REVIEW

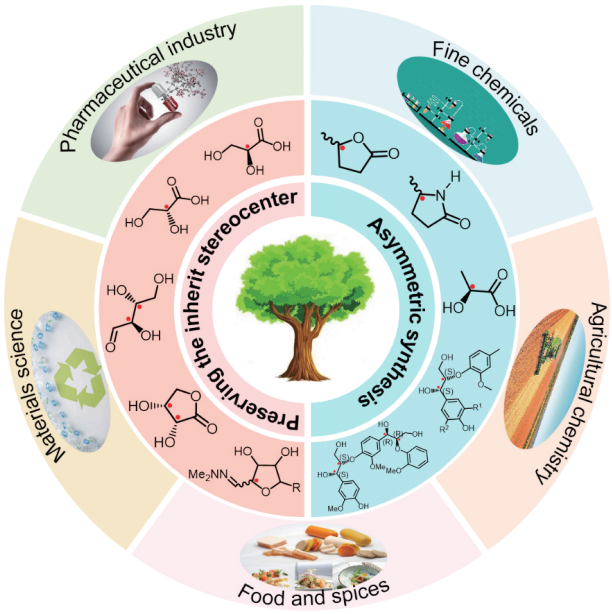
From Biomass to Chiral Chemicals via Chemocatalysis: Advances and Prospects†

Shuguang Xu[a], Shengqi Liao[b], Jianmei Li[b*], Changwei Hu[a,b*]

a. College of Chemical Engineering, Sichuan University, Chengdu 610065, China
b. Key Laboratory of Green Chemistry and Technology, Ministry of Education; National and Local Joint Engineering Laboratory of Energy Plant Biofuel Preparation and Utilization; College of Chemistry, Sichuan University, Chengdu 610064, China

(Dated: Received on April 18, 2025; Accepted on June 3, 2025)

Optically pure chiral chemicals are important building blocks with widespread applications across multiple scientific and industrial domains such as in pharmaceuticals, agrochemicals, and food, especially acting as precursors to synthesize biodegradable polymers. As an alternative to fossil resources, renewable lignocellulosic biomass has been used to access chiral chemicals, due to the versatile inherent stereostructures and multiple functional groups, such as hydroxyl, carbonyl, and phenyl ether groups. Typically, as the two main units of (hemi)cellulose components in lignocellulosic biomass, *D*-xylose and *D*-glucose bear multiple chiral centers (*e.g.*, 2*R*-3*S*-4*R* for *D*-xylose and 2*R*-3*S*-4*R*-5*R* for *D*-glucose). Lignin bears β-O-4 linkages, exhibiting (*R*,*S*/*S*,*R*) or (*R*,*R*/*S*,*S*) stereocenters at the side-chain α and β carbon atoms. The valorization of biomass into optically pure chiral chemicals is vital for developing a more sustainable future. This review discusses the production of typical chiral chemicals derived from biomass through chemocatalysis, including lactones (*e.g.*, *R*/*S*-valerolactone), carboxylic acids (*e.g.*, *D*/*L*-glyceric acid, *D*/*L*-lactic acid), polyols (*e.g.*, tetrose), furans, oligosaccharides, and others. Two strategies are generally employed. One approach involves first producing achiral platform chemicals from biomass, followed by the introduction of asymmetric catalysts to reconstruct stereocenters. The second relates to selectively preserving one or more inherent stereocenters in the natural biomass structure during complex cascade reactions in which biomass feedstock acts as a "chiral pool", thus eliminating the establishment of stereocenter. The feedstock, methods employed, and enantioselectivity and applications of the target chiral chemicals are discussed.



† Part of Special Issue dedicated to Professor Qing-shi Zhu on the occasion of his 80th birthday.

* Authors to whom correspondence should be addressed.
E-mail: lijianmei@scu.edu.cn, changweihu@scu.edu.cn

DOI: 10.1063/1674-0068/cjcp2504042

Despite these advances, the synthesis of optically pure chemicals from biomass is still in its infancy. The coming decade presents both extraordinary challenges and opportunities in biomass-derived chiral chemistry. Future research should be focused on: (1) integrating well-established asymmetric catalysis techniques and methods with biomass' inherent chiral pools, presenting an unprecedented opportunity to expand the chemical space of sustainable chiral compounds; (2) mastering polyfunctional complexity of chiral chemicals through holistic utilization of biomass' multichiral centers; (3) unlocking lignin's stereochemical treasury that represents the next frontier in biomass valorization.

Key words: Biomass valorization, Carbohydrates, Lignin, Chiral chemicals, Enantioselectivity

I. INTRODUCTION

Chirality is a fundamental and natural property that plays an important role in life. Chiral chemicals with high optical purity are employed in widespread applications such as food, cosmetics, pharmaceutical and medical industry, especially acting as an essential precursor to synthesize biodegradable polymers [1–10]. The synthesis of chiral chemicals can be achieved by microbial fermentation, however, their large-scale applications are limited by the shortcomings such as low productivities, complicated separation processes, and high cost [11, 12]. Chemocatalysis has served as a promising alternative to synthesize chiral chemicals in which asymmetric catalysis is usually adopted [13–21]. Besides, biomass can serve as a "chiral-pool" to produce chiral chemicals, that is, the chiral substructures existing in readily available biomass are directly used as raw materials in which the construction of stereostructure is not essential [22, 23]. In current market, fossil-derived chemicals are commonly employed as the feedstock to manufacture chiral chemicals.

Recently, renewable lignocellulosic biomass has served as a promising alternative to fossil-fuel-based resources to prepare valuable chemicals, due to the diminishing fossil resources and the aroused environmental issues [24–27]. Replacing fossil fuel-dependent chemistry with biomass-based processes is central to the biorefinery concept, a critical strategy for a sustainable future. Lignocellulosic biomass is recognized as the only renewable resource which possesses C, H, and O, consisting of a substantial quantity of hemicellulose, cellulose, and lignin components with diverse structures and functional groups [28–31]. Especially noteworthy is the unique intrinsic stereostructure in biomass, which is one particular advantage of biomass-based resources over fossil resource. For instance, as shown in FIG. 1, as the two main components, hemicellulose and cellulose consist of *D*-glucose and *D*-xylose units, each bearing multiple chiral centers (*e.g.* 2*R*-3*S*-4*R* for *D*-xylose, 2*R*-3*S*-4*R*-5*R* for *D*-glucose). Lignin is composed of various aromatic subunits (syringyl, hydroxylphenyl, guiacyl) with different types of linkages, depending on the type of plant. Lignin biosynthesis primarily generates β-O-4 moieties with (*R*,*S*/*S*,*R*) or (*R*,*R*/*S*,*S*) stereoisomerism at the α/β-carbons, yet the bulk polymer lacks chirality at the macroscopic level.

The multiple functional groups and versatile stereocenters in lignocellulosic biomass allow it to act as a promising feedstock to access chiral chemicals, which significantly reduces the carbon footprint of chemical industry. To date, substantial quantity of endeavors have been paid to biomass valorization, and diverse kinds of platform chemicals with short carbon-chain, such as furfural, 5-hydroxymethyl furfural, levulinic acid, γ-valerolactone, lactic acid, monophenol, and so on, have been obtained [32–35]. However, the majority of chemicals derived from biomass are achiral or racemic compounds. Biomass valorization to short-chain compounds generally passes through complicated cascade and parallel reactions, including ring-opening, isomerization, C–C cleavage, dehydration, and so on [36–38]. High reaction temperatures and Bronsted/Lewis acid or base catalysts are commonly employed to ensure high productivity [39]. Unfortunately, the chiral centers in biomass are unstable under severe reaction conditions due to the unavoidable epimerization, thereby leading to the inevitable configuration changes [40, 41]. Moreover, typical procedures like C–C breaking, dehydration, *etc.* also cause the breakage even the complete loss of intrinsic stereostructure [14]. This is the possible reason why optically pure chemicals de-

DOI: 10.1063/1674-0068/cjcp2504042

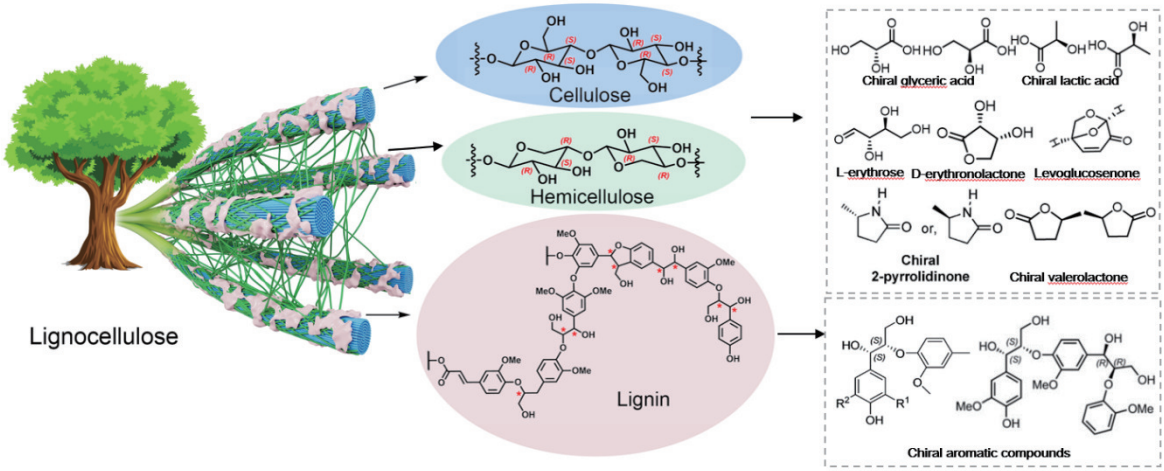


FIG. 1 The typical stereostructure contained in lignocellulosic biomass and the corresponding typically derived-chiral chemicals.

rived from biomass are predominantly produced through biocatalytic cascades [42]. Despite these great challenges in biomass valorization to chiral chemicals via chemocatalysis, some advances are available. This mini-review summarizes typical chiral chemicals (including chiral lactone, carboxylic acid, furan, *etc.*) synthesized using two strategies: one relates to the introduction of asymmetric catalysis, where the achiral platform chemicals derived from biomass via conventional homogeneous or heterogeneous catalysis are first prepared and served as the feedstocks for the next stereoselective reactions. The other approach involves the selective preservation of one or more inherent stereocenters in natural biomass during the complicated cascade reactions. The feedstocks, methods employed, enantioselectivity, and applications of the target chiral chemicals are discussed.

