

# Supporting Information

## Sodium $\beta$ -diketonate glyme adducts as precursors for fluoride phases: synthesis, characterization and functional validation

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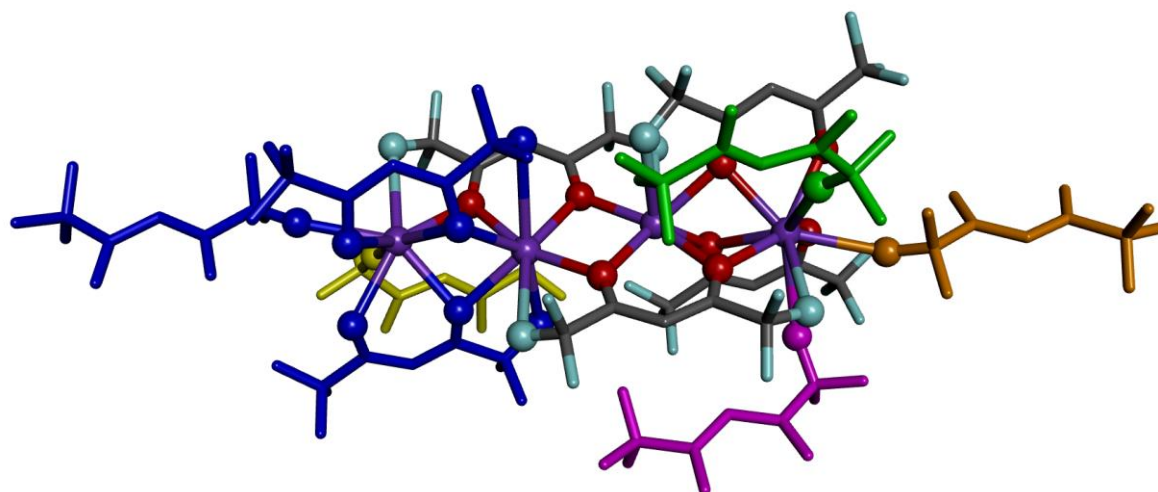
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**Figure S1.** Bridging scheme of the hfa ligand in **1**. For the sake of clarity, hydrogen atoms have been omitted. Legend: orange:  $x, y, z+1$ ; green:  $y, -x+1, -z+1$ ; magenta:  $-y+0.5, x+0.5, -z+1.5$ ; blue:  $x, y, z-1$ ; yellow:  $y-0.5, -x+0.5, -z+0.5$

**Table S1.** Na-X distances in compound **1**.

Na-X	distance (Å)	Symmetry operation
Na1-O1	2.463(8)	
Na1-O2	2.446(8)	
Na1-O3	2.442(8)	
Na1-O4	2.699(8)	
Na1-O5	2.337(8)	
Na1-F14a	2.861(8)	
Na1-F10b	2.844(8)	$-y+1/2, x+1/2, -z+3$
Na1-F15a	2.695(8)	$x, y, z+1$
Na1-F20b	2.742(7)	$y, -x+1, -z+1$
Na2-O2	2.346(8)	
Na2-O4	2.332(8)	
Na2-O5	2.351(8)	
Na2-O6	2.324(8)	
Na2-O7	2.330(8)	
Na2-F5a	2.76(1)	
Na2-F19a	2.864(8)	
Na3-O6	2.335(8)	
Na3-O7	2.346(8)	
Na3-O8	2.330(8)	
Na3-F15a	2.909(8)	
Na3-O1	2.394(8)	$x, y, z-1$
Na3-F4b	3.01(1)	$x, y, z-1$
Na3-F9a	2.682(9)	$x, y, z-1$
Na4-O8	2.323(8)	
Na4-F20a	2.835(8)	
Na4-O1	2.605(8)	$x, y, z-1$
Na4-O2	2.444(8)	$x, y, z-1$
Na4-O3	2.434(8)	$x, y, z-1$
Na4-O4	2.495(8)	$x, y, z-1$
Na4-F14b	2.425(7)	$y-1/2, -x+1/2, -z+1/2$
Na4-F19a	2.661(8)	$x, y, z-1$

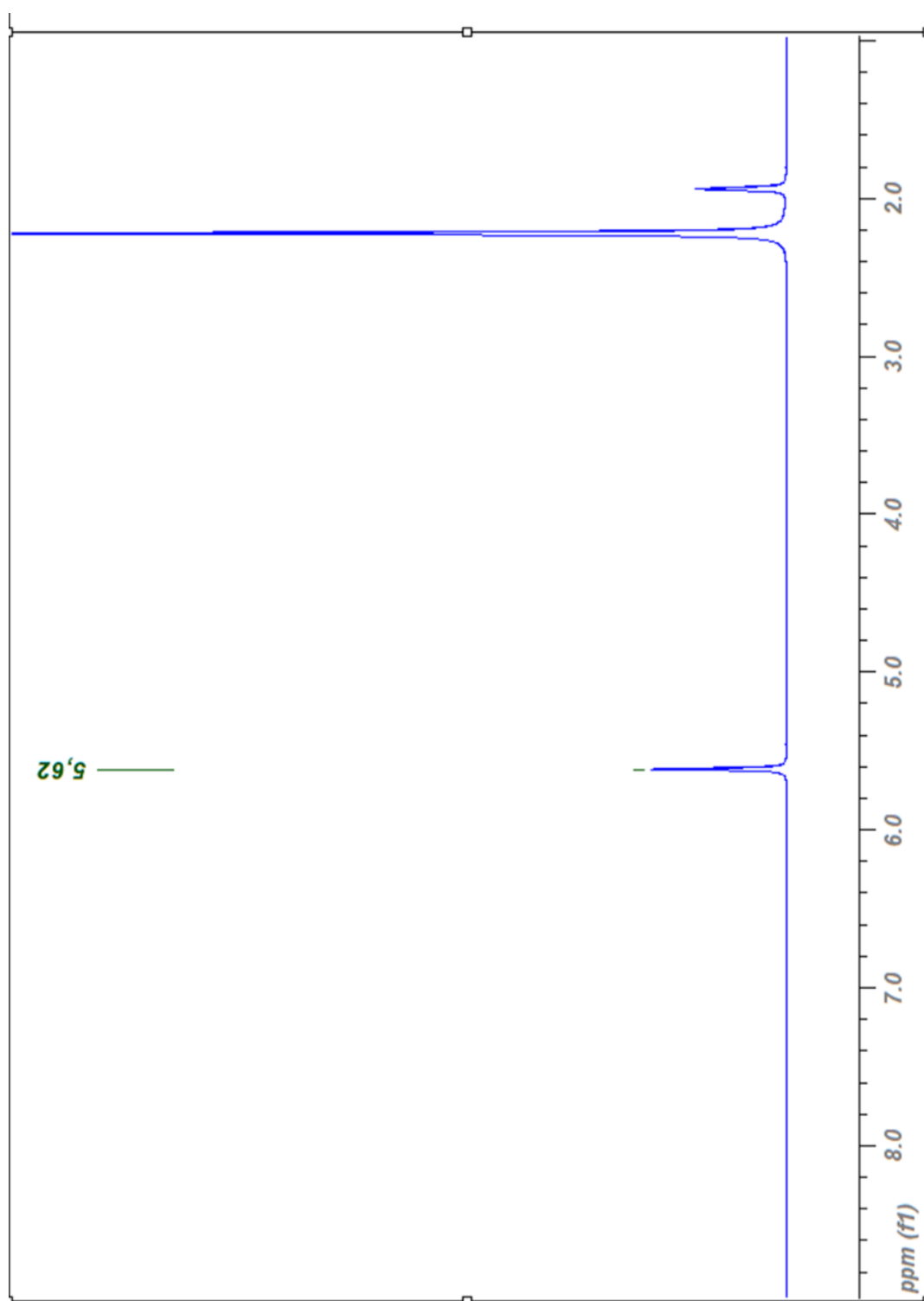
**Table S2.** Selected bond lengths in **2**.

