

クラフトリグニンの分子内エステル交換反応を利用した脂肪族性水酸基の迅速な選択的アセチル化

金大院自然 ○鈴木葉・倉知志門・和田直樹・高橋憲司

1-エチル-3-メチルイミダゾリウム酢酸塩([Emim][OAc])はリグノセルロース系バイオマスを溶解し、アセチル化剤としてイソプロペニルアセート(IPAc)を用いた脂肪族性水酸基(R-OH)・芳香族性水酸基(Ar-OH)のアセチル化、芳香族性アセート(Ar-OAc)に対する選択的な脱アセチル化の触媒としても機能する。本研究では[Emim][OAc]を利用した低分子モデル化合物とIPAcのエステル交換反応のin situ ¹H NMR解析によって、Ar-OHとIPAcのエステル交換反応速度はR-OHよりも速く、生成したAr-OAcとR-OHのエステル交換反応はIPAcよりも迅速に進行することを発見した。そこで、IPAcとクラフトリグニン分子内のAr-OHのエステル交換反応によって生じるAr-OAcを利用し、R-OHの迅速かつ選択的なアセチル化プロセスを提案した。

I.1. Introduction

Lignin

The most abundant natural aromatic polymer with various OH groups.

Kraft lignin

Waste product in pulping process, regenerated from a black liquor.

Annual emission:
> one million tons

Nippon Paper Industries Co., Ltd.,
HP: <https://www.jpia.gr.jp/>

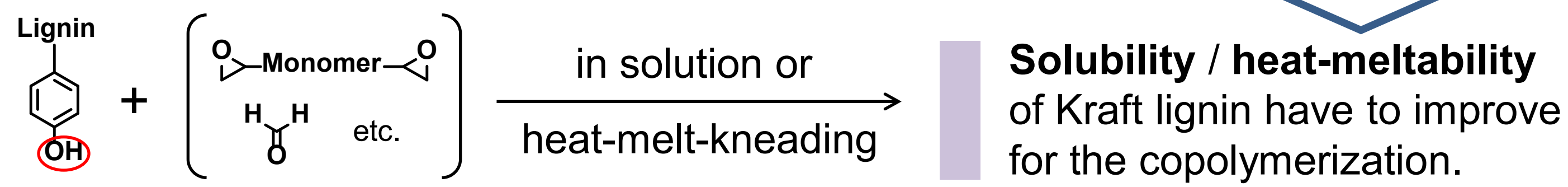
Aliphatic OH (R-OH):
2.7 ± 0.1 mmol g⁻¹

Aromatic OH (Ar-OH):
3.4 ± 0.1 mmol g⁻¹

- Insoluble in common solvents
- Non thermoplasticity
- Stiff and brittle

A certain functionalization is necessary for lignin to convert a valuable material.

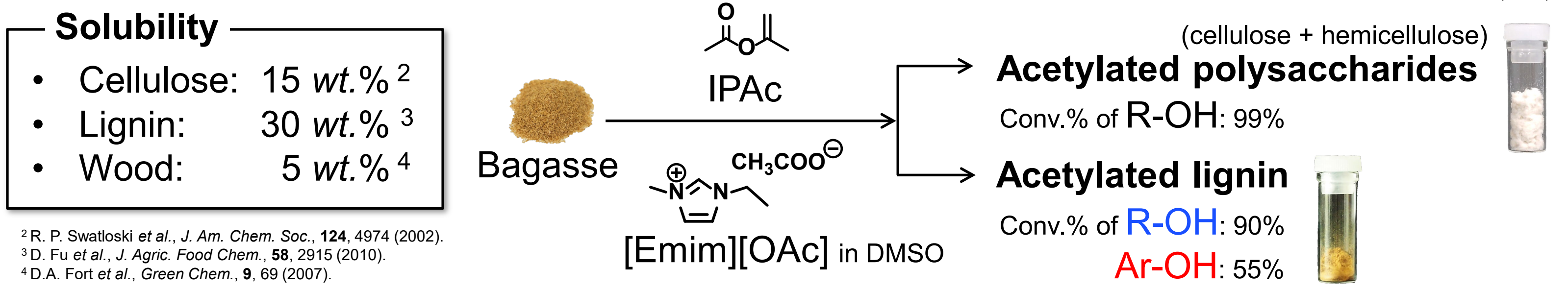
Copolymerization involving Ar-OH groups



Ionic liquid: a salt with a low melting point around room temperature

A green solvent + organocatalyst for transesterification of lignocellulosic biomass¹

¹ S. Suzuki et al., RSC Adv., 8, 21768 (2018).



I.2. This study

For valorization of Kraft lignin, an efficient synthetic protocol of **selective acetylation of R-OH groups** using [Emim][OAc] was investigated.

