Electronic Supplementary Information (ESI) for

Catalytic transformation of bio-derived furans to valuable ketoacids and diketones by water-soluble ruthenium catalysts

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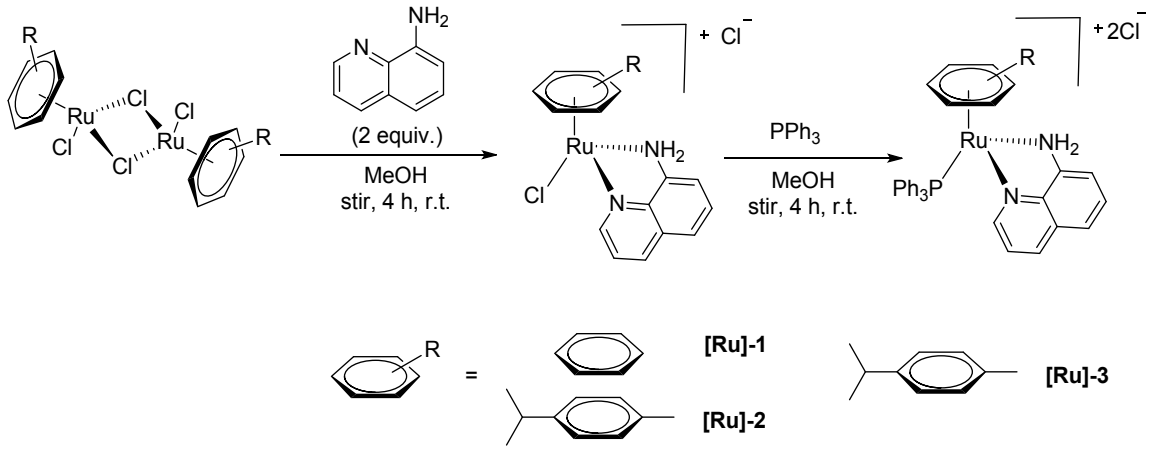
Schematic presentation for the synthesis of arene-ruthenium(II) complexes



Single-crystal X-ray diffraction studies

Single crystal X-ray structural studies of **[Ru]-1** and **[Ru]-2** were executed on a CCD Agilent Technologies (Oxford Diffraction) SUPER NOVA diffractometer. Using graphite-monochromated Mo Kα radiation ($\lambda\alpha$ = 0.71073 Å) based diffraction, data were collected at 150(2) K by the standard 'phi-omega' scan techniques, then scaled and reduced using CrysAlisPro RED software. The extracted data were evaluated using the CrysAlisPro CCD software. The structures were solved by direct methods using SHELXS-97, and refined by full matrix least-squares with SHELXL-97, refining on *F2*.[1] The positions of all the atoms were determined by direct methods. All non-hydrogen atoms were refined anisotropically. The remaining hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally 1.2*Ueq* of their parent atoms. Crystal structures were drawn with the help of ORTEP-3 (Fig. 1). The crystal and refinement data are summarized in Table S1. Bond lengths and bond angles are summarized in Table S1 and S2 (†ESI). The CCDC numbers 1401711 and 1402536 contain the supplementary crystallographic data for **[Ru]-1** and **[Ru]-2** respectively.

References

(1) G. M. Sheldrick, *Acta Crystallogr. Sect. A,* 2008, **64**, 112-122 (Program for Crystal Structure Solution and Refinement, University of Goettingen, Göttingen, Germany, **1997**).

Table S1 Single crystal X-ray refinement data for complexes **[Ru]-1** and **[Ru]-2**

	[Ru]-1	**[Ru]-2**
Empirical formula	$C_{15}H_{14}ClN_2Ru$	$C_{19}H_{22}Cl_2N_2Ru$
Formula weight (g mol^{-1})	358	450.36
Temperature (K)	150(2)	150(2)
Wavelength (Å)	1.5418	1.5418
Crystal system	Triclinic	Monoclinic
Space group	*P* -1	*P* 21/c
Crystal size (mm)	0.33 x 0.26 x 0.21	0.33 x 0.26 x 0.21
a (Å)	7.6680(5)	17.0720(2)
b (Å)	8.3022(6)	12.30860(10)
c (Å)	13.5405(6)	9.10130(10)
α (º)	83.606(5)	90
β (º)	81.922(5)	100.9000(10)
γ (º)	70.403(6)	90
V (Å^3)	802.11(9)	1877.97(3)
Z	2	4
ρ_{calcd} (g cm^{-3})	1.76	1.593
μ (mm^{-1})	11.044	9.382
F(000)	424	912
θ range, (º)	3.30 to 72.68	4.46 to 71.35
Index ranges	-9<=h<=6;	-19<=h<=20;

	-9<=k<=10;	-14<=k<=13;
	-16<=l<=16	-11<=l<=9
Completeness to θ_{max}	94.6%	98.4 %
No. of data collected/unique data	4800 / 3022 [*R*(int) =	11844 / 3586 [R(int) =
	0.0300]	0.0199]
Absorption correction	Semi-empirical from	Semi-empirical from
	equivalents	equivalents
No. of parameters/restraints	3022 / 0 / 208	0.2433 and 0.1478
Refinement method	full-matrix least-squares	full-matrix least-squares
	on F^2	on F^2
Goodness of fit on F^2	1.093	1.057
R1 [$I > 2\sigma(I)$]	R1 = 0.0489	0.0267
wR2 [$I > 2\sigma(I)$]	0.1363	0.0705
R indices (all data)	R1 = 0.0493, wR2 =	R1 = 0.0271, wR2 =
	0.1368	0.0709
Largest diff peak and hole, e Å^{-3}	2.989 and -4.032	0.628 and -0.723

Table S2 Selected bond lengths (Å) for complex **[Ru]-1** and **[Ru]-2**

[Ru]-1		**[Ru]-2**	
Ru(1)-N(1)	2.097(4)	Ru(1)-N(1)	2.0940(18)
Ru(1)-N(2)	2.126(4)	Ru(1)-N(2)	2.1336(18)
Ru(1)-C(12)	2.164(5)	Ru(1)-C(15)	2.164(2)
Ru(1)-C(14)	2.175(5)	Ru(1)-C(13)	2.167(2)
Ru(1)-C(11)	2.184(5)	Ru(1)-C(16)	2.189(2)
Ru(1)-C(10)	2.186(5)	Ru(1)-C(12)	2.193(2)
Ru(1)-C(13)	2.195(5)	Ru(1)-C(14)	2.198(2)
Ru(1)-C(15)	2.201(5)	Ru(1)-C(11)	2.223(2)
N(2)-H(2A)	2.4085(11)	Ru(1)-Cl(1)	2.3984(6)
N(2)-H(2B)	1.322(7)	N(1)-C(1)	1.325(3)
C(1)-C(2)	1.376(6)	N(1)-C(9)	1.375(3)
C(2)-C(3)	1.443(6)	N(2)-C(8)	1.452(3)
C(3)-C(4)	0.9200	N(2)-H(1N)	0.91(4)
C(4)-C(5)	0.9200	N(2)-H(2N)	0.93(4)
C(4)-C(9)	1.415(7)	C(1)-C(2)	1.408(3)
C(5)-C(6)	1.358(8)	C(2)-C(3)	1.359(4)
C(6)-C(7)	1.404(8)	C(3)-C(4)	1.412(4)
C(7)-C(8)	1.417(8)	C(4)-C(9)	1.411(3)
C(8)-C(9)	1.418(7)	C(4)-C(5)	1.414(4)
C(10)-C(11)	1.374(9)	C(5)-C(6)	1.362(5)

C(10)-C(15)	1.399(8)	C(6)-C(7)	1.412(4)
C(11)-C(12)	1.374(7)	C(7)-C(8)	1.360(3)
C(12)-C(13)	1.411(7)	C(8)-C(9)	1.404(3)
C(13)-C(14)	1.393(9)	C(10)-C(11)	1.498(4)
C(14)-C(15)	1.406(9)	C(11)-C(16)	1.408(4)
	1.409(8)	C(11)-C(12)	1.419(4)
	1.407(8)	C(12)-C(13)	1.405(4)
	1.415(8)	C(13)-C(14)	1.426(4)
	1.403(8)	C(14)-C(15)	1.402(4)
		C(14)-C(17)	1.512(3)
		C(15)-C(16)	1.421(3)
		C(17)-C(19)	1.509(5)
		C(17)-C(18)	1.511(4)

Table S3 Selected bond angles (°) for complex **[Ru]-1** and **[Ru]-2**

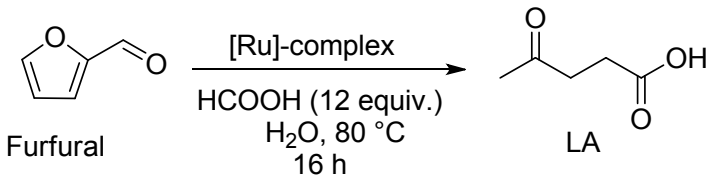
[Ru]-1		**[Ru]-2**	
N(1)-Ru(1)-N(2)	78.66(16)	N(1)-Ru(1)-N(2)	78.71(7)
N(1)-Ru(1)-C(12)	132.07(18)	N(1)-Ru(1)-C(15)	146.96(8)
N(2)-Ru(1)-C(12)	90.49(18)	N(2)-Ru(1)-C(15)	91.87(8)
N(1)-Ru(1)-C(14)	93.31(18)	N(1)-Ru(1)-C(13)	131.34(9)
N(2)-Ru(1)-C(14)	142.72(19)	N(2)-Ru(1)-C(13)	148.45(9)
C(12)-Ru(1)-C(14)	68.0(2)	C(15)-Ru(1)-C(13)	67.69(9)
N(1)-Ru(1)-C(11)	169.56(19)	N(1)-Ru(1)-C(16)	111.66(8)
N(2)-Ru(1)-C(11)	101.73(19)	N(2)-Ru(1)-C(16)	98.99(9)
C(12)-Ru(1)-C(11)	37.8(2)	C(15)-Ru(1)-C(16)	38.09(9)
C(14)-Ru(1)-C(11)	80.0(2)	C(13)-Ru(1)-C(16)	79.91(9)
N(1)-Ru(1)-C(10)	146.3(2)	N(1)-Ru(1)-C(12)	101.29(8)
N(2)-Ru(1)-C(10)	133.4(2)	N(2)-Ru(1)-C(12)	165.47(9)
C(12)-Ru(1)-C(10)	67.6(2)	C(15)-Ru(1)-C(12)	80.23(9)
C(14)-Ru(1)-C(10)	67.3(2)	C(13)-Ru(1)-C(12)	37.58(10)
C(11)-Ru(1)-C(10)	37.2(2)	C(16)-Ru(1)-C(12)	67.31(9)
N(1)-Ru(1)-C(13)	101.89(18)	N(1)-Ru(1)-C(14)	169.35(8)
N(2)-Ru(1)-C(13)	107.85(19)	N(2)-Ru(1)-C(14)	111.92(8)
C(12)-Ru(1)-C(13)	37.6(2)	C(15)-Ru(1)-C(14)	37.49(9)
C(14)-Ru(1)-C(13)	37.8(2)	C(13)-Ru(1)-C(14)	38.12(9)
C(11)-Ru(1)-C(13)	67.9(2)	C(16)-Ru(1)-C(14)	68.36(9)
C(10)-Ru(1)-C(13)	79.9(2)	C(12)-Ru(1)-C(14)	68.61(9)

