Electronic Supplementary Material (ESI) for Green Chemistry.

Electronic Supplementary Information for

Catalytic hydrodeoxygenation of neat levulinic acid into 2-methyltetrahydrofuran using cobalt phosphine complex and $Sc(OTf)_3$ co-catalytic system

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1. Literature overview

Table S1 Conversion of GVL into 2-MeTHF

Entry	Catalyst	Additive	Reaction conditions			Solvent	H source	Conv.(%)	2-MeTHF yield (%)	STY [a] (mol/(L*h))	Ref.
			H_2 (MPa)	T (℃)	t (h)						
Noble metal-based catalysts											
1	$Ru(acac)_3$-PBu_3 (S/C = 420)	NH_4PF_6	8.3	200	46	Solvent free (100 wt%)	H_2	-	-	-	1
2	$Ru(acac)_3$-triphos (S/C = 1000)	aIL	10	160	18	Solvent free (100 wt%)	H_2	-	95	0.528	2
3	[(TriPhos)Ru(CO)$(H)_2$] (S/C = 1000)	aIL	10	160	18	Solvent free (100 wt%)	H_2	-	96	0.533	2
4	5%Ru/C (S/C = 427)	-	10	190	24	Solvent free (100 wt%)	H_2	>99	43	0.179	3
5	[Cp*Ir(bpy-OMe)OH_2][$OTf]_2$ (S/C = 5194)	$Sc(OTf)_3$	3	100	16	Solvent free (100 wt%)	H_2	-	4	0.025	4

Non-noble metal-based catalysts											
6	30 wt% Cu/ZrO_2-OG (S/C = 10.6)	-	6	240	6	Ethanol (6 wt%)	H_2	98	91.1	0.0759	5
7	Cu/Al_2O_3 (S/C = 12.7)	-	4	200	2	1,4-dioxane (1.9 wt%)	H_2	91	73.7	0.0723	6
8	$Ni\text{-}Cu/Al_2O_3$	-				2-propanol	2-propanol + H_2	44.1	30.3	-	7
9	$Ni\text{-}Cu/Al_2O_3$	-	5	230	5	2-butanol	H_2	80	64	0.0558	8
10	Ni_2Cu_1/Al_2O_3	-	5	200	5	2-propanol	2-propanol + H_2	100	88.1	0.0678	9
11	$Ni\text{-}MoOx/Al_2O_3$-600 (S/C = 15.3)	-	4	200	4	Mesitylene (5.4 wt%)	H_2	95	29.5	0.0351	10
12	Co/ZrO_2 (S/C = 5.9)	-	4	230	2	1,4-dioxane (0.64 wt%)	H_2	97.0	72.2	0.0239	11
13	$Co(OAc)_2$-triphos (S/C = 100)	$Sc(OTf)_3$	5	150	24	Solvent free (100 wt%)	H_2	100	97.2	0.405	This work

[a] STY: Space-time yield.

Table S2 Conversion of LA into 2-MeTHF

Entry	Catalyst	Additive	Reaction conditions			Solvent	H source	Conv. (%)	2-MeTHF yield [a] (%)	STY [b] (mol/(L*h))	Ref.
			H_2 (MPa)	T (℃)	t (h)						
Noble metal-based catalysts											
1	$Ru(acac)_3$-triphos (S/C = 1000)	aIL+NH_4PF_6	10	160	18	Solvent free (100 wt%)	H_2	100	92	0.511	12
2	$Ru(acac)_3$-triphos (S/C = 1000)	$Al(OTf)_3$	5.5	140	30	THF (3.2 wt%)	H_2	100	88	7.15×10^{-3}	13
3	$RuH_2(PPh_3)$-{$N(CH_2PPh_2)_3$-κ^3P} (S/C = 200)	$HN(Tf)_2$	6.5	150	25	THF (6 wt%)	H_2	100	87	0.0166	14
4	2% Ru/1.07% FeSBA-15	-	3	250	LHSV 1.5 h^{-1}	1,4-dioxane (10 wt%)	H_2	93.2	67	-	15
5	5%Ru/GO	-	2.5	265	WHSV 0.512 h^{-1}	1,4-dioxane (10 wt%)	H_2	100	48	-	16
6	Pt−Mo/H-β (S/C = 50)	-	5	130	24	Water (3.7 wt%)	H_2	>99	86	0.0116	17
7	5% Pd/C (S/C = 21)	Microwave	-	150	0.5	Formic acid	HCOOH	78	72	-	18

