Supporting Information for

Synthesis of Hindered Phenolic Esters over Ion-Exchange Resins

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S1. General information of experiment

The ion-exchange resins (NKC-9, D072, D001-CC, D001-SS, 001×4, 001×7, 001×14.5, D113), HY and γ -Al₂O₃ were obtained from the Chemical Plant of Nankai University (China) and the main parameters of the sulphonic acid functionalized resins were shown in Table S1. These catalysts were used after they have been dried under vacuum at 333 K for 48 h. Other chemicals were purchased from commercial suppliers and used without further purification unless otherwise noted. HPLC were used to monitor the esterification. HPLC analyses were performed on a Agilent 1100 Series instrument at ambient temperature using Zorbax Eclipse XDB-C18 column (reverse phase, 4.6 mm × 250 mm, 5-Micron), mobile phase: 90% methanol and aqueous acetic acid(0.5%, W/W). Column chromatography was performed using 200-300 mesh silica gel (Qingdao Haiyang). ¹H NMR and ¹³C NMR spectra were recorded on Bruker AVANCE III 600MHz NMR spectrometer, using TMS as an internal standard. High-resolution mass spectra were measured with a Bruker Daltonics micrOTOF-Q II instrument (ESI). Elemental Analysis data were measured using an Elementar Vario Micro cube instrument.

Table S1 Main parameters of sulphonic acid functionalized resins^a.

Catalyst ^b	Structure	Acidity (mmol/g) ^c	S _{BET} (m ² /g)	The ratio of acidity and S _{BET}	Pore volume (cm ³ /g)	Average pore diameter (nm)	T _{max} (°C)
NKC-9	MR	4.8	11.94	0.40	0.030	10.09	100
D072	MR	4.4	15.79	0.28	0.044	11.03	120
D001-CC	MR	4.1	22.86	0.18	0.073	12.82	120
D001-SS	MR	4.2	-	-	-	-	120
001×4	G	4.5	-	-	-	-	120
001×7	G	4.5	-	-	-	-	120
001×14.5	G	3.8	-	-	-	-	120

MR: macroporous structure. G: gel type polymer.

^a Date taken from reference^[1].

^b The particle size of ion-exchange resins is 0.3-1.25 mm.

^c The acidity of dry ion-exchange resins was detected.

S2. ¹H and ¹³C NMR information of products:

hexadecyl 3,5-di-*tert*-butyl-4-hydroxybenzoate^[2]

¹H NMR (CDCl₃, 600 MHz): δ = 0.88(t, J_{HH}= 6.6Hz, 3H, CH₃), 1.25-1.43 (m, 26H, C₁₃H₂₆), 1.46(s, 18H, 2C(CH₃)₃), 1.75(m, 2H, CH₂) 4.27(t, J_{HH}= 6.6Hz, 2H, COOCH₂), 5.64(s, 1H, OH), 7.9 (s, 2H; ArH).

¹³C NMR (CDCl₃, 150 MHz): δ =14.13, 22.71, 26.11, 28.85, 29.32, 29.39, 29.60, 29.72, 30.16, 31.95, 34.33, 64.68, 121.60, 127.00, 135.67, 158.05, 167.21 ppm.

Elemental Analysis: Anal. Calcd for C₃₁H₅₄O₃: C, 78.43; H, 11.46; O, 10.11. Found: C, 78.44; H, 11.43; O, 10.13.

HRMS (ESI Positive) calc. for C₃₁H₅₄O₃, [M+H]⁺ 475.4146, found 475.4146 .

tetradecyl 3,5-di-*tert*-butyl-4-hydroxybenzoate

^1H NMR (CDCl_3 , 600 MHz): δ = 0.88(t, J_{HH} = 6.6Hz, 3H, CH_3), 1.25-1.43(m, 22H, $\text{C}_{11}\text{H}_{22}$), 1.46(s, 18H, $2\text{C}(\text{CH}_3)_3$), 1.74(m, 2H, CH_2), 4.28(t, J_{HH} = 6.6Hz, 2H, COOCH_2), 5.65(s, 1H, OH), 7.91(s, 2H; ArH).

^{13}C NMR (CDCl_3 , 150 MHz): δ = 14.13, 22.71, 26.11, 28.85, 29.32, 29.38, 29.60, 29.71, 30.16, 31.95, 34.33, 64.69, 121.59, 127.00, 135.68, 158.06, 167.24 ppm.

