SUPPLEMENTARY INFORMATION

Quantifying Variation in Cooperative B-H Bond Activations by Os(II) and Os(III) κ^2-*N,S*-chelated Complexes: Same, but Different

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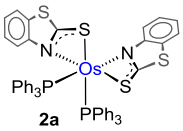
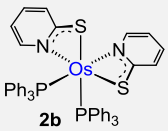
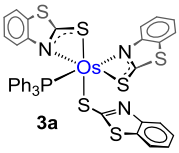
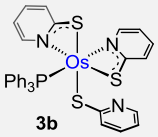
Table S1. g-values of **3a-b** determined by EPR spectroscopy in CH_2Cl_2 at 77 K and redox Potentials of **2a-b** and **3a-b** determined by Cyclic Voltammetry.

Complexes	g-value	Redox Potentials			
		E^1,V	E^2,V	E^3,V	E^4,V
 **2a**	-	0.029 (red) 0.162 (ox)	0.793 (red) 1.104 (ox)	-	-
 **2b**	-	-0.378 (red) -0.196 (ox)	0.635 (red) 0.892 (ox)	-	-
 **3a**	2.157	-1.046 (red) -0.965 (ox)	-0.023 (red) 0.084 (ox)	0.429 (red) 0.555 (ox)	0.942 (red) 1.050 (ox)
 **3b**	2.136	-1.190 (red) -1.063 (ox)	-0.601 (red) -0.032 (ox)	0.458 (ox)	1.103 (ox)

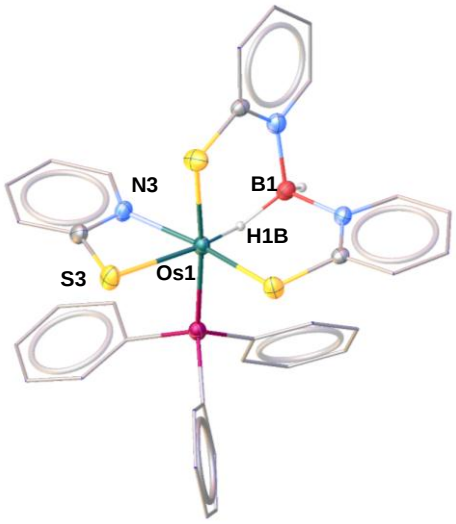


Figure S1. Molecular structure and labelling diagram of *cis*-**7**. Selected bond lengths (Å) and bond angles (˚) of *cis*-**7**: Os1-P1 2.3048(16), Os1-B1 2.394(7), Os1-S1 2.3385(17), Os1-S2 2.4011(18), N3-Os1-P1 92.68(14).

II Experimental Details

General Procedures and Instrumentation

All manipulations were carried out using standard Schlenk line and glove box techniques under inert atmosphere of dry argon. Solvents such as toluene, hexane and THF were distilled through Na/benzophenoneketyl and dichloromethane was dried over calcium hydride prior to use under argon. Chloroform-d was degassed by three freeze-thaw cycles, dried over calcium hydride for 12 h, and stored over 4 Å molecular sieves in a Young's ampoule under argon. $[Os(PPh_3)_3Cl_2]$ was synthesized according to the literature procedure[1] and other chemical such as 2-mercaptobenzothiazole, 2-mercaptopyridine, $BH_3{\cdot}SMe_2$ were obtained commercially (Sigma Aldrich) and used as received. The external reference for the ^{11}B NMR spectroscopy, $[Bu_4N][(B_3H_8)]$ was synthesized according to the literature method.[2] The ^{1}H, $^{11}B\{^{1}H\}$, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra were recorded on Bruker 400 and 500 MHz instruments. The residual solvent protons were used as reference (δ, ppm, benzene-d_6, 7.16, $CDCl_3$, 7.26, Toluene-d_8, 7.09 ppm), while a sealed tube containing $[Bu_4N][(B_3H_8)]$ in benzene-d_6 ($^{\delta}B$, ppm, -30.07) was used as an external reference for $^{11}B\{^{1}H\}$ NMR spectra. ^{1}H decoupled $^{11}B\{^{1}H\}$ spectra of all compounds were processed with a backward linear prediction algorithm to remove the broad $^{11}B\{^{1}H\}$ background signal of the NMR tube.[3] The preparative TLC was performed with Merck 105554 TLC silica gel 60 F254 and thickness of layer 250 µm on aluminum sheets with 20x20 cm size. Mass spectra were carried out using Qtof Micro YA263 HRMS instrument and Bruker MicroTOF-II mass spectrometer in ESI ionization mode. UV-vis absorption spectra were gained from Jasco V-650 spectrometer. Infrared spectra were obtained on a Jasco FT/IR–1400 spectrometer. 6X-ray photoelectron spectroscopy The X-ray photoelectron spectroscopy (XPS) was carried out in the Omicron ESCA probe TPD instrument. Aluminium source (1486.7 eV) was used to generate non-monochromatic X-rays from a dual anode source with an X-ray power of 300 W. The survey scan was done from 0 to 1100 eV with a pass energy of 50 eV and a step size of 0.5 eV to identify all the elements present in the sample. Detailed scans were done for all the elements of interest with a pass energy of 20 eV and a step size of 0.1 eV to get better resolution for the peaks.

II.1 Synthesis and Characterizations

Syntheses of 2a and 3a: In a flame-dried Schlenk tube, $[Os(PPh_3)_3Cl_2]$, **1** (0.500 g, 0.955 mmol) dissolved in 25 mL of toluene, was added to the solution of $K[L^a]$ (L^a = 2-mercaptobenzothiazole, (0.980g, 4.775 mmol) in 30 mL of THF and was thermalized for 12h at 60 °C. The colour of the reaction mixture changed from green to orange (L^a). The solvent was evaporated in vacuum; residue was extracted into hexane/CH_2Cl_2 (80:20 v/v) and passed through Celite. After the removal of solvent from filtrate, the residue was subjected to chromatographic work-up using silica-gel TLC plates. Elution with hexane/CH_2Cl_2 (70:30 v/v) yielded orange **2a** (0.210 g, 42%) and green **3a** (0.095 g, 21%).

Modified Syntheses of 2a and 3a: In a flame-dried Schlenk tube, $[Os(PPh_3)_3Cl_2]$, **1** (0.500 g, 0.955 mmol) dissolved in 25 mL of toluene, was added to the solution of $K[L^a]$ (L^a = 2-mercaptobenzothiazole, (0.980g, 4.775 mmol) in 30 mL of THF. Then, an excess amount of triethylamine (NEt_3) was added to the mixture and was thermalized for 8h at 45 °C. The colour of the reaction mixture changed from green to yellow (L^a). The solvent was evaporated in vacuum; residue was extracted into hexane/CH_2Cl_2 (80:20 v/v) and passed through Celite. After the removal of solvent from filtrate, the residue was subjected to chromatographic work-up using silica-gel TLC plates. Elution with hexane/CH_2Cl_2 (70:30 v/v) yielded orange **2a** (0.175 g, 30%) and green **3a** (0.158 g, 35%).

2a: MS (ESI$^+$): *m/z* calculated for [M+H]$^+$: 1049.1084, found: 1049.1018; ^{1}H NMR (500 MHz, $CDCl_3$, 22 °C): δ = 7.94 (d, J = 8.04 Hz, 2H $Ar_{(mbz)}$), 7.15 (d, J = 8.22 Hz, 2H $Ar_{(mbz)}$), 6.84 – 7.25 (m, 30H, $Ar_{(Phosphine)}$ + 4H, $Ar_{(mbz)}$) ppm; $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 22 °C): δ = -5.5 (s, 2P); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 22 °C): δ = 185.7 (s, C=S, mbz), 149.7 (s, C-N, mbz), 137.4–117.8 (s, Ar) ppm.

3a: MS (ESI$^+$): *m/z* calculated for [M+Na]$^+$: 974.9771, found: 974.9754.

Syntheses of 2b and 3b: Under similar reactions conditions as above, reaction of $[Os(PPh_3)_3Cl_2]$, **1** (0.500 g, 0.955 mmol) and $K[L^b]$ (L^b = 2-mercaptopyridine , 0.712 g, 4.775 mmol) yielded yellow solid **2b** (0.205 g, 46%) and violet **3b** (0.097 g,18%).

Modified Syntheses of 2b and 3b: Under similar reactions conditions as above, reaction of $[Os(PPh_3)_3Cl_2]$, **1** (0.500 g, 0.955 mmol) and $K[L^b]$ (L^b = 2-mercaptopyridine , 0.712 g, 4.775 mmol) in the presence of excess NEt_3 yielded yellow solid **2b** (0.142 g, 32%) and violet **3b** (0.135 g,25%).

2b: MS (ESI$^+$): *m/z* calculated for [M]$^+$: 936.1569, found: 936.1434; ^{1}H NMR (500 MHz, $CDCl_3$, 22 °C): δ 7.57 (d, J = 5.2 Hz, 2H $Ar_{(mp)}$), 6.81 (t, J = 7.90 Hz, 2H $Ar_{(mp)}$), 6.23 (d, J = 6.36 Hz, 2H $Ar_{(mp)}$), 6.14 (t, J = 6.36 Hz, 2H $Ar_{(mp)}$), 7.21 (m, 12H $Ar_{(Phosphine)}$), 6.97 (m, 12H $Ar_{(Phosphine)}$), 7.08 (m, 6H $Ar_{(Phosphine)}$), $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 22 °C): δ = -4.3 (s, 2P); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 22 °C): δ = 184.3 (s, C=S, mp), 144.5 (s, C-N, mp), 137.5–115.2 (s, Ar) ppm.

3b: MS (ESI$^+$): *m/z* calculated for [M+H]$^+$: 785.0796, found: 785.0740.

Syntheses of 4a and **4b**: In a flame-dried Schlenk tube, $[(PPh_3)_2Os(\kappa^2\text{-}N,S\text{-}C_7H_4NS_2)_2]$, **2a** (100 mg, 0.093 mmol) in 15 mL dry toluene was treated with stoichiometric $BH_3{\cdot}SMe_2$ at room temperature. The reaction mixture was allowed to stir at room temperature for 12 h. The volatile components were removed under vacuum and the remaining residue was extracted into hexane/CH_2Cl_2 (80:20 v/v) and passed through Celite. After removal of the solvent, the residue was subjected to chromatographic work-up by using TLC plates. Elution with hexane/CH_2Cl_2 (80:20 v/v) mixture yielded yellow solid **4a** (27 mg, 28%).

Under similar reaction conditions, reaction of $[(PPh_3)_2Os(\kappa^2\text{-}N,S\text{-}C_5H_4NS)_2]$, **2b** (100 mg, 0.106 mmol) with stoichiometric $BH_3{\cdot}SMe_2$ yielded orange solid **4b** (17 mg, 16%).

4a: MS (ESI$^+$): *m/z* calculated for [M-H]$^+$: 1061.1258, found: 1061.1318; $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$, 22 °C): δ = -3.3 (br, 1B) ppm; δ = 7.89 (d, J = 8.35 Hz, 2H $Ar_{(mbz)}$), 7.29 (d, J = 8.06 Hz, 2H $Ar_{(mbz)}$), 7.07 (d, J = 7.46 Hz, 2H $Ar_{(mbz)}$), 7.03 (t, J = 7.75 Hz, 2H $Ar_{(mbz)}$), 6.95-7.77 (m, 30H, $Ar_{(Phosphine)}$) 3.55 (br, B-H_t), -7.78 (br,1H, Os-H_b-B), -13.26 (br,1H, Os-H_t) ppm; $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 22 °C): δ = 19.2 (s, 2P) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 22 °C): δ = 197.0 (s, C=S, mbz), 143.3 (s, C-N, mbz), 136.7–115.6 (s, Ar) ppm; IR (dicholoromethane, cm^{-1}): $\tilde{\nu}$ = 2537 (BH_t), 1073 (C=S).

4b: MS (ESI$^+$): *m/z* calculated for [M-BH_3]$^+$: 936.1569, found: 936.1506; $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$, 22 °C): δ = 10.1 (br, 1B) ppm ^{1}H NMR (500 MHz, $CDCl_3$, 22 °C): δ = 7.60-6.95 (m, H_{Ar}) {Due to the presence of an inseparable impurity, we were unable to assign the aromatic protons of **4b**), 3.55 (br, B-H_t), -9.36 (br,1H, Os-H_b-B), -12.57 (br,1H, Os-H_t) ppm; $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 22 °C): δ = 28.9 (s, 2P) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 22 °C): δ = 146.1 (s, C-N, mbz), 135.6–114.0 (s, Ar) ppm; IR (dicholoromethane, cm^{-1}): $\tilde{\nu}$ = 2477 (BH_t), 1032 (C=S).

Synthesis of 5: In a flame-dried Schlenk tube **3b** (100 mg, 0.142 mmol) in 15 mL dry toluene was treated with stoichiometric $BH_3{\cdot}SMe_2$ at room temperature. The reaction mixture was allowed to stir

at room temperature for 2 h. The volatile components were removed under vacuum and the remaining residue was extracted into hexane/CH_2Cl_2 (60:40 v/v) and passed through Celite. After removal of the solvent, the residue was subjected to chromatographic work-up by using TLC plates. Elution with hexane/CH_2Cl_2 (65:35 v/v) mixture yielded orange solid **5** (18 mg, 18%).

5: MS (ESI$^+$): *m/z* calculated for [M-H]$^+$: 703.0854, found: 703.0827; $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$, 22 °C): δ = 62.5 (br, 1B) ppm; ^1H NMR (500 MHz, $CDCl_3$, 22 °C):): δ 8.38 (d, J = 6.26 Hz, 2H $Ar_{(mp)}$), 8.23 (d, J = 6.67 Hz, 1H $Ar_{(mp)}$), 7.79 (d, J = 8.62 Hz, 1H $Ar_{(mp)}$), 6.92 (t, J = 7.67 Hz, 1H $Ar_{(mp)}$), 6.72 (t, J = 6.89 Hz, 1H $Ar_{(mp)}$), 6.47 (d, J = 8.25 Hz, 1H $Ar_{(mp)}$), 6.28 (d, J = 6.31 Hz, 1H $Ar_{(mp)}$), 7.28-7.61 (m, 15H $Ar_{(Phosphine)}$, 3.90 (br, O*H*), -13.66 (br, 1H, Os-H_b-B), -13.81 (br,1H, Os-H_b-B) ppm; $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 22 °C): δ = 16.4 (s, 1P) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 22 °C): δ = 182.4 (s, C=S, mp), 150.7, 146.9 (s, C-N, mp), 138.2–113.5 (s, Ar) ppm; IR (dicholoromethane, cm^{-1}): $\tilde{\nu}$ = 3393 (OH), 1070 (C=S).

Synthesis of *trans*-**6**: In a flame-dried Schlenk tube **3a** (100 mg, 0.106 mmol) in 10 mL dry toluene was treated with stoichiometric $BH_3{\cdot}SMe_2$ at room temperature. The reaction mixture was allowed to stir at room temperature for 2 h. The volatile components were removed under vacuum and the remaining residue was extracted into hexane/CH_2Cl_2 (85:15 v/v) and passed through Celite. After removal of the solvent, the residue was subjected to chromatographic work-up by using TLC plates. Elution with a *n*-hexane/CH_2Cl_2 (70:30 v/v) mixture yielded red solid *trans*-**6** (21 mg, 21%).

trans-**6:** MS (ESI$^+$): *m/z* calculated for [M]$^+$: 965.0124, found: 965.0099; $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$, 22 °C): δ = -3.7 (br, 1B) ppm;^1H NMR (500 MHz, $CDCl_3$, 22 °C): 7.92 (d, J = 8.58 Hz, 2H $Ar_{(mbz)}$), 7.65 (d, J = 8.08 Hz, 2H $Ar_{(mbz)}$), 6.93 (t, J = 7.66 Hz, 1H $Ar_{(mbz)}$), 7.00 (t, J = 7.67 Hz, 1H $Ar_{(mbz)}$), 7.11-7.47 (m, 15H, $Ar_{(Phosphine)}$ + 6H, $Ar_{(mbz)}$), 5.15 (br, B-H_t) -4.56 (br,1H, Os-H_b-B) ppm; $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 22 °C): δ = 9.1 (s, 1P) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 22 °C): δ = 193.4, 185.0 (s, C=S, mbz), 149.7-143.5 (s, C-N, mbz), 132.9–114.9 (s, Ar) ppm; IR (dicholoromethane, cm^{-1}): $\tilde{\nu}$ = 2563 (BH_t), 1037 (C=S).

Synthesis of *cis*-**6 and** *cis*-**7**: In a flame-dried Schlenk tube, $[Os(PPh_3)_3Cl_2]$, **1** (0.100 g, 0.191 mmol) dissolved in 10 mL of toluene, was added to the solution of $Na[(H_2B)(L^a)_2]$ (L^a = 2-mercaptobenzothiazole, 0.141 g, 0.382 mmol) in 10 mL of THF and was thermalized for 12h at 60 °C. The colour of the reaction mixture changed from green to red (L^a). The solvent was evaporated in vacuum; residue was extracted into hexane/CH_2Cl_2 (60:40 v/v) and passed through Celite. After the removal of solvent from filtrate, the residue was subjected to chromatographic work-up using silica-gel TLC plates. Elution with hexane/CH_2Cl_2 (80:20 v/v) yielded yellow *cis*-**6** (20 mg, 11%).

Under similar reaction conditions as above, reaction of $[Os(PPh_3)_3Cl_2]$, **1** (0.100 g, 0.191 mmol) and $Na[(H_2B)(L^b)_2]$ (L^b = 2-mercaptopyridine, 0.94 g, 0.382 mmol) yielded red solid *cis*-**7** (20mg, 13%).

cis-**6:** MS (ESI$^+$): *m/z* calculated for [M]$^+$: 965.0124, found: 965.0106; $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$, 22 °C): δ = -3.6 (br, 1B) ppm;^1H NMR (500 MHz, $CDCl_3$, 22 °C): 8.26 (d, J = 8.28 Hz, 1H $Ar_{(mbz)}$), 7.81 (d, J = 7.95 Hz, 2H $Ar_{(mbz)}$), 7.36 (d, J = 8.35 Hz, 1H $Ar_{(mbz)}$), 7.31 (d, J = 7.75 Hz, 2H $Ar_{(mbz)}$), 7.08 (t, J = 7.65 Hz, 1H $Ar_{(mbz)}$), 6.73 (t, J = 7.49 Hz, 1H $Ar_{(mbz)}$), 6.58 (t, J = 7.49 Hz, 1H $Ar_{(mbz)}$), 6.45 (d, J = 8.21 Hz, 1H $Ar_{(mbz)}$), 7.03-7.61 (m, 15H, $Ar_{(Phosphine)}$ + 2H, $Ar_{(mbz)}$), 5.74 (br, B-H_t), -13.83 (br,1H, Os-H_b-B) ppm; $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 22 °C): δ = 4.6 (s, 1P) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 22 °C): δ = 184.7, 183.1 (s, C=S, mbz), 148.0-144.1 (s, C-N, mbz), 135.6–115.0 (s, Ar) ppm; IR (dicholoromethane, cm^{-1}): $\tilde{\nu}$ = 2475 (BH_t), 1025 (C=S).

cis-**7**: *m/z* calculated for [M]$^+$: 797.0968, found: 797.0968; $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$, 22 °C): δ = 13.9 (br, 1B) ppm; ^1H NMR (500 MHz, $CDCl_3$, 22 °C): 8.22 (d, J = 6.24 Hz, 2H $Ar_{(mp)}$), 7.76 (d, J = 6.52 Hz,

2H $Ar_{(mp)}$), 6.59 (t, J = 6.52 Hz, 2H $Ar_{(mp)}$), 6.44 (t, J = 6.22 Hz, 2H $Ar_{(mp)}$), 6.25 (d, J = 8.08 Hz, 2H $Ar_{(mp)}$), 6.09 (t, J = 6.43 Hz, 2H $Ar_{(mp)}$), 6.17-7.35 (m, 15H, $Ar_{(Phosphine)}$),4.55 (br, B-H_t), -12.46 (br,1H, Os-H_b-B) ppm; $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 22 °C): δ = 2.9 (s, 1P) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 22 °C): δ = 197.8, 182.2, 182.1 (s, C=S, mp), 150.1-143.5 (s, C-N, mp), 134.3–114.4 (s, Ar) ppm; IR (dicholoromethane, cm^{-1}): $\tilde{\nu}$ = 2572 (BH_t), 1110 (C=S).

II.2 Spectroscopic details

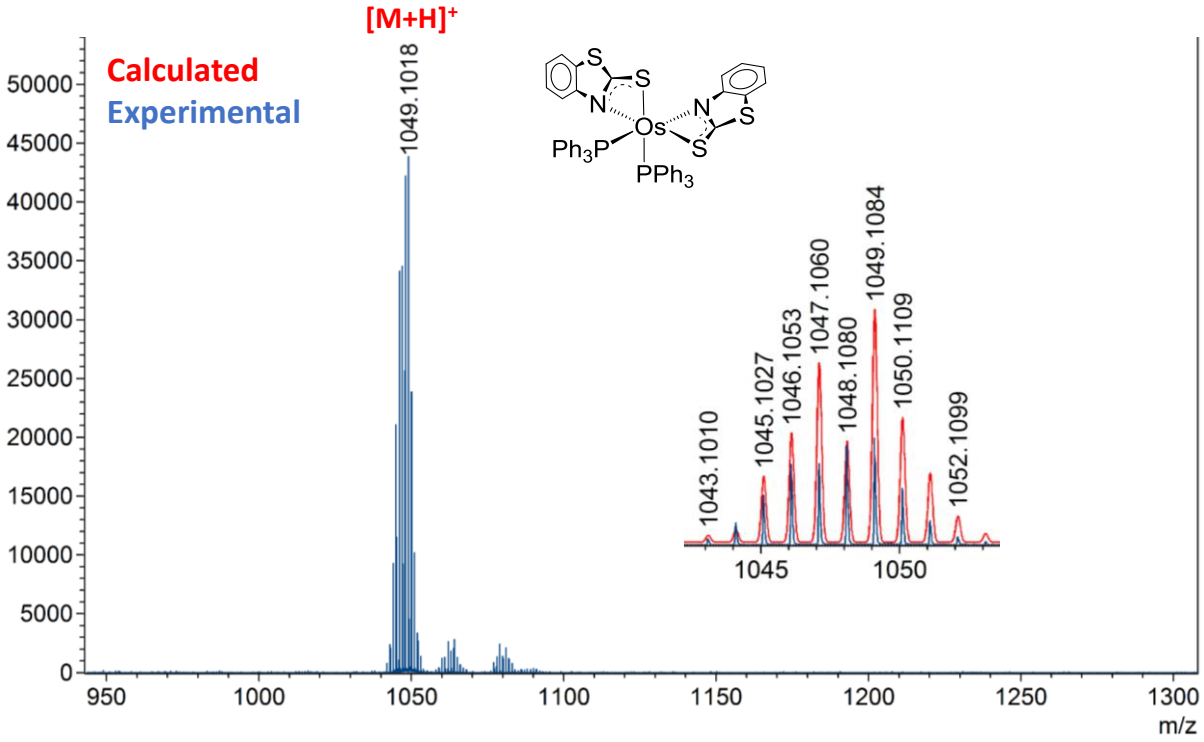


Figure S2. ESI-MS spectrum of **2a**.

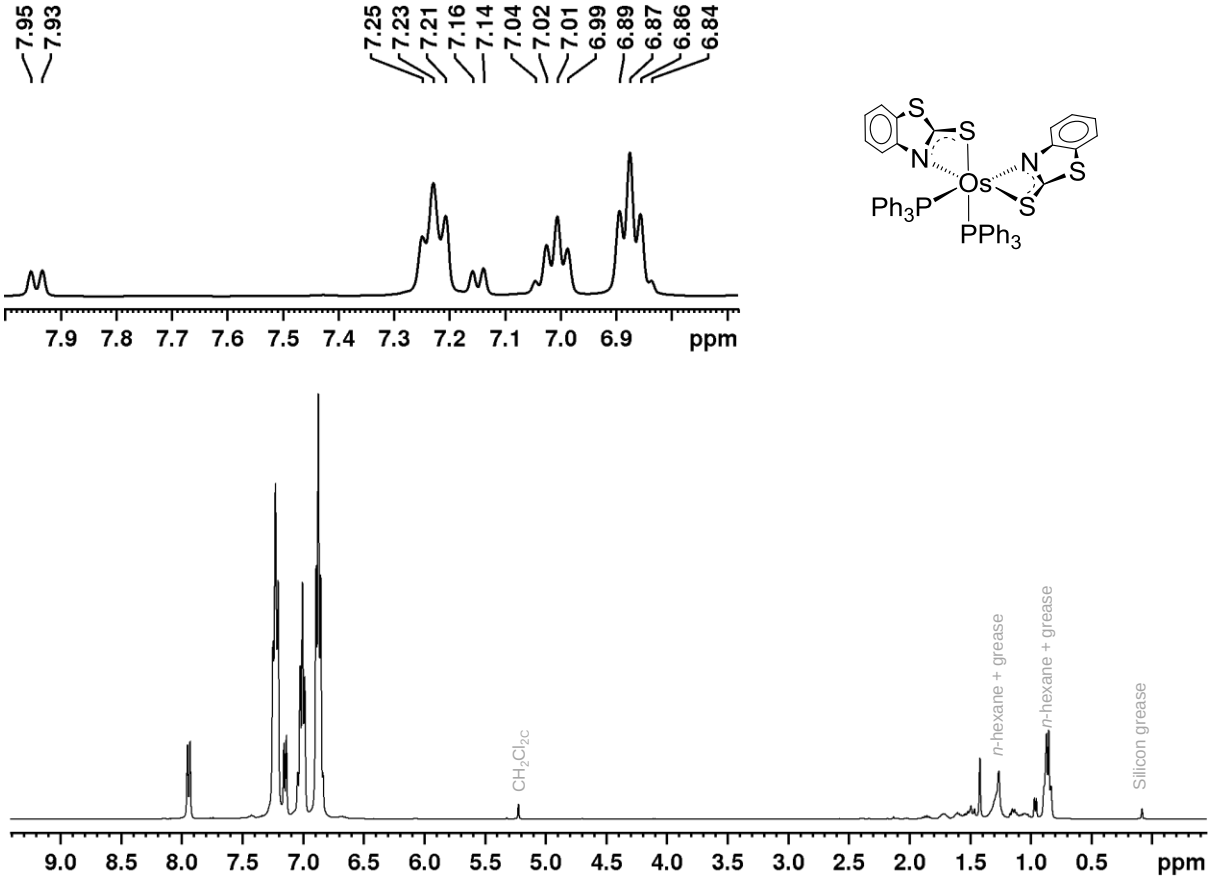


Figure S3. ^{1}H NMR spectrum of **2a** in $CDCl_3$.

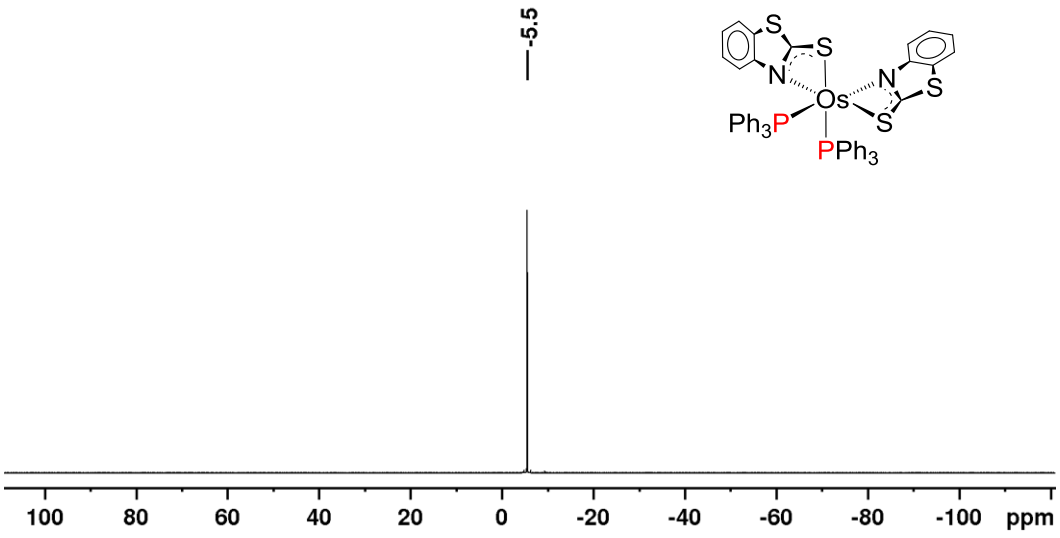


Figure S4. $^{31}P\{^{1}H\}$ NMR spectrum of **2a** in $CDCl_3$.

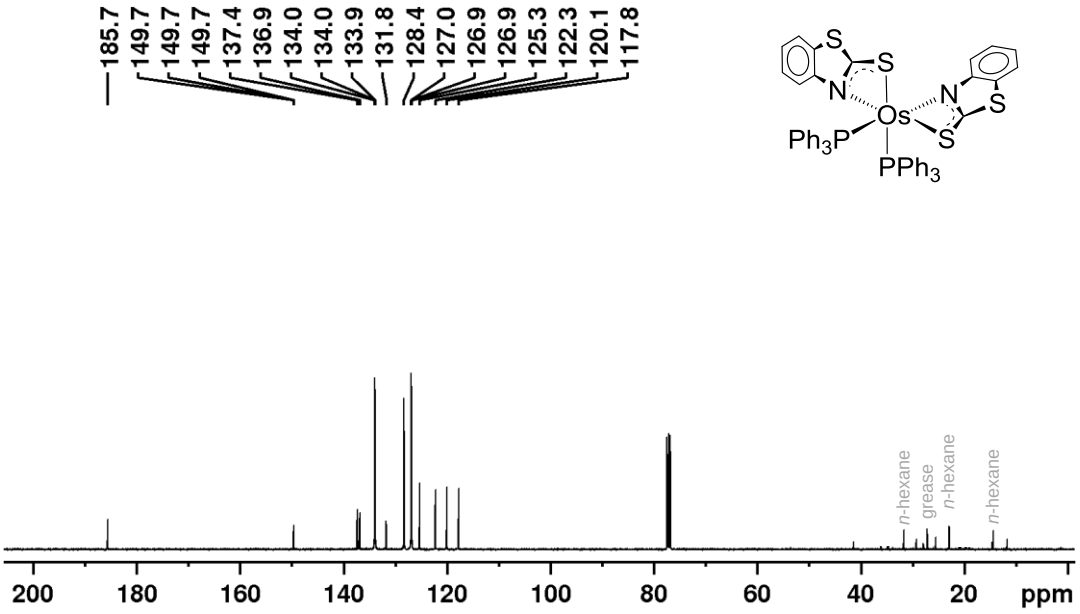


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of **2a** in $CDCl_3$.

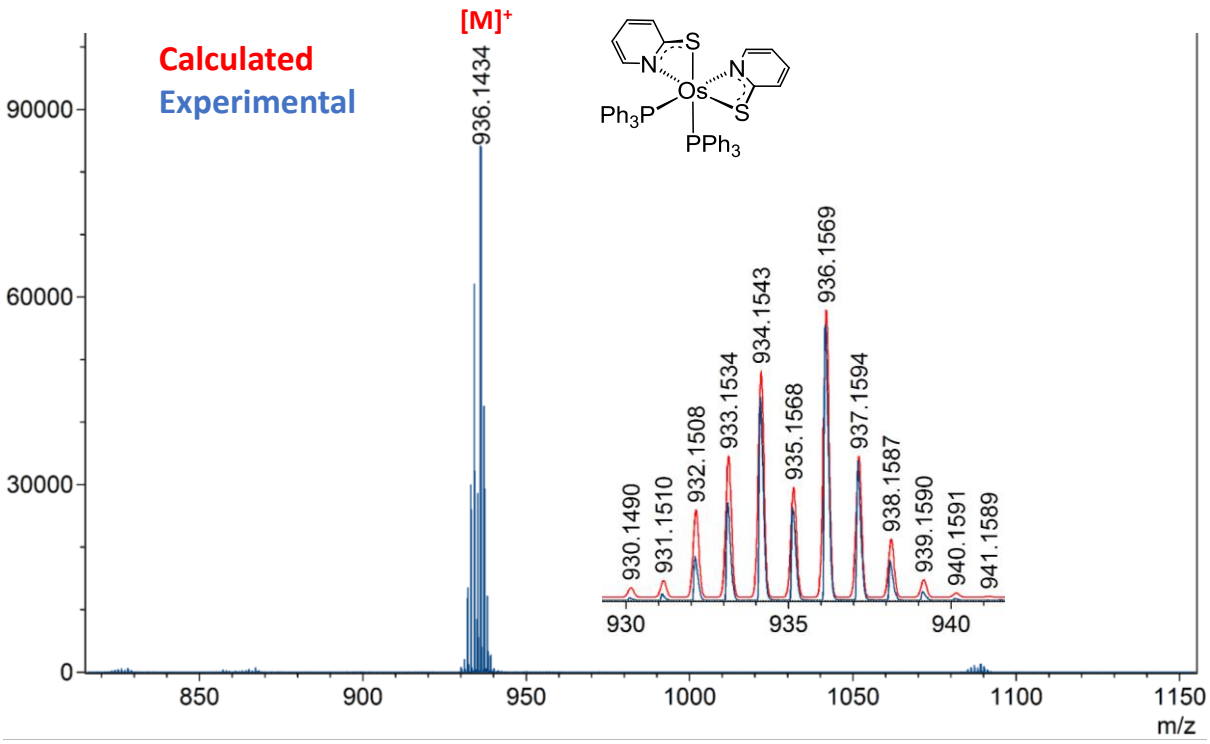


Figure S6. ESI-MS spectrum of **2b**.

