

Supporting Information

# Kinetic Effects of Sulfur Oxidation on Catalytic Nitrile Hydration: Nitrile Hydratase Insights from Bioinspired Ruthenium(II) Complexes

Davinder Kumar,<sup>a</sup> Tho N. Nguyen<sup>a</sup> and Craig A. Grapperhaus\*<sup>a</sup>

Department of Chemistry, University of Louisville, Louisville, KY 40292, USA

\*Corresponding author. Tel. +1 502852-5932; fax: +1 502852-8149.

E-mail address: [grapperhaus@louisville.edu](mailto:grapperhaus@louisville.edu) (C.A. Grapperhaus)

## Table of Contents

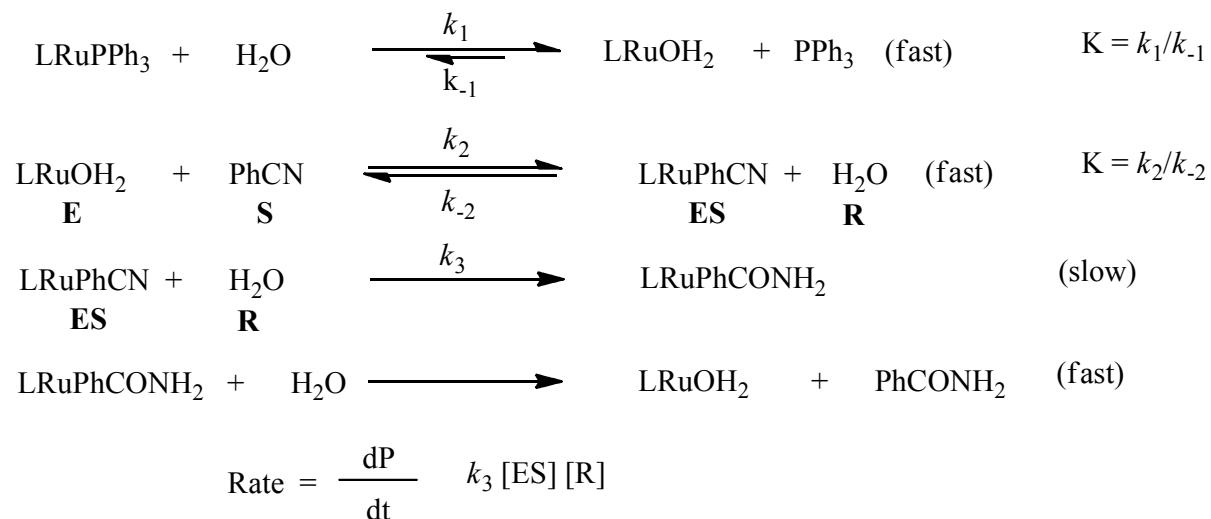
Derivation of Rate Law.....	S5
Figure S1. Kinetic traces for L <sup>1</sup> RuPPh <sub>3</sub> under conditions: [PhCN] = 4.0M, [H <sub>2</sub> O] = 11M and [Cat.] = 0.21mM (A), 0.42mM (B), and 0.84 mM (C) .....	S6
Figure S2. Kinetic traces for L <sup>1</sup> RuPPh <sub>3</sub> under conditions: [PhCN] = 0.97M, and [H <sub>2</sub> O] = 2.8M (A), 8.3M (B), 11M (C), 14M (D), and 17M (E), and [Cat.] = 0.21mM.....	S7
Figure S3. Kinetic traces for L <sup>1</sup> RuPPh <sub>3</sub> under conditions: [PhCN] = 0.12M (A), 0.49M (B), 0.97M (C), 1.9 (D), and 4.0M (E), [H <sub>2</sub> O] = 11M and [Cat.] = 0.42mM .....	S8
Figure S4. Arrhenius plot for L <sup>1</sup> RuPPh <sub>3</sub> in the temperature range 368-398K under conditions [Cat.] = 0.42mM, [PhCN] = 0.97M, and [H <sub>2</sub> O] = 11M equation: y = -8668.3x + 22.6 .....	S9
Figure S5. Eyring plot for L <sup>1</sup> RuPPh <sub>3</sub> in the temperature range 368-398K under conditions [Cat.] = 0.42mM, [PhCN] = 0.97M, and [H <sub>2</sub> O] = 11M equation: y = -8285.8x + 15.6 .....	S9
Figure S6. The kinetic traces for L <sup>2</sup> RuPPh <sub>3</sub> under conditions: [PhCN] = 4.0M, [H <sub>2</sub> O] = 11M, and [Cat.] = 0.056mM (A), 0.084mM (B), and 0.112 mM (C) .....	S10
Figure S7. The kinetic traces for L <sup>2</sup> RuPPh <sub>3</sub> under conditions: [PhCN] = 0.97M, [H <sub>2</sub> O] = 2.8M (A), 5.5M (B), 11M (C), 14M (D), and 17M (E), and [Cat.] = 0.056mM.....	S11
Figure S8. The kinetic traces for L <sup>2</sup> RuPPh <sub>3</sub> under conditions: [PhCN] = 0.49M (A), 0.97M (B), 1.9M (C), 2.9M (D), and 4.0M (E), [H <sub>2</sub> O] = 11M and [Cat.] = 0.056mM .....	S12
Figure S9. The plots for L <sup>2</sup> RuPPh <sub>3</sub> showing linear dependence of rate vs [Cat.] and k <sub>obs</sub> <sup>-1</sup> vs [PhCN] <sup>-1</sup> and [H <sub>2</sub> O] <sup>-1</sup> .....	S13
Figure S10. The Arrhenius plot for L <sup>2</sup> RuPPh <sub>3</sub> in the temperature range 368-398K under conditions: [Cat.] = 0.056mM, [PhCN] = 2.9M, and [H <sub>2</sub> O] = 11M equation: y = -5457.4x + 15.8 ...	S14
Figure S11. The Eyring plot for L <sup>2</sup> RuPPh <sub>3</sub> in the temperature range 368-398K under conditions: [Cat.] = 0.056mM, [PhCN] = 2.9M, and [H <sub>2</sub> O] = 11M equation: y = -5074.8x + 8.88.....	S14

Figure S12. The kinetic traces for $L^3RuPPh_3$ under conditions: [PhCN] = 4.0M, [H <sub>2</sub> O] = 11M, and [Cat.] = 0.112mM (A), 0.168M (B), and 0.224mM (C) .....	S15
Figure S13. The kinetic traces for $L^3RuPPh_3$ under conditions: [PhCN] = 0.97M, [H <sub>2</sub> O] = 2.8M (A), 8.3M(B), 11M (C), 17M (D), and 19M (E), and [Cat.] = 0.112mM .....	S16
Figure S14. The kinetic traces for $L^3RuPPh_3$ under conditions: [PhCN] = 0.24M (A), 0.49M (B), 0.97M (C), 1.4M (D), and 2.9M (E), and [H <sub>2</sub> O] = 11M, and [Cat.] = 0.112mM .....	S17
Figure S15. The plots for $L^3RuPPh_3$ showing linear dependence of rate vs [Cat.] and $k_{obs}^{-1}$ vs [PhCN] <sup>-1</sup> and $k_{obs}$ vs [H <sub>2</sub> O] .....	S18
Figure S16. The Arrhenius plot for the catalyst $L^3RuPPh_3$ in the temperature range 368–398K under conditions: [Cat.] = 0.112mM, [PhCN] = 1.9M, and [H <sub>2</sub> O] = 11M equation: $y = -5170.4x + 15.9$ .....	S19
Figure S17. The Eyring plot for $L^3RuPPh_3$ in the temperature range 368–398K under conditions [Cat.] = 0.112mM, [PhCN] = 1.9M, and [H <sub>2</sub> O] = 11M equation: $y = -4787.9x + 8.94$ .....	S19
Optimized coordinates for benzonitrile hydration with water in gas phase.....	S20
Table S1 Benzonitrile (gas phase) .....	S20
Table S2 Water (gas phase).....	S20
Table S3 Benziminol (gas phase).....	S20
Table S4 Benzamide (gas phase).....	S20
Table S5 Transition State for Benzonitrile Hydration with water (gas phase) .....	S21
Table S6 PPh <sub>3</sub> (gas phase) .....	S21
Gas Phase DFT Studies optimized coordinates for Catalyst $L^1RuPPh_3$ and derivatives .....	S22
Table S7 Optimized coordinates for $L^1RuPPh_3$ (gas Phase) .....	S22
Table S8 Optimized coordinates for $L^1Ru(PhCN)$ (gas Phase).....	S23
Table S9 Optimized coordinates for $L^1 Ru(H_2O)$ (gas Phase) .....	S25
Table S10 Optimized coordinates for $L^1Ru$ (gas phase) .....	S26
Table S11 Optimized coordinates for $L^1Ru(PhCONH_2)$ (gas Phase) .....	S27
Table S12 Optimized coordinates for $L^1Ru(PhC(OH)NH)$ (Gas Phase) .....	S28
Table S13 Optimized coordinates for L1 RuTS (gas Phase).....	S29
Gas Phase DFT Studies optimized coordinates for Catalyst $L^2RuPPh_3$ and derivatives .....	S30
Table S14 Optimized coordinates for $L^2RuPPh_3$ (Gas Phase): .....	S30
Table S15 Optimized coordinates for $L^2Ru(PhCN)$ (gas Phase):.....	S32
Table S16 Optimized coordinates for $L^2Ru(H_2O)$ (gas Phase):.....	S33
Table S17 Optimized coordinates for $L^2Ru$ (gas Phase): .....	S34
Table S18 Optimized coordinates for $L^2Ru(PhCONH_2)$ (gas Phase) .....	S35
Table S19 Optimized coordinates for $L^2Ru(PhC(OH)NH)$ (gas Phase): .....	S36

Table S20 Optimized coordinates for L <sup>2</sup> RuTS (gas Phase): .....	S38
Gas Phase DFT Studies optimized coordinates for Catalyst L <sup>3</sup> RuPPh <sub>3</sub> and derivatives .....	S39
Table S21 Optimized coordinates for L <sup>3</sup> RuPPh <sub>3</sub> (gas Phase) .....	S39
Table S22 Optimized coordinates for L <sup>3</sup> Ru(PhCN) (gas Phase). ....	S41
Table S23 Optimized coordinates for L <sup>3</sup> Ru(H <sub>2</sub> O) (gas Phase) .....	S42
Table S24 Optimized coordinates for L <sup>3</sup> Ru (gas Phase) .....	S43
Table S25 Optimized coordinates for L <sup>3</sup> Ru(PhCONH <sub>2</sub> ) (gas Phase): .....	S44
Table S26 Optimized coordinates for L <sup>3</sup> Ru(PhC(OH)NH) (gas Phase).....	S45
Table S27 Optimized coordinates for L <sup>3</sup> RuTS (gas Phase): .....	S47
Optimized Coordinates for Solution Phase (n,n'-dimethylformamide (DMF)) DFT Studies for benzonitrile hydration with water(Å) .....	S48
Table S28 Optimized coordinates for benzonitrile (DMF phase) .....	S48
Table S29 Optimized coordinates for water (DMF phase) .....	S48
Table S30 Optimized coordinates for benziminol (DMF phase) .....	S48
Table S31 Optimized coordinates for benzamide (DMF phase) .....	S49
Table S32 Optimized coordinates for transition state for benzonitrile hydration with Water (DMF phase).....	S49
Table S33 Optimized coordinates for PPh <sub>3</sub> (DMF phase) .....	S50
Optimized Coordinates for Solution Phase (DMF) DFT Studies for Catalyst L <sup>1</sup> RuPPh <sub>3</sub> and derivatives.....	S50
Table S34 Optimized coordinates for L <sup>1</sup> RuPPh3 (DMF phase) .....	S50
Table S35 Optimized coordinates for L <sup>1</sup> Ru(PhCN) (DMF Phase) .....	S52
Table S36 Optimized coordinates for L <sup>1</sup> Ru(H <sub>2</sub> O) (DMF Phase).....	S53
Table S37 Optimized coordinates for L <sup>1</sup> Ru (DMF phase).....	S54
Table S38 Optimized coordinates for L <sup>1</sup> Ru(PhCONH <sub>2</sub> ) (DMF Phase).....	S55
Table S39 Optimized coordinates for L <sup>1</sup> Ru(PhC(OH)NH) (DMF Phase) .....	S56
Table S40 Optimized coordinates for L <sup>1</sup> RuTS (DMF phase).....	S57
Optimized Coordinates for Solution Phase (DMF) DFT Studies for Catalyst L <sup>2</sup> RuPPh3 and its' derivatives.....	S59
Table S41 Optimized coordinates for L <sup>2</sup> RuPPh <sub>3</sub> (DMF phase).....	S59
Table S42 Optimized coordinates for L <sup>2</sup> Ru(PhCN) (DMF Phase) .....	S60
Table S43 Optimized coordinates for L <sup>2</sup> Ru(H <sub>2</sub> O) (DMF Phase).....	S61
Table S44 Optimized coordinates for L <sup>2</sup> Ru (DMF phase).....	S62
Table S45 Optimized coordinates for L <sup>2</sup> Ru(PhCONH <sub>2</sub> ) (DMF Phase).....	S63

Table S46 Optimized coordinates for L <sup>2</sup> Ru(PhC(OH)NH) (DMF Phase) .....	S65
Table S47 Optimized coordinates for L <sup>2</sup> RuTS (DMF phase):.....	S66
Optimized Coordinates for Solution Phase (DMF) DFT Studies for Catalyst L <sup>3</sup> RuPPh <sub>3</sub> and derivatives.....	S67
Table S48 Optimized coordinates for L <sup>3</sup> RuPPh <sub>3</sub> (DMF phase).....	S67
Table S49 Optimized coordinates for L <sup>3</sup> Ru(PhCN) (DMF Phase) .....	S69
Table S50 Optimized coordinates for L <sup>3</sup> Ru(H <sub>2</sub> O) (DMF Phase).....	S70
Table S51 Optimized coordinates for L <sup>3</sup> Ru (DMF phase).....	S71
Table S52 Optimized coordinates for L <sup>3</sup> Ru(PhCONH <sub>2</sub> ) (DMF Phase).....	S72
Table S53 Optimized coordinates for L <sup>3</sup> Ru(PhC(OH)NH) (DMF Phase) .....	S73
Table S54 Optimized coordinates for L <sup>3</sup> RuTS (DMF phase).....	S75
Optimized Coordinates for O-bound Benzamide (Gas Phase Studies) (Å) for L <sup>1-3</sup> Ru(O-benzamide) .....	S76
Table S55 Optimized coordinates for L <sup>1</sup> Ru(O-benzamide) (gas phase).....	S76
Table S56 Optimized coordinates for L <sup>2</sup> Ru(O-benzamide) (gas phase).....	S77
Table S57 Optimized coordinates for L <sup>3</sup> Ru(O-benzamide) (gas phase).....	S79
Optimized Coordinates for O-bound Benzamide (DMF Phase Studies) (Å) for L <sup>1-3</sup> Ru(O-benzamide) .....	S80
Table S58 Optimized coordinates for L <sup>1</sup> Ru(O-benzamide) (DMF phase) .....	S80
Table S59 Optimized coordinates for L <sup>2</sup> Ru(O-benzamide) (DMF phase) .....	S81
Table S60 Optimized coordinates for L <sup>3</sup> Ru(O-benzamide) (DMF phase) .....	S83
Table S61 DFT calculated gas and DMF phase (in parenthesis) natural charges for L <sup>1-3</sup> RuNCPh .....	S84
Table S62 DFT calculated gas and DMF phase (in parenthesis) bond distances for L <sup>1-3</sup> NCPh	S85

## Derivation of Rate Law



Applying Steady-State approximation to [ES] and under reaction conditions  $k_1 \gg k_{-1}$ :

$$\frac{d[\text{ES}]}{dt} = k_2 [\text{E}] [\text{S}] - k_{-2} [\text{ES}] [\text{R}] - k_3 [\text{ES}] [\text{R}] = 0$$

$$\text{Also, } [\text{E}] = [\text{E}_T] - [\text{ES}] \quad [\text{E}_T] = \text{total concentration of catalyst}$$

$$[\text{ES}] = \frac{k_2 [\text{E}_T] [\text{S}]}{(k_{-2} + k_3) [\text{R}] + k_2 [\text{S}]}$$

$$\text{Rate} = \frac{k_2 k_3 [\text{E}_T] [\text{S}] [\text{R}]}{(k_{-2} + k_3) [\text{R}] + k_2 [\text{S}]}$$

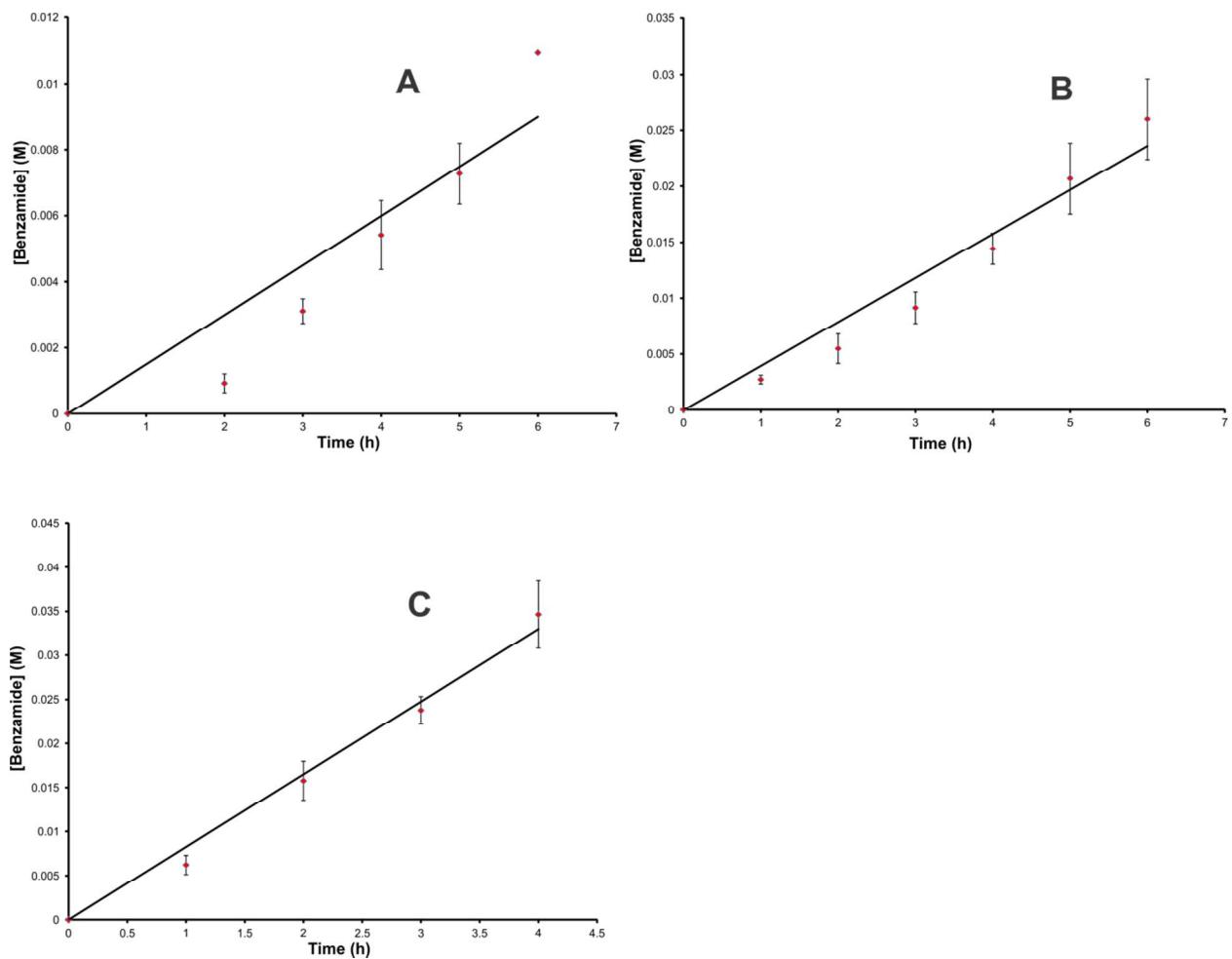
Assuming,  $k_{-2} \gg k_3$

$$\text{Rate} = \frac{k_2 k_3 [\text{E}_T] [\text{S}] [\text{R}]}{k_3 [\text{R}] + k_2 [\text{S}]} = k_{\text{obs}} [\text{E}_T]$$

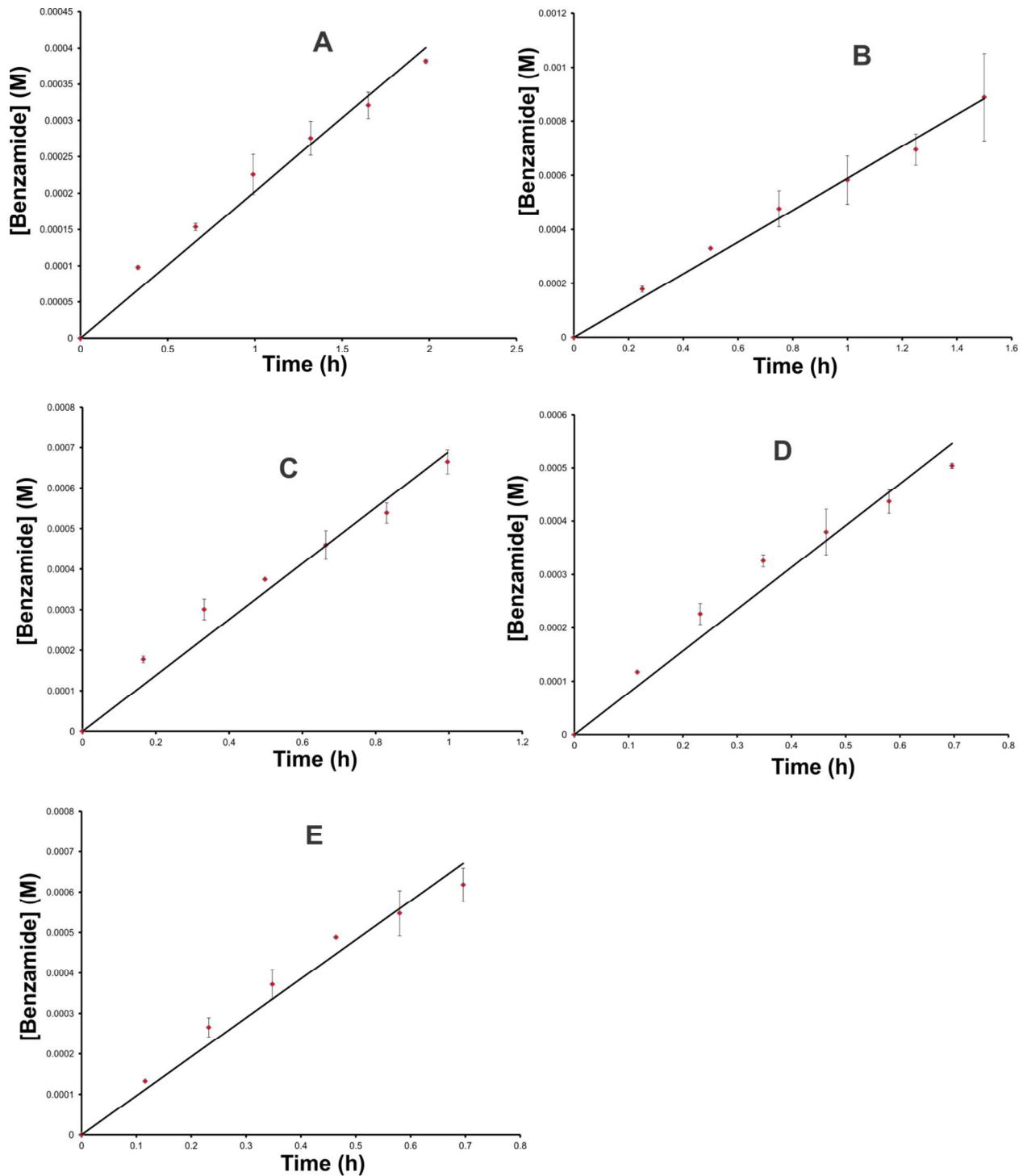
$$\frac{1}{k_{\text{obs}}} = \frac{1}{K_2 k_3 [\text{S}]} + \frac{1}{k_3} \left( \frac{1}{[\text{R}]} \right) \quad \text{slope gives } k_3$$

$$\frac{1}{k_{\text{obs}}} = \frac{1}{K_2 k_3} \left( \frac{1}{[\text{S}]} \right) + \frac{1}{k_3 [\text{R}]} \quad \text{slope gives } K_2$$

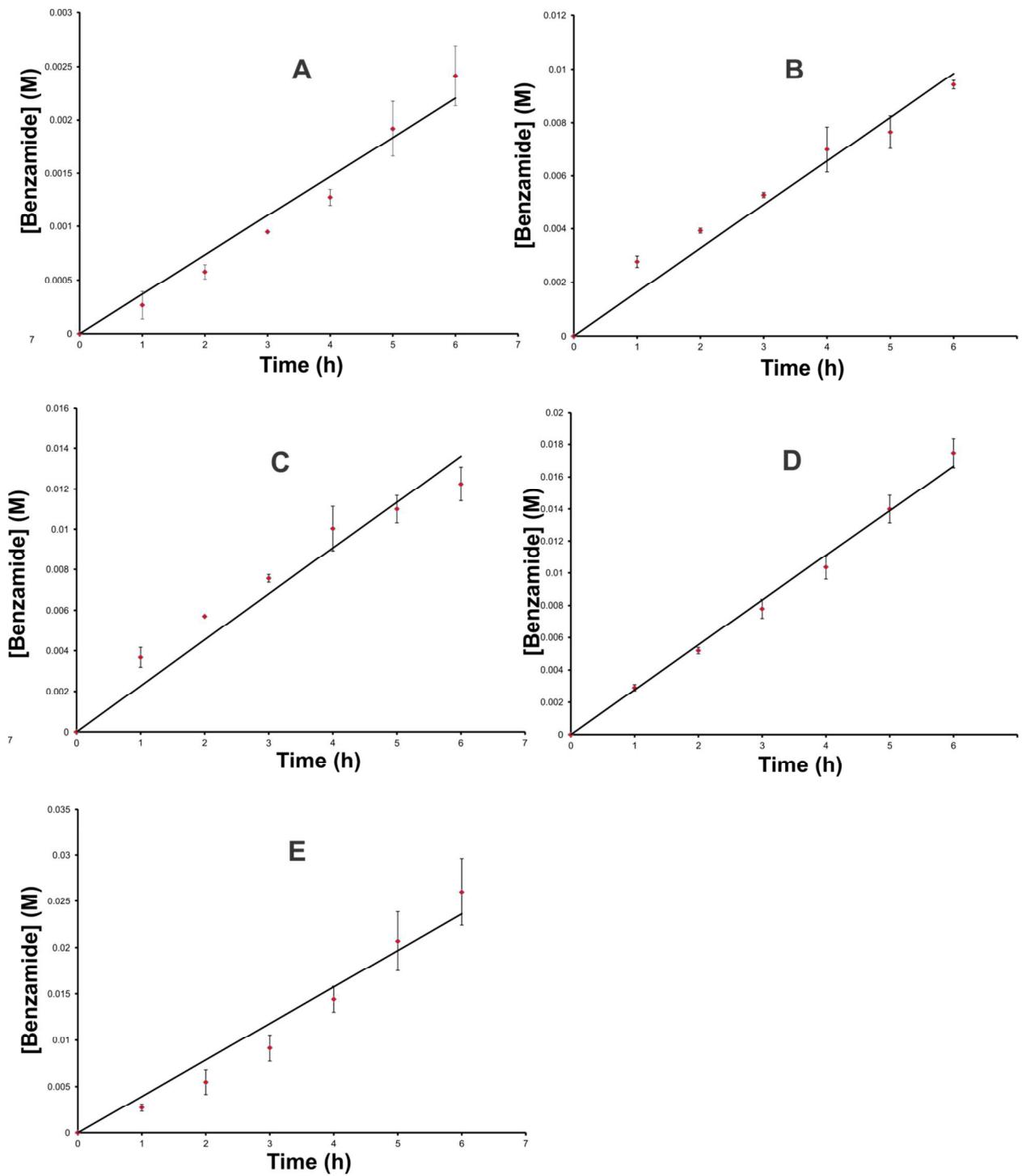
In our experiments, we have varied both benzonitrile and water concentrations. The slopes from the inverse plots slopes are utilized to calculate the  $k_3$  and  $K_2$ . Except in case of  $L^3RuPPh_3$ ,  $k_3$  is calculated from the normal plot of  $k_{obs}$  vs.  $[H_2O]$ .



