Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

A Photochemical Route to a Square Planar, Ruthenium(IV)-bis(Imide)

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Experimental

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All manipulations were carried out under inert atmosphere, either in an N_2 atmosphere MBraun glovebox or using standard Schlenk techniques. THF and *n*-hexane were dried over Na and distilled under N_2. Toluene, Et_2O, and pentane were dried by passage over activated alumina and sparged with N_2. NMR solvents C_6D_6 and toluene-d_8 were dried over CaH_2 and distilled under N_2. Hexamethyldisiloxane was dried over CaH_2 and distilled under N_2. N_3Ar and N_3Mes were synthesized according to literature procedures.[1] However, the purification of the organic azide by silica gel chromatography was omitted as the crude product was found to be pure by ^1H and ^{13}C NMR after removal of volatiles. N_3TMS was purchased from Alfa Aesar and used as received. H_2NAr and H_2NMes were purchased from Oakwood and distilled in vacuo from CaH_2. *cis*-$RuCl_2(PMe_3)_4$, $Ru(NAr)(PMe_3)_3$, and $Ru(NAr^*)(PMe_3)_3$ were prepared according to published procedures.[2] [3] LiNHR salts (where R = 2,-diisopropylphenyl or mesityl) were prepared by adding 2.5 M ^nBuLi (in hexanes, 1 equiv) to a chilled solution (liquid N_2 coldwell) of the respective H_2NR (1 equiv) in hexane. The reaction was warmed to room temperature, while stirring, which resulted in the precipitation of a white or pale yellow powder. This powder was collected by filtration, rinsed several times with *n*-hexane, and dried in vacuo. The LiNHR product was used without further purification and was stored in the glovebox freezer (–35 °C). The phosphines PMe_3 and $PPhMe_2$ were purchased from Strem Chemical Co. and used as received. They were stored in sealed containers in an N_2 glovebox.

Instrumentation

All NMR data was collected at the Max T. Rogers NMR facility. Routine characterization spectra were obtained using an Agilent DDR2 500 MHz NMR spectrometer equipped with a 5 mm PFG OneProbe operating at 499.84 MHz (^1H), 125.73 MHz (^{13}C), and 202.35 MHz (^{31}P). Additional experiments, including ^{14}N and variable temperature NMR measurements were done using: a UNITYplus 500 spectrometer equipped with a 5 mm switchable broadband probe operating at 36.12 MHz (^{14}N); a Varian Inova 500 spectrometer equipped with a 5mm pulse-field-gradient (PFG) switchable broadband probe operating at 499.84 MHz (^1H); or a Varian Inova 600 spectrometer equipped with a 5 mm PFG switchable broadband probe operating at 599.89 MHz (^1H). ^1H NMR chemical shifts are reported relative to residual C_6HD_5 in C_6D_6 as 7.16 ppm. ^{13}C NMR chemical shifts are reported relative to $(^{13}C)C_5D_6$ as 128.06 ppm. ^{14}N NMR shifts are referenced to the internal peak for dissolved N_2 in NMR solvent (309.6 ppm vs. external nitromethane as 381.6 ppm, or NH_3 as 0 ppm).

All crystallographic data was collected at the Michigan State University Center for X-ray Crystallography. All structures were collected on Bruker AXS instruments operating with either copper or molybdenum radiation sources. Data was collected at 173 K. Structure solutions were typically found using XT Intrinsic Phasing and refined by least squares using Olex software. For further information please see the .cif files provided as supplementary information.

Photolysis experiments were carried out using an Oriel Instruments Mercury Arc Lamp (Model #66921) operating between 450-1000 W; typical operating voltage for these experiments was set to 800 W. An ≈15 cm H_2O column was used as an IR filter between the lamp and the jacketed chiller, fitted with a quartz window. This reduced the temperature at the quartz window between incoming light and the reaction vessel, which was important for some experiments. A picture of the photolysis set-up is shown below.

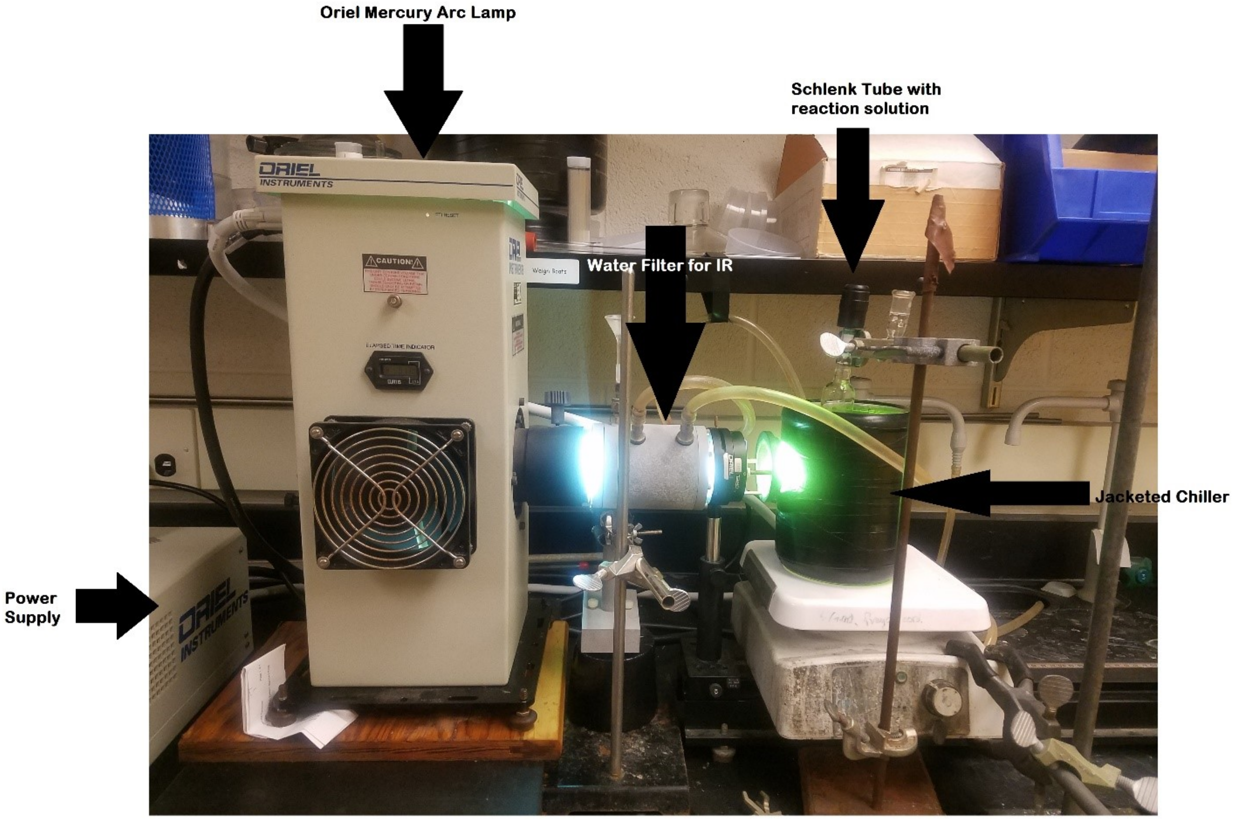
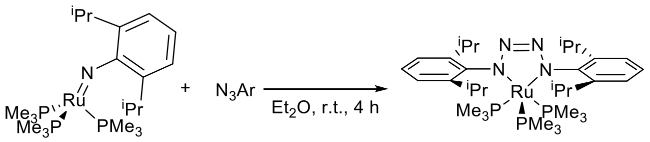


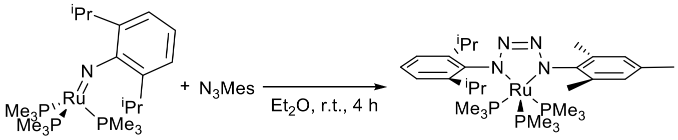
Figure S1. *Photolysis apparatus used to irradiate samples with high intensity UV-Vis light. The Oriel Instruments described are shown here operating at 800 W.*

UV-Vis spectra were collected using an Ocean Optics DH-mini UV-Vis-NIR spectrophotometer in an N_2 glovebox. Experiments were performed in THF using a quartz cell. The raw data was fit with gaussians peaks using OriginPro 9.0 software to aid accurate peak separation and assignment of maxima.

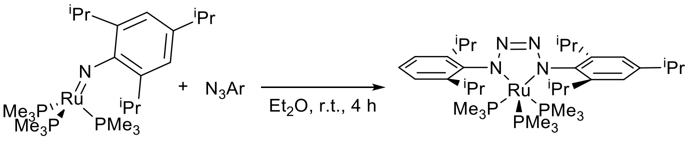
Synthetic Procedures



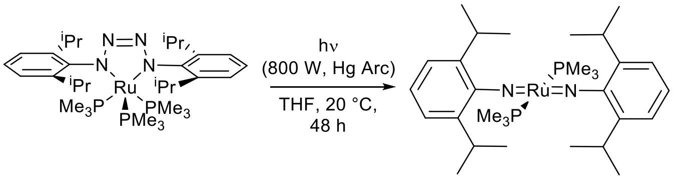
*Ru(N$_4$Ar$_2$)(PMe$_3$)$_3$ (3a)***:** A scintillation vial was charged with Ru(NAr)(PMe$_3$)$_3$ (150 mg, 1 equiv, 0.3 mmol), a stir bar, and Et$_2$O (5 mL). As this solution was stirred in the glovebox, N$_3$Ar (60 mg, 1 equiv, 0.3 mmol) in Et$_2$O (2 mL) was added dropwise. After 10 min of stirring at room temperature, a fine orange precipitate started to form. The reaction was stirred another 2 h at room temperature, at which time the fine orange powder was collected by filtration and rinsed with *n*-hexane. The powder was dried in vacuo and found to be analytically pure, giving 120 mg (57%) of **3a**. Chilling the original filtrate (–35 °C) resulted an additional 52 mg (25%) of **3a**. X-ray quality crystals were grown from concentrated THF layered with hexane at –35 °C. ^{1}H NMR (500 MHz, benzene-*d*$_6$): 7.39 (dd, *J* = 8.2, 7.1 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 4H), 3.15 (p, *J* = 6.8 Hz, 4H), 1.39 (d, *J* = 6.6 Hz, 12H), 1.31 (d, *J* = 6.9 Hz, 12H), 1.01-0.81 (m, 26H). ^{13}C{^{1}H} NMR (126 MHz, benzene-*d*$_6$): 154.58, 145.76, 125.93, 122.41, 27.59, 27.10, 24.50-23.66 (m), 21.83. ^{31}P NMR (202 MHz, benzene-*d*$_6$): 6.50. ^{14}N NMR shows no resonances for this complex, perhaps due to extreme broadening. Elemental analysis calc'd for RuC$_{33}$H$_{61}$P$_3$N$_4$: C, 55.99, H, 8.69, N, 7.92; found, C, 55.46, H, 8.47, N, 7.83. UV-vis, λ$_{max}$ nm (ε M^{-1}cm^{-1}): 478 (2347), 349 (4081).



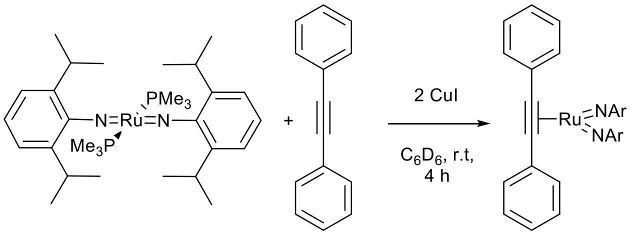
Ru{N$_4$(Ar)Mes}(PMe$_3$)$_3$ (3b): The same procedure used for **3a** above was used for the preparation of **3b** utilizing Ru(NAr)(PMe$_3$)$_3$ (76 mg, 1 equiv, 0.15 mmol) and N$_3$Mes (32 mg, 1 equiv, 0.15 mmol). This yielded crude **3b** (79 mg, 73%). X-ray quality crystals were grown from concentrated THF layered with hexane at –35 °C. ^{1}H NMR (500 MHz, benzene-*d*$_6$): 7.45 – 7.36 (m, 1H), 7.30 (d, *J* = 7.6 Hz, 2H), 6.95 (s, 2H), 3.20 (p, *J* = 6.8 Hz, 2H), 2.33 (s, 3H), 2.20 (s, 6H), 1.40 (d, *J* = 6.7 Hz, 6H), 1.30 (d, *J* = 7.0 Hz, 6H), 0.93 (dd, *J* = 4.6, 2.5 Hz, 28H). ^{13}C{^{1}H} NMR (126 MHz, benzene-*d*$_6$): 154.91, 154.52, 145.65, 135.19, 133.79, 128.64, 125.87, 122.51, 27.55, 26.85, 24.28-23.58 (m), 22.03, 20.82, 20.16. ^{31}P NMR (202 MHz, Benzene-*d*$_6$): 6.43. ^{14}N NMR shows no resonances for this complex, perhaps due to extreme broadening. Elemental analysis calc'd for Ru$C_{30}H_{55}P_3N_4$: C, 54.12, H, 8.33, N, 8.42; found, C, 54.10, H, 8.64, N, 8.19. UV-vis, λ_{max} nm (ε $M^{-1}cm^{-1}$): 490 (2052), 339 (3796).



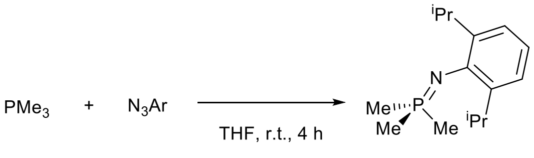
Ru{N$_4$(Ar)Ar}(PMe$_3$)$_3$ (**3c**)*: A scintillation vial was charged with Ru(NAr*)(PMe$_3$)$_3$ (70 mg, 0.128 mmol, 1 equiv), THF (5 mL), and a stir bar. With stirring, a solution of N$_3$Ar (29 mg, 0.128 mmol, 1 equiv) in THF (1 mL) was added dropwise. The solution was stirred for 4 h at room temperature and an orange-red precipitate formed. The solution was decanted from the precipitate, and the precipitate was rinsed with hexane and dried. This yielded crude powder (68 mg), which was recrystallized from hexamethyldisiloxane to give X-ray quality crystals (24 mg). Additional powder was precipitated from the mother liquor of the reaction by chilling the solution to –35 °C. This provided a total yield of **3c** of 53 mg (55%). ^{1}H NMR (500 MHz, benzene-*d*$_6$): 7.39 (dd, *J* = 8.2, 7.0 Hz, 1H), 7.33-7.28 (m, 2H), 7.25 (s, 2H), 3.16 (hept, *J* = 6.7 Hz, 4H), 3.02 (hept, *J* = 7.0 Hz, 1H), 1.46-1.38 (m, 18H), 1.36 (d, *J* = 6.9 Hz, 6H), 1.32 (d, *J* = 6.9 Hz, 6H), 0.97-0.85 (m, 27H). ^{31}P NMR (202 MHz, benzene-*d*$_6$): 6.51. ^{13}C NMR (126 MHz, benzene-*d*$_6$): 155.02, 152.88, 146.37, 146.17, 145.77, 126.31, 122.80, 120.39, 34.85, 28.05 (d), 27.59 (d), 24.91, 24.68, 24.60 (d), 24.54, 24.47, 22.31 (d), 2.10. ^{14}N NMR shows no resonances for this complex, perhaps due to extreme broadening. Elemental analysis calc'd for Ru$C_{36}H_{67}P_3N_4$: C, 57.66, H, 9.01, N, 7.47; found, C, 57.33, H, 9.04, N, 6.80. UV-vis, λ_{max} nm (ε $M^{-1}cm^{-1}$): 474 (1600), 34 (3620).



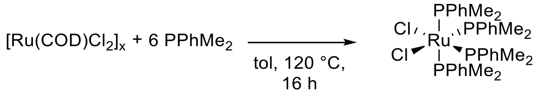
*Ru(NAr)₂(PMe₃)₂ (**1**)*: A 500 mL Schlenk tube fitted with a Teflon stopper was charged with of **3a** (75 mg, 0.11 mmol), a stir bar, and THF (200 mL), giving a 5.5 mM solution. The Schlenk tube was sealed and transferred from the glovebox to the photolysis apparatus. The Schlenk tube was submerged in a water-jacketed chiller, which maintained a temperature of about 16 °C during the photolysis process. The jacketed chiller was placed on a stir plate in the path of the light from a Hg-Arc lamp with the quartz window of the jacketed chiller aligned with the lamp. The lamp was then run at 800 W, irradiating the stirred solution in the Schlenk flask for 48 h. After the photolysis period, the vessel was returned to the glovebox. The volatiles removed in vacuo to provide a tacky, dark brown residue. This residue was extracted with cold *n*-hexane until the extracts came off colorless. The extract was filtered through Celite, and then concentrated in vacuo to about 1 mL. This solution was stored at –35 °C for several days to provide 38 mg of crystals of $Ru(NAr)_2(PMe_3)_2$, mixed with crystals of **3a** and $ArN{=}PMe_3$. To obtain a purer sample of $Ru(NAr)_2(PMe_3)_2$, 2 more recrystallizations from *n*-hexane were preformed successively. ^1H NMR (500 MHz, benzene-d_6): 6.93-6.90 (m, 4H), 6.85-6.81 (m, 2H), 4.45 (hept, J = 7.0 Hz, 4H), 1.28 (d, J = 6.9 Hz, 26H), 1.23 (t, J = 2.6 Hz, 19H). ^{31}P NMR (202 MHz, benzene-d_6): –20.90. ^{14}N NMR (36 MHz, benzene-d_6): 303.30. UV-vis, λ_{max} nm (ε $M^{-1}cm^{-1}$): 675 (4034), 484 (1776), 344 (1997), 300 (8200). Repeated attempts to obtain adequate elemental analysis failed. HRMS was instead attempted. A peak for the species $\{Ru(NAr)(PMe_3)_2H\}^+$ was observed by QTOF-HRMS running in positive ion mode. HRMS calc'd for $RuNP_2C_{18}H_{36}^+$: 429.1296; found: 429.1096. The parent bis(imide) complex was not observed by this technique. The X-ray diffraction data, ^1H NMR spectroscopy, and ^{13}C NMR spectroscopy are consistent with Wilkinson's report.



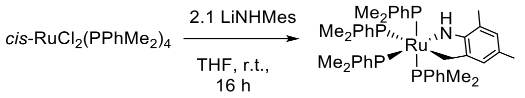
Ru(NAr)$_2$(η$_2$-diphenylacetylene) (in situ): A scintillation vial was charged with **1** (12 mg, 1 equiv, 0.021 mmol), diphenylacetylene (5.5 mg, 1.5 equiv, 0.031 mmol), a stir bar, and C_6D_6 (2 mL). To the stirred solution was added of CuI (8 mg 2 equiv, 0.042 mmol) portion-wise as a solid. The reaction solution was stirred vigorously for 4 h, over which time it went from deep blue to reddish-purple in color. The reaction mixture was filtered over a pad of Celite, and the filtrate was transferred to an NMR tube. ^{1}H NMR (600 MHz, benzene-*d*$_6$): 8.36 (d, *J* = 7.4 Hz, 4H), 7.22 (t, *J* = 8.6 Hz, 6H), 6.92 – 6.86 (m, 7H), 3.73 (p, *J* = 6.9 Hz, 4H), 1.14 (d, 28H). ^{13}C{^{1}H} NMR (151 MHz, benzene-*d*$_6$): 200.41. The full ^{13}C NMR spectrum could not be assigned due to the presence of excess diphenylacetylene, in addition to other impurities. However, this new resonance noted at >200 ppm is close to the observed ^{13}C resonance for the acetylenic carbon in the Os derivative of this molecule previously reported.^{14}N NMR (36 MHz, THF-*d*$_8$): 387.11. Attempts to grow X-ray quality crystals from this reaction solution did not result in the isolation of a new complex.



