

Molecular Redox: Revisiting the Electronic Structures of the Group 9 Metallocorroles

Supporting Information

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Cartesian Coordinates for Geometry Optimized Structures

| | |
|--|----|
| [(tpfc)Co(py) ₂] ⁺ | 7 |
| [(tpfc)Rh(py) ₂] ⁺ | 8 |
| (tpfc)Ir(py) ₂ | 10 |
| [(tpfc)Ir(py) ₂] ⁺ | 13 |
| (tpfc)Ir(cnpy) ₂ | 15 |
| [(tpfc)Ir(cnpy) ₂] ⁺ | 17 |
| (tpfc)Ir(meopy) ₂ | 19 |
| [(tpfc)Ir(meopy) ₂] ⁺ | 21 |
| (tpfc)Ir(dmap) ₂ | 23 |
| [(tpfc)Ir(dmap) ₂] ⁺ | 25 |

Equations

| | |
|---|----|
| Eq. S1. LF derived g-matrix of a low-spin d ⁵ system with a mixed d _{xz/yz} SOMO. | 28 |
|---|----|

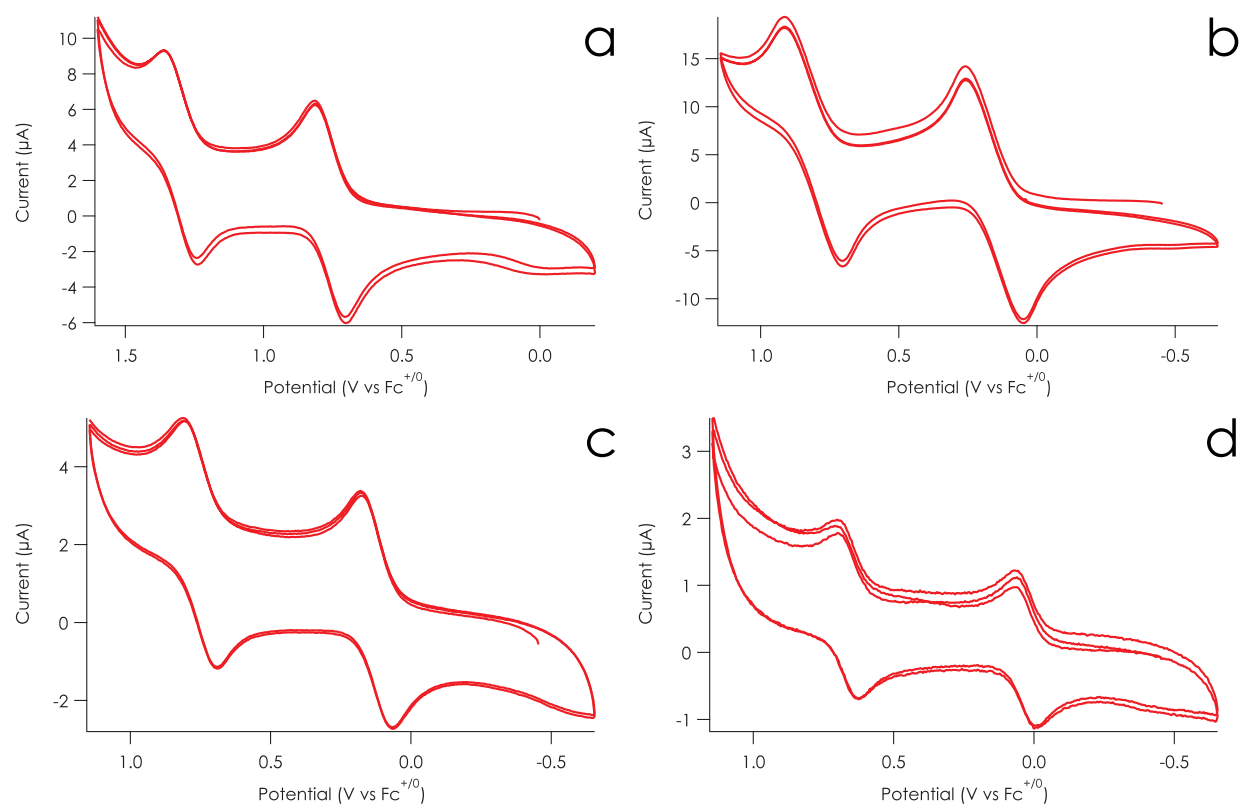


Figure S1. CV of $[\text{tpfcIrL}_2]^{+/0}$ complexes. L = cnpy (a), py (b), meopy (c), dmap (d). Potentials are referenced to $\text{Fc}^{+/0}$.

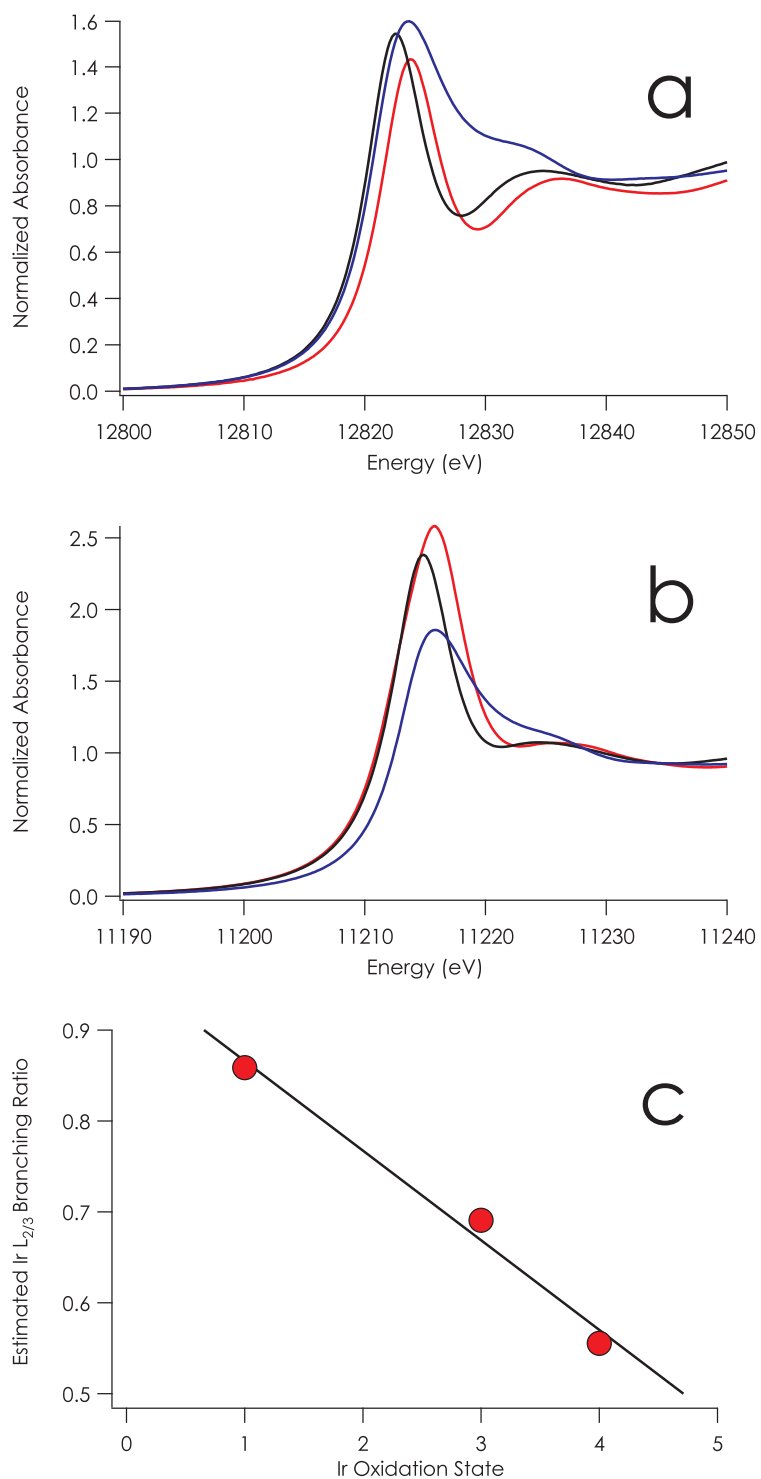


Figure S2. Ir L₂ (a) and L₃-edge (b) XAS of [(cod)Ir^ICl]₂ (blue), K₃Ir^{III}Cl₆ (black), and K₂Ir^{IV}Cl₆ (red). (c) Plot of estimated L_{2/3} branching ratio against physical Ir oxidation state of aforementioned compounds.

