Supporting Information

Sustainable Synthesis Methods of Lignin-Based Copolymers: Recyclable Non-Carbodiimide Catalytic Systems in Aqueous Solvent

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1. Synthesis of Acetic Acid and Succinic Acid Modified Capped Lignin

Lignin (2 g), Succinic Acid (1.68 g), Acetic Acid (0.81 mL), and Triethylamine (3.01 mL) were added to a THF-water cosolvent (38 mL) using an equal ratio mixture of THF and water in a double-necked flask and stirred until dissolved. A second mixture of catalyst (2.3 g) and an equal ratio of THF and Water was created by stirring until dissolved. Both mixtures were degassed under an argon atmosphere for 15 minutes. At this time, the mixture of catalyst was added to the initial mixture of Lignin, Succinic Acid, Acetic Acid, and Triethylamine. The combined mixture was refluxed for 48 hours at 50 ^{o}C. Proceed to precipitate the solution in HCl at 0 ^{o}C. Vacuum filter the mixture and rinse with water to collect a brown solid product. To ensure quality, the final product was rinsed multiple times until the de-ionized water was mostly transparent. This reaction was scaled up to 5 grams of lignin and proceeded successfully. NMR spectra, Figures S1 and S2, confirm that the lignin modification proceeded successfully as intended. The same lignin modification using DMF was previously reported in our earlier publication (*ACS Sustainable Chem. Eng.* 2023, 11, 1709).

In addition to the experiments described in the main text, the above experiment was conducted to demonstrate that the water/THF cosolvent system can be successfully applied to other types of lignin modification reactions. The successful results confirmed that the water/THF cosolvent is compatible with lignin modifications involving both acetic acid and succinic acid. This outcome serves as a strong example of the broader applicability of the water/THF cosolvent system in various lignin modification processes.