Non-noble metal-based catalysts											
8	Cu-MINT (S/C = 121)	Microwave	-	150	0.5	Formic acid (11 wt%)	HCOOH	>90	67.5	-	18
9	80 wt%Cu/SiO_2	-	2.5	265	WHSV 0.513 h^{-1}	1,4-dioxane (10 wt%)	H_2	100	64	-	19
10	35 wt% Cu/Al_2O_3 (S/C = 16)	-	7	250	24	2-propanol (5 wt%)	2-propanol+H_2	100	75	0.0269	20
11	Cu-Ni/Al_2O_3-ZrO_2(9) (S/C = 25)	-	3	220	10	2-butanol (7.6 wt%)	H_2	100	99.8	0.0538	21
12	$Co(BF_4)_2{\cdot}6H_2O$-triphos (S/C = 10)	-	8	100	22	THF (2 wt%)	H_2	>99	14	9.40×10^{-4}	22
13	$Mn(CO)_5Br$ (S/C = 40)	HCl	-	100	24	Toluene (3.2 wt%)	$PhSiH_3$	100	99 (95)	9.89×10^{-3}	23
14	$Co(OAc)_2$-triphos (S/C = 100)	$Sc(OTf)_3$	5	150	24	Solvent free (100 wt%)	H_2	100	97.0	0.404	This work

[a] Isolated yield is given in parentheses. [b] STY: Space-time yield.

