Supplementary Information

Pushing steric limits in osmium(IV) tetraaryl complexes

Joseph M. Parr,[a] Clarissa Olivar,[a] Thomas Saal, Ralf Haiges, and Michael S. Inkpen*

Department of Chemistry, University of Southern California, Los Angeles, California 90089, United States

[a] J.M.P. and C.O. contributed equally to this work.

E-mail: inkpen@usc.edu

Contents

1. Additional Synthetic Details 2

2. X-ray Crystallography 4

3. Electrochemistry 21

4. IR Spectra 22

5. NMR Spectra 24

6. References 34

1. Additional Synthetic Details

General Synthesis of Aryl Grignard Reagents

Magnesium turnings (15 mmol) were mechanically stirred[1] overnight under nitrogen in a 3-neck round-bottomed flask connected to a reflux condenser. THF (5 mL) and 1,2-dibromoethane (0.2 mL) were added, whereby a solution containing the appropriate aryl bromide (5 mmol) in THF (10 mL) was added dropwise to the stirred mixture. This was maintained at a gentle reflux for 10 min using a heat gun. The flask was then immersed in an oil bath and heated at reflux for an additional 1 h. After cooling to room temperature, the solution was filtered via cannula then titrated (approximate yields 60-85%, based on concentration and volume of acquired Grignard reagent).[2]

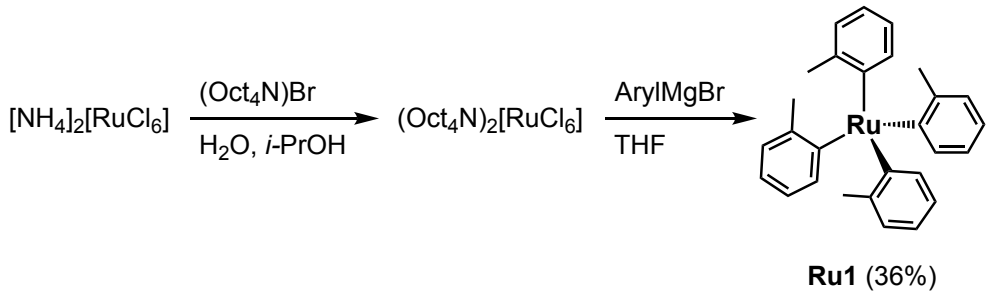


Figure S1. Synthetic route to **Ru1**.

Table S1. Selected reaction parameters for the synthesis of Ru(aryl)$_4$ complexes.

compound	metal salt	yield (%)	reference
Ru(2-tolyl)$_4$ (**Ru1**)	$Ru_2(\mu\text{-}O_2CMe)_4$	24	[3]
	$(NEt_4)[RuCl_5(MeCN)]$	34	[3]
	$(NEt_4)[RuCl_5(THF)]$	48	[3]
	$(Oct_4N)_2[RuCl_6]$	36	this work
Ru(2,4,5-trimethylphenyl)$_4$	$Ru(acac)_3$	37	[4]
Ru(2,5-xylyl)$_4$ (**Ru2m**)	$Ru(acac)_3$	34	[5]
Ru(4-MeO-2-tolyl)$_4$	$Ru(acac)_3$	29	[5]
Ru(2,6-xylyl)$_4$	$(Et_4N)[RuCl_5(MeCN)]$	13	[3]
	$(Et_4N)[RuCl_5(THF)]$	21	[3]
Ru(mesityl)$_4$ (**Ru3**)	$Ru_2(O_2CMe)_4$	21	[3]
	$RuCl_3(tht)_3$	18	[6]
Ru(p-*t*-butylphenyl)$_4$	$(Et_4N)[RuCl_5(THF)]$	20	[3]

Table S2. Selected reaction parameters for the synthesis of $Os(aryl)_4$ complexes.

$M(aryl)_4$	metal precursor	yield (%)	reference
$Os(2\text{-tolyl})_4$ (**Os1**)	OsO_4	27	[7]
		55 [a]	[8]
	$(Oct_4N)_2[OsCl_6]$	30	this work
	$(Oct_4N)_2[OsBr_6]$	73	this work
$Os(2,5\text{-xylyl})_4$ (**Os2**)	OsO_4	34	[9]
		6 [b]	this work
	$(Oct_4N)_2[OsCl_6]$	40	this work
	$(Oct_4N)_2[OsBr_6]$	55-61	this work
$Os(2,4\text{-xylyl})_4$	OsO_4	50	[8]
$Os(mesityl)_4$ (**Os3**)	OsO_4	- [c]	[10]
	$(Oct_4N)_2[OsBr_6]$	5	this work
Os(2-ethylphenyl) (**Os1-Et**)	$(Oct_4N)_2[OsBr_6]$	41	this work
Os(2-*iso*-propylphenyl) (**Os1-*i*Pr**)	$(Oct_4N)_2[OsBr_6]$	14	this work
$Os(4\text{-fluoro-}2\text{-tolyl})_4$	OsO_4	34	[8]
$Os(phenyl)_4$ [d]	OsO_4	24	[11]

[a] Attempts by us and others[9] failed to reproduce yields ≥50% following the reported methods. [b] Low isolated yields of the pure material are a result of challenging separation from closely eluting $OsO(2,5\text{-xylyl})_4$[9] species. [c] Reported attempts for this and structurally similar 2,6-dimethylated aryls resulted only in isolation of dioxoaryl osmium(VI) complexes (aryl = 2,6-xylyl, 2,4,6-mesityl, 2,3,5,6-tetramethylphenyl. 2,4,6-triisopropylphenyl).[10,12,13] [d] Slowly decomposes over several days.[11]

2. X-Ray Crystallography

Table S3. Sample and crystal data for Os(2,5-xylyl)$_4$ (**Os2**).

Chemical formula	$C_{32}H_{36}Os$	
Formula weight	610.81 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.022 x 0.167 x 0.187 mm	
Crystal habit	dark red plate	
Crystal system	monoclinic	
Space group	C 1 c 1	
Unit cell dimensions	a = 12.9059(19) Å	α = 90°
	b = 12.9355(18) Å	β = 98.736(2)°
	c = 15.837(2) Å	γ = 90°
Volume	2613.2(7) Å^3	
Z	4	
Density (calculated)	1.553 g/cm^3	
Absorption coefficient	4.897 mm^{-1}	
F(000)	1216	

Table S4. Data collection and structure refinement for Os(2,5-xylyl)$_4$ (**Os2**).

Diffractometer	Bruker APEX DUO
Radiation source	fine-focus tube (MoKα , λ = 0.71073 Å)
Theta range for data collection	2.24 to 30.52°
Index ranges	-18<=h<=18, -18<=k<=18, -22<=l<=22
Reflections collected	32067
Independent reflections	7862 [R(int) = 0.0465]
Coverage of independent reflections	99.5%
Absorption correction	multi-scan
Max. and min. transmission	0.9000 and 0.4610
Structure solution technique	direct methods
Structure solution program	SHELXTL XT 2014/5 (Bruker AXS, 2014)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXTL XL 2018/3 (Bruker AXS, 2018)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	7862 / 2 / 306
Goodness-of-fit on F^2	0.952
Δ/σ_{max}	0.001
Final R indices	7265 data; I>2σ(I) R1 = 0.0221, wR2 = 0.0406
	all data R1 = 0.0268, wR2 = 0.0416
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0012P)^2]$ where $P=(F_o^2+2F_c^2)/3$
Absolute structure parameter	0.005(6)
Largest diff. peak and hole	0.613 and -0.535 eÅ^{-3}
R.M.S. deviation from mean	0.096 eÅ^{-3}

Table S5. Sample and crystal data for Os(mesityl)$_4$ (**Os3**).

Chemical formula	$C_{36}H_{44}Os$	
Formula weight	666.96 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.051 x 0.069 x 0.489 mm	
Crystal habit	dark black rod	
Crystal system	monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 16.265(3) Å	
	b = 24.149(5) Å	α = 90°
	c = 14.951(3) Å	β = 93.736(3)°
Volume	5860.(2) Å^3	γ = 90°
Z	8	
Density (calculated)	1.512 g/cm^3	
Absorption coefficient	4.374 mm^{-1}	
F(000)	2688	

Table S6. Data collection and structure refinement for Os(mesityl)$_4$ (**Os3**).

Diffractometer	Bruker APEX II CCD Bruker APEX DUO	
Radiation source	fine-focus tube (MoKα , λ = 0.71073 Å)	
Theta range for data collection	1.51 to 27.48°	
Index ranges	-21<=h<=21, -31<=k<=31, -19<=l<=19	
Reflections collected	59569	
Independent reflections	6726 [R(int) = 0.0501]	
Coverage of independent reflections	99.9%	
Absorption correction	multi-scan	
Max. and min. transmission	0.8040 and 0.2230	
Structure solution technique	direct methods	
Structure solution program	SHELXTL XT 2014/5 (Bruker AXS, 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXTL XL 2018/3 (Bruker AXS, 2018)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	6726 / 0 / 346	
Goodness-of-fit on F^2	1.160	
Δ/σ_{max}	0.005	
Final R indices	5752 data; I>2σ(I)	R1 = 0.0257, wR2 = 0.0621
	all data	R1 = 0.0333, wR2 = 0.0676
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0244P)^2+29.8209P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.992 and -1.230 eÅ^{-3}	
R.M.S. deviation from mean	0.124 eÅ^{-3}	

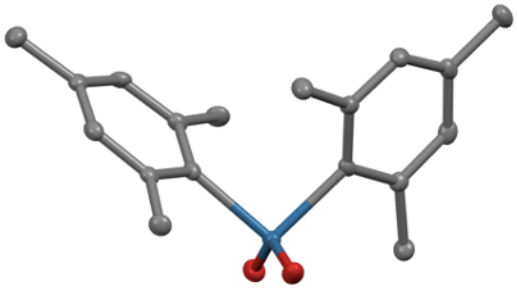


Figure S2. X-ray crystal structure of $OsO_2(mes)_2$ (50% probability ellipsoids). Hydrogen atoms are omitted for clarity (Os = teal, O = red, C = grey). Selected bond lengths (Å) and angles (°) are consistent with previously reported values.[10]

Table S7. Sample and crystal data for $OsO_2(mes)_2$.

Chemical formula	$C_{18}H_{22}O_2Os$	
Formula weight	460.55 g/mol	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal size	0.066 x 0.194 x 0.209 mm	
Crystal habit	clear dark green prism	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 12.6400(4) Å	α = 90°
	b = 15.1376(5) Å	β = 98.2720(10)°
	c = 8.2955(3) Å	γ = 90°
Volume	1570.74(9) $Å^3$	
Z	4	
Density (calculated)	1.948 g/cm^3	
Absorption coefficient	15.341 mm^{-1}	
F(000)	888	

Table S8. Data collection and structure refinement for $OsO_2(mes)_2$.

Diffractometer	Bruker APEX II CCD Bruker APEX DUO
Radiation source	IuS microsource (CuKα , λ = 1.54178 Å)
Theta range for data collection	3.53 to 71.92°
Index ranges	-15<=h<=15, -18<=k<=18, -10<=l<=10
Reflections collected	22437
Independent reflections	3056 [R(int) = 0.0671]
Coverage of independent reflections	98.7%
Absorption correction	multi-scan
Max. and min. transmission	0.4310 and 0.1420
Structure solution technique	direct methods
Structure solution program	SHELXTL XT 2014/4 (Bruker AXS, 2014)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXTL XL 2014/7 (Bruker AXS, 2014)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	3056 / 0 / 196
Goodness-of-fit on F^2	1.062
Δ/σ_{max}	0.002
Final R indices	2876 data; $I>2\sigma(I)$ R1 = 0.0237, wR2 = 0.0571 all data R1 = 0.0265, wR2 = 0.0584
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0288P)^2+1.5592P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.825 and -1.406 eÅ^{-3}
R.M.S. deviation from mean	0.177 eÅ^{-3}

Table S9. Sample and crystal data for Os(2-ethylphenyl)$_4$ (**Os1-Et**).

Chemical formula	$C_{32}H_{36}Os$	
Formula weight	610.81 g/mol	
Temperature	100.01(10) K	
Wavelength	0.71073 Å	
Crystal size	0.24 x 0.17 x 0.11 mm	
Crystal habit	black plate	
Crystal system	tetragonal	
Space group	$I4_1/a$	
Unit cell dimensions	a = 15.7666(3) Å	α = 90°
	b = 15.7666(3) Å	β = 90°
	c = 10.3145(2) Å	γ = 90°
Volume	2564.04(11) Å^3	
Z	4	
Density (calculated)	1.582 g/cm^3	
Absorption coefficient	4.991 mm^{-1}	
F(000)	1261	

Table S10. Data collection and structure refinement for Os(2-ethylphenyl)$_4$ (**Os1-Et**).

Diffractometer	XtaLAB Synergy, Dualflex, HyPix
Radiation source	fine-focus tube (MoKα , λ = 0.71073 Å)
Theta range for data collection	2.360 to 32.857°
Index ranges	-22<=h<=17, -21<=k<=23, -11<=l<=15
Reflections collected	10077
Independent reflections	2114 [R(int) = 0.0331]
Coverage of independent reflections	88.6%
Absorption correction	gaussian
Max. and min. transmission	0.134 and 0.419
Structure solution technique	dual methods
Structure solution program	ShelXT 2018/2 (Sheldrick, 2018) with Olex2 1.5 (Dolomanov *et al*., 2009)
Refinement method	Full-matrix least-squares on F^2
Refinement program	ShelXL 2017/1 (Sheldrick, 2015)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	2114 / 0 / 76
Goodness-of-fit on F^2	1.082
Δ/σ_{max}	0.000
Final R indices	1863 data; I≥2σ(I) R1 = 0.0185, wR2 = 0.0384
	all data R1 = 0.0228, wR2 = 0.0396
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0097P)^2+4.2545P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.826 and -0.0580 eÅ^{-3}
R.M.S. deviation from mean	0.099 eÅ^{-3}

Table S11. Sample and crystal data for Os(2-*iso*-propylphenyl)$_4$ (**Os1-*i*Pr**).

