

Fused Metallacyclopropenes from Alkynylphenols

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supporting Information

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1. Experimental details

General information. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques unless otherwise stated. Solvents were purged with a nitrogen flow before use. $\text{OsCl}_2(\text{PPh}_3)_3$,¹ 2-ethynylphenol,² 2-ethynyl-4-methylphenol,² 2-ethynyl-4-fluorophenol,³ 2-(1-hexyn-1-yl)phenol,⁴ 2-(1-octyn-1-yl)phenol⁵ were prepared according to literature methods. Other reagents were used as purchased. ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ spectra were collected on a Bruker Avance II (400 MHz) or a Bruker Avance III (500 MHz). ^1H and ^{13}C NMR shifts are relative to TMS, and ^{31}P chemical shifts relative to 85% H_3PO_4 . Electron spin resonance (EPR) spectrum was collected on a Bruker E500. A Synapt G2-Si was used to measure high-resolution mass (HRMS). Element Vario EL cube elemental analyzer was used for elemental analyses (EA).

Synthesis of complex 1a. A mixture of 2-ethynylphenol (0.019 g, 0.161 mmol) and $\text{OsCl}_2(\text{PPh}_3)_3$ (0.100 g, 0.095 mmol) in toluene (5 mL) was stirred at room temperature for 4 h, producing a dark green solution. The volume was concentrated to about 1 mL and *n*-hexane (10 mL) was added to precipitate a yellowish-green solid, which was filtered and washed with ether (5 mL \times 2). The resulting yellowish-green solid was further purified by column chromatography (eluent: DCM). The green band was collected and dried under vacuum. Yield: 40.2 mg, 46.6 %. $^{31}\text{P}\{^1\text{H}\}$ NMR (162.0 MHz, CD_2Cl_2): $\delta = -15.4$. ^1H NMR (400.1 MHz, CD_2Cl_2): $\delta = 7.57$ -7.53 (m, 12H, Ph), 7.35-7.24 (m, 18H, Ph), 7.02 (d, $J = 8.2$ Hz, 1H, Ph), 6.81 (t, $J = 7.8$ Hz, 1H, Ph), 6.55 (t, $J = 7.4$ Hz, 1H, Ph), 6.33 (d, $J = 8.9$ Hz, 1H, Ph), 4.19 (t, $J = 3.8$ Hz, 2H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.0 MHz, CD_2Cl_2): $\delta = 266.6$ (t, $^1J(\text{PC}) = 3.8$ Hz, Os=C), 191.9 (s, C-O), 137.6-117.7 (multiple ^{13}C signals of Ar), 37.7 (CH_2). Anal. Calcd. For $\text{C}_{44}\text{H}_{36}\text{Cl}_2\text{OOsP}_2$: C, 58.47; H, 4.01. Found: C, 58.57; H, 4.11.

Synthesis of complex 1b. A mixture of 4-methyl-2-ethynylphenol (0.0378 g, 0.286 mmol) and $\text{OsCl}_2(\text{PPh}_3)_3$ (0.200 g, 0.191 mmol) in toluene (10 mL) was stirred at room temperature for 4 h, producing a dark green solution. The volume was concentrated to about 1 mL and *n*-hexane (10 mL) was added to it to precipitate a green solid, which was filtered and washed with ether (5 mL \times 3). The resulting green solid was further purified by column chromatography (eluent: DCM). The green band was collected and dried under vacuum. Yield: 73.3 mg, 41.8 %. $^{31}\text{P}\{^1\text{H}\}$ NMR (162.0 MHz, CD_2Cl_2): $\delta = -15.2$. ^1H NMR (400.1 MHz, CD_2Cl_2): $\delta = 7.54$ -7.24 (m, 30H, Ph), 6.77 (s, 1H, Ph), 6.69 (d, $J = 8.8$ Hz, 1H, Ph), 6.22 (d, $J = 9.0$ Hz, 1H, Ph), 4.15 (s, 2H, CH_2), 2.22 (s, 3H, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.0 MHz, CD_2Cl_2): $\delta = 264.1$ (t, $^1J(\text{PC}) = 6.3$ Hz, Os=C), 191.4 (s, C-O), 140.0-120.0 (multiple ^{13}C signals of Ar), 37.5 (CH_2), 20.5 (s, Me). Anal. Calcd. For $\text{C}_{45}\text{H}_{38}\text{Cl}_2\text{OOsP}_2 \cdot 0.35\text{CH}_2\text{Cl}_2$: C, 57.48; H, 4.12. Found: C, 57.23; H, 4.48.

Synthesis of complex 1c. A mixture of 4-fluoro-2-ethynylphenol (0.0584 g, 0.429 mmol) and $\text{OsCl}_2(\text{PPh}_3)_3$ (0.300 g, 0.286 mmol) in toluene (15 mL) was stirred at room temperature for 4 h, producing a dark green solution. The volume was concentrated to about 1 mL and *n*-hexane (10 mL) was added to precipitate a yellowish-green solid, which was washed ether (5 mL \times 3). The resulting yellowish-green solid was further purified by column chromatography (eluent: DCM). The green band was collected and dried under vacuum. Yield: 142.2 mg, 53.9 %. $^{31}\text{P}\{^1\text{H}\}$ NMR (162.0 MHz, CD_2Cl_2): $\delta = -15.6$. ^1H NMR (400.1 MHz, CD_2Cl_2): $\delta = 7.56$ -7.51 (m, 12H, PPh_3), 7.35-7.24 (m, 18H, PPh_3), 6.74-6.67 (m, 2H, Ph), 6.25 (dd, $J = 9.2$ Hz, 1H, Ph), 4.27 (t, $J = 3.7$ Hz, 2H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.0 MHz, CD_2Cl_2): $\delta = 264.1$ (m, Os=C), 188.8 (s, C-O), 156.0-107.6 (multiple ^{13}C signals of Ar), 38.1 (CH_2). Anal. Calcd. For $\text{C}_{45}\text{H}_{35}\text{Cl}_2\text{FOOsP}_2 \cdot 0.45\text{CH}_2\text{Cl}_2$: C, 55.61; H, 3.77. Found: C, 55.32; H, 3.96.

Synthesis of complex 2a. A mixture of 2-(1-hexyn-1-yl)phenol (0.0499 g, 0.287 mmol) and $\text{OsCl}_2(\text{PPh}_3)_3$ (0.200 g, 0.191 mmol) in toluene (10 mL) was stirred at room temperature for 24 h, producing a dark green solution. The volume was concentrated to about 1 mL and *n*-hexane (10 mL) was added to precipitate a dark green solid, which was washed with ether (5 mL \times 3) and dried under vacuum. Yield: 84.6 mg, 47.9 %. HRMS (ESI, *m/z*): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{48}\text{H}_{43}\text{Cl}_2\text{OOsP}_2\text{Na}$, 982.1655; found, 982.1642.

Synthesis of complex 2b. A mixture of 2-(1-octyn-1-yl)phenol (0.087 g, 0.429 mmol) and $\text{OsCl}_2(\text{PPh}_3)_3$ (0.300 g, 0.286 mmol) in toluene (15 mL) was stirred at room temperature for 24 h, producing a dark green solution. The volume was concentrated to about 1 mL and *n*-hexane (10 mL) was added to precipitate a dark green solid, which was washed with ether (5 mL \times 3) and dried under vacuum. Yield: 148.3 mg, 52.4 %. HRMS (ESI, *m/z*): $[\text{M}-\text{Cl}]^+$ calcd for $\text{C}_{50}\text{H}_{48}\text{ClOOsP}_2$, 952.2390; found, 952.2403.

Synthesis of complex 3a. Complex **2a** (0.100 g, 0.104 mmol) in DCM (10 mL) was stirred at room temperature under air for 2 h, producing a yellowish-brown solution. The volume was concentrated to about 1 mL and *n*-hexane (10 mL) was added to it to precipitate a yellowish-brown solid, which was washed with ether (5 mL \times 3). The resulting yellowish-brown solid was further purified by column chromatography (eluent: DCM). The green band was collected and dried under vacuum. Yield: 82.6 mg, 82.6 %. $^{31}\text{P}\{^1\text{H}\}$ NMR (162.0 MHz, CDCl_3): $\delta = -15.4$. ^1H NMR (400.1 MHz, CDCl_3): $\delta = 7.50$ -7.48 (m, 12H, Ph), 7.26-7.16 (m, 18H, Ph), 7.01 (d, $J = 8.2$ Hz, 1H), 6.77 (t, $J = 7.7$ Hz, 1H, Ph), 6.57-6.51 (m, 2H, Ph), 5.05 (t, $J = 6.4$ Hz, 1H, Os-C=CH), 2.04 (q, $J = 7.1$ Hz, 2H, =CHCH₂), 1.18-1.13 (m, 2H, CH₂), 0.79 (t, $J = 7.2$ Hz, 3H, CH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.0 MHz, CDCl_3): $\delta = 230.4$ (br t, $^1J(\text{PC}) = 3.8$ Hz, Os=C), 190.3 (s, C-O), 137.2-116.0 (multiple ^{13}C signals of Ar and C=C), 39.2 (s), 21.6 (s), 13.9 (s). HRMS (ESI, *m/z*): $[\text{M}-\text{Cl}]^+$ calcd for $\text{C}_{48}\text{H}_{42}\text{ClOOsP}_2$, 923.2001; found, 923.1983.

Synthesis of complex 3b. Complex **2b** (0.0500 g, 0.051 mmol) in DCM (5 mL) was stirred at 40 °C under air for 2 h, producing a yellowish-brown solution. The volume was concentrated to about 1 mL and *n*-hexane (10 mL) was added to it to precipitate a yellowish-brown solid, which was washed with ether (5 mL \times 3). The resulting yellowish-brown solid was further purified by column chromatography (eluent: DCM). The yellowish-brown band was collected and dried under vacuum. Yield: 38.6 mg, 77.4 %. $^{31}\text{P}\{^1\text{H}\}$ NMR (162.0 MHz, CDCl_3): $\delta = -15.3$. ^1H NMR (400.1 MHz, CDCl_3): $\delta = 7.50$ -7.48 (m, 12H, Ph), 7.24-7.16 (m, 18H, Ph), 7.02 (d, $J = 8.2$ Hz, 1H), 6.77 (t, $J = 7.7$ Hz, 1H, Ph), 6.54 (t, $J = 12.0$ Hz, 2H, Ph), 5.04 (t, $J = 6.1$ Hz, 1H, Os-C=CH), 2.03 (br q, 2H, =CHCH₂), 1.29-1.13 (m, 6H, (CH₂)₃), 0.91 (t, $J = 8.1$ Hz, 3H, CH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.0 MHz, CDCl_3): $\delta = 230.5$ (br m, Os=C), 190.5 (s, C-O), 137.7-116.2 (multiple ^{13}C signals of Ar and C=C), 37.3 (s), 31.9 (s), 28.2 (s), 22.7 (s), 14.3 (s). HRMS (ESI, *m/z*): $[\text{M}-\text{Cl}]^+$ calcd for $\text{C}_{50}\text{H}_{46}\text{ClOOsP}_2$, 951.2314; found, 951.2322.

Synthesis of complex 4a. Complex **2a** (0.050 g, 0.052 mmol) was placed in a flask and stirred at 100 °C under air for 24 h, producing a dark solid. The solid was then purified by flash column chromatography (eluent: DCM). The brownish red band was collected and dried under vacuum. Yield: 26.8 mg, 51.9 %. HRMS (ESI, *m/z*): $[\text{M}-\text{Cl}]^+$ calcd for $\text{C}_{48}\text{H}_{43}\text{ClO}_3\text{OsP}_2$, 956.1977; found, 956.1976.

Synthesis of complex 4b. Complex **2b** (0.050 g, 0.051 mmol) was placed in a flask and stirred at 100 °C under air for 72 h, producing a dark solid. The solid was then purified by flash column chromatography (eluent: DCM). The brownish red band was collected and dried under vacuum. Yield: 7.8 mg, 15.2 %. HRMS (ESI, *m/z*): $[\text{M}-\text{Cl}]^+$ calcd for $\text{C}_{50}\text{H}_{47}\text{ClO}_3\text{OsP}_2$, 984.2291; found, 984.2292.

