

## **Heteroleptic six-coordinate bismuth(III) complexes with 2-acetylthiophene thiosemicarbazones: synthesis, characterization, and biological properties**

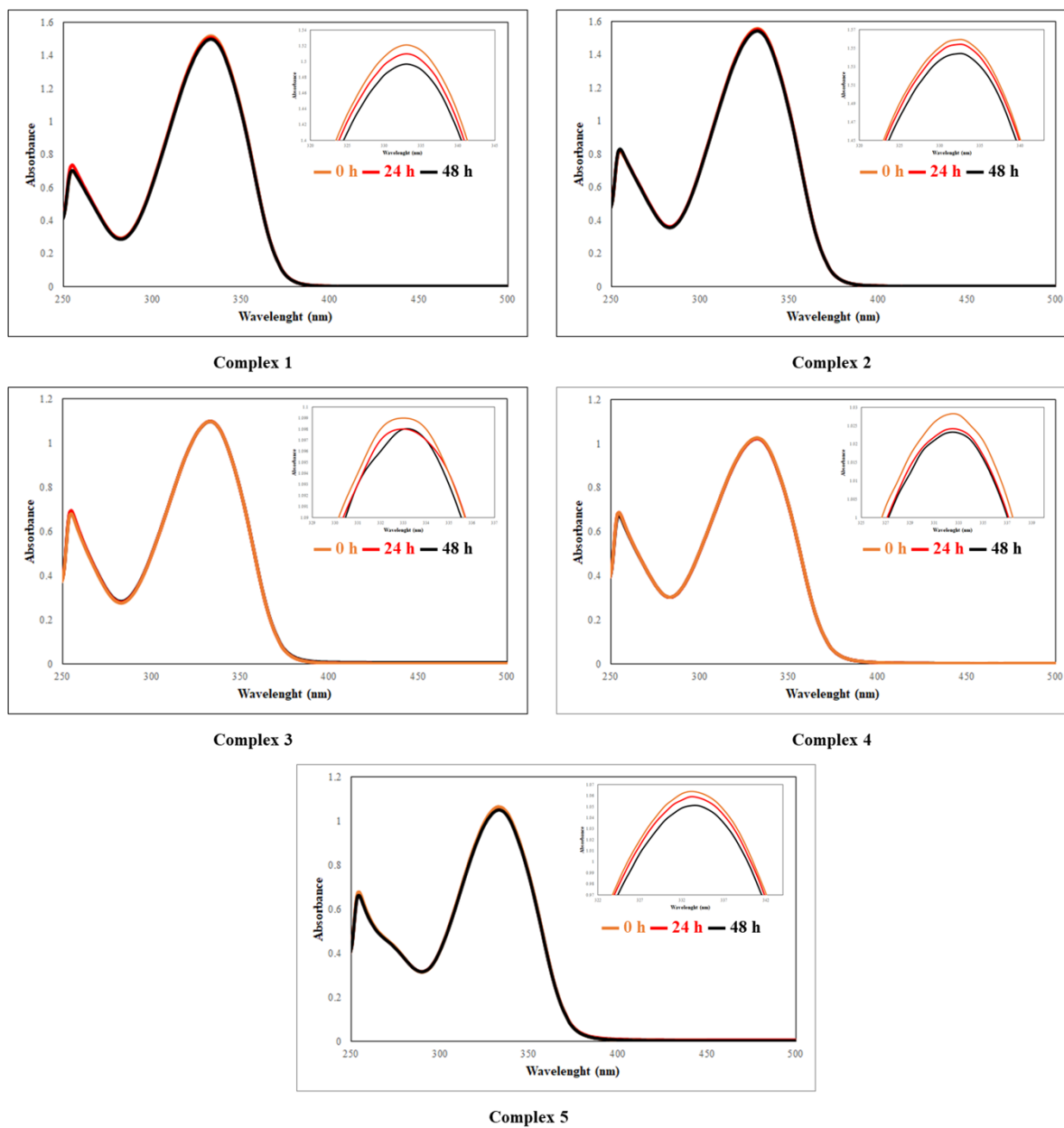
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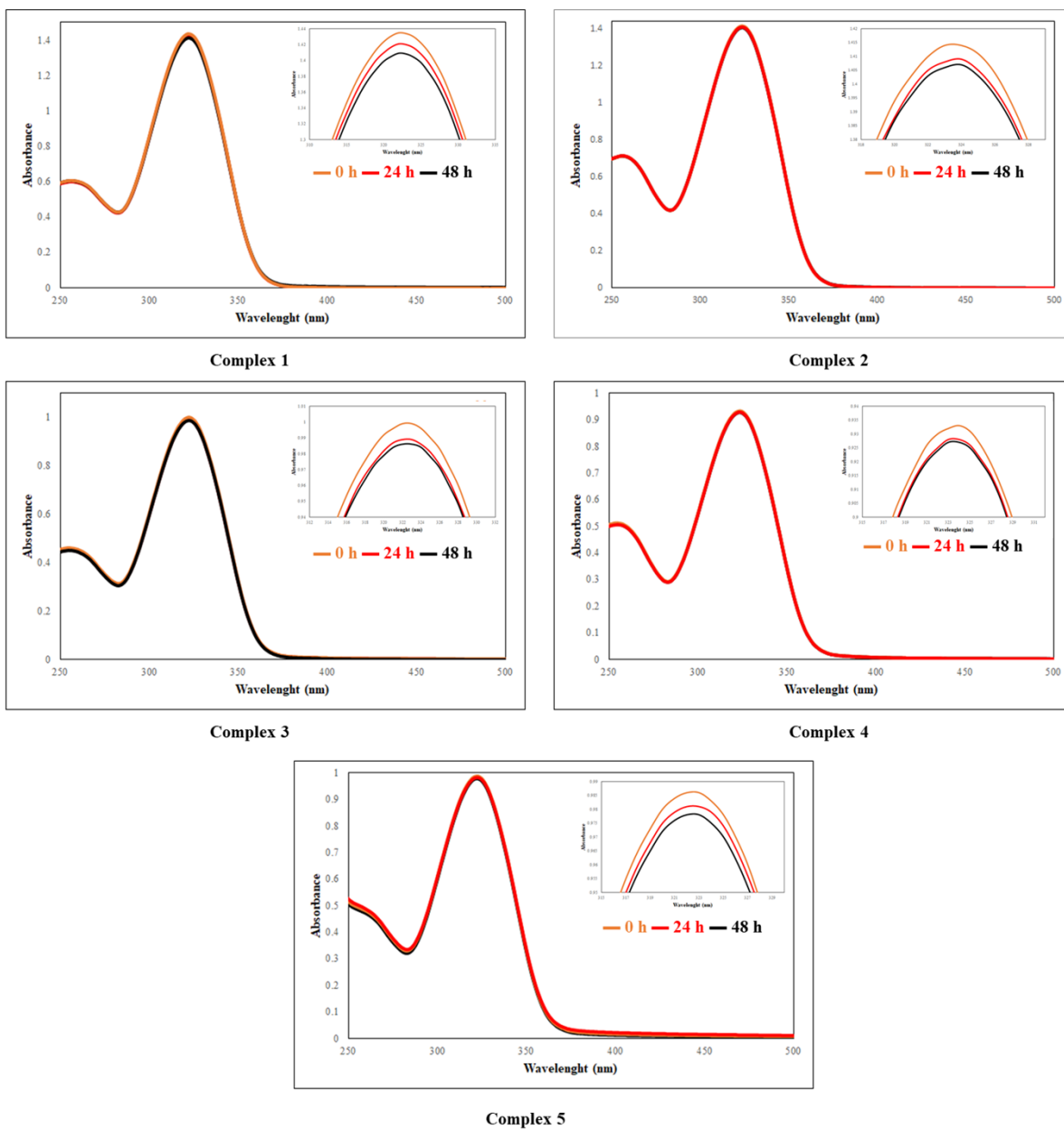
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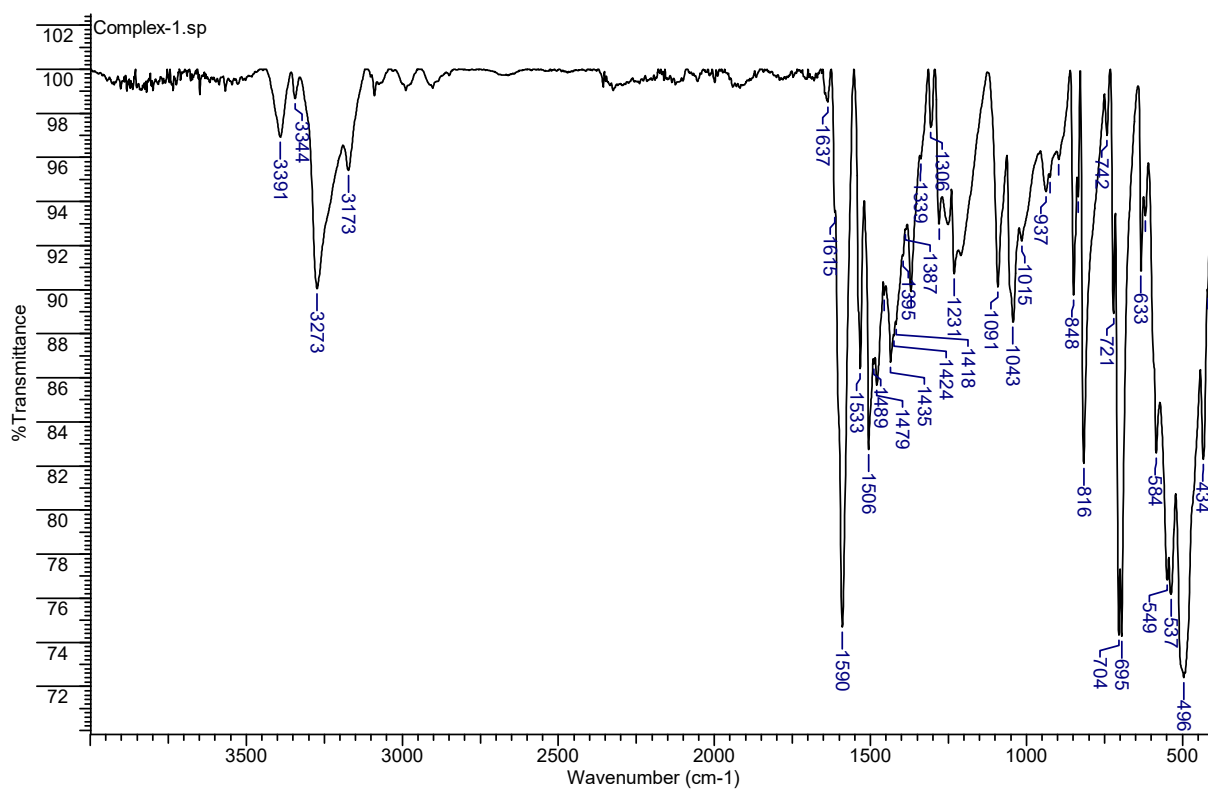
*<sup>d</sup>University Research Center of Ioannina (URCI), Institute of Materials Science and Computing, Ioannina, Greece*



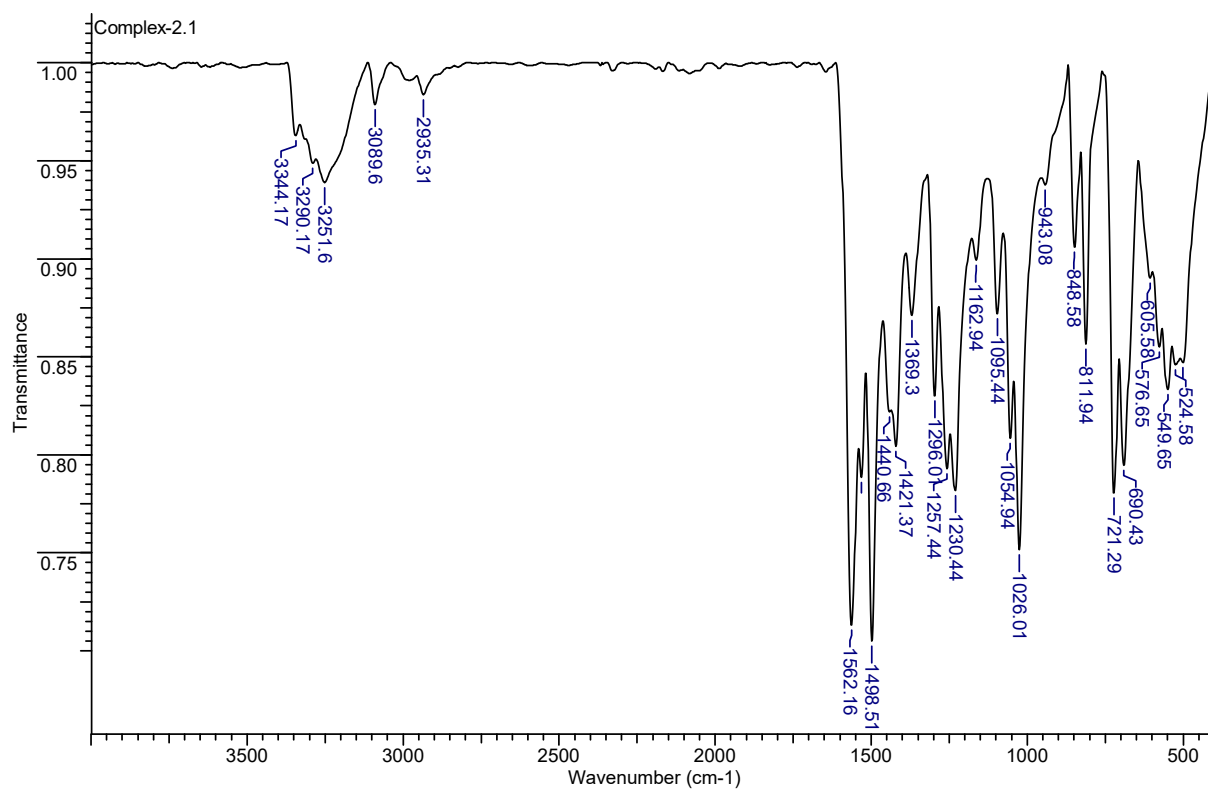
**Figure S1.** UV-Vis spectra of the Bi(III) complexes (1-5) for 0 h, 24 h and 48 h. Spectra were recorded at room temperature and in DMSO solution (20  $\mu$ M).