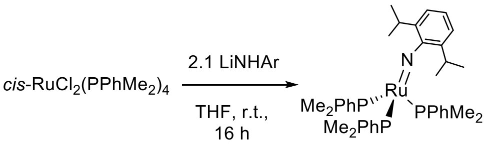
Me$_3$P=NAr: A scintillation vial was charged with PMe$_3$ (38 mg, 0.5 mmol, 1.2 equiv), THF (3 mL), and a stir bar. At room temperature, N$_3$Ar (78 mg, 0.4 mmol, 1 equiv) in THF (1 mL) was added dropwise to the stirred PMe$_3$ solution. Bubbles were noticed on addition. The reaction was allowed to stir for 4 h, and the volatiles were removed in vacuo, resulting in yellow ArN=PMe_3 (90 mg, 94%). The crude product was used without further purification. X-ray quality crystals can be grown from n-hexane at –35 °C. ^{1}H NMR (500 MHz, benzene-*d*$_6$): 7.24 (dd, *J* = 7.6, 1.5 Hz, 2H), 7.08 (td, *J* = 7.5, 2.8 Hz, 1H), 3.58 (septet, *J* = 6.9 Hz, 2H), 1.34 (d, *J* = 6.9 Hz, 12H), 0.93 (d, *J* = 12.0 Hz, 9H). ^{13}C{^{1}H} NMR (126 MHz, benzene-*d*$_6$): 142.51 (d), 128.35, 122.97 (d), 119.72 (d), 28.71, 24.21, 17.61 (d). ^{31}P NMR (202 MHz, benzene-*d*$_6$): –7.57. Elemental analysis calc'd for $C_{15}H_{26}PN$: C, 71.68, H, 10.43, N, 5.57; found, C, 71.25, H, 9.78, N, 5.61.



Cis-RuCl$_2$(PPhMe$_2$)$_4$: A 35 mL pressure tube was charged with {$RuCODCl_2$}$_x$ (0.506 g, 1.9 mmol, 1 equiv), a stir bar, and toluene (3 mL). To the stirred solution was added $PPhMe_2$ (1.4 g, 9.5 mmol, 5 equiv). The pressure tube was sealed and transferred from the glovebox to a 120 °C oil bath. The pressure tube was heated, with stirring, for 16 h, over which time the opaque, brown suspension turned an orange-yellow. The pressure tube was removed from the bath and cooled ambiently, resulting in the precipitation of copious amounts of yellow solids, which was an assortment of various sized crystals. From this precipitate, X-ray quality crystals were obtained. When the pressure tube was cooled, it was returned to the glovebox. The mother liquor was decanted, and the solids dried in vacuo to yield cis-$RuCl_2(PPhMe_2)_4$ (1.1 g, 80%). The compound has poor solubility in most organic solvents. The complex demonstrates marked color changes when dissolved in DMSO-d$_6$ or MeOD indicative of reaction. Consequently, adequate NMR spectra were not be obtained. The collected precipitate was found to be analytically pure by elemental analysis, without further treatment, and was used in subsequent reactions. Elemental analysis calc'd for $RuC_{32}H_{44}P_4Cl_2$: C, 53.05, H, 6.12, N, 0.00; found, C, 52.72, H, 6.29, N, 0.06.



Ru(κ$_2$(N,C)-1-(NH)-2-(CH$_2$)-4,6-Me$_2$C$_6$H$_2$)(PPhMe$_2$)$_4$ ***(5)***: A scintillation vial was loaded with *cis*-RuCl$_2$(PPhMe$_2$)$_4$ (124 mg, 0.16 mmol, 1 equiv), a stir bar, and THF (5 mL). To this stirring solution at room temperature was added LiNHMes (48 mg, 0.34 mmol, 2.1 equiv) in THF. Upon addition, the solution went from a pale-yellow suspension to an intense red solution. The reaction was stirred for 8 h, and the volatiles removed in vacuo. The residue was extracted with hexane and filtered through Celite until the filtrate came out colorless. The reddish-pink filtrate solution was concentrated under reduced pressure and stored at –35 °C for 24 h to yield pure **5** (46 mg, 42%) as X-ray quality crystals. ^{1}H NMR (500 MHz, benzene-*d*$_6$): 7.34 (s, 1H), 7.20 (t, *J* = 7.2 Hz, 8H), 7.04 (t, *J* = 7.6 Hz, 11H), 6.97 (s, 1H), 4.11 (s, 1H), 2.88 (s, 2H), 2.56 (s, 3H), 2.23 (s, 3H), 1.19 (d, *J* = 4.8 Hz, 24H). ^{13}C{^{1}H} NMR (126 MHz, benzene-*d*$_6$): 162.16, 144.15 (d, *J* = 26.8 Hz), 130.64 (d, *J* = 10.4 Hz), 128.35, 127.98 (d, *J* = 3.5 Hz), 126.41, 120.84, 119.66, 31.98, 21.57, 18.85, 18.13. ^{31}P NMR (202 MHz, benzene-*d*$_6$): 7.44. Elemental analysis calc'd for $RuC_{41}H_{55}P_4N$: C, 62.58, H, 7.05, N, 1.78; found, C, 62.36, H, 7.16, N, 1.85.



Ru(NAr)(PPhMe$_2$)$_3$ ***(4):*** A scintillation vial was charged with *cis*-RuCl$_2$(PPhMe$_2$)$_4$ (194 mg, 1 equiv, 0.25 mmol), a stir bar, and THF (8 mL). To this stirred solution at room temperature, LiNHAr (100 mg, 2.1 equiv, 0.52 mmol) in THF (2 mL) was added dropwise. The solution rapidly changed color from pale yellow to bright red. The solution was stirred for 16 h at room temperature, and the volatiles were removed in vacuo. This yielded a dark red residue, which was extracted with *n*-hexane and filtered through Celite until the filtrate came off colorless. The filtrate was concentrated to 2 mL and chilled to –35 °C to give pure **4** (124 mg, 67%) as amorphous crystals. ^{1}H NMR (500 MHz, benzene-d_6): 7.63 (ddt, *J* = 8.8, 4.5, 1.9 Hz, 6H), 7.22 (s, 3H), 7.08 (t, *J* = 7.5 Hz, 6H), 7.04-6.93 (m, 3H), 4.62 (septet, *J* = 6.9 Hz, 2H), 1.40 (d, *J* = 7.0 Hz, 12H), 1.39-1.36 (m, 18H). ^{13}C{ NMR (126 MHz, benzene-d_6): 157.68, 146.15-143.90 (m), 140.54 (q, *J* = 6.2 Hz), 130.59 (dd, *J* = 7.6, 3.7 Hz), 128.34, 128.14 (dd, *J* = 6.1, 3.2 Hz), 122.78, 120.49, 26.68, 23.99, 23.72 – 22.74 (m). ^{31}P NMR (202 MHz, benzene-d_6): 34.62. Elemental analysis calc'd for $RuC_{36}H_{50}P_3N$: C, 62.59, H, 7.30, N, 2.03; found, C, 62.13, H, 7.49, N, 2.11.

Spectral Data for Ru Complexes

$Ru(N_4Ar_2)(PMe_3)_3$ (**3a**)

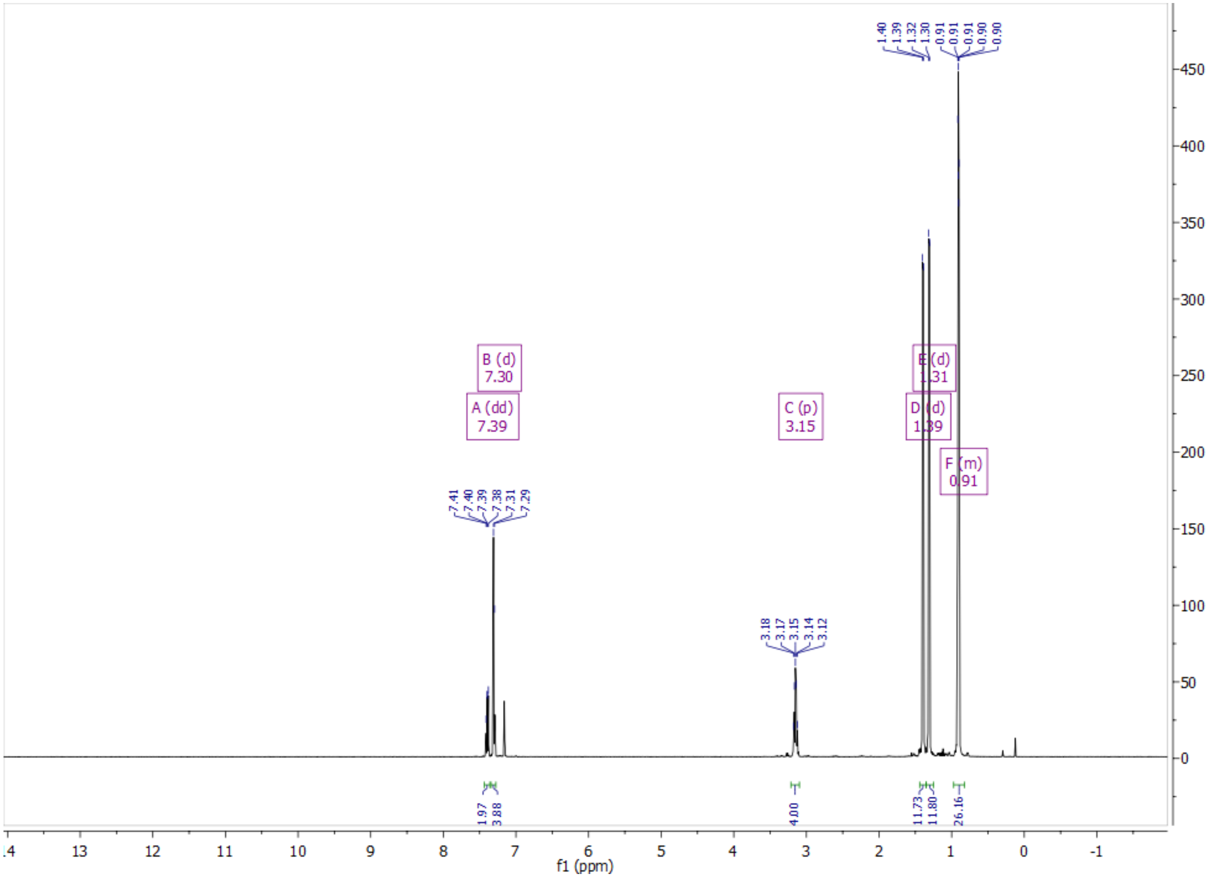


Figure S2. *^{1}H NMR spectrum of* $Ru(N_4Ar_2)(PMe_3)_3$ (**3a**) *in C_6D_6.*

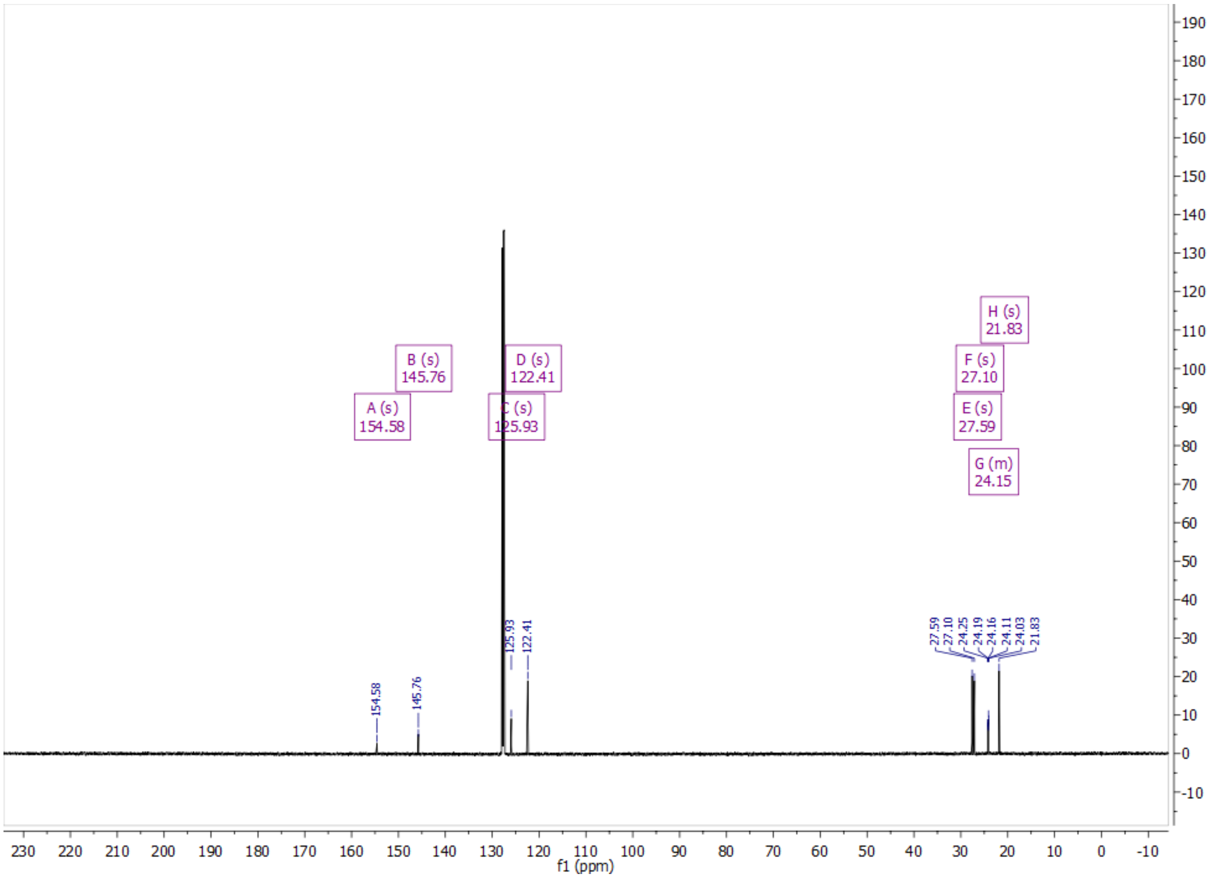


Figure S3. *^{13}C NMR spectrum of* Ru(N_4Ar_2)(PMe_3)$_3$ (**3a**) *in C_6D_6.*

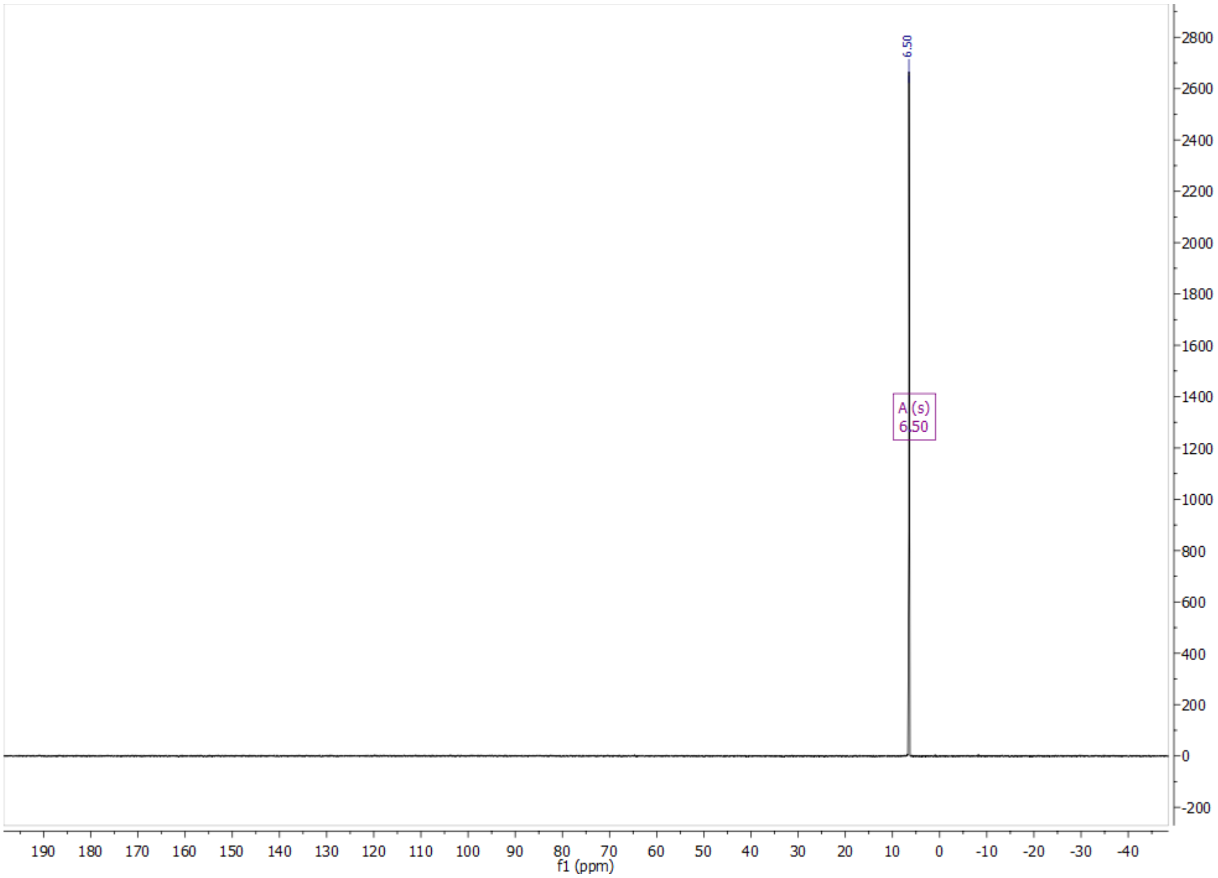


Figure S4. *^{31}P NMR spectrum of* $Ru(N_4Ar_2)(PMe_3)_3$ (**3a**) *in C_6D_6.*

Ru{N_4Ar(Mes)}(PMe_3)$_3$ (**3b**)