I.3. Previous study

In situ ¹H NMR of model reactions

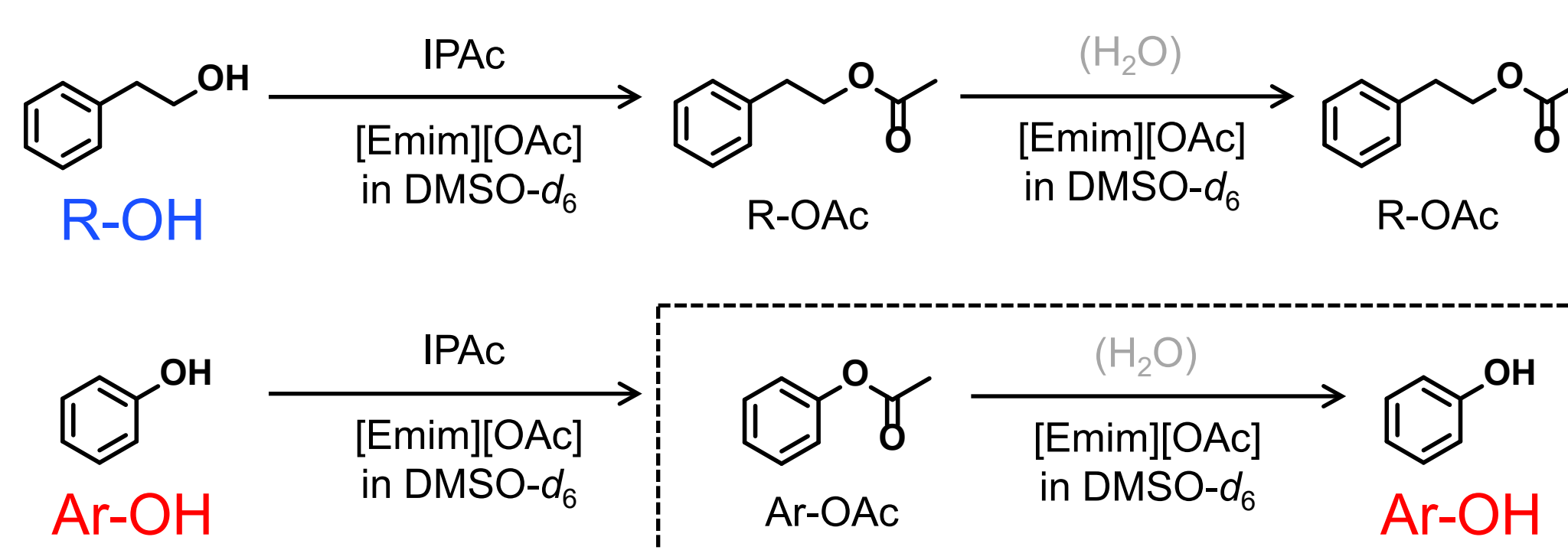
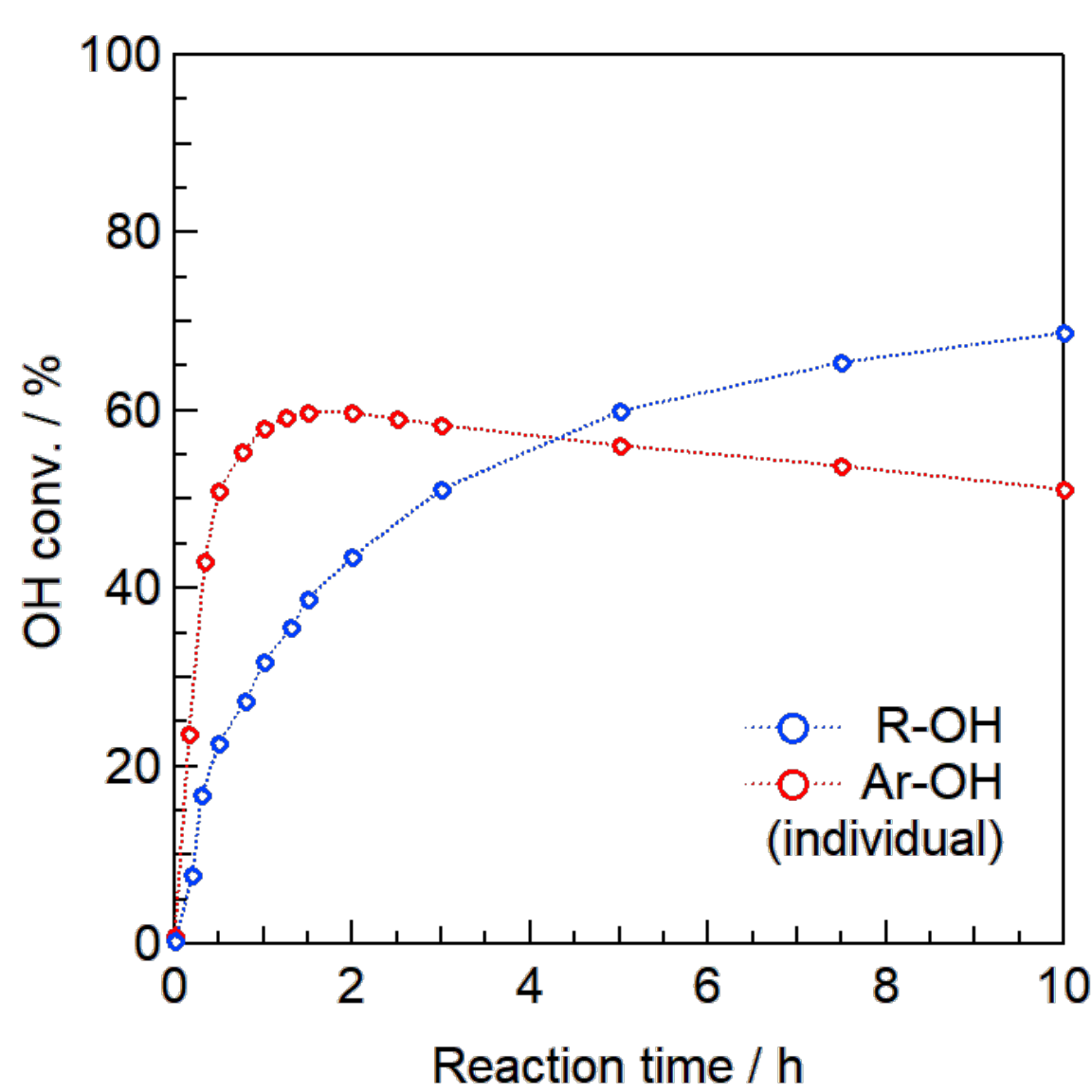
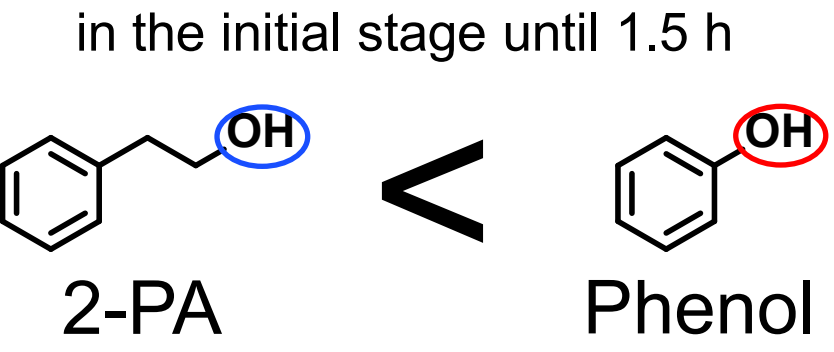
S. Suzuki et al., Chem. Lett., 47, 860 (2018).

