

The Mechanism of Acceptorless Amine Double Dehydrogenation by *N,N,N*-Amide Ruthenium (II) Hydrides: A Combined Experimental and Computational Study

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General Considerations

All reactions were conducted under a dry nitrogen atmosphere using standard Schlenk techniques, or under nitrogen atmosphere in a glovebox, unless otherwise stated. All reagents were purchased from commercial vendors. NaO^tBu (Sigma-Aldrich), NaHBET₃ (Sigma-Aldrich), and (trimethylsilyl)methylolithium (Sigma-Aldrich) was used without further purification. 1-octylamine, benzylamine, 4-methylbenzylamine, and benzonitrile were distilled from CaH₂ under a nitrogen atmosphere and then stored over 3 Å molecular sieves for at least 24 h. Toluene-*d*₈ and C₆D₆ were degassed using evacuation/refill cycles and then stored over 3 Å molecular sieves for at least 24 h. The following compounds were synthesized according to literature methods: HRu(bMepi)(PPh₃)₂ (**1**),¹ Ru(bMepi)(PPh₃)Cl (**2**),¹ Ru(bpi)(PPh₃)Cl,² 6-(1-methylethyl)-2-pyridinamine,³ and Hb'Prpi.¹ The 3 Å molecular sieves were dried at 250 °C under dynamic vacuum for 24 h. Tetrahydrofuran (THF), dichloromethane (DCM), diethyl ether (Et₂O), pentane, and benzene (C₆H₆) were purified using a Glass Contour solvent purification system consisting of a copper catalyst, neutral alumina, and activated molecular sieves then passed through an in-line, 2 µm filter immediately before being dispensed.

NMR spectra were recorded on Varian Inova 500, Varian MR400, Varian vnmrs 500 and Varian vnmrs 700 spectrometers at ambient temperature, unless otherwise stated. ¹H and ¹³C shifts are reported in parts per million (ppm) relative to TMS with the residual solvent peak used as an internal reference. ³¹P spectra were referenced on a unified scale to their respective ¹H NMR spectra. The following abbreviations are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), multiplet (m), and triphenyl phosphine (PPh₃). ¹³C NMR resonances were observed as singlets unless otherwise stated. Solid state IR spectra were collected using a Nicolet iS10 spectrometer equipped with a diamond attenuated total reflectance (ATR) accessory. Elemental analyses were performed by Midwest Microlab, LLC and Atlantic Microlab, Inc.

General procedure for rate studies 1-octylamine dehydrogenation catalyzed by **1**

1-octylamine (82 µL, 0.5 mmol) was added to a 20 mL vial charged with **1** (4.7 mg, 0.005 mmol), dioxane (2.5 µL, 0.03 mmol), and toluene-*d*₈ (0.600 µL). The liquid was then transferred to a NMR tube equipped with a J Young valve. The sealed NMR tube was frozen and evacuated until reaching 0.200 Torr, then thawed. This process was repeated until a consistent atmosphere of 0.200 Torr was maintained. An initial ¹H NMR spectrum was then obtained. The NMR tube was then heated to the desired temperature

(100, 110, 120, 130, 140 °C), using an oil bath such that the NMR tube was completely submerged in oil. The formation of 1-octanenitrile was monitored by analyzing the ^1H NMR spectrum against dioxane as the internal standard. To confirm reproducibility, all kinetic experiments were performed in triplicate.

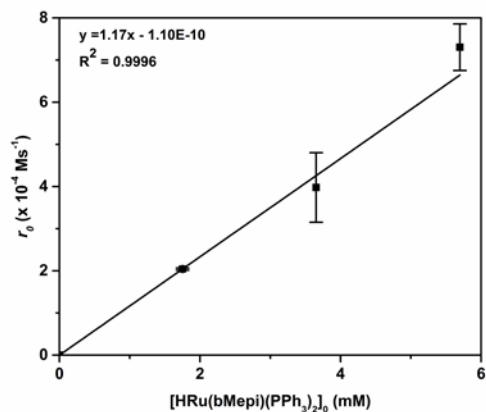


Figure S1. 1-octylamine dehydrogenation rate dependence on [1]

