Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Formic Acid Dehydrogenation by [Ru(η^6-benzene)(L)Cl] catalysts: L = 2-methylquinolin-8-olate and quinolin-8-olate

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Supporting Information

Material and methods

Materials. All the chemicals used in this work were of reagent grade. The benzeneruthenium(II) chloride dimer was purchased from TCI chemicals; 8-Hydroxy-2-methyl quinoline and 8-hydroxy quinolone were purchased from Alfa Aesar and used without further purifications. The solvents like acetone, diethyl, petroleum, dichloromethane, methanol, and ethanol were purchased from Merck and dried before use. In all the experiments, Milli-Q- purified distilled water was used.

Optical Spectra. All the UV-Visible spectroscopic experiments and analyses were performed with an Agilent Cary 8454 photodiode array UV-Visible spectrophotometer.

NMR Spectroscopy and Mass Spectrometry. At room temperature, ^{1}H and ^{13}C NMR spectra were recorded on Bruker Ultrashield spectrometer. High-resolution ESI mass spectrometry was recorded with Waters UPLC TQD and Bruker micrOTOF-Q II instruments.

X-ray crystallographic analysis. All the suitable single crystals of [Ru(η^6-benzene)(L)Cl] were mounted on a Rigaku SuperNova G8910B EosS2 single-crystal X-ray diffractometer using Mo Kα radiation (λ = 0.71073 Å). The crystal data were collected at 293(2) K. Using Olex2, the structure was solved with the olex2.solve structure solution program using Charge Flipping.

Gas chromatography analysis. The gas chromatography of the gas evolved during dehydrogenation reactions was recorded on the MICHRO-9100 gas chromatograph on Netel (India) Limited.

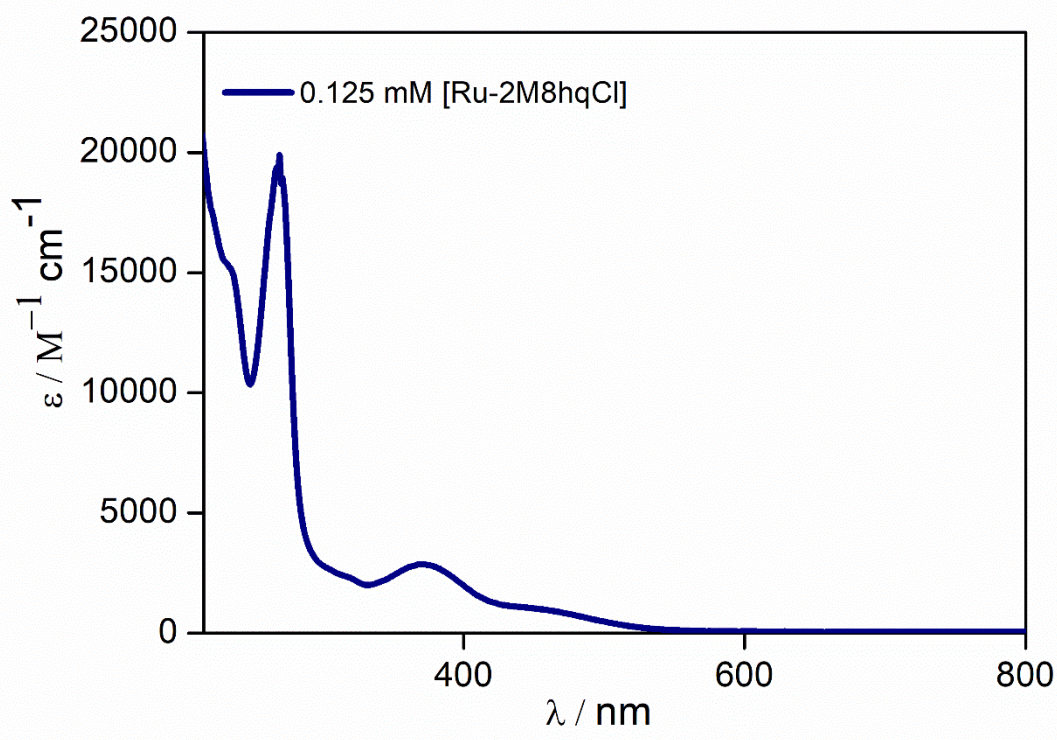


Figure S1. UV-Visible spectra of complex **1**.

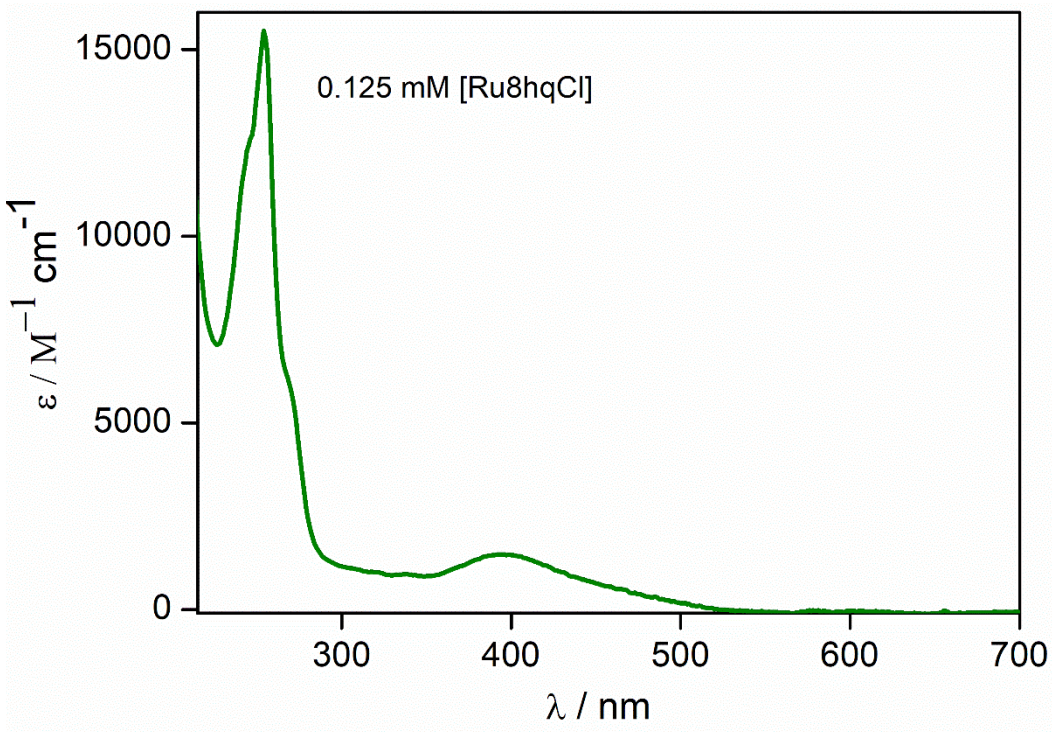


Figure S2. UV-Visible spectra of complex **2**.

