

## *Supporting Information*

### **Highly Hydroxylated Hafnium Clusters Are Accessible to High Resolution EUV Photoresists under Small Energy Doses**

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**KEYWORDS:** Hexameric Hf oxide clusters, partially decarboxylation, photoresist, EUV lithography, line/space/edge character.

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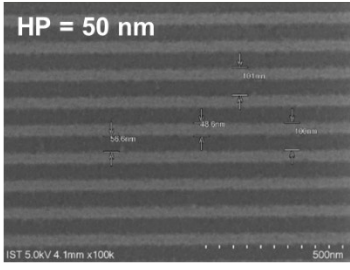
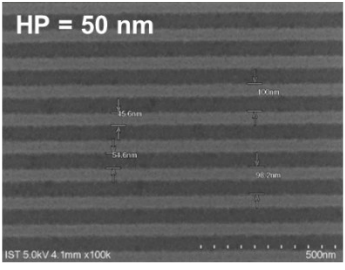
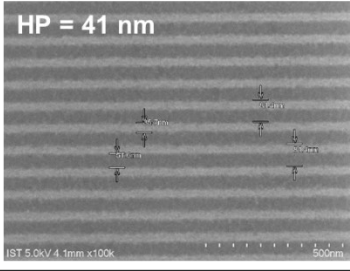
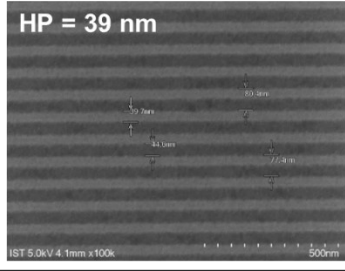
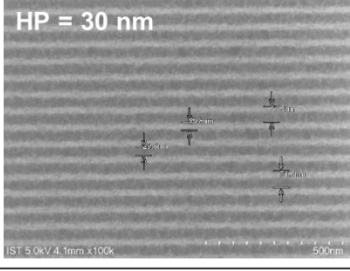
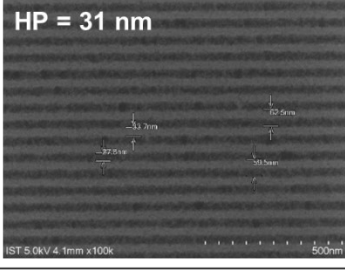
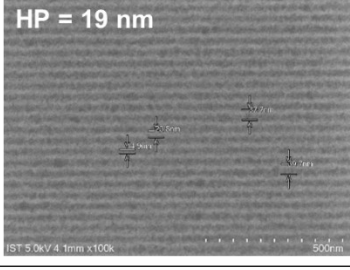
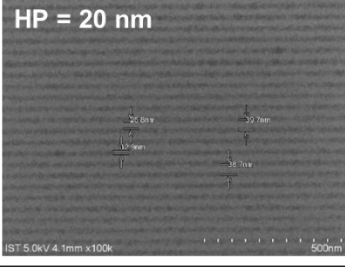
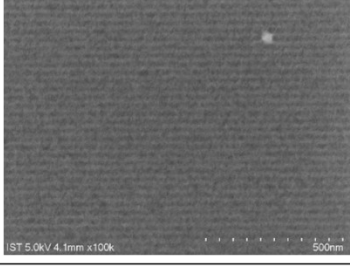
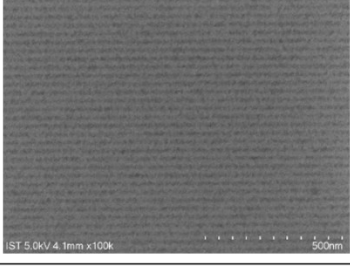
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## **1. Representative synthetic procedures**

