Supporting Information

The Development of a Platform for Near-Infrared Photoredox Catalysis

Benjamin D. Ravetz,1 Nicholas E. S. Tay, 1 Candice L. Joe,2* Melda Sezen-Edmonds,2 Michael A. Schmidt,2 Yichen Tan,2 Jacob M. Janey,2 Martin D. Eastgate,2 Tomislav Rovis1*

Correspondence to: candice.joe@bms.com; tr2504@columbia.edu

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Materials and Methods

General Comments
Unless noted, all reactions were performed in oven-dried glassware and carried out under an atmosphere of argon or nitrogen with magnetic stirring. The reactions in the general procedures section are tolerant of non flame-dried vials. All column chromatography was performed using general flash techniques on SiliCycle® SilicaFlash® P60, 40-63 μm 60 Å. For particularly difficult separations, on Teledyne Isco CombiFlash using CombiFlash gold pre-packed columns. Thin layer chromatography was performed on SiliCycle® 250 μm 60 Å plates. Visualization was accomplished with 254 nm UV light, KMnO$_4$ stain, or I$_2$.

NMR spectra were recorded on Bruker 400 and 500 MHz spectrometers at ambient temperature. Chemical shifts (δ) are reported in parts per million (ppm) from CDCl$_3$ (1H: 7.26 ppm, 13C: 77.16 ppm), CD$_2$Cl$_2$ (1H: 5.32 ppm, 13C: 54.0 ppm), CD$_3$OD (1H: 4.78, 3.31 ppm, 13C: 49.15 ppm), DMSO-d$_6$ (1H: 2.50 ppm, 13C: 39.53 ppm or CD$_3$CN (1H: 1.94 ppm, 13C: 1.32 ppm) with multiplicity (s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, and m = multiplet) and coupling constants (in Hz). Diastereomer ratios for all compounds were determined by 1H NMR analysis of the unpurified reaction mixtures. Mass spectra were recorded on a Waters Acquity H UPLC-MS. Infrared spectra were collected on a Perkin Elmer Spectrum Two FT-IR spectrometer. Gel permeation chromatography (GPC) was performed using a Waters 1515 isocratic HPLC pump with a 2990 photodiode array detector and 2414 refractive index detector. Samples run in THF and calibrated with polystyrene (PS) standards of narrow dispersity.

Solutions of Os catalysts were prepared from anhydrous toluene, acetonitrile, methanol or DMF in a nitrogen glovebox. Solutions were made in 1 cm x 1 cm quartz cuvettes from Spectrocell and were degassed by sparging with nitrogen for 30 seconds then sealed before removing from glovebox for measurement. Absorption spectra were obtained on an Agilent Technologies Cary 60 UV-Vis spectrophotometer. Fluorimetry spectra were obtained on Perkin Elmer LS-55.

Lamp information is listed below. Reactions were placed approximately 5 cm from lamps. Alternative light sources also perform adequately such as far Red 700-800 nm and deep red 660nm LED lamps from powerPAR and 730 nm far red growspot from Agroxmax LED and Kessil.

**PR160L-456**
Radiant Flux (optical output): 11,905mW (11.91W)
Intensity at 1cm from light: 447mW/cm$^2$
Power Consumption: Max. 50W

**PR160L-660-C**
Radiant Flux (optical output): 10,220mW (10.22W)
Intensity at 1cm from light: 384.42mW/cm$^2$
Power Consumption: Max. 35W

**PR160L-740-C**
Radiant Flux (optical output): 8,180mW (8.18W)
Intensity at 1cm from light: 308.43mW/cm$^2$
Power Consumption: Max. 30W
The NMR experiments were performed with parts from Goldstone Marketing LLC. Specifically, led heads Mic-LED-390L, Mic-LED-420Z, Mic-LED-655A, Mic-LED-730L were used. Additionally current controller BLCC-04, fiber coupling adapter FCA-SMA, and Fiber Patch cord (Extra Long) were purchased.

Unless otherwise stated, all starting materials were obtained from commercial sources including Sigma-Aldrich, TCI, Matrix, Alfa-Aesar, and Oakwood Scientific.

Safety Statement:
OsO$_4$ is a known toxin. The low-valent Os(II) octahedral complexes used in this study are known to have low toxicity.$^1$ Upon exposure to oxygen and under light irradiation or mild heating, we observe no oxidation to high valent Os (Figure S2). Nevertheless, precautions have been and should be taken. We synthesize the Os complexes under an inert atmosphere. The corresponding Os-contaminated waste is contained separately from other waste streams and is treated with corn oil to quench any possible OsO$_4$ generated over time. While we have not observed any decomposition of the Os complexes used in this study to OsO$_4$ while storing in a desiccator on the benchtop, we recommend storing the complexes in the glovebox to limit exposure to moisture and oxygen.
Starting Material Preparation

To a 100 mL RBF, open to air, was added sulfonyl chloride (1.1 equiv), dichloromethane, 4-dimethylaminopyridine (0.2 equiv), 2-bromo-2,2-difluoroethanol (1.0 equiv) and triethylamine (1.2 equiv). The reaction stirred at room temperature for 12 hours. The reaction mixture was then washed with water (50 mL) and saturated NaHCO₃ (50 mL) and then dried with Na₂SO₄ before the solvent was removed in vacuo to give crude product which was purified via silica gel chromatography to give the requisite sulfonate which matched literature values.²

A flame-dried flask was charged with a stir bar and dicarbonyl compound (1 equivalent) under ambient conditions. Anhydrous acetonitrile (0.25 M to dicarbonyl) was then added followed by potassium carbonate (3.5 equivalents). After, propargyl bromide (2.5 equivalents – 80% solution in toluene) was added to the flask and the vessel was vigorously stirred. After complete starting material consumption (~24h), the reaction was concentrated in vacuo and the residue was immediately suspended in ethyl ether. The resulting solution was then filtered to remove inorganic salts and the filtrate was added directly to a separatory funnel. The organic layer was washed two times with water and then dried over sodium sulfate. After, the drying agent was removed by gravity filtration through cotton and the organic layer was concentrated again in vacuo. The compound was then purified by column chromatography using an ethyl acetate:hexane gradient (0-25%) unless otherwise noted. Note: many compounds were not visible by UV light and were visualized with KMnO₄. The characterization of this compound matched literature values ³.

In a 250 mL round bottom flask containing a stir-bar, aldehyde, ethanol, KOH, 2-acetylene, and aqueous ammonia (28% ammonia in water) were added in that order under open atmosphere. The reaction was stirred for 12 hours and a precipitate formed. The solid was collected via filtration and washed with water and then ethanol to provide pure ligand.

OsL2 Off-white solid (85%)

¹H NMR (400 MHz, CDCl₃): δ 8.95 (d, J = 4.8 Hz, 4H), 8.85 (s, 2H), 7.94 – 7.83 (m, 2H), 7.57 – 7.42 (m, 3H), 7.32 (t, J = 4.8 Hz, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 163.9, 157.8, 155.9, 150.6, 138.0, 129.4, 129.2, 127.4, 122.7, 120.5 ppm. MS (ASAP+, pos): m/z = 312.1254 [M+H]+; calculated m/z = 312.1249 [M+H]+. IR (neat): 2215.21, 1676.21, 1562.12, 1423.95, 1386.97, 1270.74, 719.60 ν cm⁻¹.
OsL16. Yellow solid (58%) \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 9.00 (d, J = 4.9\) Hz, 4H), 8.88 (s, 1H), 8.28 (s, 2H), 8.00 (s, 1H), 7.40 (t, \(J = 4.8\) Hz, 2H). ppm. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(-62.78\) ppm. \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 82.4, 77.2, 75.5, 67.0, 59.6, 52.1\) (q, \(J = 33.6\) Hz), 46.9, 43.9, 42.3, 42.0, 41.1, 40.2. ppm. MS (ASAP\(^+\), pos): \(m/z = 448.0999 [M+H]^+\); calculated \(m/z = 449.0997 [M+H]^+\). IR (neat): \(\nu 2293.32, 1836.20, 1672.21, 1562.86, 1425.54, 1382.61, 1279.73, 1173.08, 1121.19, 905.54, 729.80\) cm\(^{-1}\).

