*Supporting Information*

# Novel Hexameric Tin Carboxylate Clusters as Efficient Negative-Tone EUV Photoresists: High resolution with Well-Defined Patterns using Low Energy Doses

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**Content:**

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

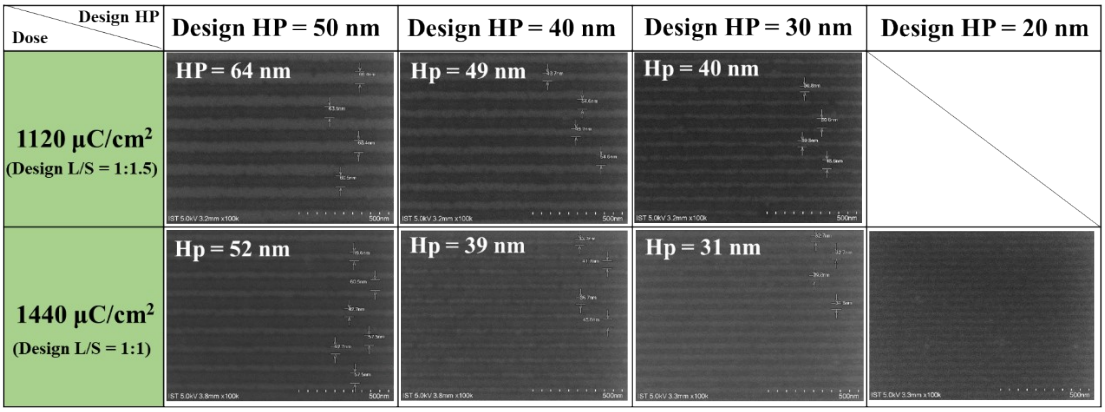



**Figure S1.** SEM images of E-beam lithography patterns for cluster **1**; Process parameter: 1.5 wt%, THK = 20.9 nm, Developer: 2-Heptanone 60 s, PEB= 80℃ 60 s

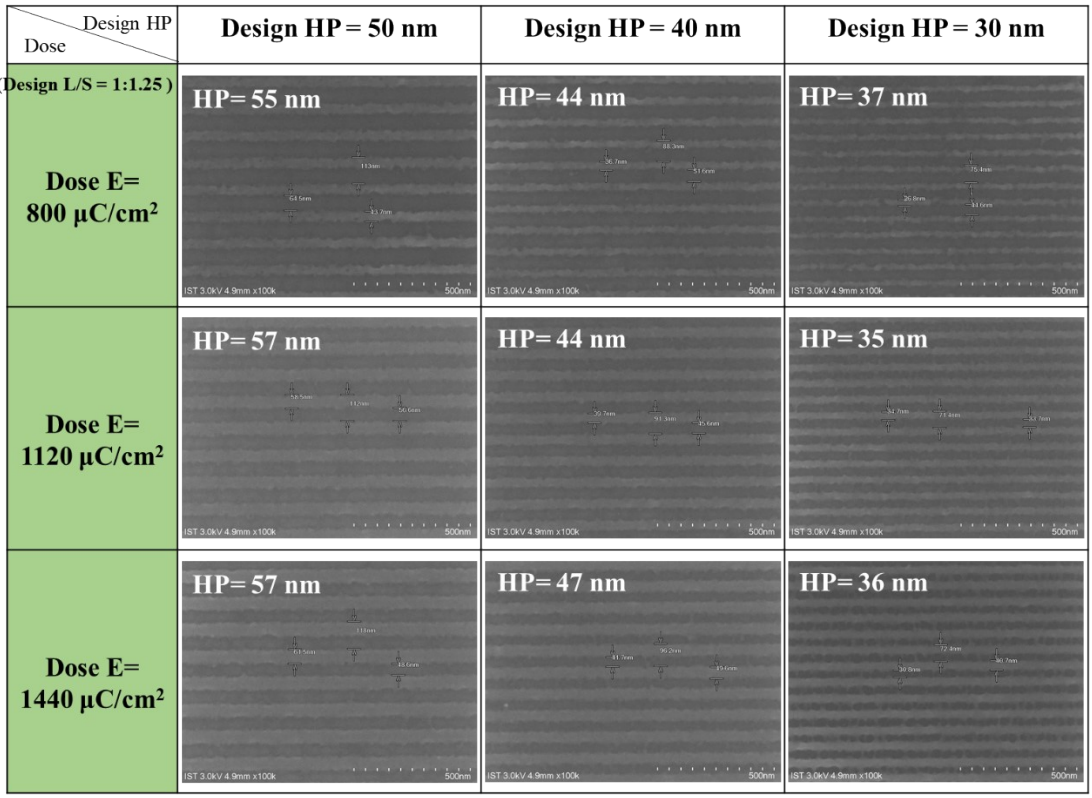



**Figure S2.** SEM images of E-beam lithography patterns for cluster **2**; Process parameter: 1.75 wt%, THK = 22.9 nm, Developer: 2-Heptanone 60 s, PEB = 80℃ 60 s

## 2. SEM image of EUV lithography patterns


**Figure S3.** SEM images of EUV lithography patterns for cluster **1:** HP=50, 35, 25 nm at different dose. Process parameter: 1.5 wt%, THK = 20.9 nm, Developer: 2-Heptanone 60 s, PEB= 80℃ 60 s