Unless otherwise noted, all reactions were carried out under nitrogen atmosphere in oven-dried glassware using standard syringe, cannula and septa apparatus. Dichloromethane and toluene were dried over  $\text{CaH}_2$  and distilled. Reagents were purchased from commercial sources and used without purification, unless otherwise stated.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker 400 MHz and Bruker 500 MHz spectrometers using chloroform-d ( $\text{CDCl}_3$ ) as the internal standard. The ESI-Mass were performed using JEOL JMS-700. The EA analysis was performed by elemental vario EL cube. The TGA were performed using Mettler-Toledo 2-HT. FTIR Spectroscopy of powder samples was in a Bruker Vertex 80v spectrometer. The AFM measurements were using SEIKO SPA-300HV. Electron-beam lithography was done by utilizing Elionix ELS-7800 with an accelerating voltage of 80 kV and a beam current of 200 pA. The EUV-IL system at the Swiss Light Sources (SLS), Paul Scherrer Institute, utilizes 13.5 nm EUV light. HRXPS measurements were performed in a ULVAC-PHI Quantera II, with a monochromatic Al K $\alpha$  source (energy of 1486.7 eV).

### 3. SEM image of E-beam lithography patterns

Dose Design HP	800 $\mu\text{C}/\text{cm}^2$	1120 $\mu\text{C}/\text{cm}^2$
Design HP = 50 nm	HP = 50 nm 	HP = 50 nm 
Design HP = 40 nm	HP = 41 nm 	HP = 39 nm 
Design HP = 30 nm	HP = 30 nm 	HP = 31 nm 
Design HP = 20 nm	HP = 19 nm 	HP = 20 nm 
Design HP = 15 nm		

**Figure S1.** SEM images of E-beam lithography patterns on **3**. Process parameter: 2 wt%, THK= 24 nm, Developer: 2-Heptanone : Hexane = 1 : 1 60 s, **no PEB**

Dose Design HP		800 $\mu\text{C}/\text{cm}^2$	1120 $\mu\text{C}/\text{cm}^2$
		Design HP = 50 nm	<p>HP = 50 nm</p>
Design HP = 40 nm	<p>HP = 39 nm</p>	<p>HP = 42 nm</p>	
Design HP = 30 nm	<p>HP = 31 nm</p>	<p>HP = 29 nm</p>	
Design HP = 20 nm		<p>HP = 20 nm</p>	
Design HP = 15 nm			

**Figure S2.** SEM images of E-beam lithography patterns on **3**. Process parameter: 2 wt%, THK= 24 nm, Developer: 2-Heptanone : Hexane = 1 : 1 60 s, PEB= 80°C, 60s

#### 4. SEM image of EUV lithography patterns

Dose Design HP	~ 10 mJ/cm <sup>2</sup>	~ 30 mJ/cm <sup>2</sup>
	Design HP = 50 nm	<p>HP = 52 nm (11 mJ/cm<sup>2</sup>)</p> <p>52.5 nm, 53.1 nm, 51.4 nm</p> <p>IST 5.0kV 3.4mm x100k 500nm</p>
Design HP = 35 nm	<p>HP = 36 nm (10 mJ/cm<sup>2</sup>)</p> <p>35.9 nm, 35.0 nm, 34.4 nm</p> <p>IST 5.0kV 3.4mm x100k 500nm</p>	<p>HP = 34 nm (30 mJ/cm<sup>2</sup>)</p> <p>34.5 nm, 34.2 nm, 34.5 nm</p> <p>IST 5.0kV 3.3mm x100k 500nm</p>
Design HP = 25 nm	<p>HP = 24 nm (9 mJ/cm<sup>2</sup>)</p> <p>24.2 nm, 24.8 nm, 24.2 nm</p> <p>IST 5.0kV 3.4mm x100k 500nm</p>	<p>HP = 25 nm (27 mJ/cm<sup>2</sup>)</p> <p>25.0 nm, 25.2 nm, 25.1 nm</p> <p>IST 5.0kV 3.3mm x100k 500nm</p>
Design HP = 22 nm	<p>HP = 21 nm (9 mJ/cm<sup>2</sup>)</p> <p>21.7 nm, 21.5 nm, 21.2 nm</p> <p>IST 5.0kV 3.4mm x100k 500nm</p>	<p>HP = 22 nm (27 mJ/cm<sup>2</sup>)</p> <p>22.0 nm, 22.1 nm, 22.1 nm</p> <p>IST 5.0kV 3.3mm x100k 500nm</p>
Design HP = 18 nm	<p>HP = 19 nm (10 mJ/cm<sup>2</sup>)</p> <p>19.2 nm, 19.2 nm, 19.4 nm</p> <p>IST 5.0kV 3.4mm x100k 500nm</p>	<p>HP = 18 nm (30 mJ/cm<sup>2</sup>)</p> <p>18.3 nm, 18.2 nm, 18.3 nm</p> <p>IST 5.0kV 3.3mm x100k 500nm</p>

