

## Supporting information for

# Synthesis, characterization and catalytic activity of novel large network polystyrene-immobilized organic bases

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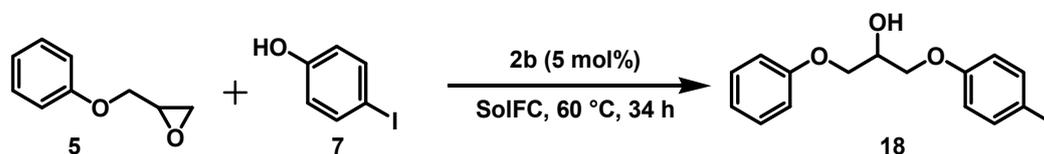
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<b>Chem. Name</b>	<b>1,3-Diphenoxypropan-2-ol (17)</b>			
<b>Lit. Ref.</b>	<i>Chem. Lett.</i> <b>2005</b> ,34,1142-1143 <i>Adv.Synth.Catal.</i> <b>2010</b> ,352,2489-2496			
<b>METHOD:</b> In a screw capped small vial equipped with a magnetic stirrer <b>2b</b> (0.021 g, 0,05 mmol, 2,43 mmol/g), phenol ( <b>6</b> ) (0.094 g, 1.0 mmol) and 2-(phenoxy)methyl oxirane ( <b>5</b> ) (0.150 g, 1.0 mmol) were consecutively added and the resulting mixture was left under stirring at 60°C. After 20 hours EtOAc (1 ml) was added and the reaction mixture filtered. The catalyst was washed using additional 2x2 ml of EtOAc. Organic layers were collected and solvent was removed under vacuum to give 1,3-diphenoxypropan-2-ol ( <b>17</b> ) as a white solid (0.240 g, 97% yield).				
<b>Mol Formula</b>	C <sub>15</sub> H <sub>16</sub> O <sub>3</sub>	<b>m.p.</b>	76-78°C	
<b>Elemental Analysis:</b> Calcd. C, 55.75; H, 4.68. Found C, 55.66; H, 4.72.				
<b><sup>1</sup>H NMR</b> <b>400 MHz</b> <b>CDCl<sub>3</sub></b>	<b>δ value</b>	<b>No. H</b>	<b>Mult.</b>	<b>j value/Hz</b>
	2.29	1	<i>br s</i>	
	4.10 – 4.25	4	<i>m</i>	
	4.40	1	<i>quintet</i>	5.5
	6.85 – 7.05	6	<i>m</i>	
	7.20 – 7.35	4	<i>m</i>	
<b><sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ :</b> 68.6, 68.8, 114.6, 121.3, 129.6, 158.4				
<b>TLC-R<sub>f</sub> (Eluant) :</b> 0.28 (Hex:EtOAc = 3:1)				

Chem. Name	1-(4-iodophenoxy)-3-phenoxypropan-2-ol ( <b>18</b> )
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Lit. Ref.	---
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**METHOD:**

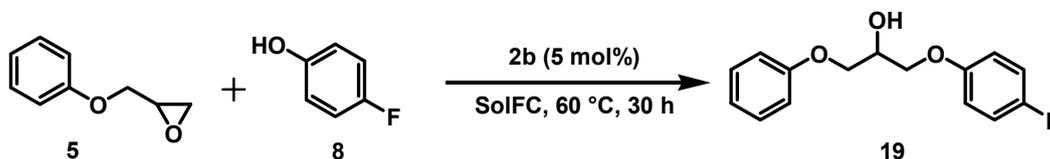
In a screw capped vial equipped with a magnetic stirrer **2b** (0,021 g, 0.05 mmol, 2,43 mmol/g), 4-iodophenol (**7**) (0.220 g, 1.0 mmol) and 2-(phenoxy)methyl oxirane (**5**) (0.150 g, 1.0 mmol) were consecutively added and the resulting mixture was left under stirring at 60°C. After 34 hours EtOAc (1 ml) was added and the reaction mixture filtered. The catalyst was washed using additional 2x2 ml of EtOAc. Organic layers were collected and solvent was removed under vacuum and the crude product was purified by washing with EtP to give 1-(4-iodophenoxy)-3-phenoxypropan-2-ol (**18**) as white solid (0.363 g, 98% yield).

<b>Mol Formula</b>	C <sub>15</sub> H <sub>15</sub> O <sub>3</sub> I			<b>m.p.</b>	66 – 67 °C
<b><sup>1</sup>H NMR</b> <b>400 MHz</b> <b>CDCl<sub>3</sub></b>	<b>δ value</b>	<b>No. H</b>	<b>Mult.</b>	<b>j value/Hz</b>	
	2.60	1	<i>br, s</i>		
	4.06 – 4.17	4	<i>m</i>		
	4.34 – 4.39	1	<i>m</i>		
	6.84 – 6.87	2	<i>m</i>		
	6.91 – 6.99	5	<i>m</i>		
	7.23 – 7.30	2	<i>m</i>		

**<sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ :** 68.6, 68.8, 69.4, 114.5, 115.5, 115.6, 115.8, 116.0, 121.3, 129.6, 154.5, 156.3, 158.3, 158.7

Chem. Name	1-(4-fluorophenoxy)-3-phenoxypropan-2-ol ( <b>19</b> )
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Lit. Ref.	
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**METHOD:**

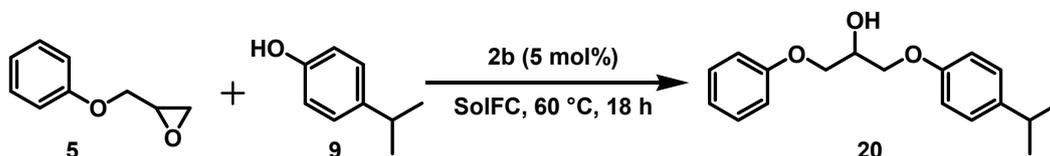
In a screw capped vial equipped with a magnetic stirrer **2b** (0,021 g, 0,05 mmol, 2,43 mmol/g), 4-fluorophenol (**8**) (0.112 g, 1.0 mmol) and 2-(phenoxy)methyl oxirane (**5**) (0.150 g, 1.0 mmol) were consecutively added and the resulting mixture was left under stirring at 60°C. After 30 hours EtOAc (1 ml) was added and the reaction mixture filtered. The catalyst was washed using additional 2x2 ml of EtOAc. Organic layers were collected and solvent was removed under vacuum and the crude product was purified by washing with EtP to give 1-(4-fluorophenoxy)-3-phenoxypropan-2-ol (**19**) as a pale yellow solid (0.257 g, 98% yield).

