Supporting Information For:

Mild sp²Carbon–Oxygen Bond Activation by an Isolable Ruthenium(II) bis(Dinitrogen) Complex: Experiment and Theory

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1. General Experimentation

All manipulations were carried out under standard Schlenk-line and glovebox techniques under an inert atmosphere of argon or dinitrogen. An MBraun Labmaster glovebox was employed operating at <0.1 ppm O₂ and <0.1 ppm H₂O. Solvents were dried over activated alumina from an SPS (solvent purification system) based upon the Grubbs design and degassed before use. Glassware was dried for 12 hours at 120°C prior to use. d₆-Benzene and d₈-toluene were freeze-pump-thaw degassed and stored over molecular sieves prior to use.

NMR spectra were obtained on BRUKER 400 or 500 MHz machines, all peaks are references against residual solvent peak or internal standard peak with values quoted in ppm. Data were processed in Topspin or MestReNova. Infrared spectra were recorded on a Perkin Elmer FT-IR Paragon 1000 spectrometer with the solid sample impregnated into KBr disk.

2. Materials

1,5-Cyclooctadiene was freeze-pump-thaw degassed and stored over molecular sieves prior to use. Ethanol was dried over magnesium, distilled and stored over molecule sieve prior to use. Chemicals purchased from Sigma Aldrich, Alfa Aesar and Fluorochem and used without further purification unless stated.

Synthesis of [Ru(η⁴-1,5-COD)(η⁶-1,3,5-COT)] follows procedure from literature.¹ RuCl₃•nH₂O (2.0 g, 1 mmol) was weighed into an ampoule and dissolved in EtOH (30 mL). 1,5-Cyclooctadiene (40 mL, 1 mmol) and Zn powder (4.0 g, 1 mmol) were
added into the ampoule and the reaction mixture was sealed and left to stir at 80 °C. The reaction mixture was allowed to cool to 25 °C then filtered and concentrated in vacuo giving a straw brown oily residue. The residue was extracted with n-hexane (30 mL) and filtered through Al₂O₃ resulting in a deep yellow solution. The volume of the yellow solution was reduced and left in freezer at -35 °C to give yellow sharp needles as the product (0.98 g, 41% yield).

\(^1\)H-NMR (C₆D₆, 400 MHz, 298 K) δ/ppm: 0.82 (m, 2H), 1.68 (m, 2H), 2.24 (br, 8H), 2.91 (br, 4H), 3.77 (m, 2H), 4.71 (t, J_HH = 7.6 Hz, 2H), 5.19 (dd, J_HH = 5.1 Hz and 1.6 Hz, 2H).

\(^{13}\)C\(^{(1)}\)H-NMR (C₆D₆, 125 MHz, 298 K) δ/ppm: 31.7, 33.9, 76.5, 99.2, 101.4.

[Literature data: \(^1\)H-NMR (C₆D₆, 60 MHz, 298 K) δ 0.90 (m, 2H), 1.64 (m, 2H), 2.22 (m, 8H), 2.92 (m, 4H), 3.79 (m, 2H), 4.78 (m, 2H), 5.22 (dd, 2H). \(^{13}\)C\(^{(1)}\)H-NMR (C₆D₆, 22.63 MHz, 298 K) δ/ppm: 31.6 (CH₂), 33.0 (CH₂), 70.1 (CH), 76.7 (CH), 99.3 (CH), 101.4 (CH).]

\[\text{Synthesis of } [\text{Ru}(\eta^2\text{-H})_2(N_2)_2(PCy}_3)_2] \text{ (1) follows procedure from literature.}^2 \]

In a dinitrogen glovebox, \([\text{Ru}(\eta^4\text{-1,5-COD})(\eta^6\text{-1,3,5-COT})] (0.60 g, 1.9 mmol) and PCy₃ (1.0 g, 3.7 mmol) were weighed into an ampoule and dissolved in n-hexane (40 mL). The ampoule was removed from the glovebox and hydrogen gas (1.01 bar) was bubbled through the solution for 3 h resulting in formation of a colorless precipitate \([\text{RuH}_2(\eta^2\text{-H})(PCy}_3)_2] \). The precipitate was isolated and washed with n-hexane (3 x 10 mL) then recrystallised and dried under an atmosphere of dinitrogen allowing for the conversion of \([\text{Ru}(\eta^2\text{-H})(PCy}_3)_2] \) into the \([\text{Ru}(\eta^2\text{-H})(PCy}_3)_2] \) complex. The product was collected as pale yellow crystals (0.57 g, 41% yield).

\(^1\)H-NMR (C₆D₆, 400 MHz, 298 K) δ/ppm: -12.96 (br, 2H, RuH), 1.15 – 2.25 (m, 66H, Cy); \(^{31}\)P\(^{(1)}\)H-NMR (C₆D₆, 162 MHz, 298 K) δ/ppm: 59.3; \(^{13}\)C\(^{(1)}\)H-NMR (C₆D₆, 100 MHz, 298 K) δ/ppm: 27.2 (m, Cy), 28.2 (m, Cy), 30.4 (m, Cy), 37.2 (t, \(^{1}J_{CP} = 8.9 \text{ Hz, Cy})\). FT-IR (ν/cm\(^{-1}\)) 1918, 1986 (Ru–H), 2131, 2163 (N≡N). **Elemental Analysis** calc. for C₃₆H₆₈N₄P₂Ru C, 60.06; H 9.52; N, 7.78 found C, 59.94; H, 9.61; N, 7.67. \(T_1 (\text{Tol-D}_8, 193 \text{ K}) = 1.08 \text{ s (Ru–H)}\).

[Literature data: \(^1\)H-NMR (C₆D₆, 200.13 MHz, 298 K) δ/ppm: -12.83 (t, \(^{1}J_{HP} = 22 \text{ Hz, 2H, RuH}); \text{FT-IR (ν/cm}^{-1}\)) 2126, 2163 (N≡N)].
acetate (0.5 mL, 5 mmol, 0.5 equiv) were dissolved in toluene (100 mL). A reflux was set up and the reaction mixture was left to heat at 110 °C under N₂ for 72 h resulting in a brown solution. The solution was cooled to rt then quenched with 9M NaOH (10 mL) and the organic layer was then washed sequentially with water (2 × 20 mL) then brine (2 × 20 mL). The organic layer was dried over MgSO₄, filtered then concentrated in vacuo leaving a brown oily residue. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 1/5) giving an off-white yellow solid (Rᵣ = 0.28). The solid was washed with cold hexane and air dried resulting in a colorless powdered solid (1.49 g, 48 %).

\[ ^{1}H\text{-NMR} (400 \text{ MHz, } C_{6}D_{6}, 298 \text{ K}) \delta/\text{ppm}: \quad 2.03 \text{ (s, 6H, ArCH₃), } 2.46 \text{ (s, 3H, COCH₃), } 6.46 \text{ (d, } J_{HH} = 8.3 \text{ Hz, 2H, ArHm), } 6.72 \text{ (t, } J_{HH} = 8.3 \text{ Hz, 1H, ArHp), } 6.85 \text{ (d, } J_{HH} = 8.3 \text{ Hz, 4H, ArH), } 6.87 \text{ (d, } J_{HH} = 8.6 \text{ Hz, 4H, ArH)} \]

\[ ^{13}C\{^{1}H\}\text{-NMR} (125 \text{ MHz, } C_{6}D_{6}, 298 \text{ K}) \delta/\text{ppm}: \quad 20.6 \text{ (ArCH₃), } 32.2 \text{ (C(O)CH₃), } 112.7 \text{ (Cₘ), } 119.8 \text{ (OCOCₘ), } 130.4 \text{ (CH₃CCₘ), } 130.6 \text{ (Cₚ), } 133.5 \text{ (CH₃C), } 155.0 \text{ (OCₘ), } 155.9 \text{ (Cₙ), } 198.6 \text{ (C=O).} \]

**Elemental Analysis** calc. for C₂₂H₂₀O₃, 79.50; H 6.07 found C, 79.38; H, 6.10.

**Synthesis of double \(^{13}\)C-labelled 2,6-dimethoxyacetophenone \(^{13}\)C₂-3a.**

2,6-dihydroxyacetophenone (0.54 g, 3.5 mmol, 1 equiv), K₂CO₃ (0.72 g, 5.2 mmol, 1.5 equiv) and \(^{13}\)CH₃I (1.0 g, 7.0 mmol, 2 equiv) were stirred in DMF (40 mL) at 100 °C under N₂ for 48 h. Reaction was quenched with 5 mol % NaOH and water and then extracted with Et₂O (2 × 20 mL). The organic layers were combined and washed sequentially with H₂O (2 × 20 mL) then with brine (2 × 20 mL). The organic layer was dried over MgSO₄, filtered then concentrated in vacuo resulting in an off yellow solid (0.20 g, 34 %).

\[ ^{1}H\text{-NMR} (400 \text{ MHz, } C_{6}D_{6}, 298 \text{ K}) \delta/\text{ppm}: \quad 2.43 \text{ (s, 3H, C(O)CH₃), } 3.19 \text{ (d, } J_{CH} = 144.2 \text{ Hz, 6H, OCH₃), } 6.18 \text{ (d, } J_{HH} = 8.4 \text{ Hz, 2H, ArHm), } 6.97 \text{ (t, } J_{HH} = 8.4 \text{ Hz, 1H, ArHp)} \]

\[ ^{13}C\{^{1}H\}\text{-NMR} (125 \text{ MHz, } C_{6}D_{6}, 298 \text{ K}) \delta/\text{ppm}: \quad 32.32 \text{ (C(O)CH₃), } 55.40 \text{ (OCH₃), } 104.31 \text{ (Cₘ), } 130.14 \text{ (Cₚ), } 157.11 \text{ (Cₙ), } 199.95 \text{ (C=O).} \]

**ESI-MS (Hi-res. for C₈\(^{13}\)C₂H₁₂O₃):** calc. 183.0932 [M+H]+, found 183.0934 [M+H]+.

**Synthesis of S1.** In a dinitrogen glovebox, \([Ru(η^{4}-1,5-COD)(η^{6}-1,3,5-COT)](0.93 \text{ g, } 3.0 \text{ mmol) and PCy₃ (1.65 g, 5.9 mmol) were weighed into an ampoule and dissolved in n-hexane (40 mL). The ampoule was removed from the glovebox and hydrogen gas (1.01 bar) was bubbled through the solution for 3 h resulting in formation of a**
colorless precipitate, [RuH₂(η²-H₂)(PCy₃)₂]. The precipitate was collected and hydrogen gas (1.01 bar) was bubbled through the mother liquor once more for 3 h. The ampoule was sealed up and purple crystals formed over 3 weeks. The purple crystals were isolated and washed with cold hexane giving the dimer, [Ru₂H(μ-H)₃(N₂)(PCy₃)₄], as product (0.58 g, 29 % yield).