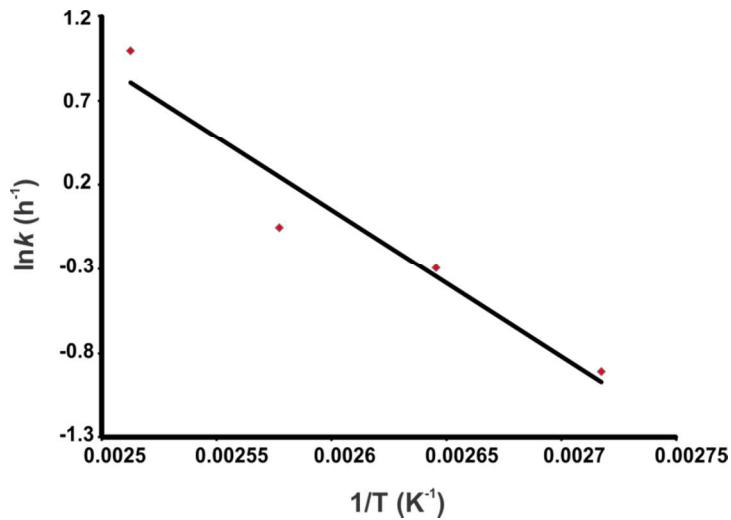
**Figure S1.** Kinetic traces for  $L^1RuPPh_3$  under conditions:  $[PhCN] = 4.0\text{M}$ ,  $[H_2O] = 11\text{M}$  and  $[Cat.] = 0.21\text{mM}$  (A),  $0.42\text{mM}$  (B), and  $0.84\text{mM}$  (C)



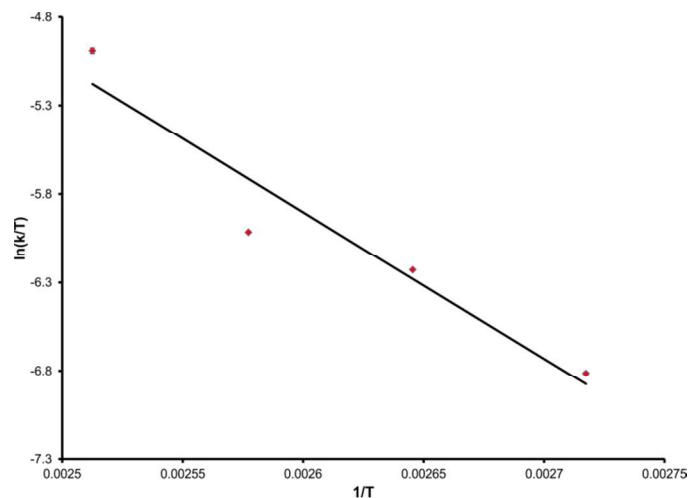
**Figure S2.** Kinetic traces for  $\text{L}^1\text{RuPPh}_3$  under conditions:  $[\text{PhCN}] = 0.97\text{M}$ , and  $[\text{H}_2\text{O}] = 2.8\text{M}$  (A),  $8.3\text{M}$  (B),  $11\text{M}$  (C),  $14\text{M}$  (D), and  $17\text{M}$  (E), and  $[\text{Cat.}] = 0.21\text{mM}$



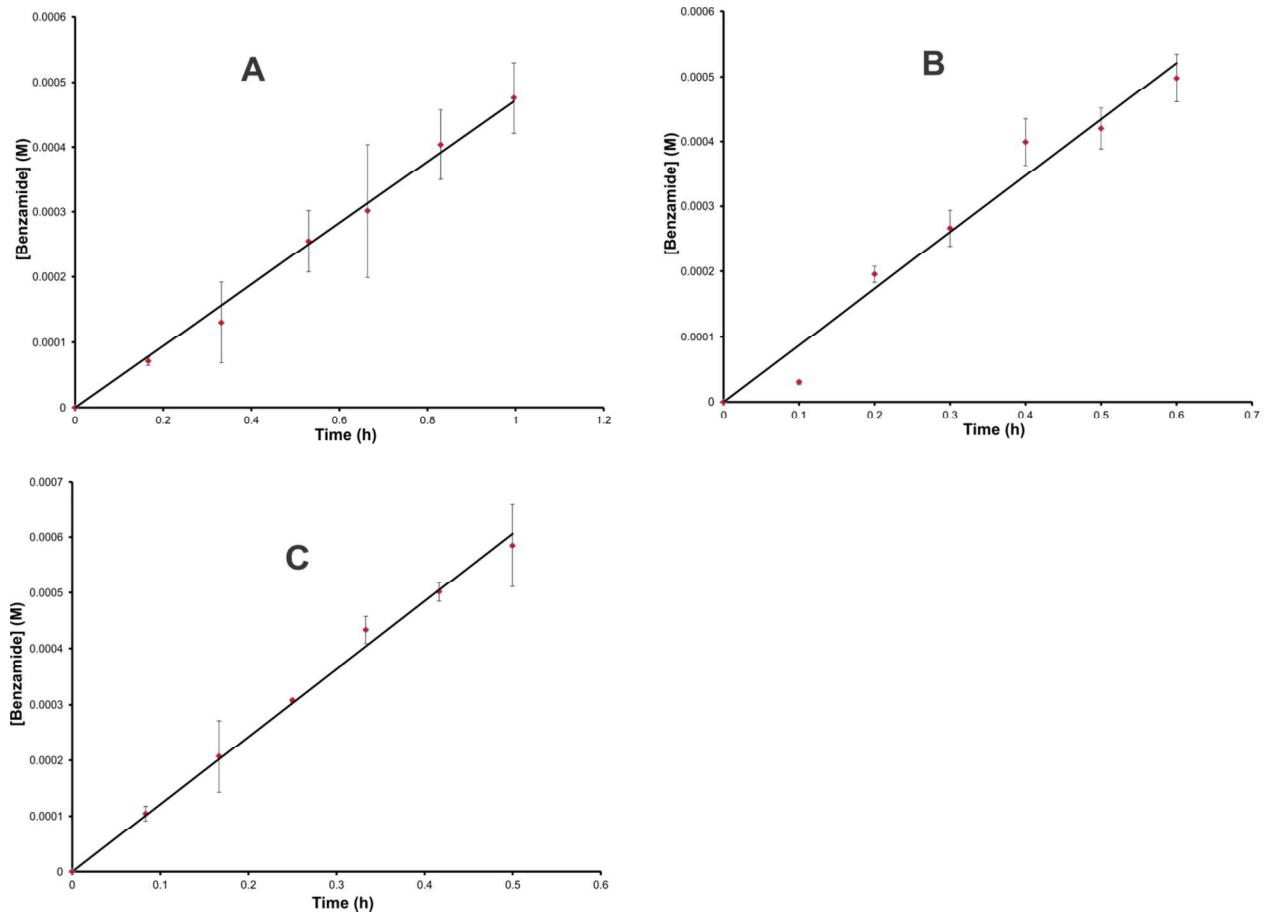
**Figure S3.** Kinetic traces for  $\text{L}^1\text{RuPPh}_3$  under conditions:  $[\text{PhCN}] = 0.12\text{M}$  (A),  $0.49\text{M}$  (B),  $0.97\text{M}$  (C),  $1.9$  (D), and  $4.0\text{M}$  (E),  $[\text{H}_2\text{O}] = 11\text{M}$  and  $[\text{Cat.}] = 0.42\text{mM}$



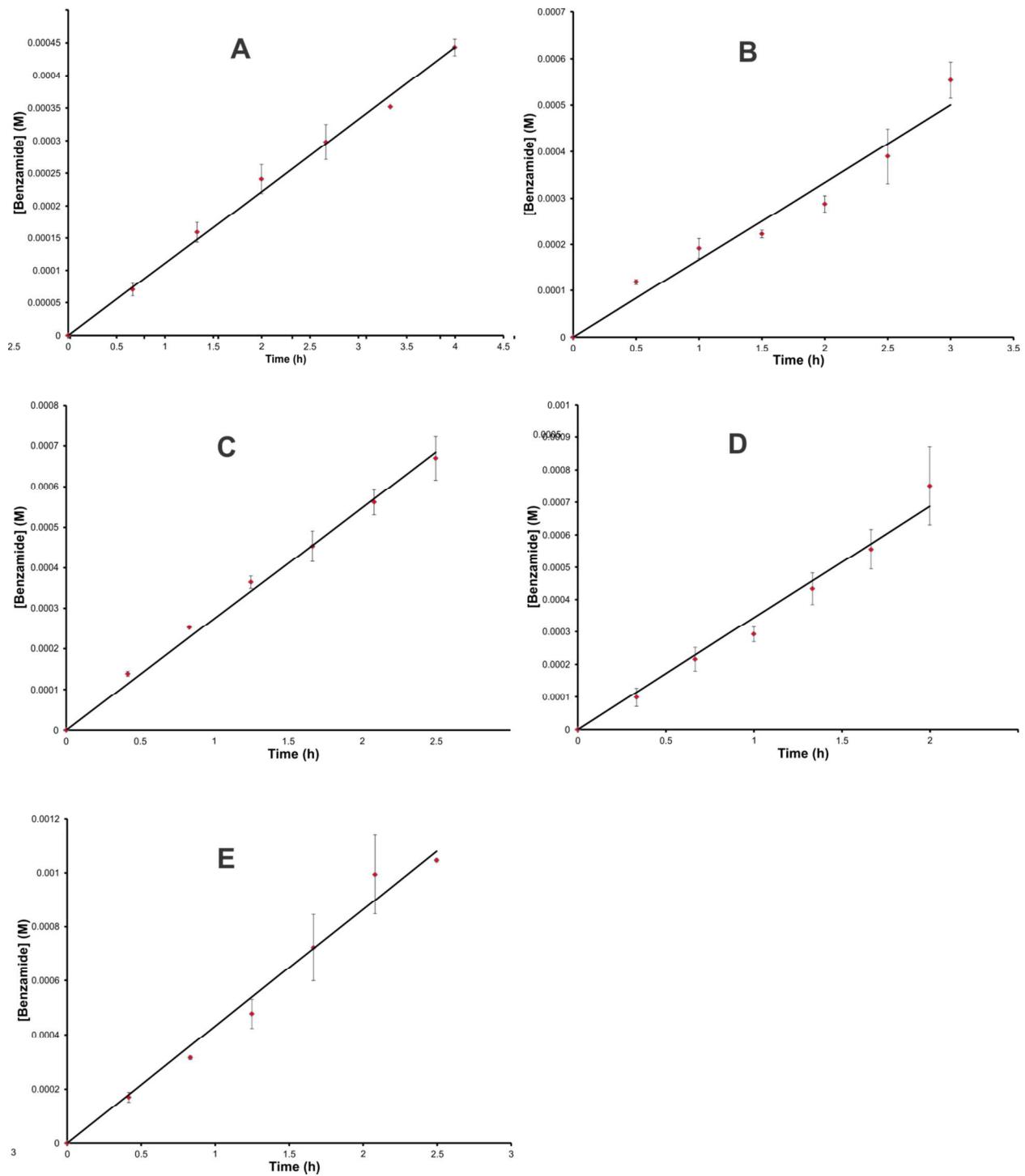
**Figure S4.** Arrhenius plot for  $\text{L}^1\text{RuPPh}_3$  in the temperature range 368-398K under conditions [Cat.] = 0.42mM, [PhCN] = 0.97M, and [H<sub>2</sub>O] = 11M equation:  $y = -8668.3x + 22.6$



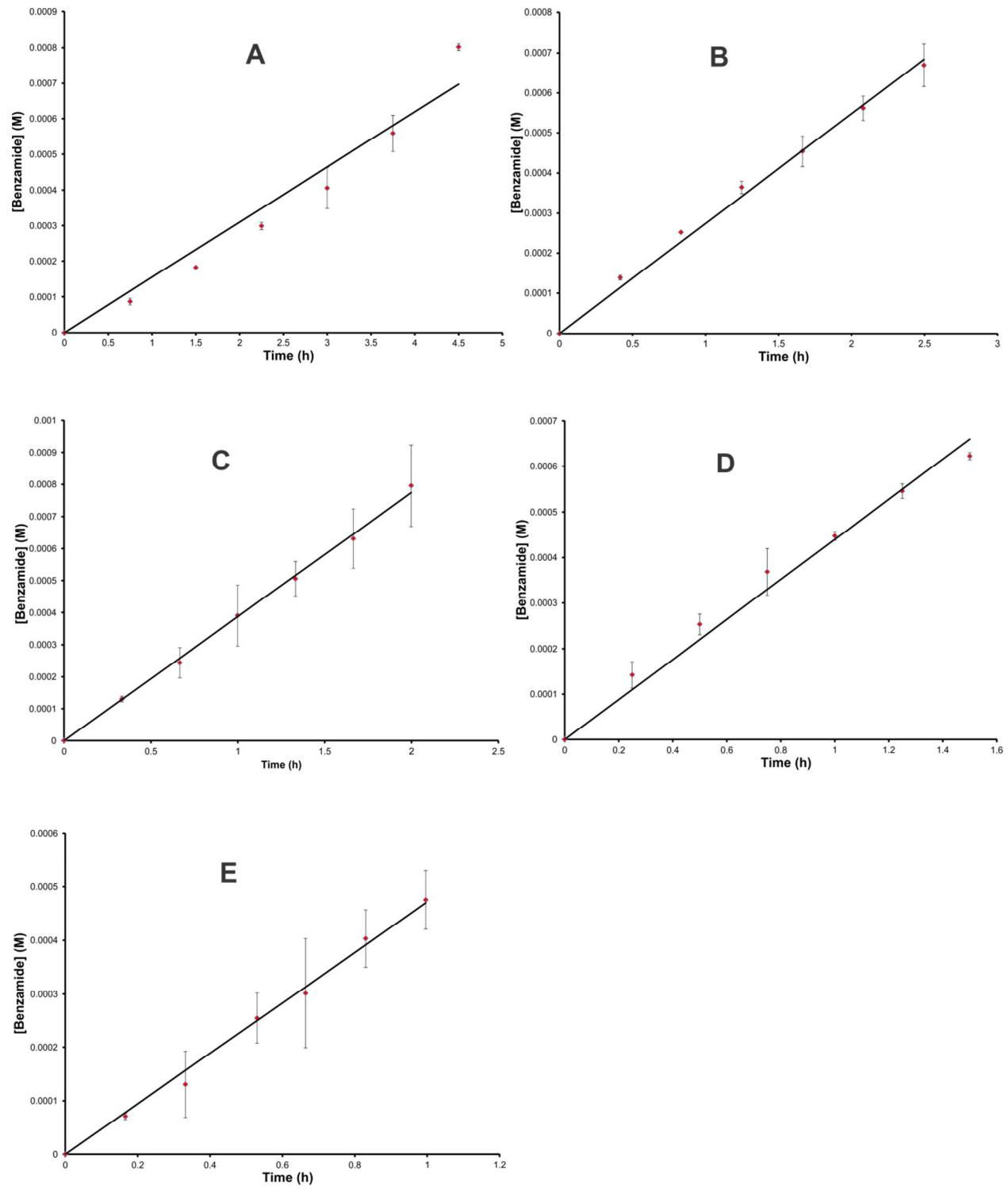
**Figure S5.** Eyring plot for  $\text{L}^1\text{RuPPh}_3$  in the temperature range 368-398K under conditions [Cat.] = 0.42mM, [PhCN] = 0.97M, and [H<sub>2</sub>O] = 11M equation:  $y = -8285.8x + 15.6$



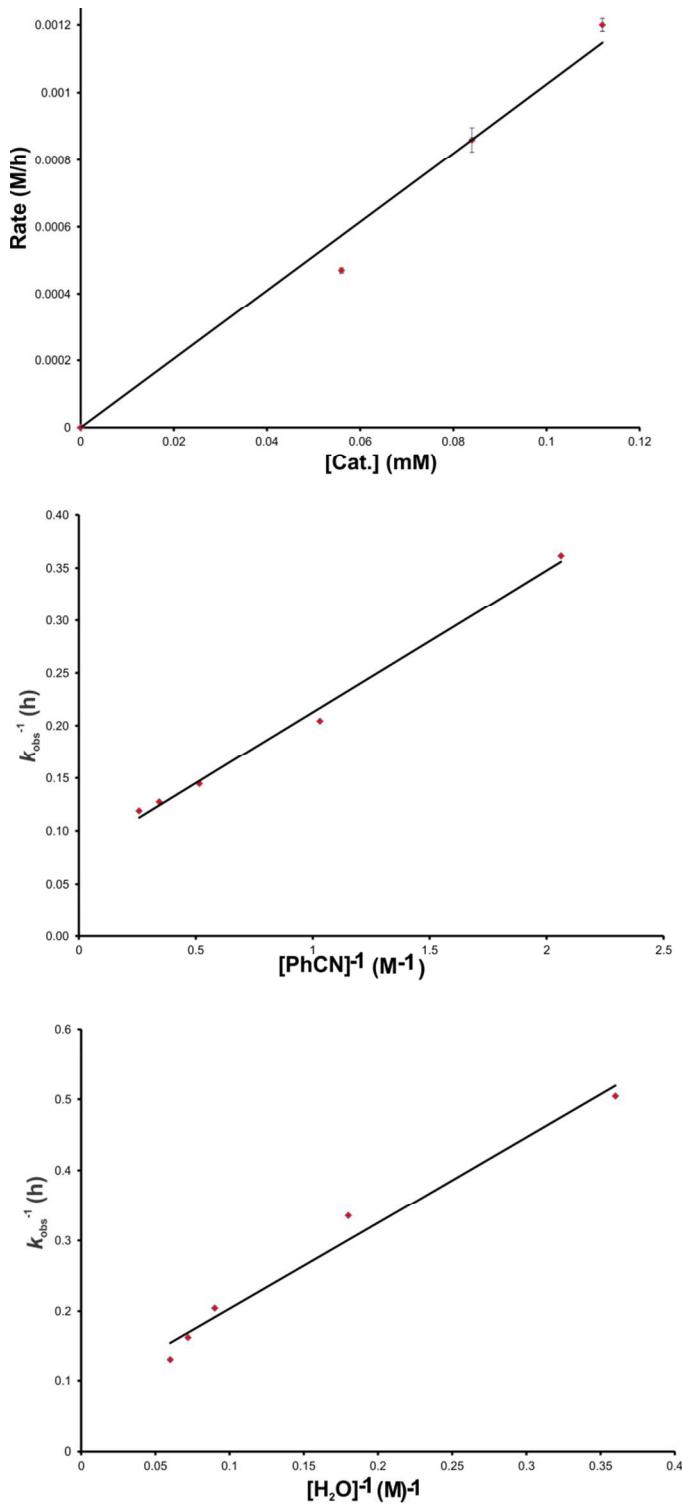
**Figure S6.** The kinetic traces for  $\text{L}^2\text{RuPPh}_3$  under conditions:  $[\text{PhCN}] = 4.0\text{M}$ ,  $[\text{H}_2\text{O}] = 11\text{M}$ , and  $[\text{Cat.}] = 0.056\text{mM}$  (A),  $0.084\text{mM}$  (B), and  $0.112\text{ mM}$  (C)



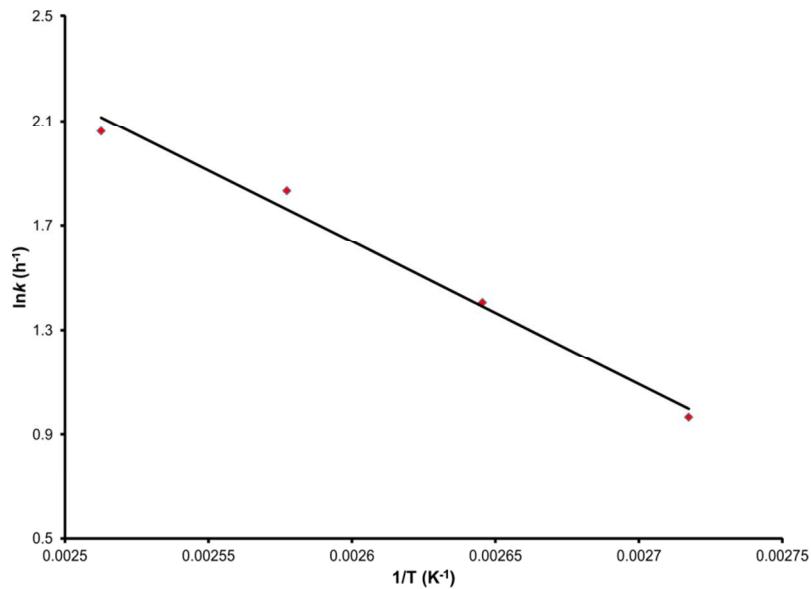
**Figure S7.** The kinetic traces for  $\text{L}^2\text{RuPPh}_3$  under conditions:  $[\text{PhCN}] = 0.97\text{M}$ ,  $[\text{H}_2\text{O}] = 2.8\text{M}$  (A),  $5.5\text{M}$  (B),  $11\text{M}$  (C),  $14\text{M}$  (D), and  $17\text{M}$  (E), and  $[\text{Cat.}] = 0.056\text{mM}$



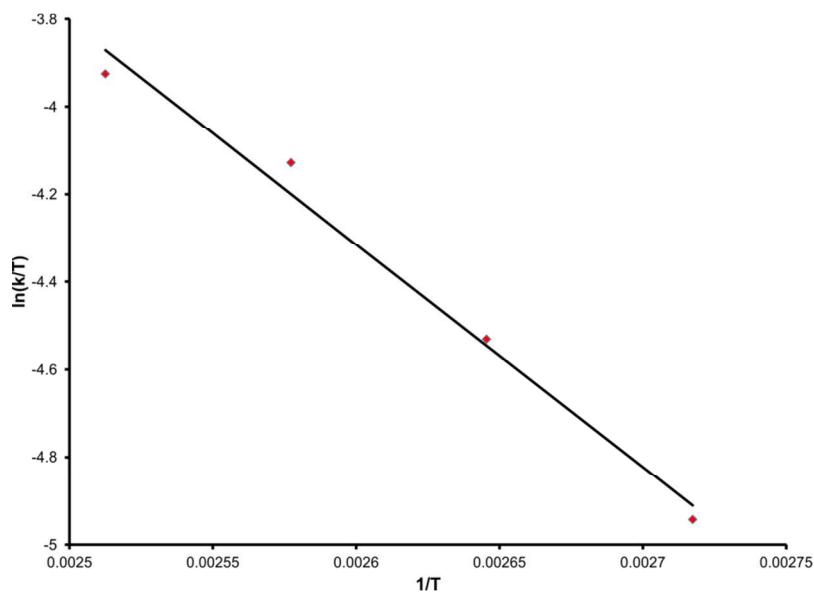
**Figure S8.** The kinetic traces for  $\text{L}^2\text{RuPPh}_3$  under conditions:  $[\text{PhCN}] = 0.49\text{M}$  (A),  $0.97\text{M}$  (B),  $1.9\text{M}$  (C),  $2.9\text{M}$  (D), and  $4.0\text{M}$  (E),  $[\text{H}_2\text{O}] = 11\text{M}$  and  $[\text{Cat.}] = 0.056\text{mM}$



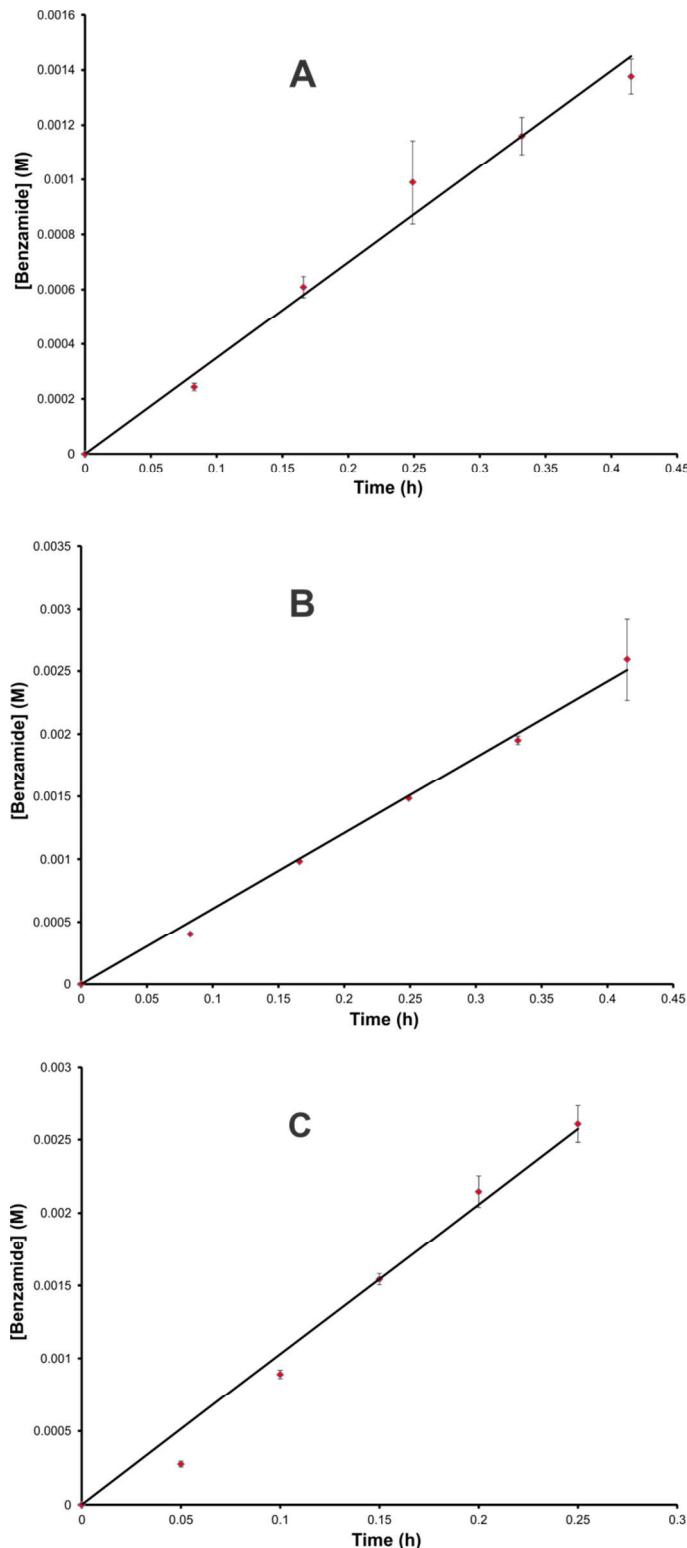
**Figure S9.** The plots for  $\text{L}^2\text{RuPPh}_3$  showing linear dependence of rate vs [Cat.] and  $k_{\text{obs}}^{-1}$  vs  $[\text{PhCN}]^{-1}$  and  $[\text{H}_2\text{O}]^{-1}$ .



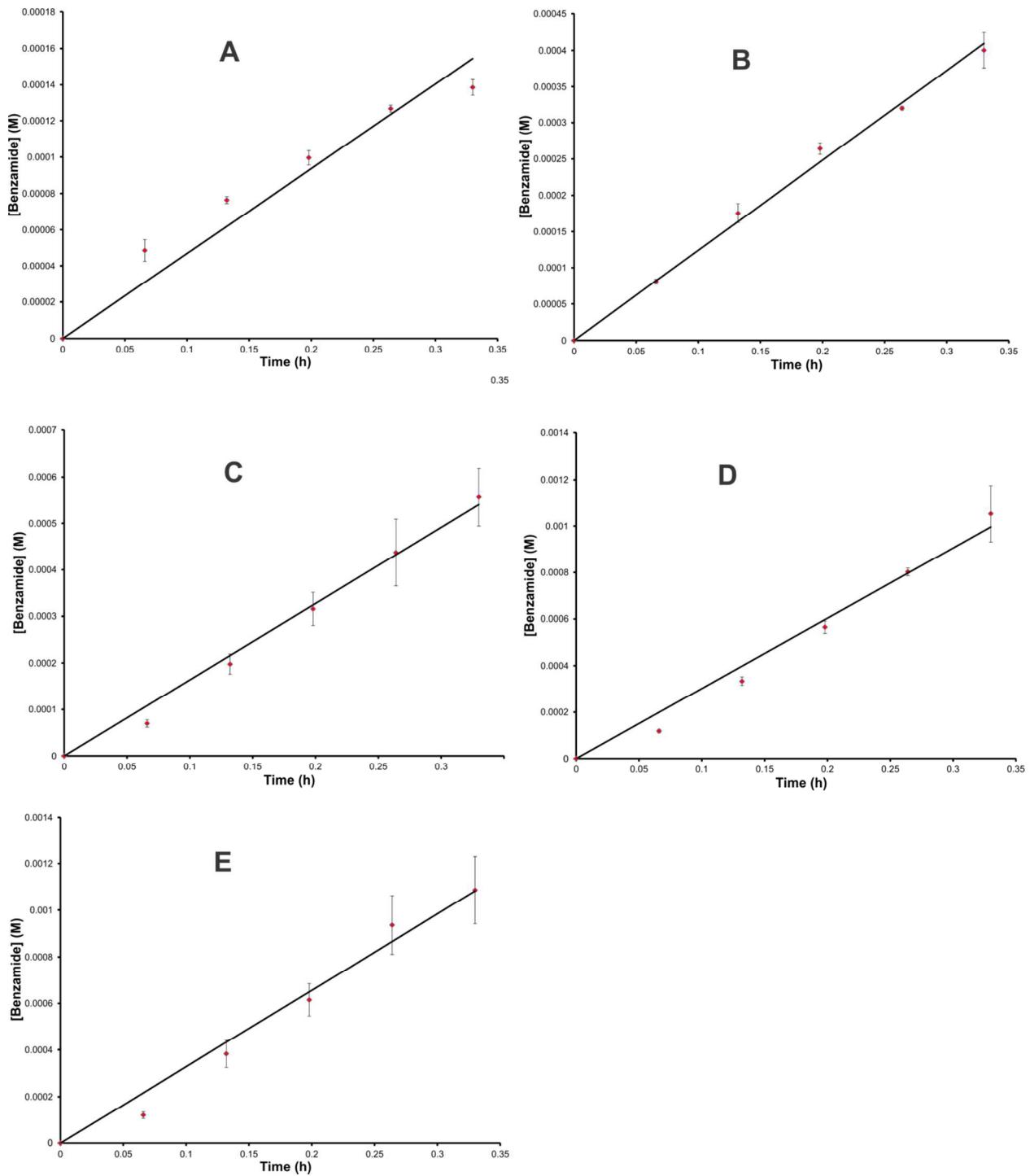
**Figure S10.** The Arrhenius plot for  $L^2\text{RuPPh}_3$  in the temperature range 368–398K under conditions: [Cat.] = 0.056mM, [PhCN] = 2.9M, and [H<sub>2</sub>O] = 11M equation:  $y = -5457.4x + 15.8$



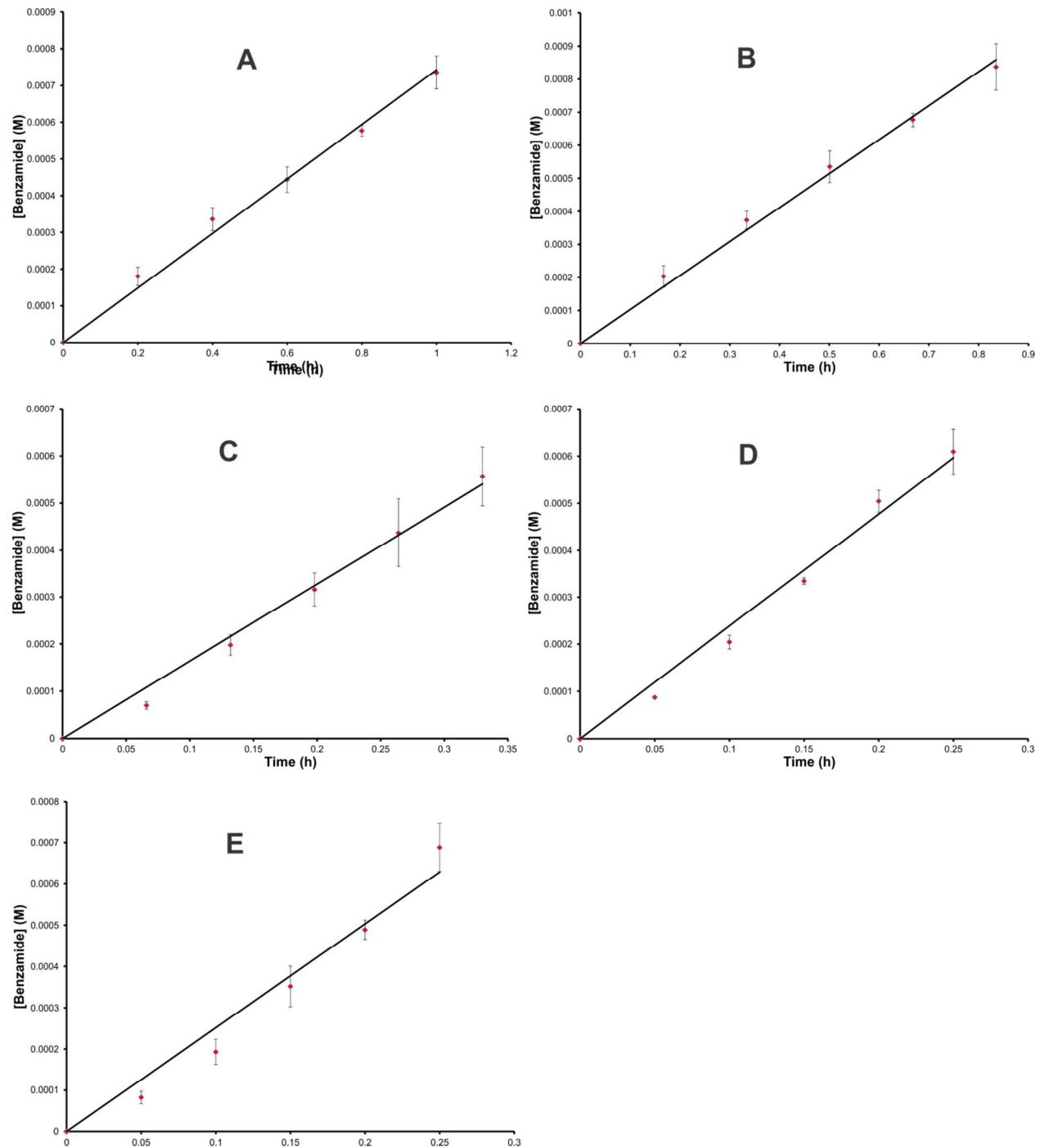
**Figure S11.** The Eyring plot for  $L^2\text{RuPPh}_3$  in the temperature range 368–398K under conditions: [Cat.] = 0.056mM, [PhCN] = 2.9M, and [H<sub>2</sub>O] = 11M equation:  $y = -5074.8x + 8.88$