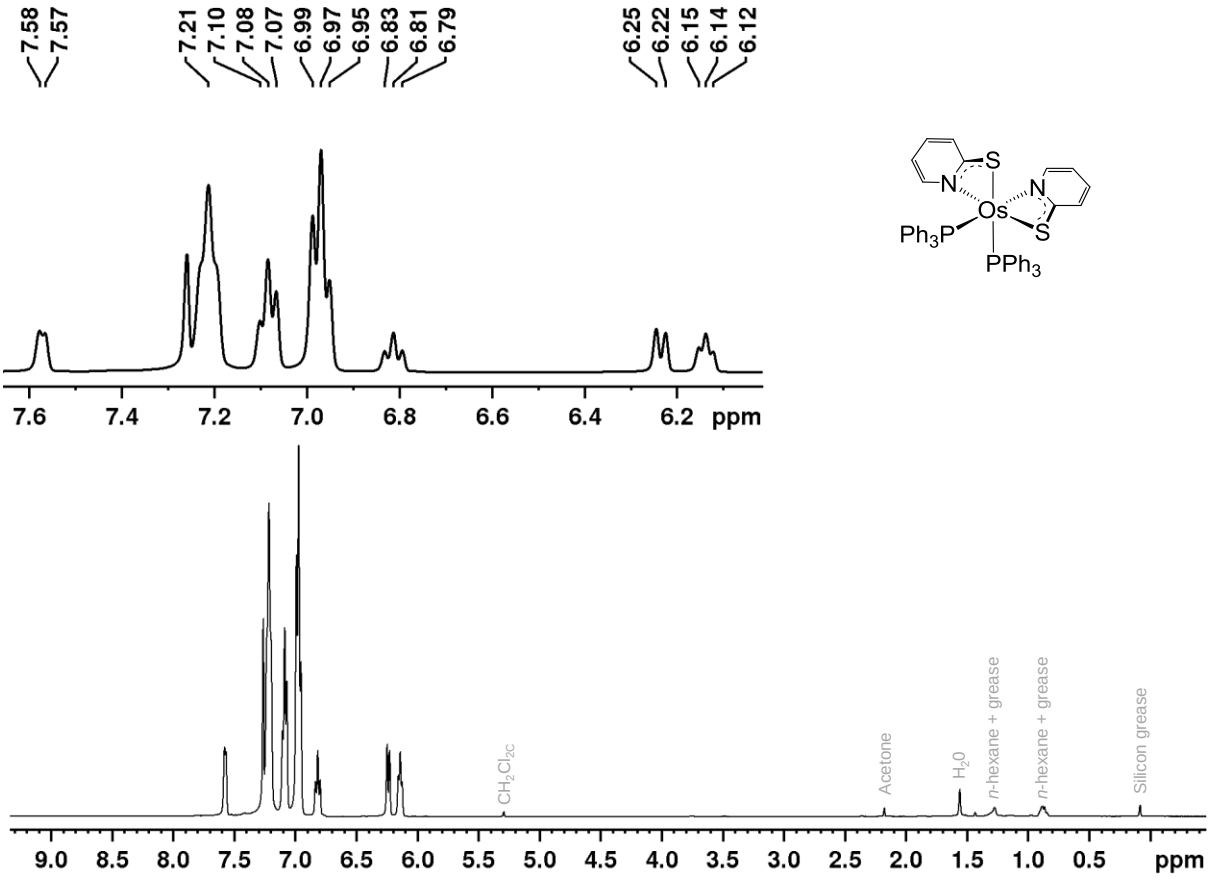


Figure S7. ^{1}H NMR spectrum of **2b** in $CDCl_3$.

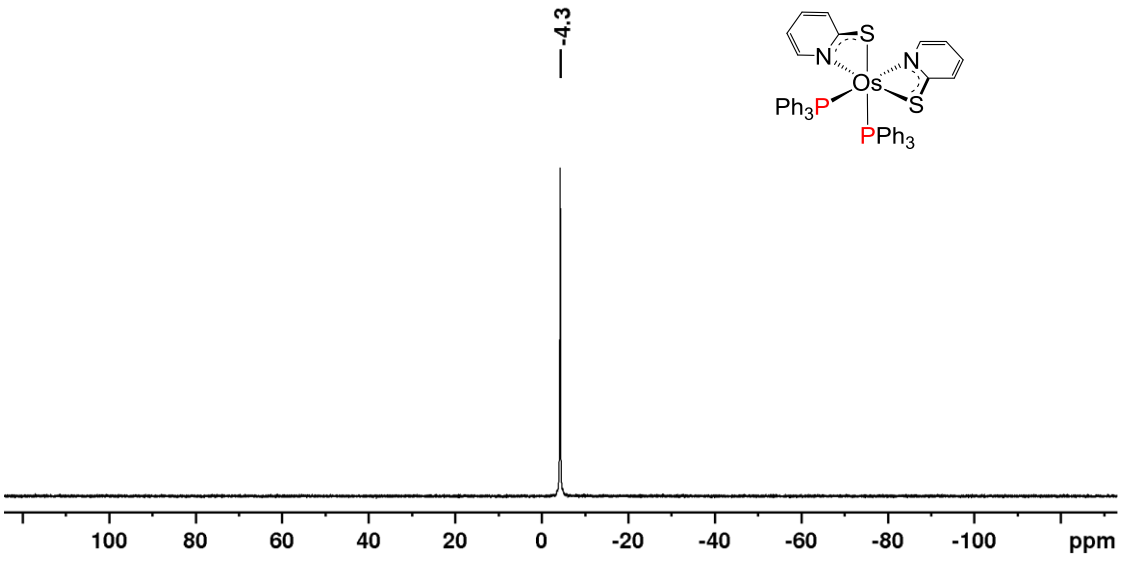


Figure S8. $^{31}P\{^{1}H\}$ NMR spectrum of **2b** in $CDCl_3$.

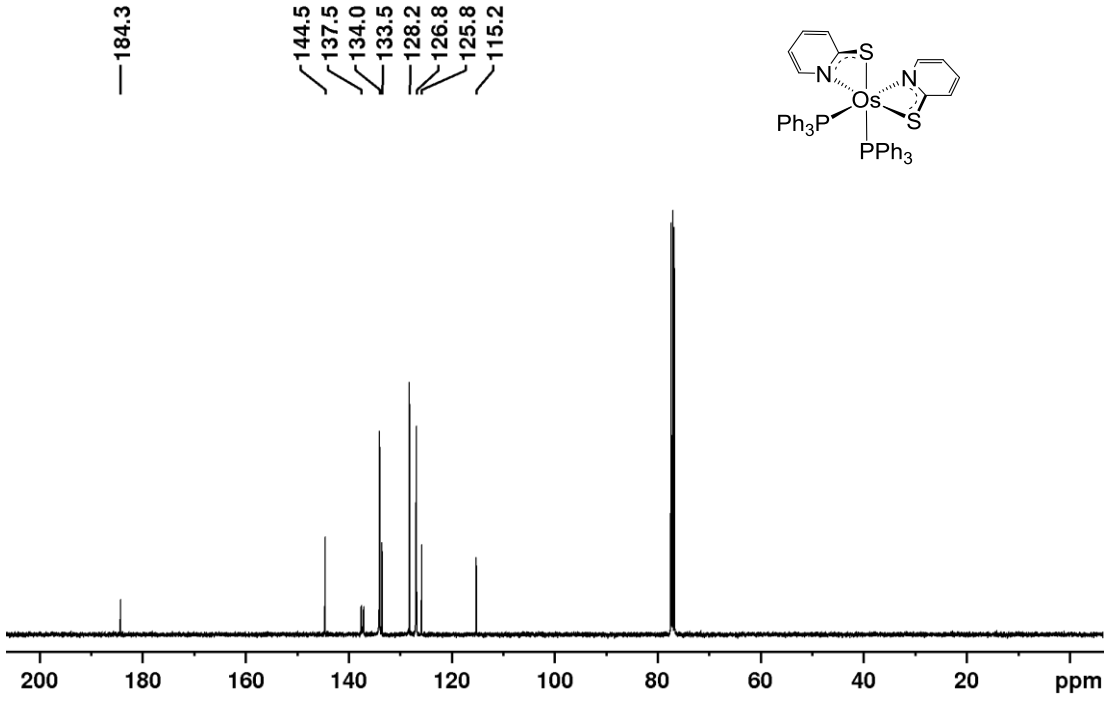


Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of **2b** in $CDCl_3$.

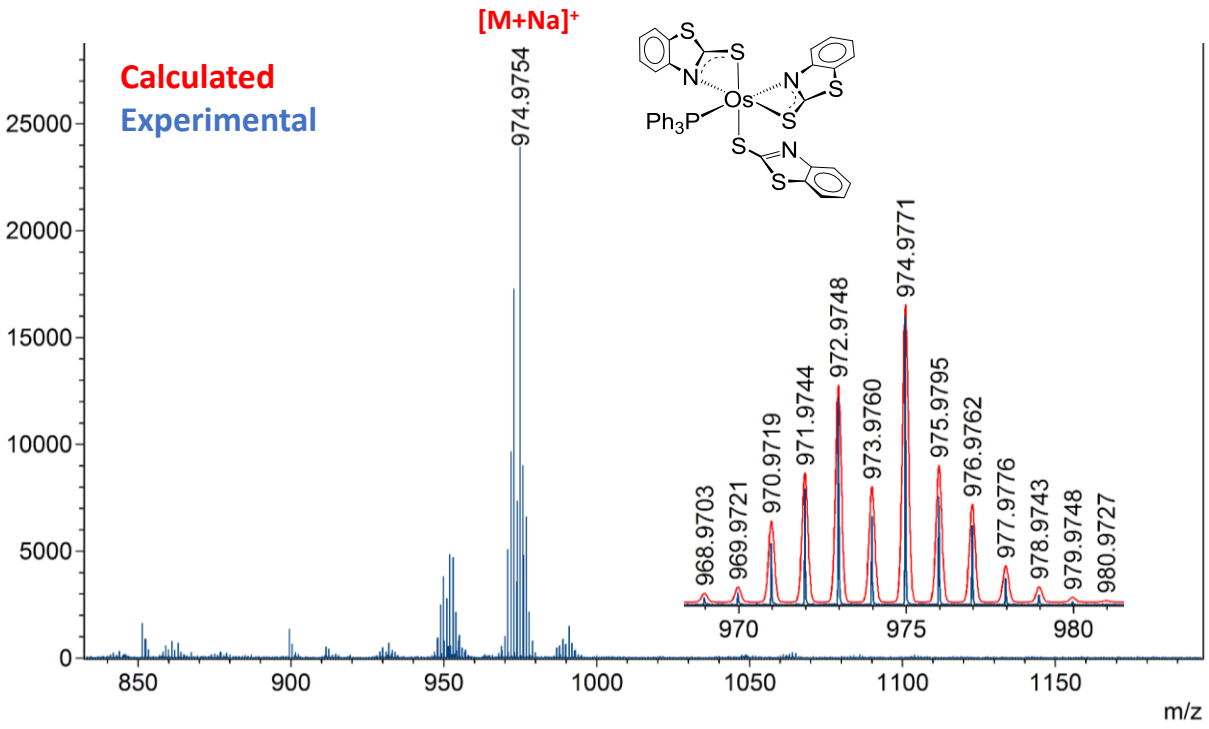


Figure S10. ESI-MS spectrum of **3a**.

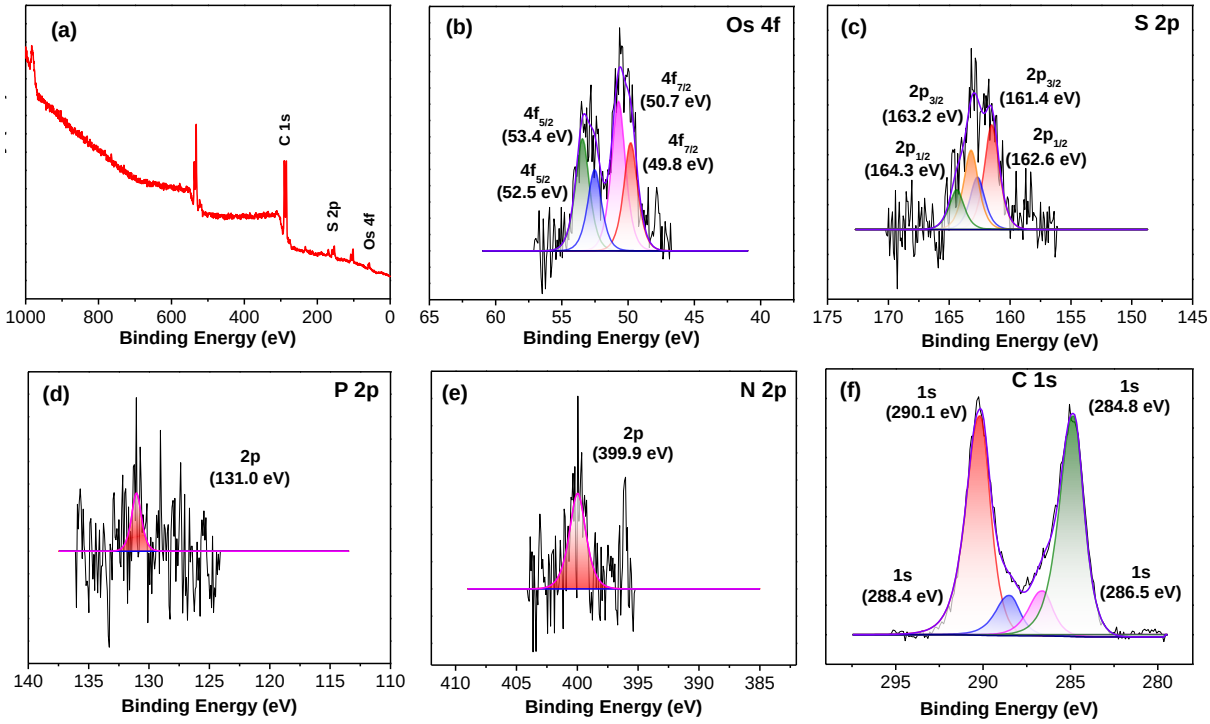


Figure S11. (a) XPS survey spectrum of **3a** and elemental spectrum of Os(b), S(c), P(d), N(e) and C(f).

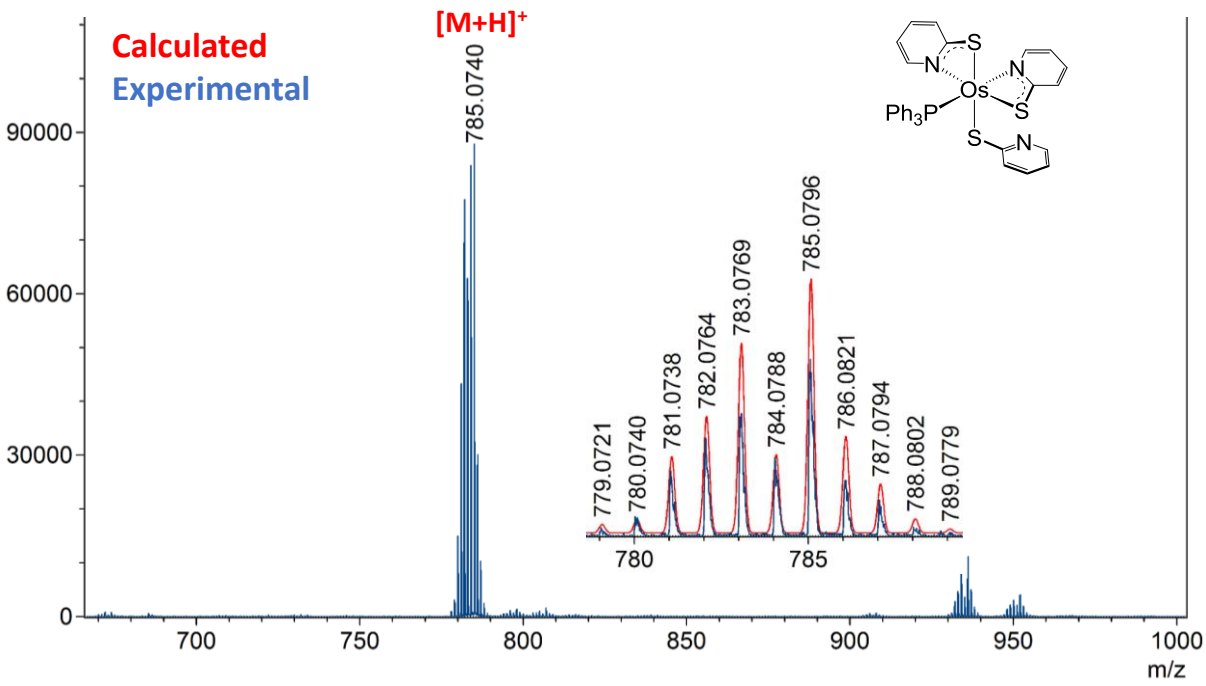


Figure S12. ESI-MS spectrum of **3b**.

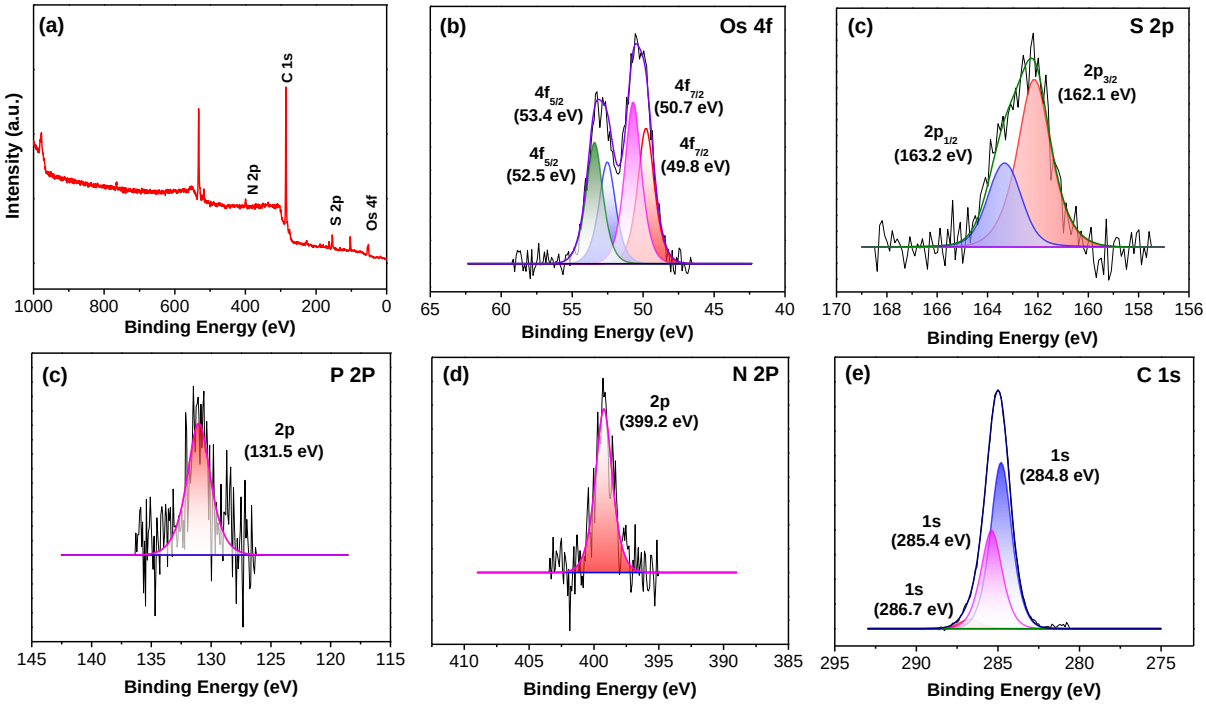


Figure S13. (a) XPS survey spectrum of **3b** and elemental spectrum of Os(b), S(c), P(d), N(e) and C(f).

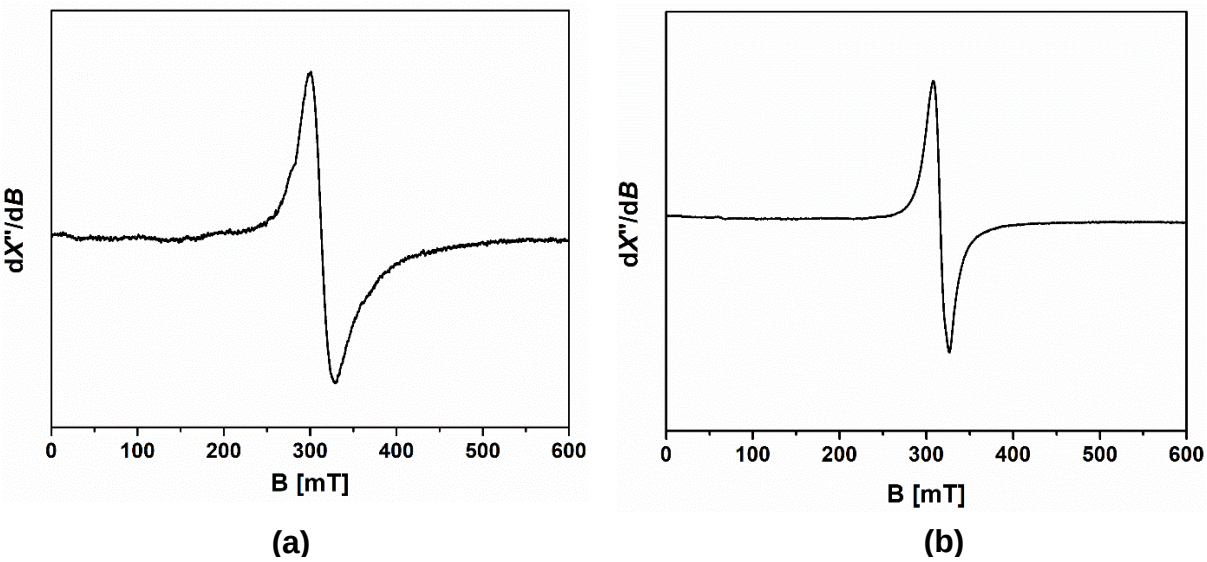


Figure S14. EPR spectrum of **3a** (a) and **3b** (b).

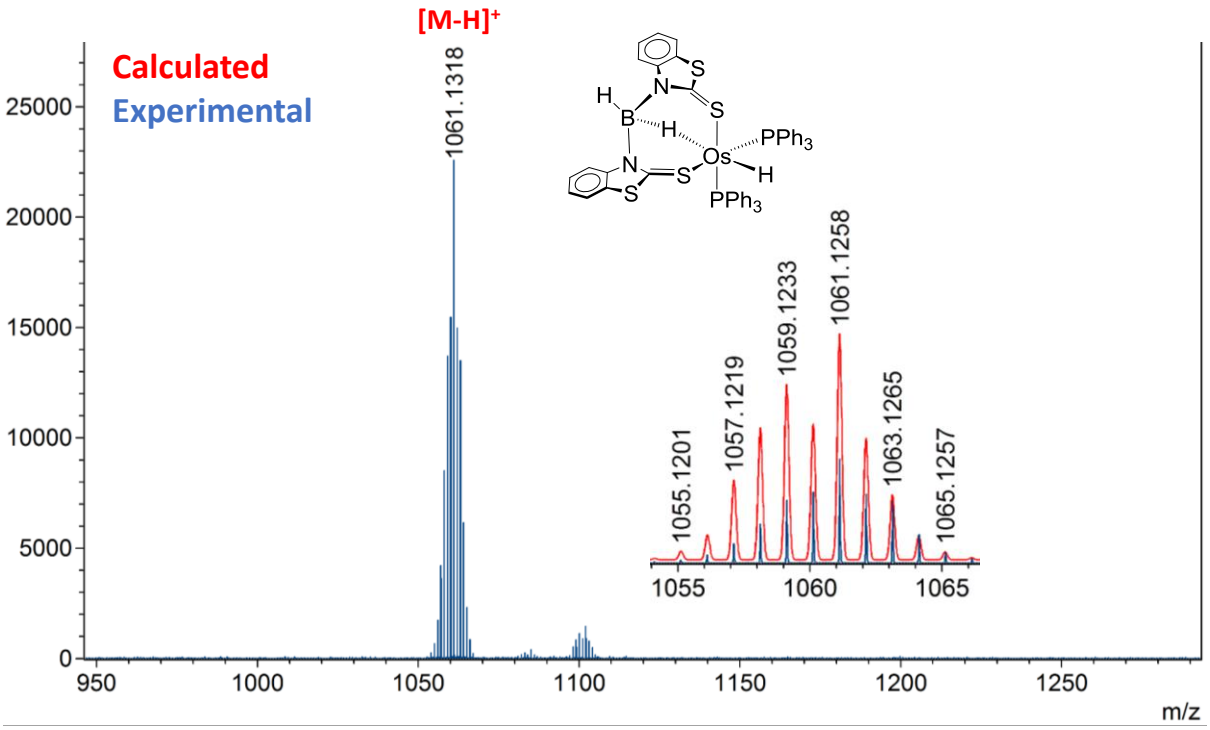


Figure S15. ESI-MS spectrum of **4a**.

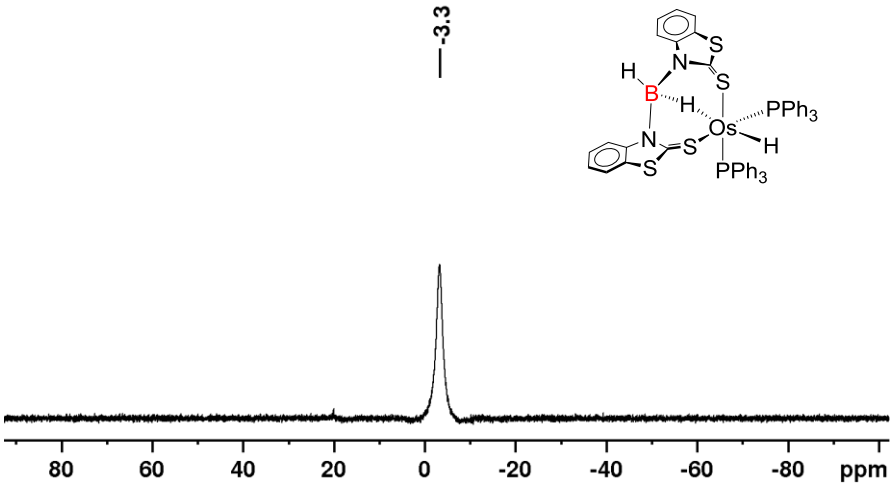


Figure S16. $^{11}B\{^{1}H\}$ NMR spectrum of **4a** in $CDCl_3$.

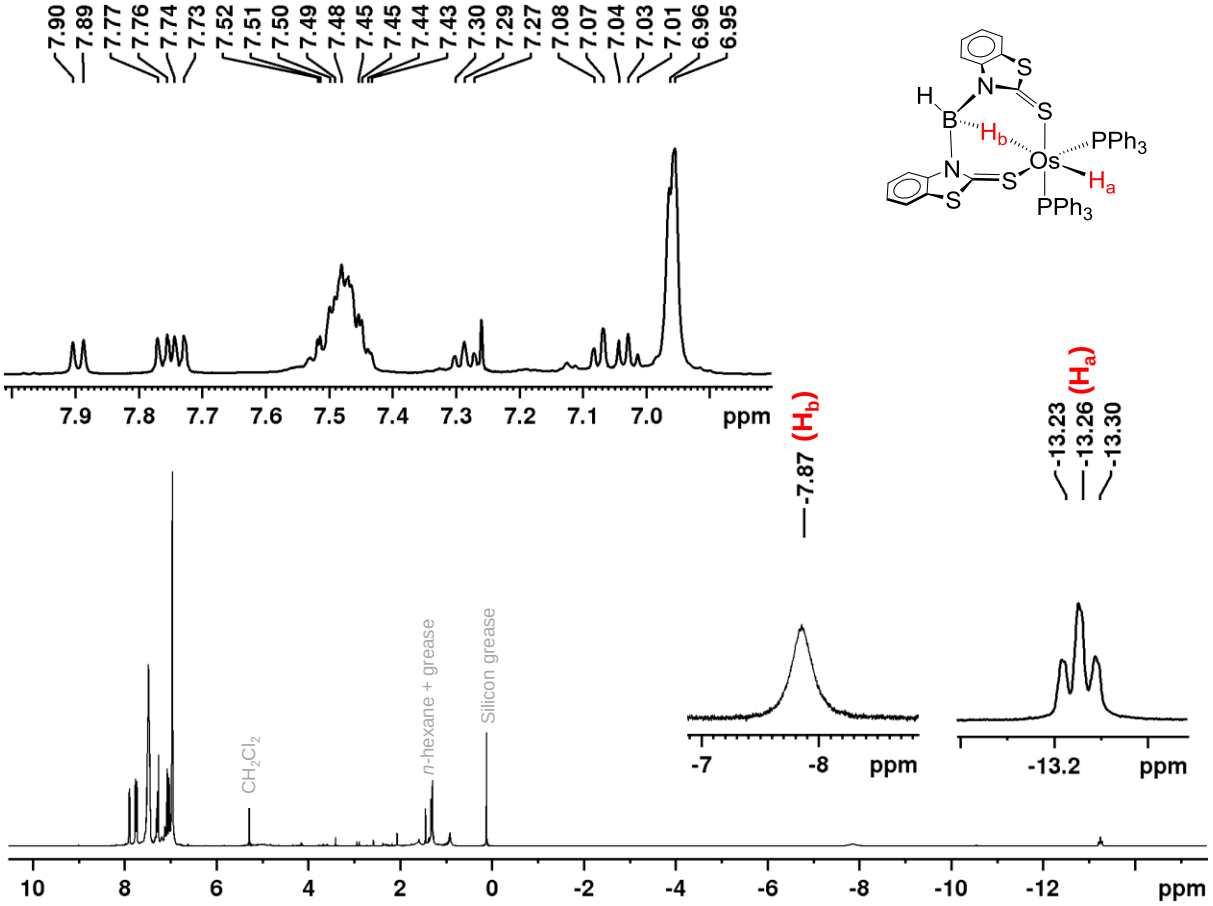


Figure S17. ^{1}H NMR spectrum of **4a** in $CDCl_3$.

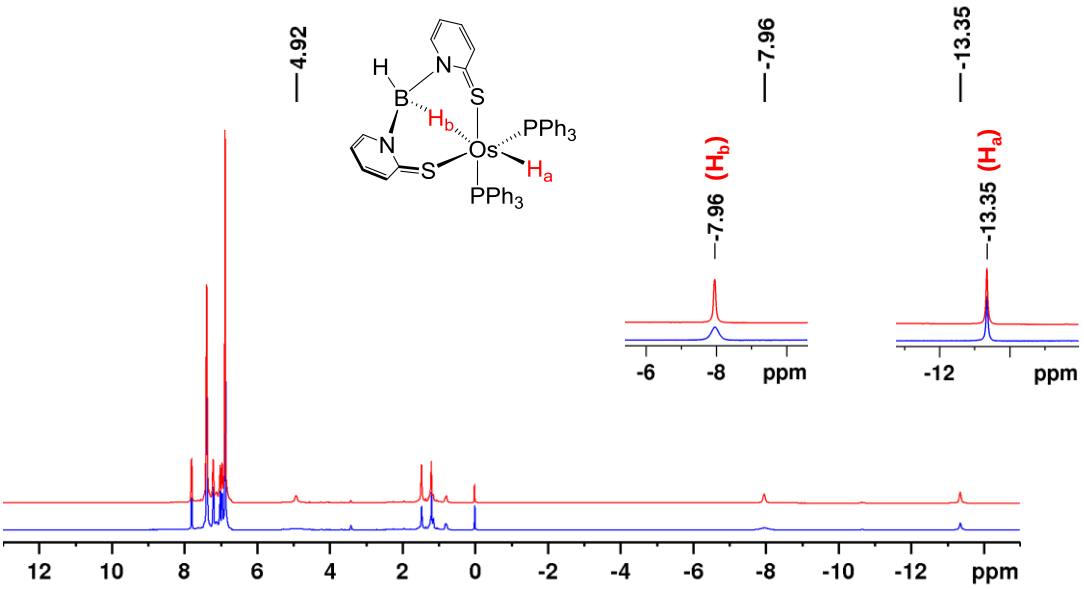


Figure S18. Stacked ^{1}H (blue) and $^{1}H\{^{11}B\}$ (red) NMR spectrum of **4a** in $CDCl_3$

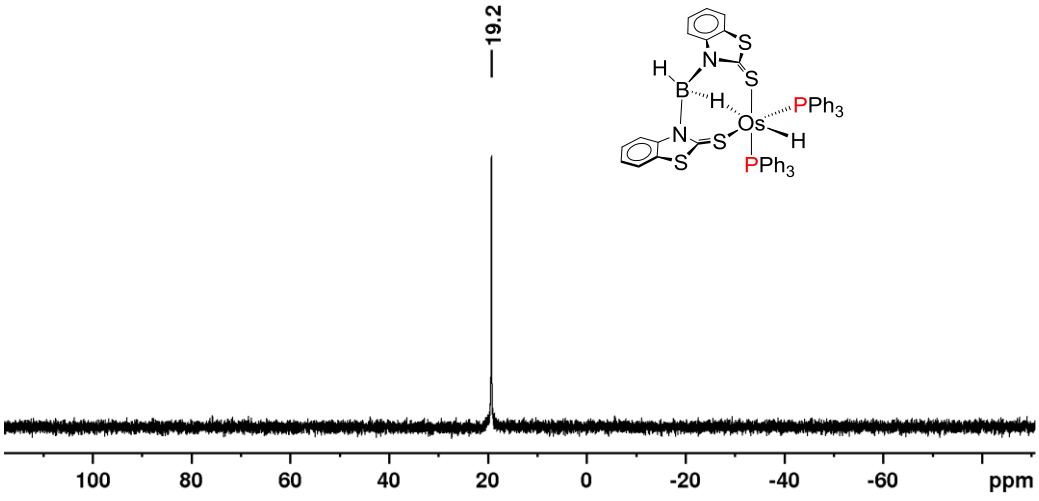


Figure S19. $^{31}P\{^{1}H\}$ NMR spectrum of **4a** in $CDCl_3$.