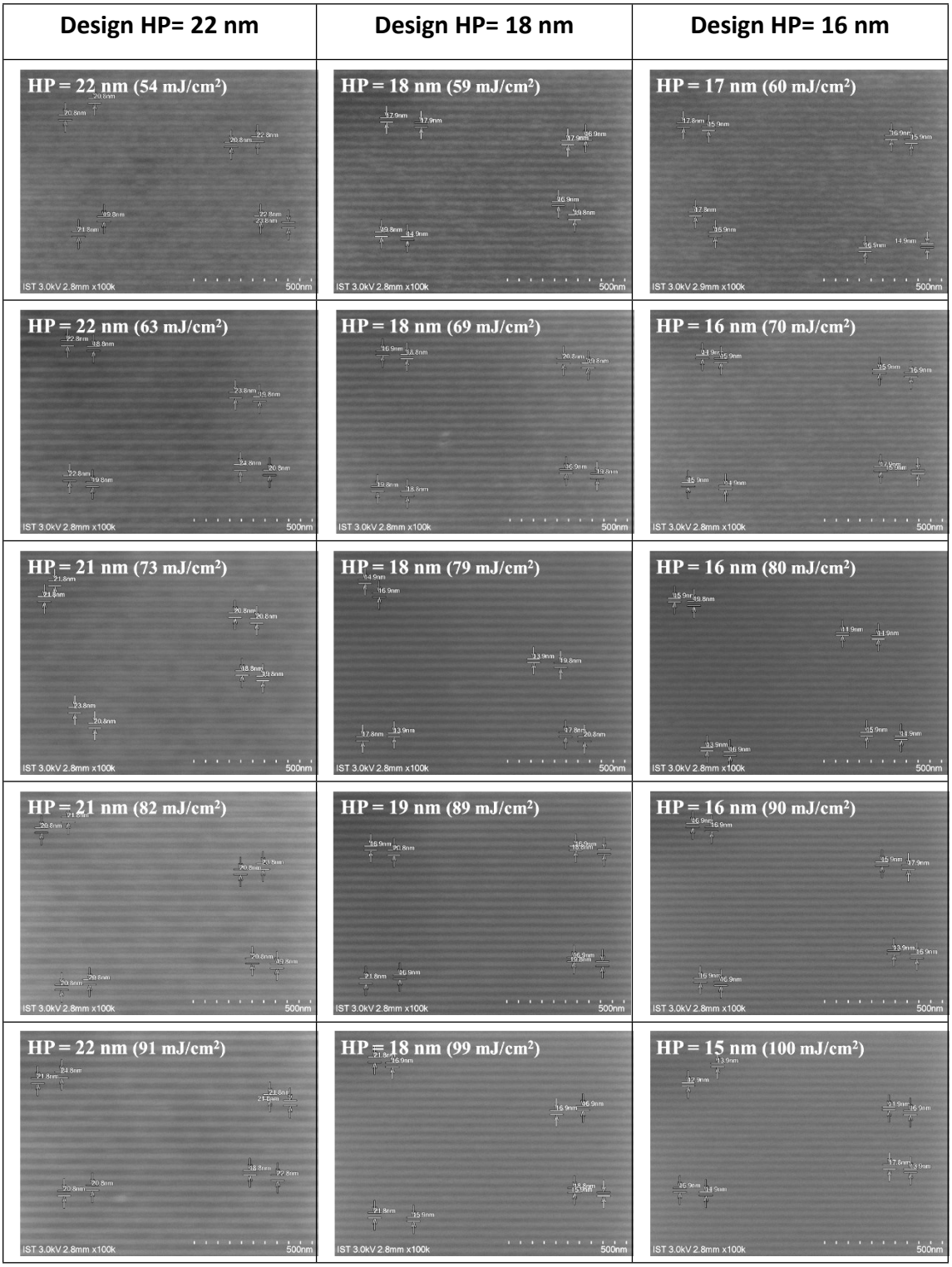



**Figure S4.** SEM images of EUV lithography patterns for cluster **1:** HP=22, 18, 16 nm at different dose. Process parameter: 1.5 wt%, THK = 20.9 nm, Developer: 2-Heptanone 60 s, PEB= 80℃ 60 s

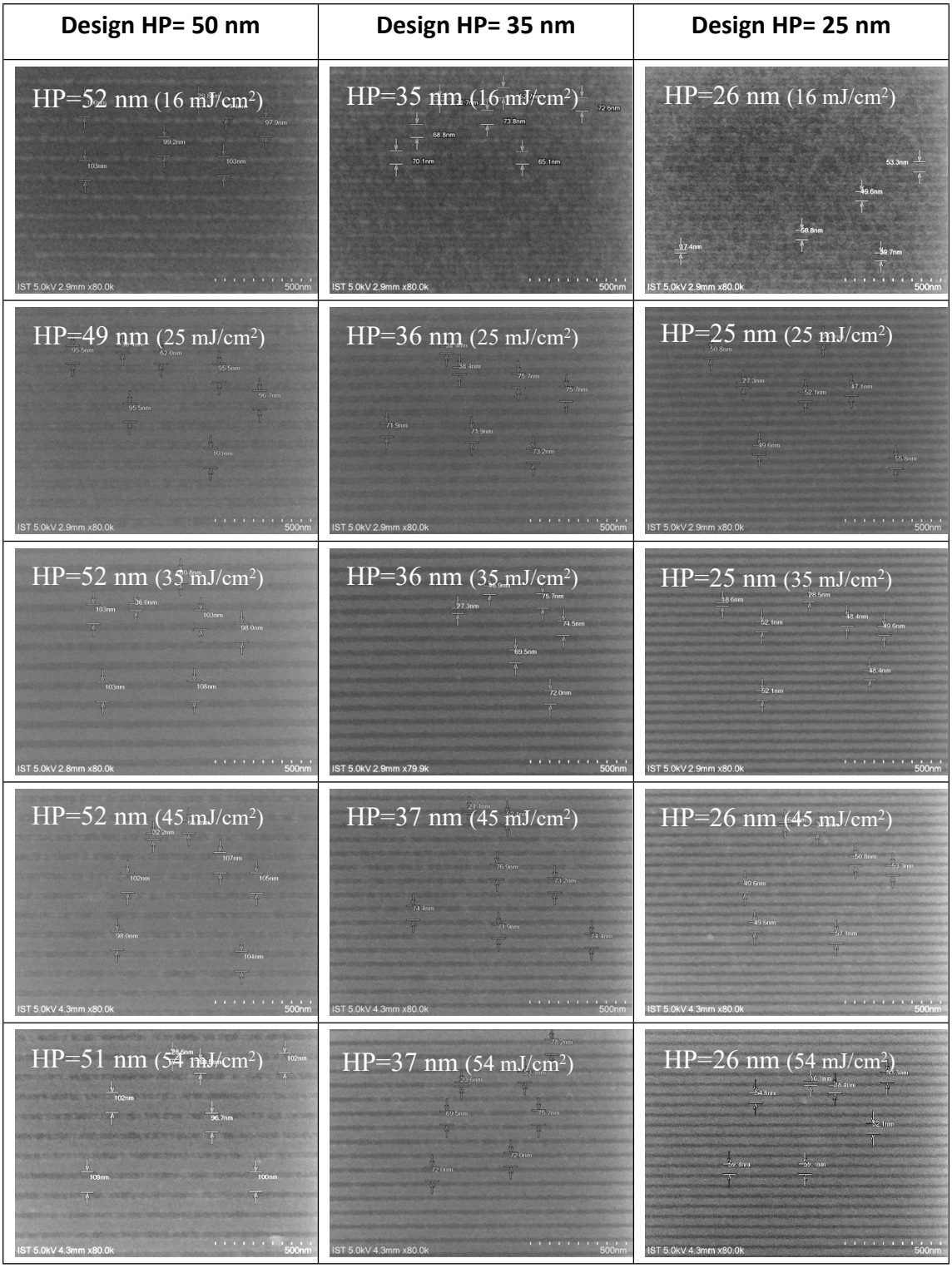



**Figure S5.** SEM images of EUV lithography patterns for cluster **2**: HP=50, 35, 25 nm at different dose. Process parameter: 1.75 wt%, PAB = 60°C 60s, THK = 22.9 nm, Developer: 2-Heptanone 60 s, No PEB.

