Supporting Information

Highly Efficient Microwave-Accelerated Transfer Hydrogenation for CO_2-Derived Carbonate Valorization by Ru(II)-Protic NHC Pincer Catalysts

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Table of Contents

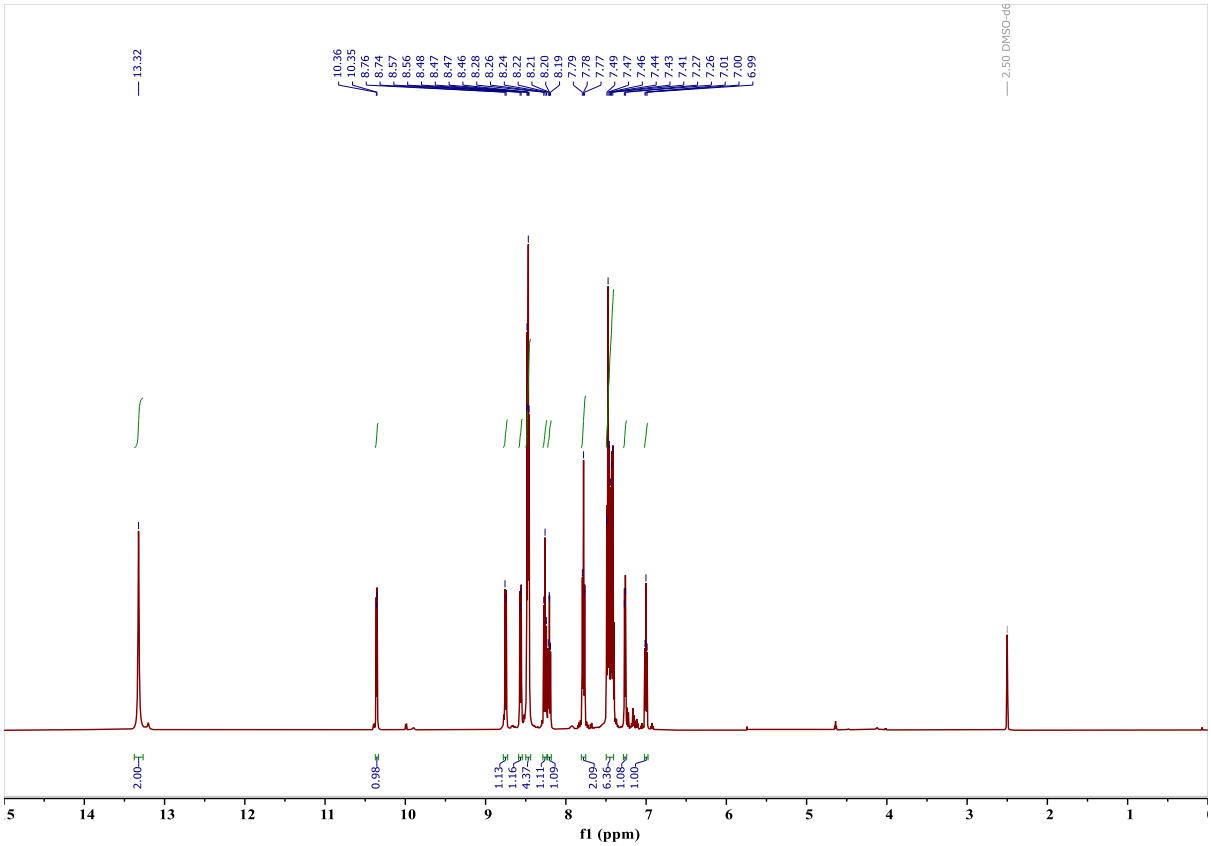

Figure S1 ^{1}H NMR of complex **Ru9** in DMSO-d_6 solution.

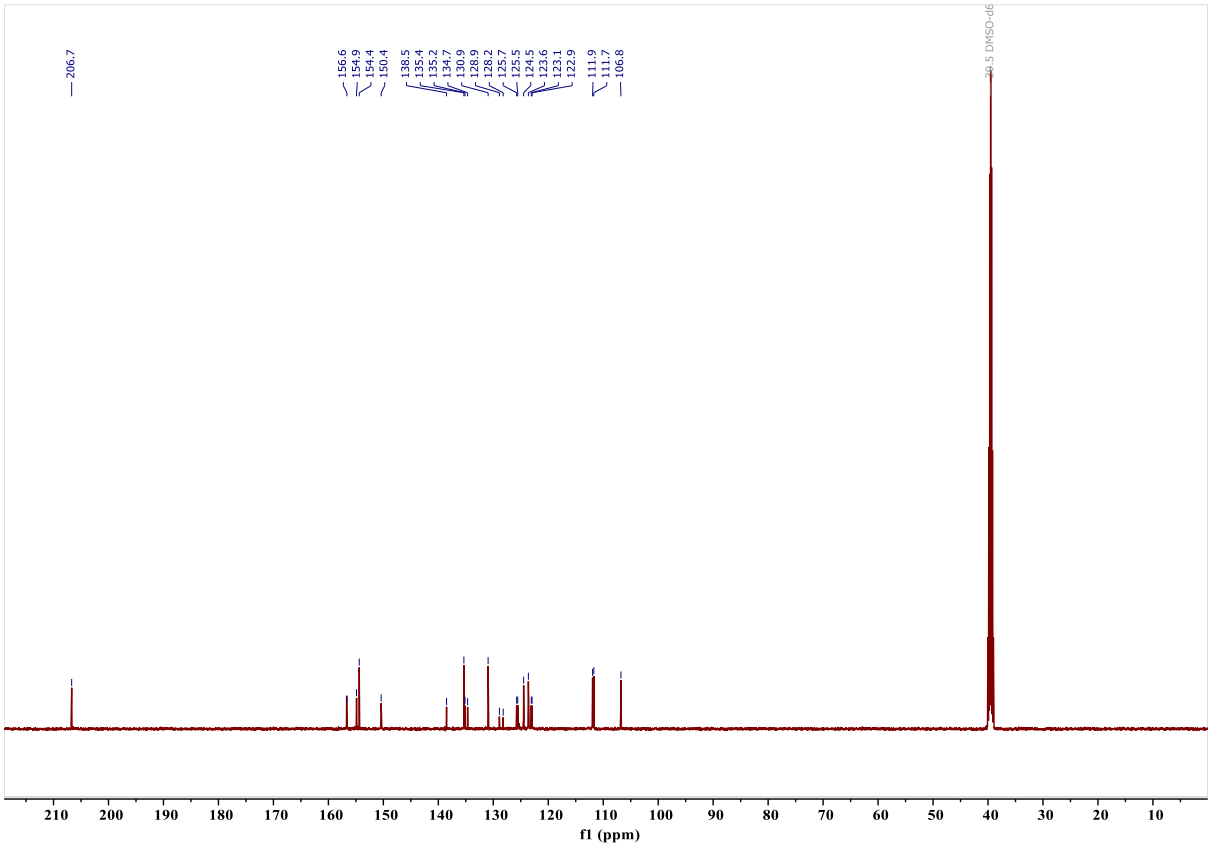

Figure S2 ^{13}C{^{1}H} NMR of complex **Ru9** in DMSO-d_6 solution.

Generic Display Report

Analysis Info

Analysis Name	D:\Documents\mass\m chem aks-as-2-227_RC1_01_15046.d	Acquisition Date	19-11-2024 11:25:46
Method	8. W M.m	Operator	Ghanashyam Bhavsar
Sample Name	m chem aks-as-2-227	Instrument	micrOTOF-Q
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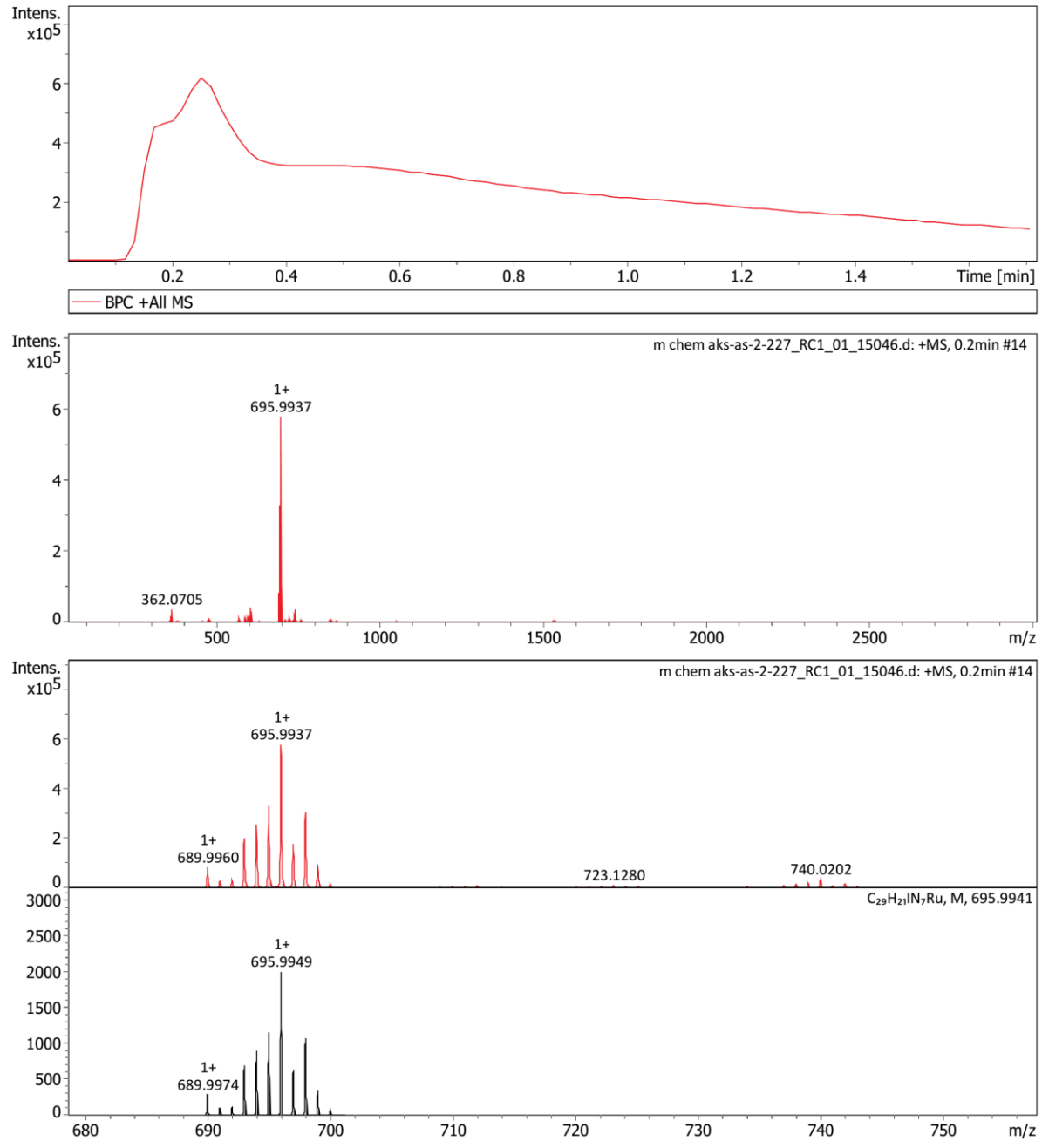


Figure S3 HRMS of complex **Ru9**.

