# Electronic Supplementary Information (ESI)

## A Conjugated Diosma-Octacyclic Complex and Its Mixed-Valence Singly Reduced State

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# 1. Experimental

**Materials:** Most materials were purchased commercially and used without further purification. Dichloromethane was distilled from calcium hydride prior to use. Ultradry methanol for syntheses was purchased from Shanghai Meryer Chemical Technology Co., Ltd. The supporting electrolyte, *n*-$Bu_4NPF_6$ (Acros-Organics), was recrystallized twice from ethanol, dried under vacuum at 353 K for 5 h and stored under argon overpressure. Just prior to an electrochemical experiment, the electrolyte was dried again in an oven at 393 K overnight, followed by 30 min under vacuum at 353 K. All manipulations were carried out under an atmosphere of dry argon (or nitrogen) gas by using standard Schlenk techniques. Osmapentalyne **1** (ref.[1]) and mononuclear **2** (ref.[2]) were synthesized according to literature procedures.

**Methods:** $^{1}H$ and $^{13}C$ NMR spectra were acquired using a Varian MERCURY Plus 400 MHz instrument or a Bruker AVANCE III HD-400 instrument. $^{31}P$ NMR spectra were measured using Bruker AVANCE III HD-400. High-resolution mass spectra (HRMS) were recorded on electrospray ionization mass spectrometry (ESI-MS). UV-vis spectra were measured with a Shimadzu UV-3600 spectrophotometer. Elemental analyses (C, H) were performed at the Shenzhen University with an Elementar Vario EL CUBE instrument.

Cyclic voltammograms of **2**−**4** were recorded with a Metrohm Autolab PGSTAT302N potentiostat operated with the NOVA 2.14 software. The air-tight single-compartment electrochemical cell, placed in Faraday cage, housed a Pt microdisc working electrode (an active area of 0.4 $mm^2$) polished with 0.25 μm diamond paste (Kemet), a coiled Pt wire counter electrode and a coiled Ag wire pseudo-reference electrode. All values are reported against the ferrocenium/ferrocene ($Fc^+$/Fc) redox couple that served as the internal standard and was added just before the ultimate potential sweep. The concentration of samples was ca. $1\times10^{-3}$ mol $dm^{-3}$.

IR spectroelectrochemical experiments at $T$ = 233 K were performed using a cryostatted OTTLE cell[3] positioned in the sample compartment of an external Bio-RAD FTS 60 MCT detector linked to a Bruker Vertex 70v FT-IR spectrometer. A Scinco S-3100 diode-array spectrophotometer served for the recording of spectral changes in the UV−vis−NIR region. The course of each spectroelectrochemical experiments was monitored by thin-layer cyclic voltammetry; the potential control was realized with a PalmSens EmStat3 potentiostat operated with the PSTrace5 software. The concentration of spectroelectrochemical samples was ca. $2\times10^{-3}$ mol dm$^{-3}$. Dry $10^{-1}$ M *n*-$Bu_4NPF_6$ was used as the supporting electrolyte.

Single-crystal X-ray analyses were performed on a Bruker Apex CCD equipped with a Mo microfocus ($\lambda$ = 0.71073 Å) or Cu microfocus ($\lambda$ = 1.54050 Å). The frames were integrated with *SAINT* v. 7.68A software package; then, the structure was solved using SHELXL-97. CCDC codes: 2024859 for **3** and 2024860 for **4-BPh$_4$**. The supplementary crystallographic data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

**Computational Details:** DFT and TD-DFT calculations were performed using the Gaussian 09 software[4] at the B3LYP[5]/6-31G* for **3** and **4** and at UWB97XD[6]/6-31G* for **4**$^-$ (Lanl2dz for the osmium atom) level of theory. Geometry optimizations and full geometry were performed without any symmetry constraints; frequency calculations on the resulting optimized geometries showed no imaginary frequencies. Electronic transitions were calculated by the TD-DFT method. The molecular orbital contributions were generated using Multiwfn_3.7_dev_bin_Win64 package[7] and plotted using VMD. The solvation effects in dichloromethane were included for a part of the calculations with the CPCM.[8] The anisotropy of the induced current density (AICD) calculations was carried out with the AICD program. To facilitate comparison with the previous study by the Xia group[2], similar simplification

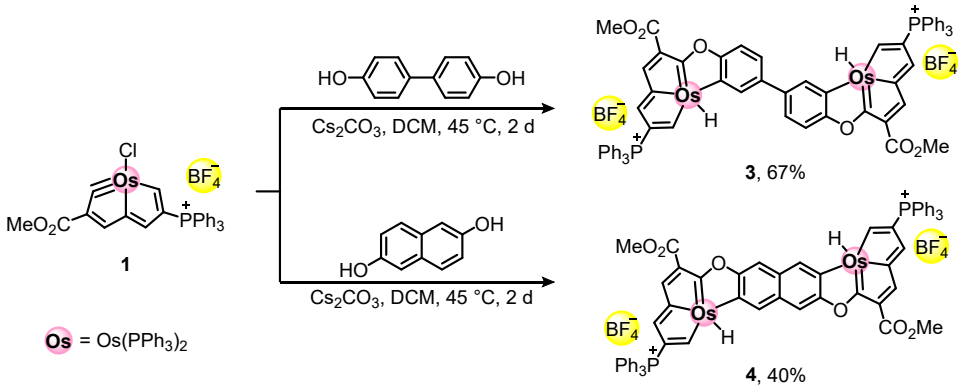
of **2**, **3**, **4** have been made by replacing the substituents on the aromatic ring skeleton with the hydrogen atoms as well as the $PPh_3$ ligands with $PH_3$. These simplified structures are denoted as **2'**, **3'** and **4'** respectively. The effective core potentials (ECPs) of Hay and Wadt with a double-ζ valence basis set (LanL2DZ) were used to describe the Os and P atoms, whereas the standard 6-311++G(d,p) basis set was used for the C, H and O atoms. Polarization functions were added for Os (ζ(f) = 0.886) and P (ζ(d) = 0.34) in optimization calculations with B3LYP method using the Gaussian 16[9]. When performing the theoretical $^1$H NMR analyses of **2**, **3** and **4**, only $PPh_3$ were replaced with $PH_3$ and the simplified structures have been denoted as **2''**, **3''** and **4''**. (The same applies for the model of the singly reduced mixed-valence species, **4''**$^-$ (cf. Fig. S5)) The basis set for the optimization of **2''**, **3''** and **4''** is the same as that for **2'**, **3'** and **4'**. CAM-B3LYP is used to calculate $^1$H NMR. In the NMR calculations, the effective core potentials (ECPs) of Hay and Wadt with a double-ζ valence basis set (LanL2DZ) were used to describe the Os and P atoms, whereas the standard 6-311++G(d,p) basis set was used for the C, N, O, and H atoms. Polarization functions were added for Os (ζ(f) = 0.886) and P (ζ(d) = 0.34).

## 2. Syntheses

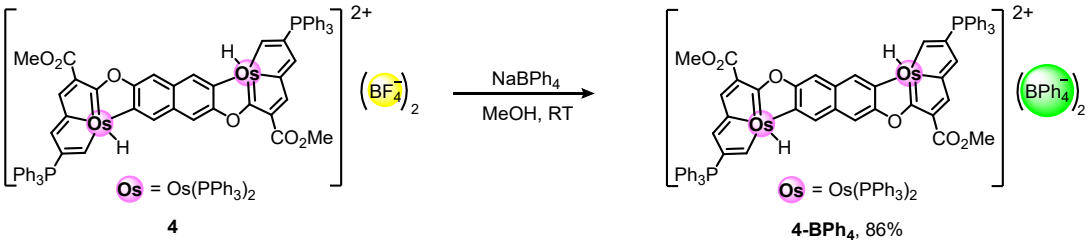
**Complex 3.** A mixture of **1** (250 mg, 2.5 equiv., 0.20 mmol), biphenol (15.0 mg, 1 equiv., 0.08 mmol) and $Cs_2CO_3$ (521 mg, 20 equiv., 1.6 mmol) in $CH_2Cl_2$ (20 mL) was refluxed at 45 °C for 2 d, and then filtrated to remove the solid suspension. The filtrate was concentrated to ca. 2 mL and then purified by column chromatography (neutral alumina, eluent: dichloromethane/methanol 50:1 → 20:1 (v/v)) to give a red solution. Red solid **3** (140 mg, 67%) was collected after vacuum solvent evaporation to dryness. $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ 12.00 (t, $J_{P\text{-}H}$ = 14 Hz, 2H), 9.42 (s, 2H), 8.67 (s, 2H), 7.69, (s, 2H), 7.91–6.67 (m, 90H, $PPh_3$), 6.54 (d, $J$ = 8.0 Hz, 2H), 6.15 (d, $J$ = 8.0 Hz, 2H), 3.90 (s, 6H, COOC$H_3$), -3.33 ppm (td, apparent q, $J_{P\text{-}H}$ = 15.6 Hz, 2H, Os−*H*). $^{31}$P{$^1$H} NMR (162 MHz, $CD_2Cl_2$): $\delta$ 13.59

(t, $J$ = 5.5 Hz, C*P*Ph$_3$), 1.14 ppm (d, $J$ = 3.9 Hz, Os*P*Ph$_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CD_2Cl_2$): $\delta$ 257.5 (t, $J_{P\text{-}C}$ = 6.2 Hz), 198.4 (d, $J_{P\text{-}C}$ = 28.2 Hz), 196.9, 169.3, 168.6, 162.6, 150.6 (d, $J_{P\text{-}C}$ = 24.4 Hz), 146.8, 146.3, 139.8 (t, $J_{P\text{-}C}$ = 11.2 Hz), 137.3, 135.0, 134.9, 134.1 (d, $J_{P\text{-}C}$ = 10.2), 133.4 (t, $J_{P\text{-}C}$ = 4.9 Hz), 131.8, 131.5, 131.3, 130.4, 130.0 (d, $J$ = 9.5 Hz), 127.8 (t, $J$ = 4.7 Hz), 124.3, 120.4 (d, $J_{P\text{-}C}$ = 88.0 Hz), 113.5, 51.9 ppm. HRMS (ESI): *m/z* calcd for $[C_{138}H_{110}O_6Os_2P_6]^{2+}$, 1215.2958; found 1215.2942. Elemental analysis. Calcd. for $C_{138}H_{110}B_2F_8O_6Os_2P_6$ (%): C 63.65, H 4.26. Found (%): C 63.38, H 4.54.

**Complex 4.** A mixture of **1** (250 mg, 2.5 equiv., 0.20 mmol), 2,6-naphthalenediol (12.9 mg, 1 eq, 0.08 mmol) and $Cs_2CO_3$ (521 mg, 20 equiv., 1.6 mmol) in $CH_2Cl_2$ (20 mL) was refluxed at 45 °C for 2 d and then the solid suspension was removed through a filter. The filtrate was concentrated to ca. 2 mL and then purified by column chromatography (neutral alumina, eluent: dichloromethane/methanol 50:1 → 20:1 (v/v)) to give an aubergine-coloured solution. Deep wine-red (aubergine) solid **4** (82.5 mg, 40%) was collected after vacuum solvent evaporation to dryness. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 12.22 (t, $J_{P-H}$ = 16 Hz, 2H), 9.68 (s, 2H),− 8.74 (s, 2H), 7.86, (s, 2H), 7.81–6.52 (m, 90H, PPh$_3$), 6.63 (s, 2H), 3.90 (s, 6H, COOC*H*$_3$), −2.92 ppm (td, apparent q, $J_{P-H}$ = 14.8 Hz, 2H, Os−*H*). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta$ 12.78 (t, $J$ = 4.2 Hz, C*P*Ph$_3$), 0.12 ppm (d, $J$ = 4.7 Hz, Os*P*Ph$_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 257.0 (unresolved splitting due to limited resolution), 197.6 (d, $J_{P-C}$ = 27.4 Hz), 197.2, 168.5, 167.7, 162.4, 152.6 (d, $J_{P-C}$ = 24.3 Hz), 146.6, 135.2, 134.6, 133.8 (d, $J_{P\text{-}C}$ = 10.0 Hz), 133.3, 131.2, 130.9, 130.7, 130.3, 130.2, 127.5, 120.4 (d, $J_{P-C}$ = 87.8 Hz), 108.6, 51.8 ppm. HRMS (ESI): *m/z* calcd for $[C_{136}H_{108}O_6Os_2P_6]^{2+}$, 1202.2880; found 1202.2822. Elemental analysis. Calcd. for $C_{136}H_{108}B_2F_8O_6Os_2P_6$ (%): C 63.36, H 4.22. Found (%): C 63.17, H 4.37.




**Complex 4-BPh$_4$.** A methanol solution of $NaBPh_4$ (63 mg, 2.5 equiv., 0.19 mmol) was slowly added to the methanol solution of **4** (200 mg, 1equiv., 0.078 mmol) under stirring. The produced precipitate was collected by filtration and dried to give deep wine-red (aubergine) solid **4-BPh$_4$** (201 mg, 86%). $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ 12.27 (t, $J_{P-H}$ = 13.2 Hz, 2H), 9.65 (s, 2H), 8.70 (s, 2H), 7.92, (s, 2H), 7.80–6.52 (m, 130H, $PPh_3$ and $BPh_4$), 6.58 (s, 2H), 3.85 (s, 6H, COOC*H*$_3$), –2.86 ppm (td, apparent q, $J_{P-H}$ = 15.3 Hz, 2H, Os–*H*). $^{31}$P{$^1$H} NMR (162 MHz, $CD_2Cl_2$): $\delta$ 12.61 (t, $J$ = 6.0 Hz, C*P*Ph$_3$), 0.02 ppm (d, $J$ = 5.8 Hz, Os*P*Ph$_3$). $^{13}$C{$^1$H} NMR (100 MHz, $CD_2Cl_2$): $\delta$ 256.3 (t, $J_{P-C}$ = 10.2 Hz), 197.1 (d, $J_{P-C}$ = 28.1 Hz), 196.6 (t, $J_{P-C}$ = 10.9 Hz), 168.0, 167.2, 164.5 (q, $J_{B-C}$ = 49.5 Hz, $BPh_4^-$), 161.4, 152.1 (d, $J_{P-C}$ = 24.3 Hz), 146.1 (d, $J_{P-C}$ = 30.0 Hz), 135.4, 134.0, 133.2 (d, $J_{P-C}$ = 19.8 Hz), 132.7, 130.6, 130.3, 130.1, 129.6, 129.5, 129.3, 126.9, 125.1, 121.2, 119.8 (d, $J_{P-C}$ = 88.2 Hz), 107.7, 50.9 ppm. Elemental analysis. Calcd. for $C_{184}H_{148}B_2O_6Os_2P_6$ (%): C 72.62, H 4.90. Found (%): C 72.24, H 5.06.