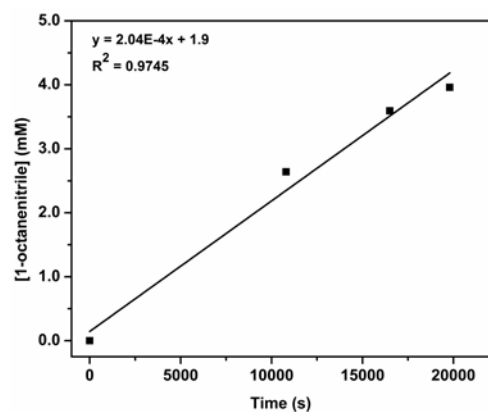


Figure S2. 1-octylamine dehydrogenation reaction profile: 0.0012M **1**

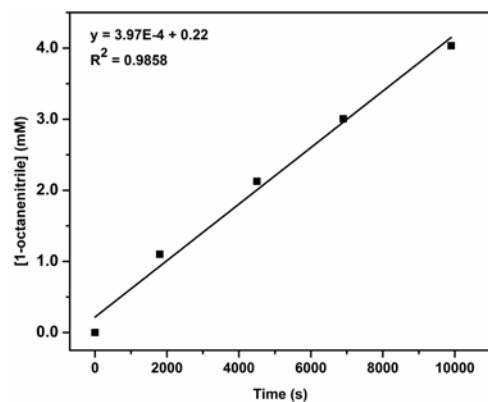


Figure S3. 1-octylamine dehydrogenation reaction profile: 0.0025M **1**

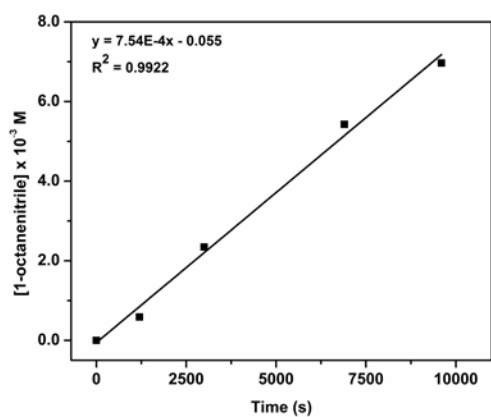


Figure S4. 1-octylamine dehydrogenation reaction profile: 0.0039M **1**

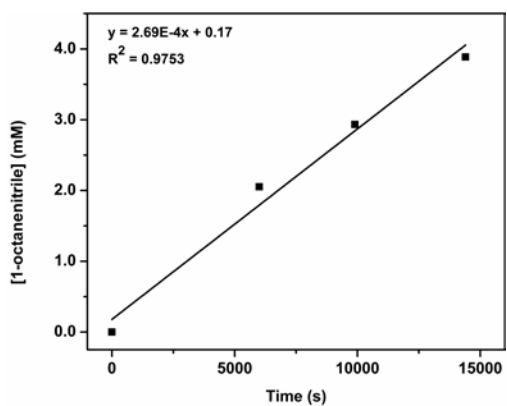


Figure S5. 1-octylamine dehydrogenation: 0.13 M 1-octylamine

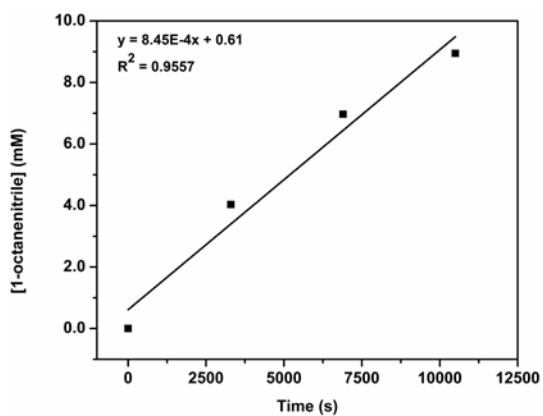


Figure S6. 1-octylamine dehydrogenation: 0.33 M 1-octylamine

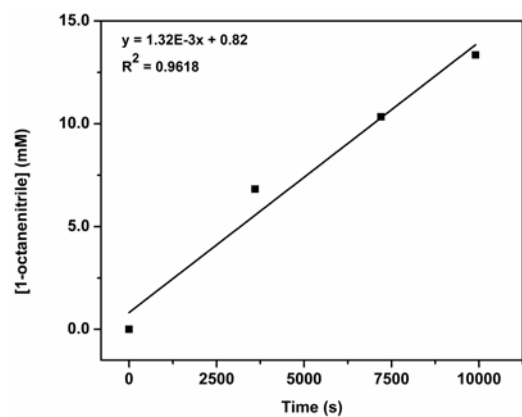


Figure S7. 1-octylamine dehydrogenation: 0.43 M 1-octylamine

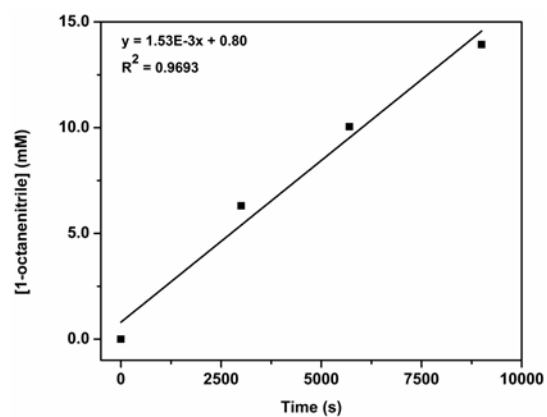


Figure S8. 1-octylamine dehydrogenation: 0.54 M 1-octylamine

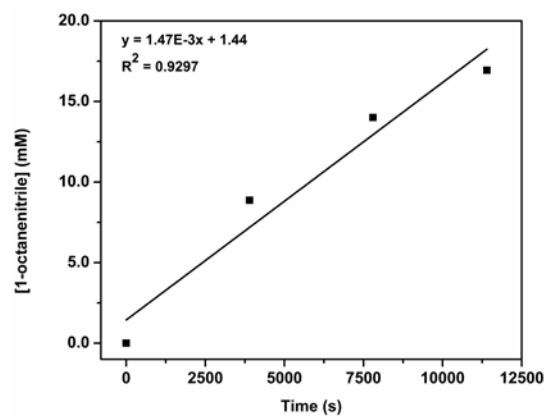


Figure S9. 1-octylamine dehydrogenation: 0.68 M 1-octylamine

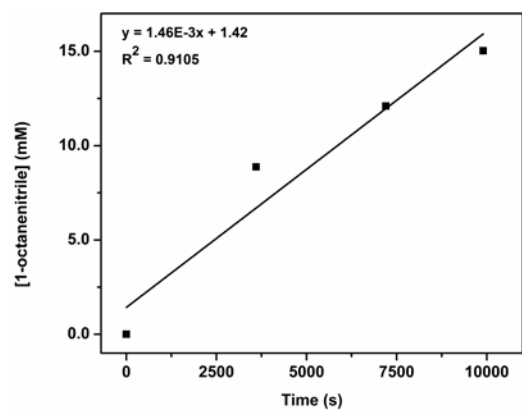


Figure S10. 1-octylamine dehydrogenation: 0.91 M 1-octylamine

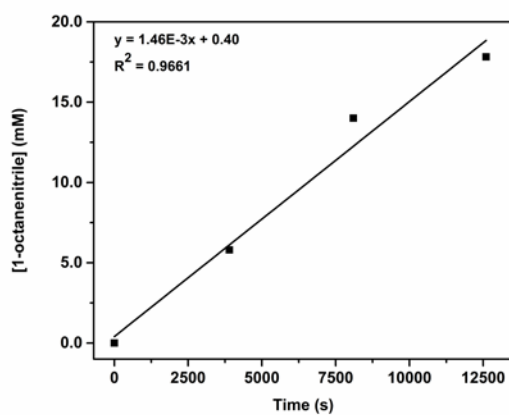


Figure S11. 1-octylamine dehydrogenation: 2 equiv PPh_3

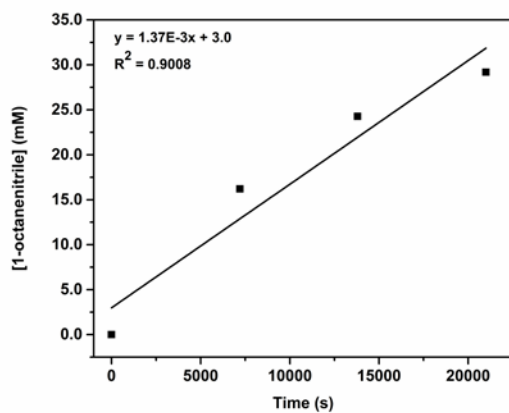


Figure S12. 1-octylamine dehydrogenation: 5 equiv PPh_3

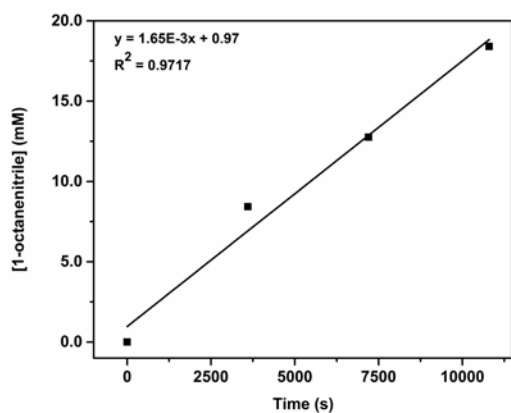


Figure S13. 1-octylamine dehydrogenation: 10 equiv PPh_3

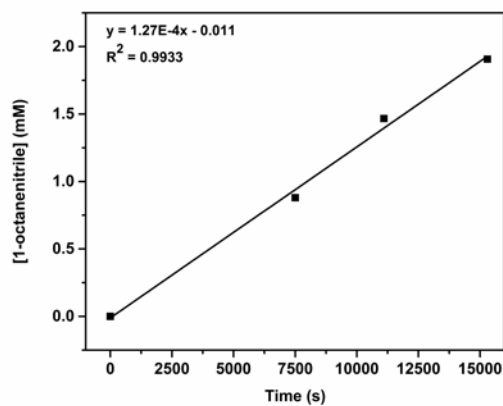


Figure S14. 1-octylamine dehydrogenation: 100 °C

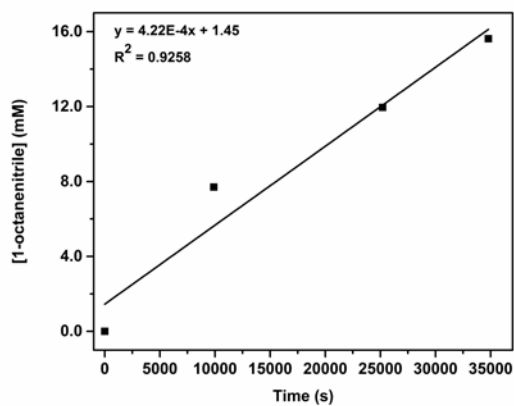


Figure S15. 1-octylamine dehydrogenation: 110 °C

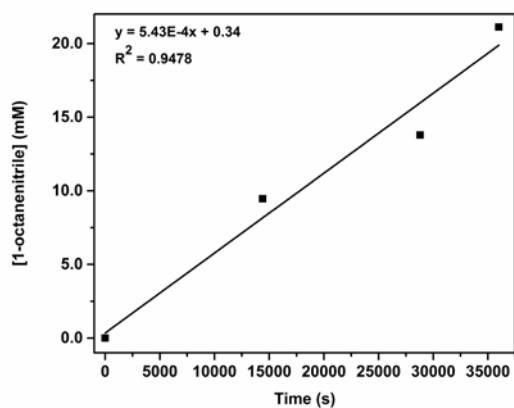


Figure S16. 1-octylamine dehydrogenation: 120 °C

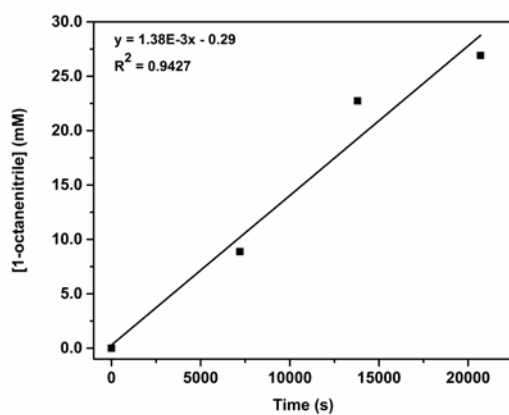


Figure S17. 1-octylamine dehydrogenation: 130 °C