¹H-NMR (C₆D₆, 400 MHz, 298 K) δ/ppm: -12.49 (br, 4H, RuH), 1.14 – 2.68 (m, 132H, Cy); ³¹P¹H-NMR (C₆D₆, 162 MHz, 298 K) δ/ppm: 75.7 (br). FT-IR (ν/cm⁻¹) 1918, 1986 (Ru–H), 2131, 2163 (N≡N). Elemental Analysis calc. for C₇₂H₁₃₆N₂P₄Ru₂: C, 63.78; H, 10.11; N, 2.07; P, 9.1; found C, 63.89; H, 9.97; N, 1.95.

[Literature data:³¹H-NMR (Tol-D₈, 250 MHz, 303 K) δ/ppm: -12.4 (s, 4H, RuH); FT-IR (ν/cm⁻¹) 2126, 2163 (N≡N). Elemental Analysis calc. for C₇₂H₁₃₆N₂P₄Ru₂: C, 63.78; H, 10.11; N, 2.07; P, 9.1; found C, 62.5; H, 9.9; N, 2.2; P, 8.2.]
3. General procedure for reduction of arylketone to arylethanol

Arylketone (4.4 mmol, 1 equiv) was weighed into a schlenk and dissolved in THF (15 mL). LiAlH₄ (2.2 mmol, 0.5 equiv) was weighed out into a separate schlenk and dissolved in THF (20 mL). LiAlH₄ solution was cooled to -78 °C and the arylketone solution was added dropwise over the course of 20 min. Once addition was completed the reaction was allowed to warm to rt and left to stir overnight. The reaction was quenched with THF/H₂O/NaOH (80/10/10) and the organic layer was then washed sequentially with H₂O (2 × 10 mL) then brine (2 × 10 mL). The organic layer was dried over MgSO₄ then concentrated in vacuo to give product. Product used in reactions without further purification.

Synthesis of 2,6-p-tolyloxy(phenyl)arylethan-1-ol (2b-H₂): Cloudy viscous liquid (0.64 g, 64 %). ¹H-NMR (400 MHz, C₆D₆, 298 K) δ/ppm: 1.48 (d, J_HH = 6.4 Hz, 3H, C(OH)CH₃), 2.07 (s, 3H, ArCH₃), 2.40 (br, 1H, OH), 5.26 (m, 1H, CH), 6.76 (dd, J_HH = 7.5 Hz and 1.8 Hz, 1H, ArH), 6.82 (d, J_HH = 8.7 Hz, 2H, ArH), 6.87 (d, J_HH = 8.4 Hz, 2H, ArH), 6.95 (m, 2H, ArH), 7.62 (dd, J_HH = 6.5 Hz and 2.6 Hz, 1H, ArH). ¹³C(¹H)-NMR (125 MHz, C₆D₆, 298 K) δ/ppm: 20.6 (ArCH₃), 24.6 (C(OH)CH₃), 65.3 (CH), 118.7 (C_m), 118.7 (OCCO), 123.9 (C_m), 127.0 (C_p), 128.3 (C_p), 130.6 (CH₃CC_m), 132.6 (CCH₃), 137.8 (C(OH)C), 154.3 (C_p), 155.7 (OC).

Elemental Analysis: calc. for C₁₅H₁₆O₂ C, 78.92; H 7.06; found C, 79.00; H, 7.14.

Synthesis of 1-(2,6-dimethoxyphenyl)ethanol-1-ol (3a-H₂): Yellow-white solid (0.565 g, 56 %). ¹H-NMR (400 MHz, C₆D₆, 298 K) δ/ppm: 1.74 (d, J_HH = 6.7 Hz, 3H, CH₃), 3.16 (s, 6H, OCH₃), 4.02 (d, J_HH = 11.8 Hz, 1H, OH), 5.84 (dq, J_HH = 13.3 Hz and 6.7 Hz, 1H, CH), 6.24 (d, J_HH = 8.4 Hz, 2H, ArH), 6.97 (t, J_HH = 8.3 Hz, 1H, ArH). ¹³C(¹H)-NMR (125 MHz, C₆D₆, 298 K) δ/ppm: 24.4 (C(OH)CH₃), 55.2 (OCH₃), 64.3 (CH), 104.6 (C_m), 159.0 (C_p). [Literature data: ¹H-NMR (400 MHz, CDCl₃, 298 K) δ/ppm: 1.50 (d, J = 6.2 Hz, 3H), 3.85 (s, 6H), 3.88 (br. S, 1H), 5.33 (m, 1H), 6.58 (d, J = 8.2 Hz, 2H), 7.16 (t, J = 8.2 Hz, 1H). ¹³C(¹H)-NMR (100 MHz, CDCl₃, 298 K) δ/ppm: 23.6 (CH₃), 55.7 (CH₃), 64.0 (CH), 104.3 (CH), 121.0 (CH), 128.1 (C), 157.4 (C)].

Synthesis of 2,6-Bis-p-tolyloxy(phenyl)arylethan-1-ol (3b-H₂): Yellow-white solid (0.41 g, 80 %). ¹H-NMR (400 MHz, C₆D₆, 298 K) δ/ppm: 1.75 (d, J_HH = 6.7 Hz, 3H, C(OH)CH₃), 2.05 (s, 6H, ArCH₃), 3.53 (d, J_HH = 11.5 Hz, 1H, OH), 5.83 (dt, J_HH = 11.3 Hz and 6.7 Hz, 1H, CH), 6.49 (d, J_HH = 8.2 Hz, 2H, ArH), 6.72 (dd, J_HH=8.5 Hz and 8.0 Hz, 1H, ArH), 6.85 (s, 8H, ArH). ¹³C(¹H)-NMR (125 MHz, C₆D₆, 298 K) δ/ppm: 20.6 (ArCH₃), 24.5 (C(OH)CH₃), 64.6 (CH), 113.6 (C_m), 119.5 (OCCO), 128.3 (C_p), 130.7 (CH₃CC_m), 133.3 (CCH₃), 155.1 (OC), 156.5 (C_p). [ESI-MS (Hi-res for C₂₂H₂₂O₃): calc. 333.1467 [M–H]^+, found 333.1491 [M–H]^+].
4. Reaction of 1 with 1-2H₂

In an argon glovebox, [Ru(H)₂(N₂)₂(PCy₃)₂] (1) (8 mg, 0.11 mmol) and [Ru(H)₂(η₂-H₂)₂(PCy₃)₂] (1-2H₂) (7 mg, 0.10 mmol) were dissolved into C₆D₆ (600 μL) by micropipette and then transferred into a J. Young NMR tube. The reaction was left at 25 °C and monitored by NMR spectroscopy.

In situ NMR data for 1 same as above.

In situ NMR data for 1-2H₂: ^1H-NMR (C₆D₆, 400 MHz, 298 K) δ/ppm: -7.84 (br, 6H, RuH); 1.08 – 2.32 (m, 66H, Cy); ^31P(^1H)-NMR (C₆D₆, 162 MHz, 298 K) δ/ppm: 76.28. T₁ (Tol-D₈, 193 K) = 52.3 ms (Ru–H). [Literature data: ^1H-NMR (Tol-D₈, 90 MHz, 298 K) δ/ppm: -7.84 (br, 6H, RuH); ^31P(^1H)-NMR (Tol-D₈, 60 MHz, 298 K) δ/ppm: 79.2).

In situ NMR data for 1-H₂/N₂: ^1H-NMR (C₆D₆, 400 MHz, 298 K) δ/ppm: -8.48 (br, 4H, RuH) 1.13 – 2.22 (m, 66H, Cy); ^31P(^1H)-NMR (C₆D₆, 162 MHz, 298 K) δ/ppm: 68.78. T₁ (Tol-D₈, 193 K) = 217 ms (Ru–H).

Figure S1. ^1H-NMR (C₆D₆, 400 MHz, 298 K) stack plot of reaction 1 with 1-2H₂. Only Ru–H region shown for clarity where (a) is a spectrum of 1, (b) is a mixture of 1 + 1-2H₂ in solution at 25 °C for 30 min and (c) is a spectrum of 1-2H₂
Figure S2. $^{31}$P{$^1$H} NMR (CD$_3$OD, 162 MHz, 298 K) stack plot of reaction 1 with 1-2H$_2$ where (a) is a spectrum of 1, (b) is a mixture of 1 + 1-2H$_2$ in solution at 25 °C for 30 min and (c) is a spectrum of 1-2H$_2$.

