Electronic Supplementary Information

For

Hetero-Carbolong Chemistry: Experimental and Theoretical Studies of Diaza-Metallapentalenes

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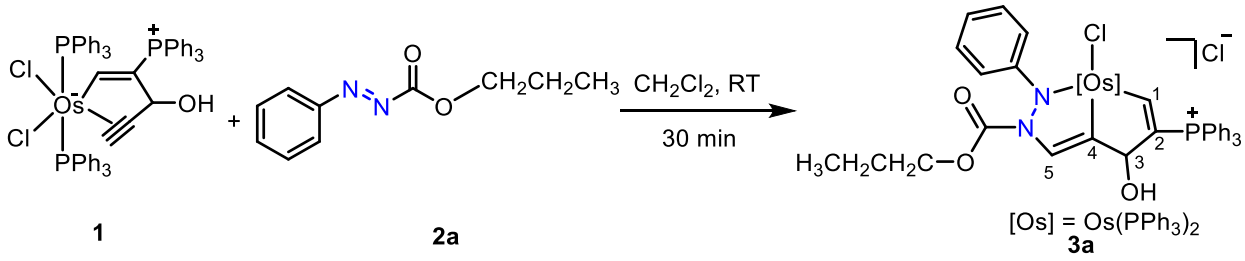
1. General Information

All syntheses were performed under an N_2 atmosphere using standard Schlenk techniques, unless otherwise stated. Diethyl ether was distilled from sodium/benzophenone and dichloromethane from calcium hydride under N_2 prior to use. The starting material complex **1** and complex **2** were synthesized according to previously published procedures.[S1, S2] Other reagents were used as received from commercial sources without further purification. NMR spectroscopic experiments were performed on Bruker AVIII-400 (^{1}H, 400.1, ^{13}C, 100.6, ^{31}P, 161.9 MHz) spectrometer or a Bruker Ascend III 600 (^{1}H, 600.1, ^{13}C, 150.9, ^{31}P, 242.9 MHz) spectrometer at room temperature. The ^{1}H NMR and ^{13}C NMR chemical shifts (δ) are reported relative to tetramethylsilane, and the ^{31}P NMR chemical shifts are relative to 85% H_3PO_4. Two-dimensional is abbreviated as HMBC (heteronuclear multiple bond coherence) and HSQC (heteronuclear single quantum coherence). The absolute values of the coupling constants are given in hertz (Hz). Multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), multiplet (m), and broad (br). High-resolution mass spectrometry (HRMS) experiments were performed on a Thermo Scientific Q Exactive instrument. Absorption spectra were recorded on a UV-2600i UV-VIS spectrophotometer.

2. Synthesis and Characterization

Synthesis and characterization of complex 3a:

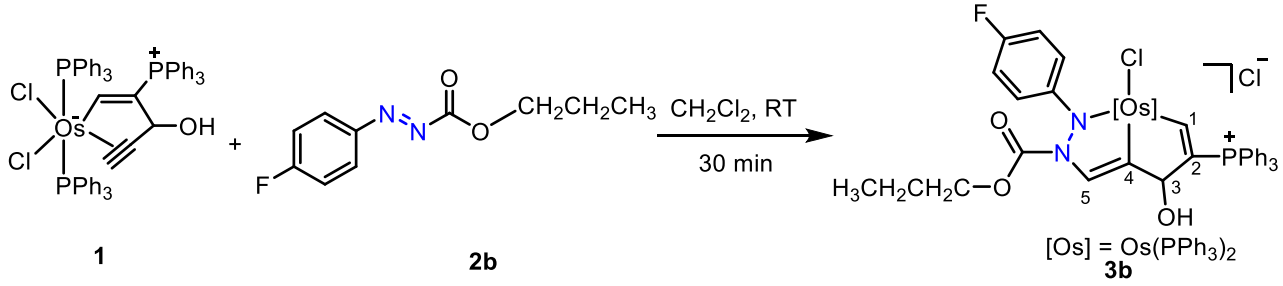


1 **2a** **3a**

To a dichloromethane (10 mL) solution of **1** (1.000 g, 0.87 mmol) was added **2a** (0.336g, 1.75 mmol). The reaction mixture was stirred at room temperature for 30 min to give a brown solution. Then, the solvent of the reaction mixture was removed under vacuum, and the residue was washed with tetrahydrofuran (3 × 2 mL) and diethyl ether (3 × 10 mL) to give a brown precipitate, which was collected by filtration and dried under vacuum. Yield, 710 mg, 61%.

^{1}H NMR (600.1 MHz, CD_2Cl_2/CD_3OD = 4/1, ppm): δ = 31.09 (d, $J_{P\text{-}H}$ = 24.0 Hz, 1H, H1), 7.73-6.28 (m, 49H, P*Ph*$_3$ and *Ph*), 5.87 (t, $J_{H\text{-}H}$ = 7.3 Hz, 1H, *Ph*), 4.83 (s, 1H, H5), 4.14-4.10 (m, 1H, $CO_2CH_2CH_2CH_3$), 4.04-4.00 (m, 2H, $CO_2CH_2CH_2CH_3$ and H3), 1.41-1.38 (m, 2H, $CO_2CH_2CH_2CH_3$), 0.65 (t, $J_{H\text{-}H}$ = 7.3 Hz, 3H, $CO_2CH_2CH_2CH_3$); ^{31}P{^{1}H} NMR (242.9 MHz, CD_2Cl_2/CD_3OD = 4/1, ppm): δ = 7.1 (s, C*P*Ph$_3$), -4.5 (d, $J_{P\text{-}P}$ = 265.0 Hz, Os*P*Ph$_3$), -23.1 (d, $J_{P\text{-}P}$ = 265.0 Hz, Os*P*Ph$_3$); ^{13}C{^{1}H} NMR (150.9 MHz, CD_2Cl_2/CD_3OD = 4/1, plus ^{13}C-dept 135, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC, ppm): δ = 212.8 (br, C4), 180.1 (br, C1), 158.8 (s, $CO_2CH_2CH_2CH_3$), 156.0 (s, *Ph*), 147.2 (s, C5), 116.6 (dd, $J_{P\text{-}C}$ = 70.7 Hz, $J_{P\text{-}C}$ = 2.5 Hz, C2), 85.8 (br, C3), 72.6 (s, $CO_2CH_2CH_2CH_3$), 22.4 (s, $CO_2CH_2CH_2CH_3$), 10.6 (s, $CO_2CH_2CH_2CH_3$); HRMS (ESI): m/z calcd for $[C_{69}H_{61}ClN_2OsO_3P_3]^+$, 1285.3193, found: 1285.3140.

Synthesis and characterization of complex 3b:

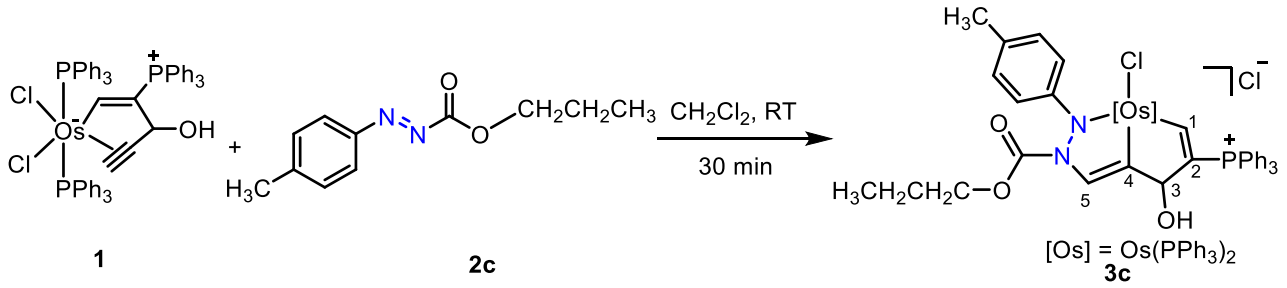


To a dichloromethane (10 mL) solution of **1** (1.000 g, 0.87 mmol) was added **2b** (0.370g, 1.76 mmol). The reaction mixture was stirred at room temperature for 30 min to give a brown solution. Then, the solvent of the reaction mixture was removed under vacuum, and the residue was washed with tetrahydrofuran (3 × 2 mL) and diethyl ether (3 × 10 mL) to give a brown precipitate, which was collected by filtration and dried under vacuum. Yield, 785 mg, 67%.

^{1}H NMR (600.1 MHz, CD_2Cl_2/CD_3OD = 4/1, ppm): δ = 31.76 (d, $J_{P\text{-}H}$ = 23.4 Hz, 1H, H1), 7.73-6.29 (m, 49H, P*Ph*$_3$ and *Ph*), 4.68 (s, 1H, H5), 4.20-4.16 (m, 1H, $CO_2CH_2CH_2CH_3$), 4.10-4.07 (m, 2H, $CO_2CH_2CH_2CH_3$ and H3), 1.47-1.45 (m, 2H, $CO_2CH_2CH_2CH_3$), 0.70 (t, $J_{H\text{-}H}$ = 7.1 Hz, 3H, $CO_2CH_2CH_2CH_3$); ^{31}P{^{1}H} NMR (242.9 MHz, CD_2Cl_2/CD_3OD = 4/1, ppm): δ = 7.3 (s, C*P*Ph$_3$), -4.8 (d, $J_{P\text{-}P}$ = 267.4 Hz, Os*P*Ph$_3$), -23.7 (d, $J_{P\text{-}P}$ = 267.4 Hz, Os*P*Ph$_3$); ^{13}C{^{1}H} NMR (150.9 MHz, CD_2Cl_2/CD_3OD = 4/1, plus ^{13}C-dept 135, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC, ppm): δ = 211.1 (br, C4), 178.8 (br, C1), 171.4 (s, *Ph*), 169.8 (s, *Ph*), 156.5 (s, $CO_2CH_2CH_2CH_3$), 155.8 (s, *Ph*), 147.9 (s, C5),

116.8 (d, $J_{P\text{-}C}$ = 69.2 Hz, C2), 85.5 (d, $J_{P\text{-}C}$ = 19.0 Hz, C3), 72.6 (s, $CO_2CH_2CH_2CH_3$), 22.5 (s, $CO_2CH_2CH_2CH_3$), 10.6 (s, $CO_2CH_2CH_2CH_3$); HRMS (ESI): m/z calcd for $[C_{69}H_{60}ClFN_2OsO_3P_3]^+$, 1303.3099, found, 1303.3046.

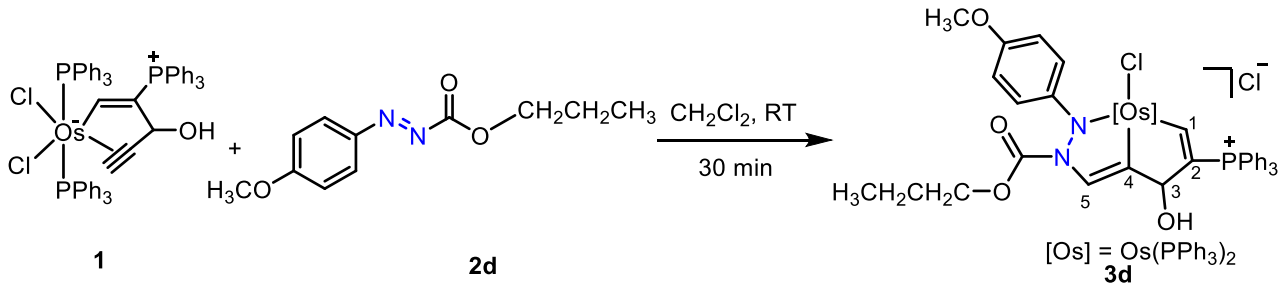
Synthesis and characterization of complex 3c:



To a dichloromethane (10 mL) solution of **1** (1.000 g, 0.87 mmol) was added **2c** (0.359g, 1.74 mmol). The reaction mixture was stirred at room temperature for 30 min to give a brown solution. Then, the solvent of the reaction mixture was removed under vacuum, and the residue was washed with tetrahydrofuran (3 × 2 mL) and diethyl ether (3 × 10 mL) to give a brown precipitate, which was collected by filtration and dried under vacuum. Yield, 810 mg, 69%.

^{1}H NMR (600.1 MHz, CD_2Cl_2/CD_3OD = 4/1, ppm): δ = 30.86 (d, $J_{P\text{-}H}$ = 23.4 Hz, 1H, H1), 7.72-6.91 (m, 49H, P*Ph*$_3$ and *Ph*), 4.58 (s, 1H, H5), 4.14-4.10 (m, 1H, $CO_2CH_2CH_2CH_3$), 4.04-4.00 (m, 1H, $CO_2CH_2CH_2CH_3$), 3.95 (br, 1H, H3), 3.11 (s, 3H, CH_3), 1.44-1.40 (br, 2H, $CO_2CH_2CH_2CH_3$), 0.65 (t, $J_{H\text{-}H}$ = 7.4 Hz, 3H, $CO_2CH_2CH_2CH_3$); ^{31}P{^{1}H} NMR (242.9 MHz, CD_2Cl_2/CD_3OD = 4/1, ppm): δ = 7.6 (s, C*P*Ph$_3$), -7.1 (d, $J_{P\text{-}P}$ = 272.7 Hz, Os*P*Ph$_3$), -27.6 (d, $J_{P\text{-}P}$ = 272.7 Hz, Os*P*Ph$_3$); ^{13}C{^{1}H} NMR (150.9 MHz, CD_2Cl_2/CD_3OD = 4/1, plus ^{13}C-dept 135, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC, ppm): δ = 207.6 (br, C4), 181.8 (br, C1), 157.0 (s, *Ph*), 156.3 (s, $CO_2CH_2CH_2CH_3$), 146.8 (s, *Ph*), 145.8 (d, $J_{P\text{-}C}$ = 2.8 Hz, C5), 116.7 (d, $J_{P\text{-}C}$ = 72.4 Hz, C2), 85.3 (d, $J_{P\text{-}C}$ = 18.7 Hz, C3), 72.3 (s, $CO_2CH_2CH_2CH_3$), 22.4 (s, $CO_2CH_2CH_2CH_3$), 19.5 (s, CH_3), 10.6 (s, $CO_2CH_2CH_2CH_3$); HRMS (ESI): m/z calcd for $[C_{69}H_{63}ClN_2OsO_3P_3]^+$, 1299.3349, found: 1299.3296

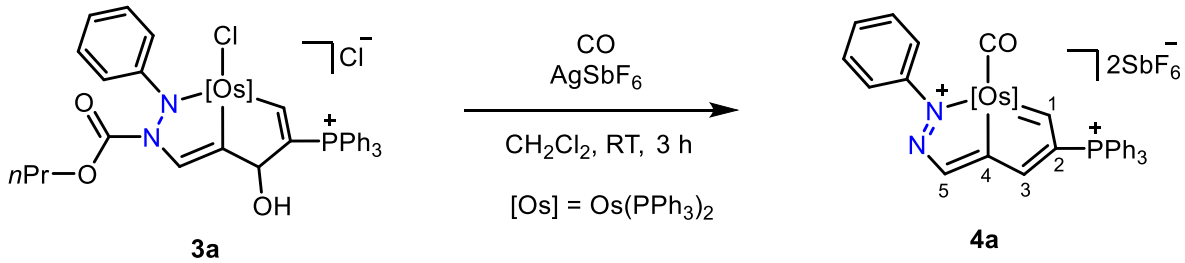
Synthesis and characterization of complex 3d:



To a dichloromethane (10 mL) solution of **1** (1.000 g, 0.87 mmol) was added **2d** (0.390g, 1.76 mmol). The reaction mixture was stirred at room temperature for 30 min to give a brown solution. Then, the solvent of the reaction mixture was removed under vacuum, and the residue was washed with tetrahydrofuran (3 × 2 mL) and diethyl ether (3 × 10 mL) to give a brown precipitate, which was collected by filtration and dried under vacuum. Yield, 790 mg, 66%.

^{1}H NMR (600.1 MHz, CD_2Cl_2/CD_3OD = 4/1, ppm): δ = 29.93 (d, $J_{P\text{-}H}$ = 20.4 Hz, 1H, H1), 7.73-6.93 (m, 47H, P*Ph*$_3$ and *Ph*), 6.61(s, $J_{H\text{-}H}$ = 8.2 Hz, 2H, *Ph*), 4.54 (s, 1H, H5), 4.11-4.09 (m, 1H, $CO_2CH_2CH_2CH_3$), 4.00 (m, 1H, $CO_2CH_2CH_2CH_3$), 3.82 (br, 1H, H3), 3.77 (s, 3H, OCH_3), 1.44 (br, 2H, $CO_2CH_2CH_2CH_3$), 0.68 (t, $J_{H\text{-}H}$ = 7.4 Hz, 3H, $CO_2CH_2CH_2CH_3$); ^{31}P{^{1}H} NMR (242.9 MHz, CD_2Cl_2/CD_3OD = 4/1, ppm): δ = 8.1 (s, C*P*Ph$_3$), -9.1 (d, $J_{P\text{-}P}$ = 276.8 Hz, Os*P*Ph$_3$), -31.1 (d, $J_{P\text{-}P}$ = 276.8 Hz, Os*P*Ph$_3$); ^{13}C{^{1}H} NMR (150.9 MHz, CD_2Cl_2/CD_3OD = 4/1, plus ^{13}C-dept 135, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC, ppm): δ = 202.2 (br, C4), 182.6 (br, C1), 167.0 (s, *Ph*), 156.5 (s, $CO_2CH_2CH_2CH_3$), 145.1 (s, *Ph*), 144.1 (s, C5), 116.8 (dd, $J_{P\text{-}C}$ = 71.7 Hz, $J_{P\text{-}C}$ = 2.5 Hz, C2), 84.9 (d, $J_{P\text{-}C}$ = 18.6 Hz, C3), 72.1 (s, $CO_2CH_2CH_2CH_3$), 56.0 (s, OCH_3), 22.5 (s, $CO_2CH_2CH_2CH_3$), 10.6 (s, $CO_2CH_2CH_2CH_3$); HRMS (ESI): m/z calcd for $[C_{69}H_{63}ClN_2OsO_4P_3]^+$, 1315.3299, found: 1315.3304

Synthesis and characterization of complex 4a:

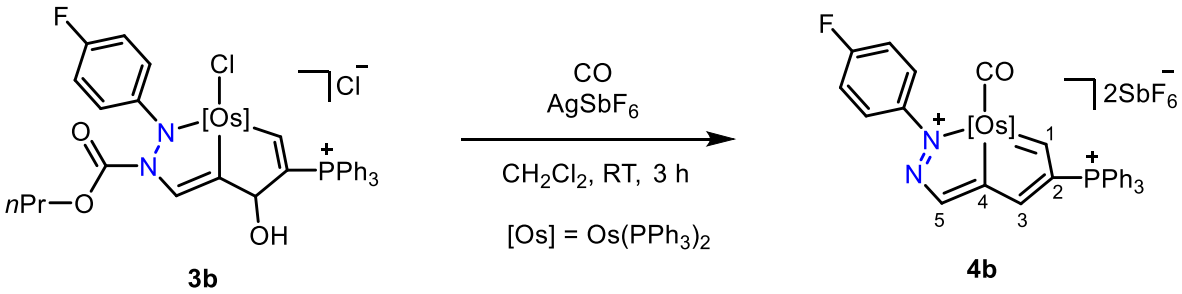


To a dichloromethane (5 mL) solution of **3a** (97 mg, 0.073 mmol) was added $AgSbF_6$ (126 mg, 0.367 mmol). The reaction mixture was stirred under CO atmosphere at room temperature for 3 h to

give a purple solution. Then, the solvent of the reaction mixture was removed under vacuum, and the residue was washed with diethyl ether (3 × 10 mL) to give a purple precipitate, which was collected by filtration and dried under vacuum. Yield, 110 mg, 92%.

^{1}H NMR (600.1 MHz, CD_2Cl_2, ppm): δ = 16.84 (dd, $J_{P\text{-}H}$ = 12.0 Hz, $J_{H\text{-}H}$ = 1.8 Hz, 1H, H1), 10.45 (s, 1H, H5), 9.78 (dd, $J_{P\text{-}H}$ = 4.5 Hz, $J_{P\text{-}H}$ = 2.2 Hz, 1H, H3), 7.91-6.83 (m, 50H, P*Ph*$_3$ and *Ph*); ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2, ppm): δ = 12.3 (t, $J_{P\text{-}P}$ = 4.4 Hz, C*P*Ph$_3$) -1.4 (d, $J_{P\text{-}P}$ = 3.8 Hz, Os*P*Ph$_3$); ^{13}C{^{1}H} NMR (150.9 MHz, CD_2Cl_2, plus ^{13}C-dept 135, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC, ppm): δ = 250.8 (br, C1), 223.3 (d, $J_{P\text{-}C}$ = 23.4 Hz, C4), 183.5 (t, $J_{P\text{-}C}$ = 10.9 Hz, *C*O), 164.8 (d, $J_{P\text{-}C}$ = 17.6 Hz, C3), 163.7 (s, C5), 163.3 (dt, $J_{P\text{-}C}$ = 63.8 Hz, $J_{P\text{-}C}$ = 3.5 Hz, C2), 160.2 (s, *Ph*); HRMS (ESI): m/z calcd for $[C_{66}H_{53}OOsN_2OP_3]^{2+}$,587.1487, found: 587.1488.

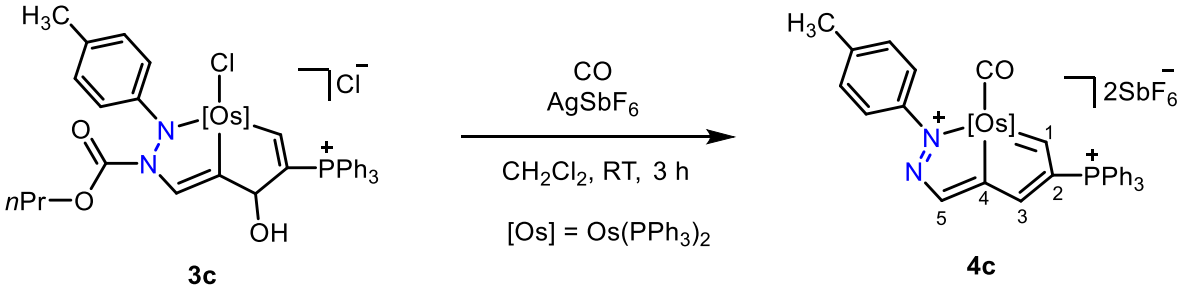
Synthesis and characterization of complex 4b:



To a dichloromethane (5 mL) solution of **3b** (93 mg, 0.070 mmol) was added $AgSbF_6$ (120 mg, 0.350 mmol). The reaction mixture was stirred under CO atmosphere at room temperature for 3 h to give a purple solution. Then, the solvent of the reaction mixture was removed under vacuum, and the residue was washed with diethyl ether (3 × 10 mL) to give a purple precipitate, which was collected by filtration and dried under vacuum. Yield, 105 mg, 91%.

^{1}H NMR (600.1 MHz, CD_2Cl_2, ppm): δ = 16.90 (dd, $J_{P\text{-}H}$ = 12.0 Hz, $J_{H\text{-}H}$ = 1.2 Hz,1H, H1), 10.48 (s, 1H, H5), 9.73 (dd, $J_{P\text{-}H}$ = 4.5 Hz, $J_{P\text{-}H}$ = 2.2 Hz, 1H, H3), 7.91-6.62 (m, 49H, P*Ph*$_3$ and *Ph*); ^{31}P{^{1}H} NMR (242.9 MHz, CD_2Cl_2, ppm): δ = 12.2 (s, C*P*Ph$_3$) -1.1 (s, Os*P*Ph$_3$); ^{13}C{^{1}H} NMR (150.9 MHz, CD_2Cl_2, plus ^{13}C-dept 135, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC, , ppm): δ = 250.9 (br, C1), 223.4 (d, $J_{P\text{-}C}$ = 23.5 Hz, C4), 183.6 (t, $J_{P\text{-}C}$ = 11.3 Hz, *C*O), 165.7 (s, *Ph*), 164.9 (d, $J_{P\text{-}C}$ = 18.0, C3), 164.0 (s, C5), 163.8 (s, *Ph*), 163.5 (dt, $J_{P\text{-}C}$ = 64.7 Hz, $J_{P\text{-}C}$ = 3.4 Hz, C2); HRMS (ESI): m/z calcd for $[C_{66}H_{52}OOsFN_2OP_3]^{2+}$, 596.1440, found: 596.1445.

Synthesis and characterization of complex 4c:

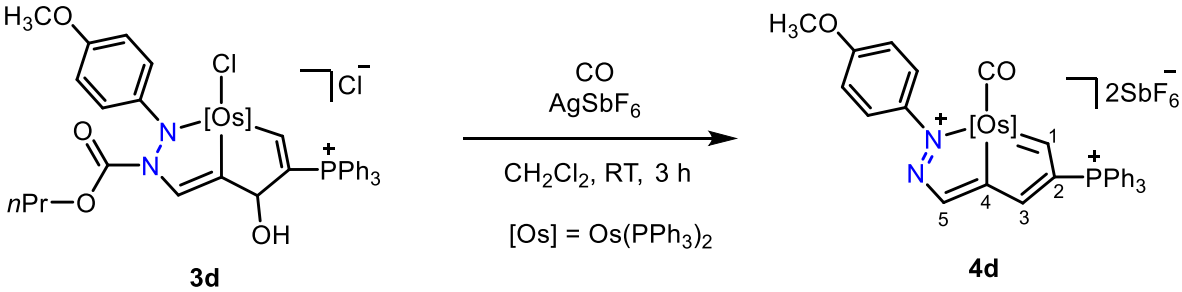


3c **4c**

To a dichloromethane (5 mL) solution of **3c** (100 mg, 0.075 mmol) was added $AgSbF_6$ (143 mg, 0.417 mmol). The reaction mixture was stirred under CO atmosphere at room temperature for 3 h to give a purple solution. Then, the solvent of the reaction mixture was removed under vacuum, and the residue was washed with diethyl ether (3 × 10 mL) to give a purple precipitate, which was collected by filtration and dried under vacuum. Yield, 122 mg, 98%.

^{1}H NMR (600.1 MHz, CD_2Cl_2, ppm): δ = 16.67 (dd, apparant d, $J_{P\text{-}H}$ = 12.0 Hz, 1H, H1), 10.37 (s, 1H, H5), 9.70 (dd, $J_{P\text{-}H}$ = 4.1 Hz, $J_{P\text{-}H}$ = 2.2 Hz, 1H, H3), 7.91-6.74 (m, 49H, P*Ph*$_3$ and *Ph*), 1.95 (s, 3H, C*H*$_3$); ^{31}P{^{1}H} NMR (242.9 MHz, CD_2Cl_2, ppm): δ = 12.2 (s, C*P*Ph$_3$) -1.3 (s, Os*P*Ph$_3$); ^{13}C{^{1}H} NMR (150.9 MHz, CD_2Cl_2, plus ^{13}C-dept 135, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC, ppm): δ = 249.5 (br, C1), 222.5 (br, C4), 183.7 (t, $J_{P\text{-}C}$ = 10.9, *C*O), 164.5 (d, $J_{P\text{-}C}$ = 18.0, C3), 163.6 (s, C5), 162.5 (dt, $J_{P\text{-}C}$ = 64.2 Hz, $J_{P\text{-}C}$ = 3.3 Hz, C2), 160.0 (s, *Ph*), 144.8 (s, *Ph*), 22.9 (s, *C*H$_3$); HRMS (ESI): m/z calcd for $[C_{67}H_{55}OOsN_2OP_3]^{2+}$, 594.1566, found: 594.1567.

Synthesis and characterization of complex 4d:



3d **4d**

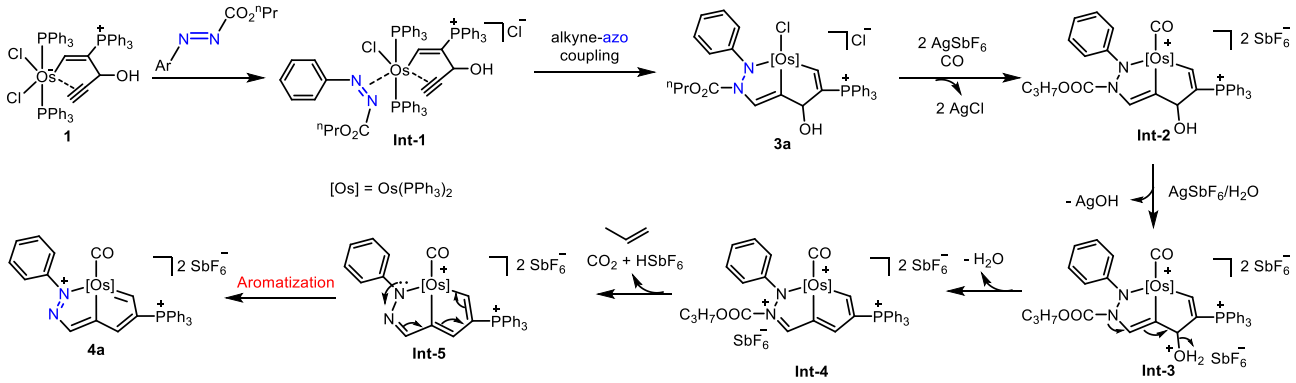
To a dichloromethane (5 mL) solution of **3d** (93 mg, 0.068 mmol) was added $AgSbF_6$ (132 mg, 0.384 mmol). The reaction mixture was stirred under CO atmosphere at room temperature for 3 h to give a blue solution. Then, the solvent of the reaction mixture was removed under vacuum, and the residue was washed with diethyl ether (3 × 10 mL) to give a blue precipitate, which was collected by

filtration and dried under vacuum. Yield, 110 mg, 96%.