2. Computational studies.

Computational details. The optimizations were performed with the Gaussian 16 software package⁶ at the B3LYP level of density functional theory (DFT).⁷ DFT/GENECP level had been done by implementing def2-TZVP basis set for Os atom.⁸ The 6-311G(2d,p) basis set had been used for the rest of atoms.⁹ Nucleus-independent chemical shift (NICS) values were calculated at the B3LYP//6-311G(2d,p)/def2-TZVP level.¹⁰ The anisotropy of the current density was calculated with the AICD 2.0 program computing the NMR properties using the CSGT method with the geometries previously obtained for **1a'** and **3a'**.¹¹

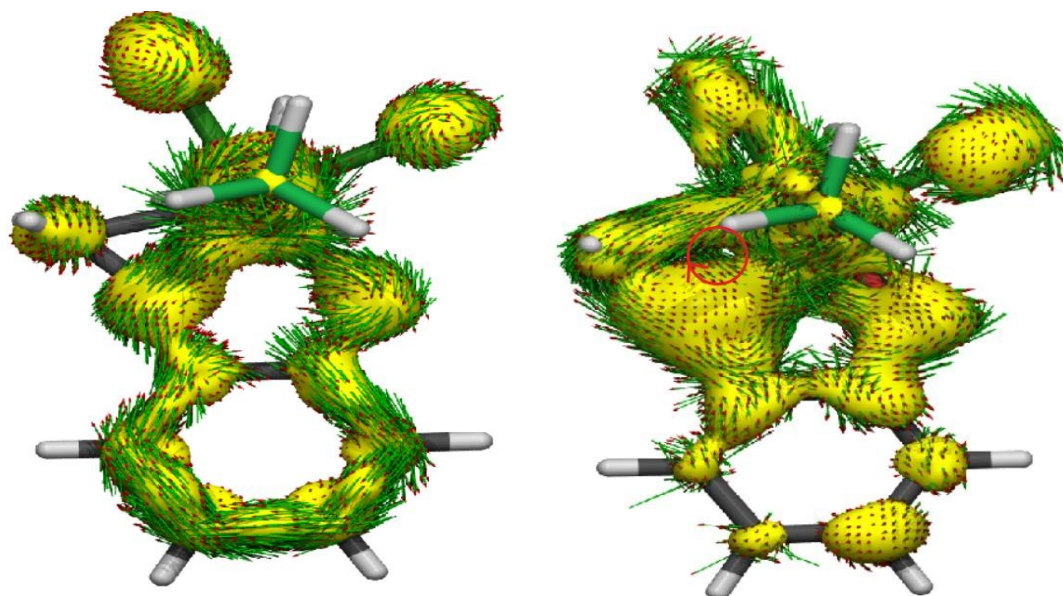


Figure S1. AICD plots of **1a'** separated into the (left) π contributions and (right) σ contributions with an isosurface value of 0.03. For AICD maps, the magnetic field vector is orthogonal with respect to the monocyclic ring plane and points downward (anti-clockwise currents are diatropic).

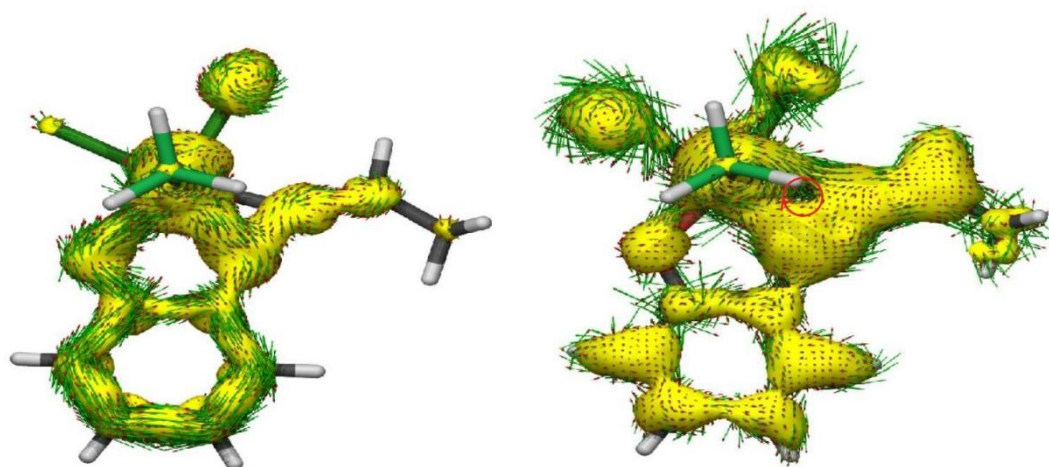


Figure S2. AICD plots of **3a'** separated into the (left) π contributions and (right) σ contributions with an isosurface value of 0.03. For AICD maps, the magnetic field vector is orthogonal with respect to the

monocyclic ring plane and points downward (anti-clockwise currents are diatropic).

3. X-ray crystallographic study

Single crystals of complexes **1a** (CCDC No.2225150), **3a** (CCDC No. 2225151), **3b** (CCDC No. 2288691), and **4a** (CCDC No.2264254) suitable for X-ray diffraction were grown from CH₂Cl₂ solution layered with *n*-hexane. Intensity data of **1a** and **4a** were collected on a Bruker Smart APEXII diffractometer using Cu-K α radiation ($\lambda = 1.54184 \text{ \AA}$), and that of **3a** and **3b** were collected on a Bruker Smart APEXII diffractometer using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Unit cell indexing was refined using SAINT, Absorption correction was applied by using multi-scan program SADABS. The structure was solved with OLEX2 software, and the SHELXT structure solution program using combined direct method.¹²⁻¹³ The crystal structure was refined by least squares using SHELXL. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to carbon atoms were placed at calculated positions and refined using a riding model approximation, with C–H = 0.95(aromatic CH) and with Uiso(H) = 1.2 Ueq(C), C–H = 1.00(-CH) and with Uiso(H) = 1.2 Ueq(C),C–H=0.99(-CH₂) and with Uiso(H) = 1.2 Ueq(C),C–H = 0.98 \AA (-CH₃) and with Uiso(H) = 1.5 Ueq(C). The crystal data are listed in Table S1.

Table S1. Crystallographic data and refinement details of **1a**, **3a**, **3b**, **4a**.

	1a	3a	3b	4a
Empirical formula	C ₄₄ H ₃₆ Cl ₂ OOSp ₂	C ₄₈ H ₄₂ Cl ₂ OOSp ₂ · CH ₂ Cl ₂	C ₅₀ H ₄₆ Cl ₂ OOSp ₂	C ₄₈ H ₄₃ Cl ₂ O ₃ Osp ₂ · CH ₂ Cl ₂
Color & habit	brown, block	brown yellow, block	brown yellow, block	brownish red, block
Crystal size (mm ³)	0.15 x 0.13 x 0.11	0.20 x 0.20 x 0.10	0.15 x 0.13 x 0.12	0.15x 0.13x 0.12
Temperature (K)	100	150	100	150
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
a (Å)	9.57540(10)	10.9207(2)	19.4318(6)	21.5392(5)
b (Å)	16.40830(10)	12.9359(2)	10.3039(2)	13.2966(3)
c (Å)	11.88330(10)	30.7710(6)	22.3306(6)	30.5699(8)
α (°) α (°)	90	90	90	90
β (°) β (°)	97.4020(10)	90	109.332(3)	99.7310(10)
γ (°) γ (°)	90	90	90	90
V(Å ³), Z	1851.50(3), 2	4346.99(13), 4	4219.0(2), 4	8629.2(4), 4
D _{cal} (Mg/m ³)	1.621	1.593	1.552	1.591
Abs. coeff.(mm ⁻¹)	8.914	3.290	3.263	8.323
2 θ range for data	5.386 to 153.254	4.882 to 52.778	4.4 to 50.054	4.162 to 133.176
Reflections collected	24556	45361	41333	80741
Indep. Reflection,	10109, 0.0257	8846, 0.0324	7456, 0.0460	15233, 0.0460
Completeness(%) of	95	99.8	99.9	99.9
Data/ restraints/	10109/15/902	8846/0/515	7456/1128/506	15233/2003/1038
Goodness-of-fit on F ²	1.074	1.010	1.016	1.083
*R ₁ [<i>I</i> >2 σ (<i>I</i>)], wR ₂	0.0196, 0.0491	0.0208, 0.0447	0.0269, 0.0586	0.0534, 0.1401
*R ₁ (all data), wR ₂	0.0198, 0.0492	0.0238, 0.0458	0.0370, 0.0633	0.0551, 0.1426

Largest diff. peak and	0.59/-0.61	0.74/-0.66	1.58/-0.83	2.83/-0.87
hole ($e \cdot \text{\AA}^{-3}$)				

$$*R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|, wR_2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(F_o^2)^2]^{1/2}, [F_o > \sigma(F_o)]$$

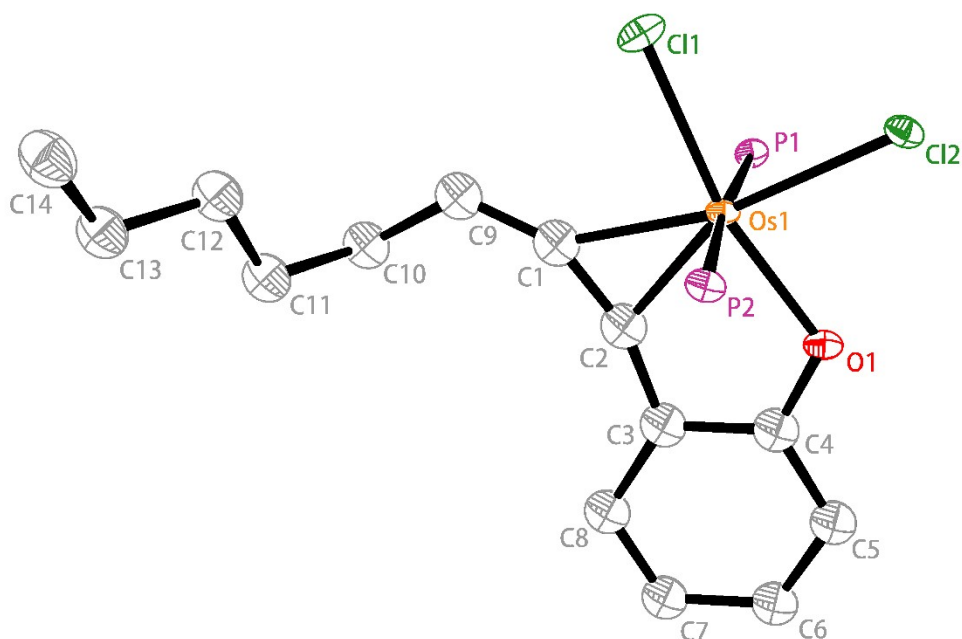


Figure S3. ORTEP drawing of complex **3b** with thermal ellipsoids set 50% probability (phenyl groups in PPh₃ are omitted for clarity). Selected bond distances (Å) and angles (°): Os1-C1 2.112(4), Os1-C2 1.982(4), Os1-O1 2.071(2), Os1-P1 2.4184(9), Os1-P2 2.4177(9), Os1-C11 2.4218(9), Os1-Cl2 2.4249(9), C1-C2 1.339(6), C2-C3 1.380(6), C3-C4 1.414(6), C4-O1 1.299(5), C4-C5 1.416(6), C5-C6 1.382(6), C6-C7 1.405(6), C7-C8 1.363(6), C8-C3 1.434(6), C1-C9 1.338(6), Os1-C1-C2 65.7(2), Os1-C2-C1 76.3(3), C1-Os1-C2 38.01(17), Os1-C2-C3 120.9(3), C2-C3-C4 109.8(4), C3-C4-O1 117.1(4), C4-O1-Os1 116.9(2), O1-Os1-C2 75.28(14), P1-Os1-P2 175.36(3).

4. NMR spectra, EPR spectra and HRMS data

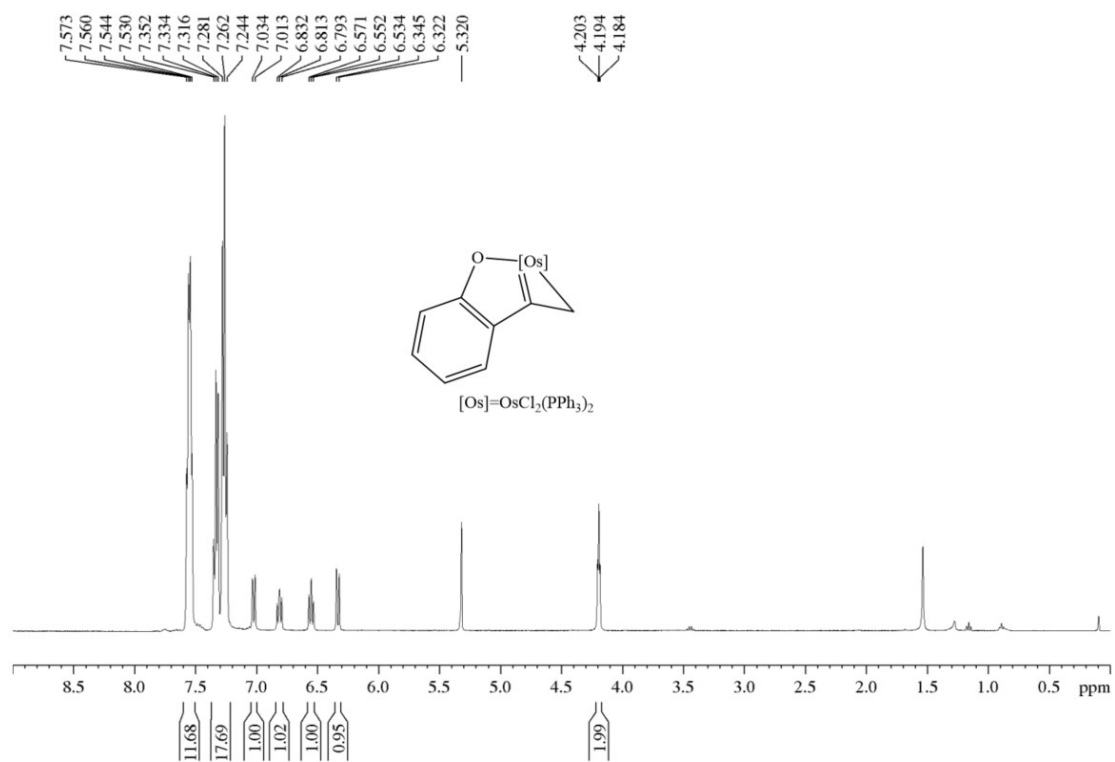


Figure S4. The ^1H NMR spectrum of complex **1a** in CD_2Cl_2 at 400.1 MHz.