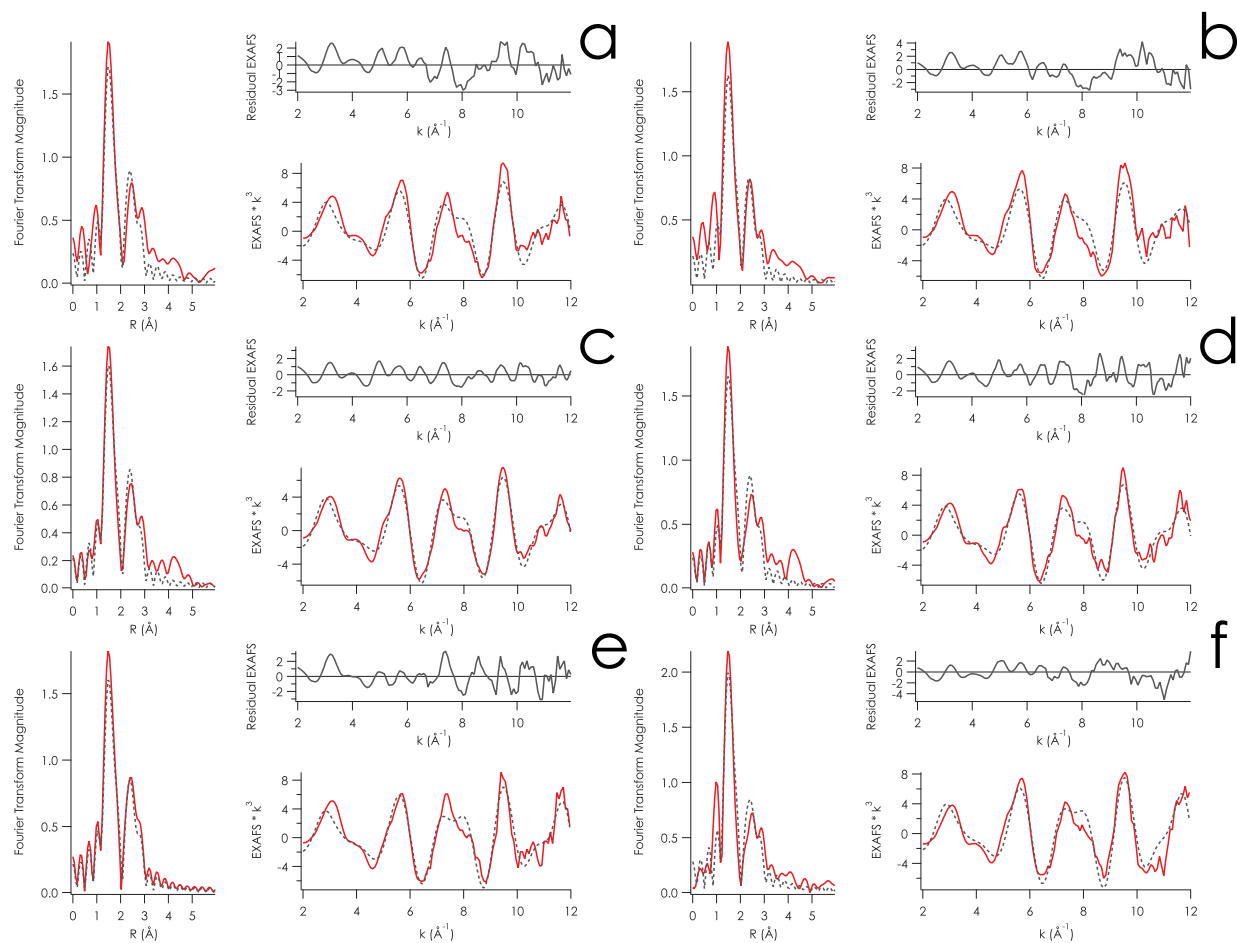


Figure S3. Ir L_3 edge EXAFS of a) **1**, b) **1⁺**, c) **2**, d) **2⁺**, e) **4**, f) **4⁺**. Experimental data are solid red lines, simulated data are dotted gray lines.

Table S1. EXAFS fitting parameters.

| 1 | | | |
|----------------------|-----------|--------------|------------------------------|
| Path | CN | R (Å) | σ^2 |
| Ir-N | 6 | 1.99 | .00245 |
| Ir-C | 12 | 2.98 | .00270 |
| E0 | -4.3723 | | |
| F | 39.00 | | |
| 1⁺ | | | |
| Path | CN | R (Å) | σ^2 |
| Ir-N | 6 | 1.99 | .00335 |
| Ir-C | 12 | 2.97 | .00255 |
| E0 | -4.3000 | | |
| F | 44.51 | | |
| 2 | | | |
| Path | CN | R (Å) | σ^2 |
| Ir-N | 6 | 1.99 | .00284 |
| Ir-C | 12 | 2.99 | .00303 |
| E0 | -4.8407 | | |
| F | 26.73 | | |
| 2⁺ | | | |
| Path | CN | R (Å) | σ^2 |
| Ir-N | 6 | 1.99 | .00262 |
| Ir-C | 12 | 2.98 | .00263 |
| E0 | -5.0330 | | |
| F | 35.06 | | |
| 4 | | | |
| Path | CN | R (Å) | σ^2 |
| Ir-N | 6 | 1.97 | .00219 |
| Ir-C | 12 | 2.99 | .00232 |
| E0 | -5.1241 | | |
| F | 38.64 | | |
| 4⁺ | | | |
| Path | CN | R (Å) | σ^2 |
| Ir-N | 6 | 1.97 | .00158 |
| Ir-C | 12 | 2.98 | .00266 |
| E0 | -4.3462 | | |
| F | 37.95 | | |

EXAFS were fit in OPT using paths calculated by FEFF7. Coordination numbers (CN) were held constant while distances (R) and Debye-Waller factors (σ^2) were allowed to float. Fits were performed over the entire (0 to 6.0 Å) Fourier transform window. Goodness of fit is measured by F, defined as $[(\sum_i^n [k_i^3 (\text{EXAFS}_{\text{obs}} - \text{EXAFS}_{\text{calc}})_i])^2 / n]^{1/2}$.

Table S2. Functional dependence of g-values and metal spin populations.

| BP86/def2-TZVP(-f)+ZORA | | | |
|---|-------------------------|---------------------------------------|-------------------|
| | g_z | $\langle g \rangle$ | Metal Spin |
| (tpfc)Co(py) ₂ ⁺ | 2.011 | 2.005 | 0.0% |
| (tpfc)Rh(py) ₂ ⁺ | 2.040 | 2.015 | 0.0% |
| (tpfc)Ir(cnpy) ₂ ⁺ | 2.494 | 2.201 | 16.4% |
| (tpfc)Ir(py) ₂ ⁺ | 2.584 | 2.237 | 18.8% |
| (tpfc)Ir(meopy) ₂ ⁺ | 2.702 | 2.280 | 20.0% |
| (tpfc)Ir(dmap) ₂ ⁺ | 3.326 | 2.494 | 22.1% |

| PW91/def2-TZVP(-f)+ZORA | | | |
|--|-------------------------|---------------------------------------|-------------------|
| | g_z | $\langle g \rangle$ | Metal Spin |
| [(tpfc)Co(py) ₂] ⁺ | 2.011 | 2.005 | 0.0% |
| [(tpfc)Rh(py) ₂] ⁺ | 2.042 | 2.015 | 0.0% |
| [(tpfc)Ir(cnpy) ₂] ⁺ | 2.503 | 2.204 | 16.5% |
| [(tpfc)Ir(py) ₂] ⁺ | 2.594 | 2.241 | 19.0% |
| [(tpfc)Ir(meopy) ₂] ⁺ | 2.715 | 2.285 | 20.2 |
| [(tpfc)Ir(dmap) ₂] ⁺ | 3.374 | 2.511 | 22.3% |

| PBE/def2-TZVP(-f)+ZORA | | | |
|--|-------------------------|---------------------------------------|-------------------|
| | g_z | $\langle g \rangle$ | Metal Spin |
| [(tpfc)Co(py) ₂] ⁺ | 2.012 | 2.006 | 0.0% |
| [(tpfc)Rh(py) ₂] ⁺ | 2.042 | 2.015 | 0.0% |
| [(tpfc)Ir(cnpy) ₂] ⁺ | 2.507 | 2.206 | 16.7% |
| [(tpfc)Ir(py) ₂] ⁺ | 2.598 | 2.243 | 19.2% |
| [(tpfc)Ir(meopy) ₂] ⁺ | 2.718 | 2.287 | |
| [(tpfc)Ir(dmap) ₂] ⁺ | 3.397 | 2.519 | 22.5% |

| B3LYP/def2-TZVP(-f)+ZORA | | | |
|--|-------------------------|---------------------------------------|-------------------|
| | g_z | $\langle g \rangle$ | Metal Spin |
| [(tpfc)Co(py) ₂] ⁺ | 2.002 | 2.002 | 0.0% |
| [(tpfc)Rh(py) ₂] ⁺ | 2.010 | 2.004 | 0.0% |
| [(tpfc)Ir(cnpy) ₂] ⁺ | 2.333 | 2.135 | 10.6% |
| [(tpfc)Ir(py) ₂] ⁺ | 2.409 | 2.167 | 12.9% |
| [(tpfc)Ir(meopy) ₂] ⁺ | 2.431 | 2.194 | 14.1 |
| [(tpfc)Ir(dmap) ₂] ⁺ | 2.677 | 2.267 | 16.3% |

TPSSH/def2-TZVP(-f)+ZORA

| | g_z | $\langle g \rangle$ | Metal Spin |
|--|-------|---------------------|------------|
| $[(\text{tpfc})\text{Co}(\text{py})_2]^+$ | 2.004 | 2.003 | 0.0% |
| $[(\text{tpfc})\text{Rh}(\text{py})_2]^+$ | 2.016 | 2.006 | 0.0% |
| $[(\text{tpfc})\text{Ir}(\text{enpy})_2]^+$ | 2.353 | 2.145 | 13.0% |
| $[(\text{tpfc})\text{Ir}(\text{py})_2]^+$ | 2.426 | 2.175 | 15.6% |
| $[(\text{tpfc})\text{Ir}(\text{meopy})_2]^+$ | 2.702 | 2.280 | 16.8% |
| $[(\text{tpfc})\text{Ir}(\text{dmap})_2]^+$ | 2.724 | 2.284 | 19.3% |

PW91/def2-TZVP(-f)+ZORA Optimized Structures [atom, x, y, z (Å)]