II. CHIRAL CHEMICAL PRODUCTION BY ASYMMETRIC SYNTHESIS

A. Levulinic acid-derived chiral chemicals

The abundant hydroxyl and carbonyl groups especially in biomass-based saccharides, enable them as a potential and perfect raw material for the production of carboxylic acids. Among saccharide-derived carboxylic acids, levulinic acid (LA) is a typical platform chemical. Many successful approaches have been achieved to afford levulinic acid from biomass feedstock with satisfied yields. LA generally serves as the potential feedstock to produce valuable optically pure chemicals, especially chiral γ-valerolactone (GVL), which can be employed as a beneficial chiral precursor to produce versatile fine chemicals [43, 44]. Notably, (*S*)-GVL has been leveraged to construct structurally diverse pharmaceuticals, such as the insect pheromone (*S*)-(+)-sulcatol and antileukemic steganacin [45–48]. On the other hand, (*R*)-GVL serves as a starting material for antihypertensive therapeutics.

In the past few decades, substantial homogeneous or heterogeneous catalysts have been developed to produce GVL from biomass-derived LA [49–52]. The catalytic asymmetric hydrogenation of LA has made great achievements to synthesize optically pure GVL in which noble metal catalysts (Rh, Ir and Ru) are usually employed [53–60]. H_2 is commonly adopted as the hydrogen source. For instance, Vinogradov *et al.* developed an Ru–BINAP–HCl system with ethanol as the solvent, achieving LA hydrogenation to GVL with an optical purity as high as 99% ee (enantiomeric excess) [61]. Mika group [43] established a catalytic system which was *in situ* prepared from (*S*)-BINAP and Ru(III)-acetylacetonate, affording (*S*)-GVL from LA with 26% ee, eliminating the use of any additive and/or solvent. When the catalyst ((*S*)-{[RuCl(SEGPHOS)]$_2$(μ-Cl)$_3$}−[$NH_2(CH_3)_2$]$^+$) was applied in methanol media, the optical purity of *S*-GVL increased sharply to 82%. Extending the feedstock to *D*-fructose gave 78% ee via a two-step strategy. In the case of "real" biomass as raw materials, including pea-pod, rice husk, corn straw, wheat straw and nut, (*S*)-GVL with 80% ee was achieved with the complete conversion of LA. Zhou and

DOI: 10.1063/1674-0068/cjcp2504042

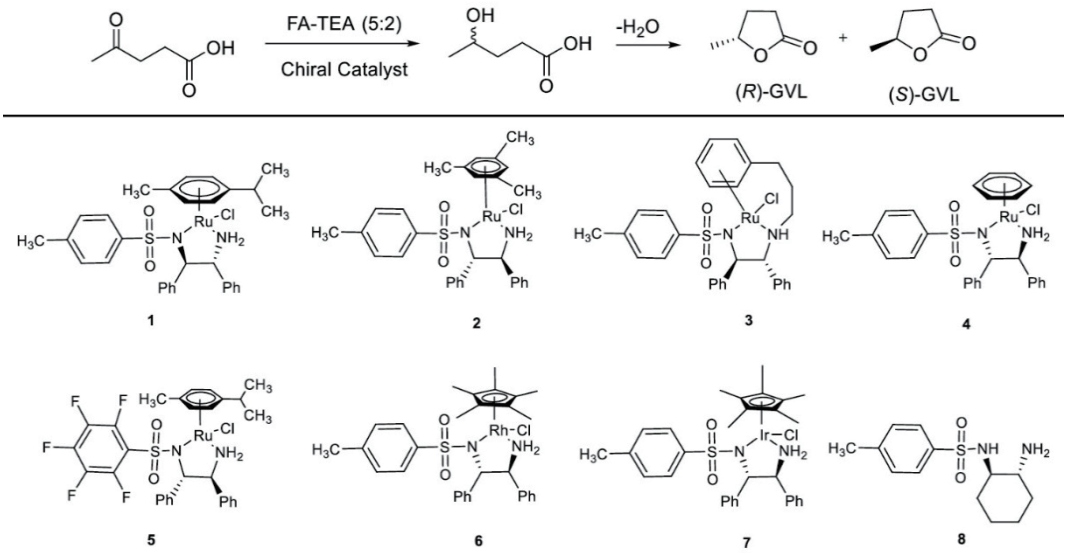


FIG. 2 Asymmetric transfer hydrogenation of LA to synthesize chiral GVL catalyzed by various chiral catalysts; adapted with permission from Ref.[45], copyright 2019 American Chemical Society.

co-workers fabricated a series of iridium complexes bearing chiral spiro phosphino-oxazoline ligands, which exhibited outstanding activity for LA hydrogenation [62]. Besides, the transfer hydrogenation of LA catalyzed by asymmetric catalyst has also proven to be efficient for chiral chemical production under mild reaction conditions [63–68]. Formic acid is also adopted as a hydrogen resource, since it is always coproduced with LA in a ratio of 1:1. Bhanage presented a report on LA conversion to chiral GVL through asymmetric transfer hydrogenation [45]. As shown in FIG. 2, RuCl-(*R*,*R*)-TsDPEN (**1** in FIG. 2) catalyst exhibited the highest activity among the selected chiral catalysts, giving chiral GVL with 93% ee and 97% yield in which formic acid was employed as hydrogen source and methanol was used as solvent. The catalytic performance of diverse organic tertiary amines was evaluated in conjunction with formic acid as a hydrogen source. Among the tested systems, a 1:1 molar combination of *N*-methylpiperidine and formic acid demonstrated optimal hydrogenation efficacy, achieving full substrate conversion and delivering enantiomerically enriched chiral GVL with 93% enantiomeric excess. When LA derived from rice husk or wheat straw was employed as raw material, chiral GVL with 82% ee was gained.

Apart from noble metal catalysts, transition metals have also been employed as the asymmetric catalysts for LA hydrogenation. Karnik *et al.* obtained optically purified *S*-GVL with moderate yields from (*S*)-bornyl esters or (*S*)-menthyl of 4-carboxylates, where sodium borohydride was used as the reductant [69]. Osawa and Tanabe fabricated a nickel catalyst modified by (*R*,*R*)-tartaric acid and NaBr, which exhibited satisfied activity for the asymmetric hydrogenation of LA to chiral GVL with a moderate enantioselectivity (60% ee) [70]. Very recently, a robust and highly active homogeneous chiral nickel–phosphine complex was established, which showed outstanding activity for LA hydrogenation to chiral GVL in high yields with excellent enantioselectivities (FIG. 3) [71, 72]. The complexation dynamics and catalytic functionality of $Ni(OTf)_2$, paired with (*S*,*S*)-Ph-BPE were investigated via high-resolution mass spectrometry (HRMS) and proton nuclear magnetic resonance (^{1}H NMR). Mechanistic analysis indicated that protonation facilitated substrate C=O bond activation, while hydrogen bonding governed enantiocontrol. This system exhibited robust applicability, enabling direct conversion of levulinic acid which was derived from *D*-fructose and even untreated bamboo powder-into enantiopure γ-valerolactone with preserved stereochemical integrity. Notably, the hydrogenation remained efficient at a 0.02 mol% catalyst loading, demonstrating scalability up to ten grams.

In addition to chiral GVL, recent attention has been focused on the development of other chiral chemicals from LA. As shown in FIG. 4, direct asymmetric reductive amination of LA to synthesize 5-methylpyrrolidinone with high optical purity was realized by using chiral Ru/bisphosphine as catalyst, wherein, H_2 was adopted as the reductant while NH_4OAc acted as nitro-

DOI: 10.1063/1674-0068/cjcp2504042

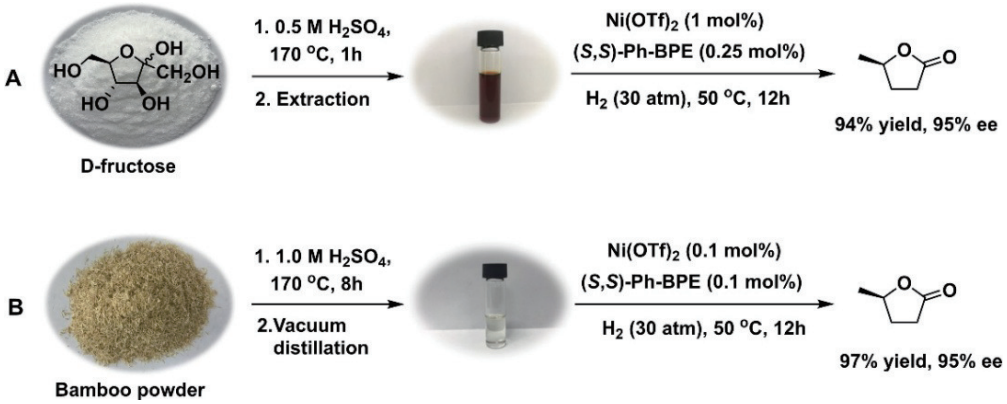


FIG. 3 The production of (*R*)-GVL from *D*-fructose and bamboo powder; adapted with permission from Ref.[71], copyright 2022 John Wiley and Sons.