2. Figures of the experimental section

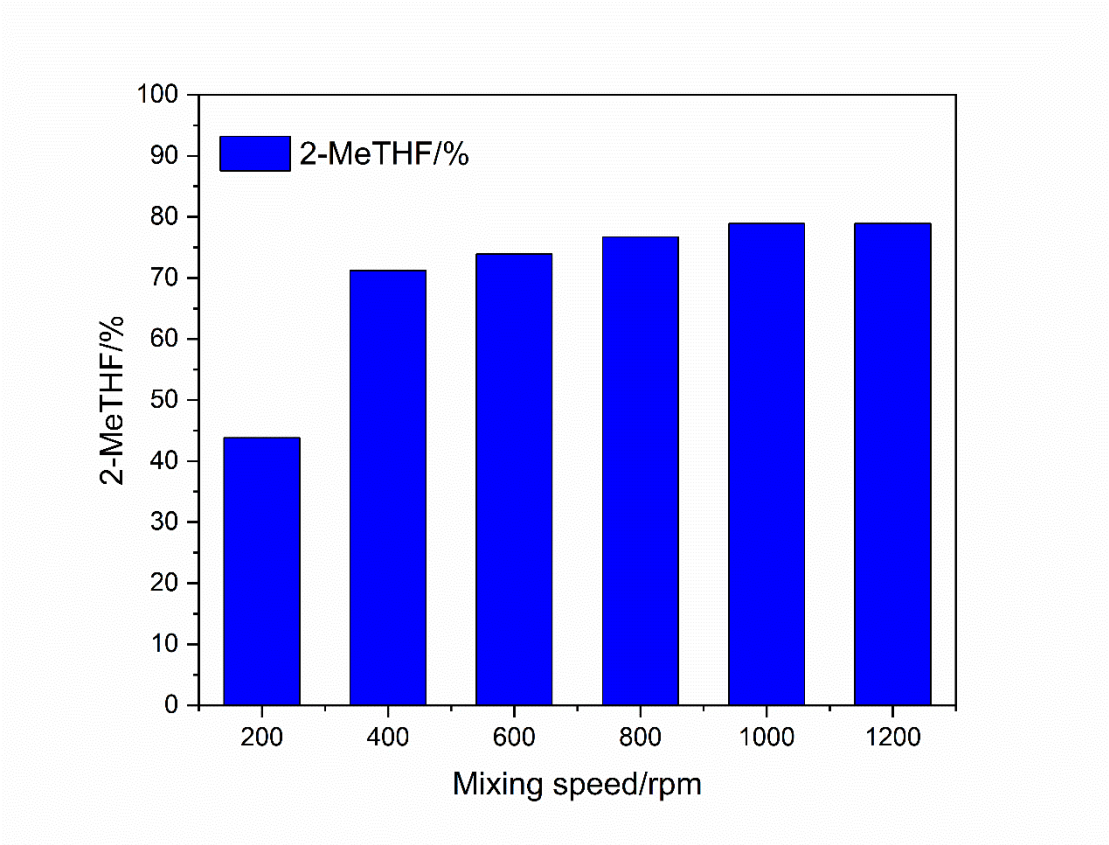


Fig. S1 The effect of mixing speed on the reaction. Reaction conditions: 6 mmol neat GVL, 1 mol% $Co(OAc)_2$/triphos, 2 mol% $Sc(OTf)_3$, 150 °C, 5 MPa H_2, 12 h. Yields were determined by GC analysis.

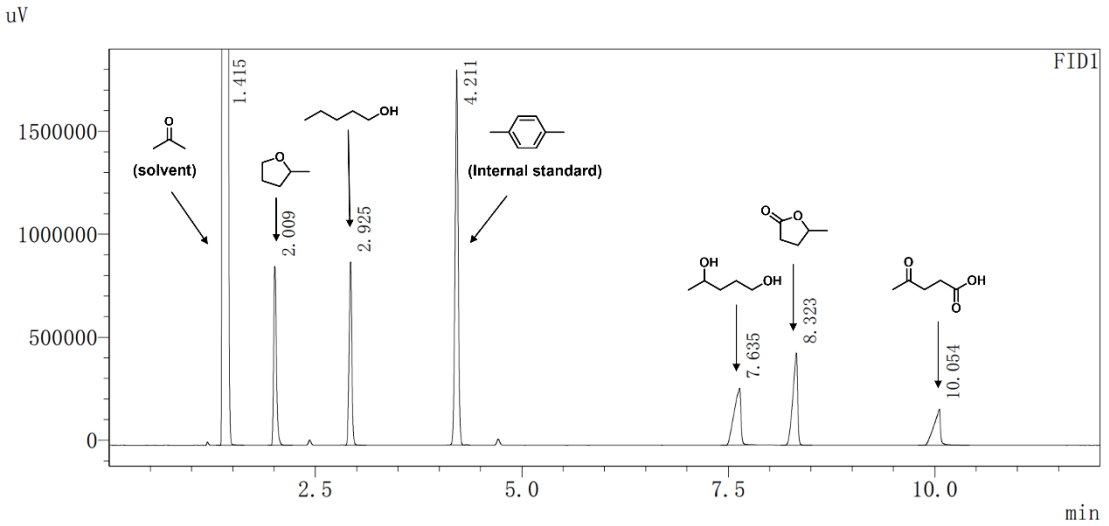


Fig. S2 A representative GC chromatogram.