Na-X	distance (Å)
Na1··Na2	3.192(5)
Na2··Na3	3.549(5)
Na3··Na4	3.174(4)
Na1-O1	2.255(7)
Na1-O2	2.364(8)
Na1-O3	2.288(8)
Na1-O4	2.349(6)
Na1-O5	2.306(8)
Na1-F14a	2.945(7)
Na2-O2	2.406(7)
Na2-O4	2.345(8)
Na2-O5	2.370(6)
Na2-O6	2.417(7)
Na2-O7	2.373(6)
Na2-F19a	2.689(6)
Na3-O6	2.343(6)
Na3-O7	2.397(7)
Na3-O8	2.373(6)
Na3-F15a	2.700(7)
Na3-O9	2.355(7)
Na3-O11	2.342(8)
Na4-O8	2.310(7)
Na4-O9	2.351(8)
Na4-O10	2.272(7)
Na4-O11	2.346(6)
Na4-O12	2.274(9)
Na5-O13	2.407(8)
Na5-O14	2.386(7)
Na5-O15	2.393(8)
Na5-O16	2.378(9)
Na5-O17	2.401(8)

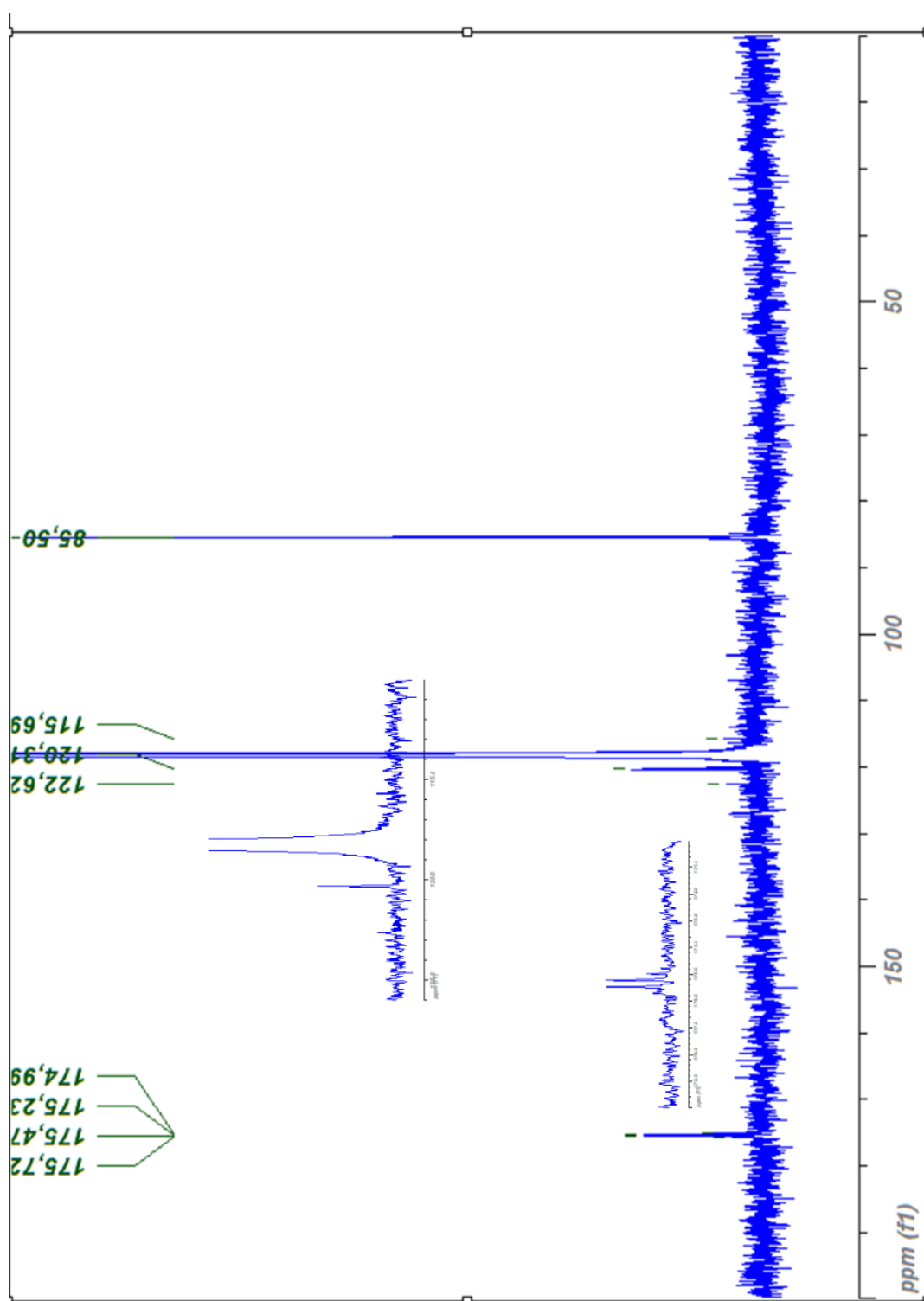
Na5-O18	2.382(7)
Na6-O19	2.401(7)
Na6-O20	2.371(8)
Na6-O21	2.377(6)
Na6-O22	2.373(9)
Na6-O23	2.409(7)
Na6-O24	2.357(8)

**Table S3.** Crystallographic data and refinement parameters for **1** and **2**.

	<b>1</b>	<b>2</b>
Empirical formula	[Na(hfa)] <sub>n</sub>	[Na <sub>4</sub> (hfa) <sub>6</sub> ] <sup>2-</sup> •2[Na(diglyme) <sub>2</sub> ] <sup>+</sup>
Formula weight	230.05	1916.97
Temperature (K)	100	100
Wavelength (Å)	1.54184	1.54184
Crystal system, space group	tetrahedral, I-4	Triclinic, P-1
Unit cell dimensions (Å, °)	a = 24.4916(7) b = 24.4916(7) c = 9.8714(3)	a = 11.460(1) α = 83.860(4) b = 17.019(1) β = 87.651(5) c = 21.816(2) γ = 71.840(4)
Volume (Å <sup>3</sup> )	5921(2)	4019.6(6)
Z, D <sub>c</sub> (mg/cm <sup>3</sup> )	8, 2.064	2, 1.584
μ (mm <sup>-1</sup> )	2.803	1.839
F(000)	3584	1936
θ range (°)	2.551-68.403	2.037-68.696
Reflections collected / unique	18361 / 5247	100935 / 14654
Data / parameters	5247 / 505	14654 / 1082
Goodness-of-fit on F <sup>2</sup>	0.993	1.927
Final R indices [I>2σ(I)]	R1 = 0.0821, wR2 = 0.2238	R1 = 0.1584, wR2 = 0.4446
R indices (all data)	R1 = 0.1087, wR2 = 0.2541	R1 = 0.1751, wR2 = 0.4627