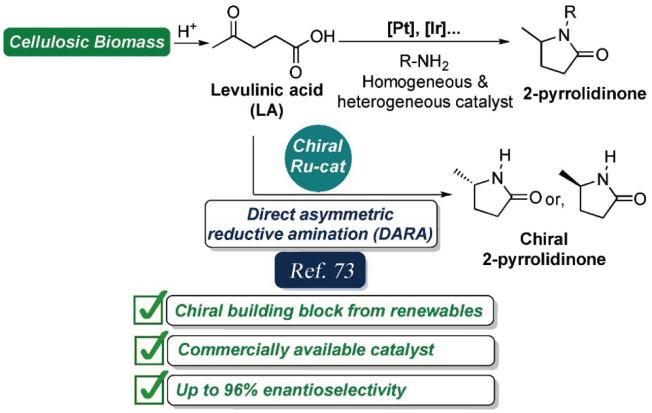


FIG. 4 Levulinic acid production directly from biomass and the further conversion into pyrrolidinone; adapted with permission from Ref.[73], copyright 2023 John Wiley and Sons.

gen source. Notably, as high as 96% ee and 89% of isolated yield were achieved [73]. Isotope-probing experiments and mass spectrometry analyses illustrated that the reaction pathway passed through imine-enamine tautomerization/cyclization, followed by cyclic enamide hydrogenation via asymmetric catalysis. It was also demonstrated that similar yield and selectivity could be obtained when methyl levulinate was used as feedstock in place of LA.

B. *D*-lactic acid synthesis

Lactic acid (LaA), a leading biomass-derived platform chemical, exists in two enantiomeric forms (*D*-LaA and *L*-LaA) and finds extensive applications in detergent formulations, cosmetic products, food processing, and as a synthetic building block [1–3]. Notably, LaA serves as the primary feedstock for polylactic acid (PLA) manufacturing, which is a frontrunner in sustainable alternatives to conventional plastics. PLA's exceptional biodegradability, tissue compatibility, and favorable material characteristics make it particularly valuable for biomedical and therapeutic uses [5, 6]. Current industrial LaA synthesis predominantly relies on microbial fermentation of food-grade biomass, with *L*-LaA constituting the major output. This preference stems from the economic viability of *L*-LaA-generating microbial strains [12]. In contrast, *D*-LaA biosynthesis faces significant hurdles, including microbial strain limitations and prohibitive production costs [74–77]. While chemical catalysis has been extensively explored as an alternative pathway, existing literature provides scarce data regarding stereochemical control in LaA [78–80]. The prevailing consensus suggests that the conventional catalytic systems employing non-chiral catalysts typically yield racemic LaA mixtures.

Recent work by Hu's research team demonstrated Y(III)-catalyzed conversion of monosaccharides and unprocessed biomass to *D*-LaA with 87% yield, but with modest enantioselectivity (<20% ee toward *D*-LaA) [81]. Building on this, they developed an innovative "MgO-*D*-LaA" catalytic system (FIG. 5) that showed remarkable cooperative effects in transforming trioses to *D*-LaA. This system delivered exceptional results, producing LaA in 90.1% yield with 77.2% ee when using pyruvaldehyde as the substrate under optimized parameters [82]. Combined experimental and computational studies identified $[Mg(OH)(H_2O)_3]^+$ as the catalytically active species, chiefly responsible for converting 1,3-dioxyacetone to pyruvaldehyde—an intermediate accessible through glucose retro-aldol cleavage from lignocellulosic biomass. Notably, mechanistic analysis revealed that pre-introduced *D*-LaA played a crucial role in directing enantioselective *D*-LaA formation from pyruvaldehyde, working in concert with solid-phase

DOI: 10.1063/1674-0068/cjcp2504042

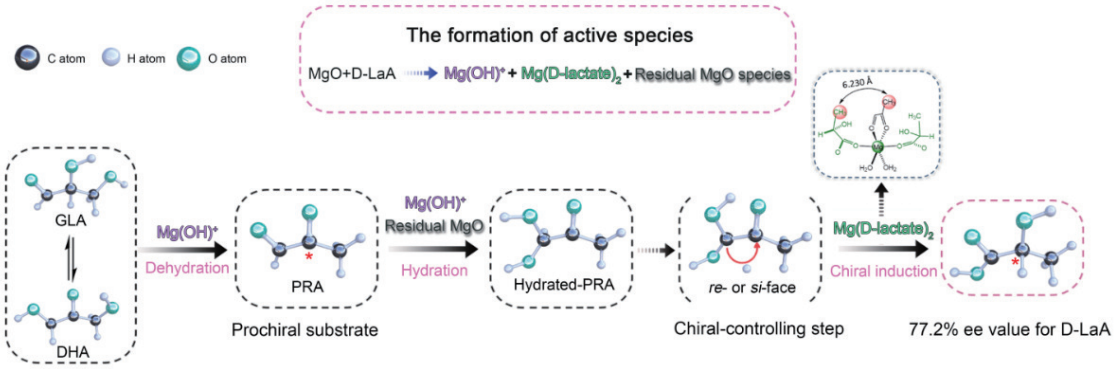


FIG. 5 The possible reaction pathway for the production of *D*-LaA from actual lignocellulosic biomass; adapted with permission from Ref.[82], copyright 2021 Elsevier.

MgO. Density functional theory calculations indicated that reduced steric constraints lowered the transition state strain energy, favoring *si*-face hydride transfer and consequently *D*-LaA formation. To broaden the system's utility, the researchers successfully adapted the protocol for glucose feedstock, attaining 80.2% LaA yield with 70.3% ee. Most remarkably, using untreated corn stover as the direct input material still afforded LaA in 57.9% yield with 49.8% ee under optimized reaction conditions.

A new "oligomer-first mechanism" was discovered in MgO-*D*-LaA system when xylose was employed as raw material to produce *D*-LaA [83]. ^{13}C NMR spectroscopy and DFT simulations confirmed that xylose initially underwent MgO-catalyzed aldol condensation, forming C_{10}/C_{15} oligomers through C–C coupling. These oligomeric species subsequently underwent selective C–C bond scission assisted by $[Mg(OH)(H_2O)_3]^+$ to generate C_3 intermediates. Remarkably, the system also demonstrated dual carbon valorization: (1) efficient recycling of glycolaldehyde (C_2 byproduct) through oligomerization to C_4/C_6 species that further participated in LaA synthesis, and (2) synergistic enhancement of carbon efficiency in hemicellulose conversion. This concerted mechanism achieved an unprecedented yield of 70.2 C-mol% LaA with 73.1% *D*-enantiomeric excess, substantially exceeding the theoretical maximum (60%) predicted by classical "3+2" transformation pathways (FIG. 6). Despite these advances, achieving perfect optical purity remained challenging. Studies revealed MgO-mediated epimerization of LaA enantiomers [84], with other alkaline earth oxides exhibiting analogous behavior. Isotope labeling experiments and computational modeling supported an "H-exchange" mechanism: the metal oxide abstracted the C2 proton, inducing electron delocalization to the carboxylate group. This transformed the C1–C2 σ bond into a σ-π hybridized system, generating a planar enolate intermediate. Subsequent protonation occurred with equal probability at either face (*re* or *si*) due to symmetric steric environments, ultimately producing racemic LaA. This fundamental racemization phenomenon explained the persistent challenge in obtaining enantiopure LaA from alkaline earth metal-catalyzed systems.

C. Lignin derivatives

Although lignin bears main β-O-4 units with (*R*,*S*/*S*,*R*) or (*R*,*R*/*S*,*S*) stereostructures, the heterogeneity of lignin structure makes it challenging to be efficiently depolymerized. Emerging research indicates that region-specific stereochemical variations may influence the enzymatic deconstruction of lignin polymers. Complementary investigations have demonstrated stereoselective lignin depolymerization activity in *Sphingobium* sp.-derived enzymes and related biocatalytic systems when acting on either native lignin or model compounds [85]. However, lignin depolymerization to chiral chemicals via chemocatalysis is still a grand challenge. The role of chiral centers in lignin biopolymers remains a pivotal yet unresolved factor affecting both biological and chemical depolymerization efficiency, thereby hindering lignin's utilization as a renewable platform chemical. To this end, the majority of endeavors have been paid to synthesize enantiomerically pure lignin models, which would act as a useful probe [86–90].

Long *et al.* [91] developed an innovative stereocontrolled synthetic route combining two established asym-

DOI: 10.1063/1674-0068/cjcp2504042

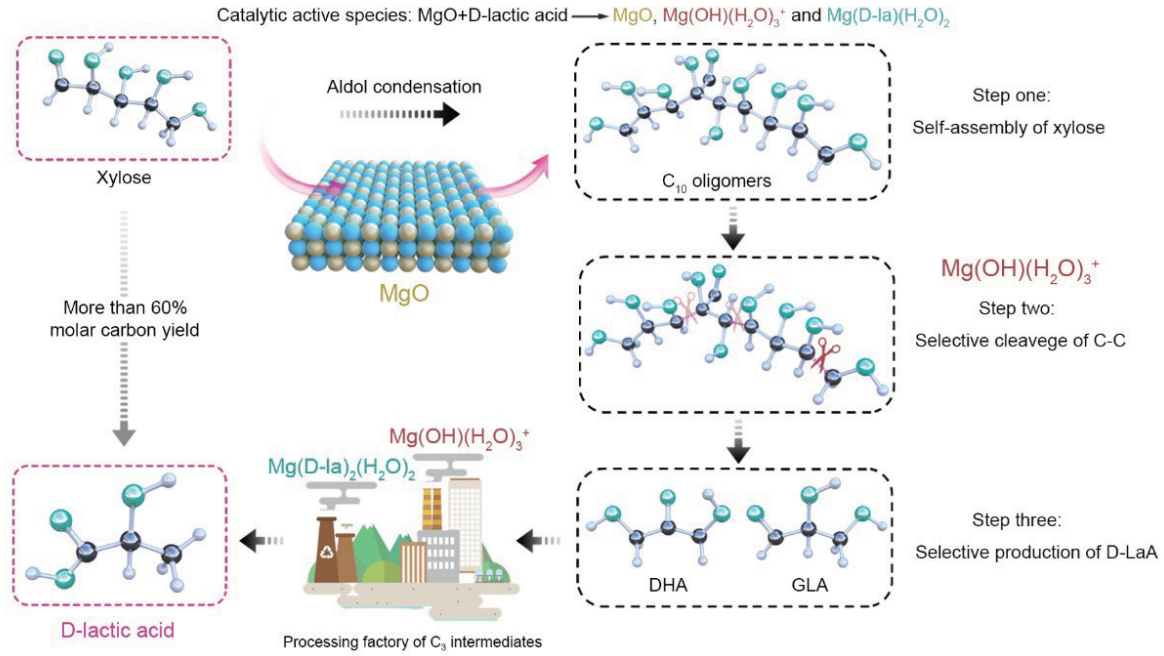


FIG. 6 The possible reaction mechanism on *D*-LaA production from xylose in MgO-*D*-LaA system; adapted with permission from Ref.[83], copyright 2021 Elsevier.