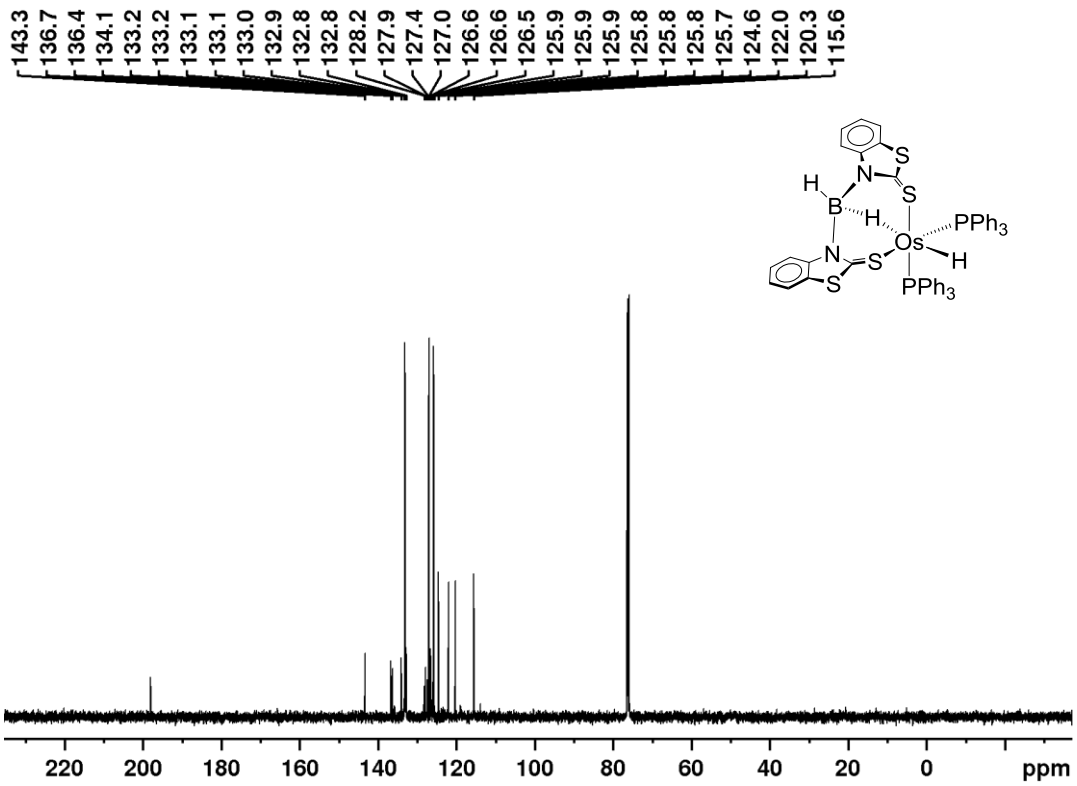


Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum of **4a** in $CDCl_3$.

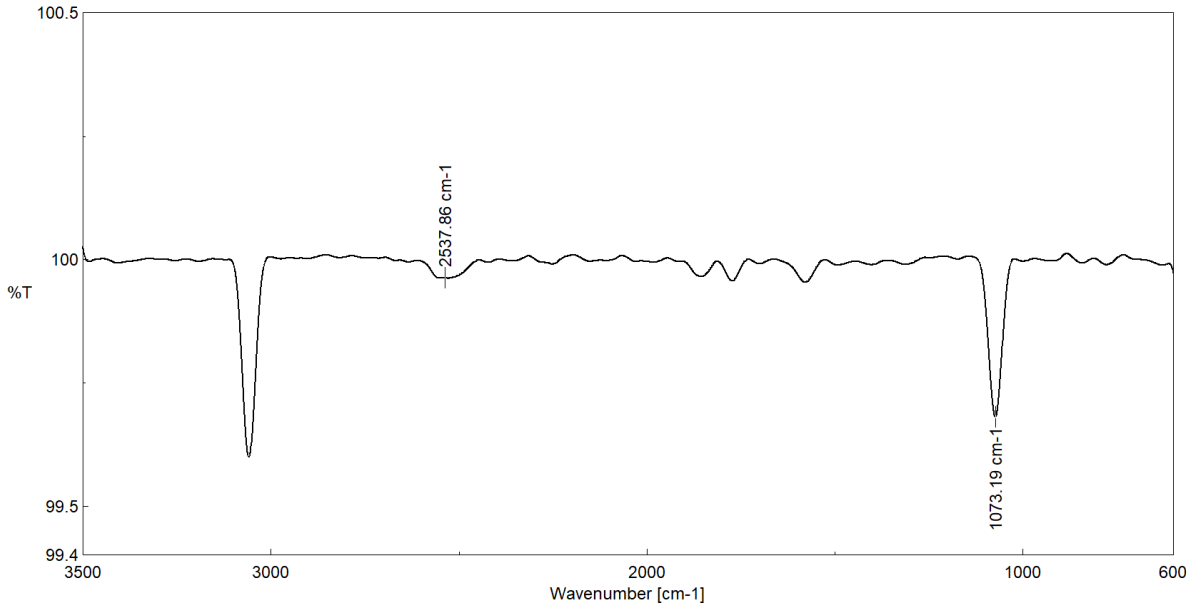


Figure S21. IR spectrum of **4a** in CH_2Cl_2.

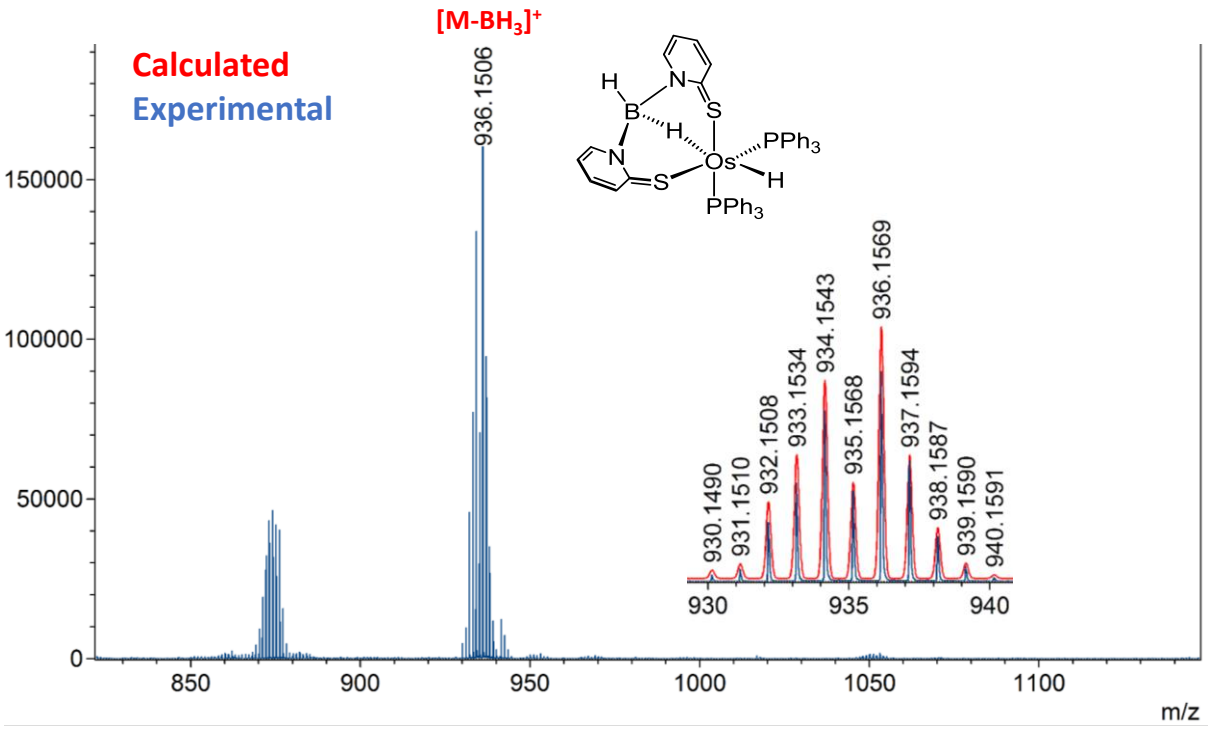


Figure S22. ESI-MS spectrum of **4b**.

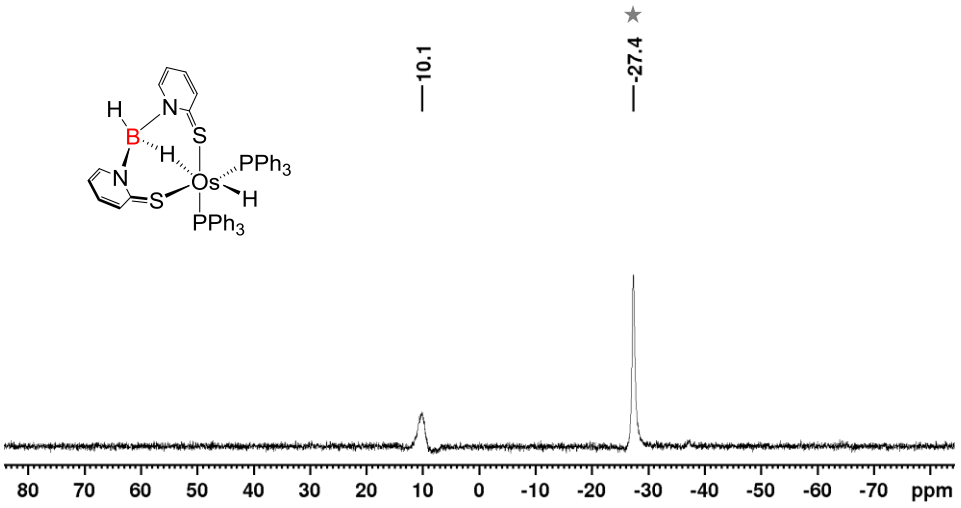


Figure S23. $^{11}B\{^{1}H\}$ NMR spectrum of **4b** in $CDCl_3$. (*inseparable impurity, which might appear due to the formation of mercaptopyridine-borane adduct)

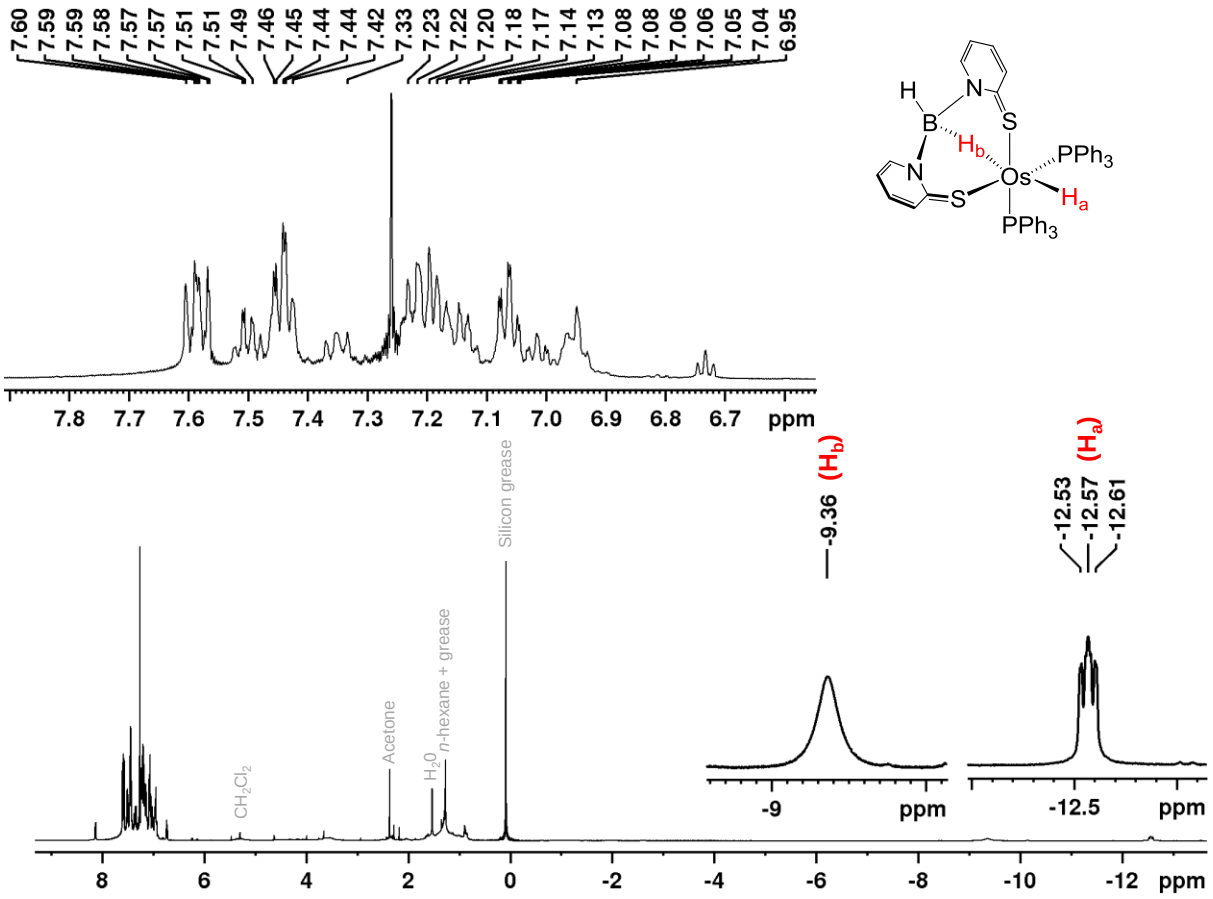


Figure S24. ^{1}H NMR spectrum of **4b** in $CDCl_3$.

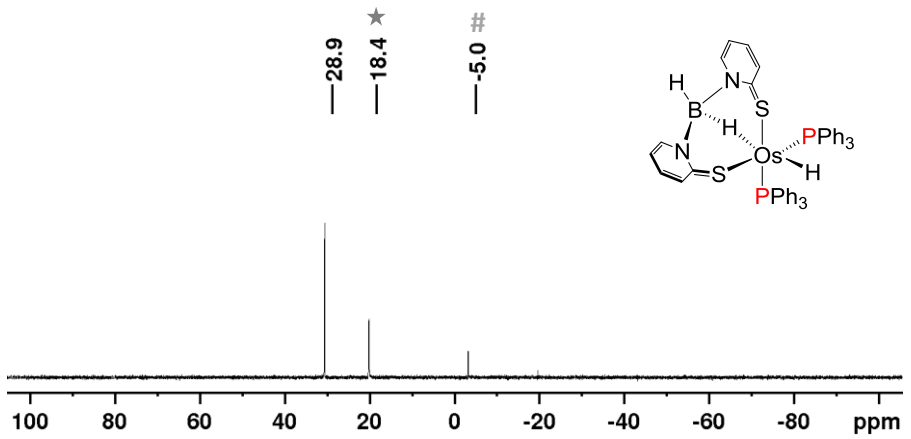


Figure S25. $^{31}P\{^{1}H\}$ NMR spectrum of **4b** in $CDCl_3$. (*inseparable impurity, which might appear due to the formation of mercaptopyridine-borane adduct; #free PPh_3)

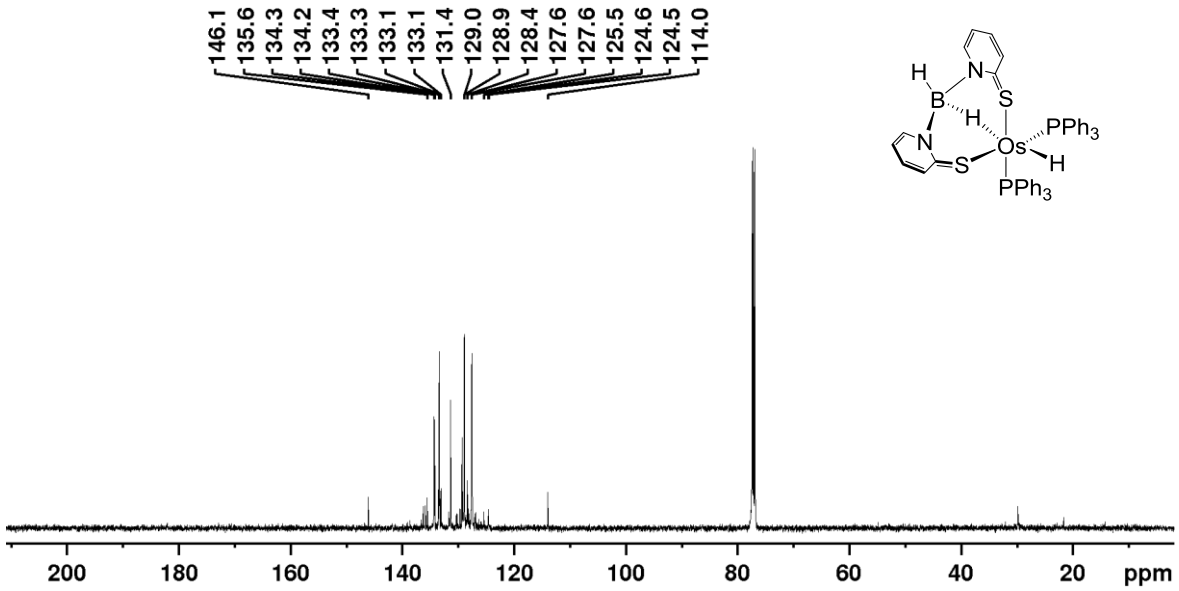


Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum of **4b** in $CDCl_3$.

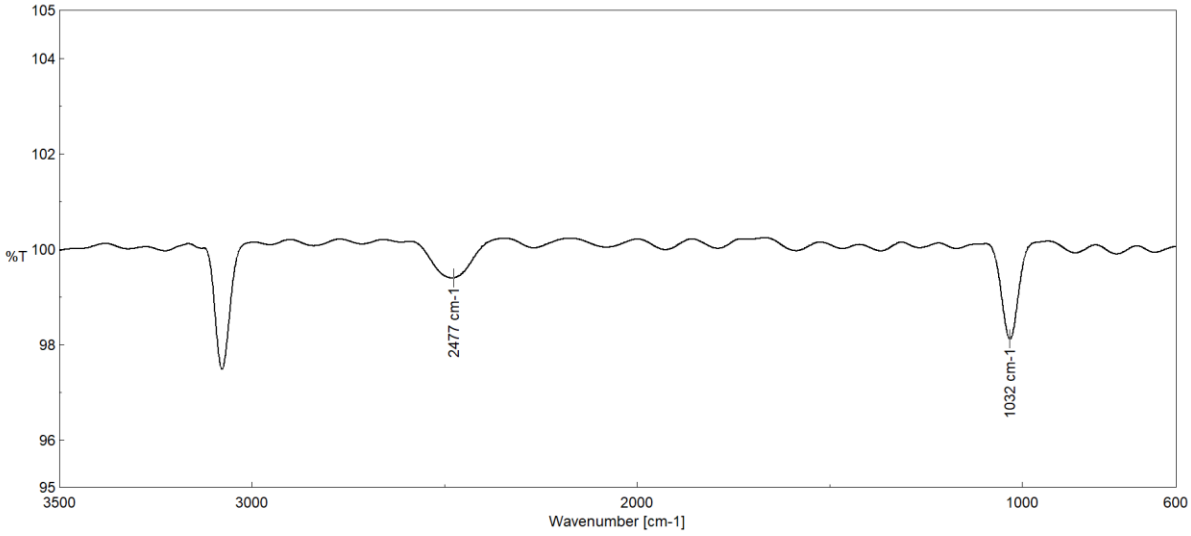


Figure S27. IR spectrum of **4b** in CH_2Cl_2.

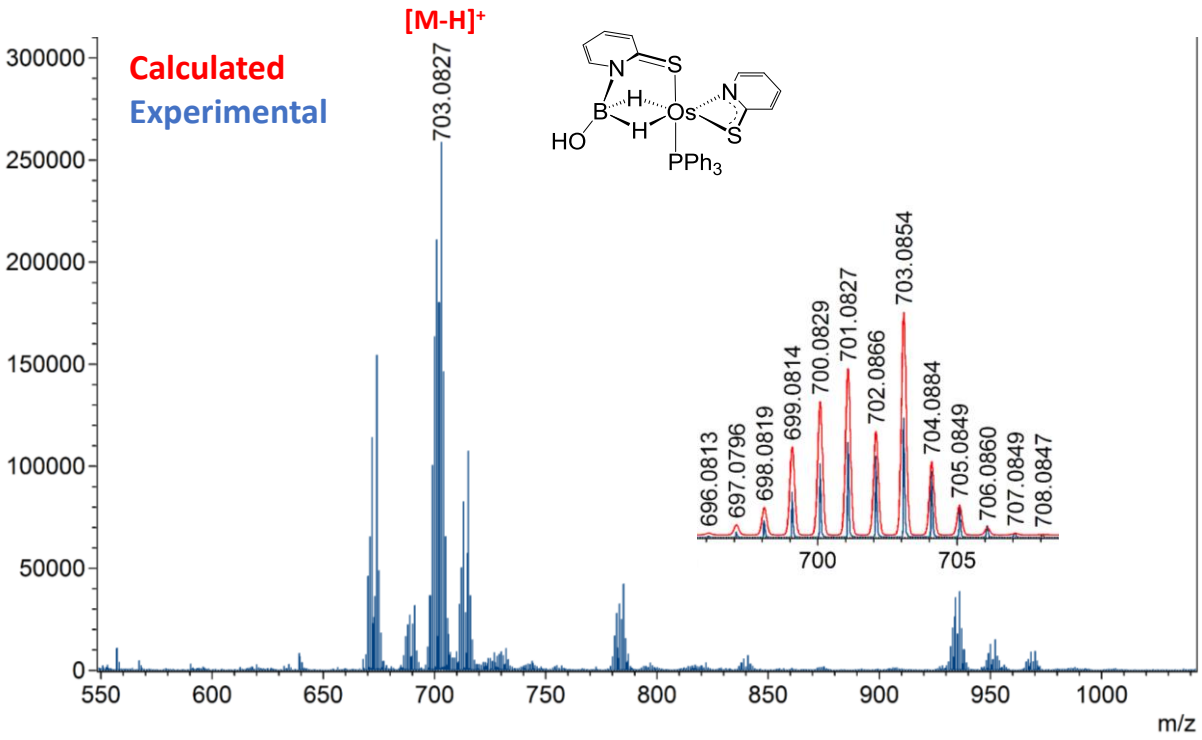


Figure S28. ESI-MS spectrum of **5**.

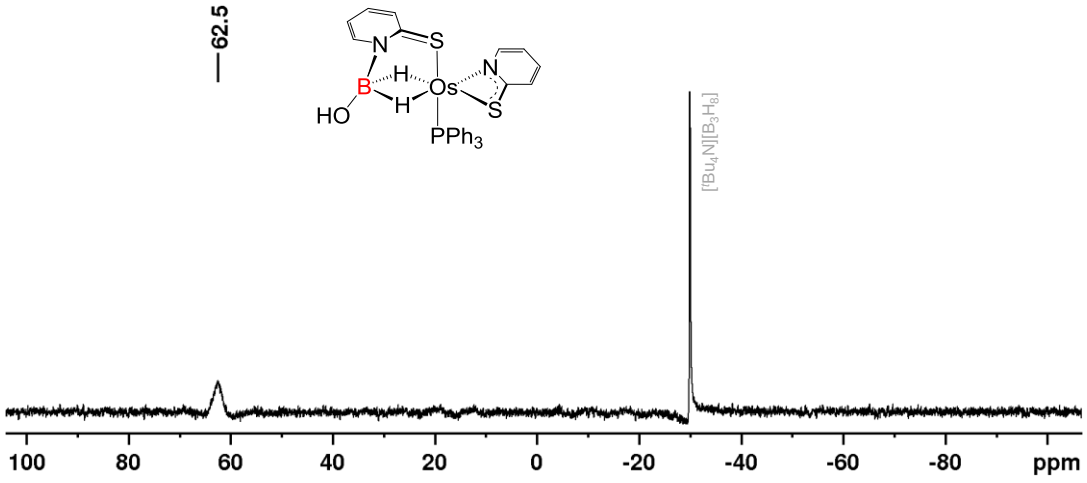


Figure S29. $^{11}B\{^{1}H\}$ NMR spectrum of **5** in $CDCl_3$.

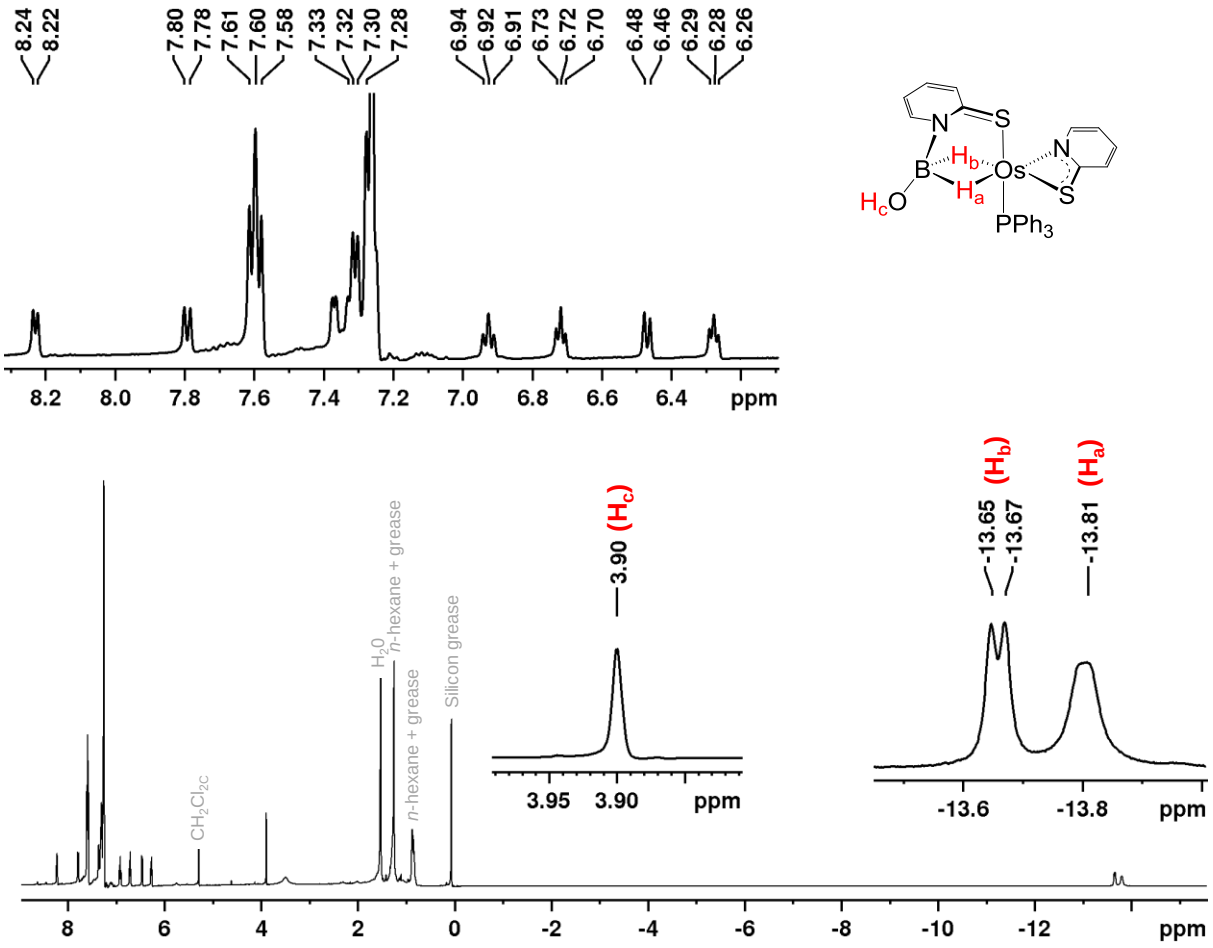


Figure S30. ^{1}H NMR spectrum of **5** in $CDCl_3$.

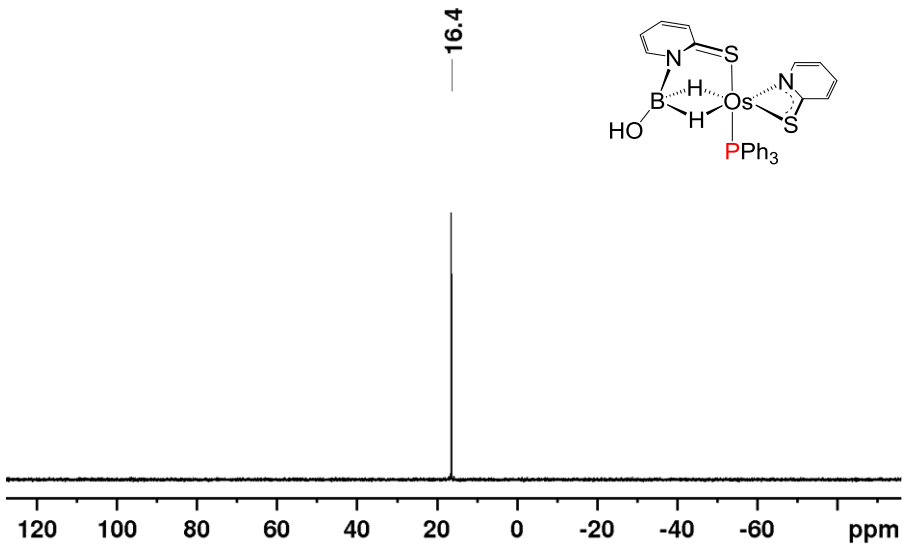


Figure S31. $^{31}P\{^{1}H\}$ NMR spectrum of **5** in $CDCl_3$.

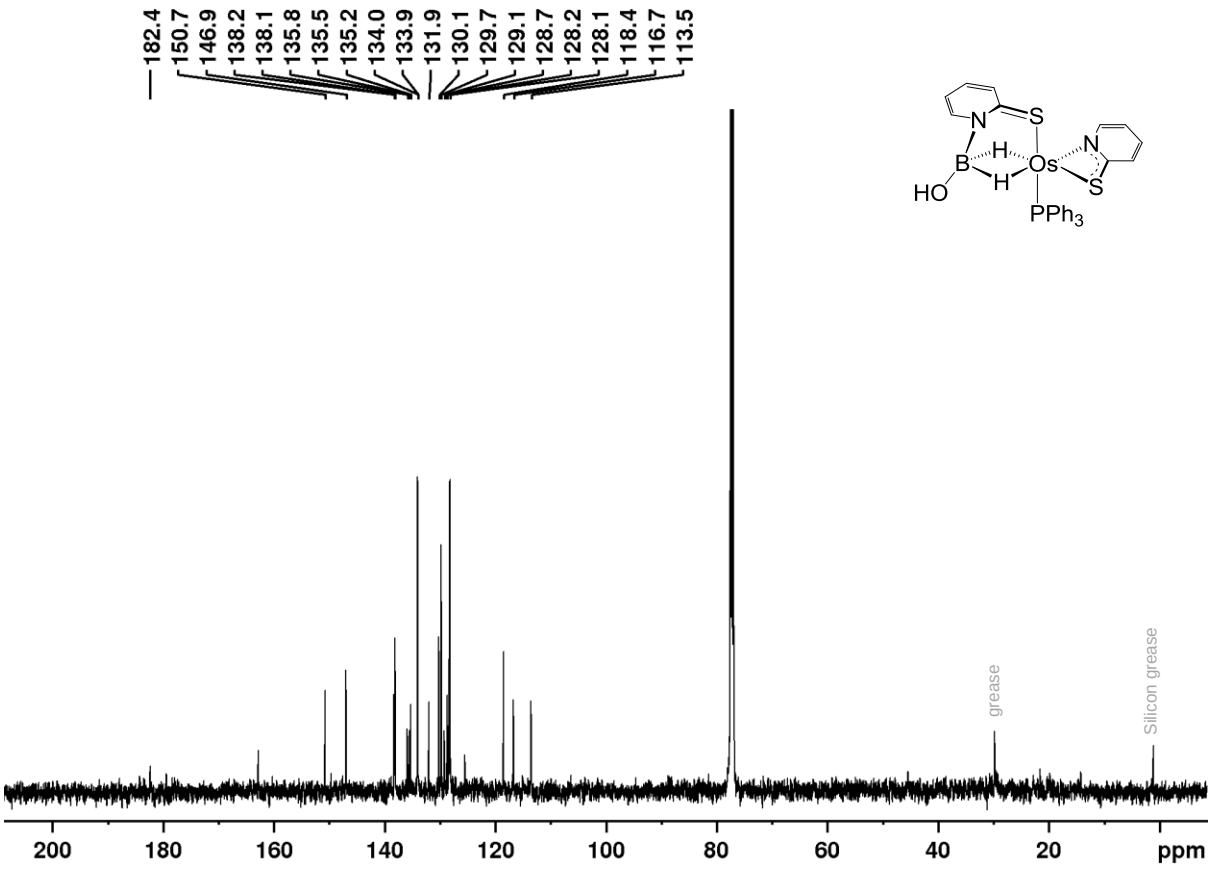


Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum of **5** in $CDCl_3$.

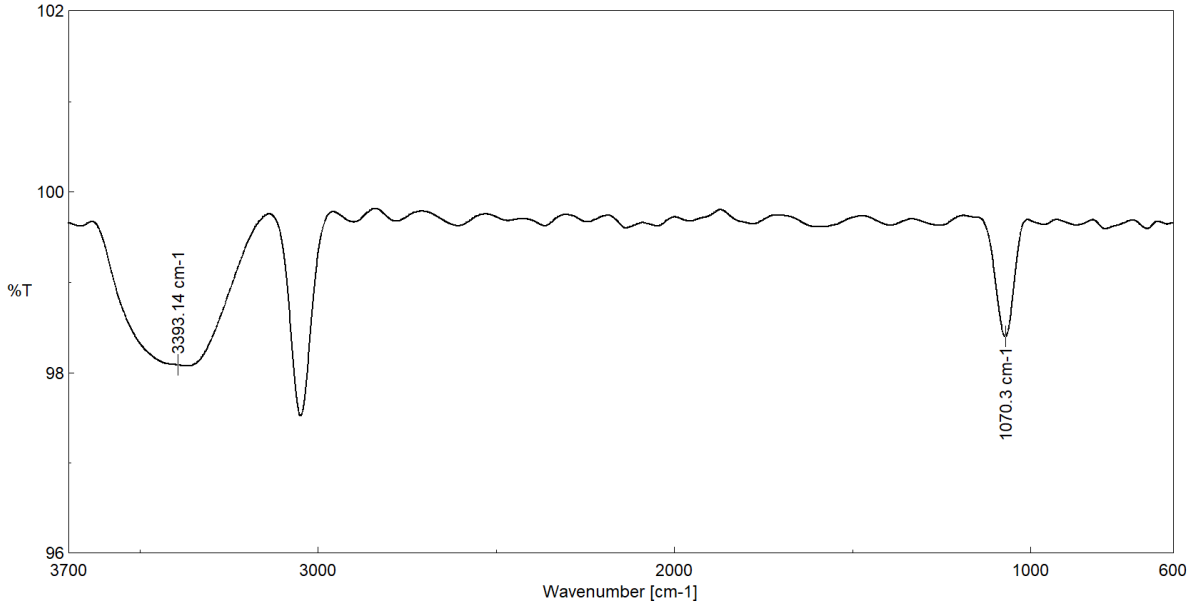


Figure S33. IR spectrum of **5** in CH_2Cl_2.