3. Research on the reaction pathway

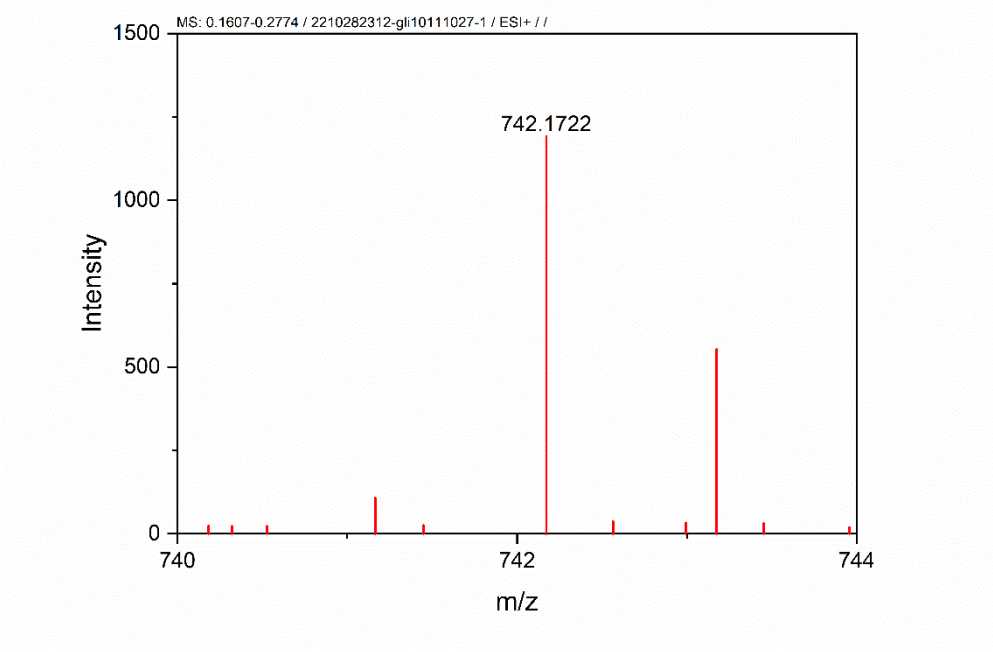
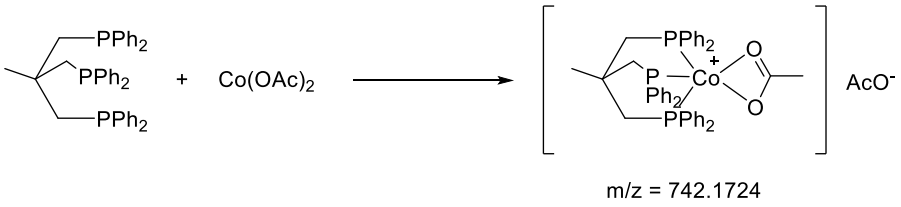


Fig. S3 The ESI-MS of the $Co(OAc)_2$/triphos = 1/1 mixture.



Scheme S1 The coordination mode of $Co(OAc)_2$ with triphos.