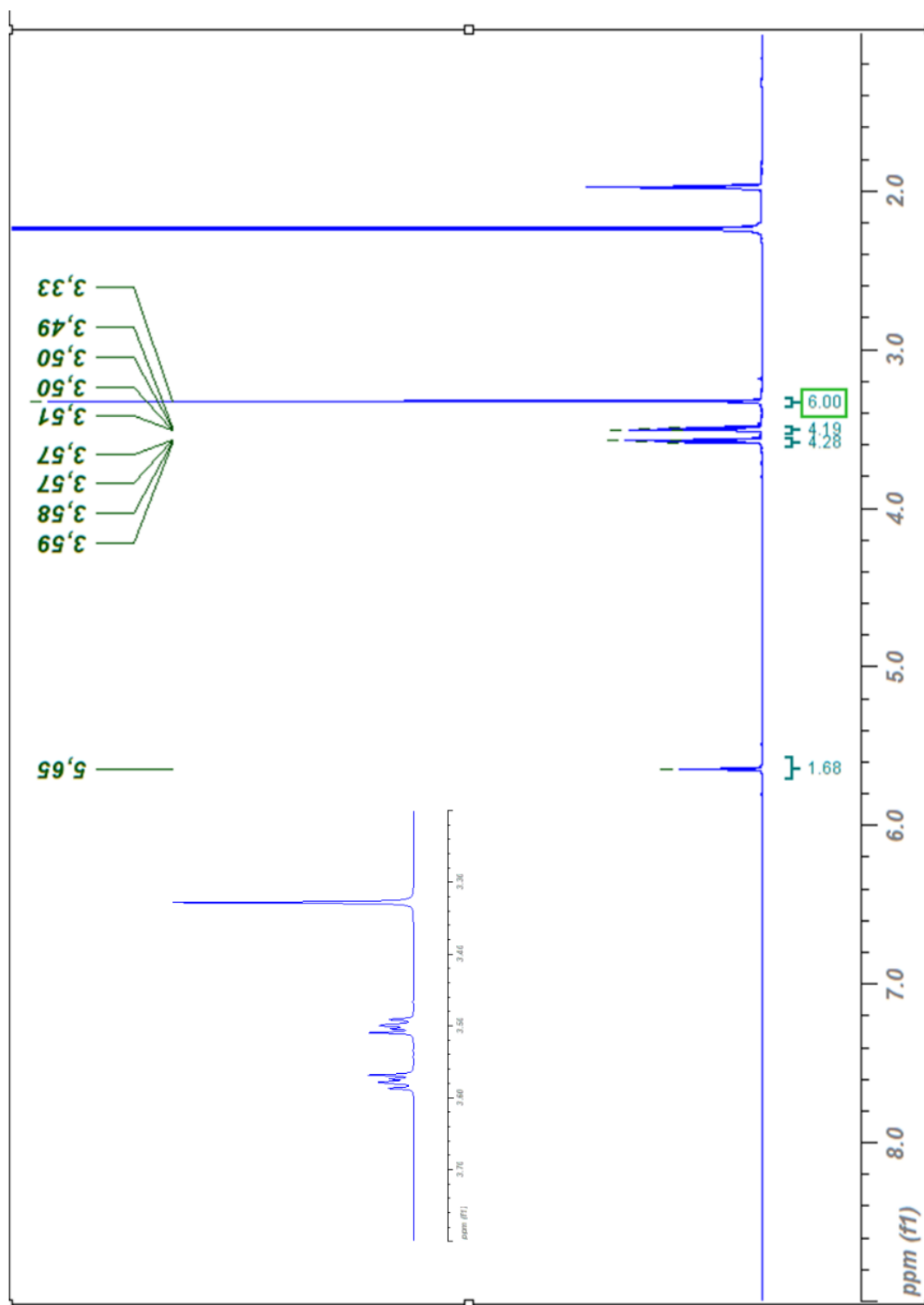


**Figure S2.**  $^1\text{H}$ -NMR spectrum of **1** ( $\text{CD}_3\text{CN}$ , 500 MHz, 27 °C)

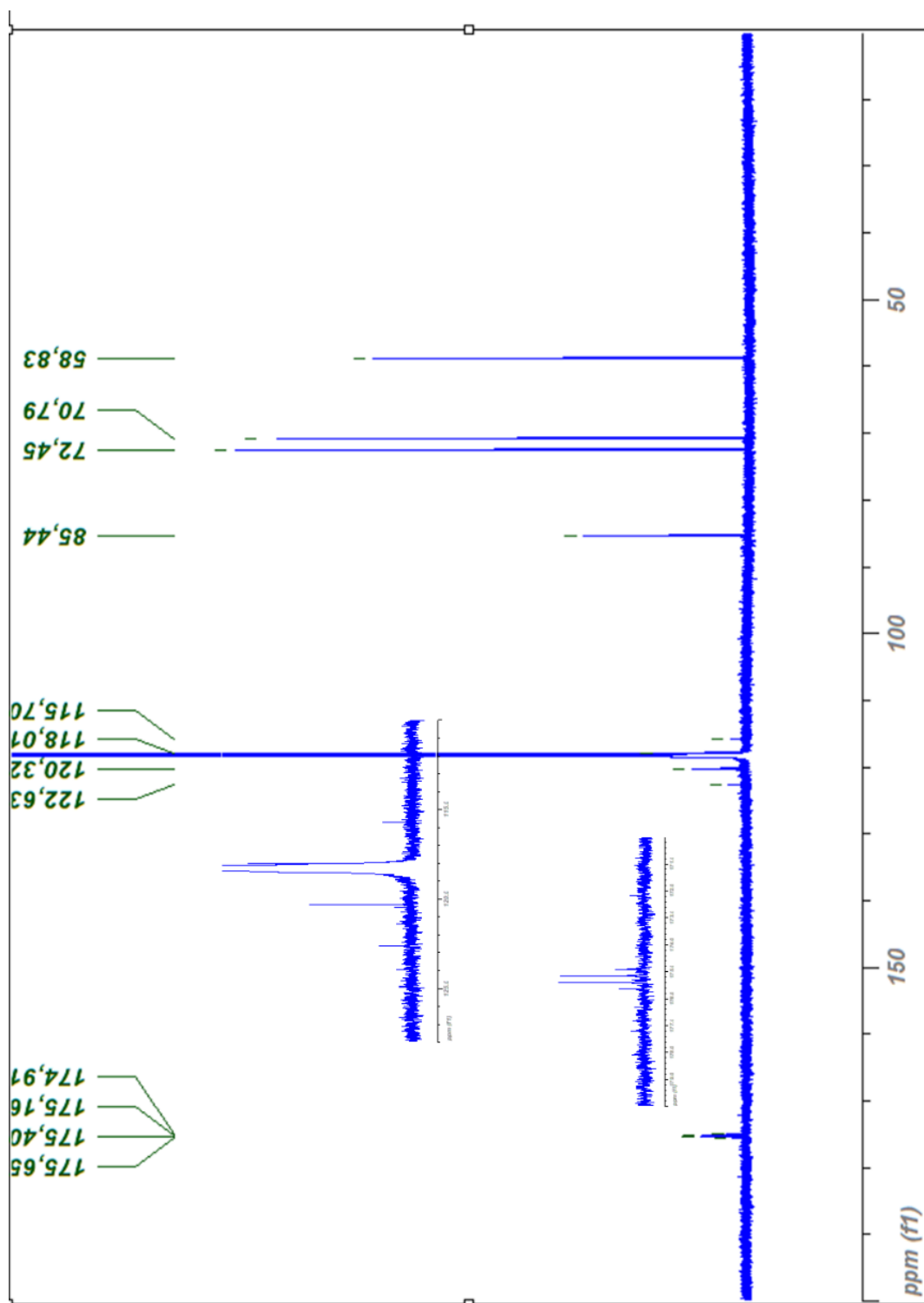


**Figure S3.**  $^{13}\text{C}$ -NMR spectrum of **1** ( $\text{CD}_3\text{CN}$ , 125 MHz, 27 °C)

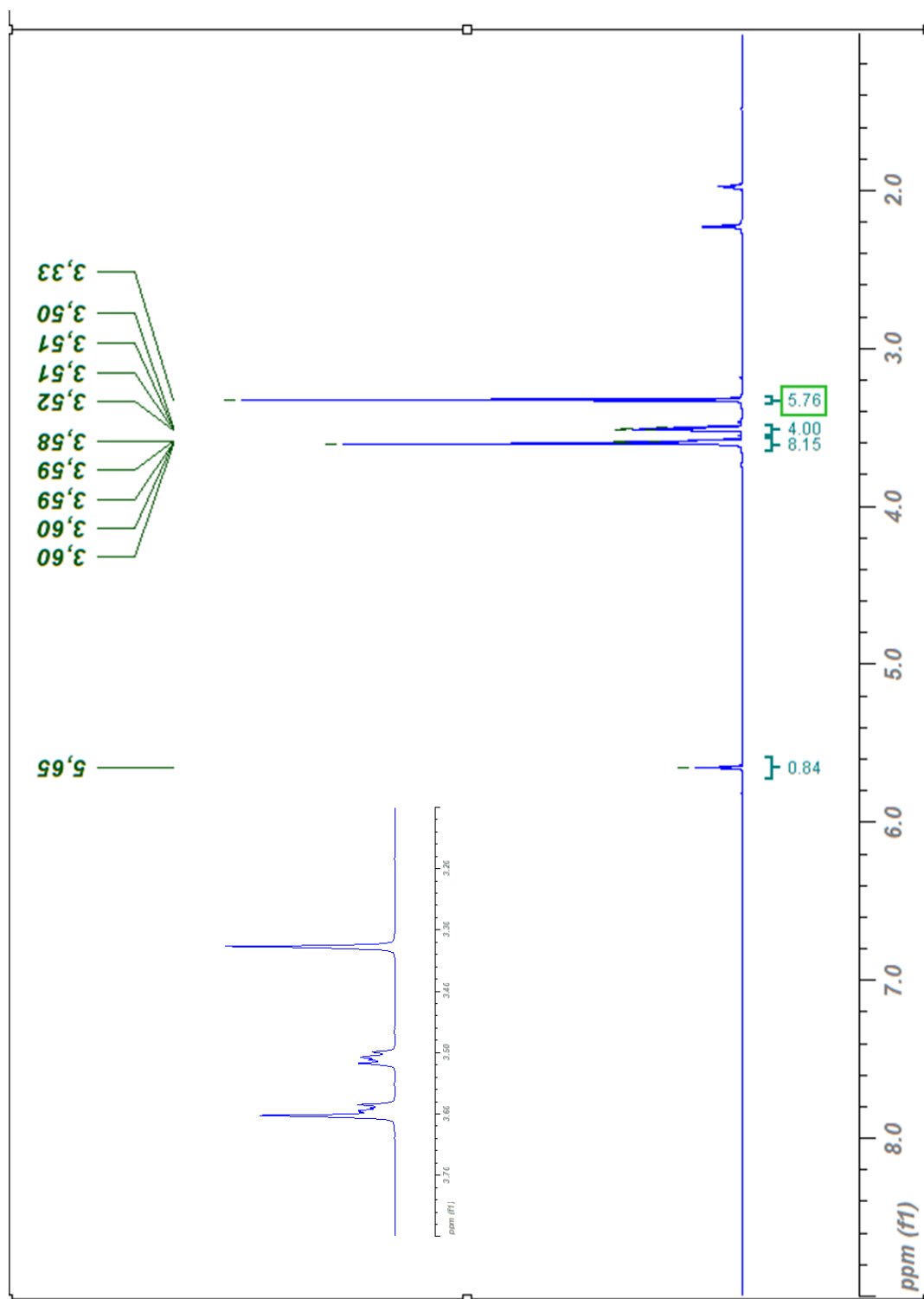




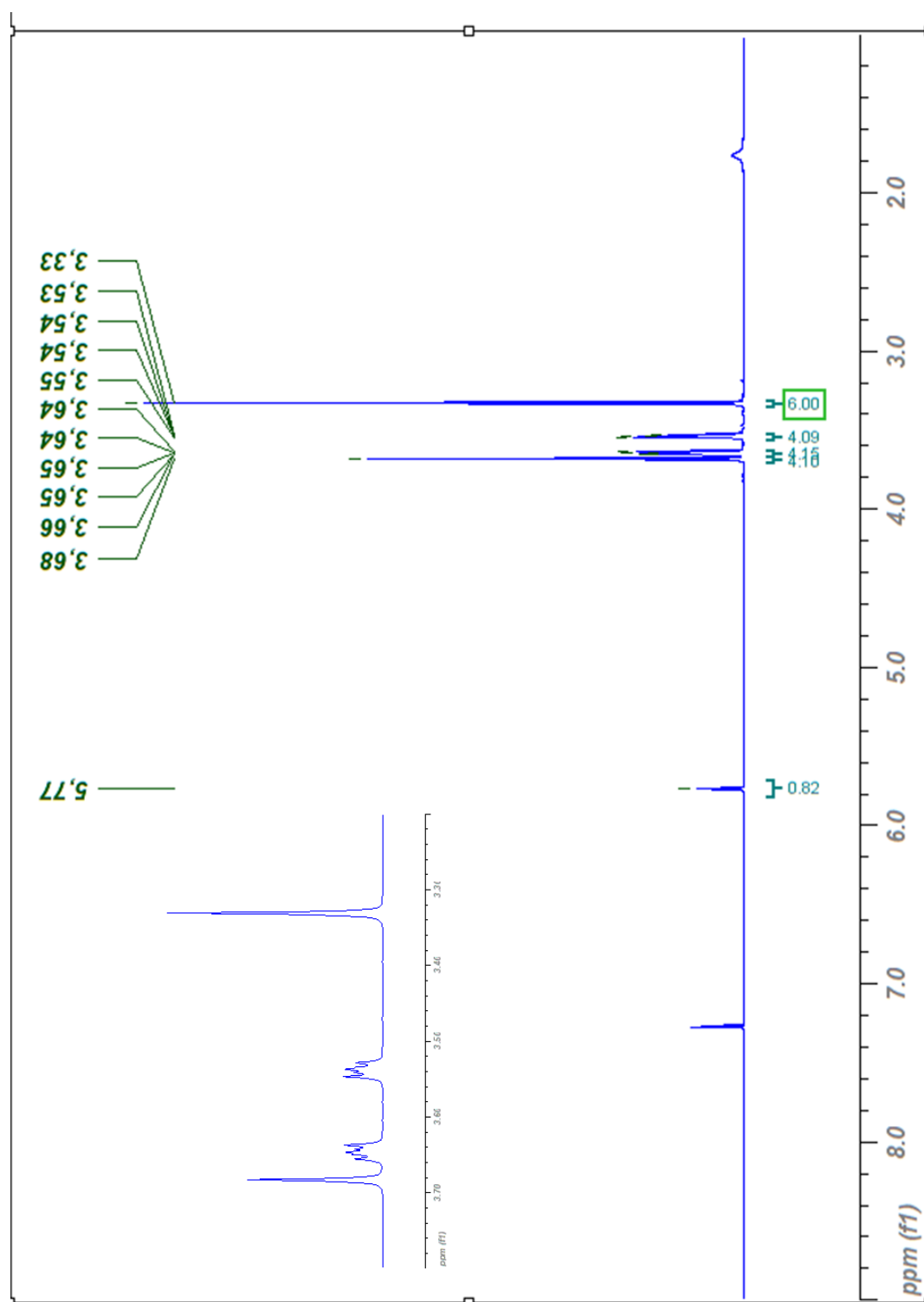
**Figure. S4.**  $^1\text{H}$ -NMR spectrum of **2** ( $\text{CD}_3\text{CN}$ , 500 MHz, 27 °C)