# 3. X-ray Crystallography

**Table S1.** Crystallographic data collected for **3** · 4 $CH_2Cl_2$ and **4-BPh$_4$** · 2 $CH_2Cl_2$.

| Compound | **3** | **4-BPh$_4$** |
|---|---|---|
| Formula | $C_{138}H_{110}O_6Os_2P_6 \cdot 4(CH_2Cl_2) \cdot 2(BF_4)$ | $C_{136}H_{108}O_6Os_2P_6 \cdot 2(CH_2Cl_2) \cdot 2(C_{24}H_{20}B)$ |
| Formula weight | 2943.80 | 3212.71 |
| Temperature (K) | 100 | 210 |
| Crystal system | Triclinic | Triclinic |
| Space group | *P*–1 | *P*–1 |
| *a* (Å) | 12.2128 (11) | 13.4602 (10) |
| *b* (Å) | 13.1403 (10) | 13.7947 (10) |
| *c* (Å) | 23.3385 (19) | 22.1507 (17) |
| $\alpha$ (°) | 105.701 (4) | 99.733 (1) |
| $\beta$ (°) | 90.316 (4) | 91.295 (1) |
| $\gamma$ (°) | 115.605 (4) | 98.543 (1) |
| *V* (Å$^3$) | 3219.0 (5) | 4003.9 (5) |
| *Z* | 1 | 1 |
| Crystal size (mm$^3$) | 0.05 × 0.03 × 0.03 | 0.12 × 0.06 × 0.02 |
| Radiation type | Cu $K_\alpha$ | Mo $K_\alpha$ |
| $R[F^2 > 2s(F^2)]$, $wR(F^2)$, *S* | 0.038, 0.114, 1.09 | 0.037, 0.085, 0.99 |
| No. of reflections | 8016 | 14719 |
| No. of parameters | 849 | 943 |
| No. of restraints | 83 | 25 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 2.60, -6.42 | 1.12, -0.99 |

Computer programs: *SAINT* v7.68A (Bruker, 2009), *SHELXT* (Sheldrick, 2015), *SHELXL* (Sheldrick, 2015), Olex2 (Dolomanov *et al.*, 2009).

**Table S2.** Selected bond lengths (Å) and angles (º) in the crystal structure of **3**·4 $CH_2Cl_2$.

| Bond lengths | | | |
|---|---|---|---|
| Os1–C1 | 2.095 (7) | Os1–C4 | 2.124 (6) |
| Os1–C7 | 2.060 (8) | Os1–C8 | 2.154 (7) |
| C1–C2 | 1.381 (10) | C2–C3 | 1.437 (10) |
| C3–C4 | 1.349 (10) | C4–C5 | 1.422 (10) |
| C5–C6 | 1.365 (10) | C6–C7 | 1.427 (10) |
| C8–C9 | 1.362 (11) | C8–C13 | 1.384 (10) |
| C9–C10 | 1.393 (10) | C10–C11 | 1.374 (10) |
| C11–C12 | 1.378 (11) | C7–O1 | 1.344 (8) |
| C9–O1 | 1.387 (8) | C12-C12' | 1.378 (11) |
| Bond angles | | | |
| C1–Os1–C4 | 73.3 (3) | C1–Os1–C8 | 140.3 (3) |
| C7–Os1–C4 | 72.8 (3) | C7–Os1–C8 | 73.4 (3) |
| C2–C1–Os1 | 119.1 (5) | C1–C2–C3 | 114.6 (6) |
| C4–C3–C2 | 112.1 (6) | C3–C4–Os1 | 120.9 (5) |
| C3–C4–C5 | 121.2 (6) | C5–C4–Os1 | 117.9 (5) |
| C6–C5–C4 | 115.8 (6) | C5–C6–C7 | 110.5 (6) |
| C6–C7–Os1 | 123.0 (5) | O1–C7–Os1 | 122.4 (5) |
| C7–O1–C9 | 111.4 (6) | C8–C9–O1 | 118.1 (6) |
| C9–C8–Os1 | 114.5 (5) | C9–C8–C13 | 116.0 (6) |
| C8–C13–C12 | 122.7 (7) | C11–C12–C13 | 117.4 (6) |
| C10–C11–C12 | 122.0 (6) | C11–C10–C9 | 117.1 (7) |

**Table S3.** Selected bond lengths (Å) and angles (º) in the crystal structure of **4-BPh$_4$** ·2 $CH_2Cl_2$.

| Bond lengths | | | |
|---|---|---|---|
| Os1–C1 | 2.089 (4) | Os1–C4 | 2.112 (4) |
| Os1–C7 | 2.048 (4) | Os1–C8 | 2.130 (4) |
| C1–C2 | 1.375 (5) | C2–C3 | 1.415 (6) |
| C3–C4 | 1.370 (5) | C4–C5 | 1.422 (5) |
| C5–C6 | 1.369 (5) | C6–C7 | 1.437 (5) |
| C7–O1 | 1.342 (4) | C8–C9 | 1.405 (5) |
| C9–O1 | 1.386 (4) | C8–C12 | 1.391 (5) |
| C11–C12 | 1.417 (5) | C11–C11$^{i}$ | 1.425 (7) |
| C10–C11 | 1.421 (5) | C9–C10 | 1.361 (5) |
| Bond angles | | | |
| C2–C1–Os1 | 118.8 (3) | C1–C2–C3 | 114.8 (4) |
| C4–C3–C2 | 112.5 (4) | C3–C4–C5 | 123.0 (4) |
| C3–C4–Os1 | 119.6 (3) | C5–C4–Os1 | 117.3 (3) |
| C6–C5–C4 | 115.7 (3) | C5–C6–C7 | 111.3 (3) |
| C6–C7–Os1 | 121.4 (3) | O1–C7–Os1 | 122.5 (3) |
| C7–O1–C9 | 112.1 (3) | O1–C9–C8 | 116.8 (3) |
| C9–C8–Os1 | 114.3 (3) | C12–C8–C9 | 116.1 (3) |
| C8–C12–C11 | 122.0 (4) | C12–C11–C11$^{i}$ | 119.4 (4) |
| C10–C11–C11$^{i}$ | 118.5 (4) | C9–C10–C11 | 119.0 (4) |

Index $^{i}$ is used to distinguish corresponding atoms in the symmetric position.

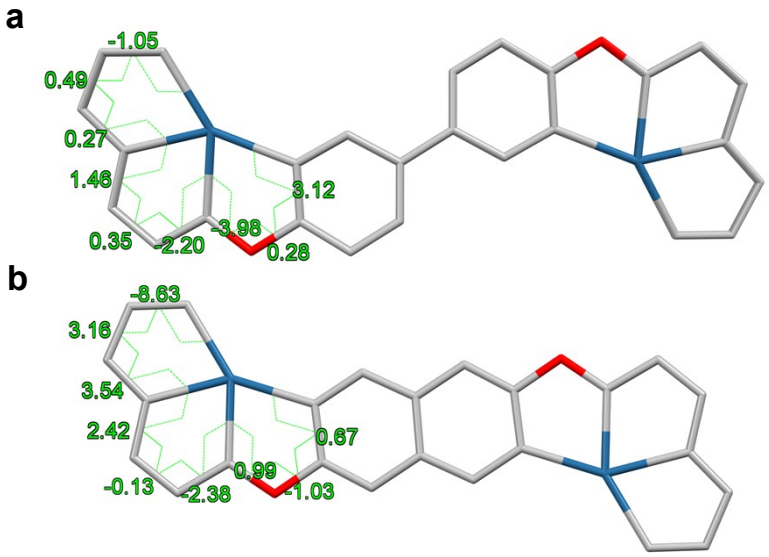



**Fig. S1.** Torsion angles exhibited by the osmacycles in the molecular structures of **3** (a) and **4-BPh$_4$** (b). They have been determined with the Mercury 2021.2.0 software, using the function (picking mode) "Measure Torsions".

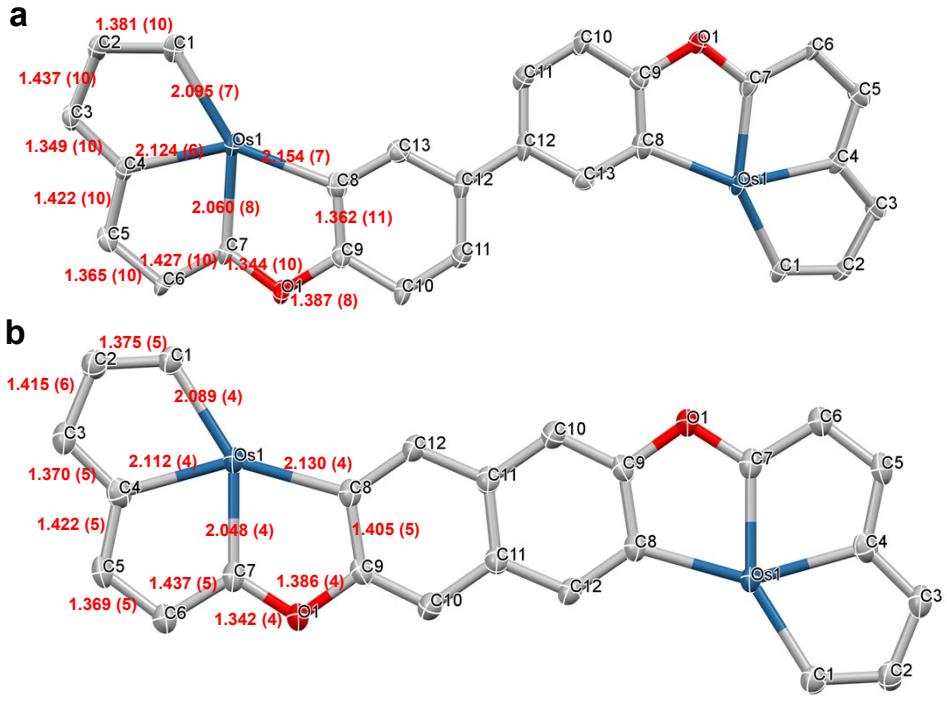



**Fig. S2.** Selected bond lengths in the molecular structures of **3** (a) and **4-BPh$_4$** (b).

# 4. Cyclic Voltammetry

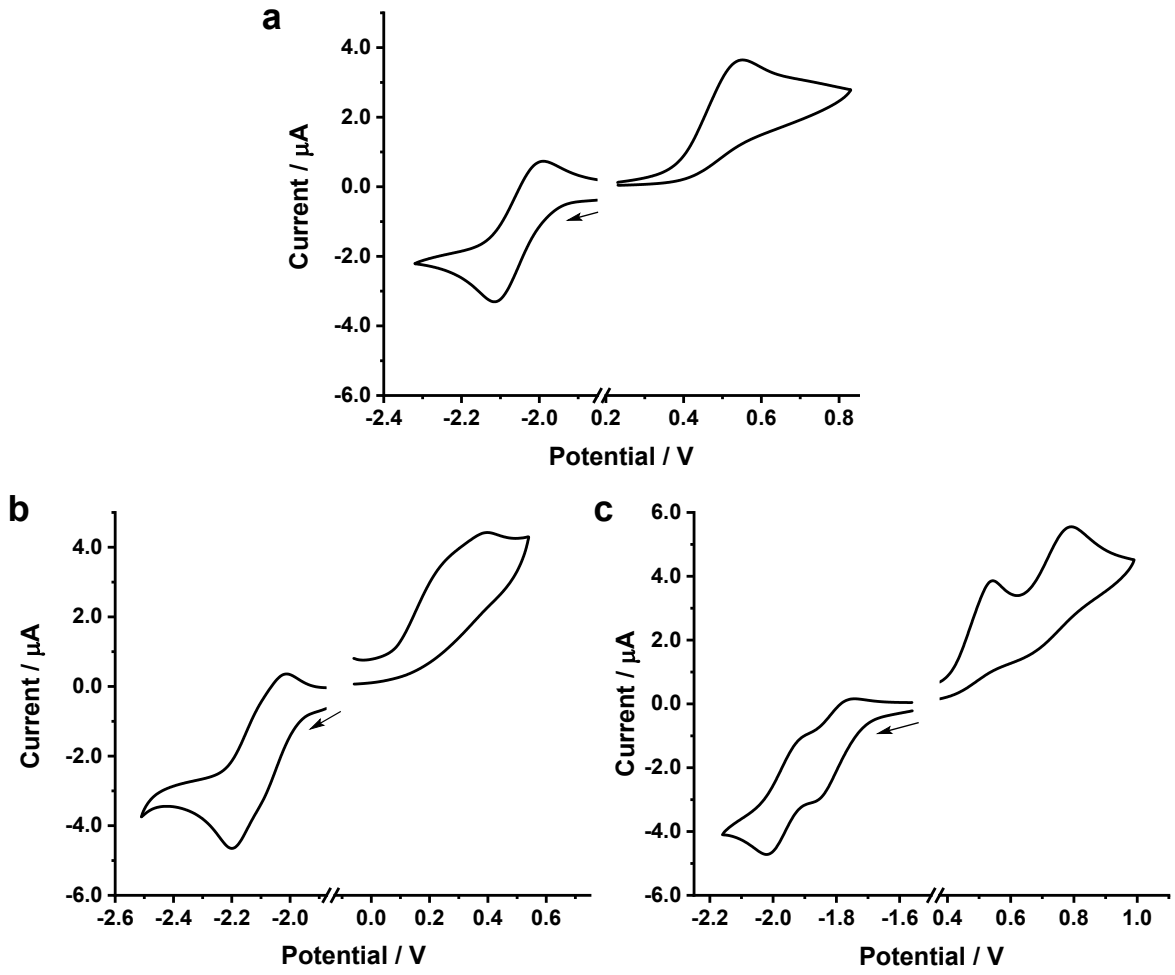



**Fig. S3.** Cyclic voltammograms of 1 mM **2** (a), **3** (b) and **4** (c) in $CH_2Cl_2$/*n*-$Bu_4NPF_6$ at $v$ = 100 mV $s^{-1}$, $T$ = 298 K. The potential scales correspond to the standard ferrocenium/ferrocene redox couple.

## 5. IR Spectroelectrochemistry

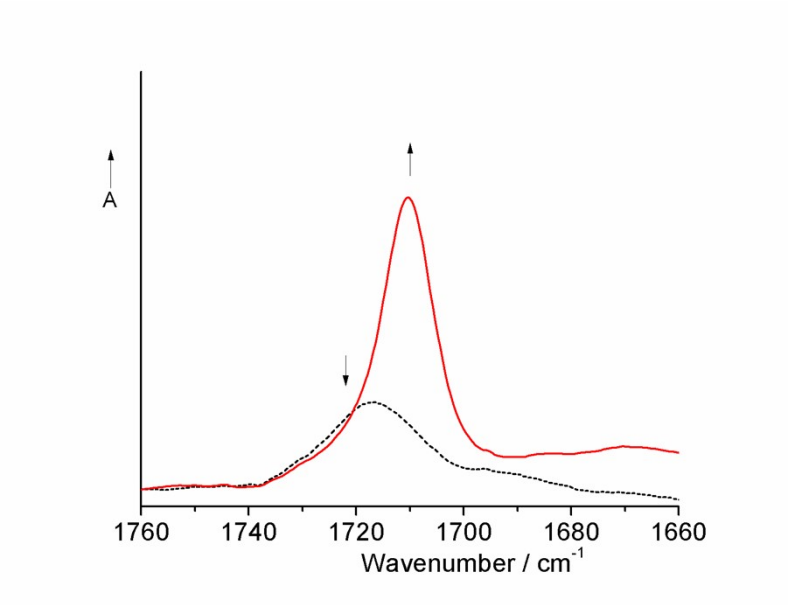



**Fig. S4.** IR ν(C=O) absorption of 2 mM **4** (black dashed line) and electrochemically reduced **4**$^{-}$ (red full line) recorded in $CH_2Cl_2$/*n*-$Bu_4NPF_6$ at $T$ = 233 K within a cryostatted OTTLE cell[3].