OsL15. The characterization of this compound matched literature values\(^4\). Off-white solid (49%) \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 8.73\) (ddd, \(J = 4.8, 1.8, 0.9\) Hz, 2H), 8.71 (s, 2H), 8.66 (dt, \(J = 8.0, 1.1\) Hz, 2H), 7.94 – 7.82 (m, 4H), 7.34 (ddd, \(J = 7.5, 4.8, 1.2\) Hz, 2H), 7.02 (d, \(J = 2.1\) Hz, 2H), 3.87 (s, 3H). ppm. \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 160.7, 156.5, 156.0, 149.9, 149.2, 137.0, 130.9, 128.7, 123.9, 121.5, 118.4, 114.4, 55.5\) ppm. MS (ASAP\(^+\)): \(m/z = 340.1449 [M+H]^+\); calculated \(m/z = 340.1450 [M+H]^+\). IR (neat): \(\nu 2023.67, 1582.83, 1514.60, 1254.48, 1180.37, 1039.81, 791.99\) cm\(^{-1}\).

OsL11. Off-white solid (86%) \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 8.96\) (d, \(J = 4.8\) Hz, 4H), 8.84 (s, 2H), 7.89 – 7.81 (m, 2H), 7.35 (t, \(J = 4.8\) Hz, 2H), 7.09 – 7.01 (m, 2H), 3.87 (s, 3H). ppm. \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 163.8, 160.9, 157.8, 155.4, 150.1, 130.1, 128.6, 122.3, 120.6, 114.7, 55.5\) ppm. MS (ASAP\(^+\)): \(m/z = 342.1352 [M+H]^+\); calculated \(m/z = 342.1355 [M+H]^+\). IR (neat): \(\nu 2218.41, 1677.10, 1596.97, 1561.58, 1515.43, 1410.23, 805.05\) cm\(^{-1}\).

OsL17. The characterization of this compound matched literature values\(^5\). Pale yellow solid (43%) \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 8.73 – 8.58\) (m, 4H), 8.42 (s, 2H), 7.83 (td, \(J = 7.7, 1.9\) Hz, 2H), 7.28 (ddd, \(J = 7.5, 4.7, 1.3\) Hz, 2H), 6.22 (s, 2H), 3.86 (s, 3H), 3.71 (s, 6H). ppm. \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 161.4, 158.5, 157.0, 154.9, 149.1, 145.3, 136.8, 124.1, 123.5, 110.6, 90.9, 56.0, 55.5\) ppm. MS (ASAP\(^+\)): \(m/z = 400.1663 [M+H]^+\); calculated \(m/z = 400.1661 [M+H]^+\). IR (neat): \(\nu 2837.76, 1608.93, 1581.83, 1464.46, 1119.62, 791.66\) cm\(^{-1}\).

OsL8. The characterization of this compound matched literature values\(^6\). White solid (69%) \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 8.75 – 8.72\) (m, 2H), 8.72 (s, 2H), 8.64 (dt, \(J = 8.0, 1.1\) Hz, 2H), 7.86 (td, \(J = 7.7, 1.8\) Hz, 2H), 7.59 (dd, \(J = 1.8, 0.7\) Hz, 1H), 7.34 (ddd, \(J = 7.5, 4.8, 1.2\) Hz, 2H), 7.11 (dd, \(J = 3.4, 0.7\) Hz, 1H). ppm. \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 156.3, 156.1, 152.1, 149.3, 143.8, 139.7, 137.0, 124.0, 121.4, 115.3, 112.2, 109.8, 109.3 ppm. MS (ASAP\(^+\)): \(m/z = 300.1137 [M+H]^+\); calculated \(m/z = 300.1137 [M+H]^+\). IR (neat): \(\nu 1607.46, 1585.73, 1562.62, 1545.03, 1402.10, 788.23, 729.71\) cm\(^{-1}\).

OsL9. The characterization of this compound matched literature values\(^7\). Yellow-Green solid (71%) \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 8.73\) (ddd, \(J = 4.8, 1.8, 0.9\) Hz, 1H), 8.70 (s, 1H), 8.65 (dt, \(J = 8.0, 1.1\) Hz, 1H), 7.93 (dd, \(J = 2.9, 1.3\) Hz, 0H), 7.86 (td, \(J = 7.7, 1.8\) Hz, 1H), 7.70 (ddd, \(J = 5.1, 1.4\) Hz, 0H), 7.45 (dd, \(J = 5.1, 2.9\) Hz, 1H), 7.37 – 7.31 (m, 1H). ppm. \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 156.4, 156.1, 149.2, 144.8, 140.1, 137.0, 126.7, 126.4, 124.0, 123.7, 121.5, 118.2\) ppm. MS (ASAP\(^+\)): \(m/z = 316.09096 [M+H]^+\); calculated \(m/z = 316.0909 [M+H]^+\). IR (neat): \(\nu 1583.57, 1466.85, 1412.89, 782.49\) cm\(^{-1}\).
OsL10. The characterization of this compound matched literature values. Tan solid (53%) $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.73 (s, 2H), 8.46 (d, $J = 7.8$ Hz, 2H), 7.95 – 7.86 (m, 2H), 7.75 (t, $J = 7.7$ Hz, 2H), 7.57 – 7.50 (m, 2H), 7.50 – 7.42 (m, 1H), 7.20 (d, $J = 7.6$ Hz, 2H), 2.67 (s, 6H). ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 158.0, 156.3, 155.9, 150.4, 139.2, 137.1, 129.0, 129.0, 127.5, 123.4, 119.1, 118.5, 24.8 ppm. MS (ASAP+): m/z = 340.1558 [M+H]$^+$; calculated m/z = 340.1562 [M+H]$^+$. IR (neat): $\nu$ 1579.91, 1547.43, 1462.49, 1397.36, 769.56, 758.11 cm$^{-1}$.

OsL6. The characterization of this compound matched literature values. White solid (51%) Note: the procedure was slightly modified by adding 10 equiv. THF to solubilize the starting aldehyde. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.81 (s, 2H), 8.75 (d, $J = 4.8$, 1.8, 0.9 Hz, 2H), 8.69 (dt, $J = 7.9$, 1.1 Hz, 2H), 8.03 – 7.98 (m, 2H), 7.87 (td, $J = 7.8$, 1.8 Hz, 2H), 7.77 – 7.71 (m, 2H), 7.70 – 7.65 (m, 2H), 7.51 – 7.45 (m, 2H), 7.42 – 7.31 (m, 4H). ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 156.4, 156.1, 149.8, 149.3, 141.9, 140.5, 137.4, 137.0, 129.0, 127.8, 127.7, 127.7, 127.2, 123.9, 121.5, 118.8 ppm. MS (ASAP+): m/z = 386.1659 [M+H]$^+$; calculated m/z = 386.1657 [M+H]$^+$. IR (neat): $\nu$ 1695.55, 1581.98, 1466.99, 1388.02, 791.71 cm$^{-1}$.

OsL7. The characterization of this compound matched literature values. White solid (56%) $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.88 (s, 2H), 8.76 (d, $J = 3.8$ Hz, 2H), 8.70 (d, $J = 8.0$ Hz, 2H), 8.41 (s, 1H), 8.06 – 7.96 (m, 3H), 7.89 (td, $J = 7.8$, 1.9 Hz, 3H), 7.59 – 7.50 (m, 2H), 7.36 (ddd, $J = 7.5$, 4.8, 1.2 Hz, 2H). ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 156.4, 156.1, 150.4, 149.3, 137.0, 135.9, 133.7, 128.8, 128.7, 127.8, 126.9, 126.8, 126.6, 125.1, 124.0, 121.6, 119.2 ppm. MS (ASAP+): m/z = 360.1508 [M+H]$^+$; calculated m/z = 360.1501 [M+H]$^+$. IR (neat): $\nu$ 1582.97, 1396.92, 791.75, 739.67 cm$^{-1}$.

OsL14. The characterization of this compound matched literature values. White solid (44%) $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.75 – 8.69 (m, 2H), 8.62 (dt, $J = 7.9$, 1.1 Hz, 2H), 8.51 (s, 2H), 7.84 (td, $J = 7.8$, 1.8 Hz, 2H), 7.31 (ddd, $J = 7.5$, 4.8, 1.2 Hz, 2H), 1.48 (s, 9H). ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.3, 156.8, 155.5, 149.2, 136.9, 123.7, 121.5, 118.3, 35.5, 30.9 ppm. MS (ASAP+): m/z = 290.1662 [M+H]$^+$; calculated m/z = 290.1657 [M+H]$^+$. IR (neat): $\nu$ 2963.81, 1583.86, 1466.68, 1396.40, 1253.68, 792.03, 740.91, 649.50 cm$^{-1}$.