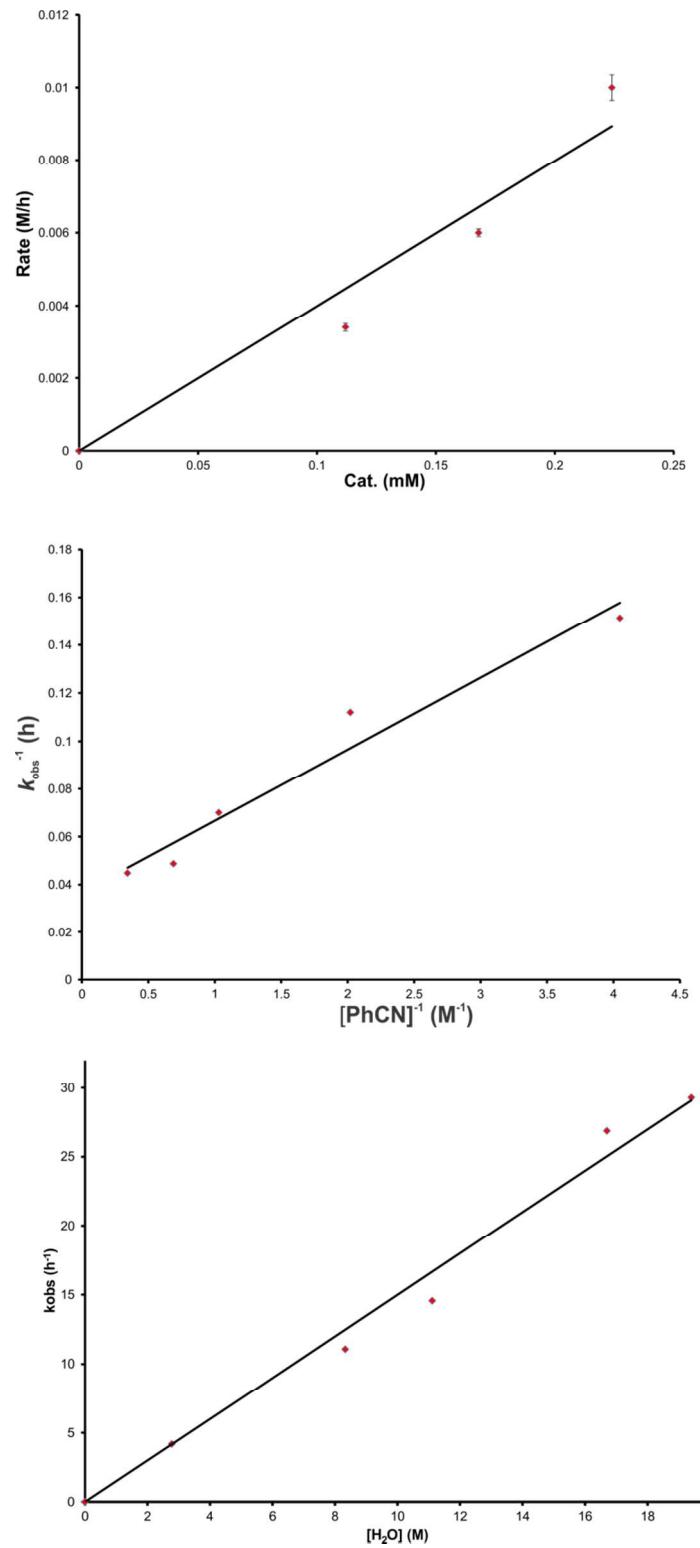
**Figure S12.** The kinetic traces for  $\text{L}^3\text{RuPPh}_3$  under conditions:  $[\text{PhCN}] = 4.0\text{M}$ ,  $[\text{H}_2\text{O}] = 11\text{M}$ , and  $[\text{Cat.}] = 0.112\text{mM}$  (A),  $0.168\text{M}$  (B), and  $0.224\text{mM}$  (C)



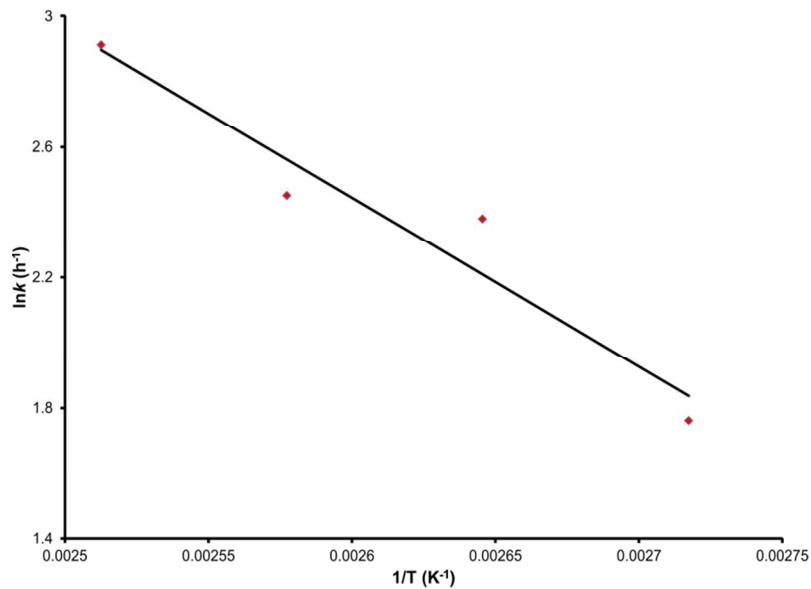
**Figure S13.** The kinetic traces for  $\text{L}^3\text{RuPPh}_3$  under conditions:  $[\text{PhCN}] = 0.97\text{M}$ ,  $[\text{H}_2\text{O}] = 2.8\text{M}$  (A),  $8.3\text{M}$ (B),  $11\text{M}$  (C),  $17\text{M}$  (D), and  $19\text{M}$  (E), and  $[\text{Cat.}] = 0.112\text{mM}$



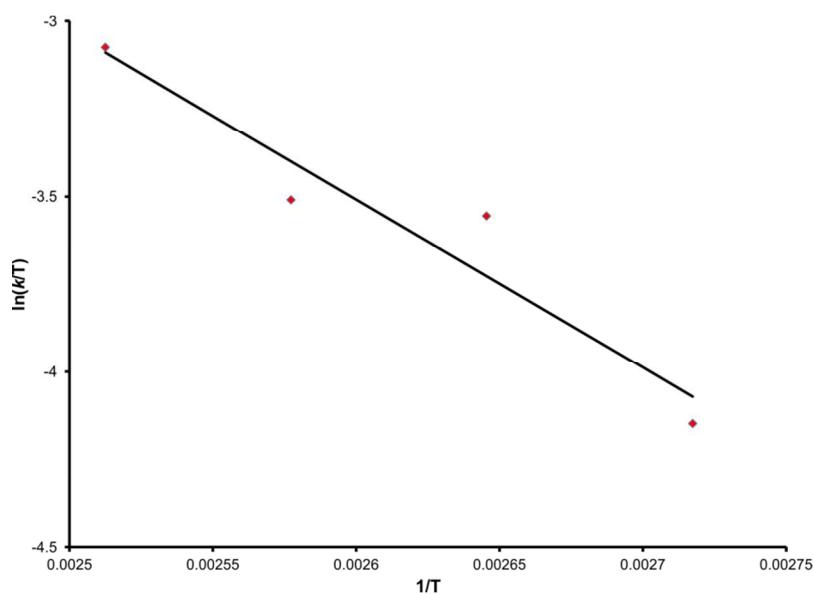
**Figure S14.** The kinetic traces for  $\text{L}^3\text{RuPPh}_3$  under conditions:  $[\text{PhCN}] = 0.24\text{M}$  (A),  $0.49\text{M}$  (B),  $0.97\text{M}$  (C),  $1.4\text{M}$  (D), and  $2.9\text{M}$  (E), and  $[\text{H}_2\text{O}] = 11\text{M}$ , and  $[\text{Cat.}] = 0.112\text{mM}$



**Figure S15. The plots for  $\text{L}^3\text{RuPPh}_3$  showing linear dependence of rate vs [Cat.] and  $k_{\text{obs}}^{-1}$  vs  $[\text{PhCN}]^{-1}$  and  $k_{\text{obs}}$  vs  $[\text{H}_2\text{O}]$**



**Figure S16.** The Arrhenius plot for the catalyst  $L^3RuPPh_3$  in the temperature range 368–398K under conditions: [Cat.] = 0.112mM, [PhCN] = 1.9M, and  $[H_2O]=11M$  equation:  $y = -5170.4x + 15.9$



**Figure S17.** The Eyring plot for  $L^3RuPPh_3$  in the temperature range 368–398K under conditions [Cat.] = 0.112mM, [PhCN] = 1.9M, and  $[H_2O]=11M$  equation:  $y = -4787.9x + 8.94$

## Optimized coordinates for benzonitrile hydration with water in gas phase

**Table S1 Benzonitrile (gas phase)**

Z	x	y	z
6	2.045308000	-0.000142000	-0.000032000
7	3.208636000	0.000074000	0.000036000
6	0.610563000	-0.000073000	-0.000017000
6	-0.091427000	-1.217654000	-0.000009000
6	-0.091292000	1.217586000	-0.000009000
6	-1.484259000	-1.211066000	0.000005000
1	0.458958000	-2.152990000	-0.000015000
6	-1.484124000	1.211153000	0.000005000
1	0.459198000	2.152861000	-0.000015000
6	-2.181209000	0.000082000	0.000012000
1	-2.026298000	-2.152234000	0.000011000
1	-2.026058000	2.152382000	0.000010000
1	-3.267607000	0.000143000	0.000023000

**Table S2 Water (gas phase)**

Z	x	y	z
8	0.000000000	0.000000000	0.119426000
1	0.000000000	0.762617000	-0.477705000
1	0.000000000	-0.762617000	-0.477705000

**Table S3 Benziminol (gas phase)**

Z	x	y	z
6	0.222894000	0.044184000	-0.001583000
6	-0.449127000	-1.184522000	0.087491000
6	-0.529300000	1.224510000	-0.097047000
6	-1.842922000	-1.226644000	0.096677000
1	0.127659000	-2.099806000	0.153933000
6	-1.921403000	1.180589000	-0.092287000
1	-0.027399000	2.183266000	-0.195253000
6	-2.582770000	-0.046087000	0.008035000
1	-2.351372000	-2.183926000	0.172202000
1	-2.489971000	2.102918000	-0.172166000
1	-3.668830000	-0.080516000	0.012528000
7	2.486324000	1.089426000	0.193710000
1	1.969562000	1.948647000	0.375641000
6	1.711143000	0.092508000	0.010124000
8	2.269174000	-1.127817000	-0.203325000
1	3.231610000	-0.981262000	-0.144720000

**Table S4 Benzamide (gas phase)**

Z	x	y	z
6	-0.220410000	-0.021856000	-0.018298000
6	0.514969000	-1.208170000	0.106893000
6	0.460703000	1.197856000	-0.141013000
6	1.907220000	-1.174522000	0.134878000
1	-0.029119000	-2.144089000	0.179763000
6	1.855468000	1.230199000	-0.120383000

1	-0.091208000	2.122010000	-0.289548000
6	2.580420000	0.045434000	0.023970000
1	2.469066000	-2.098639000	0.239991000
1	2.375305000	2.178608000	-0.225486000
1	3.666700000	0.071989000	0.042155000
7	-2.421754000	1.024799000	0.201600000
1	-3.418495000	0.900620000	0.323595000
1	-1.998184000	1.771459000	0.733561000
6	-1.718503000	-0.136782000	-0.033912000
8	-2.287623000	-1.196065000	-0.266005000

**Table S5 Transition State for Benzonitrile Hydration with water (gas phase)**

Z	x	y	z
6	1.533211000	-0.485193000	-0.000143000
7	2.485275000	-1.221780000	-0.000431000
6	0.120873000	-0.197369000	0.000043000
6	-0.769355000	-1.287312000	0.000126000
6	-0.370533000	1.114533000	-0.000055000
6	-2.141648000	-1.053519000	0.000135000
1	-0.376289000	-2.298835000	0.000181000
6	-1.745688000	1.336367000	-0.000061000
1	0.337340000	1.934162000	-0.000189000
6	-2.631370000	0.255946000	0.000040000
1	-2.829685000	-1.893920000	0.000205000
1	-2.126459000	2.353536000	-0.000145000
1	-3.703279000	0.433104000	0.000037000
1	2.813367000	1.982923000	0.000626000
8	2.664539000	1.017738000	0.000254000
1	3.198827000	-0.201136000	-0.000244000

**Table S6 PPh<sub>3</sub> (gas phase)**

Z	x	y	z
15	-0.000077000	-0.000447000	-1.206677000
6	1.333534000	-1.005927000	-0.403239000
6	2.592019000	-1.007186000	-1.029335000
6	1.160232000	-1.781318000	0.753728000
6	3.653063000	-1.744235000	-0.503180000
1	2.738537000	-0.429069000	-1.938963000
6	2.219344000	-2.528952000	1.274262000
1	0.193864000	-1.804599000	1.248222000
6	3.468110000	-2.509795000	0.650493000
1	4.620036000	-1.729517000	-0.999409000
1	2.067112000	-3.126338000	2.169739000
1	4.290500000	-3.092886000	1.056613000
6	-1.537811000	-0.651328000	-0.402357000
6	-2.115314000	-0.120494000	0.761709000
6	-2.175688000	-1.732566000	-1.034534000
6	-3.292101000	-0.663417000	1.283125000
1	-1.647321000	0.722538000	1.261126000
6	-3.344660000	-2.282211000	-0.507829000
1	-1.754097000	-2.142652000	-1.949501000
6	-3.907434000	-1.746630000	0.653011000
1	-3.727495000	-0.238450000	2.184101000
1	-3.821378000	-3.120658000	-1.009058000

1	-4.823508000	-2.166773000	1.059885000
6	0.205071000	1.657035000	-0.403331000
6	-0.421087000	2.748241000	-1.030130000
6	0.960690000	1.893503000	0.755671000
6	-0.313948000	4.035267000	-0.502860000
1	-0.993019000	2.586792000	-1.941115000
6	1.077750000	3.184077000	1.277445000
1	1.462809000	1.067724000	1.250691000
6	0.438718000	4.256692000	0.652836000
1	-0.808656000	4.865907000	-0.999637000
1	1.669057000	3.350051000	2.174518000
1	0.531792000	5.260080000	1.060031000

## Gas Phase DFT Studies optimized coordinates for Catalyst L<sup>1</sup>RuPPh<sub>3</sub> and derivatives

**Table S7 Optimized coordinates for L<sup>1</sup>RuPPh<sub>3</sub> (gas Phase)**

Z	x	y	z
44	-0.909135000	0.007027000	-0.134363000
16	-0.904598000	0.727003000	-2.415374000
16	-1.130681000	-1.212727000	1.990186000
16	-1.294225000	2.258329000	0.780950000
15	1.447272000	0.249855000	0.077742000
7	-3.155495000	0.061346000	-0.339194000
7	-1.262265000	-2.049765000	-0.980963000
6	-2.608575000	1.417672000	-2.450901000
1	-2.450684000	2.399121000	-1.997888000
1	-2.950190000	1.555788000	-3.483079000
6	-3.628491000	0.601359000	-1.658828000
1	-4.522137000	1.216701000	-1.496033000
1	-3.952814000	-0.242505000	-2.274658000
6	-3.573416000	-1.361222000	-0.209922000
1	-4.642548000	-1.484830000	-0.451569000
1	-3.414750000	-1.629391000	0.832269000
6	-2.742951000	-2.275570000	-1.101984000
1	-3.026535000	-2.134853000	-2.147695000
1	-2.977318000	-3.321032000	-0.867638000
6	-0.656477000	-2.099128000	-2.341545000
1	-0.917000000	-3.045042000	-2.848090000
1	0.426117000	-2.079926000	-2.217587000
6	-1.076946000	-0.934871000	-3.250118000
1	-2.104622000	-1.028113000	-3.612018000
1	-0.426510000	-0.926411000	-4.129679000
6	-3.708198000	0.808911000	0.840837000
1	-3.485212000	0.167387000	1.693790000
1	-4.805605000	0.872303000	0.734179000
6	-3.128511000	2.201835000	1.154958000
6	-0.921521000	-2.992384000	1.423779000
6	-0.614807000	-3.069048000	-0.095367000
1	0.455797000	-2.926145000	-0.235780000
1	-0.863564000	-4.078903000	-0.469429000
6	-2.144426000	-3.842975000	1.831444000
1	-1.974781000	-4.904570000	1.597082000
1	-3.075288000	-3.541295000	1.345928000

1	-2.304628000	-3.759368000	2.910863000
6	0.293838000	-3.595729000	2.161634000
1	0.093164000	-3.640607000	3.236624000
1	1.185575000	-2.979163000	2.025150000
1	0.508705000	-4.618729000	1.814542000
6	-3.331415000	2.432707000	2.667865000
1	-2.946473000	3.416832000	2.954072000
1	-2.797419000	1.677442000	3.251515000
1	-4.398517000	2.394887000	2.936940000
6	-3.848010000	3.343992000	0.410115000
1	-4.912949000	3.378848000	0.684748000
1	-3.783238000	3.256701000	-0.677695000
1	-3.399547000	4.304999000	0.681684000
6	2.459853000	-0.927049000	-0.964248000
6	2.739152000	-0.589173000	-2.301950000
1	2.471532000	0.394812000	-2.675334000
6	3.371862000	-1.491653000	-3.158911000
1	3.581703000	-1.199444000	-4.184919000
6	3.746808000	-2.756401000	-2.699619000
1	4.246014000	-3.456651000	-3.363980000
6	3.480384000	-3.107623000	-1.375859000
1	3.773043000	-4.084834000	-1.000166000
6	2.840461000	-2.205295000	-0.521213000
1	2.648874000	-2.501804000	0.504135000
6	2.214454000	0.162173000	1.768620000
6	3.488798000	-0.363730000	2.033111000
1	4.076192000	-0.811540000	1.238640000
6	4.027106000	-0.315966000	3.321627000
1	5.013588000	-0.733939000	3.506917000
6	3.305518000	0.271712000	4.360631000
1	3.724550000	0.310246000	5.363055000
6	2.044309000	0.812297000	4.103487000
1	1.474612000	1.274539000	4.905286000
6	1.496892000	0.753266000	2.821695000
1	0.513984000	1.172311000	2.631877000
6	2.217690000	1.857716000	-0.508425000
6	3.614128000	2.020414000	-0.442995000
1	4.237148000	1.222085000	-0.053105000
6	4.220474000	3.200275000	-0.867385000
1	5.301093000	3.302066000	-0.805994000
6	3.441867000	4.250116000	-1.363697000
1	3.913567000	5.173167000	-1.691260000
6	2.058078000	4.105514000	-1.425676000
1	1.438644000	4.918251000	-1.796303000
6	1.449943000	2.918346000	-1.002586000
1	0.370446000	2.837925000	-1.026100000

**Table S8 Optimized coordinates for L<sup>1</sup>Ru(PhCN) (gas Phase)**

Z	x	y	z
44	-0.466392000	-0.134680000	0.190615000
16	-0.964643000	-0.966484000	2.380610000
16	0.003008000	1.098676000	-1.875628000
16	-0.757402000	-2.353950000	-0.790024000
7	-2.626733000	0.005679000	-0.083325000
7	-0.723923000	1.885963000	1.044060000

6	-2.695301000	-1.472247000	2.016215000
1	-2.537187000	-2.443335000	1.542022000
1	-3.264396000	-1.612552000	2.942029000
6	-3.428389000	-0.509521000	1.082109000
1	-4.334249000	-1.000312000	0.704886000
1	-3.770025000	0.351847000	1.663888000
6	-2.866549000	1.471695000	-0.245946000
1	-3.944692000	1.701678000	-0.228963000
1	-2.464233000	1.736352000	-1.222569000
6	-2.154579000	2.294653000	0.831757000
1	-2.681270000	2.204722000	1.785310000
1	-2.203415000	3.355814000	0.560670000
6	-0.426345000	1.801234000	2.503842000
1	-0.651255000	2.759507000	3.003355000
1	0.648580000	1.627038000	2.596244000
6	-1.174730000	0.679032000	3.235587000
1	-2.243846000	0.884741000	3.334378000
1	-0.770678000	0.590094000	4.248738000
6	-2.961141000	-0.681813000	-1.382558000
1	-2.502588000	-0.050264000	-2.143914000
1	-4.055922000	-0.652803000	-1.522172000
6	-2.434880000	-2.120161000	-1.598057000
6	0.317245000	2.811327000	-1.163865000
6	0.258653000	2.806071000	0.386326000
1	1.233559000	2.478197000	0.754060000
1	0.092450000	3.834632000	0.754114000
6	-0.645304000	3.841130000	-1.792750000
1	-0.417590000	4.859229000	-1.442131000
1	-1.698221000	3.640705000	-1.578542000
1	-0.534390000	3.828547000	-2.881525000
6	1.750711000	3.244476000	-1.542084000
1	1.853663000	3.288776000	-2.630822000
1	2.487749000	2.528586000	-1.165957000
1	1.989600000	4.240767000	-1.137974000
6	-2.274550000	-2.299532000	-3.123287000
1	-1.930983000	-3.314514000	-3.347651000
1	-1.533984000	-1.598295000	-3.517989000
1	-3.229324000	-2.140700000	-3.649418000
6	-3.419700000	-3.198497000	-1.103652000
1	-4.376473000	-3.131933000	-1.643423000
1	-3.633036000	-3.129924000	-0.033266000
1	-3.001558000	-4.193906000	-1.283784000
7	1.502368000	-0.354213000	0.359853000
6	2.655552000	-0.532227000	0.329912000
6	4.060238000	-0.738905000	0.199655000
6	4.818016000	-1.253909000	1.268857000
6	4.692123000	-0.423755000	-1.020365000
6	6.188237000	-1.446664000	1.115543000
1	4.325137000	-1.502686000	2.203513000
6	6.063037000	-0.621474000	-1.157680000
1	4.096230000	-0.036250000	-1.840549000
6	6.813766000	-1.130916000	-0.093944000
1	6.769495000	-1.847029000	1.941377000
1	6.546885000	-0.380150000	-2.099845000
1	7.883164000	-1.284498000	-0.208271000

**Table S9 Optimized coordinates for L<sup>1</sup> Ru(H<sub>2</sub>O) (gas Phase)**

Z	x	y	z
44	0.009235000	0.129626000	-0.614888000
16	0.914940000	2.290298000	-0.916580000
16	-1.316026000	-1.909440000	-0.319013000
16	2.087035000	-0.891014000	-1.388428000
7	0.948634000	0.130888000	1.295111000
7	-1.655749000	1.096548000	0.451103000
6	2.227636000	2.155571000	0.373119000
1	3.016901000	1.636189000	-0.174103000
1	2.588399000	3.146069000	0.671705000
6	1.775166000	1.359728000	1.595305000
1	2.652247000	1.064337000	2.183795000
1	1.179353000	2.013017000	2.239292000
6	-0.199242000	0.065839000	2.253444000
1	0.140606000	0.234112000	3.288746000
1	-0.598674000	-0.943290000	2.183673000
6	-1.298064000	1.078397000	1.910340000
1	-0.981071000	2.084433000	2.197439000
1	-2.185876000	0.857790000	2.515218000
6	-1.751183000	2.504312000	-0.040275000
1	-2.482947000	3.076061000	0.556393000
1	-2.128220000	2.453339000	-1.064686000
6	-0.418010000	3.262544000	-0.043068000
1	-0.070240000	3.501949000	0.965375000
1	-0.553701000	4.211357000	-0.571155000
6	1.737492000	-1.154314000	1.406111000
1	0.977013000	-1.934500000	1.433952000
1	2.265855000	-1.155222000	2.375197000
6	2.721967000	-1.512136000	0.263938000
6	-2.948305000	-1.165109000	0.259003000
6	-2.934038000	0.380417000	0.139329000
1	-3.145033000	0.633058000	-0.902704000
1	-3.748336000	0.803997000	0.753864000
6	-3.294665000	-1.659559000	1.678800000
1	-2.562712000	-1.367727000	2.435242000
1	-3.340190000	-2.752878000	1.685077000
1	-4.276528000	-1.278178000	1.996008000
6	-4.067851000	-1.669197000	-0.676985000
1	-4.123360000	-2.761536000	-0.642422000
1	-3.879484000	-1.377330000	-1.715021000
1	-5.048379000	-1.270118000	-0.376476000
6	2.802212000	-3.052516000	0.222795000
1	3.516154000	-3.370028000	-0.543847000
1	1.827707000	-3.483208000	-0.024326000
1	3.136128000	-3.463692000	1.188597000
6	4.142889000	-0.972223000	0.517594000
1	4.177505000	0.117141000	0.607049000
1	4.799330000	-1.247596000	-0.313759000
1	4.565906000	-1.400766000	1.438760000
1	-1.308754000	-0.958580000	-2.346326000
8	-0.955221000	-0.078030000	-2.649458000
1	-0.175564000	-0.307591000	-3.185654000

**Table S10 Optimized coordinates for L<sup>1</sup>Ru (gas phase)**

Z	x	y	z
44	-0.045548000	0.054915000	-0.664603000
16	0.846587000	2.214777000	-1.092838000
16	-1.406314000	-1.828098000	-0.715982000
16	2.017932000	-0.990477000	-1.439262000
7	0.931959000	0.198655000	1.192458000
7	-1.714926000	1.080582000	0.342314000
6	2.182398000	2.188994000	0.179683000
1	2.980159000	1.660885000	-0.345313000
1	2.519702000	3.202817000	0.420599000
6	1.751028000	1.450025000	1.442065000
1	2.630597000	1.181961000	2.038450000
1	1.148065000	2.122055000	2.059623000
6	-0.210251000	0.150412000	2.163386000
1	0.140277000	0.372705000	3.184589000
1	-0.578569000	-0.872454000	2.149565000
6	-1.350976000	1.109503000	1.799415000
1	-1.077603000	2.134081000	2.067684000
1	-2.224006000	0.857821000	2.413791000
6	-1.803292000	2.474907000	-0.193522000
1	-2.527132000	3.068530000	0.390872000
1	-2.189772000	2.396553000	-1.212202000
6	-0.467865000	3.224136000	-0.236123000
1	-0.108794000	3.492981000	0.760788000
1	-0.606479000	4.157210000	-0.790914000
6	1.739167000	-1.075490000	1.358908000
1	0.988219000	-1.862664000	1.425540000
1	2.264838000	-1.018493000	2.327691000
6	2.716988000	-1.473367000	0.230715000
6	-2.991285000	-1.178815000	0.058820000
6	-3.004030000	0.366523000	0.047145000
1	-3.266693000	0.673050000	-0.968152000
1	-3.790426000	0.745593000	0.722901000
6	-3.212372000	-1.778207000	1.461647000
1	-4.176893000	-1.451018000	1.877133000
1	-2.433035000	-1.509324000	2.178512000
1	-3.225831000	-2.870528000	1.398989000
6	-4.165038000	-1.642831000	-0.829556000
1	-4.206221000	-2.736171000	-0.856033000
1	-4.045742000	-1.288146000	-1.858083000
1	-5.126876000	-1.277659000	-0.440139000
6	2.843743000	-3.011173000	0.291382000
1	3.550247000	-3.355800000	-0.470199000
1	1.879203000	-3.486750000	0.091769000
1	3.212235000	-3.348864000	1.273285000
6	4.127169000	-0.883023000	0.427763000
1	4.139070000	0.210025000	0.450912000
1	4.775437000	-1.192355000	-0.397973000
1	4.577337000	-1.245760000	1.364377000

**Table S11 Optimized coordinates for L<sup>1</sup>Ru(PhCONH<sub>2</sub>) (gas Phase)**

Z	x	y	z
44	-0.639833000	0.001033000	-0.301690000
16	-1.581779000	-1.167689000	-2.139389000
16	0.520994000	0.820633000	1.697644000
16	-1.575173000	2.126167000	-1.074621000
7	-2.533546000	-0.244547000	0.662955000
7	-0.222213000	-1.982576000	0.578256000
6	-3.344263000	-0.877753000	-1.695582000
1	-3.510407000	0.118328000	-2.111451000
1	-4.001250000	-1.591791000	-2.204395000
6	-3.592802000	-0.905790000	-0.189241000
1	-4.562321000	-0.440537000	0.026005000
1	-3.675952000	-1.947933000	0.131527000
6	-2.242477000	-1.121977000	1.836991000
1	-3.175088000	-1.461618000	2.317042000
1	-1.691473000	-0.507654000	2.544627000
6	-1.399794000	-2.337191000	1.440354000
1	-2.016487000	-3.059274000	0.899732000
1	-1.060854000	-2.851111000	2.347901000
6	-0.095249000	-2.956252000	-0.548588000
1	-0.008220000	-3.986911000	-0.162619000
1	0.830457000	-2.713139000	-1.074925000
6	-1.254072000	-2.908981000	-1.553217000
1	-2.184977000	-3.320716000	-1.153036000
1	-0.984388000	-3.510812000	-2.426182000
6	-2.950540000	1.114484000	1.174219000
1	-2.217749000	1.343732000	1.947987000
1	-3.941126000	1.016511000	1.651306000
6	-2.957094000	2.302074000	0.180836000
6	1.249973000	-0.786964000	2.364816000
6	1.062602000	-1.940376000	1.347020000
1	1.842024000	-1.849077000	0.587663000
1	1.210257000	-2.910151000	1.855885000
6	0.683380000	-1.108493000	3.765261000
1	1.156150000	-2.012044000	4.178926000
1	-0.397248000	-1.260002000	3.785975000
1	0.900160000	-0.277164000	4.443297000
6	2.772202000	-0.610393000	2.551452000
1	3.228554000	-1.524744000	2.960709000
1	2.971210000	0.205937000	3.253038000
1	3.267278000	-0.369612000	1.608739000
6	-2.709449000	3.573354000	1.019641000
1	-2.728450000	4.457875000	0.374901000
1	-1.731263000	3.529693000	1.506792000
1	-3.483506000	3.700570000	1.792804000
6	-4.308200000	2.469812000	-0.541243000
1	-5.116482000	2.658486000	0.181261000
1	-4.586506000	1.596877000	-1.137966000
1	-4.261649000	3.323991000	-1.224128000
6	2.395394000	-0.124177000	-1.663102000
7	1.189929000	0.617870000	-1.600635000
1	0.686554000	0.537820000	-2.480937000
8	2.399077000	-1.210660000	-2.227883000
6	3.624411000	0.468155000	-1.058753000

6	4.843489000	-0.164860000	-1.355005000
6	3.621414000	1.620119000	-0.254643000
6	6.040890000	0.351845000	-0.870203000
1	4.825801000	-1.055058000	-1.974750000
6	4.824730000	2.129797000	0.233832000
1	2.688857000	2.082504000	0.053539000
6	6.033208000	1.503723000	-0.077044000
1	6.979691000	-0.139936000	-1.109555000
1	4.813335000	3.012564000	0.866485000
1	6.967895000	1.908567000	0.302052000
1	1.276848000	1.593737000	-1.329816000