$[(\text{tpfc})\text{Co}(\text{py})_2]^+$

| | | | |
|----|-----------|-----------|-----------|
| Co | -0.001178 | 3.341533 | -0.277776 |
| F | -2.190759 | 8.127939 | 1.018635 |
| F | -2.212626 | 10.832828 | 1.281686 |
| F | -0.034285 | 12.295636 | 0.517995 |
| F | 2.171728 | 11.048252 | -0.498152 |
| F | 2.207659 | 8.339594 | -0.750696 |
| F | 2.157365 | 4.110019 | -5.187445 |
| F | 2.076117 | 4.091732 | -7.904140 |
| F | -0.200944 | 3.316979 | -9.197291 |
| F | -2.401396 | 2.556546 | -7.769693 |
| F | -2.327819 | 2.568963 | -5.051733 |
| F | 2.166990 | -1.652444 | -0.731681 |
| F | 2.134030 | -4.361199 | -0.478892 |
| F | -0.074983 | -5.611701 | 0.527059 |
| F | -2.259339 | -4.152047 | 1.279310 |
| F | -2.240239 | -1.446939 | 1.015955 |
| N | 0.001022 | 4.562915 | 1.143850 |
| N | 0.024512 | 4.755123 | -1.553411 |
| N | -0.011817 | 1.926352 | -1.550958 |
| N | -0.023958 | 2.122298 | 1.145655 |
| N | 1.990759 | 3.321747 | -0.266262 |
| N | -1.991869 | 3.361202 | -0.279724 |
| C | 0.009370 | 4.059792 | 2.402121 |
| C | 0.034357 | 5.148788 | 3.332176 |
| H | 0.047080 | 5.062597 | 4.413068 |
| C | 0.042134 | 6.311121 | 2.584627 |
| H | 0.063224 | 7.330057 | 2.956200 |
| C | 0.018567 | 5.932237 | 1.193354 |
| C | 0.025865 | 6.687719 | 0.016578 |
| C | 0.022823 | 6.106992 | -1.287430 |

| | | | |
|---|-----------|-----------|-----------|
| C | -0.020475 | 6.819455 | -2.533477 |
| H | -0.040260 | 7.898849 | -2.636041 |
| C | -0.043435 | 5.886765 | -3.539393 |
| H | -0.083857 | 6.070129 | -4.607304 |
| C | -0.012356 | 4.592319 | -2.917147 |
| C | -0.041184 | 3.339781 | -3.562087 |
| C | -0.038730 | 2.087616 | -2.914978 |
| C | -0.052084 | 0.792333 | -3.536114 |
| H | -0.064383 | 0.607267 | -4.604409 |
| C | -0.045212 | -0.139151 | -2.528848 |
| H | -0.059326 | -1.218685 | -2.630678 |
| C | -0.015958 | 0.574711 | -1.283301 |
| C | -0.019972 | -0.004160 | 0.021565 |
| C | -0.024958 | 0.752885 | 1.197205 |
| C | -0.005563 | 0.375711 | 2.588960 |
| H | 0.001023 | -0.642950 | 2.961827 |
| C | 0.004268 | 1.539140 | 3.334801 |
| H | 0.019442 | 1.626785 | 4.415546 |
| C | -0.004396 | 2.627006 | 2.403164 |
| C | 0.011472 | 8.161797 | 0.131774 |
| C | -1.099511 | 8.829922 | 0.655371 |
| C | -1.129461 | 10.215343 | 0.787866 |
| C | -0.020632 | 10.963756 | 0.392821 |
| C | 1.103267 | 10.325354 | -0.132883 |
| C | 1.104938 | 8.939182 | -0.259643 |
| C | -0.082663 | 3.337795 | -5.045615 |
| C | 1.022526 | 3.731441 | -5.805179 |
| C | 0.997002 | 3.724774 | -7.197428 |
| C | -0.163124 | 3.323962 | -7.859634 |
| C | -1.284041 | 2.930812 | -7.128855 |
| C | -1.229946 | 2.939073 | -5.737551 |
| C | -0.034784 | -1.478199 | 0.137922 |
| C | 1.062321 | -2.253902 | -0.246783 |
| C | 1.062560 | -3.639947 | -0.119263 |
| C | -0.062971 | -4.279866 | 0.401092 |
| C | -1.174935 | -3.533044 | 0.790212 |
| C | -1.146900 | -2.147588 | 0.656952 |
| C | 2.694440 | 4.472551 | -0.256529 |
| H | 2.130197 | 5.396515 | -0.256550 |
| C | 4.082531 | 4.497120 | -0.249135 |
| H | 4.593222 | 5.457718 | -0.243723 |
| C | 4.786456 | 3.296091 | -0.248094 |
| H | 5.874907 | 3.286266 | -0.244282 |
| C | 4.060669 | 2.108207 | -0.249229 |
| H | 4.553470 | 1.138296 | -0.243980 |
| C | 2.673233 | 2.158362 | -0.256656 |

| | | | |
|---|-----------|----------|-----------|
| H | 2.092317 | 1.244864 | -0.256960 |
| C | -2.674107 | 4.524556 | -0.258724 |
| H | -2.093520 | 5.438301 | -0.266388 |
| C | -4.061268 | 4.574466 | -0.229961 |
| H | -4.553836 | 5.544377 | -0.216301 |
| C | -4.786783 | 3.386480 | -0.218606 |
| H | -5.875010 | 3.396158 | -0.195835 |
| C | -4.082945 | 2.185523 | -0.235241 |
| H | -4.593189 | 1.224741 | -0.225979 |
| C | -2.695151 | 2.210228 | -0.263806 |
| H | -2.131234 | 1.286076 | -0.275772 |

[(tpfc)Rh(py)₂]⁺

| | | | |
|----|-----------|-----------|-----------|
| Rh | 0.011889 | 3.342062 | -0.276222 |
| F | -2.201332 | 8.112430 | 1.004842 |
| F | -2.251375 | 10.817300 | 1.254034 |
| F | -0.080279 | 12.297850 | 0.503068 |
| F | 2.146672 | 11.066230 | -0.488339 |
| F | 2.210001 | 8.357842 | -0.728549 |
| F | 2.146248 | 4.149943 | -5.238694 |
| F | 2.051106 | 4.118012 | -7.952598 |
| F | -0.220815 | 3.303742 | -9.231674 |
| F | -2.402053 | 2.514644 | -7.788441 |
| F | -2.314140 | 2.537295 | -5.073291 |
| F | 2.163172 | -1.656149 | -0.727826 |
| F | 2.123297 | -4.364903 | -0.482181 |
| F | -0.090585 | -5.613064 | 0.516763 |
| F | -2.272760 | -4.150017 | 1.268991 |
| F | -2.246899 | -1.444642 | 1.012968 |
| N | 0.016019 | 4.590787 | 1.223044 |
| N | 0.047122 | 4.798755 | -1.612385 |
| N | -0.004172 | 1.885198 | -1.611480 |
| N | -0.021414 | 2.094001 | 1.223404 |
| N | 2.092562 | 3.313703 | -0.256989 |
| N | -2.069069 | 3.370248 | -0.271915 |
| C | 0.014753 | 4.071398 | 2.474547 |
| C | 0.031292 | 5.182555 | 3.387633 |
| H | 0.036117 | 5.117885 | 4.470291 |
| C | 0.042912 | 6.342273 | 2.628234 |
| H | 0.059801 | 7.360748 | 3.001400 |
| C | 0.029897 | 5.955819 | 1.232930 |
| C | 0.036231 | 6.686062 | 0.024344 |
| C | 0.037832 | 6.136343 | -1.308908 |
| C | -0.012166 | 6.854040 | -2.559320 |

| | | | |
|---|-----------|-----------|-----------|
| H | -0.036726 | 7.933371 | -2.663624 |
| C | -0.033388 | 5.926798 | -3.575599 |
| H | -0.076624 | 6.128093 | -4.640366 |
| C | 0.004491 | 4.618980 | -2.968169 |
| C | -0.030160 | 3.342480 | -3.595801 |
| C | -0.031008 | 2.065229 | -2.967363 |
| C | -0.052228 | 0.757214 | -3.575427 |
| H | -0.067005 | 0.555384 | -4.640848 |
| C | -0.049586 | -0.170064 | -2.558956 |
| H | -0.069606 | -1.249421 | -2.663864 |
| C | -0.015554 | 0.547441 | -1.308070 |
| C | -0.020576 | -0.001788 | 0.025131 |
| C | -0.023037 | 0.728830 | 1.233632 |
| C | -0.005346 | 0.342526 | 2.628771 |
| H | 0.000010 | -0.676038 | 3.002043 |
| C | 0.004187 | 1.502487 | 3.387943 |
| H | 0.017685 | 1.567294 | 4.470516 |
| C | -0.002693 | 2.613528 | 2.474758 |
| C | 0.008551 | 8.162511 | 0.137182 |
| C | -1.112845 | 8.822469 | 0.648564 |
| C | -1.157442 | 10.208204 | 0.773587 |
| C | -0.052577 | 10.965560 | 0.384500 |
| C | 1.081771 | 10.335343 | -0.128527 |
| C | 1.097477 | 8.948645 | -0.249079 |
| C | -0.080195 | 3.340348 | -5.079566 |
| C | 1.013267 | 3.751604 | -5.847355 |
| C | 0.980602 | 3.738458 | -7.239413 |
| C | -0.176074 | 3.316242 | -7.894410 |
| C | -1.286369 | 2.907636 | -7.155840 |
| C | -1.224442 | 2.920577 | -5.764977 |
| C | -0.039753 | -1.478333 | 0.138715 |
| C | 1.055802 | -2.255861 | -0.246673 |
| C | 1.052739 | -3.642228 | -0.122529 |
| C | -0.075094 | -4.280910 | 0.394381 |
| C | -1.185825 | -3.532306 | 0.783671 |
| C | -1.154147 | -2.146484 | 0.654404 |
| C | 2.796697 | 4.466041 | -0.245466 |
| H | 2.231352 | 5.391651 | -0.244069 |
| C | 4.184376 | 4.484543 | -0.236482 |
| H | 4.700950 | 5.441911 | -0.229087 |
| C | 4.882965 | 3.279688 | -0.235770 |
| H | 5.971359 | 3.266500 | -0.229861 |
| C | 4.155323 | 2.092273 | -0.239859 |
| H | 4.648273 | 1.122501 | -0.235318 |
| C | 2.768473 | 2.144745 | -0.248711 |
| H | 2.180990 | 1.233111 | -0.250381 |

| | | | |
|---|-----------|----------|-----------|
| C | -2.745026 | 4.538903 | -0.246489 |
| H | -2.158521 | 5.451086 | -0.252492 |
| C | -4.131535 | 4.591141 | -0.214708 |
| H | -4.624047 | 5.560962 | -0.197122 |
| C | -4.859061 | 3.403732 | -0.205011 |
| H | -5.947172 | 3.416608 | -0.179398 |
| C | -4.160490 | 2.199137 | -0.226741 |
| H | -4.676509 | 1.241490 | -0.219084 |
| C | -2.773164 | 2.217918 | -0.257865 |
| H | -2.208872 | 1.291850 | -0.273409 |