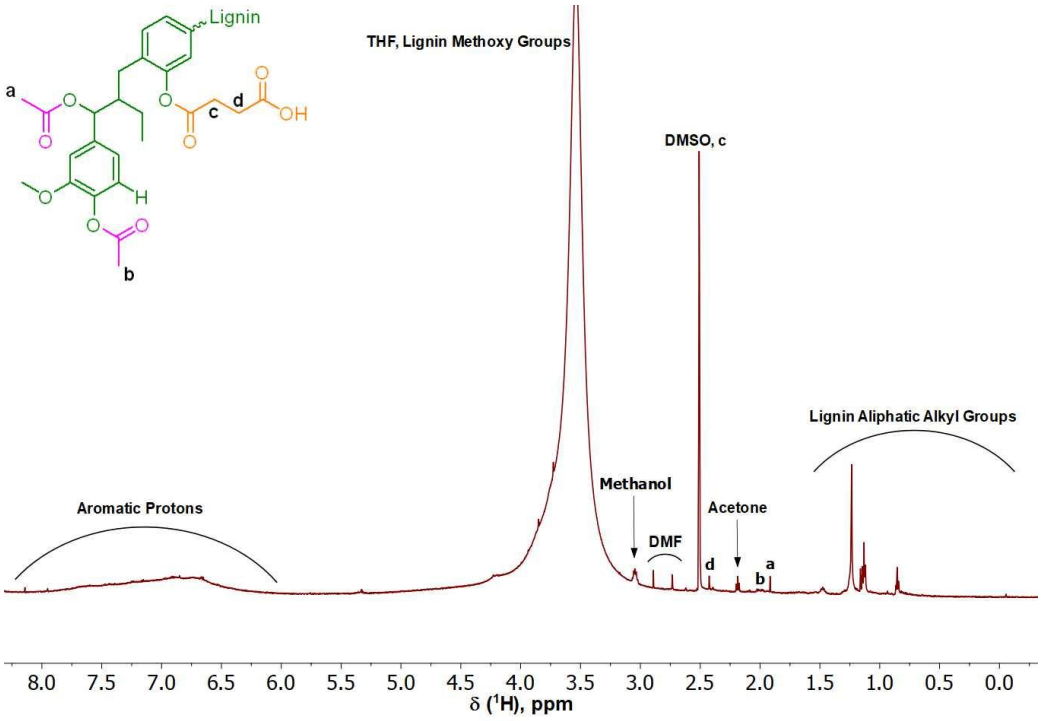

Figure S1. ^{1}H NMR of Modified Capped Lignin

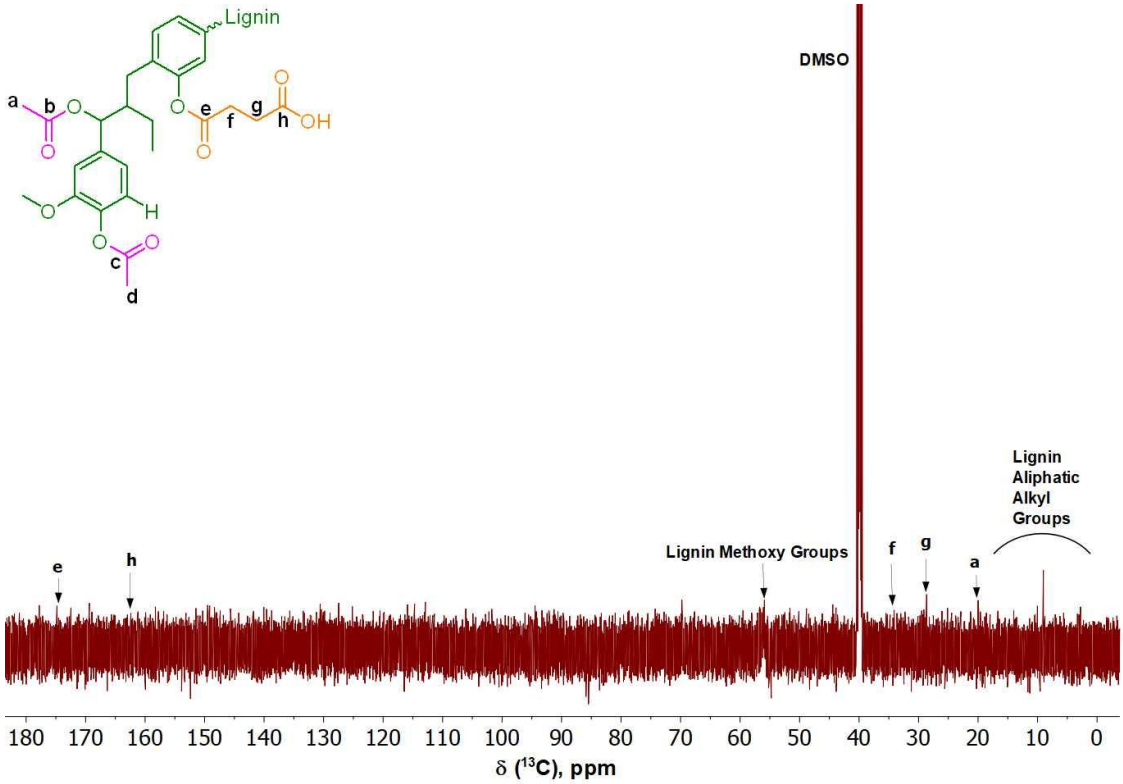

Figure S2. ^{13}C NMR of Modified Capped Lignin

Figure S3. Photo of Modified Lignin Product using DMF solvent

Figure S4. Photo of Modified Lignin Product using THF/Water cosolvent

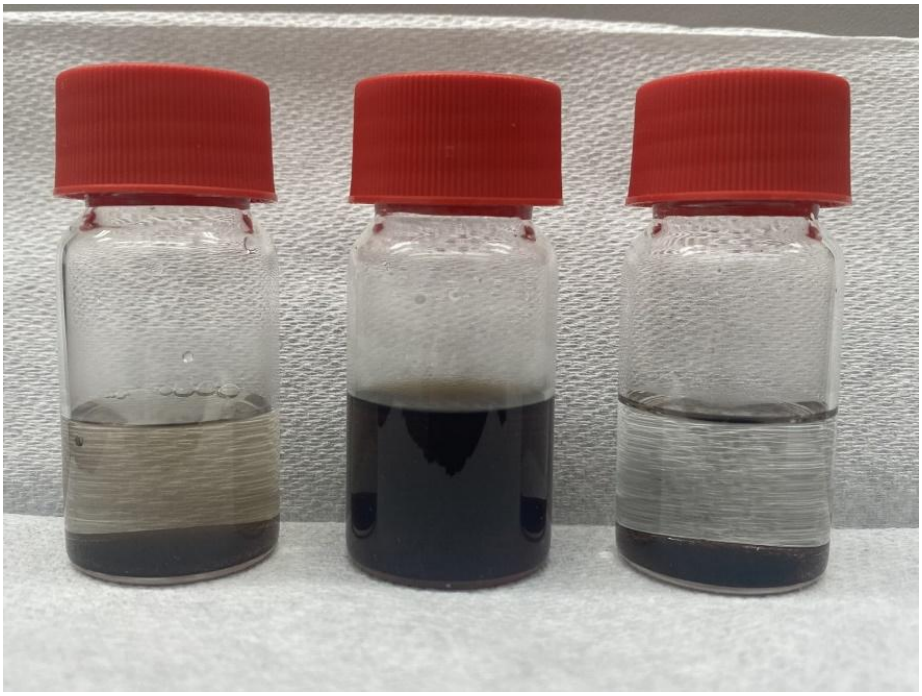

