Electronic Supplementary Information for Dalton Transactions


# Heteroditopic Ferrocene-based Ureas as Receptors for Anions and Cations

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## Electronic Supplementary Information (ESI)

**Figure I**: Electrochemical response of heteroditopic receptors **2a** and **2b** (c = $10^{-3}$ M) upon addition of increasing amounts of $F^-$ and $H_2PO_4^-$ (c = $2.5 \cdot 10^{-2}$ M) using ($n$-$Bu_4N$)$ClO_4$ (c = 0.1 M) as supporting electrolyte; CV scan rate: 100 $mVs^{-1}$.

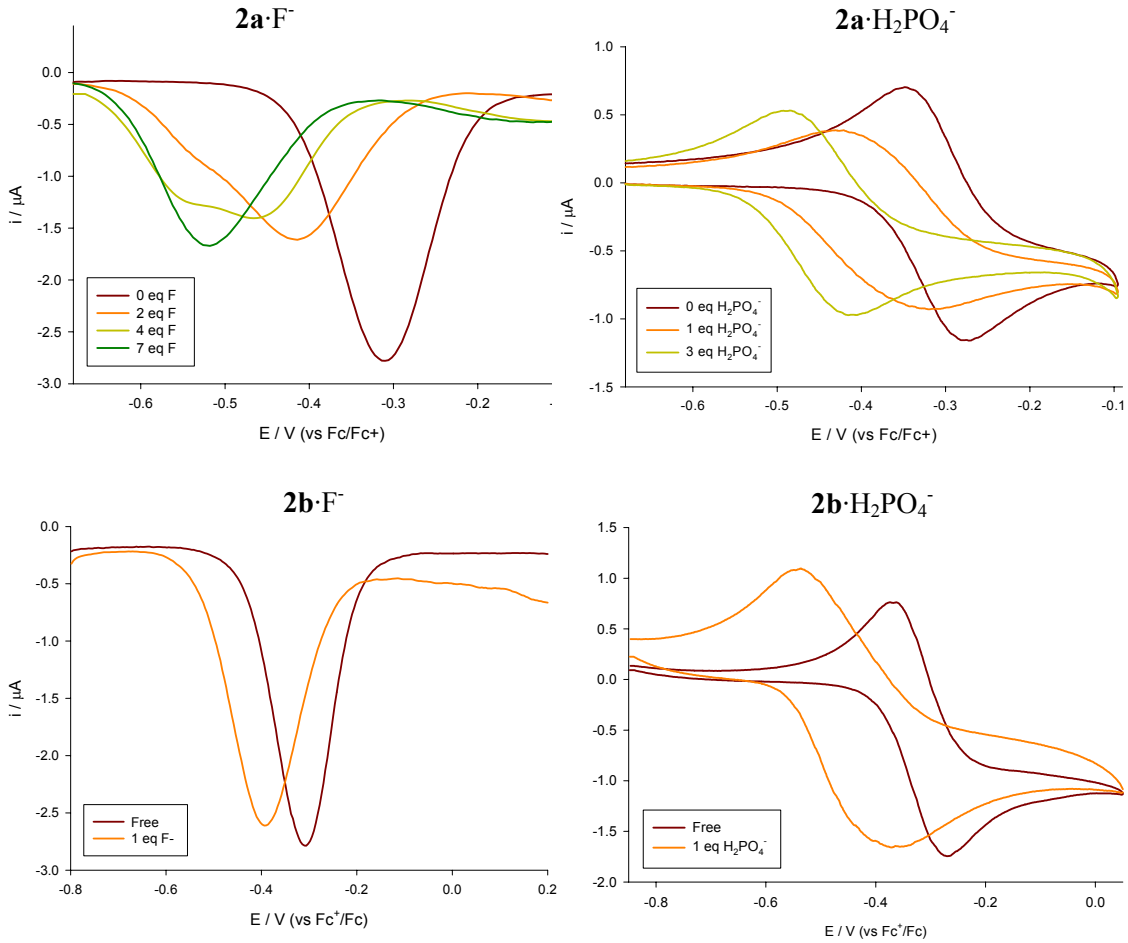


**Figure II**: Electrochemical response of heteroditopic receptor **2a** (c = $10^{-3}$ M) upon addition of increasing amounts of $Cu^{2+}$ (c = $2.5 \cdot 10^{-2}$ M) using ($n$-$Bu_4N$)$ClO_4$ (c = 0.1 M) as supporting electrolyte; CV scan rate: 100 $mVs^{-1}$.

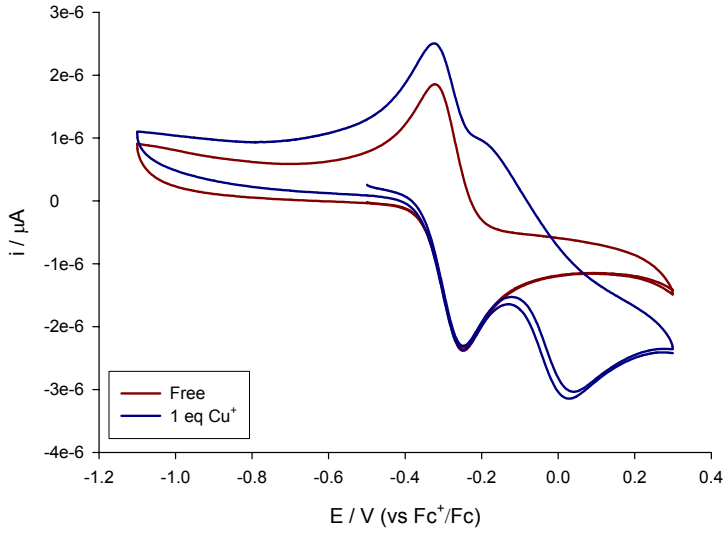


**Figure III**: Electrochemical response of heteroditopic receptors **2c** and **2d** (c = $10^{-3}$ M) upon addition of increasing amounts $F^-$, $H_2PO_4^-$ and $AcO^-$ (c = $2.5 \cdot 10^{-2}$ M) using (*n*-$Bu_4N)ClO_4$ (c = 0.1 M) as supporting electrolyte; CV scan rate: $100 mVs^{-1}$.

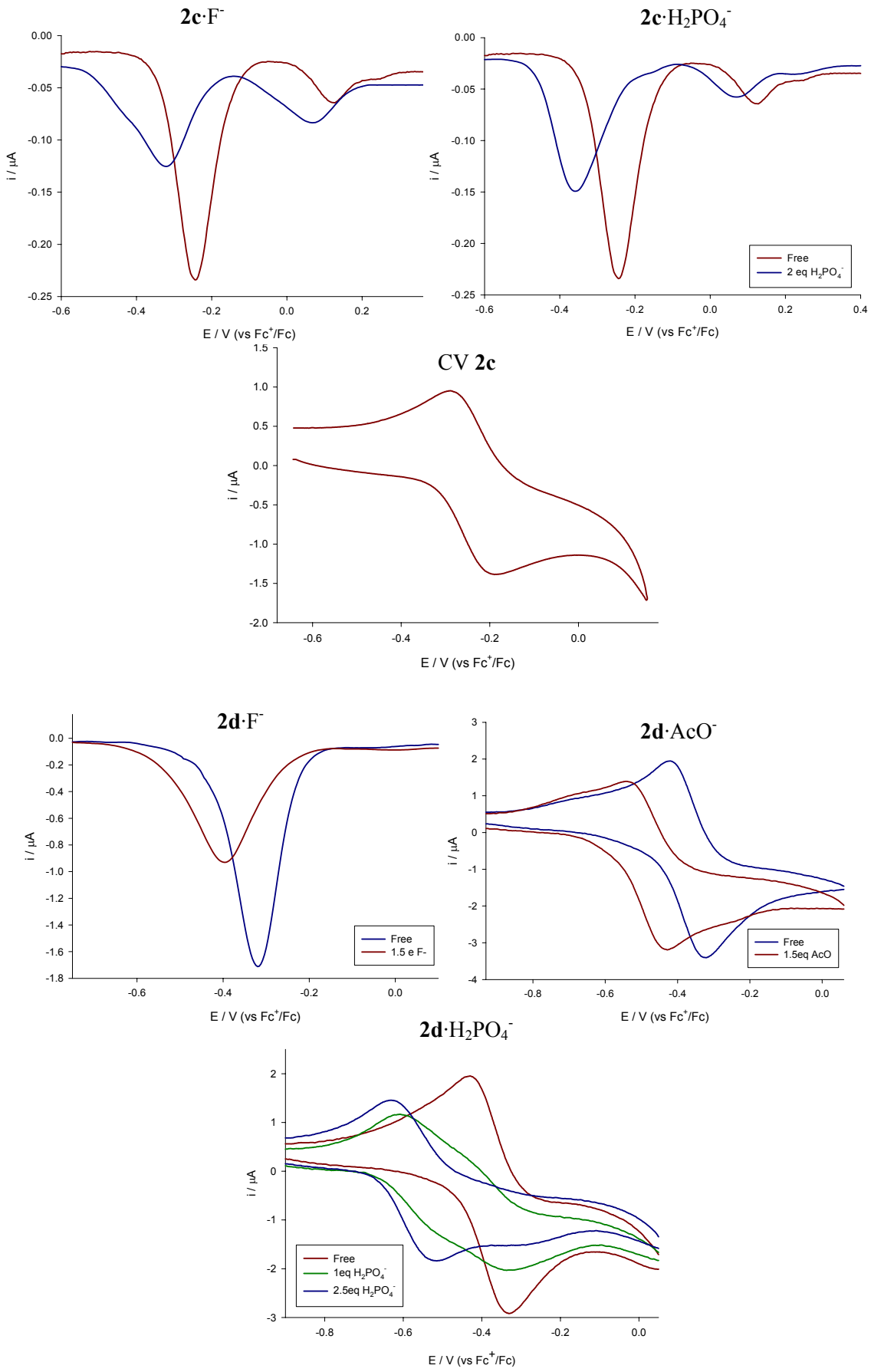


**Figure IV**: Electrochemical response of the heteroditopic receptor **2d** (c = $10^{-3}$ M) upon addition of increasing amounts of $Li^+$ (c = $2.5 \cdot 10^{-2}$ M) using ($n$-$Bu_4N$)$ClO_4$ (c = 0.1 M) as supporting electrolyte; scan rate: 100 $mVs^{-1}$.

