

## Supporting Information

### **Effect of coordinating (-CN) Vs non-coordinating (-F) substituents in 3-pyridyl urea receptors toward second sphere sulfate recognition: Selective crystallisation of CuSO<sub>4</sub> from mixtures of competing anions/ cations.**

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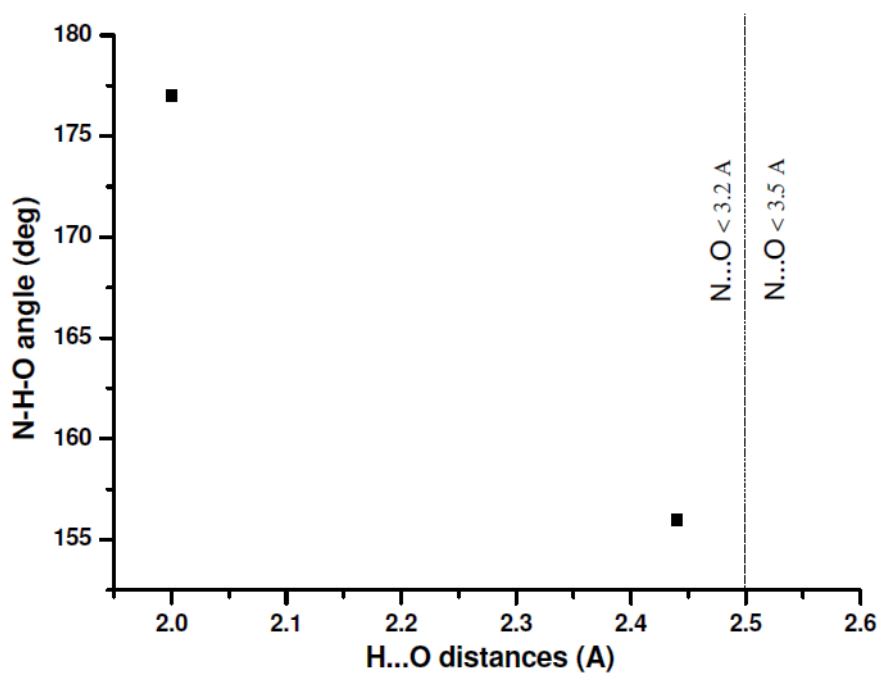
**Table 1S.** Metal-Ligand bond distances in complex **1**

Atoms	Distance (Å)
Cu1 -O3	2.2469
Cu1 -O5	2.4112
Cu1 -N1	2.0223

**Table 2S.** Hydrogen bonding table for complex **1**

D-H...A	d(H-A) Å	d(D-A) Å	<DHA (°)
N(2) --H(2) ..O(2)	2.44	3.24	156
N(3) --H(3) ..O(2)	2.00	2.85	177
C(1) --H(1) ..O(4)	2.23	2.99	138

**Figure 1S.** Scattered plot of complex **1**



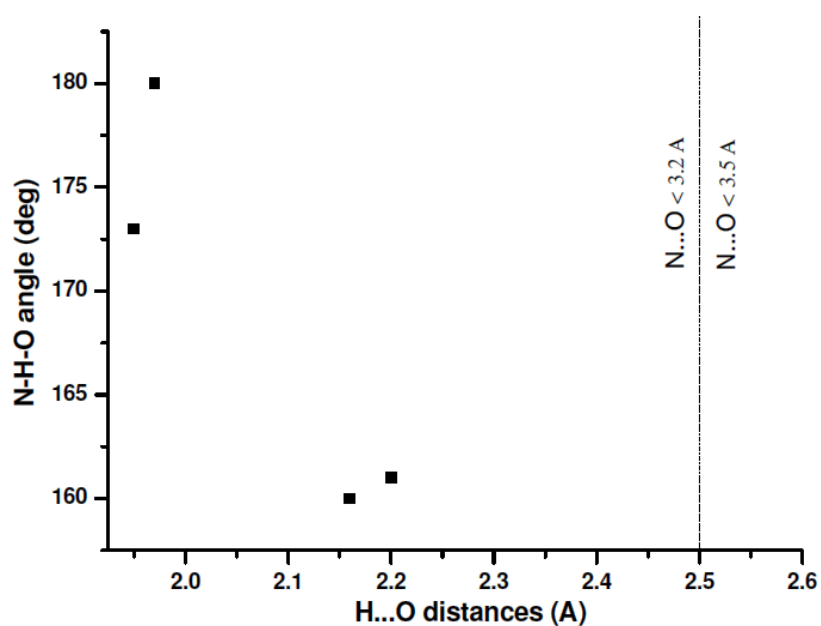
**Table 3S.** Metal-Ligand bond distances in complex **2**