Spectrometer: JNM-ECA 600 MHz NMR (Scans: each 80)

<80 °C, 0-10 h, Ar atmosphere >

- 2-Phenylethyl alcohol (2-PA, R-OH) or phenol (Ar-OH): 0.64 mmol
- [Emim][OAc]: 1 eq.
- IPAc: 1 eq.
- DMSO-d₆: 1.5 mL

Acetylation rate in the initial stage until 1.5 h



Ar-OH was once quickly acetylated, but the generated Ar-OAc was deacetylated, while the R-OAc was hardly done.

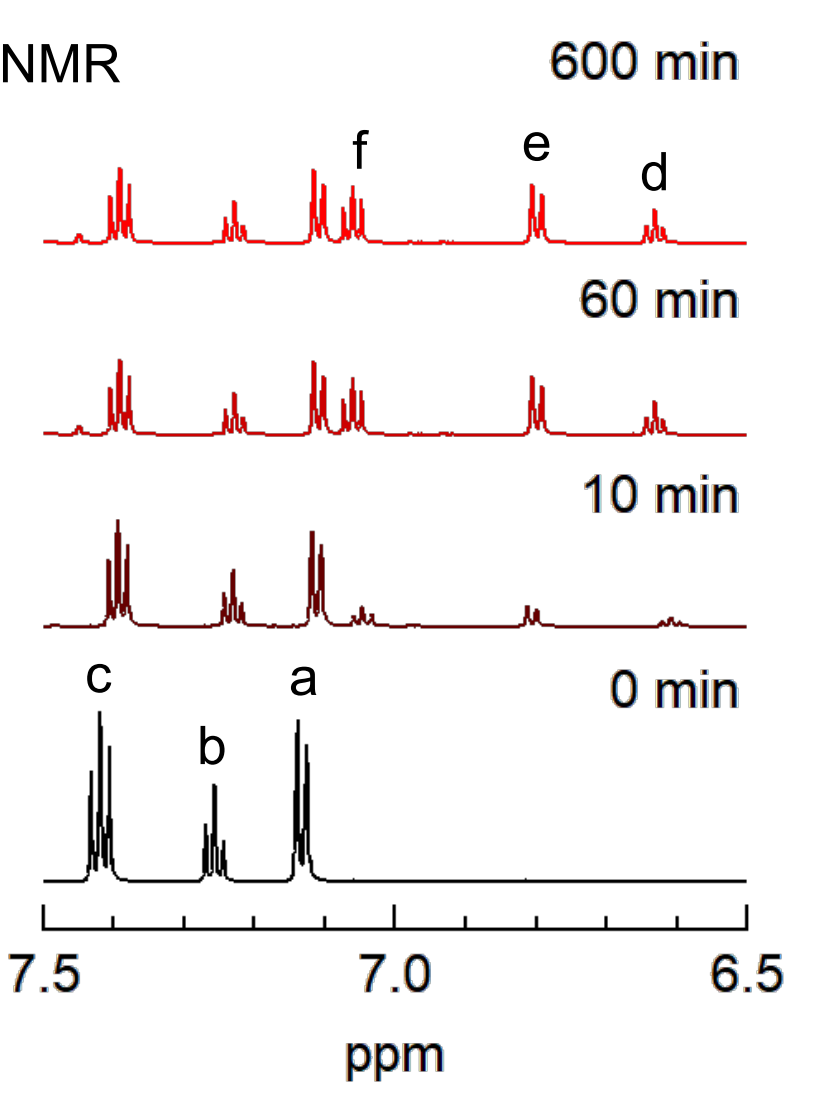
In situ ¹H NMR spectra

Spectrometer: JNM-ECA 600 MHz NMR (Scans: each 80)

<80 °C, Ar atmosphere >

- Phenyl acetate: 0.64 mmol
- [Emim][OAc]: 1 eq.
- DMSO-d₆: 1.5 mL

[Emim][OAc] has another catalytic ability in selective deacetylation of Ar-OAc.