(tpfc)Ir(py)₂

| | | | |
|----|----------|----------|----------|
| Ir | 2.04575 | -0.00002 | -0.00609 |
| F | -0.00488 | 4.95909 | 1.24137 |
| F | 0.16428 | 7.66174 | 1.44308 |
| F | 2.35640 | 8.97230 | 0.47466 |
| F | 4.39440 | 7.56680 | -0.68454 |
| F | 4.25900 | 4.85959 | -0.84633 |
| F | 4.04657 | -0.13277 | -5.21716 |
| F | 3.64533 | -0.24433 | -7.90751 |
| F | 1.10344 | -0.37814 | -8.90251 |
| F | -1.03736 | -0.40124 | -7.20633 |
| F | -0.63804 | -0.29506 | -4.51737 |
| F | 4.29561 | -4.89463 | -0.37139 |
| F | 4.46153 | -7.56875 | 0.05943 |
| F | 2.41549 | -8.88447 | 1.31067 |
| F | 0.18655 | -7.51423 | 2.10161 |
| F | -0.00716 | -4.84765 | 1.63527 |
| N | 2.04300 | 1.31422 | 1.44449 |
| N | 2.03839 | 1.39557 | -1.41296 |
| N | 2.03705 | -1.51433 | -1.28437 |
| N | 2.04300 | -1.18127 | 1.55451 |
| N | 4.09209 | -0.00000 | -0.00000 |
| N | -0.00000 | 0.00000 | 0.00000 |
| C | 2.06097 | 0.84224 | 2.73071 |
| C | 2.08725 | 2.00112 | 3.57401 |
| H | 2.10148 | 1.99990 | 4.65906 |
| C | 2.08951 | 3.12520 | 2.75410 |
| H | 2.10015 | 4.16144 | 3.07507 |
| C | 2.05893 | 2.67181 | 1.38626 |
| C | 2.06440 | 3.34769 | 0.13229 |
| C | 2.04127 | 2.75056 | -1.16231 |
| C | 1.96961 | 3.40553 | -2.44731 |
| H | 1.96041 | 4.48059 | -2.59353 |
| C | 1.91261 | 2.43340 | -3.41818 |

| | | | |
|---|----------|----------|----------|
| H | 1.84997 | 2.57714 | -4.49176 |
| C | 1.95577 | 1.15105 | -2.75521 |
| C | 1.90560 | -0.14681 | -3.31929 |
| C | 1.95377 | -1.38965 | -2.64285 |
| C | 1.91596 | -2.72584 | -3.19007 |
| H | 1.85455 | -2.96394 | -4.24680 |
| C | 1.97750 | -3.60826 | -2.13709 |
| H | 1.97282 | -4.69211 | -2.18749 |
| C | 2.04574 | -2.84192 | -0.91522 |
| C | 2.07064 | -3.32214 | 0.42653 |
| C | 2.06282 | -2.53863 | 1.61600 |
| C | 2.09546 | -2.86991 | 3.01848 |
| H | 2.10956 | -3.87395 | 3.42920 |
| C | 2.09114 | -1.67787 | 3.73612 |
| H | 2.10723 | -1.58099 | 4.81681 |
| C | 2.06164 | -0.59786 | 2.79411 |
| C | 2.12120 | 4.82419 | 0.19032 |
| C | 1.09809 | 5.57633 | 0.77798 |
| C | 1.16413 | 6.96560 | 0.88130 |
| C | 2.28009 | 7.63859 | 0.38040 |
| C | 3.31593 | 6.91885 | -0.21825 |
| C | 3.22452 | 5.53012 | -0.30252 |
| C | 1.71578 | -0.21109 | -4.79231 |
| C | 2.78857 | -0.19817 | -5.68521 |
| C | 2.59874 | -0.25424 | -7.06752 |
| C | 1.30129 | -0.32403 | -7.57857 |
| C | 0.20817 | -0.33787 | -6.71021 |
| C | 0.42981 | -0.28284 | -5.33442 |
| C | 2.13801 | -4.78724 | 0.61745 |
| C | 3.25786 | -5.52300 | 0.21527 |
| C | 3.36448 | -6.89533 | 0.43773 |
| C | 2.32471 | -7.56761 | 1.08362 |
| C | 1.19069 | -6.86405 | 1.49392 |
| C | 1.11117 | -5.49239 | 1.25436 |
| C | 4.77866 | 1.16505 | -0.03303 |
| H | 4.19010 | 2.07605 | -0.07363 |
| C | 6.16679 | 1.19989 | -0.01717 |
| H | 6.66860 | 2.16436 | -0.04908 |
| C | 6.88154 | 0.00410 | 0.03960 |
| H | 7.97006 | 0.00567 | 0.05303 |
| C | 6.16888 | -1.19349 | 0.08107 |
| H | 6.67239 | -2.15646 | 0.12850 |
| C | 4.78056 | -1.16280 | 0.06259 |
| H | 4.19390 | -2.07524 | 0.09710 |
| C | -0.68757 | 1.16407 | -0.03592 |
| H | -0.09805 | 2.07522 | -0.05978 |

| | | | |
|---|----------|----------|----------|
| C | -2.07591 | 1.19579 | -0.03569 |
| H | -2.58082 | 2.15860 | -0.06730 |
| C | -2.78841 | -0.00173 | 0.00961 |
| H | -3.87699 | -0.00262 | 0.00904 |
| C | -2.07410 | -1.19776 | 0.06566 |
| H | -2.57742 | -2.16060 | 0.11545 |
| C | -0.68592 | -1.16379 | 0.06307 |
| H | -0.09498 | -2.07279 | 0.11733 |

[(tpfc)Ir(py)₂]⁺

| | | | |
|----|-----------|-----------|-----------|
| Ir | -0.006835 | 3.340525 | -0.281329 |
| F | -2.187923 | 8.119854 | 1.037296 |
| F | -2.200651 | 10.821090 | 1.355389 |
| F | -0.020465 | 12.292615 | 0.608880 |
| F | 2.177201 | 11.055477 | -0.439994 |
| F | 2.206898 | 8.353889 | -0.737649 |
| F | 2.175334 | 4.116084 | -5.211131 |
| F | 2.126270 | 4.108622 | -7.928123 |
| F | -0.133312 | 3.331435 | -9.252772 |
| F | -2.349027 | 2.560742 | -7.852175 |
| F | -2.309778 | 2.568158 | -5.134473 |
| F | 2.149951 | -1.659294 | -0.751926 |
| F | 2.147989 | -4.358419 | -0.434026 |
| F | -0.026317 | -5.607323 | 0.648521 |
| F | -2.211574 | -4.150393 | 1.407247 |
| F | -2.229430 | -1.452075 | 1.065089 |
| N | 0.006489 | 4.592965 | 1.208234 |
| N | 0.012494 | 4.789417 | -1.622146 |
| N | -0.030730 | 1.891705 | -1.621459 |
| N | -0.024753 | 2.088681 | 1.208709 |
| N | 2.073030 | 3.315662 | -0.297499 |
| N | -2.088251 | 3.364486 | -0.271682 |
| C | 0.002555 | 4.047175 | 2.501830 |
| C | 0.012065 | 5.166034 | 3.397086 |
| H | 0.012913 | 5.110958 | 4.480132 |
| C | 0.020148 | 6.318980 | 2.632998 |
| H | 0.029021 | 7.338348 | 3.004564 |
| C | 0.013225 | 5.937168 | 1.227620 |
| C | 0.016129 | 6.687457 | 0.006704 |
| C | 0.009195 | 6.147554 | -1.303607 |
| C | -0.027469 | 6.856572 | -2.561156 |
| H | -0.045289 | 7.935712 | -2.668491 |
| C | -0.043490 | 5.930844 | -3.573046 |

| | | | |
|---|-----------|-----------|-----------|
| H | -0.077134 | 6.134515 | -4.638148 |
| C | -0.017281 | 4.609468 | -2.973615 |
| C | -0.040896 | 3.340594 | -3.608189 |
| C | -0.046038 | 2.071402 | -2.973182 |
| C | -0.065016 | 0.749829 | -3.572655 |
| H | -0.076557 | 0.545371 | -4.638046 |
| C | -0.069161 | -0.175572 | -2.560509 |
| H | -0.088372 | -1.254661 | -2.668061 |
| C | -0.043518 | 0.533076 | -1.302577 |
| C | -0.042810 | -0.006304 | 0.007575 |
| C | -0.039019 | 0.744711 | 1.228900 |
| C | -0.032939 | 0.363506 | 2.634283 |
| H | -0.039182 | -0.655221 | 3.007562 |
| C | -0.020357 | 1.516860 | 3.397799 |
| H | -0.015171 | 1.571651 | 4.480861 |
| C | -0.013648 | 2.635267 | 2.502394 |
| C | 0.008621 | 8.162926 | 0.141015 |
| C | -1.097028 | 8.827844 | 0.678827 |
| C | -1.121562 | 10.209792 | 0.843051 |
| C | -0.011677 | 10.962205 | 0.458698 |
| C | 1.107257 | 10.329173 | -0.082434 |
| C | 1.104784 | 8.944685 | -0.232984 |
| C | -0.065459 | 3.340603 | -5.093811 |
| C | 1.047127 | 3.734757 | -5.842226 |
| C | 1.038608 | 3.735695 | -7.235034 |
| C | -0.111663 | 3.334668 | -7.913315 |
| C | -1.239516 | 2.937188 | -7.196340 |
| C | -1.202449 | 2.945027 | -5.804093 |
| C | -0.042684 | -1.481371 | 0.144866 |
| C | 1.057080 | -2.256301 | -0.233949 |
| C | 1.074675 | -3.639297 | -0.071942 |
| C | -0.032114 | -4.278270 | 0.486712 |
| C | -1.144897 | -3.533071 | 0.876585 |
| C | -1.136232 | -2.152452 | 0.699599 |
| C | 2.777648 | 4.471493 | -0.305110 |
| H | 2.210431 | 5.396453 | -0.292838 |
| C | 4.163919 | 4.488677 | -0.329508 |
| H | 4.680081 | 5.446177 | -0.336984 |
| C | 4.863603 | 3.284273 | -0.343092 |
| H | 5.951702 | 3.272189 | -0.363669 |
| C | 4.137157 | 2.095950 | -0.326523 |
| H | 4.631486 | 1.126966 | -0.331725 |
| C | 2.751606 | 2.144443 | -0.302176 |
| H | 2.163903 | 1.232481 | -0.288007 |
| C | -2.767798 | 4.534945 | -0.251720 |
| H | -2.181745 | 5.447984 | -0.256910 |