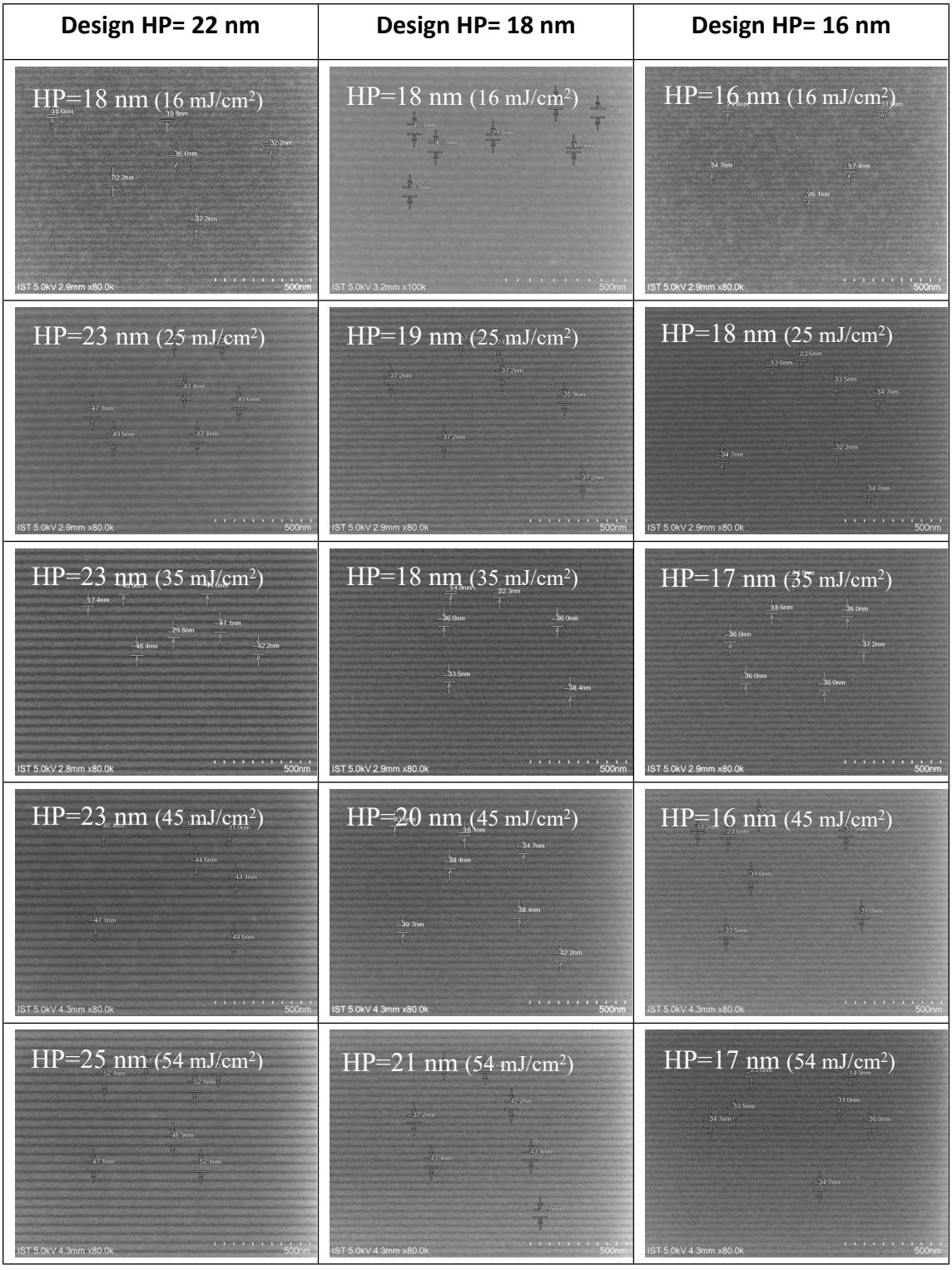



**Figure S6.** SEM images of EUV lithography patterns for cluster 2. HP=22, 18, 16 nm at different dose. Process parameter: 1.75 wt%, PAB = 60℃ 60s, THK = 22.9 nm, Developer: 2-Heptanone 60 s, No PEB.

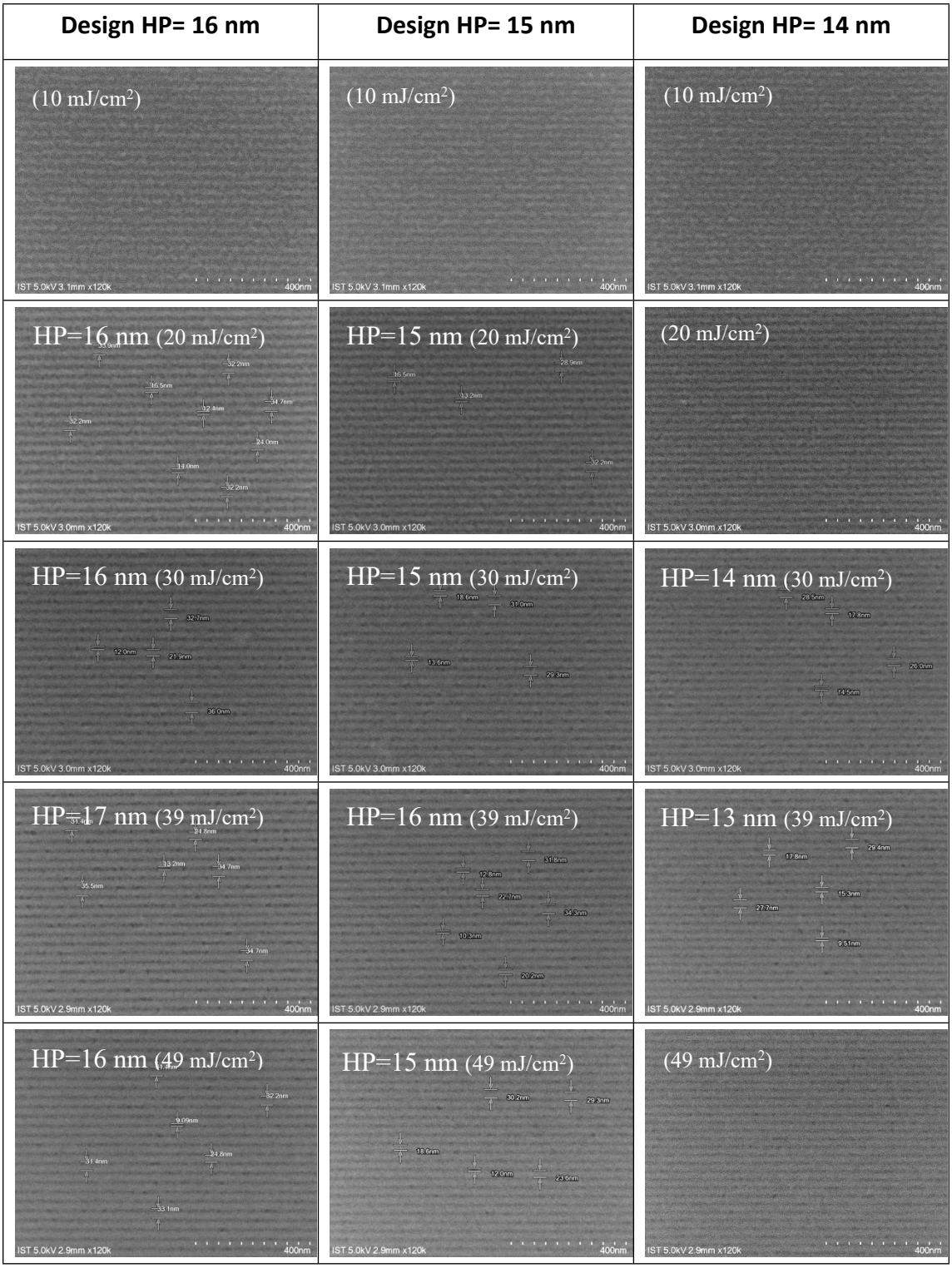



**Figure S7.** SEM images of EUV lithography patterns for cluster 2, HP=16, 15, 14 nm at different dose. Process parameter: 1.75 wt%, PAB = 60°C 40s, THK = 20.62 nm, Developer: 2-Heptanone 60 s, No PEB.

