Supporting Information

Controllable synthesis of cellulose benzoates for understanding of chiral recognition mechanism and fabrication of high-efficient chiral stationary phases

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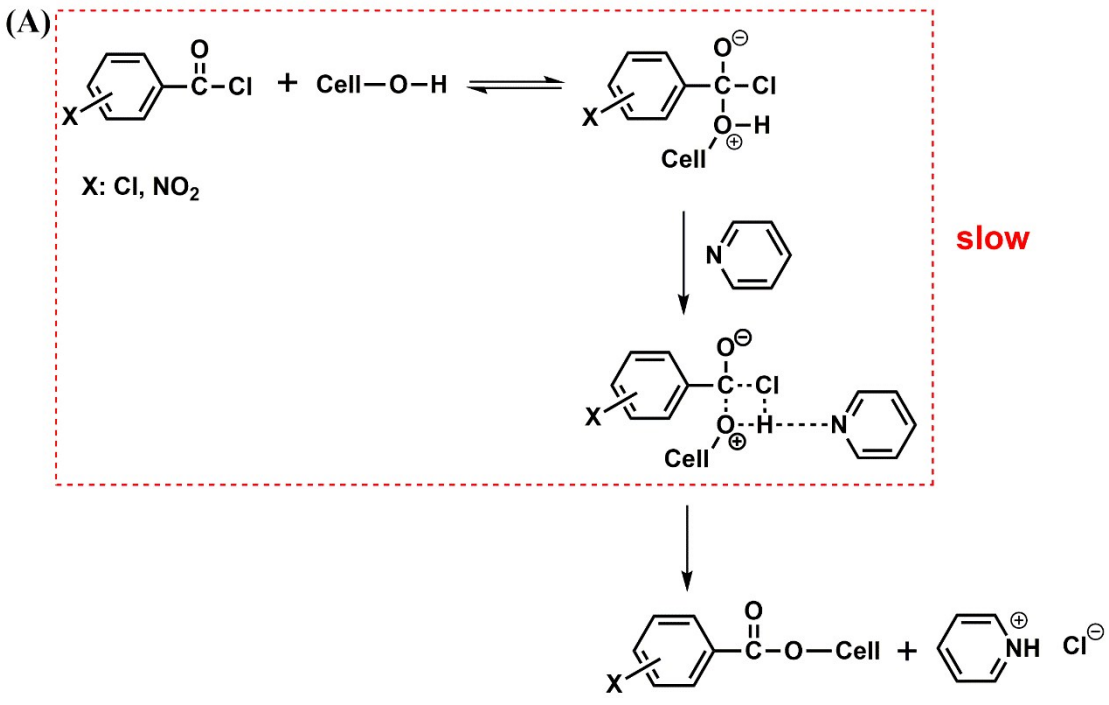