Figure S3. $^{31}$P{$^1$H} DOSY NMR of the mixture of 1-2H$_2$, 1 and 1-H$_2$/N$_2$.

| Complex      | δ / ppm | D x 10$^{-10}$ (m$^2$ s$^{-1}$) |
|--------------|---------|---------------------------------|
| 1            | 59.3    | 6.6                             |
| 1-2H$_2$     | 76.2    | 6.6                             |
| 1-H$_2$/N$_2$| 68.7    | 6.7                             |
5. Ru-Mediated C–H Bond Activation

\[
\begin{align*}
\text{Ru} & \quad \text{N} \quad \text{N} \\
\text{Cy}_3P & \quad \downarrow & \quad \text{Cy}_3P \\
\text{1 equiv.} & \quad \text{2 equiv.} & \quad \text{2 equiv.}
\end{align*}
\]

\[
\begin{align*}
\text{1} & \quad \text{2} & \quad \text{C}_6D_6 & \quad 25^\circ C \\
\text{Ru-N}_{2}(\text{N}_{2})_{2}(\text{PCy}_{3})_{2} & \quad 2\text{-methoxyacetophenone (2a)} & \quad \text{2a-H}_2 & \quad 4a \\
\quad & \quad \text{(1)} & \quad (\text{120} \mu\text{L, 0.23 M, 2 equiv}) & \quad \text{(53 mg, 57 %)}
\end{align*}
\]

C–H Activation of 2-methoxyacetophenone (2a): In a dinitrogen glovebox, [Ru(H)₂(N₂)₂(PCy₃)₂] (1) (200 µL, 0.07 M, 1 equiv), 2-methoxyacetophenone (2a) (120 µL, 0.23 M, 2 equiv) and ferrocene (80 µL, 0.17 M, 1 equiv) were added by micropipette into a J. Young NMR tube and made up to 600 µL with C₆D₆. The J. Young NMR tube was sealed and the reaction left at 25 °C for 24 h with a color change from straw yellow to deep purple/red observed. The reaction was monitored by ¹H-NMR and ³¹P{¹H}-NMR spectroscopy and yields calculated against internal standards; ferrocene for ¹H-NMR and PPh₃ in a borosilicate capillary tube for ³¹P{¹H}-NMR. Formation of 2a-H₂ was confirmed by comparison against a genuine sample of the substrate bought commercially. 4a was observed at >99 % yield and 2a-H₂ was observed at 87 % yield. Isolation of 4a was achieved from scale-up synthesis of the above reaction in toluene and recrystallization in hexamethyldisiloxane to give an orange powder as the product (53 mg, 57 %).

Data for 4a: ¹H-NMR (C₆D₆, 400 MHz, 298 K) δ/ppm: -14.90 (t, J_HP = 24.5 Hz, 1H, Ru-H), 1.03 – 2.24 (m, 66H, Cy), 2.95 (s, 3H, CH₃), 3.36 (s, 3H, OCH₃), 6.08 (d, J_HH = 7.9 Hz, 1H, Ar_Hₘ), 7.02 (t, J_HH = 7.7 Hz, 1H, Ar_Hₚ), 7.76 (d, J_HH = 7.5 Hz, 1H, Ar_Hₘ); ¹³C{¹H}-NMR (C₆D₆, 125 MHz, 298 K) δ/ppm: 27.5 (m, Cy), 28.4 (m, Cy), 30.1 (m, Cy), 31.8 (CH₃), 35.9 (t, ¹JC_P = 8.2 Hz, Cy), 54.2 (OCH₃), 100.7 (Cₘ), 130.1 (Cₚ), 136.6 (Cₘ), 162.3 (COCH₃), 204.3 (C=O), 212.3 (Ru–C); ³¹P{¹H}-NMR (C₆D₆, 162 MHz, 298 K) δ/ppm: 39.11.

FT-IR (ν/cm⁻¹): 1964 (Ru–H), 2078 (N≡N).

Due to the sensitivity of this complex repeated attempts to acquire CHN analysis failed to provide satisfactory results.

In situ NMR data for 2a-H₂: ¹H-NMR (C₆D₆, 400 MHz, 298 K) δ/ppm: 1.49 (d, J_HH = 6.5 Hz, 3H, CH₃), 3.20 (s, 3H, OCH₃), 5.17 (q, J_HH = 5.9 Hz, 1H, CH), 6.48 (d, J_HH = 8.3 Hz, 1H, Ar_Hₘ), 6.90 (t, J_HH = 7.2 Hz, 1H, Ar_Hₚ), 7.06 (td, J_HH = 9.4 Hz and 1.9z Hz, 1H, Ar_Hₘ), 7.44 (d, J_HH = 7.2 Hz, 1H, Ar_Hₚ). ¹³C{¹H}-NMR (C₆D₆, 125 MHz, 298 K) δ/ppm: 23.9 (CH₃), 54.7 (OCH₃), 66.0 (C(H)OH), 110.5 (Cₘ), 121.1 (Cₚ), 126.4 (C₀), 128.4 (Cₙ), 134.9 (C), 156.6 (C(OMe)).
Figure S4. $^1$H-NMR (C$_6$D$_6$, 400 MHz, 298 K) stack plot for C–H activation of 2-methoxyacetophenone

Figure S5. $^{31}$P-$^1$H-NMR (C$_6$D$_6$, 162 MHz, 298 K) stack plot for C–H activation of 2-methoxyacetophenone
C–H Activation of 1-(2-(p-tolyloxy)phenyl)ethanone (2b): In a dinitrogen glovebox, [Ru(H)\(_2\)(N\(_2\))\(_2\)(PCy\(_3\))\(_2\)] (1) (200 µL, 0.07 M, 1 equiv), 1-(2-(p-tolyloxy)phenyl)ethanone (2b) (120 µL, 0.23 M, 2 equiv) and ferrocene (80 µL, 0.17 M, 1 equiv) were added by micropipette into a J. Young NMR tube and made up to 600 µL with C\(_6\)D\(_6\). The J. Young NMR tube was sealed and the reaction mixture was left at 25 °C for 24 h with a color change from straw yellow to deep orange observed. The reaction was monitored by \(^1\)H-NMR and \(^{31}\)P\(^1\)H-NMR spectroscopy and yields calculated against internal standards; ferrocene for \(^1\)H-NMR and PPh\(_3\) in a borosilicate capillary tube for \(^{31}\)P\(^1\)H-NMR. Formation of 2b-H\(_2\) was confirmed by comparison against a genuine synthesised sample of the substrate. 4b was observed at 89 % yields and 2b-H\(_2\) was observed at 91 % yield. Isolation of 4b was achieved from scale-up synthesis of the above reaction in toluene and recrystallization in n-hexane to give deep purple crystalline solid as the product (26 mg, 68 %).

Data for 4b: \(^1\)H-NMR (C\(_6\)D\(_6\), 400 MHz, 298 K) δ/ppm: -14.82 (t, J = 24.1 Hz, 1H, RuH), 1.10 – 1.47 (m, 24H, Cy), 1.67 – 2.00 (m, 36H, Cy), 2.07 (s, 3H, CH\(_3\)), 2.25 (m, 6H, Cy), 2.98 (s, 3H, C(O)CH\(_3\)), 6.33 (d, J = 7.7 Hz, 1H, ArH\(_m\)), 6.92 (m, 1H, ArH\(_p\)), 6.93 (d, J = 8.6 Hz, 2H, OArH\(_p\)), 7.00 (d, J = 8.6 Hz, 2H, OArH\(_o\)), 7.81 (d, J = 7.5 Hz, 1H, ArH\(_m\)); \(^{13}\)C\(^1\)H-NMR (C\(_6\)D\(_6\), 125 MHz, 298 K) δ/ppm: 20.53 (ArCH\(_3\)), 26.7 (m, Cy), 27.7 (m, Cy), 29.9 (m, Cy), 31.3 (C(O)CH\(_3\)), 35.8 (t, J\(_{CP}\) = 8.2 Hz, Cy), 108.9 (C\(_m\)), 119.0 (OCC\(_O\)), 130.2 (C\(_p\)), 131.0 (CH\(_3\)CC\(_m\)), 138.9 (C\(_m\)), 204.3 (C=O), 212.2 (Ru–C); \(^{31}\)P\(^1\)H-NMR (C\(_6\)D\(_6\), 162 MHz, 298 K) δ/ppm: 39.87. FT-IR (ν/cm\(^{-1}\)): 1983 (Ru–H), 2106 (N≡N).

Elemental Analysis calc. for C\(_{51}\)H\(_{60}\)N\(_2\)O\(_2\)P\(_2\)Ru C, 66.86; H 8.80; N 3.06 found C, 67.11; H, 8.81; N, 2.96.