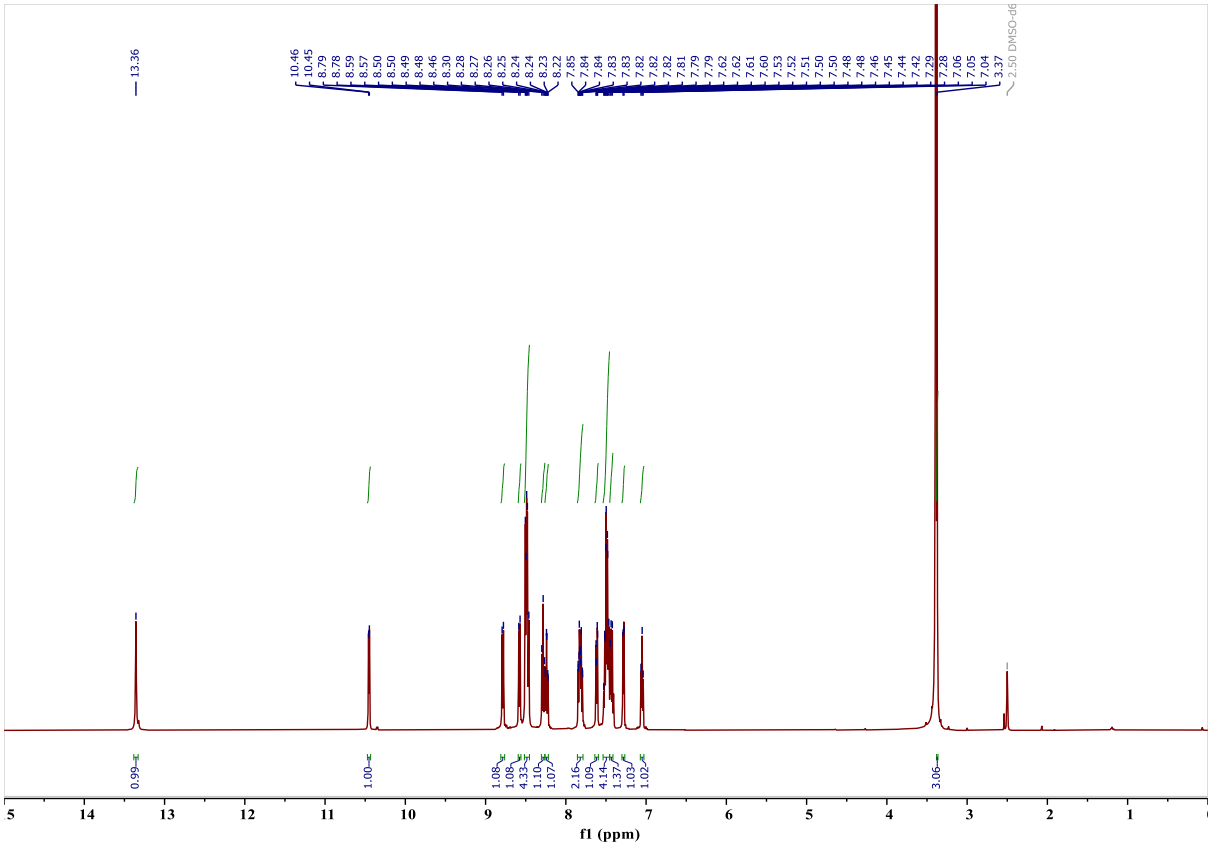


Figure S4 ^{1}H NMR of complex **Ru10** in DMSO-d_6 solution.

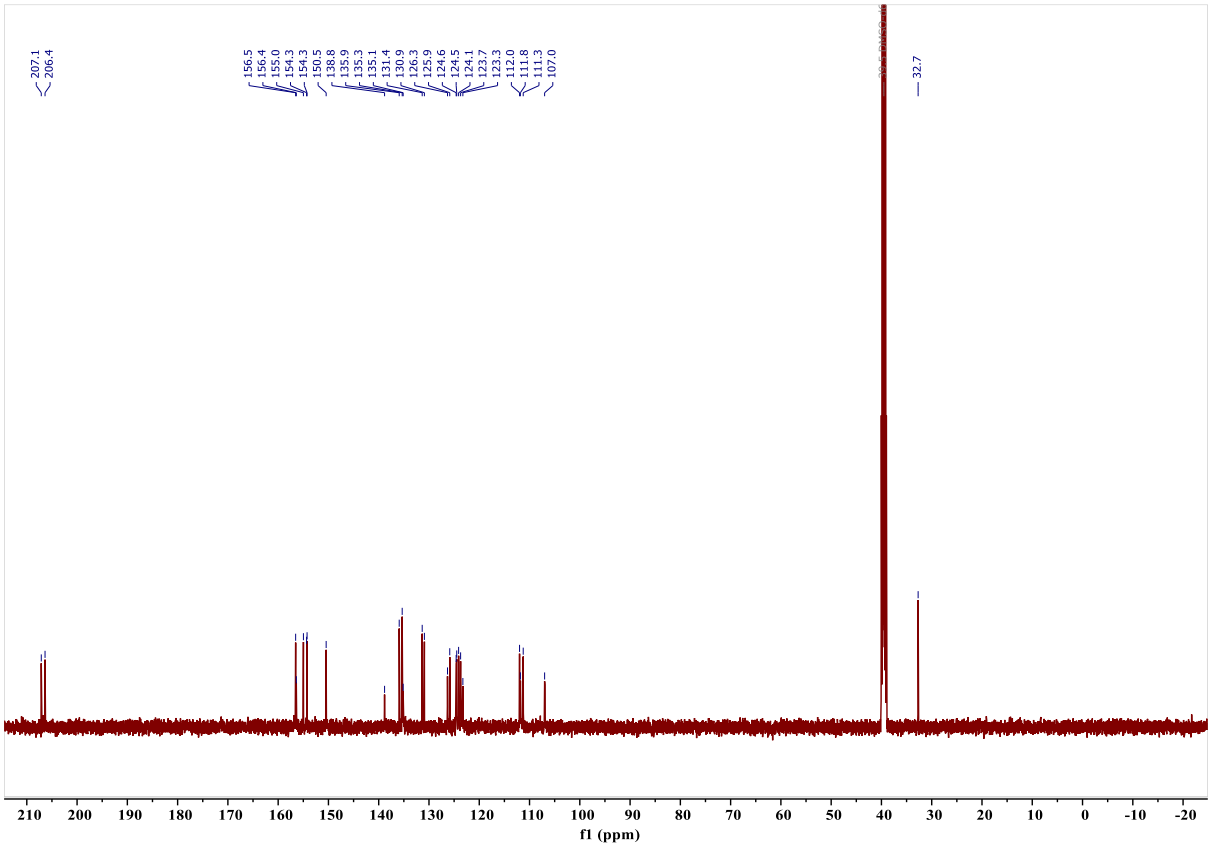


Figure S5 ^{13}C{^{1}H} NMR of complex **Ru10** in DMSO-d6 solution.

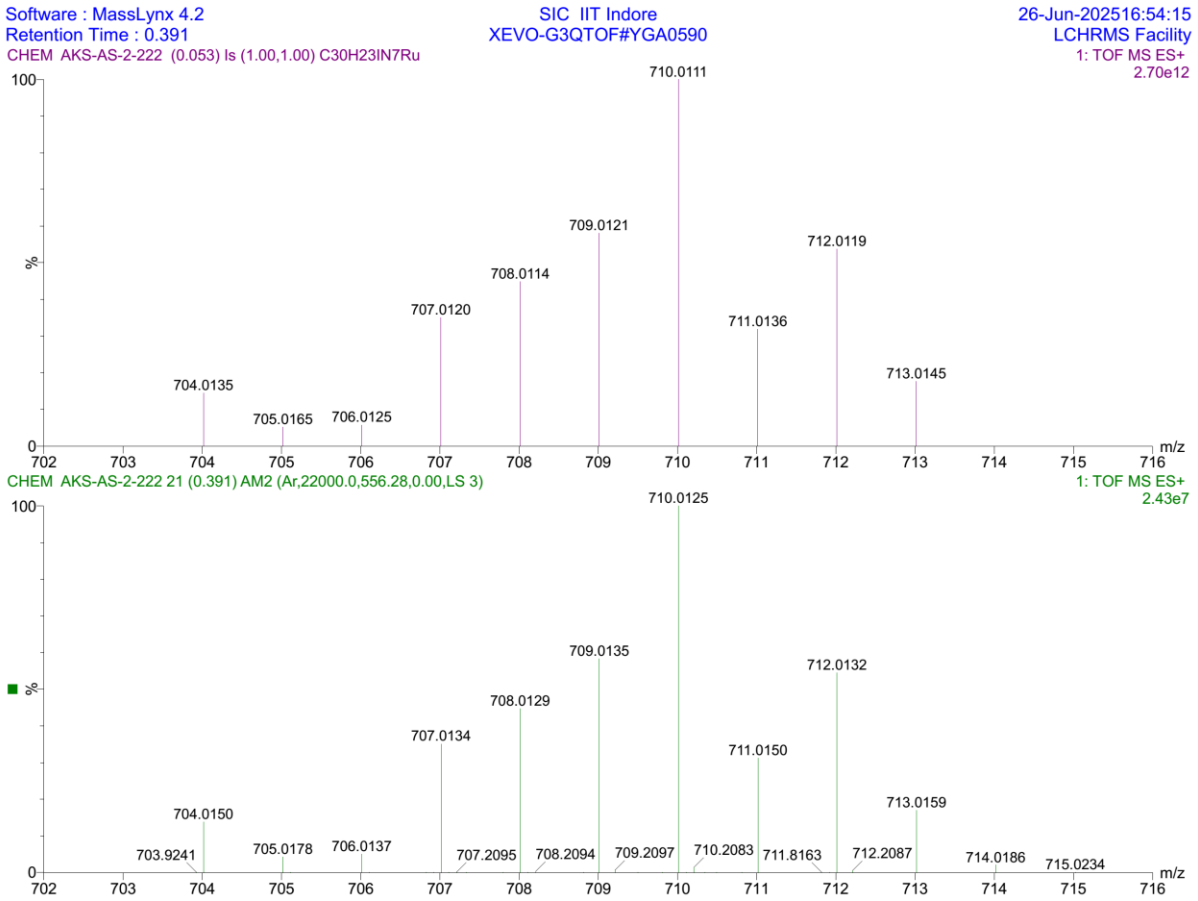


Figure S6 HRMS of complex **Ru10**.

General procedure for thermal transfer hydrogenation of inorganic carbonates using glycerol

A 60 mL pressure tube was charged with K_2CO_3 (4mmol), ethanol (0.05 mL) in glycerol (1.0 mL), and a catalyst (1.0 µmol). The sealed tube was stirred for 20 h in a silicone oil bath maintained at 160 °C. After completion, the reaction mixture was diluted with water (9 mL), and isonicotinic acid (0.05 mmol) was added as an internal standard (IS). For NMR analysis, 0.45 mL of the diluted solution was mixed with 0.15 mL of D_2O. Product quantification was carried out by comparing the integration of characteristic ^1H NMR signals with that of the internal standard. The amount of formate was determined from the integration of the formate proton signal ($HCOO^-$, δ = 8.45 ppm) relative to the internal standard signal (δ = 8.60 ppm). Turnover frequency (TOF) values after 20 h were calculated from the molar concentration of formate produced under these conditions. A representative calculation is provided below.

$$\text{mmol of formate} = \frac{(\text{integral of formate peak/no.of corresponding proton})}{(\text{integral of internal standard/no.of corresponding proton})} \text{ x (mmol of (IS)}$$

General procedure for microwave-accelerated transfer hydrogenation of inorganic carbonates using glycerol

Microwave-accelerated reactions were carried out in a Milestone Start S microwave reactor equipped with a magnetic stirrer to ensure continuous mixing and a noncontact infrared sensor for real-time monitoring and precise control of the reaction temperature. In a typical experiment, a 60 mL sealed pressure tube was charged with the hydrogen donor (1.0 mL) (ethanol (0.05 mL) in glycerol, glycerol-water mixture, methanol, ethanol, isopropanol, or ethylene glycol, carbonate salt or base (4.0 mmol), the desired carbonate salt, and the catalyst. The reaction mixture was subjected to microwave irradiation under controlled temperature and time conditions, with continuous stirring to maintain homogeneity. Upon completion, the resulting products were analyzed by NMR spectroscopy using the procedure described above.

