# Supporting Information

## Promotive Mechanism of $CO_2$ on the Hydrogenation of Levulinic Acid into γ-Valerolactone Catalyzed by $RuCl_3$ in Aqueous Solution

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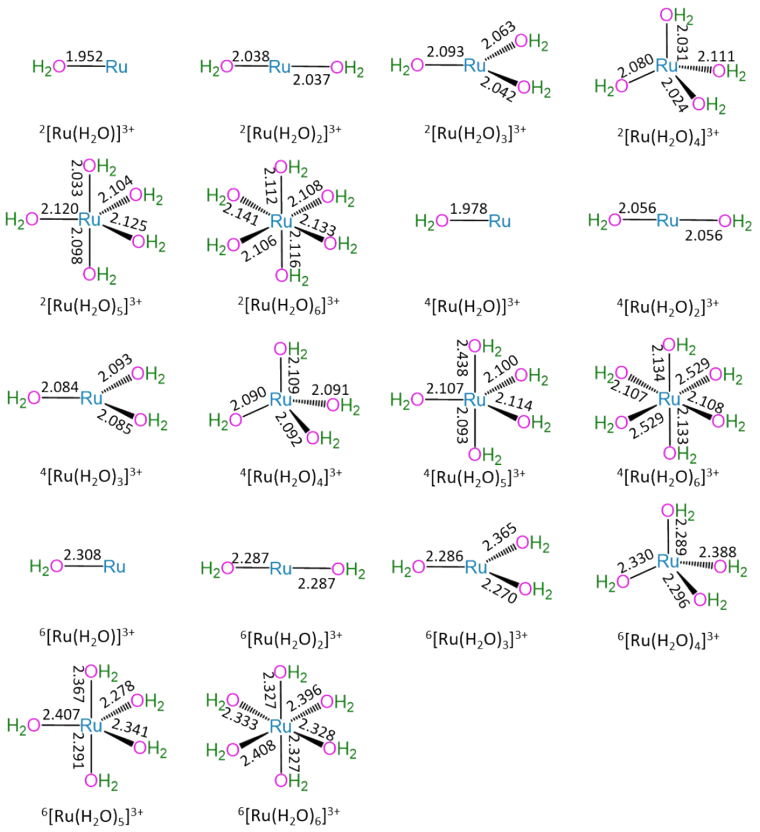
# Catalogue

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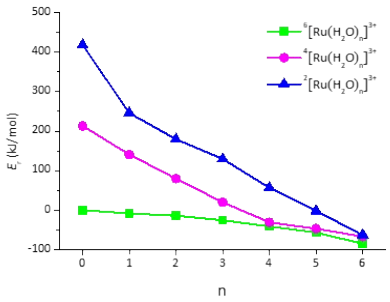


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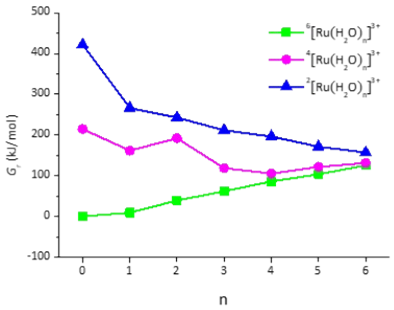



(c)

**Figure S1** The geometric structures (a), the relative energy ($E_r$, kJ mol$^{-1}$) (b) and the formed Gibbs free energies ($G_r$, kJ mol$^{-1}$) (c) for $^{x}[Ru(H_2O)_n]^{3+}$ (n=0-6) complexes as function of the number of coordinating $H_2O$ molecules (n) relative to the dissociated $^{6}Ru^{3+}$ cation and $H_2O$ in aqueous solution

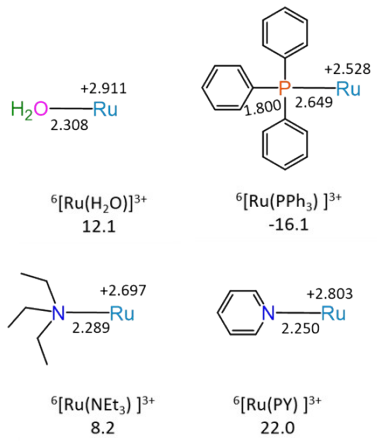
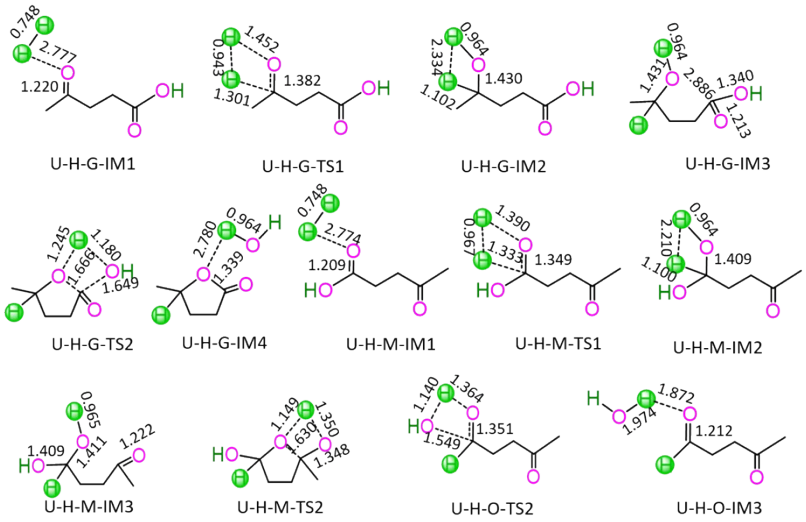
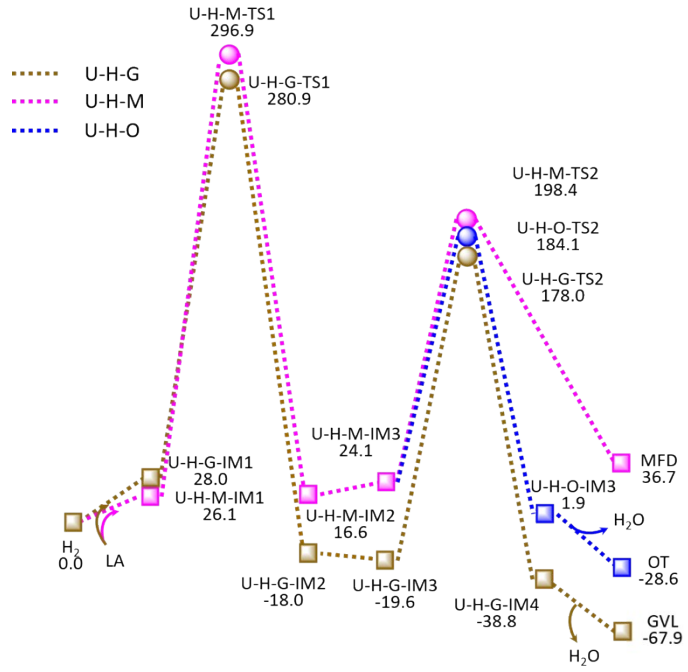



**Figure S2** The optimized geometric structures, the Gibbs free energies ($G_r$, kJ mol$^{-1}$) relative to the dissociated $^6Ru^{3+}$ cation and ligand, and the charge of natural bond orbital (NBO) of Ru-site in $^6[Ru(H_2O)]^{3+}$, $^6[Ru(PPh_3)]^{3+}$, $^6[Ru(NEt_3)]^{3+}$ and $^6[Ru(PY)]^{3+}$ complexes in aqueous solution.

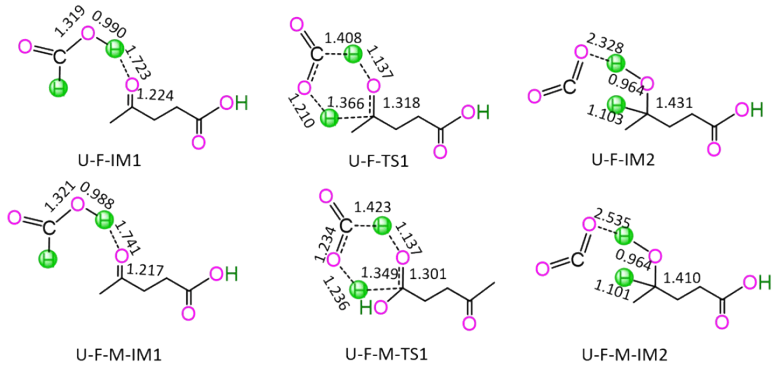



(a)

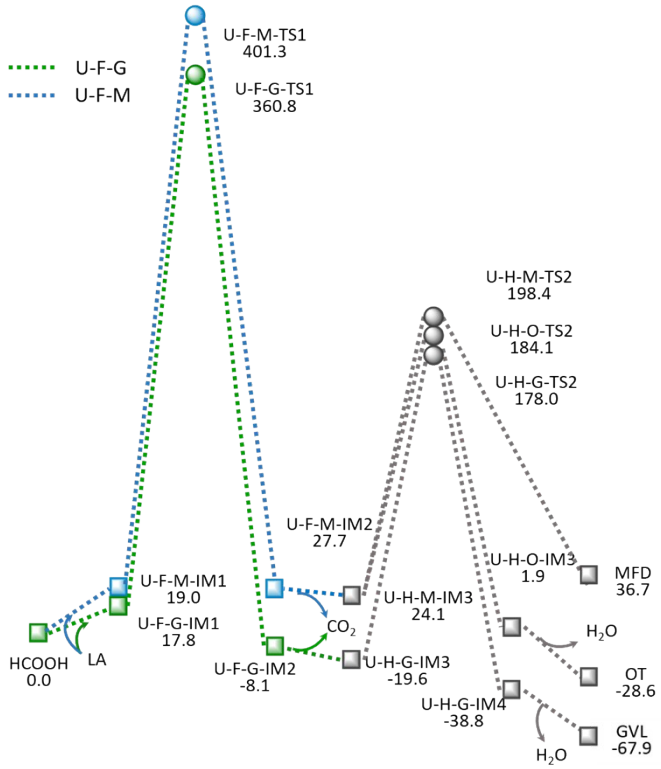



(b)

**Figure S3** The geometric structures (a) and the schematic energy diagrams (b) with the relative Gibbs free energy ($G_r$, kJ mol$^{-1}$) for the background reaction of the hydrogenation of LA to GVL, OT and MFD with $H_2$ as H-source. For clarity, hydrogen atoms on carbon are not shown. Bond lengths are reported in Å.

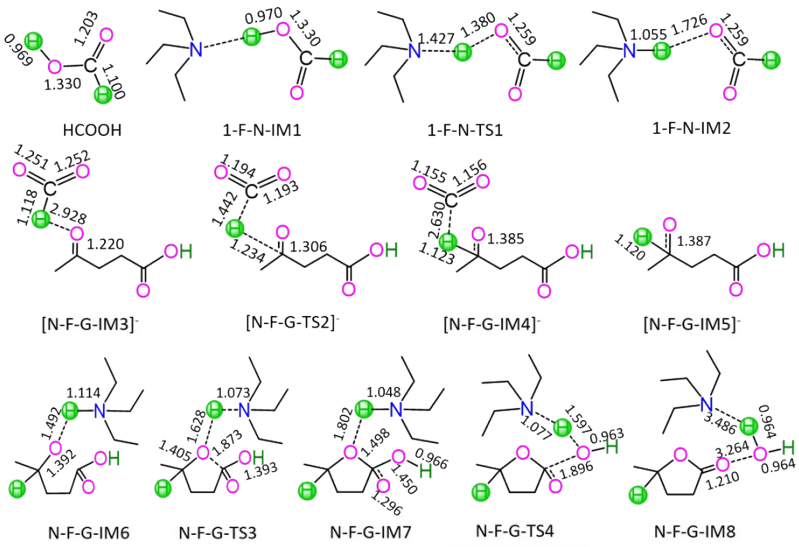



(a)

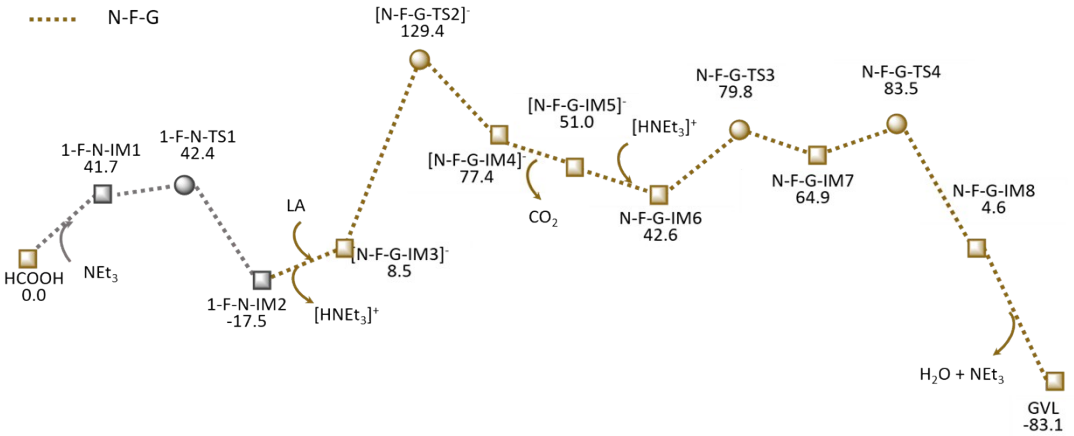



(b)

**Figure S4** The geometric structures (a) and the schematic energy diagrams (b) with the relative Gibbs free energy ($G_r$, kJ mol$^{-1}$) for the background reaction of the hydrogenation of LA to GVL, OT and MFD with HCOOH as H-source. For clarity, hydrogen atoms on carbon are not shown. Bond lengths are reported in Å.

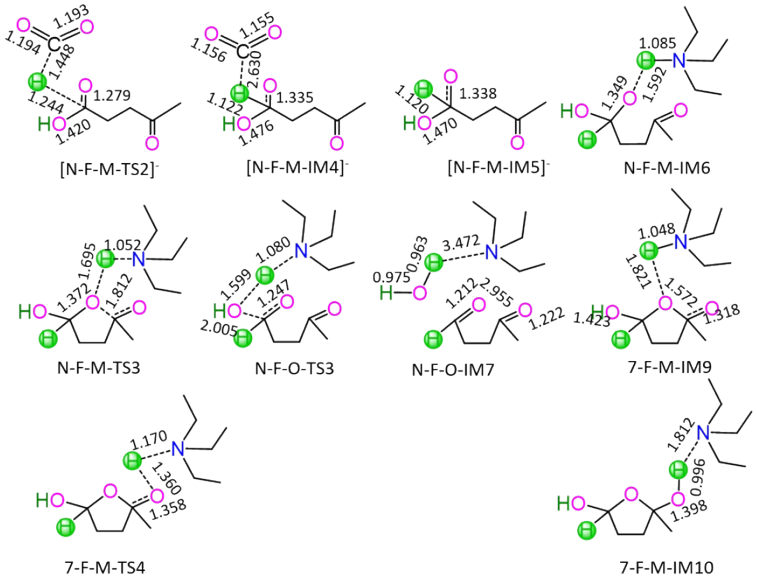



(a)

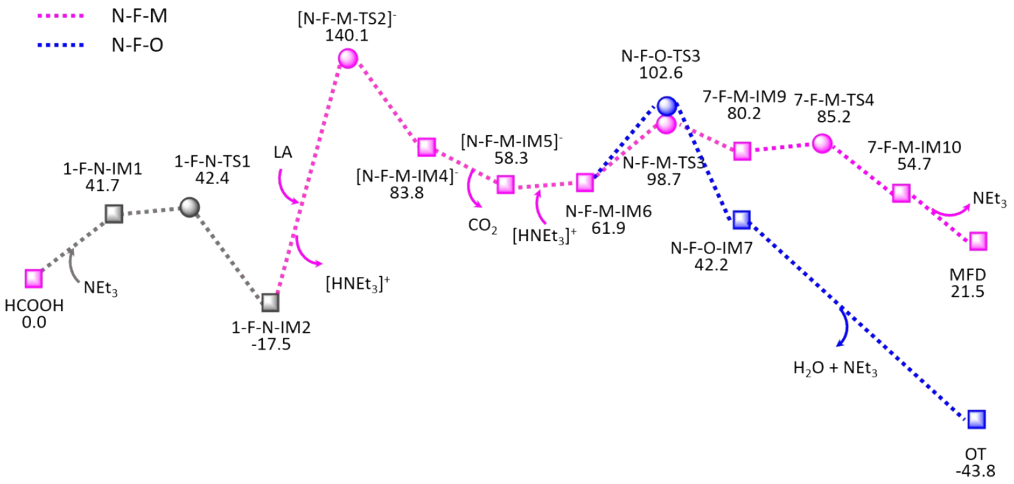



(b)

**Figure S5** The geometric structures (a) and the schematic energy diagrams (b) with the relative Gibbs free energy ($G_r$, kJ mol$^{-1}$) for the background of LA + HCOOH ⟶ GVL + $H_2O$ + $CO_2$ through hydrogenation of ketone carbonyl in the presence of $NEt_3$ ligand. For clarity, hydrogen atoms on carbon are not shown. Bond lengths are reported in Å.