^{1}H NMR (400.1 MHz, CD_2Cl_2, ppm): δ = 16.22 (dd, $J_{P\text{-}H}$ = 12.0 Hz, $J_{H\text{-}H}$ = 1.6 Hz,1H, H1), 10.29 (s, 1H, H5), 9.44 (dd, $J_{P\text{-}H}$ = 4.0 Hz, $J_{P\text{-}H}$ = 2.2 Hz, 1H, H3), 7.91-6.45 (m, 49H, P*Ph*$_3$ and *Ph*), 3.81(s, 3H, OC*H*$_3$); ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2, ppm): δ = 11.9 (t, $J_{P\text{-}P}$ = 5.6 Hz, C*P*Ph$_3$) -0.5 (d, $J_{P\text{-}P}$ = 5.6 Hz, Os*P*Ph$_3$); ^{13}C{^{1}H} NMR (150.9 MHz, CD_2Cl_2, plus ^{13}C-dept 135, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC, ppm): δ = 246.1 (br, C1), 220.5 (br, C4), 184.2 (t, $J_{P\text{-}C}$ = 10.7 Hz, *C*O), 164.6 (s, *Ph*), 164.2 (d, $J_{P\text{-}C}$ = 18.3 Hz, C3), 163.3 (s, C5), 160.4 (dt, $J_{P\text{-}C}$ = 66.1 Hz, $J_{P\text{-}C}$ = 3.4 Hz, C2), 160.0 (s, *Ph*), 117.5 (s, *Ph*), 57.5 (s, O*C*H$_3$); HRMS (ESI): m/z calcd for $[C_{67}H_{55}O_2OsN_2OP_3]^{2+}$, 602.1540, found: 602.1545.

3. Plausible Mechanism for the Formation of Diaza-Osmapentalenes 4

A plausible mechanism from **1** to **4** was postulated to elucidate the formation of the diaza-osmapentalenes **4**. Taking **4a** as an example, firstly, the coordination of the azocarboxylate **2a** to the Os center generated **Int-1**, which was followed by alkyne-azo coupling to afford **3a**.[S3] Subsequently, the abstraction of chloride by $AgSbF_6$ accompanied by the coordination of CO led to the formation of **Int-2**. Then, the hydrolysis of $AgSbF_6$ under trace of water would facilitate the dehydration to form **Int-4**. Finally, the cleavage of N-C bond by the loss of propene and CO_2[S4] followed by the aromatization process gave the final diaza-osmapentalene **4a**.



Scheme S1 Plausible Mechanism for the Formation of Diaza-Osmapentalenes **4**.

4. NMR Spectra

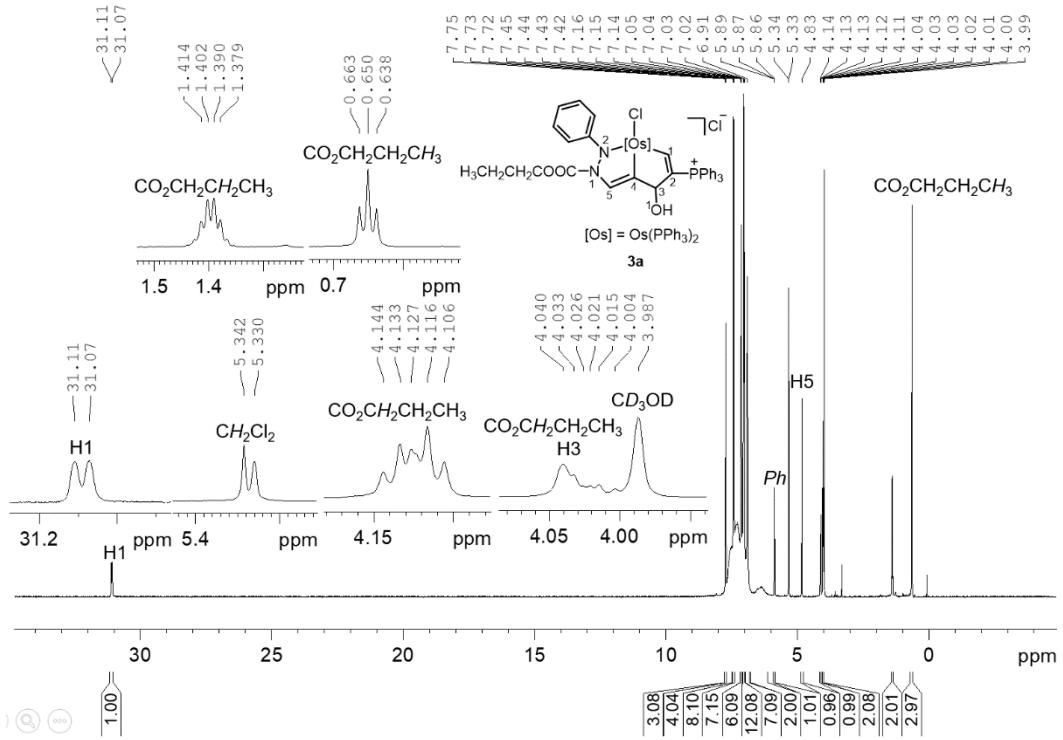


Figure S1 The ^{1}H NMR (600.1 MHz, CD_2Cl_2/CD_3OD = 4/1) spectrum for complex **3a**.

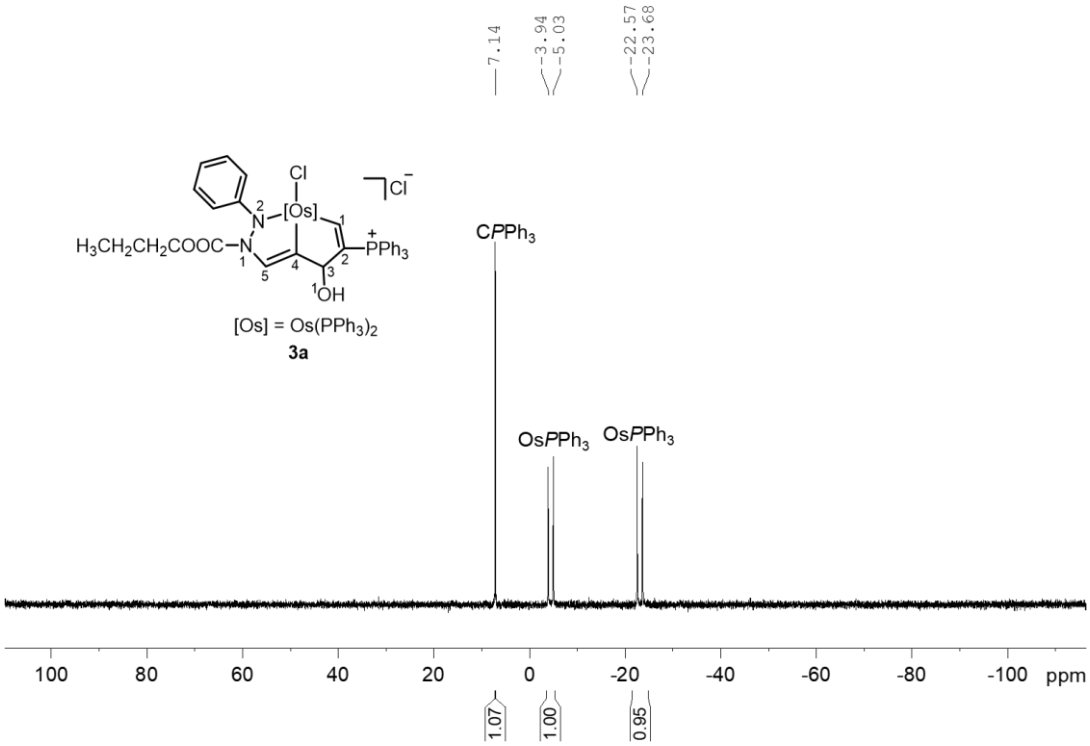


Figure S2 The $^{31}P\{^{1}H\}$ NMR (242.9 MHz, CD_2Cl_2/CD_3OD = 4/1) spectrum for complex **3a**.

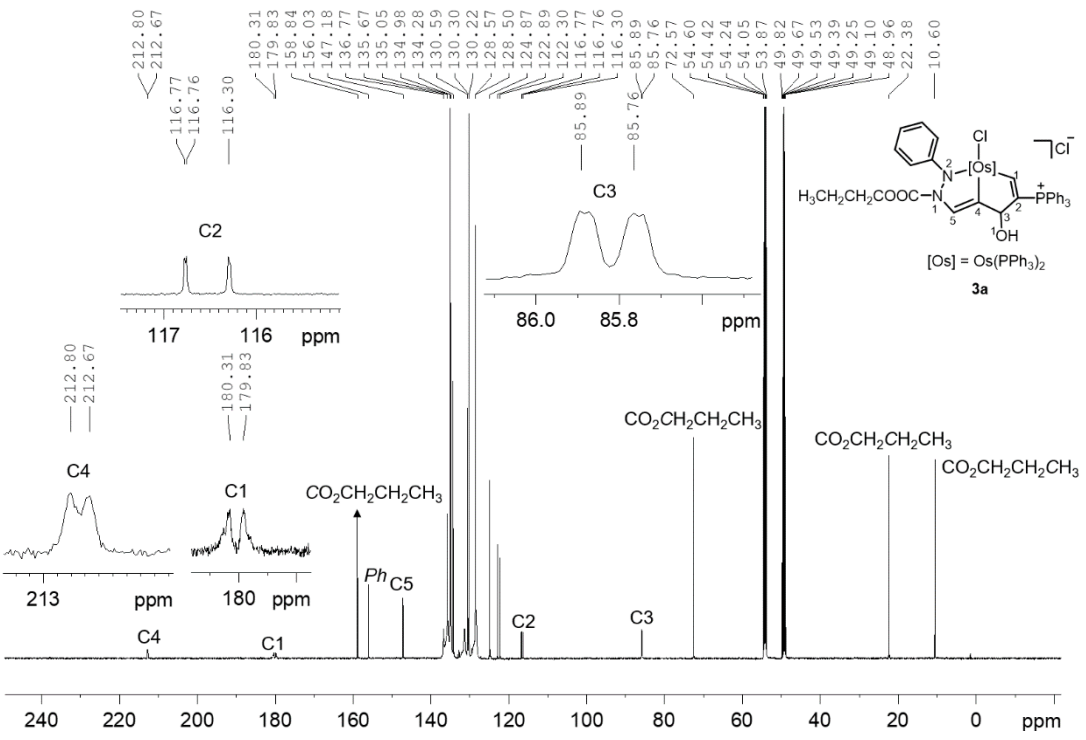


Figure S3 The $^{13}C\{^{1}H\}$ NMR (150.9 MHz, CD_2Cl_2/CD_3OD = 4/1) spectrum for complex **3a**.

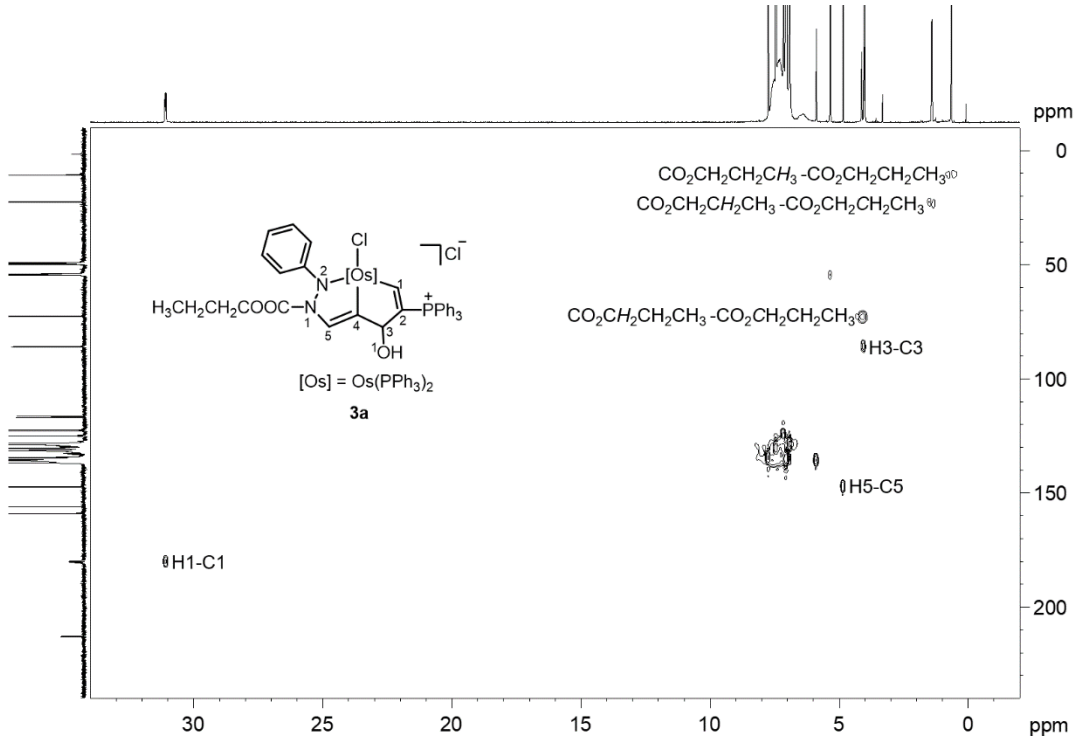


Figure S4 The ^{1}H-^{13}C HSQC spectrum for complex **3a** in CD_2Cl_2/CD_3OD = 4/1.

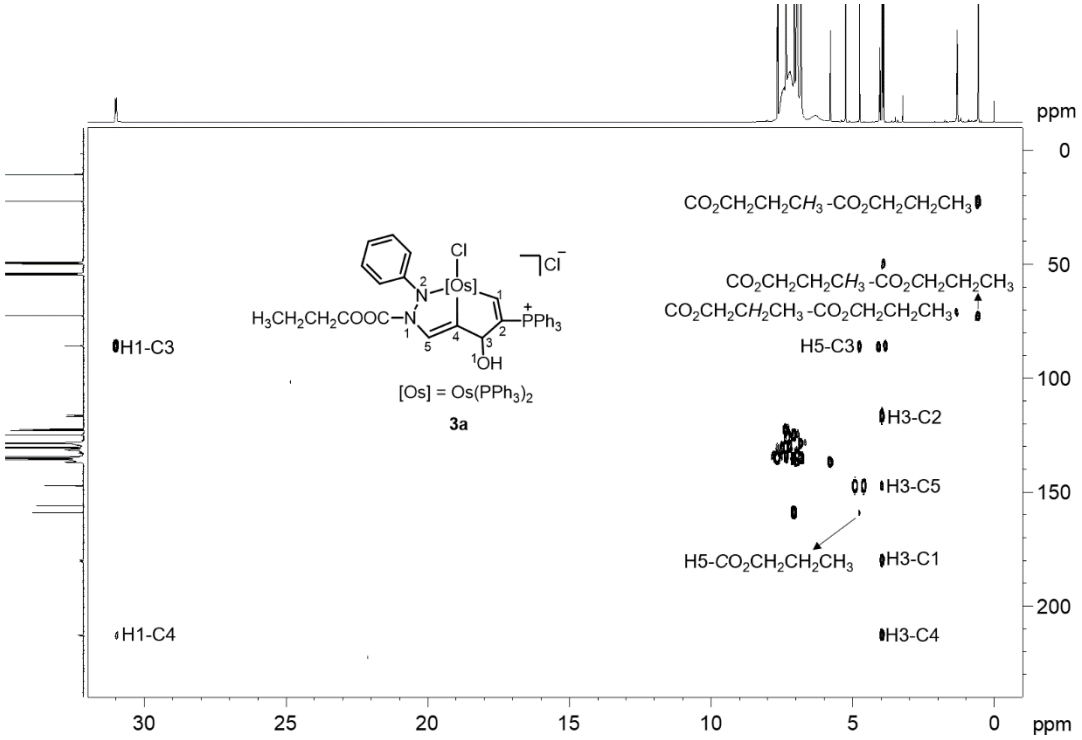


Figure S5 The ^{1}H-^{13}C HMBC spectrum for complex **3a** in CD_2Cl_2/CD_3OD = 4/1.

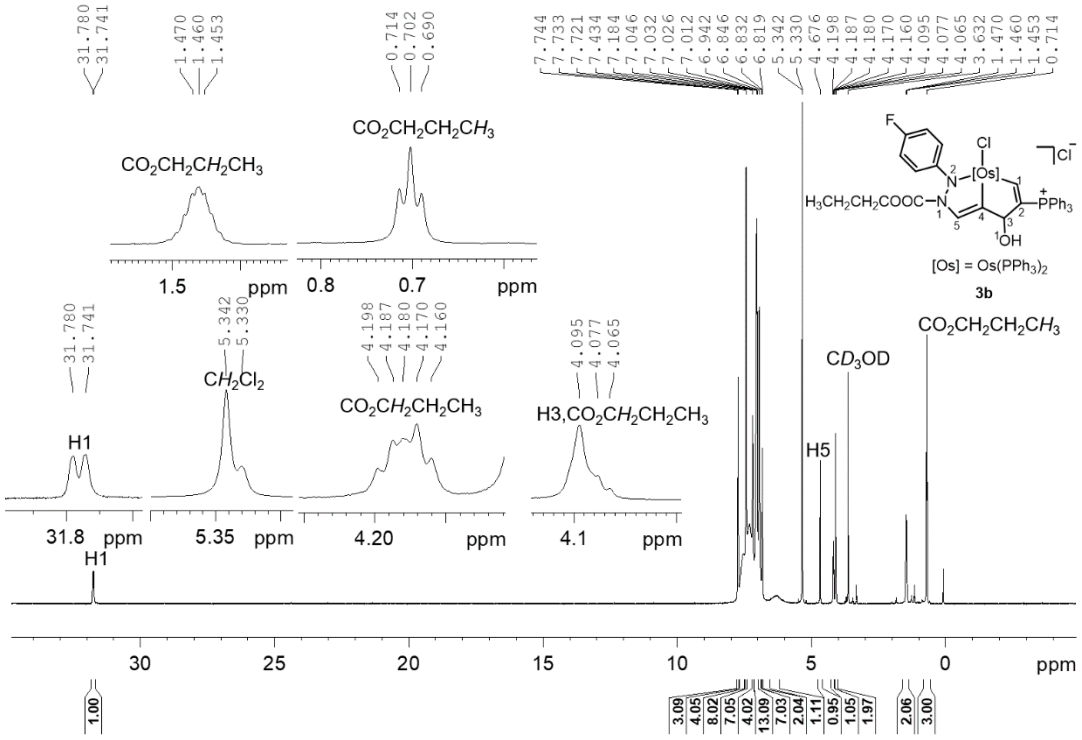


Figure S6 The ^{1}H NMR (600.1 MHz, CD_2Cl_2/CD_3OD = 4/1) spectrum for complex **3b**.

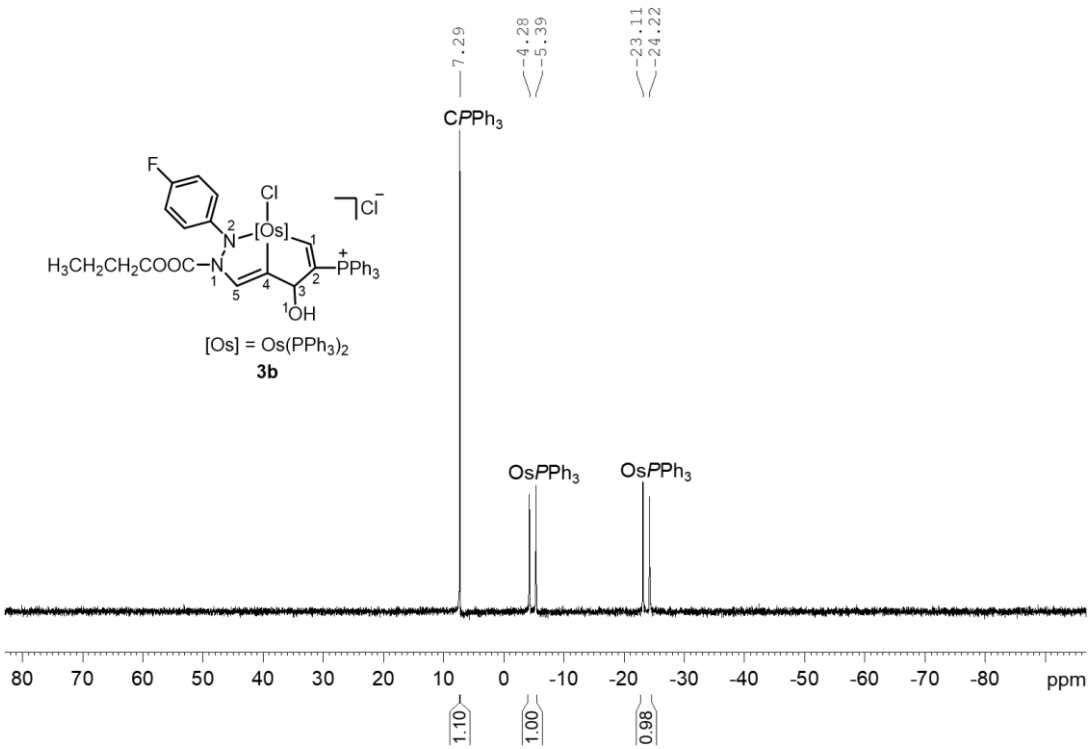


Figure S7 The $^{31}P\{^{1}H\}$ NMR (242.9 MHz, CD_2Cl_2/CD_3OD = 4/1) spectrum for complex **3b**.

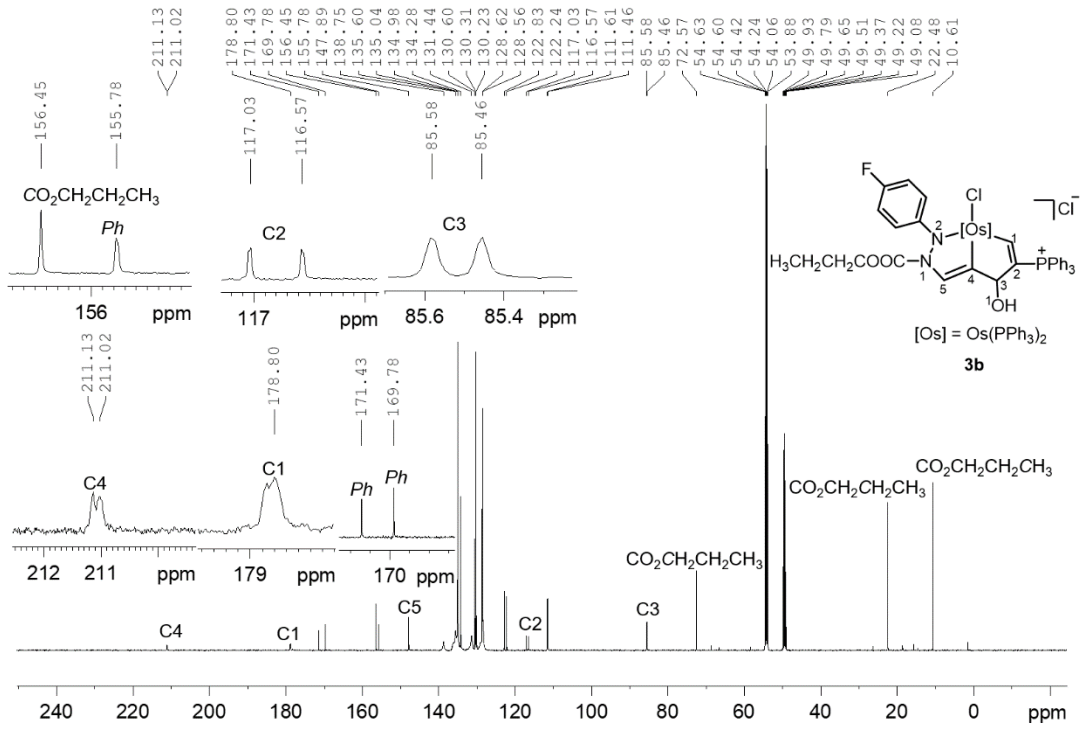


Figure S8 The $^{13}C\{^{1}H\}$ NMR (150.9 MHz, CD_2Cl_2/CD_3OD = 4/1) spectrum for complex **3b**.

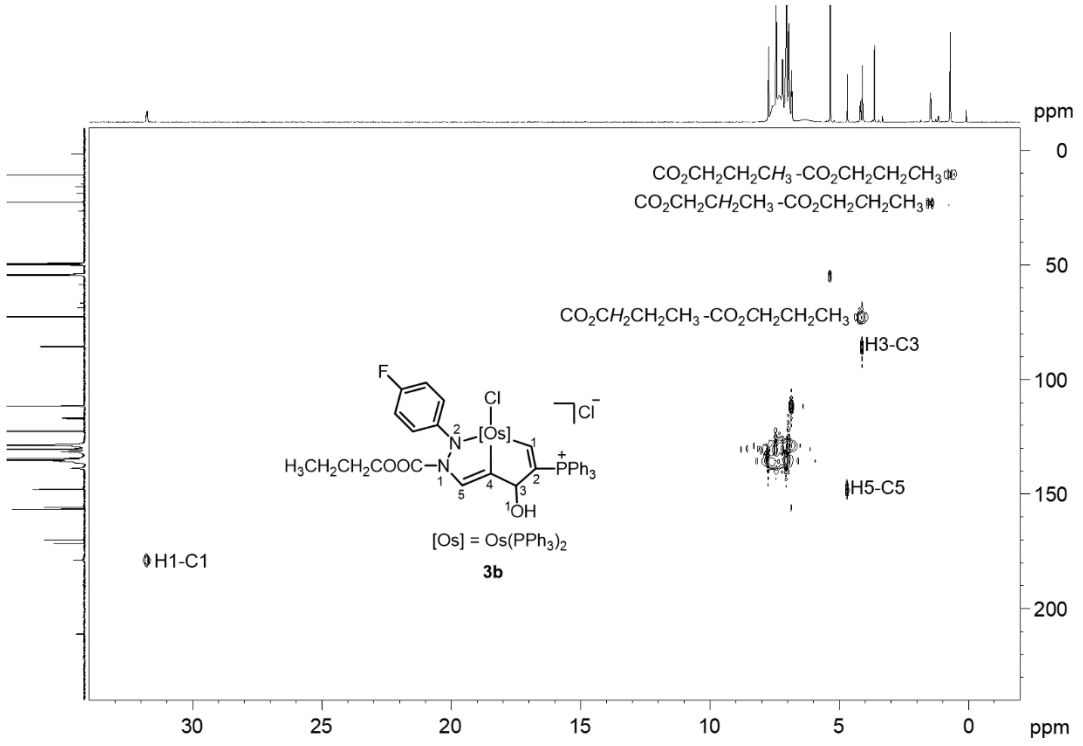


Figure S9 The ^{1}H-^{13}C HSQC spectrum for complex **3b** in CD_2Cl_2/CD_3OD = 4/1.

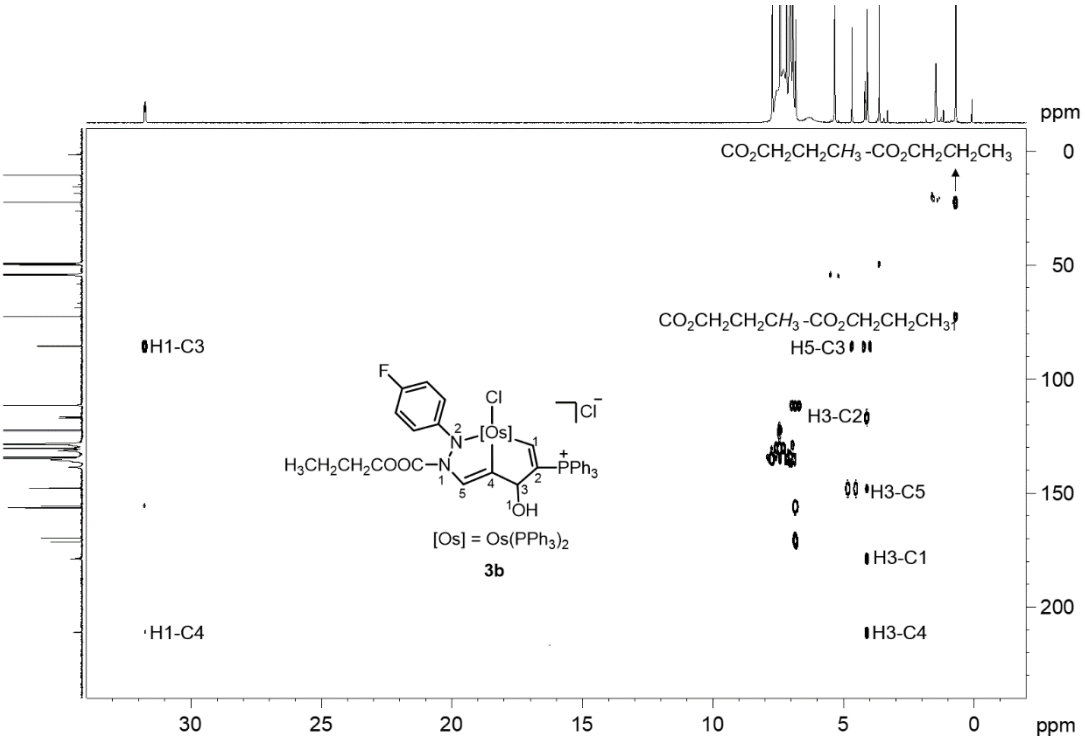


Figure S10 The ^{1}H-^{13}C HMBC spectrum for complex **3b** in CD_2Cl_2/CD_3OD = 4/1.