To a suspension of 2H-ligand (3.2 mmol) in acetone (15 mL), powdered KOH (16.0 mmol) was added. The mixture was stirred for 15 min at room temperature, followed by the addition of methyl iodide (16.0 mmol) with vigorous stirring. The reaction continued to stir for another 6 hours. The reaction mixture was poured into water. The precipitate was filtered and recrystallized from methanol to afford tan crystals.
The characterization of OsL11 matched literature values\textsuperscript{12}. Tan solid (88\%) \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 8.42 (d, J = 7.9 Hz, 2H), 8.04 (t, J = 7.9 Hz, 1H), 7.90 – 7.85 (m, 4H), 7.48 – 7.43 (m, 2H), 7.36 (ddt, J = 12.2, 7.1, 1.5 Hz, 4H), 4.24 (s, 6H). ppm. \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ 150.3, 149.7, 142.7, 138.2, 137.3, 125.4, 123.8, 123.0, 120.4, 110.0, 32.6 ppm. MS (ASAP\textsuperscript{+}): m/z = 340.1566 [M+H]\textsuperscript{+}; calculated m/z = 340.1562 [M+H]\textsuperscript{+}. IR (neat): ν 2208.46, 1569.85, 1419.28, 1327.23, 729.26 cm\textsuperscript{-1}.

Hydrazine hydrate (200 mmol, 20 equiv.) was added to a 25 mL oven-dried, argon-filled round bottom flask equipped with a magnetic stirring bar. While stirring, 2,6-difluoropyridine (10 mmol, 1 equiv.) was added cautiously. The reaction mixture was then heated to 80ºC for 24 h. While cooling, a yellow solid formed. Filtration of the resulting suspension provided a solid which was washed with isopropanol and diethyl ether. The material was carried forward to the next step without further purification.

To an oven dried flask was added one equivalent of bishydrazinepyridine, ketone (2 equiv.) and toluenesulfonic acid (2 mol\%). The flask was fitted with a Dean-Stark trap, condenser, and placed under N\textsubscript{2} and heated at 110ºC. The reaction was allowed to reflux for 12-24 h. After heating, the reaction was allowed to cool to room temperature, quenched with 1M NaOH, followed by saturated NaCl. The aqueous mixture was extracted three times with ethyl acetate (25-50 mL) and dried with Na\textsubscript{2}SO\textsubscript{4}. The crude mixture was more than 95% pure and was carried forward to the final step.

A 25.0 mL sealed tube containing 2-bromoacetophenone bis-hydrazine 7 2.07 mmol, 1.0 equiv.), CuI (0.138 mmol, 0.1 equiv.), 1,10-phenanthroline (0.26 mmol, 0.2 equiv.) and KOH (3.54 mmol, 1.71 equiv.) and 10 mL dioxane under nitrogen atmosphere was sealed and heated to reflux overnight. The reaction was cooled to room temperature and diluted with 50 mL of EtOAc. The mixture was washed once with water (100 mL) and once with sat. NaCl. The organic phase was dried with Na\textsubscript{2}SO\textsubscript{4} and the solvent was removed in vacuo to give pure 2,6-bis-(3'methylindazol-1-yl)pyridine 8 as a tan solid. The characterization of this compound matched literature values\textsuperscript{13}. OsL13 Tan solid (99\%) \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 8.68 (d, J = 8.5 Hz, 2H), 7.94 (t, J = 8.0 Hz, 1H), 7.78 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 7.9 Hz, 2H), 7.47 (t, J = 7.7 Hz, 2H), 7.29 (t, J = 7.5 Hz, 2H), 2.69 (s, 6H). ppm. \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ 152.4, 146.0, 140.5, 139.5, 128.0, 126.0, 122.1, 120.3, 115.0, 109.5, 12.3 ppm. MS (ASAP\textsuperscript{+}): m/z = 340.1565 [M+H]\textsuperscript{+}; calculated m/z = 340.1562 [M+H]\textsuperscript{+}. IR (neat): ν 1577.29, 1450.26, 1344.19, 1210.3, 1075.01, 733.87 cm\textsuperscript{-1}.

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In an over-dried pressure tube containing a stir-bar was added 2.5 equiv. ligand under open atmosphere. The tube was then pumped into the glovebox where 1 equiv. OsCl$_3$ hydrate was added followed by anhydrous ethylene glycol (0.075 M). The tube was firmly sealed and removed from the glovebox where it was heated at 230 °C in a sand bath. (Caution: all sealed tube reactions were placed behind a blast shield since pressure develops in the tube.) After 48 hours, the reaction was allowed to cool to 60°C. Then, open to air, 10 equiv. NH$_4$PF$_6$ was added to the flask followed by equal volume of distilled water. Over the course of 45 min, the dark solution formed a dark precipitate which was collected on filter paper, washed with water, methanol, DCM, and ether to yield pure catalyst. Note: the catalyst is slightly soluble in DCM so minimal DCM was used during washing.

Os8. Gray-purple solid (58%) $^1$H NMR (400 MHz, DMSO): δ 9.36 (s, 4H), 9.00 (d, $J$ = 8.2 Hz, 4H), 8.09 (s, 2H), 7.91 (t, $J$ = 7.9 Hz, 4H), 7.75 (d, $J$ = 3.5 Hz, 2H), 7.46 (d, $J$ = 5.7 Hz, 4H), 7.20 (t, $J$ = 6.7 Hz, 4H), 6.97 (s, 2H) ppm. $^{19}$F NMR (376 MHz, DMSO) δ -70.14 (d, $J$ = 711.5 Hz) ppm. $^{13}$C NMR (101 MHz, DMSO) δ 159.5, 154.7, 152.3, 149.6, 146.4, 137.8, 136.2, 128.0, 124.9, 116.1, 113.0, 112.3 ppm. MS (ESI, pos): $m/z$ = 935.1370 [Os(II)L$_2$+PF$_6$]$^+$; calculated $m/z$ = 935.1374 [Os(II)L$_2$+PF$_6$]$^+$. IR (neat): ν 1895.16, 1609.31, 1440.58, 1338.91, 1279.73, 823.09, 765.50, 555.29 cm$^{-1}$.

Os9. Gray-purple solid (43%) $^1$H NMR (400 MHz, DMSO): δ 9.50 (s, 4H), 9.03 (d, $J$ = 8.2 Hz, 4H), 8.76 (s, 2H), 8.32 (s, 2H), 7.96 (q, $J$ = 13.0, 8.6 Hz, 6H), 7.44 (d, $J$ = 5.7 Hz, 4H), 7.20 (s, 4H) ppm. $^{19}$F NMR (376 MHz, DMSO) δ -70.12 (d, $J$ = 711.8 Hz) ppm. $^{13}$C NMR (101 MHz, DMSO) δ 159.5, 154.7, 152.2, 149.6, 146.4, 137.8, 136.2, 128.0, 124.9, 116.1, 113.0, 112.3 ppm. MS (ESI, pos): $m/z$ = 967.0908 [Os(II)L$_2$+PF$_6$]$^+$; calculated $m/z$ = 967.0914 [Os(II)L$_2$+PF$_6$]$^+$. IR (neat): ν 1910.18, 1611.11, 1445.88, 1338.99, 1214.90, 813.47, 769.09, 555.38 cm$^{-1}$.

