Electronic Supplementary Material (ESI) for Dalton Transactions.

Preparation and Characterization of Nanofibrous Metal–Organic Frameworks as Efficient Catalysts for Synthesis of Cyclic Carbonates in the Solvent Free Conditions

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1. Sample preparation

1.1. Synthesis of UiO-66

Briefly, terephthalic acid (0.327 g) and $ZrCl_4$ (0.512 g) were mixed with DMF (25 mL) in a Teflon-lined bomb. The Teflon-lined bomb was then sealed and placed in an oven at 120 °C for 24 h. The final product was collected by centrifuging and washed successively with DMF and methanol several times. Finally, the UiO-66 particles were evacuated in vacuum at 100 °C for 12 h.

1.2. Synthesis of ZIF-67

2-methylimidazole (1.64 g) was dissolved in 2 mL deionized water and followed the addition of an aqueous $Co(NO_3).6H_2O$ solution (0.291 g in 2 mL deionized water) with stirring. Purple colored product was formed immediately at room temperature. Stirring kept for 2 hours and then the resulted purple powder filtered and washed with deionized water and ethanol 3 times and then kept for drying in the oven at 80°C overnight under vacuum.

2. Study of the electrospinning parameters:

For improving the fibers performances, different processing parameters such as voltage, the distance from needle to collector, PVA weight fraction in solution and MOF weight fraction relative to the polymer were optimized. The results are summarized in Table S1. As seen the best fibers were prepared with a concentration of 9% in water for PVA and 50% in DMF for PS. In the case of PVA, in concentrations of less than 9%, because of the low viscosity, the solvent was trapped into the fibers and knotted fibers were prepared and in concentrations of higher than 9%, the solution could not be passed through the needle. When the distance between the needle and the collector was 10 cm, the solvent has not enough time to evaporate, and therefore knotty fibers were obtained. For distances more than 15 cm, the electrospinning jet could not reach the collector, and no fibers were prepared.

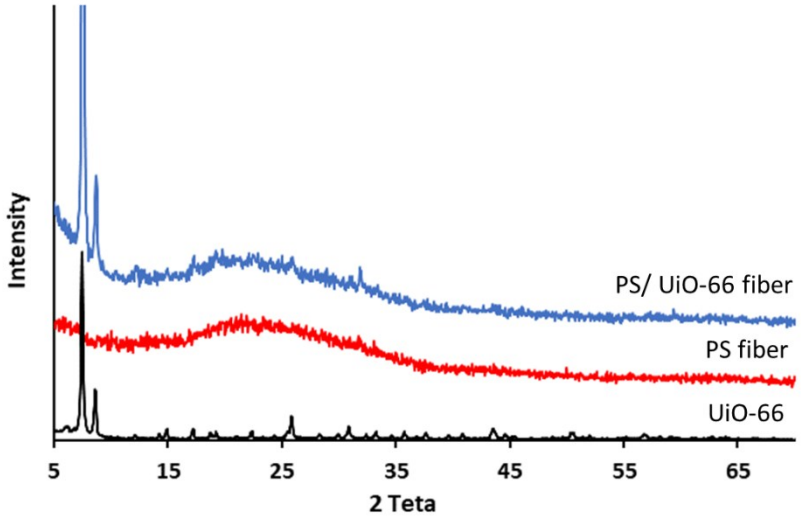

Figure S1: XRD patterns of UiO-66, PS fiber and PS-UiO-66 fiber.