Rapid and selective acetylation of model compounds

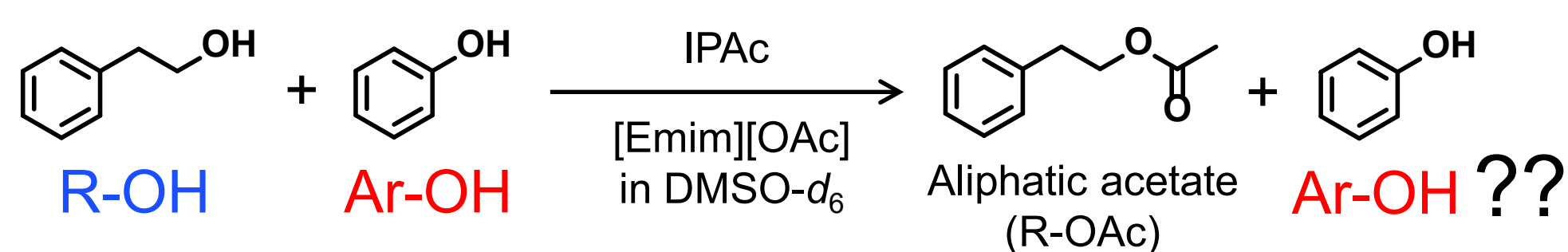
Acetylation and selective deacetylation of Kraft lignin

II.1. Experimental Acetylation of a mixture of R-OH + Ar-OH

Spectrometer: JNM-ECA 600 MHz NMR (Scans: each 80)