# 6. DFT and TD-DFT Calculations

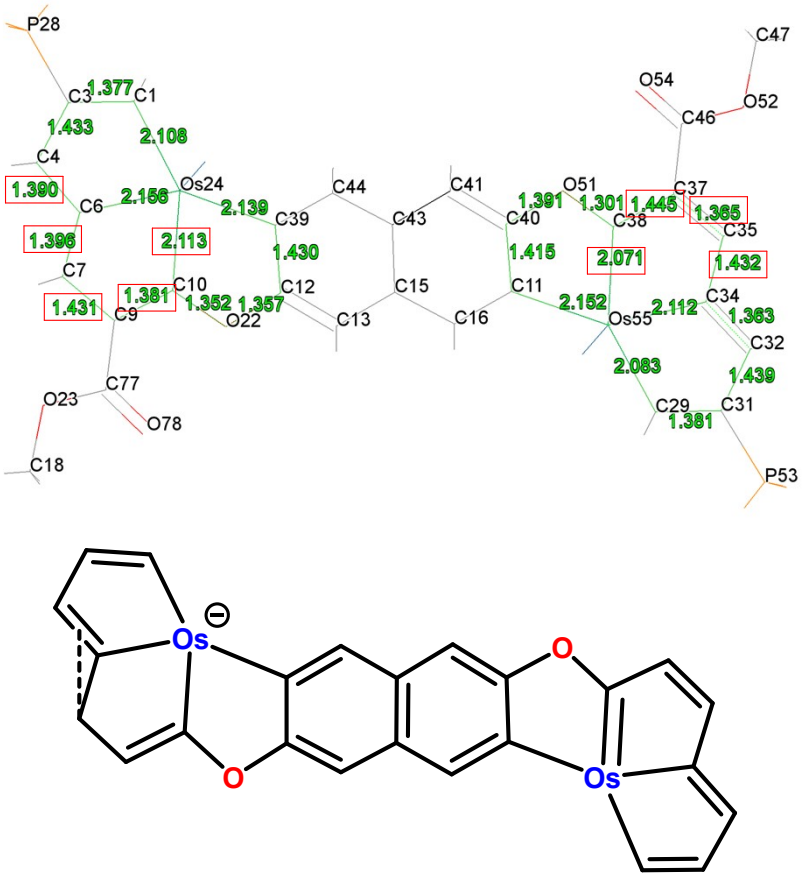



**Fig. S5**. Selected bond lengths in **4''**$^{-}$ and its schematic molecular structure.

**Table S4.** TD-DFT calculated (calc) and experimental (exp) electronic absorption of **3** and **4**.

| Complex | Excitation (percentage) | $f$ | $\lambda_{max}$(calc)/nm | $\lambda_{max}$(exp)/nm ($\varepsilon$/$10^4$ $M^{-1}cm^{-1}$) | $\Delta E_{(H-L)}$ /eV |
|---|---|---|---|---|---|
| **3** | HOMO→LUMO (86%) | 0.413 | 498 | 525 (1.04) | 2.95 |
| | HOMO-3→LUMO (32%) | 0.045 | 399 | 480 (1.13) | |
| | HOMO-3→LUMO (19%) | 0.096 | 398 | | |
| | HOMO→LUMO+2 (56%) | 0.077 | 384 | | |
| | HOMO-2→LUMO+1 (72%) | 0.132 | 368 | 383 (1.05) | |
| **4** | HOMO→LUMO (10%)<br>HOMO-1→LUMO (80%) | 0.200 | 507 | 530 (1.85)[a] | 2.89 |
| | HOMO→LUMO (84%)<br>HOMO-1→LUMO (13%) | 0.306 | 502 | | |
| | HOMO-1→LUMO+2 (63%) | 0.389 | 369 | 395 (2.83)[b] | |
| | HOMO-3→LUMO (51%) | 0.166 | 362 | | |

[a] 508 nm at $T$ = 233 K (cf. Fig. 9 in the main text). [b] 374 nm at $T$ = 233 K (cf. Fig. 9 in the main text).

**Table S5.** Isosurface plots of molecular orbitals involved in the major electronic excitations in **3**.

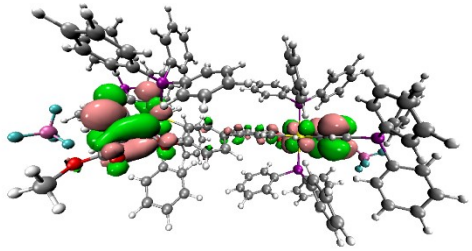
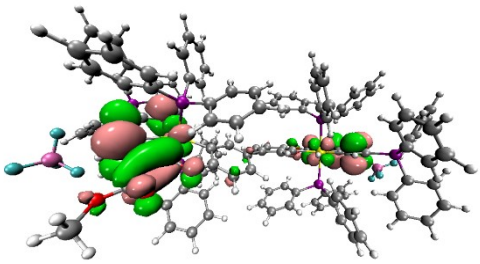
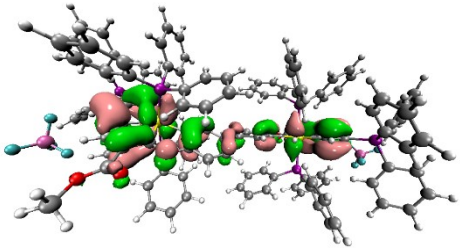
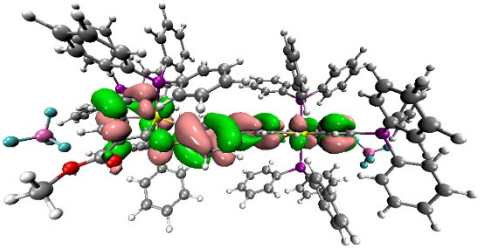
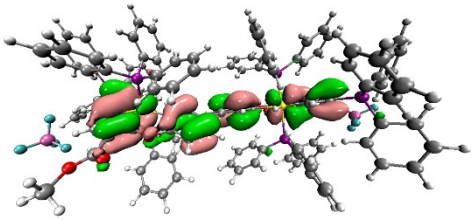
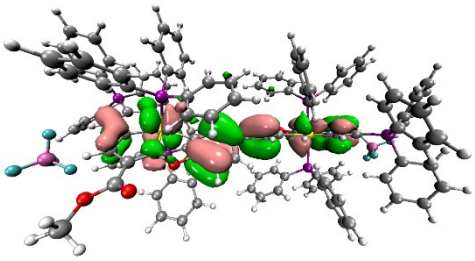
| | |
|---|---|
|  LUMO+1 (-2.16 eV) |  LUMO+2 (-1.41 eV) |
|  HOMO (-5.16 eV) |  LUMO (-2.20 eV) |
|  HOMO-3 (-6.00 eV) |  HOMO-2 (-5.96 eV) |

**Table S6.** Isosurface plots of molecular orbitals involved in the major electronic excitations in **4**.

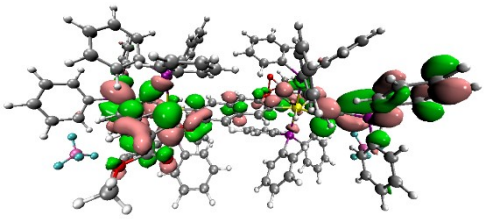
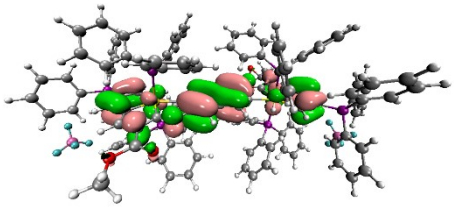
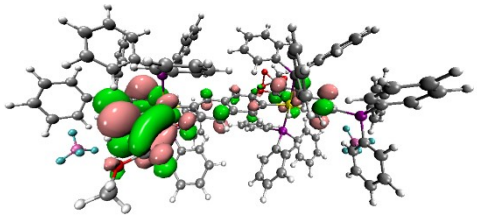
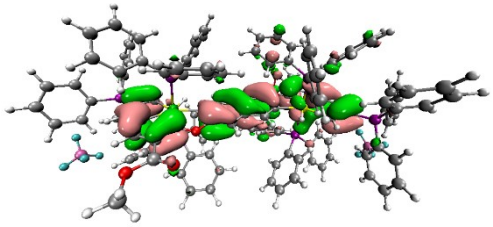
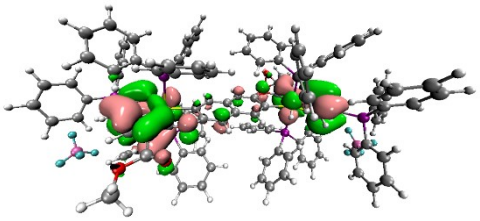
<table>
<tr><td colspan="2">  <br>LUMO+2 (-1.50 eV)</td></tr>
<tr><td>  <br>HOMO (-5.29 eV)</td><td>  <br>LUMO (-2.40 eV)</td></tr>
<tr><td>  <br>HOMO-3 (-6.21eV)</td><td>  <br>HOMO-1 (-5.38 eV)</td></tr>
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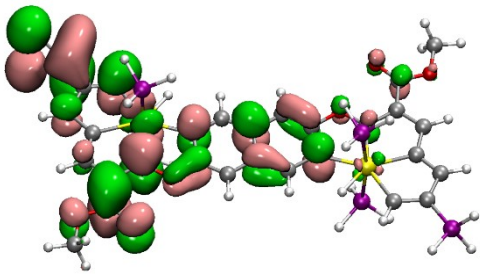
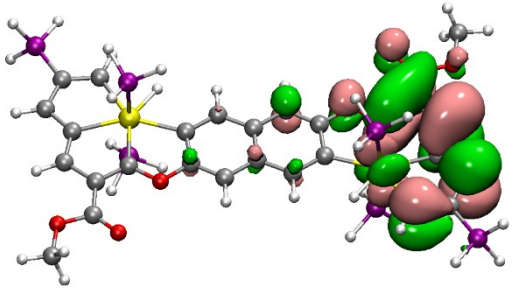
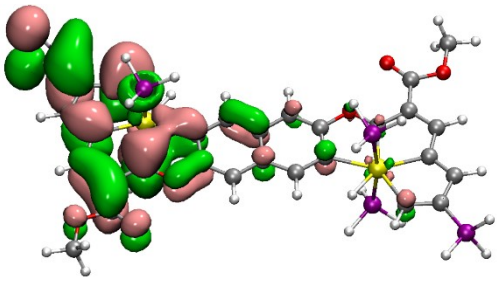
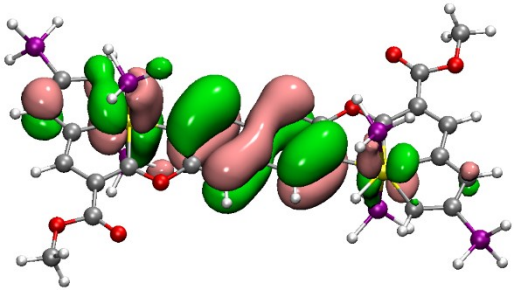
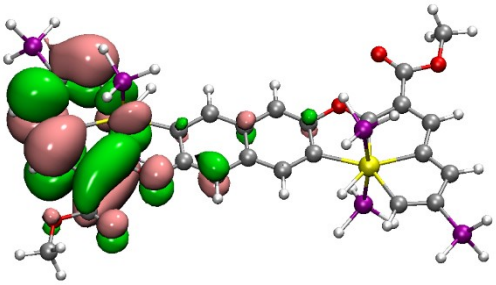
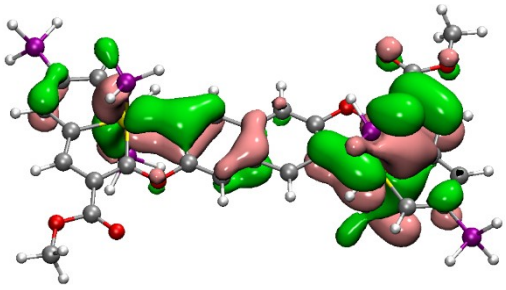
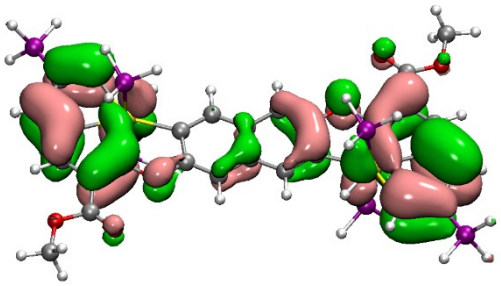
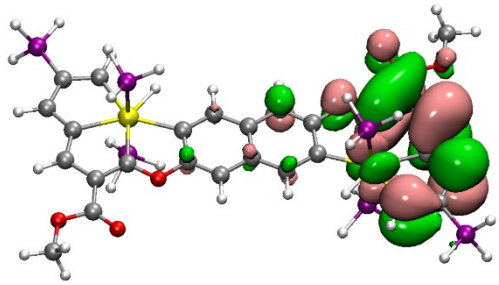
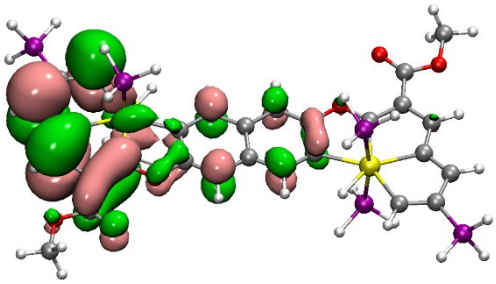
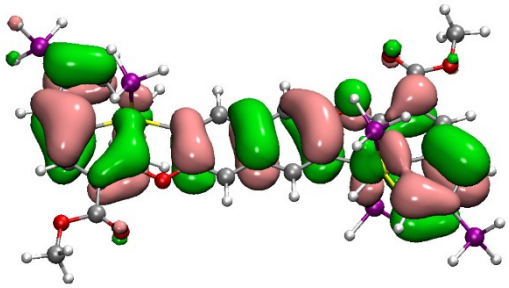
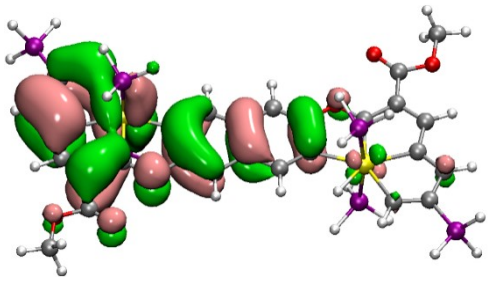
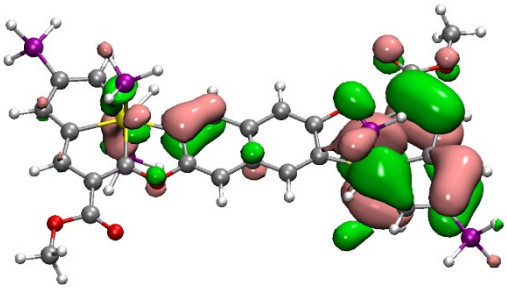
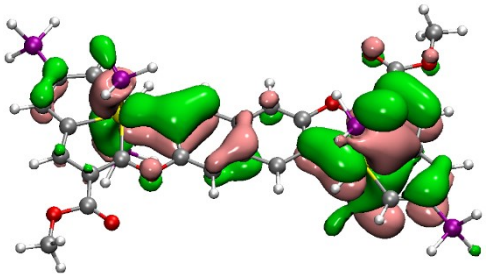
**Table S7.** Isosurface plots of molecular orbitals involved in the major electronic excitations in **4''**$^{-}$.