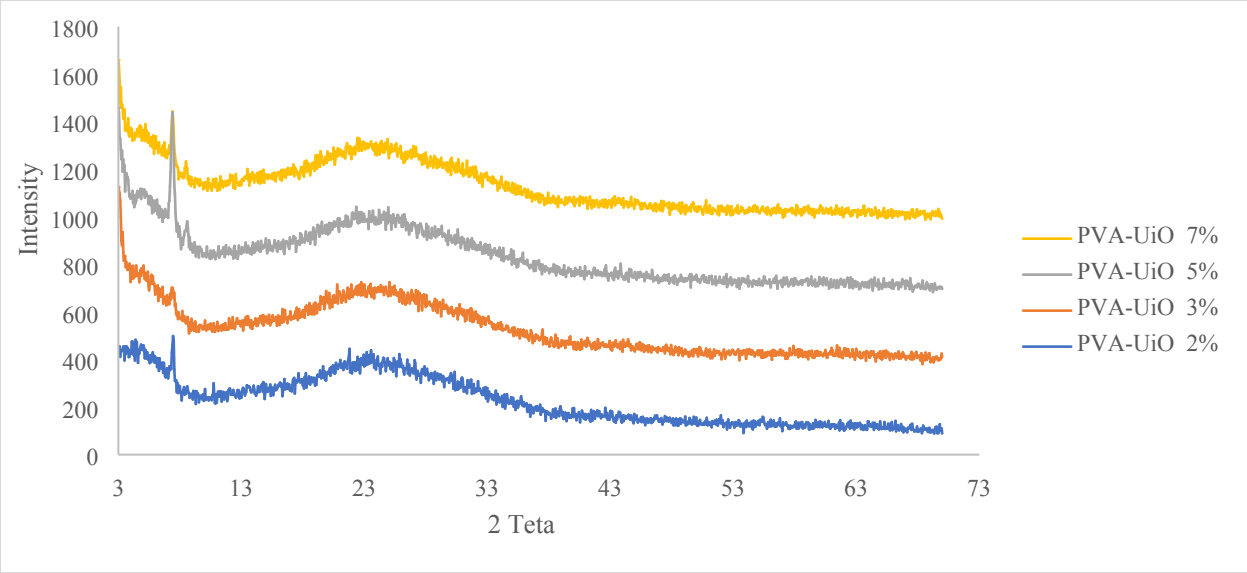

Figure S2: The XRD patterns of PVA/UiO-66 composites with different feeding weight ratio of UiO-66

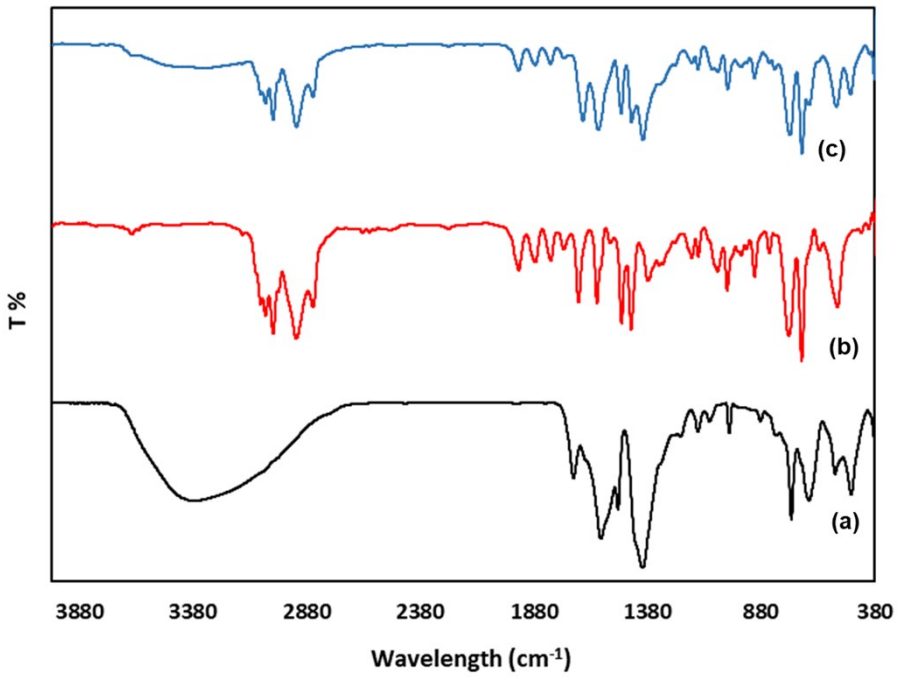

Figure S3: FT-IR spectra of (a) UiO-66, (b) PS fiber and (c) PS/UiO-66 fiber.