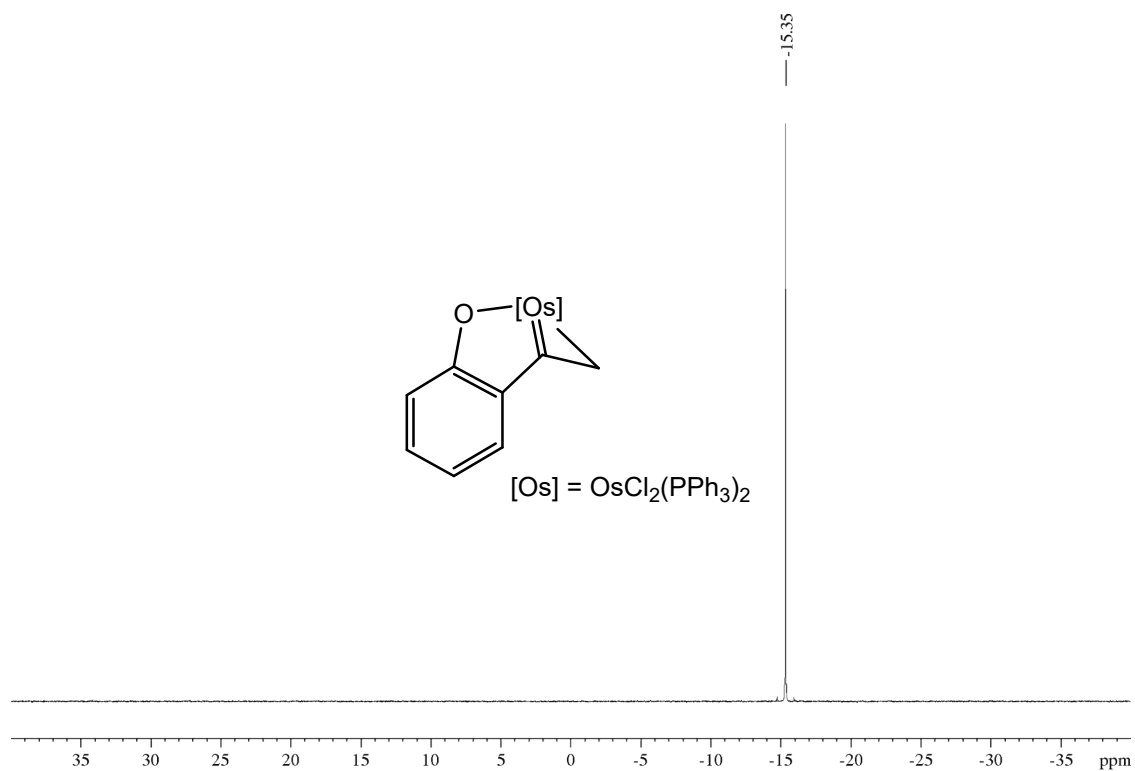


Figure S5. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex **1a** in CD_2Cl_2 at 162.0 MHz.

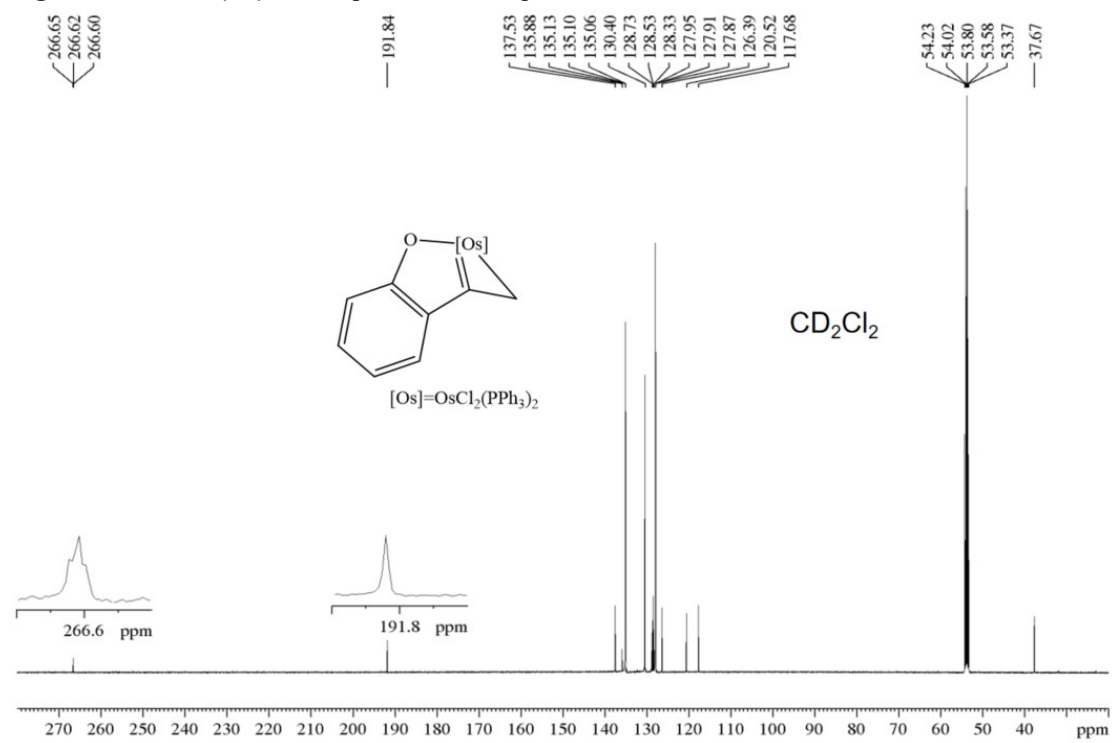


Figure S6. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex **1a** in CD_2Cl_2 at 125.0 MHz.

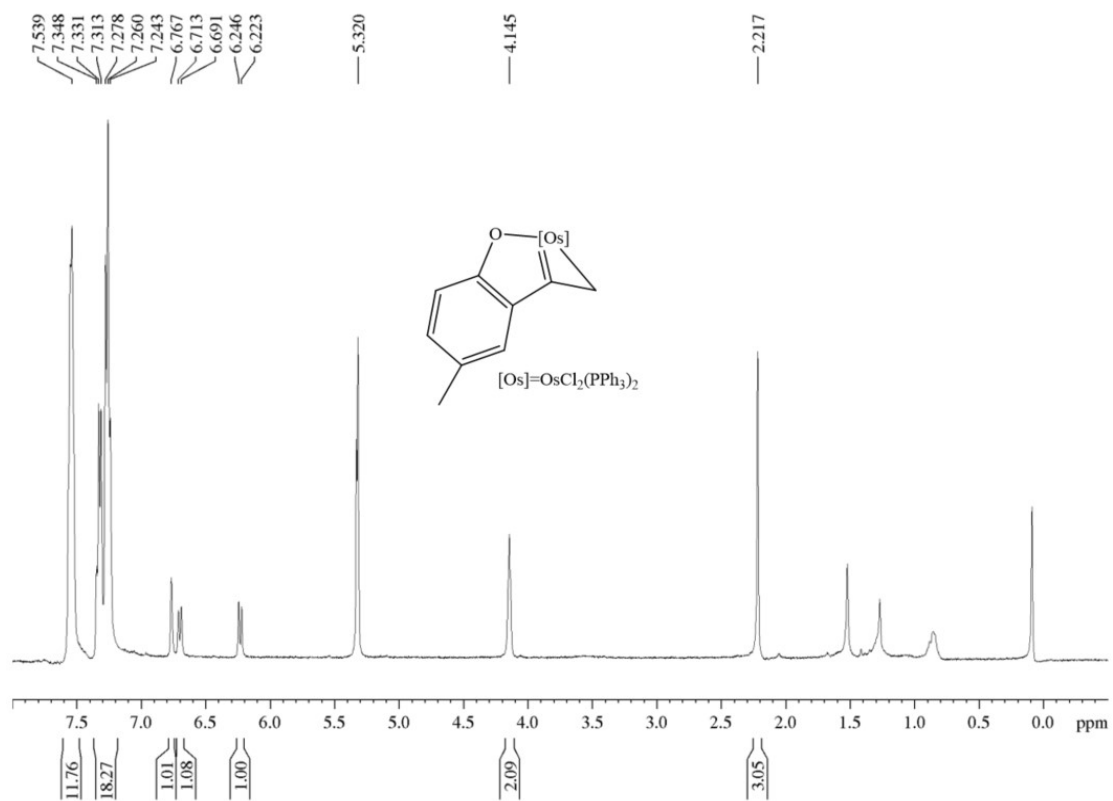


Figure S7. The ¹H NMR spectrum of complex **1b** in CD₂Cl₂ at 400.1 MHz.

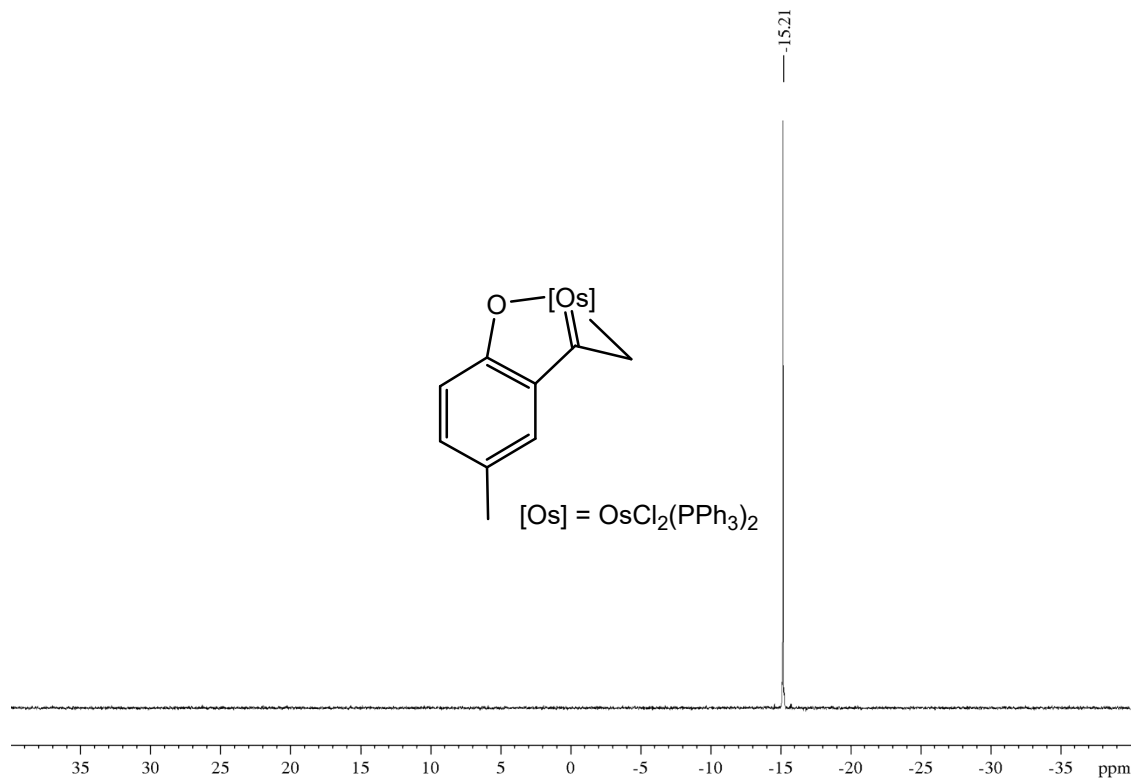


Figure S8. The ³¹P{¹H} NMR spectrum of complex **1b** in CD₂Cl₂ at 162.0 MHz.