Mol Formula	C <sub>15</sub> H <sub>15</sub> O <sub>3</sub> F			m.p.	69 – 70 °C
<sup>1</sup> H NMR 400 MHz CDCl <sub>3</sub>	δ value	No. H	Mult.	j value/Hz	
	2.75	1	<i>br, s</i>		
	4.06 – 4.16	4	<i>m</i>		
	4.33 – 4.41	1	<i>m</i>		
	6.84 – 6.87	2	<i>m</i>		
	6.91 – 6.98	5	<i>m</i>		
	7.23 – 7.30	2	<i>m</i>		

<sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ : 68.6, 68.8, 69.4, 114.5, 115.5, 115.6, 115.8, 116.0, 121.3, 129.6, 154.5, 156.3, 158.3, 158.7

Chem. Name	1-(4'-Isopropylphenoxy)-3-phenoxypropan-2-ol ( <b>20</b> )
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Lit. Ref.	<i>Adv.Synth.Catal.</i> <b>2010</b> ,352,2489-2496
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**METHOD:**

In a screw capped vial equipped with a magnetic stirrer **2b** (0,021 g, 0,05 mmol, 2,43 mmol/g), 4-isopropylphenol (**9**) (0.136 g, 1.0 mmol) and 2-(phenoxy)methyl oxirane (**5**) (0.150 g, 1.0 mmol) were consecutively added and the resulting mixture was left under stirring at 60°C. After 18 hours EtOAc (1 ml) was added and the reaction mixture filtered. The catalyst was washed using additional 2x2 ml of EtOAc. Organic layers were collected and solvent was removed under vacuum to give 1-(4'-isopropylphenoxy)-3-phenoxypropan-2-ol (**20**) as a pale yellow oil (0.277 g, 97% yield).

Mol Formula	C <sub>18</sub> H <sub>22</sub> O <sub>3</sub>	m.p.	Oil
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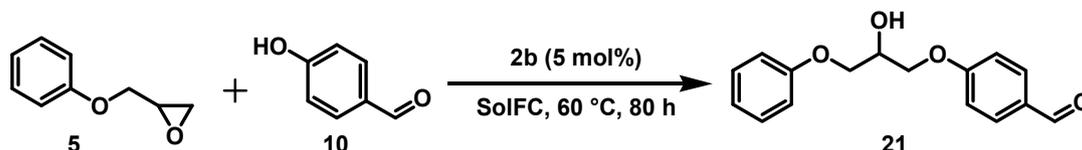
**Elemental Analysis:** Calcd. C, 75.50; H, 7.74. Found C, 75.13; H, 7.78

<sup>1</sup> H NMR 400 MHz CDCl <sub>3</sub>	δ value	No. H	Mult.	j value/Hz
	1.22	6	<i>d</i>	6.8
	2.70	1	<i>d</i>	4.9
	2.86	1	<i>septet</i>	6.9
	4.05 - 4.20	4	<i>m</i>	
	4.37	1	<i>sextet</i>	5.2
	6.86	2	<i>d</i>	8.6
	6.90 – 7.00	3	<i>m</i>	
	7.14	2	<i>d</i>	8.6
	7.25 – 7.36	2	<i>m</i>	

<sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ : 24.2, 33.3, 68.6, 68.7, 68.8, 114.4, 114.5, 121.2, 127.3, 129.5, 141.7, 156.5, 158.4

TLC-R<sub>f</sub> (Eluant) : 0.36 (Hex:EtOAc = 3:1)

<b>Chem. Name</b>	<b>4-(2-hydroxy-3-phenoxypropoxy)benzaldehyde (21)</b>
<b>Lit. Ref.</b>	<i>Chem. Commun.</i> , <b>2013</b> , 49, 5886—5888



**METHOD:**

In a screw capped vial equipped with a magnetic stirrer **2b** (0.021 g, 0.05 mmol, 2.43 mmol/g), 4-hydroxybenzaldehyde (**10**) (0.122 g, 1.0 mmol) and 2-(phenoxy)methyl oxirane (**5**) (0.150 g, 1.0 mmol) were consecutively added and the resulting mixture was left under stirring at 60°C. After 80 hours EtOAc (1 ml) was added and the reaction mixture filtered. The catalyst was washed using additional 2x2 ml of EtOAc. Organic layers were collected and solvent was removed under vacuum and the crude product was purified by silica gel flash chromatography (eluant: Petroleum ether/EtOAc, 3/1) to give 4-(2-hydroxy-3-phenoxypropoxy)benzaldehyde (**21**) as a white solid (0.264 g, 97% yield).

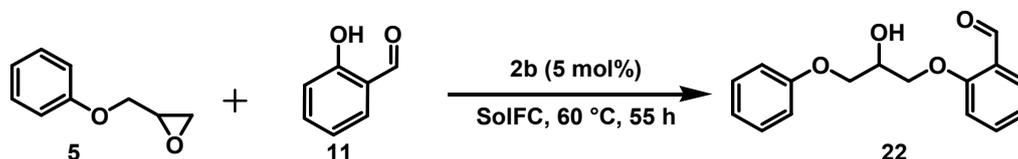
<b>Mol Formula</b>	$C_{16}H_{16}O_4$			<b>m.p.</b>	90 – 91 °C
<b><sup>1</sup>H NMR 400 MHz CDCl<sub>3</sub></b>	<b>δ value</b>	<b>No. H</b>	<b>Mult.</b>	<b>j value/Hz</b>	
	2.64	1	<i>br, s</i>	D <sub>2</sub> O exchangeable	
	4.04 – 4.20	2	<i>m</i>		
	4.23 – 4.24	2	<i>m</i>		
	4.39 – 4.47	1	<i>m</i>		
	6.93 – 6.95	2	<i>m</i>		
	6.98 – 7.00	1	<i>m</i>		
	7.03 – 7.05	2	<i>m</i>		
	7.28 – 7.32	2	<i>m</i>		
	7.82 – 7.84	2	<i>m</i>		
9.88	1	<i>s</i>			

**<sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ** : 68.4, 68.6, 69.0, 114.5, 114.8, 121.4, 129.6, 130.3, 132.0, 158.2, 163.4, 190.8

