Electronic Supplemental Information

Extension of Simmons–Smith Reaction to Metal-Carbynes: Efficient Synthesis of Metallacyclopropenes with σ-Aromaticity

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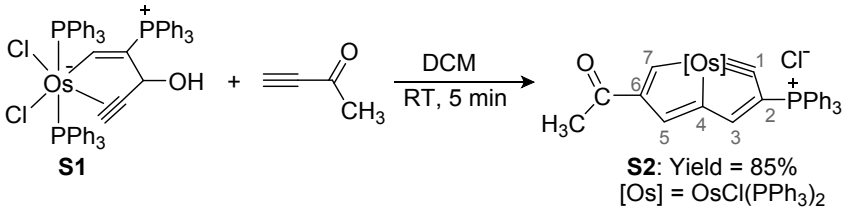
1. Experimental Procedures

General Information: All syntheses were carried out under an inert atmosphere (N_2) using standard Schlenk techniques, unless otherwise stated. Solvents were distilled from sodium/benzophenone (hexane and diethyl ether) or calcium hydride (dichloromethane) under N_2 prior to use. The metallapentalyne was synthesized according to a previously published procedure.[1] Other reagents were used as received from commercial sources without further purification. Column chromatography was performed on alumina gel (200–300 mesh) in air. Nuclear magnetic resonance (NMR) spectroscopic experiments were performed on a Bruker AV-300, a Bruker AVIII-500 or a Bruker Ascend III 600 spectrometer at room temperature. ^{1}H and ^{13}C NMR chemical shifts (δ) are relative to tetramethylsilane, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4. The absolute values of the coupling constants are given in Hertz (Hz). Multiplicities are abbreviated as singlet (s), doublet (b), triplet (t), multiplet (m), and broad (br). High-resolution mass spectroscopy (HRMS) experiments were conducted on a Bruker En Apex Ultra 7.0T FT-MS. Elemental analyses were performed on a Vario EL III elemental analyzer.

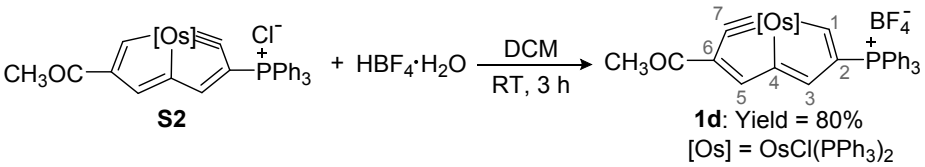
Synthesis and characterization of S2



3-Butyn-2-one (63 μL, 0.80 mmol) was added to a suspension of compound **S1** (300 mg, 0.27 mmol) in dichloromethane (15 mL). The mixture was stirred at RT for 5 min to give a yellow solution. The solution was evaporated under vacuum to a volume of ca. 2 mL and then purified by column chromatography (neutral alumina, eluent: dichloromethane/methanol = 20:1) to give complex **S2** (270 mg, 85%) as a yellow solid. ^{1}H NMR plus HMQC (500.1 MHz, CD_2Cl_2): δ = 13.88 (s, 1H, C^7H), 9.43 (s, 1H, C^5H), 8.22 (s, 1H, C^3H), 1.78 (s, 3H, $COCH_3$), 7.84-7.10 ppm (m, 45H, other aromatic protons). ^{31}P NMR (202.5 MH_Z, CD_2Cl_2): δ = 6.63 (t, $J_{P\text{-}P}$ = 4.9 Hz, $CPPh_3$), 3.26 ppm (d, $J_{P\text{-}P}$ = 4.9 Hz, $OsPPh_3$). ^{13}C NMR plus DEPT-135 and HMQC (125.8 MHz, CD_2Cl_2): δ = 324.4 (dt, $J_{P\text{-}C}$ = 14.4 Hz, 13.0 Hz, C^1), 226.5 (br, C^7), 193.8 (s, $COCH_3$, confirmed by HMBC), 182.4

(d, $J_{P\text{-}C}$ = 22.8 Hz, C^4), 162.6 (s, C^6), 160.6 (d, $J_{P\text{-}C}$ = 15.4 Hz, C^3), 152.7 (s, C^5), 119.2 (d, $J_{P\text{-}C}$ = 90.7 Hz, C^2), 25.9 (s, CO*C*H$_3$), 135.5-127.8 ppm (m, other aromatic carbons). HRMS (ESI): *m/z* calcd for $[C_{63}H_{51}ClOOsP_3]^+$, 1143.2445; found: 1143.2460. Elemental analysis calcd (%) for $C_{63}H_{51}Cl_2OP_3Os$: C 64.23, H 4.36; found: C 64.56, H 4.70.

Synthesis and characterization of 1d



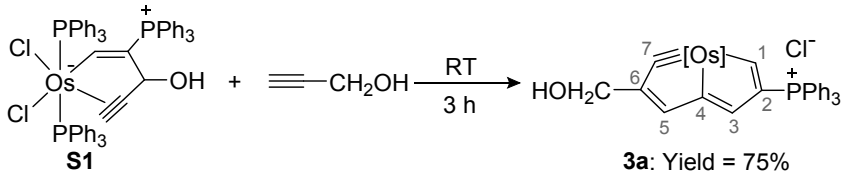
S2

1d: Yield = 80%
[Os] = $OsCl(PPh_3)_2$

To a solution of compound **S2** (295 mg, 0.25 mmol) in dichloromethane (15 mL) was added a solution of $HBF_4 \cdot H_2O$ (85 μL, 0.50 mmol). The reaction mixture was stirred at RT for 3 h to give a reddish-brown solution. The solution was evaporated under vacuum to a volume of ca. 2 mL, then diethyl ether (20 mL) was added to the solution. The yellow precipitate was collected by filtration, washed with diethyl ether (2 × 5 mL) and dried under vacuum to give **1d** (246 mg, 80%) as a yellow solid.

^{1}H NMR plus HMQC (500.1 MHz, CD_2Cl_2): δ = 13.44 (d, $J_{P\text{-}H}$ = 16.9 Hz, 1H, C^5H), 8.92 (s, 1H, C^3H), 8.04 (s, 1H, C^5H), 1.98 (s, 3H, COCH_3), 7.91-6.95 ppm (m, 45H, other aromatic protons). ^{31}P NMR (202.5 MH$_Z$, CD_2Cl_2): δ = 13.67 (t, $J_{P\text{-}P}$ = 4.9 Hz, C*P*Ph$_3$), 5.52 ppm (d, $J_{P\text{-}P}$ = 4.9 Hz, Os*P*Ph$_3$). ^{13}C NMR plus DEPT-135 and HMQC (125.8 MHz, CD_2Cl_2): δ = 332.8 (dt, $J_{P\text{-}C}$ = 15.4 Hz, 6.3 Hz, C^7), 224.5 (br, C^1), 189.0 (s, *C*OCH$_3$, confirmed by HMBC), 180.7 (d, $J_{P\text{-}C}$ = 18.6 Hz, C^4), 160.4 (s, C^5), 160.3 (s, C^6), 149.2 (d, $J_{P\text{-}C}$ = 21.4 Hz, C^3), 118.9 (d, $J_{P\text{-}C}$ = 88.6 Hz, C^2), 28.8 (s, CO*C*H$_3$), 135.4-127.7 ppm (m, other aromatic carbons). HRMS (ESI): *m/z* calcd for $[C_{63}H_{51}ClOOsP_3]^+$, 1143.2445; found: 1143.2456. Elemental analysis calcd (%) for $C_{63}H_{51}BClF_4OP_3Os$: C 64.54, H 4.18; found: C 64.28, H 4.36.

Synthesis and characterization of 3a



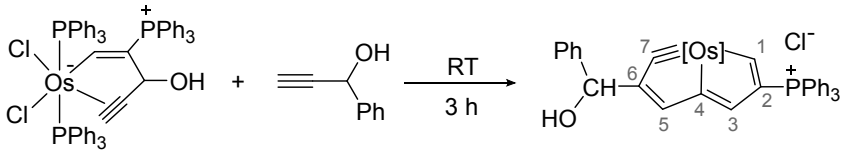
S1

3a: Yield = 75%
[Os] = $OsCl(PPh_3)_2$

Propargyl alcohol (47 μL, 0.80 mmol) was added to a suspension of compound **S1** (300 mg, 0.27 mmol) in dichloromethane (15 mL). The mixture was stirred at room temperature for 3 h to give a yellow solution. The solution was evaporated under vacuum to a volume of ca. 2 mL, then diethyl ether (20 mL) was added to the solution. The yellow precipitate was collected by filtration, washed with diethyl ether (2 × 5 mL) and dried under vacuum to give **3a** (236 mg, 75%) as a yellow solid.

^{1}H NMR plus HMQC (300.1 MHz, $CDCl_3$): δ = 13.08 (d, $J_{P\text{-}H}$ = 18.0 Hz, 1H, C^1*H*), 8.60 (s, 1H, C^3*H*), 8.08 (s, 1H, C^5*H*), 4.05 (s, 2H, C*H*$_2$OH), 1.94 (br, 1H, O*H*), 7.87-6.91 ppm (m, 45H, other aromatic protons). ^{31}P NMR (121.5 MH_Z, $CDCl_3$): δ = 13.41 (t, $J_{P\text{-}P}$ = 4.9 Hz, C*P*Ph$_3$), 6.12 ppm (d, $J_{P\text{-}P}$ = 4.9 Hz, Os*P*Ph$_3$). ^{13}C NMR plus DEPT-135 and HMQC (75.5 MHz, CD_2Cl_2): δ = 332.1 (br, C^7), 219.5 (s, C^1), 182.1 (d, $J_{P\text{-}C}$ = 21.9 Hz, C^4), 166.3 (s, C^6), 161.3 (s, C^5), 141.8 (d, $J_{P\text{-}C}$ = 22.7 Hz, C^3), 120.0 (d, $J_{P\text{-}C}$ = 88.3 Hz, C^2), 56.9 (s, *C*H$_2$OH), 137.8-127.4 ppm (m, carbons of PPh$_3$). Elemental analysis calcd (%) for $C_{62}H_{51}Cl_2OP_3Os$: C 63.86, H 4.41; found: C 63.74, H 4.55.

Synthesis and characterization of 3b



3b: Yield = 67%
[Os] = $OsCl(PPh_3)_2$

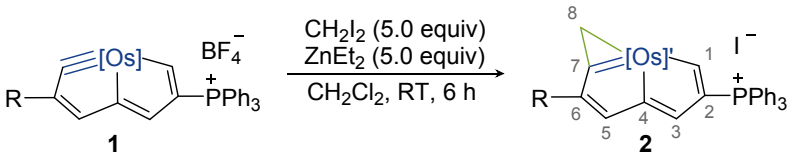
1-Phenyl-2-propyn-1-ol (97 μL, 0.80 mmol) was added to a suspension of compound **S1** (300 mg, 0.27 mmol) in dichloromethane (15 mL). The mixture was stirred at room temperature for 3 h to give a yellow solution. The solution was evaporated under vacuum to a volume of ca. 2 mL, then diethyl ether (20 mL) was added to the solution. The yellow precipitate was collected by filtration, washed with diethyl ether (2 × 5 mL) and dried under vacuum to give **3b** (225 mg, 67%) as a yellow solid.

^{1}H NMR plus HMQC (300.1 MHz, $CDCl_3$): δ = 13.01 (d, $J_{P\text{-}H}$ = 18.0 Hz, 1H, C^1*H*), 8.78 (s, 1H, C^3*H*), 8.39 (s, 1H, C^5*H*), 5.22 (s, 1H, C*H*(OH)Ph), 2.65 (br, 1H, O*H*), 7.86-6.78 ppm (m, 50H, other aromatic protons). ^{31}P NMR (121.5MH_Z, $CDCl_3$): δ = 13.37 (t, $J_{P\text{-}P}$ = 4.9 Hz, C*P*Ph$_3$), 6.41 ppm (d, $J_{P\text{-}P}$ = 4.9 Hz, Os*P*Ph$_3$). ^{13}C NMR plus DEPT-135 and HMQC (75.5 MHz, CD_2Cl_2): δ = 329.6 (br, C^7), 219.3 (s, C^1), 181.8 (d, $J_{P\text{-}C}$ = 19.1 Hz, C^4), 170.4

(s, C^6), 162.5 (s, C^5), 142.9 (d, $J_{P\text{-}C}$ = 21.5 Hz, C^3), 120.0 (d, $J_{P\text{-}C}$ = 88.3 Hz, C^2), 69.1 (s, *C*H(OH)Ph), 144.3-126.7 ppm (m, other aromatic carbons). Elemental analysis calcd (%) for $C_{68}H_{55}Cl_2OP_3Os$: C 65.75, H 4.46; found: C 66.25, H 4.81.

General Procedures A: To a solution of metallapentalyne (1.0 equiv) in CH_2Cl_2 (30 mL) was added CH_2I_2 (5.0 equiv) and $ZnEt_2$ (1 M in hexane, 5.0 equiv). The reaction mixture was stirred at room temperature for 6 hours to give a brown solution. Excess zinc salt was removed by filtration. The solution was evaporated under vacuum to a volume of ca. 4 mL, then diethyl ether (40 mL) was added to the solution. The yellow precipitate was collected by filtration, washed with diethyl ether (2 × 10 mL) and dried under vacuum.

General procedures B: CF_3COOH (2.0 equiv) was added to a solution of metallapentalyne **3** (1.0 equiv) in dichloromethane (30 mL). CH_2I_2 (5.0 equiv) and $ZnEt_2$ (1M in hexane, 5.0 equiv) were sequentially added to the reaction mixture and stirred at room temperature for 6 hours to give a brown yellow solution. Excess zinc salt was removed by filtration. The solution was evaporated under vacuum to a volume of ca. 4 mL, then diethyl ether (40 mL) was added to the solution. The yellow precipitate was collected by filtration, washed with diethyl ether (2 × 10 mL) and dried under vacuum.



[Os] = $OsCl(PPh_3)_2$, [Os]' = $OsI(PPh_3)_2$

1a: R = COOEt
1b: R = COO^{t}Bu
1c: R = COOMe
1d: R = COMe

2a: R = COOEt, 78%
2b: R = COO^{t}Bu, 76%
2c: R = COOMe, 75%
2d: R = COMe, 72%

Synthesis and characterization of complex 2a: The product was prepared by General Procedure A using 1.00 g (0.79 mmol) of metallapentalyne (**1a**) with CH_2I_2 (322 μL, 4.00 mmol) and $ZnEt_2$ (1 M, 4.00 mL, 4.00 mmol) in CH_2Cl_2 (30 mL), affording compound **2a** (870 mg, 78%) as a yellow solid.

^{1}H NMR plus HSQC (500.1 MHz, CD_2Cl_2): δ = 14.82 (d, $J_{P\text{-}H}$ = 16.5 Hz, 1H, C^1H), 9.14 (s, 1H, C^5H), 8.67 (s, 1H, C^3H), 3.96 (q, $J_{H\text{-}H}$ = 7.3 Hz, 2H, $COOCH_2CH_3$), 3.21 (t, $J_{P\text{-}H}$ = 4.7 Hz, 2H, C^8H), 1.15 (t, $J_{H\text{-}H}$ = 7.1 Hz, 3H, $COOCH_2CH_3$), 7.83-6.93 ppm (m, 45H, other aromatic protons); ^{31}P NMR (202.5 MHz, CD_2Cl_2): δ = 11.88 (s, $CPPh_3$), -20.87 ppm (s, $OsPPh_3$); ^{13}C NMR plus DEPT-135, HSQC and HMBC (125.8 MHz, CD_2Cl_2): δ = 238.8

(t, $J_{P\text{-}C}$ = 4.5 Hz, C^7), 238.1 (m, C^1), 191.1 (d, $J_{P\text{-}C}$ = 22.7 Hz, C^4), 164.6 (s, C^5), 160.3 (s, *C*$OOCH_2CH_3$), 153.5 (d, $J_{P\text{-}C}$ = 22.5 Hz, C^3), 146.8 (s, C^6), 139.3 (d, $J_{P\text{-}C}$ = 71.8 Hz, C^2), 60.5 (s, COO*C*H_2CH_3), 18.8 (s, C^8), 14.3 (s, $COOCH_2CH_3$), 135.1-118.8 ppm (m, other aromatic carbons); HRMS (ESI): *m/z* calcd for $[C_{65}H_{55}IO_2OsP_3]^+$, 1279.2075; found, 1279.2174. Elemental analysis calcd (%) for $C_{65}H_{55}I_2O_2OsP_3$: C, 55.56; H, 3.95; found: C, 55.38; H, 3.82.

Synthesis and characterization of complex 2b: The product was prepared by General Procedure A using 1.00 g (0.78 mmol) of metallapentalyne (**1b**) with CH_2I_2 (314 μL, 3.90 mmol) and $ZnEt_2$ (1 M, 3.90 mL, 3.90 mmol), affording compound **2b** (845 mg, 76%) as a yellow solid.

^{1}H NMR plus HSQC (500.1 MHz, CD_2Cl_2): δ = 14.83 (d, $J_{P\text{-}H}$ = 17.0 Hz, 1H, C^1H), 9.13 (s, 1H, C^5H), 8.70 (s, 1H, C^3H), 3.28 (s, 2H, C^8H), 1.38 (s, 9H, $COOC(CH_3)_3$, 7.90-6.93 ppm (m, 45H, other aromatic protons); ^{31}P NMR (202.5 MHz, CD_2Cl_2): δ = 13.75 (s, C*P*Ph_3), -18.97 ppm (s, Os*P*Ph_3); ^{13}C NMR plus DEPT-135, HSQC and HMBC (125.8 MHz, CD_2Cl_2): δ = 240.9 (t, $J_{P\text{-}C}$ = 4.6 Hz, C^7), 239.6 (m, C^1), 192.9 (d, $J_{P\text{-}C}$ = 22.0 Hz, C^4), 166.7 (s, C^5), 161.5 (s, *C*$OOC(CH_3)_3$), 154.9 (d, $J_{P\text{-}C}$ = 21.8 Hz, C^3), 150.4 (s, C^6), 141.0 (d, $J_{P\text{-}C}$ = 72.9 Hz, C^2), 82.9 (s, $COOC(CH_3)_3$), 29.8 (s, $COOC(CH_3)_3$), 20.4 (s, C^8), 137.7-120.8 ppm (m, other aromatic carbons); HRMS (ESI): m/z calcd for $[C_{67}H_{59}IO_2OsP_3]^+$, 1307.2388; found, 1307.2467. Elemental analysis calcd (%) for $C_{67}H_{59}I_2O_2OsP_3$: C, 56.15; H, 4.15; found: C, 56.55; H, 3.76.

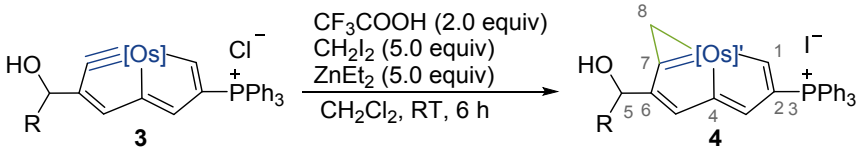
Synthesis and characterization of complex 2c: The product was prepared by General Procedure A using 1.00 g (0.80 mmol) of metallapentalyne (**1c**) with CH_2I_2 (322 μL, 4.00 mmol) and $ZnEt_2$ (1 M, 4.00 mL, 4.00 mmol), affording compound **2c** (837 mg, 75%) as a yellow solid.

^{1}H NMR plus HSQC (600.1 MHz, CD_2Cl_2): δ = 14.91 (dd, $J_{P\text{-}H}$ = 16.3 Hz, $J_{P\text{-}H}$ = 1.4 Hz, 1H, C^1H), 9.25 (s, 1H, C^5H, confirmed by HSQC), 8.76 (t, $J_{P\text{-}H}$ = 2.7 Hz, 1H, C^3H, confirmed by HSQC), 3.58 (s, 3H, $COOCH_3$), 3.29 (t, $J_{P\text{-}H}$ = 5.0 Hz, 2H, C^8H), 7.91-6.90 ppm (45H, other aromatic protons); ^{31}P NMR (242.9 MHz, CD_2Cl_2): δ = 11.83 (s, C*P*Ph_3), -20.89 ppm (s, Os*P*Ph_3); ^{13}C NMR plus DEPT-135, HSQC, and HMBC (150.9 MHz, CD_2Cl_2): δ = 239.5 (t, $J_{P\text{-}C}$ = 4.5 Hz, C^7), 239.3 (m, C^1), 191.5 (d, $J_{P\text{-}C}$ = 23.7 Hz, C^4), 165.5 (s, C^5), 161.7 (s, *C*$OOCH_3$), 154.7 (d, $J_{P\text{-}C}$ = 21.9 Hz, C^3), 147.0 (s, C^6), 140.3 (dt, $J_{P\text{-}C}$ =

72.7 Hz, $J_{P\text{-}C}$ = 3.7 Hz, C^2), 135.9-119.5 (other aromatic carbons), 52.4 (s, COO*C*H_3), 19.2 ppm (s, C^8); HRMS (ESI): *m/z* calcd for $[C_{64}H_{53}IO_2OsP_3]^+$, 1265.1918; found 1265.1971. Elemental analysis calcd (%) for $C_{64}H_{53}I_2O_2OsP_3$: C 55.26, H 3.84; found: C 55.58, H 3.89.

Synthesis and characterization of complex 2d: The product was prepared by General Procedure A using 1.00 g (0.81 mmol) of metallapentalyne (**1d**) with CH_2I_2 (378 μL, 4.55 mmol) and $ZnEt_2$ (1 M, 2.03 mL, 2.03 mmol), affording compound **2d** (805 mg, 72%) as a yellow solid.

^{1}H NMR plus HSQC (600.1 MHz, CD_2Cl_2/CD_3OD = 4/1): δ = 14.95 (d, $J_{P\text{-}H}$ = 16.2 Hz, 1H, C^1*H*), 9.30 (s, 1H, C^5*H*, confirmed by HSQC), 8.81 (s, 1H, C^3*H*, confirmed by HSQC), 3.29 (t, $J_{P\text{-}H}$ = 4.5 Hz, 2H, C^8*H*), 1.93 (s, 3H, COC*H*$_3$), 7.88-6.95 ppm (45H, other aromatic protons); ^{31}P NMR (242.9 MHz, CD_2Cl_2/CD_3OD = 4/1): δ = 11.87 (s, C*P*Ph$_3$), -20.60 ppm (s, Os*P*Ph$_3$); ^{13}C NMR plus DEPT-135, HSQC, and HMBC (150.9 MHz, CD_2Cl_2/CD_3OD = 4/1): δ = 240.4 (m, C^1), 239.0 (t, $J_{P\text{-}C}$ = 4.8 Hz,C^7), 192.0 (s, *C*OCH$_3$), 191.4 (d, $J_{P\text{-}C}$ = 24.0 Hz, C^4), 164.0 (s, C^5), 156.0 (d, $J_{P\text{-}C}$ = 21.6 Hz, C^3), 153.9 (s, C^6), 140.7 (dt, $J_{P\text{-}C}$ = 72.6 Hz, $J_{P\text{-}C}$ = 3.7 Hz, C^2), 135.3-119.6 (other aromatic carbons), 27.8 (s, CO*C*H$_3$), 19.0 ppm (s, C^8); HRMS (ESI): *m/z* calcd for $[C_{64}H_{53}IOOsP_3]^+$, 1249.1969; found: 1249.1990. Elemental analysis calcd (%) for $C_{64}H_{53}I_2OOsP_3$: C 55.90, H 3.89; found: C 55.52, H 3.80.



[Os] = $OsCl(PPh_3)_2$, [Os]' = $OsI(PPh_3)_2$

3a: R = H
3b: R = Ph

4a: R = H, 70%
4b: R = Ph, 73%

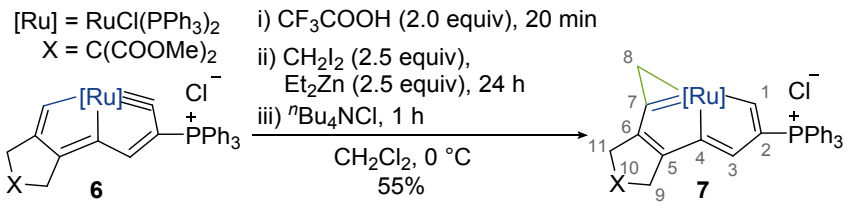
Synthesis and characterization of complex 4a: The product was prepared by General Procedure B using 1.00 g (0.82 mmol) of metallapentalyne (**3a**) with CF_3COOH (122 μL, 1.64 mmol), CH_2I_2 (330 μL, 4.10 mmol) and $ZnEt_2$ (1 M, 4.10 mL, 4.10 mmol), affording compound **4a** (784 mg, 70%) as a yellow solid.

^{1}H NMR plus (500.1 MHz, CD_2Cl_2/CD_3OD = 4/1): δ = 14.73 (d, $J_{P\text{-}H}$ = 15.7 Hz, 1H, C^1*H*), 9.03 (s, 1H, C^5*H*), 8.39 (s, 1H, C^3*H*), 4.13 (br, 1H, CH_2O*H*), 3.33 (s, 2H ,CH_2OH), 3.04 (s, 2H, C^8*H*), 7.90-6.99 ppm (m, 45H, other aromatic protons); ^{31}P NMR (202.5 MHz, CD_2Cl_2/CD_3OD = 4/1): δ = 11.59 (s, C*P*Ph$_3$), -19.43 ppm (s, Os*P*Ph$_3$); ^{13}C NMR plus DEPT-135, HSQC and HMBC (125.8 MHz, CD_2Cl_2/CD_3OD = 4/1): δ = 232.9 (s, C^7),

232.3 (m, C^1), 193.3 (d, $J_{P\text{-}C}$ = 27.8 Hz, C^4), 163.6 (s, C^5), 157.6 (s, C^6), 148.2 (d, $J_{P\text{-}C}$ = 22.3 Hz, C^3), 137.4 (d, $J_{P\text{-}C}$ = 68.2 Hz, C^2), 60.0 (s, *C*H_2OH), 19.4 (s, C^8), 135.3-119.3 ppm (m, other aromatic carbons); HRMS (ESI): *m/z* calcd for $[C_{63}H_{53}IOOsP_3]^+$, 1237.2069; found: 1237.2037. Elemental analysis calcd (%) for $C_{63}H_{53}I_2OOsP_3$: C, 55.51; H, 3.92; found: C, 55.26; H, 4.22.

Synthesis and characterization of complex 4b: The product was prepared by General Procedure B using 1.00 g (0.77 mmol) of metallapentalyne (**3b**) with CF_3COOH (114 µL, 1.54 mmol), CH_2I_2 (310 µL, 3.85 mmol) and $ZnEt_2$ (1 M, 3.85 mL, 3.85 mmol), affording compound **4b** (812 mg, 73%) as a yellow solid.

^{1}H NMR plus HSQC (500.1 MHz, CD_2Cl_2/CD_3OD): δ = 14.76 (d, $J_{P\text{-}H}$ = 16.1 Hz, 1H, C^1*H*), 9.45 (s, 1H, C^5*H*), 8.25 (s, 1H, C^3*H*), 5.66 (s, 1H, C*H*(OH)Ph), 3.91 (s, 1H, CH(O*H*)Ph), 3.32 (s, 2H, C^8*H*), 7.87-6.94 ppm (m, 50H, other aromatic protons); ^{31}P NMR (202.5 MHz, CD_2Cl_2/CD_3OD): δ = 11.61 (s, C*P*Ph_3), -21.00 ppm (d, $J_{P\text{-}P}$ = 28.5 Hz, Os*P*Ph_3); ^{13}C NMR plus DEPT-135, HSQC and HMBC (125.8 MHz, CD_2Cl_2/CD_3OD): δ = 230.62 (m, C^1), 229.1 (t, $J_{P\text{-}C}$ = 5.28 Hz, C^7), 194.4 (d, $J_{P\text{-}C}$ = 24.8 Hz, C^4), 164.4 (s, C^5), 157.6 (s, C^6), 149.3 (d, $J_{P\text{-}C}$ = 23.1 Hz, C^3), 137.2 (dt, $J_{P\text{-}C}$ = 70.5 Hz, $J_{P\text{-}C}$ = 3.31 Hz, C^2), 72.8 (s, *C*H(OH)Ph), 27.2 (s, C^8), 143.6, 135.3-119.3 ppm (m, other aromatic carbons); HRMS (ESI): *m/z* calcd for $[C_{69}H_{57}IOOsP_3]^+$, 1313.2283; found: 1313.2286. Elemental analysis calcd (%) for $C_{69}H_{57}I_2OOsP_3$: C, 57.59; H, 3.99; found: C, 57.45; H, 3.62.



Synthesis and characterization of complex 7: CF_3COOH (119 µL, 1.60 mmol) was added to a solution of **6** (1.00 g, 0.83 mmol) in dichloromethane (30 mL) and stirred at 0°C for 20 min. A solution of CH_2I_2 (168 µL, 2.08 mmol) and $ZnEt_2$ (1 M, 2.08 mL, 2.08 mmol) were sequentially added to the reaction mixture and stirred at 0°C for 24 hours to give a red solution. Excess zinc salt was removed by filtration. ^{n}Bu_4NCl (4.62 g, 16.6 mmol) was added to the filtrate and stirred at room temperature for 1 hour to give a red solution. The solution was evaporated under vacuum to a volume of approximately 3 mL and washed with n-hexane (3 × 30 mL) to give a brown solid, the solid was purified by column

chromatography (silicone, eluent: dichloromethane/methanol = 15:1) to give a brow solution. Brown solid **7** (556 mg, 55%) was collected after solvent evaporation under vacuum.

