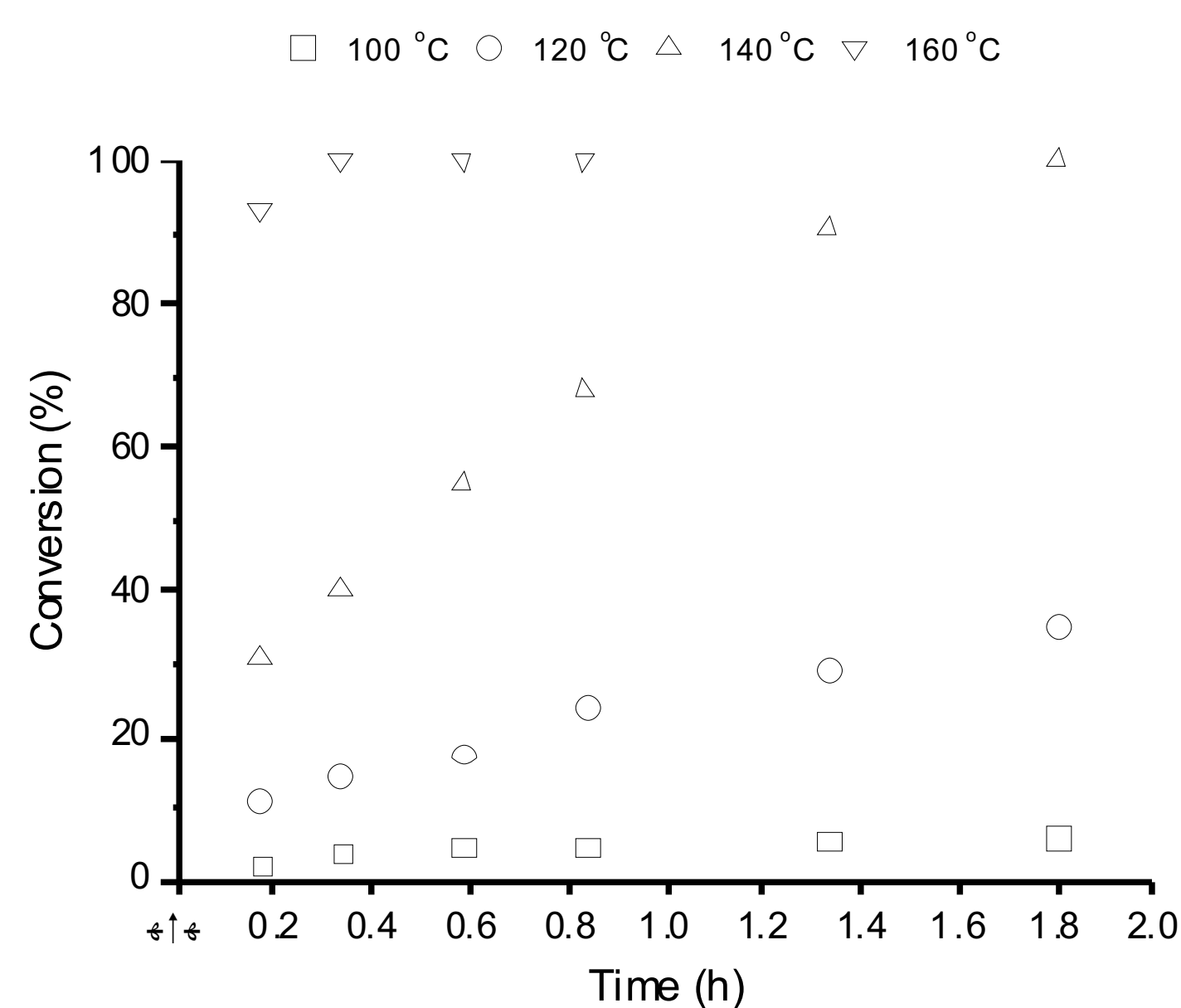
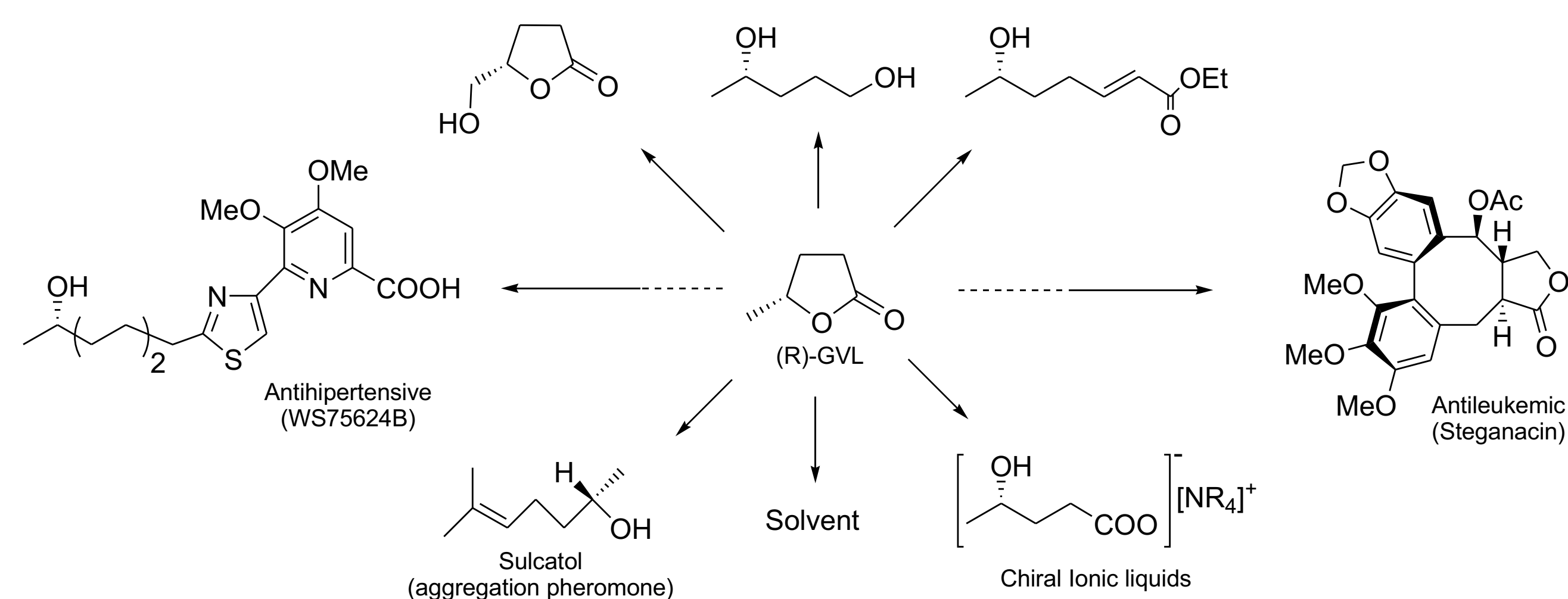
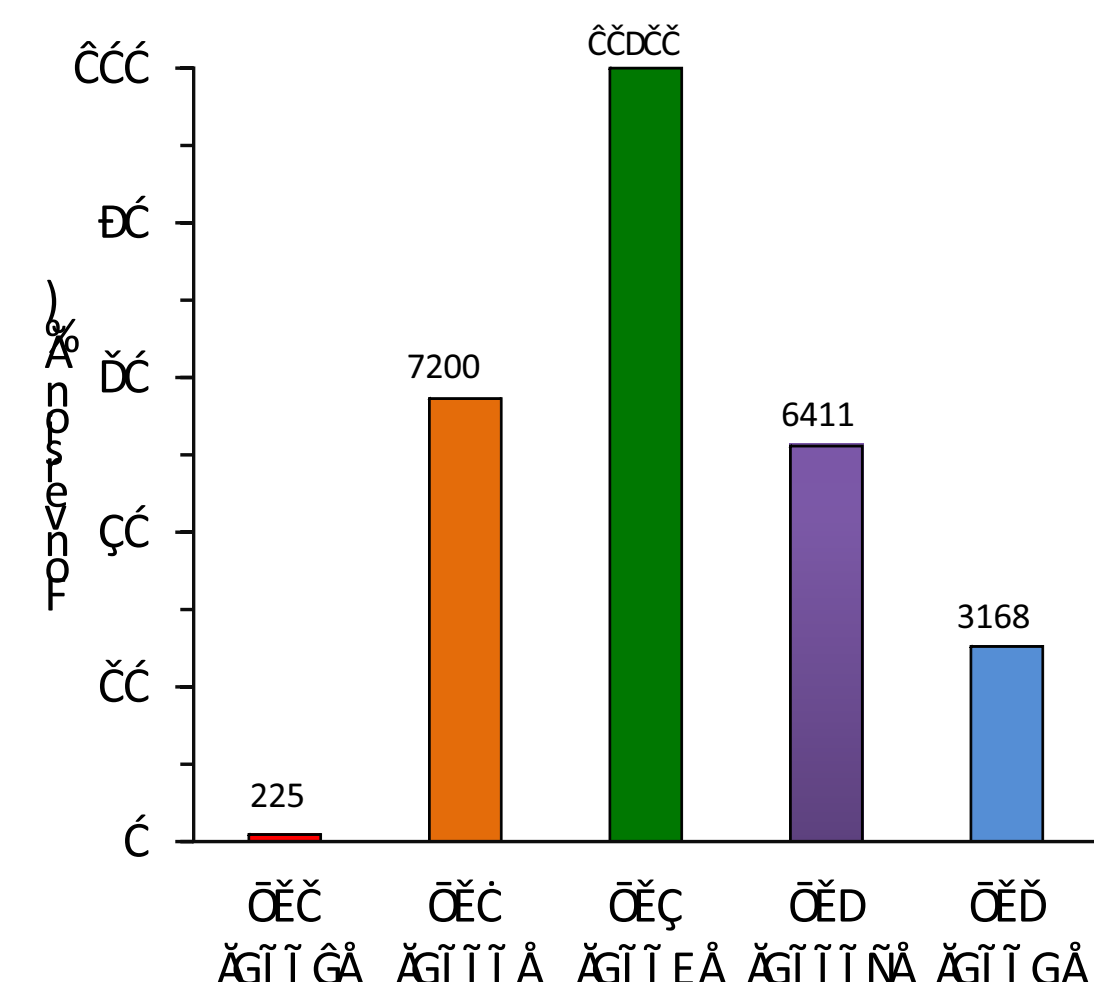
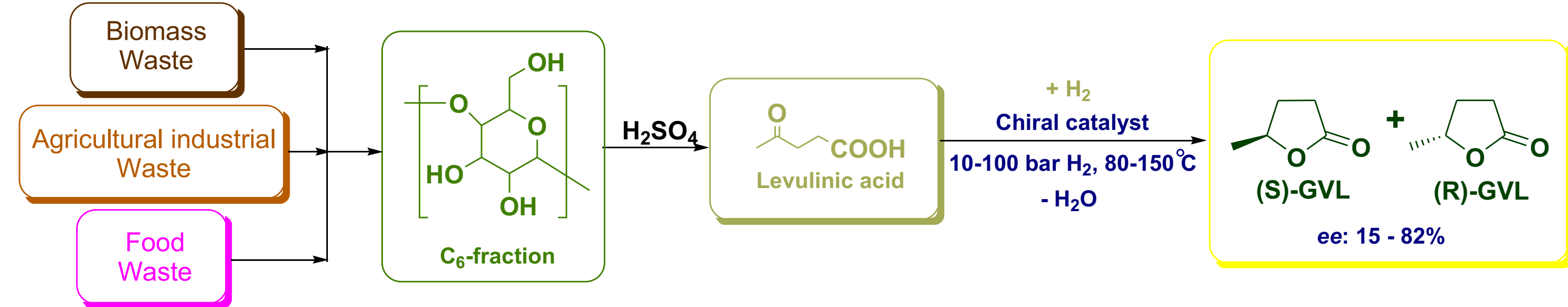


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The replacement of depleting fossil resources, which currently provide more than 95% of our energy needs and feedstock of chemical industry is one of the most pressing challenges. The production of carbon-based chemicals from fossil resources to renewables has become a key issue of sustainability, especially for goods manufactured by chemical industry. The intensive research activities on biomass conversion has led to the identification of unique platform molecules such as 5-hydroxymethyl