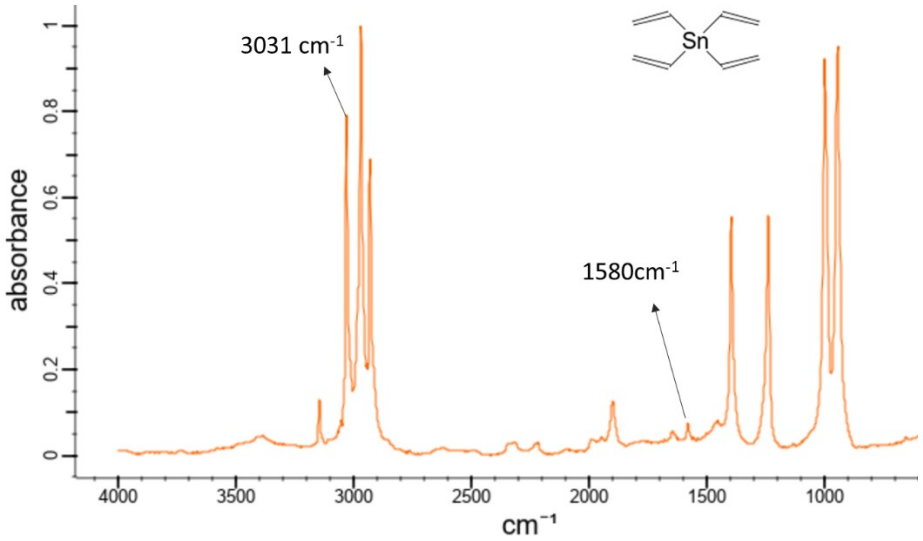



**Figure S8. IR spectra of Sn(vinyl)$_4$**

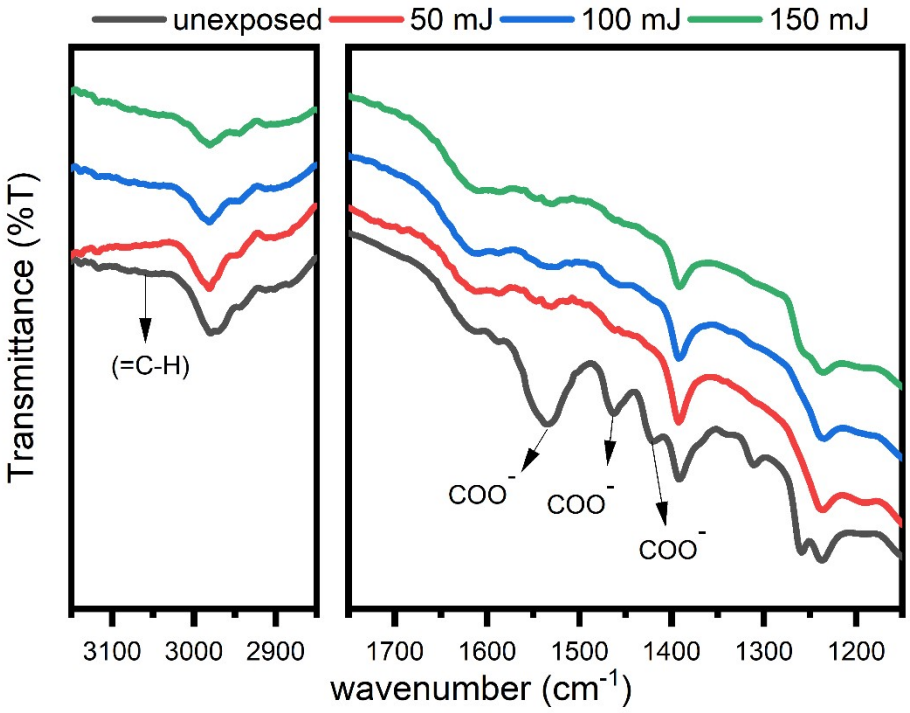



**Figure S9. Spectra of photoresist 2 in which the two regions are plotted on equal Magnitudes.**

3. **Table S1. LWR values for cluster 1 :**

| **Cluster 1 HP = 18 nm** | |
|---|---|
| Dose (mJ/cm$^2$ ) | LWR (nm) |
| 79 | 4.6 |
| 89 | 4.9 |
| 99 | 5.2 |

**The computation is based on a software: see:** l. Mochi, M. Vockenhuber, T. Allenet, Y. Ekinci, *Proc. SPIE*, 2021, **11855**, 1185502

**4. X-ray crystallographic structures and data**

**4.1 Crystal data and X-ray structure of cluster 1 :**

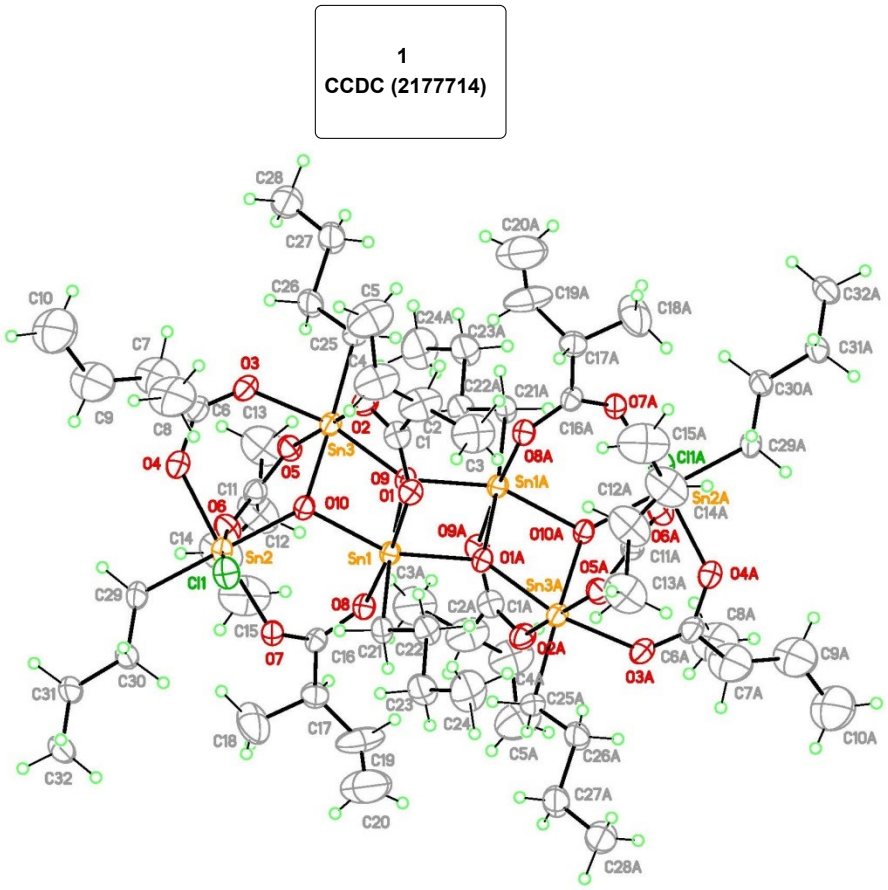



Table 1 Crystal data and structure refinement for 220347lt_auto.

| | |
|---|---|
| Identification code | 220347lt_auto |
| Empirical formula | $C_{32}H_{55}ClO_{10}Sn_3$ |
| Formula weight | 991.28 |
| Temperature/K | 99.99(10) |
| Crystal system | triclinic |

| | |
|---|---|
| Space group | P-1 |
| a/Å | 12.4749(4) |
| b/Å | 12.5391(3) |
| c/Å | 15.0700(4) |
| α/° | 90.977(2) |
| β/° | 104.825(3) |
| γ/° | 117.675(3) |
| Volume/Å$^3$ | 1992.54(11) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.652 |
| μ/mm$^{-1}$ | 15.858 |
| F(000) | 988.0 |
| Crystal size/mm$^3$ | 0.21 × 0.14 × 0.06 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 6.144 to 145.92 |
| Index ranges | -15 ≤ h ≤ 14, -13 ≤ k ≤ 15, -18 ≤ l ≤ 18 |
| Reflections collected | 26569 |
| Independent reflections | 7521 [$R_{int}$ = 0.0478, $R_{sigma}$ = 0.0387] |
| Data/restraints/parameters | 7521/317/536 |
| Goodness-of-fit on F$^2$ | 1.273 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0592, w$R_2$ = 0.1713 |
| Final R indexes [all data] | $R_1$ = 0.0678, w$R_2$ = 0.1778 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.63/-1.52 |