^{1}H NMR (600.1 MHz, CD_2Cl_2): δ = 13.91 (ddd, $J_{P\text{-}H}$ = 17.34 Hz, $J_{P\text{-}H}$ = 5.34 Hz, $J_{H\text{-}H}$ = 2.52 Hz, 1H, C^{1}*H*), 7.72 (dd, $J_{H\text{-}H}$ = 2.52 Hz, $J_{H\text{-}H}$ = 1.26 Hz, 1H, C^{3}*H*), 6.90-7.81 (m, 46H, the above-mentioned C^{3}*H* and other aromatic protons), 3.71 (s, 6H, COOC*H*$_3$), 3.67(s, 2H, C^{8}*H*), 3.06 (s, C^{11}*H*), 2.38 ppm (s, C^{9}*H*); ^{31}P NMR (242.9 MHz, CD_2Cl_2): δ = 21.71 (s, Ru*P*Ph$_3$), 9.85 ppm (s, C*P*Ph$_3$); ^{13}C NMR (150.9 MHz, CD_2Cl_2, plus HSQC and HMBC): δ = 269.4 (br, C^{1}), 250.6 (t, $J_{P\text{-}C}$ = 5.33 Hz, C^{7}), 202.4 (dt, $J_{P\text{-}C}$ = 26.75 Hz, $J_{P\text{-}C}$ = 5.65 Hz, C^{4}), 194.4 (s, C^{5}), 171.2 (s, *C*OOCH$_3$), 153.7 (s, C^{6}), 150.0 (d, $J_{P\text{-}C}$ = 22.97 Hz, C^{3}), 129.9 (dt, $J_{P\text{-}C}$ = 67.25 Hz, $J_{P\text{-}C}$ = 3.68 Hz, C^{2}), 128.3-135.5 (m, the above-mentioned C^{2} and other aromatic carbons), 119.7 (d, $J_{P\text{-}C}$ = 88.05 Hz, Ph), 65.5 (s, C^{10}), 54.4 (s, COO*C*H$_3$), 53.9 (s, COO*C*H$_3$), 45.8 (s, C^{8}), 39.2 (s, C^{9}), 35.1 ppm (s, C^{11}); HRMS (ESI): *m/z* calcd for $[C_{69}H_{59}ClO_4P_3Ru]^+$ 1181.2368, found: 1181.2372. Elemental analysis calcd (%) for $C_{69}H_{59}Cl_2O_4P_3Ru$: C, 68.09; H, 4.89; found: C, 67.68; H, 5.27.

2. X-ray Crystallographic Analysis

Single-Crystal X-Ray Diffraction Experiments. Single-crystal X-ray diffraction data were collected on a Rigaku XtaLAB Synergy, Dualflex, HyPix diffractometer with mirrormonochromated Cu Kα radiation (λ = 1.54184 Å) for **2a** and **2b**. The crystal was kept at 100.00 K during data collection. And single-crystal X-ray diffraction data were collected on an Oxford Gemini S Ultra CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) for **1d**, **3a**, **3b** and **7**. With Olex2[2], the structure was solved using the SHELXT[3] structure solution program and refined with the SHELXL[4] refinement package using least-squares minimization. Non-hydrogen atoms were refined anisotropically unless otherwise stated. Hydrogen atoms were introduced at their geometric positions and refined as riding atoms unless otherwise stated. The diffuse electron densities resulting from the residual solvent molecules in **2a**, **2b** and **6** were removed from the data set using the SQUEEZE routine of PLATON. Single crystals suitable for X-ray diffraction were grown from a solution of CH_2Cl_2 (for **1d**) or $CHCl_3$ (for **2a**, **2b**, **3a**, **3b** and **7**) layered with hexane. In solution, complex **3a** is easily oxidized to transform into **3a'** with an oxygen atom to the original carbyne carbon, therefore, in our extension attempts to grow crystals of **3a**, the cocrystals of **3a** and **3a'** were always obtained only, owing to the partially oxidation of **3a**. the composition of the cocrystal was defined as 0.7·**3a**·0.3·**3a'** by the X-ray diffraction analysis. Due to the similarity between the overall structure of **3a** and **3a'**, the structure of the cocrystal showed a disorder between **3a** and **3a'** with the O2 atom refined with 30% site occupancies. Further details on the crystal data, data collection, and refinements are provided in Tables S1 and S2. X-ray crystal structures have been deposited in the Cambridge Crystallographic Database under the deposition numbers CCDC 2005482 (**1d**), CCDC 2005483 (**2a**), CCDC 2005484 (**2b**), CCDC 2005479 (**3a**), CCDC 2005480 (**3b**), CCDC 2005481 (**7**). The data can be obtained free of charge from the CCDC (www.ccdc.cam.ac.uk/data_request/cif).

Table S1. Crystal data and structure refinement of 1d, 2a and 2b.

	1d·$3CH_2Cl_2$	**2a**	**2b**
Empirical formula	$C_{66}H_{57}BOF_4Cl_7OsP_6$	$C_{65}H_{55}I_2O_2OsP_3$	$C_{67}H_{59}I_2O_2OsP_3$
Mol. weight	1484.18	1405.00	1433.05
Temperature [K]	173	100.00(10)	100.00(10)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P-1	$P2_1/n$	$P2_1/n$
a [Å]	13.7995(6)	13.57170(10)	18.5224(2)
b [Å]	15.4786(6)	12.22040(10)	12.6665(2)
c [Å]	18.2124(7)	38.22804(6)	29.5255(4)
α [°]	65.1950(10)	90	90
β [°]	73.6760(10)	96.8380(10)	102.2220(10)
γ [°]	73.0050(10)	90	90
V [Å^3]	3370.8(2)	6295.08(10)	6770.09(16)
Z	2	4	4
ρ_{calcd} [g cm^{-3}]	1.462	1.482	1.406
μ [mm^{-1}]	2.291	12.551	11.681
F(000)	1484.0	2752.0	2816.0
Crystal size [mm^3]	0.08 × 0.08 × 0.07	0.3 × 0.3 × 0.2	0.35 × 0.35 × 0.2
Radiation	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2θ range [°]	6.07 to 50	6.694 to 150.308	5.184 to 129.996
Coll. refl.	42713	71539	46265
Indep. refl.	11805	12830	11456
data/restraints/params	11805/40/822	12830/0/659	11456/0/667
GOF on F^2	1.049	1.061	1.047
R_1/wR_2 [$I \geq 2\sigma(I)$]	0.0449/0.1131	0.0347/0.0880	0.0316/0.0774
R_1/wR_2 (all data)	0.0504/0.1179	0.0350/0.0882	0.0328/0.0781
Largest peak/hole [e Å^{-3}]	2.54/-1.87	0.90/-2.98	1.29/-1.59

Table S2. Crystal data and structure refinement of 3a, 3b and 7.

	0.7·**3a**·0.3·**3a'**·2$CHCl_3$·H_2O	**3b**·2$CHCl_3$	2·**7**
Empirical formula	$C_{64}H_{55}Cl_8O_{2.3}OsP_3$	$C_{70}H_{57}Cl_8OOsP_3$	$C_{138}H_{118}Cl_4O_8Ru_2P_6$
Mol. weight	1427.59	1480.86	2434.08
Temperature [K]	173(2)	173(2)	173.00(10)
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1
a [Å]	12.5033(6)	12.0312(5)	18.0079(6)
b [Å]	14.0801(5)	17.2019(10)	18.6935(7)
c [Å]	18.7173(8)	19.2444(11)	24.9721(9)
α [°]	80.333(3)	106.991(5)	95.726(3)
β [°]	80.005(4)	103.843(4)	110.761(3)
γ [°]	72.223(4)	105.956(4)	102.104(3)
V [Å^3]	3066.3(2)	3433.9(3)	7545.1(5)
Z	2	2	2
ρ_{calcd} [g cm^{-3}]	1.546	1.432	1..071
μ [mm^{-1}]	2.550	2.279	0.381
F(000)	1429.0	1484.0	2512.0
Crystal size [mm^3]	0.20 × 0.10 × 0.05	0.6 × 0.3 × 0.2	0.4 × 0.3 × 0.3
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range [°]	5.65 to 50	4.548 to 58.398	3.138 to 58.162
Coll. refl.	25229	35894	78787
Indep. refl.	10777	15765	34379
data/restraints/params	10777/6/753	15765/1/796	34379/0/1427
GOF on F^2	0.757	0.936	1.064
R_1/wR_2 [$I \geq 2\sigma(I)$]	0.0369/0.0411	0.0332/0.0639	0.0673/0.1356
R_1/wR_2 (all data)	0.0609/0.0434	0.0464/0.0654	0.0993/0.1499
Largest peak/hole [e Å^{-3}]	0.71/-0.56	1.65/-0.97	0.99/-0.84

Crystal Structures

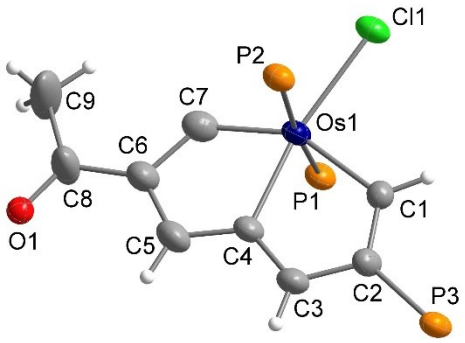


Figure S1. X-ray molecular structure of the cation of complex **1d** (ellipsoids are drawn at the 50% probability level). The phenyl groups of PPh_3 are omitted for clarity. Selected bond lengths (Å) and angles (°): Os1–C1 2.040(5), C1–C2 1.384(7), C2–C3 1.411(7), C3–C4 1.385(7), C4–C5 1.411(7), C5–C6 1.390(8), C6–C7 1.441(8), C7–Os1 1.800(6), Os1–C4 2.088(5); Os1–C1–C2 119.8(4), C1–C2–C3 113.6(4), C2–C3–C4 113.3(4), C3–C4–Os1 118.2(4), C4–Os1–C1 74.99(19), Os1–C4–C5 117.9(4), C4–C5–C6 111.4(5), C5–C6–C7 106.9(5), C6–C7–Os1 130.7(4), C7–Os1–C4 73.1(2).

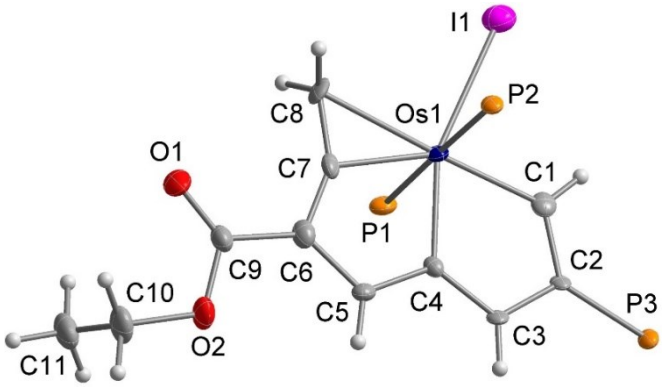


Figure S2. X-ray molecular structure for the cation of complex **2a** drawn at the 50% probability level. The phenyl groups are omitted for clarity. Selected bond lengths (Å) and angles (°): Os1–C1 2.034(4), Os1–C4 2.089(4), Os1–C7 1.991(4), Os1–C8 2.288(4), C1–C2 1.387(6), C2–C3 1.416(5), C3–C4 1.380(5), C4–C5 1.401(5), C5–C6 1.388(6), C6–C7 1.381(6), C7–C8 1.361(6); Os1–C1–C2 119.8(3), C1–C2–C3 113.5(3), C2–C3–C4 113.3(3), C3–C4–Os1 118.3(3), C4–Os1–C1 75.12(15), Os1–C4–C5 119.5(3), C4–C5–C6 112.5(3), C5–C6–C7 110.5(3), C6–C7–Os1 125.3(3), C7–Os1–C4 72.24(16), Os1–C7–C8 83.9(3), C7–C8–Os1 59.9(2), C7–Os1–C8 36.24(16).

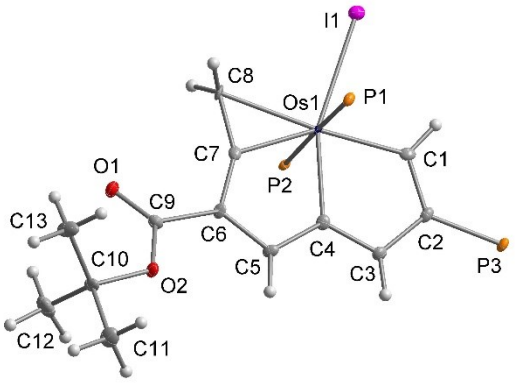


Figure S3. X-ray molecular structure of complex **2b** (ellipsoids are drawn at the 50% probability level). The phenyl groups of PPh_3 are omitted for clarity. Selected bond lengths (Å) and angles (°): Os1–C1 2.039(4), Os1–C4 2.083(4), Os1–C7 1.979(4), Os1–C8 2.297(4), C1–C2 1.391(5), C2–C3 1.411(6), C3–C4 1.395(5), C4–C5 1.411(6), C5–C6 1.393(5), C6–C7 1.380(6), C7–C8 1.384(5); Os1–C1–C2 119.6(3), C1–C2–C3 113.7(3), C2–C3–C4 113.3(3), C3–C4–Os1 118.0(3), C4–Os1–C1 75.43(15), Os1–C4–C5 119.3(3), C4–C5–C6 111.9(3), C5–C6–C7 110.9(3), C6–C7–Os1 125.1(3), C7–Os1–C4 72.78(15), Os1–C7–C8 84.2(2), C7–C8–Os1 59.0(2), C7–Os1–C8 36.83(15).

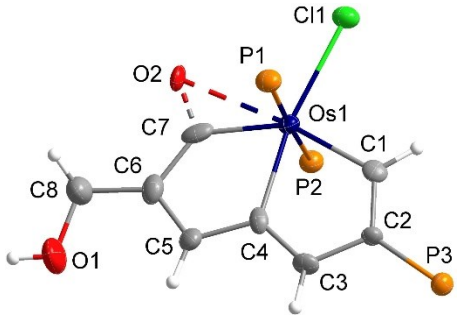


Figure S4. X-ray molecular structure of the cation of 0.7·**3**·0.3·**3a'** (ellipsoids are drawn at the 50% probability level). The phenyl groups of PPh_3 are omitted for clarity. Selected bond lengths (Å) and angles (°): Os1–C1 2.035(3), C1–C2 1.367(5), C2–C3 1.426(5), C3–C4 1.373(5), C4–C5 1.415(5), C5–C6 1.362(5), C6–C7 1.426(6), C7–Os1 1.852(4), Os1–C4 2.071(4); Os1–C1–C2 119.9(3), C1–C2–C3 113.7(3), C2–C3–C4 112.3(4), C3–C4–Os1 119.1(3), C4–Os1–C1 74.87(16), Os1–C4–C5 118.6(3), C4–C5–C6 112.9(4), C5–C6–C7 105.7(4), C6–C7–Os1 131.2(3), C7–Os1–C4 71.52(17). The structure of the cocrystal showed a disorder between **3a** (Os1–C7 carbyne bond) and **3a'** (metallacycle Os1–C7–O2), which were refined with 0.7 and 0.3 site occupancies, respectively.

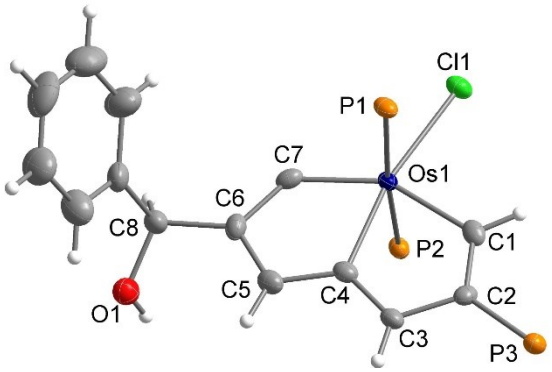


Figure S5. X-ray molecular structure of the cation of complex **3b** (ellipsoids are drawn at the 50% probability level). The phenyl groups of PPh_3 are omitted for clarity. Selected bond lengths (Å) and angles (°): Os1–C1 2.039(3), C1–C2 1.367(4), C2–C3 1.428(4), C3–C4 1.369(4), C4–C5 1.415(4), C5–C6 1.379(4), C6–C7 1.414(4), C7–Os1 1.847(3), Os1–C4 2.092(3); Os1–C1–C2 119.9(2), C1–C2–C3 113.7(3), C2–C3–C4 113.1(3), C3–C4–Os1 118.2(2), C4–Os1–C1 75.03(13), Os1–C4–C5 117.3(2), C4–C5–C6 113.0(3), C5–C6–C7 106.5(3), C6–C7–Os1 130.9(2), C7–Os1–C4 72.26(13).

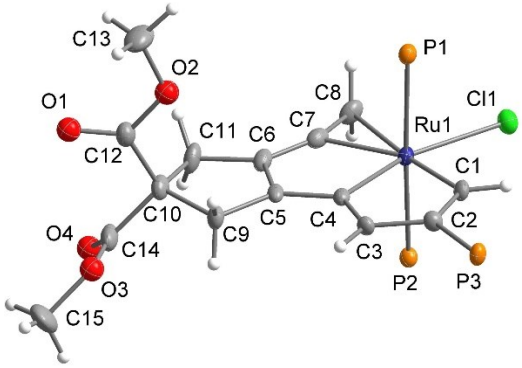


Figure S6. X-ray molecular structure for the cation of complex **7** drawn at the 50% probability level. The phenyl groups are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru1–C1 2.012(4), Ru1–C4 2.067(4), Ru1–C7 2.027(4), Ru1–C8 2.315(4), C1–C2 1.385(5), C2–C3 1.412(5), C3–C4 1.375(5), C4–C5 1.411(5), C5–C6 1.379(6), C6–C7 1.377(6), C7–C8 1.356(6); Ru1–C1–C2 119.5(3), C1–C2–C3 113.6(3), C2–C3–C4 113.0(4), C3–C4–Ru1 118.2(3), C4–Ru1–C1 75.72(15), Ru1–C4–C5 117.9(3), C4–C5–C6 113.7(4), C5–C6–C7 112.6(3), C6–C7–Ru1 121.4(3), C7–Ru1–C4 74.40(16), Ru1–C7–C8 83.9(3), C7–C8–Ru1 60.5(2), C7–Ru1–C8 35.62(16).

3. Theoretical Calculations

Computational details.

Structure **2a'** and structure **7'** were optimized at the B3LYP/6-311++G** level of DFT[5] with an SDD basis set[6] describing P, Cl, Ru, I and Os atoms. Whereas the other structures were optimized at the B3LYP/6-31G* level with an SDD basis set to describe P, Cl, Zn, Ru, I and Os atoms; our single-point energy calculations were then performed on the mechanism at the ωB97XD/def2-TZVP level[7] with the Solvation Model based on Density (SMD)[8] in dichloromethane. Frequency calculations were performed to identify all the stationary points as minima (zero imaginary frequency). The energies are given in kcal/mol and include the zero-point energy corrections. NBO calculations were carried out at the B3LYP/6-31G* level with an SDD basis set to describe P, Cl, Zn, Ru, I and Os atoms with the NBO 6.0 program.[9] Nucleus-independent chemical shift (NICS)[10] values were calculated at the B3LYP/6-311++G** level of theory. All the above calculations were performed with the Gaussian 09 software package[11]. The anisotropy of the induced current density (AICD)[12] calculations were carried out with the AICD program[12a].

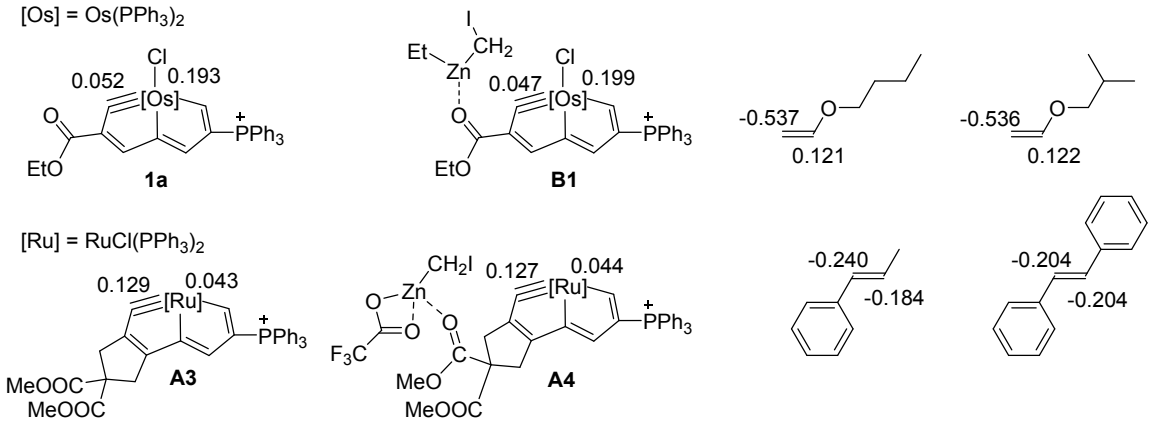


Figure S7. The natural bond orbital (NBO) charges calculated for **1a**, **B1** (at 298 K) and **A3**, **A4** (at 273 K). The B3LYP/6-31G* level with an SDD basis set was used.

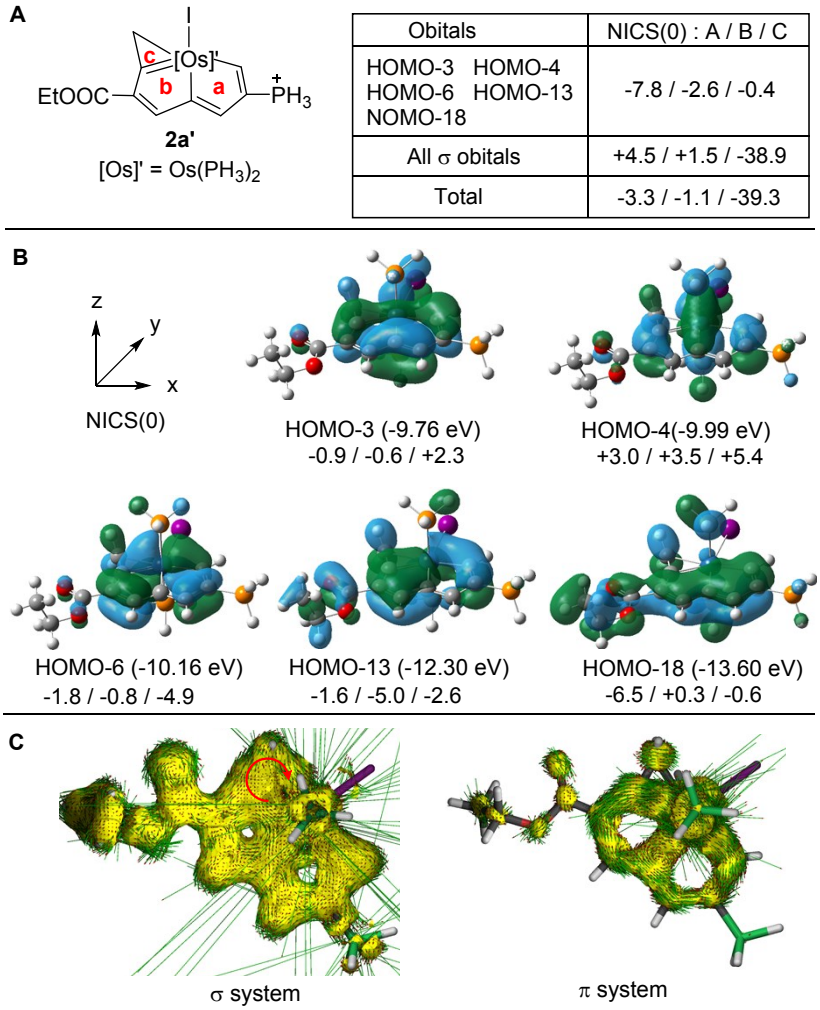


Figure S8. Aromaticity Evaluation. A) NICS(0) values for the model complex **2a′**; B) Key occupied π MOs and their energies together with contributions to NICS(0): the eigenvalues of the MOs are given within parentheses in the first line whereas the NICS(0) values of rings a, b, and c are given in the second line; C) AICD isosurfaces of **2a′** separated into the σ and π contribution. Current density vectors are plotted onto the AICD isosurface of 0.025 to indicate dia- and paratropic ring currents. The magnetic field vector is orthogonal with respect to the ring plane and points upward (clockwise currents are diatropic).

4. NMR Spectra

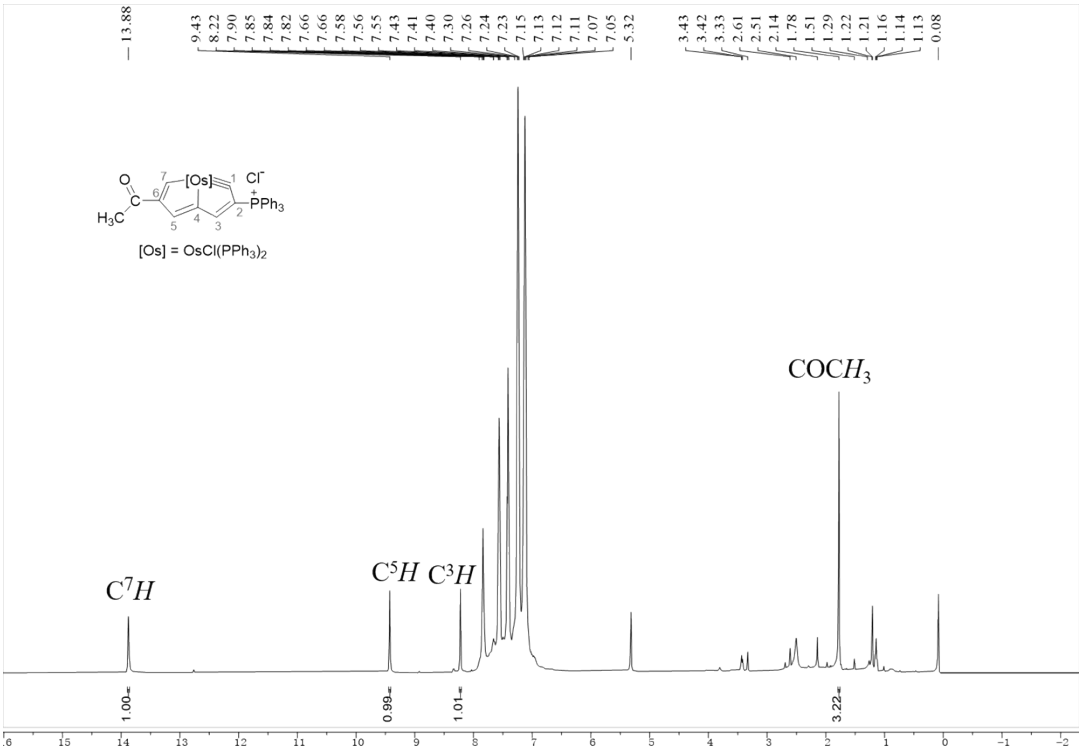


Figure S9. The ^{1}H NMR (500.1 MHz, CD_2Cl_2) spectrum for complex **1d'**.

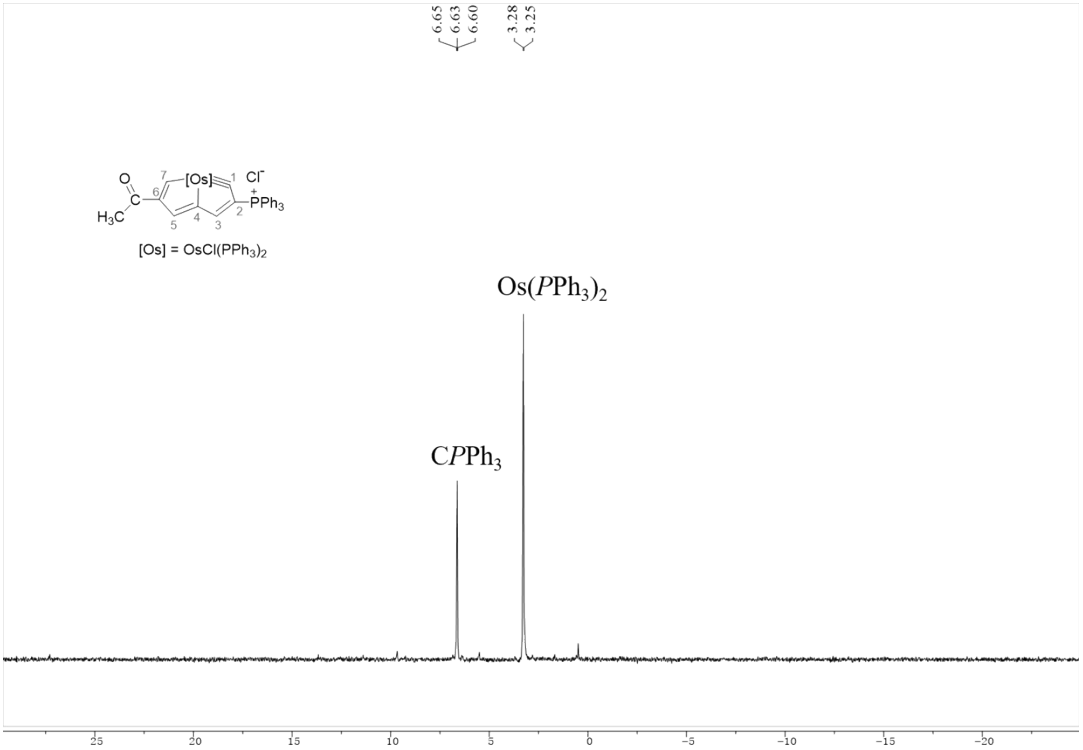


Figure S10. The $^{31}P\{^{1}H\}$ NMR (202.5 MHz, CD_2Cl_2) spectrum for complex **1d'**.