Chemical formula	$C_{36}H_{44}Os$	
Formula weight	666.91 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.033 x 0.161 x 0.242 mm	
Crystal habit	purple plate	
Crystal system	tetragonal	
Space group	P -4	
Unit cell dimensions	a = 11.904(4) Å	α = 90°
	b = 11.904(4) Å	β = 90°
	c = 10.580(3) Å	γ = 90°
Volume	1499.2(10) Å^3	
Z	2	
Density (calculated)	1.477 g/cm^3	
Absorption coefficient	4.274 mm^{-1}	
F(000)	672	

Table S12. Data collection and structure refinement for Os(2-*iso*-propylphenyl)$_4$ (**Os1-*i*Pr**).

Diffractometer	Bruker APEX II CCD Bruker APEX DUO
Radiation source	fine-focus tube (MoKα , λ = 0.71073 Å)
Theta range for data collection	1.71 to 30.55°
Index ranges	-16<=h<=16, -16<=k<=16, -15<=l<=15
Reflections collected	37981
Independent reflections	4494 [R(int) = 0.0551]
Coverage of independent reflections	98.7%
Absorption correction	multi-scan
Max. and min. transmission	0.8720 and 0.4240
Structure solution technique	direct methods
Structure solution program	SHELXTL XT 2014/5 (Bruker AXS, 2014)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXTL XL 2014/7 (Bruker AXS, 2014)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	4494 / 0 / 173
Goodness-of-fit on F^2	1.025
Δ/σ_{max}	0.000
Final R indices	3983 data; I>2σ(I) R1 = 0.0205, wR2 = 0.0397
	all data R1 = 0.0296, wR2 = 0.0420
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0186P)^2+0.2196P]$ where $P=(F_o^2+2F_c^2)/3$
Absolute structure parameter	0.231(9)
Largest diff. peak and hole	0.963 and -1.103 eÅ^{-3}
R.M.S. deviation from mean	0.098 eÅ^{-3}

Geometry Analysis

We apply **Equation S1** to calculate the "tetrahedricity"-value (*T*-value) for different tetrahedral compounds (compiled in **Table 1**), adapting an approach used by others to calculate the "octahedricity"-value (*O*-value) for a series of polypyridyl complexes.[14–16] The *T*-value is the root-mean-square deviation of a set of C–M–C angles from their ideal tetrahedral values (109.5°). The larger the *T*-value the greater the deviation of C-M-C angles from ideality and the more distorted the tetrahedral geometry, where a *T*-value = 0 indicates no deviation and a perfect tetrahedral geometry. Here, $\hat{\theta}_i$ = 109.5° for ideal C-M-C angles, and θ_i = the 6 unique experimental C-M-C angles determined from structural data. These unique angles are given for each compound in **Tables S14-S28**.

$$T\text{-value} = \sqrt{\frac{1}{6}\sum_{i=1}^{6}(\hat{\theta}_i - \theta_i)^2} \qquad \textbf{(S1)}$$

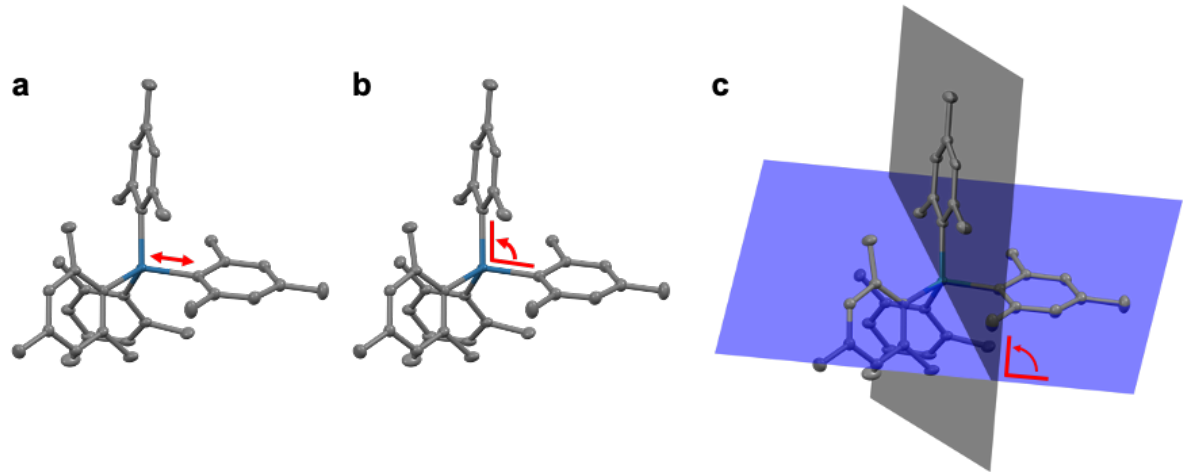


Figure S3. Illustrative definitions of selected structural parameters (red arrows) using the ellipsoid structure of **Os3** (Os = teal, C = grey). **(a)** M–C bond length, **(b)** C-M-C angle, and **(c)** aryl plane angle. Hydrogen atoms are omitted for clarity.

Table S13. Overview of additional structural parameters for selected compounds.[a]

			aryl plane (°)	
compound	M-C (Å)	C-M-C (°)	min-max	average
Os(mesityl)$_4$ (**Os3**)	2.026(3)-2.049(3)	98.4(1)-117.2(1)	63.93-82.89	70.49
Os(cyclohexyl)$_4$	2.026-2.031	105.4-117.1	-	-
Os(2-^{i}Pr-phenyl) (**Os1-*i*Pr**)	2.014(4)-2.016(3)	101.74(2)-116.84(14)	55.46-87.73	70.46
Os(2-ethylphenyl) (**Os1-Et**)	2.005(18)	104.52(10)-112.00(5)	69.09-73.37	70.52
Os(2-tolyl)$_4$ (**Os1**)	1.984-2.011	106.1-117.1	66.46-73.97	70.49
Os(4-Br-2,5-xylyl)$_4$	1.98(2)-2.03(3)	107.3(6)-111.6(7)	60.01-84.88	70.50
Os(phenyl)$_4$	1.995	107.6-110.4	62.04-86.44	70.17
Os(2,5-xylyl)$_4$ (**Os2**)	2.003(4)-2.017(4)	108.1(2)-110.9(2)	50.85-87.62	67.45
Ru(mesityl)$_4$ (**Ru3**)	2.00(1)-2.02(1)	99.1(4)-117.0(4)	64.25-81.47	70.51
Ru(cyclohexyl)$_4$	2.018-2.020	105.4-116.3	-	-
Ru(2-tolyl)$_4$ (**Ru1**)	1.943-2.047	106.3-114.9	64.83-77.36	70.46
Ru(4-MeO-2-tolyl)$_4$	1.986	106.0-111.2	61.39-87.58	70.12
Ru(4-Br-2,5-xylyl)$_4$	1.984	106.4-111.0	61.83-86.80	70.15
Ru(2,4,5-trimethylphenyl)$_4$	1.99-2.03	108.4-110.7	60.21-81.20	70.50
C(phenyl)$_4$	1.551	106.7-110.9	68.51-74.49	70.50

[a] Minimum and maximum values are provided to give an indication of range. Selected parameters are provided with estimated standard deviations (e.s.d.) in parentheses for all structures with associated e.s.d. All bond lengths and angles used are tabulated in **Tables S14-S28**. For structure identifiers and references see **Table 1**. M = Os, Ru, C.

Table S14. Selected structural parameters for Os(mesityl)$_4$ (**Os3**).[a]

M-C bond length (Å)		C-M-C angle (°)		aryl plane angle (°)	
Os1-C1	2.049(3)	C1-Os1-C10	113.8(1)	(C1-C9)-(C10-C18)	67.00
Os1-C10	2.026(3)	C1-Os1-C19	98.4(1)	(C1-C9)-(C19-C27)	74.34
Os1-C19	2.038(3)	C1-Os1-C28	117.1(1)	(C1-C9)-(C28-C36)	63.92
Os1-C28	2.033(3)	C10-Os1-C19	117.2(1)	(C10-C18)-(C19-C27)	65.59
		C10-Os1-C28	98.7(1)	(C10-C18)-(C28-C36)	82.89
		C19-Os1-C28	112.8(1)	(C19-C27)-(C28-C36)	69.20

[a] Atom labels refer to deposited crystal structure labels. Selected parameters are provided with e.s.d. in parentheses. For structure identifier and reference see **Table 1**.

Table S15. Selected structural parameters for Os(cyclohexyl)$_4$.[a]

M-C bond length (Å)		C-M-C angle (°)	
Os1-C1	2.026	C1-Os1-C1B	117.1
Os1-C1B	2.026	C1-Os1-C7	106.3
Os1-C7	2.031	C1-Os1-C7B	105.4
Os1-C7B	2.031	C1B-Os1-C7	106.4
		C1B-Os1-C7B	106.3
		C7-Os1-C7B	117.0

[a] Atom labels refer to deposited crystal structure labels. For structure identifier and reference see **Table 1**.

Table S16. Selected structural parameters for Os(2-*iso*-propylphenyl)$_4$ (**Os1-^{i}Pr**).[a]

M-C bond length (Å)		C-M-C angle (°)		aryl plane angle (°)	
Os1-C1A	2.016(3)	C1A-Os1-C1B	106.03(2)	(C1A-C6A)-(C1B-C6B)	87.73
Os1-C1B	2.016(3)	C1A-Os1-C11A	107.95(14)	(C1A-C6A)-(C9A, C11A-C15A)	78.38
Os1-C11A	2.014(4)	C1A-Os1-C11B	116.84(14)	(C1A-C6A)-(C9B, C11B-C15B)	55.46
Os1-C11B	2.014(4)	C1B-Os1-C11A	116.84(14)	(C1B-C6B)-(C9A, C11A-C15A)	55.46
		C1B-Os1-C11B	107.95(14)	(C1B-C6B)-(C9B, C11B-C15B)	78.38
		C11A-Os1-C11B	101.74(2)	(C9A, C11A-C15A)-(C9B, C11B-C15B)	67.35

[a] Atom labels refer to deposited crystal structure labels. Selected parameters are provided with e.s.d. in parentheses. For structure identifier and reference see **Table 1**.

Table S17. Selected structural parameters for Os(2-ethylphenyl)$_4$ (**Os1-Et**).[a]

M-C bond length (Å)		C-M-C angle (°)		aryl plane angle (°)	
Os1-C1A	2.005(18)	C1A-Os1-C1B	112.00(5)	(C1A-C6A)-(C1B-C6B)	69.09
Os1-C1B	2.005(18)	C1A-Os1-C1C	112.00(5)	(C1A-C6A)-(C1C-C6C)	69.09
Os1-C1C	2.005(18)	C1A-Os1-C1D	104.52(10)	(C1A-C6A)-(C1D-C6D)	73.37
Os1-C1D	2.005(18)	C1B-Os1-C1C	104.52(10)	(C1B-C6B)-(C1C-C6C)	73.37
		C1B-Os1-C1D	112.00(5)	(C1B-C6B)-(C1D-C6D)	69.09
		C1C-Os1-C1D	112.00(5)	(C1C-C6C)-(C1D-C6D)	69.09

[a] Atom labels refer to deposited crystal structure labels. Selected parameters are provided with e.s.d. in parentheses. For structure identifier and reference see **Table 1**.

Table S18. Selected structural parameters for Os(2-tolyl)$_4$ (**Os1**).[a]

M-C bond length (Å)		C-M-C angle (°)		aryl plane angle (°)	
Os1-C1	2.0106	C1-Os1-C1C	114.11	(C1-C6)-(C8-C13)	66.46
Os1-C1C	2.0106	C1-Os1-C8	106.06	(C1-C6)-(C1C-C6C)	73.97
Os1-C8	1.9835	C1-Os1-C8C	106.94	(C1-C6)-(C8C-C13C)	69.47
Os1-C8C	1.9835	C8-Os1-C8C	117.05	(C8-C13)-(C1C-C6C)	69.47
		C8-Os1-C1C	106.94	(C8-C13)-(C8C-C13C)	77.12
		C8C-Os1-C1C	106.06	(C1C-C6C)-(C8C-C13C)	66.46

[a] Atom labels refer to deposited crystal structure labels. For structure identifier and reference see **Table 1**.

Table S19. Selected structural parameters for Os(4-Br-2,5-xylyl)$_4$.[a]

M-C bond length (Å)		C-M-C angle (°)		aryl plane angle (°)	
Os1-C1	1.98(2)	C1-Os1-C9	107.3(6)	(C1-C8)-(C9-C16)	77.39
Os1-C9	2.00(2)	C1-Os1-C17	111.6(7)	(C1-C8)-(C17-C24)	60.01
Os1-C17	2.03(3)	C1-Os1-C25	109.4(7)	(C1-C8)-(C25-C32)	74.13
Os1-C28	1.99(2)	C-Os1-C17	110.7(6)	(C9-C16)-(C17-C24)	63.17
		C9-Os1-C25	110.3(6)	(C9-C16)-(C25-C32)	63.40
		C17-Os1-C25	107.5(6)	(C17-C24)-(C25-C32)	84.88

[a] Atom labels refer to deposited crystal structure labels. Selected parameters are provided with e.s.d. in parentheses. For structure identifier and reference see **Table 1**.

Table S20. Selected structural parameters for Os(phenyl)$_4$.[a]

M-C bond length (Å)		C-M-C angle (°)		aryl plane angle (°)	
Os1-C6	1.995	C6-Os1-C6A	110.4	(C1-C6)-(C1A-C6A)	62.04
Os1-C6A	1.995	C6-Os1-C6B	107.6	(C1-C6)-(C1B-C6B)	86.44
Os1-C6B	1.995	C6-Os1-C6C	110.4	(C1-C6)-(C1C-C6C)	62.04
Os1-C6C	1.995	C6A-Os1-C6B	110.4	(C1A-C6A)-(C1B-C6B)	62.04
		C6A-Os1-C6C	107.6	(C1A-C6A)-(C1C-C6C)	86.44
		C6B-Os1-C6C	110.4	(C1B-C6B)-(C1C-C6C)	62.04

[a] Atom labels refer to deposited crystal structure labels. For structure identifier and reference see **Table 1**.

