

Supporting Information

Ligand tuned catalytic activity of Ruthenium-imidazolyl amine complexes for reversible formic acid dehydrogenation and CO₂ hydrogenation to formic acid

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General procedure for TON and TOF calculation in FA dehydrogenation.

The turnover number (TON) was calculated by the following equation:

$$\text{TON} = \frac{V_{\text{corrected}}}{\left(V_{\text{m,H}_2, 25^\circ \text{C}} + V_{\text{m,CO}_2, 25^\circ \text{C}} \right) \times n_{\text{catalyst}}} = \frac{\text{Substrate}}{\text{Catalyst}} \times \frac{\text{Conversion (\%)}}{100}$$

where, V_{measured} and V_{blank} are the volume of gas measured in the catalytic reaction and blank reaction, $V_{\text{corrected}} = V_{\text{measured}} - V_{\text{blank}}$, V_{m} are the molar volume of H_2 and CO_2 , respectively, and n_{catalyst} is the molar amount of catalyst. To account for temperature changes that can affect the measurements of evolved gas volume, a blank reaction without any catalyst was performed. The blank volume (V_{blank}) was observed to be constant over the course of the reaction and was used to correct all the measured gas volumes (V_{measured}) generated during FA dehydrogenation. The turnover frequency (TOF) was calculated by the following equation:

$$\text{TOF} = \frac{\text{TON}}{\text{Time}}$$

where time is in hour.

For example, for entry 12 (Table 1) the dehydrogenation of an aqueous solution of FA (1 mmol, 0.4 M in water) with SF (0.25 mmol) at 90 °C, over *in situ* **Ru/L7** catalyst (**Ru**: 10 μmol , **L7**: 20 μmol), in the first 3 min 49 mL gas was released with complete conversion of FA. Therefore, the TON and TOF for this reaction can be calculated as follows:

$$\begin{aligned} \text{TON} &= \frac{1 \text{ mmol}}{0.01 \text{ mmol}} \times \frac{49 \text{ mL}}{49 \text{ mL}} = 100 \\ \text{TOF} &= \frac{100}{3 \text{ min}} \times 60 \text{ min} = 2000 \text{ h}^{-1} \end{aligned}$$

Table S1 Catalytic FA dehydrogenation in water over *in-situ* **Ru/Ln** catalysts

Entry	Catalysts	Volume of gas (mL)	Time (min)	TON	TOF (h ⁻¹)
1	Ru	35	390	71	193
2	Ru/L1	28	244	57	122
3	Ru/L2	26	167	53	131
4	Ru/L3	38	187	78	196
5	Ru/L4	34	176	69	81
6	Ru/L5	30	127	61	131
7	Ru/L6	49	27	100	322
8	Ru/L7	49	12	100	587
9	Ru/L8	49	19	100	322
10	Ru/L9	46	15	95	261

Reaction condition: FA (0.4 M, 2.5 mL in water), *in situ* **Ru/Ln** catalysts (**Ru**: 10 μ mol, **Ln**: 20 μ mol) at 90 °C. TON and TOF values were estimated, respectively at the end of the reaction and initial 3 min. Ru: $[(\eta^6\text{-C}_{10}\text{H}_{14})\text{RuCl}_2]_2$ and Ln: **L1-L9**.

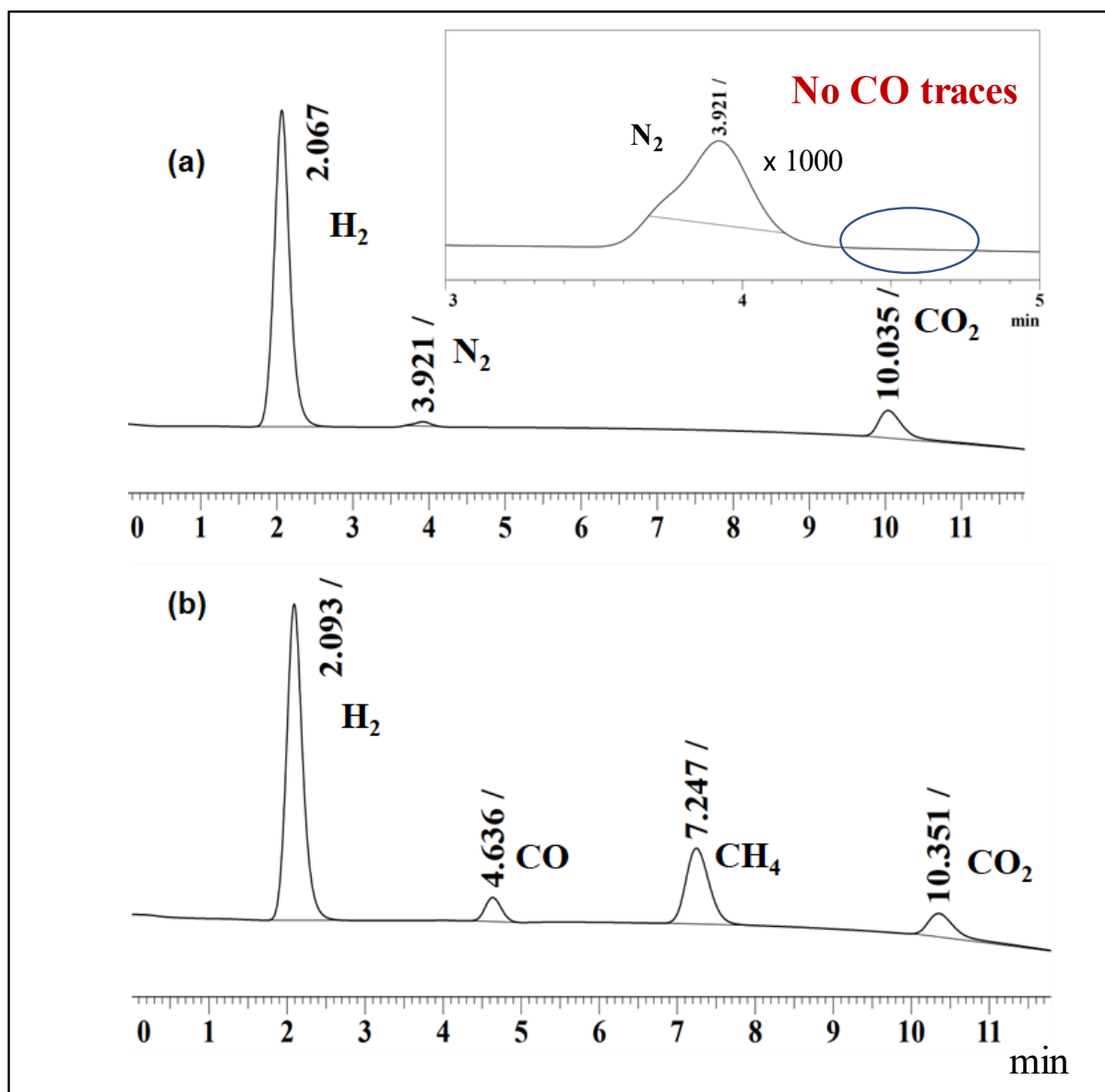


Fig. S1 GC-TCD analysis of the (a) evolved gas ($\text{H}_2\text{:CO}_2 \approx 1\text{:}1$) for the catalytic FA dehydrogenation over *in situ* **Ru/L7** catalyst (Analysis is performed using Argon as the carrier gas). No CO traces (inset). Reaction conditions: FA (0.4 M, 2.5 mL in water), SF (0.25 mmol), *in situ* **Ru/L7** catalyst (**Ru**: 10 μmol , **L7**: 20 μmol) at 90 °C. (b) Pure mixture of gas containing H_2 , CO , CH_4 , CO_2 .

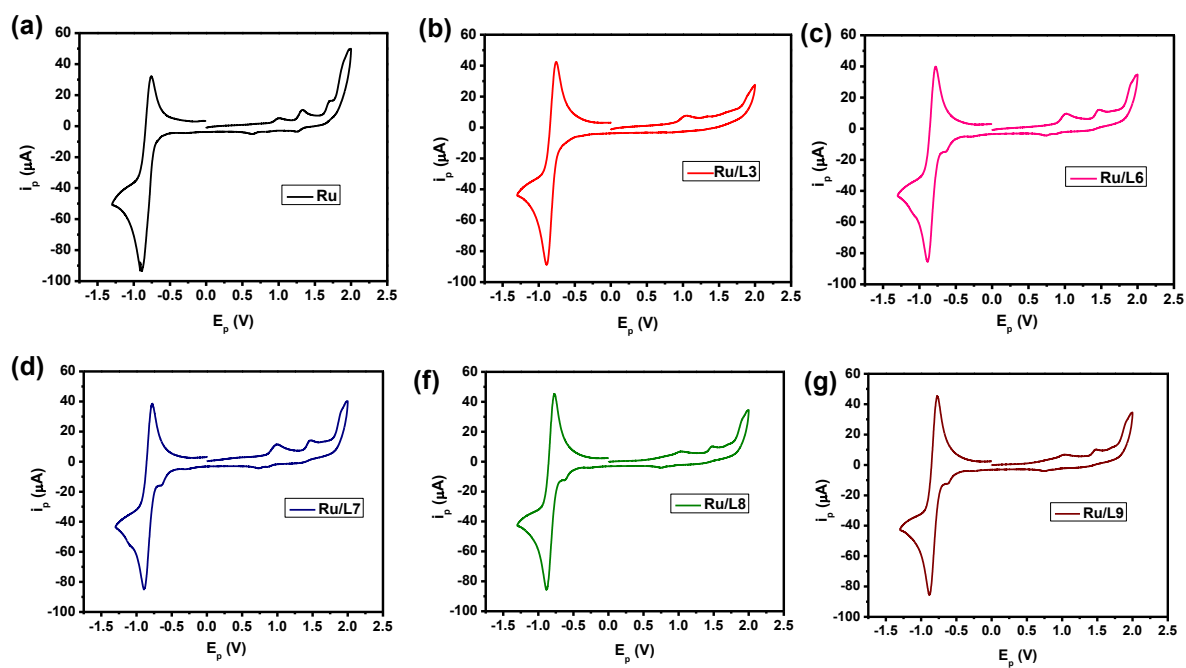


Fig. S2 Cyclic voltammograms for catalysts (1mM) (a) **Ru** (b) **Ru/L3** (c) **Ru/L6** (d) **Ru/L7** (e) **Ru/L8** and (f) **Ru/L9** in acetonitrile with 0.1 M NBu_4PF_6 as supporting electrolyte at a scan rate of 0.1 Vs^{-1} .

Table S2 Electrochemical data extracted from cyclic voltammograms of **Ru**, **Ru/L3**, **Ru/L6**, **Ru/L7**, **Ru/L8** and **Ru/L9** complexes

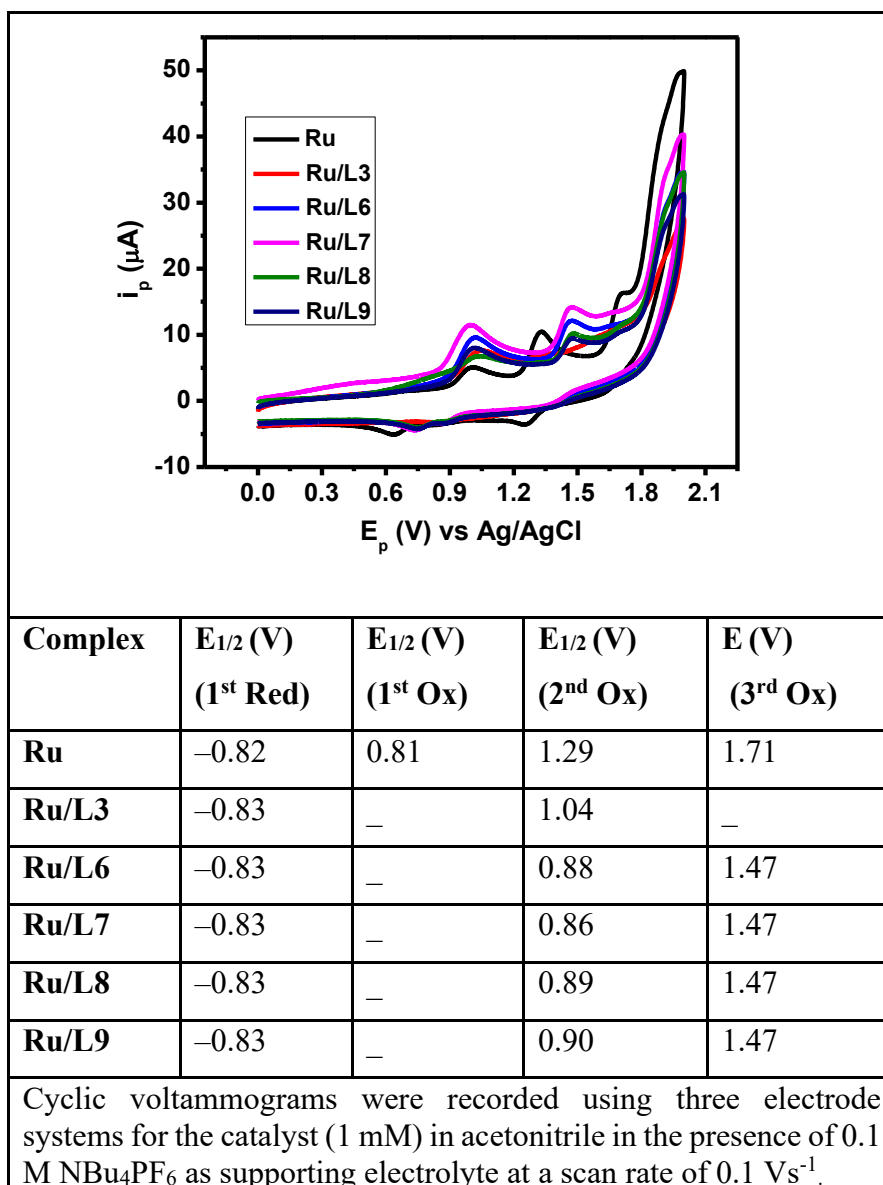


Table S3 Kinetics parameter for FA dehydrogenation over **Ru/L7** in water

Temperature (K)	$1/T \times 10^3 \text{ (K}^{-1}\text{)}$	$k \text{ (s}^{-1}\text{)}$	$\ln[k] \text{ (s}^{-1}\text{)}$
363	2.75	0.555556	-0.58779
353	2.83	0.253889	-1.37086
343	2.91	0.108889	-2.21743
333	3.00	0.054167	-2.91569
323	3.09	0.022778	-3.78197

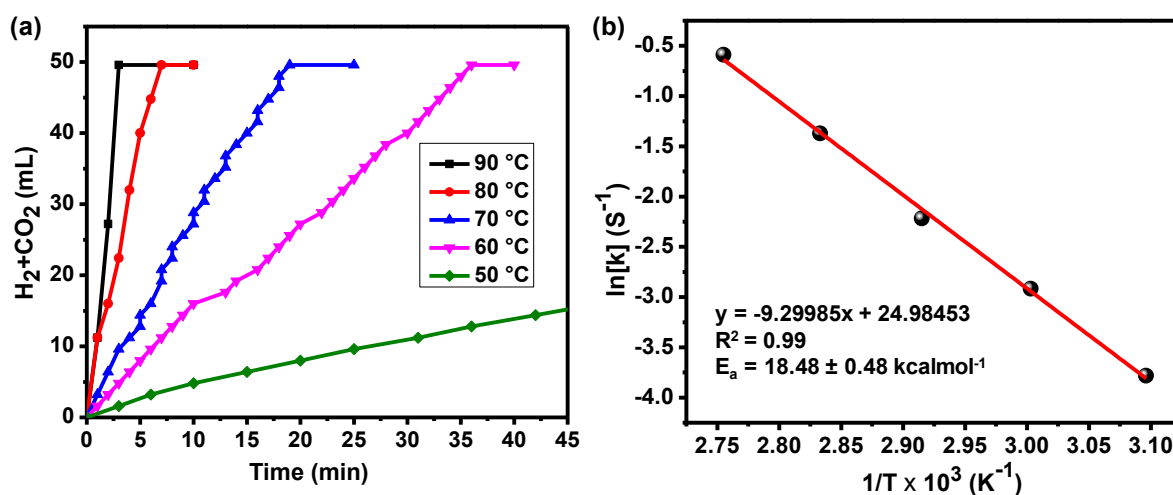


Fig. S3 (a) Temperature dependent FA dehydrogenation over *in situ* **Ru/L7** catalyst and (b) the corresponding Arrhenius plot was based on the initial rate at 3 min for FA dehydrogenation. Reaction conditions: FA (0.4 M, 2.5 mL in water), SF (0.25 mmol), *in situ* **Ru/L7** catalyst (**Ru**: 10 μ mol, **L7**: 20 μ mol), 50 °C – 90 °C.

Estimation of activation energy (E_a) using Arrhenius plot:

We know the Arrhenius equation as $k = Ae^{-E_a/RT}$

$\ln k = \ln A + (-E_a/R)1/T$, where E_a is the activation energy and R is molar gas constant (1.987 cal K⁻¹ mol⁻¹) and T is temperature in Kelvin (323 K – 363 K)

From the Arrhenius plot (**Fig. S3**): Slope = -9.29985 ± 0.23939

As from $\ln[k]$ vs. $1/T$ plot, we got slope = $-E_a/R = -9.29985 \pm 0.23939$

Therefore, $E_a = 18.48 \pm 0.48$ k cal mol⁻¹

Table S4 Activation energies (E_a) for FA dehydrogenation in water over various literature known catalysts

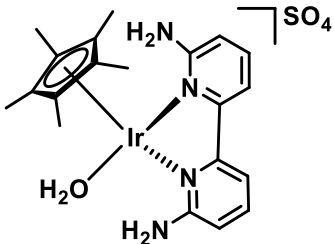
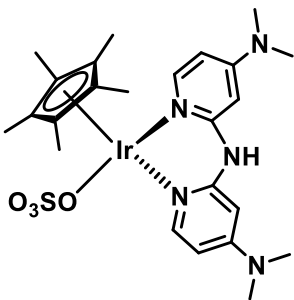
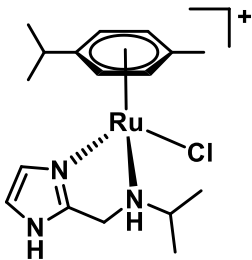
Catalysts	Reaction conditions	E_a (kcalmol ⁻¹)	Ref.
	HCOOH (1 mol/L M, 2.5 mL), H ₂ O, 50-80 °C, 10 min	19.45	S1
[Cp*Ir(pyrimidylimidazoline)H ₂ O] SO ₄	HCOOH (1 M, 10 mL), H ₂ O, 45-70 °C, 0.17 h	18.69	S2
[Cp*Ir(THBPM)(H ₂ O)]SO ₄ where THBPM: 2,2',6,6'-tetrahydroxyl-4,4'-bipyrimidine	1 M HCOOH/HCOONa (1:1, 10 mL), H ₂ O, 50-80 °C, 0.08 h	18.26	S3
	HCOOH (4 mmol), H ₂ O (1.3 mL), 60-90 °C, 5 min	18.49	S4
	HCOOH (0.4 M, 2.5 mL), HCOONa (0.25 mmol), H ₂ O, 50-90 °C, 3 min	18.48	This work

Table S5. Determination of activation parameters for FA dehydrogenation over **Ru/L7** catalyst in water

T (K)	(1/T) x 10 ³ (K ⁻¹)	k (s ⁻¹)	k/T (s ⁻¹ K ⁻¹)	[k/T x c], where c = h/k', (h = Planck's constant and k' = Boltzmann's constant)	ln[k/T x c] (e. u.)
363	2.75	0.555556	0.00153	7.3309 x 10 ⁻¹⁴	-30.2441
353	2.83	0.253889	0.000719	3.4451 x 10 ⁻¹⁴	-30.9992
343	2.91	0.108889	0.000317	1.5206 x 10 ⁻¹⁴	-31.8171
333	3.00	0.054167	0.000163	7.7916 x 10 ⁻¹⁵	-32.4857
323	3.09	0.022778	0.0000705	3.3779 x 10 ⁻¹⁵	-33.3215

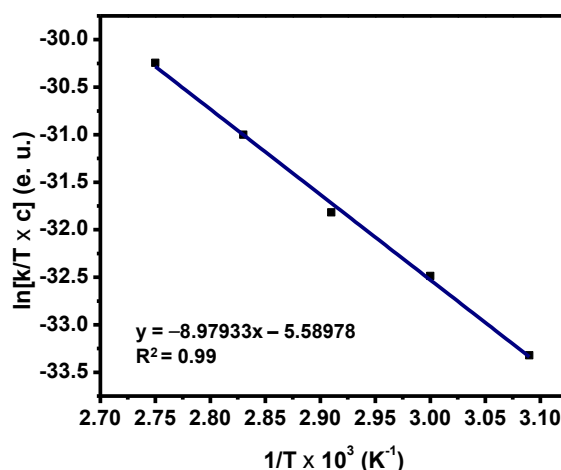


Fig. S4 Eyring plot for FA dehydrogenation. Reaction conditions: FA (0.4 M, 2.5 mL in water), SF (0.25 mmol), *in situ* **Ru/L7** catalyst (**Ru**: 10 μ mol, **L7**: 20 μ mol), 50°C – 90 °C, where e. u. is the energy unit for $\frac{\Delta S^\ddagger}{R}$ value.