**Table S12 Optimized coordinates for L<sup>1</sup>Ru(PhC(OH)NH) (Gas Phase)**

Z	x	y	z
44	-0.543736000	-0.080330000	-0.363933000
16	-2.030910000	-0.300759000	-2.217098000
16	0.865049000	-0.290753000	1.637216000
16	-0.503623000	2.355375000	-0.654157000
7	-2.328837000	0.353647000	0.810271000
7	-1.071195000	-2.175736000	0.124173000
6	-3.435591000	0.641852000	-1.492912000
1	-3.140861000	1.670871000	-1.709752000
1	-4.368698000	0.416823000	-2.021374000
6	-3.603436000	0.407227000	0.008172000
1	-4.254940000	1.187331000	0.421205000
1	-4.132905000	-0.538508000	0.156143000
6	-2.399897000	-0.783911000	1.776023000
1	-3.353931000	-0.776124000	2.329553000
1	-1.581824000	-0.634395000	2.479053000
6	-2.229771000	-2.137425000	1.081769000
1	-3.137578000	-2.391188000	0.528416000
1	-2.113425000	-2.918385000	1.842706000
6	-1.484246000	-2.849752000	-1.139700000
1	-1.871504000	-3.862927000	-0.934086000
1	-0.580290000	-2.966644000	-1.743488000
6	-2.532455000	-2.080416000	-1.955211000
1	-3.522197000	-2.100729000	-1.491736000
1	-2.631510000	-2.554457000	-2.936767000
6	-2.066860000	1.619471000	1.583093000
1	-1.276739000	1.346872000	2.283217000
1	-2.971714000	1.871197000	2.163822000
6	-1.580686000	2.860207000	0.795296000
6	0.883974000	-2.158395000	1.844134000
6	0.137770000	-2.859884000	0.682076000
1	0.828994000	-2.926642000	-0.160966000
1	-0.131727000	-3.889844000	0.978713000
6	0.341869000	-2.556681000	3.233409000
1	0.411650000	-3.644350000	3.387974000
1	-0.696596000	-2.259340000	3.398268000
1	0.938453000	-2.068886000	4.010668000
6	2.348064000	-2.643853000	1.777440000
1	2.413998000	-3.739716000	1.869247000
1	2.926541000	-2.201772000	2.594497000
1	2.818010000	-2.340793000	0.837595000
6	-0.735413000	3.698209000	1.778224000

1	-0.384157000	4.611756000	1.287382000
1	0.139610000	3.133842000	2.113448000
1	-1.322311000	3.993311000	2.662508000
6	-2.740786000	3.748992000	0.304615000
1	-3.332665000	4.123620000	1.153398000
1	-3.420727000	3.230170000	-0.376495000
1	-2.343618000	4.613746000	-0.236528000
6	2.399063000	-0.353775000	-1.795012000
7	1.125014000	-0.489208000	-1.646839000
1	0.779382000	-0.952912000	-2.489580000
8	2.942024000	-0.956630000	-2.902884000
1	3.822047000	-0.576977000	-3.061079000
6	3.357584000	0.366099000	-0.931681000
6	4.675906000	-0.116890000	-0.828789000
6	3.004979000	1.556554000	-0.278243000
6	5.626129000	0.576821000	-0.081012000
1	4.949398000	-1.060498000	-1.295785000
6	3.966853000	2.252931000	0.450093000
1	1.987510000	1.930943000	-0.348167000
6	5.273813000	1.769117000	0.553759000
1	6.635788000	0.184848000	0.006342000
1	3.687714000	3.178352000	0.945856000
1	6.014692000	2.317241000	1.130028000

**Table S13 Optimized coordinates for L1 RuTS (gas Phase)**

Z	x	y	z
44	-0.545668000	-0.004680000	0.293486000
16	-1.146341000	-0.209236000	2.573114000
16	-0.042937000	0.592785000	-2.041729000
16	-0.709549000	-2.413275000	-0.013400000
7	-2.706848000	-0.024627000	-0.132750000
7	-0.828257000	2.125737000	0.513512000
6	-2.875518000	-0.812120000	2.313168000
1	-2.728746000	-1.890892000	2.216541000
1	-3.484687000	-0.635496000	3.206894000
6	-3.570471000	-0.223280000	1.080328000
1	-4.427715000	-0.858203000	0.819228000
1	-3.987614000	0.750313000	1.353714000
6	-2.932253000	1.346217000	-0.691639000
1	-4.009178000	1.570760000	-0.773101000
1	-2.493638000	1.346473000	-1.688110000
6	-2.254712000	2.437098000	0.148472000
1	-2.814296000	2.598488000	1.073576000
1	-2.301692000	3.384924000	-0.401054000
6	-0.578020000	2.460814000	1.948368000
1	-0.794891000	3.525718000	2.139591000
1	0.488143000	2.294837000	2.118374000
6	-1.372658000	1.604689000	2.941517000
1	-2.442272000	1.833931000	2.945625000
1	-0.997438000	1.795797000	3.951497000
6	-2.914631000	-1.040610000	-1.220978000
1	-2.481406000	-0.578917000	-2.107768000
1	-3.996026000	-1.172121000	-1.395114000
6	-2.264023000	-2.452648000	-1.082354000
6	0.299122000	2.423532000	-1.821469000

6	0.187630000	2.836935000	-0.331422000
1	1.140692000	2.602555000	0.145225000
1	0.020330000	3.926059000	-0.254957000
6	-0.617548000	3.254654000	-2.742368000
1	-0.381893000	4.327107000	-2.667602000
1	-1.681537000	3.128383000	-2.523044000
1	-0.467825000	2.950478000	-3.783229000
6	1.757712000	2.702134000	-2.242340000
1	1.896495000	2.457812000	-3.300326000
1	2.449730000	2.086966000	-1.660670000
1	2.019605000	3.762874000	-2.101697000
6	-1.911043000	-2.941088000	-2.497146000
1	-1.495367000	-3.953562000	-2.461897000
1	-1.178584000	-2.278901000	-2.968302000
1	-2.808776000	-2.968019000	-3.131576000
6	-3.220807000	-3.463104000	-0.421560000
1	-4.137989000	-3.560836000	-1.017927000
1	-3.508670000	-3.166385000	0.592315000
1	-2.752788000	-4.450044000	-0.353724000
7	1.493123000	0.025383000	0.641930000
6	2.352027000	-0.703449000	0.147460000
6	3.827070000	-0.691373000	0.279060000
6	4.391812000	-0.065218000	1.405137000
6	4.686899000	-1.251289000	-0.680978000
6	5.772487000	-0.010709000	1.569469000
1	3.722996000	0.371698000	2.139625000
6	6.071879000	-1.191312000	-0.513573000
1	4.268706000	-1.704960000	-1.573399000
6	6.621060000	-0.576170000	0.611575000
1	6.190807000	0.471713000	2.449460000
1	6.721700000	-1.621889000	-1.271314000
1	7.699274000	-0.533365000	0.741463000
1	0.656462000	-2.174110000	-0.738518000
8	1.950503000	-1.878952000	-0.839064000
1	2.442459000	-2.673695000	-0.559647000

## Gas Phase DFT Studies optimized coordinates for Catalyst L<sup>2</sup>RuPPh<sub>3</sub> and derivatives

**Table S14 Optimized coordinates for L<sup>2</sup>RuPPh<sub>3</sub> (Gas Phase):**

Z	x	y	z
44	-0.896504000	-0.109404000	-0.146344000
16	-0.932950000	0.504031000	-2.474724000
16	-1.046396000	-1.258773000	2.017900000
16	-1.435823000	2.049920000	0.587814000
15	1.510531000	0.254647000	0.065533000
7	-3.141365000	-0.264904000	-0.377513000
7	-1.092074000	-2.239922000	-0.927581000
6	-2.694809000	1.027492000	-2.568492000
1	-2.622800000	2.049957000	-2.191620000
1	-3.027401000	1.042988000	-3.612323000
6	-3.649999000	0.180382000	-1.726783000
1	-4.582181000	0.740713000	-1.586587000
1	-3.917243000	-0.716026000	-2.293285000

6	-3.447272000	-1.712795000	-0.200823000
1	-4.502671000	-1.921531000	-0.440906000
1	-3.275758000	-1.933744000	0.849734000
6	-2.544533000	-2.584770000	-1.059191000
1	-2.825479000	-2.490989000	-2.110288000
1	-2.701218000	-3.638909000	-0.798344000
6	-0.461910000	-2.297193000	-2.276227000
1	-0.646172000	-3.278315000	-2.747960000
1	0.613356000	-2.197506000	-2.139133000
6	-0.948224000	-1.200282000	-3.234057000
1	-1.955154000	-1.388584000	-3.616547000
1	-0.277295000	-1.174477000	-4.097593000
6	-3.783727000	0.461042000	0.773690000
1	-3.571700000	-0.164288000	1.640462000
1	-4.874490000	0.472004000	0.616745000
6	-3.295119000	1.883977000	1.103032000
6	-0.698733000	-3.040531000	1.524011000
6	-0.385275000	-3.167152000	0.009692000
1	0.673048000	-2.963391000	-0.135871000
1	-0.564128000	-4.208315000	-0.314667000
6	-1.852929000	-3.962389000	1.973598000
1	-1.593658000	-5.017336000	1.800882000
1	-2.799426000	-3.767319000	1.463920000
1	-2.031444000	-3.832702000	3.045545000
6	0.560360000	-3.509745000	2.285489000
1	0.365738000	-3.515939000	3.362437000
1	1.403182000	-2.835578000	2.113326000
1	0.850206000	-4.529966000	1.988969000
6	-3.373898000	2.072619000	2.624785000
1	-3.044112000	3.075532000	2.905032000
1	-2.739718000	1.352945000	3.149601000
1	-4.410335000	1.936814000	2.963942000
6	-4.101831000	2.985484000	0.403653000
1	-5.136744000	2.962425000	0.771639000
1	-4.120245000	2.879680000	-0.683425000
1	-3.681271000	3.970331000	0.620386000
6	2.502571000	-0.881059000	-1.041198000
6	2.737162000	-0.487492000	-2.372291000
1	2.436650000	0.502734000	-2.700327000
6	3.363894000	-1.343523000	-3.279557000
1	3.536835000	-1.008969000	-4.299372000
6	3.781541000	-2.614767000	-2.878218000
1	4.277131000	-3.278249000	-3.581797000
6	3.564311000	-3.019021000	-1.560907000
1	3.892318000	-4.000812000	-1.228998000
6	2.928355000	-2.164019000	-0.655842000
1	2.774935000	-2.504255000	0.362035000
6	2.302113000	0.107572000	1.740030000
6	3.560988000	-0.470183000	1.973529000
1	4.127530000	-0.911686000	1.161252000
6	4.119066000	-0.471402000	3.254657000
1	5.093198000	-0.927153000	3.414166000
6	3.434711000	0.118661000	4.316980000
1	3.869393000	0.119927000	5.313451000
6	2.194107000	0.716145000	4.088550000
1	1.657624000	1.190753000	4.905737000

6	1.625053000	0.708627000	2.814680000
1	0.669622000	1.195133000	2.650324000
6	2.261340000	1.872145000	-0.499488000
6	3.642067000	2.079754000	-0.320509000
1	4.246285000	1.330586000	0.179942000
6	4.253318000	3.246691000	-0.771321000
1	5.320606000	3.387286000	-0.619672000
6	3.495868000	4.234177000	-1.408636000
1	3.971392000	5.147971000	-1.756211000
6	2.128108000	4.041261000	-1.583087000
1	1.521728000	4.807055000	-2.059432000
6	1.510867000	2.867673000	-1.134268000
1	0.438852000	2.769583000	-1.247355000
8	-0.741664000	2.621993000	1.786494000
8	-1.525743000	3.004552000	-0.588338000

**Table S15 Optimized coordinates for L<sup>2</sup>Ru(PhCN) (gas Phase):**

Z	x	y	z
44	-0.481900000	0.112700000	0.254412000
16	-0.959554000	-0.520365000	2.526951000
16	-0.197375000	1.131273000	-1.951840000
16	0.148240000	-2.055536000	-0.320683000
7	-2.507267000	-0.543017000	-0.202512000
7	-1.502318000	2.019480000	0.729737000
6	-2.364950000	-1.638895000	2.128681000
1	-1.823430000	-2.553423000	1.874144000
1	-2.981724000	-1.813401000	3.017187000
6	-3.239308000	-1.147011000	0.973861000
1	-3.855954000	-1.981290000	0.617670000
1	-3.936886000	-0.393938000	1.352060000
6	-3.202541000	0.715010000	-0.624255000
1	-4.287792000	0.550122000	-0.720313000
1	-2.796864000	0.972295000	-1.600799000
6	-2.946651000	1.869709000	0.349619000
1	-3.527727000	1.724241000	1.263419000
1	-3.316515000	2.800456000	-0.097141000
6	-1.376490000	2.248796000	2.198103000
1	-1.958033000	3.135252000	2.505363000
1	-0.322807000	2.463842000	2.392948000
6	-1.802292000	1.052956000	3.058832000
1	-2.883945000	0.893968000	3.051198000
1	-1.517500000	1.251622000	4.096695000
6	-2.430641000	-1.467218000	-1.395618000
1	-2.177619000	-0.812668000	-2.229674000
1	-3.433629000	-1.885425000	-1.578073000
6	-1.391047000	-2.614535000	-1.370842000
6	-0.547688000	2.926813000	-1.525375000
6	-0.798247000	3.116830000	-0.007023000
1	0.176013000	3.195448000	0.480677000
1	-1.334411000	4.067651000	0.163028000
6	-1.702016000	3.470398000	-2.393057000
1	-1.859151000	4.543813000	-2.209477000
1	-2.653183000	2.958814000	-2.223433000
1	-1.456270000	3.344042000	-3.452067000
6	0.709674000	3.756538000	-1.865503000

1	0.925990000	3.689040000	-2.936100000
1	1.582754000	3.378394000	-1.325492000
1	0.569273000	4.819519000	-1.614265000
6	-0.911108000	-2.847141000	-2.810460000
1	-0.184605000	-3.662830000	-2.842540000
1	-0.426685000	-1.956330000	-3.218980000
1	-1.761309000	-3.111862000	-3.454849000
6	-1.942782000	-3.923868000	-0.793508000
1	-2.731227000	-4.310797000	-1.453807000
1	-2.364349000	-3.809543000	0.207920000
1	-1.153085000	-4.675638000	-0.721206000
7	1.468435000	0.536715000	0.586683000
6	2.631331000	0.497880000	0.570138000
6	4.029425000	0.238714000	0.436869000
6	5.001480000	1.094574000	0.981417000
6	4.404354000	-0.922916000	-0.268167000
6	6.350032000	0.787910000	0.820146000
1	4.696067000	1.985405000	1.521829000
6	5.758347000	-1.212021000	-0.418192000
1	3.627676000	-1.565462000	-0.676544000
6	6.728670000	-0.362664000	0.122016000
1	7.106192000	1.445802000	1.238941000
1	6.056307000	-2.105351000	-0.959411000
1	7.782644000	-0.597105000	-0.000567000
8	0.101588000	-2.972629000	0.880185000
8	1.349306000	-2.247476000	-1.197282000

**Table S16 Optimized coordinates for L<sup>2</sup>Ru(H<sub>2</sub>O) (gas Phase):**

Z	x	y	z
44	-0.062470000	0.120528000	-0.518231000
16	0.743925000	2.308880000	-0.993915000
16	-1.320524000	-1.940234000	-0.057770000
16	1.994725000	-0.781552000	-0.897403000
7	0.595325000	0.444963000	1.489509000
7	-1.927570000	1.109182000	0.201760000
6	1.864689000	2.441075000	0.466267000
1	2.757614000	1.939866000	0.086701000
1	2.096256000	3.490503000	0.678148000
6	1.310943000	1.761147000	1.718781000
1	2.127572000	1.599809000	2.432664000
1	0.603884000	2.437484000	2.207144000
6	-0.670091000	0.431898000	2.293805000
1	-0.478878000	0.754607000	3.329709000
1	-1.010094000	-0.600613000	2.310758000
6	-1.758905000	1.317990000	1.676644000
1	-1.526808000	2.371817000	1.851416000
1	-2.705301000	1.128919000	2.197840000
6	-2.030478000	2.418679000	-0.506048000
1	-2.873146000	3.011118000	-0.108979000
1	-2.250907000	2.191953000	-1.552246000
6	-0.756706000	3.269363000	-0.446953000
1	-0.569050000	3.675823000	0.550486000
1	-0.875169000	4.121695000	-1.122912000
6	1.420984000	-0.768493000	1.879646000
1	0.686936000	-1.564192000	2.000228000

1	1.880404000	-0.571880000	2.860707000
6	2.508038000	-1.286667000	0.896131000
6	-3.050488000	-1.244004000	0.199105000
6	-3.108449000	0.263392000	-0.152658000
1	-3.196143000	0.347074000	-1.239113000
1	-4.020257000	0.707497000	0.285384000
6	-3.557044000	-1.555531000	1.623164000
1	-2.955871000	-1.101973000	2.414403000
1	-3.540356000	-2.636878000	1.789968000
1	-4.593557000	-1.210602000	1.750068000
6	-4.003028000	-1.963358000	-0.780626000
1	-4.004055000	-3.039795000	-0.584027000
1	-3.691934000	-1.814347000	-1.819498000
1	-5.034830000	-1.597733000	-0.670627000
6	2.526524000	-2.819719000	0.963043000
1	3.292436000	-3.220649000	0.293881000
1	1.564975000	-3.242402000	0.658829000
1	2.749720000	-3.154778000	1.985455000
6	3.902814000	-0.726905000	1.200419000
1	3.926998000	0.365644000	1.222513000
1	4.621162000	-1.044770000	0.440969000
1	4.242624000	-1.098506000	2.176965000
1	-1.098797000	-1.320217000	-2.244508000
8	-0.586239000	-0.558204000	-2.616219000
1	0.267905000	-0.988832000	-2.841818000
8	3.052030000	0.223465000	-1.286530000
8	1.958990000	-2.008334000	-1.769271000

**Table S17 Optimized coordinates for L<sup>2</sup>Ru (gas Phase):**

Z	x	y	z
44	-0.142643000	0.040997000	-0.540623000
16	0.636105000	2.228131000	-1.142240000
16	-1.386727000	-1.911961000	-0.549336000
16	1.927007000	-0.889486000	-1.012738000
7	0.635403000	0.484641000	1.375081000
7	-1.978547000	1.057973000	0.192723000
6	1.831255000	2.452508000	0.242848000
1	2.712491000	1.944479000	-0.152626000
1	2.055548000	3.513819000	0.394209000
6	1.329455000	1.827312000	1.539736000
1	2.162317000	1.705050000	2.241243000
1	0.616967000	2.506715000	2.016047000
6	-0.596991000	0.459240000	2.234532000
1	-0.363624000	0.820597000	3.248760000
1	-0.894568000	-0.583552000	2.309312000
6	-1.758792000	1.279787000	1.658382000
1	-1.584073000	2.346209000	1.826657000
1	-2.666389000	1.029320000	2.221284000
6	-2.101502000	2.365769000	-0.522738000
1	-2.925432000	2.963324000	-0.096514000
1	-2.366357000	2.132193000	-1.556419000
6	-0.824268000	3.209153000	-0.530671000
1	-0.589128000	3.620844000	0.454368000
1	-0.972800000	4.058520000	-1.204635000
6	1.511125000	-0.685188000	1.788580000

1	0.812969000	-1.505356000	1.956102000
1	1.976986000	-0.433311000	2.754353000
6	2.582761000	-1.182182000	0.796531000
6	-3.066058000	-1.310910000	0.036943000
6	-3.183178000	0.220293000	-0.130318000
1	-3.379469000	0.406478000	-1.188637000
1	-4.049610000	0.599367000	0.438737000
6	-3.353881000	-1.794022000	1.471571000
1	-4.367568000	-1.503207000	1.783575000
1	-2.652357000	-1.401558000	2.211374000
1	-3.288612000	-2.885308000	1.515279000
6	-4.125061000	-1.947047000	-0.888405000
1	-4.091359000	-3.037676000	-0.804902000
1	-3.942852000	-1.686160000	-1.935635000
1	-5.138029000	-1.617949000	-0.615037000
6	2.736947000	-2.697201000	0.991603000
1	3.495350000	-3.089687000	0.310117000
1	1.803089000	-3.224579000	0.777783000
1	3.044548000	-2.922528000	2.022831000
6	3.944669000	-0.500348000	0.972603000
1	3.892640000	0.590265000	0.934862000
1	4.631517000	-0.810840000	0.181601000
1	4.378109000	-0.787426000	1.940816000
8	2.865686000	0.169125000	-1.542274000
8	2.007683000	-2.214139000	-1.691510000

**Table S18 Optimized coordinates for L<sup>2</sup>Ru(PhCONH<sub>2</sub>) (gas Phase)**

Z	x	y	z
44	-0.601451000	-0.127207000	-0.290990000
16	-1.883317000	-0.646342000	-2.242519000
16	0.791227000	-0.056704000	1.723905000
16	-1.134968000	2.094823000	-0.384681000
7	-2.431890000	-0.362467000	0.819549000
7	-0.455702000	-2.329851000	0.014720000
6	-3.523076000	-0.227867000	-1.515624000
1	-3.538979000	0.854810000	-1.663675000
1	-4.331321000	-0.687103000	-2.095096000
6	-3.652172000	-0.611717000	-0.040894000
1	-4.506281000	-0.077630000	0.392717000
1	-3.890064000	-1.676835000	0.026173000
6	-2.192427000	-1.561340000	1.683834000
1	-3.123856000	-1.880113000	2.178449000
1	-1.480332000	-1.247559000	2.443046000
6	-1.604309000	-2.730983000	0.890503000
1	-2.374414000	-3.188800000	0.264730000
1	-1.288086000	-3.511651000	1.593208000
6	-0.573000000	-2.969515000	-1.328121000
1	-0.612362000	-4.068829000	-1.234400000
1	0.337474000	-2.713757000	-1.876413000
6	-1.791373000	-2.503757000	-2.136887000
1	-2.737470000	-2.877586000	-1.735865000
1	-1.702808000	-2.889169000	-3.157138000
6	-2.563972000	0.850943000	1.717143000
1	-1.791226000	0.709142000	2.472125000
1	-3.546979000	0.810985000	2.212383000

6	-2.357753000	2.260870000	1.100743000
6	1.326072000	-1.859662000	1.854756000
6	0.877749000	-2.664420000	0.609115000
1	1.598893000	-2.481221000	-0.189778000
1	0.906213000	-3.744716000	0.838998000
6	0.849027000	-2.478911000	3.186315000
1	1.233866000	-3.503630000	3.296633000
1	-0.236626000	-2.519181000	3.297877000
1	1.233334000	-1.886179000	4.022240000
6	2.869129000	-1.910746000	1.882462000
1	3.226846000	-2.948876000	1.957941000
1	3.246895000	-1.361454000	2.750509000
1	3.302384000	-1.458940000	0.987998000
6	-1.698566000	3.153594000	2.161635000
1	-1.550086000	4.164044000	1.771732000
1	-0.722141000	2.763583000	2.460650000
1	-2.338588000	3.216943000	3.052537000
6	-3.662478000	2.904078000	0.614523000
1	-4.316193000	3.097496000	1.475972000
1	-4.210090000	2.278918000	-0.095380000
1	-3.461489000	3.853542000	0.112688000
6	2.433406000	-0.101787000	-1.592386000
7	1.183499000	0.575986000	-1.576663000
1	0.750975000	0.507711000	-2.495878000
8	2.521384000	-1.173297000	-2.178550000
6	3.586409000	0.551428000	-0.914023000
6	4.856579000	-0.006676000	-1.137419000
6	3.459965000	1.689357000	-0.098465000
6	5.987065000	0.566797000	-0.564291000
1	4.932076000	-0.885751000	-1.768878000
6	4.597845000	2.255347000	0.476195000
1	2.489149000	2.122997000	0.121220000
6	5.857951000	1.700790000	0.243947000
1	6.966853000	0.133986000	-0.746509000
1	4.494712000	3.129969000	1.111723000
1	6.739788000	2.150480000	0.692960000
1	1.223234000	1.555285000	-1.280233000
8	-1.978482000	2.471257000	-1.581803000
8	0.033309000	3.022935000	-0.152221000

**Table S19 Optimized coordinates for L<sup>2</sup>Ru(PhC(OH)NH) (gas Phase):**

Z	x	y	z
44	0.541420000	-0.167780000	0.301116000
16	2.013430000	-0.474825000	2.191324000
16	-0.899159000	-0.347500000	-1.668092000
16	0.827717000	2.137823000	0.316936000
7	2.361175000	-0.195133000	-0.904822000
7	0.701131000	-2.380228000	0.042768000
6	3.536807000	0.137150000	1.366079000
1	3.407593000	1.215690000	1.484291000
1	4.428087000	-0.189683000	1.912794000
6	3.637680000	-0.282188000	-0.100127000
1	4.408957000	0.324891000	-0.589933000
1	3.990145000	-1.316274000	-0.147938000
6	2.225012000	-1.427158000	-1.743108000

1	3.162921000	-1.640121000	-2.281561000
1	1.442418000	-1.213015000	-2.469037000
6	1.828592000	-2.649058000	-0.910519000
1	2.686977000	-3.003917000	-0.335168000
1	1.561385000	-3.470280000	-1.585987000
6	1.004287000	-2.977344000	1.373420000
1	1.194879000	-4.060849000	1.281945000
1	0.106265000	-2.856429000	1.985382000
6	2.190213000	-2.326275000	2.096128000
1	3.147838000	-2.562900000	1.624802000
1	2.234552000	-2.714176000	3.118562000
6	2.327895000	1.001904000	-1.822633000
1	1.528734000	0.778590000	-2.530000000
1	3.278887000	1.045589000	-2.378478000
6	2.025847000	2.382251000	-1.198551000
6	-1.243868000	-2.194679000	-1.678261000
6	-0.619374000	-2.888800000	-0.442561000
1	-1.299571000	-2.740464000	0.399269000
1	-0.543325000	-3.975990000	-0.624854000
6	-0.797902000	-2.823032000	-3.015500000
1	-1.063369000	-3.890207000	-3.055446000
1	0.274461000	-2.737333000	-3.206079000
1	-1.308696000	-2.320177000	-3.842556000
6	-2.769652000	-2.406109000	-1.572555000
1	-3.025268000	-3.477307000	-1.559897000
1	-3.271807000	-1.950301000	-2.431408000
1	-3.170394000	-1.937988000	-0.669950000
6	1.284751000	3.217362000	-2.252839000
1	1.056373000	4.212078000	-1.862699000
1	0.339805000	2.749414000	-2.541145000
1	1.908545000	3.329265000	-3.151118000
6	3.275036000	3.142525000	-0.736339000
1	3.888160000	3.405445000	-1.609544000
1	3.899821000	2.574107000	-0.043816000
1	2.992051000	4.064644000	-0.222770000
6	-2.379533000	0.094181000	1.886984000
7	-1.123075000	-0.118448000	1.695571000
1	-0.716740000	-0.319483000	2.611274000
8	-2.845684000	-0.156469000	3.150069000
6	-3.395178000	0.568298000	0.924270000
6	-4.694311000	0.028001000	0.987286000
6	-3.108975000	1.599030000	0.018310000
6	-5.693204000	0.501142000	0.139034000
1	-4.912733000	-0.787823000	1.673140000
6	-4.123684000	2.079733000	-0.809778000
1	-2.115510000	2.038282000	-0.010974000
6	-5.407684000	1.534014000	-0.758014000
1	-6.688269000	0.066639000	0.179082000
1	-3.901524000	2.886851000	-1.501785000
1	-6.187667000	1.912533000	-1.413729000
8	1.667388000	2.562187000	1.501813000
8	-0.334550000	3.047137000	0.037755000
1	-3.716641000	0.263198000	3.247481000

**Table S20 Optimized coordinates for L<sup>2</sup>RuTS (gas Phase):**

Z	x	y	z
44	-0.490884000	0.115854000	0.108810000
16	-0.334625000	-0.788277000	2.335371000
16	-0.725792000	1.427366000	-1.936257000
16	-0.485665000	-1.833497000	-1.057957000
7	-2.665834000	-0.178553000	0.338700000
7	-0.903820000	2.026343000	1.103528000
6	-1.981428000	-1.594222000	2.387238000
1	-1.769022000	-2.559213000	1.924912000
1	-2.294241000	-1.773291000	3.422032000
6	-3.071893000	-0.820548000	1.640011000
1	-3.920253000	-1.493011000	1.459289000
1	-3.448192000	-0.032120000	2.297231000
6	-3.179678000	1.225146000	0.287713000
1	-4.250042000	1.267978000	0.550118000
1	-3.051393000	1.556296000	-0.741768000
6	-2.396387000	2.160516000	1.221023000
1	-2.674329000	1.969839000	2.261128000
1	-2.697298000	3.194457000	1.015817000
6	-0.272184000	2.015441000	2.454525000
1	-0.546493000	2.921839000	3.020265000
1	0.808148000	2.038471000	2.293287000
6	-0.618376000	0.782003000	3.293285000
1	-1.652643000	0.787719000	3.647767000
1	0.025733000	0.759631000	4.177240000
6	-3.142186000	-0.942105000	-0.864946000
1	-3.058762000	-0.236423000	-1.693172000
1	-4.206071000	-1.201196000	-0.738838000
6	-2.363572000	-2.222735000	-1.273106000
6	-0.565662000	3.155960000	-1.228050000
6	-0.257710000	3.108652000	0.286862000
1	0.812477000	2.924374000	0.395729000
1	-0.488010000	4.085808000	0.747532000
6	-1.809892000	4.001323000	-1.569446000
1	-1.692385000	5.035723000	-1.213229000
1	-2.736689000	3.603260000	-1.148001000
1	-1.943331000	4.035364000	-2.655320000
6	0.650799000	3.834348000	-1.895411000
1	0.486195000	3.922881000	-2.973804000
1	1.555111000	3.238681000	-1.743764000
1	0.815551000	4.846341000	-1.493515000
6	-2.592295000	-2.432513000	-2.780122000
1	-2.074660000	-3.329963000	-3.127042000
1	-2.222900000	-1.589384000	-3.367863000
1	-3.666532000	-2.555509000	-2.970606000
6	-2.779299000	-3.501575000	-0.535263000
1	-3.813694000	-3.749092000	-0.808475000
1	-2.731358000	-3.427117000	0.550951000
1	-2.138704000	-4.335986000	-0.830089000
7	1.576774000	0.289537000	0.035992000
6	2.509818000	-0.466768000	0.168589000
6	3.973286000	-0.380164000	0.052464000
6	4.526050000	0.896254000	-0.167915000
6	4.831419000	-1.486920000	0.136906000

6	5.902629000	1.059274000	-0.288124000
1	3.856842000	1.746260000	-0.250513000
6	6.210804000	-1.315999000	0.011273000
1	4.401287000	-2.467810000	0.289251000
6	6.752703000	-0.047220000	-0.197215000
1	6.313824000	2.051021000	-0.458409000
1	6.863448000	-2.183012000	0.073502000
1	7.827832000	0.080241000	-0.293820000
8	-0.012594000	-3.024587000	-0.087567000
8	0.134215000	-1.985892000	-2.398955000
1	2.143467000	-2.115271000	1.594125000
8	2.187044000	-2.172746000	0.624770000
1	1.022469000	-2.669231000	0.246639000

## Gas Phase DFT Studies optimized coordinates for Catalyst L<sup>3</sup>RuPPh<sub>3</sub> and derivatives

**Table S21 Optimized coordinates for L<sup>3</sup>RuPPh<sub>3</sub> (gas Phase)**

Z	x	y	z
44	-0.870029000	-0.075584000	-0.227489000
16	-0.733696000	0.769351000	-2.532695000
16	-1.049653000	-1.336618000	1.821651000
16	-1.403421000	2.023355000	0.691583000
15	1.567435000	0.238551000	0.103139000
7	-3.076469000	-0.127914000	-0.611002000
7	-1.034610000	-2.099823000	-1.232731000
6	-2.470666000	1.357261000	-2.627066000
1	-2.394533000	2.316735000	-2.109776000
1	-2.755780000	1.523905000	-3.671822000
6	-3.476923000	0.426979000	-1.954192000
1	-4.427565000	0.963282000	-1.844671000
1	-3.678455000	-0.416207000	-2.620427000
6	-3.416993000	-1.583043000	-0.557131000
1	-4.459761000	-1.746855000	-0.875377000
1	-3.328728000	-1.872354000	0.491887000
6	-2.490373000	-2.411279000	-1.436632000
1	-2.727151000	-2.252424000	-2.491385000
1	-2.670245000	-3.476396000	-1.247890000
6	-0.357549000	-2.041625000	-2.560169000
1	-0.536204000	-2.974738000	-3.121852000
1	0.713122000	-1.970573000	-2.375015000
6	-0.787534000	-0.856907000	-3.433872000
1	-1.790137000	-0.980931000	-3.851508000
1	-0.095896000	-0.785685000	-4.278496000
6	-3.802018000	0.528380000	0.539446000
1	-3.673620000	-0.168802000	1.368662000
1	-4.870990000	0.588380000	0.280530000
6	-3.306763000	1.902656000	1.022525000
6	-0.687243000	-3.121405000	1.131324000
6	-0.362155000	-3.128363000	-0.378808000
1	0.704916000	-2.958715000	-0.509454000
1	-0.577816000	-4.130676000	-0.790626000
6	-1.860498000	-4.037466000	1.504568000
1	-1.579421000	-5.080120000	1.302385000