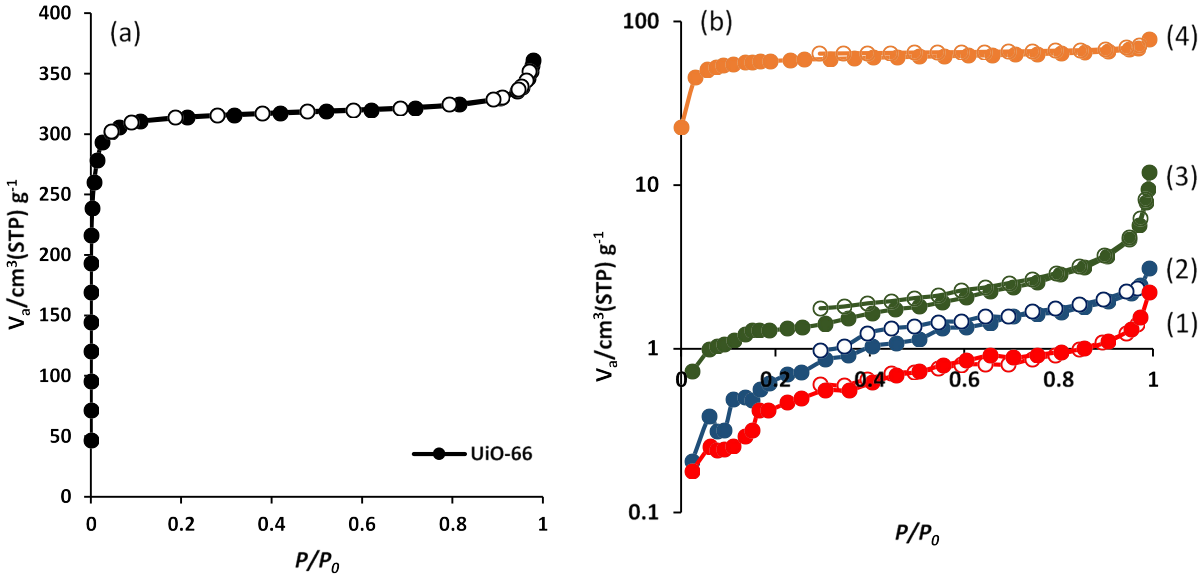

Figure S4: (a) N_2 isotherms of UiO-66 and (b) N_2 adsorption and desorption of (1) Ps fiber, (2) PS/UiO-66 fiber, (3) PVA fiber and (4) PVA/UiO-66 fiber (● = sorption, ○ = desorption).