Estimation of activation parameters using Eyring plot:

We know the Eyring equation as $k = \frac{k'T}{h} e^{-\frac{\Delta H^\ddagger}{RT}} e^{\frac{\Delta S^\ddagger}{R}}$

So,

$$\frac{k}{T} \frac{h}{k'} = e^{-\frac{\Delta H^\ddagger}{RT}} e^{\frac{\Delta S^\ddagger}{R}}$$

Now

$$\ln\left(\frac{k}{T} \frac{h}{k'}\right) = -\frac{\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R}$$

Considering $\frac{h}{k'}$ as constant $c = 4.79 \times 10^{-11} \text{ s K}$, where h =Planck's constant and k' =Boltzman's constant

Therefore

$$\ln\left(\frac{k}{T} \times c\right) = -\frac{\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R}$$

Now from the Eyring plot (**Fig. S4**) $\ln\left(\frac{k}{T} \times c\right)$ vs. $1/T$, we got slope $-\frac{\Delta H^\ddagger}{R} = -8.97933 \pm 0.24469$

Therefore, $\Delta H^\ddagger = 17.84 \pm 0.49 \text{ kcalmol}^{-1}$

Again, we got intercept as $\frac{\Delta S^\ddagger}{R} = -5.58978 \pm 0.71414$

Therefore, $\Delta S^\ddagger = -11.11 \pm 1.42 \text{ calK}^{-1}\text{mol}^{-1}$

And $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$

Therefore, at 298 K $\Delta G^\ddagger = 21.15 \pm 0.65 \text{ kcalmol}^{-1}$

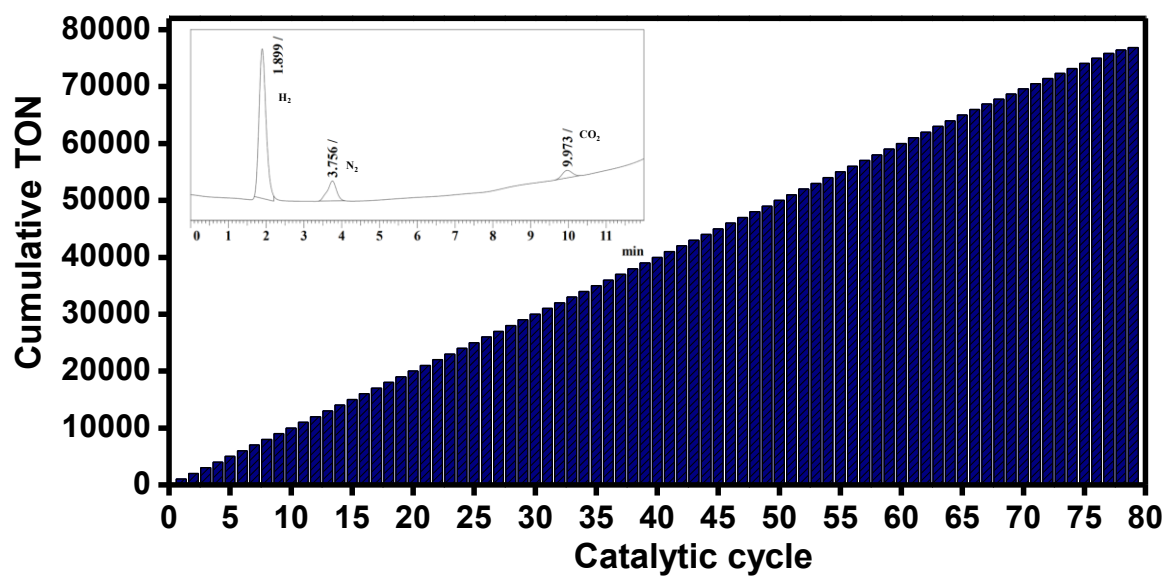
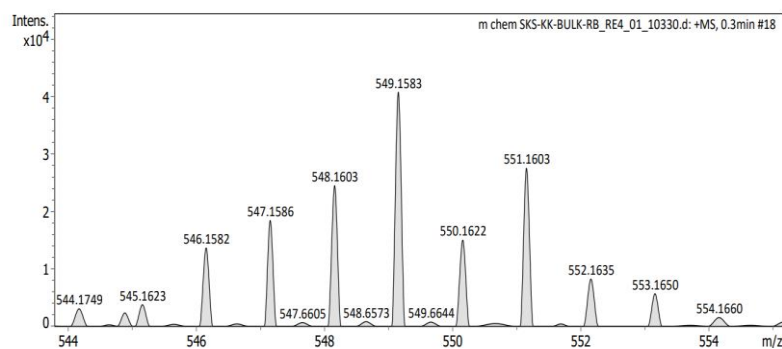
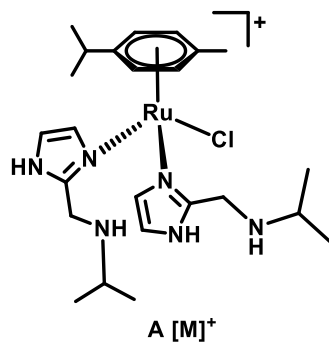


Fig. S5 Recyclability plot for catalytic FA dehydrogenation over *in situ* **Ru/L7** catalyst. Reaction conditions: FA (0.4 M, 25 mL in water), SF (2.5 mmol), *in situ* **Ru/L7** catalyst (**Ru**: 10 μ mol, **L7**: 20 μ mol) at 90°C. FA (380 μ L) was added after each catalytic run. GC-TCD analysis after 80 catalytic runs (inset).

(a)



(b)

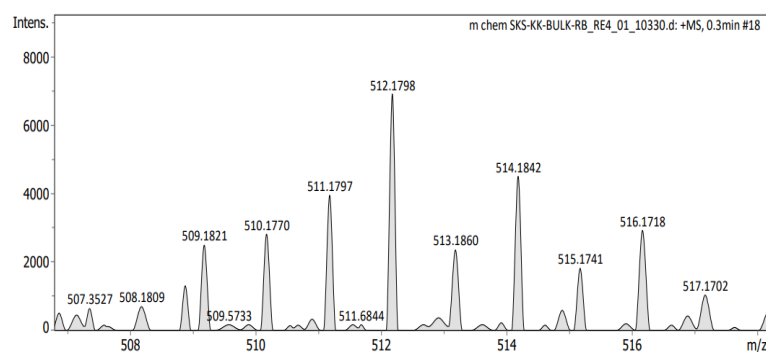
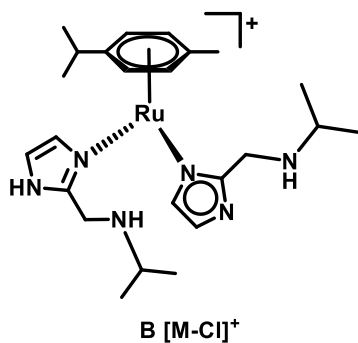


Fig. S6 Minor Ru/(Ln)₂ species observed after 70 catalytic runs for FA dehydrogenation over Ru/L7 catalyst.

Table S6 Upscaling the catalytic FA dehydrogenation over *in situ* **Ru/L7** catalyst

Entry	FA (mmol)	Volume of gas (mL)	Time (min)	TON	TOF (h ⁻¹)
1 ^a	1	49	3	100	2000
2 ^b	10	489	60	1000	1078
3 ^c	20	979	280	2000	530
4 ^d	30	1469	520	3000	471
5 ^e	50	2448	780	5000	451

Reaction conditions: ^aFA (0.4 M, 2.5 mL in water), ^bFA (0.4 M, 25 mL in water), ^cFA (0.4 M, 50 mL in water), ^dFA (0.4 M, 75 mL in water), ^eFA (0.4 M, 120 mL in water), with SF (0.25 equiv. of FA), *in situ* **Ru/L7** catalyst (**Ru**: 10 μ mol, **L7**: 20 μ mol) at 90°C. TON are calculated the end of the reaction. ^aTOF (initial 3 min). ^{b-e}TOF (initial 10 min).

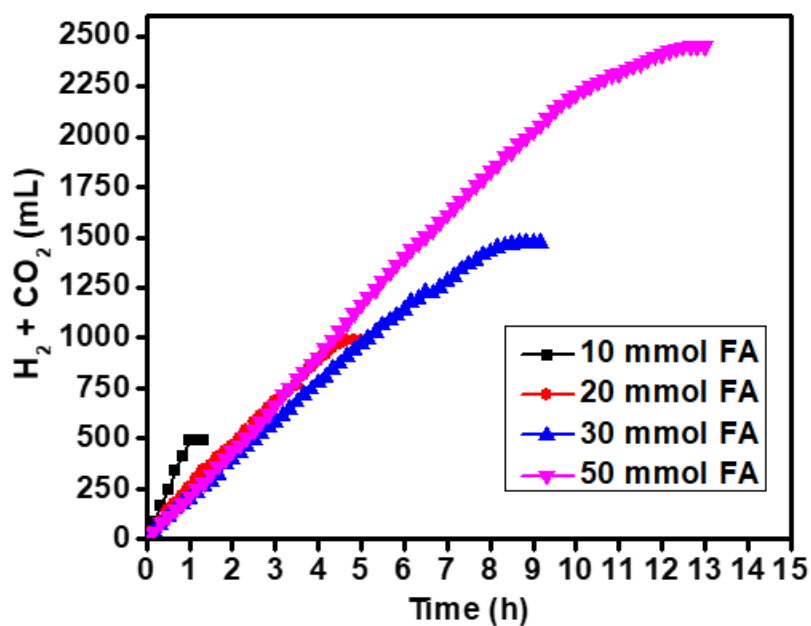


Fig. S7 Gas evolution plot for upscaling the catalytic FA dehydrogenation over *in situ* **Ru/L7** catalyst (**Ru**: 10 μ mol, **L7**: 20 μ mol) at 90°C. Reaction conditions: 10 fold: FA (0.4 M, 25 mL in water), SF (2.5 mmol); 20 fold: FA (0.4 M, 50 mL in water), SF (5 mmol); 30 fold: FA (0.4 M, 75 mL in water), SF (7.5 mmol); and 50 fold: FA (0.4 M, 125 mL in water), SF (12.5 mmol).

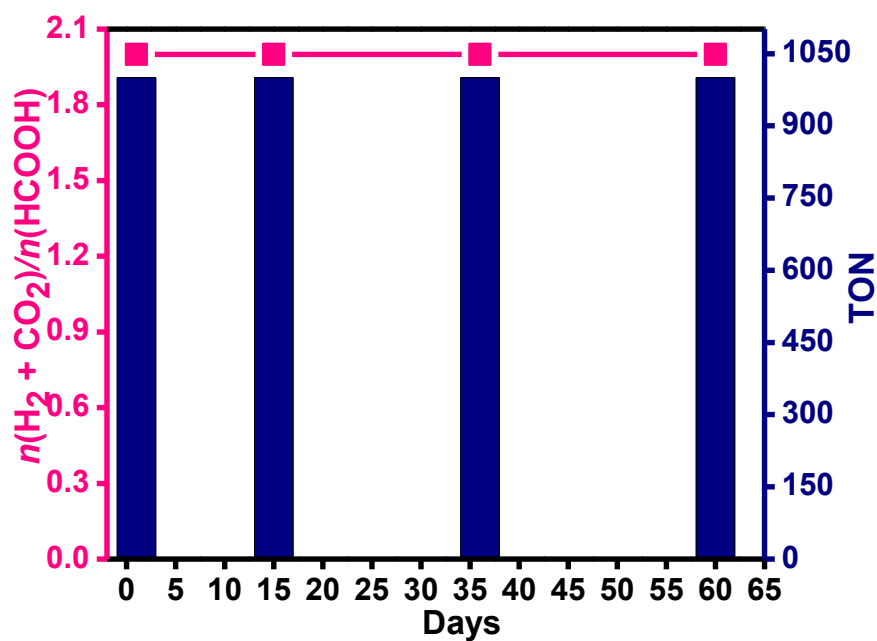


Fig. S8 Long-term stability of the catalytic FA dehydrogenation over *in situ* **Ru/L7** catalyst in water at 90 °C, FA (380 μL) was added after days 15, 36 and 60 days in the same reaction mixture. Reaction conditions: FA (0.4 M, 25 mL in water), SF (2.5 mmol), *in situ* **Ru/L7** catalyst (**Ru**: 10 μmol , **L7**: 20 μmol) at 90°C.

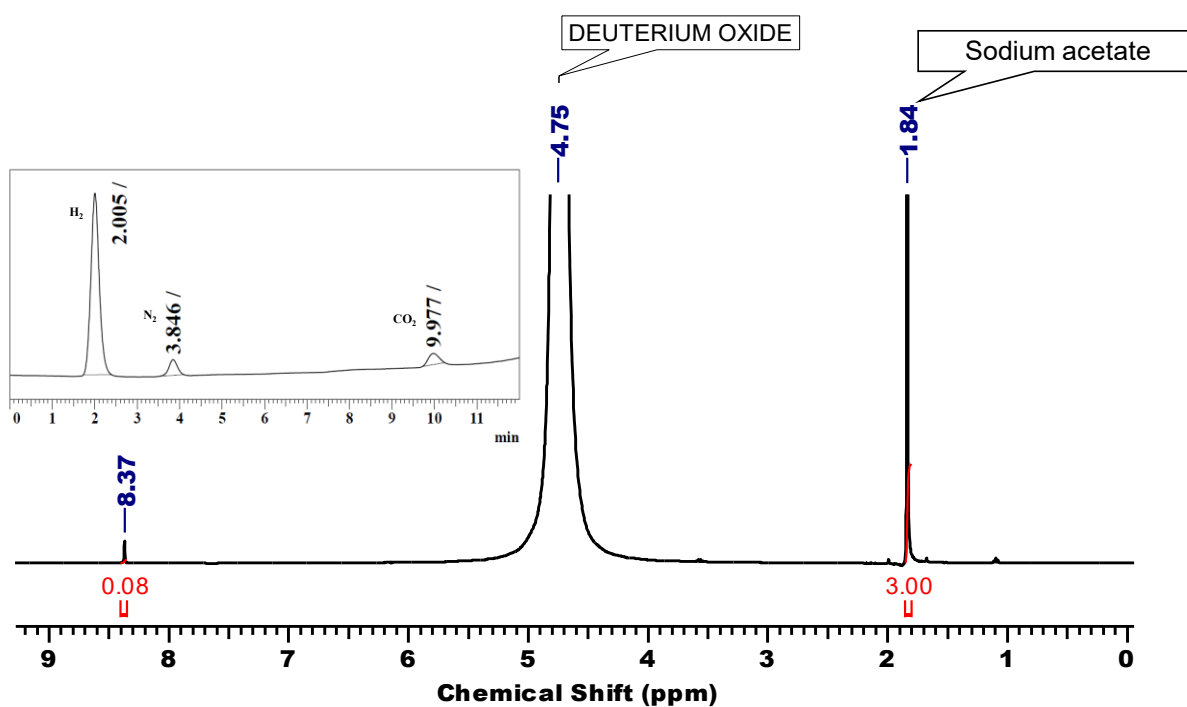


Fig. S9 ^1H NMR of reaction aliquot of the catalytic FA dehydrogenation over *in situ* **Ru/L7** catalyst in a high pressure reactor (Closed system) GC-TCD analysis of the evolved gas (inset) Reaction conditions: FA (0.4 M, 25 mL in water), SF (2.5 mmol), *in situ* **Ru/L7** catalyst (**Ru**: 10 μmol , **L7**: 20 μmol), at 90 $^\circ\text{C}$. NMR yield is calculated by using sodium acetate (0.05 mmol) as internal standard.

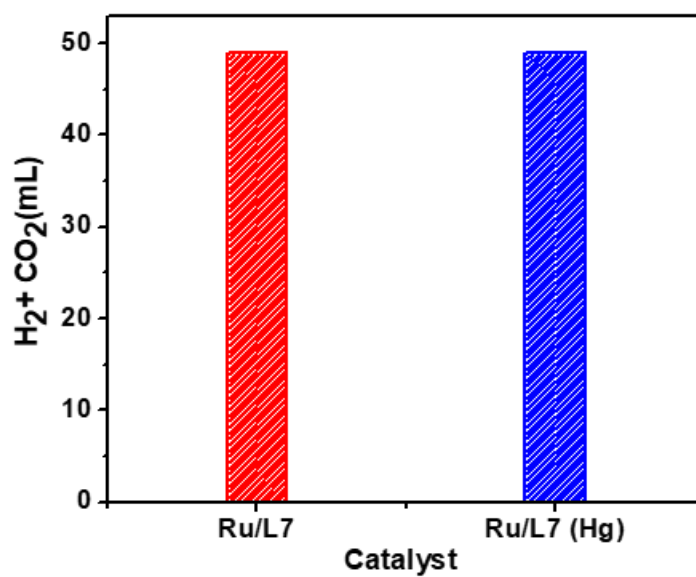


Fig. S10 Control Hg(0) poisoning experiment, with and without a large excess of elemental Hg(0). Reaction conditions: FA (0.4 M, 2.5 mL in water), *in situ* **Ru/L7** catalyst (**Ru**: 10 μ mol, **L7**: 20 μ mol), SF (0.25 mmol), 90 °C.

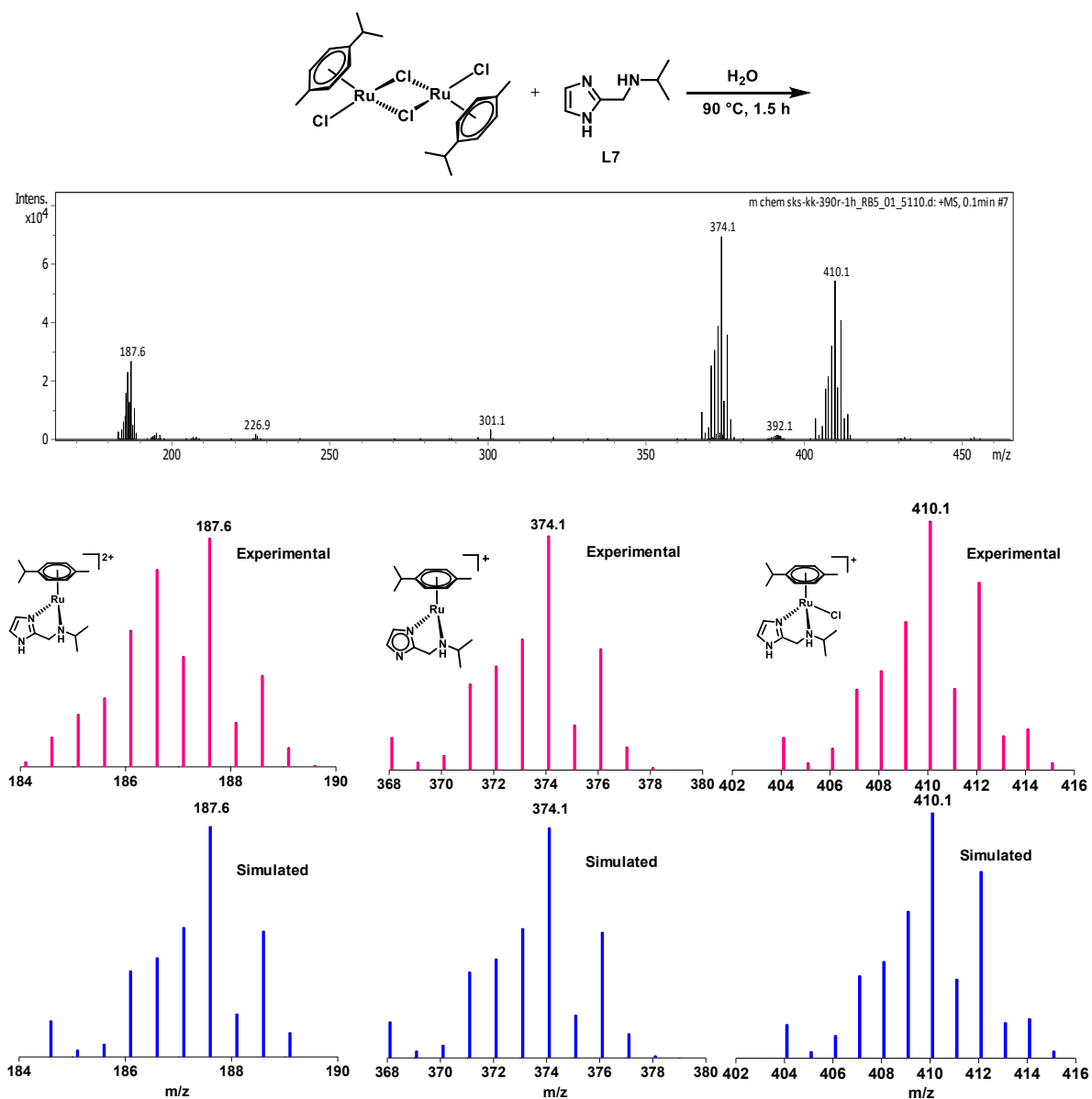


Fig. S11 Mass analysis of various species formed during the *in situ* generation of **Ru/L7** catalyst. Reaction conditions: **Ru** (10 μmol), **L7** (20 μmol), H_2O (2.5 mL), 90 $^\circ\text{C}$, 1.5 h.