Elemental Analysis: Anal. Calcd for $\text{C}_{29}\text{H}_{50}\text{O}_3$: C, 77.97; H, 11.28; O, 10.74. Found: C, 77.82; H, 11.29; O, 10.89.

HRMS (ESI Positive) calc. for $\text{C}_{29}\text{H}_{50}\text{O}_3$, $[\text{M}+\text{H}]^+$ 447.3833, found 447.3833.

octyl 3,5-di-*tert*-butyl-4-hydroxybenzoate

^1H NMR (CDCl_3 , 600 MHz): δ = 0.88(t, J_{HH} = 6.6Hz, 3H, CH_3), 1.28-1.44(m, 10H, C_5H_{10}), 1.46(s, 18H, $2\text{C}(\text{CH}_3)_3$), 1.74(m, 2H, CH_2), 4.28(t, J_{HH} = 6.6Hz, 2H, COOCH_2), 5.65(s, 1H, OH), 7.90(s, 2H; ArH).

^{13}C NMR (CDCl_3 , 150 MHz): δ =14.10, 22.67, 26.10, 28.84, 29.25, 30.16, 31.79, 34.34, 64.69, 121.58, 127.00, 135.69, 158.07, 167.24 ppm.

Elemental Analysis: Anal. Calcd for $\text{C}_{23}\text{H}_{38}\text{O}_3$: C, 76.20; H, 10.56; O, 13.24. Found: C, 76.11; H, 10.60; O, 13.28.

HRMS (ESI Positive) calc. for $\text{C}_{23}\text{H}_{38}\text{O}_3$, $[\text{M}+\text{H}]^+$ 363.2894, found 363.2894.

hexadecyl 3-(*tert*-butyl)-4-hydroxybenzoate^[3]

¹H NMR (CDCl₃, 600 MHz): δ = 0.88(t, J_{HH}= 7.2Hz, 3H, CH₃), 1.25-1.41(m, 26H, C₁₃H₂₆), 1.42(s, 9H, C(CH₃)₃), 1.75(m, 2H, CH₂), 4.28(t, J_{HH} = 6.6Hz, 2H, COOCH₂), 5.70 (s, 1H, OH), 6.71(d, J_{HH} = 7.8, 1H, ArH), 7.78 (dd, J_{HH} = 1.8 and 8.4 Hz, 1H, ArH), 8.00(d, J_{HH}=1.8 Hz, 1H, ArH).

¹³C NMR (CDCl₃, 150 MHz): δ =14.13, 22.71, 26.08, 28.79, 29.32, 29.36, 29.61, 29.68, 29.72, 31.95, 34.67, 65.11, 116.36, 121.99, 129.25, 136.17, 159.29, 167.7 ppm.

Elemental Analysis: Anal. Calcd for C₂₇H₄₆O₃: C, 77.46; H, 11.07; O, 11.46. Found: C, 77.41; H, 11.09; O, 11.49.

HRMS (ESI Positive) calc. for C₂₇H₄₆O₃, [M+H]⁺ 419.3520, found 419.3521.

hexadecyl 4-hydroxybenzoate^[3]

^1H NMR (CDCl_3 , 600MHz): δ = 0.86(t, J_{HH} = 7.2Hz, 3H, CH_3), 1.25-1.46(m, 26H, $\text{C}_{13}\text{H}_{26}$), 1.74(m, 2H, CH_2), 4.28 (t, J_{HH} = 6.6Hz, 2H, COOCH_2), 5.47 (s, 1H, OH), 6.86 (dd, J_{HH} = 2.4 and 7.2 Hz, 2H; ArH), 7.96 (dd, J_{HH} = 3 and 9.6 Hz, 2H; ArH).

^{13}C NMR (CDCl_3 , 150 MHz): δ = 14.13, 22.70, 26.06, 28.74, 29.31, 29.38, 29.55, 29.61, 29.67, 29.71, 31.94, 65.26, 115.31, 122.47, 131.93, 160.43, 167.26 ppm.

Elemental Analysis: Anal. Calcd for $\text{C}_{23}\text{H}_{38}\text{O}_3$: C, 76.20; H, 10.56; O, 13.24. Found: C, 76.22; H, 10.60; O, 13.18.

HRMS (ESI Positive) calc. for $\text{C}_{23}\text{H}_{38}\text{O}_3$, $[\text{M}+\text{Na}]^+$ 385.2713, found 385.2711.

Reference

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