In situ NMR data for 2b-H\(_2\): \(^1\)H-NMR (400 MHz, 298 K, C\(_6\)D\(_6\)) δ/ppm: 1.46 (d, J\(_{HH}\) = 6.4 Hz, 3H, C(OH)CH\(_3\)), 2.06 (s, 3H, ArCH\(_3\)), 5.20 (m, 1H, CH), 6.77 (dd, J\(_{HH}\) = 7.4 Hz and 1.9 Hz, 1H, ArH\(_m\)), 6.82 (d, J\(_{HH}\) = 8.7 Hz, 2H, ArH\(_o\)), 6.86 (d, J\(_{HH}\) = 8.7 Hz, 2H, ArH\(_m\)), 6.94 (m, 2H, ArH), 7.58 (dd, J\(_{HH}\) = 6.8 Hz and 2.5 Hz, 1H, ArH\(_o\)). \(^{13}\)C \(^1\)H-NMR (125 MHz, 298 K, C\(_6\)D\(_6\)) δ/ppm: 20.6 (ArCH\(_3\)), 26.5 (C(OH)CH\(_3\)), 118.7 (C\(_m\)), 118.7 (OCC\(_O\)), 123.8 (C\(_m\)), 128.4 (C\(_o\)), 128.4 (C\(_p\)), 130.6 (CH\(_3\)CC\(_m\)), 132.6 (CCH\(_3\)), 154.4 (C\(_o\)), 155.7 (OC\(_i\)).
**Figure S6.** $^1$H–NMR ($C_6D_6$, 400 MHz, 298 K) stack plot of C–H activation of 1-(2-(p-tolyl)oxy)phenyl)ethanone

**Figure S7.** $^{31}$P${[^1]H}$–NMR ($C_6D_6$, 162 MHz, 298 K) stack plot of C–H activation of 1-(2- (p-tolyl)oxy)phenyl)ethanone
6. Ru-Mediated C–O Bond Activation

C–O Activation of 2,6-Dimethoxyacetophenone (3a): In a dinitrogen glovebox, [Ru(H)₂(N₂)₂(PCy₃)₂] (1) (200 µL, 0.07 M, 1 equiv), 2,6-dimethoxyacetophenone (3a) (120 µL, 0.23 M, 2 equiv) and ferrocene (80 µL, 0.17 M, 1 equiv) were added by micropipette into a J. Young NMR tube and made up to 600 µL with C₆D₆. The J. Young NMR tube was sealed and the reaction mixture heated at 40 °C for 24 h with a color change from straw yellow to deep red observed. The reaction was monitored by ¹H-NMR and ³¹P{¹H}-NMR spectroscopy and yields calculated against internal standards; ferrocene for ¹H-NMR and PPh₃ for ³¹P{¹H}-NMR in a borosilicate capillary tube. Formation of 3a-H₂ was confirmed by comparison against a genuine synthesised sample of the substrate. 4a was observed at 52 % yield and 3a-H₂ was observed at 98 % yield.

In situ NMR data for 4a same as above.

In situ NMR data for 3a-H₂: ¹H-NMR (C₆D₆, 400 MHz, 298 K) δ/ppm: 1.73 (d, J = 6.6 Hz, 3H, C-H₃), 3.17 (s, 6H, OCH₃), 5.82 (dt, J = 13.3 and 6.7 Hz, 1H, CH), 6.25 (d, J = 8.3 Hz, 2H, ArHₘ), 6.97 (t, J = 8.4 Hz, 1H, ArHₚ). ¹³C{¹H}-NMR (C₆D₆, 125 MHz, 298 K) δ/ppm: 24.2 (CH₃), 55.2 (OCH₃), 64.1 (COH), 104.6 (Cₘ), 158.0 (Cₚ).

A peak in ³¹P{¹H}-NMR at 64.43 ppm was identified as the major by-product [RuH₂(CO)(N₂)(PCy₃)₂] (5-N₂) in this reaction. The yield of 5-N₂ was 28 %.
Figure S8. $^1$H-NMR (C$_6$D$_6$, 400 MHz, 298 K) stack plot of C–O activation of 2,6-dimethoxyacetophenone.
**Figure S9.** $^{31}$P$_1$($^1$H)–NMR ($C_6D_6$, 162 MHz, 298 K) stack plot of C–O activation of 2,6-dimethoxyacetophenone.

C–O Activation of 2,6-bis-p-tolyloxyphenylacetophenone (3b): In a dinitrogen glovebox, [Ru(H)₂(N₂)₂(PCy₃)₂] (1) (200 µL, 0.07 M, 1 equiv), 2,6-bis-p-tolyloxy(phenyl)acetophenone (3b) (120 µL, 0.23 M, 2 equiv) and ferrocene (80 µL, 0.17 M, 1 equiv) were added by micropipette into a J. Young NMR tube and made up to 600 µL with $C_6D_6$. The J. Young NMR tube was sealed and the reaction mixture left to react at 40 °C for 24 h with a color change from straw yellow to deep orange observed. The reaction was monitored by $^1$H-NMR and $^{31}$P$[^1$H]–NMR spectroscopy and yields calculated against internal standards; ferrocene for $^1$H-NMR and PPh₃ in a borosilicate capillary tube for $^{31}$P$[^1$H]–NMR. Formation of 3b-H₂ was confirmed by comparison against a genuine synthesised sample of the substrate. 4b was observed at 54 % yield and 3b-H₂ was observed at 96 % yield.

*In situ* NMR data for 4b same as above.
In situ NMR data for 3b-H2: $^1\text{H}-\text{NMR (400 MHz, C}_6\text{D}_6, 298 \text{ K)} \delta/\text{ppm:}$ 1.75 (d, $J_{HH} = 6.3$ Hz, 3H, C(OH)CH$_3$), 2.05 (s, 6H, ArCH$_3$), 5.84 (dq, $J_{HH} = 13.4$ Hz and 6.8 Hz, 1H, CH), 6.50 (d, $J_{HH} = 8.2$ Hz, 2H, ArH$_m$), 6.73 (d, $J_{HH} = 8.3$ Hz, 1H, ArH$_p$), 6.85 (s, 8H, ArH); $^{13}\text{C}^1\text{H-}\text{NMR (125 MHz, C}_6\text{D}_6, 298 \text{ K)} \delta/\text{ppm:}$ 20.6 (ArCH$_3$), 24.4 (C(OH)CH$_3$), 113.6 (C$_m$), 119.5 (OCC$_D$), 128.2 (C$_p$), 130.6 (CH$_3$CC$_m$), 133.3 (CCH$_3$), 155.1 (OC$_d$), 156.7 (C$_o$).

A peak in $^1\text{H}-\text{NMR at } -25.87$ ppm (t, $J_{HP} = 19.8$ Hz, 1H, RuH) and a peak in $^{31}\text{P}^1\text{H-}\text{NMR at } 42.94$ ppm was identified as the major by-product in this reaction 6a [RuH(N$_2$)(p-OC$_6$H$_4$(CH$_3$))(PCy$_3$)$_2$]. The yield of 6a was 20 %. In addition, 7a and 8a were observed as minor by-products in <5 % yield.
Figure S10. $^1$H–NMR ($\text{C}_6\text{D}_6$, 400 MHz, 298 K) stack plot of C–O activation of 2,6-bis-$p$-tolyloxy(phenyl)acetophenone.

Figure S11. $^{31}$P{$^1$H}–NMR ($\text{C}_6\text{D}_6$, 162 MHz, 298 K) stack plot of C–O activation of 2,6-bis-$p$-tolyloxy(phenyl)acetophenone.
C–O Activation of double $^{13}$C-labelled 2,6-dimethoxyacetophenone ($^{13}$C$_2$-3a): In a dinitrogen glovebox, [Ru(H)$_2$(N$_2$)$_2$(PCy$_3$)$_2$] (1) (200 µL, 0.07 M, 1 equiv), $^{13}$C$_2$-3a (120 µL, 0.23 M, 2 equiv) and ferrocene (80 µL, 0.17 M, 1 equiv) were added by micropipette into a J. Young NMR tube and made up to 600 µL with C$_6$D$_6$. The J. Young NMR tube was sealed and the reaction mixture heated at 40 °C for 24 h with a color change from straw yellow to deep orange observed. The reaction was monitored by $^1$H-NMR and $^{31}$P{${^1}$H}-NMR spectroscopy. Structure determination of $^{13}$C$_2$-3a-H$_2$ and $^{13}$C-4a were compared to NMR data obtained for 3a-H$_2$ and 4a as the chemical shifts of the signals are anticipated to be near identical except for the $^{13}$C-labelled carbon atoms on methoxy group.

In situ NMR data for $^{13}$C-4a: $^1$H-NMR (C$_6$D$_6$, 400 MHz, 298 K) δ/ppm: -14.89 (t, $J_{HP}$ = 24.2 Hz, 1H, RuH), 0.95 – 2.31 (m, 66H, Cy), 3.36 (d, $J_{CH}$ = 143.6 Hz, 3H, O$^{13}$CH$_3$), 6.09 (d, $J_{HH}$ = 7.8 Hz, 1H, ArH$_m$), 7.02 (t, $J_{HHH}$ = 7.7 Hz, 1H, ArH$_p$), 7.77 (d, $J_{HHH}$ = 7.5 Hz, 1H, ArH$_m$); $^{13}$C{$^1$H}-NMR (C$_6$D$_6$, 125 MHz, 298 K) δ/ppm: 26.7 (m, Cy), 27.9 (m, Cy), 29.9 (m, Cy), 31.6 (CH$_3$), 35.8 (t, $J_{CP}$ = 8.3 Hz, Cy), 54.2 (O$^{13}$CH$_3$), 100.7 (C$_m$), 130.2 (C$_p$), 136.6 (C$_m$), 162.4 (COCH$_3$), 207.3 (C=O), 212.4 (Ru–C); $^{31}$P{$^1$H}-NMR (C$_6$D$_6$, 162 MHz, 298 K) δ/ppm: 39.06.

In situ NMR data for $^{13}$C$_2$-3a-H$_2$: $^1$H-NMR (C$_6$D$_6$, 400 MHz, 298 K) δ/ppm: 1.72 (s, 3H, CH$_3$), 3.17 (d, $J_{CH}$ = 144.1 Hz, 6H, O$^{13}$CH$_3$), 5.82 (m, 1H, CH), 6.25 (d, $J_{HH}$ = 8.3 Hz, 2H, ArH$_m$), 6.97 (t, $J_{HHH}$ = 8.4 Hz, 1H, ArH$_p$); $^{13}$C{$^1$H}-NMR (C$_6$D$_6$, 125 MHz, 298 K) δ/ppm: 24.2 (CH$_3$), 55.2 (O$^{13}$CH$_3$), 64.0 (COH), 104.6 (C$_m$), 158.0 (C$_p$).