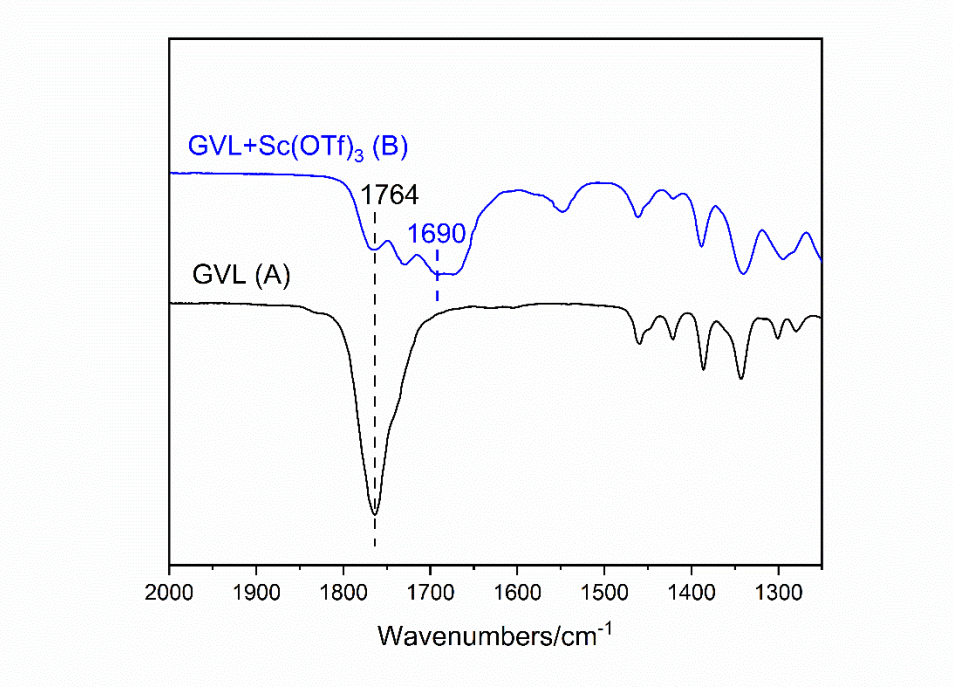
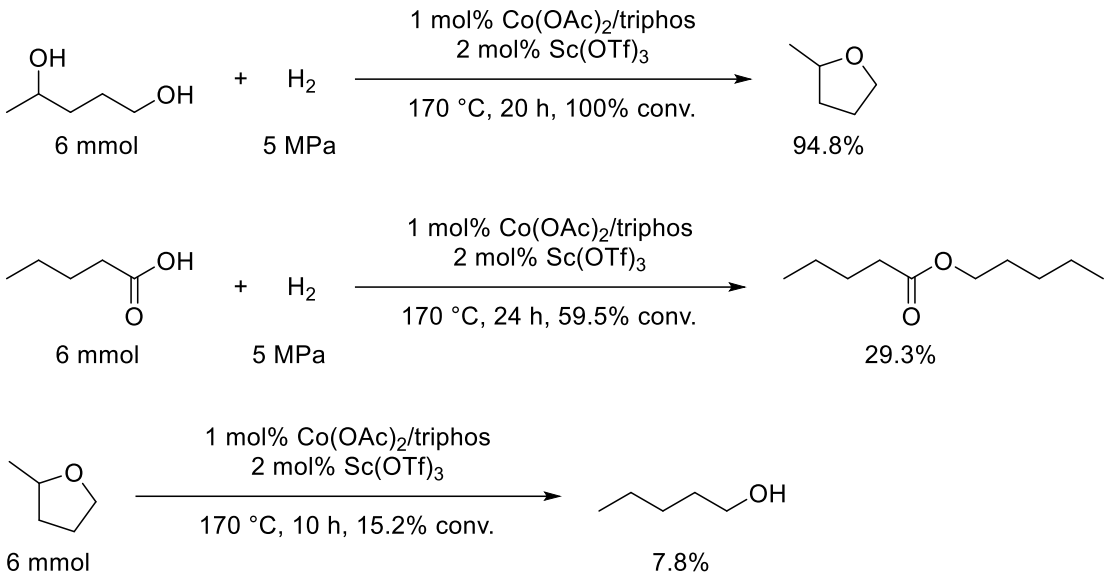
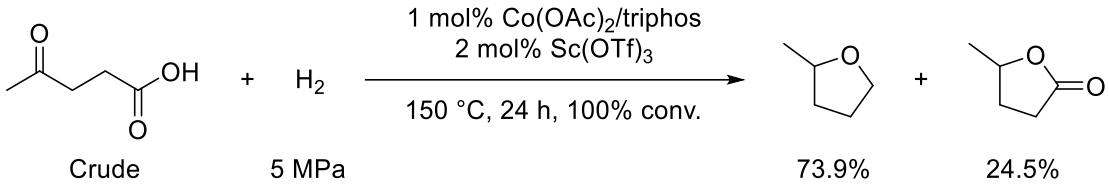


Fig. S4 FTIR spectroscopy of GVL (A), and the mixture of GVL and $Sc(OTf)_3$ (B).



Scheme S2 Experiments for the by-product 1-PeOH.

4. Hydrodeoxygenation of fructose-derived LA



Scheme S3 Hydrodeoxygenation of fructose-derived LA with 1 mol% $Co(OAc)_2$.

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