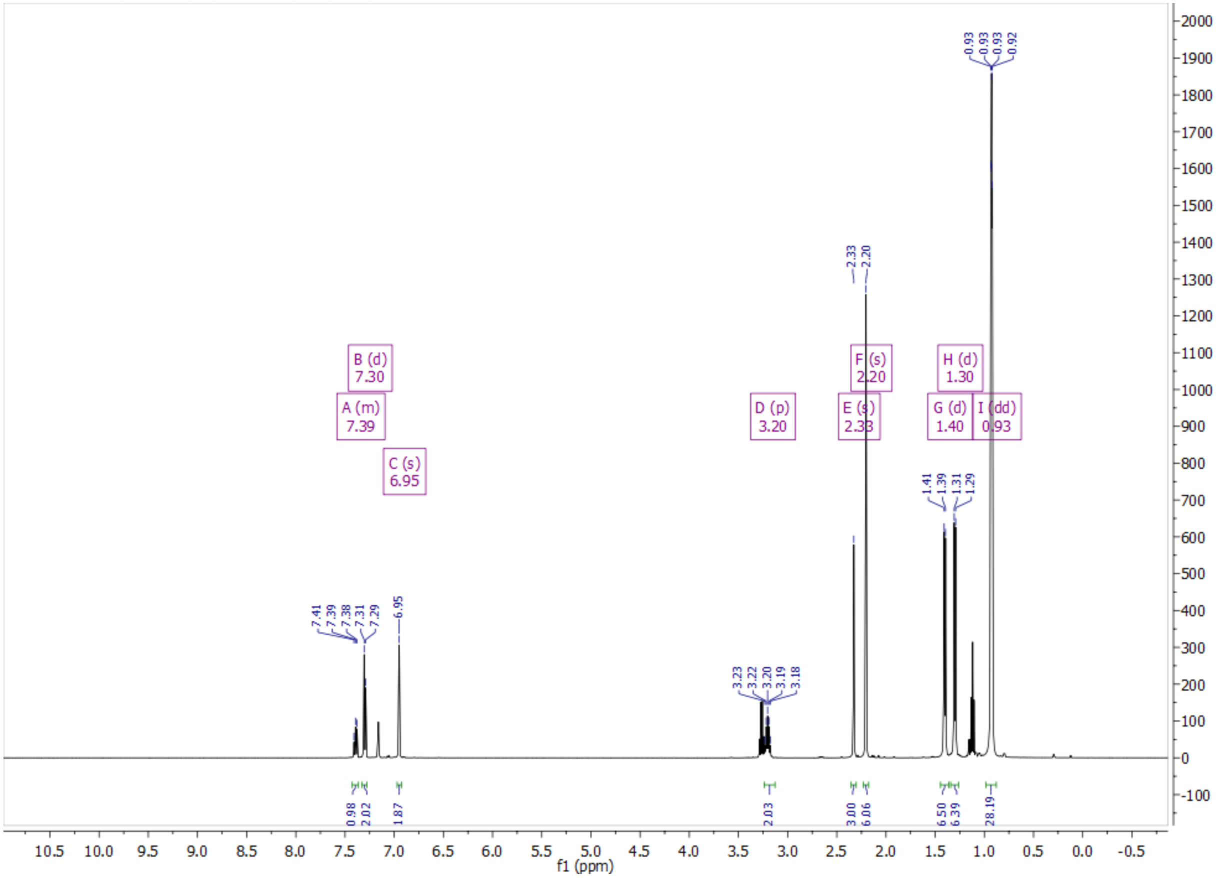


Figure S5. *^{1}H NMR spectrum of* Ru{N_4(Ar)Mes}(PMe_3)$_3$ (**3b**) *in C_6D_6.*

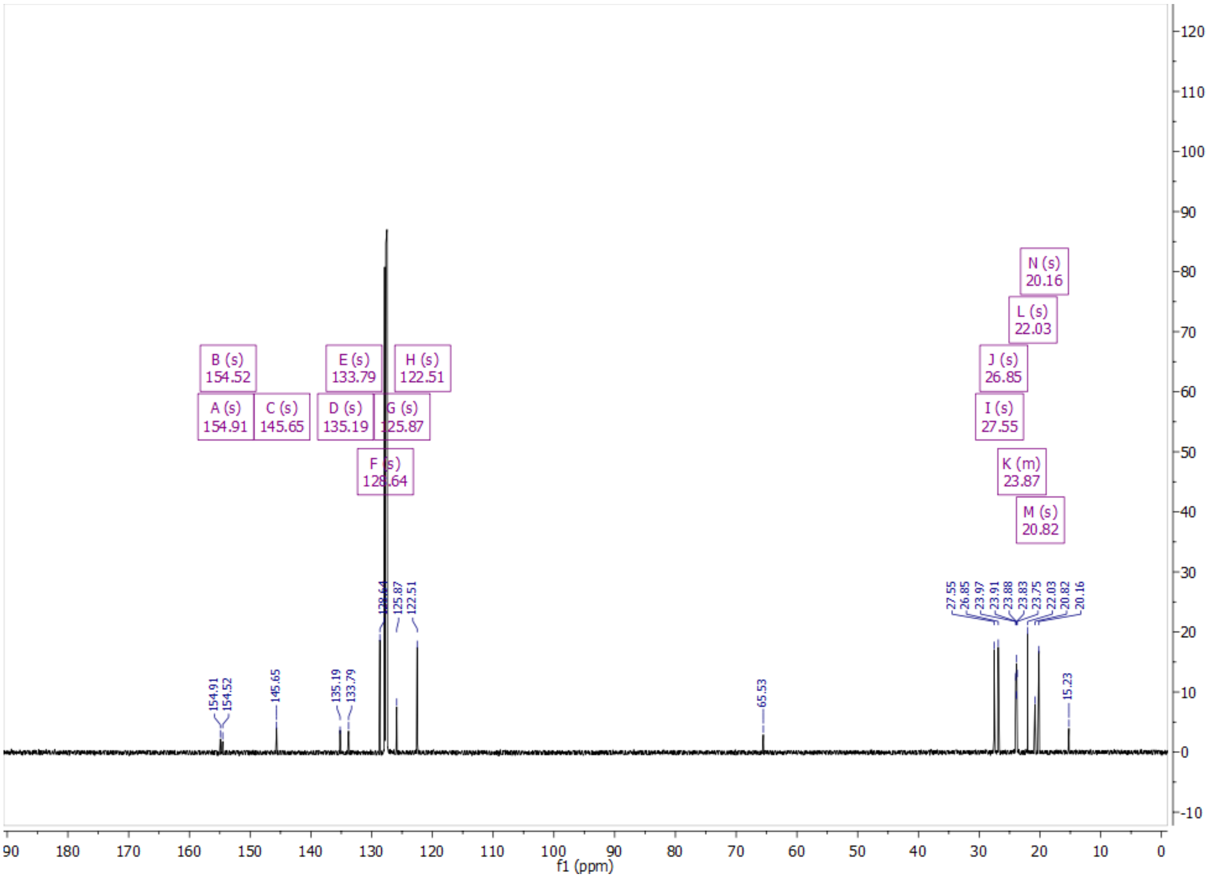


Figure S6. *^{13}C NMR spectrum of* Ru{N_4(Ar)Mes}(PMe_3)$_3$ (**3b**) *in C_6D_6.*

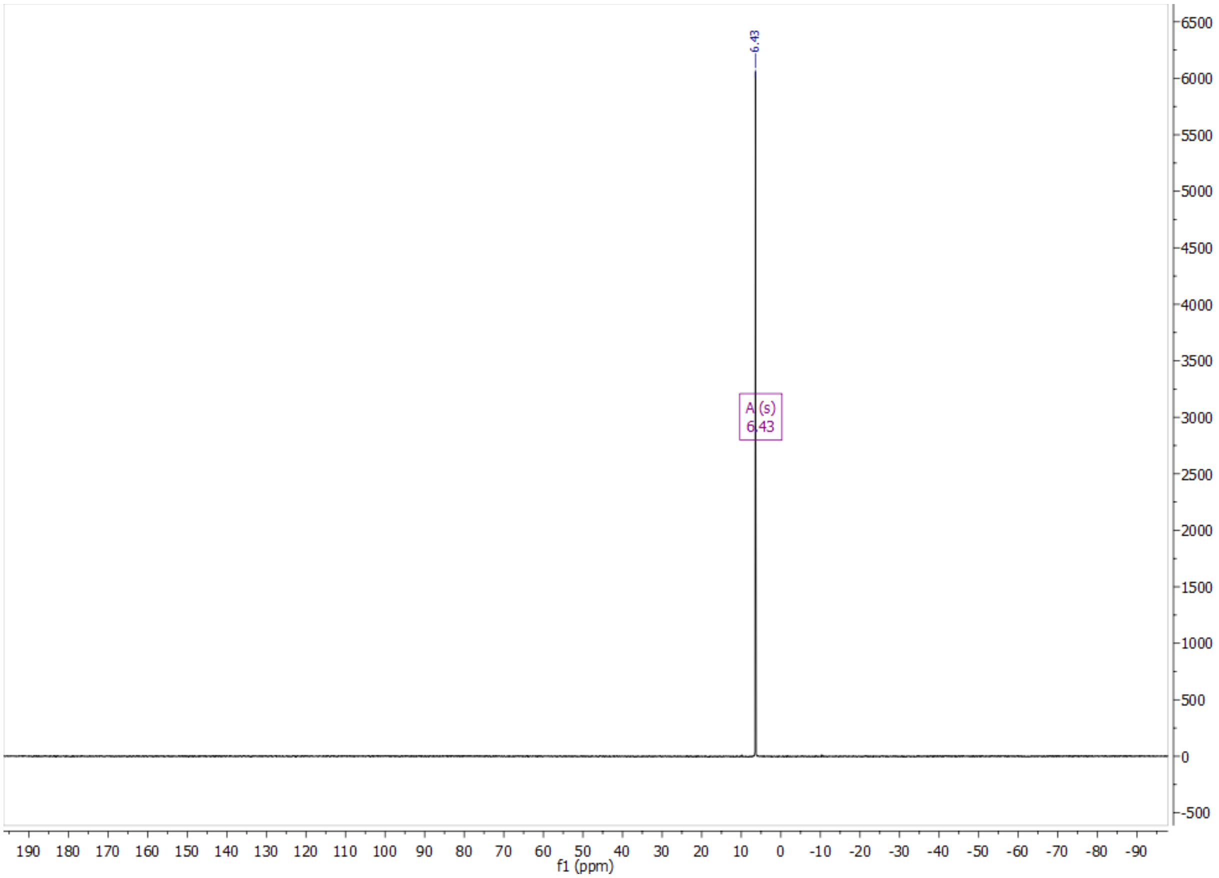


Figure S7. *^{31}P NMR spectrum of* Ru{N_4(Ar)Mes}(PMe_3)$_3$ (**3b**) *in C_6D_6.*

Ru{N_4(Ar)Ar*}(PMe_3)$_3$ (**3c**)

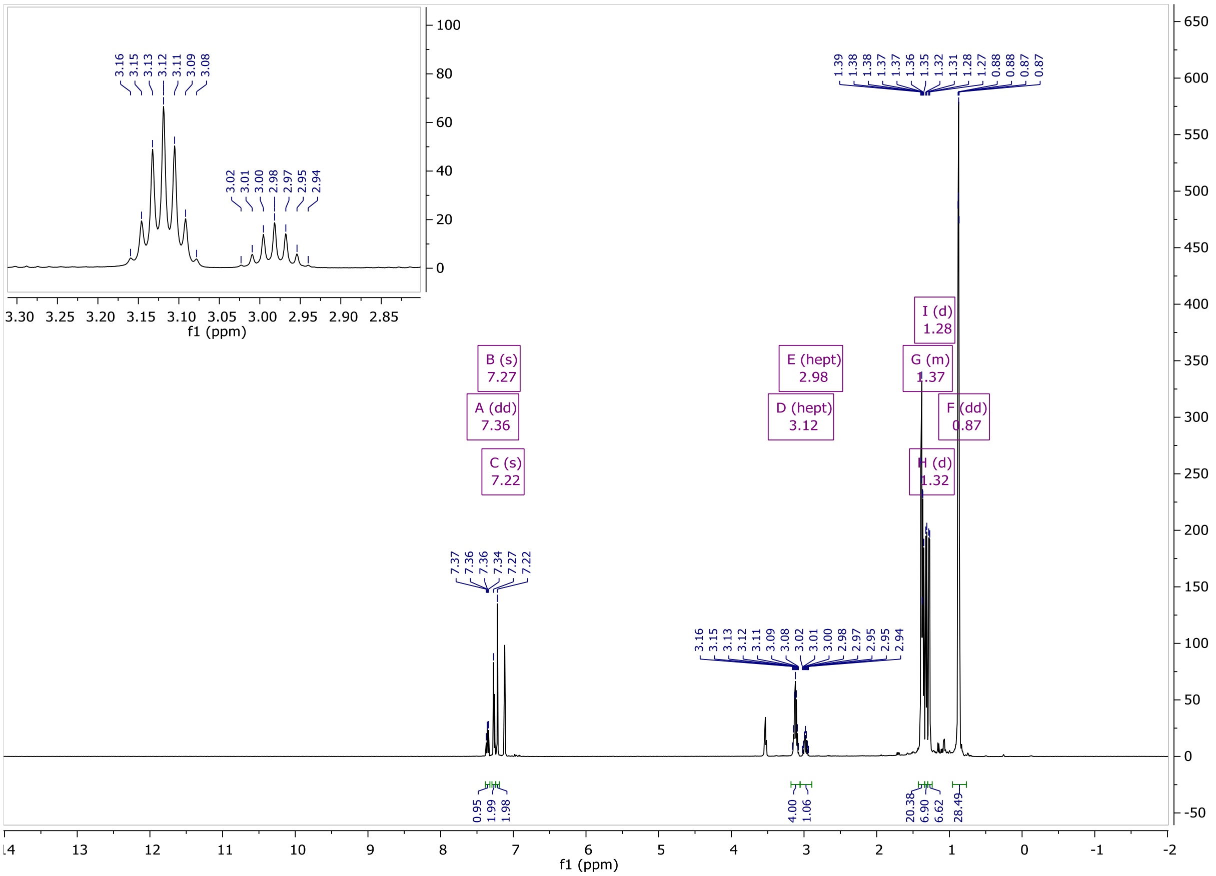


Figure S8. *^{1}H NMR spectrum of Ru{N_4(Ar)Ar*}(PMe_3)$_3$ (**3c**) in C_6D_6.*

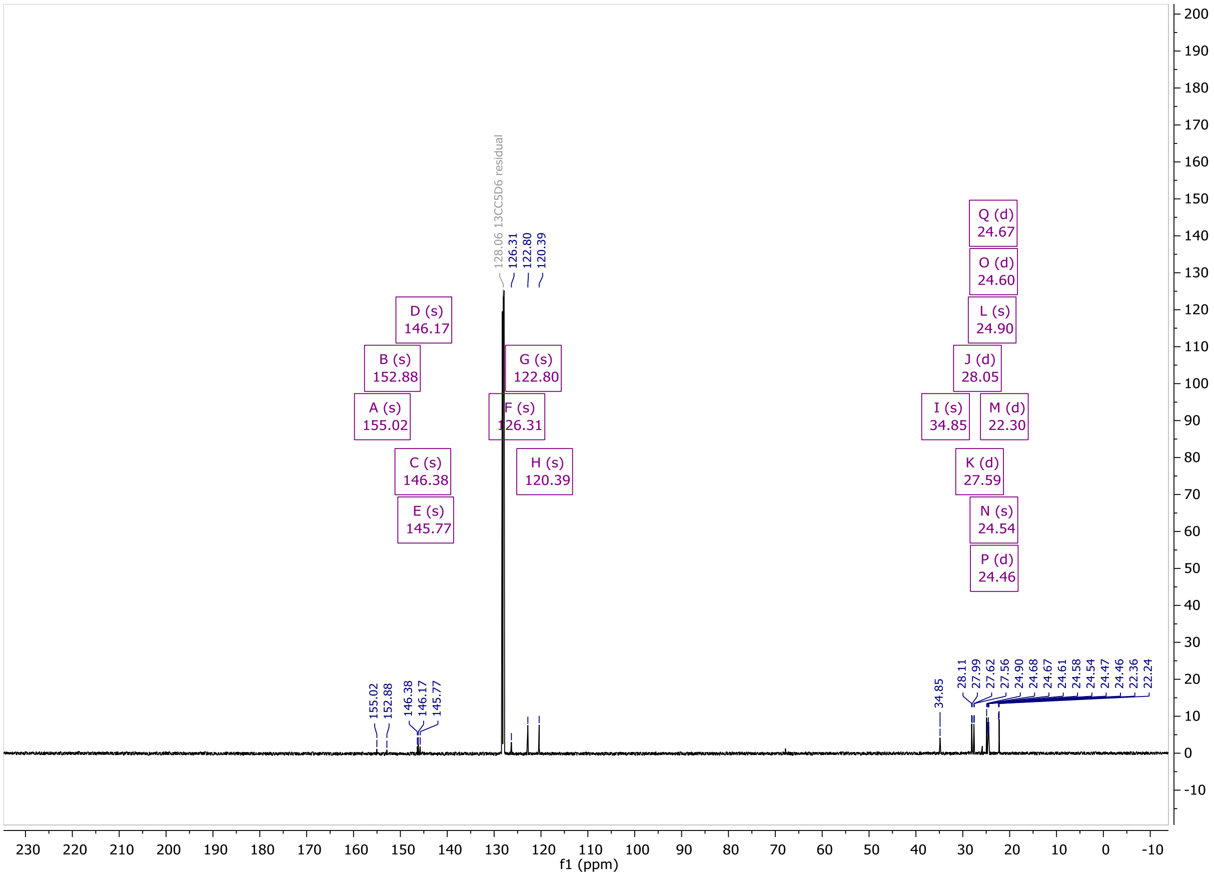


Figure S9. ^{13}C NMR spectrum of Ru{N_4(Ar)Ar*}(PMe_3)$_3$ (**3c**) in C_6D_6.