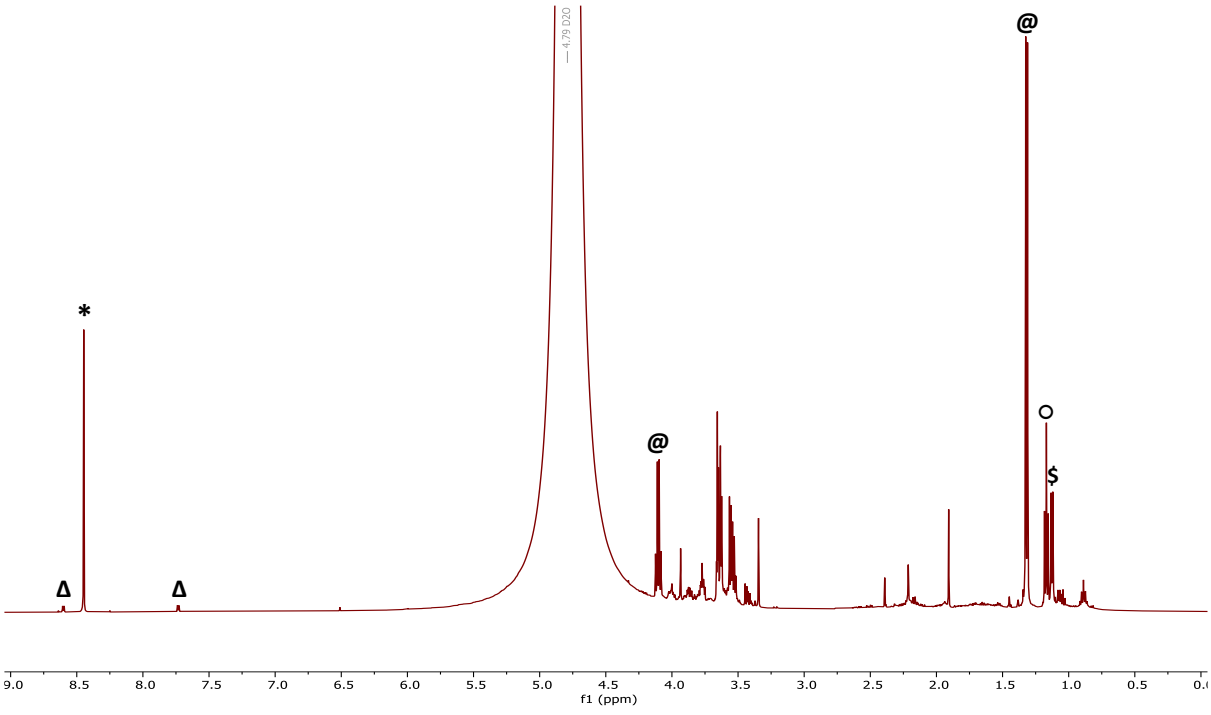


Figure S7 ^{1}H NMR spectrum of an aliquot of the reaction mixture obtained using glycerol as the hydrogen donor. Peaks are assigned as follows: Δ = internal NMR standard (isonicotinic acid); * = formate (HCO_2^-); @ = lactate; ○ = ethanol, $ = 1,2-PDO

Table S1. Catalytic activity of Ru(II) NHC complexes in the microwave-accelerated transfer hydrogenation of varying amounts of carbonate salt using glycerol as the hydrogen source. The activity is expressed in terms of turnover numbers (TON) and turnover frequencies (TOF) for the formation of 1,2-propanediol (1,2-PDO), formic acid (FA), and lactic acid (LA). The corresponding results are graphically represented in Figure 4

Complexes	TON			TOF (h^{-1})		
	1,2-PDO	Formate	Lactate	1,2-PDO	Formate	Lactate
[Ru1]	4,523	9,286	11,190	38,768	79,592	95,914
[Ru5]	952	4,643	6,667	8,160	39,796	57,146
[Ru9]	3,809	5,714	9,167	32,648	48,979	78,574
[Ru10]	4,523	10,714	18,214	38,768	91,836	156,120
[Ru11]	4,167	8,928	10,357	35,717	76,530	88,774

Table S2. Catalytic performance of **Ru10** in the microwave-accelerated transfer hydrogenation of various carbonate salts using glycerol as the hydrogen source. The activity is expressed in terms of turnover numbers (TON) and turnover frequencies (TOF) for the formation of 1,2-propanediol (1,2-PDO), formic acid (FA), and lactic acid (LA). The corresponding data are graphically illustrated in Figure 3. Relative excess terms are defined as follows:

$$\text{Rel. excess}_{AD/TH} = \frac{[LA] - ([FA] + [1,2-PDO])}{[FA] + [1,2-PDO]} \times 100$$

Entry	Base	TON			TOF (h^{-1})			Relative excess AD/TH
		1,2-PDO	Formate	Lactate	1,2-PDO	Formate	Lactate	
1.	$KOH + CO_2$	714	2,500	6,666	6,120	21,428	57,137	107
2.	$NaHCO_3$	238	1,071	4,761	2,040	9,180	40,808	264
3.	$KHCO_3$	1,071	4,642	14,523	9,180	39,788	1,24,483	154
4.	$CaCO_3$	0	0	0	0	0	0	0
5.	Li_2CO_3	0	125	2,381	0	1,071	20,408	1,804
6.	Na_2CO_3	833	357	11,785	7,140	3,060	1,01,014	890
7.	K_2CO_3	4,523	10,714	18,214	38,768	91,836	1,56,120	19.5
8.	Cs_2CO_3	5,000	18,571	67,619	42,857	159,180	579,591	187

9.	K_2CO_3:Cs_2CO_3 (9:1)	4,643	16,785	62,200	39,797	143,871	533,142	190

Table S3. Catalytic activity of **Ru10** in the microwave-accelerated transfer hydrogenation of varying amounts of carbonate salt using glycerol as the hydrogen source. The activity is expressed in terms of turnover numbers (TON) and turnover frequencies (TOF) for the formation of 1,2-propanediol (1,2-PDO), formic acid (FA), and lactic acid (LA). The corresponding results are graphically represented in Figure 4.

Base amount (mmol)	TON			TOF			Rel. excess % AD/TH
	1,2-PDO	Formate	Lactate	1,2-PDO	Formate	Lactate	
1	714	1,071	12,262	6,120	9,180	105,102	587
2	952	2,142	12,857	8,160	18,360	110,202	315
3	1,190	2,857	13,452	10,200	24,488	115,302	232
4	4,523	10,714	18,214	38,768	91,834	156,120	19
5	4,643	11,071	18,452	39,797	94,894	158,160	17

Procedure for time-dependent monitoring of the catalytic reaction

In thermal conditions (Figures 5a and 5b)

The general catalytic protocol outlined in Section III was adapted by employing ethanol (0.05 mL) in glycerol (1 mL), K_2CO_3 (4 mmol), and **Ru10** (0.14 µmol). Reactions were carried out at 160 °C for up to 24 h. At predetermined time intervals, aliquots of the reaction mixture were collected and analyzed by ^{1}H NMR spectroscopy to quantify turnover numbers (TON) at each time point. Each experiment was repeated four times to evaluate reproducibility, and the data presented in Figure 5b include error bars reflecting the observed experimental variations.

Table S4. Table summarizing the activity of **Ru10** for the thermal-accelerated transfer hydrogenation of different amounts of carbonate salts from glycerol at different times.

Time (h)	TON of 1,2-PDO	TON of Formate	TON of Lactate
1	0	78	357
2	0	154	833
3	0	157	595
4	119	300	2,262
5	119	357	2,024
6	238	714	4,762
8	238	1,428	7,500
10	238	1,786	10,476
15	476	2,857	15,119
20	595	3,214	18,809
24	833	2,143	19,048

In microwave heating conditions (Figures 6a and 6b)

The general catalytic protocol outlined in Section III was adapted by employing ethanol (0.05 mL) in glycerol (1 mL), K_2CO_3 (4 mmol), and **Ru10** (0.14 µmol). Reactions were carried out at 50 °C for up to 20 min. At predetermined time intervals, aliquots of the reaction mixture were collected and analyzed by ^{1}H NMR spectroscopy to quantify turnover numbers (TON) at each time point. Each experiment was repeated four times to evaluate reproducibility, and the data presented in Figure 6b include error bars reflecting the observed experimental variations.

Table S5. Table summarizing the activity of **Ru10** for the microwave-accelerated transfer hydrogenation of different amounts of carbonate salts from glycerol at different times up to 20 mins.

Time (min)	TON of 1,2-PDO	TON of Formate	TON of Lactate
3	357	1,788	11,190
5	1,309	7,142	13,571
7	4,523	10,714	18,214
10	4,643	10,714	18,452
20	4,880	10,714	36,905

Mechanistic Investigation

I. NMR experiment for evaluating the regeneration of the protic-NHC complex in the presence of glycerol

All NMR experiments were carried out under an inert nitrogen atmosphere within a glovebox to exclude air and moisture. In situ monitoring of the reaction was performed using a J. Young NMR tube, which was charged with complex **Ru10** (35 mg, 0.041 mmol) dissolved in DMSO-d_6 (0.5 mL). The progress of the reaction was followed by recording ^{1}H NMR spectra on a 500 MHz spectrometer. The characteristic ^{1}H NMR resonances of the protic NHC complex were observed at δ 13.36 (s, 1H), 10.45 (d, J = 4.4 Hz, 1H), 8.79 (d, J = 8.2 Hz, 1H), 8.58 (d, J = 8.2 Hz, 1H), 8.54–8.44 (m, 4H), 8.28 (t, J = 8.3 Hz, 1H), 8.24 (td, J = 7.9, 1.6 Hz, 1H), 7.86–7.76 (m, 2H), 7.61 (dd, J = 7.2, 2.1 Hz, 1H), 7.54–7.46 (m, 4H), 7.47–7.38 (m, 1H), 7.28 (d, J = 5.9 Hz, 1H), 7.05 (t, J = 6.7 Hz, 1H), and 3.37 (s, 3H).