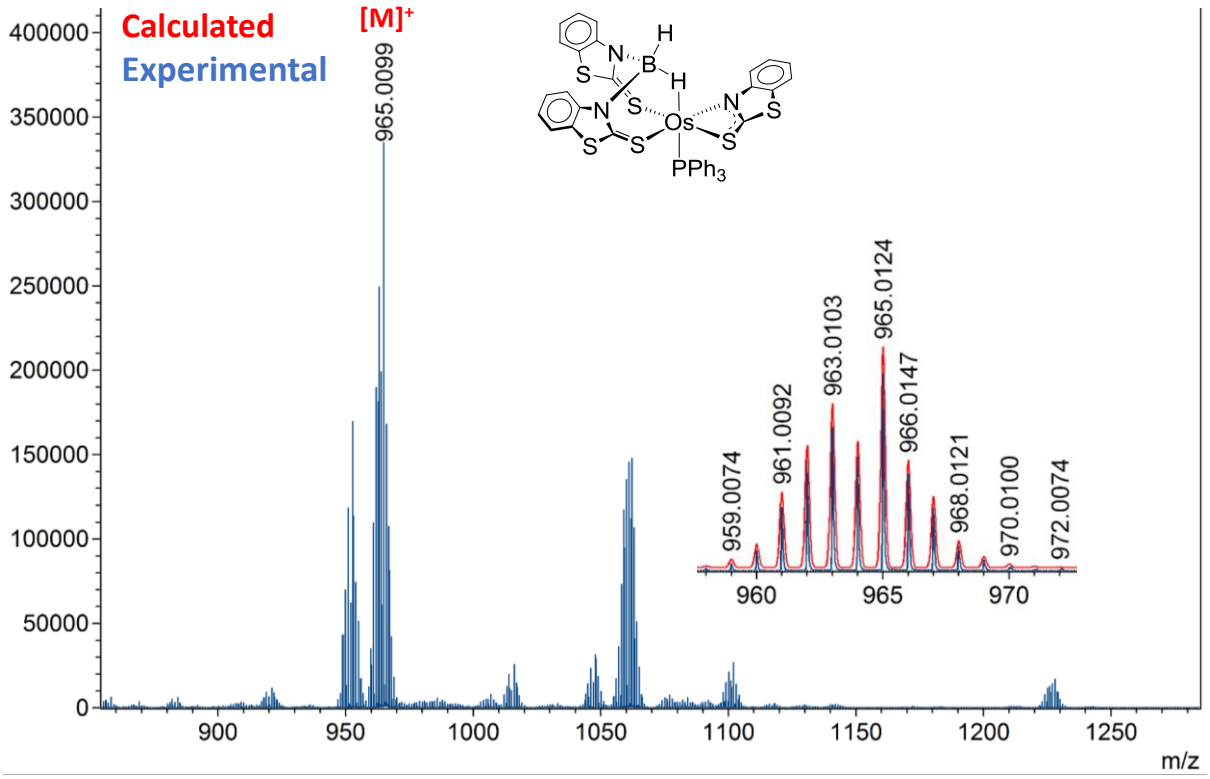


Figure S34. ESI-MS spectrum of *trans*-**6**.

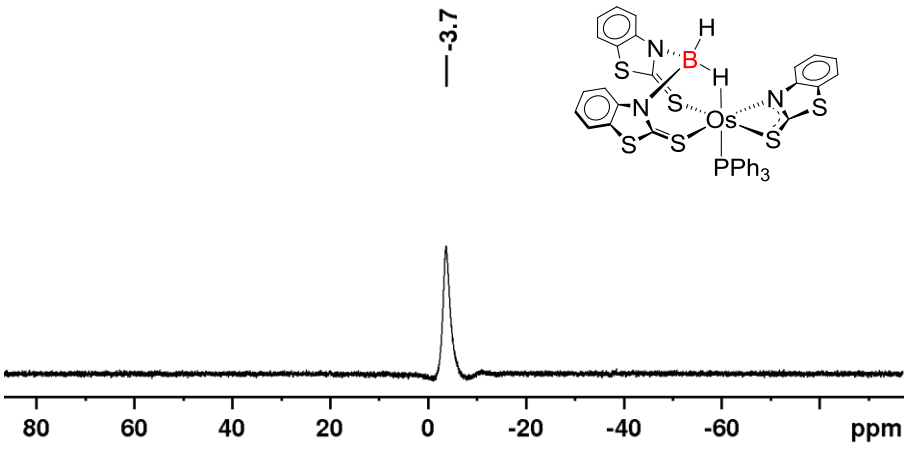


Figure S35. $^{11}B\{^{1}H\}$ NMR spectrum of *trans*-**6** in $CDCl_3$.

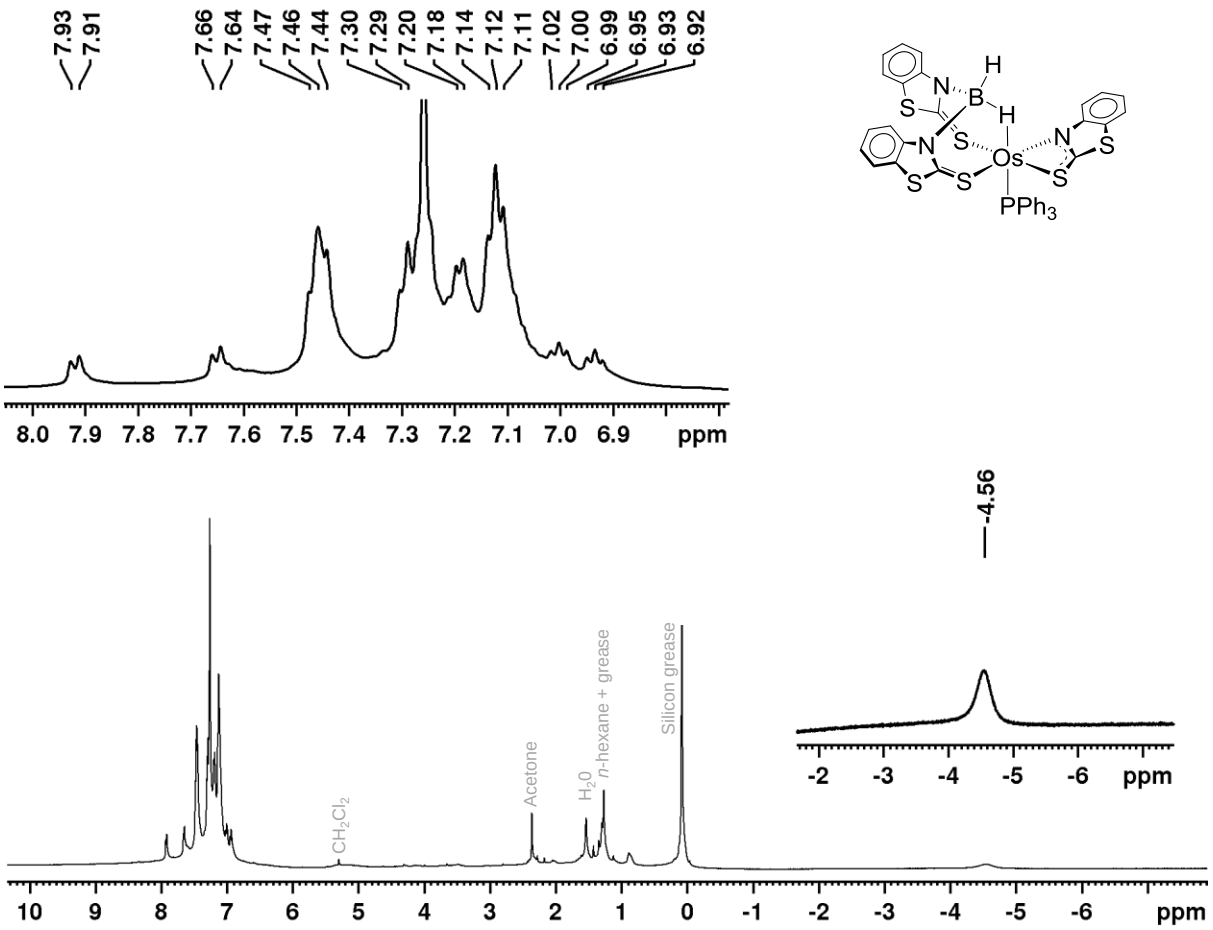


Figure S36. ^{1}H NMR spectrum of *trans*-**6** in $CDCl_3$.

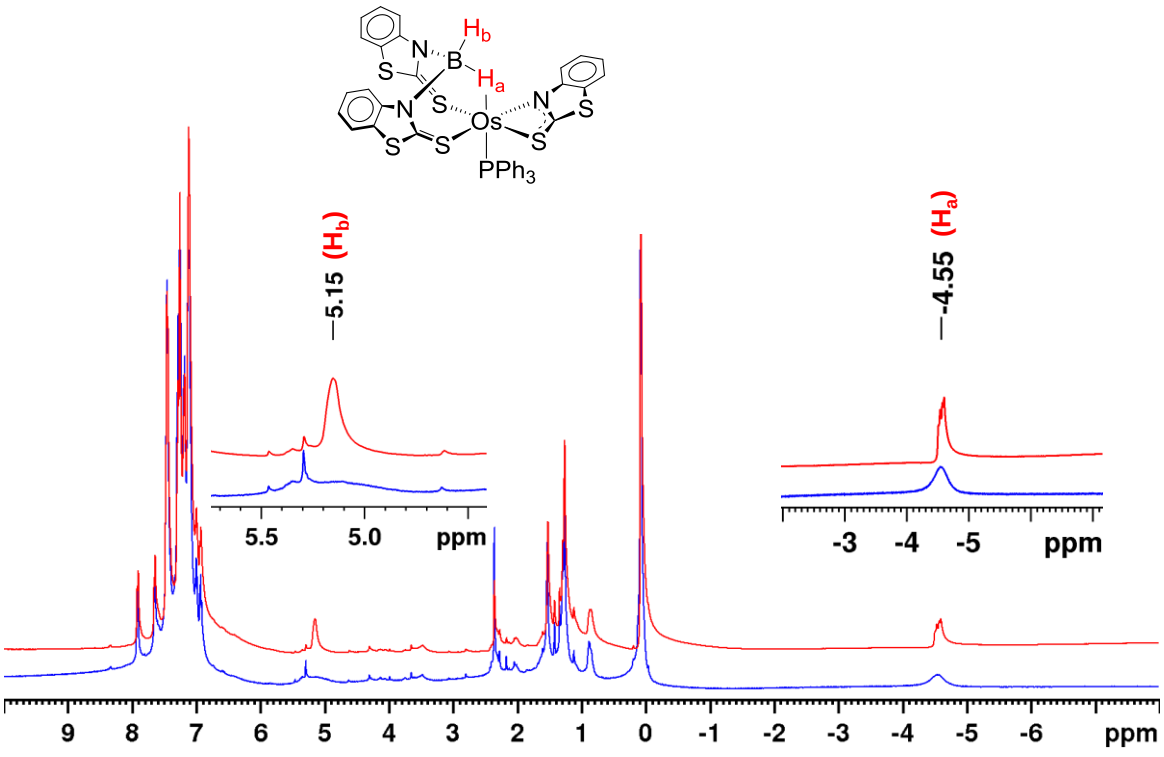


Figure S37. Stacked ^{1}H (blue) and $^{1}H\{^{11}B\}$ (red) NMR spectrum of *trans*-**6** in $CDCl_3$.

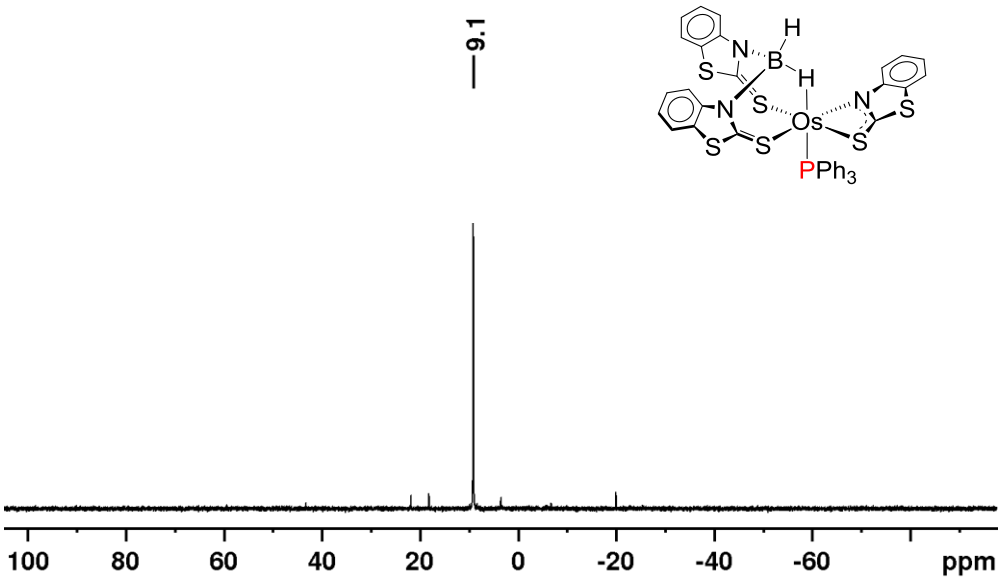


Figure S38. $^{31}P\{^{1}H\}$ NMR spectrum of *trans*-**6** in $CDCl_3$.

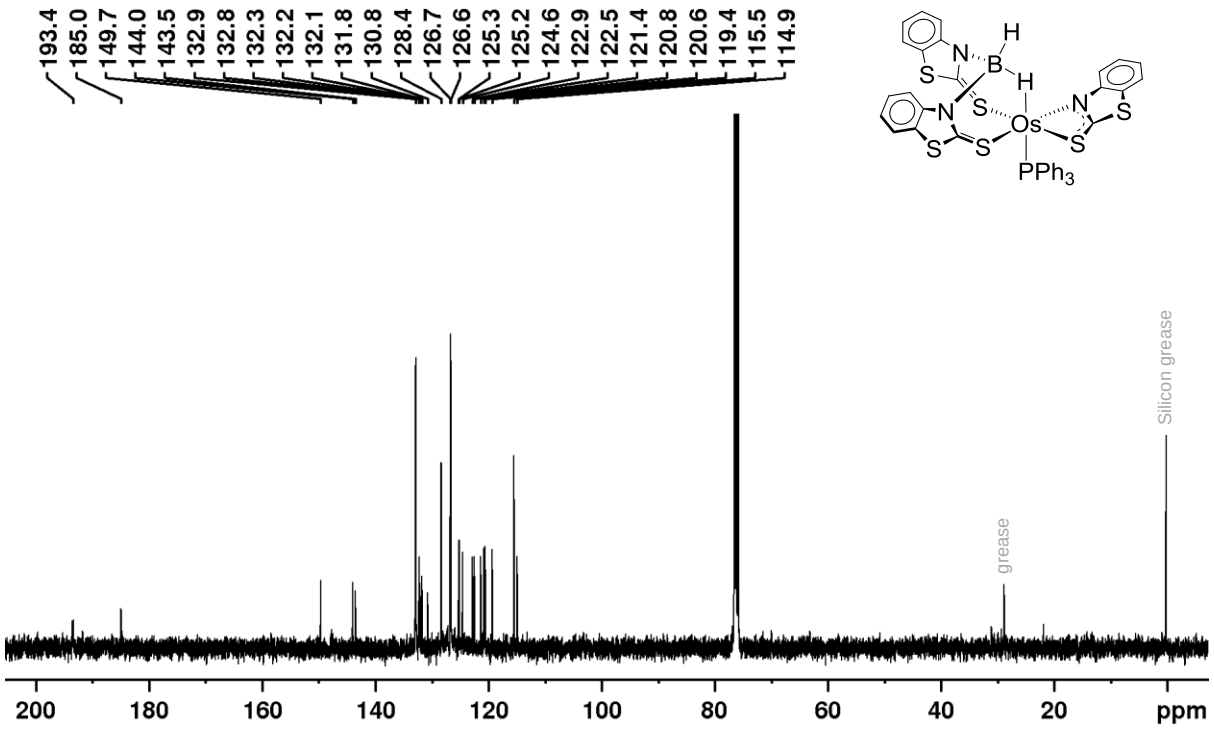


Figure S39. $^{13}C\{^{1}H\}$ NMR spectrum of *trans*-**6** in $CDCl_3$.

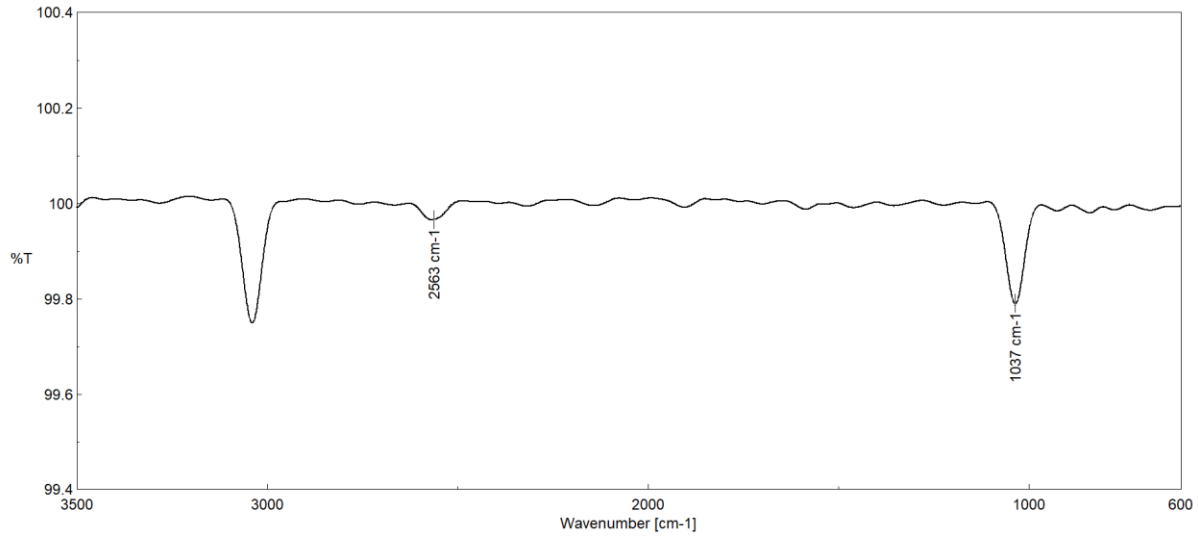


Figure S40. IR spectrum of *trans*-**6** in CH_2Cl_2.

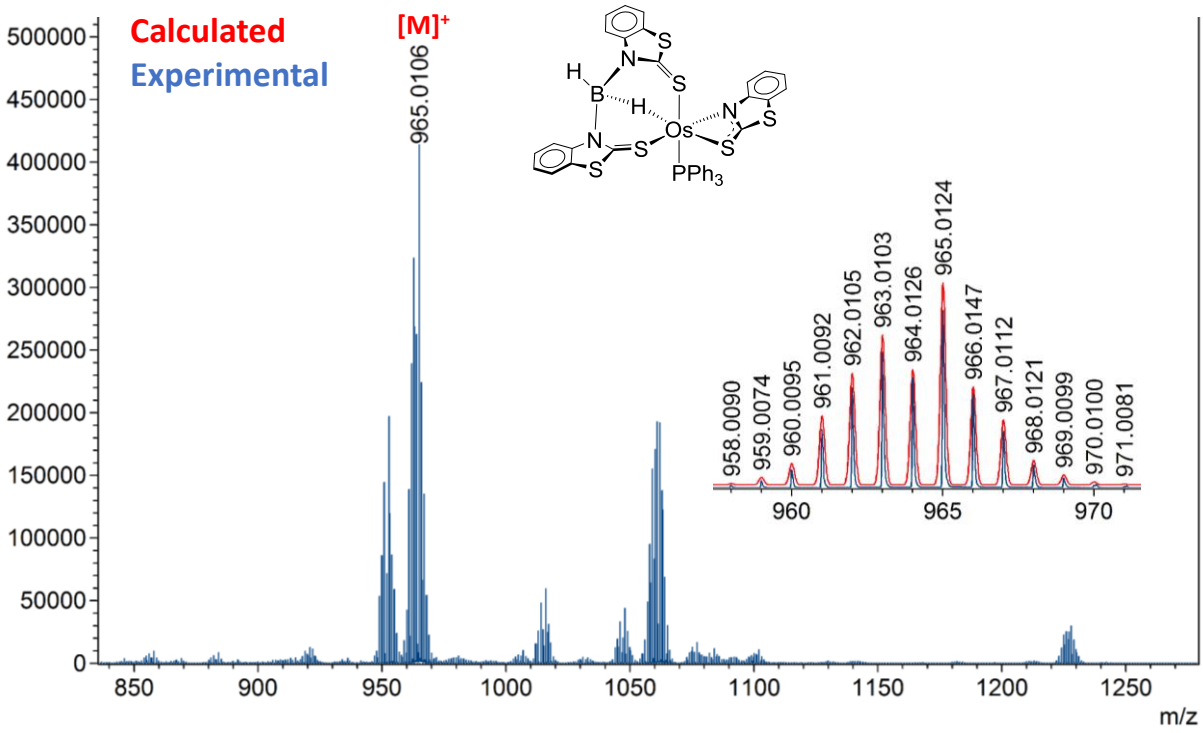


Figure S41. ESI-MS spectrum of *cis*-**6**.

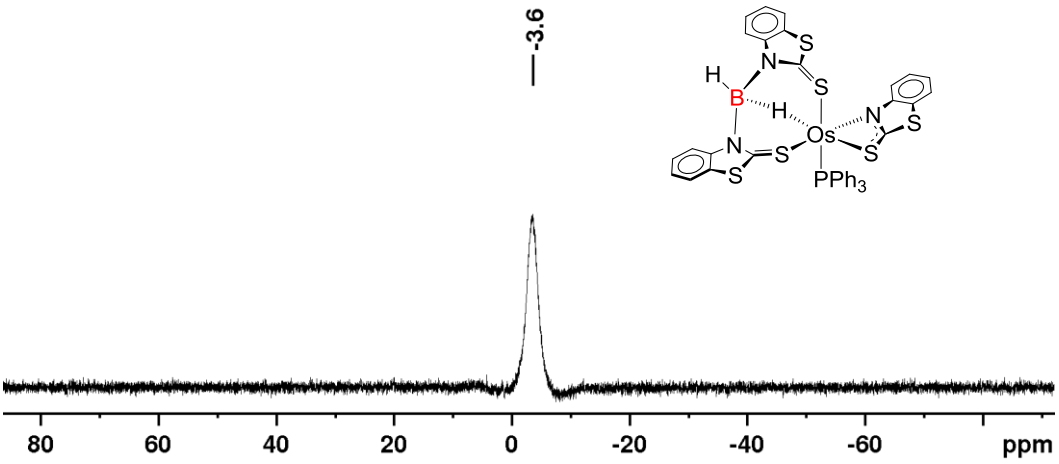


Figure S42. $^{11}B\{^{1}H\}$ NMR spectrum of *cis*-**6** in $CDCl_3$.

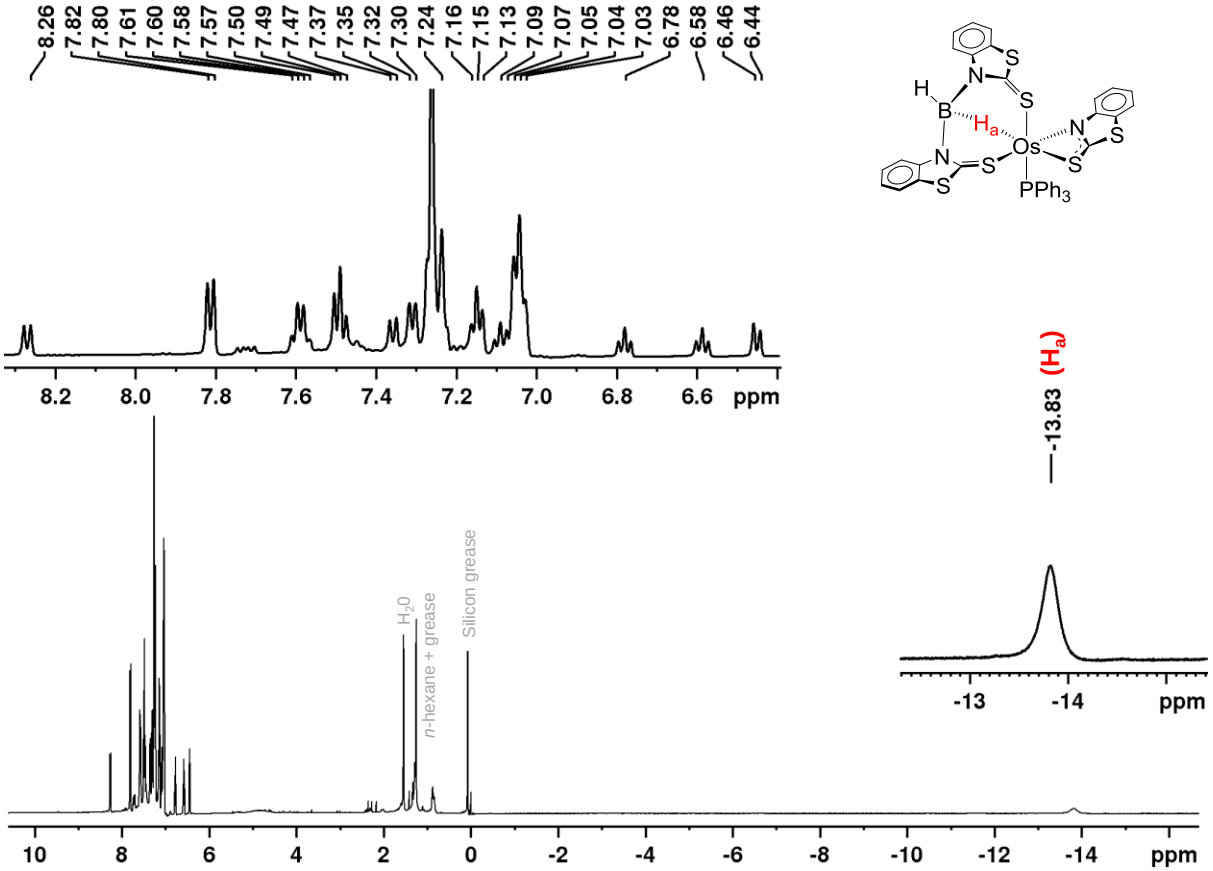


Figure S43. ^{1}H NMR spectrum of *cis*-**6** in $CDCl_3$.

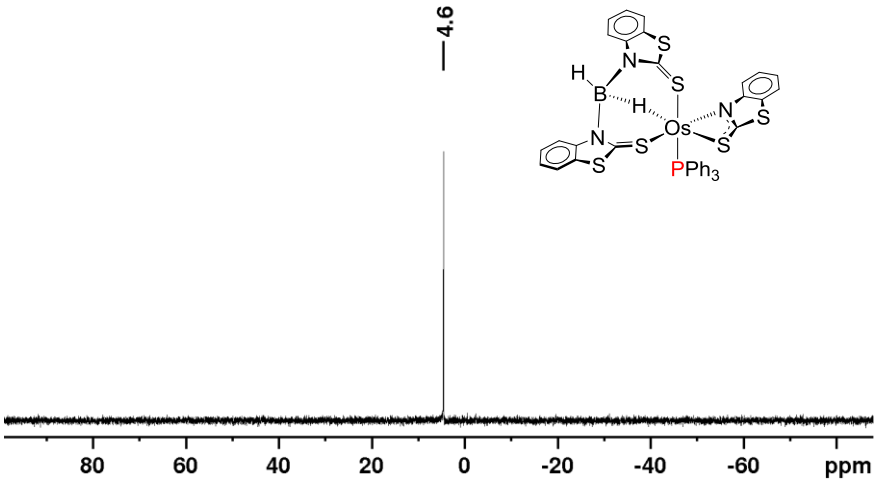


Figure S44. $^{31}P\{^{1}H\}$ NMR spectrum of *cis*-**6** in $CDCl_3$.

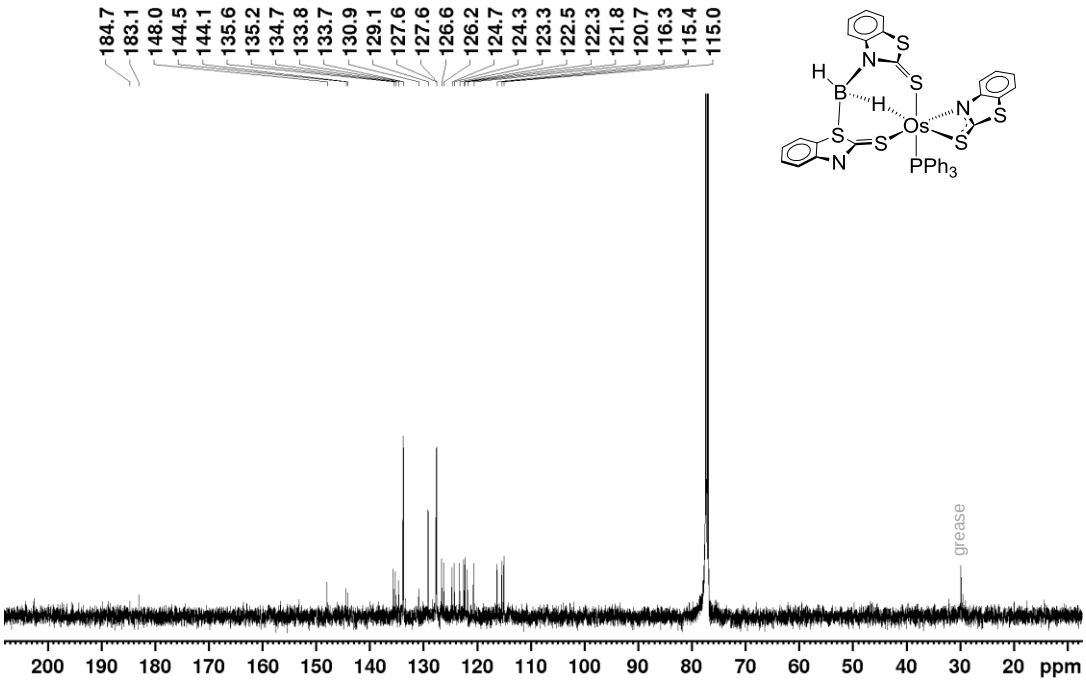


Figure S45. $^{13}C\{^{1}H\}$ NMR spectrum of *cis*-**6** in $CDCl_3$.

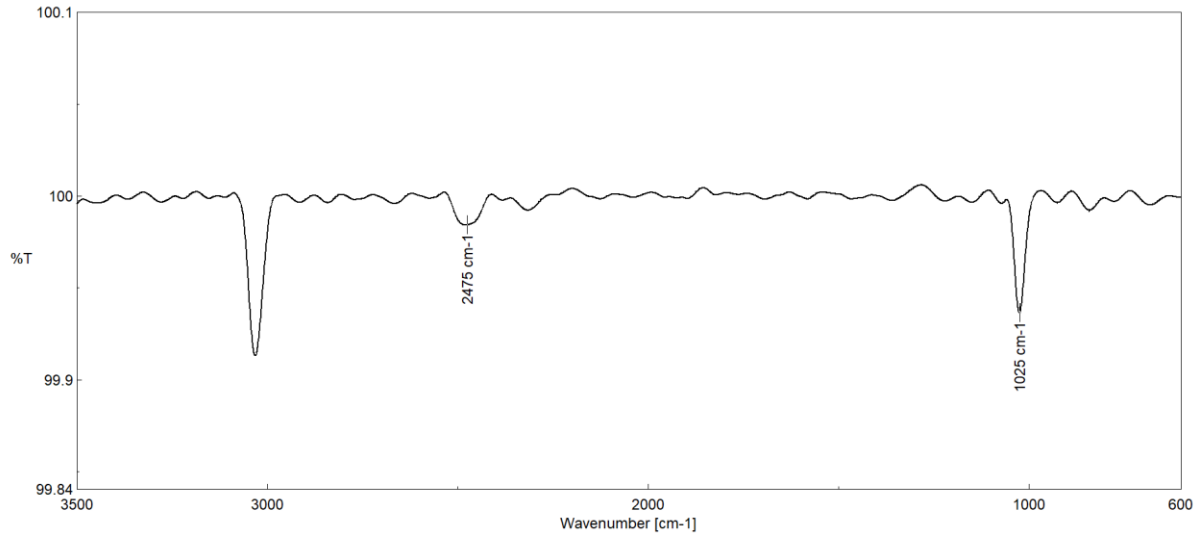


Figure S46. IR spectrum of *cis*-**6** in CH_2Cl_2.

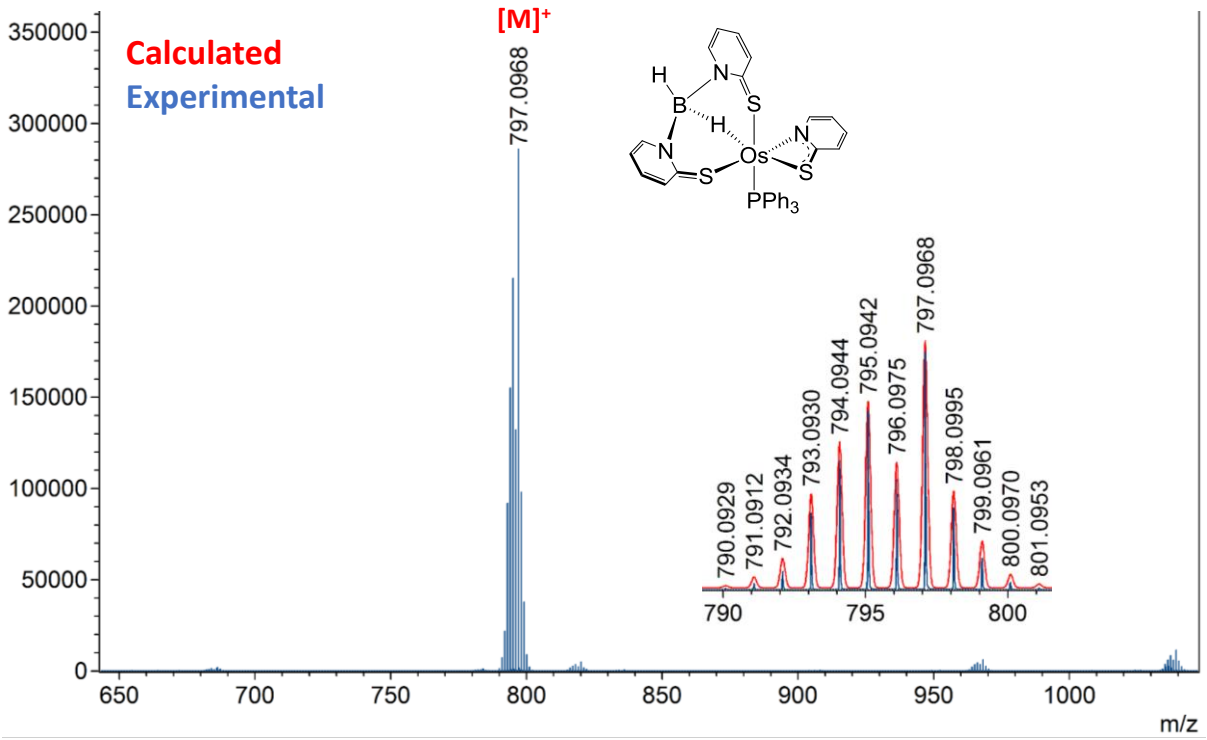


Figure S47. ESI-MS spectrum of *cis*-**7**.