Figure S5a. Photo of Natural Lignin Solubility (Natural Lignin in Deionized Water (Left). Natural Lignin in the 50:50 cosolvent of THF and Deionized Water (Center). Natural Lignin in Pure THF (Right)

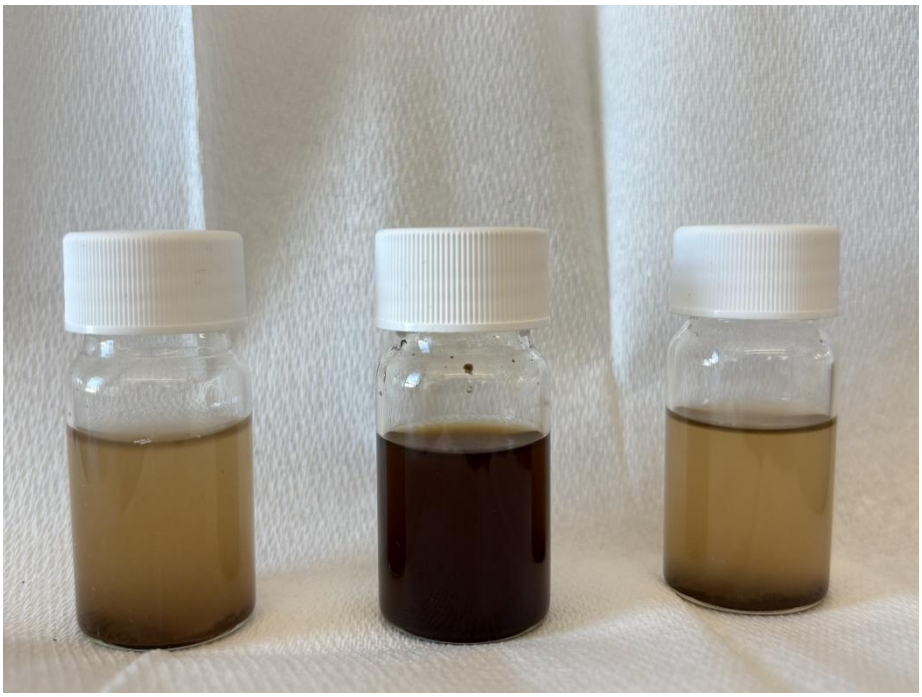

Figure S5b. Photo of Modified Lignin Solubility (Modified Lignin in Deionized Water (Left). Modified Lignin in the 50:50 cosolvent of THF and Deionized Water (Center). Modified Lignin in Pure THF (Right)