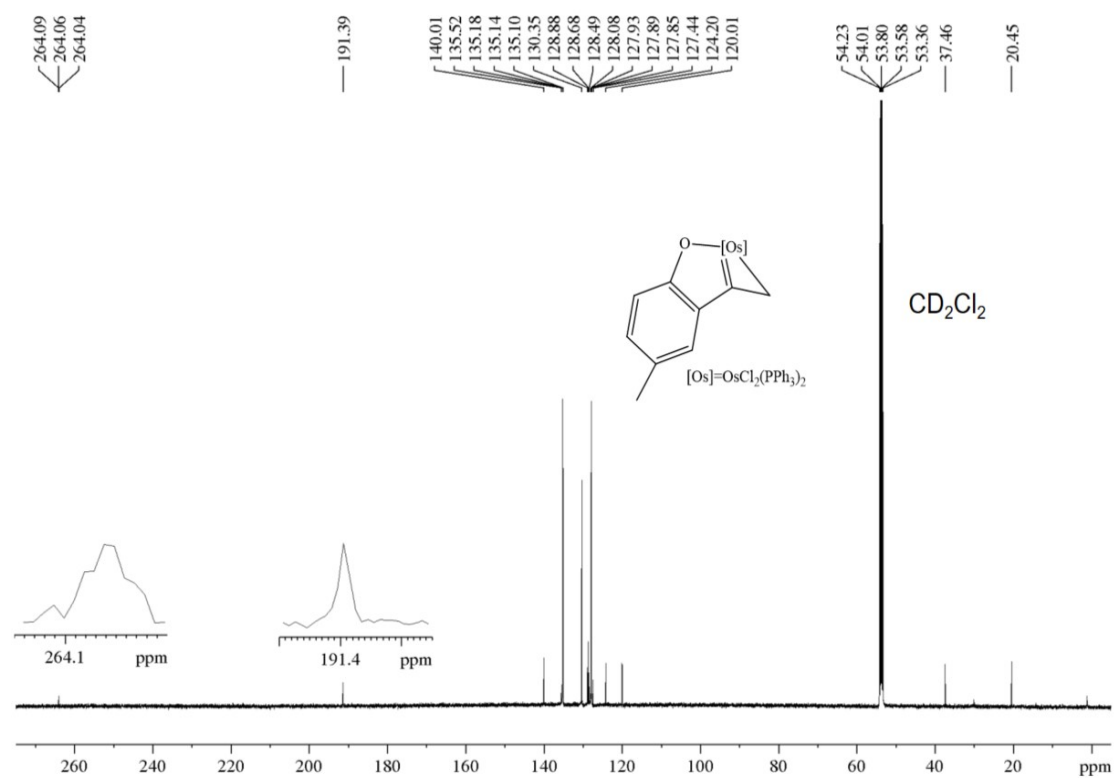


Figure S9. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex **1b** in CD_2Cl_2 at 125.0 MHz.

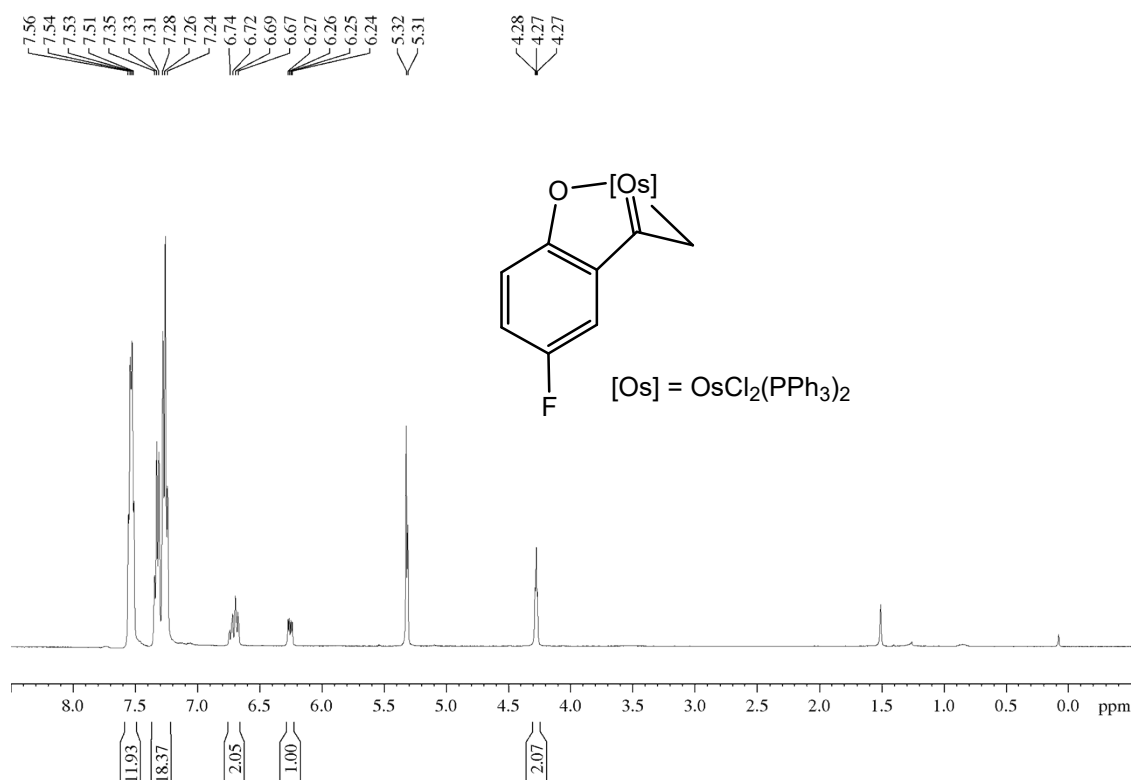


Figure S10. The ^1H NMR spectrum of complex **1c** in CD_2Cl_2 at 400.1 MHz.

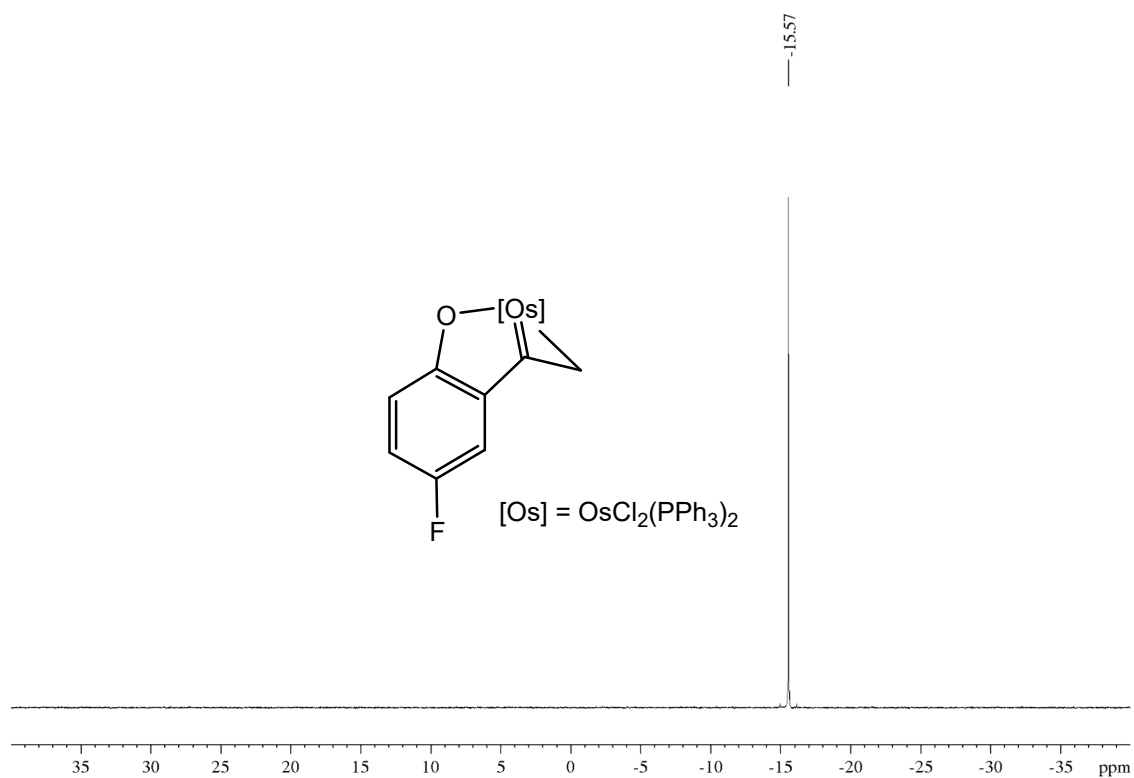


Figure S11. The $^{31}P\{^1H\}$ NMR spectrum of complex **1c** in CD_2Cl_2 at 162.0 MHz.

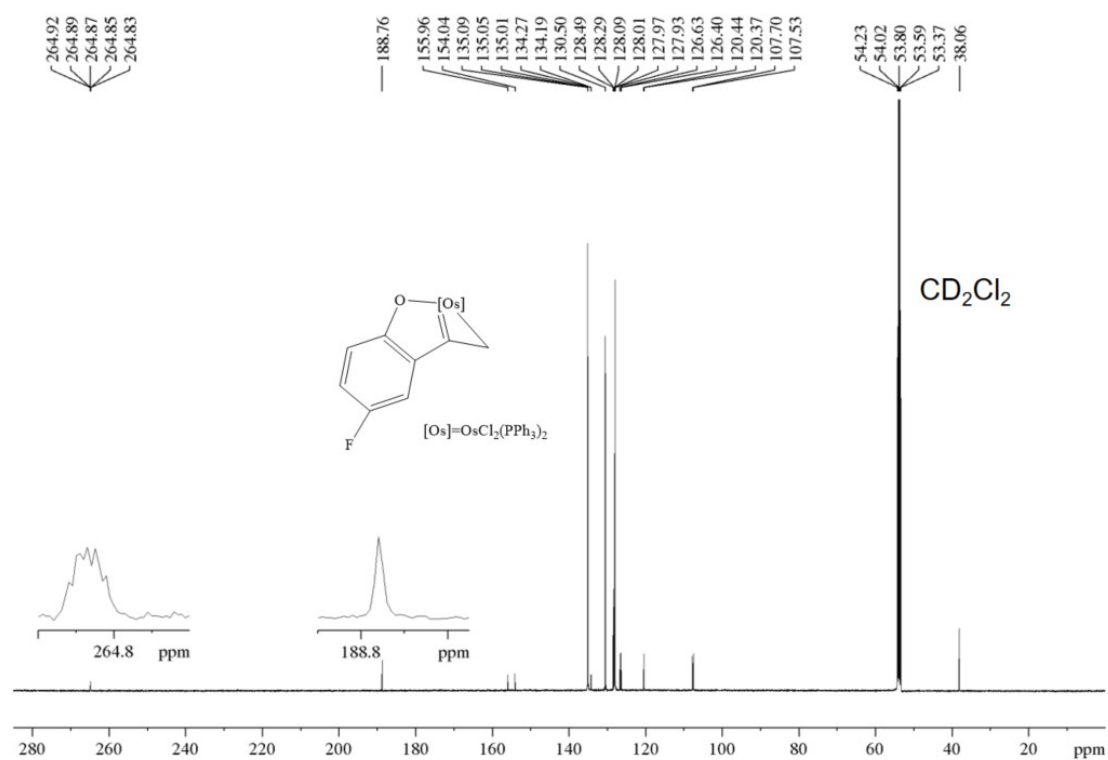


Figure S12. The $^{13}C\{^1H\}$ NMR spectrum of complex **1c** in CD_2Cl_2 at 125.0 MHz.