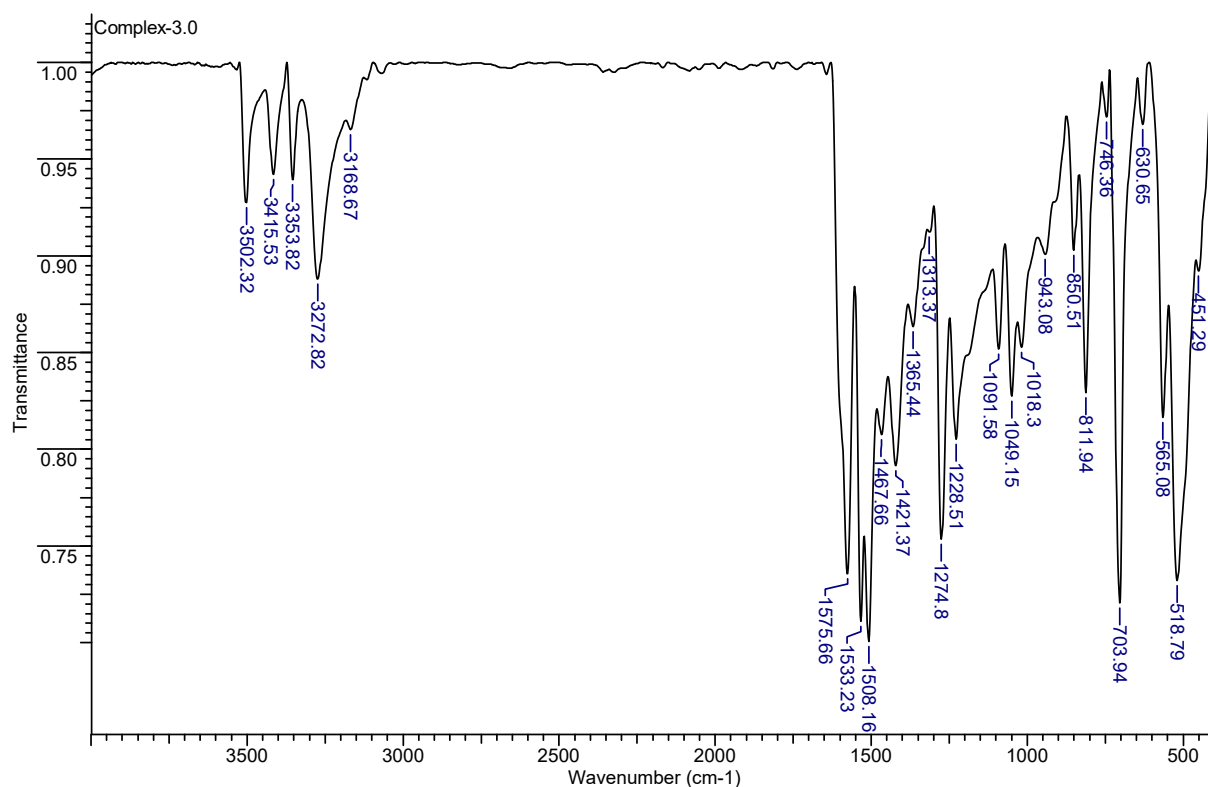
**Figure S2.** UV spectra of the Bi(III) complexes (1-5) for 0 h, 24 h and 48 h in PBS (20 $\mu$ M).



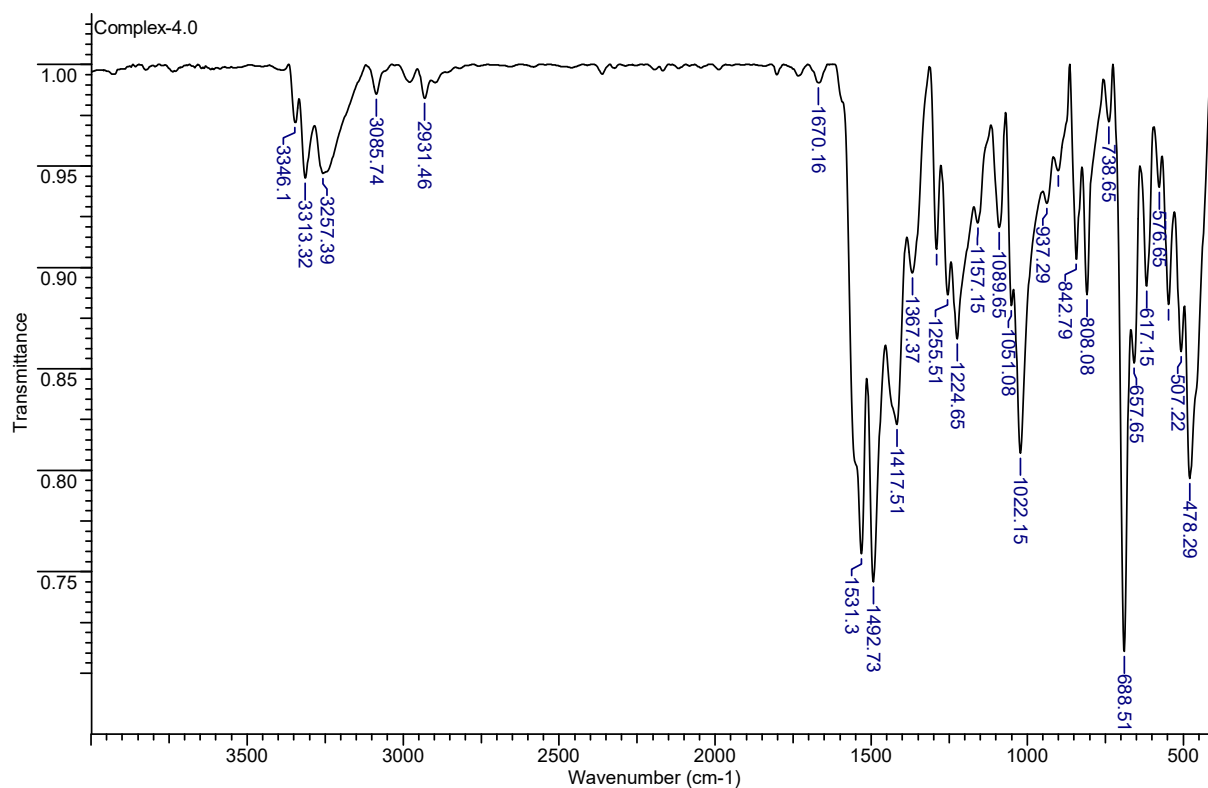
**Figure S3.** FT-IR spectrum of  $[\text{BiCl}_3(\eta^1\text{-S-Hattsc})_3]$  (**1**).



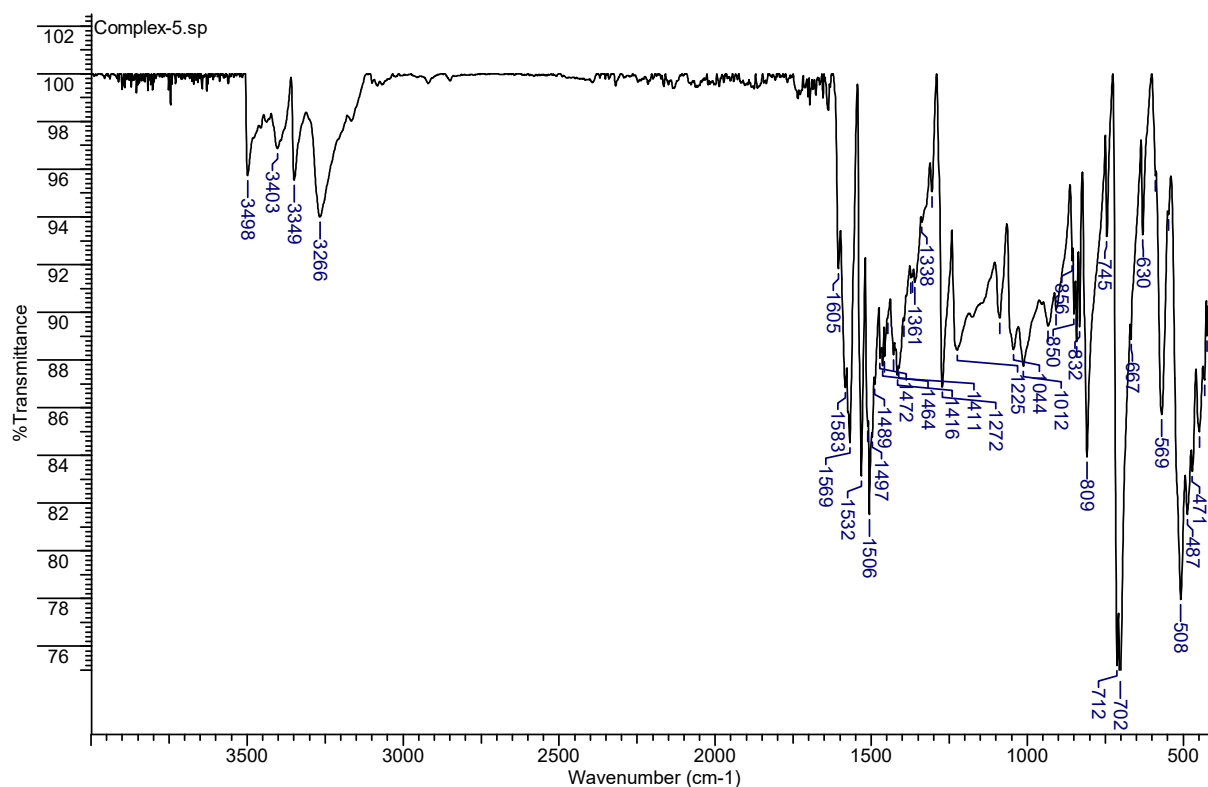
**Figure S4.** FT-IR spectrum of  $\{[\text{mer-BiCl}_3(\eta^1\text{-S-Hatmtsc})_3][\text{fac-SbCl}_3(\eta^1\text{-S-Hatmtsc})_3] \cdot 2\text{CH}_3\text{OH}\}$  (**2**)



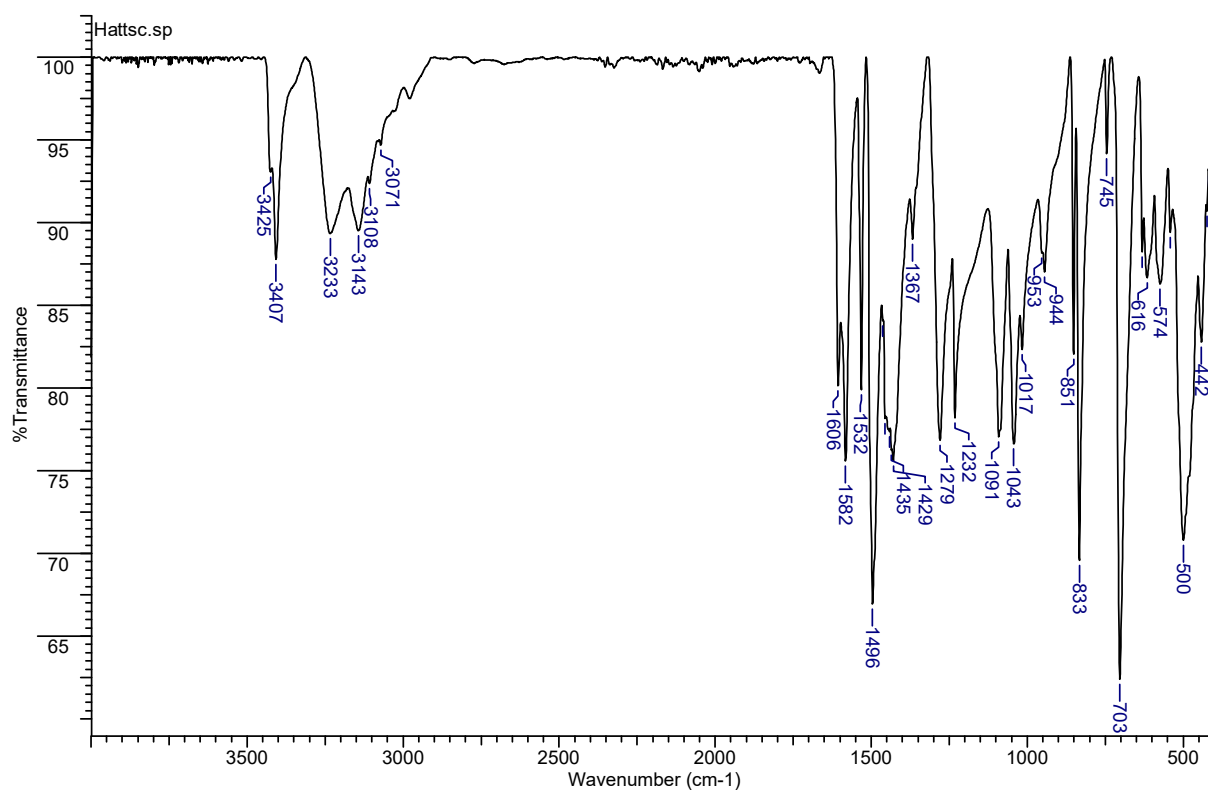
**Figure S5.** FT-IR spectrum of  $\{[\text{BiBr}_2(\mu_2\text{-Br})(\eta^1\text{-S-Hattsc})_2]_2\}$  (**3**).