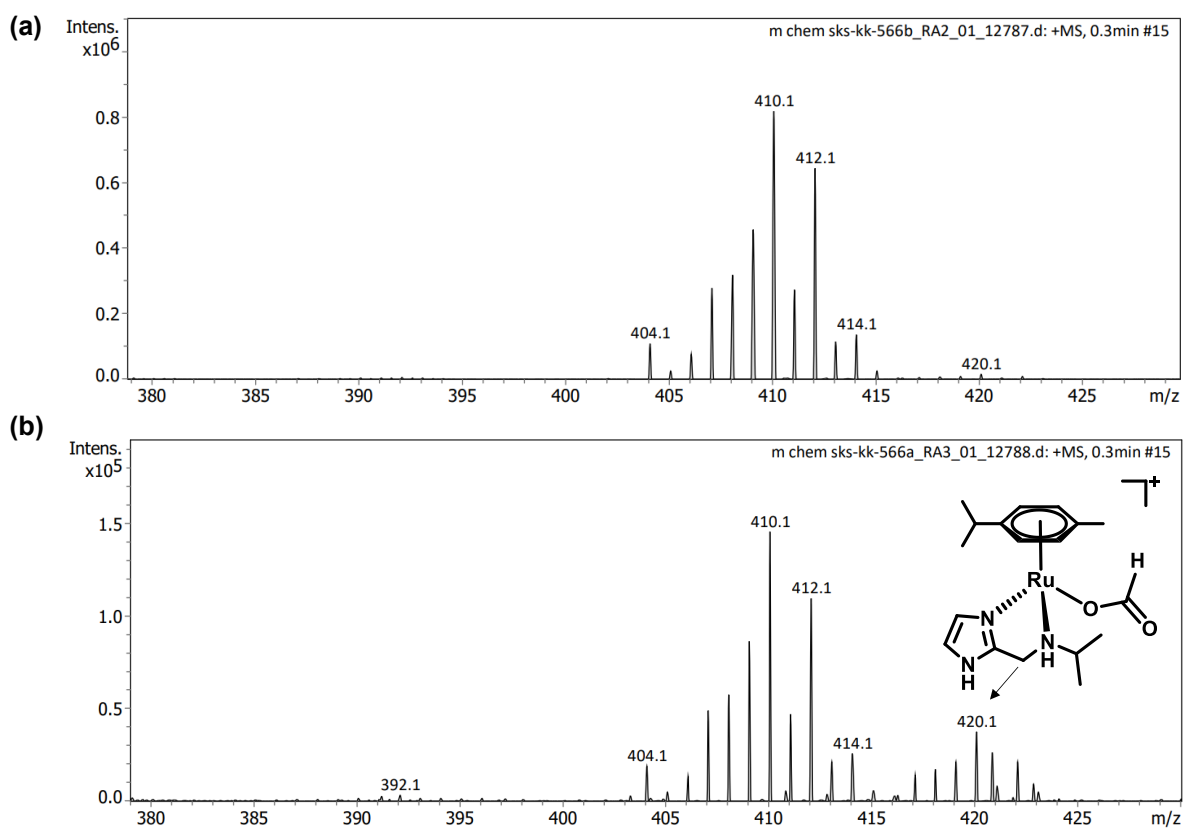
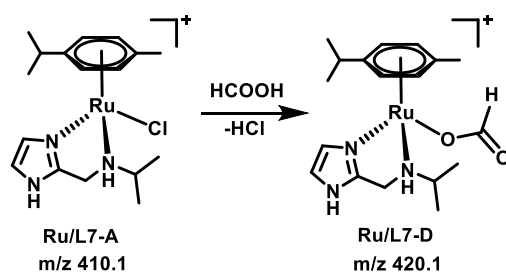


Fig. S12 Formation Ru-formato species **Ru/L7-B**. (a) Reaction conditions: **Ru** (10 μmol), **L7** (20 μmol), FA (1 mmol), H₂O (2.5 mL), 90 °C, 15 min. (b) Reaction conditions: **Ru** (10 μmol), **L7** (20 μmol), FA (1 mmol), SF (0.25 mmol), H₂O (2.5 mL), 90 °C, 2 min.

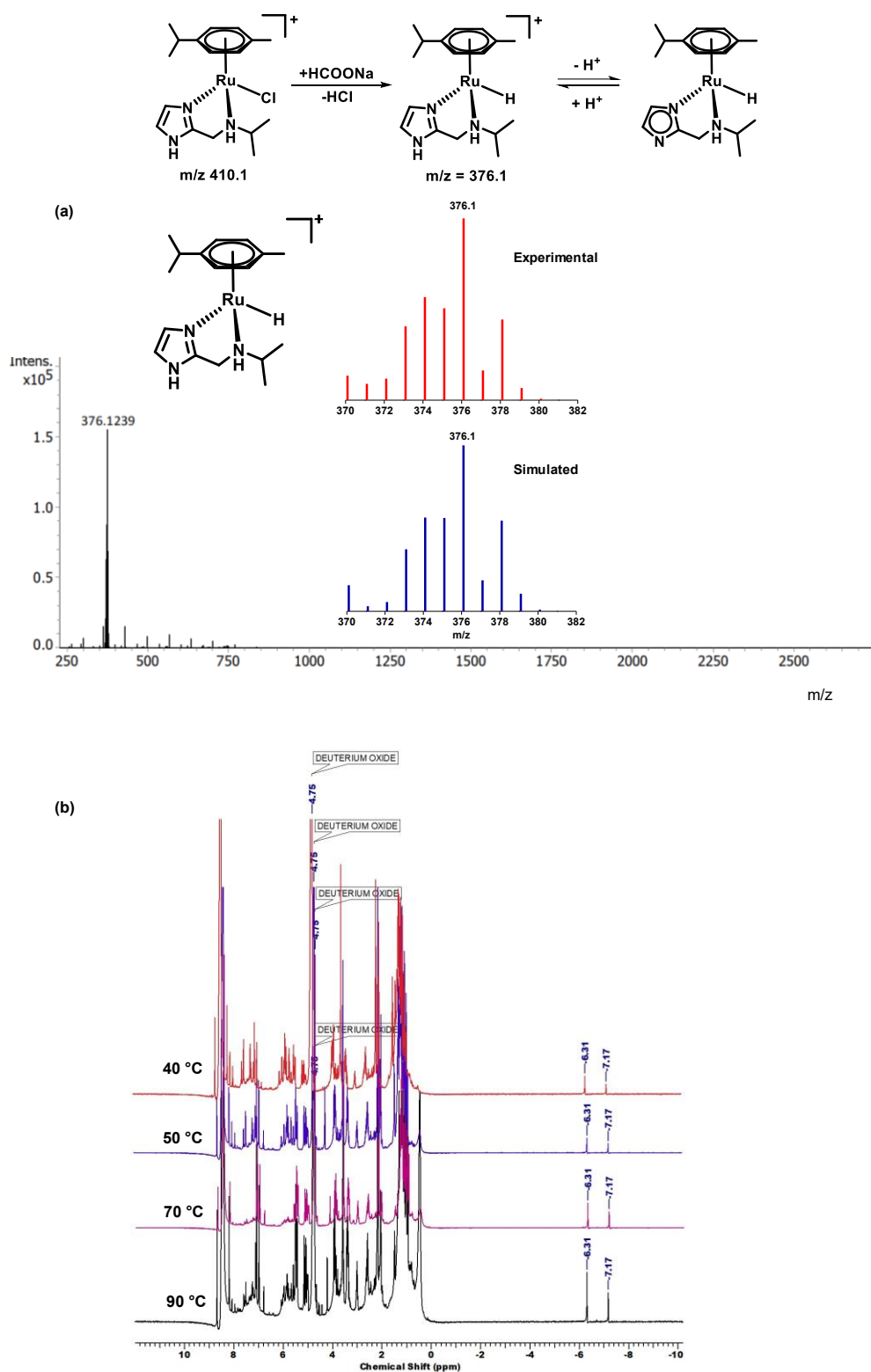


Fig. S13 (a) Mass analysis of Ru hydrido species **Ru/L7-C**. (b) Temperature dependent ^1H NMR analysis in D_2O . Reaction conditions: **Ru** (10 μmol), **L7** (20 μmol), SF (1 mmol), D_2O (2.5 mL), at 40, 50, 70 and 90 $^\circ\text{C}$ for 10 min each.

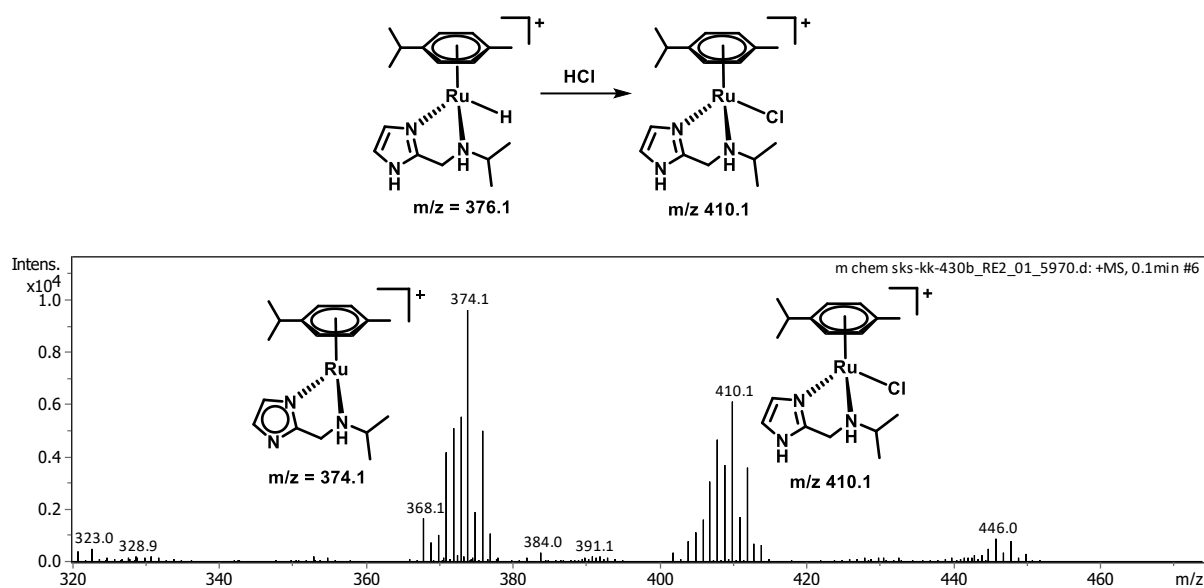


Fig. S14 Mass investigation of the reaction mixture of *in situ* **Ru** (10 μmol), **L7** (20 μmol), treated with SF (1 mmol) in water (2.5 mL) stirred at 90 $^{\circ}\text{C}$ for 10 min in step 1, and further with 1 M HCl (1 mL) in the step 2.

Table S7 Single crystal X-ray refinement data for **Ru/L7**

Identification Code	Ru/L7
Formula	C ₁₇ H ₂₇ N ₃ RuCl ₂
Molecular weight	445.39
Crystal system	triclinic
Space group	P -1
Temperature/K	296
Wavelength	0.71073
a/Å	8.4626(4)
b/Å	8.6713(4)
c/Å	13.9310(7)
α /°	95.566(1)
β /°	102.413(1)
γ /°	92.563(1)
V/ Å ³	991.41(8)
Z	2
Density/gcm ⁻³	1.492
Absorption Coefficient	9.258
Absorption Correction	spherical harmonics- Frame scaling
F(000)	456.0
Total no of reflections	4915
Reflections, I>2 σ (I)	4629
Max. 2 θ /°	28.278
Ranges (h, k, l)	-11 ≤ h ≤ 10 -9 ≤ k ≤ 11 -18 ≤ l ≤ 18
Complete to 2 θ (%)	99.7
Refinement method	'SHELXL 2014/7 (Sheldrick, 2015)
Goof (F ²)	1.039
R indices [I>2 σ (I)]	0.0228
R Indices (all data)	0.0246

Table S8 Selected bond lengths (Å) for complex **Ru/L7**

Ru1 C11	2.4182(5)
Ru1 N1	2.0773(15)
Ru1 N2	2.1949(15)
Ru1 C2	2.2107(18)
Ru1 C3	2.1771(17)
Ru1 C4	2.1699(18)
Ru1 C5	2.2017(17)
Ru1 C6	2.1754(18)
Ru1 C7	2.1956(18)
N1 C11	1.385(2)
N1 C13	1.328(2)
N2 C14	1.490(2)
N2 C15	1.506(2)
N3 C12	1.380(2)
N3 C13	1.338(2)
C1 C2	1.497(3)
C2 C3	1.411(3)
C2 C7	1.432(3)
C3 C4	1.427(3)
C4 C5	1.409(2)
C5 C6	1.434(3)
C5 C8	1.517(3)
C6 C7	1.403(3)
C8 C9	1.532(3)
C8 C10	1.521(3)
C11 C12	1.363(3)
C13 C14	1.488(3)
C15 C16	1.517(3)
C15 C17	1.525(3)

Table S9 Selected bond angles (°) for **Ru/L7**

N1 Ru1 Cl1	84.30(4)
N1 Ru1 N2	75.16(6)
N1 Ru1 C2	126.10(6)
N1 Ru1 C3	98.32(6)
N1 Ru1 C4	93.77(6)
N1 Ru1 C5	115.32(6)
N1 Ru1 C6	152.12(7)
N1 Ru1 C7	164.00(7)
N2 Ru1 Cl1	87.99(4)
N2 Ru1 C2	93.16(6)
N2 Ru1 C5	169.48(6)
N2 Ru1 C7	101.76(7)
C2 Ru1 Cl1	148.81(5)
C3 Ru1 Cl1	159.91(5)
C3 Ru1 N2	111.98(6)
C3 Ru1 C2	37.51(7)
C3 Ru1 C5	68.76(7)
C3 Ru1 C7	67.93(7)
C4 Ru1 Cl1	121.83(5)
C4 Ru1 N2	147.46(6)
C4 Ru1 C2	68.46(7)
C4 Ru1 C3	38.33(7)
C4 Ru1 C5	37.60(6)
C4 Ru1 C6	68.11(7)
C4 Ru1 C7	80.45(7)
C5 Ru1 Cl1	92.03(5)
C5 Ru1 C2	81.39(7)
C6 Ru1 Cl1	87.71(5)
C6 Ru1 N2	131.28(6)
C6 Ru1 C2	68.29(7)
C6 Ru1 C3	80.72(7)

C6 Ru1 C5	38.25(7)
C6 Ru1 C7	37.45(7)
C7 Ru1 C11	111.46(5)
C7 Ru1 C2	37.91(7)
C7 Ru1 C5	68.46(7)
C11 N1 Ru1	136.52(12)
C13 N1 Ru1	115.85(12)
C13 N1 C11	106.74(15)
C14 N2 Ru1	109.76(11)
C14 N2 C15	113.39(15)
C15 N2 Ru1	120.95(11)
C13 N3 C12	107.88(15)
C1 C2 Ru1	130.85(13)
C3 C2 Ru1	69.95(10)
C3 C2 C1	120.92(17)
C3 C2 C7	118.49(17)
C7 C2 Ru1	70.47(11)
C7 C2 C1	120.58(17)
C2 C3 Ru1	72.54(10)
C2 C3 C4	120.54(16)
C4 C3 Ru1	70.56(10)
C3 C4 Ru1	71.11(10)
C5 C4 Ru1	72.43(10)
C5 C4 C3	121.35(16)
C4 C5 Ru1	69.98(10)
C4 C5 C6	117.69(16)
C4 C5 C8	122.48(16)
C6 C5 Ru1	69.88(10)
C6 C5 C8	119.79(16)
C8 C5 Ru1	129.71(12)
C5 C6 Ru1	71.87(10)
C7 C6 Ru1	72.06(10)
C7 C6 C5	121.33(17)

C2 C7 Ru1	71.62(10)
C6 C7 Ru1	70.49(11)
C6 C7 C2	120.57(17)
C5 C8 C9	108.91(16)
C5 C8 C10	113.66(16)
C10 C8 C9	111.5(2)
C12 C11 N1	108.40(16)
C11 C12 N3	106.43(16)
N1 C13 N3	110.55(16)
N1 C13 C14	119.90(16)
N3 C13 C14	129.56(16)
C13 C14 N2	105.87(14)
N2 C15 C16	112.86(17)
N2 C15 C17	111.72(15)
C16 C15 C17	111.35(17)

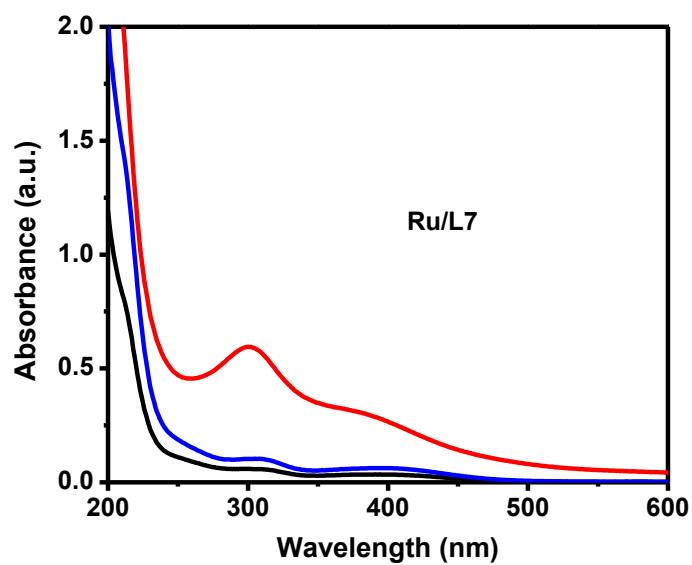


Fig. S15 UV-vis spectra of (a) aqueous solution of **Ru/L7** (black line), (b) aqueous solution of **Ru/L7** with the addition of SF (red line), and (c) after adding aqueous HCl to an aqueous solution of **Ru/L7** with the addition of SF (blue line).

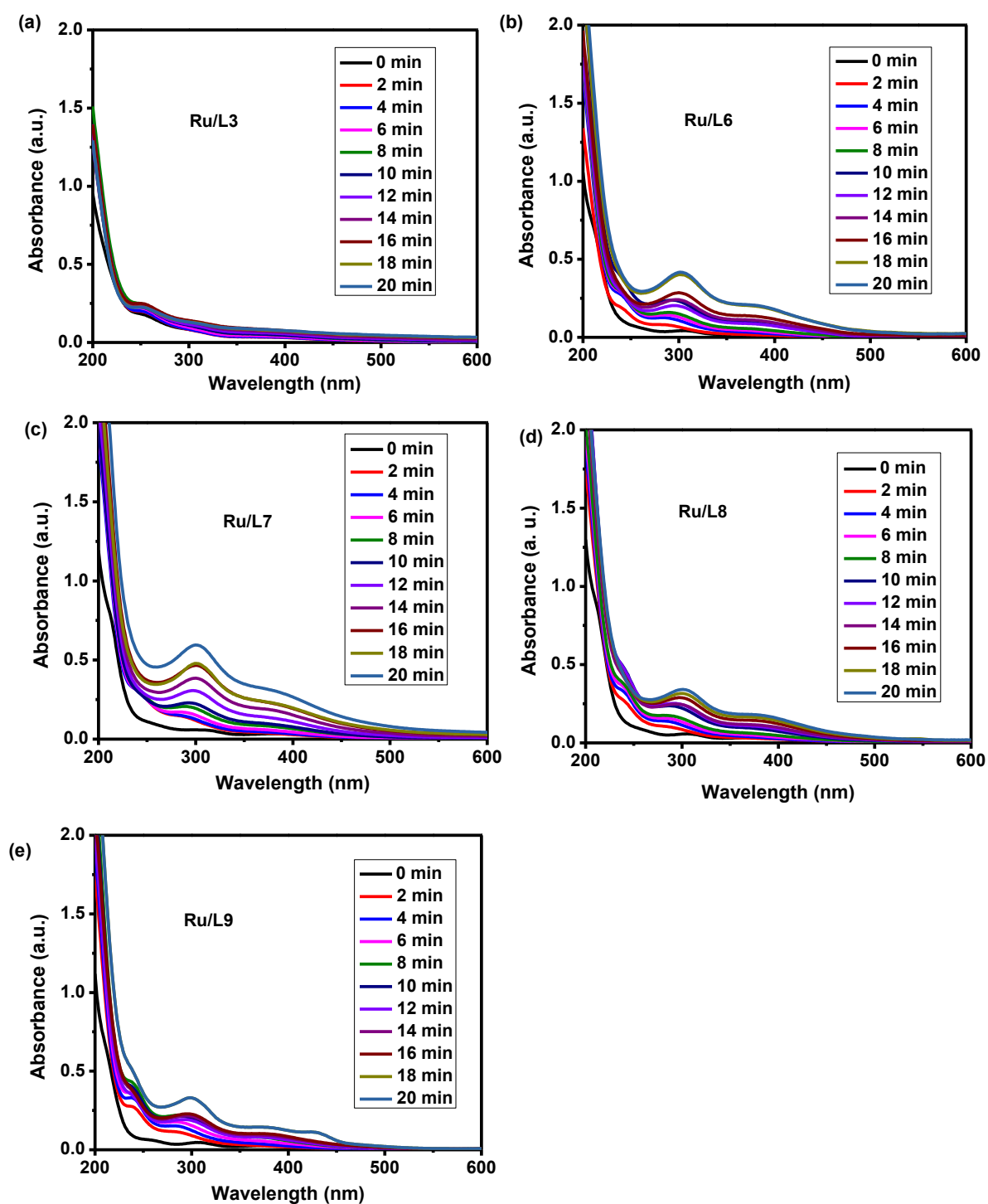


Fig. S16 UV-vis spectra of aqueous solution of **Ru/Ln** upon the addition of SF.