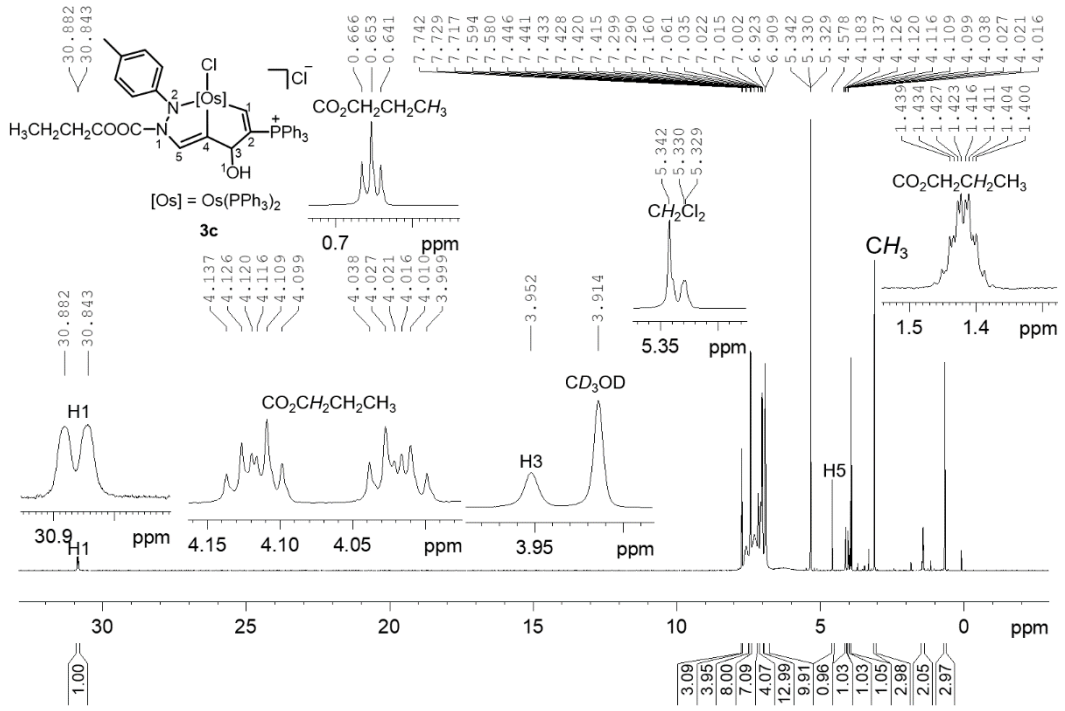


Figure S11 The ^{1}H NMR (600.1 MHz, CD_2Cl_2/CD_3OD = 4/1) spectrum for complex **3c**.

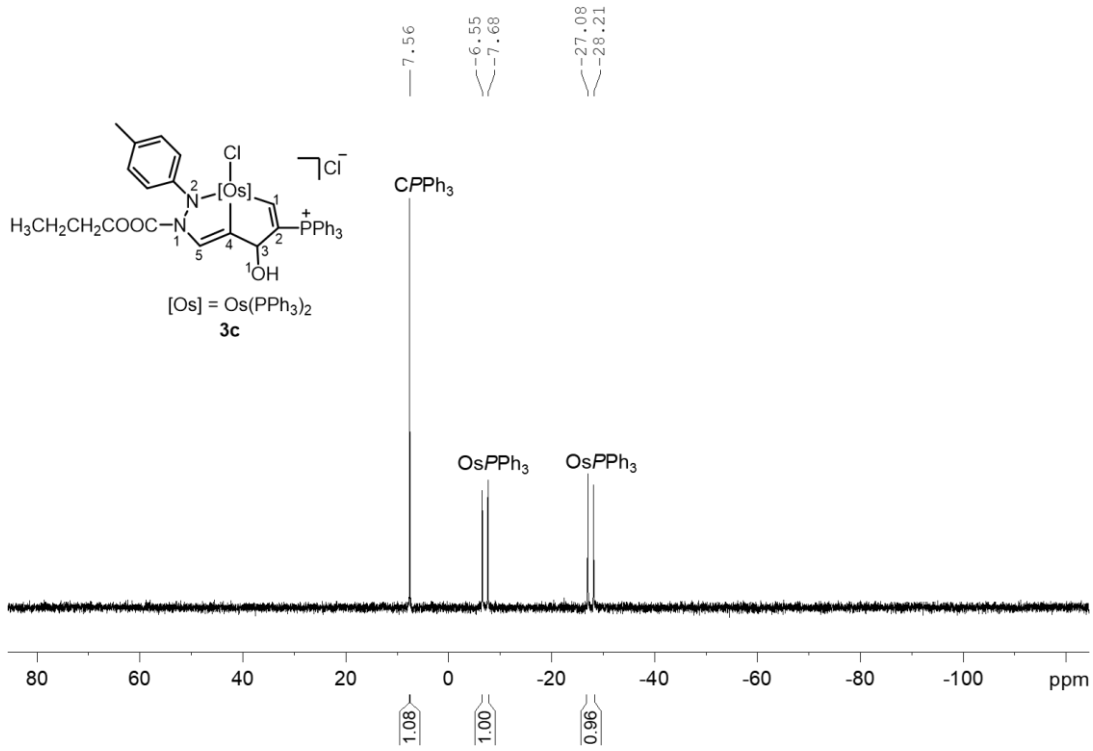


Figure S12 The $^{31}P\{^{1}H\}$ NMR (242.9 MHz, CD_2Cl_2/CD_3OD = 4/1) spectrum for complex **3c**.

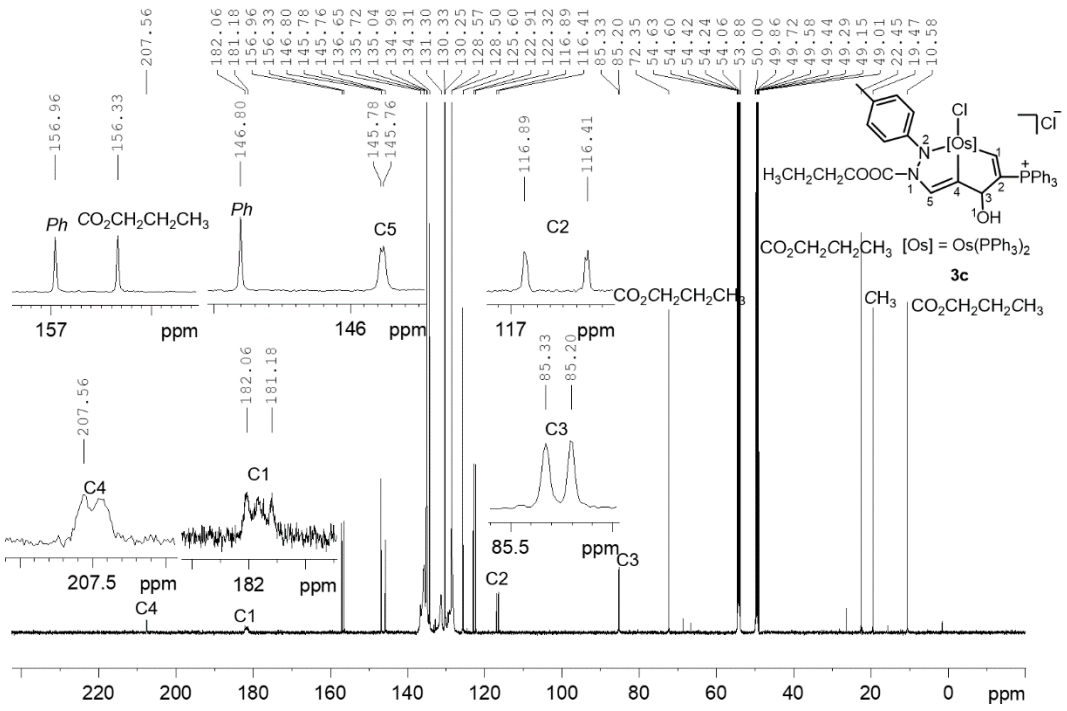


Figure S13 The $^{13}C\{^{1}H\}$ NMR (150.9 MHz, CD_2Cl_2/CD_3OD = 4/1) spectrum for complex **3c**.

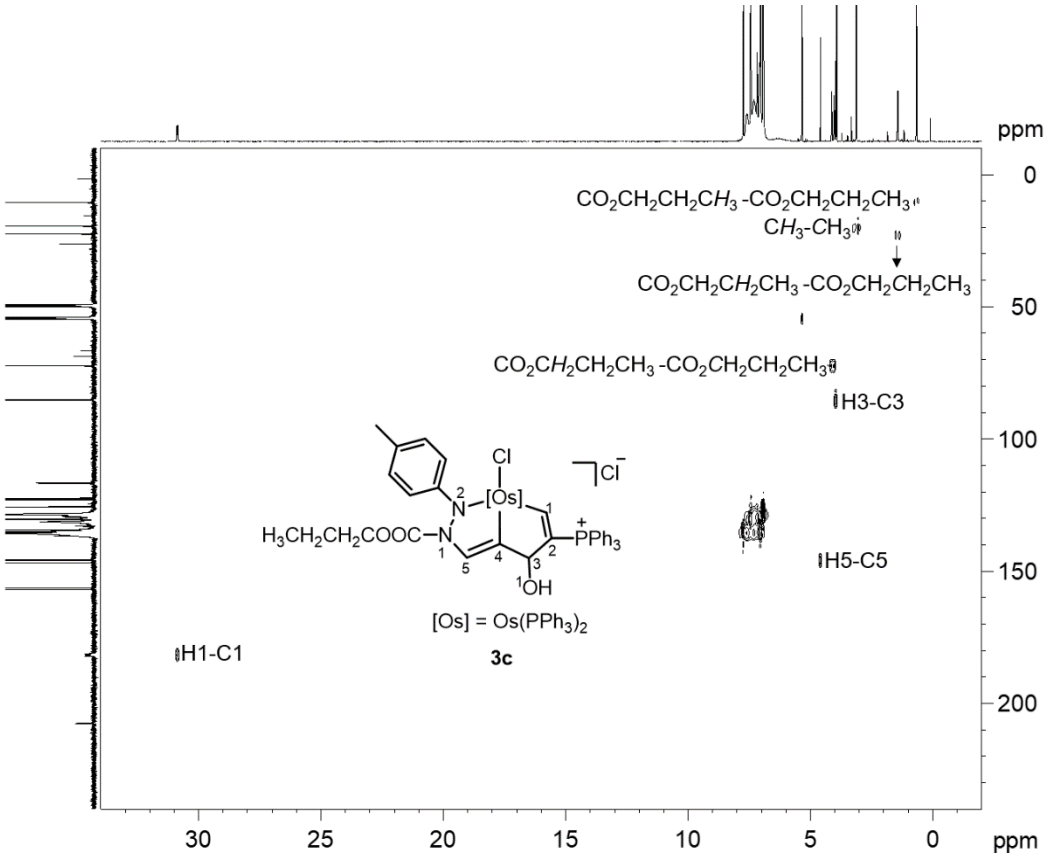


Figure S14 The ^{1}H-^{13}C HSQC spectrum for complex **3c** in CD_2Cl_2/CD_3OD = 4/1.

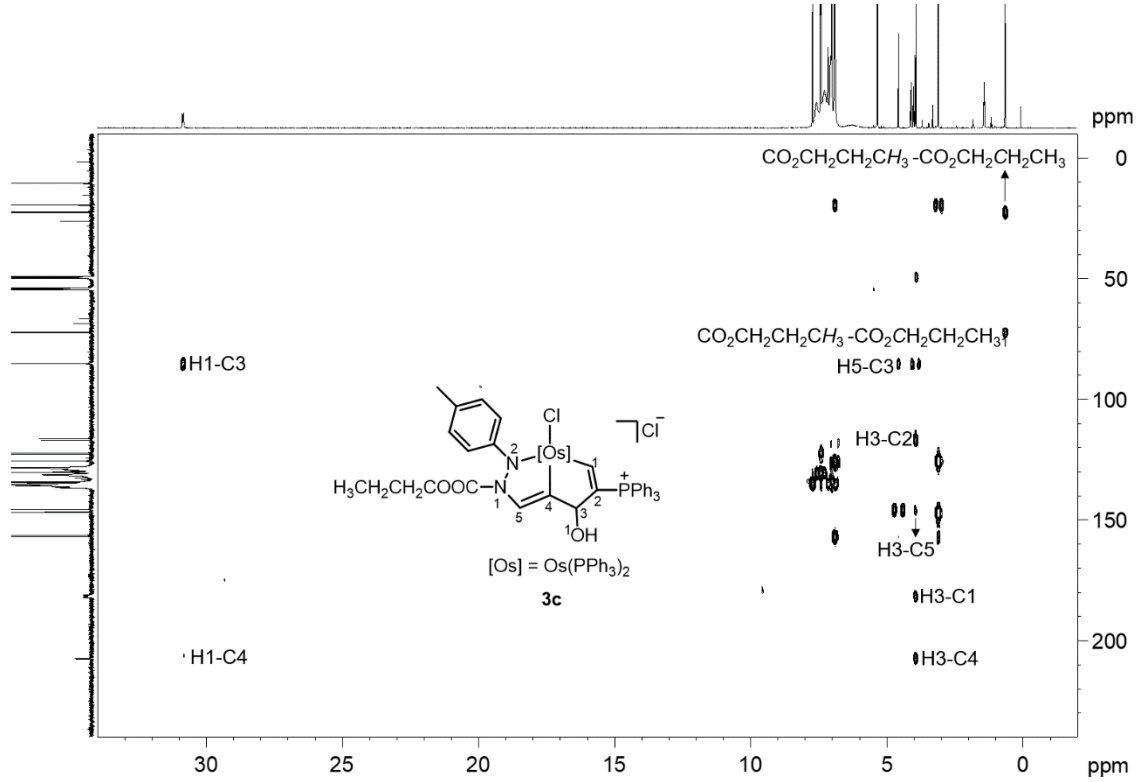


Figure S15 The ^{1}H-^{13}C HMBC spectrum for complex **3c** in CD_2Cl_2/CD_3OD = 4/1.

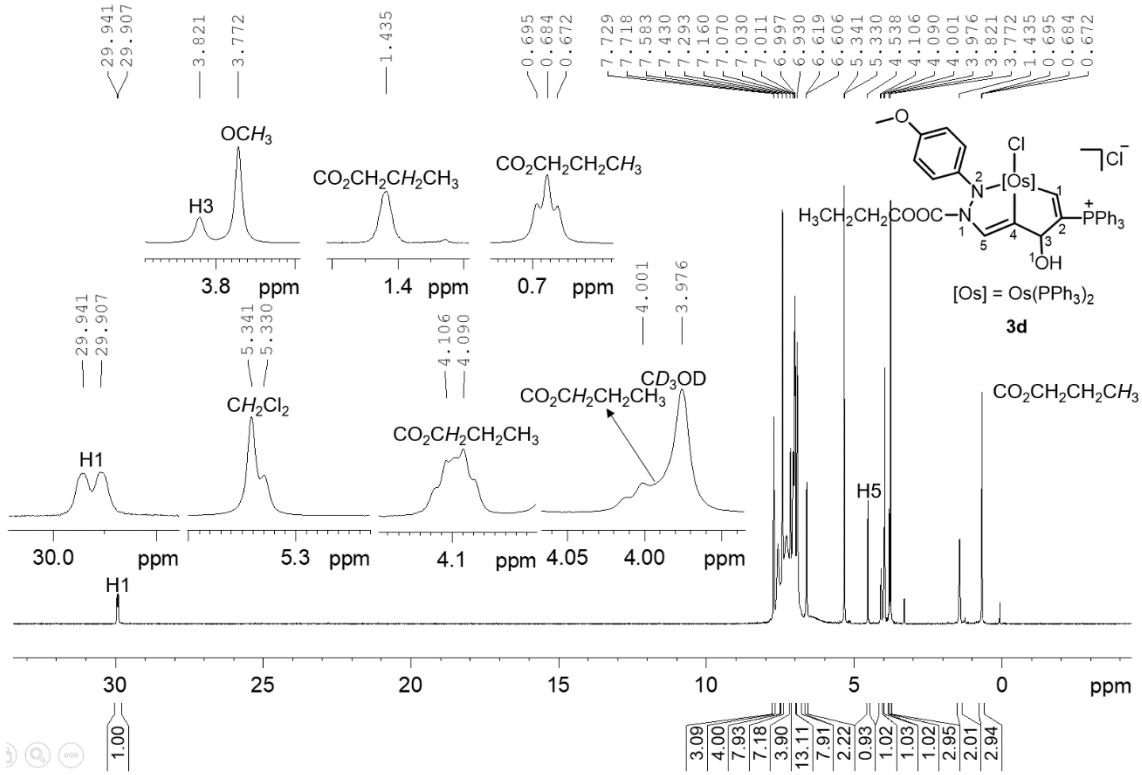


Figure S16 The ^{1}H NMR (600.1 MHz, CD_2Cl_2/CD_3OD = 4/1) spectrum for complex **3d**.

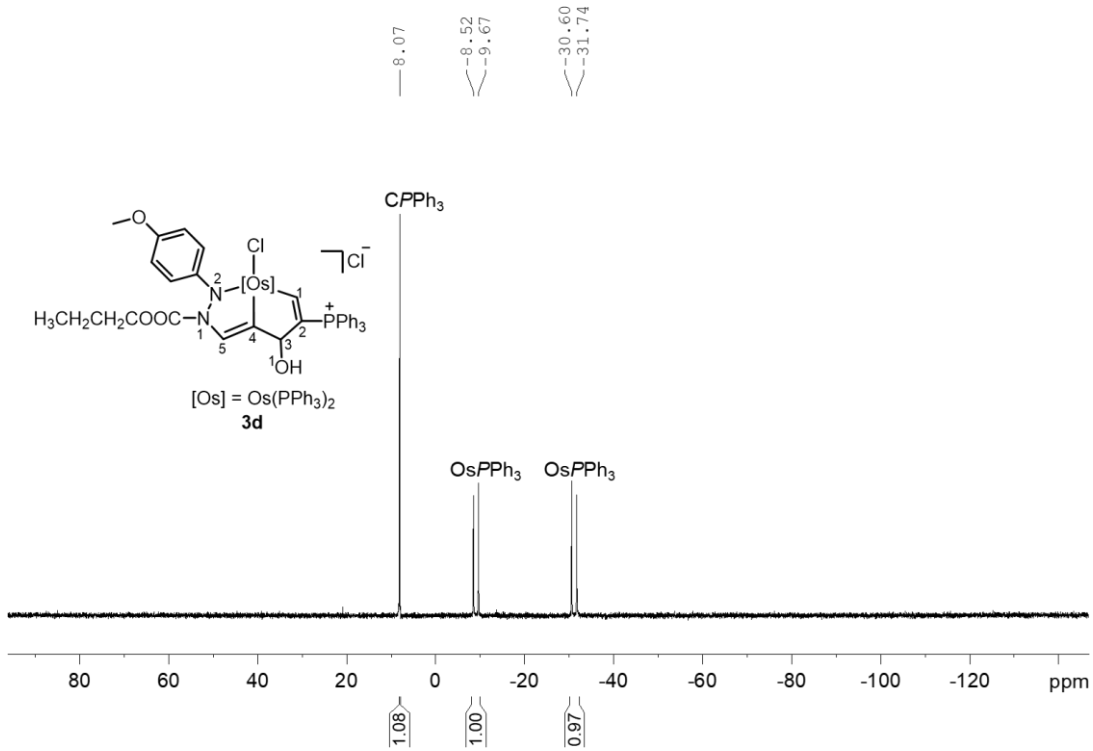


Figure S17 The $^{31}P\{^{1}H\}$ NMR (242.9 MHz, CD_2Cl_2/CD_3OD = 4/1) spectrum for complex **3d**.

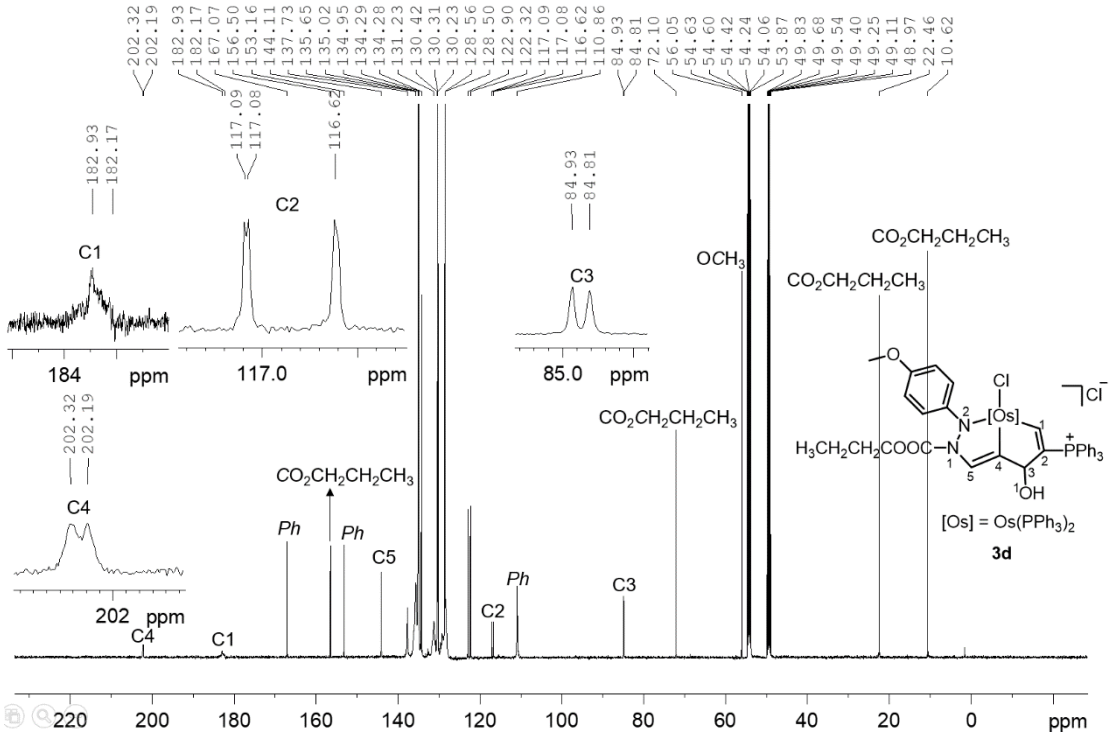


Figure S18 The $^{13}C\{^{1}H\}$ NMR (150.9 MHz, CD_2Cl_2/CD_3OD = 4/1) spectrum for complex **3d**.

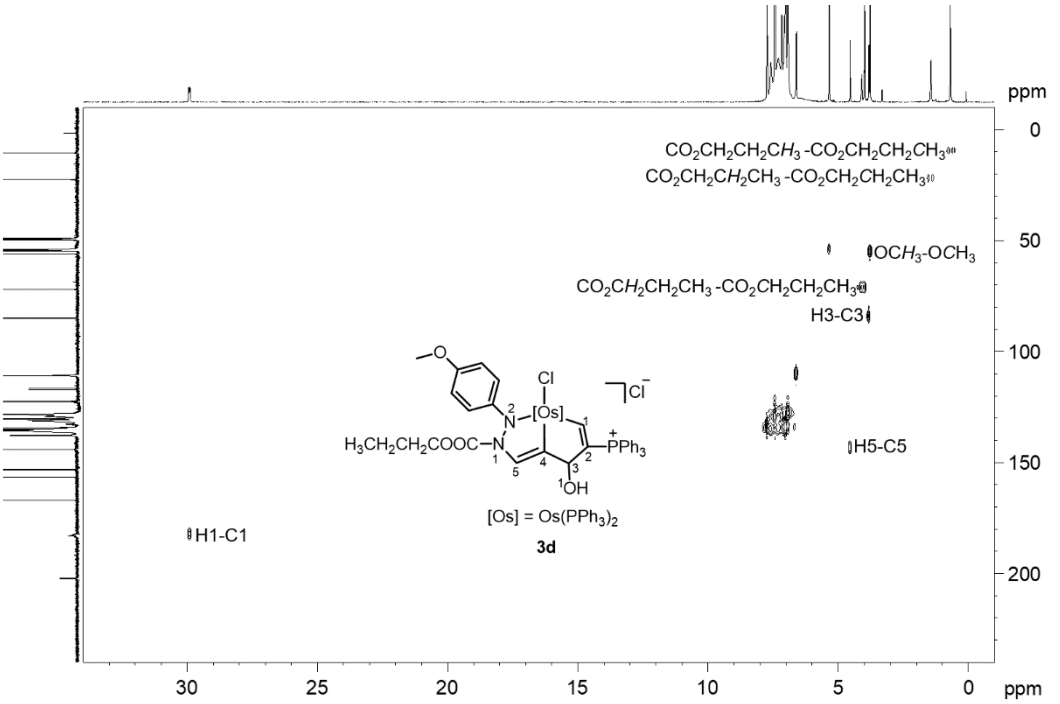


Figure S19 The ^{1}H-^{13}C HSQC spectrum for complex **3d** in CD_2Cl_2/CD_3OD = 4/1.

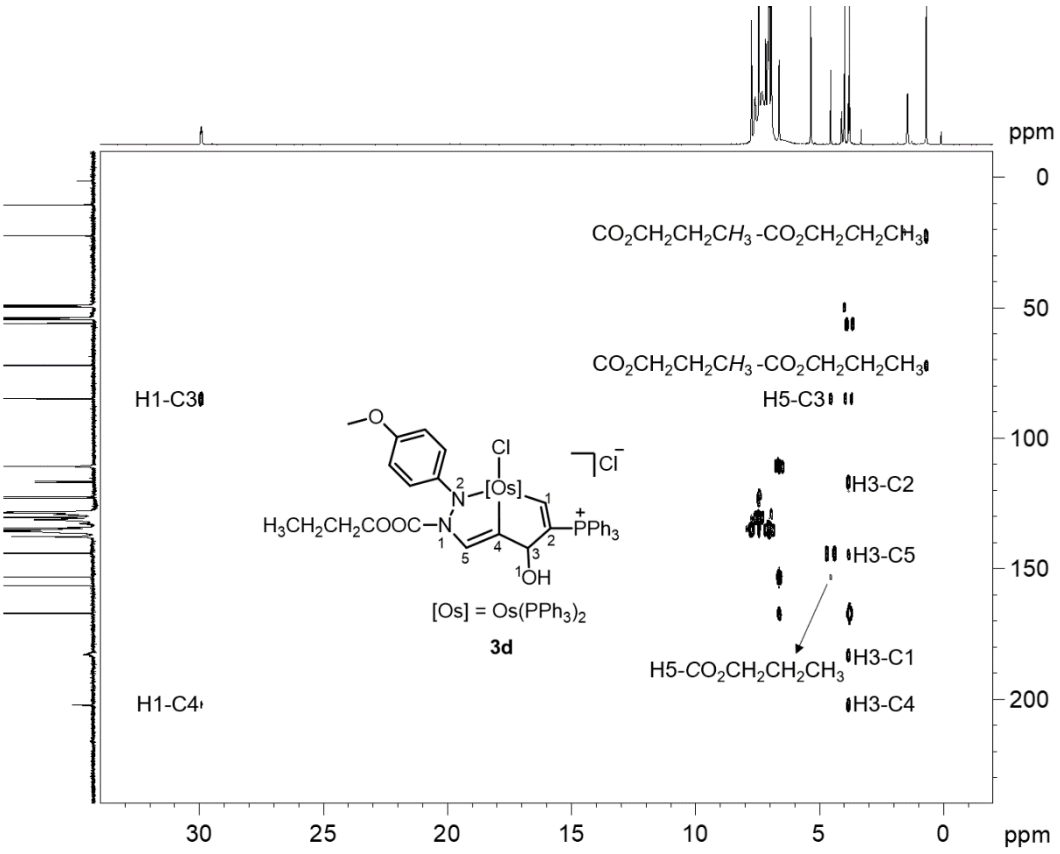


Figure S20 The ^{1}H-^{13}C HMBC spectrum for complex **3d** in CD_2Cl_2/CD_3OD = 4/1.

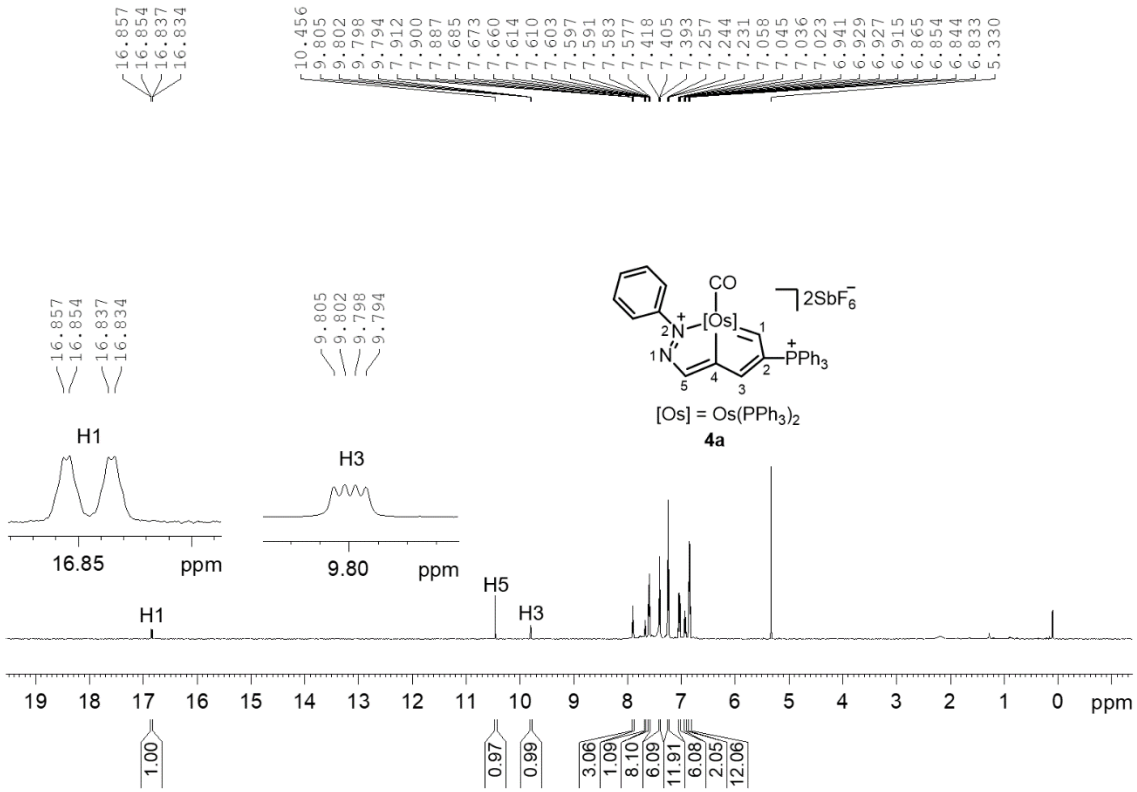


Figure S21 The ^{1}H NMR (600.1 MHz, CD_2Cl_2) spectrum for complex **4a**.