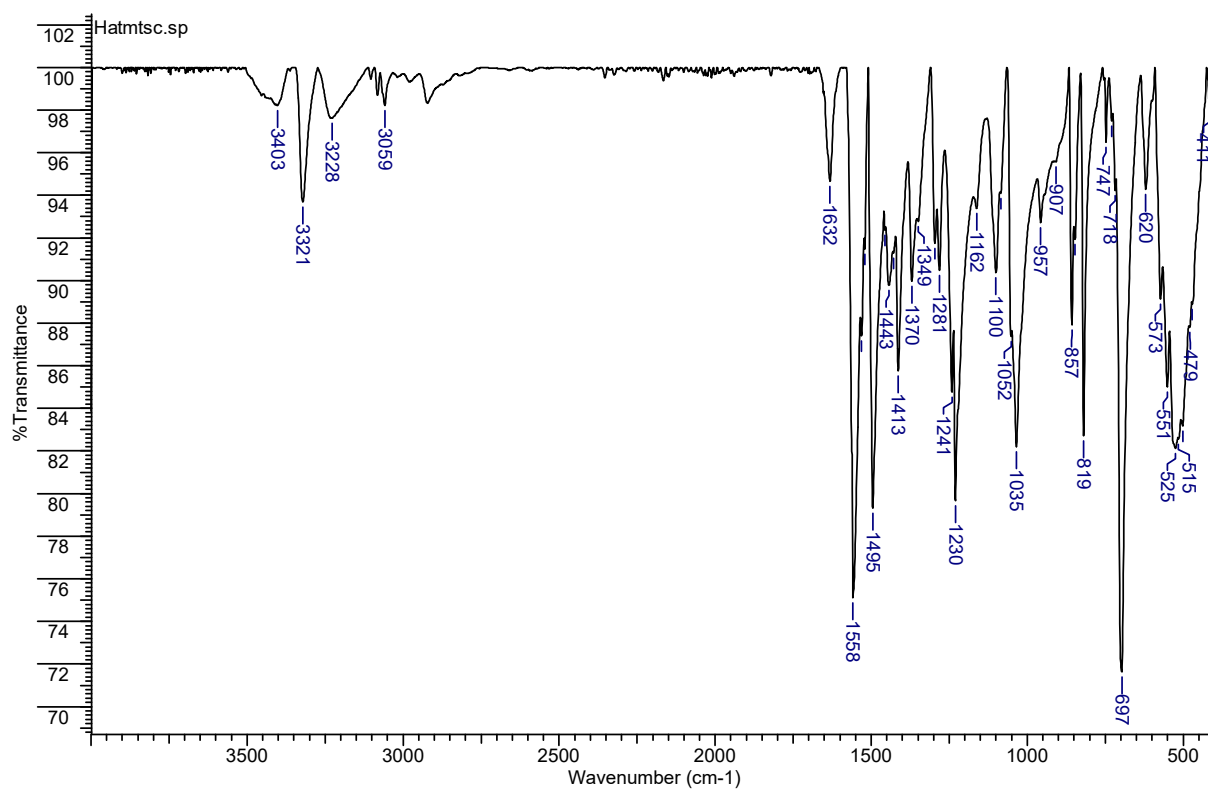
**Figure S6.** FT-IR spectrum of  $\{[\text{BiBr}_2(\mu_2\text{-Br})(\eta^1\text{-S-Hatmtsc})_2]_2\}$  (**4**).



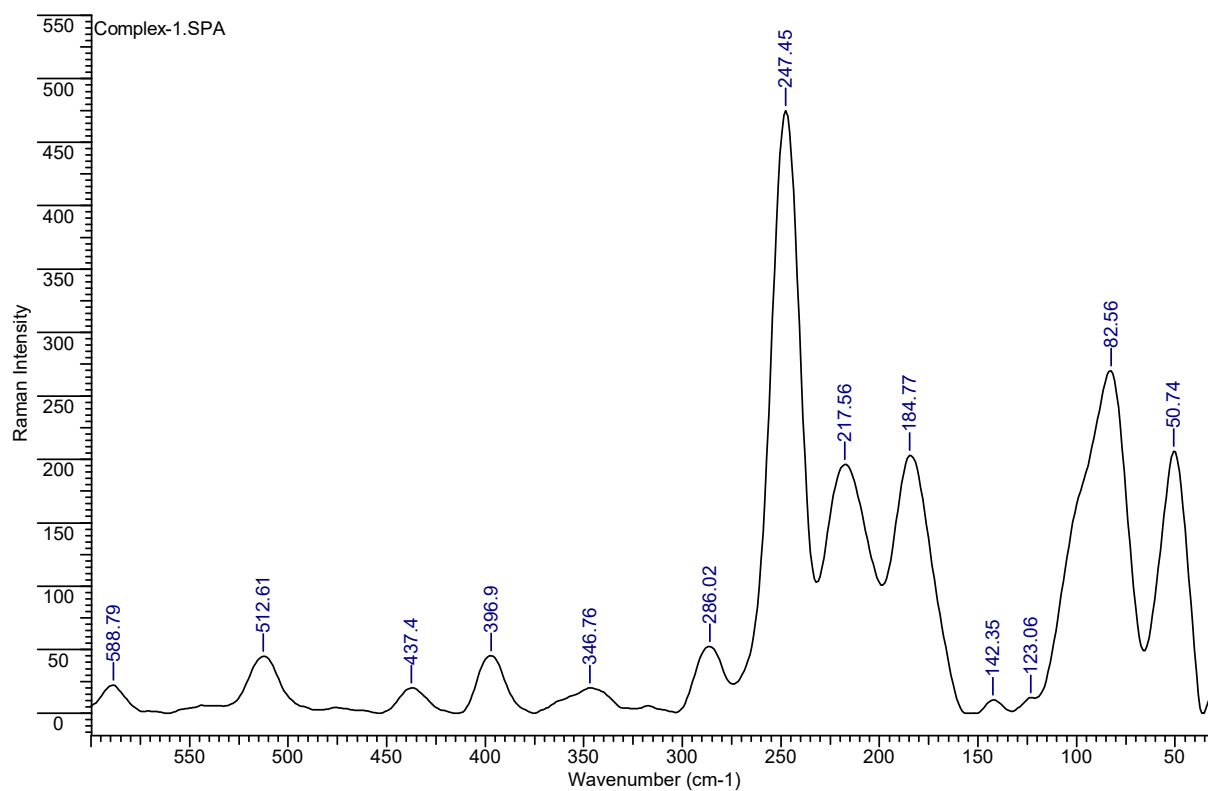
**Figure S7.** FT-IR spectrum of  $\{[\text{BiI}_2(\mu_2\text{-I})(\eta^1\text{-S-Hattsc})_2]_2\}$  (**5**).



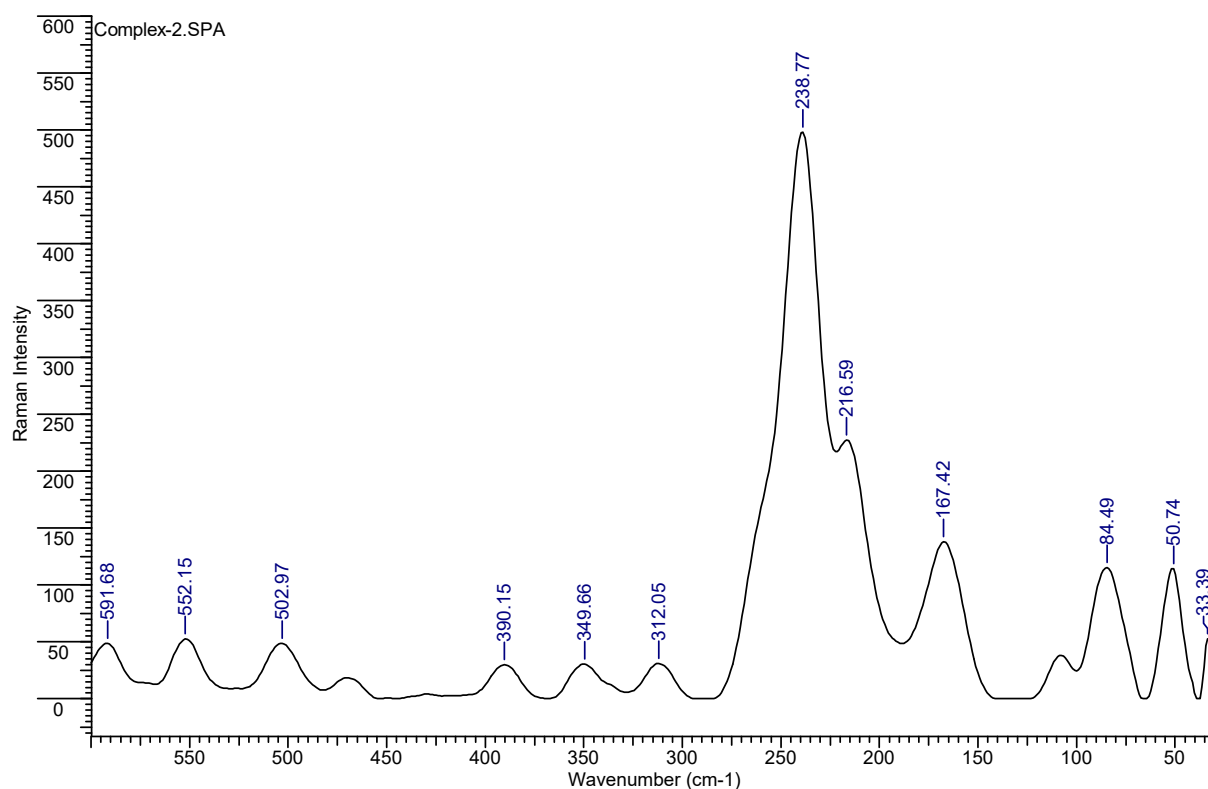
**Figure S8.** FT-IR spectrum of 2-acetylthiophene thiosemicarbazone (Hattsc)



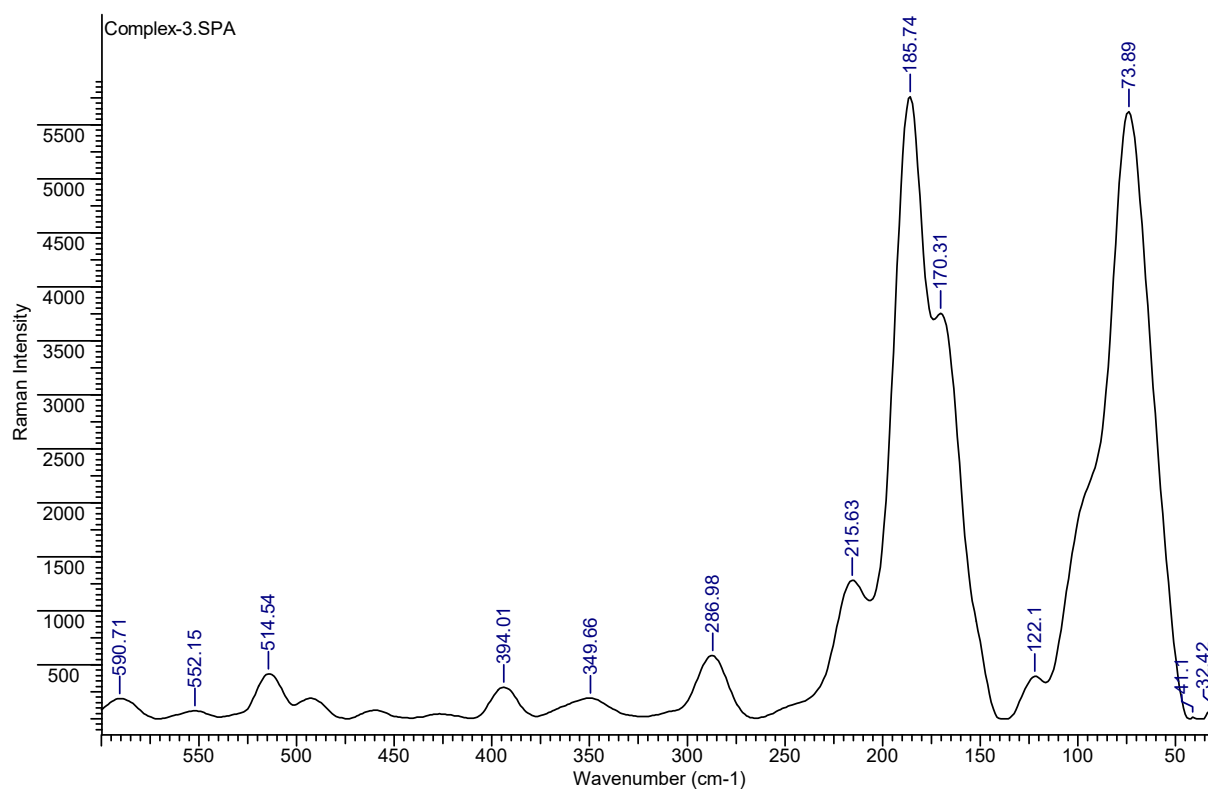
**Figure S9.** FT-IR spectrum of 2-acetylthiophene-N-methyl thiosemicarbazone (Hatmtsc)