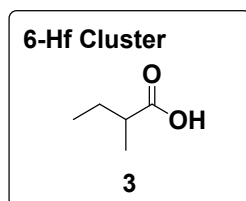
**Figure S3.** SEM images of EUV lithography patterns on **3** HP= 50, 35, 25, 22, 18 nm at different dose. Process parameter: 2.0 wt%, THK= 24 nm, Developer: 2-Heptanone : Hexane = 1 : 1 60 s, PEB= 80°C 60 s

Dose Design HP	$\sim 90 \text{ mJ/cm}^2$	$\sim 100 \text{ mJ/cm}^2$
	Design HP = 50 nm	
Design HP = 35 nm		
Design HP = 25 nm		
Design HP = 22 nm		
Design HP = 18 nm		

**Figure S4.** SEM images of EUV lithography patterns on **3** HP= 50, 35, 25, 22, 18 nm at different dose. Process parameter: 2.0 wt%, THK= 24 nm, Developer: 2-Heptanone : Hexane = 1 : 1 60 s, PEB= 80°C 30 s

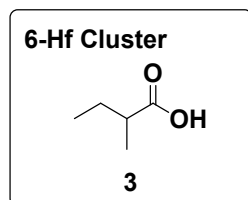
## 6. Spectral data of key compounds.

### 6.1 Spectral data for highly decarboxylated 6-Hafnium Cluster with 2-methylbutanoic acid ligand 3.



White solid (59%) ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ) :  $\delta$  2.11 (s, 8H), 1.65 (s, 8H), 1.30 (s, 8H), 1.03 (s, 24H), 0.84 (s, 24H) ;  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ) :  $\delta$  181.9, 42.8, 26.6, 16.2, 11.9. ; **EA Anal.** Calcd. for  $\text{C}_{40}\text{H}_{80}\text{O}_{28}\text{Hf}_6$  : C : 23.10% ; H : 3.88%, found : C : 23.11% ; H : 4.17

## 7. $^1\text{H}$ and $^{13}\text{C}$ NMR of cluster 3



Current Data Parameters  
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 PROCNO 1

F2 - Acquisition Parameters  
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 Time 20.06  
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 PULPROG zg30  
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 NS 19  
 DS 0  
 SWH 6410.256 Hz  
 FIDRES 0.195625 Hz  
 AQ 2.5559039 sec  
 RG 161  
 DW 78.000 usec  
 DE 6.00 usec  
 TE 300.0 K  
 D1 2.00000000 sec  
 TDO 1

===== CHANNEL f1 =====  
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 PL1 -2.40 dB  
 SFO1 400.1528010 MHz