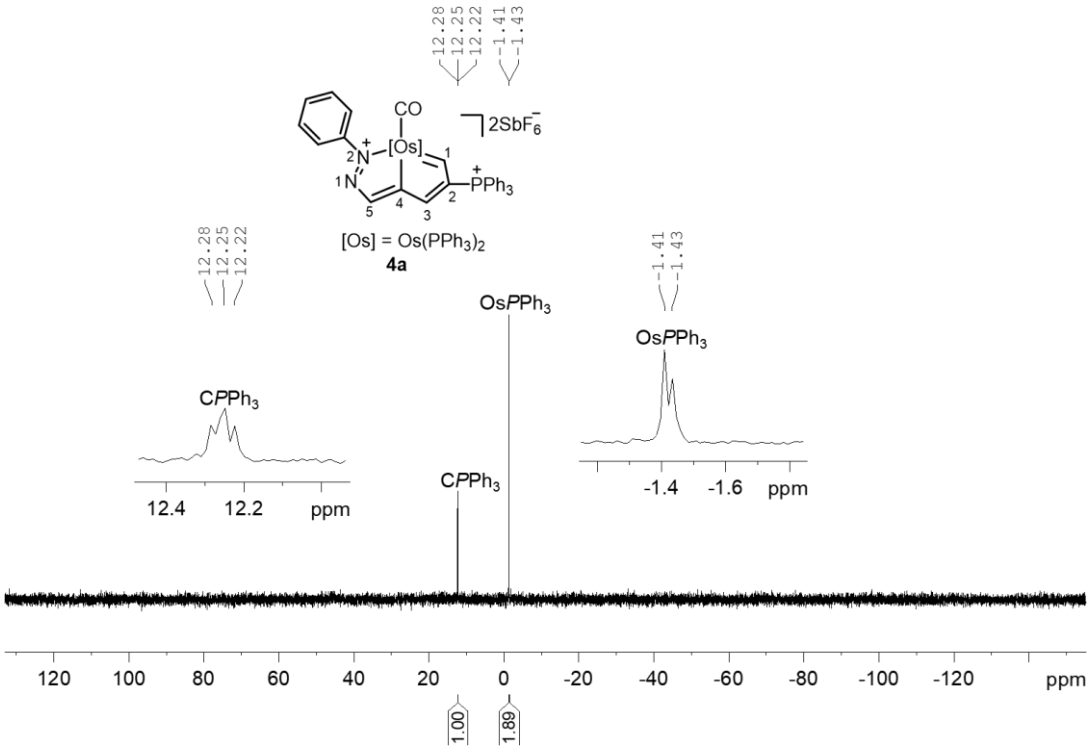


Figure S22 The $^{31}P\{^{1}H\}$ NMR (161.9 MHz, CD_2Cl_2) spectrum for complex **4a**.

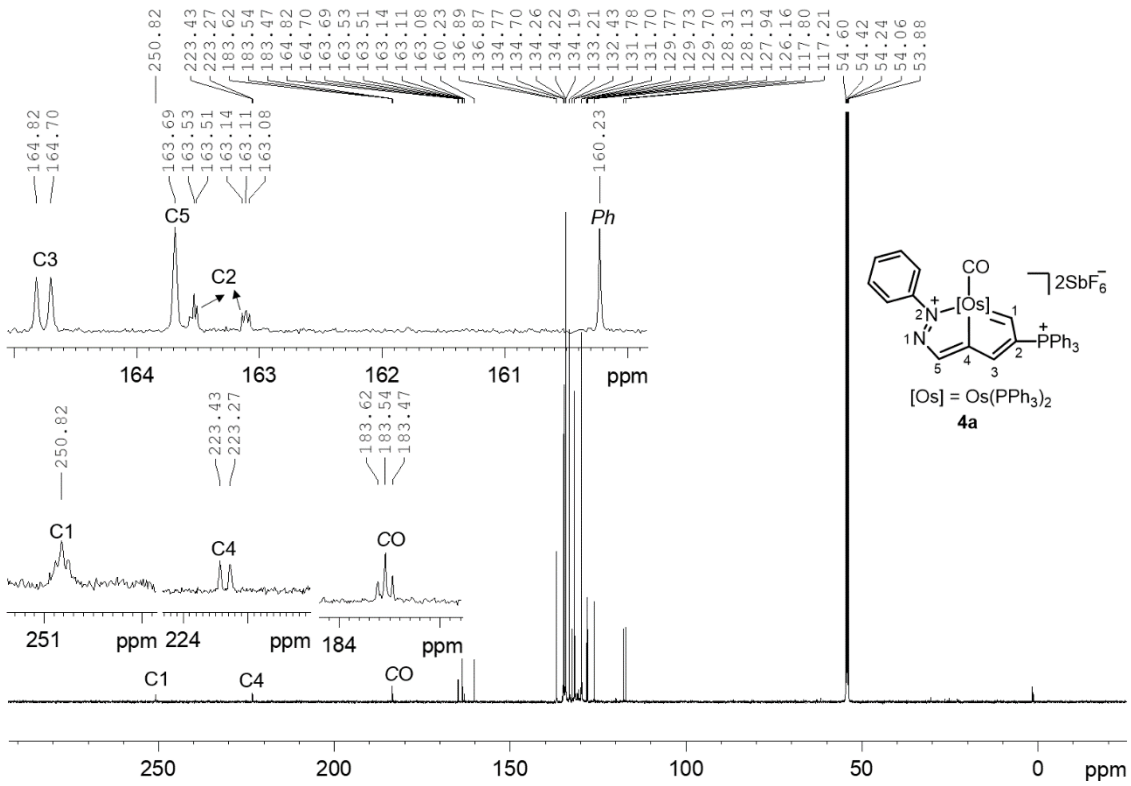


Figure S23 The $^{13}C\{^{1}H\}$ NMR (150.9 MHz, CD_2Cl_2) spectrum for complex **4a**.

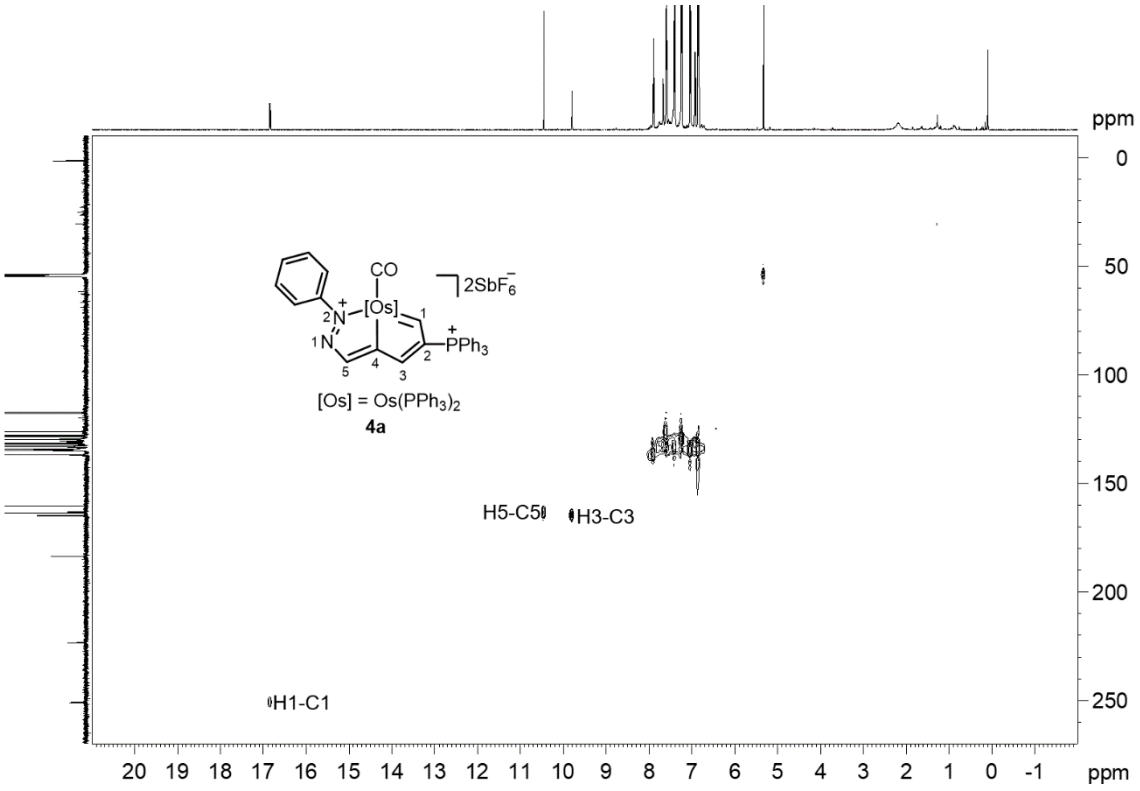


Figure S24 The ^{1}H-^{13}C HSQC spectrum for complex **4a** in CD_2Cl_2.

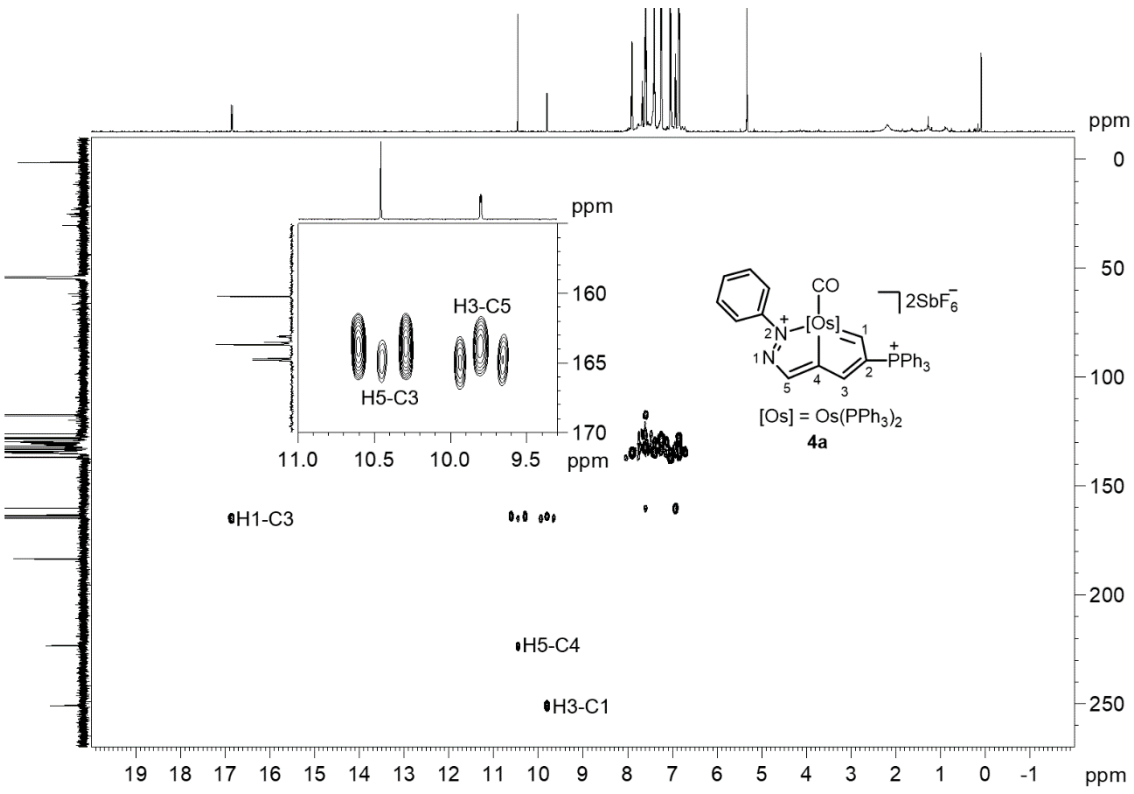


Figure S25 The ^{1}H-^{13}C HMBC spectrum for complex **4a** in CD_2Cl_2.

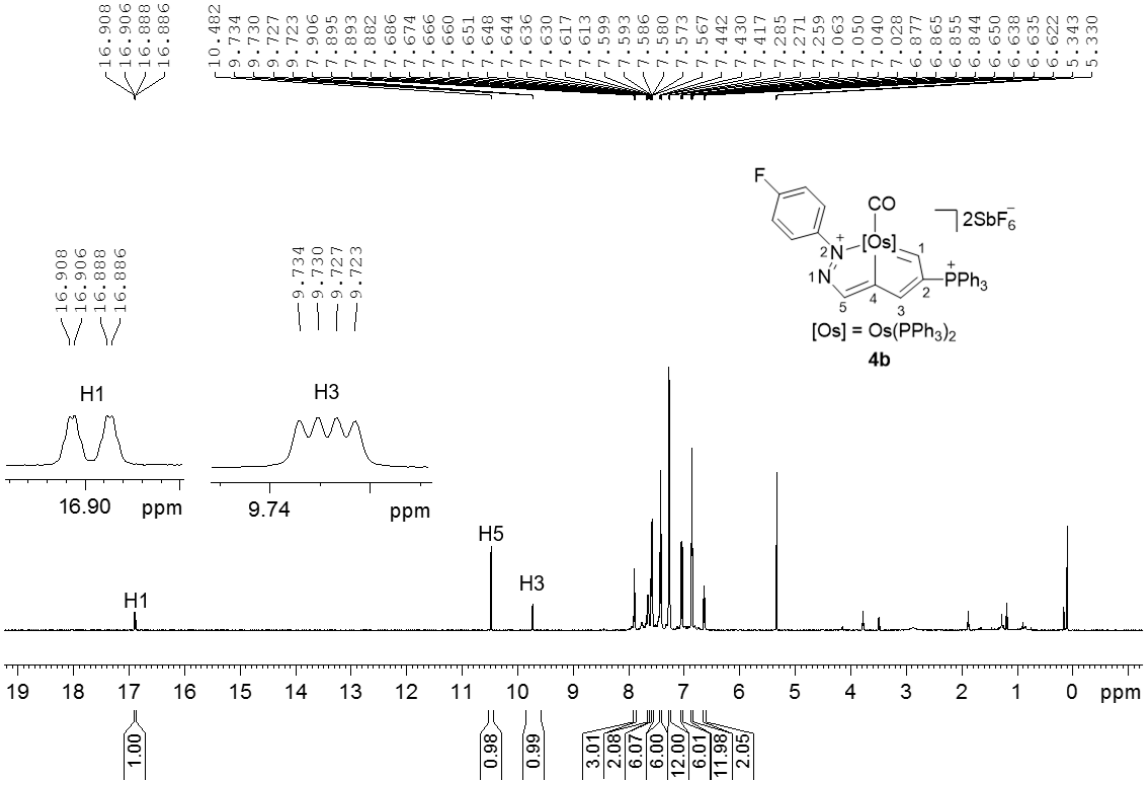


Figure S26 The ^{1}H NMR (600.1 MHz, CD_2Cl_2) spectrum for complex **4b**.

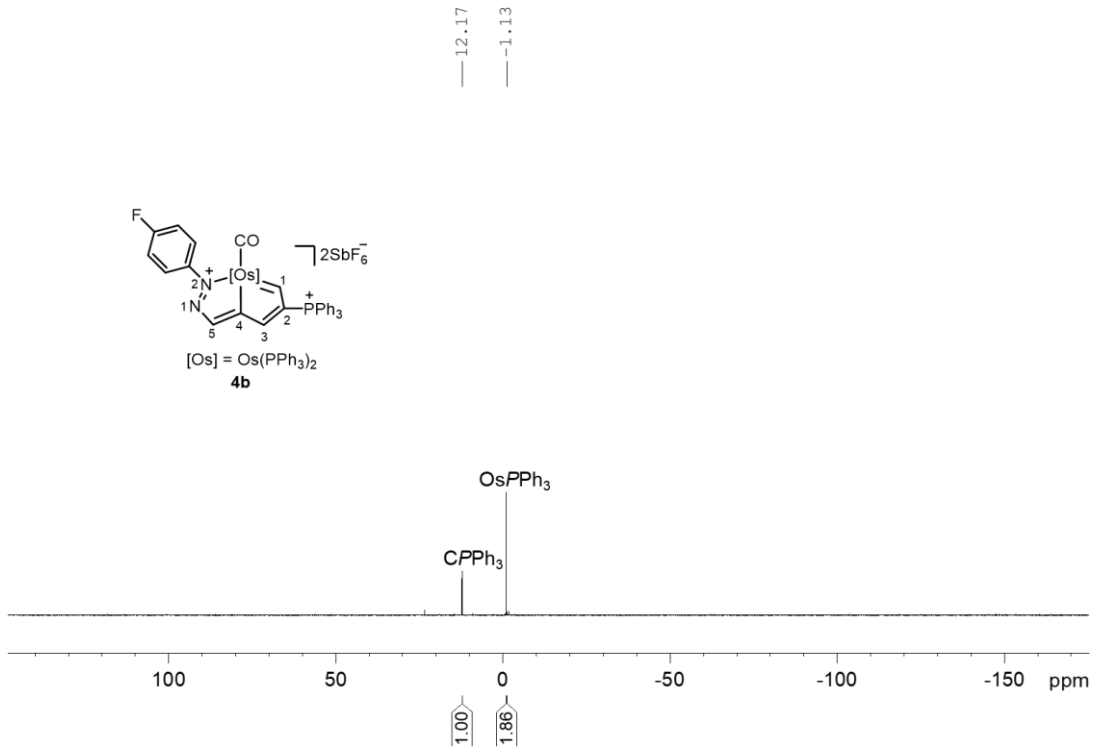


Figure S27 The $^{31}P\{^{1}H\}$ NMR (242.9 MHz, CD_2Cl_2) spectrum for complex **4b**.

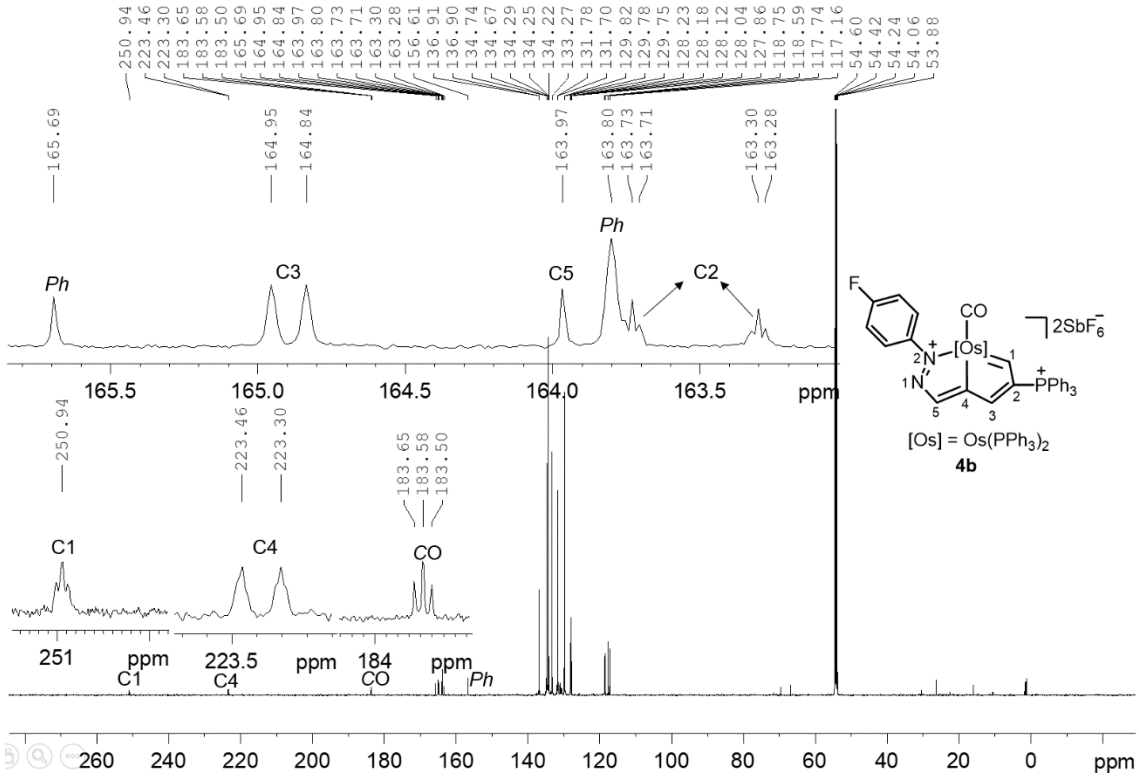


Figure S28 The $^{13}C\{^{1}H\}$ NMR (150.9 MHz, CD_2Cl_2) spectrum for complex **4b**.

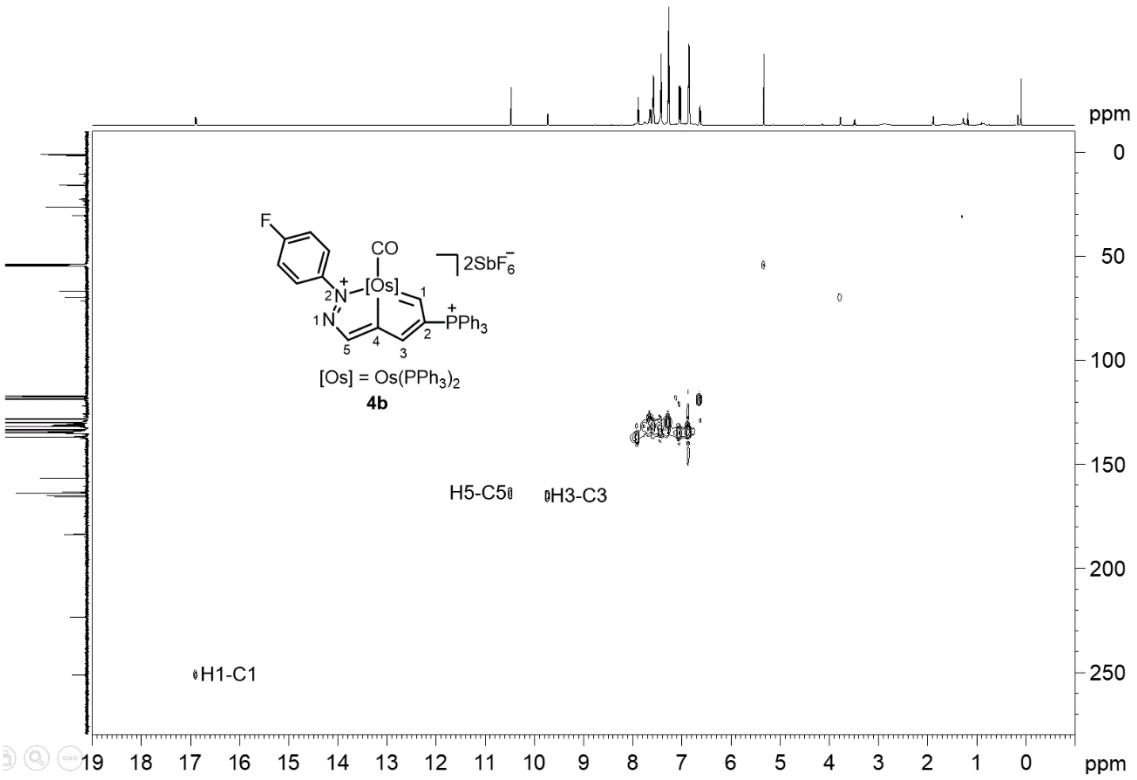


Figure S29 The ^{1}H-^{13}C HSQC spectrum for complex **4b** in CD_2Cl_2.

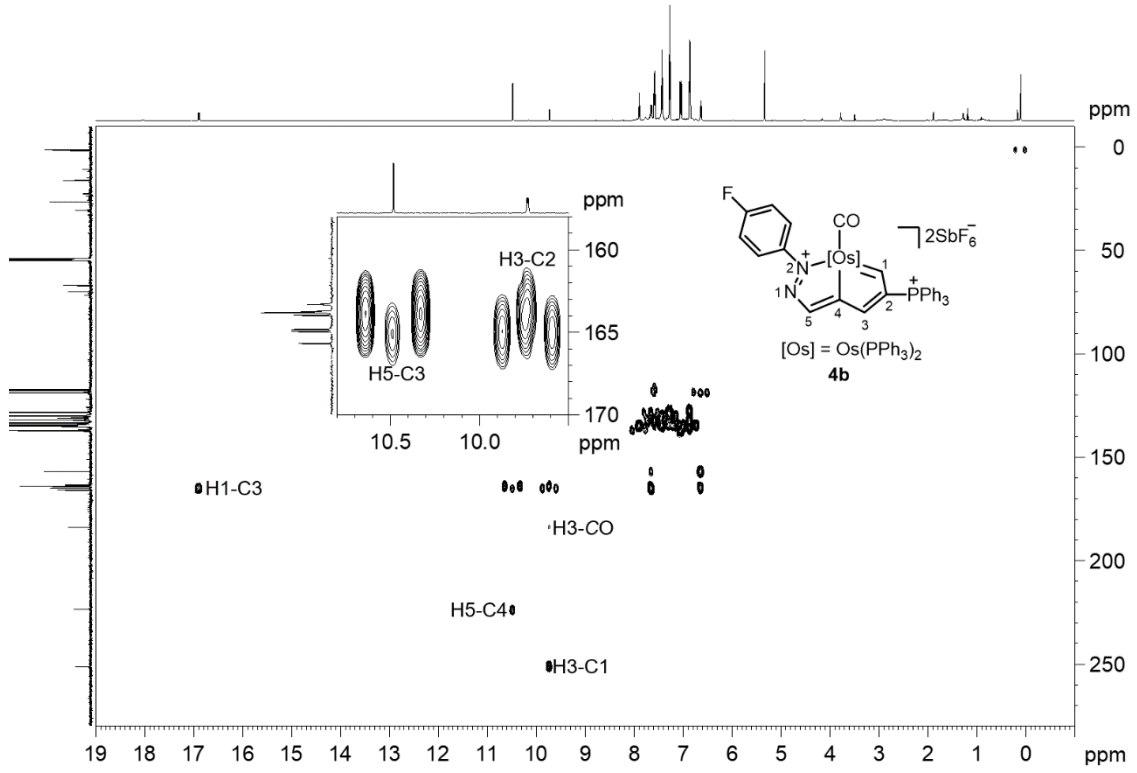


Figure S30 The ^{1}H-^{13}C HMBC spectrum for complex **4b** in CD_2Cl_2.

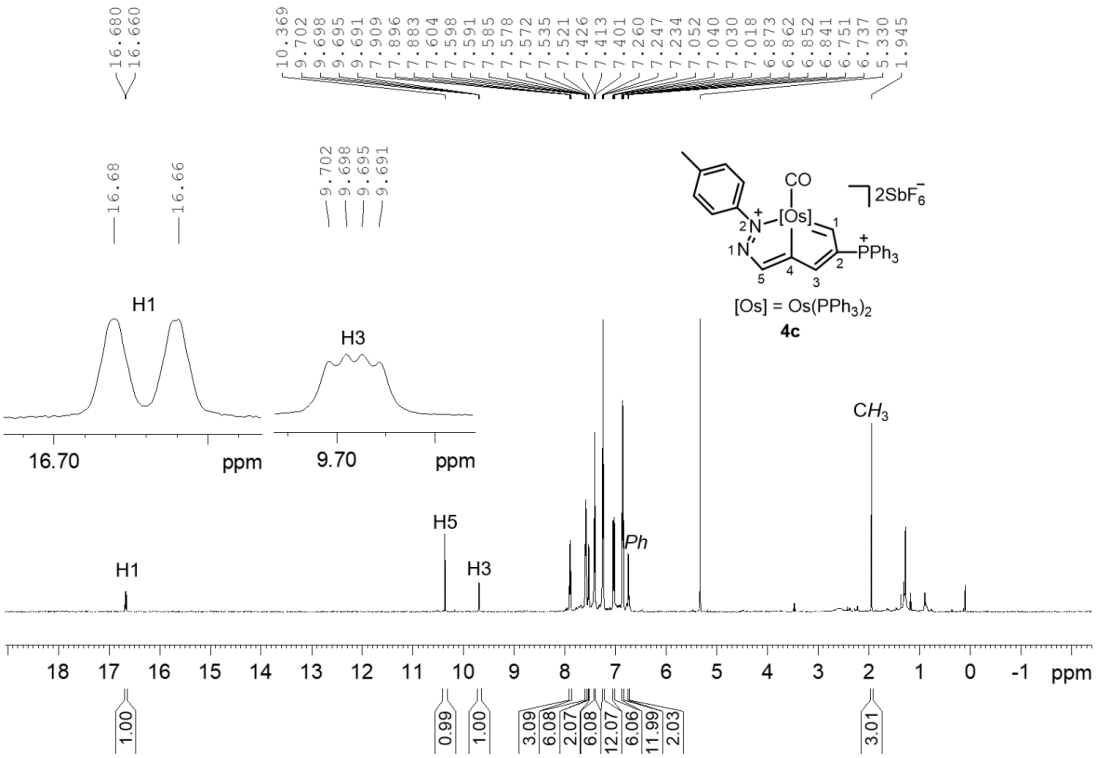


Figure S31 The ^{1}H NMR (600.1 MHz, CD_2Cl_2) spectrum for complex **4c**.