metric methodologies—sharpless asymmetric epoxidation (SAE) and Jacobson hydrolytic kinetic resolution (employing chiral salen-Co(III)OAc complexes)— to construct β-O-4 lignin dimer analogs incorporating S, G, and H subunits with exceptional enantiopurity (>99% ee) and satisfactory yields. The protocol first afforded both enantiomeric forms of diols **7a–7c** (FIG. 7) with ≥99% ee. Subsequent protection of the primary hydroxyl groups as *tert*-butyldimethylsilyl (TBS) – yielded optically pure intermediates **8a–8c**. These were then subjected to Mitsunobu coupling with 4-hydroxy-3-methoxybenzaldehyde, achieving complete β-carbon inversion to furnish protected (*S*,*S*)-configured dimers **9a–9c**. Sequential deprotection steps—fluoride-mediated TBS cleavage followed by palladium-catalyzed hydrogenolytic removal of benzyl groups in ethanolic medium— delivered the target enantiomerically enriched compounds **11a–11c**, with concurrent aldehyde reduction occurring during the final step. Hartwig's team [92] subsequently reported an optimized five-step enantioselective synthesis of β-O-4-linked (*R*,*R*)- and (*S*,*S*)-lignin dimers, featuring an Evans aldol reaction as the stereo determining step. Strategic Mitsunobu inversions enabled access to (*R*,*S*)- and (*S*,*R*)-diastereomers. Notably, this methodology permitted multigram-scale preparation of lignin models, overcoming previous synthetic limitations. The strategy was successfully adapted for constructing a lignin trimer analog while maintaining >99% ee and high overall yields (FIG. 8).

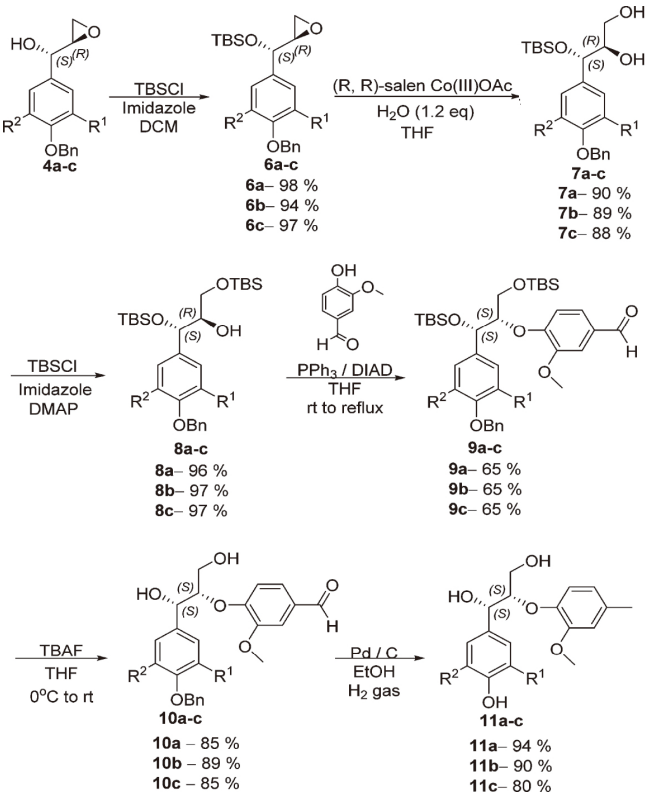


FIG. 7 The production of (*S*,*S*)-lignin dimers; adapted with permission from ref.[91], copyright 2015 American Chemical Society.

Two-dimensional POF (porous organic frameworks) heterogeneous catalysts were developed to explore the

DOI: 10.1063/1674-0068/cjcp2504042

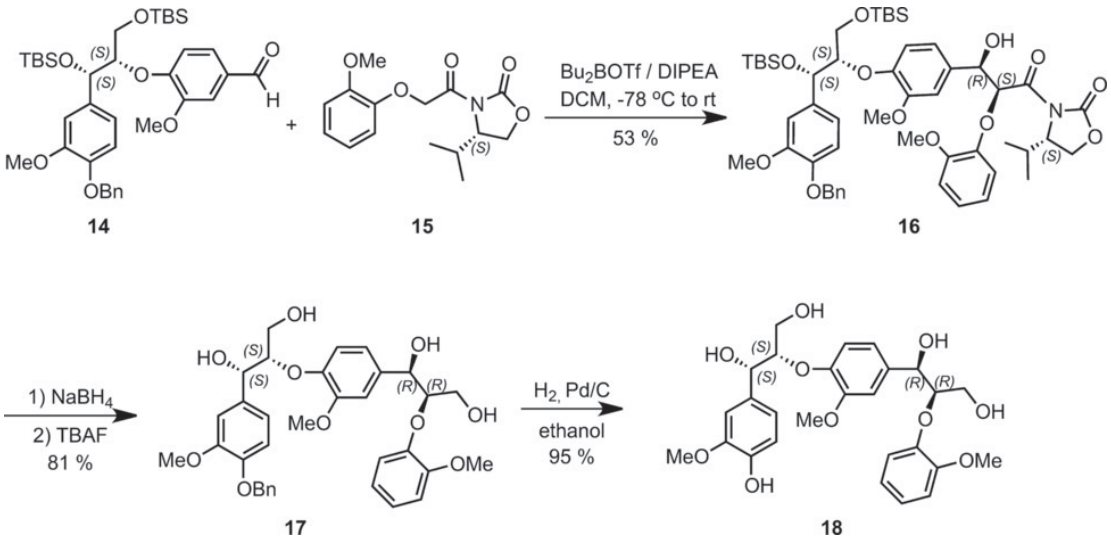


FIG. 8 Synthesis of enantiomerically pure lignin trimer model; adapted with permission from Ref.[92], copyright 2016 John Wiley and Sons.

special interactions for asymmetric catalysis of lignin-derived compounds [93]. Studies demonstrated that POF material exhibited exceptional aromatic compound sequestration capabilities, capturing>90% of such species within its porous matrix. This remarkable performance stemmed from the cooperative effects between the conjugated framework structure and π-electron system, showing binding affinities 10–100 times greater than conventional porous materials. Structural analysis revealed that phenyl moieties within the framework established strong π-π stacking interactions, creating sterically constrained environments around metallic active sites to enhance asymmetric induction. The catalytic system achieved near-quantitative conversion and exceptional stereocontrol (>99% ee) for diverse substrates including 2-acetonaphthone, 3-methylbutanone, 4-acetyl-biphenyl, 4'-methoxyacetophenone, 3',5'-bis(trifluoromethyl)-acetophenone, and 4'-chloroacetophenone. Mechanistic investigations employed (*S*)-tert-butyl (4-chloro-3-oxo-1-phenylbutan-2-yl) carbamate as a chiral probe in Ru/POF-L2 mediated transformations. The (*R*)-configured POF catalyst displayed 96.7% substrate conversion, stereoselectively transforming the (*S*)-precursor to (2*R*,3*S*)-1-chloro-2-hydroxy-3-(N-benzylamino)-4-phenylbutane with 90.3% ee.

III. CHIRAL CHEMICAL PRODUCTION BY PRESERVING THE INHERIT STEREOCENTER

In comparison to the conventional asymmetric catalysis, preserving the inherit stereocenter in lignocellulosic biomass has emerged as a potential approach to access optically pure chemicals with biomass feedstock acting as a chiral pool. For instance, short-chain chiral polyols and carboylic acids can be theoretically produced from C5–C6 monosaccharides derived from (hemi)cellulose components in biomass, where retro-aldol condensation is an effective method to shorten the carbon chain. However, little success has been achieved in using lignin as a chiral pool to produce optically pure chemicals. The precise cleavage of C–C bond while inhibiting configuration changes even loss of inherent stereocenters at the special sites is a key challenge, which only a minority of reports are available.

A. The reserve of one chiral center in saccharides

Glyceric acid (GA), a chiral molecule, was first isolated from tobacco leaves in 1956 and initially characterized as *D*-(*R*)-enantiomer. Research indicates that *D*-glyceric acid exhibits bioactivity, including hepatostimulatory effects, whereas *L*-glyceric acid serves as a potential precursor for synthesizing biologically relevant *L*-sugars [94]. Currently, microbial biocatalysis remains the predominant method for the enantioselective synthesis of glyceric acid.