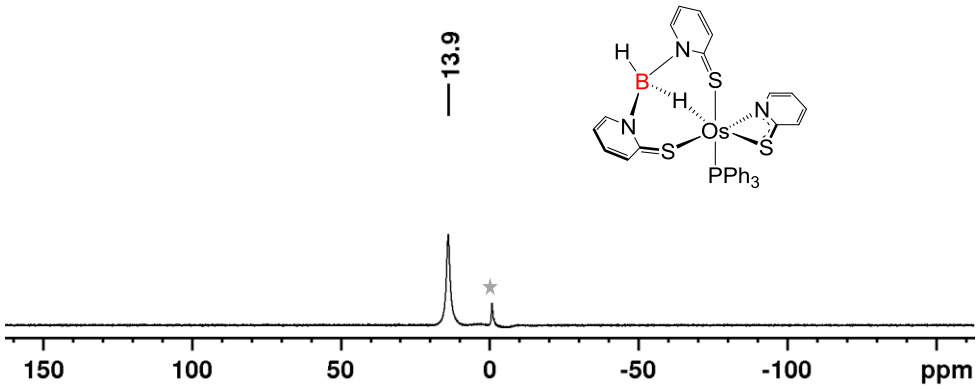


Figure S48. $^{11}B\{^{1}H\}$ NMR spectrum of *cis*-**7** in $CDCl_3$. (*inseparable impurity)

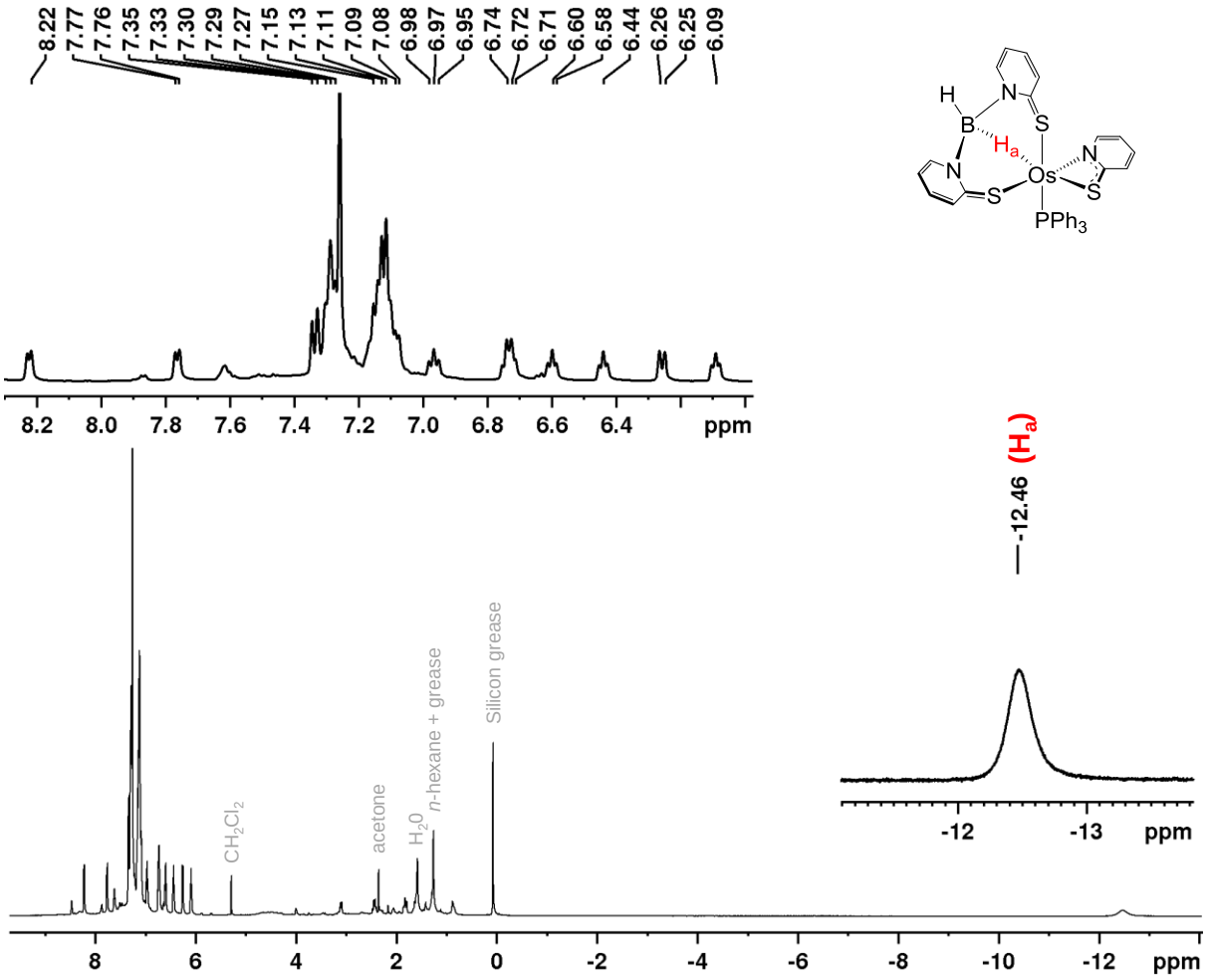


Figure S49. ^{1}H NMR spectrum of *cis*-**7** in $CDCl_3$.

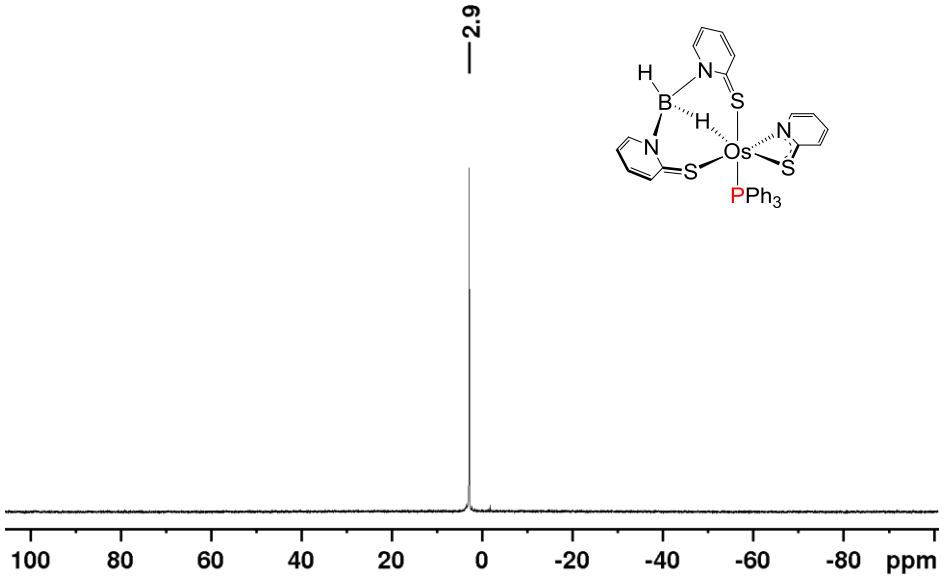


Figure S50. $^{31}P\{^{1}H\}$ NMR spectrum of *cis*-**7** in $CDCl_3$.

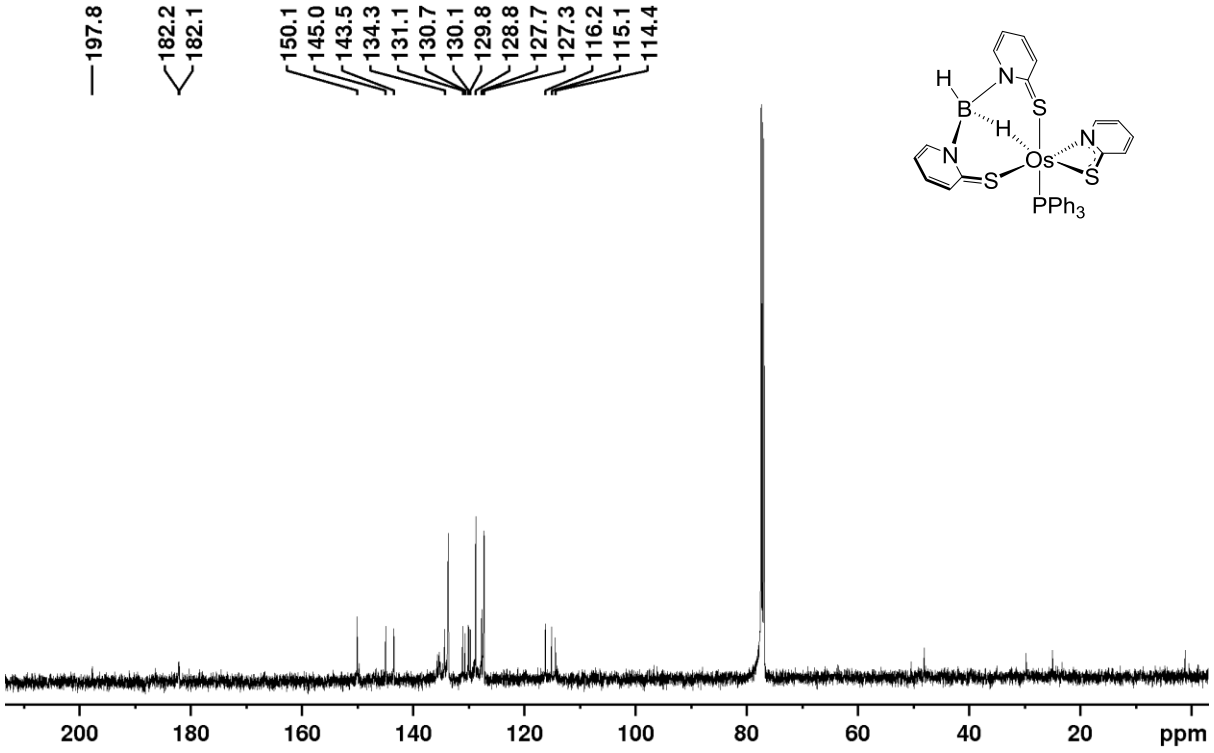


Figure S51. $^{13}C\{^{1}H\}$ NMR spectrum of *cis*-**7** in $CDCl_3$.

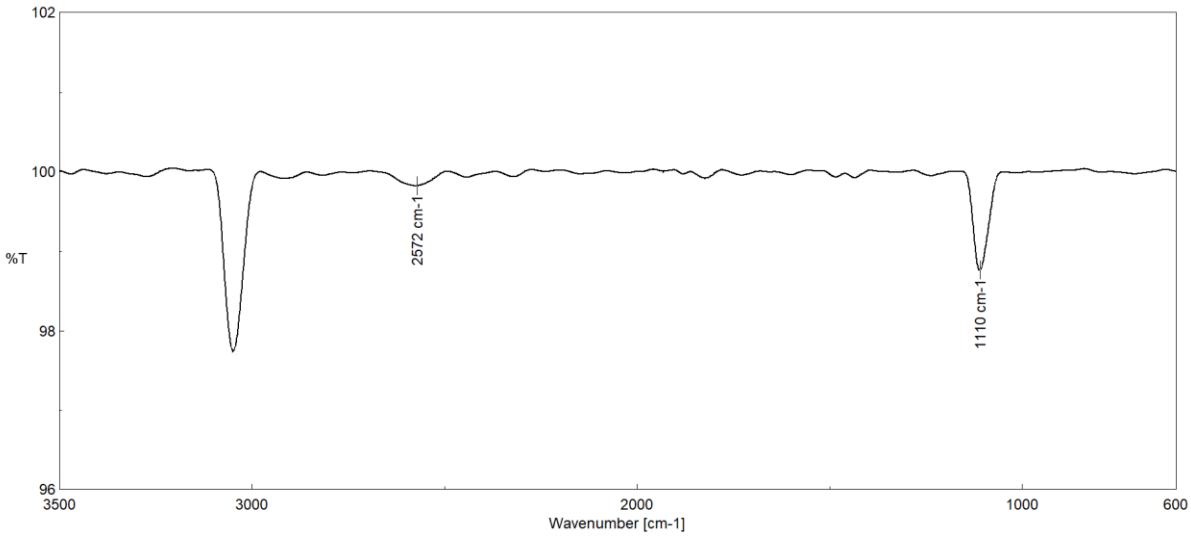


Figure S52. IR spectrum of *cis*-**7** in CH_2Cl_2.

II.3 X-ray Analysis Details

Suitable X-ray quality crystals of **2b, 4a**, **5**, cis-**6,** *trans*-**6** and *cis*-**7** were grown by slow diffusion of a hexane-CH_2Cl_2 solution at -4 ˚C. Crystal data of **4a**, **5**, *trans*-**6** and *cis*-**7** were obtained and integrated using a D8 VENTURE Bruker AXS diffractometer with PHOTON II detector with graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation at 298(2) K for **5**, *trans*-**6** and *cis*-**7** and at 296(2) K for **4a**. Crystal data of **2b**, cis-**6** was obtained and integrated using a Bruker APEX-II CCD diffractometer with graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation at 296(2) K. All the structures were solved using SHELXT-2018 and SHELXS-97[4] and refined using SHELXL−2018, SHELXL-2014 and SHELXL-2019[5]. Using Olex2 all the molecular structures were drawn.[6] Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no CCDC-2353030 (**4a**), 2353031 (**4a**), 2353032 (**5**), 2353033 (***trans*-6**), 2353034 (***cis*-6**) and 2353035 (***cis*-7**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for **2b***:* $C_{47}H_{40}Cl_2N_2OsP_2S_2$, M_r= 1019.97, triclinic, space group *P*-1, *a* = 11.6034(3) Å, *b* = 12.2578(3) Å, *c* = 17.0531(4) Å, *α* = 74.1121(10)°, *β* = 85.1640(11)°, *γ* = 64.8014(10)°, *V* = 2109.39(9) Å^3, *Z* = 2, ρ_{calcd} = 1.606 g/cm3, μ = 3.361 mm^{-1}, *F*(000) = 1016.0, R_1 = 0.0291, wR_2 = 0.0683, 7396 independent reflections [2θ ≤ 50.000°] and 505 parameters.

Crystal data for **4a***:* $C_{50}H_{40}N_2OsP_2S_4B$, M_r = 1060.03, triclinic, space group *P*-1, *a* = 9.6569(8) Å, *b* = 11.9102(8) Å, *c* = 20.8069(16) Å, *α* = 86.218(4)°, *β* = 84.416(4)°, *γ* = 69.354(4)°, *V* = 2227.5(3) Å^3, *Z* = 2, ρ_{calcd} = 1.580 g/cm3, μ = 3.160 mm^{-1}, *F*(000) = 1058.0, R_1 = 0.0390, wR_2 = 0.0771, 11172 independent reflections [2θ ≤ 56.866°] and 549 parameters.

Crystal data for **5***:* $C_{28}H_{25}POsS_2BON_2$, M_r = 701.60, triclinic, space group *P*-1, *a* = 9.7769(3) Å, *b* = 11.7895(4) Å, *c* = 13.7966(6) Å, *α* = 69.327(2)°, *β* = 85.219(2)°, *γ* = 68.070(1)°, *V* = 1378.05(9) Å^3, *Z* = 2,

ρ_{calcd} = 1.691 g/cm3, μ = 4.860 mm^{-1}, F(000) = 686.0, R_1 = 0.0177, wR_2 = 0.0441, 5124 independent reflections [2θ ≤ 50.992°] and 336 parameters.

*Crystal data for trans-***6***:* $C_{40}H_{31}BPS_6OsCl_2N_3$, M_r = 1048.92, monoclinic, space group *C*2/c, *a* = 36.1185(15) Å, *b* = 36.1185(15) Å, *c* = 28.0264(12) Å, *α* = 90°, *β* = 127.780(1)°, *γ* = 90°, *V* = 8143.9(6) Å^3, *Z* = 8, ρ_{calcd} = 1.711 g/cm3, μ = 3.645 mm^{-1}, *F*(000) = 4144.0, R_1 = 0.0456, wR_2 = 0.1081, 8348 independent reflections [2θ ≤ 52.866°] and 493 parameters.

*Crystal data for cis-**6**:* $C_{39}H_{29}N_3PS_6OsB$, M_r = 963.99, monoclinic, space group $P2_1/c$, *a* = 10.9773(4) Å, *b* = 23.2835(8) Å, *c* = 14.8343(5) Å, *α* = 90°, *β* = 103.8767(15)°, *γ* = 90°, *V* = 3680.8(2) Å^3, *Z* = 4, ρ_{calcd} = 1.740 g/cm3, μ = 3.883 mm^{-1}, *F*(000) = 1904.0, R_1 = 0.0402, wR_2 = 0.0868, 6473 independent reflections [2θ ≤ 49.996°] and 468 parameters.

*Crystal data for cis-**7**:* $C_{33}H_{29}N_3S_3PBOs$, M_r = 795.75, monoclinic, space group $P2_1/n$, *a* = 9.516(3) Å, *b* = 19.737(7) Å, *c* = 19.416(6) Å, *α* = 90°, *β* = 93.665(9)°, *γ* = 90°, *V* = 3639(2) Å^3, *Z* = 4, ρ_{calcd} = 1.452 g/cm3, μ = 3.745 mm^{-1}, *F*(000) = 1568.0, R_1 = 0.0378, wR_2 = 0.0787, 6387 independent reflections [2θ ≤ 49.994°] and 385 parameters.

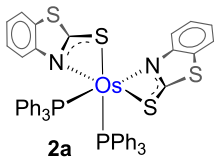
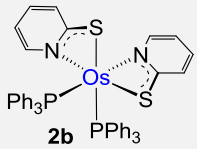
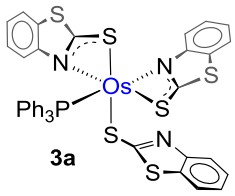
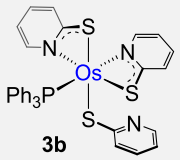
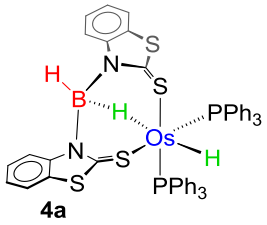
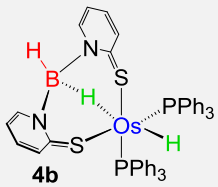
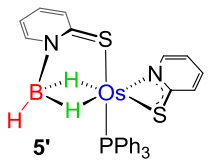
III Computational Details

All molecules were fully optimized with the Gaussian 16 program[7] using the gradient-corrected Becke–Lee–Yang–Parr (B3LYP) functional[8] in conjunction with the 6-31g(d)-LANL2DZ basis set from the EMSL Basis Set Exchange Library[9]. The model compounds were fully optimized starting from X-ray coordinates in the gaseous state (no solvent effect). Frequency calculations were carried out for the verification of the nature of the stationary state and to confirm the absence of any imaginary frequency which eventually confirmed the minima on the potential energy hypersurface for all structures. Furthermore, the gauge including atomic orbital (GIAO)[10] method was employed to compute the ^{11}B chemical shifts. Wiberg bond indices (WBI)[11] was generated from natural bond orbital analysis (NBO)[12]. All the optimized geometries and orbital pictures were drawn by Chemcraft[13] visualization programs. Laplacian electronic distribution plots and Two-dimensional electron density and were generated using the Multiwfn package.[14]

Table S2. Selected geometrical parameters and Wiberg Bond Indices (WBI) of **2a-b**, **3a-b**, **4a-b**, **5'**, *trans*-**6** and *cis*-**6**.

2a				**2b**			
	Expt.	Cal.	WBI		Expt.	Cal.	WBI
Os1-S1	-	2.529	0.675	Os1-S1	2.4317(10)	2.518	0.719
Os1-S2	-	2.521	0.682	Os1-S2	2.4285(10)	2.506	0.729
Os1-N1	-	2.210	0.453	Os1-N1	2.142(3)	2.157	0.504
Os1-N2	-	2.198	0.454	Os1-N2	2.135(3)	2.147	0.503
3a				**3b**			
	Expt.	Cal.	WBI		Expt.	Cal.	WBI
Os1-S1	-	2.336	0.961	Os1-S1	-	2.357	0.956
Os1-S3	-	2.583	0.646	Os1-S2	-	2.548	0.694
Os1-S5	-	2.425	0.829	Os1-S3	-	2.410	0.861
Os1-N1	-	2.168	0.506	Os1-N1	-	2.140	0.532
Os1-N2	-	2.165	0.488	Os1-N2	-	2.130	0.516
4a				**4b**			
	Expt.	Cal.	WBI		Expt.	Cal.	WBI
Os1-B1	2.689	2.799	0.188	Os1-B1	-	2.691	0.227
Os1-H2A	-	1.616	0.758	Os1-H2A	-	1.623	0.749
Os1-H1B	1.69(4)	1.843	0.237	Os1-H1B	-	1.799	0.261
B1-H1B	1.31(4)	1.254	0.685	B1-H1B	-	1.262	0.655
Os1-S2	2.3985(11)	2.444	0.703	Os1-S1	-	2.419	0.747
5'							
	Expt.	Cal.	WBI				
Os1-B1	-	2.067	0.686				
Os1-H2B	-	1.701	0.474				
B1-H2B	-	1.494	0.408				
Os1-S1	-	2.434	0.745				
Os1-S2	-	2.558	0.694				
trans-**6**				*cis*-**6**			
	Expt.	Cal.	WBI		Expt.	Cal.	WBI
Os1-B1	2.712	2.772	0.194	Os1-B1	2.497(8)	2.602	0.286
Os1-H1A	1.76(5)	1.799	0.277	Os1-H1A	1.71(6)	1.715	0.350
B1-H1A	1.21(2)	1.251	0.645	B1-H1A	1.31(6)	1.305	0.554
Os1-S5	2.4816(15)	2.549	0.649	Os1-S4	2.4741(18)	2.537	0.696
Os1-N3	2.127(4)	2.168	0.508	Os1-N3	2.138(5)	2.145	0.520

Table S3. Experiment and calculated ^{11}B NMR, calculated natural charge and HOMO-LUMO energy gap of **2a-b**, **3a-b**, **4a-b**, **5'**, *trans*-**6** and *cis*-**6**.

Complexes	^{11}B NMR (ppm)		Natural Charge (q)				ΔE_{H-L} (eV)
	Expt	Calc	q_{Os}	q_B	q_N	q_S	
 **2a**	-	-	-0.800	-	-0.505	0.057 (S1) 0.070 (S2)	3.810
 **2b**	-	-	-0.845	-	-0.453	0.002 (S1) 0.016 (S2)	3.520
 **3a**	-	-	-0.556	-	-0.497 (N1) -0.497 (N2) -0.502 (N3)	0.218 (S1) 0.094 (S3) 0.183 (S5)	2.072
 **3b**	-	-	-0.582	-	-0.449 (N1) -0.430 (N2) -0.490 (N3)	0.145 (S1) 0.056 (S2) 0.133 (S3)	2.126
 **4a**	-3.3	-8.4	-1.483	-0.412	-0.607 (N1) -0.622 (N2)	0.272 (S2) 0.235 (S4)	3.467
 **4b**	10.3	13.2	-1.554	-0.418	-0.568 (N1) -0.575 (N2)	0.235 (S1) 0.202 (S2)	2.922
 **5'**	62.5 (**5**)	46.2	-1.072	0.2873	-0.585 (N1) -0.433 (N2)	0.219 (S1) 0.029 (S2)	2.929

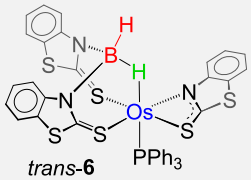
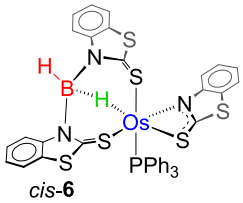
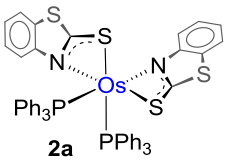
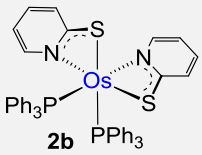
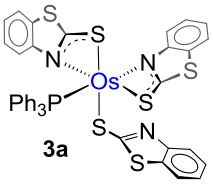
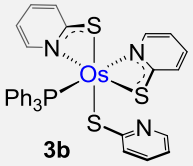
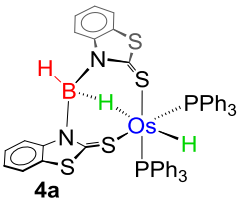
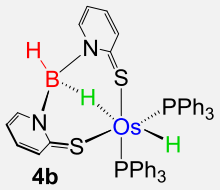
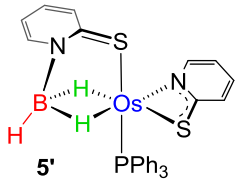
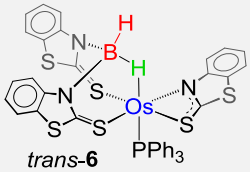
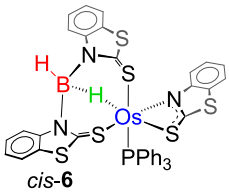
 *trans*-**6**	-3.6	-6.7	-0.900	0.438	-0.613 (N1) -0.600 (N2) -0.484 (N3)	0.240 (S1) 0.252 (S3) 0.098 (S5)	2.987
 *cis*-**6**	-3.7	-5.7	-0.970	0.455	-0.474 (N1) -0.623 (N2) -0.611 (N3)	0.110 (S4) 0.251 (S5) 0.256 (S6)	3.175

Table S4. Topological parameters at selected bond critical points (BCPs) of **2a-b**, **3a-b**, **4a-b**, **5'**, *trans*-**6** and *cis*-**6**.

Complexes	BCP	*ρ(r)*	*H(r)*	*∇²ρ(r)*	*ELF*	*ϵ*
 **2a**	Os1-S1	0.067	-0.018	0.122	0.301	0.555
	Os1-S2	0.034	-0.019	0.124	0.305	0.447
	Os1-N1	0.077	-0.015	0.292	0.172	0.288
	Os1-N2	0.079	-0.017	0.300	0.177	0.284
 **2b**	Os1-S1	0.070	-0.019	0.119	0.327	0.519
	Os1-S2	0.071	-0.020	0.120	0.330	0.401
	Os1-N1	0.088	-0.020	0.340	0.340	0.250
	Os1-N2	0.090	-0.021	0.348	0.296	0.262
 **3a**	Os1-S1	0.096	-0.030	0.205	0.347	0.212
	Os1-S2	0.061	-0.012	0.114	0.313	0.528
	Os1-S3	0.084	-0.024	0.147	0.377	0.226
	Os1-N1	0.088	-0.018	0.329	0.210	0.469
 **3b**	Os1-S1	0.090	-0.028	0.193	0.332	0.262
	Os1-S2	0.067	-0.018	0.107	0.336	0.565
	Os1-S3	0.085	-0.027	0.144	0.374	0.236
	Os1-N1	0.093	-0.022	0.344	0.211	0.554
 **4a**	Os1-H2A	0.144	-0.081	0.132	0.513	0.250
	Os1- H1B	0.068	-0.017	0.256	0.142	0.187
	Os1-S2	0.073	-0.019	0.236	0.357	0.122
	B1-H1B	0.141	-0.131	-0.106	0.526	0.251

 **4b**	Os1-H2A	0.145	-0.079	0.119	0.545	0.246
	Os1- H1B	0.078	-0.026	0.273	0.377	0.198
	Os1-S2	0.079	-0.019	0.205	0.271	0.094
	B1-H1B	0.140	-0.138	-0.105	0.483	0.253
 **5'**	Os1-H2A	0.109	-0.044	0.322	0.259	1.546
	Os1- B1	0.121	-0.071	-0.225	0.641	0.600
	B1-H2A	0.120	-0.076	-0.153	0.831	0.530
	B1-H2B	0.112	-0.062	-0.102	0.811	0.783
 *trans*-**6**	Os1-H1A	0.077	-0.022	0.254	0.182	0.059
	Os1- S5	0.064	-0.017	0.118	0.291	0.472
	Os1-N3	0.084	-0.018	0.326	0.183	0.382
	B1-H1A	0.138	-0.126	-0.055	0.473	0.266
 *cis*-**6**	Os1-H2B	0.097	-0.037	0.281	0.238	0.112
	Os1- S4	0.065	-0.017	0.121	0.295	0.478
	Os1-N1	0.088	-0.019	0.354	0.182	0.379
	B1-H2B	0.126	-0.109	-0.085	0.514	0.445

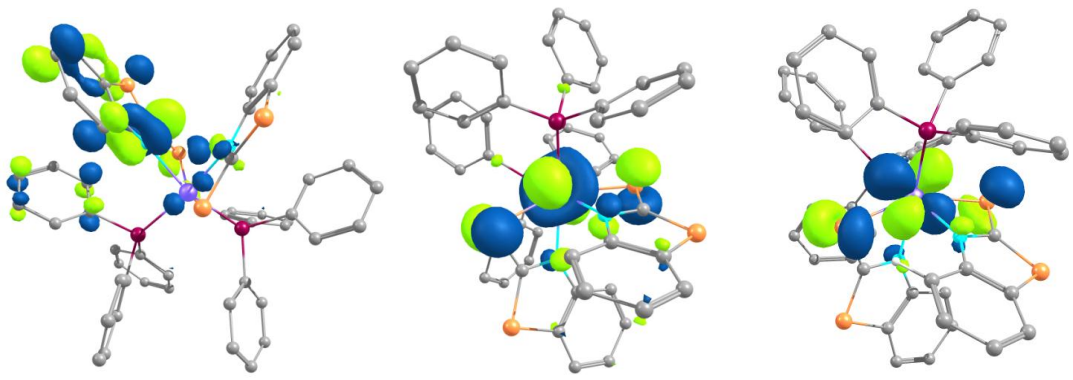


Figure S53. Selected molecular orbitals of **2a** (isocontour values: ±0.043 [e.bohr^{-3}]$^{1/2}$).

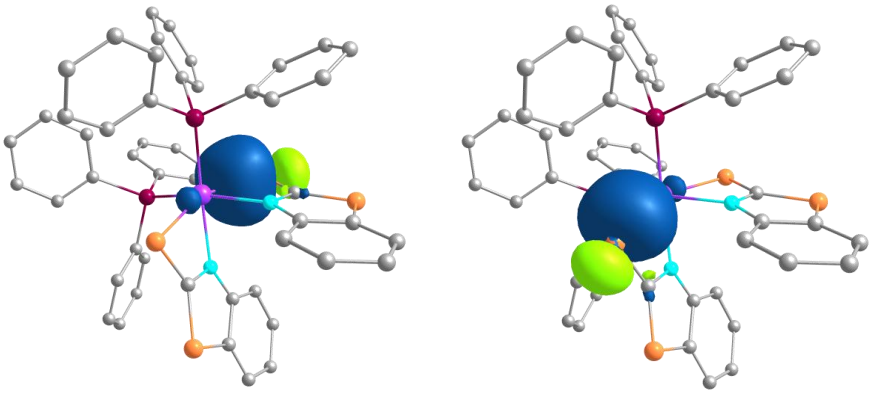


Figure S54. Selected NBOs of **2a** (isocontour values: ±0.043 [e.bohr^{-3}]$^{1/2}$).

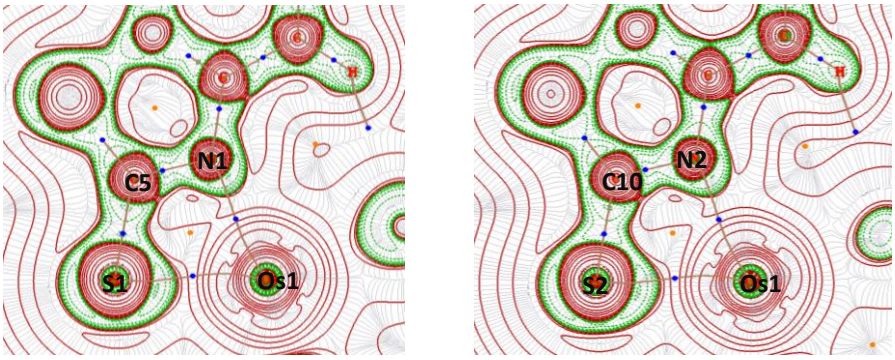


Figure S55. Contour-line diagram of the Laplacian of electron density in the Os1-N1-C5-S1 (a) and Os1-N2-C10-S2 (b) planes of **2a**, respectively. The solid brown lines are bond paths, while blue spheres indicate the bond critical points and orange sphere indicates ring critical points. Area of charge concentration [$\nabla^2\rho(r)<0$] are indicated by solid lines and area of charge depletion [$\nabla^2\rho(r)>0$] are shown by dashed lines.

