## Supporting Information for

# Troponate-/Aminotroponate Ruthenium-Arene complexes: Synthesis, Structure and Ligand Tuned Mechanistic Pathway for Direct C-H bond Arylation with Arylchlorides in water 

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General Information, Materials and Instrumentation. All reactions were performed under open atmosphere except the catalytic reactions which were performed under Ar atmosphere using chemicals of high purity purchased from Sigma Aldrich and Alfa Aesar. Dichloro bridged arene-ruthenium(II) precursors $\left[\left\{\left(\eta^{6}-\mathrm{C}_{6} \mathrm{H}_{6}\right) \mathrm{RuCl}_{2}\right\}_{2}\right]$ and $\left[\left\{\left(\eta^{6}-\mathrm{C}_{10} \mathrm{H}_{14}\right) \mathrm{RuCl}_{2}\right\}_{2}\right]$ were synthesized according to the literature procedures. ${ }^{51}{ }^{1} \mathrm{H}$ NMR ( 400 MHz ), ${ }^{13} \mathrm{C}$ NMR ( 100 MHz ), and ${ }^{31} \mathrm{P}$ NMR ( 161.97 MHz ) spectra were recorded at 298 K using $\mathrm{CDCl}_{3}$ or DMSO$d_{6}$ as the solvent on a Bruker Avance 400 spectrometer. Tetramethylsilane (TMS) was used as an external standard and the chemical shifts in ppm are reported relative to the centre of the singlet at 7.26 ppm for $\mathrm{CDCl}_{3}$ and 2.49 ppm for DMSO- $d_{6}$ in ${ }^{1} \mathrm{H}$ NMR, and to the centre of the triplet at 77.0 ppm for $\mathrm{CDCl}_{3}$ and 39.50 ppm for DMSO- $d_{6}$ in ${ }^{13} \mathrm{C}$ NMR. Suitable single crystals of complexes $[\mathbf{R u}] \mathbf{- 1}$ and $[\mathbf{R u}] \mathbf{- 3}$ along with the single crystal of ligand $\mathbf{L 3}$ were subjected to single-crystal X-ray structural studies using Agilent Technologies Supernova CCD system. ESI (positive and negative mode), and high-resolution mass spectra (HRMS) were recorded on a micro TF-Q II mass spectrometer. The voltammograms were recorded on a CHI620D electrochemical analyser in dichloromethane as the solvent and 0.1 $\mathrm{M} \mathrm{TBAF}_{6}$ as the supporting electrolyte. The electrodes used were glassy carbon as a working electrode, a Pt wire as a counter electrode and the Silver as a reference electrode. Infrared spectra ( 4000 to $500 \mathrm{~cm}^{-1}$ ) were recorded with a BRUKER TENSOR 27 instrument in KBr pellets. CCDC deposition numbers of the ligand $\mathbf{L 3}$, and complexes $[\mathbf{R u}]-\mathbf{1}$ and $[\mathbf{R u}]-\mathbf{3}$ are 1431337, 1431336 and 1441581, respectively.


Table S1. Crystal data and structure refinement details for Ligand L3.

| Crystal parameters | Ligand (L3) |
| :--- | :--- |
| empirical formula | $\mathrm{C}_{13} \mathrm{H}_{17} \mathrm{~N}$ O |
| Fw | 203.28 |
| $T(\mathrm{~K})$ | $293(2)$ |
| $\lambda(\AA)$ | 1.54184 |
| Cryst system | $\mathrm{P} 21 / \mathrm{n}$ |
| space group | $0.14 \times 0.12 \times 0.11$ |
| Cryst size, mm | $12.1210(7)$ |
| $a, \AA$ | $8.5610(5)$ |
| $b, \AA$ | $12.4050(8)$ |
| $c, \AA$ | 90.00 |
| $\alpha$, deg | $111.635(7)$ |
| $\beta$, deg | 90.00 |
| $\gamma$, deg |  |


| $V, \AA^{3}$ | $1196.56(12)$ |
| :--- | :--- |
| $Z$ | 4 |
| $\rho_{\text {calcd }}, \mathrm{g} \mathrm{cm}^{-3}$ | 1.128 |
| $\mu, \mathrm{~mm}^{-1}$ | 0.554 |
| $F(000)$ | 440 |
| $\theta$ range, deg | $6.43-73.23$ |
| completeness to $\theta_{\max }$ | $[73.2$ |
| no. of data collected/unique data | $13562 / 1916$ |
| params/restraints | 1.042 |
| goodness of fit on $F^{2}$ | $\mathrm{R} 1=0.0607 \mathrm{wR} 2=0.1627$ |
| Final R indices $[I>2 \sigma(I)]$ | $\mathrm{R} 1=0.0517 \mathrm{wR} 2=0.1499$ |
| R indices (all data) |  |