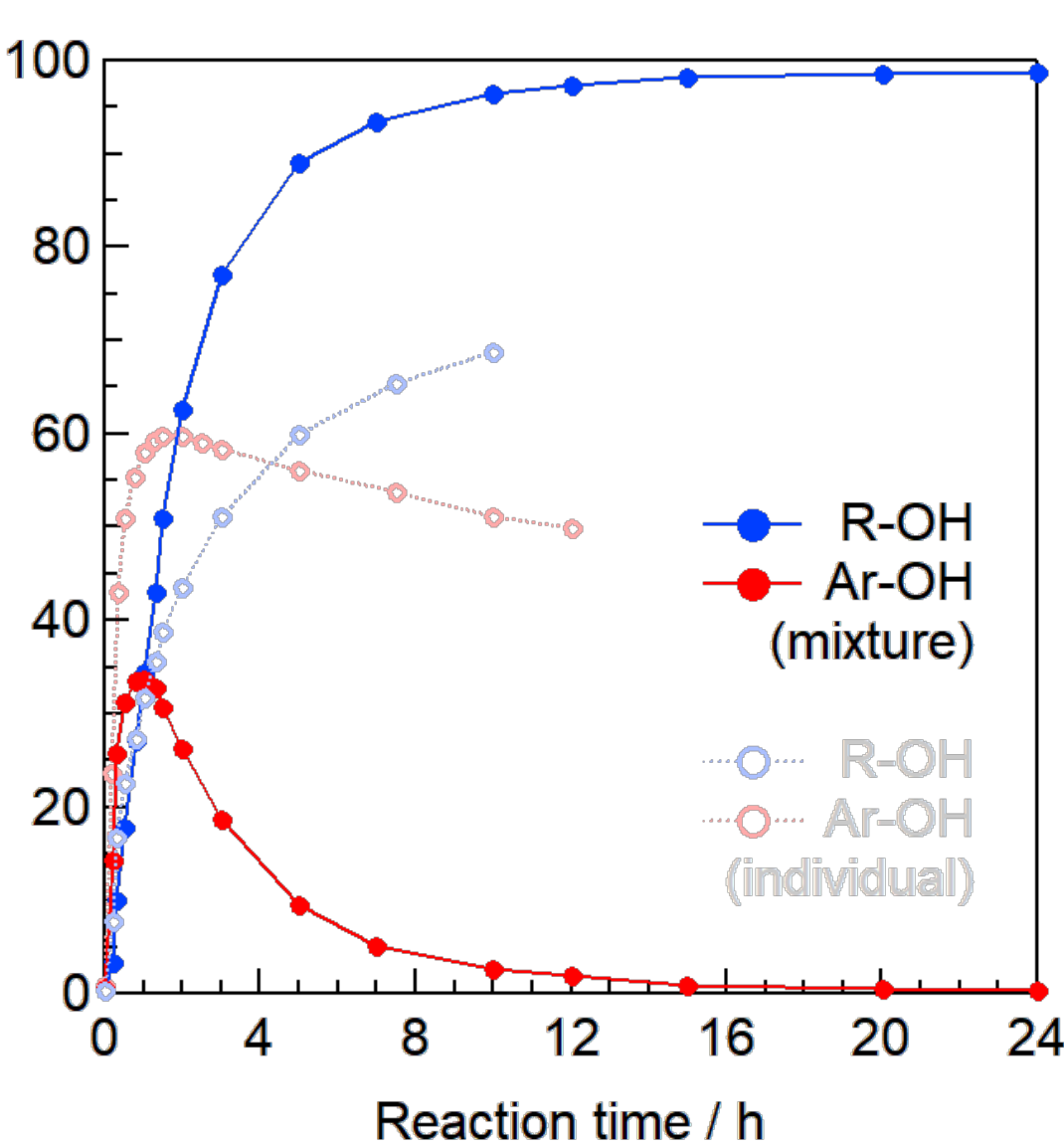
<80 °C, 0-24 h, Ar atmosphere >

- A mixture of 2-PA (R-OH) and phenol (Ar-OH): each 0.64 mmol
- [Emim][OAc]: 1 eq./[R-OH]
- IPAc: 1 eq./[R-OH]
- DMSO-d₆: 1.5 mL

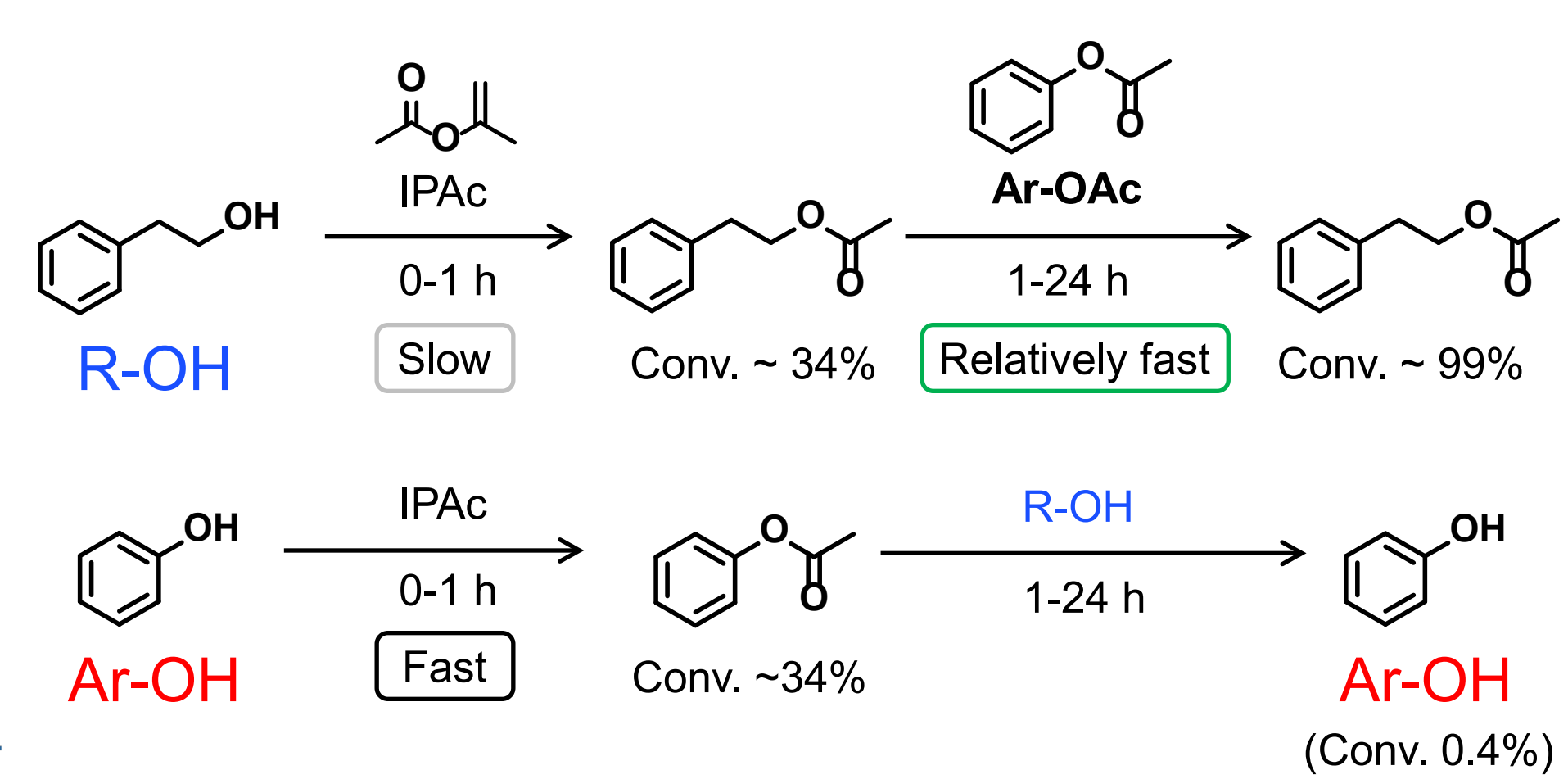


Can the bifunctional catalytic ability of [Emim][OAc] enable a selective acetylation of R-OH?

II.2. Result & Discussion



Each reaction behaviors of R-OH and Ar-OH



- R-OH in the mixture with Ar-OH was completely acetylated at 80 °C until 24 h,
- The reaction rate in the latter stage was clearly faster than that of 2-PA alone.
- Ar-OH was quickly acetylated until 1 h, and then the generated Ar-OAc was perfectly deacetylated until 24 h, via intramolecular transesterification with R-OH.