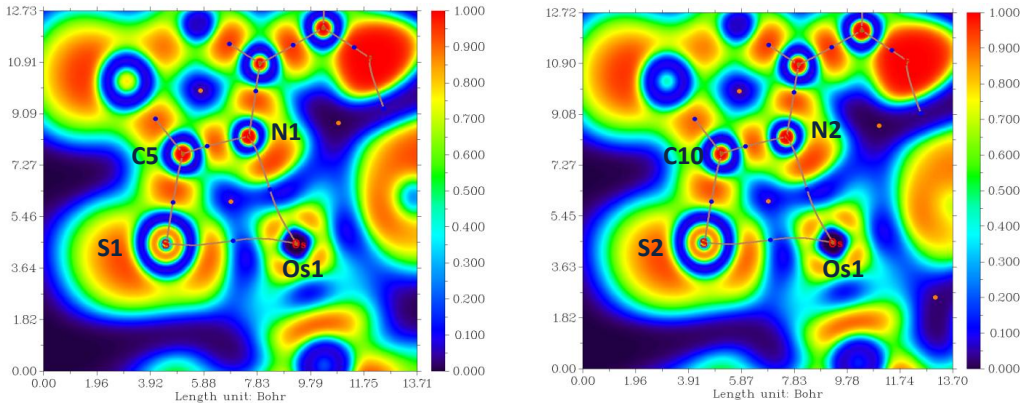


Figure S56. ELF plot in the Os1-N1-C5-S1 (a) and Os1-N2-C10-S2 (b) planes of **2a**, respectively.

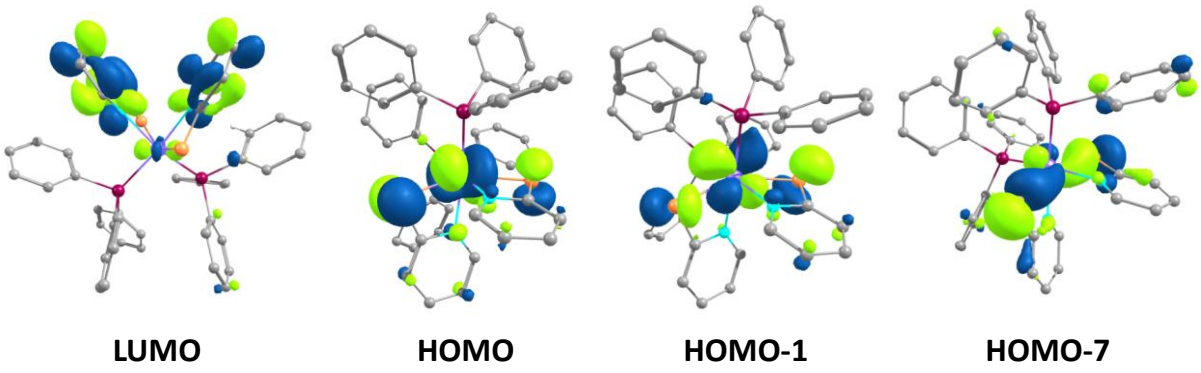


Figure S57. Selected molecular orbitals of **2b** (isocontour values: ±0.043 [e.bohr^{-3}]$^{1/2}$).

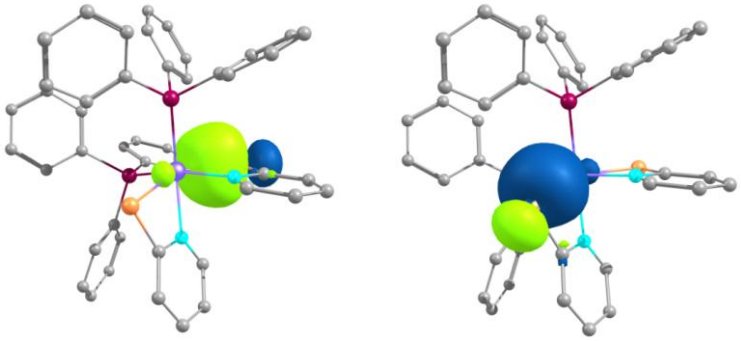


Figure S58. Selected NBOs of **2b** (isocontour values: ±0.043 [e.bohr^{-3}]$^{1/2}$).

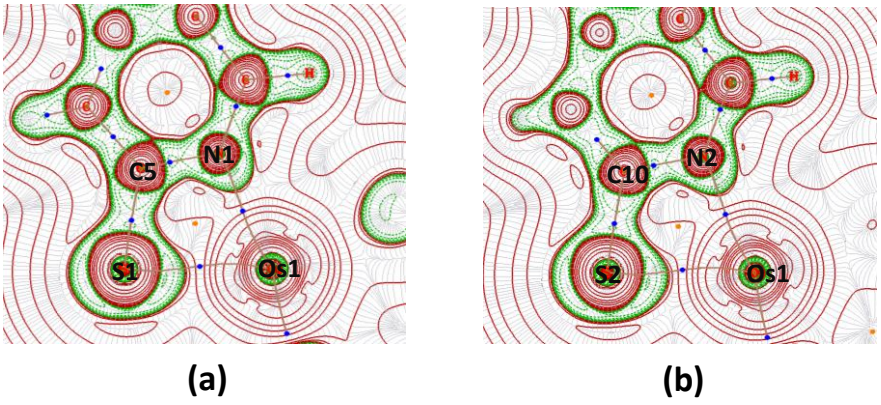
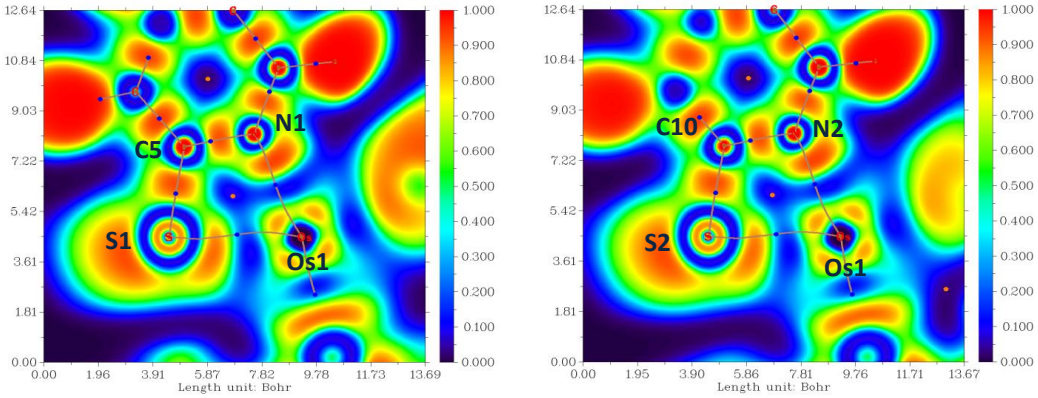
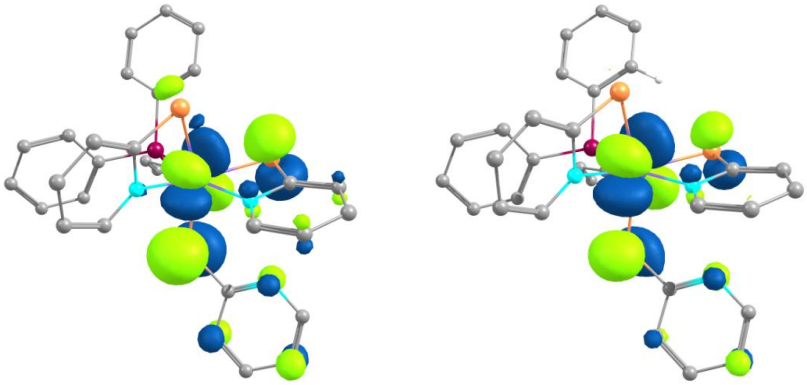


Figure S59. Contour-line diagram of the Laplacian of electron density in the Os1-N1-C5-S1 (a) and Os1-N2-C10-S2 (b) planes of **2b**, respectively. The solid brown lines are bond paths, while blue spheres indicate the bond critical points and orange sphere indicates ring critical points. Area of charge concentration [$\nabla^2\rho(r)<0$] are indicated by solid lines and area of charge depletion [$\nabla^2\rho(r)>0$] are shown by dashed lines.



(a) **(b)**

Figure S60. ELF plot in the Os1-N1-C5-S1 (a) and Os1-N2-C10-S2 (b) planes of **2b**, respectively.



HOMO **LUMO**

Figure S61. Selected molecular orbitals of **3a** (isocontour values: ±0.043 [e.bohr^{-3}]$^{1/2}$).

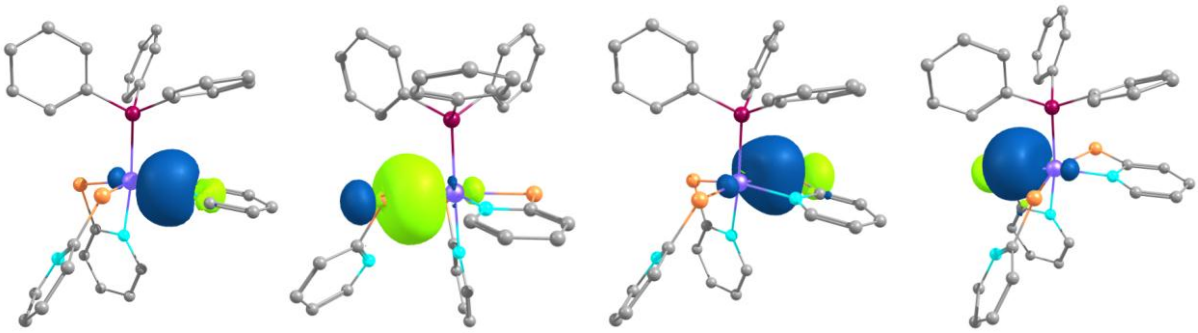


Figure S62. Selected NBOs of **3a** (isocontour values: ±0.043 [e.bohr^{-3}]$^{1/2}$).

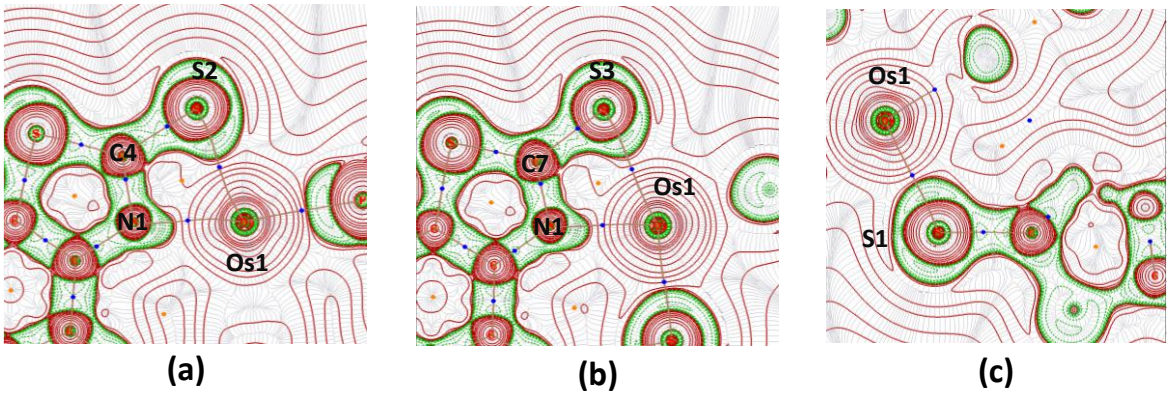


Figure S63. Contour-line diagram of the Laplacian of electron density in the Os1-N1-C4-S2 (a), Os1-N2-C8-S3 (b) planes and Os1-S1 (c) bond of **3a**, respectively. The solid brown lines are bond paths, while blue spheres indicate the bond critical points and orange sphere indicates ring critical points. Area of charge concentration [$\nabla^2\rho(r)<0$] are indicated by solid lines and area of charge depletion [$\nabla^2\rho(r)>0$] are shown by dashed lines.

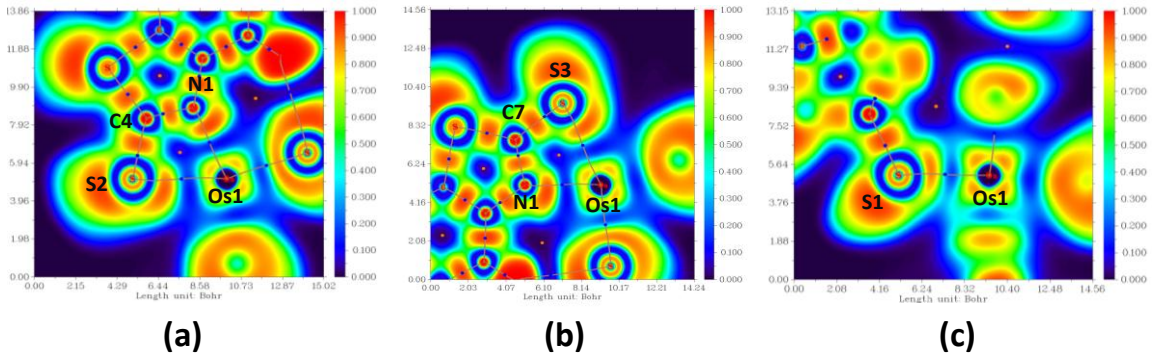


Figure S64. ELF plot in the Os1-N1-C5-S1 (a) and Os1-N2-C10-S2 (b) planes of **3a**, respectively.

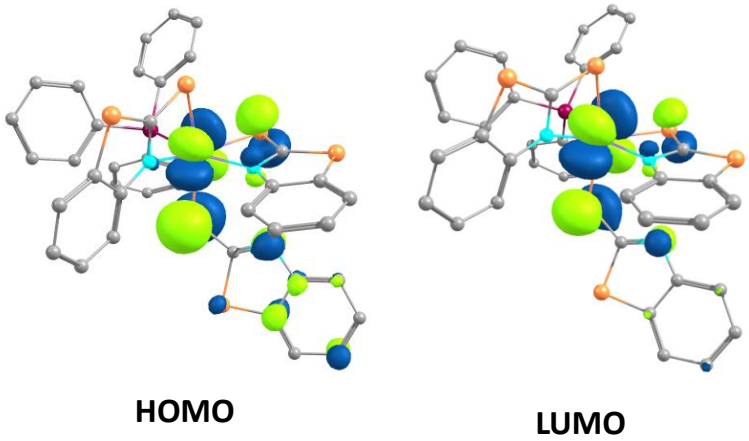


Figure S65. Selected molecular orbitals of **3b** (isocontour values: ±0.043 [e.bohr^{-3}]$^{1/2}$).

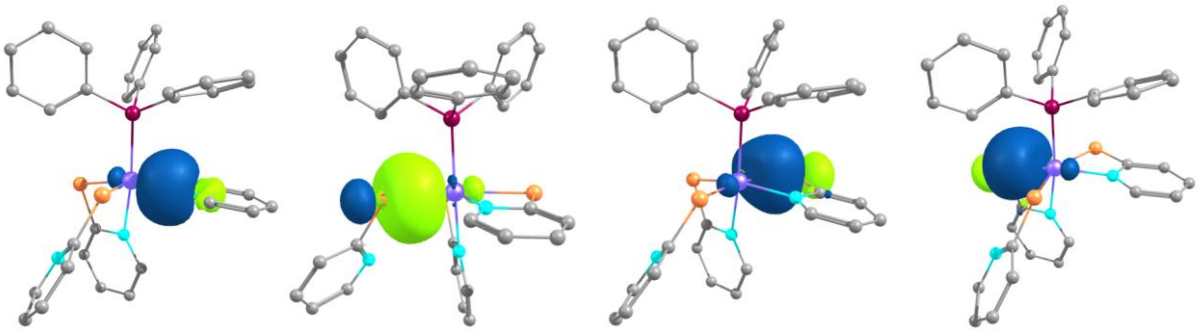


Figure S66. Selected NBOs of **3b** (isocontour values: ±0.043 [e.bohr^{-3}]$^{1/2}$).

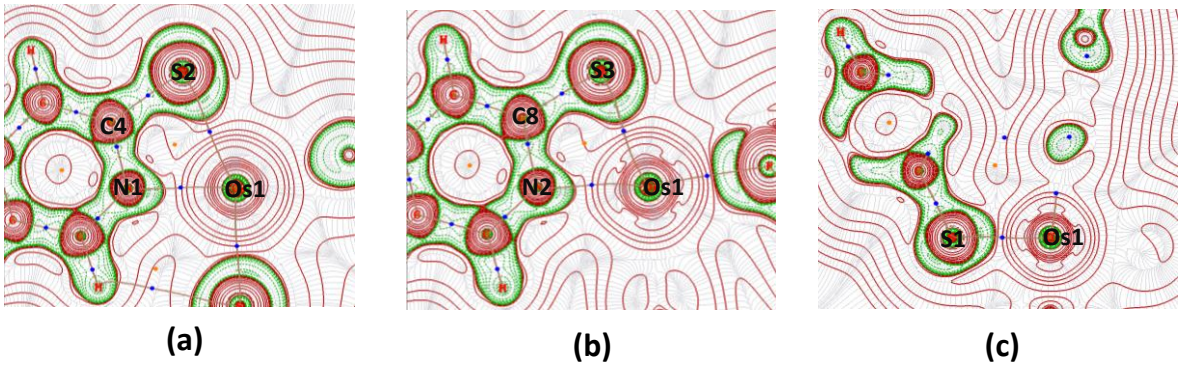


Figure S67. Contour-line diagram of the Laplacian of electron density in the Os1-N1-C4-S2 (a), Os1-N2-C8-S3 (b) planes and Os1-S1 (c) bond of **3b**, respectively. The solid brown lines are bond paths, while blue spheres indicate the bond critical points and orange sphere indicates ring critical points. Area of charge concentration [$\nabla^2\rho(r)<0$] are indicated by solid lines and area of charge depletion [$\nabla^2\rho(r)>0$] are shown by dashed lines.

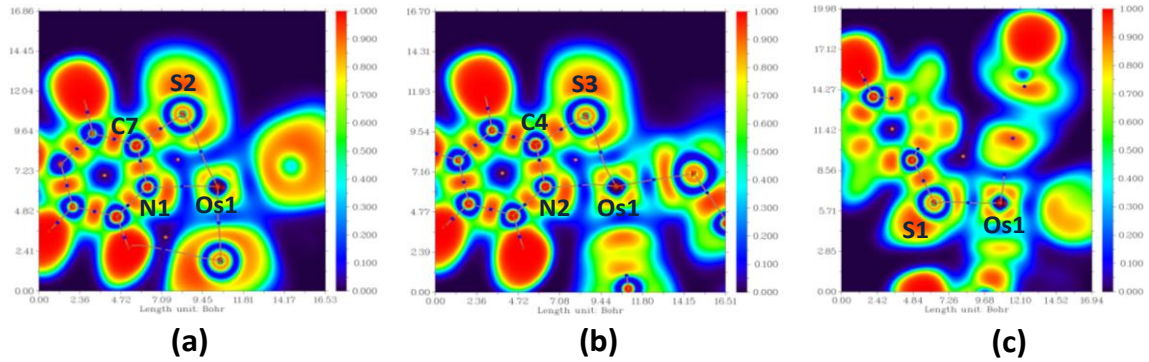


Figure S68. ELF plot in the Os1-N1-C5-S1 (a) and Os1-N2-C10-S2 (b) planes of **3b**, respectively.

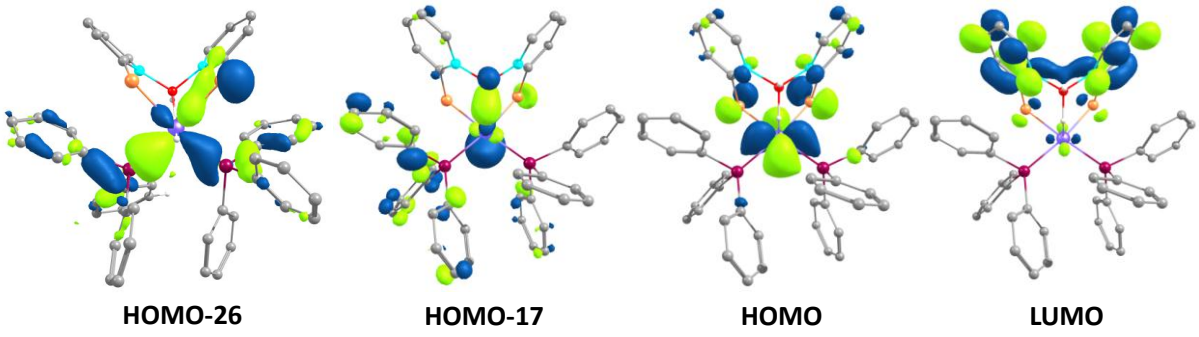


Figure S69. Selected molecular orbitals of **4a** (isocontour values: ±0.043 [e.bohr^{-3}]$^{1/2}$).

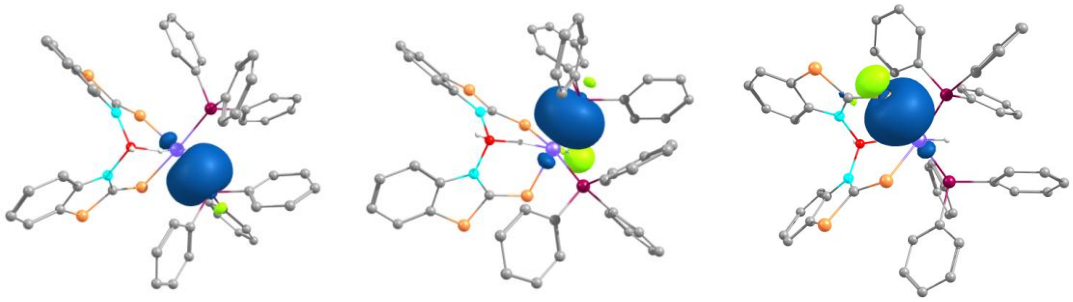
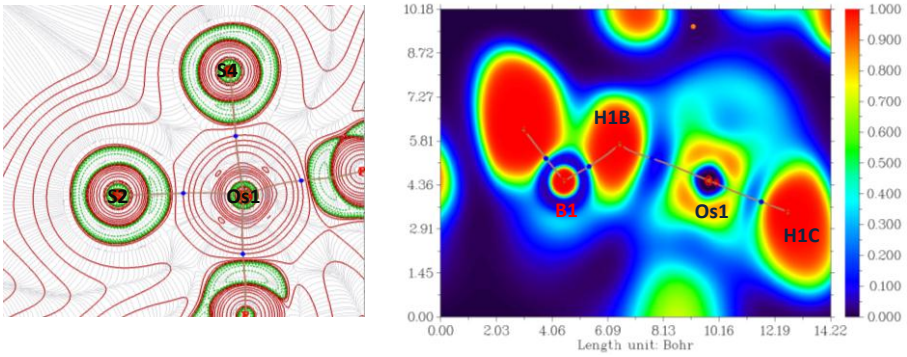


Figure S70. Selected NBOs of **4a** (isocontour values: ±0.043 [e.bohr^{-3}]$^{1/2}$).



(a) **(b)**

Figure S71. (a) Contour-line diagram of the Laplacian of electron density along Os-S and OS-P bonds in the Os1-S2-S1-P1-P2 planes and of **4a**. The solid brown lines are bond paths, while blue spheres indicate the bond critical points and orange sphere indicates ring critical points. Area of charge concentration [$\nabla^2\rho(r)<0$] are indicated by solid lines and area of charge depletion [$\nabla^2\rho(r)>0$] are shown by dashed lines.; (b) **.** ELF plot in the H1C-Os1-H2B-B1 plane.

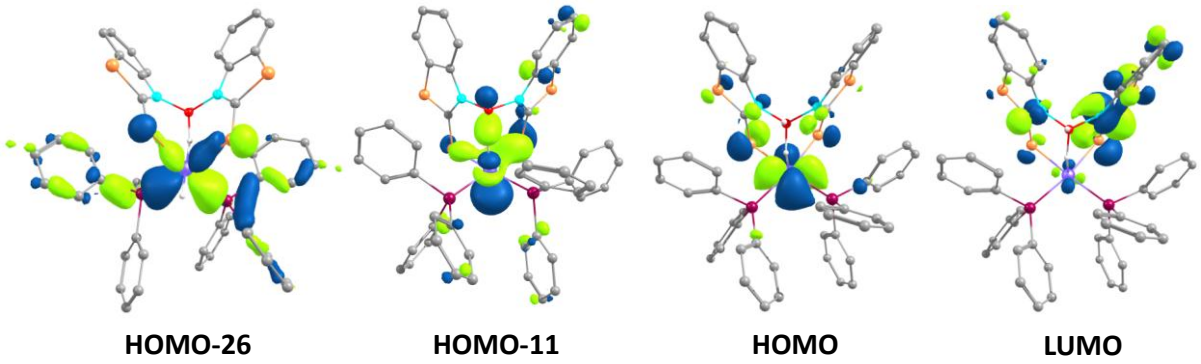


Figure S72. Selected molecular orbitals of **4b** (isocontour values: ±0.043 [e.bohr^{-3}]$^{1/2}$).

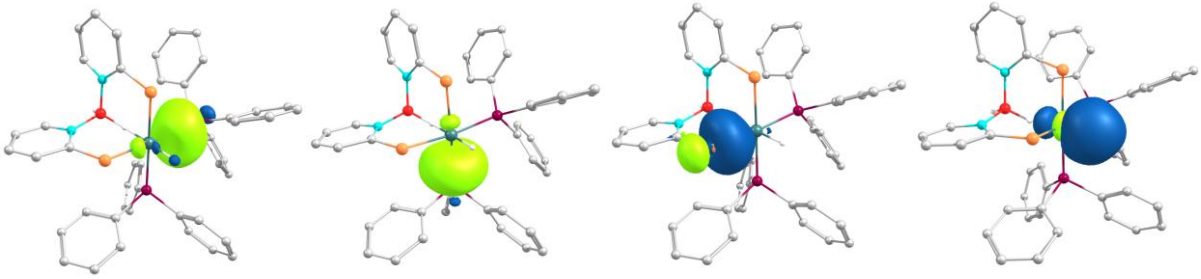


Figure S73. Selected NBOs of **4b** (isocontour values: ±0.043 [e.bohr^{-3}]$^{1/2}$).

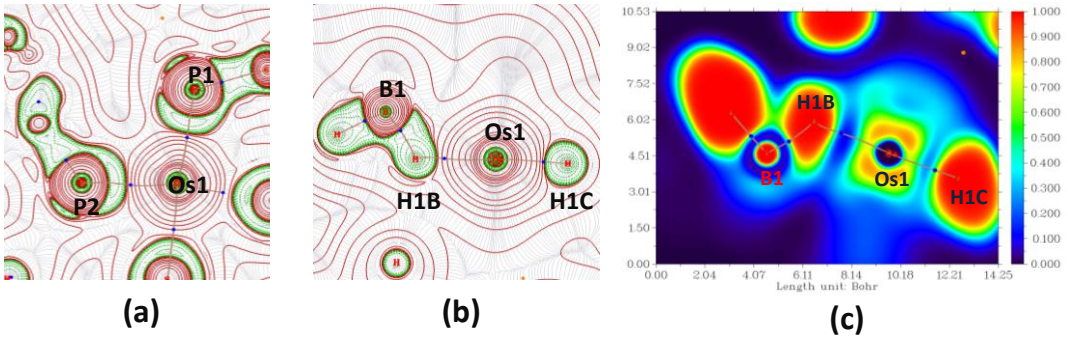


Figure S74. Contour-line diagram of the Laplacian of electron density along Os-S and OS-P bonds in the Os1-S2-S1-P1-P2 (a) and H1C-Os1-H2B-B1 (b) planes and of **4b**. The solid brown lines are bond paths, while blue spheres indicate the bond critical points and orange sphere indicates ring critical points. Area of charge concentration [$\nabla^2\rho(r)<0$] are indicated by solid lines and area of charge depletion [$\nabla^2\rho(r)>0$] are shown by dashed lines.; (b) ELF plot in the H1C-Os1-H2B-B1 plane of **4b**.

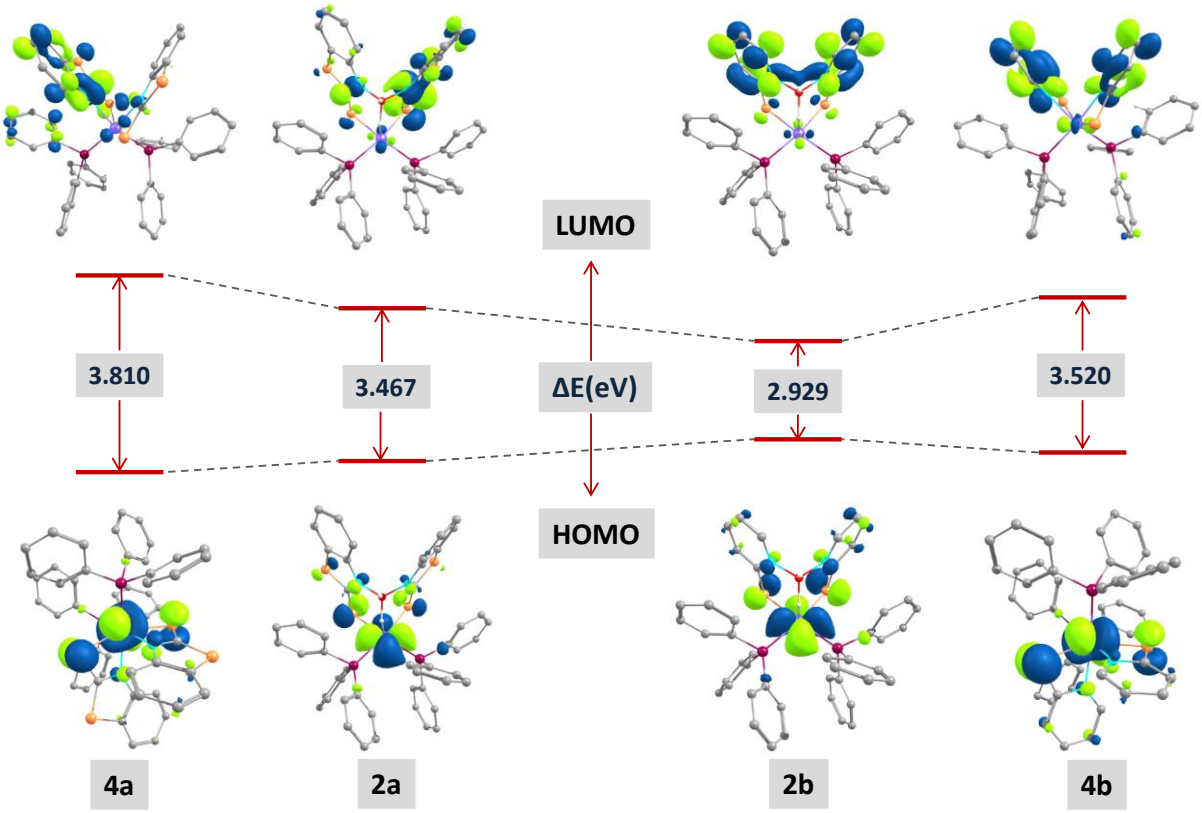


Figure S75. Comparison of HOMO-LUMO gap between **2a-b** and **4a-b**.

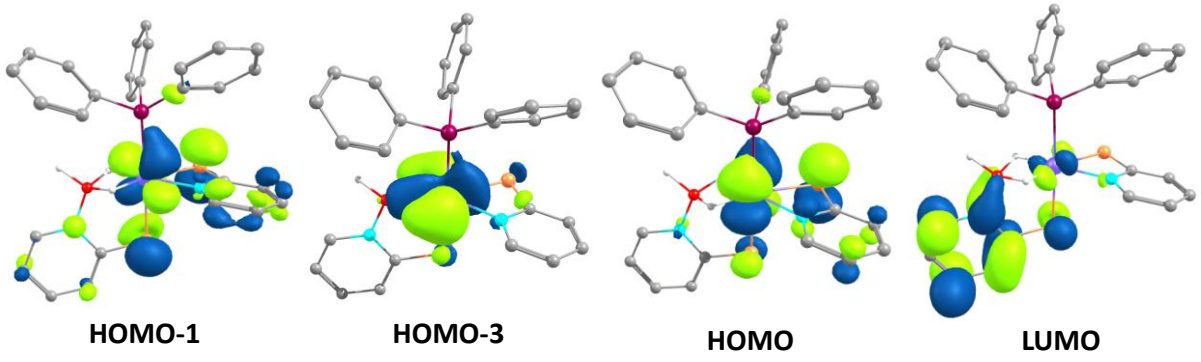


Figure S76. Selected molecular orbitals of **5'** (isocontour values: ±0.043 [e.bohr^{-3}]$^{1/2}$).

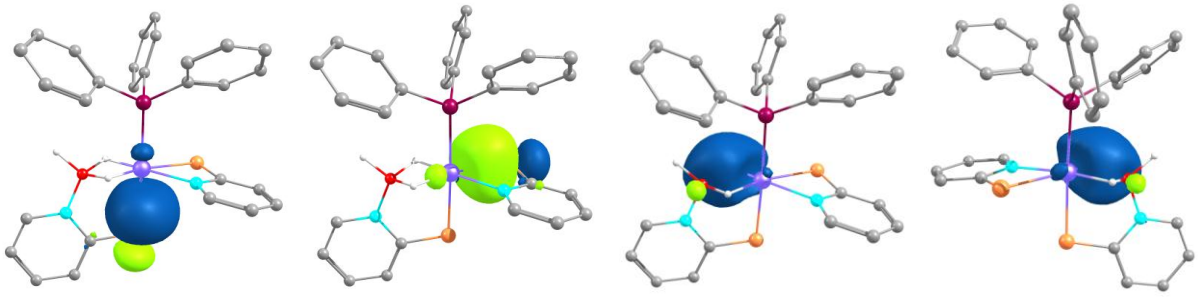


Figure S77. Selected NBOs of **5'** (isocontour values: ±0.043 [e.bohr^{-3}]$^{1/2}$).