Os11. Red-purple solid (83%) $^1$H NMR (400 MHz, DMSO): δ 8.99 (d, $J$ = 6.4 Hz, 4H), 7.86 (bs, 3H), 7.69 (d, $J$ = 8.2 Hz, 2H), 7.37 (bs, 4H), 6.96 (t, $J$ = 7.7 Hz, 4H), 6.10 (d, $J$ = 8.1 Hz, 4H), 5.75 (bs, 1H), 4.66 (bs, 12H) ppm. $^{19}$F NMR (376 MHz, DMSO) δ -70.13 (d, $J$ = 711.3 Hz) ppm. $^{13}$C NMR (101 MHz, DMSO) δ 155.2, 148.4, 140.0, 134.8, 133.7, 125.5, 125.1, 122.8, 113.9, 113.3, 32.5 ppm. MS (ESI, pos): $m/z$ = 1015.2217 [Os(II)L$_2$+PF$_6$]$^+$; calculated $m/z$ = 1015.2227 [Os(II)L$_2$+PF$_6$]$^+$. IR (neat): ν 2048.76, 1980.72, 1927.22, 1600.35, 1509.83, 831.02, 555.88 cm$^{-1}$.
Os13. Red-orange solid (85%) $^1$H NMR (400 MHz, DMSO): δ 8.82 (d, J = 8.5 Hz, 4H), 8.70 (d, J = 8.7 Hz, 4H), 8.47 (t, J = 8.5 Hz, 2H), 7.80 – 7.69 (m, 9H), 7.52 – 7.45 (m, 4H), 1.94 (s, 12H) ppm. $^{19}$F NMR (376 MHz, DMSO) δ -70.14 (d, J = 711.2 Hz) ppm. $^{13}$C NMR (101 MHz, DMSO) δ 154.1, 149.4, 139.9, 131.2, 128.1, 124.4, 123.9, 121.9, 110.8, 105.3, 9.0 ppm. MS (ESI, pos): m/z = 1015.2209 [Os(II)L$_2$+PF$_6$]$^+$; calculated m/z = 1015.2227 [Os(II)L$_2$+PF$_6$]$^+$. IR (neat): ν 2060.36, 1995.98, 1928.80, 1651.87, 1614.43, 1449.34, 1472.67, 829.04, 739.05, 555.15 cm$^{-1}$.

Os6. Black solid (82%) $^1$H NMR (400 MHz, DMSO): δ 9.59 (s, 4H), 9.15 (d, J = 8.1 Hz, 4H), 8.55 (d, J = 8.0 Hz, 4H), 8.11 (d, J = 8.0 Hz, 4H), 8.00 – 7.89 (m, 8H), 7.59 (t, J = 7.6 Hz, 4H), 7.47 (d, J = 5.8 Hz, 6H), 7.24 (t, J = 6.6 Hz, 4H) ppm. $^{19}$F NMR (376 MHz, DMSO) δ -70.14 (d, J = 711.3 Hz) ppm. $^{13}$C NMR (101 MHz, DMSO) δ 159.8, 154.7, 152.2, 145.6, 141.8, 138.9, 137.8, 134.3, 129.1, 128.6, 128.2, 128.0, 127.2, 126.9, 125.0, 119.5 ppm. MS (ESI, pos): m/z = 1107.2417 [Os(II)L$_2$+PF$_6$]$^+$; calculated m/z = 1107.2418 [Os(II)L$_2$+PF$_6$]$^+$.

Os7. Dark brown solid (41%) $^1$H NMR (400 MHz, DMSO): δ 9.67 (bs, 4H), 9.16 (bs, 4H), 9.01 (bs, 2H), 8.58 (bs, 2H), 8.41 (bs, 2H), 8.16 (bs, 4H), 7.97 (bs, 4H), 7.70 (d, J = 13.3 Hz, 4H), 7.50 (bs, 4H), 7.25 (bs, 4H) ppm. $^{19}$F NMR (376 MHz, DMSO) δ -70.15 (d, J = 711.2 Hz) ppm. $^{13}$C NMR (101 MHz, DMSO) δ 159.8, 154.7, 152.3, 137.8, 134.6, 132.5, 128.8, 128.0, 127.7, 127.0, 124.4, 119.9 ppm. MS (ESI, pos): m/z = 1055.2096 [Os(II)L$_2$+PF$_6$]$^+$; calculated m/z = 1055.2106 [Os(II)L$_2$+PF$_6$]$^+$.

Os10. Gray-purple solid (20%) $^1$H NMR (400 MHz, DMSO): δ 9.49 (bs, 2H), 8.99 (d, J = 7.4 Hz, 2H), 8.66 (bs, 4H), 8.45 (bs, 2H), 7.90 (bs, 6H), 7.79 (bs, 2H), 7.67 – 7.49 (m, 4H), 7.38 (m, 4H), 7.26 (bs, 2H), 2.62 (bs, 12H) ppm. $^{19}$F NMR (376 MHz, DMSO) δ -70.16 (d, J = 711.2 Hz) ppm. $^{13}$C NMR (101 MHz, DMSO) δ 157.7, 155.8, 154.4, 150.0, 137.3, 134.4, 130.1, 128.1, 126.9, 124.4, 118.0, 117.9, 24.3 ppm. MS (ESI, pos): m/z = 1014.2146 [Os(II)L$_2$+PF$_6$]$^+$; calculated m/z = 1014.2148 [Os(II)L$_2$+PF$_6$]$^+$.

Os9. Green-brown solid (89%) $^1$H NMR (400 MHz, DMSO): δ 9.22 (bs, 4H), 8.91 (bs, 4H), 8.27 (bs, 4H), 7.98 (bs, 4H), 7.76 (bs, 4H), 7.62 (bs, 2H), 7.36 (bs, 4H) ppm. $^{19}$F NMR (376 MHz, DMSO) δ -70.16 (d, J = 711.3 Hz) ppm. $^{13}$C NMR (101 MHz, DMSO) δ 157.6, 160.9, 156.9, 153.2, 146.9, 135.2, 130.5, 129.2, 127.5, 123.1, 122.9 ppm. MS (ESI, pos): m/z = 959.1609 [Os(II)L$_2$+PF$_6$]$^+$; calculated

m/z = 959.1600 [Os(II)L₂+PF₆]⁺. IR (neat): ν 1991.67, 1578.48, 1390.48, 811.01, 554.66 cm⁻¹.

Os₁₆. Black solid (48%) ¹H NMR (400 MHz, DMSO): δ 9.52 (s, 4H), 8.93 (dd, J = 4.7, 1.9 Hz, 4H), 8.90 (s, 4H), 8.35 (s, 2H), 7.97 (dd, J = 5.9, 1.9 Hz, 4H), 7.39 (dd, J = 5.9, 4.7 Hz, 4H ppm. ¹⁷F NMR (376 MHz, DMSO) δ -60.99, -70.18 (d, J = 711.5 Hz ppm. ¹³C NMR (101 MHz, DMSO) δ 167.4, 160.8, 157.1, 153.1, 144.3, 138.1, 131.2 (q, J =33.2 Hz), 129.4, 124.7, 124.6, 123.2, 122.0 ppm. MS (ESI, pos): m/z = 1231.1085 [Os(II)L₂+PF₆]⁺; calculated m/z = 1231.1096 [Os(II)L₂+PF₆]⁺. IR (neat): ν 1997.21, 1622.91, 1591.34, 1393.99, 1016.29, 811.35, 693.14, 554.77 cm⁻¹.

Os₁. Brown solid (85%). ¹H NMR (400 MHz, DMSO): δ 9.17 (s, 4H), 8.88 (d, J = 2.9 Hz, 4H), 8.24 (d, J = 8.2 Hz, 4H), 7.99 (d, J = 5.8 Hz, 4H), 7.36 – 7.25 (m, 8H), 3.94 (s, 6H ppm. ¹⁷F NMR (376 MHz, DMSO) δ -70.17 (d, J = 711.3 Hz ppm. ¹³C NMR (101 MHz, DMSO) δ 167.7, 161.4, 160.9, 156.8, 153.1, 146.6, 129.3, 127.2, 123.1, 122.0, 115.0, 55.5 ppm. MS (ESI, pos): m/z = 1019.1807 [Os(II)L₂+PF₆]⁺; calculated m/z = 1019.1812 [Os(II)L₂+PF₆]⁺. IR (neat): ν 1981.29, 1541.34, 1578.49, 1398.47, 1239.25, 1100.50, 800.25, 553.39 cm⁻¹.

Os₁₅. Black solid (80%). ¹H NMR (400 MHz, DMSO): δ 9.46 (s, 4H), 9.09 (d, J = 8.2 Hz, 4H), 8.40 (d, J = 8.9 Hz, 4H), 7.97 – 7.89 (m, 4H), 7.43 (d, J = 5.5 Hz, 4H), 7.32 (d, J = 8.9 Hz, 4H), 7.21 (t, J = 7.3 Hz, 4H), 3.97 (s, 6H ppm. ¹⁷F NMR (376 MHz, DMSO) δ -70.13 (d, J = 711.3 Hz ppm. ¹³C NMR (101 MHz, DMSO) δ 161.3, 159.9, 154.7, 152.1, 146.0, 137.6, 129.5, 127.9, 127.6, 124.9, 118.9, 114.5, 55.5 ppm. MS (ESI, pos): m/z = 1015.2006 [Os(II)L₂+PF₆]⁺; calculated m/z = 1015.2003 [Os(II)L₂+PF₆]⁺. IR (neat): ν 1897.19, 1634.34, 1488.12, 1454.39, 1239.43, 1050.54, 1027.31, 824.09, 760.21, 559.30 cm⁻¹.