**TLC-R<sub>f</sub> (Eluant)** : 0.51 (EtP:EtOAc = 3:1)

Chem. Name	2-(2'-Hydroxy-3'-phenoxypropoxy)-benzaldehyde ( <b>22</b> )
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Lit. Ref.	<i>Adv.Synth.Catal.</i> <b>2010</b> ,352,2489-2496
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**METHOD:**

In a screw capped vial equipped with a magnetic stirrer **2b** (0.021 g, 0.05 mmol, 2.43 mmol/g), 2-hydroxybenzaldehyde (**11**) (0.122 g, 1.0 mmol) and 2-(phenoxy)methyl oxirane (**5**) (0.150 g, 1.0 mmol) were consecutively added and the resulting mixture was left under stirring at 60°C. After 28 hours EtOAc (1 ml) was added and the reaction mixture filtered. The catalyst was washed using additional 2x2 ml of EtOAc. Organic layers were collected, solvent was removed under vacuum and the crude product was purified by silica gel chromatography (eluant: Petroleum ether/EtOAc, 4/1) to give 2-(2'-Hydroxy-3'-phenoxypropoxy)-benzaldehyde (**22**) as a yellow viscous oil (94% yield).

Mol Formula	C <sub>16</sub> H <sub>16</sub> O <sub>4</sub>	m.p.	Oil
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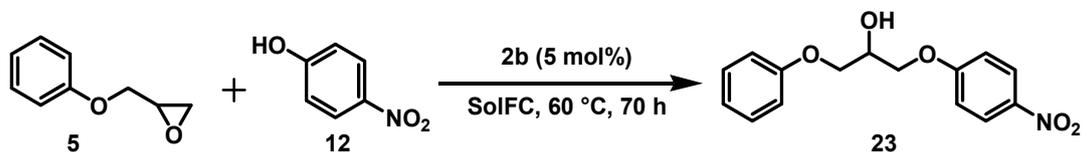
**Elemental Analysis:** Calcd. C, 70.57; H, 5.92. Found C, 70.89; H, 5.95

<sup>1</sup> H NMR 400 MHz CDCl <sub>3</sub>	δ value	No. H	Mult.	j value/Hz
	3.00 – 3.40	1	<i>bs</i>	
	4.18	2	<i>d</i>	5.3
	4.23 – 4.35	2	<i>m</i>	
	4.40 – 4.50	1	<i>m</i>	
	6.80 – 7.10	5	<i>m</i>	
	7.25 – 7.35	2	<i>m</i>	
	7.50 – 7.60	1	<i>m</i>	
	7.81	1	<i>dd</i>	1.4 and 7.6

<sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ : 68.4, 68.6, 69.6, 112.9, 114.5, 121.3, 121.4, 125.0, 129.6, 129.7, 136.0, 158.3, 160.5, 189.7

Chem. Name	1-(4'-Nitrophenoxy)-3-phenoxypropan-2-ol ( <b>23</b> )
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Lit. Ref.	<i>Adv.Synth.Catal.</i> <b>2010</b> ,352,2489-2496
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**METHOD:**

In a screw capped vial equipped with a magnetic stirrer **2b** (0,021 g, 0,05 mmol, 2,43 mmol/g), 4-nitrophenol (**12**) (0.139 g, 1.0 mmol) and 2-(phenoxy)methyl oxirane (**5**) (0.150 g, 1.0 mmol) were consecutively added and the resulting mixture was left under stirring at 60°C. After 70 hours EtOAc (1 ml) was added and the reaction mixture filtered. The catalyst was washed using additional 2x2 ml of EtOAc. Organic layers were collected and solvent was removed under vacuum and the crude product was purified by silica gel flash chromatography (eluant: Petroleum ether/EtOAc, 3/1) to give 1-(4'-nitrophenoxy)-3-phenoxy-propan-2-ol (**23**) as a pale yellow solid (0.251 g, 87% yield).

Mol Formula	C <sub>15</sub> H <sub>15</sub> NO <sub>5</sub>	m.p.	85 – 87 °C
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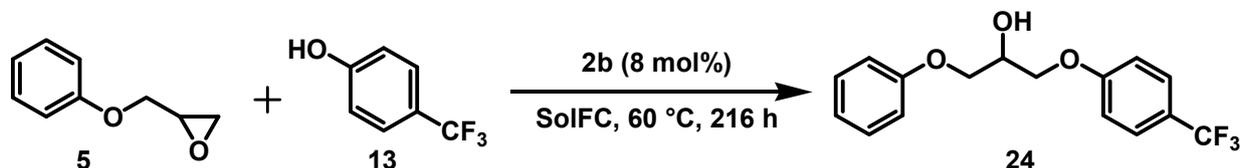
**Elemental Analysis:** Calcd. C, 62.28; H, 5.23; N, 4.84. Found C, 62.34; H, 5.22; N, 4.82

<sup>1</sup> H NMR 400 MHz CDCl <sub>3</sub>	δ value	No. H	Mult.	j value/Hz
	2.90	1	<i>d</i>	5.3
	4.10 – 4.30	4	<i>m</i>	
	4.35 – 4.50	1	<i>m</i>	
	6.85 – 7.05	5	<i>m</i>	
	7.20 – 7.35	2	<i>m</i>	
	8.17	2	<i>d</i>	9.2

<sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ : 68.3, 68.5, 69.4, 114.4, 114.5, 121.4, 125.8, 129.5, 141.7, 158.1, 163.4

TLC-R<sub>f</sub> (Eluant) : 0.21 (Hex:EtOAc = 3:1)

Chem. Name	1-phenoxy-3-(4-(trifluoromethyl)phenoxy)propan-2-ol ( <b>24</b> )
Lit. Ref.	---



**METHOD:**

In a screw capped vial equipped with a magnetic stirrer **2b** (0,034 g, 0,08 mmol, 2,43 mmol/g), 4-trifluoromethyl-phenol (**13**) (0.162 g, 1.0 mmol) and 2-(phenoxy)methyl oxirane (**5**) (0.150 g, 1.0 mmol) were consecutively added and the resulting mixture was left under stirring at 60°C. After 28 hours EtOAc (1 ml) was added and the reaction mixture filtered. The catalyst was washed using additional 2x2 ml of EtOAc. Organic layers were collected and solvent was removed under vacuum and the crude product was purified by silica gel chromatography (eluant: Petroleum ether/EtOAc, 4/1) to give 1-phenoxy-3-(4-(trifluoromethyl)phenoxy)propan-2-ol (**24**) as white solid (64% yield).