| | |
|---|---|
|  α-LUSO+6 | |
|  α-LUSO |  α-LUSO+2 |
|  α-HOSO-1 |  α-HOSO |
|  α-HOSO-9 |  α-HOSO-3 |

| | |
|---|---|
|  β-LUSO |  β-LUSO+2 |
|  β-HOSO-2 |  β-HOSO |
|  β-HOSO-9 |  β-HOSO-8 |

## 7. NMR Spectroscopy

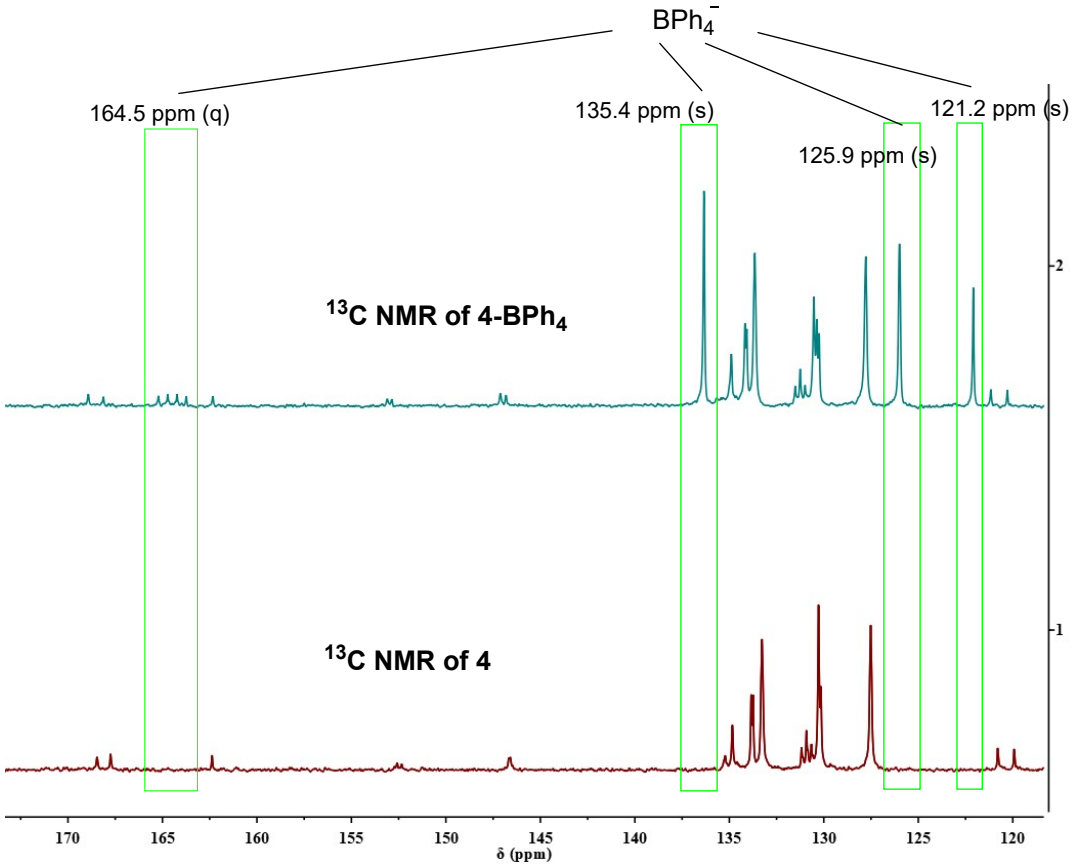



**Fig. S6**. Section of $^{13}C$ NMR (100 MHz, $CD_2Cl_2$, 298 K) spectra of **4** (bottom) and **4-BPh$_4$** (top).

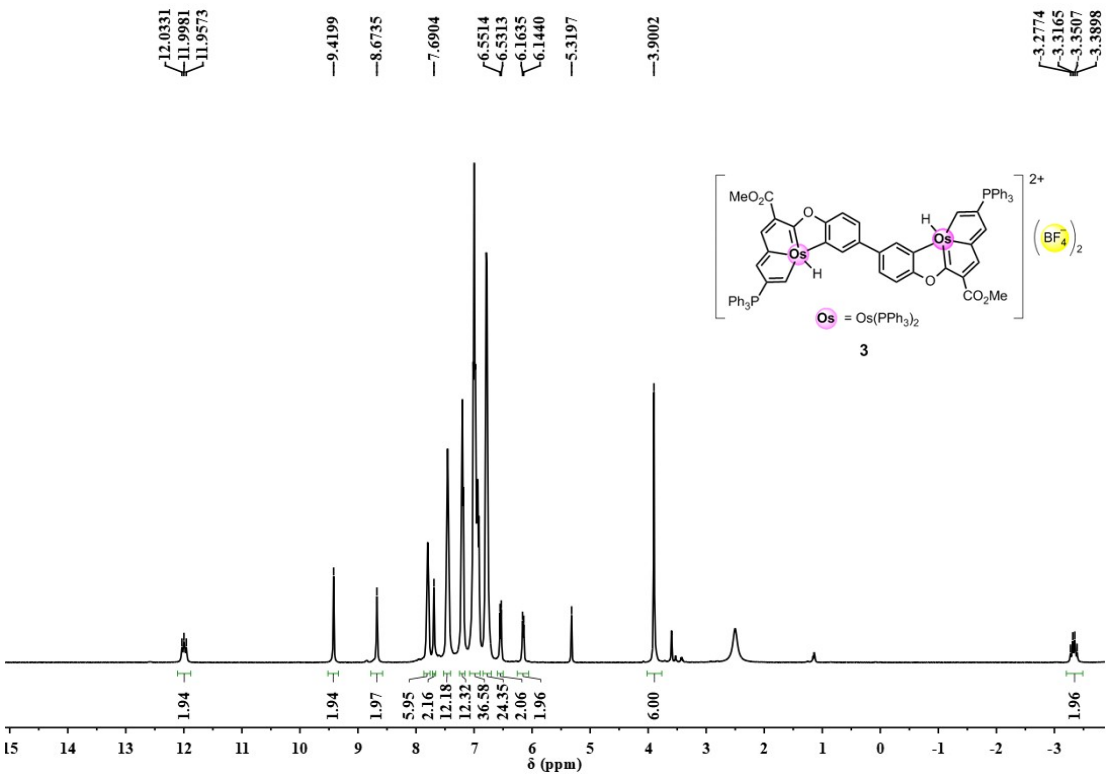



**Fig. S7**. $^{1}H$ NMR (400 MHz, $CD_2Cl_2$, 298 K) spectrum of **3**.

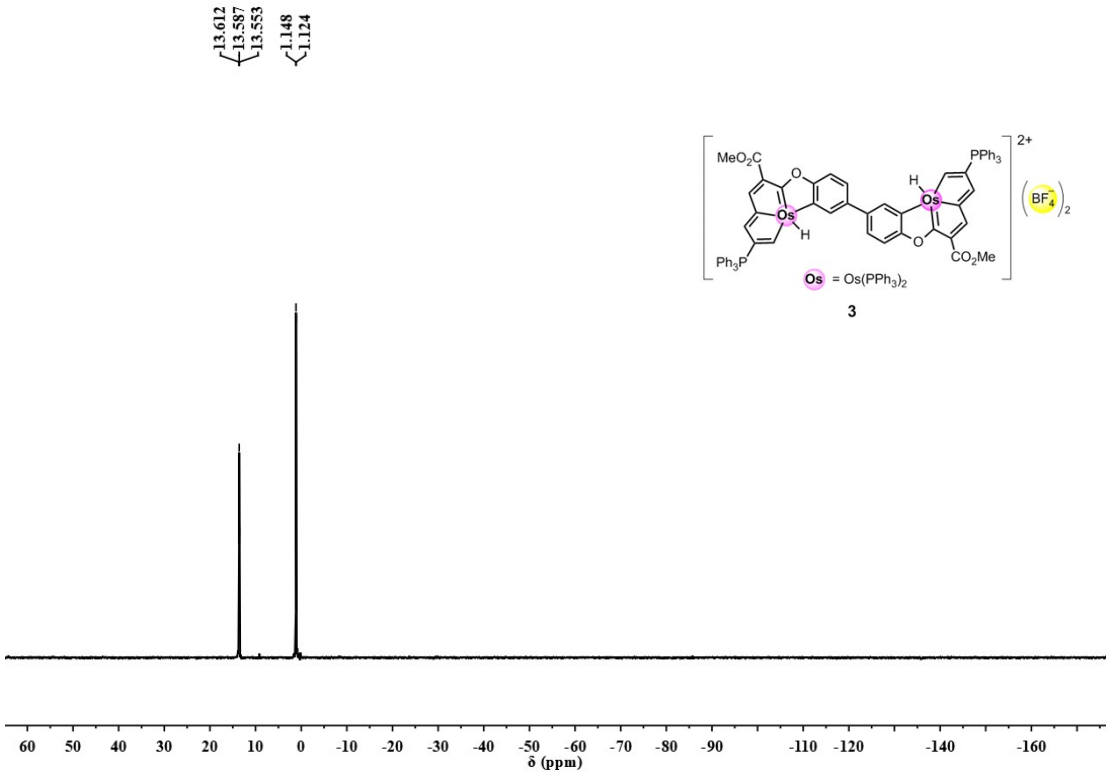



**Fig. S8**. $^{31}P$ NMR (162 MHz, $CD_2Cl_2$, 298 K) spectrum of **3**.

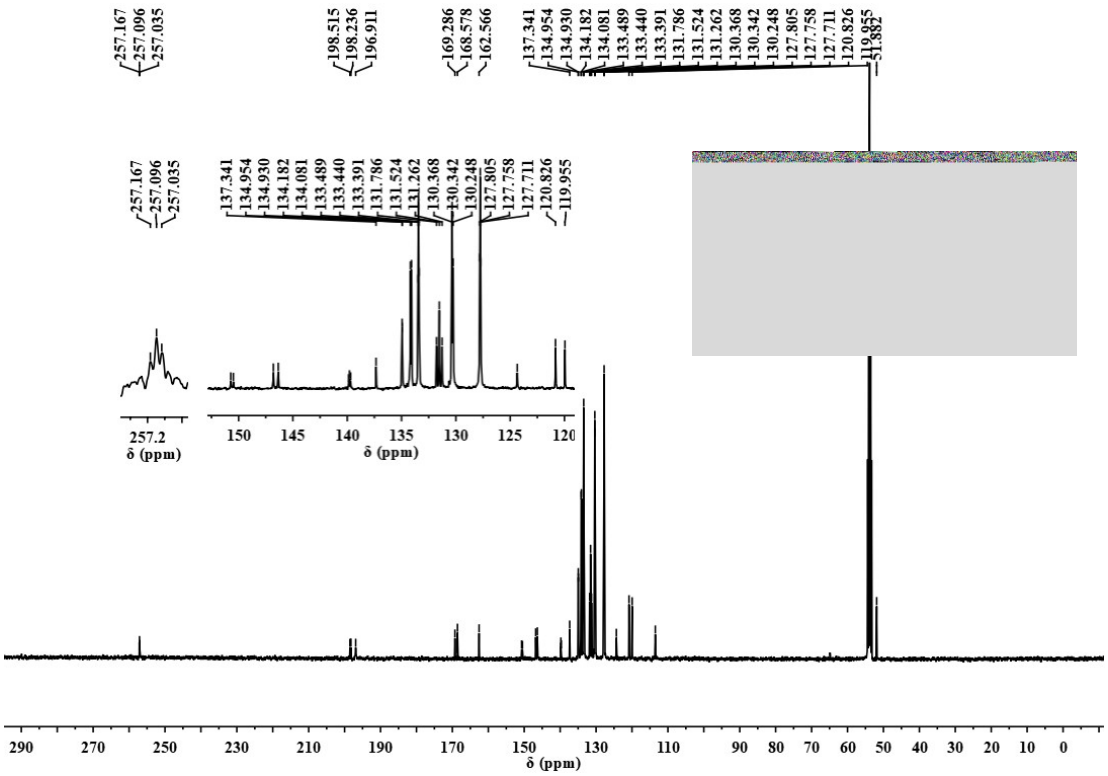



**Fig. S9**. $^{13}C$ NMR (100 MHz, $CD_2Cl_2$, 298 K) spectrum of **3**.

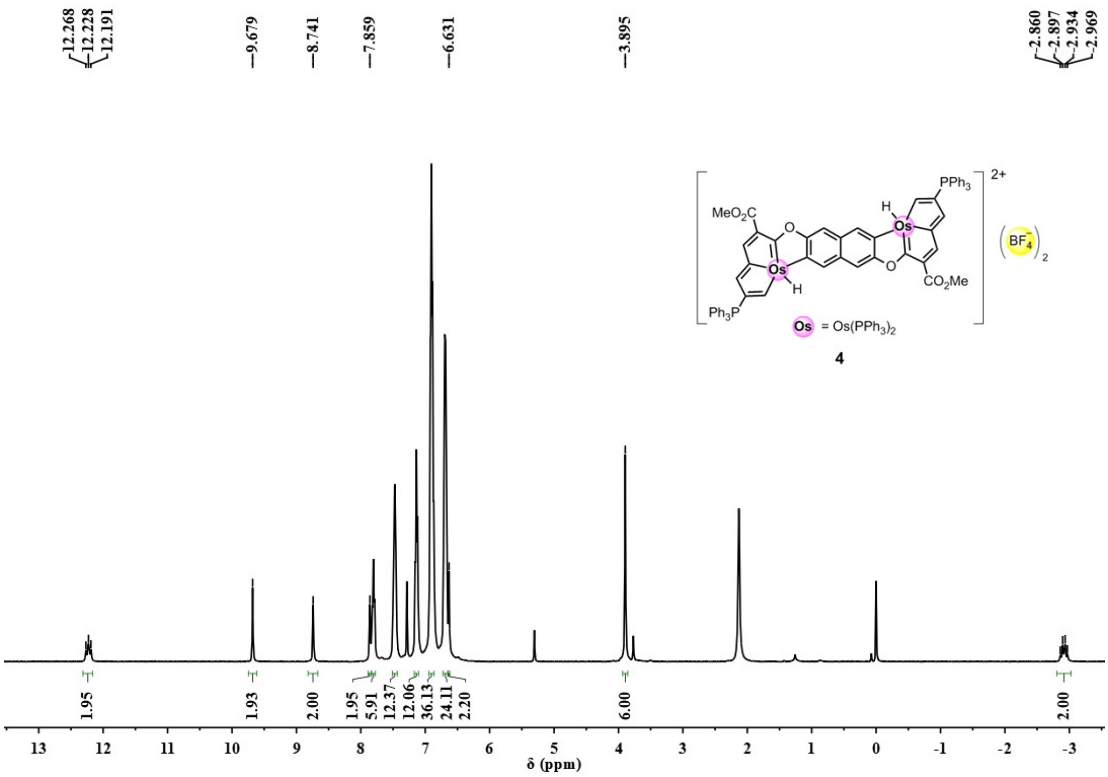