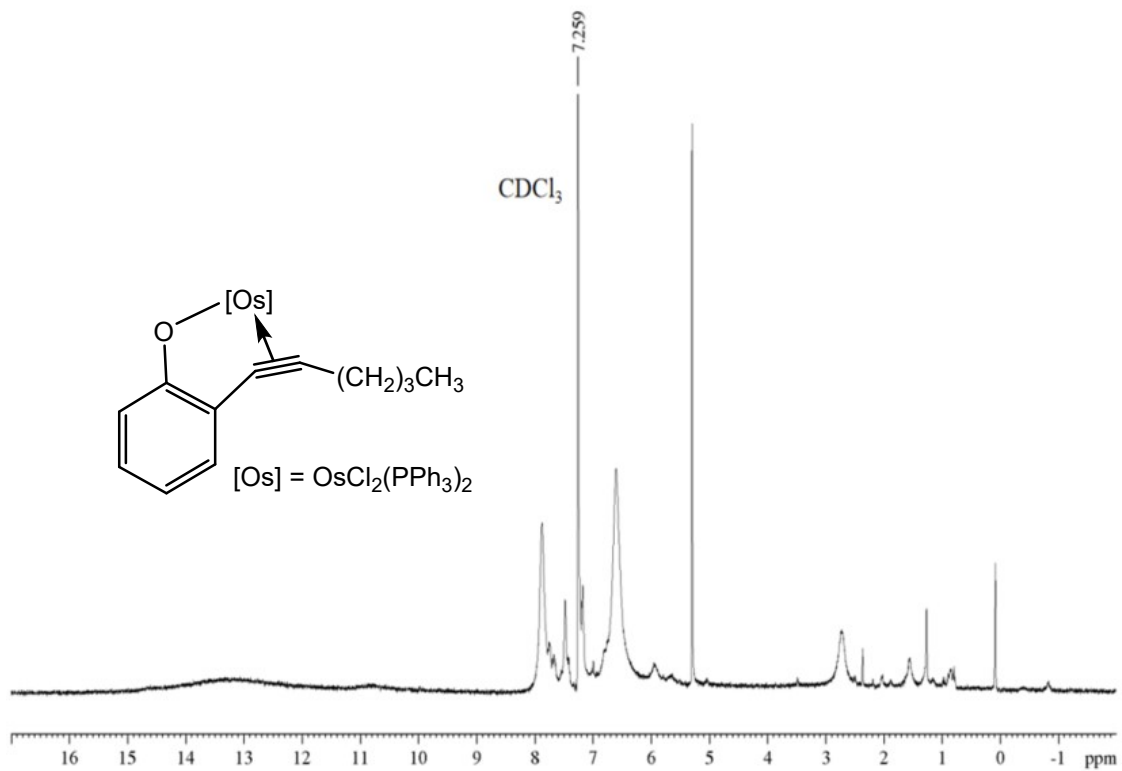


Figure S13. The ¹H NMR spectrum of complex 2a in CDCl₃ at 400.1 MHz.

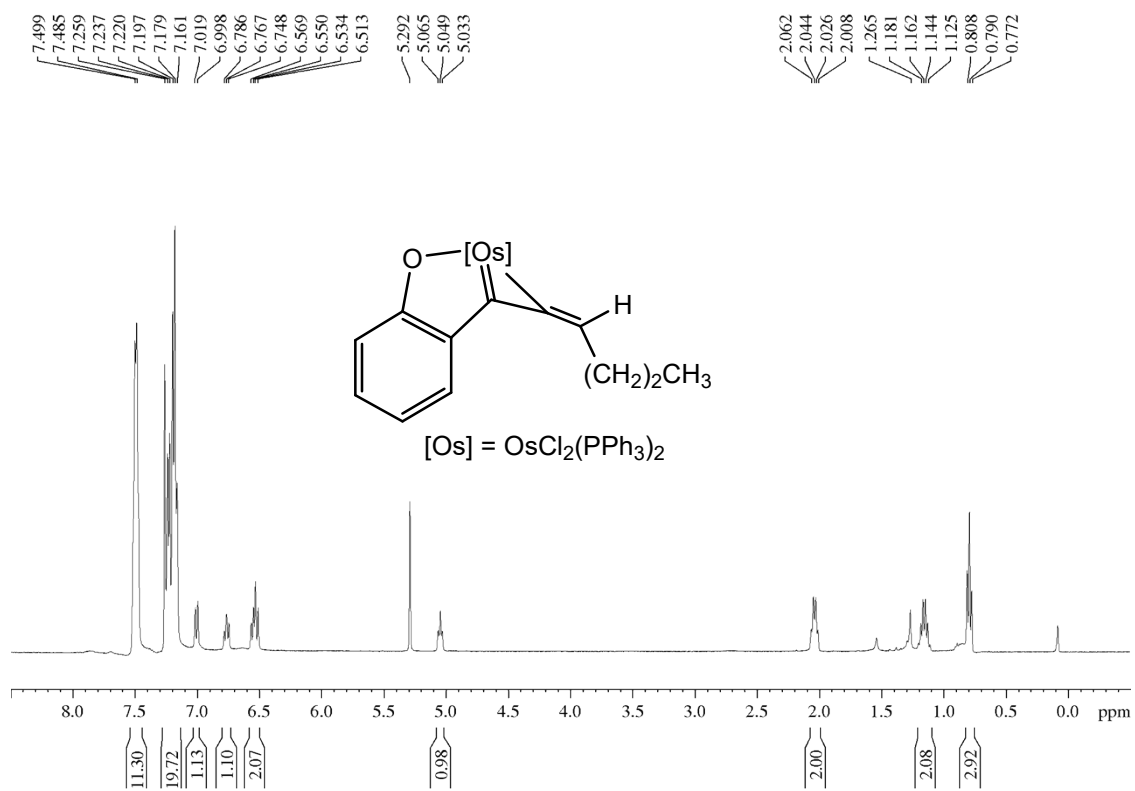


Figure S14. The ¹H NMR spectrum of complex 3a in CDCl₃ at 400.1 MHz.

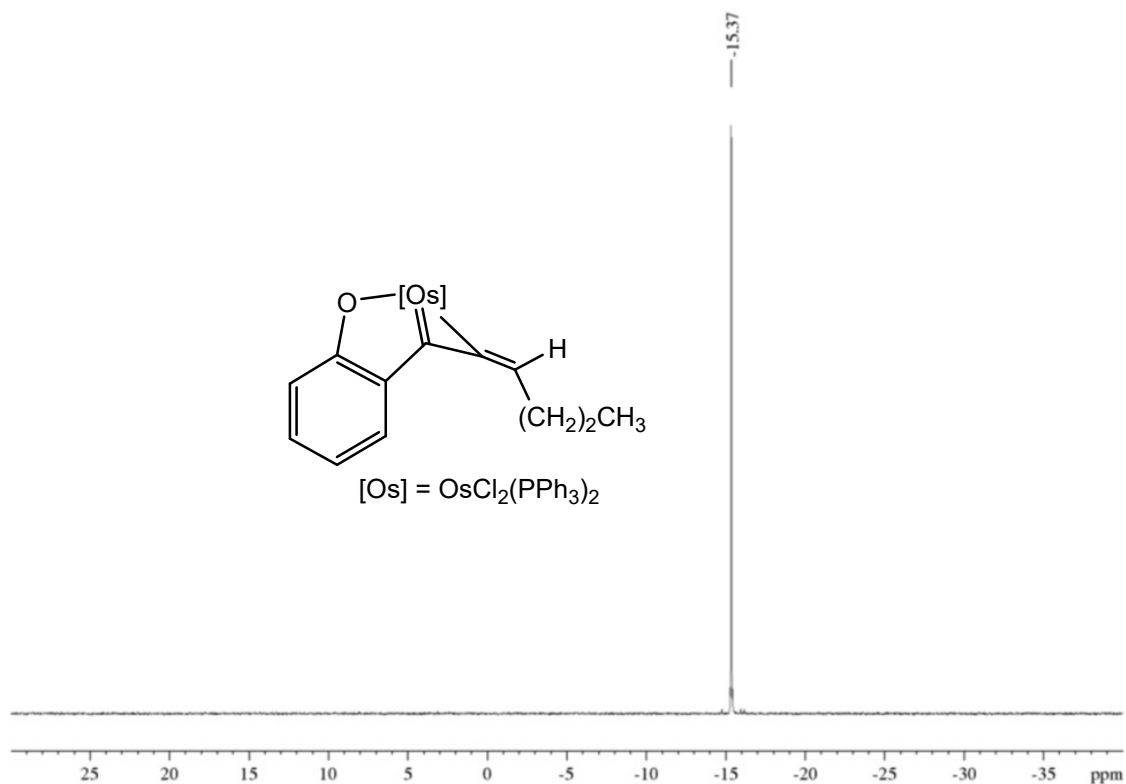


Figure S15. The $^{31}P\{^1H\}$ NMR spectrum of complex **3a** in $CDCl_3$ at 162.0 MHz.

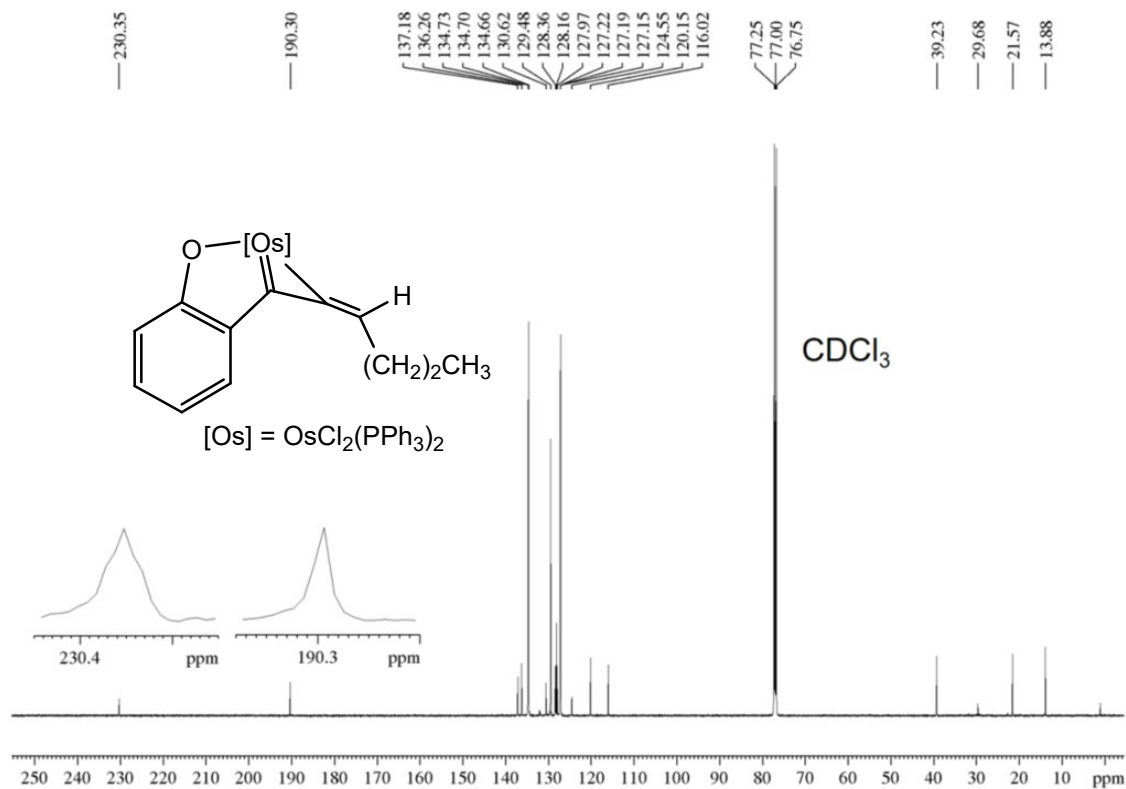


Figure S16. The $^{13}C\{^1H\}$ NMR spectrum of complex **3a** in $CDCl_3$ at 125.0 MHz.

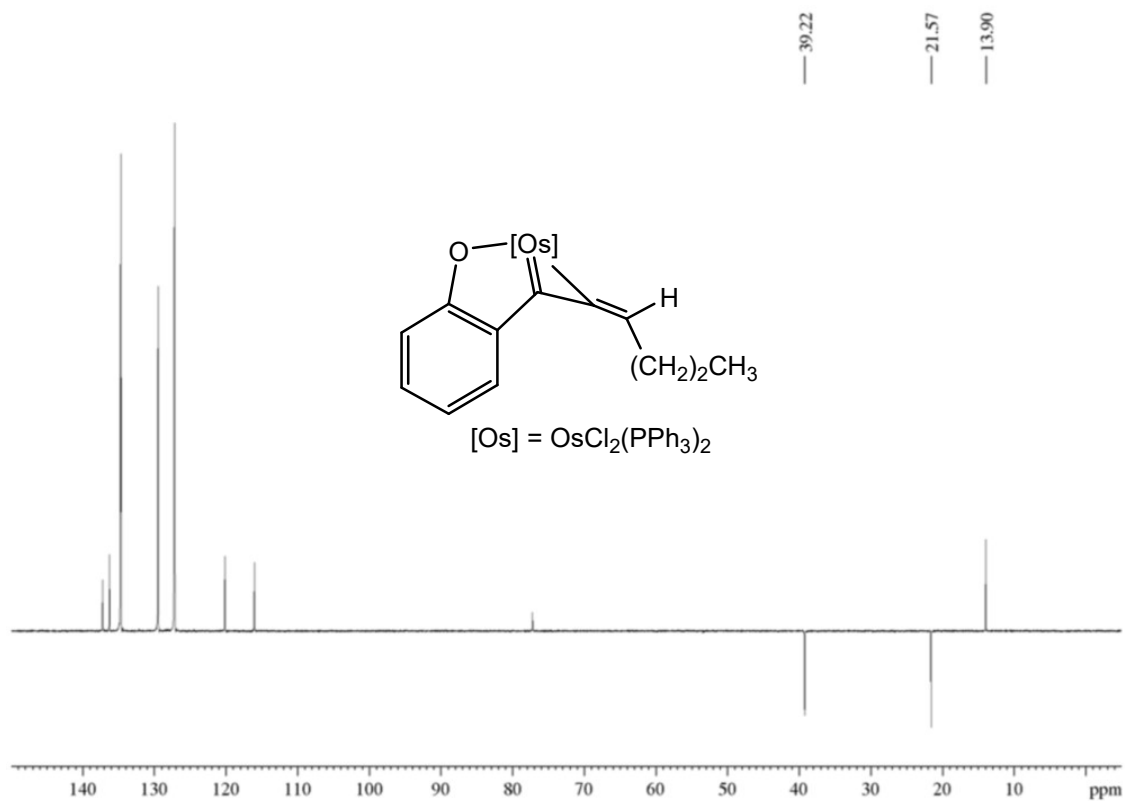


Figure S17. The ¹³C DEPT-135 NMR spectrum of complex **3a** in CDCl₃ at 125.0 MHz.