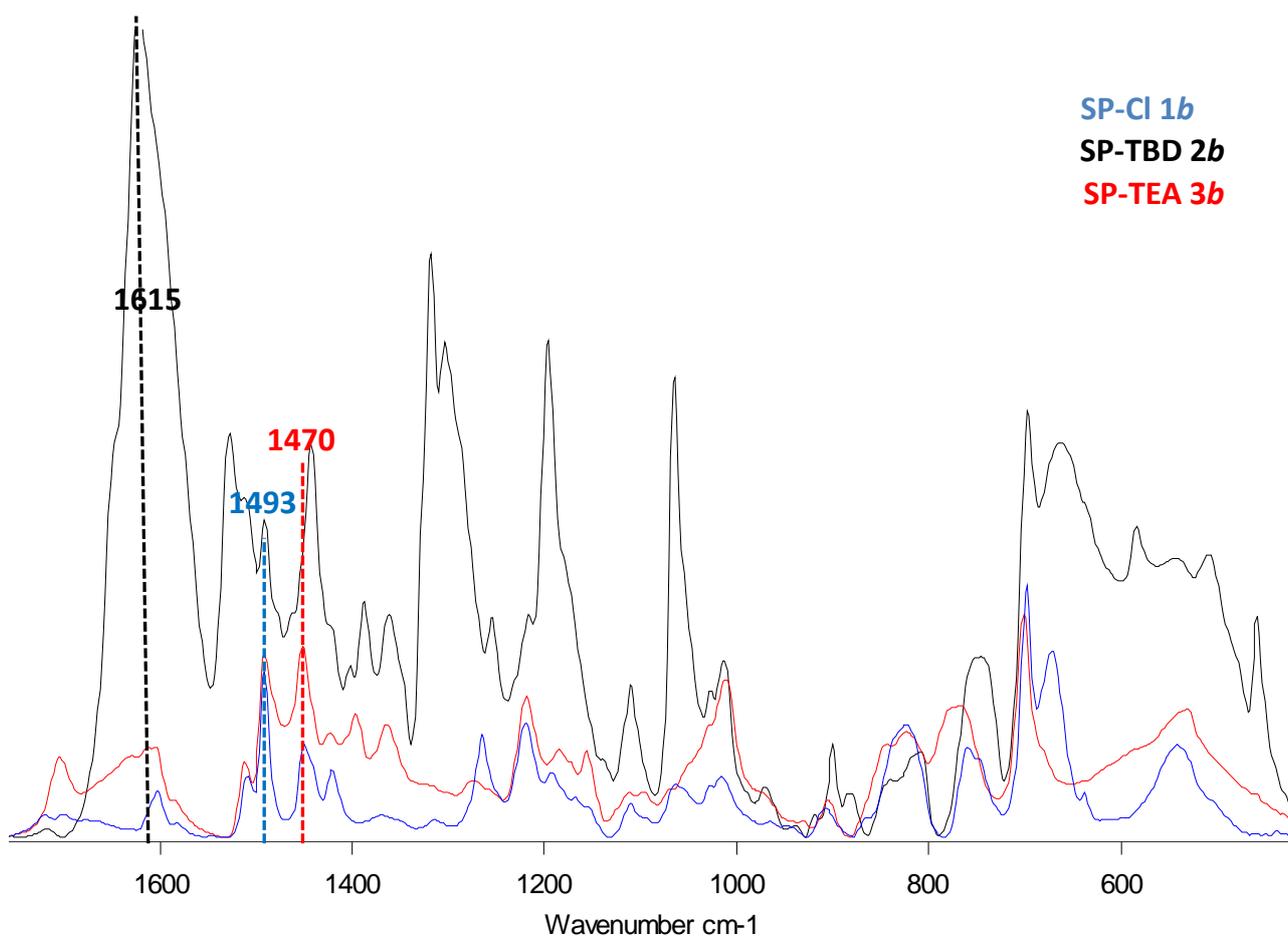
<b>Mol Formula</b>	C <sub>16</sub> H <sub>15</sub> O <sub>3</sub> F <sub>3</sub>			<b>m.p.</b>	60 - 62 °C
<b><sup>1</sup>H NMR</b> <b>400 MHz</b> <b>CDCl<sub>3</sub></b>	<b>δ value</b>	<b>No. H</b>	<b>Mult.</b>	<b>j value/Hz</b>	
	2,75 – 2.79	1	<i>br, s</i>		
	4.11 – 4.22	4	<i>m</i>		
	4.39 – 4.42	1	<i>m</i>		
	6.89 – 6.99	5	<i>m</i>		
	7.27 – 7.31	2	<i>m</i>		
	7.52 – 7.55	2	<i>m</i>		

**<sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ** : 68.6, 68.8, 69.1, 82.8, 84.5, 114.5, 115.4, 121.4, 123.3, 123.6, 125.7, 126.9, 127.0, 129.6, 158.2, 160.8