N(1)-Ru(1)-C(15)	111.7(2)	N(1)-Ru(1)-C(11)	92.81(8)
N(2)-Ru(1)-C(15)	169.24(19)	N(2)-Ru(1)-C(11)	128.11(9)
C(12)-Ru(1)-C(15)	80.3(2)	C(15)-Ru(1)-C(11)	68.15(9)
C(14)-Ru(1)-C(15)	37.4(2)	C(13)-Ru(1)-C(11)	67.82(9)
C(11)-Ru(1)-C(15)	67.6(2)	C(16)-Ru(1)-C(11)	37.23(9)
C(10)-Ru(1)-C(15)	37.4(2)	C(12)-Ru(1)-C(11)	37.49(9)
C(13)-Ru(1)-C(15)	67.9(2)	C(14)-Ru(1)-C(11)	81.13(9)
N(1)-Ru(1)-Cl(1)	84.43(11)	N(1)-Ru(1)-Cl(1)	85.66(5)
N(2)-Ru(1)-Cl(1)	84.98(12)	N(2)-Ru(1)-Cl(1)	84.18(6)
C(12)-Ru(1)-Cl(1)	141.50(15)	C(15)-Ru(1)-Cl(1)	125.21(7)
C(14)-Ru(1)-Cl(1)	130.87(15)	C(13)-Ru(1)-Cl(1)	88.49(7)
C(11)-Ru(1)-Cl(1)	106.01(16)	C(16)-Ru(1)-Cl(1)	162.68(7)
C(10)-Ru(1)-Cl(1)	88.22(14)	C(12)-Ru(1)-Cl(1)	110.35(7)
C(13)-Ru(1)-Cl(1)	166.50(15)	C(14)-Ru(1)-Cl(1)	94.59(7)
C(15)-Ru(1)-Cl(1)	98.73(15)	C(11)-Ru(1)-Cl(1)	146.78(7)
C(1)-N(1)-C(9)	118.2(4)	C(1)-N(1)-C(9)	117.90(19)
C(1)-N(1)-Ru(1)	126.4(3)	C(1)-N(1)-Ru(1)	126.28(16)
C(9)-N(1)-Ru(1)	115.2(3)	C(9)-N(1)-Ru(1)	115.76(14)
C(8)-N(2)-Ru(1)	112.2(3)	C(8)-N(2)-Ru(1)	111.72(13)
C(8)-N(2)-H(2A)	109.2	C(8)-N(2)-H(1N)	111(2)
Ru(1)-N(2)-H(2A)	109.2	Ru(1)-N(2)-H(1N)	109(2)
C(8)-N(2)-H(2B)	109.2	C(8)-N(2)-H(2N)	102(2)
Ru(1)-N(2)-H(2B)	109.2	Ru(1)-N(2)-H(2N)	112(2)

H(2A)-N(2)-H(2B)	107.9	H(1N)-N(2)-H(2N)	111(3)
N(1)-C(1)-C(2)	122.4(5)	N(1)-C(1)-C(2)	122.9(2)
C(3)-C(2)-C(1)	120.1(5)	C(3)-C(2)-C(1)	119.6(2)
C(2)-C(3)-C(4)	119.4(5)	C(2)-C(3)-C(4)	119.6(2)
C(3)-C(4)-C(5)	124.3(5)	C(9)-C(4)-C(3)	117.4(2)
C(3)-C(4)-C(9)	117.7(5)	C(9)-C(4)-C(5)	118.4(2)
C(5)-C(4)-C(9)	118.0(5)	C(3)-C(4)-C(5)	124.2(2)
C(6)-C(5)-C(4)	120.5(5)	C(6)-C(5)-C(4)	119.8(2)
C(5)-C(6)-C(7)	121.0(5)	C(5)-C(6)-C(7)	121.4(3)
C(8)-C(7)-C(6)	120.3(5)	C(8)-C(7)-C(6)	119.7(3)
C(7)-C(8)-C(9)	119.8(5)	C(7)-C(8)-C(9)	120.1(2)
C(7)-C(8)-N(2)	124.2(5)	C(7)-C(8)-N(2)	123.4(2)
C(9)-C(8)-N(2)	116.1(4)	C(9)-C(8)-N(2)	116.54(19)
N(1)-C(9)-C(8)	117.3(4)	N(1)-C(9)-C(8)	117.07(19)
N(1)-C(9)-C(4)	122.2(4)	N(1)-C(9)-C(4)	122.5(2)
C(8)-C(9)-C(4)	120.5(4)	C(8)-C(9)-C(4)	120.4(2)
C(11)-C(10)-C(15)	121.2(5)	C(16)-C(11)-C(12)	118.4(2)
C(11)-C(10)-Ru(1)	71.3(3)	C(16)-C(11)-C(10)	120.9(2)
C(15)-C(10)-Ru(1)	71.9(3)	C(12)-C(11)-C(10)	120.7(2)
C(10)-C(11)-C(12)	119.5(5)	C(16)-C(11)-Ru(1)	70.09(13)
C(10)-C(11)-Ru(1)	71.5(3)	C(12)-C(11)-Ru(1)	70.12(13)
C(12)-C(11)-Ru(1)	70.3(3)	C(10)-C(11)-Ru(1)	130.76(18)
C(13)-C(12)-C(11)	120.7(5)	C(13)-C(12)-C(11)	120.3(2)

C(13)-C(12)-Ru(1)	72.4(3)	C(13)-C(12)-Ru(1)	70.22(13)
C(11)-C(12)-Ru(1)	71.9(3)	C(11)-C(12)-Ru(1)	72.39(13)
C(12)-C(13)-C(14)	118.6(5)	C(12)-C(13)-C(14)	121.9(2)
C(12)-C(13)-Ru(1)	70.0(3)	C(12)-C(13)-Ru(1)	72.19(13)
C(14)-C(13)-Ru(1)	70.4(3)	C(14)-C(13)-Ru(1)	72.09(13)
C(15)-C(14)-C(13)	121.2(5)	C(15)-C(14)-C(13)	117.1(2)
C(15)-C(14)-Ru(1)	72.3(3)	C(15)-C(14)-C(17)	123.8(2)
C(13)-C(14)-Ru(1)	71.9(3)	C(13)-C(14)-C(17)	119.1(2)
C(14)-C(15)-C(10)	118.8(5)	C(15)-C(14)-Ru(1)	69.97(13)
C(14)-C(15)-Ru(1)	70.3(3)	C(13)-C(14)-Ru(1)	69.79(13)
C(10)-C(15)-Ru(1)	70.7(3)	C(17)-C(14)-Ru(1)	129.82(17)
		C(14)-C(15)-C(16)	121.6(2)
		C(14)-C(15)-Ru(1)	72.54(13)
		C(16)-C(15)-Ru(1)	71.90(13)
		C(11)-C(16)-C(15)	120.7(2)
		C(11)-C(16)-Ru(1)	72.68(14)
		C(15)-C(16)-Ru(1)	70.01(13)
		C(19)-C(17)-C(18)	111.6(3)
		C(19)-C(17)-C(14)	114.1(3)
		C(18)-C(17)-C(14)	109.2(2)

Table S4 Catalytic transformation of furfural to LA in aqueous medium with different arene-ruthenium(II) complexes based catalysts. Reaction Conditions: furfural (1.0 mmol), catalyst (1 mol%), formic acid (12 equiv.) and water (10 mL), *T* = 80 °C.



Entry	Catalyst	Conv./Sel.
1.	[Ru]-2	>99/>99
2.	[Ru]-3	17.6/>99
3.	[Ru]-4	27/>99
4.	[Ru]-5	50/>99

Table S5 Influence of additives on the catalytic transformation of furfural to LA in the presence of **[Ru]-2**. Reaction Conditions: furfural (1.0 mmol), **[Ru]-2** (1 mol%), and water (10 mL).

Entry	Additive	*T* (°C) / *t* (h)	Conv. (%)
1	formic acid[a]	100/7	>99
2	formic acid[a]	80/16	>99
3	formic acid[a]	60/16	23
4	H_2 gas[b]	80/16	n.r.
5	acetic acid[a]	80/16	~2
6	propionic acid[a]	80/16	n.r.
7	*iso*-butyric acid[a]	80/16	n.r.

[a]12 equivalents. [b]from balloon.

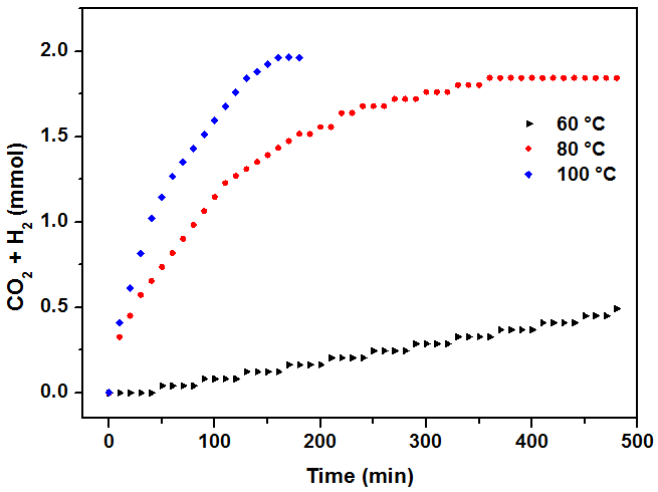


Figure S1 Influenece of temperature on the decomposition of formic acid (1 mmol) to CO_2 and H_2 with **[Ru]-2** catalyst (0.01 mmol).