furfural (5-HMF), levulinic acid (LA) and γ -valerolactone (GVL). The hydrogenation of LA to 4-hydroxyvaleric acid (4-HVA) followed by the intramolecular dehydration of 4-HVA to GVL is a key step of the conversion of carbohydrate-based biomass to GVL, which can be used for the production of both energy and carbon-based products [1, 3]. GVL is renewable, easy and safe to store and move globally in large quantities, because it has low melting, high boiling and flash points, definite but acceptable smell, is stable under air and miscible with water assisting biodegradation [3]. It was demonstrated that the application of bidentate phosphines as ligands for the Ru catalyzed selective reduction of LA to GVL significantly increased the efficiency of the transformation compared to the utilization of alkyl-bis(*m*-sulfonated-phenyl)phosphine ligands, with TOF of 21233 h⁻¹ in a solvent-, chlorine- and additive-free reaction environment [2]. Although, the green catalytic reductions of LA to GVL has been studied, the enantioselective hydrogenation has not been reported yet. The selective asymmetric reduction of LA leads to the formation of (R)-GVL or (S)-GVL, which can be used as an optically active platform molecule for the production of chiral chemicals. Both *in situ* generated and prepared Ru-based catalysts were tested for increasing the chiral induction in the conversion of LA to optically active GVL [4].