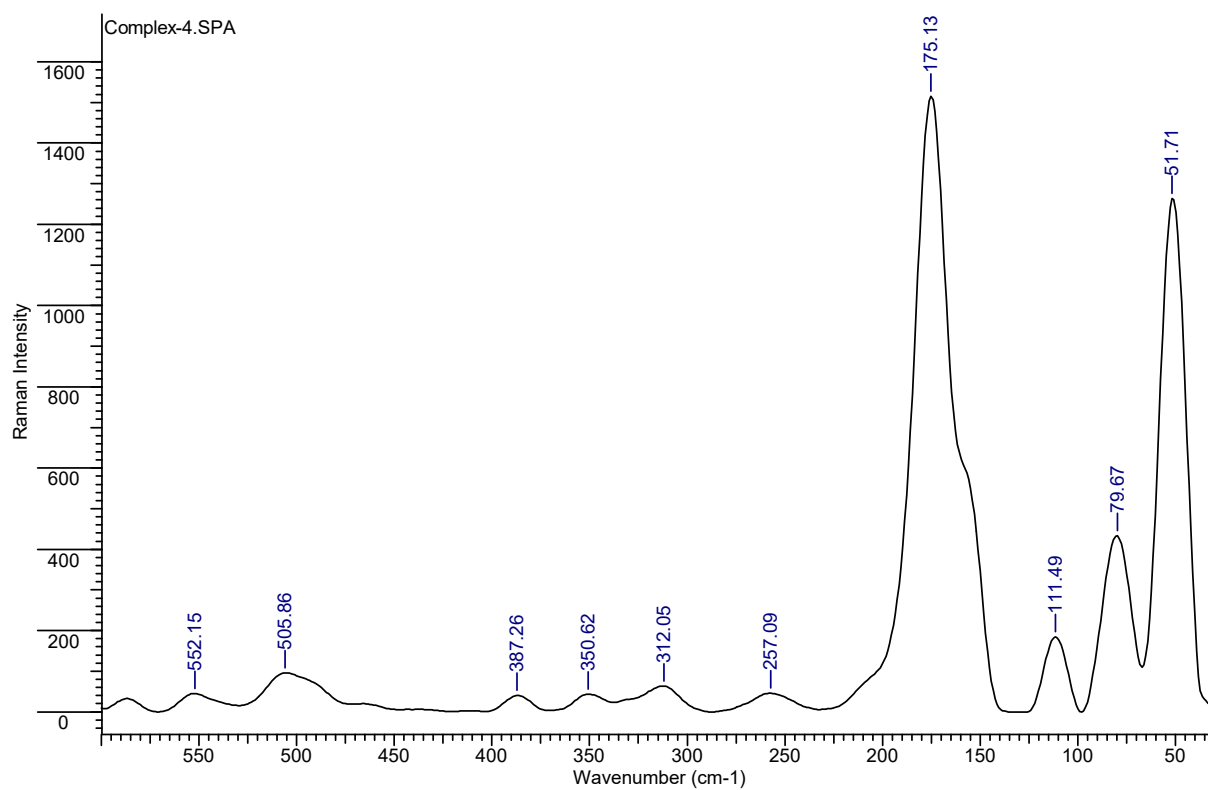
**Figure S10.** Raman spectrum of  $[\text{BiCl}_3(\eta^1\text{-S-Hattsc})_3]$  (**1**).



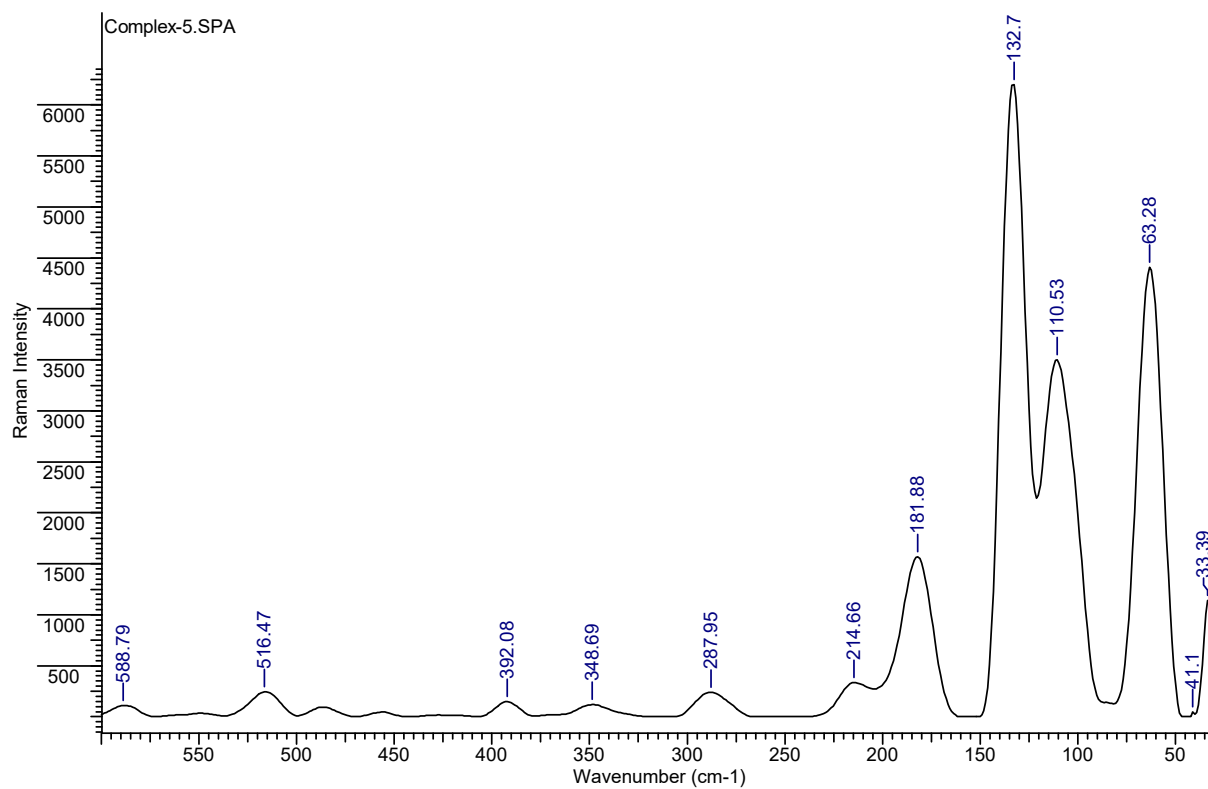
**Figure S11.** Raman spectrum of {[mer-BiCl<sub>3</sub>(η<sup>1</sup>-S-Hatmtsc)<sub>3</sub>][fac-SbCl<sub>3</sub>(η<sup>1</sup>-S-Hatmtsc)<sub>3</sub>].2CH<sub>3</sub>OH} (**2**)



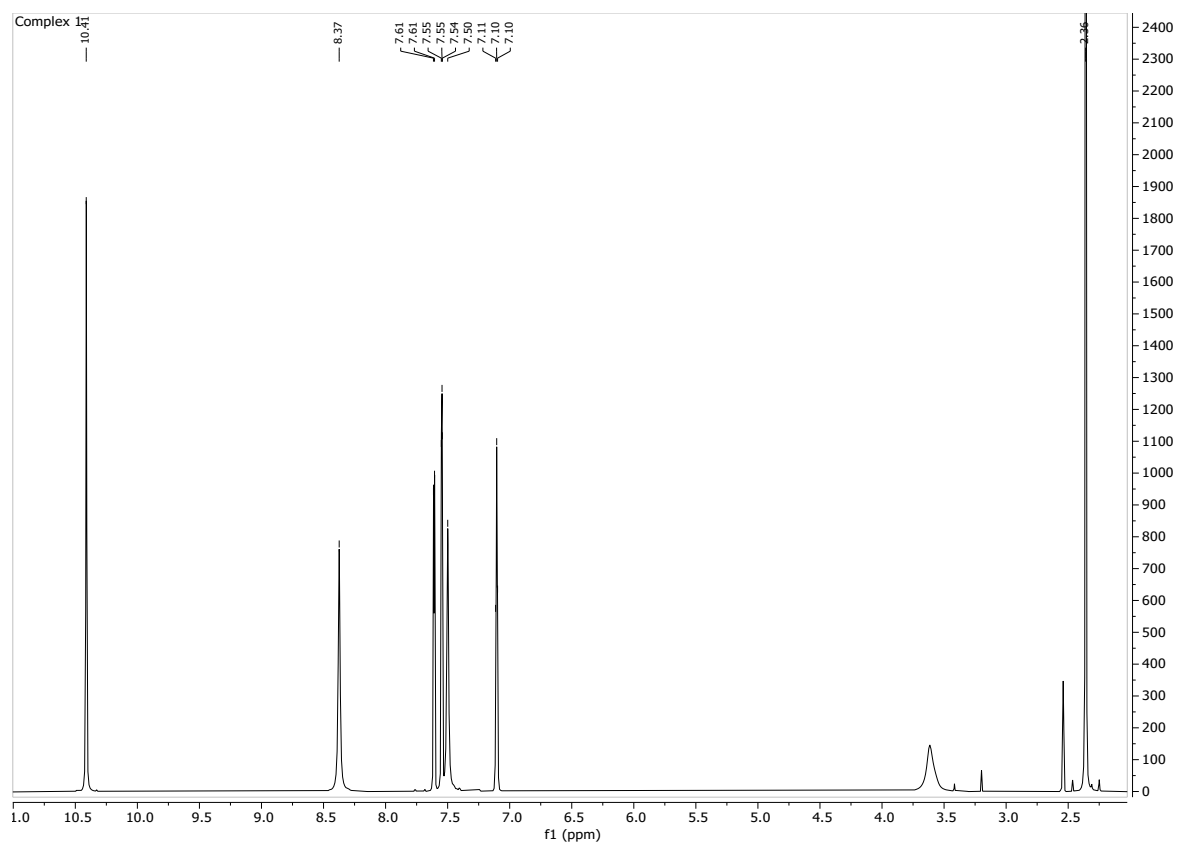
**Figure S12.** Raman spectrum of {[BiBr<sub>2</sub>(μ<sub>2</sub>-Br)(η<sup>1</sup>-S-Hattsc)<sub>2</sub>]} (**3**).