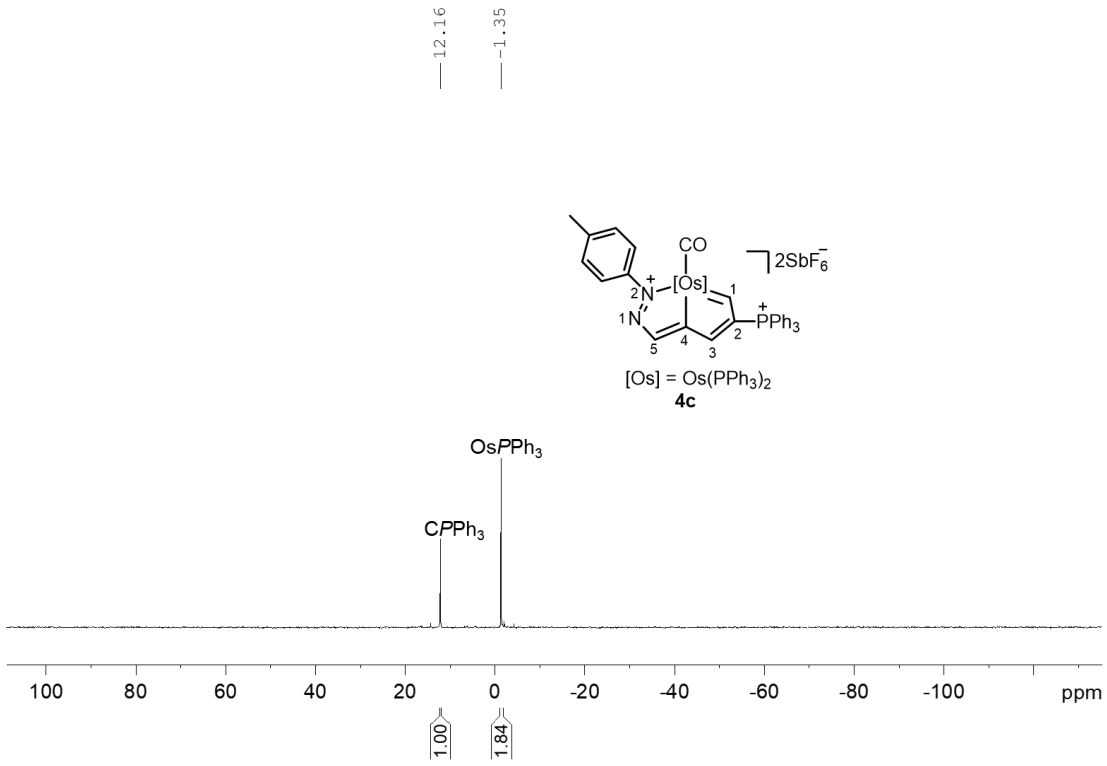


Figure S32 The $^{31}P\{^{1}H\}$ NMR (242.9 MHz, CD_2Cl_2) spectrum for complex **4c**.

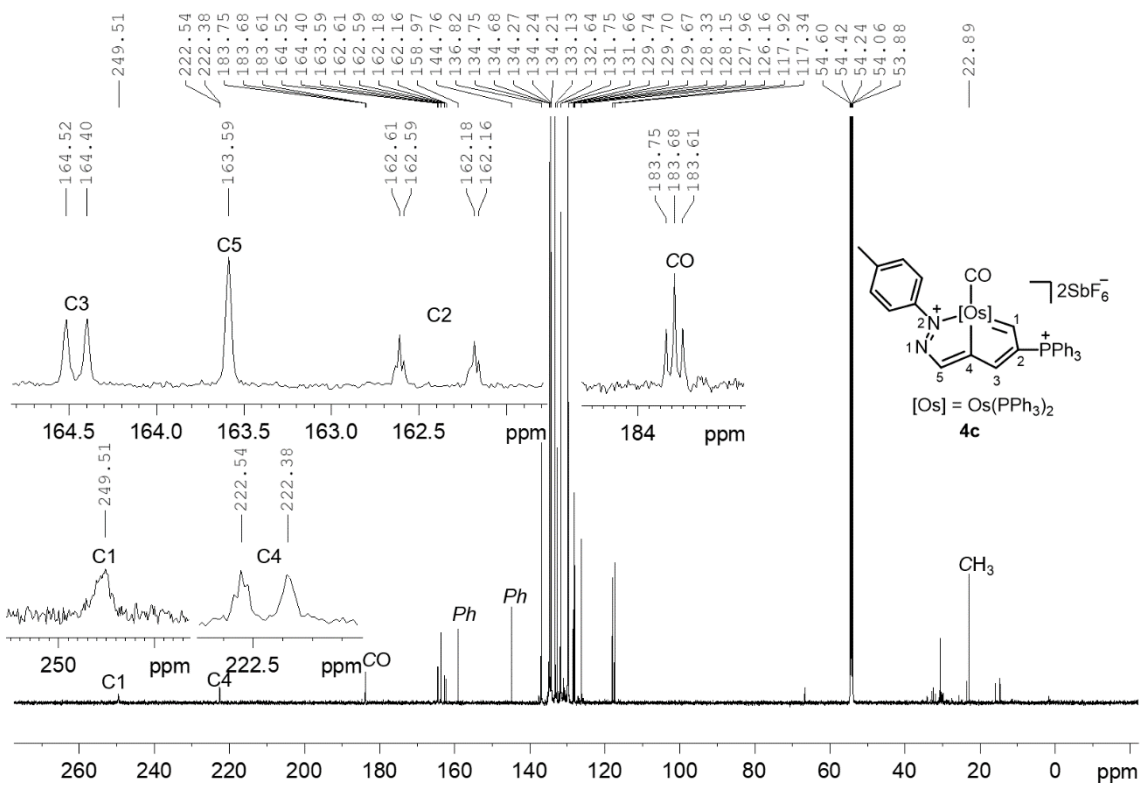


Figure S33 The $^{13}C\{^{1}H\}$ NMR (150.9 MHz, CD_2Cl_2) spectrum for complex **4c**.

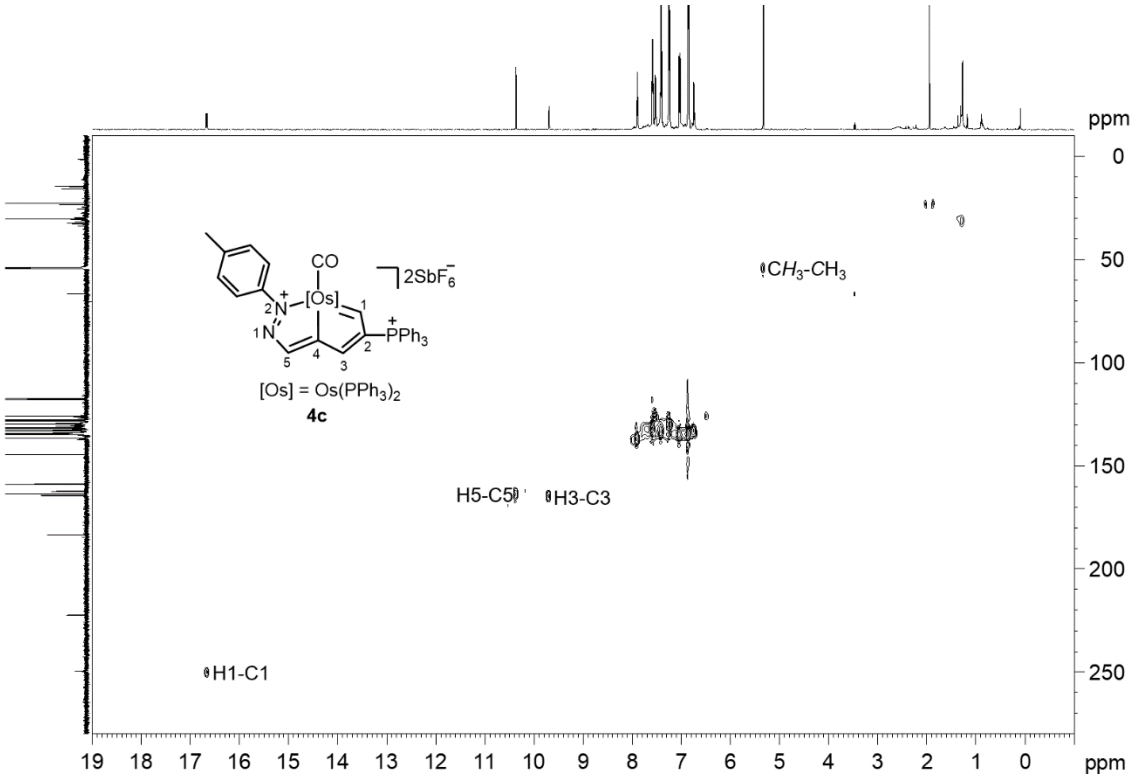


Figure S34 The ^{1}H-^{13}C HSQC spectrum for complex **4c** in CD_2Cl_2.

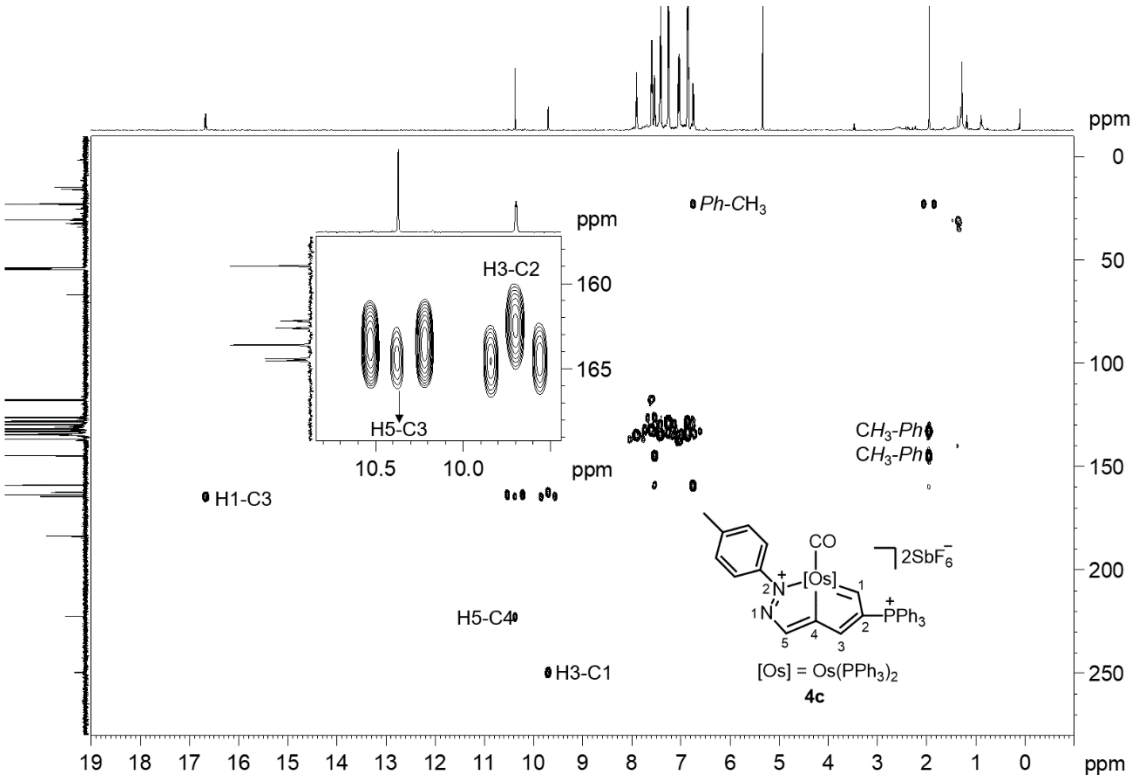


Figure S35 The ^{1}H-^{13}C HMBC spectrum for complex **4c** in CD_2Cl_2.

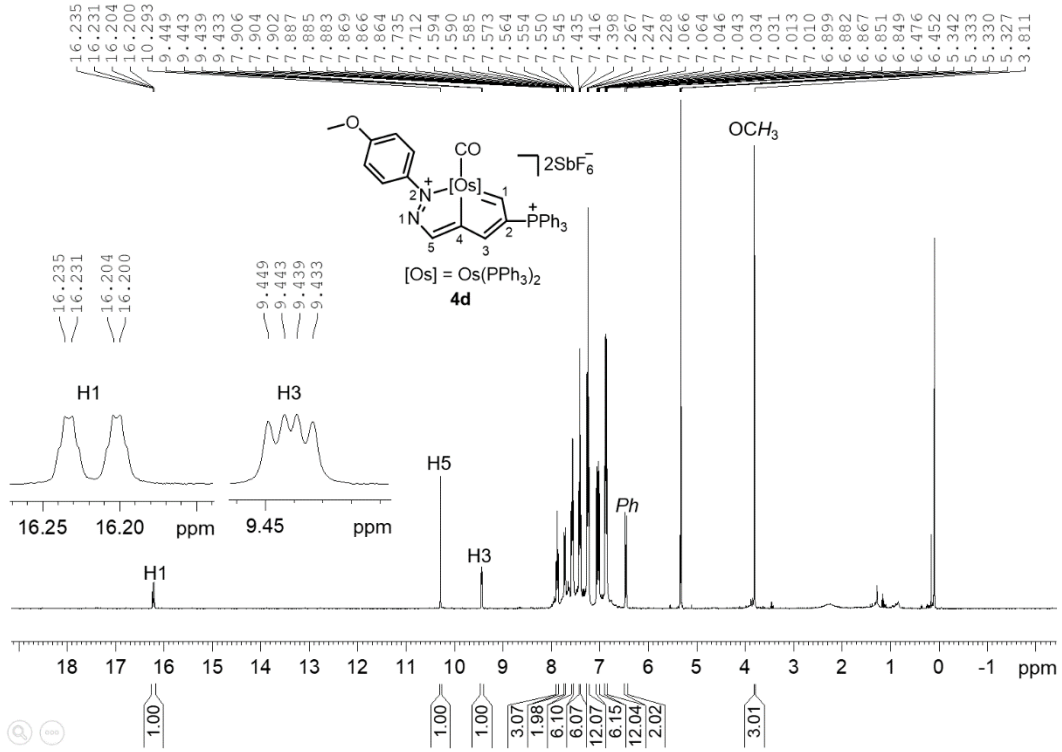


Figure S36 The ^{1}H NMR (400.1 MHz, CD_2Cl_2) spectrum for complex **4d**.

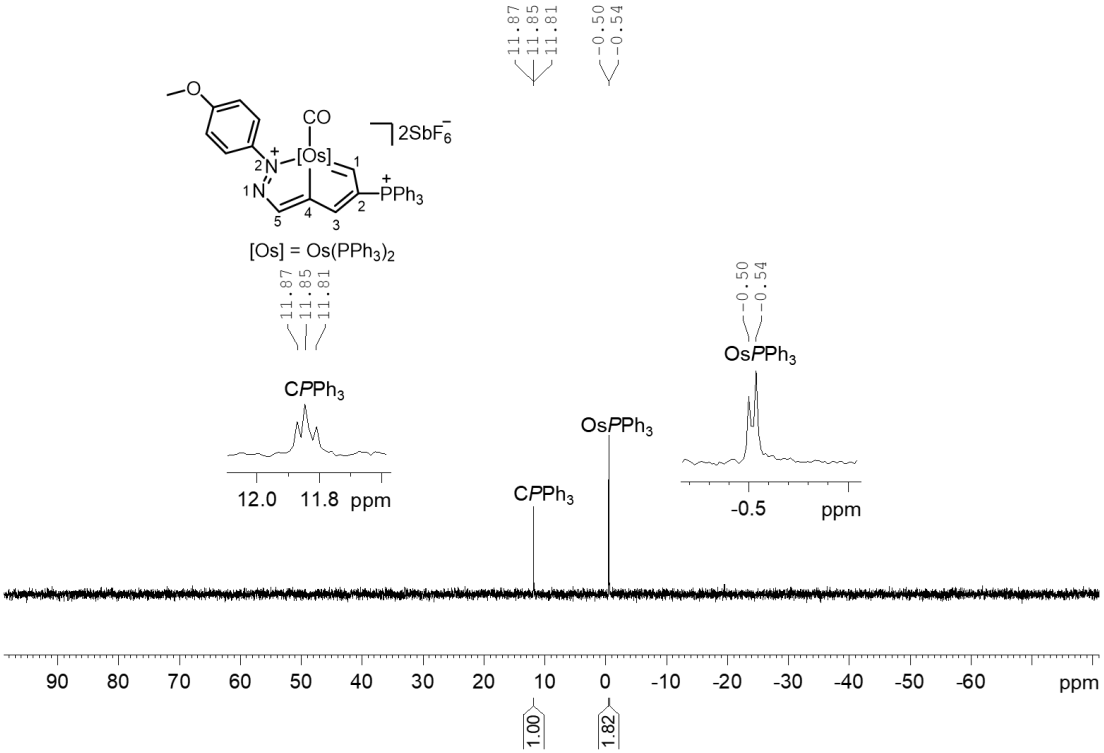


Figure S37 The $^{31}P\{^{1}H\}$ NMR (161.9 MHz, CD_2Cl_2) spectrum for complex **4d**.

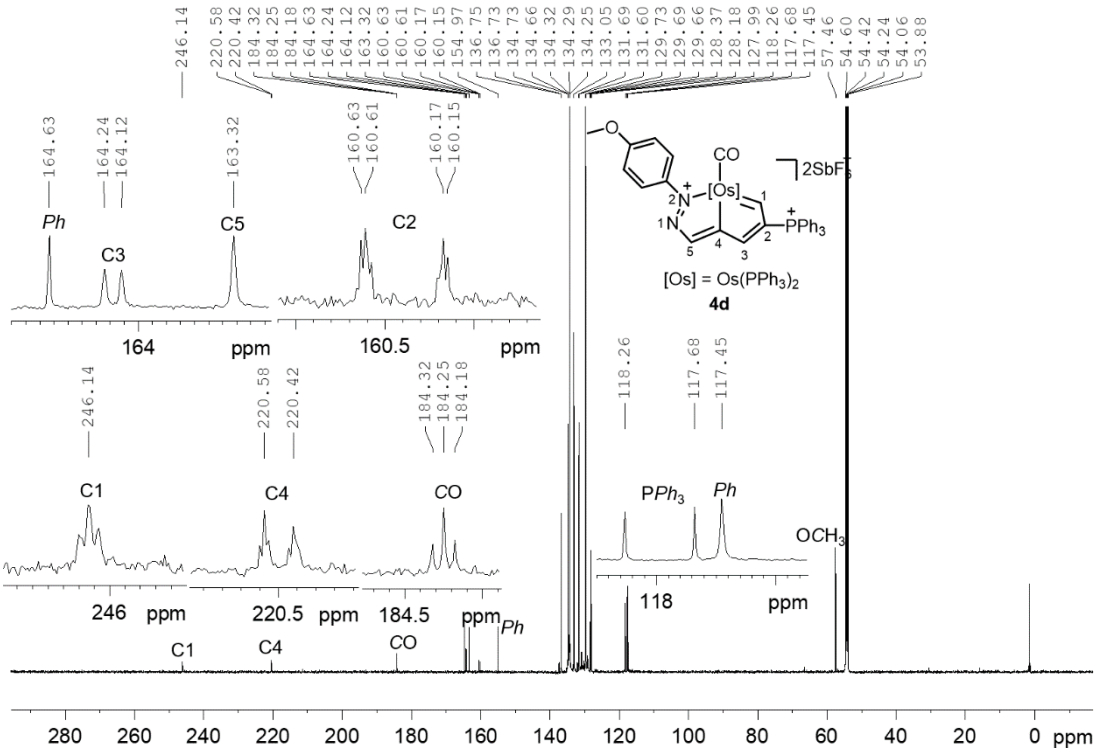


Figure S38 The $^{13}C\{^{1}H\}$ NMR (150.9 MHz, CD_2Cl_2) spectrum for complex **4d**.

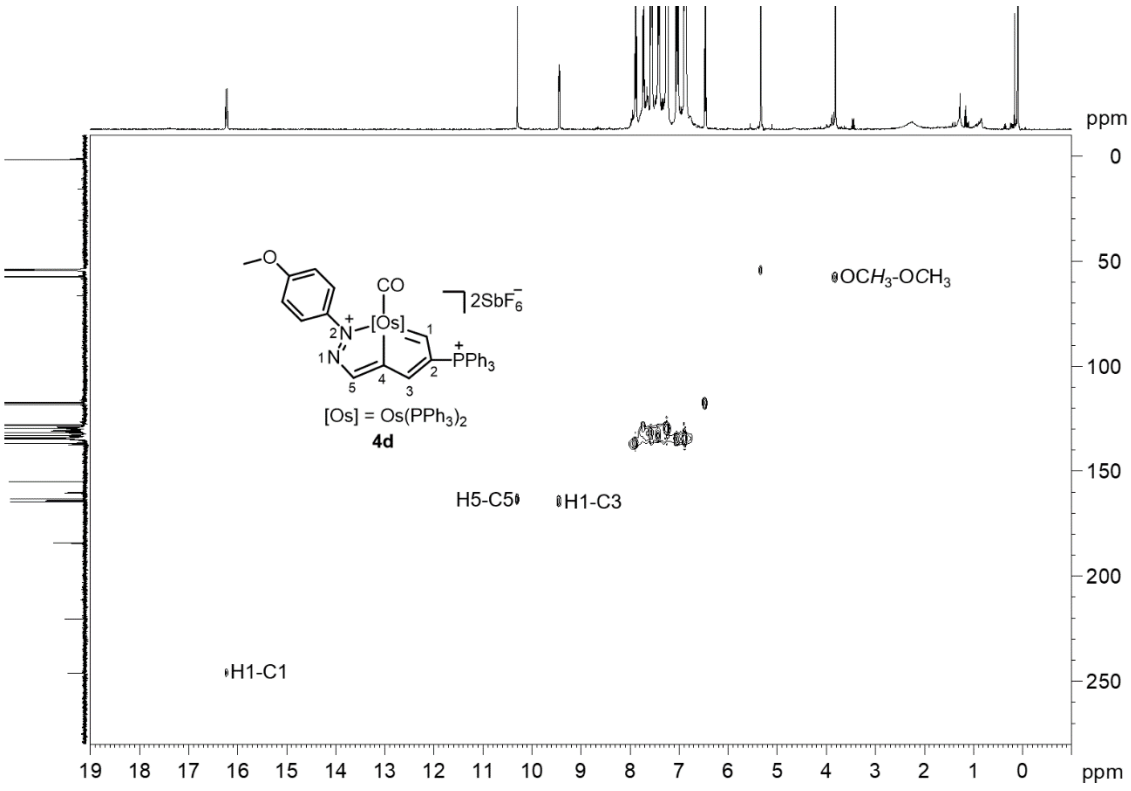


Figure S39 The ^{1}H-^{13}C HSQC spectrum for complex **4d** in CD_2Cl_2.

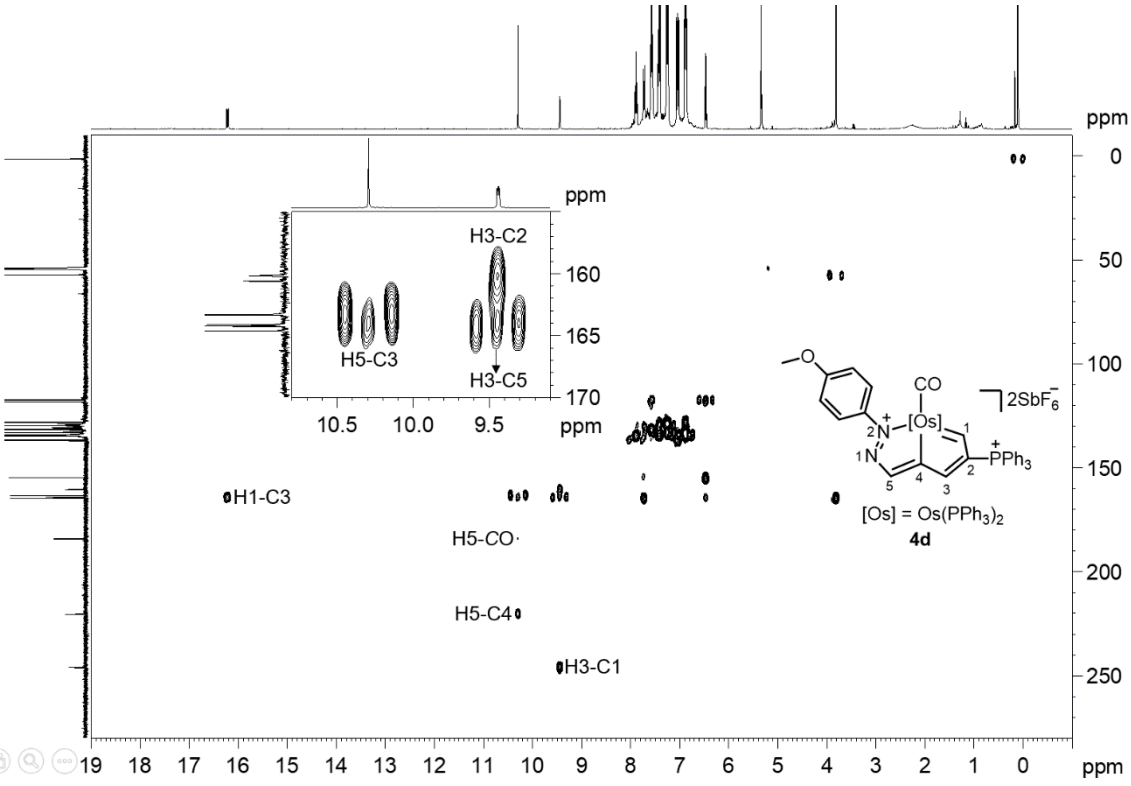


Figure S40 The ^{1}H-^{13}C HMBC spectrum for complex **4d** in CD_2Cl_2.

5. HRMS Spectra

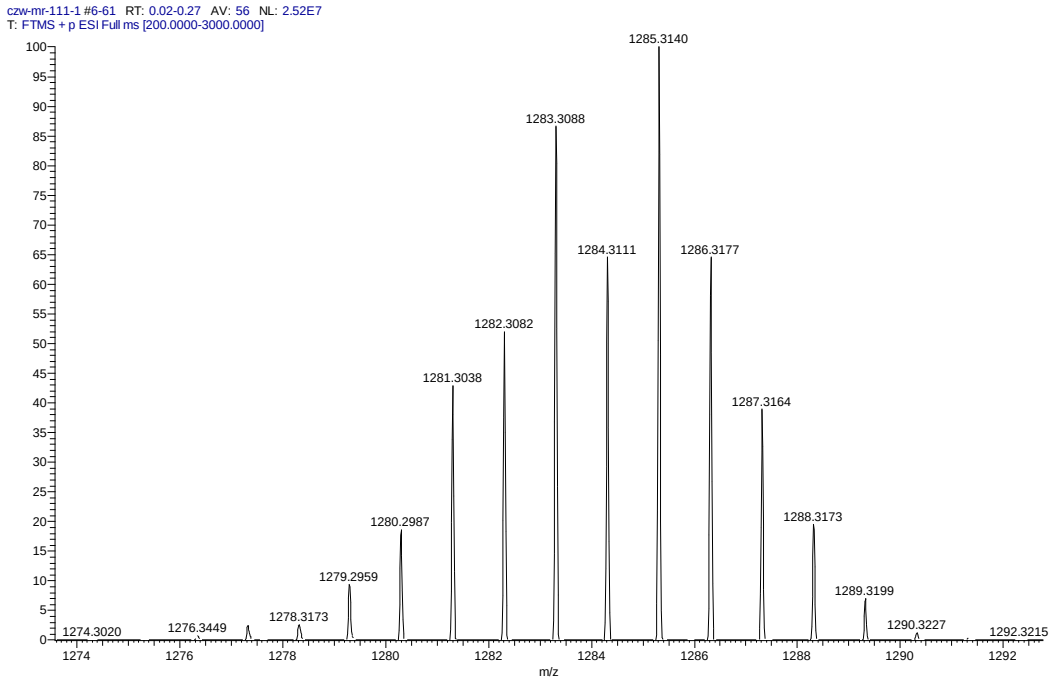


Figure S41 Positive ion ESI-MS spectrum of **[3a-Cl]**$^+$ $[C_{69}H_{61}ClN_2O_3OsP_3]^+$ measured in dichloromethane.