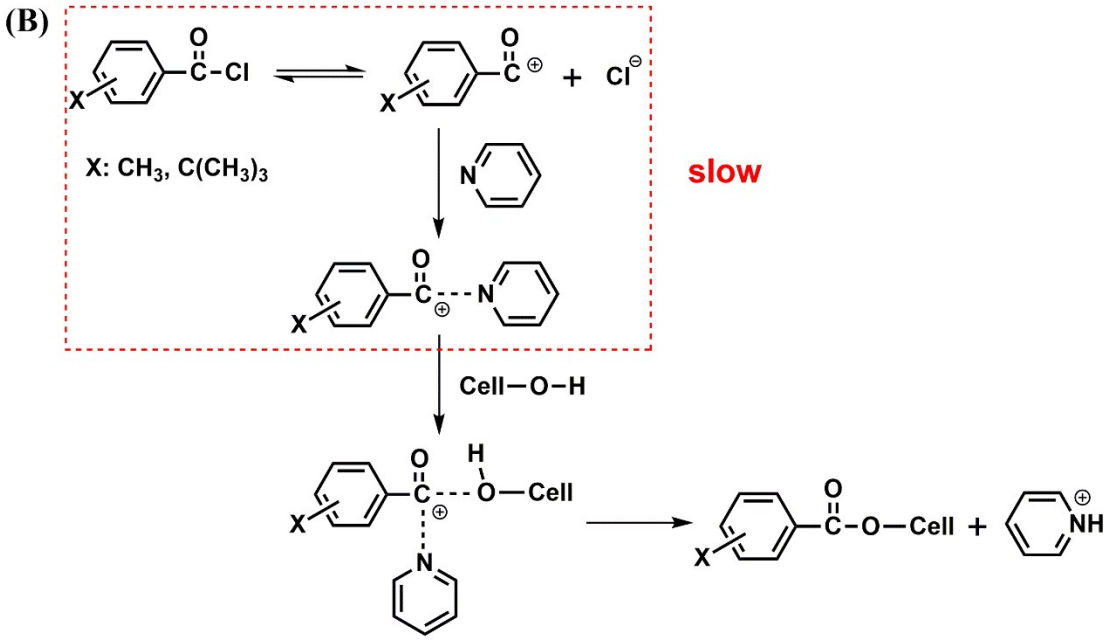


Figure S1. The possible mechanism of homogeneous benzoylation of cellulose with pyridine as the catalyst. (A) Addition-elimination mechanism, (B) Ionization mechanism.

Table S1. Solubility of cellulose benzoates with different DS in organic solvents

DS	Solvents							
	DMSO	Pyridine	DMF	THF	Chloroform	Dichloromethane	Acetone	Ethyl acetate
1.50	+	+	+	+	±	-	-	-
1.98	+	+	+	+	+	±	+	-
2.42	+	+	+	+	+	+	+	+
3.0	+	+	+	+	+	+	-	-

+, Soluble; ±, Swollen; -, Insoluble

Table S2. Solubility of cellulose 2-methylbenzoates with different DS in organic solvents

DS	Solvents							
	DMSO	Pyridine	DMF	THF	Chloroform	Dichloromethane	Acetone	Ethyl acetate
1.06	+	+	+	+	±	±	±	-
1.48	+	+	+	+	±	-	-	-
2.05	+	+	+	+	+	+	-	-
2.52	+	+	+	+	+	+	+	+
3.0	+	+	+	+	+	+	+	+

+, Soluble; ±, Swollen; -, Insoluble

Table S3. Solubility of cellulose 3-methylbenzoates with different DS in organic solvents

DS	Solvents							
	DMSO	Pyridine	DMF	THF	Chloroform	Dichloromethane	Acetone	Ethyl acetate
0.95	+	+	+	±	±	-	-	-
1.58	+	+	+	+	±	-	+	-
1.91	+	+	+	+	±	+	+	-
2.45	+	+	+	+	+	+	+	±
3.0	+	+	+	+	+	+	-	-

+, Soluble; ±, Swollen; -, Insoluble

Table S4. Solubility of cellulose 4-methylbenzoates with different DS in organic solvents

DS	Solvents							
	DMSO	Pyridine	DMF	THF	Chloroform	Dichloromethane	Acetone	Ethyl acetate
1.05	+	+	+	-	-	-	-	-
1.52	+	+	+	+	±	±	±	±
1.99	+	+	+	+	+	+	±	±
2.52	+	+	+	+	+	+	+	+
3.0	+	+	+	+	+	+	+	+

+, Soluble; ±, Swollen; -, Insoluble

Table S5. Solubility of cellulose 3,5-dimethylbenzoates with different DS in organic solvents

DS	Solvents							
	DMSO	Pyridine	DMF	THF	Chloroform	Dichloromethane	Acetone	Ethyl acetate
0.93	+	+	+	-	-	-	-	-
1.79	-	+	+	+	+	+	+	-
2.09	-	+	+	+	+	+	+	+
2.45	-	±	-	-	+	-	-	-
2.91	-	+	-	-	+	+	-	-

+, Soluble; ±, Swollen; -, Insoluble

Table S6. Solubility of cellulose 4-tert-butylbenzoates with different DS in organic solvents

DS	Solvents							
	DMSO	Pyridine	DMF	THF	Chloroform	Dichloromethane	Acetone	Ethyl acetate
1.03	+	+	+	-	-	-	-	-
1.59	+	+	+	+	-	±	±	±
2.05	-	+	+	+	+	+	+	+
2.47	-	+	+	+	+	+	+	+
3.0	-	+	±	+	+	+	±	+

+, Soluble; ±, Swollen; -, Insoluble

38 **Table S7.** Solubility of cellulose 4-chlorobenzoates with different DS in organic solvents

DS	Solvents							
	DMSO	Pyridine	DMF	THF	Chloroform	Dichloromethane	Acetone	Ethyl acetate
1.45	+	+	±	±	-	-	-	-
2.04	+	+	+	+	±	±	±	±
2.49	+	+	+	+	±	±	±	±
3.0	+	+	+	+	+	±	±	±

