Supporting Information

Isolation and purification of 4-propylguaiacol and 4-propylsyringol by extraction and crystallization from the products of reductive catalytic fractionation processes

Tianyu Ren,[a,†] Zhaofeng Zhang,[a,†] Shengping You,[*,a,d] Wei Qi,[*,a,b,c,d], Rongxin Su[a,b,c,d] and Zhimin He [a]

[a] Chemical Engineering Research Center, School of Chemical Engineering and Technology, Tianjin University, Tianjin, 300072, China

[b] State Key Laboratory of Chemical Engineering, Tianjin University, Tianjin, 300072, China

[c] Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin, 300072, China

[d] Tianjin Key Laboratory of Membrane Science and Desalination Technology, Tianjin University, Tianjin, 300072, China

[†] These authors contributed equally to this work.

[*] Corresponding author at: Chemical Engineering Research Center, School of Chemical Engineering and Technology, Tianjin University, Tianjin, 300072, China

E-mail address: qiwei@tju.edu.cn (Wei Qi); ysp@tju.edu.cn (Shengping You)

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S1. Material

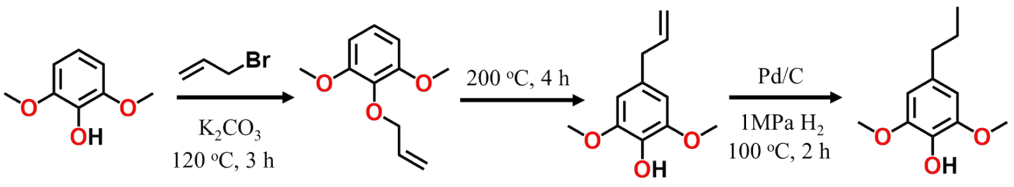
Poplar was from Taian, Shandong Provence, China, and is the same with that used in our previous work.[1] Poplar was crashed and sieved. The part of > 60 mesh was used for reaction. The composition of poplar: lignin: 21.0 wt.%; cellulose: 44.5 wt.%; hemicellulose: 14.8 wt.%; and water: 6.3 wt.%.

Phenol (99%), 4-methylphenol (99%), guaiacol (98%), 4-methylguaiacol (98%), 4-propylguaiacol (98%), allyl bromide (98%), Methyl 3-(4-hydroxyphenyl)propionate (98%), potassium carbonate (98%), sodium hydroxide (96%), 5%Pd/C and 5%Ru/C were from Shanghai Aladin chemical corporation; 4-ethylphenol (97%), 4-propylphenol (99%), and DMSO-d6 (with 0.03% tetramethylsilane) were from Tianjin Heowns chemical corporation; 4-ethylguaiacol (99%) was from Shanghai Yuanye chemical corporation; syringol (98%) was from Adamas corporation; potassium hydroxide (85%) was from Tianjin Kemel chemical corporation; hydrochloric acid (AR) was from Tianjin Jiangtian chemical corporation; dichloromethane (99%), n-hexane (99%), acetone (99%), ethylene glycol (99%) and methanol (99%) were from Tianjin Concord chemical corporation.

It should be highlighted that the purity of potassium hydroxide is typically 85% for AR or technical grade. The impurities may include water, K_2CO_3, KCl, etc. Due to the low content, 10% more KOH was added when preparing the KOH solution.

For the sake of simplification, in this work, we designated some lignin-based monomers as A-B, where A = H, G, or S (for hydroxylphenyl, guaiacyl or syringyl, respectively), and B = 0, 1, 2, 3 or 4 (for no sidechain, 4-methyl-, 4-ethyl-, 4-propyl- or 4-butyl-, respectively). For example, H-0 and G-3 represent phenol and propylguaiacol, respectively. Likewise, the sodium and potassium phenolate were designated as A-BNa and A-BK, respectively.

Preparation of 4-propanylsyringol (S-3): the method was modified from a protocol in the literature.[2] The pathway is presented in. In a typical reaction, 10 g (~65 mmol) S-0, 17 g (~123 mmol) K_2CO_3, 8.5 g (~70 mmol) allyl bromide were mixed into 50 ml acetone. The mixture was stirred and heated to 120 °C for 4 h in an autoclave in oil bath. Afterwards, the product was filtered and rotary-evaporated. The red-brown mixture (rich in 2,6-dimethoxy-O-allylphenol) was transferred into an autoclave and stirred and heated to 200 °C for 4 h. Then, the as-formed product (rich in allylsyringol) was dissolved into 50 ml methanol and 0.2 g 5%Pd/C was added. The mixture was hydrogenated under 1 MPa H_2 at 100 °C for 2 h to generate S-3. The product was filtered and rotary-evaporated. Typically, the distribution of products was: S-3: ~70%; S-0: ~20%; 2,6-dimethoxy-O-allylphenol: ~8%; and dimers: ~2%. Thus, a purification method was developed. The product was extracted with hexane to separate dimers and rotary-evaporated. Next, the mixture was dissolved in DCM and extracted with 0.05-0.1 mol/L KOH solution until S-0 was completely removed, followed by extraction with 0.4-0.6 mol/L KOH solution to extract S-3. Afterwards, the KOH solution was acidified and reversely extracted with DCM which was subsequently evaporated. The final product was ~9 g with 97+% S-3.



Scheme S1 Reaction pathway for synthesis of S-3

S2. Experimental

S2.1 Determination of solubility of G-3 and S-3 in alkali solution

To a KOH or NaOH solution (0.2 – 3 mol/L, 10 or 20 ml) was added G-3 and/or S-3 and an equivalent mol amount of KOH or NaOH. The mixture was heated to ensure a completely dissolved solution. Afterwards, the solution was cooled down to 65, 15, or 4 °C to crystallize. A double-layer beaker and a water bath circulator were used to maintain a stable temperature environment which was accurately measured by a K-type thermal couple. If no crystal formed, reheat the solution and add more phenols and alkali. When the solution stopped crystallization and was maintained for more than 1 h, a liquor of supernatant was sampled. It was acidified with hydrochloric acid and extracted with DCM for 2 times. The DCM phase was rotary-evaporated and the residual was dissolved in methanol containing internal standard, followed by detection with GC-FID (the conditions can be found in Section S2.6).

S2.2 Typical RCF and ARCF reactions

The reaction conditions were modified from our previous work, and the yield of G-3, S-3, and main impurities in the product were close to those reported in the work.[1]

RCF: 8 g poplar sawdust and 0.8 g 5%Ru/C were put into 80 ml methanol. The mixture was transferred to a stainless-steel reactor. After replacing the air with pressured H_2 for 3 times, the mixture was pressured with H_2 to 3MPa. Then, the mixture was heated in an oven to 230 °C and stirred at 500 rpm for 3 h. Then, the reactor was removed from the oven and cooled to room temperature. After filtering the mixture, the liquid product was obtained. The reaction was repeated 10 times to prepare the product used for the isolation discribed in the main text.