Os₁₇. Black solid (56%). ¹H NMR (400 MHz, DMSO): δ 9.06 (s, 4H), 8.84 (d, J = 8.2 Hz, 4H), 7.90 – 7.82 (m, 4H), 7.27 (d, J = 7.3 Hz, 8H), 6.58 (s, 4H), 3.96 (s, 6H), 3.93 (s, 12H ppm. ¹⁷F NMR (376 MHz, DMSO) δ -70.16 (d, J = 711.2 Hz ppm. ¹³C NMR (101 MHz, DMSO) δ 162.3, 159.8, 158.7, 153.5, 151.7, 141.7, 137.8, 128.0, 125.0, 124.6, 106.7, 91.3, 56.3, 55.7 ppm. MS (ESI, pos): m/z = 1135.2412 [Os(II)L₂+PF₆]⁺; calculated m/z = 1135.2426 [Os(II)L₂+PF₆]⁺. IR (neat): ν 1921.23, 1431.29, 965.22, 831.89, 749.20, 559.18 cm⁻¹.

Os₃. The characterization of this compound matched literature values. Dark green solid (56%) ¹H NMR (400 MHz, DMSO): δ 9.42 (s, 4H), 9.00 (d, J = 8.1 Hz, 4H), 8.31 (d, J = 8.2 Hz, 4H), 7.95 (d, J = 8.2 Hz, 4H), 7.90 (t, J = 7.8 Hz, 4H), 7.40 (d, J = 5.6 Hz, 4H), 7.20 (t, J = 6.8 Hz, 4H). ppm. ¹⁷F NMR (376 MHz, DMSO) δ -70.11 (d, J = 711.4 Hz ppm. ¹³C NMR (101 MHz, DMSO) δ 159.9, 154.9, 152.4, 145.3, 138.2, 135.1, 132.4, 130.3, 128.3, 125.2, 124.3, 120.0 ppm. MS (ESI, pos): m/z = 1110.9956 [Os(II)L₂+PF₆]⁺; calculated m/z = 1110.9966 [Os(II)L₂+PF₆]⁺. IR (neat): ν 1801.99, 1601.62, 1486.91, 1241.89, 1050.97, 841.27, 556.41 cm⁻¹.

S10
Os4. The characterization of this compound matched literature values.\(^{15}\) Black solid (75%)\(^1\)H NMR (400 MHz, DMSO): \(\delta\) 9.02 (d, \(J = 7.9\) Hz, 1H), 8.73 (d, \(J = 8.1\) Hz, 1H), 7.99 (t, \(J = 7.9\) Hz, 0H), 7.84 (t, \(J = 7.6\) Hz, 1H), 7.36 – 7.12 (m, 2H) ppm. \(^{19}\)F NMR (376 MHz, DMSO) \(\delta\) -70.10 (d, \(J = 711.3\) Hz) ppm. \(^{13}\)C NMR (101 MHz, DMSO) \(\delta\) 159.8, 154.6, 152.2, 138.2, 135.4, 128.2, 124.9, 123.0 ppm. MS (ESI, pos): m/z = 803.1165 [Os(II)L\(_2\)+PF\(_6\)]\(^+\); calculated m/z = 803.1164 [Os(II)L\(_2\)+PF\(_6\)]\(^+\). IR (neat): \(\nu\) 1897.13, 1602.30, 1448.58, 1337.99, 1282.03, 824.09, 761.59, 555.13 cm\(^{-1}\).

Os14. Black solid (25%)\(^1\)H NMR (400 MHz, CD\(_3\)CN): \(\delta\) 8.75 (s, 4H), 8.56 (d, \(J = 8.2\) Hz, 4H), 7.76 (td, \(J = 7.9, 1.5\) Hz, 4H), 7.20 (d, \(J = 5.7\) Hz, 4H), 7.07 (ddd, \(J = 7.3, 5.7, 1.3\) Hz, 4H), 1.71 (s, 18H) ppm. \(^{19}\)F NMR (376 MHz, CD\(_3\)CN) \(\delta\) -72.78 (d, \(J = 711.3\) Hz) ppm. \(^{13}\)C NMR (101 MHz, CD\(_3\)CN) \(\delta\) 161.3, 161.1, 155.6, 153.3, 138.5, 128.5, 125.4, 120.8, 118.3, 36.6, 31.5 ppm. MS (ESI, pos): m/z = 915.2413 [Os(II)L\(_2\)+PF\(_6\)]\(^+\); calculated m/z = 915.2416 [Os(II)L\(_2\)+PF\(_6\)]\(^+\). IR (neat): \(\nu\) 1888.47, 1371.39, 1057.91, 959.02, 835.79, 555.26 cm\(^{-1}\).

In an over-dried pressure tube containing a stir-bar was added 3.5 equiv. ligand under open atmosphere. The tube was then pumped into the glovebox where 1 equiv. OsCl\(_3\) hydrate was added followed by anhydrous ethylene glycol (0.075 M). The tube was firmly sealed and removed from the glovebox where it was heated at 230 °C in a sand bath. (Caution: all sealed tube reactions were placed behind a blast shield since pressure develops in the tube.) After 48 hours, the reaction was allowed to cool to 60°C. Then, 10 equiv. NH\(_4\)PF\(_6\) was added to the flask followed by equal volume of distilled water. Over the course of 45 min, the dark solution formed a dark precipitate which was collected on filter paper, washed with water and ether to yield pure catalyst.

Os5. The characterization of this compound matched literature values.\(^{16}\) Dark green solid (45%)\(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) 8.32 (s, 6H), 8.18 (s, 6H), 7.99 (s, 6H), 7.66 (s, 6H) ppm. \(^{19}\)F NMR (376 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) -72.71 (d, \(J = 711.3\) Hz) ppm. \(^{13}\)C NMR (101 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 152.9, 150.4, 137.1, 131.7, 128.9, 127.1 ppm. MS (ESI, pos): m/z = 877.1309 [Os(II)L\(_3\)+PF\(_6\)]\(^+\); calculated m/z = 877.1321 [Os(II)L\(_3\)+PF\(_6\)]\(^+\). IR (neat): \(\nu\) 1611.23, 1499.10, 1391.23, 811.87, 541.23 cm\(^{-1}\).
Os12. The characterization of this compound matched literature values\textsuperscript{17}. Dark green solid (75\%)\textsuperscript{1H NMR} (400 MHz, DMSO): $\delta$ 8.74 (d, $J$ = 8.2 Hz, 6H), 7.93 (td, $J$ = 7.9, 1.4 Hz, 6H), 7.63 (d, $J$ = 6.2 Hz, 6H), 7.41 (ddd, $J$ = 7.3, 5.7, 1.3 Hz, 6H) ppm. \textsuperscript{19F NMR} (376 MHz, DMSO) $\delta$ -70.10 (d, $J$ = 711.4 Hz) ppm. \textsuperscript{13C NMR} (101 MHz, DMSO) $\delta$ 158.7, 150.5, 137.5, 128.6, 124.9 ppm. MS (ESI, pos): m/z = 805.1326 [Os(II)L\textsubscript{3}+PF\textsubscript{6}]\textsuperscript{+}; calculated m/z = 805.1320 [Os(II)L\textsubscript{2}+PF\textsubscript{6}]\textsuperscript{+}. IR (neat): $\nu$ 1601.33, 1469.29, 1367.89, 811.21, 551.39 cm\textsuperscript{-1}.