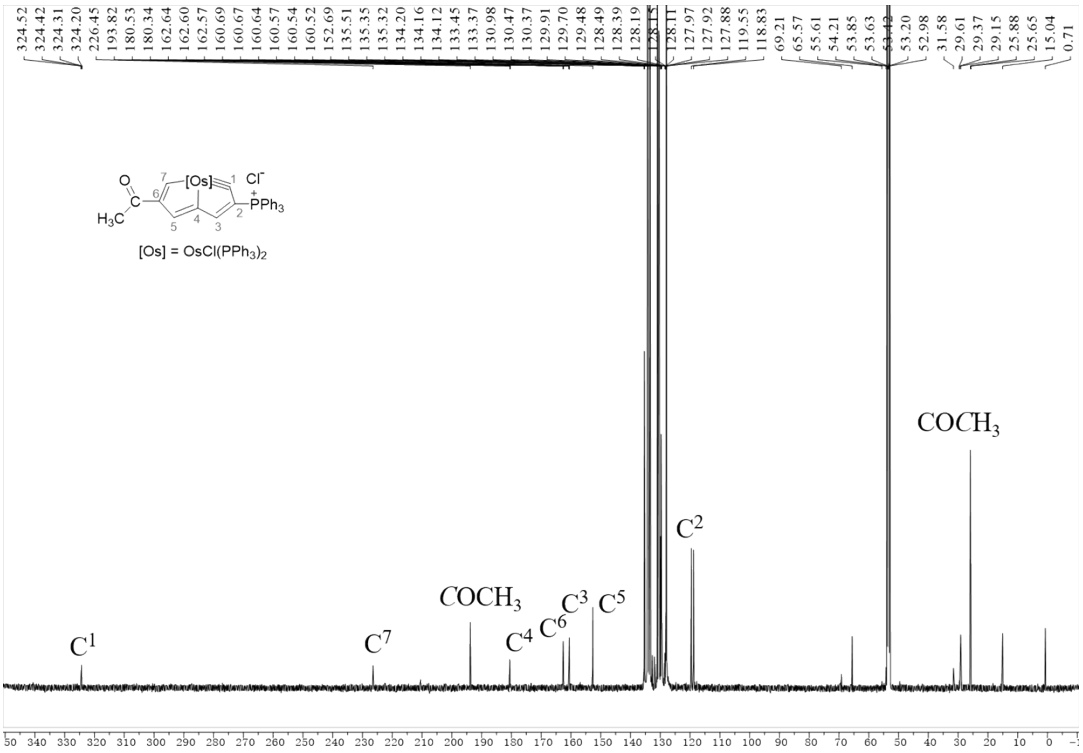


Figure S11. The $^{13}C\{^{1}H\}$ NMR (125.8 MHz, CD_2Cl_2) spectrum for complex **1d'**.

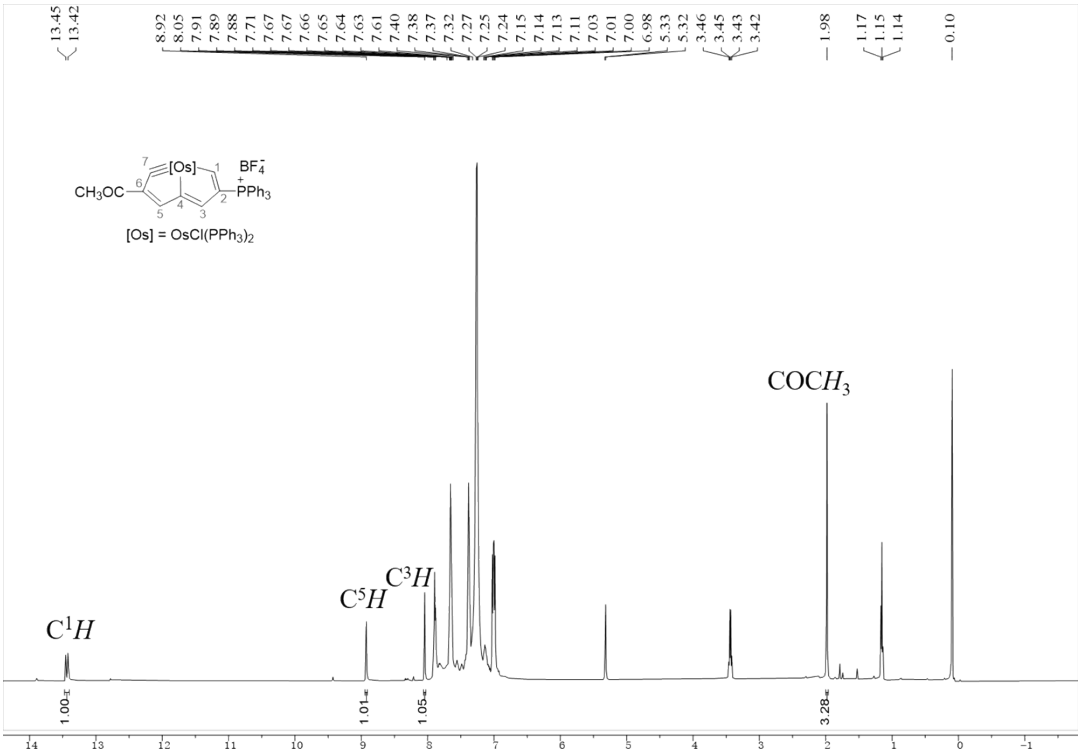


Figure S12. The ^{1}H NMR (500.1 MHz, CD_2Cl_2) spectrum for complex **1d**.

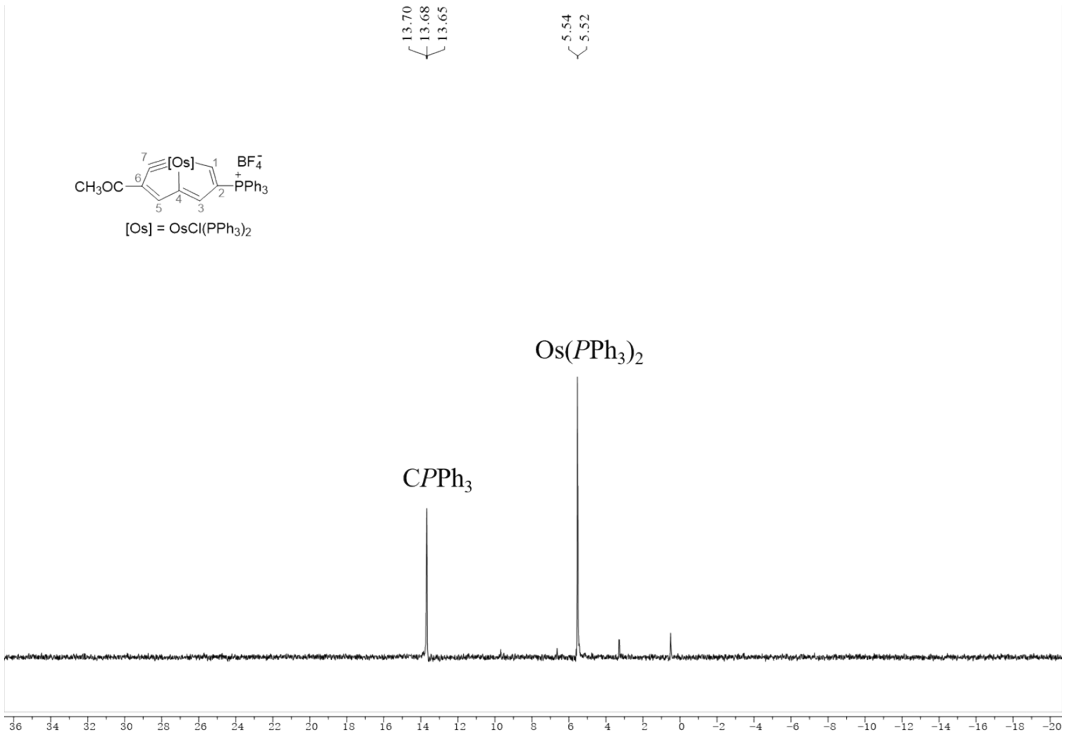


Figure S13. The $^{31}P\{^{1}H\}$ NMR (202.5 MHz, CD_2Cl_2) spectrum for complex **1d**.

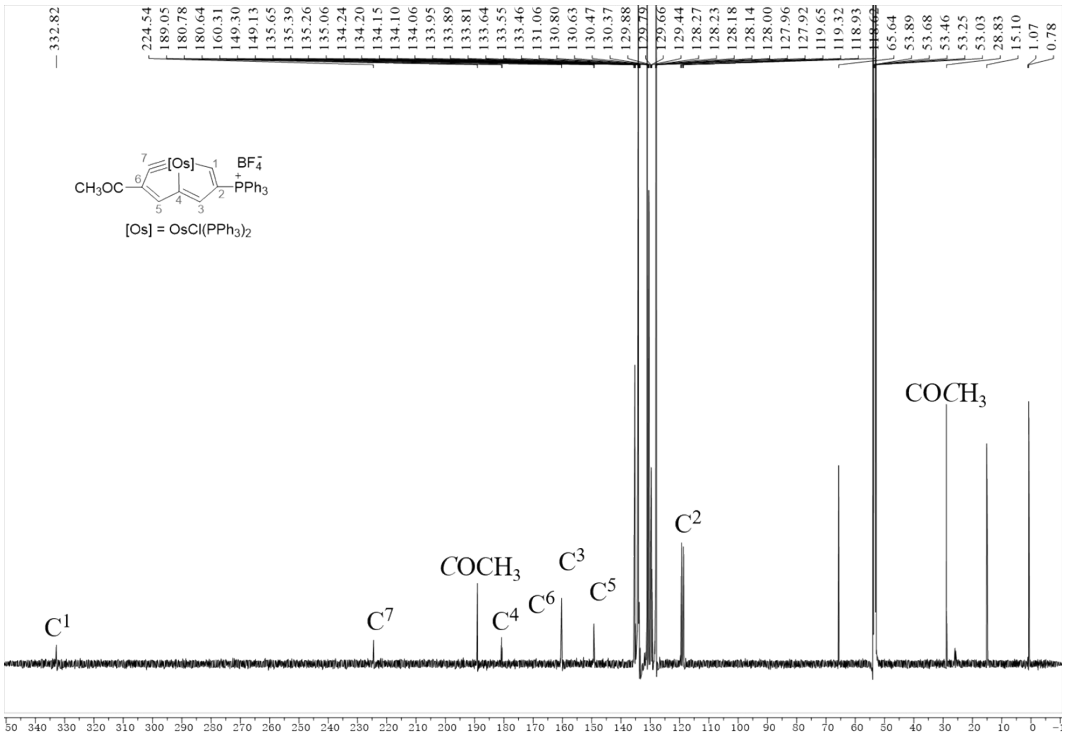


Figure S14. The $^{13}C\{^{1}H\}$ NMR (125.8 MHz, CD_2Cl_2) spectrum for complex **1d**.

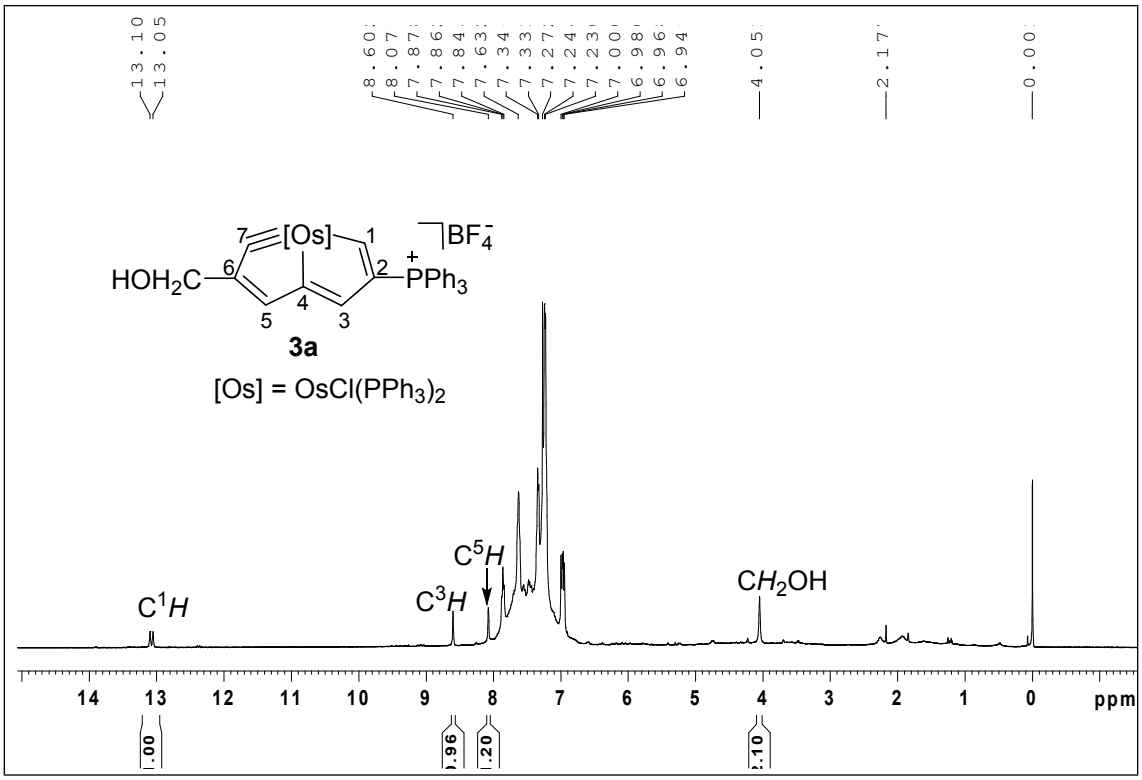


Figure S15. The ^{1}H NMR (300.1 MHz, $CDCl_3$) spectrum for complex **3a**.

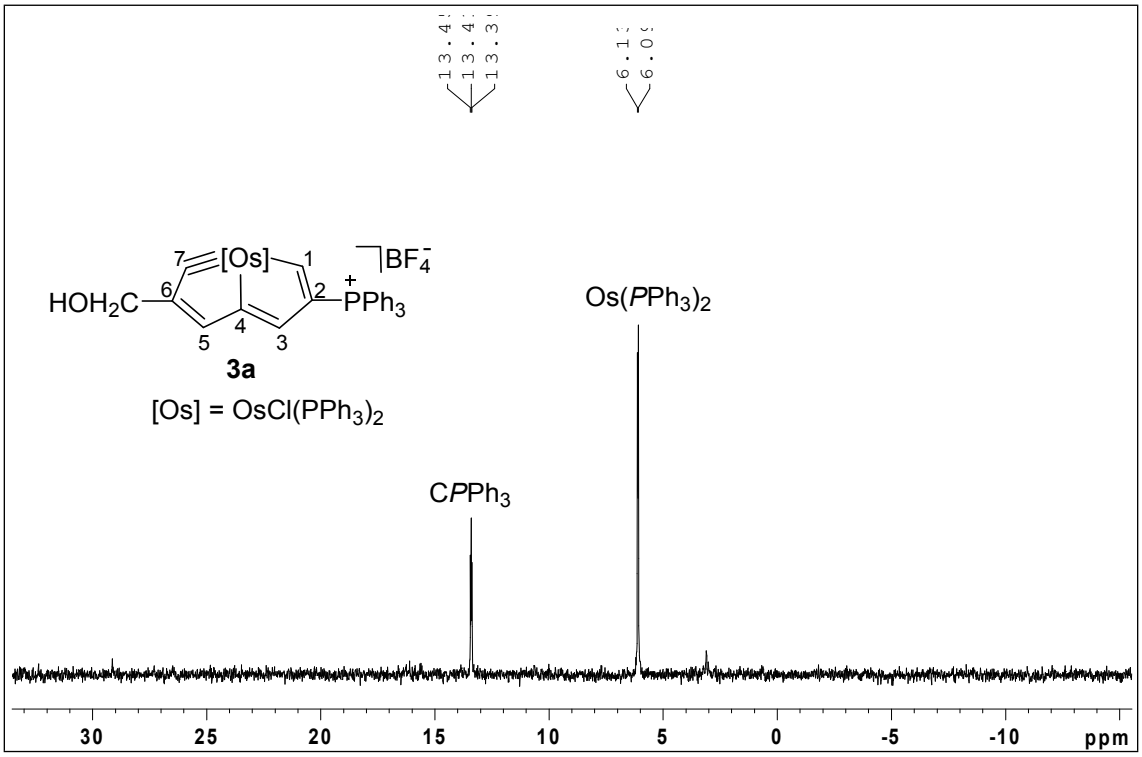


Figure S16. The $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$) spectrum for complex **3a**.

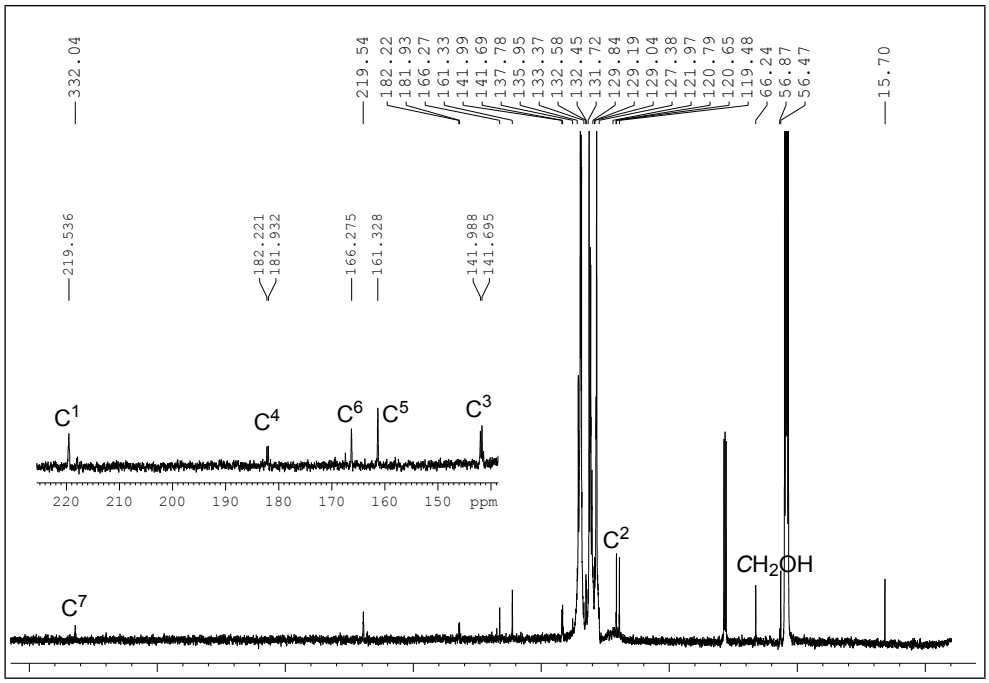


Figure S17. The $^{13}C\{^{1}H\}$ NMR (75.5 MHz, CD_2Cl_2) spectrum for complex **3a**.

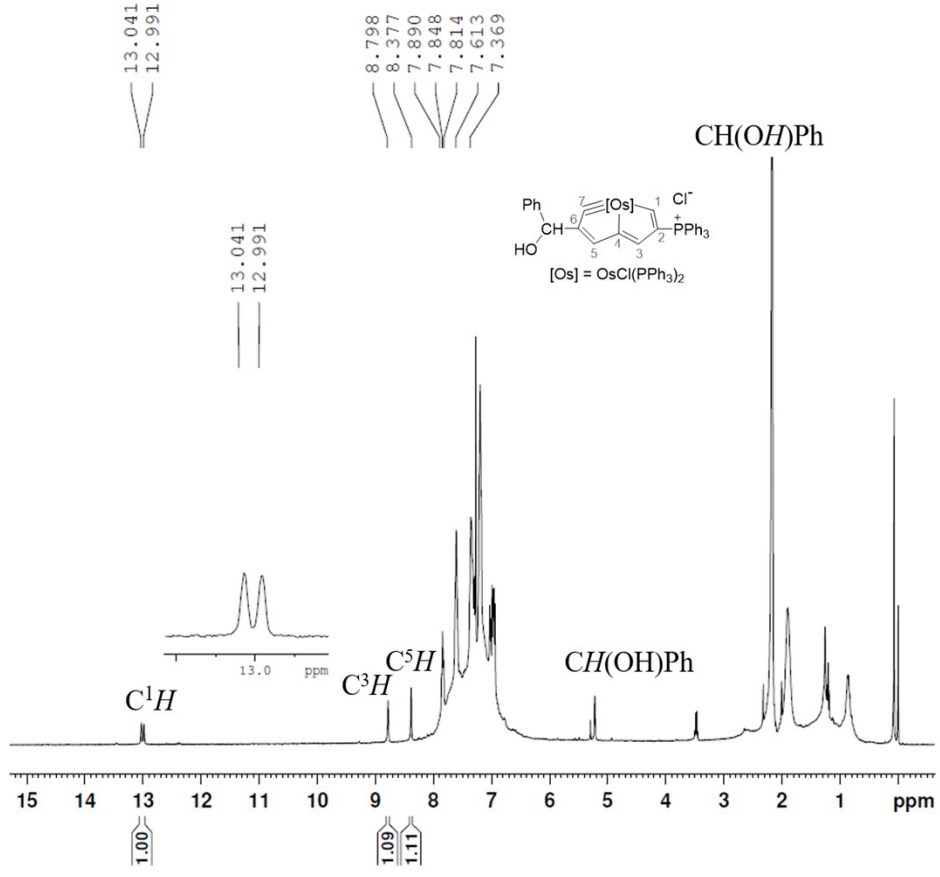


Figure S18. The ^{1}H NMR (300.1 MHz, $CDCl_3$) spectrum for complex **3b**.

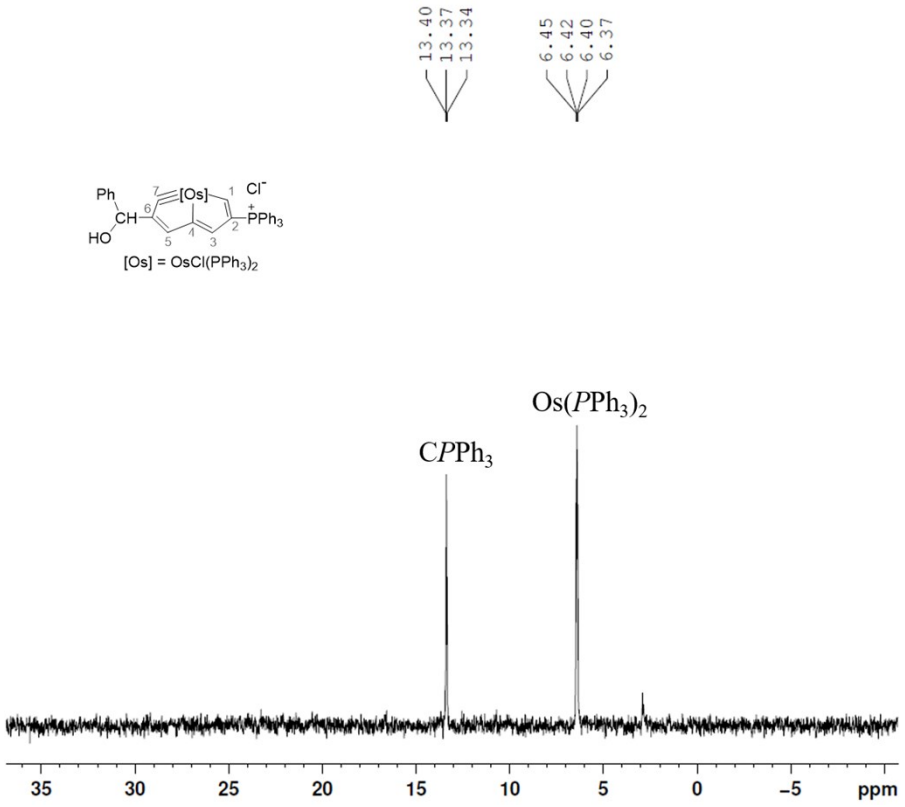


Figure S19. The $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$) spectrum for complex **3b**.

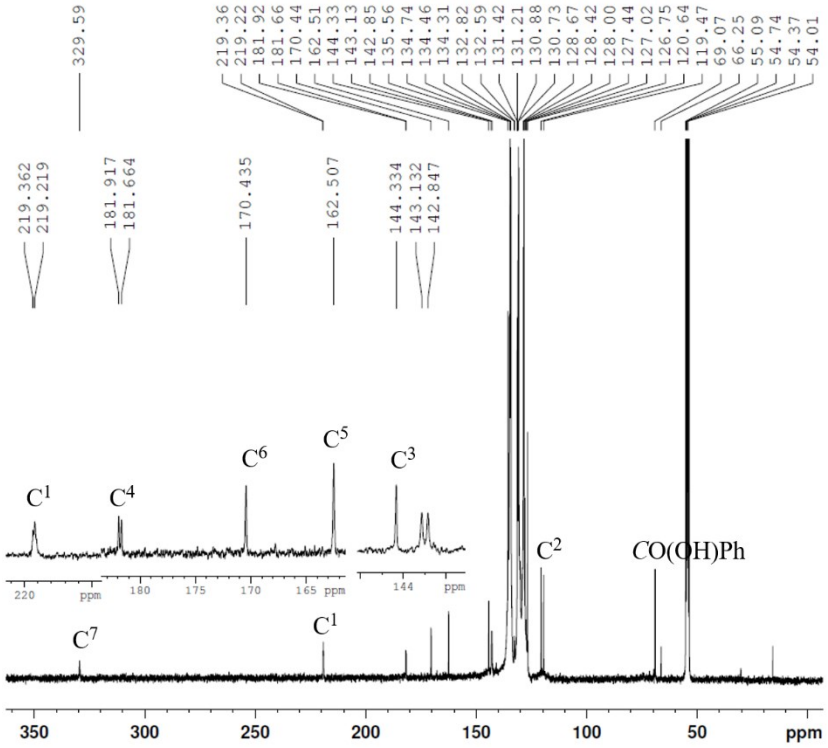


Figure S20. The $^{13}C\{^{1}H\}$ NMR (75.5 MHz, CD_2Cl_2) spectrum for complex **3b**.

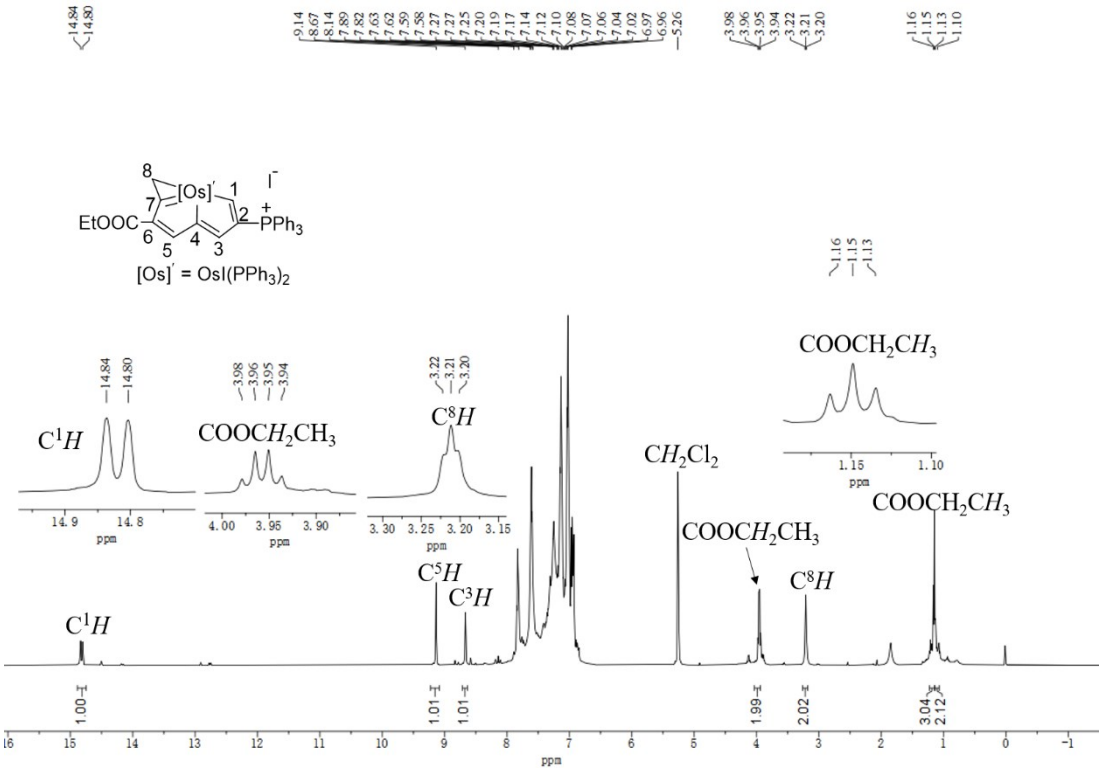


Figure S21. The ^{1}H NMR (500.1 MHz, CD_2Cl_2) spectrum for complex **2a**.