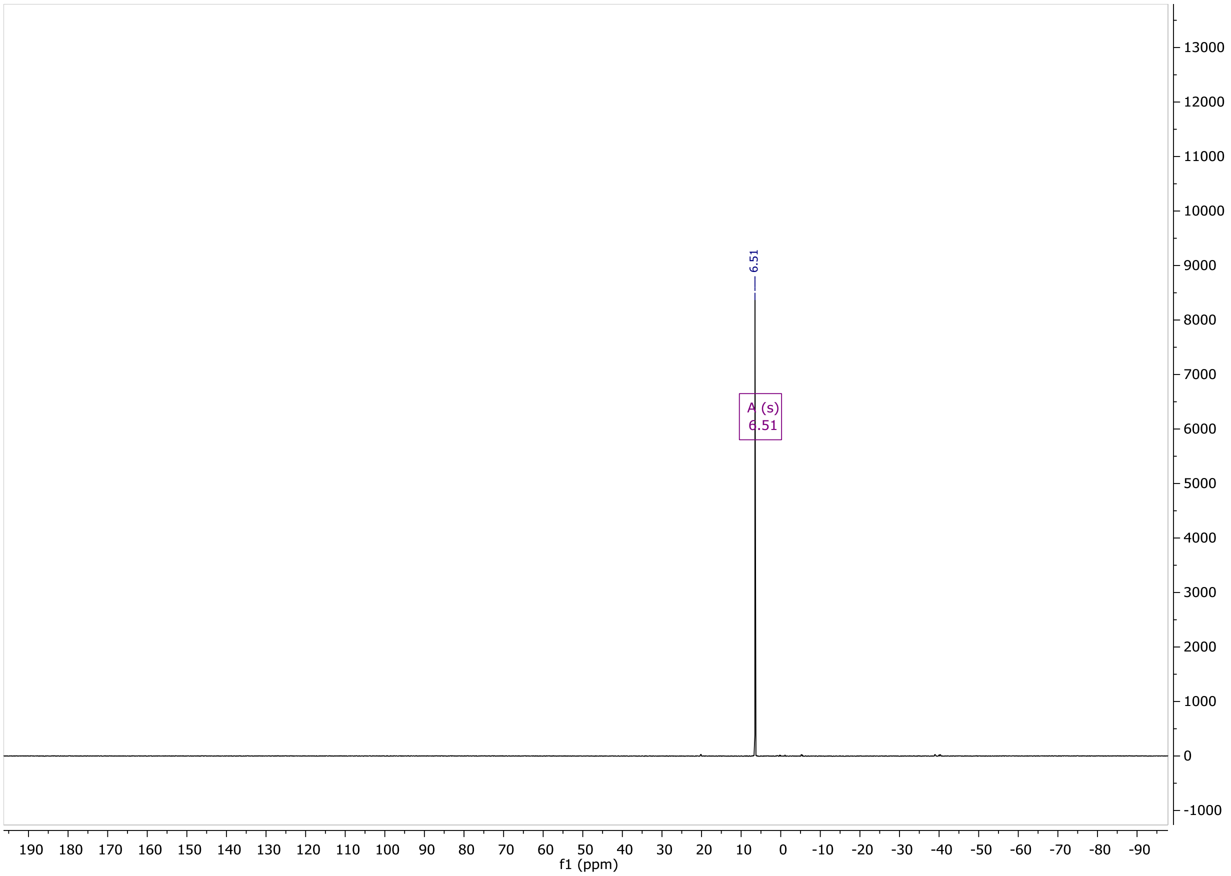


Figure S10. *^{31}P NMR spectrum of Ru{N_4(Ar)Ar*}(PMe_3)$_3$ (**3c**) in C_6D_6.*

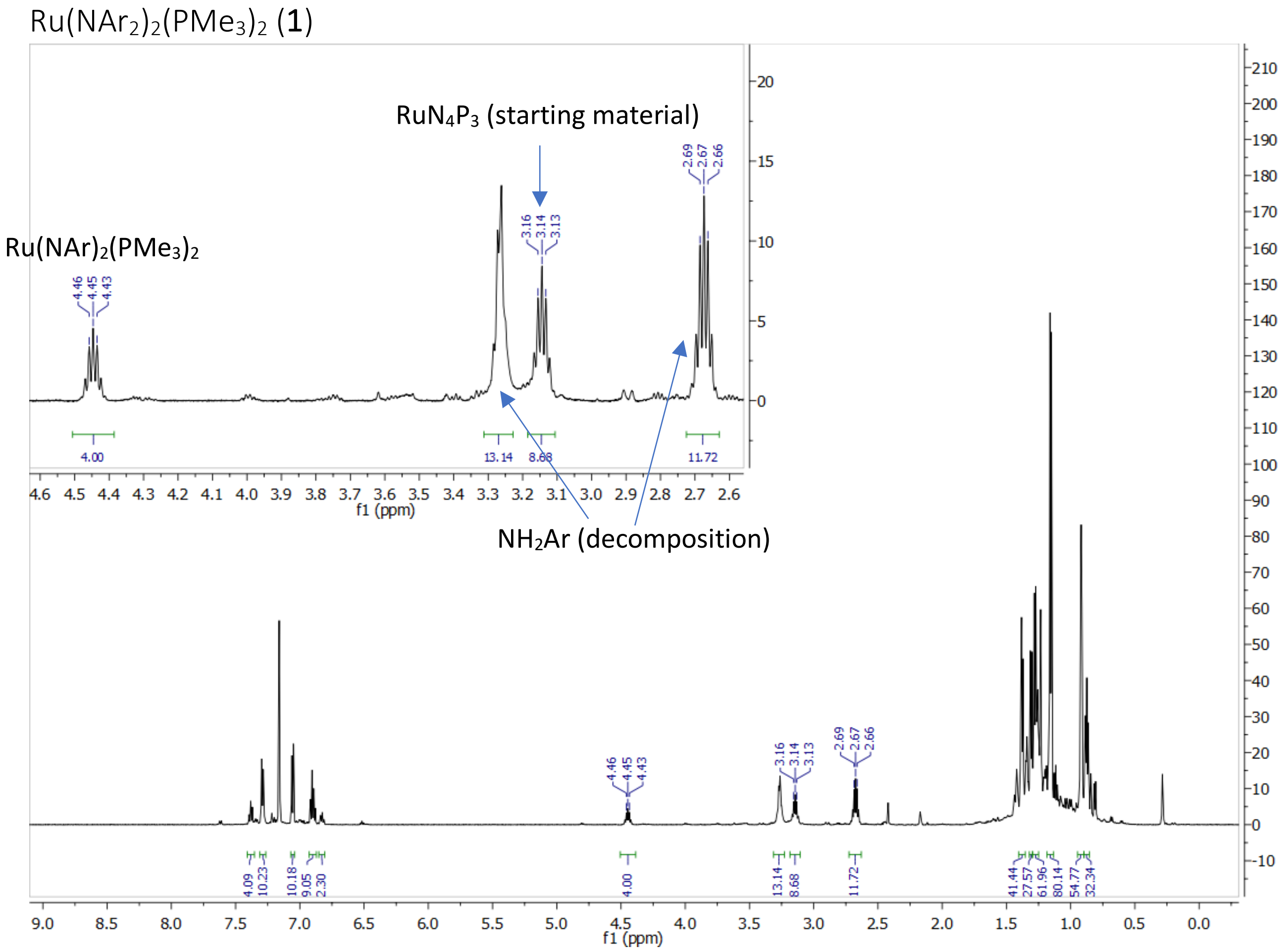


Figure S11. *^{1}H NMR of photolysis reaction containing a mixture of Ru(NAr)$_2$(PMe$_3$)$_2$ (**1**), **3a** (starting material), and H$_2$NAr (decomposition byproduct).*

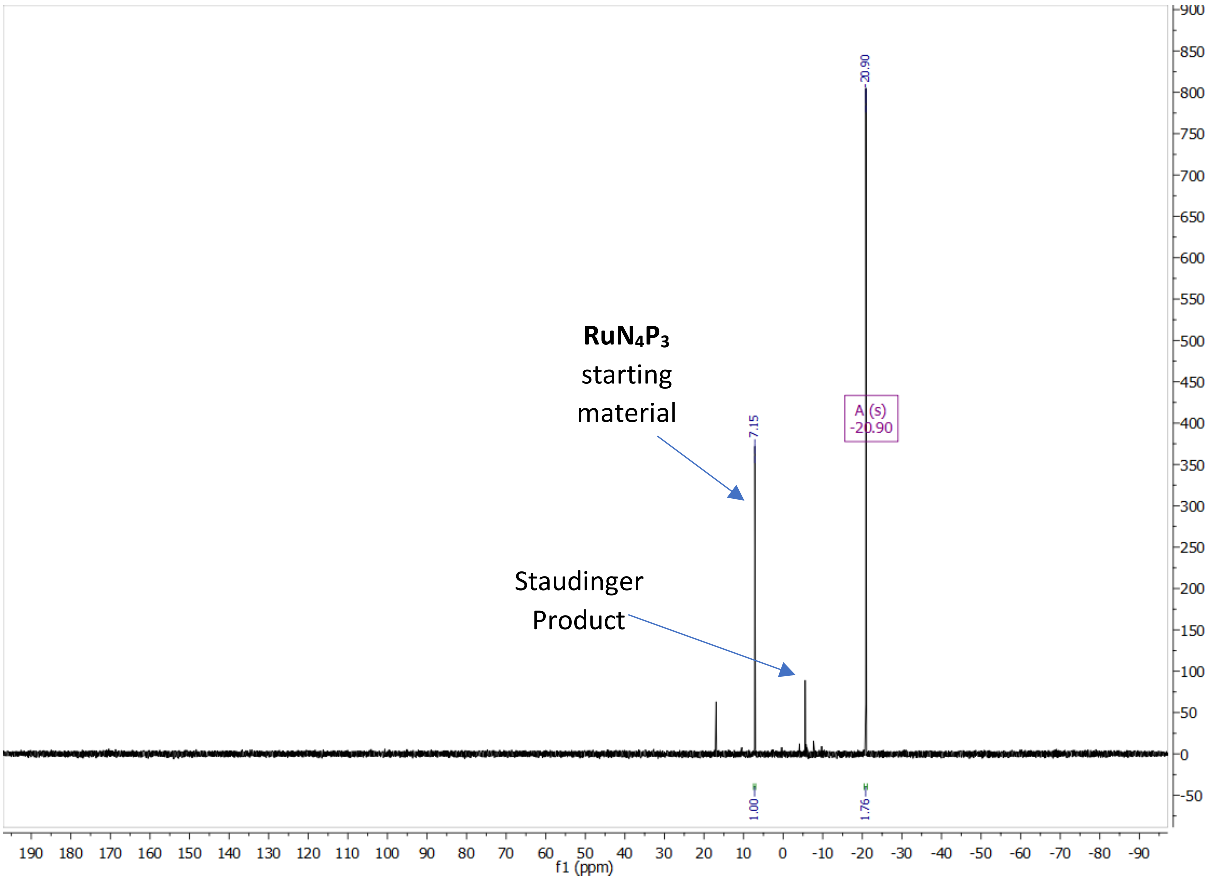


Figure S12. *^{31}P NMR spectrum of Ru(NAr)$_2$(PMe$_3$)$_2$ (**1**) after extraction and repeated recrystallization in C$_6$D$_6$.*

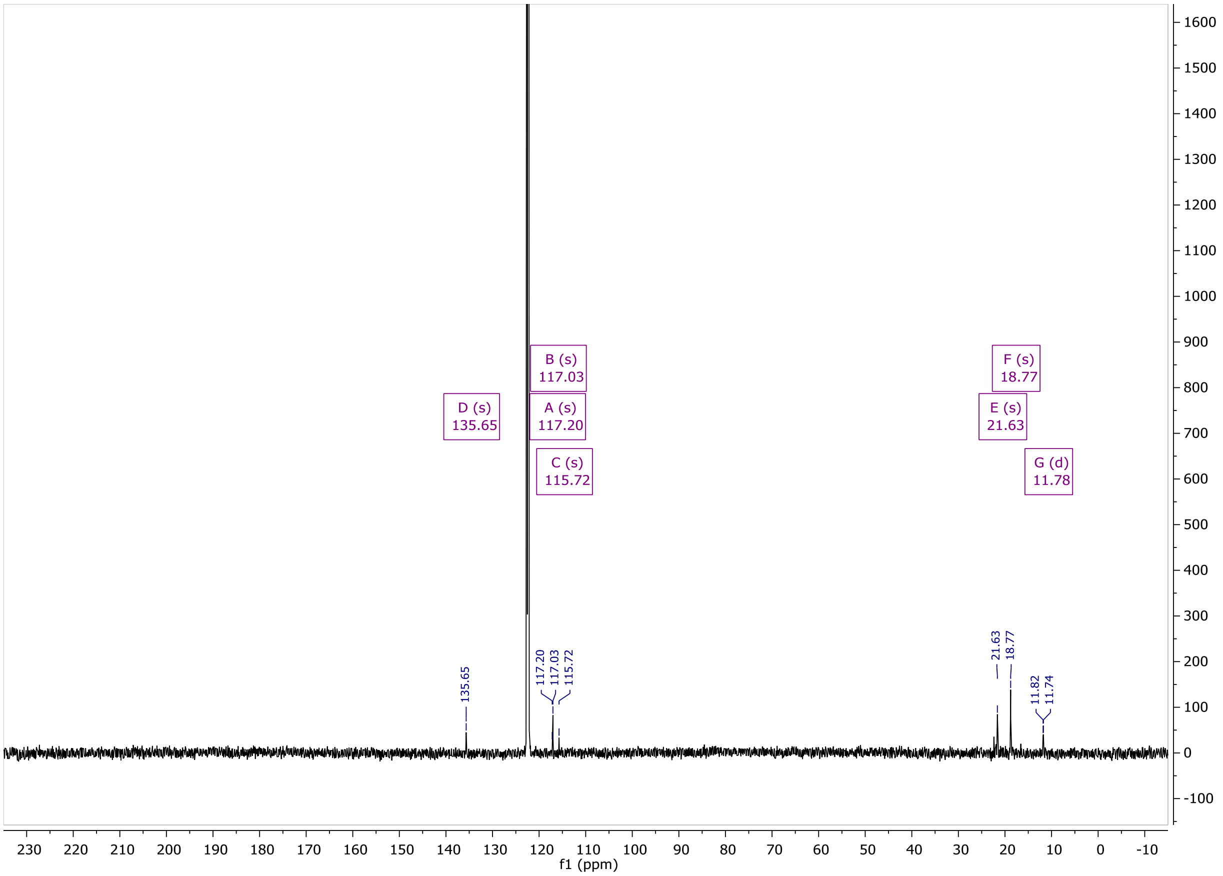


Figure S13. *^{13}C NMR spectrum of $Ru(NAr)_2(PMe_3)_2$ (**1**) in C_6D_6.*

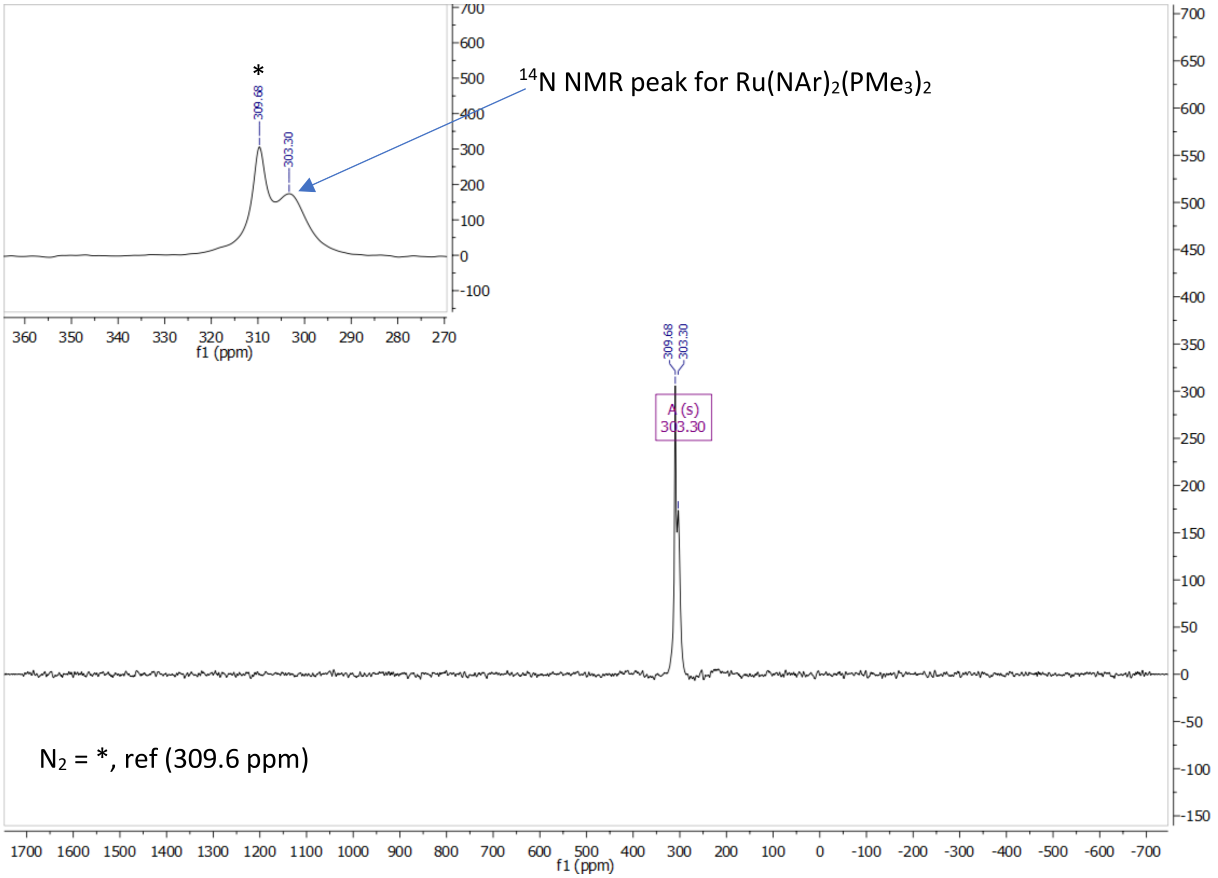


Figure S14. *^{14}N NMR of Ru(NAr)$_2$(PMe$_3$)$_2$ (**1**) in C_6D_6.*

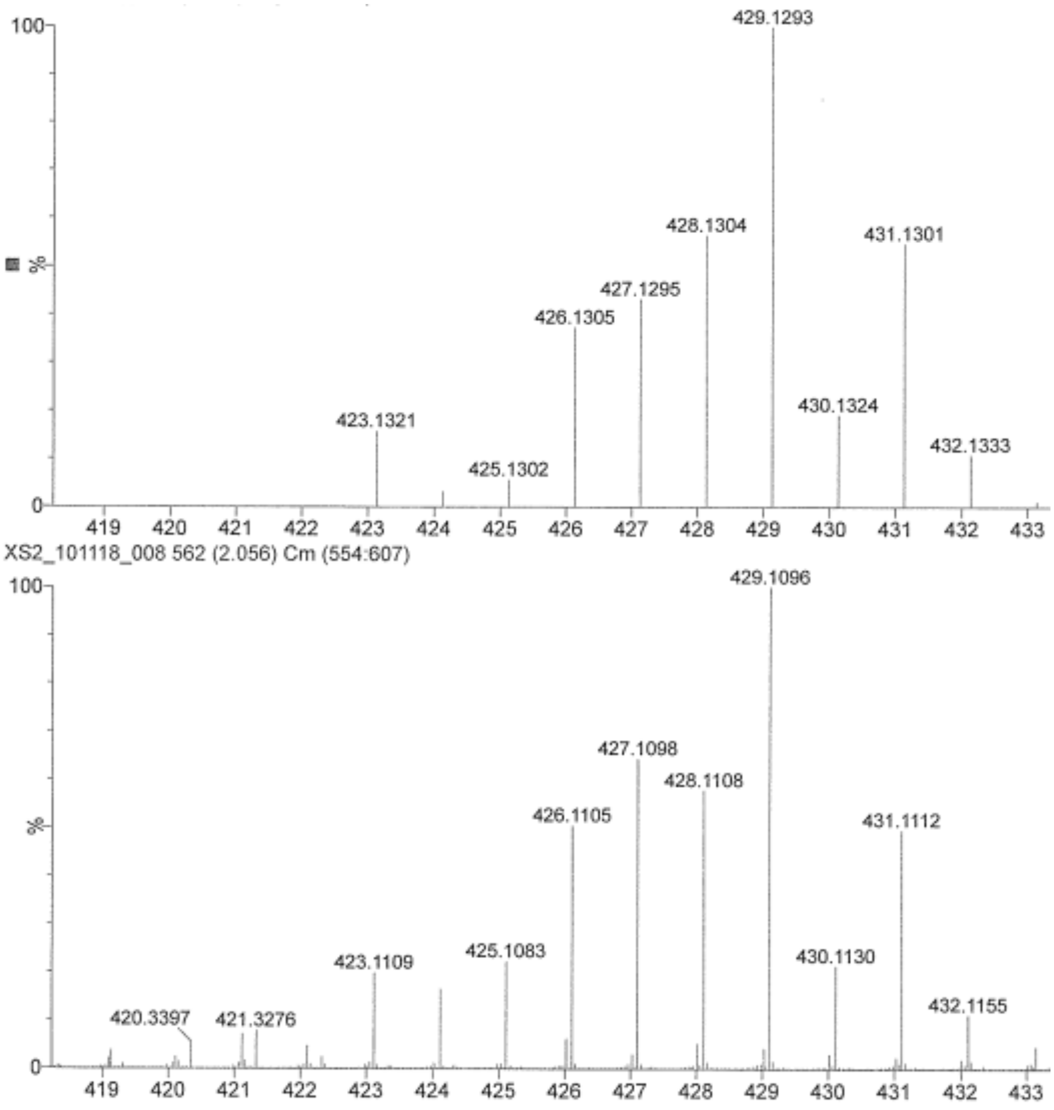


Figure S15. *QTOF-HRMS fragmentation patterns (*top*) calculated and (*bottom*) experimental for $Ru(NAr)_2(PMe_3)_2$ (**1**).*