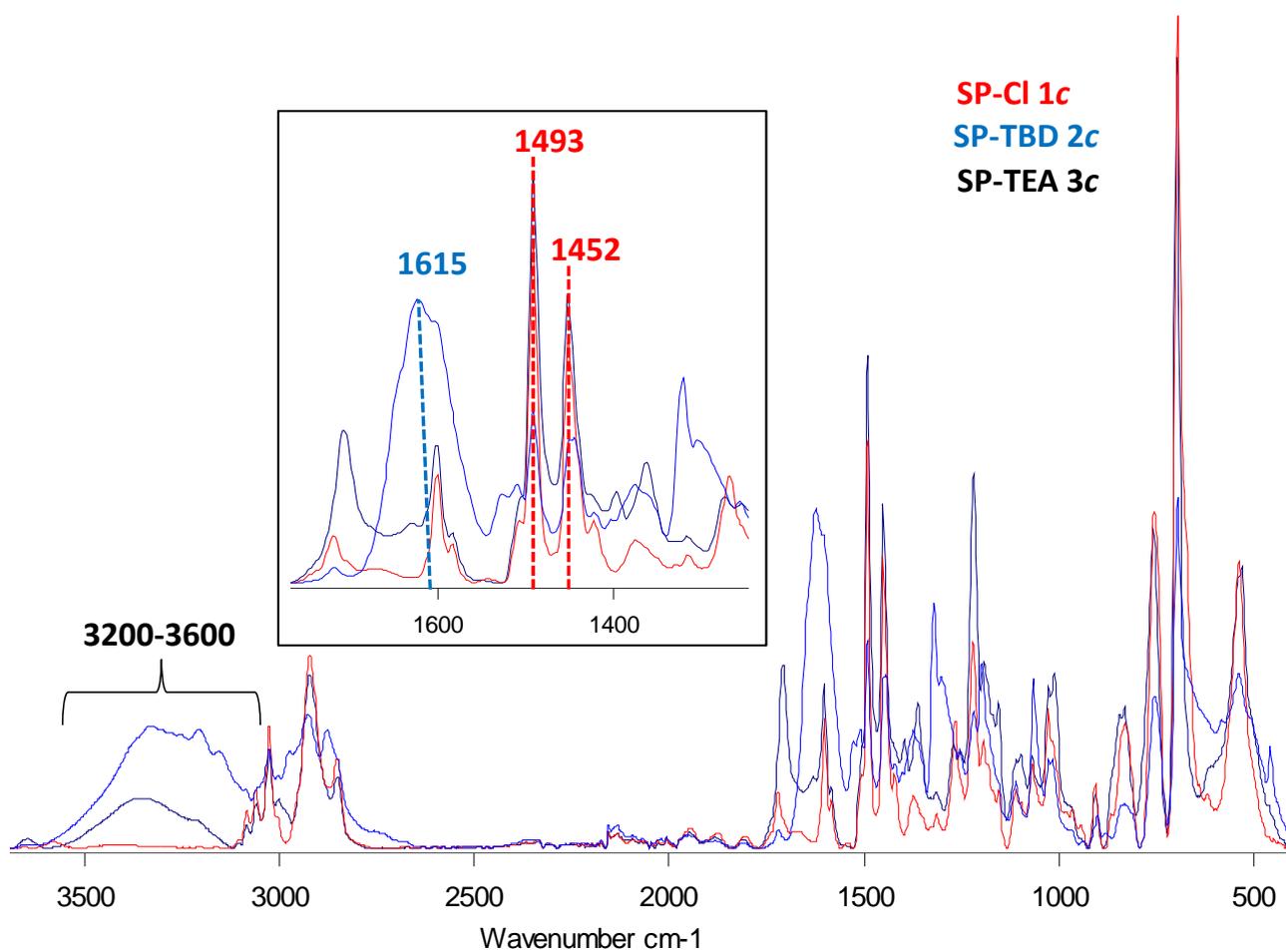
**TLC-R<sub>f</sub> (Eluant)** : 0.44 (EtP :EtOAc = 4 :1)

**Table S1.** Recycling of catalyst **2b** in the reaction of epoxide **5** and phenol **6**

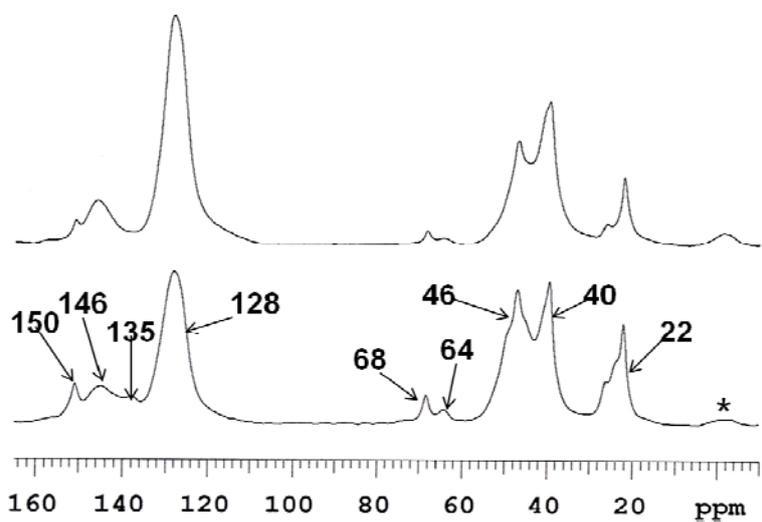
<i>Run</i>	<i>Conversion (%)</i>
1	97
2	95
3	93
4	86
5	81
6	56



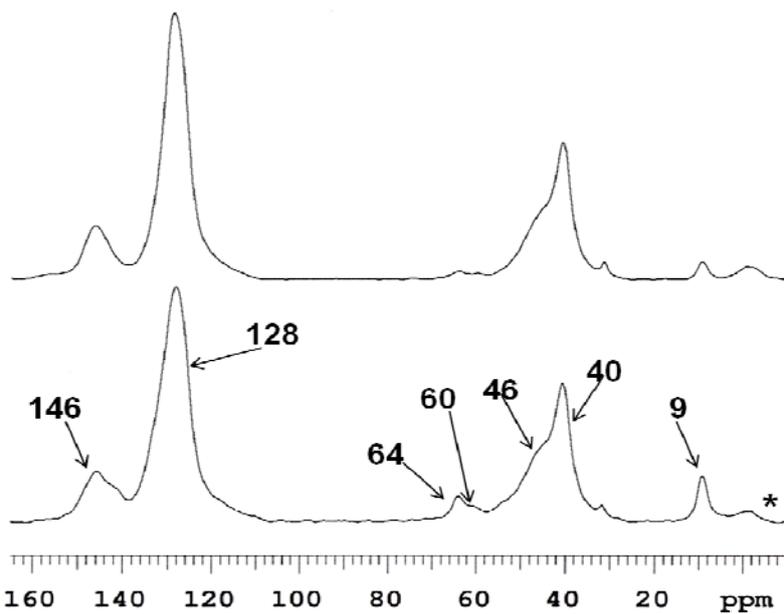
**Figure S1.** Partial FTIR spectra of SP-CI **1b**, SP-TBD **2b** and SP-TEA **3b**



