

## Supporting information

### 1. Experimental

#### 1.1. Synthesis of catalyst

##### Synthesis of Poly-OC<sub>4</sub>Br

The monomer was firstly synthesized by the reaction between 2,4,6-tribromophenol and 1,4-dibromobutane. 1.32 g (4 mmol) of 2,4,6-tribromophenol and 1.08 mL (9 mmol) 1,4-dibromobutane were added in 60 mL of acetone, and then 0.552 g (4 mmol) of K<sub>2</sub>CO<sub>3</sub> was added to the mixture. The mixture was refluxed at 60°C under magnetic stirring overnight. After the solid K<sub>2</sub>CO<sub>3</sub> was removed by centrifugation, the solvent was evaporated. The obtained slurry crude product was not purified with column chromatography because the left 1,4-dibromobutane residue has no influence in the next step (Figure S1). Next, the crude product and 0.756 g (6 mmol) of 1,4-diethynylbenzene, 0.121 g (0.173 mmol) of bis(triphenylphosphine) palladium (II) dichloride and 0.06 g (0.316 mmol) of CuI were added in dry toluene (10 mL) and 6 mL of degassed N, N-diisopropylethylamine (DIPEA). The whole mixture was stirred at 60°C for 6 h in dark. After isolated by filtration, the obtained solid was washed with H<sub>2</sub>O, CH<sub>2</sub>Cl<sub>2</sub> and methanol. Finally, the synthesized sample was purified using Soxhlet extraction with methanol as the solvent for 2.5 days and then dried under vacuum. The yield of this cross-coupling reaction was about 70%. The resulting powder was denoted as Poly-OC<sub>4</sub>Br (yield 70%).

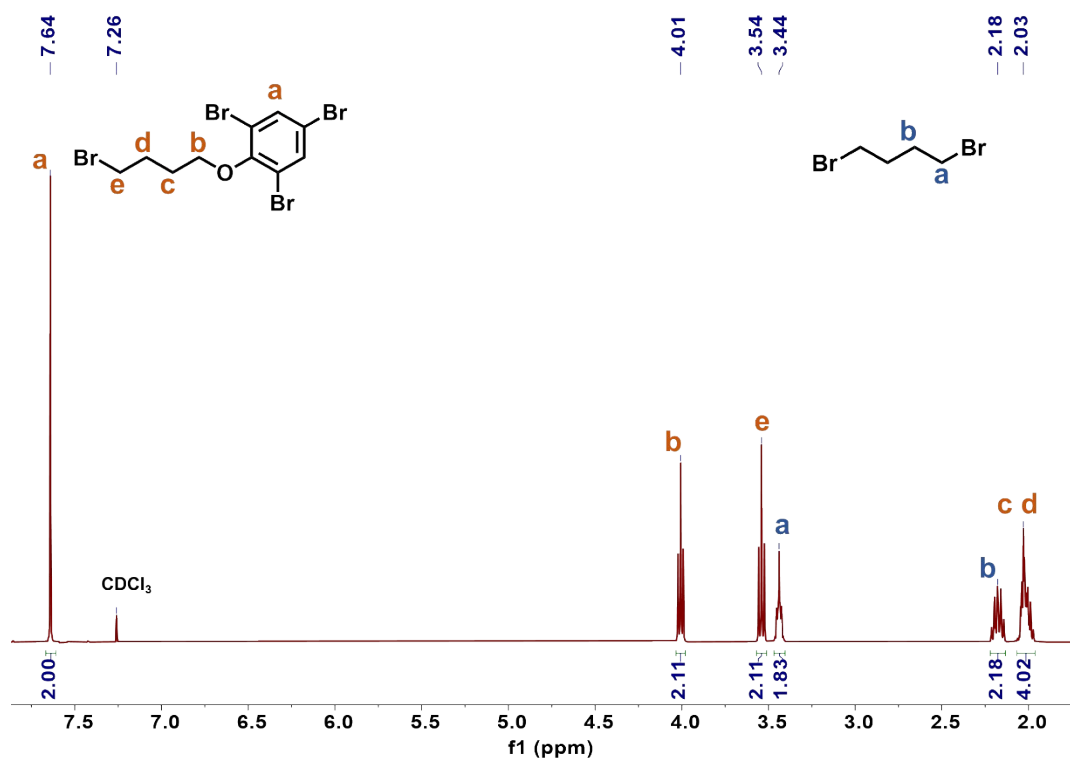


Figure S1. <sup>1</sup>H-NMR spectrum of 1,3,5-tribromo-2-(4-bromobutoxy) benzene in CDCl<sub>3</sub>

### Synthesis of Poly-OC<sub>4</sub>Br-VcB1

0.2 g of Poly-OC<sub>4</sub>Br and 6 mL of 4-methyl-5-thiazoleethanol was added to 50 mL of acetonitrile. The mixture was refluxed at 75°C for 48 h. After that, the solid sample was collected by centrifugation and washed with acetonitrile(4x35 mL) and acetone(2x35 mL). The Poly-OC<sub>4</sub>Br-VcB1 was dried at 60°C under vacuum for 12h.

### Synthesis of Poly-OC<sub>4</sub>Br-VcB1-TMSiLi

Poly-OC<sub>4</sub>Br-VcB1 (60mg) was dispersed in tetrahydrofuran (THF; 20mL), and 2mL of (trimethylsilyl)methyl lithium solution (TMSiLi in hexanes 0.55 M) was then slowly added. The whole mixture was stirred at 25 °C for 4h. After that, the powder collected by centrifugation was washed with THF (5x10 mL) in a glove filled with Argon and dried under vacuum.

### **Synthesis of Poly-OC<sub>4</sub>Br-TMSiLi**

The synthesis procedure of Poly-OC<sub>4</sub>Br-TMSiLi was the same as that of Poly-OC<sub>4</sub>Br-VcB1-TMSiLi. Poly-OC<sub>4</sub>Br (60mg) was dispersed in tetrahydrofuran (THF; 20 mL), then 2mL of (trimethylsilyl)methylolithium solution (TMSiLi in hexanes 0.55M) was added dropwise to the mixture. After stirring at 25°C for 4h, the powder was collected by centrifugation, washed with THF (5 × 10 mL) and dried under vacuum.

### **Synthesis of Poly-OC<sub>4</sub>Br-VcB1-MeOK and Poly-OC<sub>4</sub>Br-VcB1-tBuOK**

Poly-OC<sub>4</sub>Br-VcB1 (60 mg) and 84 mg of potassium methoxide (MeOK) were added to the methanol (MeOH; 30 mL). The whole mixture was stirred at 25°C for 4 h. After that, the powder collected by centrifugation was washed with MeOH (5 × 20 mL) and dried under vacuum. The synthesis procedure of Poly-OC<sub>4</sub>Br-VcB1-tBuOK was almost the same as the Poly-OC<sub>4</sub>Br-VcB1-MeOK. Poly-OC<sub>4</sub>Br-VcB1 (60 mg) and potassium t-butoxide (t-BuOK 134 mg) were added to the t-butanol (30 mL). After stirring at 25°C for 4h, the powder was isolated by centrifugation and washed with t-butanol (5 × 20 mL) and dried under vacuum.

### **Synthesis of Poly-OH**

1.322g (4 mmol) of 2,4,6-Tribromophenol, 0.756g (6 mmol) of 1,4-diethynylbenzene, 0.200g (0.173mmol) of tetrakis(triphenylphosphine) palladium and 0.06 g (0.316 mmol) CuI were added in extra-dry toluene (10 mL), then 10ml of degassed triethylamine (Et<sub>3</sub>N) was added. The whole mixture was stirred at 60°C for

6 h (protect from light during the polymerization reaction ). After removing the solvent by filtration, the obtained solid sample was washed with H<sub>2</sub>O, CH<sub>2</sub>Cl<sub>2</sub> and methanol. Finally, the synthesized sample was further purified by using Soxhlet extraction with methanol as the solvent for 2.5 days and then dried under vacuum.

### **Synthesis of 3-(4-bromobutyl)-5-(2-hydroxyethyl)-4- methyl thiazolium salt**

4-methyl-5-thiazoleethanol (6 mmol) and 1,4-dibromobutane (12 mmol) were added in acetonitrile(50 mL). This solution was refluxed at 75 °C for 48 h. After reaction, the acetonitrile solvent was evaporated. 40 mL acetone was then added to the resulting colloidal sample, and the formed white precipitate was isolated by centrifugation. After the solvents were removed by distillation, the colloidal sample was washed with ethyl ether. The <sup>1</sup>H-NMR spectrum of the colloidal sample is seen in Figure S2.