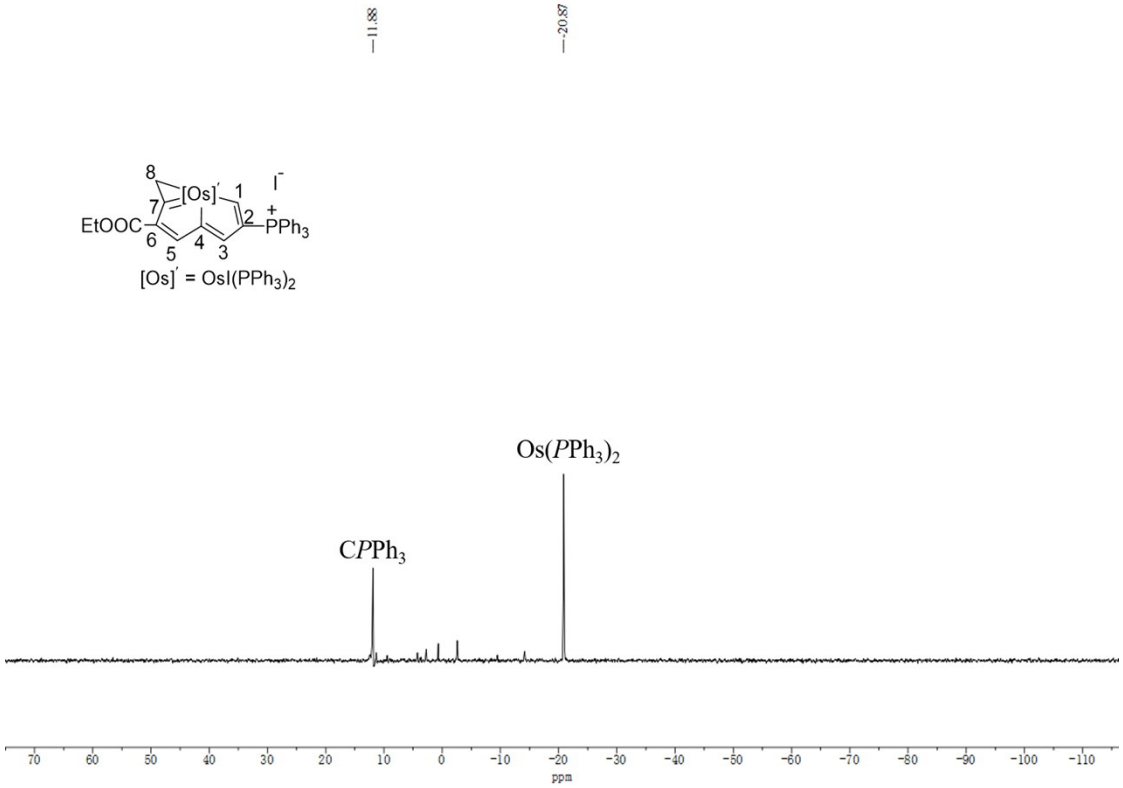


Figure S22. The $^{31}P\{^{1}H\}$ NMR (202.5 MHz, CD_2Cl_2) spectrum for complex **2a**.

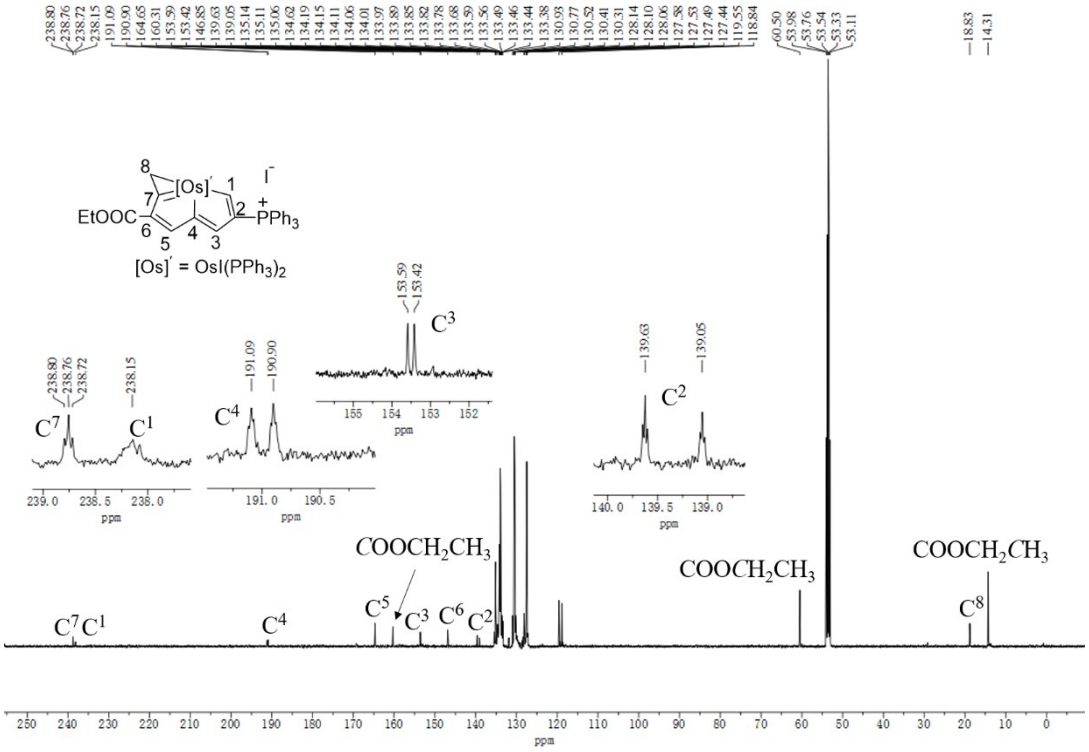


Figure S23. The $^{13}C\{^{1}H\}$ NMR (125.8 MHz, CD_2Cl_2) spectrum for complex **2a**.

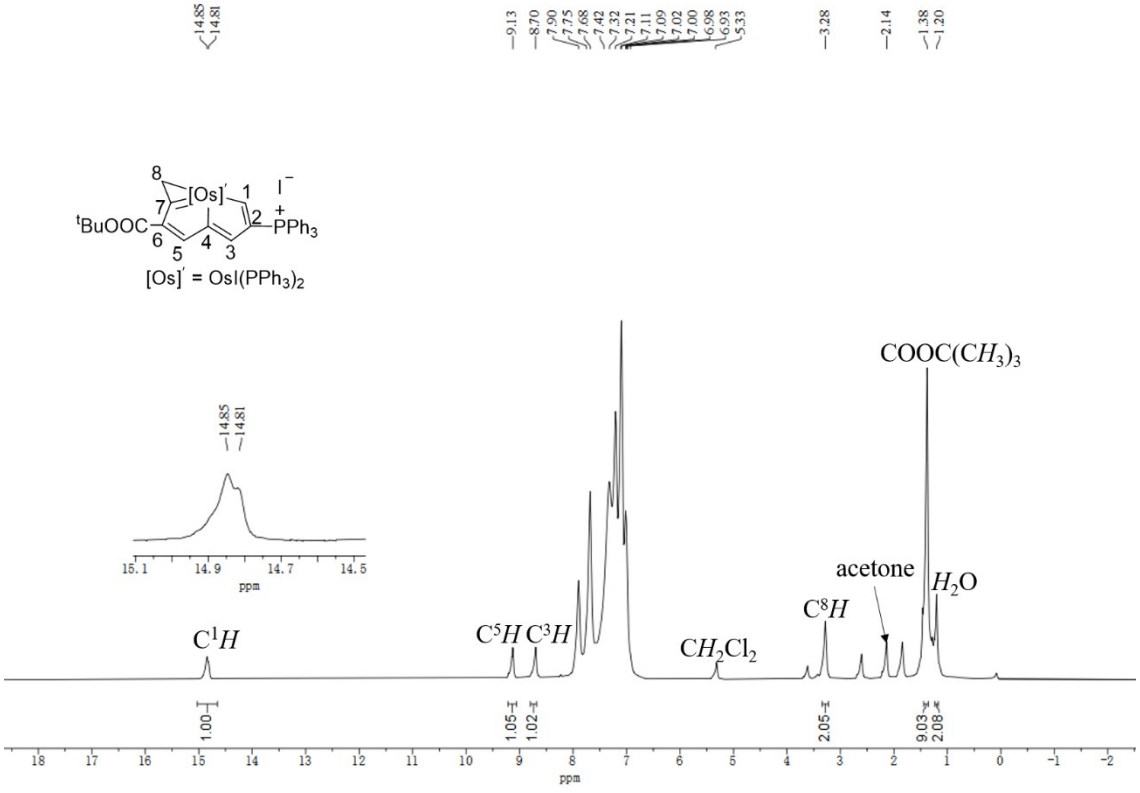


Figure S24. The ^{1}H NMR (500.1 MHz, CD_2Cl_2) spectrum for complex **2b**.

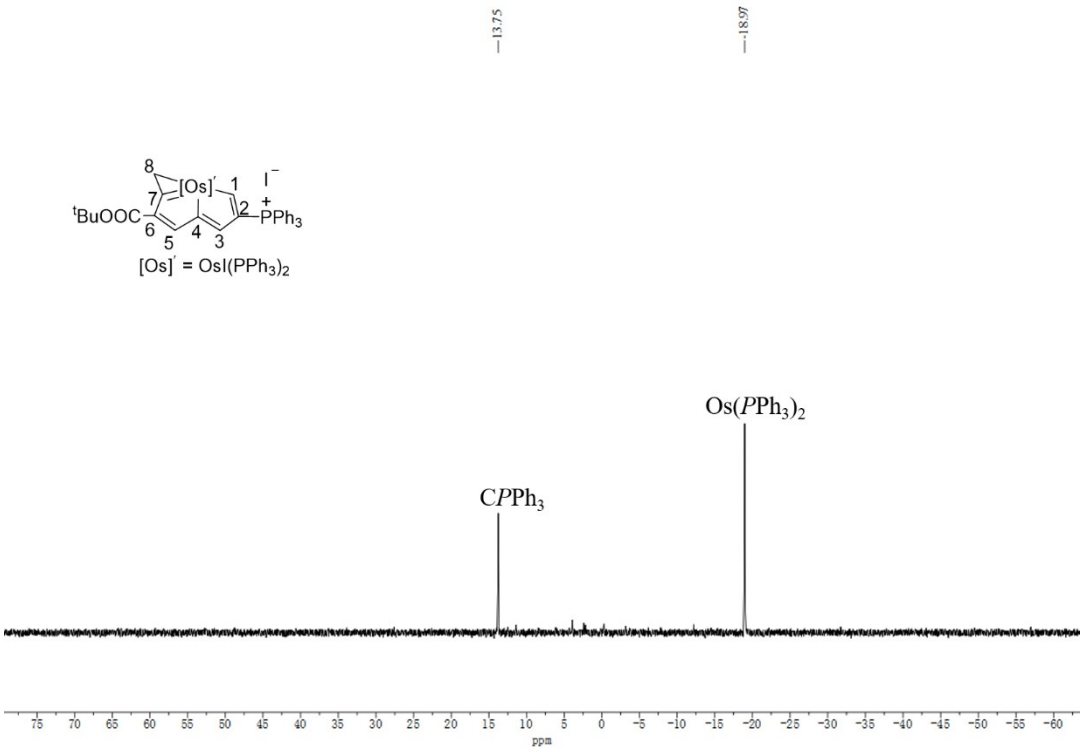


Figure S25. The $^{31}P\{^{1}H\}$ NMR (205.5 MHz, CD_2Cl_2) spectrum for complex **2b**.

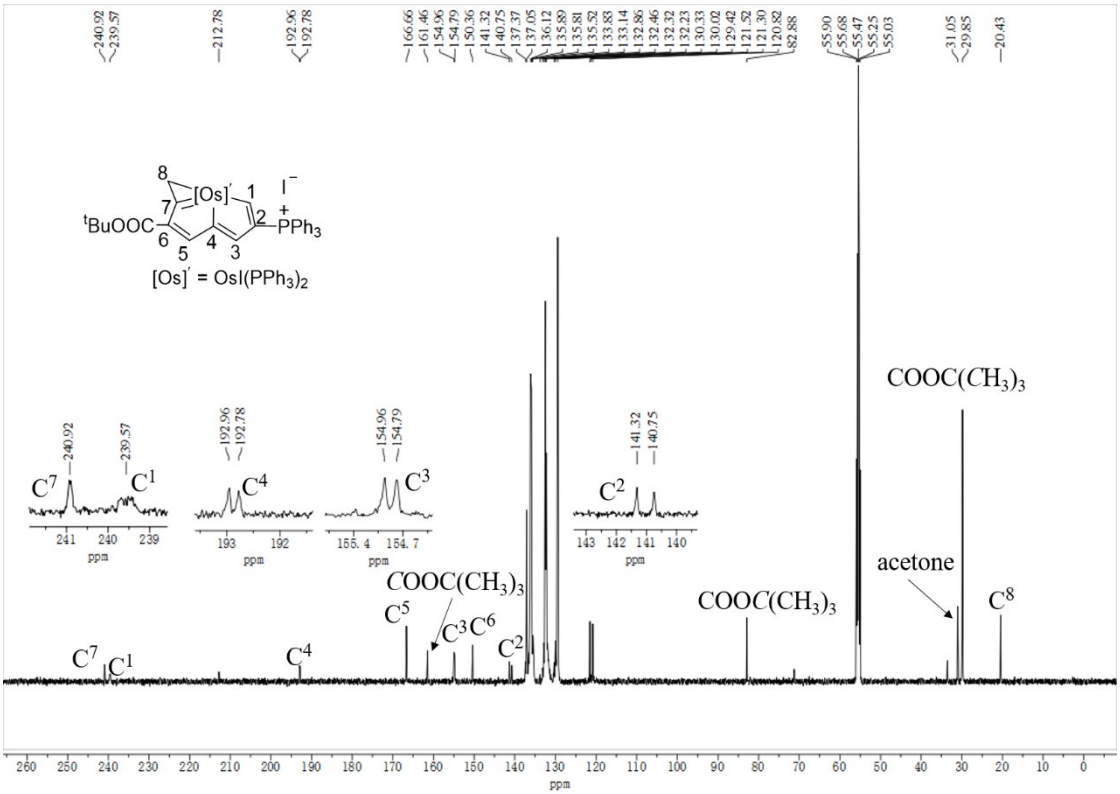


Figure S26. The $^{13}C\{^{1}H\}$ NMR (125.8 MHz, CD_2Cl_2) spectrum for complex **2b**.

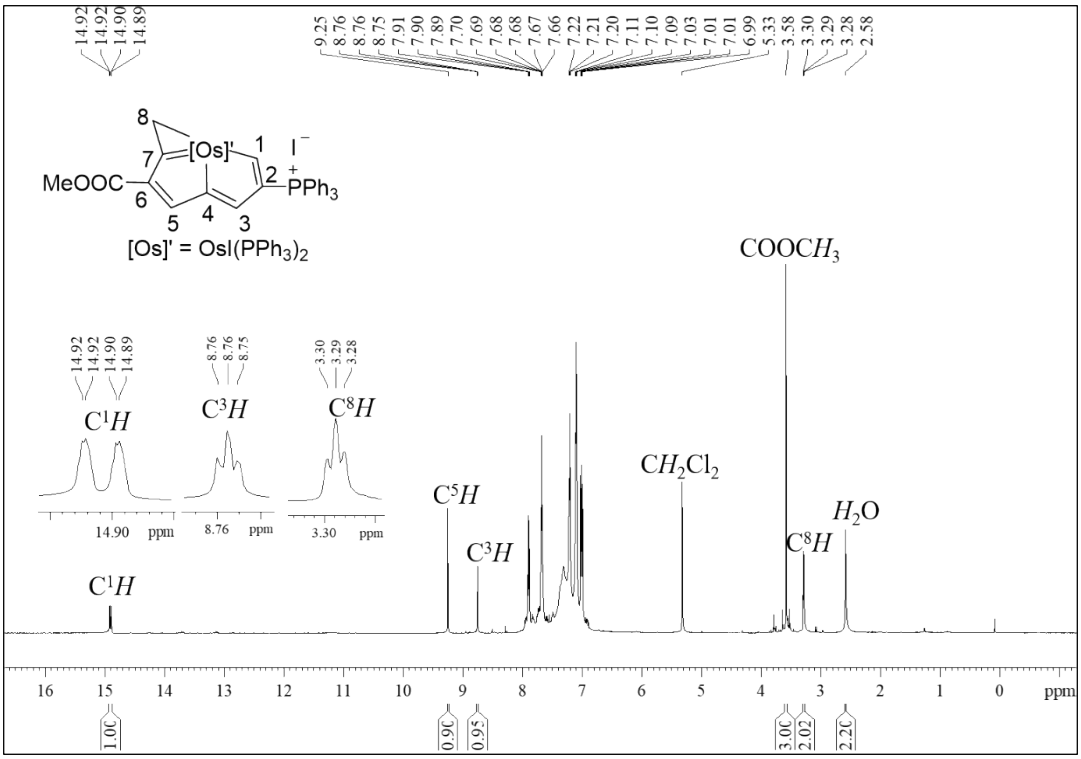


Figure S27. The ^{1}H NMR (600.1 MHz, CD_2Cl_2) spectrum for complex **2c**.

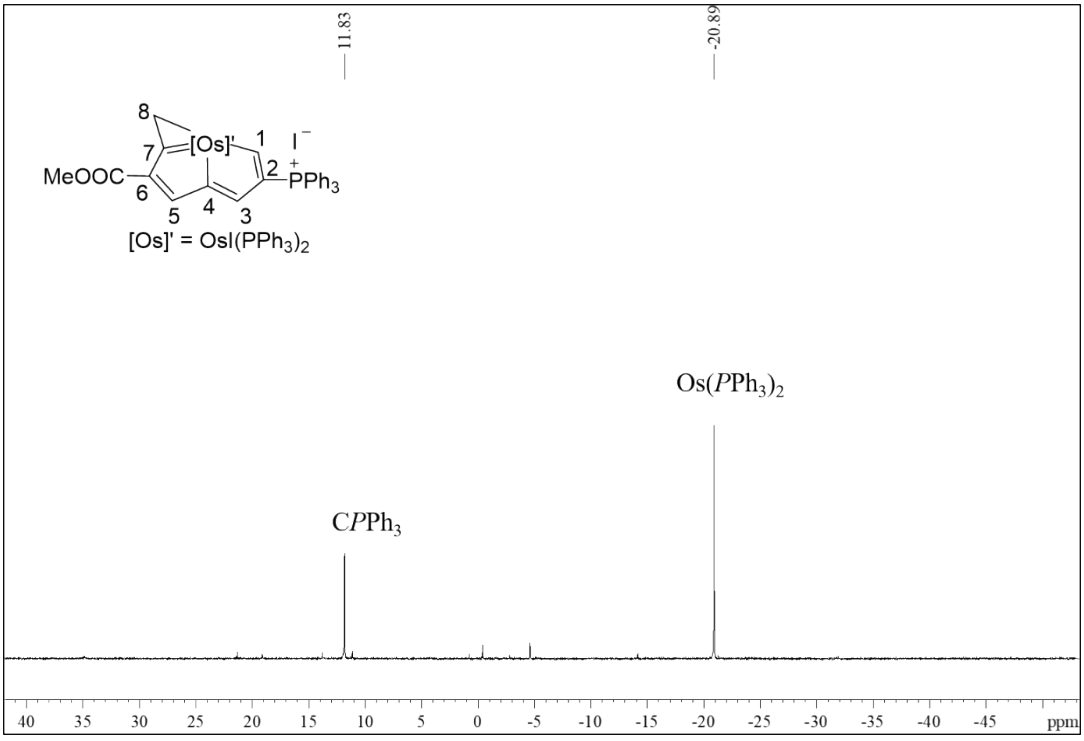


Figure S28. The $^{31}P\{^{1}H\}$ NMR (242.9 MHz, CD_2Cl_2) spectrum for complex **2c**.

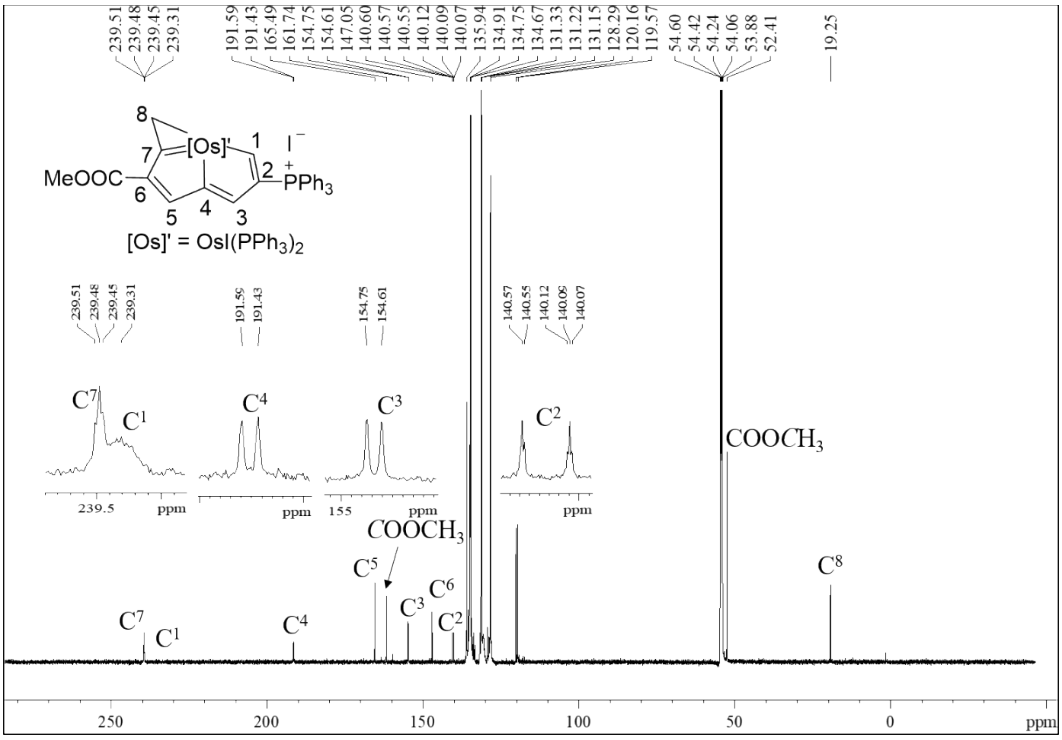


Figure S29. The $^{13}C\{^{1}H\}$ NMR (150.9 MHz) spectrum for complex **2c**.

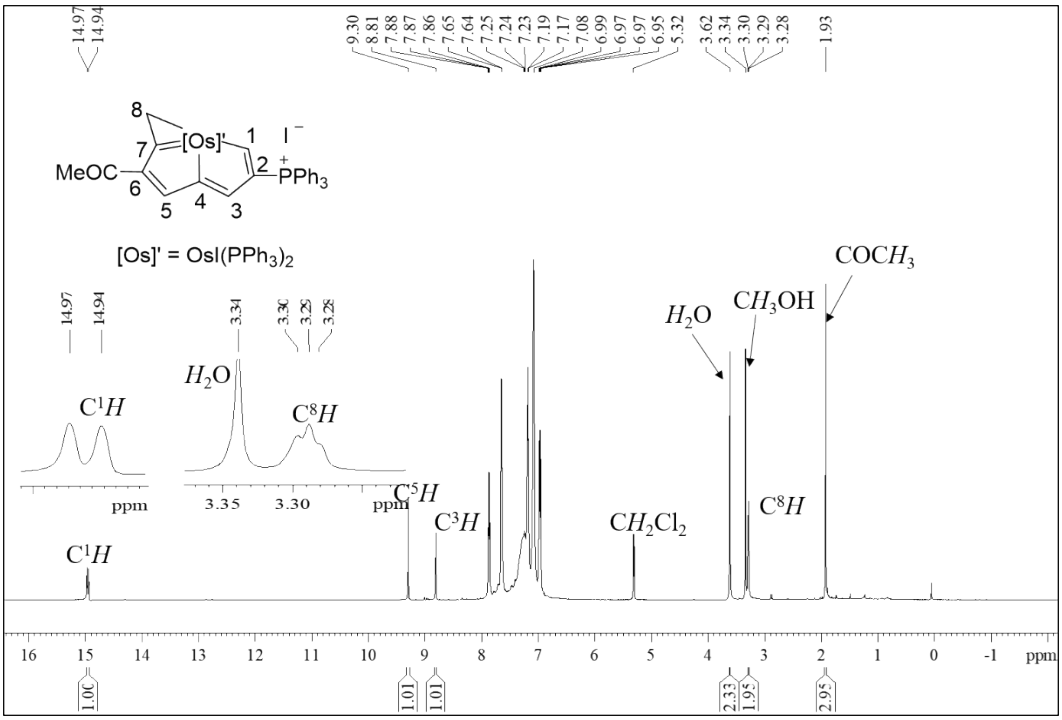


Figure S30. The ^{1}H NMR (600.1 MHz, CD_2Cl_2/CD_3OD = 4/1) spectrum for complex **2d**.

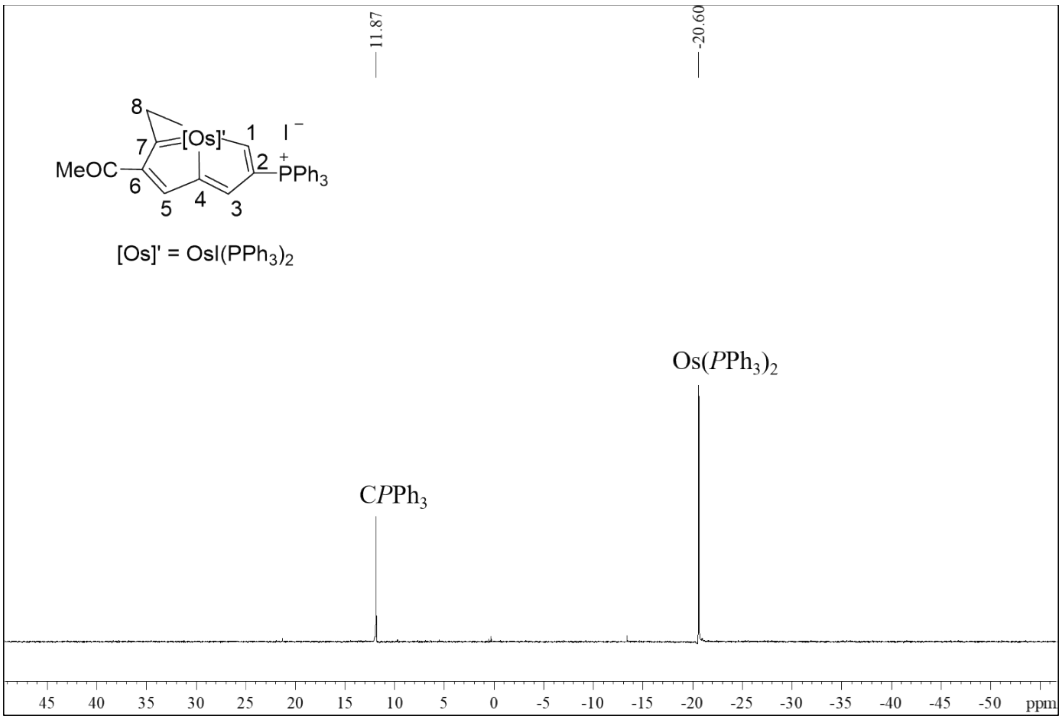


Figure S31. The $^{31}P\{^{1}H\}$ NMR (242.9 MHz, CD_2Cl_2/CD_3OD = 4/1) spectrum for complex **2d**.

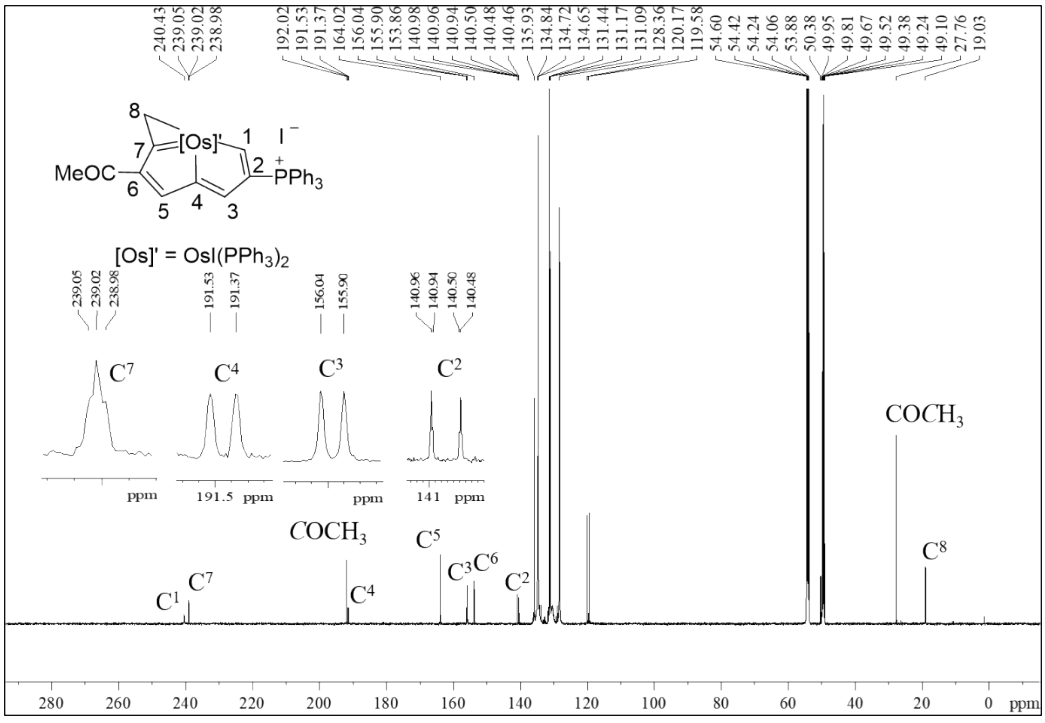


Figure S32. The $^{13}C\{^{1}H\}$ NMR (150.9 MHz, CD_2Cl_2/CD_3OD = 4/1) spectrum for complex **2d**.