ARCF: 15 g poplar sawdust and 1.5 g 5%Ru/C were well mixed in 300 ml EG solution of 0.4 g/L sulfuric acid. The mixture and a magnetic stir bar were transferred into a 500 ml beaker. The mixture were heated to 190 °C and stirred at 500 rpm for 3 h. After filtering the mixture, the liquid product was obtained.

S2.3 Determination of solubilities of G-3 and S-3 in alkali solution

To a KOH or NaOH solution (0.2 – 3 mol/L, 10 or 20 ml) was added proper amount of G-3 and/or S-3 and an equivalent mol amount of KOH or NaOH. The mixture was heated to ensure a completely dissolved solution. Afterwards, the solution was cooled down to 65, 15, or 4 °C to crystallize. A double-layer beaker and a water bath circulator were used to maintain a stable temperature environment which was accurately measured by a K-type thermal couple. If no crystal formed, reheat the solution and add more phenols and alkali. When the solution stopped crystallization and was maintained for more than 1 h, a liquor of supernatant was sampled. It was acidified with hydrochloric acid and extracted with DCM for 2 times. The DCM phase was rotary-evaporated and the residual was dissolved in methanol containing internal standard, followed by detection with GC-FID (the GC conditions can be found in Section S2.6).

S2.4 Preparation of monomer-enriched oil

The method was modified from a protocol in the literature.[3]

(1) Removing solvent:

From RCF: the product solution of RCF was rotary-evaporated to yield the product oil.

From ARCF: the product solution of ARCF was diluted with 3 times the volume of water and extracted with 0.5 times the volume of DCM for 5 times. The DCM phase was rotary-evaporated to yield the product oil.

(2) Preparation of monomer-enriched oil: the product oil was dissolved in ~50 ml methanol and reduced at 150 °C for 2 h under 3 MPa H_2 catalyzed by 0.5 g 5%Ru/C. Then, the solution was filtered and evaporated to yield hydrogenated product oil. The hydrogenated product oil (containing ~6 g (RCF) or ~3 g (ARCF) phenolic monomers) was dissolved in 30 ml DCM and extracted with 30 ml water for 5 times. The DCM phase was rotary-evaporated to yield lignin oil, which was subsequently extracted with 50 ml hexane for 4 times at 65 °C. The hexane phase was concentrated to less than 100 ml and stored at -20 °C. Then, the hexane phase was transferred. Adding 50 ml hexane twice to re-extract the as-formed precipitate and storing the mixture at -20 °C. Finally, the hexane phases were combined and rotary-evaporated to yield the monomer-enriched oil. We obtained 4.54 g monomer-enriched oil from RCF of 80 g poplar, containing 33% G-3 and 53% S-3; and 2.48 g from ARCF of ~50 g poplar, containing 31% G-3 and 56% S-3.

S2.5 Separation and purification of G-3 and S-3 from ARCF/RCF derived monomer-enriched oil

We conducted and compared two separation protocols with and without recycling residual KOH and DCM phases. During the isolation, small amount of components were sampled at due time and analyzed to study the process, which is described in Section S2.6.

For RCF monomer-enriched oil (recycle residual components twice): a total of ~4.38 g monomer-enriched oil (containing 1.35 g G-3 and 2.19 g S-3) was used for separation. In the first cycle, 1.61 g monomer-enriched oil was dissolved into 15 ml DCM. Then, the DCM phase was consecutively extracted with 15 ml 0.4, 0.5, 0.5 and 0.6 mol/L KOH solution. The KOH solutions were filtered, combined, and concentrated to ~39 ml using a rotary evaporator, followed by slowly cooling down to 4 °C to form S-3K crystal which was washed with 4 ml cold 2.5 mol/L KOH solution (S-3(1) GC purity: 98.3%, Fig. S9). Then, in the second cycle, to the residual DCM solution was added 1.50 g monomer-enriched oil. The DCM phase was extracted with the residual KOH solution (combined with the KOH solution used for washing S-3K, and containing G-3K and minor S-3K) diluted with water (~15 ml × 4 times, 63 ml in total). The aqueous KOH phase was filtered and added with 2 ml 10 mol/L KOH to increase KOH concentration. Then, the solution was cooled to 4 °C to yield S-3K crystal (washed, S-3(2) GC purity: 96.7%). Afterwards, the solution was further concentrated to ~33 ml using a rotary evaporator and cooled to 4 °C to further yield more S-3K crystal (washed, S-3(3) GC purity: 95.4%). Lastly, in the third cycle, 1.27 g monomer-enriched oil was added into the residual DCM solution, followed by extraction with diluted residual KOH solution (~15 ml × 4 times, 55 ml in total). The DCM phase was further extracted with fresh aqueous KOH (~10 ml 1 mol/L KOH, 2 times). The aqueous solutions were combined and concentrated to ~40 ml and cooled to yield S-3K (washed, S-3(4) GC purity: 96.6%). Then, the filtrate was further concentrated to ~17 ml and cooled to further remove minor S-3K (as an impurity to G-3), followed by acidifying to ~0.7 mol/L KOH and extracting with DCM. Removing DCM yielded the isolated G-3 product (1.23 g, GC purity: 88.4%). Combining and acidifying four S-3K crystals (Fig. S9), multiply extracting with DCM, and removing DCM yielded the isolated S-3 product (2.02 g, GC purity: 96.4%).

For ARCF monomer-enriched oil (without recycling): ~2.48 g monomer-enriched oil (containing 0.73 g G-3 and 1.30 g S-3) was dissolved into 15 ml DCM. Then, the DCM phase was consecutively extracted with 20 ml 0.4, 0.45, 0.6, and 0.75 mol/L KOH solution. The KOH phase was filtered, combined, and concentrated to ~30 ml using a rotary-evaporator. During the concentration, S-3K crystals were formed. Reheat the concentrated KOH solution in a water bath to ensure a transparent solution and slowly decrease the temperature to 4 °C to crystallize S-3K. Afterwards, S-3K crystals were filtered and washed with 8 ml 2.5 mol/L cold KOH solution. Acidifying S-3K, extracting with DCM, and removing DCM finally yielded isolated S-3 product (1.00 g, GC purity: 95.9%). The KOH filtrate was further concentrated to 20 ml and cooled in iced water to further remove minor S-3K as an impurity to G-3. Then, the solution was filtrated and acidified to ~1.3 mol/L KOH, followed by multiple extraction with DCM. Removing DCM yielded G-3 product (0.65 g, GC purity: 84.3%).

Further purification by crystallization: a sample of S-3K crystal (containing ~0.65 g S-3, 95.5%) produced from RCF monomer-enriched oil was dissolved into 10 ml 0.7 mol/L KOH at 70 °C. Then, the solution was slowly cooled down to 4 °C to recrystallize. The crystal was filtered, acidified, and extracted with DCM, without the need to wash. Removing DCM yielded ~0.45 g S-3 with 98.3% GC purity. As for G-3, 0.30 g G-3 (88.4%, as mentioned above) was dissolved in 10 ml 1 mol/L aqueous NaOH. Filtrate the solution to remove a small amount of undissolved S-3Na. Then, 1.5 ml 10 mol/L aqueous NaOH were added to increase the concentration. G-3Na was crystallized at 4 °C, followed by filtration, acidification, and extraction with DCM. Remove DCM to obtain ~0.24 g G-3 with 93.1% GC purity.