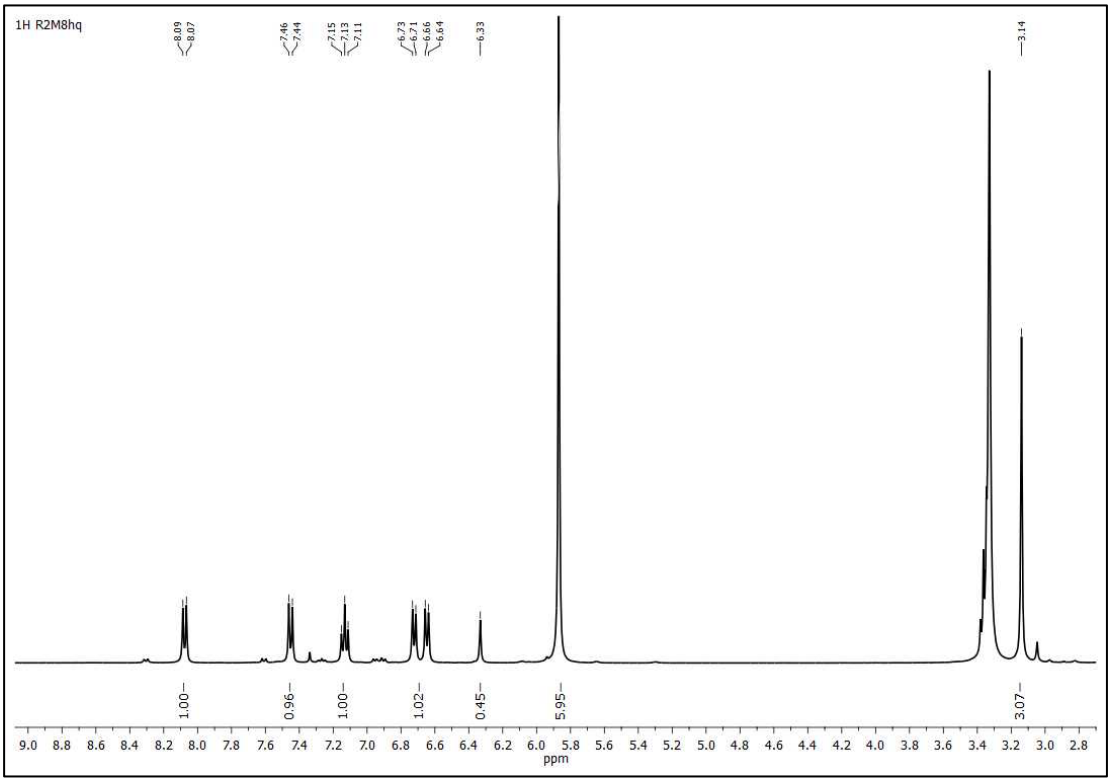


Figure S3. ^{1}H NMR of complex **1** in DMSO-d_6

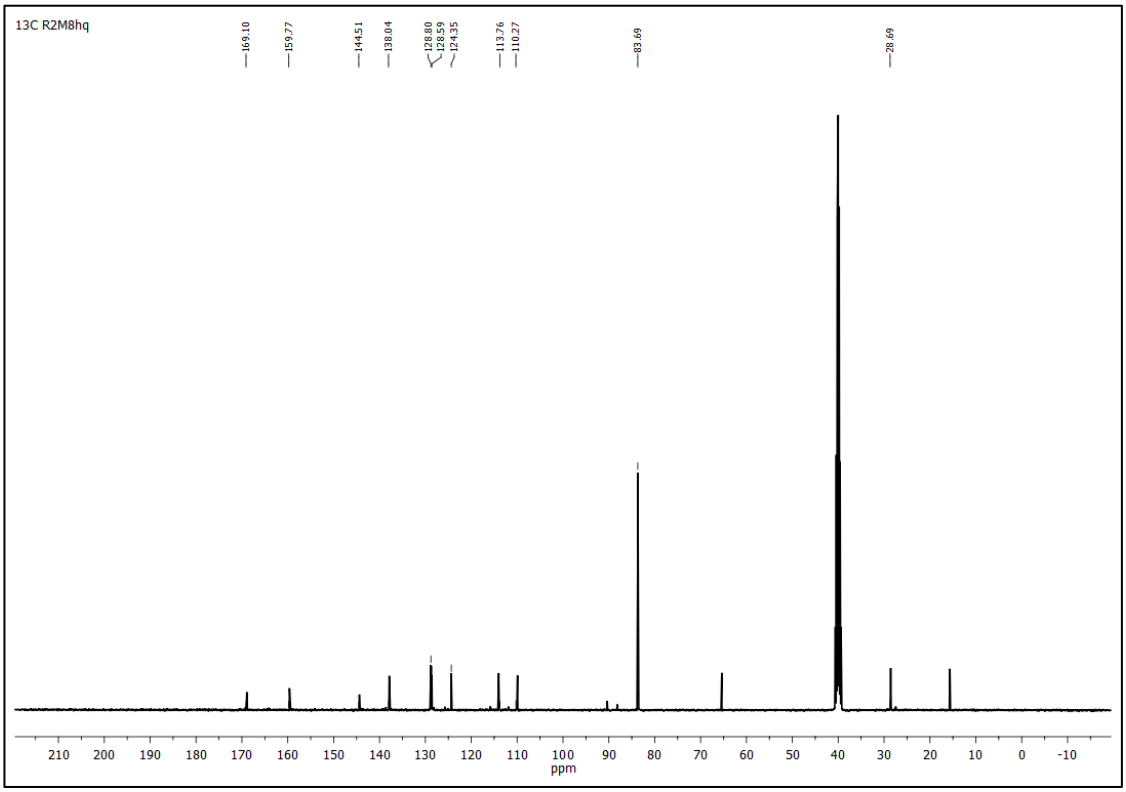


Figure S4. ^{13}C NMR of complex **1** in DMSO-d_6

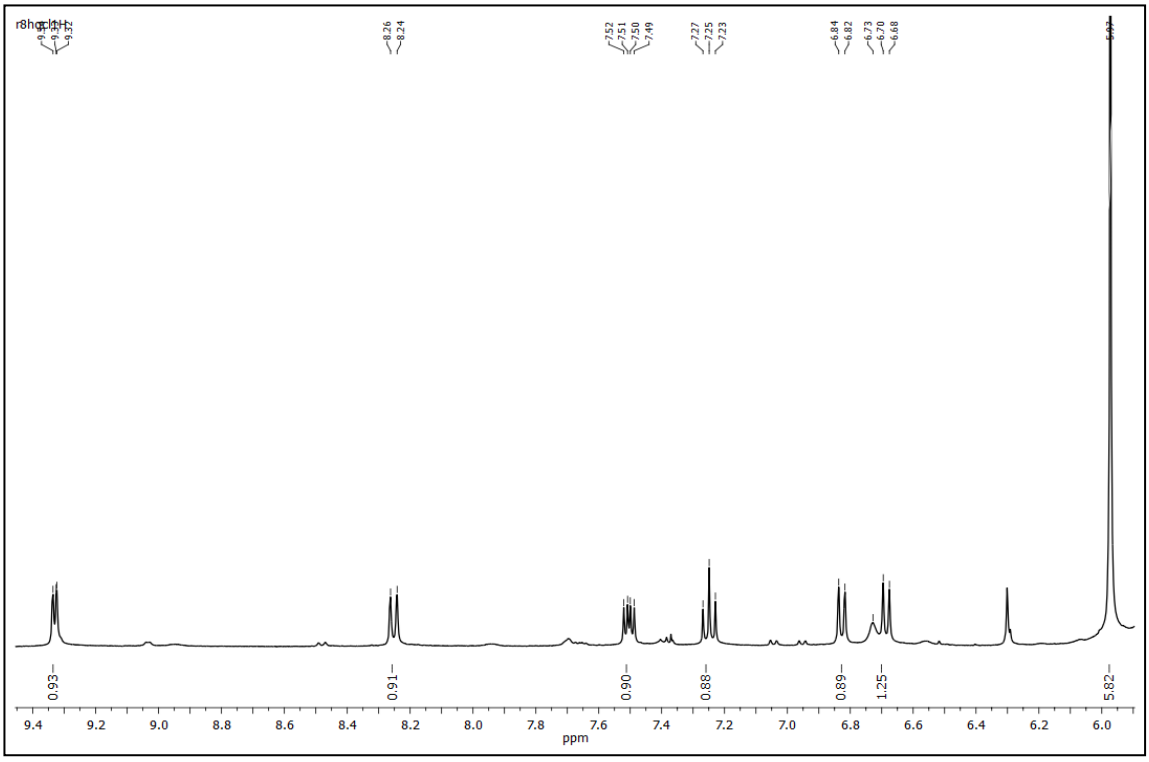


Figure S5. ^{1}H NMR Spectra of the Complex **2** in DMSO-d_6

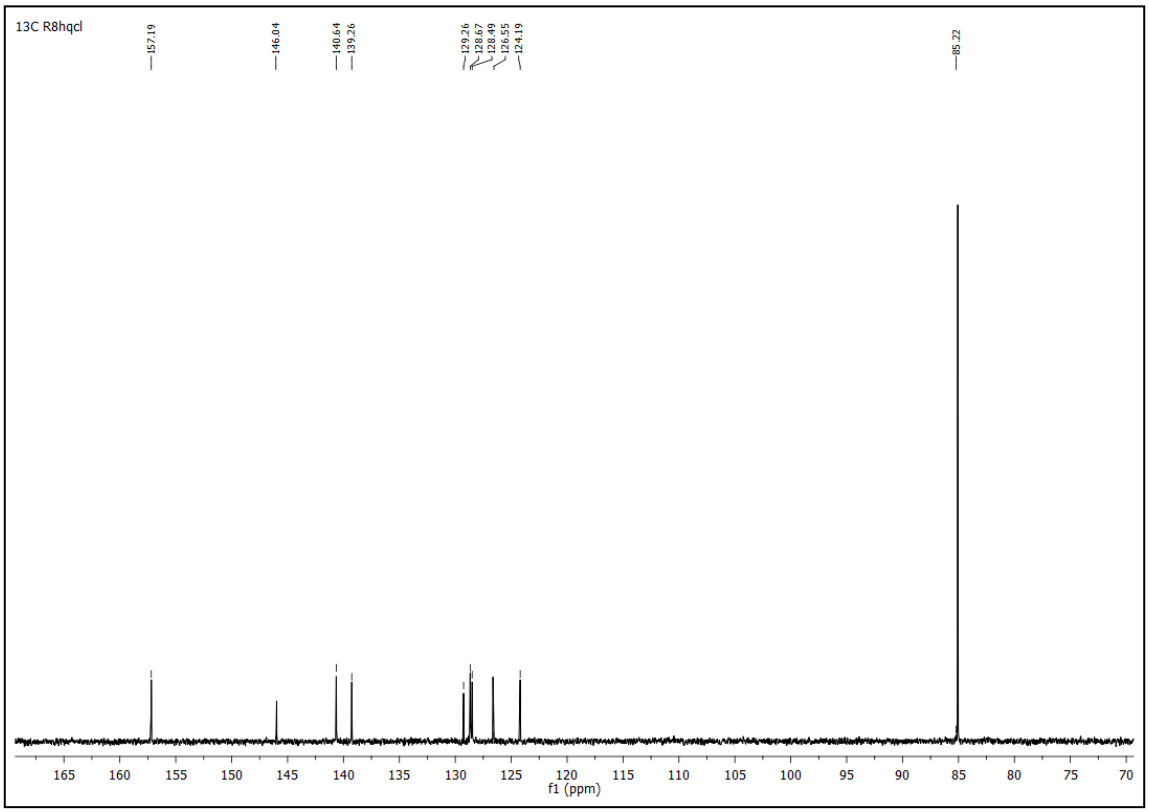


Figure S6. ^{13}C NMR Spectra of Complex **2** in DMSO-d_6.

