANL2DZ level for Re(I) complexes 1-3.

| Transition | Complex |
|------------|---------|
|            | 1       | 2       | 3       |
| **1**      | $E (\lambda)$ | 2.38 (521) | 2.78 (446) | 3.05 (407) |
|            | $f$     | 0.1459   | 0.0676   | 0.1335   |
| **2**      | $E (\lambda)$ | 2.89 (428) | 3.16 (392) | 3.26 (381) |
|            | $f$     | 0.0577   | 0.0066   | 0.0060   |
| **3**      | $E (\lambda)$ | **3.18 (390)** | 3.29 (376) | **3.33 (373)** |
|            | $f$     | 0.0606   | 0.0122   | **0.3587** |
| **4**      | $E (\lambda)$ | 3.36 (369) | 3.57 (347) | 3.62 (343) |
|            | $f$     | 0.0062   | 0.0443   | 0.0089   |
| **5**      | $E (\lambda)$ | 3.44 (361) | **3.63 (341)** | 3.67 (338) |
|            | $f$     | 0.0058   | **0.1115** | 0.0016   |
| **6**      | $E (\lambda)$ | 3.45 (359) | 3.79 (327) | 3.70 (335) |
|            | $f$     | 0.0025   | 0.0122   | 0.0129   |
| **7**      | $E (\lambda)$ | 3.49 (356) | 3.85 (322) | 3.92 (316) |
|            | $f$     | 0.0146   | 0.0832   | 0.0361   |
| **8**      | $E (\lambda)$ | 3.78 (328) | 3.90 (318) | 3.94 (315) |
|            | $f$     | 0.0056   | 0.0078   | 0.0203   |
| **9**      | $E (\lambda)$ | **3.79 (327)** | 3.92 (316) | 3.97 (312) |
|            | $f$     | **0.2133** | 0.0103   | 0.0048   |
| **10**     | $E (\lambda)$ | 3.81 (325) | 3.95 (314) | 3.99 (311) |
|            | $f$     | 0.0006   | 0.0220   | 0.0076   |
Table S10. B3LYP-D3/6-31+G(d)-LANL2DZ relevant optimized geometry data for Re(I) complexes 1-3 and 1a-1s in their triplet excited states. Bond distances, bond angles, and dihedral angles are given in Å, degrees, and degrees, respectively. The atom numbering used is collected for complex 1.\(^a\)

|       | Re-C1 | Re-C2 | Re-L3\(^a\) | Re-N4 | Re-N5 | Re-N6 | N4-Re-N7 | L3-Re-N7 | C8-N4-Re-N7 | C9-N5-N6-C10 |
|-------|-------|-------|-------------|-------|-------|-------|-----------|-----------|-------------|-------------|
| 1     | 1.936 | 1.926 | 1.935       | 2.164 | 2.236 | 2.260 | 74.3      | 100.7     | -84.9       | 0.9         |
| 2     | 1.933 | 1.928 | 1.930       | 2.174 | 2.209 | 2.268 |          |           |             | 1.0         |
| 3     | 1.934 | 1.930 | 1.929       | 2.153 | 2.192 | 2.270 |          |           |             | -1.3        |
| 1a    | 1.940 | 1.925 | 1.936       | 2.161 | 2.237 | 2.259 | 75.4      | 99.7      | -82.6       | -0.1        |
| 1b    | 1.937 | 1.926 | 1.936       | 2.162 | 2.237 | 2.260 | 74.6      | 100.4     | -84.1       | 0.5         |
| 1c    | 1.936 | 1.925 | 1.934       | 2.164 | 2.234 | 2.261 | 74.0      | 100.8     | -85.9       | 0.7         |
| 1d    | 1.934 | 1.924 | 1.932       | 2.168 | 2.235 | 2.263 | 74.0      | 100.5     | -85.4       | 0.2         |
| 1e    | 1.939 | 1.924 | 1.935       | 2.162 | 2.235 | 2.261 | 75.2      | 99.7      | -83.0       | -0.4        |
| 1f    | 1.937 | 1.923 | 1.932       | 2.168 | 2.237 | 2.262 | 75.3      | 99.4      | -83.2       | -0.8        |
| 1g    | 1.940 | 1.926 | 1.936       | 2.162 | 2.238 | 2.258 | 75.8      | 99.4      | -83.6       | 0.3         |
| 1h    | 1.937 | 1.924 | 1.935       | 2.163 | 2.235 | 2.261 | 74.5      | 100.4     | -84.7       | -0.03       |
| 1i    | 1.927 | 1.902 | 2.396       | 2.129 | 2.248 | 2.228 | 81.4      | 91.0      | -83.0       | -0.4        |
| 1j    | 1.931 | 1.903 | 2.399       | 2.120 | 2.250 | 2.229 | 82.4      | 89.8      | -82.8       | -0.5        |
| 1k    | 1.923 | 1.905 | 2.369       | 2.221 | 2.250 | 2.147 | 85.1      | 85.7      | -82.2       | -3.5        |
| 1l    | 1.935 | 1.902 | 2.401       | 2.118 | 2.246 | 2.227 | 82.3      | 90.5      | -81.9       | -0.6        |
| 1m    | 1.929 | 1.900 | 2.395       | 2.129 | 2.247 | 2.228 | 82.0      | 90.4      | -81.7       | -0.7        |
| 1n    | 1.938 | 1.902 | 2.401       | 2.133 | 2.246 | 2.228 | 84.1      | 88.4      | -82.0       | 0.5         |
| 1o    | 1.932 | 1.900 | 2.397       | 2.124 | 2.248 | 2.229 | 83.5      | 88.4      | -81.9       | 0.2         |
| 1p    | 1.931 | 1.902 | 2.403       | 2.122 | 2.248 | 2.227 | 81.1      | 90.8      | -82.8       | -0.1        |
| 1q    | 1.925 | 1.900 | 2.395       | 2.132 | 2.249 | 2.229 | 81.4      | 90.8      | -82.8       | -0.7        |
| 1r    | 1.936 | 1.903 | 2.401       | 2.114 | 2.249 | 2.229 | 82.4      | 89.8      | -82.8       | -0.4        |
| 1s    | 1.928 | 1.900 | 2.398       | 2.128 | 2.249 | 2.230 | 82.8      | 88.9      | -83.3       | 0.1         |

\(^a\) L3 is the carbon atom of the carbonyl ligand in \textit{trans} disposition to the pyridine ligand for complexes 1-3 and 1a-1h or the phosphorus atom of the phosphine ligand in \textit{trans} disposition to the pyridine ligand for complexes 1i-1s.
Table S11. Energies in the singlet ground state and triplet excited state \((E_S \text{ and } E_T)\) in hartree, respectively), difference between \(E_T\) and \(E_S\) (\(\Delta E_{ST}\), in kcal/mol), excitation energy in nm and eV \((\lambda_{max} (E))\), oscillator strength \((f)\), dominant orbital excitations with their corresponding coefficients for the lowest-lying absorption band, HOMO and LUMO energies \((E_H \text{ and } E_L)\) in eV, respectively, and difference between \(E_i\) and \(E_{H-L}\) (\(\Delta E_{H-L}\)) in eV of the Re(I) complexes 1-3 and 1a-1s calculated at the PCM-M06/6-31+G(d)-LANL2DZ/B3LYP-D3/6-31+G(d)-LANL2DZ level.