Very recently, Hu's group explored an innovative strategy that inherited the special chiral center in biomass, and achieved *D*-glyceric acid production via chemocatalysis with the highest yield and excellent ee up to date [42]. This approach eliminated the use of chi-

DOI: 10.1063/1674-0068/cjcp2504042

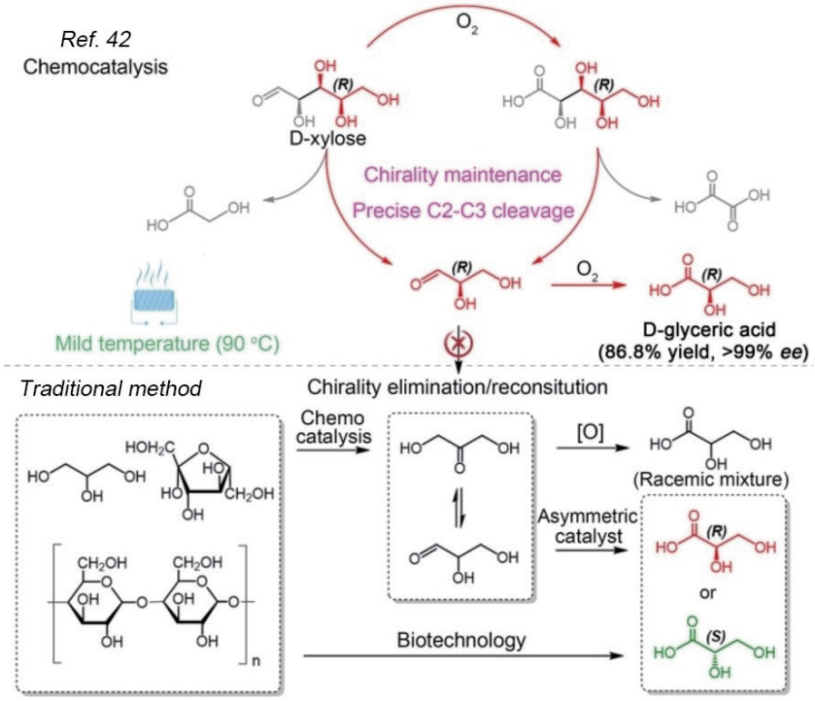


FIG. 9 The comparison for chiral glyceric acid production from biomass-based derivatives in this work with those in literature; adapted with permission from Ref.[42], copyright 2024 John Wiley and Sons.

ral catalysts/additives. Instead, an achiral heterogeneous Ag/γ-Al_2O_3 catalyst, consisting of both Ag_2O and metallic Ag active centers, was established. Ag^+ and Ag^0 species on the Ag/γ-Al_2O_3 catalyst exhibited remarkable cooperative-roles in *D*-xylose conversion to *D*-glyceric acid under relatively mild conditions. In detail, Ag^+ was responsible for low-temperature activation of *D*-xylose while Ag^0 facilitated the generation of active O* from O_2. The synergistic action of Ag^+ and active O* facilitated the selective scission of the C2–C3 bond. Crucially, active O* enabled rapid oxidation of the transient *D*-glyceraldehyde intermediate to form stable *D*-glyceric acid, effectively suppressing side reactions that would lead to chiral center loss (FIG. 9). Thorough experiments and characterization, including isotopic tracing combined with quantum chemical calculations, proved that the stereostructure at C4 of *D*-xylose was preserved and successfully transferred to C2 in *D*-glyceric acid in the process of C2–C3 cleavage. The starting material could also be extended to other *D*-pentoses. When *D*-ribose or *D*-arabinose was used as raw material, *D*-glyceric acid was produced as the major product with >99% ee. Using *L*-xylose as feedstock, as expected, *L*-glyceric acid was obtained with 75.1% yield and >99% ee. Similarly, *L*-ribose or *L*-arabinose as starting material produced *L*-glyceric acid with >99% ee.

B. The reserve of two chiral centers in saccharides

The multiple stereocenters in monosaccharides allow them to serve as the feedstock to produce chiral chemicals with more than one chiral center. Theoretically, *D*-tetroses (possessing two stereogenic centers) could be derived from *D*-glucose via retro-aldol cleavage. However, this process typically competes with dehydration pathways, yielding byproducts including methyl vinylglycolate, methyl-4-methoxy-2-hydroxybutanoate, and vinylglycolate. Notably, the C4-skeleton compound *D*-(−)-erythrose and its tautomer *D*-(+)-erythrulose represent particularly valuable chiral building blocks among these tetroses. *D*-(−)-erythrose demonstrates significant pharmaceutical utility as a versatile synthon. Through synthetic transformations involving erythritol, (+)-tanikolide, 2,4-di-O-benzyl-1-deoxymannojirimycin, and epimuricatacin intermediates, it can be efficiently converted to the non-natural enantiomer *L*-(+)-erythrose. Furthermore, oxidative modification of its aldehyde functionality followed by intramolecular cyclization produces *D*-(−)-erythronolactone (another widely employed chiral template in asymmetric synthesis).

Tang and Zhang developed a strategy for the catalytic conversion of *D*-hexoses to *D*-tetroses (mainly *D*-(+)-erythrulose and *D*-(−)-erythrose) via retro-aldol condensation [95]. Various homogeneous Lewis acid catalysts were screened, and molybdic and tungstic cata-

DOI: 10.1063/1674-0068/cjcp2504042

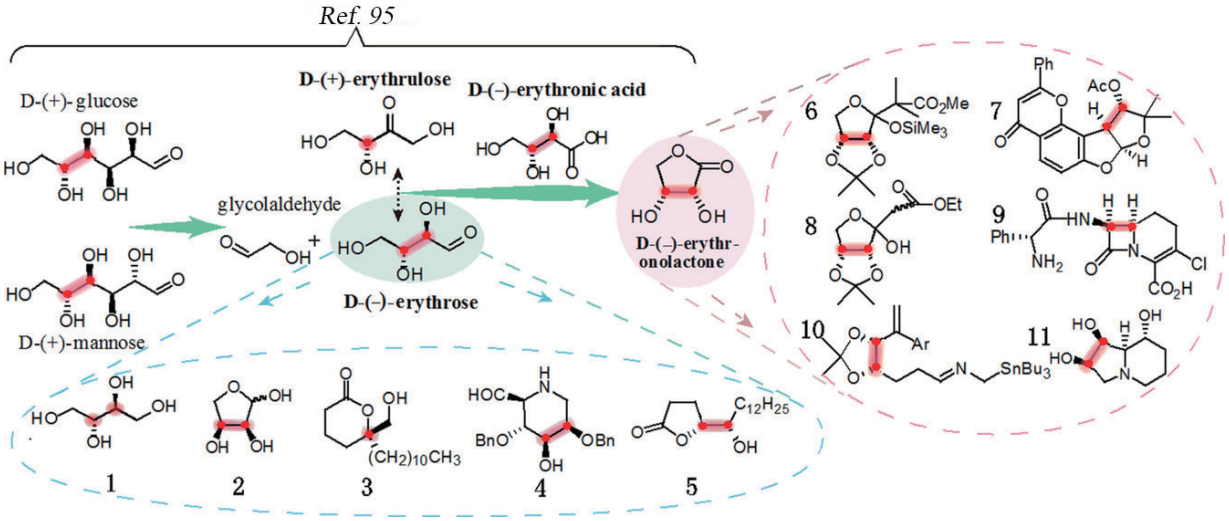


FIG. 10 The production of *D*-tetrose and *D*-(−)-erythronolactone from *D*-hexose and other potential target chiral chemicals, where the chirality of natural carbohydrates was retained and transferred to the target products. **1**: Erythritol, **2**: *L*-(+)-erythrose, **3**: (+)-tanikolide, **4**: 2,4-di-O-benzyl-1-deoxymannojirimicyn, **5**: (−)-2-epimuricatacin, **6**: isopropyildene-2,2-dimethyl-3-O-trimeth-ylsilyl-a-d-erythro-3,6-furanoso-3-hexulosonate, **7**: (−)-semiglabrin, **8**: lactol, **9**: loracarbef, **10**: (2-aza-allyl)stannane, and **11**: (−)-swainsonine; adapted with permission from Ref.[95], copyright 2017 John Wiley and Sons.

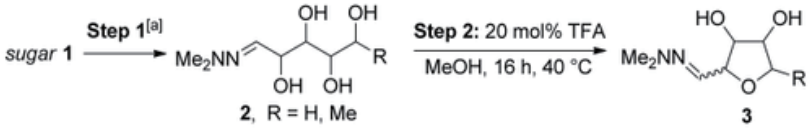
lysts exhibited outstanding activity for the transformation of *D*-(+)-glucose, yielding tetrose and glycolaldehyde. 46.1% yield of tetrose was obtained when ammonium tungstate was adopted as the catalyst (FIG. 10). In addition, several byproducts, including dehydration products derived from tetrose and a few C_3 compounds, were also detected. Among them, erythrose was the main tetrose product by the catalysis of a series of tungstic compounds, while erythrulose was obtained in the case of molybdic species as catalyst. Mass spectrometry, specific rotation, ^{1}H NMR and ^{13}C NMR analyses were employed to verify the production of erythrose and its chirality, which well matched with those of commercial *D*-(−)-erythrose. It was suggested that the production of C_4 compounds greatly depended on the relative isomerization and epimerization rates of *D*-(−)-fructose, *D*-(+)-glucose, and *D*-(+)-mannose. During the retro-aldol process of glucose, erythrose could sequentially be transformed into glyceric acid, whereas the generated glyceric acid could be further converted to erythrose again via an aldol condensation reaction. When the produced *D*-(−)-erythrose was employed as the feedstock, the chiral centers could be completely retained in the final chiral synthon.

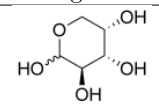
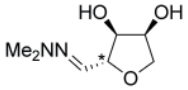
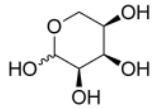
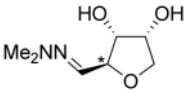
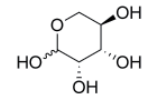
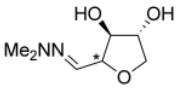
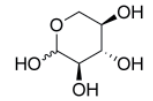
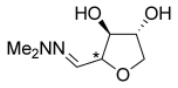
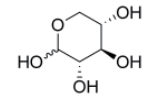
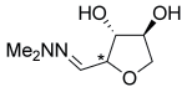
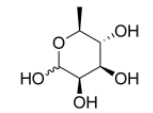
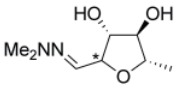
L-arabinose, a byproduct in sugar beet industry with abundant reserves, has been employed as a raw material to produce chiral tetrahydrofuran (THF) through a hydrazone-based strategy [96]. In detail, *N*,*N*-dimethylhydrazine and Amberlyst 15 acidic resin in methanol at room temperature gave hydrazone **2a** in 99% yield (Table I). When stirring hydrazone **2a** was performed in methanol with 20 mol% TFA at 40 °C for 16 h, the complete conversion of **2a** was obtained. As a consequence, THF **3a** was obtained in 67% yield containing two stereoisomers in a ratio of 75:25 (mixture). This approach could be extended to other biomass-derived reducing sugars. For example, the enantiomeric THF ent-**3a** could be synthesized from *D*-ribose in a 59% yield with two steps. The substrate could be extended to *D*-lyxose, yielding hydrazone as the major product with 98% yield. The cyclization reaction mediated by TFA produced THF derivative **3b** in 66% yield, showing a 55:45 diastereomeric ratio (dr). Alternatively, **3b** was synthesized from *D*-xylose in two steps with 61% overall yield and the same diastereoselectivity. Using *L*-rhamnose as the starting material afforded THF **3c** in 69% yield with a 60:40 dr. This approach proved versatile for preparing various functionalized chiral tetrahydrofurans and enabled the formal synthesis of 3*R*-3-hydroxymuscarine. A proposed reaction mechanism featurs a key vinyldiazenium intermediate in the cyclization step.