| | | | |
|---|-----------|----------|-----------|
| C | -4.153420 | 4.582542 | -0.227826 |
| H | -4.647794 | 5.551401 | -0.214921 |
| C | -4.879415 | 3.393928 | -0.220692 |
| H | -5.967562 | 3.405178 | -0.201717 |
| C | -4.178745 | 2.190207 | -0.236710 |
| H | -4.693779 | 1.232113 | -0.231048 |
| C | -2.792431 | 2.208450 | -0.260081 |
| H | -2.225726 | 1.283151 | -0.272271 |

(tpfc)Ir(cnp₂)₂

| | | | |
|----|-----------|-----------|-----------|
| Ir | -0.050114 | 0.000639 | 0.004397 |
| F | -2.153246 | -4.853264 | -1.453107 |
| F | -2.038047 | -7.543403 | -1.787384 |
| F | 0.129045 | -8.946566 | -0.884383 |
| F | 2.200734 | -7.638539 | 0.328325 |
| F | 2.121096 | -4.940772 | 0.623198 |
| F | 2.056519 | -1.176599 | 4.908753 |
| F | 2.039725 | -1.207573 | 7.610700 |
| F | 0.006864 | -0.001062 | 8.990455 |
| F | -2.038223 | 1.206613 | 7.629452 |
| F | -2.078345 | 1.178133 | 4.927758 |
| F | 2.172219 | 4.946904 | 0.563835 |
| F | 2.241355 | 7.644208 | 0.254731 |
| F | 0.141509 | 8.944357 | -0.916079 |
| F | -2.043846 | 7.534757 | -1.764227 |
| F | -2.148393 | 4.845866 | -1.412523 |
| N | -0.077938 | -1.249872 | -1.504338 |
| N | -0.025077 | -1.454601 | 1.350854 |
| N | -0.025932 | 1.456787 | 1.350011 |
| N | -0.075605 | 1.249872 | -1.505095 |
| N | 1.993046 | -0.003025 | -0.029306 |
| N | -2.091340 | 0.004109 | 0.020710 |
| C | -0.075095 | -0.721806 | -2.769147 |
| C | -0.060816 | -1.841967 | -3.663436 |
| H | -0.057490 | -1.793178 | -4.748433 |
| C | -0.051537 | -3.002018 | -2.892055 |
| H | -0.043540 | -4.023749 | -3.259115 |
| C | -0.065136 | -2.608904 | -1.506094 |
| C | -0.050011 | -3.338559 | -0.282049 |
| C | -0.044889 | -2.798543 | 1.036314 |
| C | -0.080265 | -3.511935 | 2.290534 |
| H | -0.106331 | -4.592749 | 2.389556 |
| C | -0.078743 | -2.586197 | 3.306684 |
| H | -0.101504 | -2.786740 | 4.373029 |
| C | -0.034911 | -1.272405 | 2.705600 |

| | | | |
|---|-----------|-----------|-----------|
| C | -0.018425 | 0.001502 | 3.335712 |
| C | -0.006532 | 1.275160 | 2.704795 |
| C | 0.038223 | 2.589343 | 3.304957 |
| H | 0.066254 | 2.790447 | 4.371053 |
| C | 0.030341 | 3.514750 | 2.288572 |
| H | 0.051952 | 4.595574 | 2.387697 |
| C | -0.005339 | 2.800744 | 1.034576 |
| C | -0.024095 | 3.339171 | -0.284255 |
| C | -0.057398 | 2.608665 | -1.507368 |
| C | -0.046828 | 3.001327 | -2.893524 |
| H | -0.036702 | 4.022940 | -3.260928 |
| C | -0.059796 | 1.840938 | -3.664404 |
| H | -0.057694 | 1.791681 | -4.749380 |
| C | -0.075055 | 0.721167 | -2.769588 |
| C | -0.018641 | -4.811722 | -0.406277 |
| C | -1.058024 | -5.514191 | -1.024478 |
| C | -1.020351 | -6.896365 | -1.194167 |
| C | 0.080887 | -7.614923 | -0.729334 |
| C | 1.132128 | -6.946152 | -0.102474 |
| C | 1.070125 | -5.562724 | 0.048675 |
| C | -0.011091 | 0.001337 | 4.817283 |
| C | 1.018141 | -0.602904 | 5.549850 |
| C | 1.032396 | -0.618209 | 6.942881 |
| C | 0.001053 | -0.000324 | 7.648560 |
| C | -1.036286 | 0.618413 | 6.952444 |
| C | -1.034024 | 0.604499 | 5.559391 |
| C | 0.008934 | 4.812053 | -0.413926 |
| C | 1.107432 | 5.565590 | 0.011189 |
| C | 1.164102 | 6.948464 | -0.147963 |
| C | 0.098015 | 7.613453 | -0.753538 |
| C | -1.012782 | 6.891812 | -1.189817 |
| C | -1.044992 | 5.510623 | -1.011695 |
| C | 2.677674 | -1.171732 | -0.042654 |
| H | 2.089572 | -2.084343 | -0.037874 |
| C | 4.061826 | -1.216434 | -0.063298 |
| H | 4.572991 | -2.175961 | -0.071251 |
| C | 4.777375 | -0.010516 | -0.076955 |
| C | 6.203799 | -0.013980 | -0.097117 |
| C | 4.068119 | 1.199117 | -0.076619 |
| H | 4.584163 | 2.155904 | -0.094816 |
| C | 2.683737 | 1.161691 | -0.055859 |
| H | 2.100740 | 2.077477 | -0.061394 |
| C | -2.781034 | -1.161046 | -0.001178 |
| H | -2.196685 | -2.076287 | -0.008005 |
| C | -4.165471 | -1.198709 | -0.016017 |
| H | -4.681488 | -2.155523 | -0.029755 |

| | | | |
|---|-----------|-----------|-----------|
| C | -4.874713 | 0.010962 | -0.015156 |
| C | -6.301210 | 0.013708 | -0.029518 |
| C | -4.159677 | 1.217309 | -0.004607 |
| H | -4.671250 | 2.176612 | -0.009342 |
| C | -2.775396 | 1.172964 | 0.010011 |
| H | -2.186266 | 2.085280 | 0.012138 |
| N | 7.366999 | -0.015191 | -0.113697 |
| N | -7.464486 | 0.014423 | -0.040319 |

[(tpfc)Ir(enpy)₂]⁺

| | | | |
|----|-----------|-----------|-----------|
| Ir | 0.000000 | 0.000000 | 0.000000 |
| F | -2.248240 | -4.752780 | -1.301670 |
| F | -2.295730 | -7.453640 | -1.619670 |
| F | -0.127550 | -8.951200 | -0.890150 |
| F | 2.092830 | -7.740520 | 0.141620 |
| F | 2.157130 | -5.039510 | 0.439060 |
| F | 2.211000 | -0.802080 | 4.912680 |
| F | 2.183150 | -0.794310 | 7.629970 |
| F | -0.056610 | 0.009690 | 8.972160 |
| F | -2.273780 | 0.806960 | 7.588830 |
| F | -2.255750 | 0.799350 | 4.870910 |
| F | 2.219990 | 4.973640 | 0.453860 |
| F | 2.247820 | 7.672620 | 0.136000 |
| F | 0.080240 | 8.947540 | -0.929600 |
| F | -2.128100 | 7.516910 | -1.671320 |
| F | -2.175550 | 4.818960 | -1.329060 |
| N | -0.013230 | -1.252360 | -1.489630 |
| N | 0.012430 | -1.449150 | 1.340610 |
| N | 0.003840 | 1.448870 | 1.340290 |
| N | -0.014540 | 1.252120 | -1.489840 |
| N | 2.080080 | 0.000000 | -0.000000 |
| N | -2.081570 | 0.000920 | 0.006530 |
| C | -0.020690 | -0.706430 | -2.783150 |
| C | -0.031520 | -1.825230 | -3.678470 |
| H | -0.038430 | -1.770060 | -4.761480 |
| C | -0.031280 | -2.978270 | -2.914470 |
| H | -0.037480 | -3.997630 | -3.286100 |
| C | -0.022710 | -2.596540 | -1.509080 |
| C | -0.019280 | -3.346940 | -0.288230 |
| C | -0.009580 | -2.807120 | 1.022100 |
| C | -0.044940 | -3.515780 | 2.279890 |
| H | -0.074820 | -4.594640 | 2.387350 |
| C | -0.042020 | -2.590030 | 3.291880 |
| H | -0.069820 | -2.793390 | 4.357210 |
| C | -0.004680 | -1.269000 | 2.692280 |