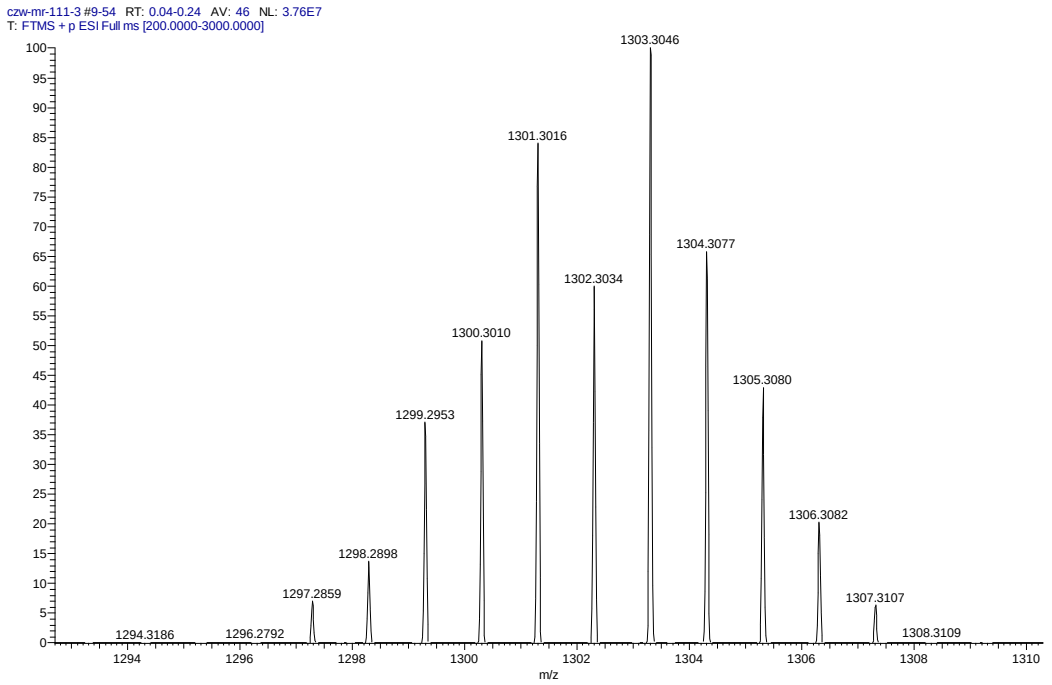


Figure S42 Positive ion ESI-MS spectrum of **[3b-Cl]**$^+$ $[C_{69}H_{60}ClFN_2O_3OsP_3]^+$ measured in dichloromethane.

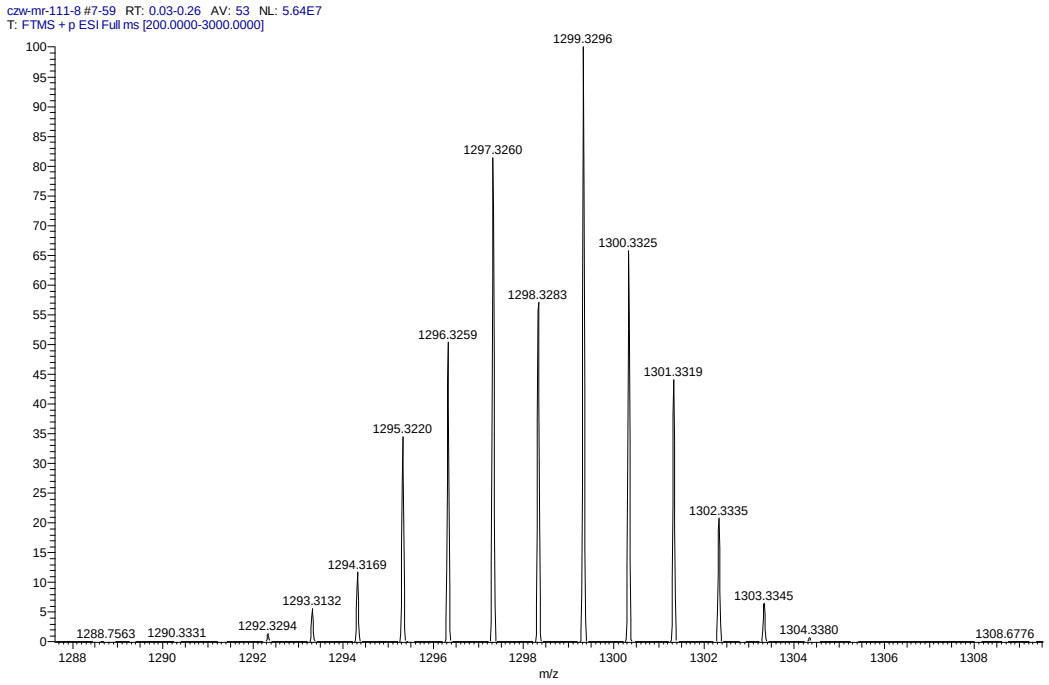


Figure S43 Positive ion ESI-MS spectrum of **[3c-Cl]**$^+$ $[C_{70}H_{63}ClN_2O_3OsP_3]^+$ measured in dichloromethane.

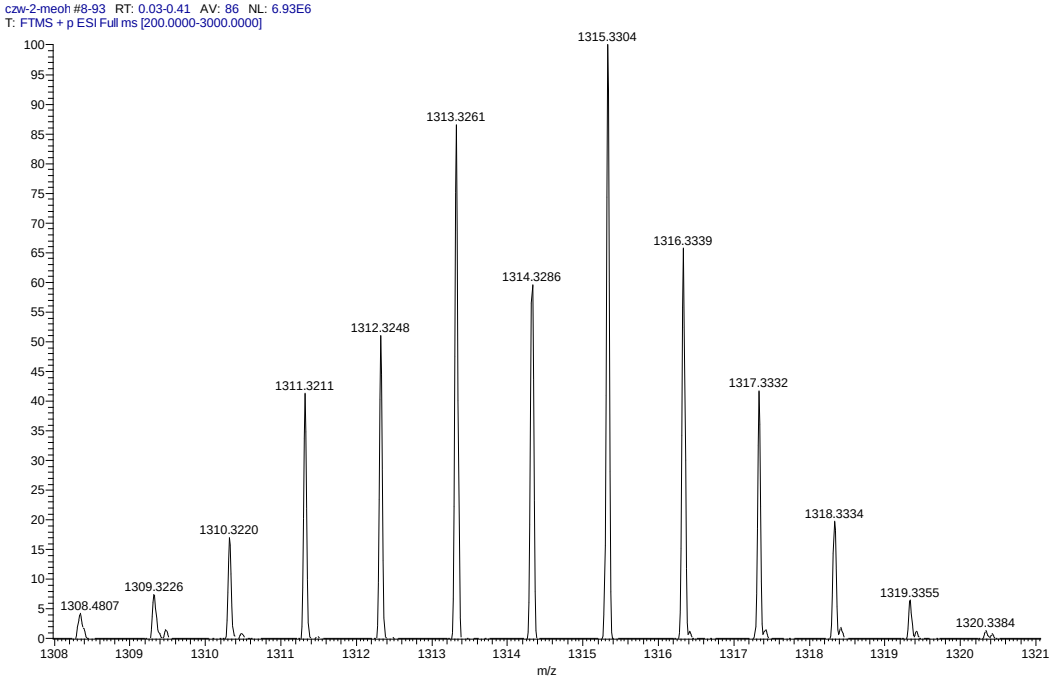


Figure S44 Positive ion ESI-MS spectrum of **[3d-Cl]**$^+$ $[C_{70}H_{63}ClN_2O_4OsP_3]^+$ measured in dichloromethane.

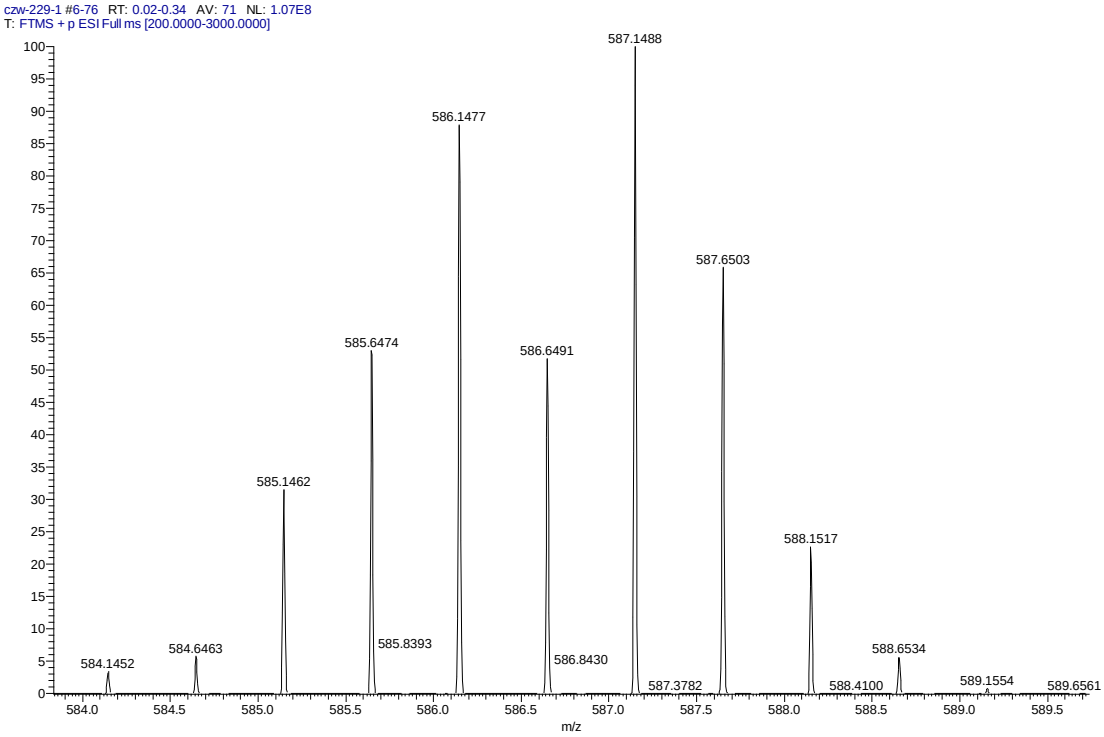


Figure S45 Positive ion ESI-MS spectrum of **[4a-2SbF$_6$]$^{2+}$** $[C_{66}H_{53}N_2OOsP_3]^{2+}$ measured in dichloromethane.

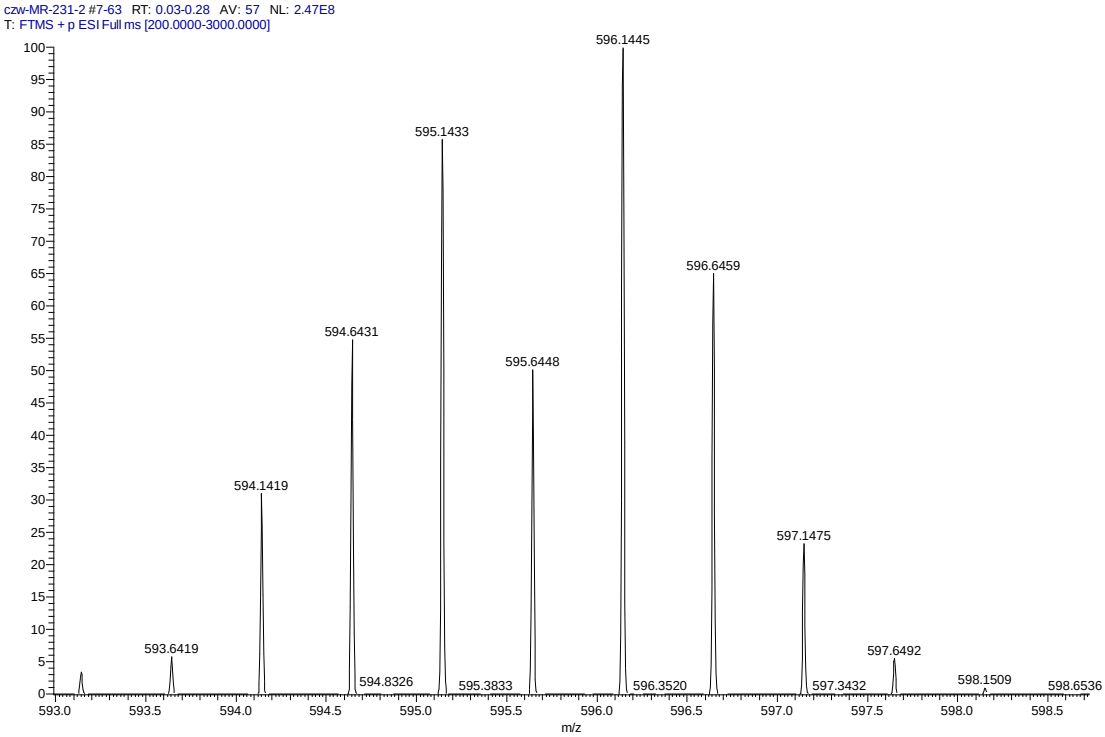


Figure S46 Positive ion ESI-MS spectrum of **[4b-2SbF$_6$]$^{2+}$** $[C_{66}H_{52}FN_2OOsP_3]^{2+}$ measured in dichloromethane.

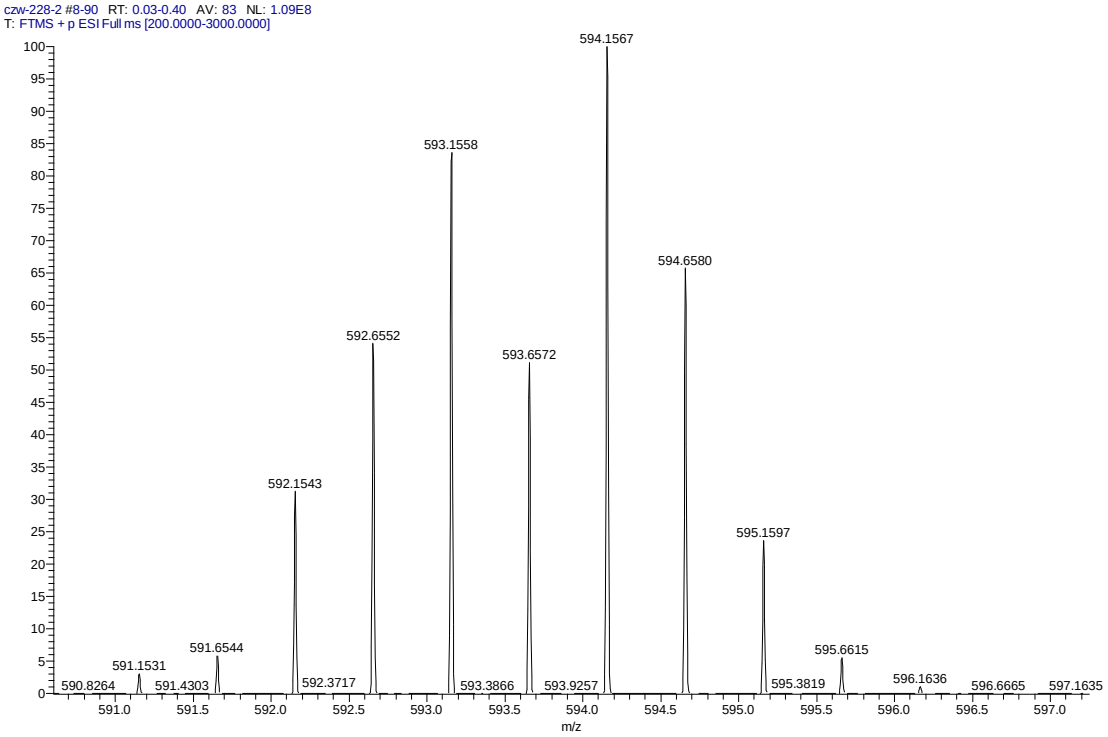


Figure S47 Positive ion ESI-MS spectrum of **[4c-2SbF$_6$]$^{2+}$** $[C_{67}H_{55}N_2OOsP_3]^{2+}$ measured in dichloromethane.

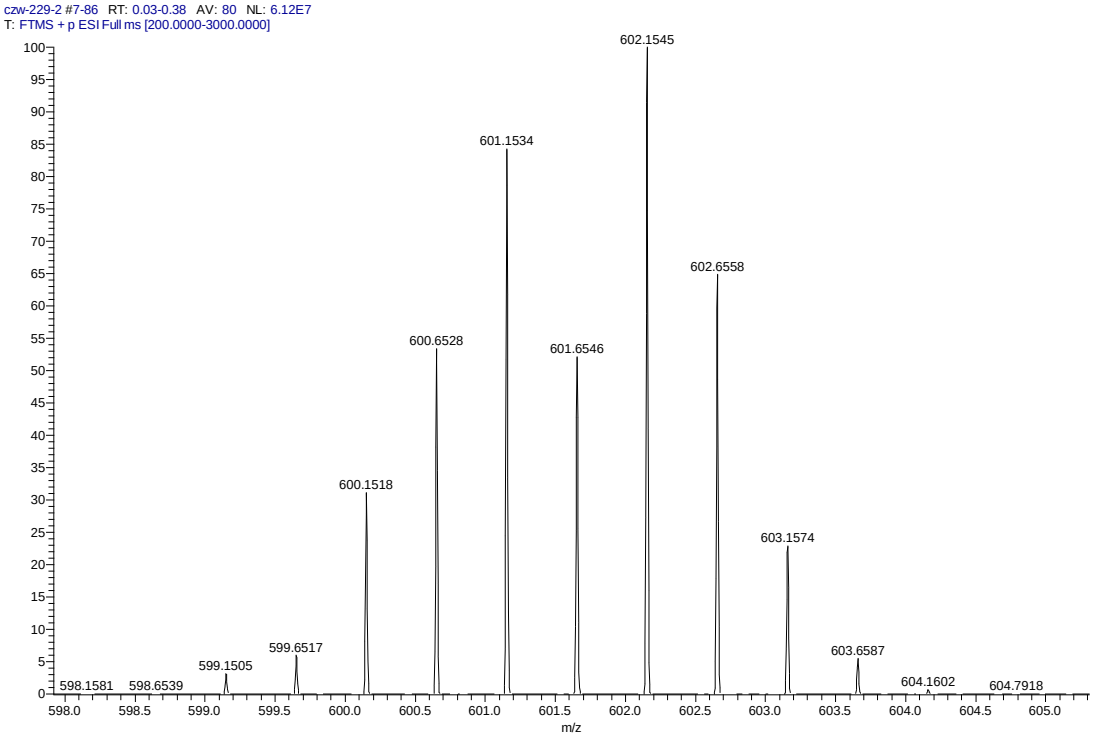


Figure S48 Positive ion ESI-MS spectrum of **[4d-2SbF$_6$]$^{2+}$** $[C_{67}H_{55}N_2O_2OsP_3]^{2+}$ measured in dichloromethane.

6. Crystallographic Details

Crystallographic Details. Single-crystal X-ray diffraction data were collected on a Bruker CMOS area detector (for **3b**, **3d**, **4b** and **4d**) and Bruker APEX-II CCD area detector (for **3a**, **3c**, **4a** and **4c**) with graphite-monochromated GaKa radiation (λ = 1.34139 Å) for **4c**, and CuKα (λ = 1.54184) for **3a-d**, **4a**, **4b** and **4d**. All the Data were corrected for absorption effects using the multi-scan technique. Using Olex2,[S5] the structures were solved with the ShelXT[S6] structure solution program using Charge Flipping and refined with the ShelXL[S7] refinement package using Least Squares minimization. Non-H atoms were refined anisotropically unless otherwise stated. Hydrogen atoms were introduced at their geometric positions and refined as riding atoms unless otherwise stated. The disordered parts containing solvent CH_2Cl_2, phenyl groups on PPh_3 and counter anion SbF_6^- were refined by using restraints. The crystals suitable for X-ray diffraction were grown from the CH_2Cl_2 solution layered with *n*-hexane for complexes **3a-d** and **4a-d**. CCDC-2233810 (**3a**), CCDC-2233811 (**3b**), CCDC-2233812 (**3c**), CCDC-2233813 (**3d**), CCDC-2233814 (**4a**), CCDC-2233815 (**4b**), CCDC-2233816 (**4c**) and CCDC-2233817 (**4d**) contain the supplementary crystallographic data for this paper, and the data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures. For further details on the crystal data, data collection, and refinements, see **Tables S1-S4**.

Table S1 Crystal data and structure refinement for **3a** and **3b**.

	3a $3.5CH_2Cl_2$	**3b** $3CH_2Cl_2$
Formula	$C_{72.5}H_{68}Cl_9OsN_2O_3P_3$	$C_{72}H_{65}Cl_8FOsN_2O_3P_3$
Mr	1617.44	1591.97
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a [Å]	13.1837(3)	13.0268(7)

b [Å]	20.2111(5)	20.4321(11)
c [Å]	26.5287(7)	26.2852(12)
α [°]	90	90
β [°]	98.736 (2)	97.885(3)
γ [°]	90	90
V [Å^3]	6986.8(3)	6930.0(6)
Z	4	4
ρ_{calcd} [gcm^{-3}]	1.538	1.526
μ [mm^{-1}]	7.650	7.378
F(000)	3260.0	3204.0
Crystal size [mm^3]	0.10 × 0.06 × 0.04	0.08×0.06×0.04
2θ range [℃]	5.52 to 139.178	5.498 to 133.786
Reflns collected	75298	55649
Independent reflns	12963	12247
Observed reflns [$I \geq 2\sigma$]	11183	9924
Data/restraints/params	12963/163/921	12247/0/813
GOF on F^2	1.198	1.031
R_1/wR_2[$I \geq 2\sigma(I)$]	0.0661/0.1461	0.0429/0.1080
R_1/wR_2 (all data)	0.0767/0.1510	0.0583/0.1161
Largest peak/hole [e Å^{-3}]	1.64/-1.23	2.62/-1.41

Table S2 Crystal data and structure refinement for **3c** and **3d**.

	3c $3CH_2Cl_2$	**3d** $3CH_2Cl_2$
Formula	$C_{73}H_{69}Cl_8OsN_2O_3P_3$	$C_{73}H_{69}Cl_8OsN_2O_4P_3$
Mr	1589.01	1605.01
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a [Å]	12.9751(11)	12.8076(5)
b [Å]	20.5087(17)	20.4760(8)
c [Å]	26.253(2)	26.9271(10)
α [°]	90	90
β [°]	100.951(3)	97.668(2)
γ [°]	90	90
V [Å^3]	6858.9(10)	6998.4(5)
Z	4	4
ρ_{calcd} [gcm^{-3}]	1.539	1.523
μ [mm^{-1}]	7.431	7.300
F(000)	3208.0	3240.0
Crystal size [mm^3]	0.16 ×0.12 ×0.1	0.16×0.10×0.08
2θ range [°]	5.506 to 134.148	5.44 to 133.272
Reflns collected	54402	61949
Independent reflns	11981	12350

Observed reflns [$I \geq 2\sigma$]	11686	11856
Data/restraints/params	11981/0/814	12350/18/823
GOF on F^2	1.082	1.027
$R_1/wR_2[I \geq 2\sigma(I)]$	0.0313/0.0841	0.0209/0.0484
R_1/wR_2 (all data)	0.0327/0.0882	0.0228/0.0490
Largest peak/hole [e Å^{-3}]	2.53/-0.80	1.08/-0.90

Table S3 Crystal data and structure refinement for **4a** and **4b**.

	4a CH_2Cl_2	**4b** $2CH_2Cl_2$
Formula	$C_{133}H_{108}Cl_2F_{24}Os_2N_4O_2P_6Sb_4$	$C_{68}H_{56}Cl_4F_{13}OsN_2OP_3Sb_2$
Mr	3374.35	1832.55
Crystal system	triclinic	triclinic
Space group	*P*-1	*P*-1
a [Å]	11.6995(9)	11.7175(7)
b [Å]	21.8835(15)	13.7798(8)
c [Å]	25.5349(19)	21.3973(9)
α [°]	104.879(4)	98.994(2)
β [°]	91.321(4)	98.356(2)
γ [°]	95.310(4)	94.226(4)
V [Å^3]	6283.8(8)	3359.7(3)
Z	2	2

ρ_{calcd} [gcm^{-3}]	1.783	1.811
μ [mm^{-1}]	12.319	12.672
F(000)	3292.0	1788.0
Crystal size [mm^3]	0.12 ×0.08 ×0.06	0.18×0.06×0.04
2θ range [°]	4.2 to 124.992	4.234 to 133.286
Reflns collected	75780	46595
Independent reflns	19902	11820
Observed reflns [$I \geq 2\sigma$]	14923	11356
Data/restraints/params	19902/156/1657	11820/0/847
GOF on F^2	1.056	1.062
R_1/wR_2[$I \geq 2\sigma(I)$]	0.0539/0.1341	0.0230/0.0524
R_1/wR_2 (all data)	0.0749/0.1448	0.0242/0.0531
Largest peak/hole [e Å^{-3}]	1.90/-1.66	1.90/-0.94

Table S4 Crystal data and structure refinement for **4c** and **4d**.

	4c $2CH_2Cl_2$	**4d**
Formula	$C_{69}H_{59}Cl_4F_{12}Os_2N_2OP_3Sb_2$	$C_{67}H_{55}F_{12}OsN_2O_2P_3Sb_2$
Mr	1828.59	1674.74
Crystal system	triclinic	monoclinic
Space group	*P*-1	$P2_1/n$
a [Å]	11.1145(5)	11.9962(3)

b [Å]	13.6851(6)	20.0596(5)
c [Å]	23.2566(10)	26.3587(6)
α [°]	81.356(2)	90
β [°]	78.117(2)	98.0180(10)
γ [°]	84.437(2)	90
V [Å^3]	3414.3(3)	6280.9(3)
Z	2	4
ρ_{calcd} [gcm^{-3}]	1.779	1.771
μ [mm^{-1}]	8.436	11.949
F(000)	1788.0	3272.0
Crystal size [mm^3]	0.06 × 0.05 × 0.03	0.06 × 0.04 × 0.04
2θ range [°]	3.408 to 105.962	5.556 to 145.196
Reflns collected	67848	62215
Independent reflns	12009	12297
Observed reflns [$I \geq 2\sigma$]	10818	10621
Data/restraints/params	12009/0/788	12297/0/803
GOF on F^2	1.133	1.077
R_1/wR_2[$I \geq 2\sigma(I)$]	0.0368/0.0899	0.0443/0.1065
R_1/wR_2 (all data)	0.0411/0.0958	0.0528/0.1113
Largest peak/hole [e Å^{-3}]	1.25/-1.78	3.05/-1.60

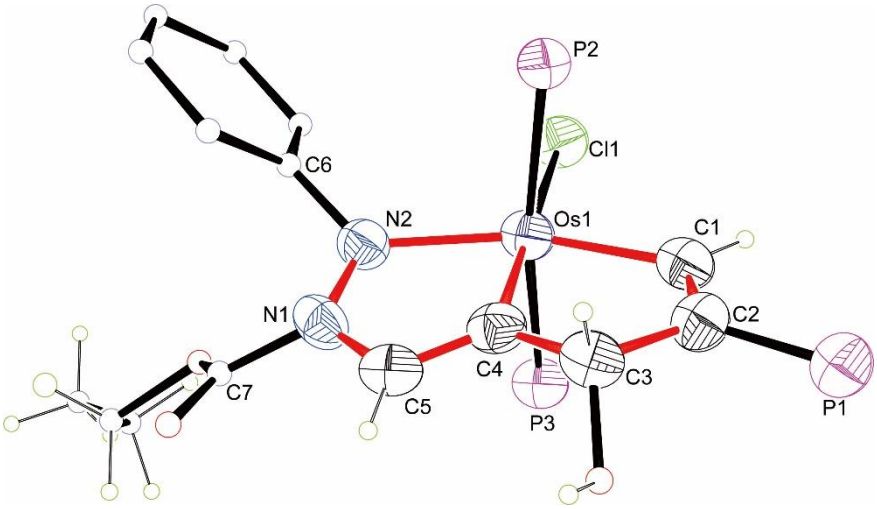


Figure S49. X-ray molecular structure for the cation of complex **3a** (ellipsoids are at the 50% probability level, the phenyl groups in PPh_3 and hydrogen atoms of phenyl group have been omitted for clarity). Selected bond distances (Å) and angles (deg): Os1-C1 2.067(8), Os1-C4 1.960(7), Os1-N2 2.066(7), Os1-Cl1 2.5058(17), C1-C2 1.349(11), C2-C3 1.528 (10), C3-C4 1.509(11), C4-C5 1.362 (10), C5-N1 1.388(10), N1-N2 1.370(8), C3-O1 1.433(8); Os1-C1-C2 117.9(6), C1-C2-C3 116.2(7), C2-C3-C4 105.3(6), C3-C4-Os1 120.9(5), C4-Os1-C1 78.3(3), Os1-C4-C5 116.3(6), C4-C5-N1 114.6(7), C5-N1-N2 116.3(6), N1-N2-Os1 111.6(5), N2-Os1-C4 79.0(3).

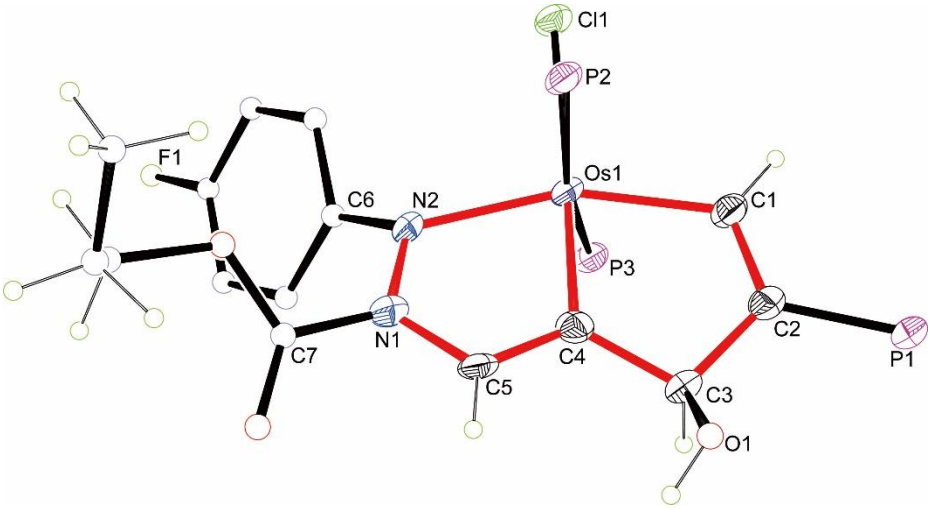


Figure S50. X-ray molecular structure for the cation of complex **3b** (ellipsoids are at the 50% probability level, the phenyl groups in PPh_3 and hydrogen atoms of phenyl group have been omitted for clarity). Selected bond distances (Å) and angles (deg): Os1-C1 2.070(5), Os1-C4 1.954(5), Os1-N2 2.088(4), Os1-Cl1 2.5136(10), C1-C2 1.353(7), C2-C3 1.508(7), C3-C4 1.527(16), C4-C5 1.372(12), C5-N1 1.373(6), N1-N2 1.369(6), C3-O1 1.439(6); Os1-C1-C2 116.9(4), C1-C2-C3 117.3(4), C2-C3-C4 105.2(4), C3-C4-Os1 120.1(3), C4-Os1-C1 78.74(19), Os1-C4-C5 116.2(3), C4-C5-N1

115.0(4), C5-N1-N2 117.2(4), N1-N2-Os1 110.6(3), N2-Os1-C4 79.14(17).