Table S21. Selected structural parameters for Os(2,5-xylyl)$_4$ (**Os2**).[a]

M-C bond length (Å)		C-M-C angle (°)		aryl plane angle (°)	
Os1-C1	2.003(4)	C1-Os1-C9	108.1(2)	(C1-C8)-(C9-C16)	61.93
Os1-C9	2.017(4)	C1-Os1-C17	108.6(2)	(C1-C8)-(C17-C24)	50.85
Os1-C17	2.005(5)	C1-Os1-C25	109.5(2)	(C1-C8)-(C25-C32)	85.02
Os1-C28	2.006(4)	C9-Os1-C17	108.7(2)	(C9-C16)-(C17-C24)	87.62
		C9-Os1-C25	110.9(2)	(C9-C16)-(C25-C32)	61.51
		C17-Os1-C25	110.9(2)	(C17-C24)-(C25-C32)	57.75

[a] Atom labels refer to deposited crystal structure labels. Selected parameters are provided with e.s.d. in parentheses. For structure identifier and reference see **Table 1**.

Table S22. Selected structural parameters for Ru(mesityl)$_4$ (**Ru3**).[a]

M-C bond length (Å)		C-M-C angle (°)		aryl plane angle (°)	
Ru1-C1	2.00(1)	C1-Ru1-C7	113.6(4)	(C1-C6)-(C7-C12)	66.99
Ru1-C7	2.02(1)	C1-Ru1-C13	99.6(4)	(C1-C6)-(C13-C18)	81.47
Ru1-C13	2.01(1)	C1-Ru1-C19	116.0(4)	(C1-C6)-(C19-C24)	66.59
Ru1-C19	2.01(1)	C7-Ru1-C13	117.0(4)	(C7-C12)-(C13-C18)	64.25
		C7-Ru1-C19	99.1(4)	(C7-C12)-(C19-C24)	73.80
		C13-Ru1-C19	112.5(4)	(C13-C18)-(C19-C24)	69.96

[a] Atom labels refer to deposited crystal structure labels. Selected parameters are provided with e.s.d. in parentheses. For structure identifier and reference see **Table 1**.

Table S23. Selected structural parameters for Ru(cyclohexyl)$_4$.[a]

M-C bond length (Å)		C-M-C angle (°)	
Ru1-C1	2.020	C1-Ru1-C1B	116.3
Ru1-C1B	2.020	C1-Ru1-C7	107.1
Ru1-C7	2.018	C1-Ru1-C7B	105.4
Ru1-C7B	2.018	C1B-Ru1-C7	105.4
		C1B-Ru1-C7B	107.1
		C7-Ru1-C7B	107.1

[a] Atom labels refer to deposited crystal structure labels. For structure identifier and reference see **Table 1**.

Table S24. Selected structural parameters for Ru(2-tolyl)$_4$ (**Ru1**).[a]

M-C bond length (Å)		C-M-C angle (°)		aryl plane angle (°)	
Ru1-C1	2.047	C1-Ru1-C1C	114.9	(C1-C6)-(C8-C13)	70.24
Ru1-C1C	2.047	C1-Ru1-C8	106.3	(C1-C6)-(C1C-C6C)	75.28
Ru1-C8	1.943	C1-Ru1-C8C	107.8	(C1-C6)-(C8C-C13C)	64.83
Ru1-C8C	1.943	C8-Ru1-C1C	107.8	(C8-C13)-(C1C-C6C)	64.83
		C8-Ru1-C8C	113.9	(C8-C13)-(C8C-C13C)	77.36
		C8C-Ru1-C1C	106.3	(C1C-C6C)-(C8C-C13C)	70.24

[a] Atom labels refer to deposited crystal structure labels. For structure identifier and reference see **Table 1**.

Table S25. Selected structural parameters for Ru(4-MeO-2-tolyl)$_4$.[a]

M-C bond length (Å)		C-M-C angle (°)		aryl plane angle (°)	
Ru1-C1	1.986	C1-Ru1-C1	111.2	(C1-C6)-(C6-C1)	61.39
Ru1-C1	1.986	C1-Ru1-C1	111.2	(C1-C6)-(C6-C1)	87.58
Ru1-C1	1.986	C1-Ru1-C1	106.0	(C1-C6)-(C6-C1)	61.39
Ru1-C1	1.986	C1-Ru1-C1	106.0	(C1-C6)-(C6-C1)	61.39
		C1-Ru1-C1	111.2	(C1-C6)-(C6-C1)	61.39
		C1-Ru1-C1	111.2	(C1-C6)-(C6-C1)	87.58

[a] Atom labels refer to deposited crystal structure labels. For structure identifier and reference see **Table 1**.

Table S26. Selected structural parameters for Ru(4-Br-2,5-xylyl)$_4$.[a]

M-C bond length (Å)		C-M-C angle (°)		aryl plane angle (°)	
Ru1-C1	1.984	C1-Ru1-C1	111.0	(C1-C6)-(C6-C1)	61.83
Ru1-C1	1.984	C1-Ru1-C1	111.0	(C1-C6)-(C6-C1)	86.80
Ru1-C1	1.984	C1-Ru1-C1	106.4	(C1-C6)-(C6-C1)	61.83
Ru1-C1	1.984	C1-Ru1-C1	111.0	(C1-C6)-(C6-C1)	86.80
		C1-Ru1-C1	106.4	(C1-C6)-(C6-C1)	61.83
		C1-Ru1-C1	111.0	(C1-C6)-(C6-C1)	61.83

[a] Atom labels refer to deposited crystal structure labels. For structure identifier and reference see **Table 1**.

Table S27. Selected structural parameters for Ru(2,4,5-trimethylphenyl)$_4$.[a]

M-C bond length (Å)		C-M-C angle (°)		aryl plane angle (°)	
Ru1-C11	2.03(1)	C11-Ru1-C21	109.4(5)	(C11-C16)-(C21-C26)	81.20
Ru1-C21	2.00(1)	C11-Ru1-C31	108.7(5)	(C11-C16)-(C31-C36)	70.92
Ru1-C31	1.92(1)	C11-Ru1-C41	110.5(4)	(C11-C16)-(C41-C46)	67.64
Ru1-C41	1.99(1)	C21-Ru1-C31	110.7(5)	(C21-C26)-(C31-C36)	60.21
		C21-Ru1-C41	109.2(5)	(C21-C26)-(C41-C46)	67.33
		C31-Ru1-C41	108.4(4)	(C31-C36)-(C41-C46)	75.72

[a] Atom labels refer to deposited crystal structure labels. Selected parameters are provided with e.s.d. in parentheses. For structure identifier and reference see **Table 1**.

Table S28. Selected structural parameters for tetraphenylmethane, C(phenyl)$_4$.[a]

C-C bond length (Å)		C-M-C angle (°)		aryl plane angle (°)	
C7-C1	1.5509	C1-C7-C1	110.86	(C1-C6)-(C6-C1)	68.51
C7-C1	1.5509	C1-C7-C1	106.72	(C1-C6)-(C6-C1)	68.51
C7-C1	1.5509	C1-C7-C1	110.86	(C1-C6)-(C6-C1)	74.49
C7-C1	1.5509	C1-C7-C1	106.72	(C1-C6)-(C6-C1)	68.51
		C1-C7-C1	110.86	(C1-C6)-(C6-C1)	68.51
		C1-C7-C1	110.86	(C1-C6)-(C6-C1)	74.49

[a] Atom labels refer to deposited crystal structure labels. For structure identifier and reference see **Table 1**.

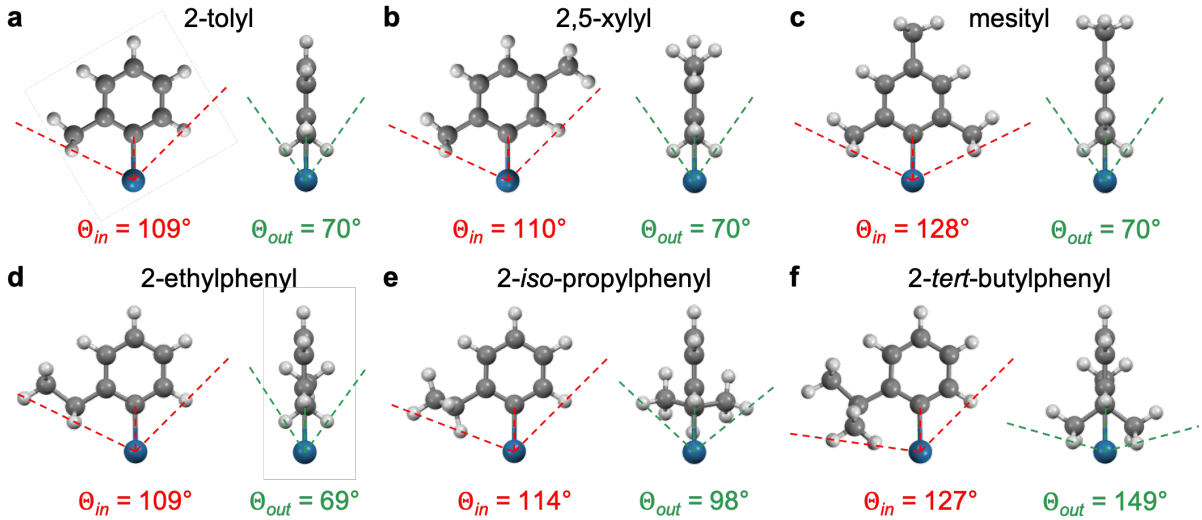


Figure S4. Ball and stick models illustrating the *in-plane* (Θ_{in}) and *out-of-plane* (Θ_{out}) cone angles for different Os-aryl ligand geometries (Os = teal, C = grey, H = white). Parameters for each σ-aryl ligand are given in **Table 2**.

3. Electrochemistry

Table S29. Electrochemical data for Os(aryl)$_4$ complexes.[a]

	redox transition	E_{pa} (V)	E_{pc} (V)	ΔE	i_{pa}/i_{pc}
Os(2-tolyl)$_4$ (**Os1**)	1−/0	−1.918	−2.004	0.086	0.97
	0/1+	0.366	0.287	0.079	0.98
Os(2,5-xylyl)$_4$ (**Os2**)	1−/0	−1.969	−2.047	0.078	0.98
	0/1+	0.281	0.208	0.073	1.00
Os(mesityl)$_4$ (**Os3**)	1−/0	−1.992	−2.064	0.072	0.98
	0/1+	0.187	0.120	0.067	1.00
	1+/2+	1.155	1.079	0.093	1.14 [b]
Os(2-ethylphenyl)$_4$	1−/0	−1.991	−2.061	0.070	1.00
(**Os1-Et**)	0/1+	0.390	0.308	0.082	1.02
Os(2-^{i}Pr-phenyl)$_4$	1−/0	−2.038	−2.112	0.074	1.02
(**Os1-*i*Pr**)	0/1+	0.374	0.298	0.076	0.99

[a] Scan rate = 0.1 V s^{-1}; NBu_4PF_6 supporting electrolyte; working electrode: glassy carbon; reference electrode, counter electrode: Pt. All potentials corrected for iR_u and reported relative to $[Cp_2Fe]^+/Cp_2Fe$. [b] Redox feature overlap with onset of solvent oxidation makes it difficult to define peak baselines and accurately determine i_{pa}/i_{pc}. Overlaid cyclic voltammograms for **Os3** recorded at different scan rates are presented in **Figure S5**.