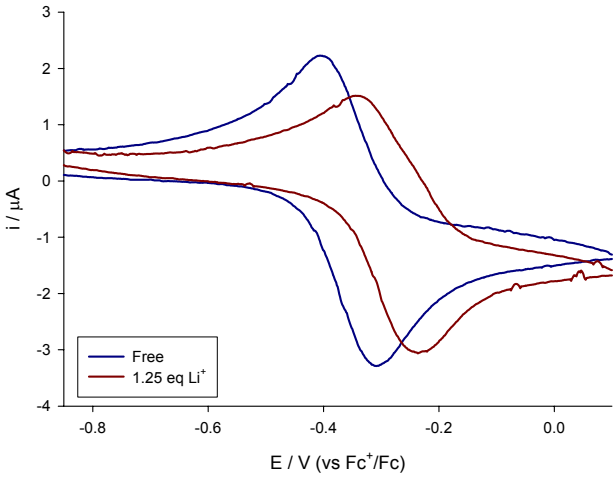


**Figure V**: $^{1}$H-NMR spectral changes observed for the urea NH protons upon addition of increasing amounts $F^-$ and $H_2PO_4^-$ anions (c = 0.1 M) to the heteroditopic receptor **2a** (c = $5 \cdot 10^{-3}$ M).

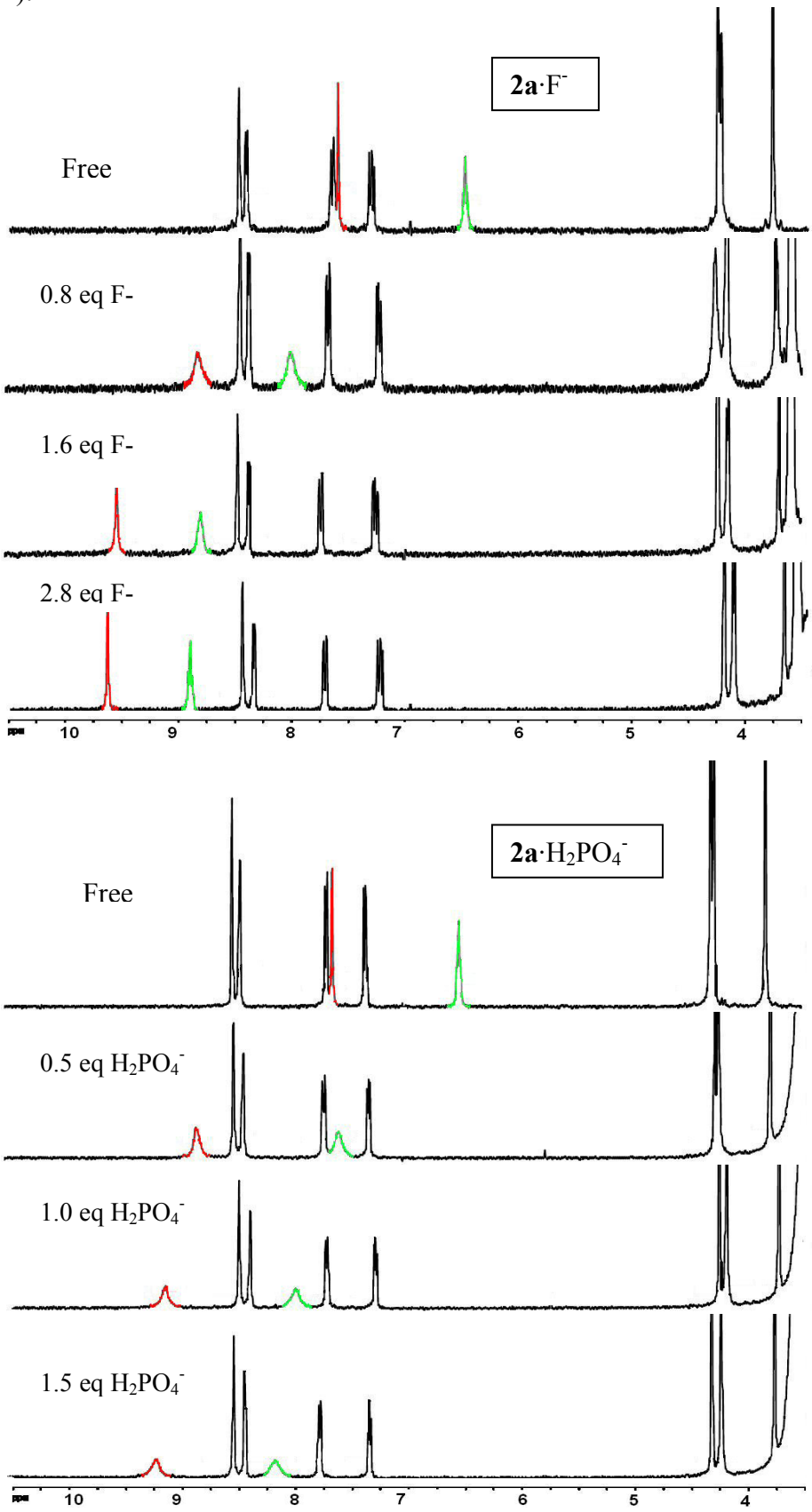


**Figure VI**: $^{1}$H-NMR spectral changes observed for the urea NH protons upon addition of increasing amounts of $F^-$ (c = 0.1 M) to the heteroditopic receptor **2b** (c = $5{:}10^{-3}$ M).

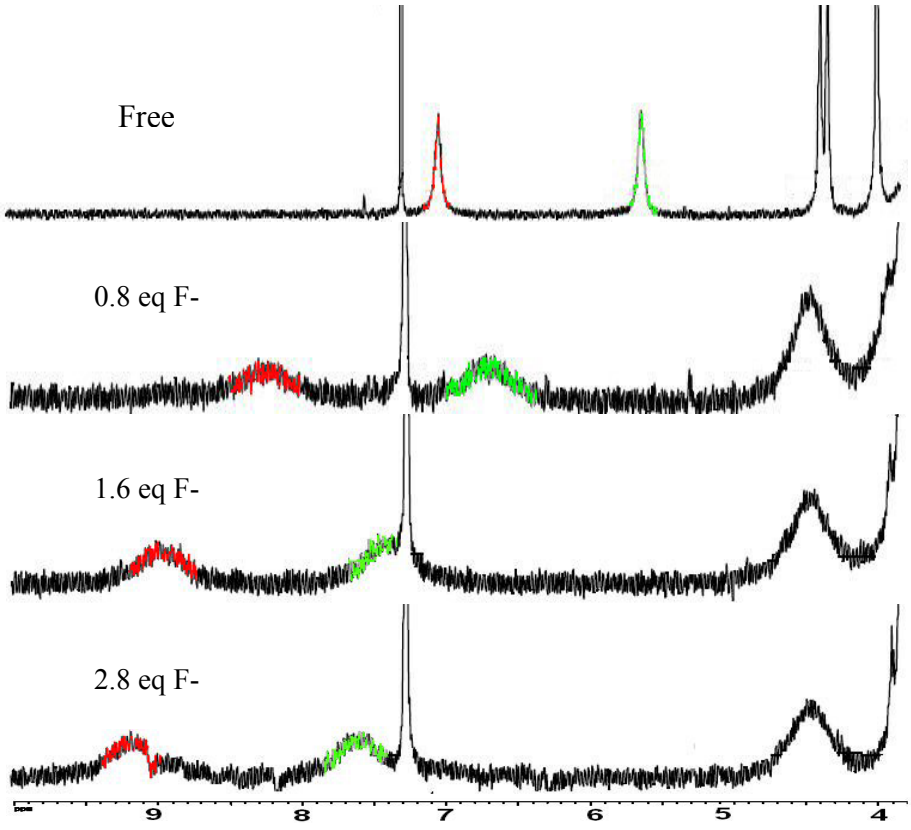


**Figure VII**: $^{1}$H-NMR spectral changes observed for the urea NH protons upon addition of increasing amounts of $K^+$ (c = 0.1 M) for the heteroditopic receptor **2b** (c = $5 \cdot 10^{-3}$M).

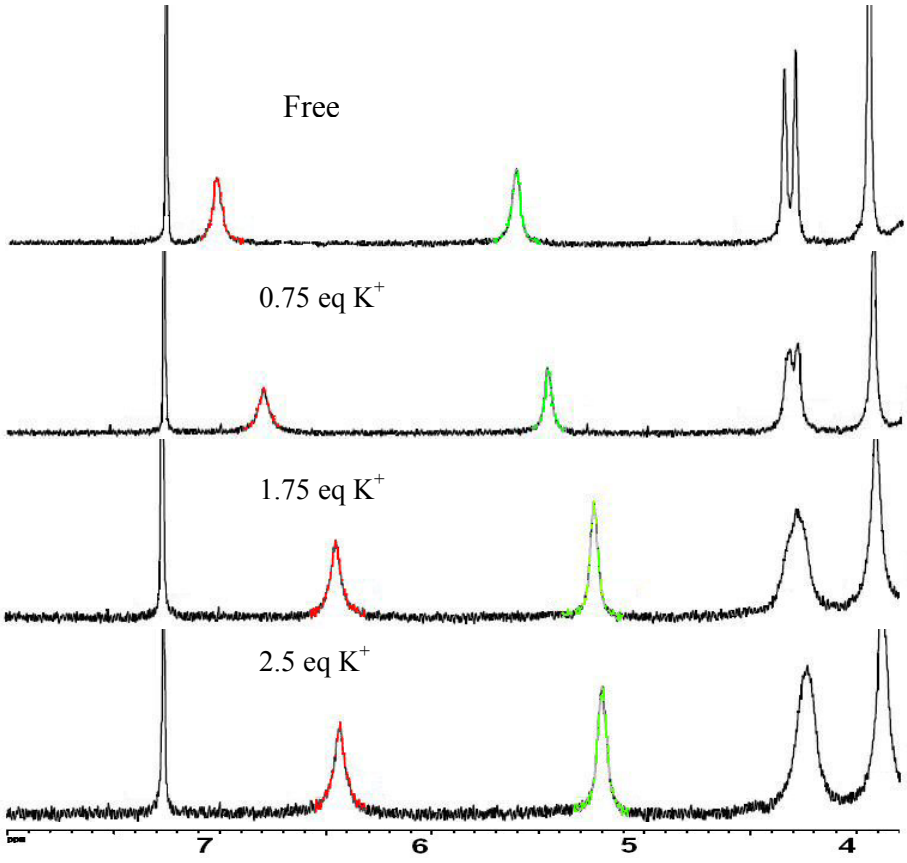


**Figure VIII**: $^{1}$H-NMR spectral changes observed for the urea NH protons upon addition of increasing amounts of $H_2PO_4^-$ anion (c = 0.1 M) to the heteroditopic receptor **2d** (c = $5 \cdot 10^{-3}$M).