F2 - Processing parameters  
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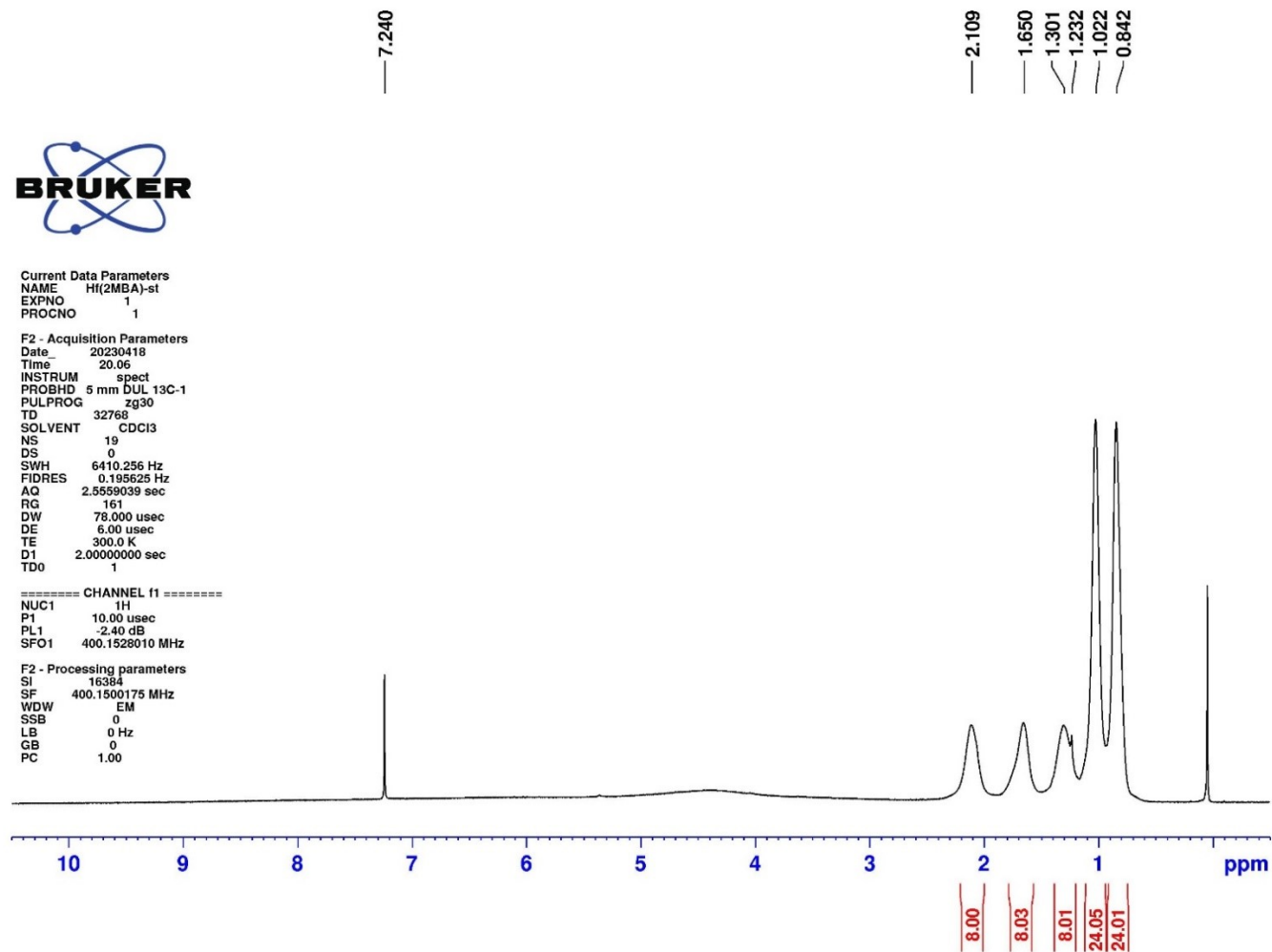
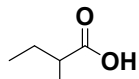


Figure S5.  $^1\text{H}$  NMR of cluster 3



6-Hf Cluster



3



Current Data Parameters  
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PROCNO 1

