- 1 Supporting Information
- Controllable synthesis of cellulose benzoates for understanding of chiral 2
- recognition mechanism and fabrication of high-efficient chiral stationary 3
- 4

### phases

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

	Solvents									
DS	DMSO	Duriding	DMF	THF	Chlorofor	Dichloromethan	Aceton	Ethyl		
		i ynunic			m	е	е	acetate		
1.50	+	+	+	+	±	-	-	-		
1.98	+	+	+	+	+	±	+	-		
2.42	+	+	+	+	+	+	+	+		
3.0	+	+	+	+	+	+	-	-		

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

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

	Solvents									
DS	DMSO	Dyriding	DME	тис	Chlorofor	Dichloromethan	Aceton	Ethyl		
	511100	i yname	Bivii		m e	е	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 

	Solvents									
DS	DMSO	Duridino	DMF	тыс	Chlorofor	Dichloromethan	Aceton	Ethyl		
	DIVISO	i yndine		1111	m e	е	acetate			
0.95	+	+	+	±	±	-	-	-		
1.58	+	+	+	+	±	-	+	-		
1.91	+	+	+	+	±	+	+	-		
2.45	+	+	+	+	+	+	+	±		
3.0	+	+	+	+	+	+	-	-		

+, Soluble; ±, Swollen; -, Insoluble 

29	Table

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

	Solvents									
DS	DMSO	Duridino	DMF	тис	Chlorofor	Dichloromethan	Aceton	Ethyl		
	DIVISO	i ynanie		ППГ	m e	е	acetate			
1.05	+	+	+	-	-	-	-	-		
1.52	+	+	+	+	±	±	±	±		
1.99	+	+	+	+	+	+	±	±		
2.52	+	+	+	+	+	+	+	+		
3.0	+	+	+	+	+	+	+	+		

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

31

32

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

	Solvents									
DS	DMSO	Pyridine	DMF	TUE	Chlorofor	Dichloromethan	Aceton	Ethyl		
					m e	е	acetate			
0.93	+	+	+	-	-	-	-	-		
1.79	-	+	+	+	+	+	+	-		
2.09	-	+	+	+	+	+	+	+		
2.45	-	±	-	-	+	-	-	-		
2.91	-	+	-	-	+	+	-	-		

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

34 35

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

	Solvents									
DS	DMSO	Duriding	DME	тис	Chlorofor	Dichloromethan	Aceton	Ethyl		
		i yname	DIVII		m e	е	acetate			
1.03	+	+	+	-	-	-	-	-		
1.59	+	+	+	+	-	±	±	±		
2.05	-	+	+	+	+	+	+	+		
2.47	-	+	+	+	+	+	+	+		
3.0	-	+	±	+	+	+	±	+		

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

	Solvents									
DS	DMSO	Duridino		тыс	Chlorofor Dichloromethan Ace THF m e e	Aceton	Ethyl			
	DIVISO	Pynume	DIVIF	INF		е	е	acetate		
1.45	+	+	±	±	-	-	-	-		
2.04	+	+	+	+	±	±	±	±		
2.49	+	+	+	+	±	±	±	±		
3.0	+	+	+	+	+	±	±	±		

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

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

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

	Solvents									
DS	DMSO	Pyridine	DMF	THF	Chlorofor	Dichloromethan	Aceton	Ethyl		
					m	е	е	acetate		
0.76	+	+	+	+	±	±	±	-		
1.69	+	+	+	+	±	-	-	-		
2.05	+	+	+	+	+	+	-	-		
2.50	+	+	+	+	+	+	+	+		
2.90	+	+	+	+	+	+	+	+		