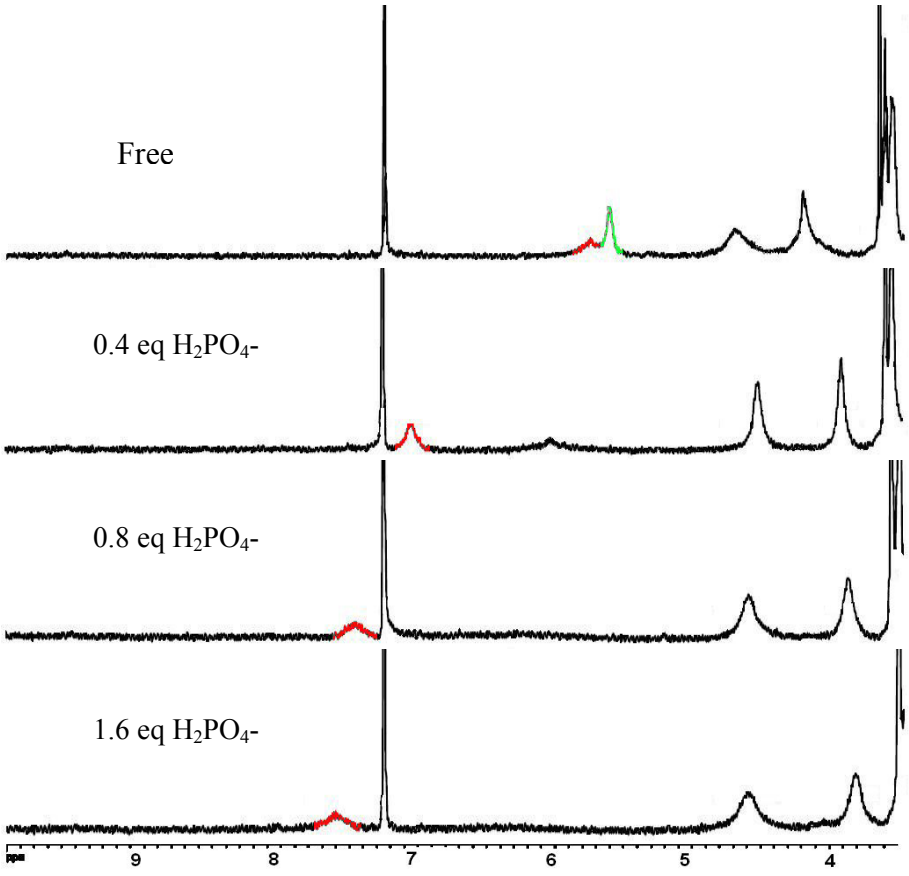


**Figure IX**: Binding profiles associated with the observed chemical shifts of the NH urea protons upon addition of increasing amounts of $F^-$, $H_2PO_4^-$ and $AcO^-$ (c = 0.1 M) to the heteroditopic receptors **2** (c = $5 \cdot 10^{-3}$ M).

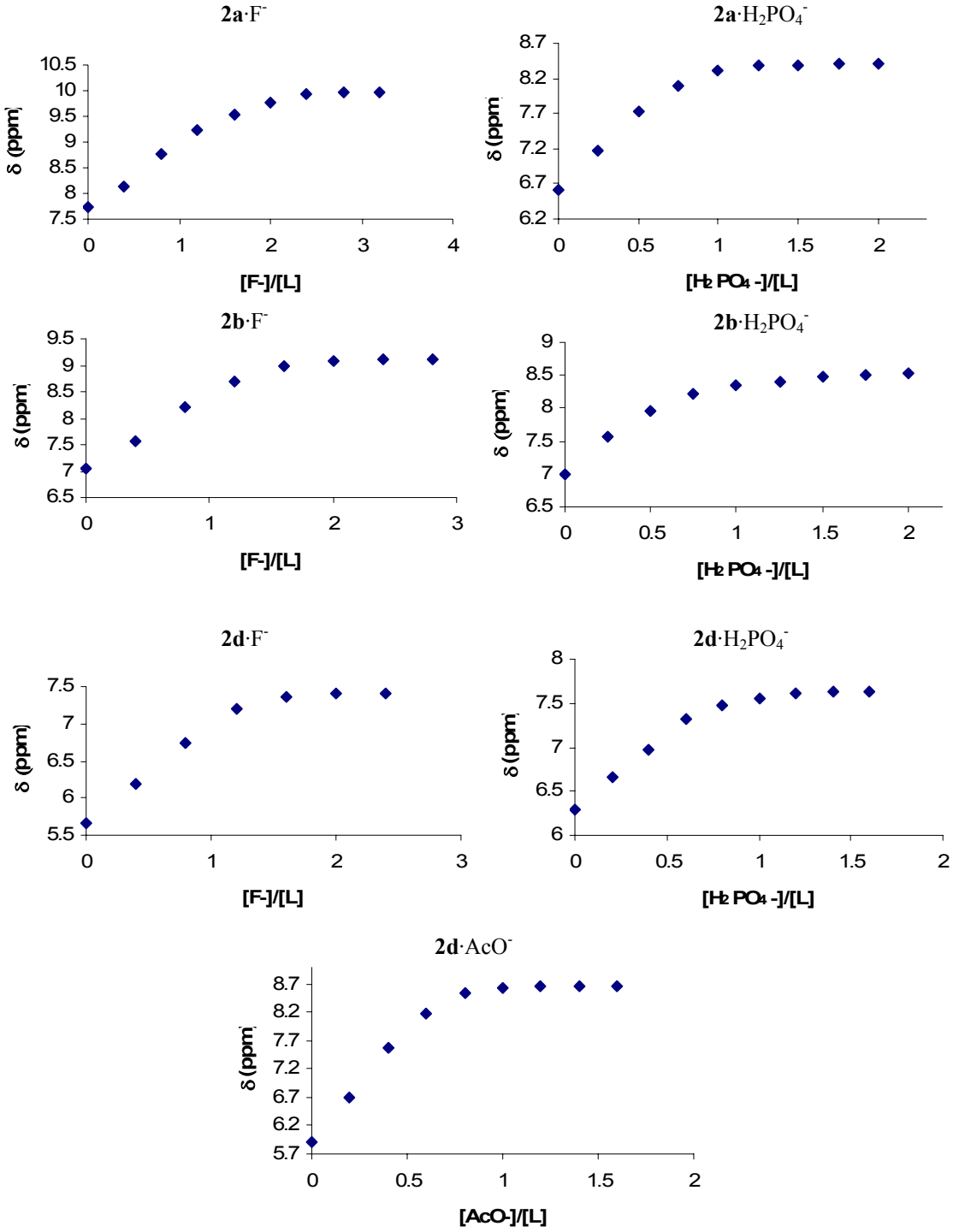


**Figure X**: Binding profiles associated with the observed chemical shifts of the NH urea protons upon addition of increasing amounts of $K^+$ (c = 0.1 M) to the heteroditopic receptor **2b** (c = $5 \cdot 10^{-3}$ M) and $H_2PO_4^-$ ( c = 0.1 M) to the complex [**2b**·$K^+$] (c = $5 \cdot 10^{-3}$ M).

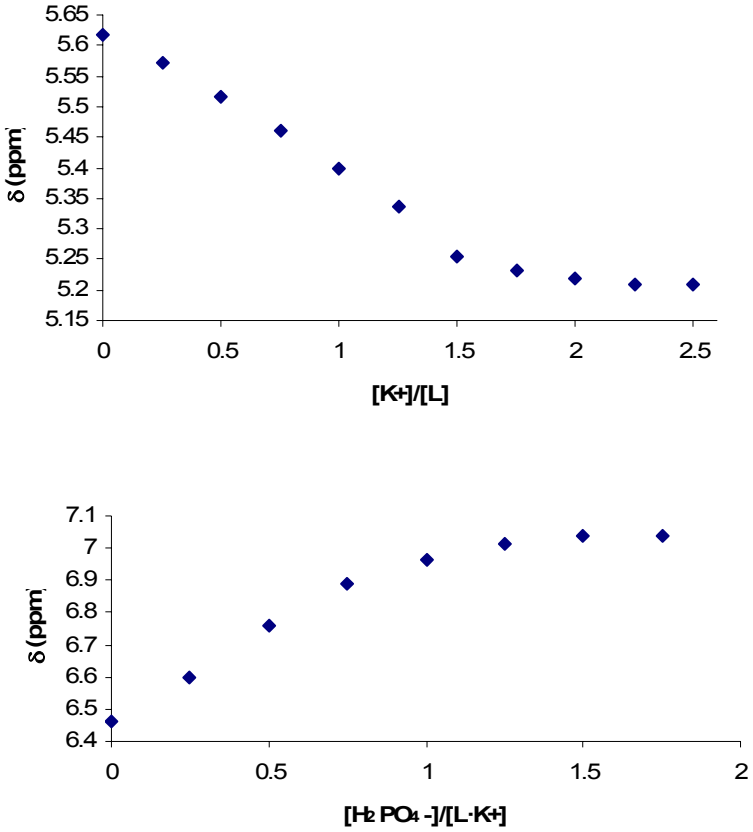



**Figure XI**: Binding profiles associated with the observed chemical shift of the NH urea protons upon addition of increasing amounts of $Li^+$ (c = 0.1 M) to the heteroditopic receptor **2d** (c = $5 \cdot 10^{-3}$ M).

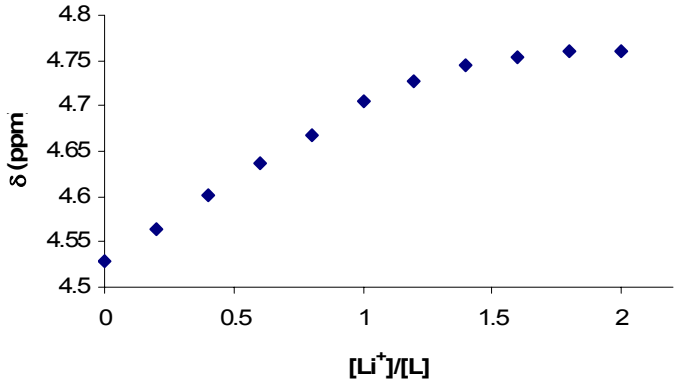


**Figure XII**: UV-vis-NIR spectra obtained for the free receptor **2a**; for the electrochemically oxidized **2a**$^{+}$ and for the complex [**2a**·$Cu^{2+}$].