**Fig. S10**. $^{1}H$ NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **4**.

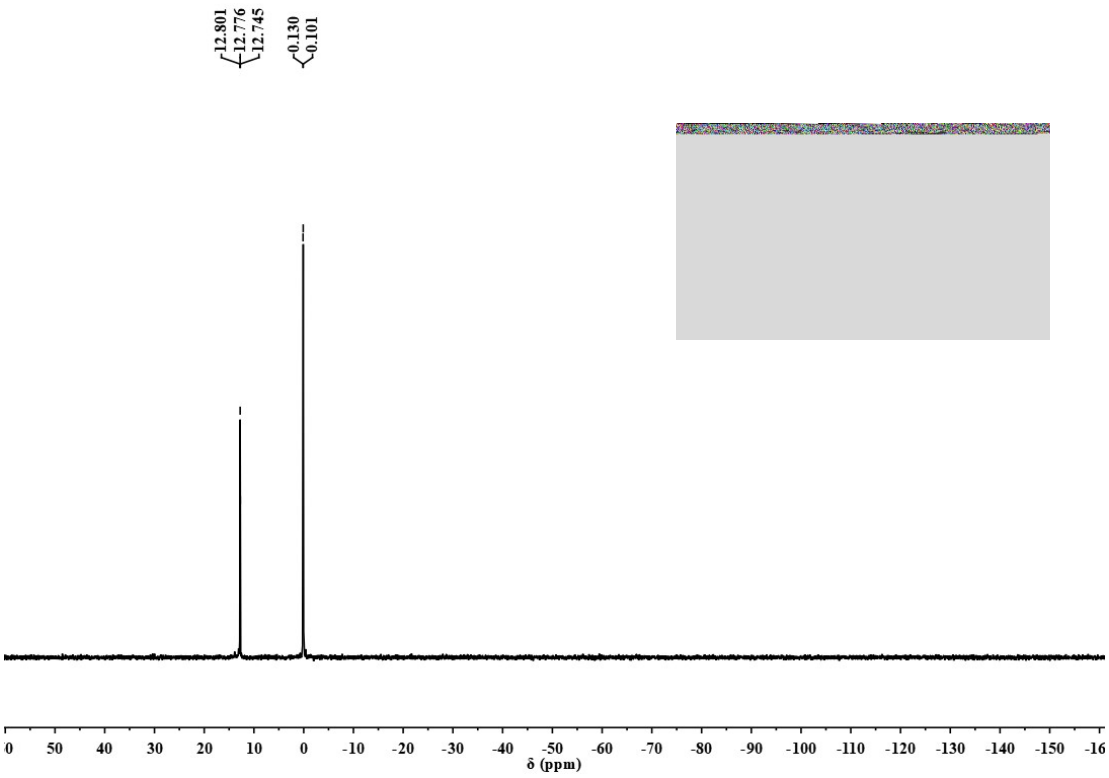



**Fig. S11**. $^{31}P$ NMR (162 MHz, $CDCl_3$, 298 K) spectrum of **4**.

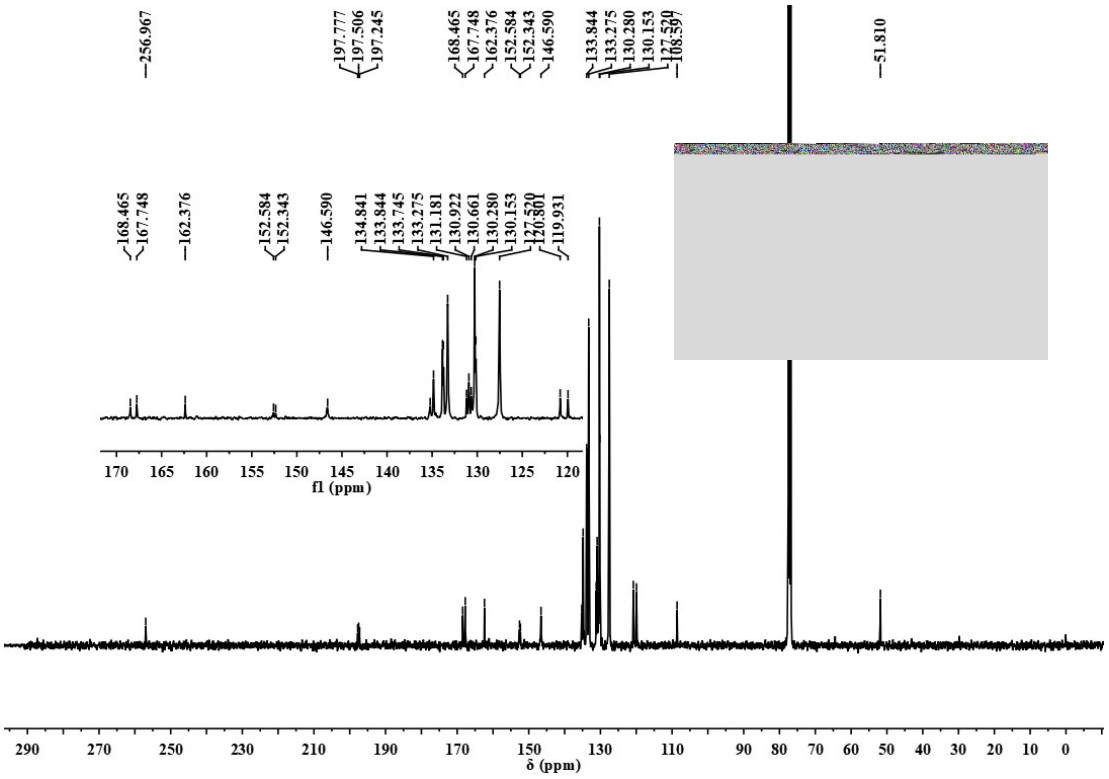



**Fig. S12**. $^{13}C$ NMR (100 MHz, $CDCl_3$, 298 K) spectrum of complex **4**.

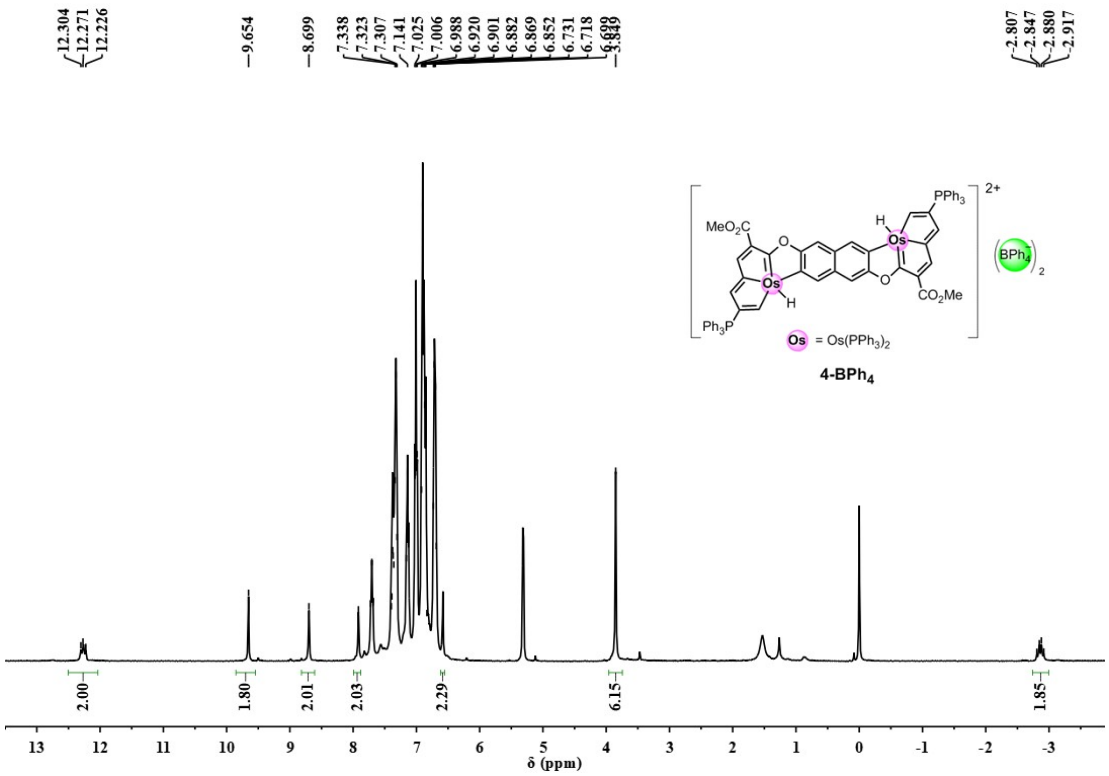



**Fig. S13**. $^{1}H$ NMR (400 MHz, $CD_2Cl_2$, 298 K) spectrum of **4-BPh$_4$**.

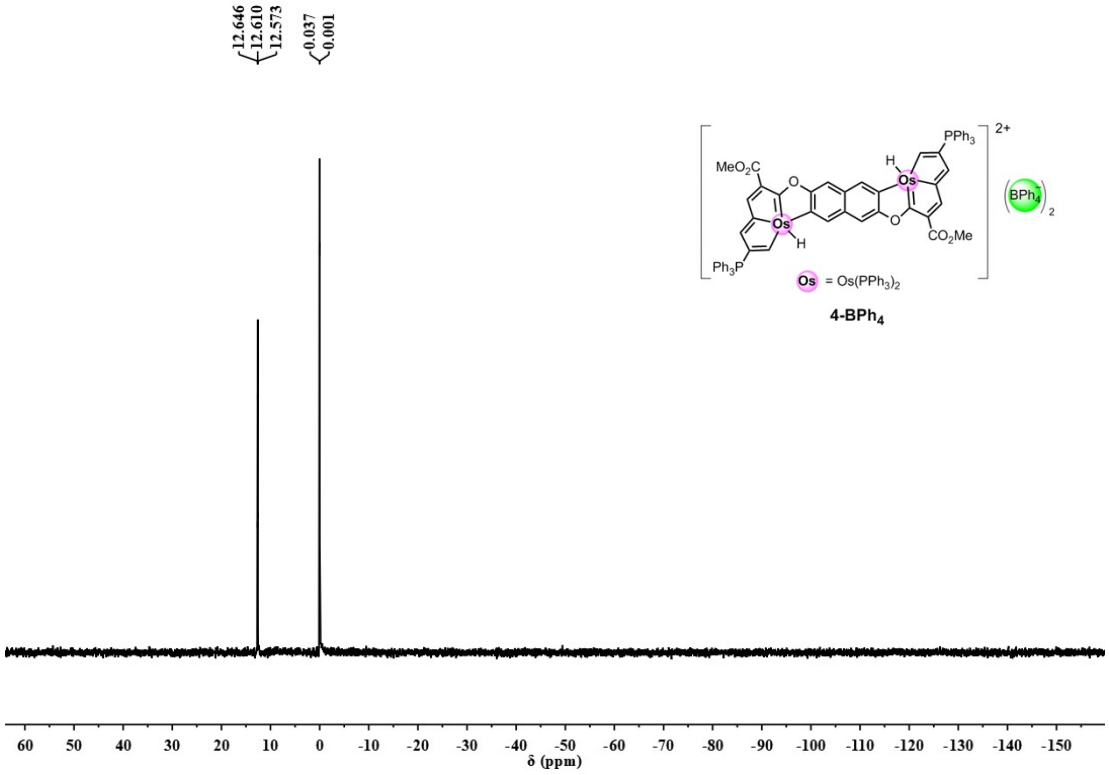



**Fig. S14**. $^{31}P$ NMR (162 MHz, $CD_2Cl_2$, 298 K) spectrum of **4-BPh$_4$**.

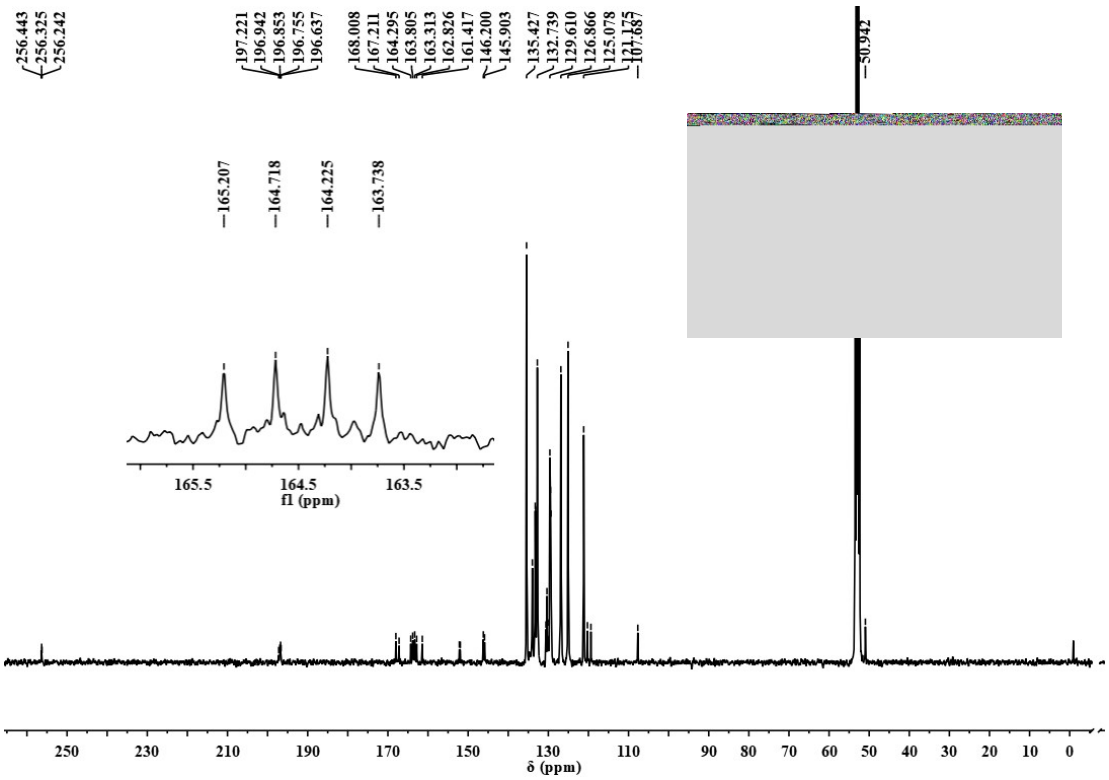
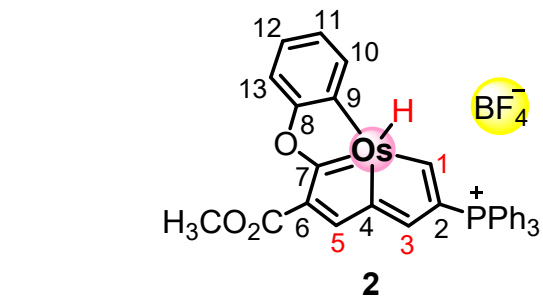
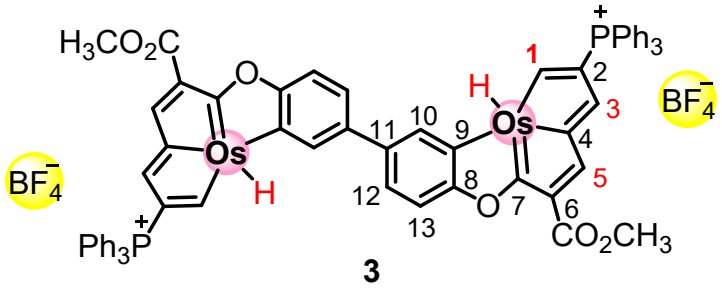