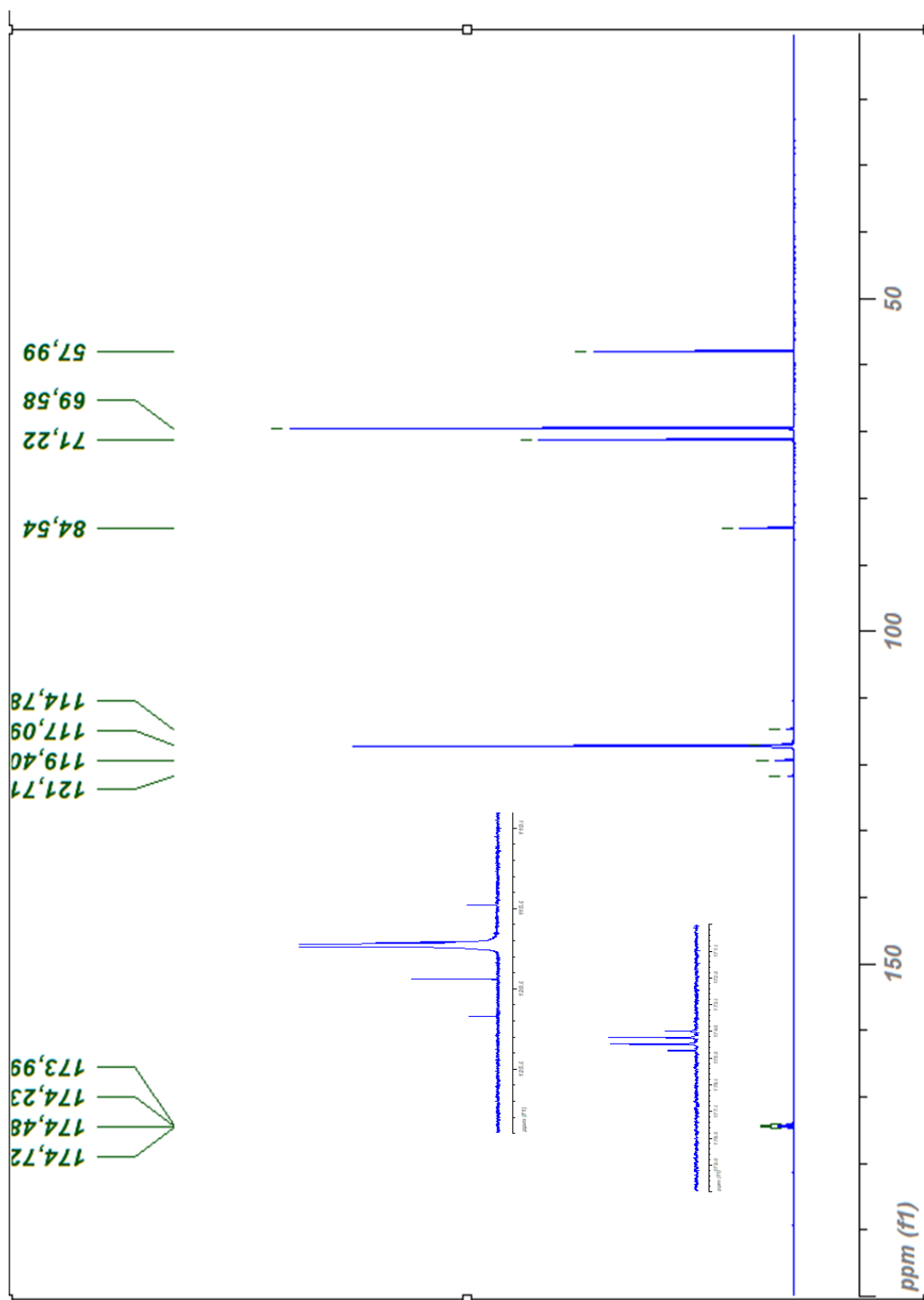
**Figure S5.**  $^{13}\text{C}$ -NMR spectrum of **2** ( $\text{CD}_3\text{CN}$ , 125 MHz, 27 °C)



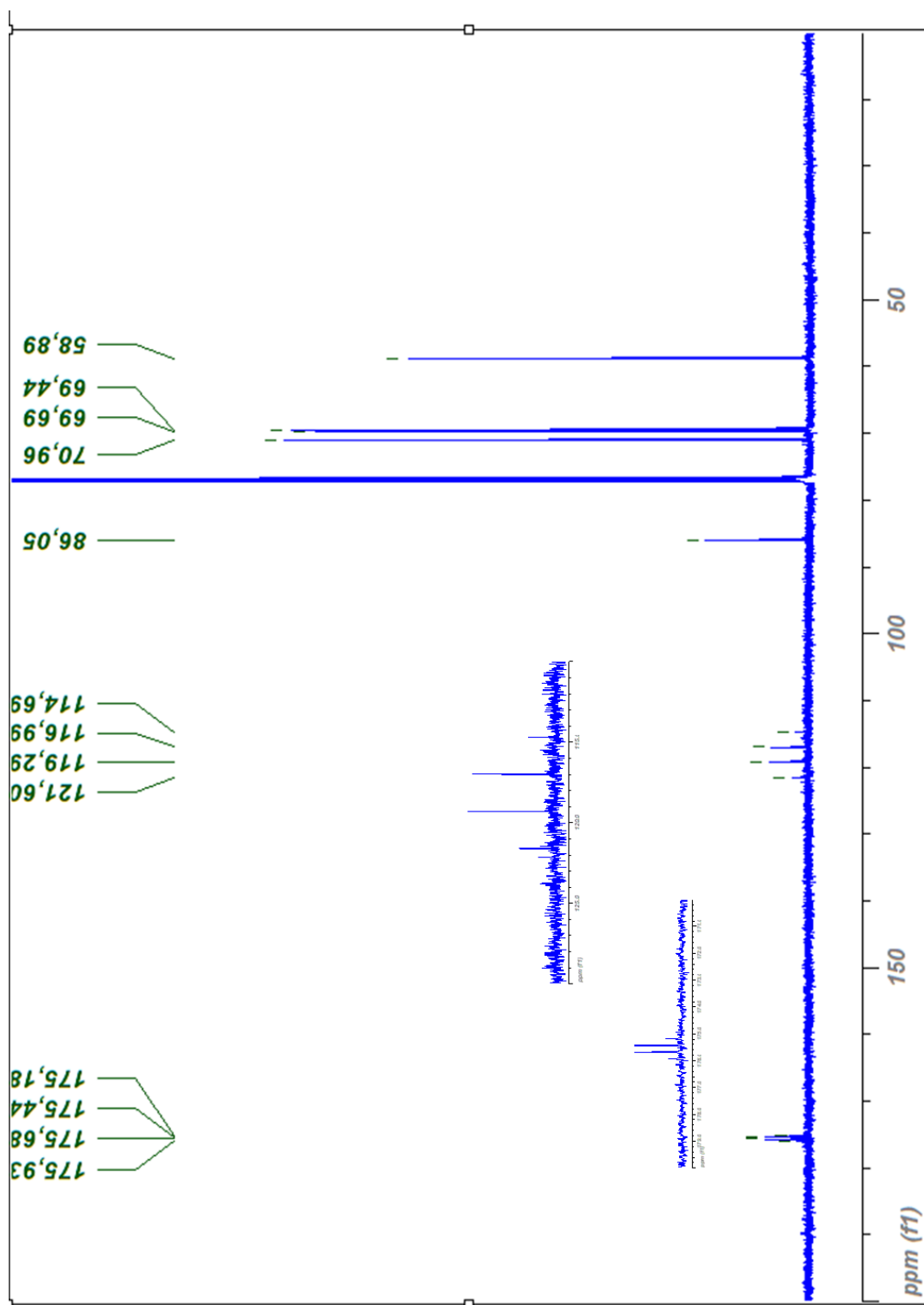
**Figure. S6.**  $^1\text{H}$ -NMR spectrum of **3** ( $\text{CD}_3\text{CN}$ , 500 MHz, 27 °C)