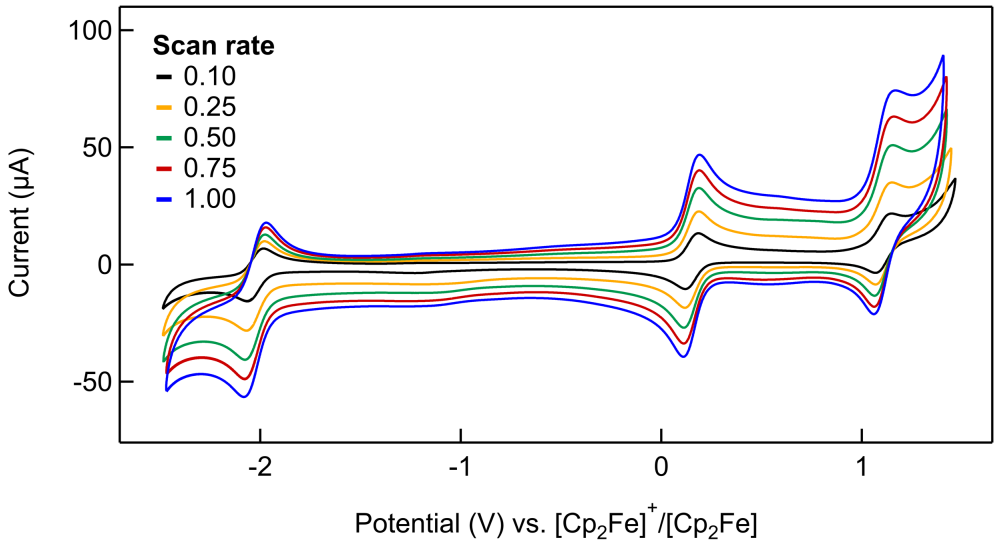
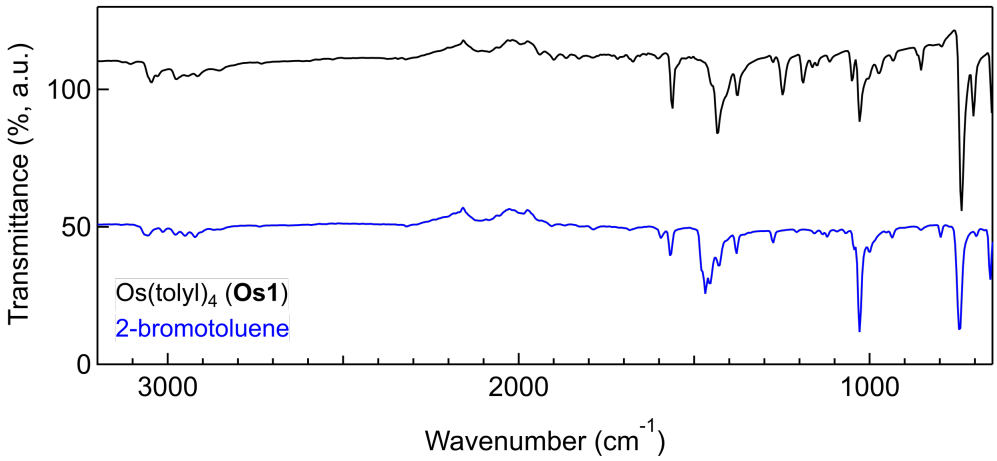
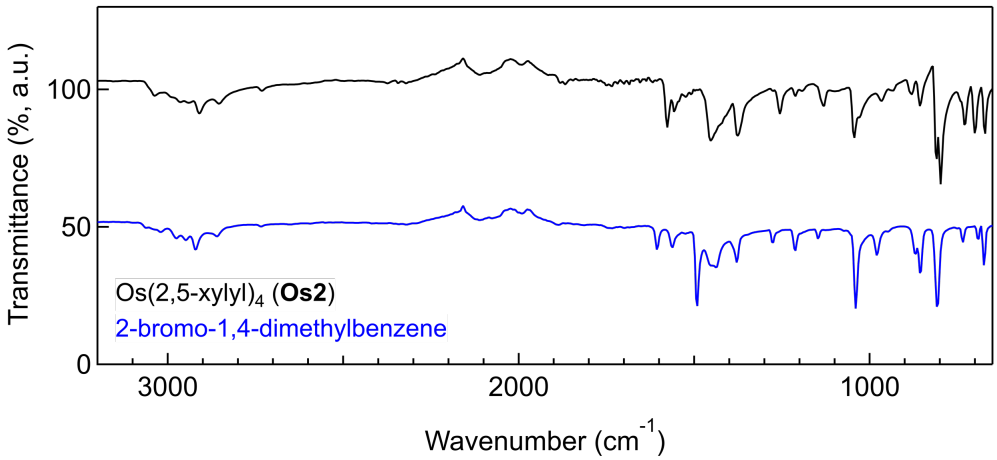
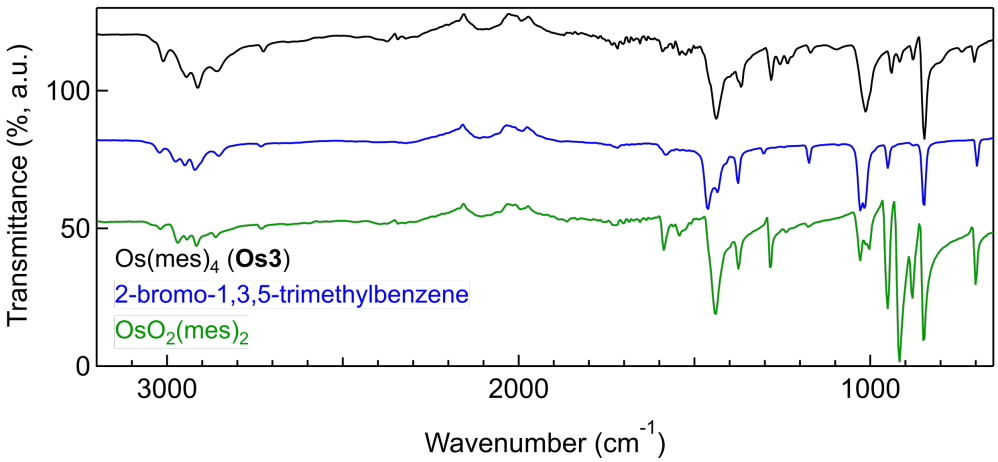


Figure S5. Overlaid voltammograms showing the dependence of current on scan rate for Os(mesityl)$_4$ (**Os3**). Potentials are reported relative to $[Cp_2Fe]^+/[Cp_2Fe]$, corrected for iR_u. For conditions see main text.

4. IR Spectra


Transmittance (%, a.u.)
100
50
0
Os(tolyl)4 (Os1)
2-bromotoluene
3000
2000
1000
Wavenumber (cm-1)


Transmittance (%, a.u.)
100
50
0
Os(2,5-xylyl)4 (Os2)
2-bromo-1,4-dimethylbenzene
3000
2000
1000
Wavenumber (cm-1)


Transmittance (%, a.u.)
100
50
0
Os(mes)4 (Os3)
2-bromo-1,3,5-trimethylbenzene
OsO2(mes)2
3000
2000
1000
Wavenumber (cm-1)

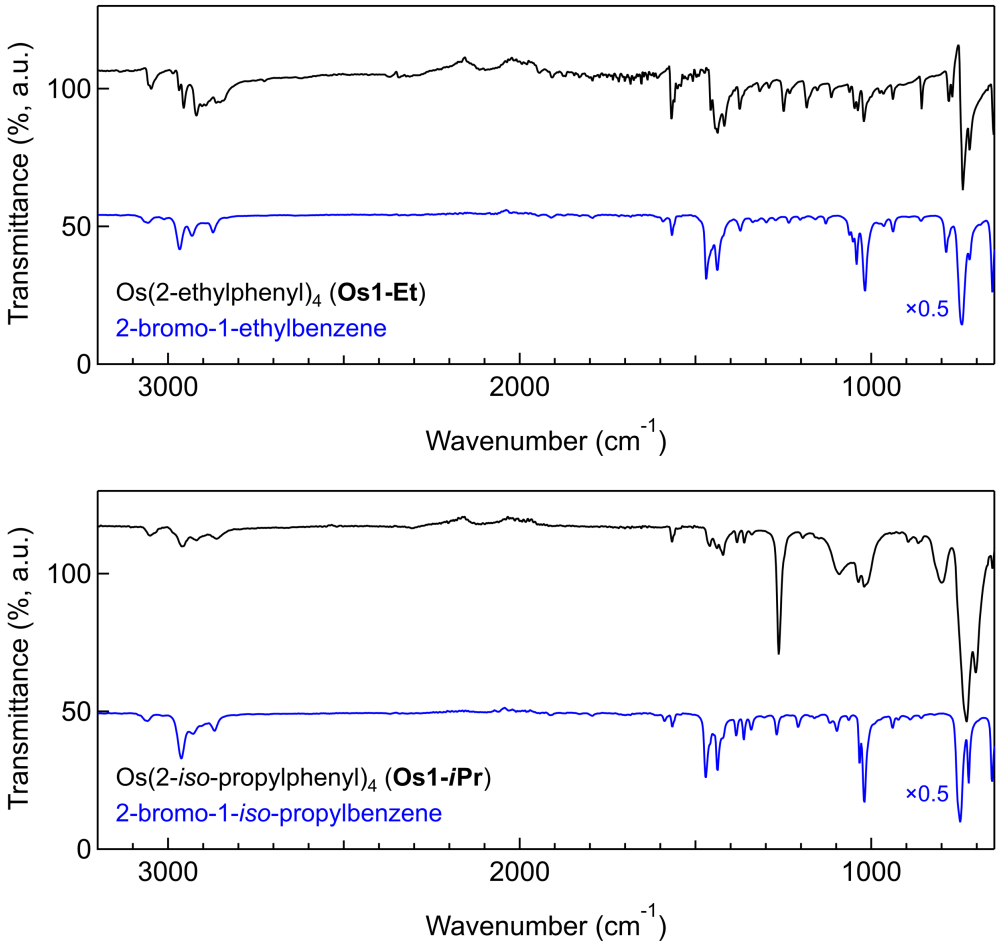


Figure S6. Infrared spectra (ATR) of **Os1-3**, **Os1-Et**, and **Os1-*i*Pr** (black), their aryl bromide ligand precursors (blue), and selected dioxo complexes (green); displaced along the y-axis for clarity. Spectra of Os(aryl)$_4$ are broadly comparable to those of their bromoaryl precursors. Features attributable to Os=O in $OsO_2(mes)_2$ appear between 920-880 cm^{-1} and are absent in the tetraaryl analogues.[10]

5. NMR Spectra

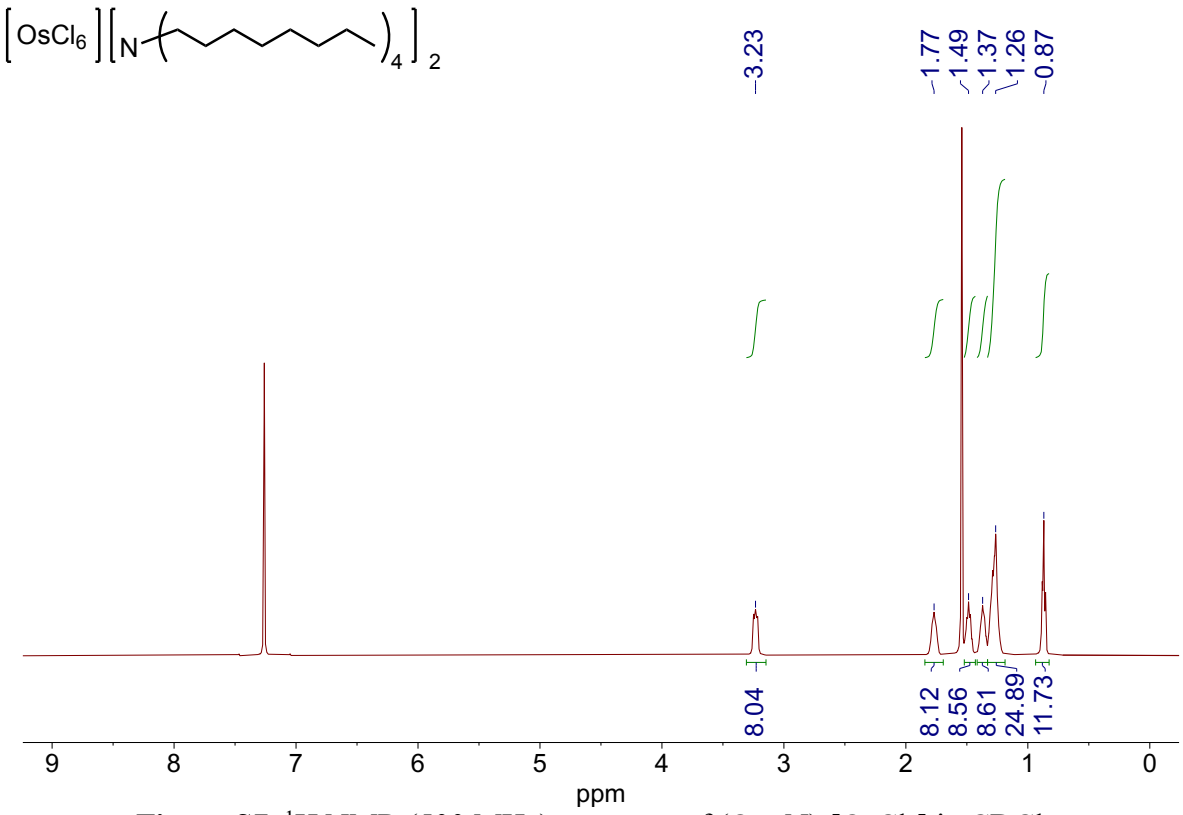


Figure S7. ^{1}H NMR (500 MHz) spectrum of $(Oct_4N)_2[OsCl_6]$ in $CDCl_3$.

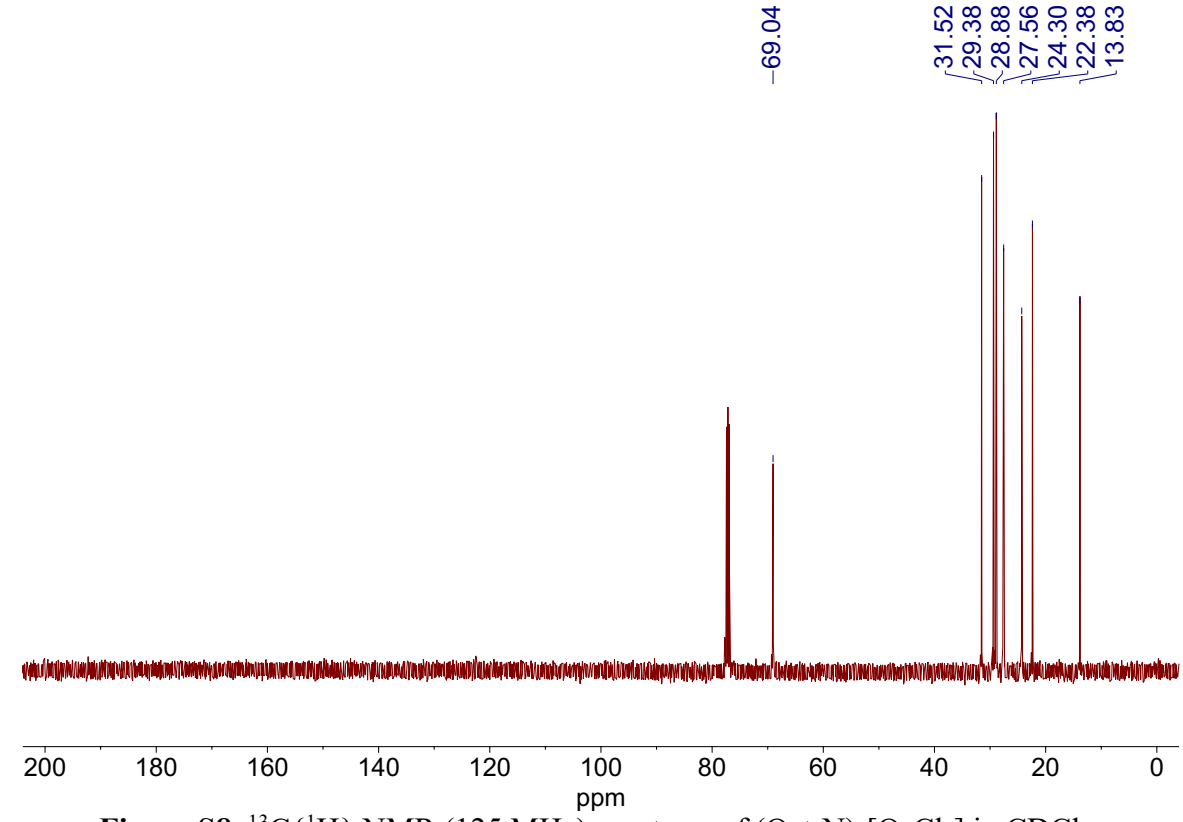


Figure S8. $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of $(Oct_4N)_2[OsCl_6]$ in $CDCl_3$.