**Fig. S15**. $^{13}C$ NMR (100 MHz, $CD_2Cl_2$, 298 K) spectrum of **4-BPh$_4$**.



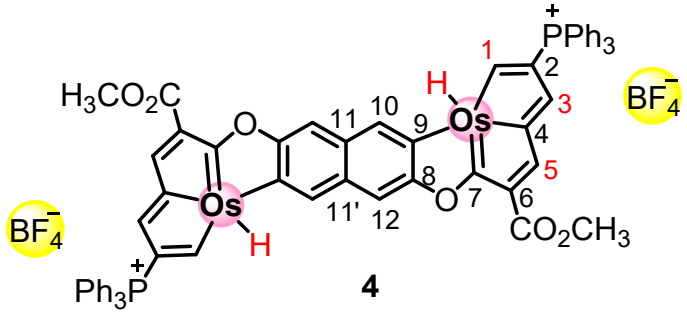

**2**

| Experiment | DFT |
|---|---|
| H1: 11.80, t | 11.89 |
| H3: 8.54, s | 8.29 |
| H5: 9.36, s | 10.04 |
| OsH: - 3.41, s | - 0.38 |




**3**

| Experiment | DFT |
|---|---|
| H1: 12.00, t | 11.91 |
| H3: 8.67, s | 8.37 |
| H5: 9.42, s | 10.06 |
| OsH: - 3.33, s | - 0.25 |




**4**

| Experiment | DFT |
|---|---|
| H1: 12.22, t | 12.00 |
| H3: 8.74, s | 8.41 |
| H5: 9.68, s | 10.14 |
| OsH: - 2.92, s | - 0.04 |

**Fig. S16**. Experimental $^{1}$H NMR shifts (ppm versus tetramethylsilane) recorded for **2**–**4** and calculated (DFT) for their models **2''**–**4''** (with $PPh_3$ replaced by $PH_3$).

## 8. High-Resolution Mass Spectrometry

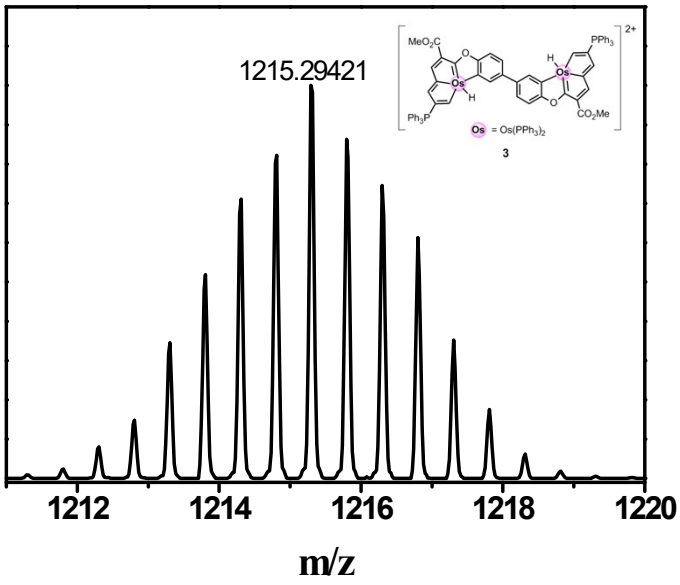



**Fig. S17**. HR-MS (ESI+) spectrum of dication **3**.

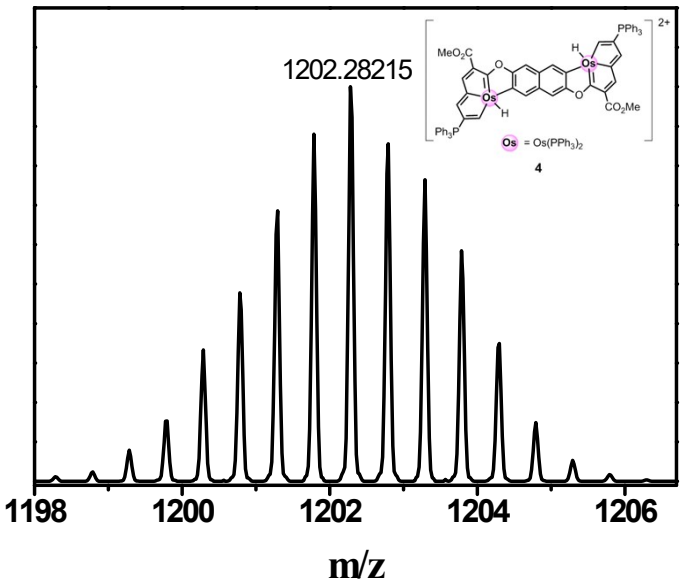



**Fig. S18**. HR-MS (ESI+) spectrum of dication **4**.

## 9. EDDB Analysis

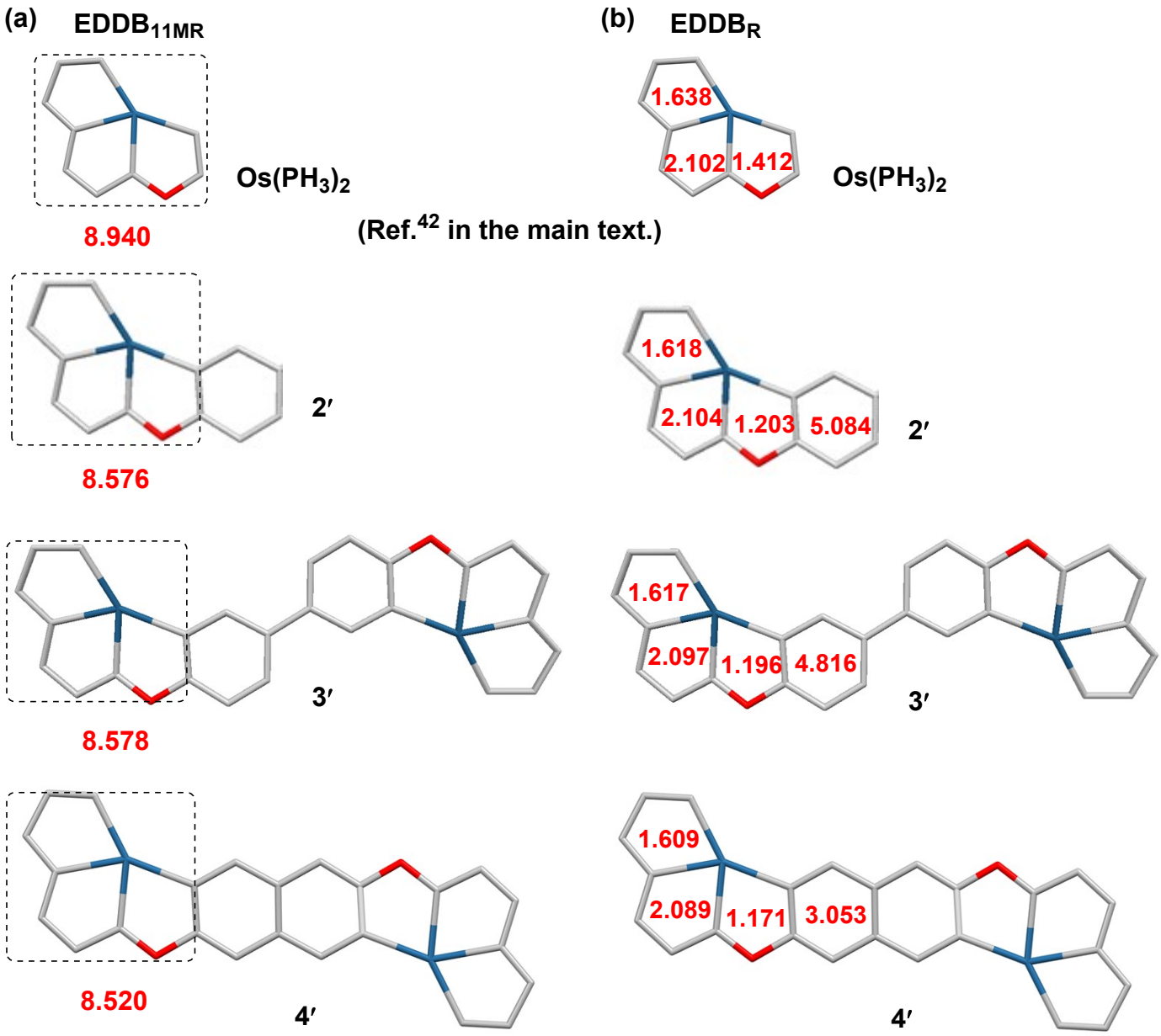



**Fig. S19**. EDDB analysis of the ring aromaticity in **2'**, **3'** and **4'**. (a) EDDB values for the 11-membered ring and (b) separate EDDB values for each ring, including the additional benzene ring in the bridge fused to the osmafuran moiety.

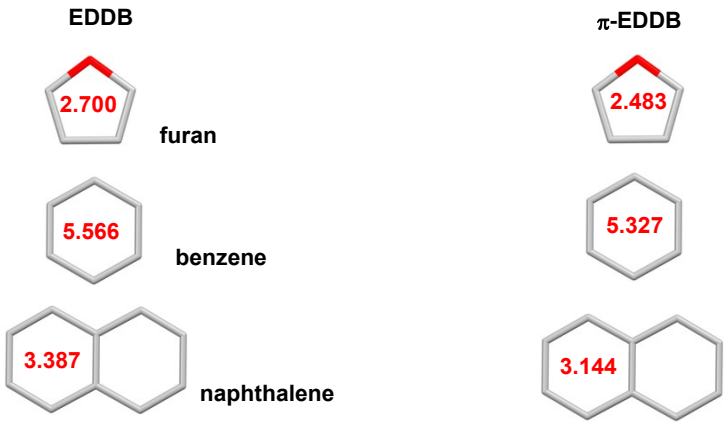



**Fig. S20**. EDDB/π- EDDB analysis of furan, benzene, and naphthalene rings.

## 10. Analysis of Aromaticity

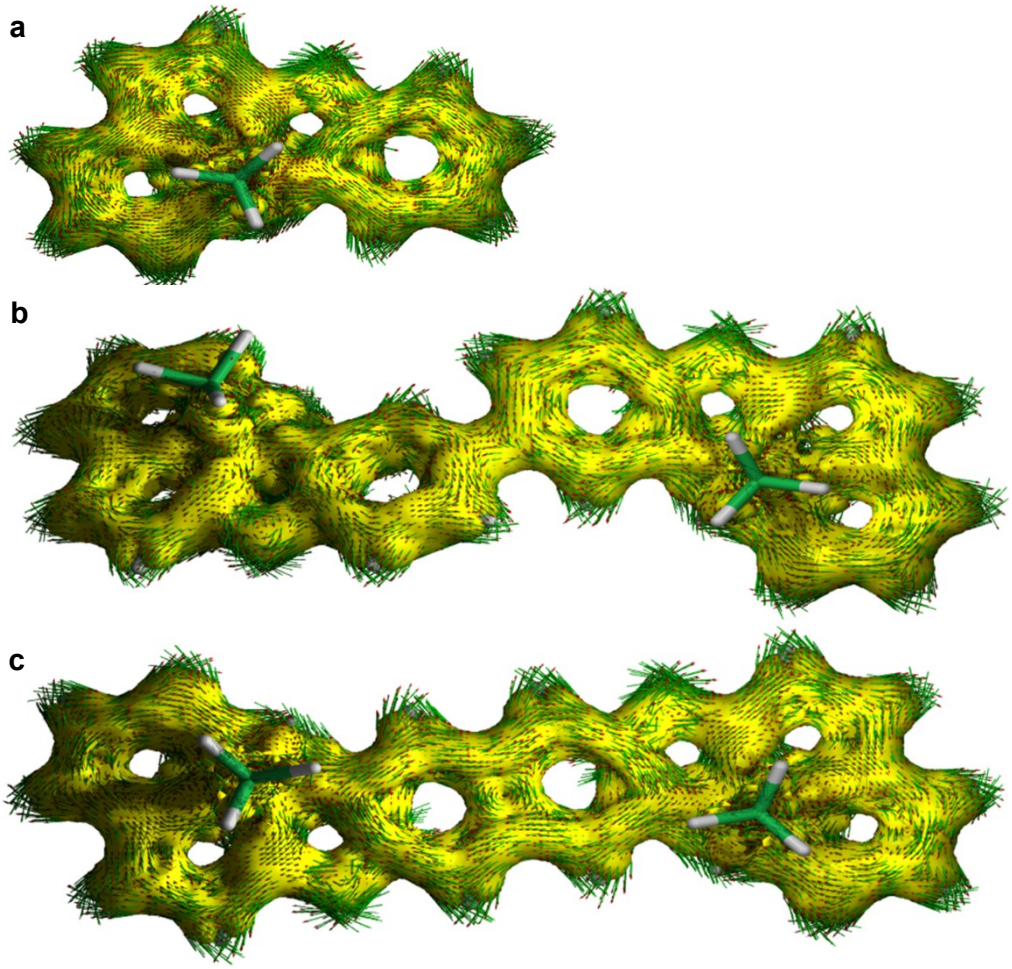



**Fig. S21**. AICD plots of **2'**, **3'** and **4'** by π-ring current contributions. Current density vectors are plotted onto the AICD isosurface of 0.030 to indicate diatropic ring currents.