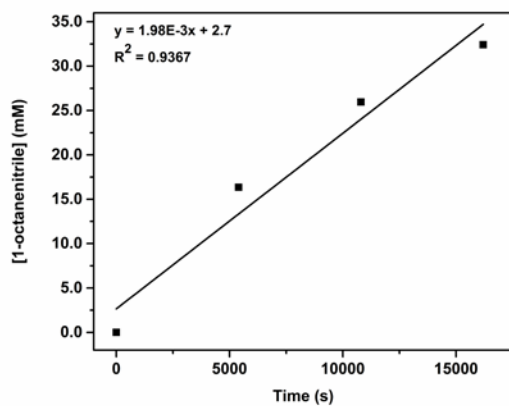


Figure S18. 1-octylamine dehydrogenation: 140 °C

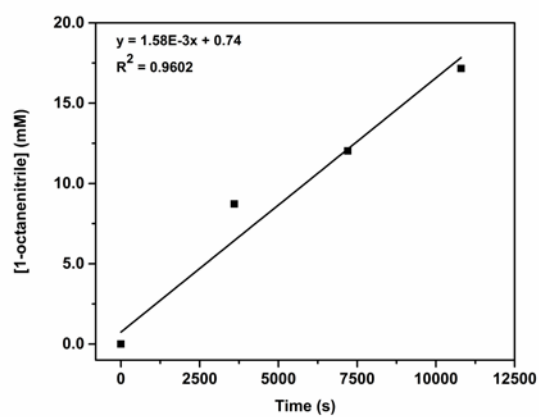


Figure S19. 1-octylamine dehydrogenation: Ru(bMepi)(PPh₃)Cl (2)

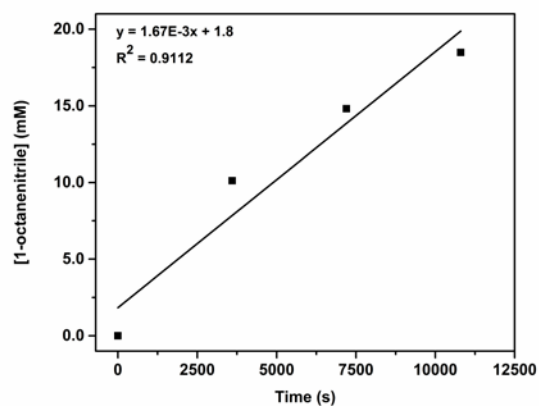


Figure S20. 1-octylamine dehydrogenation: Ru(bMepi^{Me})(PPh₃)(OTf)₂ (4)

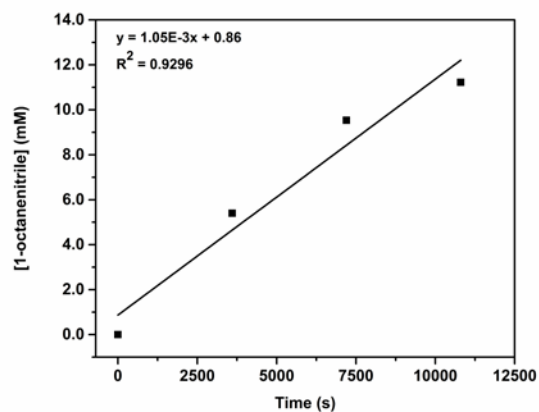


Figure S21. 1-octylamine dehydrogenation: Ru(bⁱPrpi)(PPh₃)Cl (5)

Ru(*b*ⁱPrpi)(PPh₃)Cl (5). THF (10 mL) was added to a 20 mL vial charged with biPrpi[−] K⁺ (81.6 mg, 0.194 mmol), RuCl₂(PPh₃)₃ (186 mg, 0.194 mmol), and a stir bar. The resulting solution was stirred at 70 °C for 20 h. THF was removed under vacuum. The crude product was extracted with DCM (20 mL), and the DCM was then removed under vacuum. The purple solid was washed with Et₂O (4 x 5 mL), and pentane (4 x 10 mL). Yield: 78 mg (52%). Crystals were obtained by allowing pentane to diffuse into a C₆H₆ solution. ¹H NMR (700 MHz, C₆D₆): δ 7.98 (m, 2H), 7.56 (d, *J*_{HH} = 7.9 Hz, 2H), 7.20 (t, *J*_{HH} = 7.6 Hz, 2H), 7.01 (m, 2H), 6.83 (t, *J*_{HH} = 8.6 Hz, 6H), 6.79 (t, *J*_{HH} = 7.2 Hz, 3H), 6.68 (t, *J*_{HH} = 7.4 Hz, 6H), 6.44 (d, *J*_{HH} = 7.3 Hz, 2H), 1.66 (d, *J*_{HH} = 6.4 Hz, 6H), 0.92 (d, *J*_{HH} = 6.3 Hz, 6H), −0.01 (p, *J*_{HH} = 6.5 Hz, 2H). ¹³C{¹H} NMR (700 MHz, C₆D₆): δ 170.2, 156.0, 153.3, 141.7, 135.5, 135.3, 135.1, 133.5, 133.4, 129.2, 128.6, 126.2, 120.4, 37.4, 25.1, 23.4. ³¹P{¹H} NMR (700 MHz, C₆D₆): δ 45.8 (s, PPh₃). IR (ATR, cm^{−1}): 3074, 1570, 1515, 1466, 1434, 1402, 1316, 1217, 1191, 1111, 1089, 850, 830, 807, 782, 748, 696. Anal. Calculated (Found): C, 64.57 (64.60); H, 5.03 (5.01); N, 8.96 (8.87).