Peaks in $^{31}$P{$^1$H}-NMR at 64.45 ppm and in $^{13}$C{$^1$H}-NMR at 207.3 ppm ($^{13}$C=O) allowed identification of [RuH$_2$(CO)(N$_2$)(PCy$_3$)$_2$] ($^{13}$C-5-N$_2$) as the major by-product in this reaction.
Figure S12. \(^1\)H–NMR (C\(_6\)D\(_6\), 400 MHz, 298 K) of C–O activation of \(^{13}\)C-labelled 2,6-dimethoxyacetophenone.

Figure S13. \(^{13}\)C–\(^1\)H–NMR (C\(_6\)D\(_6\), 125 MHz, 298 K) of C–O activation of double \(^{13}\)C-labelled 2,6-dimethoxyacetophenone.
Figure S14. $^{13}$C-1H-NMR (C$_6$D$_6$, 125 MHz, 298 K) stack plot showing only Ru-CO peak for comparison where (a) is the C-O cleavage reaction with $^{13}$C$_2$-3a, (b) is 5-N$_2$ and (c) is 5-H$_2$. 
7. Identification of By-products from C–O Bond Activation

A number of literature known carbonyl complexes and arene complexes of the \{Ru(PCy3)2\} fragment are known. Selected examples, including spectroscopic data, are included below for reference.\textsuperscript{2,6-9}

Figure S15. Previously identified \{Ru(PCy3)2\} complexes relevant to by-product identification.
For C–O Activation of 2,6-Dimethoxyacetophenone with 1

Reaction of 1 with ethanol: In a dinitrogen glovebox, \([\text{Ru(H)}_2(\text{N}_2)_2(\text{PCy}_3)_2]\) (1) (200 µL, 0.07 M, 1 equiv) and ethanol (1 µL, 0.02 mmol, 1 equiv) were added by micropipette into a J. Young NMR tube and made up to 600 µL with Tol-D_8. The J. Young NMR tube was sealed and removed from the glovebox. The reaction mixture was subjected to a freeze-pump-thaw procedure and then exposed to a dihydrogen atmosphere (1 bar). The J. Young NMR tube was sealed and then heated at 40 °C for 48 h. A color change from straw yellow to deep yellow was observed. The reaction was monitored by ^1H-NMR and ^31P{^1H}-NMR spectroscopy showing clean formation of 5-H_2 and methane. The J. Young tube was taken back into the glovebox and left open to the dinitrogen atmosphere for 3 h. ^1H-NMR and ^31P{^1H}-NMR spectroscopy showed a mixture of both 5-H_2 and 5-N_2 as the products.

In situ NMR data for 5-H_2: ^1H-NMR (Tol-D_8, 400 MHz, 233 K) δ/ppm: -7.08 (br s, 4H, RuH), 1.12 – 2.26 (m, 66H, Cy); ^31P{^1H}-NMR (Tol-D_8, 162 MHz, 233K) δ/ppm: 71.57; isolated ^13C{^1H}-NMR data for 5-H_2: ^13C{^1H}-NMR (C_6D_6, 125 MHz, 298 K) δ/ppm: 27.2 (m, Cy), 28.2 (t, J_CP = 4.9 Hz, Cy), 30.6 (m, Cy), 38.6 (t, J_CP = 10.5 Hz, Cy), 204.5 (t, J_CP = 8.3 Hz, C=O).

[Literature data for 5-H_2: ^1H-NMR (C_6D_6, 400 MHz, 301 K) δ/ppm: -7.0 (br s, 4H, RuH), 2.28 – 1.29 (m, 66H, Cy); ^31P{^1H}-NMR (C_6D_6, 162 MHz, 301K) δ/ppm: 72.1; ^13C{^1H}-NMR (C_6D_6, 100 MHz, 301 K) δ/ppm: 27.0 (s, Cy), 28.0 (t, J_CP = 5.1 Hz), 30.3 (s, Cy), 38.3 (t, J_CP = 10.7 Hz), 204.2 (t, J_CP = 3.7 Hz, C=O)].

In situ NMR data for 5-N_2: ^1H-NMR (Tol-D_8, 400 MHz, 233 K) δ/ppm: -13.51 (td, J_HH = 21.4 Hz and J_HH = 6.6 Hz, 1H, RuH), -6.68 (td, J_HH = 23.4 Hz and J_HH = 6.3 Hz, RuH) 1.03 – 2.38 (m, 66H, Cy); ^31P{^1H}-NMR (Tol-D_8, 162 MHz, 233K) δ/ppm: 63.86; isolated ^13C{^1H} NMR data for 5-N_2: ^13C{^1H}-NMR (C_6D_6, 125 MHz, 298 K) δ/ppm: 27.1 (m, Cy), 28.2 (t, J_CP = 4.8 Hz, Cy), 30.4 (m, Cy), 37.9 (t, J_CP = 8.2 Hz, Cy), 205.6 (m, C=O).

Comparison of the multinuclear NMR data allowed identification of 5-N_2 as the major by-product of C–O cleavage of 2,6-dimethoxyacetophenone.
**Figure S16.** VT $^1$H-NMR on a mixed sample of 5-N$_2$ and 5-H$_2$ generated from the reaction of I and EtOH dissolved in Tol-D$_8$. Only Ru–H region shown for clarity.

**Figure S17.** VT $^{31}$P{$^1$H} -NMR on a mixed sample of 5-N$_2$ and 5-H$_2$ generated from the reaction of I and EtOH dissolved in Tol-D$_8$. 
Figure S18. \(^1\text{H}-^{31}\text{P}\{^1\text{H}\}\) HMBC on a mixed sample of 5-N\(_2\) and 5-H\(_2\) generated from the reaction of 1 and EtOH at 193 K dissolved in Tol-D\(_8\)
For C–O Bond Activation of 2,6-bis-p-tolyloxy(phenyl)acetophenone with 1

In order to identify the major by-product during C–O bond activation of 2,6-bis-p-tolyloxy(phenyl)acetophenone with 1, reactions were carried out with both 4-methylphenol and 4-tert-butylphenol. The latter was used as a surrogate for the former in order to facilitate product separation and purification by crystallization. A combination of NMR spectroscopy and single x-ray crystallography was used to determine the structures of the products from both the reaction of 1 with 4-methylphenol and 4-tert-butyl phenol.

Reaction of 1 with 4-methylphenol: In a dinitrogen glovebox, [Ru(H₂)(N₂)₂(PCy₃)₂] (1) (54 mg, 0.08 mmol, 1 equiv) and 4-methylphenol (9 mg, 0.08 mmol, 1 equiv) were weighed into a 20 mL scintillation vial and dissolved in toluene (2 mL). The mixture was left to stir in the glovebox at 25 °C for 24 h. A color change from straw yellow to deep orange/brown was observed. The solvent was removed in vacuo to leave a brown oily residue which was extracted with n-hexane (2 mL) resulting in a yellow precipitate forming in the brown solution. The yellow precipitate was isolated and washed with cold pentane (1 mL) and left to dry to give a yellow powder as a mixed product of 7a/8a (22 mg). The mother liquor from this reaction was reduced in vacuo to give a brown powder as 6a contaminated with the decomposition product [Ru(H₂)(η⁶-C₆D₆)PCy₃]₁₀. Multiple attempts to isolate 6a cleanly were unsuccessful.

In situ NMR data for 6a: ¹H-NMR (C₆D₆, 500 MHz, 298 K) δ/ppm: -25.86 (t, J_HH = 19.2 Hz, 1H, RuH); ³¹P{¹H}-NMR (C₆D₆, 162 MHz, 298 K) δ/ppm: 41.94.

NMR data for 7a: ¹H-NMR (C₆D₆, 400 MHz, 298 K) δ/ppm: -11.51 (br s, 1H, RuH), 1.06 – 2.09 (m, 66H, Cy), 1.93 (s, 3H, CH₃), 5.01 (d, J_HH = 5.6 Hz, 2H, ArHm), 5.16 (d, J_HH = 5.6 Hz, 2H, ArHg); ¹³C{¹H}-NMR (C₆D₆, 125 MHz, 298 K) δ/ppm: 27.1 (s, Cy), 28.3 (br s, Cy), 31.0 (m, Cy), 35.2 (CH₃), 77.3 (Cm), 95.8 (Co), 137.0 (Cp), 163.0 (C=O); ³¹P{¹H}-NMR (C₆D₆, 162 MHz, 298 K) δ/ppm: 50.44 (br).

NMR data for 8a: ¹H-NMR (C₆D₆, 400 MHz, 298 K) δ/ppm: -11.51 (br s, 2H, RuH), 1.06 – 2.09 (m, 33H, Cy), 2.16 (s, 3H, CH₃), 7.05 (d, J_HH = 8.1 Hz, 2H, ArHm), 7.38 (d, J_HH = 7.9 Hz, 2H, ArHg), 11.66 (s, 1H, OH); ¹³C{¹H}-NMR (C₆D₆, 125 MHz, 298 K) δ/ppm: 20.4 (CH₃), 27.1 (s, Cy), 28.3 (br s, Cy), 31.0 (m, Cy), 116.0 (Co), 127.0 (Cp), 128.3 (Ci), 130 (Co); ³¹P{¹H}-NMR (C₆D₆, 162 MHz, 298 K) δ/ppm: 50.44 (br).
Comparison of the multinuclear NMR data (including those for reaction of 4-tert-butyl phenol below) allowed identification of 6a as the major by-product of C–O cleavage of 2,6-bis-p-tolylxy(phenyl)acetophenone.