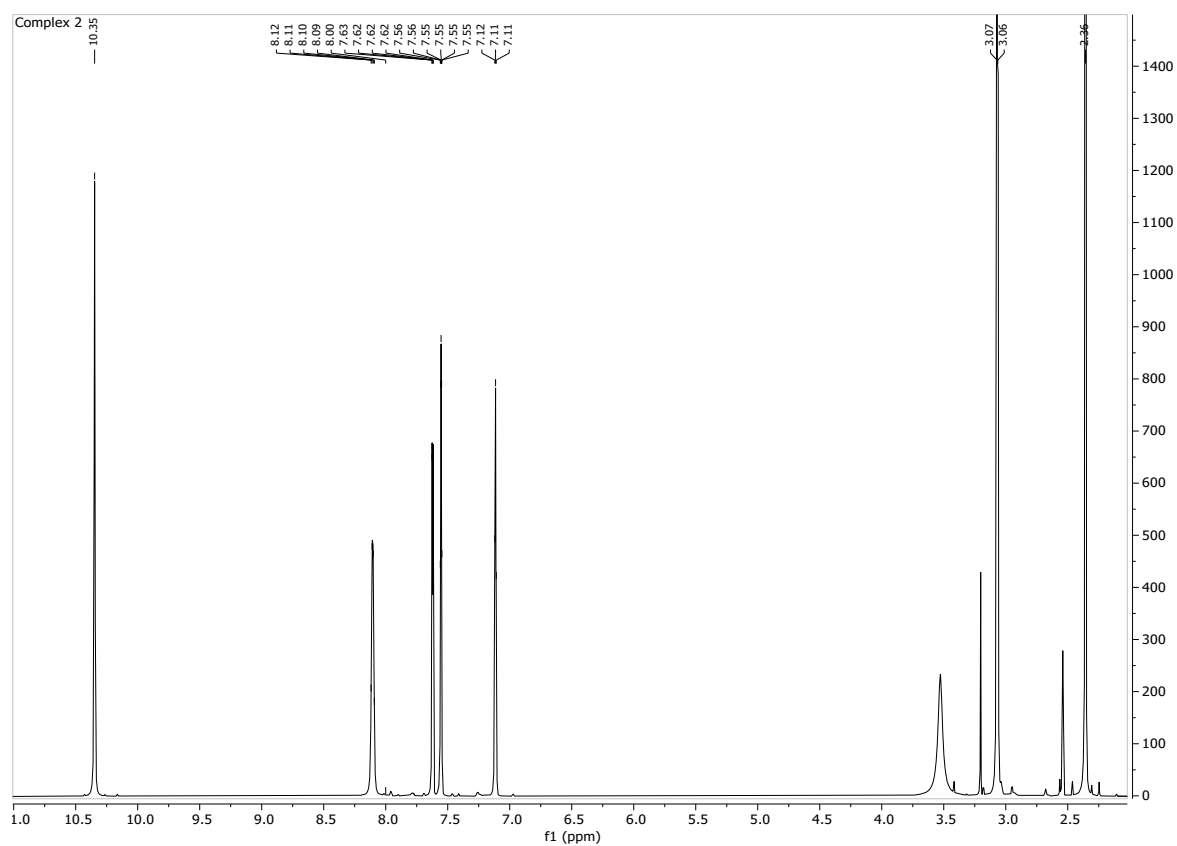
**Figure S13.** Raman spectrum of  $\{[\text{BiBr}_2(\mu_2\text{-Br})(\eta^1\text{-S-Hatmtsc})_2]_2\}$  (**4**).



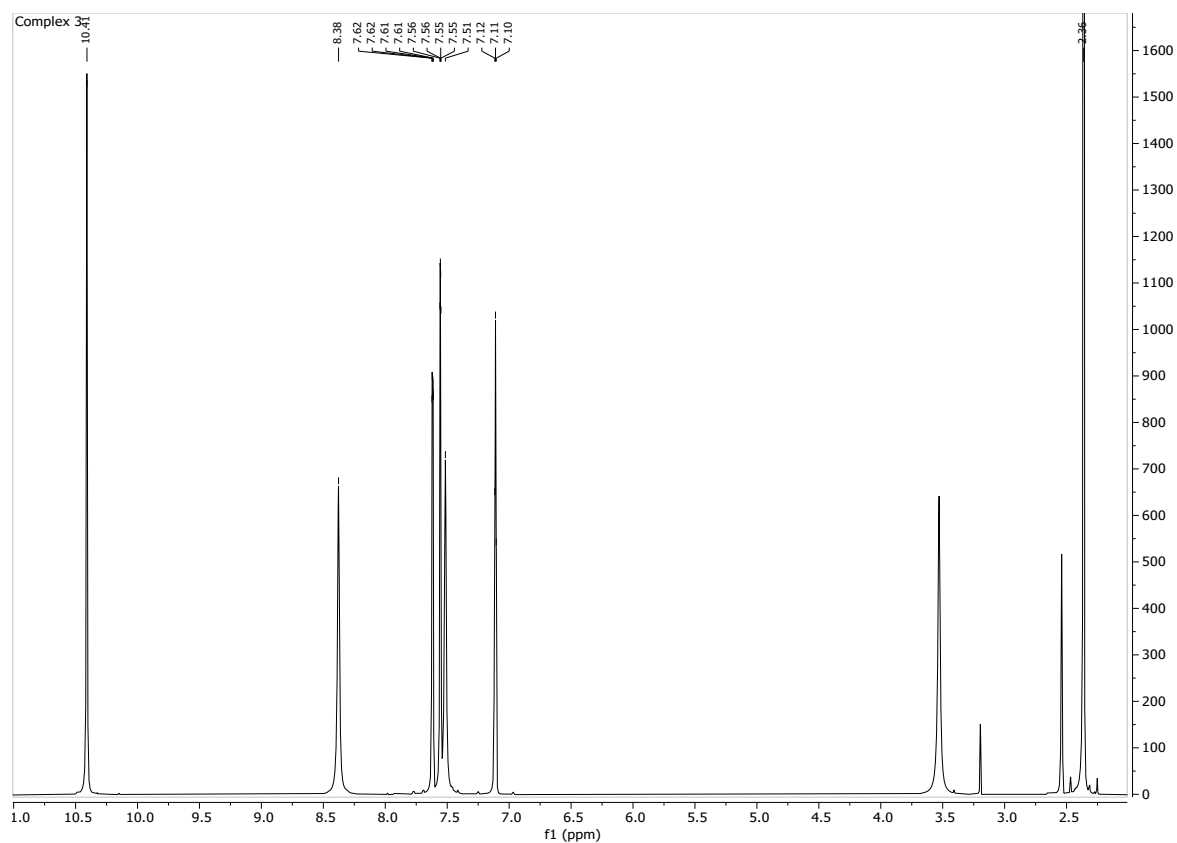
**Figure S14.** Raman spectrum of  $\{[\text{BiI}_2(\mu_2\text{-I})(\eta^1\text{-S-Hattsc})_2]_2\}$  (**5**).



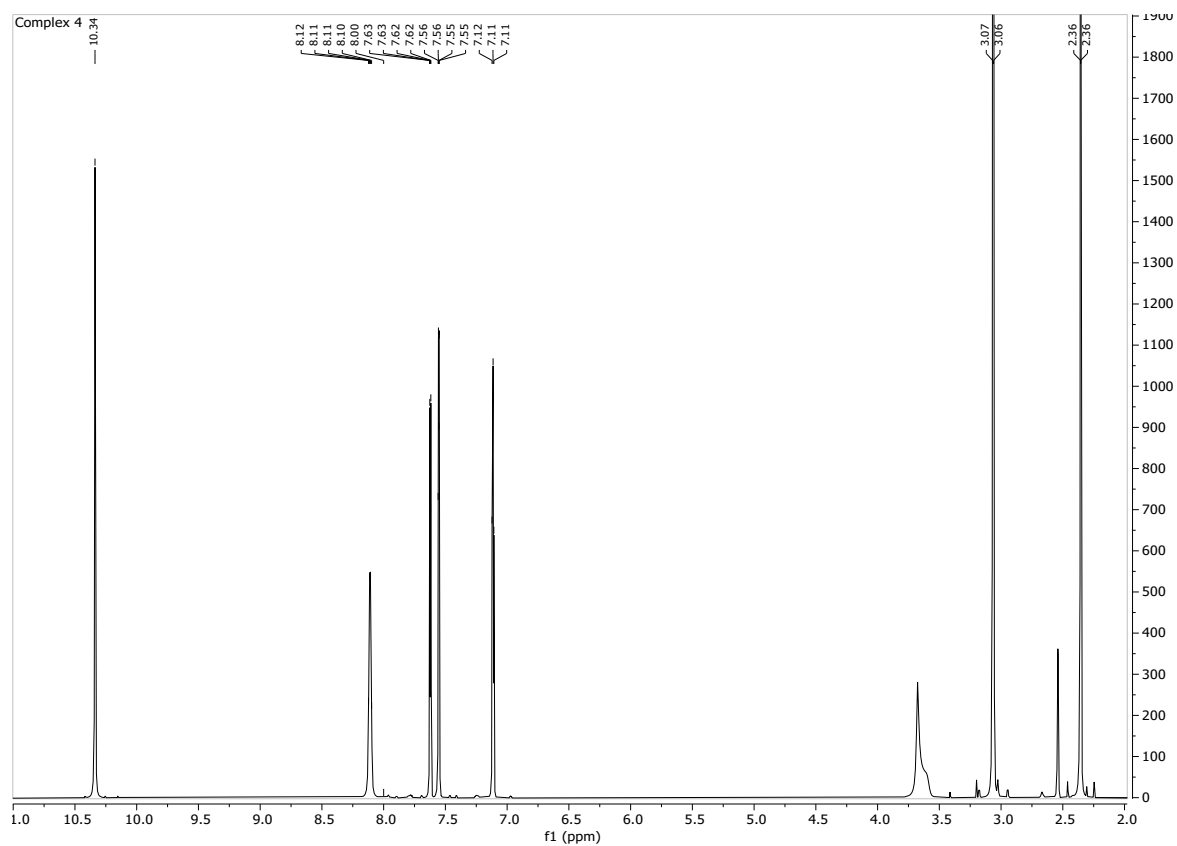
**Figure S15.**  $^1\text{H}$ -NMR spectrum of  $[\text{BiCl}_3(\eta^1\text{-S-Hattsc})_3]$  (**1**).



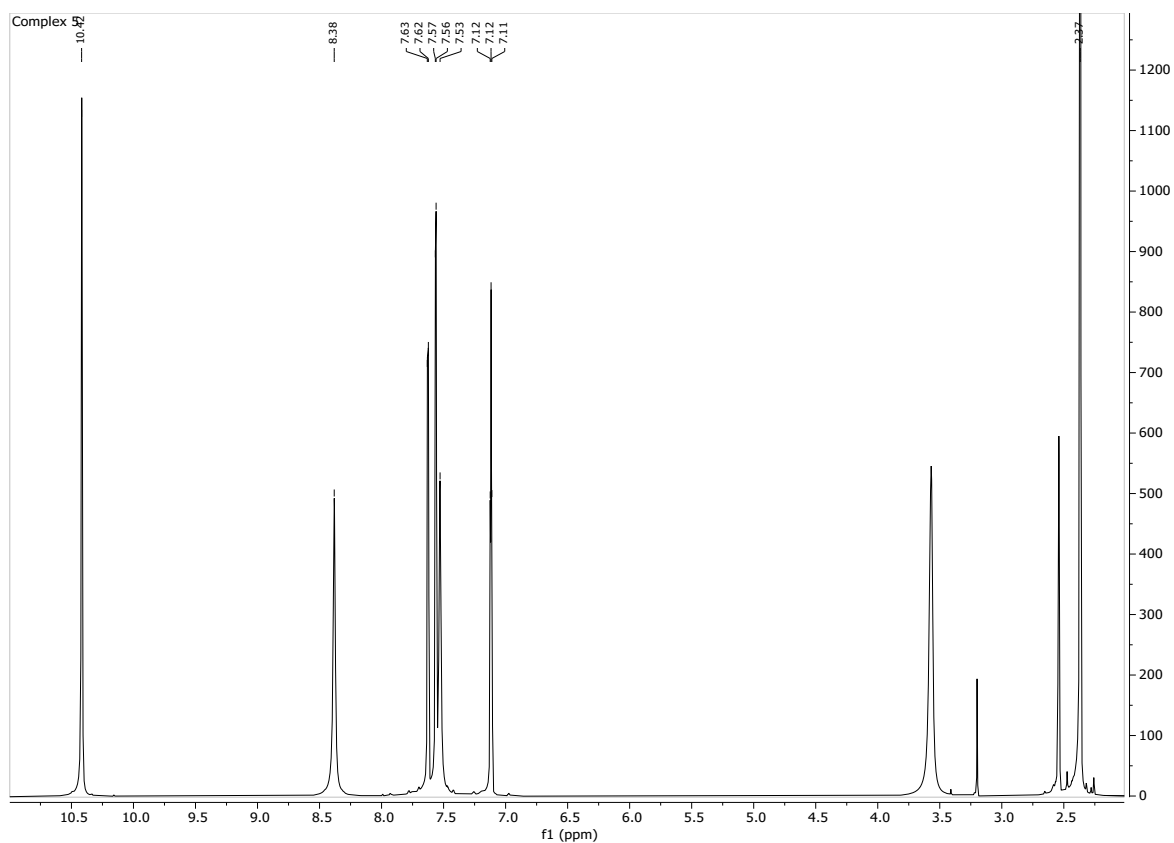
**Figure S16.**  $^1\text{H}$ -NMR spectrum of  $\{[\text{mer-BiCl}_3(\eta^1\text{-S-Hatmtsc})_3][\text{fac-SbCl}_3(\eta^1\text{-S-Hatmtsc})_3] \cdot 2\text{CH}_3\text{OH}\}$  (**2**)