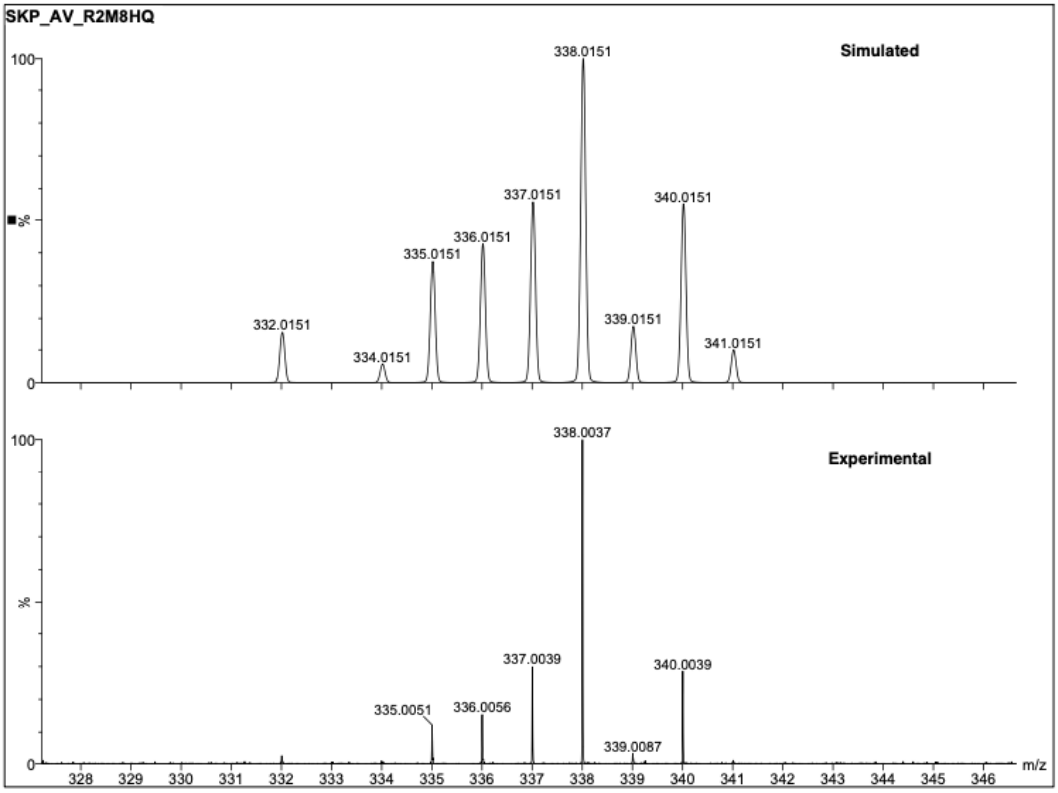


Figure S7. Mass Spectra of the Complex **1**.

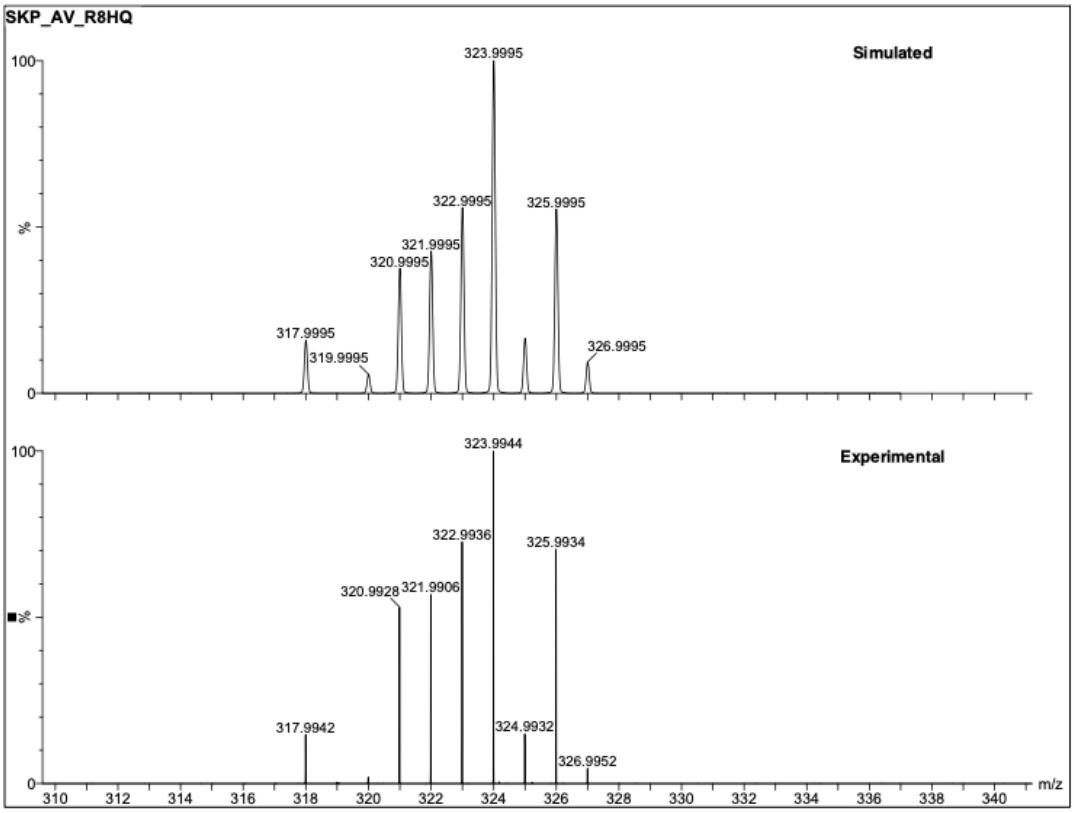


Figure S8. Mass Spectra of the Complex **2**.

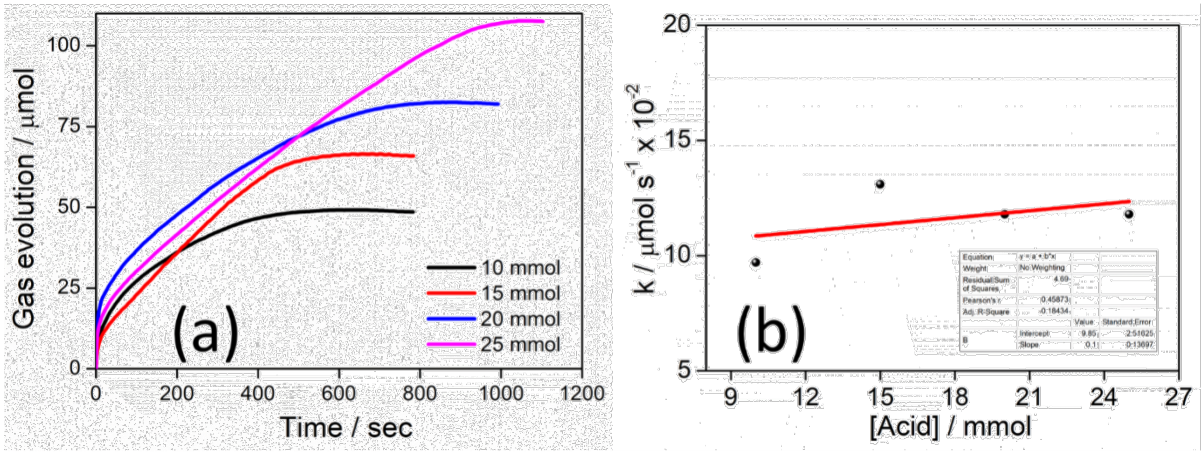


Figure S9. (a) Gas evolution by complex **1** with a variation of acid concentration in the presence of 1.0 mM of complex and 15 mmol of HCOONa at 70 °C in water. **(b)** Rate of gas evolution *vs.* acid in water.

