

Electronic Supplementary Information

Nanoparticles of Aromatic Biopolymers Catalyze CO₂ Cycloaddition to epoxides under Atmospheric Conditions

*Wimalin Jaroonwatana,¹ Tharinee Theerathanagorn,¹ Man Theerasilp,¹ Silvano Del Gobbo,¹
Dungporn Yiamsawas,² Valerio D'Elia,^{1*} and Daniel Crespy^{1*}*

¹ Department of Materials Science and Engineering, School of Molecular Science and
Engineering, Vidyasirimedhi Institute of Science and Technology (VISTEC), Rayong 21210,
Thailand

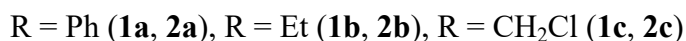
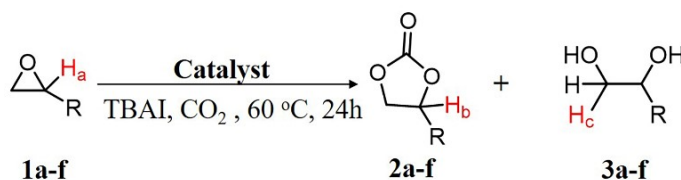
² National Nanotechnology Center (NANOTEC), National Science and Technology
Development Agency (NSTDA), Pathumthani 12120, Thailand

Determination of the conversion

The conversion of epoxides **1a-1f** was determined from ^1H NMR spectroscopy measurements by comparing the integrals of OCH_2CHR protons in the starting material (H_a) and in the product (H_b) according to Equation S1 below and to the chemical shifts reported in Table S1.

Equation S1. Conversion as calculated from the intensities (I_H) of the corresponding signals of OCH_2CHR protons in the starting material (H_a), cyclic carbonate product (H_b) and diol by-product (H_c).

$$\text{Conversion} = \frac{I_{Hb} + I_{Hc}}{(I_{Ha} + I_{Hb} + I_{Hc})} \quad (\text{eq. S1})$$



Scheme S1. CO_2 conversion with epoxides into cyclic carbonates

Table S1. Chemical shifts (δ , ppm, CDCl_3) for the corresponding OCH_2CHR protons in the epoxides, cyclic carbonate products and diol by-product.

Entry	δH_a (ppm)	δH_b (ppm)	δH_c (ppm)
1a/2a	3.86	5.68	-
1b/2b	2.89	4.66	-
1c/2c/3c	3.24	4.94	3.62

1d/2d	3.21	4.83	-
1e/2e/3e	3.25	4.97	3.73
1f/2f/3f	3.35	5.02	3.84

Determination of the selectivity

The selectivity for the carbonate product was determined via ^1H NMR from the integrals of protons of carbonated product (**Hb**) and diol by-product (**Hc**) shown in **Scheme S1** according to **Equation S2**. The selectivity was calculated from the integral values(I) of the RHCOCOOCH_2 protons in cyclic carbonate product (**Hb**) and RHCOHCOHH_2 protons in diol by-product (**Hc**).

$$\text{Selectivity of cyclic carbonates (\%)} = \frac{I_{\text{Hb}}}{(I_{\text{Hb}} + I_{\text{Hc}})} \times 100 \quad (\text{eq. S2})$$

