Electronic Supplementary Material (ESI) for Nanoscale Advances.
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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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1. Representative synthetic procedures

Unless otherwise noted, all reactions were carried out under nitrogen atmosphere inoven-dried glassware using standard syringe, cannula and septa apparatus. Dichloromethane and toluene were dried over CaH_2 and distilled. Reagents were purchased from commercial sources and used without purification, unless otherwise stated. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 MHz and Bruker 500 MHz spectrometers using chloroform-d ($CDCl_3$) as the internal standard. The ESI-Mass were perdormed using JEOL JMS-700. The EA analysis was performed by elementar vario EL cube. The TGA were performed using Mettler-Toledo 2-HT. FTIR Spectroscopy of power 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 Ka source (energy of 1486.7 eV).

3. SEM image of E-beam lithography patterns

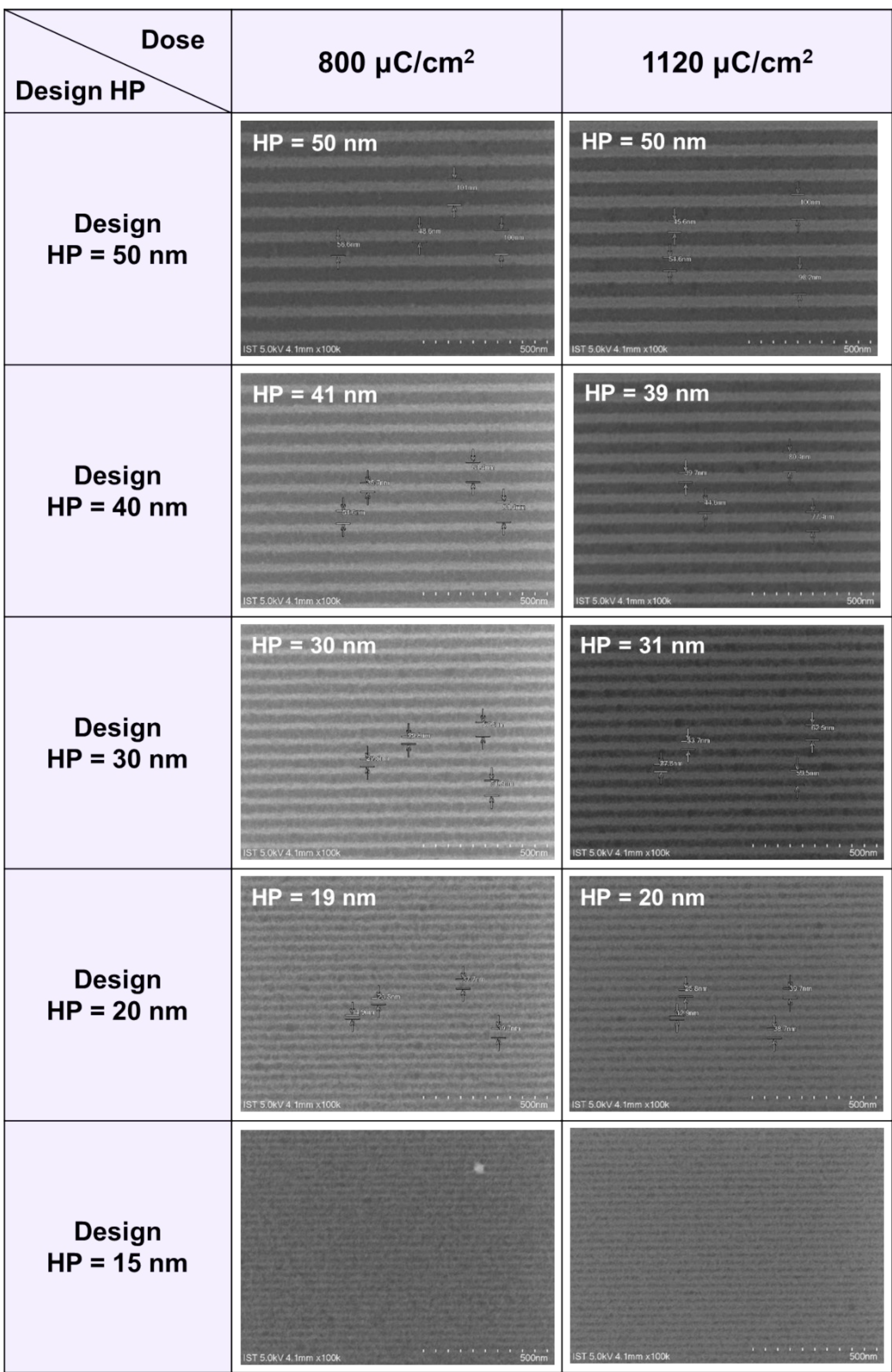


Figure S1. SEM images of E-beam lithography patterns on **3**. Process parameter: 2 wt%, THK= 24 nm, Developer: 2-Heptanone : Hexane = 1 : 1 60 s, **no PEB**