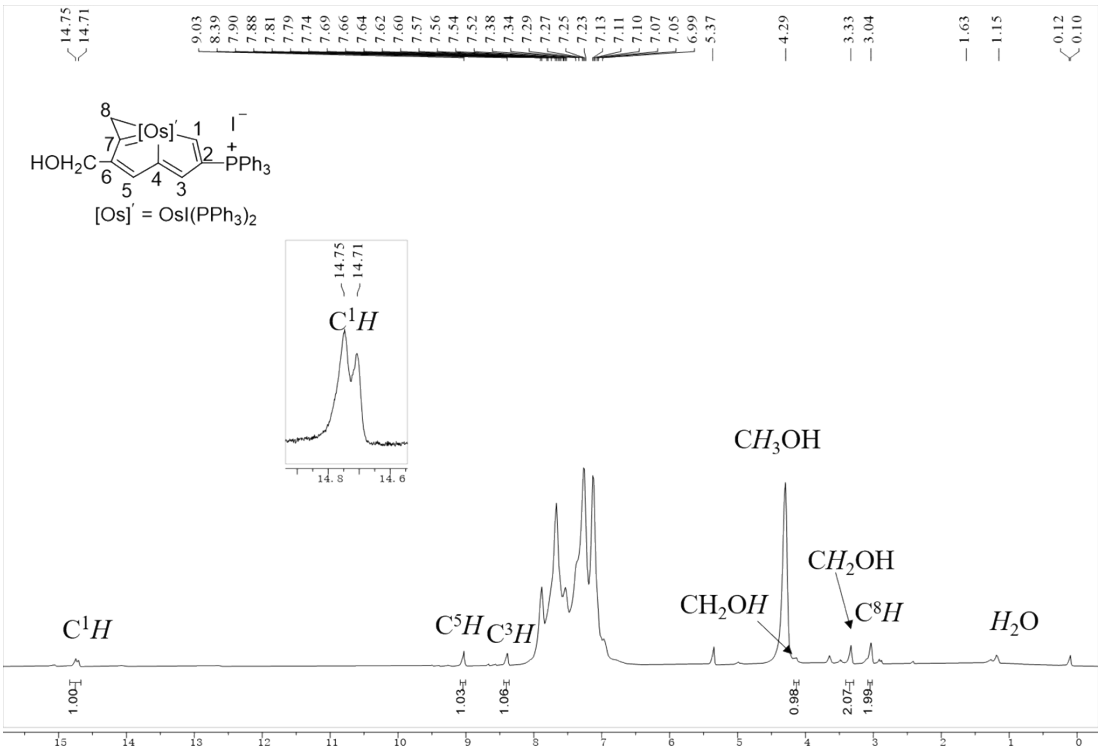


Figure S33. The ^{1}H NMR (500.1 MHz, CD_2Cl_2/CD_3OD = 4/1) spectrum for complex **4a**.

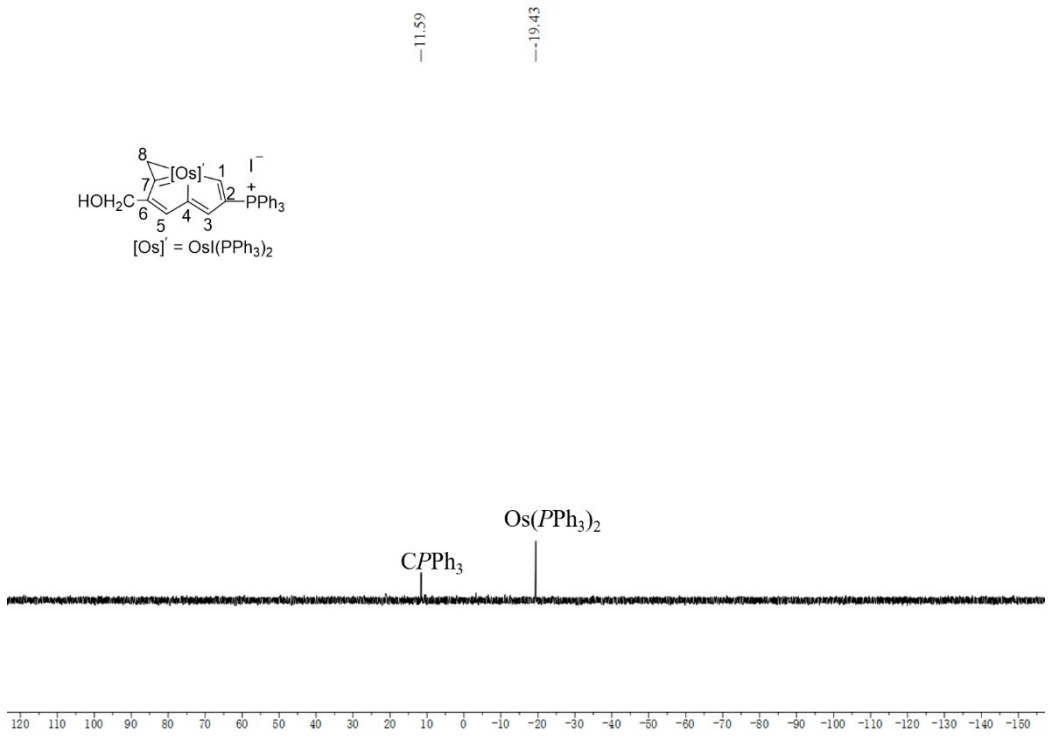


Figure S34. The ^{31}P{^{1}H} NMR (202.5 MHz, CD_2Cl_2/CD_3OD = 4/1) spectrum for complex **4a**.

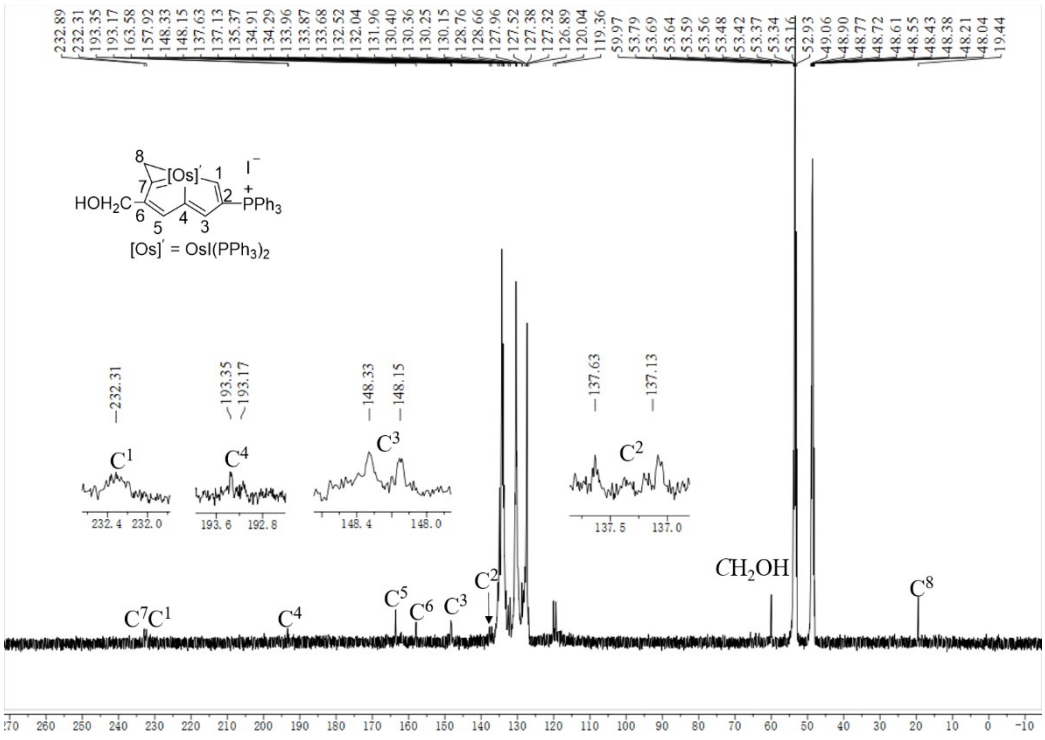


Figure S35. The $^{13}C\{^{1}H\}$ NMR (125.8 MHz, CD_2Cl_2/CD_3OD = 4/1) spectrum for complex **4a**.

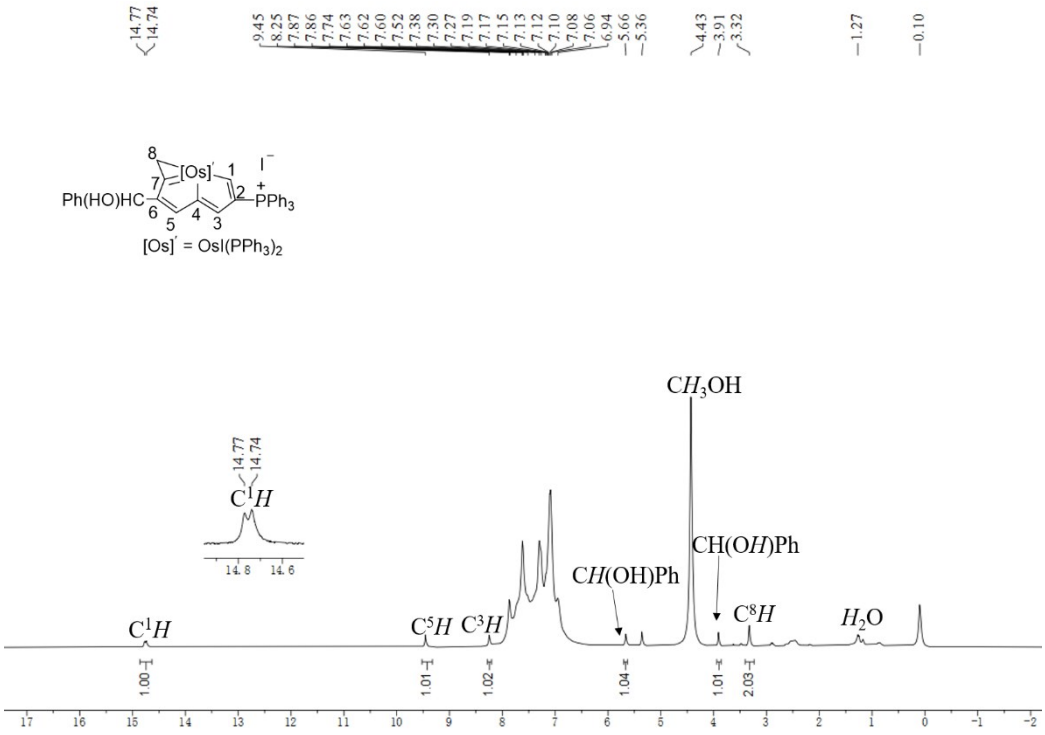


Figure S36. The ^{1}H NMR (500.1 MHz, CD_2Cl_2/CD_3OD = 4/1) spectrum for complex **4b**.

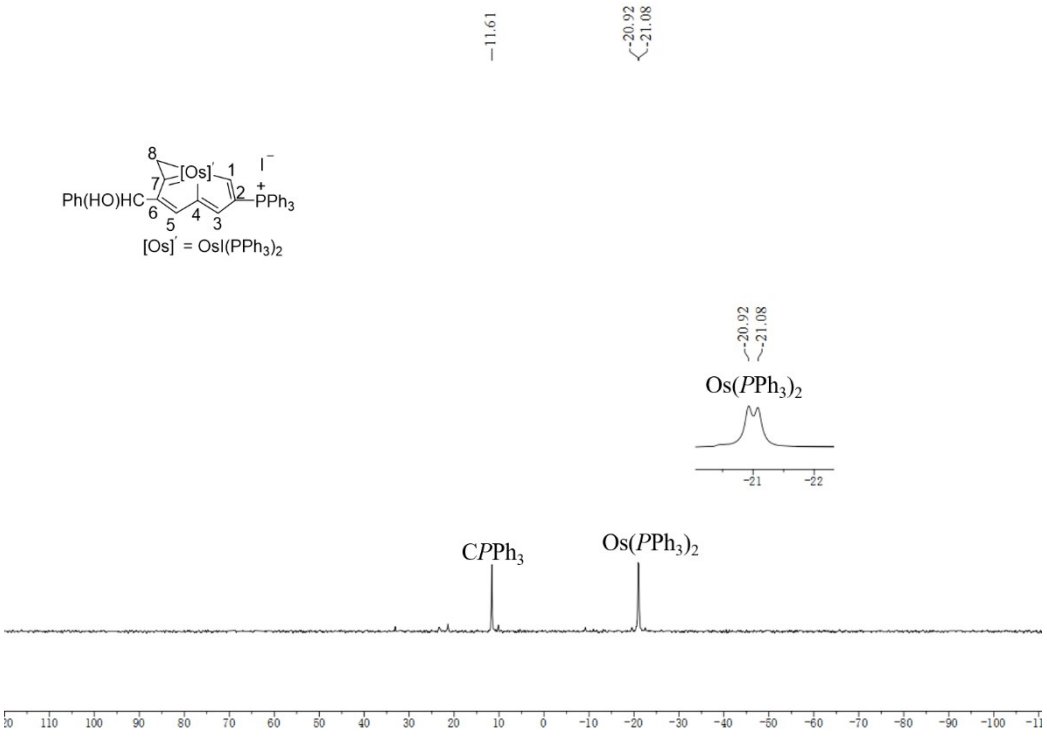


Figure S37. The $^{31}P\{^{1}H\}$ NMR (202.5 MHz, CD_2Cl_2/CD_3OD = 4/1) spectrum for complex **4b**.

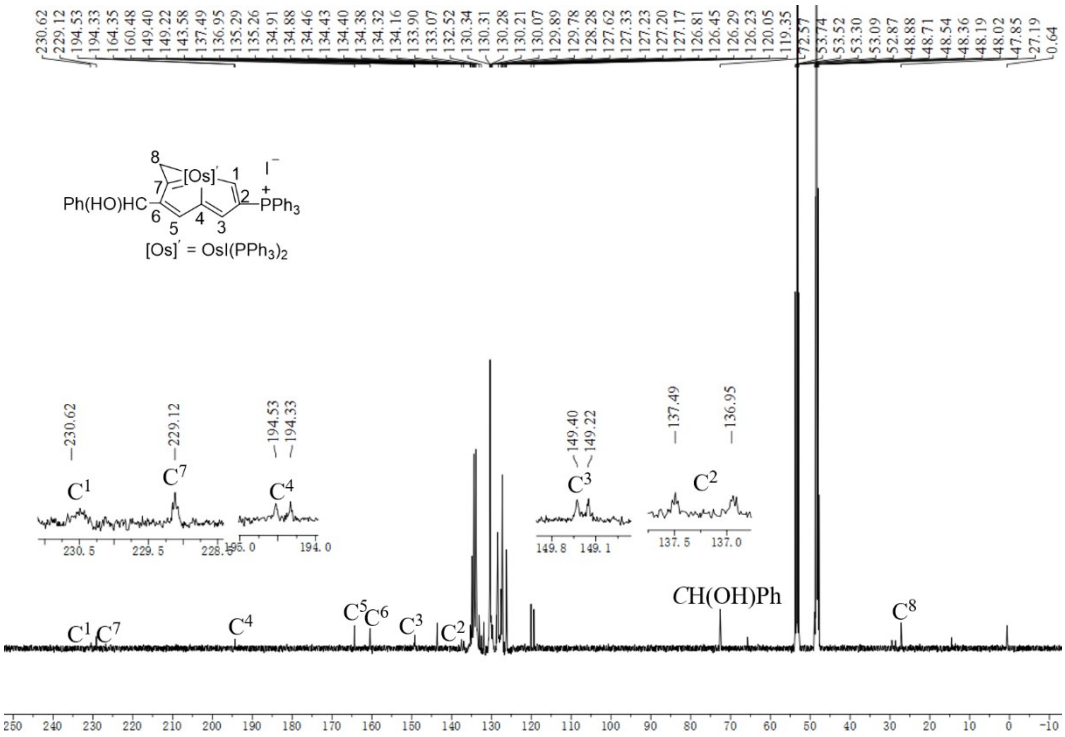


Figure S38. The $^{13}C\{^{1}H\}$ NMR (125.8 MHz, CD_2Cl_2/CD_3OD = 4/1) spectrum for complex **4b**.

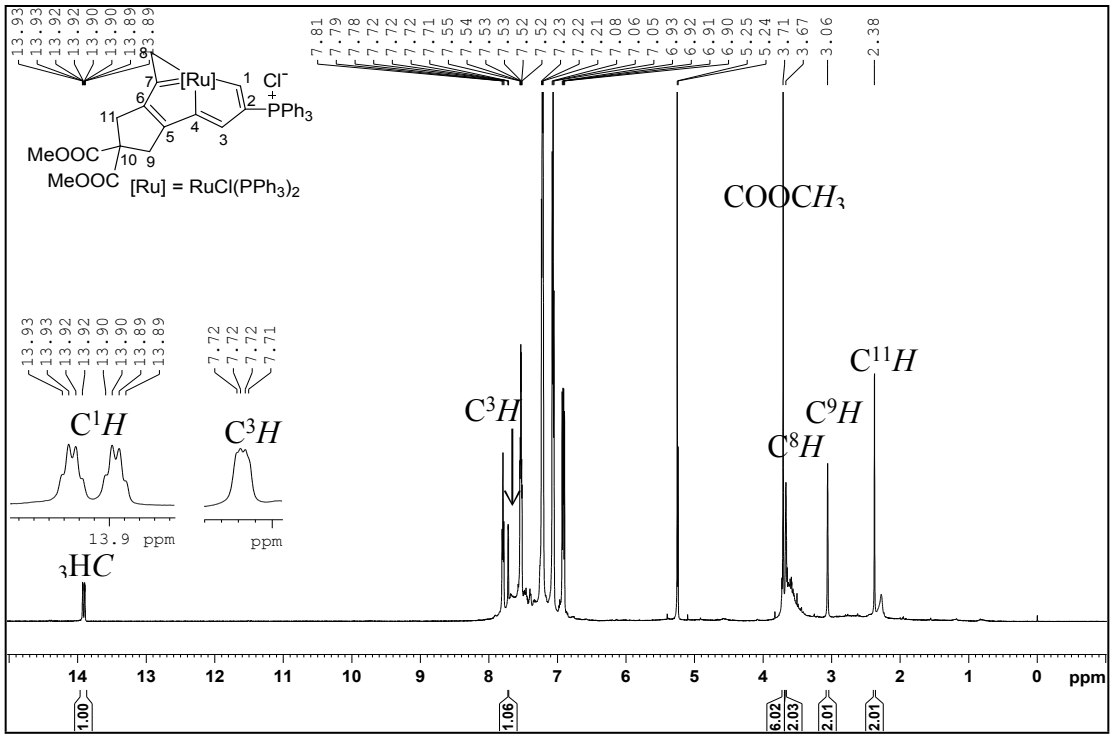


Figure S39. The ^{1}H NMR (600.1 MHz, CD_2Cl_2) spectrum for complex **6**.

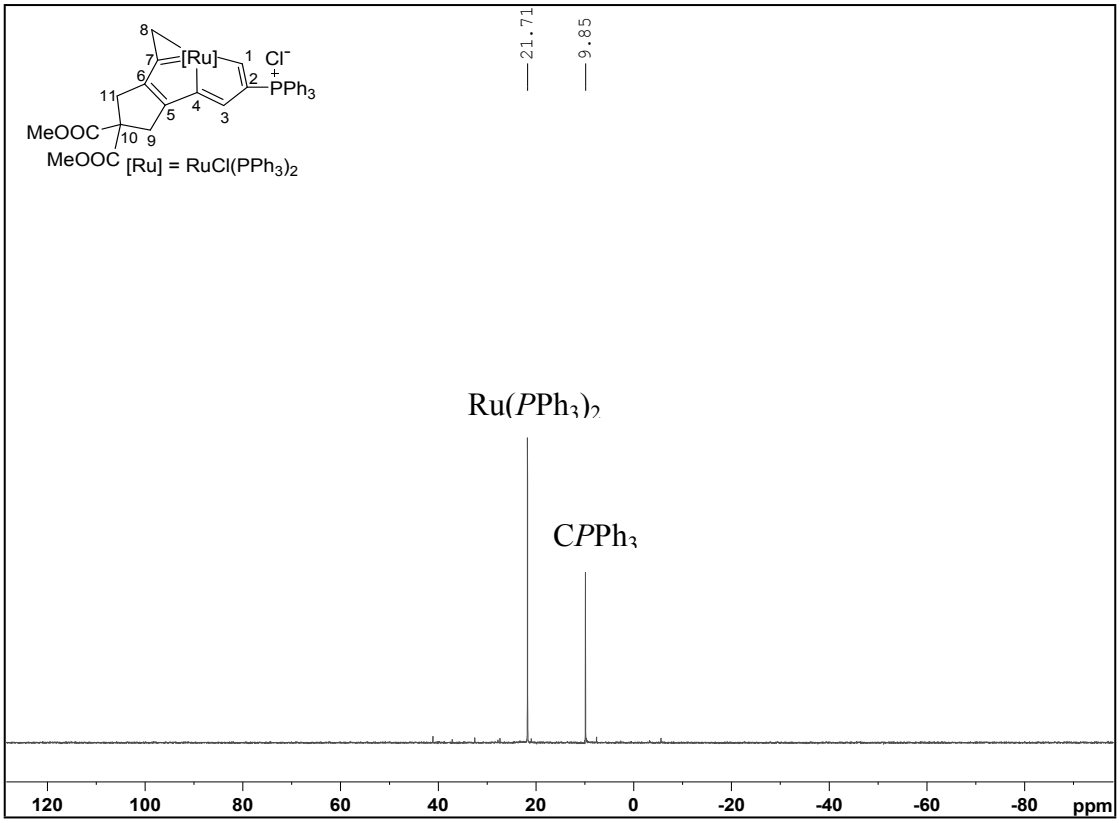


Figure S40. The $^{31}P\{^{1}H\}$ NMR (242.9 MHz, CD_2Cl_2) spectrum for complex **7**.

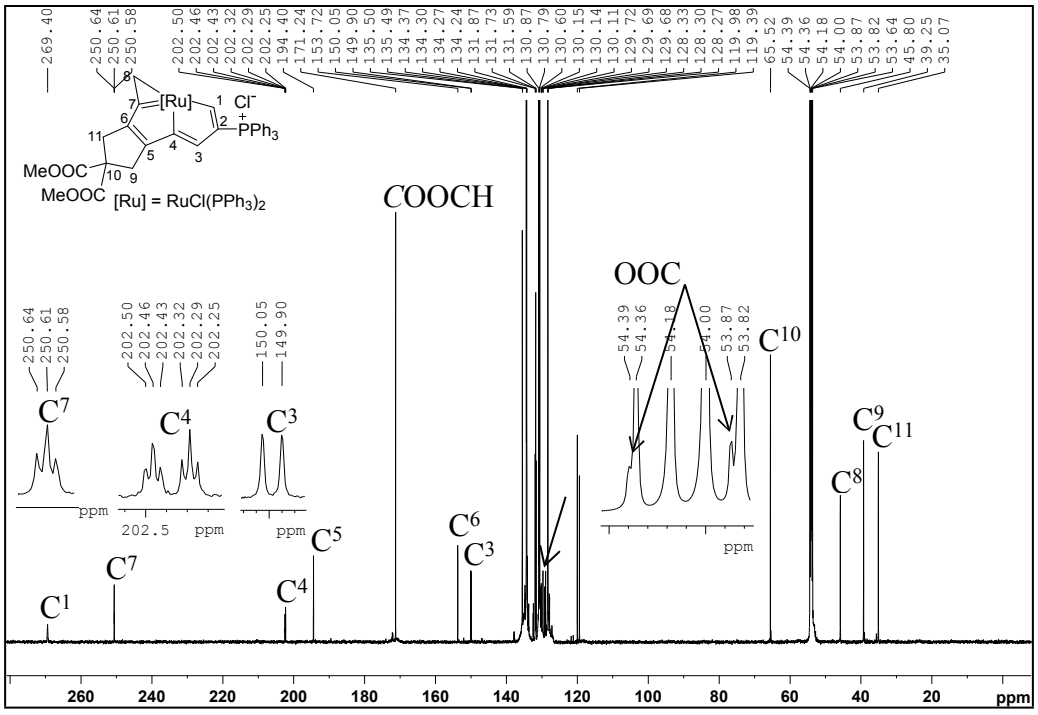


Figure S41. The $^{13}C\{^{1}H\}$ NMR (150.9 MHz, CD_2Cl_2) spectrum for complex **7**.

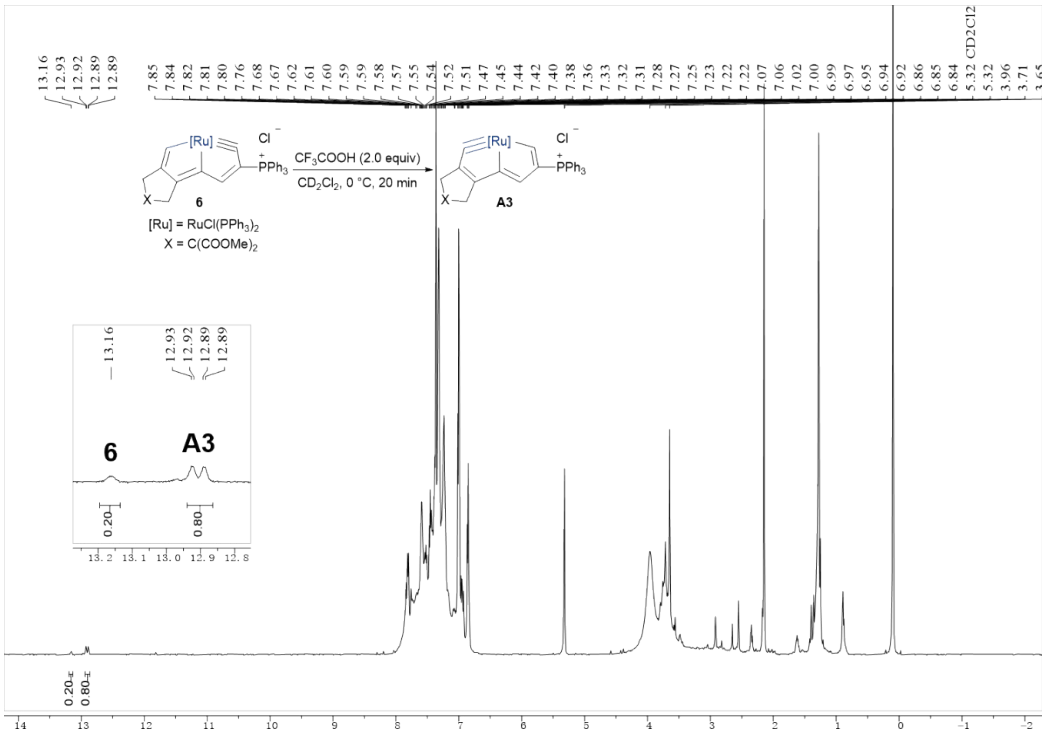


Figure S42. The *in situ* $^{31}P\{^{1}H\}$ NMR (202.5 MHz, CD_2Cl_2) spectrum for the reaction of **6** with CF_3COOH.

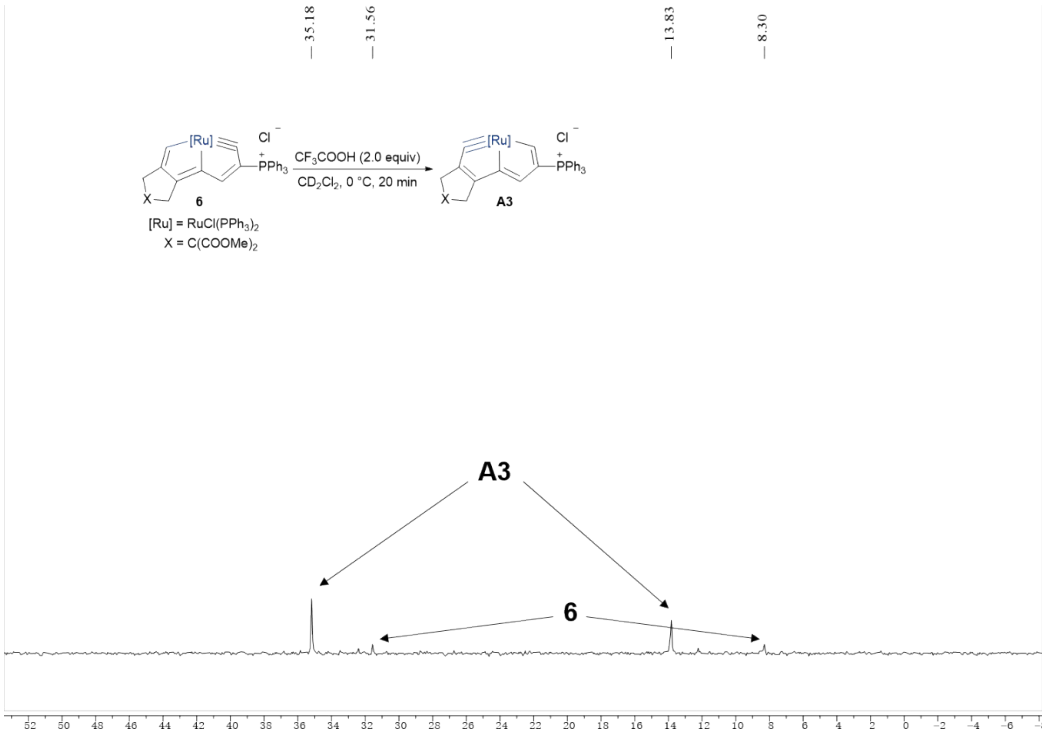


Figure S43. The *in situ* ^{1}H NMR (500.1 MHz, CD_2Cl_2) spectrum for the reaction of **6** with CF_3COOH.