Table S2. Selected bond lengths and bond angles for Ligand L3.

| Bond lengths (Å) |  |
| :---: | :---: |
| O1-C13 | $1.2478(18)$ |
| C13-C7 | $1.488(2)$ |
| C13-C12 | $1.414(2)$ |
| C7-C8 | $1.393(2)$ |
| N1-C7 | $1.3317(19)$ |
| N1-C1 | $1.4548(19)$ |


| C1-C2 | $1.513(3)$ |
| :---: | :---: |
| Bond angles ( ${ }^{\circ}$ ) |  |
| C1-N1-C7 | $128.62(13)$ |
| N1-C7-C13 | $111.27(12)$ |
| N1-C7-C8 | $122.60(14)$ |
| N1-C1-C2 | $108.38(16)$ |
| N1-C1-C6 | $110.53(15)$ |
| O1-C13-C7 | $116.37(13)$ |
| O1-C13-C12 | $120.07(14)$ |

Table S3. Selected bond lengths and bond angles for complexes [Ru]-1 and [Ru]-3.

| Bond lengths (̊) | $[\mathbf{R u}]-\mathbf{1}$ | $[\mathbf{R u}] \mathbf{- 3}$ |
| :--- | :---: | :---: |
| Ru1-O1 | $2.0789(18)$ | $2.0463(19)$ |
| Ru1-O2 | $2.079(2)$ | - |
| Ru1-N1 | - | $2.115(3)$ |
| Ru1-C | 1.645 | 1.676 |
| Ru1-C $\mathrm{C}_{\text {avg. }}$ | 2.167 | 2.188 |
| Ru1-Cl1 | $2.4094(8)$ | $2.4196(8)$ |
| O1-C1 | $1.284(3)$ | $1.277(4)$ |
| O2-C7 | $1.289(3)$ | - |
| N1-C7 | - | $1.319(4)$ |
| N1-C8 | - | $1.479(4)$ |
| C1-C7 | $1.454(4)$ | $1.468(4)$ |


| C1-C2 | 1.403(4) | 1.386(4) |
| :---: | :---: | :---: |
| C2-C3 | 1.382(4) | 1.384(5) |
| Bond angles ( ${ }^{\circ}$ ) |  |  |
| O1-Ru1-O2 | 76.63(7) | - |
| O1-Ru-N1 | - | 75.86(9) |
| O1-Ru1-Cl1 | 84.48(6) | 85.93(6) |
| O2-Ru1-Cl1 | 84.47(6) | - |
| N1-Ru-Cl1 | - | 84.68(7) |
| $\mathrm{C}_{\mathrm{t}}$-Ru1-O1 | 131.17 | 126.70 |
| $\mathrm{C}_{\mathrm{t}}$-Ru1-O2 | 131.60 | - |
| $\mathrm{C}_{\mathrm{t}}$-Ru-N1 | - | 136.67 |
| $\mathrm{C}_{\mathrm{t}}$-Ru1-Cl1 | 129.63 | 128.18 |
| O1-Ru-C11 | 91.76(9) | - |
| O1-Ru-C13 | 149.20(10) | 86.99(10) |
| O1-Ru-C15 | - | 129.76(10) |
| O2-Ru-C11 | 144.18(11) | - |
| N1-Ru-C13 | - | 140.67(11) |
| O2-Ru-C13 | 133.18(9) | - |
| N1-Ru-C15 | - | 96.90(11) |

Table S4. Cyclic voltammetric data of ruthenium complexes.