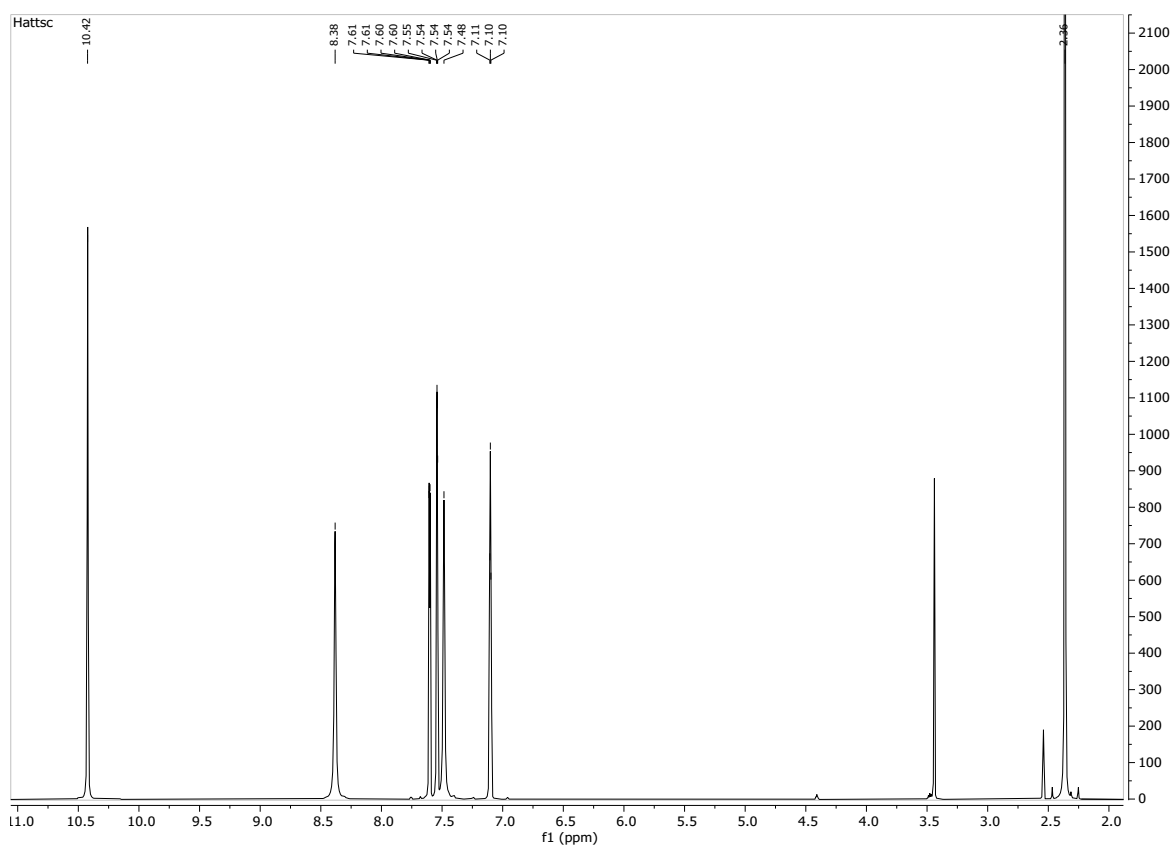
**Figure S17.**  $^1\text{H}$ -NMR spectrum of  $\{[\text{BiBr}_2(\mu_2\text{-Br})(\eta^1\text{-S-Hattsc})_2]_2\}$  (**3**).



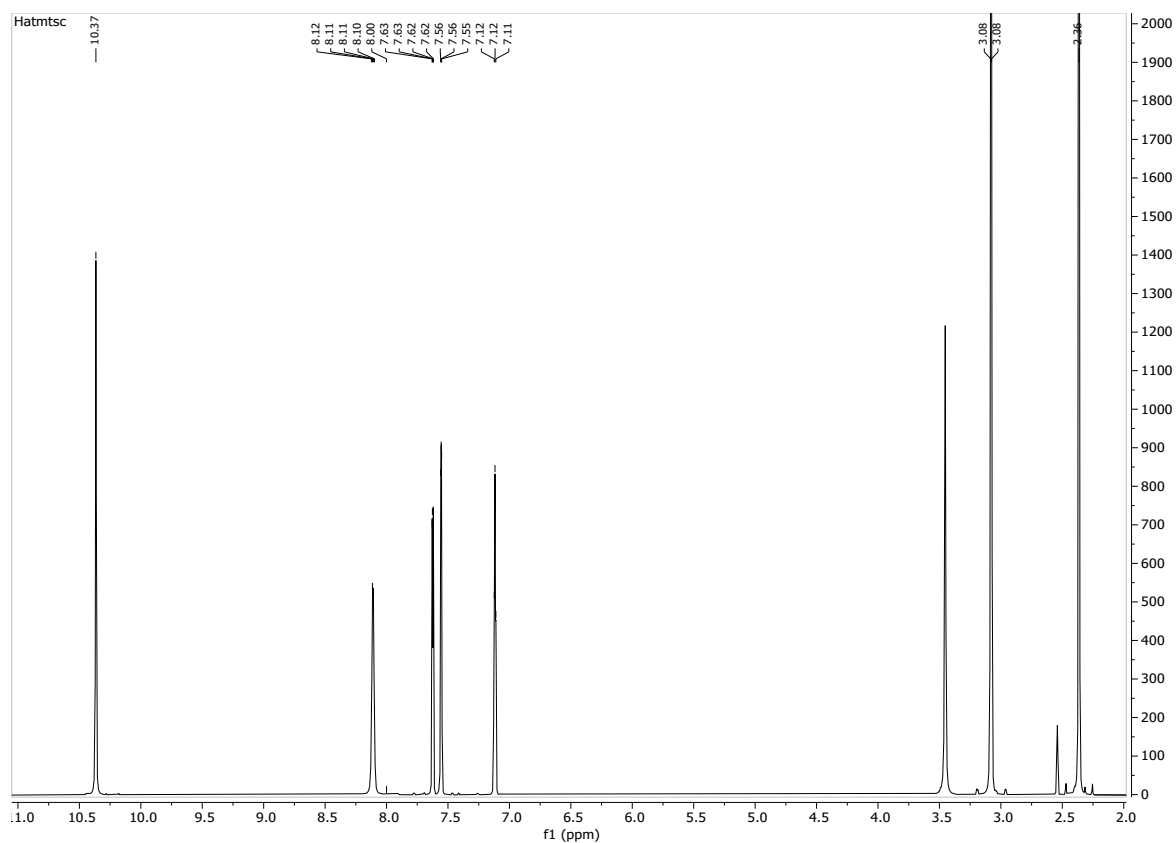
**Figure S18.**  $^1\text{H}$ -NMR spectrum of  $\{[\text{BiBr}_2(\mu_2\text{-Br})(\eta^1\text{-S-Hatmtsc})_2]_2\}$  (**4**).



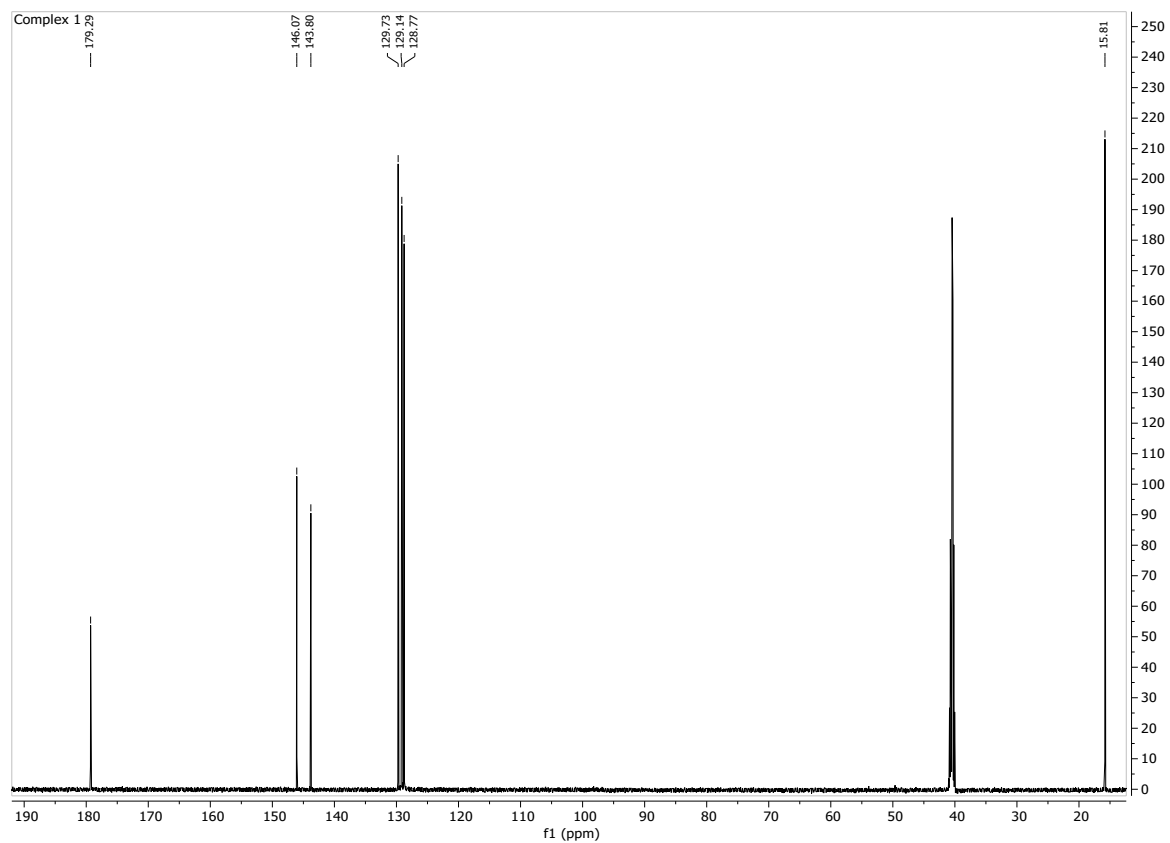
**Figure S19.**  $^1\text{H}$ -NMR spectrum of  $\{[\text{BiI}_2(\mu_2\text{-I})(\eta^1\text{-S-Hattsc})_2]_2\}$  (5).



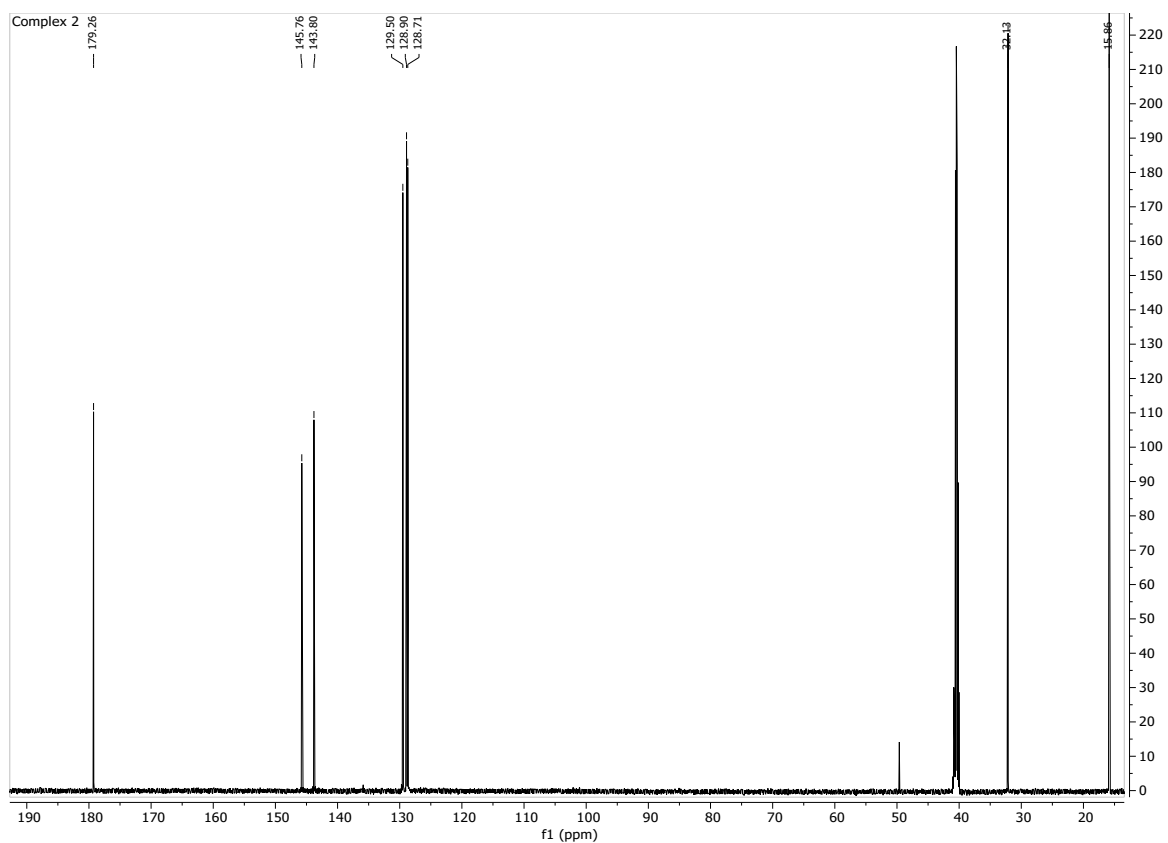
**Figure S20.**  $^1\text{H}$ -NMR spectrum of 2-acetylthiophene thiosemicarbazone (Hattsc).



