Direct asymmetric reduction of levulinic acid to gamma-valerolactone: synthesis of a chiral platform molecule

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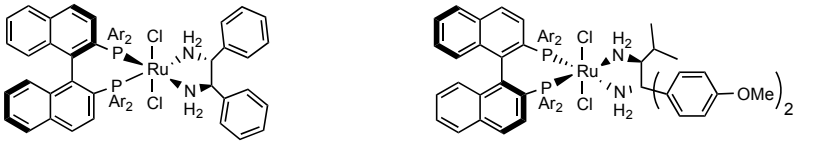
Electronic Supplementary Information (ESI)

Materials

Levulinic acid, (*R*)-Ru(OAc)$_2$(BINAP), RuCl$_2$[(*S*)-(DM-BINAP))((*S*,*S*)-DPEN)], (*R*)-RuCl[(*p*-cymene)(SEGPHOS)]Cl, (*S*)-[(RuCl(SEGPHOS))$_2$(μ-Cl)$_3$][NH$_2$Me$_2$], RuCl$_2$[(*S*)-(DM-SEGPHOS)][(*S*)-DAIPEN], (*S*)-Ru(OAc)$_2$(SEGPHOS), RuCl$_2$[(*R*)-xylbinap][(*R*,*R*)-DPEN], (*R*)-RuCl[(*p*-cymene)(DM-SEGPHOS)]Cl, (±)-BINAP, (*R*)-RuCl[(*p*-cymene)(DTMB-SEGPHOS)]Cl, RuCl$_2$[(*S*)-(DM-SEGPHOS)][(*S*,*S*)-DPEN], butanol, heptanol were purchased from Sigma-Aldrich Ltd., Budapest, Hungary and used as received. Methanol, ethanol, 2-propanol, toluene were obtained from Molar Chemicals Ltd., Budapest, Hungary. and used without further purification



RuCl$_2$[(R)-(XylBINAP)][(R,R)-DPEN)] (**1**) RuCl$_2$[(S)-(XylBINAP)][(S,S)-DAIPEN)] (**2**)

Figure S1. XylBINAP modified Ru catalysts

ESI-Table S1. Solvent screening for reduction of levulinic acid

Entry	Catalyst	Solvent	Base	Conv (%)	ee
1	**1**	-	-	100	11
2	**1**	methanol	-	100	13
3	**1**	methanol	$(CH_3)_3COK$	100	14
4	**2**	methanol	-	100	13
5	**1**	ethanol	$(CH_3)_3COK$	50	17
6	**1**	2-propanol	$(CH_3)_3COK$	96	1
7	**1**	2-propanol	-	100	13
8	**1**	butanol	$(CH_3)_3COK$	68	13
9	**1**	heptanol	$(CH_3)_3COK$	100	3.6
10	**1**	ethanol/2-propanol	$(CH_3)_3COK$	100	10

Conditions: 1 mL (9.8 mmol) LA, 1.4 mL solvent, T = 140 °C, t = 20 h, p = 60 bar, catalyst: 0.006 mmol, S/C = 1600.

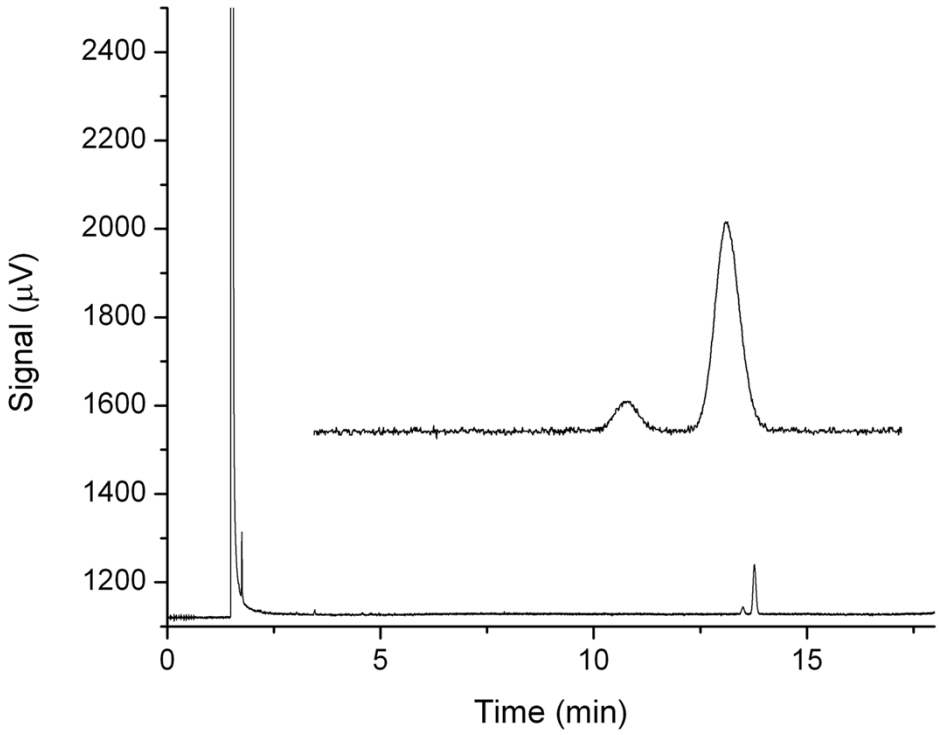


Figure S2. Chromatogram of reaction mixture with 82 % of ee.