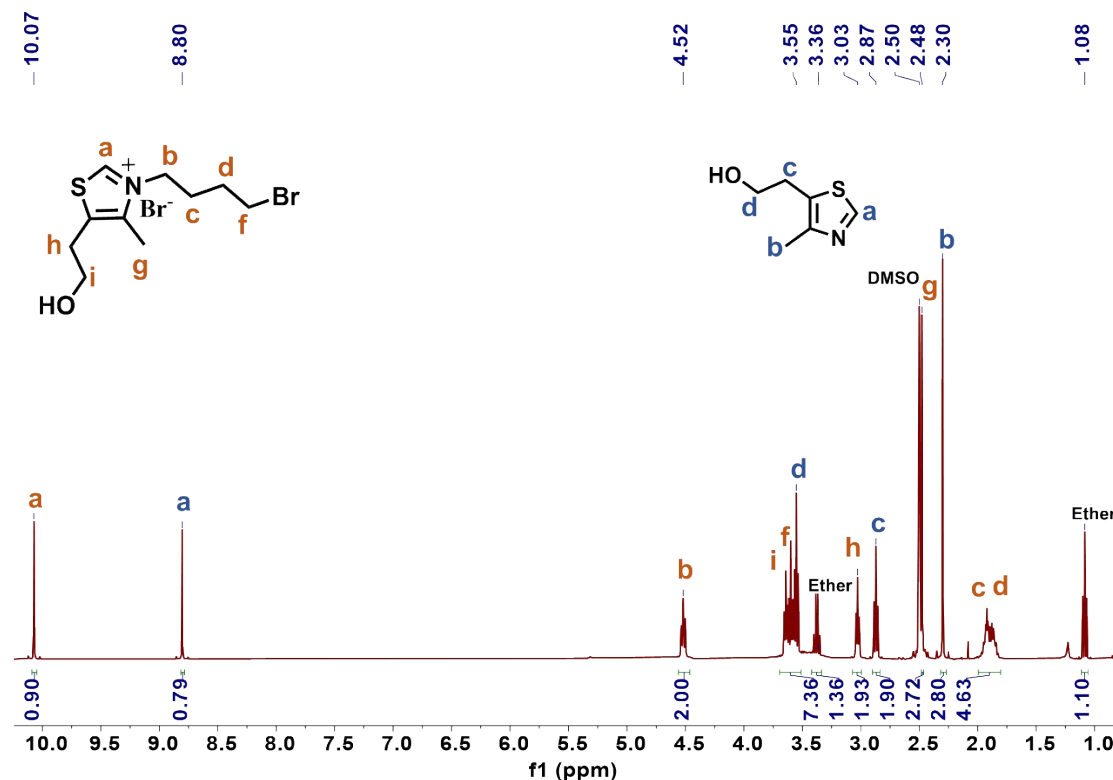


Figure S2. <sup>1</sup>H-NMR spectrum of 3-(4-bromobutyl)-5-(2-hydroxyethyl)-4-methylthiazolium salt in DMSO.

## 1.2. Catalyst characterization

<sup>1</sup>H-NMR spectra and <sup>13</sup>C-NMR spectra were recorded on a Bruker Nuclear Magnetic Resonance (NMR) DPX-500 spectrometer. The solid-state <sup>13</sup>C-NMR spectra were recorded on 600MHz WB Solid-State NMR spectrometer. Thermogravimetric analysis (TGA) was carried out on SHIMADZU thermogravimetric analyzer. The temperature was increased to 800°C from 25°C under air atmosphere with a heating rate of 5°C/min. Transmission electron microscope (TEM, Tecnai G2 F30 S-Twin, Philips-FEI Co.) and EDX mapping was used to observe the morphologies of the catalysts and metal element dispersion. The powders were ultrasonically dispersed in the ethanol to form a suspension, and it was doped to the porous copper grid coated with carbon film for TEM observation. Elemental analysis was performed on Thermo Fisher

Scientific Flash Smart CHNS/O elemental analyzer. Powder X-ray diffraction (PXRD) experiments were carried out on a Bruker D8 Venture (Cu K $\alpha$  radiation). The X-ray diffraction patterns were collected from  $2\theta = 3^\circ$  to  $80^\circ$ . The voltage and current were operated at 40 kV and 300 mA, and the scanning speed was  $10^\circ / \text{min}$ . N<sub>2</sub> adsorption experiment was carried out on a Micromeritics instrument (ASAP2040). Before N<sub>2</sub> physical adsorption, the sample (~0.1 g) was degassed at 383 K for 6 h under the vacuum. The specific surface area was calculated according to the BET method.

### **1.3. Catalytic reaction**

#### **Catalytic reaction under batch conditions**

60mg of the catalyst, 180 mg of paraformaldehyde powder, 84  $\mu\text{L}$  of triethylamine (NEt<sub>3</sub>) and 1 mL of DMF were loaded to the 10 mL Schlenk tube and heated to  $90^\circ\text{C}$  under stirring for 2 h by using an aluminum heating block. In order to exclude the influence of air and water, the loading process was conducted in a glovebox filled with Argon. After catalytic reaction, the Schlenk tube was allowed to cool to room temperature. To 300  $\mu\text{L}$  of the reaction solution was added 200  $\mu\text{L}$  of DMSO-d<sub>6</sub> and 40  $\mu\text{L}$  of toluene as an internal standard. the reaction solution was analyzed by <sup>1</sup>H-NMR. (For Table 1 entries 1a and 8d, no NEt<sub>3</sub> was added in the catalytic reaction system)

#### **Catalytic reaction using Soxhlet extractor reactor**

The Poly-OC<sub>4</sub>Br-VcB1-TMSiLi catalyst ( 60 mg) and paraformaldehyde powder(

180 mg) loaded in filter cartridge were placed inside the "extraction tube". The Soxhlet extractor was modified to have a minimum liquid retention volume. The dioxane solvent was loaded in the flask. The temperature of the heater and the water flowing in the reflux condenser were 120 °C and 85 °C, respectively. During the reaction, the dioxane vapour flooded into the "extraction tube", and was cooled by the reflux condenser (85 °C) to condense; then the warm solvent (~85 °C) dripped into the filter cartridge, where the catalytic reaction occurred. The dissolved reaction products were transported to the distillation flask with the drops. The product DHA could not evaporate due to its higher boiling point and accumulated in the still pot.

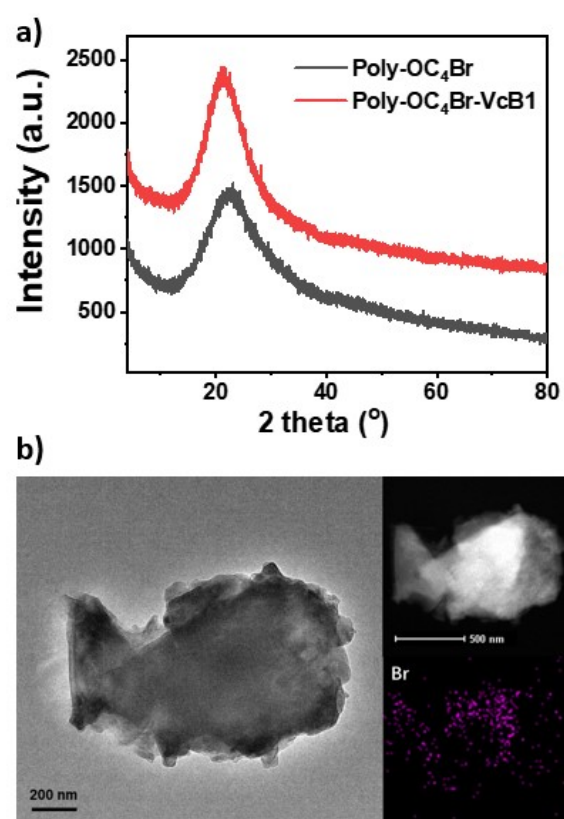


Figure S3. (a) The Powder X-ray diffraction (XRD) of the prepared samples; (b) TEM image, dark-field TEM image and the corresponding EDS mapping of Poly-OC<sub>4</sub>Br



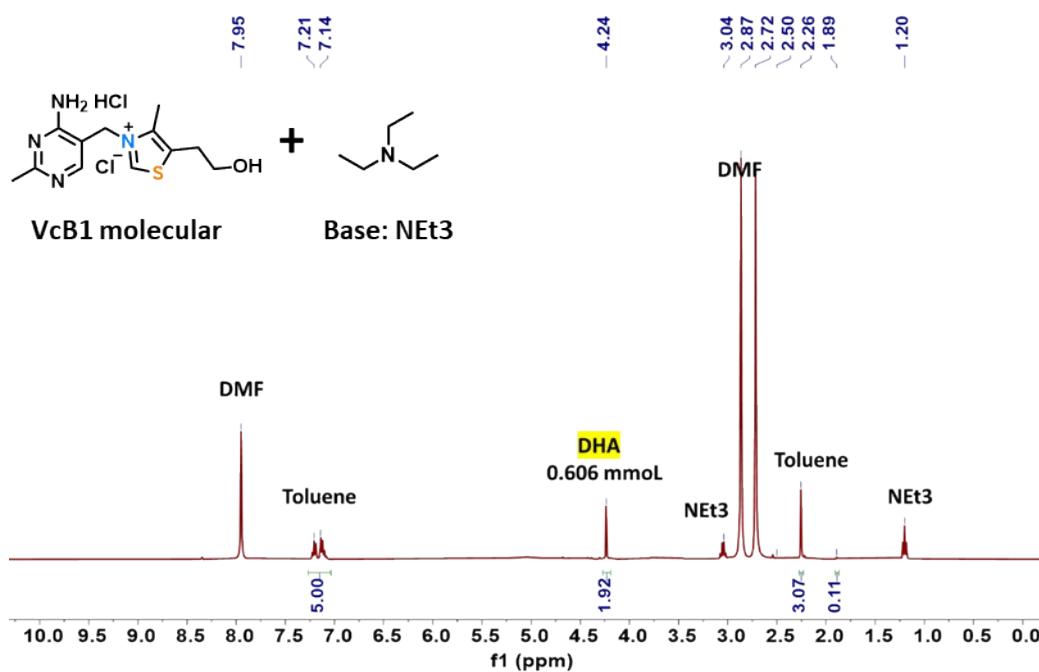


Figure S4. <sup>1</sup>H-NMR spectrum of the formaldehyde condensation mixture catalyzed by thiamine hydrochloride in the presence of base (Cat 0.3mmol; paraformaldehyde 6 mmol; NEt<sub>3</sub> 0.6mmol; DMF 1mL; 90°C; 2h). Toluene was used as an internal standard.