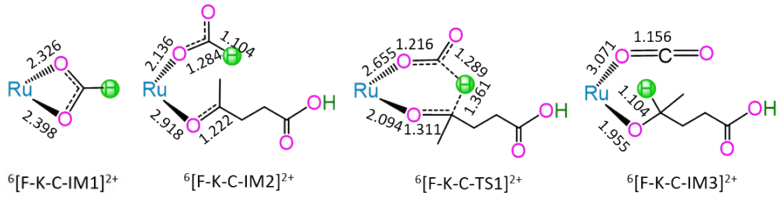



(a)

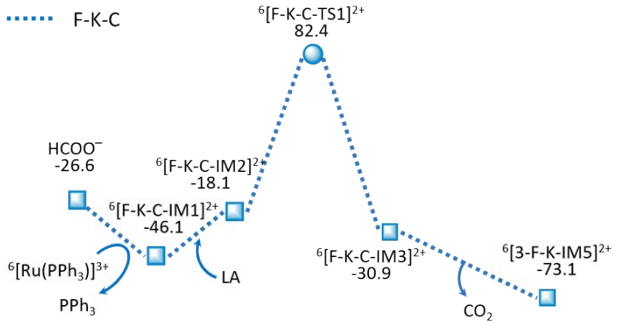



(b)

**Figure S6** The geometric structures (a) and the schematic energy diagrams (b) with the relative Gibbs free energy ($G_r$, kJ mol$^{-1}$) for the background reactions of LA + HCOOH ⟶ OT + $H_2O$ + $CO_2$ and LA + HCOOH ⟶ MFD + $CO_2$ through hydrogenation of carboxyl carbonyl in the presence of $NEt_3$ ligand. For clarity, hydrogen atoms on carbon are not shown. Bond lengths are reported in Å.

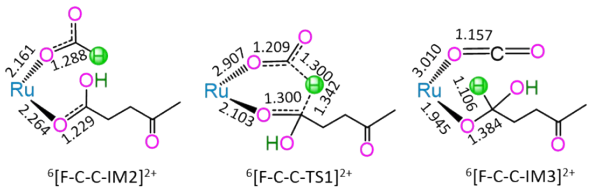



(a)

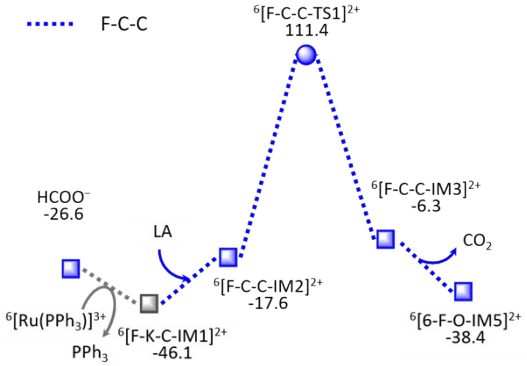



(b)

**Figure S7** The geometric structures (a) and the schematic energy diagrams (b) with the relative Gibbs free energy ($G_r$, kJ mol$^{-1}$) for the reaction stage of $^6[Ru(PPh_3)]^{3+}$ + $HCOO^-$ + LA $\rightarrow$ $^6[3\text{-F-K-IM5}]^{2+}$ + $CO_2$ + $PPh_3$ through hydrogenation of ketone carbonyl. For clarity, hydrogen atoms on carbon are not shown. Bond lengths reported in Å.

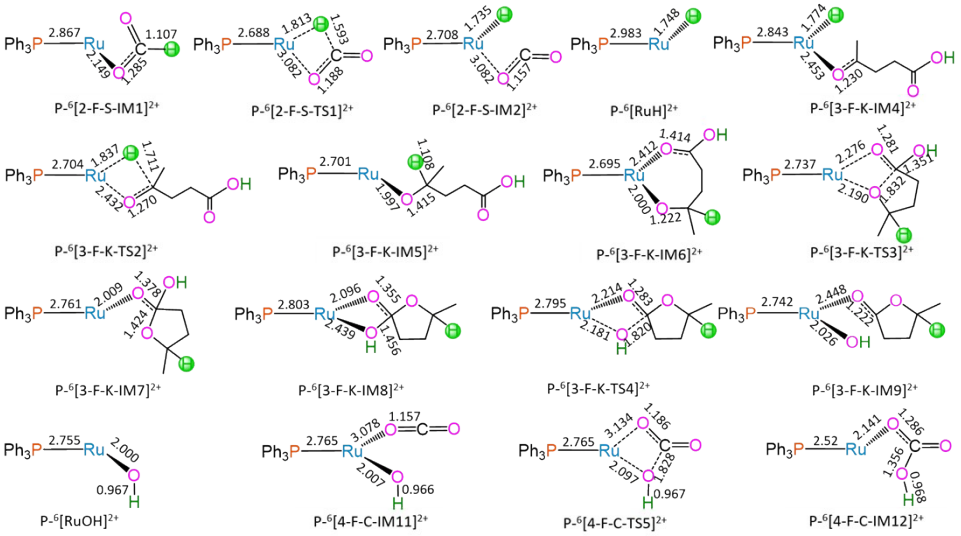



(a)

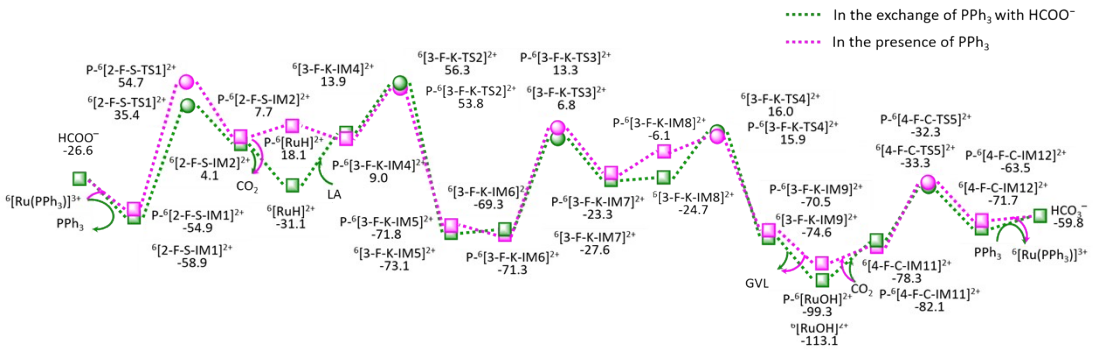



(b)

**Figure S8.** The geometric structures (a) and the schematic energy diagrams (b) with the relative Gibbs free energy ($G_r$, kJ mol$^{-1}$) for the reaction stage of $^6[Ru(PPh_3)]^{3+}$ + $HCOO^-$ + LA ⟶ $^6$[6-F-O-IM5]$^{2+}$ + $CO_2$ + $PPh_3$ through hydrogenation of carboxyl carbonyl. For clarity, hydrogen atoms on carbon are not shown. Bond lengths reported in Å.




(a)




(b)

**Figure S9.** The geometric structures (a) and the schematic energy diagrams (b) with the relative Gibbs free energy ($G_r$, kJ mol$^{-1}$) for the reaction stage of $HCOO^-$ + LA ⟶ GVL + $HCO_3^-$. For clarity, hydrogen atoms on carbon are not shown. Bond lengths reported in Å.

**NOTES: Evaluation of rate constants:**

The rate constants *k*(T) were evaluated according to conventional transition state theory *k'*(T), including the tunneling correction *κ*(T) based on Wigner's formulation as follows:[1]

$$k^{'} = \frac{k_B T}{hc^0} \bullet e^{\frac{-\Delta G^{\neq}}{RT}}$$

$$\kappa\ (T)\ = 1 + \frac{1}{24}|\frac{w^{\neq} h}{k_B T}|^2$$

$$k = \kappa\ (T)\ \times k^{'}$$

$$\ln k = -\frac{E_a}{RT} + \ln A$$

$$k = A \bullet e^{\frac{-E_a}{RT}}$$

where $k_B$ is Boltzmann's constant, T is the absolute temperature, *h* is Planck's constant, $c^0$ is the standard concentration (1 mol $dm^{-3}$), $\Delta G^{\neq}$ is the activation Gibbs free energy barrier and $\omega^{\neq}$ is the imaginary frequency of the TS.

**References:**

1. E. Wigner, *J. Chem. Phys*., 1937, **5**, 720–723.

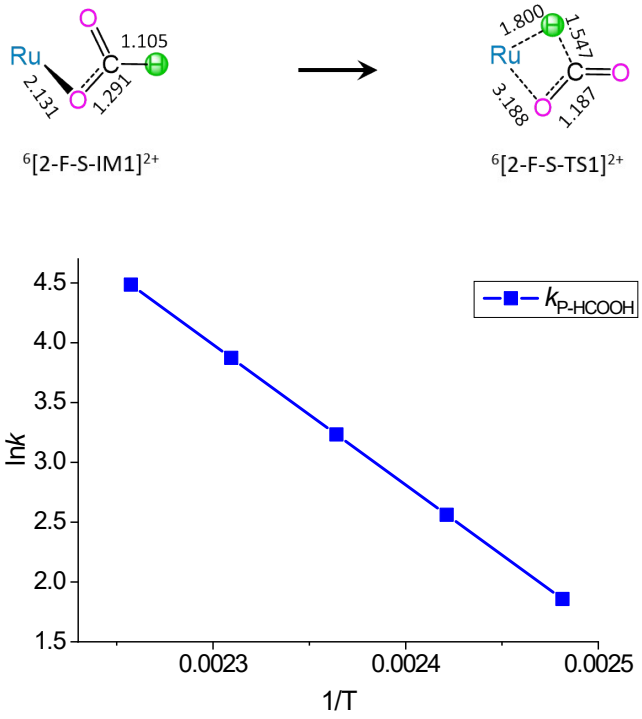



**Figure S10.** Arrhenius plots of rate constants for the selective control step for the reaction stage of $^{6}[Ru(PPh_3)]^{3+}$ + HCOOH + $NEt_3$ ⟶ $^{6}[RuH]^{2+}$ + $[HNEt_3]^{+}$ + $PPh_3$ + $CO_2$ in aqueous solution.

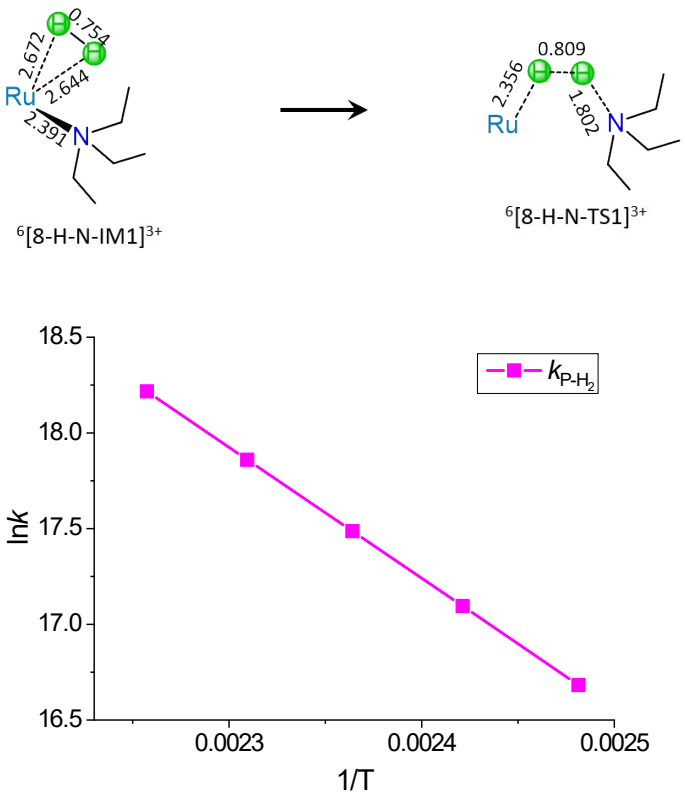
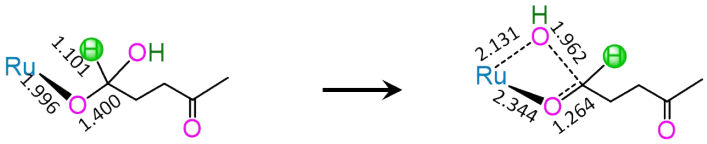


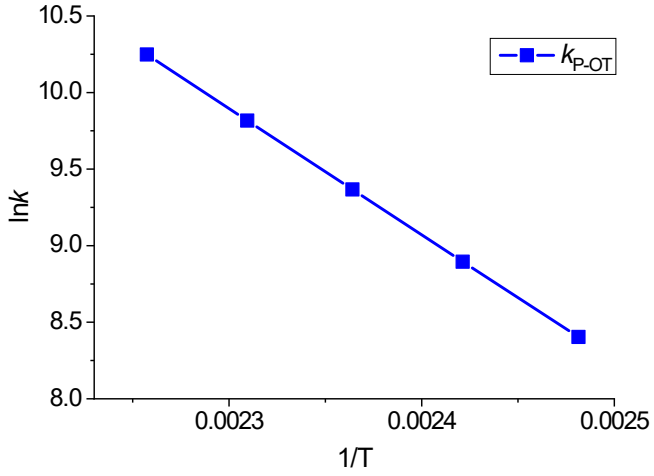

**Figure S11.** Arrhenius plots of rate constants for the selective control step for the reaction stage of $^{6}[Ru(PPh_3)]^{3+}$ + $H_2$ + $NEt_3$ ⟶ $^{6}[RuH]^{2+}$ + $[HNEt_3]^{+}$ + $PPh_3$ in aqueous solution.

**Table S1.** The reaction rate comparation of $^{6}[Ru(PPh_3)]^{3+}$ + HCOOH + $NEt_3$ → $^{6}[RuH]^{2+}$ + $[HNEt_3]^{+}$ + $PPh_3$ + $CO_2$ and $^{6}[Ru(PPh_3)]^{3+}$ + $H_2$ + $NEt_3$ → $^{6}[RuH]^{2+}$ + $[HNEt_3]^{+}$ + $PPh_3$ under the temperature range of 403 − 443 K.

| T /K | P-HCOOH | P-$H_2$ | |
|---|---|---|---|
| | 2.80× 10^13 exp(-97523/RT) | 4.17× 10^14 exp(-56892/RT) | $k_{P\text{-}H_2}/k_{P\text{-}HCOOH}$ |
| 403 | 6.4E+00 | 1.8E+07 | 2.8E+06 |
| 413 | 1.3E+01 | 2.7E+07 | 2.1E+06 |
| 423 | 2.5E+01 | 3.9E+07 | 1.6E+06 |
| 433 | 4.8E+01 | 5.7E+07 | 1.2E+06 |
| 443 | 8.9E+01 | 8.2E+07 | 9.2E+05 |

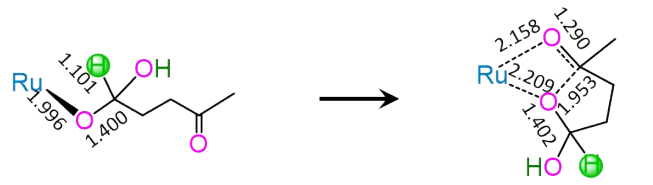



$^{6}$[6-F-O-IM5]$^{2+}$ $^{6}$[6-F-O-TS3]$^{2+}$

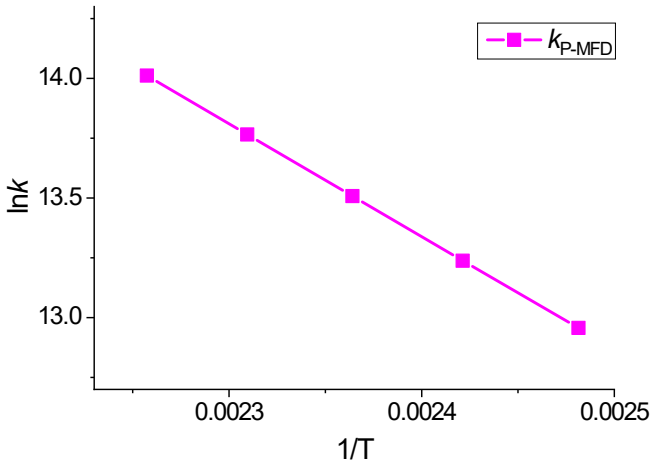



$$k_{\text{P-OT}} = 3.33\times10^{12}\exp(-68457/RT)$$

**Figure S12.** Arrhenius plots of rate constants for the selective control step for the reaction stage of $^{6}$[6-F-O-IM5]$^{2+}$ + $[HNEt_3]^+$ + $PPh_3$ ⟶ OT + $^{6}$[Ru($PPh_3$)]$^{3+}$ + $H_2O$ + $NEt_3$ in aqueous solution.