Adsorption-desorption isotherms

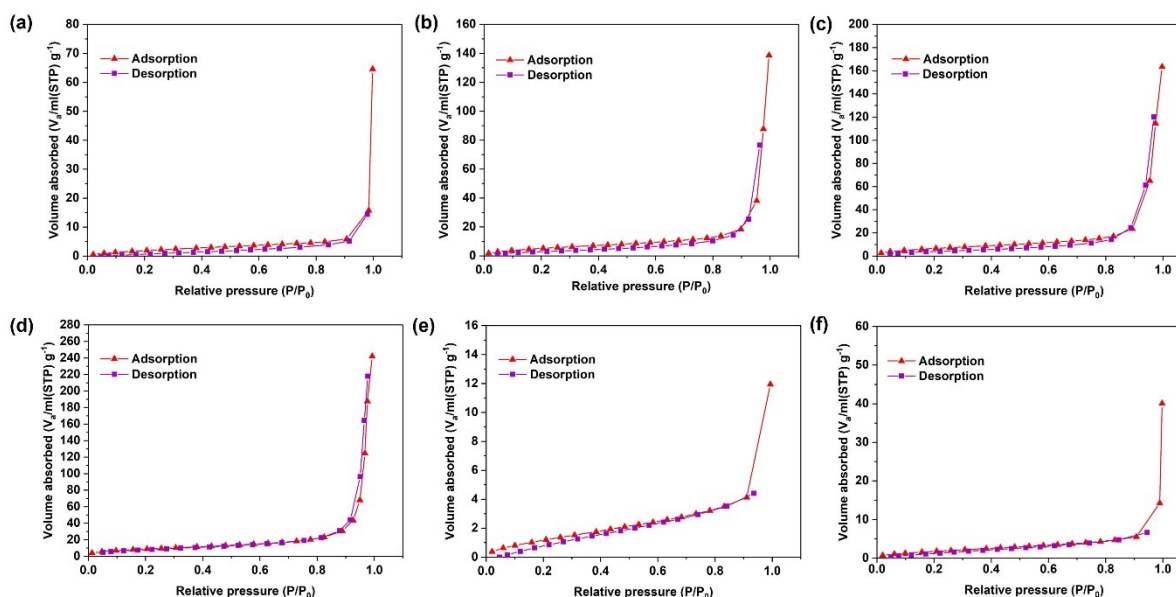


Figure S1. Nitrogen adsorption and desorption isotherm of (a) melanin microparticles from human hair, nanoparticles of (b) squid ink, (c) cuttlefish ink, (d) synthetic melanin, (e) lignin and (f) phenolated lignin.

XPS measurements

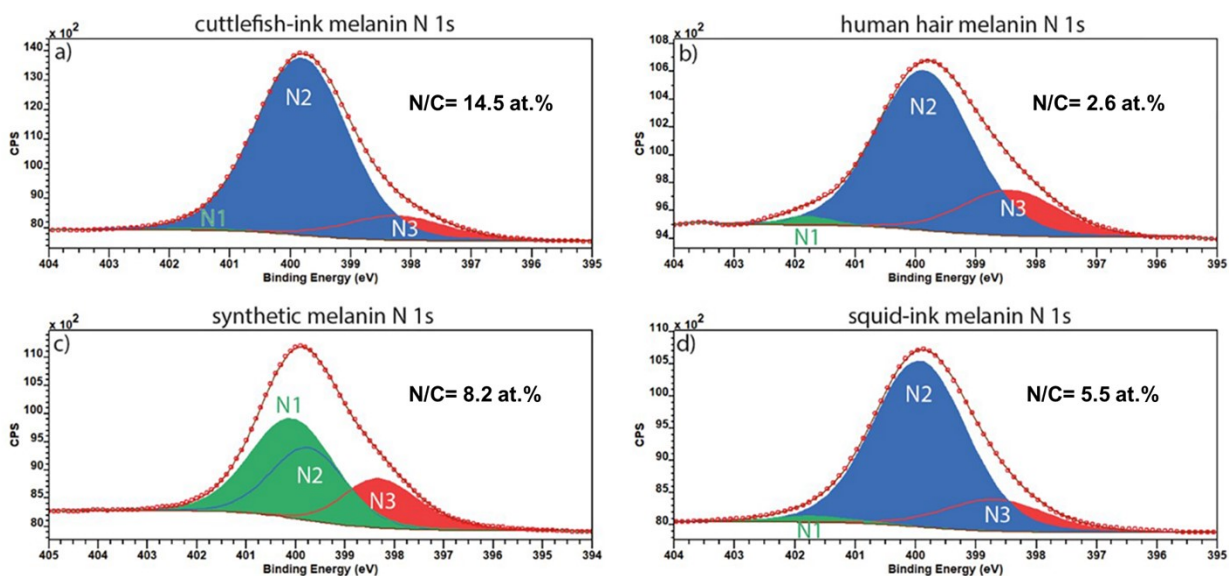


Figure S2. High resolution N 1s XPS spectra of a) cuttlefish ink melanin, b) human hair melanin, c) synthetic melanin, and d) squid ink melanin. The N/C atomic ratios estimated by XPS are given in each figure.