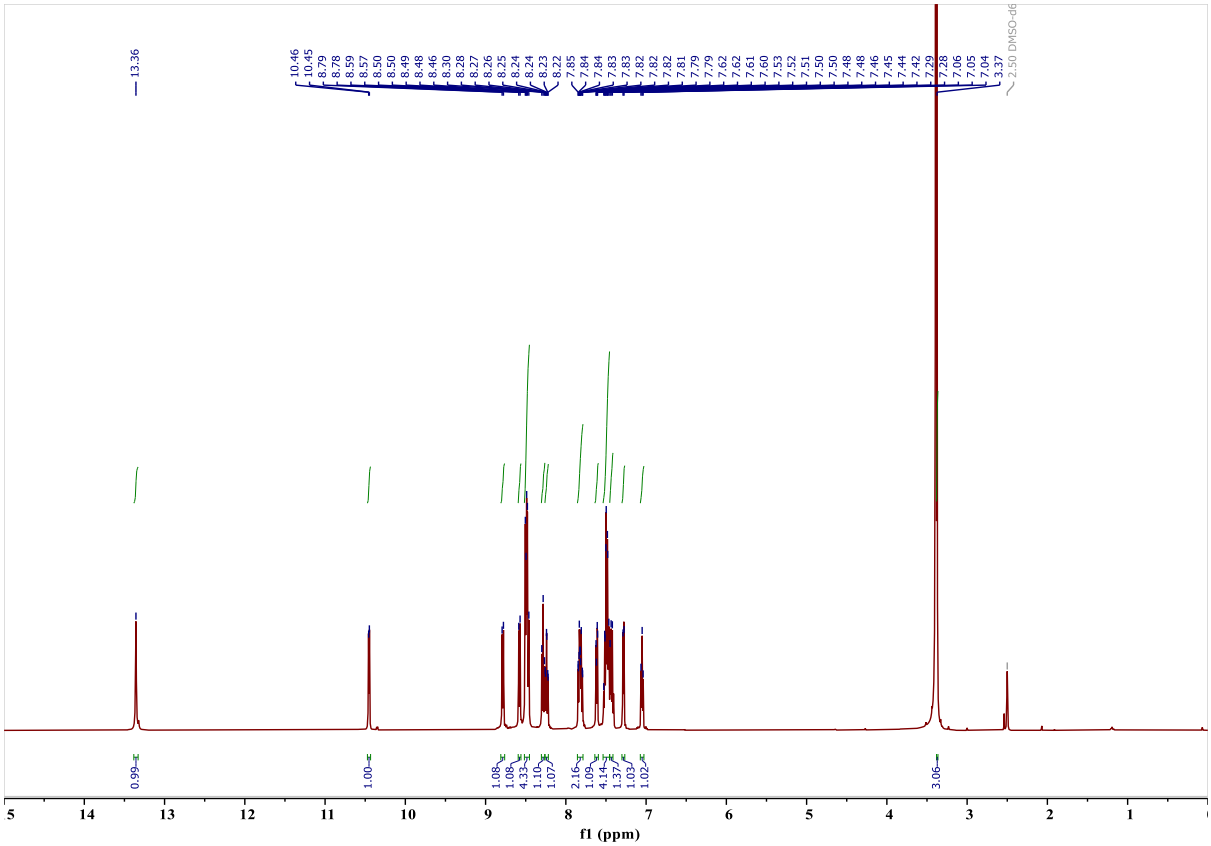
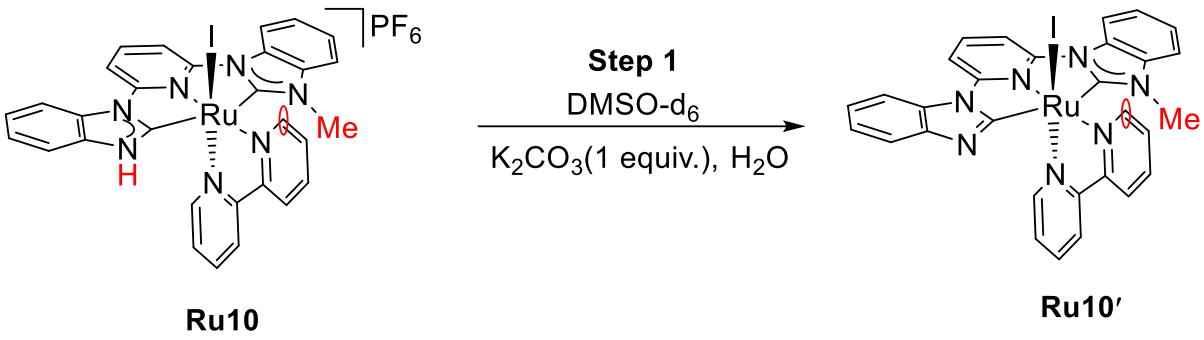


Figure S8 ^{1}H NMR of complex **Ru10** in DMSO-d6

Step 1: In situ generation of Ru10′: Following the initial NMR characterization of complex **Ru10** (35 mg, 0.041 mmol), an equimolar amount of K_2CO_3 (5.66 mg, 0.041 mmol) dissolved in H_2O was introduced into the J. Young NMR tube containing the complex in DMSO-d_6 (0.5 mL). The addition immediately induced a distinct color change to orange-red, indicative of the in-situ formation of a new species, designated as **Ru10′**. The tube was sealed with a Teflon screw-cap to maintain an inert environment, briefly agitated to ensure homogeneity, and subsequently subjected to NMR analysis. The **^{1}H NMR** spectrum recorded at 500 MHz (DMSO-d_6) displayed resonances at δ 9.99 (d, J = 4.5 Hz, 1H), 8.71 (d, J = 6.9 Hz, 1H), 8.58 (d, J = 8.2 Hz, 1H), 8.48 (d, J = 8.1 Hz, 1H), 8.43 (t, J = 8.2 Hz, 1H), 8.37 (d, J = 8.2 Hz, 1H), 8.20 (t, J = 7.7 Hz, 2H), 8.04 (d, J = 7.1 Hz, 1H), 7.88–7.78 (m, 2H), 7.66 (d, J = 6.7 Hz, 1H), 7.59–7.48 (m, 2H), 7.32 (dd, J = 7.4, 1.6 Hz, 1H), 7.20–7.03 (m, 4H), and 3.45 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, DMSO-d_6) δ 202.6, 194.3, 155.4, 154.4, 154.2, 153.8, 153.6, 148.6, 147.8, 143.0, 137.5, 136.4, 136.2, 133.1, 131.6, 126.6, 125.2, 125.1, 124.3, 123.6, 122.8, 121.5, 117.5, 112.8, 112.1, 110.9, 106.6, and 33.7.



Scheme S1 In situ formation of **Ru10'**

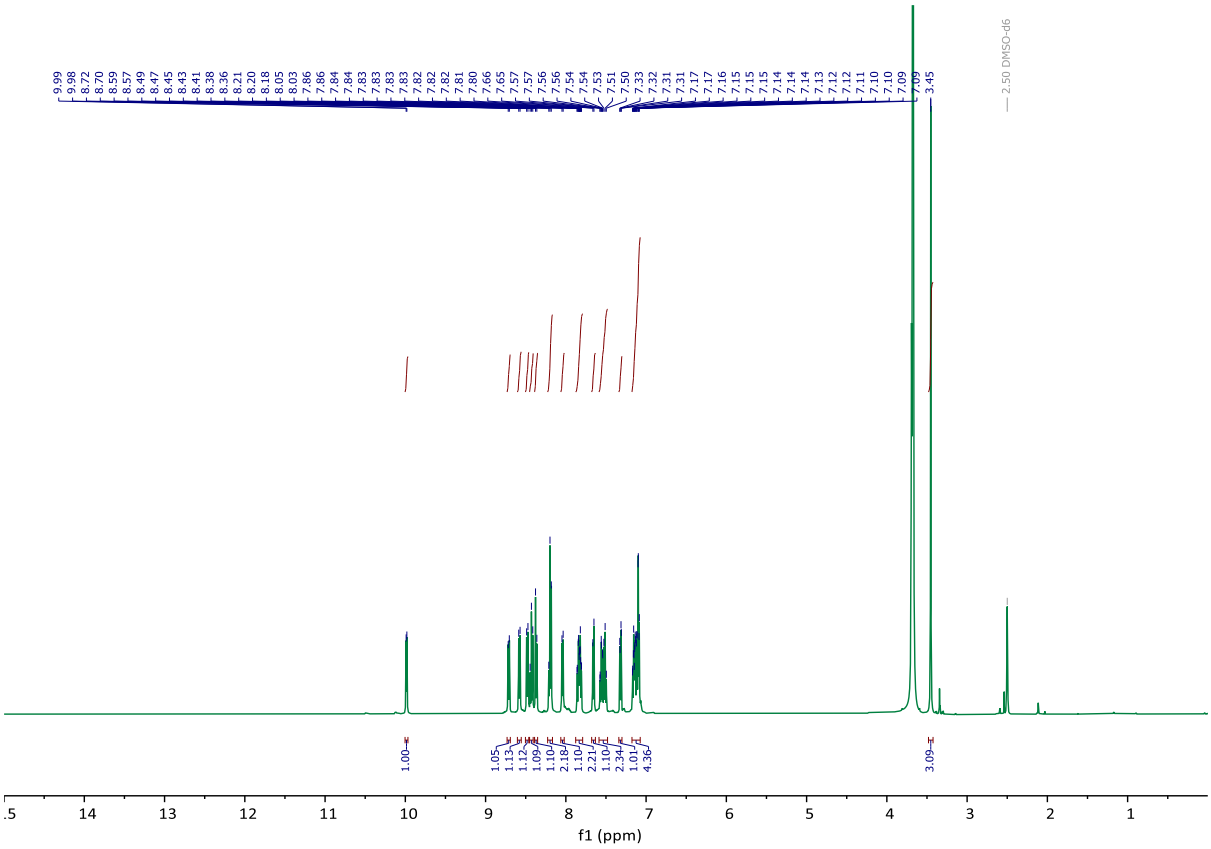


Figure S9 ^{1}H NMR of complex **Ru10'** in DMSO-d6

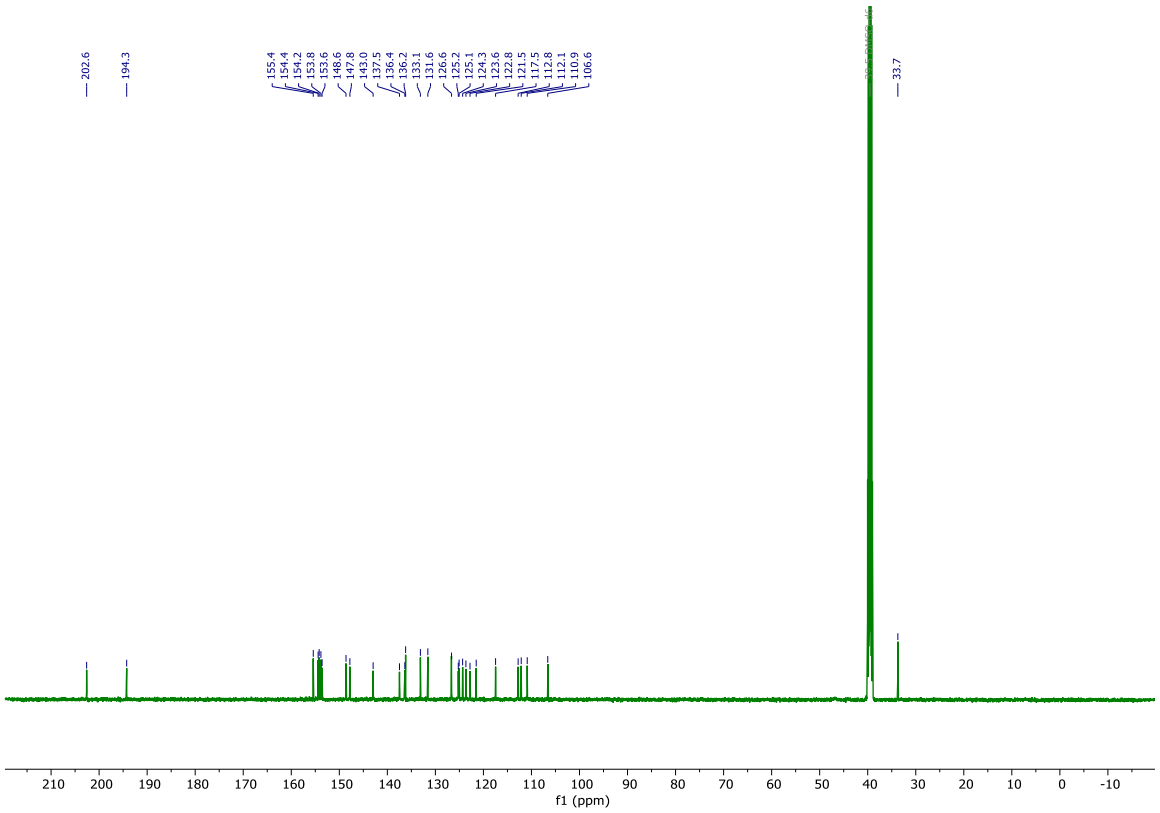
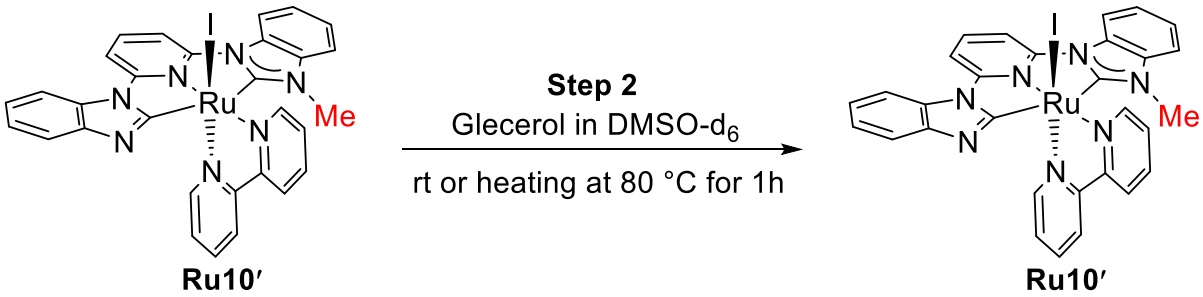


Figure S10 ^{13}C NMR of complex **Ru10'** in DMSO-d6

Step 2: No Regeneration of complex Ru10: In the subsequent experiment, two equivalents of glycerol were introduced into the J. Young NMR tube containing **Ru10′**. The tube was sealed with a Teflon screw-cap to ensure an airtight environment, vigorously agitated, and allowed to stand overnight at room temperature. The reaction progress was monitored by recording ^{1}H NMR spectra on a 500 MHz spectrometer. The resulting spectra revealed no evidence for the regeneration of the protic NHC complex **Ru10**, as indicated by the absence of the diagnostic NH resonance. Moreover, no appreciable change in the chemical shifts of the observed signals was detected. Even upon heating the NMR tube to 80 °C for 1 h, the ^{1}H NMR spectrum remained essentially unchanged, thereby confirming that glycerol does not promote the in situ regeneration of **Ru10** under the examined conditions (Scheme S2).