## 11. References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## 12. Cartesian Coordinates

**Complex 2'**

| | | | |
|---|---|---|---|
| C | −2.07117600 | −1.61927800 | 0.25773600 |
| C | −3.34646500 | −1.11582800 | 0.13726300 |
| C | −3.42219500 | 0.28041200 | −0.09986600 |
| H | −4.36541900 | 0.81132300 | −0.22039700 |
| C | −2.19236600 | 0.90019100 | −0.17661000 |
| C | −2.00168000 | 2.27854200 | −0.41485000 |
| H | −2.83435100 | 2.96971700 | −0.53591200 |
| C | −0.68365100 | 2.68637900 | −0.48936800 |
| C | 0.22554500 | 1.62467600 | −0.30544100 |
| C | 1.73800600 | −0.36955400 | 0.07373400 |
| C | 2.36042200 | 0.86314300 | −0.16725800 |
| C | 3.73307800 | 1.07251600 | −0.21344100 |
| H | 4.12422300 | 2.06464600 | −0.40583300 |
| C | 4.57178800 | −0.01933600 | −0.00641800 |
| H | 5.64762400 | 0.11004600 | −0.03567200 |
| C | 4.01375500 | −1.27422700 | 0.23795800 |
| C | 2.62721300 | −1.44051200 | 0.27588600 |
| H | 2.23103400 | −2.43100900 | 0.46795400 |
| O | 1.52785200 | 1.95313900 | −0.37231400 |
| H | −1.98637500 | −2.68826000 | 0.43790300 |
| Os | −0.42274100 | −0.30331600 | 0.06625900 |
| H | 0.09890600 | −1.80967600 | 0.42672300 |
| H | 4.65988700 | −2.13043100 | 0.40065600 |
| P | −0.47870200 | 0.10480900 | 2.39159400 |
| H | −0.70718000 | 1.43777700 | 2.84627300 |
| H | −1.47132900 | −0.56033800 | 3.16756300 |

| | | | |
|---|---|---|---|
| H | 0.66871900 | −0.19697000 | 3.18282900 |
| P | −0.42625600 | −0.90823600 | −2.21560400 |
| H | −0.13846400 | −2.25893800 | −2.56501400 |
| H | −1.63757100 | −0.74720700 | −2.95002000 |
| H | 0.46805000 | −0.26274800 | −3.12050900 |
| H | −4.23581100 | −1.73693900 | 0.22097600 |
| H | −0.35567500 | 3.70459000 | −0.67046100 |

**Complex 3'**

| | | | |
|---|---|---|---|
| C | −5.99235700 | 2.03169600 | 0.83933200 |
| C | −7.34979500 | 2.01797500 | 1.06582100 |
| C | −7.98602800 | 0.77186600 | 0.83292400 |
| H | −9.05587600 | 0.61799100 | 0.96669200 |
| C | −7.12817500 | −0.22135700 | 0.40857400 |
| C | −7.52031000 | −1.54160000 | 0.09750100 |
| H | −8.55017000 | −1.88182600 | 0.19468700 |
| C | −6.50585900 | −2.36828300 | −0.34567800 |
| C | −5.25619000 | −1.71731900 | −0.39537200 |
| C | −3.07404200 | −0.42994400 | −0.40114500 |
| C | −3.02856200 | −1.76370800 | −0.82629200 |
| C | −1.87899200 | −2.42182200 | −1.24126200 |
| H | −1.93033800 | −3.45516500 | −1.56401200 |
| C | −0.67930300 | −1.71989900 | −1.24319100 |
| H | 0.22503700 | −2.20740100 | −1.58748900 |
| C | −0.63934200 | −0.37888000 | −0.83112600 |
| C | −1.83669700 | 0.23360100 | −0.41993000 |
| H | −1.78878800 | 1.26157200 | −0.08135000 |
| O | −4.22412500 | −2.46530700 | −0.82287600 |
| Os | −5.04066000 | 0.25843100 | 0.17907100 |

| | | | |
|---|---|---|---|
| H | −5.48129200 | 2.97648100 | 1.00845800 |
| H | −3.93417800 | 1.43833500 | 0.41049000 |
| C | 5.99236100 | −2.03173600 | 0.83922300 |
| C | 7.34979000 | −2.01800700 | 1.06576700 |
| C | 7.98601400 | −0.77187600 | 0.83296400 |
| H | 9.05585500 | −0.61799500 | 0.96677800 |
| C | 7.12816400 | 0.22135800 | 0.40863200 |
| C | 7.52029700 | 1.54161600 | 0.09762200 |
| H | 8.55015100 | 1.88184500 | 0.19484500 |
| C | 6.50585100 | 2.36830800 | −0.34555300 |
| C | 5.25618700 | 1.71733700 | −0.39530000 |
| C | 3.07404100 | 0.42996000 | −0.40113500 |
| C | 3.02856100 | 1.76373900 | −0.82623100 |
| C | 1.87899100 | 2.42187000 | −1.24117600 |
| H | 1.93033800 | 3.45522500 | −1.56388800 |
| C | 0.67930100 | 1.71994800 | −1.24313000 |
| H | −0.22503800 | 2.20746300 | −1.58740900 |
| C | 0.63934000 | 0.37891500 | −0.83111200 |
| C | 1.83669500 | −0.23358200 | −0.41994000 |
| H | 1.78878500 | −1.26156700 | −0.08139900 |
| O | 4.22412400 | 2.46533900 | −0.82278600 |
| H | 5.48130400 | −2.97653800 | 1.00827400 |
| Os | 5.04066000 | −0.25844200 | 0.17904400 |
| H | 3.93418700 | −1.43837100 | 0.41036500 |
| P | −4.66051900 | −0.37191800 | 2.42241100 |
| H | −3.32272200 | −0.56440600 | 2.87730500 |
| H | −5.12875300 | 0.49375600 | 3.45271600 |
| H | −5.22504300 | −1.59391800 | 2.89588400 |
| P | −5.38662800 | 1.08889800 | −2.00288000 |

| | | | |
|---|---|---|---|
| H | −6.72077300 | 1.39337100 | −2.40353100 |
| H | −4.76564400 | 2.31663300 | −2.37230400 |
| H | −4.99170900 | 0.30717700 | −3.12913700 |
| P | 5.38664900 | −1.08877400 | −2.00295300 |
| H | 6.72082200 | −1.39299800 | −2.40370300 |
| H | 4.76586300 | −2.31660800 | −2.37237600 |
| H | 4.99152000 | −0.30708500 | −3.12915900 |
| P | 4.66051400 | 0.37176500 | 2.42242500 |
| H | 3.32270000 | 0.56383900 | 2.87744200 |
| H | 5.12910400 | −0.49378800 | 3.45267100 |
| H | 5.22470700 | 1.59392800 | 2.89586900 |
| H | 6.62892000 | 3.40765400 | −0.63158700 |
| H | −6.62893000 | −3.40761600 | −0.63176000 |
| H | −7.90021800 | 2.89394300 | 1.40275900 |
| H | 7.90021300 | −2.89398600 | 1.40267600 |

**Complex 4'**

| | | | |
|---|---|---|---|
| C | −6.19776100 | −1.82627800 | −0.06343900 |
| H | −5.96859400 | −2.88900300 | −0.08816000 |
| C | −7.53038700 | −1.48427400 | −0.09403600 |
| C | −7.79363700 | −0.09062200 | −0.06328900 |
| H | −8.80091800 | 0.32306700 | −0.08717500 |
| C | −6.65825000 | 0.69097900 | −0.01438400 |
| C | −6.65651800 | 2.10301500 | 0.01231700 |
| H | −7.57544000 | 2.68726000 | 0.01893900 |
| C | −5.40594800 | 2.68960100 | 0.02268900 |
| C | −4.35981900 | 1.74322500 | 0.00835200 |
| C | 2.58859600 | 0.07483500 | 0.01145300 |
| C | −2.13295800 | 1.27323700 | 0.01008200 |

| | | | |
|---|---|---|---|
| C | −0.82129500 | 1.67079700 | 0.01160300 |
| H | −0.56962600 | 2.72557000 | 0.01237400 |
| C | 0.19788700 | 0.68724700 | 0.01200500 |
| C | 1.57989100 | 1.02479500 | 0.01222100 |
| H | 1.83231000 | 2.07979300 | 0.01208500 |
| O | −3.11609400 | 2.25142000 | 0.01012400 |
| Os | −4.74164800 | −0.28874900 | 0.00701900 |
| H | −4.01961800 | −1.75246700 | 0.08117200 |
| C | 6.19776100 | 1.82627700 | −0.06344200 |
| H | 5.96859400 | 2.88900300 | −0.08816300 |
| C | 7.53038700 | 1.48427300 | −0.09403700 |
| C | 7.79363700 | 0.09062100 | −0.06328800 |
| H | 8.80091800 | −0.32306800 | −0.08717300 |
| C | 6.65825000 | −0.69097900 | −0.01438200 |
| C | 6.65651800 | −2.10301600 | 0.01232300 |
| H | 7.57544000 | −2.68726100 | 0.01894700 |
| C | 5.40594800 | −2.68960100 | 0.02269600 |
| C | 4.35981900 | −1.74322600 | 0.00835400 |
| C | −2.58859600 | −0.07483600 | 0.01145400 |
| C | 2.13295800 | −1.27323800 | 0.01008400 |
| C | 0.82129500 | −1.67079700 | 0.01160700 |
| H | 0.56962600 | −2.72557100 | 0.01238100 |
| C | −0.19788700 | −0.68724800 | 0.01200700 |
| C | −1.57989100 | −1.02479500 | 0.01222400 |
| H | −1.83231000 | −2.07979300 | 0.01209100 |
| O | 3.11609400 | −2.25142000 | 0.01012800 |
| Os | 4.74164800 | 0.28874900 | 0.00701900 |
| H | 4.01961800 | 1.75246700 | 0.08116600 |
| P | −4.70038700 | −0.44892100 | −2.34752900 |

| | | | |
|---|---|---|---|
| H | −4.24744800 | −1.66224000 | −2.94086600 |
| H | −5.93081300 | −0.30828900 | −3.05437700 |
| H | −3.90646700 | 0.46287300 | −3.10506400 |
| P | −4.80108600 | −0.33505600 | 2.36646500 |
| H | −5.20156500 | 0.84282700 | 3.06547300 |
| H | −5.67360600 | −1.26632000 | 3.00033600 |
| H | −3.60449900 | −0.61681700 | 3.08963900 |
| P | 4.80108000 | 0.33506300 | 2.36646400 |
| H | 5.20156300 | −0.84281500 | 3.06547800 |
| H | 5.67359500 | 1.26633300 | 3.00033500 |
| H | 3.60449000 | 0.61682100 | 3.08963400 |
| P | 4.70039200 | 0.44891500 | −2.34753000 |
| H | 4.24745300 | 1.66223300 | −2.94087100 |
| H | 5.93081900 | 0.30828300 | −3.05437400 |
| H | 3.90647400 | −0.46288000 | −3.10506500 |
| H | 5.21882300 | −3.75821900 | 0.03790500 |
| H | −5.21882300 | 3.75821900 | 0.03789500 |
| H | −8.32847900 | −2.22263900 | −0.13431200 |
| H | 8.32847900 | 2.22263800 | −0.13431400 |

**Complex 2"**

| | | | |
|---|---|---|---|
| C | 0.390570172 | 1.244376858 | −0.011746589 |
| C | −0.939044528 | 0.864739453 | 0.023138928 |
| C | −1.217569575 | −0.541048616 | 0.027795078 |
| H | −2.218566970 | −0.965585277 | 0.056301996 |
| C | −0.062468106 | −1.280934748 | 0.000552712 |
| C | −0.062468106 | −2.704186773 | 0.000552712 |
| H | −0.975250333 | −3.291847202 | 0.001514083 |
| C | 1.176405023 | −3.301134759 | 0.003569812 |

| | | | |
|---|---|---|---|
| C | 2.238342488 | −2.329020433 | 0.000552712 |
| C | 3.979643868 | −0.474111200 | −0.024385971 |
| C | 4.439516616 | −1.794374820 | 0.003478819 |
| C | 5.769908338 | −2.187821782 | 0.017589933 |
| H | 6.025785827 | −3.239907282 | 0.037450111 |
| C | 6.738032572 | −1.188972232 | 0.006098502 |
| H | 7.788358595 | −1.453431560 | 0.016040055 |
| C | 6.345432216 | 0.150047807 | −0.018593504 |
| C | 4.993738364 | 0.499497306 | −0.032341431 |
| H | 4.732115758 | 1.550751892 | −0.051710338 |
| C | 1.381089478 | −4.781979473 | 0.012288422 |
| C | 0.267044138 | −6.871653236 | −0.003446904 |
| H | 0.810122954 | −7.227249739 | −0.879186889 |
| H | 0.769161808 | −7.219486539 | 0.899450446 |
| H | −0.765490385 | −7.210874592 | −0.025758716 |
| O | 3.467410309 | −2.791435225 | 0.016500368 |
| O | 2.447767826 | −5.341762548 | 0.037654599 |
| O | 0.195338210 | −5.428174170 | −0.011414124 |
| H | 0.610022130 | 2.309397248 | −0.011667013 |
| Os | 1.828512035 | −0.287132948 | −0.039740128 |
| H | 2.559503217 | 1.166532395 | −0.137049210 |
| H | 7.097300361 | 0.931040969 | −0.027995109 |
| P | −2.239523681 | 2.094470148 | 0.056327703 |
| H | −3.150129793 | 2.061738159 | −1.033104244 |
| H | −3.097552717 | 2.057134228 | 1.187510429 |
| H | −1.689718476 | 3.394661534 | 0.045866292 |
| P | 1.904592323 | −0.290921273 | −2.421666541 |
| H | 1.290313142 | −1.365676277 | −3.126145412 |
| H | 1.312116354 | 0.799401704 | −3.118322344 |

| | | | |
|---|---|---|---|
| H | 3.188009581 | −0.301032003 | −3.033057052 |
| P | 2.007141454 | −0.120604401 | 2.331062844 |
| H | 2.525338100 | 1.088938806 | 2.869572499 |
| H | 0.830870516 | −0.244555332 | 3.125776583 |
| H | 2.844301522 | −1.053253147 | 3.002432443 |