Atoms	Distance (Å)
Cd1 -O3	2.2699
Cd1 -O4	2.2687
Cd1 -N1	2.3394
Cd1 -N2	2.3812

**Table 4S.** Hydrogen bonding table for complex **2**

D-H...A	d(H-A) Å	d(D-A) Å	<DHA (°)
N(3) --H(3) ..O(1)	2.20	3.02	161
N(4) --H(4) ..O(1)	1.95	2.81	173
N(5) --H(5) ..O(2)	2.16	2.98	160
N(6) --H(6) ..O(2)	1.97	2.83	180
C(3) --H(3A) ..O(1)	2.48	2.83	142

**Figure 2S.** Scattered plot of complex **2**



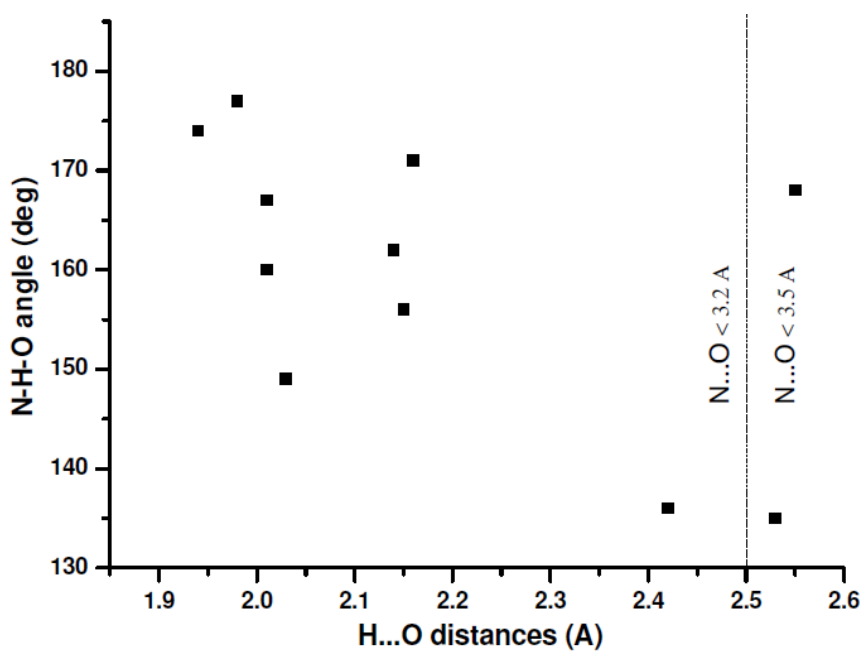
**Table 5S.** Metal-Ligand bond distances in complex **3**

Atoms	Distance (Å)
Cu1 -N1	2.0178
Cu1 -N2	2.0140
Cu1 -N3	2.0183
Cu1 -N4	2.0350
Cu1 -N13	2.5759
Cu1 -N16	2.6716

**Table 6S.** Hydrogen bonding table for complex **3**

D-H...A	d(H-A) Å	d(D-A) Å	<DHA (°)
N(5) --H(5) ..O(4)	1.94	2.79	174
N(6) --H(6) ..O(3)	2.14	2.97	162
N(7) --H(7) ..O(1)	2.03	2.80	149
N(8) --H(8A) ..O(1)	2.14	2.95	156
N(8) --H(8A) ..O(2)	2.42	3.09	136
N(9) --H(9) ..O(1)	2.01	2.85	168
N(10) --H(10) ..O(4)	1.98	2.84	177
N(11) --H(11) ..O(2)	2.01	2.83	160
N(12) --H(12) ..O(3)	2.15	3.00	171
C(8) --H(8) ..O(3)	2.53	3.24	135
C(11) --H(11A) ..O(1)	2.55	3.47	169