## 4.3 Crystal data and X-ray structure of cluster 2 :

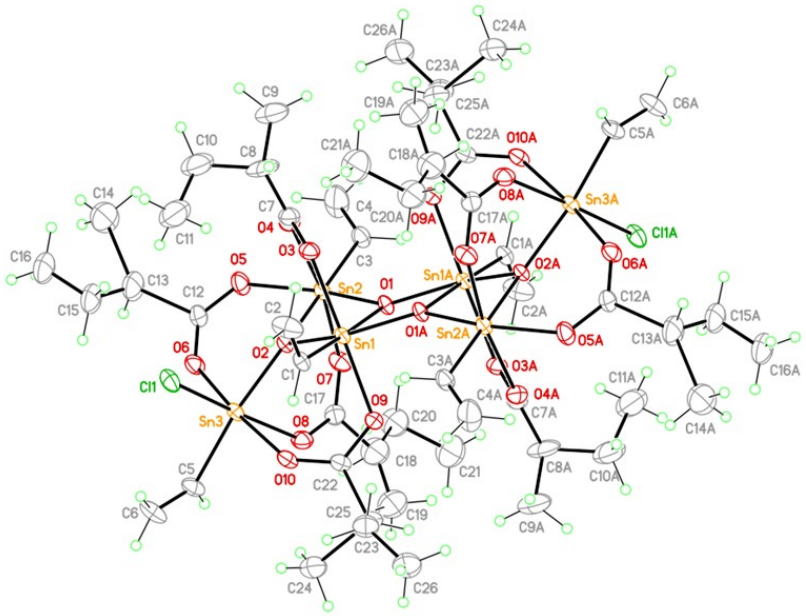



Table 1. Crystal data and structure refinement for 210753lt_0m_a.

| | | |
|---|---|---|
| Identification code | 210753lt_0m_a | |
| Empirical formula | C52 H90 Cl2 O20 Sn6 | |
| Formula weight | 1818.27 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | P-1 | |
| Unit cell dimensions | a = 10.7499(9) Å | α= 67.810(4)°. |
| | b = 13.2738(11) Å | β= 71.148(4)°. |
| | c = 14.0693(11) Å | γ = 73.030(4)°. |
| Volume | 1725.8(3) Å$^3$ | |
| Z | 1 | |
| Density (calculated) | 1.750 Mg/m$^3$ | |
| Absorption coefficient | 2.278 mm$^{-1}$ | |
| F(000) | 896 | |
| Crystal size | 0.23 x 0.20 x 0.06 mm$^3$ | |
| Theta range for data collection | 1.610 to 26.514°. | |
| Index ranges | -13<=h<=12, -16<=k<=16, -17<=l<=16 | |
| Reflections collected | 28957 | |
| Independent reflections | 7053 [R(int) = 0.0502] | |
| Completeness to theta = 25.242° | 99.6 % | |

| | |
|---|---|
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7454 and 0.6419 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 7053 / 414 / 525 |
| Goodness-of-fit on $F^2$ | 1.080 |
| Final R indices [I>2sigma(I)] | R1 = 0.0406, wR2 = 0.1111 |
| R indices (all data) | R1 = 0.0539, wR2 = 0.1288 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 1.401 and -1.066 e.$Å^{-3}$ |

## 5. Spectral data of key compounds

### 5.1 Spectral data for cluster 1 :

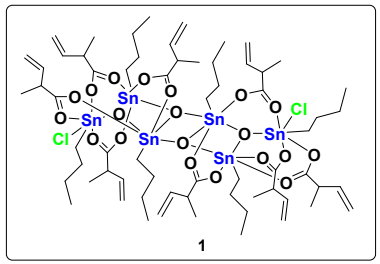
Transparent crystal (59%) ; $^{1}$H NMR (400 MHz, $CDCl_3$) : δ 5.92-5.88 (m, 8H), 5.12-5.07 (m, 16H), 3.12-3.04 (m, 8H), 1.73-1.62 (m, 24H), 1.34-1.32 (m, 12H), 1.24-1.18 (m, 24H), 0.88 (d, $J$ = 7.1 Hz, 18H)；$^{13}$C NMR (125 MHz, $CDCl_3$) : δ 182.7, 181.8, 138.7, 137.9, 137.7, 115.8, 115.4, 115.1, 114.9, 114.5, 114.4, 46.5, 46.5, 46.3, 46.2, 35.6, 35.5, 27.7, 27.5, 27.2, 27.1, 26.7, 26.4, 26.2, 26.1, 25.7, 17.2, 17.0；$^{119}$Sn NMR (186 MHz, $CDCl_3$) : δ -483.9, -522.3, -523.6, -551.1；HRMS (ESI+, m/z) Calcd. For $^{12}C_{64}{}^{1}H_{110}{}^{35}Cl_2{}^{16}O_{20}{}^{120}Sn_6$ $[M+H]^+$ : 1989.11, found : 1989.87; EA Anal. Calcd. for $C_{64}H_{110}Cl_2O_{20}Sn_6$ : C : 38.77% ; H : 5.59%, found : C : 38.65% ; H : 5.58%.

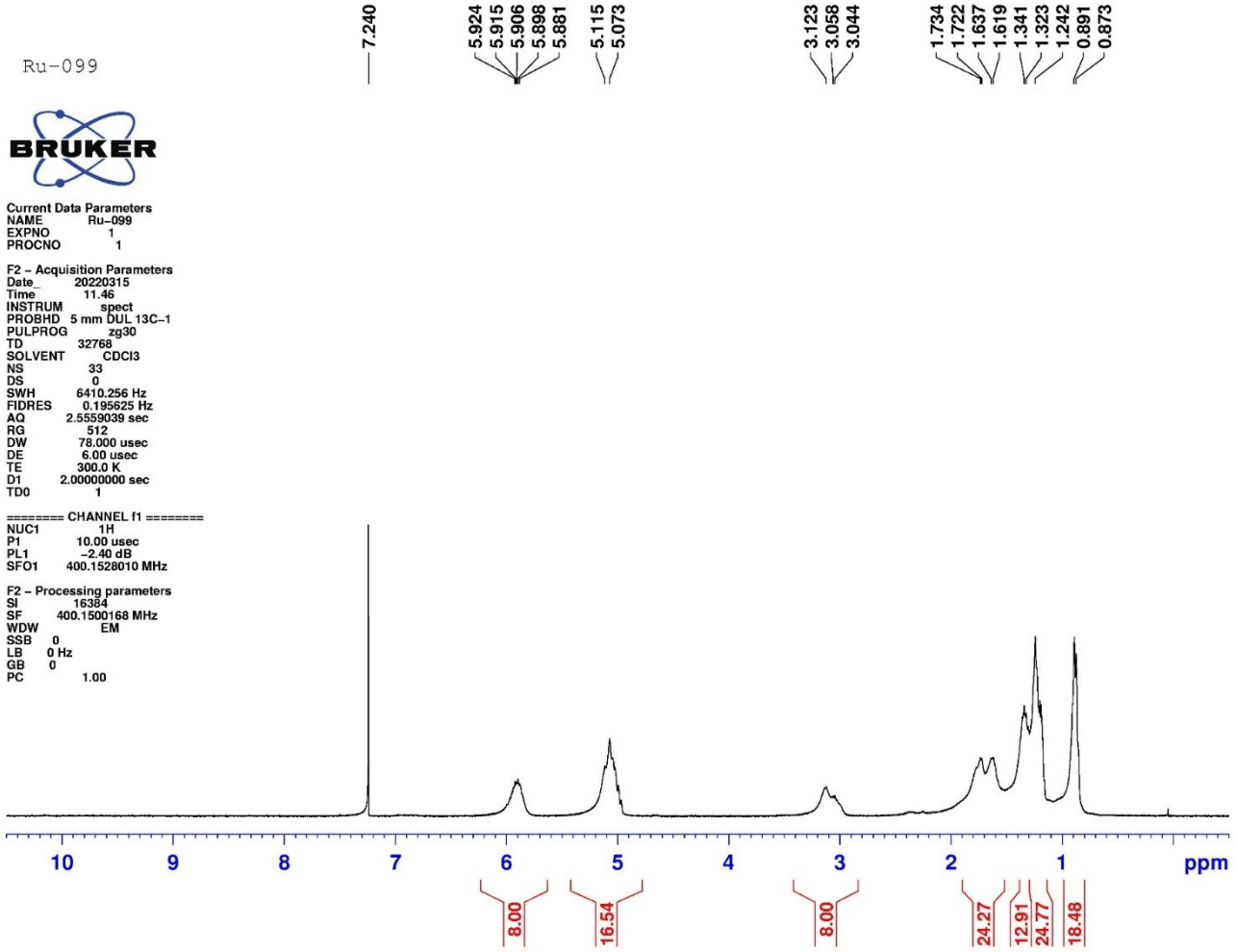
### 5.2 Spectral data for cluster 2 :