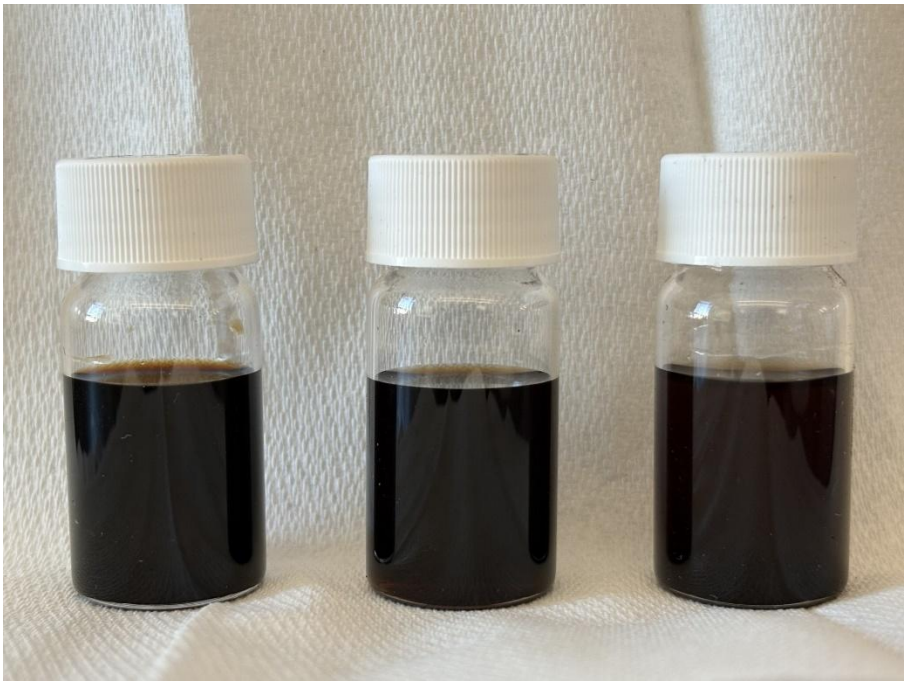

Figure S5c. Photo of Natural Lignin Solubility (Natural Lignin in DMF (Left). Natural Lignin in DMSO (Center). Natural Lignin in NMP (Right)

Figure S5d. Photo of Modified Lignin Solubility (Modified Lignin in DMF (Left). Modified Lignin in DMSO (Center). Modified Lignin in NMP (Right)

6. **Degree of acid modification**

Internal standard: 1,3,5-trioxane (Molecular weight 90.08 g mol^{-1})

Sample preparation: 23.3 mg of modified lignin and 3.2 mg trioxane were taken in NMR tube. DMSO-d_6 used as NMR solvent.

Integration values from ^{1}H NMR: Six proton atoms from trioxane at 5.12 ppm (**6**), COO<u>H</u> (one proton) peak at 12.0 ppm (**3.38**)

3.2 mg trioxane = 0.0356 mmol

Amount of COOH groups (0.0356 × 3.38) mmol = 0.120071 mmol

Hence, 0.0233 gram of modified lignin contained 0.120071 mmol COOH groups

*So, 1 gram of modified lignin contained (*0.120071 */*0.0233*) mmol =* ***5.1532 mmol COOH groups***

Hence, the degree of acid modification is 5.1532 mmol g^{-1}.

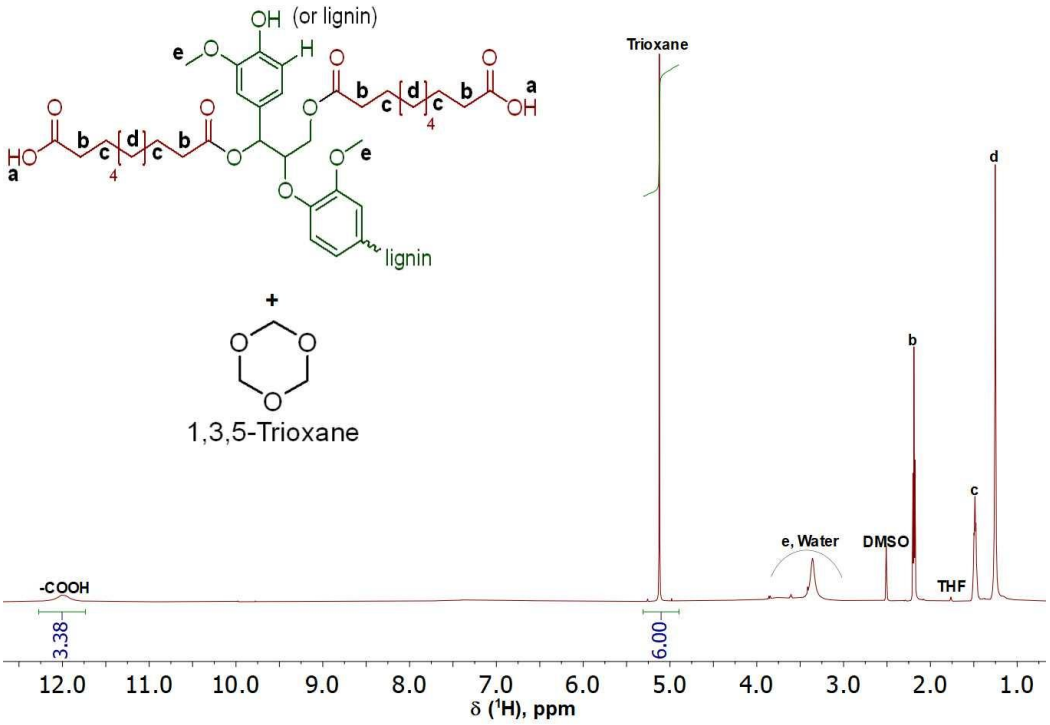

Figure S6. [1]H NMR of Modified Lignin and Trioxane for Determining Degree of Acid Modification