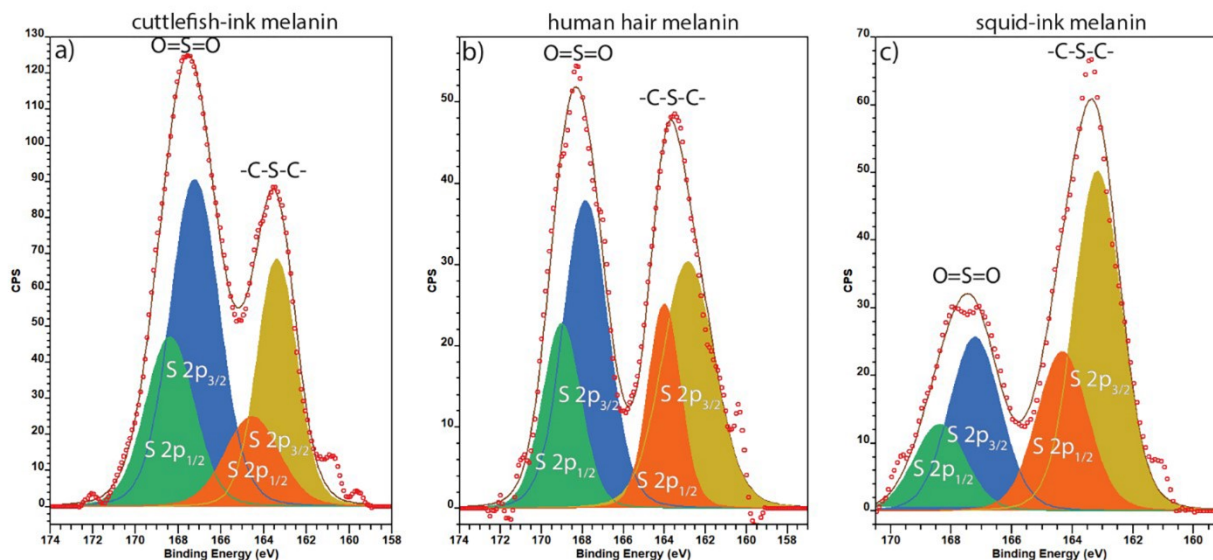


Figure S3. High resolution S 2p XPS spectra of a) cuttlefish-ink melanin, b) human hair melanin, and c) squid-ink melanin.

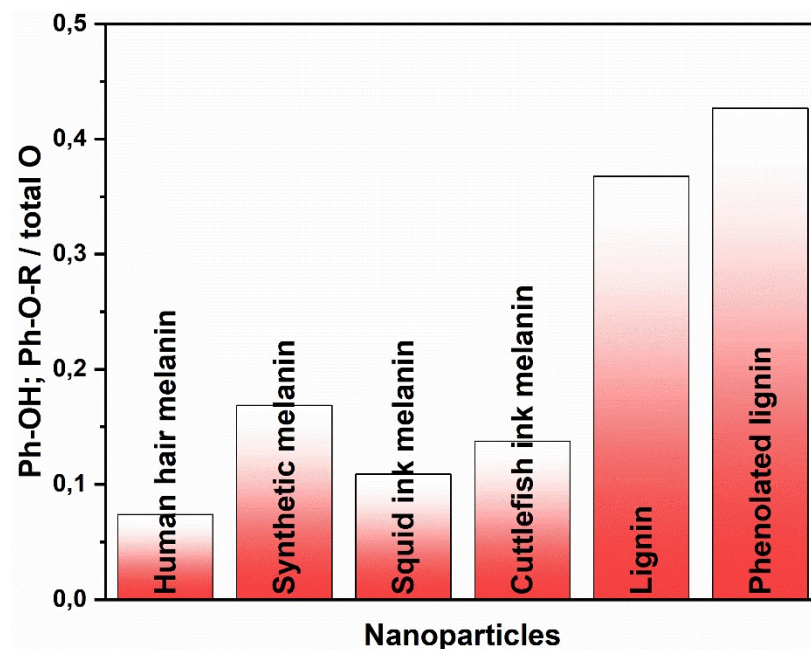


Figure S4. Ratio between phenolic oxygen atoms and total oxygen atoms based on deconvoluted O 1s components, as determined by XPS measurements.

Table S2. Binding energies of deconvoluted C 1s signals from melanin and lignin samples prepared in this work.

Material	C 1s components (eV)						
	π - π^* shake-up	O-C=O (C1)	C=O (C2)	C-O (C3)	C-N; C-S (C4)	C(sp ³) (C5)	C(sp ²) (C6)
Melanin microparticles from human hair	-	289.01	287.92	286.61	285.92	285.12	284.59
Synthetic melanin nanoparticles	290.52	288.45	287.28	286.62	285.71	284.77	284.18
Nanoparticles from squid ink		288.05	287.05	286.45	285.85	285.30	284.72
Nanoparticles from cuttlefish ink	289.83	287.99	287.65	286.22		285.00	284.36
Lignin nanoparticles		-	-	286.37		285.20	284.65

Phenolated lignin nanoparticles	288.86	287.01	286.20		285.35	284.48

Table S3. Binding energies of deconvoluted O 1s signals from melanin and lignin samples prepared in this work.