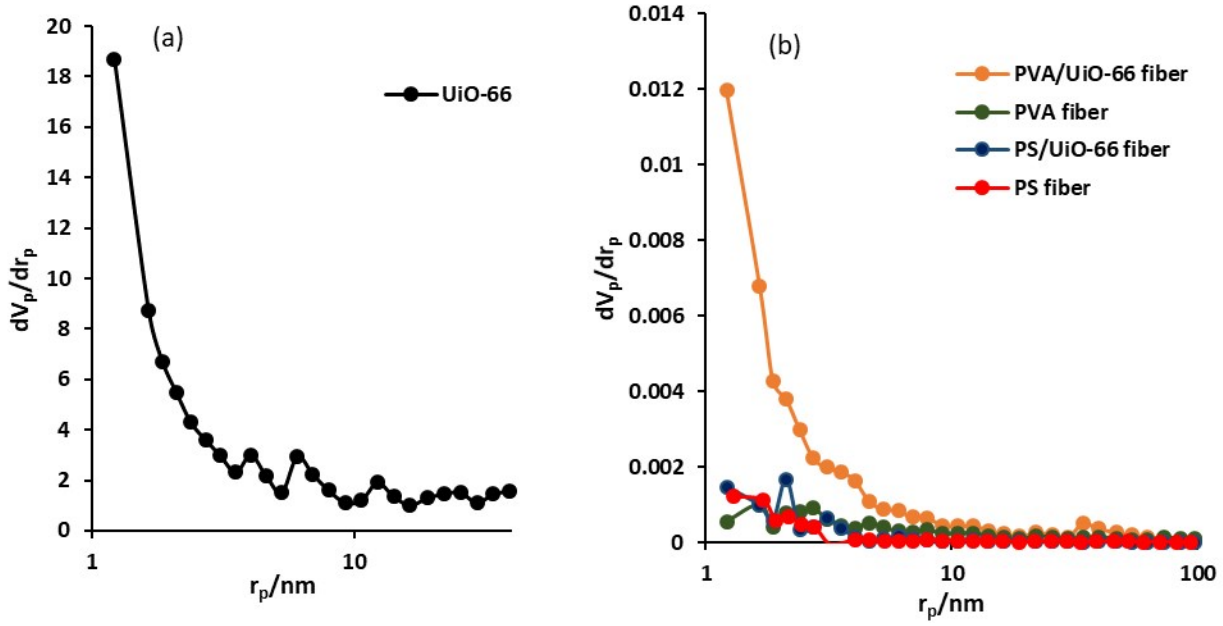

Figure S5: BJH plots of (a) UiO-66 and (b) PS fiber, PS/UiO-66 fiber, PVA fiber and PVA/UiO-66 fiber

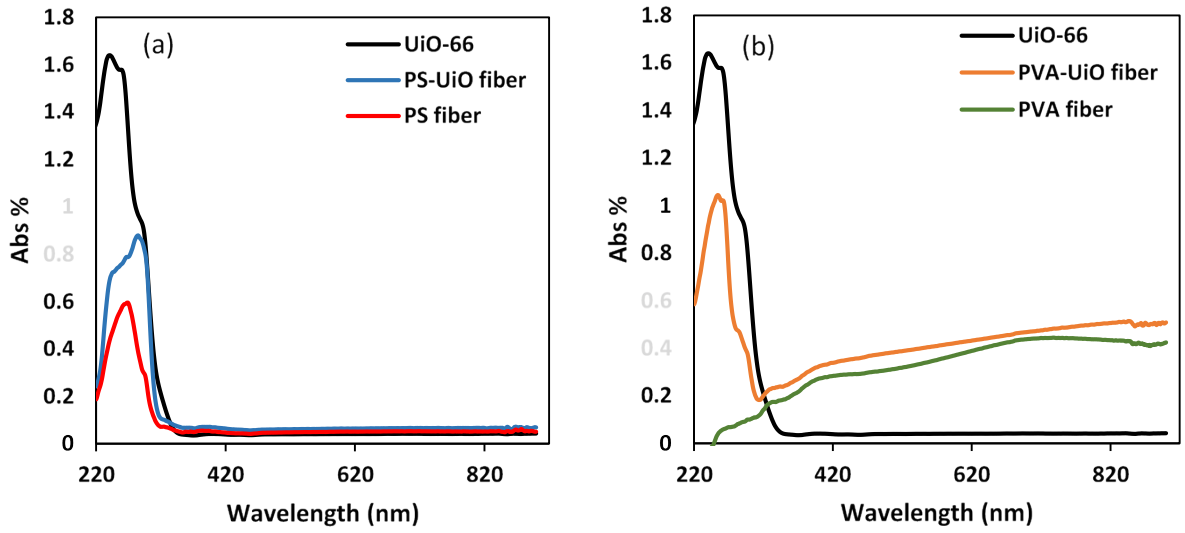

Figure S6: UV-Vis spectra of UiO-66, PS fiber, PS/UiO-66 fiber, PVA fiber and PVA/UiO-66 fiber.