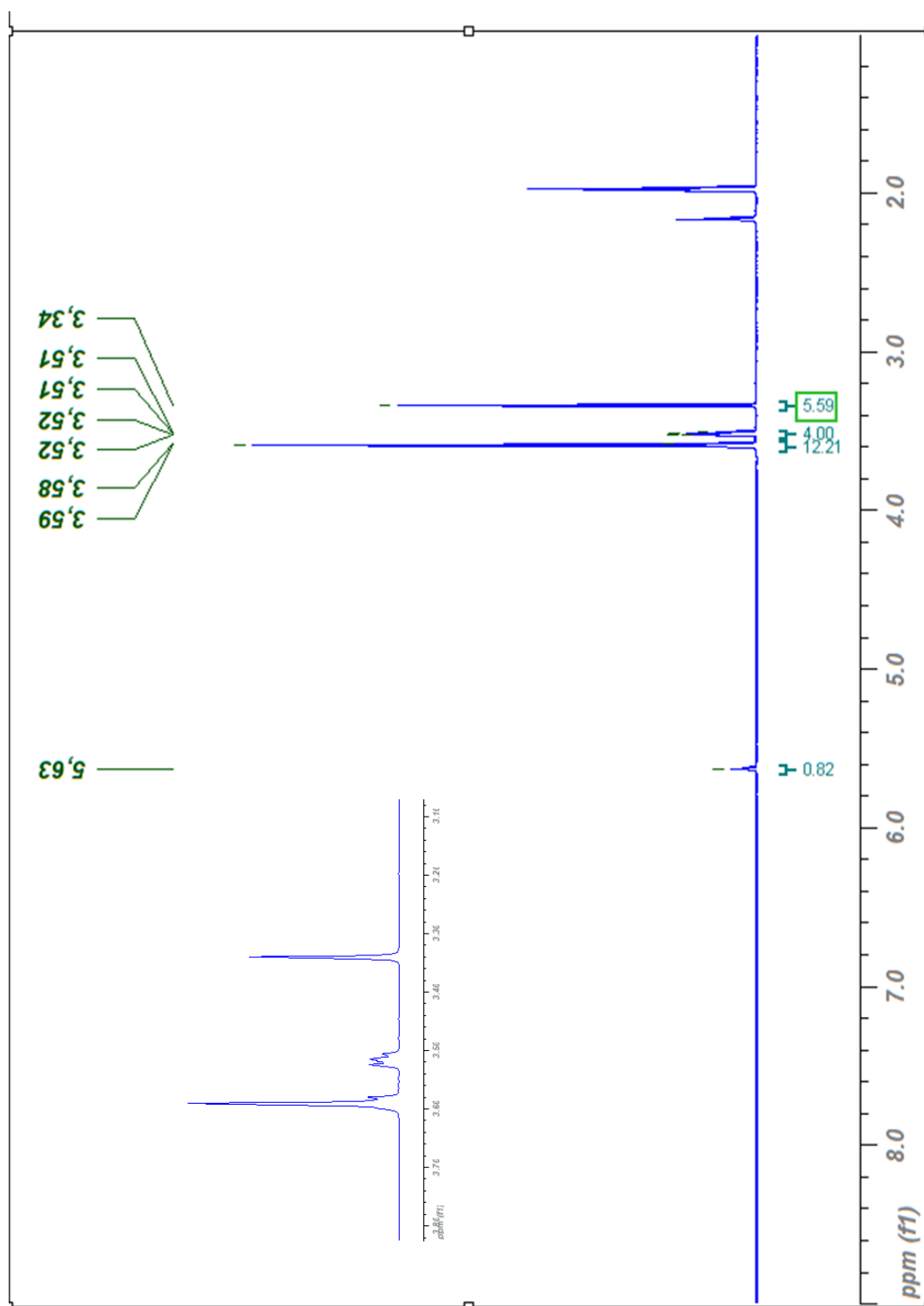
**Figure. S7.**  $^1\text{H}$ -NMR spectrum of **3** ( $\text{CDCl}_3$ , 500 MHz, 27 °C)



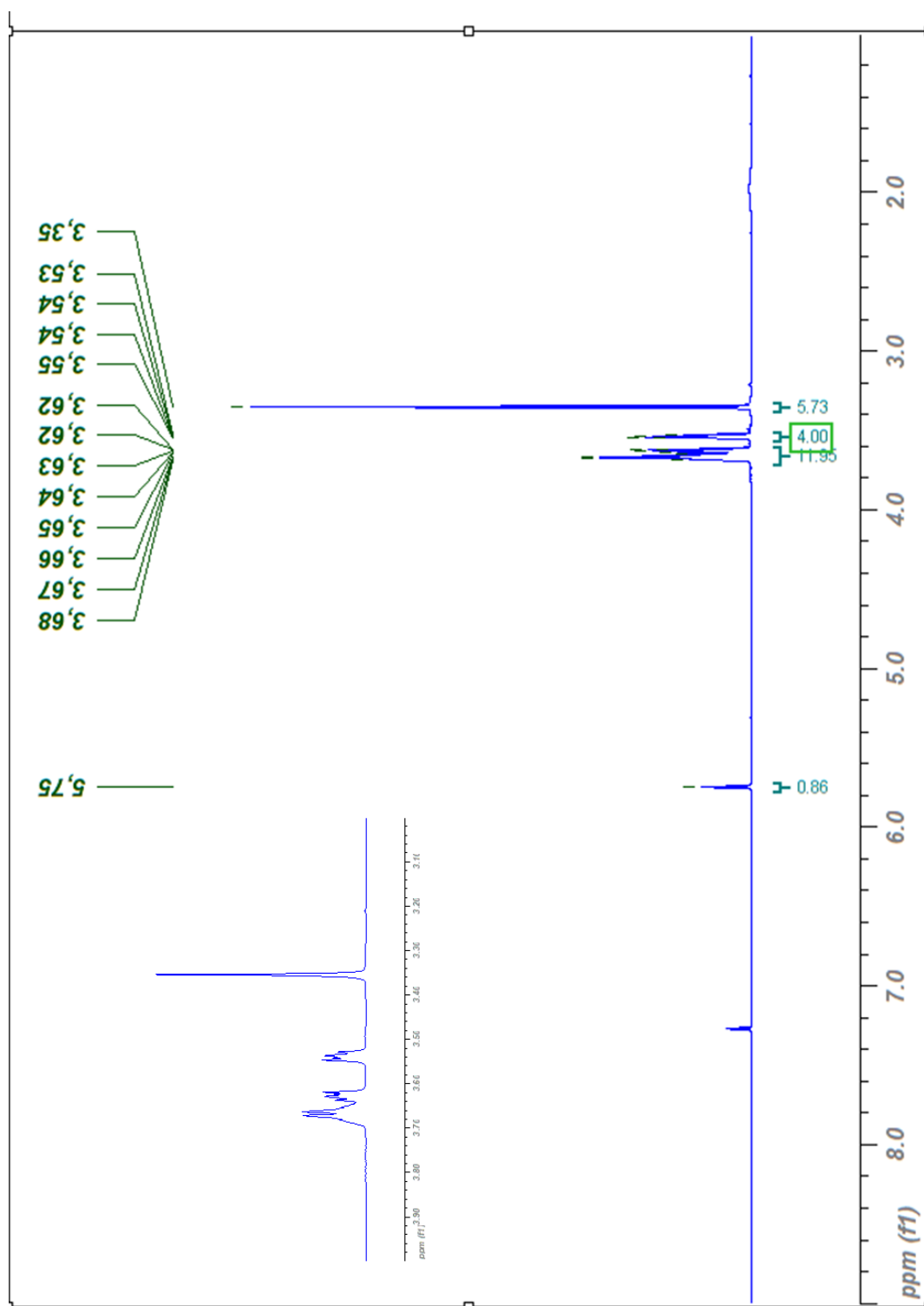
**Figure. S8.** <sup>13</sup>C-NMR spectrum of **3** (CD<sub>3</sub>CN, 125 MHz, 27 °C)