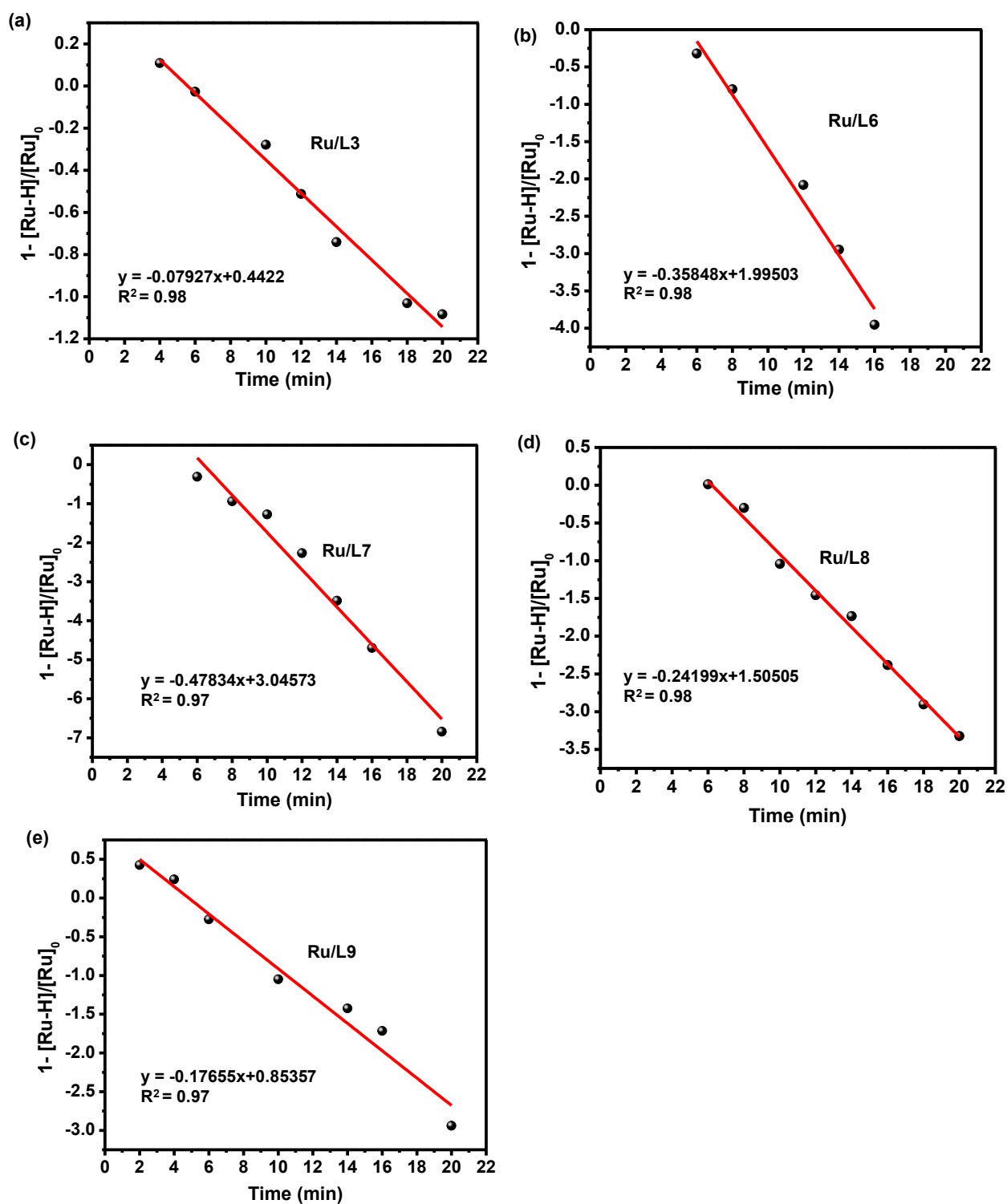


Fig. S17 Ru-hydride formation rate based on the change in absorption at 400 nm for **Ru/Ln** complexes in the presence of SF.

Table S10 Ru-hydride formation rates for **Ru/Ln** catalysts in the presence of SF

Catalysts	Hydride formation rate ($v_{\text{Ru-H}} \times 10^{-3} \mu\text{mol s}^{-1}$)
Ru/L3	1.3
Ru/L6	5.9
Ru/L7	8.0
Ru/L8	4.0
Ru/L9	2.9

CO₂ capture and hydrogenation

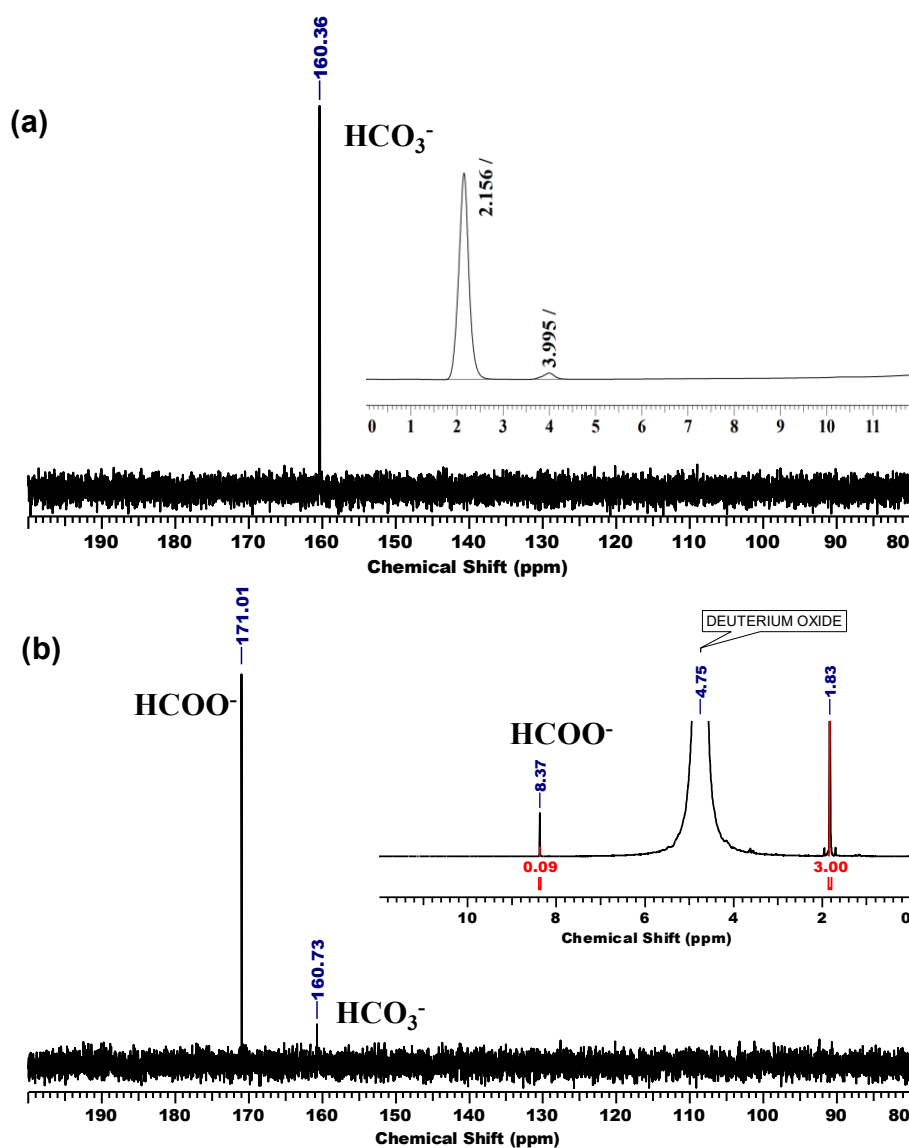
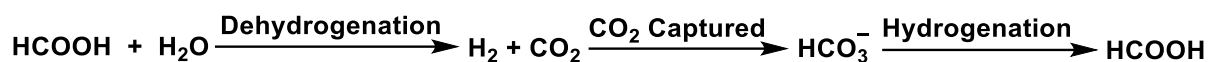


Fig. S18 CO₂ capture and hydrogenation. **Dehydrogenation** of FA, Reaction conditions: Reaction conditions: FA (0.4 M, 25 mL in water), *in situ* Ru/L7 catalyst (Ru: 10 μmol, L7: 20 μmol), SF (2.5 mmol), 90 °C. **CO₂ captured** (a) ¹³C NMR of CO₂ captured reaction aliquot (5 mL of 2 M KOH), GC TCD analysis of effluent gas (inset). **Hydrogenation** of bicarbonate, Reaction conditions: *in situ* Ru/L7 catalyst (Ru: 10 μmol, L7: 20 μmol), H₂ (20 bar), 80 °C, 48 h. (b) ¹H (inset) and ¹³C NMR (in D₂O) of reutilization of captured CO₂ reaction aliquot (hydrogenation of HCO₃⁻).

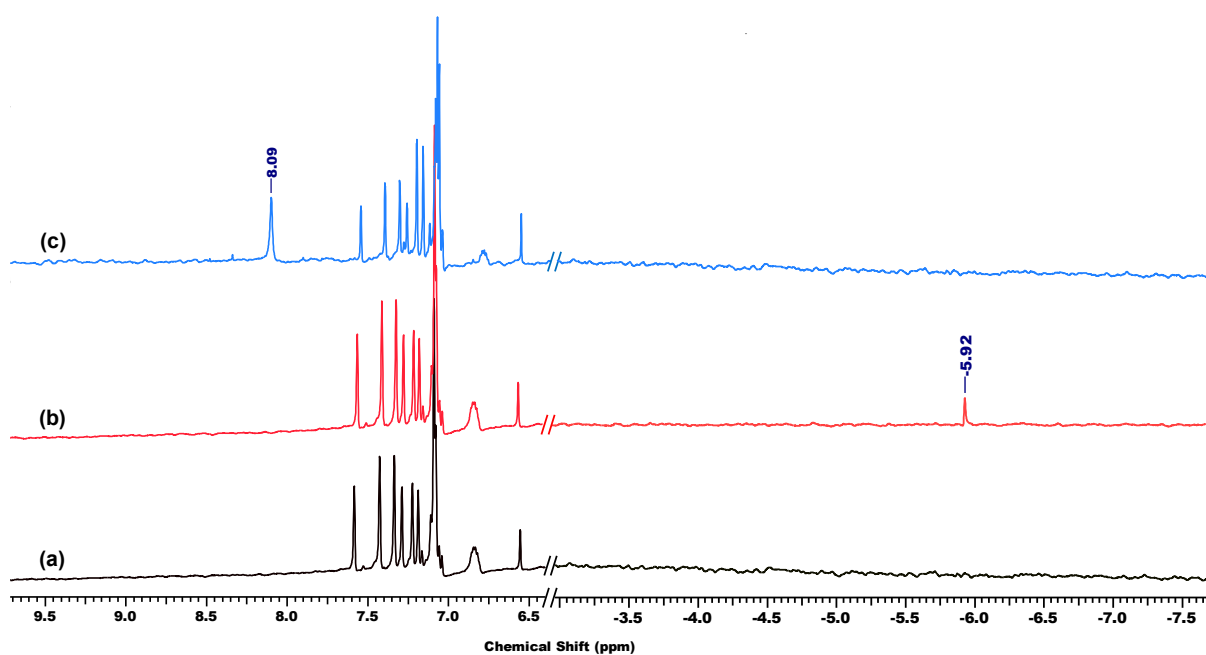


Fig. S19 ^1H NMR spectrum (in DMSO-d_6) for generation of Ru-hydrido species and Ru-formato species involved in CO_2 hydrogenation. Reaction conditions: (a) *ex situ* **Ru/L7** (0.02 mmol) in DMSO (1.5 mL). (b) **Ru/L7** (0.02 mmol) in DMSO (1.5 mL), H_2 (20 bar), 80°C , 2.5 h. (c) *ex situ* **Ru/L7** (0.02 mmol) in DMSO (1.5 mL), H_2 (10 bar), CO_2 (10 bar), 80°C , 2.5 h.

General Procedure for the Synthesis of Ligands (L2 -L9)

L2

Ligand **L2** is synthesized by reducing 2-thiophenecarboxaldehyde (5 mmol, 0.5 mL) with NaBH₄ (7 mmol, 265 mg) in 15 mL of methanol at room temperature for 2 h. Completion of the reaction is monitored by thin layer chromatography. Further, all the volatiles are removed under reduced pressure, followed by extraction with dichloromethane (3 × 15 mL)/water. Then, the organic layer is dried over anhydrous Na₂SO₄, and further the solvent was evaporated under reduced pressure to get the desired oily product (70% yield). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.27-7.26 (d, J = 5 Hz, 1H), 6.99-6.97 (m, 2H), 4.78 (s, 2H), 2.35 (s, 1H); ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 144.18, 127.07, 125.80, 125.69, 60.14.

L3

Ligand **L3** is synthesized by reducing 2-imidazolecarboxaldehyde (5 mmol, 480 mg) with NaBH₄ (2.5 mmol, 95 mg) in 15 mL of ethanol at room temperature for 2 h. Completion of the reaction is monitored by thin layer chromatography. Further, all the volatiles are removed under reduced pressure then the product is recrystallized with diethyl ether in methanol to obtain the desired pure product (72% yield). ¹H NMR: (500 MHz, DMSO-d₆) δ (ppm) 11.86 (s, 1H), 6.90 (s, 2H), 5.29 (s, 1H), 4.44 (s, 2H); ¹³C NMR (125 MHz, DMSO-d₆) δ 147.95, 122.04, 57.03.

L4

Ligand **L4** is synthesized by condensation of furfural (5 mmol, 0.414 mL) with n-propylamine (25 mmol, 2.1 mL) for 12h, followed by reduction with NaBH₄ (5.1 mmol, 193 mg) in 15 mL of ethanol at room temperature for 2 h. Completion of the reaction is monitored by thin layer chromatography. Further, all the volatiles are removed under reduced pressure, followed by extraction with dichloromethane (3 × 15 mL)/water. Then, the organic layer is dried over anhydrous Na₂SO₄, and further the solvent was evaporated under reduced pressure to get the desired oily product (75 % yield). ¹H NMR (500 MHz, CDCl₃): δ (ppm) δ 7.36 (s, 1H), 6.31(s, 1H), 6.18 (s, 1H), 3.78 (s, 2H), 2.60-2.57 (t, J₁ =10 Hz, J₂ = 5 Hz, 2H), 1.80 (s, 1H), 1.54-1.49 (m, 2H), 0.93-0.90 (t, J₁ = 10 Hz, J₂ = 5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 153.94, 141.71, 110.04, 106.77, 50.98, 46.13, 22.99, 11.70. HRMS calcd for [M + H]⁺ [C₈H₁₃NO] 140.1070, observed 140.1098

L5

Ligand **L5** is synthesized by condensation of 2-thiophenecarboxaldehyde (5 mmol, 0.5 mL) with n-propylamine (25 mmol, 2.1 mL) for 12 h, followed by reduction with NaBH₄ (5.1 mmol, 193 mg) in 15 mL of ethanol at room temperature for 2 h. Completion of the reaction is monitored by thin layer chromatography. Further, all the volatiles are removed under reduced pressure, followed by extraction with dichloromethane (3 × 15 mL)/water. Then, the organic layer is dried over anhydrous Na₂SO₄, and further the solvent was evaporated under reduced pressure to get the desired oily product (75 % yield). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.22-7.21 (d, *J* = 5 Hz, 1H), 6.96-6.94 (m, 2 H), 4.00 (s, 2H), 2.65-2.63 (t, *J* = 5 Hz, 2 H), 1.70 (s, 1H), 1.58-1.51 (m, 2H), 0.95-0.92 (t, *J*₁ = 10 Hz, *J*₂ = 5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 143.91, 126.31, 124.54, 123.99, 50.72, 48.05, 22.75, 11.46. HRMS calcd for [M + H]⁺ [C₈H₁₃NS] 156.0841, observed 156.0851.

L6

Ligand **L6** is synthesized by condensation of with 2-imidazolecarboxaldehyde (4 mmol, 384.24 mg) with n-propylamine (20 mmol, 1.6 mL) for 12 h, followed by reduction with NaBH₄ (2.5 mmol, 95 mg) in 25 mL of methanol at room temperature for 2 h. Completion of the reaction is monitored by thin layer chromatography. Further, all the volatiles are removed under reduced pressure, followed by extraction with dichloromethane (3 × 15 mL)/water. Then, the organic layer is dried over anhydrous Na₂SO₄, and further the solvent was evaporated under reduced pressure to get the desired oily product (78 % yield). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 6.96 (s, 2H), 3.89 (s, 2H), 2.61-2.58 (t, *J*₁ = 5 Hz, *J*₂ = 10 Hz, 2H), 1.54-1.48 (m, 2H), 0.92-0.89 (t, *J*₁ = 10 Hz, *J*₂ = 5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 147.22, 122.01, 51.71, 47.24, 23.12, 11.87. HRMS calcd for [M + H]⁺ [C₇H₁₃N₃] 140.1182, observed 140.1199.

L7

Ligand **L7** is synthesized by condensation of with 2-imidazolecarboxaldehyde (4 mmol, 384.24 mg) with iso-propylamine (20 mmol, 1.7 mL) for 12 h, followed by reduction with NaBH₄ (2.5 mmol, 95 mg) in 25 mL of methanol at room temperature for 2 h. Completion of the reaction is monitored by thin layer chromatography. Further, all the volatiles are removed under reduced pressure, followed by extraction with dichloromethane (3 × 15 mL)/water. Then, the organic layer is dried over anhydrous Na₂SO₄, and further the solvent was evaporated under reduced pressure to get the desired oily product (80 % yield). ¹H NMR (500 MHz, CDCl₃): δ (ppm) δ 6.95 (s, 2H), 3.89 (s, 2H), 2.87-2.81 (m, 1H), 1.08-1.07 (d, *J* = 5 Hz, 6H); ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 146.90, 121.41, 48.57, 44.51, 22.38. HRMS calcd for [M + H]⁺ [C₇H₁₃N₃] 140.1182, observed 140.1198.

L8

Ligand **L8** is synthesized by condensation of with 2-imidazolecarboxaldehyde (4 mmol, 384.24 mg) with n-butylamine (10 mmol, 0.98 mL) for 12 h, followed by reduction with NaBH₄ (2.5 mmol, 95 mg) in 25 mL of methanol at room temperature for 2 h. Completion of the reaction is monitored by thin layer chromatography. Further, all the volatiles are removed under reduced pressure, followed by extraction with dichloromethane (3 × 15 mL)/water. Then, the organic layer is dried over anhydrous Na₂SO₄, and further the solvent was evaporated under reduced pressure to get the desired oily product (73 % yield). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 6.97 (s, 2H), 3.90 (s, 2H), 2.65-2.62 (t, *J*₁ = 10 Hz, *J*₂ = 5 Hz, 2 H), 1.50-1.44 (m, 2H), 1.37-1.30 (m, 2H), 0.91-0.89 (t, *J* = 5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 146.96, 122.07, 49.52, 47.21, 32.02, 31.14, 20.55, 14.12. HRMS calcd for [M + H]⁺ [C₈H₁₅N₃] 154.1339, observed 154.1351.