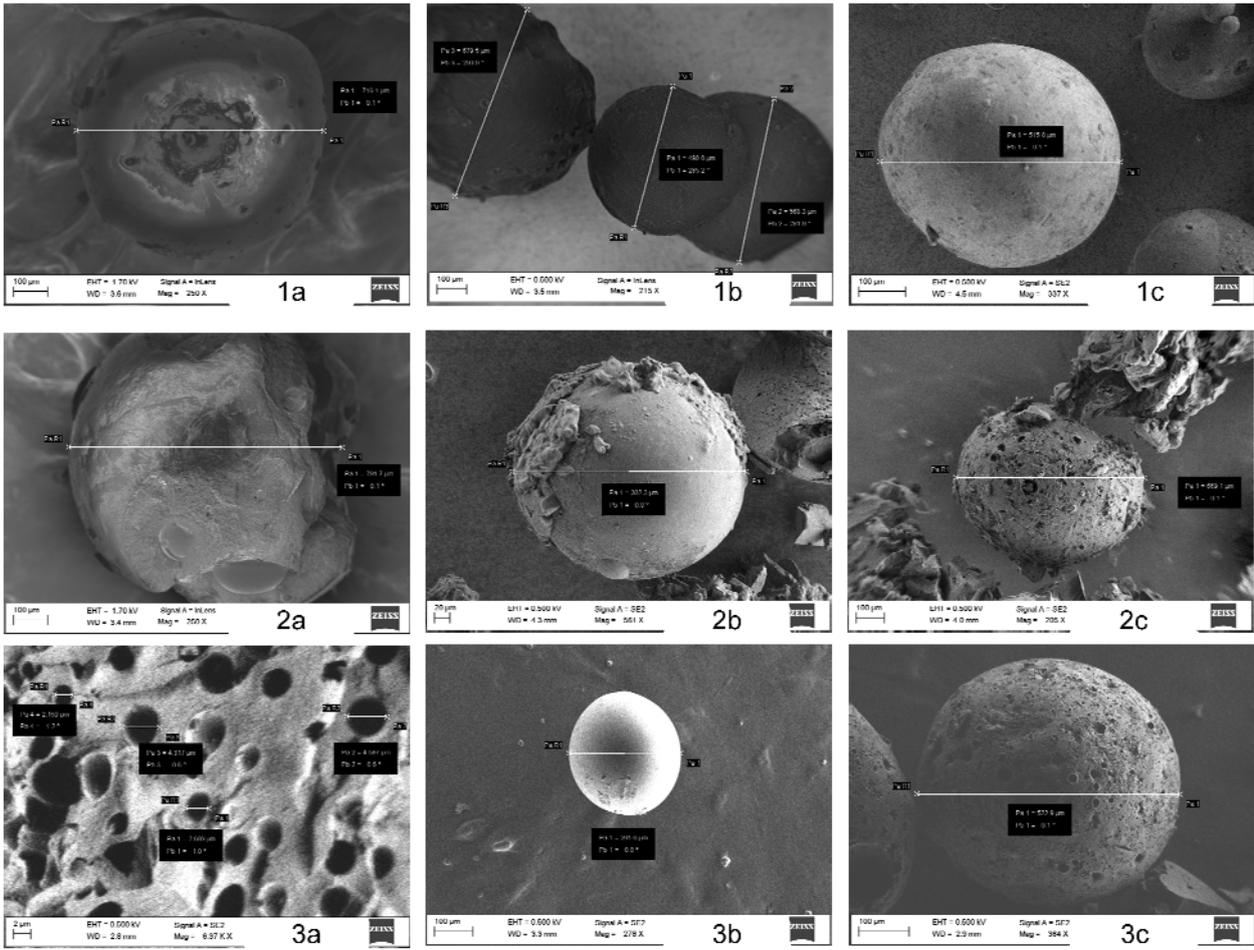
**Figure S2.** Full FTIR spectra of SP-Cl **1c**, SP-TBD **2c** and SP-TEA **3c**. The inset shows the expanded spectral region between 1150  $\text{cm}^{-1}$  and 1750  $\text{cm}^{-1}$ .



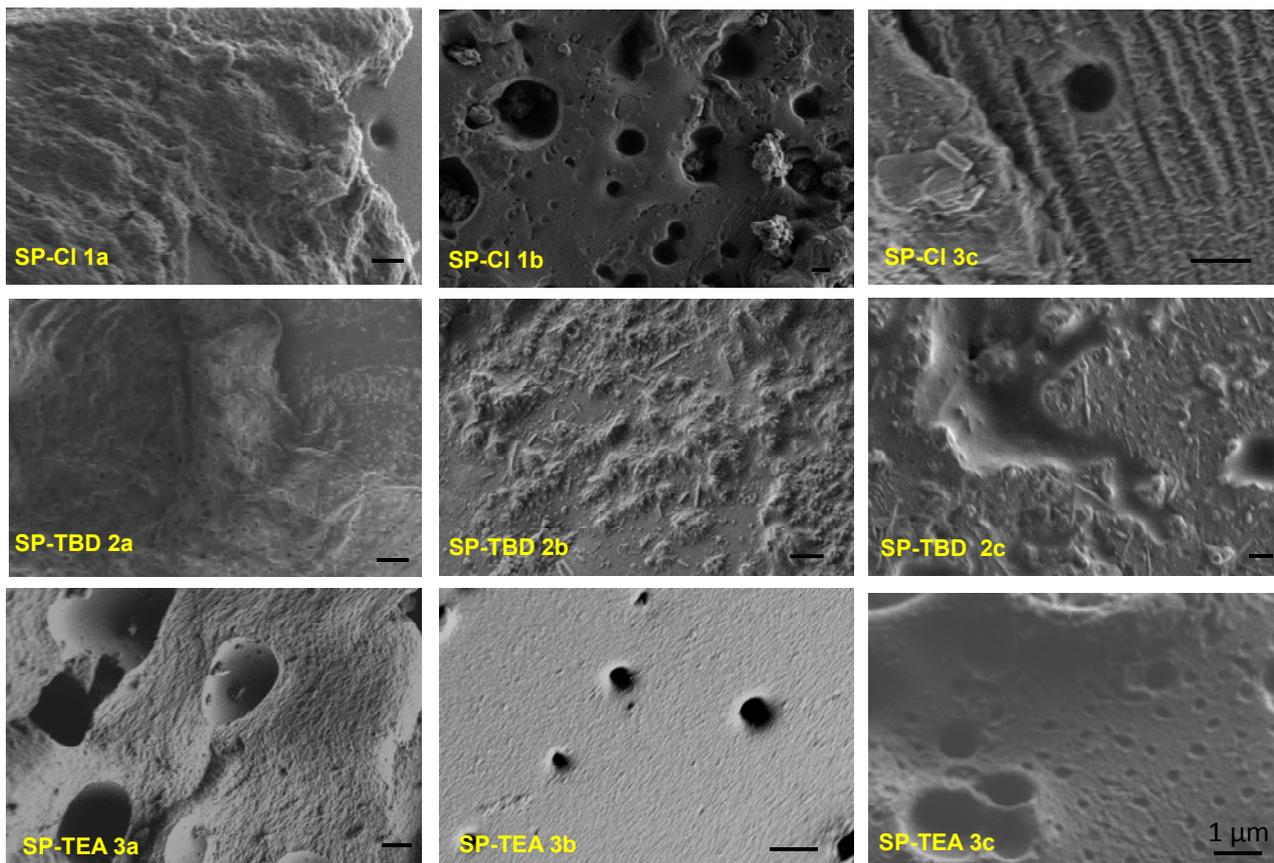
**Figure S3**  $^{13}\text{C}$ -CP/MAS SS-NMR spectra of SP-TBD **2b** and **2c**.