S2.6 Sampling and components analysis

During the separation from monomer-enriched oil, samples were taken at the due time to detect and study the components in each part. In order not to lose too much products, small amounts of samples were taken. For the DCM phase, ~0.2 ml was sampled directly for GC detection; for alkali solution, 0.5 ml was sampled, followed by acidification and extraction with 0.5 ml DCM. The DCM phase was used for GC detection; for S-3K crystals, a small piece (~3% weight of each S-3K crystal product) was sampled, followed by acidification and extraction with 0.5 ml DCM. The DCM phase was used for GC detection; for isolated G-3 and S-3 products, directly dissolve the sample using DCM to a high concentration of > 150 mg/ml and detect using GC.

All samples were quantitatively analyzed by GC-FID (Agilent 7890B). Injector temperature: 300 °C; detector temperature: 300 °C; column: HP-5 (30 m × 0.320 mm × 0.25 μm); column temperature: 70 °C-2 min-8 °C/min-150 °C-15 °C/min-300 °C-8 min. The structure of impurities was determined using GC-MS (Agilent 7890B-5977A). The injector and column temperature were the same with GC-FID, while the column was HP-5ms (30 m × 0.250 mm × 0.25 μm).

Purity is considered the most important information of this work. Thus, all samples from the separation of monomer-enriched oil were analyzed using external standard method, because (1) adding internal standard dilutes the sample, (2) the GC peak of internal standard may cover impurities' peaks, and (3) internal standard could contain trace amount of impurities, all interfering the identification of impurities in the sample and calculation of the purity.

It is not possible to accurately calculate the content of each impurity. Thus, for simplification, apart from S-3 which using effective carbon number method to evaluate the response factor, all other impurities were supposed to have the same response factors with G-3. The purity of compound i is calculated as follow:

$$GC\ purity_i = \frac{A_i\ (i \neq S-3)\ or\ A_{S-3} \times 1.18}{A_{G-3} + A_{S-3} \times 1.18 + A_{all\ impurities}} \times 100\%$$

where A is the area of GC peak; $A_{\text{all impurities}}$ is the total area of all peaks excluding solvent, G-3, and S-3; 1.18 is the relative response factor of S-3 to G-3.

S2.7 Extraction of phenolics by KOH solution

All the extraction were conducted at room temperature (19 ± 3 °C). In an extraction, shake violently to mix the two phases, and it takes several seconds to 2 mins for phase separation.

Single extraction: 2.4 mmol phenols was dissolved in 8 ml DCM containing dodecane as internal standard. 1 ml DCM solution was extracted with 1 ml KOH solution with concentration of 0.05, 0.1, 0.3, 0.6, 1.0, and 1.5 mol/L. Then, the DCM phase, as well as the starting DCM solution, were detected by GC-FID.

Co-extraction of G-3 and S-3: 0.4 g (2.4 mmol) G-3 and 0.8 g (4.1 mmol) S-3 were dissolved in 10 ml DCM. 1 ml DCM solution was extracted with 1 ml KOH solution with a concentration of 0.1 - 0.5 mol/L. Then, the DCM phase, as well as the starting DCM solution, were detected by GC-FID.

S2.8 Preparation of monomer-enriched oil rich in 4-propanolguaiacol (G-3OH) and 4-propanolsyringol (S-3OH) and the attempt for the isolation

The two monomers were produced via RCF process catalyzed by Pd/C. The conditions were similar to the RCF condition described in Section S2.2, but 5%Pd/C was used instead of 5%Ru/C. The product was rotary-evaporated to remove the solvent. The residual was dissolved in DCM at ratio of 1 g: 10 ml. The same volume of 0.2 mol/L aqueous NaOH solution was added twice to extract the phenols. The NaOH extracting solution were combined and acidified with hydrochloric acid. The as-formed solution was extracted with equivalent volume of 90% hexane - 10% ethyl acetate solution for 3 times. Then, extracting the aqueous phase with equivalent volume of DCM twice. After removing DCM, the monomer-enriched oil containing 29% G-3OH and 59% S-3OH was obtained.

G-3OH and S-3OH have high polarity and solubility in water. Their solubilities are > 30 mg/ml in water. When they become salts of Li, Na, and K, their solubility increases sharply. Thus, no crystals can be found. The precipitate of the sodium salt of S-3OH began to form when NaOH concentration was > 4 mol/L which is far from a practical condition. Moreover, the purity and yield of the as-formed precipitate were still not satisfactory.

S2.9 Characterization

Nuclear Magnetic Resonance (NMR): Each sample was weighed and dissolved in DMSO-d6 (containing tetramethylsilane as internal reference) to form a solution of 20 mg/ml. The mixture was transferred to NMR tubes and detected with JEOL JNM ECZ600R (600 MHz) for 1H spectra and AVANCE IIITM HD 400 MHz NanoBAY (400MHz) for 13C spectra. The spectra were processed with MestReNova software.

Powder X-ray diffraction (XRD): The crystals of S-3K and G-3Na were grounded into powder, followed by loading them in a XRD sample stage. The samples were tested with a Rigaku Smartlab (8 kW) using Cu-Kα radiation.

S3. Figures and Tables

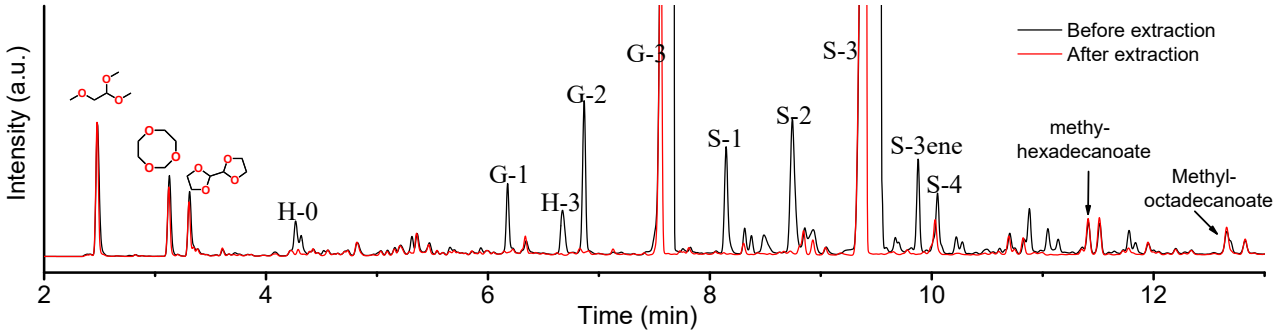


Fig. S1 Enlarged GC spectrum (region of monomers) of DCM-dissolved monomer-enriched oil before extraction (black line) and after extraction with KOH solution and recycling twice (red line). The spectra are overlapped for better comparison. Abbreviations: H = hydroxyphenyl, G = guaiacyl, S = syringyl, 0 = without side chain, 1 = 4-methyl, 2 = 4-ethyl, 3 = 4-propyl, 3ene = 4-propenyl, 4 = 4-butyl.