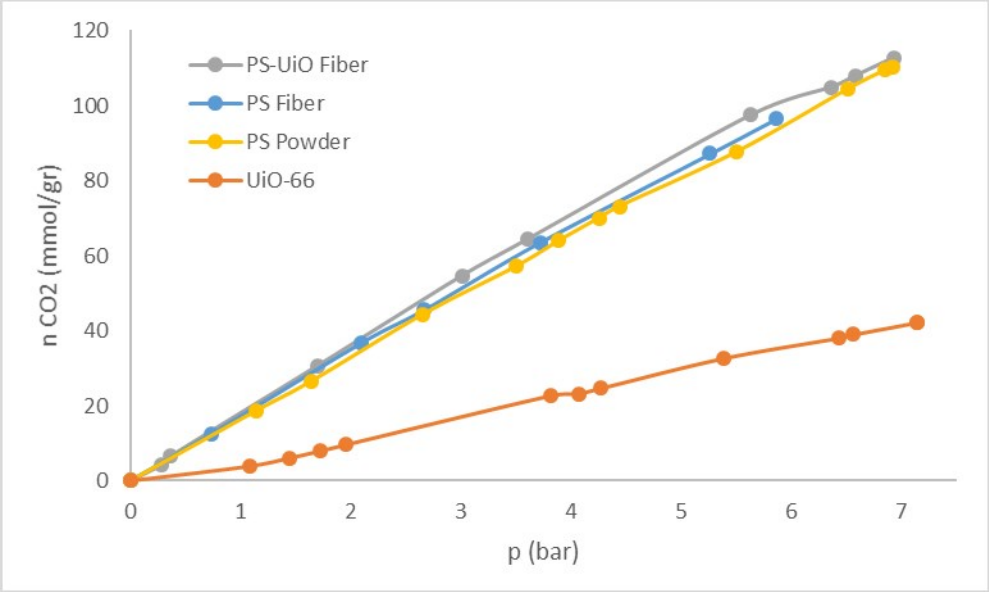

Figure S7. CO_2 adsorption capacity of UiO-66, PS powder, PS fiber and PS/UiO-66 fiber at 298.2 K.

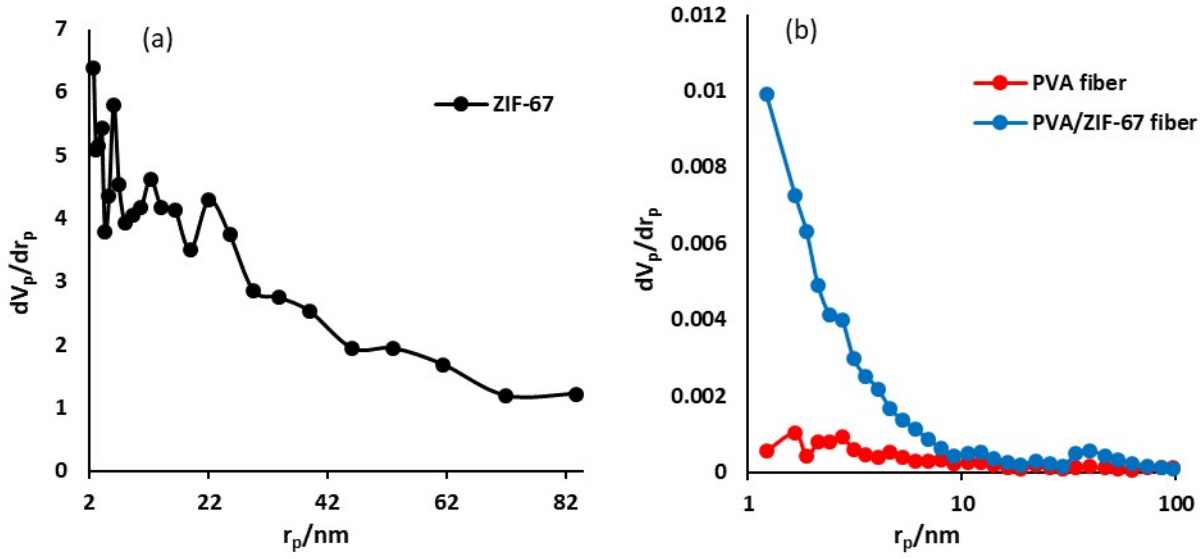

Figure S8: BJH plots of (a) ZIF-67 and (b) PVA fiber and PVA/ZIF-67 fiber.