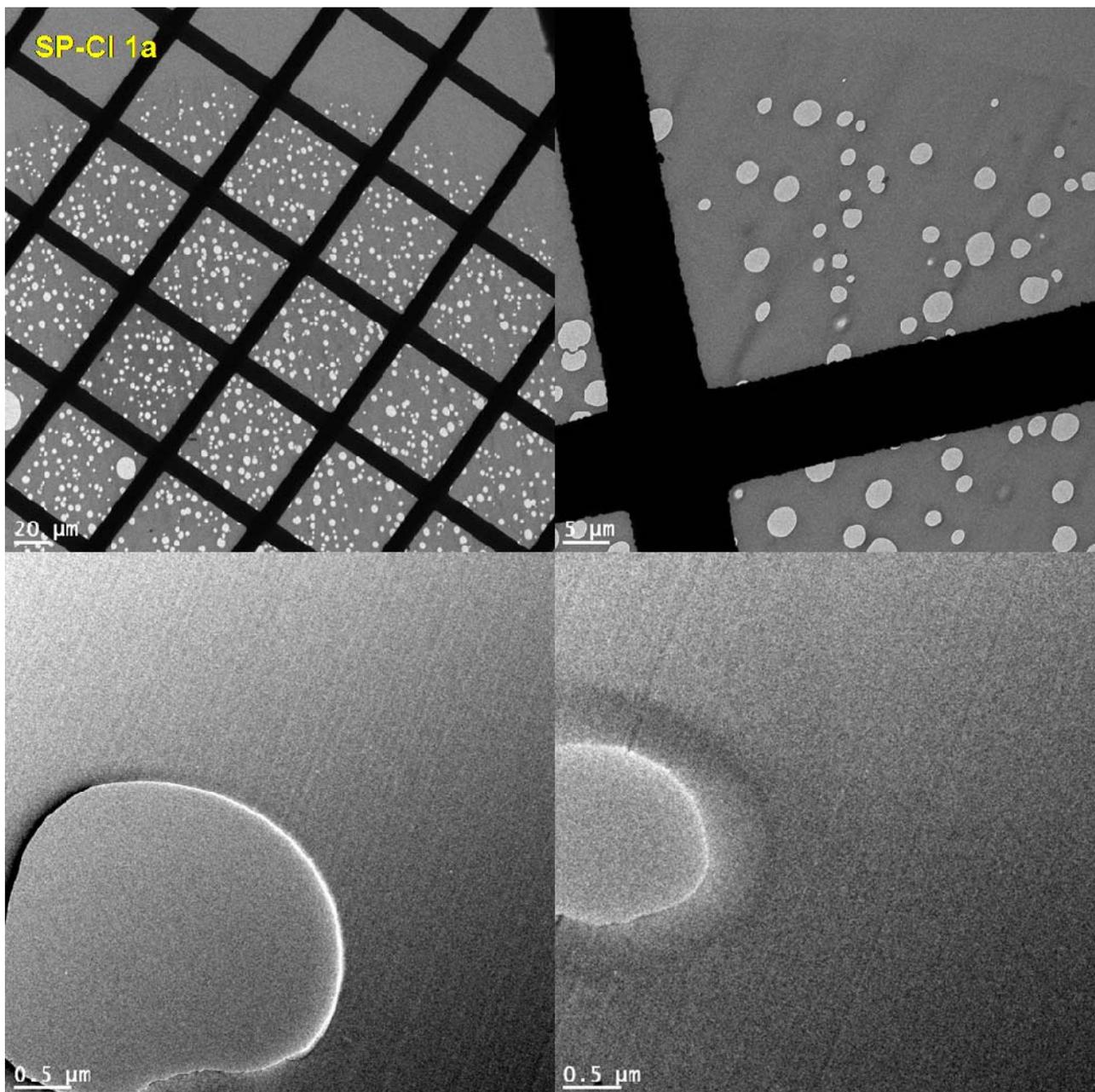
**Figure S4**  $^{13}\text{C}$ -CP/MAS NMR spectra of SP-TEA **3b** and **3c**.