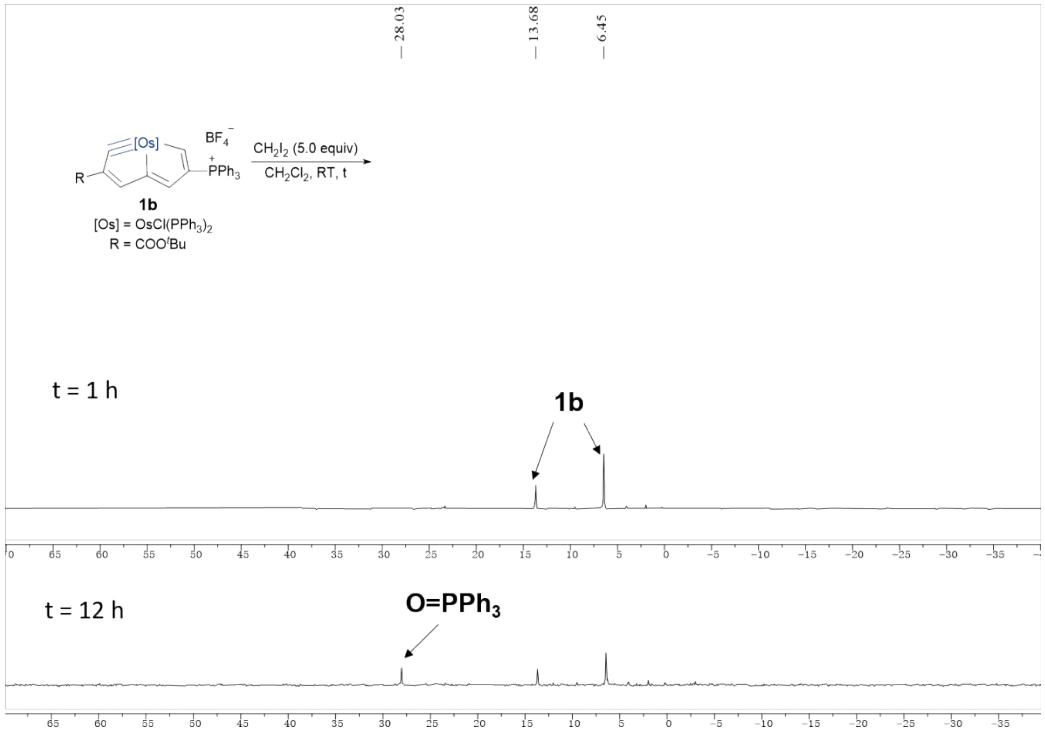


Figure S44. The *in situ* $^{31}P\{^{1}H\}$ NMR (202.5 MHz, CD_2Cl_2) spectrum for the reaction of **1b** with CH_2I_2.

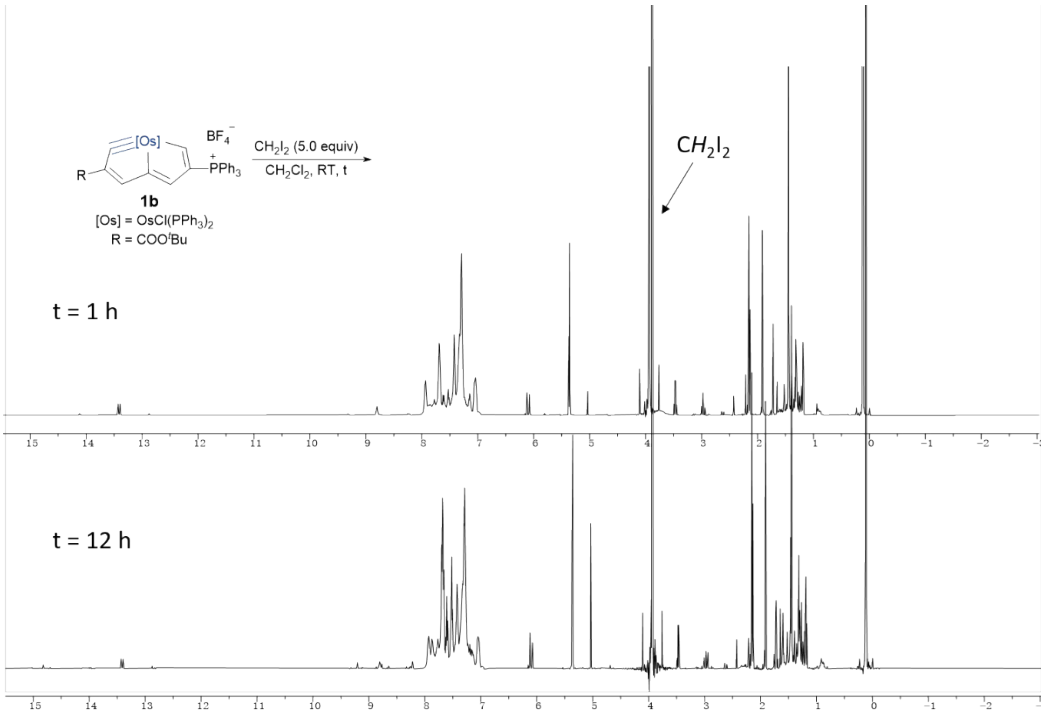


Figure S45. The *in situ* ^{1}H NMR (500.1 MHz, CD_2Cl_2) spectrum for the reaction of **1b** with CH_2I_2.

5. HRMS spectra

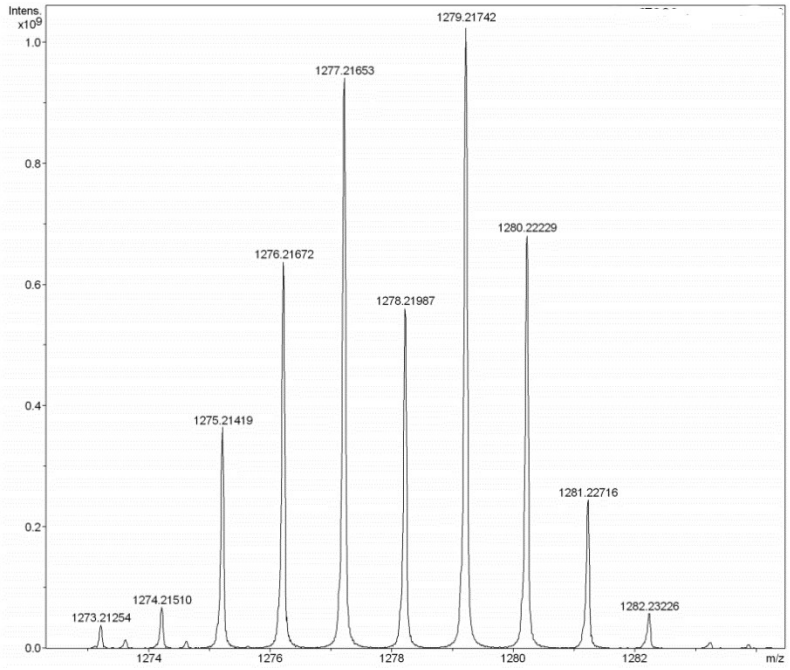


Figure 46. Positive ion ESI-MS spectrum of [**2a**]$^+$ $[C_{65}H_{55}IO_2OsP_3]^+$ measured in methanol.

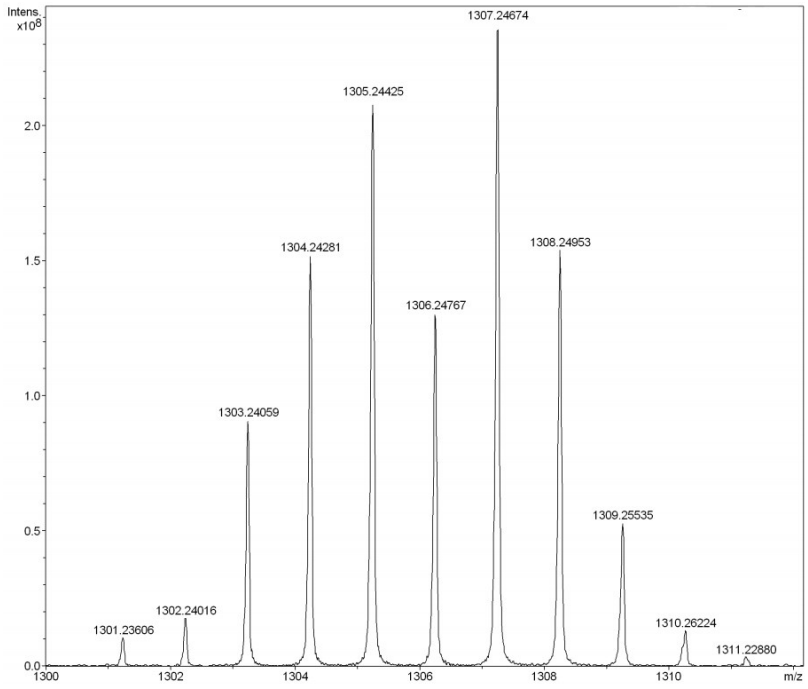


Figure 47. Positive ion ESI-MS spectrum of [**2b**]$^+$ $[C_{67}H_{59}IO_2OsP_3]^+$ measured in methanol.

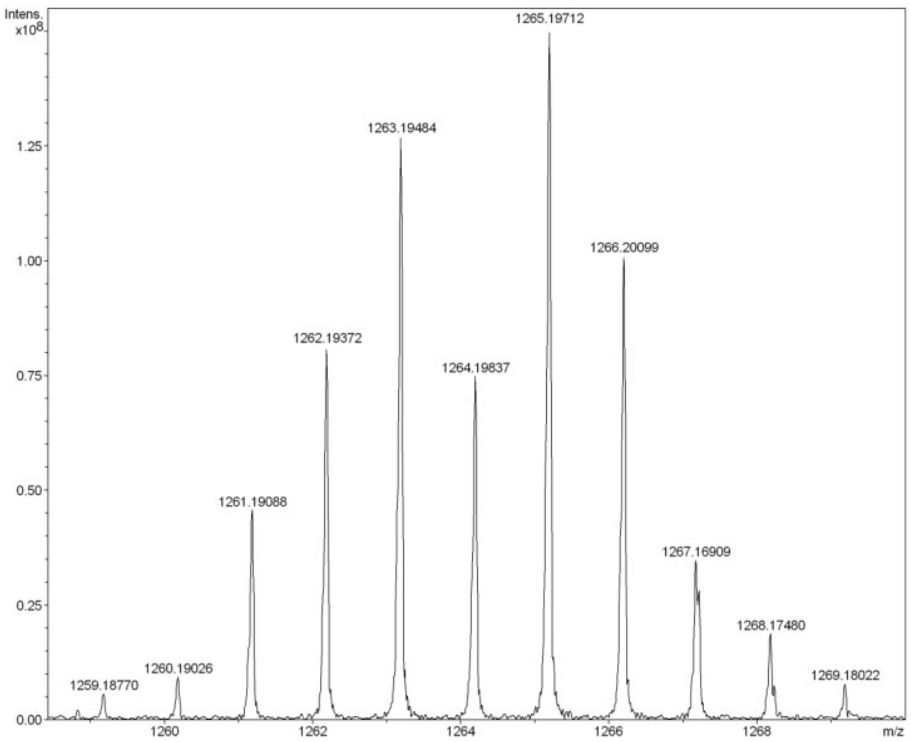


Figure 48. Positive ion ESI-MS spectrum of [**2c**]$^+$ $[C_{64}H_{53}IO_2OsP_3]^+$ measured in methanol.

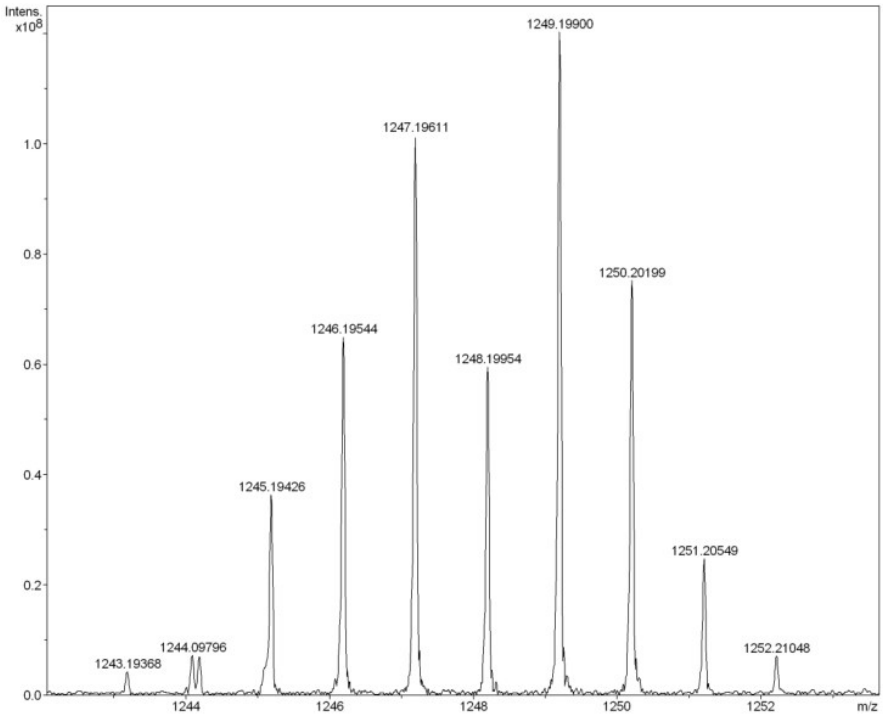


Figure 49. Positive ion ESI-MS spectrum of [**2d**]$^+$ $[C_{64}H_{53}IOOsP_3]^+$ measured in methanol.

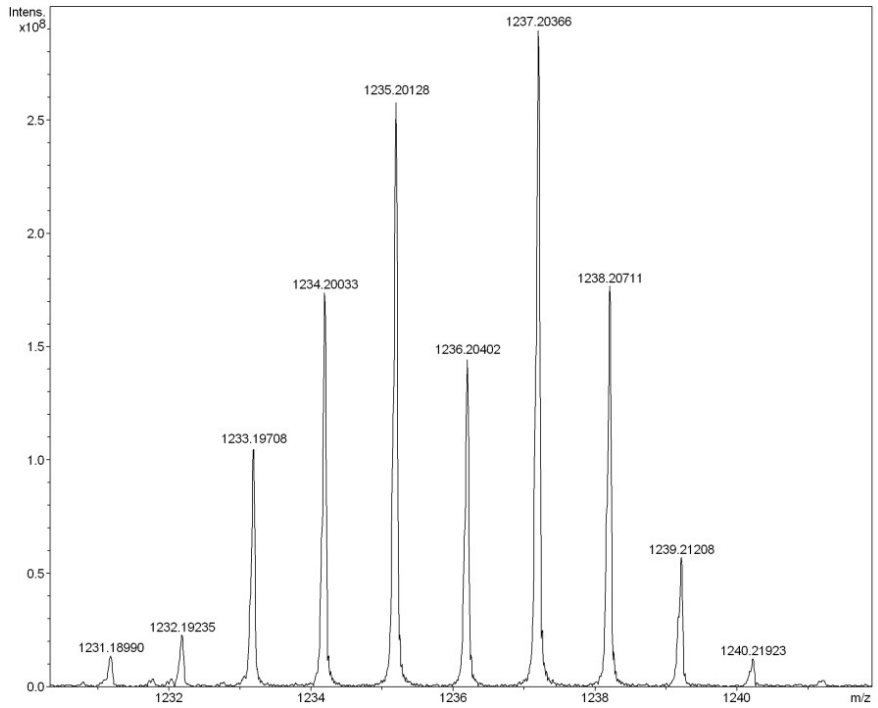


Figure 50. Positive ion ESI-MS spectrum of [**4a**]$^+$ $[C_{63}H_{53}IOOsP_3]^+$ measured in methanol.

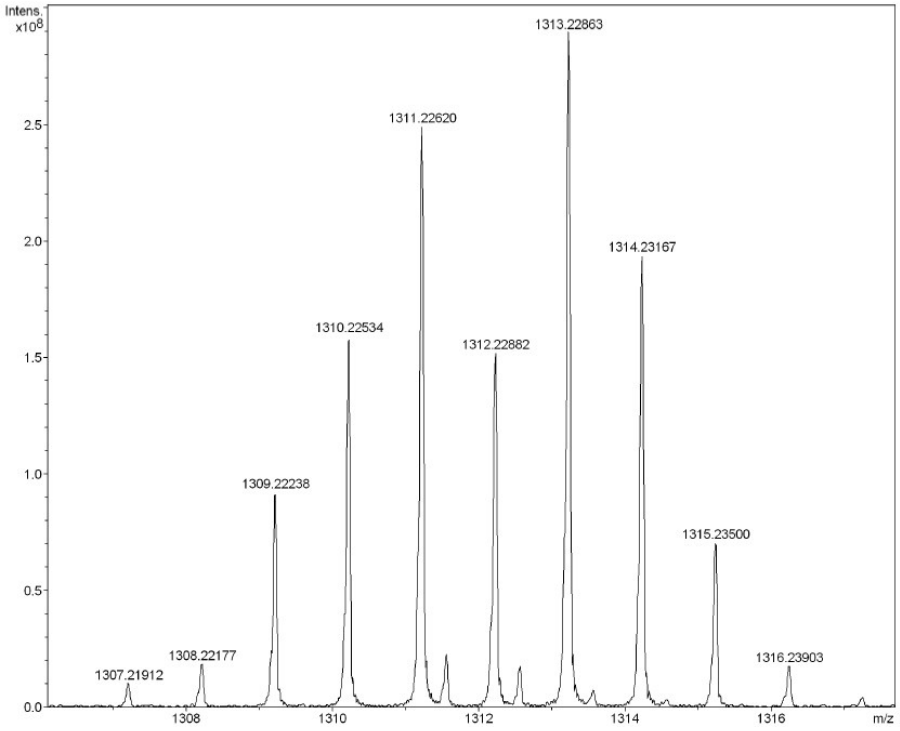


Figure 51. Positive ion ESI-MS spectrum of [**4b**]$^+$ $[C_{69}H_{57}IOOsP_3]^+$ measured in methanol.

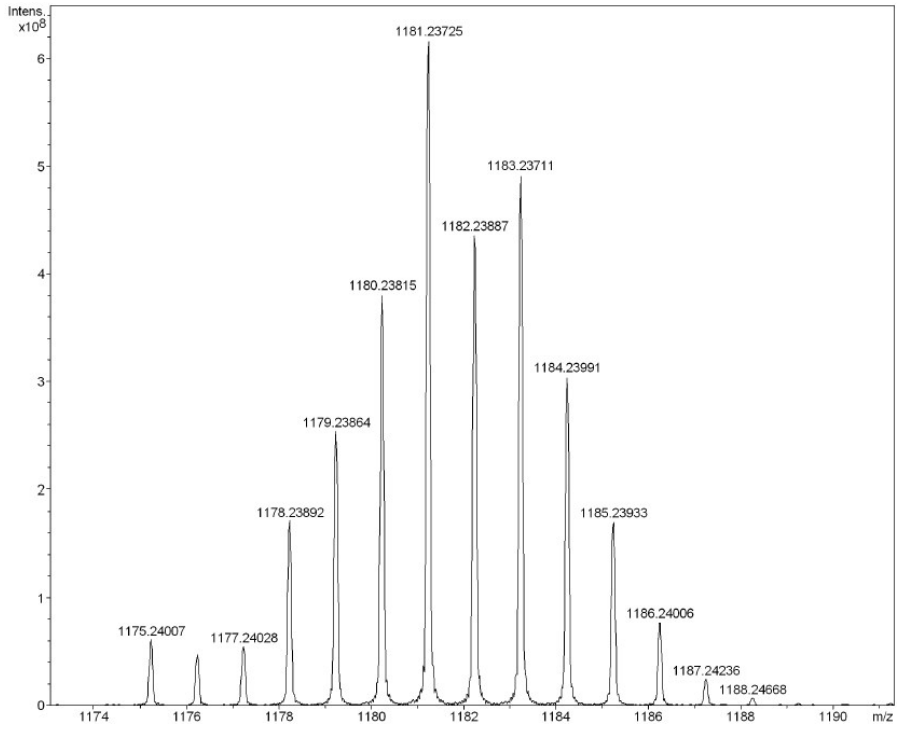
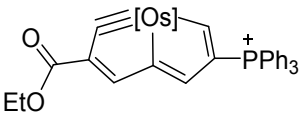


Figure 52. Positive ion ESI-MS spectrum of [**7**]$^+$ $[C_{69}H_{59}ClO_4OsP_3]^+$ measured in methanol.

6. Cartesian Coordinates



[Os] = $OsCl(PPh_3)_2$

124

1a$^+$ E = -4196.28116761 a.u.

Os	1.000360	0.020883	-0.511234
P	1.091645	-2.481412	-0.739120
P	1.177053	2.523261	-0.642638
P	-3.619603	0.019593	0.667938
Cl	1.173228	0.051695	-3.039439
O	5.051214	-0.117884	2.025881
O	3.847895	-0.152878	3.948372
C	-1.060424	0.078872	-0.596861
H	-1.581558	0.142010	-1.552126
C	-1.776734	0.033389	0.583000
C	-0.979655	-0.053604	1.764325
H	-1.390643	-0.134117	2.770227
C	0.376165	-0.045655	1.497979
C	1.397847	-0.096261	2.486940
H	1.217235	-0.143669	3.559708
C	2.671012	-0.078793	1.921483
C	2.517353	-0.030482	0.518770
C	3.983965	-0.117839	2.607716
C	-0.436384	-3.313946	-1.446569
C	-0.915003	-4.530036	-0.939924
H	-0.423433	-5.003063	-0.096661
C	-2.020676	-5.150783	-1.529777
H	-2.376669	-6.099253	-1.136246
C	-2.648590	-4.567152	-2.631259
H	-3.500828	-5.056583	-3.094864
C	-2.163660	-3.362681	-3.146457
H	-2.635995	-2.910257	-4.013882
C	-1.062105	-2.736019	-2.560814
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C	2.324556	-4.201245	-2.649902
H	1.392244	-4.755893	-2.639938
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H	3.249971	-5.534481	-4.061212
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H	5.400971	-4.286548	-4.105418
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H	5.670495	-2.241970	-2.714001
C	3.684361	-2.343156	-1.898542
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C	1.421385	-3.392392	0.869010
C	0.445299	-3.411257	1.876204
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C	0.687977	-4.068177	3.082706
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H	2.103281	-5.211543	4.243259
C	2.891049	-4.677710	2.308453
H	3.846861	-5.168261	2.469092
C	2.646772	-4.029900	1.094145
H	3.413444	-4.026167	0.327377
C	1.496281	3.346469	1.012675
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H	3.502944	3.977624	0.526737
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H	3.930474	4.993578	2.732954
C	1.982205	4.510920	3.520521
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C	4.756950	4.058233	-3.219301
H	5.593517	4.423051	-3.808612
C	3.632634	4.863889	-3.027790
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H	-3.232381	5.327007	-3.090914
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H	-3.640256	1.961543	-1.529187
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C	4.714537	-0.228540	6.177512
H	5.678871	0.686951	4.449661
H	5.649670	-1.079063	4.401256
H	5.625031	-0.262140	6.785183
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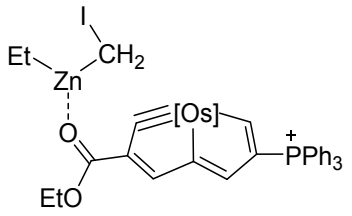

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136

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C	-2.237400	0.083472	-0.604667
H	-2.745288	0.242634	-1.555814
C	1.319612	0.147371	0.579530
C	1.451060	-0.091690	1.966580
C	-5.232653	-2.044492	1.235808
C	2.736064	-0.116571	2.693119
C	-2.181850	-0.385391	1.711312
H	-2.596790	-0.653218	2.682559
C	-0.828191	-0.211282	1.486983
C	2.116342	-4.508103	1.858210
H	3.132013	-4.857109	2.019541
C	2.740102	-3.942474	-3.764029
H	2.753685	-4.830088	-4.390297
C	-1.948910	-2.453967	-2.910097
H	-1.645877	-1.451995	-3.198565
C	-1.023503	3.029548	2.444852
H	-1.880069	2.419581	2.178681
C	-6.973739	1.235880	1.346647
H	-7.505945	0.763054	0.526978
C	-1.820209	3.535406	-0.944583
C	-2.131077	3.353540	-2.301199
H	-1.500815	2.722269	-2.919873
C	1.629100	-3.684122	-2.959665
H	0.791056	-4.373547	-2.969052
C	-5.632266	0.917107	1.601987
C	-6.223531	-2.194928	2.212261
H	-6.751480	-1.330326	2.600641
C	-2.966559	-0.196764	0.535143
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C	1.600414	-2.539742	-2.152557
C	2.329816	2.933813	-1.436001
H	2.475187	1.911783	-1.105805
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H	2.661022	-0.759340	-1.552557
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H	-1.631085	3.241683	4.500040
C	-7.625582	2.177267	2.143730
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C	-3.238189	3.996955	-2.856462
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H	4.315499	3.104214	-2.238995
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H	4.634753	-1.230612	-2.958239
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H	-1.491628	-3.225586	1.270872

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H	2.710144	0.338012	6.585445
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H	1.783472	4.392775	1.087978
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H	-5.830706	2.167669	-3.562198
C	0.920689	4.891850	-1.663600
H	-0.025100	5.399264	-1.502824
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C	-5.853380	-4.586849	2.197119
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H	1.809028	6.581196	-2.654201
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H	-6.917432	0.251986	-4.720622
C	0.225557	4.266971	4.107475
H	0.338262	4.624049	5.127222
C	-1.640808	-4.426035	-1.537841
H	-1.117373	-4.957467	-0.750388
C	0.175176	-0.308075	2.487809
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C	-6.943631	2.802818	3.189918
H	-7.452565	3.538004	3.806225
C	-3.337301	-4.408763	-3.266786
H	-4.127917	-4.914156	-3.814716
C	-6.609469	-1.113130	-3.082721
H	-7.085846	-1.951075	-3.582699
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H	3.989314	5.442351	-3.030038
C	-3.747056	4.990842	-0.715699
H	-4.364175	5.635204	-0.095515
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H	2.046442	5.185542	3.408033
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Cl	0.008283	0.586329	-2.965966
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H	4.978397	-3.067737	0.885585
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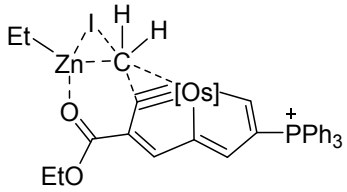

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O	2.581723	-0.026936	4.137853
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C	1.659685	-0.062103	0.555629
C	1.706245	-0.157352	1.974063
C	-5.090632	-1.447608	1.611799
C	2.895724	-0.241276	2.857017
C	-1.936874	-0.101300	1.689886
H	-2.367190	-0.203422	2.685628
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H	3.003970	-5.091755	2.366781
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H	2.292207	-5.980900	-3.613699
C	-1.988071	-2.721945	-2.629406
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H	-1.432167	2.383556	-2.856438
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C	-6.060433	-1.271536	2.604943
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C	1.451846	-3.117190	-1.975026
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H	2.110967	1.773198	-2.699833
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C	0.657491	3.221458	1.221671
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C	0.506450	-3.383103	0.805275
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C	-5.878831	-3.616601	3.176379
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H	2.380618	6.703738	-2.214550
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H	1.669076	4.371011	4.805612
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H	-1.500122	-4.893126	-0.047151
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H	-1.581213	4.739847	0.749749
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C	-3.109722	5.141149	-0.704145
H	-3.564767	5.923487	-0.102992
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H	3.334011	4.424663	2.953873
C	-3.625386	4.834777	-1.962857
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H	4.441246	0.610508	4.807923
H	3.293418	0.608338	-1.327405
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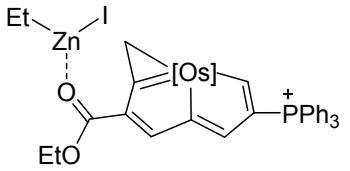
H	5.394337	-3.391565	-0.414803
H	4.872420	-3.466344	1.262397

H	7.370675	-3.774208	1.112447
H	7.530401	-2.209451	0.303773
H	7.004918	-2.280186	1.984522



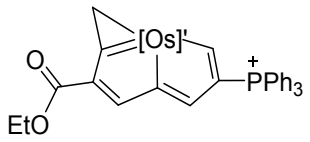
[Os] = $OsCl(PPh_3)_2$

136

B1$^+$ E = -6392.17765302 a.u.