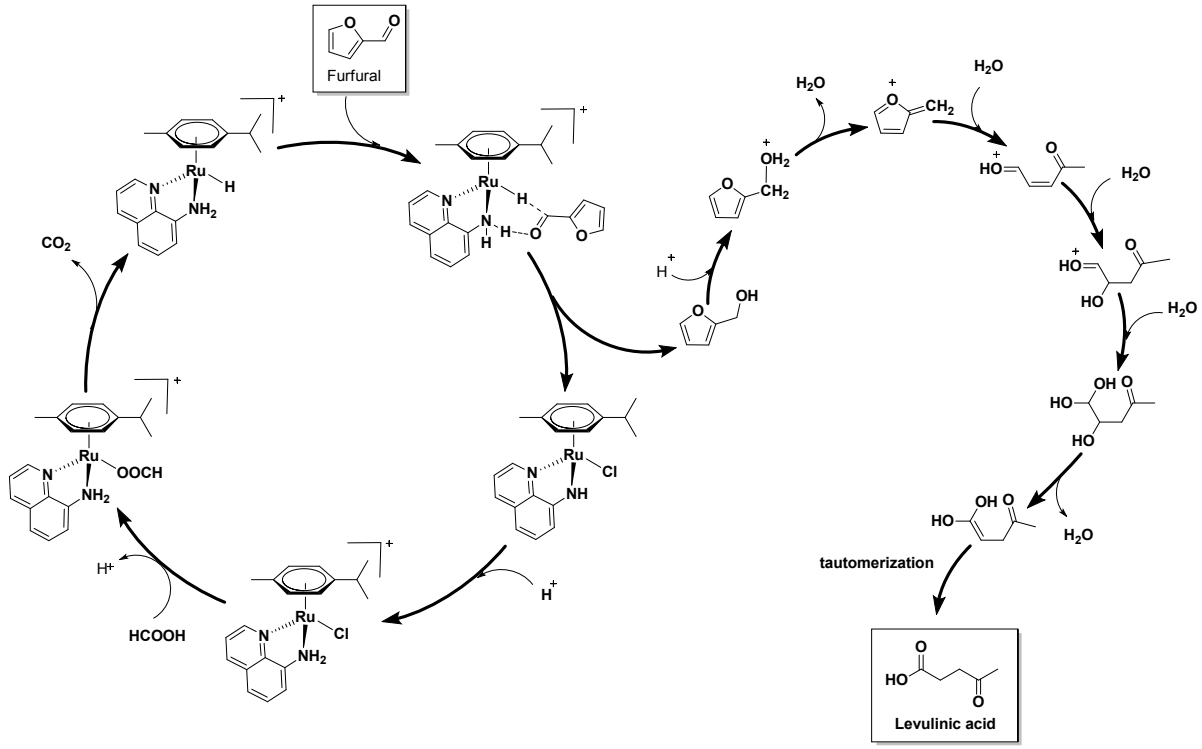


Figure S2 Possible reaction mechanism for the transformation of furfural to LA.

The thermal stability studies were performed in NMR tubes by dissolving ca. 4 mg of each catalyst in 0.5 mL of D_2O and heating the solution at 80 or 100 °C. The decomposition of the catalyst was monitored by ^1H NMR spectra taken at certain intervals of time (0, 24, 48 and 72 h).

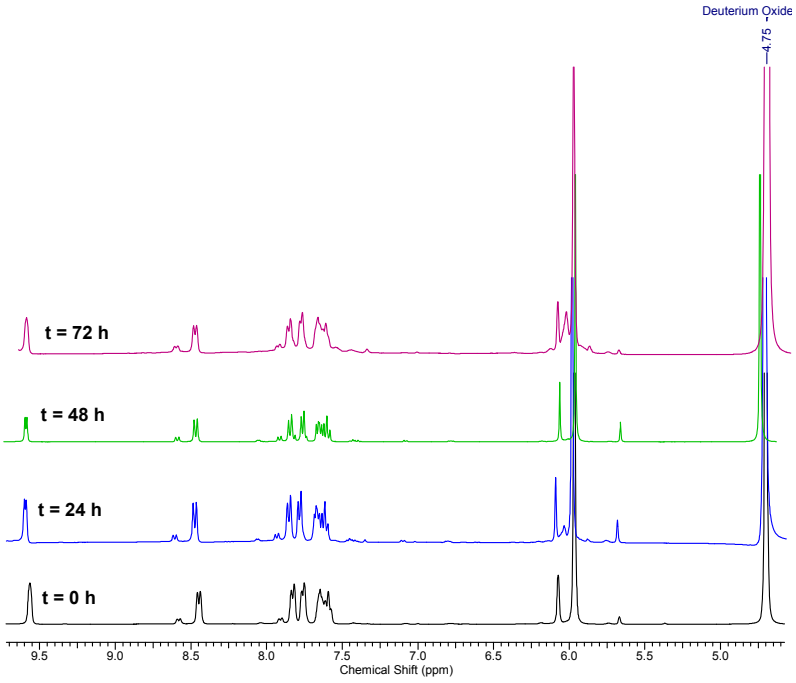


Figure S3 ^1H NMR spectra for the thermal stability of **[Ru]-1** catalyst at 80 °C in D_2O.

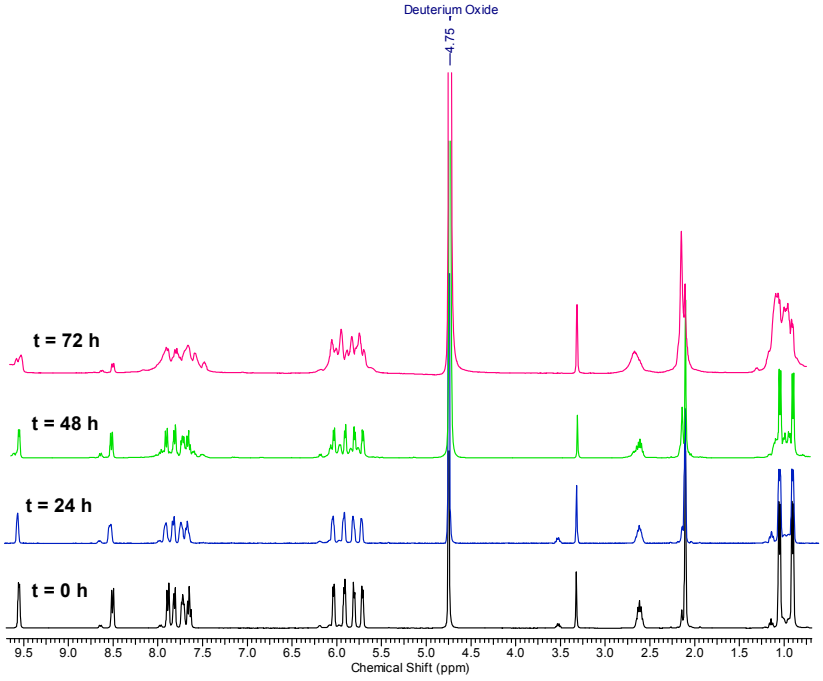


Figure S4 ^1H NMR spectra for the thermal stability of **[Ru]-2** catalyst at 80 °C in D_2O.

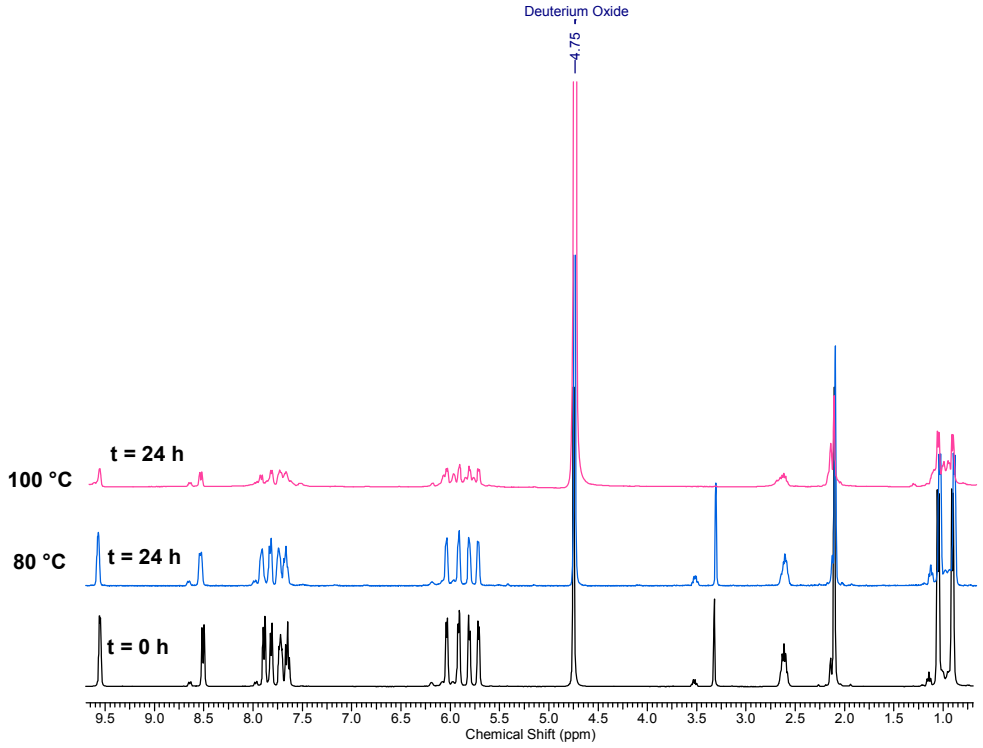


Figure S5 ^{1}H NMR spectra for the thermal stability of **[Ru]-2** catalyst at 80 °C and 100 °C in D_2O.

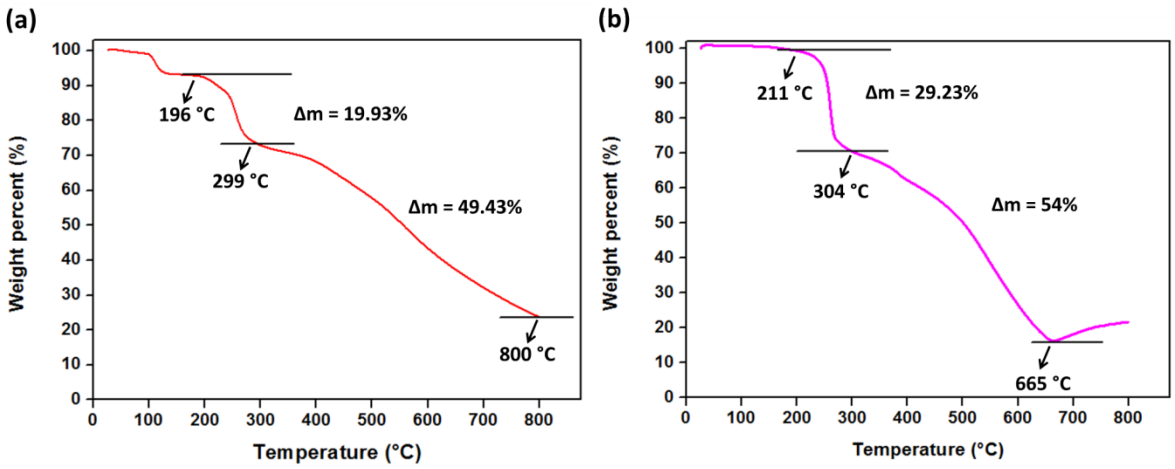


Figure S6 Thermal gravimetric analysis (TGA) graph of a) **[Ru]-1** and b) **[Ru]-2**.