| Species | \(E_S\) | \(E_T\) | \(\Delta E_{ST}\) | \(\lambda_{max} (E)\) | \(f\) | Configuration | \(E_H\) | \(E_L\) | \(\Delta E_{H-L}\) |
|---------|---------|---------|-----------------|-----------------|-----|---------------|---------|---------|-----------------|
| 1       | -1633.912888 | -1633.851279 | 38.7 | 521 (2.38) | 0.1459 | H → L (0.6960) | -5.98 | -2.82 | 3.16 |
| 2       | -1353.183798 | -1353.108711 | 47.1 | 446 (2.78) | 0.0676 | H → L (0.6993) | -5.64 | -1.98 | 3.66 |
| 3       | -1277.008324 | -1276.930089 | 49.1 | 373 (3.33) | 0.3587 | H-1 → L (0.6718)/H → L (-0.1659) | -5.73 | -1.88 | 3.85 |
| 1a      | -1900.959515 | -1900.899520 | 37.7 | 534 (3.22) | 0.1386 | H → L (0.6937) | -6.05 | -2.96 | 3.09 |
| 1b      | -1733.125226 | -1733.064473 | 38.1 | 532 (2.33) | 0.1435 | H → L (0.6967) | -6.04 | -2.93 | 3.11 |
| 1c      | -1748.373801 | -1748.317551 | 35.3 | 565 (2.19) | 0.1292 | H → L (0.6978) | -5.75 | -2.80 | 2.95 |
| 1d      | -1767.776972 | -1767.732364 | 28.0 | 659 (1.88) | 0.1007 | H → L (0.6998) | -5.35 | -2.77 | 2.58 |
| 1e      | -2015.420137 | -2015.365833 | 34.1 | 579 (2.14) | 0.1415 | H → L (0.6942) | -5.81 | -2.94 | 2.87 |
| 1f      | -2034.824141 | -2034.781497 | 26.8 | 678 (1.83) | 0.1312 | H → L (0.6935)/H → L+1 (-0.1110) | -5.40 | -2.94 | 2.46 |
| 1g      | -2168.011959 | -2167.948813 | 39.6 | 517 (2.40) | 0.1537 | H → L (0.6945) | -6.21 | -3.04 | 3.17 |
| 1h      | -1847.585859 | -1847.531178 | 34.3 | 578 (2.14) | 0.1292 | H → L (0.6994) | -5.80 | -2.91 | 2.89 |
| 1i      | -1981.602431 | -1981.546457 | 35.1 | 584 (2.12) | 0.0979 | H-1 → L (0.1119)/H → L (0.6897) | -5.61 | -2.74 | 2.87 |
| 1j      | -2379.582469 | -2379.527312 | 34.6 | 611 (2.03) | 0.0767 | H-1 → L (-0.3159)/H → L (0.6171) | -5.44 | -2.75 | 2.69 |
| 1k      | -2528.857023 | -2528.798015 | 37.0 | 559 (2.22) | 0.1017 | H-1 → L (0.1114)/H → L (0.6898) | -5.77 | -2.80 | 2.97 |
| 1l      | -2248.648310 | -2248.595150 | 33.4 | 608 (2.04) | 0.0945 | H-1 → L (0.1233)/H → L (0.6875) | -5.66 | -2.88 | 2.78 |
| 1m      | -2363.109107 | -2363.059803 | 30.9 | 631 (1.96) | 0.1161 | H → L (0.6924) | -5.54 | -2.86 | 2.68 |
| 1n      | -2646.628760 | -2646.577198 | 32.4 | 644 (1.92) | 0.0698 | H-1 → L (-0.3458)/H → L (0.6007) | -5.48 | -2.89 | 2.59 |
| 1o      | -2761.089141 | -2761.040814 | 30.3 | 653 (1.90) | 0.0934 | H-1 → L (-0.2543)/H → L (0.6431) | -5.45 | -2.87 | 2.58 |
| 1p      | -2080.815019 | -2080.760020 | 34.5 | 601 (2.06) | 0.0860 | H-1 → L (0.1407)/H → L (0.6839) | -5.67 | -2.84 | 2.83 |
| 1q      | -2195.275858 | -2195.225650 | 31.5 | 627 (1.98) | 0.0995 | H-1 → L (-0.1015)/H → L (0.6926) | -5.54 | -2.81 | 2.63 |
| 1r      | -2478.794985 | -2478.741640 | 33.5 | 632 (1.96) | 0.0651 | H-2 → L (0.1021)/H-1 → L (-0.4084)/H → L (0.5515) | -5.48 | -2.85 | 2.63 |
| 1s      | -2593.255739 | -2593.206056 | 31.2 | 645 (1.93) | 0.0822 | H-2 → L (0.1029)/H-1 → L (-0.2869)/H → L (0.6261) | -5.45 | -2.82 | 2.63 |
Table S12. Variations of some relevant bond distances (in Å), bond angles (in degrees), and dihedral angles (in degrees) when going from their singlet ground states to their corresponding triplet excited states of Re(I) complexes 1-3 and 1a-1s at the B3LYP-D3/6-31+G(d)-LANL2DZ level of theory. The atom numbering used is collected for complex 1.a

|     | Re-C1 | Re-C2 | Re-L3\(^a\) | Re-N4 | Re-N5 | Re-N6 | N4-Re-N7 | C3-Re-N7 | C8-N4-Re-N7 | C9-N5-N6-C10 |
|-----|-------|-------|-------------|-------|-------|-------|----------|----------|-------------|-------------|
| 1   | 0.008 | 0.002 | 0.004       | -0.017| -0.015| 0.001 | -1.4     | 2.4      | -4.5        | -0.4        |
| 2   | 0.005 | 0.005 | 0.001       | -0.004| -0.045| 0.007 |          |          |             |             |
| 3   | 0.005 | 0.003 | 0.001       | -0.005| -0.032| 0.005 | -0.008   | -0.004   | -0.045      | -0.005      |
| 1a  | 0.009 | 0.002 | 0.005       | -0.022| -0.017| 0.001 | -1.1     | 1.6      | -3.5        | -0.1        |
| 1b  | 0.008 | 0.002 | 0.004       | -0.019| -0.017| 0.002 | -1.4     | 2.2      | -4.7        | -0.7        |
| 1c  | 0.007 | 0.001 | 0.003       | -0.014| -0.017| 0.001 | -1.4     | 2.1      | -6.6        | -0.6        |
| 1d  | 0.005 | 0.000 | 0.001       | -0.009| -0.016| 0.003 | -1.4     | 1.9      | -5.6        | -1.0        |
| 1e  | 0.008 | 0.002 | 0.004       | -0.018| -0.019| 0.002 | -1.0     | 1.4      | -4.6        | -0.9        |
| 1f  | 0.006 | -0.003| 0.001       | -0.011| -0.017| 0.004 | -0.9     | 1.1      | -4.7        | -1.4        |
| 1g  | 0.010 | 0.003 | 0.004       | -0.023| -0.016| 0.001 | -1.2     | 1.8      | -3.5        | 0.7         |
| 1h  | 0.007 | 0.001 | 0.003       | -0.015| -0.019| 0.002 | -1.3     | 1.6      | -6.1        | -0.7        |
| 1i  | 0.025 | 0.002 | 0.015       | -0.065| -0.010| 0.003 | 0.2      | 0.9      | -6.2        | 1.6         |
| 1j  | 0.030 | 0.003 | 0.017       | -0.079| -0.010| 0.003 | 0.3      | 1.5      | -5.8        | 1.4         |
| 1k  | 0.017 | 0.002 | 0.010       | -0.050| -0.013| 0.004 | -2.8     | 3.7      | -6.2        | -2.4        |
| 1l  | 0.030 | 0.003 | 0.021       | -0.078| -0.013| 0.003 | 0.4      | 0.6      | -5.2        | 1.5         |
| 1m  | 0.024 | 0.001 | 0.015       | -0.064| -0.012| 0.004 | 0.4      | 0.3      | -5.7        | 1.2         |
| 1n  | 0.034 | 0.003 | 0.018       | -0.067| -0.015| 0.003 | 1.0      | 0.4      | -5.3        | 2.4         |
| 1o  | 0.028 | 0.002 | 0.015       | -0.074| -0.013| 0.003 | 1.0      | 0.4      | -5.9        | 2.2         |
| 1p  | 0.028 | 0.002 | 0.021       | -0.072| -0.009| 0.001 | 0.5      | 0.5      | -6.6        | 1.9         |
| 1q  | 0.021 | 0.000 | 0.013       | -0.059| -0.009| 0.003 | 0.1      | 0.6      | -7.3        | 1.6         |
| 1r  | 0.034 | 0.003 | 0.016       | -0.085| -0.010| 0.002 | 0.1      | 1.1      | -6.4        | 1.4         |
| 1s  | 0.026 | 0.001 | 0.014       | -0.068| -0.011| 0.003 | 0.1      | 0.6      | -8.0        | 2.1         |

\(^a\) L3 is the carbon atom of the carbonyl ligand in *trans* disposition to the pyridine ligand for complexes 1-3 and 1a-1h or the phosphorus atom of the phosphine ligand in *trans* disposition to the pyridine ligand for complexes 1i-1s.
Figure S5. B3LYP-D3/6-31+G(d)-LANL2DZ optimized structures in the singlet ground state of Re(I) complexes 1a-1s. For clarity, two views are given for each species.
Figure S5. (cont.)