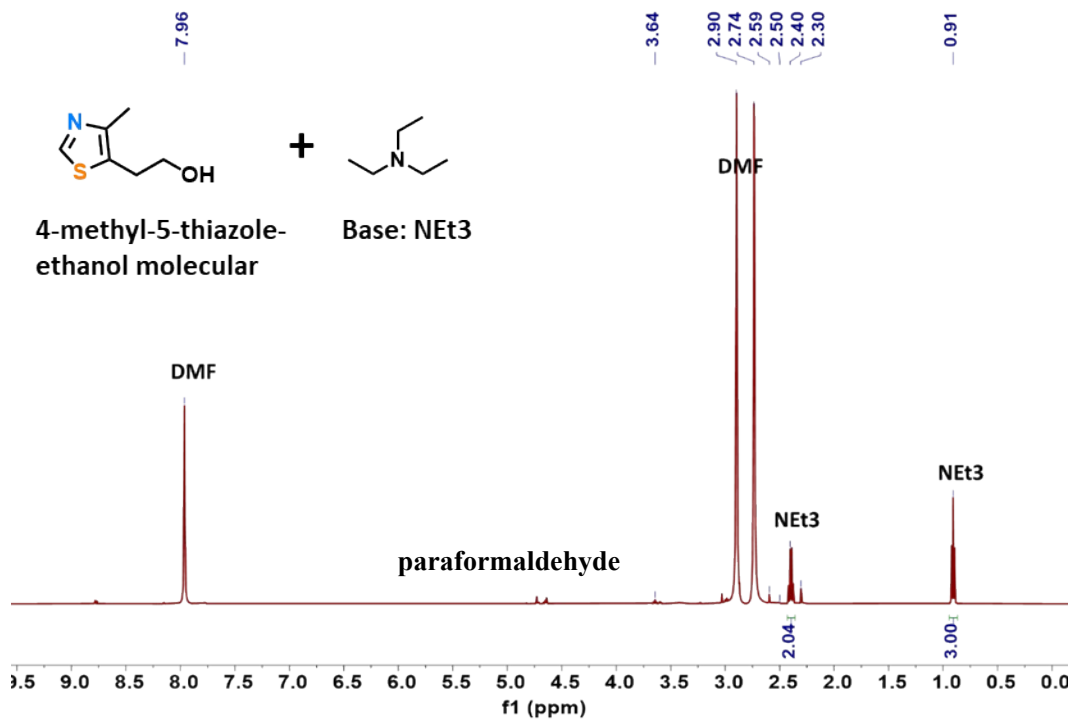


Figure S5. <sup>1</sup>H-NMR spectrum of the formaldehyde condensation mixture catalyzed by 4-methyl-5-thiazoleethanol in the presence of base (Cat 0.3mmol; paraformaldehyde 6 mmol; NEt<sub>3</sub> 0.6 mmol; DMF 1mL; 90°C; 2h).

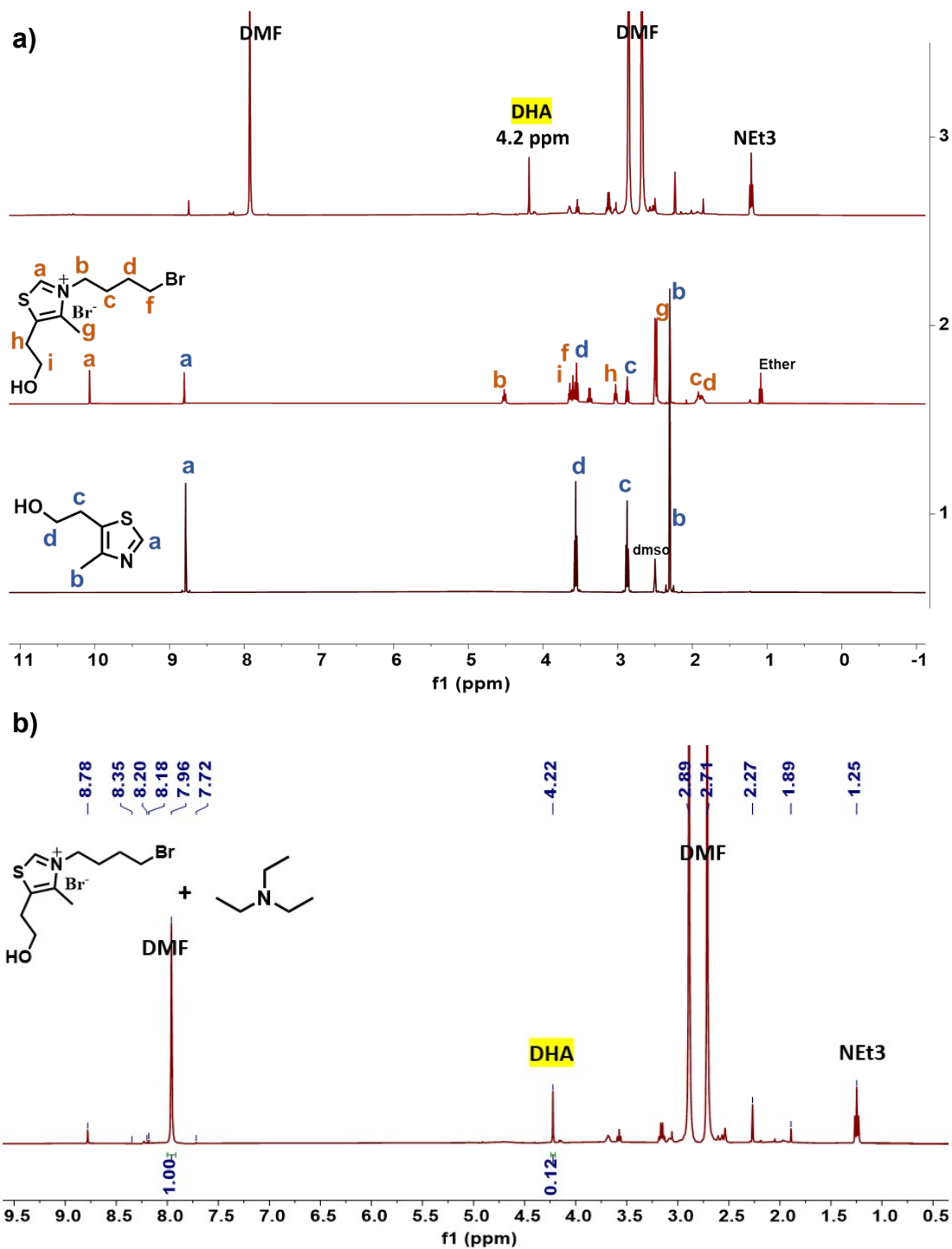


Figure S6. a)  $^1\text{H-NMR}$  spectrum of the formaldehyde condensation mixture catalyzed by 3-(4-bromobutyl)-5-(2-hydroxyethyl)-4-methylthiazolium salt in the presence of  $\text{NEt}_3$  (paraformaldehyde 6 mmol;  $\text{NEt}_3$  0.6 mmol; DMF 1 mL;  $90^\circ\text{C}$ ; 2 h; the top);  $^1\text{H-NMR}$  spectrum of 3-(4-bromobutyl)-5-(2-hydroxyethyl)-4-methylthiazolium salt (the center) and 4-methyl-5-thiazoleethanol (the bottom). b) the DHA produced is about 0.4 mmol calculated based on the DMF.