Os	-0.062235	-0.224165	-0.763912
P	-4.434869	0.634798	0.931283
P	-0.418294	-2.740696	-0.675622
P	0.434984	2.259682	-1.012904
O	4.180541	-1.090203	1.596865
O	3.118640	-0.543846	3.503599
C	-2.065819	0.165986	-0.634354
H	-2.703519	0.247128	-1.513932
C	1.697605	-0.488580	0.144269
C	1.866059	-0.472165	1.526899
C	-5.067365	-0.657258	2.099291
C	3.163097	-0.728426	2.185924
C	-1.726898	0.200520	1.702720
H	-2.008746	0.267499	2.753265
C	-0.419738	-0.047144	1.284161
C	1.795317	-4.373086	2.445057
H	2.797029	-4.774929	2.568365
C	1.217766	-6.067406	-2.551487
H	1.253223	-7.134956	-2.353217
C	-2.932796	-2.784344	-1.976630
H	-2.525442	-1.955242	-2.547221
C	-0.105574	3.503751	1.501989
H	-1.134675	3.562728	1.162927
C	-6.012347	2.903677	1.478275
H	-6.761822	2.423643	0.856967
C	-0.915086	3.388049	-1.692265
C	-1.752061	2.916759	-2.711518
H	-1.666478	1.889982	-3.052428
C	0.575865	-5.220427	-1.649405
H	0.119635	-5.643044	-0.759861
C	-4.761696	2.302327	1.677680
C	-5.826997	-0.304743	3.220253
H	-6.052052	0.735819	3.429213
C	-2.636630	0.332115	0.628411
C	-2.173351	-3.367842	-0.953495
C	1.380816	-3.939505	1.183096
H	2.066913	-4.014976	0.345933
C	0.526855	-3.838041	-1.888495
C	2.084899	2.013660	-3.324111
H	1.480864	1.140384	-3.547821
C	-6.356146	-0.437679	-0.853676
H	-6.543930	-1.190399	-0.096001
C	1.859146	2.745472	-2.150560
C	1.102596	-3.319545	-3.052933
H	1.021119	-2.263129	-3.276355
C	2.154944	-0.645175	-1.155247
C	0.225592	3.966678	2.776637
H	-0.548160	4.385622	3.415360
C	-6.291649	4.133475	2.075371
H	-7.259547	4.599330	1.916691
C	-2.657487	3.784675	-3.329533
H	-3.280908	3.413535	-4.139058
C	-3.796614	2.931517	2.473097
H	-2.823304	2.477931	2.625558
C	4.358390	-0.749747	4.243850
C	-4.775052	-2.003099	1.832391
H	-4.186827	-2.283055	0.963181
C	-5.393515	0.556692	-0.648246
C	3.073503	2.425176	-4.221590
H	3.242126	1.850278	-5.127871
C	1.743330	-4.175464	-3.954534
H	2.185080	-3.762015	-4.856739
C	0.885396	2.986964	0.655362
C	-4.084862	4.162034	3.065697
H	-3.335068	4.650904	3.680616
C	0.089691	-3.428021	0.996283
C	-0.770256	-3.337942	2.099659
H	-1.768067	-2.927504	1.982276
C	-4.193102	-3.298037	-2.292286
H	-4.768893	-2.842000	-3.092536
C	4.071387	-0.441049	5.699589
H	3.744821	0.596139	5.823809
H	4.983124	-0.585894	6.288400
H	3.295751	-1.102455	6.098756
C	2.206346	2.917241	1.117938
H	2.998055	2.519001	0.490887
C	-5.158715	1.531992	-1.628962
H	-4.417763	2.311171	-1.478136
C	-5.887180	1.499831	-2.817240
H	-5.702531	2.252852	-3.577127
C	2.607849	3.904084	-1.902149
H	2.433525	4.496993	-1.011027
C	-5.253876	-2.992772	2.690547
H	-5.034329	-4.034419	2.477109
C	1.808009	-5.545200	-3.705289
H	2.307793	-6.206031	-4.407864
C	-6.294300	-1.303520	4.077426
H	-6.880608	-1.030364	4.949607
C	-3.941994	-4.988842	-0.587547
H	-4.320041	-5.858871	-0.057052
C	-0.357108	-3.778408	3.358377
H	-1.041387	-3.716386	4.200362
C	0.926827	-4.298561	3.534610

H	1.245739	-4.645875	4.513258
C	-6.010253	-2.644261	3.813128
H	-6.378307	-3.417930	4.480618
C	3.595818	4.305924	-2.802102
H	4.176939	5.199843	-2.594627
C	-6.849519	0.508293	-3.026407
H	-7.417696	0.490988	-3.951788
C	1.546246	3.907556	3.227049
H	1.803463	4.276804	4.215853
C	-2.679398	-4.481336	-0.268173
H	-2.094877	-4.963956	0.507831
C	0.652127	-0.209650	2.179597
H	0.562115	-0.147384	3.260845
C	-5.329559	4.762899	2.868110
H	-5.549137	5.721327	3.329099
C	-4.702903	-4.396370	-1.597358
H	-5.679194	-4.799985	-1.851445
C	-7.083587	-0.456512	-2.045760
H	-7.835115	-1.224537	-2.202227
C	-0.981012	4.737423	-1.317209
H	-0.315382	5.132471	-0.557643
C	3.834842	3.564737	-3.960664
H	4.606089	3.878635	-4.658189
C	-1.898460	5.594500	-1.927562
H	-1.940236	6.637119	-1.624798
C	2.533776	3.379114	2.395266
H	3.567043	3.325860	2.725881
C	-2.741121	5.120759	-2.934572
H	-3.442444	5.793562	-3.420356
Zn	5.720857	-0.648696	0.013470
I	6.226078	1.751645	0.713345
H	4.676251	-1.785747	4.093717
H	5.121085	-0.091163	3.819693
H	2.397733	-1.636083	-1.533505
H	2.677449	0.167290	-1.655356
Cl	-0.573015	-0.347767	-3.317878
C	5.956882	-2.294699	-1.043472
C	5.711089	-3.596130	-0.266838
H	6.972194	-2.279202	-1.456919
H	5.274091	-2.225032	-1.900415
H	5.811115	-4.477826	-0.915812
H	6.424702	-3.719255	0.556713
H	4.705705	-3.624647	0.171312



[Os]' = OsI(PPh$_3$)$_2$

127

2a$^+$ E = -4073.18723152 a.u.

Os	0.946556	0.058733	-0.464864
I	0.634656	0.064099	-3.402965
P	-3.644767	-0.206542	0.824639
P	1.199252	-2.469584	-0.518816
P	0.886074	2.614827	-0.448870
O	3.699101	0.265908	4.110321
O	5.023962	0.380595	2.268599
C	0.365041	0.025687	1.547823
C	2.655181	0.175545	2.013032
C	-1.105902	-0.088147	-0.526484
H	-1.676407	-0.136998	-1.453305
C	-4.221741	-1.834614	1.501610
C	-0.993382	-0.045228	1.837446
H	-1.385620	-0.026938	2.854336
C	-3.677007	2.421662	1.807329
H	-2.952783	2.626017	1.024339
C	-4.202315	1.132491	1.978074
C	3.926266	0.282125	2.778620
C	-3.098623	4.847634	-1.522856
H	-3.997003	5.386173	-1.811897
C	0.506518	3.290494	2.312743
H	-0.526361	2.991762	2.166634
C	-1.549063	3.013758	-1.856787
H	-1.240453	2.143499	-2.426897
C	2.752372	3.001762	-2.627786
H	2.668566	1.938689	-2.808152
C	2.022937	3.600556	-1.597882
C	3.236109	0.212378	-0.618773
H	3.759598	-0.664789	-0.991418
H	3.634216	1.153790	-0.990297
C	0.924290	3.703034	3.579377
H	0.209896	3.731851	4.397868
C	-2.710718	3.700663	-2.217825
H	-3.303705	3.339188	-3.052845
C	2.623429	0.168069	0.622112
C	-0.693868	-4.619866	-0.103380
H	-0.112190	-4.895686	0.768557
C	0.999162	-3.189430	2.248138
H	-0.052582	-2.942561	2.150436
C	-1.781518	-5.416323	-0.474129
H	-2.034847	-6.287230	0.124203
C	1.407340	3.265211	1.239008
C	-1.804142	-0.119045	0.678465
C	1.844442	-3.099811	1.133459
C	-1.148546	4.629275	-0.102892
H	-0.544287	5.012815	0.711421
C	-0.349740	-3.494264	-0.861792
C	-3.379830	-2.607680	2.308492
H	-2.362947	-2.286668	2.507273
C	1.362780	0.092640	2.541795
H	1.161203	0.084779	3.609628
C	-5.023680	3.197536	3.662770
H	-5.343794	4.001167	4.319521
C	-4.095330	3.451713	2.649561

H	-3.693466	4.450555	2.509342
C	2.399346	-3.291289	-1.729171
C	-0.762068	3.470149	-0.791278
C	-2.313844	5.310548	-0.465311
H	-2.594859	6.213651	0.070219
C	3.642186	5.159984	-3.276155
H	4.270054	5.763448	-3.925544
C	2.544801	-4.686063	-1.657064
H	1.984032	-5.260743	-0.926430
C	-2.170130	-3.997021	-2.383771
H	-2.719318	-3.765426	-3.293001
C	-4.467410	0.016806	-0.816803
C	2.740144	3.633476	1.464239
H	3.457752	3.616715	0.650951
C	-5.220909	1.163755	-1.089721
H	-5.329511	1.944205	-0.344762
C	-5.531063	-2.260236	1.236972
H	-6.184030	-1.669342	0.602130
C	2.098933	4.991288	-1.421208
H	1.534970	5.478505	-0.632421
C	-3.849800	-3.803758	2.852666
H	-3.194428	-4.404679	3.476019
C	2.252904	4.074657	3.794708
H	2.577267	4.395309	4.780593
C	3.159604	4.034462	2.735238
H	4.196637	4.318144	2.889804
C	-5.154417	-4.227730	2.593453
H	-5.516707	-5.159481	3.017792
C	3.121561	-2.577428	-2.688868
H	2.985938	-1.509674	-2.794621
C	-1.095269	-3.188276	-2.008872
H	-0.819622	-2.338063	-2.625472
C	3.203303	-3.401672	1.289510
H	3.878887	-3.335748	0.443677
C	2.905645	5.764567	-2.253861
H	2.956218	6.839468	-2.104561
C	3.412494	-5.350377	-2.521775
H	3.515531	-6.429746	-2.454151
C	-5.134687	0.874977	2.989429
H	-5.540427	-0.121968	3.126150
C	4.141724	-4.631067	-3.472503
H	4.816819	-5.149097	-4.147764
C	3.991602	-3.248328	-3.554825
H	4.542432	-2.680476	-4.299153
C	-2.522271	-5.108984	-1.614605
H	-3.355942	-5.739192	-1.911629
C	1.495104	-3.604703	3.484942
H	0.823407	-3.685772	4.335521
C	5.505861	-0.984750	5.205949
H	6.331208	-0.883768	5.919709
H	5.906714	-1.390838	4.273117
H	4.778036	-1.691144	5.618486
C	-5.993426	-3.456843	1.785489
H	-7.007055	-3.786350	1.577903
C	3.701902	-3.803002	2.531713
H	4.757904	-4.036205	2.632893
C	3.561079	3.781456	-3.461303
H	4.119414	3.301350	-4.259859
C	-5.540503	1.911949	3.832240
H	-6.260404	1.711768	4.620151
C	2.849386	-3.912601	3.630354
H	3.235414	-4.237579	4.592293
C	4.864857	0.373612	4.966722
H	4.476555	0.803920	5.892875
H	5.571181	1.069968	4.508914
C	-5.839310	1.300786	-2.334359
H	-6.430930	2.187038	-2.543583
C	-4.332986	-0.991907	-1.782033
H	-3.758435	-1.889094	-1.572329
C	-5.700606	0.304044	-3.301237
H	-6.181345	0.415299	-4.268676
C	-4.947356	-0.839983	-3.024483
H	-4.839336	-1.617237	-3.774942

5

CH_2I_2 E = -634.876560049 a.u.

C	0.000000	0.000000	1.057325
H	-0.899514	0.000000	1.664053
H	0.899514	0.000000	1.664053
I	0.000000	1.852908	-0.091246
I	0.000000	-1.852908	-0.091246

5

CH_2ICl E = -797.305246600 a.u.

C	0.811834	-1.095374	0.000000
H	1.403544	-1.196110	0.903987
H	1.403544	-1.196110	-0.903987
I	0.000000	0.940747	0.000000
Cl	-0.451652	-2.405594	0.000000

8

EtI E = -377.019220101 a.u.

C	2.451769	-0.434584	0.000070
C	1.446596	0.700086	0.000051
H	3.464377	-0.007336	0.000094
H	2.349107	-1.065492	0.887504
H	2.349149	-1.065485	-0.887374
H	1.503435	1.322976	0.891832
H	1.503490	1.322995	-0.891713
I	-0.652071	-0.039635	-0.000020

9

EtZnI E = -2156.55815840 a.u.

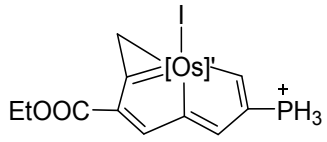
Zn	-0.888883	-0.245453	0.000046
C	-2.828293	-0.513087	-0.000081
C	-3.656381	0.781891	-0.000006

H	-3.060926	-1.125147	0.879834
H	-3.060858	-1.124992	-0.880121
H	-4.731606	0.556832	-0.000002
H	-3.454506	1.398116	0.883424
H	-3.454518	1.398187	-0.883389
I	1.572396	0.087694	-0.000012

15

$ZnEt_2$ E = -1937.91545370 a.u.

Zn	0.000003	0.000013	-0.050660
C	1.843934	0.677774	-0.050083
C	2.936905	-0.393235	0.129367
H	1.929264	1.432055	0.745130
H	2.007487	1.221055	-0.991696
H	3.944736	0.046069	0.121664
H	2.830274	-0.931722	1.079381
H	2.909447	-1.144024	-0.670256
C	-1.843919	-0.677770	-0.050091
C	-2.936931	0.393194	0.129370
H	-1.929222	-1.432065	0.745113
H	-2.007451	-1.221049	-0.991710
H	-3.944744	-0.046149	0.121659
H	-2.830322	0.931674	1.079391
H	-2.909499	1.143995	-0.670243

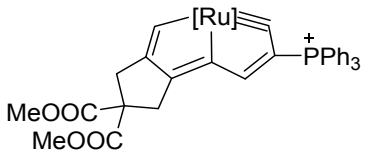


[Os]' = $Os(PH_3)_2$

37

2a'$^+$ E = -1707.11246024 a.u.

Os	0.436846	-0.083473	0.019833
I	2.772726	-1.763096	-0.088685
P	2.212242	4.284276	-0.089370
P	0.465853	-0.225052	-2.418025
P	0.697381	-0.216718	2.444964
O	-4.868637	0.419940	0.301557
O	-4.175599	-1.737378	0.290418
C	-0.825321	1.585504	0.078183
C	-2.566104	0.015781	0.175036
C	1.748327	1.506552	-0.049965
H	2.831896	1.400360	-0.104529
C	-0.241382	2.841582	0.043900
H	-0.804562	3.772179	0.068622
C	-3.945647	-0.553397	0.258661
C	-0.777685	-2.011678	0.082076
H	-0.762930	-2.603024	-0.829137
H	-0.667735	-2.604395	0.985749
C	-1.432037	-0.797249	0.116010
C	1.175185	2.769596	-0.027457
C	-2.223639	1.366946	0.152287
H	-2.964677	2.159491	0.189486
C	-6.862006	-0.237084	-0.984708
H	-7.926172	-0.465913	-0.882007
H	-6.381314	-1.085346	-1.474991
H	-6.765312	0.647008	-1.618974
C	-6.270328	0.010767	0.390358
H	-6.751943	0.848533	0.893322
H	-6.327804	-0.876282	1.020856
H	0.010986	-1.443226	-2.967540
H	-0.295223	0.697351	-3.174694
H	1.725301	-0.108010	-3.036619
H	0.303737	-1.437091	3.035783
H	0.002959	0.701915	3.267436
H	2.007620	-0.088886	2.944656
H	2.105853	5.138362	1.025289
H	3.567526	3.924227	-0.162730
H	1.982575	5.128769	-1.192626



[Ru] = $RuCl(PPh_3)_2$

134

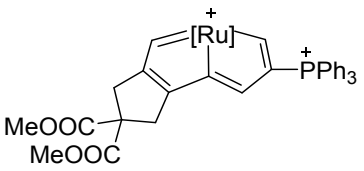
Temperature = 273.15 K

6$^+$ E = -4505.74797628 a.u.

C	-1.313282	-0.096887	-0.368954
C	-1.585553	-0.153909	0.997122
C	-0.380155	0.021343	1.724947
H	-0.313842	0.021463	2.813852
C	0.702097	0.172255	0.861697
C	2.031306	0.400428	1.221150
C	2.927294	0.461037	0.137840
C	2.327474	0.293879	-1.094434
H	2.924089	0.249716	-2.008566
C	2.742437	0.620078	2.530974
H	2.460220	-0.085013	3.316373
H	2.534681	1.635267	2.895033
C	4.257618	0.469088	2.157305
C	4.341273	0.711458	0.611433
H	4.648966	1.749726	0.441280
H	5.090775	0.072261	0.136034
C	4.729167	-0.955756	2.478322
C	6.616920	-2.374042	2.532286
H	6.443439	-2.668689	3.569961
H	7.683003	-2.269232	2.333485
H	6.170303	-3.115577	1.865348
C	5.100843	1.484559	2.936751
C	5.959615	2.005766	5.073508
H	5.488458	2.991372	5.101746
H	6.982405	2.106964	4.703005
H	5.950232	1.544937	6.060939

C	2.292202	-2.856318	-2.228191
C	3.100146	-3.838293	-1.641341
H	2.792539	-4.335306	-0.728608
C	4.314652	-4.195831	-2.234468
H	4.930509	-4.961475	-1.770246
C	4.727878	-3.584399	-3.417900
H	5.670256	-3.867182	-3.878843
C	3.917919	-2.613610	-4.011553
H	4.224752	-2.137888	-4.938993
C	2.706040	-2.248488	-3.423964
H	2.079278	-1.498806	-3.896625
C	-0.601344	-3.163172	-2.665461
C	-0.244570	-4.320471	-3.370477
H	0.752645	-4.736975	-3.270477
C	-1.168977	-4.942236	-4.211508
H	-0.881398	-5.836237	-4.757732
C	-2.453793	-4.414726	-4.352656
H	-3.170614	-4.896664	-5.011821
C	-2.810142	-3.262240	-3.650825
H	-3.805035	-2.840383	-3.762725
C	-1.887389	-2.633317	-2.812984
H	-2.159615	-1.724373	-2.288095
C	0.510916	-3.418831	0.051702
C	-0.396573	-4.481459	0.148499
H	-1.083636	-4.687855	-0.664800
C	-0.404221	-5.299778	1.282864
H	-1.102790	-6.130519	1.337980
C	0.495860	-5.068036	2.325106
H	0.507906	-5.724165	3.191878
C	1.394089	-4.000138	2.240539
H	2.107668	-3.803499	3.034856
C	1.396487	-3.178468	1.112731
H	2.115692	-2.370152	1.057437
C	-1.641599	3.177804	-1.701754
C	-2.428849	2.431213	-2.591106
H	-2.026809	1.527415	-3.038605
C	-3.708250	2.876003	-2.932177
H	-4.301641	2.304438	-3.641399
C	-4.215924	4.057460	-2.385286
H	-5.210566	4.401659	-2.655442
C	-3.431654	4.803858	-1.505147
H	-3.811272	5.731858	-1.086415
C	-2.145251	4.371805	-1.170300
H	-1.538644	4.974524	-0.502791
C	1.100385	3.427368	-2.732004
C	2.467080	3.155879	-2.879074
H	2.958407	2.452007	-2.217310
C	3.211081	3.784286	-3.877782
H	4.270324	3.563893	-3.976797
C	2.595139	4.682653	-4.750755
H	3.172226	5.166042	-5.533837
C	1.234047	4.952129	-4.613088
H	0.743434	5.646869	-5.288973
C	0.488890	4.331476	-3.607975
H	-0.568176	4.553521	-3.520412
C	1.838461	4.217751	0.268533
H	2.484001	4.286304	-0.599617
C	0.620800	3.532081	0.191866
C	-0.202884	3.483407	1.326302
H	-1.155802	2.965875	1.284506
C	0.184860	4.111874	2.509689
H	-0.473212	4.082240	3.374416
C	1.408352	4.783501	2.583833
H	1.709978	5.271985	3.506201
C	2.233293	4.832862	1.460487
H	3.184850	5.354819	1.502553
C	-3.918493	1.284624	2.340670
C	-3.146974	2.025560	3.247205
H	-2.168732	1.671341	3.559522
C	-3.641789	3.224530	3.758014
H	-3.047134	3.795319	4.465179
C	-4.900899	3.687696	3.364915
H	-5.283029	4.622747	3.763686
C	-5.667547	2.947846	2.464802
H	-6.647344	3.302911	2.159899
C	-5.181369	1.742516	1.951622
H	-5.783455	1.170406	1.254273
C	-3.205804	-1.488961	3.159147
C	-2.321334	-2.575061	3.149743
H	-1.642509	-2.733352	2.317705
C	-2.317090	-3.460905	4.228213
H	-1.626890	-4.298066	4.221489
C	-3.188122	-3.267772	5.302482
H	-3.177906	-3.959576	6.139761
C	-4.071770	-2.185864	5.304571
H	-4.749119	-2.033562	6.139490
C	-4.083317	-1.291606	4.234218
H	-4.765342	-0.447391	4.241928
C	-4.415460	-0.988269	0.432427
C	-5.138535	-2.160907	0.678139
H	-5.013929	-2.699619	1.611605
C	-6.024392	-2.638825	-0.289409
H	-6.585166	-3.549153	-0.100389
C	-6.188537	-1.947924	-1.490920
H	-6.882324	-2.319597	-2.239413
C	-5.464228	-0.776953	-1.731703
H	-5.590705	-0.236973	-2.665300
C	-4.573162	-0.291062	-0.774582
H	-4.012597	0.616594	-0.974893
Cl	0.191279	0.193233	-3.716300
P	0.625896	-2.358333	-1.497033
P	0.112745	2.599182	-1.360770
P	-3.256468	-0.335752	1.714560
Ru	0.302825	0.102407	-1.222063
O	6.051288	-1.072199	2.282538
O	4.012347	-1.872619	2.824297

O	5.207758	1.114064	4.226391
O	5.560758	2.507769	2.483143



[Ru] = $RuCl(PPh_3)_2$

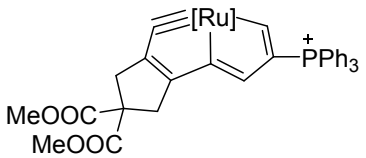
135

Temperature = 273.15 K

A2$^+$ E = -4506.19180472 a.u.

C	-1.419207	0.028551	-0.368699
C	-1.631816	-0.097465	0.979893
C	-0.405723	-0.112837	1.695012
H	-0.331735	-0.221294	2.775401
C	0.682698	0.006520	0.857633
C	2.018888	0.074968	1.289426
C	2.924449	0.126960	0.225271
C	2.241636	0.120345	-0.963937
H	2.677659	0.081653	-1.972493
C	2.722727	0.146030	2.609695
H	2.364952	-0.581730	3.345845
H	2.603296	1.139363	3.062565
C	4.238678	-0.049062	2.244941
C	4.356431	0.166358	0.688901
H	4.819582	1.132629	0.461659
H	4.971524	-0.612398	0.231794
C	4.622556	-1.492526	2.603115
C	5.401157	-2.904283	4.338202
H	4.520629	-3.550786	4.370641
H	5.801331	-2.751568	5.339296
H	6.153279	-3.340936	3.678607
C	1.975587	-2.760642	-2.694294
C	2.808255	-3.827654	-2.334879
H	2.575605	-4.449667	-1.478788
C	3.952494	-4.106085	-3.087721
H	4.590816	-4.936048	-2.799512
C	4.268297	-3.331942	-4.204179
H	5.156108	-3.554261	-4.788680
C	3.429991	-2.277353	-4.575024
H	3.656612	-1.682198	-5.455016
C	2.287984	-1.989095	-3.826299
H	1.628346	-1.187661	-4.144230
C	-0.985425	-3.007646	-2.803081
C	-0.711173	-3.759075	-3.951361
H	0.312254	-3.966171	-4.242079
C	-1.759897	-4.246174	-4.735046
H	-1.536481	-4.824714	-5.626397
C	-3.083614	-3.993438	-4.376090
H	-3.895995	-4.372781	-4.988790
C	-3.360303	-3.252379	-3.224751
H	-4.387788	-3.053517	-2.935126
C	-2.316483	-2.757551	-2.443521
H	-2.547142	-2.187170	-1.549065
C	0.451457	-3.525014	-0.254065
C	-0.517769	-4.523143	-0.089370
H	-1.327503	-4.625293	-0.803157
C	-0.426282	-5.420288	0.980003
H	-1.171427	-6.204166	1.084037
C	0.634370	-5.333512	1.883657
H	0.718473	-6.049322	2.696622
C	1.604411	-4.341066	1.718901
H	2.454559	-4.277553	2.390911
C	1.512271	-3.437370	0.660165
H	2.301128	-2.704982	0.531673
C	-1.371592	3.453615	-1.123606
C	-2.367722	2.997155	-2.001283
H	-2.153723	2.194660	-2.700594
C	-3.620487	3.613832	-2.018398
H	-4.374181	3.274326	-2.723908
C	-3.893580	4.681542	-1.158641
H	-4.865524	5.165794	-1.180957
C	-2.902671	5.139206	-0.289885
H	-3.098858	5.981266	0.367408
C	-1.642365	4.534559	-0.274741
H	-0.875798	4.924684	0.385213
C	1.069955	3.433184	-2.781610
C	2.229172	2.893263	-3.353988
H	2.703064	2.018717	-2.922061
C	2.796944	3.480309	-4.484750
H	3.695856	3.052941	-4.919310
C	2.206189	4.607805	-5.058919
H	2.643477	5.060720	-5.943563
C	1.052767	5.149599	-4.491470
H	0.589228	6.028175	-4.930139
C	0.485237	4.568724	-3.355245
H	-0.409091	5.005285	-2.925305
C	2.544173	4.084740	-0.083029
H	2.903391	4.195097	-1.100152
C	1.329142	3.436768	0.172166
C	0.873213	3.334869	1.495402
H	-0.076938	2.854168	1.705434
C	1.622628	3.869236	2.544057
H	1.256292	3.796306	3.564447
C	2.844495	4.497187	2.286173
H	3.432508	4.899595	3.104850
C	3.298496	4.606920	0.972104
H	4.237115	5.110274	0.759220
C	-3.753036	1.417534	2.565046
C	-2.772021	2.190303	3.200616
H	-1.731826	1.879637	3.196566
C	-3.136630	3.367791	3.852463
H	-2.377820	3.967539	4.345678
C	-4.474494	3.771199	3.874814
H	-4.755672	4.686894	4.386093

C	-5.450725	2.996771	3.245512
H	-6.491089	3.306371	3.265089
C	-5.096010	1.816457	2.589098
H	-5.860987	1.219901	2.103287
C	-3.196596	-1.487106	3.110585
C	-2.481386	-2.670962	2.877181
H	-1.953295	-2.833829	1.941904
C	-2.449421	-3.654428	3.865916
H	-1.891941	-4.568253	3.687592
C	-3.124020	-3.460146	5.074279
H	-3.094873	-4.228888	5.840620
C	-3.834619	-2.279382	5.300705
H	-4.357152	-2.126779	6.239912
C	-3.874189	-1.286815	4.320775
H	-4.423987	-0.369193	4.502911
C	-4.575333	-0.647032	0.538905
C	-5.197609	-1.900221	0.593358
H	-4.931561	-2.617555	1.362617
C	-6.180777	-2.219749	-0.346132
H	-6.673525	-3.185959	-0.297985
C	-6.536556	-1.296840	-1.331807
H	-7.308426	-1.545300	-2.054103
C	-5.910089	-0.047715	-1.383959
H	-6.191532	0.671960	-2.146550
C	-4.931046	0.286215	-0.448489
H	-4.468009	1.268550	-0.483849
Cl	-0.454856	0.338212	-3.557813
P	0.408814	-2.369100	-1.728991
P	0.336564	2.679692	-1.226488
P	-3.292983	-0.199467	1.790519
Ru	0.318585	0.131042	-1.282511
O	5.033531	-1.586144	3.869585
O	4.492814	-2.433144	1.845223
H	-2.208995	0.107973	-1.115936
C	5.112265	0.959335	3.005815
O	4.685835	1.815846	3.748915
O	6.399991	0.784464	2.691482
C	7.342545	1.663524	3.349103
H	7.283237	1.531159	4.431407
H	8.321455	1.367610	2.974902
H	7.127274	2.703914	3.095903

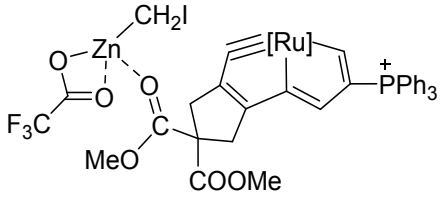


[Ru] = $RuCl(PPh_3)_2$

134
Temperature = 273.15 K
A3$^+$ E = -4505.74863959 a.u.

C	1.500647	0.071412	-0.493647
C	1.661932	-0.034449	0.868261
C	0.445793	-0.151784	1.620064
H	0.419270	-0.218335	2.707609
C	-0.673730	-0.149049	0.824928
C	-2.025642	-0.310122	1.242813
C	-2.927955	-0.259413	0.186741
C	-2.205676	-0.057969	-0.992067
C	-2.728043	-0.576724	2.548882
H	-2.454666	0.125696	3.341032
H	-2.497052	-1.590585	2.899174
C	-4.250326	-0.434633	2.188883
C	-4.349081	-0.489539	0.620332
H	-4.711913	-1.478757	0.321205
H	-5.057018	0.246439	0.228378
C	-4.777558	0.920581	2.684518
C	-6.721358	2.245422	2.902536
H	-6.562389	2.416407	3.969803
H	-7.781697	2.123643	2.684060
H	-6.302740	3.080011	2.334924
C	-5.060109	-1.564162	2.838669
C	-5.850312	-2.387868	4.905854
H	-5.378486	-3.365207	4.777670
H	-6.884780	-2.439765	4.558313
H	-5.808102	-2.072499	5.948031
C	-1.988713	3.206542	-2.177867
C	-2.642459	4.369830	-1.752123
H	-2.285235	4.917057	-0.886493
C	-3.764611	4.835949	-2.441856
H	-4.266901	5.737044	-2.100705
C	-4.232561	4.152854	-3.564942
H	-5.103341	4.518644	-4.102028
C	-3.572394	3.001490	-4.000020
H	-3.923794	2.470728	-4.880581
C	-2.456689	2.524238	-3.310233
H	-1.937056	1.639245	-3.662471
C	0.966355	3.362758	-2.228337
C	0.738229	4.154725	-3.357988
H	-0.271123	4.314958	-3.719375
C	1.811643	4.736176	-4.037023
H	1.620917	5.343855	-4.917041
C	3.118003	4.537745	-3.591668
H	3.950547	4.991078	-4.122435
C	3.350207	3.751920	-2.460647
H	4.363663	3.587886	-2.105032
C	2.280701	3.164255	-1.785719
H	2.474453	2.551559	-0.911193
C	-0.494443	3.518753	0.330735
C	0.366822	4.594322	0.586072
H	1.112812	4.884538	-0.145149
C	0.255524	5.319084	1.777735
H	0.919694	6.161296	1.954039
C	-0.717122	4.980841	2.720409
H	-0.812387	5.556439	3.637486
C	-1.581474	3.911541	2.470476

H	-2.352807	3.636221	3.182557
C	-1.469098	3.187430	1.283449
H	-2.162483	2.376309	1.096570
C	1.366615	-3.184702	-1.814485
C	2.295753	-2.556787	-2.658231
H	2.027987	-1.634145	-3.165258
C	3.548321	-3.136301	-2.871868
H	4.251095	-2.652272	-3.545392
C	3.888948	-4.338845	-2.246438
H	4.862290	-4.789805	-2.419877
C	2.963370	-4.968425	-1.414168
H	3.210951	-5.912326	-0.936200
C	1.704204	-4.398786	-1.202926
H	0.989609	-4.913217	-0.570105
C	-1.212762	-2.951543	-3.203706
C	-2.181864	-2.139307	-3.801815
H	-2.396899	-1.160890	-3.388551
C	-2.859613	-2.583866	-4.939291
H	-3.606776	-1.944652	-5.401323
C	-2.568856	-3.832644	-5.489327
H	-3.092547	-4.172393	-6.378489
C	-1.597401	-4.642293	-4.897139
H	-1.362191	-5.614306	-5.321600
C	-0.920808	-4.205279	-3.757925
H	-0.164776	-4.842368	-3.309631
C	-2.480704	-3.917562	-0.513564
H	-2.960666	-3.799812	-1.479421
C	-1.197347	-3.399518	-0.299833
C	-0.595480	-3.571025	0.954859
H	0.400239	-3.179148	1.134489
C	-1.259227	-4.261489	1.970579
H	-0.772594	-4.406238	2.932211
C	-2.543760	-4.766647	1.753568
H	-3.064726	-5.297976	2.544838
C	-3.153331	-4.588542	0.511429
H	-4.153796	-4.972025	0.335862
C	3.745307	-1.742751	2.357330
C	2.747610	-2.558872	2.905846
H	1.713533	-2.230159	2.918856
C	3.084904	-3.803324	3.437606
H	2.309818	-4.435810	3.860197
C	4.413450	-4.234830	3.425954
H	4.672747	-5.204865	3.839705
C	5.407641	-3.419375	2.883520
H	6.441688	-3.750762	2.873162
C	5.078464	-2.171907	2.349041
H	5.856409	-1.545425	1.925280
C	3.255390	1.092734	3.174225
C	2.488133	2.263297	3.102444
H	1.896932	2.490164	2.220253
C	2.478075	3.143700	4.185341
H	1.875839	4.044580	4.128394
C	3.225647	2.858875	5.330043
H	3.211185	3.545378	6.171615
C	3.988303	1.690586	5.397891
H	4.566932	1.465726	6.288848
C	4.005164	0.803087	4.321783
H	4.592733	-0.107553	4.381125
C	4.642336	0.480412	0.566608
C	5.317670	1.686288	0.788394
H	5.065966	2.309246	1.640299
C	6.326940	2.084217	-0.091313
H	6.855964	3.015911	0.085764
C	6.657234	1.284311	-1.186809
H	7.443704	1.594980	-1.868328
C	5.980115	0.081553	-1.406024
H	6.234632	-0.541433	-2.258014
C	4.973576	-0.327946	-0.531859
H	4.459276	-1.267845	-0.709820
Cl	0.400851	0.289478	-3.620402
P	-0.455935	2.569613	-1.294747
P	-0.335549	-2.400879	-1.637081
P	3.301977	-0.054957	1.721166
Ru	-0.403118	0.064131	-1.257340
O	-6.103132	1.006797	2.498787
O	-4.097365	1.813166	3.145810
O	-5.126733	-1.381189	4.170431
O	-5.532486	-2.515080	2.258464
H	2.359943	0.164513	-1.157236



[Ru] = $RuCl(PPh_3)_2$

146

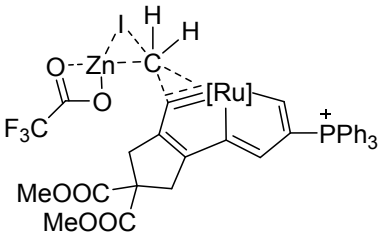
Temperature = 273.15 K

A4$^+$ E = -7148.64859189 a.u.