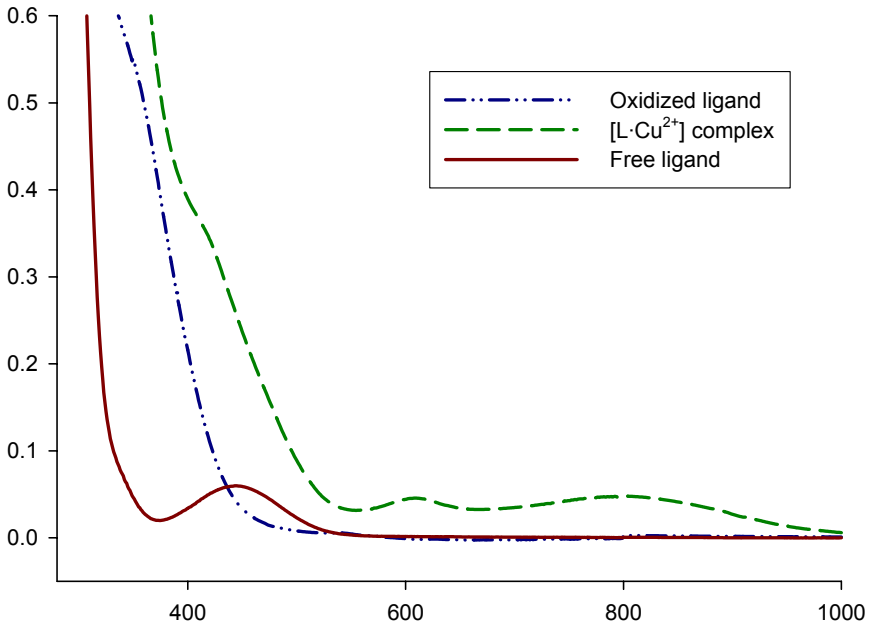
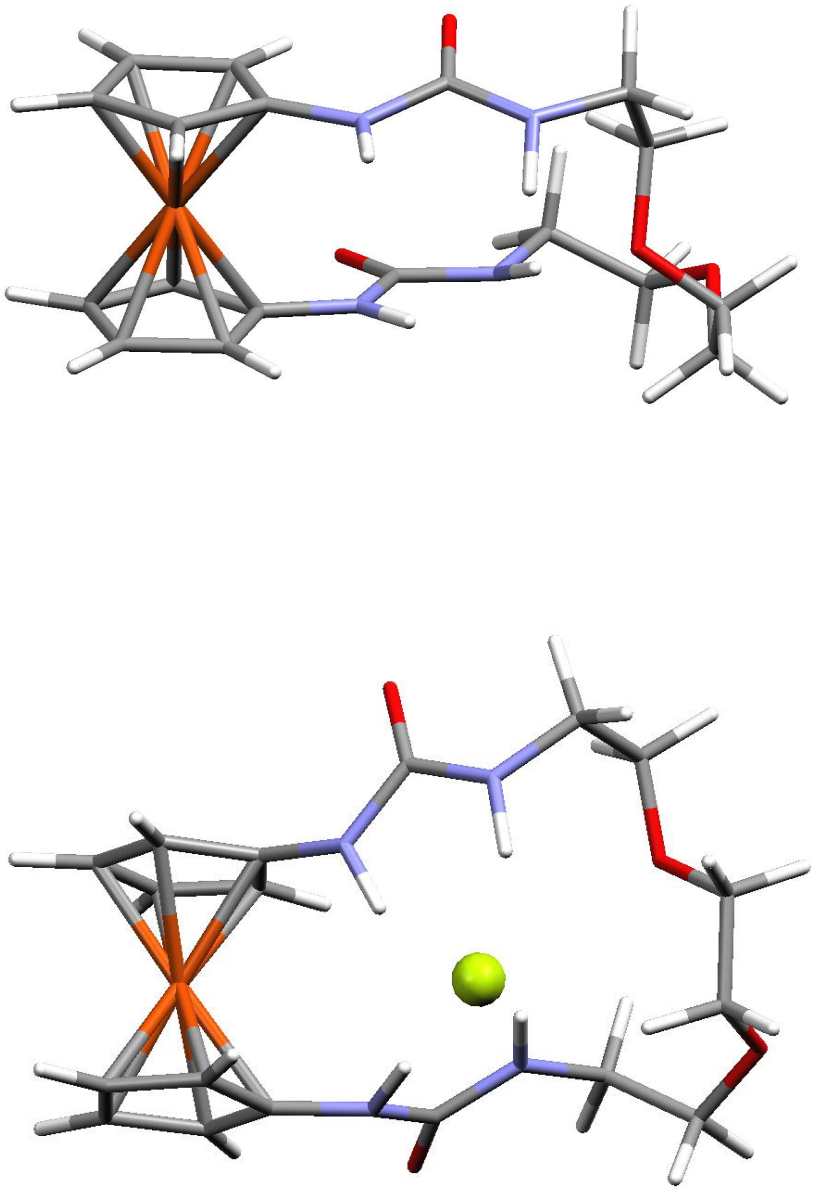
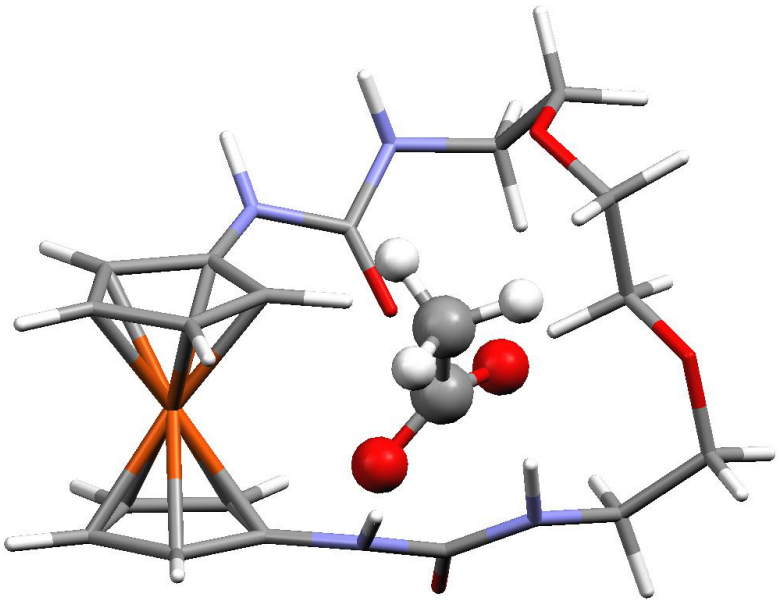


**Figure XIII**: Calculated (B3LYP/6-31G*) structures for compounds **2d**, **2d**·$F^-$, **2d**·$AcO^-$ and **2d**·$H_2PO_4^-$.





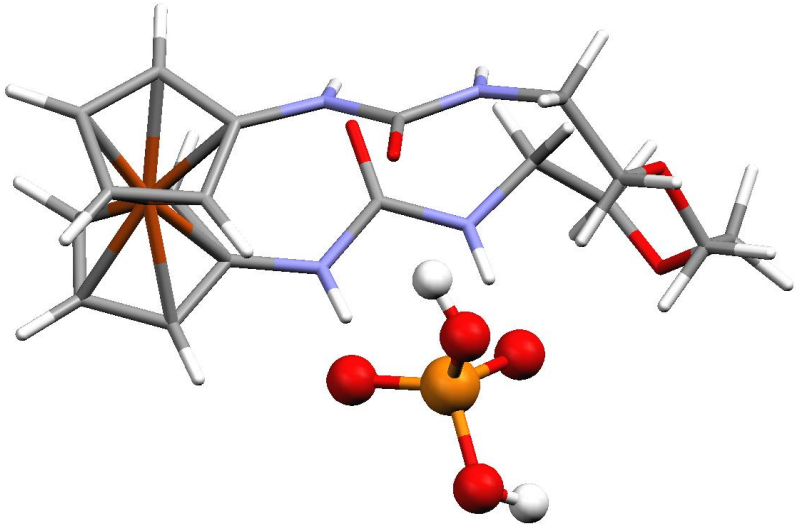
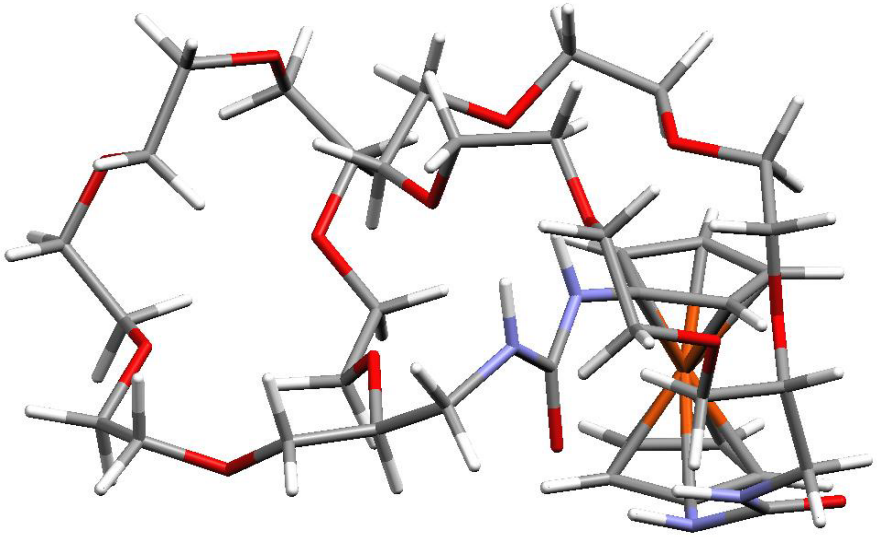
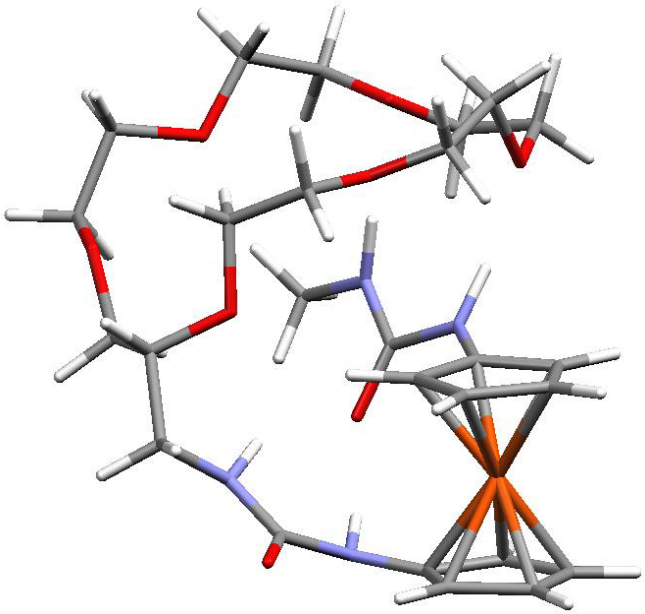


**Figure XIV**: Calculated (B3LYP/3-21G*) structures for compounds **2b**, and **3**.





Calculated energies (B3LYP/6-31G*) and Cartesian coordinates for compounds **2b**, **2b**·$KH_2PO_4$, **2d**, **2d**·$F^-$, **2d**·$AcO^-$, **2d**·$H_2PO_4^-$, **2d**·$Li^+$, **3** and **3**·$KH_2PO_4$.