**Figure 3S.** Scattered plot of complex **3**



**Table 7S.** Metal-Ligand bond distances in complex **4**

Atoms	Distance (Å)
Co1 -O1	2.1106
Co1 -O2	2.1131
Co1 -N1	2.1467

**Table 8S.** Hydrogen bonding table for complex **4**

D-H...A	d(H-A) Å	d(D-A) Å	<DHA (°)
N(2) --H(2) ..O(4A)	2.04	2.90	173
N(3) --H(3) ..O(5A)	2.15	2.98	160
C(8) --H(8) ..O(5A)	2.46	3.24	142
C(11) --H(11) ..O(3)	2.35	3.26	165
C(16) --H(16C) ..N(4)	2.59	3.50	158

**Figure 4S.** Scattered plot of complex **4**

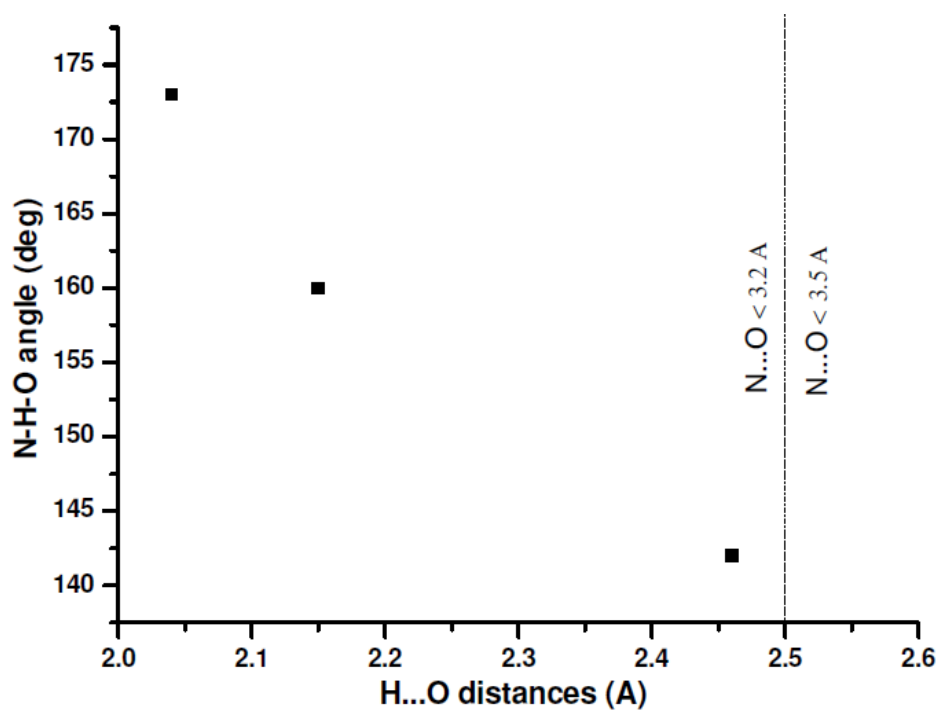