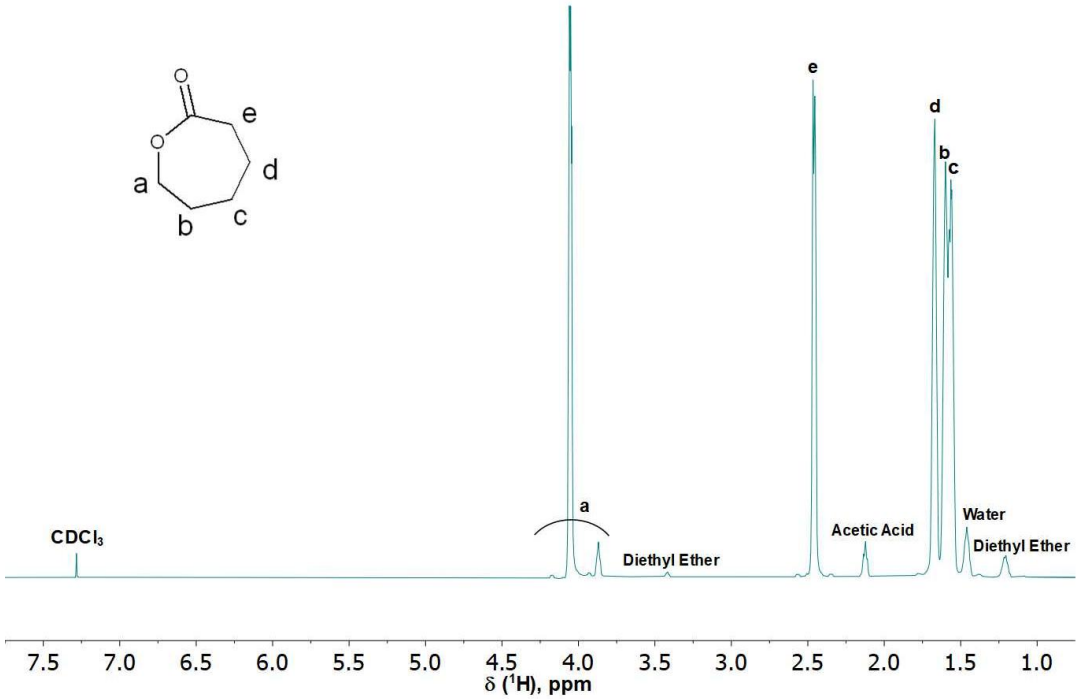

Figure S7. [1]H NMR of ε-Caprolactone

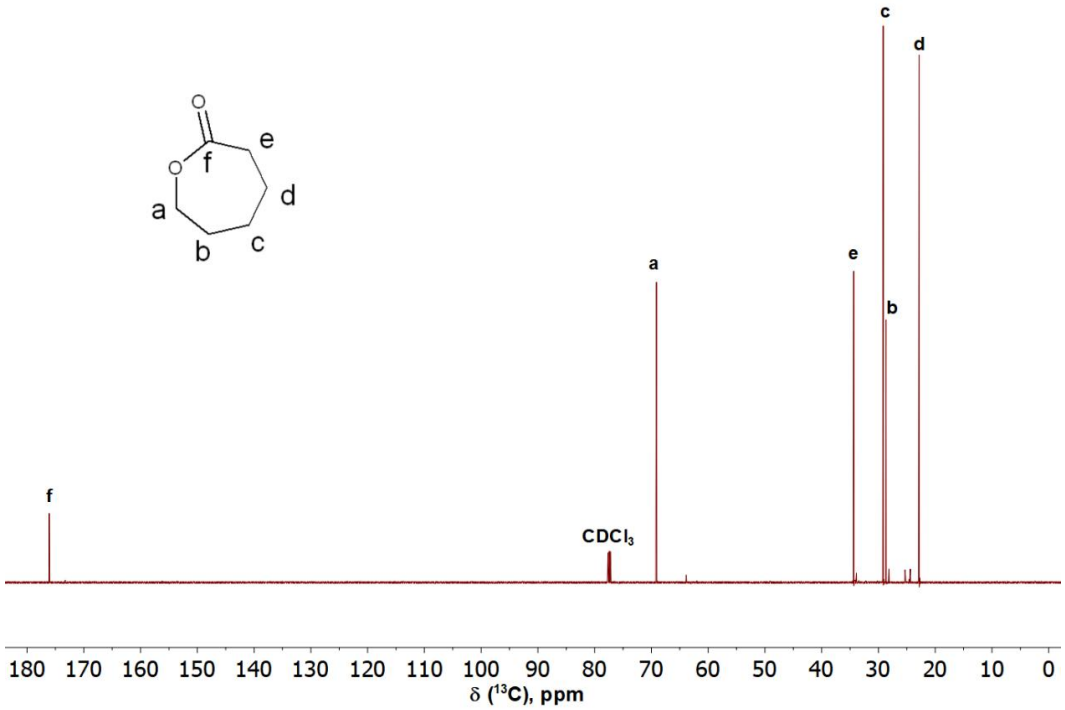

Figure S8. ^{13}C NMR of ε-Caprolactone

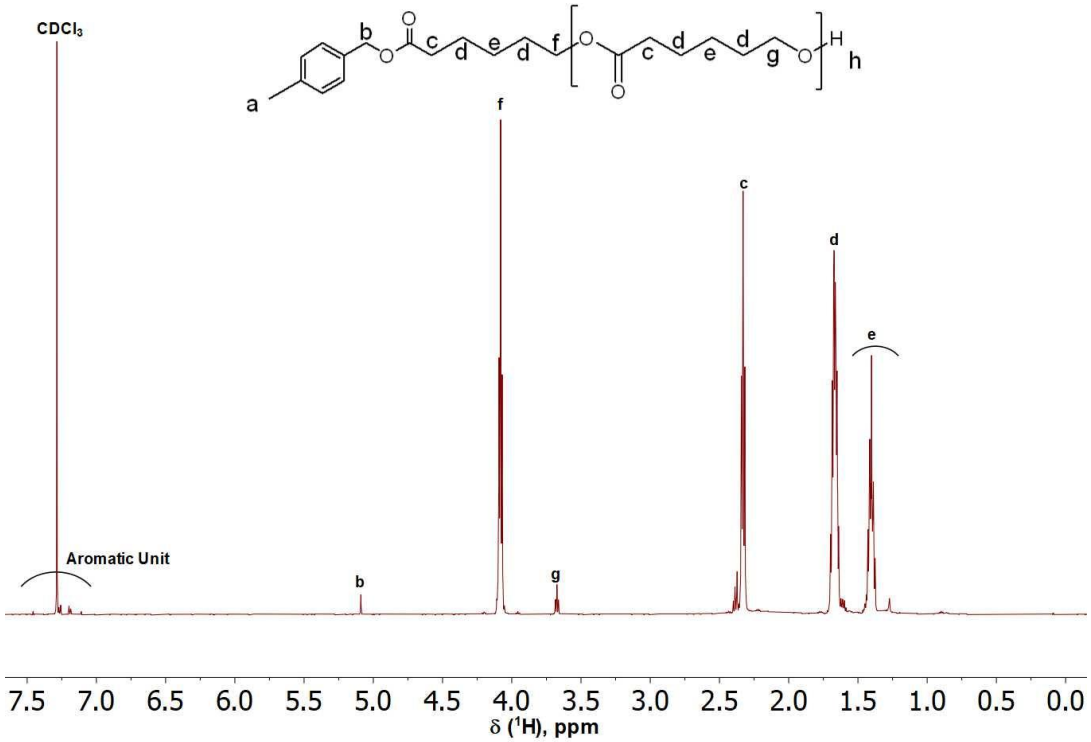

Figure S9. ^{1}H NMR of ROP of ε-Caprolactone Without Use of PS-TBD Catalyst

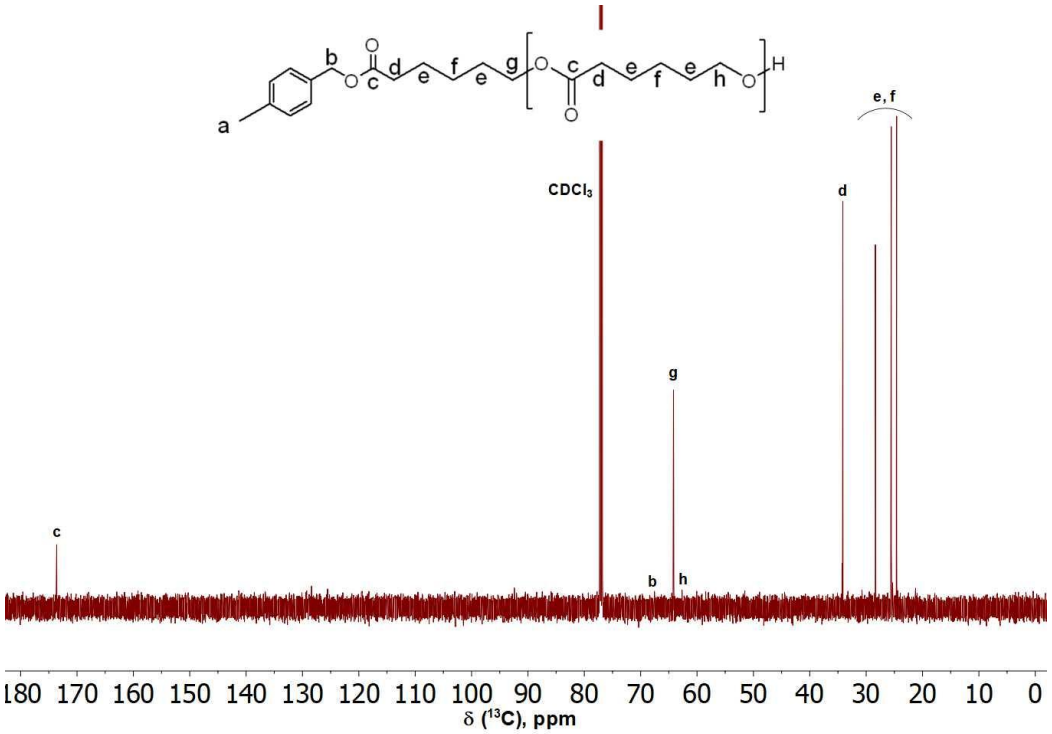

Figure S10. ^{13}C NMR of ROP of ε-Caprolactone Without Use of PS-TBD Catalyst

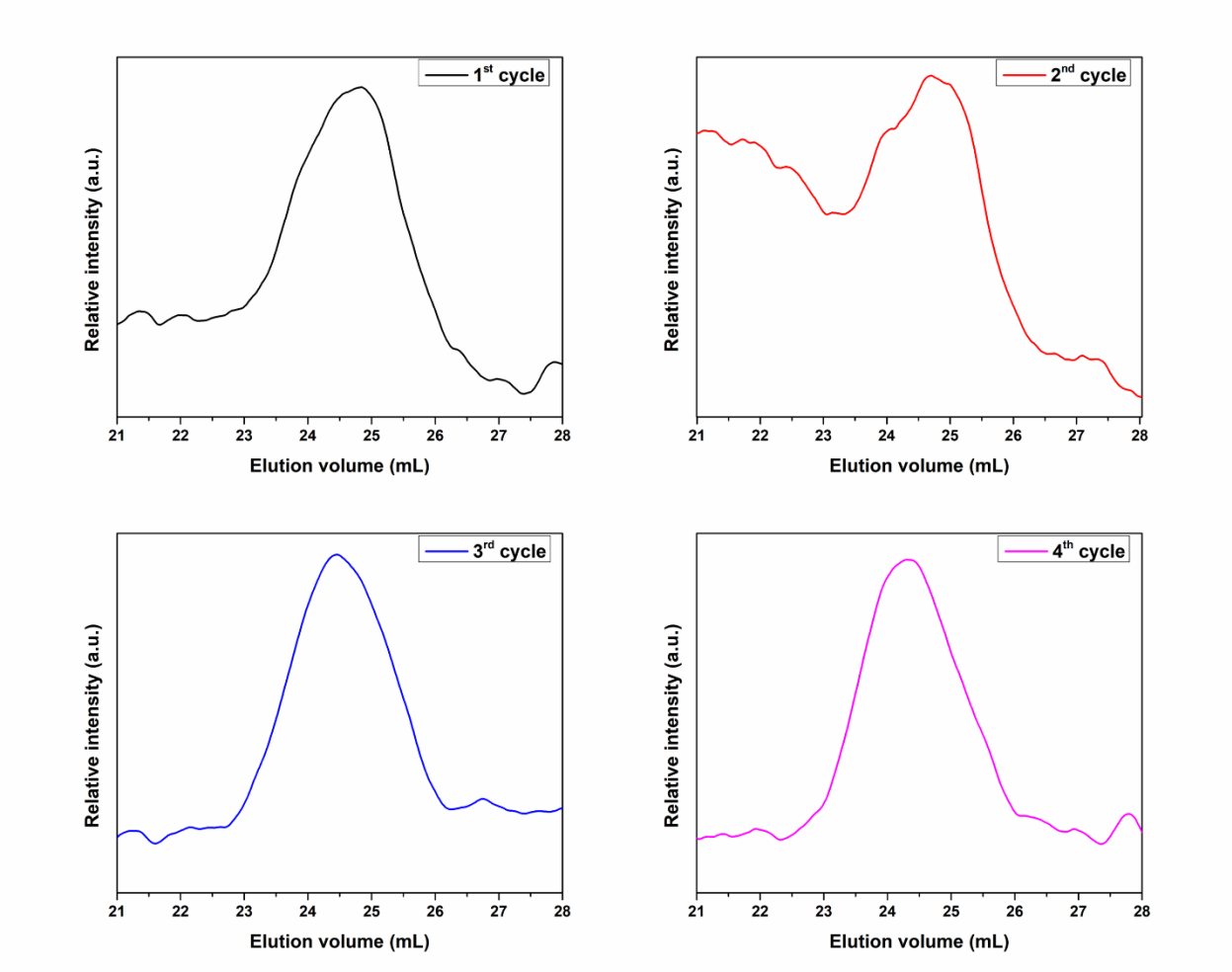