Compound **2b** E = -4020.96532275 au

$G_{chloroform}$ = -4020.953080 au

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O | 4.598509 | 0.472223 | 2.879382 | C | -3.007952 | -1.447429 | 1.224183 |
| C | 5.792108 | 1.043873 | 2.250831 | C | -1.455569 | -4.948337 | -0.190404 |
| C | 6.071028 | 0.531877 | 0.837912 | C | -3.292419 | -2.471187 | 2.192255 |
| O | 6.905392 | -0.676657 | 1.003700 | C | -2.807304 | -5.192832 | 0.237882 |
| C | 7.318717 | -1.284439 | -0.257793 | C | -2.042170 | -3.036051 | 2.635452 |
| C | 6.135649 | -1.778776 | -1.093819 | C | -3.677292 | -4.284208 | -0.464354 |
| O | 5.498788 | -0.655229 | -1.799920 | C | -0.980708 | -2.371875 | 1.926378 |
| C | 5.835039 | -0.511623 | -3.213152 | C | -4.368550 | -1.645075 | -1.824112 |
| C | 4.962845 | 0.628781 | -3.729671 | Fe | -2.270372 | -3.260528 | 0.625019 |
| O | 3.580813 | 0.167327 | -3.725858 | H | -2.388850 | -1.811730 | -2.328925 |
| C | 2.594011 | 1.203319 | -3.419731 | N | -4.221736 | -0.312171 | -2.172066 |
| C | 1.431311 | 0.545035 | -2.682532 | N | -3.220875 | -2.383986 | -2.113402 |
| O | 1.884066 | 0.064750 | -1.381498 | O | -5.395965 | -2.107859 | -1.291592 |
| C | 2.462086 | -1.292219 | -1.410878 | H | -3.292570 | 0.019190 | -2.417106 |
| C | 2.365550 | -1.835515 | 0.002153 | C | -1.486236 | -3.880911 | -1.154368 |
| O | 3.497019 | -1.300949 | 0.776179 | O | 0.672695 | 1.097240 | 2.445706 |
| C | 3.304857 | -1.493242 | 2.214854 | C | 1.892821 | 1.928560 | 2.356840 |
| C | 4.561083 | -1.000445 | 2.924319 | C | 2.159892 | 2.280521 | 0.900752 |
| H | 6.688707 | 0.861615 | 2.857249 | O | 1.093928 | 3.067031 | 0.257732 |
| H | 5.134731 | 0.290711 | 0.334952 | C | 0.754878 | 4.353734 | 0.875431 |
| H | 6.626270 | 1.285674 | 0.260534 | C | -0.701116 | 4.294062 | 1.324960 |
| H | 7.917128 | -0.579597 | -0.855312 | O | -1.567692 | 4.118948 | 0.151771 |
| H | 7.950363 | -2.128281 | 0.036551 | C | -2.064538 | 5.363560 | -0.424896 |
| H | 6.450073 | -2.558807 | -1.799787 | C | -2.861253 | 4.963764 | -1.662832 |
| H | 5.367537 | -2.154044 | -0.414667 | O | -3.949796 | 4.073057 | -1.273608 |
| H | 6.895299 | -0.256715 | -3.356444 | C | -3.745708 | 2.683695 | -1.718335 |
| H | 5.607072 | -1.430138 | -3.768277 | C | -4.792433 | 1.826636 | -0.989100 |
| H | 5.091797 | 1.483789 | -3.053209 | O | -4.283448 | 1.290211 | 0.272512 |
| H | 5.284729 | 0.921256 | -4.739156 | C | -4.016946 | 2.343575 | 1.270967 |
| H | 3.027982 | 1.956287 | -2.748047 | C | -3.512409 | 1.681788 | 2.552665 |
| H | 2.243718 | 1.700119 | -4.336807 | O | -2.039780 | 1.662393 | 2.532518 |
| H | 1.863308 | -1.921100 | -2.082458 | C | -1.466547 | 0.816849 | 3.581004 |
| H | 3.493516 | -1.234110 | -1.745957 | C | -0.009777 | 1.236397 | 3.736823 |
| H | 1.414026 | -1.505434 | 0.429507 | H | 1.741678 | 2.837743 | 2.955874 |
| H | 2.403106 | -2.935005 | -0.000866 | H | 2.230744 | 1.383555 | 0.279698 |
| H | 2.419729 | -0.935709 | 2.549825 | H | 3.111464 | 2.830284 | 0.856427 |
| H | 3.161474 | -2.560682 | 2.447043 | H | 0.897006 | 5.136659 | 0.121810 |
| H | 5.441768 | -1.406301 | 2.422511 | H | 1.404261 | 4.570657 | 1.731624 |
| H | 4.539168 | -1.314805 | 3.974832 | H | -0.972235 | 5.199158 | 1.887547 |
| H | 5.588475 | 2.118349 | 2.226031 | H | -0.886126 | 3.399963 | 1.922756 |
| H | 1.034298 | -0.297390 | -3.256412 | H | -1.246619 | 6.040325 | -0.714179 |
| C | -2.863679 | -3.491731 | -1.341950 | H | -2.718778 | 5.880461 | 0.289395 |
| C | -1.579561 | -1.381284 | 1.052015 | H | -2.184920 | 4.478060 | -2.376227 |

| | | | |
|---|---|---|---|
| H | -3.290138 | 5.857817 | -2.131253 |
| H | -2.741706 | 2.332428 | -1.458485 |
| H | -3.897712 | 2.621785 | -2.806478 |
| H | -4.952768 | 2.882677 | 1.480003 |
| H | -3.270135 | 3.046553 | 0.898057 |
| H | -3.913098 | 0.665644 | 2.611359 |
| H | -3.852290 | 2.253781 | 3.429227 |
| H | -1.544947 | -0.237756 | 3.307022 |
| H | -1.970952 | 0.977460 | 4.546729 |
| H | 0.019628 | 2.288300 | 4.050904 |
| H | 0.475606 | 0.624408 | 4.508376 |
| H | 2.769406 | 1.390476 | 2.732886 |
| H | -0.650053 | -3.442149 | -1.668524 |
| H | -0.581290 | -5.495203 | 0.119685 |
| H | -3.123638 | -5.953791 | 0.931093 |
| H | -4.743628 | -4.199343 | -0.388715 |
| C | -5.279185 | 0.637833 | -1.835263 |
| H | -5.759304 | 1.043279 | -2.737105 |
| H | -6.018579 | 0.063736 | -1.271942 |
| H | -5.655613 | 2.485970 | -0.807086 |
| N | -0.857668 | -0.331878 | 0.424180 |
| H | -0.418752 | 0.326139 | 1.083853 |
| C | -0.834599 | 0.009829 | -0.905243 |
| N | -0.416003 | 1.294100 | -1.151665 |
| H | -0.142607 | 1.930746 | -0.393310 |
| C | 0.290870 | 1.574950 | -2.405187 |
| H | 0.720668 | 2.570598 | -2.265574 |
| H | -0.388995 | 1.584202 | -3.261790 |
| O | -1.127457 | -0.749948 | -1.876952 |
| H | -4.273423 | -2.756715 | 2.533966 |
| H | -1.922964 | -3.806777 | 3.378778 |
| H | 0.075041 | -2.531871 | 2.059904 |
| H | -3.700789 | -0.764178 | 0.763405 |

Compound **2b**·$KH_2PO_4$ E = -5264.55587944 au

$G_{chloroform}$ = -5264.566840 au

| | | | |
|---|---|---|---|
| C | 0.000000 | 0.000000 | 0.000000 |
| C | 1.439558 | 0.000000 | 0.000000 |
| C | 1.875036 | 1.376456 | 0.000000 |
| C | 0.705980 | 2.218507 | -0.018189 |
| C | -0.452937 | 1.368397 | -0.039220 |
| H | 2.047755 | -0.882530 | 0.030053 |
| H | 2.897129 | 1.711523 | 0.055400 |
| H | 0.697697 | 3.295149 | 0.006429 |
| H | -1.494191 | 1.639865 | -0.067968 |
| Fe | 0.748820 | 0.991412 | -1.650320 |
| C | 0.403910 | -0.271152 | -3.198255 |
| C | -0.512631 | 0.838949 | -3.249215 |
| C | 0.270994 | 2.041127 | -3.340352 |
| C | 1.666159 | 1.681944 | -3.335485 |
| C | 1.753213 | 0.249613 | -3.255715 |
| H | -1.586334 | 0.773124 | -3.215854 |
| H | -0.125319 | 3.038719 | -3.424341 |
| H | 2.497003 | 2.361275 | -3.425223 |
| H | 2.652466 | -0.342775 | -3.269099 |
| N | -0.899840 | -1.064152 | -0.014691 |
| N | 0.118530 | -1.657516 | -3.121121 |
| H | -1.911350 | -0.742505 | -0.058546 |
| H | 0.582237 | -2.177733 | -2.353196 |
| C | -0.560100 | -2.345758 | -0.343227 |
| C | -0.869521 | -2.275083 | -3.837157 |
| O | 0.641564 | -2.725788 | -0.560612 |
| O | -1.848694 | -1.705197 | -4.392726 |
| N | -1.634936 | -3.195805 | -0.486241 |
| N | -0.704061 | -3.652260 | -3.955516 |
| H | -2.559649 | -2.794928 | -0.807447 |
| H | 0.197427 | -4.037005 | -3.693797 |
| C | -1.370862 | -4.590495 | -0.826422 |
| H | -0.354282 | -4.672996 | -1.219958 |
| H | -2.083477 | -4.929278 | -1.574681 |
| C | -1.545868 | -4.389651 | -4.899990 |
| H | -2.317440 | -3.682042 | -5.205503 |
| H | -0.970958 | -4.660664 | -5.799340 |
| P | -3.959844 | -0.676083 | -1.637309 |
| O | -3.259859 | 0.055785 | -0.502449 |
| O | -3.842838 | -2.198825 | -1.629076 |
| O | -3.527502 | -0.131119 | -3.087014 |
| H | -2.932623 | -0.755395 | -3.635809 |
| O | -5.534515 | -0.263636 | -1.573246 |
| H | -5.673233 | 0.408960 | -0.857482 |
| H | -0.639757 | -5.140458 | 1.106154 |
| C | -1.448510 | -5.459575 | 0.433532 |
| C | -2.761391 | -5.325955 | 1.194930 |
| O | -1.223283 | -6.866645 | 0.027561 |
| O | -3.848483 | -5.944929 | 0.411499 |
| H | -2.696018 | -5.841668 | 2.162213 |
| H | -2.951175 | -4.260560 | 1.356877 |
| K | -3.389883 | -7.861285 | -1.498960 |
| C | -0.588747 | -7.631954 | 1.105448 |
| C | -5.043414 | -6.186227 | 1.222908 |