Material	O 1s components (eV)				
	Ph-OH (aromatic) (O1)	-O- C=O (O2)	-C-OH -C-O-C- (aliphatic) (O3)	-O-C=O (O4)	-C=O (O5)
Melanin microparticles from human hair	533.31	532.60		532.00	531.40
Synthetic melanin nanoparticles	533.35	532.54		531.82	531.19
Nanoparticles from squid ink	533.40	532.67		532.00	531.35
Nanoparticles from cuttlefish ink	533.29	532.60		531.79	531.08
	Ph-OH+ Ph-OR (aromatic) (O1*)				
Lignin nanoparticles	532.96		532.39		531.42
Phenolated lignin nanoparticles	533.30		532.42		531.46

Table S4. Binding energies of deconvoluted N 1s signals from melanin and lignin samples prepared in this work.

Material	N 1s components (eV)		
	R-NH ₂ /R-NH ₃ ⁺ (N1)	R ₂ NH (N2)	=NR (N3)
Melanin microparticles from human hair	401.78	399.88	398.50
Synthetic melanin nanoparticles	401.85	399.91	398.42
Nanoparticles from squid ink	401.73	399.93	398.69

Nanoparticles from cuttlefish ink	401.53	399.81	398.24
-----------------------------------	--------	--------	--------

Table S5. Binding energies of deconvoluted S 2p signals from melanin and lignin samples prepared in this work.

Material	S 2p components (eV)	
	C-S-C (S1)	SO ₂ (S2)
Melanin microparticles from human hair	2p ^{3/2} 162.85 2p ^{1/2} 164.01	2p ^{3/2} 167.85 2p ^{1/2} 169.01
Nanoparticles from squid ink	2p ^{3/2} 163.17 2p ^{1/2} 164.33	2p ^{3/2} 167.22 2p ^{1/2} 168.38
Nanoparticles from cuttlefish ink	2p ^{3/2} 163.38 2p ^{1/2} 164.55	2p ^{3/2} 167.23 2p ^{1/2} 168.39

Titration of phenolic groups of melanin nanoparticles

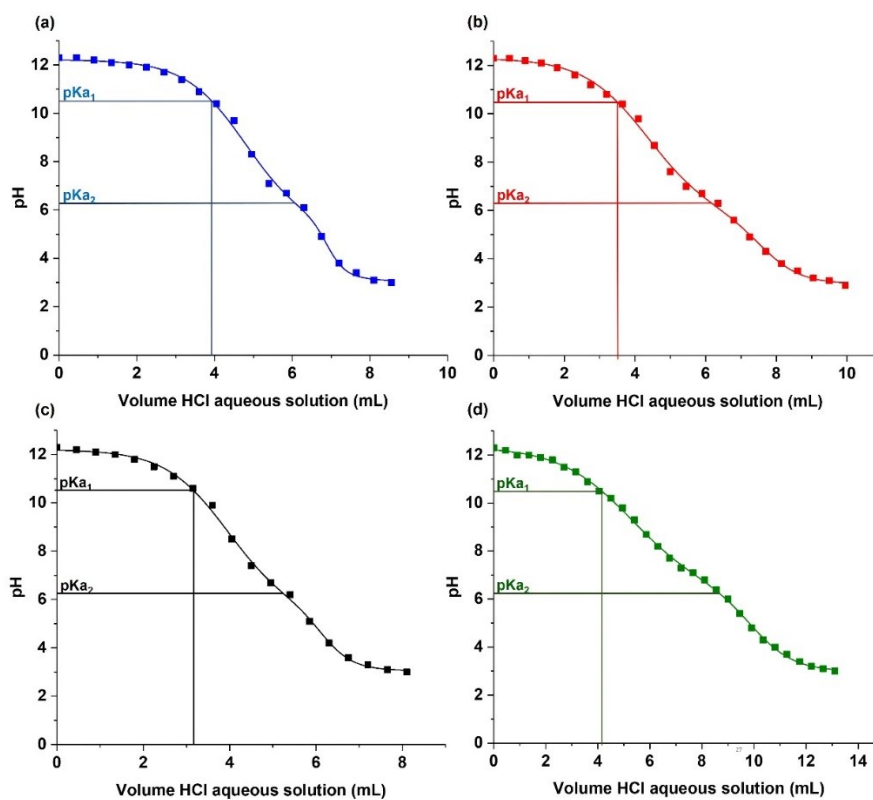


Figure S5. pH titration back-titration curves of the phenolic groups in melanin nanoparticles of (a) squid ink, (b) cuttlefish, (c) melanin microparticles from human hair, and (d) synthetic melanin nanoparticles.