**Complex 3"**

| | | | |
|---|---|---|---|
| C | 8.229218520 | −9.811607516 | −2.896115190 |
| C | 8.775572920 | −11.037327401 | −3.226944878 |
| C | 8.096393043 | −12.204695595 | −2.747427043 |
| H | 8.425483539 | −13.223852318 | −2.936492629 |
| C | 6.985722785 | −11.875144494 | −2.013270242 |
| C | 6.139934115 | −12.854079899 | −1.420653519 |
| H | 6.311658888 | −13.920877855 | −1.526082026 |
| C | 5.077247563 | −12.363661850 | −0.698164762 |
| C | 5.059208557 | −10.926834954 | −0.684999316 |
| C | 5.166455289 | −8.383454483 | −0.776513649 |
| C | 4.146330229 | −8.966221213 | −0.018629833 |
| C | 3.183040937 | −8.268940428 | 0.694386758 |
| H | 2.434871566 | −8.805180536 | 1.265017113 |
| C | 3.228168544 | −6.881980868 | 0.663708864 |
| H | 2.507789026 | −6.315925076 | 1.240980866 |
| C | 4.217521580 | −6.214398571 | −0.076697462 |
| C | 5.164303211 | −6.979459734 | −0.783046279 |
| H | 5.908223481 | −6.453827306 | −1.368784988 |
| C | 4.060198714 | −13.230354551 | −0.025127189 |
| C | 3.553892379 | −15.459171198 | 0.599357405 |
| H | 2.610328827 | −15.469897793 | 0.053729798 |
| H | 3.369392375 | −15.191739298 | 1.639657412 |

| | | | |
|---|---|---|---|
| H | 4.051104045 | −16.423148121 | 0.530886251 |
| O | 4.104824894 | −10.352953724 | 0.017297959 |
| O | 3.009891105 | −12.848075014 | 0.426079239 |
| O | 4.468700734 | −14.513986299 | −0.003728569 |
| Os | 6.483838856 | −9.816932661 | −1.720164645 |
| H | 8.740132108 | −8.920034517 | −3.251329616 |
| H | 6.887274927 | −8.286660235 | −2.115131608 |
| C | −0.635496415 | −1.138499979 | 0.011767542 |
| C | −1.273299206 | 0.086517598 | 0.065128368 |
| C | −0.443994955 | 1.255092656 | 0.039137002 |
| H | −0.822544972 | 2.273869408 | 0.078140675 |
| C | 0.885937194 | 0.927262340 | −0.031477166 |
| C | 1.916805586 | 1.907623334 | −0.064451597 |
| H | 1.714456217 | 2.974194412 | −0.052204514 |
| C | 3.201475875 | 1.418884512 | −0.114869955 |
| C | 3.226034415 | −0.017874541 | −0.107749678 |
| C | 3.089324845 | −2.561449163 | −0.105156183 |
| C | 4.359272888 | −1.976734294 | −0.107073276 |
| C | 5.558811307 | −2.672160963 | −0.105156183 |
| H | 6.498848433 | −2.134424786 | −0.095233200 |
| C | 5.506425475 | −4.059177641 | −0.096426196 |
| H | 6.429796503 | −4.623645330 | −0.059412775 |
| C | 4.271738897 | −4.728676325 | −0.098454917 |
| C | 3.089324845 | −3.965459155 | −0.105156183 |
| H | 2.143686322 | −4.492673152 | −0.129824551 |
| C | 4.417973304 | 2.287058379 | −0.185098810 |
| C | 5.193850036 | 4.517624889 | 0.006021655 |
| H | 5.963601814 | 4.253639867 | 0.730987955 |
| H | 5.624644201 | 4.525723548 | −0.995222027 |

| | | | |
|---|---|---|---|
| H | 4.752802452 | 5.481744876 | 0.244991785 |
| O | 4.411862948 | −0.589904343 | −0.109556262 |
| O | 5.530391089 | 1.905439235 | −0.449231177 |
| O | 4.101292868 | 3.571070068 | 0.071863170 |
| H | −1.256051167 | −2.030935106 | 0.035921266 |
| Os | 1.466853381 | −1.130372616 | −0.084555748 |
| H | 0.909881606 | −2.661877581 | −0.153781514 |
| P | 10.268727868 | −11.147151842 | −4.214176781 |
| H | 10.731204646 | −9.857750170 | −4.555549266 |
| H | 11.368433765 | −11.793064143 | −3.590591089 |
| H | 10.138989213 | −11.843030800 | −5.444769275 |
| P | 5.089775673 | −9.789225390 | −3.652212573 |
| H | 3.992070557 | −8.885149174 | −3.659570100 |
| H | 5.678704277 | −9.462434996 | −4.905630731 |
| H | 4.417443359 | −10.987923904 | −4.025074729 |
| P | 7.855776802 | −9.604005087 | 0.218910012 |
| H | 8.862785680 | −10.582526899 | 0.457487106 |
| H | 8.640786016 | −8.425572268 | 0.350295648 |
| H | 7.220011766 | −9.603698163 | 1.490864680 |
| P | 1.521434867 | −1.331384786 | 2.291180142 |
| H | 0.857510773 | −0.347450121 | 3.078310148 |
| H | 0.967131932 | −2.505679556 | 2.870842695 |
| H | 2.790383203 | −1.331167848 | 2.932916769 |
| P | 1.434594858 | −1.169580275 | −2.466678108 |
| H | 2.306363488 | −2.081896465 | −3.122468281 |
| H | 0.212745695 | −1.492314640 | −3.120618160 |
| H | 1.759230658 | 0.023889330 | −3.172480882 |
| P | −3.060842566 | 0.194142809 | 0.161814669 |
| H | −3.573118517 | 0.845511800 | 1.314507051 |

| | | | |
|---|---|---|---|
| H | −3.691191684 | 0.883315986 | −0.907358314 |
| H | −3.633754795 | −1.096081211 | 0.170320373 |

**Complex 4"**

| | | | |
|---|---|---|---|
| C | 1.302984202 | 0.006709213 | −0.014422958 |
| H | 2.385338188 | −0.094190554 | −0.035476670 |
| C | 0.551370020 | −1.153174279 | −0.038848705 |
| C | −0.874113729 | −1.003945641 | −0.014975305 |
| H | −1.575542474 | −1.834905270 | −0.034305106 |
| C | −1.242461035 | 0.316580840 | 0.024779324 |
| C | −2.602821057 | 0.733043097 | 0.049584479 |
| H | −3.432010850 | 0.032570679 | 0.060894005 |
| C | −2.809835866 | 2.093248574 | 0.053116577 |
| C | −1.569388052 | 2.821386650 | 0.039338173 |
| C | 2.103606102 | 8.929283943 | 0.038029240 |
| C | −0.428048959 | 4.783043058 | 0.034922470 |
| C | −0.428048959 | 6.152197626 | 0.034922470 |
| H | −1.365112802 | 6.696461219 | 0.034936179 |
| C | 0.813747752 | 6.831359538 | 0.034617602 |
| C | 0.895471801 | 8.252315285 | 0.036500255 |
| H | −0.038944709 | 8.801977269 | 0.038301960 |
| C | −4.166335538 | 2.723920872 | 0.065352967 |
| C | −6.490283317 | 2.267014425 | 0.148307107 |
| H | −6.651887202 | 2.911652880 | 1.012201094 |
| H | −7.111133540 | 1.377050569 | 0.209285447 |
| H | −6.699999963 | 2.823504274 | −0.765147158 |
| O | −1.655802480 | 4.135646479 | 0.035046670 |
| O | −5.127585092 | 1.781770675 | 0.135596491 |
| Os | 0.262220540 | 1.833829866 | 0.043467646 |

| | | | |
|---|---|---|---|
| H | 1.869096202 | 2.100535786 | 0.113221178 |
| O | −4.386874987 | 3.908253606 | 0.017312771 |
| C | 1.520959036 | 12.869968442 | −0.011893283 |
| H | 0.438572873 | 12.970875447 | −0.031166558 |
| C | 2.272535376 | 14.029860380 | −0.037058522 |
| C | 3.698054454 | 13.880618423 | −0.015537937 |
| H | 4.399453586 | 14.711584350 | −0.035658125 |
| C | 4.066461836 | 12.560074619 | 0.023091409 |
| C | 5.426859488 | 12.143605884 | 0.045546239 |
| H | 6.256065845 | 12.844074114 | 0.055789706 |
| C | 5.633882512 | 10.783398881 | 0.048248136 |
| C | 4.393413317 | 10.055265361 | 0.036144550 |
| C | 0.720418198 | 3.947369615 | 0.038082483 |
| C | 3.252066371 | 8.093612298 | 0.032700257 |
| C | 3.252065529 | 6.724456926 | 0.032127257 |
| H | 4.189129313 | 6.180194238 | 0.030434547 |
| C | 2.010270615 | 6.045294409 | 0.033505124 |
| C | 1.928549244 | 4.624337963 | 0.034922470 |
| H | 2.862966362 | 4.074675956 | 0.035011764 |
| C | 6.990400748 | 10.152725971 | 0.058169739 |
| C | 9.314496280 | 10.609644329 | 0.136795538 |
| H | 9.522548824 | 10.052897317 | −0.776881543 |
| H | 9.935459644 | 11.499622847 | 0.196393152 |
| H | 9.477669223 | 9.965248911 | 1.000574937 |
| O | 4.479819285 | 8.741007876 | 0.031152057 |
| O | 7.951779121 | 11.094889812 | 0.126428162 |
| Os | 2.561812252 | 11.042820452 | 0.043573074 |
| H | 0.955048990 | 10.776085601 | 0.115750495 |
| O | 7.210853164 | 8.968383786 | 0.009945970 |

| | | | |
|---|---|---|---|
| P | 1.338747790 | −2.763696647 | −0.092937806 |
| H | 1.054380452 | −3.620403384 | 1.002751885 |
| H | 1.019320833 | −3.562585416 | −1.222124200 |
| H | 2.743541562 | −2.625282352 | −0.111215489 |
| P | 1.485073997 | 15.640406349 | −0.089211385 |
| H | 1.771131620 | 16.496626468 | 1.006419220 |
| H | 1.802760227 | 16.439795384 | −1.218534267 |
| H | 0.080254124 | 15.501998596 | −0.105379692 |
| P | 0.423167873 | 1.941303787 | −2.333419035 |
| H | 1.722668369 | 2.019069041 | −2.905309313 |
| H | −0.110137692 | 0.872108134 | −3.108924995 |
| H | −0.189554109 | 3.040551180 | −2.995676212 |
| P | 0.311273002 | 1.866230668 | 2.427604541 |
| H | −0.900020237 | 1.630025792 | 3.138154728 |
| H | 1.150589934 | 0.932593288 | 3.096932915 |
| H | 0.734231489 | 3.067306821 | 3.060622931 |
| P | 2.516517317 | 11.009407772 | 2.427770592 |
| H | 3.728839046 | 11.245730435 | 3.136527095 |
| H | 1.677925470 | 11.942472720 | 3.098802980 |
| H | 2.094960195 | 9.807920882 | 3.060943423 |
| P | 2.397104152 | 10.936355003 | −2.333100651 |
| H | 1.096694030 | 10.859042805 | −2.902979941 |
| H | 2.929368525 | 12.005783001 | −3.109002343 |
| H | 3.008600705 | 9.837278714 | −2.996774910 |

**Complex 4''$^{-}$**

| | | | |
|---|---|---|---|
| C | 5.91023 | 2.37198 | −0.00605 |
| H | 5.57614 | 3.40873 | −0.00397 |

| | | | |
|---|---|---|---|
| C | 7.26553 | 2.12992 | −0.01768 |
| C | 7.72381 | 0.77219 | −0.01855 |
| H | 8.77294 | 0.47983 | −0.02191 |
| C | 6.65798 | −0.1204 | −0.00562 |
| C | 6.79962 | −1.50879 | 0.00339 |
| H | 7.76548 | −2.00607 | 0.00091 |
| C | 5.57385 | −2.24654 | 0.01509 |
| C | 4.46325 | −1.42535 | 0.01387 |
| C | −2.57589 | −0.29809 | −0.00912 |
| C | 2.21445 | −1.10992 | 0.01307 |
| C | 0.93898 | −1.60812 | 0.01114 |
| H | 0.78039 | −2.68208 | 0.01472 |
| C | −0.15392 | −0.7104 | 0.00367 |
| C | −1.4996 | −1.16536 | −0.00206 |
| H | −1.66195 | −2.23994 | −0.00244 |
| C | 6.81396 | −5.67108 | 0.04608 |
| H | 6.32247 | −6.07113 | 0.93737 |
| H | 7.87359 | −5.9294 | 0.04996 |
| H | 6.32475 | −6.08796 | −0.83872 |
| O | 3.23923 | −2.00005 | 0.02051 |
| O | 6.76505 | −4.25153 | 0.03258 |
| Os | 4.65533 | 0.67867 | 0.00333 |
| H | 3.78333 | 2.07078 | 0.00313 |
| P | 4.68194 | 0.61744 | −2.31773 |
| P | 4.69104 | 0.63111 | 2.32467 |
| P | 8.37094 | 3.49057 | −0.04817 |
| C | −5.97488 | −2.31192 | −0.04498 |
| H | −5.65708 | −3.3541 | −0.07686 |
| C | −7.33405 | −2.06732 | −0.0093 |

| | | | |
|---|---|---|---|
| C | −7.73293 | −0.68513 | 0.02669 |
| H | −8.76827 | −0.34664 | 0.05069 |
| C | −6.64802 | 0.13916 | 0.01854 |
| C | −6.78678 | 1.56414 | 0.03624 |
| H | −7.75502 | 2.05878 | 0.0587 |
| C | −5.6168 | 2.26794 | 0.01892 |
| C | −4.46864 | 1.39052 | −0.00257 |
| C | 2.55386 | 0.27914 | 0.00637 |
| C | −2.23407 | 1.07534 | −0.00608 |
| C | −0.96691 | 1.5853 | −0.00336 |
| H | −0.80694 | 2.65921 | −0.00203 |
| C | 0.1238 | 0.68601 | −0.00002 |
| C | 1.47371 | 1.13782 | 0.00087 |
| H | 1.63505 | 2.21232 | −0.0038 |
| C | −5.54087 | 3.75687 | 0.02219 |
| C | −6.8102 | 5.72269 | 0.12618 |
| H | −6.38164 | 6.12087 | −0.79638 |
| H | −7.86499 | 5.98276 | 0.20412 |
| H | −6.25303 | 6.11794 | 0.97861 |
| O | −3.30254 | 1.96637 | −0.00126 |
| O | −6.76875 | 4.29361 | 0.12196 |
| P | −8.48131 | −3.39972 | 0.00009 |
| O | −4.52906 | 4.40919 | −0.05665 |
| Os | −4.6963 | −0.66763 | −0.02398 |
| H | −3.8285 | −2.05799 | −0.05696 |
| P | −4.47546 | −0.77839 | 2.31008 |
| P | −4.50242 | −0.69176 | −2.36251 |
| H | 9.19908 | 3.61044 | −1.17537 |
| H | 9.30053 | 3.5684 | 1.00083 |

| | | | |
|---|---|---|---|
| H | 7.67917 | 4.70246 | 0.00546 |
| H | 5.48976 | 1.53814 | −3.0154 |
| H | 3.48459 | 0.79169 | −3.04048 |
| H | 5.13705 | −0.56737 | −2.92787 |
| H | 5.45166 | 1.59407 | 3.01843 |
| H | 3.48698 | 0.74807 | 3.04784 |
| H | 5.206 | −0.52701 | 2.93891 |
| H | −3.91923 | 0.33524 | 2.96098 |
| H | −3.65013 | −1.78966 | 2.82504 |
| H | −5.61953 | −0.96818 | 3.10787 |
| H | −3.65495 | 0.26851 | −2.93864 |
| H | −3.98493 | −1.85215 | −2.95944 |
| H | −5.648 | −0.50947 | −3.15971 |
| H | −7.80929 | −4.61914 | −0.09928 |
| H | −9.41926 | −3.41314 | −1.04116 |
| H | −9.28269 | −3.52235 | 1.14358 |
| C | 5.5163 | −3.71948 | 0.0272 |
| O | 4.52411 | −4.41622 | 0.03305 |