Figure 5S. ESI-MS spectrum of L<sup>1</sup>

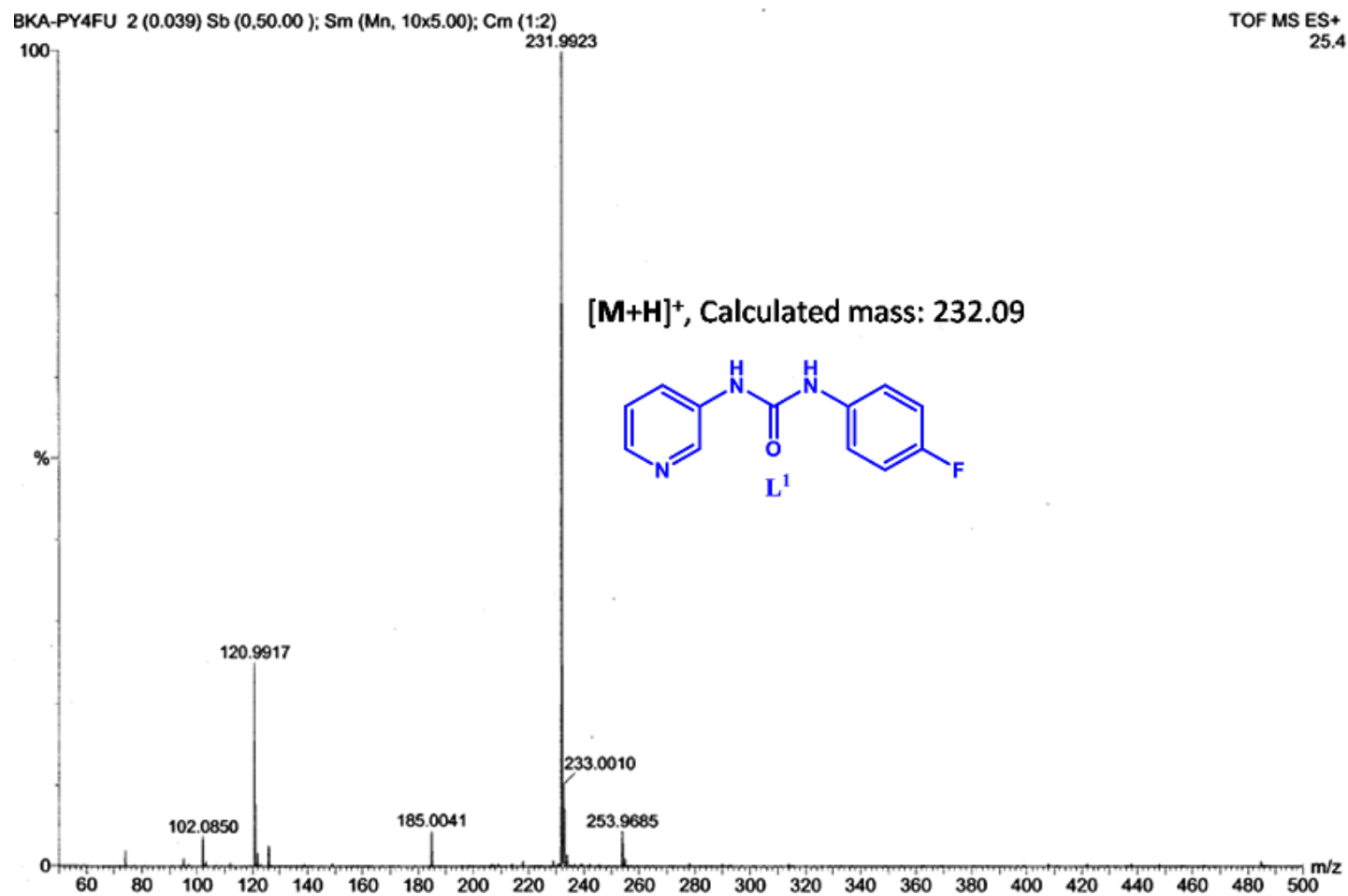




Figure 6S.  $^1\text{H-NMR}$  spectrum of  $\text{L}^1$