Figure S11. GPC Curves for the Four Cycles*

*Each cycle represent one repetitive and independent use of the same PS-TBD catalyst in four consecutive reactions, testing the catalyst's recyclability. These GPC data represent the molecular weight of the ring-opened polycaprolactone product.

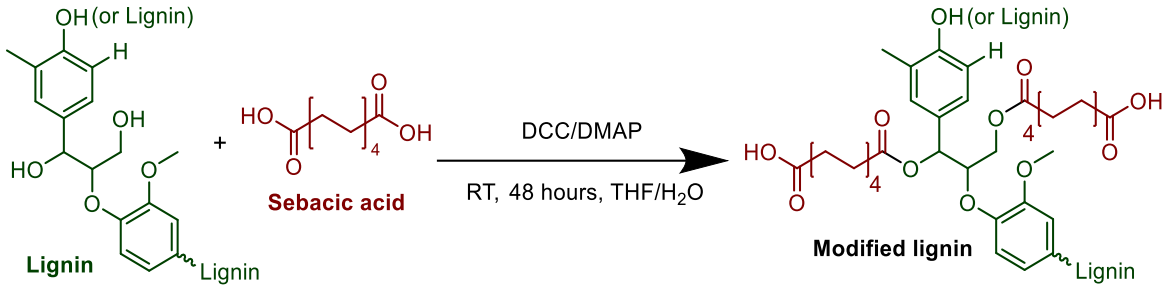

Figure S12. Synthesis of Modified Lignin using DCC/DMAP and THF/Water Cosolvent System