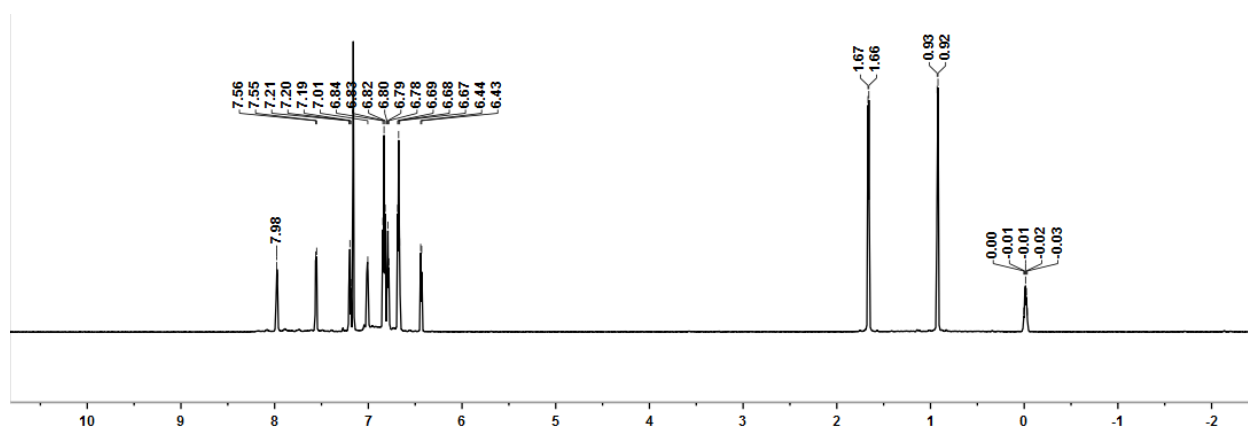


Figure S22. ¹H NMR spectrum of **5** in C₆D₆

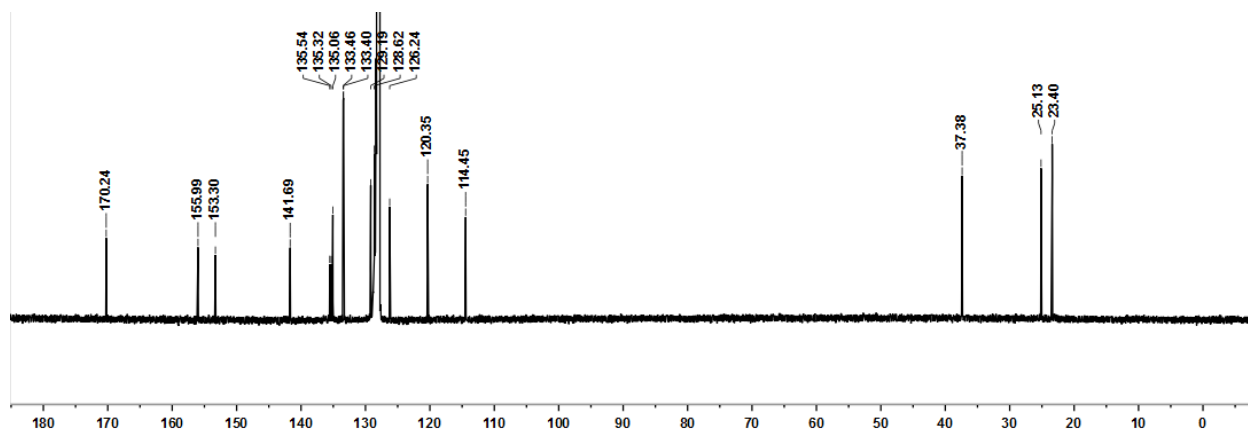


Figure S23. ¹³C NMR spectrum of **5** in C₆D₆

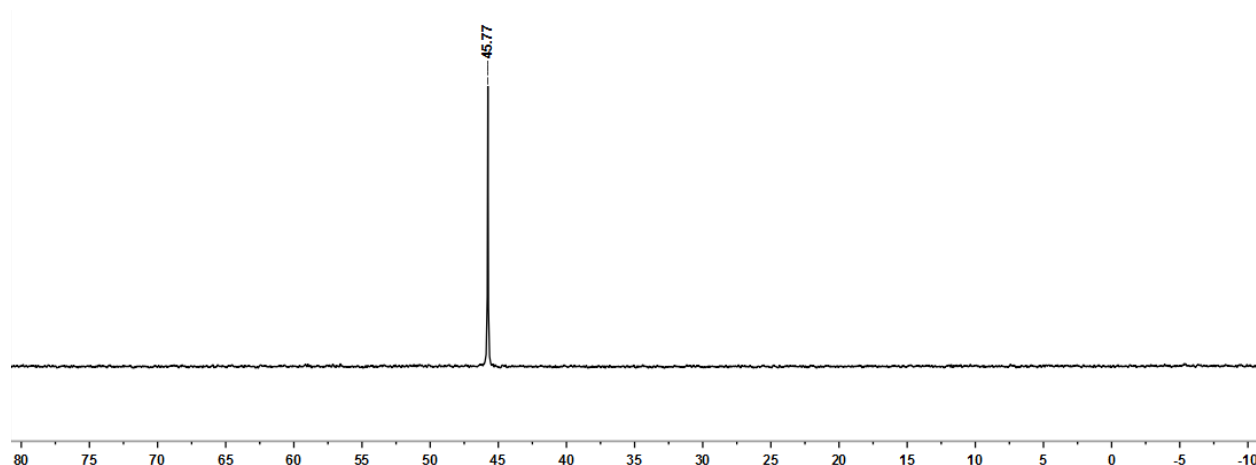


Figure S24. ^{31}P NMR spectrum of **5** in C_6D_6

HRu(bMepi)(PMe₃)₂ (1-PMe₃). PMe₃ (150 μL , 1.45 mmol) was added to a 20 mL vial charged with ClRu(bMepi)(PPh₃) (106 mg, 0.146 mmol) and THF (10 mL). The resulting solution stirred at room temperature for 20 h, resulting in a purple solid precipitate, [Ru(bMepi)(PMe₃)₂]Cl. The solid was filtered and washed with THF (4 x 5 mL), then Et₂O (4 x 5 mL) and used without further purification. Yield: 72.7 mg (82%). This compound ([Ru(bMepi)(PMe₃)₂]Cl; 15.4 mg, 0.025 mmol), was added to a 20 mL vial and charged with C₆H₆ (10 mL) followed by PMe₃ (0.004 mL, 0.039 mmol), and a stir bar. NaHEt₃B (0.026 mL, 0.026 mmol) was added to the solution, and the reaction solution color changed from purple to green immediately. The reaction solution was allowed to stir for 1 h. The C₆H₆ solvent was removed under vacuum, and the crude product was extracted with pentane (4 x 5 mL). Evaporation of the volatiles under vacuum afforded the product as a green powder. Yield: 12.7 mg (88%). Crystals were obtained by cooling a pentane solution to $-35\text{ }^\circ\text{C}$. ^1H NMR (400 MHz, C₆D₆): δ 8.48 (dd, $J_{\text{HH}} = 5.6$, 3.2 Hz, 2H), 7.78 (dd, $J_{\text{HH}} = 8.0$, 1.2 Hz, 2H), 7.35 (dd, $J_{\text{HH}} = 5.6$, 3.2 Hz, 2H), 7.11 (t, $J_{\text{HH}} = 7.6$ Hz, 2H), 6.63 (dd, $J_{\text{HH}} = 7.2$, 1.6 Hz, 2H), 3.17 (s, 6H), 0.27 (t, $J_{\text{HH}} = 2.4$ Hz, 18H), -10.77 (t, $J_{\text{PH}} = 23.0$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (700 MHz, C₆D₆): 164.4, 160.9, 151.2, 142.9, 131.1, 128.6, 126.4, 120.9, 116.6, 35.3, 15.1. ^{31}P NMR (162 MHz, C₆D₆): δ 2.14 (d, $J_{\text{PH}} = 22.7$ Hz). IR (ATR, cm^{-1}): 3066, 2962, 2918, 2885, 2796, 2105, 1969, 1605, 1569, 1505, 1418, 1374, 1197, 1123, 772, 713, 683, 658. Anal. Calculated (Found): C, 53.79 (53.63); H, 6.08 (6.05); N, 12.06 (12.02).