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FIDRES 0.908261 Hz  
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RG 191.01  
DW 16.800 usec  
DE 6.50 usec  
TE 300.3 K  
D1 2.0000000 sec  
D11 0.0300000 sec  
TD0 1  
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NUC1 13C  
P1 10.00 usec  
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NUC2 1H  
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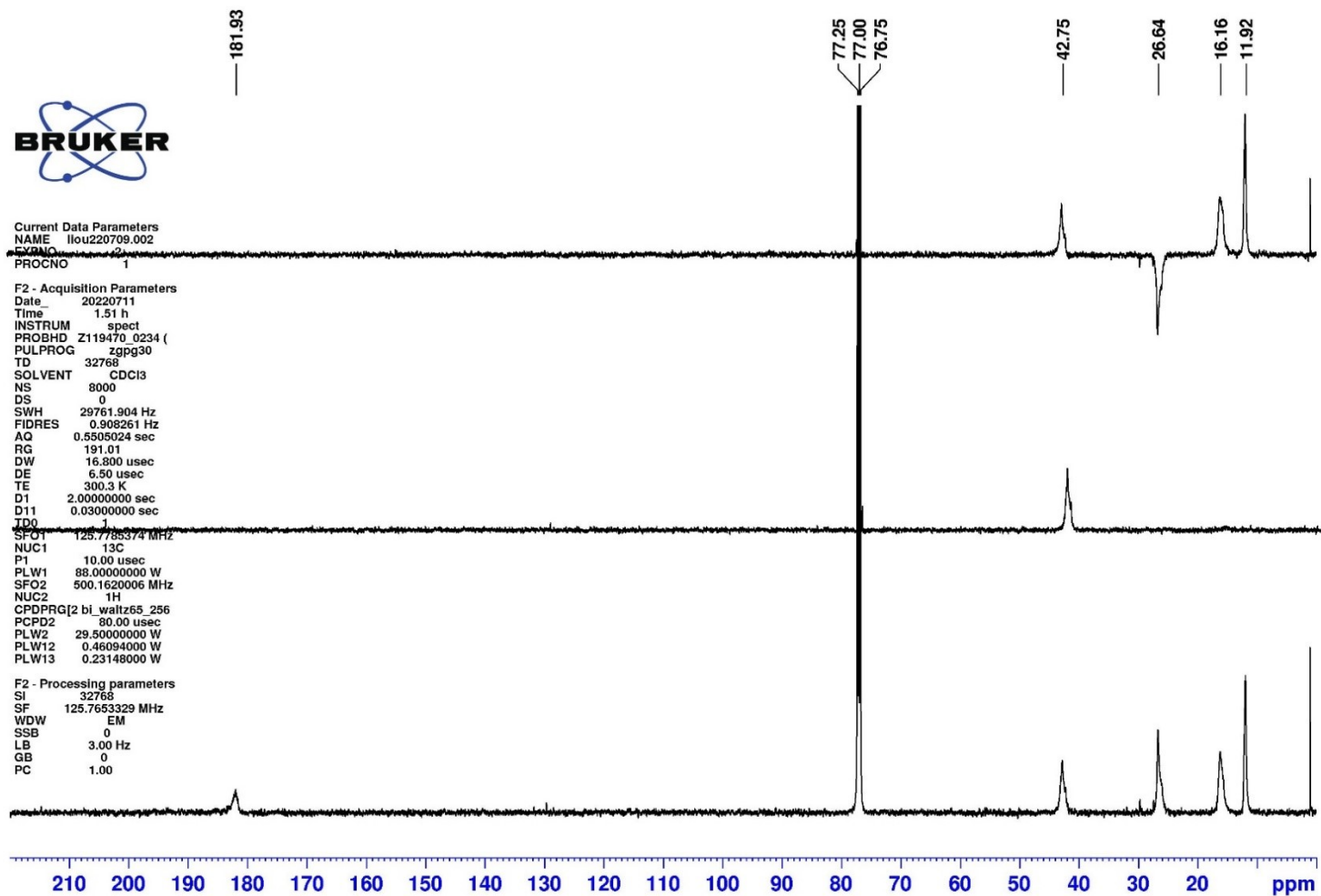