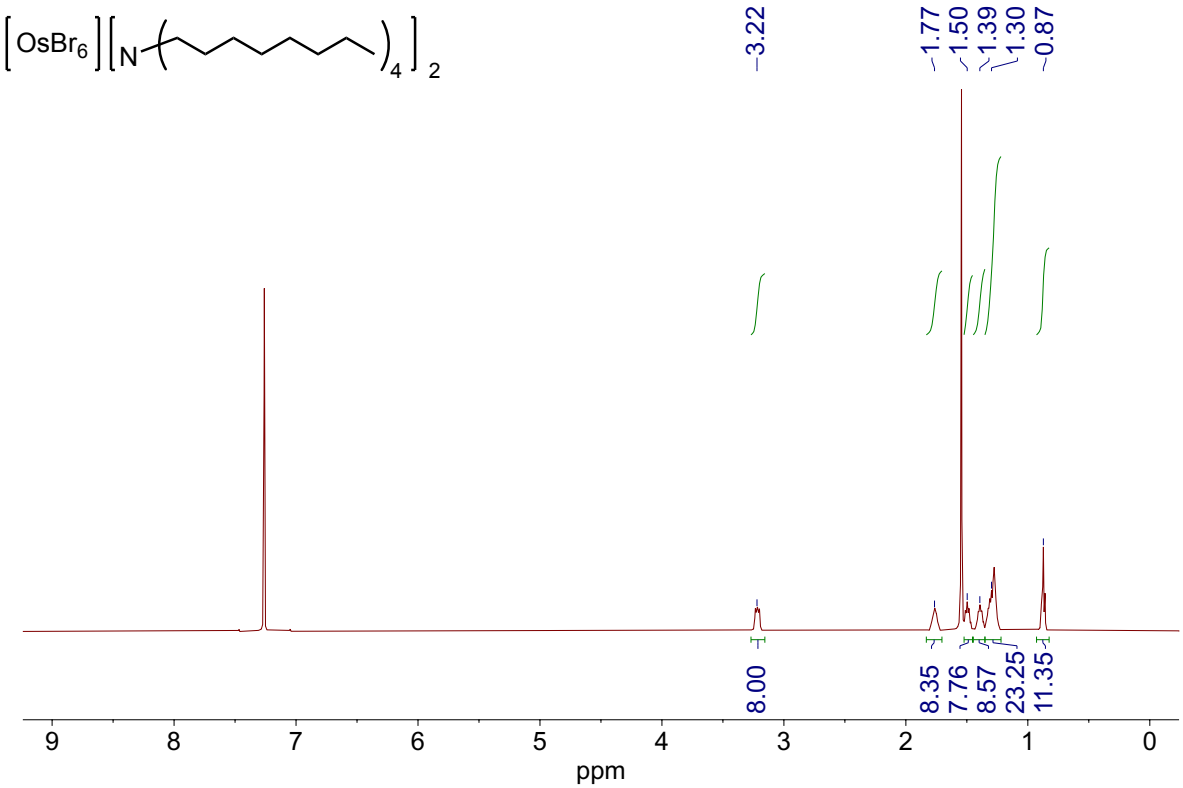


Figure S9. ^{1}H NMR (500 MHz) spectrum of $(Oct_4N)_2[OsBr_6]$ in $CDCl_3$.

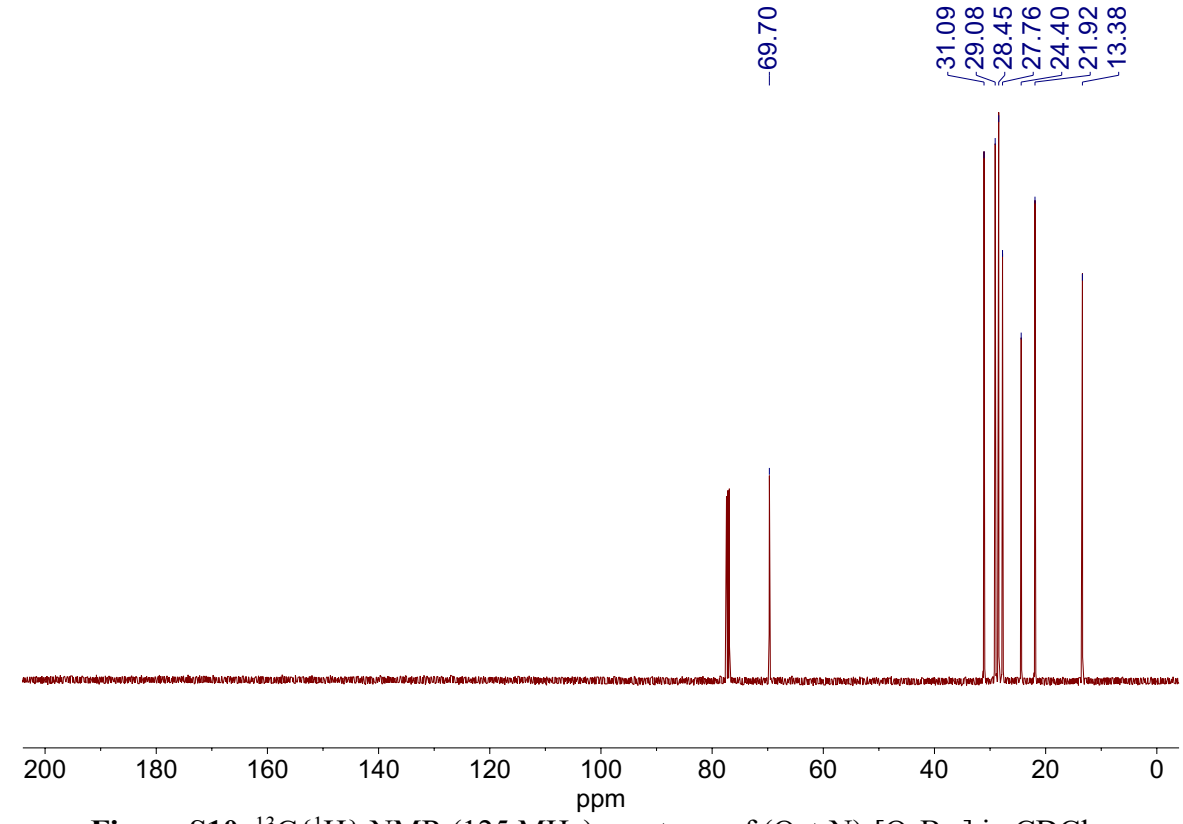


Figure S10. $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of $(Oct_4N)_2[OsBr_6]$ in $CDCl_3$.

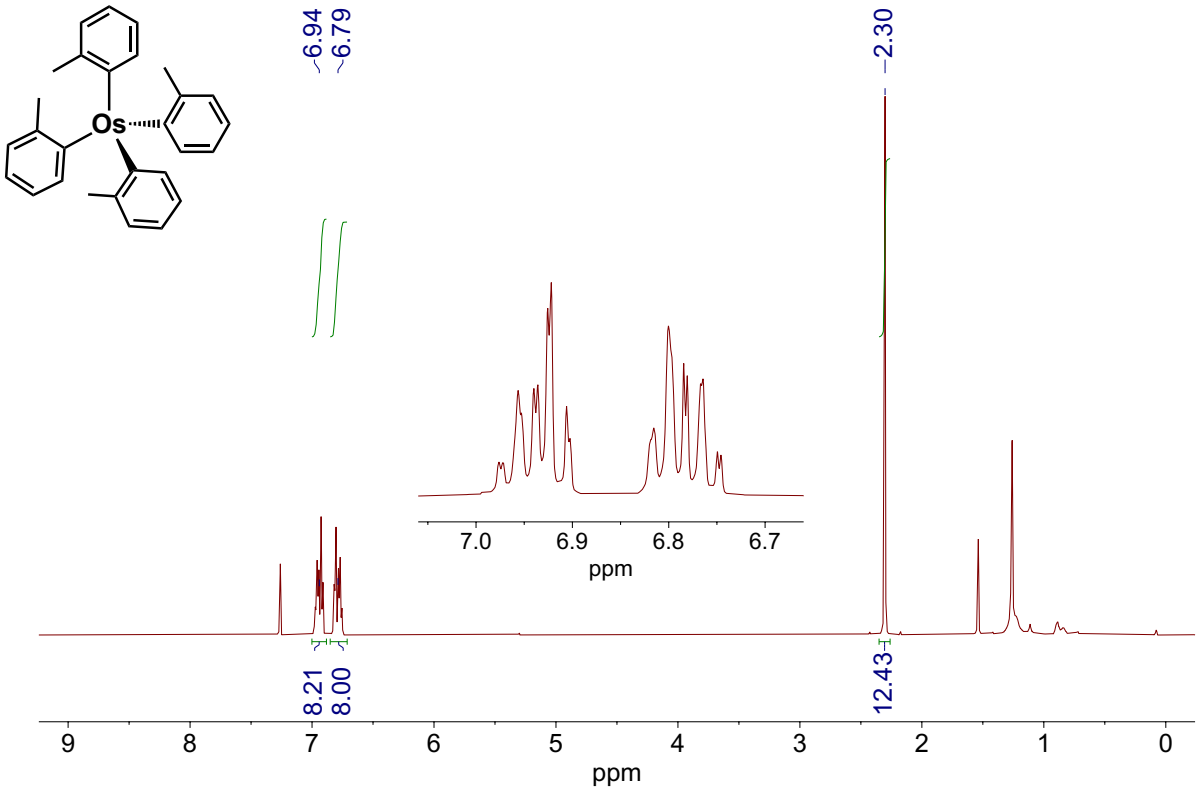


Figure S11. ^{1}H NMR (400 MHz) spectrum of Os(2-tolyl)$_4$ **(Os1)** in $CDCl_3$.

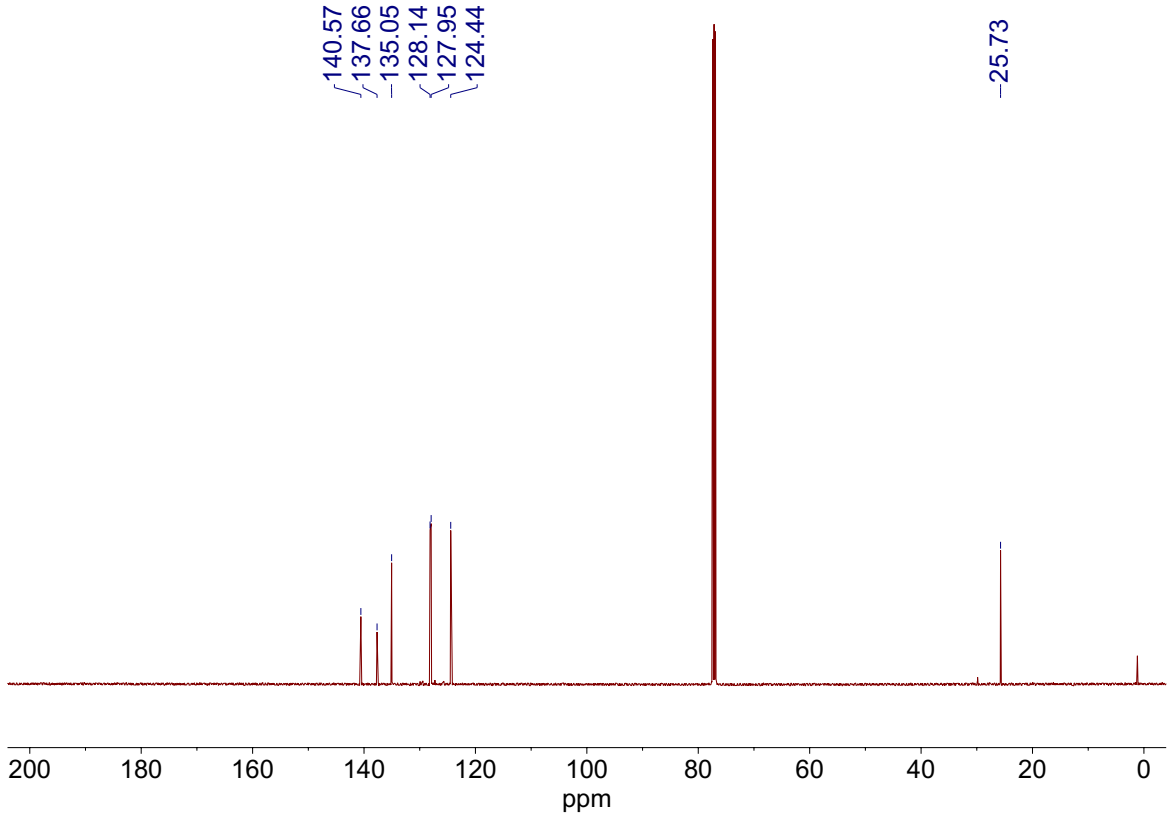


Figure S12. ^{13}C{^{1}H} NMR (125 MHz) spectrum of Os(2-tolyl)$_4$ **(Os1)** in $CDCl_3$.