1e

1f

1g

1h
Figure S5. (cont.)
Figure S5. (cont.)
Figure S5. (cont.)
Figure S6. Contour maps of the spin density distribution (isovalue 0.0004) for the triplet excited state of the Re(I) complexes 1a-1s. For clarity, two views are given for each species.
Figure S6. (cont.)

1e

1f

1g

1h
Figure S6. (cont.)

1i

1j

1k

1l
Figure S6. (cont.)

1q

1r

1s
Table S13. B3LYP-D3/6-31+G(d)-LANL2DZ variations of some relevant bond distances (in Å), bond angles (in degrees), and dihedral angles (in degrees) of complexes 1a-1h compared to complex 1. The atom numbering used is collected for complex 1.\textsuperscript{a}

![Chemical structure diagram](image)

| Complexes | Re-C1 (Å) | Re-C2 (Å) | Re-L3\textsuperscript{a} (Å) | Re-N4 (Å) | Re-N5 (Å) | Re-N6 (Å) | N4-Re-N7 (°) | N5-Re-N7 (°) | C3-Re-N7 (°) | C8-N4-Re-N7 (°) | C9-N5-N6-C10 (°) |
|-----------|-----------|-----------|-----------------|-----------|-----------|-----------|-------------|-------------|-------------|----------------|-----------------|
| 1a        | 0.003     | -0.001    | 0.000           | 0.002     | 0.003     | -0.001    | 0.8         | -0.2        | 1.3         | -0.6           |
| 1b        | 0.001     | 0.000     | 0.001           | 0.000     | 0.003     | -0.001    | 0.3         | -0.1        | 1.0         | -0.3           |
| 1c        | 0.001     | 0.000     | 0.000           | -0.003    | 0.000     | 0.001     | -0.3        | 0.4         | 1.1         | 0.0            |
| 1d        | 0.001     | 0.000     | 0.000           | -0.004    | 0.000     | 0.001     | -0.3        | 0.3         | 0.6         | -0.1           |
| 1e        | 0.003     | -0.002    | 0.000           | -0.001    | 0.003     | 0.000     | 0.5         | 0.0         | 2.0         | -0.8           |
| 1f        | 0.003     | 0.002     | 0.000           | -0.002    | 0.003     | -0.001    | 0.5         | 0.0         | 1.9         | -0.7           |
| 1g        | 0.002     | -0.001    | 0.001           | 0.004     | 0.003     | -0.002    | 1.3         | -0.7        | 0.3         | -0.3           |
| 1h        | 0.002     | -0.001    | 0.001           | -0.003    | 0.003     | 0.000     | 0.1         | 0.5         | 1.8         | -0.6           |

\textsuperscript{a} L3 is the carbon atom of the carbonyl ligand in \textit{trans} disposition to the pyridine ligand for complexes 1 and 1a-1h.
Table S14. Excitation energies in eV ($E$) and nm ($\lambda$), and oscillator strengths ($f$) of the first ten lowest-lying singlet-singlet electron transitions calculated at the PCM-TD-M06/6-31+G(d)-LANL2DZ//B3LYP-D3/6-31+G(d)-LANL2DZ level for Re(I) complexes 1a-1h. For comparison purposes, the data obtained for complex 1 are also included.

| Transition | 1  | 1a  | 1b  | 1c  | 1d  | 1e  | 1f  | 1g  | 1h  |
|------------|----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1          | $E$ ($\lambda$) | 2.38 (521) | 2.32 (534) | 2.33 (532) | 2.19 (565) | 1.88 (659) | 2.14 (579) | 1.83 (678) | 2.40 (517) | 2.14 (578) |
|            | $f$ | 0.1459 | 0.1386 | 0.1435 | 0.1292 | 0.1007 | 0.1415 | 0.1312 | 0.1537 | 0.1292 |
| 2          | $E$ ($\lambda$) | 2.89 (428) | 2.80 (443) | 2.83 (439) | 2.63 (471) | 2.64 (470) | 2.38 (521) | 2.88 (430) | 2.77 (448) |
|            | $f$ | 0.0577 | 0.0083 | 0.0669 | 0.0490 | 0.0423 | 0.0048 | 0.0348 | 0.0100 | 0.0770 |
| 3          | $E$ ($\lambda$) | 3.18 (390) | 2.96 (418) | 3.15 (394) | 2.98 (416) | 2.74 (452) | 2.84 (436) | 2.64 (470) | 3.05 (406) | 2.94 (421) |
|            | $f$ | 0.0606 | 0.1024 | 0.0300 | 0.0943 | 0.1465 | 0.1196 | 0.1325 | 0.1053 | 0.0397 |
| 4          | $E$ ($\lambda$) | 3.36 (369) | 3.25 (381) | 3.29 (377) | 3.26 (381) | 2.96 (419) | 3.24 (383) | 2.98 (416) | 3.24 (383) | 3.28 (379) |
|            | $f$ | 0.0062 | 0.0030 | 0.0156 | 0.0063 | 0.0035 | 0.0052 | 0.0035 | 0.0075 | 0.0221 |
| 5          | $E$ ($\lambda$) | 3.44 (361) | 3.33 (372) | 3.36 (369) | 3.36 (369) | 3.30 (376) | 3.29 (376) | 3.19 (389) | 3.31 (375) | 3.29 (376) |
|            | $f$ | 0.0058 | 0.0037 | 0.0008 | 0.0091 | 0.0303 | 0.0032 | 0.0300 | 0.0018 | 0.0042 |
| 6          | $E$ ($\lambda$) | 3.45 (359) | 3.37 (368) | 3.40 (364) | 3.43 (361) | 3.40 (365) | 3.32 (373) | 3.25 (381) | 3.35 (370) | 3.35 (371) |
|            | $f$ | 0.0025 | 0.0139 | 0.0145 | 0.0131 | 0.0247 | 0.0100 | 0.0333 | 0.0185 | 0.0166 |
| 7          | $E$ ($\lambda$) | 3.49 (356) | 3.48 (356) | 3.48 (356) | 3.43 (362) | 3.37 (368) | 3.26 (380) | 3.61 (344) | 3.39 (366) |
|            | $f$ | 0.0146 | 0.0150 | 0.0137 | 0.0038 | 0.0601 | 0.0037 | 0.1678 | 0.0308 | 0.0066 |
| 8          | $E$ ($\lambda$) | 3.78 (328) | 3.61 (343) | 3.76 (330) | 3.64 (340) | 3.47 (357) | 3.50 (354) | 3.35 (370) | 3.66 (339) | 3.62 (343) |
|            | $f$ | 0.0056 | 0.4810 | 0.2128 | 0.0119 | 0.0473 | 0.4735 | 0.1614 | 0.4517 | 0.0633 |
| 9          | $E$ ($\lambda$) | 3.79 (327) | 3.70 (335) | 3.78 (328) | 3.67 (338) | 3.48 (356) | 3.52 (352) | 3.38 (367) | 3.76 (330) | 3.66 (339) |
|            | $f$ | 0.2133 | 0.0882 | 0.0101 | 0.0660 | 0.0075 | 0.0457 | 0.0406 | 0.0002 | 0.0835 |
| 10         | $E$ ($\lambda$) | 3.81 (325) | 3.77 (329) | 3.80 (327) | 3.70 (335) | 3.54 (351) | 3.69 (336) | 3.48 (356) | 3.77 (329) | 3.68 (337) |
|            | $f$ | 0.0006 | 0.0002 | 0.0005 | 0.2316 | 0.1401 | 0.0050 | 0.0089 | 0.0181 | 0.1738 |
Table S15. B3LYP-D3/6-31+G(d)-LANL2DZ variations of some relevant bond distances (in Å), bond angles (in degrees), and dihedral angles (in degrees) of complexes 1i-1s compared to complex 1. The atom numbering used is collected for complex 1.a