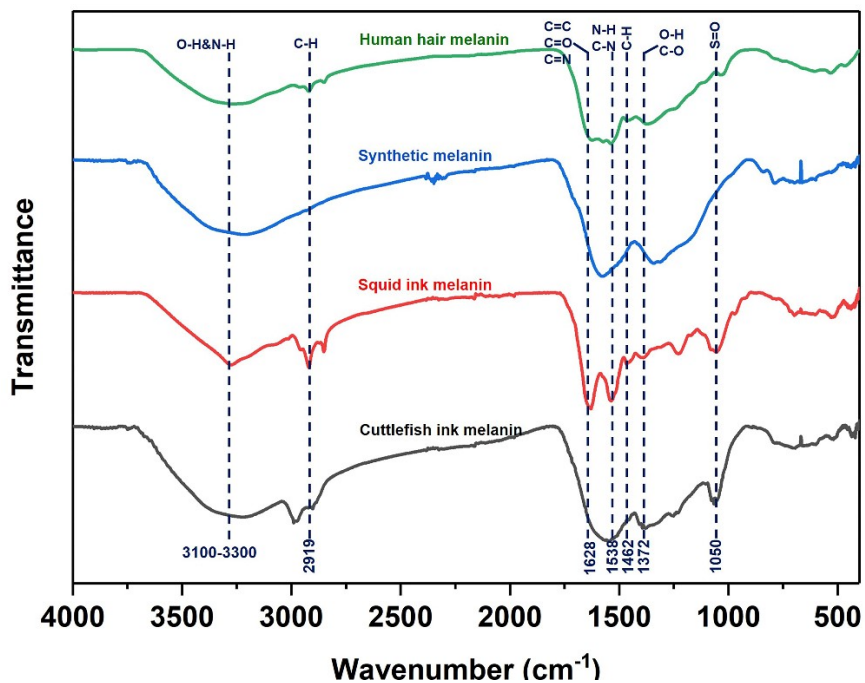


Figure S6. FTIR spectra of natural melanin particles from human hair, squid ink, cuttlefish ink, and synthetic melanin particles.

¹H NMR spectra of the products

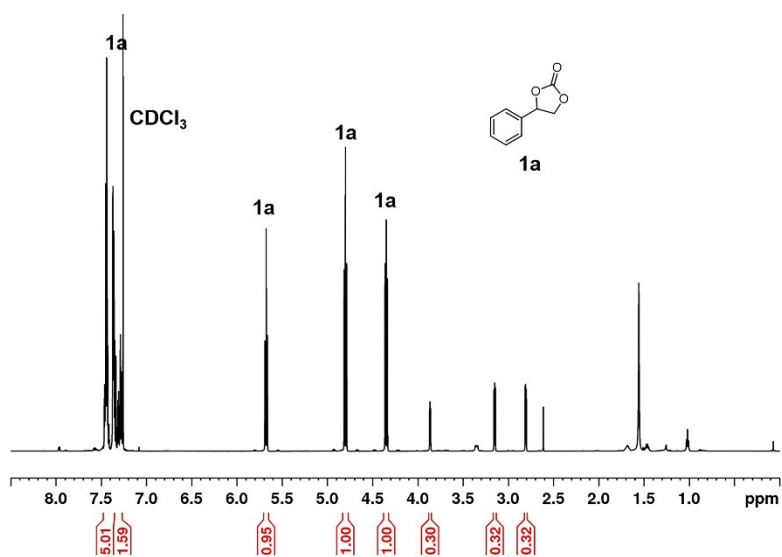


Figure S7. (4-phenyl-1,3-dioxolan-2-one) (1): ¹H NMR (CDCl₃, 600 MHz): δ 7.47-7.35 (m, 5H), 5.70-5.65 (t, 1H, *J* = 8.0 Hz), 4.83 -4.77 (t, 1H, *J* = 8.4 Hz), and 4.37-4.32 ppm (dd, 1H, *J* = 8.7, 7.8 Hz).