| S.No. | Complexes | Anodic pot. <br> $\left(\mathbf{E}_{\mathbf{p a}}\right)$ | Cathodic pot. <br> $\left(\mathbf{E}_{\mathbf{p c}}\right)$ | Oxidation half <br> wave potential <br> $\mathbf{E}_{1 / 2}(\mathbf{m V})$ | $\Delta \mathbf{E}(\mathbf{m V})$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathbf{1}$ | $[\mathbf{R u}]-\mathbf{1}$ | 1.108 | 0.770 | 0.939 | 0.338 |
| $\mathbf{2}$ | $[\mathbf{R u}]-\mathbf{2}$ | 1.220 | 1.142 | 1.181 | 0.078 |
| $\mathbf{3}$ | $[\mathbf{R u}]-\mathbf{3}$ | 1.213 | 1.133 | 1.173 | 0.080 |
| $\mathbf{4}$ | $[\mathbf{R u}]-\mathbf{5}$ | 1.023 | 0.759 | 1.023 | 0.529 |
| $\mathbf{5}$ | $[\mathbf{R u}]-6$ | 1.237 | 1.168 | 1.202 | 0.069 |



Figure S1. Cyclic voltammogram of [Ru]-1 in dichloromethane.


Figure S2. Cyclic voltammogram of [Ru]-5 in dichloromethane.

## Catalytic C-H bond arylation reactions

## ${ }^{1}$ H NMR spectra of compounds C-H arylated products



2-(4'-methoxy-[1,1'-biphenyl]-2-yl)pyridine: Yield: 0.112 g ( $43 \%$ ). ${ }^{\mathbf{1}} \mathbf{H}$ NMR ( $\mathbf{4 0 0} \mathbf{~ M H z , ~}$ $\left.\mathbf{C D C l}_{3}\right): \delta(\mathrm{ppm})=8.64(\mathrm{~d}, J=4.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.70-7.65(\mathrm{~m}, 1 \mathrm{H}), 7.47-7.36(\mathrm{~m}, 4 \mathrm{H}), 7.12-7.05$ $(\mathrm{m}, 3 \mathrm{H}), 6.90(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 6.79(\mathrm{~d}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 3.78(\mathrm{~s}, 3 \mathrm{H}),{ }^{\mathbf{1 3}} \mathbf{C}$ NMR ( $\mathbf{1 0 0}$ $\left.\mathbf{M H z}, \mathbf{C D C l}_{3}\right): \delta(\mathrm{ppm})=159.48,158.54,149.42,140.21,139.37,135.25,133.73,130.77$, 130.44, 128.52, 127.29, 125.43, 121.29, 113.59, 55.19, HRMS (ESI) m/z: calculated $262.1226\left[\left(\mathrm{C}_{18} \mathrm{H}_{15} \mathrm{NO}+\mathrm{H}\right)\right]^{+}$, Found: $262.1276\left[\left(\mathrm{C}_{18} \mathrm{H}_{15} \mathrm{NO}+\mathrm{H}\right)\right]^{+}$.


2-(4,4'-dimethoxy-[1,1',3',1'-terphenyl]-2'-yl)pyridine: ${ }^{1} \mathrm{H}$ NMR (400 MHz, $\mathrm{CDCl}_{3}$ ): $\delta(\mathrm{ppm})=8.36(\mathrm{~d}, J=4.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.50-7.46(\mathrm{~m}, 1 \mathrm{H}), 7.41-7.39(\mathrm{~m}, 2 \mathrm{H}), 7.35-7.31(\mathrm{~m}, 1 \mathrm{H})$, $7.02(\mathrm{~m}, 4 \mathrm{H}), 6.94-6.87(\mathrm{~m}, 2 \mathrm{H}), 6.70-6.65(\mathrm{~m}, 4 \mathrm{H}), 3.74(\mathrm{~s}, 6 \mathrm{H}),{ }^{13} \mathbf{C}$ NMR ( $\mathbf{1 0 0} \mathbf{~ M H z}$, $\left.\mathbf{C D C l}_{3}\right): \delta(\mathrm{ppm})=159.24,158.08,148.50,141.43,138.36,135.09,134.06,130.68,129.18$, 128.15, 126.83, 120.86, 113.11, 55.12, HRMS (ESI) m/z: calculated: $368.1645\left[\left(\mathrm{C}_{25} \mathrm{H}_{21} \mathrm{NO}_{2}\right.\right.$ $+\mathrm{H})]^{+}$, Found: $368.1694\left[\left(\mathrm{C}_{25} \mathrm{H}_{21} \mathrm{NO}_{2}+\mathrm{H}\right)\right]^{+}$.