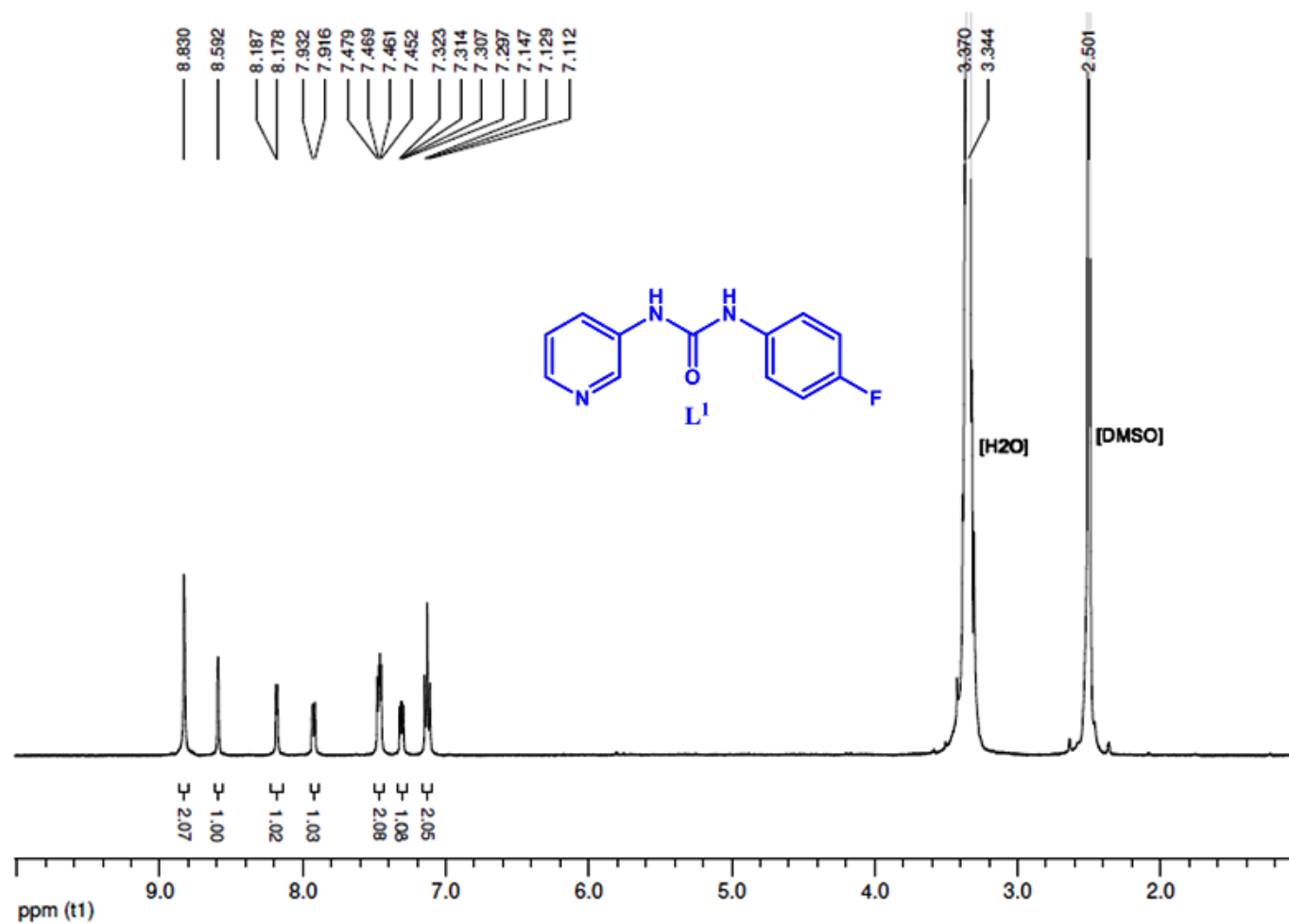


Figure 7S.  $^{13}\text{C}$ -NMR spectrum of  $\text{L}^1$

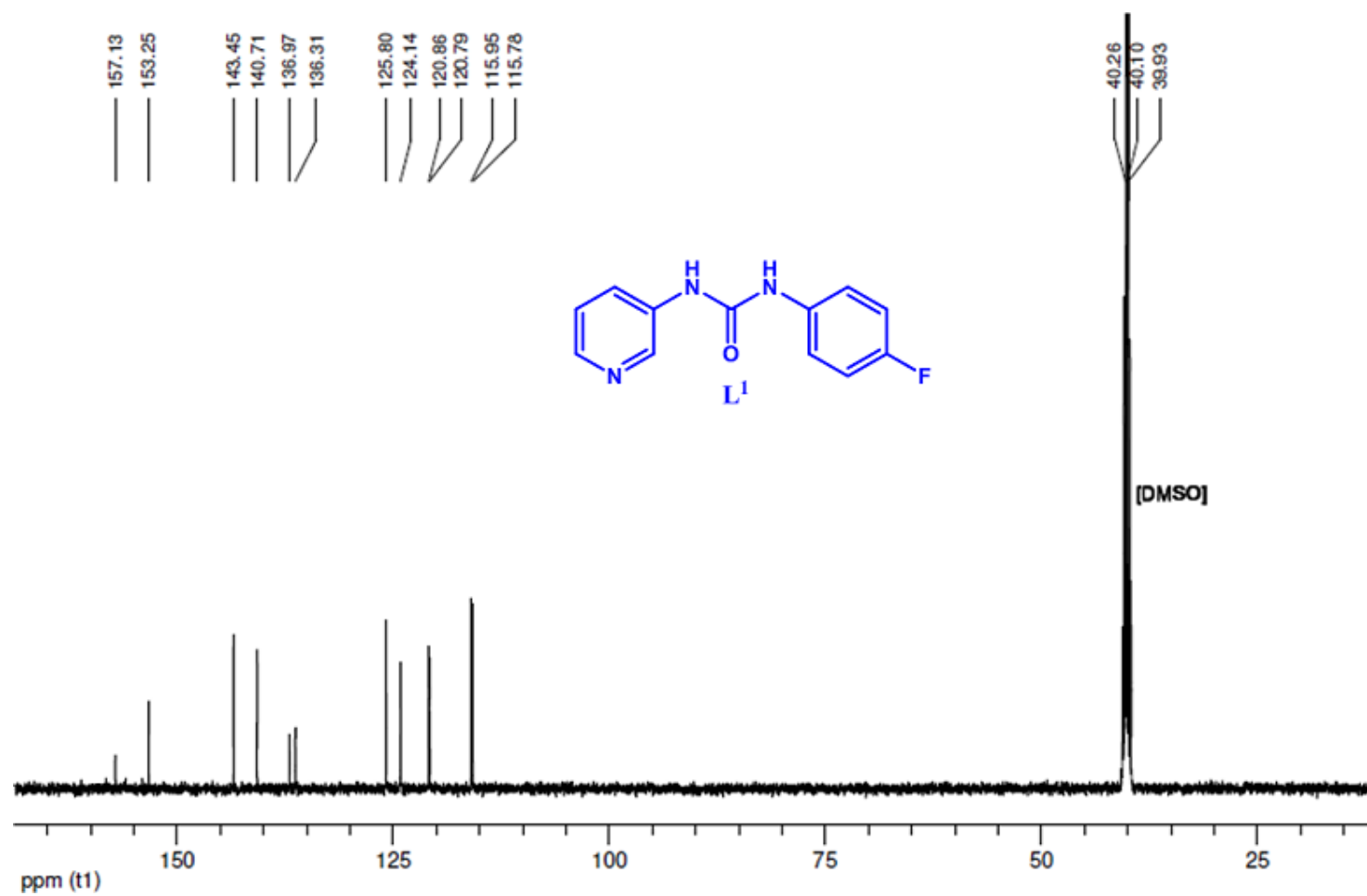


Figure 8S. ESI-MS spectrum of  $L^2$