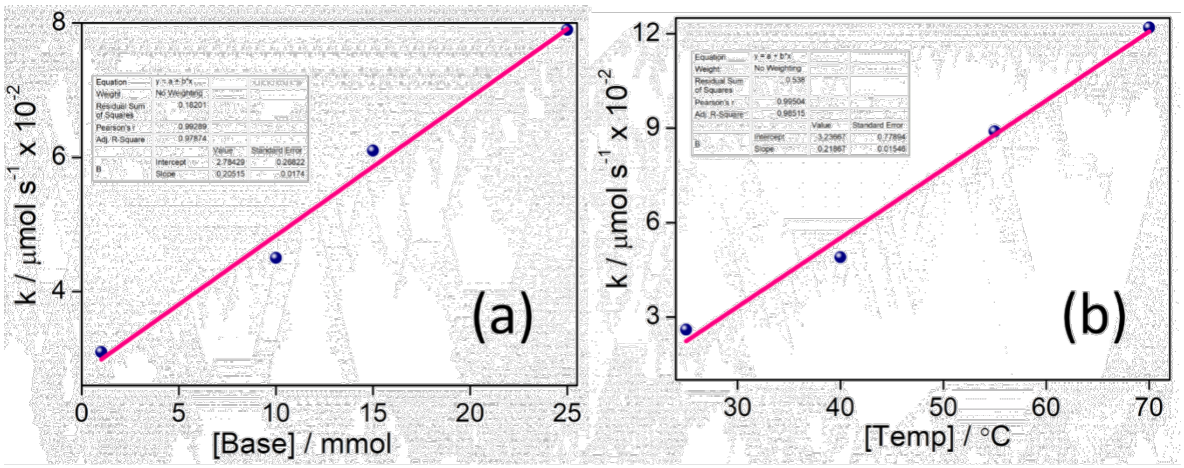


Figure S10. (a) Rate of gas evolution by complex **1** *vs.* HCOONa in water. **(b)** Rate of gas evolution by complex **1** *vs.* temperature in water.

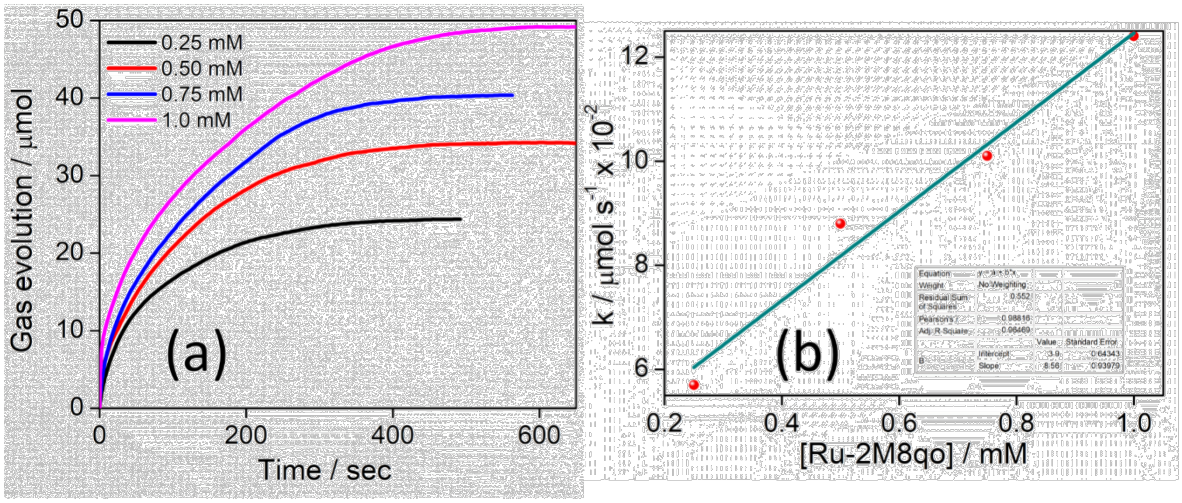


Figure S11. (a) Gas evolution by complex **1** with a variety of complex concentrations in the presence of 10 mmol of acid and 15 mmol of the HCOONa at 70 °C in water. **(b)** Rate of gas evolution *vs.* complex in water.

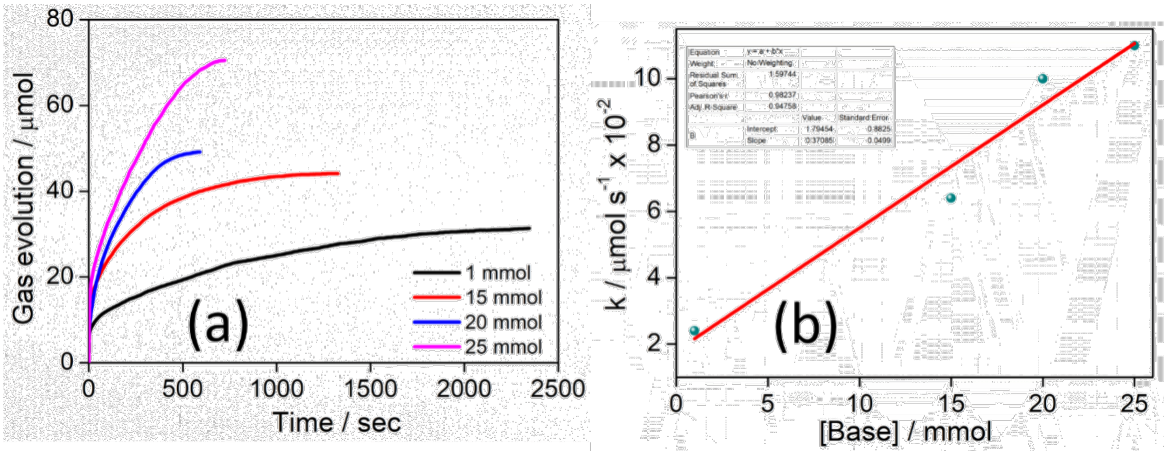


Figure S12. (a) Gas evolution by complex **2** with a variety of HCOONa concentrations in the presence of 10 mmol of acid and 1.0 mM of the complex at 70 °C in water. **(b)** Rate of gas evolution *vs.* HCOONa in water.

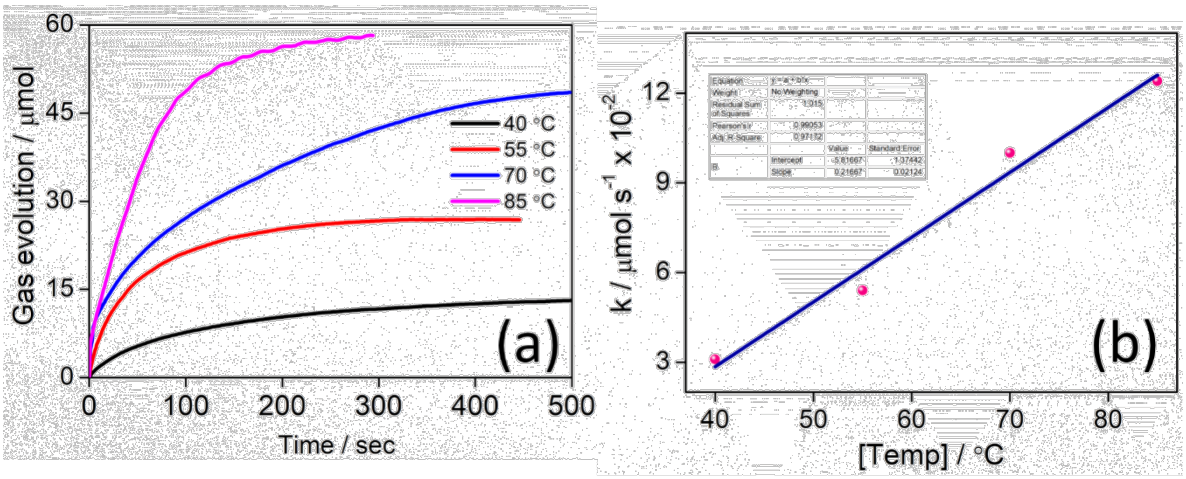
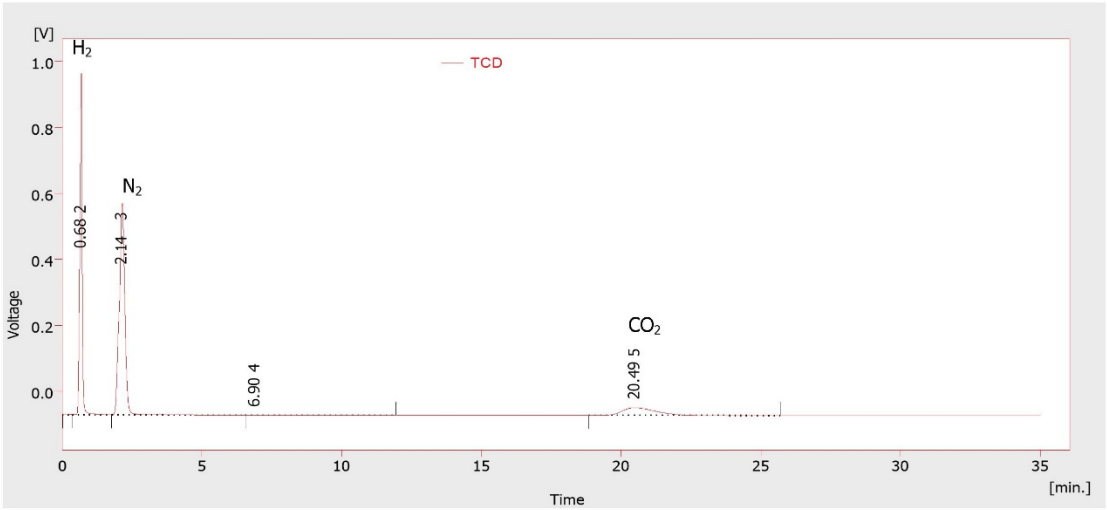