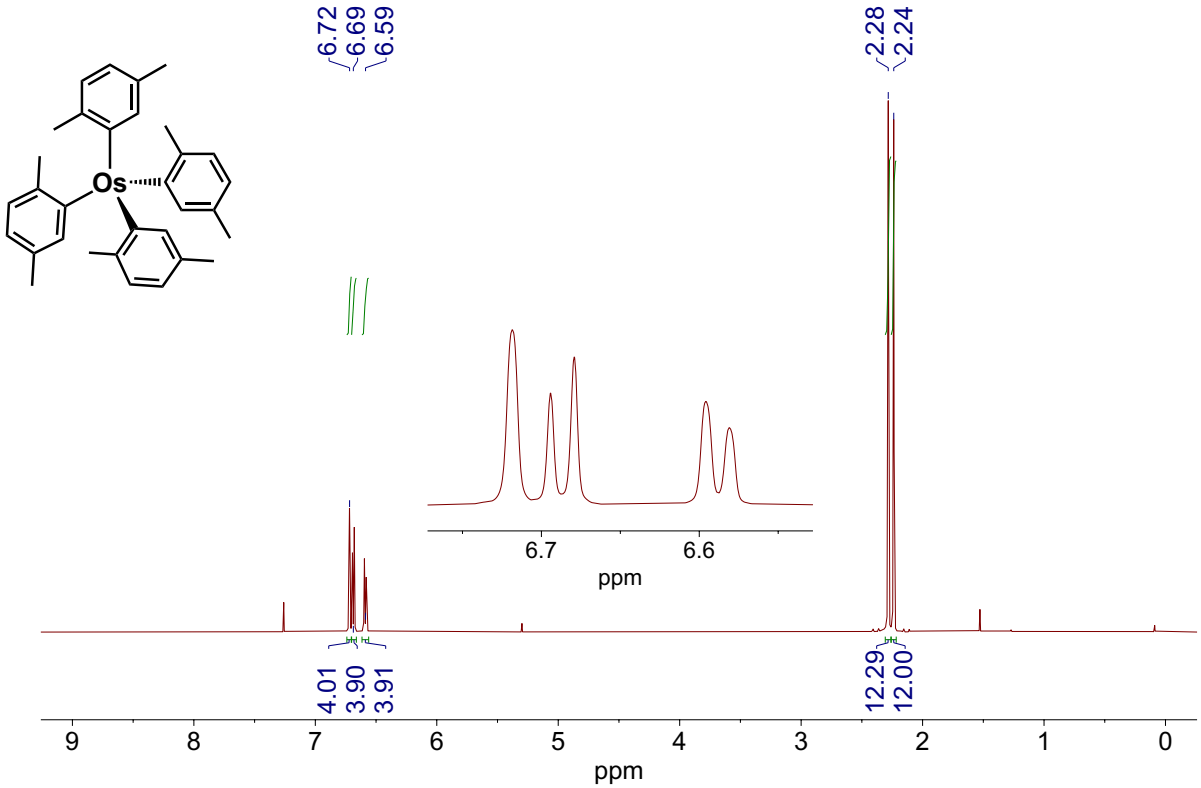


Figure S13. ^{1}H NMR (500 MHz) spectrum of Os(2,5-xylyl)$_4$ **(Os2)** in $CDCl_3$.

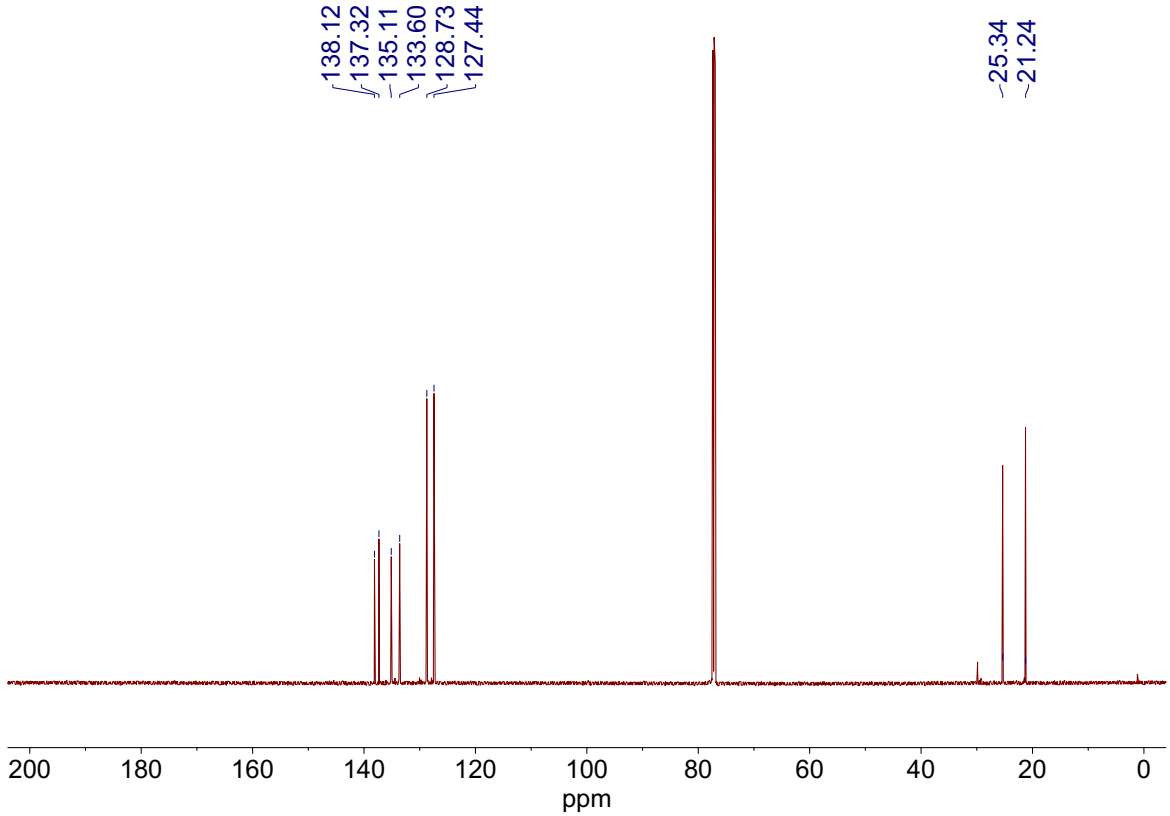


Figure S14. ^{13}C{^{1}H} NMR (150 MHz) spectrum of Os(2,5-xylyl)$_4$ **(Os2)** in $CDCl_3$.

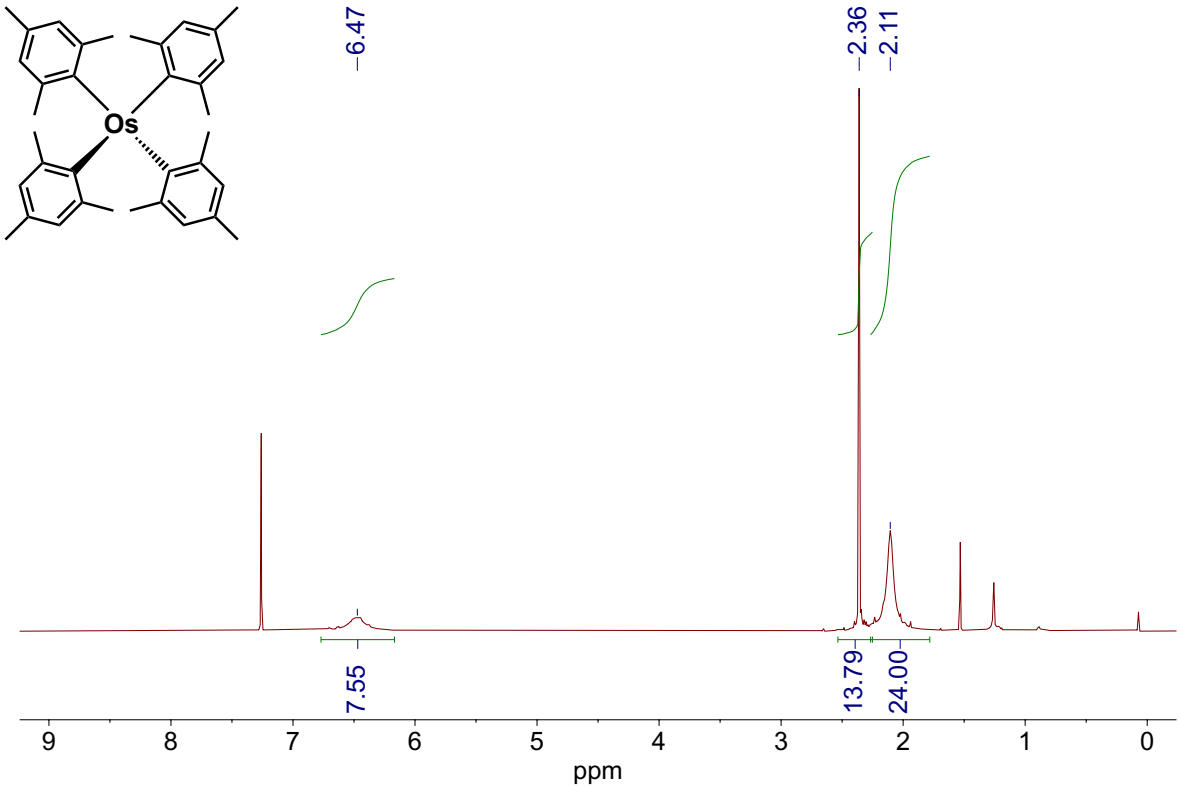


Figure S15. ^{1}H NMR (500 MHz) spectrum of Os(mesityl)$_4$ **(Os3)** in $CDCl_3$.

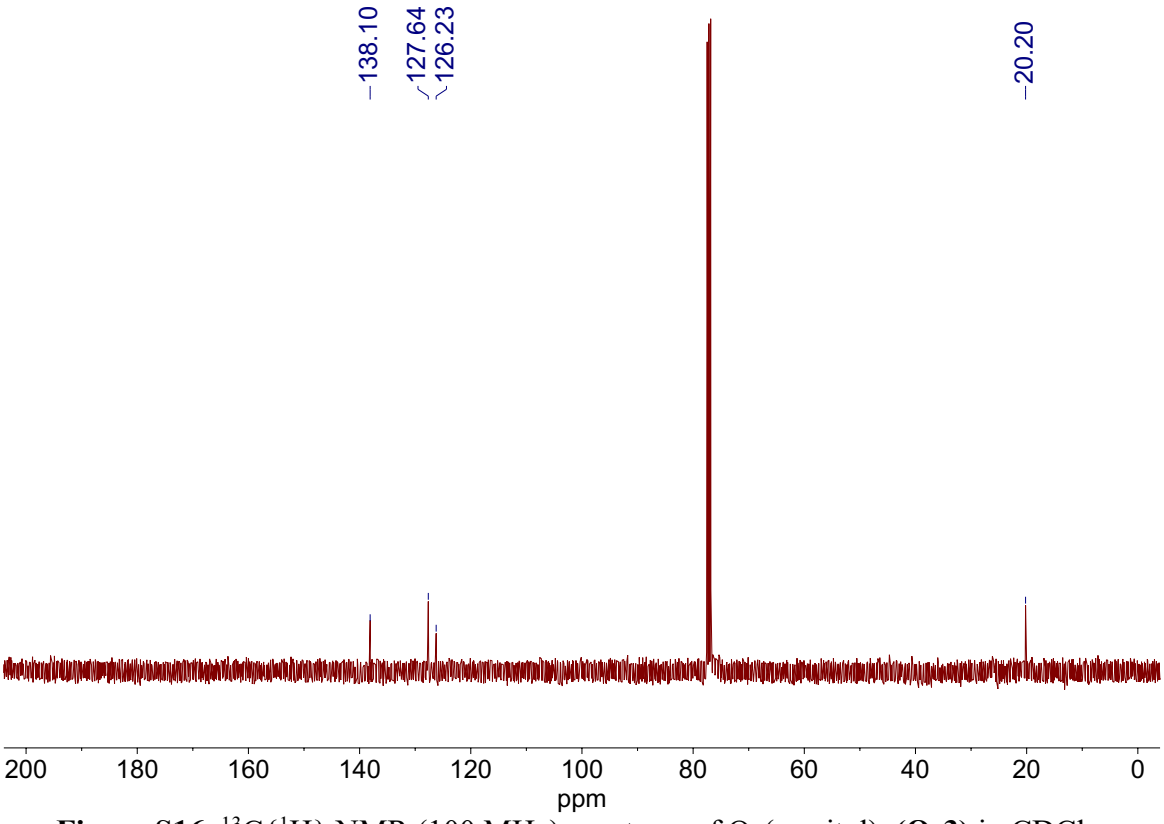


Figure S16. $^{13}C\{^{1}H\}$ NMR (100 MHz) spectrum of Os(mesityl)$_4$ **(Os3)** in $CDCl_3$.