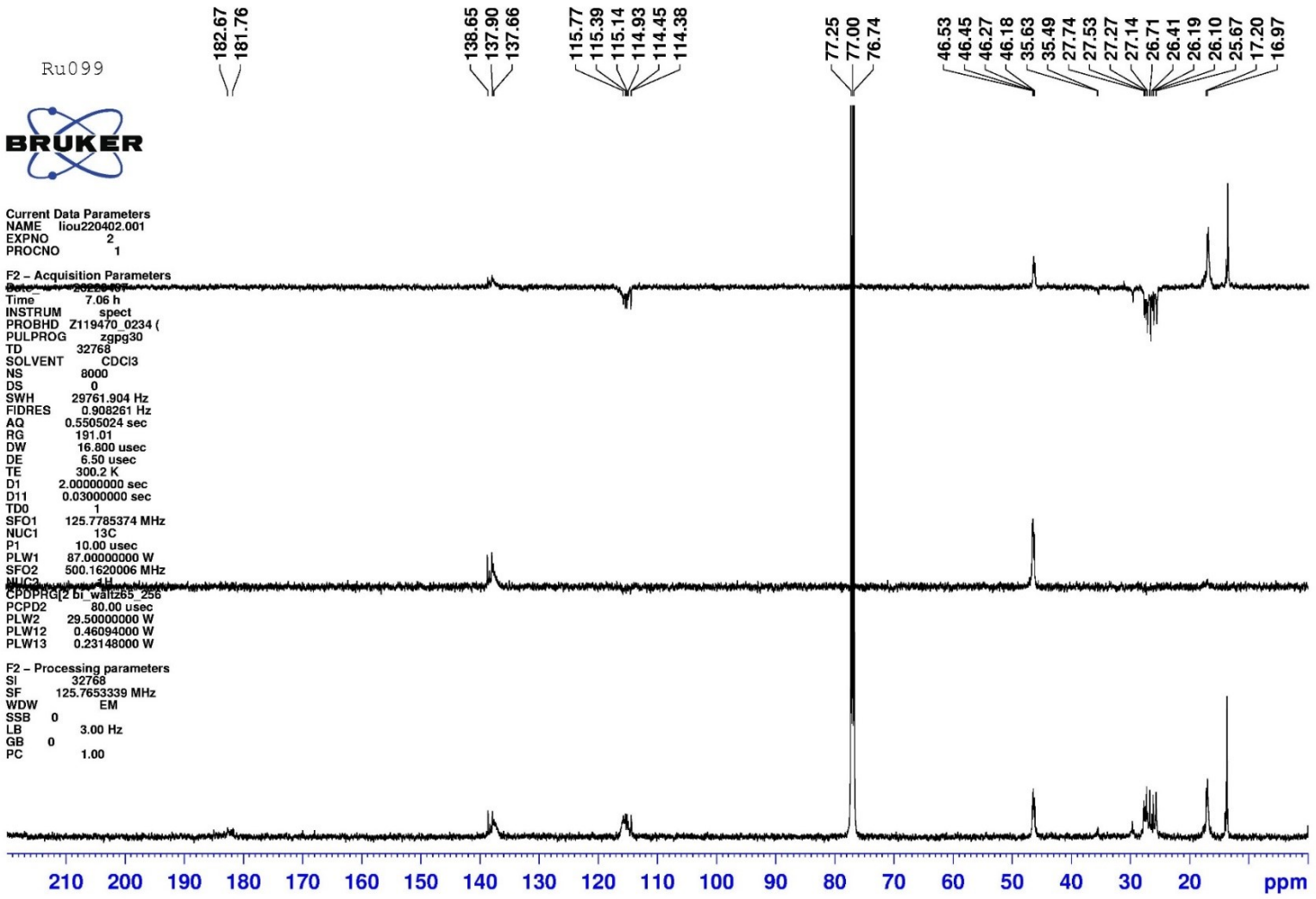
Transparent crystal (65%)；$^{1}$H NMR（500 MHz, $CDCl_3$）：δ 6.22-5.91（m, 18H）, 2.44-2.24（m, 8H）, 1.72-1.35（m, 16H）, 1.17-1.07（m, 24H）, 0.93-0.85（m, 24H）；$^{13}$C NMR（125 MHz, $CDCl_3$）：δ 186.0, 185.4, 185.2, 185.1, 184.6, 184.1, 183.5, 145.2, 141.9, 141.1, 140.8, 139.7, 139.3, 138.7, 138.3, 138.1, 136.3, 135.5, 135.1, 134.5, 133.9, 133.5, 133.0, 132.1, 131.8, 131.2, 123.0, 43.9, 43.8, 43.8, 43.6, 40.5, 27.3, 27.2, 27.1, 26.8, 16.9, 16.8, 16.7, 16.5, 11.7, 11.5；$^{119}$Sn NMR（186 MHz, $CDCl_3$）：δ -183.96, -539.25, -542.63, -547.88. HRMS（ESI+, m/z）Calcd. For $C_{52}H_{90}Cl_2O_{20}Sn_6$ $[M+H]^+$：1823.95, found：1824.75；EA Anal. Calcd. for $C_{52}H_{90}Cl_2O_{20}Sn_6$：C：34.35%；H：4.99%, found：C：34.32%；H：4.94%.