| | | | |
|---|---|---|---|
| O | -5.266353 | -9.923644 | -2.264184 |
| C | -0.436017 | -9.082338 | 0.698023 |
| H | -1.208300 | -7.596442 | 2.013007 |
| H | 0.398360 | -7.207896 | 1.326984 |
| C | -5.690597 | -7.494699 | 0.794648 |
| H | -4.756657 | -6.285110 | 2.276943 |
| H | -5.753412 | -5.356554 | 1.121652 |
| C | -4.659123 | -11.268060 | -2.268495 |
| C | -6.338711 | -9.803753 | -3.263901 |
| O | 0.537519 | -9.148101 | -0.413040 |
| H | -1.390717 | -9.525637 | 0.409970 |
| H | -0.053155 | -9.644700 | 1.556850 |
| O | -4.691392 | -8.553200 | 1.034926 |
| H | -6.571955 | -7.668498 | 1.431787 |
| H | -6.015733 | -7.505004 | -0.250773 |
| C | -3.559488 | -11.367781 | -3.313046 |
| H | -4.215899 | -11.373876 | -1.277757 |
| H | -5.429545 | -12.031697 | -2.440664 |
| C | -6.768354 | -8.356717 | -3.362948 |
| H | -7.192812 | -10.424064 | -2.966094 |
| H | -5.979200 | -10.130835 | -4.248969 |
| C | 1.459004 | -10.277267 | -0.318824 |
| C | -5.315428 | -9.879911 | 1.040498 |
| O | -2.453733 | -10.540964 | -2.815280 |
| H | -3.242132 | -12.414326 | -3.426339 |
| H | -3.897564 | -10.992199 | -4.287724 |
| O | -7.487240 | -8.012917 | -2.129056 |
| H | -7.446112 | -8.257019 | -4.225470 |
| H | -5.915194 | -7.693762 | -3.508101 |
| C | 0.783706 | -11.581703 | -0.726113 |
| H | 1.847853 | -10.374170 | 0.703682 |
| H | 2.285626 | -10.051341 | -0.998736 |
| C | -4.299034 | -10.883840 | 1.559665 |
| H | -6.178653 | -9.879890 | 1.723516 |
| H | -5.648111 | -10.134590 | 0.030235 |
| C | -1.397589 | -10.328113 | -3.813875 |
| C | -8.153314 | -6.709537 | -2.246428 |
| O | -0.246519 | -11.853691 | 0.273707 |
| H | 0.332062 | -11.447990 | -1.716208 |
| H | 1.514564 | -12.401518 | -0.775440 |
| O | -3.257696 | -11.104683 | 0.543515 |
| H | -3.849463 | -10.506321 | 2.485125 |
| H | -4.819172 | -11.829911 | 1.770258 |
| C | -0.694852 | -9.030104 | -3.465330 |
| H | -1.842294 | -10.223988 | -4.810853 |
| H | -0.692508 | -11.169851 | -3.811576 |
| C | -7.239649 | -5.567706 | -1.810323 |
| H | -9.035336 | -6.748548 | -1.599693 |
| H | -8.477465 | -6.550793 | -3.283881 |
| C | -1.439717 | -12.494996 | -0.277299 |
| C | -2.535986 | -12.370110 | 0.774495 |
| O | -1.691382 | -7.974260 | -3.708713 |
| H | -0.352358 | -9.018295 | -2.423795 |
| H | 0.163479 | -8.896166 | -4.140984 |
| O | -5.983618 | -5.702176 | -2.533521 |
| H | -7.076655 | -5.611887 | -0.725708 |
| H | -7.724238 | -4.606118 | -2.036494 |
| H | -1.247842 | -13.556388 | -0.492945 |
| H | -1.758093 | -11.971764 | -1.186245 |
| H | -2.070260 | -12.382743 | 1.766697 |
| H | -3.243578 | -13.207638 | 0.697084 |
| C | -1.081085 | -6.652373 | -3.882062 |
| C | -5.106657 | -4.525731 | -2.324171 |
| C | -2.166681 | -5.700693 | -4.371480 |
| H | -0.671069 | -6.294925 | -2.932945 |
| H | -0.282778 | -6.716551 | -4.636692 |
| C | -4.111477 | -4.475816 | -3.458548 |
| H | -4.600685 | -4.612073 | -1.362808 |
| H | -5.688569 | -3.600539 | -2.338551 |
| O | -3.115490 | -5.562077 | -3.263498 |
| H | -2.675736 | -6.176827 | -5.224192 |
| H | -3.623568 | -3.503488 | -3.402129 |
| H | -4.628008 | -4.622632 | -4.415974 |

Compound **2d** E = -2483.90482239 au

$G_{DMSO}$ = -2483.918037 au

| | | | |
|---|---|---|---|
| C | 2.498449 | 3.113295 | -0.067178 |
| C | -2.178383 | 1.636573 | -0.294992 |
| C | -1.386845 | -1.526374 | 0.792470 |
| C | -2.109611 | -0.960985 | 1.887289 |
| C | -3.620539 | 0.453251 | -1.646600 |
| C | -3.482162 | -1.346657 | 1.758694 |
| C | -4.376809 | 0.976486 | -0.557366 |
| C | -3.602472 | -2.131224 | 0.575110 |
| C | -3.482455 | 1.703169 | 0.288775 |
| C | -2.313215 | -2.230852 | -0.035055 |
| C | 3.005279 | -1.917518 | -1.396211 |
| C | 0.762478 | -1.941122 | -0.388834 |
| C | 0.160582 | 2.467142 | -0.385066 |
| Fe | -2.908416 | -0.260731 | 0.131850 |

| | | | |
|---|---|---|---|
| H | -2.055275 | -2.750206 | -0.943755 |
| H | -1.165041 | 2.668646 | 1.174139 |
| H | 0.456773 | -0.752992 | 1.270364 |
| H | -4.514213 | -2.567719 | 0.188497 |
| H | -4.279788 | -1.083724 | 2.441030 |
| H | 2.313586 | -0.701810 | 0.171512 |
| H | -1.684317 | -0.359145 | 2.681898 |
| H | 2.449048 | 3.638465 | -1.024959 |
| H | 2.644027 | -2.848544 | -1.841016 |
| N | -0.003736 | -1.378081 | 0.623618 |
| N | 2.090637 | -1.561936 | -0.321953 |
| N | 1.140774 | 2.993313 | 0.455711 |
| N | -1.037277 | 2.237891 | 0.268860 |
| O | 0.348975 | 2.254527 | -1.575897 |
| O | 0.319406 | -2.724347 | -1.220110 |
| H | 1.105389 | 2.676776 | 1.417322 |
| H | 3.007554 | -1.153523 | -2.188089 |
| C | -2.255971 | 0.847133 | -1.479228 |
| C | 3.195976 | 1.769983 | -0.275470 |
| H | 4.222559 | 1.918644 | -0.627650 |
| H | 2.655139 | 1.197082 | -1.033457 |
| C | 4.428955 | -2.098521 | -0.876452 |
| H | 5.091086 | -2.345736 | -1.714411 |
| H | 4.471240 | -2.923039 | -0.152297 |
| O | 4.937912 | -0.894587 | -0.296190 |
| O | 3.189058 | 1.022513 | 0.956164 |
| C | 4.461735 | 0.645290 | 1.482687 |
| H | 5.236508 | 1.339065 | 1.131075 |
| H | 4.402690 | 0.729258 | 2.575533 |
| C | 4.834811 | -0.785307 | 1.115003 |
| H | 5.795868 | -1.038135 | 1.593783 |
| H | 4.074799 | -1.471725 | 1.508673 |
| H | 3.066278 | 3.734037 | 0.634616 |
| H | -3.743300 | 2.223725 | 1.202306 |
| H | -5.438238 | 0.847072 | -0.391238 |
| H | -4.002250 | -0.152427 | -2.457813 |
| H | -1.425714 | 0.609219 | -2.125018 |

Compound **2d**·$F^-$ E = -2583.84572074 au

$G_{DMSO}$ = -2583.904572 au

| | | | |
|---|---|---|---|
| C | -1.639198 | 1.589950 | -0.227274 |
| C | -1.816532 | 0.915702 | -1.475883 |
| C | -3.202549 | 0.952993 | -1.812117 |
| C | -3.890495 | 1.652845 | -0.771041 |
| C | -2.927235 | 2.044483 | 0.205018 |
| H | -1.025939 | 0.435941 | -2.037460 |
| H | -3.656553 | 0.514498 | -2.692142 |
| H | -4.956249 | 1.842712 | -0.729233 |
| H | -3.113793 | 2.583496 | 1.124762 |
| C | -1.903223 | -1.659433 | 0.753639 |
| C | -2.603795 | -0.945051 | 1.776884 |
| C | -3.997269 | -0.936666 | 1.448525 |
| C | -4.153208 | -1.622042 | 0.205942 |
| C | -2.860041 | -2.052155 | -0.232395 |
| H | -2.141792 | -0.488993 | 2.643446 |
| H | -4.785433 | -0.486048 | 2.038643 |
| H | -5.085020 | -1.788485 | -0.320611 |
| H | -2.614748 | -2.590339 | -1.134830 |
| Fe | -2.939874 | 0.003143 | -0.015205 |
| N | -0.428701 | 1.745503 | 0.485691 |
| N | -0.525275 | -1.850746 | 0.758789 |
| H | -0.038867 | 0.942298 | 1.001229 |
| H | 0.024000 | -1.214588 | 1.365174 |
| C | 0.537895 | 2.656547 | 0.089481 |
| C | 0.198281 | -2.291898 | -0.355645 |
| O | 0.371925 | 3.538352 | -0.754891 |
| O | -0.232739 | -3.097826 | -1.185609 |
| N | 1.713993 | 2.478814 | 0.803184 |
| N | 1.443857 | -1.726603 | -0.383016 |
| H | 1.779244 | 1.556338 | 1.257500 |
| H | 1.591883 | -0.946671 | 0.276880 |
| C | 2.940084 | 3.043699 | 0.290843 |
| H | 2.716686 | 4.026429 | -0.136730 |
| H | 3.634507 | 3.197254 | 1.127778 |
| C | 3.593964 | 2.180307 | -0.803885 |
| H | 2.966124 | 2.214787 | -1.699235 |
| H | 4.590854 | 2.583512 | -1.062416 |
| O | 3.682012 | 0.802595 | -0.470976 |
| C | 4.615532 | 0.469908 | 0.536550 |
| H | 4.493174 | 1.101102 | 1.430849 |
| H | 5.646316 | 0.607790 | 0.164039 |
| C | 4.393812 | -0.977288 | 0.949991 |
| H | 3.364377 | -1.081553 | 1.308350 |
| H | 5.070667 | -1.203367 | 1.791199 |
| O | 4.703547 | -1.850927 | -0.130709 |
| C | 3.709072 | -2.788573 | -0.526874 |
| H | 3.362511 | -3.384725 | 0.332451 |
| H | 4.240209 | -3.461990 | -1.212031 |
| C | 2.489757 | -2.198185 | -1.259406 |
| H | 2.041661 | -2.976364 | -1.886372 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 2.846587 | -1.390918 | -1.911642 | F | 1.216900 | -0.061226 | 1.698506 |