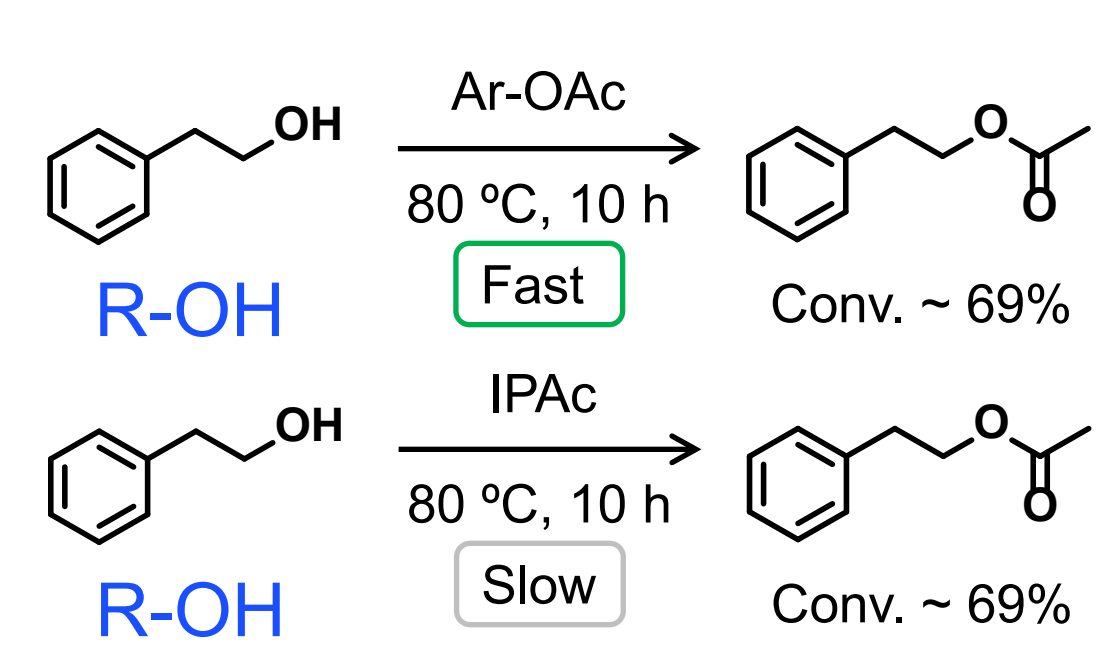
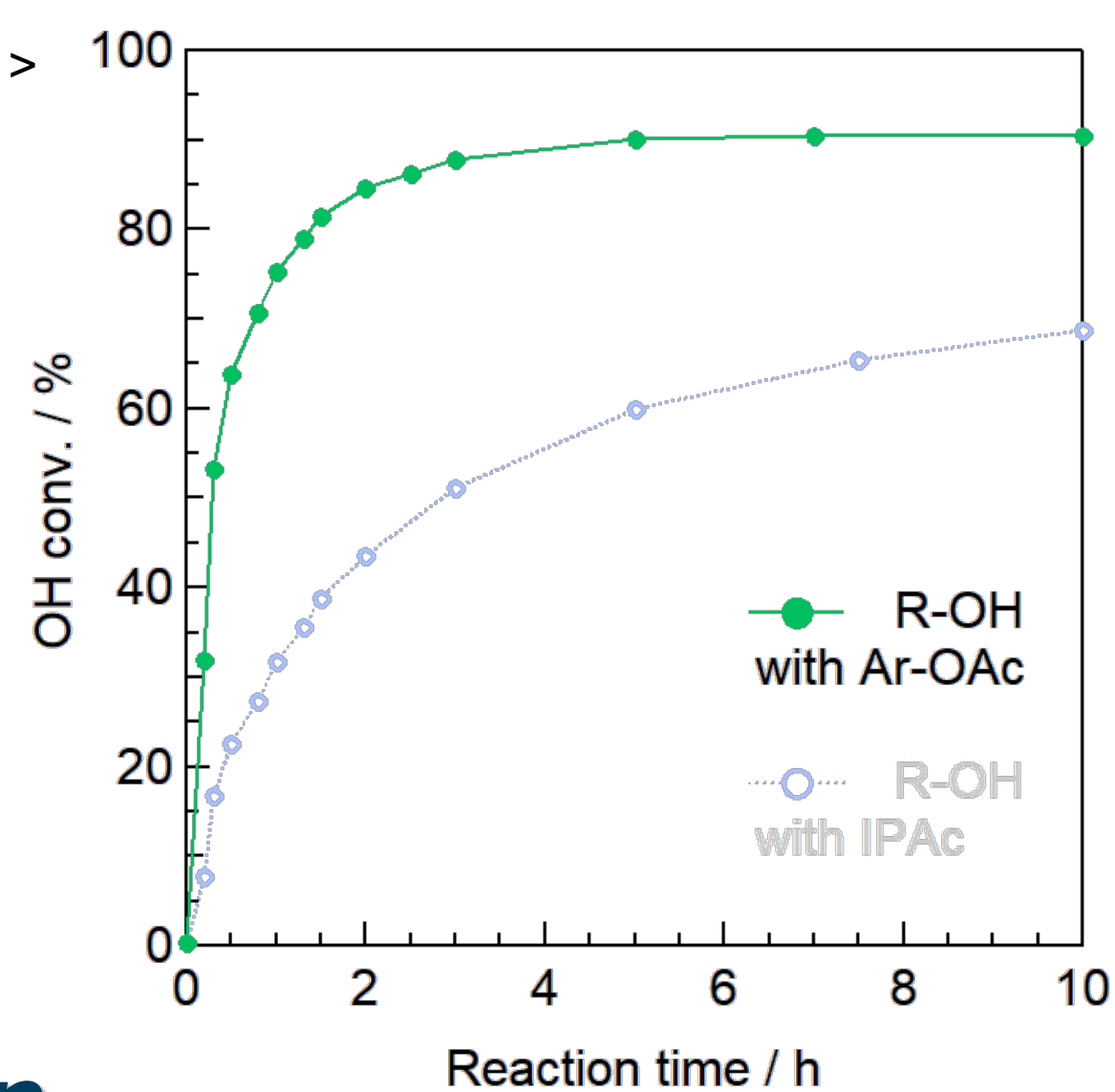
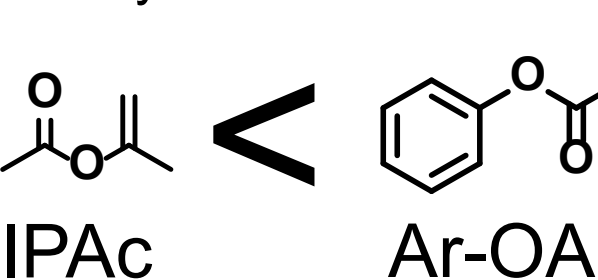
II.3. Appendix Comparison of IPAc / Ar-OAc as acetyl donors