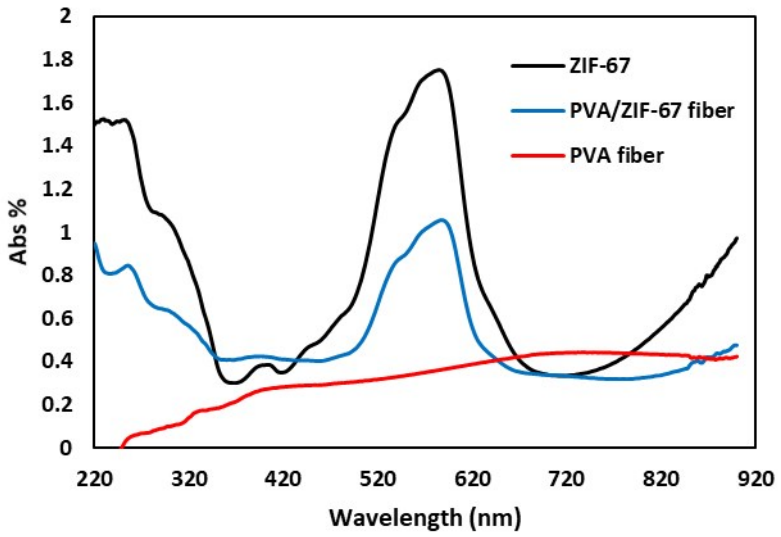

Figure S9: UV-Vis spectra of ZIF-67 fiber, PVA fiber and PVA/ZIF-67 fiber.

Table S1. Optimization of electrospinning parameters

	PVA/UiO-66 & PVA/ZIF-67	PS/UiO-66
Applied voltage (kV)	10, 15, 20	10, 15, 18, 20, 22
Flow rate (mL/h)	0.3, 0.5, 0.8	0.5, 1, 2, 3
Collection distance (cm)	10, 12, 15, 20	10- 15- 20
PVA weight fraction in solution (%)	5, 7, 9, 12	5, 10, 20, 30, 40, 50, 60
MOF weight fraction relative to the polymer solution (%)	2, 3, 5, 7	3, 5, 7, 8, 10

Table S2: Sorption data for UiO-66, PS fiber, PS/UiO-66 fiber, PVA fiber and PVA/UiO-66 fiber

Sample	S_{BET} (m^2 g^{-1})	Total pore volume (P/P_0=0.990) (cm^3 g^{-1})	Mean pore diameter (nm)
UiO-66	1315.5	0.5585	1.6983
PS fiber	1.6536	0.0032871	7.9514
PS/UiO-66 fiber	3.0412	0.0046288	6.0881
PVA fiber	4.8378	0.015581	12.883
PVA/UiO-66 fiber	220.96	0.1181	2.1372

Table S3: Cycloaddition of CO_2 to styrene epoxide[a]

Catalyst	Amount (mg)	Conversion[b] (%)	Selectivity[b] (%)
-	-	43	65
UiO-66 powder	40	66	71
PS powder	40	39	73
PS fiber	40	50	78
PS/UiO-66 fiber	40	65	72
PS/UiO-66 fiber	80	93	83
PVA powder	40	40	67
PVA fiber	40	43	81
PVA/(5%)UiO-66 fiber	40	65	70
PVA/(5%)UiO-66 fiber	80	90	84
PVA/(2%)UiO-66 fiber	80	50	58
PVA/(3%)UiO-66 fiber	80	45	55
PVA/(7%)UiO-66 fiber	80	40	49

[a]Reaction condition: Styrene epoxide (10 mmol), P_{CO2} (2.0 MPa), TBABr (0.3 gr) and T (120 °C) for 4h.
[b]Yields were determined by GC analysis.