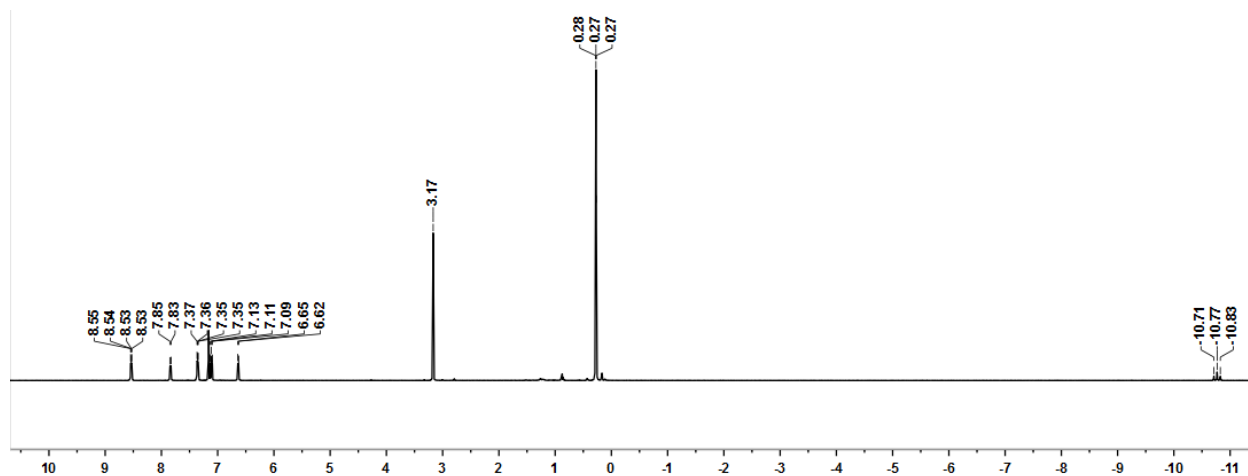


Figure S25. ¹H NMR spectrum of 1-PMe₃ in C₆D₆

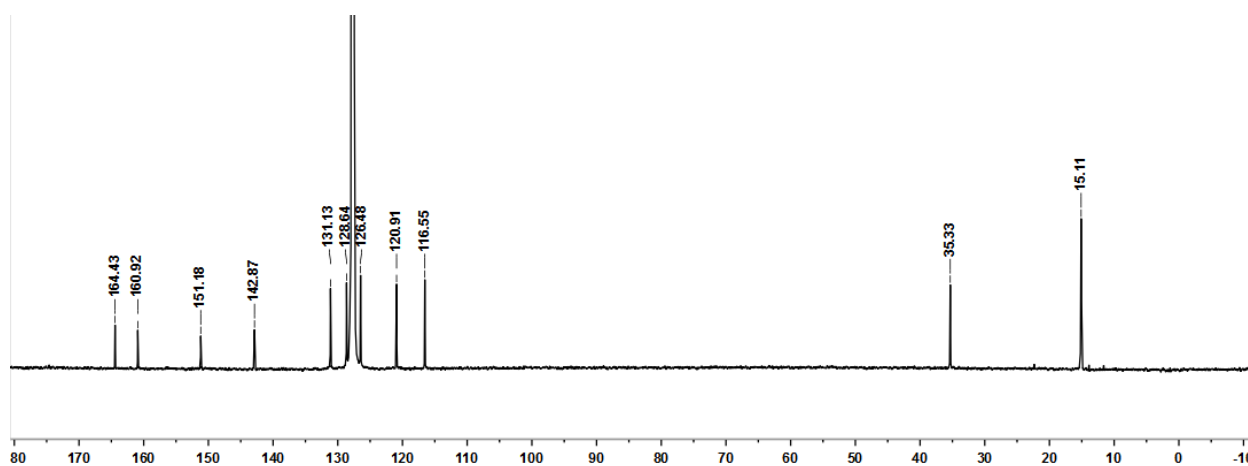


Figure S26. ¹³C NMR spectrum of 1-PMe₃ in C₆D₆

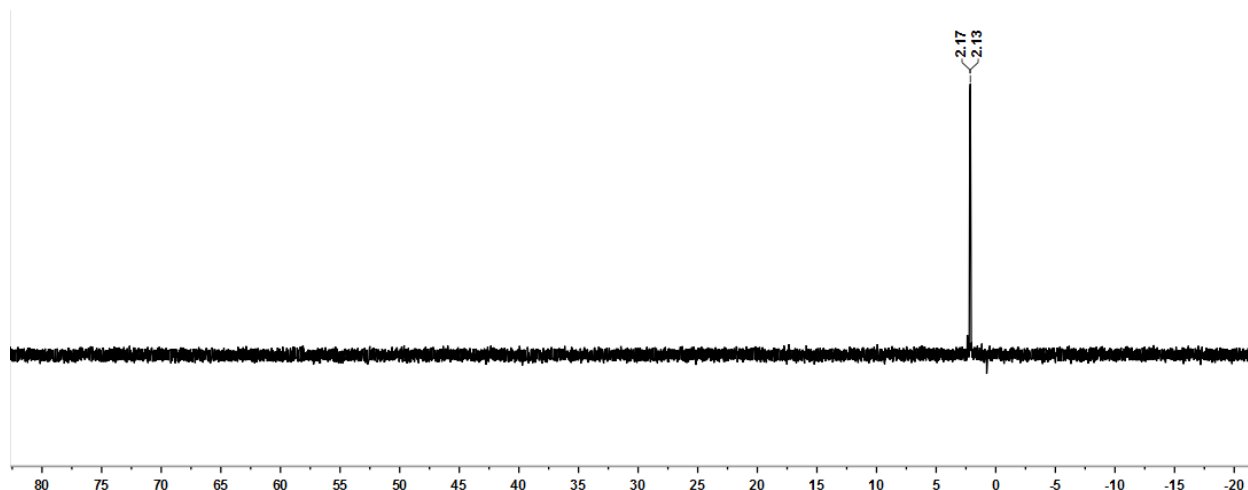


Figure S27. ^{31}P NMR spectrum of **1-PMe₃** in C_6D_6

HRu(bpi)(PPh₃)₂ (1-bpi). $\text{ClRu(bpi)(PPh}_3)_2$ (100 mg, 0.104 mmol) was dissolved in THF (10 mL) in a 20 mL vial charged with a stir bar. While stirring, NaHEt_3B (110 μL , 0.110 mmol) was added to the solution, and the reaction solution color immediately changed from green to black. After stirring at room temperature for 30 minutes THF was removed under vacuum. The black solid was extracted with C_6H_6 (10 mL). C_6H_6 was removed under vacuum and the gray product was washed with pentane (4 x 10 mL), affording 62.4 mg (65%). ^1H NMR (700 MHz, C_6D_6): δ 8.61 (d, $J_{\text{HH}} = 6.0$ Hz, 2H), 8.39 (m, 2H), 7.37 (d, $J_{\text{HH}} = 8.1$ Hz, 2H), 7.30 (t, $J_{\text{HH}} = 5.7$ Hz, 14H), 6.82 (m, 16H), 6.68 (t, $J_{\text{HH}} = 7.6$ Hz, 2H), 5.34 (t, $J_{\text{HH}} = 6.6$ Hz, 2H), -10.77 (t, $J_{\text{PH}} = 23.3$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (700 MHz, C_6D_6): δ 163.7, 158.8, 152.8, 142.6, 134.7 (t, $J_{\text{CP}} = 16.6$ Hz, *ipso*-CP), 133.5, 131.5, 128.4, 120.6, 113.5. $^{31}\text{P}\{^1\text{H}\}$ NMR (700 MHz, C_6D_6): δ 55.59 (s, PPh_3). IR, neat (cm^{-1}): 3048, 1842, 1545, 1499, 1435, 1379, 1311, 1286, 1194, 1114, 1089, 1006, 906, 769, 694. Anal. Calculated (Found): C, 70.12 (67.81); H, 4.69 (4.66); N, 7.57 (7.45).