General Procedures

To a 1 dram vial equipped with a stir bar was added Umemoto’s reagent (1.5 equiv.) The vial was pumped into the glovebox and dry chloroform (0.2 M), styrene (0.31 mmol), Os(bptpy)$_2$(PF\textsubscript{6})\textsubscript{2} (0.01 mol\%), from stock soln' in MeCN, and trimethylsilyl chloride (2 equiv.) were added. The vial was equipped with a screw-on cap, removed from the glovebox, and placed in front of a 740 nm lamp for 2 hours at 22°C. The reaction was concentrated down and the residue was loaded onto a silica column and eluted with an ethyl acetate:hexane gradient from 0-20%. The product matched literature values\textsuperscript{18}.\textsuperscript{1H NMR} (400 MHz, CDCl\textsubscript{3}): $\delta$ 7.42 – 7.38 (m, 2H), 7.34 – 7.30 (m, 2H), 5.11 (dd, $J$ = 7.9, 6.0 Hz, 1H), 3.08 – 2.80 (m, 2H), 1.32 (s, 9H) ppm. \textsuperscript{19F NMR} (376 MHz, CDCl\textsubscript{3}) $\delta$ -64.09 (t, $J$ = 9.9 Hz). \textsuperscript{13C NMR} (101 MHz, CDCl\textsubscript{3}) $\delta$ 152.4, 136.9, 126.6, 123.3 (q, $J$ = 221.8 Hz), 54.8 (q, $J$ = 3.6 Hz), 43.9 (q, $J$ = 28.4 Hz), 34.8, 31.4 ppm.

To a 1 dram vial equipped with a stir bar was added CuCl\textsubscript{2} (0.02 equiv.). The vial was pumped into the glovebox and dry acetonitrile (0.2 M), PMDETA (4 mol\%), Os(bptpy)$_2$(PF\textsubscript{6})\textsubscript{2} (0.05 mol\%, from stock soln' in MeCN) phenylacetylene (0.31 mmol), and benzyl azide (2 equiv.) were added. The vial was equipped with a screw-on cap, removed from the glovebox, and placed in front of a 740 nm lamp for 4 hours at 22°C. The reaction was concentrated down and the residue was loaded onto a silica column and eluted with an ethyl acetate:hexane gradient from 0-20%. The product matched literature values\textsuperscript{19}.\textsuperscript{1H NMR} (400 MHz, CDCl\textsubscript{3}): $\delta$ 7.83 – 7.77 (m, 2H), 7.67 (s, 1H), 7.43 – 7.27 (m, 8H), 5.55 (s, 2H) ppm. \textsuperscript{13C NMR} (101 MHz, CDCl\textsubscript{3}) $\delta$ 148.2, 134.8, 130.6, 129.2, 128.9, 128.8, 128.2, 128.1, 125.8, 119.6, 54.2 ppm.
To a 1 dram vial equipped with a stir bar was added initiator (0.5 mol%). The vial was pumped into the glovebox and dry DMSO (0.2 M), methylacrylate (0.31 mmol), and Os(bptpy)$_2$(PF$_6$)$_2$ (0.1 mol%, from stock soln' in MeCN) were added. The vial was equipped with a screw-on cap, removed from the glovebox, and placed in front of a 740 nm lamp for 5 hours at 22°C. After, the reaction was dripped into excess methanol and the polymer was precipitated. The product matched literature values and a proton and GPC trace are provided.20
To a 1 dram vial equipped with a stir bar was added initiator (0.5 mol%). The vial was pumped into the glovebox and epoxide (1 mmol), and Os(bptpy)$_2$(PF$_6$)$_2$ (0.1 mol%, from stock soln’ in MeCN) were added. The vial was equipped with a screw-on cap, removed from the glovebox, and placed in front of a 740 nm lamp for 4 hours at 22°C. After, the reaction was dripped into excess methanol and the polymer was precipitated. The product matched literature values and a proton and GPC trace are provided$^{21}$. 
To a 1 dram vial equipped with a stir bar was added initiator (0.5 mol%). The vial was pumped into the glovebox and MeCN (0.8M), styrene (1 mmol), and Os(bptpy)₂(PF₆)₂ (0.1 mol%, from stock soln' in MeCN) were added. The vial was equipped with a screw-on cap, removed from the glovebox, and placed in front of a 740 nm lamp for 24 hours at 22°C. After, the reaction was dripped into excess methanol and the polymer was precipitated. The product matched literature values and a proton and GPC trace are provided²².

To a 1 dram vial equipped with a stir bar was added furfural (0.40 mmol), dry methanol(d₄) (0.5 M), and Os(bptpy)₂(PF₆)₂ (0.01 mol%, from stock soln' in MeCN). The vial was flushed with oxygen gas for 5 minutes, capped, and placed in front of a 740 nm lamp for 4 hours at 22 °C under an O₂ atmosphere. The product yield (¹H NMR) was calculated using 0.20 mmol of an
internal standard (HMDS, hexamethyl-disiloxane). The proton and carbon NMRs of the crude reactions are provided as the product was not isolated. $^1$H NMR (400 MHz, MeOD-$d_4$) δ 7.38 (dd, J = 5.8, 1.1 Hz, 1H), 6.21 (dd, J = 5.7, 1.2 Hz, 1H), 6.18 (s, 1H). $^{13}$C NMR (101 MHz, MeOD-$d_4$) δ 173.3, 154.7, 124.6, 100.7.

To a 1.5 dram vial equipped with a stir bar was added methyl 3-((2-bromo-2,2-difluoroethoxy)sulfonyl)-thiophene-2-carboxylate (0.40 mmol). The vial was pumped into the glovebox and dry DMSO (0.14 M), NBu$_3$ (1.50 equiv), Os(bptpy)$_2$(PF$_6$)$_2$ (0.01 mol%, from stock soln' in MeCN), and formic acid (1.50 equiv) were added. The vial was equipped with a screw-on cap, removed from the glovebox, and placed in front of a 740 nm lamp for 12 hours at 22°C. After, the reaction was concentrated down and the residue was loaded onto a silica column and eluted with an ethyl acetate:hexane gradient from 10-50%. The product matched literature values$^2$. $^1$H NMR (376 MHz, CDCl$_3$): δ 7.51 (d, J = 5.2 Hz, 1H), 7.28 (d, J = 5.2 Hz, 1H), 4.23 (t, J = 13.6 Hz, 2H), 3.89 (s, 3H), 2.77 (s, 1H) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -99.05 (t, J = 13.6 Hz) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 161.7, 140.6 (t, J = 28.8 Hz), 130.9 (t, J = 4.4 Hz), 130.7, 128.8 (t, J = 6.8 Hz), 119.8 (t, J = 244.6 Hz), 65.6 (t, J = 31.3 Hz), 52.9 ppm.

To a 1.5 dram vial equipped with a stir bar was added 4-methoxyphenylboronic acid (0.40 mmol, dry methanol (0.5 M), Os(bptpy)$_2$(PF$_6$)$_2$ (0.1 mol%, from stock soln' in MeCN), and DIPEA (2 equiv.). The vial was flushed with oxygen gas for 90 seconds, capped, and placed in front of a 740 nm lamp for 24 hours at 22°C under an O$_2$ atmosphere. The reaction was concentrated down and the residue was loaded onto a silica column and eluted with an ethyl acetate:hexane gradient from 10-30%. The product matched literature values$^2$. $^1$H NMR (400 MHz, CDCl$_3$): δ 6.83 – 6.73 (m, 4H), 4.75 (s, 1H), 3.77 (s, 3H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 153.9, 149.6, 116.2, 115.0, 56.0 ppm.
2H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 175.7, 139.8, 139.3, 136.5, 131.0, 128.7, 128.5, 128.2, 127.7, 50.3, 31.3, 19.1 ppm.

Under ambient conditions, an oven dried 1-dram vial was charged with a stir bar. Diyne (0.3 mmol, 1.0 equiv.) and cobalt pre-catalyst (0.015 mmol, 0.05 equiv.) were weighed directly into the vial. The vial was fitted with a teflon cap, pumped into the glove box and charged with degassed DCE (0.1 M), alkyne coupling partner (0.6 mmol, 2.0 equiv), diisopropylamine (DIPEA – 0.09 mmol, 0.3 equiv), and Os(tpy)$_2$(PF$_6$)$_2$ (0.01 mol% from stock soln’ in MeCN). The vial was then firmly sealed, removed from the glove box, and placed in front of the desired light source. After completion (24 hours), celite was added to the reaction and the solvent was removed in vacuo. After the celite was loaded onto a column and eluted with an ethyl acetate:hexane gradient from 0-20%. The product matched literature values.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.55 (dd, $J$ = 7.6, 2.0 Hz, 2H), 7.46 – 7.37 (m, 4H), 7.36 – 7.30 (m, 1H), 7.26 (d, $J$ = 7.8 Hz, 1H), 3.57 (d, $J$ = 7.9 Hz, 4H), 2.49 (q, $J$ = 7.2 Hz, 4H), 1.08 (t, $J$ = 7.2 Hz, 6H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 207.9, 141.3, 140.7, 140.5, 139.2, 128.8, 127.3, 127.2, 126.3, 124.8, 123.3, 74.8, 37.9, 37.6, 32.4, 8.4 ppm.