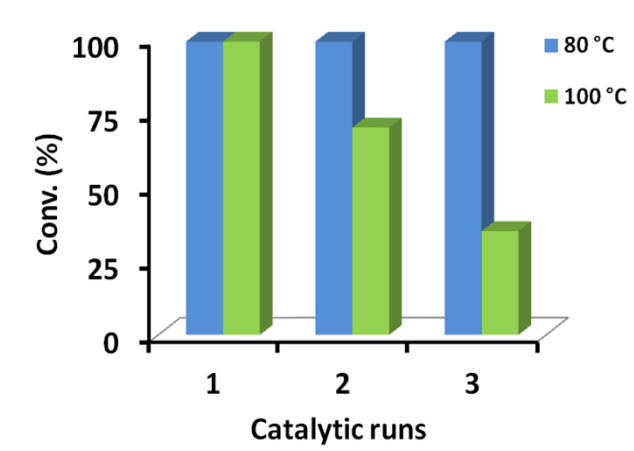
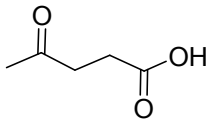
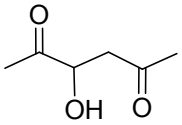


Figure S7 Stability of **[Ru]-2** catalyst towards recyclability for the catalytic transformation of furfural to LA at 80 and 100 °C.

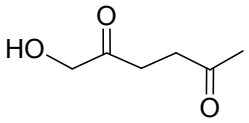
Spectral data of products obtained by catalytic transformation of bio-derived furans



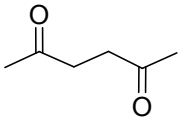
Levulinic acid (LA): ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.73 (t, 2H, J = 8 Hz), 2.59 (t, 2H, J = 8 Hz), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 206.65, 177.53, 37.69, 29.78, 27.64. HRMS (ESI) m/z: calculated 139.04 [$C_5H_8O_3 + Na^+$], found 139.036 [$C_5H_8O_3 + Na^+$].



3-Hydroxyhexane-2,5-dione (3-HHD): ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.33-4.30 (m, 1H), 3.75 (br, 1H) 2.95 (dd, 1H, J_1 = 16 Hz, J_2 = 4Hz), 2.82 (dd, 1H, J = 16 Hz, J_2 = 4Hz), 2.22 (s, 3H), 2.18 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 209.15, 207.09, 73.76, 46.11, 30.81, 25.38. HRMS (ESI) m/z: calculated 153.05 [$C_5H_{10}O_3 + Na^+$], found 153.05 [$C_5H_{10}O_3 + Na^+$].



1-Hydroxyhexane-2,5-dione (1-HHD): ^{1}H NMR (400MHz, $CDCl_3$): δ (ppm) = 4.31 (s, 2H), 2.82 (t, 2H, J = 8 Hz), 2.61 (t, 2H, J = 8 Hz), 2.17 (s, 3H).



Hexane-2,5-dione (HD): ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.69 (s, 4H), 2.18 (s, 6H).

NMR Spectra of arene-ruthenium(II) complexes

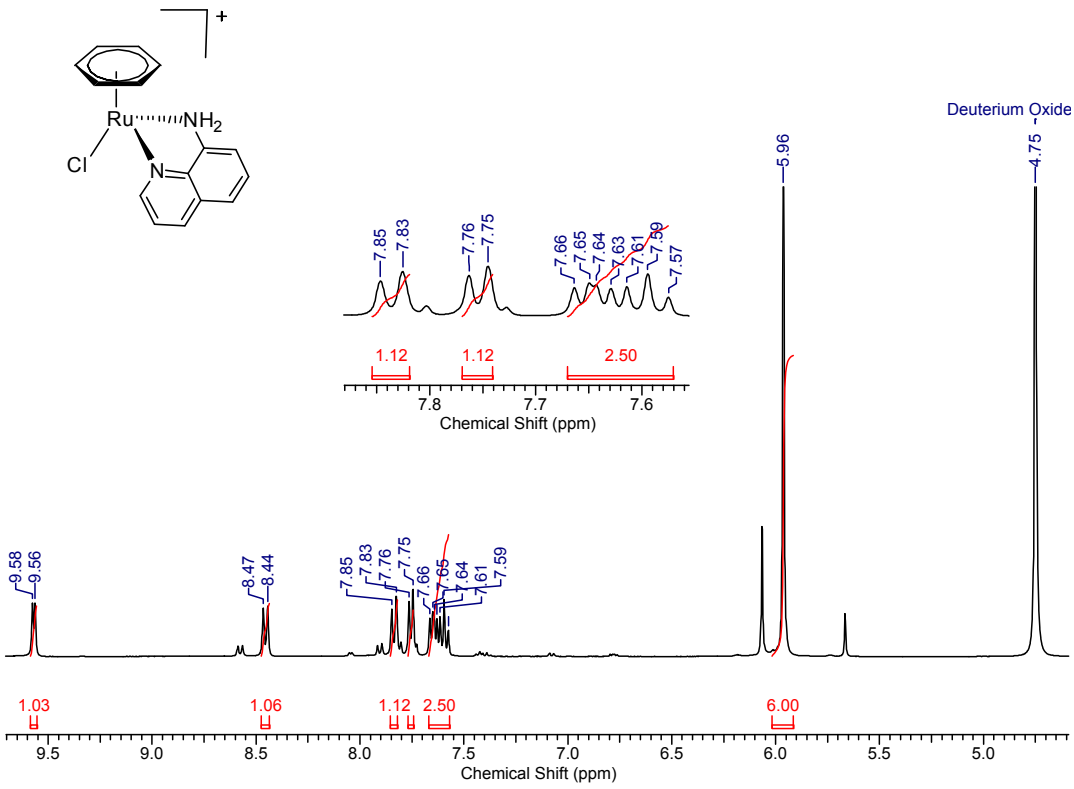


Figure S8 ^{1}H NMR spectrum of complex **[Ru]-1**.

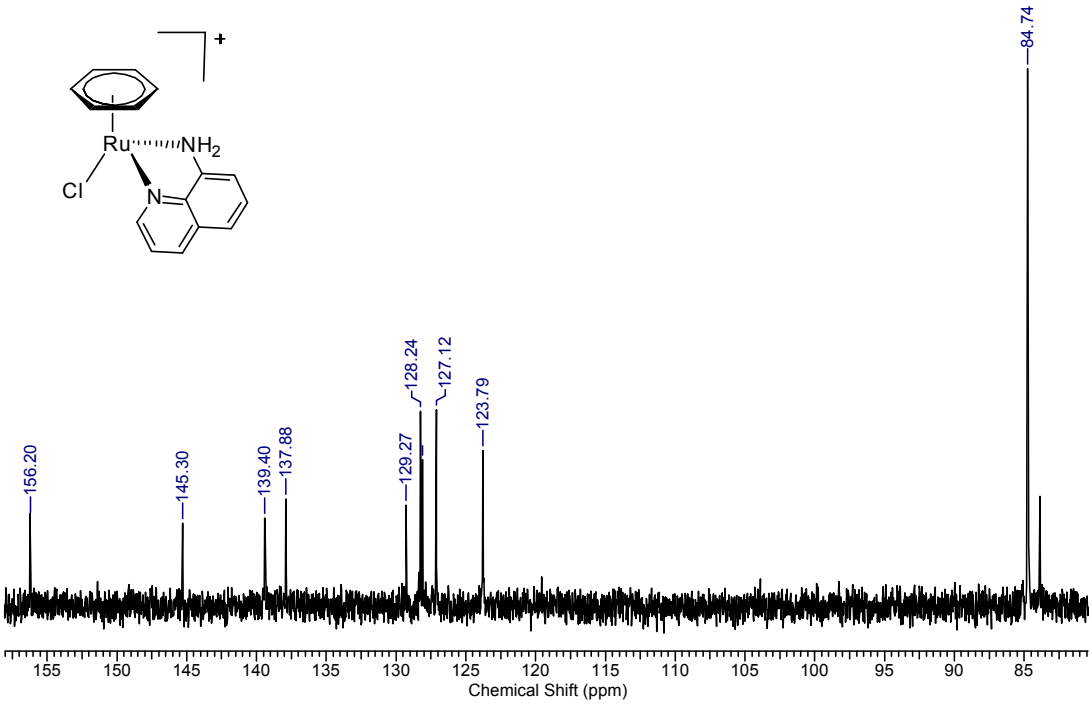


Figure S9 ^{13}C NMR spectrum of complex **[Ru]-1**.

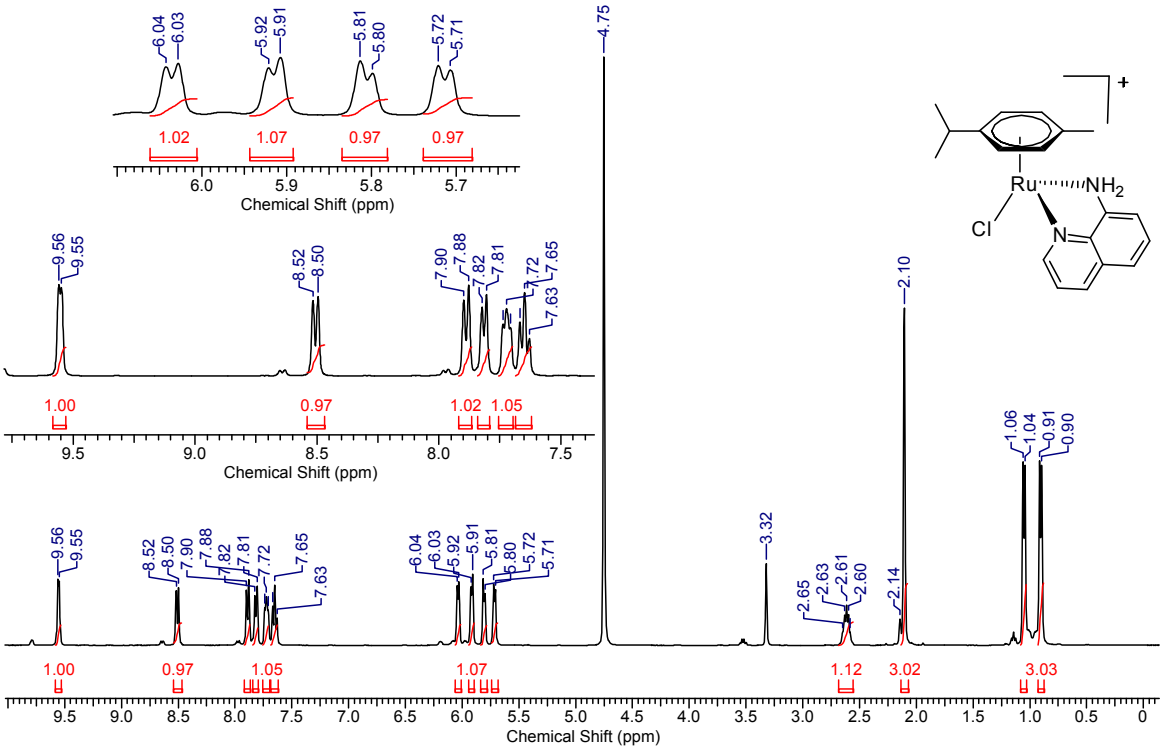


Figure S10 ^{1}H NMR spectrum of complex **[Ru]-2**.