$^6$[6-F-O-IM5]$^{2+}$ $^6$[7-F-M-TS3]$^{2+}$

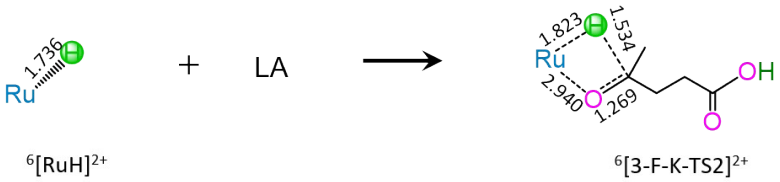



$$k_{\text{P-MFD}} = 5.00\times10^{10}\exp(-39136/RT)$$

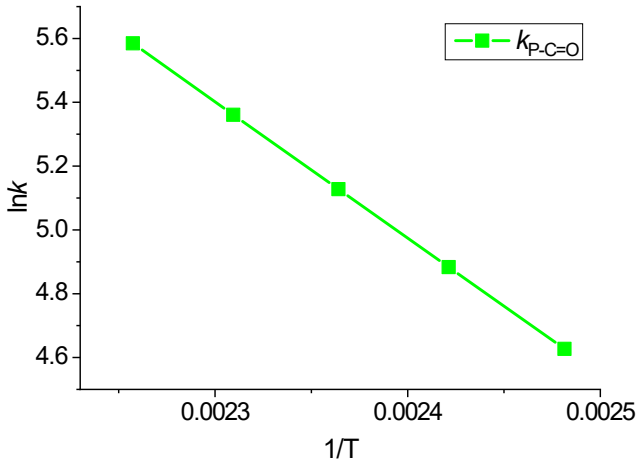
**Figure S13.** Arrhenius plots of rate constants for the selective control step for the reaction stage of $^6$[6-F-O-IM5]$^{2+}$ + $[HNEt_3]^+$ + $PPh_3$ ⟶ MFD + $^6$[Ru($PPh_3$)]$^{3+}$ + $NEt_3$ in aqueous solution

**Table S2.** The reaction rate comparation of $^{6}[6\text{-F-O-IM5}]^{2+} + [HNEt_3]^{+} + PPh_3 \rightarrow OT + {}^{6}[Ru(PPh_3)]^{3+} + H_2O + NEt_3$ and $^{6}[6\text{-F-O-IM5}]^{2+} + [HNEt_3]^{+} + PPh_3 \rightarrow MFD + {}^{6}[Ru(PPh_3)]^{3+} + NEt_3$ under the temperature range of 403 − 443 K.

| T /K | P-OT | P-MFD | | | |
|---|---|---|---|---|---|
| | 3.33×10^12 exp(-68457/RT) | 5.00× 10^10 exp(-39136/RT) | $k_{P\text{-}MFD}/k_{P\text{-}OT}$ | OT(%) | MFD(%) |
| 403 | 4.5E+03 | 2.5E+05 | 9.5E+01 | 1.0% | 99.0% |
| 413 | 7.3E+03 | 4.8E+05 | 7.7E+01 | 1.3% | 98.7% |
| 423 | 1.2E+04 | 8.8E+05 | 6.3E+01 | 1.6% | 98.4% |
| 433 | 1.8E+04 | 1.6E+05 | 5.2E+01 | 1.9% | 98.1% |
| 443 | 2.8E+04 | 2.7E+06 | 4.3E+01 | 2.3% | 97.7% |

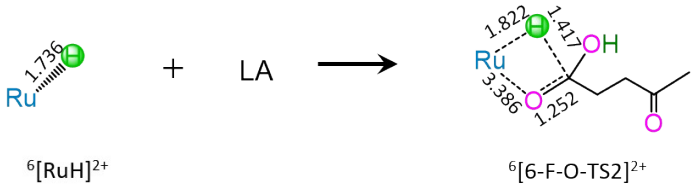



$^6$[RuH]$^{2+}$ $^6$[3-F-K-TS2]$^{2+}$

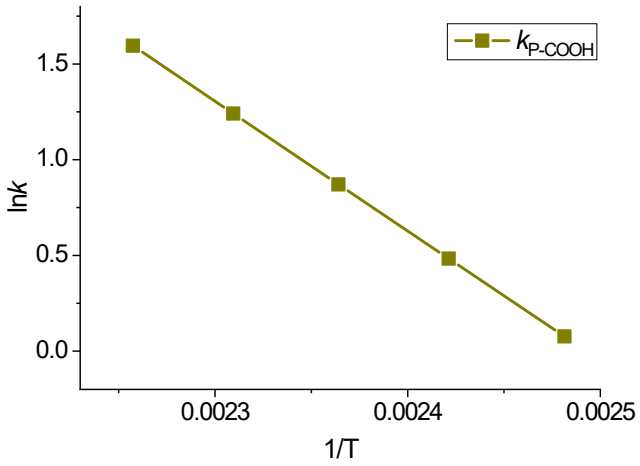



$$k_{\text{P-C=O}} = 4.12\times10^{6}\exp(-35530/RT)$$

**Figure S14.** Arrhenius plots of rate constants for the selective control step of $^6$[RuH]$^{2+}$ + LA ⟶ $^6$[3-F-K-TS2]$^{2+}$ in aqueous solution.




$^6$[RuH]$^{2+}$ $^6$[6-F-O-TS2]$^{2+}$




$$k_{\text{P-COOH}} = 2.17 \times 10^{7} \exp(-56342/RT)$$

**Figure S15.** Arrhenius plots of rate constants for the selective control step for the reaction stage of $^6$[RuH]$^{2+}$ + LA → $^6$[6-F-O-TS2]$^{2+}$ in aqueous solution.

**Table S3.** The reaction rate comparation of $^{6}[RuH]^{2+}$ + LA → $^{6}[3\text{-F-K-TS2}]^{2+}$ and $^{6}[RuH]^{2+}$ + LA → $^{6}[6\text{-F-O-TS2}]^{2+}$ under the temperature range of 403 − 443 K.

| T /K | P-C=O | P-COOH | | | |
|---|---|---|---|---|---|
| | 4.12× 10^6 exp(-35530/RT) | 2.17× 10^7 exp(-56342/RT) | $k_{P\text{-}C=O}/k_{P\text{-}COOH}$ | P-C=O(%) | P-COOH(%) |
| 403 | 1.0E+02 | 1.1E+00 | 9.5E+01 | 99.0% | 1.0% |
| 413 | 1.3E+02 | 1.6E+00 | 8.1E+01 | 98.8% | 1.2% |
| 423 | 1.7E+02 | 2.4E+00 | 7.1E+01 | 98.6% | 1.4% |
| 433 | 2.1E+02 | 3.5E+00 | 6.2E+01 | 98.4% | 1.6% |
| 443 | 2.7E+02 | 4.9E+00 | 5.4E+01 | 98.2% | 1.8% |

**Table S4.** Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy ($G_0$, hartree), total energies ($E_c$, hartree) corrected by *ZPE*, sum of electronic and thermal free energies ($G_c$, hartree) with *ZPE* and thermal corrections, and relative energies ($E_r$, kJ mol$^{-1}$) and relative Gibbs free energies ($G_r$, kJ mol$^{-1}$) relative to $^6Ru^{3+}$ and $H_2O$ for $^x[Ru(H_2O)_n]^{3+}$ ( n = 0-6) at M06/def2TZVP, 6-311++G(d,p) level in aqueous solution.

| Species | *ZPE* | $E_c$ | $G_0$ | $G_c$ | $E_r$ | $G_r$ |
|---|---|---|---|---|---|---|
| $^6Ru^{3+}$ | 0.00000 | -94.43419 | -0.02116 | -94.45535 | | |
| $^4Ru^{3+}$ | 0.00000 | -94.35303 | -0.02062 | -94.37365 | | |
| $^2Ru^{3+}$ | 0.00000 | -94.27499 | -0.01969 | -94.29468 | | |
| $H_2O$ | 0.02128 | -76.41073 | -0.00070 | -76.43271 | | |
| | | | | | | |
| $^6Ru^{3+}$ | 0.00000 | -94.43419 | -0.02116 | -94.45535 | | |
| $^6Ru^{3+} + 6*H_2O$ | 0.12767 | -552.89858 | -0.02535 | -553.05161 | 0.0 | 0.0 |
| $^6[Ru(H_2O)]^{3+}$ | 0.02407 | -170.84812 | -0.01128 | -170.88347 | | |
| $^6[Ru(H_2O)]^{3+} + 5*H_2O$ | 0.13047 | -552.90178 | -0.01477 | -553.04701 | -8.4 | 12.1 |
| $^6[Ru(H_2O)_2]^{3+}$ | 0.04943 | -247.26098 | 0.00763 | -247.30279 | | |
| $^6[Ru(H_2O)_2]^{3+} + 4*H_2O$ | 0.13455 | -552.90392 | 0.00484 | -553.03363 | -14.0 | 47.2 |
| $^6[Ru(H_2O)_3]^{3+}$ | 0.07488 | -323.67609 | 0.02583 | -323.72514 | | |
| $^6[Ru(H_2O)_3]^{3+} + 3*H_2O$ | 0.13872 | -552.90829 | 0.02374 | -553.02327 | -25.5 | 74.4 |
| $^6[Ru(H_2O)_4]^{3+}$ | 0.10062 | -400.09272 | 0.04691 | -400.14643 | | |
| $^6[Ru(H_2O)_4]^{3+} + 2*H_2O$ | 0.14318 | -552.91419 | 0.04552 | -553.01184 | -41.0 | 104.4 |
| $^6[Ru(H_2O)_5]^{3+}$ | 0.12691 | -476.50939 | 0.06863 | -476.56767 | | |
| $^6[Ru(H_2O)_5]^{3+} + H_2O$ | 0.14819 | -552.92012 | 0.06794 | -553.00038 | -56.6 | 134.5 |
| $^6[Ru(H_2O)_6]^{3+}$ | 0.15012 | -552.93090 | 0.08537 | -552.99564 | -84.9 | 146.9 |
| | | | | | | |
| $^4Ru^{3+}$ | 0.00000 | -94.35303 | -0.02062 | -94.37365 | | |
| $^4Ru^{3+} + 6*H_2O$ | 0.12767 | -552.81743 | -0.02480 | -552.96991 | 213.1 | 214.5 |
| $^4[Ru(H_2O)]^{3+}$ | 0.02480 | -170.79132 | -0.00911 | -170.82523 | | |
| $^4[Ru(H_2O)]^{3+} + 5*H_2O$ | 0.13120 | -552.84498 | -0.01260 | -552.98878 | 140.7 | 165.0 |
| $^4[Ru(H_2O)_2]^{3+}$ | 0.05089 | -247.22532 | 0.01143 | -247.26478 | | |
| $^4[Ru(H_2O)_2]^{3+} + 4*H_2O$ | 0.13600 | -552.86825 | 0.00864 | -552.99561 | 79.6 | 147.0 |
| $^4[Ru(H_2O)_3]^{3+}$ | 0.07697 | -323.65876 | 0.03039 | -323.70534 | | |
| $^4[Ru(H_2O)_3]^{3+} + 3*H_2O$ | 0.14081 | -552.89096 | 0.02830 | -553.00347 | 20.0 | 126.4 |
| $^4[Ru(H_2O)_4]^{3+}$ | 0.10432 | -400.08881 | 0.05456 | -400.13857 | | |
| $^4[Ru(H_2O)_4]^{3+} + 2*H_2O$ | 0.14688 | -552.91027 | 0.05317 | -553.00398 | -30.7 | 125.0 |
| $^4[Ru(H_2O)_5]^{3+}$ | 0.13031 | -476.50577 | 0.07513 | -476.56095 | | |
| $^4[Ru(H_2O)_5]^{3+} + H_2O$ | 0.15159 | -552.91650 | 0.07443 | -552.99366 | -47.0 | 152.2 |
| $^4[Ru(H_2O)_6]^{3+}$ | 0.15399 | -552.92391 | 0.09189 | -552.98601 | -66.5 | 172.2 |
| | | | | | | |
| $^2Ru^{3+}$ | 0.00000 | -94.27499 | -0.01969 | -94.29468 | | |
| $^2Ru^{3+} + 6*H_2O$ | 0.12767 | -552.73939 | -0.02388 | -552.89094 | 418.0 | 421.8 |
| $^2[Ru(H_2O)]^{3+}$ | 0.02461 | -170.75134 | -0.00846 | -170.78441 | | |
| $^2[Ru(H_2O)]^{3+} + 5*H_2O$ | 0.13100 | -552.80501 | -0.01194 | -552.94795 | 245.7 | 272.1 |
| $^2[Ru(H_2O)_2]^{3+}$ | 0.05166 | -247.18733 | 0.01246 | -247.22653 | | |
| $^2[Ru(H_2O)_2]^{3+} + 4*H_2O$ | 0.13677 | -552.83026 | 0.00967 | -552.95736 | 179.4 | 247.5 |
| $^2[Ru(H_2O)_3]^{3+}$ | 0.07882 | -323.61706 | 0.03477 | -323.66111 | | |
| $^2[Ru(H_2O)_3]^{3+} + 3*H_2O$ | 0.14266 | -552.84926 | 0.03268 | -552.95924 | 129.5 | 242.5 |
| $^2[Ru(H_2O)_4]^{3+}$ | 0.10642 | -400.05557 | 0.05864 | -400.10335 | | |
| $^2[Ru(H_2O)_4]^{3+} + 2*H_2O$ | 0.14898 | -552.87704 | 0.05725 | -552.96877 | 56.6 | 217.5 |
| $^2[Ru(H_2O)_5]^{3+}$ | 0.13203 | -476.48854 | 0.07921 | -476.54136 | | |
| $^2[Ru(H_2O)_5]^{3+} + H_2O$ | 0.15331 | -552.89927 | 0.07851 | -552.97407 | -1.8 | 203.6 |
| $^2[Ru(H_2O)_6]^{3+}$ | 0.15826 | -552.92269 | 0.09993 | -552.98102 | -63.3 | 185.3 |

**Table S5.** Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy ($G_0$, hartree), total energies ($E_c$, hartree) corrected by *ZPE*, sum of electronic and thermal free energies ($G_c$, hartree) with *ZPE* and thermal corrections, and relative energies ($E_r$, kJ mol$^{-1}$) and relative Gibbs free energies ($G_r$, kJ mol$^{-1}$) relative to $^6Ru^{3+}$, $PPh_3$, $NEt_3$ and PY for $^6[Ru(H_2O)]^{3+}$, $^6[Ru(PPh_3)]^{3+}$, $^6[Ru(NEt_3)]^{3+}$ and $^6[Ru(PY)]^{3+}$ complexes at M06/def2TZVP, 6-311++G(d,p) level in aqueous solution.

| Species | *ZPE* | $E_c$ | $G_0$ | $G_c$ | $E_r$ | $G_r$ |
|---|---|---|---|---|---|---|
| $^6Ru^{3+}$ | 0.00000 | -94.43419 | -0.02116 | -94.45535 | | |
| $H_2O$ | 0.02128 | -76.41073 | -0.00070 | -76.43271 | | |
| $PPh_3$ | 0.27244 | -1035.47240 | 0.20382 | -1035.54102 | | |
| $NEt_3$ | 0.20387 | -292.05597 | 0.15681 | -292.10303 | | |
| PY | 0.08809 | -248.07271 | 0.05210 | -248.10871 | | |
| $^6Ru^{3+} + H_2O + PPh_3 + NEt_3 + PY$ | 0.58568 | -1746.44599 | 0.39087 | -1746.64081 | 0.0 | 0.0 |
| $^6[Ru(H_2O)]^{3+}$ | 0.02440 | -170.84837 | -0.01069 | -170.88345 | | |
| $^6[Ru(H_2O)]^{3+} + PPh_3 + NEt_3 + PY$ | 0.58880 | -1746.44944 | 0.40203 | -1746.63620 | -9.1 | 12.1 |
| $^6[Ru(PPh_3)]^{3+}$ | 0.27415 | -1129.92479 | 0.19644 | -1130.00251 | | |
| $^6[Ru(PPh_3)]^{3+} + NEt_3 + PY + H_2O$ | 0.58740 | -1746.46420 | 0.40465 | -1746.64695 | -47.8 | -16.1 |
| $^6[Ru(NEt_3)]^{3+}$ | 0.20889 | -386.50218 | 0.15581 | -386.55526 | | |
| $^6[Ru(NEt_3)]^{3+} + PY + H_2O + PPh_3$ | 0.59070 | -1746.45802 | 0.41103 | -1746.63769 | -31.6 | 8.2 |
| $^6[Ru(PY)]^{3+}$ | 0.09029 | -342.51063 | 0.04525 | -342.55568 | | |
| $^6[Ru(PY)]^{3+} + H_2O + PPh_3 + NEt_3$ | 0.58788 | -1746.44973 | 0.40518 | -1746.63243 | -9.8 | 22.0 |

**Table S6.** Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy ($G_0$, hartree), total energies ($E_c$, hartree) corrected by *ZPE*, sum of electronic and thermal free energies ($G_c$, hartree) with *ZPE* and thermal corrections, and relative energies ($E_r$, kJ mol$^{-1}$) and relative Gibbs free energies ($G_r$, kJ mol$^{-1}$) relative to the reactants for hydrogenation of LA to GVL, OT and MFD with $H_2$ as H-source at M06/def2TZVP, 6-311++G(d,p) level in aqueous solution.