| Complexes | Re-C1  | Re-C2  | Re-L3\(^a\) | Re-N4  | Re-N5  | Re-N6  | N4-Re-N7 | C3-Re-N7 | C8-N4-Re-N7 | C9-N5-N6-C10 |
|-----------|--------|--------|-------------|--------|--------|--------|----------|-----------|-------------|--------------|
| 1i        | -0.026 | -0.024 | 0.450       | -0.034 | 0.007  | 0.013  | 5.9      | -8.2      | 3.6         | -3.3         |
| 1j        | -0.027 | -0.024 | 0.451       | -0.033 | 0.009  | 0.018  | 7.0      | -10.0     | 3.4         | -3.2         |
| 1k        | -0.022 | -0.021 | 0.428       | -0.042 | 0.012  | 0.016  | 12.2     | -16.3     | 4.4         | -7.2         |
| 1l        | -0.023 | -0.025 | 0.449       | -0.035 | 0.008  | 0.015  | 6.2      | -8.4      | 3.7         | -3.4         |
| 1m        | -0.023 | -0.025 | 0.449       | -0.035 | 0.008  | 0.012  | 5.9      | -8.2      | 4.4         | -3.2         |
| 1n        | -0.024 | -0.025 | 0.452       | -0.034 | 0.010  | 0.019  | 7.4      | -10.3     | 3.7         | -3.2         |
| 1o        | -0.024 | -0.026 | 0.451       | -0.033 | 0.010  | 0.017  | 6.8      | -9.8      | 4.4         | -3.3         |
| 1p        | -0.025 | -0.024 | 0.451       | -0.033 | 0.006  | 0.013  | 5.9      | -8.0      | 4.2         | -3.3         |
| 1q        | -0.024 | -0.024 | 0.451       | -0.033 | 0.007  | 0.010  | 5.8      | -8.1      | 4.9         | -3.6         |
| 1r        | -0.026 | -0.024 | 0.454       | -0.032 | 0.008  | 0.018  | 6.6      | -9.6      | 4.0         | -3.1         |
| 1s        | -0.026 | -0.025 | 0.453       | -0.032 | 0.009  | 0.015  | 7.0      | -10.0     | 5.1         | -3.3         |

\(^a\) L3 is the carbon atom of the carbonyl ligand in \textit{trans} disposition to the pyridine ligand for complex 1 and the phosphorus atom of the phosphine ligand in \textit{trans} disposition to the pyridine ligand for complexes 1i-1s.
Table S16. Excitation energies in eV ($E$) and nm ($\lambda$), and oscillator strengths ($f$) of the first ten lowest-lying singlet-singlet electron transitions calculated at the PCM-TD-M06/6-31+G(d)-LANL2DZ/B3LYP-D3/6-31+G(d)-LANL2DZ level for Re(I) complexes 1i-1s. For comparison purposes, the data obtained for complex 1 are also included.

| Transition | 1 | 1i | 1j | 1k | 1l | 1m | 1n | 1o | 1p | 1q | 1r | 1s |
|------------|---|----|----|----|----|----|----|----|----|----|----|----|
| $E (\lambda)$ | 2.38 (521) | 2.12 (584) | 2.03 (611) | 2.22 (559) | 2.04 (608) | 1.96 (631) | 1.92 (644) | 1.90 (653) | 2.06 (601) | 1.98 (627) | 1.96 (632) | 1.92 (645) |
| $f$ | 0.1459 | 0.0979 | 0.0767 | 0.1017 | 0.0945 | 0.1161 | 0.0698 | 0.0934 | 0.0860 | 0.0995 | 0.0651 | 0.0822 |
| 2 | $E (\lambda)$ | 2.89 (428) | 2.47 (503) | 2.14 (579) | 2.56 (484) | 2.37 (523) | 2.38 (520) | 2.02 (614) | 2.04 (607) | 2.41 (514) | 2.43 (510) | 2.06 (603) | 2.08 (596) |
| $f$ | 0.0577 | 0.0557 | 0.0083 | 0.0323 | 0.0580 | 0.0374 | 0.0076 | 0.0111 | 0.0791 | 0.0674 | 0.0129 | 0.0154 |
| 3 | $E (\lambda)$ | 3.18 (390) | 2.78 (446) | 2.28 (545) | 2.81 (441) | 2.57 (483) | 2.45 (505) | 2.16 (575) | 2.17 (571) | 2.73 (454) | 2.64 (471) | 2.20 (564) | 2.21 (560) |
| $f$ | 0.0606 | 0.0297 | 0.0232 | 0.0309 | 0.0069 | 0.0248 | 0.0276 | 0.0256 | 0.0394 | 0.0461 | 0.0296 | 0.2073 |
| 4 | $E (\lambda)$ | 3.36 (369) | 2.94 (422) | 2.56 (485) | 2.99 (414) | 2.78 (446) | 2.67 (465) | 2.45 (505) | 2.35 (528) | 2.86 (434) | 2.79 (445) | 2.49 (497) | 2.39 (519) |
| $f$ | 0.0062 | 0.0003 | 0.0472 | 0.0408 | 0.0275 | 0.0497 | 0.0340 | 0.0275 | 0.0005 | 0.0168 | 0.0527 | 0.0359 |
| 5 | $E (\lambda)$ | 3.44 (361) | 2.96 (418) | 2.80 (443) | 3.03 (409) | 2.83 (438) | 2.85 (436) | 2.51 (494) | 2.43 (510) | 2.91 (426) | 2.87 (432) | 2.76 (450) | 2.70 (459) |
| $f$ | 0.0058 | 0.0603 | 0.0027 | 0.0305 | 0.0015 | 0.0024 | 0.0146 | 0.0168 | 0.0541 | 0.0441 | 0.0255 | 0.0011 |
| 6 | $E (\lambda)$ | 3.45 (359) | 3.00 (414) | 2.90 (428) | 3.06 (405) | 2.94 (422) | 2.87 (433) | 2.68 (463) | 2.67 (465) | 2.97 (418) | 2.88 (430) | 2.83 (437) | 2.80 (442) |
| $f$ | 0.0025 | 0.0336 | 0.0870 | 0.0111 | 0.0367 | 0.0475 | 0.0029 | 0.0038 | 0.0167 | 0.0181 | 0.0540 | 0.0929 |
| 7 | $E (\lambda)$ | 3.49 (356) | 3.19 (389) | 2.93 (423) | 3.31 (374) | 3.02 (410) | 3.00 (413) | 2.79 (445) | 2.77 (448) | 3.21 (386) | 3.14 (395) | 2.85 (435) | 2.87 (432) |
| $f$ | 0.0146 | 0.0256 | 0.0002 | 0.0372 | 0.0450 | 0.0236 | 0.0006 | 0.0002 | 0.0255 | 0.0220 | 0.0056 | 0.0007 |
| 8 | $E (\lambda)$ | 3.78 (328) | 3.32 (374) | 3.01 (412) | 3.40 (364) | 3.19 (389) | 3.12 (398) | 2.80 (443) | 2.80 (443) | 3.32 (373) | 3.31 (375) | 2.94 (421) | 2.93 (423) |
| $f$ | 0.0056 | 0.0368 | 0.0006 | 0.0250 | 0.0202 | 0.0178 | 0.0463 | 0.0632 | 0.0318 | 0.0267 | 0.0001 | 0.0081 |
| 9 | $E (\lambda)$ | 3.79 (327) | 3.49 (356) | 3.04 (408) | 3.60 (344) | 3.36 (369) | 3.26 (380) | 2.82 (440) | 2.84 (437) | 3.52 (352) | 3.47 (358) | 2.99 (414) | 2.99 (415) |
| $f$ | 0.2133 | 0.0791 | 0.0046 | 0.0910 | 0.0205 | 0.0091 | 0.0333 | 0.0027 | 0.0680 | 0.0921 | 0.0035 | 0.0019 |
| 10 | $E (\lambda)$ | 3.81 (325) | 3.63 (342) | 3.11 (398) | 3.67 (338) | 3.47 (357) | 3.35 (370) | 2.93 (423) | 2.92 (425) | 3.58 (346) | 3.53 (351) | 3.10 (401) | 3.03 (409) |
| $f$ | 0.0006 | 0.0776 | 0.0274 | 0.0174 | 0.0921 | 0.0661 | 0.0035 | 0.0173 | 0.1234 | 0.1008 | 0.0253 | 0.0237 |
**Figure S7.** PCM-TD-M06/6-31+G(d)-LANL2DZ//B3LYP-D3/6-31+G(d)-LANL2DZ electronic absorption spectra of Re(I) pyridocarbazole complexes bearing the phosphine ligands DAPTA (1k), PMe$_3$ (1p and 1q), and CAP (1r and 1s).

