

Electronic Supplementary Information for

**Solvent-free transformation of levulinic acid into valeric acid
and its esters using nickel phosphine complex and metal triflate
co-catalytic system**

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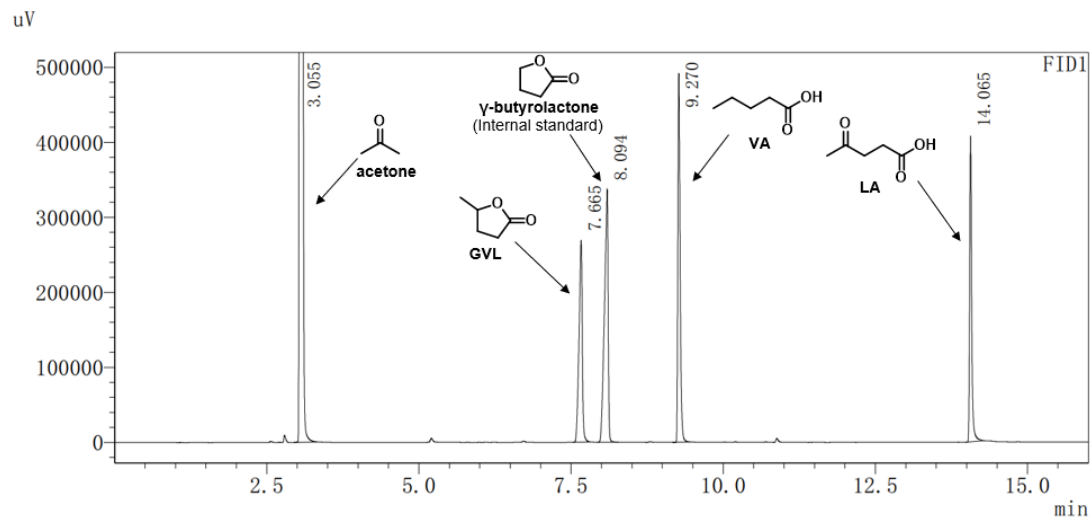


Fig.S1 Gas chromatogram of the reaction.

Table S1 GVL as substrate ^a

entry	ligands	Conversion (%)	VA Yield (%) ^b
1	triphos	100	99.0
2	PP ₂	84.3	83.4
3	PP ₃	79.4	79.0
4	DPPB	8.0	-
5	DPPE	2.5	-
6	DCyPE	4.0	-
7	R-BINAP	5.4	4.7
8	DPPP	3.0	-
9 ^c	PPh ₃	4.9	-

^areaction conditions: 6 mmol GVL, 1 mol% Ni(OAc)₂·4H₂O, 1 mol% ligand, 2 mol% Zr(OTf)₄, 180°C, 1 MPa, 10 h, solvent-free. ^bYield determined by GC analysis. ^c2 mol% ligand.

Table S2 Effect of ligands at the use of 1 mol% Zr(OTf)₄^a

Entry	Ligand	Conversion (%)	Yields (%) ^b	
			VA	GVL
1	triphos	100	37.2	62.3
2	PP ₂	100	36.7	5.6
3	PP ₃	100	34.2	7.4
4	DPPB	100	-	99.0
5	DPPE	100	3.0	96.0
6	DCyPE	100	2.5	96.6
7	R-BINAP	100	-	47.2
8	DPPP	100	4.0	95.1
9 ^c	PPh ₃	100	-	-

^a Reaction conditions: 6 mmol LA, 1 mol% Ni(OAc)₂·4H₂O/ligand, 1 mol% Zr(OTf)₄, 180°C, 1 MPa, 10 h, solvent-free. ^b Yield determined by GC analysis. ^c 2 mol% PPh₃.