Dose / Design HP	800 μC/cm^2	1120 μC/cm^2
Design HP = 50 nm	HP = 50 nm	HP = 51 nm
Design HP = 40 nm	HP = 39 nm	HP = 42 nm
Design HP = 30 nm	HP = 31 nm	HP = 29 nm
Design HP = 20 nm		HP = 20 nm
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℃, 60s

.

4. SEM image of EUV lithography patterns

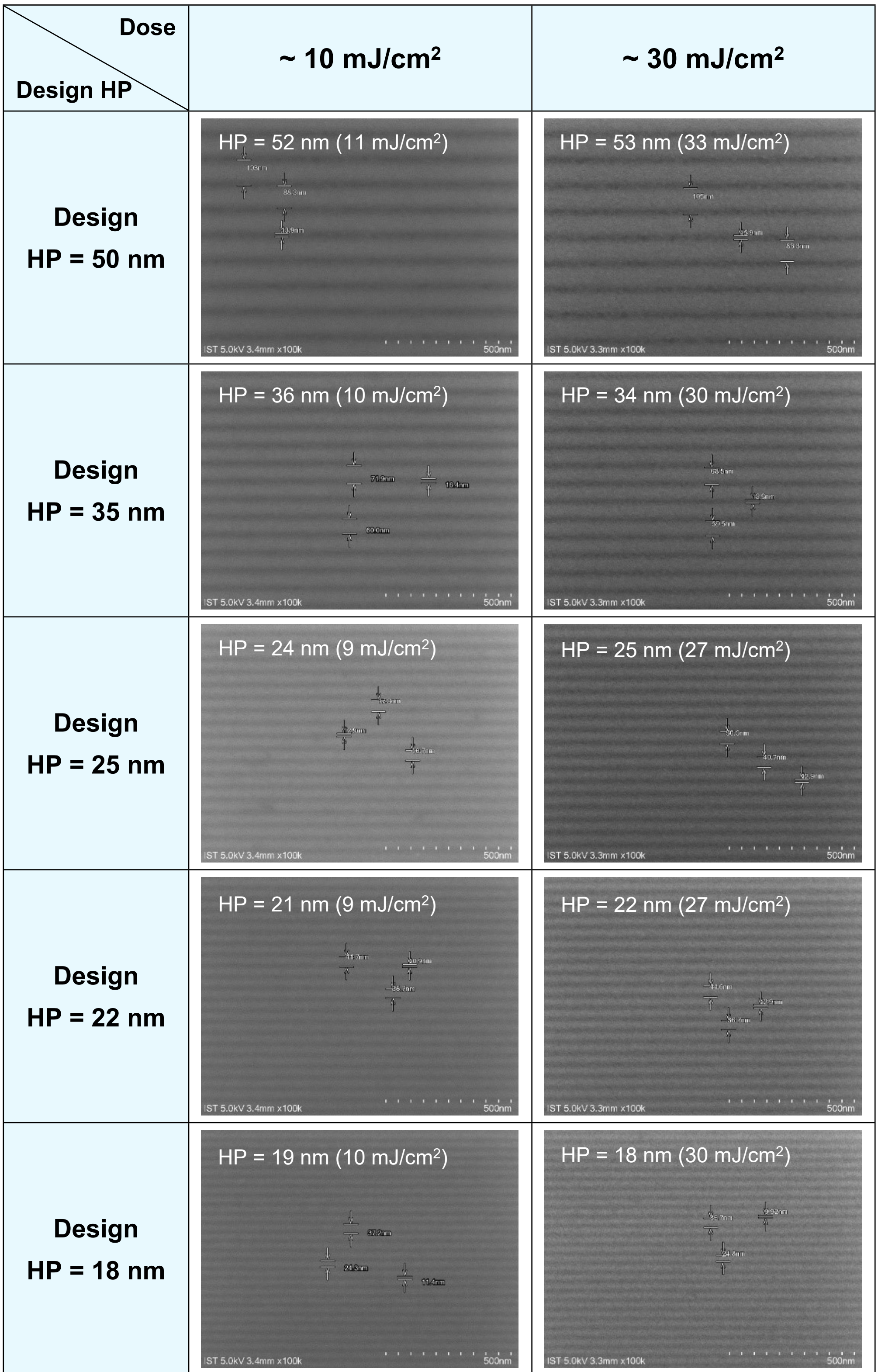


Figure S3. SEM images of EUV lithography patterns on **3** HP= 50, 35, 25, 22, 18 nm at different dose. Process parameter: 2.0 wt%, THK= 24 nm, Developer: 2-Heptanone : Hexane = 1 : 1 60 s, PEB= 80°C 60 s

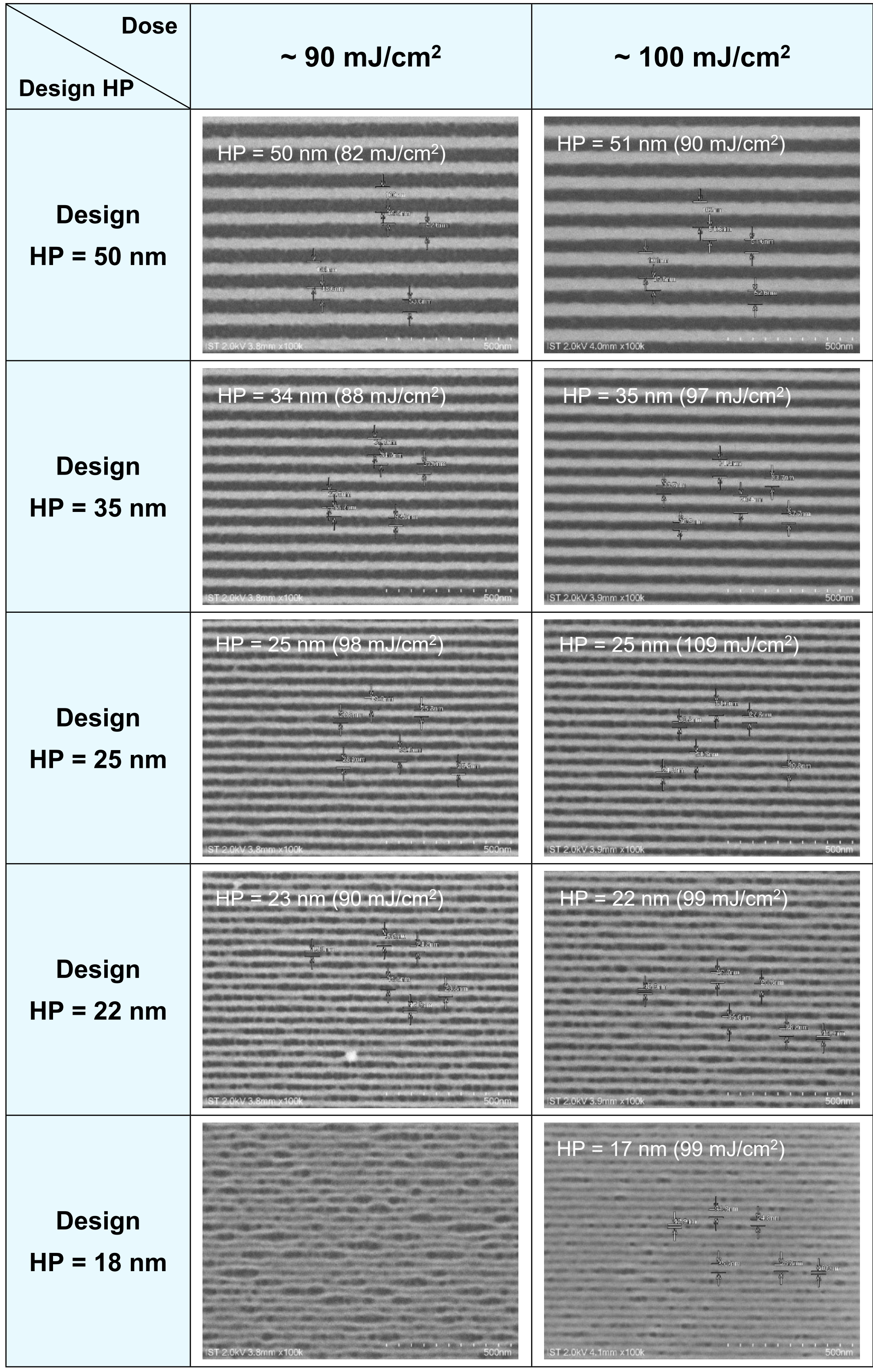
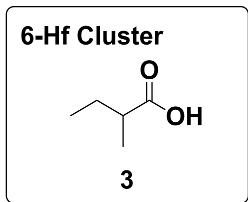