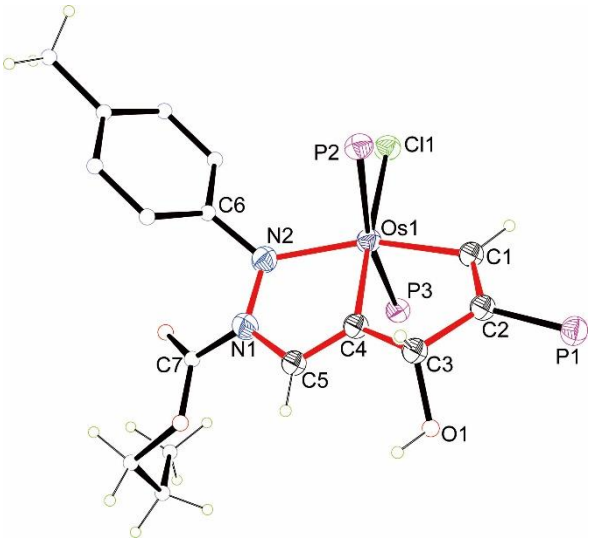


Figure S51. X-ray molecular structure for the cation of complex **3c** (ellipsoids are at the 50% probability level, the phenyl groups in PPh_3 and hydrogen atoms of phenyl group have been omitted for clarity). Selected bond distances (Å) and angles (deg): Os1-C1 2.081(3), Os1-C4 1.976(3), Os1-N2 2.052(3), Os1-Cl1 2.5025(7), C1-C2 1.356(4), C2-C3 1.520(4), C3-C4 1.510(4), C4-C5 1.367(4), C5-N1 1.398(4), N1-N2 1.384(4), C3-O1 1.425(3); Os1-C1-C2 117.3(3), C1-C2-C3 117.0(3), C2-C3-C4 105.1(2), C3-C4-Os1 120.9(2), C4-Os1-C1 77.90(12), Os1-C4-C5 115.5(2), C4-C5-N1 114.8(3), C5-N1-N2 115.3(4), N1-N2-Os1 111.80(18), N2-Os1-C4 79.03(11).

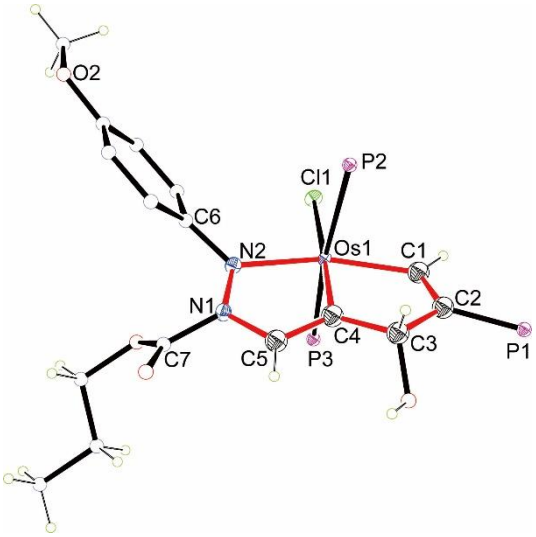


Figure S52. X-ray molecular structure for the cation of complex **3d** (ellipsoids are at the 50% probability level, the phenyl groups in PPh_3 and hydrogen atoms of phenyl group have been omitted for clarity). Selected bond distances (Å) and angles (deg): Os1-C1 2.0710(19), Os1-C4 1.955(2), Os1-N2 2.0716(16), Os1-Cl1 2.5221(4), C1-C2 1.354(3), C2-C3 1.516(3), C3-C4 1.519(3), C4-C5 1.377(3),

C5-N1 1.376(3), N1-N2 1.368(2), C3-O1 1.429(2); Os1-C1-C2 116.73(14), C1-C2-C3 117.54(16), C2-C3-C4 104.98(15), C3-C4-Os1 120.85(14), C4-Os1-C1 78.73(8), Os1-C4-C5 115.99(4), C4-C5-N1 114.48(17), C5-N1-N2 117.36(16), N1-N2-Os1 111.01(11), N2-Os1-C4 79.47(7).

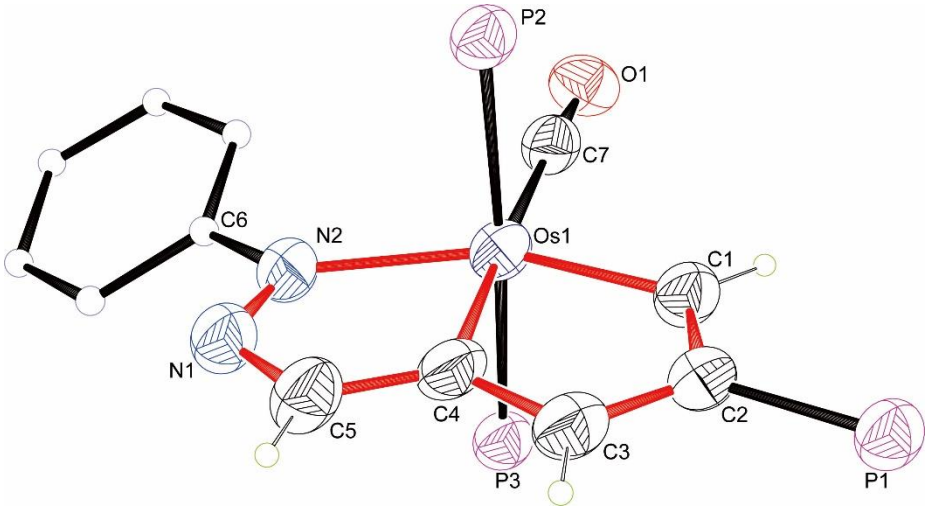


Figure S53. X-ray molecular structure for the cation of complex **4a** (ellipsoids are at the 50% probability level, the phenyl groups in PPh_3 and hydrogen atoms of phenyl group have been omitted for clarity). Selected bond distances (Å) and angles (deg): Os1-C1 1.987(7), Os1-C4 2.040(8), Os1-N2 2.144(6), Os1-C7 1.926(9), C1-C2 1.432(11), C2-C3 1.378(11), C3-C4 1.431(11), C4-C5 1.380(12), C5-N1 1.345(10), N1-N2 1.297(10), C7-O1 1.148(10); Os1-C1-C2 117.5(5), C1-C2-C3 115.3(7), C2-C3-C4 111.9(7), C3-C4-Os1 117.5(6), C4-Os1-C1 77.7(3), Os1-C4-C5 116.2(6), C4-C5-N1 117.0(8), C5-N1-N2 115.6(7), N1-N2-Os1 116.6(5), N2-Os1-C4 74.5(3).

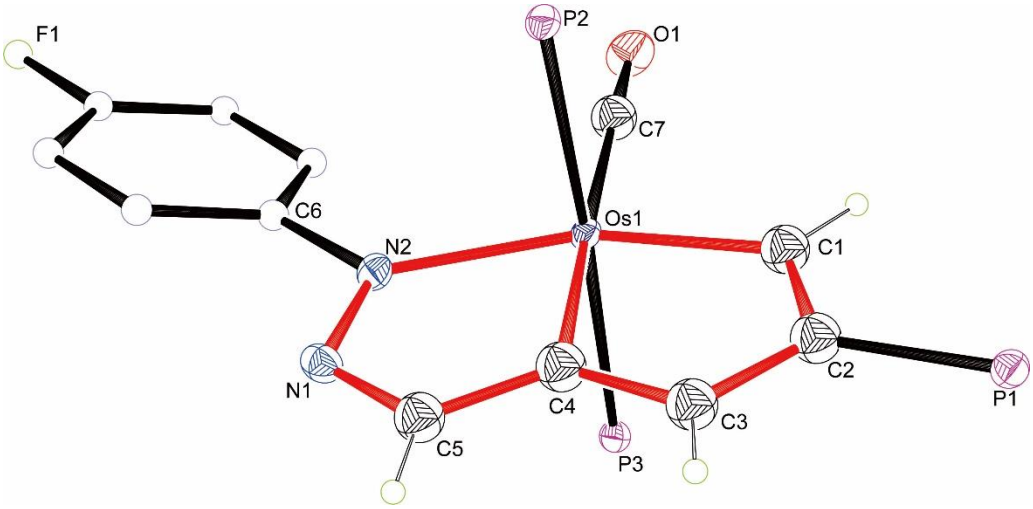


Figure S54. X-ray molecular structure for the cation of complex **4b** (ellipsoids are at the 50% probability level, the phenyl groups in PPh_3 and hydrogen atoms of phenyl group have been omitted for

clarity). Selected bond distances (Å) and angles (deg): Os1-C1 1.994(4), Os1-C4 2.020(3), Os1-N2 2.091(2), Os1-C7 1.963(3), C1-C2 1.437(4), C2-C3 1.390(4), C3-C4 1.423(4), C4-C5 1.385(4), C5-N1 1.345(4), N1-N2 1.333(3), C7-O1 1.135(4); Os1-C1-C2 115.3(2), C1-C2-C3 115.9(2), C2-C3-C4 112.6(2), C3-C4-Os1 116.7(2), C4-Os1-C1 79.43(11), Os1-C4-C5 114.5(2), C4-C5-N1 118.5(2), C5-N1-N2 113.7(2), N1-N2-Os1 116.72(18), N2-Os1-C4 76.37(10).

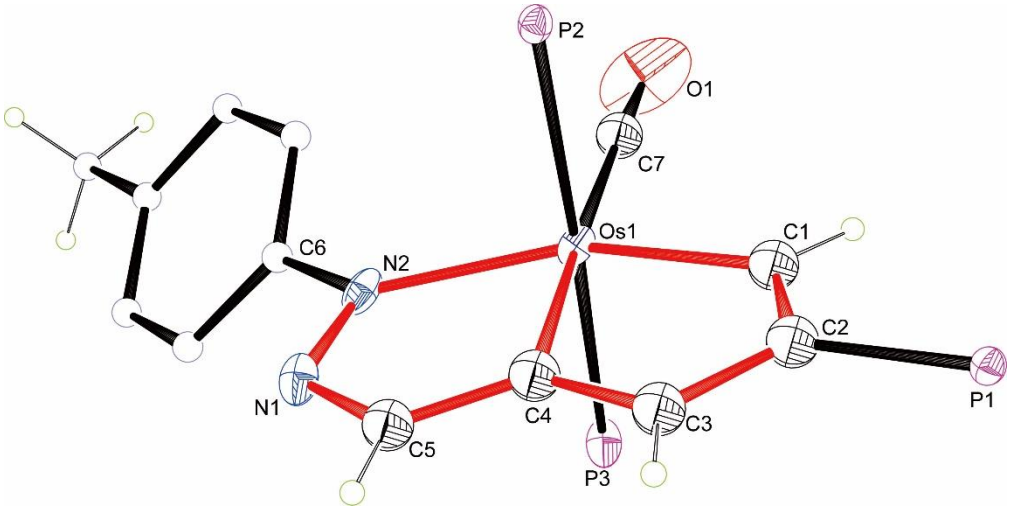


Figure S55. X-ray molecular structure for the cation of complex **4c** (ellipsoids are at the 50% probability level, the phenyl groups in PPh_3 and hydrogen atoms of phenyl group have been omitted for clarity). Selected bond distances (Å) and angles (deg): Os1-C1 1.983(4), Os1-C4 2.040(4), Os1-N2 2.106(4), Os1-C7 1.934(5), C1-C2 1.432(6), C2-C3 1.395(6), C3-C4 1.411(6), C4-C5 1.388(6), C5-N1 1.350(6), N1-N2 1.329(6), C7-O1 1.139(6); Os1-C1-C2 115.9(3), C1-C2-C3 115.6(4), C2-C3-C4 112.6(4), C3-C4-Os1 116.5(3), C4-Os1-C1 78.92(17), Os1-C4-C5 115.0(3), C4-C5-N1 118.6(4), C5-N1-N2 113.0(4), N1-N2-Os1 118.0(3), N2-Os1-C4 75.38(16).

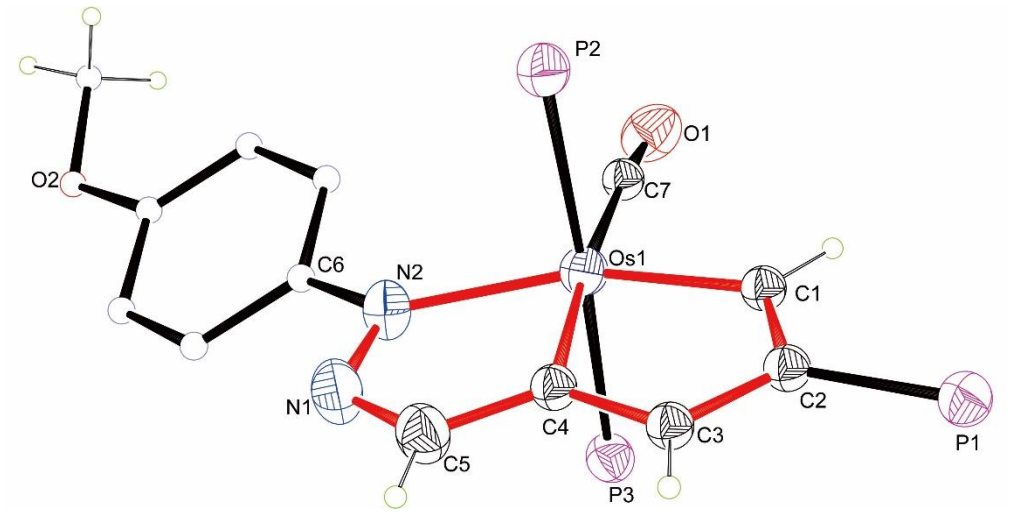


Figure S56. X-ray molecular structure for the cation of complex **4d** (ellipsoids are at the 50% probability level, the phenyl groups in PPh_3 and hydrogen atoms of phenyl group have been omitted for clarity). Selected bond distances (Å) and angles (deg): Os1-C1 1.986(5), Os1-C4 2.034(5), Os1-N2 2.126(6), Os1-C7 1.944(5), C1-C2 1.430(7), C2-C3 1.387(7), C3-C4 1.416(7), C4-C5 1.388(7), C5-N1 1.336(7), N1-N2 1.326(7), C7-O1 1.133(7); Os1-C1-C2 116.6(3), C1-C2-C3 115.7(4), C2-C3-C4 112.0(4), C3-C4-Os1 117.5(4), C4-Os1-C1 78.3(2), Os1-C4-C5 114.8(4), C4-C5-N1 119.1(5), C5-N1-N2 113.8(4), N1-N2-Os1 116.7(3), N2-Os1-C4 75.42(19).

7. UV-vis-NIR Absorption Spectra of 3 and 4.

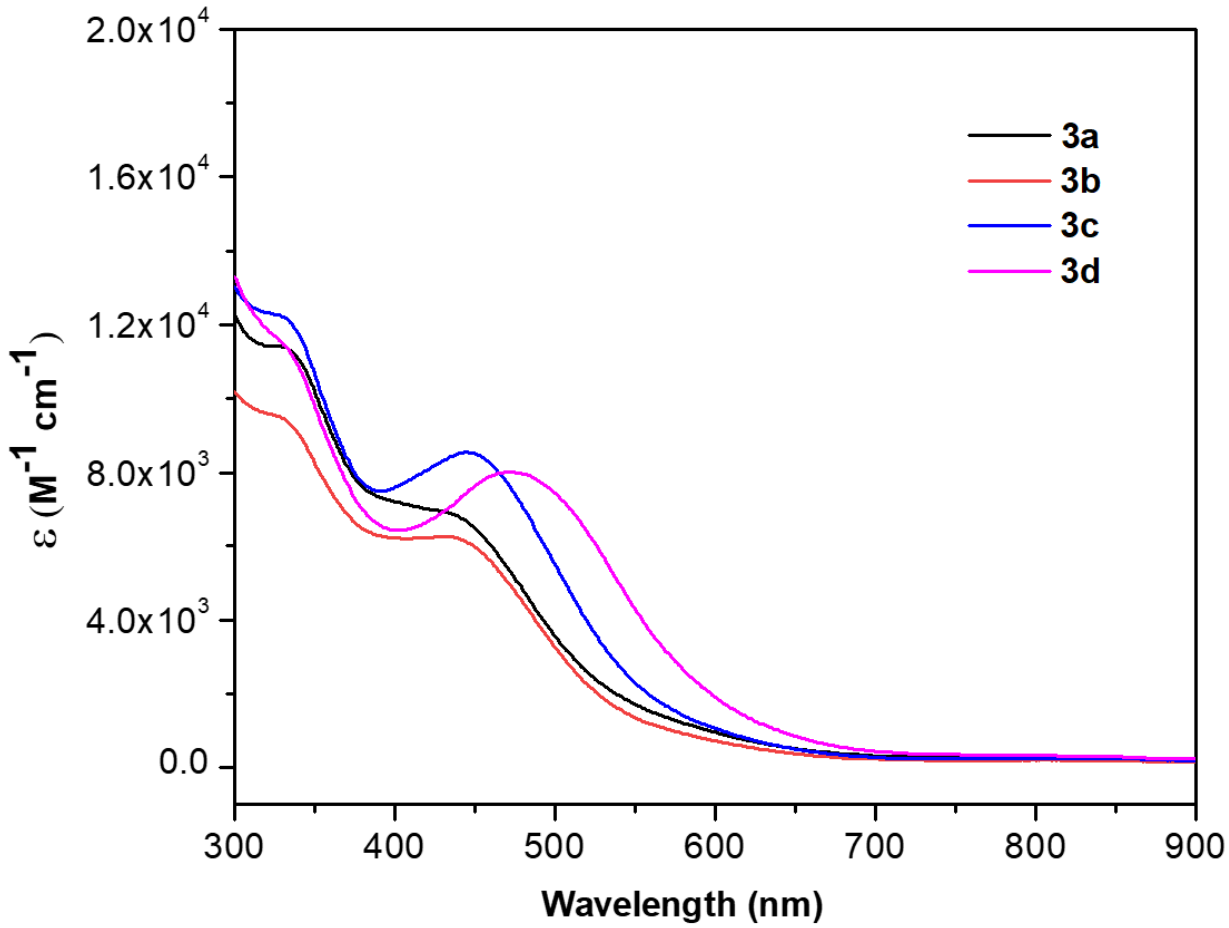


Figure S57. UV-vis-NIR absorption spectra of **3** measured in CH_2Cl_2 (2.0 * 10^{-4} M) at room temperature.

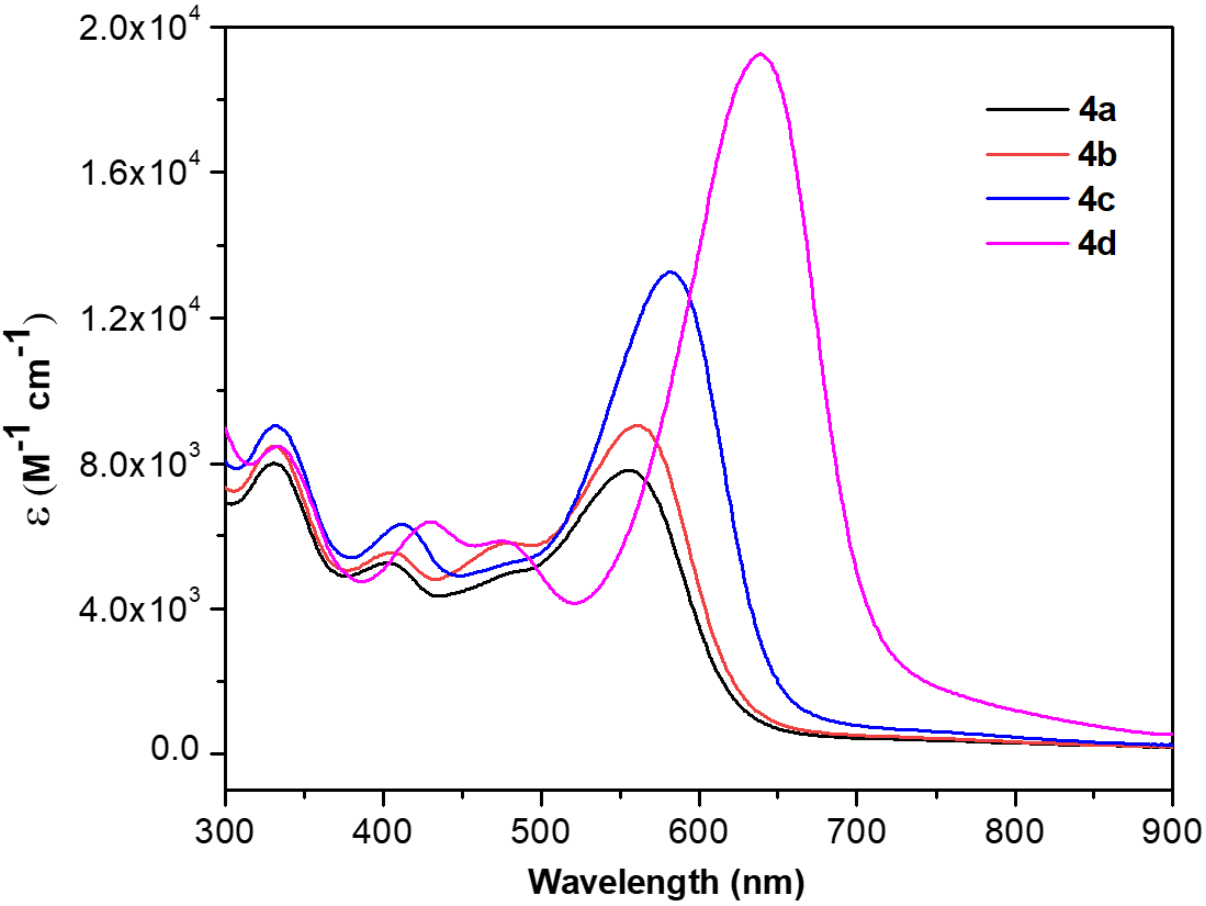


Figure S58. UV-vis-NIR absorption spectra of **4** measured in CH_2Cl_2 (2.0 * 10^{-4} M) at room temperature.

8. Experimental and Calculated Absorption Spectral Data for 4a-d.

Compound	Experimental (nm)	Calculated (nm)	*f*	Contribution (H = HOMO, L = LUMO)
4a$^+$	556 nm	593 nm	0.0935	H→L (41%) H-1→L (51%)
4b$^+$	562 nm	596 nm	0.0971	H→L (43%) H-1→L (45%)
4c$^+$	583 nm	599 nm	0.1774	H→L (47%) H-1→L (42%)

4d^{+}	639 nm	615 nm	0.3836	H→L (61%) H-1→L (30%)

Table S5. Experimental and calculated absorption spectral data for **4a-d**.

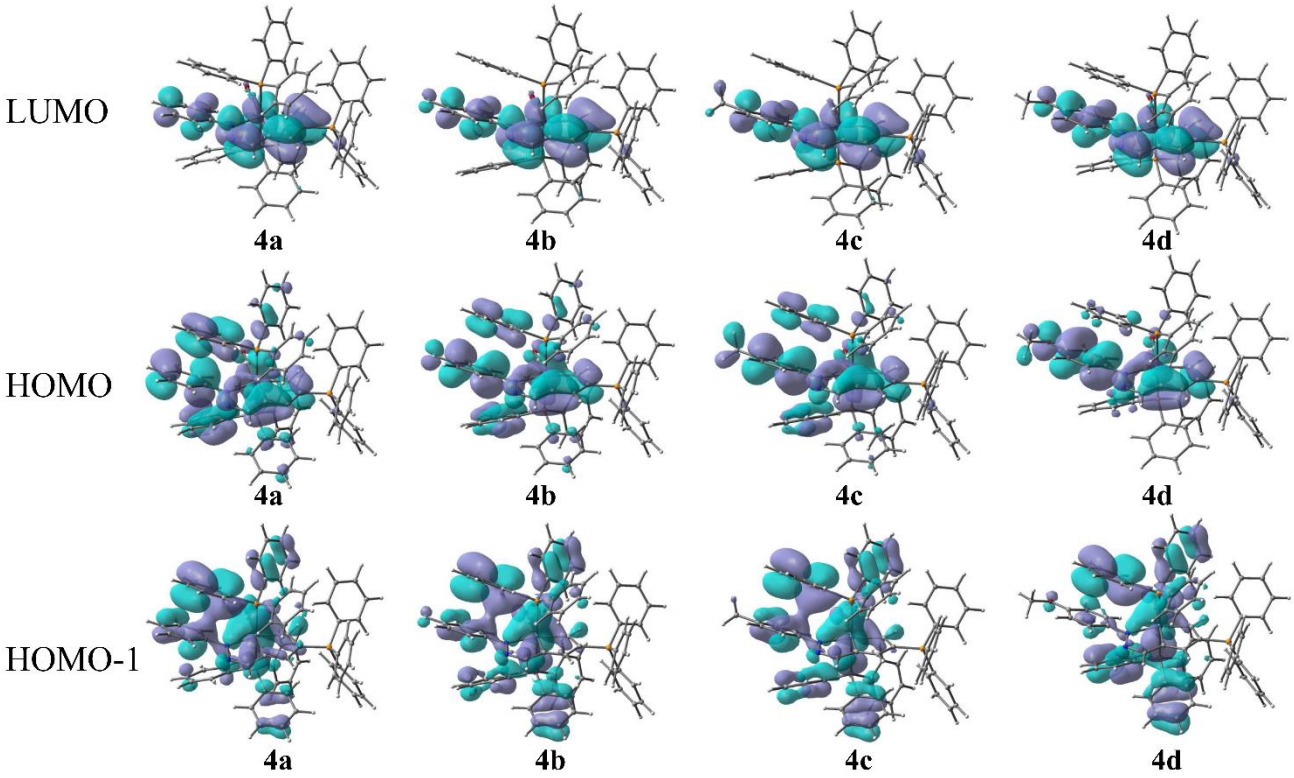


Figure S59. DFT calculated lowest unoccupied molecular orbitals (LUMO), the highest occupied molecular orbitals (HOMO) and HOMO-1 for the cations of complexes **4a-d**.

9. Theoretical Calculations

Computational details. All optimizations were performed with the Gaussian 16 software package.[S8] All of these structures evaluated were optimized at the B3LYP level[S9-11] of density functional theory (DFT) with a SDD basis set to describe Os atom[S12] and the standard 6-31G* basis set was used for the C, O, N, P, F and H atoms for the cation of **4a-d**, whereas the standard 6-311++G** basis set was used for C, O, N, P, F and H atoms for other complexes.[S13] Frequency analyses have been performed to validate the stationary points as intermediate with zero imaginary frequency. The D3 dispersion correction was also applied to the single-point energy calculations. To understand the absorption spectra, we performed time-dependent density functional theory (TD-DFT) calculations

on the cationic of complexes **4a-d** at the B3LYP/6-31g* level.[S14] In the TD-DFT calculations, the polarizable continuum model was used with dichloromethane as the solvent. Nucleus-independent chemical shift (NICS) values were calculated at the B3LYP-GIAO/6-31G* level.[S15] Anisotropy of the induced current density (ACID) calculations were carried out with the ACID program.[S16]

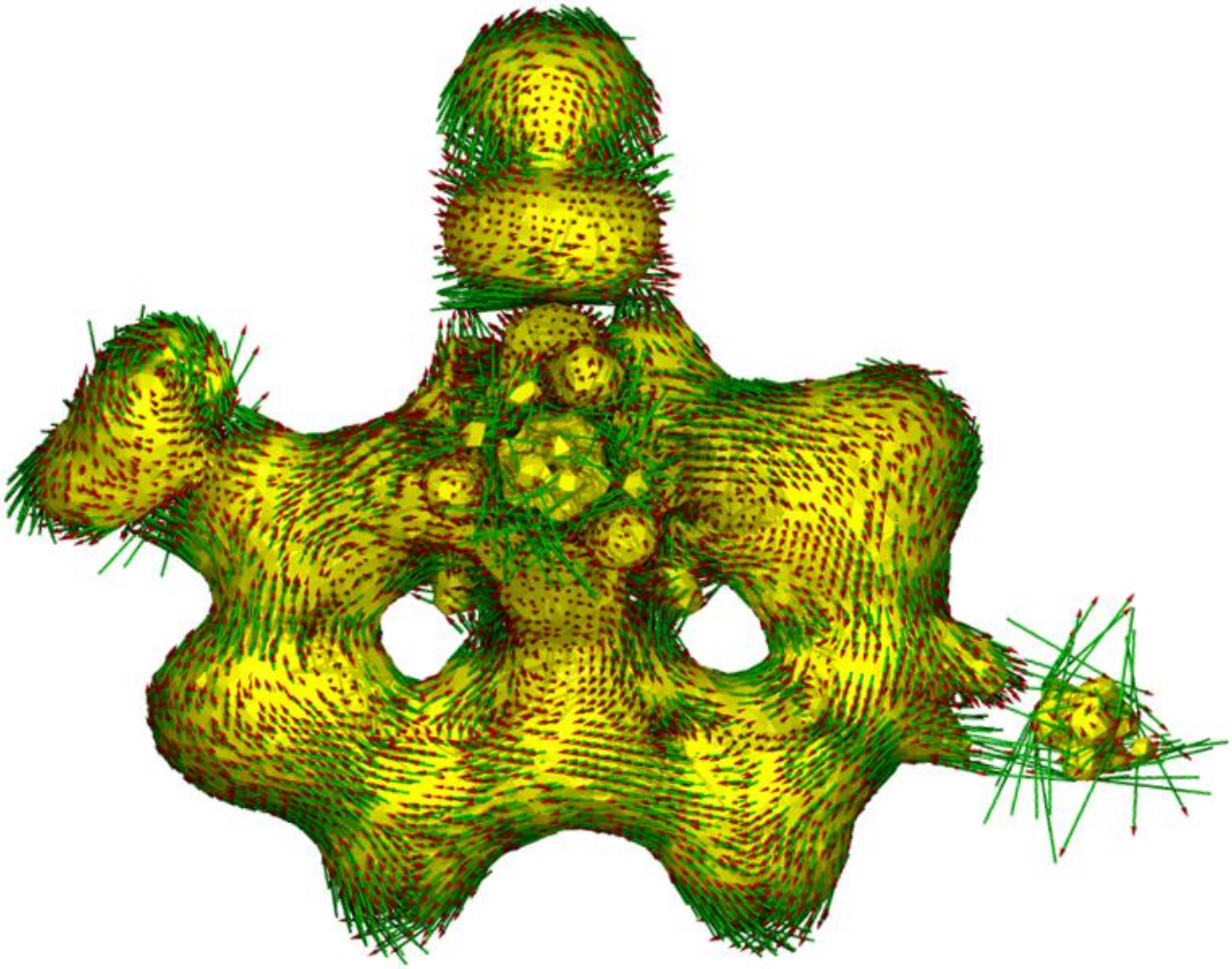


Figure S60. ACID isosurfaces of **4'**. Current density vectors are plotted onto the ACID isosurface of 0.040 to indicate diatropic ring currents. The magnetic field vector is orthogonal with respect to the ring plane and points upward (clockwise currents are diatropic).