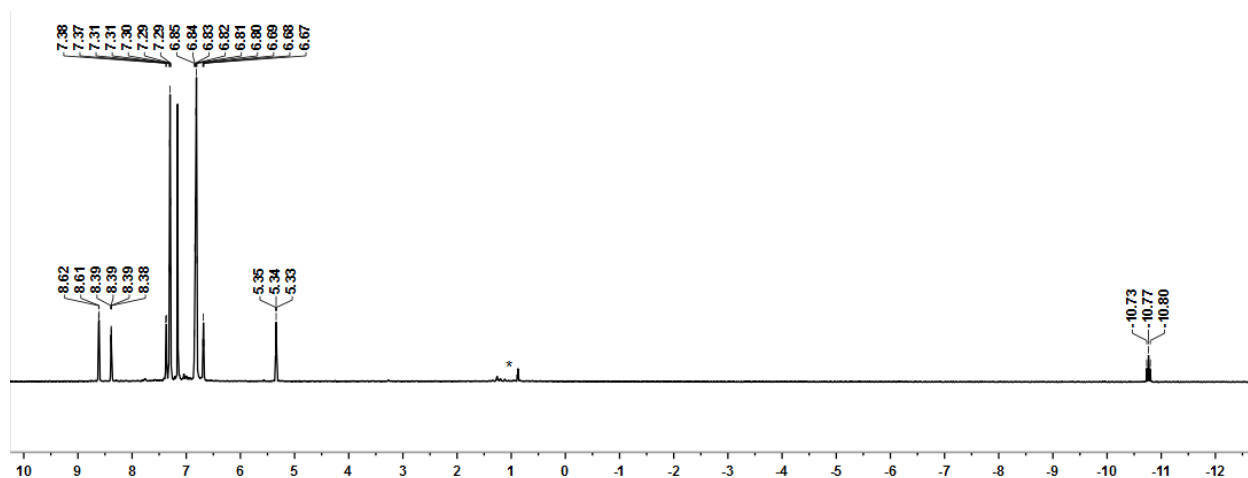


Figure S28. ^1H NMR spectrum of **1-bpi** in C_6D_6 . * = pentane

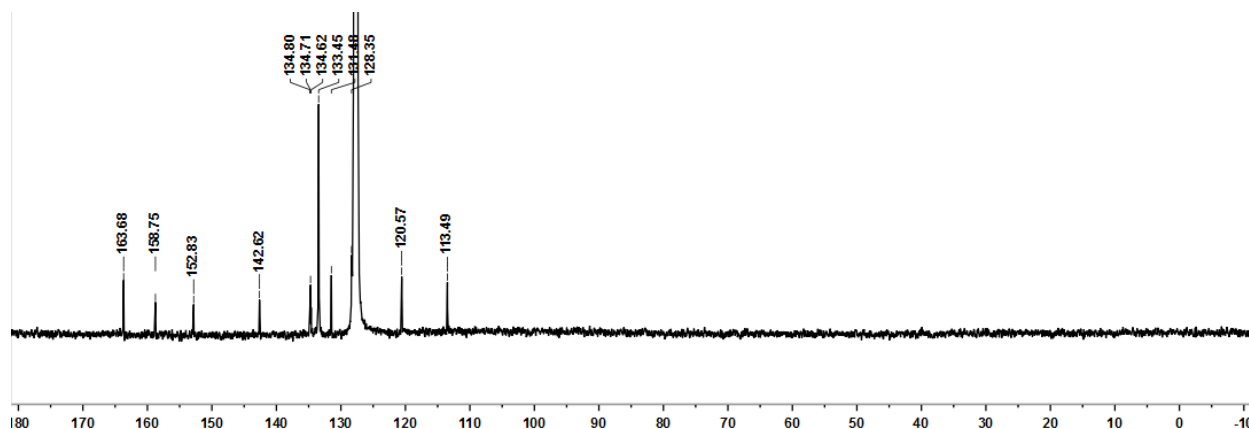


Figure S29. ¹³C NMR spectrum of **1-bpi** in C₆D₆

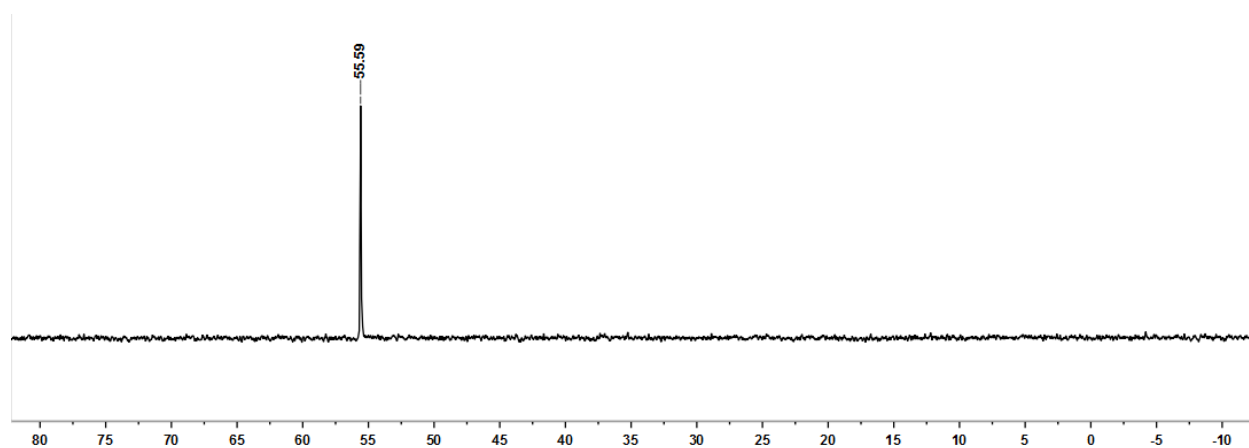


Figure S30. ³¹P NMR spectrum of **1-bpi** in C₆D₆

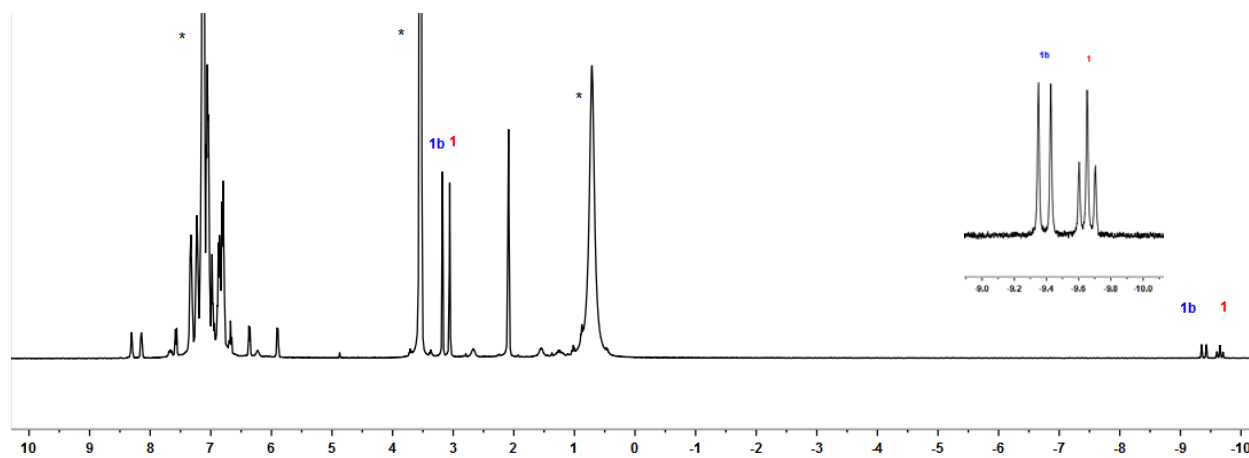


Figure S31. 10 equiv benzylamine added to HRu(bMepi)(PPh₃)₂ (**1**) in toluene-*d*₈. * = benzylamine