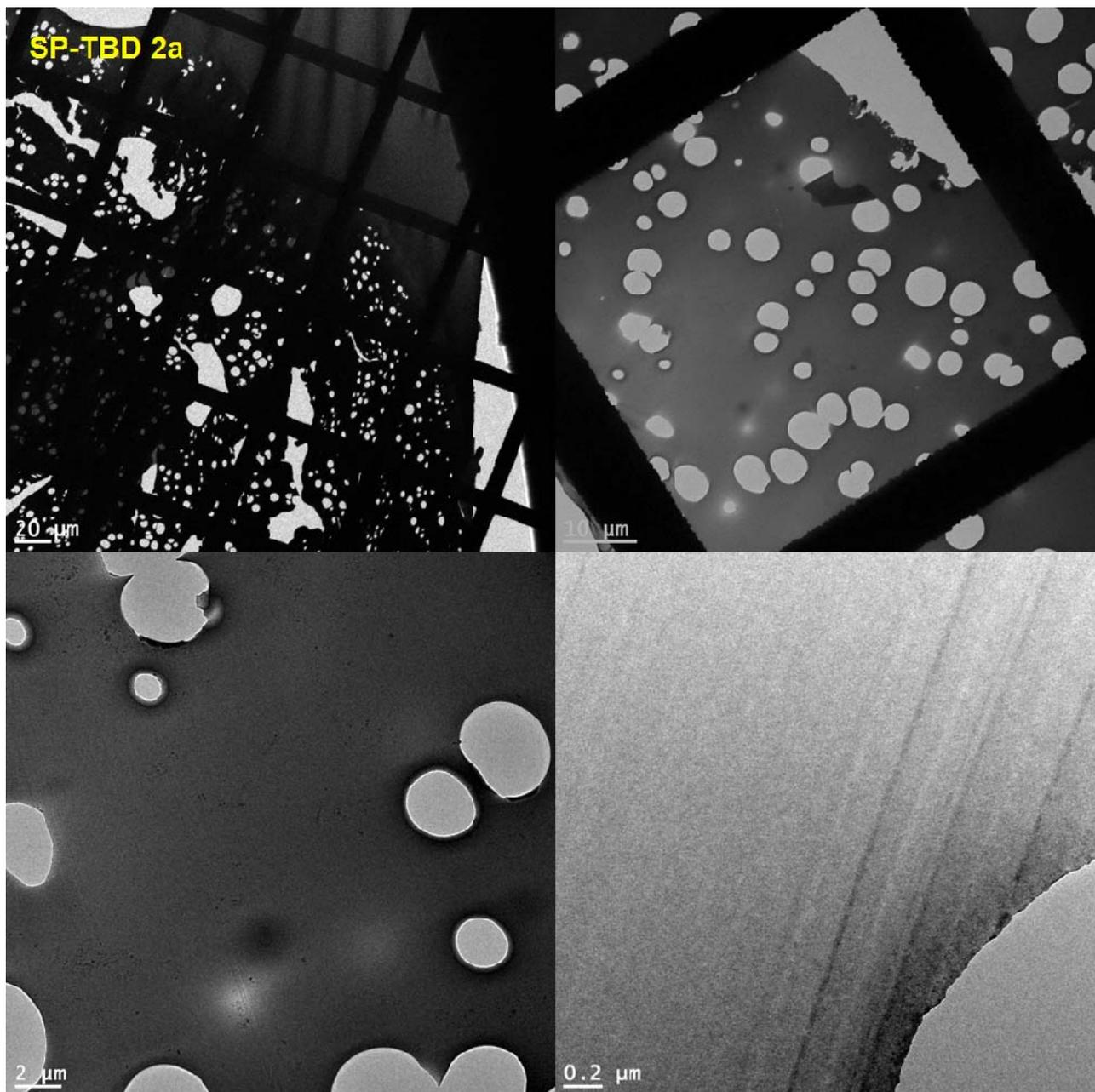
**Figure S5.** SEM Images of SP-CI **1a-c**, SP-TBD **2a-c**, and SP-TEA **3a-c**.



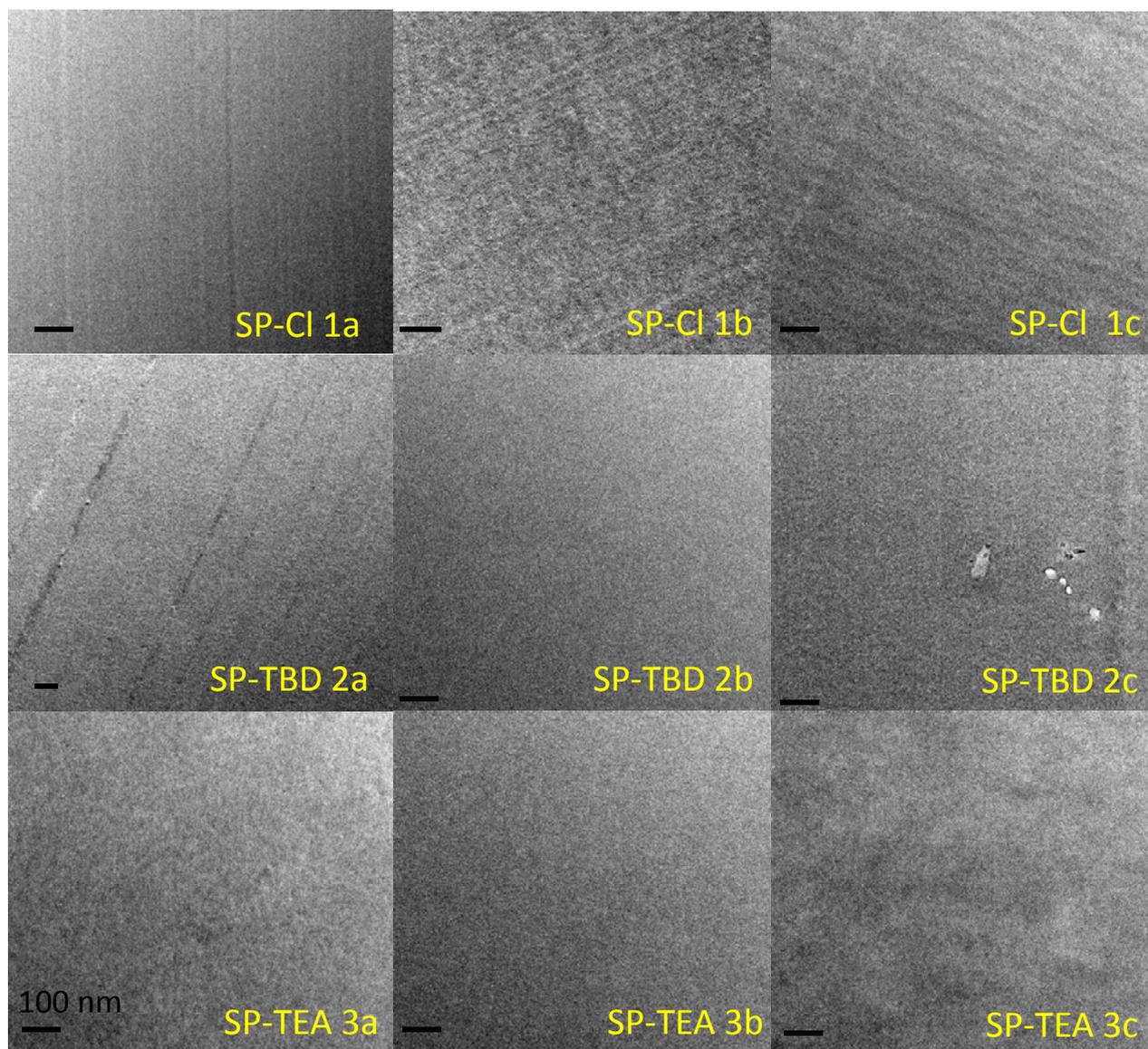
**Figure S6.** Additional SEM Images of SP-CI **1a-c**, SP-TBD **2a-c**, and SP-TEA **3a-c** (all scale bars are 1 micron)



**Figure S7 .** Additional TEM Images of SP-CI **1a** at various magnifications



**Figure S8.** Additional TEM Images of SP-TBD **2a** at various magnifications



**Figure S9.** TEM Images of SP-Cl **1a-c**, SP-TBD **2a-c**, and SP-TEA **3a-c** (all scale bars are 100 nm)