Scheme S2 Addition of glycerol to **Ru10'** at rt and heating at 80 °C.

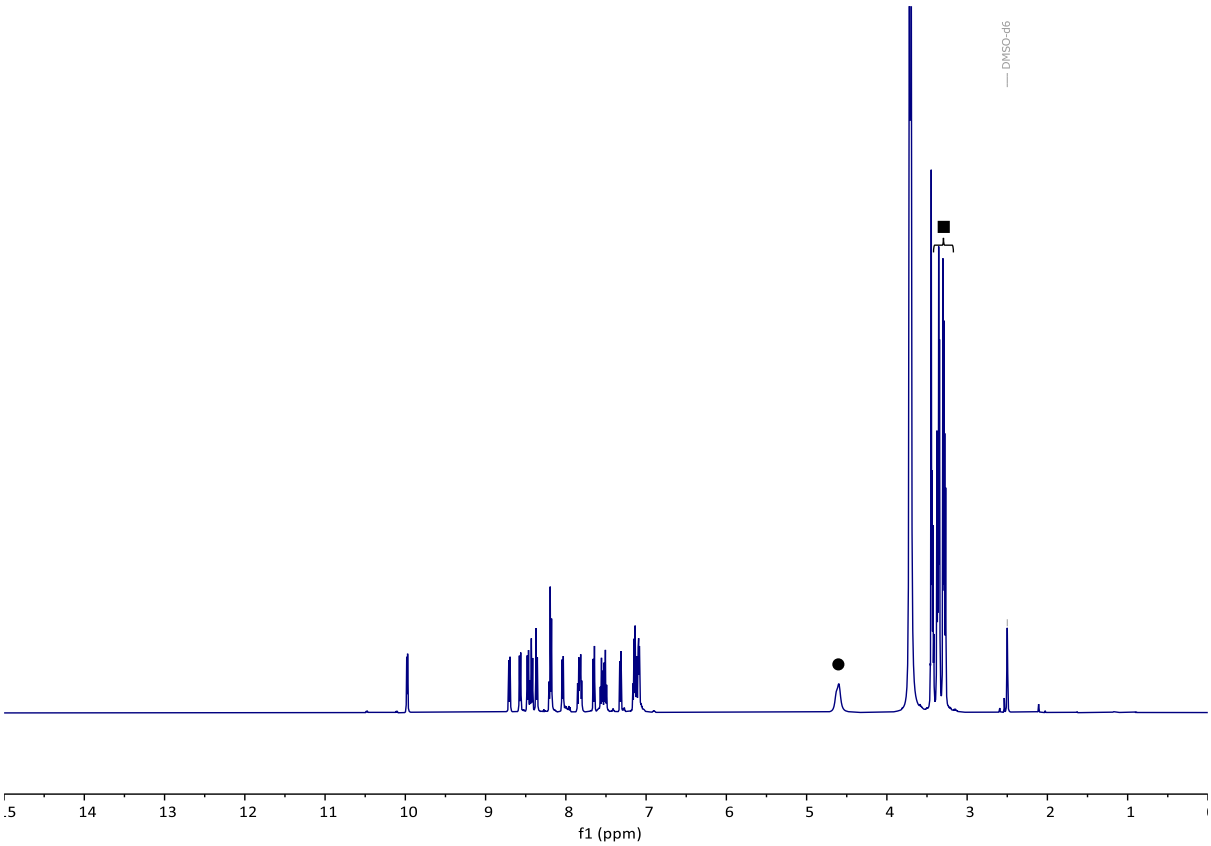


Figure S11 ^{1}H NMR spectra of **Ru10′** after the addition of glycerol and K_2CO_3, recorded at room temperature and upon heating to 80 °C. • denotes the OH resonance of glycerol; ▪ denotes the CH_2 resonance of glycerol.

Reaction of Ru10 with $KHCO_3$: Following the initial NMR characterization of complex **Ru10** (35 mg, 0.041 mmol), an equimolar amount of $KHCO_3$ (4.1 mg, 0.041 mmol) dissolved in H_2O was introduced into the J. Young NMR tube containing the complex in DMSO-d_6 (0.5 mL). The addition didn't show any color change. The tube was sealed with a Teflon screw-cap to maintain an inert environment, briefly agitated to ensure homogeneity, and subsequently subjected to NMR analysis, which confirmed that the complex Ru10 remained intact in the presence of $KHCO_3$.

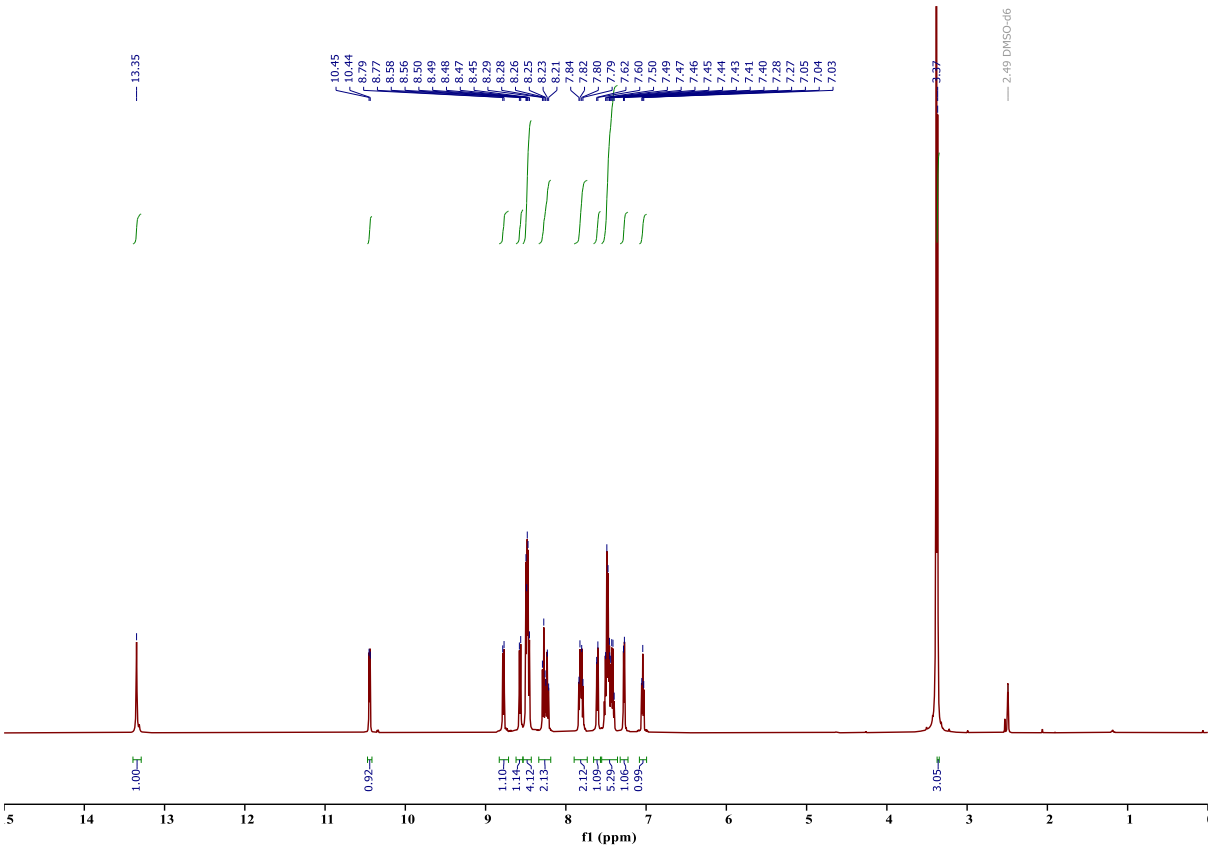


Figure S12 ^{1}H NMR of complex **Ru10** in DMSO-d6 in presence of $KHCO_3$.

II. In situ generation of Ru–hydride complex: The deprotonated complex **Ru10′** (0.05 mmol, 35 mg) was dissolved in DMSO-d_6 (300 µL) in a J. Young NMR tube. To this solution, glycerol (2 equiv., 0.10 mmol, 7.3 µL) and K_2CO_3 (2 equiv., 0.10 mmol, 13.8 mg, dissolved in 200 µL H_2O) were added sequentially. The NMR tube was sealed with a Teflon screw-cap and heated at 90 °C. The reaction progress was monitored on a 500 MHz NMR spectrometer. Analysis of the resulting mixture by ^{1}H NMR spectroscopy revealed the appearance of a characteristic hydride resonance at δ -7.75 ppm (Figure S12).