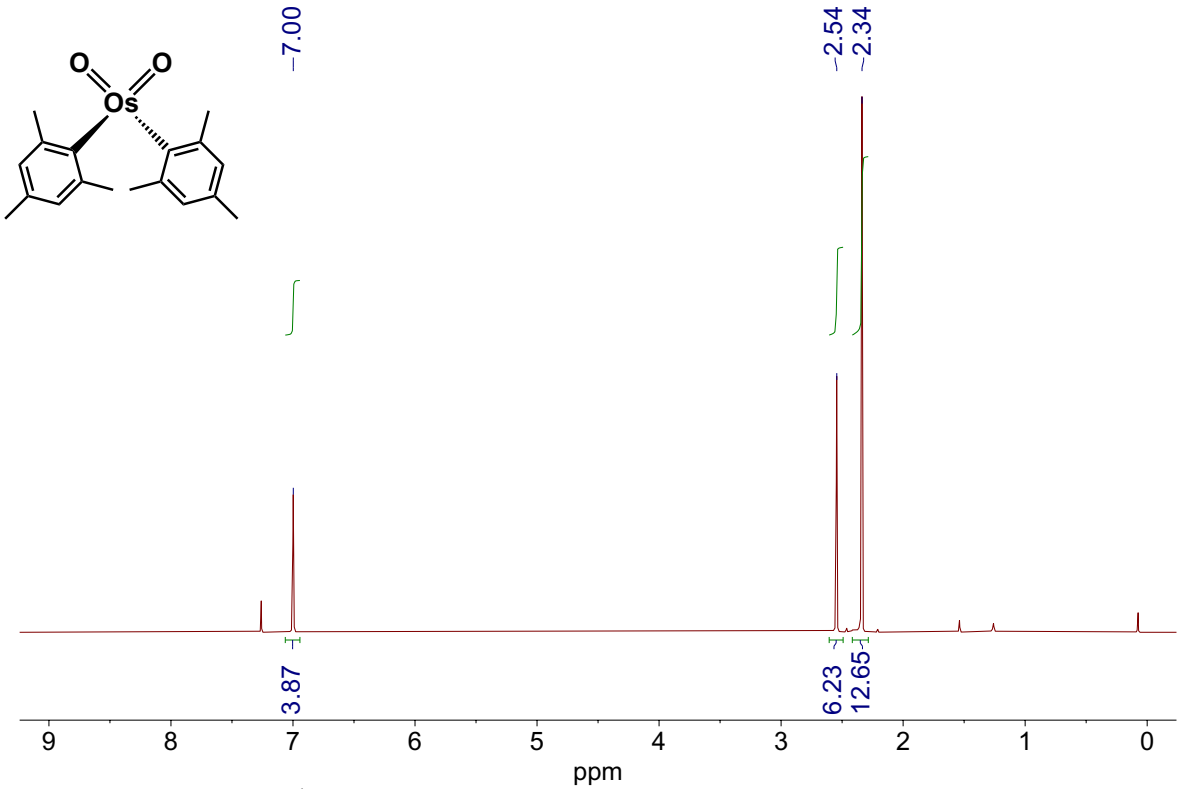


Figure S17. ^{1}H NMR (500 MHz) spectrum of OsO_2(mesityl)$_2$ in $CDCl_3$.

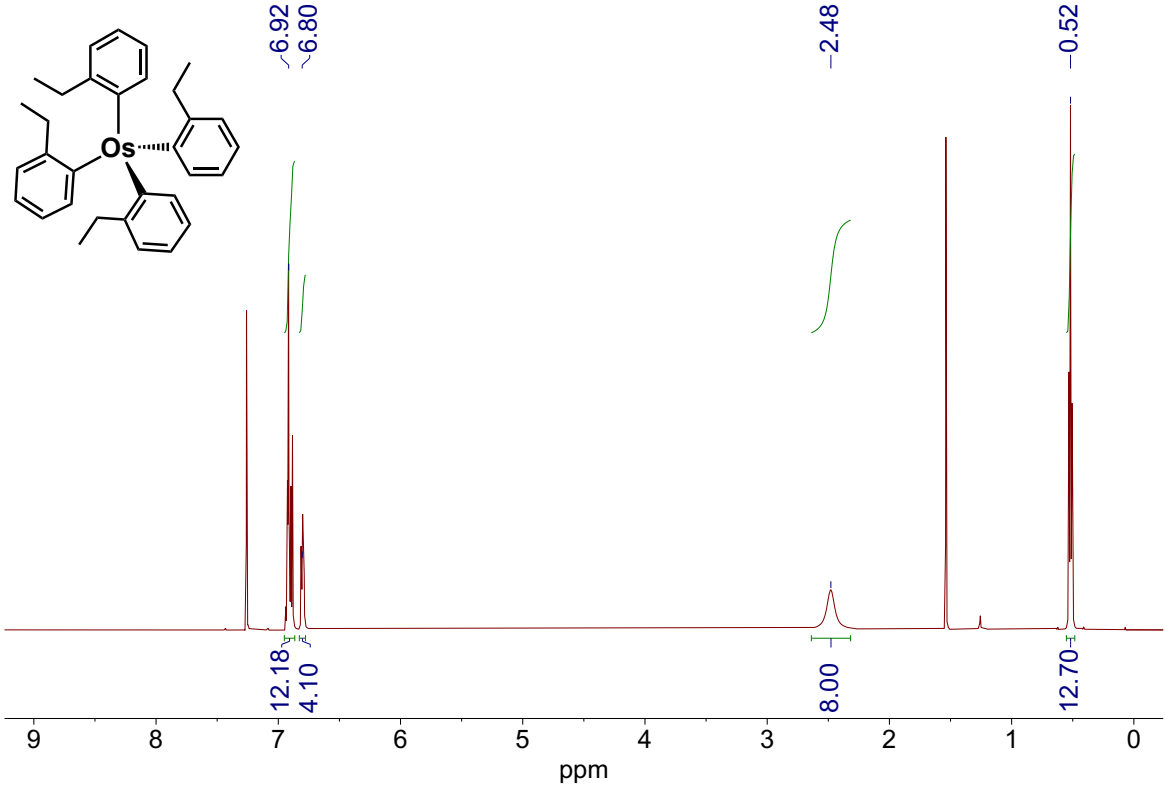


Figure S18. ^{1}H NMR (600 MHz) spectrum of Os(2-ethylphenyl)$_4$ (**Os1-Et**) in $CDCl_3$.

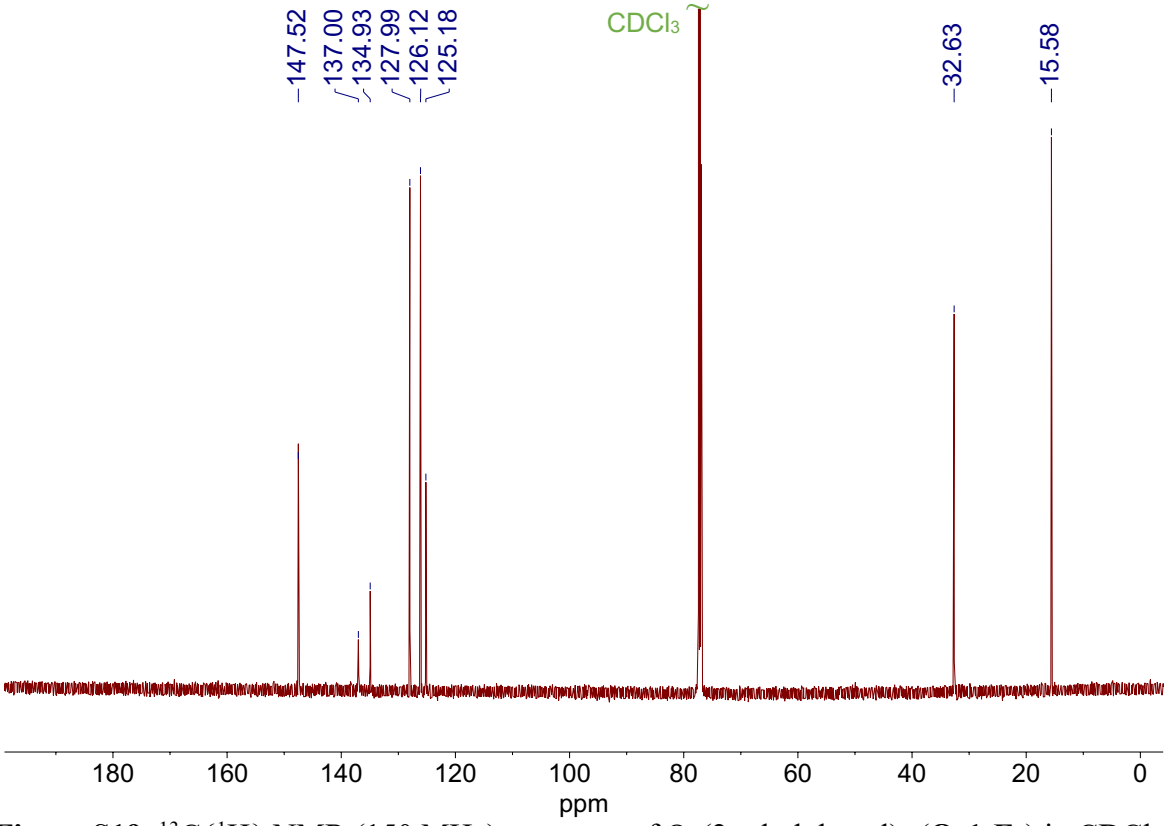


Figure S19. ^{13}C{^{1}H} NMR (150 MHz) spectrum of Os(2-ethylphenyl)$_4$ (**Os1-Et**) in $CDCl_3$.

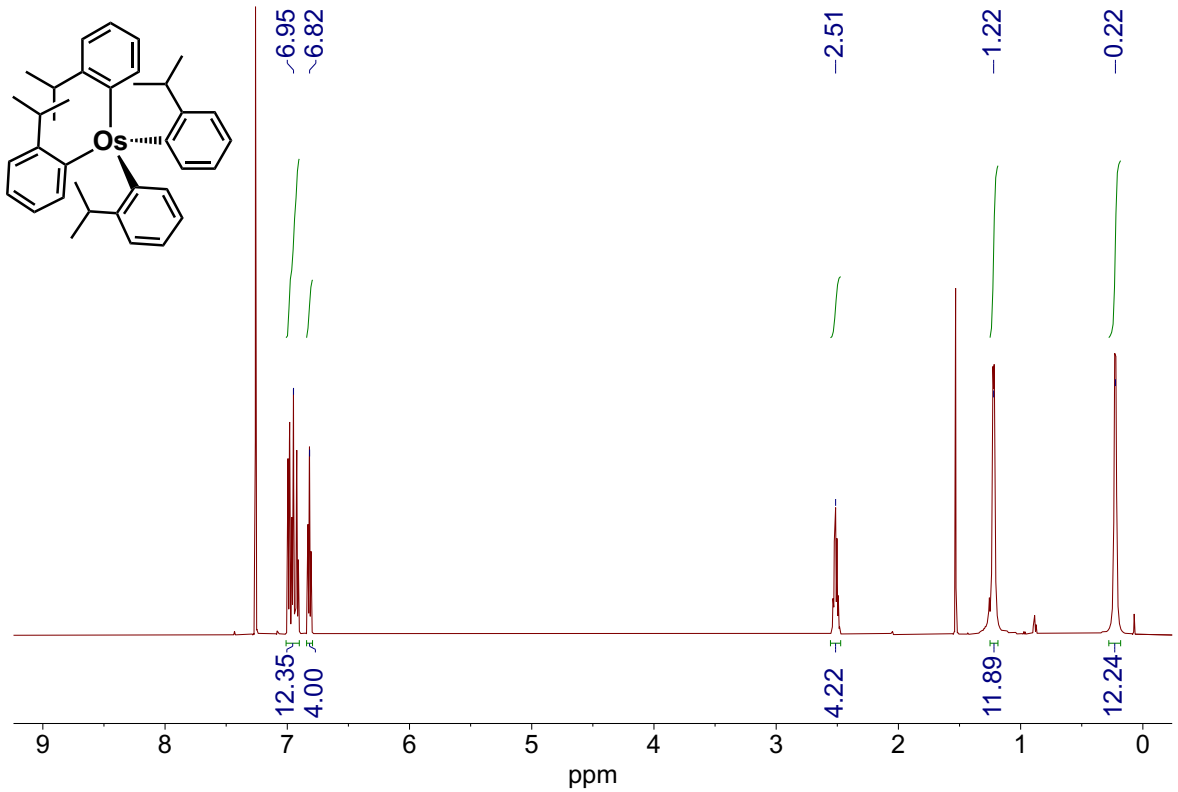


Figure S20. ^{1}H NMR (600 MHz) spectrum of Os(2-*iso*-propylphenyl)$_4$ (**Os1-*i*Pr**) in $CDCl_3$.

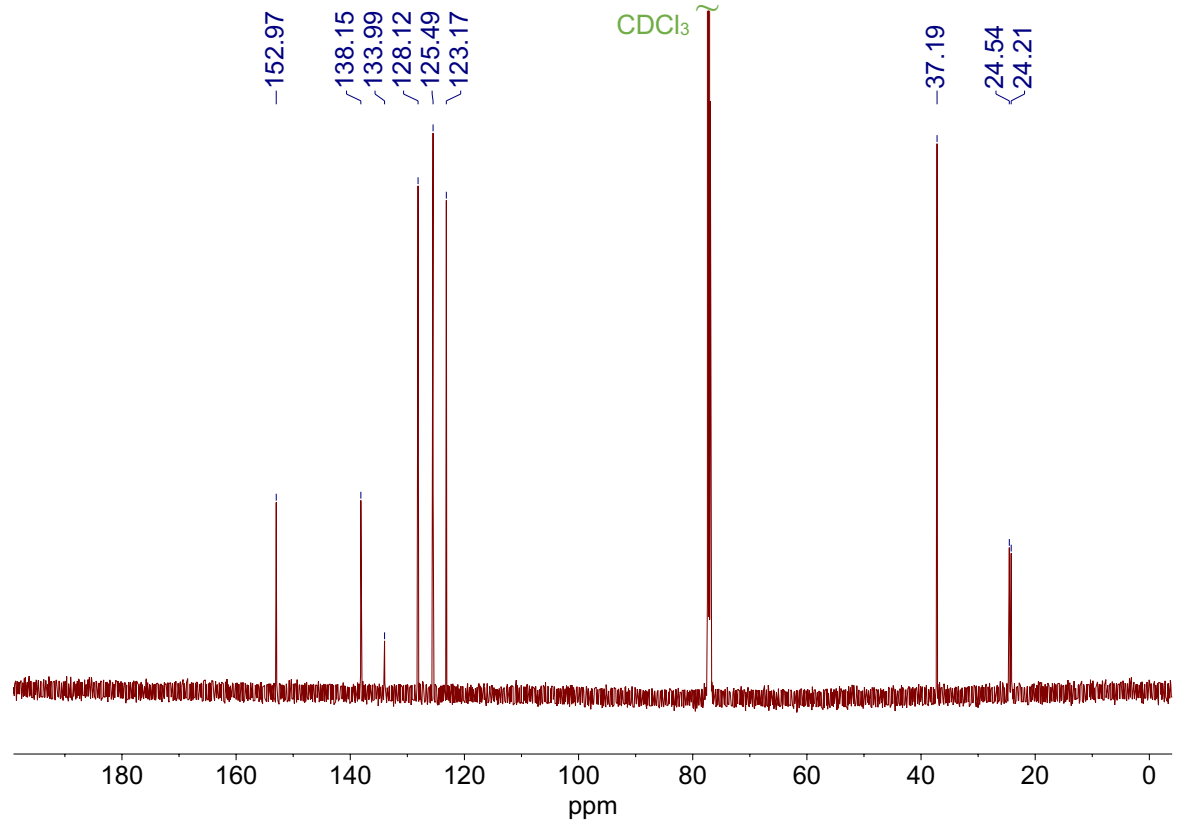


Figure S21. ^{13}C{^{1}H} NMR (150 MHz) spectrum of Os(2-*iso*-propylphenyl)$_4$ (**Os1-*i*Pr**) in $CDCl_3$.