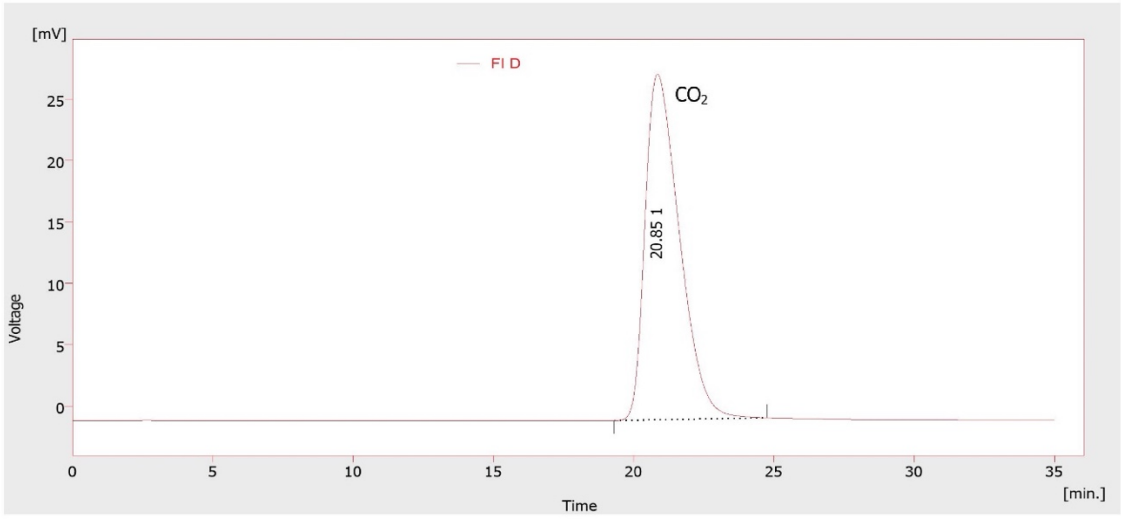
Figure S13. (a) Gas evolution by complex **2** with the temperature variation in the presence of 1.0 mM of complex, 15 mmol of the HCOONa, and 10 mmol of acid in water. **(b)** Rate of gas evolution *vs.* temperature in water.



Result Table

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	0.211	29.362	2.271	0.2	0.1
2	0.681	6144.158	1036.200	35.8	60.8
3	2.143	8927.545	642.069	52.0	37.7
4	6.901	86.601	0.495	0.5	0.0
5	20.493	1990.351	23.591	11.6	1.4
	Total	17178.018	1704.626	100.0	100.0

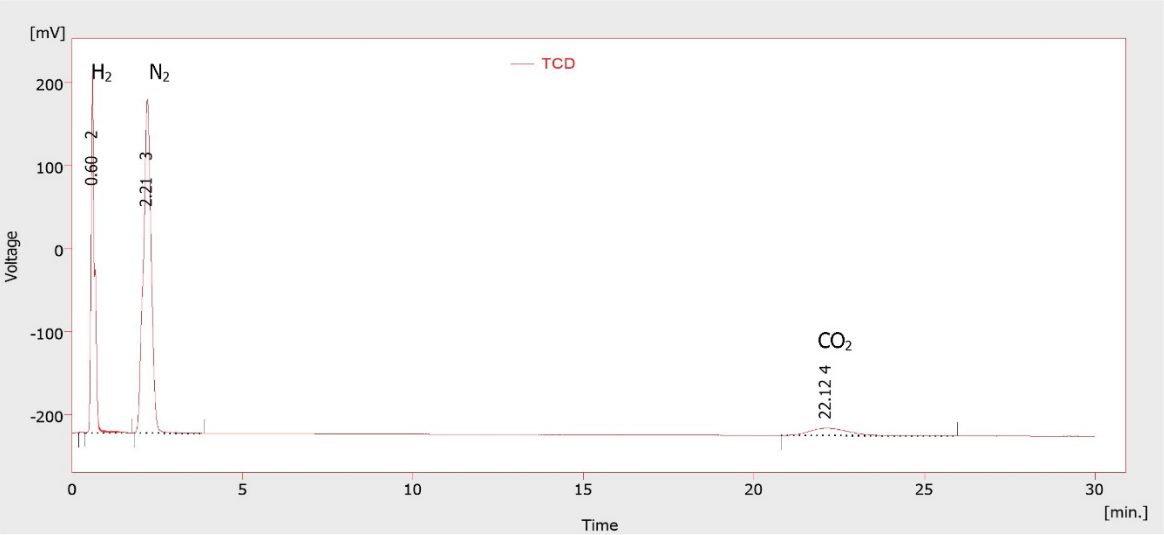
Figure S14. Gas chromatography TCD file for the dehydrogenation using 1.0 mM complex **1 in the presence of** 10 mmol of formic acid and 15 mmol of sodium formate at 90 °C.



Result Table

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	20.853	2396.361	28.152	100.0	100.0
	Total	2396.361	28.152	100.0	100.0

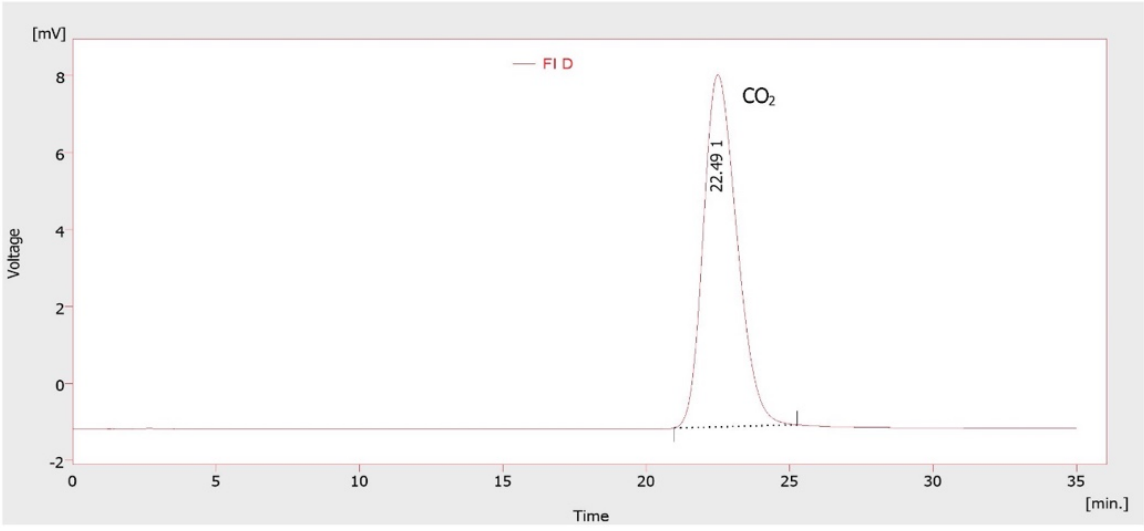
Figure S15. Gas chromatography FID file for the dehydrogenation using 1.0 mM complex **1** in the presence of 10 mmol of formic acid and 15 mmol of sodium formate at 90 °C.



Result Table

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	0.217	8.874	0.903	0.1	0.1
2	0.604	3042.580	431.812	29.8	51.1
3	2.207	6415.499	402.663	62.8	47.7
4	22.124	742.375	9.021	7.3	1.1
	Total	10209.329	844.399	100.0	100.0

Figure S16. Gas chromatography TCD file for the dehydrogenation using 1.0 mM complex **2 in the presence of** 10 mmol of formic acid and 15 mmol of sodium formate at 90 °C.