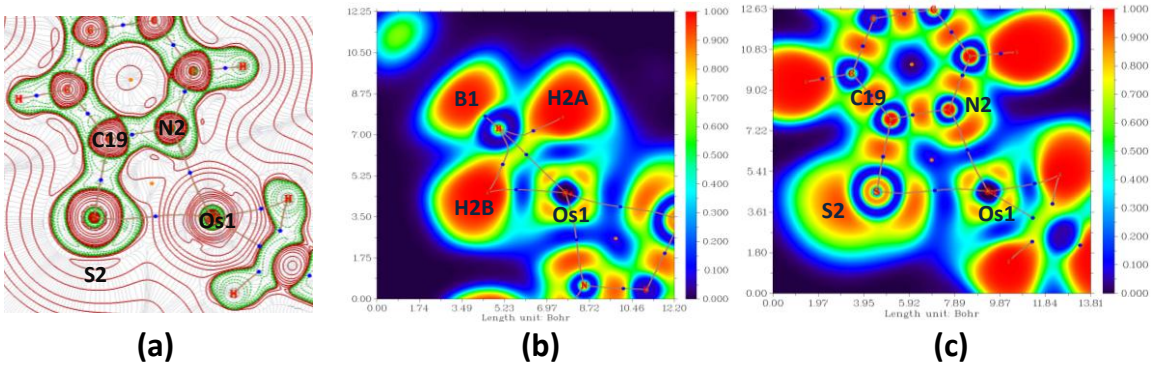


Figure S78. (a) Contour-line diagram of the Laplacian of electron density in the Os1-N2-C19-S2 plane of **5'**. The solid brown lines are bond paths, while blue spheres indicate the bond critical points and orange sphere indicates ring critical points. Area of charge concentration [$\nabla^2\rho(r)<0$] are indicated by solid lines and area of charge depletion [$\nabla^2\rho(r)>0$] are shown by dashed lines ; ELF plot in Os1-H2A-B1-H2B (b) and Os1-N2-C19-S2 (c) planes of **5'**.

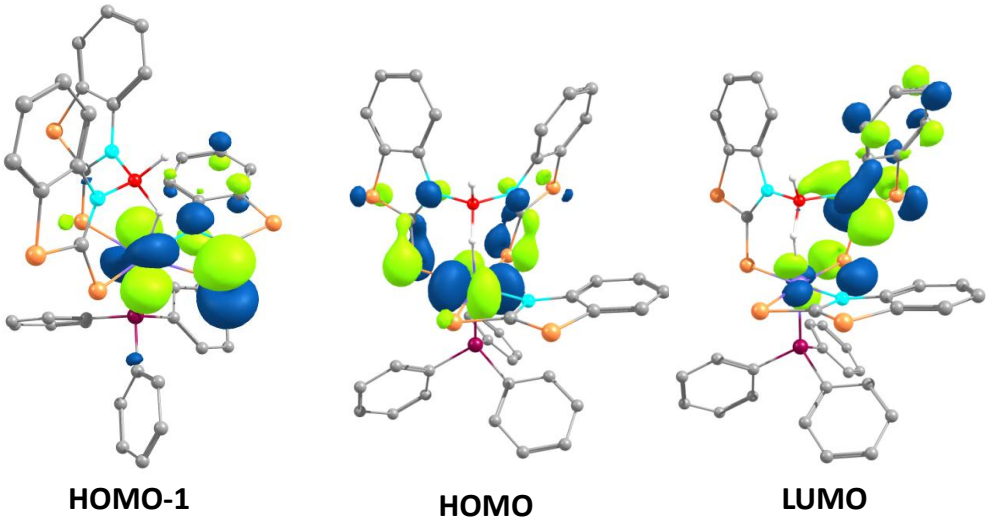


Figure S79. Selected molecular orbitals of *trans*-**6** (isocontour values: ±0.043 [e.bohr^{-3}]$^{1/2}$).

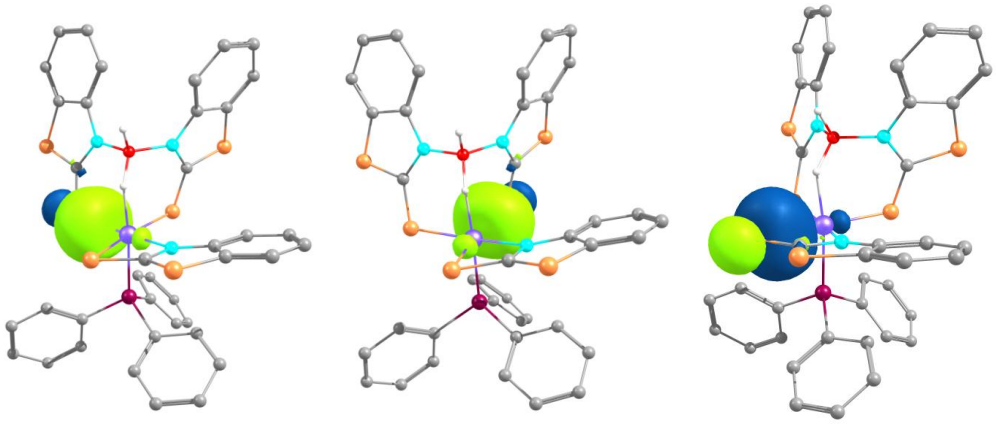


Figure S80. Selected NBOs of *trans*-**6** (isocontour values: ±0.043 [e.bohr^{-3}]$^{1/2}$).

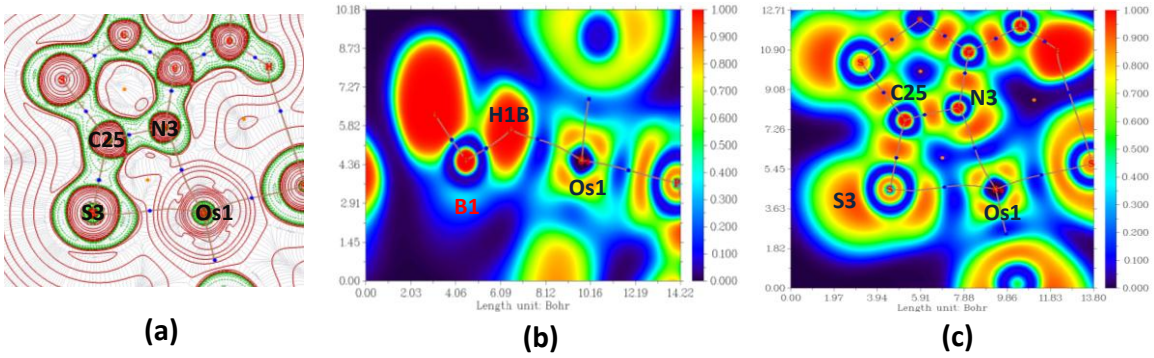


Figure S81. (a) Contour-line diagram of the Laplacian of electron density in the Os1-N3-C25-S3 plane of *trans*-**6**. The solid brown lines are bond paths, while blue spheres indicate the bond critical points and orange sphere indicates ring critical points. Area of charge concentration [$\nabla^2\rho(r)<0$] are indicated by solid lines and area of charge depletion [$\nabla^2\rho(r)>0$] are shown by dashed lines; ELF plot in Os1-H1B-B1 (b) and the Os1-N3-C25-S3 (c) planes of *trans*-**6**, respectively.

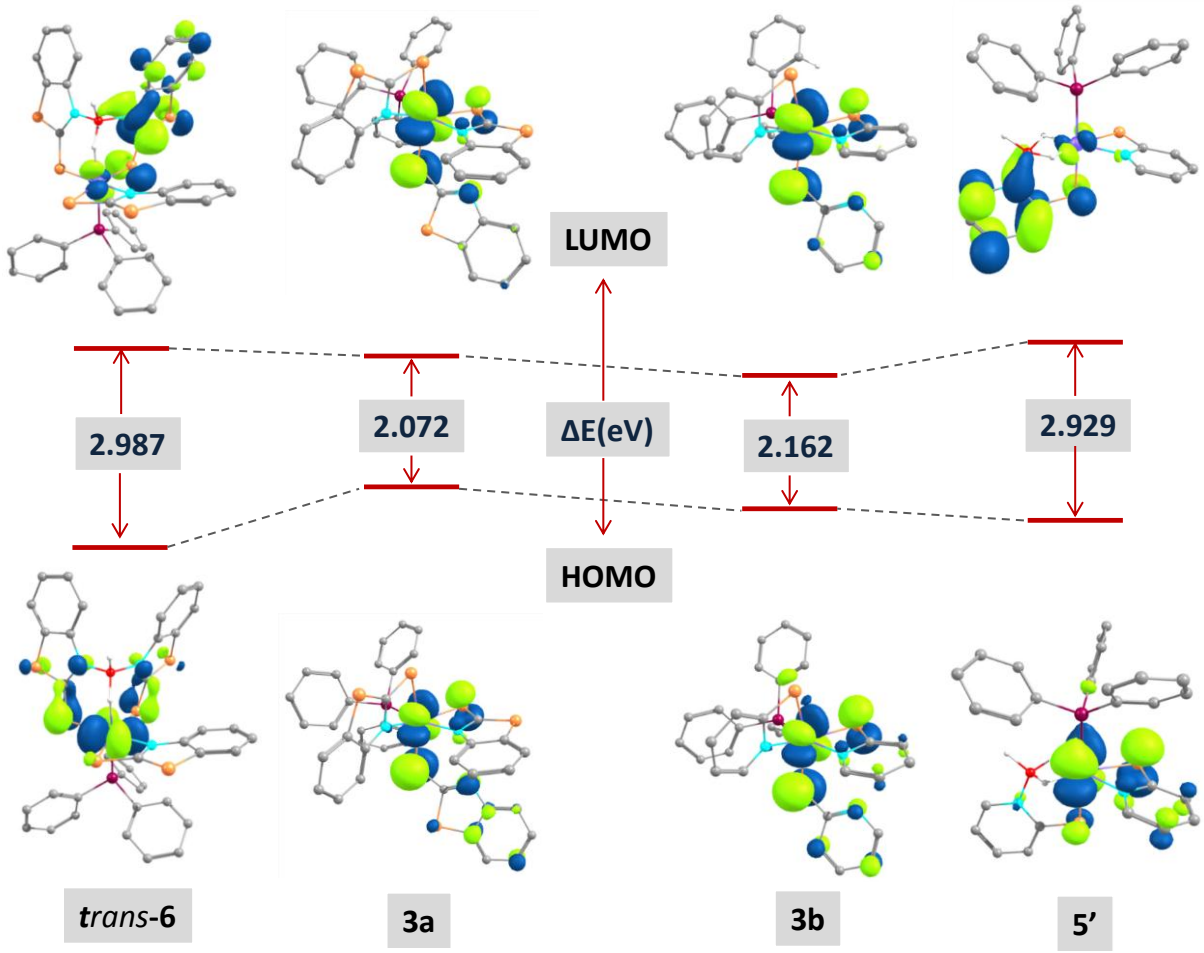


Figure S82. Comparison of HOMO-LUMO gap between **3a-b** and **5'**, *trans*-**6**.

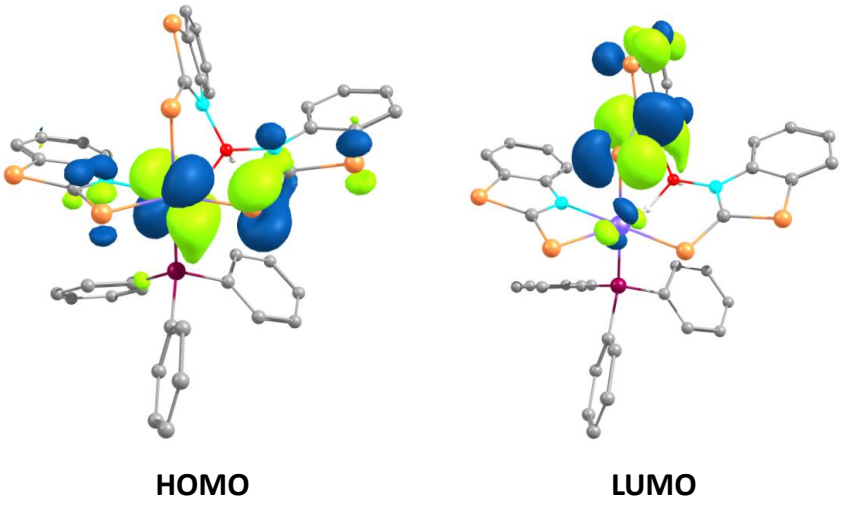


Figure S83. Selected molecular orbitals of *cis*-**6** (isocontour values: ±0.043 [e.bohr^{-3}]$^{1/2}$).

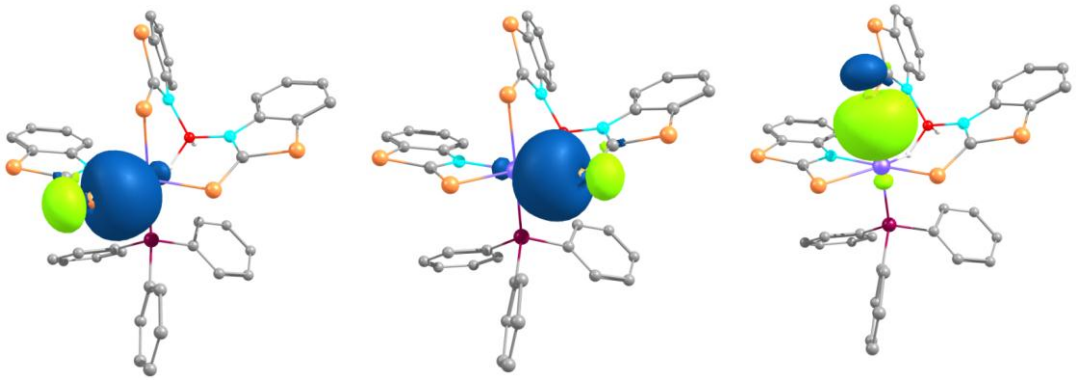


Figure S84. Selected NBOs of *cis*-**6** (isocontour values: ±0.043 [e.bohr^{-3}]$^{1/2}$).

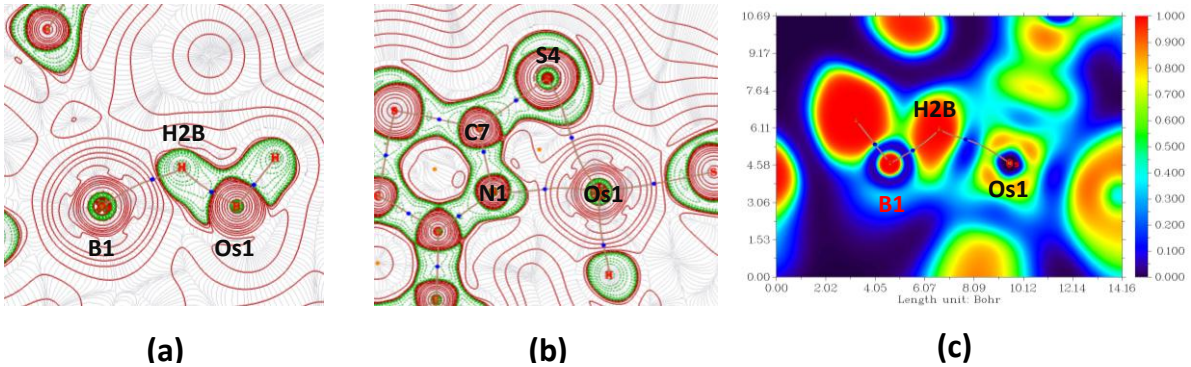


Figure S85. Contour-line diagram of the Laplacian of electron density in the Os1-H2B-B1 (a) and Os1-N1-C7-S4 (b) planes of *cis*-**6**, respectively. The solid brown lines are bond paths, while blue spheres indicate the bond critical points and orange sphere indicates ring critical points. Area of charge concentration [$\nabla^2\rho(r)<0$] are indicated by solid lines and area of charge depletion [$\nabla^2\rho(r)>0$] are shown by dashed lines ; (c) ELF plot in Os1H2BB1 of *cis*-**6**.

IV Cartesian Coordinates of all Optimized Structures

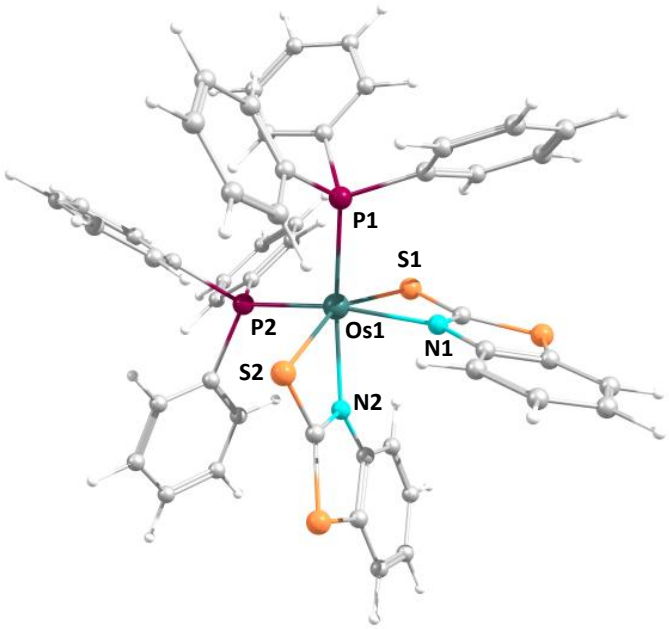


Figure S86. Optimized geometry of **2a**.
Total energy = -4405.03037684 a.u.
Cartesian coordinates for the calculated structure **2a** (in Å)

Os	-0.277369000	0.031039000	0.019350000	H	1.562534000	2.279118000	-4.957811000
P	1.030701000	-1.929131000	0.087659000	C	3.532202000	2.524497000	-4.118010000
P	1.412027000	1.697068000	-0.021537000	H	4.007607000	2.728268000	-5.071161000
S	-0.810590000	-0.318831000	-2.427751000	C	1.773100000	-3.898476000	2.040234000
S	-0.859861000	0.378308000	2.447690000	H	1.604701000	-4.638249000	1.268007000
C	2.301175000	1.988083000	-1.641701000	C	0.179813000	3.709223000	1.549135000
N	-2.094438000	-1.165758000	-0.369182000	H	0.133193000	2.942216000	2.311992000
C	1.562385000	-2.536592000	1.770810000	C	-0.858144000	-4.038009000	0.266615000
C	2.608364000	-2.084623000	-0.904523000	H	-1.054576000	-3.655026000	1.260255000
N	-1.841342000	1.534406000	0.372102000	C	0.799716000	4.439707000	-0.655276000
C	3.722344000	0.551981000	1.132355000	H	1.239602000	4.260593000	-1.626401000
H	3.526035000	-0.265917000	0.454248000	C	-2.781113000	2.367512000	-0.214989000
C	-2.144090000	-1.108056000	-1.687331000	C	4.281892000	2.521416000	-2.944772000
C	0.112564000	-3.430994000	-0.541401000	H	5.346810000	2.724029000	-2.978295000
C	1.786256000	-1.616121000	2.799272000	C	3.186042000	2.713849000	2.027887000
H	1.634315000	-0.562034000	2.616765000	H	2.572109000	3.602182000	2.061224000
C	2.868640000	1.662556000	1.158300000	C	2.203064000	-2.037528000	4.061587000
C	2.686076000	-1.450976000	-2.150761000	H	2.364960000	-1.303330000	4.842683000
H	1.853884000	-0.857201000	-2.501012000	C	-4.169202000	-2.174667000	-0.774126000
C	-1.999738000	1.413998000	1.677123000	C	1.556739000	2.005336000	-2.828848000
C	3.704813000	-2.845315000	-0.474828000	H	0.490608000	1.823459000	-2.798610000
H	3.683244000	-3.340243000	0.486826000	C	3.821200000	-1.579311000	-2.949507000
C	-3.224063000	-1.751846000	0.186815000	H	3.856384000	-1.077850000	-3.909925000
C	3.672171000	2.261293000	-1.717370000	C	4.905207000	-2.335689000	-2.510978000
H	4.276648000	2.274355000	-0.820940000	H	5.791510000	-2.431066000	-3.128493000
C	2.162914000	2.270576000	-4.054725000	C	0.747847000	3.418084000	0.299702000

C	4.848136000	0.486488000	1.948638000
H	5.491640000	-0.384829000	1.900580000
C	0.333135000	-3.951140000	-1.821096000
H	1.072919000	-3.504979000	-2.472086000
C	2.188191000	-4.320948000	3.300943000
H	2.339106000	-5.378496000	3.488347000
C	-0.319632000	4.977309000	1.831811000
H	-0.753766000	5.174880000	2.805673000
C	-1.575365000	-5.142371000	-0.184058000
H	-2.320134000	-5.595707000	0.460481000
C	5.142420000	1.531719000	2.821851000
H	6.015712000	1.481697000	3.462749000
C	4.843758000	-2.965368000	-1.269255000
H	5.683166000	-3.553663000	-0.914516000
C	-3.702097000	2.914235000	0.705944000
C	-1.340846000	-5.657718000	-1.458387000
H	-1.898301000	-6.518642000	-1.810447000
C	0.294215000	5.709850000	-0.373493000
H	0.344571000	6.482954000	-1.132394000
C	-0.388161000	-5.055919000	-2.275274000
H	-0.199221000	-5.443929000	-3.270202000
C	4.306573000	2.644158000	2.856821000
H	4.526069000	3.470511000	3.524115000
C	-0.266507000	5.984670000	0.869332000
H	-0.658488000	6.971800000	1.087704000
C	2.403289000	-3.390957000	4.317430000
H	2.720668000	-3.720848000	5.300551000
S	-3.596567000	-1.799224000	-2.399120000
C	-5.358024000	-2.796649000	-0.403632000
C	-3.484679000	-1.961717000	1.545204000
C	-4.673879000	-2.580490000	1.913225000
C	-5.604618000	-2.995952000	0.952102000
H	-6.074621000	-3.116598000	-1.150798000
H	-6.526186000	-3.474166000	1.262946000
H	-4.884156000	-2.741455000	2.964449000
H	-2.766323000	-1.631874000	2.284190000
S	-3.349956000	2.332870000	2.334674000
C	-4.715111000	3.776538000	0.296586000
C	-2.885452000	2.691890000	-1.570992000
C	-4.804842000	4.092716000	-1.056408000
C	-3.897868000	3.552468000	-1.977663000
H	-3.988852000	3.807212000	-3.027362000
H	-5.587344000	4.760493000	-1.397434000
H	-5.417388000	4.190028000	1.010651000
H	-2.192352000	2.257488000	-2.279207000

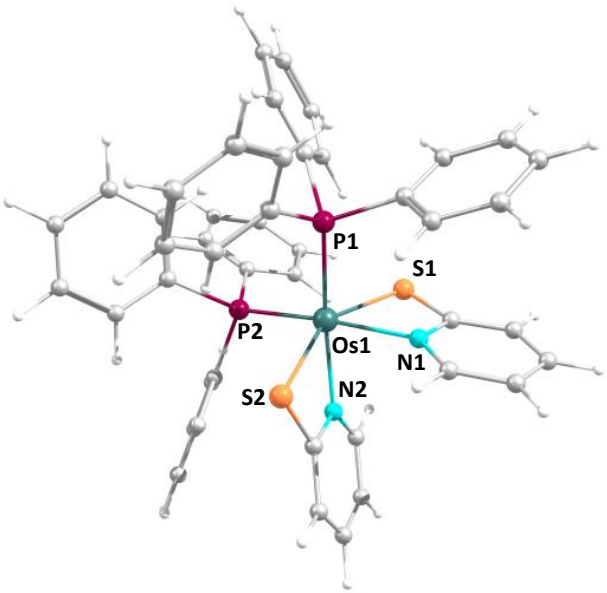


Figure S87. Optimized geometry of **2b**.
Total energy = -3456.12698883 a.u.
Cartesian coordinates for the calculated structure **2b** (in Å)

Os	-0.016575000	-0.829918000	0.005001000	H	-2.276699000	-3.751887000	3.259831000
P	-1.772439000	0.748396000	-0.179520000	C	3.707253000	-0.793528000	-1.413809000
P	1.833124000	0.670867000	0.136839000	H	2.912376000	-0.837599000	-2.148104000
S	-0.535890000	-1.380699000	2.406276000	C	-4.110093000	-0.770722000	-0.714577000
S	0.325287000	-1.541462000	-2.373108000	H	-3.676239000	-0.920273000	-1.696149000
C	2.203601000	1.462179000	1.792060000	C	4.540011000	-0.112792000	0.736148000
N	-1.430996000	-2.436280000	0.271218000	H	4.415467000	0.383445000	1.688533000
C	-2.126996000	1.446842000	-1.872902000	C	1.941269000	-3.344306000	0.608872000
C	-1.812690000	2.271623000	0.906750000	H	1.933223000	-3.066669000	1.655674000
N	1.283495000	-2.523244000	-0.222579000	C	3.050521000	3.270476000	3.178159000
C	1.057969000	3.231977000	-0.775868000	H	3.446895000	4.277116000	3.255175000
H	0.358351000	3.198609000	0.047313000	C	2.836479000	2.258504000	-2.062517000
C	-1.500621000	-2.599533000	1.617418000	H	3.547131000	1.467742000	-2.255200000
C	-3.441385000	0.016478000	0.233161000	C	-1.334447000	2.028785000	-4.094207000
C	-1.103039000	1.504467000	-2.822631000	H	-0.524405000	2.058397000	-4.814027000
H	-0.120703000	1.130355000	-2.572141000	C	-2.884107000	-4.534440000	1.337247000
C	1.936807000	2.161451000	-0.994452000	H	-3.458991000	-5.356335000	1.749890000
C	-1.290034000	2.181262000	2.203173000	C	-2.788053000	-4.368510000	-0.049792000
H	-0.857035000	1.249315000	2.539339000	H	-3.279202000	-5.048007000	-0.734258000
C	1.221655000	-2.799970000	-1.552844000	C	2.045873000	0.691790000	2.950859000
C	-2.365877000	3.492365000	0.495936000	H	1.672364000	-0.320898000	2.876587000
H	-2.763067000	3.603736000	-0.503791000	C	-1.326228000	3.274890000	3.067229000
C	-2.051032000	-3.304368000	-0.543399000	H	-0.912920000	3.179384000	4.064973000
H	-1.929697000	-3.124122000	-1.604414000	C	-1.877617000	4.482890000	2.647518000
C	2.725991000	2.755304000	1.923462000	H	-1.900314000	5.336252000	3.316346000
H	2.888639000	3.370041000	1.048795000	C	3.491440000	-0.139168000	-0.191827000
C	2.376673000	1.202192000	4.204579000	C	1.825699000	-3.948292000	-2.077669000
H	2.244278000	0.583494000	5.085401000	H	1.751259000	-4.154566000	-3.137978000
C	2.874023000	2.498532000	4.324076000	C	1.076218000	4.358414000	-1.592751000
H	3.127818000	2.900274000	5.298934000	H	0.386955000	5.171652000	-1.394479000
C	-3.396444000	1.928736000	-2.231557000	C	-4.029886000	0.186826000	1.490878000
H	-4.214948000	1.884594000	-1.523853000	H	-3.537789000	0.784552000	2.246569000
C	-2.236055000	-3.648546000	2.183051000	C	2.578047000	-4.487156000	0.149762000

H	3.109076000	-5.125434000	0.843894000
C	-3.628618000	2.453007000	-3.500658000
H	-4.617859000	2.815644000	-3.758320000
C	4.931659000	-1.391868000	-1.700356000
H	5.072636000	-1.888633000	-2.654078000
C	-5.340986000	-1.351121000	-0.421032000
H	-5.844728000	-1.949144000	-1.172670000
C	1.970195000	4.437834000	-2.659005000
H	1.983787000	5.312834000	-3.299357000
C	-2.394926000	4.587678000	1.357489000
H	-2.821953000	5.524702000	1.016362000
C	2.511563000	-4.790659000	-1.215027000
H	2.993995000	-5.683101000	-1.598564000
C	-5.923562000	-1.164759000	0.831819000
H	-6.884205000	-1.613173000	1.060039000
C	5.764386000	-0.718820000	0.451328000
H	6.559512000	-0.684410000	1.188253000
C	-5.261088000	-0.398611000	1.786871000
H	-5.701570000	-0.248494000	2.766533000
C	2.847980000	3.382967000	-2.889680000
H	3.555274000	3.431499000	-3.710597000
C	5.967141000	-1.357896000	-0.768004000
H	6.919993000	-1.825756000	-0.989971000
C	-2.596421000	2.504787000	-4.437276000
H	-2.778656000	2.907760000	-5.427565000

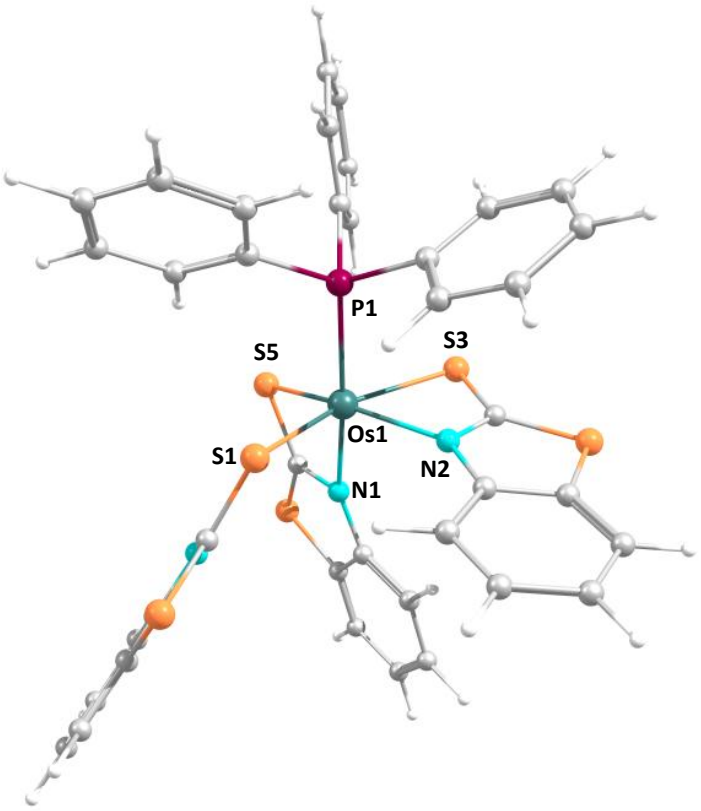


Figure S88. Optimized geometry of **3a**.
Total energy = -4488.96109316 a.u.
Cartesian coordinates for the calculated structure **3a** (in Å)

C	2.408433000	-1.209489000	1.411572000
C	4.486950000	-1.707898000	0.828006000
C	5.554509000	-2.026507000	-0.021839000
H	5.380193000	-2.090425000	-1.088928000
C	6.808977000	-2.255804000	0.525545000
H	7.640479000	-2.503946000	-0.124172000
C	7.017233000	-2.172859000	1.911150000
H	8.005388000	-2.355576000	2.317602000
C	5.970932000	-1.861071000	2.773211000
H	6.134968000	-1.801001000	3.842474000
C	4.709763000	-1.630501000	2.223922000
C	1.789403000	-0.658048000	-2.276497000
C	2.709419000	1.274223000	-1.573502000
C	2.885722000	2.448636000	-0.836829000
H	2.163227000	2.726315000	-0.080571000
C	4.003852000	3.233157000	-1.088655000
H	4.152119000	4.144839000	-0.521768000
C	4.943781000	2.864548000	-2.060900000
H	5.808040000	3.493112000	-2.240148000
C	4.783184000	1.695485000	-2.798840000
H	5.511509000	1.407978000	-3.547591000
C	3.664168000	0.906645000	-2.546476000
C	-1.079270000	2.511761000	-0.915913000
C	-0.403761000	2.788810000	1.228846000

C	0.116889000	2.485606000	2.490734000
H	0.418339000	1.471340000	2.715796000
C	0.241794000	3.505699000	3.427195000
H	0.648782000	3.278557000	4.405753000
C	-0.143452000	4.818545000	3.127470000
H	-0.036189000	5.597273000	3.873381000
C	-0.658478000	5.135608000	1.873445000
H	-0.952497000	6.150715000	1.634597000
C	-0.780673000	4.117227000	0.932526000
N	-0.600166000	1.916548000	0.164434000
N	1.669503000	0.368660000	-1.463292000
N	3.188680000	-1.467422000	0.414456000
P	-2.388831000	-0.870099000	0.059359000
S	0.668505000	-0.940755000	1.430384000
S	3.205401000	-1.230255000	3.023741000
S	-1.275642000	1.506203000	-2.288739000
S	-1.370764000	4.233273000	-0.725695000
S	3.204625000	-0.619040000	-3.306982000
S	0.482368000	-1.790460000	-2.131973000
C	-3.471488000	0.428421000	0.808991000
C	-3.161467000	0.928424000	2.081469000
C	-4.541365000	0.991877000	0.105434000
C	-3.924153000	1.944562000	2.649561000
H	-2.321477000	0.525303000	2.635271000
C	-5.298896000	2.016785000	0.672458000
H	-4.787612000	0.635805000	-0.886563000
C	-4.998116000	2.490197000	1.946695000
H	-3.673090000	2.315174000	3.636908000
H	-6.124057000	2.443391000	0.113140000
H	-5.590436000	3.284109000	2.387701000
C	-3.445573000	-1.574231000	-1.299490000
C	-3.057168000	-1.516271000	-2.640179000
C	-4.656234000	-2.206129000	-0.976140000
C	-3.861569000	-2.069504000	-3.637446000
H	-2.121494000	-1.051497000	-2.913275000
C	-5.460958000	-2.751512000	-1.971118000
H	-4.972631000	-2.280927000	0.057214000
C	-5.065360000	-2.683807000	-3.307458000
H	-3.539869000	-2.017784000	-4.671456000
H	-6.393457000	-3.235118000	-1.702144000
H	-5.689846000	-3.113508000	-4.082792000
C	-2.454634000	-2.284484000	1.261253000
C	-1.636940000	-3.392803000	1.000036000
C	-3.322793000	-2.330856000	2.356845000
C	-1.689479000	-4.519567000	1.814049000
H	-0.951056000	-3.376006000	0.161721000
C	-3.367361000	-3.458807000	3.177611000
H	-3.971329000	-1.493155000	2.578210000
C	-2.553085000	-4.554976000	2.908490000
H	-1.048494000	-5.366644000	1.597434000
H	-4.042798000	-3.476224000	4.025857000
H	-2.588797000	-5.430907000	3.546531000
Os	-0.237367000	-0.097687000	-0.551223000