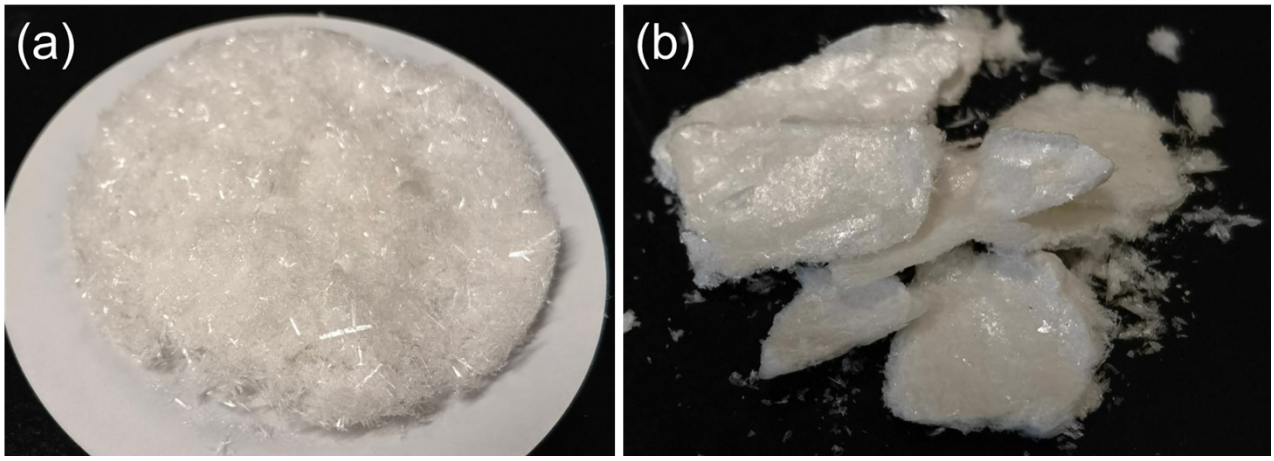


Fig. S2 Enlarged pictures of insets in Scheme 1. (a) S-3K crystal; (b) G-3Na crystal.

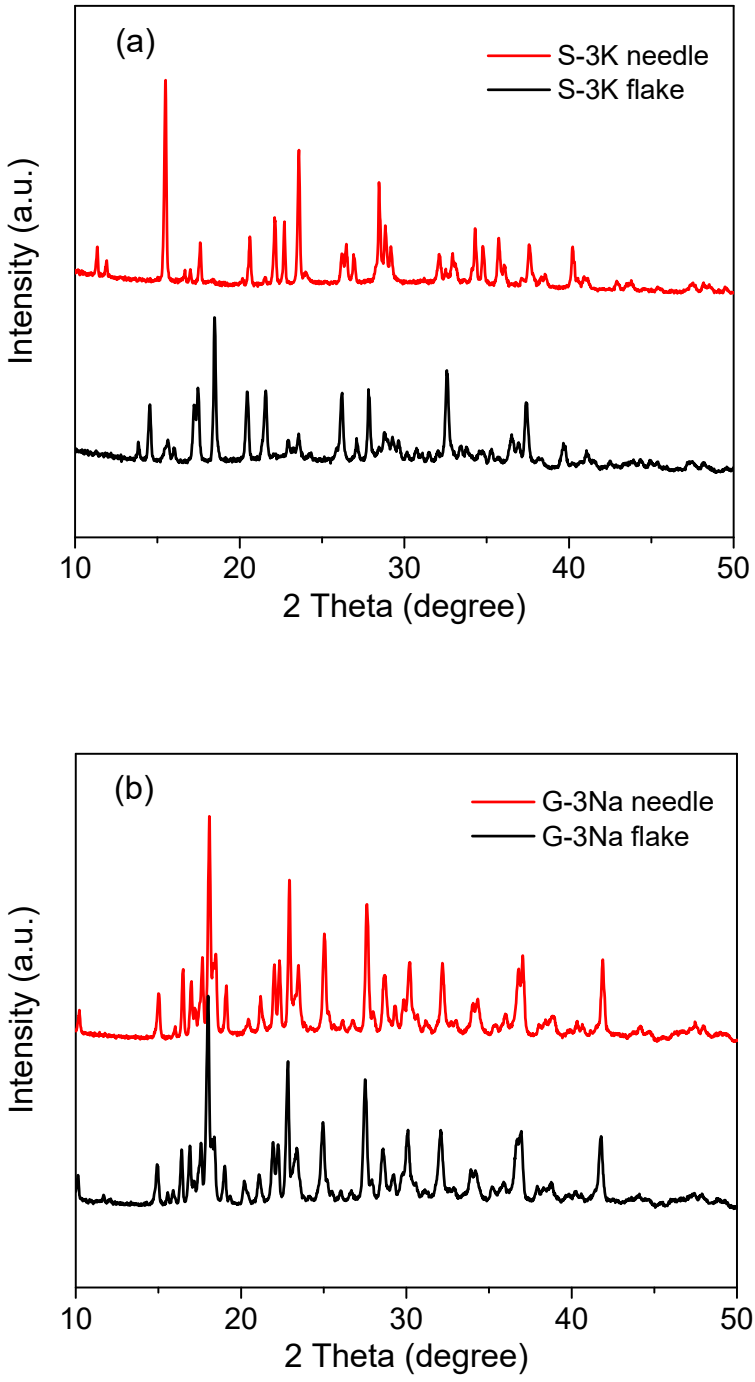


Fig. S3 XRD patterns of (a)S-3K and (b) G-3Na crystals in the form of needle and flake. No evident peak found at $2\theta > 50°$. Sample preparation condition: S-3K: 0.3 g S-3 dissolved in 10 ml 1 M KOH, slowly cool down to 4 °C (needle) or directly store at 4 °C (flake); G-3Na: 0.3 g G-3 dissolved in 10 ml 2.5 or 2.0 M NaOH, slowly cool down to 4 °C (needle) or directly store at 4 °C (flake).