L9

Ligand **L9** is synthesized by condensation of with 2-imidazolecarboxaldehyde (4 mmol, 384.24 mg) with iso-butylamine (15 mmol, 1 mL) for 12 h, followed by reduction with NaBH₄ (2.5 mmol, 95 mg) in 10 mL of ethanol at room temperature for 2 h. Completion of the reaction is monitored by thin layer chromatography. Further, all the volatiles are removed under reduced pressure, followed by extraction with dichloromethane (3 × 15 mL)/water. Then, the organic layer is dried over anhydrous Na₂SO₄, and further the solvent was evaporated under reduced pressure to get the desired oily product (76 % yield). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 6.95 (s, 2H), 5.64 (s, 2H), 3.87 (s, 2H) 2.43-2.42 (d, *J* = 5 Hz, 2 H), 1.77-1.69 (m, 1H), 0.89-0.87 (d, *J* = 10 Hz, 6H); ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 147.12, 121.99, 57.71, 47.27, 28.32, 20.74. HRMS calcd for [M + H]⁺ [C₈H₁₅N₃] 154.1339, observed 154.1352.

Synthesis of [(η⁶-C₁₀H₁₄)Ru(L7)Cl]⁺ (Ru/L7)

Ex situ **Ru/L7** catalyst is synthesized by treating [(η⁶-C₁₀H₁₄)RuCl₂]₂ (0.05 mmol, 30.6 mg) and **L7** (0.12 mmol, 16.7 mg) in acetonitrile (15 mL) under reflux for 12 h. The volume of the reaction mixture is reduced to 1 mL under reduced pressure, followed by precipitation with excess of diethyl ether to obtain yellow solid. The identity of the synthesised *ex situ* complex is confirmed by NMR, HRMS and single-crystal X-ray diffraction. ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) 13.04 (s, NH), 7.63 (s, 1H), 7.31 (s, 1H), 5.88-5.87 (d, *J* = 4 Hz, 2H), 5.69-5.68 (d, *J* = 4 Hz, 2H), 3.70-3.65 (m, 1H), 3.26-3.19 (m, 2H), 2.85-2.79 (m, 1H), 2.05 (s, 3H), 1.18-1.16 (d, *J* = 8 Hz, 3H), 1.14-1.12 (d, *J* = 8 Hz, 3H), 0.94-0.91 (m, 6H); ¹³C NMR (100 MHz, DMSO-d₆): δ (ppm) 149.33, 128.61, 118.57, 104.27, 82.86, 81.85, 81.31, 80.42, 50.33, 30.28, 27.71, 20.88, 19.79, 17.40, 13.83. HRMS calcd for [M]⁺ [C₁₇H₂₇N₃RuCl] 410.0933, observed 410.0944.

Characterization of ligand L2-L9 and metal complexes (Ru/L7)

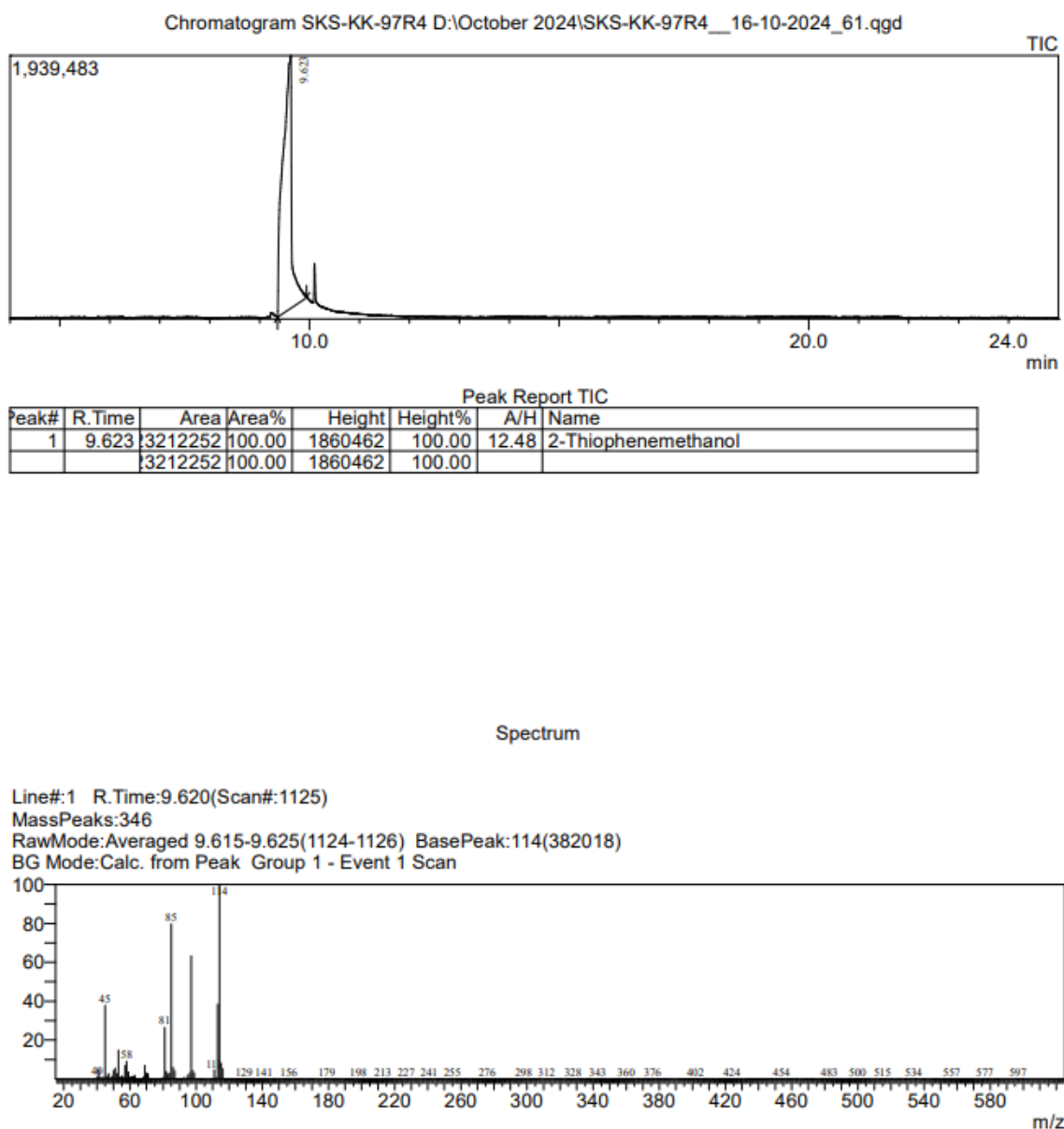


Fig. S20 GC-MS data of L2

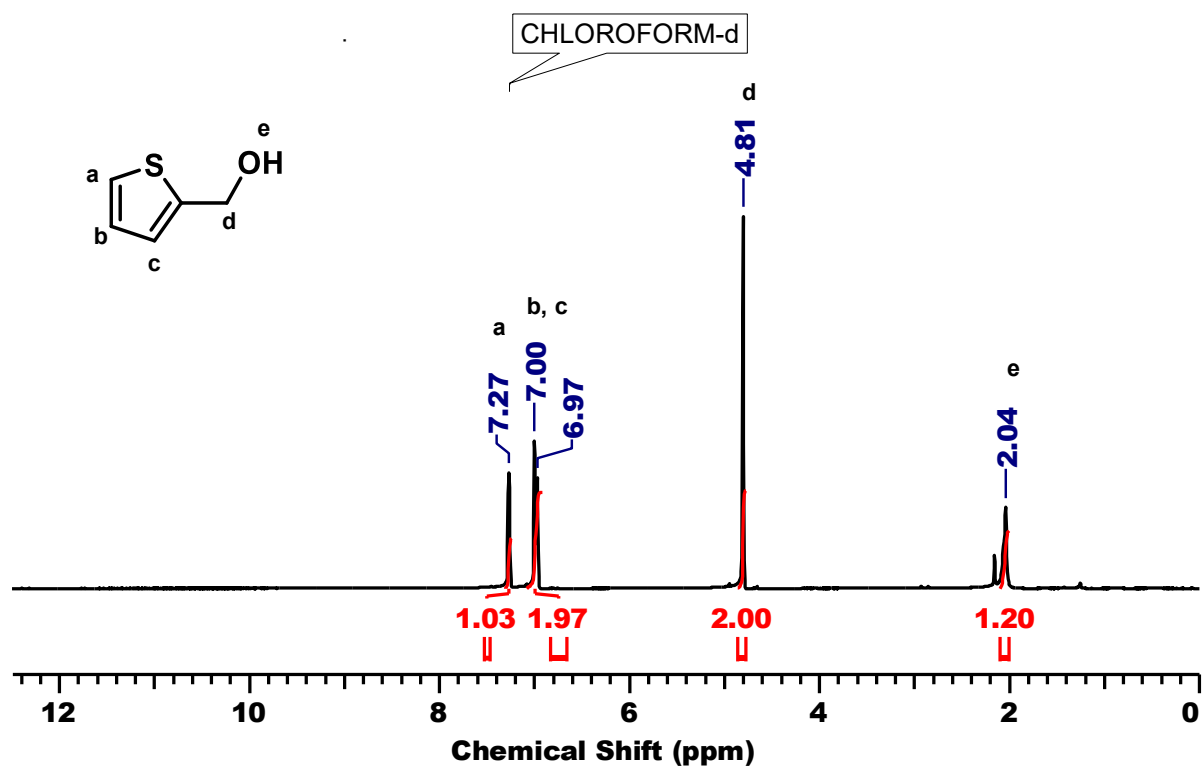


Fig. S21 ¹H NMR of L2

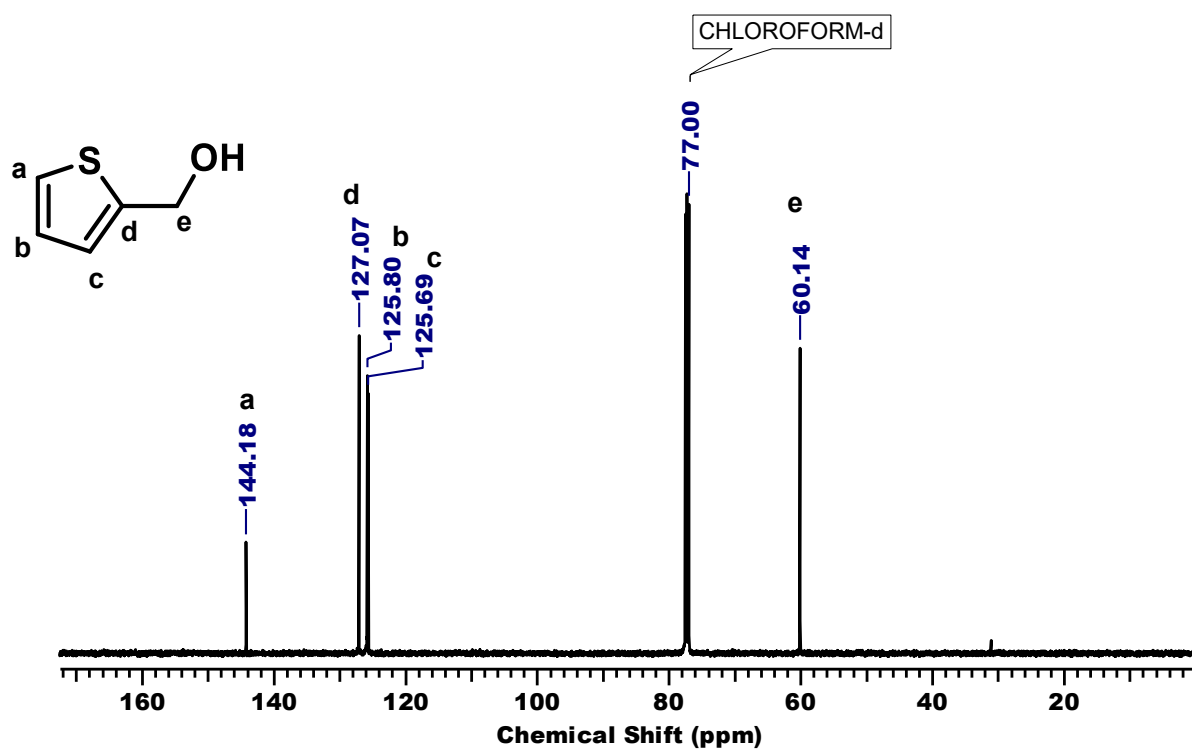
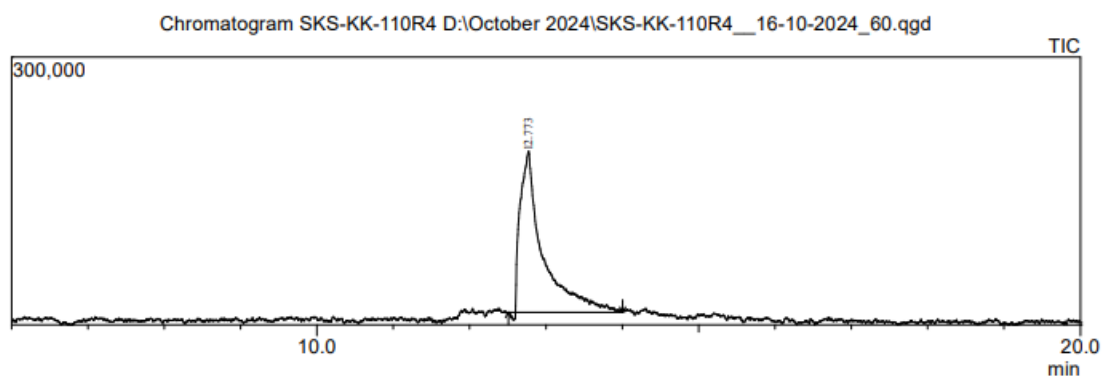


Fig. S22 ¹³C NMR of L2



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
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		3606165	100.00	177172	100.00		