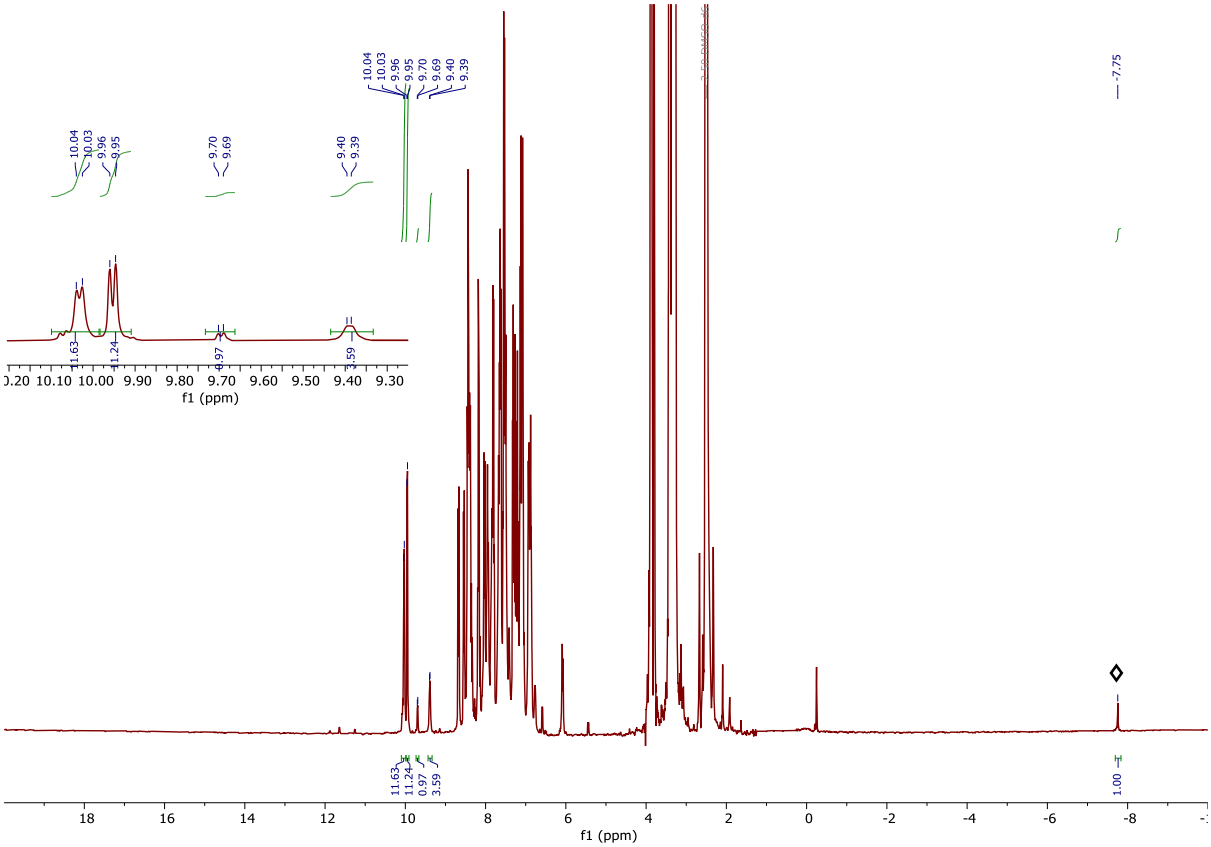


Figure S13 ^{1}H NMR spectrum in DMSO-d_6 showing the in situ generation of the ruthenium–hydride intermediate, ◊ indicates a Ru-H peak

III. To check the generation of free CO_2: The reaction was performed with **Ru10** with the addition of two equivalents of glycerol and K_2CO_3 into the J. Young NMR. The tube was sealed with a Teflon screw-cap to ensure an airtight environment, vigorously agitated, and allowed to stand overnight at room temperature. The reaction progress was monitored by recording ^{13}C NMR spectra on a 500 MHz spectrometer. The resulting spectra revealed no extra peak at δ 125, which is evidence for the generation of CO_2.

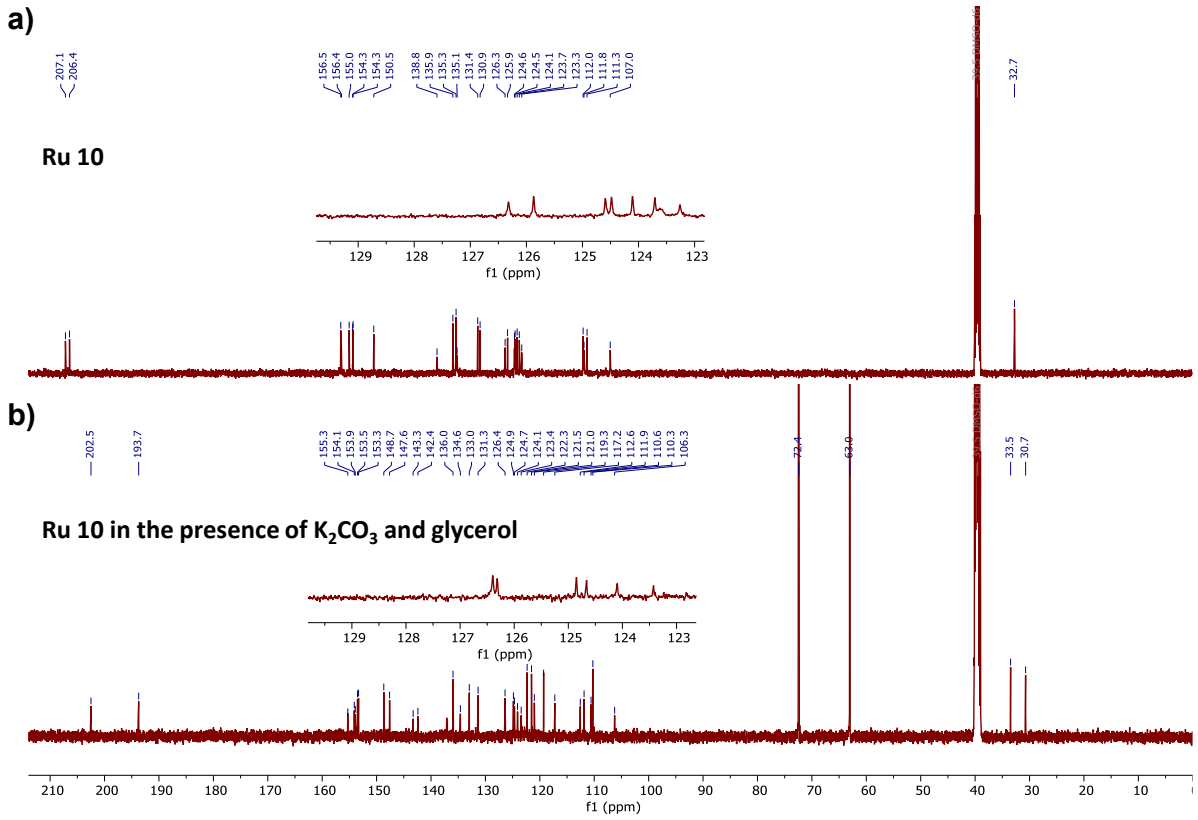
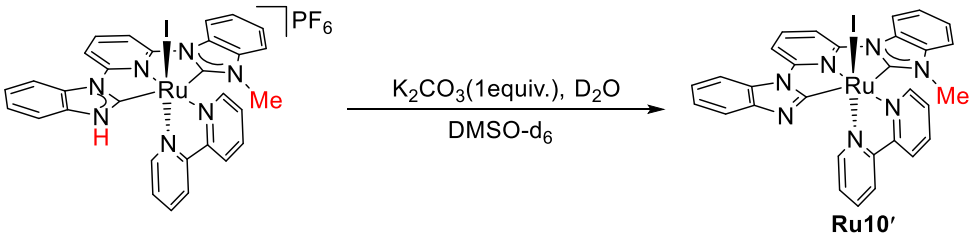


Figure S14 ^{13}C NMR spectrum in DMSO-d_6 showing a) complex Ru10 and b) complex Ru10 in presence of K_2CO_3 and glycerol (δ 72.4 and 63.0)

Mechanistic investigation using mass spectrometry.

To gain further insight into the mechanistic pathway, mass spectrometric analysis was performed. In experiment (**a**), the deprotonated species of complex **Ru10** was examined. The NMR sample obtained after the addition of K_2CO_3 to complex **Ru10** (step 1) was subjected to mass analysis, which confirmed the successful deprotonation of **Ru10**. Notably, when methanol was employed as a protic solvent during data collection, the deprotonated complex **Ru10'** was observed by LC-MS as the ion $[M–I]^+$ with the molecular formula $C_{30}H_{22}N_7Ru$. The experimental m/z value of 581.9619 closely matched the calculated value of 582.0988, thereby corroborating the structural assignment.



Scheme S3. Deprotonation of complex **Ru10**.

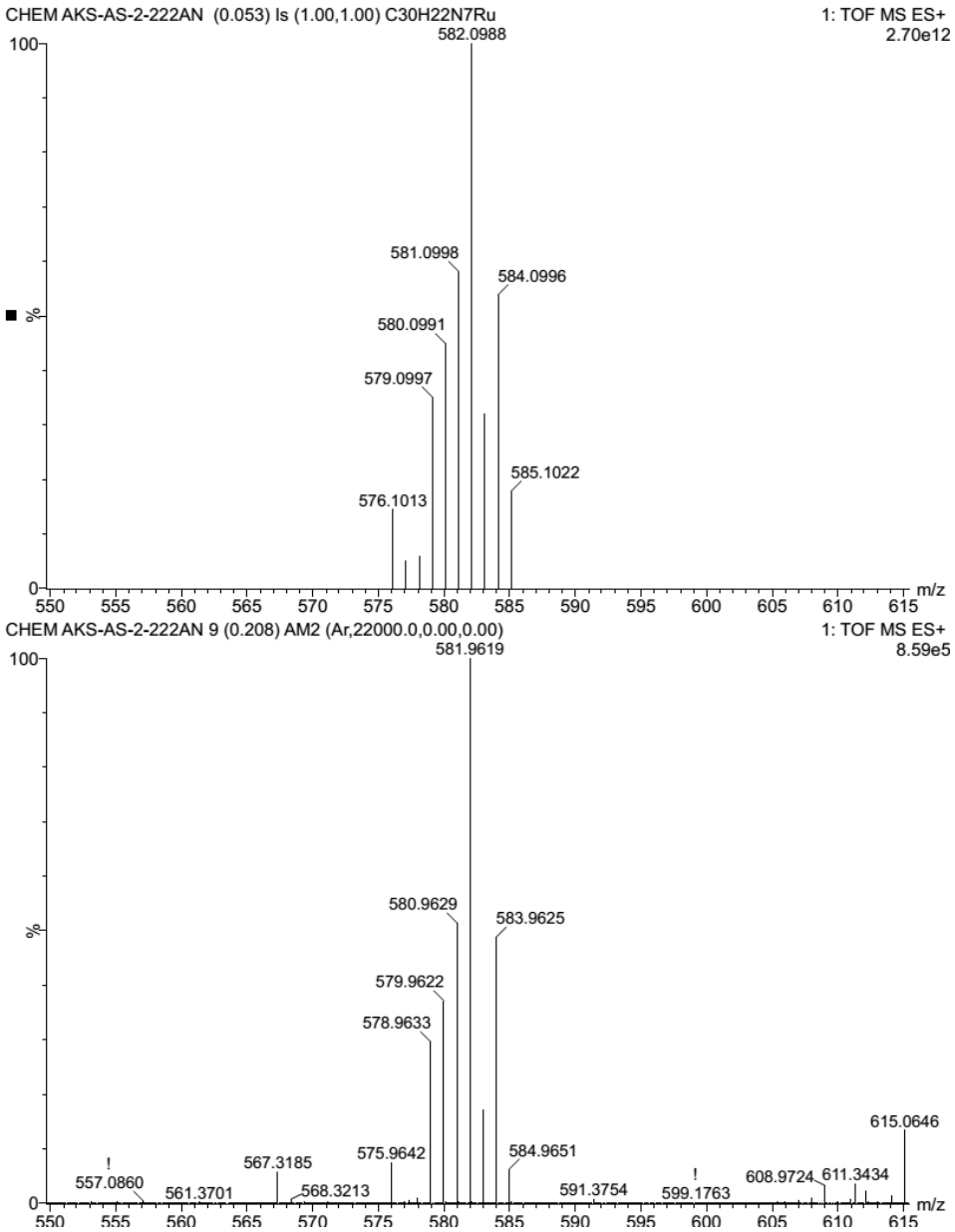


Figure S15 LC-MS spectrum of the NMR sample from experiment **step 1**, collected in acetonitrile (ACN).

(b) Detection of alkoxy intermediate I: Further mechanistic insight was obtained from LC-MS analysis of the catalytic reaction mixture, which provided clear evidence for the generation of a key transient alkoxy intermediate. This species, designated as intermediate I, was detected with the molecular formula $C_{33}H_{29}N_7O_3Ru$. The LC-MS showed an experimental m/z value of 673.1044, in close agreement with the calculated value of 673.1384, thereby supporting the involvement of this alkoxy intermediate in the catalytic cycle.