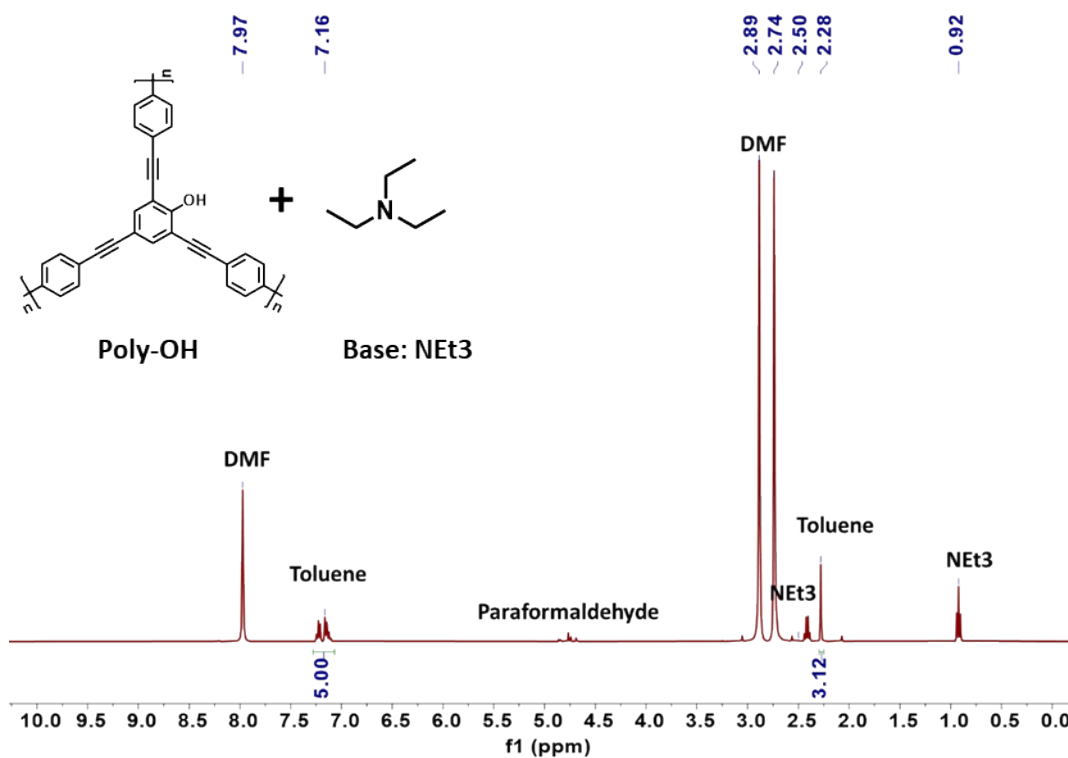


Figure S7. <sup>1</sup>H-NMR spectrum of the formaldehyde condensation mixture catalyzed by Poly-OH in the presence of NEt<sub>3</sub> (Cat 60 mg; paraformaldehyde 6 mmol; NEt<sub>3</sub> 0.6 mmol; DMF 1mL; 90°C; 2h). Toluene was used as an internal standard.

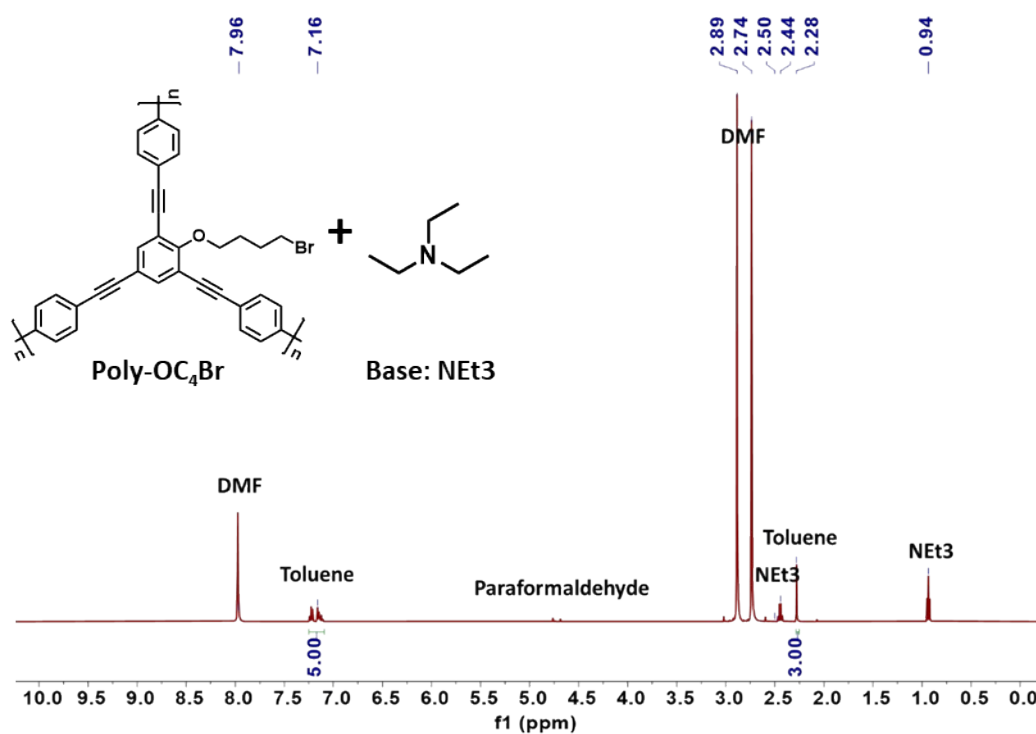


Figure S8. <sup>1</sup>H-NMR spectrum of the formaldehyde condensation mixture catalyzed by Poly-OC<sub>4</sub>Br in the presence of NEt<sub>3</sub> (Cat 60 mg; paraformaldehyde 6 mmol; NEt<sub>3</sub> 0.6 mmol; DMF 1mL; 90°C; 2h). Toluene was used as an internal standard.

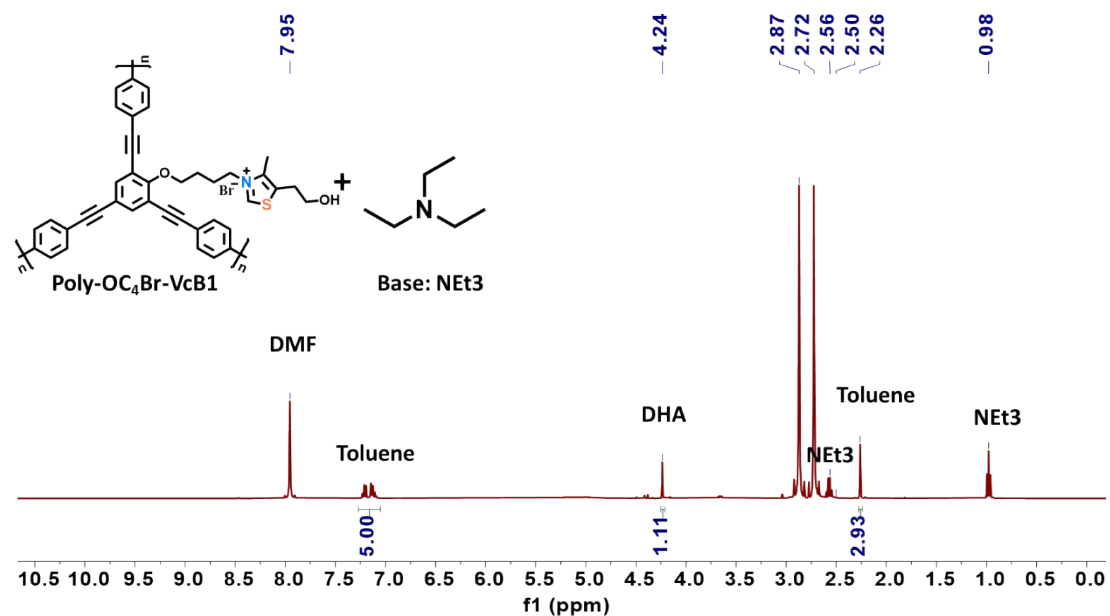


Figure S9. <sup>1</sup>H-NMR spectrum of the formaldehyde condensation mixture catalyzed by Poly-OC<sub>4</sub>Br-VcB1 in the presence of NEt<sub>3</sub> (Cat 60 mg; paraformaldehyde 6 mmol; NEt<sub>3</sub> 0.6 mmol; DMF 1mL; 90°C; 2h). Toluene was used as an internal standard.