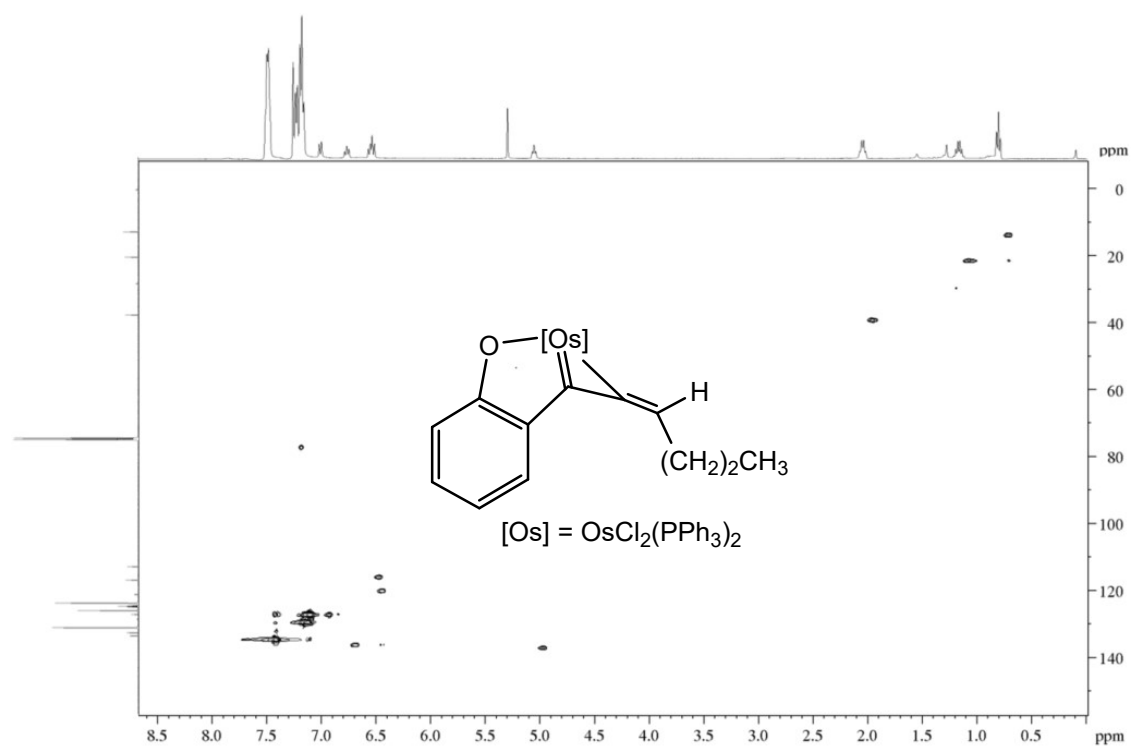


Figure S18. The ¹H-¹³C HSQC and expanded NMR spectrum of complex **3a** in CDCl₃ at 125.0 MHz.

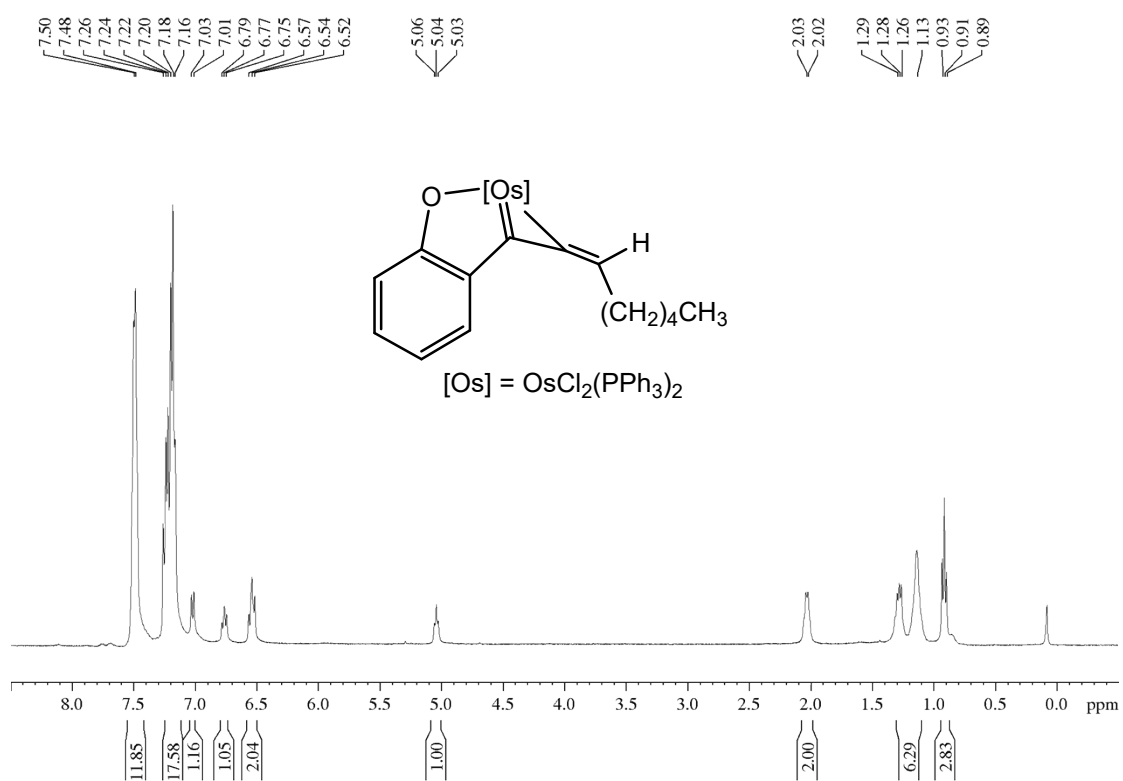


Figure S19. The 1H NMR spectrum of complex **3b** in CDCl₃ at 400.1 MHz.

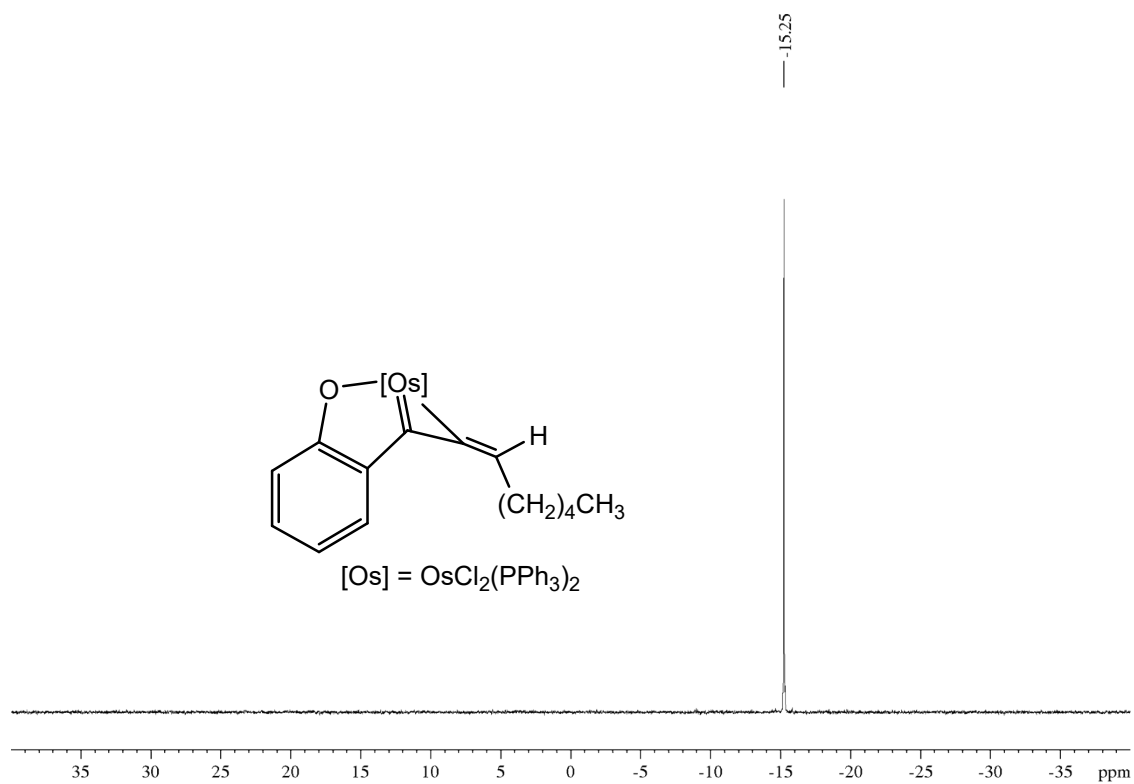


Figure S20. The $^{31}P\{^1H\}$ NMR spectrum of complex **3b** in CDCl₃ at 162.0 MHz.

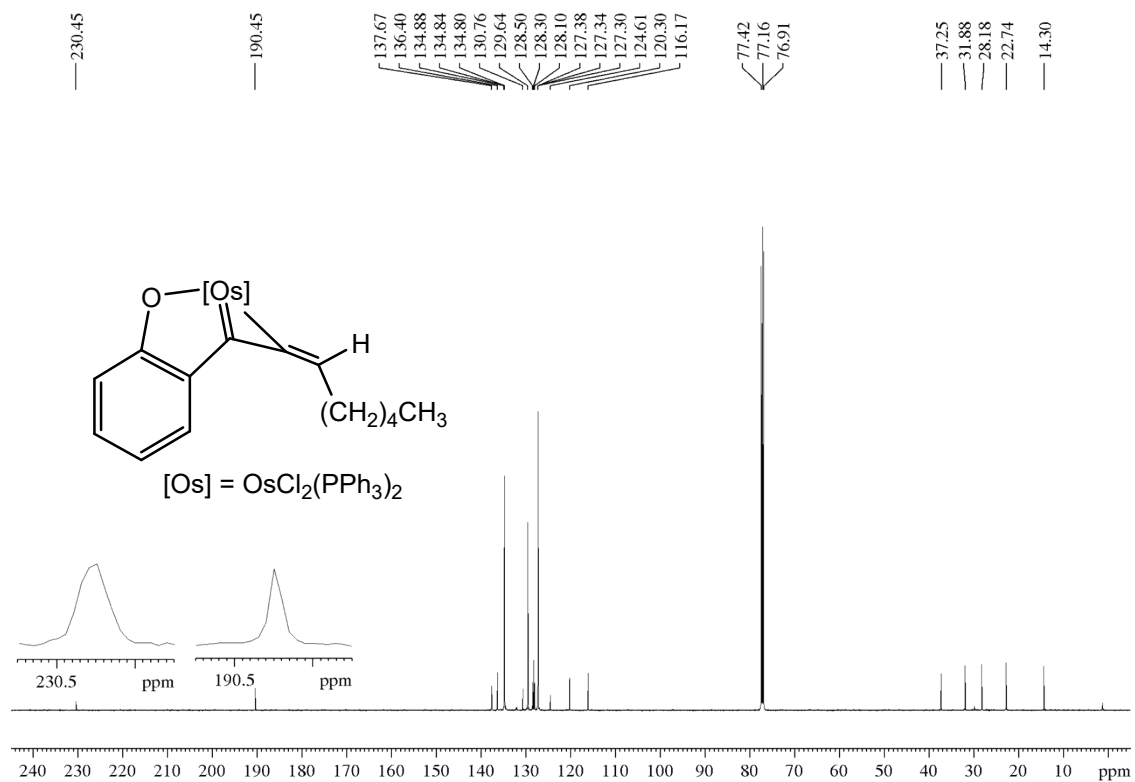


Figure S21. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex **3b** in CDCl_3 at 125.0 MHz.