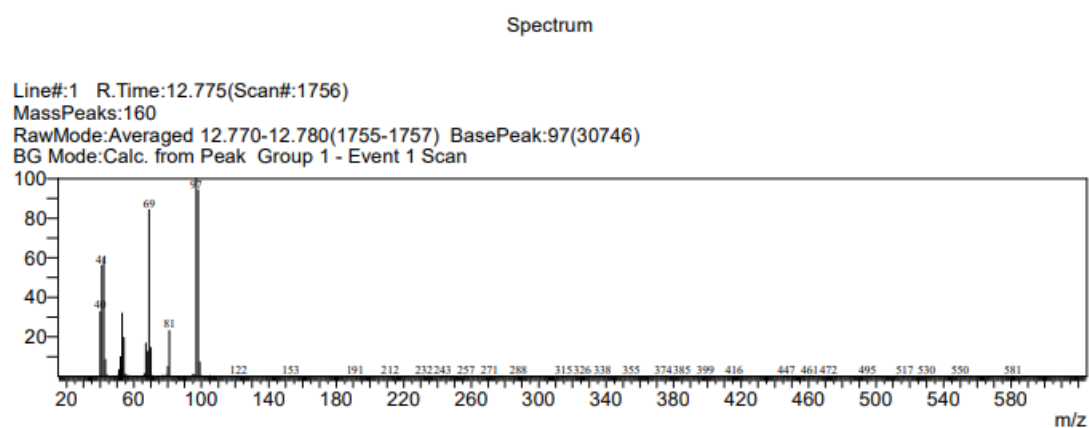


Fig. S23 GC-MS data of L3

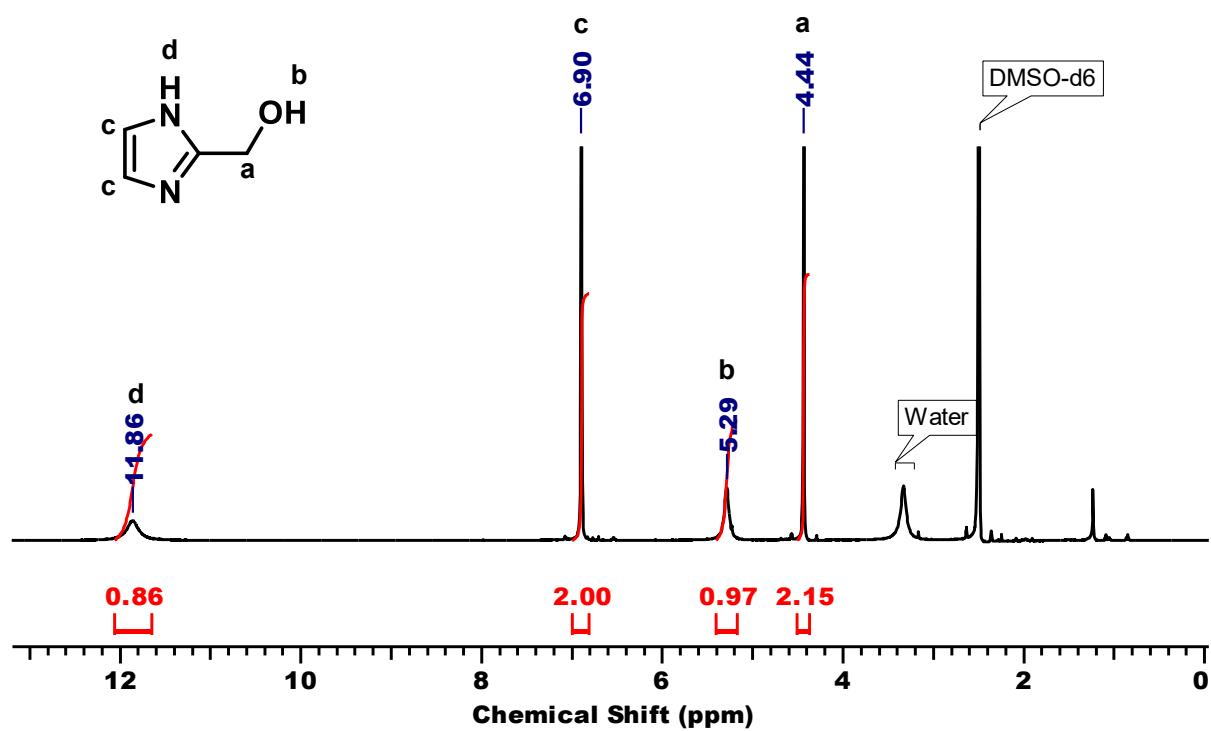


Fig. S24 ¹H NMR of L3

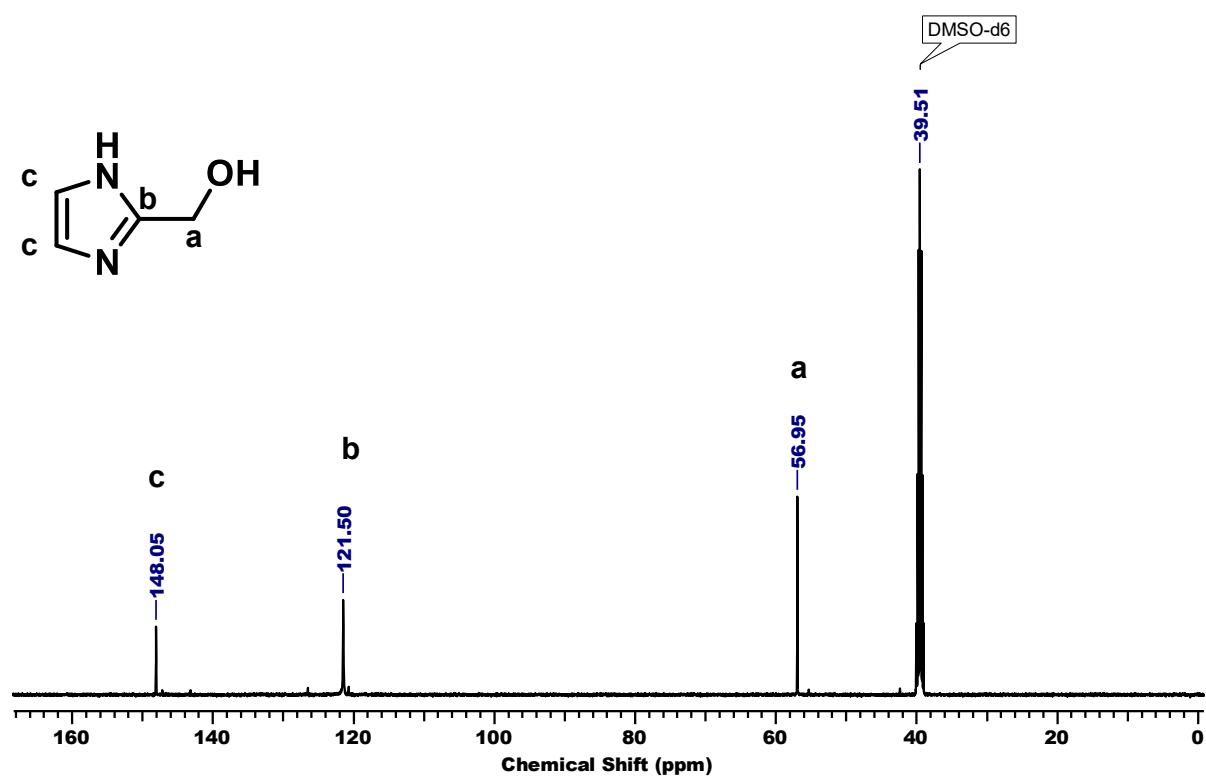


Fig. S25 ¹³C NMR of L3

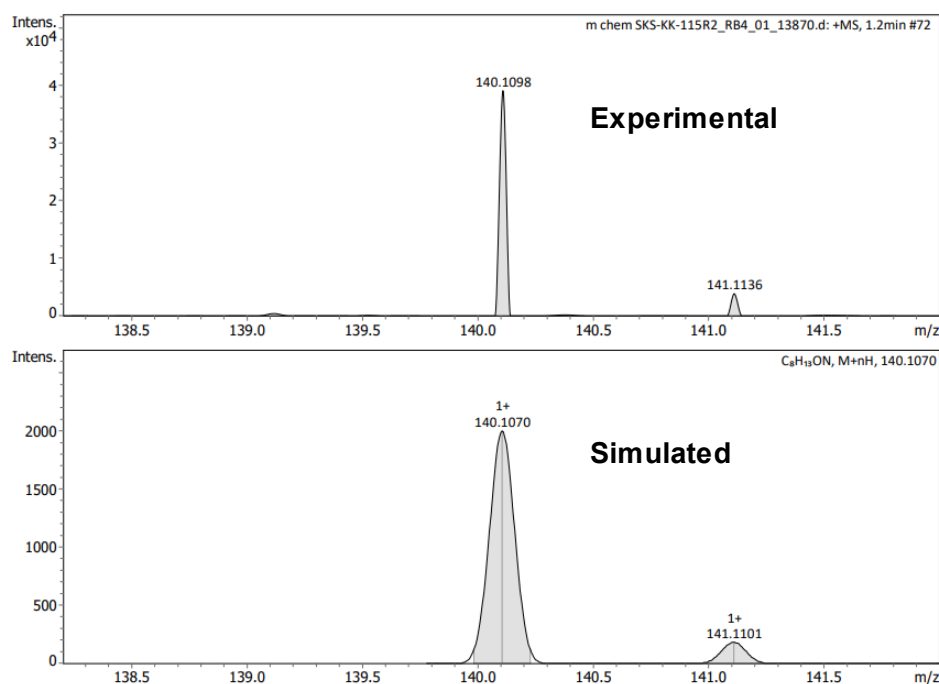


Fig. S26 HR-MS spectrum of L4

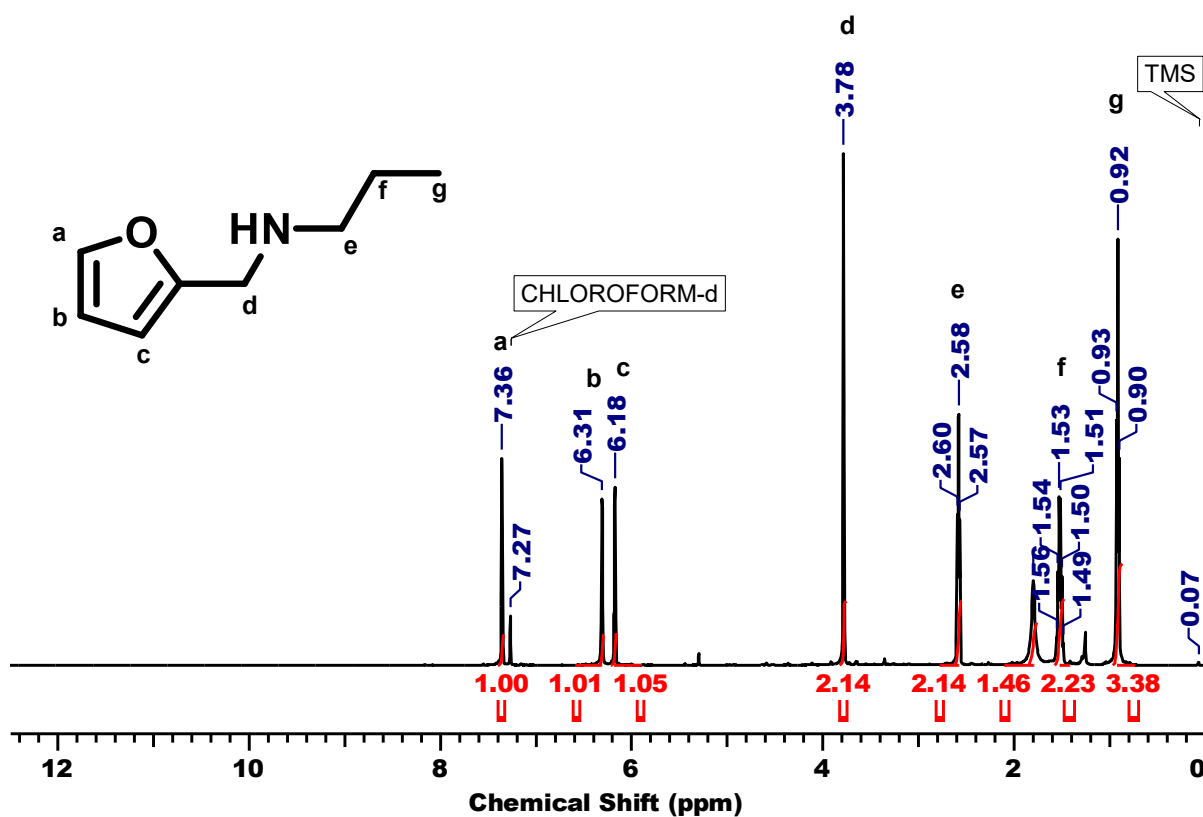


Fig. S27 ¹H NMR of L4

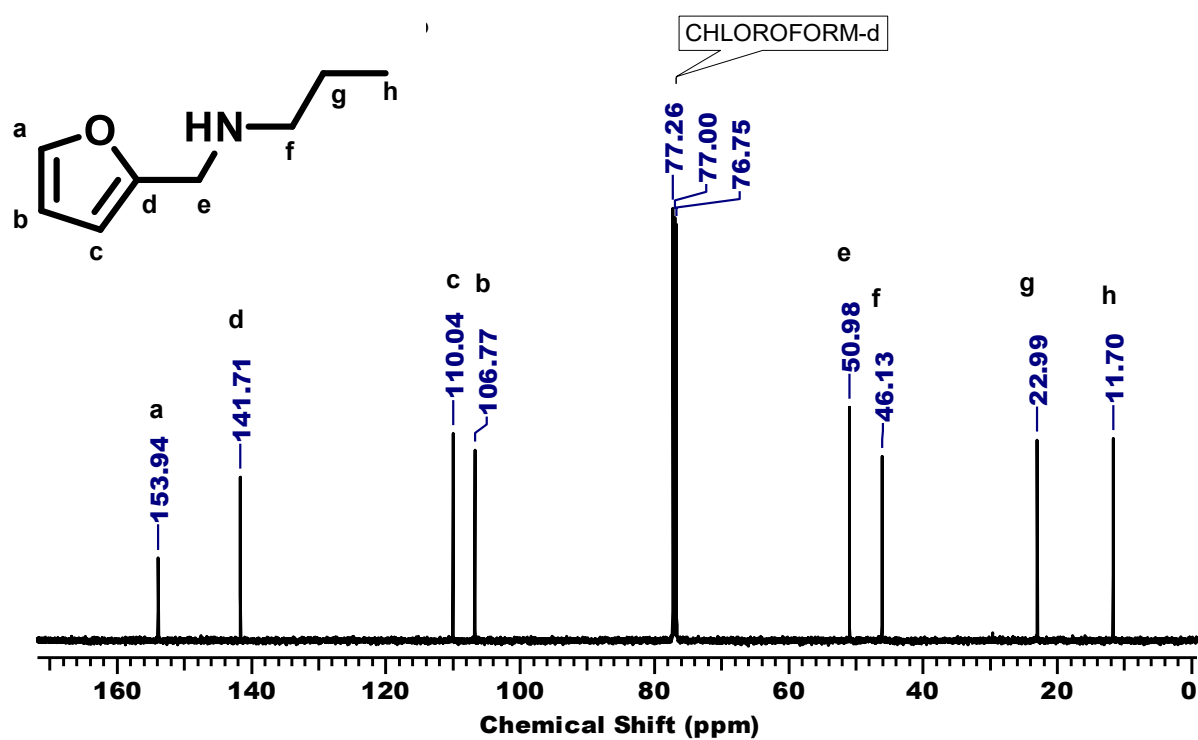


Fig.S28 ¹³C NMR of L4

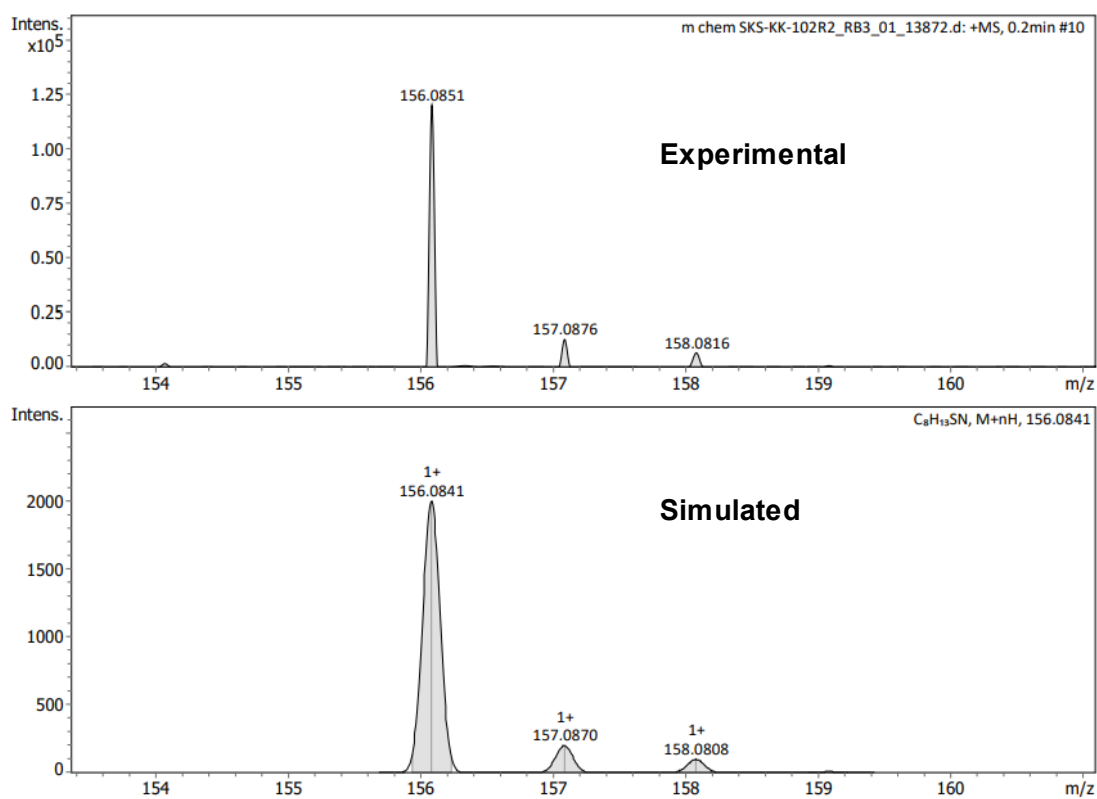


Fig. S29 HR-MS spectrum of L5