Table S4: Conditions optimization of cycloaddition of CO_2 to styrene epoxide catalyzed by PVA/UiO-66 fiber

entry	Catalyst (mg)	time (h)	T (°C)	Epoxide (mmol)	P_{CO2} (bar)	TBABr (mg)	Conv.[a] (%)	Sel.[a] (%)
1	30	4	120	10	20	300	63	78
2	60	4	120	10	20	300	81	82
3	80	4	120	10	20	300	91	84
4	100	4	120	10	20	300	85	79
5	80	3	120	10	20	300	75	75
6	80	4	120	10	20	300	91	83
7	80	5	120	10	20	300	82	84
8	80	4	90	10	20	300	50	78
9	80	4	100	10	20	300	84	83
10	80	4	110	10	20	300	87	74
11	80	4	120	10	20	300	91	83
12	80	4	130	10	20	300	85	81
13	80	4	120	7	20	300	73	82
14	80	4	120	10	20	300	91	84
15	80	4	120	13	20	300	74	81
16	80	4	120	10	14	300	76	82
17	80	4	120	10	16	300	82	83
18	80	4	120	10	20	300	91	83.5
19	80	4	120	10	24	300	86	83.5
20	80	4	120	10	20	25	87	95
21	80	4	120	10	20	50	95	94
22	80	4	120	10	20	100	91	91
23	80	4	120	10	20	200	90	85
24	80	4	120	10	20	300	91	84

[a]Yields were determined by GC analysis.

Table S5: Conditions optimization of cycloaddition of CO_2 to styrene epoxide catalyzed by PS/UiO-66 fiber[a]

entry	T (°C)	TBABr (mg)	Conversion[b] (%)	Selectivity[b](%)
1	90	300	72	80
2	100	300	81	84
3	110	300	86	81
4	120	300	94	83
5	130	300	86	82
6	120	200	87	85
7	120	300	94	83
8	120	400	88	81

[a]Reaction condition: Catalyst =80 mg, epoxide=10 mmol, P_{CO2}=20 bar, for 4 h.
[b]Yields were determined by GC analysis.

Table S6: Sorption data for ZIF-67, PVA fiber and PVA/ZIF-67 fiber.

Sample	S_{BET} (m^2 g^{-1})	Total pore volume (P/P_0=0.990) (cm^3 g^{-1})	Mean pore diameter (nm)
ZIF-67	260.91	0.3284	5.0348
PVA fiber	4.8378	0.015581	12.883
PVA/ZIF-67 fiber	115.47	0.084734	2.9352

Table S7: Conditions optimization of cycloaddition of CO_2 to styrene epoxide catalyzed by PVA/ZIF-67 fiber

entry	Catalyst (mg)	time (h)	Epoxide (mmol)	TBABr (mg)	T (°C)	P_{CO2} (bar)	Conv.[a] (%)	Sel.[a] (%)
1	20	6	25	300	120	10	95	82
2	30	6	25	300	120	10	91	89
3	60	6	25	300	120	10	88	89
4	80	6	25	300	120	10	90	86
5	30	2	25	300	120	10	84	88
6	30	3	25	300	120	10	91	89
7	30	4	25	300	120	10	88	89
8	30	5	25	300	120	10	88	87
9	30	3	15	300	120	10	85	83
10	30	3	20	300	120	10	94	88
11	30	3	25	300	120	10	91	88
12	30	3	20	50	120	10	74	94
13	30	3	20	100	120	10	91	91
14	30	3	20	200	120	10	90	91
15	30	3	20	300	120	10	74	88
16	30	3	20	100	110	10	75	92
17	30	3	20	100	120	10	90	91
18	30	3	20	100	130	10	91	84
19	30	3	20	100	120	6	87	93
20	30	3	20	100	120	8	86	95
21	30	3	20	100	120	10	90	91
22	30	3	20	100	120	15	88	92

[a]Yields were determined by GC analysis.