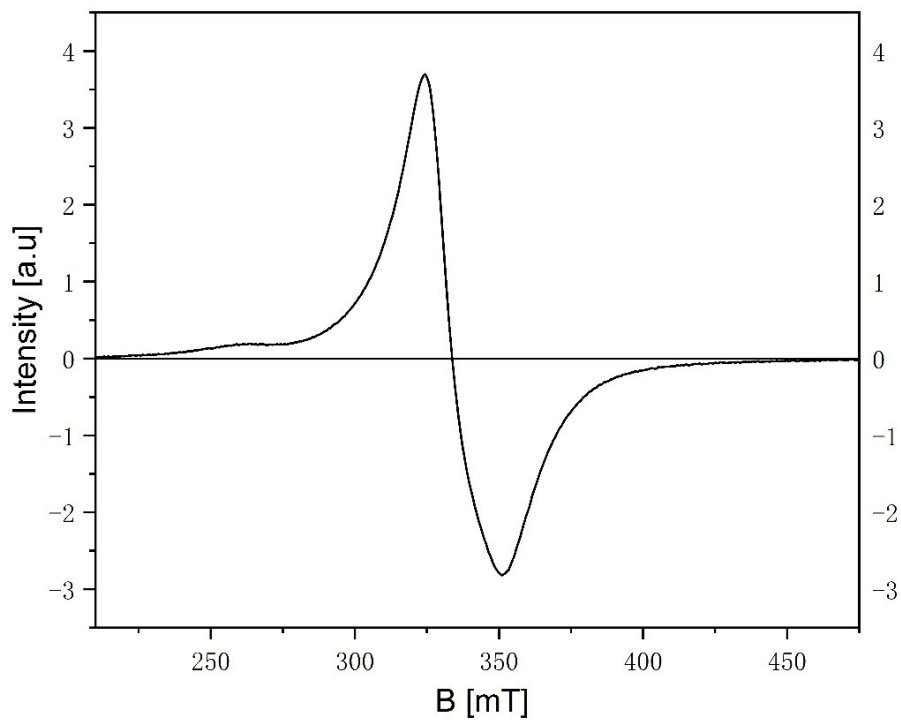


Figure S22. The EPR spectrum of complex **2a** (powder) at room temperature.

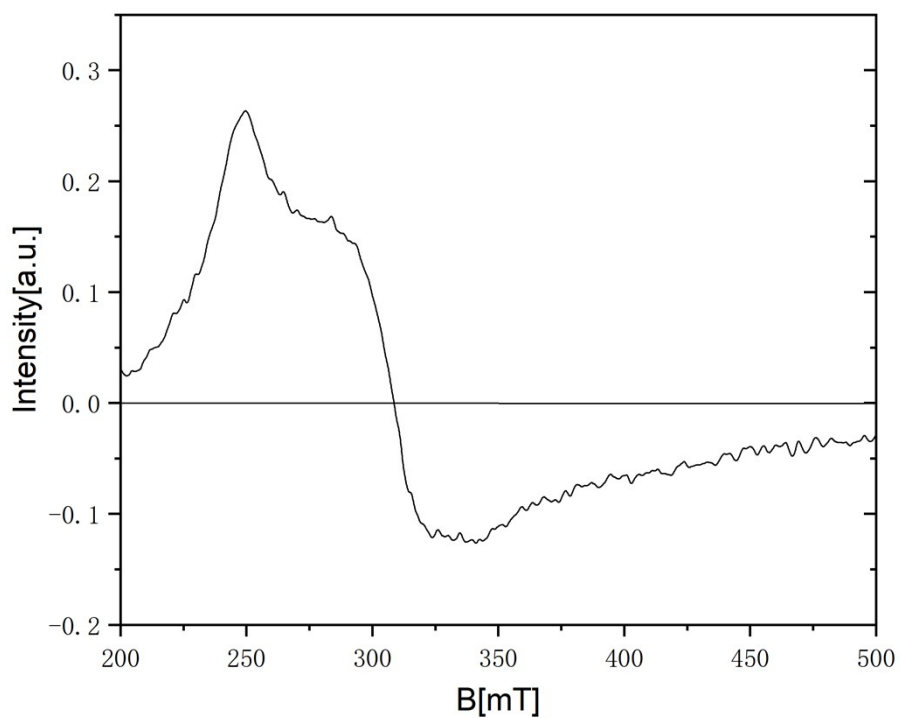


Figure S23. The EPR spectrum of complex **4a** (powder) at room temperature.

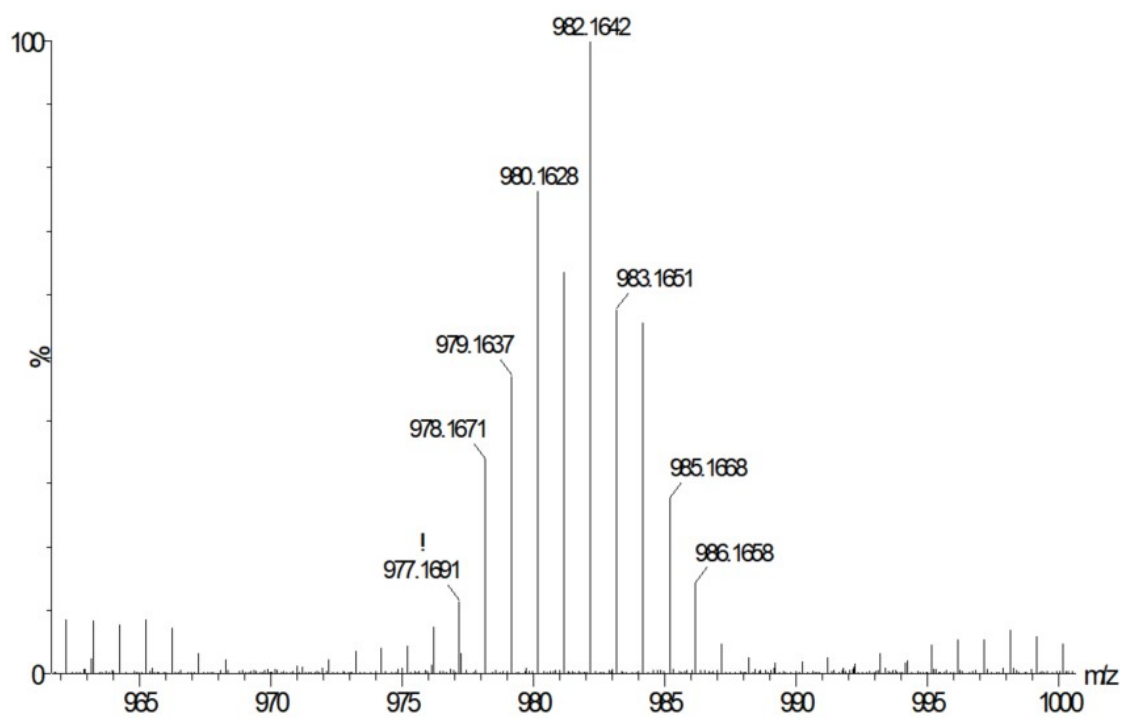


Figure S24. Positive ion ESI-HRMS data of **[2a-Cl]⁺** $[\text{C}_{48}\text{H}_{43}\text{ClOOSp}_2]^+$ measured in DCM.

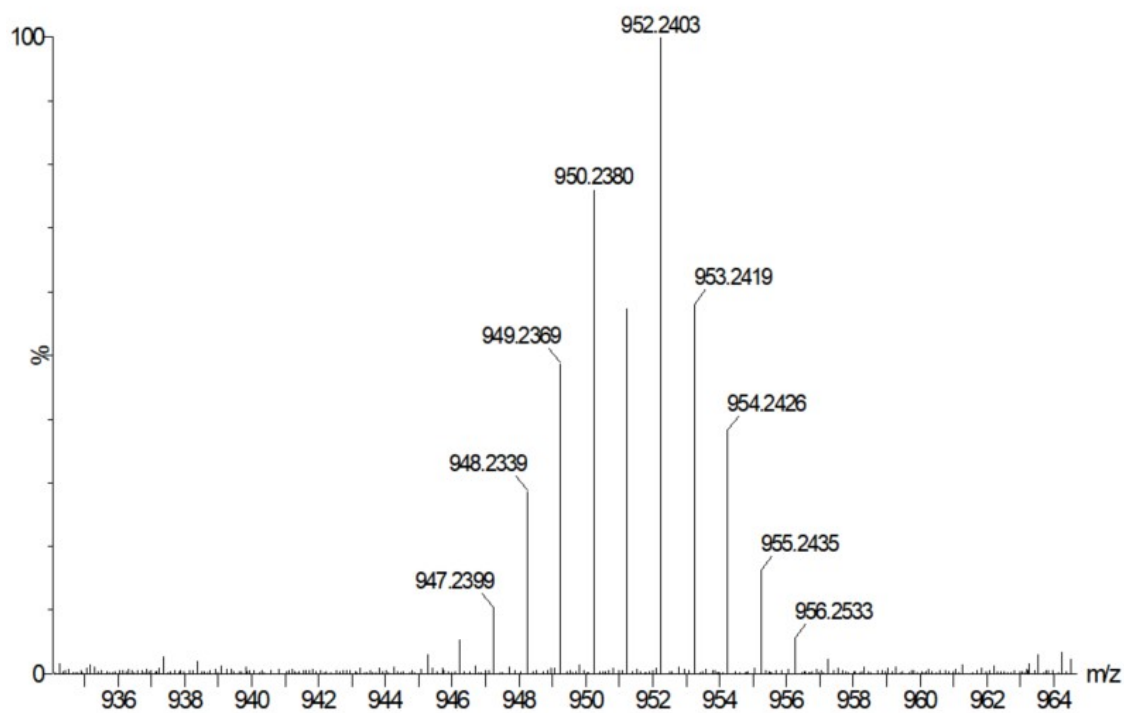


Figure S25. Positive ion ESI-HRMS data of $[2b-Cl]^+$ $[C_{50}H_{48}ClOOSp_2]^+$ measured in DCM.

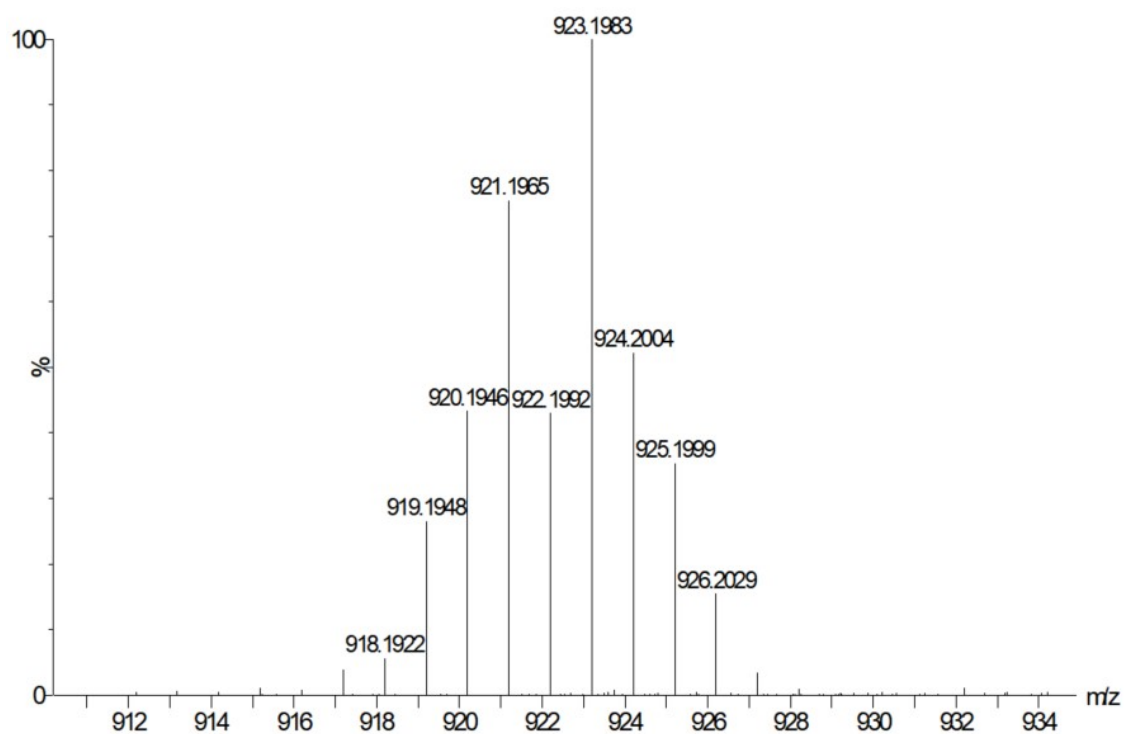


Figure S26. Positive ion ESI-HRMS data of $[3a-Cl]^+$ $[C_{48}H_{42}ClOOSp_2]^+$ measured in DCM.