Figure S4. SEM images of EUV lithography patterns on **3** HP= 50, 35, 25, 22, 18 nm at different dose. Process parameter: 2.0 wt%, THK= 24 nm, Developer: 2-Heptanone : Hexane = 1 : 1 60 s, PEB= 80℃ 30 s

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}**H NMR** (400 MHz, $CDCl_3$) : δ 2.11 (s, 8H), 1.65 (s, 8H), 1.30 (s, 8H), 1.03 (s, 24H), 0.84 (s, 24H) ; ^{13}**C NMR** (125 MHz, $CDCl_3$) : δ 181.9, 42.8, 26.6, 16.2, 11.9. ; **EA Anal.** Calcd. for $\mathbf{C_{40}H_{80}O_{28}Hf_6}$: C : 23.10% ; H : 3.88%, found : C : 23.11% ; H : 4.17

7. ^{1}H and ^{13}C NMR of cluster 3

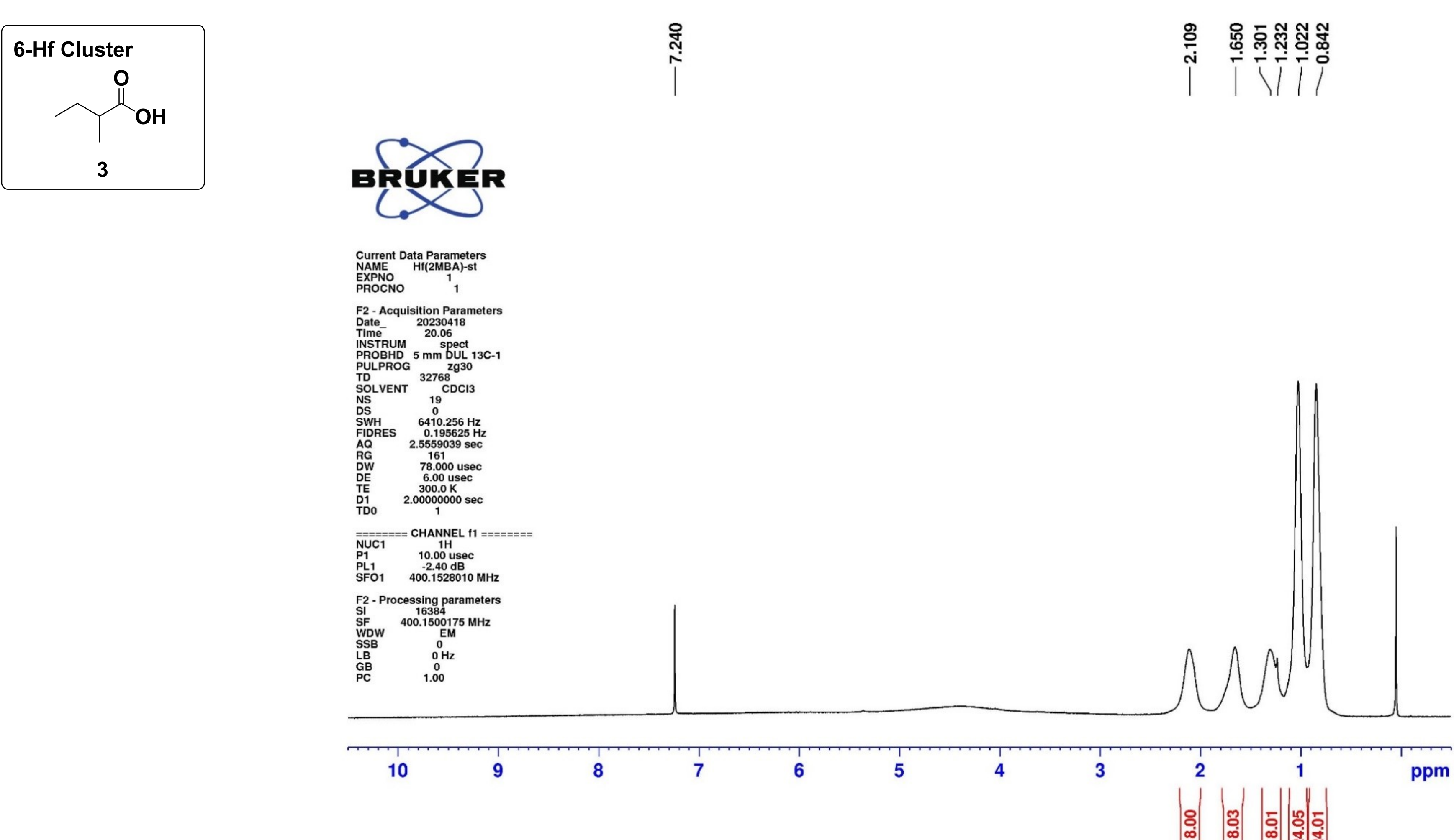


Figure S5. 1H NMR of cluster **3**

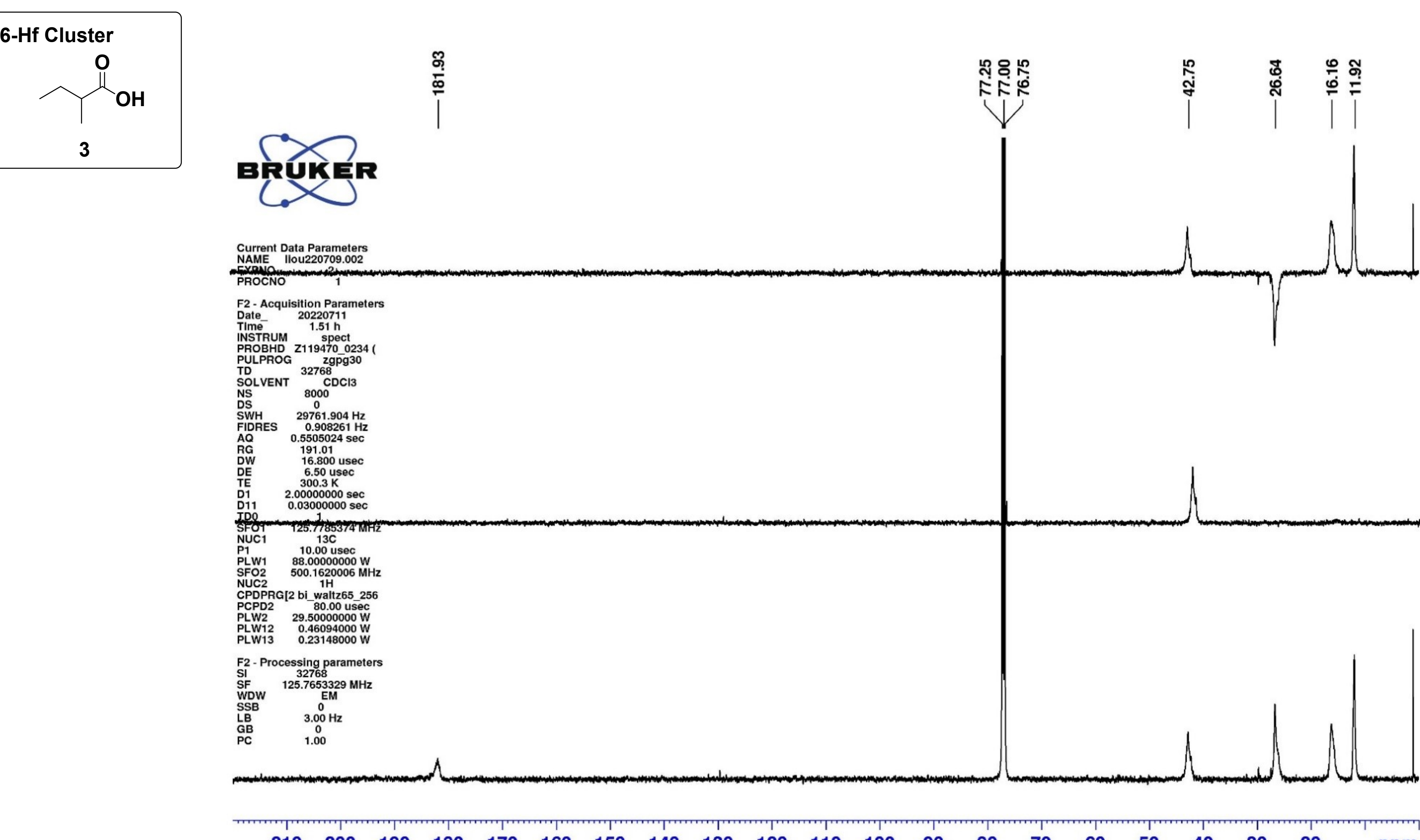


Figure S6. ^{13}C NMR of cluster **3**

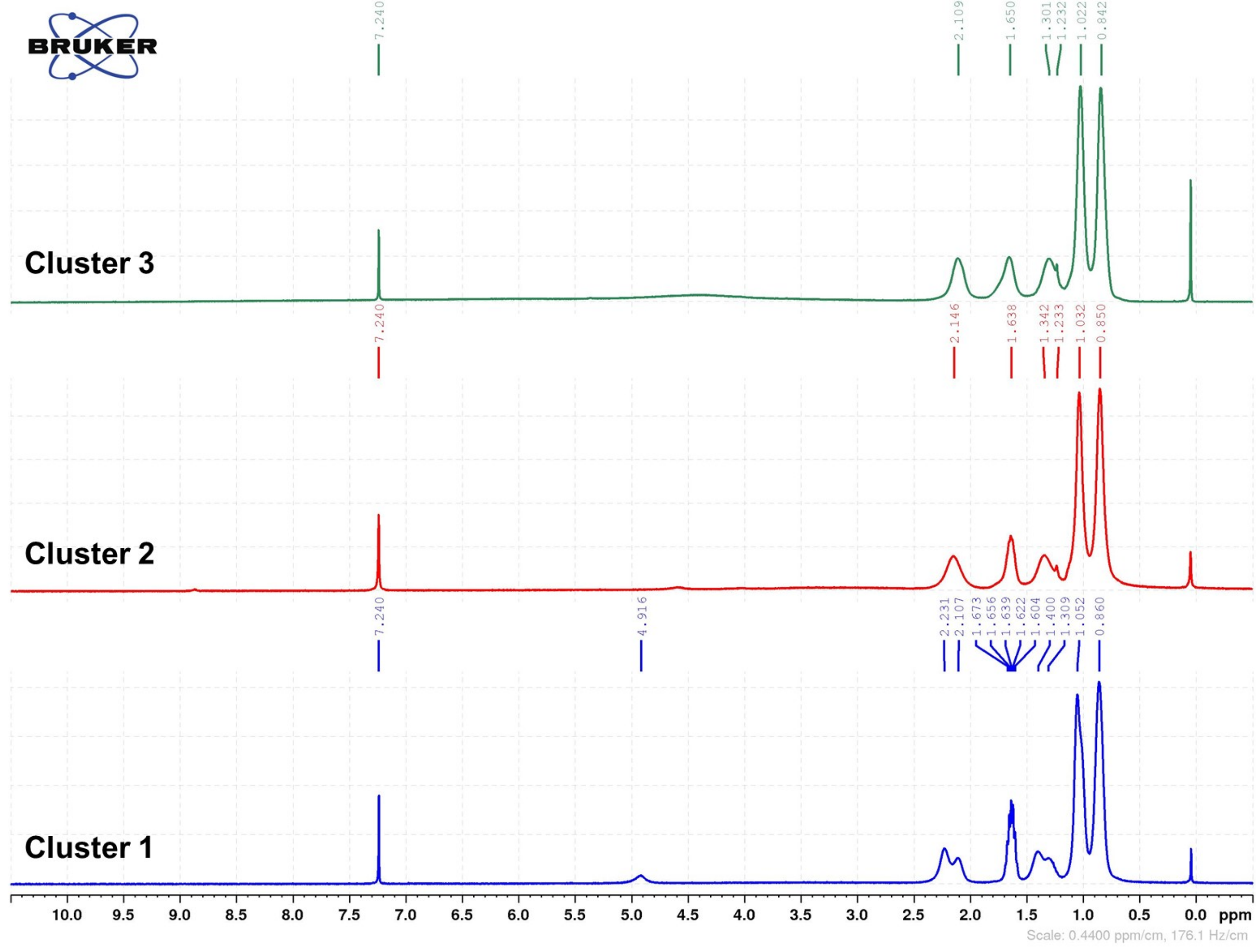


Figure S7. ^{1}H NMR of cluster **1**, **2** and **3**