| Species | *ZPE* | $E_c$ | $G_0$ | $G_c$ | $E_r$ | $G_r$ |
|---|---|---|---|---|---|---|
| LA | 0.12706 | -420.80704 | 0.07904 | -420.85507 | | |
| $H_2$ | 0.00981 | -1.15796 | -0.00228 | -1.17005 | | |
| HCOOH | 0.03342 | -189.70312 | 0.00298 | -189.73356 | | |
| $NEt_3$ | 0.20387 | -292.05597 | 0.15681 | -292.10303 | | |
| $H_2O$ | 0.02128 | -76.41073 | -0.00070 | -76.43271 | | |
| GVL | 0.12519 | -345.57698 | 0.08391 | -345.61826 | | |
| OT | 0.12081 | -345.55701 | 0.07452 | -345.60330 | | |
| MFD | 0.15403 | -421.96688 | 0.10976 | -422.01115 | | |
| LA + HCOOH + $H_2$ + $NEt_3$ | 0.37416 | -903.72409 | 0.23655 | -903.86170 | 0.0 | 0.0 |
| $H_2$ | 0.00981 | -1.15796 | -0.00228 | -1.17005 | | |
| $H_2$ + LA + HCOOH + $NEt_3$ | 0.37416 | -903.72409 | 0.23655 | -903.86170 | 0.0 | 0.0 |
| U-H-G-IM1 | 0.14178 | -421.96102 | 0.08835 | -422.01445 | | |
| U-H-G-IM1 + HCOOH + $NEt_3$ | 0.37907 | -903.72011 | 0.24815 | -903.85103 | 10.5 | 28.0 |
| U-H-G-TS1 | 0.14368 | -421.87004 | 0.09560 | -421.91812 | | |
| U-H-G-TS1 + HCOOH + $NEt_3$ | 0.38097 | -903.62912 | 0.25539 | -903.75470 | 249.3 | 280.9 |
| U-H-G-IM2 | 0.15125 | -421.98331 | 0.10259 | -422.03196 | | |
| U-H-G-IM2 + HCOOH + $NEt_3$ | 0.38854 | -903.74239 | 0.26239 | -903.86854 | -48.0 | -18.0 |
| U-H-G-IM3 | 0.15203 | -421.98579 | 0.10522 | -422.03259 | | |
| U-H-G-IM3 + HCOOH + $NEt_3$ | 0.38932 | -903.74487 | 0.26502 | -903.86917 | -54.6 | -19.6 |
| U-H-G-TS2 | 0.14649 | -421.91313 | 0.10229 | -421.95734 | | |
| U-H-G-TS2 + HCOOH + $NEt_3$ | 0.38379 | -903.67221 | 0.26208 | -903.79392 | 136.2 | 178.0 |
| U-H-G-IM4 | 0.14989 | -421.98840 | 0.09838 | -422.03991 | | |
| U-H-G-IM4 + HCOOH + $NEt_3$ | 0.38718 | -903.74748 | 0.25817 | -903.87649 | -61.4 | -38.8 |
| GVL | 0.12519 | -345.57698 | 0.08391 | -345.61826 | | |
| GVL + HCOOH + $NEt_3$ + $H_2O$ | 0.38376 | -903.74680 | 0.24300 | -903.88755 | -59.6 | -67.9 |
| U-H-M-IM1 | 0.14173 | -421.96106 | 0.08761 | -422.01518 | | |
| U-H-M-IM1 + HCOOH + $NEt_3$ | 0.37902 | -903.72014 | 0.24740 | -903.85176 | 10.4 | 26.1 |
| U-H-M-TS1 | 0.14101 | -421.86143 | 0.09041 | -421.91203 | | |
| U-H-M-TS1 + HCOOH + $NEt_3$ | 0.37830 | -903.62051 | 0.25020 | -903.74861 | 271.9 | 296.9 |
| U-H-M-IM2 | 0.15071 | -421.96828 | 0.10022 | -422.01878 | | |
| U-H-M-IM2 + HCOOH + $NEt_3$ | 0.38800 | -903.72737 | 0.26001 | -903.85536 | -8.6 | 16.6 |
| U-H-M-IM3 | 0.15132 | -421.96761 | 0.10299 | -422.01594 | | |
| U-H-M-IM3 + HCOOH + $NEt_3$ | 0.38861 | -903.72669 | 0.26278 | -903.85252 | -6.8 | 24.1 |
| U-H-M-TS2 | 0.14708 | -421.90574 | 0.10326 | -421.94956 | | |
| U-H-M-TS2 + HCOOH + $NEt_3$ | 0.38437 | -903.66482 | 0.26306 | -903.78614 | 155.6 | 198.4 |
| MFD | 0.15403 | -421.96688 | 0.10976 | -422.01115 | | |
| MFD + HCOOH + $NEt_3$ | 0.39132 | -903.72596 | 0.26955 | -903.84773 | -4.9 | 36.7 |
| U-H-O-TS2 | 0.14479 | -421.90582 | 0.09560 | -421.95502 | | |
| U-H-O-TS2 + HCOOH + $NEt_3$ | 0.38208 | -903.66491 | 0.25539 | -903.79160 | 155.4 | 184.1 |
| U-H-O-IM3 | 0.14516 | -421.96767 | 0.08844 | -422.02439 | | |
| U-H-O-IM3 + HCOOH + $NEt_3$ | 0.38245 | -903.72675 | 0.24823 | -903.86097 | -7.0 | 1.9 |
| OT | 0.12081 | -345.55701 | 0.07452 | -345.60330 | | |
| OT + HCOOH + $NEt_3$ + $H_2O$ | 0.37938 | -903.72683 | 0.23361 | -903.87259 | -7.2 | -28.6 |

**Table S7.** Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy ($G_0$, hartree), total energies ($E_c$, hartree) corrected by *ZPE*, sum of electronic and thermal free energies ($G_c$, hartree) with *ZPE* and thermal corrections, and relative energies ($E_r$, kJ mol$^{-1}$) and relative Gibbs free energies ($G_r$, kJ mol$^{-1}$) relative to the reactants for hydrogenation of LA to GVL, OT and MFD with HCOOH as H-source at M06/def2TZVP, 6-311++G(d,p) level in aqueous solution.

| Species | *ZPE* | $E_c$ | $G_0$ | $G_c$ | $E_r$ | $G_r$ |
|---|---|---|---|---|---|---|
| LA | 0.12706 | -420.80704 | 0.07904 | -420.85507 | | |
| $H_2$ | 0.00981 | -1.15796 | -0.00228 | -1.17005 | | |
| HCOOH | 0.03342 | -189.70312 | 0.00298 | -189.73356 | | |
| $NEt_3$ | 0.20387 | -292.05597 | 0.15681 | -292.10303 | | |
| $H_2O$ | 0.02128 | -76.41073 | -0.00070 | -76.43271 | | |
| GVL | 0.12519 | -345.57698 | 0.08391 | -345.61826 | | |
| OT | 0.12081 | -345.55701 | 0.07452 | -345.60330 | | |
| MFD | 0.15403 | -421.96688 | 0.10976 | -422.01115 | | |
| LA + HCOOH + $H_2$ + $NEt_3$ | 0.37416 | -903.72409 | 0.23655 | -903.86170 | 0.0 | 0.0 |
| HCOOH | 0.03342 | -189.70312 | 0.00298 | -189.73356 | | |
| HCOOH + LA + $H_2$ + $NEt_3$ | 0.37416 | -903.72409 | 0.23655 | -903.86170 | 0.0 | 0.0 |
| U-F-G-IM1 | 0.16220 | -610.51861 | 0.09897 | -610.58183 | | |
| U-F-G-IM1 + $H_2$ + $NEt_3$ | 0.37587 | -903.73253 | 0.25351 | -903.85490 | -22.2 | 17.8 |
| U-F-G-TS1 | 0.15552 | -610.39456 | 0.09888 | -610.45120 | | |
| U-F-G-TS1 + $H_2$ + $NEt_3$ | 0.36920 | -903.60849 | 0.25341 | -903.72427 | 303.5 | 360.8 |
| U-F-G-IM2 | 0.16509 | -610.53180 | 0.10518 | -610.59171 | | |
| U-F-G-IM2 + $H_2$ + $NEt_3$ | 0.37877 | -903.74572 | 0.25971 | -903.86478 | -56.8 | -8.1 |
| U-F-M-IM1 | 0.162556 | -610.519321 | 0.10048 | -610.58139 | | |
| U-F-M-IM1 + $H_2$ + $NEt_3$ | 0.37624 | -903.73325 | 0.25502 | -903.85447 | -24.0 | 19.0 |
| U-F-M-TS1 | 0.15473 | -610.37850 | 0.09746 | -610.43578 | | |
| U-F-M-TS1 + $H_2$ + $NEt_3$ | 0.36841 | -903.59243 | 0.25199 | -903.70885 | 345.7 | 401.3 |
| U-F-M-IM2 | 0.164444 | -610.51666 | 0.10304 | -610.57807 | | |
| U-F-M-IM2 + $H_2$ + $NEt_3$ | 0.37812 | -903.73059 | 0.25757 | -903.85114 | -17.1 | 27.7 |

**Table S8.** Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy ($G_0$, hartree), total energies ($E_c$, hartree) corrected by *ZPE*, sum of electronic and thermal free energies ($G_c$, hartree) with *ZPE* and thermal corrections, and relative energies ($E_r$, kJ mol$^{-1}$) and relative Gibbs free energies ($G_r$, kJ mol$^{-1}$) relative to the reactants for the reaction of LA + HCOOH → GVL + $H_2O$ + $CO_2$ through hydrogenation of ketone carbonyl in the presence of $NEt_3$ ligand at M06/def2TZVP, 6-311++G(d,p) level in aqueous solution.

| Species | *ZPE* | $E_c$ | $G_0$ | $G_c$ | $E_r$ | $G_r$ |
|---|---|---|---|---|---|---|
| LA | 0.12706 | -420.80704 | 0.07904 | -420.85507 | | |
| $H_2$ | 0.00981 | -1.15796 | -0.00228 | -1.17005 | | |
| HCOOH | 0.03342 | -189.70312 | 0.00298 | -189.73356 | | |
| $NEt_3$ | 0.20387 | -292.05597 | 0.15681 | -292.10303 | | |
| $H_2O$ | 0.02128 | -76.41073 | -0.00070 | -76.43271 | | |
| GVL | 0.12519 | -345.57698 | 0.08391 | -345.61826 | | |
| OT | 0.12081 | -345.55701 | 0.07452 | -345.60330 | | |
| MFD | 0.15403 | -421.96688 | 0.10976 | -422.01115 | | |
| $[HNEt_3]^+$ | 0.21950 | -292.50499 | 0.17264 | -292.55185 | | |
| $CO_2$ | 0.01180 | -188.54399 | -0.01351 | -188.56930 | | |
| LA + HCOOH + $H_2$ + $NEt_3$ | 0.37416 | -903.72409 | 0.23655 | -903.86170 | 0.0 | 0.0 |
| HCOOH | 0.033418 | -189.703116 | 0.002979 | -189.733555 | | |
| HCOOH + LA + $H_2$ + $NEt_3$ | 0.374161 | -903.724086 | 0.236551 | -903.861696 | 0.0 | 0.0 |
| 1-F-N-IM1 | 0.24078 | -481.76171 | 0.18177 | -481.82072 | | |
| 1-F-N-IM1 + LA + $H_2$ | 0.37765 | -903.72671 | 0.25853 | -903.84583 | -6.9 | 41.7 |
| 1-F-N-TS1 | 0.23486 | -481.76264 | 0.17707 | -481.82043 | | |
| 1-F-N-TS1 + LA + $H_2$ | 0.37173 | -903.72764 | 0.25383 | -903.84554 | -9.3 | 42.4 |
| 1-F-N-IM2 | 0.24136 | -481.78477 | 0.18288 | -481.84325 | | |
| N-F-G-IM2 + LA + $H_2$ | 0.378231 | -903.749777 | 0.259639 | -903.868369 | -67.4 | -17.5 |
| $[N\text{-}F\text{-}G\text{-}IM3]^-$ | 0.149705 | -610.075691 | 0.088829 | -610.136568 | | |
| $[N\text{-}F\text{-}G\text{-}IM3]^-$ + $H_2$ + $[HNEt_3]^+$ | 0.379014 | -903.738641 | 0.259188 | -903.858468 | -38.2 | 8.5 |
| $[N\text{-}F\text{-}G\text{-}TS2]^-$ | 0.146803 | -610.031776 | 0.088081 | -610.090499 | | |
| $[N\text{-}F\text{-}G\text{-}TS2]^-$ + $H_2$ + $[HNEt_3]^+$ | 0.376112 | -903.694726 | 0.25844 | -903.812399 | 77.1 | 129.4 |
| $[N\text{-}F\text{-}G\text{-}IM4]^-$ | 0.150561 | -610.050162 | 0.090403 | -610.110321 | | |
| $[N\text{-}F\text{-}G\text{-}IM4]^-$ + $H_2$ + $[HNEt_3]^+$ | 0.37987 | -903.713112 | 0.260762 | -903.832221 | 28.8 | 77.4 |
| $[N\text{-}F\text{-}G\text{-}IM5]^-$ | 0.13729 | -421.50307 | 0.08926 | -421.55109 | | |
| $[N\text{-}F\text{-}G\text{-}IM4]^-$ + $H_2$ + $[HNEt_3]^+$ + $CO_2$ | 0.37840 | -903.71001 | 0.24611 | -903.84229 | 37.0 | 51.0 |
| N-F-G-IM6 | 0.35631 | -714.03415 | 0.28434 | -714.10612 | | |
| N-F-G-IM6 + $H_2$ + $CO_2$ | 0.37791 | -903.73611 | 0.26856 | -903.84546 | -31.6 | 42.6 |
| N-F-G-TS3 | 0.35931 | -714.02496 | 0.29230 | -714.09197 | | |
| N-F-G-TS3 + $H_2$ + $CO_2$ | 0.38092 | -903.72691 | 0.27652 | -903.83131 | -7.4 | 79.8 |
| N-F-G-IM7 | 0.36020 | -714.02917 | 0.29175 | -714.09762 | | |
| N-F-G-IM7 + $H_2$ + $CO_2$ | 0.38180 | -903.73113 | 0.27596 | -903.83696 | -18.5 | 64.9 |
| N-F-G-TS4 | 0.35742 | -714.01997 | 0.28683 | -714.09056 | | |
| N-F-G-TS4 + $H_2$ + $CO_2$ | 0.37902 | -903.72193 | 0.27104 | -903.82991 | 5.7 | 83.5 |
| N-F-G-IM8 | 0.35766 | -714.04773 | 0.28477 | -714.12062 | | |
| N-F-G-IM8 + $H_2$ + $CO_2$ | 0.37926 | -903.74968 | 0.26898 | -903.85996 | -67.2 | 4.6 |
| GVL | 0.12519 | -345.57698 | 0.08391 | -345.61826 | | |
| GVL + $H_2$ + $CO_2$ + H2O + $NEt_3$ | 0.37194 | -903.74564 | 0.22424 | -903.89334 | -56.6 | -83.1 |

**Table S9.** Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy ($G_0$, hartree), total energies ($E_c$, hartree) corrected by *ZPE*, sum of electronic and thermal free energies ($G_c$, hartree) with *ZPE* and thermal corrections, and relative energies ($E_r$, kJ mol$^{-1}$) and relative Gibbs free energies ($G_r$, kJ mol$^{-1}$) relative to the reactants for the reactions of LA + HCOOH → MFD + $H_2O$ + $CO_2$ and LA + HCOOH → OT + $CO_2$ through carboxyl carbonyl hydrogenation in the presence of $NEt_3$ ligand at M06/def2TZVP, 6-311++G(d,p) level in aqueous solution.