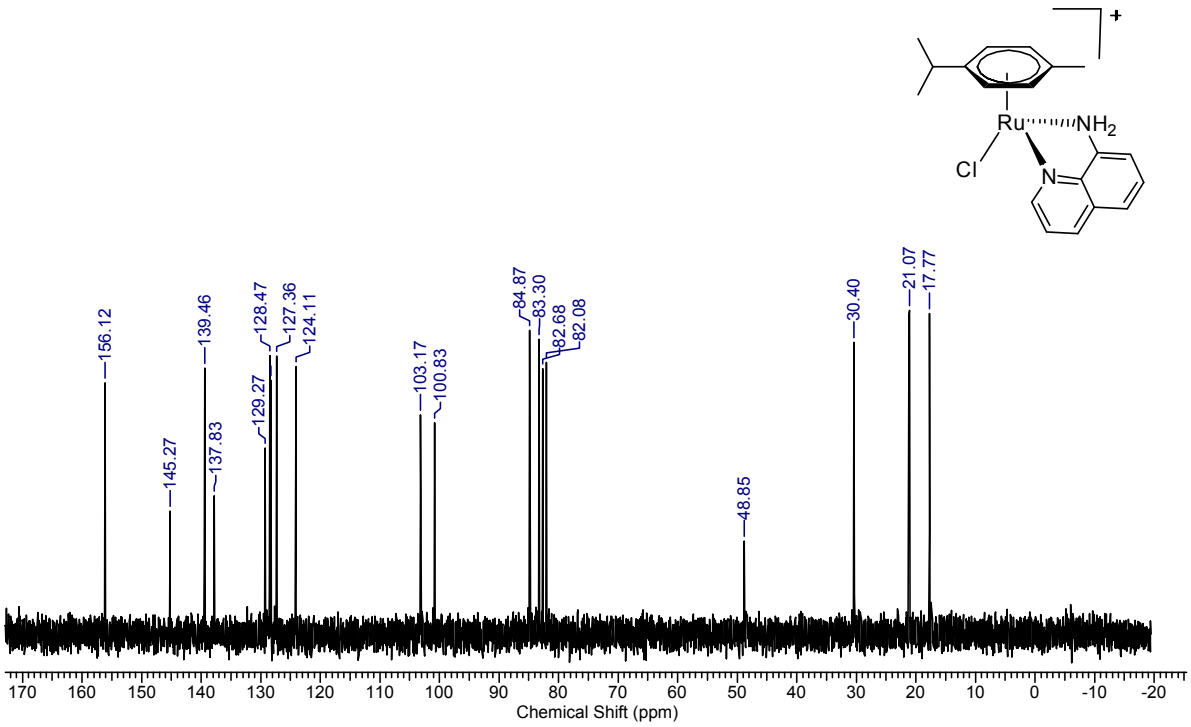


Figure S11 ^{13}C NMR spectrum of complex **[Ru]-2**.

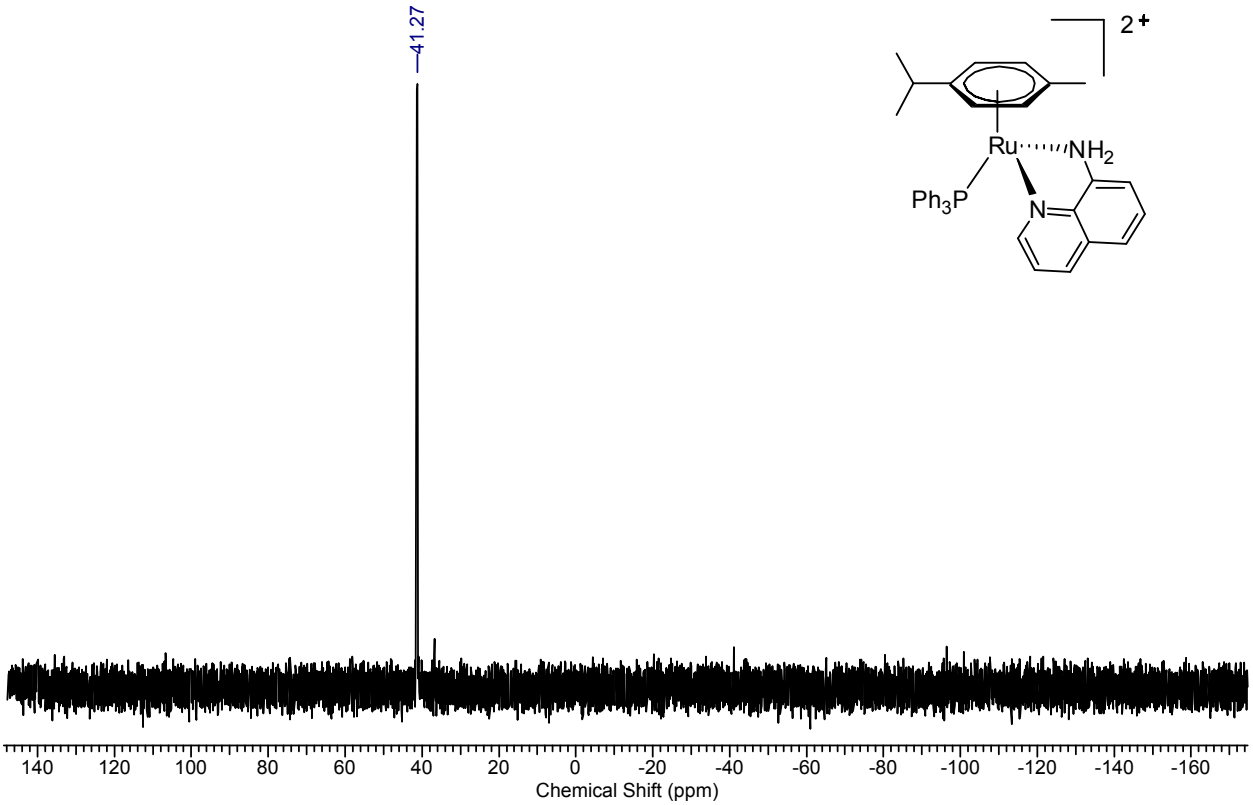


Figure S12 ^{31}P NMR spectrum of complex **[Ru]-3**.