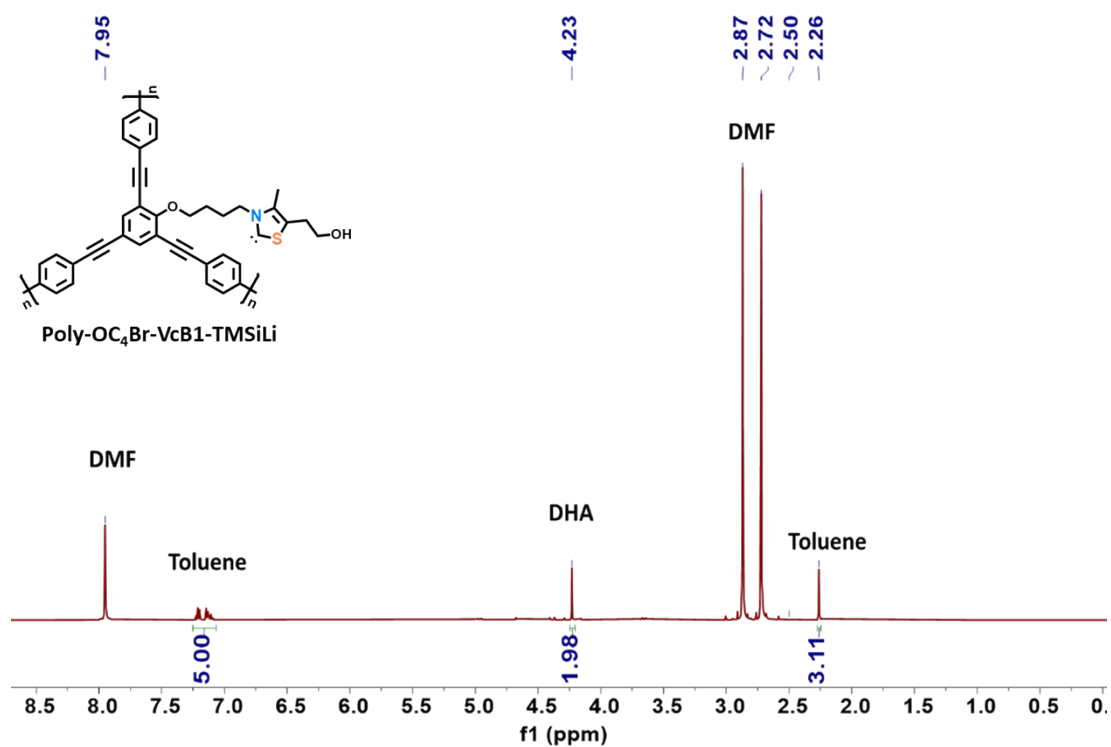


Figure S10. <sup>1</sup>H-NMR spectrum of the formaldehyde condensation mixture catalyzed by Poly-OC<sub>4</sub>Br-VcB1-TMSiLi (paraformaldehyde 6 mmol; Cat 60 mg; DMF 1mL; 90°C; 2h). Toluene was used as an internal standard.

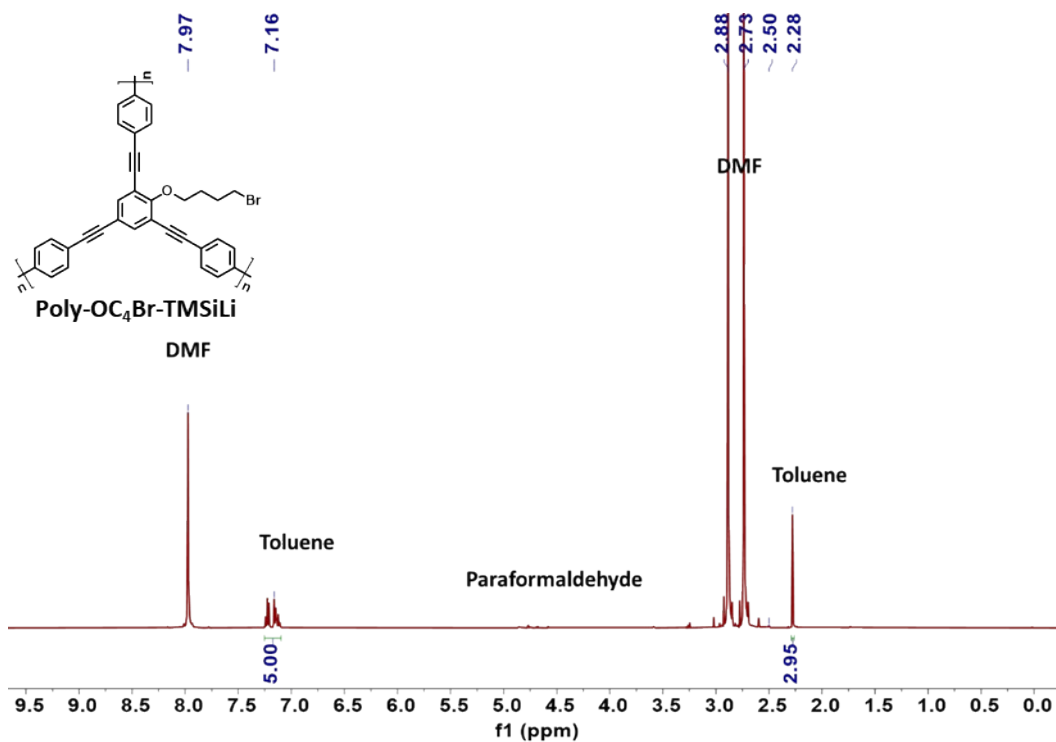


Figure S11. <sup>1</sup>H-NMR spectrum of the formaldehyde condensation mixture catalyzed by Poly-OC<sub>4</sub>Br-TMSiLi (Cat 60 mg; paraformaldehyde 6 mmol; DMF 1mL; 90°C; 2h). Toluene was used as an internal standard.



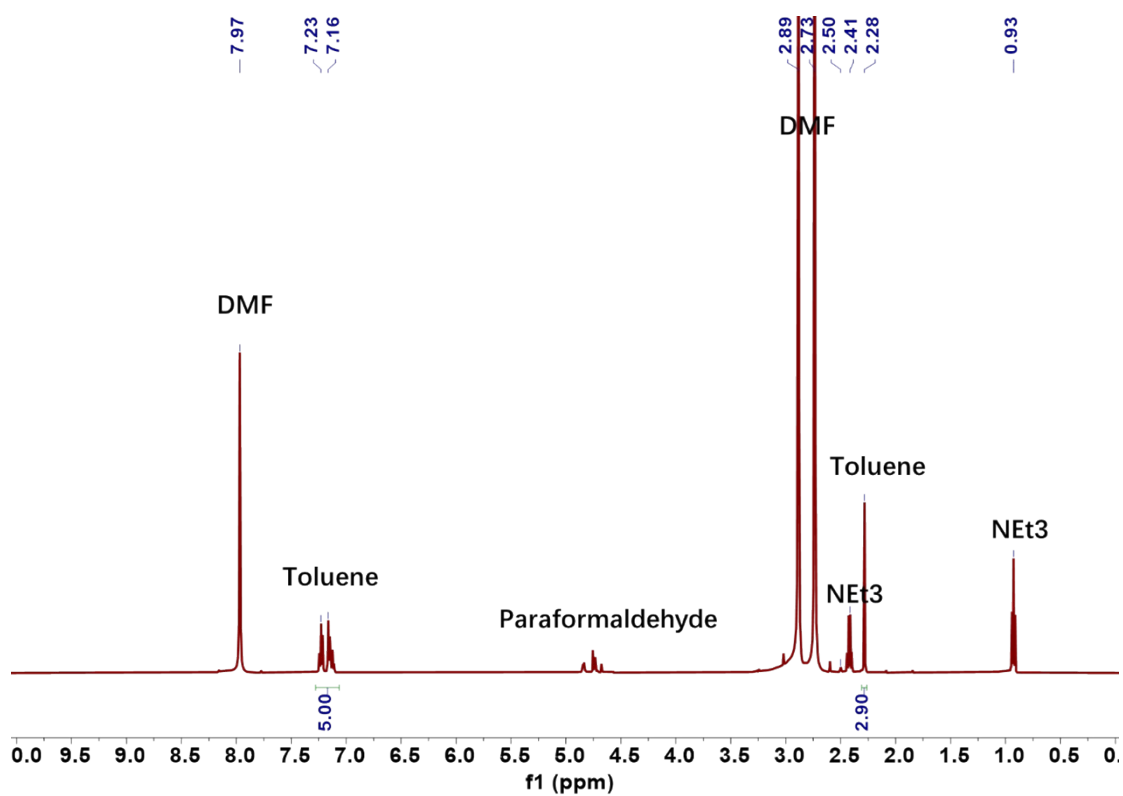


Figure S12.  $^1\text{H-NMR}$  spectrum of the formaldehyde condensation mixture catalyzed by  $\text{NEt}_3$  (paraformaldehyde 6 mmol;  $\text{NEt}_3$  0.6 mmol; DMF 1 mL;  $90^\circ\text{C}$ ; 2h). Toluene was used as an internal standard.