1k
($R^1 = H, R^2 = H, R^3 = \text{DAPTA}$)

1p
($R^1 = F, R^2 = H, R^3 = \text{PMe}_3$)

1q
($R^1 = F, R^2 = \text{OMe}, R^3 = \text{PMe}_3$)

1r
($R^1 = F, R^2 = H, R^3 = \text{CAP}$)

1s
($R^1 = F, R^2 = \text{OMe}, R^3 = \text{CAP}$)
Figure S8. Contour maps of the frontier Kohn-Sham orbitals involved in the main orbital transition of the lowest-lying absorption band found for Re(I) dicarbonyl pyridyl complexes containing the phosphine ligands DAPTA (1k), PMe₃ (1p and 1q), and CAP (1r and 1s). Two views are given for each orbital.
Table S17. B3LYP-D3/6-31+G(d)-LANL2DZ cartesian coordinates, in Å, of the optimized structures in their singlet ground states of all Re(I) complexes investigated.

| X   | Y   | Z   |
|-----|-----|-----|
| C   | -1.024946 | 0.217753 | -0.386651 |
| N   | 0.061628 | 1.035618 | -0.428157 |
| C   | -0.446574 | 2.318033 | -0.324976 |
| C   | 0.250431 | 3.536985 | -0.308205 |
| C   | -0.794804 | 4.711963 | -0.173828 |
| C   | -1.893202 | 4.693307 | -0.059022 |
| C   | -2.594511 | 3.490826 | -0.076685 |
| C   | -1.882998 | 2.287043 | -0.207235 |
| C   | -2.253905 | 0.893530 | -0.254624 |
| C   | -3.451977 | 0.972923 | -0.250840 |
| C   | -3.379199 | -1.264612 | -0.296007 |
| C   | 1.936996 | -2.301058 | 1.779526 |
| C   | 1.403377 | -2.580447 | 4.192469 |
| C   | 0.634663 | -0.571740 | 5.503605 |
| C   | 0.441943 | 1.630585 | 4.295821 |
| C   | 0.998819 | 1.723454 | 1.875311 |
| C   | 1.445459 | -3.420405 | -0.814011 |
| C   | -2.826763 | -4.003261 | -0.521655 |
| C   | 1.331865 | 3.556613 | -0.407357 |
| C   | 0.036988 | 5.666159 | -0.162846 |
| C   | -3.768801 | 3.483111 | 0.009465 |
| C   | -4.408939 | 0.606303 | -0.107336 |
| C   | -4.291857 | -1.853969 | -0.264674 |
| C   | 2.080263 | 0.227345 | 4.079599 |
| C   | 2.158135 | 0.099372 | -3.561650 |
| C   | -0.531868 | -4.953770 | -0.772040 |
| C   | -2.432619 | 5.631561 | 0.045032 |

| X   | Y   | Z   |
|-----|-----|-----|
| C   | 1.820259 | -0.091711 | -0.490398 |
| C   | 3.298898 | -1.327869 | -0.414134 |
| C   | 4.152399 | -2.418720 | -0.498781 |
| C   | 3.033174 | 1.382911 | -0.228592 |
| C   | 3.757876 | 2.273790 | -0.042271 |
| C   | 1.424284 | -0.268688 | 1.732475 |
| C   | 1.574017 | -1.440772 | 2.382344 |
| C   | 1.292765 | -1.593919 | 3.736706 |
| C   | 0.839811 | -0.488256 | 4.460342 |
| C   | 0.686019 | 0.727211 | 3.792670 |
| C   | 0.984230 | 0.796663 | 2.434192 |
| C   | 0.249300 | -1.661020 | -0.596894 |
| C   | 0.872722 | 1.298457 | -2.411902 |
| C   | 0.536171 | -3.930320 | -0.732205 |
| C   | 1.858404 | -3.489132 | -0.562396 |
| C   | 2.106920 | -2.133355 | 0.423049 |
| C   | 1.036765 | -1.217215 | -0.478566 |
| C   | -0.194703 | 0.521234 | -3.266950 |
| C   | -0.049393 | 0.984102 | -0.428798 |
| C   | -0.454261 | 2.289383 | -0.336551 |
| C   | 0.314308 | 3.740002 | -0.368694 |
| C   | -0.345006 | 4.684000 | -0.233194 |
| C   | -1.753981 | 4.748886 | -0.068737 |
| C   | -2.523272 | 3.597038 | -0.039118 |
| C   | 3.366083 | -1.374313 | -0.407931 |
| C   | 2.411099 | -2.175308 | -0.336069 |
| C   | 3.110805 | 1.373772 | -0.239972 |
| C   | 0.816019 | 2.281935 | 0.066231 |
| C   | 0.770516 | -0.227791 | 1.727291 |
| C   | 1.046756 | -1.458266 | 2.374687 |
| C   | 1.303388 | -1.065960 | 3.725132 |
| C   | 0.807144 | -0.489889 | 4.478775 |
| C   | 0.770166 | 0.732142 | 3.783184 |
| C   | 1.086387 | 0.796680 | 2.428795 |
| C   | 0.324876 | -1.075979 | -0.596054 |
| C   | 0.439575 | -3.015105 | -0.707277 |
| C   | -0.682113 | -3.882865 | -0.678826 |
| C   | -1.957504 | -3.349732 | -0.541595 |
| C   | -2.128601 | -1.951369 | -0.434322 |
| C   | -0.931000 | -1.177692 | -0.472231 |

| X   | Y   | Z   |
|-----|-----|-----|
| C   | 0.206231 | 0.142686 | -3.560685 |
| X      | Y      | Z      |
|--------|--------|--------|
| -3.523689 | -1.272923 | -0.350640 |
| -5.276030 | -2.956950 | -0.624732   |
| 5.388491  | -4.681025 | 0.746530    |
| 5.542752  | -4.578860 | -1.037913   |
| -5.539845 | 1.611487  | -0.053729   |
| 6.940914  | -4.196197 | 0.007096    |
| -2.077781 | 2.289441  | 0.132242    |
| -2.071553 | 4.677506  | 0.406226    |
| 4.857590  | -0.290603 | 0.022196    |
| 4.357519  | 8.440319  | 0.098232    |
| -1.826380 | -2.382680 | -2.397368   |
| -1.830649 | -3.34275   | -3.553275   |
| -3.182526 | 4.380019   | -0.638739   |
| 5.545942  | -2.747146 | -0.031997   |
| 5.854869  | -4.131846 | -0.083677   |
| 6.940914  | -4.196197 | 0.007096    |
| 5.942752  | -5.578600 | -1.037913   |
| 5.388491  | -4.681025 | 0.746530    |
| 4.857590  | -0.290603 | 0.022196    |
| 4.357519  | 8.440319  | 0.098232    |
| -1.826380 | -2.382680 | -2.397368   |
| -1.830649 | -3.34275   | -3.553275   |
| -3.182526 | 4.380019   | -0.638739   |
| 5.545942  | -2.747146 | -0.031997   |
| 5.854869  | -4.131846 | -0.083677   |