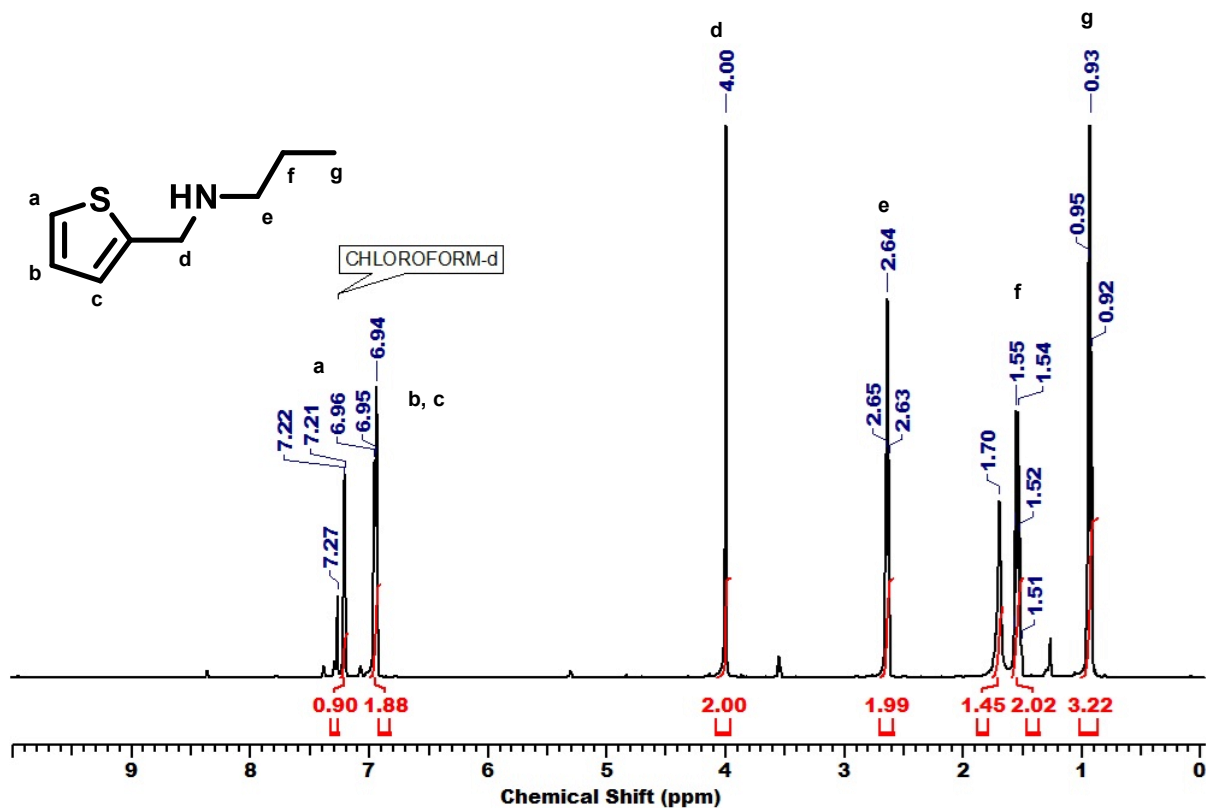


Fig. S30 ¹H NMR of L5

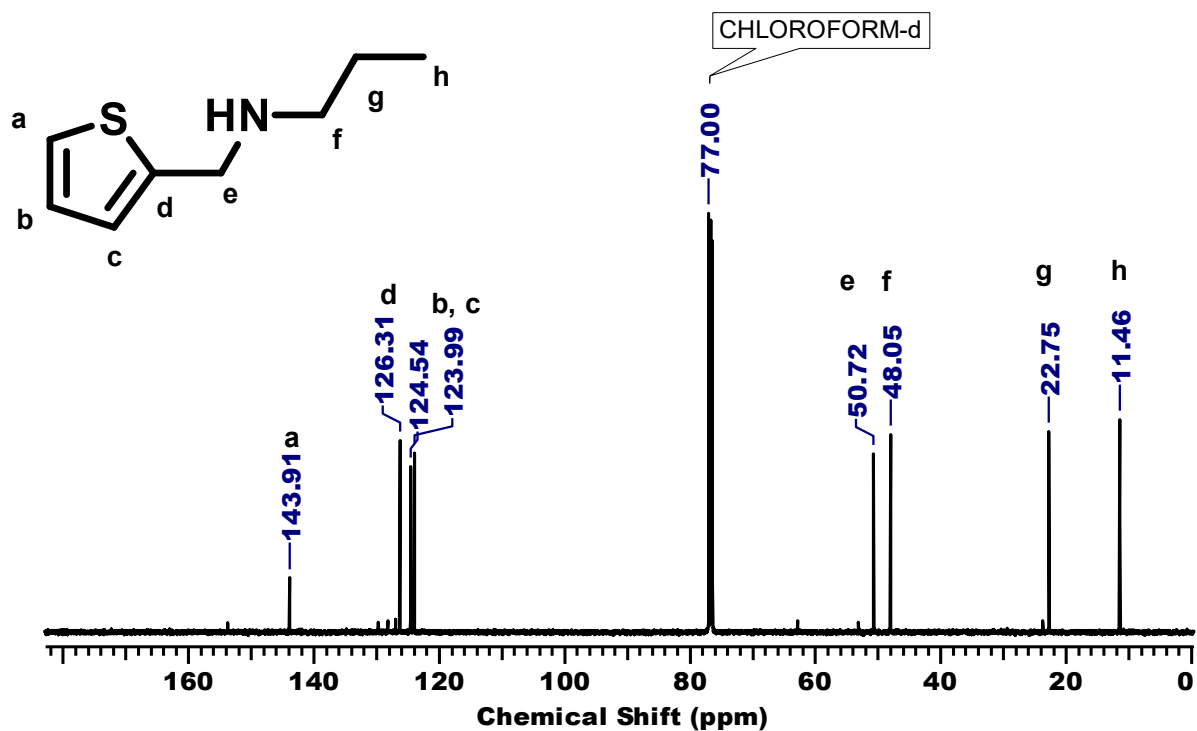


Fig. S31 ¹³C NMR of L5

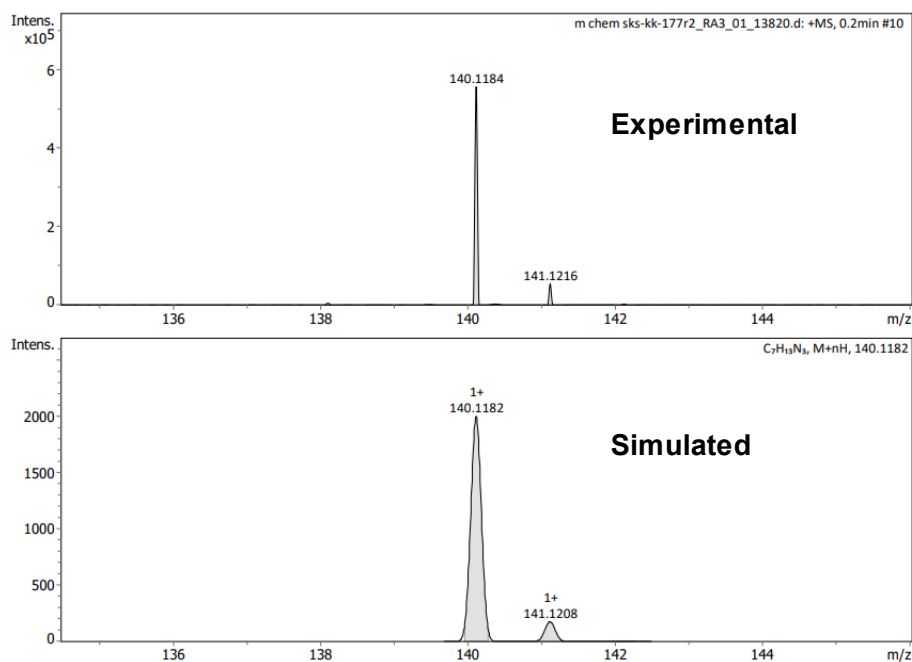


Fig. S32 HR-MS spectrum of L6

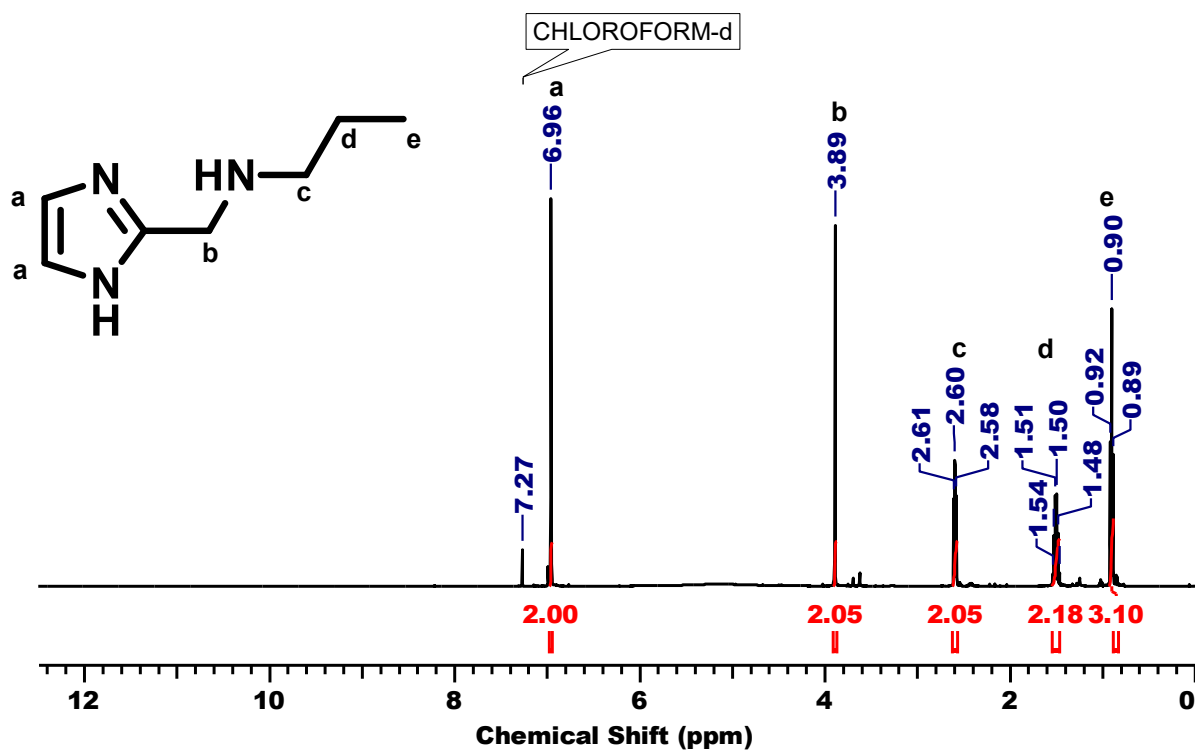


Fig. S33 ¹H NMR of L6

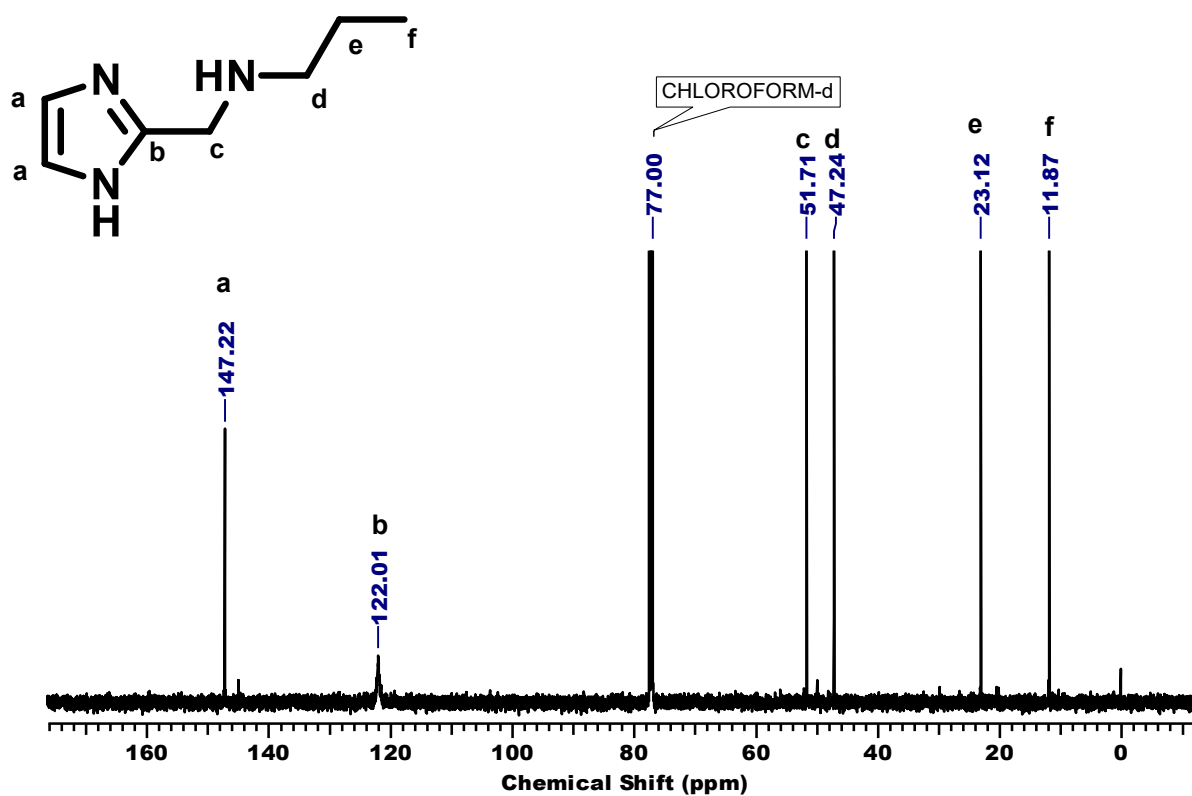


Fig. S34 ¹³C NMR of L6

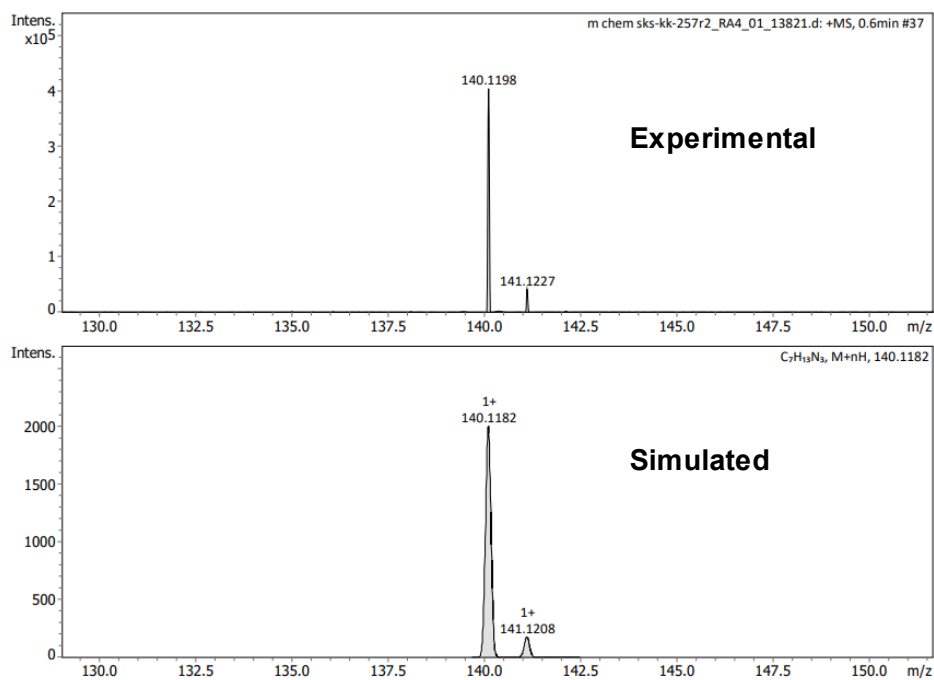


Fig. S35 HR-MS spectrum of L7

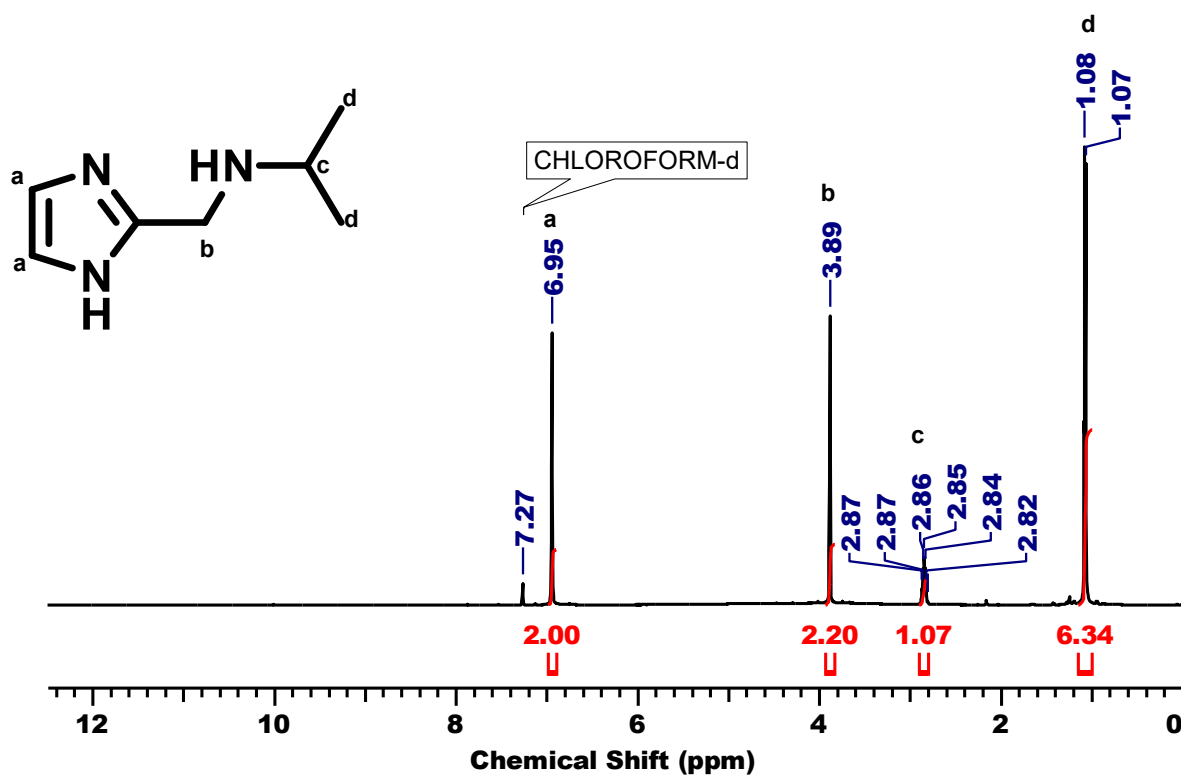


Fig.