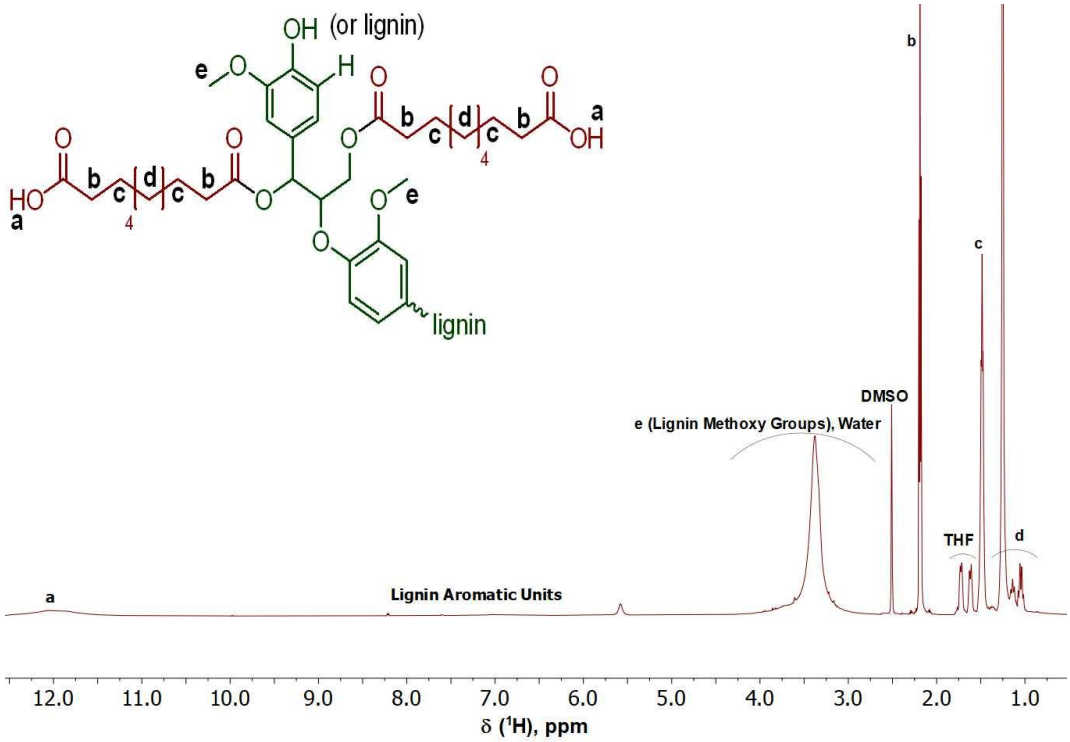

Figure S13. ^{1}H NMR of Modified Lignin using Figure S12

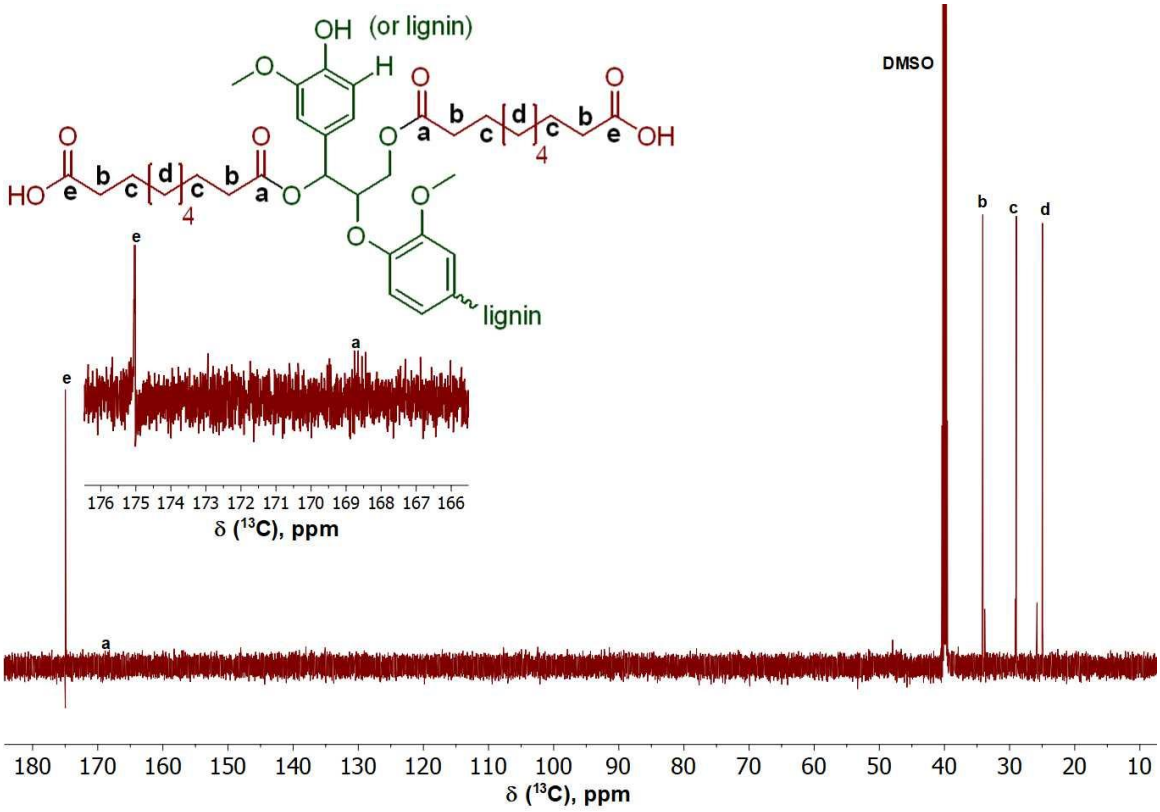

Figure S14. ^{13}C NMR of Modified Lignin using Figure S12

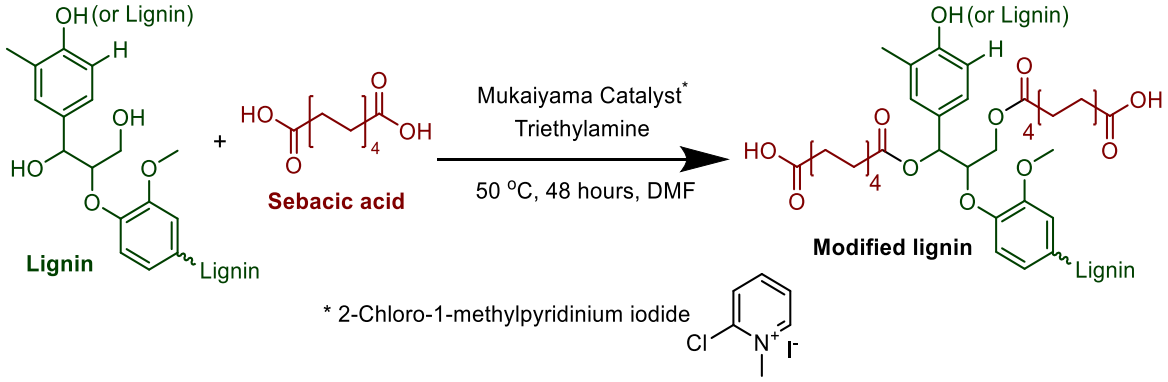

Figure S15. Synthesis of Modified Lignin using Mukaiyama Reagent System and DMF Solvent