**1j**

| X      | Y      | Z      |
|--------|--------|--------|
| -5.141100 | 1.612999 | -0.068549 |
| -1.507981 | 2.688070 | -1.282552 |
| 0.229599  | 3.321832 | -0.098156 |
| 0.138523  | 2.380827 | 1.435051  |
| -0.905325 | 2.831702 | 2.385553  |
| 1.234658  | 2.987380 | 0.024207  |
| 1.626019  | 3.707806 | -1.048623 |
| 2.748872  | 4.503978 | -1.048623 |
| 3.506478  | 4.682355 | 0.130449  |
| 3.104177  | 3.889910 | 1.242429  |
| 1.972111  | 0.849299 | -1.51985  |
| 0.692497  | 0.610883 | -1.695197 |
| 0.641215  | 0.782224 | -0.018124 |
| 1.466192  | 0.061895 | -3.904822 |
| 2.371380  | -0.871319 | -4.205511 |
| 2.455506  | -1.080670 | -0.203177 |
| 1.583981  | -0.297950 | -1.204416 |
| 1.613778  | -0.459843 | -0.198510 |
| 0.810820  | 0.241370 | 1.025632  |
| 1.109360  | -0.212152 | 2.304461  |
| 0.547545  | 0.002960 | 3.520277  |
| 1.008174  | -0.402881 | 4.689302  |
| 2.008255  | -1.400422 | 4.660919  |
| 2.574181  | -1.819130 | 3.458445  |
| 2.127922  | -1.226271 | 2.264646  |
| 2.458307  | -1.388554 | 0.872109  |
| 3.302501  | -1.245863 | 0.050229  |
| 4.306889  | -3.390563 | 0.101022  |
| 4.608039  | -3.624716 | 1.511086  |
| 4.851376  | -3.611853 | -0.804885 |
| 4.297194  | -2.933559 | -1.910160 |
| 4.615513  | -3.285185 | -0.073688 |
| 3.307813  | -1.999275 | -1.342374 |
| 1.008072  | 3.613429 | -1.933596 |
| 3.012297  | 0.584992 | -1.933175 |
| 4.386003  | 5.264648 | 0.171869  |
| 3.654659  | 3.927514 | 2.178976  |
| 1.635077  | 2.491920 | 1.993173  |
| 0.080670  | 1.051431 | -3.381819 |
| 3.010565  | -1.443450 | -4.085216 |
| 0.224872  | 0.364272 | 3.541843  |
| 0.585912  | -0.103703 | 5.448486  |
| 3.343043  | -2.589497 | 3.426312  |
| 5.566103  | -4.322795 | -0.888605 |
| 0.084317  | -0.137783 | -0.136154 |
| 3.931198  | 0.379915 | -0.020625 |
| 4.123309  | -0.612190 | -0.391143 |
| 5.422031  | -1.413699 | 0.766718  |
| 4.389797  | -1.781164 | 1.867257  |
| 2.013995  | 1.179974 | 4.826308  |
| 1.701831  | 1.490965 | 2.425120  |
\[
\begin{array}{cccc}
C & -2.021551 & -1.355035 & 1.299431 \\
C & -5.029786 & -1.149700 & -1.683965 \\
C & -4.239626 & -2.446610 & -2.007856 \\
N & -2.845809 & -2.484181 & -1.598076 \\
C & -2.417556 & -3.527424 & -0.686280 \\
C & -3.053452 & -3.558841 & 0.730067 \\
C & -2.059762 & -1.275323 & -1.639901 \\
H & -3.103996 & 0.887091 & 0.863871 \\
C & -0.097399 & 1.191552 & -0.856635 \\
C & -6.255241 & -0.901372 & 1.281043 \\
H & -5.844284 & -2.334618 & 0.348190 \\
H & -4.195433 & -0.895880 & 2.484258 \\
H & -4.880350 & -2.508865 & 2.531185 \\
H & -3.938687 & -0.735829 & 2.201148 \\
H & -1.066640 & -1.881881 & 1.219755 \\
H & -4.713956 & -0.357425 & -2.373264 \\
H & -0.684887 & -1.353396 & -1.925592 \\
H & -4.744636 & -3.300661 & -1.541760 \\
H & -4.329264 & -2.598094 & -3.099311 \\
H & -1.328898 & -3.442159 & -0.586540 \\
H & -2.601002 & -4.513801 & -1.140792 \\
H & -0.478563 & -3.939908 & 0.655880 \\
H & -2.486884 & -3.412877 & 1.306360 \\
H & -5.972939 & -0.207382 & -1.143035 \\
H & -1.000466 & -1.532061 & -1.766034 \\
H & 1.374883 & 0.243893 & -4.971146 \\
H & 2.339421 & -1.847959 & 5.594222 \\
\end{array}
\]

\[1k \]

\[
\begin{array}{cccc}
C & 0.333227 & 2.716393 & 0.567852 \\
O & -1.424203 & -1.439960 & -0.055252 \\
C & -1.788986 & -2.869262 & -1.261845 \\
O & -2.001456 & -3.710269 & -2.054557 \\
C & -1.671115 & -2.567777 & 1.457833 \\
O & -1.821196 & -2.335957 & 2.408420 \\
N & -3.503706 & -0.670594 & -0.024524 \\
C & -4.299629 & -0.738908 & -1.112853 \\
C & -5.585279 & -0.207382 & -3.121801 \\
C & -6.085854 & 0.420751 & -0.001008 \\
C & -5.269415 & 0.490173 & 1.128584 \\
C & -3.992384 & -0.061332 & 1.078027 \\
C & -1.128931 & 0.883847 & -1.697553 \\
C & -2.069132 & -0.060903 & -0.312288 \\
C & -0.892453 & 0.979345 & -3.918430 \\
C & -0.467868 & 2.210923 & -3.441978 \\
C & -0.374761 & 2.407927 & -2.040476 \\
C & -0.739578 & 1.307608 & -2.147040 \\
C & -1.686334 & 4.200541 & -1.854718 \\
N & -0.961922 & 0.413880 & -1.029459 \\
C & -0.628565 & 0.891295 & 2.303621 \\
C & -0.802211 & 0.215634 & 3.526270 \\
C & -4.431252 & -0.855042 & 4.685503 \\
C & -0.051333 & 2.222320 & 4.642009 \\
C & -1.073781 & 2.094423 & 3.434412 \\
C & -0.192392 & 2.242009 & 2.250390 \\
C & -0.179867 & 2.593481 & -0.852100 \\
C & 0.179660 & 3.662606 & 0.018372 \\
C & 0.726287 & 5.013724 & 0.366941 \\
O & 0.973727 & 5.477201 & 1.466135 \\
C & 0.903970 & 5.666073 & -0.854847 \\
C & 0.535345 & 4.860462 & -1.954077 \\
C & 0.597293 & 5.201121 & -3.121801 \\
C & 0.075530 & 3.581963 & -1.372455 \\
C & -3.880313 & -1.240765 & -1.976940 \\
C & -6.177057 & -0.292728 & -2.048941 \\
C & -7.086691 & 0.842962 & 0.008271 \\
C & -2.965767 & -0.171188 & 1.931283 \\
C & -3.327174 & 0.171188 & -1.379117 \\
C & -1.506223 & -1.041368 & -3.379117 \\
C & -0.196608 & 3.018884 & -4.113668 \\
C & -1.611642 & -0.808916 & 3.560593 \\
C & -0.511523 & 0.390046 & 5.644696 \\
C & 0.546851 & 3.922984 & 3.388606 \\
C & 1.268931 & 6.599713 & -0.947128 \\
P & 0.897380 & -1.858747 & -0.099170 \\
\end{array}
\]
| C   | -2.684269 | 3.663251 | -2.559495 |
| O   | -3.871075 | 3.600131 | -2.843736 |
| N   | -1.872819 | 2.800649 | -1.682600 |
| H   | -2.007741 | -0.671387 | 3.561124 |
| H   | -2.826571 | 1.08270 | 5.209362 |
| H   | -1.377200 | 3.297060 | 5.754469 |
| H   | 0.840478 | 3.502746 | 4.575575 |
| H   | 1.491154 | 1.756681 | 2.930199 |
| O   | -0.856133 | -1.050735 | 1.186005 |
| C   | -4.374807 | 1.529089 | -1.462373 |
| H   | 3.734371 | 0.731521 | 1.381555 |
| H   | 5.482445 | 2.311737 | 0.647510 |
| H   | 2.630619 | 4.505324 | -1.794944 |
| H   | 2.073551 | 5.379600 | -3.684743 |
| P   | 1.008362 | -2.139182 | -0.289710 |
| O   | 0.454392 | -3.904095 | 0.414422 |
| C   | 1.725003 | -4.770284 | -1.097361 |
| O   | 3.003347 | -4.788589 | -1.789797 |
| C   | 3.764036 | -3.437821 | -0.987959 |
| O   | 3.021041 | -2.268277 | -2.303075 |
| C   | 2.453225 | -1.430400 | -1.276163 |
| C   | 0.537756 | -1.575380 | -1.822899 |
| C   | 0.115275 | -4.331721 | -0.356619 |
| N   | 0.205523 | -2.889556 | -2.880751 |
| C   | 0.913038 | -2.063943 | -0.733235 |
| C   | 2.452745 | -2.244686 | -3.638929 |
| C   | -0.323490 | -2.338013 | -1.610581 |
| N   | 2.463115 | -3.857137 | 0.637427 |
| C   | 0.776441 | -4.371284 | -1.365201 |
| C   | 3.696570 | -5.502313 | -1.306793 |
| C   | 2.827964 | -5.171787 | -2.799873 |
| C   | 4.199475 | -3.206078 | -0.900674 |
| C   | 4.671881 | -3.599662 | -2.557155 |
| C   | 3.218480 | -1.092387 | 0.321227 |
| C   | 2.133933 | -0.471559 | -1.698277 |
| C   | -0.289379 | -0.195311 | -1.03454 |
| C   | 0.654135 | -6.219237 | -1.74202 |
| C   | 0.794882 | -4.547046 | -3.889112 |
| C   | 0.875995 | -4.711235 | -3.36521 |
| C   | 0.663158 | -1.018882 | -3.514711 |
| C   | 0.636958 | -2.224397 | -4.787429 |
| C   | 2.736041 | -3.179041 | -4.137397 |
| C   | 2.896405 | -1.429291 | -2.392536 |
| C   | 1.131349 | -2.938584 | -1.755551 |
| C   | -0.743008 | -1.335808 | -1.764258 |
| C   | -0.510181 | -0.729588 | -0.015296 |
| O   | -0.530863 | -1.719115 | 0.665619 |
| O   | -6.045963 | -0.119557 | -0.754468 |
| O   | -3.774554 | -0.600198 | 0.691192 |
| C   | -8.257697 | 0.146139 | -1.615256 |
| C   | -7.721258 | -0.703837 | 0.322874 |
| C   | -7.309607 | -1.738687 | -0.015427 |
| C   | -8.293352 | -1.82496 | -1.263235 |
| C   | -9.276888 | -0.257486 | -1.616629 |
| C   | -7.882407 | 0.144461 | -2.644083 |
| O   | 5.081269 | 4.415922 | -1.045083 |
| C   | 6.428906 | 4.294228 | -0.617073 |
| O   | 6.867480 | 3.336594 | -0.931468 |
| C   | 6.517080 | 4.394435 | 0.474052 |
| C   | 6.967771 | 5.112778 | -1.098466 |