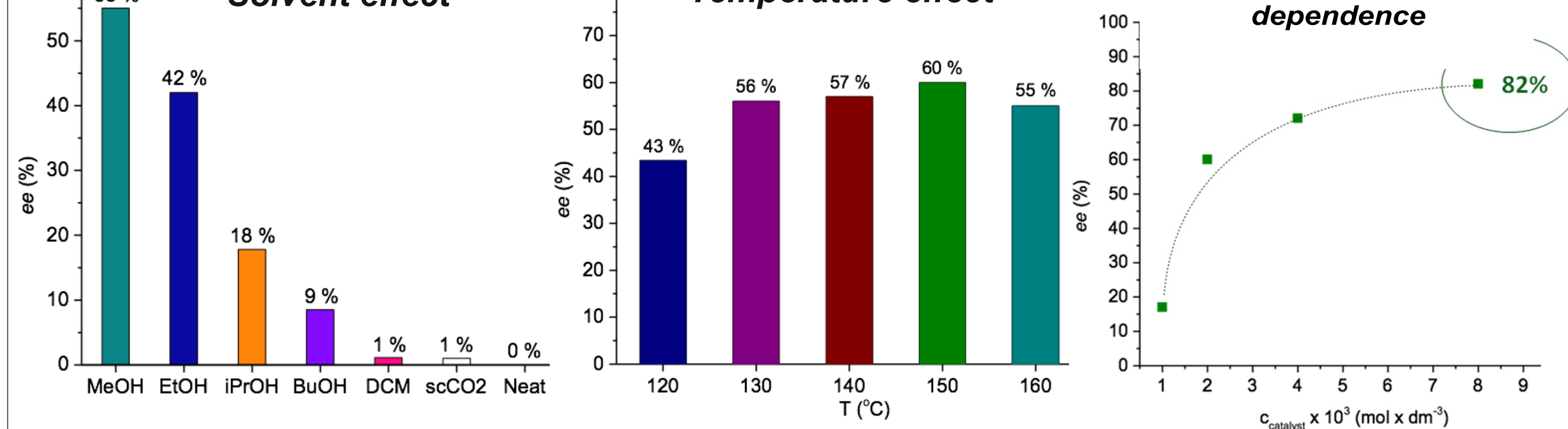
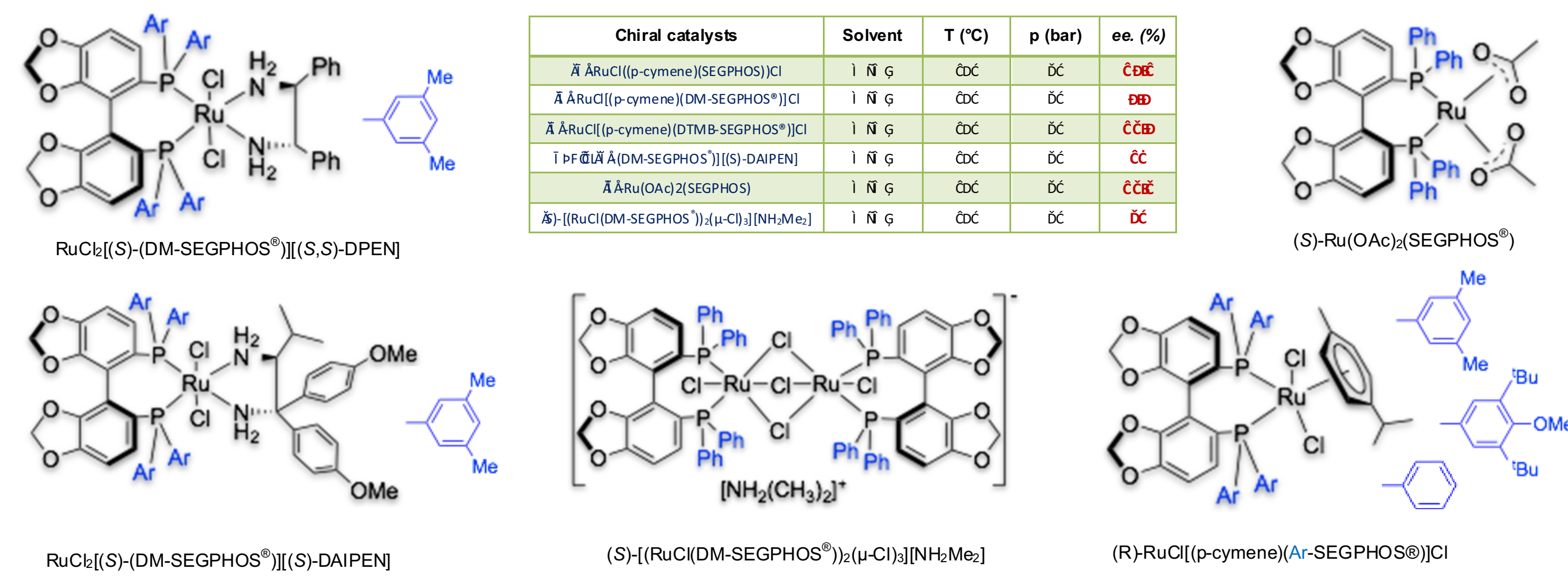


[Ru] = $0.775 \times 10^{-3} \text{ mol dm}^{-3}$ ($8 \times 10^{-3} \text{ mol\%}$),
[DPPB] = $7.75 \times 10^{-3} \text{ mol dm}^{-3}$, 100 bar H_2 .

Entry	[Ru] × 10 ³ (mol dm ⁻³)	Ligand	[Ligand] × 10 ³ (mol dm ⁻³)	T (°C)	P(H ₂) (bar)	Time (h)	Yield (%)	TON	TOF (h ⁻¹)
1	1.55	-	-	140	100	2.0	0	0	0
2 ^a	1.55	Bu-DPPDS	15.5	140	100	1.8	>99.9	6370	3538
3 ^a	1.55	DPPB	15.5	140	100	1.0	>99.9	6370	6370
4	0.775	DPPE	7.75	140	100	1.8	1.8	226	125
5	0.775	DPPPr	7.75	140	100	1.8	57.5	7325	4069
6	0.775	DPPB	7.75	140	100	1.8	>99.9	12740	7077
7	0.775	DPPPe	7.75	140	100	1.8	51.2	6522	3623
8	0.775	DPPH	7.75	140	100	1.8	25.3	3223	1790
9	0.775	(±)-BINAP	7.75	140	100	1.8	98.6	12561	6978
10	0.775	DPPB	7.75	140	75	1.8	>99.9	12740	7077
11	0.775	DPPB	7.75	140	50	1.8	>99.9	12740	7077
12	0.775	DPPB	7.75	140	25	1.8	>50.6	6446	3581
13	0.775	DPPB	7.75	140	10	1.8	26.3	3350	1861
14	0.775	DPPB	7.75	140	10	4.5	70	8918	1981
15	0.775	DPPB	7.75	160	100	0.6	>99.9	12740	21233
16	0.775	DPPB	7.75	120	100	1.8	35.7	4548	2526
17	0.775	DPPB	7.75	100	100	1.8	6.4	815	453

Reaction conditions: 30 mL (293.02 mmol) LA, Ru precursor: Ru(acac)₃, Ligand/Ru = 10, TON defined as mol of substrate converted per mol of Ru.

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- We have demonstrated that the catalyst in situ generated from Ru(III)-acetylacetonate and 1,4-bis(diphenylphosphino)butane (DPPB) can be used for the efficient conversion of biomass derived levulinic acid to gamma-valerolactone representing TOF of 21233 h⁻¹.
 - Levulinic acid was successfully converted to (R)-GVL (ee. = 82 %) in the presence of Ru-SEGPHOS based catalyst under optimized conditions:
 - Solvent: MeOH
 - Temperature: 150 °C
 - No base, no additive were used
 - Catalyst concentration: 0.008 mol/L
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This work was supported by the Budapest University of Technology and Economics under project number KMR_12-1-2012-0066. The authors would like to thank Prof. László Kollár (University of Pécs) for helpful discussions and the scholarship of Campus Hungary program.