Mass Spectra of arene ruthenium complexes

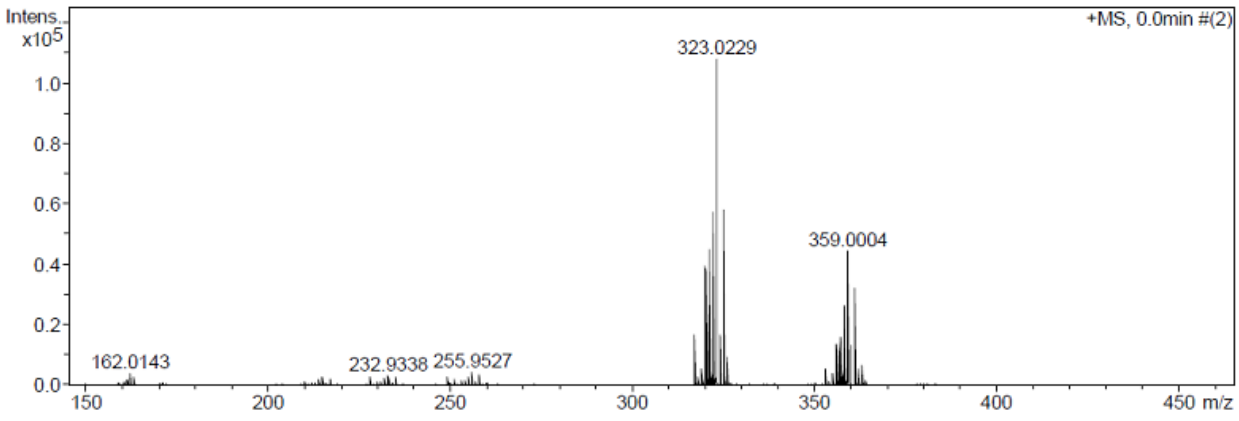


Figure S13 Mass spectrum of complex **[Ru]-1**

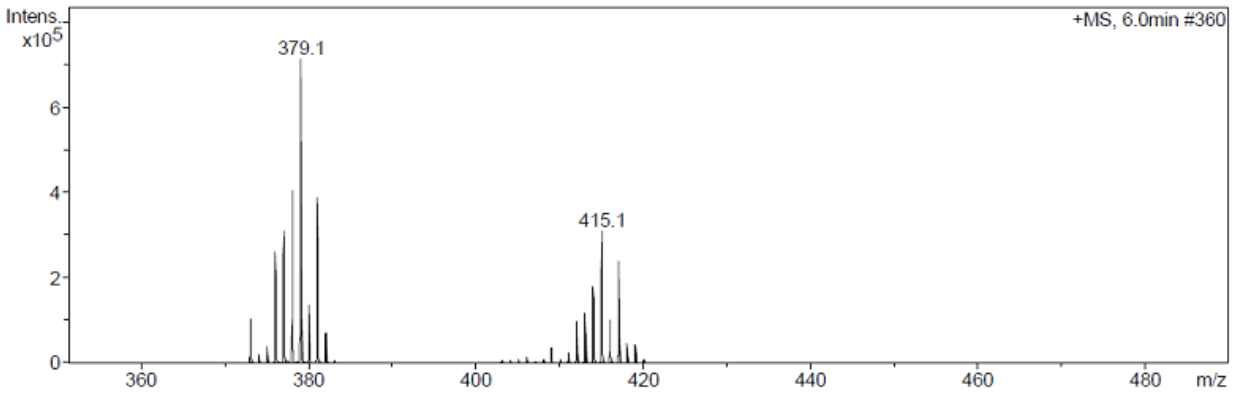


Figure S14 Mass spectrum of complex **[Ru]-2**

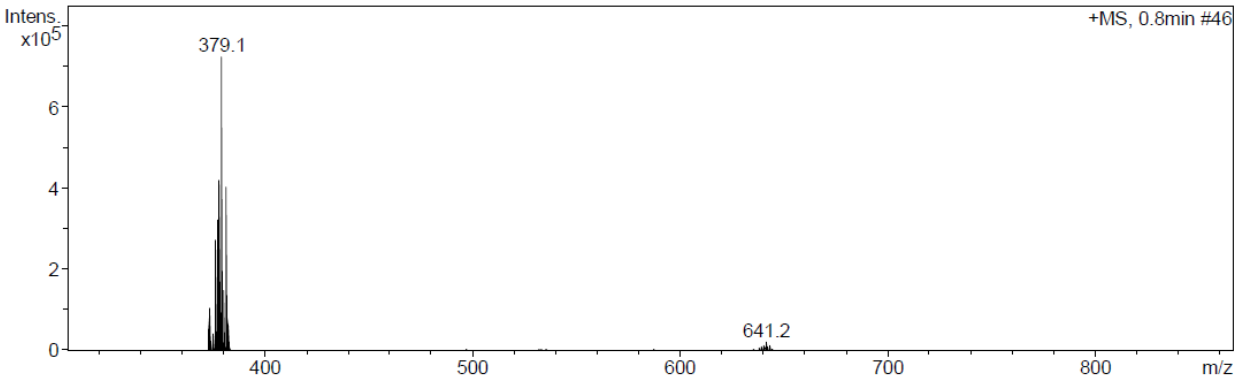
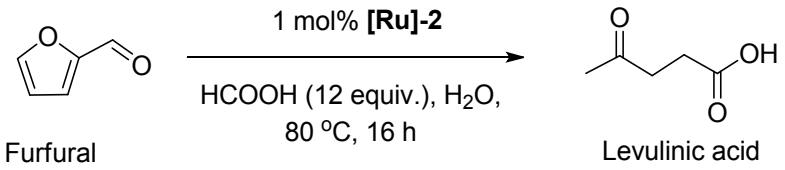


Figure S15 Mass spectrum of complex **[Ru]-3**

NMR Spectra of products obtained by catalytic transformation of bio-derived furans



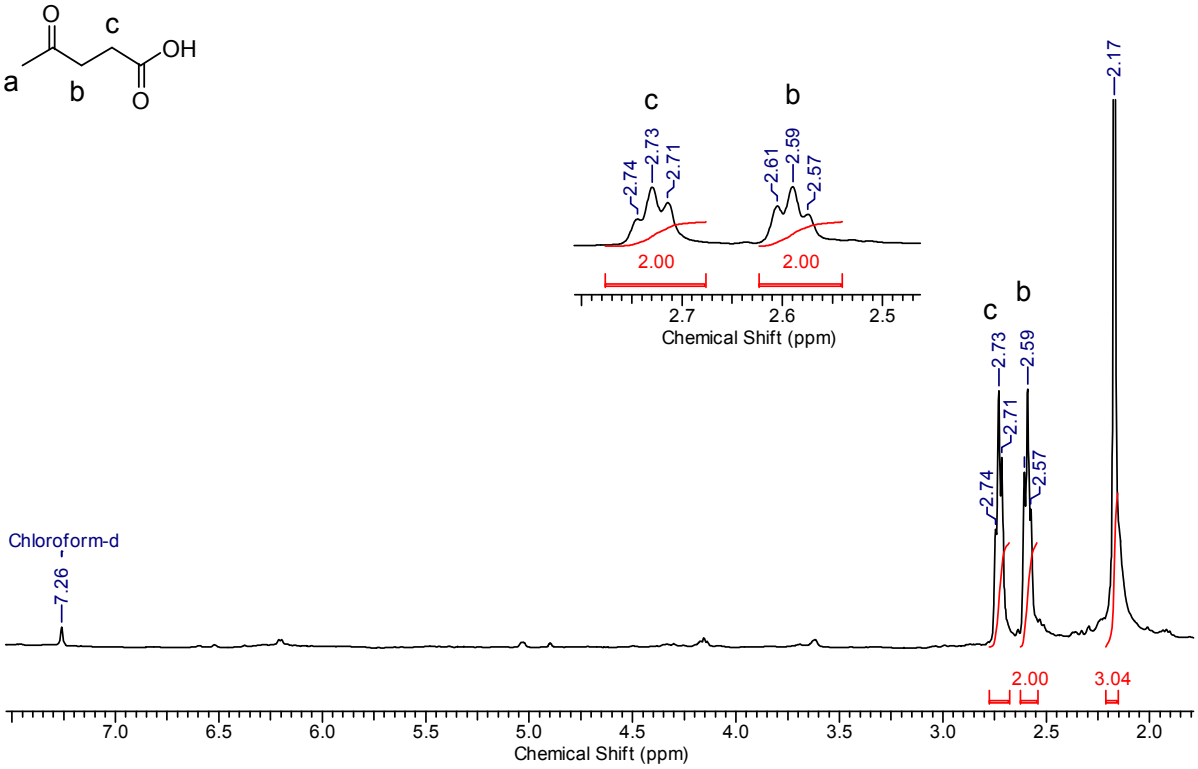


Figure S16 ^{1}H NMR spectrum of Levulinic acid.

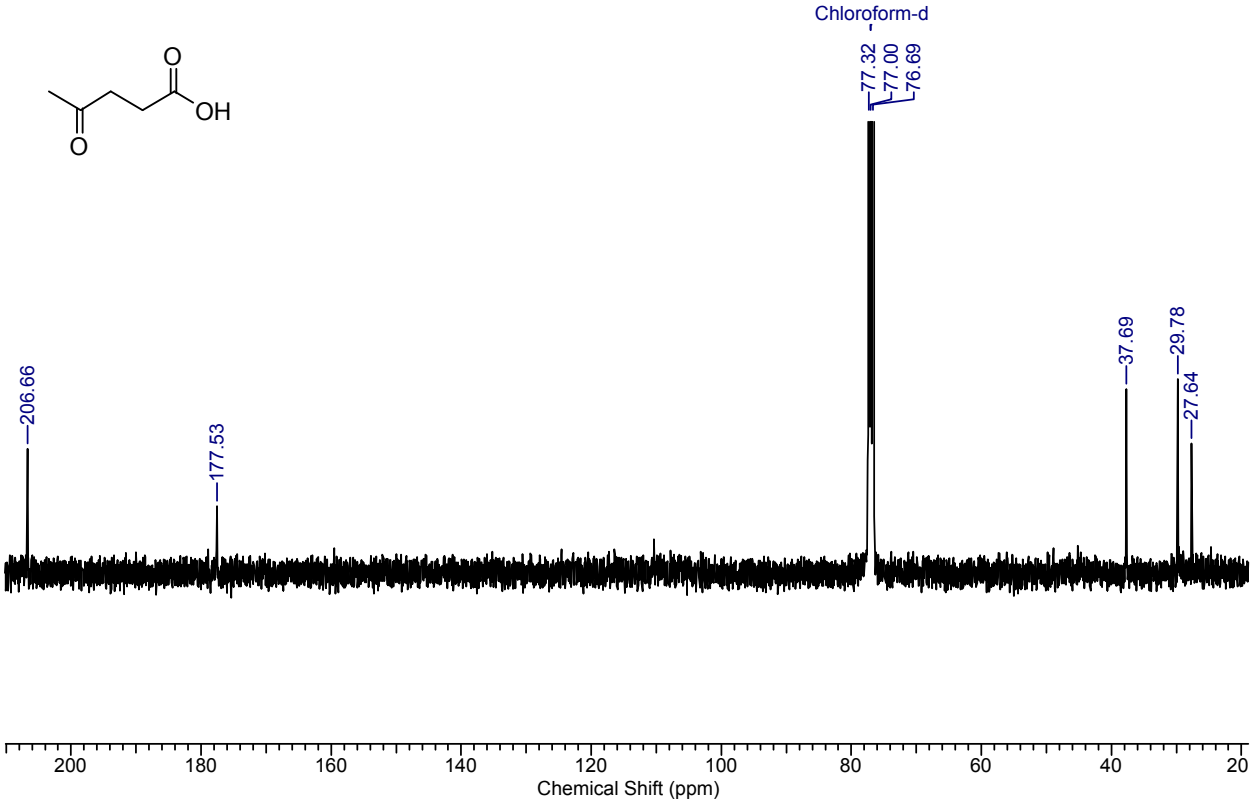


Figure S17 ^{13}C NMR spectrum of Levulinic acid.

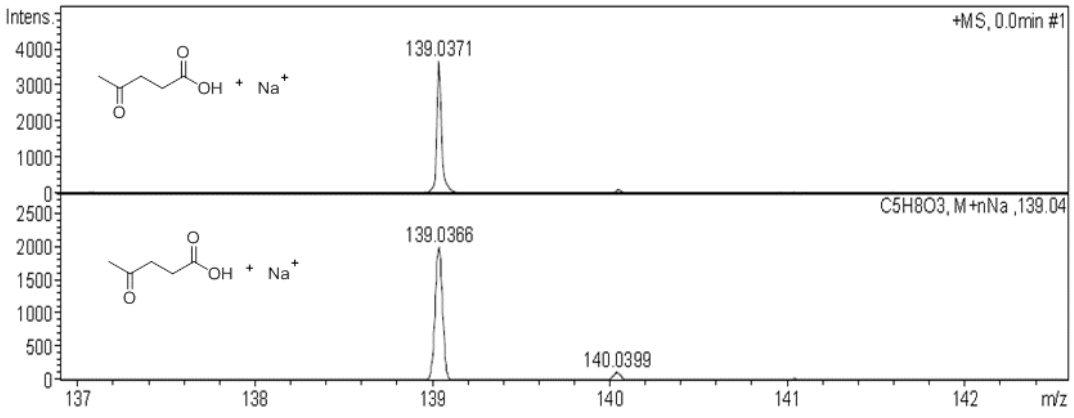


Figure S18 HRMS data of levulinic acid obtained from furfural.