Levoglucosenone (LGO), bearing six different functional carbon atoms with two chiral centers, can be prepared from biomass and has been intensively used in myriad applications. For instance, LGO has been widely used to produce monomers that act as the precursor to synthesize polymers (*e.g.*, polyacrylates, polyolefins,

DOI: 10.1063/1674-0068/cjcp2504042

TABLE I The synthesis of THFs 3 via a two-step reaction using sugar as feedstock; adapted with permission from Ref.[96], copyright 2015 John Wiley and Sons.



Entry	Suger 1	Step 1 yield/%	THF 3[b]	Step 2 yield/%	dr[c]
1	 L-arabinose **1a**	99	 **3a**	67 (66)[d]	75:25
2	 D-ribose **1b**	98	 *ent*-**3a**	59	75:25
3	 D-lyxose **1c**	98	 **3b**	66	55:45
4	 D-xylose **1d**	not isolated	 **3b**	61[e]	55:45
5	 L-xylose *ent*-**1d**	not isolated	 *ent*-**3b**	57	55:45
6	 L-rhamnose **1e**	99	 **3c**	69	60:40

[a] Substrates and Reaction conditions: Amberlyst®15, NH_2NMe_2 (2.0 equiv), 24 h, MeOH, RT.
[b] Unless otherwise stated, the reaction was conducted on a 6.0–6.7 mmol scale.
[c] Based on the results of crude ^{1}H NMR.
[d] The reaction was performed using 20.0 g (104 mmol) of hydrazone **2a**.
[e] Yield over two steps from xylose.

photo-crosslinkable polycarbonates and polyesters). LGO is also employed as a raw material to synthesize chiral ligands, auxiliaries, and bioactive chemicals such as pheromones (*e.g.*, anticancer drugs, antifungi, and japonilure) and flavors (*e.g.*, dairy lactone). These works have certified the significant applications of LGO as a chiral synthon to synthesize valuable commodities and molecules. A mini-review [97] described the production of LGO through various strategies from different raw materials, including pure cellulose, lignocellulosic biomass, and non-sugar compounds. It was pointed out that the pyrolysis process by the catalysis of phosphoric acid catalyst obviously improved LGO selectivity to 30% using glucose, cellulose, even birch, and pine wood as biomass sources. When zeolites were employed as acid catalyst, LGO selectivity could be enhanced up to 40%, while the yields of other valuable oxygenated products like furfural were also increased. LGO also acted as a feedstock to produce other chiral chemicals. Sn-Beta and related metallozeolites effectively catalyzed the oxidative conversion of LGO to enantiomerically enriched (*S*)-γ-hydroxymethyl-α,β-butenolide (HBO) (FIG. 11) [44]. A one-pot catalytic system employing H_2O_2 as the oxidant and Sn-Beta as the catalyst afforded the target butenolide in 75% yield. Significant yield enhancement to 90% was achieved through a sequential two-step protocol combining Sn-Beta with acidic Amberlyst-15 resin.

DOI: 10.1063/1674-0068/cjcp2504042

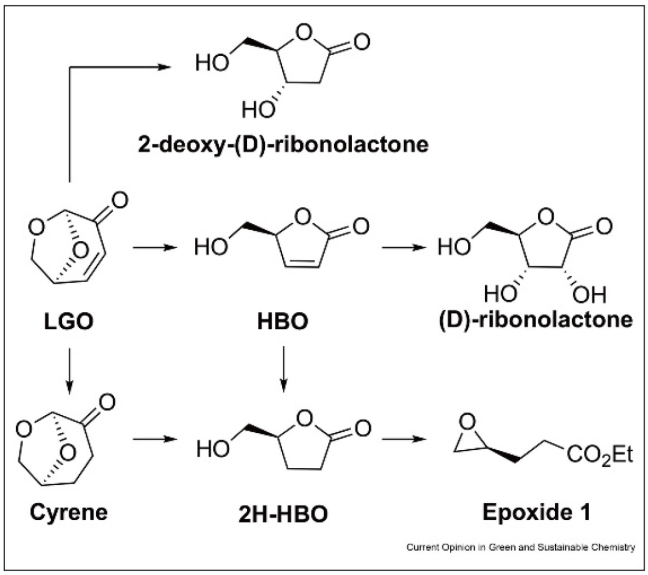


FIG. 11 The production of cyrene and high-value chiral building blocks from LGO; adapted with permission from Ref. [97], Copyright 2023 Elsevier.

C. The complete reserve of stereostructure in monosaccharides

The stereocontrolled assembly of oligosaccharides from monosaccharide building blocks presents significant synthetic challenges, requiring precise orchestration of regio-, stereo-, and chemoselective transformations while preserving native carbohydrate configurations. Niu's team pioneered an innovative O-glycosylation paradigm that substantially reduced protecting group manipulation through catalyst-mediated control, enabling direct 1,2-*cis*-glycosidic bond formation with programmable site-selectivity [98]. This catalytic approach circumvented traditional –deprotection complications by employing designed aminoboronic acid catalysts that governed glycosyl transfer through a sophisticated interplay of dynamic covalent B–O bonds and directional hydrogen bonding networks. The catalyst architecture dictated reaction outcomes by modulating spatial proximity between glycosyl donors and acceptors, with catalyst variations enabling programmable site-switching of glycosylation. Notably, this system operated through a robust catalyst-determined mechanism rather than substrate-directed control, exhibiting broad functional group tolerance across diverse monosaccharides (glucose, galactose, fructose, arabinose) and compatibility with various protecting groups (silyl, ester, benzylidene). The methodology's versatility extended to complex disaccharide donors, facilitating access to architecturally sophisticated oligosaccharides. The same group [99] developed stable ortho-iodobiphenyl sulfide glycosyl donors for phenol glycosylation via Pd-catalyzed SN2 displacement. This bench-stable system preserved carbohydrate integrity while enabling late-stage diversification of pharmaceuticals and natural products through stereo-defined glycosylation, offering new avenues for modulating bioactive compound properties.

IV. CONCLUSIONS AND PROSPECTS

In summary, the three major components in lignocellulosic biomass all show the potential for producing chiral compounds. As the most abundant linear polysaccharide in nature, the conversion of cellulose component in biomass typically involves cascade steps such as depolymerization, isomerization, C–C bond cleavage, and asymmetric hydrogenation or oxidation. Chiral carboxylic acids (*e.g.*, saccharic acid, lactic acid, glyceric acid, erythritic acid, *etc.*), lactone (*e.g.*, GVL), and polyols (*e.g.* erythritol; erythrol) with various carbon chains and their derivatives can be produced depending on the different reaction pathways and reaction conditions. The hemicellulose component enriches in C_5-sugar stereochemistry. The branched structure of hemicellulose presents unique opportunities for chiral lactone synthesis. The key challenge in (hemi)cellulose transformation to chiral chemicals relates to the competing polymerization and epimerization during sugar decomposition, which might significantly reduce chiral yields. Different from (hemi)cellulose, lignin's complexity and irregular structure mainly yields chiral aromatic compounds, while innovative strategies to maintain optical purity during depolymerization are also highly required. For instance, radical recombination usually happens during lignin depolymerization, yielding new polymer with high molecular weight which is resistant to be further converted. In biomass transformation to produce chiral chemicals, two strategies including asymmetric catalysis and the reserve of inherent stereocenters in the original structure, have been adopted. Through the introduction of asymmetric catalyst in the key reaction steps, the functional groups of target chemicals can be modulated by conventional asymmetric catalysis, thereby affording various kinds of chiral chemicals. However, some issues are encountered, such as the complicated process to synthesize asymmetric catalyst, as well as its recyclability and high cost. Moreover, the reaction con-

DOI: 10.1063/1674-0068/cjcp2504042

ditions for biomass conversion are generally harsh, discovering asymmetric ligands and catalysts that remain effective under such conditions remains a significant challenge. Alternatively, chiral chemicals prepared by preserving the chiral centers in natural biomass structure avoids the reconstruction of chiral center, which aligns with the principles of green chemistry and sustainable development. Nevertheless, the structure and diversity of target chiral chemicals are significantly dependent on the inherent stereostructure of biomass, where adjusting the functional groups is quite challenging under the premise of chiral preservation. Despite the state-of-the-art progresses, the current processes for producing chiral compounds from biomass are in its infancy stage. Biomass feedstock contains numerous chiral units with diverse structure, however, the multitude of reaction types involved in biomass conversion makes it challenging to control the preservation of chiral centers during the process. The kinds of chiral chemicals derived from biomass remain limited, and the optical purity is required to be improved.

As the global scientific community intensifies its focus on sustainable chemistry, the field of biomass-derived chiral chemicals stands at a pivotal juncture. Building upon three decades of progress since Prof. Qingshi Zhu's visionary insights, we identify four transformative research directions that promise to redefine the stereoselective synthesis of chiral chemicals from renewable resources.