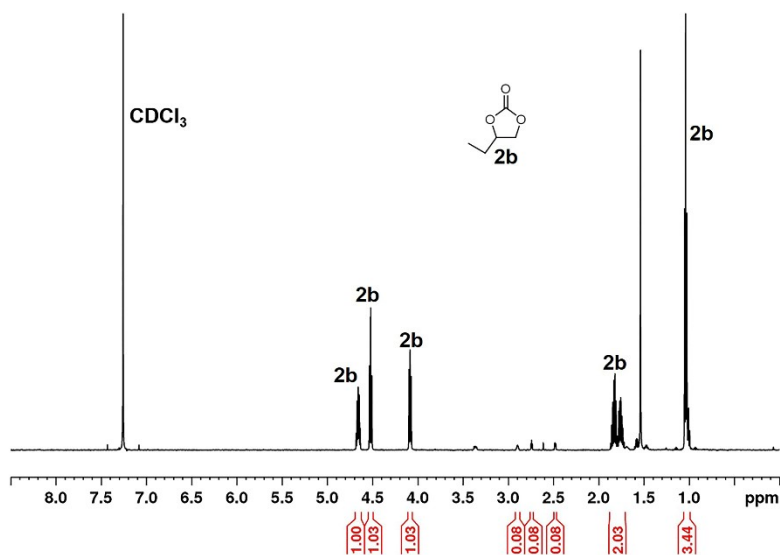


Figure S8. (4-ethyl-1,3-dioxolan-2-one) (2): ^1H NMR (CDCl_3 , 600 MHz): δ 4.62-4.55 (m, 1H), 4.48-4.42 (t, 1H, $J = 8.1$ Hz), 4.04-3.99 (dd, 1H, $J = 8.4, 7.0$ Hz), 1.82-1.75 (m, 2H), and 1.03-0.99 ppm (t, 3H, $J = 7.5$ Hz).

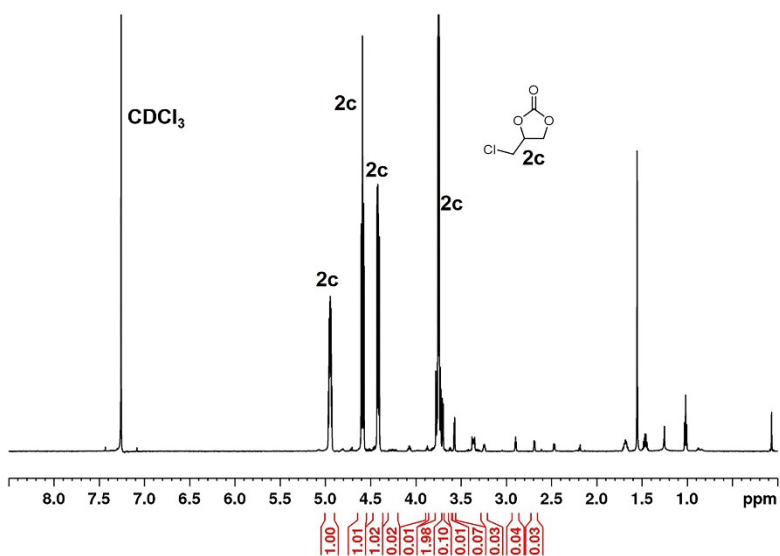


Figure S9. (4-(chloromethyl)-1,3-dioxolan-2-one) (3): ^1H NMR (CDCl_3 , 600 MHz): δ 5.00-4.90 (m, 1H), 4.64-4.54 (t, 1H, $J = 8.5$ Hz), 4.47-4.36 (dd, 1H, $J = 8.9, 5.7$ Hz), and 3.78-3.71 ppm (t, 2H, $J = 4.7$ Hz).