| Species | *ZPE* | $E_c$ | $G_0$ | $G_c$ | $E_r$ | $G_r$ |
|---|---|---|---|---|---|---|
| LA | 0.12706 | -420.80704 | 0.07904 | -420.85507 | | |
| $H_2$ | 0.00981 | -1.15796 | -0.00228 | -1.17005 | | |
| HCOOH | 0.03342 | -189.70312 | 0.00298 | -189.73356 | | |
| $NEt_3$ | 0.20387 | -292.05597 | 0.15681 | -292.10303 | | |
| $H_2O$ | 0.02128 | -76.41073 | -0.00070 | -76.43271 | | |
| GVL | 0.12519 | -345.57698 | 0.08391 | -345.61826 | | |
| OT | 0.12081 | -345.55701 | 0.07452 | -345.60330 | | |
| MFD | 0.15403 | -421.96688 | 0.10976 | -422.01115 | | |
| $[HNEt_3]^+$ | 0.21950 | -292.50499 | 0.17264 | -292.55185 | | |
| $CO_2$ | 0.01180 | -188.54399 | -0.01351 | -188.56930 | | |
| LA + HCOOH + $H_2$ + $NEt_3$ | 0.37416 | -903.72409 | 0.23655 | -903.86170 | 0.0 | 0.0 |
| HCOOH | 0.03342 | -189.70312 | 0.00298 | -189.73356 | | |
| HCOOH + LA + $H_2$ + $NEt_3$ | 0.37416 | -903.72409 | 0.23655 | -903.86170 | 0.0 | 0.0 |
| 1-F-N-IM1 | 0.24078 | -481.76171 | 0.18177 | -481.82072 | | |
| 1-F-N-IM1 + LA + $H_2$ | 0.37765 | -903.72671 | 0.25853 | -903.84583 | -6.9 | 41.7 |
| 1-F-N-TS1 | 0.23486 | -481.76264 | 0.17707 | -481.82043 | | |
| 1-F-N-TS1 + LA + $H_2$ | 0.37173 | -903.72764 | 0.25383 | -903.84554 | -9.3 | 42.4 |
| 1-F-N-IM2 | 0.24136 | -481.78477 | 0.18288 | -481.84325 | | |
| N-F-G-IM2 + LA + $H_2$ | 0.378231 | -903.749777 | 0.259639 | -903.868369 | -67.4 | -17.5 |
| $[N\text{-}F\text{-}M\text{-}TS2]^-$ | 0.14559 | -610.02588 | 0.08504 | -610.08643 | | |
| $[N\text{-}F\text{-}M\text{-}TS2]^-$ + $H_2$ + $[HNEt_3]^+$ | 0.37489 | -903.68883 | 0.25540 | -903.80833 | 92.6 | 140.1 |
| $[N\text{-}F\text{-}M\text{-}IM4]^-$ | 0.14896 | -610.04621 | 0.08729 | -610.10789 | | |
| $[N\text{-}F\text{-}M\text{-}IM4]^-$ + $H_2$ + $[HNEt_3]^+$ | 0.37827 | -903.70916 | 0.25765 | -903.82979 | 39.2 | 83.8 |
| $[N\text{-}F\text{-}M\text{-}IM5]^-$ | 0.13611 | -421.49887 | 0.08670 | -421.54828 | | |
| $[N\text{-}F\text{-}M\text{-}IM5]^-$ + $H_2$ + $[HNEt_3]^+$ + $CO_2$ | 0.37722 | -903.70581 | 0.24355 | -903.83948 | 48.0 | 58.3 |
| N-F-M-IM6 | 0.35679 | -714.02646 | 0.28447 | -714.09878 | | |
| N-F-M-IM6 + $H_2$ + $CO_2$ | 0.37840 | -903.72841 | 0.26869 | -903.83812 | -11.4 | 61.9 |
| N-F-M-TS3 | 0.35883 | -714.01769 | 0.29177 | -714.08475 | | |
| N-F-M-TS3 + $H_2$ + $CO_2$ | 0.38043 | -903.71964 | 0.27599 | -903.82409 | 11.7 | 98.7 |
| 7-F-M-IM9 | 0.35886 | -714.02138 | 0.28842 | -714.09181 | | |
| 7-F-M-IM9 + $H_2$ + $CO_2$ | 0.38046 | -903.72333 | 0.27264 | -903.83116 | 2.0 | 80.2 |
| 7-F-M-TS4 | 0.35578 | -714.02324 | 0.28912 | -714.08991 | | |
| 7-F-M-TS4 + $H_2$ + $CO_2$ | 0.37739 | -903.72520 | 0.27333 | -903.82925 | -2.9 | 85.2 |
| 7-F-M-IM10 | 0.36016 | -714.03203 | 0.29067 | -714.10152 | | |
| 7-F-M-IM10 + $H_2$ + $CO_2$ | 0.38177 | -903.73399 | 0.27489 | -903.84087 | -26.0 | 54.7 |
| MFD | 0.15403 | -421.96688 | 0.10976 | -422.01115 | | |
| MFD + $H_2$ + $CO_2$ + $NEt_3$ | 0.37951 | -903.72480 | 0.25079 | -903.85352 | -1.9 | 21.5 |
| N-F-O-TS3 | 0.35422 | -714.01086 | 0.28180 | -714.08328 | | |
| N-F-O-TS3 + $H_2$ + $CO_2$ | 0.37582 | -903.71282 | 0.26602 | -903.82262 | 29.6 | 102.6 |
| N-F-O-IM7 | 0.35292 | -714.02726 | 0.27388 | -714.10630 | | |
| N-F-O-IM7 + $H_2$ + $CO_2$ | 0.37453 | -903.72922 | 0.25810 | -903.84564 | -13.5 | 42.2 |
| OT | 0.12081 | -345.55701 | 0.07452 | -345.60330 | | |
| OT + $H_2$ + $CO_2$ + $H_2O$ + $NEt_3$ | 0.36756 | -903.72567 | 0.21485 | -903.87838 | -4.1 | -43.8 |

**Table S10.** Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy ($G_0$, hartree), total energies ($E_c$, hartree) corrected by *ZPE*, sum of electronic and thermal free energies ($G_c$, hartree) with *ZPE* and thermal corrections, and relative energies ($E_r$, kJ mol$^{-1}$) and relative Gibbs free energies ($G_r$, kJ mol$^{-1}$) relative to the reactants for the reaction of $^6[Ru(PPh_3)]^{3+}$ + $HCOO^-$ + LA → $^6$[3-F-K-IM5]$^{2+}$ + $CO_2$ + $PPh_3$ through hydrogenation of ketone carbonyl at M06/def2TZVP, 6-311++G(d,p) level in aqueous solution.

| Species | *ZPE* | $E_c$ | $G_0$ | $G_c$ | $E_r$ | $G_r$ |
|---|---|---|---|---|---|---|
| $^6[Ru(PPh_3)]^{3+}$ | 0.27415 | -1129.92479 | 0.19644 | -1130.00251 | | |
| $PPh_3$ | 0.27244 | -1035.47240 | 0.20382 | -1035.54102 | | |
| $NEt_3$ | 0.20387 | -292.05597 | 0.15681 | -292.10303 | | |
| $[HNEt_3]^+$ | 0.21950 | -292.50499 | 0.17264 | -292.55185 | | |
| PY | 0.08809 | -248.07271 | 0.05210 | -248.10871 | | |
| LA | 0.12706 | -420.80704 | 0.07904 | -420.85507 | | |
| HCOOH | 0.03342 | -189.70312 | 0.00298 | -189.73356 | | |
| $H_2$ | 0.00981 | -1.15796 | -0.00228 | -1.17005 | | |
| $CO_2$ | 0.011798 | -188.543994 | -0.013507 | -188.569298 | | |
| $^6[Ru(PPh_3)]^{3+}$ + $PPh_3$ + $NEt_3$ + PY + LA + HCOOH + $H_2$ | 1.008843 | -3317.193988 | 0.688905 | -3317.513926 | 0.0 | 0.0 |
| $HCOO^-$ | 0.020569 | -189.264961 | -0.009333 | -189.294864 | | |
| $HCOO^-$ + $^6[Ru(PPh_3)]^{3+}$ + $PPh_3$ + PY + LA + $H_2$ + $[HNEt_3]^+$ | 1.011624 | -3317.204854 | 0.692416 | -3317.524064 | -28.5 | -26.6 |
| $^6$[F-K-C-IM1]$^{2+}$ | 0.022604 | -283.723514 | -0.017665 | -283.763782 | | |
| $^6$[F-K-C-IM1]$^{2+}$ + 2*$PPh_3$ + PY + LA + $H_2$ + $[HNEt_3]^+$ | 1.011941 | -3317.211013 | 0.691461 | -3317.531491 | -44.7 | -46.1 |
| $^6$[F-K-C-IM2]$^{2+}$ | 0.152587 | -704.541107 | 0.085512 | -704.608182 | | |
| $^6$[F-K-C-IM2]$^{2+}$ + 2*$PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ | 1.01486 | -3317.221565 | 0.715602 | -3317.520821 | -72.4 | -18.1 |
| $^6$[F-K-C-TS1]$^{2+}$ | 0.148068 | -704.504859 | 0.083008 | -704.569918 | | |
| $^6$[F-K-C-TS1]$^{2+}$ + 2*$PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ | 1.010341 | -3317.185317 | 0.713098 | -3317.482557 | 22.8 | 82.4 |
| $^6$[F-K-C-IM3]$^{2+}$ | 0.153525 | -704.545771 | 0.086247 | -704.613049 | | |
| $^6$[F-K-C-IM3]$^{2+}$ + 2*$PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ | 1.015798 | -3317.226229 | 0.716337 | -3317.525688 | -84.6 | -30.9 |
| $^6$[3-F-K-IM5]$^{2+}$ | 0.14037 | -516.00242 | 0.08295 | -516.05984 | | |
| $^6$[3-F-K-IM5]$^{2+}$ + 2*$PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + $CO_2$ | 1.01444 | -3317.22687 | 0.69953 | -3317.54178 | -86.3 | -73.1 |

**Table S11.** Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy ($G_0$, hartree), total energies ($E_c$, hartree) corrected by *ZPE*, sum of electronic and thermal free energies ($G_c$, hartree) with *ZPE* and thermal corrections, and relative energies ($E_r$, kJ mol$^{-1}$) and relative Gibbs free energies ($G_r$, kJ mol$^{-1}$) relative to the reactants for the reaction of $^6[Ru(PPh_3)]^{3+}$ + $HCOO^-$ + LA → $^6$[6-F-O-IM5]$^{2+}$ + $CO_2$ + $PPh_3$ through hydrogenation of carboxyl carbonyl at M06/def2TZVP, 6-311++G(d,p) level in aqueous solution.

| Species | *ZPE* | $E_c$ | $G_0$ | $G_c$ | $E_r$ | $G_r$ |
|---|---|---|---|---|---|---|
| $^6[Ru(PPh_3)]^{3+}$ | 0.27415 | -1129.92479 | 0.19644 | -1130.00251 | | |
| $PPh_3$ | 0.27244 | -1035.47240 | 0.20382 | -1035.54102 | | |
| $NEt_3$ | 0.20387 | -292.05597 | 0.15681 | -292.10303 | | |
| $[HNEt_3]^+$ | 0.21950 | -292.50499 | 0.17264 | -292.55185 | | |
| PY | 0.08809 | -248.07271 | 0.05210 | -248.10871 | | |
| LA | 0.12706 | -420.80704 | 0.07904 | -420.85507 | | |
| HCOOH | 0.03342 | -189.70312 | 0.00298 | -189.73356 | | |
| $H_2$ | 0.00981 | -1.15796 | -0.00228 | -1.17005 | | |
| $CO_2$ | 0.01180 | -188.54399 | -0.01351 | -188.56930 | | |
| $^6[Ru(PPh_3)]^{3+}$ + $PPh_3$ + $NEt_3$ + PY + LA + HCOOH + $H_2$ | 1.00884 | -3317.19399 | 0.68891 | -3317.51393 | 0.0 | 0.0 |
| $HCOO^-$ | 0.02057 | -189.26496 | -0.00933 | -189.29486 | | |
| $HCOO^-$ + $^6[Ru(PPh_3)]^{3+}$ + $PPh_3$ + PY + LA + $H_2$ + $[HNEt_3]^+$ | 1.01162 | -3317.20485 | 0.69242 | -3317.52406 | -28.5 | -26.6 |
| $^6[F\text{-}K\text{-}C\text{-}IM1]^{2+}$ | 0.02260 | -283.72351 | -0.01767 | -283.76378 | | |
| $^6[F\text{-}K\text{-}C\text{-}IM1]^{2+}$ + 2*$PPh_3$ + PY + LA + $H_2$ + $[HNEt_3]^+$ | 1.01194 | -3317.21101 | 0.69146 | -3317.53149 | -44.7 | -46.1 |
| $^6[F\text{-}C\text{-}C\text{-}IM2]^{2+}$ | 0.15287 | -704.54330 | 0.08816 | -704.60800 | | |
| $^6[F\text{-}C\text{-}C\text{-}IM2]^{2+}$ + 2*$PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ | 1.01514 | -3317.22375 | 0.71825 | -3317.52064 | -78.1 | -17.6 |
| $^6[F\text{-}C\text{-}C\text{-}TS1]^{2+}$ | 0.14712 | -704.49225 | 0.08052 | -704.55885 | | |
| $^6[F\text{-}C\text{-}C\text{-}TS1]^{2+}$ + 2*$PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ | 1.00939 | -3317.17271 | 0.71061 | -3317.47149 | 55.9 | 111.4 |
| $^6[F\text{-}C\text{-}C\text{-}IM3]^{2+}$ | 0.15167 | -704.53562 | 0.08359 | -704.60370 | | |
| $^6[F\text{-}C\text{-}C\text{-}IM3]^{2+}$ + 2*$PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ | 1.01394 | -3317.21608 | 0.71368 | -3317.51634 | -58.0 | -6.3 |
| $^6[6\text{-}F\text{-}O\text{-}IM5]^{2+}$ | 0.13940 | -515.98718 | 0.07994 | -516.04664 | | |
| $^6[6\text{-}F\text{-}O\text{-}IM5]^{2+}$ + 2*$PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + $CO_2$ | 1.01347 | -3317.21163 | 0.69653 | -3317.52857 | -46.3 | -38.4 |

**Table S12.** Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy ($G_0$, hartree), total energies ($E_c$, hartree) corrected by *ZPE*, sum of electronic and thermal free energies ($G_c$, hartree) with *ZPE* and thermal corrections, and relative energies ($E_r$, kJ mol$^{-1}$) and relative Gibbs free energies ($G_r$, kJ mol$^{-1}$) relative to the reactants for the reaction stage (i) of HCOOH + L → $HCOO^-$ + $[HL]^+$ (L= $PPh_3$, $NEt_3$, and PY) at M06/def2TZVP, 6-311++G(d,p) level in aqueous solution.

| Species | *ZPE* | $E_c$ | $G_0$ | $G_c$ | $E_r$ | $G_r$ |
|---|---|---|---|---|---|---|
| $^6[Ru(PPh_3)]^{3+}$ | 0.27415 | -1129.92479 | 0.19644 | -1130.00251 | | |
| $PPh_3$ | 0.27244 | -1035.47240 | 0.20382 | -1035.54102 | | |
| $[HPPh_3]^+$ | 0.28366 | -1035.91017 | 0.21535 | -1035.97848 | | |
| $NEt_3$ | 0.20387 | -292.05597 | 0.15681 | -292.10303 | | |
| $[HNEt_3]^+$ | 0.21950 | -292.50499 | 0.17264 | -292.55185 | | |
| PY | 0.08809 | -248.07271 | 0.05210 | -248.10871 | | |
| $[HPY]^+$ | 0.10172 | -248.51019 | 0.06550 | -248.54641 | | |
| LA | 0.12706 | -420.80704 | 0.07904 | -420.85507 | | |
| HCOOH | 0.03342 | -189.70312 | 0.00298 | -189.73356 | | |
| $H_2$ | 0.00981 | -1.15796 | -0.00228 | -1.17005 | | |
| $^6[Ru(PPh_3)]^{3+} + PPh_3 + NEt_3 + PY + LA + HCOOH + H_2$ | 1.00884 | -3317.19399 | 0.68891 | -3317.51393 | 0.0 | 0.0 |
| HCOOH | 0.03342 | -189.70312 | 0.00298 | -189.73356 | | |
| $HCOOH + {}^6[Ru(PPh_3)]^{3+} + PPh_3 + NEt_3 + PY + LA + H_2$ | 1.00884 | -3317.19399 | 0.68891 | -3317.51393 | 0.0 | 0.0 |
| 1-F-P-IM1 | 0.30780 | -1225.18671 | 0.22956 | -1225.26496 | | |
| $1\text{-F-P-IM1} + {}^6[Ru(PPh_3)]^{3+} + NEt_3 + PY + LA + H_2$ | 1.01079 | -3317.20519 | 0.71167 | -3317.50431 | -29.4 | 25.3 |
| 1-F-P-TS1 | 0.30224 | -1225.17795 | 0.22356 | -1225.25662 | | |
| $1\text{-F-P-TS1} + {}^6[Ru(PPh_3)]^{3+} + NEt_3 + PY + LA + H_2$ | 1.00523 | -3317.19642 | 0.70567 | -3317.49598 | -6.4 | 47.1 |
| 1-F-P-IM2 | 0.30540 | -1225.18435 | 0.22305 | -1225.26670 | | |
| $1\text{-F-P-IM2} + {}^6[Ru(PPh_3)]^{3+} + NEt_3 + PY + LA + H_2$ | 1.00839 | -3317.20283 | 0.70516 | -3317.50606 | -23.2 | 20.7 |
| $HCOO^-$ | 0.02057 | -189.26496 | -0.00933 | -189.29486 | | |
| $HCOO^- + {}^6[Ru(PPh_3)]^{3+} + NEt_3 + PY + LA + H_2 + [HPPh_3]^+$ | 1.00722 | -3317.19361 | 0.68813 | -3317.51270 | 1.0 | 3.2 |
| 1-F-N-IM1 | 0.24078 | -481.76171 | 0.18177 | -481.82072 | | |
| $1\text{-F-N-IM1} + {}^6[Ru(PPh_3)]^{3+} + PPh_3 + PY + LA + H_2$ | 1.01233 | -3317.19662 | 0.71088 | -3317.49806 | -6.9 | 41.7 |
| 1-F-N-TS1 | 0.23486 | -481.76264 | 0.17707 | -481.82043 | | |
| $1\text{-F-N-TS1} + {}^6[Ru(PPh_3)]^{3+} + PPh_3 + PY + LA + H_2$ | 1.00641 | -3317.19754 | 0.70618 | -3317.49777 | -9.3 | 42.4 |
| 1-F-N-IM2 | 0.24136 | -481.78477 | 0.18288 | -481.84325 | | |
| $1\text{-F-N-IM2} + {}^6[Ru(PPh_3)]^{3+} + PPh_3 + PY + LA + H_2$ | 1.01291 | -3317.21968 | 0.71199 | -3317.52060 | -67.4 | -17.5 |
| $HCOO^-$ | 0.02057 | -189.26496 | -0.00933 | -189.29486 | | |
| $HCOO^- + {}^6[Ru(PPh_3)]^{3+} + PPh_3 + PY + LA + H_2 + [HNEt_3]^+$ | 1.01162 | -3317.20485 | 0.69242 | -3317.52406 | -28.5 | -26.6 |
| 1-F-Y-IM1 | 0.12248 | -437.78748 | 0.07183 | -437.83813 | | |
| $1\text{-F-Y-IM1} + {}^6[Ru(PPh_3)]^{3+} + PPh_3 + NEt_3 + LA + H_2$ | 1.00981 | -3317.20565 | 0.70566 | -3317.50979 | -30.6 | 10.9 |
| 1-F-Y-TS1 | 0.11869 | -437.78861 | 0.07018 | -437.83712 | | |
| $1\text{-F-Y-TS1} + {}^6[Ru(PPh_3)]^{3+} + PPh_3 + NEt_3 + LA + H_2$ | 1.00602 | -3317.20677 | 0.70401 | -3317.50878 | -33.6 | 13.5 |
| 1-F-Y-IM2 | 0.12282 | -437.78894 | 0.07153 | -437.84023 | | |
| $1\text{-F-Y-IM2} + {}^6[Ru(PPh_3)]^{3+} + PPh_3 + NEt_3 + LA + H_2$ | 1.01015 | -3317.20711 | 0.70536 | -3317.51190 | -34.4 | 5.3 |
| $HCOO^-$ | 0.02057 | -189.26496 | -0.00933 | -189.29486 | | |
| $HCOO^- + {}^6[Ru(PPh_3)]^{3+} + PPh_3 + NEt_3 + LA + H_2 + [HPY]^+$ | 1.00962 | -3317.19331 | 0.68999 | -3317.51294 | 1.8 | 2.6 |