| | | | |
|---|-----------|-----------|-----------|
| C | -0.008200 | 0.000000 | 3.327020 |
| C | -0.003100 | 1.269230 | 2.692090 |
| C | -0.001620 | 2.590870 | 3.291700 |
| H | -0.002440 | 2.795350 | 4.357150 |
| C | -0.002570 | 3.516360 | 2.279620 |
| H | -0.008050 | 4.595590 | 2.387330 |
| C | 0.004820 | 2.807580 | 1.021530 |
| C | 0.001790 | 3.347050 | -0.288590 |
| C | -0.012890 | 2.596170 | -1.509910 |
| C | -0.013180 | 2.977410 | -2.915300 |
| H | -0.010150 | 3.996180 | -3.288510 |
| C | -0.020320 | 1.824070 | -3.678900 |
| H | -0.024210 | 1.769330 | -4.761970 |
| C | -0.020020 | 0.705570 | -2.783580 |
| C | -0.045470 | -4.822200 | -0.422490 |
| C | -1.163140 | -5.473800 | -0.951700 |
| C | -1.205460 | -6.855340 | -1.115740 |
| C | -0.101700 | -7.621000 | -0.740030 |
| C | 1.028900 | -7.001440 | -0.207610 |
| C | 1.044140 | -5.617040 | -0.057030 |
| C | -0.021210 | 0.000140 | 4.812790 |
| C | 1.092370 | -0.407360 | 5.552530 |
| C | 1.094670 | -0.408340 | 6.945360 |
| C | -0.045420 | 0.006340 | 7.632570 |
| C | -1.173980 | 0.417340 | 6.924390 |
| C | -1.147830 | 0.409200 | 5.531900 |
| C | 0.018480 | 4.822020 | -0.425860 |
| C | 1.130340 | 5.583710 | -0.055600 |
| C | 1.163200 | 6.966420 | -0.217730 |
| C | 0.059820 | 7.618630 | -0.767760 |
| C | -1.064790 | 6.886820 | -1.148980 |
| C | -1.071250 | 5.506180 | -0.972070 |
| C | 2.770870 | -1.164170 | 0.002120 |
| H | 2.192560 | -2.082280 | -0.005750 |
| C | 4.156980 | -1.197930 | 0.015740 |
| H | 4.661700 | -2.161530 | 0.019200 |
| C | 4.871100 | -0.001970 | 0.023900 |
| C | 6.305370 | 0.023880 | -0.081280 |
| C | 4.158800 | 1.194950 | 0.012990 |
| H | 4.664700 | 2.157960 | 0.014350 |
| C | 2.772620 | 1.163020 | -0.000590 |
| H | 2.195770 | 2.081950 | -0.010180 |
| C | -2.775190 | -1.161330 | -0.008150 |
| H | -2.200070 | -2.081310 | -0.007530 |
| C | -4.161430 | -1.192360 | -0.021270 |
| H | -4.667430 | -2.155240 | -0.030340 |

| | | | |
|---|-----------|-----------|-----------|
| C | -4.873190 | 0.004850 | -0.022750 |
| C | -6.309110 | -0.027280 | 0.061370 |
| C | -4.158080 | 1.200110 | -0.012170 |
| H | -4.661660 | 2.164290 | -0.013820 |
| C | -2.771950 | 1.165290 | 0.000420 |
| H | -2.194140 | 2.083750 | 0.008210 |
| N | 7.453040 | 0.076270 | -0.220670 |
| N | -7.462410 | -0.096850 | 0.127630 |

(tpfc)Ir(meopy)₂

| | | | |
|----|-----------|-----------|-----------|
| Ir | -0.044364 | 3.339751 | -0.283700 |
| F | -2.052272 | 8.235925 | 1.216542 |
| F | -1.887459 | 10.923061 | 1.526978 |
| F | 0.281411 | 12.287314 | 0.566941 |
| F | 2.305834 | 10.936887 | -0.681511 |
| F | 2.180707 | 8.241151 | -0.949685 |
| F | 2.016451 | 4.495519 | -5.205267 |
| F | 1.974927 | 4.534652 | -7.906071 |
| F | -0.081333 | 3.349972 | -9.271134 |
| F | -2.125845 | 2.158890 | -7.894589 |
| F | -2.145112 | 2.185419 | -5.193168 |
| F | 2.091321 | -1.658995 | -0.837047 |
| F | 2.089146 | -4.357339 | -0.536219 |
| F | -0.051314 | -5.607363 | 0.617596 |
| F | -2.204165 | -4.144251 | 1.458087 |
| F | -2.236274 | -1.452034 | 1.116381 |
| N | -0.035523 | 4.588466 | 1.224059 |
| N | -0.024662 | 4.793349 | -1.629770 |
| N | -0.057200 | 1.885222 | -1.629429 |
| N | -0.062257 | 2.092266 | 1.224460 |
| N | 2.010874 | 3.321822 | -0.284327 |
| N | -2.098271 | 3.357507 | -0.270157 |
| C | -0.027664 | 4.061840 | 2.488572 |
| C | 0.007519 | 5.181680 | 3.384071 |
| H | 0.020475 | 5.132517 | 4.469204 |
| C | 0.023291 | 6.341843 | 2.612904 |
| H | 0.045670 | 7.363559 | 2.979799 |
| C | -0.008732 | 5.947113 | 1.226597 |
| C | 0.000238 | 6.676075 | 0.002715 |
| C | -0.020974 | 6.136129 | -1.315832 |
| C | -0.062783 | 6.852345 | -2.569257 |
| H | -0.075813 | 7.933637 | -2.667258 |
| C | -0.085534 | 5.927508 | -3.585861 |
| H | -0.118379 | 6.128503 | -4.652019 |

| | | | |
|---|-----------|-----------|-----------|
| C | -0.051569 | 4.612865 | -2.983706 |
| C | -0.057927 | 3.339092 | -3.614362 |
| C | -0.054801 | 2.065142 | -2.983751 |
| C | -0.036063 | 0.750158 | -3.585903 |
| H | -0.025795 | 0.548624 | -4.652386 |
| C | -0.043388 | -0.174532 | -2.568756 |
| H | -0.038090 | -1.255854 | -2.666945 |
| C | -0.052308 | 0.542296 | -1.315052 |
| C | -0.067970 | 0.004343 | 0.003881 |
| C | -0.075592 | 0.733641 | 1.226959 |
| C | -0.067963 | 0.337863 | 2.613315 |
| H | -0.077895 | -0.684294 | 2.979759 |
| C | -0.052480 | 1.498110 | 3.384464 |
| H | -0.044919 | 1.546956 | 4.469662 |
| C | -0.047538 | 2.618597 | 2.488828 |
| C | 0.059284 | 8.148586 | 0.123742 |
| C | -0.954298 | 8.873064 | 0.759978 |
| C | -0.891261 | 10.255799 | 0.918096 |
| C | 0.209600 | 10.954532 | 0.423713 |
| C | 1.235842 | 10.264375 | -0.220564 |
| C | 1.149497 | 8.880966 | -0.358790 |
| C | -0.063948 | 3.340318 | -5.095628 |
| C | 0.964921 | 3.935030 | -5.837052 |
| C | 0.967124 | 3.953523 | -7.230126 |
| C | -0.075555 | 3.346690 | -7.928367 |
| C | -1.112183 | 2.736305 | -7.224196 |
| C | -1.098616 | 2.748567 | -5.831092 |
| C | -0.072040 | -1.469147 | 0.131523 |
| C | 1.007866 | -2.250251 | -0.291193 |
| C | 1.027476 | -3.634835 | -0.136857 |
| C | -0.058636 | -4.274232 | 0.460206 |
| C | -1.152259 | -3.525188 | 0.893133 |
| C | -1.146833 | -2.142823 | 0.720718 |
| C | 2.715577 | 4.473479 | -0.287475 |
| H | 2.141344 | 5.395590 | -0.283833 |
| C | 4.101491 | 4.509342 | -0.295358 |
| H | 4.603002 | 5.472964 | -0.299667 |
| C | 4.810407 | 3.298585 | -0.294984 |
| O | 6.152798 | 3.192765 | -0.305527 |
| C | 4.077175 | 2.100568 | -0.277119 |
| H | 4.590924 | 1.141271 | -0.267220 |
| C | 2.698225 | 2.152031 | -0.270000 |
| H | 2.106445 | 1.241434 | -0.252124 |
| C | -2.785033 | 4.527044 | -0.238164 |
| H | -2.192694 | 5.437711 | -0.237411 |
| C | -4.163687 | 4.577707 | -0.205121 |

| | | | |
|---|-----------|----------|-----------|
| H | -4.677576 | 5.536651 | -0.182616 |
| C | -4.896246 | 3.379133 | -0.198340 |
| O | -6.238450 | 3.484212 | -0.168724 |
| C | -4.187094 | 2.168666 | -0.218034 |
| H | -4.687928 | 1.204798 | -0.206493 |
| C | -2.801558 | 2.205345 | -0.250806 |
| H | -2.226202 | 1.283821 | -0.260101 |
| C | 6.901250 | 4.427017 | -0.326465 |
| C | -6.986408 | 2.249537 | -0.159893 |
| H | -8.039405 | 2.544334 | -0.138612 |
| H | -6.735122 | 1.658945 | 0.732946 |
| H | -6.769321 | 1.666874 | -1.066824 |
| H | 7.954234 | 4.131652 | -0.337940 |
| H | 6.679352 | 5.021715 | 0.571427 |
| H | 6.655060 | 5.005743 | -1.228450 |