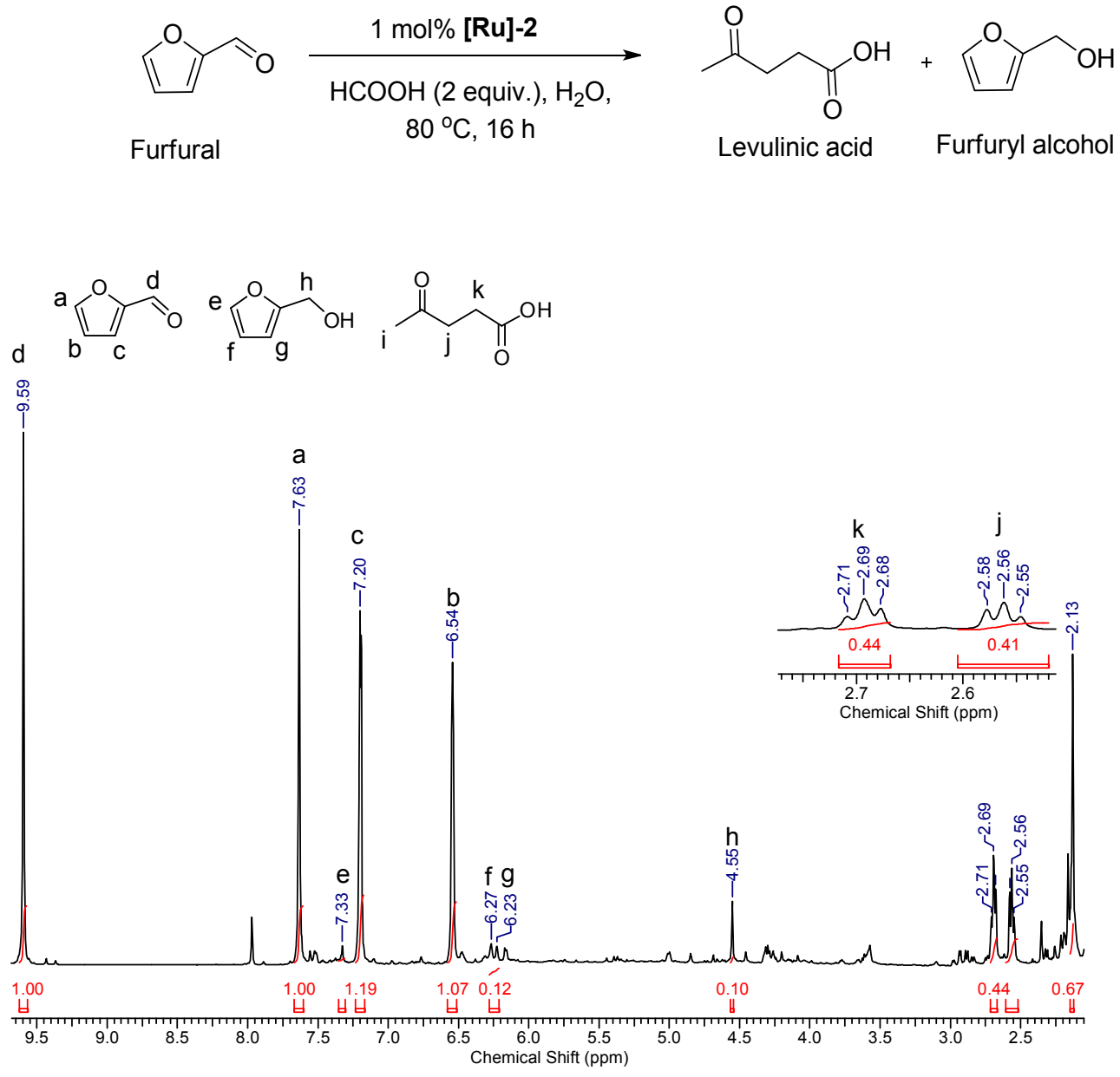


Figure S19 ^{1}H NMR spectrum of the products obtained from the catalytic transformation of furfural with 2 equivalents of formic acid.

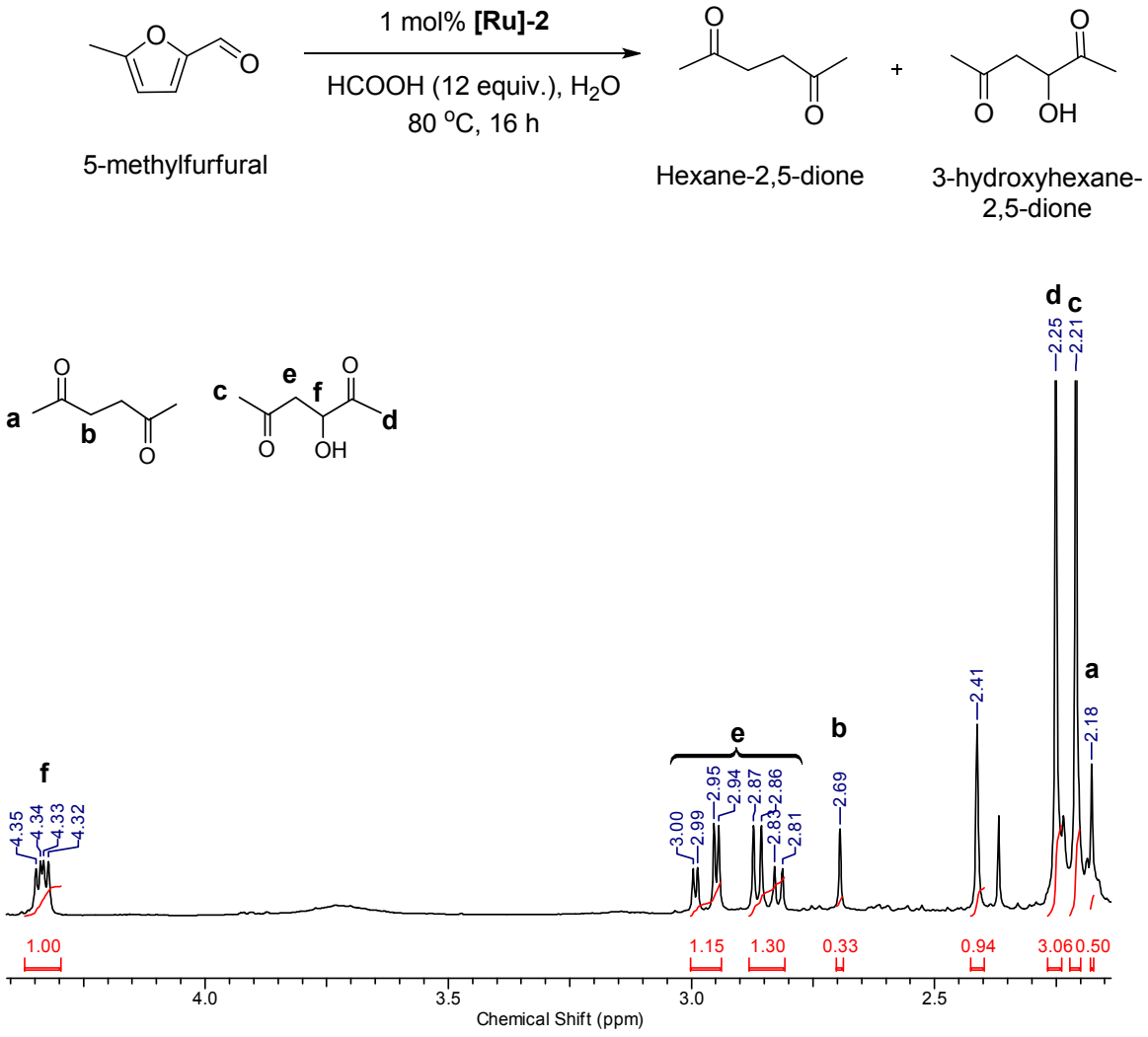


Figure S20 ^{1}H NMR spectrum of the products obtained from the catalytic transformation of 5-methylfurfuraldehyde.

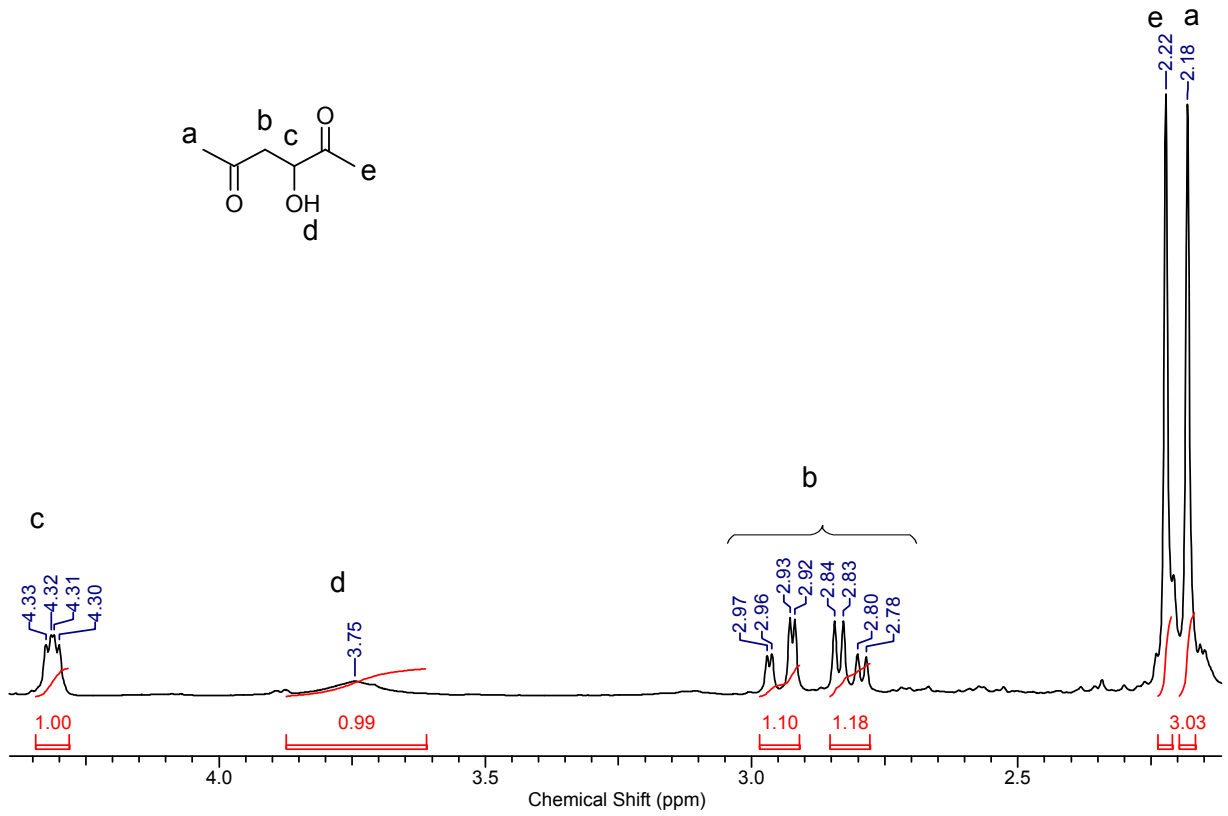


Figure S21 ^{1}H NMR spectrum of 3-hydroxyhexane-2,5-dione (after purification) obtained from 5-methyl furfural.