$Ru(NAr_2)_2(\eta_2\text{-diphenylacetylene})$

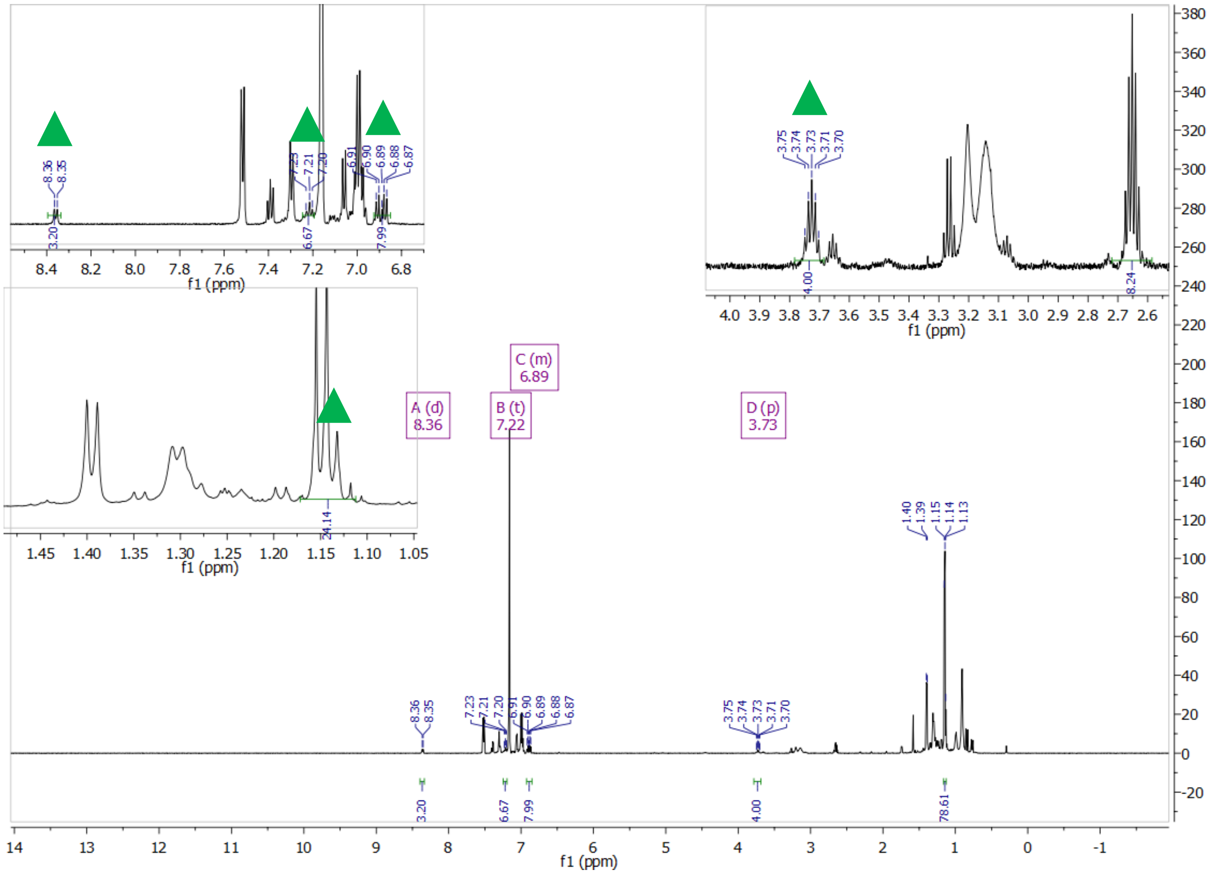


Figure S16. *^1H NMR spectrum of $Ru(NAr)_2(\eta_2\text{-diphenylacetylene})$ containing diphenylacetylene (excess) and H_2NAr impurities.*

Note: in the above spectrum, peaks assigned with multiplet values and denoted by green triangles correspond to the title complex formed *in situ*. The peaks noted match very closely the splitting pattern and chemical shifts of those reported for the osmium analogue of this complex by Schrock, et. al.[4]

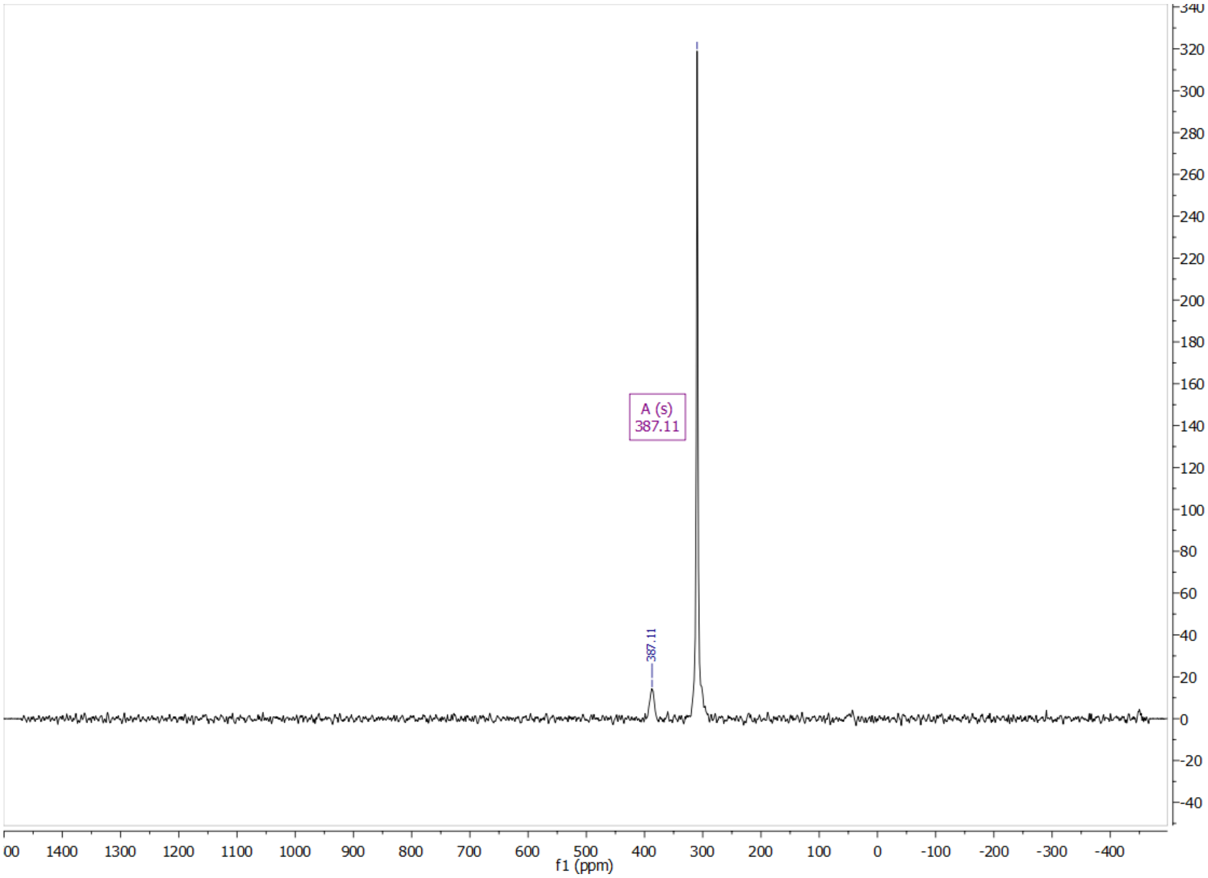


Figure S17. *^{14}N NMR spectrum of Ru(NAr)$_2$(η_2-diphenylacetylene) in C_6D_6.*

$Ru(\kappa_2(N,C)\text{-}1\text{-}(NH)\text{-}2\text{-}(CH_2)\text{-}4,6\text{-}Me_2C_6H_2)(PPhMe_2)_4$ (***5***)

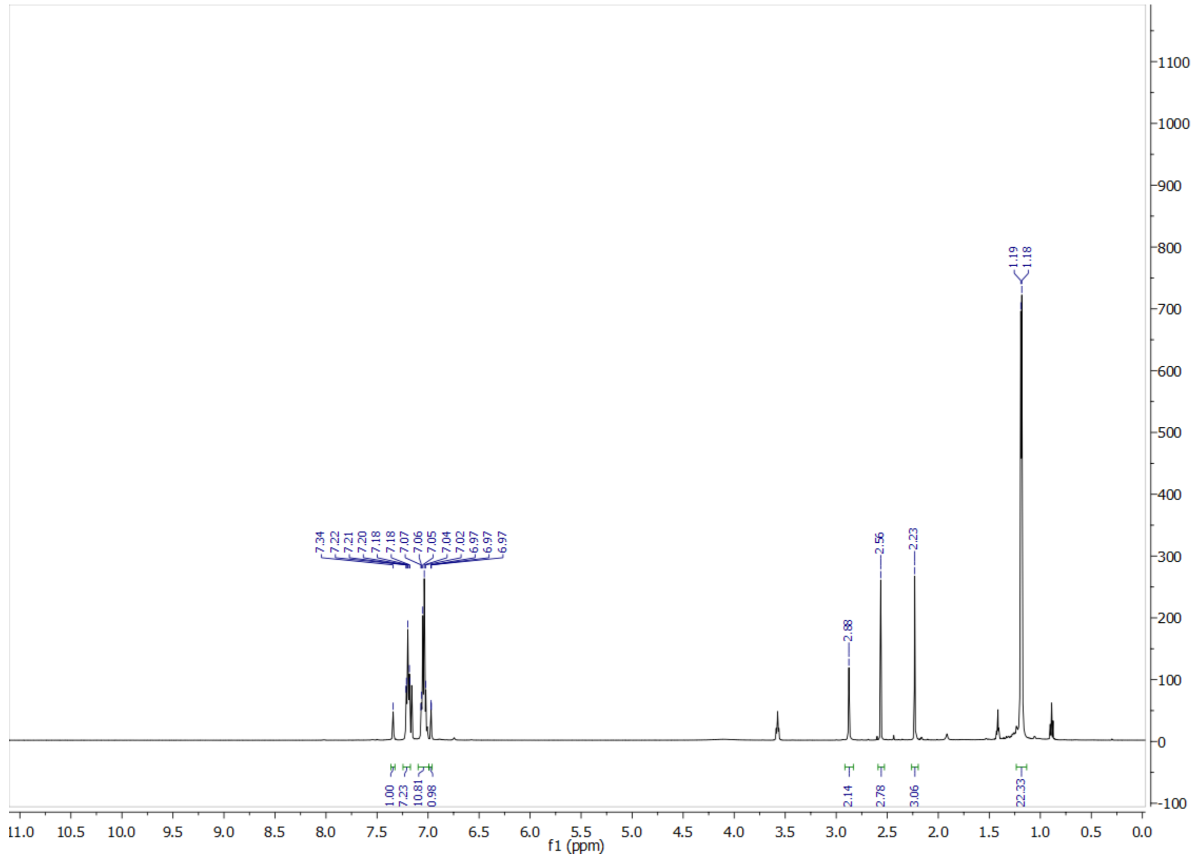


Figure S18. ^1H NMR of *$Ru(\kappa_2(N,C)\text{-}1\text{-}(NH)\text{-}2\text{-}(CH_2)\text{-}4,6\text{-}Me_2C_6H_2)(PPhMe_2)_4$* (***5***) in C_6D_6.

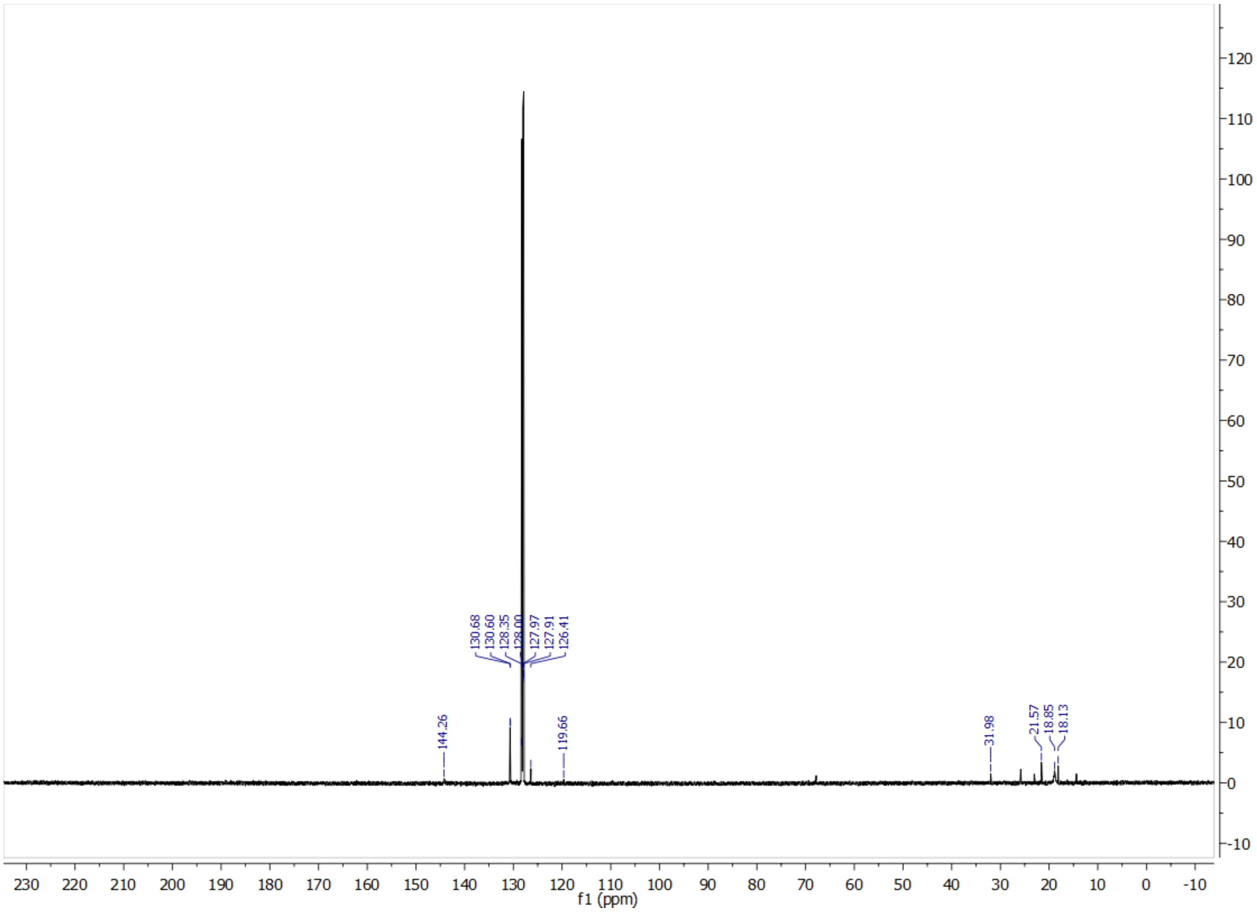


Figure S19. *^{13}C NMR of Ru(κ_2(N,C)-1-(NH)-2-(CH$_2$)-4,6-Me$_2$C$_6$H$_2$)(PPhMe$_2$)$_4$ (**5**) in C$_6$D$_6$.*

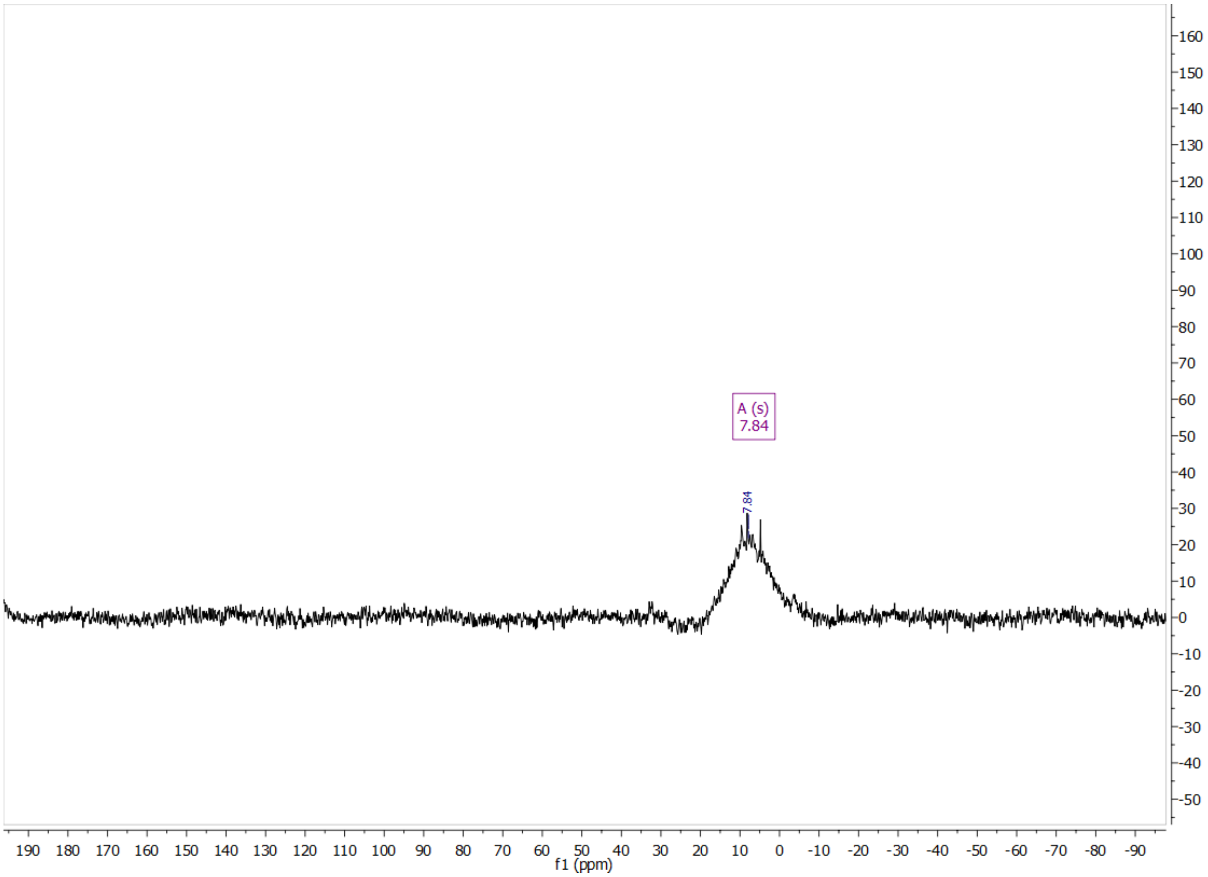


Figure S20. *^{31}P NMR of Ru(κ_2(N,C)-1-(NH)-2-(CH$_2$)-4,6-Me$_2$C$_6$H$_2$)(PPhMe$_2$)$_4$ (**5**) in C$_6$D$_6$.*