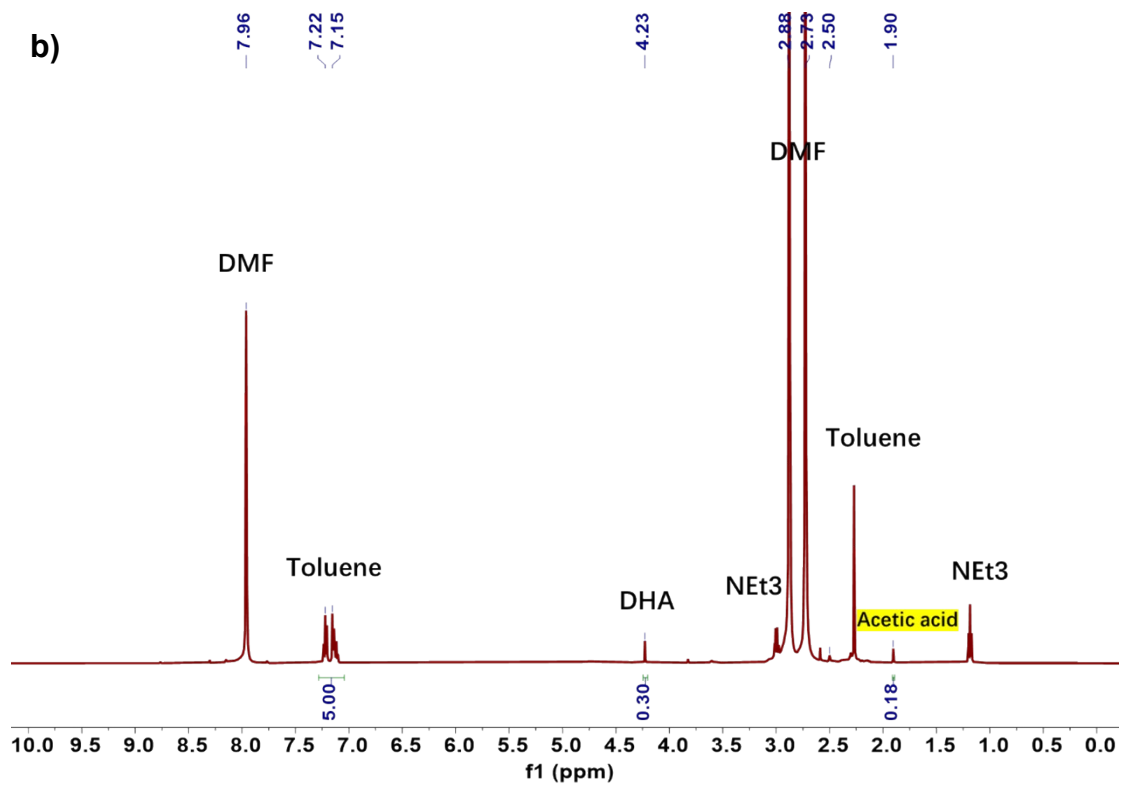
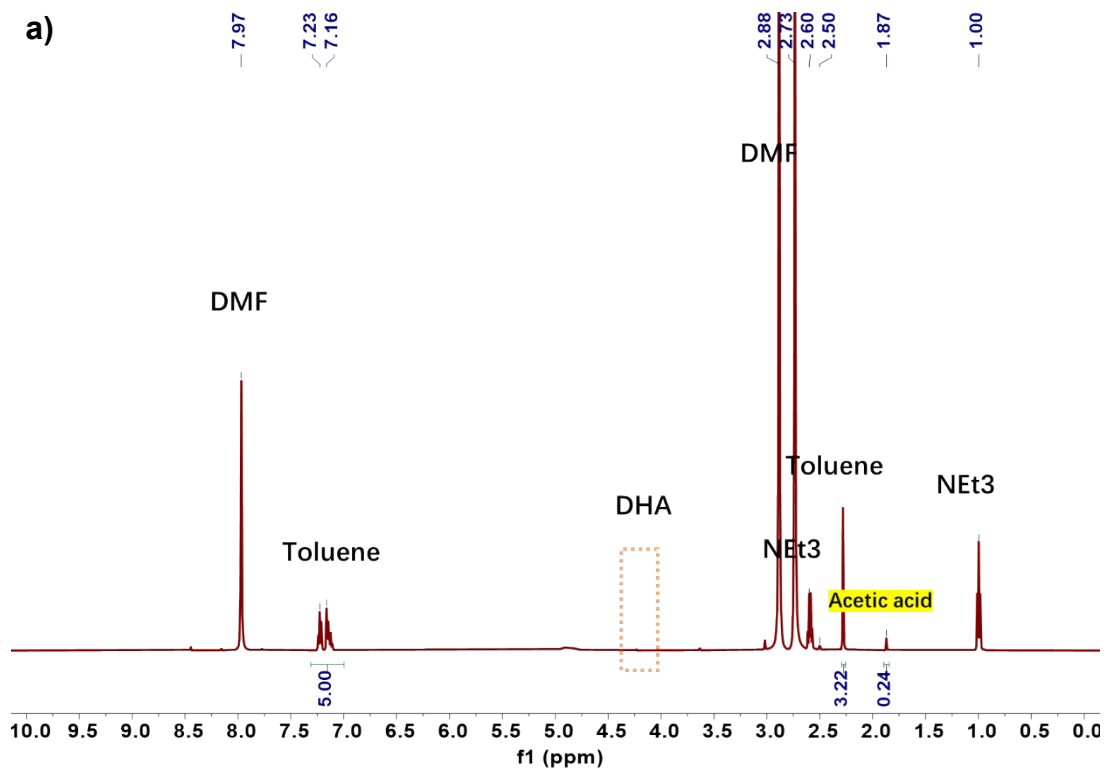


Figure S13.  $^1\text{H-NMR}$  spectrum of the DHA degradation in alkaline medium (a:  $\text{NEt}_3$  0.6 mmol; DHA 0.5 mmol and b: DHA 0.5 mmol; VcB1 0.3mmol;  $\text{NEt}_3$  0.6 mmol in 1mL

DMF at 90°C for 10h).

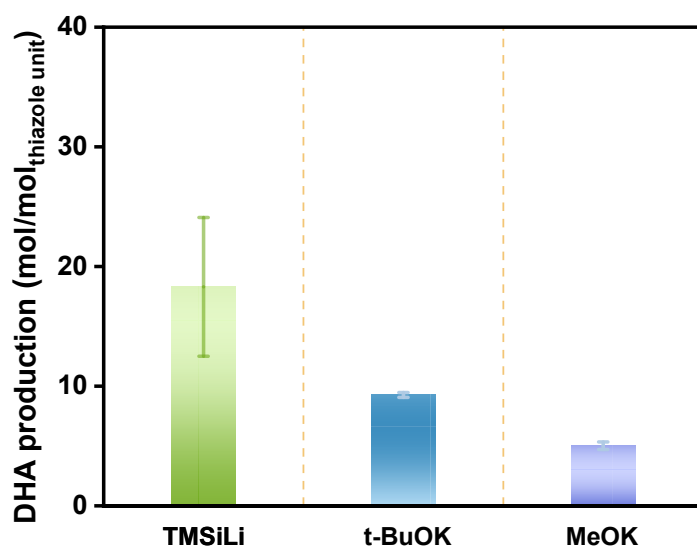


Figure S14. The DHA production of the Poly-OC<sub>4</sub>Br-VcB1 pre-activated with different bases (TMSiLi, t-BuOK, MeOK). (Cat. 60mg; paraformaldehyde 6mmol; 1mL of DMF at 90°C for 2h)

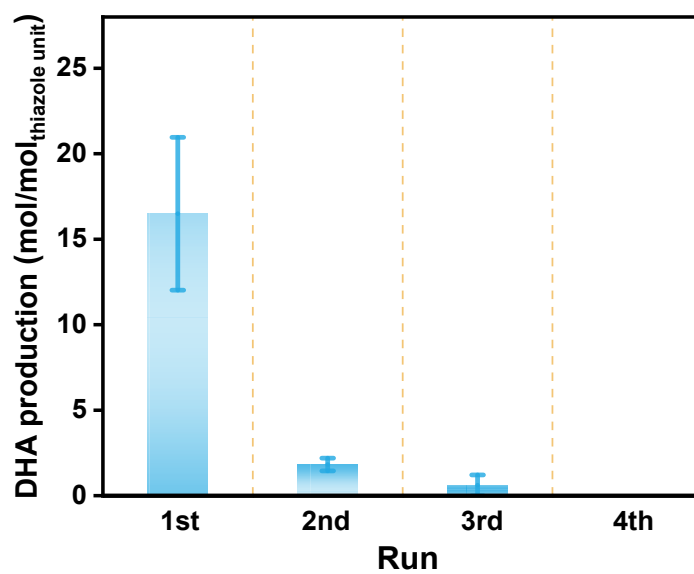


Figure S15. Reusability of Poly-OC<sub>4</sub>Br-VcB1 in the reaction of formaldehyde condensation under batch conditions in the presence of NEt<sub>3</sub> base (paraformaldehyde 6mmol, cat 60mg, 1mL DMF, 90°C, 2h, and 0.6mmol of NEt<sub>3</sub> was added in the batch reactor for each cycle).