Result Table

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	22.488	744.757	9.157	100.0	100.0
	Total	744.757	9.157	100.0	100.0

Figure S17. Gas chromatography FID file for the dehydrogenation using 1.0 mM complex **2** in the presence of 10 mmol of formic acid and 15 mmol of sodium formate at 90 °C.

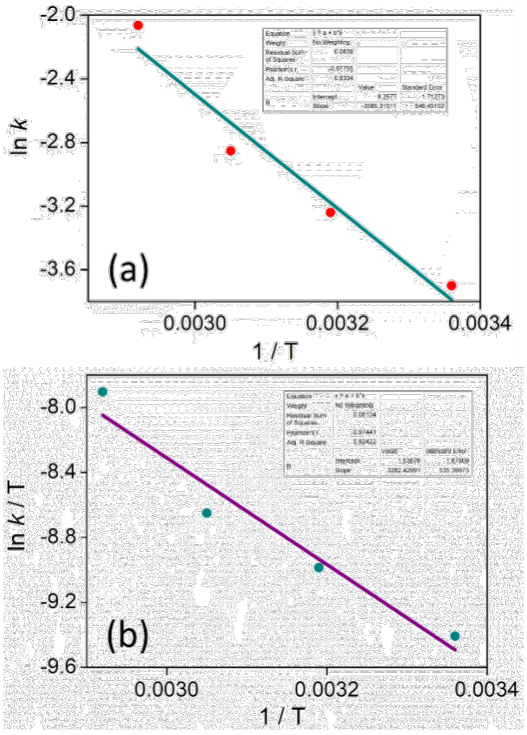


Figure S18. (a) Arrhenius plot for complex **1**. **(b)** Eyring plot for complex **1**.

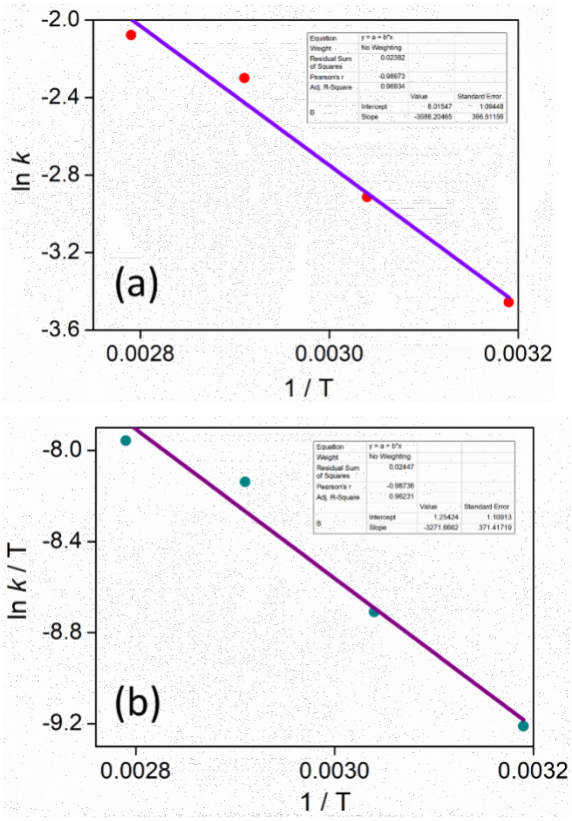


Figure S19. (a) Arrhenius plot for complex **2**. **(b)** Eyring plot for complex **2**.

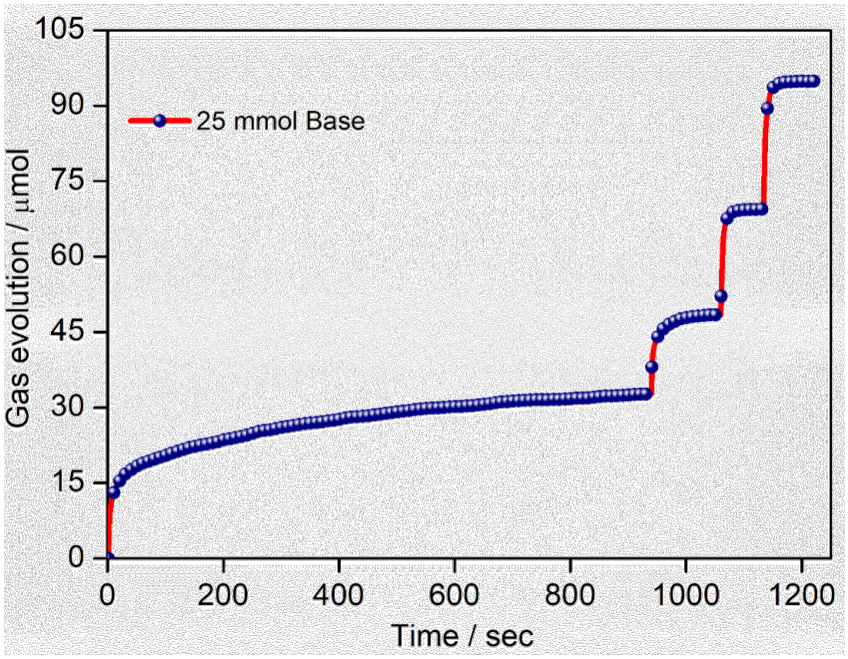


Figure S20. Catalytic cycles for complex **1** with the iteration of 25 mmol of HCOONa in the presence of 1.0 mM complex and 20 mmol acid in deionized water at 70 °C

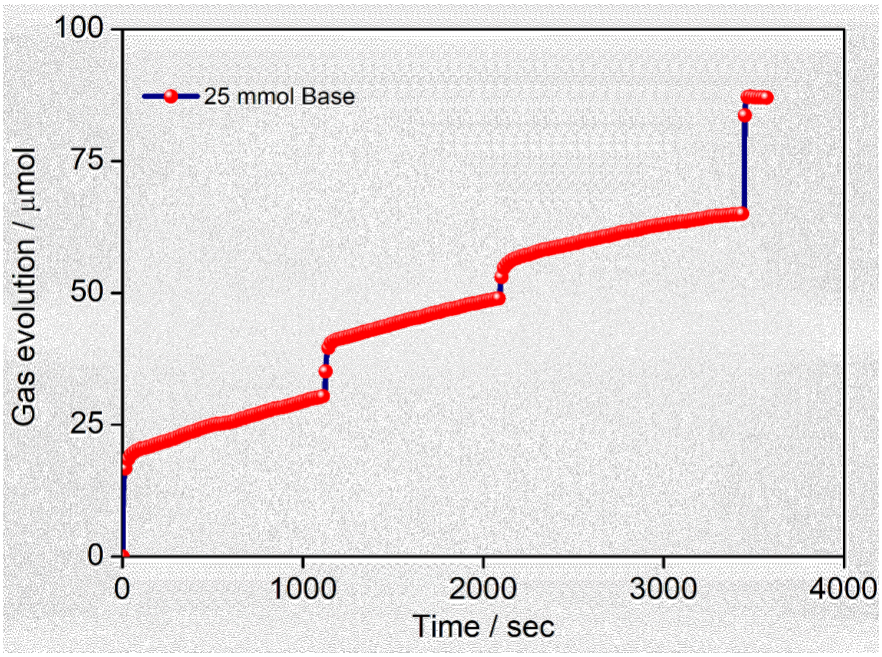


Figure S21. Catalytic cycles for complex **2** with the iteration of 25 mmol of HCOONa in the presence of 1.0 mM complex and 20 mmol acid in deionized water at 70 °C.