S38 ¹H NMR of L7

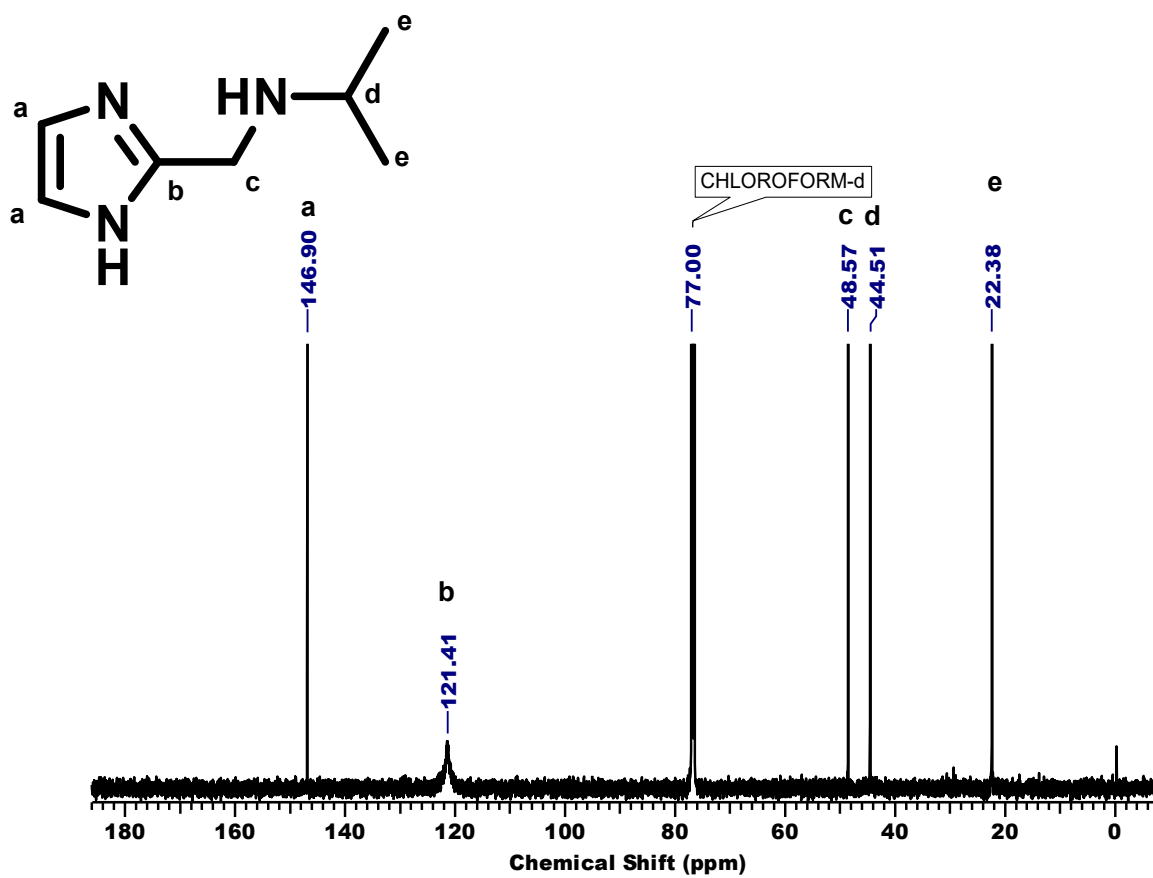


Fig. S37 ¹³C NMR of L7

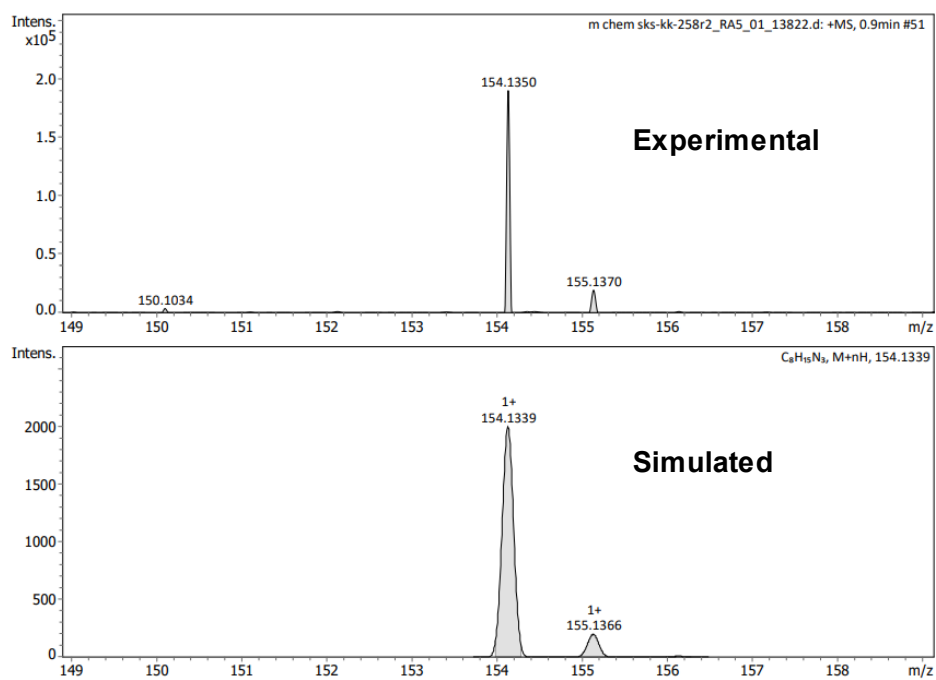


Fig. S38 HR-MS spectrum of L8

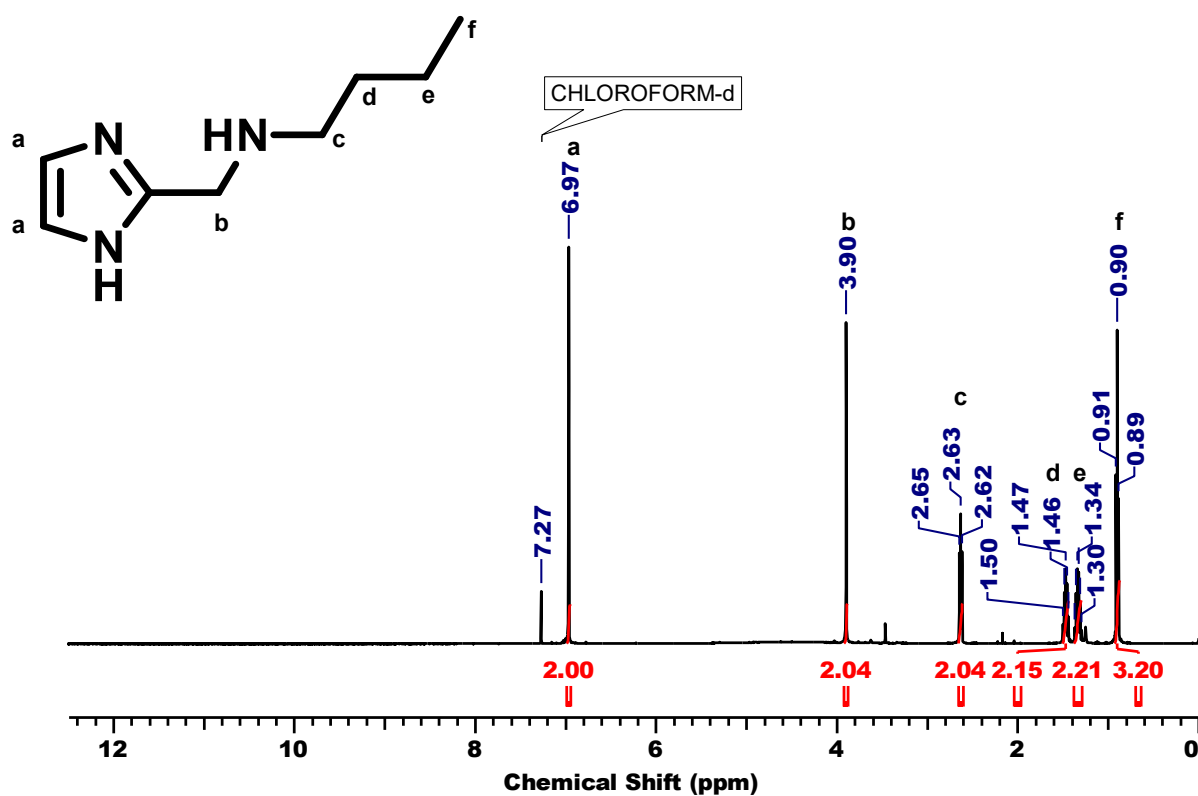


Fig. S39 ¹H NMR of L8

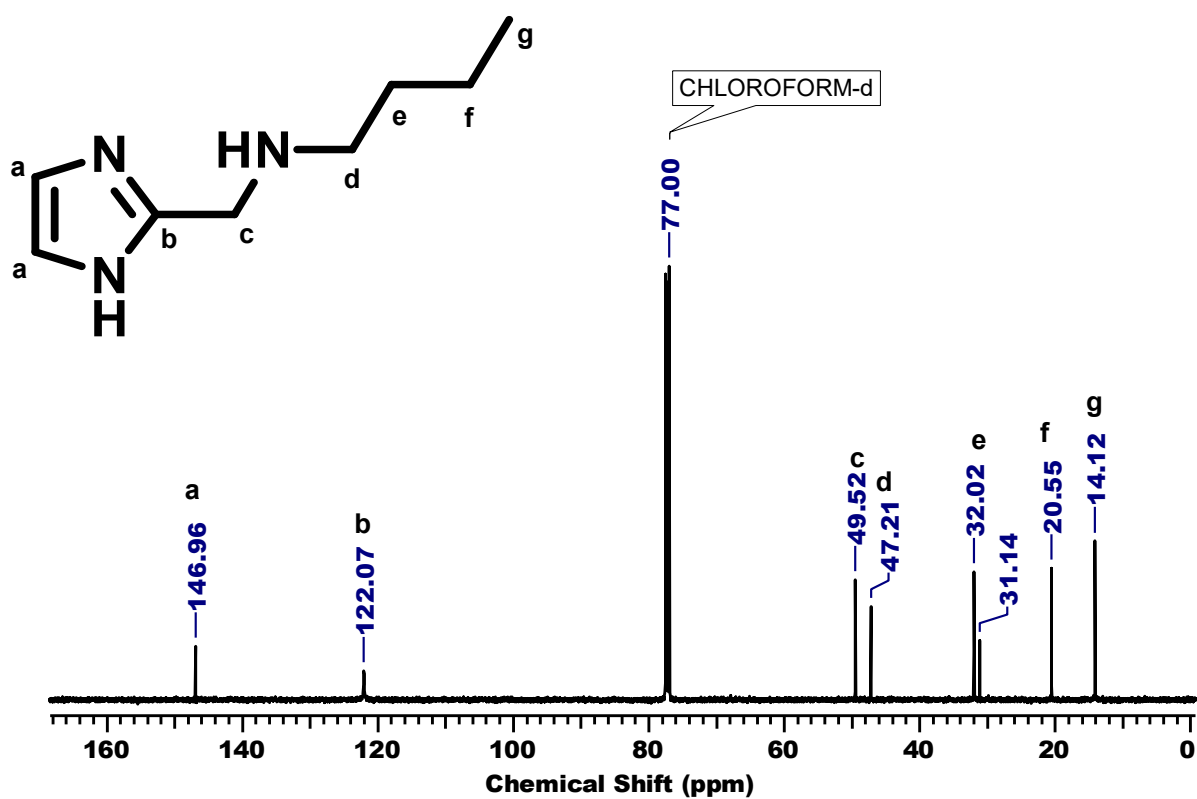


Fig. S40 ¹³C NMR of L8

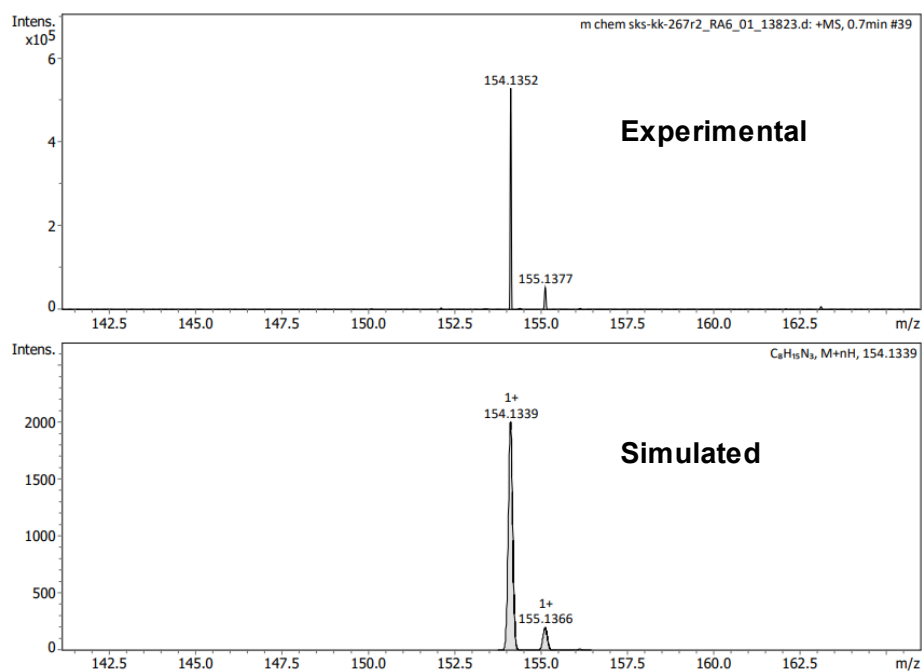


Fig. S41 HR-MS spectrum of L9

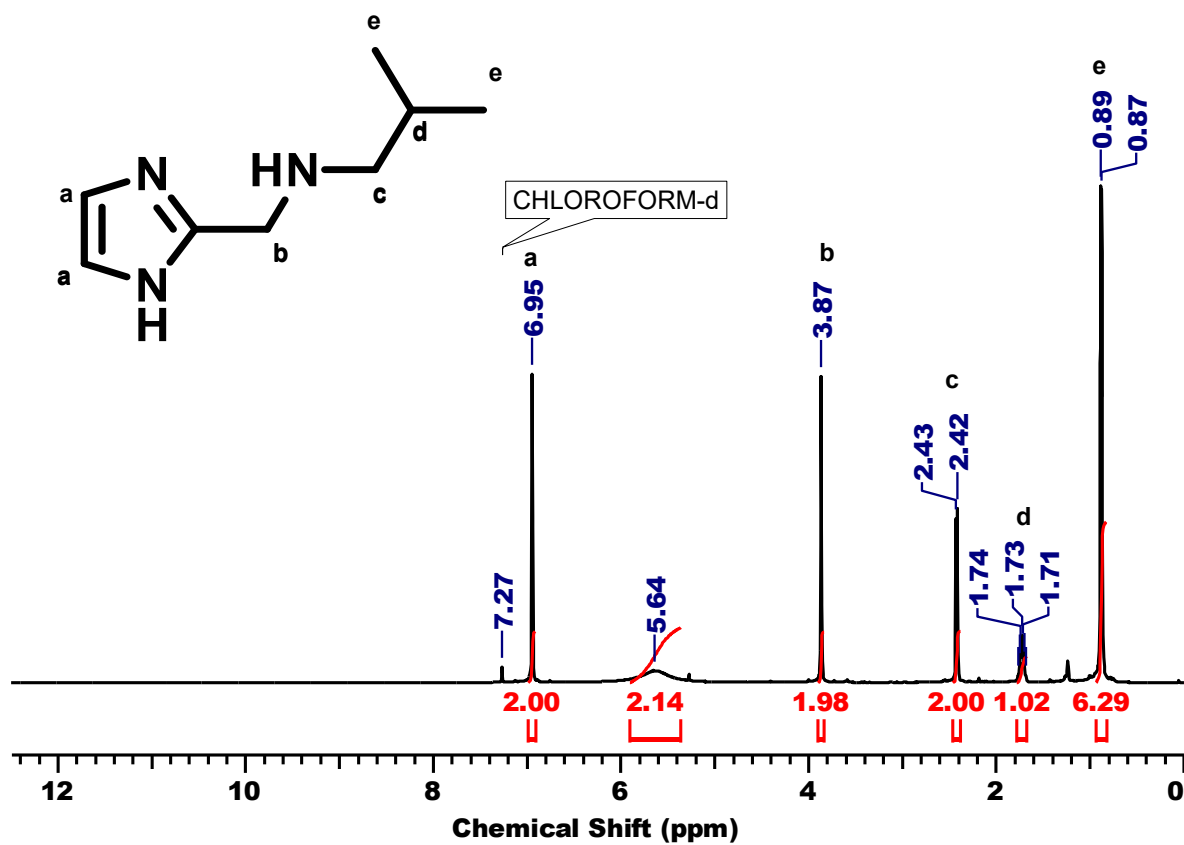


Fig.

S42 ¹H NMR of L9

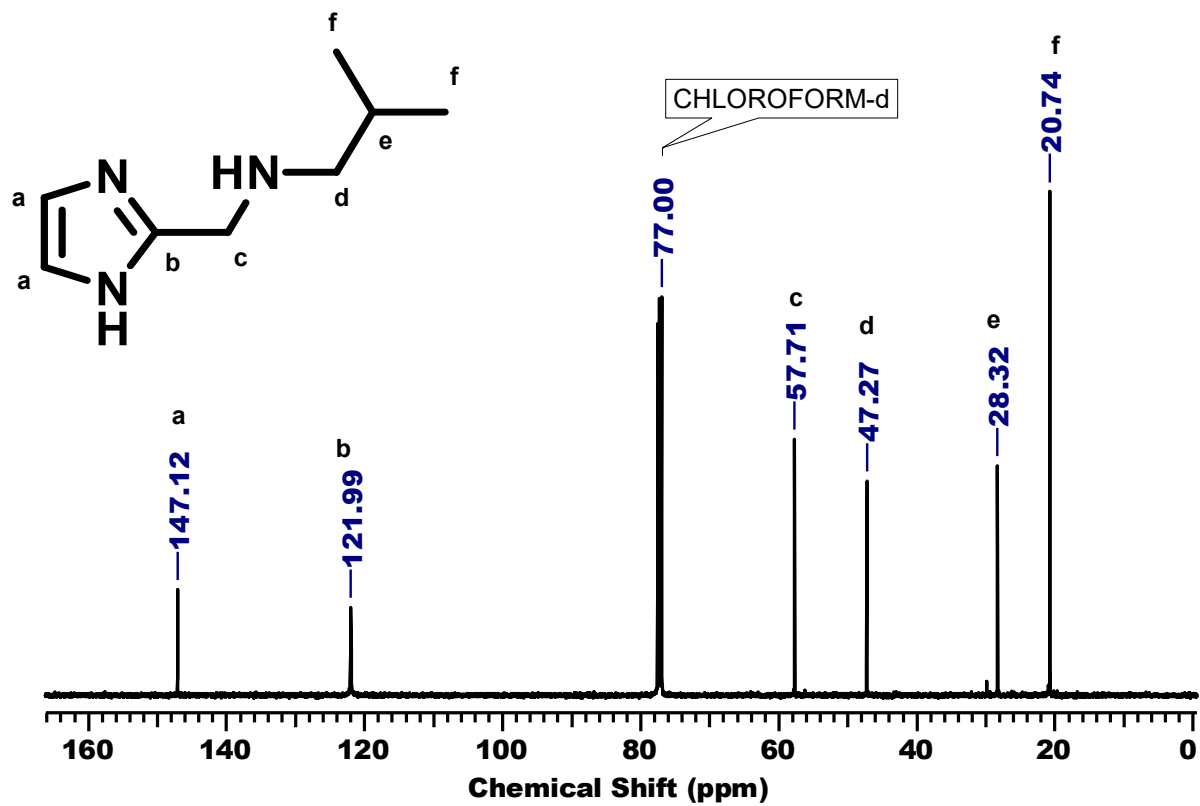


Fig. S43 ¹³C NMR of L9

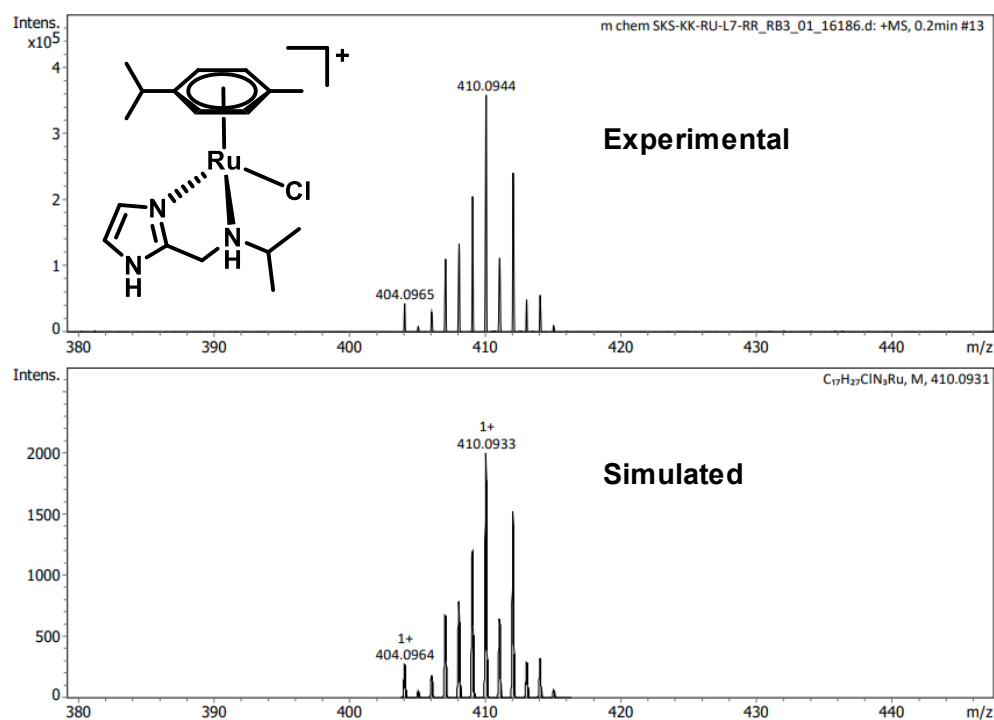


Fig. S44 HR-MS spectrum of Ru/L7

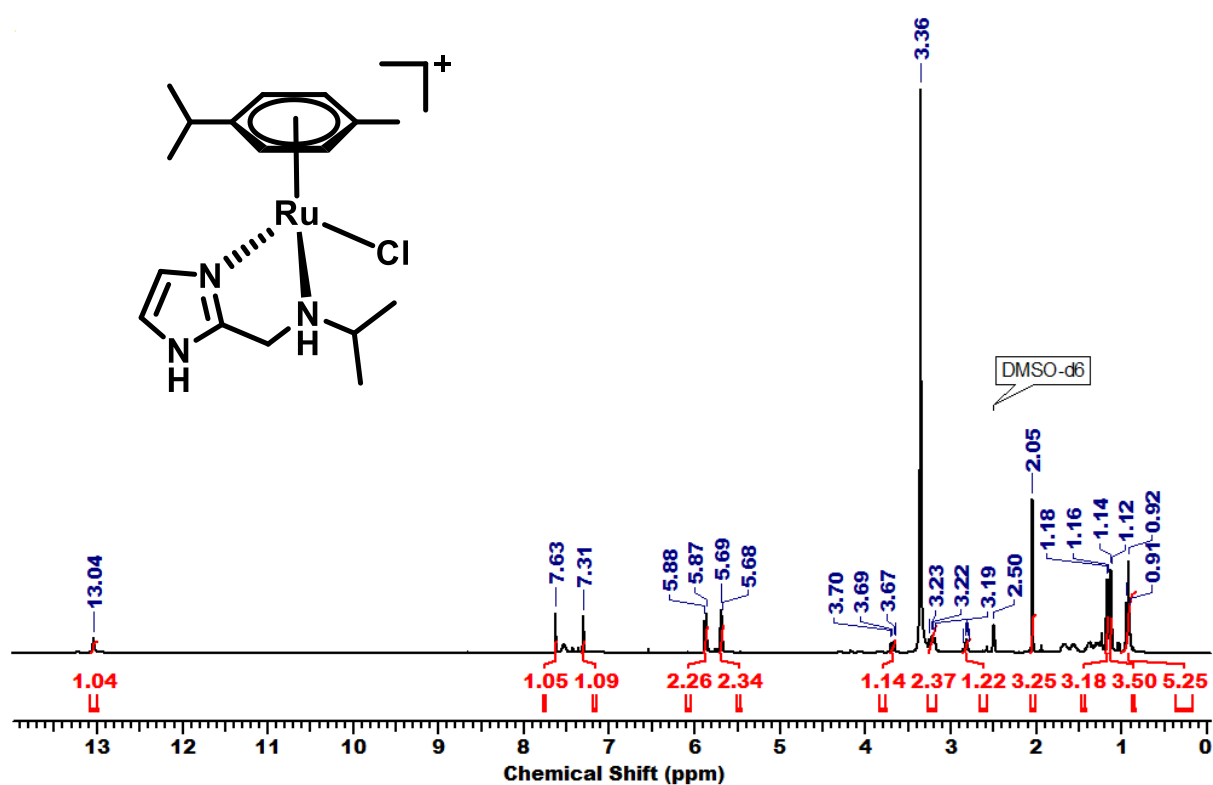


Fig. S45 ¹H NMR of Ru/L7

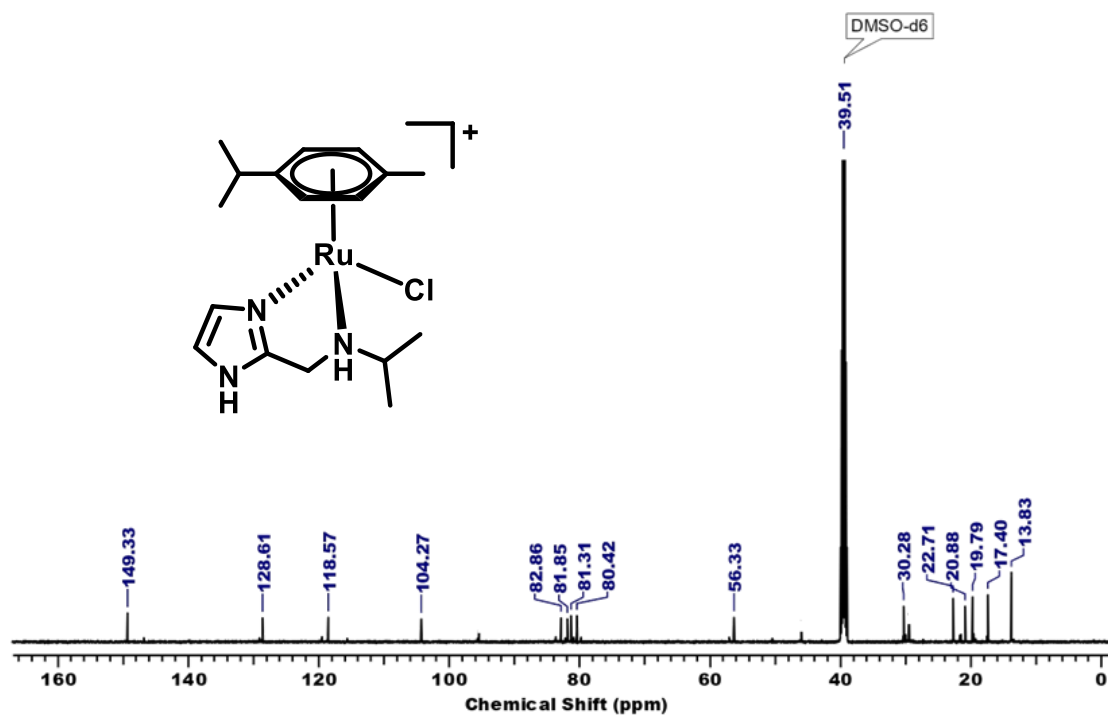
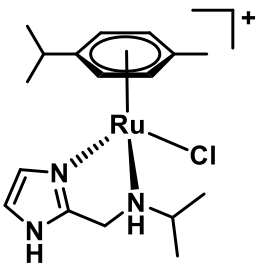
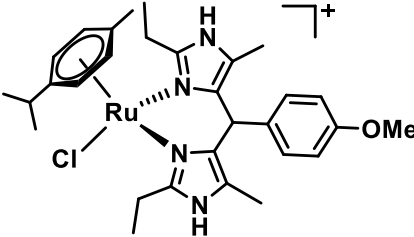
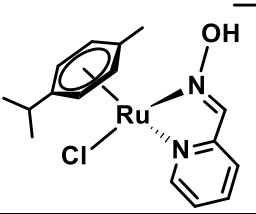
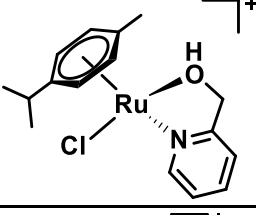
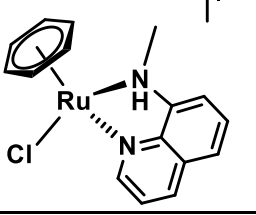
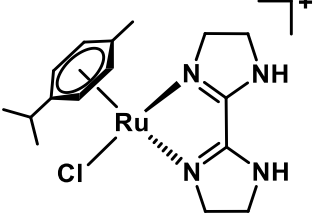
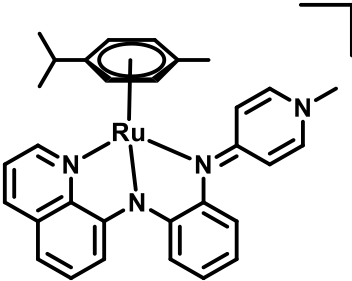
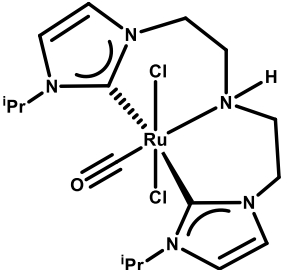
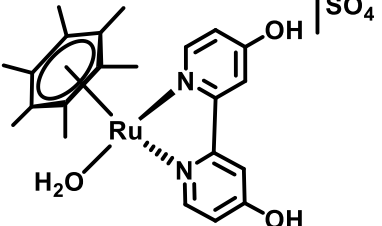
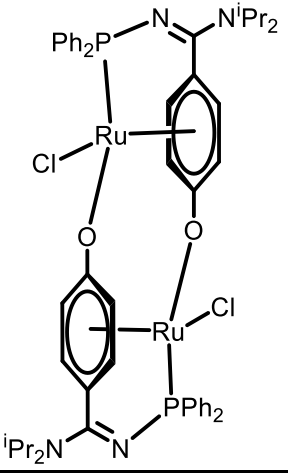


Fig. S46 ^{13}C NMR of Ru/L7

Table S11 Comparative catalytic activity of previous literature work and the current work for formic acid dehydrogenation.

Catalyst	Substrate	Solvent	T (°C)	t (h)	TON	TOF(h ⁻¹)	Ref.
 <i>in situ catalyst</i>	HCOOH/ HCOONa	H ₂ O	90	80	76,840	2000	This work
	HCOOH/ HCOONa	H ₂ O	90	0.33	8830	1545	S5
	HCOOH/ HCOONa	H ₂ O	90	1.56	500	296	S6
	HCOOH/ HCOONa	H ₂ O	90	0.25	6050	1548	S7
	HCOOH/ HCOONa	H ₂ O	90	0.25	2248	940	S8
[RuCl ₂ (C ₁₀ H ₁₄)] ₂	HCOOH	HexNMe ₂	40	3	30	10	S9
[RuCl ₂ (PPh ₃) ₃]	HCOOH/ NEt ₃	DMF	40	0.3	891	2688	S10
[RuCl ₂ (C ₆ H ₆) ₂]/DPPE	HCOOH	Me ₂ NHex	80	NA	NA	47970	S11
[RuCl ₂ (C ₆ H ₆) ₂]/DPPE	HCOOH	DMOA	25	1080	>100000 0	1000	S12
[(PNP ³)Ru(H)Cl(CO)]	HCOOH / NHex ₃	DMF	90	3	706500	256000	S13
[(PNNP ²)RuH ₂ (CO)]	HCOOH/ NEt ₃	DMSO	90	150	1100000	7300	S14

	HCOOH/ HCOONa	H ₂ O	90	29	350000	12000	S15
	HCOOH	DMSO	80	NA	2200	10000	S16
	HCOOH	1-ethyl-3-methylimidazolium diethylphosphate	100	3	2000	820	S17
	HCOOH	H ₂ O	60	24	3700	94	S18
	HCOOH	DMSO	90	0.33	202	95	S19

HexNMe₂ = N,N-dimethylhexylamine; DMOA = dimethyloctylamine; DPPE = 1,2- Bis(diphenylphosphino)ethane.

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