## Mass spectral study of the reaction of [Ru]-1 with potassium acetate (KOAc).

To trap the carboxylate coordinated cyclometallated species, [Ru]-1 ( $0.025 \mathrm{mmol}, 0.0098 \mathrm{~g}$ ) was added with potassium acetate $(0.05 \mathrm{mmol}, 0.0049 \mathrm{~g})$ and 5 mL water to the two necked round bottom flask. Reaction vessel was then provided with magnetic bar and was degassed with vacuum pump followed by the gassing with Argon. Reaction mixture was stirred for 3 h at $100^{\circ} \mathrm{C}$ and after the completion of reaction time, mixture was cooled down. Crude reaction mixture was filtered through filter tip of $1000 \mu \mathrm{~L}$ and mixture was diluted with acetonitrile. ESI-MS was recorded in positive mode and analyzed further.

## Mass spectral study of the reaction of [Ru]-1 with potassium pivalate (KOPiv).

To trap the carboxylate coordinated cyclometallated species, [Ru]-1 ( $0.025 \mathrm{mmol}, 0.0098 \mathrm{~g}$ ) was added with potassium pivalate $(0.05 \mathrm{mmol}, 0.0070 \mathrm{~g})$ and 5 mL water to the two necked round bottom flask. Reaction vessel was then provided with magnetic bar and was degassed with vacuum pump followed by the gassing with Argon. Reaction mixture was stirred for 3 h at $100^{\circ} \mathrm{C}$ and after the completion of reaction time, mixture was cooled down. Crude reaction mixture was filtered through filter tip of $1000 \mu \mathrm{~L}$ and mixture was diluted with acetonitrile. ESI-MS was recorded in positive mode and analyzed further.

## Mass spectral study of the reaction of [Ru]-1 with 2-phenylpyridine in different catalyst to substrate ratio

[ $\mathbf{R u} \mathbf{u} \mathbf{- 1}$ was added with 2-phenylpyridine and 4-chloroanisole in $\mathrm{C}: \mathrm{S}$ ratio 1:1, 1:2 and 1:5 in water ( 5 mL ) followed by addition of potassium carbonate (3 equiv.). Reaction mixture was heated at $100{ }^{\circ} \mathrm{C}$ for 3 h under Ar atmosphere. After completion of reaction time, crude reaction mixture was filtered through filter tip of $1000 \mu \mathrm{~L}$ and mixture was diluted with acetonitrile. ESI-MS was recorded in positive mode and analyzed further (Figure S3).


Figure S3. Relative abundance of $\mathrm{Ru}(I I)$ cyclometallated species ([Ru]-A and [Ru]B) with different catalyst to substrate ratio with [Ru]-1 catalyst under similar reaction conditions.

Time dependent mass spectral study of the reaction of [Ru]-1 with 2phenylpyridine (S/C ratio 2:1).

To perform the time dependent study of two intermediates ([Ru]-A and $[\mathbf{R u}]-\mathbf{B}$ ), a two necked round bottom flask was charged with $[\mathbf{R u}]-1$ catalyst $(0.05 \mathrm{mmol}, 0.0196 \mathrm{~g})$ and 2 phenylpyridine ( $0.1 \mathrm{mmol}, 14.3 \mu \mathrm{~L}$ ). Reaction was carried out in water ( 5 mL ) at $100{ }^{\circ} \mathrm{C}$ under Ar atmosphere for $3 \mathrm{~h} .100 \mu \mathrm{~L}$ of aliquot was withdrawn at $5 \mathrm{~min}, 10 \mathrm{~min}, 15 \mathrm{~min}, 30$ $\mathrm{min}, 45 \mathrm{~min}, 60 \mathrm{~min}, 90 \mathrm{~min}, 120 \mathrm{~min}, 150 \mathrm{~min}$ and 180 min . Crude reaction mixture was filtered through filter tip of $1000 \mu \mathrm{~L}$ and further diluted with acetonitrile. ESI-MS was recorded in positive mode and analyzed further.