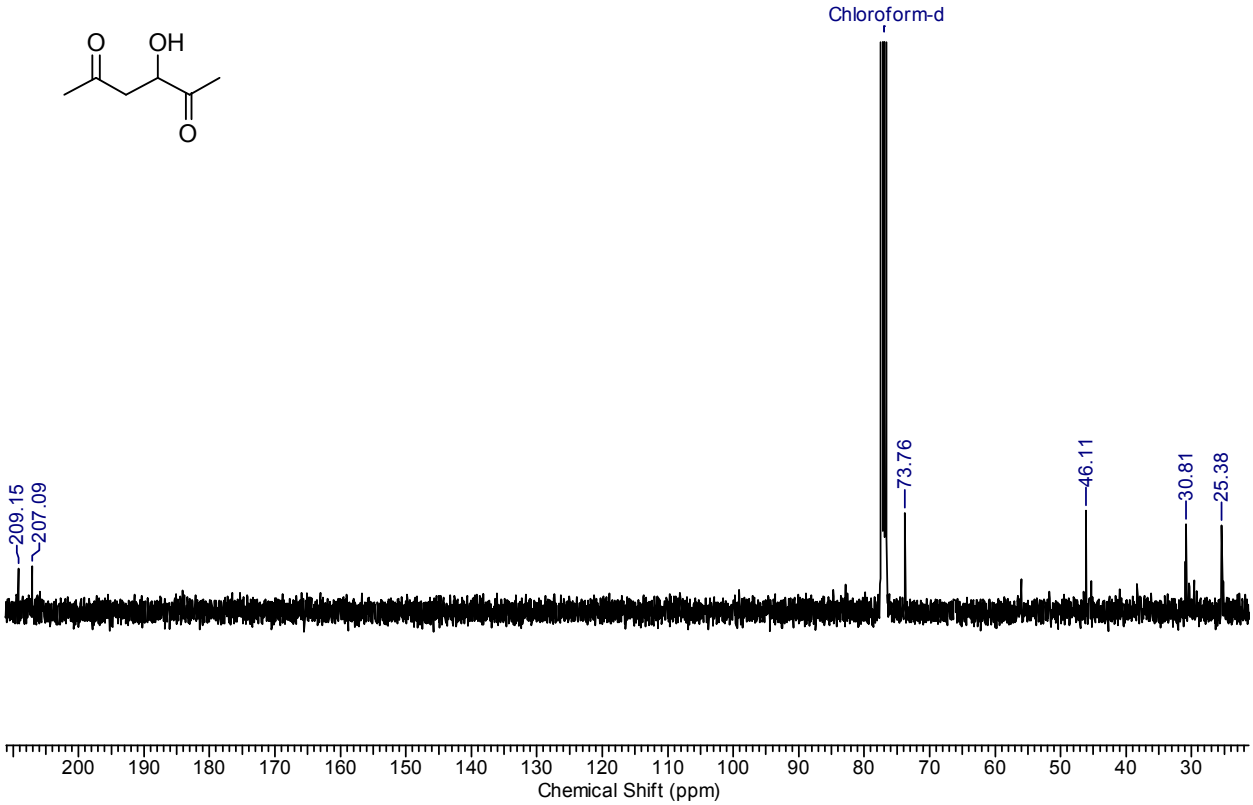


Figure S22 ^{13}C NMR spectrum of 3-hydroxyhexane-2,5-dione (after purification) obtained from 5-methyl furfural.

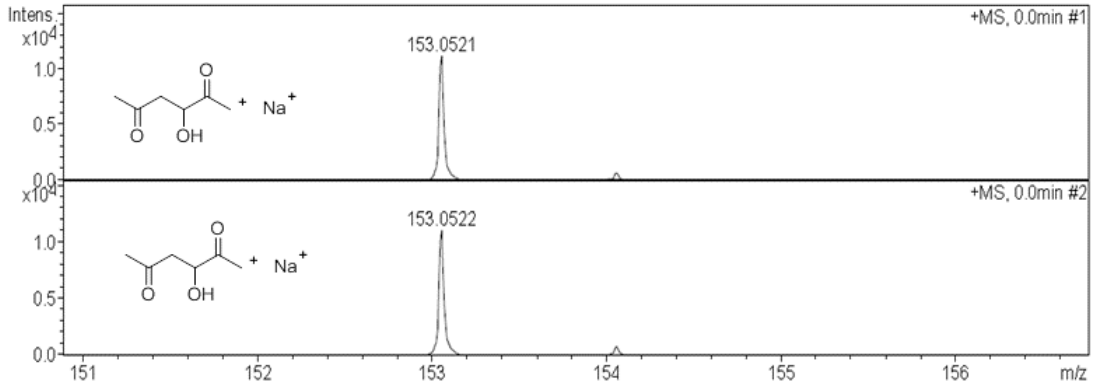
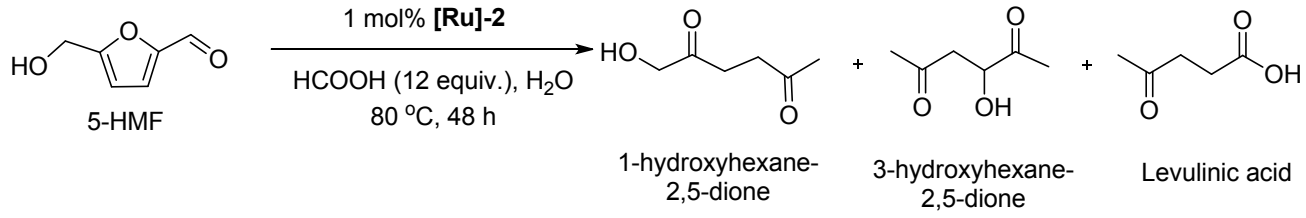


Figure S23 HRMS data of 3-hydroxyhexane-2,5-dione obtained from 5-methyl furfural.



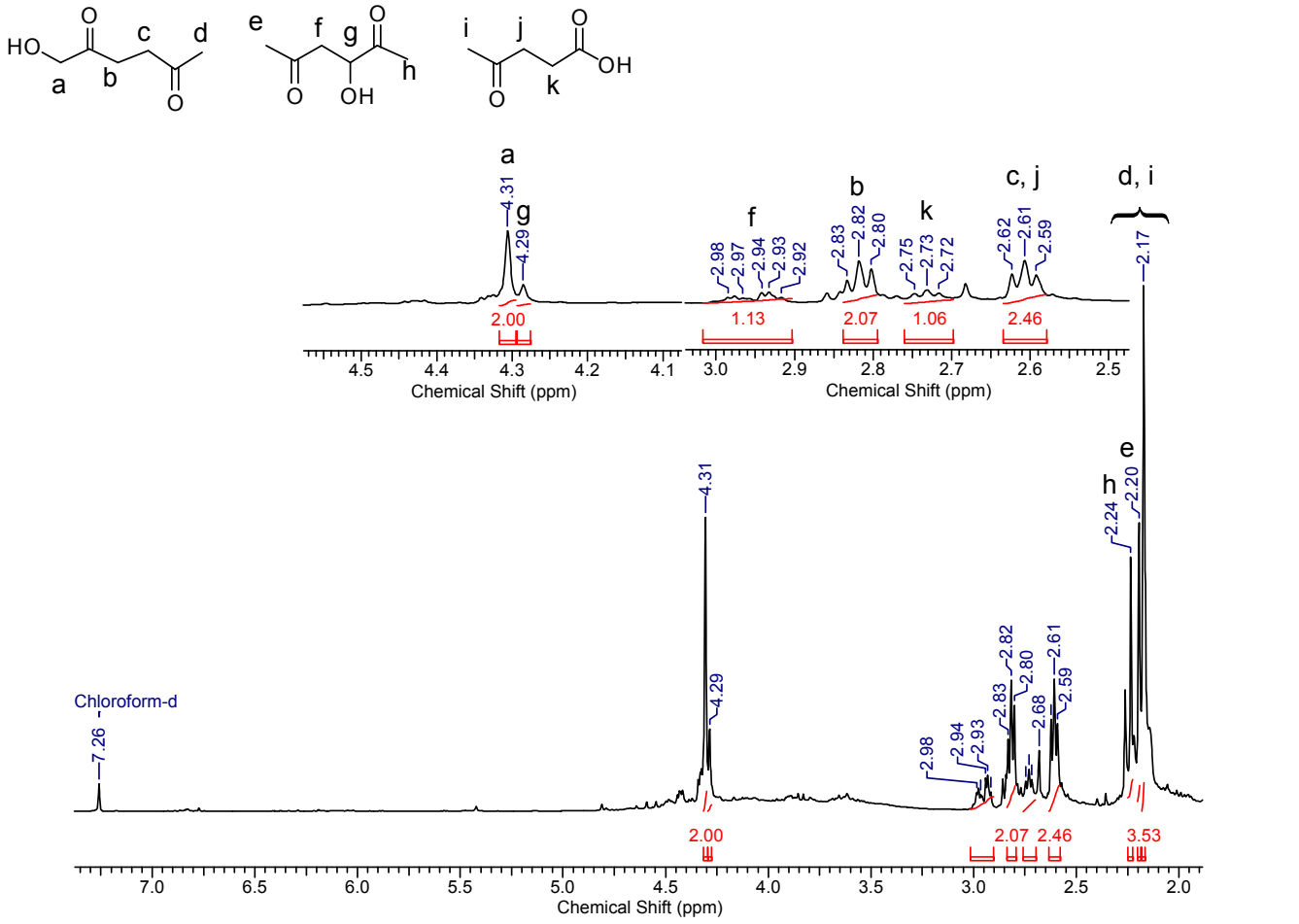


Figure S24 ^{1}H NMR spectrum of the products obtained from the catalytic transformation of 5-hydroxymethyl-2-furfual (5-HMF).