**Table S13.** Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy ($G_0$, hartree), total energies ($E_c$, hartree) corrected by *ZPE*, Sum of electronic and thermal free energies ($G_c$, hartree) with *ZPE* and thermal corrections, and relative energies ($E_r$, kJ mol$^{-1}$) and relative Gibbs free energies ($G_r$, kJ mol$^{-1}$) relative to the reactants for the reaction stage (ii) of $HCOO^-$ + $^6[Ru(PPh_3)]^{3+}$ → $^6[RuH]^{2+}$ + $PPh_3$ + $CO_2$ at M06/def2TZVP, 6-311++G(d,p) level in aqueous solution.

| Species | *ZPE* | $E_c$ | $G_0$ | $G_c$ | $E_r$ | $G_r$ |
|---|---|---|---|---|---|---|
| $^6[Ru(PPh_3)]^{3+}$ | 0.27415 | -1129.92479 | 0.19644 | -1130.00251 | | |
| $PPh_3$ | 0.27244 | -1035.47240 | 0.20382 | -1035.54102 | | |
| $NEt_3$ | 0.20387 | -292.05597 | 0.15681 | -292.10303 | | |
| $[HNEt_3]^+$ | 0.21950 | -292.50499 | 0.17264 | -292.55185 | | |
| PY | 0.08809 | -248.07271 | 0.05210 | -248.10871 | | |
| LA | 0.12706 | -420.80704 | 0.07904 | -420.85507 | | |
| HCOOH | 0.03342 | -189.70312 | 0.00298 | -189.73356 | | |
| $H_2$ | 0.00981 | -1.15796 | -0.00228 | -1.17005 | | |
| $CO_2$ | 0.01180 | -188.54399 | -0.01351 | -188.56930 | | |
| $^6[Ru(PPh_3)]^{3+}$ + $PPh_3$ + $NEt_3$ + PY + LA + HCOOH + $H_2$ | 1.00884 | -3317.19399 | 0.68891 | -3317.51393 | 0.0 | 0.0 |
| $HCOO^-$ | 0.02057 | -189.26496 | -0.00933 | -189.29486 | | |
| $HCOO^-$ + $^6[Ru(PPh_3)]^{3+}$ + $PPh_3$ + PY + LA + $H_2$ + $[HNEt_3]^+$ | 1.01162 | -3317.20485 | 0.69242 | -3317.52406 | -28.5 | -26.6 |
| $^6[2\text{-F-S-IM1}]^{2+}$ | 0.02222 | -283.72747 | -0.01894 | -283.76864 | | |
| $^6[2\text{-F-S-IM1}]^{2+}$ + 2*$PPh_3$ + PY + LA + $H_2$ + $[HNEt_3]^+$ | 1.01156 | -3317.21497 | 0.69018 | -3317.53635 | -55.1 | -58.9 |
| $^6[2\text{-F-S-TS1}]^{2+}$ | 0.01698 | -283.69093 | -0.02481 | -283.73272 | | |
| $^6[2\text{-F-S-TS1}]^{2+}$ + 2*$PPh_3$ + PY + LA + $H_2$ + $[HNEt_3]^+$ | 1.00632 | -3317.17843 | 0.68431 | -3317.50043 | 40.9 | 35.4 |
| $^6[2\text{-F-S-IM2}]^{2+}$ | 0.01866 | -283.70367 | -0.02233 | -283.74466 | | |
| $^6[2\text{-F-S-IM2}]^{2+}$ + 2*$PPh_3$ + PY + LA + $H_2$ + $[HNEt_3]^+$ | 1.00800 | -3317.19117 | 0.68680 | -3317.51237 | 7.4 | 4.1 |
| $^6[RuH]^{2+}$ | 0.00420 | -95.16229 | -0.02229 | -95.18878 | | |
| $^6[RuH]^{2+}$ + 2*$PPh_3$ + PY + LA + $H_2$ + $[HNEt_3]^+$ + $CO_2$ | 1.00533 | -3317.19378 | 0.67333 | -3317.52579 | 0.5 | -31.1 |

**Table S14.** Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy ($G_0$, hartree), total energies ($E_c$, hartree) corrected by *ZPE*, Sum of electronic and thermal free energies ($G_c$, hartree) with *ZPE* and thermal corrections, and relative energies ($E_r$, kJ mol$^{-1}$) and relative Gibbs free energies ($G_r$, kJ mol$^{-1}$) relative to the reactants for the reaction stage (**ii**i) of $^6[RuH]^{2+}$ + LA → $^6[RuOH]^{2+}$ + GVL through the hydrogenation of ketone carbonyl at M06/def2TZVP, 6-311++G(d,p) level in aqueous solution.

| Species | *ZPE* | $E_c$ | $G_0$ | $G_c$ | $E_r$ | $G_r$ |
|---|---|---|---|---|---|---|
| $^6[Ru(PPh_3)]^{3+}$ | 0.27415 | -1129.92479 | 0.19644 | -1130.00251 | | |
| $PPh_3$ | 0.27244 | -1035.47240 | 0.20382 | -1035.54102 | | |
| $NEt_3$ | 0.20387 | -292.05597 | 0.15681 | -292.10303 | | |
| $[HNEt_3]^+$ | 0.21950 | -292.50499 | 0.17264 | -292.55185 | | |
| PY | 0.08809 | -248.07271 | 0.05210 | -248.10871 | | |
| LA | 0.12706 | -420.80704 | 0.07904 | -420.85507 | | |
| HCOOH | 0.03342 | -189.70312 | 0.00298 | -189.73356 | | |
| $H_2$ | 0.00981 | -1.15796 | -0.00228 | -1.17005 | | |
| $CO_2$ | 0.01180 | -188.54399 | -0.01351 | -188.56930 | | |
| GVL | 0.12519 | -345.57698 | 0.08391 | -345.61826 | | |
| $^6[Ru(PPh_3)]^{3+}$ + $PPh_3$ + $NEt_3$ + PY + LA + HCOOH + $H_2$ | 1.00884 | -3317.19399 | 0.68891 | -3317.51393 | 0.0 | 0.0 |
| $^6[RuH]^{2+}$ | 0.00420 | -95.16229 | -0.02229 | -95.18878 | | |
| $^6[RuH]^{2+}$ + 2*$PPh_3$ + PY + LA + $H_2$ + $[HNEt_3]^+$ + $CO_2$ | 1.00533 | -3317.19378 | 0.67333 | -3317.52579 | 0.5 | -31.1 |
| $^6$[3-F-K-IM4]$^{2+}$ | 0.13541 | -515.96925 | 0.07797 | -516.02670 | | |
| $^6$[3-F-K-IM4]$^{2+}$ + 2*$PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + $CO_2$ | 1.00948 | -3317.19371 | 0.69455 | -3317.50864 | 0.7 | 13.9 |
| $^6$[3-F-K-TS2]$^{2+}$ | 0.13570 | -515.95439 | 0.07955 | -516.01053 | | |
| $^6$[3-F-K-TS2]$^{2+}$ + 2*$PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + $CO_2$ | 1.00977 | -3317.17884 | 0.69613 | -3317.49247 | 39.8 | 56.3 |
| $^6$[3-F-K-IM5]$^{2+}$ | 0.14037 | -516.00242 | 0.08295 | -516.05984 | | |
| $^6$[3-F-K-IM5]$^{2+}$ + 2*$PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + $CO_2$ | 1.01444 | -3317.22687 | 0.69953 | -3317.54178 | -86.3 | -73.1 |
| $^6$[3-F-K-IM6]$^{2+}$ | 0.14086 | -516.00375 | 0.08621 | -516.05840 | | |
| $^6$[3-F-K-IM6]$^{2+}$ + 2*$PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + $CO_2$ | 1.01493 | -3317.22821 | 0.70280 | -3317.54033 | -89.8 | -69.3 |
| $^6$[3-F-K-TS3]$^{2+}$ | 0.14018 | -515.97845 | 0.08921 | -516.02941 | | |
| $^6$[3-F-K-TS3]$^{2+}$ + 2*$PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + $CO_2$ | 1.01425 | -3317.20290 | 0.70579 | -3317.51135 | -23.4 | 6.8 |
| $^6$[3-F-K-IM7]$^{2+}$ | 0.14233 | -515.98966 | 0.08947 | -516.04252 | | |
| $^6$[3-F-K-IM7]$^{2+}$ + 2*$PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + $CO_2$ | 1.01641 | -3317.21411 | 0.70605 | -3317.52446 | -52.8 | -27.6 |
| $^6$[3-F-K-IM8]$^{2+}$ | 0.14165 | -515.98835 | 0.08862 | -516.04138 | | |
| $^6$[3-F-K-IM8]$^{2+}$ + 2*$PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + $CO_2$ | 1.01572 | -3317.21280 | 0.70521 | -3317.52332 | -49.4 | -24.7 |
| $^6$[3-F-K-TS4]$^{2+}$ | 0.13977 | -515.97382 | 0.08768 | -516.02591 | | |
| $^6$[3-F-K-TS4]$^{2+}$ + 2*$PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + $CO_2$ | 1.01384 | -3317.19828 | 0.70427 | -3317.50785 | -11.3 | 16.0 |
| $^6$[3-F-K-IM9]$^{2+}$ | 0.13998 | -516.00549 | 0.08506 | -516.06041 | | |
| $^6$[3-F-K-IM9]$^{2+}$ + 2*$PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + $CO_2$ | 1.01405 | -3317.22994 | 0.70164 | -3317.54235 | -94.4 | -74.6 |
| $^6[RuOH]^{2+}$ | 0.01137 | -170.42314 | -0.02230 | -170.45681 | | |
| $^6[RuOH]^{2+}$ + 2*$PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + $CO_2$ + GVL | 1.01063 | -3317.22457 | 0.67819 | -3317.55701 | -80.3 | -113.1 |
| $^6$[3-F-C-IM4]$^{2+}$ | 0.13780 | -515.96972 | 0.08001 | -516.02750 | | |
| $^6$[3-F-C-IM4]$^{2+}$ + 2*$PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + $CO_2$ | 1.01187 | -3317.19417 | 0.69660 | -3317.50943 | -0.5 | 11.8 |
| $^6$[3-F-C-TS2]$^{2+}$ | 0.13559 | -515.95117 | 0.08090 | -516.00587 | | |
| $^6$[3-F-C-TS2]$^{2+}$ + 2*$PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + $CO_2$ | 1.00966 | -3317.17563 | 0.69748 | -3317.48780 | 48.2 | 68.6 |

**Table S15.** Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy ($G_0$, hartree), total energies ($E_c$, hartree) corrected by *ZPE*, Sum of electronic and thermal free energies ($G_c$, hartree) with *ZPE* and thermal corrections, and relative energies ($E_r$, kJ mol$^{-1}$) and relative Gibbs free energies ($G_r$, kJ mol$^{-1}$) relative to the reactants for the reaction stage (iv) of $^6[RuOH]^{2+}$ + $CO_2$ + $PPh_3$ → $^6[Ru(PPh_3)]^{3+}$ + $HCO_3^-$ at M06/def2TZVP, 6-311++G(d,p) level in aqueous solution.

| Species | *ZPE* | $E_c$ | $G_0$ | $G_c$ | $E_r$ | $G_r$ |
|---|---|---|---|---|---|---|
| $^6[Ru(PPh_3)]^{3+}$ | 0.27415 | -1129.92479 | 0.19644 | -1130.00251 | | |
| $PPh_3$ | 0.27244 | -1035.47240 | 0.20382 | -1035.54102 | | |
| $NEt_3$ | 0.20387 | -292.05597 | 0.15681 | -292.10303 | | |
| $[HNEt_3]^+$ | 0.21950 | -292.50499 | 0.17264 | -292.55185 | | |
| PY | 0.08809 | -248.07271 | 0.05210 | -248.10871 | | |
| LA | 0.12706 | -420.80704 | 0.07904 | -420.85507 | | |
| HCOOH | 0.03342 | -189.70312 | 0.00298 | -189.73356 | | |
| $H_2$ | 0.00981 | -1.15796 | -0.00228 | -1.17005 | | |
| $CO_2$ | 0.01180 | -188.54399 | -0.01351 | -188.56930 | | |
| GVL | 0.12519 | -345.57698 | 0.08391 | -345.61826 | | |
| $OH^-$ | 0.00893 | -75.92761 | -0.00988 | -75.94642 | | |
| $^6[Ru(PPh_3)]^{3+}$ + $PPh_3$ + $NEt_3$ + PY + LA + HCOOH + $H_2$ | 1.00884 | -3317.19399 | 0.68891 | -3317.51393 | 0.0 | 0.0 |
| 6[RuOH]2+ | 0.01137 | -170.42314 | -0.02230 | -170.45681 | | |
| $^6[RuOH]^{2+}$ + 2*$PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + $CO_2$ + GVL | 1.01063 | -3317.22457 | 0.67819 | -3317.55701 | -80.3 | -113.1 |
| $OH^-$ | 0.00893 | -75.92761 | -0.00988 | -75.94642 | | |
| $^6[Ru(PPh_3)]^{3+}$ + $PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + $CO_2$ + GVL | 1.00991 | -3317.18144 | 0.68323 | -3317.50811 | 33.0 | 15.3 |
| $^6[4\text{-F-C-IM11}]^{2+}$ | 0.02502 | -358.96581 | -0.02205 | -359.01287 | | |
| $^6[4\text{-F-C-IM11}]^{2+}$ + 2*$PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + GVL | 1.01248 | -3317.22325 | 0.69195 | -3317.54377 | -76.8 | -78.3 |
| $^6[4\text{-F-C-TS5}]^{2+}$ | 0.02497 | -358.95103 | -0.01972 | -358.99572 | | |
| $^6[4\text{-F-C-TS5}]^{2+}$ + 2*$PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + GVL | 1.01243 | -3317.20847 | 0.69428 | -3317.52662 | -38.0 | -33.3 |
| $^6[4\text{-F-C-IM12}]^{2+}$ | 0.02890 | -358.96785 | -0.01359 | -359.01034 | | |
| $^6[4\text{-F-C-IM12}]^{2+}$ + 2*$PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + GVL | 1.01636 | -3317.22529 | 0.70041 | -3317.54124 | -82.2 | -71.7 |
| $HCO_3^-$ | 0.02645 | -264.51134 | -0.00655 | -264.54433 | | |
| $HCO_3^-$ + $^6[Ru(PPh_3)]^{3+}$ + $PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + GVL | 1.01562 | -3317.22117 | 0.70007 | -3317.53672 | -71.4 | -59.8 |

**Table S16.** Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy ($G_0$, hartree), total energies ($E_c$, hartree) corrected by *ZPE*, Sum of electronic and thermal free energies ($G_c$, hartree) with *ZPE* and thermal corrections, and relative energies ($E_r$, kJ mol$^{-1}$) and relative Gibbs free energies ($G_r$, kJ mol$^{-1}$) relative to the reactants for the reaction stage (v) of $HCO_3^-$ + $[HL]^+$ → L + $CO_2$ + $H_2O$ (L = $PPh_3$, $NEt_3$, and PY) at M06/def2TZVP, 6-311++G(d,p) level in aqueous solution.