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Abundance of [Ru]-A and [Ru]-B species with different Ru(II) catalysts ([Ru]-1
to [Ru]-3)
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To strengthen the presence of species $[\mathbf{R u} \mathbf{]} \mathbf{- A}$ and $[\mathbf{R u}]-\mathbf{B}$ with different catalysts, 0.025 $\mathrm{mmol} \mathrm{Ru}($ II $)$ catalyst ([Ru]-1 to $[\mathbf{R u}]-\mathbf{3}$ ) were taken separately in a two necked round bottom flask with 3 equiv. of $\mathrm{K}_{2} \mathrm{CO}_{3}$ and 0.05 mmol 2-phenylpyridine keeping S/C ratio 2:1 in 5 mL water under Ar atmosphere. Reaction was performed at $100^{\circ} \mathrm{C}$ for 3 h and crude reaction mixture was filtered through filter tip of $1000 \mu \mathrm{~L}$ and further diluted with acetonitrile. ESIMS was recorded in positive mode and analyzed further.


Figure S4. Relative abundance of Ru(II) cyclometallated intermediates [Ru]-A and $[R u]-B$ with different ruthenium(II) catalysts ([Ru]-1 to $[R u]-3)$.

## Mass spectral investigation for stability of complexes [Ru]-1 and [Ru]-2 in

 waterTo check the stability of the complexes in water, a series of experiments were performed by stirring 0.010 g of ruthenium complexes ([Ru]-1 or $[\mathbf{R u}]-\mathbf{2}$ ) dissolved in water ( 5 mL ) at room temperature or heating at $100{ }^{\circ} \mathrm{C}$, with or without added $\mathrm{K}_{2} \mathrm{CO}_{3}(0.207 \mathrm{~g})$ under Ar atmosphere. For mass spectral analysis, $100 \mu \mathrm{~L}$ of aliquots were withdrawn at different intervals of time as at $0 \mathrm{sec}, 10 \mathrm{~min}, 1 \mathrm{~h}, 5 \mathrm{~h}, 10 \mathrm{~h}, 1$ day, 3 days and 1 week from the crude reaction mixture, which were filtered and diluted with methanol before analysis by ESI-MS.


Figure S5. Mass spectral investigation for the stability of [Ru]-1 complex in water.


Figure S6. Mass spectral investigation for stability of [Ru]-2 complex in water.


Figure S7. Mass spectral investigation for stability of [Ru]-1 complex in water with $\mathrm{K}_{2} \mathrm{CO}_{3}$.


Figure S8. Mass spectral investigation for stability of [Ru]-2 complex in water with $\mathrm{K}_{2} \mathrm{CO}_{3}$.

## Preparation of intermediate species $\left[\left(\eta^{6}-p\right.\right.$-cymene $) \mathrm{Ru}\left(\kappa^{2}-C, N-2-\right.$ phenylpyridine)CI]

Reaction vessel was charged with the $\left[\left\{\left(\eta^{6}-p \text {-cymene }\right) \mathrm{RuCl}_{2}\right\}_{2}\right](0.5 \mathrm{mmol}, 0.306 \mathrm{~g})$ and potassium acetate ( $3.0 \mathrm{mmol}, 0.294 \mathrm{~g}$ ) in 25 mL of methanol under Ar atmosphere. Solution was stirred for 24 h at room temperature and the product was isolated by reducing volume under vacuum. Product was precipitated with ether and washed with $n$-hexane several times to remove excess/unreacted 2-phenylpyridine. Product was air dried and analyzed by ${ }^{1} \mathrm{H}$ NMR.

${ }^{1} \mathbf{H}$ NMR ( $\left.\mathbf{4 0 0} \mathbf{~ M H z}, \mathbf{C D C l}_{3}\right): \delta(\mathrm{ppm})=9.24(\mathrm{~d}, J=4.0 \mathrm{~Hz}, 1 \mathrm{H}), 8.16(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H})$, $7.71(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.68-7.64(\mathrm{~m}, 1 \mathrm{H}), 7.62(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.19-7.17(\mathrm{~m}, 1 \mathrm{H})$, 7.06-7.01 (m, 2H), 5.59-5.55 (m, 2H), $5.17(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.98(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H})$, 2.45-2.42 (m, 1H), $2.05(\mathrm{~s}, 3 \mathrm{H}), 0.97(\mathrm{~d}, J=4.0 \mathrm{~Hz}, 3 \mathrm{H}), 0.85(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 3 \mathrm{H})$.