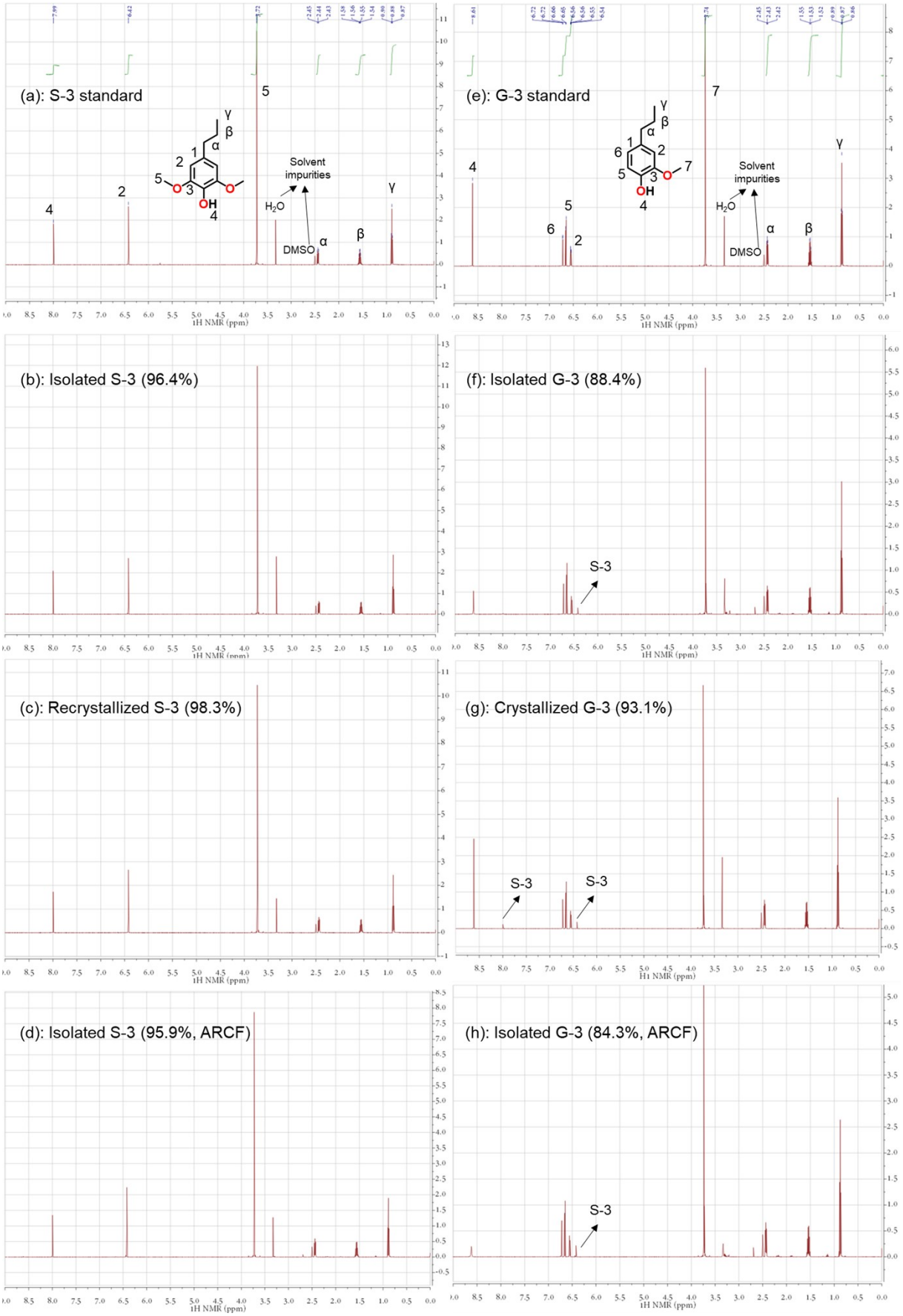


Fig. S4 1H NMR spectra of the standards and the 6 products of S-3 and G-3 (Fig. S7). The numbers in parathesis are GC purities. The solvent used for the test was DMSO-d6. H_2O and DMSO are impurities of the solvent.

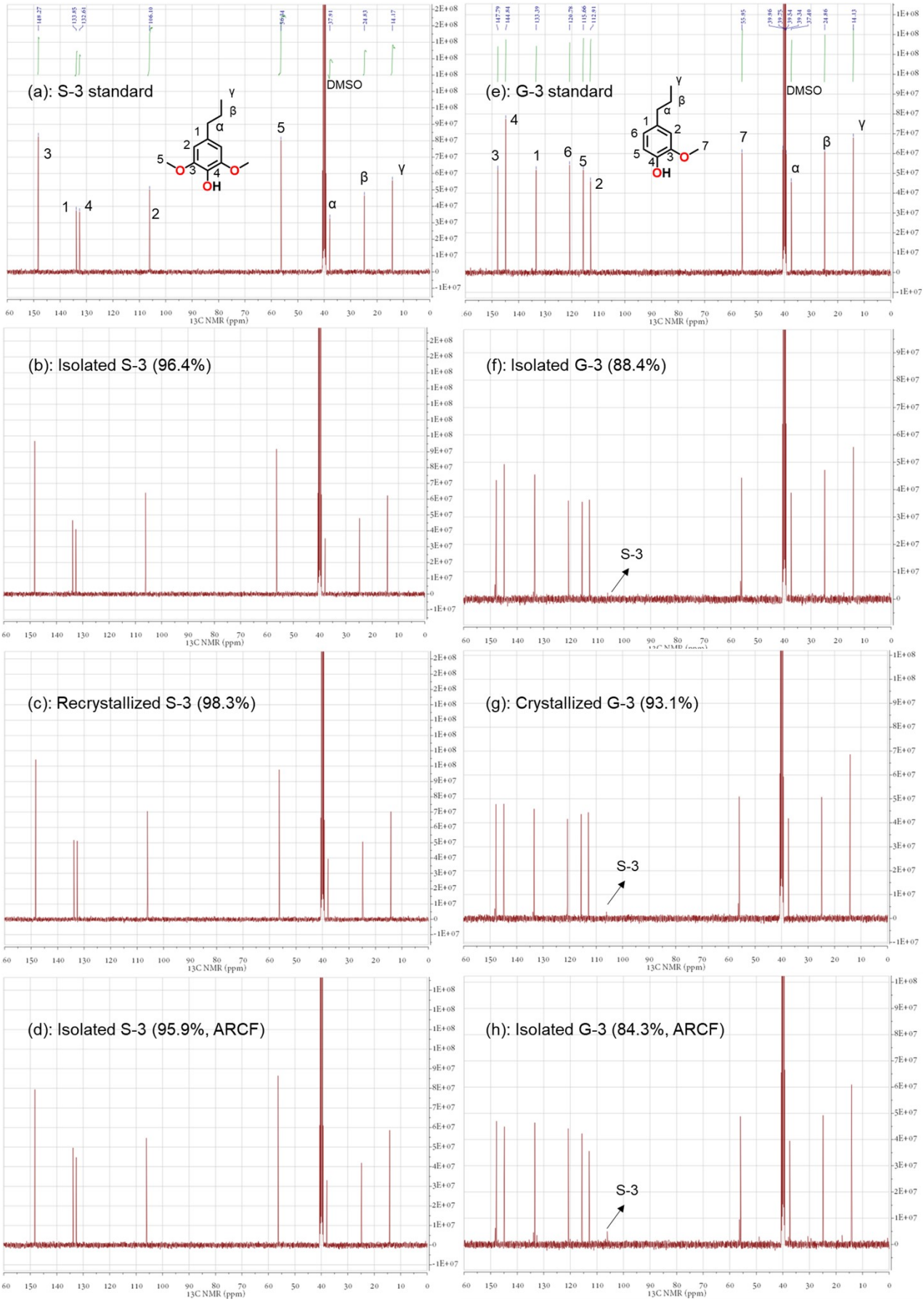


Fig. S5 13C NMR spectra of the standards and the 6 products of S-3 and G-3 (Fig. S7). The numbers in parathesis are GC purities. The solvent used for the test was DMSO-d6.