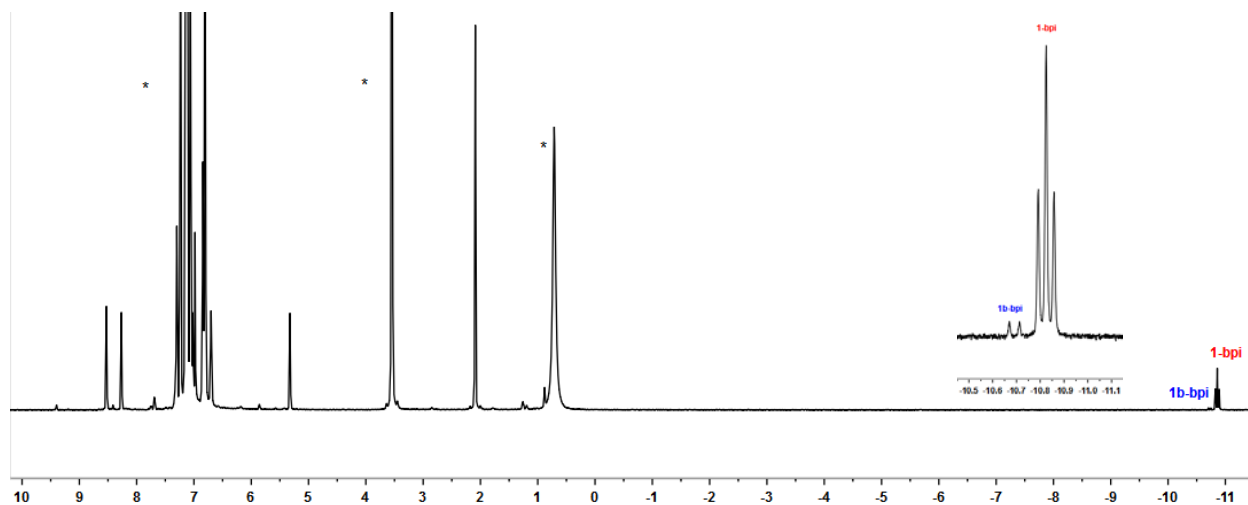


Figure S32. 10 equiv benzylamine added to HRu(bpi)(PPh₃)₂ (**1-bpi**) in toluene-*d*₈. * = benzylamine

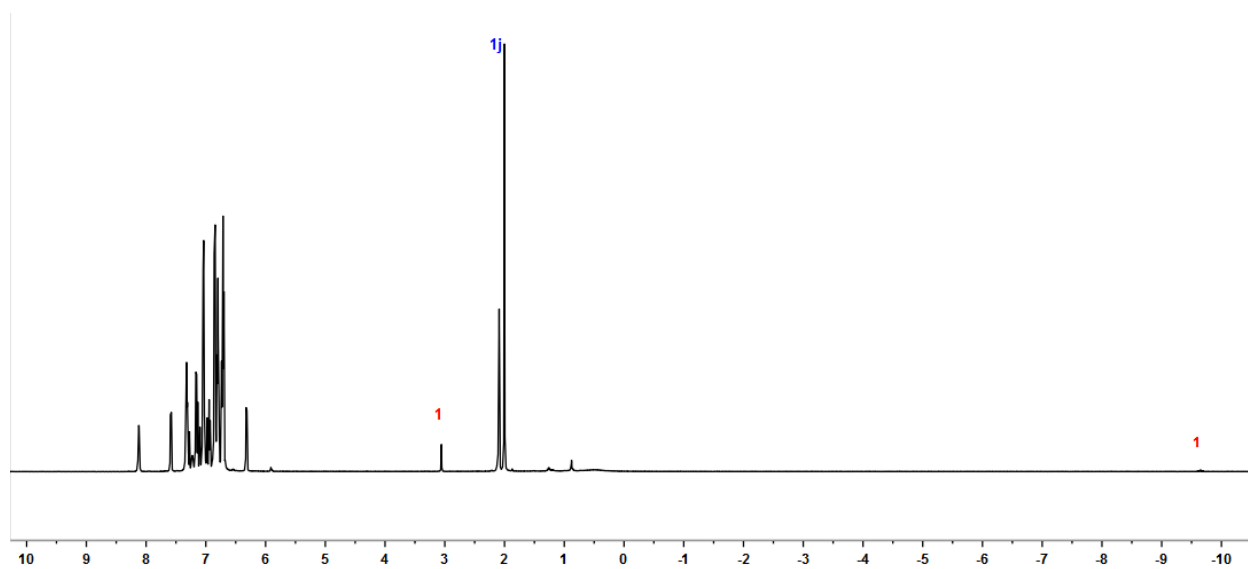


Figure S33. 5 equiv 4-CF₃-benzonitrile added to HRu(bMepi)(PPh₃)₂ (**1**) in toluene-*d*₈

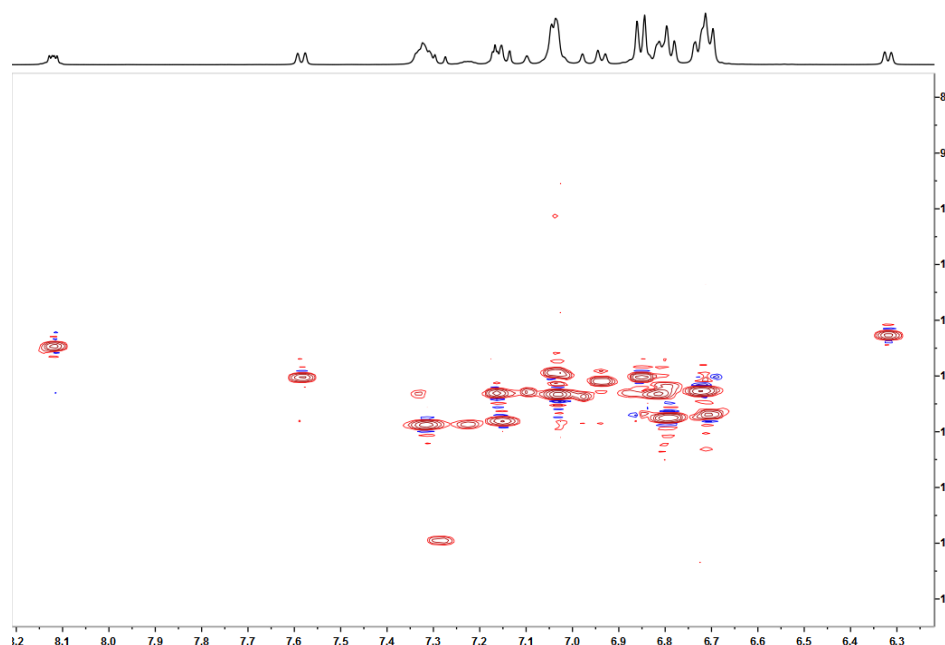


Figure S34. $^1\text{H}/^{13}\text{C}$ -HSQC: observation of imine proton in **1j** with crosspeak at δ 160 and 7.29 with 5 equiv 4- CF_3 -benzonitrile added to $\text{HRu}(\text{bMepi})(\text{PPh}_3)_2$ (**1**).

In situ synthesis of $\text{Ru}(-\text{CH}_2\text{CH}_3\text{pi})(\text{PPh}_3)(\text{NH}_2\text{C}_6\text{H}_9)$ (6**).** A 20 mL vial was charged with trimethylsilylmethyl lithium (3.9 mg, 0.041 mmol) and THF (1 mL), and was cooled to -78°C . A solution of 4-methylbenzylamine (5.3 μL , 0.042 mmol) in THF (1 mL) was added drop-wise to the trimethylsilylmethyl lithium solution, and stirred for 30 minutes at -78°C . This solution was then added to $\text{Ru}(\text{bMepi})(\text{PPh}_3)\text{Cl}$ (29.8 mg, 0.041 mmol) dissolved in THF (10 mL). After stirring at -78°C for 15 minutes, THF was removed under vacuum. The dark green solid was extracted with C_6D_6 and ^1H and ^{31}P NMR spectra were obtained. Crystals were obtained by diffusion of pentane into a solution of C_6H_6 , at -35°C . ^1H NMR (500 MHz, C_6D_6): δ 8.49–8.47 (m, 1H), 8.42–8.41 (m, 1H), 7.79 (d, $J_{\text{HH}} = 7.8$ Hz, 1H), 7.59 (d, $J_{\text{HH}} = 8.3$ Hz, 1H), 7.29 (dd, $J_{\text{HH}} = 5.4, 3.0$ Hz, 2H), 7.22 (t, $J_{\text{HH}} = 7.8$ Hz, 1H), 7.05 (t, $J_{\text{HH}} = 7.5$ Hz, 1H), 6.96 (t, $J_{\text{HH}} = 8.3$ Hz, 6 H, PPh_3), 6.82–6.76 (m, 9H, PPh_3), 6.49 (d, $J_{\text{HH}} = 7.7$ Hz, 2H), 6.43 (d, $J_{\text{HH}} = 6.3$ Hz, 1H), 6.14 (d, $J_{\text{HH}} = 7.1$ Hz, 1H), 5.98 (d, $J_{\text{HH}} = 7.8$ Hz, 2H), 2.79 (s, 3H), 2.26 (t, $J = 12.1$ Hz, 2H), 1.98–1.87 (m, 1H), 1.86 (s, 3H), 1.81–1.71 (m, 1H), 1.51 (s, 2H). $^{31}\text{P}\{^1\text{H}\}$ NMR (500 MHz, C_6D_6): δ 62.55 (s, PPh_3).