To a 1 dram vial equipped with a stir bar was added $N$-vinyl carbazole (0.80 mmol, 1 equiv.). The vial was pumped into the glovebox and dry MeCN (0.40 M), propylene oxide (3.0 equiv mmol), and Os(bpm-pmp-py)$_2$(PF$_6$)$_2$ (0.1 mol%, from stock soln’ in MeCN) were added. The vial was equipped with a screw-on cap, removed from the glovebox, and placed in front of a 660 nm lamp for 36 hours at 22°C. After, the reaction was concentrated down and the residue was loaded onto a silica column and eluted with an ethyl acetate:hexane gradient from 0-30%. The product matched literature values. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.09 (d, $J$ = 7.7 Hz, 4H), 7.59 (d, $J$ = 8.3 Hz, 4H), 7.42 (t, $J$ = 7.2 Hz, 4H), 7.24 (t, $J$ = 6.9 Hz, 4H), 6.36 – 6.27 (m, 2H), 3.12 (dtt, $J$ = 14.0, 9.4, 5.1 Hz, 2H), 2.84 – 2.68 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 140.1, 125.9, 123.7, 120.6, 119.5, 109.8, 54.6, 21.0.

To a 2 dram vial equipped with a stir bar was added caffeine (0.40 mmol). The vial was pumped into the glovebox and dry acetonitrile/TFA (1:1, 0.1 M), tert-butylperacetate (50 wt. % in mineral spirits, 3.0 equiv), Os(bpmppy)$_2$(PF$_6$)$_2$ (0.1 mol%, from stock soln’ in MeCN) were added. The vial was equipped with a screw-on cap, removed from the glovebox, and placed in front of a 740 nm lamp for 12 hours at 22°C. After, the reaction was concentrated down and the residue was loaded onto a silica column and eluted with a methanol:DCM gradient from 0-1%. The isolated product was then triturated with Et$_2$O (5 mL x 3) to remove nonpolar impurities.
The product matched literature values.\textsuperscript{26} \textbf{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}): \(\delta\) 3.89 (s, 1H), 3.53 (s, 1H), 3.37 (s, 1H), 2.44 (s, 1H) ppm. \textbf{\textsuperscript{13}C NMR} (101 MHz, CDCl\textsubscript{3}) \(\delta\) 155.3, 151.8, 150.8, 148.0, 107.5, 32.0, 29.8, 28.0, 13.2 ppm.

To a 1 dram vial equipped with a stir bar was added DABCO (2.0 equiv.). The vial was pumped into the glovebox and NiBr\textsubscript{2}(glyme) (5 mol%), dry DMA (0.4 M), aryl bromide (0.31 mmol), pyrrolidine (3 equiv.), and Os(phen),(PF\textsubscript{6})\textsubscript{2} (0.1 mol%, from stock soln' in MeCN) were added. The vial was equipped with a screw-on cap, removed from the glovebox, and placed in front of a 660 nm lamp for 15 hours at 22°C. After, the reaction was concentrated down and the residue was loaded onto a silica column and eluted with an ethyl acetate:hexane gradient from 0-20%. The product matched literature values.\textsuperscript{27} \textbf{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}): \(\delta\) 7.44 (d, \(J = 8.2\) Hz, 1H), 6.55 (d, \(J = 6.5\) Hz, 1H), 3.37 – 3.26 (m, 2H), 2.08 – 1.97 (m, 3H) ppm. \textbf{\textsuperscript{19}F NMR} (376 MHz, CDCl\textsubscript{3}) \(\delta\) -60.61 ppm. \textbf{\textsuperscript{13}C NMR} (101 MHz, CDCl\textsubscript{3}) \(\delta\) 149.9, 129.5, 126.9, 126.5 (q, \(J = 3.7\) Hz), 125.5 (q, \(J = 270.0\) Hz), 116.8 (q, \(J = 32.5\) Hz), 111.0, 47.7, 25.6 ppm.

To a 1 dram vial equipped with a stir bar was added the N-oxide derivative (0.44 mmol, 1.4 equiv.), Os(tpy),(PF\textsubscript{6})\textsubscript{2} (0.1 mol%, from stock soln' in MeCN), and substrate (0.31 mmol) under argon/nitrogen atmosphere. The combined materials were then dissolved in dry MeCN (1 ml) and stirred briefly (~2 minutes). Trifluoroacetic anhydride (0.37 mmol, 1.2 equiv.) was then added to the resulting solution. The vial was equipped with a screw-on cap and placed in front of a 740 nm lamp for 24 hours at 22°C. The reaction was then quenched with water, extracted with DCM, and concentrated down. After, the residue was loaded onto a silica column and eluted with an ethyl acetate:hexane gradient from 0-40%. The product matched literature values.\textsuperscript{28} For scale up or \textit{in situ} monitoring, the yield was determined by NMR using DCE or fluorobenzene as internal standard. \textbf{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}): \(\delta\) 7.72 (d, \(J = 7.1\) Hz, 1H), 7.52 (d, \(J = 8.9\) Hz, 1H), 6.27 – 6.14 (m, 1H), 3.58 (s, 3H) ppm. \textbf{\textsuperscript{19}F NMR} (376 MHz, CDCl\textsubscript{3}) \(\delta\) -65.16 ppm. \textbf{\textsuperscript{13}C NMR} (101 MHz, CDCl\textsubscript{3}) \(\delta\) 159.0, 142.4, 138.9 (q, \(J = 5.1\) Hz), 122.9 (q, \(J = 271.6\) Hz), 120.5 (q, \(J = 30.8\) Hz), 104.0, 37.9 ppm.
**Fig. S1.** The reaction was monitored by NMR to reveal that the 420 nm light starts the reaction faster, but soon slows. The 660 nm light starts the reaction slower since less light is absorbed by the reaction due to a ~10 fold decrease in extinction coefficient; however, the overall yield remains higher. Experimental procedure adapted from Lehnerr *et al.* 29
Fig. S2. The Os3 was stressed under acidic and basic conditions to determine the stability of the catalyst. The acidic conditions are DMSO:6M HCl 1:1 (10^{-4} M), under O\textsubscript{2}, with 740 nm light irradiation for 16h. The basic conditions are DMSO:6M NaOH 1:1 (10^{-4} M), under O\textsubscript{2}, with 740 nm light irradiation for 16h. As seen by UV/Vis, there is no decomposition of the catalyst under acidic or basic conditions. A concern that we considered is the generation of OsO\textsubscript{4} under reaction conditions, but we have no evidence to support that even under highly stressful conditions.
| Catalyst                              | E_{ox} V | E_{red} V | T (eV) | λ_{em} (nm) | E'_{ox} V | E'_{red} V | T_1 (kcal/mol) |
|--------------------------------------|----------|-----------|--------|-------------|-----------|-----------|----------------|
| Os3 - Os(4'(4-BrPh)-2,2':6',2''-tpy)2(PF_6)_2 | 1.077    | -0.821    | 1.75   | 742.5       | -0.673    | 0.929     | 40.4           |
| Os6 - Os(4'(1,1'-bPh)-2,2':6',2''-tpy)2(PF_6)_2 | 1.03     | -0.866    | 1.75   | 744         | -0.72     | 0.884     | 40.4           |
| Os7 - Os(4'(Np)-2,2':6',2''-tpy)2(PF_6)_2     | 1.05     | -0.95     | 1.74   | 744.5       | -0.69     | 0.79      | 40.1           |
| Os8 - Os(4'(3-Fu)-2,2':6',2''-tpy)2(PF_6)_2   | 1.058    | -0.964    | 1.72   | 762.5       | -0.662    | 0.756     | 39.7           |
| Os9 - Os(4'(3-T)-2,2':6',2''-tpy)2(PF_6)_2    | 1.024    | -0.83     | 1.75   | 745.5       | -0.726    | 0.92      | 40.4           |
| Os10 - Os(s6,s6-dMe-4-Ph-2,2':6',2''-tpy)2(PF_6)_2 | 1.037    | -0.79     | 1.69   | 748.5       | -0.653    | 0.9       | 39             |
| Os2 - Os(4'-ppy-2,6-dpm)2(PF_6)_2             | 1.247    | -0.765    | 1.77   | 737.5       | -0.523    | 1.005     | 40.8           |
| Os4 - Os(tpy)2(PF_6)_2                     | 0.98     | -1.2      | 1.77   | 730         | -0.79     | 0.57      | 40.8           |
| Os11 - Os(2,6-bis(1-Me-1H-benzim)py)2(PF_6)_2 | 0.812    | -0.94     | 1.71   | 756         | -0.898    | 0.77      | 39.4           |
| Os12 - Os(bpy)2(PF_6)_2                    | 0.83     | -1.37     | 1.75   | 707         | -0.92     | 0.38      | 40.4           |
| Os5 - Os(phen)2(PF_6)_2                    | 0.9      | -1.38     | 1.8    | 690         | -0.9      | 0.42      | 41.5           |
| Os13 - Os(2,6-(3-Me-2H-Indz)py)2(PF_6)_2    | 1.25     | -1.3      | 1.96   | 676         | -0.71     | 0.66      | 45.2           |
| Os14 - Os(4'-(tBu)-2,2':6',2''-tpy)2(PF_6)_2 | 1.11     | -1.01     | 1.8    | 715         | -0.69     | 0.79      | 41.5           |
| Os15 - Os(4'(4-MeOPh)-2,2':6',2''-tpy)2(PF_6)_2 | 1.18     | -0.90     | 1.76   | 734.0       | -0.580    | 0.86      | 40.7           |
| Os1 - Os(4-pMeOppy-2,6-dpm)2(PF_6)_2        | 1.37     | -0.59     | 1.79   | 731.0       | -0.420    | 1.20      | 41.3           |
| Os16 - Os(4-dCF3ppy-2,6-dpm)2(PF_6)_2       | 1.54     | -0.54     | 1.78   | 742.0       | -0.240    | 1.24      | 41.0           |
| Os17 - Os(4'(2,4,6-MeOPh)-2,2':6',2''-tpy)2(PF_6)_2 | 1.14     | -0.97     | 1.79   | 725.0       | -0.650    | 0.82      | 41.3           |