Compound **2d**·$AcO^-$ E = -2712.45790746 au

$G_{DMSO}$ = -2712.523958 au

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 0.000000 | 0.000000 | 0.000000 | N | 1.261315 | -0.527139 | -0.507558 |
| C | 4.823996 | 0.000000 | 0.000000 | N | 3.586638 | -0.406037 | -0.575704 |
| C | 5.570999 | 3.654914 | 0.000000 | O | 2.331201 | 1.498534 | -0.262329 |
| C | 6.984652 | 3.444171 | 0.047122 | O | 3.151934 | 5.140315 | -0.255735 |
| C | 7.093154 | -0.012629 | 0.432965 | H | 1.420441 | -1.497450 | -0.259031 |
| C | 7.390923 | 2.836982 | -1.183409 | H | 0.972099 | 4.591717 | 0.844149 |
| C | 6.431900 | 0.640314 | 1.519568 | C | 6.098681 | -0.397543 | -0.520662 |
| C | 6.222894 | 2.661304 | -1.989110 | H | 6.261356 | -0.912341 | -1.459984 |
| C | 5.030137 | 0.644110 | 1.259782 | C | -0.263967 | -0.390697 | 1.465285 |
| C | 5.099621 | 3.143435 | -1.250406 | H | -0.391233 | -1.485085 | 1.520481 |
| C | 1.361292 | 5.072617 | 1.752174 | H | -1.212270 | 0.058400 | 1.801934 |
| C | 3.540621 | 4.698849 | 0.829146 | C | 0.470217 | 4.746321 | 2.948565 |
| C | 2.398393 | 0.287803 | -0.408320 | H | -0.565537 | 5.022863 | 2.672243 |
| Fe | 6.064222 | 1.628855 | -0.229302 | H | 0.758900 | 5.351566 | 3.815536 |
| H | 4.064516 | 3.134168 | -1.552418 | O | 0.515258 | 3.409006 | 3.415608 |
| H | 3.502570 | -1.409318 | -0.683765 | O | 0.809425 | -0.058601 | 2.318380 |
| H | 5.089663 | 3.900388 | 2.000962 | C | 0.639528 | 1.077851 | 3.168813 |
| H | 6.190852 | 2.232534 | -2.983282 | H | -0.206908 | 0.910905 | 3.855949 |
| H | 6.892847 | 1.120411 | 2.372439 | H | 1.563944 | 1.160180 | 3.745561 |
| H | 8.404051 | 2.563427 | -1.452567 | C | 0.459144 | 2.399248 | 2.422214 |
| H | 2.969236 | 3.996143 | 2.678131 | H | 1.263006 | 2.497552 | 1.687457 |
| H | 0.053950 | 1.084086 | -0.110995 | H | -0.509144 | 2.437828 | 1.886400 |
| H | 8.160804 | -0.161794 | 0.329369 | C | 5.134307 | 1.777103 | 5.372502 |
| H | 7.616480 | 3.687676 | 0.891189 | H | 5.261627 | 0.729547 | 5.068484 |
| H | -0.830562 | -0.368631 | -0.620001 | H | 4.331399 | 1.808215 | 6.116522 |
| H | 1.272350 | 6.153962 | 1.568700 | H | 6.074392 | 2.120765 | 5.815283 |
| H | 4.267958 | 1.095525 | 1.882276 | C | 4.762264 | 2.620011 | 4.135631 |
| N | 4.815049 | 4.192907 | 1.040694 | O | 3.546106 | 2.602953 | 3.790552 |
| N | 2.750710 | 4.708713 | 1.960211 | O | 5.706295 | 3.222841 | 3.552251 |

Compound **2d**·$H_2PO_4^-$ E = -3127.56937981 au

$G_{DMSO}$ = -3127.635402 au

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 2.432484 | -1.241299 | 2.664298 | C | -2.913536 | 2.187711 | -0.551100 |
| C | -2.301707 | -0.499357 | 1.545085 | C | 2.441100 | 2.400468 | 0.445937 |
| C | -2.019137 | 1.274640 | -1.193715 | C | 0.166641 | 1.896441 | -0.261663 |
| C | -2.804417 | 0.363354 | -1.970766 | C | 0.060408 | -1.013924 | 2.011461 |
| C | -4.613147 | -0.478388 | 1.456735 | Fe | -3.398487 | 0.258843 | -0.012316 |
| C | -4.177642 | 0.734640 | -1.837948 | H | -2.612990 | 2.972232 | 0.124532 |
| C | -4.141497 | -1.540819 | 0.623890 | H | -0.779781 | 0.870104 | 1.841275 |
| C | -4.246308 | 1.858532 | -0.959265 | H | -0.248152 | 0.358171 | -1.607171 |
| C | -2.714087 | -1.547485 | 0.667415 | H | -5.145758 | 2.376773 | -0.649965 |

| | | | |
|---|---|---|---|
| H | -4.756046 | -2.214459 | 0.040356 |
| H | -5.015673 | 0.238830 | -2.311957 |
| H | 1.849859 | 0.916412 | -0.978107 |
| H | 2.936473 | -0.822951 | 3.545781 |
| H | -5.648007 | -0.208450 | 1.627007 |
| H | -2.389661 | -0.469999 | -2.521472 |
| H | 2.074929 | -2.242611 | 2.916676 |
| H | 1.892424 | 3.207768 | 0.939677 |
| H | -2.048352 | -2.188727 | 0.110315 |
| N | -0.623674 | 1.212974 | -1.160495 |
| N | 1.512966 | 1.736949 | -0.450625 |
| N | 1.252134 | -0.439115 | 2.386917 |
| N | -0.985172 | -0.126384 | 1.894251 |
| O | -0.057510 | -2.237145 | 1.851270 |
| O | -0.300981 | 2.625838 | 0.638922 |
| H | 1.347720 | 0.565819 | 2.354166 |
| H | 2.815630 | 1.713134 | 1.213927 |
| C | -3.474786 | 0.164240 | 2.032716 |
| H | -3.480896 | 1.009985 | 2.708606 |
| C | 3.436374 | -1.361955 | 1.523672 |
| H | 2.932866 | -1.665920 | 0.601798 |
| H | 4.178662 | -2.136742 | 1.792528 |
| C | 3.641273 | 2.999316 | -0.283601 |
| H | 4.235165 | 3.587612 | 0.439361 |
| H | 3.289971 | 3.676251 | -1.070388 |
| O | 4.476422 | 2.062438 | -0.946261 |
| O | 4.094956 | -0.111285 | 1.340422 |
| C | 4.920111 | -0.103765 | 0.181350 |
| H | 5.816078 | -0.726149 | 0.368482 |
| H | 4.372623 | -0.513780 | -0.676468 |
| C | 5.380841 | 1.312770 | -0.148521 |
| H | 5.628373 | 1.850603 | 0.781195 |
| H | 6.302346 | 1.231034 | -0.742038 |
| P | 1.227832 | -1.883109 | -1.788685 |
| O | 2.292983 | -0.820309 | -1.555442 |
| O | -0.194372 | -1.413382 | -2.005488 |
| O | 1.752048 | -2.802701 | -3.054853 |
| H | 2.563230 | -2.365021 | -3.355956 |
| O | 1.262073 | -3.033431 | -0.624384 |
| H | 0.695611 | -2.785085 | 0.138635 |

Compound **2d**·$Li^+$ E = -2491.37997253 au
$G_{DMSO}$ = -2491.447737 au

| | | | |
|---|---|---|---|
| Li | 0.000000 | 0.000000 | -2.098746 |
| Fe | 0.000000 | 0.000000 | 2.822831 |
| C | 0.604799 | 1.749201 | 1.916483 |
| C | -0.604799 | -1.749201 | 1.916483 |
| C | 0.358707 | 1.959347 | 3.309003 |
| C | -0.358707 | -1.959347 | 3.309003 |
| C | 1.231199 | 1.098552 | 4.039135 |
| C | -1.231199 | -1.098552 | 4.039135 |
| C | 1.999446 | 0.353101 | 3.098637 |
| C | -1.999446 | -0.353101 | 3.098637 |
| C | 1.615697 | 0.749077 | 1.781228 |
| C | -1.615697 | -0.749077 | 1.781228 |
| H | -0.354883 | 2.656634 | 3.730692 |
| H | 0.354883 | -2.656634 | 3.730692 |
| H | 1.287578 | 1.023730 | 5.116679 |
| H | -1.287578 | -1.023730 | 5.116679 |
| H | 2.747513 | -0.391338 | 3.337424 |
| H | -2.747513 | 0.391338 | 3.337424 |
| H | 2.010254 | 0.375057 | 0.850039 |
| H | -2.010254 | -0.375057 | 0.850039 |
| N | -0.022570 | 2.525487 | 0.915293 |
| N | 0.022570 | -2.525487 | 0.915293 |
| H | -0.534102 | 3.326866 | 1.259008 |
| H | 0.534102 | -3.326866 | 1.259008 |
| C | 0.000000 | 2.303337 | -0.429099 |
| C | 0.000000 | -2.303337 | -0.429099 |
| O | 0.661529 | 1.389701 | -0.954021 |
| O | -0.661529 | -1.389701 | -0.954021 |
| N | -0.770481 | 3.159729 | -1.182247 |
| N | 0.770481 | -3.159729 | -1.182247 |
| H | -1.259128 | 3.898583 | -0.694814 |
| H | 1.259128 | -3.898583 | -0.694814 |
| C | -0.470925 | 3.426929 | -2.590255 |
| C | 0.470925 | -3.426929 | -2.590255 |
| H | 0.612656 | 3.409970 | -2.751167 |
| H | -0.612656 | -3.409970 | -2.751167 |
| H | -0.823598 | 4.441632 | -2.798276 |
| H | 0.823598 | -4.441632 | -2.798276 |
| C | -1.126654 | 2.495677 | -3.607585 |
| C | 1.126654 | -2.495677 | -3.607585 |
| H | -2.184311 | 2.323419 | -3.365553 |
| H | 2.184311 | -2.323419 | -3.365553 |
| H | -1.069842 | 2.976306 | -4.593687 |
| H | 1.069842 | -2.976306 | -4.593687 |
| O | -0.418008 | 1.254709 | -3.659941 |
| O | 0.418008 | -1.254709 | -3.659941 |
| C | -0.548419 | 0.523933 | -4.880234 |
| C | 0.548419 | -0.523933 | -4.880234 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -1.538999 | 0.051776 | -4.939429 | H | -0.423049 | 1.191740 | -5.743101 |
| H | 1.538999 | -0.051776 | -4.939429 | H | 0.423049 | -1.191740 | -5.743101 |