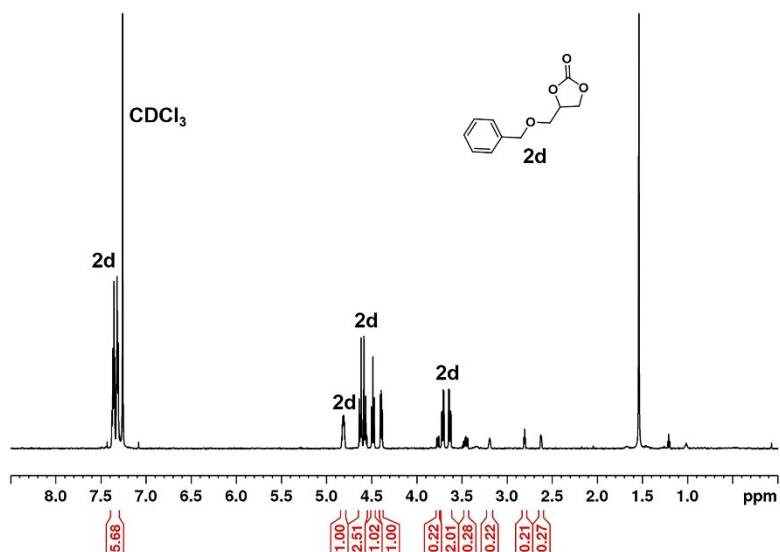


Figure S10. (4-(benzyloxymethyl)-1,3-dioxolan-2-one) (4): ^1H NMR (CDCl_3 , 600 MHz): δ 7.39-7.29 (m, 5H), 4.84-4.78 (dq, 1H, J = 9.0, 4.1 Hz), 4.64-4.54 (m, 2H), 4.51-4.46 (t, 1H, J = 8.3 Hz), 4.41-4.37 (dd, 1H, J = 8.3, 6.0 Hz), and 3.71 (dd, 1H, J = 10.9, 4.1 Hz) and 3.63 ppm (dd, 1H, J = 10.9, 3.8 Hz).

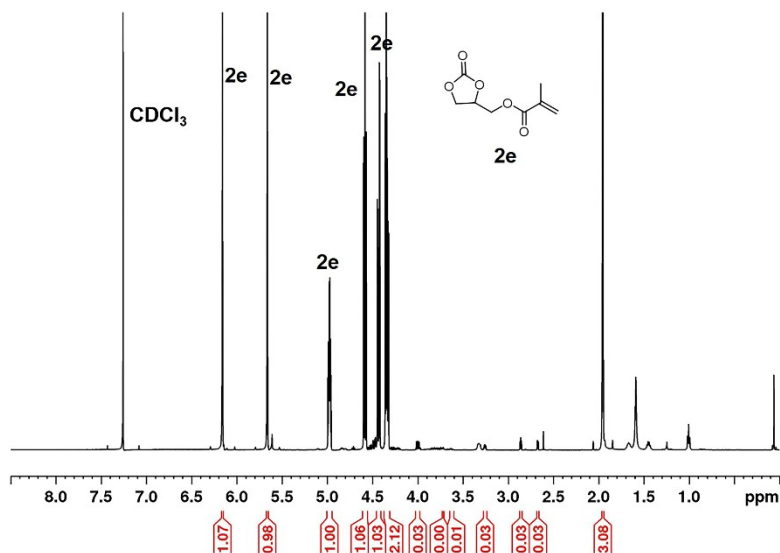


Figure S11. (2-oxo-1,3-dioxolan-4-yl)methyl methacrylate) (5): ^1H NMR (CDCl_3 , 600 MHz): δ 6.17-6.15 (q, 1H, J = 1.0 Hz), 5.67-5.65 (quint, 1H, J = 1.6 Hz), 5.00-4.95 (m, 1H), 4.60-4.56 (t, 1H, J = 8.6 Hz), 4.45-4.41 (dd, 1H, J = 12.6, 3.2 Hz), and 4.36-4.31 ppm (m, 2H).

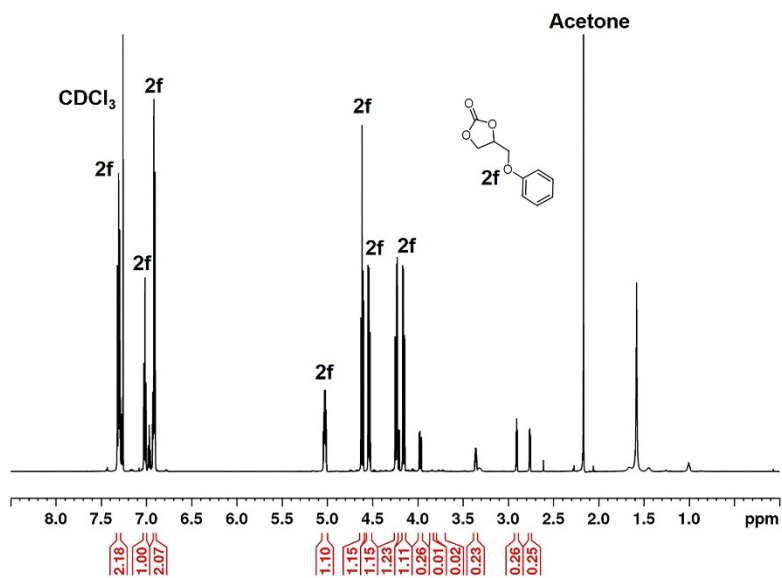
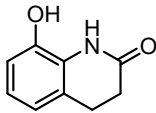
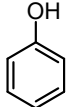