[(tpfc)Ir(meopy)₂]⁺

| | | | |
|----|-----------|-----------|-----------|
| Ir | -0.008957 | 3.341741 | -0.277151 |
| F | -2.149947 | 8.165254 | 1.076813 |
| F | -2.092236 | 10.862823 | 1.418340 |
| F | 0.106233 | 12.289989 | 0.641020 |
| F | 2.254786 | 11.011704 | -0.457651 |
| F | 2.218402 | 8.312339 | -0.773673 |
| F | 2.186762 | 4.104603 | -5.199276 |
| F | 2.149380 | 4.092429 | -7.916695 |
| F | -0.105742 | 3.316527 | -9.249520 |
| F | -2.329059 | 2.553079 | -7.857128 |
| F | -2.301788 | 2.565564 | -5.139225 |
| F | 2.135966 | -1.704630 | -0.697267 |
| F | 2.059221 | -4.404777 | -0.405651 |
| F | -0.172261 | -5.609095 | 0.611950 |
| F | -2.338392 | -4.103429 | 1.331989 |
| F | -2.278040 | -1.403176 | 1.020234 |
| N | -0.003288 | 4.595539 | 1.209712 |
| N | 0.000707 | 4.788163 | -1.619868 |
| N | -0.022698 | 1.891419 | -1.615544 |
| N | -0.017799 | 2.092220 | 1.213482 |
| N | 2.072323 | 3.334297 | -0.296029 |
| N | -2.091413 | 3.349220 | -0.267505 |
| C | -0.002090 | 4.051686 | 2.504112 |
| C | 0.009945 | 5.171175 | 3.397979 |
| H | 0.013896 | 5.118285 | 4.481150 |
| C | 0.017130 | 6.323433 | 2.632263 |
| H | 0.028023 | 7.342697 | 3.004095 |
| C | 0.004829 | 5.940048 | 1.227638 |

| | | | |
|---|-----------|-----------|-----------|
| C | 0.010234 | 6.688559 | 0.005903 |
| C | -0.000062 | 6.146759 | -1.303765 |
| C | -0.029929 | 6.853925 | -2.562180 |
| H | -0.045783 | 7.932949 | -2.671334 |
| C | -0.043080 | 5.926580 | -3.573110 |
| H | -0.071452 | 6.128872 | -4.638660 |
| C | -0.021020 | 4.606695 | -2.971454 |
| C | -0.037347 | 3.336918 | -3.604237 |
| C | -0.038858 | 2.068822 | -2.967686 |
| C | -0.056449 | 0.746998 | -3.565412 |
| H | -0.067205 | 0.541024 | -4.630551 |
| C | -0.061180 | -0.177165 | -2.551496 |
| H | -0.079723 | -1.256448 | -2.657535 |
| C | -0.035560 | 0.533898 | -1.295209 |
| C | -0.039852 | -0.003794 | 0.016042 |
| C | -0.034035 | 0.747715 | 1.235309 |
| C | -0.034345 | 0.367940 | 2.640812 |
| H | -0.043367 | -0.650483 | 3.015089 |
| C | -0.022536 | 1.522386 | 3.403266 |
| H | -0.020860 | 1.578402 | 4.486292 |
| C | -0.012376 | 2.639505 | 2.506154 |
| C | 0.030433 | 8.163729 | 0.140446 |
| C | -1.049789 | 8.850060 | 0.702746 |
| C | -1.038407 | 10.230840 | 0.878983 |
| C | 0.081038 | 10.960851 | 0.479844 |
| C | 1.174567 | 10.306740 | -0.087192 |
| C | 1.137263 | 8.923962 | -0.247772 |
| C | -0.056362 | 3.334422 | -5.090005 |
| C | 1.060320 | 3.724630 | -5.834429 |
| C | 1.057987 | 3.722863 | -7.227260 |
| C | -0.090009 | 3.322606 | -7.909761 |
| C | -1.221684 | 2.928872 | -7.196927 |
| C | -1.190805 | 2.939546 | -5.804497 |
| C | -0.070636 | -1.479002 | 0.152083 |
| C | 1.017751 | -2.277796 | -0.207963 |
| C | 0.996253 | -3.662407 | -0.059930 |
| C | -0.139741 | -4.278481 | 0.464847 |
| C | -1.242217 | -3.508785 | 0.835815 |
| C | -1.193369 | -2.127141 | 0.674559 |
| C | 2.774422 | 4.489336 | -0.312233 |
| H | 2.205652 | 5.413639 | -0.300365 |
| C | 4.156152 | 4.534398 | -0.345207 |
| H | 4.644217 | 5.504339 | -0.358386 |
| C | 4.875883 | 3.329622 | -0.359154 |
| O | 6.211760 | 3.225763 | -0.393958 |
| C | 4.146839 | 2.128547 | -0.331353 |

| | | | |
|---|-----------|----------|-----------|
| H | 4.665578 | 1.172563 | -0.335096 |
| C | 2.771189 | 2.169602 | -0.299466 |
| H | 2.196739 | 1.249016 | -0.277667 |
| C | -2.790684 | 4.513580 | -0.252633 |
| H | -2.217327 | 5.435051 | -0.262281 |
| C | -4.166557 | 4.554284 | -0.229568 |
| H | -4.685013 | 5.510347 | -0.221095 |
| C | -4.895778 | 3.353157 | -0.217539 |
| O | -6.231985 | 3.456602 | -0.196086 |
| C | -4.175530 | 2.148743 | -0.227404 |
| H | -4.662881 | 1.178412 | -0.217897 |
| C | -2.793604 | 2.194259 | -0.250373 |
| H | -2.225573 | 1.269521 | -0.257534 |
| C | 6.985260 | 4.447777 | -0.427678 |
| C | -7.005502 | 2.234235 | -0.183344 |
| H | -8.049434 | 2.554973 | -0.168078 |
| H | -6.781417 | 1.645104 | 0.715616 |
| H | -6.808372 | 1.643413 | -1.087496 |
| H | 8.028717 | 4.126551 | -0.457566 |
| H | 6.803018 | 5.045043 | 0.475372 |
| H | 6.746710 | 5.030593 | -1.327020 |

(tpfc)Ir(dmap)₂

| | | | |
|----|-----------|-----------|-----------|
| Ir | -0.048723 | 3.339655 | -0.280518 |
| F | -2.069236 | 8.214392 | 1.226239 |
| F | -1.931499 | 10.902452 | 1.536853 |
| F | 0.219663 | 12.290136 | 0.570377 |
| F | 2.254873 | 10.960942 | -0.684193 |
| F | 2.158714 | 8.264369 | -0.950533 |
| F | 2.006061 | 4.499227 | -5.204469 |
| F | 1.961893 | 4.537566 | -7.904566 |
| F | -0.094289 | 3.350310 | -9.267984 |
| F | -2.136078 | 2.156638 | -7.888792 |
| F | -2.153382 | 2.184267 | -5.188053 |
| F | 2.116190 | -1.617189 | -0.872683 |
| F | 2.175301 | -4.313410 | -0.567523 |
| F | 0.084645 | -5.605092 | 0.630900 |
| F | -2.081749 | -4.184464 | 1.510044 |
| F | -2.178659 | -1.496213 | 1.162159 |
| N | -0.035270 | 4.587138 | 1.226920 |
| N | -0.025720 | 4.793509 | -1.625394 |
| N | -0.064818 | 1.885987 | -1.626021 |
| N | -0.067145 | 2.092241 | 1.226563 |
| N | 2.007963 | 3.314580 | -0.284002 |
| N | -2.103267 | 3.363908 | -0.270651 |

| | | | |
|---|-----------|-----------|-----------|
| C | -0.022101 | 4.060902 | 2.491003 |
| C | 0.016135 | 5.180161 | 3.387435 |
| H | 0.032982 | 5.130396 | 4.472593 |
| C | 0.027285 | 6.340882 | 2.616636 |
| H | 0.050061 | 7.362688 | 2.983584 |
| C | -0.009669 | 5.945725 | 1.230347 |
| C | -0.004420 | 6.674974 | 0.007346 |
| C | -0.024653 | 6.135697 | -1.311355 |
| C | -0.072633 | 6.853067 | -2.564111 |
| H | -0.088199 | 7.934438 | -2.661769 |
| C | -0.096040 | 5.928639 | -3.581236 |
| H | -0.132244 | 6.130220 | -4.647253 |
| C | -0.057228 | 4.613920 | -2.978881 |
| C | -0.065690 | 3.340320 | -3.610074 |
| C | -0.062332 | 2.066173 | -2.979815 |
| C | -0.038591 | 0.751601 | -3.583480 |
| H | -0.027902 | 0.550399 | -4.650105 |
| C | -0.040978 | -0.173467 | -2.566543 |
| H | -0.030855 | -1.254781 | -2.665349 |
| C | -0.052752 | 0.543428 | -1.312684 |
| C | -0.059484 | 0.004929 | 0.005893 |
| C | -0.068080 | 0.733638 | 1.228998 |
| C | -0.042709 | 0.336632 | 2.615070 |
| H | -0.042100 | -0.685802 | 2.981090 |
| C | -0.028931 | 1.496889 | 3.386574 |
| H | -0.010772 | 1.545560 | 4.471760 |
| C | -0.041371 | 2.617384 | 2.490833 |
| C | 0.041431 | 8.147698 | 0.128925 |
| C | -0.978028 | 8.862084 | 0.767568 |
| C | -0.929431 | 10.245446 | 0.925408 |
| C | 0.162000 | 10.956175 | 0.427577 |
| C | 1.193370 | 10.276773 | -0.219763 |
| C | 1.121971 | 8.892314 | -0.356974 |
| C | -0.073379 | 3.341957 | -5.091018 |
| C | 0.953585 | 3.938174 | -5.834286 |
| C | 0.954481 | 3.956315 | -7.227344 |
| C | -0.087527 | 3.347629 | -7.924861 |
| C | -1.122252 | 2.735772 | -7.219316 |
| C | -1.107446 | 2.748405 | -5.826242 |
| C | -0.033978 | -1.468140 | 0.133928 |
| C | 1.053944 | -2.228546 | -0.306996 |
| C | 1.105856 | -3.611926 | -0.149885 |
| C | 0.045745 | -4.272470 | 0.470055 |
| C | -1.054421 | -3.545010 | 0.922428 |
| C | -1.082318 | -2.163365 | 0.745960 |
| C | 2.731092 | 4.459270 | -0.287651 |