<80 °C, 0-10 h, Ar atmosphere >

- 2-PA (R-OH) : 0.64 mmol
- [Emim][OAc]: 1 eq.
- IPAc or Ar-OAc: 1 eq.
- DMSO-d₆: 1.5 mL

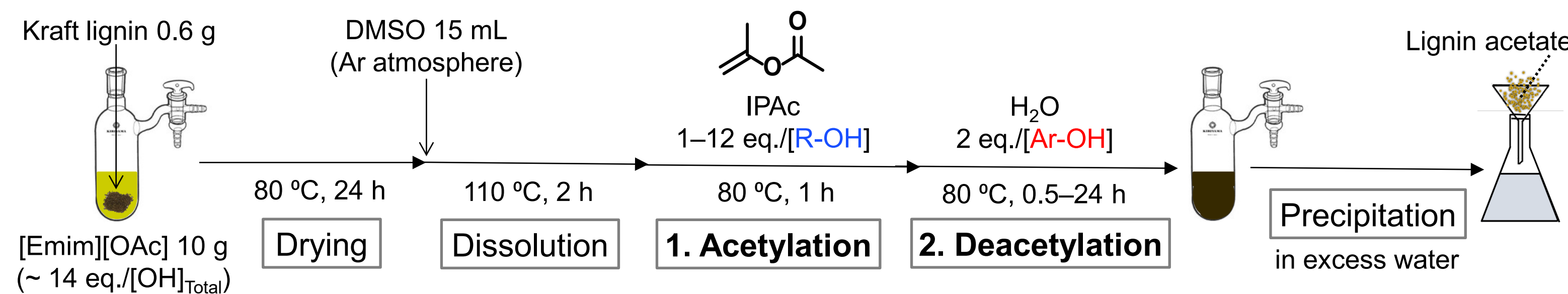
Acetyl donor

Acetylation rate of 2-PA



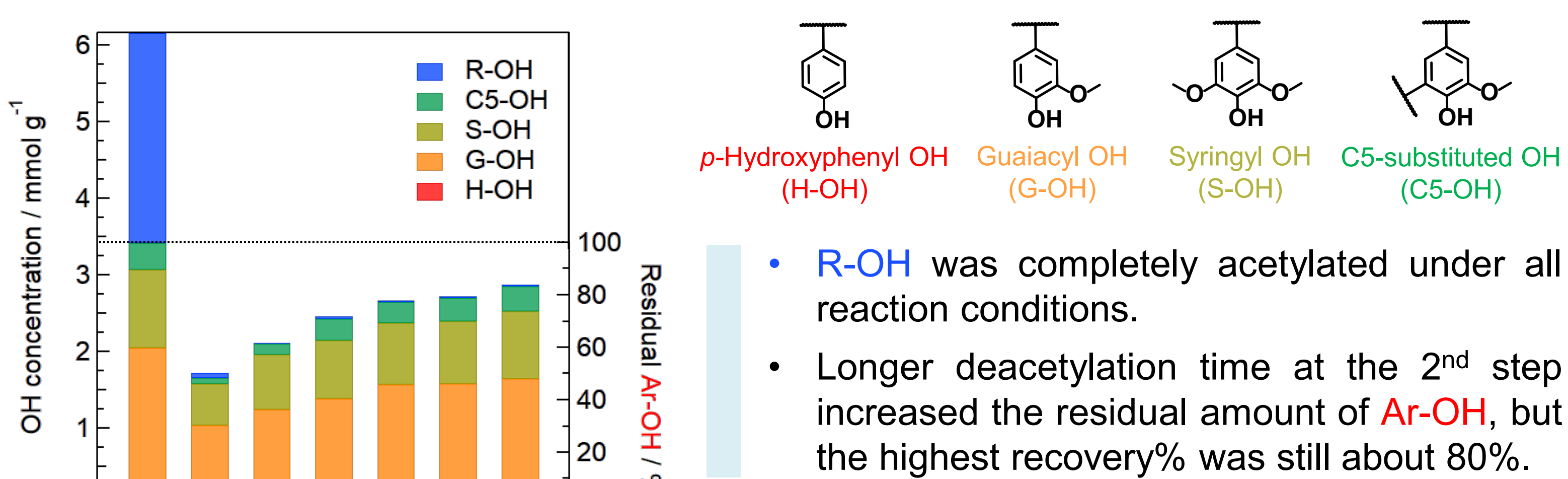
It was proved that the Ar-OAc was a better acetyl reagent for R-OH than IPAc.