1	-2.779137000	-3.824109000	0.955279000
1	-2.100778000	-3.939131000	2.565142000
6	0.558015000	-3.601151000	1.898921000
1	0.325788000	-3.721948000	2.961618000
1	1.383103000	-2.886421000	1.827213000
1	0.905796000	-4.572567000	1.517566000
6	-3.516434000	1.976391000	2.542719000
1	-3.139517000	2.922858000	2.937608000
1	-3.004292000	1.157545000	3.052953000
1	-4.589228000	1.905419000	2.769816000
6	-4.007487000	3.088464000	0.346700000
1	-5.070862000	3.075053000	0.621641000
1	-3.936548000	3.068496000	-0.743234000
1	-3.578796000	4.037240000	0.678147000
6	2.590246000	-0.778744000	-1.087316000
6	2.889509000	-0.229943000	-2.348784000
1	2.619106000	0.798717000	-2.564699000
6	3.545368000	-0.980201000	-3.326269000
1	3.767378000	-0.526986000	-4.289042000
6	3.930453000	-2.297304000	-3.065716000
1	4.450001000	-2.878246000	-3.822888000
6	3.649834000	-2.855352000	-1.818479000
1	3.951985000	-3.875385000	-1.595243000
6	2.982491000	-2.106793000	-0.844357000
1	2.778905000	-2.567734000	0.115218000
6	2.276677000	-0.106420000	1.784721000
6	3.491880000	-0.770722000	2.022502000
1	4.081292000	-1.158056000	1.199077000
6	3.976701000	-0.926071000	3.323415000
1	4.917751000	-1.445648000	3.485779000
6	3.263673000	-0.406165000	4.404211000
1	3.641849000	-0.525777000	5.416268000
6	2.069502000	0.278402000	4.175011000
1	1.512973000	0.701426000	5.006823000
6	1.572665000	0.426673000	2.879085000
1	0.654991000	0.985466000	2.717559000
6	2.367114000	1.894809000	-0.232289000
6	3.739638000	2.046419000	0.042054000
1	4.302412000	1.231337000	0.484967000
6	4.394819000	3.241936000	-0.239892000
1	5.454291000	3.339498000	-0.016835000
6	3.690434000	4.312767000	-0.798992000
1	4.200146000	5.248639000	-1.013915000
6	2.331162000	4.173487000	-1.065985000
1	1.765371000	5.002760000	-1.482072000
6	1.669054000	2.971606000	-0.787924000
1	0.602141000	2.911539000	-0.961913000
8	-0.781719000	2.423485000	1.996449000
8	-1.347558000	3.095750000	-0.381402000
8	-2.509702000	-1.434402000	2.370201000

**Table S22 Optimized coordinates for L<sup>3</sup>Ru(PhCN) (gas Phase)**

Z	x	y	z
44	-0.457780000	0.099161000	0.297221000
16	-0.761270000	-0.597136000	2.629407000
16	-0.233140000	1.117464000	-1.866226000
16	0.142257000	-2.048892000	-0.369543000
7	-2.496203000	-0.565999000	-0.001812000
7	-1.433727000	1.988053000	0.920903000
6	-2.176062000	-1.714557000	2.281681000
1	-1.651558000	-2.612061000	1.945788000
1	-2.724729000	-1.934951000	3.203940000
6	-3.135903000	-1.173387000	1.221516000
1	-3.804525000	-1.983799000	0.905515000
1	-3.774802000	-0.411629000	1.676771000
6	-3.209129000	0.704719000	-0.369496000
1	-4.299245000	0.544540000	-0.395278000
1	-2.870935000	0.954642000	-1.378918000
6	-2.897470000	1.848704000	0.603628000
1	-3.434191000	1.704970000	1.545351000
1	-3.278624000	2.785319000	0.179371000
6	-1.230500000	2.166428000	2.388889000
1	-1.794847000	3.041513000	2.754262000
1	-0.167864000	2.377023000	2.533284000
6	-1.600468000	0.944898000	3.236953000
1	-2.678880000	0.771227000	3.272859000
1	-1.273177000	1.126115000	4.265555000
6	-2.526179000	-1.488605000	-1.204445000
1	-2.368892000	-0.823962000	-2.055694000
1	-3.534556000	-1.925325000	-1.275478000
6	-1.468700000	-2.618720000	-1.291299000
6	-0.519319000	2.962195000	-1.316231000
6	-0.760831000	3.114745000	0.202559000
1	0.211931000	3.214865000	0.689809000
1	-1.318425000	4.048913000	0.392618000
6	-1.655399000	3.539925000	-2.167753000
1	-1.753373000	4.615589000	-1.965901000
1	-2.620574000	3.064624000	-1.977522000
1	-1.447505000	3.402341000	-3.231115000
6	0.793532000	3.690384000	-1.654092000
1	0.973647000	3.677787000	-2.733486000
1	1.649337000	3.210283000	-1.165969000
1	0.759322000	4.740292000	-1.327986000
6	-1.112230000	-2.813979000	-2.772865000
1	-0.340351000	-3.579650000	-2.883867000
1	-0.744275000	-1.887363000	-3.219283000
1	-2.003249000	-3.133708000	-3.330724000
6	-1.941037000	-3.950373000	-0.694163000
1	-2.776247000	-4.338611000	-1.293101000
1	-2.278233000	-3.864334000	0.341788000
1	-1.135776000	-4.689344000	-0.706905000
7	1.521547000	0.522211000	0.523642000
6	2.684478000	0.465065000	0.497601000
6	4.081016000	0.199613000	0.369484000
6	5.050489000	1.046068000	0.934657000
6	4.458359000	-0.954974000	-0.345813000

6	6.399162000	0.736559000	0.783295000
1	4.742271000	1.930879000	1.483400000
6	5.812830000	-1.247156000	-0.485524000
1	3.684094000	-1.590311000	-0.769654000
6	6.780176000	-0.407171000	0.074984000
1	7.153442000	1.386670000	1.217562000
1	6.113666000	-2.134856000	-1.034069000
1	7.834382000	-0.643755000	-0.039749000
8	0.216015000	-2.976344000	0.821862000
8	1.277850000	-2.193044000	-1.339587000
8	-1.415451000	0.811620000	-2.839729000

**Table S23 Optimized coordinates for L<sup>3</sup>Ru(H<sub>2</sub>O) (gas Phase)**

Z	x	y	z
44	-0.052371000	0.236484000	-0.514775000
16	0.810494000	2.492231000	-0.850525000
16	-1.252655000	-1.806356000	-0.175454000
16	1.946294000	-0.736698000	-0.968930000
7	0.629961000	0.401608000	1.498381000
7	-1.875273000	1.238607000	0.272055000
6	1.953006000	2.415697000	0.591699000
1	2.805165000	1.886313000	0.158924000
1	2.265688000	3.424601000	0.881959000
6	1.364839000	1.684665000	1.799449000
1	2.172085000	1.473820000	2.511856000
1	0.669459000	2.352858000	2.314464000
6	-0.638407000	0.338089000	2.303708000
1	-0.439341000	0.578260000	3.360374000
1	-0.979931000	-0.698757000	2.241935000
6	-1.711560000	1.294389000	1.766109000
1	-1.474686000	2.325871000	2.041807000
1	-2.664664000	1.062795000	2.256596000
6	-1.946635000	2.615533000	-0.295786000
1	-2.766514000	3.187518000	0.172009000
1	-2.189924000	2.505933000	-1.356059000
6	-0.649863000	3.423536000	-0.176119000
1	-0.432006000	3.718455000	0.853648000
1	-0.759620000	4.345996000	-0.754776000
6	1.447896000	-0.844870000	1.805030000
1	0.703008000	-1.639576000	1.882908000
1	1.925792000	-0.704133000	2.786160000
6	2.518598000	-1.313249000	0.777269000
6	-3.042069000	-1.068920000	-0.021534000
6	-3.074828000	0.467618000	-0.180189000
1	-3.170009000	0.695717000	-1.244932000
1	-3.975414000	0.866964000	0.319297000
6	-3.648385000	-1.553529000	1.300227000
1	-3.152336000	-1.139554000	2.181317000
1	-3.571392000	-2.639764000	1.382769000
1	-4.709541000	-1.272139000	1.338740000
6	-3.825572000	-1.677245000	-1.198280000
1	-3.889782000	-2.764958000	-1.094823000
1	-3.335415000	-1.457852000	-2.153450000
1	-4.850190000	-1.279571000	-1.238029000
6	2.548870000	-2.849080000	0.784374000

1	3.270409000	-3.221901000	0.052030000
1	1.567509000	-3.266152000	0.548481000
1	2.846877000	-3.210569000	1.777855000
6	3.920587000	-0.758845000	1.059595000
1	3.944251000	0.331302000	1.134915000
1	4.617260000	-1.039438000	0.266065000
1	4.288559000	-1.173449000	2.007639000
1	0.136357000	-1.130323000	-2.667431000
8	-0.454632000	-0.331651000	-2.706892000
1	0.050123000	0.294015000	-3.253899000
8	3.030290000	0.214173000	-1.416434000
8	1.765198000	-1.937464000	-1.875819000
8	-0.996511000	-2.511138000	1.195885000

**Table S24 Optimized coordinates for L<sup>3</sup>Ru (gas Phase)**

Z	x	y	z
44	-0.077912000	0.228793000	-0.618178000
16	0.758128000	2.530129000	-0.908652000
16	-1.246527000	-1.780768000	-0.442462000
16	1.973356000	-0.716858000	-1.081954000
7	0.578915000	0.326448000	1.382042000
7	-1.918894000	1.200891000	0.179562000
6	1.880172000	2.397667000	0.542506000
1	2.736966000	1.890635000	0.092326000
1	2.181184000	3.395443000	0.879688000
6	1.296727000	1.616439000	1.720774000
1	2.104090000	1.388683000	2.426281000
1	0.590435000	2.254168000	2.258197000
6	-0.693200000	0.230518000	2.175692000
1	-0.494405000	0.427454000	3.240692000
1	-1.030276000	-0.803011000	2.077045000
6	-1.762736000	1.208038000	1.672364000
1	-1.519445000	2.227011000	1.983510000
1	-2.718100000	0.965947000	2.153115000
6	-2.005925000	2.594213000	-0.347007000
1	-2.833571000	3.140888000	0.136297000
1	-2.248411000	2.514125000	-1.410517000
6	-0.718058000	3.413006000	-0.205055000
1	-0.505023000	3.682638000	0.832803000
1	-0.843763000	4.350483000	-0.755660000
6	1.406093000	-0.911883000	1.678156000
1	0.681058000	-1.728956000	1.673774000
1	1.816431000	-0.803710000	2.693824000
6	2.534466000	-1.279654000	0.688658000
6	-3.051607000	-1.112861000	-0.172263000
6	-3.106995000	0.424519000	-0.297816000
1	-3.200820000	0.677445000	-1.358351000
1	-4.017275000	0.798131000	0.202633000
6	-3.595456000	-1.649135000	1.156724000
1	-4.673651000	-1.449555000	1.217372000
1	-3.122010000	-1.206724000	2.035935000
1	-3.432472000	-2.726851000	1.223439000
6	-3.878630000	-1.709444000	-1.326116000
1	-3.909362000	-2.800844000	-1.249701000
1	-3.447445000	-1.456069000	-2.301506000

1	-4.913539000	-1.339276000	-1.302850000
6	2.662989000	-2.810437000	0.671138000
1	3.435204000	-3.119775000	-0.037910000
1	1.722633000	-3.283500000	0.380306000
1	2.943083000	-3.174159000	1.669575000
6	3.892368000	-0.651184000	1.024224000
1	3.856848000	0.435884000	1.128850000
1	4.621004000	-0.870118000	0.239990000
1	4.264407000	-1.070197000	1.969237000
8	2.990972000	0.333496000	-1.457358000
8	1.955432000	-1.935009000	-1.945343000
8	-0.965949000	-2.667652000	0.803628000

**Table S25 Optimized coordinates for L<sup>3</sup>Ru(PhCONH<sub>2</sub>) (gas Phase):**

Z	x	y	z
44	-0.595374000	-0.158688000	-0.327416000
16	-1.897805000	-0.729673000	-2.323019000
16	0.796609000	-0.000354000	1.614049000
16	-1.077946000	2.073211000	-0.503302000
7	-2.444972000	-0.302241000	0.756000000
7	-0.513629000	-2.354552000	0.023018000
6	-3.507226000	-0.225095000	-1.593817000
1	-3.481406000	0.854038000	-1.763466000
1	-4.335907000	-0.662554000	-2.161164000
6	-3.649996000	-0.575602000	-0.112204000
1	-4.509671000	-0.029890000	0.295773000
1	-3.892220000	-1.637930000	-0.021638000
6	-2.219600000	-1.463598000	1.679136000
1	-3.157559000	-1.746838000	2.183622000
1	-1.515406000	-1.109312000	2.434514000
6	-1.661617000	-2.683073000	0.935639000
1	-2.447028000	-3.155636000	0.339946000
1	-1.352442000	-3.435699000	1.670536000
6	-0.667632000	-3.045042000	-1.290956000
1	-0.741642000	-4.137022000	-1.148163000
1	0.246410000	-2.845809000	-1.856775000
6	-1.872232000	-2.575778000	-2.115748000
1	-2.827659000	-2.892388000	-1.689546000
1	-1.805283000	-3.022091000	-3.112647000
6	-2.586663000	0.952316000	1.598885000
1	-1.830482000	0.833377000	2.377718000
1	-3.586347000	0.943866000	2.059713000
6	-2.342471000	2.331212000	0.927552000
6	1.318609000	-1.869833000	1.791823000
6	0.821022000	-2.711353000	0.599418000
1	1.528670000	-2.5955595000	-0.225019000
1	0.820086000	-3.779481000	0.881530000
6	0.858186000	-2.385110000	3.161996000
1	1.301833000	-3.373991000	3.340416000
1	-0.223775000	-2.478375000	3.265526000
1	1.187800000	-1.705798000	3.950895000
6	2.857939000	-1.888049000	1.775132000
1	3.233599000	-2.918518000	1.852752000
1	3.254725000	-1.321325000	2.623459000
1	3.264611000	-1.450484000	0.860221000

6	-1.697761000	3.258201000	1.969405000
1	-1.472902000	4.233419000	1.528935000
1	-0.772637000	2.829973000	2.361366000
1	-2.390104000	3.408599000	2.808892000
6	-3.614129000	2.979885000	0.366307000
1	-4.289409000	3.227146000	1.196334000
1	-4.155370000	2.335448000	-0.331107000
1	-3.375633000	3.901436000	-0.170367000
6	2.445864000	-0.192129000	-1.680300000
7	1.188627000	0.470654000	-1.679633000
1	0.729844000	0.331711000	-2.577770000
8	2.544289000	-1.286374000	-2.220375000
6	3.588082000	0.497255000	-1.018455000
6	4.861494000	-0.073280000	-1.189735000
6	3.448428000	1.673561000	-0.260342000
6	5.980964000	0.523776000	-0.620172000
1	4.946995000	-0.981148000	-1.777635000
6	4.576098000	2.261869000	0.312903000
1	2.477093000	2.129014000	-0.087601000
6	5.838445000	1.693661000	0.133428000
1	6.963076000	0.081389000	-0.761899000
1	4.462296000	3.165720000	0.903948000
1	6.712011000	2.160875000	0.580416000
1	1.224076000	1.468928000	-1.453583000
8	-1.864275000	2.408240000	-1.751152000
8	0.114332000	2.975813000	-0.282149000
8	0.031590000	0.310630000	2.942360000

**Table S26 Optimized coordinates for L<sup>3</sup>Ru(PhC(OH)NH) (gas Phase)**

Z	x	y	z
44	-0.541495000	-0.186543000	-0.325679000
16	-2.003760000	-0.528946000	-2.301283000
16	0.887914000	-0.271723000	1.579739000
16	-0.788729000	2.126396000	-0.396748000
7	-2.393553000	-0.149492000	0.811528000
7	-0.753757000	-2.389285000	-0.056135000
6	-3.503375000	0.152692000	-1.496055000
1	-3.332562000	1.224852000	-1.619031000
1	-4.400660000	-0.142509000	-2.050910000
6	-3.640826000	-0.256045000	-0.030854000
1	-4.431693000	0.349814000	0.428930000
1	-3.987643000	-1.291938000	0.014558000
6	-2.281564000	-1.357365000	1.694240000
1	-3.234892000	-1.547438000	2.214219000
1	-1.523229000	-1.109922000	2.442107000
6	-1.887113000	-2.612393000	0.907378000
1	-2.743135000	-2.989299000	0.341786000
1	-1.623944000	-3.407345000	1.614585000
6	-1.066098000	-3.015835000	-1.372389000
1	-1.278814000	-4.091750000	-1.249439000
1	-0.163102000	-2.933087000	-1.983899000
6	-2.230480000	-2.363854000	-2.126242000
1	-3.195209000	-2.555186000	-1.649447000
1	-2.281208000	-2.797051000	-3.130113000
6	-2.395300000	1.075384000	1.697791000

1	-1.629627000	0.863563000	2.446659000
1	-3.376120000	1.140488000	2.195578000
6	-2.049549000	2.434378000	1.049687000
6	1.220776000	-2.190317000	1.615630000
6	0.557346000	-2.919916000	0.430297000
1	1.226694000	-2.844567000	-0.430374000
1	0.448900000	-3.992959000	0.670173000
6	0.802301000	-2.731764000	2.987888000
1	1.117298000	-3.780786000	3.075964000
1	-0.272205000	-2.681981000	3.171896000
1	1.278174000	-2.156035000	3.784615000
6	2.744164000	-2.351728000	1.470784000
1	3.026346000	-3.414741000	1.444652000
1	3.260086000	-1.887433000	2.317015000
1	3.115060000	-1.878566000	0.556536000
6	-1.343411000	3.287582000	2.115062000
1	-1.049155000	4.255104000	1.700966000
1	-0.448578000	2.789135000	2.494447000
1	-2.025244000	3.461747000	2.959250000
6	-3.261485000	3.201991000	0.506451000
1	-3.909484000	3.495984000	1.343483000
1	-3.864491000	2.625237000	-0.198676000
1	-2.941169000	4.107308000	-0.015334000
6	2.384019000	0.030014000	-1.959896000
7	1.136367000	-0.192342000	-1.727701000
1	0.704631000	-0.422416000	-2.624555000
8	2.824296000	-0.244071000	-3.225237000
6	3.413261000	0.527709000	-1.022490000
6	4.707672000	-0.025936000	-1.079607000
6	3.141154000	1.584205000	-0.141562000
6	5.713973000	0.457801000	-0.247101000
1	4.915399000	-0.857595000	-1.749475000
6	4.163210000	2.070979000	0.674999000
1	2.153376000	2.040473000	-0.119841000
6	5.441368000	1.511734000	0.630090000
1	6.705343000	0.014695000	-0.282471000
1	3.950977000	2.895457000	1.349294000
1	6.227376000	1.896214000	1.274780000
8	-1.557015000	2.523916000	-1.638225000
8	0.384758000	3.014850000	-0.091656000
8	0.159054000	0.017896000	2.932596000
1	3.689063000	0.179991000	-3.353662000

**Table S27 Optimized coordinates for L<sup>3</sup>RuTS (gas Phase):**

Z	x	y	z
44	-0.460013000	0.087294000	0.178495000
16	-0.233133000	-0.934200000	2.408486000
16	-0.652200000	1.415915000	-1.797291000
16	-0.471463000	-1.813738000	-1.073196000
7	-2.608735000	-0.248923000	0.460824000
7	-0.847360000	1.937052000	1.294367000
6	-1.863940000	-1.764860000	2.409446000
1	-1.645227000	-2.683623000	1.863448000
1	-2.161235000	-2.033702000	3.429192000
6	-2.971267000	-0.943250000	1.745424000
1	-3.833866000	-1.598408000	1.567387000
1	-3.312482000	-0.183471000	2.453794000
6	-3.135407000	1.156047000	0.469810000
1	-4.197319000	1.176713000	0.767325000
1	-3.052513000	1.510031000	-0.562060000
6	-2.343155000	2.067513000	1.420220000
1	-2.612286000	1.858151000	2.459436000
1	-2.642418000	3.106004000	1.237143000
6	-0.213127000	1.856053000	2.643591000
1	-0.485904000	2.734291000	3.252418000
1	0.867051000	1.887115000	2.482920000
6	-0.549954000	0.584693000	3.425704000
1	-1.586446000	0.562665000	3.771871000
1	0.086842000	0.538381000	4.314181000
6	-3.128846000	-0.970591000	-0.755997000
1	-3.092655000	-0.222335000	-1.551491000
1	-4.177736000	-1.259840000	-0.583268000
6	-2.346281000	-2.215338000	-1.259368000
6	-0.441601000	3.155735000	-0.973945000
6	-0.194237000	3.061776000	0.545508000
1	0.875209000	2.906013000	0.697670000
1	-0.467985000	4.017197000	1.026564000
6	-1.651908000	4.019101000	-1.346208000
1	-1.491583000	5.045515000	-0.988750000
1	-2.591349000	3.651403000	-0.927609000
1	-1.785746000	4.045917000	-2.430088000
6	0.827623000	3.747399000	-1.613087000
1	0.680560000	3.900975000	-2.686753000
1	1.681767000	3.074278000	-1.482200000
1	1.079877000	4.718491000	-1.162578000
6	-2.611338000	-2.331023000	-2.771356000
1	-2.073321000	-3.182273000	-3.195625000
1	-2.299239000	-1.429772000	-3.302774000
1	-3.686296000	-2.481820000	-2.935206000
6	-2.718728000	-3.544260000	-0.589872000
1	-3.753857000	-3.795059000	-0.856278000
1	-2.651008000	-3.530879000	0.498338000
1	-2.070207000	-4.348521000	-0.945500000
7	1.616716000	0.287450000	0.044752000
6	2.556011000	-0.466496000	0.133484000
6	4.016991000	-0.380767000	-0.004750000
6	4.574674000	0.904066000	-0.151046000
6	4.867682000	-1.496522000	-0.012536000

6	5.949423000	1.066045000	-0.292058000
1	3.912205000	1.763426000	-0.156799000
6	6.244907000	-1.326263000	-0.159186000
1	4.433931000	-2.482325000	0.088703000
6	6.791876000	-0.049827000	-0.295794000
1	6.364920000	2.064291000	-0.403112000
1	6.891954000	-2.199479000	-0.169143000
1	7.865484000	0.076778000	-0.408204000
8	0.049781000	-3.029960000	-0.167629000
8	0.127981000	-1.881545000	-2.432178000
1	2.195503000	-2.155212000	1.521943000
8	2.243030000	-2.190021000	0.551627000
1	1.099815000	-2.666598000	0.167712000
8	-2.107774000	1.411860000	-2.367055000

## Optimized Coordinates for Solution Phase (n,n'-dimethylformamide (DMF)) DFT Studies for benzonitrile hydration with water(Å)

**Table S28 Optimized coordinates for benzonitrile (DMF phase)**

Z	x	y	z
6	2.042493000	-0.000372000	-0.000096000
7	3.206562000	0.000193000	0.000110000
6	0.608770000	-0.000182000	-0.000050000
6	-0.090308000	-1.220553000	-0.000027000
6	-0.089967000	1.220385000	-0.000027000
6	-1.483298000	-1.212573000	0.000015000
1	0.457824000	-2.156969000	-0.000044000
6	-1.482959000	1.212794000	0.000015000
1	0.458426000	2.156647000	-0.000044000
6	-2.179099000	0.000208000	0.000036000
1	-2.025711000	-2.153025000	0.000032000
1	-2.025110000	2.153397000	0.000031000
1	-3.265157000	0.000360000	0.000069000

**Table S29 Optimized coordinates for water (DMF phase)**

Z	x	y	z
8	0.000000000	0.000000000	0.120461000
1	0.000000000	0.759875000	-0.481845000
1	0.000000000	-0.759875000	-0.481845000

**Table S30 Optimized coordinates for benziminol (DMF phase)**

Z	x	y	z
6	0.224137000	0.042821000	-0.000490000
6	-0.448940000	-1.185422000	0.100490000
6	-0.526468000	1.224317000	-0.108244000
6	-1.843303000	-1.226934000	0.108875000
1	0.123299000	-2.102657000	0.180119000
6	-1.919347000	1.180176000	-0.105000000
1	-0.026321000	2.182660000	-0.214797000
6	-2.581973000	-0.045709000	0.006731000
1	-2.352273000	-2.182749000	0.194812000
1	-2.487007000	2.101768000	-0.194820000

1	-3.667797000	-0.079225000	0.010210000
7	2.480899000	1.091169000	0.219200000
1	1.948886000	1.937147000	0.421090000
6	1.712413000	0.091174000	0.011962000
8	2.270046000	-1.122501000	-0.231444000
1	3.235447000	-0.997653000	-0.165410000

**Table S31 Optimized coordinates for benzamide (DMF phase)**

Z	x	y	z
6	-0.221875000	-0.020521000	-0.013835000
6	0.514863000	-1.206711000	0.114833000
6	0.460387000	1.199191000	-0.141492000
6	1.907985000	-1.175050000	0.138660000
1	-0.022736000	-2.145317000	0.199168000
6	1.855735000	1.229554000	-0.125986000
1	-0.087084000	2.126433000	-0.283003000
6	2.581587000	0.044479000	0.019387000
1	2.468793000	-2.099006000	0.248260000
1	2.374767000	2.177677000	-0.233690000
1	3.667633000	0.070574000	0.034044000
7	-2.422051000	1.013250000	0.217432000
1	-3.424303000	0.917866000	0.319299000
1	-1.995877000	1.796668000	0.691515000
6	-1.720333000	-0.131019000	-0.031395000
8	-2.287117000	-1.197147000	-0.282331000

**Table S32 Optimized coordinates for transition state for benzonitrile hydration with Water (DMF phase)**

Z	x	y	z
6	-1.581536000	-0.409345000	-0.041586000
7	-2.492358000	-1.213809000	-0.111203000
6	-0.150943000	-0.158212000	-0.015831000
6	0.698869000	-1.278334000	0.050349000
6	0.390491000	1.134132000	-0.071085000
6	2.079208000	-1.096932000	0.063606000
1	0.269891000	-2.274377000	0.091642000
6	1.774214000	1.304198000	-0.058118000
1	-0.276602000	1.986440000	-0.128139000
6	2.618625000	0.192802000	0.009685000
1	2.734340000	-1.961274000	0.116756000
1	2.192597000	2.305203000	-0.101904000
1	3.696002000	0.329960000	0.020787000
1	-2.563714000	1.417655000	0.945770000
8	-2.554564000	1.077260000	0.028809000
1	-3.143059000	-0.054878000	-0.019089000

**Table S33 Optimized coordinates for PPh<sub>3</sub> (DMF phase)**

Z	x	y	z
15	-0.006942000	-0.004684000	-1.199961000
6	-1.612246000	-0.461851000	-0.396246000
6	-2.427300000	-1.382278000	-1.078014000
6	-2.068975000	0.066162000	0.822803000
6	-3.657950000	-1.778197000	-0.549434000
1	-2.099015000	-1.789328000	-2.031820000
6	-3.304149000	-0.323068000	1.348115000
1	-1.462318000	0.786533000	1.363843000
6	-4.099124000	-1.247796000	0.665679000
1	-4.273499000	-2.492367000	-1.089671000
1	-3.643279000	0.096931000	2.291542000
1	-5.060628000	-1.547115000	1.074728000
6	0.401033000	1.616052000	-0.400512000
6	1.193892000	1.757759000	0.749579000
6	-0.102706000	2.775242000	-1.017010000
6	1.468868000	3.024401000	1.272323000
1	1.599540000	0.877482000	1.238934000
6	0.161864000	4.039756000	-0.488638000
1	-0.704318000	2.687731000	-1.919216000
6	0.951889000	4.167241000	0.657544000
1	2.085876000	3.116339000	2.162475000
1	-0.239640000	4.923995000	-0.976537000
1	1.167410000	5.151156000	1.065084000
6	1.204866000	-1.164796000	-0.412613000
6	2.468663000	-1.273969000	-1.019934000
6	0.932297000	-1.954076000	0.715982000
6	3.441354000	-2.128694000	-0.499183000
1	2.693119000	-0.685812000	-1.907433000
6	1.901921000	-2.820123000	1.230103000
1	-0.038328000	-1.893323000	1.197365000
6	3.158811000	-2.906289000	0.627965000
1	4.414833000	-2.192843000	-0.977019000
1	1.674350000	-3.423719000	2.105365000
1	3.911966000	-3.578252000	1.030743000

## Optimized Coordinates for Solution Phase (DMF) DFT Studies for Catalyst L<sup>1</sup>RuPPh<sub>3</sub> and derivatives

**Table S34 Optimized coordinates for L<sup>1</sup>RuPPh<sub>3</sub> (DMF phase)**

Z	x	y	z
44	-0.919412000	-0.004576000	-0.111185000
16	-0.890722000	0.683823000	-2.399416000
16	-1.117062000	-1.235663000	2.033178000
16	-1.358201000	2.247640000	0.838097000
15	1.456910000	0.250537000	0.070257000
7	-3.154359000	0.030128000	-0.357493000
7	-1.225394000	-2.058878000	-0.938172000
6	-2.601083000	1.346002000	-2.499302000
1	-2.478201000	2.353922000	-2.098707000
1	-2.916021000	1.425025000	-3.544557000
6	-3.618429000	0.536009000	-1.701132000

1	-4.523358000	1.138421000	-1.563532000
1	-3.921023000	-0.325149000	-2.300274000
6	-3.560916000	-1.398347000	-0.215846000
1	-4.621738000	-1.533081000	-0.476529000
1	-3.424197000	-1.651940000	0.832167000
6	-2.705257000	-2.308457000	-1.084102000
1	-2.971877000	-2.181354000	-2.134144000
1	-2.926743000	-3.354730000	-0.847718000
6	-0.599867000	-2.129324000	-2.293929000
1	-0.851762000	-3.083946000	-2.782278000
1	0.480216000	-2.103462000	-2.154899000
6	-1.016857000	-0.985523000	-3.224312000
1	-2.033488000	-1.094291000	-3.608276000
1	-0.346866000	-0.971320000	-4.087792000
6	-3.755870000	0.786818000	0.789309000
1	-3.548734000	0.169133000	1.663465000
1	-4.849069000	0.826842000	0.651921000
6	-3.217249000	2.198180000	1.092763000
6	-0.919094000	-3.019251000	1.466978000
6	-0.582599000	-3.076207000	-0.045597000
1	0.489472000	-2.920425000	-0.161354000
1	-0.812053000	-4.083650000	-0.431198000
6	-2.156499000	-3.861462000	1.846372000
1	-1.999422000	-4.915519000	1.576897000
1	-3.080888000	-3.532371000	1.369310000
1	-2.315856000	-3.815247000	2.929015000
6	0.276069000	-3.648080000	2.215943000
1	0.066575000	-3.695255000	3.289952000
1	1.187676000	-3.060779000	2.080249000
1	0.466867000	-4.673748000	1.866917000
6	-3.528427000	2.477042000	2.579101000
1	-3.174125000	3.474029000	2.862577000
1	-3.042491000	1.744535000	3.231150000
1	-4.611777000	2.441291000	2.766378000
6	-3.899633000	3.309746000	0.270841000
1	-4.983875000	3.313670000	0.452708000
1	-3.740031000	3.212955000	-0.804691000
1	-3.507900000	4.288206000	0.569967000
6	2.490798000	-0.959748000	-0.904058000
6	2.760240000	-0.696264000	-2.260254000
1	2.460268000	0.250882000	-2.698130000
6	3.418214000	-1.632263000	-3.060683000
1	3.615523000	-1.400902000	-4.103972000
6	3.826751000	-2.855474000	-2.523199000
1	4.343338000	-3.582146000	-3.143861000
6	3.567162000	-3.133654000	-1.180327000
1	3.882568000	-4.078709000	-0.746597000
6	2.901873000	-2.198293000	-0.382362000
1	2.716060000	-2.439741000	0.658444000
6	2.248902000	0.275296000	1.758412000
6	3.546348000	-0.187374000	2.031393000
1	4.137876000	-0.660516000	1.255573000
6	4.102426000	-0.047845000	3.306640000
1	5.106131000	-0.419189000	3.496406000
6	3.376882000	0.570183000	4.326290000
1	3.810582000	0.681008000	5.316633000