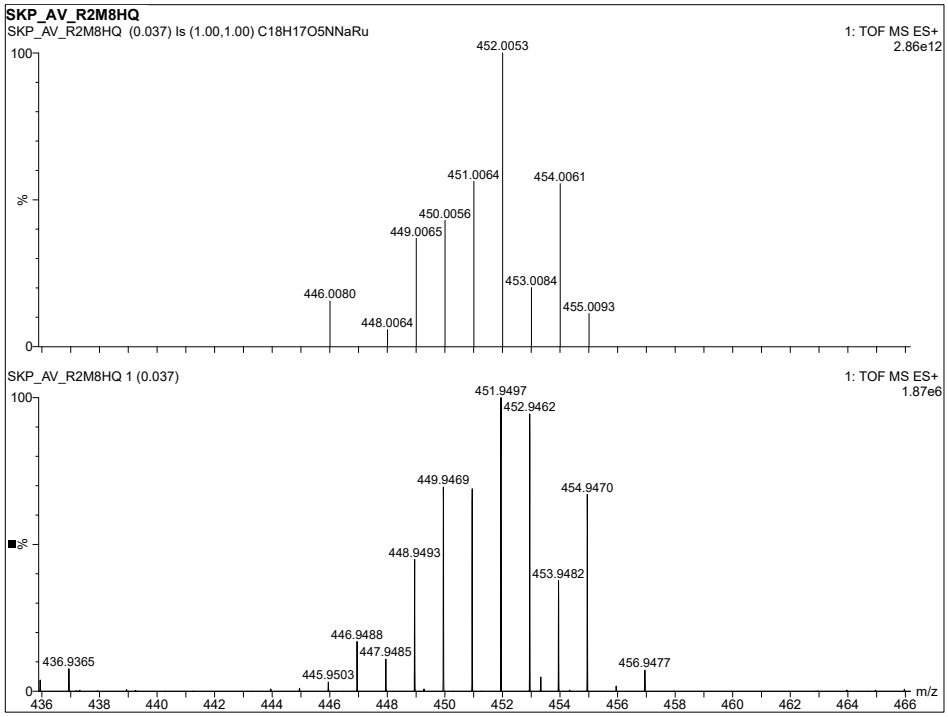


Figure S22. ESI-mass spectra of complex **1** with the addition of HCOOH and HCOONa; Calcd. for [Ru(η^6-benzene)(2M8hq)OOCH]+ HCOONa] + H$^+$ (m/z 452.005), Found (m/z = 451.9497).

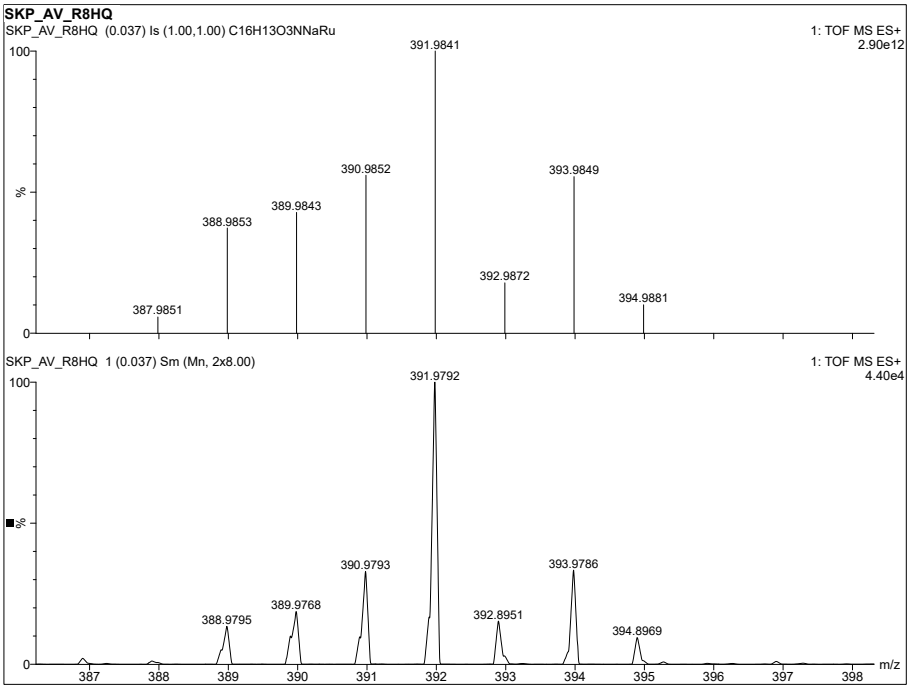


Figure S23. ESI-mass spectra of complex **2** with the addition of HCOOH and HCOONa for Calcd. for [Ru(η^6-benzene)(8hq)OOCH] + Na$^+$ (m/z 391.9841), Found (m/z = 391.9792).

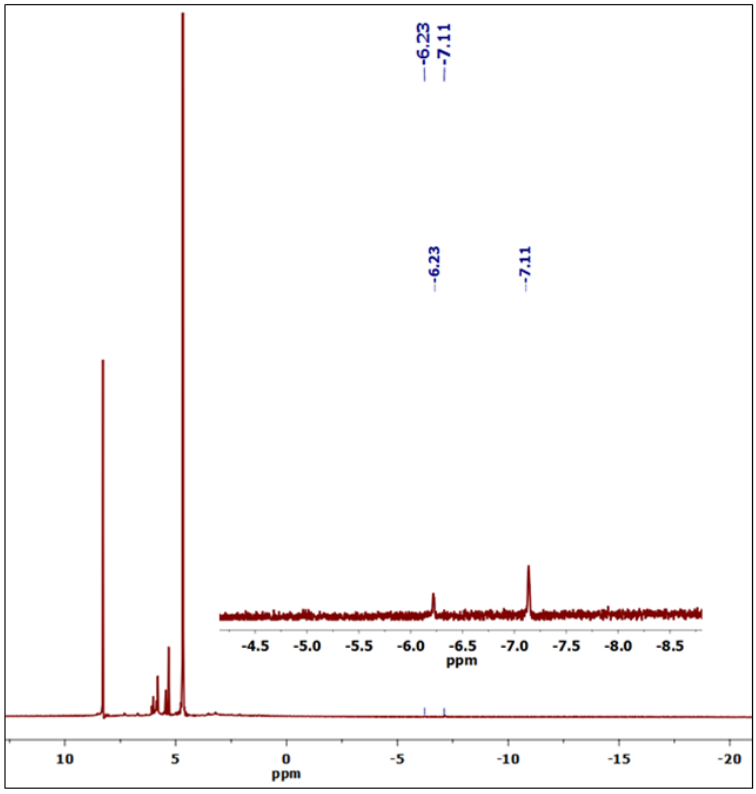


Figure S24. ^{1}H NMR of complex **1 in the presence of** HCOOH and HCOONa after heating at 90 °C.

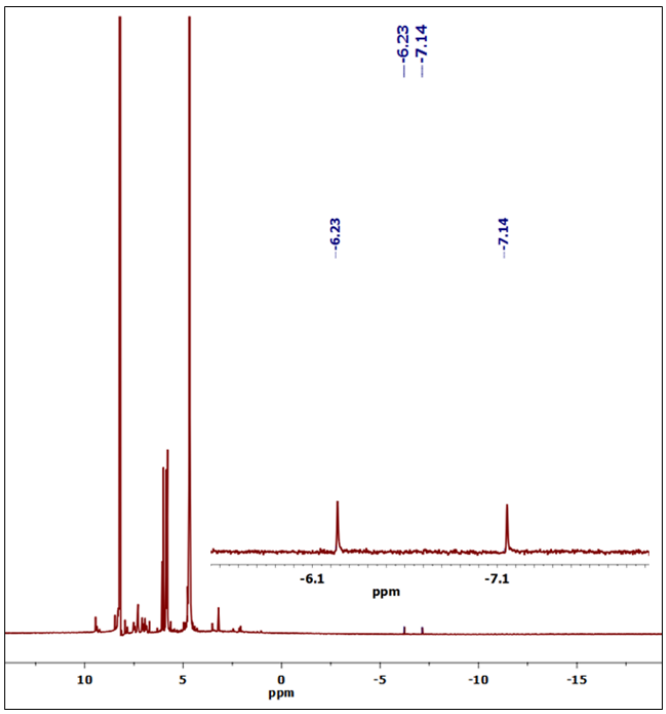


Figure S25. ^{1}H NMR of complex **2** in the presence of HCOOH and HCOONa after heating at 90 °C.