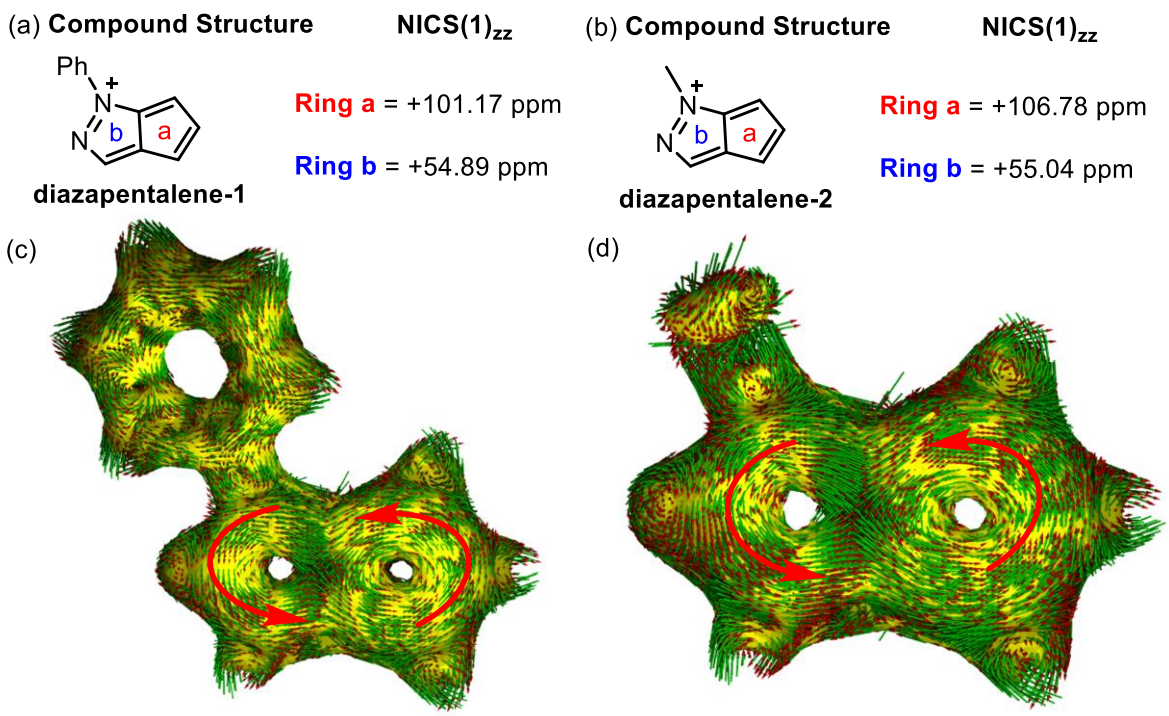


Figure S61. The NICS(1)zz values (ppm) for **diazapentalene-1** (a) and **diazapentalene-2** (b), describing the zz component 1.0 Å above the ring center. ACID isosurfaces of **diazapentalene-1** (c) and **diazapentalene-2** (d). Current density vectors are plotted onto the ACID isosurface of 0.050 to indicate diatropic ring currents. The magnetic field vector is orthogonal with respect to the ring plane and points upward (clockwise currents are diatropic).

10. Reference

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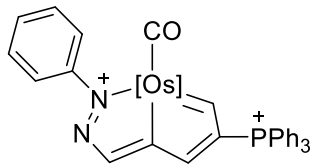
11. Cartesian Coordinates



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H	1.89409400	-0.09057900	-2.64825100
C	-2.95211100	4.02770100	1.33820300
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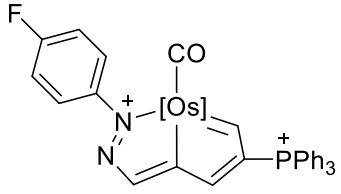

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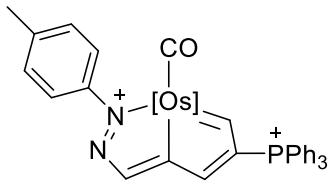

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H	-4.51373500	-4.66550600	-2.61265100
C	0.47946000	2.55074300	2.67627000
H	0.17751900	1.51367500	2.74495500
C	4.49847700	-0.98278500	-1.66629900
C	2.34670000	3.51968100	-2.38740900
H	3.42943200	3.44982200	-2.31902200
C	1.56728300	3.14317000	-1.29530200
H	2.05541900	2.78649700	-0.39920600
C	1.53699600	4.48189300	3.68261600
H	2.05562900	4.94180600	4.51881900
C	0.17750900	3.29876000	1.53022800

C	3.21069800	-2.32544500	1.56027800
H	2.35782600	-2.53485300	0.92675700
C	-2.39813500	3.39303000	0.18229800
C	-0.10017200	-2.40870900	2.86437200
H	0.31857300	-1.43140200	2.66557600
C	-0.86953900	-3.05650800	1.88872900
C	0.12206000	-3.00829400	4.10540600
H	0.71370600	-2.48995500	4.85429600
C	-3.02366700	-3.66823300	-1.42415900
H	-2.21691800	-3.94939500	-2.09145400
C	5.17240600	-0.98208800	2.08745800
H	5.83072200	-0.14644000	1.87199700
C	1.23408200	5.23702900	2.54458000
H	1.51818900	6.28387000	2.49238800
C	-4.09424200	4.58785800	1.44549300
H	-4.40220700	5.08270000	2.36168500
C	-5.37424300	-3.77090800	-0.84961900
H	-6.38304500	-4.10389200	-1.07491200
C	-3.82980600	-2.60865200	0.60233700
H	-3.64492600	-2.04246900	1.51045600
C	4.92047600	-2.32032400	-1.62603200
H	4.86103800	-2.88880800	-0.70399800
C	4.43165500	3.44840700	1.41755100
H	3.96004600	4.06076400	2.17867200
C	-4.78228400	-0.33415800	-2.06648500
H	-4.37353900	-0.67380600	-3.00907200
C	0.16752400	3.25248500	-1.33568600
C	-5.12290000	-3.03525300	0.31206200
H	-5.93353600	-2.78756900	0.99020300
C	-1.41460500	-4.32138700	2.17661400
H	-2.01451900	-4.83872700	1.43465200
C	5.42257100	-1.79654400	3.19136500
H	6.27973100	-1.59293700	3.82552200
C	3.46551600	-3.12923500	2.66976700
H	2.79373800	-3.94932300	2.90326700
C	-4.96683500	4.51620200	0.35836400
H	-5.95751200	4.95574400	0.42482700
C	1.73577200	4.00779200	-3.54591400
H	2.33722500	4.30795600	-4.39889100
C	0.55961000	4.65126700	1.47446000
H	0.33047000	5.24638700	0.59576800
C	4.57639700	-0.25355600	-2.86919200
H	4.25517900	0.78397600	-2.90921600

C	5.56210300	3.90603500	0.73261600
H	5.97852600	4.88146600	0.96518900
C	5.41952800	-2.92202100	-2.78218400
H	5.75405500	-3.95425300	-2.74765300
C	4.57080400	-2.86594500	3.48382500
H	4.76863700	-3.49262100	4.34832300
C	5.49793800	-2.19857200	-3.97343300
H	5.89253200	-2.66932300	-4.86880300
C	4.48453700	1.40238300	0.12019000
C	-0.43647000	3.76497200	-2.49165800
H	-1.50752700	3.90714500	-2.54513300
C	0.10386300	-3.26491100	-0.82937200
C	-3.29474700	3.30061700	-0.89747000
H	-3.02525100	2.76038700	-1.79706300
C	-3.90987600	0.13898600	-1.06154300
C	5.07644400	-0.86513800	-4.01663300
H	5.14351100	-0.30144200	-4.94205000
C	2.01146000	-4.58585600	-2.42423900
H	2.74915300	-5.09194900	-3.03949500
C	-4.44615600	0.55923800	0.16919100
H	-3.79477200	0.97255900	0.92519700
C	-1.19066900	-4.91792200	3.41655000
H	-1.62033100	-5.89221300	3.62902400
C	0.98365900	-4.20233600	-0.26516100
H	0.92728700	-4.43808700	0.79180200
C	-6.14282300	-0.39567900	-1.82209600
H	-6.80324200	-0.78581200	-2.59173100
C	5.63182400	1.85338800	-0.55103200
H	6.11509300	1.23569100	-1.29989700
C	-4.56295300	3.87222800	-0.81293600
H	-5.24052600	3.79534800	-1.65785000
C	-0.42235400	-4.26299400	4.38381900
H	-0.25668200	-4.72671000	5.35170700
C	3.89484100	2.19894800	1.11907100
H	3.01672000	1.85888900	1.66047200
C	6.16362000	3.10768000	-0.24237500
H	7.05074800	3.45566000	-0.76242500
C	1.11682600	-3.68210400	-3.00326500
H	1.14950300	-3.49005700	-4.07181500
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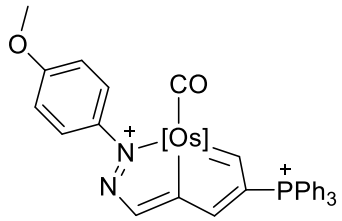
H	-0.51377300	-2.33166200	-2.67949500
C	-5.81490600	0.51374100	0.38869400
H	-6.21239200	0.86856500	1.33504200

C	-6.69088800	0.02608400	-0.59385900
C	0.34665300	4.13639900	-3.58888500
H	-0.13559000	4.54232500	-4.47318400
C	1.93577200	-4.84997600	-1.05674200
H	2.60879900	-5.57003000	-0.60023300
C	-8.17178200	-0.07130600	-0.34692500
H	-8.74318200	0.31418600	-1.19869900
H	-8.47039300	-1.11967900	-0.21295300
H	-8.47352300	0.47754800	0.5493670



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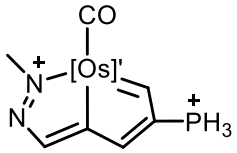
P	-1.00239800	-2.31985500	0.25383200
P	-0.60639200	2.59630300	0.14148000
O	-2.05137100	0.24540100	3.00276300
N	-2.12139200	0.26518900	-2.50457300
N	-2.43148700	0.23628900	-1.20631300
C	2.07216600	-0.11258400	-0.47777000
C	1.17256300	-0.03064500	0.62342900
H	1.63893400	-0.09512200	1.60975200
C	0.08890700	0.09823800	-1.70234600
C	4.19063900	-1.28635700	1.20331300
C	-0.80676500	0.22069100	-2.76553300
H	-0.54183000	0.28042800	-3.81947000
C	-1.57481000	0.20425000	1.94670200
C	-2.68502500	-2.88921900	-0.19850200
C	1.38511900	3.13908600	3.73185000
H	1.62486700	2.54886500	4.61151800
C	1.48379900	-0.04351500	-1.75707900
H	2.05111500	-0.12015900	-2.68024000
C	-2.64294600	4.04388100	1.42981800
H	-1.96112800	4.11300200	2.27036000
C	-4.27862400	-4.01718900	-1.63536100
H	-4.48598600	-4.59100300	-2.53377300

C	0.67843500	2.55417800	2.67749700
H	0.37436000	1.51820200	2.75195000
C	4.57017600	-1.02563700	-1.73876300
C	2.45374900	3.50709500	-2.41354500
H	3.53650300	3.42158700	-2.36648700
C	1.68993500	3.12948400	-1.31113100
H	2.18960500	2.75615900	-0.42838800
C	1.76727400	4.48014300	3.66017500
H	2.30720700	4.93729600	4.48433900
C	0.35382400	3.30393900	1.53889600
C	3.33629000	-2.35660900	1.51248400
H	2.46891000	-2.55781100	0.89631600
C	-2.24642800	3.41024800	0.24014200
C	0.04639200	-2.40335600	2.88285300
H	0.48031900	-1.43530000	2.67184100
C	-0.75677700	-3.03812000	1.92595900
C	0.28423900	-3.00430800	4.12027000
H	0.90271900	-2.49605200	4.85424800
C	-2.96744900	-3.61812700	-1.36125400
H	-2.17428800	-3.90319200	-2.04298600
C	5.31949200	-1.03061000	2.00023100
H	5.98053900	-0.20060700	1.77171200
C	1.44182200	5.23710500	2.52960700
H	1.72962800	6.28261400	2.47116000
C	-3.91972600	4.59805400	1.54031600
H	-4.21183800	5.08587000	2.46543100
C	-5.31007900	-3.69941500	-0.75158000
H	-6.32544800	-4.02226200	-0.96241000
C	-3.73033500	-2.56529900	0.68431600
H	-3.52526000	-2.00864100	1.59408100
C	4.97948300	-2.36723000	-1.70731300
H	4.93190200	-2.93561400	-0.78452100
C	4.61143400	3.40756100	1.33980200
H	4.15927300	4.02731700	2.10680900
C	-4.71479100	-0.23860000	-1.96812800
H	-4.33043500	-0.56077900	-2.92683800
C	0.29124800	3.25757800	-1.32373400
C	-5.03304100	-2.97461800	0.41105600
H	-5.83035000	-2.72344400	1.10389600
C	-1.31929500	-4.29159000	2.22914200
H	-1.94373600	-4.79994200	1.50138300
C	5.58471100	-1.84733800	3.09897100
H	6.45607000	-1.65112700	3.71590300

C	3.60639200	-3.16294800	2.61653000
H	2.93247300	-3.97747700	2.86310600
C	-4.81016800	4.53677500	0.46714700
H	-5.79892500	4.97716600	0.55354800
C	1.82784100	4.01568900	-3.55516200
H	2.41719900	4.31676200	-4.41624200
C	0.74057800	4.65470200	1.47500000
H	0.49481900	5.25093800	0.60154800
C	4.63218400	-0.29671100	-2.94257600
H	4.32018600	0.74387300	-2.97577200
C	5.73634700	3.84981400	0.63598100
H	6.16831600	4.82060200	0.85951200
C	5.45011400	-2.97330200	-2.87308000
H	5.77476900	-4.00890300	-2.84539900
C	4.72984100	-2.90940600	3.40846300
H	4.93948500	-3.53789300	4.26887100
C	5.51285700	-2.25000500	-4.06533200
H	5.88537400	-2.72416200	-4.96834300
C	4.61814600	1.35826800	0.04615800
C	-0.32725500	3.79041700	-2.46254400
H	-1.39704700	3.94788500	-2.49411600
C	0.17320000	-3.26608100	-0.80296000
C	-3.16054000	3.32883600	-0.82586400
H	-2.90540400	2.79672600	-1.73452000
C	-3.80713700	0.19234900	-0.97219000
C	5.10393500	-0.91246000	-4.09977100
H	5.15860900	-0.34887000	-5.02608400
C	2.04102700	-4.62012500	-2.41760800
H	2.76374400	-5.13852900	-3.04037900
C	-4.31779800	0.59390800	0.28511600
H	-3.64367100	0.97845100	1.03581400
C	-1.08054800	-4.88919800	3.46586900
H	-1.52416100	-5.85454400	3.69026600
C	1.04471800	-4.21657700	-0.24751000
H	0.99822500	-4.44858800	0.81073600
C	-6.07178800	-0.29321200	-1.71234700
H	-6.74170300	-0.66051200	-2.47996800
C	5.76001100	1.79382200	-0.64410400
H	6.22325500	1.16892700	-1.39967000
C	-4.42602700	3.90234300	-0.71596700
H	-5.11684900	3.83559000	-1.55109700
C	-0.27867300	-4.24723600	4.41430100
H	-0.10076600	-4.71189000	5.37957300

C	4.05466600	2.16422300	1.05245400
H	3.18070900	1.83619900	1.60780600
C	6.31218400	3.04206600	-0.34674300
H	7.19492400	3.37813300	-0.88191200
C	1.15446400	-3.70297900	-2.98763800
H	1.17872700	-3.51208400	-4.05663000
C	0.23188600	-3.02978800	-2.18764800
H	-0.44931400	-2.32503400	-2.64726400
C	-5.66976400	0.56606900	0.53796100
H	-6.07274600	0.89781400	1.48840400
C	-6.56779200	0.10767200	-0.45158200
C	0.44010000	4.16303200	-3.57053800
H	-0.05312100	4.58470000	-4.44134100
C	1.97695400	-4.88076500	-1.04882800
H	2.64410100	-5.61022600	-0.59865800
O	-7.85672700	0.08767400	-0.09756800
C	-8.85022200	-0.34525800	-1.03755100
H	-8.68091100	-1.38765300	-1.33044700
H	-9.80190100	-0.25995700	-0.51415500
H	-8.85564600	0.29827300	-1.92413900



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4'

E = -1574.92678334 a.u.

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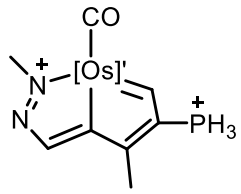
P	4.27992400	-0.19643600	-0.00004500
P	-0.44474800	-0.23553000	-2.42288400
P	-0.44528200	-0.23829600	2.42265900
O	-1.84149900	-3.02689100	-0.00158500
N	-1.54450000	2.45481900	0.00110100
N	-1.89375800	1.21087900	0.00043700
C	2.50320700	0.16171700	0.00023500
C	1.52851800	-0.89657900	-0.00026700
H	1.91985600	-1.91846000	-0.00072200
C	0.62457400	1.54719500	0.00085400
C	-0.19116600	2.66645400	0.00140000
H	0.11615300	3.70721300	0.00197000
C	-1.31815700	-2.01614800	-0.00109400
C	2.04070500	1.48195500	0.00082700

H	2.69214200	2.35320100	0.00125300
H	5.03865300	0.98507600	-0.00034400
H	4.67234200	-0.94437800	-1.12346900
H	4.67299000	-0.94414100	1.12331300
H	0.71294400	0.24086300	-3.06596300
H	-1.43760100	0.58671900	-2.98847400
H	-0.66318200	-1.46112300	-3.07704700
H	-0.66417000	-1.46463000	3.07527700
H	0.71232800	0.23709500	3.06662100
H	-1.43813700	0.58345900	2.98897300
C	-3.34555700	1.00730900	0.00015200
H	-3.86690800	1.96293200	0.00032300
H	-3.61045900	0.41663300	-0.88072300
H	-3.61071800	0.41620300	0.88066700



4'-1

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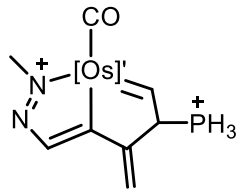
P	0.18725600	0.21860600	2.40333600
P	0.43174900	0.47284800	-2.42922900
O	-0.33142300	3.38511100	0.15189200
N	-1.15551400	-2.22298900	-0.22668500
N	-1.40015000	-0.92343800	-0.13233000
C	3.16861500	-0.49865800	0.06230700
C	2.36355100	0.67203000	0.12399400
H	2.88393500	1.62400100	0.24941600
C	1.10983400	-1.58207500	-0.10491100
C	0.13640900	-2.57651600	-0.22808600
H	0.32002900	-3.64355400	-0.32514200
C	-0.12929600	2.26319500	0.08768800
C	2.50028900	-1.73924900	-0.05567500
H	5.61376900	-0.93960500	-0.98847800
H	5.52668800	-1.08558500	1.24150500
H	5.36946900	0.93076400	0.24598300
H	1.14483100	-0.56120700	3.08213200
H	-1.00798000	-0.33564100	2.90298600

H	0.25578200	1.42291800	3.12903800
H	0.48368700	1.74908700	-3.02103000
H	1.50686600	-0.17037100	-3.07421500
H	-0.66386700	-0.10091600	-3.10408700
C	-2.83413774	-0.60913667	-0.05621284
H	-3.40391153	-1.49546564	-0.24243522
H	-3.06587999	-0.23445632	0.91888211
H	-3.07640827	0.13128905	-0.78968046
C	3.22403219	-3.09748946	-0.11025206
H	3.87438235	-3.12121507	-0.95959402
H	3.79829649	-3.23176075	0.78254788
H	2.50227800	-3.88320471	-0.19163046



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4'-2

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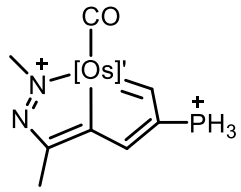
P	-0.49542000	-0.88373500	-2.21309900
P	-1.06257100	0.66150200	2.26698400
O	-2.21136000	-2.80939000	0.76964300
N	-1.16560400	2.37343300	-1.02278100
N	-1.74968300	1.28808300	-0.71117000
C	1.20868800	-1.12216000	0.68158700
H	1.40466800	-2.14626100	1.02055700
C	0.78921400	1.32561400	-0.21199700
C	0.19197300	2.42155000	-0.77705100
H	0.66308100	3.35854300	-1.04873200
C	-1.59108900	-1.88834100	0.52307000
H	4.96719500	-0.25357900	-0.33839400
H	3.33795800	-0.89385300	-1.75857700
H	4.04386800	-2.31495800	-0.14486100
H	-0.03966500	0.12495900	-3.08302500
H	-1.77871800	-1.16298900	-2.71409600
H	0.22817500	-2.00986700	-2.64615100
H	-1.46011200	-0.22634300	3.28182800
H	-0.07251100	1.43395000	2.89954400
H	-2.14070200	1.56084700	2.19676800

C	-3.19909900	1.26494100	-0.93637000
H	-3.52204000	2.18969000	-1.41297000
H	-3.45569900	0.40270200	-1.55604000
H	-3.70304800	1.13805000	0.02583800
C	2.17205700	1.19728800	0.26222200
C	3.04733600	2.19759900	0.45085000
H	4.02722900	2.04829500	0.89385900
H	2.79665100	3.21937600	0.19200500
C	2.46803100	-0.24820900	0.69097700
H	2.93199800	-0.29805600	1.68750300



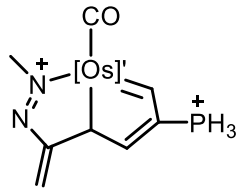
[Os]' = $Os(PH_3)_2$

4'-3

E = -1614.26869618 a.u.

Os	0.40088800	-0.41468000	0.00011300
P	-4.24599900	-0.50354400	0.00012800
P	0.45181200	-0.38569500	2.41793100
P	0.45112900	-0.38888500	-2.41770500
O	1.94323500	-3.13494800	0.00175600
N	1.48794900	2.33179600	-0.00093100
N	1.86596600	1.10126200	-0.00074900
C	-2.48434100	-0.08969200	0.00020300
C	-1.48605200	-1.11343400	0.00038800
H	-1.84289000	-2.14770200	0.00071000
C	-0.65575000	1.37001000	-0.00035100
C	0.11849900	2.53300600	-0.00069700
C	1.39203300	-2.13800900	0.00102800
C	-2.06052100	1.25105900	-0.00014500
H	-2.74902100	2.09288700	-0.00014600
H	-5.04449600	0.65136300	0.01236800
H	-4.61759700	-1.27296200	1.11613600
H	-4.62394900	-1.25269000	-1.12758500
H	-0.73866100	0.01841700	3.05120700
H	1.38408700	0.49677100	2.99689200
H	0.73953900	-1.59255300	3.08051100
H	0.73007200	-1.59865900	-3.07871500
H	-0.73680300	0.02265000	-3.05099000
H	1.38930600	0.48614500	-2.99840500

C	3.32369300	0.93479400	-0.00129900
H	3.82122100	1.90297700	-0.00231900
H	3.60182700	0.35086300	0.87968500
H	3.60098300	0.34936700	-0.88154800
C	-0.31889100	3.95624100	-0.00095100
H	0.08619200	4.47366300	-0.87667100
H	-1.40317400	4.05728900	-0.00081600
H	0.08640900	4.47405000	0.87446200



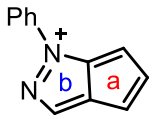
[Os]' = $Os(PH_3)_2$

4'-4

E = -1614.24299188 a.u.

Os	-0.39269300	-0.43245100	-0.02885100
P	4.25752200	-0.40839600	0.17491800
P	-0.10564500	0.42023400	-2.27130900
P	-0.92305000	-1.42302400	2.10615100
O	-1.59717000	-2.92702800	-1.27633300
N	-1.58370800	2.36633200	0.34599100
N	-1.92322200	1.17031700	0.19616200
C	2.50514400	-0.02888100	0.11780700
C	1.56938300	-1.05074200	-0.00262900
H	1.93987700	-2.07470900	-0.06332300
C	-1.16463100	-1.98036200	-0.80210400
C	2.05526200	1.35631400	0.19524200
H	2.69969200	2.18108300	-0.09810600
H	5.01318600	0.35517300	-0.73371000
H	4.45719400	-1.75789000	-0.14985200
H	4.87193500	-0.19807000	1.42456000
H	1.22437300	0.68201700	-2.65474900
H	-0.73097300	1.64910200	-2.55936000
H	-0.56153100	-0.39360200	-3.32449500
H	-0.75525100	-2.81743200	2.18793200
H	-0.20890300	-0.99054100	3.24151700
H	-2.25036100	-1.26946300	2.55203300
C	-3.37552300	0.95330100	0.11694200
H	-3.90985400	1.89565600	0.22893600
H	-3.59511100	0.48634900	-0.84583400
H	-3.65903500	0.24938600	0.90218200

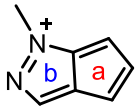
C	-0.19797200	2.68343300	0.43329600
C	0.10004600	3.99376100	0.45552100
H	1.12171400	4.34347600	0.53658500
H	-0.68979300	4.73228300	0.39548700
C	0.74077900	1.54657800	0.51340500
H	0.37606000	0.78055200	1.25715100



diazapentalene-1

E = -571.984457429 a.u.

C	-3.22295400	-1.52726900	0.31086400
C	-1.76457800	-1.54067700	0.31044300
C	-1.34429300	-0.25866900	-0.01976800
C	-1.95777000	1.85256600	-0.24471900
H	-3.83377700	-2.39616300	0.50387600
H	-1.15643300	-2.39960700	0.56239700
H	-2.43629300	2.81648500	-0.33052700
C	-3.66454000	-0.26320700	0.04735800
H	-4.69212900	0.06568800	-0.00760500
C	-2.46275400	0.58807900	-0.14373400
N	-0.56191900	1.81599600	-0.23061700
N	-0.21091600	0.56547500	-0.09476200
C	1.14890000	0.18798600	-0.04562500
C	1.51849600	-1.11203900	-0.42434100
C	2.10365400	1.13074200	0.36699700
C	2.85646100	-1.47092400	-0.37039500
H	0.78337300	-1.80670300	-0.80914600
C	3.43487600	0.75155500	0.41677000
H	1.78790900	2.12391300	0.65607700
C	3.81427900	-0.54501400	0.05304300
H	3.15874900	-2.46422400	-0.67765900
H	4.18150100	1.46324600	0.74630800
H	4.85827700	-0.83171100	0.09257600



diazapentalene-2

E = -380.192178105 a.u.

C	-2.31521000	-0.79494500	-0.00011100
C	-0.98452200	-1.42486600	0.00008700

C	-0.05583700	-0.40438600	0.00031500
C	0.27855800	1.78018700	-0.00001700
H	-3.24025100	-1.35174600	-0.00020400
H	-0.80728200	-2.49377800	-0.00002100
H	0.27156900	2.85916500	-0.00021400
C	-2.17849900	0.55565700	-0.00012800
H	-2.97121900	1.28950400	-0.00023200
C	-0.70964200	0.84874100	0.00013000
N	1.53645500	1.12638900	-0.00003600
N	1.31360200	-0.13982100	0.00014900
C	2.42209500	-1.09987100	-0.00017300
H	2.35349100	-1.72195300	0.89342400
H	2.35445500	-1.72038100	-0.89495200
H	3.34717100	-0.52988700	0.00079500