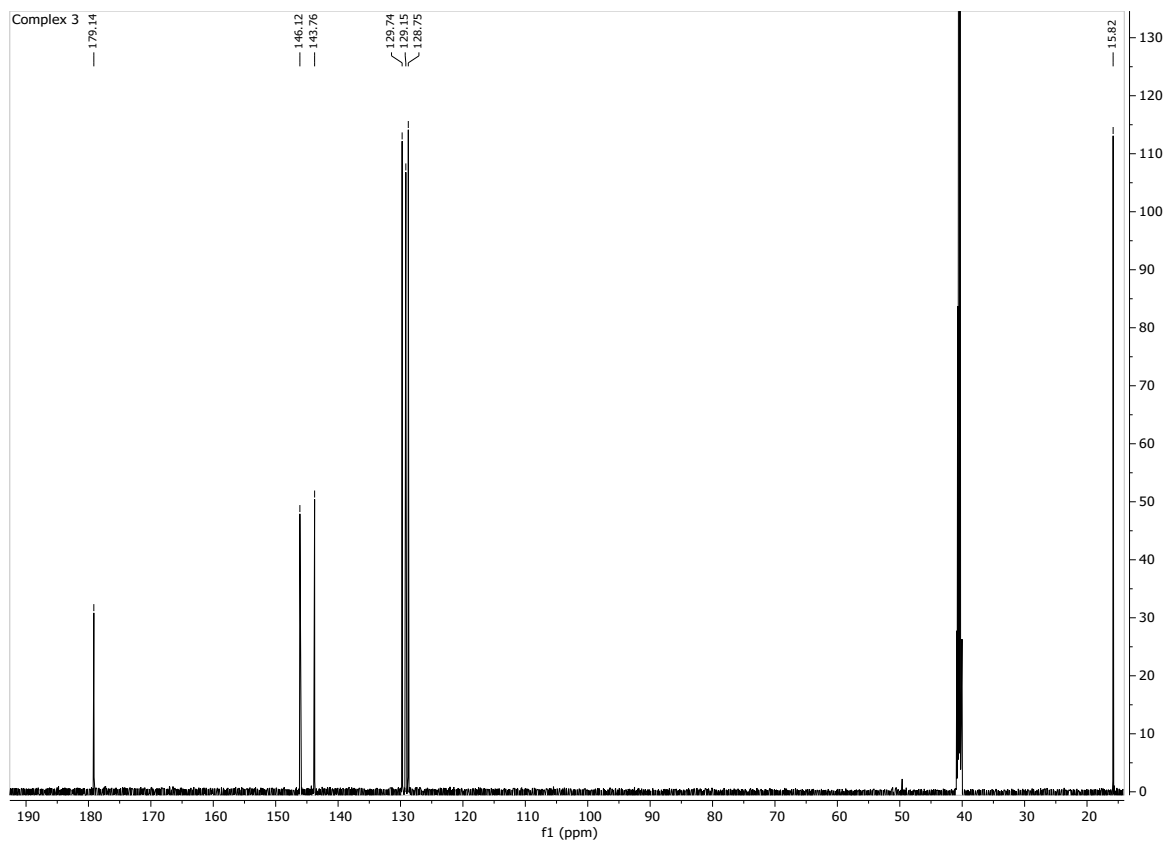
**Figure S21.**  $^1\text{H}$ -NMR spectrum of 2-acetylthiophene-N-methyl thiosemicarbazone (Hatmtsc).



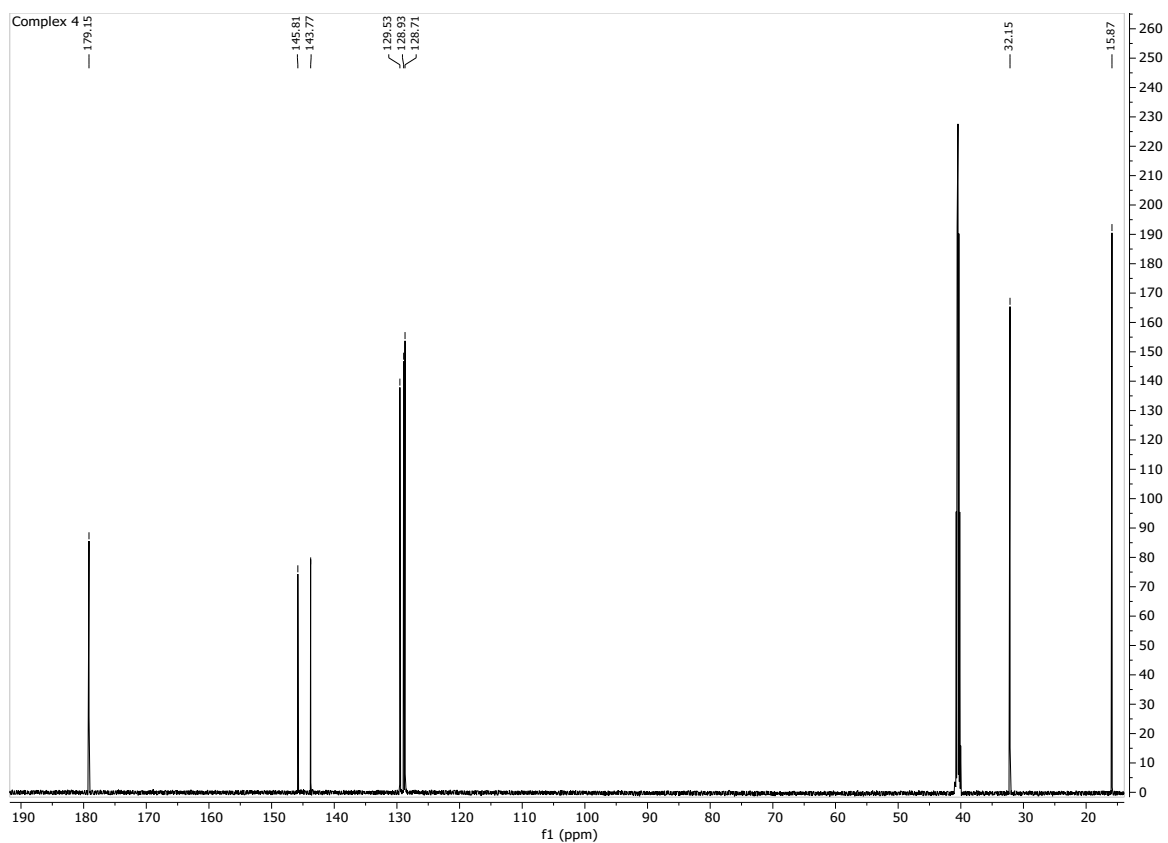
**Figure S22.**  $^{13}\text{C}$ -NMR spectrum of  $[\text{BiCl}_3(\eta^1\text{-S-Hattsc})_3]$  (1).



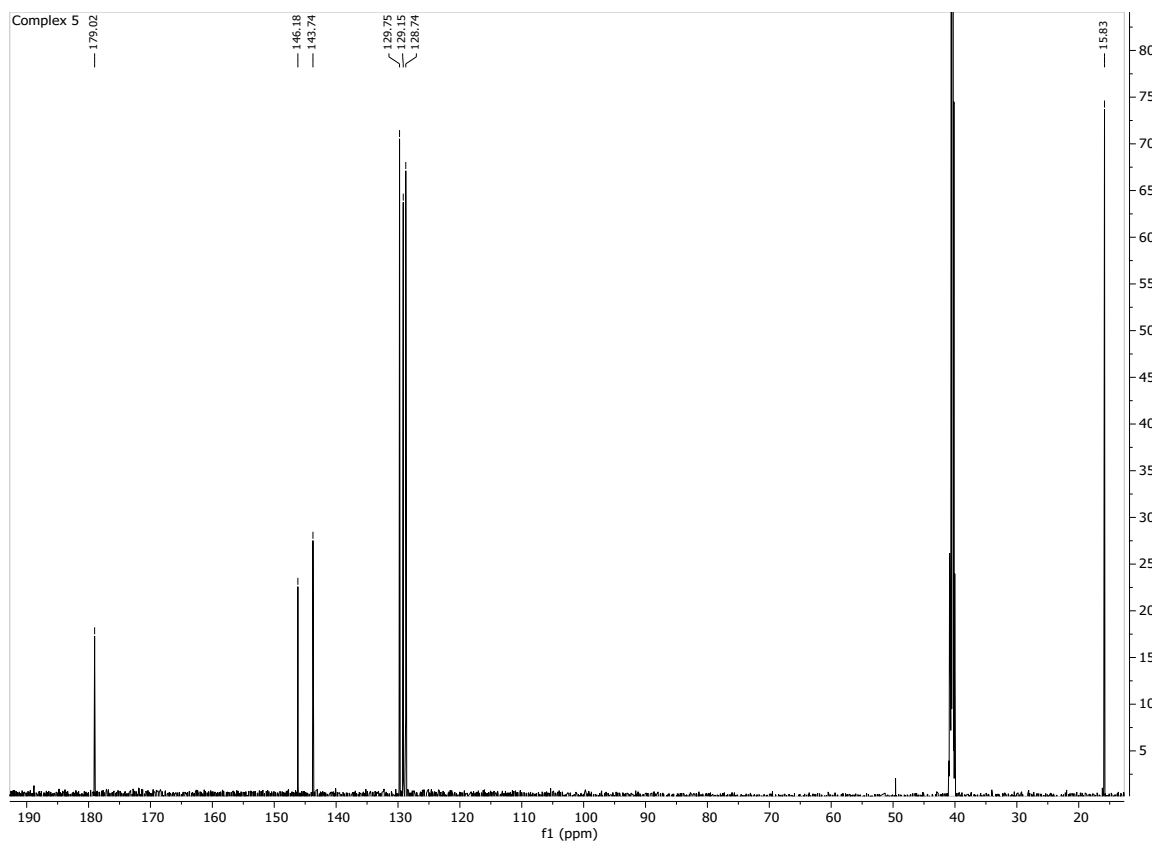
**Figure S23.**  $^{13}\text{C}$ -NMR spectrum of  $\{[\text{mer-BiCl}_3(\eta^1\text{-S-Hatmtsc})_3][\text{fac-SbCl}_3(\eta^1\text{-S-Hatmtsc})_3]\cdot 2\text{CH}_3\text{OH}\}$  (**2**)



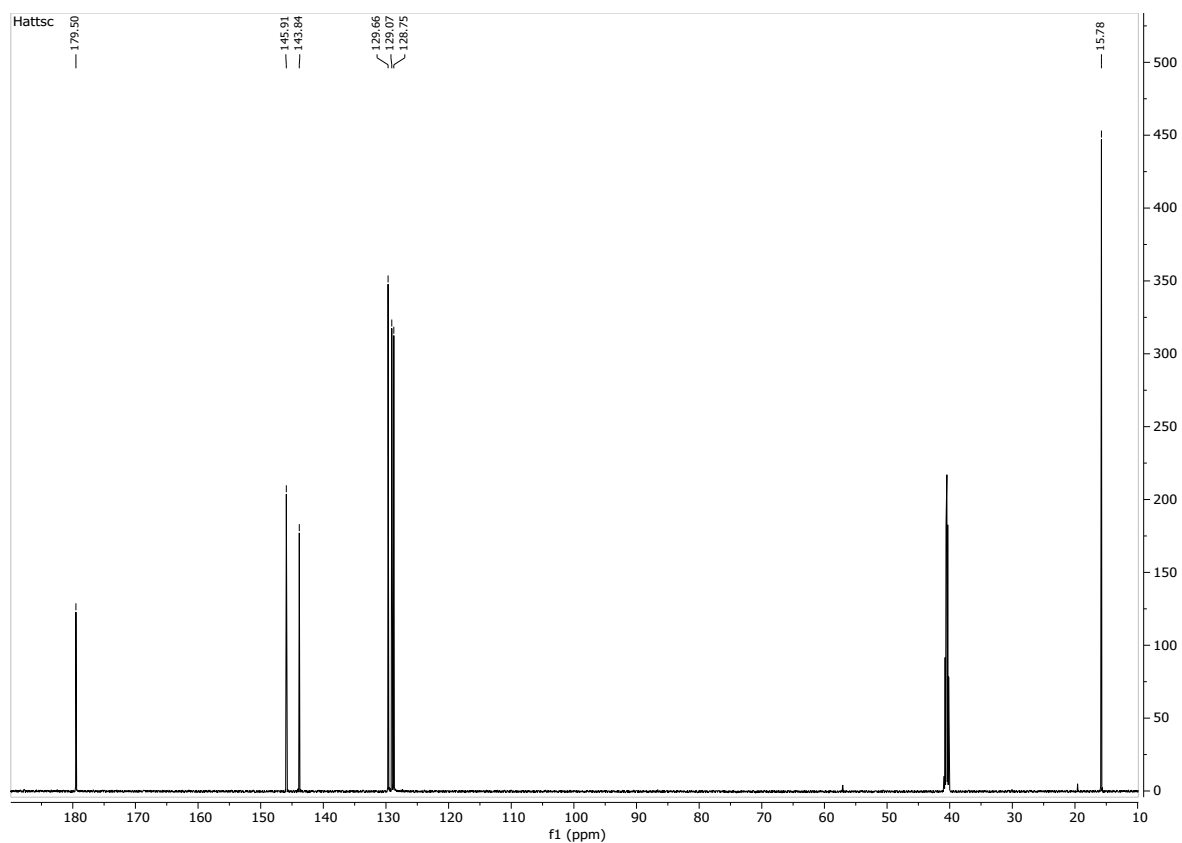
**Figure S24.**  $^{13}\text{C}$ -NMR spectrum of  $\{[\text{BiBr}_2(\mu_2\text{-Br})(\eta^1\text{-S-Hattsc})_2]\}_2$  (**3**).