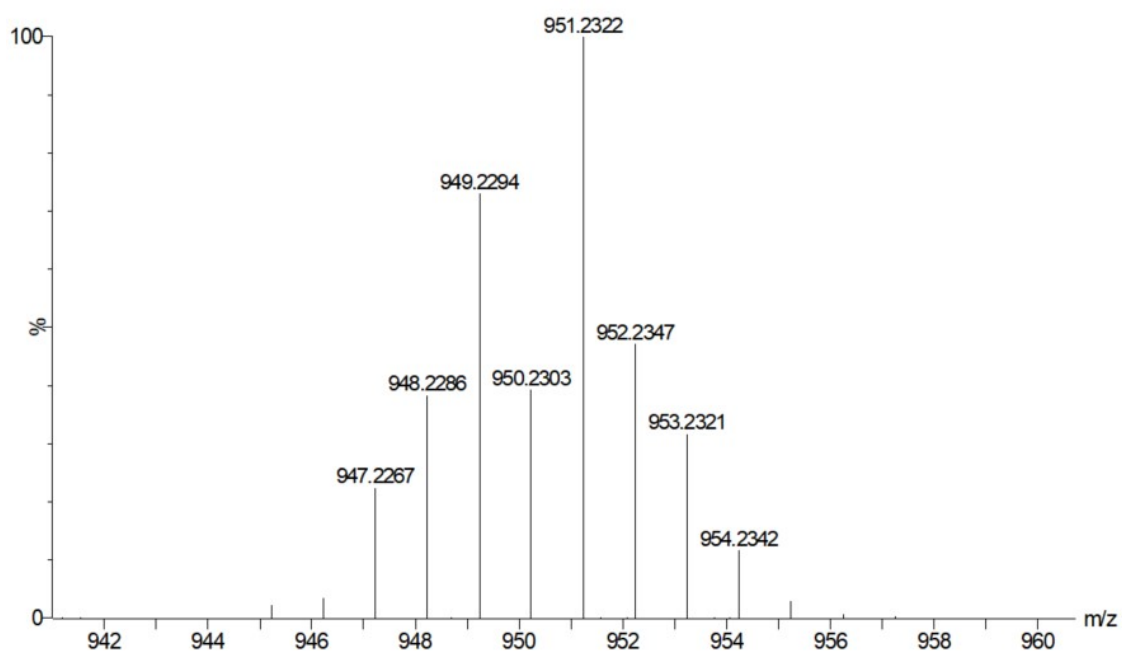


Figure S27. Positive ion ESI-HRMS data of **[3b-Cl]⁺** [C₅₀H₄₆ClO₃OsP₂]⁺ measured in DCM.

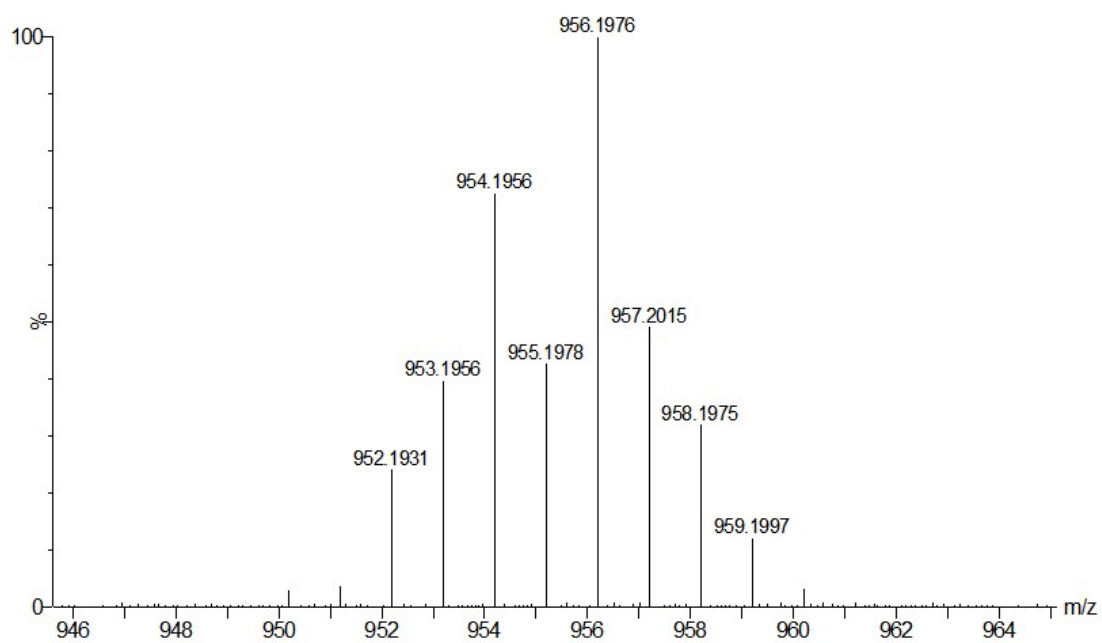


Figure S28. Positive ion ESI-HRMS data of **[4a-Cl]⁺** [C₄₈H₄₃ClO₃OsP₂]⁺ measured in DCM.

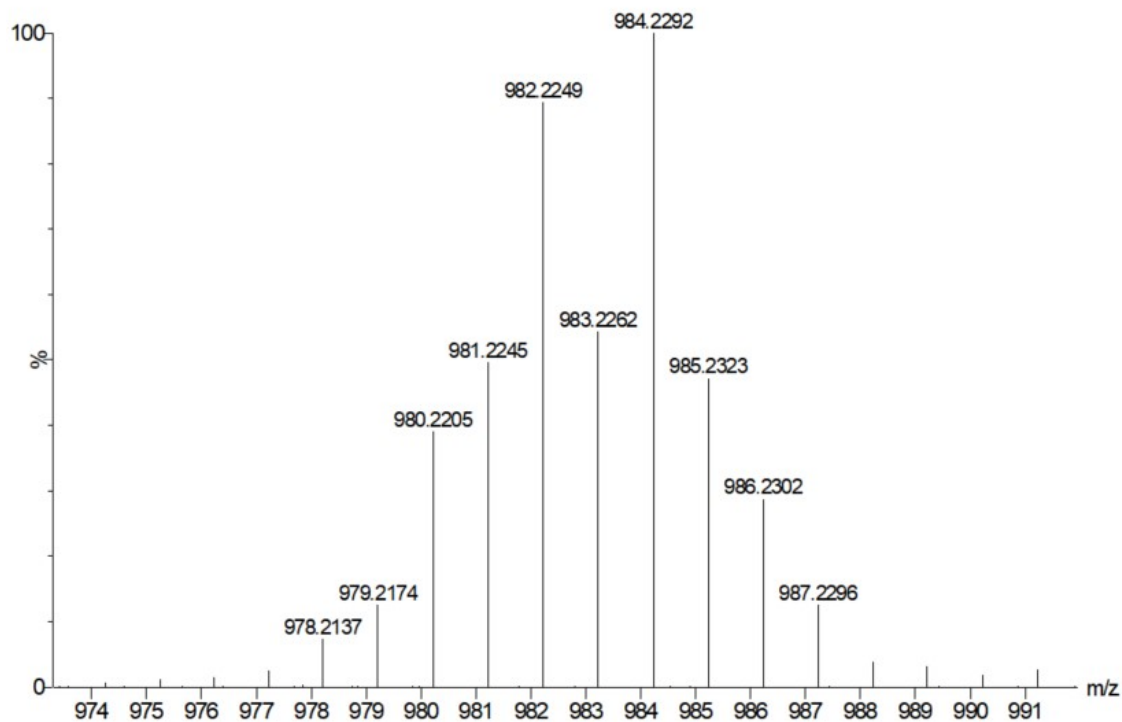
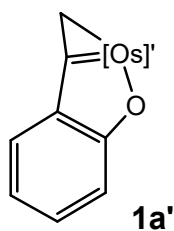


Figure S29. Positive ion ESI-HRMS data of **[4b-Cl]⁺** [C₅₀H₄₇ClO₃OsP₂]⁺ measured in DCM.

5. The Calculated Cartesian Coordinates with Electronic Energies

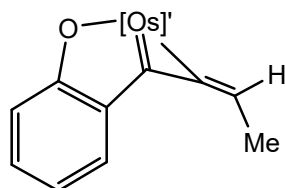


E = -2081.282678 a.u.

Os	-0.6080000	0.0020000	-0.0650000
O	1.0480000	-0.0330000	1.2670000
C	0.0050000	0.0560000	-2.1820000
H	-0.2400000	-0.8400000	-2.7440000
H	-0.2410000	0.9790000	-2.6970000
C	2.2180000	-0.0190000	0.7260000
C	3.5200000	0.0370000	-1.3870000
H	3.5410000	0.0650000	-2.4700000
C	4.6720000	0.0180000	-0.6510000

H	5.63700000	0.03000000	-1.14100000
C	4.61400000	-0.02000000	0.77000000
H	5.54600000	-0.03400000	1.32400000
C	2.27300000	0.01900000	-0.70700000
C	3.43000000	-0.03800000	1.46200000
H	3.39500000	-0.06600000	2.54300000
C	0.98900000	0.03200000	-1.21000000
Cl	-2.83000000	0.03000000	-1.12200000
Cl	-1.81300000	-0.05400000	2.07000000
P	-0.85100000	-2.36000000	0.01300000
H	-2.15300000	-2.79300000	0.29800000
H	-0.56700000	-3.13400000	-1.13200000
H	-0.10900000	-3.07400000	0.97300000
P	-0.85200000	2.35600000	0.13300000
H	-0.10500000	3.02300000	1.12200000
H	-0.57600000	3.18700000	-0.97400000
H	-2.15300000	2.77200000	0.44700000

[Os]' = OsCl₂(PH₃)₂



3a'

E = -2158.671828 a.u.

Os	-0.61800000	-0.19300000	0.00000000
Cl	-1.85300000	-2.31100000	0.00000000
Cl	-2.84000000	0.86100000	0.00100000
O	1.01700000	-1.54500000	0.00000000
C	4.59500000	-1.13800000	0.00000000
H	5.51200000	-1.71700000	0.00000000
C	2.20000000	-1.02700000	0.00000000
C	4.69000000	0.28100000	0.00000000
H	5.66800000	0.74700000	0.00000000
C	2.29300000	0.40200000	0.00000000
C	1.01900000	0.94800000	0.00000000
C	3.39200000	-1.79500000	0.00000000
H	3.32600000	-2.87600000	0.00000000
C	3.55700000	1.04600000	0.00000000
H	3.60900000	2.12800000	0.00000000

C	0.02200000	1.84300000	0.00000000
C	-0.40800000	3.10200000	-0.00100000
H	-1.48100000	3.26900000	-0.00100000
P	-0.85300000	-0.31400000	-2.36300000
H	-0.15400000	-1.32300000	-3.05200000
H	-2.16500000	-0.55100000	-2.79700000
H	-0.51300000	0.80300000	-3.15500000
P	-0.85200000	-0.31400000	2.36400000
H	-2.16300000	-0.55300000	2.79700000
H	-0.15100000	-1.32100000	3.05300000
H	-0.51500000	0.80400000	3.15400000
C	0.48200000	4.30700000	-0.00100000
H	0.28300000	4.93200000	-0.87800000
H	0.28300000	4.93200000	0.87600000
H	1.53900000	4.03900000	-0.00100000

Reference

1. P. R. Hoffmann and K. G. Caulton, *J. Am. Chem. Soc.*, 1975, **97**, 4221-4228.
2. J. Bucher, T. Wurm, K. S. Nalivela, M. Rudolph, F. Rominger and A. S. K. Hashmiet, *Angew. Chem., Int. Ed.*, 2014, **53**, 3854-3858.
3. Z. Rong, W. Hu, N. Dai and G. Qian, *Org. Lett.*, 2020, **22**, 3286-3290.
4. S. Ohno, R. F. Avena, H. Aoyama, H. Fujioka and M. Arisawa, *Green Chem.*, 2020, **22**, 1220-1228.
5. Martínez, C., R. Álvarez and J.M. Aurrecoechea, *Org. Lett.*, 2009, **11**, 1083-1086.
6. Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
7. a) A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648-5652; b) B. Miehlich, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett.* 1989, **157**, 200-206; c) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B.* 1988, **37**, 785-789.
8. a) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* 2005, **7**, 3297-3305; b) F. Weigend, *Phys. Chem. Chem. Phys.* 2006, **8**, 1057-1065.
9. P. J. Hay and W. R. Wadt, *J. Chem. Phys.* 1985, **82**, 299-310.

10. a) P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao and N. J. R. v. E. Hommes, *J. Am. Chem. Soc.* 1996, **118**, 6317-6318; b) Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta and P. v. R. Schleyer, *Chem. Rev.* 2005, **105**, 3842-3888; c) H. Fallah-Bagher-Shaidaei, C. S. Wannere, C. Corminboeuf, R. Puchta and P. v. R. Schleyer, *Org. Lett.* 2006, **8**, 863-866.
11. a) R. Herges and D. Geuenich, *J. Phys. Chem. A* 2001, **105**, 3214-3220; b) D. Geuenich, K. Hess, F. Kçhler and R. Herges, *Chem. Rev.* 2005, **105**, 3758-3772.
12. G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112-122.
13. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. J. Puschmann, *Appl. Cryst.*, 2009, **42**, 339-341.