6	2.090478000	1.047377000	4.062101000
1	1.517590000	1.533191000	4.848028000
6	1.528177000	0.895140000	2.793168000
1	0.525170000	1.260026000	2.595053000
6	2.196938000	1.847039000	-0.589656000
6	3.594765000	2.015012000	-0.608905000
1	4.244246000	1.217997000	-0.261853000
6	4.171462000	3.195878000	-1.073609000
1	5.253304000	3.299982000	-1.079725000
6	3.361339000	4.241518000	-1.528900000
1	3.809725000	5.162952000	-1.890794000
6	1.975745000	4.091140000	-1.510807000
1	1.334107000	4.897404000	-1.857217000
6	1.398636000	2.903141000	-1.045769000
1	0.320146000	2.810052000	-1.015898000

**Table S35 Optimized coordinates for L<sup>1</sup>Ru(PhCN) (DMF Phase)**

Z	x	y	z
44	-0.457102000	-0.161217000	0.077098000
16	-0.629104000	-1.373421000	2.127947000
16	-0.256138000	1.454847000	-1.782189000
16	-0.958714000	-2.135725000	-1.317249000
7	-2.625833000	0.009909000	0.182637000
7	-0.510673000	1.646262000	1.303820000
6	-2.410986000	-1.802028000	2.001470000
1	-2.385766000	-2.707117000	1.392893000
1	-2.811517000	-2.057810000	2.987168000
6	-3.254251000	-0.703262000	1.358169000
1	-4.214948000	-1.127549000	1.045831000
1	-3.489637000	0.044741000	2.117552000
6	-2.848496000	1.484175000	0.335409000
1	-3.900737000	1.699227000	0.573261000
1	-2.609511000	1.929905000	-0.627636000
6	-1.949389000	2.083685000	1.417292000
1	-2.312722000	1.805048000	2.407732000
1	-2.010881000	3.176046000	1.373750000
6	0.024985000	1.309274000	2.662872000
1	-0.097454000	2.164558000	3.344587000
1	1.095942000	1.130388000	2.544558000
6	-0.620327000	0.076215000	3.300294000
1	-1.645984000	0.253889000	3.630830000
1	-0.041301000	-0.209951000	4.182037000
6	-3.199640000	-0.426526000	-1.137737000
1	-2.861161000	0.330689000	-1.845286000
1	-4.298749000	-0.373479000	-1.081119000
6	-2.772567000	-1.804392000	-1.698345000
6	0.186783000	3.009897000	-0.816464000
6	0.373405000	2.691410000	0.689715000
1	1.388829000	2.314130000	0.827221000
1	0.283950000	3.621893000	1.273362000
6	-0.857137000	4.117119000	-1.071434000
1	-0.575506000	5.041595000	-0.547654000
1	-1.865955000	3.846834000	-0.752892000
1	-0.904473000	4.341771000	-2.142396000
6	1.544895000	3.544983000	-1.319691000

1	1.476957000	3.820561000	-2.377443000
1	2.331713000	2.791546000	-1.214758000
1	1.846751000	4.441834000	-0.758787000
6	-2.957403000	-1.727948000	-3.228955000
1	-2.686683000	-2.682634000	-3.692759000
1	-2.328721000	-0.946355000	-3.666231000
1	-4.004819000	-1.514481000	-3.488981000
6	-3.652303000	-2.964578000	-1.192854000
1	-4.703450000	-2.798863000	-1.468946000
1	-3.608787000	-3.101026000	-0.110750000
1	-3.331093000	-3.905303000	-1.653035000
7	1.538004000	-0.382993000	0.015884000
6	2.693313000	-0.546592000	-0.036523000
6	4.102682000	-0.760186000	-0.114946000
6	4.738607000	-1.617658000	0.805004000
6	4.857127000	-0.117938000	-1.117137000
6	6.112672000	-1.825610000	0.716852000
1	4.153008000	-2.111191000	1.573866000
6	6.230371000	-0.336298000	-1.191925000
1	4.362031000	0.540091000	-1.823832000
6	6.859967000	-1.187853000	-0.278468000
1	6.600924000	-2.487798000	1.425477000
1	6.810075000	0.158401000	-1.965379000
1	7.931143000	-1.354813000	-0.342675000

**Table S36 Optimized coordinates for L<sup>1</sup>Ru(H<sub>2</sub>O) (DMF Phase)**

Z	x	y	z
44	0.002746000	0.124487000	-0.621051000
16	0.884060000	2.297386000	-0.901036000
16	-1.344626000	-1.922108000	-0.355639000
16	2.060839000	-0.972553000	-1.425455000
7	0.977566000	0.118100000	1.272423000
7	-1.639999000	1.068566000	0.466520000
6	2.208014000	2.192450000	0.375022000
1	3.029467000	1.732997000	-0.176077000
1	2.516230000	3.193934000	0.690009000
6	1.789635000	1.360395000	1.584363000
1	2.679037000	1.069366000	2.153781000
1	1.194451000	1.987744000	2.250603000
6	-0.161039000	0.033238000	2.246831000
1	0.192873000	0.193180000	3.275942000
1	-0.552593000	-0.978401000	2.173349000
6	-1.265223000	1.043594000	1.926346000
1	-0.950404000	2.048024000	2.215576000
1	-2.145503000	0.818103000	2.537780000
6	-1.767962000	2.486079000	-0.005081000
1	-2.493502000	3.032673000	0.616614000
1	-2.166703000	2.444598000	-1.021091000
6	-0.448834000	3.260511000	-0.020651000
1	-0.088099000	3.506284000	0.980376000
1	-0.596336000	4.203164000	-0.553904000
6	1.788768000	-1.148322000	1.379561000
1	1.047189000	-1.946636000	1.408763000
1	2.320088000	-1.144210000	2.344658000
6	2.780582000	-1.482461000	0.238200000

6	-2.958423000	-1.185621000	0.283901000
6	-2.929049000	0.359494000	0.173435000
1	-3.159889000	0.619416000	-0.862220000
1	-3.725961000	0.784365000	0.804743000
6	-3.262301000	-1.692468000	1.708354000
1	-2.498124000	-1.428402000	2.441417000
1	-3.342869000	-2.784577000	1.703034000
1	-4.220468000	-1.287468000	2.062685000
6	-4.111673000	-1.669751000	-0.621037000
1	-4.186189000	-2.761749000	-0.590278000
1	-3.957043000	-1.369798000	-1.662510000
1	-5.073427000	-1.257909000	-0.283284000
6	2.967610000	-3.014437000	0.259565000
1	3.682107000	-3.320119000	-0.512335000
1	2.021854000	-3.532516000	0.072586000
1	3.359981000	-3.350793000	1.230828000
6	4.170854000	-0.851205000	0.446555000
1	4.149422000	0.239828000	0.470161000
1	4.842495000	-1.146807000	-0.366656000
1	4.614145000	-1.199429000	1.390375000
1	-1.426371000	-0.857920000	-2.362089000
8	-1.073378000	0.033851000	-2.618788000
1	-0.372737000	-0.154448000	-3.266994000

**Table S37 Optimized coordinates for L<sup>1</sup>Ru (DMF phase)**

Z	x	y	z
44	-0.039453000	0.070880000	-0.687078000
16	0.840420000	2.244887000	-1.061242000
16	-1.412083000	-1.861789000	-0.670602000
16	2.019536000	-1.044486000	-1.456035000
7	0.925285000	0.177044000	1.174663000
7	-1.702044000	1.063020000	0.321182000
6	2.158597000	2.221400000	0.225090000
1	2.995930000	1.752970000	-0.292971000
1	2.444367000	3.240962000	0.499569000
6	1.728310000	1.438371000	1.459525000
1	2.605053000	1.167696000	2.056473000
1	1.113674000	2.083972000	2.089447000
6	-0.223294000	0.108862000	2.145667000
1	0.127677000	0.314164000	3.166861000
1	-0.591275000	-0.913721000	2.114271000
6	-1.351004000	1.080011000	1.787166000
1	-1.073598000	2.099320000	2.063446000
1	-2.231767000	0.834069000	2.389653000
6	-1.814015000	2.469126000	-0.193785000
1	-2.544730000	3.035506000	0.403112000
1	-2.199979000	2.403023000	-1.213335000
6	-0.492624000	3.235951000	-0.216697000
1	-0.138923000	3.501204000	0.781662000
1	-0.631532000	4.167228000	-0.771634000
6	1.748271000	-1.081918000	1.343770000
1	1.012606000	-1.883467000	1.409044000
1	2.268406000	-1.021930000	2.312177000
6	2.747093000	-1.463861000	0.226688000
6	-3.008619000	-1.187764000	0.063049000

6	-2.994428000	0.356806000	0.018893000
1	-3.240094000	0.649592000	-1.004737000
1	-3.783564000	0.755964000	0.675267000
6	-3.256193000	-1.761116000	1.471982000
1	-4.208429000	-1.389427000	1.874989000
1	-2.471467000	-1.511942000	2.188527000
1	-3.316728000	-2.853329000	1.423874000
6	-4.177914000	-1.647884000	-0.832808000
1	-4.240711000	-2.741051000	-0.844231000
1	-4.049411000	-1.303027000	-1.863923000
1	-5.134755000	-1.261042000	-0.455122000
6	2.940453000	-2.992166000	0.324713000
1	3.656794000	-3.331476000	-0.431029000
1	1.996435000	-3.521427000	0.160961000
1	3.332756000	-3.279483000	1.311483000
6	4.132436000	-0.814052000	0.405769000
1	4.106227000	0.276363000	0.367125000
1	4.808201000	-1.151291000	-0.387475000
1	4.573731000	-1.106977000	1.368962000

**Table S38 Optimized coordinates for L<sup>1</sup>Ru(PhCONH<sub>2</sub>) (DMF Phase)**

Z	x	y	z
44	-0.813837000	0.006333000	0.187874000
16	-1.439698000	-1.023458000	2.235473000
16	0.171810000	1.421046000	-1.430109000
16	-0.109753000	-2.135725000	-0.810822000
7	-2.734048000	-0.526478000	-0.479334000
7	-1.771523000	1.808292000	0.954007000
6	-2.849274000	-2.024803000	1.605021000
1	-2.362209000	-2.932366000	1.246762000
1	-3.527032000	-2.291589000	2.421191000
6	-3.607054000	-1.299851000	0.499230000
1	-4.217694000	-2.012995000	-0.063744000
1	-4.300889000	-0.590021000	0.952491000
6	-3.370830000	0.812142000	-0.742325000
1	-4.444025000	0.690494000	-0.946669000
1	-2.898484000	1.204198000	-1.639816000
6	-3.179644000	1.795043000	0.416072000
1	-3.860411000	1.554207000	1.234961000
1	-3.462505000	2.796435000	0.075006000
6	-1.793470000	1.742519000	2.454430000
1	-2.395360000	2.568331000	2.862251000
1	-0.764138000	1.885639000	2.790014000
6	-2.314790000	0.422462000	3.018365000
1	-3.389397000	0.292965000	2.875656000
1	-2.124021000	0.396507000	4.094265000
6	-2.585549000	-1.237835000	-1.806184000
1	-2.211646000	-0.474025000	-2.487780000
1	-3.588559000	-1.534129000	-2.149475000
6	-1.619666000	-2.443237000	-1.889269000
6	-0.446854000	3.113068000	-0.884811000
6	-0.986990000	3.029696000	0.560468000
1	-0.120456000	3.032542000	1.225996000
1	-1.582681000	3.927106000	0.789667000
6	-1.465716000	3.680874000	-1.891565000

1	-1.791658000	4.683293000	-1.581688000
1	-2.356532000	3.060988000	-2.005693000
1	-1.003043000	3.769658000	-2.879985000
6	0.759812000	4.074227000	-0.856572000
1	0.455244000	5.074805000	-0.519465000
1	1.187952000	4.175870000	-1.859290000
1	1.544362000	3.708497000	-0.186288000
6	-1.176821000	-2.541574000	-3.364401000
1	-0.502343000	-3.393527000	-3.501060000
1	-0.650028000	-1.635837000	-3.680957000
1	-2.042064000	-2.688716000	-4.027518000
6	-2.289113000	-3.780825000	-1.520435000
1	-3.138077000	-3.983494000	-2.188563000
1	-2.656947000	-3.810396000	-0.493181000
1	-1.571826000	-4.600639000	-1.633466000
6	3.869734000	-0.903274000	1.759445000
7	2.521352000	-0.974281000	1.567042000
1	1.969125000	-1.364412000	2.319725000
8	4.381109000	-1.165661000	2.851660000
6	4.702106000	-0.466936000	0.586715000
6	6.083831000	-0.696979000	0.656179000
6	4.167855000	0.166287000	-0.546299000
6	6.917956000	-0.320367000	-0.394775000
1	6.485375000	-1.175607000	1.543191000
6	5.005939000	0.549488000	-1.595050000
1	3.106649000	0.392246000	-0.613528000
6	6.379554000	0.303290000	-1.524552000
1	7.985861000	-0.510721000	-0.333685000
1	4.584392000	1.045475000	-2.464817000
1	7.028297000	0.600292000	-2.344007000
1	2.100415000	-0.997469000	0.646996000

**Table S39 Optimized coordinates for L<sup>1</sup>Ru(PhC(OH)NH) (DMF Phase)**

Z	x	y	z
44	-0.514792000	-0.063206000	-0.345151000
16	-1.888193000	-0.304830000	-2.277550000
16	0.820791000	-0.293195000	1.729856000
16	-0.517007000	2.414924000	-0.526767000
7	-2.385275000	0.293434000	0.722382000
7	-0.992881000	-2.169755000	0.068405000
6	-3.375217000	0.563285000	-1.636251000
1	-3.132374000	1.608453000	-1.833298000
1	-4.258880000	0.289516000	-2.220624000
6	-3.617547000	0.301717000	-0.152708000
1	-4.326777000	1.042393000	0.233886000
1	-4.108548000	-0.667612000	-0.048452000
6	-2.477623000	-0.866756000	1.664167000
1	-3.467172000	-0.903568000	2.144732000
1	-1.725118000	-0.699617000	2.430898000
6	-2.212775000	-2.194999000	0.955017000
1	-3.072681000	-2.468004000	0.341186000
1	-2.115600000	-2.990928000	1.700881000
6	-1.311512000	-2.851101000	-1.226083000
1	-1.684168000	-3.870436000	-1.041480000
1	-0.372890000	-2.948248000	-1.777739000

6	-2.333593000	-2.106493000	-2.090503000
1	-3.349078000	-2.166923000	-1.692906000
1	-2.349300000	-2.555292000	-3.087039000
6	-2.239409000	1.551013000	1.530034000
1	-1.477128000	1.309642000	2.271316000
1	-3.185642000	1.743887000	2.062007000
6	-1.782334000	2.835923000	0.798903000
6	0.844566000	-2.165738000	1.917469000
6	0.193788000	-2.843039000	0.686856000
1	0.941798000	-2.873176000	-0.108039000
1	-0.072319000	-3.883623000	0.936070000
6	0.203409000	-2.593699000	3.254654000
1	0.244177000	-3.686218000	3.373022000
1	-0.838250000	-2.284791000	3.359267000
1	0.757589000	-2.148792000	4.088277000
6	2.310505000	-2.650386000	1.955777000
1	2.362166000	-3.745656000	2.048357000
1	2.829419000	-2.218945000	2.818496000
1	2.853573000	-2.356004000	1.052866000
6	-1.116925000	3.730142000	1.867084000
1	-0.787682000	4.675474000	1.422179000
1	-0.243997000	3.238113000	2.307048000
1	-1.822721000	3.968919000	2.676650000
6	-2.951063000	3.642182000	0.198105000
1	-3.659244000	3.939843000	0.984705000
1	-3.509745000	3.094416000	-0.563483000
1	-2.571524000	4.556134000	-0.271777000
6	2.498318000	-0.410395000	-1.702788000
7	1.219291000	-0.515132000	-1.566651000
1	0.890618000	-1.094720000	-2.341789000
8	3.063184000	-1.151467000	-2.702718000
1	3.955914000	-0.818669000	-2.896554000
6	3.429854000	0.414501000	-0.903943000
6	4.744665000	-0.039625000	-0.690559000
6	3.046687000	1.670161000	-0.409889000
6	5.657018000	0.746908000	0.012780000
1	5.048977000	-1.022239000	-1.041387000
6	3.968264000	2.457741000	0.277722000
1	2.028308000	2.014851000	-0.554923000
6	5.272744000	2.001001000	0.492717000
1	6.664403000	0.378977000	0.184406000
1	3.665767000	3.432679000	0.650187000
1	5.985188000	2.618666000	1.032512000

**Table S40 Optimized coordinates for L<sup>1</sup>RuTS (DMF phase)**

Z	x	y	z
44	-0.524146000	-0.018890000	0.280851000
16	-1.073768000	-0.396295000	2.552682000
16	-0.059206000	0.814376000	-2.019541000
16	-0.542820000	-2.417061000	-0.175084000
7	-2.676886000	-0.165172000	-0.103312000
7	-0.969426000	2.071599000	0.647344000
6	-2.756161000	-1.113774000	2.292820000
1	-2.539641000	-2.174294000	2.142294000
1	-3.351521000	-1.019251000	3.206132000

6	-3.510048000	-0.504603000	1.108492000
1	-4.319329000	-1.182796000	0.813212000
1	-3.995006000	0.413772000	1.446445000
6	-3.034039000	1.213101000	-0.569199000
1	-4.125704000	1.346460000	-0.609716000
1	-2.635831000	1.313007000	-1.575881000
6	-2.429919000	2.291379000	0.333941000
1	-2.975676000	2.332605000	1.277893000
1	-2.567521000	3.272142000	-0.133624000
6	-0.721371000	2.345384000	2.099266000
1	-1.034803000	3.369722000	2.354358000
1	0.358117000	2.277364000	2.248154000
6	-1.418621000	1.367085000	3.047500000
1	-2.500949000	1.507674000	3.093890000
1	-1.029145000	1.514784000	4.058176000
6	-2.846195000	-1.123708000	-1.248707000
1	-2.440988000	-0.592567000	-2.109240000
1	-3.919720000	-1.293896000	-1.426255000
6	-2.133496000	-2.507326000	-1.191388000
6	0.046091000	2.662883000	-1.679287000
6	-0.050286000	2.936792000	-0.158957000
1	0.936939000	2.761945000	0.272751000
1	-0.311657000	3.994908000	0.009528000
6	-1.009362000	3.431433000	-2.502532000
1	-0.922337000	4.513579000	-2.328429000
1	-2.037375000	3.139684000	-2.279595000
1	-0.846912000	3.252469000	-3.571034000
6	1.426491000	3.186020000	-2.132751000
1	1.553785000	3.034901000	-3.210120000
1	2.241356000	2.667656000	-1.618923000
1	1.524023000	4.263619000	-1.933064000
6	-1.804671000	-2.923199000	-2.634467000
1	-1.339388000	-3.914214000	-2.655059000
1	-1.123497000	-2.207798000	-3.105585000
1	-2.722307000	-2.969772000	-3.236755000
6	-3.011634000	-3.594324000	-0.544598000
1	-3.946253000	-3.703235000	-1.109422000
1	-3.271956000	-3.366002000	0.492818000
1	-2.496163000	-4.560076000	-0.552555000
7	1.537737000	0.024554000	0.608565000
6	2.422589000	-0.629288000	0.064951000
6	3.897007000	-0.618017000	0.213334000
6	4.445355000	-0.125293000	1.412836000
6	4.774501000	-1.043200000	-0.799677000
6	5.824793000	-0.067746000	1.594972000
1	3.770721000	0.206839000	2.195516000
6	6.157643000	-0.979776000	-0.615268000
1	4.375257000	-1.404099000	-1.741382000
6	6.689497000	-0.496007000	0.581263000
1	6.227908000	0.309483000	2.531175000
1	6.818721000	-1.306900000	-1.413410000
1	7.765622000	-0.451188000	0.724203000
1	0.781721000	-2.089522000	-0.932614000
8	2.049997000	-1.711826000	-1.075253000
1	2.585714000	-2.511316000	-0.911640000

# Optimized Coordinates for Solution Phase (DMF) DFT Studies for Catalyst L<sup>2</sup>RuPPh<sub>3</sub> and its' derivatives

**Table S41 Optimized coordinates for L<sup>2</sup>RuPPh<sub>3</sub> (DMF phase)**

Z	x	y	z
44	-0.910442000	-0.123331000	-0.135394000
16	-0.922977000	0.463607000	-2.468707000
16	-1.033766000	-1.268677000	2.046076000
16	-1.501863000	2.039298000	0.594050000
15	1.519175000	0.252492000	0.058462000
7	-3.134441000	-0.312947000	-0.395373000
7	-1.046827000	-2.242588000	-0.892392000
6	-2.687700000	0.968433000	-2.589923000
1	-2.642368000	1.995715000	-2.225170000
1	-3.002226000	0.970497000	-3.637893000
6	-3.635801000	0.106637000	-1.760777000
1	-4.584918000	0.640106000	-1.641113000
1	-3.868921000	-0.799218000	-2.322761000
6	-3.428624000	-1.766516000	-0.211527000
1	-4.472707000	-1.986090000	-0.478068000
1	-3.289062000	-1.977771000	0.844764000
6	-2.494640000	-2.626315000	-1.043610000
1	-2.760251000	-2.553581000	-2.098574000
1	-2.627378000	-3.679942000	-0.775303000
6	-0.402184000	-2.314777000	-2.239371000
1	-0.573836000	-3.304538000	-2.690389000
1	0.670177000	-2.200489000	-2.095413000
6	-0.898548000	-1.243859000	-3.216695000
1	-1.897078000	-1.450786000	-3.607372000
1	-0.219787000	-1.208967000	-4.072505000
6	-3.815388000	0.411667000	0.730232000
1	-3.596521000	-0.185639000	1.614724000
1	-4.902287000	0.385410000	0.562894000
6	-3.379942000	1.857794000	1.029757000
6	-0.674180000	-3.053478000	1.559600000
6	-0.335461000	-3.162969000	0.050503000
1	0.721597000	-2.941500000	-0.077262000
1	-0.491538000	-4.202383000	-0.281809000
6	-1.831667000	-3.980807000	1.987729000
1	-1.572203000	-5.029696000	1.787453000
1	-2.776634000	-3.772665000	1.483106000
1	-2.007684000	-3.881408000	3.064085000
6	0.574519000	-3.527082000	2.334647000
1	0.370164000	-3.538980000	3.410564000
1	1.427402000	-2.864576000	2.165081000
1	0.858966000	-4.547096000	2.037435000
6	-3.548216000	2.095404000	2.537431000
1	-3.274036000	3.119192000	2.803496000
1	-2.928073000	1.413010000	3.124860000
1	-4.597156000	1.935900000	2.819502000
6	-4.185901000	2.912723000	0.260223000
1	-5.238588000	2.843009000	0.562460000
1	-4.135219000	2.790817000	-0.823073000
1	-3.832171000	3.920468000	0.493336000

6	2.544725000	-0.893207000	-0.999817000
6	2.785502000	-0.538363000	-2.340583000
1	2.456894000	0.426825000	-2.713010000
6	3.448046000	-1.407831000	-3.209062000
1	3.620425000	-1.107267000	-4.238905000
6	3.893445000	-2.652399000	-2.756539000
1	4.413846000	-3.327058000	-3.430286000
6	3.666168000	-3.018839000	-1.429379000
1	4.010846000	-3.980800000	-1.060187000
6	2.994534000	-2.151160000	-0.563143000
1	2.832726000	-2.465210000	0.461658000
6	2.318808000	0.191895000	1.739489000
6	3.592274000	-0.343371000	1.993695000
1	4.164777000	-0.810775000	1.201089000
6	4.156135000	-0.272557000	3.271585000
1	5.141302000	-0.697334000	3.445196000
6	3.463254000	0.347228000	4.311896000
1	3.902511000	0.404360000	5.304334000
6	2.204370000	0.900594000	4.064137000
1	1.660244000	1.394848000	4.865120000
6	1.632094000	0.819631000	2.793228000
1	0.658231000	1.261819000	2.610481000
6	2.246855000	1.871631000	-0.547040000
6	3.625342000	2.109823000	-0.383741000
1	4.249975000	1.381372000	0.122230000
6	4.213163000	3.278311000	-0.864271000
1	5.278927000	3.439795000	-0.725478000
6	3.435054000	4.237521000	-1.521161000
1	3.892465000	5.149258000	-1.896113000
6	2.069471000	4.014262000	-1.684649000
1	1.451229000	4.754993000	-2.185564000
6	1.477422000	2.839437000	-1.203095000
1	0.407893000	2.711520000	-1.308265000
8	-0.860963000	2.613513000	1.839076000
8	-1.533923000	3.048785000	-0.544820000

**Table S42 Optimized coordinates for L<sup>2</sup>Ru(PhCN) (DMF Phase)**

Z	x	y	z
44	-0.443677000	0.005262000	0.146205000
16	-0.578361000	-0.860124000	2.379741000
16	-0.248980000	1.288807000	-1.936917000
16	-0.971206000	-2.036267000	-0.865129000
7	-2.595910000	0.283664000	0.290001000
7	-0.396766000	1.993735000	1.084908000
6	-2.374489000	-1.243802000	2.356643000
1	-2.382759000	-2.227682000	1.885741000
1	-2.753864000	-1.338283000	3.378399000
6	-3.201204000	-0.217133000	1.586232000
1	-4.191402000	-0.636780000	1.377265000
1	-3.369649000	0.648332000	2.229493000
6	-2.772249000	1.773957000	0.226419000
1	-3.807245000	2.050970000	0.472167000
1	-2.572944000	2.064735000	-0.802248000
6	-1.812374000	2.501063000	1.169336000
1	-2.149614000	2.400849000	2.201928000

1	-1.838937000	3.573824000	0.951208000
6	0.177303000	1.846192000	2.460230000
1	0.116152000	2.800793000	3.004061000
1	1.234486000	1.601907000	2.336708000
6	-0.489898000	0.755014000	3.300877000
1	-1.497530000	1.021533000	3.626881000
1	0.106863000	0.589975000	4.201578000
6	-3.238369000	-0.321089000	-0.930138000
1	-2.940649000	0.331781000	-1.750757000
1	-4.331350000	-0.258437000	-0.824996000
6	-2.844442000	-1.766190000	-1.314244000
6	0.281202000	2.959325000	-1.248901000
6	0.503920000	2.885312000	0.283210000
1	1.508868000	2.494276000	0.453844000
1	0.469222000	3.901494000	0.707455000
6	-0.726189000	4.052242000	-1.660799000
1	-0.394984000	5.036771000	-1.301932000
1	-1.735320000	3.880025000	-1.281013000
1	-0.794439000	4.100812000	-2.752845000
6	1.642630000	3.335720000	-1.871109000
1	1.551327000	3.426505000	-2.958560000
1	2.398799000	2.574766000	-1.655668000
1	2.000426000	4.300699000	-1.483091000
6	-2.994059000	-1.898842000	-2.837140000
1	-2.744216000	-2.911614000	-3.164581000
1	-2.343143000	-1.200625000	-3.369492000
1	-4.032863000	-1.692905000	-3.126814000
6	-3.701774000	-2.843438000	-0.637394000
1	-4.738727000	-2.746648000	-0.983717000
1	-3.707148000	-2.779791000	0.451665000
1	-3.345104000	-3.841824000	-0.903469000
7	1.563001000	-0.278922000	0.085555000
6	2.713152000	-0.465043000	0.061523000
6	4.120768000	-0.705383000	0.031762000
6	4.763891000	-1.247381000	1.161588000
6	4.859763000	-0.402529000	-1.128309000
6	6.135985000	-1.481430000	1.123510000
1	4.187081000	-1.480092000	2.050742000
6	6.231189000	-0.642892000	-1.150161000
1	4.355854000	0.013090000	-1.994645000
6	6.869847000	-1.180797000	-0.028361000
1	6.632886000	-1.900068000	1.993296000
1	6.801916000	-0.410822000	-2.044073000
1	7.939567000	-1.366466000	-0.051932000
8	-0.988397000	-3.205370000	0.104077000
8	-0.285713000	-2.379365000	-2.166657000

**Table S43 Optimized coordinates for L<sup>2</sup>Ru(H<sub>2</sub>O) (DMF Phase)**

Z	x	y	z
44	-0.083992000	0.116038000	-0.515760000
16	0.682430000	2.317122000	-0.990757000
16	-1.320612000	-1.967166000	-0.129099000
16	1.969080000	-0.856126000	-0.943239000
7	0.643603000	0.431750000	1.467522000
7	-1.910786000	1.070874000	0.256836000

6	1.852040000	2.454601000	0.423261000
1	2.745337000	1.976472000	0.019147000
1	2.073842000	3.505208000	0.632173000
6	1.338990000	1.765724000	1.684440000
1	2.168558000	1.621241000	2.384569000
1	0.630188000	2.428216000	2.183541000
6	-0.597467000	0.397791000	2.314964000
1	-0.372713000	0.722018000	3.340737000
1	-0.917655000	-0.640300000	2.347781000
6	-1.712110000	1.271099000	1.735234000
1	-1.494724000	2.325740000	1.913618000
1	-2.643675000	1.064295000	2.272574000
6	-2.066219000	2.394246000	-0.428733000
1	-2.899334000	2.960245000	0.014979000
1	-2.326999000	2.180958000	-1.467773000
6	-0.808402000	3.264370000	-0.402540000
1	-0.590466000	3.673231000	0.586338000
1	-0.952299000	4.111758000	-1.077735000
6	1.504344000	-0.748219000	1.847946000
1	0.805119000	-1.577488000	1.954167000
1	1.952766000	-0.555017000	2.833258000
6	2.608701000	-1.190012000	0.857654000
6	-3.039111000	-1.288288000	0.246039000
6	-3.105913000	0.226429000	-0.071198000
1	-3.238770000	0.333284000	-1.150423000
1	-3.995685000	0.660587000	0.411764000
6	-3.462846000	-1.632811000	1.688274000
1	-2.809490000	-1.209703000	2.452824000
1	-3.461129000	-2.719191000	1.825014000
1	-4.482076000	-1.271547000	1.881638000
6	-4.045872000	-1.982823000	-0.696244000
1	-4.047085000	-3.063793000	-0.521519000
1	-3.797303000	-1.809067000	-1.748235000
1	-5.065258000	-1.613195000	-0.517112000
6	2.809253000	-2.703263000	1.026658000
1	3.597703000	-3.065692000	0.361350000
1	1.895408000	-3.259476000	0.802274000
1	3.105416000	-2.925946000	2.060106000
6	3.951262000	-0.481506000	1.080326000
1	3.883984000	0.606481000	1.031883000
1	4.682202000	-0.796711000	0.331197000
1	4.338783000	-0.750639000	2.071194000
1	-1.252474000	-1.174812000	-2.267488000
8	-0.900402000	-0.300227000	-2.577937000
1	-0.136800000	-0.527419000	-3.137282000
8	3.004377000	0.091836000	-1.525906000
8	1.960559000	-2.193993000	-1.649730000