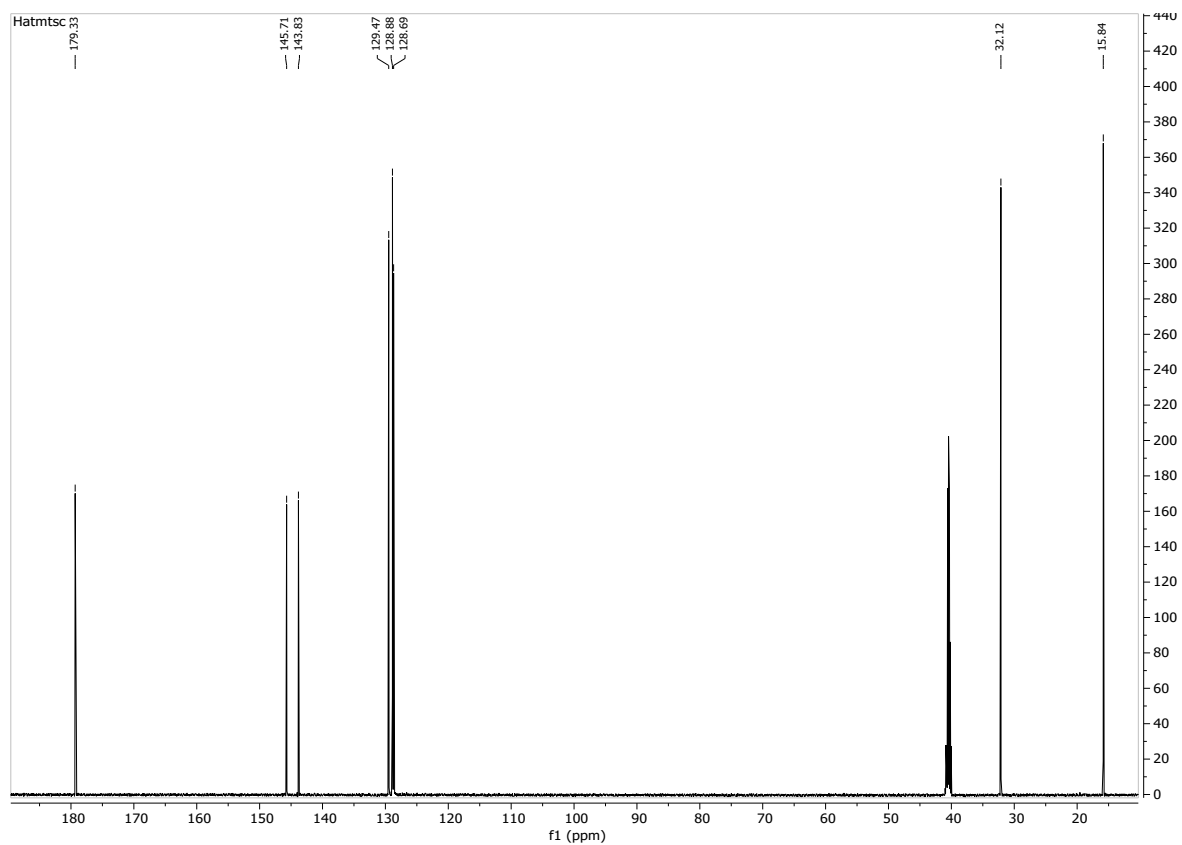
**Figure S25.**  $^{13}\text{C}$ -NMR spectrum of  $\{[\text{BiBr}_2(\mu_2\text{-Br})(\eta^1\text{-S-Hatmtsc})_2]_2\}$  (**4**).



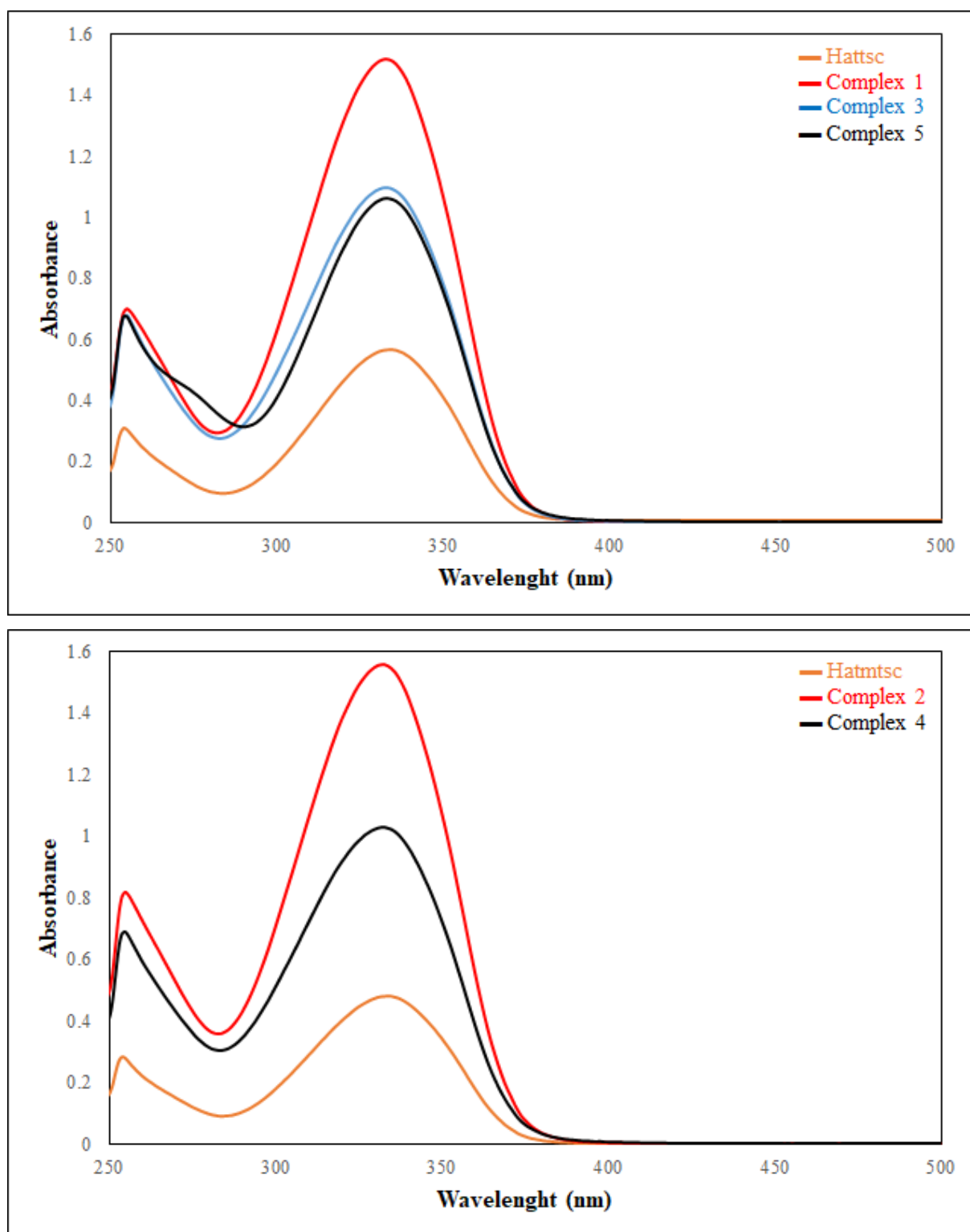
**Figure S26.**  $^{13}\text{C}$ -NMR spectrum of  $\{[\text{BiI}_2(\mu_2\text{-I})(\eta^1\text{-S-Hattsc})_2]_2\}$  (**5**).



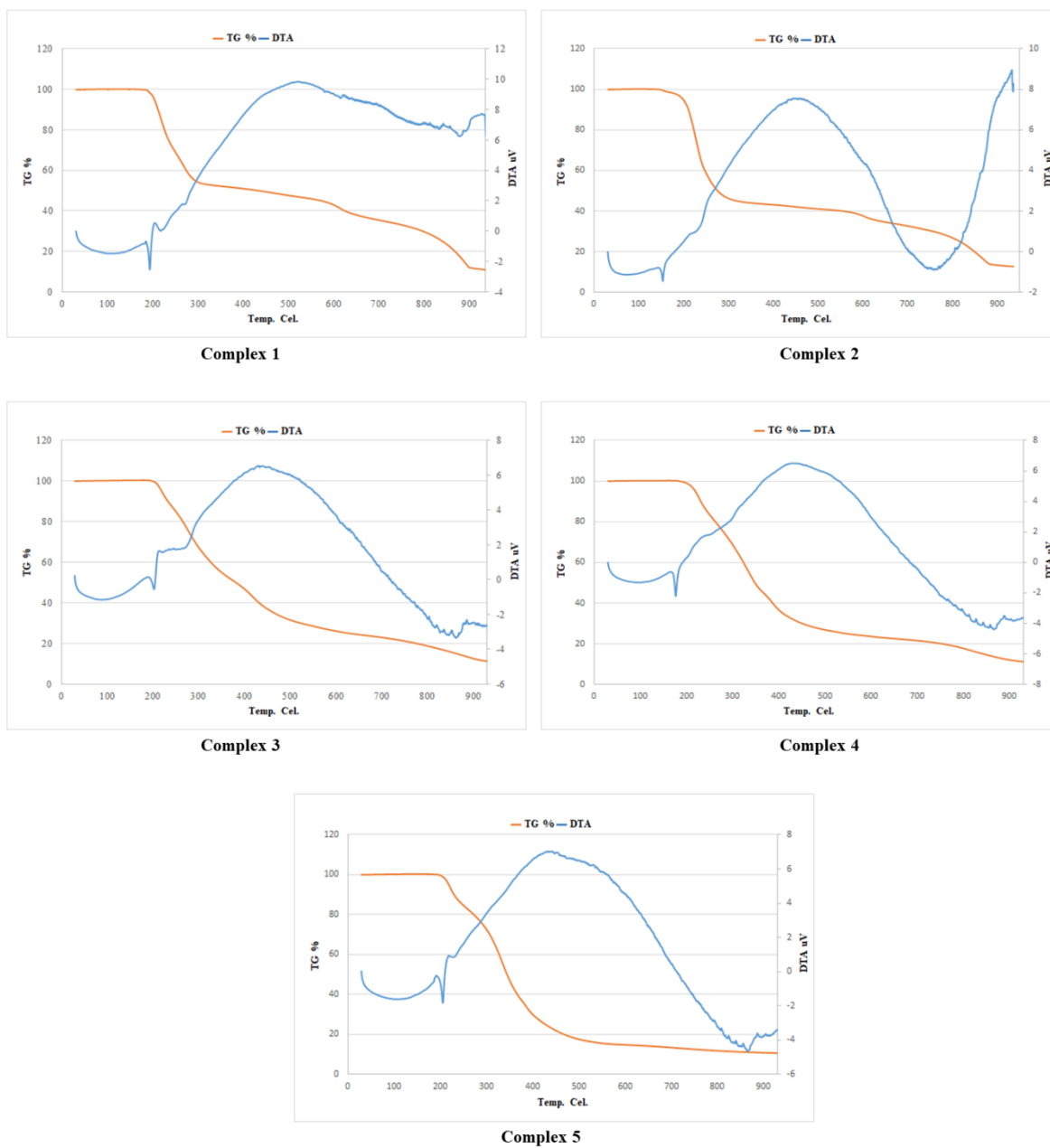
**Figure S27.** <sup>13</sup>C-NMR spectrum of 2-acetylthiophene thiosemicarbazone (Hattsc)



**Figure S28.** <sup>13</sup>C-NMR spectrum of 2-acetylthiophene-N-methyl thiosemicarbazone (Hatmtsc)



**Figure S29.** UV-Vis absorption spectra of bismuth(III) complexes (1-5) and free ligands. Spectra were recorded at room temperature and in DMSO solution (20  $\mu$ M).



**Figure S30.** TG-DTA curves of bismuth(III) complexes (1-5).

**Table S1.** Molar conductivity values of the bismuth(III) complexes **1-5** for 0 h, 24 h and 48 h in DMSO.

| Compounds | 0 h        | 24 h       | 48 h       |
|-----------|------------|------------|------------|
| <b>1</b>  | 10.72±0.42 | 10.85±0.18 | 10.92±0.21 |
| <b>2</b>  | 4.73±0.26  | 4.79±0.12  | 4.81±0.16  |
| <b>3</b>  | 12.95±0.48 | 13.01±0.54 | 13.08±0.25 |
| <b>4</b>  | 15.48±0.54 | 15.51±0.29 | 15.58±0.35 |
| <b>5</b>  | 35.23±0.18 | 35.38±0.14 | 35.42±0.32 |