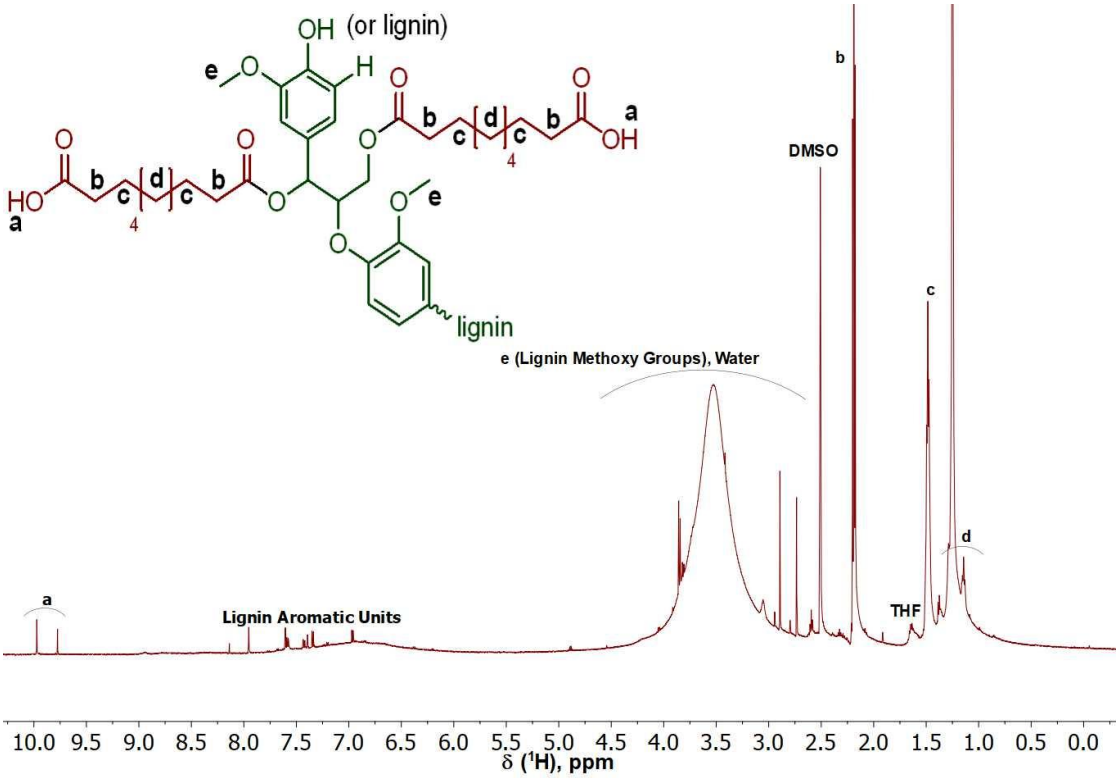

Figure S16. ^{1}H NMR of Modified Lignin using Figure S15

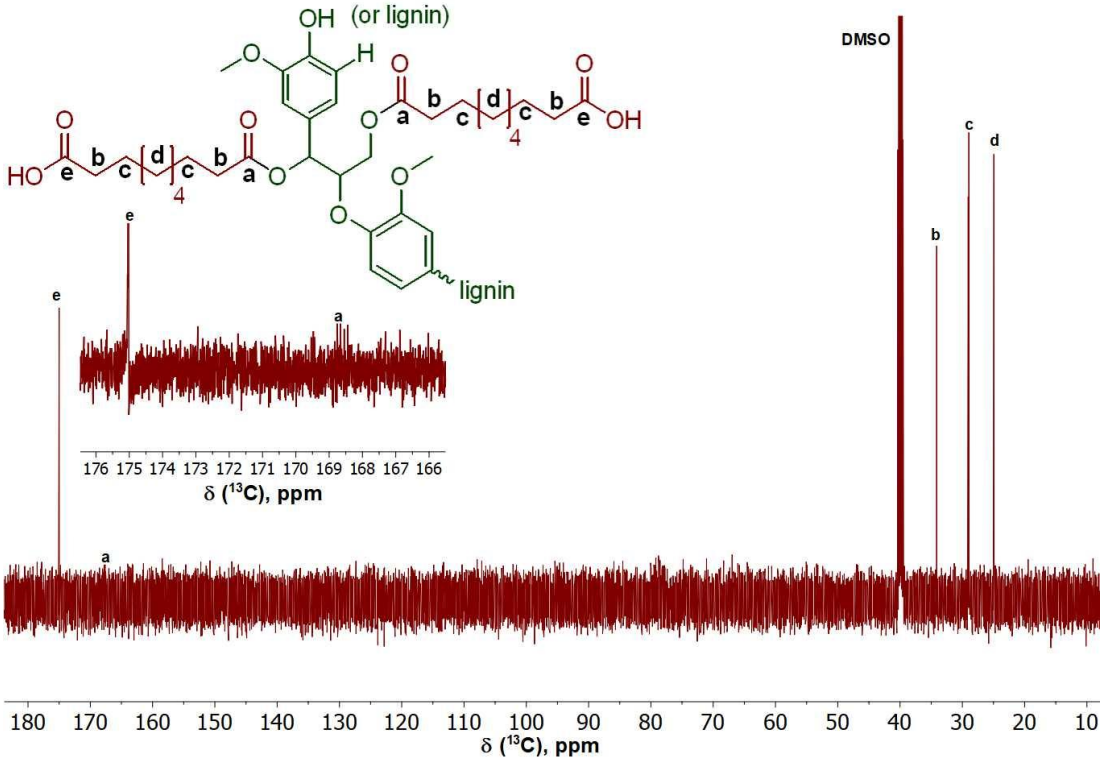

Figure S17. ^{13}C NMR of Modified Lignin using Figure S15

Table S1 Comparative Table with Four Reaction Conditions for Lignin Modification

Reaction Condition	Yield (grams)	Yield (Weight %)
Cosolvent and Mukaiyama Reagent	**3.14 g**	**82 %**
Cosolvent and DCC/DMAP	**2.72 g**	**71 %**
DMF and DCC/DMAP	**2.38 g**	**62 %**
DMF and Mukaiyama Reagent	**2.64 g**	**69 %**

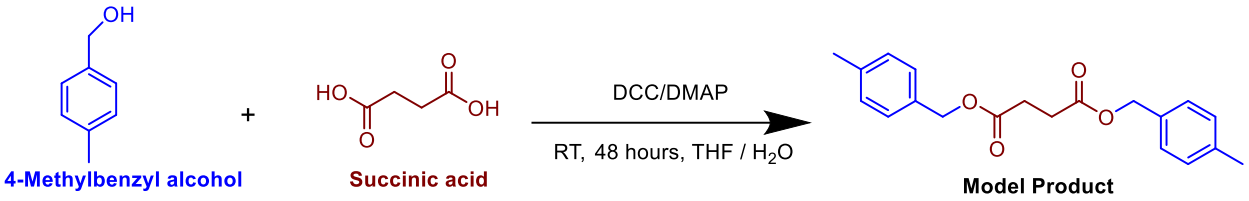

Figure S18. Synthesis of Model Product using DCC/DMAP and THF/Water Cosolvent System