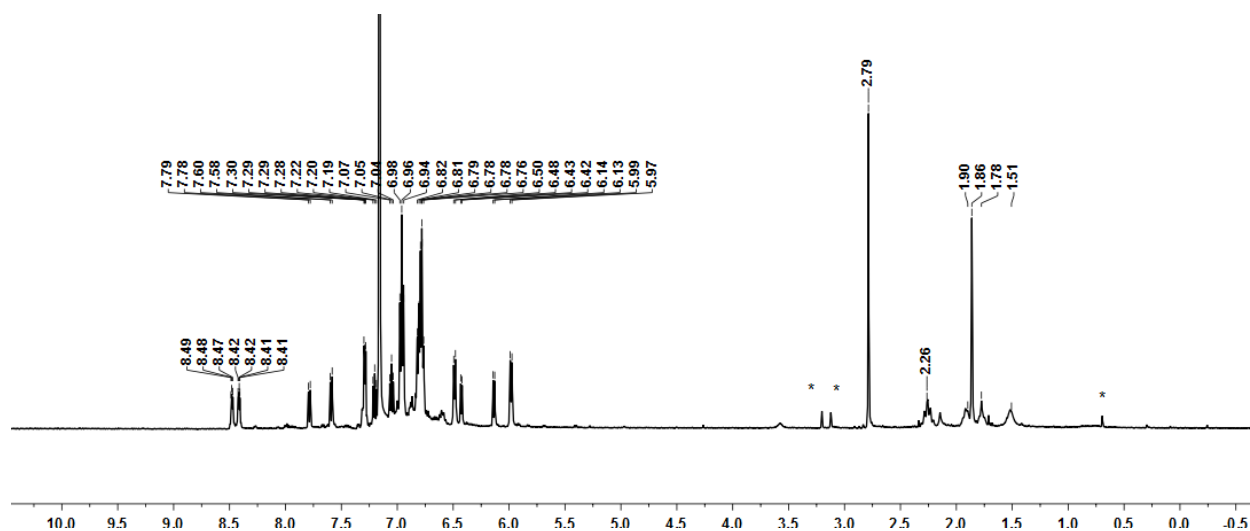


Figure S35. ^1H NMR spectrum of $\text{Ru}(-\text{CH}_2\text{CH}_3\text{pi})(\text{PPh}_3)(\text{NH}_2\text{C}_8\text{H}_9)$ (**6**) formed *in situ* in C_6D_6 . * = $[\text{Ru}(\text{CH}_2\text{Mepi})\text{PPh}_3]_2$.²

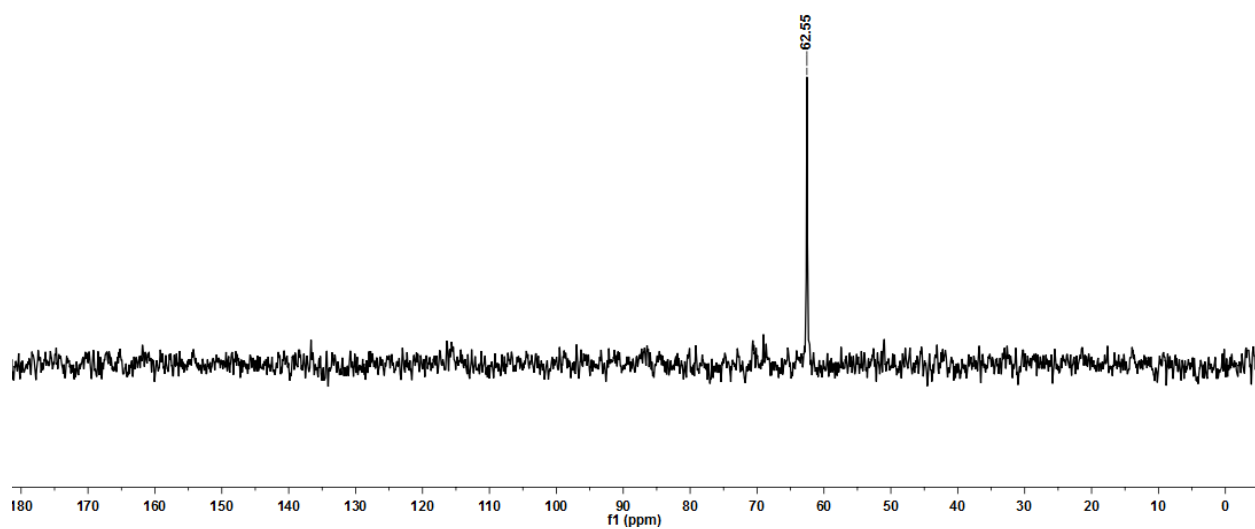


Figure S36. ^{31}P NMR spectrum of $\text{Ru}(-\text{CH}_2\text{CH}_3\text{pi})(\text{PPh}_3)(\text{NH}_2\text{C}_8\text{H}_9)$ (**6**) formed *in situ* in C_6D_6

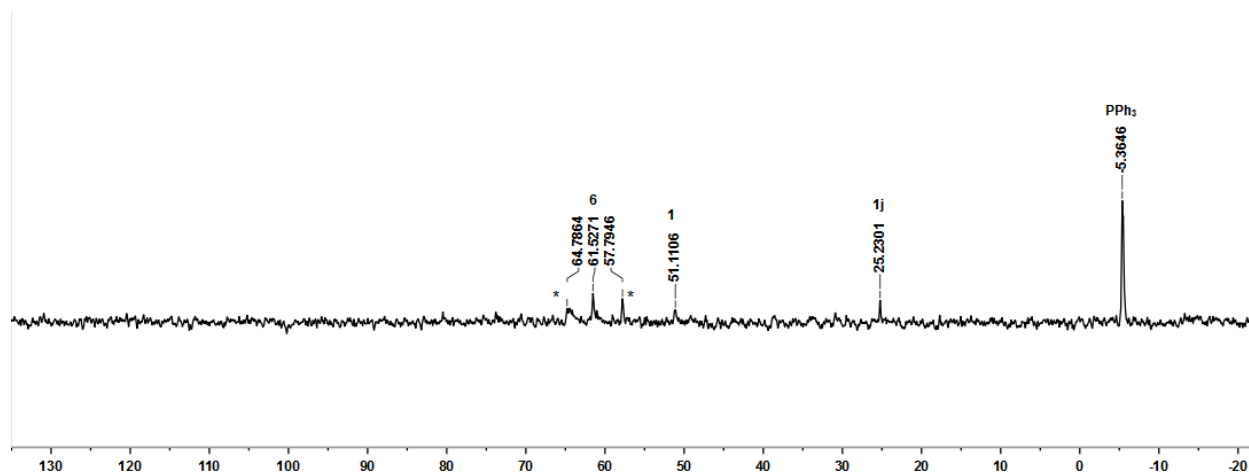


Figure S37. ^{31}P NMR spectrum during dehydrogenation of 1-octylamine with **1**. * = unknown intermediates.

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