39 +, Soluble; ±, Swollen; -, Insoluble

40

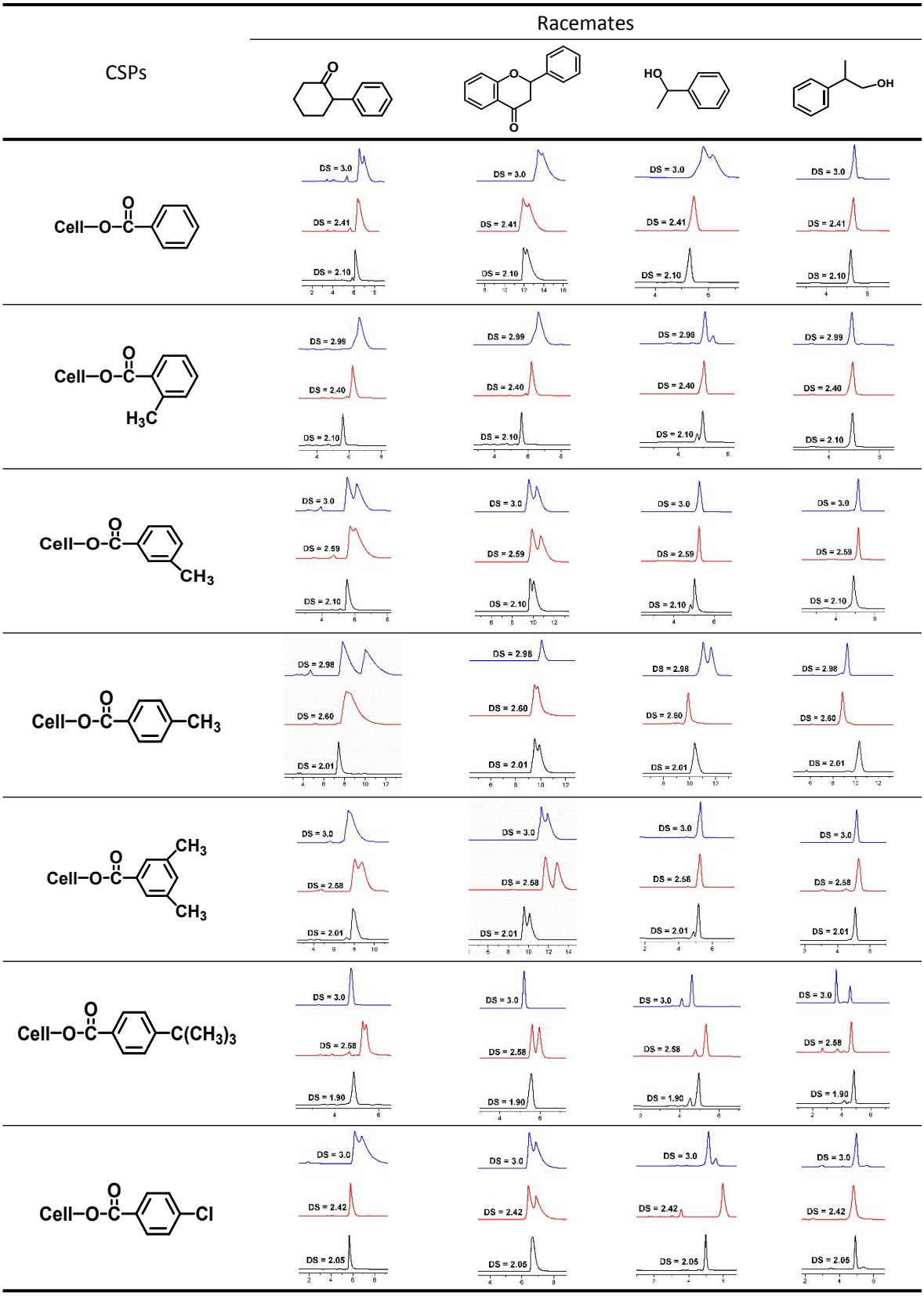
41 **Table S8.** Solubility of cellulose 4-nitrobenzoates with different DS in organic solvents

DS	Solvents							
	DMSO	Pyridine	DMF	THF	Chloroform	Dichloromethane	Acetone	Ethyl acetate
0.76	+	+	+	+	±	±	±	-
1.69	+	+	+	+	±	-	-	-
2.05	+	+	+	+	+	+	-	-
2.50	+	+	+	+	+	+	+	+
2.90	+	+	+	+	+	+	+	+

42 +, Soluble; ±, Swollen; -, Insoluble

43

Figure S2. Chromatographic resolution of four racemates, (A) 2-phenyl cyclohexanone, (B) flavanone, (C) 1-phenyl-1-ethanol and (D) 2-phenyl-1-propanol, on HPLC columns of cellulose benzoates with different substituted groups and DS values.