## 6. $^{1}H$ and $^{13}C$ NMR of key compounds

### 6.1 Spectral data for cluster 1

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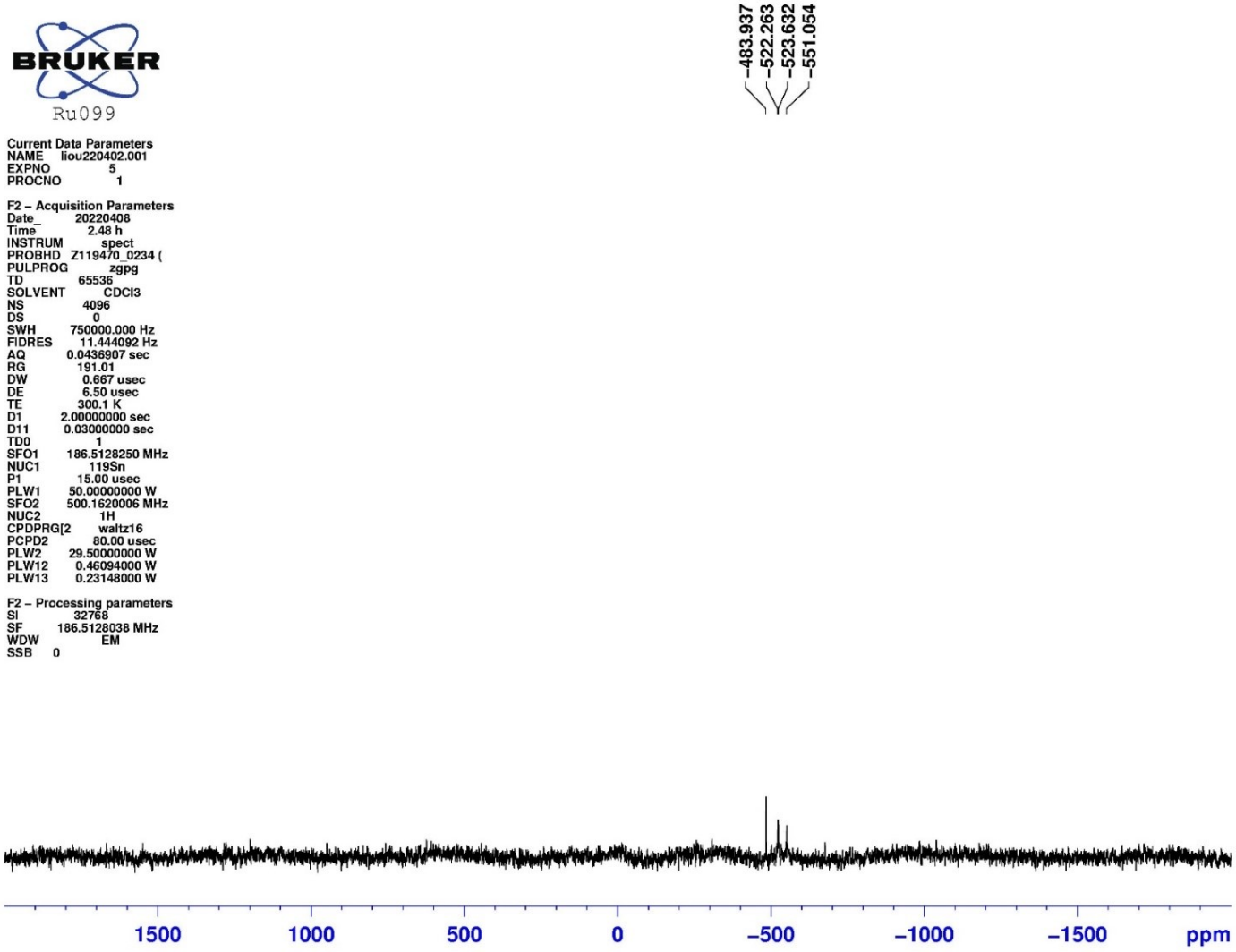


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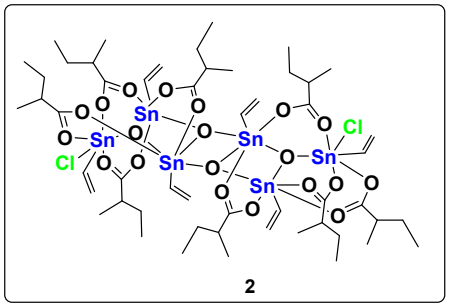
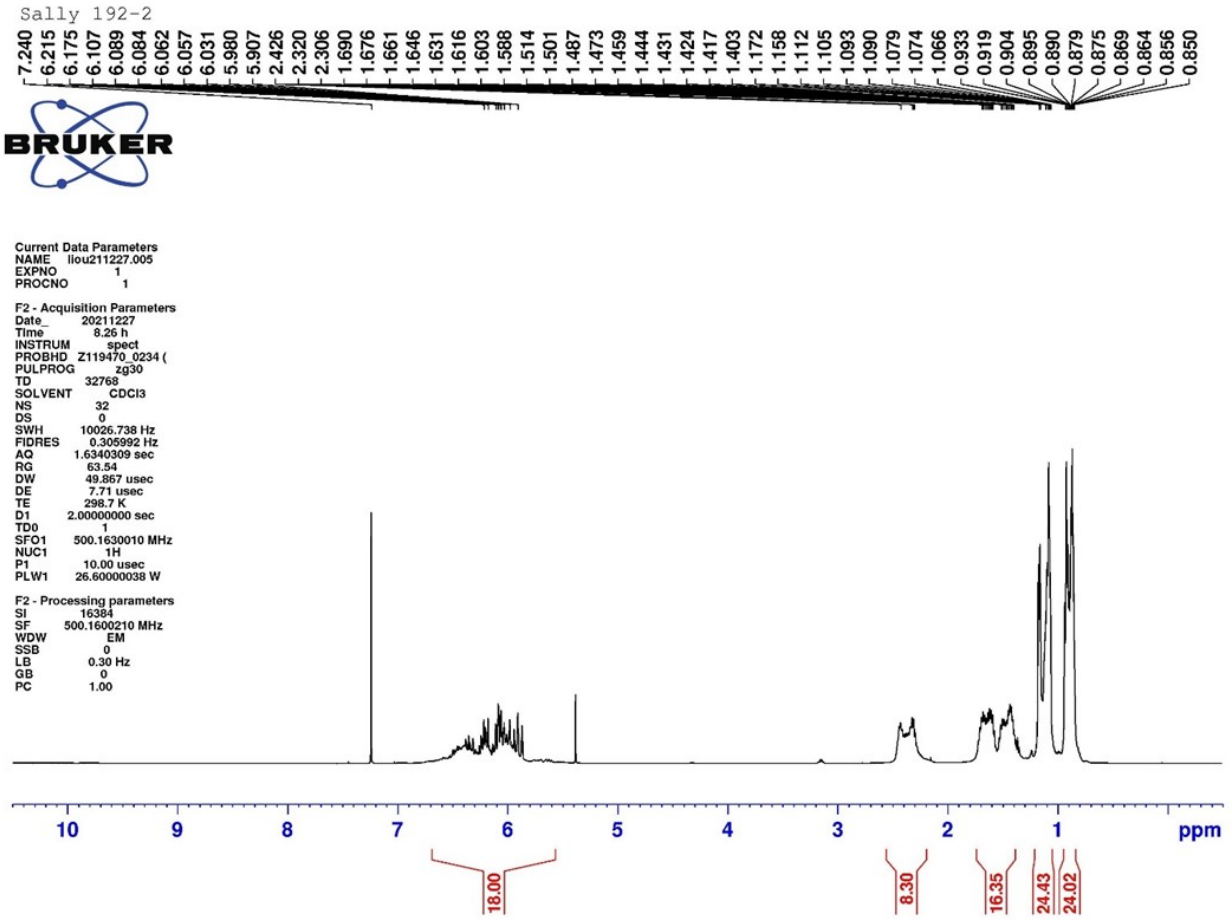
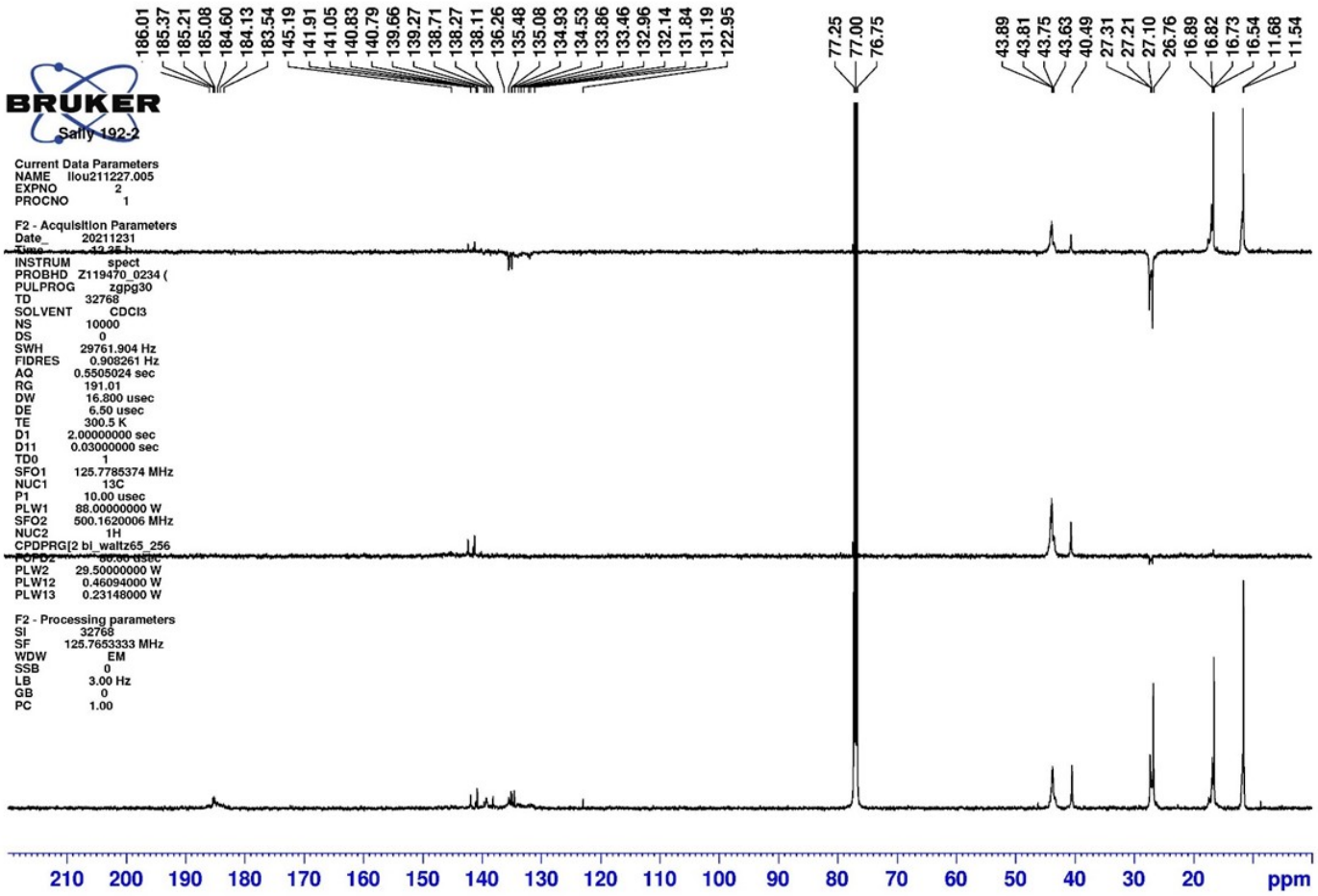
## 6.2 Spectral data for cluster 2