Reaction of 1 with 4-tert-butyl phenol: In a dinitrogen glovebox, [Ru(H)2(N2)2(PCy3)2] (1) (33 mg, 0.05 mmol, 1 equiv) and 4-tert-butyl phenol (8 mg, 0.05 mmol, 1 equiv) were weighed into a scintillation vial and dissolved in toluene (2 mL). The mixture was left to stir in the glovebox at 25 °C for 24 h. A color change from straw yellow to deep orange/red was observed. The solvent was removed in vacuo to leave a dark red oily residue which was extracted with hexane (2 mL) resulting in a yellow precipitate forming in an orange solution. The yellow precipitate was isolated and washed with cold pentane (1 mL) and left to dry to give a yellow powder as a mixed product of 7b/8b (<10 mg). The mother liquor from this reaction was left in glovebox freezer at -35 °C overnight to give red crystals 6b (15 mg, 49 %).

NMR data for 6b: 1H-NMR (Tol-D8, 500 MHz, 298 K) δ/ppm: -25.80 (t, JHP = 18.7 Hz, 1H, RuH), 1.03 – 2.30 (m, 66H, Cy), 1.39 (s, 9H, C(CH3)3), 6.67 (d, JHH = 8.6 Hz, 2H, ArHn), 7.27 (d, JHH = 8.7 Hz, 2H, ArHd); 13C{1H}-NMR (C6D6, 125 MHz, 298 K) δ/ppm: 27.13 (s, Cy), 28.2 (m, Cy), 30.3 (s, Cy), 30.8 (s, Cy) 32.3 (C(CH3)3), 33.6 (t, JCP = 8.4 Hz, Cy), 33.9 (C(CH3)3), 118.5 (Cp), 125.9 (Cm), 135.2(Cp), 167.0 (C–O); 3P{1H}-NMR (Tol-D8, 162 MHz, 298 K) δ/ppm: 41.9.

FT-IR (v/cm−1): 1893 (Ru–H), 2044 (N≡N).

NMR data for 7b: 1H-NMR (C6D6, 400 MHz, 298 K) δ/ppm: -11.09 (br s, 1H, RuH), 0.97 (s, 9H, C(CH3)3), 1.06 – 2.35 (m, 66H, Cy), 5.30 (d, JHP = 7.0 Hz, 2H, ArH), 5.44 (d, JHP = 6.8 Hz, 2H, ArHd); 13C{1H}-NMR (C6D6, 125 MHz, 298 K) δ/ppm: 31.7 (C(CH3)3), 33.8 (C(CH3)3), 84.1 (Cp), 96.3 (Cm), 111.0 (Cp), 164.5 (C=O); 3P{1H}-NMR (C6D6, 162 MHz, 298 K) δ/ppm: 75.1.

NMR data for 8b: 1H-NMR (400 MHz, C6D6, 298 K) δ/ppm: -11.07 (d, JHP = 17.0 Hz, 2H, RuH), 1.06 – 2.35 (m, 33H, Cy), 1.26 (s, 9H, (C(CH3)3), 7.23 (m, 4H, ArH), 10.11 (s, 1H, OH); 13C{1H}-NMR (C6D6, 125 MHz, 298 K) δ/ppm: 31.9 (C(CH3)3), 34.0 (C(CH3)3), 115.8 (Cm), 126.4 (Cp), 141.1 (Cp), 156.7 (C–OH); 3P{1H}-NMR (C6D6, 162 MHz, 298 K) δ/ppm: 75.1.

1 The remaining 13C resonances of the PCy3 ligands could not be assigned due to the overlapping signals in the mixture of 8a/8b which could not be resolved by HSQC, HMBC or DEPT NMR experiments.
8. Competition and Inhibition reactions

Intermolecular C–H bond versus C–O bond activation: In a dinitrogen glovebox, 
[Ru(H)₂(N₂)₂(PCy)₃] (1) (200 µL, 0.07 M, 1 equiv), 2,6-dimethoxycetophenone (3a) (120 µL, 0.23 M, 2 equiv), 2,2-dimethylpropiophenone (4.7 µL, 0.028 mmol, 2 equiv) and ferrocene (80 µL, 0.17 M, 1 equiv) were added by micropipette into a J. Young NMR tube and made up to 600 µL with C₆D₆. The J. Young NMR tube was sealed and the reaction left at 25 °C for 24 h with a color change from straw yellow to deep red observed. The reaction was monitored by ¹H-NMR and ³¹P{¹H}-NMR spectroscopy and yields calculated against the internal standard ferrocene. 4c was observed at >99 % yield, 3c-H₂ was observed in 59 % yield and 3a-H₂ was observed in 27 % yield.

In situ NMR data for 4c: ¹H-NMR (C₆D₆, 400 MHz, 298 K) δ/ppm: -14.76 (t, J_{HP} = 25.7 Hz, 1H, RuH), 0.86 – 1.03 (m, 6H, Cy), 1.20 – 1.35 (m, 12H, Cy), 1.40 – 2.00 (m, 42H, Cy), 1.52 (s, 9H, C(CH₃)₃), 2.10 – 2.25 (m, 6H, Cy), 6.77 (t, J_{HH} = 7.4 Hz, 1H, ArHₘ), 7.00 (m, 1H, ArHₚ), 7.96 (dd, J_{HH} = 8.1 Hz and 1.3 Hz, 1H, ArHₒ), 8.21 (d, J_{HH} = 7.6 Hz, 1H, ArHᵢₐₗ); ¹³C{¹H}-NMR (CsD₆, 125 MHz, 298 K) δ/ppm: 27.4 (m, Cy), 29.3 (C(CH₃)₃), 29.7 (s, Cy), 30.1 (s, Cy), 36.1 (t, J_{CP} = 8.4 Hz), 43.6 (C(CH₃)₃), 117.8 (Cₘ), 128.7 (Cₚ), 130.5 (Cₒ), 144.9 (Cₗ), 209.6 (Ru–C), 211.4 (C=O); ³¹P{¹H}-NMR (CsD₆, 162 MHz, 298 K) δ/ppm: 36.9. FT-IR (ν/cm⁻¹): 2046 (Ru–H), 2089 (N≡N). Elemental Analysis calc. for C₄₇H₈₀N₂O₂P₂Ru C, 66.24; H, 9.46; N, 3.29 found C, 66.33; H, 9.27; N, 3.15.

In situ NMR data for 3c-H₂: ¹H-NMR (C₆D₆, 400 MHz, 298 K) δ/ppm: 0.91 (s, 9H, C(CH₃)₃), 4.05 (d, J_{HH} = 2.9 Hz, 1H, CH), 7.09-7.21 (m, 5H, ArH); ¹³C{¹H}-NMR (CsD₆, 125 MHz, 298 K) δ/ppm: 26.1 (C(CH₃)₃), 35.6 (C(CH₃)₃), 82.13 (CH), 128.0 (Cₘ).

In situ NMR data for 3a-H₂ same as above.
Complexation of CO versus N\textsubscript{2} to ruthenium: In a dinitrogen glovebox, [RuH(N\textsubscript{2})(o-C\textsubscript{6}H\textsubscript{4}C(O)OMe)(PCy\textsubscript{3})\textsubscript{2}] (4a) (5 mg, 0.006 mmol) was weighed and dissolved in C\textsubscript{6}D\textsubscript{6} (500 µL) and transferred in to a J. Young NMR tube. A ferrocene internal standard capillary insert was added to the J. Young NMR tube. The J. Young NMR tube was sealed and removed from the glovebox. The reaction mixture was subjected to a freeze-pump-thaw procedure and then exposed to a CO atmosphere (1.05 bar) resulting in an immediate color change from orange to straw yellow. \textsuperscript{1}H and \textsuperscript{31}P{\textsuperscript{1}H}-NMR confirmed full conversion of 4a into [RuH(CO)(o-C\textsubscript{6}H\textsubscript{4}C(O)OMe)(PCy\textsubscript{3})\textsubscript{2}] (4a-CO). Solvent removed \textit{in vacuo} to remove any excess CO in the reaction solution leaving a yellow solid. [RuH\textsubscript{2}(N\textsubscript{2})\textsubscript{2}(PCy\textsubscript{3})\textsubscript{2}] (1) (100 µL, 0.07 M) was added by micropipette into the J. Young NMR tube and made up to 500 µL with C\textsubscript{6}D\textsubscript{6} then the reaction mixture was heated at 40 °C for 24 h. The reaction was monitored by \textsuperscript{1}H-NMR and \textsuperscript{31}P{\textsuperscript{1}H}-NMR spectroscopy and yields calculated against the internal standard. 4a was observed at <10 % yield.

\textit{In situ} NMR data for 4a-CO: \textsuperscript{1}H-NMR (C\textsubscript{6}D\textsubscript{6}, 400 MHz, 298 K) δ/ppm: -15.19 (t, J\textsubscript{HP} = 23.4 Hz, 1H, RuH), 0.91 – 2.37 (m, 66H, Cy), 2.88 (s, 3H, CH\textsubscript{3}), 3.36 (s, 3H, OCH\textsubscript{3}), 6.21 (d, J\textsubscript{HH} = 7.8 Hz, 1H, ArH\textsubscript{m}), 7.12 (t, J\textsubscript{HH} = 7.4 Hz, 1H, ArH\textsubscript{p}), 8.00 (d, J\textsubscript{HH} = 7.1 Hz, 1H, ArH\textsubscript{m}); \textsuperscript{31}P{\textsuperscript{1}H}-NMR (C\textsubscript{6}D\textsubscript{6}, 162 MHz, 298 K) δ/ppm: 41.9.

\textit{In situ} NMR data for 4a same as above.