Note: Eluent for racemate A-C, hexane/2-propanol (98:2, v/v); eluent for racemate D, hexane/2-propanol (90:10, v/v). Flow rate, 1 mL/min.

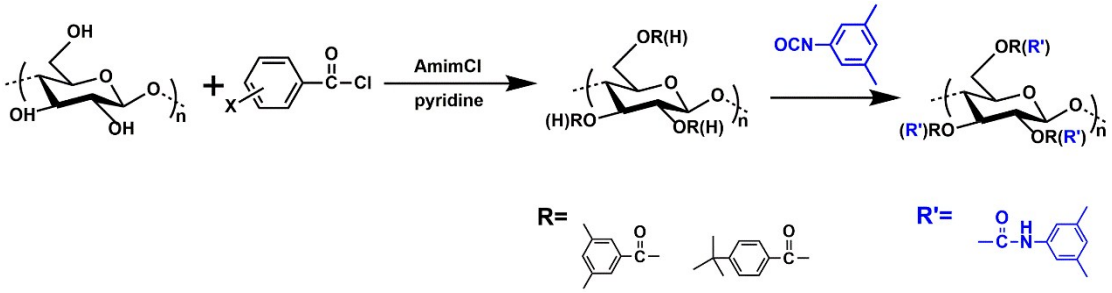


Figure S3. Synthesis route of cellulose mixed esters, cellulose benzoate 3,5-dimethyl phenylcarbamate, in AmimCl via a "one-pot, two-step" process.

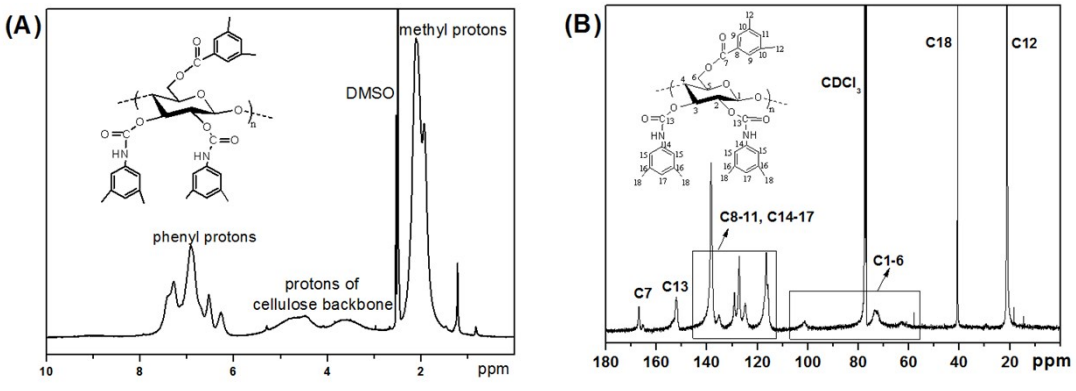


Figure S4. (A) ^{1}H-NMR and (B) ^{13}C-NMR spectra of cellulose 3,5-dimethylbenzoate 3,5-dimethyl phenylcarbamate.

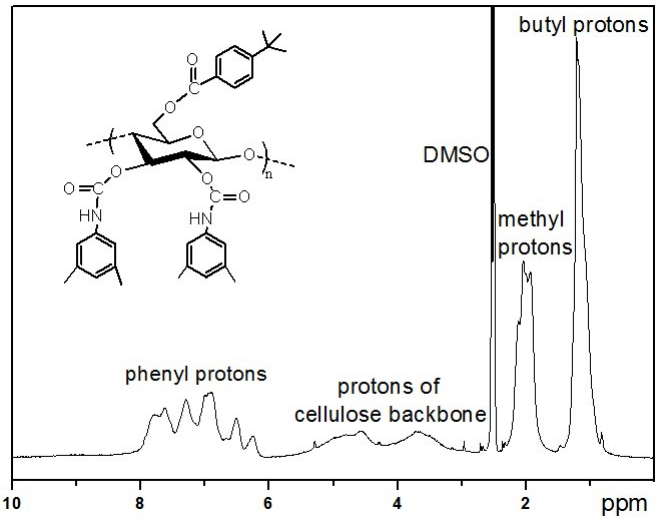


Figure S5. ^{1}H-NMR spectrum of cellulose 4-tert-butylbenzoate 3,5-dimethyl phenylcarbamate.