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DE 6.50 usec
TE 300.5 K
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SFO2 500.1620006 MHz
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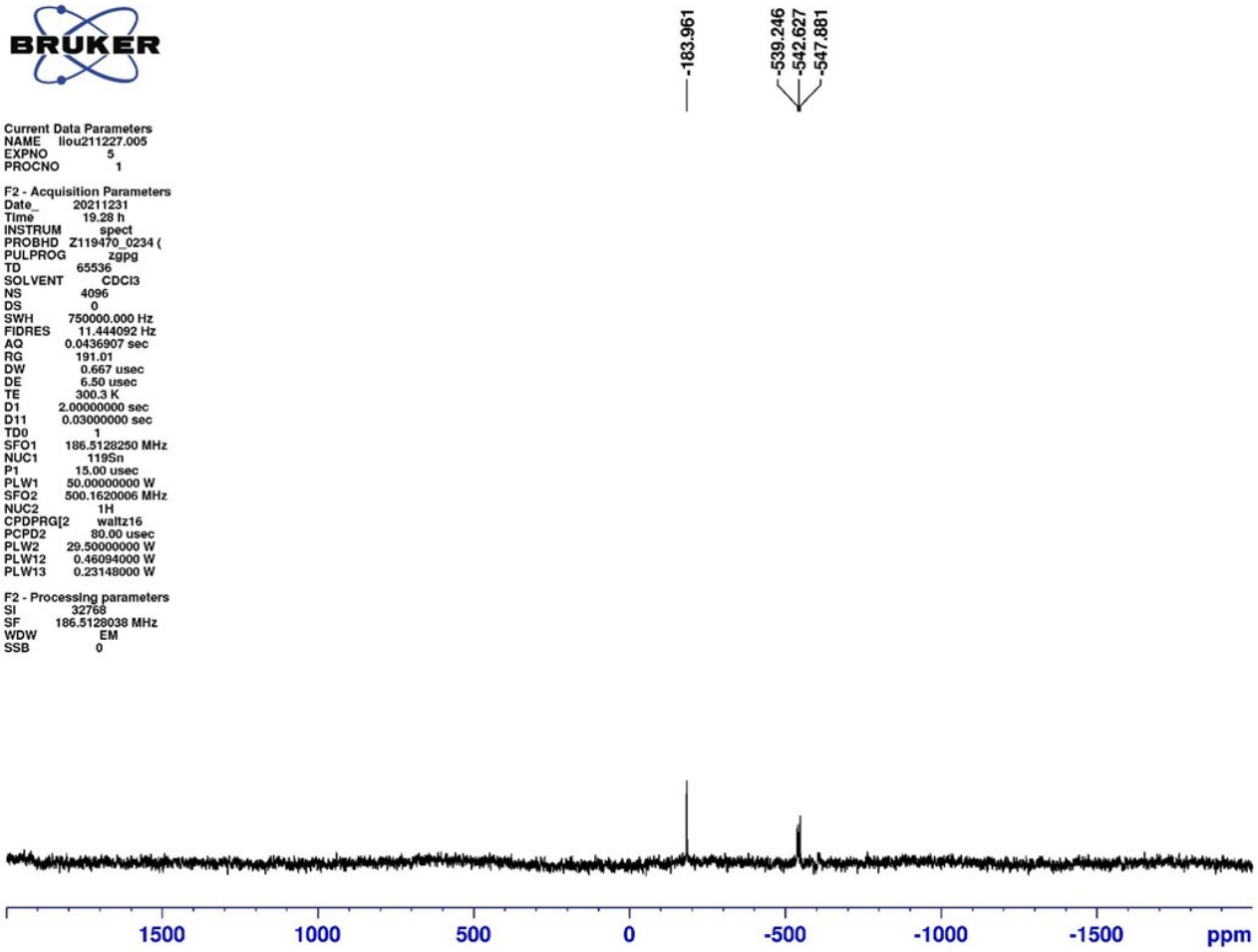
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