\textit{In situ} NMR data for 5-N\textsubscript{2} same as above.
Conversion of 6b into 7b and 8b: In a dinitrogen glovebox, [RuH(κ1-OC₆H₄C(CH₃)₃)(N₂)(PCy₃)₂] (6b) (15 mg, 0.02 mmol) was dissolved in benzene (1.8 mL) and transferred into a J. Young NMR tube along with ferrocene (50 μL, 0.17 M). The J. Young NMR tube was sealed and removed from the glovebox. The reaction mixture was subjected to a freeze-pump-thaw procedure and then exposed to a dihydrogen atmosphere (1.01 bar). The reaction was monitored by ¹H-NMR and ³¹P{¹H}-NMR spectroscopy and yields calculated against ferrocene showing the conversion of 6b into 7b and 8b.

In situ NMR data for 6b, 7b and 8b same as above.
Table S1. Comparison of C–O cleavage reactions under different conditions.

| [Ru] complex                  | Ru : 3a | Temp / °C | Time / h | Atmosphere | Yield 4a / % | T\(_{1/2}\) / h\(^*\) |
|-------------------------------|---------|-----------|----------|------------|--------------|----------------|
| [Ru(H\(_2\))(N\(_2\))(PCy\(_3\))\(_2\)]  | 1 : 2   | 25        | 72       | N\(_2\)    | 35           | n/a            |
| [Ru(H\(_2\))(N\(_2\))(PCy\(_3\))\(_2\)]  | 1 : 2   | 40        | 24       | N\(_2\)    | 52           | 6.0            |
| [Ru(H\(_2\))(N\(_2\))(PCy\(_3\))\(_2\)]  | 1 : 2   | 40        | 5        | Ar         | 50           | 1.6            |
| [Ru(H\(_2\))(\eta\(_2\)-H\(_2\))(PCy\(_3\))\(_2\)] | 1 : 2   | 25        | 24       | H\(_2\)    | 0            | n/a            |
| [Ru(H\(_2\))(\eta\(_2\)-H\(_2\))(PCy\(_3\))\(_2\)] | 1 : 2   | 25        | 24       | Ar         | 0            | n/a            |
| [Ru(H\(_2\))(\eta\(_2\)-H\(_2\))(PCy\(_3\))\(_2\)] | 1 : 4   | 25        | 24       | Ar         | 0            | n/a            |

\(^*\)Time taken for 25\% of 4a to form in C–O cleavage reaction
9. Xray Data

The X-ray crystal structure of 1

The two Ru–H hydrogen atoms in the structure of 1 were located from ΔF maps and refined freely.

The X-ray crystal structure of 4a

The Ru–H hydrogen atom in the structure of 4a was located from a ΔF map and refined freely. The included toluene solvent molecule was found to be disordered across a centre of symmetry, and two unique orientations of ca. 29 and 21% occupancy were identified (with the action of the inversion centre generating two further orientations of the same occupancies). The geometries of both orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and all of the atoms were refined isotropically.

The X-ray crystal structure of 4b

The Ru–H hydrogen atom in the structure of 4b was located from a ΔF map and refined freely.

The X-ray crystal structure of 4c

The Ru–H hydrogen atom in the structure of 4c was located from a ΔF map and refined freely. The complex lists across a mirror plane that passes through Ru1, H1, C1 to C7, O7, C8, C10, N11 and N12. When refined using AFIX 137, the methyl hydrogen atoms on C10 would not settle, and so the AFIX 33 command was used instead. The included benzene solvent molecule was found to be disordered across a mirror plane, and this was modelled using one complete 50% occupancy molecule (with the action of the mirror plane generating a second 50% occupancy orientation). The geometry of the unique orientation was optimised, and all of the non-hydrogen atoms were refined anisotropically.

The X-ray crystal structure of 6b

The Ru–H hydrogen atom in the structure of 6b was located from a ΔF map and refined freely. The included solvent was found to be highly disordered, and the best approach to handling this diffuse electron density was found to be the SQUEEZE routine of PLATON[1]. This suggested a total of 73 electrons per unit cell, equivalent to 36.5 electrons per asymmetric unit. Before the use of SQUEEZE the solvent clearly resembled a straight chain disordered across a centre of symmetry, but the length of the chain was uncertain. Pentane (C\textsubscript{5}H\textsubscript{12}, 42 electrons) was chosen as it was the most recently used crystallisation solvent. 0.85 pentane molecules corresponds to 35.7 electrons, so this was used as the solvent present. As a result, the atom list for the asymmetric unit is low by 0.85(C\textsubscript{5}H\textsubscript{12}) = C\textsubscript{4.25}H\textsubscript{10.2} (and that for the unit cell low by C\textsubscript{8.5}H\textsubscript{20.4}) compared to what is actually presumed to be present.

The X-ray crystal structure of 8a

The Ru–H hydrogen atom in the structure of 8a was located from a ΔF map and refined freely. The O–H hydrogen atoms of the O50- and O60-based included 4-methylphenol moieties
were also located from ΔF maps, and were refined freely subject to an O–H distance constraint of 0.90 Å. The included heptane solvent molecule was found to be disordered. Three orientations were identified of ca. 51, 28 and 21% occupancy, their geometries were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientations were refined isotropically).

The X-ray crystal structure of S1

The presumed one terminal and three bridging Ru–H and Ru–H–Ru hydrogen atoms in the structure of S1 could not be located; their presence (which would give both ruthenium atoms an octahedral coordination geometry) was inferred by analogy with the closely related species dinitrogen-tris(μ2-hydrido)-hydrido-tetrakis(triphenylphosphine)-di-ruthenium (CCDC refcode BUGSIF10) which has triphenyl phosphine ligands where S1 has tricyclohexyl phsophines. As a consequence the atom list is low by 4 hydrogen atoms. The included solvent was found to be highly disordered, and the best approach to handling this diffuse electron density was found to be the SQUEEZE routine of PLATON. This suggested a total of 219 electrons per unit cell, equivalent to 109.5 electrons per asymmetric unit. Before the use of SQUEEZE the solvent clearly resembled heptane (C7H16, 58 electrons), and 2 heptane molecules corresponds to 116 electrons, so this was used as the solvent present. As a result, and taking into account the 4 “missing” hydrides, the atom list for the asymmetric unit is low by 2(C7H16) + 4H = C14H36 (and that for the unit cell low by C28H72) compared to what is actually presumed to be present.

Figure. S19    The crystal structure of I (50% probability ellipsoids).
**Figure. S20**  The crystal structure of 4a (50% probability ellipsoids).

**Figure. S21**  The crystal structure of 4b (50% probability ellipsoids).
Figure. S22  The crystal structure of the $C_2$-symmetric complex 4e (50% probability ellipsoids). The mirror plane passes through Ru1, H1, the N$_2$ unit, and all of the phenyl-tert-butyl ketone ligand with the exception of two of the t-Bu methyl groups.

Figure. S23  The crystal structure of 6b (50% probability ellipsoids).
Figure. S24  The crystal structure of 8a (50% probability ellipsoids).

Figure. S25  The crystal structure of S1.
Figure. S26a  The crystal structure of S1 (50% probability ellipsoids).

Figure. S26b  Line drawing of S1 including the one terminal and three bridging Ru–H and Ru–H–Ru hydrogen atoms.
10. DFT Studies
Computational Details

DFT calculations were run using Gaussian 09 (Revision D.01)\textsuperscript{13} using the BP86 density functional.\textsuperscript{14-16} Ru and P centres were described with Stuttgart RECPs and associated basis sets (ECP28MWB for Ru and ECP10MWB for P).\textsuperscript{17-19} The P basis set was augmented with the addition of d-orbital polarisation ($\zeta = 0.387$).\textsuperscript{20} 6-31+G* basis sets were used for N and O and 6-31G** basis sets were used for all other atoms.\textsuperscript{21-23}

Geometry optimisation calculations were performed without symmetry constraints. The Gaussian 09 default optimisation criteria were tightened to $10^{-9}$ on the density matrix and $10^{-7}$ on the energy matrix. The default numerical integration grid was also improved using a pruned grid with 99 radial shells and 590 angular points per shell. Frequency analyses for all stationary points were performed using the enhanced criteria to confirm the nature of the structures as either minima (no imaginary frequency) or transition states (only one imaginary frequency). Intrinsic reaction coordinate (IRC) calculations were used to connect transition states and minima located on the potential energy surface allowing a full energy profile (calculated at 298.15 K, 1 atm) of the reaction to be constructed.\textsuperscript{24,25} Free energies reported within the main text are corrected for the effects of benzene solvent ($\varepsilon = 2.2706$) using the integral equation formalism polarizable continuum model (IEFPCM).\textsuperscript{26} In addition, single point dispersion corrections were applied to the BP86 optimised geometries employing Grimme’s D3 parameter set with the Becke-Johnson (BJ) damping as implemented in Gaussian.\textsuperscript{27}

The graphical user interface used to visualise the various properties of the intermediates and transition states was GaussView 5.0.9.\textsuperscript{28} Natural Bond Orbital analysis was carried out using NBO 5.9.\textsuperscript{29,30} The topology of the electron density for selected systems within the QTAIM framework was carried out using the AIMALL software.\textsuperscript{31-33} Weak interactions were identified using the Non Covalent Interaction (NCI) approach.\textsuperscript{34} The analysis was carried out with the NCIplot software and visualized using the VMD interface.\textsuperscript{35,36}
Figure S27. Mechanisms for the formation of Ru(0). A transition state structure was not identified for $\text{TS}_{\text{N}_2\text{-diss}}$. 
Figure S28. Mechanisms for the ketone transfer hydrogenation. Reaction profile in grey outlines a higher energy pathway involving Ru(0).
Figure S29. C–H Activation Mechanisms at Ru(0) intermediate.
Figure S30. C–O Activation Mechanisms at Ru(0) intermediate.
**Figure S31.** Nucleophilic Aromatic Substitution Mechanism.
Assessment of DFT Functional Effects