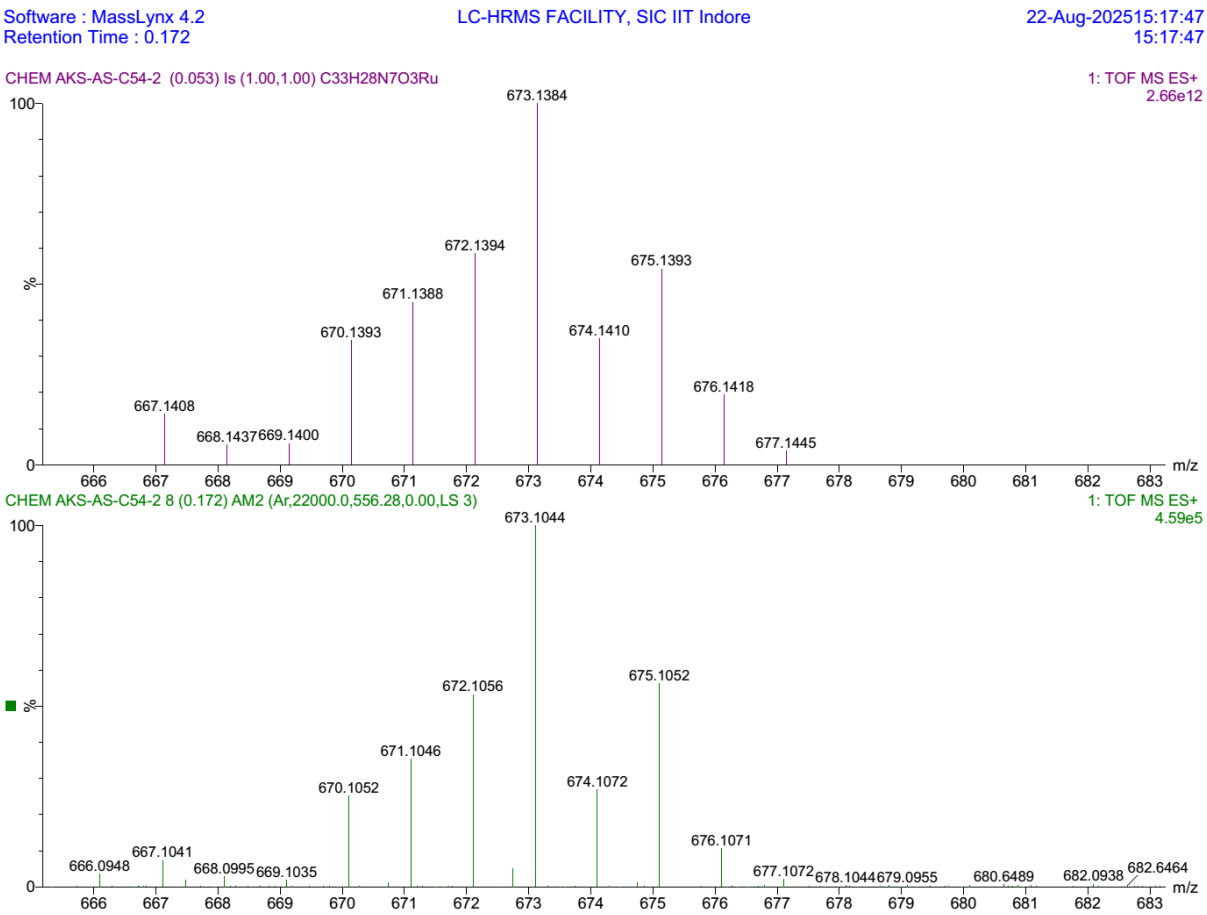


Figure S16 LC-MS spectrum showing the detection of the Ru–alkoxy intermediate (intermediate **I**) in the catalytic reaction mixture.

(c) Detection of formate intermediate VII: LC-MS analysis of the catalytic reaction mixture provided compelling evidence for the formation of a key transient formate intermediate. This species, designated as intermediate **VII**, corresponds to a Ru–OOCH complex with the molecular formula $C_{31}H_{24}N_7O_2Ru$. LC-MS confirmed its identity, showing an experimental m/z value of 628.1043, which is in close agreement with the calculated value of 628.1402. These results strongly support the participation of a Ru–formate species in the catalytic cycle.

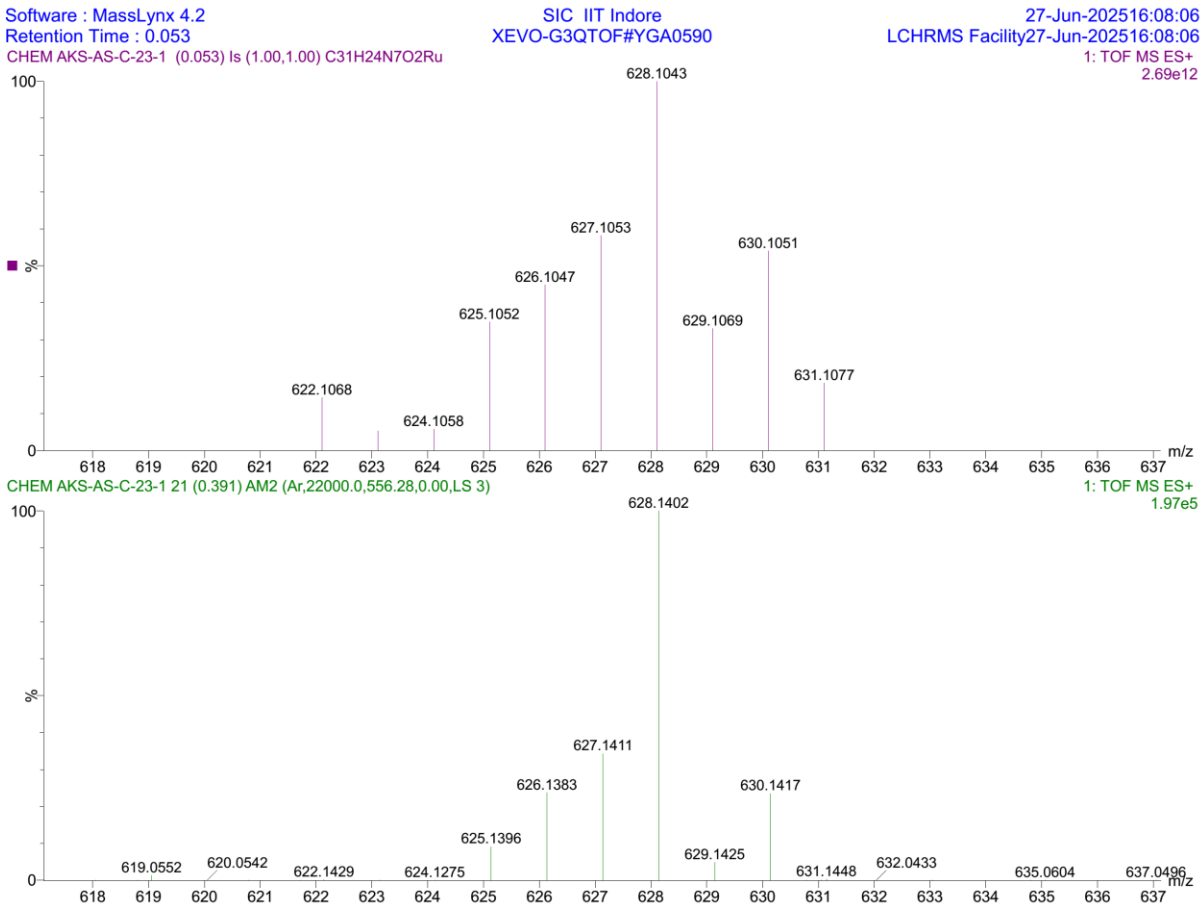


Figure S17 LC-MS spectrum showing the detection of the Ru–formate intermediate (intermediate **VII**) in the catalytic reaction mixture

Mercury Test/Homogeneous Test

An oven-dried 60 mL pressure tube was charged with ethanol (0.05 mL) in glycerol (1.0 mL), mercury (1 equiv.), and a catalyst **Ru10** (0.14 µmol). The sealed tube was stirred for 20 h in a silicone oil bath maintained at 160 °C. After completion, product quantification was carried out by the aforesaid method.

Radical trapping experiment

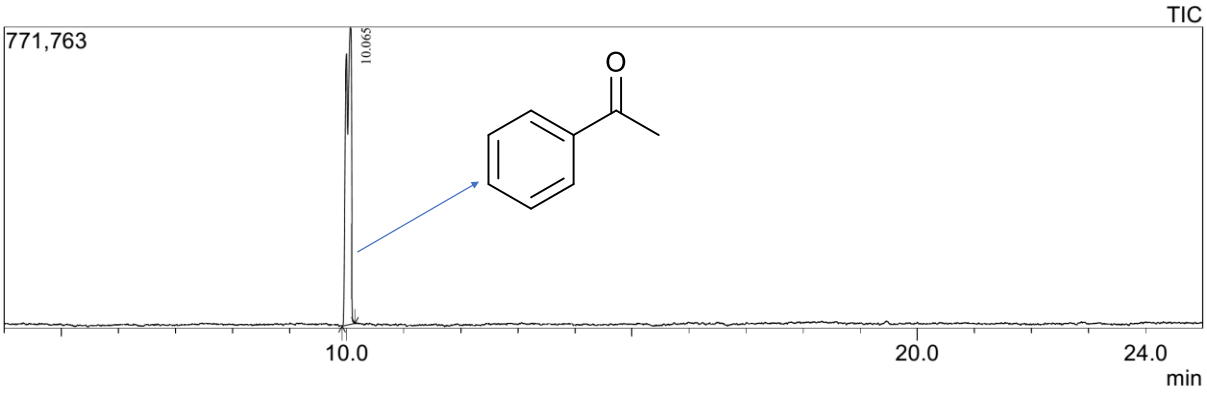
An oven-dried 60 mL pressure tube was charged with ethanol (0.05 mL) in glycerol (1.0 mL), 4-hydroxy-TEMPO (1 equiv.), and a catalyst **Ru10** (0.14 µmol). The reaction mixture was subjected to microwave irradiation under controlled temperature (50 ± 2 °C) for 7 minutes, with continuous stirring to maintain homogeneity. Upon completion, the resulting products were analyzed by NMR spectroscopy using the procedure described above.

Crystallographic Data: Table S6 Crystal data and structure refinement parameters.

	Ru9
Empirical formula	$C_{29}H_{21}F_6IN_7PRu$
Formula weight	840.47
Temperature/K	298
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.2849(4)
b/Å	34.0048(12)
c/Å	10.4093(3)
α/°	90
β/°	111.852(4)
γ/°	90
Volume/Å^3	3378.9(2)
Z	4
ρ_{calc}g/cm^3	1.652
μ/mm^{-1}	1.488
F(000)	1640.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.96 to 58.452
Reflections collected	35146
Independent reflections	8326 [R_{int} = 0.0971]
Data/restraints/parameters	8326/0/434
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0667, wR_2 = 0.179
Final R indexes [all data]	R_1 = 0.1004, wR_2 = 0.1996

General method for transfer hydrogenation of acetophenone

An oven-dried Schlenk tube equipped with a magnetic stirring bar was loaded with catalyst **Ru10** (0.25 mol%), KO^{t}Bu (10 mol%), and anhydrous solvent (methanol or ethanol or 2-propanol) (3 mL). Next, add the acetophenone (1 mmol) to the reaction mixture. After that, the Schlenk tube was placed in a preheated oil bath (70 °C for methanol, 85 °C for ethanol or 2-propanol) with stirring. At the end of the reaction catalytic solution was analyzed on a GC-MS QP 2010 ultra-mass spectrometer equipped with an FID detector.