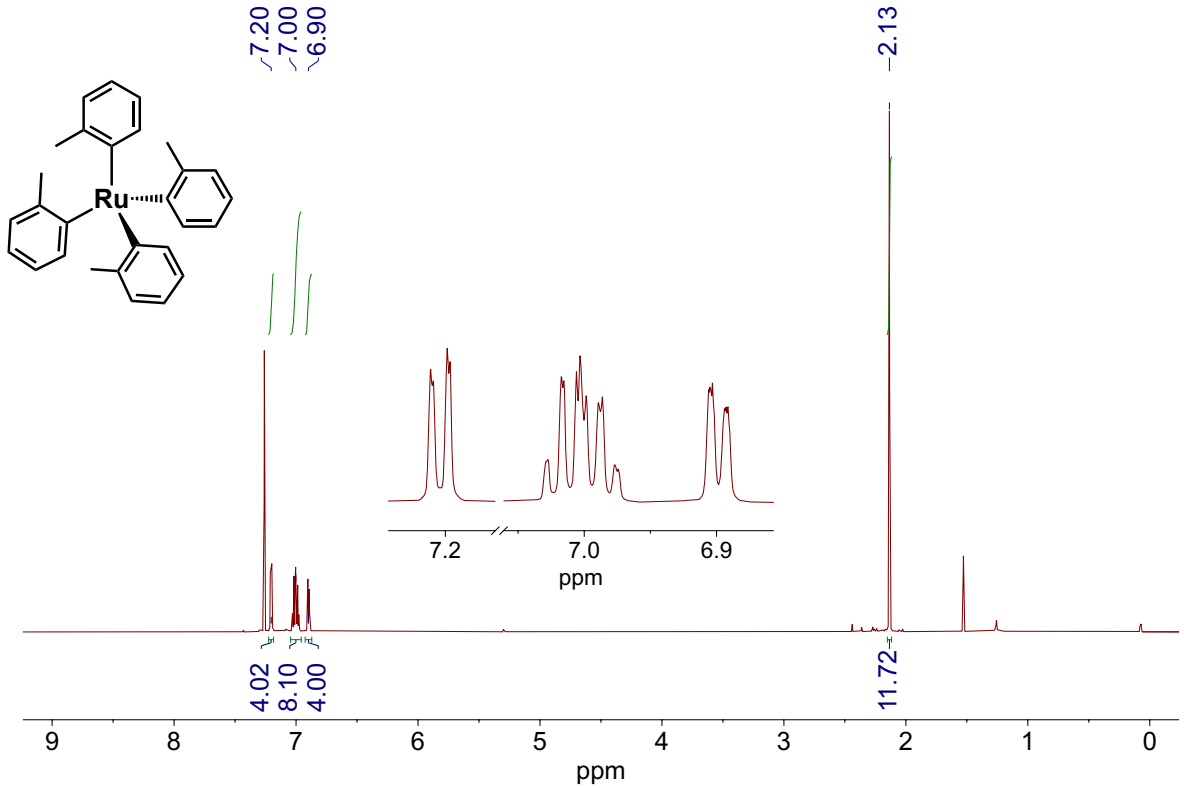


Figure S22. ^{1}H NMR (600 MHz) spectrum of Ru(2-tolyl)$_4$ (**Ru1**) in $CDCl_3$.

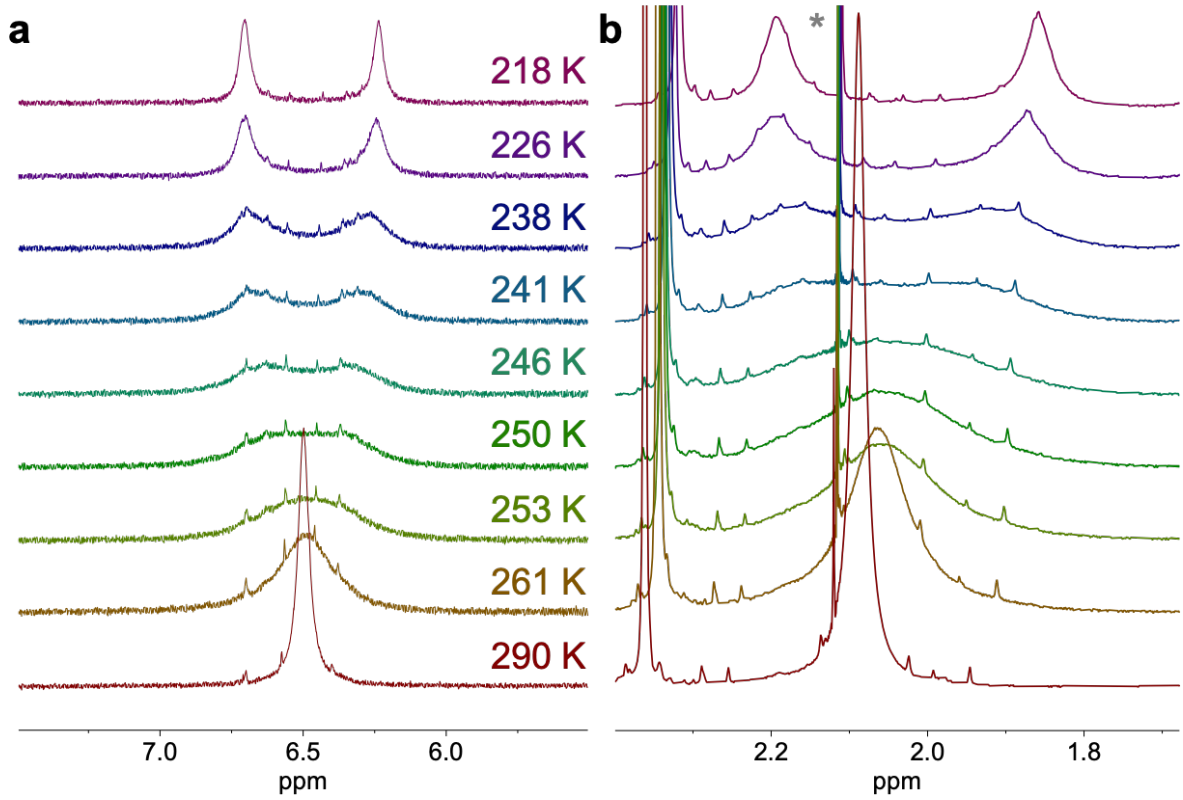


Figure S23. Variable-temperature NMR (600 MHz) spectra of **Os3** in CD_2Cl_2, showing the evolution of aryl-*H* **(a)**, and *ortho*-methyl C-*H* **(b)** resonances with temperature (* = acetone).

Table S30. Activation parameters for the rotation of mesityl ligands about the M-C bond in CD_2Cl_2 solutions of $M(mes)_4$.[a]

compound	$Ru(mes)_4$	$Os(mes)_4$
$\Delta\nu$, 2-CH_3 (Hz)	108.5	203.9
T_c, 2-CH_3 (K)	253	244
$\Delta\nu$, 3,5-H (Hz)	108.5	281.9
T_c, 3,5-H (K)	253	250
$\Delta G^{\ddagger}$, 2-CH_3 (kJ mol^{-1})	50.1	46.9
$\Delta G^{\ddagger}$, 3,5-H (kJ mol^{-1})	50.1	47.5
M–C_{av} (Å)	2.01(1)	2.037(3)
reference	6	this work

[a] Adapted from Hay-Motherwell *et al.*[6] Using $\Delta G^{\ddagger} = -RT_c\ln\pi\Delta\nu h 2^{-1/2}(kT_c)^{-1}$ following Hay-Motherwell *et al.*[17] Here, $\Delta\nu$ = separation between resonances in Hz; T_c = coalescence temperature in K; R, h, and k = gas, Planck, and Boltzmann constants, respectively.

5. References

(1) Baker, K. V.; Brown, J. M.; Hughes, N.; Skarnulis, A. J.; Sexton, A. Mechanical Activation of Magnesium Turnings for the Preparation of Reactive Grignard Reagents. *J. Org. Chem.* **1991**, *56* (2), 698–703.

(2) Love, B. E.; Jones, E. G. The Use of Salicylaldehyde Phenylhydrazone as an Indicator for the Titration of Organometallic Reagents. *J. Org. Chem.* **1999**, *64* (10), 3755–3756.

(3) Savage, P. D.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. Synthesis of Homoleptic Tetrahedral Aryls of Rhenium(IV) and Ruthenium(IV). X-Ray Crystal Structures of Tetrakis(o-Methylphenyl)Rhenium(IV), Tetrakis(*o*-Methylphenyl)Oxorhenium(VI), and Tetrakis(*o*-Methylphenyl)-Ruthenium(IV). *Dalton Trans.* **1988**, *3*, 669–673.

(4) Wang, C.-J.; Wu, X.-L.; Ma, X.-F.; Jia, A.-Q.; Zhang, Q.-F. Synthesis and Crystal Structure of a New Homoleptic Tetraarylruthenium(IV) Complex Ru(2,4,5-$Me_3C_6H_2)_4$. *Z. Naturforsch* **2017**, *72* (7), 523–525.

(5) So, S. C.; Cheung, W. M.; Wang, G. C.; Kwan Huang, E.; Lau, M. K.; Zhang, Q. F.; Sung, H. H. Y.; Williams, I. D.; Leung, W. H. Migratory Insertion and Reductive Coupling of Tetraarylruthenium(IV) Complexes. *Organometallics* **2014**, *33* (17), 4497–4502.

(6) Hay-Motherwell, R.; Wilkinson, G.; Hussain-Bates, B.; Hurthouse, M. Homoleptic Mesityls of Iridium(III,IV,V) and Ruthenium(IV,V). *Dalton Trans.* **1992**, 3477–3482.

(7) Tooze, R. P.; Stavropoulos, P.; Motevalli, M.; Hursthouse, M. B.; Wilkinson, G. Synthesis and X-Ray Crystal Structures of the First Tetrahedral Osmium(IV) Compounds, Tetrakis(Cyclohexyl)Osmium(IV) and Tetrakis(*o*-Methylphenyl)Osmium(IV). *J. Chem. Soc. Chem. Commun.* **1985**, 1139–1140.

(8) Hardy, D. T.; Wilkinson, G.; Young, G. B. Mechanistic Studies of Ligand-Induced Thermolytic Reductive Elimination of Biaryl from Tetraarylosmium(IV). *Polyhedron* **1996**, *15* (8), 1363–1373.

(9) Lau, M.-K.; Chim, J. L.; Wong, W.-T.; Williams, I. D.; Leung, W.-H. Synthesis and Molecular Structures of Monooxo Aryl Complexes of Osmium(VI). *Can. J. Chem.* **2001**, *79* (5–6), 607–612.

(10) Stravropoulos, P.; Edwards, P. G.; Behling, T.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. Oxoaryls of Rhenium-(V) and -(VI) and Osmium(VI). X-Ray Crystal Structures of Dimesityldioxorhenium(VI), Tetramesityloxorhenium(VI), and

Dimesityldioxoosmium(VI). *Dalton Trans.* **1987**, *1*, 169–175.

(11) Stavropoulos, P.; Savage, P. D.; Tooze, R. P.; Wilkinson, G.; Hussain, B.; Motevalli, M.; Hursthouse, M. B. The Synthesis and X-Ray Crystal Structures of Homoleptic Tetrahedral Aryls of Osmium(IV) and of Cyclohexyls of Ruthenium(IV), Osmium(IV), and Chromium(IV). *Dalton Trans.* **1987**, *3*, 557–562.

(12) Longley, C. J.; Savage, P. D.; Wilkinson, G.; Hussain, B.; Hurthouse, M. Alkylimido and Oxo Aryls of Rhenium. X-Ray Structures of $(ButN)_2ReCl_2(o\text{-}MeC_6H_4)$ and $MO_2(2,6\text{-}Me_2C_6H_3)_2$, M = Re and Os. *Polyhedron* **1988**, *7* (12), 1079–1088.

(13) Murrer, B. A. Use of Osmium Compounds for the Treatment of Bacterial and Fungal Infections. B. A. Murrer, WO Pat., 10177, 1991.

(14) Brown, C. M.; Arsenault, N. E.; Cross, T. N. K.; Hean, D.; Xu, Z.; Wolf, M. O. Structural, Electrochemical and Photophysical Behavior of Ru(II) Complexes with Large Bite Angle Sulfur-Bridged Terpyridyl Ligands. *Inorg. Chem. Front.* **2020**, *7*, 117–127.

(15) Österman, T.; Abrahamsson, M.; Becker, H.-C.; Hammarström, L.; Persson, P. Influence of Triplet State Multidimensionality on Excited State Lifetimes of Bis-Tridentate RuII Complexes: A Computational Study. *J. Phys. Chem. A* **2012**, *116* (3), 1041–1050.

(16) Lundqvist, M. J. Quantum Chemical Modeling of Dye-Sensitized Titanium Dioxide: Ruthenium Polypyridyl and Perylene Dyes, TiO_2 Nanoparticles, and Their Interfaces, Ph.D. Thesis, Uppsala University, 2006.

(17) Hay-Motherwell, R. S.; Hussain-Bates, B.; Hursthouse, M. B.; Wilkinson, G. Synthesis and X-Ray Crystal Structure of Trimesitylrhodium(III). *J. Chem. Soc. Chem. Commun.* **1990**, *18*, 1242–1243.