**Table. S1.** A library of catalysts have been prepared and their characterization data are summarized in the table. Cyclic voltammetry was performed in acetonitrile vs. Ag/AgCl. All oxidations are reversible, all reductions appear quasi-reversible. λ_{em} energies are the maximum peak intensity for measured fluorescence spectra. T_1 energies are estimated by the point of intersection between normalized absorption and emission spectra.
**Fig. S3.** The mechanism of Stephenson’s trifluoromethylation is shown for reference. The charge transfer complexes absorb blue light which can be seen in Stephenson’s research. Prior to scale-up, we noted this secondary electron donor-acceptor (EDA) mechanism in which blue-light excitation of the EDA complex initiates trifluoromethyl radical formation and decreases light penetration throughout the solution. However, this charge transfer complex is not sensitized by NIR light, thus limiting competitive light absorption for the transition metal photocatalyst.
Fig. S4. Os3 was oxidized with CAN and the spectra of the resulting Os(III) species is shown. There are new ligand-to-metal-charge-transfer bands formed\textsuperscript{30}. The Os(III) complex competes for light absorption under blue light conditions.
**Fig. S5.** Analysis of theoretical light penetration into trifluoromethylation run at 0.2M showing NIR penetrates much further than blue light into solution.
Fig. S6. There is a trend when monitoring yield against vessel cross-sectional distance, surface area, and volume. We are currently investigating these effects. Note: lowering Ru loading below 0.1 mol% to match the extinction coefficient of Os4 results in decreases in yield.
Fig. S7. Side-by-side comparison of reaction conditions in this work and published conditions\textsuperscript{2,3,18,19,20,23,24,25,26,27}. The substrates chosen are representative of the published transformations.
Fig. S8 The plot describes how the number of lamps per reaction compares to reaction volume as the reaction is scaled up. On 1 mole scale (2500 mL), we used 8 lamps meaning there are 312 mL solution per lamp. On 10 mmol scale (25 mL), we used 2 lamps meaning there are 12.5 mL solution per lamp. If we wanted to to achieve 12.5 mL solution /lamp on 2500 mL scale, we require 200 lamps.
NMR Spectra
C_{21}H_{21}F_3N_3
Exact Mass: 447.09
C_{22}H_{13}N_{3}O
Exact Mass: 339.14
C_{19}H_{12}N_{2}O

Exact Mass: 299.11
$\text{C}_{52}\text{H}_{64}\text{F}_{12}\text{N}_{20}\text{OsP}_{3}$

Exact Mass: 1160.19

$2^+ \quad \text{2PF}_6$
C_{42}H_{34}F_{12}N_{12}OsP_{2}
Exact Mass: 1160.19

BR-3-Os(bisbenzpyrazolepyr)2.1.fid

2+ 2PF_{6}
C_{60}H_{39}F_{2}N_{6}O_{2}Os_{2}P_{2}
Exact Mass: 1164.15

2^+ 2PF_{6}
C_{42}H_{54}F_{12}N_{4}O_{3}Os_{2}
Exact Mass: 1160.16

2+ 2PF_6
C_{30}H_{22}F_{14}N_{2}OsP_{2}

Exact Mass: 946.08
$\text{(ppm)}$

$\text{NT-01-168-column.3.fid}$

$\text{C}_{28}\text{H}_{18}\text{F}_{12}\text{N}_{4}\text{OsF}_{2}$

Exact Mass: 1080.21
C_{39}H_{29}F_{16}N_2OsP_2
Exact Mass: 1022.10

2+ 2PF_6
C$_{22}$H$_{24}$F$_{12}$N$_{6}$OsP$_{2}$

Exact Mass: 959.10
NT-01-220-1.1.fid
NT-01-220-1

NT-01-220-1.2.fid
NT-01-220-1
$\text{C}_2\text{H}_3\text{F}_3\text{NO}$

Exact Mass: 177.04
Crude scale-up $^1$H NMR
Scale-up $^{19}$F NMR yield calculations:

1) 3.958 g aliquot removed at the end of rxn from 2562 g total mass.

$$\frac{3.958}{2562} = 0.00154$$

0.00154 x 1 mole SM = 0.00154 mol product in aliquot based off theoretical 100% yield.

2) 121.5 mg fluorobenzene and added as standard, 0.00126 mol.

$$\frac{0.00126}{0.00154} = 0.82.$$ 

3) Integrate fluorobenzene fluorine peak to 0.82, divide product integration by 3 for 62% yield.

$^{19}$F NMR with fluorobenzene NMR standard.
**Single crystal X-ray diffraction.** Data for all compounds was collected on an Agilent SuperNova diffractometer using mirror-monochromated Mo Kα radiation. Data collection, integration, scaling (ABSPACK) and absorption correction (face-indexed Gaussian integration\(^{31}\) or numeric analytical methods\(^{32}\) were performed in CrysAlisPro.\(^{33}\) Structure solution was performed using ShelXT\(^{34}\). Subsequent refinement was performed by full-matrix least-squares on \(F^2\) in ShelXL.\(^{34}\) Olex2 \(^{35}\) was used for viewing and to prepare CIF files. PLATON\(^{36}\) was used extensively for SQUEEZE,\(^{37}\) ADDSYM \(^{38}\) and TwinRotMat. Many disordered solvent molecules were modeled as rigid fragments from the Idealized Molecular Geometry Library.\(^{39}\) ORTEP graphics were prepared in CrystalMaker.\(^{40}\) Thermal ellipsoids are rendered at the 50% probability level. Unless noted, C-H hydrogens were placed in calculated positions and refined with riding isotropic ADPs and coordinates.

**Crystal structure:**

An initial data set was collected at 100 K and showed weak superstructure reflections and a strongly featured difference map. The temperature was increased to 220 K and a second data set was collected. This data set showed no superstructure reflections, and structure solution in Fddd (ShelXT) and refinement proceeded routinely. A PF\(_6\) anion was disordered over a twofold rotation axis and additionally disordered over two independent positions; these were each modeled as variable-metric rigid bodies as described above. A continuous channel along the 101 direction appeared to contain disordered dimethylformamide, but it was not possible to find a satisfactory atomic model. The disordered solvent was treated as a diffuse contribution to the overall scattering using PLATON SQUEEZE.
Figure S9. Molecular structure of \( \text{Os(bptpy)}_2(\text{PF}_6)_2 \). Black, carbon; blue, nitrogen; navy, osmium; brown, bromine. A PF\(_6\) counterion is omitted for clarity.
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