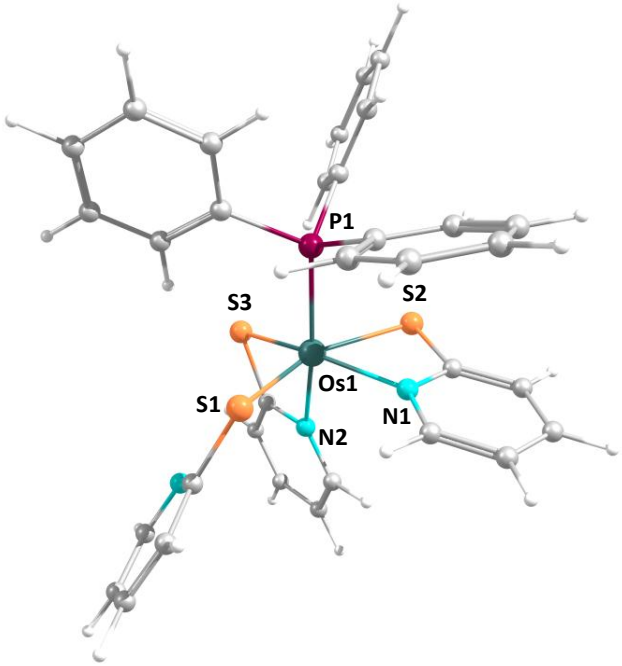


Figure S89. Optimized geometry of **3b**.
Total energy = -3065.59923664 a.u.
Cartesian coordinates for the calculated structure **3b** (in Å)

C	-2.955098000	1.413279000	1.503447000
C	-4.939916000	1.922308000	0.474980000
C	-5.577209000	2.203678000	1.678699000
C	-2.589418000	-0.000004000	-2.154158000
C	-3.373986000	-1.691057000	-0.749607000
C	-4.536416000	-1.817285000	-1.497226000
C	0.117635000	-2.994727000	-0.051222000
C	-0.417811000	-2.301970000	2.126235000
C	-0.274394000	-3.590392000	2.611920000
N	-0.228973000	-2.015132000	0.827020000
N	-2.429444000	-0.801936000	-1.072679000
N	-3.662332000	1.538335000	0.378103000
P	1.726389000	0.494076000	-0.007119000
S	-1.215642000	1.003928000	1.457908000
S	0.295682000	-2.339128000	-1.651575000
S	-1.172073000	1.029177000	-2.294315000
C	2.521633000	-0.297603000	1.462653000
C	2.397554000	0.274770000	2.735118000
C	3.123739000	-1.557713000	1.345259000
C	2.893542000	-0.383913000	3.859172000
H	1.915125000	1.237444000	2.853122000
C	3.618625000	-2.213504000	2.470303000
H	3.208548000	-2.029749000	0.373569000
C	3.510578000	-1.626515000	3.729931000
H	2.797140000	0.077747000	4.835773000
H	4.087891000	-3.184901000	2.360509000
H	3.900219000	-2.135877000	4.604335000
C	2.947369000	0.229412000	-1.383121000
C	2.486951000	0.219944000	-2.704162000
C	4.326018000	0.144344000	-1.149816000
C	3.383600000	0.128363000	-3.766794000
H	1.425478000	0.280379000	-2.907885000
C	5.220983000	0.044594000	-2.212924000
H	4.712002000	0.146551000	-0.138177000
C	4.752270000	0.037363000	-3.525325000
H	3.007267000	0.120961000	-4.783627000
H	6.284582000	-0.027100000	-2.013338000
H	5.449102000	-0.039554000	-4.352595000
C	1.963624000	2.314751000	0.281221000
C	0.968346000	3.216627000	-0.108074000
C	3.166830000	2.817803000	0.796083000
C	1.171767000	4.591144000	0.015505000
H	0.029936000	2.849823000	-0.500897000
C	3.364766000	4.189151000	0.927206000
H	3.955663000	2.142116000	1.103025000
C	2.366386000	5.080947000	0.535021000
H	0.388507000	5.275272000	-0.291172000
H	4.299468000	4.560666000	1.332684000
H	2.521446000	6.149632000	0.634457000
Os	-0.484739000	-0.270123000	-0.384951000
C	0.272911000	-4.320203000	0.379901000
C	0.075578000	-4.612531000	1.719082000
H	-0.689432000	-1.465908000	2.757707000
H	-0.430375000	-3.789201000	3.664086000
H	0.190834000	-5.630713000	2.074328000
H	0.540704000	-5.083994000	-0.339027000
C	-3.511572000	1.670351000	2.772319000
C	-4.835669000	2.071087000	2.854207000
H	-5.477464000	2.010936000	-0.465585000
H	-6.614537000	2.515397000	1.693984000
H	-5.285918000	2.276129000	3.819599000
H	-2.903116000	1.557112000	3.661159000

C	-3.724137000	-0.078794000	-2.959370000
C	-4.707740000	-0.998268000	-2.616968000
H	-3.819816000	0.567325000	-3.822445000
H	-5.604074000	-1.082986000	-3.221364000
H	-5.286940000	-2.542077000	-1.209786000
H	-3.184135000	-2.302299000	0.124235000

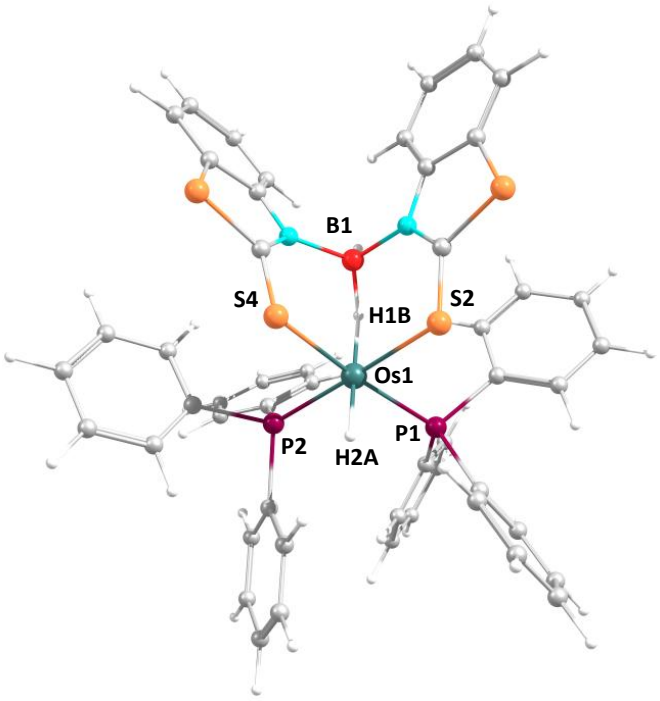


Figure S90. Optimized geometry of **4a**.
Total energy = -4431.72328713 a.u.
Cartesian coordinates for the calculated structure **4a** (in Å)

Os	0.352347000	-0.073333000	-0.843174000
C	2.951066000	-1.250503000	1.610810000
C	2.721494000	-1.743037000	2.901353000
H	1.877013000	-2.389342000	3.098017000
C	3.585332000	-1.429946000	3.951131000
H	3.387568000	-1.826931000	4.941021000
C	4.699347000	-0.625694000	3.729146000
H	5.373957000	-0.386927000	4.543889000
C	4.943643000	-0.136907000	2.446973000
H	5.810563000	0.485103000	2.255066000
C	4.078331000	-0.444879000	1.400645000
H	4.297364000	-0.067839000	0.410718000
C	3.104962000	-2.400451000	-0.988032000
C	4.199005000	-3.118305000	-0.480639000
H	4.340227000	-3.208442000	0.589284000
C	5.117875000	-3.720269000	-1.336716000
H	5.958316000	-4.266576000	-0.922586000
C	4.959050000	-3.619681000	-2.718445000
H	5.675152000	-4.086850000	-3.385618000
C	3.876048000	-2.912894000	-3.233834000
H	3.741949000	-2.826415000	-4.306541000
C	2.958404000	-2.306664000	-2.375573000
H	2.132063000	-1.742539000	-2.785463000
C	0.946319000	-3.150930000	0.799096000
C	1.273945000	-4.454719000	0.411328000
H	2.069241000	-4.627785000	-0.300779000
C	0.574963000	-5.549170000	0.921345000
H	0.841813000	-6.549410000	0.597810000
C	-0.459703000	-5.362424000	1.833546000
H	-1.001382000	-6.214042000	2.229907000
C	-0.800725000	-4.068455000	2.223870000
H	-1.611704000	-3.905983000	2.925335000
C	-0.110203000	-2.976253000	1.704151000
H	-0.407074000	-1.978704000	2.002609000
C	-2.107239000	-2.264737000	-1.195527000
C	-3.880804000	-2.168585000	0.262713000
C	-4.678095000	-1.771126000	1.338988000
H	-4.392988000	-0.933553000	1.953702000
C	-5.852882000	-2.466300000	1.612358000
H	-6.467938000	-2.150210000	2.446860000
C	-6.250041000	-3.555153000	0.832409000
H	-7.169825000	-4.081098000	1.059151000
C	-5.461446000	-3.970234000	-0.236494000
H	-5.750718000	-4.818291000	-0.845620000
C	-4.286989000	-3.274108000	-0.504415000
C	-2.572743000	1.431545000	-1.344802000

C	-4.643237000	2.431041000	-0.359247000
C	-5.772208000	3.130061000	0.056267000
H	-6.341534000	3.727567000	-0.645742000
C	-6.140489000	3.060793000	1.397498000
H	-7.013547000	3.601187000	1.743450000
C	-5.371561000	2.319871000	2.299338000
H	-5.644113000	2.301344000	3.348204000
C	-4.248873000	1.612258000	1.878358000
H	-3.643800000	1.067948000	2.589902000
C	-3.892115000	1.639667000	0.527267000
C	1.114566000	2.341731000	1.791036000
C	0.785199000	1.327708000	2.693383000
H	0.634213000	0.323943000	2.323067000
C	0.639762000	1.594787000	4.054620000
H	0.387837000	0.789309000	4.735543000
C	0.816008000	2.888671000	4.535802000
H	0.700482000	3.099780000	5.593287000
C	1.135145000	3.914954000	3.646564000
H	1.264567000	4.929127000	4.008627000
C	1.280472000	3.644653000	2.288470000
H	1.506309000	4.459610000	1.611762000
C	0.553115000	3.503169000	-0.743868000
C	-0.649876000	4.008208000	-0.232119000
H	-1.131383000	3.517425000	0.605506000
C	-1.235534000	5.147947000	-0.775848000
H	-2.163615000	5.523701000	-0.359210000
C	-0.634508000	5.801379000	-1.850876000
H	-1.089768000	6.689507000	-2.274891000
C	0.554508000	5.302468000	-2.374891000
H	1.032569000	5.800130000	-3.211644000
C	1.144025000	4.163696000	-1.825163000
H	2.073191000	3.800640000	-2.244779000
C	3.092888000	2.238090000	-0.377613000
C	3.621260000	1.791182000	-1.596700000
H	2.988136000	1.234493000	-2.275463000
C	4.951791000	2.033344000	-1.934107000
H	5.336345000	1.675643000	-2.882940000
C	5.785324000	2.720515000	-1.053876000
H	6.822311000	2.904614000	-1.312299000
C	5.274724000	3.161993000	0.164718000
H	5.914256000	3.690114000	0.863915000
C	3.941817000	2.925059000	0.498649000
H	3.579071000	3.263807000	1.459005000
N	-2.665212000	-1.590463000	-0.163674000
N	-2.791543000	1.002940000	-0.077510000
P	1.837775000	-1.636306000	0.154660000
P	1.279553000	1.935883000	-0.024700000
S	-3.886379000	2.445945000	-1.946885000
S	-1.193339000	1.169612000	-2.271281000
S	-3.105206000	-3.605702000	-1.754984000
S	-0.617924000	-2.015998000	-1.948426000
B	-2.088995000	-0.276846000	0.512152000
H	-2.329571000	-0.334077000	1.682785000
H	-0.835890000	-0.226083000	0.558471000
H	1.413132000	0.050741000	-2.057002000

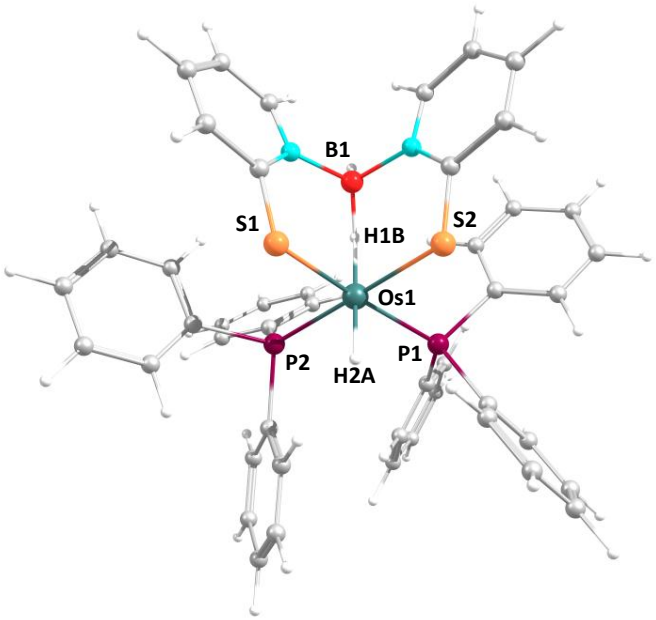


Figure S91. Optimized geometry of **4b**.
Total energy = -3482.80211904 a.u.
Cartesian coordinates for the calculated structure **4b** (in Å)

s	0.158274000	0.353974000	-0.702398000
C	-2.502828000	-1.543199000	1.182515000
C	-2.997803000	-1.335320000	2.475381000
H	-3.147127000	-0.331438000	2.849092000
C	-3.326936000	-2.413886000	3.297466000
H	-3.711096000	-2.226945000	4.294576000
C	-3.176021000	-3.719226000	2.839013000
H	-3.436961000	-4.557272000	3.475862000
C	-2.693047000	-3.938557000	1.549794000
H	-2.575336000	-4.948866000	1.174698000
C	-2.358949000	-2.862530000	0.732430000
H	-1.999650000	-3.055407000	-0.269936000
C	-3.272735000	-0.573085000	-1.358441000
C	-4.537516000	-1.100433000	-1.053905000
H	-4.811826000	-1.292808000	-0.023806000
C	-5.453522000	-1.389690000	-2.061862000
H	-6.423879000	-1.799635000	-1.803482000
C	-5.122368000	-1.158178000	-3.396773000
H	-5.833780000	-1.386287000	-4.183027000
C	-3.870417000	-0.637479000	-3.711334000
H	-3.599360000	-0.456594000	-4.745777000
C	-2.952769000	-0.348829000	-2.700536000
H	-1.975404000	0.035980000	-2.955738000
C	-2.898763000	1.290886000	0.839107000
C	-4.094512000	1.854151000	0.380215000
H	-4.575973000	1.460167000	-0.504407000
C	-4.677383000	2.934636000	1.043046000
H	-5.600665000	3.358134000	0.662588000
C	-4.081285000	3.468066000	2.182446000
H	-4.538617000	4.303925000	2.700287000
C	-2.884719000	2.923080000	2.645127000
H	-2.403056000	3.333905000	3.525910000
C	-2.295895000	1.854943000	1.972392000
H	-1.352079000	1.464776000	2.333472000
C	-0.522599000	3.656190000	-0.703163000
C	0.357181000	4.676213000	1.240717000
C	-0.892561000	6.025939000	-0.273967000
C	3.010761000	2.127107000	-0.838290000
C	5.083879000	3.333358000	-0.416529000
C	3.401986000	3.148770000	1.263887000
C	1.456931000	-1.940764000	1.850534000
C	0.638301000	-1.265883000	2.758123000
H	-0.085143000	-0.556757000	2.383033000
C	0.749690000	-1.486029000	4.131038000
H	0.099720000	-0.951527000	4.814991000
C	1.691354000	-2.386373000	4.620023000
H	1.782170000	-2.557878000	5.687067000
C	2.524279000	-3.061687000	3.727547000
H	3.268957000	-3.758025000	4.097773000
C	2.410279000	-2.838742000	2.358011000
H	3.081706000	-3.355638000	1.683289000
C	3.110599000	-1.682657000	-0.427687000
C	4.031913000	-0.931379000	0.314702000
H	3.692641000	-0.337549000	1.155613000
C	5.386538000	-0.944223000	-0.002629000
H	6.081890000	-0.359723000	0.590082000
C	5.848422000	-1.703849000	-1.077585000
H	6.904201000	-1.716389000	-1.325127000
C	4.941751000	-2.446712000	-1.827539000
H	5.286698000	-3.042185000	-2.665960000
C	3.583873000	-2.437448000	-1.504156000
H	2.900029000	-3.029790000	-2.097972000
C	0.706925000	-3.224005000	-0.681870000
C	0.289890000	-3.258946000	-2.019994000

H	0.265855000	-2.339104000	-2.590237000
C	-0.114051000	-4.452969000	-2.614485000
H	-0.432511000	-4.453361000	-3.651225000
C	-0.119388000	-5.636902000	-1.879075000
H	-0.439562000	-6.565643000	-2.338451000
C	0.283318000	-5.613576000	-0.545901000
H	0.275153000	-6.525574000	0.041529000
C	0.694578000	-4.419668000	0.046231000
H	0.985613000	-4.429046000	1.087457000
N	0.226024000	3.567350000	0.447388000
N	2.562928000	2.468506000	0.420226000
P	-2.057811000	-0.156527000	0.002697000
P	1.294421000	-1.591933000	0.021408000
S	2.143652000	1.086981000	-1.873511000
S	-0.875707000	2.316907000	-1.703792000
B	1.066976000	2.300937000	0.919382000
H	1.118035000	2.376979000	2.119715000
H	0.514038000	1.167595000	0.862873000
H	-0.186826000	-0.461316000	-2.063719000
C	-1.062900000	4.924514000	-1.065467000
C	-0.170080000	5.897846000	0.933461000
H	0.915239000	4.519919000	2.152048000
H	-0.030323000	6.730895000	1.608869000
H	-1.319079000	6.979764000	-0.563068000
H	-1.628278000	4.974596000	-1.986608000
C	4.279905000	2.619796000	-1.261095000
C	4.645724000	3.584476000	0.904930000
H	3.007742000	3.319717000	2.255127000
H	5.261780000	4.108944000	1.622621000
H	6.053913000	3.684081000	-0.750460000
H	4.594319000	2.375930000	-2.267347000

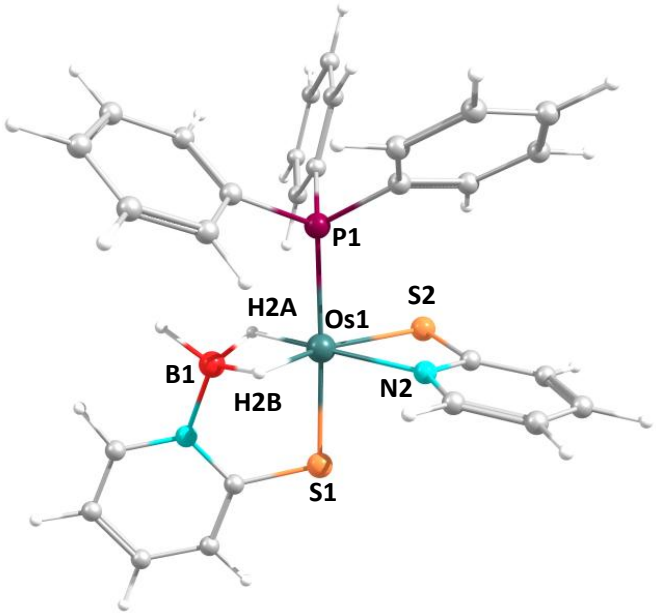


Figure S92. Optimized geometry of **5'**.
Total energy = -2446.30688610 a.u.
Cartesian coordinates for the calculated structure **5'** (in Å)

Os	-0.861100000	0.376672000	0.219700000
C	1.195292000	-2.184642000	-1.114328000
C	1.646866000	-3.440533000	-0.696183000
H	2.050304000	-3.569396000	0.299575000
C	1.577349000	-4.543694000	-1.548881000
H	1.926536000	-5.509877000	-1.201360000
C	1.064930000	-4.407156000	-2.835459000
H	1.015291000	-5.263765000	-3.498468000
C	0.608269000	-3.160288000	-3.262993000
H	0.200100000	-3.042497000	-4.260938000
C	0.663895000	-2.064504000	-2.406895000
H	0.279101000	-1.108468000	-2.742401000
C	2.017051000	-1.325397000	1.536704000
C	3.385868000	-1.623919000	1.590401000
H	4.012562000	-1.454136000	0.722846000
C	3.956028000	-2.133911000	2.754330000
H	5.017003000	-2.357265000	2.779933000
C	3.167157000	-2.350256000	3.883993000
H	3.612165000	-2.742533000	4.791802000
C	1.807707000	-2.050890000	3.842560000
H	1.189071000	-2.204208000	4.719879000
C	1.237332000	-1.539241000	2.677378000
H	0.184665000	-1.287673000	2.655935000
C	2.620353000	0.322763000	-0.722848000
C	3.104096000	1.398214000	0.037372000
H	2.673969000	1.605856000	1.010299000
C	4.136791000	2.198261000	-0.442741000
H	4.498668000	3.023078000	0.161222000

C	4.704212000	1.942488000	-1.690898000
H	5.509757000	2.565802000	-2.063113000
C	4.231480000	0.877879000	-2.452671000
H	4.669472000	0.663693000	-3.421585000
C	3.197530000	0.072326000	-1.972453000
H	2.858806000	-0.759977000	-2.575289000
C	-4.083810000	0.058146000	0.183003000
C	-5.499130000	0.163074000	0.225124000
H	-5.927096000	1.121883000	0.486736000
C	-6.288164000	-0.920446000	-0.059287000
H	-7.367972000	-0.830285000	-0.026600000
C	-5.688515000	-2.157807000	-0.396540000
H	-6.282844000	-3.031625000	-0.626155000
C	-4.325564000	-2.232762000	-0.424755000
H	-3.793037000	-3.141608000	-0.669377000
C	-0.178434000	2.802320000	-1.770512000
H	-0.483402000	2.161323000	-2.588419000
C	0.207941000	4.116947000	-1.969364000
H	0.218777000	4.532002000	-2.968602000
C	0.577320000	4.882864000	-0.855183000
H	0.878992000	5.916788000	-0.981691000
C	0.552700000	4.318617000	0.409212000
H	0.823962000	4.883435000	1.292048000
C	0.157319000	2.979688000	0.543754000
P	1.221699000	-0.682661000	-0.015808000
S	-3.058832000	1.375372000	0.533192000
S	0.023250000	2.007884000	1.980606000
B	-1.995943000	-1.303845000	-0.184588000
N	-3.525800000	-1.157977000	-0.142306000
N	-0.200868000	2.249356000	-0.547841000
H	-1.410710000	-0.379325000	-1.202331000
H	-1.421578000	-1.000628000	1.098667000
H	-1.701950000	-2.419120000	-0.490542000

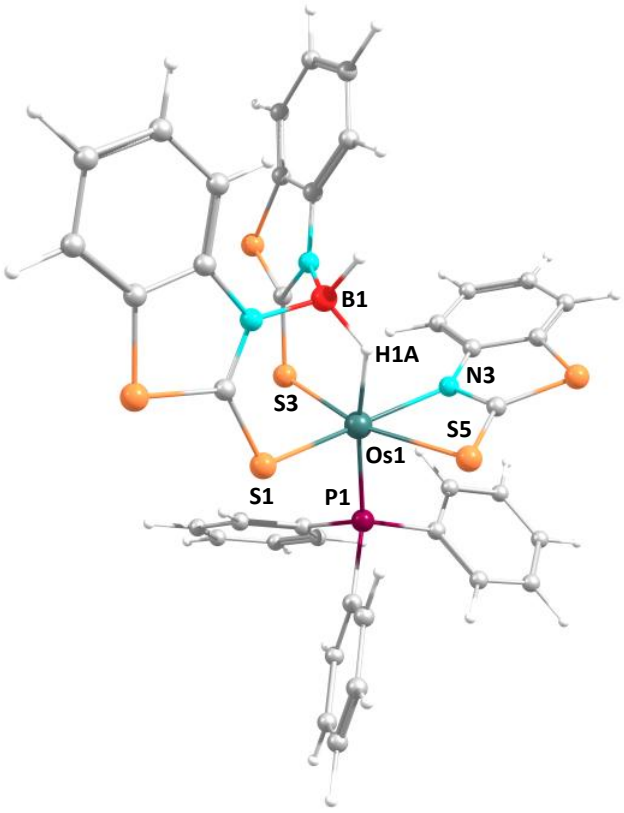


Figure S93. Optimized geometry of *trans*-**6**.
Total energy = -4515.07831409 a.u.
Cartesian coordinates for the calculated structure *trans*-**6** (in Å)

Os	-0.339195000	-0.281233000	-0.424968000
C	-3.407211000	-2.141476000	-0.376943000
C	-3.013635000	-2.710124000	-1.592112000
H	-2.162845000	-2.307788000	-2.122423000
C	-3.707560000	-3.795004000	-2.128060000
H	-3.384308000	-4.222899000	-3.070370000
C	-4.803986000	-4.327384000	-1.455838000
H	-5.341354000	-5.172833000	-1.871074000
C	-5.204287000	-3.770255000	-0.241507000
H	-6.054029000	-4.180636000	0.292878000
C	-4.511564000	-2.687809000	0.293612000
H	-4.832246000	-2.272216000	1.241000000
C	-2.703045000	-1.015486000	2.145222000
C	-1.920662000	-2.041765000	2.693957000
H	-1.211906000	-2.575211000	2.070950000
C	-2.043934000	-2.388909000	4.035785000

H	-1.430836000	-3.186254000	4.440862000
C	-2.945074000	-1.711373000	4.856558000
H	-3.037224000	-1.978561000	5.903433000
C	-3.726038000	-0.690542000	4.322272000
H	-4.432830000	-0.159128000	4.950207000
C	-3.610486000	-0.347170000	2.974265000
H	-4.238917000	0.438294000	2.575597000
C	-3.702405000	0.714425000	0.008709000
C	-4.767632000	0.584474000	-0.888617000
H	-4.939778000	-0.355870000	-1.395833000
C	-5.615873000	1.662460000	-1.142498000
H	-6.434749000	1.544222000	-1.843487000
C	-5.412467000	2.882362000	-0.503456000
H	-6.073659000	3.718895000	-0.700589000
C	-4.347221000	3.025248000	0.385385000
H	-4.171759000	3.973771000	0.880379000
C	-3.495316000	1.952580000	0.632233000
H	-2.663771000	2.084754000	1.313709000
C	1.907529000	-2.638783000	-0.502215000
C	4.261688000	-3.455748000	-0.678308000
C	5.502303000	-4.077442000	-0.773932000
H	5.591174000	-5.151880000	-0.666970000
C	6.622972000	-3.287330000	-1.013391000
H	7.600016000	-3.749168000	-1.090515000
C	6.487008000	-1.904505000	-1.157342000
H	7.362736000	-1.295222000	-1.347801000
C	5.243480000	-1.286005000	-1.059829000
H	5.165558000	-0.216987000	-1.173285000
C	4.111104000	-2.065493000	-0.813924000
C	2.103366000	0.631285000	1.564486000
C	3.879726000	1.601622000	0.476302000
C	4.640422000	2.116437000	-0.577151000
H	4.375966000	1.892865000	-1.601361000
C	5.724154000	2.941557000	-0.289171000
H	6.310677000	3.345048000	-1.106280000
C	6.058135000	3.265900000	1.028757000
H	6.907544000	3.907064000	1.231727000
C	5.286577000	2.788371000	2.084944000
H	5.518428000	3.057395000	3.108463000
C	4.197366000	1.973697000	1.793646000
C	-1.030832000	1.708229000	-2.203754000
C	-0.530361000	3.108841000	-0.500458000
C	-0.165569000	3.538920000	0.779570000
H	0.036055000	2.809505000	1.553125000
C	-0.074286000	4.903658000	1.030301000
H	0.210441000	5.243767000	2.019433000
C	-0.342380000	5.844325000	0.027628000
H	-0.263287000	6.903152000	0.244503000
C	-0.709858000	5.430691000	-1.250769000
H	-0.919044000	6.155380000	-2.028787000
C	-0.799721000	4.065284000	-1.504613000
P	-2.510415000	-0.668529000	0.327108000
S	0.216344000	-2.590946000	-0.430750000
S	2.701662000	-4.208171000	-0.400488000
S	0.554956000	-0.008098000	1.788634000
S	2.998279000	1.332937000	2.912173000
S	-1.156916000	0.108393000	-2.807581000
S	-1.237640000	3.259762000	-3.012229000
N	2.751568000	0.764808000	0.385515000
N	2.778127000	-1.620010000	-0.690455000
N	-0.676917000	1.799253000	-0.930530000
B	2.391311000	-0.102769000	-0.870025000
H	2.974791000	0.325805000	-1.820625000
H	1.214738000	0.043274000	-1.272104000

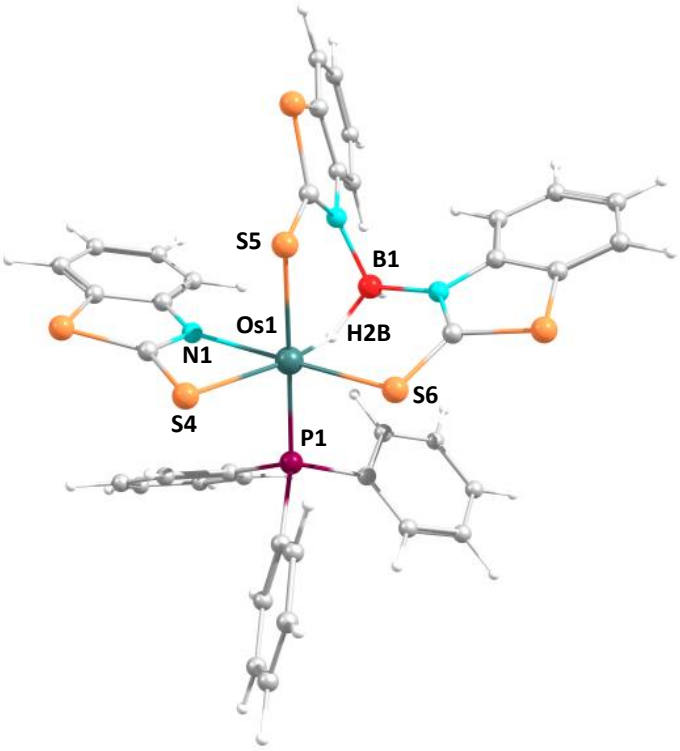


Figure S94. Optimized geometry of *cis*-**6**.
Total energy = -2446.30688610 a.u.
Cartesian coordinates for the calculated structure *cis*-**6** (in Å)

B	-1.782311000	-0.332702000	0.409994000
C	1.428149000	4.293929000	-0.283282000
C	1.299407000	5.519348000	0.363405000
H	1.793869000	6.404703000	-0.018417000
C	0.516790000	5.581427000	1.514179000
H	0.402550000	6.526832000	2.031362000
C	-0.121420000	4.435483000	2.006177000
H	-0.725252000	4.504447000	2.903667000
C	0.005837000	3.211198000	1.360738000
H	-0.483391000	2.322078000	1.736919000
C	0.785167000	3.134476000	0.203752000
C	1.809641000	2.240550000	-1.602121000
C	-4.305155000	2.503975000	-0.182730000
C	-5.326617000	3.283778000	0.350080000
H	-5.910658000	3.938797000	-0.285138000
C	-5.567826000	3.215938000	1.719427000
H	-6.355020000	3.818510000	2.156414000
C	-4.784968000	2.390112000	2.531353000
H	-4.964388000	2.362544000	3.599852000
C	-3.768788000	1.604037000	1.994895000
H	-3.161160000	0.980818000	2.636230000
C	-3.535350000	1.641060000	0.616891000
C	-2.462529000	1.332740000	-1.393326000
C	-3.563514000	-2.232486000	0.176109000
C	-4.488861000	-1.701371000	1.077041000
H	-4.304023000	-0.762633000	1.573590000
C	-5.668239000	-2.397065000	1.331200000
H	-6.383783000	-1.979673000	2.029994000
C	-5.942948000	-3.613298000	0.701799000
H	-6.867737000	-4.137735000	0.910623000
C	-5.027599000	-4.156966000	-0.195263000
H	-5.224322000	-5.102103000	-0.687024000
C	-3.849994000	-3.460326000	-0.444500000
C	-1.644603000	-2.470927000	-1.064749000
C	3.008588000	0.227017000	3.003480000
H	2.438448000	-0.533447000	3.520425000
C	3.715933000	1.168737000	3.753393000
H	3.671866000	1.131120000	4.836473000
C	4.478975000	2.143559000	3.118099000
H	5.028178000	2.874139000	3.701445000
C	4.537761000	2.169718000	1.724528000
H	5.135205000	2.919512000	1.217928000
C	3.831205000	1.234138000	0.975915000
H	3.900930000	1.256054000	-0.105288000
C	3.052459000	0.251768000	1.606024000
C	3.475197000	-2.264235000	-1.621572000
H	2.569821000	-2.096939000	-2.187916000
C	4.537902000	-2.942512000	-2.217589000
H	4.441717000	-3.296152000	-3.237969000
C	5.717828000	-3.156063000	-1.509955000
H	6.546166000	-3.678947000	-1.975098000
C	5.830548000	-2.687932000	-0.201227000
H	6.746759000	-2.845406000	0.357170000
C	4.768091000	-2.012433000	0.393768000
H	4.873112000	-1.652054000	1.410014000
C	3.574714000	-1.793329000	-0.309322000

C	1.522013000	-2.247957000	1.677321000
C	0.526833000	-1.926561000	2.612152000
H	0.143910000	-0.915657000	2.670353000
C	0.012272000	-2.893394000	3.471489000
H	-0.752401000	-2.620436000	4.190464000
C	0.469984000	-4.208613000	3.400855000
H	0.064791000	-4.964274000	4.064522000
C	1.445201000	-4.544052000	2.466363000
H	1.802659000	-5.565363000	2.394699000
C	1.969587000	-3.572389000	1.613479000
H	2.726604000	-3.856302000	0.894690000
N	1.022605000	2.008354000	-0.564460000
N	-2.561084000	0.931257000	-0.107781000
N	-2.326065000	-1.675279000	-0.208231000
Os	0.466144000	-0.040528000	-0.867184000
P	2.137409000	-0.939415000	0.508782000
S	2.344745000	3.914428000	-1.744241000
S	-3.723800000	2.472421000	-1.842875000
S	-2.531877000	-3.925210000	-1.506130000
S	2.123245000	0.854301000	-2.567291000
S	-1.231334000	0.882417000	-2.450514000
S	-0.093407000	-2.214472000	-1.671702000
H	-1.959898000	-0.393092000	1.594426000
H	-0.490482000	-0.203474000	0.547577000

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