Figure S6. <sup>13</sup>C NMR of cluster 3

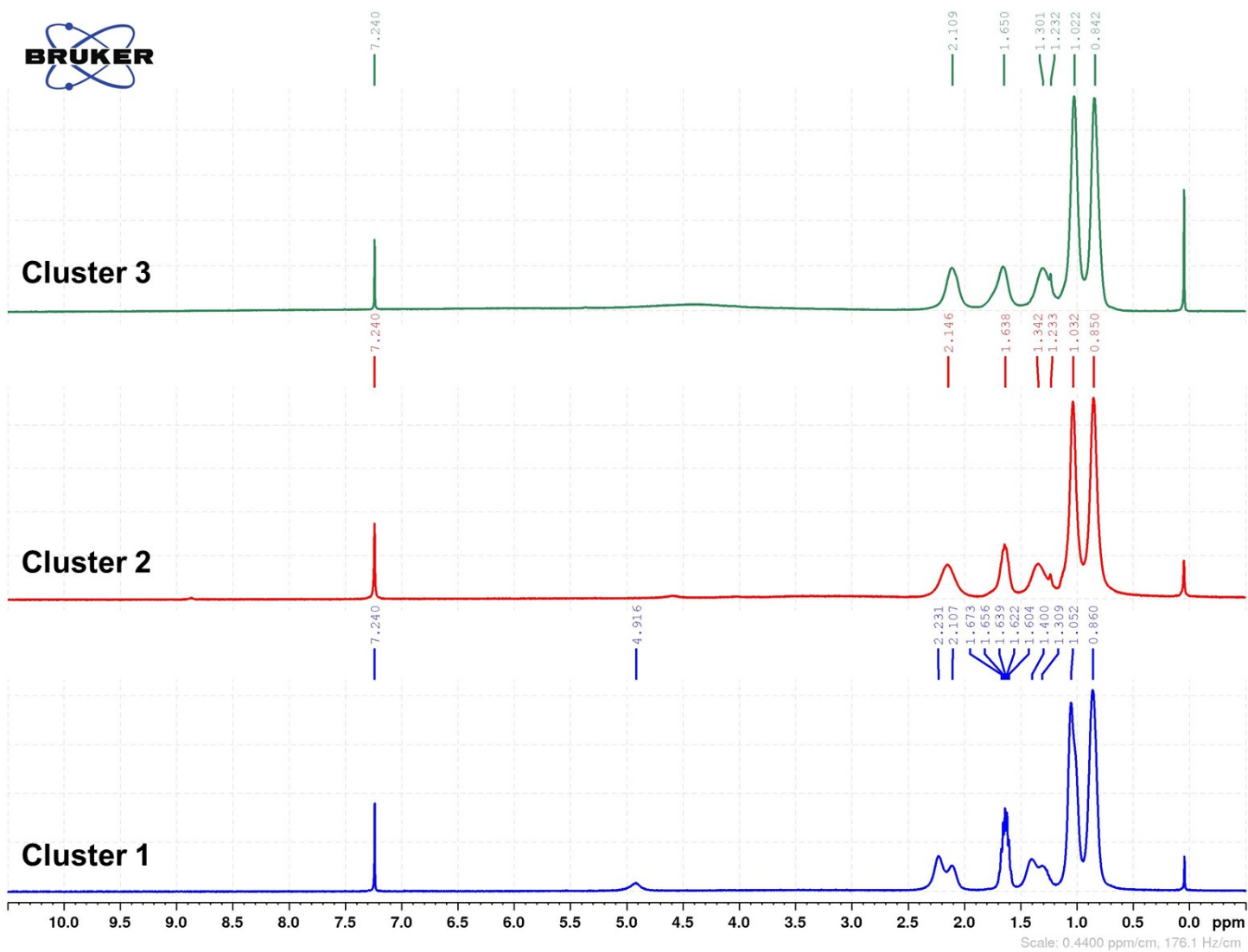


Figure S7.  $^1\text{H}$  NMR of cluster 1, 2 and 3