Ru(NAr)(PPhMe$_2$)$_3$ (**4**)

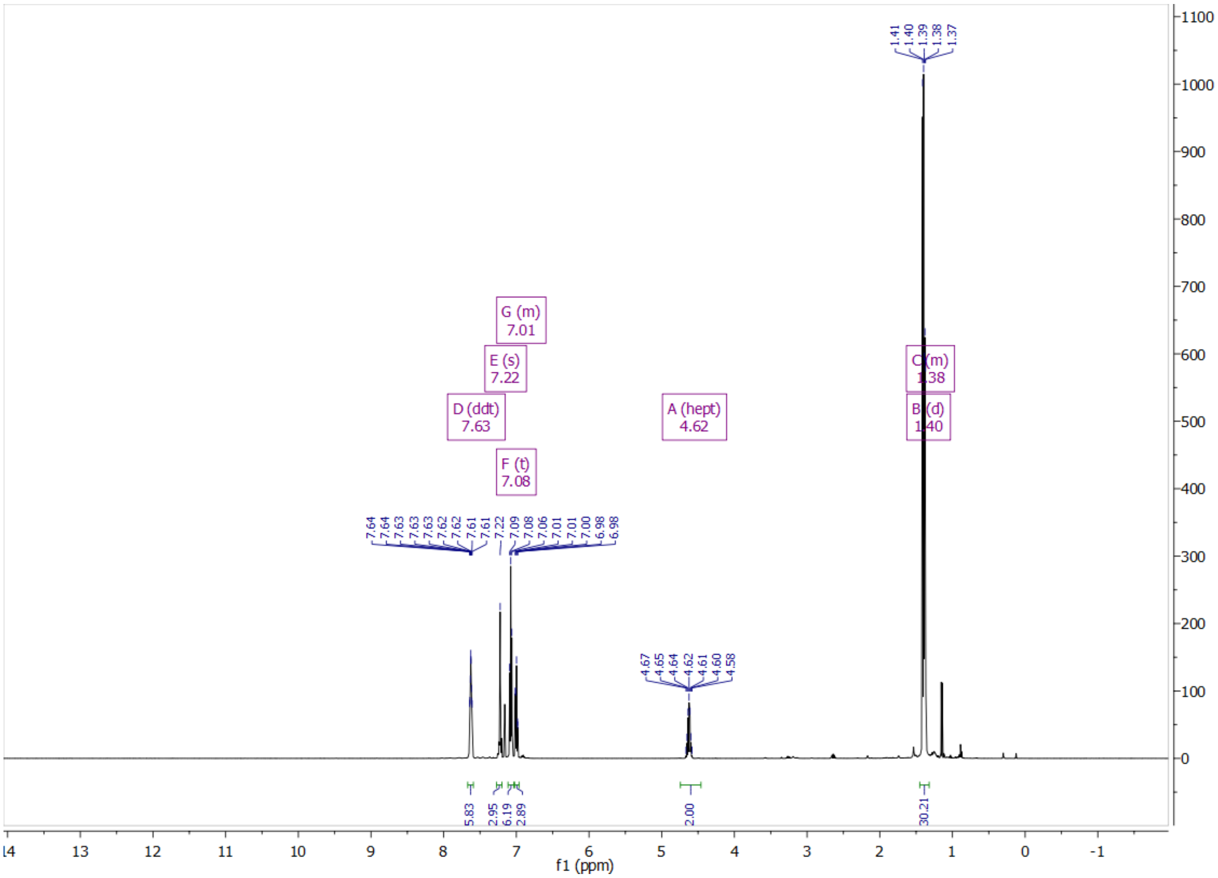


Figure S21. *^{1}H NMR of Ru(=NAr)(PPhMe$_2$)$_3$ (**4**) in C_6D_6.*

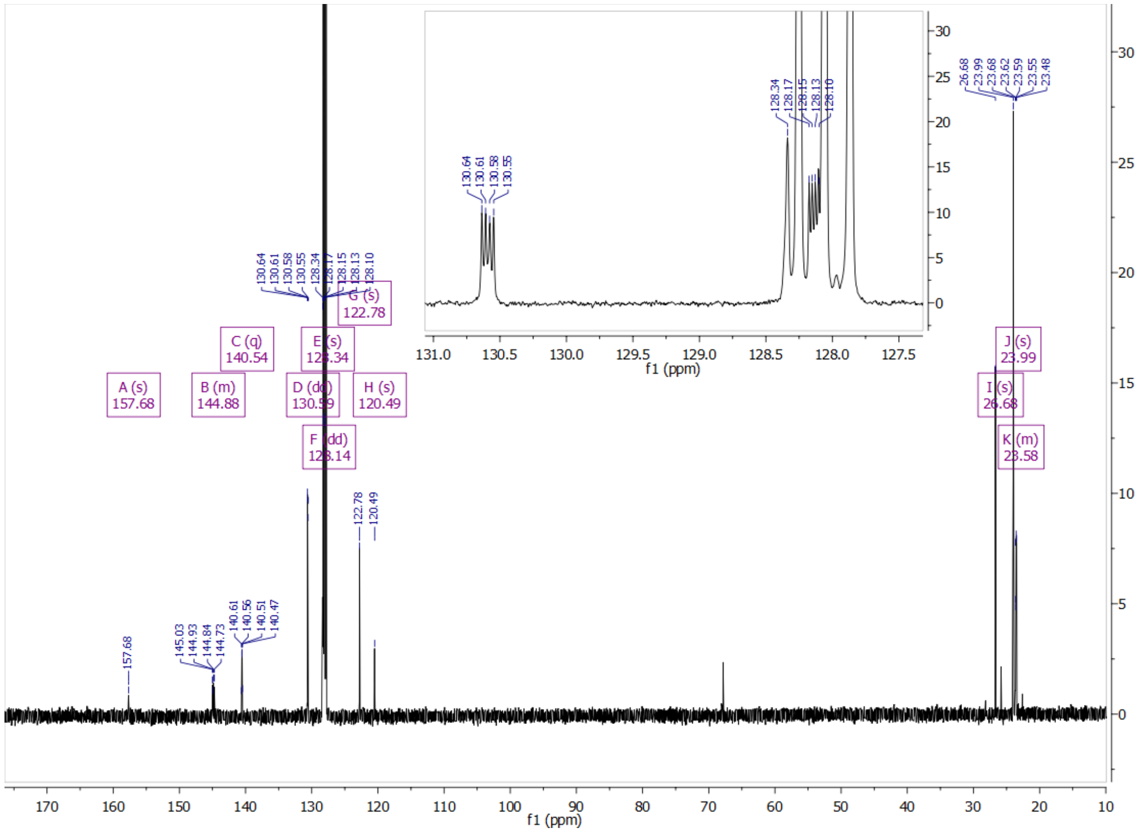


Figure S22. *^{13}C NMR of Ru(=NAr)(PPhMe$_2$)$_3$ (**4**) in C_6D_6.*

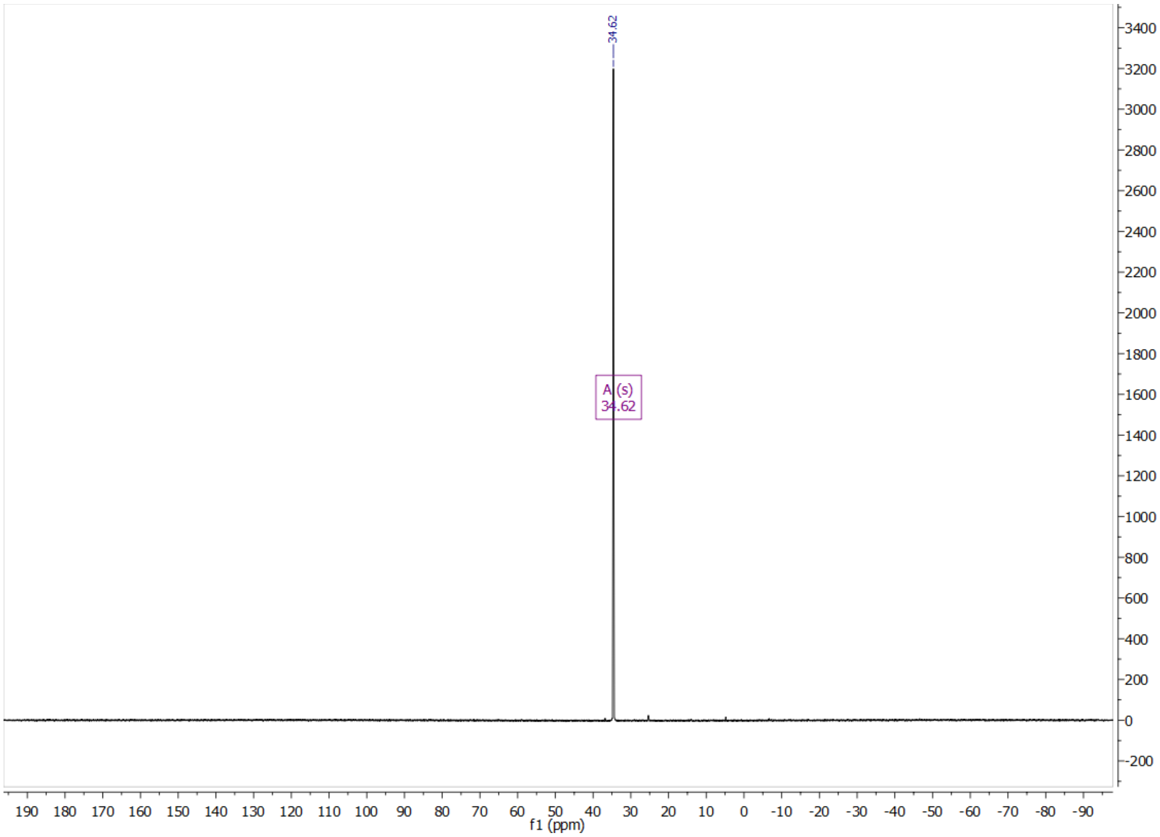


Figure S23. *^{31}P NMR of Ru(=NAr)($PPhMe_2$)$_3$ (**4**) in C_6D_6.*

Crude NMR Spectra for Photolysis of **3c**

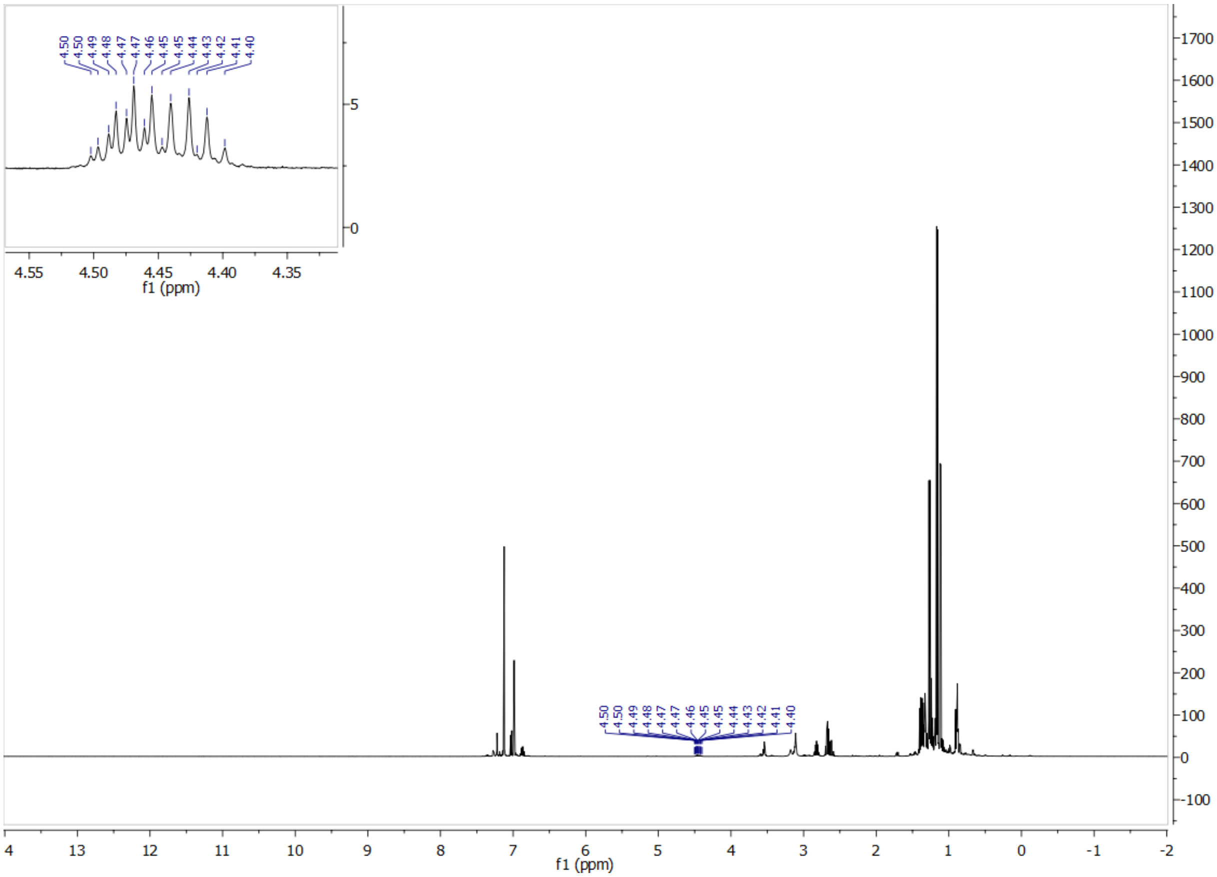


Figure S24. *^{1}H NMR after photolysis of Ru{N_4(Ar)Ar*}(PMe_3)$_3$ (**3c**). Spectrum in C_6D_6.*

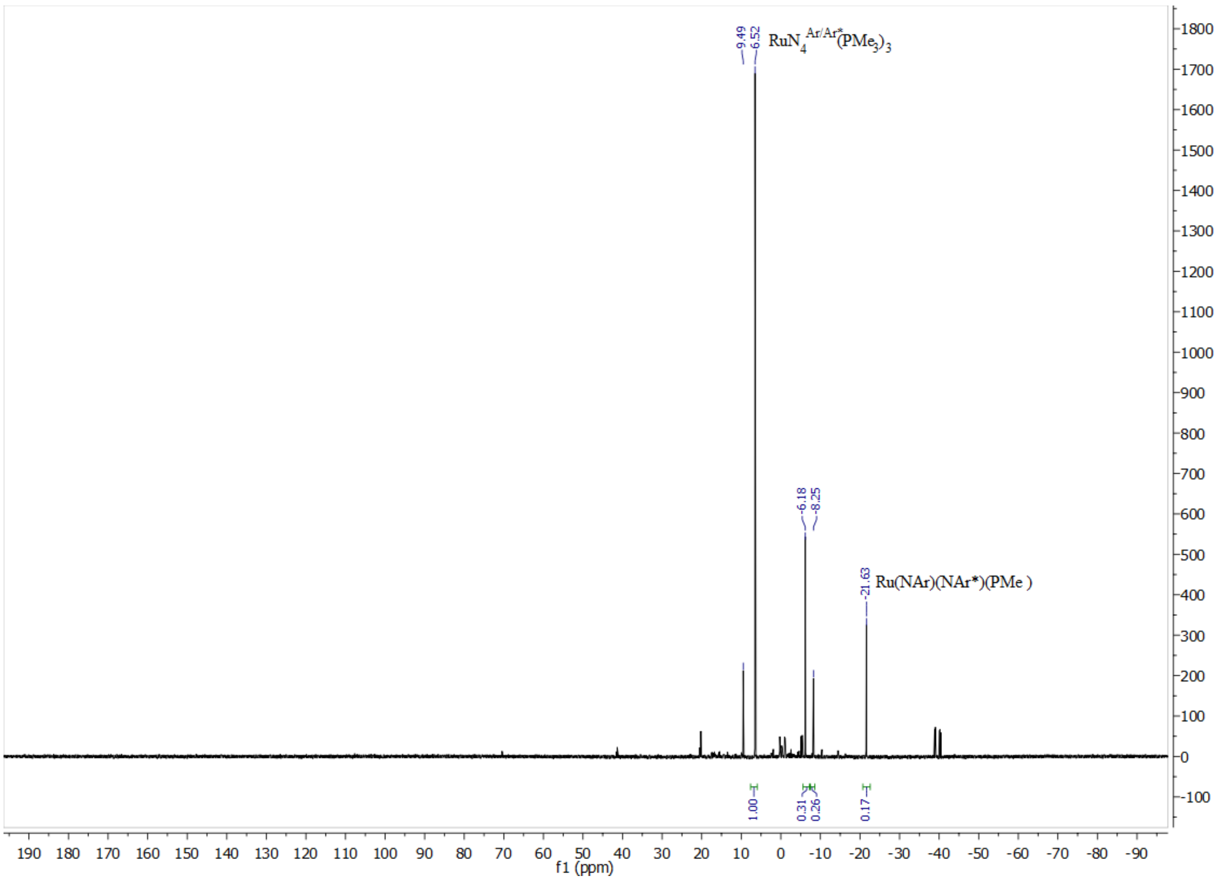


Figure S25. *^{31}P NMR after photolysis of Ru{N$_4$(Ar)Ar*}(PMe$_3$)$_3$ (**3c**). Spectrum in C$_6$D$_6$.*

^{14}N NMR Spectra of Planar $Os(NAr)_2(X/L)_2$ Complexes

$Os(NAr)_2(PMe_3)_2$

The complex $Os(NAr)_2(PMe_3)_2$ has been previously reported. The complex was prepared according to the reported procedure, and spectral properties matched those previously reported (^{1}H, ^{13}C, and ^{31}P NMR; unit cell determination by single crystal X-ray diffraction).[5] Here we report the ^{14}N NMR spectrum of the complex for comparison to the Ru analogue.