**Figure. S9.** <sup>13</sup>C-NMR spectrum of **3** (CDCl<sub>3</sub>, 125 MHz, 27 °C)

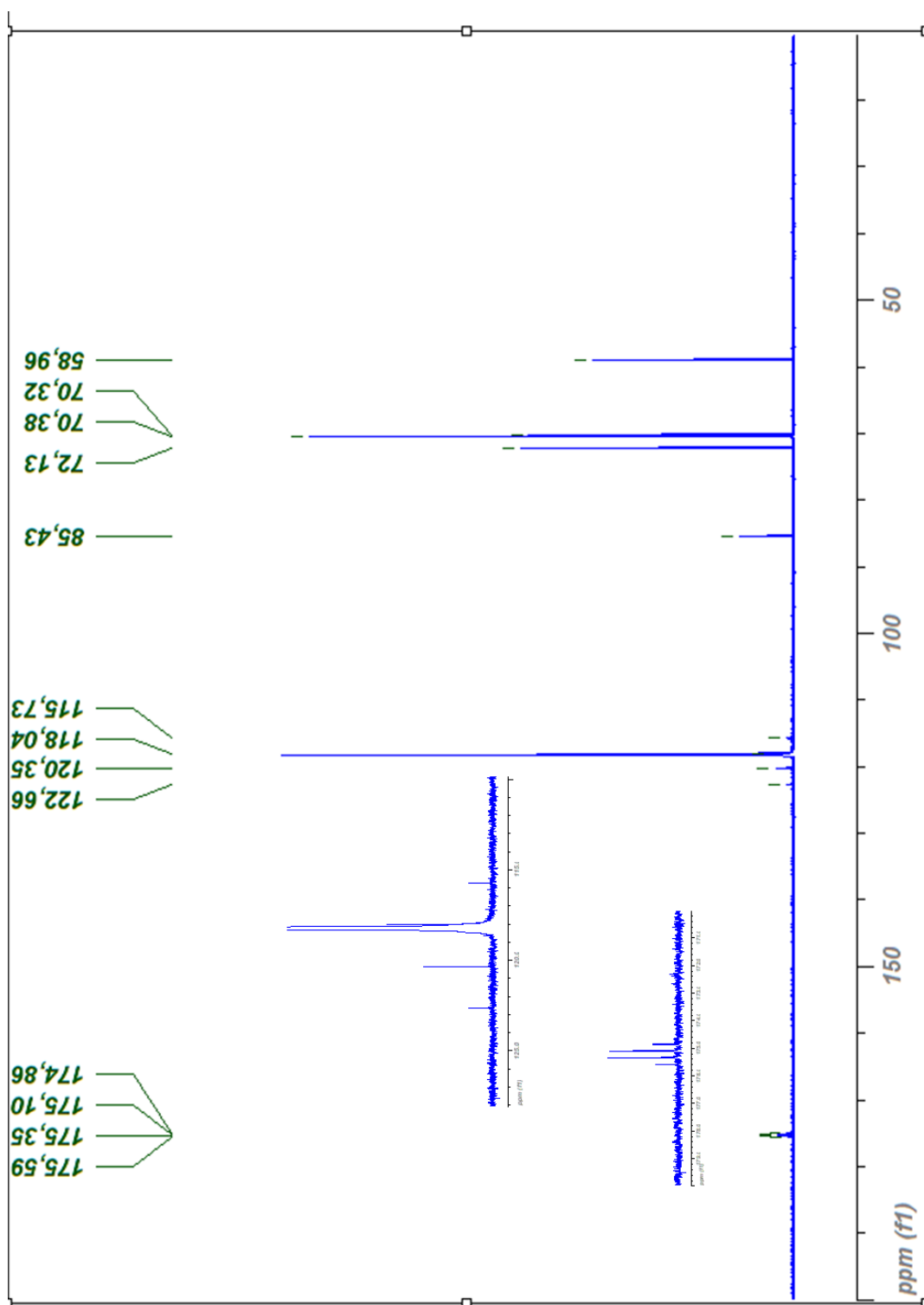


**Figure. S10.**  $^1\text{H}$ -NMR spectrum of **4** ( $\text{CD}_3\text{CN}$ , 500 MHz, 27 °C)

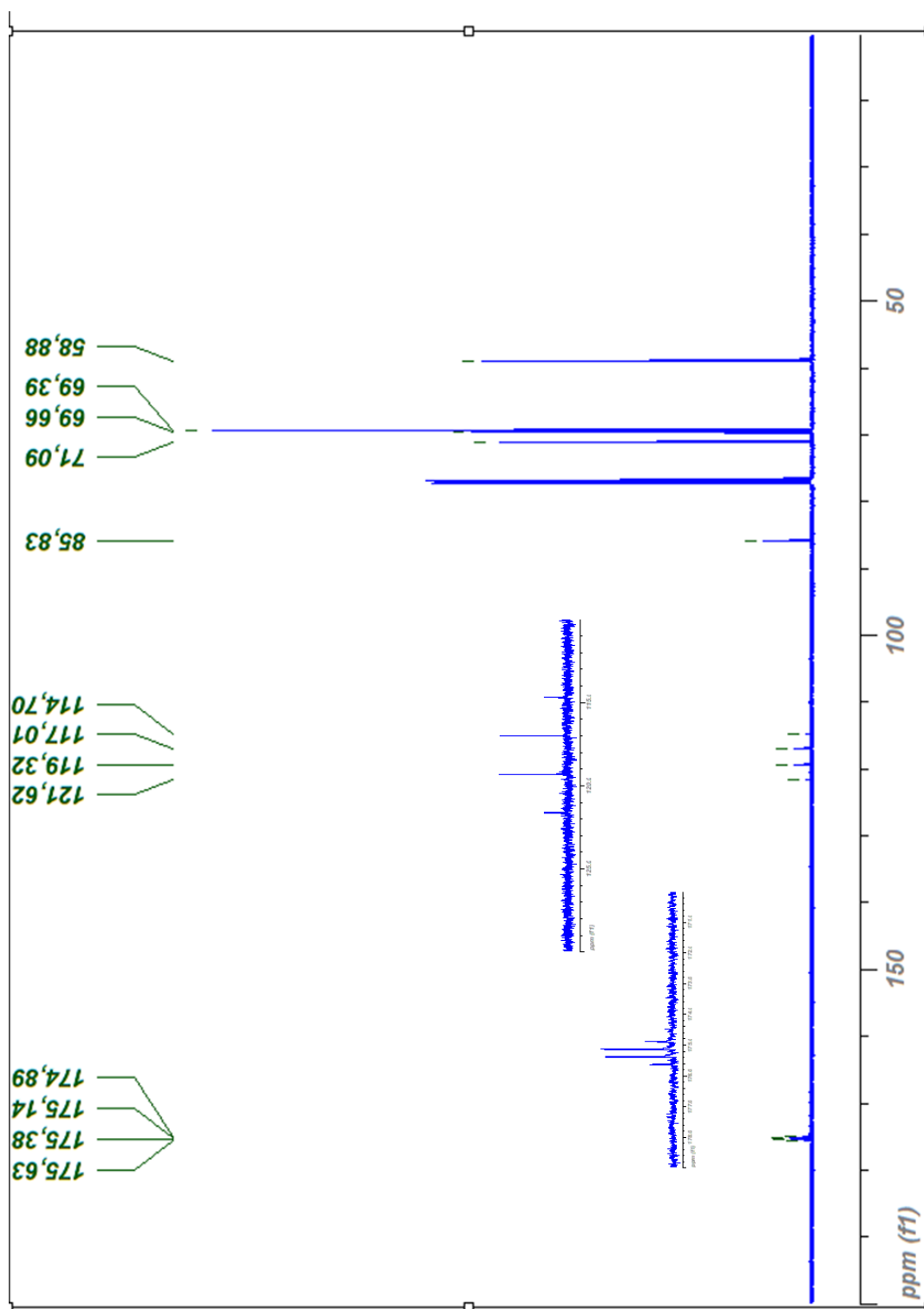


**Figure. S11.**  $^1\text{H}$ -NMR spectrum of **4** ( $\text{CDCl}_3$ , 500 MHz, 27 °C)

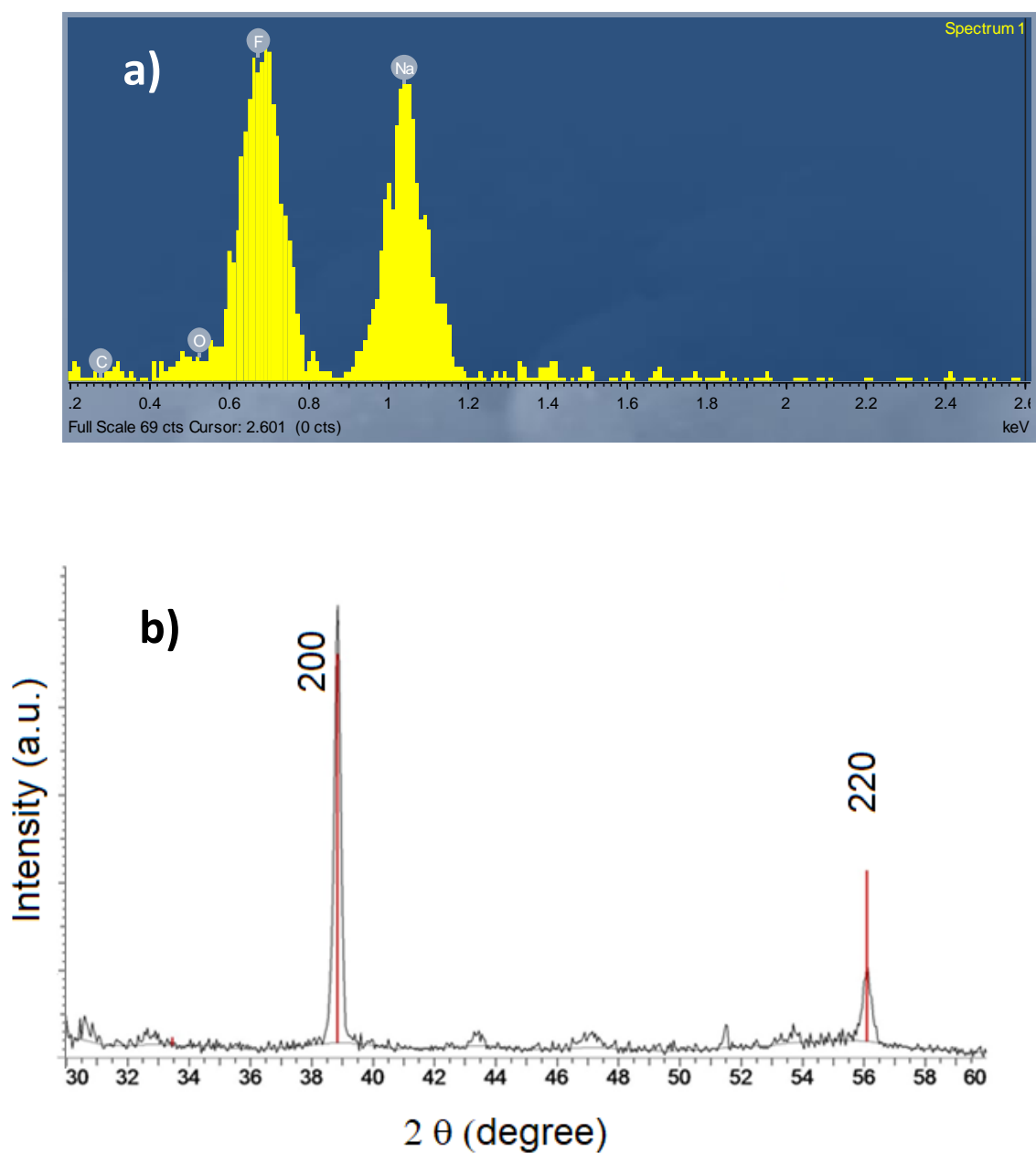




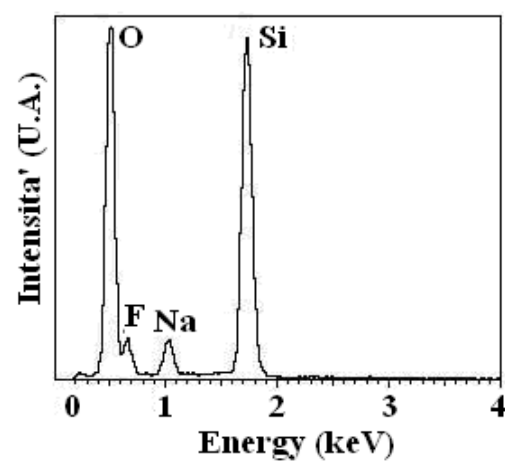
**Figure. S12.** <sup>13</sup>C-NMR spectrum of **4** (CD<sub>3</sub>CN, 125 MHz, 27 °C)



**Figure S13.** <sup>13</sup>C-NMR spectrum of **4** (CDCl<sub>3</sub>, 125 MHz, 27 °C)



**Figure S14.** a) EDX spectrum of the TGA residue of the adduct **2**; b) XRD pattern of the powder obtained after treatment at 350 °C of the adduct **2**.



**Figure S15.** EDX spectrum of the NaF nanocubes deposited through MOCVD.