A range of DFT exchange-correlation functionals were chosen to assess the influence of functional on key steps in the C–H and C–O bond activation pathways (Table S6 and S7). The functionals include GGA functionals (BP86\textsuperscript{14–16}, PBE\textsuperscript{39}) and hybrid-GGA functionals (B3LYP\textsuperscript{38,40}, PBE0\textsuperscript{39,41}); hybrid Minnesota functionals, M06L\textsuperscript{42} and M11L, long range-corrected functional, ωB97X\textsuperscript{43}, and Grimme’s D2 dispersion corrected ωB97X-D\textsuperscript{43}. The BP86-optimized coordinates for each conformer were re-optimised using the new functional.
Table S2. Relative free energies of key transition states and preceding intermediates re-optimised using specified density functionals. All values single point corrected for solvent. Dispersion single point correction using D3(BJ) for BP86, PBE, PBE0 and B3LYP, D2 correction for ωB97X.

|                          | BP86  | PBE   | B3LYP | PBE0  | ωB97X | ωB97XD | M06L | M11L |
|--------------------------|-------|-------|-------|-------|-------|--------|------|------|
| Ru(0) Formation          |       |       |       |       |       |        |      |      |
| TS-H₂-diss-2             | 38.4  | 43.3  | 40.4  | 46.3  | 44.5  | 45.5   | -    | 36.0 |
| Int-s7-3                 | 5.5   | 10.3  | 3.1   | 6.0   | 2.2   | 3.0    | 10.2 | 6.5  |
| TS-s7-5                  | 32.6  | 36.4  | 33.8  | 35.3  | 33.8  | 34.6   | 38.3 | 35.8 |
| 2nd Hydrogenation TS of Aryl. Ketone |       |       |       |       |       |        |      |      |
| TS-s7-4                  | 29.4  | 29.9  | 28.3  | 24.5  | 20.0  | -      | -    | 30.8 |
| CH Activation @ Ru(II)   |       |       |       |       |       |        |      |      |
| Int-2                    | 19.2  | 25.9  | 16.4  | 20.2  | 14.9  | 14.5   | 25.1 | 21.0 |
| TS-2                     | 23.4  | 27.1  | 18.9  | 22.5  | 16.1  | 17.2   | 28.4 | 26.1 |
| CO Activation @ Ru(II)   |       |       |       |       |       |        |      |      |
| Int-7                    | 23.7  | 28.6  | 17.5  | 21.7  | 13.4  | 15.2   | 26.2 | 22.4 |
| TS-5                     | 32.0  | 36.6  | 33.3  | 32.9  | 28.0  | 28.9   | 37.0 | 35.6 |
| Hydride Attack Mechanism |       |       |       |       |       |        |      |      |
| Int-1'                   | 9.7   | 10.7  | 8.9   | 10.2  | 4.6   | 5.5    | 10.3 | 8.7  |
| TS-s9-1                  | 33.8  | 38.3  | 37.3  | 38.5  | 36.0  | 35.8   | 38.2 | 41.9 |
| CO Activation @ Ru(0)    |       |       |       |       |       |        |      |      |
| Int-13                   | 24.8  | 29.7  | 24.6  | 31.6  | 28.1  | 30.3   | 26.6 | 20.4 |
| TS-s8-3                  | 27.1  | 36.0  | 32.6  | 40.3  | 41.1  | 42.1   | 36.9 | 33.3 |

(a) Reported in main article
Figure S32. (left) NBO and (right) QTAIM data on Int-4, TS-4 and Int-5
Figure S33. CH Activation with experimental system (a) and model system [Ru(H)2(N2)(PMe3)2] (b). Calculations performed using B3PW91 density functional concurrent with Clot et al. 37.
Figure S34. Int-6 (a) Int-11 (b) and Int-12 (c) featuring stabilizing CH agostic interactions (Å).
Figure S35. Isomerization of Int-11 to Int-12: cis- to trans- movement of phosphine ligands
Figure S36. High energy MeOH formation pathways from Int-9.
**Figure S37.** Mechanism for Formaldehyde formation involving β-hydride elimination from Ru-OMe intermediate.
Figure S38. Mechanism for MeOH decomposition leading to the experimentally observed product, 5-N₂.
|                  | σ-Complex Formation | C-X Bond Formation |
|------------------|---------------------|--------------------|
| CH Activation    | *Int-2*             | *TS-2*             |
| P–Ru–P (°)       | 156.7               | 160.3              |
|                  | *Int-3*             | *TS-3*             |
|                  | 147.2               | 147.4              |
|                  | *Int-4*             |                    |
|                  | 160.7               |                    |
| CO Activation    | *Int-7*             | *TS-5*             |
| P–Ru–P (°)       | 153.5               | 131.5              |
|                  | *Int-8*             | *TS-6*             |
|                  | 125.6               | 122.3              |
|                  | *Int-9*             |                    |
|                  | 113.8               |                    |

*Table S3.* Comparison of P–Ru–P bond angles of intermediates involved in σ-Complex and C-X bond formation steps. For reference, *Int-1* P–Ru–P = 160.1°.
Figure S39. NCI Plots of Int-7 and Int-2.

(a) Int-7 (b) Int-2

strong attraction

weak attraction
| Donor → Acceptor Interactions | $E^2$ (kcal/mol) |
|--------------------------------|-----------------|
| **BD(1) C1–H3 → BD*(1) Ru–H1** | 65.73           |
| **LP(2) Ru → BD*(1) C1–H3**    | 5.74            |
| **LP(3) Ru → BD*(1) C1–H3**    | 13.18           |

*Table S4.* Second order perturbation estimates ($E^2$ values, kcal mol$^{-1}$) of donor (filled orbital) to acceptor (empty orbital) interactions within **Int-3** (CH Activation).

| Donor → Acceptor Interactions | $E^2$ (kcal/mol) |
|--------------------------------|-----------------|
| **BD(1) Ru–C5 → BD*(1) Ru–H1** | 67.54           |
| **BD(1) Ru–H1 → BD*(1) Ru–C5** | 46.39           |
| **BD(1) C5–O2 → BD*(1) Ru–H1** | 9.83            |
| **LP(2) O2→ BD*(1) Ru–H1**     | 21.17           |

*Table S5.* Second order perturbation estimates ($E^2$ values, kcal mol$^{-1}$) of donor (filled orbital) to acceptor (empty orbital) interactions within **Int-8** (CO Activation).
Figure S40. QTAIM analysis of Int-7 and Int-8. ρ<sub>b</sub> in bold and ∇<sup>2</sup>ρ<sub>b</sub> in italics

|      | Int-7 | | | Int-8 | | |
|------|-------|----|----|-------|----|----|---|
|      | G<sub>b</sub> (au) | V<sub>b</sub> (au) | H<sub>b</sub> (au) | Å | G<sub>b</sub> (au) | V<sub>b</sub> (au) | H<sub>b</sub> (au) | Å |
| Ru–C5 | - | - | - | 3.53 | +0.0549 | -0.0857 | -0.0308 | 2.22 |
| Ru–O2 | +0.0318 | -0.0311 | +0.0007 | 2.52 | +0.0902 | -0.0918 | -0.0016 | 2.19 |
| C5–O2 | +0.3200 | -0.7302 | -0.4102 | 1.38 | +0.1402 | -0.3478 | -0.2076 | 1.51 |

Table S6. Bond lengths (Å), local electron kinetic (G<sub>b</sub>), potential (V<sub>b</sub>) and total (H<sub>b</sub>) energy densities for Ru–C5, Ru–O2 and C5–O2 interactions in Int-7 and Int-8.
Figure S41. NBO analysis of Int-2, Int-3, Int-7 and Int-8. NPA charges.

**C–H Activation**

![C–H Activation Diagram]

**C–O Activation**

![C–O Activation Diagram]
11. Multinuclear NMR data of substrates

Figure S42. $^1$H NMR of 1

Figure S43. $^{31}$P{$^1$H} NMR of 1
Figure S44. $^1$H NMR of 3b

Figure S45. $^{13}$C ($^1$H) NMR of 3b
Figure S46. $^1$H NMR of $^{13}$C$_2$-3a

Figure S47. $^{13}$C{$_1^1$H} NMR of $^{13}$C$_2$-3b
Figure S48. $^1$H NMR of transfer hydrogenation product of 2b

Figure S49. $^{13}$C[$^1$H] NMR of transfer hydrogenation product of 2b
Figure S50. $^1$H NMR of transfer hydrogenation product of 3b

Figure S51. $^{13}$C($^1$H) NMR of transfer hydrogenation product of 3b
Figure S52. $^1$H NMR of 4a

Figure S53. $^{31}$P {$^1$H} NMR of 4a
Figure S54. HSQC NMR of the reaction of 1 with 2a

Figure S55. HMBC NMR of the reaction of 1 with 2a
Figure S56. $^1$H NMR of 4b

Figure S57. $^{31}$P{$^1$H} NMR of 4b
Figure S58. HSQC NMR of the reaction of 1 with 3a

Figure S59. HMBC NMR of the reaction of 1 with 3a
Figure S60. $^1$H NMR of 7a/8a

Figure S61. $^{31}$P{${^1}$H} NMR of 7a/8a
Figure S62. $^1$H NMR of 6b

Figure S63. $^{31}$P{$^1$H} NMR of 6b
Figure S64. $^1$H NMR of 7b/8b

Figure S65. $^{31}$P{H} NMR of 7b/8b
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