Table S1 The mass purities of the products (compared with the purities based on GC peak area).[a,b,c]

Sample	Isolated S-3 (RCF)	Recrystallized S-3 (RCF)	Isolated S-3 (ARCF)
Purity (based on mass, wt%)	95.9±1.5	100.9±1.3	97.0±1.3
Purity (based on GC peak area, %)	96.4	98.3	95.9
Sample	Isolated G-3 (RCF)	Crystallized G-3 (RCF)	Isolated G-3 (ARCF)
Purity (based on mass, wt%)	86.8±0.8	92.0±0.7	85.3±1.3
Purity (based on GC peak area, %)	88.4	93.1	84.3

[a] Detection procedure: Weigh and dissolve a sample in an ethanol solution with dodecane as internal standard. Detect the mixture using GC-FID. The purities were calculated by the following equation: Purity = Area of S-3 (or G-3) × correction factor of S-3 (or G-3) / (Area of dodecane / Mass of dodecane), where correction factors of S-3 (or G-3) were measured with standards. For all S-3 products and isolated G-3 (ARCF), as least 3 samples were prepared for the detection, while 1 sample was prepared and multiply detected for isolated G-3 (RCF) and crystallized G-3 (RCF) due to lack of enough sample (Fig. S7).

[b] The two purities are close, indicating that all the products did not contain too much GC-undetectable impurities such as oligomers and decomposable substances.

[c] The detection of mass purity depends on the accurate detection of the correction factors (or responds factor) of G-3 and S-3, which requires highly pure standards. However, the purities of the two standards are 98% for G-3 and 97% for S-3 (maybe even lower), which are not high enough. Thus, the mass purities were considered less accurate and the purities based on GC peak area are more suitable and convenient for the research.

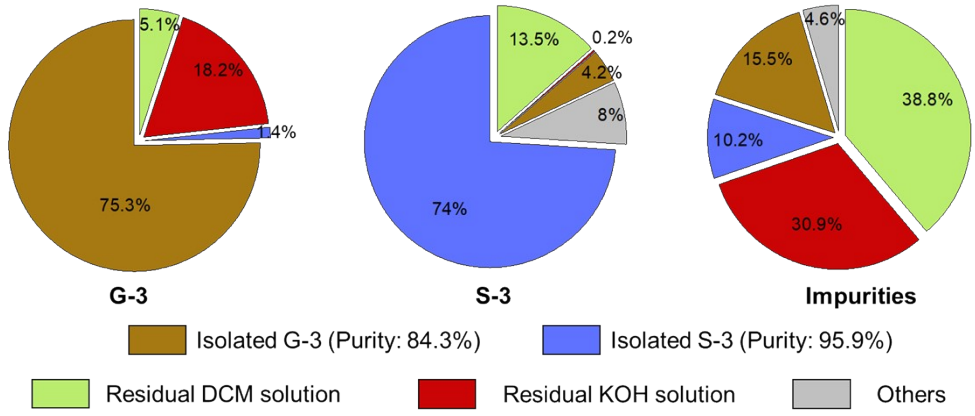


Fig. S6 The distributions of G-3, S-3, and impurities after the primary isolation of the monomer-enriched oil from ARCF case. Impurities are all other components in the monomer-enriched oil. The distribution of impurities can be found in Fig. S1. “Others” (light gray) represents the part of missing sample due to sampling, uncollectable sample, and detection and calculation errors.

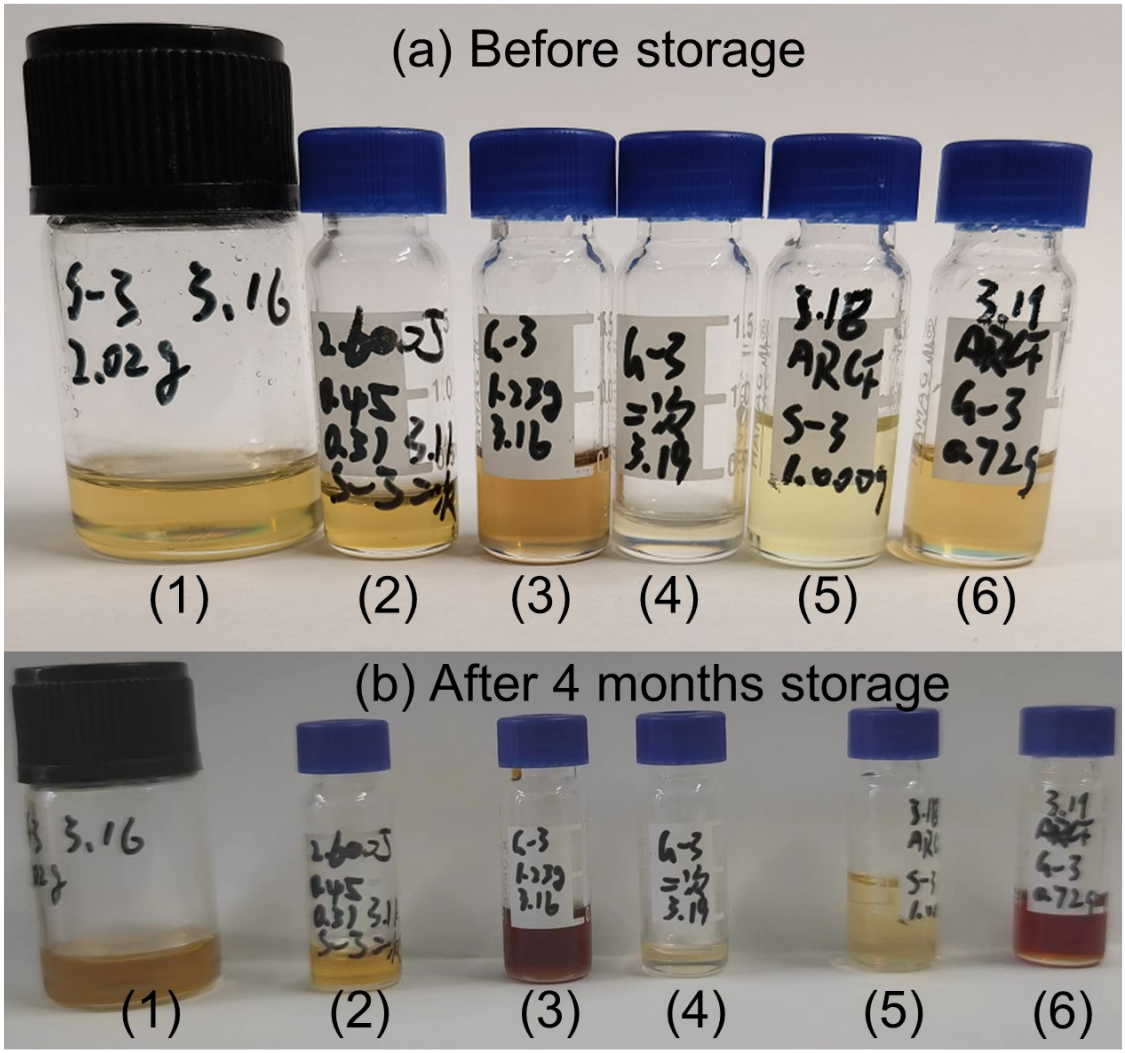


Fig. S7 G-3 and S-3 products before (a) and after 4 months storage (b). (1) isolated S-3, (2) recrystallized S-3, (3) isolated G-3, and (4) crystallized G-3 from RCF case; (5) isolated S-3 and (6) isolated G-3 from ARCF case.