C	2.985810	-0.544852	0.400648
C	3.119517	-0.416887	-0.962780
C	1.993301	0.166240	-1.632364
H	1.947938	0.307854	-2.712211
C	0.980246	0.508842	-0.770124
C	-0.236466	1.173798	-1.095768
C	-1.044042	1.392375	0.013220
C	-0.393806	0.875217	1.137253
C	-0.843071	1.775827	-2.337637
H	-0.839523	1.105559	-3.204425
H	-0.314922	2.689814	-2.635291
C	-2.297481	2.173905	-1.888800
C	-2.295628	2.158595	-0.313405
H	-2.228787	3.183597	0.070938
H	-3.212561	1.724244	0.090343

C	-3.279356	1.143989	-2.444604
C	-1.284551	-2.363647	2.231502
C	-2.243507	-3.333677	1.905984
H	-2.081968	-4.008642	1.071702
C	-3.416861	-3.439775	2.656167
H	-4.158776	-4.188991	2.394378
C	-3.635788	-2.585634	3.739472
H	-4.550949	-2.667262	4.318790
C	-2.672153	-1.634296	4.077712
H	-2.830249	-0.976408	4.927668
C	-1.498831	-1.519577	3.328453
H	-0.745002	-0.792194	3.606863
C	1.427402	-3.531915	2.000420
C	1.039030	-4.231342	3.147552
H	0.084001	-4.024538	3.616504
C	1.885714	-5.192009	3.705066
H	1.574336	-5.723525	4.599738
C	3.122418	-5.465241	3.121559
H	3.778408	-6.213404	3.557668
C	3.514533	-4.769591	1.975882
H	4.477802	-4.969864	1.515126
C	2.674171	-3.803943	1.421839
H	2.994504	-3.263870	0.536567
C	-0.197041	-2.964808	-0.411322
C	0.258171	-4.212238	-0.855079
H	0.952009	-4.787038	-0.251889
C	-0.200141	-4.741998	-2.067175
H	0.147486	-5.720612	-2.387924
C	-1.118644	-4.034156	-2.842838
H	-1.486177	-4.454250	-3.775192
C	-1.580361	-2.791191	-2.400168
H	-2.310240	-2.237497	-2.983903
C	-1.123323	-2.259740	-1.194477
H	-1.509936	-1.305823	-0.853344
C	4.097906	2.442087	1.860818
C	4.779601	1.485199	2.628760
H	4.222153	0.701652	3.133927
C	6.166875	1.561220	2.768449
H	6.681188	0.829058	3.385867
C	6.887002	2.582178	2.141570
H	7.965679	2.642585	2.258311
C	6.210198	3.536076	1.381398
H	6.758302	4.342769	0.902347
C	4.820015	3.472334	1.245704
H	4.307985	4.236102	0.670917
C	1.701931	3.021293	3.459946
C	0.505221	2.611327	4.057467
H	-0.103271	1.850318	3.582882
C	0.102819	3.171618	5.271564
H	-0.825400	2.844108	5.731289
C	0.894950	4.133682	5.899533
H	0.583399	4.562123	6.847992
C	2.092536	4.539793	5.307893
H	2.716400	5.285975	5.791896
C	2.496223	3.987683	4.091425
H	3.429503	4.311529	3.641844
C	0.770062	4.668030	0.990643
H	0.388900	4.681213	2.006090
C	1.698592	3.694651	0.601733
C	2.185567	3.706773	-0.713296
H	2.909678	2.961701	-1.025933
C	1.755239	4.677046	-1.619475
H	2.147073	4.682593	-2.633490
C	0.817509	5.636752	-1.229921
H	0.469936	6.379533	-1.941150
C	0.329685	5.630000	0.076774
H	-0.391071	6.378567	0.393989
C	5.608315	0.566089	-2.483954
C	4.937954	1.714476	-2.924676
H	3.854615	1.766663	-2.891158
C	5.667391	2.799957	-3.409212
H	5.145885	3.690280	-3.747780
C	7.062289	2.742317	-3.457646
H	7.627664	3.589371	-3.834770
C	7.729470	1.596566	-3.021779
H	8.813678	1.547976	-3.057555
C	7.006659	0.505292	-2.535251
H	7.532962	-0.380178	-2.194449
C	4.123568	-1.859855	-3.414777
C	2.999611	-2.694192	-3.350061
H	2.408823	-2.762007	-2.441575
C	2.632051	-3.439704	-4.470979
H	1.755983	-4.078368	-4.418378
C	3.379548	-3.354158	-5.647631
H	3.088391	-3.933932	-6.518715
C	4.499346	-2.521381	-5.708377
H	5.079597	-2.450888	-6.623498
C	4.874759	-1.770651	-4.593894
H	5.741103	-1.119003	-4.648223
C	5.745985	-1.950335	-0.872155
C	5.955086	-3.295088	-1.200196
H	5.470959	-3.731833	-2.067407
C	6.799655	-4.075272	-0.407160
H	6.968963	-5.116023	-0.666892
C	7.427408	-3.516991	0.707970
H	8.084579	-4.125594	1.322134
C	7.215273	-2.174521	1.033036
H	7.701962	-1.738569	1.900108
C	6.378363	-1.384422	0.245539
H	6.227242	-0.340656	0.504372
Cl	2.017466	-0.554144	3.575065
P	0.309736	-2.227990	1.246334
P	2.220406	2.337511	1.790020
P	4.630709	-0.905059	-1.910992
Ru	1.249330	0.093111	1.283449
O	-3.685586	0.166880	-1.818805

H	3.783711	-0.973417	1.007036
Zn	-5.486874	-0.562962	-0.736056
C	-5.562988	-2.504684	-0.631399
H	-5.715597	-2.999490	-1.590725
H	-4.702588	-2.946614	-0.129793
I	-7.306537	-3.141602	0.592585
O	-6.632326	1.053051	-1.589140
C	-6.348802	1.675439	-0.533615
O	-5.618255	1.180330	0.374931
C	-6.927852	3.082583	-0.297181
F	-5.992259	3.897462	0.221479
F	-7.953644	3.007378	0.562716
F	-7.368680	3.630590	-1.441935
O	-3.589093	1.382657	-3.708429
C	-4.555616	0.512093	-4.349166
H	-5.520744	0.616602	-3.850002
H	-4.609660	0.861924	-5.378831
H	-4.213678	-0.524351	-4.309451
C	-2.683364	3.571128	-2.400885
O	-1.932566	4.345720	-2.948675
O	-3.964938	3.828709	-2.100254
C	-4.465663	5.127425	-2.491337
H	-4.335929	5.269916	-3.566270
H	-5.518467	5.119567	-2.220184
H	-3.929300	5.911679	-1.952218



[Ru] = $RuCl(PPh_3)_2$

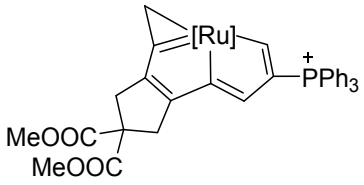
146

Temperature = 273.15 K

TSA4$^+$ E = -7148.61844020 a.u.

C	-2.630335	-0.642141	0.104748
C	-3.126453	0.594991	-0.231076
C	-2.125851	1.590891	-0.459557
H	-2.352138	2.625652	-0.714630
C	-0.850008	1.103570	-0.307963
C	0.350583	1.829068	-0.517749
C	1.489280	1.071200	-0.273050
C	1.109169	-0.220096	0.102232
C	0.691287	3.217944	-0.986124
H	0.153878	4.000867	-0.438923
H	0.455433	3.352833	-2.048355
C	2.248496	3.312970	-0.795914
C	2.755022	1.855464	-0.484220
H	3.341583	1.463445	-1.320989
H	3.396769	1.867831	0.401385
C	2.530534	4.235355	0.397856
C	0.996555	-0.973325	3.537105
C	1.885738	-0.063362	4.117991
H	1.656340	0.994944	4.154221
C	3.085452	-0.515109	4.679087
H	3.767971	0.202378	5.125790
C	3.397603	-1.874350	4.675444
H	4.327609	-2.223181	5.114711
C	2.503830	-2.786503	4.107119
H	2.736781	-3.847291	4.101396
C	1.310811	-2.342516	3.535170
H	0.627277	-3.057369	3.087466
C	-1.875096	-1.389928	3.827912
C	-1.537455	-1.709860	5.150777
H	-0.557023	-1.460602	5.541479
C	-2.458824	-2.354087	5.977943
H	-2.180678	-2.600138	6.998810
C	-3.726792	-2.681971	5.495894
H	-4.440440	-3.189645	6.138777
C	-4.070917	-2.355996	4.183585
H	-5.053060	-2.609466	3.795013
C	-3.149519	-1.714158	3.354118
H	-3.426618	-1.475618	2.336454
C	-0.903621	1.321791	3.331258
C	-1.948046	1.651386	4.206442
H	-2.629042	0.884838	4.558130
C	-2.105295	2.965843	4.657178
H	-2.907471	3.198993	5.352782
C	-1.219943	3.963014	4.244978
H	-1.328881	4.978752	4.615545
C	-0.180272	3.641740	3.369777
H	0.536094	4.393978	3.055340
C	-0.028866	2.333290	2.907724
H	0.795063	2.109803	2.240607
C	-2.161682	-2.282204	-2.873700
C	-2.903021	-3.213208	-2.130458
H	-2.561883	-3.515856	-1.144223
C	-4.057432	-3.782228	-2.672980
H	-4.607549	-4.522857	-2.097896
C	-4.488631	-3.424251	-3.953147
H	-5.383528	-3.873191	-4.375235
C	-3.748331	-2.504686	-4.695823
H	-4.063473	-2.232631	-5.699468
C	-2.584034	-1.942276	-4.164361
H	-2.006977	-1.253741	-4.771245
C	0.565559	-3.160028	-2.585561
C	1.103390	-4.010506	-1.615598
H	0.900090	-3.838374	-0.566451
C	1.866029	-5.118414	-2.002154
H	2.280424	-5.770309	-1.238963
C	2.087981	-5.385260	-3.351827
H	2.681906	-6.245125	-3.648064
C	1.536188	-4.546057	-4.323939

H	1.695450	-4.751591	-5.378784
C	0.774346	-3.442297	-3.945104
H	0.347651	-2.803096	-4.711987
C	1.463055	-0.306333	-3.627271
H	2.133168	-1.095184	-3.302024
C	0.105887	-0.344716	-3.278803
C	-0.734031	0.689087	-3.715576
H	-1.784570	0.683404	-3.445326
C	-0.232345	1.724565	-4.506756
H	-0.897312	2.512918	-4.850054
C	1.119876	1.754309	-4.853632
H	1.511831	2.569588	-5.452890
C	1.965117	0.736901	-4.408984
H	3.019083	0.746545	-4.672362
C	-5.450016	1.133137	-2.173298
C	-4.580181	1.721090	-3.100329
H	-3.589011	2.042753	-2.797140
C	-4.990693	1.894730	-4.421788
H	-4.314607	2.348962	-5.139988
C	-6.266215	1.486239	-4.819129
H	-6.583345	1.622770	-5.848766
C	-7.133638	0.903869	-3.893665
H	-8.125727	0.585232	-4.199148
C	-6.730371	0.725678	-2.568605
H	-7.408496	0.267408	-1.856209
C	-5.271718	2.603166	0.425768
C	-4.552823	2.960866	1.574252
H	-3.775410	2.314714	1.970836
C	-4.835573	4.170070	2.211011
H	-4.269912	4.447683	3.094651
C	-5.827134	5.015024	1.707811
H	-6.041172	5.956563	2.205137
C	-6.541578	4.654481	0.563050
H	-7.309988	5.312031	0.167803
C	-6.265986	3.449092	-0.082930
H	-6.816881	3.177141	-0.977661
C	-5.949656	-0.338045	0.391019
C	-6.651831	-0.065614	1.570772
H	-6.608759	0.920203	2.021576
C	-7.416121	-1.071229	2.166240
H	-7.965982	-0.857740	3.077870
C	-7.476899	-2.340758	1.588447
H	-8.075525	-3.119814	2.051362
C	-6.772638	-2.609823	0.411465
H	-6.818465	-3.596615	-0.039122
C	-6.008951	-1.612133	-0.194247
H	-5.472214	-1.831477	-1.112552
Cl	-1.029773	-3.289834	0.970693
P	-0.640559	-0.452458	2.760382
P	-0.529276	-1.689839	-2.135851
P	-4.925542	0.981806	-0.399940
Ru	-0.612697	-0.916733	0.265593
O	2.628464	3.861040	1.548236
H	-3.295789	-1.487373	0.270860
Zn	4.626647	-0.723280	0.269656
C	3.004141	-1.775617	0.397353
H	2.557864	-2.058894	1.344031
H	2.602456	-2.316859	-0.451380
I	5.043271	-3.431631	0.659627
O	5.859143	0.749202	0.910753
C	6.204872	0.967741	-0.292117
O	5.733914	0.308080	-1.251381
C	7.224124	2.093029	-0.543962
F	7.466591	2.249660	-1.853799
F	8.378091	1.815731	0.075959
F	6.744194	3.255262	-0.065090
O	2.584313	5.519625	0.017042
C	2.826534	6.486322	1.059808
H	3.737245	6.232669	1.606293
H	2.933092	7.442023	0.547881
H	1.981974	6.515321	1.753268
C	2.934319	3.873297	-2.049578
O	2.369371	4.236854	-3.057325
O	4.265183	3.874513	-1.878035
C	5.051002	4.386245	-2.975076
H	4.823610	5.442688	-3.136330
H	6.086707	4.249210	-2.672318
H	4.836544	3.824941	-3.887279



[Ru] = $RuCl(PPh_3)_2$

137
Temperature = 273.15 K
7$^+$ E = -4545.07942884 a.u.

Ru	0.371020	-0.073834	-1.318194
P	0.116058	2.421654	-1.663291
Cl	-0.816275	-0.510928	-3.576327
P	0.449522	-2.618080	-1.274621
P	-3.117480	0.011143	1.891344
C	-1.541586	0.025967	0.920125
C	-0.290924	0.180104	1.581030
H	-0.191493	0.269990	2.663133
C	-1.459750	-0.108209	-0.461955
H	-2.370736	-0.218758	-1.049421
C	0.713574	-3.517855	0.364617
C	0.845376	2.499675	-4.410242
H	0.390034	1.514022	-4.447339
C	2.316050	0.021749	-2.565439
H	2.543075	-0.916384	-3.062768
H	2.328001	0.900229	-3.205513
C	0.919834	3.192555	-3.193607

C	-1.072518	-3.513776	-1.941838
C	-3.556743	1.675523	2.595735
C	-4.539097	-0.531729	0.841356
C	-2.040999	-3.190553	4.254709
H	-1.413109	-4.069224	4.148184
C	0.841170	3.390761	-0.228424
C	4.448278	0.604682	0.415988
H	4.803671	1.586863	0.086788
H	5.156282	-0.134778	0.030791
C	2.794618	4.286928	0.914570
H	3.865893	4.459198	0.935596
C	2.395625	0.141324	-1.207231
C	-2.597204	2.330893	-2.522292
H	-2.356849	1.320607	-2.838689
C	3.021081	0.347221	0.001791
C	2.855158	0.681575	2.367841
H	2.622202	-0.021418	3.172552
H	2.600989	1.689373	2.719082
C	-1.628661	3.112436	-1.879712
C	-2.943036	-1.152498	3.322839
C	1.829859	-3.309732	-2.355046
C	2.132740	0.383910	1.079999
C	2.221446	3.634308	-0.179705
H	2.857376	3.329824	-1.004911
C	1.957365	5.061404	-4.339088
H	2.380483	6.061647	-4.305325
O	6.294032	-0.770445	2.278190
C	-2.143868	-2.295610	3.188530
H	-1.598797	-2.490218	2.269957
C	0.785069	0.185690	0.708462
C	-0.028707	-4.660461	0.696528
H	-0.799958	-5.024559	0.028066
C	4.974414	-0.724616	2.516064
O	5.579100	2.718845	1.982140
C	-2.339356	-3.187851	-1.443919
H	-2.447083	-2.394185	-0.715030
O	4.351280	-1.616902	3.051511
O	5.255882	1.614675	3.925187
C	1.900517	4.362728	-5.546014
H	2.284694	4.814790	-6.456155
C	1.717833	-3.086645	1.243246
H	2.313060	-2.213596	1.004070
C	1.338004	3.086227	-5.578536
H	1.275705	2.539351	-6.515268
C	1.463366	4.484188	-3.167500
H	1.501813	5.050633	-2.243658
C	5.153822	1.763362	2.592570
C	0.230740	-5.353518	1.882664
H	-0.344990	-6.245496	2.116132
C	-3.851777	2.874381	-2.816996
H	-4.584264	2.265700	-3.341436
C	-6.016209	-0.139378	-1.030802
H	-6.318296	0.471358	-1.876048
C	-5.228713	-1.711141	1.146290
H	-4.927856	-2.321803	1.990985
C	-6.708391	-1.314973	-0.728119
H	-7.554347	-1.618025	-1.338058
C	-4.152887	4.192425	-2.470956
H	-5.127256	4.612375	-2.705289
C	-4.933692	0.259958	-0.247747
H	-4.410301	1.180206	-0.488938
C	-3.182901	4.977815	-1.845427
H	-3.397267	6.012092	-1.590513
C	-3.472846	-3.878420	-1.871490
H	-4.446787	-3.604117	-1.476530
C	5.956811	2.663317	4.623714
H	6.980076	2.747455	4.250478
H	5.950602	2.367388	5.672346
H	5.444345	3.618889	4.488140
C	3.846712	-4.295833	-4.038911
H	4.626602	-4.680022	-4.690378
C	2.889326	-4.054485	-1.826093
H	2.935343	-4.270157	-0.764397
C	-6.315798	-2.098105	0.358939
H	-6.855270	-3.009041	0.600765
C	1.784648	-3.059951	-3.737620
H	0.966568	-2.477151	-4.153126
C	2.787409	-3.556573	-4.571843
H	2.739070	-3.361823	-5.639651
C	-2.729961	-2.947459	5.444768
H	-2.644286	-3.644705	6.273178
C	1.992927	4.698970	1.980974
H	2.434130	5.220024	2.826206
C	-0.959495	-4.560953	-2.863900
H	0.008778	-4.850427	-3.253185
C	0.048841	3.786666	0.857730
H	-1.019226	3.597988	0.851559
C	4.377245	0.587219	1.984568
C	0.620661	4.443540	1.949680
H	-0.012856	4.767922	2.771114
C	3.895311	-4.541079	-2.666974
H	4.711146	-5.121209	-2.244383
C	-1.923603	4.446256	-1.562408
H	-1.174447	5.083449	-1.104608
C	1.236470	-4.918409	2.747703
H	1.446791	-5.467533	3.661792
C	-2.554144	2.476061	3.158581
H	-1.515329	2.164197	3.128871
C	1.981254	-3.781635	2.425628
H	2.772569	-3.428095	3.078127
C	-2.096217	-5.248596	-3.297041
H	-1.989187	-6.053618	-4.018716
C	6.978192	-1.959091	2.723518
H	6.869172	-2.074870	3.804391
H	8.023048	-1.809214	2.453919
H	6.571965	-2.840608	2.221650

C	-3.355849	-4.908181	-2.806751
H	-4.238429	-5.442676	-3.147000
C	-3.525965	-1.806862	5.574832
H	-4.059241	-1.614545	6.501049
C	-3.634808	-0.905139	4.516084
H	-4.248497	-0.016417	4.623877
C	-5.222041	3.311530	3.232545
H	-6.258929	3.633016	3.257887
C	-4.893163	2.092470	2.635600
H	-5.675213	1.477621	2.203220
C	-4.224459	4.109423	3.793639
H	-4.483249	5.055639	4.259554
C	-2.892515	3.689631	3.757447
H	-2.115123	4.305807	4.199563

7
Temperature = 273.15 K
CF_3COO^- E = -526.420939699 a.u.

C	-1.066804	0.009776	-0.000022
O	-1.592252	1.139976	-0.000042
O	-1.532909	-1.147993	-0.000096
C	0.513669	0.013435	0.000024
F	1.080968	1.250871	-0.000025
F	1.032822	-0.629553	1.089004
F	1.032887	-0.629666	-1.088858

8
Temperature = 273.15 K
CF_3COOH E = -526.884339105 a.u.

C	-0.934653	0.160088	-0.000050
O	-1.498219	1.222252	-0.000067
O	-1.521575	-1.046192	-0.000039
H	-2.486281	-0.894765	-0.000062
C	0.601048	-0.000919	0.000019
F	1.188283	1.196239	0.000002
F	0.997271	-0.679678	1.090394
F	0.997364	-0.679753	-1.090274

9
Temperature = 273.15 K
$CF_3COOZnI$ E = -2603.64237173 a.u.

Zn	0.394077	-0.005083	-0.000036
O	-1.356200	-1.083006	-0.000021
C	-1.963015	0.026816	-0.000002
O	-1.346214	1.126739	-0.000023
C	-3.508295	0.005300	0.000082
F	-4.027225	1.245846	-0.000427
F	-3.960631	-0.644707	1.096369
F	-3.960791	-0.645671	-1.095558
I	2.833258	0.000202	-0.000048

5
Temperature = 273.15 K
CH_2I_2 E = -634.876560049 a.u.

C	0.000000	0.000000	1.057325
H	-0.899514	0.000000	1.664053
H	0.899514	0.000000	1.664053
I	0.000000	1.852908	-0.091246
I	0.000000	-1.852908	-0.091246

8
Temperature = 273.15 K
Ethane E = -79.8349434909 a.u.

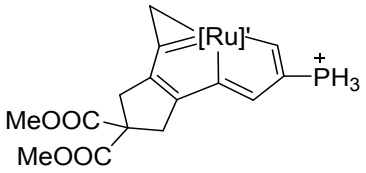
C	-0.765067	0.000001	-0.000005
C	0.765067	-0.000001	0.000005
H	-1.164334	-0.963801	-0.336678
H	-1.164264	0.190321	1.003025
H	-1.164292	0.773515	-0.666291
H	1.164332	0.963809	0.336655
H	1.164293	-0.773499	0.666310
H	1.164265	-0.190344	-1.003020

8
Temperature = 273.15 K
EtI E = -377.019220101 a.u.

C	2.451769	-0.434584	0.000070
C	1.446596	0.700086	0.000051
H	3.464377	-0.007336	0.000094
H	2.349107	-1.065492	0.887504
H	2.349149	-1.065485	-0.887374
H	1.503435	1.322976	0.891832
H	1.503490	1.322995	-0.891713
I	-0.652071	-0.039635	-0.000020

15
Temperature = 273.15 K
$ZnEt_2$ E = -1937.91545370 a.u.

Zn	-0.000003	-0.000013	-0.050660
C	-1.843934	-0.677774	-0.050083
C	-2.936905	0.393235	0.129367
H	-1.929264	-1.432055	0.745130
H	-2.007487	-1.221055	-0.991696
H	-3.944736	-0.046069	0.121664
H	-2.830274	0.931722	1.079381
H	-2.909447	1.144024	-0.670256
C	1.843919	0.677770	-0.050091
C	2.936931	-0.393194	0.129370
H	1.929222	1.432065	0.745113
H	2.007451	1.221049	-0.991710
H	3.944744	0.046149	0.121659
H	2.830322	-0.931674	1.079391
H	2.909499	-1.143995	-0.670243



[Ru]' = $RuCl(PH_3)_2$

47

7'$^+$ E = -2465.44100759 a.u.

Ru	-2.007989	-0.602401	-0.145629
P	-2.517231	-0.312272	-2.492688
Cl	-4.225020	-1.833364	-0.051668
P	-1.871268	-1.060537	2.223851
P	-3.229135	3.819700	0.798175
C	-2.387963	2.234820	0.393004
C	-0.975796	2.170965	0.202318
H	-0.318021	3.034888	0.280877
C	-3.097888	1.056478	0.276223
H	-4.179023	1.025223	0.412508
C	-1.096889	-2.640676	-0.593501
H	-1.198694	-3.329409	0.239642
H	-1.423612	-3.043838	-1.547177
C	2.373369	-1.259469	-0.787868
H	2.586771	-1.406869	-1.850269
H	2.678360	-2.169761	-0.271036
C	-0.260632	-1.560520	-0.525853
C	0.933875	-0.876153	-0.555026
C	2.120686	1.183224	-0.345408
H	2.271358	1.888248	0.472111
H	2.226868	1.732334	-1.288482
C	0.788983	0.488910	-0.307459
O	4.567014	-1.113351	1.250927
C	-0.551019	0.889427	-0.082177
C	3.572001	-0.223225	1.181096
O	4.614188	-0.217900	-2.208241
O	3.047290	0.294783	2.136393
O	5.113639	1.276293	-0.595952
C	4.375621	0.304716	-1.150631
C	6.303393	1.673966	-1.319713
H	6.977559	0.823986	-1.423000
H	6.757120	2.456590	-0.717422
H	6.035073	2.049415	-2.307139
C	3.149327	0.003141	-0.280095
C	5.063954	-1.432706	2.572107
H	5.443054	-0.532448	3.055366
H	5.863115	-2.151298	2.411264
H	4.268861	-1.866902	3.178389
H	-3.107620	-1.084889	2.899743
H	-1.350162	-2.318978	2.603200
H	-1.113209	-0.222690	3.074925
H	-3.885615	-0.151009	-2.788455
H	-2.198511	-1.388226	-3.353042
H	-1.958787	0.755380	-3.235341
H	-4.608491	3.598179	0.939297
H	-2.820701	4.434922	1.997681
H	-3.107480	4.840598	-0.164810

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