| Species | *ZPE* | $E_c$ | $G_0$ | $G_c$ | $E_r$ | $G_r$ |
|---|---|---|---|---|---|---|
| $^6[Ru(PPh_3)]^{3+}$ | 0.27415 | -1129.92479 | 0.19644 | -1130.00251 | | |
| $PPh_3$ | 0.27244 | -1035.47240 | 0.20382 | -1035.54102 | | |
| $[HPPh_3]^+$ | 0.28366 | -1035.91017 | 0.21535 | -1035.97848 | | |
| $NEt_3$ | 0.20387 | -292.05597 | 0.15681 | -292.10303 | | |
| $[HNEt_3]^+$ | 0.21950 | -292.50499 | 0.17264 | -292.55185 | | |
| PY | 0.08809 | -248.07271 | 0.05210 | -248.10871 | | |
| $[HPY]^+$ | 0.10172 | -248.51019 | 0.06550 | -248.54641 | | |
| LA | 0.12706 | -420.80704 | 0.07904 | -420.85507 | | |
| HCOOH | 0.03342 | -189.70312 | 0.00298 | -189.73356 | | |
| $H_2$ | 0.00981 | -1.15796 | -0.00228 | -1.17005 | | |
| $CO_2$ | 0.01180 | -188.54399 | -0.01351 | -188.56930 | | |
| GVL | 0.12519 | -345.57698 | 0.08391 | -345.61826 | | |
| $H_2O$ | 0.02128 | -76.41073 | -0.00070 | -76.43271 | | |
| $^6[Ru(PPh_3)]^{3+}$ + $PPh_3$ + $NEt_3$ + PY + LA + HCOOH + $H_2$ | 1.00884 | -3317.19399 | 0.68891 | -3317.51393 | 0.0 | 0.0 |
| $HCO_3^-$ | 0.02645 | -264.51134 | -0.00655 | -264.54433 | | |
| $HCO_3^-$ + $^6[Ru(PPh_3)]^{3+}$ + $[HPPh_3]^+$ + PY + $H_2$ + $NEt_3$ + GVL | 1.01122 | -3317.20993 | 0.69579 | -3317.52535 | -41.8 | -30.0 |
| 5-B-P-IM1 | 0.31186 | -1300.43267 | 0.22889 | -1300.51563 | | |
| 5-B-P-IM1 + $^6[Ru(PPh_3)]^{3+}$ + PY + $H_2$ + $NEt_3$ + GVL | 1.01297 | -3317.22108 | 0.71587 | -3317.51818 | -71.1 | -11.1 |
| 5-B-P-TS1 | 0.30690 | -1300.40860 | 0.22524 | -1300.49026 | | |
| 5-B-P-TS1 + $^6[Ru(PPh_3)]^{3+}$ + PY + $H_2$ + $NEt_3$ + GVL | 1.00802 | -3317.19701 | 0.71222 | -3317.49281 | -7.9 | 55.5 |
| 5-B-P-IM2 | 0.31032 | -1300.44082 | 0.22668 | -1300.52446 | | |
| 5-B-P-IM2 + $^6[Ru(PPh_3)]^{3+}$ + PY + $H_2$ + $NEt_3$ + GVL | 1.01143 | -3317.22924 | 0.71367 | -3317.52700 | -92.5 | -34.3 |
| $HCO_3^-$ | 0.02645 | -264.51134 | -0.00655 | -264.54433 | | |
| $HCO_3^-$ + $^6[Ru(PPh_3)]^{3+}$ + $PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + GVL | 1.01562 | -3317.22117 | 0.70007 | -3317.53672 | -71.4 | -59.8 |
| 5-B-N-IM1 | 0.24732 | -557.03079 | 0.18682 | -557.09129 | | |
| 5-B-N-IM1 + $^6[Ru(PPh_3)]^{3+}$ + $PPh_3$ + PY + $H_2$ + GVL | 1.01700 | -3317.23563 | 0.72080 | -3317.53183 | -109.3 | -47.0 |
| 5-B-N-TS1 | 0.24103 | -557.00196 | 0.18183 | -557.06116 | | |
| 5-B-N-TS1 + $^6[Ru(PPh_3)]^{3+}$ + $PPh_3$ + PY + $H_2$ + GVL | 1.01070 | -3317.20681 | 0.71582 | -3317.50170 | -33.7 | 32.1 |
| 5-B-N-IM2 | 0.24340 | -557.01940 | 0.18153 | -557.08127 | | |
| 5-B-N-IM2 + $^6[Ru(PPh_3)]^{3+}$ + $PPh_3$ + PY + $H_2$ + GVL | 1.01307 | -3317.22425 | 0.71551 | -3317.52181 | -79.4 | -20.7 |
| $HCO_3^-$ | 0.02645 | -264.51134 | -0.00655 | -264.54433 | | |
| $HCO_3^-$ + $^6[Ru(PPh_3)]^{3+}$ + $PPh_3$ + $[HPY]^+$ + $H_2$ + $NEt_3$ + GVL | 1.01362 | -3317.20963 | 0.69765 | -3317.52560 | -41.1 | -30.6 |
| 5-B-Y-IM1 | 0.12935 | -513.02994 | 0.07597 | -513.08332 | | |
| 5-B-Y-IM1 + $^6[Ru(PPh_3)]^{3+}$ + $PPh_3$ + $H_2$ + $NEt_3$ + GVL | 1.01481 | -3317.21804 | 0.71467 | -3317.51818 | -63.1 | -11.1 |
| 5-B-Y-TS1 | 0.12432 | -513.01262 | 0.07180 | -513.06514 | | |
| 5-B-Y-TS1 + $^6[Ru(PPh_3)]^{3+}$ + $PPh_3$ + $H_2$ + $NEt_3$ + GVL | 1.00977 | -3317.20072 | 0.71050 | -3317.49999 | -17.7 | 36.6 |
| 5-B-Y-IM2 | 0.12575 | -513.03316 | 0.06671 | -513.09221 | | |
| 5-B-Y-IM2 + $^6[Ru(PPh_3)]^{3+}$ + $PPh_3$ + $H_2$ + $NEt_3$ + GVL | 1.01120 | -3317.22127 | 0.70541 | -3317.52707 | -71.6 | -34.5 |
| $CO_2$ | 0.01180 | -188.54399 | -0.01351 | -188.56930 | | |
| $CO_2$ + $^6[Ru(PPh_3)]^{3+}$ + $PPh_3$ + PY + $NEt_3$ + $H_2$ + GVL + $H_2O$ | 1.00663 | -3317.21554 | 0.67659 | -3317.54557 | -56.6 | -83.1 |

**Table S17.** Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy ($G_0$, hartree), total energies ($E_c$, hartree) corrected by *ZPE*, Sum of electronic and thermal free energies ($G_c$, hartree) with *ZPE* and thermal corrections, and relative energies ($E_r$, kJ mol$^{-1}$) and relative Gibbs free energies ($G_r$, kJ mol$^{-1}$) relative to the reactants for the reaction stage (vi) of $^6[RuH]^{2+}$ + LA ⟶ $^6[RuOH]^{2+}$ + OT through the hydrogenation of carboxyl carbonyl at M06/def2TZVP, 6-311++G(d,p) level in aqueous solution.

| Species | *ZPE* | $E_c$ | $G_0$ | $G_c$ | $E_r$ | $G_r$ |
|---|---|---|---|---|---|---|
| $^6[Ru(PPh_3)]^{3+}$ | 0.27415 | -1129.92479 | 0.19644 | -1130.00251 | | |
| $PPh_3$ | 0.27244 | -1035.47240 | 0.20382 | -1035.54102 | | |
| $[HPPh_3]^+$ | 0.28366 | -1035.91017 | 0.21535 | -1035.97848 | | |
| $NEt_3$ | 0.20387 | -292.05597 | 0.15681 | -292.10303 | | |
| $[HNEt_3]^+$ | 0.21950 | -292.50499 | 0.17264 | -292.55185 | | |
| PY | 0.08809 | -248.07271 | 0.05210 | -248.10871 | | |
| $[HPY]^+$ | 0.10172 | -248.51019 | 0.06550 | -248.54641 | | |
| LA | 0.12706 | -420.80704 | 0.07904 | -420.85507 | | |
| HCOOH | 0.03342 | -189.70312 | 0.00298 | -189.73356 | | |
| $H_2$ | 0.00981 | -1.15796 | -0.00228 | -1.17005 | | |
| $CO_2$ | 0.01180 | -188.54399 | -0.01351 | -188.56930 | | |
| OT | 0.12081 | -345.55701 | 0.07452 | -345.60330 | | |
| $^6[Ru(PPh_3)]^{3+} + PPh_3 + NEt_3 + PY + LA + HCOOH + H_2$ | 1.00884 | -3317.19399 | 0.68891 | -3317.51393 | 0.0 | 0.0 |
| $^6[RuH]^{2+}$ | 0.00420 | -95.16229 | -0.02229 | -95.18878 | | |
| $^6[RuH]^{2+} + 2*PPh_3 + PY + LA + H_2 + [HNEt_3]^+ + CO_2$ | 1.00533 | -3317.19378 | 0.67333 | -3317.52579 | 0.5 | -31.1 |
| $^6[3\text{-F-C-IM4}]^{2+}$ | 0.13780 | -515.96972 | 0.08001 | -516.02750 | | |
| $^6[3\text{-F-C-IM4}]^{2+} + 2*PPh_3 + PY + H_2 + [HNEt_3]^+ + CO_2$ | 1.01187 | -3317.19417 | 0.69660 | -3317.50943 | -0.5 | 11.8 |
| $^6[6\text{-F-O-TS2}]^{2+}$ | 0.13485 | -515.94716 | 0.07718 | -516.00483 | | |
| $^6[6\text{-F-O-TS2}]^{2+} + 2*PPh_3 + PY + H_2 + [HNEt_3]^+ + CO_2$ | 1.00893 | -3317.17161 | 0.69376 | -3317.48677 | 58.8 | 71.3 |
| $^6[6\text{-F-O-IM5}]^{2+}$ | 0.13940 | -515.98718 | 0.07994 | -516.04664 | | |
| $^6[6\text{-F-O-IM5}]^{2+} + 2*PPh_3 + PY + H_2 + [HNEt_3]^+ + CO_2$ | 1.01347 | -3317.21163 | 0.69653 | -3317.52857 | -46.3 | -38.4 |
| $^6[6\text{-F-O-TS3}]^{2+}$ | 0.13572 | -515.96212 | 0.07863 | -516.01920 | | |
| $^6[6\text{-F-O-TS3}]^{2+} + 2*PPh_3 + PY + H_2 + [HNEt_3]^+ + CO_2$ | 1.00979 | -3317.18657 | 0.69522 | -3317.50114 | 19.5 | 33.6 |
| $^6[6\text{-F-O-IM6}]^{2+}$ | 0.13497 | -515.98151 | 0.07362 | -516.04285 | | |
| $^6[6\text{-F-O-IM6}]^{2+} + 2*PPh_3 + PY + H_2 + [HNEt_3]^+ + CO_2$ | 1.00904 | -3317.20596 | 0.69020 | -3317.52479 | -31.4 | -28.5 |
| $^6[RuOH]^{2+}$ | 0.01137 | -170.42314 | -0.02230 | -170.45681 | | |
| $^6[RuOH]^{2+} + 2*PPh_3 + PY + H_2 + [HNEt_3]^+ + CO_2 + OT$ | 1.00625 | -3317.20460 | 0.66880 | -3317.54205 | -27.9 | -73.8 |

**Table S18.** Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy ($G_0$, hartree), total energies ($E_c$, hartree) corrected by *ZPE*, Sum of electronic and thermal free energies ($G_c$, hartree) with *ZPE* and thermal corrections, and relative energies ($E_r$, kJ mol$^{-1}$) and relative Gibbs free energies ($G_r$, kJ mol$^{-1}$) relative to the reactants for the reaction stage (vii) of $^6[RuH]^{2+}$ + LA + $[HNEt_3]^+$ + $PPh_3$ → $^6[Ru(PPh_3)]^{3+}$ + $NEt_3$ + MFD through the hydrogenation of carboxyl carbonyl at M06/def2TZVP, 6-311++G(d,p) level in aqueous solution.

| Species | *ZPE* | $E_c$ | $G_0$ | $G_c$ | $E_r$ | $G_r$ |
|---|---|---|---|---|---|---|
| $^6[Ru(PPh_3)]^{3+}$ | 0.27415 | -1129.92479 | 0.19644 | -1130.00251 | | |
| $PPh_3$ | 0.27244 | -1035.47240 | 0.20382 | -1035.54102 | | |
| $[HPPh_3]^+$ | 0.28366 | -1035.91017 | 0.21535 | -1035.97848 | | |
| $NEt_3$ | 0.20387 | -292.05597 | 0.15681 | -292.10303 | | |
| $[HNEt_3]^+$ | 0.21950 | -292.50499 | 0.17264 | -292.55185 | | |
| PY | 0.08809 | -248.07271 | 0.05210 | -248.10871 | | |
| $[HPY]^+$ | 0.10172 | -248.51019 | 0.06550 | -248.54641 | | |
| LA | 0.12706 | -420.80704 | 0.07904 | -420.85507 | | |
| HCOOH | 0.03342 | -189.70312 | 0.00298 | -189.73356 | | |
| $H_2$ | 0.00981 | -1.15796 | -0.00228 | -1.17005 | | |
| $CO_2$ | 0.01180 | -188.54399 | -0.01351 | -188.56930 | | |
| MFD | 0.15379 | -421.96692 | 0.10937 | -422.01134 | | |
| $^6[Ru(PPh_3)]^{3+}$ + $PPh_3$ + $NEt_3$ + PY + LA + HCOOH + $H_2$ | 1.00884 | -3317.19399 | 0.68891 | -3317.51393 | 0.0 | 0.0 |
| $^6[RuH]^{2+}$ | 0.00420 | -95.16229 | -0.02229 | -95.18878 | | |
| $^6[RuH]^{2+}$ + 2*$PPh_3$ + PY + LA + $H_2$ + $[HNEt_3]^+$ + $CO_2$ | 1.00533 | -3317.19378 | 0.67333 | -3317.52579 | 0.5 | -31.1 |
| $^6$[3-F-C-IM4]$^{2+}$ | 0.13780 | -515.96972 | 0.08001 | -516.02750 | | |
| $^6$[3-F-C-IM4]$^{2+}$ + 2*$PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + $CO_2$ | 1.01187 | -3317.19417 | 0.69660 | -3317.50943 | -0.5 | 11.8 |
| $^6$[6-F-O-TS2]$^{2+}$ | 0.13485 | -515.94716 | 0.07718 | -516.00483 | | |
| $^6$[6-F-O-TS2]$^{2+}$ + 2*$PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + $CO_2$ | 1.00893 | -3317.17161 | 0.69376 | -3317.48677 | 58.8 | 71.3 |
| $^6$[6-F-O-IM5]$^{2+}$ | 0.13940 | -515.98718 | 0.07994 | -516.04664 | | |
| $^6$[6-F-O-IM5]$^{2+}$ + 2*$PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + $CO_2$ | 1.01347 | -3317.21163 | 0.69653 | -3317.52857 | -46.3 | -38.4 |
| $^6$[7-F-M-IM6]$^{2+}$ | 0.14032 | -515.98897 | 0.08483 | -516.04445 | | |
| $^6$[7-F-M-IM6]$^{2+}$ + 2*$PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + $CO_2$ | 1.01439 | -3317.21342 | 0.70141 | -3317.52639 | -51.0 | -32.7 |
| $^6$[7-F-M-TS3]$^{2+}$ | 0.13959 | -515.97139 | 0.08624 | -516.02474 | | |
| $^6$[7-F-M-TS3]$^{2+}$ + 2*$PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + $CO_2$ | 1.01366 | -3317.19584 | 0.70282 | -3317.50668 | -4.9 | 19.0 |
| $^6$[7-F-M-IM7]$^{2+}$ | 0.14262 | -515.98518 | 0.08943 | -516.03837 | | |
| $^6$[7-F-M-IM7]$^{2+}$ + 2*$PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + $CO_2$ | 1.01669 | -3317.20963 | 0.70602 | -3317.52030 | -41.1 | -16.7 |
| [7-F-M-IM8]$^-$ | 0.13908 | -421.49519 | 0.09502 | -421.53925 | | |
| [7-F-M-IM8]$^-$ + $^6[Ru(PPh_3)]^{3+}$ + $PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + $CO_2$ | 1.01487 | -3317.17204 | 0.70423 | -3317.48268 | 57.6 | 82.0 |
| 7-F-M-IM9 | 0.35886 | -714.02138 | 0.28842 | -714.09181 | | |
| 7-F-M-IM9 + $^6[Ru(PPh_3)]^{3+}$ + $PPh_3$ + PY + $H_2$ + $CO_2$ | 1.01514 | -3317.19324 | 0.72499 | -3317.48339 | 2.0 | 80.2 |
| 7-F-M-TS4 | 0.35578 | -714.02324 | 0.28912 | -714.08991 | | |
| 7-F-M-TS4 + $^6[Ru(PPh_3)]^{3+}$ + $PPh_3$ + PY + $H_2$ + $CO_2$ | 1.01207 | -3317.19510 | 0.72569 | -3317.48148 | -2.9 | 85.2 |
| 7-F-M-IM10 | 0.36016 | -714.03203 | 0.29067 | -714.10152 | | |
| 7-F-M-IM10 + $^6[Ru(PPh_3)]^{3+}$ + $PPh_3$ + PY + $H_2$ + $CO_2$ | 1.01645 | -3317.20389 | 0.72724 | -3317.49310 | -26.0 | 54.7 |
| MFD | 0.15379 | -421.96692 | 0.10937 | -422.01134 | | |
| MFD + $^6[Ru(PPh_3)]^{3+}$ + $PPh_3$ + PY + $H_2$ + $CO_2$ + $NEt_3$ | 1.01395 | -3317.19474 | 0.70275 | -3317.50594 | -2.0 | 21.0 |