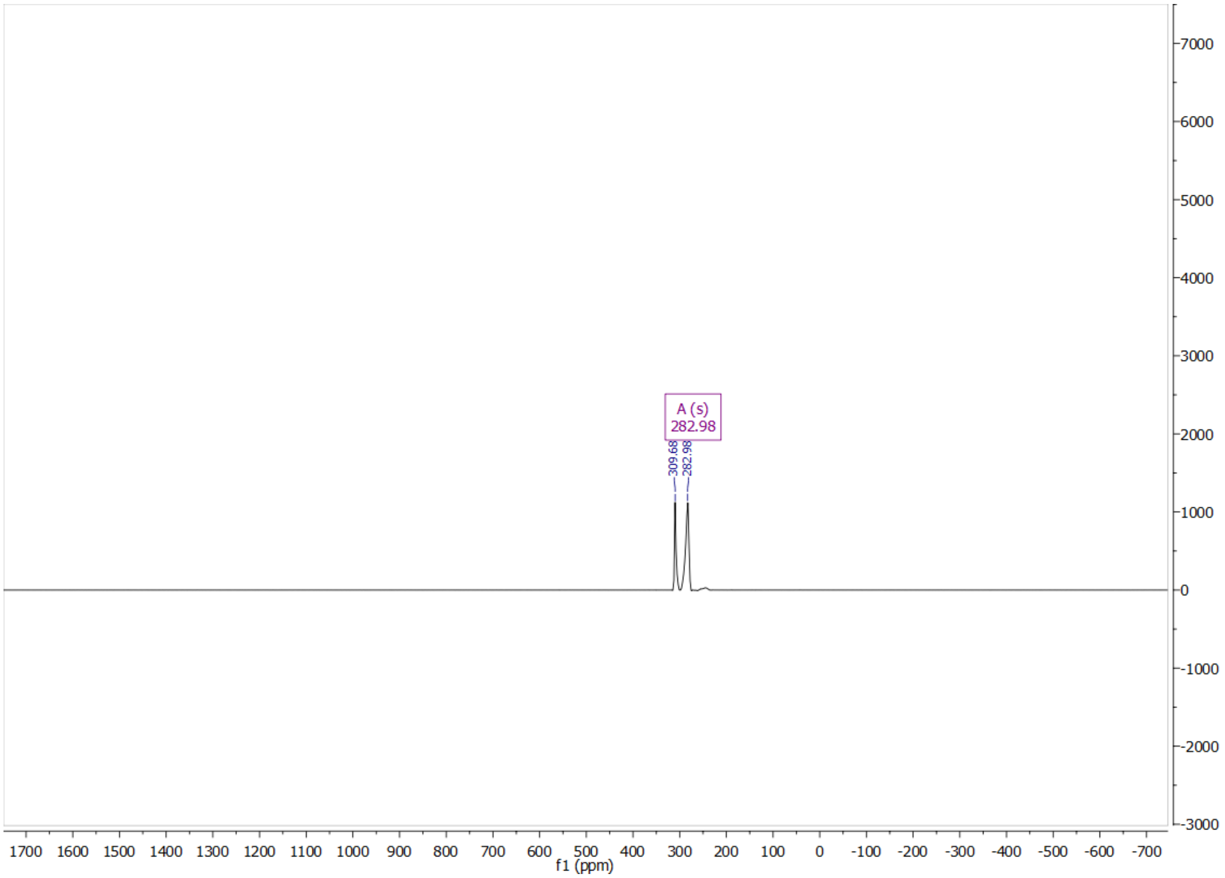


Figure S26. *^{14}N NMR spectrum of $Os(NAr)_2(PMe_3)_2$ in C_6D_6. The peak for the complex is at 282.9 ppm; the peak at 309.6 ppm is for dissolved N_2.*

Os(NAr)$_2$(η_2-diphenylacetylene)

The complex Os(NAr)$_2$(η_2-diphenylacetylene) has been previously reported. The complex was prepared according to the reported procedure, and spectral properties matched those previously reported (^{1}H and ^{13}C NMR).[5] Here we report the ^{14}N NMR spectrum of the complex for comparison to the Ru analogue.

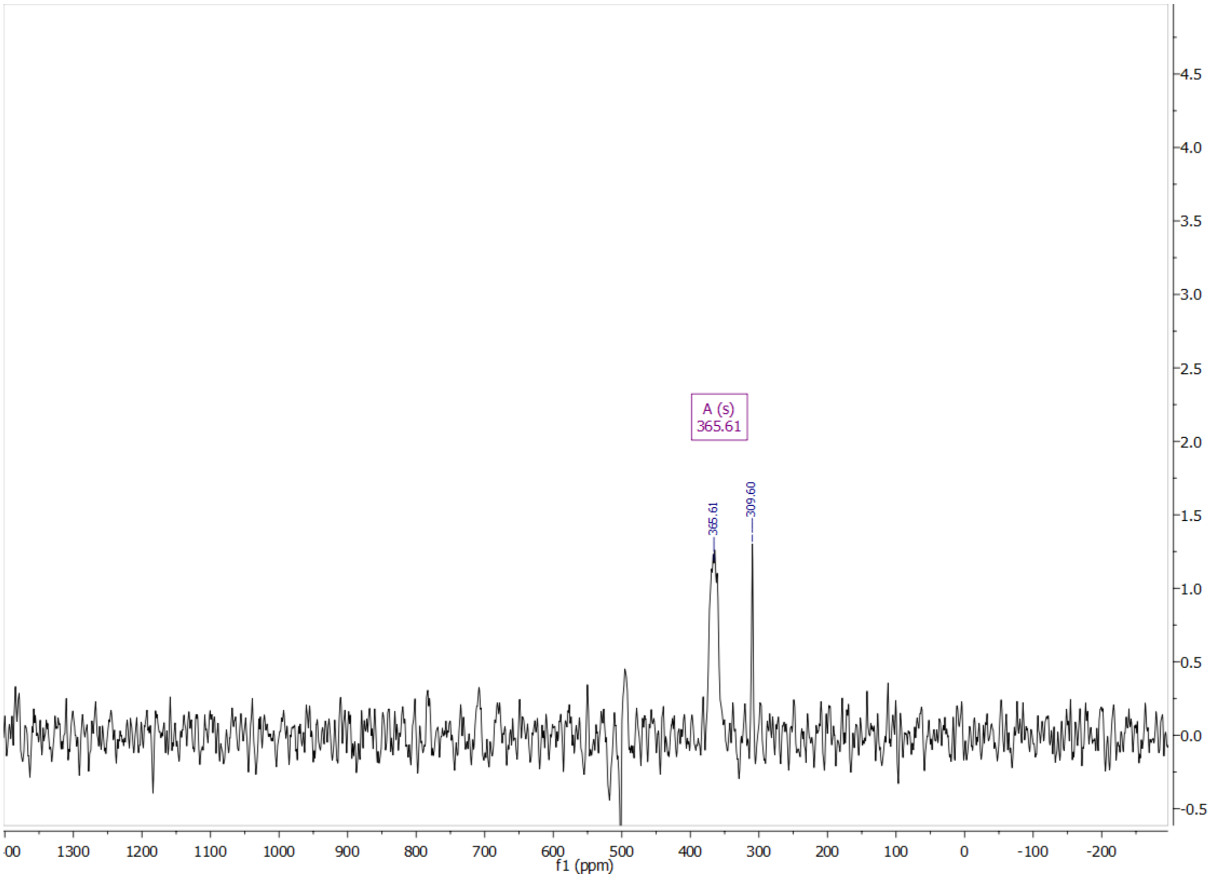


Figure S27. *^{14}N NMR spectrum of Os(NAr)$_2$(η_2-diphenylacetylene) in C_6D_6. The peak for the complex is at 365.6 ppm; the peak at 309.6 ppm is for dissolved N_2.*

Os(NAr)$_2$O$_2$

The complex Os(NAr)$_2$(O)$_2$ has been previously reported. The complex was prepared according to the reported procedure, and spectral properties matched those previously reported (^{1}H and ^{13}C NMR).[4] Here we report the ^{14}N NMR spectrum of the complex for comparison of the imido N shifts to the other oxidation states of Os(NAr)$_2$(L)$_x$ complexes (above) and the Ru analogues.

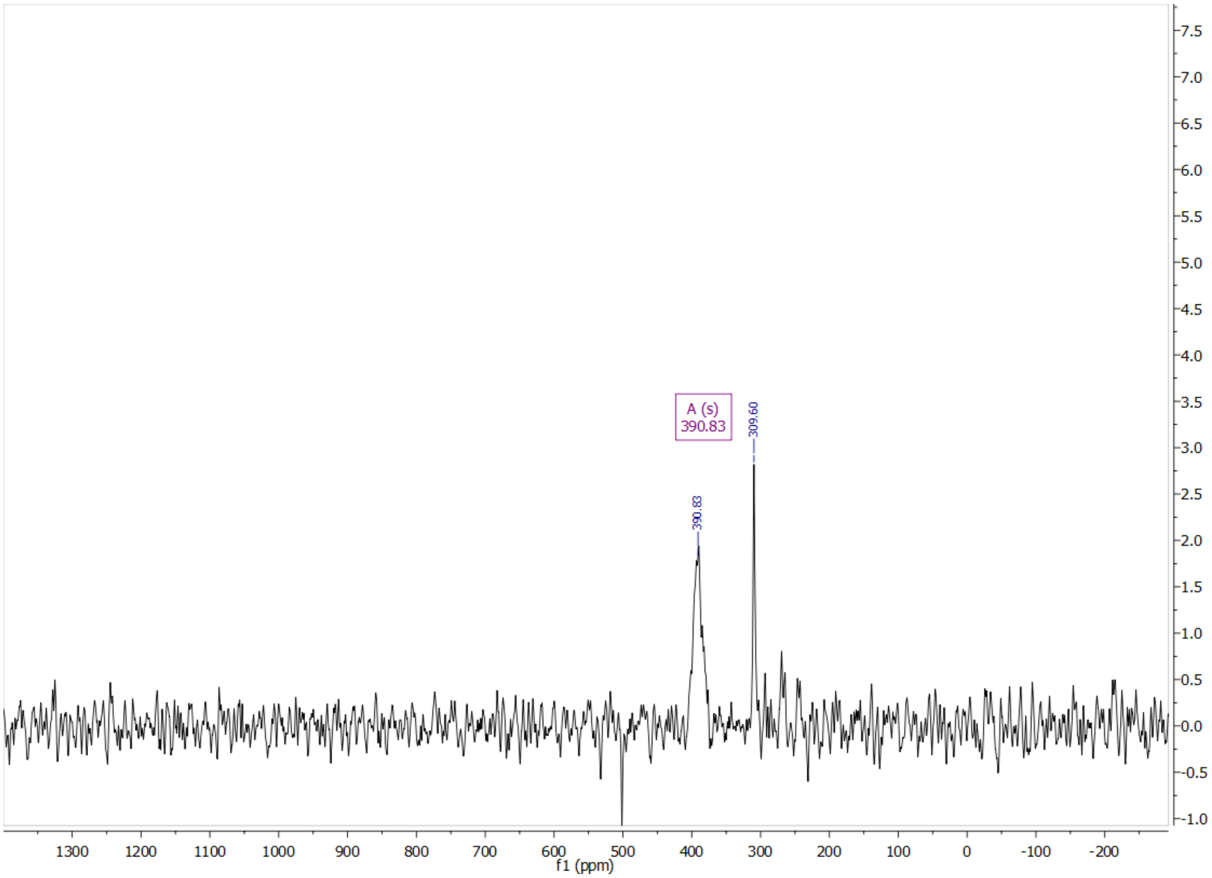


Figure S28. *^{14}N NMR spectrum of Os(NAr)$_2$O$_2$ in C$_6$D$_6$. The peak for the complex is at 390.8 ppm; the peak at 309.6 ppm is for dissolved N$_2$.*

Staudinger product: Me_3PNAr

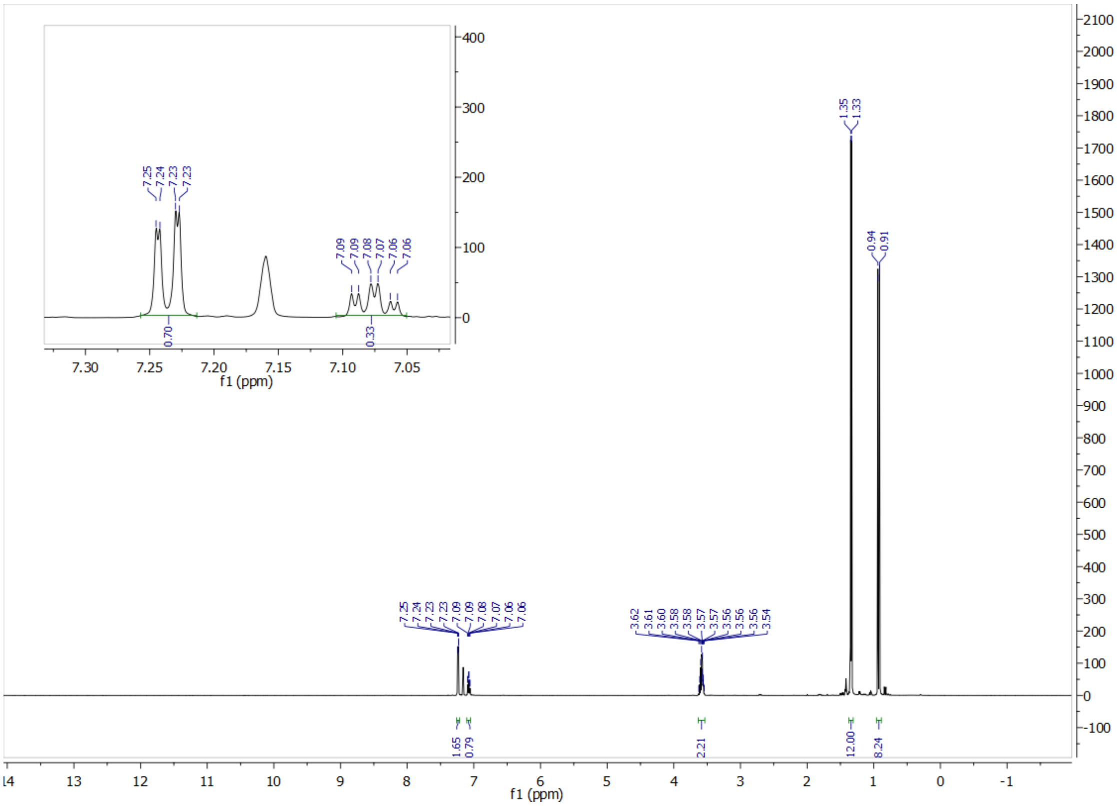


Figure S29. ^1H NMR of Me_3PNAr in C_6D_6.

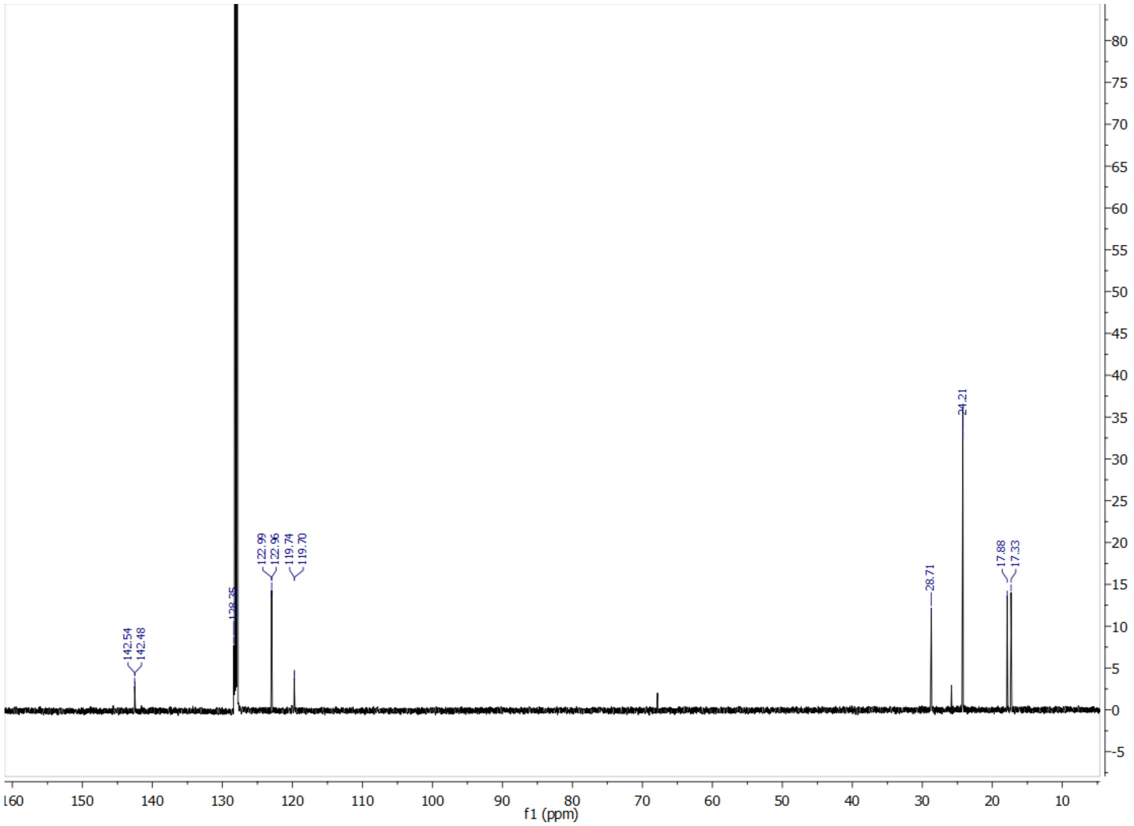


Figure S30. *^{13}C NMR of Me_3PNAr in C_6D_6.*

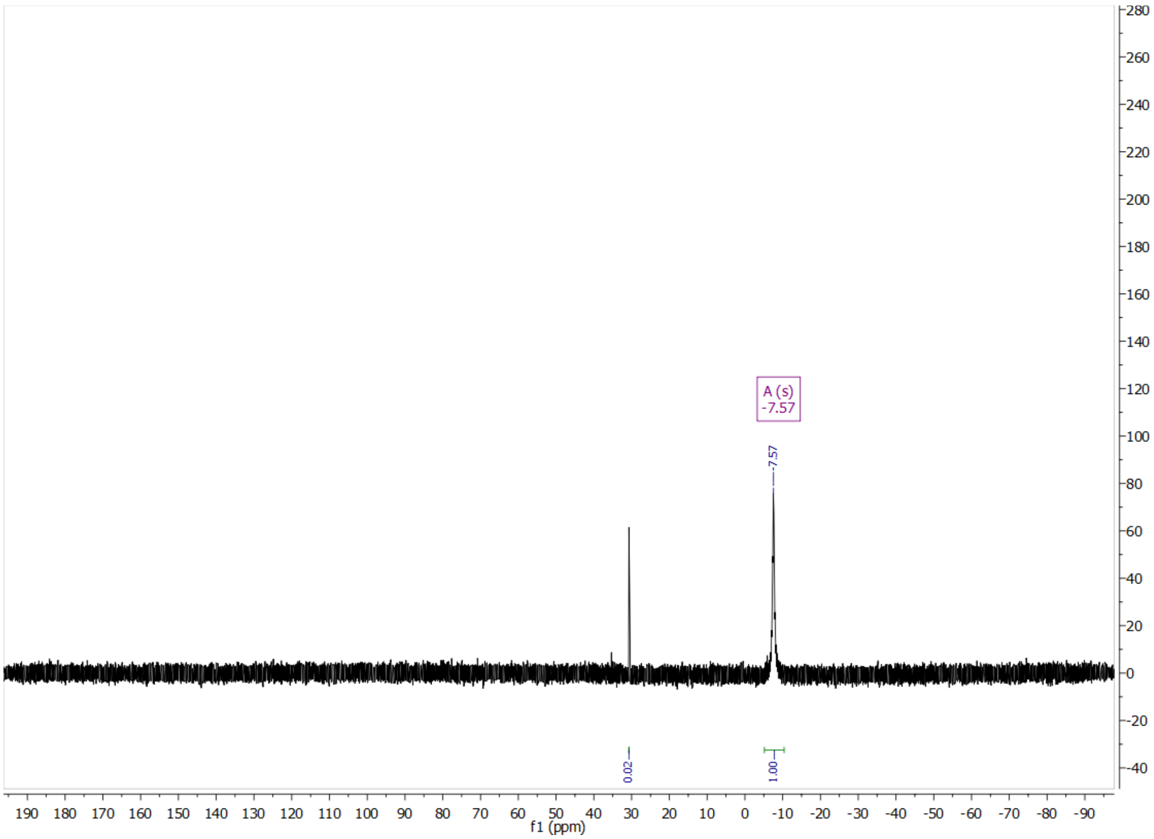


Figure S31. *^{31}P NMR spectrum of P(NAr)Me$_3$ in C$_6$D$_6$.*

UV-Vis Spectra for Ru Complexes

$Ru(N_4Ar_2)(PMe_3)_3$ (**3a**)