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	10.065	4962732	100.00	761615	100.00	6.52	Acetophenone
		4962732	100.00	761615	100.00		

Spectrum

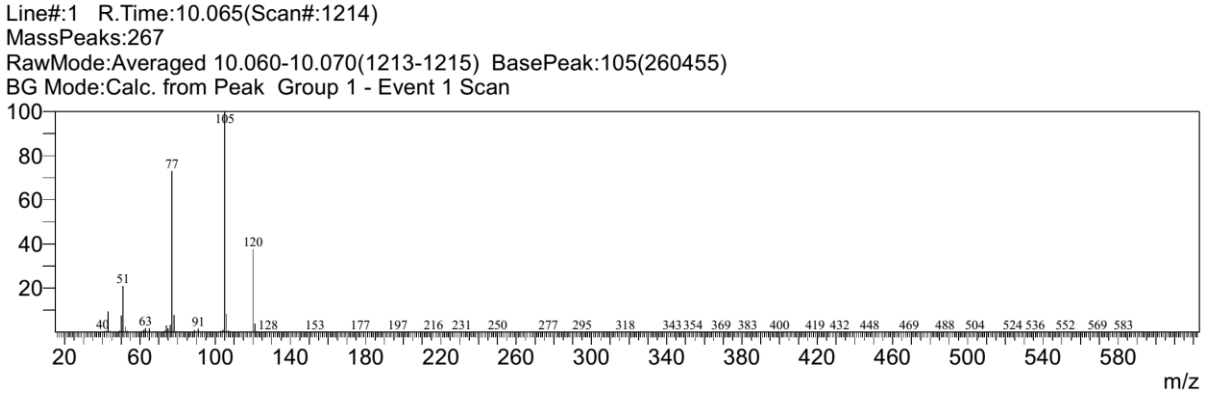
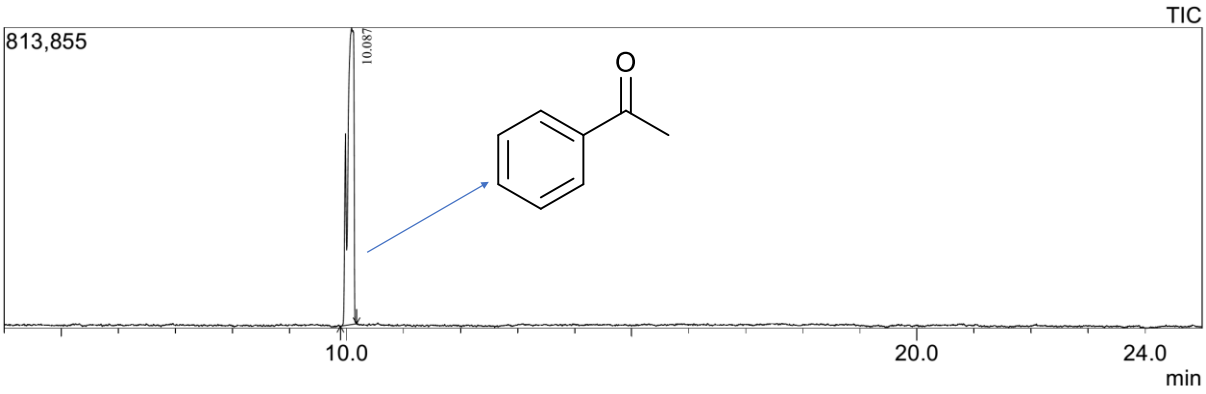


Figure S18 GC-MS analysis for the transfer hydrogenation of acetophenone by catalyst **Ru10** using methanol



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	10.087	6372420	100.00	806945	100.00	7.90	Acetophenone
		6372420	100.00	806945	100.00		

Spectrum

Line#:1 R.Time:10.085(Scan#:1218)
MassPeaks:291
RawMode:Averaged 10.080-10.090(1217-1219) BasePeak:105(271350)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan

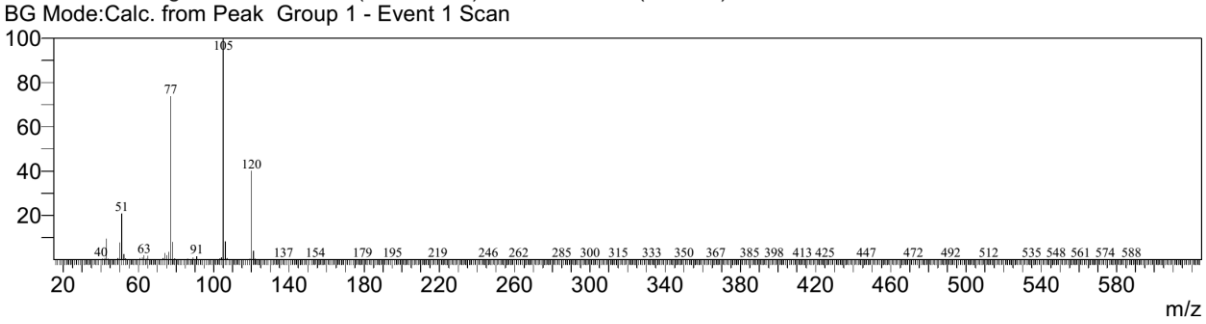
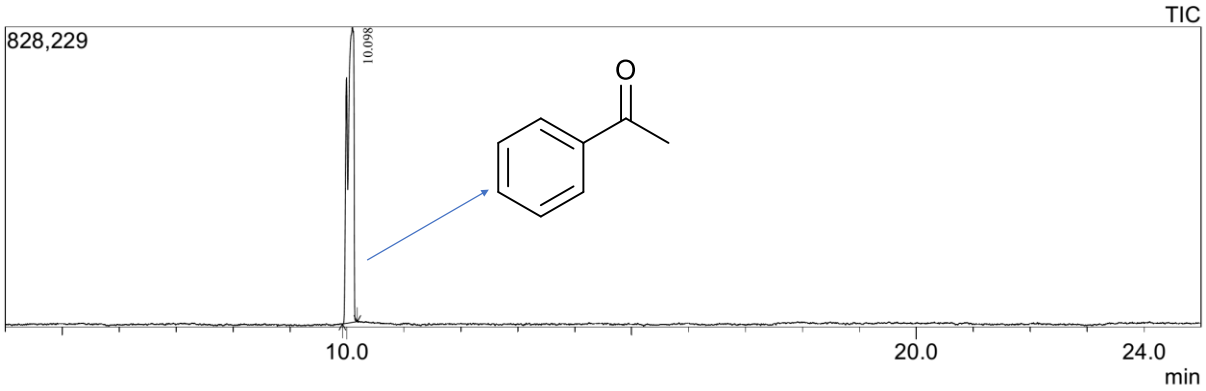


Figure S19 GC-MS analysis for the transfer hydrogenation of acetophenone by catalyst **Ru10** using ethanol



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	10.098	6564558	100.00	815201	100.00	8.05	Acetophenone
		6564558	100.00	815201	100.00		

Spectrum

Line#:1 R.Time:10.100(Scan#:1221)
MassPeaks:309
RawMode:Averaged 10.095-10.105(1220-1222) BasePeak:105(268183)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan

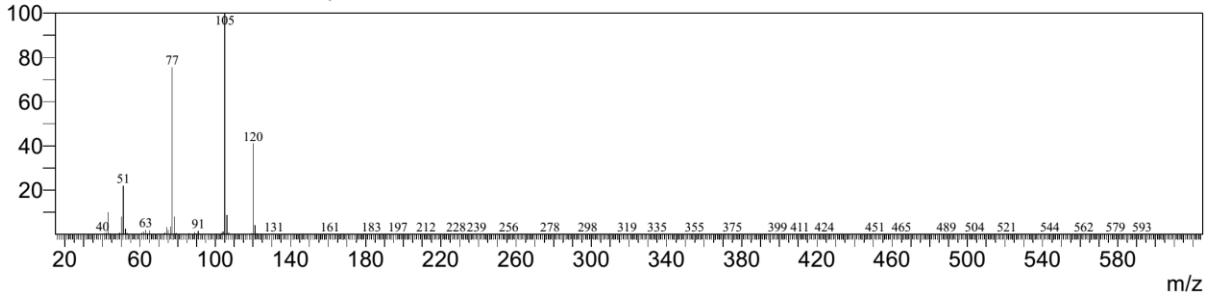


Figure S20 GC-MS analysis for the transfer hydrogenation of acetophenone by catalyst **Ru10** using 2-propanol

Transfer hydrogenation of acetophenone using glycerol as solvent

An oven-dried Schlenk tube equipped with a magnetic stirring bar was loaded with catalyst **Ru10** (0.25 mol%), KO^{t}Bu (10 mol%), and glycerol (3 mL). Next, add the acetophenone (1 mmol) to the reaction mixture. After that, the Schlenk tube was placed in a preheated oil bath (100 °C) with stirring. At the end of the reaction catalytic solution was analyzed by NMR.

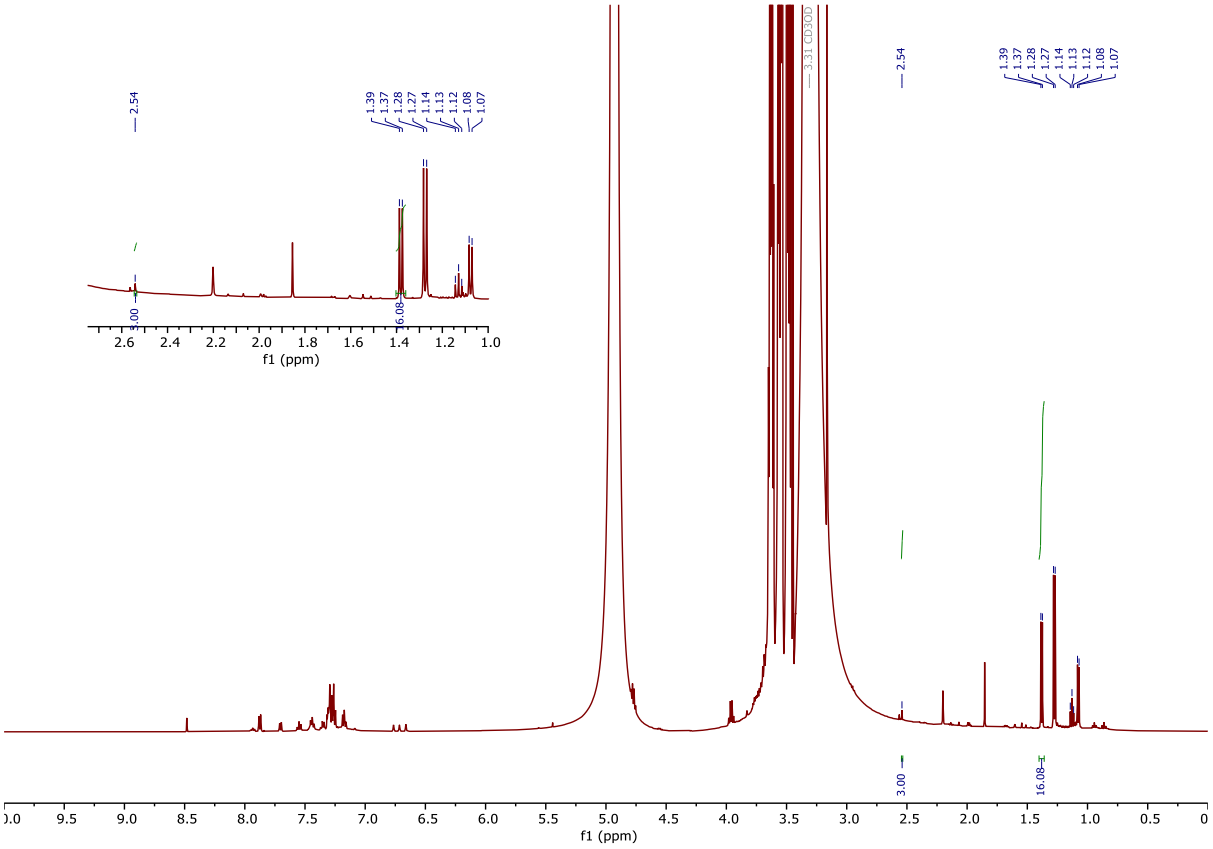


Figure S21 NMR analysis for the transfer hydrogenation of acetophenone by catalyst **Ru10** using glycerol