| | | | |
|---|-----------|----------|-----------|
| H | 2.167171 | 5.388267 | -0.281167 |
| C | 4.108757 | 4.487185 | -0.298964 |
| H | 4.580840 | 5.464469 | -0.300395 |
| C | 4.864584 | 3.281383 | -0.305535 |
| N | 6.222828 | 3.265106 | -0.326135 |
| C | 4.081169 | 2.093615 | -0.284359 |
| H | 4.529997 | 1.105446 | -0.275186 |
| C | 2.704581 | 2.153763 | -0.272878 |
| H | 2.120502 | 1.237741 | -0.253982 |
| C | -2.799158 | 4.524475 | -0.237114 |
| H | -2.213463 | 5.439968 | -0.226853 |
| C | -4.175674 | 4.583548 | -0.212814 |
| H | -4.625100 | 5.571095 | -0.188490 |
| C | -4.958296 | 3.395003 | -0.217368 |
| N | -6.316728 | 3.410284 | -0.203189 |
| C | -4.202049 | 2.189505 | -0.233004 |
| H | -4.673547 | 1.212056 | -0.223582 |
| C | -2.824564 | 2.218389 | -0.257066 |
| H | -2.258463 | 1.290396 | -0.263515 |
| C | 7.055630 | 4.459028 | -0.348811 |
| C | 7.026873 | 2.051354 | -0.328515 |
| H | 6.418579 | 1.146391 | -0.302165 |
| H | 7.693400 | 2.053658 | 0.548360 |
| H | 7.651181 | 2.028873 | -1.235814 |
| H | 6.468677 | 5.378312 | -0.358372 |
| H | 7.695099 | 4.440132 | -1.245428 |
| H | 7.707463 | 4.466788 | 0.539171 |
| C | -7.149071 | 2.215831 | -0.207539 |
| C | -7.121531 | 4.623340 | -0.181931 |
| H | -6.562011 | 1.296953 | -0.234232 |
| H | -7.811261 | 2.236534 | -1.087488 |
| H | -7.777991 | 2.205407 | 0.696774 |
| H | -6.513535 | 5.528781 | -0.168735 |
| H | -7.765403 | 4.618312 | 0.711700 |
| H | -7.768909 | 4.647565 | -1.072892 |

[(tpfc)Ir(dmap)₂]⁺

| | | | |
|----|-----------|-----------|-----------|
| Ir | -0.004510 | 3.340544 | -0.276179 |
| F | -2.191955 | 8.127641 | 1.025419 |
| F | -2.200287 | 10.828064 | 1.339805 |
| F | -0.012944 | 12.294784 | 0.603415 |
| F | 2.188349 | 11.051092 | -0.431105 |
| F | 2.215198 | 8.350101 | -0.723461 |
| F | 2.187839 | 4.105525 | -5.202069 |
| F | 2.144559 | 4.098224 | -7.918788 |

| | | | |
|---|-----------|-----------|-----------|
| F | -0.114150 | 3.326708 | -9.248637 |
| F | -2.335272 | 2.562652 | -7.852615 |
| F | -2.302967 | 2.571390 | -5.135472 |
| F | 2.154949 | -1.678443 | -0.706854 |
| F | 2.116691 | -4.378381 | -0.409453 |
| F | -0.092405 | -5.611554 | 0.621673 |
| F | -2.276028 | -4.134746 | 1.348847 |
| F | -2.256340 | -1.435065 | 1.028858 |
| N | 0.005856 | 4.593143 | 1.209760 |
| N | 0.012682 | 4.787698 | -1.617223 |
| N | -0.024839 | 1.891273 | -1.614751 |
| N | -0.019869 | 2.090582 | 1.211823 |
| N | 2.075734 | 3.320628 | -0.293778 |
| N | -2.086396 | 3.360459 | -0.268362 |
| C | 0.000891 | 4.049151 | 2.503454 |
| C | 0.007377 | 5.167578 | 3.398496 |
| H | 0.006728 | 5.113867 | 4.481685 |
| C | 0.015755 | 6.320804 | 2.633314 |
| H | 0.023065 | 7.340010 | 3.005687 |
| C | 0.011099 | 5.938189 | 1.229003 |
| C | 0.016382 | 6.686575 | 0.009127 |
| C | 0.011272 | 6.145381 | -1.300823 |
| C | -0.021014 | 6.853777 | -2.557961 |
| H | -0.036886 | 7.932951 | -2.666377 |
| C | -0.035620 | 5.926768 | -3.570022 |
| H | -0.065583 | 6.129943 | -4.635413 |
| C | -0.012503 | 4.607326 | -2.969032 |
| C | -0.034356 | 3.338121 | -3.602347 |
| C | -0.039532 | 2.069626 | -2.966987 |
| C | -0.056572 | 0.749137 | -3.566032 |
| H | -0.066867 | 0.543946 | -4.631385 |
| C | -0.060700 | -0.176173 | -2.552378 |
| H | -0.078543 | -1.255451 | -2.659285 |
| C | -0.036511 | 0.534123 | -1.296109 |
| C | -0.038690 | -0.004786 | 0.014769 |
| C | -0.035490 | 0.745622 | 1.233398 |
| C | -0.034353 | 0.365353 | 2.638303 |
| H | -0.042789 | -0.653198 | 3.012442 |
| C | -0.023275 | 1.519895 | 3.401530 |
| H | -0.021239 | 1.575422 | 4.484627 |
| C | -0.012977 | 2.636753 | 2.504656 |
| C | 0.010561 | 8.162327 | 0.141776 |
| C | -1.096383 | 8.831086 | 0.672310 |
| C | -1.118964 | 10.213462 | 0.834394 |
| C | -0.005937 | 10.963441 | 0.455256 |
| C | 1.114374 | 10.327069 | -0.078550 |

| | | | |
|---|-----------|-----------|-----------|
| C | 1.109979 | 8.942293 | -0.226805 |
| C | -0.056003 | 3.337128 | -5.087982 |
| C | 1.059143 | 3.727780 | -5.834622 |
| C | 1.053905 | 3.728493 | -7.227481 |
| C | -0.095580 | 3.330343 | -7.908482 |
| C | -1.225810 | 2.936208 | -7.193807 |
| C | -1.192044 | 2.944490 | -5.801392 |
| C | -0.052217 | -1.480324 | 0.150058 |
| C | 1.045480 | -2.265312 | -0.212971 |
| C | 1.044350 | -3.649715 | -0.061507 |
| C | -0.079919 | -4.280587 | 0.470459 |
| C | -1.191114 | -3.525461 | 0.844723 |
| C | -1.163002 | -2.143537 | 0.679353 |
| C | 2.800695 | 4.467440 | -0.300770 |
| H | 2.244969 | 5.400168 | -0.284462 |
| C | 4.174097 | 4.498717 | -0.328706 |
| H | 4.642024 | 5.477793 | -0.330908 |
| C | 4.937087 | 3.296710 | -0.351328 |
| N | 6.290151 | 3.285610 | -0.385877 |
| C | 4.154044 | 2.107544 | -0.331298 |
| H | 4.605417 | 1.120723 | -0.337644 |
| C | 2.781251 | 2.161824 | -0.303108 |
| H | 2.209895 | 1.238609 | -0.289230 |
| C | -2.792310 | 4.518897 | -0.246284 |
| H | -2.222017 | 5.442761 | -0.251087 |
| C | -4.165193 | 4.573008 | -0.220393 |
| H | -4.616125 | 5.559929 | -0.206818 |
| C | -4.948456 | 3.383957 | -0.212318 |
| N | -6.301791 | 3.394877 | -0.189658 |
| C | -4.185003 | 2.182254 | -0.228126 |
| H | -4.652210 | 1.202896 | -0.219164 |
| C | -2.811544 | 2.213761 | -0.253918 |
| H | -2.256775 | 1.280513 | -0.264865 |
| C | 7.109806 | 4.490556 | -0.407135 |
| C | 7.089904 | 2.067386 | -0.406091 |
| H | 6.474144 | 1.168795 | -0.381566 |
| H | 7.762459 | 2.052453 | 0.463109 |
| H | 7.699852 | 2.041853 | -1.320376 |
| H | 6.508477 | 5.399170 | -0.401344 |
| H | 7.737243 | 4.494436 | -1.309549 |
| H | 7.765961 | 4.506072 | 0.474814 |
| C | -7.121536 | 2.189841 | -0.181303 |
| C | -7.101743 | 4.612979 | -0.170944 |
| H | -6.520397 | 1.281375 | -0.204431 |
| H | -7.786543 | 2.189457 | -1.056420 |
| H | -7.739868 | 2.170563 | 0.727495 |

| | | | |
|---|-----------|----------|-----------|
| H | -6.485487 | 5.511565 | -0.168482 |
| H | -7.736979 | 4.624101 | 0.725951 |
| H | -7.749809 | 4.642264 | -1.058513 |

g-matrix for LS d⁵ System with SOMO Described by Eq S1.

$$\begin{vmatrix}
 2\lambda \left(\frac{\alpha_{xz}^2}{\delta_{xy}} + \frac{\alpha_{yz}^2}{\delta_{x^2-y^2}} + \frac{3\alpha_{yz}^2}{\delta_{z^2}} \right) + g_e & -2\lambda(3\alpha_{yz}\alpha_{xz}) & 0 \\
 -2\lambda(3\alpha_{yz}\alpha_{xz}) & 2\lambda \left(\frac{\alpha_{yz}^2}{\delta_{xy}} + \frac{\alpha_{xz}^2}{\delta_{x^2-y^2}} + \frac{3\alpha_{xz}^2}{\delta_{z^2}} \right) + g_e & 0 \\
 0 & 0 & 2\lambda \left(\frac{\alpha_{yz}^2}{\delta_{xz}} + \frac{\alpha_{xz}^2}{\delta_{yz}} \right) + g_e
 \end{vmatrix} \quad (S1)$$