Compound **3**

E = -3099.20933820 au

$G_{chloroform}$ = -3099.208388 au

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -3.922607 | 0.768400 | -1.209111 | H | 6.344092 | -0.104414 | -0.000155 |
| C | -1.595882 | -1.369167 | 0.263255 | H | 5.068227 | -0.738103 | 1.082958 |
| C | -1.917871 | -0.294461 | 1.165389 | H | 6.085535 | 2.141344 | -0.385037 |
| C | -5.006392 | -1.294036 | -1.294596 | H | 5.214886 | 2.206202 | 1.178821 |
| C | -2.989389 | -0.740337 | 2.017955 | H | 3.869276 | 2.930503 | -1.442407 |
| C | -5.572423 | -0.531213 | -0.213935 | H | 4.765524 | 4.138949 | -0.482613 |
| C | -3.327613 | -2.091579 | 1.649656 | H | 1.619302 | 2.956478 | -1.008419 |
| C | -4.890942 | 0.736783 | -0.148838 | H | 1.713625 | 4.658979 | -0.458154 |
| C | -2.478228 | -2.477645 | 0.551434 | H | 2.094047 | 2.014943 | 2.661566 |
| C | -2.585186 | 2.675952 | -0.496316 | H | 2.576789 | 1.087916 | 1.220334 |
| Fe | -3.574584 | -0.823294 | 0.078604 | H | 0.238860 | 0.089378 | 2.833403 |
| H | -2.126958 | 1.313967 | -1.948436 | H | 1.884627 | -0.156932 | 3.486460 |
| N | -1.236879 | 2.993148 | -0.559494 | H | 0.060944 | -2.537313 | 2.059796 |
| N | -2.934511 | 1.722428 | -1.459751 | H | 1.396901 | -2.450619 | 3.243698 |
| O | -3.369271 | 3.154085 | 0.346526 | H | 2.978833 | -3.113986 | 1.401107 |
| H | -0.637168 | 2.283432 | -0.991681 | H | 1.836317 | -4.408001 | 1.920245 |
| C | -3.970654 | -0.496569 | -1.899879 | H | 1.835742 | -4.719660 | -1.600221 |
| O | 1.426850 | -3.529070 | 0.044875 | H | -3.365199 | -0.766760 | -2.747974 |
| C | 2.401015 | -4.154173 | -0.853384 | H | -5.329970 | -2.265388 | -1.627870 |
| C | 3.274340 | -3.112849 | -1.560691 | H | -6.395760 | -0.833548 | 0.410781 |
| O | 3.775653 | -2.182569 | -0.535598 | H | -5.072715 | 1.554243 | 0.520764 |
| C | 4.991043 | -1.473504 | -0.941074 | C | -0.675780 | 3.813773 | 0.516905 |
| C | 5.279720 | -0.367759 | 0.074440 | H | -0.596220 | 4.870433 | 0.225134 |
| O | 4.454185 | 0.806362 | -0.233231 | H | -1.358489 | 3.755714 | 1.370159 |
| C | 5.097939 | 2.085405 | 0.095782 | H | 1.033818 | 3.839384 | 1.840012 |
| C | 4.198160 | 3.198985 | -0.431531 | N | -0.457710 | -1.464787 | -0.567530 |
| O | 3.074063 | 3.327199 | 0.483801 | H | 0.163365 | -2.265671 | -0.380182 |
| C | 1.780509 | 3.608416 | -0.142715 | C | 0.106347 | -0.433224 | -1.281399 |
| C | 0.720012 | 3.316028 | 0.924145 | N | 1.459383 | -0.566254 | -1.457010 |
| O | 0.602325 | 1.880765 | 1.176725 | H | 2.008485 | -1.035358 | -0.733052 |
| C | 1.752215 | 1.302036 | 1.900393 | C | 2.164184 | 0.325592 | -2.388346 |
| C | 1.298267 | 0.012629 | 2.568978 | H | 2.468249 | -0.203950 | -3.302762 |
| O | 1.544320 | -1.086154 | 1.631546 | H | 3.044625 | 0.723791 | -1.885654 |
| C | 1.138632 | -2.378610 | 2.175394 | H | 1.478840 | 1.128247 | -2.666060 |
| C | 1.936745 | -3.431833 | 1.428601 | O | -0.532401 | 0.533999 | -1.792604 |
| H | 3.030669 | -4.849464 | -0.285530 | H | -3.442276 | -0.164827 | 2.807887 |
| H | 2.680537 | -2.552203 | -2.288013 | H | -4.068935 | -2.712263 | 2.124312 |
| H | 4.101589 | -3.626947 | -2.069854 | H | -2.455776 | -3.437781 | 0.063695 |
| H | 4.880321 | -1.016813 | -1.931262 | H | -1.377637 | 0.636005 | 1.213216 |
| H | 5.837548 | -2.175208 | -0.965598 | | | | |

Compound **3**·$KH_2PO_4$ E = -4342.80229680 au

$G_{chloroform}$ = -4342.812772 au

| | | | |
|---|---|---|---|
| C | 3.731937 | 1.467545 | 0.856508 |
| C | 3.008340 | 0.272509 | 1.210023 |
| C | 3.959688 | -0.671156 | 1.736789 |
| C | 5.263064 | -0.065202 | 1.714290 |
| C | 5.128125 | 1.257652 | 1.162359 |
| H | 1.962072 | 0.089278 | 1.075660 |
| H | 3.726190 | -1.672940 | 2.055029 |
| H | 6.176158 | -0.505025 | 2.076182 |
| H | 5.914013 | 1.988522 | 1.061873 |
| Fe | 4.457257 | -0.143003 | -0.159911 |
| C | 3.497605 | -1.376370 | -1.533999 |
| C | 3.753451 | -0.066772 | -2.081725 |
| C | 5.175641 | 0.156223 | -2.050600 |
| C | 5.789906 | -0.996465 | -1.442077 |
| C | 4.750129 | -1.938526 | -1.110572 |
| H | 2.980759 | 0.552994 | -2.504973 |
| H | 5.693488 | 1.006022 | -2.462917 |
| H | 6.846550 | -1.155972 | -1.308851 |
| H | 4.851697 | -2.906495 | -0.659696 |
| N | 3.256395 | 2.696272 | 0.349444 |
| N | 2.211359 | -1.855694 | -1.344884 |
| H | 3.987238 | 3.371901 | 0.144606 |
| H | 1.464694 | -1.297761 | -1.816464 |
| C | 1.977055 | 3.023406 | 0.002489 |
| C | 1.900815 | -2.790639 | -0.366563 |
| O | 0.959612 | 2.303231 | 0.269520 |
| O | 2.711753 | -3.612250 | 0.114822 |
| N | 1.838442 | 4.215465 | -0.648164 |
| N | 0.588949 | -2.687902 | 0.052387 |
| H | 2.657119 | 4.741542 | -0.929092 |
| H | 0.149054 | -1.755843 | 0.052777 |
| C | 0.518366 | 4.687968 | -1.103905 |
| H | -0.131178 | 4.904630 | -0.248826 |
| H | 0.035059 | 3.937752 | -1.734403 |
| H | 0.667881 | 5.604079 | -1.677648 |
| C | 0.030351 | -3.707084 | 0.936454 |
| H | 0.187890 | -4.699895 | 0.501133 |
| H | 0.517286 | -3.717520 | 1.923466 |
| C | -1.476835 | -3.446052 | 1.096048 |
| H | -1.947114 | -4.226673 | 1.707399 |
| O | -1.691356 | -2.126141 | 1.716019 |
| C | -1.382379 | -2.011686 | 3.141711 |
| H | -0.692289 | -2.800113 | 3.464897 |
| H | -2.307748 | -2.071245 | 3.726301 |
| C | -0.711651 | -0.662219 | 3.351099 |
| H | 0.143999 | -0.587145 | 2.671400 |
| H | -0.367241 | -0.566202 | 4.391285 |
| O | -1.692366 | 0.385140 | 3.043588 |
| C | -1.081706 | 1.719988 | 3.054024 |
| H | -0.276026 | 1.787845 | 2.314291 |
| H | -0.688038 | 1.949878 | 4.055014 |
| C | -2.162441 | 2.721363 | 2.686951 |
| H | -1.781037 | 3.741170 | 2.843743 |
| H | -3.049738 | 2.564524 | 3.314340 |
| O | -2.484358 | 2.506156 | 1.276574 |
| C | -3.421426 | 3.499490 | 0.738281 |
| H | -2.956247 | 4.496273 | 0.740245 |
| H | -4.341680 | 3.523624 | 1.336539 |
| C | -3.749770 | 3.068005 | -0.680087 |
| H | -2.824665 | 2.795555 | -1.199658 |
| H | -4.274517 | 3.877593 | -1.209136 |
| O | -4.624735 | 1.894495 | -0.553273 |
| C | -4.849398 | 1.219284 | -1.845111 |
| H | -3.923784 | 0.738522 | -2.185122 |
| H | -5.205368 | 1.945814 | -2.591633 |
| C | -5.940733 | 0.192543 | -1.589192 |
| H | -6.225517 | -0.275307 | -2.540372 |
| H | -6.811221 | 0.696164 | -1.155415 |
| O | -5.472283 | -0.823259 | -0.635756 |
| C | -5.582304 | -2.218213 | -1.086914 |
| H | -6.219252 | -2.279436 | -1.978354 |
| H | -6.038562 | -2.789931 | -0.273729 |
| C | -4.210463 | -2.798448 | -1.388495 |
| H | -3.616125 | -2.101067 | -1.991201 |
| H | -4.316351 | -3.762453 | -1.909645 |
| O | -3.555358 | -2.999034 | -0.084205 |
| C | -2.149258 | -3.369128 | -0.273732 |
| H | -1.662018 | -2.615068 | -0.894197 |
| H | -2.068637 | -4.351841 | -0.762175 |
| H | -0.453239 | 2.263866 | -0.823860 |
| O | -0.975810 | 1.891361 | -1.601583 |
| P | -0.715846 | 0.270355 | -1.711243 |
| O | -2.042224 | -0.424244 | -1.923366 |
| O | 0.503507 | -0.047927 | -2.540563 |
| O | -0.315605 | 0.004670 | -0.105750 |
| H | 0.310883 | 0.714620 | 0.235190 |
| K | -3.035490 | -0.141796 | 0.606226 |

Electronic Supplementary Information for Dalton Transactions