| 1O | Re  | 0.400946 | -0.839872 | 1.617257 |
|    | C   | -0.444787 | -2.325130 | 2.456138 |
|    | O   | -1.031859 | -3.529519 | 2.961601 |
|    | C   | 0.203697 | -2.141191 | 2.440066 |
|    | O   | 3.110293 | -1.458901 | 2.926329 |
|    | N   | -0.226942 | 0.628561 | 3.167603 |
|    | C   | -1.410376 | 0.518194 | 3.038278 |
|    | C   | -7.705801 | -2.998183 | -0.537860 |
|    | C   | -6.862219 | -3.946167 | -1.780706 |
|    | C   | -7.848664 | -4.770481 | -0.552299 |
|    | C   | 2.301597 | 6.045983 | -2.138589 |
| 1p | Re  | 0.400946 | -0.839872 | 1.617257 |
|    | C   | -0.444787 | -2.325130 | 2.456138 |
|    | O   | -1.031859 | -3.529519 | 2.961601 |
|    | C   | 0.203697 | -2.141191 | 2.440066 |
|    | O   | 3.110293 | -1.458901 | 2.926329 |
|    | N   | -0.226942 | 0.628561 | 3.167603 |
|    | C   | -1.410376 | 0.518194 | 3.038278 |
|    | C   | -7.705801 | -2.998183 | -0.537860 |
|    | C   | -6.862219 | -3.946167 | -1.780706 |
|    | C   | -7.848664 | -4.770481 | -0.552299 |
|    | C   | 2.301597 | 6.045983 | -2.138589 |
|   | X       | Y       | Z       |
|---|---------|---------|---------|
| H | 4.344003| -2.87517| -1.74558|
| O | 0.475941| -3.01698| -2.89692|
| C | 3.330942| -1.96585| -1.17986|
| H | 1.074838| 3.68443 | 0.62899 |
| H | 1.093511| 5.13275 | -1.47632|
| H | 4.385037| 5.19136 | 0.68689 |
| H | 3.563120| 3.76375 | 2.59410|
| H | 1.540232| 2.36060 | 2.25743|
| H | 0.094167| 1.63165 | -3.24591|
| H | 3.165097| -1.28134| -3.92695|
| H | -0.426212| 0.788005| 3.65901|
| C | 0.282539| -0.37070 | 5.74896 |
| H | 3.137937| -2.76479 | 3.56522 |
| H | 5.561743| -4.31379 | -0.72487|
| C | -2.160797|-0.123784|-0.134113|
| H | -3.950101| 0.427874|-0.311376|
| H | -9.428733| -0.579825|-0.636437|
| H | -5.546383| -1.349524| 0.430671|
| H | -4.66692| -1.666326| 1.684335|
| H | -3.326743| -2.231835| 1.384162|
| H | -2.225740| -1.303148| 1.334723|
| H | -4.881941|-1.151276|-1.967402|
| H | -4.075419|-2.462928|-2.169234|
| H | -0.130501|-2.980415|-1.511666|
| H | -5.422079|-3.523331|-0.626504|
| H | -3.210434|-3.513241| 0.711454 |
| H | -1.937193|-1.300411|-1.591953|
| H | -3.938000| 1.203936| -1.087750|
| H | -4.222717| 0.940701| 0.618665 |
| H | -6.425921|-0.817465| 0.836169 |
| H | -5.929461|-2.277481|-0.009331|
| H | -5.413014|-0.796862| 2.260802|
| H | -5.215536|-2.409265| 2.720308|
| H | -2.236793|-0.659206| 2.22040|
| H | -1.271374|-1.838568| 1.374738|
| H | -4.482807|-0.379407|-2.636308|
| H | -5.905827|-1.352521|-2.320145|
| H | -4.638268|-3.299918|-1.740551|
| H | -1.270443|-2.641978|-1.259521|
| H | -1.350169|-3.444210|-0.409398|
| H | -2.568427|-4.519540|-1.073863|
| H | -4.224840|-3.888906| 0.534462|
| H | -2.718201|-4.255731| 1.365509|
| H | -0.873317|-1.569114|-1.591492|
| H | -2.101953|-0.724683|-2.510691|
| F | 1.563669| 0.501368|-5.022679|
| C | 2.033609|-2.120284| 5.704857|

**1s**

|   | X       | Y       | Z       |
|---|---------|---------|---------|
| Re | -0.809188|-0.976482|-1.281752|
| C | -2.129024|-2.326089|-1.517973|
| O | -2.921137|-3.191013|-1.690911|
| C | -1.419536|-0.008454|-2.797494|
| O | -1.770759| 0.618734|-3.725095|
| N | 0.782045|-2.068427|-2.395717|
| C | 0.655499|-3.416563|-2.380384|
| O | 1.873281|-4.124833|-0.012245|
| C | 2.863860|-3.420365|-3.699066|
| C | 2.504018|-2.026888|-3.721649|
| C | 1.742923|-1.391684|-3.060003|
| C | 0.703051|-1.980415| 1.116666 |
| C | -0.209399|-1.324060| 1.109998|
| C | 0.501332|-3.585370| 2.230361|
| C | 1.566439|-2.900748| 2.776657|
| C | 1.943516|-1.686082| 2.155135|