**Table S44 Optimized coordinates for L<sup>2</sup>Ru (DMF phase)**

Z	x	y	z
44	-0.132091000	0.067850000	-0.564124000
16	0.625420000	2.275801000	-1.101786000
16	-1.368228000	-1.939452000	-0.486449000
16	1.933905000	-0.892074000	-1.008616000
7	0.612702000	0.455018000	1.365406000

7	-1.965661000	1.037115000	0.163193000
6	1.804027000	2.467337000	0.298208000
1	2.702886000	1.990096000	-0.093350000
1	2.011871000	3.525429000	0.480393000
6	1.291876000	1.804646000	1.570181000
1	2.113381000	1.676574000	2.281879000
1	0.567146000	2.464412000	2.049563000
6	-0.629099000	0.407063000	2.219372000
1	-0.399763000	0.749009000	3.237702000
1	-0.922828000	-0.638022000	2.270608000
6	-1.773309000	1.243401000	1.641472000
1	-1.594764000	2.304895000	1.823324000
1	-2.693638000	0.996867000	2.181031000
6	-2.114787000	2.359746000	-0.530616000
1	-2.949198000	2.927250000	-0.092123000
1	-2.372561000	2.142495000	-1.569425000
6	-0.858074000	3.228313000	-0.508821000
1	-0.636782000	3.636110000	0.479537000
1	-1.004481000	4.076160000	-1.182824000
6	1.493137000	-0.708198000	1.770496000
1	0.806160000	-1.544398000	1.899358000
1	1.934793000	-0.480278000	2.750559000
6	2.600603000	-1.157220000	0.791108000
6	-3.068758000	-1.328200000	0.034801000
6	-3.165468000	0.198609000	-0.179494000
1	-3.327807000	0.362389000	-1.247324000
1	-4.043388000	0.596206000	0.352863000
6	-3.403629000	-1.775363000	1.470878000
1	-4.419395000	-1.456384000	1.741156000
1	-2.720672000	-1.379682000	2.224434000
1	-3.365964000	-2.867371000	1.539174000
6	-4.106193000	-1.979869000	-0.903929000
1	-4.083882000	-3.069419000	-0.797218000
1	-3.906334000	-1.735081000	-1.952065000
1	-5.121071000	-1.639795000	-0.656267000
6	2.827203000	-2.660978000	1.007922000
1	3.624222000	-3.028356000	0.356062000
1	1.924696000	-3.240410000	0.796478000
1	3.123523000	-2.847254000	2.048417000
6	3.932275000	-0.420234000	0.981663000
1	3.845959000	0.664970000	0.912826000
1	4.657395000	-0.737625000	0.227765000
1	4.339295000	-0.662671000	1.971501000
8	2.926291000	0.076726000	-1.627200000
8	1.968403000	-2.251619000	-1.665625000

**Table S45 Optimized coordinates for L<sup>2</sup>Ru(PhCONH<sub>2</sub>) (DMF Phase)**

Z	x	y	z
44	0.566841000	-0.008022000	-0.179645000
16	1.198062000	0.432420000	-2.437215000
16	-0.401117000	-0.105854000	2.069839000
16	1.820409000	-1.935111000	0.006043000
7	2.358213000	1.034192000	0.386493000
7	-0.289742000	2.033856000	-0.185650000
6	2.978130000	0.747574000	-2.102830000

1	3.385322000	-0.264556000	-2.104420000
1	3.427721000	1.309455000	-2.926962000
6	3.224162000	1.473172000	-0.782379000
1	4.276970000	1.366637000	-0.500128000
1	3.057295000	2.540726000	-0.933457000
6	1.875021000	2.258974000	1.105555000
1	2.706552000	2.954969000	1.285907000
1	1.496192000	1.921292000	2.066419000
6	0.772158000	2.970466000	0.323907000
1	1.198919000	3.502955000	-0.527512000
1	0.321121000	3.740283000	0.959141000
6	-0.644420000	2.391505000	-1.595879000
1	-0.948646000	3.447682000	-1.659061000
1	-1.503163000	1.779860000	-1.876308000
6	0.482171000	2.144231000	-2.603158000
1	1.299547000	2.863960000	-2.518602000
1	0.075879000	2.234821000	-3.613735000
6	3.102013000	0.170498000	1.375280000
1	2.481456000	0.184397000	2.271365000
1	4.060945000	0.653016000	1.614038000
6	3.355075000	-1.311160000	1.006401000
6	-1.465360000	1.452244000	2.072015000
6	-1.533367000	2.066839000	0.651893000
1	-2.279786000	1.509211000	0.082022000
1	-1.889377000	3.107735000	0.721193000
6	-0.987167000	2.449251000	3.148769000
1	-1.653253000	3.322755000	3.182413000
1	0.029623000	2.814966000	2.999410000
1	-1.017497000	1.969781000	4.132900000
6	-2.907907000	1.058343000	2.454616000
1	-3.567060000	1.938619000	2.451171000
1	-2.927934000	0.633254000	3.463921000
1	-3.317029000	0.315990000	1.765719000
6	3.435228000	-2.110238000	2.315511000
1	3.639058000	-3.165345000	2.113045000
1	2.503581000	-2.047766000	2.883167000
1	4.249563000	-1.719635000	2.939459000
6	4.640139000	-1.543922000	0.201328000
1	5.505280000	-1.276137000	0.821078000
1	4.694544000	-0.958131000	-0.717219000
1	4.732821000	-2.596905000	-0.077388000
6	-2.276704000	-0.970194000	-1.547218000
7	-1.116387000	-1.455622000	-0.894515000
1	-0.530904000	-1.966682000	-1.553205000
8	-2.172042000	-0.486704000	-2.668033000
6	-3.583392000	-1.041385000	-0.833909000
6	-4.616943000	-0.206392000	-1.294183000
6	-3.840663000	-1.937880000	0.216740000
6	-5.874445000	-0.248112000	-0.699330000
1	-4.414607000	0.470189000	-2.117549000
6	-5.107068000	-1.988752000	0.799840000
1	-3.074312000	-2.617137000	0.575636000
6	-6.121630000	-1.140875000	0.348974000
1	-6.662703000	0.409676000	-1.053194000
1	-5.299881000	-2.691484000	1.604684000
1	-7.104657000	-1.179194000	0.809481000

1	-1.264331000	-2.000149000	-0.048091000
8	2.391488000	-2.430461000	-1.313234000
8	1.205466000	-3.059276000	0.813072000

**Table S46 Optimized coordinates for L<sup>2</sup>Ru(PhC(OH)NH) (DMF Phase)**

Z	x	y	z
44	-0.530302000	-0.168049000	-0.286292000
16	-1.923558000	-0.535390000	-2.218866000
16	0.873117000	-0.291856000	1.725227000
16	-0.840015000	2.145990000	-0.322103000
7	-2.393262000	-0.198618000	0.843583000
7	-0.659405000	-2.355132000	0.000967000
6	-3.493882000	0.054357000	-1.473403000
1	-3.406746000	1.132560000	-1.614431000
1	-4.348632000	-0.314747000	-2.047930000
6	-3.641471000	-0.335011000	-0.005811000
1	-4.444162000	0.260183000	0.443607000
1	-3.970291000	-1.374115000	0.049315000
6	-2.273786000	-1.415115000	1.712309000
1	-3.230524000	-1.631591000	2.209176000
1	-1.532421000	-1.176021000	2.470964000
6	-1.824324000	-2.637566000	0.913606000
1	-2.650226000	-3.016543000	0.309799000
1	-1.568178000	-3.446692000	1.605200000
6	-0.895854000	-2.999446000	-1.328274000
1	-1.080020000	-4.077611000	-1.204870000
1	0.027068000	-2.891648000	-1.902691000
6	-2.056748000	-2.389543000	-2.118996000
1	-3.033947000	-2.644039000	-1.703744000
1	-2.030894000	-2.778550000	-3.140088000
6	-2.430534000	1.011182000	1.735768000
1	-1.649457000	0.831917000	2.475081000
1	-3.397323000	1.039794000	2.260337000
6	-2.156248000	2.387337000	1.090155000
6	1.218138000	-2.140767000	1.798410000
6	0.642274000	-2.854416000	0.550151000
1	1.357863000	-2.729451000	-0.265072000
1	0.553642000	-3.934456000	0.751760000
6	0.714344000	-2.739310000	3.128680000
1	0.959752000	-3.809144000	3.187938000
1	-0.361958000	-2.635751000	3.279306000
1	1.207611000	-2.238101000	3.968437000
6	2.745946000	-2.362248000	1.761164000
1	2.988163000	-3.435084000	1.786047000
1	3.218477000	-1.894357000	2.631427000
1	3.190220000	-1.928591000	0.861037000
6	-1.545444000	3.289813000	2.172840000
1	-1.346830000	4.289900000	1.778780000
1	-0.605067000	2.884371000	2.554782000
1	-2.247256000	3.385110000	3.011908000
6	-3.406023000	3.075607000	0.526503000
1	-4.097613000	3.296407000	1.349725000
1	-3.944436000	2.476396000	-0.208816000
1	-3.139711000	4.020302000	0.044923000
6	2.459202000	-0.088795000	-1.827669000

7	1.191160000	-0.239613000	-1.642046000
1	0.815345000	-0.620651000	-2.512469000
8	2.955467000	-0.564397000	-3.005159000
6	3.442702000	0.540324000	-0.920568000
6	4.757497000	0.040068000	-0.876788000
6	3.101599000	1.668476000	-0.161051000
6	5.717421000	0.656090000	-0.074458000
1	5.025877000	-0.848853000	-1.441891000
6	4.074738000	2.290356000	0.621457000
1	2.088719000	2.058951000	-0.190770000
6	5.378365000	1.788118000	0.671243000
1	6.725397000	0.253753000	-0.034659000
1	3.810926000	3.172540000	1.198600000
1	6.127842000	2.276336000	1.288198000
8	-1.552854000	2.621372000	-1.580371000
8	0.295830000	3.075614000	0.056835000
1	3.844873000	-0.202497000	-3.159788000

**Table S47 Optimized coordinates for L<sup>2</sup>RuTS (DMF phase):**

Z	x	y	z
44	-0.487722000	0.106871000	0.089908000
16	-0.223477000	-0.795728000	2.300405000
16	-0.787050000	1.461019000	-1.944173000
16	-0.560581000	-1.822371000	-1.097133000
7	-2.638425000	-0.190797000	0.431946000
7	-0.846365000	2.008010000	1.107034000
6	-1.867090000	-1.588096000	2.472051000
1	-1.695882000	-2.581531000	2.056919000
1	-2.115814000	-1.709916000	3.530514000
6	-2.990329000	-0.834841000	1.757048000
1	-3.834702000	-1.516667000	1.607969000
1	-3.354619000	-0.048875000	2.420014000
6	-3.167116000	1.212223000	0.419966000
1	-4.216206000	1.240306000	0.749022000
1	-3.117680000	1.552081000	-0.612044000
6	-2.334969000	2.134609000	1.318049000
1	-2.547054000	1.921589000	2.366846000
1	-2.648232000	3.171148000	1.156193000
6	-0.137222000	2.005689000	2.425776000
1	-0.394973000	2.907395000	3.001276000
1	0.931977000	2.044071000	2.207070000
6	-0.426152000	0.772855000	3.280737000
1	-1.428830000	0.775220000	3.713268000
1	0.284342000	0.738565000	4.110259000
6	-3.188624000	-0.949892000	-0.741358000
1	-3.161823000	-0.246245000	-1.574655000
1	-4.239687000	-1.211917000	-0.553410000
6	-2.437402000	-2.233899000	-1.193951000
6	-0.652051000	3.188772000	-1.218397000
6	-0.266928000	3.117220000	0.277783000
1	0.812387000	2.964774000	0.333362000
1	-0.496731000	4.078987000	0.764163000
6	-1.942145000	3.992200000	-1.482214000
1	-1.845730000	5.015151000	-1.092166000
1	-2.833788000	3.546748000	-1.036941000

1	-2.119602000	4.062700000	-2.560811000
6	0.499048000	3.933014000	-1.928834000
1	0.284610000	4.032954000	-2.998084000
1	1.444565000	3.393277000	-1.820406000
1	0.626481000	4.944555000	-1.516525000
6	-2.779493000	-2.465884000	-2.675289000
1	-2.287432000	-3.365920000	-3.052633000
1	-2.477081000	-1.623760000	-3.301462000
1	-3.863084000	-2.601987000	-2.773644000
6	-2.790099000	-3.504368000	-0.410261000
1	-3.857883000	-3.712886000	-0.547762000
1	-2.599464000	-3.437414000	0.659219000
1	-2.226116000	-4.358556000	-0.792975000
7	1.595222000	0.258108000	-0.058479000
6	2.530590000	-0.497265000	0.077246000
6	3.997613000	-0.393491000	-0.009388000
6	4.543690000	0.892963000	-0.192187000
6	4.867727000	-1.492680000	0.069973000
6	5.921160000	1.071591000	-0.287883000
1	3.872433000	1.743030000	-0.257163000
6	6.248128000	-1.307113000	-0.029424000
1	4.451135000	-2.481628000	0.206919000
6	6.781176000	-0.028952000	-0.206772000
1	6.324868000	2.070969000	-0.426091000
1	6.907937000	-2.168369000	0.032264000
1	7.856103000	0.110767000	-0.281565000
8	0.031150000	-3.057478000	-0.256120000
8	-0.028231000	-1.904559000	-2.498303000
1	2.171577000	-2.166144000	1.464788000
8	2.212064000	-2.197976000	0.492869000
1	1.041519000	-2.666591000	0.109618000

## Optimized Coordinates for Solution Phase (DMF) DFT Studies for Catalyst L<sup>3</sup>RuPPh<sub>3</sub> and derivatives

**Table S48 Optimized coordinates for L<sup>3</sup>RuPPh<sub>3</sub> (DMF phase)**

Z	x	y	z
44	-0.880377000	-0.083479000	-0.228374000
16	-0.739416000	0.780673000	-2.515079000
16	-1.023629000	-1.373310000	1.807254000
16	-1.452729000	1.994520000	0.746290000
15	1.577832000	0.235049000	0.096078000
7	-3.068509000	-0.164634000	-0.624151000
7	-0.995113000	-2.081900000	-1.244038000
6	-2.482131000	1.347170000	-2.624579000
1	-2.433614000	2.311896000	-2.117346000
1	-2.755713000	1.507020000	-3.671949000
6	-3.477617000	0.397920000	-1.966490000
1	-4.437114000	0.914886000	-1.854849000
1	-3.662601000	-0.439521000	-2.640957000
6	-3.391450000	-1.627147000	-0.590700000
1	-4.427545000	-1.798009000	-0.918479000
1	-3.307612000	-1.929158000	0.452655000
6	-2.445260000	-2.424631000	-1.471909000

1	-2.674526000	-2.257147000	-2.525000000
1	-2.602336000	-3.494912000	-1.301996000
6	-0.306683000	-2.011949000	-2.571398000
1	-0.475663000	-2.943545000	-3.132635000
1	0.761688000	-1.932163000	-2.379039000
6	-0.749255000	-0.832323000	-3.440543000
1	-1.743125000	-0.966815000	-3.872446000
1	-0.048740000	-0.732144000	-4.273450000
6	-3.811075000	0.461385000	0.526112000
1	-3.649913000	-0.227512000	1.356668000
1	-4.882761000	0.480975000	0.278464000
6	-3.368377000	1.855511000	0.999428000
6	-0.661851000	-3.145046000	1.104627000
6	-0.317176000	-3.117903000	-0.401592000
1	0.749447000	-2.933768000	-0.514089000
1	-0.512899000	-4.112517000	-0.833297000
6	-1.832533000	-4.075780000	1.448218000
1	-1.547262000	-5.106770000	1.203370000
1	-2.753276000	-3.847756000	0.909864000
1	-2.060760000	-4.026875000	2.515328000
6	0.579463000	-3.637951000	1.872031000
1	0.345058000	-3.773366000	2.933045000
1	1.410231000	-2.929096000	1.804101000
1	0.921149000	-4.604325000	1.476753000
6	-3.656176000	1.950118000	2.505538000
1	-3.351586000	2.922291000	2.901959000
1	-3.131783000	1.166437000	3.056381000
1	-4.734151000	1.832438000	2.678012000
6	-4.071619000	3.012702000	0.278333000
1	-5.147788000	2.951446000	0.484734000
1	-3.935430000	2.998366000	-0.804094000
1	-3.711428000	3.978610000	0.641629000
6	2.625543000	-0.739611000	-1.101179000
6	2.927899000	-0.166305000	-2.350479000
1	2.635511000	0.856993000	-2.562083000
6	3.609331000	-0.890947000	-3.330197000
1	3.829068000	-0.422814000	-4.285707000
6	4.014330000	-2.204509000	-3.081822000
1	4.550015000	-2.766438000	-3.841491000
6	3.727302000	-2.786902000	-1.846512000
1	4.040107000	-3.805628000	-1.635319000
6	3.035044000	-2.064853000	-0.870140000
1	2.825594000	-2.547640000	0.077253000
6	2.300202000	-0.109788000	1.775463000
6	3.528563000	-0.752733000	2.003717000
1	4.118837000	-1.129197000	1.176600000
6	4.025652000	-0.902954000	3.301844000
1	4.976211000	-1.406808000	3.454727000
6	3.312850000	-0.398640000	4.390548000
1	3.701130000	-0.513400000	5.398973000
6	2.102332000	0.263186000	4.172106000
1	1.545521000	0.670890000	5.011921000
6	1.594493000	0.403030000	2.878964000
1	0.659229000	0.932759000	2.722074000
6	2.333154000	1.920821000	-0.207537000
6	3.677498000	2.144408000	0.146368000

1	4.248825000	1.368044000	0.644002000
6	4.297154000	3.361427000	-0.131400000
1	5.335191000	3.512323000	0.152762000
6	3.586230000	4.382260000	-0.770901000
1	4.068677000	5.331664000	-0.987250000
6	2.254105000	4.172159000	-1.121965000
1	1.687355000	4.960377000	-1.610917000
6	1.629829000	2.949615000	-0.844425000
1	0.582567000	2.828021000	-1.084250000
8	-0.886525000	2.329942000	2.109489000
8	-1.344442000	3.159476000	-0.225072000
8	-2.465981000	-1.467621000	2.429001000

**Table S49 Optimized coordinates for L<sup>3</sup>Ru(PhCN) (DMF Phase)**

Z	x	y	z
44	-0.423920000	0.001191000	0.222261000
16	-0.540608000	-0.699243000	2.560371000
16	-0.160235000	1.016308000	-1.938167000
16	-0.991660000	-2.109095000	-0.613405000
7	-2.556837000	0.308010000	0.375893000
7	-0.320774000	2.042024000	1.027690000
6	-2.341235000	-1.053871000	2.551282000
1	-2.364948000	-2.065115000	2.142849000
1	-2.724622000	-1.076601000	3.575497000
6	-3.152112000	-0.066382000	1.715299000
1	-4.154919000	-0.477541000	1.553699000
1	-3.291864000	0.851321000	2.289273000
6	-2.691942000	1.792336000	0.166797000
1	-3.722336000	2.117196000	0.372042000
1	-2.478215000	1.964112000	-0.888829000
6	-1.727262000	2.584556000	1.051182000
1	-2.072989000	2.589163000	2.086310000
1	-1.727537000	3.632195000	0.732866000
6	0.239783000	1.994600000	2.416682000
1	0.191002000	2.990971000	2.880346000
1	1.294015000	1.724772000	2.323053000
6	-0.447514000	0.985036000	3.337468000
1	-1.456022000	1.287753000	3.625845000
1	0.136975000	0.896587000	4.256798000
6	-3.233382000	-0.385916000	-0.780081000
1	-2.930612000	0.191970000	-1.655120000
1	-4.322062000	-0.297334000	-0.652901000
6	-2.867095000	-1.863627000	-1.051235000
6	0.434388000	2.767322000	-1.359444000
6	0.613112000	2.845176000	0.173751000
1	1.609665000	2.471993000	0.416720000
1	0.574562000	3.899242000	0.489901000
6	-0.521439000	3.827225000	-1.920098000
1	-0.119842000	4.823886000	-1.696038000
1	-1.530537000	3.769316000	-1.507377000
1	-0.610508000	3.728709000	-3.004523000
6	1.822971000	2.962082000	-1.997345000
1	1.747677000	2.978636000	-3.089362000
1	2.510034000	2.156643000	-1.715255000
1	2.266888000	3.913529000	-1.673952000

6	-3.040313000	-2.110151000	-2.558149000
1	-2.776976000	-3.139316000	-2.817261000
1	-2.417029000	-1.433036000	-3.146588000
1	-4.088878000	-1.944813000	-2.838610000
6	-3.723015000	-2.876168000	-0.280051000
1	-4.764806000	-2.789063000	-0.613793000
1	-3.707824000	-2.730880000	0.800980000
1	-3.387416000	-3.897715000	-0.477157000
7	1.595750000	-0.309561000	0.155420000
6	2.744343000	-0.504265000	0.129422000
6	4.150245000	-0.752895000	0.082774000
6	5.041004000	0.113557000	0.745569000
6	4.637712000	-1.863593000	-0.633138000
6	6.409769000	-0.135848000	0.687298000
1	4.656750000	0.967400000	1.294406000
6	6.009309000	-2.098676000	-0.681416000
1	3.943107000	-2.525094000	-1.140365000
6	6.894638000	-1.238244000	-0.023991000
1	7.099073000	0.530894000	1.196735000
1	6.387470000	-2.953998000	-1.232925000
1	7.963388000	-1.426799000	-0.066031000
8	-0.999752000	-3.186204000	0.457745000
8	-0.322556000	-2.566448000	-1.888744000
8	-1.494805000	1.261937000	-2.730251000

**Table S50 Optimized coordinates for L<sup>3</sup>Ru(H<sub>2</sub>O) (DMF Phase)**

Z	x	y	z
44	-0.056399000	0.242563000	-0.509874000
16	0.788593000	2.498359000	-0.827719000
16	-1.253742000	-1.809186000	-0.224669000
16	1.939730000	-0.755028000	-1.003700000
7	0.648931000	0.385732000	1.488008000
7	-1.856274000	1.215274000	0.291680000
6	1.942282000	2.430300000	0.604396000
1	2.810298000	1.933611000	0.167531000
1	2.227241000	3.443144000	0.903804000
6	1.378863000	1.673601000	1.805454000
1	2.194105000	1.456420000	2.504561000
1	0.685789000	2.324863000	2.340240000
6	-0.612158000	0.311918000	2.309164000
1	-0.398655000	0.542825000	3.362522000
1	-0.951951000	-0.722365000	2.244853000
6	-1.686650000	1.271504000	1.788105000
1	-1.443062000	2.299338000	2.063366000
1	-2.637428000	1.047182000	2.283253000
6	-1.958831000	2.600345000	-0.269382000
1	-2.778579000	3.149991000	0.217535000
1	-2.215882000	2.495592000	-1.326250000
6	-0.674968000	3.424194000	-0.155385000
1	-0.450404000	3.728492000	0.869120000
1	-0.791374000	4.337838000	-0.744002000
6	1.471164000	-0.852967000	1.778049000
1	0.737245000	-1.659935000	1.823730000
1	1.935738000	-0.736861000	2.767497000
6	2.558577000	-1.275332000	0.752447000

6	-3.032028000	-1.092586000	0.025342000
6	-3.058162000	0.441565000	-0.153385000
1	-3.150872000	0.654861000	-1.220827000
1	-3.956293000	0.847476000	0.338731000
6	-3.582903000	-1.563788000	1.376165000
1	-3.044451000	-1.157375000	2.234174000
1	-3.536009000	-2.652775000	1.451572000
1	-4.633314000	-1.257325000	1.459942000
6	-3.883752000	-1.704134000	-1.102740000
1	-3.948824000	-2.791564000	-0.991089000
1	-3.453747000	-1.486600000	-2.086505000
1	-4.905205000	-1.300333000	-1.080965000
6	2.667034000	-2.806888000	0.789111000
1	3.419583000	-3.160363000	0.077985000
1	1.709844000	-3.274830000	0.549673000
1	2.969682000	-3.131877000	1.793156000
6	3.936125000	-0.659909000	1.027267000
1	3.922288000	0.430691000	1.072805000
1	4.652630000	-0.946867000	0.253245000
1	4.306708000	-1.030952000	1.991408000
1	-0.105913000	-0.932108000	-2.823178000
8	-0.672419000	-0.146411000	-2.672340000
1	-0.299134000	0.541654000	-3.250184000
8	3.033779000	0.161963000	-1.522340000
8	1.790066000	-2.003936000	-1.858361000
8	-0.941163000	-2.637233000	1.075382000

**Table S51 Optimized coordinates for L<sup>3</sup>Ru (DMF phase)**

Z	x	y	z
44	-0.084740000	0.240621000	-0.615804000
16	0.735715000	2.530501000	-0.916412000
16	-1.257066000	-1.792448000	-0.446177000
16	1.959494000	-0.753569000	-1.080015000
7	0.582470000	0.351983000	1.371439000
7	-1.904866000	1.187019000	0.164203000
6	1.862986000	2.437126000	0.532024000
1	2.742300000	1.959576000	0.097143000
1	2.133018000	3.444417000	0.862134000
6	1.292343000	1.652402000	1.711271000
1	2.098691000	1.433109000	2.418656000
1	0.581487000	2.283447000	2.245822000
6	-0.687630000	0.259060000	2.177786000
1	-0.480001000	0.472018000	3.235298000
1	-1.018764000	-0.775899000	2.096001000
6	-1.759666000	1.222744000	1.662047000
1	-1.524026000	2.246408000	1.957359000
1	-2.715855000	0.986608000	2.140402000
6	-2.019618000	2.577106000	-0.383888000
1	-2.855031000	3.107720000	0.096571000
1	-2.259355000	2.478459000	-1.445571000
6	-0.750566000	3.418817000	-0.244791000
1	-0.541218000	3.713630000	0.785709000
1	-0.877615000	4.338386000	-0.821738000
6	1.414948000	-0.872696000	1.679215000
1	0.699939000	-1.698085000	1.667051000

1	1.818283000	-0.765420000	2.695950000
6	2.556968000	-1.229639000	0.700012000
6	-3.046112000	-1.133540000	-0.144336000
6	-3.090888000	0.400683000	-0.308473000
1	-3.171349000	0.625598000	-1.375386000
1	-4.001834000	0.788509000	0.173077000
6	-3.568705000	-1.638550000	1.205567000
1	-4.634106000	-1.391318000	1.291625000
1	-3.056092000	-1.209162000	2.067690000
1	-3.460042000	-2.723574000	1.272232000
6	-3.906464000	-1.745994000	-1.266223000
1	-3.945488000	-2.836035000	-1.169187000
1	-3.503317000	-1.506478000	-2.256565000
1	-4.935481000	-1.365518000	-1.217034000
6	2.747848000	-2.753327000	0.752300000
1	3.536004000	-3.069222000	0.063131000
1	1.825696000	-3.275978000	0.490323000
1	3.042173000	-3.052968000	1.766746000
6	3.894206000	-0.547153000	1.013200000
1	3.837223000	0.541962000	1.041260000
1	4.646428000	-0.814464000	0.266308000
1	4.250258000	-0.889344000	1.993335000
8	3.017370000	0.214610000	-1.580527000
8	1.927708000	-2.038427000	-1.876365000
8	-0.931928000	-2.731270000	0.766261000

**Table S52 Optimized coordinates for L<sup>3</sup>Ru(PhCONH<sub>2</sub>) (DMF Phase)**

Z	x	y	z
44	-0.598302000	-0.162154000	-0.326825000
16	-1.879430000	-0.752301000	-2.318439000
16	0.806148000	0.016499000	1.603245000
16	-1.078944000	2.083478000	-0.499938000
7	-2.451547000	-0.307478000	0.736533000
7	-0.508419000	-2.336753000	0.036743000
6	-3.508015000	-0.268510000	-1.618113000
1	-3.522705000	0.805239000	-1.810750000
1	-4.314540000	-0.742182000	-2.185573000
6	-3.657353000	-0.597022000	-0.134383000
1	-4.519458000	-0.051672000	0.265020000
1	-3.894873000	-1.656853000	-0.030979000
6	-2.237702000	-1.465860000	1.670279000
1	-3.181784000	-1.745469000	2.159270000
1	-1.548094000	-1.110294000	2.434541000
6	-1.666844000	-2.680733000	0.936672000
1	-2.440414000	-3.157759000	0.332753000
1	-1.359751000	-3.433299000	1.670499000
6	-0.639548000	-3.049189000	-1.274515000
1	-0.712168000	-4.135629000	-1.112939000
1	0.281635000	-2.855145000	-1.829169000
6	-1.834577000	-2.598441000	-2.117918000
1	-2.794682000	-2.925278000	-1.713189000
1	-1.742534000	-3.035785000	-3.115470000
6	-2.607694000	0.943002000	1.572478000
1	-1.839475000	0.846418000	2.342211000
1	-3.598796000	0.922341000	2.047723000

6	-2.399610000	2.318806000	0.887313000
6	1.299910000	-1.846660000	1.831912000
6	0.817546000	-2.692420000	0.634977000
1	1.538880000	-2.583392000	-0.177823000
1	0.811161000	-3.756037000	0.922873000
6	0.811229000	-2.348606000	3.197383000
1	1.220919000	-3.351523000	3.371778000
1	-0.272955000	-2.410573000	3.292781000
1	1.167424000	-1.689273000	3.992239000
6	2.840056000	-1.886558000	1.844595000
1	3.194542000	-2.922189000	1.936964000
1	3.231670000	-1.321404000	2.697000000
1	3.270120000	-1.465276000	0.932272000
6	-1.825445000	3.279813000	1.939304000
1	-1.636987000	4.265537000	1.504526000
1	-0.893154000	2.893099000	2.356685000
1	-2.546427000	3.400639000	2.758399000
6	-3.679764000	2.917704000	0.291855000
1	-4.395415000	3.105011000	1.102352000
1	-4.163140000	2.267640000	-0.439570000
1	-3.471214000	3.869976000	-0.203279000
6	2.494266000	-0.261671000	-1.659071000
7	1.222534000	0.372588000	-1.705478000
1	0.779126000	0.162782000	-2.598004000
8	2.621848000	-1.377339000	-2.147892000
6	3.617080000	0.474927000	-1.015346000
6	4.900591000	-0.087714000	-1.130668000
6	3.453254000	1.690688000	-0.327388000
6	6.003325000	0.553155000	-0.574065000
1	5.012979000	-1.024948000	-1.664916000
6	4.562411000	2.325563000	0.232244000
1	2.472884000	2.140711000	-0.199487000
6	5.834953000	1.762224000	0.109317000
1	6.991752000	0.114115000	-0.671949000
1	4.430561000	3.261309000	0.767295000
1	6.694441000	2.263859000	0.545008000
1	1.260116000	1.382310000	-1.567945000
8	-1.807079000	2.471000000	-1.776463000
8	0.087189000	3.015475000	-0.214144000
8	0.091151000	0.422296000	2.945438000