A. Synergizing asymmetric catalysis with the native chirality in biomass

The integration of well-established asymmetric catalysis techniques with biomass' inherent chiral pools presents an unprecedented opportunity to expand the chemical space of sustainable chiral compounds. Future research should focus on: (i) developing hybrid catalytic systems that synergistically combine organo-, metal-, and bio-catalysis with biomass-derived chiral synthons; (ii) designing cascade reactions that preserve and amplify the stereochemical information embedded in biomass components; (iii) creating computational tools to predict optimal combinations of catalytic systems and biomass feedstocks for target molecular architectures. This integrated approach could yield novel classes of pharmaceuticals, specialty chemicals, and advanced materials with precisely engineered stereochemical properties while dramatically reducing the environmental footprint of chiral synthesis.

B. Mastering polyfunctional complexity: holistic utilization of biomass' multichiral centers

Current methodologies often treat biomass' multiple stereocenters as synthetic challenges rather than opportunities. A paradigm shift is needed to develop: (i) selective yet flexible transformation strategies that can simultaneously address multiple chiral centers; (ii) novel protecting-group-free methodologies that leverage the inherent reactivity patterns of polyfunctional biomass molecules; (iii) stereodivergent synthesis platforms capable of generating diverse stereoisomers from single biomass precursors. Particular attention should be paid to dynamic kinetic resolution and parallel kinetic resolution that can efficiently convert complex biomass mixtures into enantiopure products. These advancements enable access to molecular complexity rivaling natural products while maintaining atom economy and process efficiency.

C. Unlocking lignin's stereochemical treasury: the next frontier in biomass valorization

While carbohydrates have dominated biomass chiral chemistry, lignin— nature's most abundant source of aromatic chirality—remains largely untapped. Key research priorities include: (i) developing mild, selective depolymerization methods that preserve lignin's stereochemical integrity; (ii) establishing robust catalytic systems for the asymmetric functionalization of lignin-derived phenols and other aromatic chiral building blocks; (iii) creating structure-property relationships for lignin-based chiral compounds to guide application development; (iv) investigating the potential of lignin's unique C–C bonded architectures to create novel chiral scaffolds unavailable from other biomass sources. The successful exploitation of lignin's stereochemical diversity could revolutionize sustainable chiral chemistry, providing access to entirely new classes of compounds with large-scale applications.

Success in these endeavors will require close collaboration across catalysis, synthetic methodology, process engineering, and computational chemistry. Ultimately, these advances will not only honor the prophetic vision of pioneers like Prof. Zhu but also contribute significantly to the development of a truly sustainable chemical industry grounded in the principles of green chem-

DOI: 10.1063/1674-0068/cjcp2504042

istry and circular economy.

D. Developing cost-effective reaction system to reduce production cost

Current biomass-to-chiral routes remain energy-intensive, but life-cycle analysis suggests carbon-negative benefits could offset costs to some extent. Enhancing the economic viability of biomass represents a critical factor in improving its competitiveness against conventional fossil resources. The economic viability of biomass-derived chiral chemicals hinges on three pivotal factors: feedstock availability and pretreatment costs, catalytic system efficiency, and product separation/purification requirements. (i) Raw lignocellulosic biomass offers a cost advantage over petrochemical routes; however, pretreatment processes (*e.g.*, steam explosion, acid hydrolysis) to extract the target components account for a high fraction of total production costs, necessitating optimization of delignification and saccharification steps. The coproduction of value-added byproducts from different component in biomass (*e.g.*, lignin-derived aromatics and sugar-based chiral chemicals) is a potential strategy. (ii) The development of heterogeneous chemo-catalysts seems to be more cost-effectiveness compared to expensive enzymatic approaches. Moreover, scale-up from the present refined sugar and lignin models to demonstration plants could achieve cost parity with conventional synthesis through integration of continuous flow reactors. (iii) The energy-intensive nature of chiral separation (*e.g.*, simulated moving bed chromatography, membrane-assisted resolution) shows potential for reducing separation costs.

V. ACKNOWLEDGEMENTS

This work is supported by the National Natural Science Foundation of China (Nos. 22478263, 22308230), Natural Science Foundation of Sichuan (No.2024NSFSC1134), China Postdoctoral Science Foundation (No.2024T170612), 111 center (B17030), and the Fundamental Research Funds for the Central Universities.

This work is dedicated to the 80th anniversary of Prof. Qingshi Zhu, who, in as early as the 1990s, foresaw the shift in chemical research from fossil resources to the utilization of renewable biomass. Moreover, he emphasized the importance of leveraging natural chiral units derived from biomass in his 973 Program application. Over the past three decades, significant progress has been made in this field.

[1] F. A. Castillo Martinez, E. M. Balciunas, J. M. Salgado, J. M. Domínguez González, A. Converti, and R. P. de S. Oliveira, Trends Food Sci. Technol. **30**, 70 (2013).
[2] M. Dusselier, P. Van Wouwe, A. Dewaele, E. Makshina, and B. F. Sels, Energy Environ. Sci. **6**, 1415 (2013).
[3] M. Morales, P. Y. Dapsens, I. Giovinazzo, J. Witte, C. Mondelli, S. Papadokonstantakis, K. Hungerbühler, and J. Pérez-Ramírez, Energy Environ. Sci. **8**, 558 (2015).
[4] G. A. Martau, V. Coman, and D. C. Vodnar, Crit. Rev. Biotechnol. **40**, 608 (2020).
[5] M. Murariu and P. Dubois, Adv. Drug Deliv. Rev. **107**, 17 (2016).
[6] N. G. Ricapito, C. Ghobril, H. Zhang, M. W. Grinstaff, and D. Putnam, Chem. Rev. **116**, 2664 (2016).
[7] W. S. Chow, E. L. Teoh, and J. Karger-Kocsis, Express Polym. Lett. **12**, 396 (2018).
[8] M. Nofar, D. Sacligil, P. J. Carreau, M. R. Kamal, and M. C. Heuzey, Int. J. Biol. Macromol. **125**, 307 (2019).
[9] D. J. Garlotta, Polym. Environ. **9**, 63 (2001).
[10] H. Tsuji and Y. Arakawa, Polym. Chem. **9**, 2446 (2018).
[11] S. Klotz, N. Kaufmann, A. Kuenz, and U. Prusse, Appl. Microbiol. Biotechnol. **100**, 9423 (2016).
[12] M. A. Abdel-Rahman, Y. Tashiro, and K. Sonomoto, Biotechnol. Adv. **31**, 877 (2013).
[13] R. Gerardy, D. P. Debecker, J. Estager, P. Luis, and J. M. Monbaliu, Chem. Rev. **120**, 7219 (2020).
[14] B. Zhang, B. K. Biswal, J. Zhang, and R. Balasubramanian, Chem. Rev. **123**, 7193 (2022).
[15] J. Iglesias, I. Martinez-Salazar, P. Maireles-Torres, D. Martin Alonso, R. Mariscal, and M. Lopez Granados, Chem. Soc. Rev. **49**, 5704 (2020).
[16] L. T. Mika, E. Csefalvay, and A. Nemeth, Chem. Rev. **118**, 505 (2018).
[17] M. Wang, J. Ma, H. Liu, N. Luo, Z. Zhao, and F. Wang, ACS Catal. **8**, 2129 (2018).
[18] A. Kumar, P. Daw, and D. Milstein, Chem. Rev. **122**, 385 (2022).
[19] L. Lin, X. Han, B. Han, and S. Yang, Chem. Soc. Rev. **50**, 11270 (2021).
[20] Z. Zhang, J. Song, and B. Han, Chem. Rev. **117**, 6834 (2017).
[21] Z. Zhang and G. W. Huber, Chem. Soc. Rev. **47**, 1351 (2018).
[22] J. Li, W. Zhang, S. Xu, and C. Hu, Front. Chem. **8**, 70 (2020).
[23] M. Tamura, N. Yuasa, J. Cao, Y. Nakagawa, and K. Tomishige, Angew. Chem. Int. Ed. **57**, 8058 (2018).
[24] C. Espro, E. Paone, F. Mauriello, R. Gotti, E. Uliassi,