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

<sup>40</sup> 

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

_		Racema	tes	
CSPs	$\sim$		HO	ОН
	DS = 3.0	DS = 3.0	DS = 3.0	DS = 3.0
Cell—O–C	DS = 2.41	DS = 2.41	DS = 2.41	DS = 2.41
	DS = 2.10	$\frac{DS = 2.10}{\frac{1}{10} \frac{1}{12} \frac{1}{14} \frac{1}{18}}$	DS = 2.10	DS = 2.10
0 _	DS = 2.99	DS = 2.99	DS = 2.99	DS = 2.99
Cell–O–Ü–	DS = 2.40	DS = 2.40	DS = 2.40	DS = 2.40
H₃C	DS = 2.10	DS = 2.10	DS = 2.10	DS = 2.10
	DS = 3.0	DS = 3.0	D\$ = 3.0	DS = 3.0
Cell-O-Ċ-	DS = 2.59	DS = 2.59	DS = 2.59	DS = 2.59
СН3	DS = 2.10	DS = 2.10	DS = 2.10 /	DS = 2.10
	DS = 2.98	DS = 2.98	DS = 2.98	DS = 2.98
О Сеll−О-Ё–∕́У–СН₃	DS = 2.60	DS = 2.60	DS = 2.60	DS = 2.60
	$\mathbf{DS} = 2.01 \sqrt{\frac{1}{2} \frac{1}{6} \frac{1}{6} \frac{1}{10} \frac{1}{12}}$	DS = 2.01	DS = 2.01	DS = 2.01
CH₂	DS = 3.0	DS = 3.0	DS = 3.0	DS = 3.0
Cell-O-Ċ	DS = 2.68	D\$ = 2.58	DS = 2.58	DS = 2.58
`CH₃	DS = 2.01	DS = 2.01	DS = 2.01	DS = 2.01
° _	DS = 3.0	DS = 3.0	DS = 3.0	DS = 3.0
Cell–O-Ċ–🧹 –C(CH <sub>3</sub> ) <sub>3</sub>	DS = 2.58	DS = 2.58	DS = 2.58	DS = 2.58
	DS = 1.90	DS = 1.90	DS = 1.90	DS = 1.90
	DS = 3.0	DS = 3.0	DS = 3.0	DS = 3.0
O Cell−O-Ċ−∕◯∕−Cl	DS = 2.42	DS = 2.42	DS = 2.42	DS = 2.42
	DS = 2.05	DS = 2.05	DS = 2.05	DS = 2.05

47 Note: Eluent for racemate A-C, hexane/2-propanol (98:2, v/v); eluent for racemate D, hexane/2-

<sup>48</sup> propanol (90:10, v/v). Flow rate, 1 mL/min.



**Figure S3.** Synthesis route of cellulose mixed esters, cellulose benzoate 3,5-dimethyl 52 phenylcarbamate, in AmimCl via a "one-pot, two-step" process.



**Figure S4.** (A) <sup>1</sup>H-NMR and (B) <sup>13</sup>C-NMR spectra of cellulose 3,5-dimethylbenzoate 3,5-dimethyl 56 phenylcarbamate.

50 prienvicarbania



**Figure S5.** <sup>1</sup>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 63 64 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/2-65 propanol/trifluoroacetic acid (90:9.8:0.2, v/v); Flow rate, 1 mL/min. (B) DL-Propranolol 66 hydrochloride was separated on cellulose 4-tert-butylbenzoate 3,5-dimethyl phenylcarbamate. 67 Eluent, hexane/2-propanol (50:50, v/v); Flow rate, 0.5 mL/min. (C) Tebuconazole was separated 68 69 on cellulose 4-tert-butylbenzoate 3,5-dimethyl phenylcarbamate. Eluent, hexane/2-propanol 70 (98:2, v/v); Flow rate, 1 mL/min. (D) DL-α-Tocopherol was separated on cellulose 4-tertbutylbenzoate 3,5-dimethyl phenylcarbamate. Eluent, hexane/2-propanol (90:10, v/v); Flow rate, 71 1 mL/min. (E) DL-Propranolol hydrochloride was separated on cellulose 3,5-dimethylbenzoate 3,5-72 73 dimethylphenylcarbamate. Eluent, hexane/2-propanol/triethylamine (50:49.8:0.2, v/v); Flow rate, 74 0.5 mL/min. (F) DL- $\alpha$ -Tocopherol was separated on cellulose 3,5-dimethylbenzoate 3,5-75 dimethylphenylcarbamate. Eluent, hexane/2-propanol (90:10, v/v); Flow rate, 1 mL/min. 76