**Table S53 Optimized coordinates for L<sup>3</sup>Ru(PhC(OH)NH) (DMF Phase)**

Z	x	y	z
44	-0.537978000	-0.197032000	-0.319173000
16	-1.948579000	-0.653513000	-2.293409000
16	0.886039000	-0.173769000	1.594836000
16	-0.828452000	2.121723000	-0.453844000
7	-2.406892000	-0.160530000	0.778332000
7	-0.689060000	-2.368561000	0.029663000
6	-3.493490000	-0.002085000	-1.553436000
1	-3.386604000	1.068842000	-1.729591000
1	-4.360775000	-0.370323000	-2.109493000
6	-3.644006000	-0.342595000	-0.073994000
1	-4.456387000	0.260395000	0.347225000
1	-3.963708000	-1.382072000	0.015485000

6	-2.280450000	-1.330806000	1.712195000
1	-3.236844000	-1.522798000	2.220582000
1	-1.544641000	-1.036602000	2.461350000
6	-1.841594000	-2.597019000	0.975760000
1	-2.674252000	-3.009578000	0.404074000
1	-1.575383000	-3.366593000	1.707283000
6	-0.949656000	-3.072686000	-1.265500000
1	-1.142007000	-4.141107000	-1.085537000
1	-0.032885000	-3.004343000	-1.855861000
6	-2.111012000	-2.492000000	-2.075495000
1	-3.085560000	-2.701332000	-1.629594000
1	-2.107356000	-2.947144000	-3.069197000
6	-2.460135000	1.091701000	1.613855000
1	-1.682716000	0.944773000	2.366358000
1	-3.438916000	1.140333000	2.114300000
6	-2.175862000	2.436261000	0.909874000
6	1.231360000	-2.074383000	1.752741000
6	0.618188000	-2.857839000	0.573250000
1	1.314042000	-2.806443000	-0.267019000
1	0.519059000	-3.919378000	0.851302000
6	0.770415000	-2.562846000	3.131840000
1	1.062994000	-3.613609000	3.253358000
1	-0.306196000	-2.492346000	3.290687000
1	1.250041000	-1.980787000	3.922579000
6	2.761107000	-2.233208000	1.672766000
1	3.041729000	-3.294987000	1.708332000
1	3.244643000	-1.729805000	2.516611000
1	3.165277000	-1.807703000	0.749457000
6	-1.581064000	3.384946000	1.962488000
1	-1.345365000	4.357802000	1.522865000
1	-0.669909000	2.972360000	2.400597000
1	-2.311679000	3.540620000	2.767379000
6	-3.409413000	3.103853000	0.288183000
1	-4.112521000	3.368970000	1.088107000
1	-3.941158000	2.471386000	-0.423476000
1	-3.130676000	4.022410000	-0.235583000
6	2.444091000	-0.167574000	-1.910113000
7	1.183244000	-0.327962000	-1.684616000
1	0.785277000	-0.735243000	-2.532564000
8	2.915378000	-0.663009000	-3.086543000
6	3.442117000	0.484336000	-1.033981000
6	4.750434000	-0.032951000	-0.980258000
6	3.120388000	1.641999000	-0.310822000
6	5.721252000	0.594189000	-0.201012000
1	5.003622000	-0.941612000	-1.520259000
6	4.104763000	2.272341000	0.451344000
1	2.115369000	2.053186000	-0.353920000
6	5.400545000	1.752714000	0.512222000
1	6.723932000	0.179971000	-0.152959000
1	3.855571000	3.175836000	1.001047000
1	6.159035000	2.248096000	1.111988000
8	-1.501231000	2.539512000	-1.753153000
8	0.313522000	3.049930000	-0.088521000
8	0.181171000	0.234130000	2.942874000
1	3.802226000	-0.306036000	-3.265977000

**Table S54 Optimized coordinates for L<sup>3</sup>RuTS (DMF phase)**

Z	x	y	z
44	-0.454947000	0.073252000	0.175259000
16	-0.172059000	-0.960223000	2.380662000
16	-0.661930000	1.447405000	-1.773397000
16	-0.537679000	-1.787264000	-1.128630000
7	-2.586617000	-0.245404000	0.523883000
7	-0.784057000	1.911333000	1.312198000
6	-1.818368000	-1.752753000	2.483934000
1	-1.652454000	-2.716324000	2.001839000
1	-2.074503000	-1.945669000	3.530029000
6	-2.933862000	-0.942980000	1.819989000
1	-3.792388000	-1.602168000	1.649393000
1	-3.275772000	-0.183406000	2.524728000
6	-3.104352000	1.165279000	0.563710000
1	-4.154325000	1.186315000	0.891951000
1	-3.054515000	1.533652000	-0.462003000
6	-2.275757000	2.046267000	1.506917000
1	-2.502692000	1.801078000	2.545779000
1	-2.575713000	3.091147000	1.375851000
6	-0.090019000	1.826690000	2.637687000
1	-0.341338000	2.701281000	3.255691000
1	0.981750000	1.861551000	2.431873000
6	-0.397929000	0.556745000	3.426183000
1	-1.409869000	0.538918000	3.835999000
1	0.293527000	0.487350000	4.269564000
6	-3.151928000	-0.946587000	-0.681362000
1	-3.113762000	-0.198303000	-1.476367000
1	-4.201453000	-1.213521000	-0.491302000
6	-2.411437000	-2.208673000	-1.207602000
6	-0.490404000	3.179144000	-0.944610000
6	-0.170496000	3.054030000	0.558790000
1	0.906207000	2.907541000	0.659596000
1	-0.427390000	3.996426000	1.067599000
6	-1.742053000	4.011329000	-1.245748000
1	-1.598195000	5.026643000	-0.854978000
1	-2.653778000	3.604779000	-0.805342000
1	-1.907613000	4.080145000	-2.323853000
6	0.724309000	3.841775000	-1.621155000
1	0.529481000	4.010031000	-2.685534000
1	1.618815000	3.216005000	-1.531892000
1	0.942055000	4.814347000	-1.159178000
6	-2.780699000	-2.361982000	-2.693300000
1	-2.278817000	-3.227396000	-3.133947000
1	-2.512320000	-1.474024000	-3.268417000
1	-3.863252000	-2.517395000	-2.774764000
6	-2.738593000	-3.522028000	-0.487077000
1	-3.809597000	-3.725760000	-0.605481000
1	-2.518364000	-3.516205000	0.578739000
1	-2.184823000	-4.352093000	-0.933271000
7	1.628701000	0.255304000	-0.015885000
6	2.564137000	-0.507924000	0.071715000
6	4.028641000	-0.407973000	-0.050436000
6	4.572267000	0.877479000	-0.246889000
6	4.898114000	-1.508565000	0.014002000

6	5.947692000	1.053657000	-0.371261000
1	3.901478000	1.728776000	-0.299020000
6	6.276440000	-1.325102000	-0.113302000
1	4.483746000	-2.496737000	0.162361000
6	6.807368000	-0.048088000	-0.304555000
1	6.350075000	2.051980000	-0.520134000
1	6.936233000	-2.186973000	-0.061950000
1	7.880765000	0.089886000	-0.401016000
8	0.098841000	-3.057474000	-0.387696000
8	-0.037245000	-1.757190000	-2.544847000
1	2.148075000	-2.189479000	1.415724000
8	2.246360000	-2.211080000	0.447497000
1	1.113567000	-2.664735000	0.008464000
8	-2.095844000	1.417431000	-2.417634000

## Optimized Coordinates for O-bound Benzamide (Gas Phase Studies) (Å) for L<sup>1-3</sup>Ru(O-benzamide)

**Table S55 Optimized coordinates for L<sup>1</sup>Ru(O-benzamide) (gas phase)**

Z	x	y	z
44	-0.505176000	-0.090783000	0.137656000
16	-0.369880000	-1.047172000	2.291870000
16	-0.661930000	1.253200000	-1.926139000
16	-0.675544000	-2.287016000	-0.934925000
7	-2.630735000	-0.248656000	0.318247000
7	-0.788205000	1.843786000	1.124587000
6	-2.055705000	-1.779704000	2.303643000
1	-1.887138000	-2.716070000	1.767686000
1	-2.381669000	-2.006659000	3.325056000
6	-3.092924000	-0.909360000	1.597010000
1	-3.984537000	-1.511503000	1.383585000
1	-3.415020000	-0.120516000	2.282828000
6	-3.097050000	1.174758000	0.309698000
1	-4.160911000	1.241873000	0.591238000
1	-2.985940000	1.526411000	-0.714068000
6	-2.269145000	2.062820000	1.247589000
1	-2.556471000	1.880329000	2.286550000
1	-2.513311000	3.113427000	1.049109000
6	-0.161451000	1.751000000	2.477353000
1	-0.372920000	2.658619000	3.069008000
1	0.917700000	1.702240000	2.313946000
6	-0.587840000	0.519619000	3.287407000
1	-1.624001000	0.579413000	3.631972000
1	0.043802000	0.450360000	4.178555000
6	-3.159167000	-0.936278000	-0.916701000
1	-2.969614000	-0.224666000	-1.720299000
1	-4.251614000	-1.055592000	-0.809853000
6	-2.511343000	-2.280711000	-1.327110000
6	-0.367356000	2.963389000	-1.201978000
6	-0.082576000	2.893964000	0.323367000
1	0.978008000	2.664834000	0.449688000
1	-0.268766000	3.884857000	0.775782000
6	-1.554867000	3.887084000	-1.543847000
1	-2.505292000	3.540281000	-1.130037000

1	-1.680395000	3.938623000	-2.629865000
1	-1.377226000	4.908284000	-1.174676000
6	0.890306000	3.575835000	-1.854244000
1	0.741508000	3.678956000	-2.933792000
1	1.765832000	2.938636000	-1.694935000
1	1.107579000	4.575016000	-1.445950000
6	-2.692275000	-2.400935000	-2.855731000
1	-2.272936000	-3.348711000	-3.208596000
1	-2.172173000	-1.589244000	-3.372554000
1	-3.756748000	-2.374647000	-3.138938000
6	-3.204338000	-3.498668000	-0.683860000
1	-3.166108000	-3.488193000	0.408497000
1	-2.712940000	-4.420138000	-1.011651000
1	-4.262023000	-3.553567000	-0.984199000
1	1.299242000	0.135039000	-2.224672000
8	1.711244000	0.005604000	0.224050000
7	2.251980000	-0.166960000	-1.975280000
6	2.562608000	-0.196762000	-0.673328000
6	3.980485000	-0.480687000	-0.286012000
6	4.854537000	-1.187633000	-1.125163000
6	4.440058000	-0.039099000	0.962267000
6	6.168403000	-1.434114000	-0.727581000
1	4.502347000	-1.584180000	-2.073427000
6	5.755698000	-0.276485000	1.353801000
1	3.751968000	0.489290000	1.613268000
6	6.624076000	-0.973080000	0.509064000
1	6.832491000	-1.993748000	-1.380392000
1	6.104270000	0.078237000	2.319959000
1	7.648752000	-1.162999000	0.816883000
1	2.967637000	-0.195758000	-2.684579000

**Table S56 Optimized coordinates for L<sup>2</sup>Ru(O-benzamide) (gas phase)**

Z	x	y	z
44	-0.505811000	0.087830000	0.128330000
16	-0.662618000	-0.622689000	2.429527000
16	-0.282113000	1.196622000	-2.022823000
16	-0.927283000	-1.984788000	-0.775210000
7	-2.647469000	0.331176000	0.204466000
7	-0.498605000	2.146997000	0.936025000
6	-2.450418000	-1.035580000	2.382873000
1	-2.418631000	-2.045910000	1.971717000
1	-2.867640000	-1.076489000	3.395242000
6	-3.272984000	-0.080098000	1.519319000
1	-4.253243000	-0.529938000	1.319781000
1	-3.466386000	0.830330000	2.093119000
6	-2.834843000	1.806080000	0.012679000
1	-3.883816000	2.093533000	0.191768000
1	-2.582424000	2.008015000	-1.026998000
6	-1.918188000	2.629495000	0.926114000
1	-2.294271000	2.611961000	1.952573000
1	-1.957458000	3.679214000	0.611133000
6	0.033219000	2.103485000	2.326307000
1	-0.043159000	3.094020000	2.807548000
1	1.094766000	1.856915000	2.244734000
6	-0.642777000	1.061180000	3.224665000

1	-1.667400000	1.335753000	3.489961000
1	-0.080041000	0.986006000	4.160256000
6	-3.251771000	-0.389675000	-0.975223000
1	-2.942320000	0.197196000	-1.841034000
1	-4.350126000	-0.339972000	-0.896465000
6	-2.812737000	-1.851449000	-1.223977000
6	0.231867000	2.909670000	-1.453394000
6	0.424471000	2.962279000	0.082696000
1	1.416859000	2.562375000	0.297984000
1	0.398789000	4.012143000	0.426368000
6	-0.752410000	3.976969000	-1.975182000
1	-1.772063000	3.849888000	-1.601875000
1	-0.805184000	3.923165000	-3.067129000
1	-0.416710000	4.989319000	-1.704037000
6	1.613902000	3.217735000	-2.070677000
1	1.544869000	3.220526000	-3.162962000
1	2.341960000	2.453462000	-1.784514000
1	1.985411000	4.204775000	-1.752412000
6	-2.942852000	-2.124660000	-2.730458000
1	-2.651641000	-3.152934000	-2.958518000
1	-2.299396000	-1.463796000	-3.315693000
1	-3.985071000	-1.979754000	-3.047720000
6	-3.624380000	-2.903176000	-0.457425000
1	-3.677069000	-2.725487000	0.617934000
1	-3.186231000	-3.894847000	-0.595180000
1	-4.652793000	-2.922892000	-0.843502000
8	1.677226000	-0.052112000	0.173857000
8	-0.867249000	-3.032959000	0.342366000
8	-0.247137000	-2.424962000	-2.030708000
6	2.409168000	-1.058010000	0.331247000
6	3.890250000	-0.891674000	0.174909000
6	4.709943000	-1.935892000	-0.277278000
6	4.466332000	0.352934000	0.463625000
6	6.083715000	-1.741428000	-0.421824000
1	4.274866000	-2.890213000	-0.561502000
6	5.839969000	0.542301000	0.330914000
1	3.824607000	1.163797000	0.791019000
6	6.652703000	-0.505328000	-0.110415000
1	6.706516000	-2.553017000	-0.787359000
1	6.277358000	1.508681000	0.566511000
1	7.723228000	-0.355427000	-0.220836000
7	1.958245000	-2.274179000	0.672136000
1	0.958019000	-2.524165000	0.662235000
1	2.612765000	-3.035748000	0.767913000

**Table S57 Optimized coordinates for L<sup>3</sup>Ru(O-benzamide) (gas phase)**

Z	x	y	z
44	-0.483639000	0.074157000	0.218733000
16	-0.657468000	-0.738766000	2.544301000
16	-0.210696000	1.181116000	-1.871216000
16	-0.800701000	-1.983194000	-0.769542000
7	-2.634901000	0.195232000	0.257937000
7	-0.578905000	2.083403000	1.120502000
6	-2.411666000	-1.246978000	2.381311000
1	-2.302424000	-2.223371000	1.905166000
1	-2.868189000	-1.380332000	3.368514000
6	-3.253570000	-0.281034000	1.548763000
1	-4.219099000	-0.752863000	1.326868000
1	-3.478474000	0.600041000	2.155864000
6	-2.876579000	1.669995000	0.097136000
1	-3.938919000	1.910525000	0.267781000
1	-2.630039000	1.898183000	-0.943926000
6	-2.019700000	2.511792000	1.054475000
1	-2.430049000	2.473801000	2.067589000
1	-2.082265000	3.562077000	0.746007000
6	-0.113878000	2.016426000	2.535107000
1	-0.256036000	2.988152000	3.038644000
1	0.960573000	1.818038000	2.501144000
6	-0.779311000	0.919288000	3.371510000
1	-1.830270000	1.131740000	3.584015000
1	-0.265595000	0.856808000	4.335919000
6	-3.195281000	-0.514373000	-0.952227000
1	-2.911259000	0.124241000	-1.791912000
1	-4.293527000	-0.531352000	-0.868712000
6	-2.674958000	-1.939004000	-1.253031000
6	0.281737000	2.931130000	-1.188784000
6	0.357182000	2.966551000	0.353120000
1	1.353798000	2.628711000	0.644679000
1	0.242462000	4.007352000	0.704760000
6	-0.680230000	3.968858000	-1.777256000
1	-1.711864000	3.842415000	-1.441389000
1	-0.700108000	3.897448000	-2.867039000
1	-0.346449000	4.977885000	-1.498229000
6	1.700889000	3.183838000	-1.728321000
1	1.691172000	3.234950000	-2.821629000
1	2.380715000	2.376462000	-1.435608000
1	2.106934000	4.133449000	-1.348823000
6	-2.755260000	-2.147435000	-2.774206000
1	-2.365723000	-3.131130000	-3.048521000
1	-2.178413000	-1.391381000	-3.310901000
1	-3.803218000	-2.084701000	-3.098153000
6	-3.437651000	-3.069703000	-0.551067000
1	-3.511409000	-2.949409000	0.531379000
1	-2.951191000	-4.031246000	-0.733790000
1	-4.459113000	-3.118413000	-0.951965000
8	1.707961000	-0.049187000	0.178794000
8	-0.700269000	-3.071621000	0.308315000
8	-0.052332000	-2.322757000	-2.019252000
6	2.463742000	-1.036794000	0.349321000
6	3.937770000	-0.845403000	0.163080000

6	4.760190000	-1.877638000	-0.311084000
6	4.504338000	0.404461000	0.448379000
6	6.128072000	-1.665931000	-0.483101000
1	4.329543000	-2.835795000	-0.589601000
6	5.872859000	0.610830000	0.288063000
1	3.861288000	1.205150000	0.798029000
6	6.688283000	-0.424568000	-0.176637000
1	6.753008000	-2.468148000	-0.865349000
1	6.304156000	1.580456000	0.521615000
1	7.754491000	-0.261359000	-0.308005000
7	2.043814000	-2.249947000	0.732099000
1	1.049483000	-2.532489000	0.706656000
1	2.719745000	-2.992491000	0.831905000
8	-1.553324000	1.421131000	-2.634732000

## Optimized Coordinates for O-bound Benzamide (DMF Phase Studies) (Å) for L<sup>1-3</sup>Ru(O-benzamide)

**Table S58 Optimized coordinates for L<sup>1</sup>Ru(O-benzamide) (DMF phase)**

Z	x	y	z
44	-0.519229000	-0.131059000	0.084884000
16	-0.384143000	-1.319787000	2.125964000
16	-0.605637000	1.478038000	-1.805396000
16	-0.914910000	-2.177874000	-1.253452000
7	-2.644621000	-0.174131000	0.354134000
7	-0.628595000	1.679621000	1.291199000
6	-2.115932000	-1.930682000	2.165867000
1	-2.055217000	-2.842117000	1.569746000
1	-2.404668000	-2.200755000	3.186305000
6	-3.110884000	-0.930953000	1.583389000
1	-4.047668000	-1.447093000	1.346959000
1	-3.357151000	-0.196825000	2.352580000
6	-3.012250000	1.271406000	0.523013000
1	-4.054313000	1.370628000	0.861114000
1	-2.925583000	1.729107000	-0.459758000
6	-2.087983000	1.982080000	1.515728000
1	-2.342423000	1.694762000	2.537555000
1	-2.261238000	3.061963000	1.459301000
6	0.047131000	1.410328000	2.600670000
1	-0.090167000	2.260972000	3.285755000
1	1.114326000	1.319602000	2.387562000
6	-0.427404000	0.132465000	3.296623000
1	-1.437568000	0.216745000	3.703231000
1	0.242172000	-0.085673000	4.132702000
6	-3.284552000	-0.685194000	-0.909904000
1	-3.081825000	0.089278000	-1.649821000
1	-4.374805000	-0.734725000	-0.757592000
6	-2.776070000	-2.027151000	-1.489247000
6	-0.232614000	3.078729000	-0.882834000
6	0.108031000	2.787172000	0.600920000
1	1.158046000	2.491119000	0.647498000
1	-0.002833000	3.714114000	1.187440000
6	-1.396987000	4.076483000	-1.051148000
1	-2.350111000	3.701906000	-0.672540000

1	-1.537794000	4.306443000	-2.112748000
1	-1.174521000	5.019045000	-0.531440000
6	1.020100000	3.738019000	-1.497889000
1	0.840300000	3.989962000	-2.548400000
1	1.886207000	3.070871000	-1.450757000
1	1.273162000	4.668353000	-0.968799000
6	-3.092225000	-1.996744000	-2.999878000
1	-2.778595000	-2.933908000	-3.472407000
1	-2.570136000	-1.174009000	-3.497728000
1	-4.171860000	-1.877867000	-3.175719000
6	-3.501361000	-3.253384000	-0.900255000
1	-3.357097000	-3.365222000	0.175968000
1	-3.132624000	-4.169248000	-1.374805000
1	-4.582686000	-3.190850000	-1.089737000
1	1.449439000	0.643328000	-2.201310000
8	1.716999000	-0.198784000	0.113335000
7	2.382205000	0.242550000	-2.015460000
6	2.624283000	-0.138595000	-0.749612000
6	4.019067000	-0.524894000	-0.370975000
6	4.963127000	-0.939316000	-1.323950000
6	4.382257000	-0.489822000	0.983806000
6	6.250240000	-1.302358000	-0.926404000
1	4.692818000	-1.012247000	-2.373325000
6	5.671642000	-0.843288000	1.377406000
1	3.646273000	-0.178446000	1.717337000
6	6.608905000	-1.250237000	0.422989000
1	6.969674000	-1.631747000	-1.670425000
1	5.945328000	-0.803601000	2.427884000
1	7.612491000	-1.530755000	0.730085000
1	3.143737000	0.477080000	-2.636174000

**Table S59 Optimized coordinates for L<sup>2</sup>Ru(O-benzamide) (DMF phase)**

Z	x	y	z
44	-0.498540000	0.066080000	0.094643000
16	-0.431222000	-0.762716000	2.347670000
16	-0.444931000	1.321928000	-2.011921000
16	-1.071496000	-1.927785000	-0.904359000
7	-2.607634000	0.340715000	0.418162000
7	-0.351051000	2.061764000	1.002492000
6	-2.220477000	-1.140112000	2.499879000
1	-2.273882000	-2.141606000	2.070645000
1	-2.510087000	-1.198312000	3.553355000
6	-3.110514000	-0.137940000	1.769321000
1	-4.108911000	-0.569122000	1.640068000
1	-3.240944000	0.739930000	2.403780000
6	-2.788688000	1.830452000	0.344020000
1	-3.800067000	2.113477000	0.669212000
1	-2.672371000	2.101257000	-0.702596000
6	-1.754018000	2.571373000	1.195214000
1	-2.006453000	2.484325000	2.253271000
1	-1.800930000	3.640987000	0.964812000
6	0.340278000	1.935169000	2.323145000
1	0.334547000	2.899067000	2.854502000
1	1.380352000	1.678782000	2.109517000
6	-0.255746000	0.862816000	3.236520000

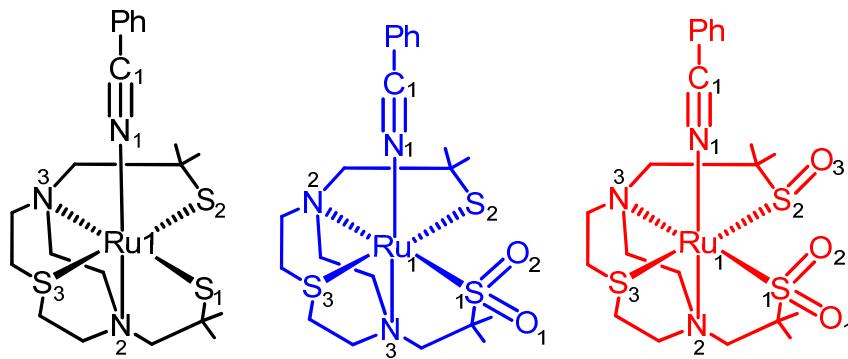
1	-1.230049000	1.140062000	3.644827000
1	0.416560000	0.706328000	4.083936000
6	-3.359156000	-0.292564000	-0.723579000
1	-3.142163000	0.339015000	-1.585545000
1	-4.438048000	-0.231499000	-0.519519000
6	-2.992395000	-1.746387000	-1.104535000
6	0.118133000	3.005311000	-1.388146000
6	0.485934000	2.931264000	0.113450000
1	1.490075000	2.509459000	0.182189000
1	0.517979000	3.949134000	0.535502000
6	-0.932422000	4.088445000	-1.709106000
1	-1.904852000	3.907272000	-1.247282000
1	-1.092757000	4.138745000	-2.791493000
1	-0.581583000	5.075722000	-1.376935000
6	1.412064000	3.398426000	-2.133733000
1	1.221401000	3.479352000	-3.209112000
1	2.199125000	2.653639000	-1.982459000
1	1.785272000	4.372881000	-1.785909000
6	-3.339477000	-1.933860000	-2.589844000
1	-3.112742000	-2.952600000	-2.915715000
1	-2.781431000	-1.243138000	-3.226284000
1	-4.412368000	-1.758318000	-2.741377000
6	-3.726551000	-2.822739000	-0.294650000
1	-3.581854000	-2.744461000	0.782577000
1	-3.395359000	-3.819948000	-0.596541000
1	-4.803313000	-2.747606000	-0.492605000
8	1.690975000	-0.120597000	-0.056451000
8	-0.876400000	-3.120718000	0.039588000
8	-0.553398000	-2.231587000	-2.291546000
6	2.435862000	-1.118898000	0.111267000
6	3.918111000	-0.931438000	0.023955000
6	4.772904000	-1.965826000	-0.388004000
6	4.461173000	0.322038000	0.342960000
6	6.149149000	-1.750845000	-0.467294000
1	4.369537000	-2.930828000	-0.681039000
6	5.837338000	0.531135000	0.273186000
1	3.797916000	1.122765000	0.651794000
6	6.684457000	-0.504924000	-0.131515000
1	6.800459000	-2.554657000	-0.797629000
1	6.249379000	1.501955000	0.533091000
1	7.756531000	-0.340008000	-0.190498000
7	1.980785000	-2.352232000	0.373922000
1	0.979930000	-2.583105000	0.372028000
1	2.629339000	-3.103182000	0.561050000

**Table S60 Optimized coordinates for L<sup>3</sup>Ru(O-benzamide) (DMF phase)**

Z	x	y	z
44	-0.473885000	0.036130000	0.181776000
16	-0.447940000	-0.904205000	2.445371000
16	-0.309814000	1.262523000	-1.850654000
16	-1.053032000	-1.911404000	-0.907564000
7	-2.579350000	0.310893000	0.487852000
7	-0.307074000	1.974879000	1.195817000
6	-2.244633000	-1.255675000	2.513318000
1	-2.303283000	-2.230578000	2.028775000
1	-2.568392000	-1.366421000	3.552580000
6	-3.099246000	-0.198742000	1.816321000
1	-4.108708000	-0.598118000	1.668698000
1	-3.209199000	0.657752000	2.483363000
6	-2.726647000	1.808361000	0.442716000
1	-3.741532000	2.104654000	0.746155000
1	-2.580418000	2.093313000	-0.600393000
6	-1.708591000	2.508115000	1.349526000
1	-1.998095000	2.404983000	2.396912000
1	-1.725533000	3.583176000	1.141143000
6	0.332294000	1.786030000	2.536162000
1	0.321331000	2.730105000	3.101409000
1	1.375880000	1.521896000	2.351423000
6	-0.304658000	0.689083000	3.388111000
1	-1.294502000	0.957559000	3.762902000
1	0.331222000	0.507268000	4.258464000
6	-3.329304000	-0.276073000	-0.682102000
1	-3.091697000	0.385885000	-1.517550000
1	-4.408102000	-0.217240000	-0.476422000
6	-2.969773000	-1.718102000	-1.114476000
6	0.325513000	2.943995000	-1.139511000
6	0.586948000	2.858146000	0.380117000
1	1.588004000	2.448628000	0.522658000
1	0.581394000	3.872592000	0.809492000
6	-0.648186000	4.059834000	-1.534920000
1	-1.632008000	3.964711000	-1.071874000
1	-0.799756000	4.072150000	-2.617080000
1	-0.224387000	5.027001000	-1.235658000
6	1.681405000	3.194533000	-1.825510000
1	1.551446000	3.320963000	-2.905582000
1	2.368630000	2.358392000	-1.657951000
1	2.152045000	4.106388000	-1.432849000
6	-3.300083000	-1.840167000	-2.611124000
1	-3.051572000	-2.837167000	-2.985115000
1	-2.752613000	-1.102905000	-3.201516000
1	-4.375515000	-1.678129000	-2.760665000
6	-3.714186000	-2.826390000	-0.359284000
1	-3.581240000	-2.795808000	0.721944000
1	-3.385630000	-3.811714000	-0.701346000
1	-4.788510000	-2.737119000	-0.564290000
8	1.710548000	-0.129585000	0.004951000
8	-0.860058000	-3.138449000	-0.007756000
8	-0.517842000	-2.153634000	-2.301027000
6	2.455769000	-1.137118000	0.121139000
6	3.934833000	-0.952229000	0.001900000

6	4.769408000	-1.970279000	-0.485435000
6	4.495531000	0.281153000	0.366068000
6	6.143942000	-1.758672000	-0.596372000
1	4.350140000	-2.917389000	-0.812495000
6	5.870367000	0.485867000	0.264645000
1	3.848612000	1.069204000	0.735736000
6	6.697447000	-0.533463000	-0.216633000
1	6.779586000	-2.548525000	-0.985497000
1	6.296818000	1.440163000	0.559889000
1	7.768273000	-0.371390000	-0.300445000
7	1.998993000	-2.373615000	0.356514000
1	0.997129000	-2.601646000	0.357102000
1	2.647327000	-3.134670000	0.499248000
8	-1.681459000	1.585088000	-2.550287000

**Table S61 DFT calculated gas and DMF phase (in parenthesis) natural charges for  $L^{1-3}RuNCPh$**



Atom type	<sup>1</sup> L RuNCPh	<sup>2</sup> L RuNCPh	<sup>3</sup> L RuNCPh
Ru	- 0.504(-0.479)	- 0.624(-0.618)	- 0.671(-0.668)
N1	- 0.205(-0.230)	- 0.240(-0.242)	- 0.266(-0.287)
C1	+ 0.373(+0.383)	+ 0.422(+0.413)	+ 0.423(+0.425)
S1	- 0.099(-0.230)	+ 1.931(+1.893)	+ 1.922(+1.866)
S2	- 0.108(-0.214)	- 0.097(-0.188)	+ 0.985(+0.935)
S3	+ 0.554 (+0.541)	+ 0.566(+0.547)	+ 0.538(+0.520)
O1, O2	-----	- 0.998(-1.026) - 0.970 (-1.014)	- 0.996 (-1.026), - 0.971(-1.015)
O3	-----	-----	- 0.967(-1.002)
N2	-0.422(-0.418)	-0.424(-0.421)	-0.425(-0.420)
N3	-0.430 (-0.419)	-0.438(-0.429)	-0.445(-0.435)

**Table S62 DFT calculated gas and DMF phase (in parenthesis) bond distances for L<sup>1-3</sup>NCPh**

Bond type	<sup>1</sup> L RuNCPh	<sup>2</sup> L RuNCPh	<sup>3</sup> L RuNCPh
Ru1-N1	1.988(2.008)	2.023(2.028)	2.036(2.045)
C1-N1	1.167(1.168)	1.164(1.165)	1.165(1.165)
Ru1-S1	2.443(2.469)	2.330(2.339)	2.328(2.340)
Ru1-S2	2.451(2.472)	2.447(2.455)	2.402(2.402)
Ru1-S3	2.395(2.389)	2.407(2.399)	2.453(2.444)
Ru1-N2	2.182(2.178)	2.177(2.175)	2.165(2.160)
Ru1-N3	2.209(2.185)	2.214(2.199)	2.216(2.196)