Table S2 The usage and chemical cost in RCF case.

	Chemicals used in RCF case	Usage[a]	Chemical cost (US$)[b]	Comments
Primary isolation	Monomer-enriched oil (g)	~4.38		
	Containing G-3 / S-3	1.35 / 2.19		
	Obtaining G-3 (purity: 88.4%) / S-3 (purity: 96.4%) (g)	1.23 / 2.02		
	DCM (for dissolving monomer-enriched oil, ml)	15	0.0112	Recyclable
	DCM (for extracting G-3, ml)	50	0.0373	Recyclable
	DCM (for extracting S-3, ml)	15	0.0112	Recyclable
	Solid KOH (85%, g)	6.2	0.00556	~50% recyclable
	Water (ml)	150	-	Recyclable
	Hydrochloric acid (HCL, 37%, ml）	~4	0.000416	Consumed
		Total:	0.0657	
Purification of S-3 (1 g, from S-3K)[a,c]	Solid KOH (85%, g)	0.6	0.000538	Recyclable
	Water (ml)	15	-	Recyclable
	Hydrochloric acid (HCL, 37%, ml）	0.4	0.0000416	It is a part of HCL used in primary isolation
	DCM	15	0.0112	Recyclable
		Total:	0.0118	
Purification G-3 (1 g, from G-3, 88.4%)[a,c]	Solid NaOH (96%, g)	3.3	0.00222	~90% recyclable
	Water (ml)	15	-	Recyclable
	Hydrochloric acid (HCL, 37%, ml）	0.5	0.000052	Consumed
	DCM	15	0.0112	Recyclable
		Total:	0.0135	

Chemical cost for production of 1 kg S-3 (96.4%) +0.62 kg G-3 (88.4%) ($): 3.2 (unrecyclable) + 62.5 (recyclable)

Chemical cost for purification for 1 kg S-3 (recrystallized, 98.3%) ($): 0.04 (unrecyclable) + 11.7 (recyclable)

Chemical cost for purification for 1 kg G-3 (crystallized, 93.1%) ($): 0.27 (unrecyclable) + 13.2 (recyclable)

[a] The usage in the region of primary isolation is calculated according the experimental procedures (Section S2.5). The usage for purification is evaluated based on the experimental procedures and magnified proportionally to 1 g product.

[b] The chemical price was searched on www.molbase.cn, b2b.baidu.com, and www.1688.com. The prices are: DCM 567 US$/ton, solid KOH (85%, technical grade) 896 US$/ton, solid NaOH 672 US$/ton, and hydrochloric acid (technical grade)104 US$/ton.

[c] The usages are based on processing 1 g S-3 or G-3. Since the alkaline solutions used for (re)crystallization are recyclable, we consider that the samples are not lost in the alkaline solutions.

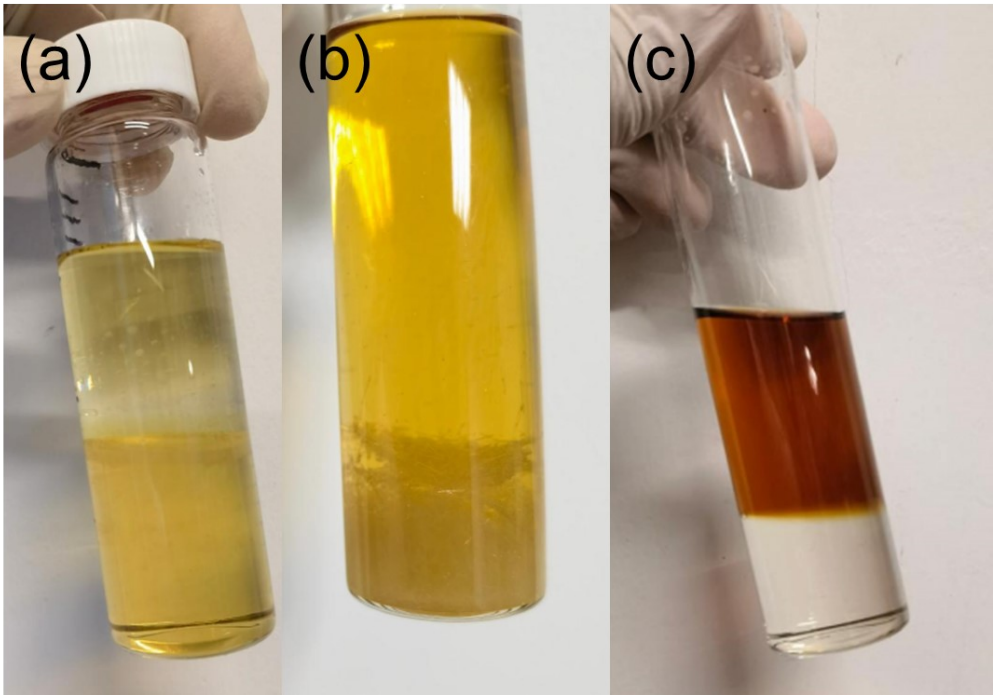


Fig. S8 Pictures of the prototol. (a) extraction of the DCM-dissolved monomer-enriched oil (bottom phase) with aqueous KOH solution (upper phase); (b) S-3K crystal formed and deposited in the KOH solution; (c) revere extraction of KOH solution (upper phase) with DCM (lower phase). The color of KOH solution mainly depends on the concentration of phenolic impurities. The DCM solution of G-3 or S-3 are almost colorless; while the NaOH or KOH solution of G-3 or S-3 are light yellow.