**Table S19.** Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy ($G_0$, hartree), total energies ($E_c$, hartree) corrected by *ZPE*, Sum of electronic and thermal free energies ($G_c$, hartree) with *ZPE* and thermal corrections, and relative energies ($E_r$, kJ mol$^{-1}$) and relative Gibbs free energies ($G_r$, kJ mol$^{-1}$) relative to the reactants for the reaction stage (viii) of $^6[Ru(PPh_3)]^{3+} + H_2 + L \rightarrow {}^6[RuH]^{2+} + [HL]^+ + PPh_3$ (L = $PPh_3$, $NEt_3$, and PY) and $^6[Ru(PPh_3)]^{3+} + H_2 \rightarrow {}^6[Ru(H)_2]^{3+} + PPh_3$ at M06/def2TZVP, 6-311++G(d,p) level in aqueous solution.

| Species | *ZPE* | $E_c$ | $G_0$ | $G_c$ | $E_r$ | $G_r$ |
|---|---|---|---|---|---|---|
| $^6[Ru(PPh_3)]^{3+}$ | 0.27415 | -1129.92479 | 0.19644 | -1130.00251 | | |
| $PPh_3$ | 0.27244 | -1035.47240 | 0.20382 | -1035.54102 | | |
| $[HPPh_3]^+$ | 0.28366 | -1035.91017 | 0.21535 | -1035.97848 | | |
| $NEt_3$ | 0.20387 | -292.05597 | 0.15681 | -292.10303 | | |
| $[HNEt_3]^+$ | 0.21950 | -292.50499 | 0.17264 | -292.55185 | | |
| PY | 0.08809 | -248.07271 | 0.05210 | -248.10871 | | |
| $[HPY]^+$ | 0.10172 | -248.51019 | 0.06550 | -248.54641 | | |
| LA | 0.12706 | -420.80704 | 0.07904 | -420.85507 | | |
| HCOOH | 0.03342 | -189.70312 | 0.00298 | -189.73356 | | |
| $H_2$ | 0.00981 | -1.15796 | -0.00228 | -1.17005 | | |
| $CO_2$ | 0.01180 | -188.54399 | -0.01351 | -188.56930 | | |
| | | | | | | |
| $^6[Ru(PPh_3)]^{3+} + PPh_3 + NEt_3 + PY + LA + HCOOH + H_2$ | 1.00884 | -3317.19399 | 0.68891 | -3317.51393 | 0.0 | 0.0 |
| $H_2$ | 0.009806 | -1.157963 | -0.002277 | -1.170046 | | |
| $H_2 + {}^6[Ru(PPh_3)]^{3+} + PPh_3 + NEt_3 + PY + LA + HCOOH$ | 1.008843 | -3317.193988 | 0.688905 | -3317.513926 | 0.0 | 0.0 |
| $^6[Ru(H_2)]^{3+}$ | 0.013971 | -95.588856 | -0.016603 | -95.61943 | | |
| $^6[Ru(H_2)]^{3+} + 2*PPh_3 + NEt_3 + PY + LA + HCOOH$ | 1.01129 | -3317.172487 | 0.681956 | -3317.501819 | 56.5 | 31.8 |
| $^6[Ru(H)_2]^{3+}$ | 0.005147 | -95.438249 | -0.022271 | -95.465667 | | |
| $^6[Ru(H)_2]^{3+} + 2*PPh_3 + NEt_3 + PY + LA + HCOOH$ | 1.002466 | -3317.02188 | 0.676288 | -3317.348056 | 451.9 | 435.5 |
| $^6[8\text{-H-P-IM1}]^{3+}$ | 0.293057 | -1131.078501 | 0.213197 | -1131.158361 | | |
| $^6[8\text{-H-P-IM1}]^{3+} + PPh_3 + NEt_3 + PY + LA + HCOOH$ | 1.01794 | -3317.18973 | 0.70794 | -3317.49973 | 11.2 | 37.3 |
| $^6[8\text{-H-P-TS1}]^{3+}$ | 0.28697 | -1131.06014 | 0.20840 | -1131.13872 | | |
| $^6[8\text{-H-P-TS1}]^{3+} + PPh_3 + NEt_3 + PY + LA + HCOOH$ | 1.01185 | -3317.17138 | 0.70314 | -3317.48009 | 59.4 | 88.8 |
| $^6[8\text{-H-P-IM2}]^{3+}$ | 0.29269 | -1131.07826 | 0.21771 | -1131.15324 | | |
| $^6[8\text{-H-P-IM2}]^{3+} + PPh_3 + NEt_3 + PY + LA + HCOOH$ | 1.01757 | -3317.18950 | 0.71245 | -3317.49461 | 11.8 | 50.7 |
| $^6[RuH]^{2+}$ | 0.00420 | -95.16229 | -0.02229 | -95.18878 | | |
| $^6[RuH]^{2+} + PPh_3 + NEt_3 + PY + LA + HCOOH + [HPPh_3]^+$ | 1.01274 | -3317.18370 | 0.68780 | -3317.50863 | 27.0 | 13.9 |
| $^6[8\text{-H-N-IM1}]^{3+}$ | 0.22797 | -387.65914 | 0.17408 | -387.71303 | | |
| $^6[8\text{-H-N-IM1}]^{3+} + 2*PPh_3 + PY + LA + HCOOH$ | 1.02141 | -3317.18680 | 0.71582 | -3317.49239 | 18.9 | 56.5 |
| $^6[8\text{-H-N-TS1}]^{3+}$ | 0.22128 | -387.63858 | 0.16380 | -387.69606 | | |
| $^6[8\text{-H-N-TS1}]^{3+} + 2*PPh_3 + PY + LA + HCOOH$ | 1.01472 | -3317.16624 | 0.70554 | -3317.47542 | 72.8 | 101.1 |
| $^6[8\text{-H-N-IM2}]^{3+}$ | 0.22697 | -387.66630 | 0.16687 | -387.72639 | | |
| $^6[8\text{-H-N-IM2}]^{3+} + 2*PPh_3 + PY + LA + HCOOH$ | 1.02041 | -3317.19396 | 0.70862 | -3317.50576 | 0.1 | 21.5 |
| $^6[RuH]^{2+}$ | 0.00420 | -95.16229 | -0.02229 | -95.18878 | | |
| $^6[RuH]^{2+} + 2*PPh_3 + PY + LA + HCOOH + [HNEt_3]^+$ | 1.01715 | -3317.19494 | 0.69209 | -3317.52000 | -2.5 | -15.9 |
| $^6[8\text{-H-Y-IM1}]^{3+}$ | 0.10688 | -343.66627 | 0.05929 | -343.71385 | | |
| $^6[8\text{-H-Y-IM1}]^{3+} + 2*PPh_3 + NEt_3 + LA + HCOOH$ | 1.01610 | -3317.17719 | 0.70575 | -3317.48754 | 44.1 | 69.3 |
| $^6[8\text{-H-Y-TS1}]^{3+}$ | 0.10619 | -343.64604 | 0.05710 | -343.69513 | | |
| $^6[8\text{-H-Y-TS1}]^{3+} + 2*PPh_3 + NEt_3 + LA + HCOOH$ | 1.01542 | -3317.15696 | 0.70356 | -3317.46882 | 97.2 | 118.4 |
| $^6[8\text{-H-Y-IM2}]^{3+}$ | 0.10954 | -343.66745 | 0.06248 | -343.71451 | | |
| $^6[8\text{-H-Y-IM2}]^{3+} + 2*PPh_3 + NEt_3 + LA + HCOOH$ | 1.01877 | -3317.17837 | 0.70894 | -3317.48819 | 41.0 | 67.6 |
| $^6[RuH]^{2+}$ | 0.00420 | -95.16229 | -0.02229 | -95.18878 | | |
| $^6[RuH]^{2+} + 2*PPh_3 + NEt_3 + LA + HCOOH + [HPY]^+$ | 1.01515 | -3317.18340 | 0.68967 | -3317.50888 | 27.8 | 13.3 |

**Table S20.** Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy ($G_0$, hartree), total energies ($E_c$, hartree) corrected by *ZPE*, Sum of electronic and thermal free energies ($G_c$, hartree) with *ZPE* and thermal corrections, and relative energies ($E_r$, kJ mol$^{-1}$) and relative Gibbs free energies ($G_r$, kJ mol$^{-1}$) relative to the reactants for the reaction stage of $HCOO^-$ + LA → GVL + $HCO_3^-$ in presence of $PPh_3$ at M06/def2TZVP, 6-311++G(d,p) level in aqueous solution.

| Species | *ZPE* | $E_c$ | $G_0$ | $G_c$ | $E_r$ | $G_r$ |
|---|---|---|---|---|---|---|
| $^6[Ru(PPh_3)]^{3+}$ | 0.27415 | -1129.92479 | 0.19644 | -1130.00251 | | |
| $PPh_3$ | 0.27244 | -1035.47240 | 0.20382 | -1035.54102 | | |
| $NEt_3$ | 0.20387 | -292.05597 | 0.15681 | -292.10303 | | |
| $[HNEt_3]^+$ | 0.21950 | -292.50499 | 0.17264 | -292.55185 | | |
| PY | 0.08809 | -248.07271 | 0.05210 | -248.10871 | | |
| LA | 0.12706 | -420.80704 | 0.07904 | -420.85507 | | |
| HCOOH | 0.03342 | -189.70312 | 0.00298 | -189.73356 | | |
| $H_2$ | 0.00981 | -1.15796 | -0.00228 | -1.17005 | | |
| $CO_2$ | 0.01180 | -188.54399 | -0.01351 | -188.56930 | | |
| GVL | 0.12519 | -345.57698 | 0.08391 | -345.61826 | | |
| $^6[Ru(PPh_3)]^{3+}$ + $PPh_3$ + $NEt_3$ + PY + LA + HCOOH + $H_2$ | 1.00884 | -3317.19399 | 0.68891 | -3317.51393 | 0.0 | 0.0 |
| $HCOO^-$ | 0.02057 | -189.26496 | -0.00933 | -189.29486 | | |
| $HCOO^-$ + $^6[Ru(PPh_3)]^{3+}$ + $PPh_3$ + PY + LA + $H_2$ + $[HNEt_3]^+$ | 1.01162 | -3317.20485 | 0.69242 | -3317.52406 | -28.5 | -26.6 |
| P-$^6$[2-F-S-IM1]$^{2+}$ | 0.29696 | -1319.22254 | 0.21134 | -1319.30816 | | |
| P-$^6$[2-F-S-IM1]$^{2+}$ + $PPh_3$ + PY + LA + $H_2$ + $[HNEt_3]^+$ | 1.01386 | -3317.23764 | 0.71665 | -3317.53485 | -114.6 | -54.9 |
| P-$^6$[2-F-S-TS1]$^{2+}$ | 0.29350 | -1319.18214 | 0.20922 | -1319.26641 | | |
| P-$^6$[2-F-S-TS1]$^{2+}$ + $PPh_3$ + PY + LA + $H_2$ + $[HNEt_3]^+$ | 1.01040 | -3317.19724 | 0.71453 | -3317.49311 | -8.5 | 54.7 |
| P-$^6$[2-F-S-IM2]$^{2+}$ | 0.29414 | -1319.19972 | 0.20954 | -1319.28431 | | |
| P-$^6$[2-F-S-IM2]$^{2+}$ + $PPh_3$ + PY + LA + $H_2$ + $[HNEt_3]^+$ | 1.01104 | -3317.21482 | 0.71485 | -3317.51101 | -54.7 | 7.7 |
| P-$^6$[RuH]$^{2+}$ | 0.28238 | -1130.63208 | 0.20340 | -1130.71107 | | |
| P-$^6$[RuH]$^{2+}$ + $PPh_3$ + PY + LA + $H_2$ + $[HNEt_3]^+$ + $CO_2$ | 1.01108 | -3317.19118 | 0.69520 | -3317.50706 | 7.4 | 18.1 |
| P-$^6$[3-F-K-IM4]$^{2+}$ | 0.41221 | -1551.47355 | 0.31620 | -1551.56956 | | |
| P-$^6$[3-F-K-IM4]$^{2+}$ + $PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + $CO_2$ | 1.01385 | -3317.22560 | 0.72897 | -3317.51048 | -83.0 | 9.0 |
| P-$^6$[3-F-K-TS2]$^{2+}$ | 0.41078 | -1551.45526 | 0.31351 | -1551.55253 | | |
| P-$^6$[3-F-K-TS2]$^{2+}$ + $PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + $CO_2$ | 1.01241 | -3317.20731 | 0.72627 | -3317.49345 | -35.0 | 53.8 |
| P-$^6$[3-F-K-IM5]$^{2+}$ | 0.41533 | -1551.50415 | 0.31911 | -1551.60037 | | |
| P-$^6$[3-F-K-IM5]$^{2+}$ + $PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + $CO_2$ | 1.01697 | -3317.25620 | 0.73188 | -3317.54129 | -163.3 | -71.8 |
| P-$^6$[3-F-K-IM6]$^{2+}$ | 0.41705 | -1551.50419 | 0.32109 | -1551.60016 | | |
| P-$^6$[3-F-K-IM6]$^{2+}$ + $PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + $CO_2$ | 1.01869 | -3317.25624 | 0.73385 | -3317.54108 | -163.4 | -71.3 |
| P-$^6$[3-F-K-TS3]$^{2+}$ | 0.41660 | -1551.47458 | 0.32325 | -1551.56794 | | |
| P-$^6$[3-F-K-TS3]$^{2+}$ + $PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + $CO_2$ | 1.01824 | -3317.22664 | 0.73601 | -3317.50886 | -85.7 | 13.3 |
| P-$^6$[3-F-K-IM7]$^{2+}$ | 0.41726 | -1551.48799 | 0.32335 | -1551.58190 | | |
| P-$^6$[3-F-K-IM7]$^{2+}$ + $PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + $CO_2$ | 1.01889 | -3317.24004 | 0.73611 | -3317.52282 | -120.9 | -23.3 |
| P-$^6$[3-F-K-IM8]$^{2+}$ | 0.41743 | -1551.48094 | 0.32302 | -1551.57534 | | |
| P-$^6$[3-F-K-IM8]$^{2+}$ + $PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + $CO_2$ | 1.01906 | -3317.23299 | 0.73579 | -3317.51626 | -102.4 | -6.1 |
| P-$^6$[3-F-K-TS4]$^{2+}$ | 0.41526 | -1551.47375 | 0.32205 | -1551.56696 | | |
| P-$^6$[3-F-K-TS4]$^{2+}$ + $PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + $CO_2$ | 1.01689 | -3317.22581 | 0.73481 | -3317.50788 | -83.5 | 15.9 |
| P-$^6$[3-F-K-IM9]$^{2+}$ | 0.41486 | -1551.50210 | 0.31710 | -1551.59987 | | |
| P-$^6$[3-F-K-IM9]$^{2+}$ + $PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + $CO_2$ | 1.01650 | -3317.25416 | 0.72986 | -3317.54079 | -158.0 | -70.5 |
| P-$^6$[RuOH]$^{2+}$ | 0.28700 | -1205.91067 | 0.20511 | -1205.99256 | | |
| P-$^6$[RuOH]$^{2+}$ + $PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + $CO_2$ + GVL | 1.01383 | -3317.23970 | 0.70179 | -3317.55174 | -120.0 | -99.3 |
| P-$^6$[4-F-C-IM11]$^{2+}$ | 0.30034 | -1394.46490 | 0.20993 | -1394.55531 | | |
| P-$^6$[4-F-C-IM11]$^{2+}$ + $PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + GVL | 1.01536 | -3317.24994 | 0.72011 | -3317.54520 | -146.9 | -82.1 |
| P-$^6$[4-F-C-TS5]$^{2+}$ | 0.30027 | -1394.44970 | 0.21361 | -1394.53637 | | |
| P-$^6$[4-F-C-TS5]$^{2+}$ + $PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + GVL | 1.01530 | -3317.23475 | 0.72379 | -3317.52625 | -107.0 | -32.3 |
| P-$^6$[4-F-C-IM12]$^{2+}$ | 0.30417 | -1394.46484 | 0.22076 | -1394.54824 | | |
| P-$^6$[4-F-C-IM12]$^{2+}$ + $PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + GVL | 1.01920 | -3317.24988 | 0.73094 | -3317.53813 | -146.7 | -63.5 |
| $HCO_3^-$ | 0.02645 | -264.51134 | -0.00655 | -264.54433 | | |
| $HCO_3^-$ + $^6[Ru(PPh_3)]^{3+}$ + $PPh_3$ + PY + $H_2$ + $[HNEt_3]^+$ + GVL | 1.01562 | -3317.22117 | 0.70007 | -3317.53672 | -71.4 | -59.8 |