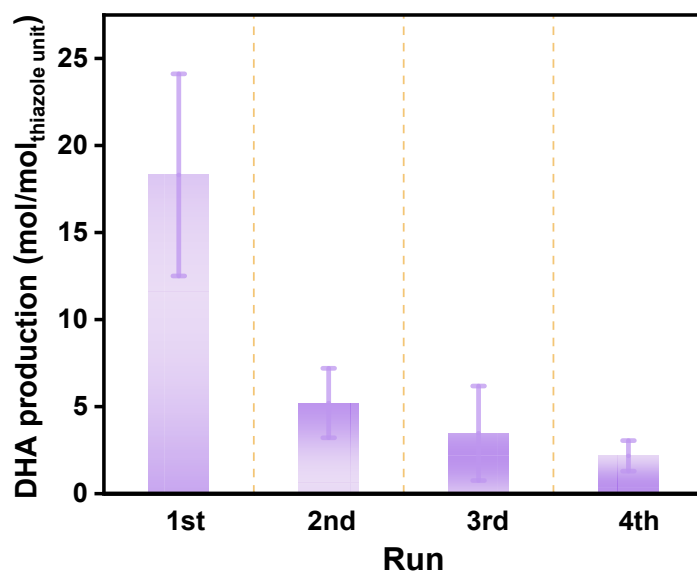


Figure S16. Reusability of Poly-OC4Br-VcB1-TMSiLi in the reaction of formaldehyde condensation under base-free batch conditions (paraformaldehyde 6mmol, cat 60mg, 1mL DMF, 90°C, 2h)

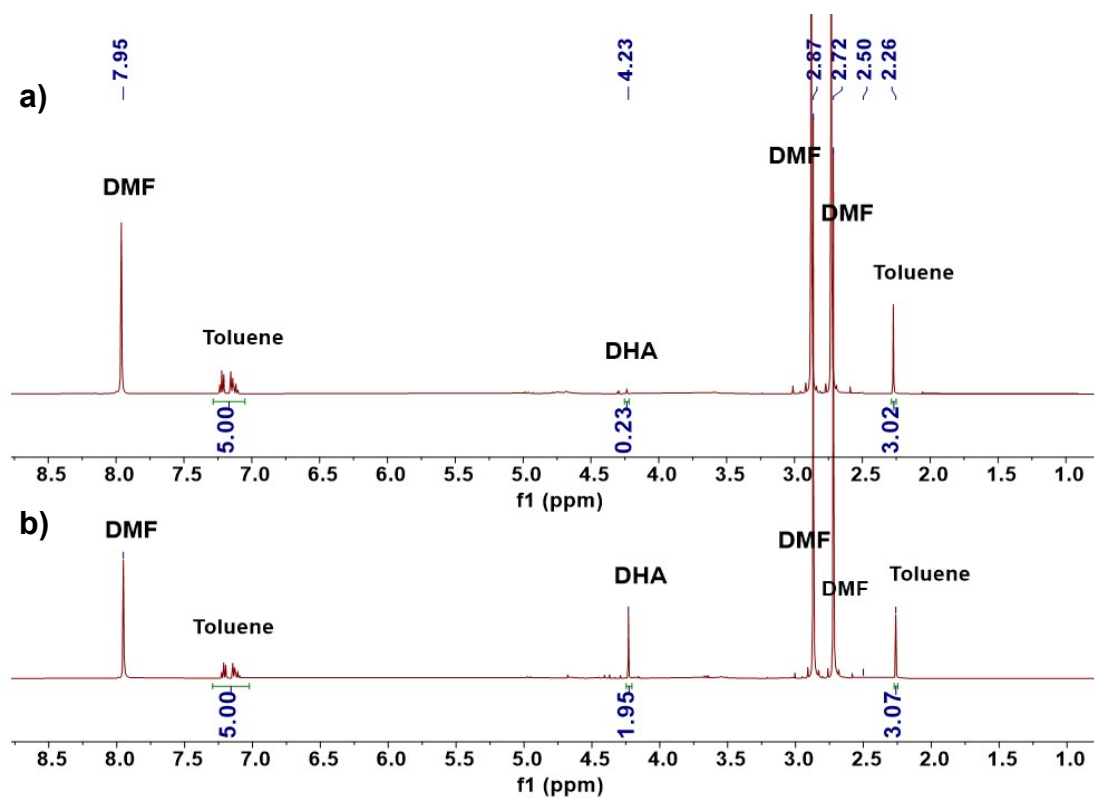


Figure S17. The DHA production of Poly-OC<sub>4</sub>Br-VcB1-TMSiLi catalyst a) pretreated with DHA prior to the catalytic reaction in batch reactor; b) without DHA treatment (Cat. 60mg; paraformaldehyde 6mmol; 1mL of DMF at 90 °C for 2h). This result conforms that the DHA product can poison the active site.

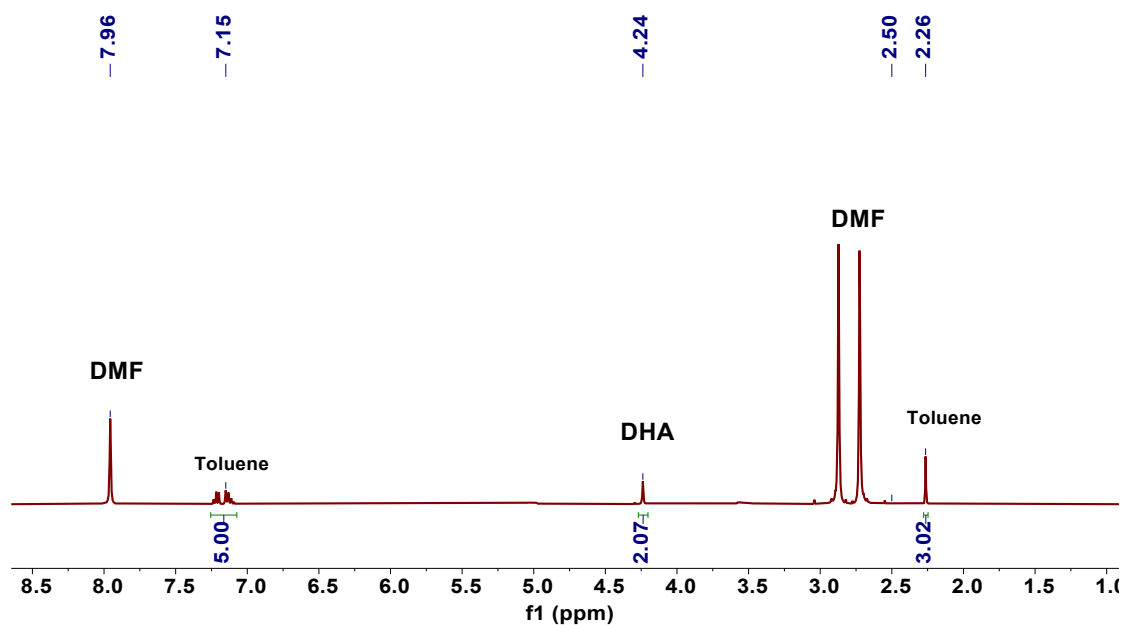


Figure S18. The DHA production of Poly-OC<sub>4</sub>Br-VcB1-TMSiLi pre-treated with methanol prior to the catalytic reaction in batch reactor. (60mg of Poly-OC<sub>4</sub>Br-VcB1-TMSiLi pretreated in 1mL of methanol at 90°C for 2h, paraformaldehyde 6mmol, 1mL of DMF at 90 °C for 2h; DHA product 0.65mmol)

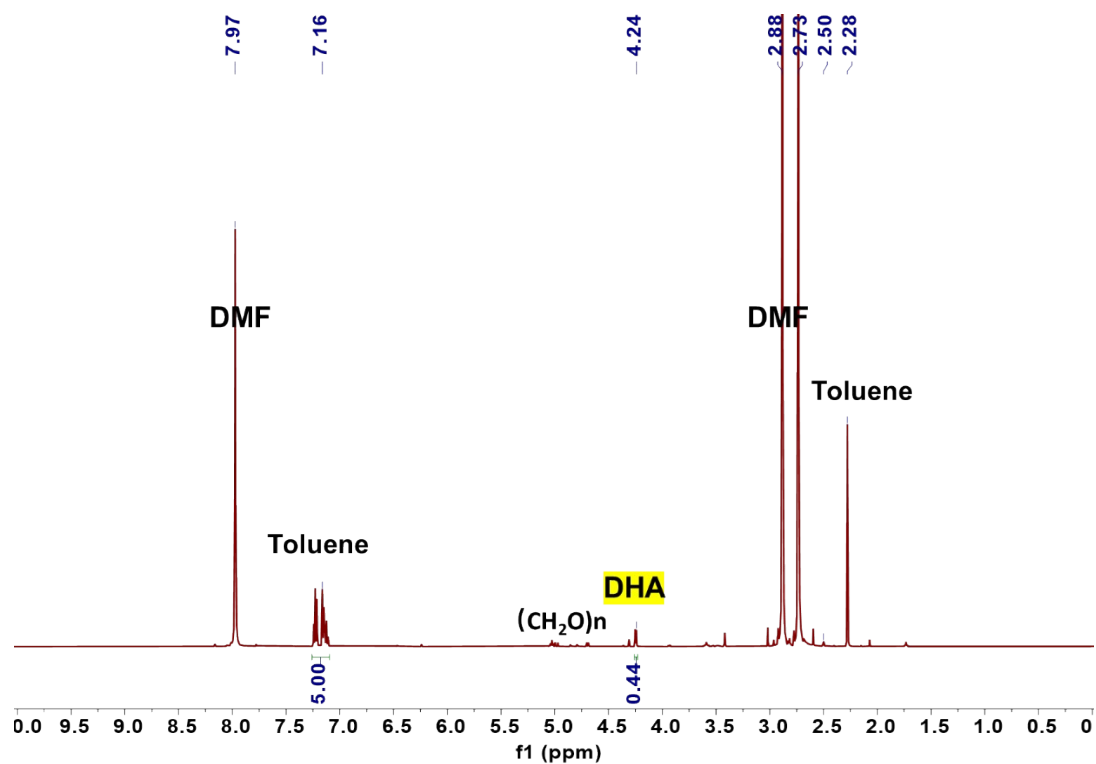


Figure S19. The DHA production of Poly-OC<sub>4</sub>Br-VcB1-TMSiLi pre-treated with acetone prior to the catalytic reaction in batch reactor. (60mg of Poly-OC<sub>4</sub>Br-VcB1-TMSiLi pretreated in 1mL of acetone at 90 °C for 2h; paraformaldehyde 6mmol; 1mL of DMF at 90 °C for 2h)