**S55**
|   | Re   | C    | N    | C    | C    | C    | C    | C    | C    | C    | C    | C    | C    | C    | C    | C    |
|---|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| 1 | 3.005145 | -0.108745 | -0.465515 | 3.365436 | -1.373508 | -0.334252 | 4.210226 | -2.166443 | -0.248092 | 3.096111 | 1.375681 | -0.150592 | 3.783265 | 2.286406 | 0.063311 | 1.412854 | -0.321376 | 1.732012 |
|   | -2.328036 | 5.674720 | 0.043060 | -0.490872 | -2.952116 | 0.903901 | -3.733553 | 2.809209 | -0.014903 | 4.199124 | -2.266890 | -0.190910 | 5.123653 | -1.220020 | 0.060808 | 4.699634 | 0.121647 | -0.471722 |
|   | 1.314442 | -1.708953 | 3.654102 | 0.671584 | -0.589821 | 4.413474 | 0.714174 | 0.666625 | 3.807743 | 1.092085 | 0.758594 | 2.471810 | 0.129683 | -1.684470 | -0.647960 | 1.700803 | -1.782399 | -0.518365 |
|   | 6.182609 | 0.051595 | 0.556077 | 1.664008 | 0.079131 | 2.775665 | 3.085407 | -2.962762 | -0.281773 | 3.330363 | -1.261546 | -0.318098 | 1.642291 | -2.379141 | 1.695139 | 0.995854 | -2.708681 | 4.075813 |
|   | 0.479068 | -0.596828 | 5.454498 | 0.454027 | 1.568669 | 4.351879 | 1.124101 | 1.714950 | 1.963223 | 1.462838 | -3.412555 | -0.928001 | 2.819175 | -4.020615 | -0.592869 | 3.389421 | 3.524821 | -0.234396 |
|   | -0.134175 | 5.667069 | -0.182786 | -0.621757 | 3.517175 | 0.025803 | -6.522679 | -0.729157 | 0.004756 | 2.152686 | 0.051197 | -2.377667 | 0.440864 | -1.892270 | -1.352121 | 0.490872 | -4.952116 | -0.903901 |
|   | -2.328036 | 5.674720 | 0.043060 | -0.490872 | -2.952116 | 0.903901 | -3.733553 | 2.809209 | -0.014903 | 4.199124 | -2.266890 | -0.190910 | 5.123653 | -1.220020 | 0.060808 | 4.699634 | 0.121647 | -0.471722 |

Table S18. B3LYP-D3/6-31+G(d)-LANL2DZ cartesian coordinates, in Å, of the optimized structures in their triplet excited states of all Re(I) complexes investigated.
| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| C    | 0.047337 | 2.956402 | -0.38939 |
| C    | -0.317368 | 1.569472 | -0.450352 |
| C    | 0.702331 | 0.600445 | -0.374687 |
| H    | 0.817706 | -0.524703 | 0.437301 |
| C    | 1.650657 | -1.394567 | -0.36770 |
| C    | 1.896875 | -2.767908 | -0.393227 |
| C    | 2.232282 | -3.197332 | -0.292327 |
| C    | 4.014823 | -0.865536 | -0.133207 |
| C    | 2.705533 | -0.443229 | -0.234000 |
| C    | 2.075899 | 0.874310 | -0.245143 |
| C    | 2.450180 | 2.213771 | -0.169659 |
| C    | 3.747552 | 2.859384 | -0.021998 |
| C    | 4.872603 | 2.368984 | 0.079713 |
| C    | 3.460358 | 4.239978 | -0.011904 |
| C    | 2.096532 | 4.538194 | -0.231813 |
| O    | 1.608715 | 5.666143 | -0.153091 |
| C    | 1.429881 | 3.230282 | -0.242183 |
| C    | 0.022241 | 0.716879 | 1.750586 |
| C    | -2.747295 | 1.355368 | 4.140685 |
| O    | -0.934182 | 0.246881 | 5.491962 |
| C    | 0.511351 | -1.473081 | 4.354162 |
| O    | 0.095812 | -1.991133 | 1.958403 |
| C    | 3.607735 | 1.689156 | 0.819094 |
| C    | -0.808984 | 4.968821 | -0.45834 |
| C    | 1.092387 | -3.488658 | -0.495664 |
| C    | 4.332973 | -2.457985 | -0.320013 |
| C    | 4.832568 | -0.157593 | -0.03496 |
| C    | 5.371194 | -4.951861 | -0.075791 |
| C    | -1.801222 | -1.357120 | -2.365278 |
| O    | -1.839935 | -1.490415 | -3.515222 |
| F    | -3.330739 | 4.268089 | -0.742179 |
| O    | 5.580380 | -2.596337 | -0.063121 |
| C    | 5.983733 | -3.970783 | -1.050783 |
| C    | 6.664936 | -4.431769 | -1.056392 |
| C    | 7.046359 | -3.977173 | -0.051490 |
| C    | 5.517427 | -4.527843 | 0.730983 |

**lj**

| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| Re   | 1.722959 | -0.119089 | -0.025284 |
| C    | 3.184082 | -1.373903 | -0.075631 |
| O    | 4.036297 | -2.173272 | -0.127272 |
| C    | 2.897359 | 1.346099 | 0.263347 |
| O    | 3.600681 | 2.272275 | 0.437225 |
| N    | 1.318511 | -0.449952 | 2.141839 |
| C    | 1.325056 | -1.687971 | 2.678149 |
| C    | 0.928878 | -1.936395 | 4.007871 |
| C    | 0.637234 | -0.866215 | 4.827894 |
| O    | 0.620968 | 0.416525 | 4.277535 |
| C    | 0.962883 | 0.582538 | 2.939037 |
| N    | 0.153627 | -1.705392 | -0.298455 |
| C    | -0.076009 | -3.053780 | -0.478641 |
| C    | -0.830629 | -3.884222 | -0.616857 |
| C    | -2.134960 | -3.363459 | -0.581553 |
| C    | -2.297990 | -1.968237 | -0.406217 |
| C    | -1.102405 | -1.193190 | -0.268236 |
| C    | -1.210294 | 0.202463 | -0.108198 |
| N    | -0.091144 | 0.994133 | 0.007655 |
| C    | -0.569311 | 2.299885 | 0.123919 |
| C    | 0.182213 | 3.481596 | 0.264672 |
| C    | -0.552228 | 4.683488 | 0.365508 |
| C    | -1.955627 | 4.703691 | 0.325375 |
| C    | -2.697060 | 3.517508 | 0.182466 |
| C    | -2.002558 | 2.316189 | 0.081770 |
| C    | -2.418220 | 0.926673 | -0.074561 |
| C    | -5.199270 | 1.934174 | -1.163324 |
| C    | -4.998201 | 0.590418 | -0.020411 |
| N    | -5.514684 | 1.704958 | -0.093679 |
| N    | -5.705063 | -0.616315 | -0.367223 |
| O    | -4.892084 | -1.715053 | -0.469845 |
| O    | -5.320324 | -2.900639 | -0.320097 |
| O    | 1.597971 | -2.493893 | 0.028190 |
| C    | 1.024323 | -2.954527 | 4.382895 |

**S60**
### 1o

| Re  | 0.412900 | 0.774480 | 1.626584 |
|-----|----------|----------|----------|
| Im  | 0.530472 | 2.167612 | 2.576066 |
| Re  | 1.129900 | 3.001985 | 3.131784 |
| Im  | 0.207519 | 1.293233 | 2.386927 |
| Re  | -0.119613 | 1.591675 | 2.833062 |
| Im  | 0.956800 | -0.772960 | 3.164663 |
| Re  | 1.263878 | -0.859593 | 3.729138 |
| Im  | 1.610155 | -1.859747 | 4.634702 |
| Re  | 0.655711 | -2.818928 | 4.976531 |
| Im  | 0.877443 | -2.436099 | -0.858450 |
| Re  | 2.126304 | -1.818787 | -0.943385 |
| Im  | 1.149358 | -1.116240 | -0.164852 |
| Re  | -0.190043 | -1.508258 | -0.232101 |
| Im  | -1.178455 | -0.839810 | -0.477072 |
| Re  | -2.361295 | -1.488132 | -1.598303 |
| Im  | -3.657623 | -1.215233 | -0.602774 |
| Re  | -4.711474 | -2.004917 | -0.134817 |
| Im  | -4.472003 | -3.060734 | -0.769391 |
| Re  | -3.165698 | -3.349793 | -1.225271 |
| Im  | -2.565729 | -2.567638 | -0.761873 |
| Re  | -0.685403 | -2.570189 | -0.101520 |
| Im  | 0.243025 | -2.376945 | -1.774126 |
| Re  | 0.029520 | -4.408646 | -2.689574 |

### 1p

| Re  | 1.740478 | -0.068018 | -0.004699 |
|-----|----------|----------|----------|
| Im  | 3.153051 | -1.385925 | -0.467550 |
| Re  | 3.971461 | -2.218118 | -0.009985 |
| Im  | 2.973207 | 1.362877 | 0.223325 |
| Re  | 3.712918 | 2.262421 | 0.357727 |
| Im  | 1.312454 | -0.292583 | 1.269581 |
| Re  | 1.275814 | -1.506327 | -0.684177 |
| Im  | 0.932304 | -1.684871 | 4.049848 |
| Re  | 0.607531 | -0.567574 | 4.865622 |
| Im  | 0.642783 | 0.690183 | 2.620964 |
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