III.1. Experimental One-pot two-steps transesterification



III.2. Result & Discussion

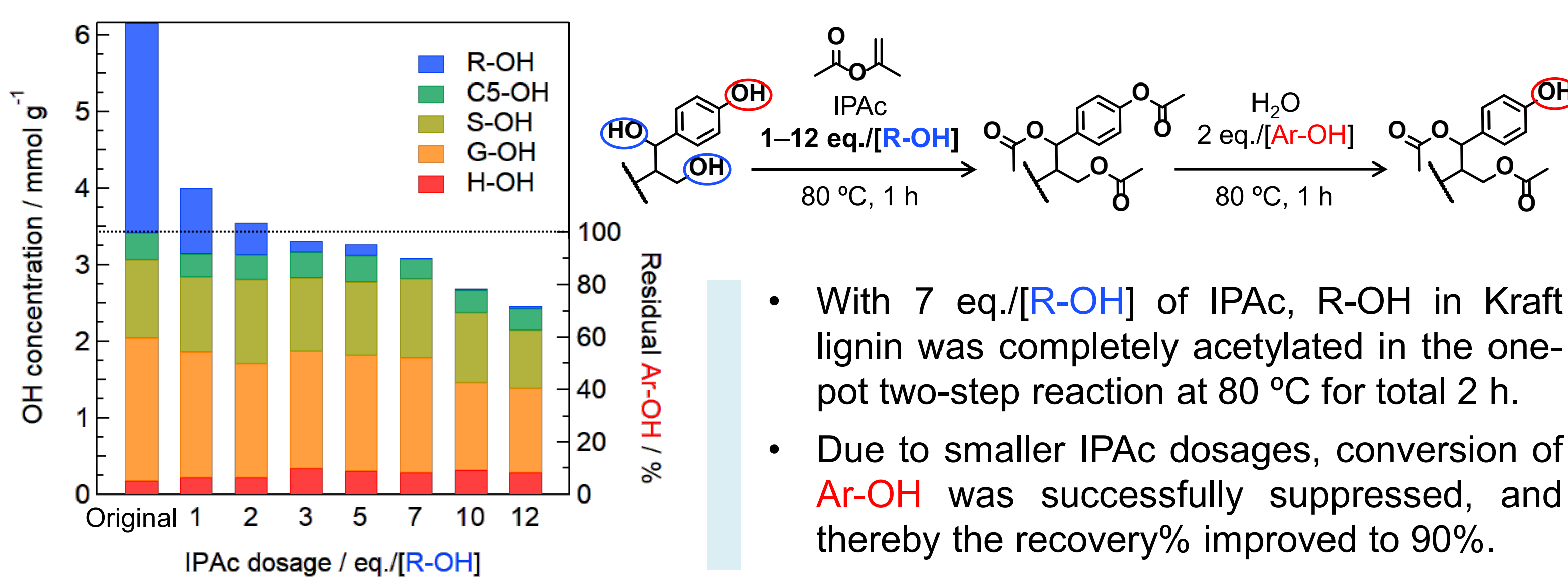
III.2.1. Effect of deacetylation time (IPAc: 12 eq./[R-OH])



- R-OH was completely acetylated under all reaction conditions.
- Longer deacetylation time at the 2nd step increased the residual amount of Ar-OH, but the highest recovery% was still about 80%.

Too much Ar-OH was acetylated by excess IPAc in the acetylation at the 1st step?

III.2.2. Effect of IPAc dosage (Acetylation & deacetylation time: each 1 h)



- With 7 eq./[R-OH] of IPAc, R-OH in Kraft lignin was completely acetylated in the one-pot two-step reaction at 80 °C for total 2 h.
- Due to smaller IPAc dosages, conversion of Ar-OH was successfully suppressed, and thereby the recovery% improved to 90%.

Rapid and selective acetylation of R-OH succeeded in one-pot two-step reaction at 80 °C for total 2 h. The average conv. (N=5): R-OH = 97 ± 4%, Ar-OH = 10 ± 1.

IV. Conclusion

[Emim][OAc]触媒条件下、クラフトリグニンのAr-OHとIPAcのエステル交換反応によって生成したAr-OAcは、クラフトリグニン分子内のR-OHに対する優れたアセチル化剤として機能することが示唆された。クラフトリグニンのR-OH量に対して7当量のIPAcを使用し、80 °C、計2時間の温和かつ迅速な条件下でのワンポット二段階反応によって、クラフトリグニンの約9割のAr-OHを未修飾のまま残す一方、全てのR-OHをアセチルする、効率的な選択的アセチル化プロセスを開発した。