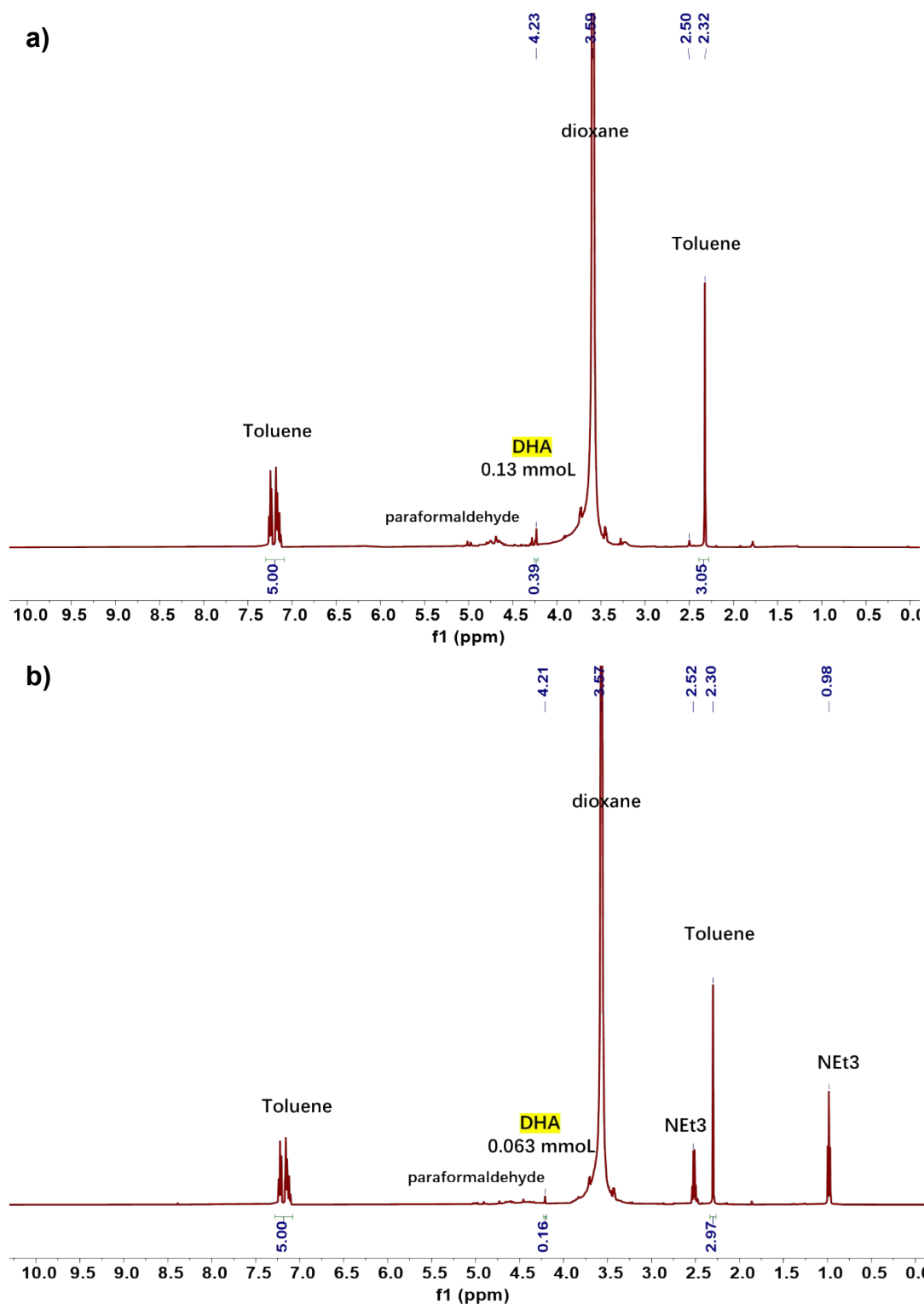


Figure S20. a)  $^1\text{H-NMR}$  spectrum of the formaldehyde condensation mixture catalyzed by Poly-OC<sub>4</sub>Br-VcB1-TMSiLi in dioxane (Cat 60 mg; paraformaldehyde 6 mmol; dioxane 1mL; 90°C; 2h); b)  $^1\text{H-NMR}$  spectrum of the formaldehyde condensation mixture catalyzed by Poly-OC<sub>4</sub>Br-VcB1 in dioxane with the presence of NEt<sub>3</sub> (Cat 60 mg; paraformaldehyde 6 mmol; NEt<sub>3</sub> 0.6 mmol; dioxane 1mL; 90°C; 2h). Toluene was used as an internal standard. The activity of Poly-OC<sub>4</sub>Br-VcB1-TMSiLi in dioxane under batch condition (7.7 mol/ mol thiazole unit) is lower than that in DMF (18.3 mol/mol thiazole unit)

Table S1. Porosity parameters of prepared polymers determined by N<sub>2</sub> adsorption.

<b>Samples</b>	<b>BET Surface Area</b> <b>(cm<sup>2</sup>/g)</b>	<b>Pore Volume</b> <b>(cm<sup>3</sup>/g)</b>	<b>Pore Size</b> <b>(nm)</b>
Poly-OH	690	0.020	6.9
Poly-OC <sub>4</sub> Br	668	0.021	8.9
Poly-OC <sub>4</sub> Br-VcB1	194	0.004	5.6

Table S2. Catalytic performance of different formaldehyde condensation catalysts.

Entry	Catalyst	Base	Temperature (°C)	Solvent	Reaction Time (min)	Active Species/CH <sub>2</sub> O	DHA Yield (%)	TON <sup>a</sup>	DHA selectivity (%)	Ref.	
1	CaOH-K <sub>2</sub> HPO <sub>4</sub>	Base catalyzed	200	Formaldehyde solution	~1.0	1/10	2.4	0.04	25.1	1	
2	Thiamin hydrochloride	LiOH	100	DMF	8	1/39	19.3	2.53	19.3	2	
3	Homogeneous Catalysis	Thiamin hydrochloride	DMEA	100	DMF	30	1/39	35.7	4.7	39.3	2
4		3-Ethylbenzothiazolium bromide	NEt <sub>3</sub>	100	DMF	60	1/20	87.2	5.8	89	3
5		3-Ethylthiazolium bromide	NEt <sub>3</sub>	100	EtOH	60	1/20	29.4	1.96	30	3
6		Hexylbenzothiazolium bromide pretreated with NEt <sub>3</sub>	---	100	Dioxane	60	1/10	85	28	85	4
7	PTS(15)-DVB	NEt <sub>3</sub>	70	DMF	360	1/100	75.5	25.2	No available data	5	
8	Heterogeneous Catalysis	Poly-OC <sub>4</sub> Br-VcB1	NEt <sub>3</sub>	90	DMF	600	1/150	2.0	1.0	33	
9		Poly-OC <sub>4</sub> Br-VcB1-TMSiLi	---	90	DMF	600	1/150	34.0	20.0	~99	This work
10		Poly-OC <sub>4</sub> Br-VcB1-TMSiLi	---	90	DMF	120	1/150	31.3	18.4	~99	

a. calculated based on the amount of DHA

1. Kopetzki, D.; Antonietti, M., Hydrothermal formose reaction. *New J. Chem* **2011**, 35 (9), 1787-1794.
2. Shigemasa, Y.; Sasaki, Y.; Ueda, N.; Nakashima, R., Formose Reactions. XXI. A Selective Formation of dihydroxyacetone in the formose reaction in N, N-Dimethylformamide. *Bull. Chem. Soc. Jpn.* **1984**, 57(10): 2761-2767.
3. Matsumoto, T.; Yamamoto, H.; Inoue, S., Selective formation of triose from formaldehyde catalyzed by thiazolium salt. *J. Chem. Soc.* **1984**, 106 (17), 4829-4832.
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