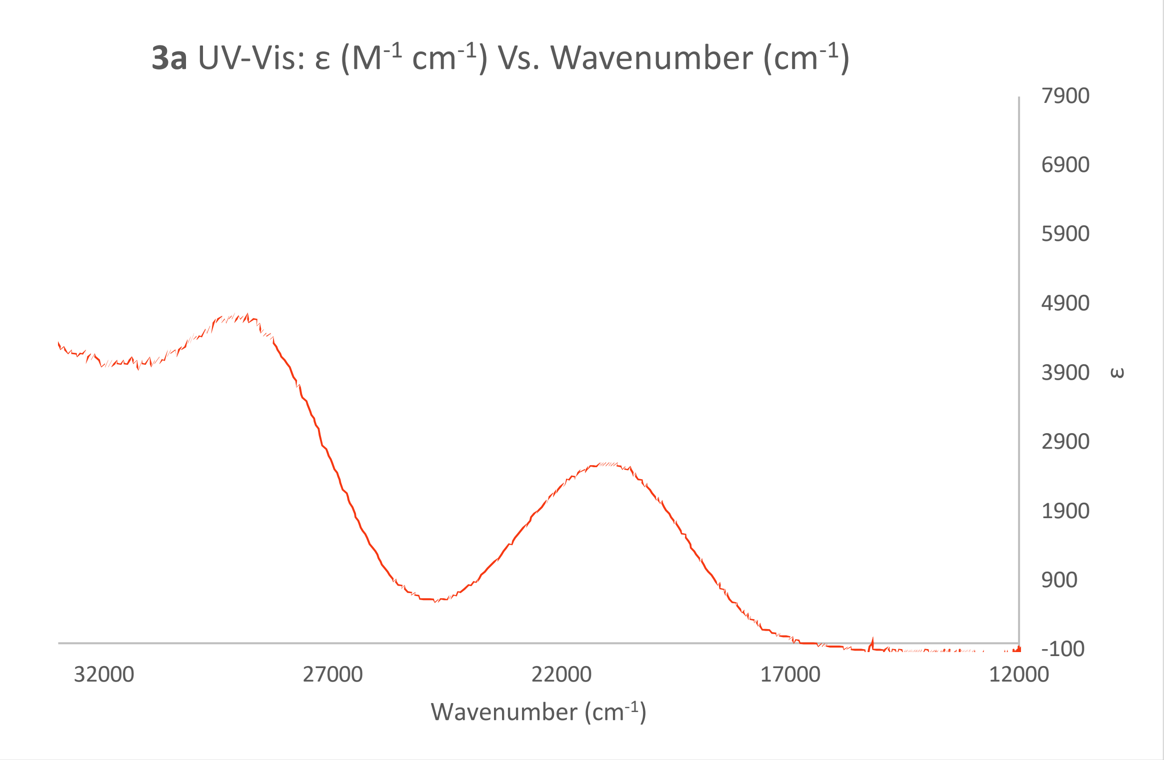


Figure S32. *Plot of ε vs. wavenumber for **3a** (0.000203 M in THF).*

Ru(NAr)$_2$(PMe$_3$)$_2$ (**1**)

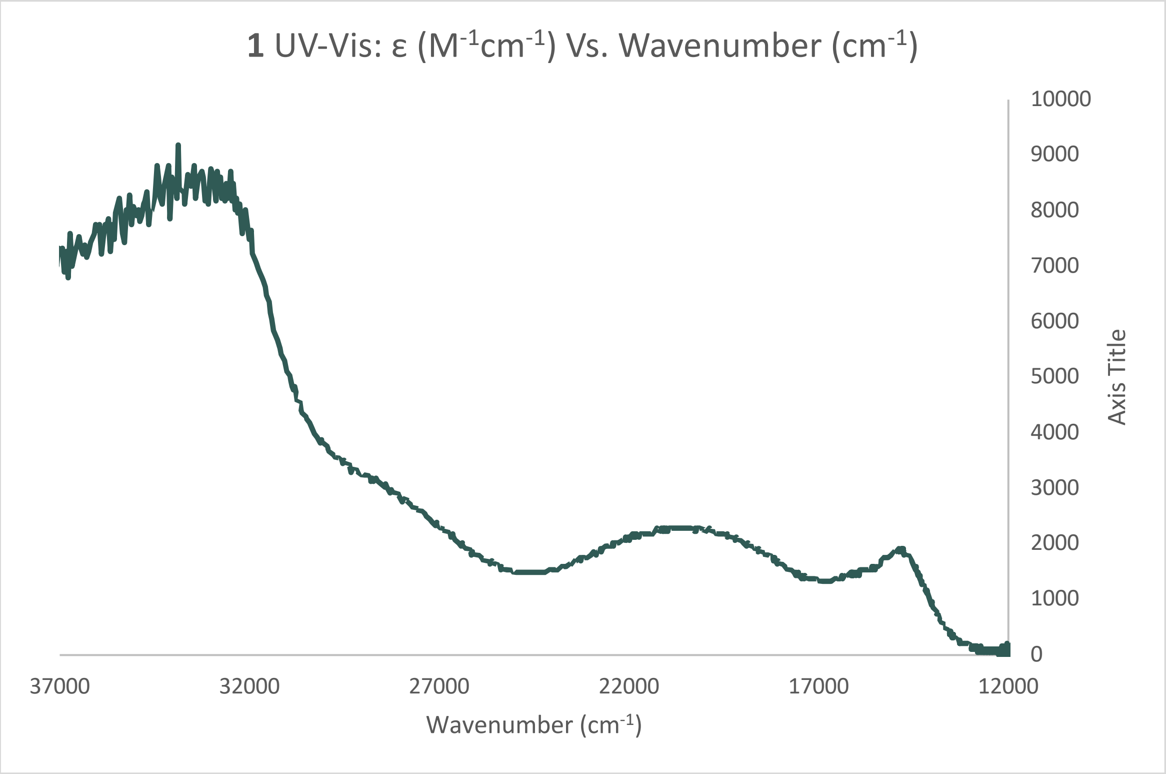


Figure S33. *Plot of ε vs wavenumber for Ru(NAr)$_2$(PMe$_3$)$_2$ (**1**) (0.000188 M in THF).*

Ru{N_4Ar(Mes)}(PMe_3)$_3$ (**3b**)

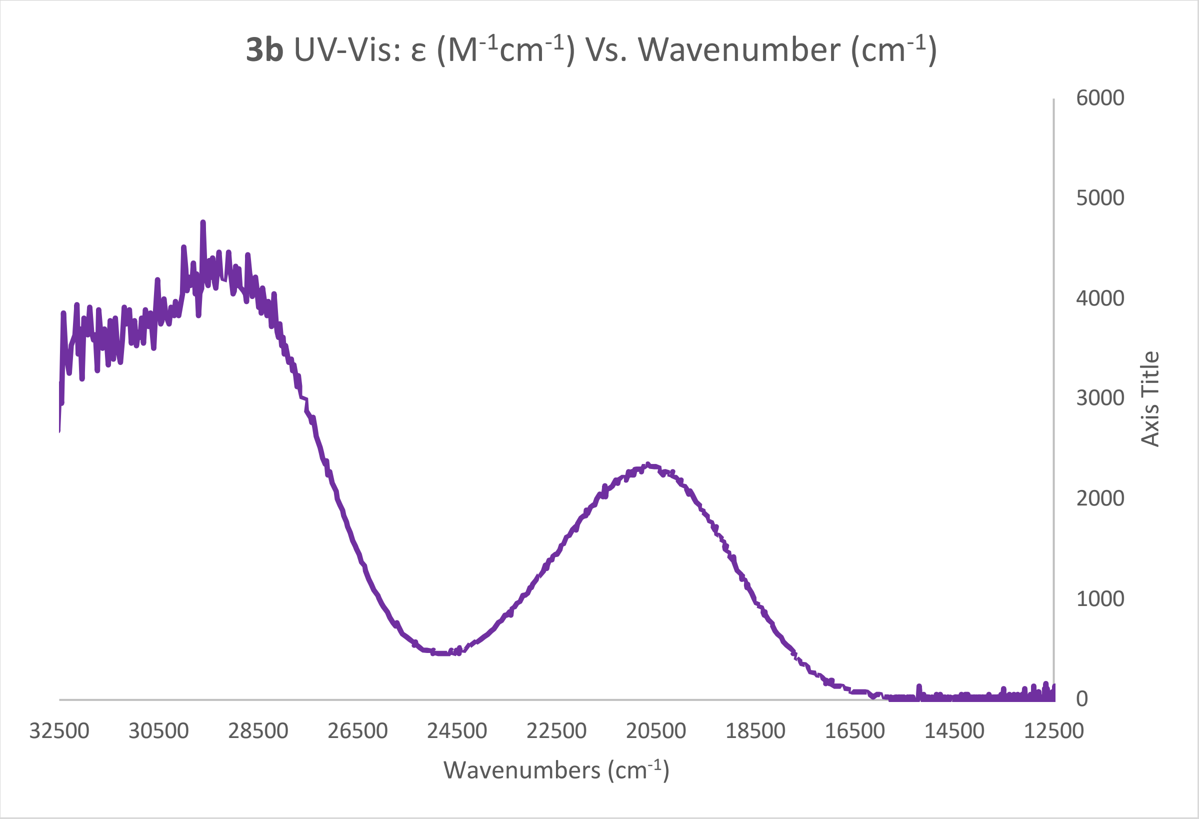


Figure S34. *Plot of ε vs wavenumber for **3b** (0.00030 M in THF)*

Ru{N_4Ar(Ar*)}($(PMe_3)_3$) (**3c**)

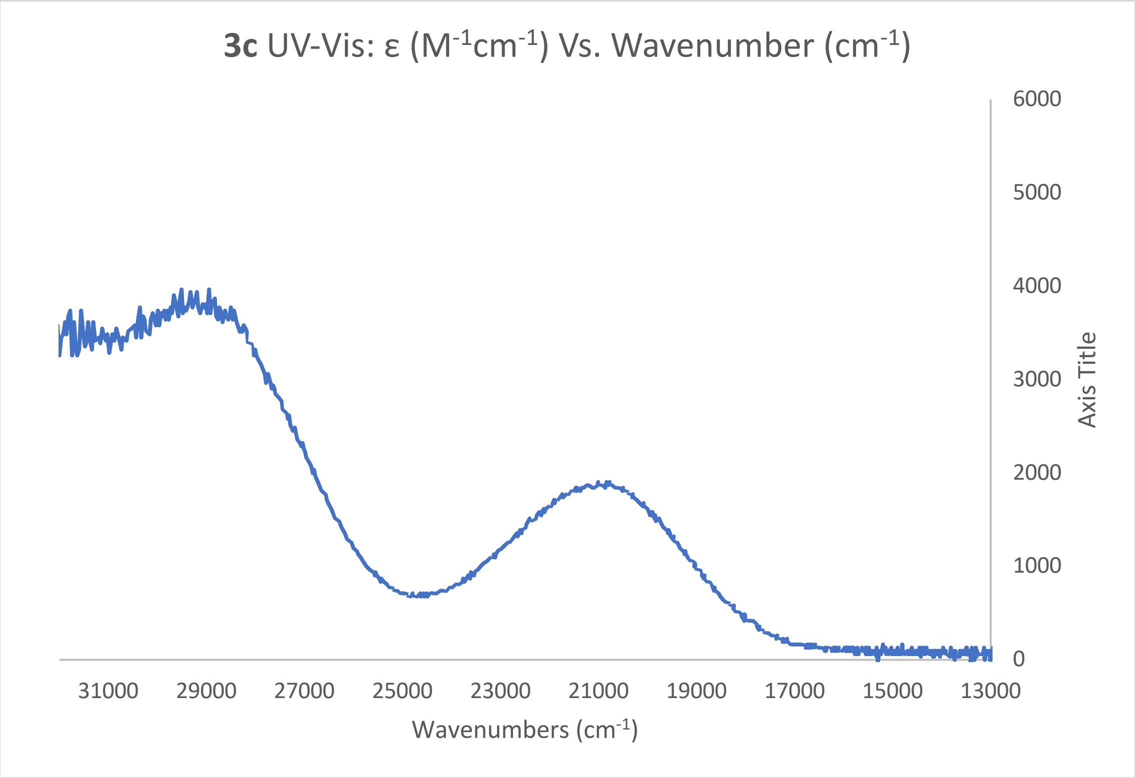


Figure S35. *Plot of ε vs wavenumber for* ***3c*** *(0.00031 M in THF).*

Absorption Spectrum Overlay for **3a** and **1** (0.0002 M in THF)

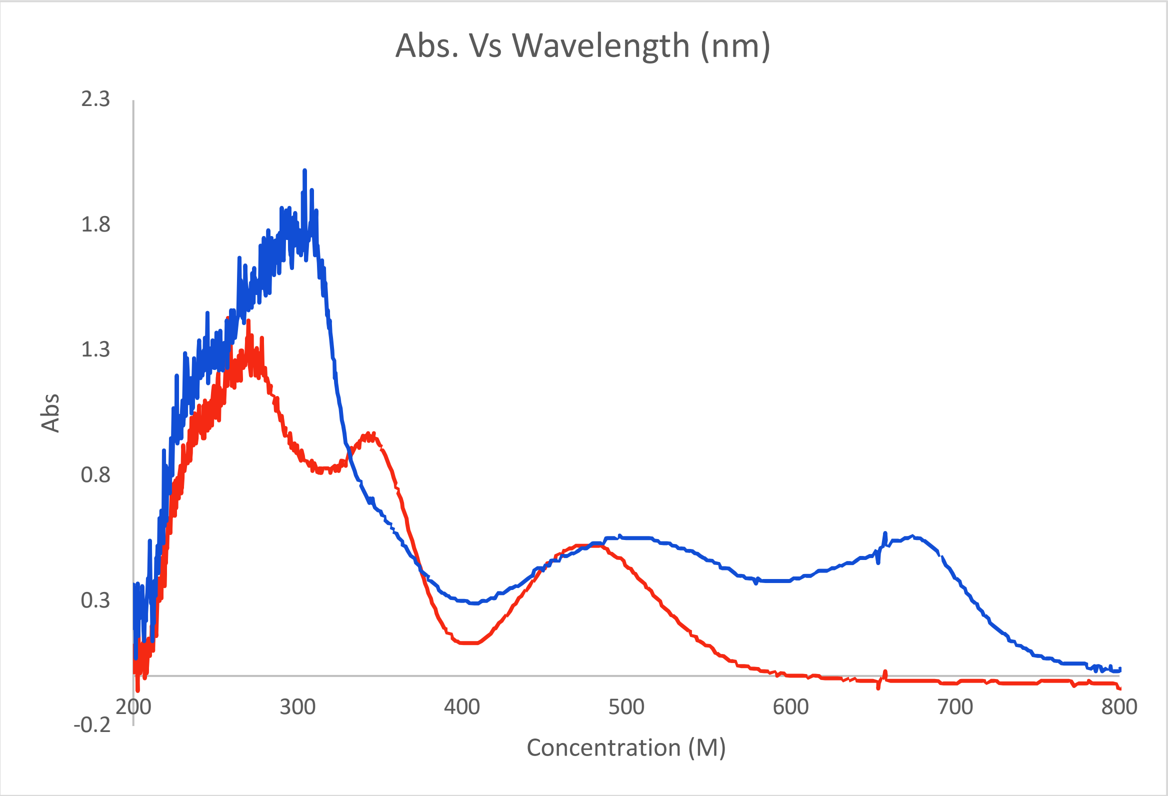


Figure S36. Overlay of plots of Abs Vs Wavelength for tetrazene **3a** (orange) starting material and Ru(NAr)$_2$(PMe$_3$)$_2$ (**1**) (blue) product for the photochemical synthesis process. Both plots were recorded at a concentration of 0.0002 M in THF, which was the typical concentration employed for bulk photolysis. Competing strong absorption features dominate the spectrum, which is the major proposed reason for the conversion limit of 25%.

References:

1. Park, J. Y.; Kim, Y.; Bae, D. Y.; Rhee, Y. H.; Park, J., Ruthenium Bisammine Complex and Its Reaction with Aryl Azides. *Organometallics* **2017,** *36* (18), 3471-3476.

2. Aldrich, K. E. F., B. S.; Singh, A. K.; Staples, R. J.; McCracken, J.; Levine, B.; Smith, M. R.; Odom, A. L. , *Inorganic chemistry* **2019**.

3. Singh, A. K.; Levine, B. G.; Staples, R. J.; Odom, A. L., A 4-coordinate Ru(II) imido: unusual geometry, synthesis, and reactivity. *Chemical communications* **2013,** *49* (92), 10799-801.

4. Schofield, M. H.; Kee, T. P.; Anhaus, J. T.; Schrock, R. R.; Johnson, K. H.; Davis, W. M., Osmium imido complexes: synthesis, reactivity, and SCF-X.alpha.-SW electronic structure. *Inorganic chemistry* **1991,** *30* (19), 3595-3604.

5. Wolf, J. R.; Bazan, G. C.; Schrock, R. R., Exchange of oxo ligands in osmium tetroxide with imido ligands in bis(arylimido)bis(tert-butoxo)molybdenum complexes, Mo(NAr)2(O-tert-Bu)2. A facile route to Os(NAr)2O2 and Os(NAr)3O and osmium(IV) complexes of the type Os(NAr)2L2 (NAr = N-2,6-C6H3-iso-Pr2; L = a phosphine). *Inorganic chemistry* **1993,** *32* (19), 4155-4156.