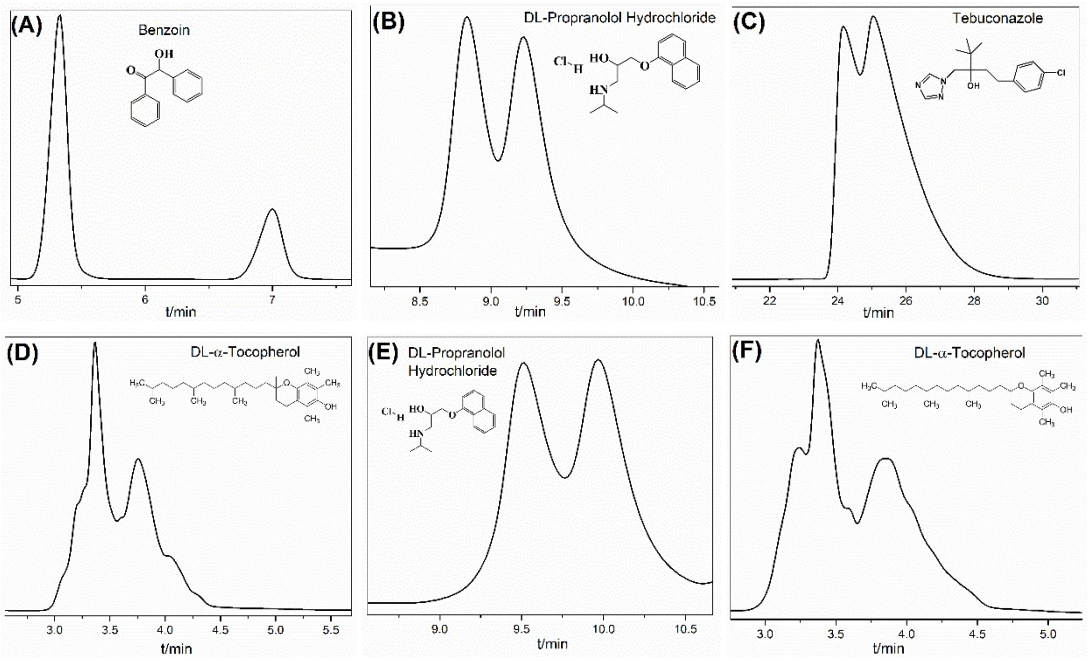


Figure S6. Chromatographic resolution of some chiral drug and pesticide molecules on HPLC columns of cellulose benzoates with different substituted groups and DS values. (A) Benzoin was separated on cellulose 4-tert-butylbenzoate with DS = 2.58. Eluent, hexane/2-propanol/trifluoroacetic acid (90:9.8:0.2, v/v); Flow rate, 1 mL/min. (B) DL-Propranolol hydrochloride was separated on cellulose 4-tert-butylbenzoate 3,5-dimethyl phenylcarbamate. Eluent, hexane/2-propanol (50:50, v/v); Flow rate, 0.5 mL/min. (C) Tebuconazole was separated on cellulose 4-tert-butylbenzoate 3,5-dimethyl phenylcarbamate. Eluent, hexane/2-propanol (98:2, v/v); Flow rate, 1 mL/min. (D) DL-α-Tocopherol was separated on cellulose 4-tert-butylbenzoate 3,5-dimethyl phenylcarbamate. Eluent, hexane/2-propanol (90:10, v/v); Flow rate, 1 mL/min. (E) DL-Propranolol hydrochloride was separated on cellulose 3,5-dimethylbenzoate 3,5-dimethylphenylcarbamate. Eluent, hexane/2-propanol/triethylamine (50:49.8:0.2, v/v); Flow rate, 0.5 mL/min. (F) DL-α-Tocopherol was separated on cellulose 3,5-dimethylbenzoate 3,5-dimethylphenylcarbamate. Eluent, hexane/2-propanol (90:10, v/v); Flow rate, 1 mL/min.