Figure S12. (4-(phoxymethyl)-1,3-dioxolan-2-one) (6): ^1H NMR (CDCl_3 , 600 MHz): δ 7.31 (m, 2H), 7.02 (tt, 1H, $J = 7.4, 1.0$ Hz), 6.92-6.89 (m, 2H), 5.03 (m, 1H), 4.61 (t, 1H, $J = 8.4$ Hz), 4.54 (dd, 1H, $J = 8.6, 5.9$ Hz), 4.23 (dd, 1H, 10.5, 4.3 Hz), and 4.15 ppm (dd, 1H, $J = 10.5, 3.6$ Hz).

Table S6. Comparison of catalytic performance of soluble model hydrogen bond donors in the cycloaddition of CO_2 to styrene oxide under standard reaction conditions.

Entry	Catalyst ^a	Conversion ^b (%)	Selectivity ^b
1	 8-Hydroxy-3,4-dihydro-2(1H)-quinolinone	46 ± 1	100
2	 Phenol	58 ± 1	100

^a Reaction conditions: styrene oxide (25 mmol, 2.83 mL), 0.1 mol % hydrogen bond donor, TBAI (1 mol%), 1 bar CO₂ (balloon), 60 °C, and 24 h.

^b Conversion and selectivity measured by ¹H NMR spectroscopy.

Recycling of the catalyst

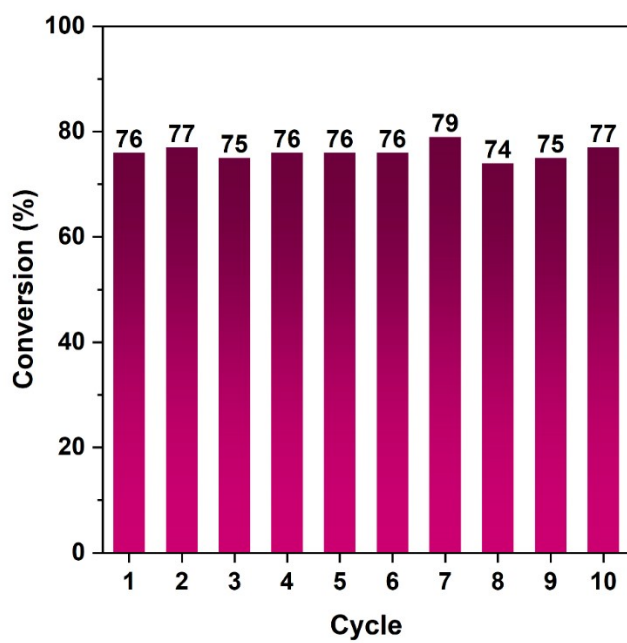


Figure S13. Reusability of phenolated lignin nanoparticles for the synthesis of styrene carbonate from CO₂ and styrene oxide. Reaction condition: styrene oxide (8.82 mmol), 35 mg phenolated lignin nanoparticles, TBAI (1 mol% compared with styrene oxide), 1 bar CO₂ (balloon), 60 °C, and 24 h.

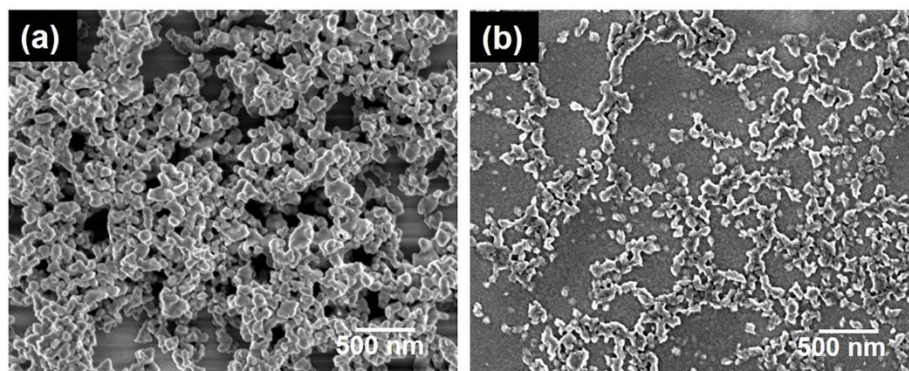


Figure S14. SEM micrographs of phenolated lignin nanoparticles after the first cycle (a) and the tenth cycle of catalysis (b).