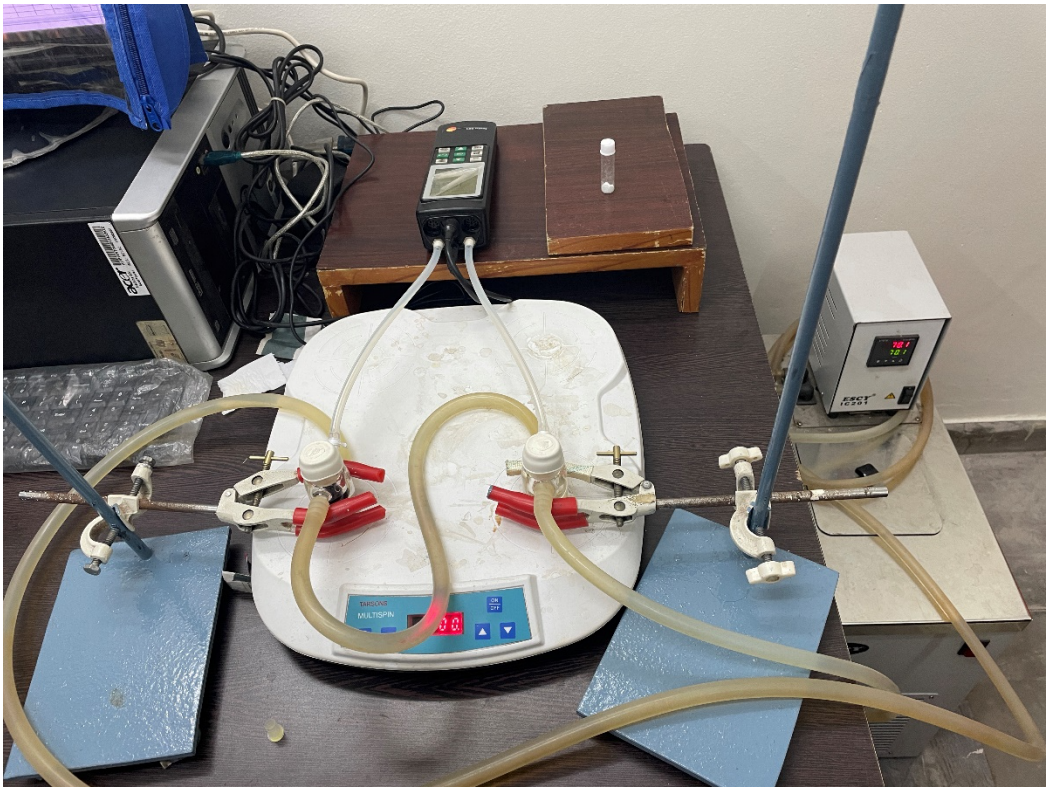


Figure S26. The presentation of the setup used for the dehydrogenation of formic acid.

Table S1. Crystal data and structure refinement for 1.

Identification code	2112742
Empirical formula	$C_{16}H_{14}NOClRu$
Formula weight	745.63
Temperature/K	293.2
Crystal system	triclinic
Space group	P-1
a/Å	7.5620(7)
b/Å	9.2366(8)
c/Å	9.7047(8)
α/°	91.151(7)
β/°	91.017(7)
γ/°	98.196(7)
Volume/Å^3	670.64(10)
Z	1
ρ_{calc}g/cm^3	1.8461
μ/mm^{-1}	1.361
F(000)	369.9
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.2 to 50
Index ranges	-10 ≤ h ≤ 10, -12 ≤ k ≤ 12, -12 ≤ l ≤ 13
Reflections collected	10363
Independent reflections	2331 [R_{int} = 0.0671, R_{sigma} = 0.0690]
Data/restraints/parameters	2331/0/182
Goodness-of-fit on F^2	0.989
Final R indexes [I>=2σ (I)]	R_1 = 0.0331, wR_2 = 0.0661
Final R indexes [all data]	R_1 = 0.0404, wR_2 = 0.0680

Table S2. Selected Bond Lengths for 1.

Atom	Atom	Length/Å
Ru1	N1	2.142(3)
Ru1	O1	2.051(2)
Ru1	C16	2.214(3)
Ru1	C11	2.182(3)
Ru1	C12	2.174(3)
Ru1	C13	2.169(3)
Ru1	C14	2.197(3)
Ru1	C15	2.175(3)
Ru1	Cl1	2.4180(9)

Table S3. Selected Bond Angles for 1.

Atom	Atom	Atom	Angle/°
O1	Ru1	N1	79.54(10)
C16	Ru1	N1	113.60(13)
C16	Ru1	O1	165.34(12)
C11	Ru1	N1	146.99(13)
C11	Ru1	O1	131.80(13)
C11	Ru1	C16	37.35(14)
C12	Ru1	N1	172.15(11)
C12	Ru1	O1	98.39(12)
C12	Ru1	C16	67.70(14)
C12	Ru1	C11	37.59(13)
C13	Ru1	N1	133.98(12)
C13	Ru1	O1	85.92(12)
C13	Ru1	C16	80.17(14)
C13	Ru1	C11	68.17(14)
C13	Ru1	C12	38.17(13)
C14	Ru1	N1	104.78(12)
C14	Ru1	O1	103.45(12)
C14	Ru1	C16	67.82(13)
C14	Ru1	C11	80.33(13)
C14	Ru1	C12	68.20(14)
C14	Ru1	C13	37.40(14)
C15	Ru1	N1	96.20(12)
C15	Ru1	O1	138.99(12)
C15	Ru1	C16	37.39(12)
C15	Ru1	C11	67.59(13)
C15	Ru1	C12	80.34(14)
C15	Ru1	C13	67.78(14)
C15	Ru1	C14	37.75(13)
Cl1	Ru1	N1	83.42(7)
Cl1	Ru1	O1	87.21(7)
Cl1	Ru1	C16	100.34(9)
Cl1	Ru1	C11	87.65(9)
Cl1	Ru1	C12	104.10(10)
Cl1	Ru1	C13	139.47(11)
Cl1	Ru1	C14	167.46(9)
Cl1	Ru1	C15	133.19(10)

Table S4. Crystal data and structure refinement for 2.

Identification code	2112741
Empirical formula	$C_{15}H_{14}ClNORu$
Formula weight	358.78
Temperature/K	293.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	7.3837(9)
b/Å	15.434(2)
c/Å	12.6134(18)
α/°	90
β/°	117.249(10)
γ/°	90
Volume/Å^3	1277.9(3)
Z	4
ρ_{calc}g/cm^3	1.8648
μ/mm^{-1}	1.424
F(000)	712.0
Crystal size/mm^3	0.26 × 0.23 × 0.21
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.048 to 50
Index ranges	-9 ≤ h ≤ 9, -20 ≤ k ≤ 18, -17 ≤ l ≤ 10
Reflections collected	5778
Independent reflections	2257 [R_{int} = 0.0349, R_{sigma} = 0.0563]
Data/restraints/parameters	2257/0/172
Goodness-of-fit on F^2	1.016
Final R indexes [I>=2σ (I)]	R_1 = 0.0378, wR_2 = 0.0665
Final R indexes [all data]	R_1 = 0.0544, wR_2 = 0.0723
Largest diff. peak/hole / e Å^{-3}	0.75/-0.63

Table S5. Selected Bond Lengths for 2.

Atom	Atom	Length/Å
Ru1	Cl1	2.4281(11)
Ru1	O1	2.048(3)
Ru1	N1	2.097(4)
Ru1	C13	2.168(5)
Ru1	C15	2.140(6)
Ru1	C12	2.183(5)
Ru1	C11	2.175(5)
Ru1	C10	2.155(6)
Ru1	C14	2.175(5)

Table S6. Selected Bond Angles for 2.

Atom	Atom	Atom	Angle/°
O1	Ru1	Cl1	87.08(9)
N1	Ru1	Cl1	85.00(10)
N1	Ru1	O1	78.61(13)
C13	Ru1	Cl1	90.17(16)
C13	Ru1	O1	153.3(2)
C13	Ru1	N1	127.6(2)
C15	Ru1	Cl1	150.1(3)
C15	Ru1	O1	122.0(3)
C15	Ru1	N1	93.8(2)
C15	Ru1	C13	67.0(3)
C12	Ru1	Cl1	94.10(15)
C12	Ru1	O1	117.0(2)
C12	Ru1	N1	164.3(2)
C12	Ru1	C13	36.7(2)
C12	Ru1	C15	79.2(2)
C11	Ru1	Cl1	121.79(19)
C11	Ru1	O1	92.29(18)
C11	Ru1	N1	151.5(2)
C11	Ru1	C13	66.9(2)
C11	Ru1	C15	68.0(3)
C11	Ru1	C12	36.9(2)
C10	Ru1	Cl1	159.4(2)
C10	Ru1	O1	94.6(2)
C10	Ru1	N1	115.4(2)
C10	Ru1	C13	79.2(2)
C10	Ru1	C15	37.7(3)
C10	Ru1	C12	66.9(2)
C10	Ru1	C11	37.7(3)
C14	Ru1	Cl1	113.1(2)
C14	Ru1	O1	159.6(3)
C14	Ru1	N1	99.3(2)
C14	Ru1	C13	36.8(2)
C14	Ru1	C15	37.6(3)
C14	Ru1	C12	66.6(3)
C14	Ru1	C11	79.9(2)
C14	Ru1	C10	67.8(3)

Table S7. The calculation for the Arrhenius plot and Eyring plot for **1**.

Temperature / [K]	$\frac{1}{T}$	k	$ln\ k$	$ln\ \frac{k}{T}$
298	0.00336	-3.699	-9.408	**298**
313	0.00319	-3.240	-8.987	**313**
328	0.00305	-2.852	-8.650	**328**
343	**0.00292**	**-2.064**	**-7.904**	**343**

Table S8. The calculation for the Arrhenius plot and Eyring plot for **2**.

Temperature / [K]	$\frac{1}{T}$	k	$ln\ k$	$ln\ \frac{k}{T}$
298	313	0.00319	-3.461	**-9.2379**
313	328	0.00304	-2.9132	**-8.9380**
328	343	0.00291	-2.2990	**-8.8724**
343	**358**	**0.00279**	**-2.0768**	**-8.7384**