M. L. Bolognesi, D. Rodriguez-Padron, and R. Luque, Chem. Soc. Rev. **50**, 11191 (2021).
[25] M. Besson, P. Gallezot, and C. Pinel, Chem. Rev. **114**, 1827 (2014).
[26] I. Delidovich, P. J. Hausoul, L. Deng, R. Pfutzenreuter, M. Rose, and R. Palkovits, Chem. Rev. **116**, 1540 (2016).
[27] A. Farran, C. Cai, M. Sandoval, Y. Xu, J. Liu, M. J. Hernaiz, and R. J. Linhardt, Chem. Rev. **115**, 6811 (2015).
[28] A. R. Morais, A. M. da Costa Lopes, and R. Bogel-Lukasik, Chem. Rev. **115**, 3 (2015).
[29] X. Zhang, K. Wilson, and A. F. Lee, Chem. Rev. **116**, 12328 (2016).
[30] T. Ennaert, J. Van Aelst, J. Dijkmans, R. De Clercq, W. Schutyser, M. Dusselier, D. Verboekend, and B. F. Sels, Chem. Soc. Rev. **45**, 584 (2016).
[31] W. Schutyser, T. Renders, S. Van den Bosch, S. F. Koelewijn, G. T. Beckham, and B. F. Sels, Chem. Soc. Rev. **47**, 852 (2018).
[32] J. C. Serrano-Ruiz, R. Luque, and A. Sepulveda-Escribano, Chem. Soc. Rev. **40**, 5266 (2011).
[33] P. Sudarsanam, E. Peeters, E. V. Makshina, V. I. Parvulescu, and B. F. Sels, Chem. Soc. Rev. **48**, 2366 (2019).
[34] X. Liu, Z. Jiang, S. Feng, H. Zhang, J. Li, and C. Hu, Fuel **244**, 247 (2018).
[35] Y. M. Questell-Santiago, M. V. Galkin, K. Barta, and J. S. Luterbacher, Nat. Rev. Chem. **4**, 311 (2020).
[36] E. Calcio Gaudino, G. Cravotto, M. Manzoli, and S. Tabasso, Chem. Soc. Rev. **50**, 1785 (2021).
[37] M. J. Climent, A. Corma, and S. Iborra, Green Chem. **16**, 516 (2014).
[38] J. S. Luterbacher, D. Martin Alonso, and J. A. Dumesic, Green Chem. **16**, 4816 (2014).
[39] P. Y. Dapsens, C. Mondelli, and J. Perez-Ramirez, Chem. Soc. Rev. **44**, 7025 (2015).
[40] G. Yang and L. Zhou, ACS Catal. **8**, 6691 (2018).
[41] X. Li, J. Wu, and W. J. Tang, Am. Chem. Soc. **144**, 3727 (2022).
[42] R. Yang, S. Xu, X. Wang, Y. Xiao, J. Li, and C. Hu, Angew. Chem. Int. Ed. **63**, e202403547 (2024).
[43] J. M. Tukacs, B. Fridrich, G. Dibó, E. Székely, and L. T. Mika, Green Chem. **17**, 5189 (2015).
[44] C. Paris, M. Moliner, and A. Corma, Green Chem. **15**, 2101 (2013).
[45] V. S. Shende, A. B. Raut, P. Raghav, A. A. Kelkar, and B. M. Bhanage, ACS Omega **4**, 19491 (2019).
[46] K. Götz, A. Liese, M. Ansorge-Schumacher, and L. Hilterhaus, Appl. Microbiol. Biotbiotechnol. **97**, 3865 (2013).
[47] S. H. Lee and O. J. Park, Appl. Microbiol. Biotechnol. **84**, 817 (2009).
[48] T. Osawa and Y. Tanabe, Catal. Lett. **148**, 824 (2018).
[49] C. Zhou, Y. Xiao, S. Xu, J. Li, and C. Hu, Ind. Eng. Chem. Res. **59**, 17228 (2020).
[50] X. Li, J. Li, X. Liu, Q. Tian, and C. Hu, Catalysts **8**, 241 (2018).
[51] N. Arai, T. Namba, K. Kawaguchi, Y. Matsumoto, and T. Ohkuma, Angew. Chem. Int. Ed. **130**, 1400 (2018).
[52] Q. Hu, Z. Zhang, Y. Liu, T. Imamoto, and W. Zhang, Angew. Chem. Int. Ed. **54**, 2260 (2015).
[53] J. H. Xie, X. Y. Liu, X. H. Yang, J. B. Xie, L. X. Wang, and Q. L. Zhou, Angew. Chem. Int. Ed. **51**, 201 (2012).
[54] T. Touge, T. Hakamata, H. Nara, T. Kobayashi, N. Sayo, T. Saito, Y. Kayaki, and T. Ikariya, J. Am. Chem. Soc. **133**, 14960 (2011).
[55] F. H. Zhang, F. J. Zhang, M. L. Li, J. H. Xie, and Q. L. Zhou, Nat. Catal. **3**, 621 (2020).
[56] W. Li, J. H. Xie, H. Lin, and Q. L. Zhou, Green Chem. **14**, 2388 (2012).
[57] J. Deng, Y. Wang, T. Pan, Q. Xu, Q. X. Guo, and Y. Fu, ChemSusChem **6**, 1163 (2013).
[58] U. Omoruyi, S. Page, J. Hallett, and P. W. Miller, ChemSusChem **9**, 2037 (2016).
[59] W. R. H. Wright, and R. Palkovits, ChemSusChem **5**, 1657 (2012).
[60] T. Ohkuma, M. Kitamura, and R. Noyori, Tetrahedron Lett. **31**, 5509 (1990).
[61] E. V. Starodubtseva, O. V. Turova, M. G. Vinogradov, L. S. Gorshkova, and V. A. Ferapontov, Russ. Chem. Bull. **54**, 2374 (2005).
[62] M. L. Li, Y. Li, J. B. Pan, Y. H. Li, S. Song, S. F. Zhu, and Q. L. Zhou, ACS Catal. **10**, 10032 (2020).
[63] R. Noyori and S. Hashiguchi, Acc. Chem. Res. **30**, 97 (1997).
[64] S. Gladiali and E. Alberico, Chem. Soc. Rev. **35**, 226 (2006).
[65] X. Wu, C. Wang, and J. Xiao, Platinum Met. Rev. **54**, 3 (2010).
[66] F. Foubelo and M. Yus, Chem. Rec. **15**, 907 (2015).
[67] J. Václavík, P. Šot, B. Vilhanová, J. Pecháček, M. Kuzma, and P. Kačer, Molecules **18**, 6804 (2013).
[68] T. Koike and T. Ikariya, Adv. Synth. Catal. **346**, 37 (2004).
[69] A. V. Karnik, S. T. Patil, S. S. Patnekar, and A. Semwal, New J. Chem. **28**, 1420 (2004).
[70] H. Jacobs, K. Berryman, J. Jones, and A. Gopalan, Synth. Commun. **20**, 999 (1990).
[71] C. Q. Deng, J. Liu, J. H. Luo, L. J. Gan, J. Deng, and Y. Fu, Angew. Chem. Int. Ed. **61**, e202115983 (2021).
[72] J. Cha, Y. Choi, C. Sung, M. Kim, W. K. Park, and K. Min, Bioresour. Technol. **418**, 131895 (2025).
[73] S. Chakrabortty, S. Zheng, F. Kallmeier, E. Baráth, S. Tin, and J. G. de Vries, ChemSusChem **16**, e202202353 (2023).
[74] X. Wang, G. Wang, X. Yu, H. Chen, Y. Sun, and G. Chen, Bioresour. Technol. **239**, 490 (2017).
[75] H. J. Park, J. H. Bae, H. J. Ko, S. H. Lee, B. H. Sung, J. I. Han, and J. H. Sohn, Biotechnol. Bioeng. **115**, 2232 (2018).
[76] Y. Zhang, M. Yoshida, and P. V. Vadlani, Biotechnol. Lett. **40**, 1167 (2018).

DOI: 10.1063/1674-0068/cjcp2504042

[77] Y. Zhang, A. Kumar, P. R. Hardwidge, T. Tanaka, A. Kondo, and P. V. Vadlani, Biotechnol. Prog. **32**, 271 (2016).
[78] W. Deng, P. Wang, B. Wang, Y. Wang, L. Yan, Y. Li, Q. Zhang, Z. Cao, and Y. Wang, Green Chem. **20**, 735 (2018).
[79] Y. Wang, W. Deng, B. Wang, Q. Zhang, X. Wan, Z. Tang, Y. Wang, C. Zhu, Z. Cao, G. Wang, and H. Wan, Nat. Commun. **4**, 2141 (2013).
[80] Z. Tang, W. Deng, Y. Wang, E. Zhu, X. Wan, Q. Zhang, and Y. Wang, ChemSusChem **7**, 1557 (2014).
[81] S. Xu, J. Li, Y. Wu, Y. Xiao, and C. Hu, iScience **12**, 132 (2019).
[82] S. Xu, T. He, J. Li, Z. Huang, and C. Hu, Appl. Catal. B: Environ. **292**, 120145 (2021).
[83] S. Xu, Y. Xiao, J. Li, W. Zhang, and C. Hu, Chem. Eng. J. **432**, 134359 (2022).
[84] W. Zhang, S. Xu, X. Wang, Y. Liu, R. Yang, J. Li, and C. Hu, Ind. Crop. Prod. **193**, 116260 (2023).
[85] C. W. Lahive, P. J. Deuss, C. S. Lancefield, Z. Sun, D. B. Cordes, C. M. Young, F. Tran, A. M. Z. Slawin, J. G. de Vries, P. C. J. Kamer, N. J. Westwood, and K. Barta, J. Am. Chem. Soc. **138**, 8900 (2016).
[86] J. Ralph, J. Peng, F. Lu, R. D. Hatfield, and R. F. Helm, J. Agric. Food Chem. **47**, 2991 (1999).
[87] L. Jösson, O. Karlsson, K. Lundquist, and P. O. Nyman, FEBS Lett. **276**, 45 (1990).
[88] D. L. Gall, H. Kim, F. C. Lu, T. J. Donohue, D. R. Noguera, and J. J. Ralph, Biol. Chem. **289**, 8656 (2014).
[89] D. L. Gall, J. Ralph, T. J. Donohue, and D. R. Noguera, Environ. Sci. Technol. **48**, 12454 (2014).
[90] E. Masai, A. Ichimura, Y. Sato, K. Miyauchi, Y. Katayama, and M. J. Fukuda, Bacteriology **185**, 1768 (2003).
[91] C. Njiojob, J. L. Rhinehart, J. Bozell, and B. L. J. Long, Org. Chem. **80**, 1771 (2015).
[92] C. N. Njiojob, J. J. Bozell, B. K. Long, T. Elder, R. E. Key, and W. T. Hartwig, Chem. Eur. J. **22**, 12506 (2016).
[93] Y. Yang, D. Deng, S. Zhang, Q. Meng, Z. Li, Z. Wang, H. Sha, R. Faller, Z. Bian, X. Zou, G. Zhu, and Y. Yuan, Adv. Mater. **32**, 1908243 (2020).
[94] S. J. Sato, Ole. Sci. **70**, 289 (2021).
[95] S. Lin, X. Guo, K. Qin, L. Feng, Y. Zhang, and Y. Tang, ChemCatChem **9**, 4179 (2017).
[96] R. W. Foster, C. J. Tame, D. K. Bučar, H. C. Hailes, and T. D. Sheppard, Chem. Eur. J. **21**, 15947 (2015).
[97] F. Allais, Curr. Opin. Green Sust. Chem. **40**, 100744 (2023).
[98] Q. D. Dang, Y. H. Deng, T. Y. Sun, Y. Zhang, J. Li, X. Zhang, Y. D. Wu, and D. Niu, Nature **632**, 313 (2024).
[99] L. Deng, Y. Wang, S. Xu, A. Shen, H. Zhu, S. Zhang, X. Zhang, and D. Niu, Science **382**, 928 (2023).

DOI: 10.1063/1674-0068/cjcp2504042