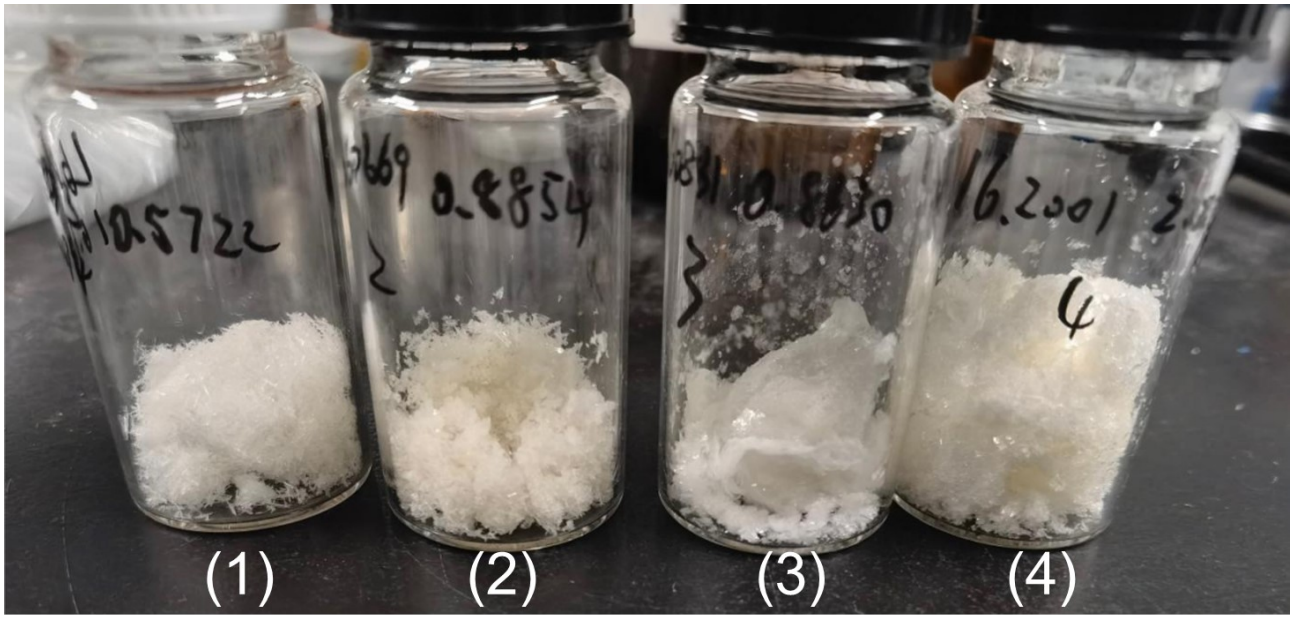


Fig. S9 Four S-3K crystals obtained from RCF case. Procedures and purities are described in Section S2.5. The overall purity of the four crystals is 96.4% (Fig. 5a).

S4. Suggestions and details for a successful isolation

It should be highlighted that the information given above and in the main text may not be enough for an experimenter to reproduce the isolation results because many factors and details could affect the isolation results. Experimenters should understand the mechanism of each step as much as possible to ensure a successful isolation. Therefore, suggestions and details are given here to help.

(1) RCF reactions: High yield and selectivity of G-3 and S-3 are conductive to good isolation. Thus, reaction conditions should be optimized. Wood type can lead special impurities. For instance, two main impurities, phenol and methyl 4-hydroxyphenylpropionate, are from depolymerization of poplar lignin.[1] A choice of wood type is necessary.

(2) Re-hydrogenation: 4-propenylguaiacol and 4-propenylsyrinol could be formed in the products. They should be re-hydrogenated and removed (Section S2.4) even though they are in trace amount, because they are similar in structure with G-3 and S-3 and could largely remain in the final products.

(3) Alkane extraction: In the extraction of lignin oil with alkanes (hexane used in this work), minor dimers and larger molecules were simultaneously extracted. Thus, the alkane solution is strongly suggested to be concentrated and cooled (e.g., to -20 °C, Section S2.4) to let the large impurities precipitate out. Thus, the as-formed monomer-enriched oil could be significantly purified in the GC range of dimers (Fig. S10).

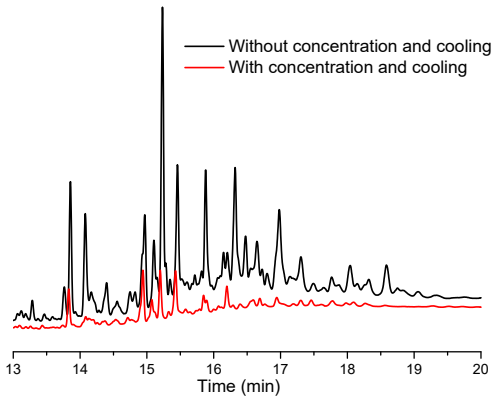


Fig. S10 Comparison of GC spectra of monomer-enriched oil (region of dimers) on handling ways on the hexane extracting solution. The concentration of sample of black is 3 times of the red. Even though, it can be identified that the dimer impurities of the red are much less than the black.

(4-1) IMPORTANT! Extraction of DCM-dissolved monomer-enriched oil with KOH solution: If the concentration of KOH and the monomer-enriched oil are both high, the extraction leads to formation of large amount of S-3K precipitate and makes the mixture a slurry. If this happen, add small amount of water to dilute the KOH solution, so S-3K could be effectively re-dissolved. An effective extraction features that the two phases are almost clear (Fig. S8).

(4-2) Extraction of DCM-dissolved monomer-enriched oil with KOH solution: After extraction, the KOH solution is recommended to be filtered since the extraction may produce trace amount of precipitate. They may be the

salts of dimers, but we could not detect them due to low content.

(5) IMPORTANT! Concentration: The KOH solution was rotary-evaporated to partially remove water. During the evaporation, bumping may easily happen since the salts of phenols served as surfactant and favored bubble formation. If this happens, slow down evaporation speed by slow down rotation speed, lower evaporation temperature and vacuum degree.

(6) Crystallization: If the KOH solution is diluted (e.g., 0.5 – 0.7 mol/L) and less crystal forms, the crystal will be needle-like and high purity; while if the KOH solution is concentrated (e.g., > 1 mol/L) and more crystal formed, the crystal will be flake-like and low purity. Thus, experimenters can multiply crystallize S-3K under relatively low concentration to reach high S-3 purity, and are not recommended to crystallize all S-3K in one step.

(7) Filtrating and washing S-3K crystal: During filtration, certain amount of KOH solution may remain and attach on the crystal, which is the most contribution of impurities in isolated S-3. Less solution remains on big and needle-like crystals, while more solution remains in flake-like crystal. Washing the crystal using cold and concentrated KOH may be necessary.

(8) Recycling KOH solution: The KOH solution can be properly diluted to certain concentration and used in the same way of fresh aqueous KOH solution.

(9) Re-extraction: Since the recycled KOH solution contains G-3K, it cannot completely extract G-3 in DCM. Thus, extraction using fresh KOH solution in the last cycle is necessary.

(10) Concentration before reverse extraction: Between crystallization and reverse extraction, we recommend to further concentrate the KOH solution to a high concentration (e.g., > 2 mol/L), and then, crystallize in iced water. Therefore, the removal of S-3K could be maximized.

(11) Reverse extraction: According to Fig. 4, we recommend to acidify or dilute the KOH solution to 0.7 ~ 1.3 mol/L before reverse extraction.

(12) Evaluation of KOH concentration: The KOH concentration after extraction can be evaluated as follow. Thus, detection of components in each phase (especially, DCM phase) may be necessary.

$$KOH\ concentration = \frac{mol\ amount\ of\ KOH - mol\ amount\ of\ phenols\ extracted}{volume\ of\ solvent}$$

S5. Reference

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