Reaction of the cycloruthenated species, [Ru]-A, with 4-chloroanisole. Cyclometallated species [Ru]-A was taken ( $0.1 \mathrm{mmol}, 0.039 \mathrm{~g}$ ) in a two necked round bottom flask under Ar atmosphere followed by the addition of base $\left(\mathrm{K}_{2} \mathrm{CO}_{3}, 0.3 \mathrm{mmol}\right.$, 0.0414 g ) with 2.5 equivalent of 4-chloroanisole ( $0.25 \mathrm{mmol}, 30 \mu \mathrm{~L}$ ). 5 mL water was added and reaction mixture was stirred for 8 h at $100^{\circ} \mathrm{C}$. Resulting reaction mixture was cooled
down to room temperature and extracted with ethyl acetate $(3 \times 10 \mathrm{~mL})$ and solvent volume was reduced under pressure. Crude reaction mixture was analyzed with ${ }^{1} \mathrm{H}$ NMR.

## Computational Study

Density functional theory (DFT) calculations were carried out using Gaussian 09 package ${ }^{\text {S2 }}$ using Becke's three parameter exchange and the Lee-Yang-Parr's correlation functional (B3LYP). ${ }^{\mathrm{S} 3} 6-311 \mathrm{G}(\mathrm{d}, \mathrm{p})^{\mathrm{S} 4-\mathrm{S} 5}$ basis functions are used for non-metals ( $\mathrm{C}, \mathrm{H}, \mathrm{O}, \mathrm{N}, \mathrm{P}$ and Cl ), whereas LANL2DZ-ECP (effective core potentials) ${ }^{\text {S6-S7 }}$ is used for Ru. Water is used as an implicit solvent using the polarizable continuum model (PCM) as implemented in Gaussian 09. ${ }^{\text {S8-S10 }}$ In all the calculations, D3 version of Grimme's dispersion corrections is included for long range interactions. ${ }^{\text {S11 }}$ Harmonic vibrational frequencies are calculated to characterize the nature of the stationary points. Zero-point energy and entropy corrections (at 298.15 K ) are included for the free energy calculations.

[Ru]-1

[Ru]-2

[Ru]-3

## Optimized structures of [Ru]-1, [Ru]-2, and [Ru]-3. Here white, skyblue, blue, red, turquoise, green and teal colour balls denote the hydrogen, carbon, nitrogen, oxygen, phosphorous, chlorine, and ruthenium atoms, respectively.

The reaction free energies $\left(\Delta G_{A}\right.$ for $[\mathbf{R u}]-\mathbf{A}$ and $\Delta G_{B}$ for $\left.[\mathbf{R u}]-\mathbf{B}\right)$ are calculated for the formation of $[\mathbf{R u}]-\mathbf{A}$ and $[\mathbf{R u}]-\mathbf{B}$ are using the following equations:

$$
\begin{gathered}
\Delta \mathrm{G}_{\mathrm{A}}=\left(\mathrm{G}_{\mathrm{A}}+\mathrm{G}_{\mathrm{H} 3 \mathrm{O}+}+\mathrm{G}_{\mathrm{Cl}-}+\mathrm{G}_{\text {troponate/aminotroponate }}\right)-\left(\mathrm{G}_{[\mathrm{Ru}] \text {-cat }}+2 \mathrm{G}_{\mathrm{H} 2 \mathrm{O}}+\mathrm{G}_{\mathrm{phpy}}\right) \\
\Delta \mathrm{G}_{\mathrm{B}}=\left(\mathrm{G}_{\mathrm{B}}+\mathrm{G}_{\mathrm{H} 3 \mathrm{O}+}+\mathrm{G}_{\mathrm{Cl}-}+\mathrm{G}_{p \text {-cymene }}\right)-\left(\mathrm{G}_{[\mathrm{Ru}]-\text { cat }}+3 \mathrm{G}_{\mathrm{H} 2 \mathrm{O}}+\mathrm{G}_{\mathrm{phpy}}\right)
\end{gathered}
$$

where $\mathrm{G}_{\mathrm{A}}, \mathrm{G}_{\mathrm{H} 3 \mathrm{O}+}, \mathrm{G}_{\mathrm{Cl}}, \mathrm{G}_{\text {troponat//aminotroponate }}, \mathrm{G}_{[\mathrm{Ru}]-\text { cat }}, \mathrm{G}_{\mathrm{H} 2 \mathrm{O}}, \mathrm{G}_{\text {phpy }}, \mathrm{G}_{\mathrm{B}}$ and $\mathrm{G}_{p \text {-cymene }}$ are the total free energies (with zero point and entropy corrections) of $[\mathbf{R u}]-\mathbf{A}, \mathbf{H}_{\mathbf{3}} \mathbf{O}^{+}, \mathbf{C l}^{-}$, troponato/aminotroponato, [Ru]-catalysts, $\mathbf{H}_{2} \mathbf{O}$, 2-phenylpyridine, $[\mathrm{Ru}]-\mathrm{B}$ and $p$ cymene, respectively.

We have calculated the binding energy $\left(\mathrm{E}_{\mathrm{B}}\right)$ (Table 1) of the leaving groups ( $p$-cymene and troponate/aminotroponate) to understand such trend. The binding energies are calculated using the following formula:

$$
\left.\begin{array}{c}
\mathrm{E}_{\mathrm{B}}=\mathrm{E}_{[\mathrm{Ru}]-\text { cat }}-\left(\mathrm{E}_{(\text {Ruu }] \text {-cat })-(p \text {-cymene })}+\mathrm{E}_{(p \text {-cymene })}\right) \\
\mathrm{E}_{\mathrm{B}}=\mathrm{E}_{[\mathrm{Ru}]-\mathrm{Cat}}-\left(\mathrm{E}_{(\text {Ru] }] \text { cat })}-(\text { (roponate/aminotroponate })\right.
\end{array}+\mathrm{E}_{(\text {(roponate/aminotroponate })}\right)
$$

where $\mathrm{E}_{([\mathrm{Ru}] \text {-cat }) ~-~(p-c y m e n e) ~}$ is the single point energy of the catalyst without p-cymene ligand, $\mathrm{E}_{(p \text {-cymene })}$ is the single point energy of the $p$-cymene within the geometry of catalyst, $\mathrm{E}_{([\mathrm{Ru}] \text {-cat })-}$ (troponato/aminotroponato) is the single point energy of the catalyst without troponate/aminotroponate ligand, and $\mathrm{E}_{\text {(troponate/aminotroponate) }}$ is the single point energy of the troponate/aminotroponate within the geometry of catalyst.

Table S5. The binding energies ( $\mathrm{kcal} / \mathrm{mol}$ ) calculated for p-cymene and troponate/aminotroponate ligands in ruthenium catalysts.

|  | $[\mathbf{R u}]-\mathbf{1}$ | $[\mathbf{R u}]-2$ | $[\mathbf{R u}]-3$ |
| :--- | :--- | :--- | :--- |
| $\boldsymbol{p}$-cymene | -43.7 | -37.6 | -41.2 |
| troponate/aminotroponate | -68.8 | -85.8 | -87.2 |

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${ }^{1} \mathrm{H}$ NMR of 2-(isopropylamino)cyclohepta-2,4,6-trienone (L2).


${ }^{1} \mathrm{H}$ NMR of [Ru]-1

${ }^{13} \mathrm{C}$ NMR of [Ru]-1


Mass spectra of [Ru]-1

${ }^{1} \mathrm{H}$ NMR of $[\mathrm{Ru}]-2$


Mass spectra of [Ru]-2


Mass spectra of [Ru]-3


Mass spectra of [Ru]-4


## ${ }^{1} \mathrm{H}$ NMR of [Ru]-5




Mass spectra of [Ru]-5


Mass spectra of [Ru]-6


Mass spectra of [Ru]-7


Mass spectra of [Ru]-8



${ }^{1}$ H NMR of 2-(4'-methoxy-[1,1'-biphenyl]-2-yl)pyridine


${ }^{13} \mathrm{C}$ NMR of 2-(4'-methoxy-[1, 1'-biphenyl]-2-yl)pyridine


${ }^{1}$ H NMR of 2-(4,4'-dimethoxy-[1, 1',3',1"-terphenyl]-2'-yl)pyridine


${ }^{13} \mathrm{C}$ NMR of 2-(4,4'-dimethoxy-[1,1',3',1"-terphenyl]-2'-yl)pyridine



${ }^{1} \mathrm{H}$ NMR of cyclometallated species $\left[\left(\eta^{6}-p\right.\right.$-cymene $) \operatorname{RuCl}\left(\kappa^{2}-C, N\right.$-phenylpyridine $\left.)\right]$


IR data of [Ru]-1


IR data of [Ru]-5