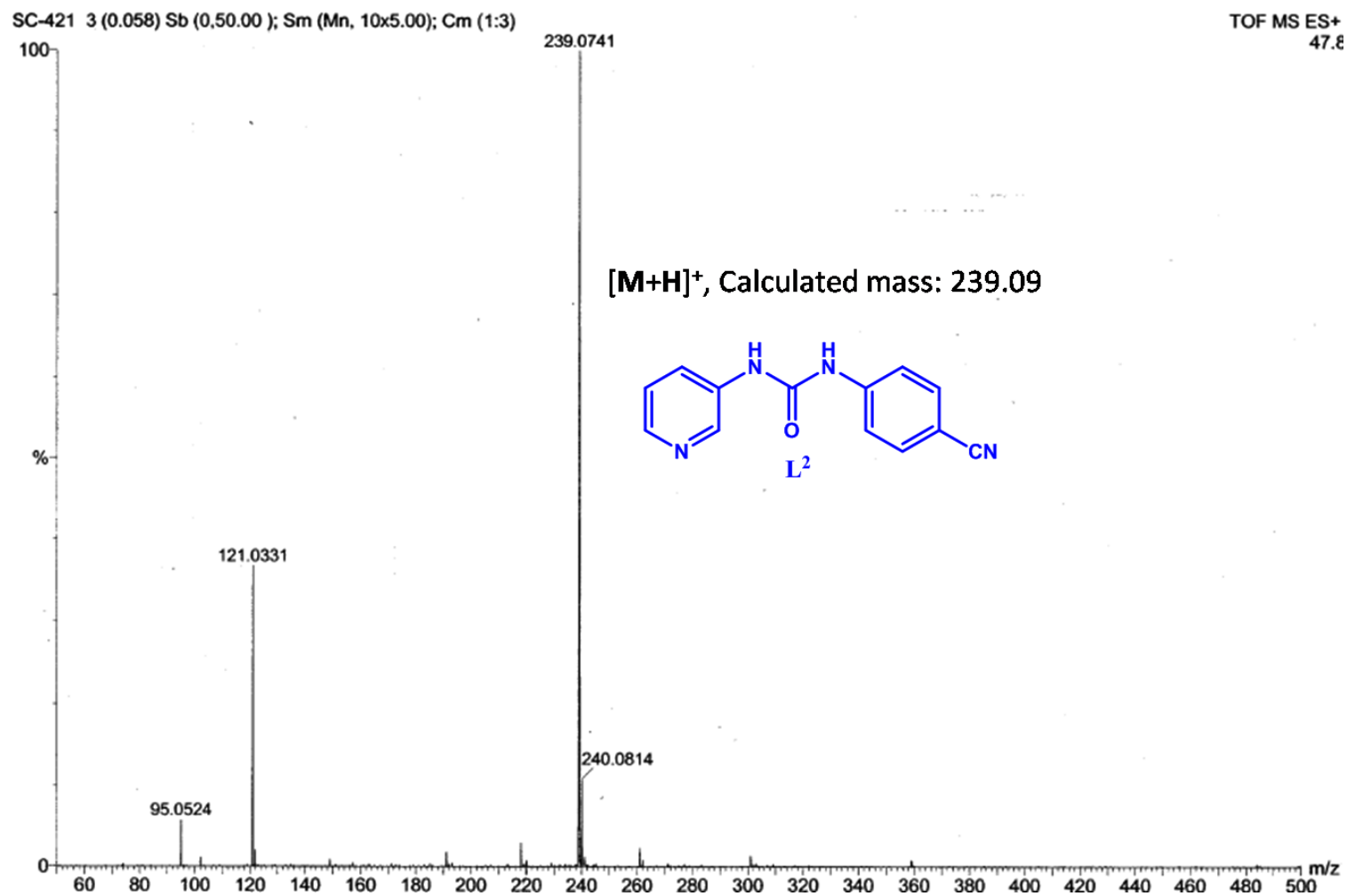


Figure 9S:  $^1\text{H-NMR}$  spectrum of  $\text{L}^2$

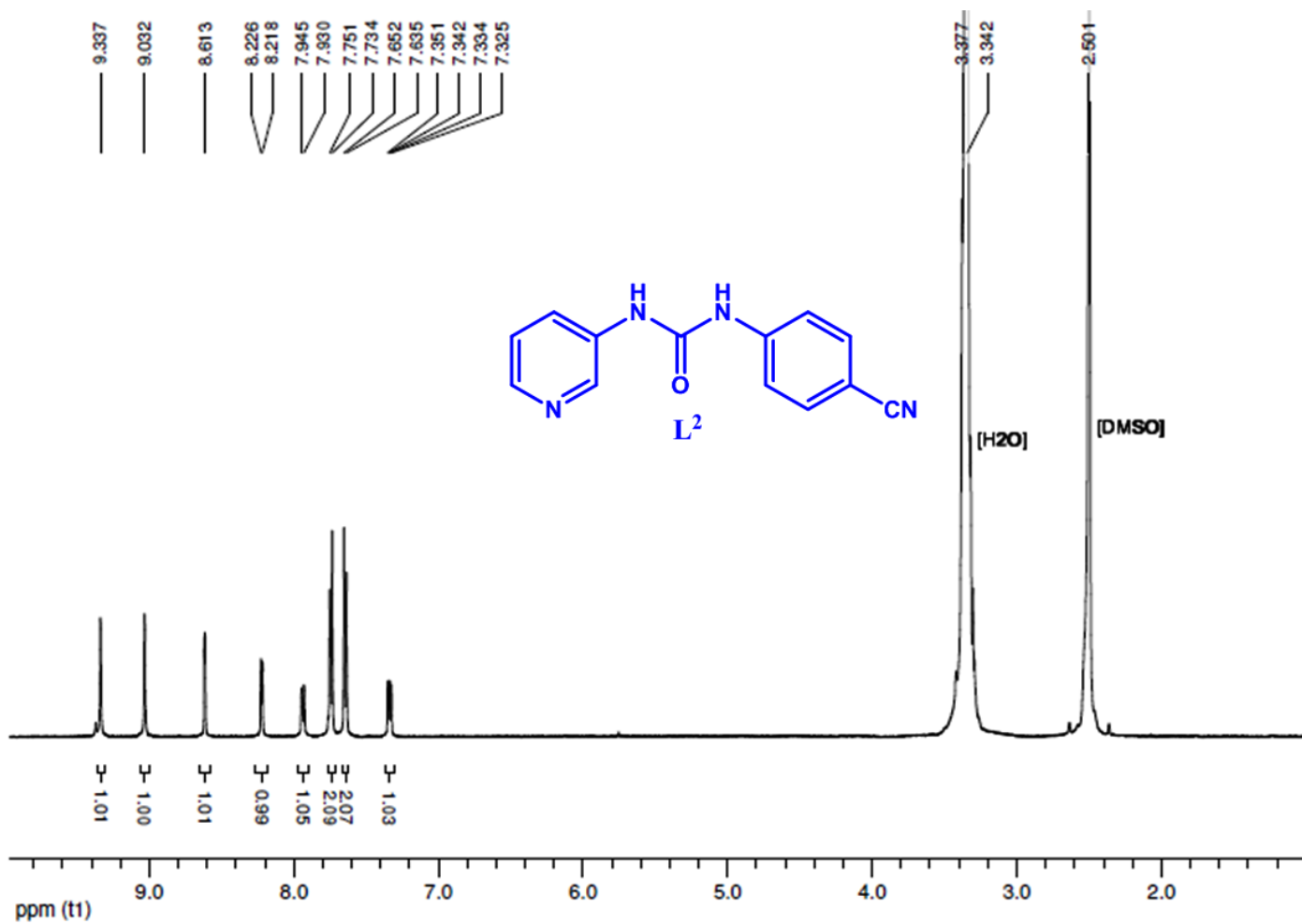
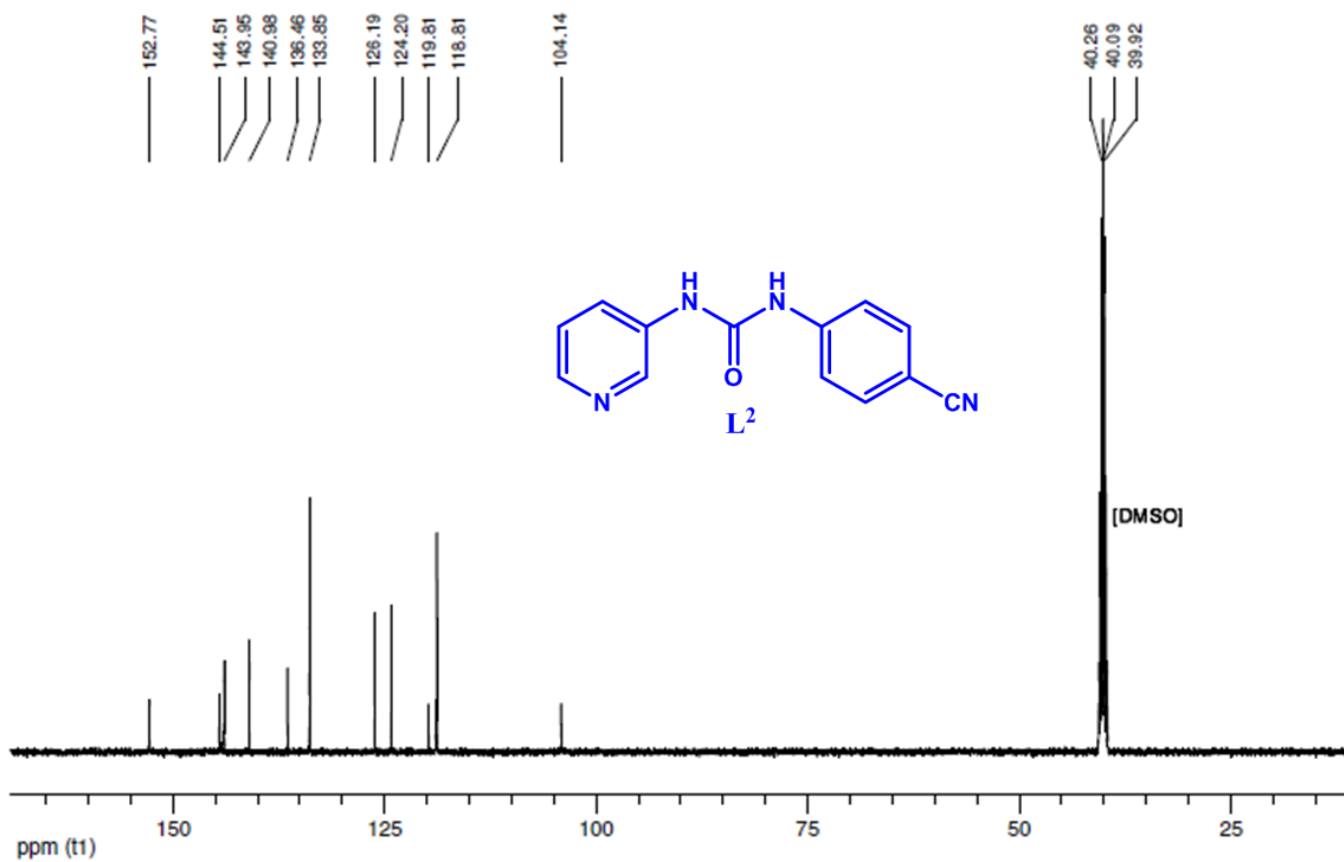
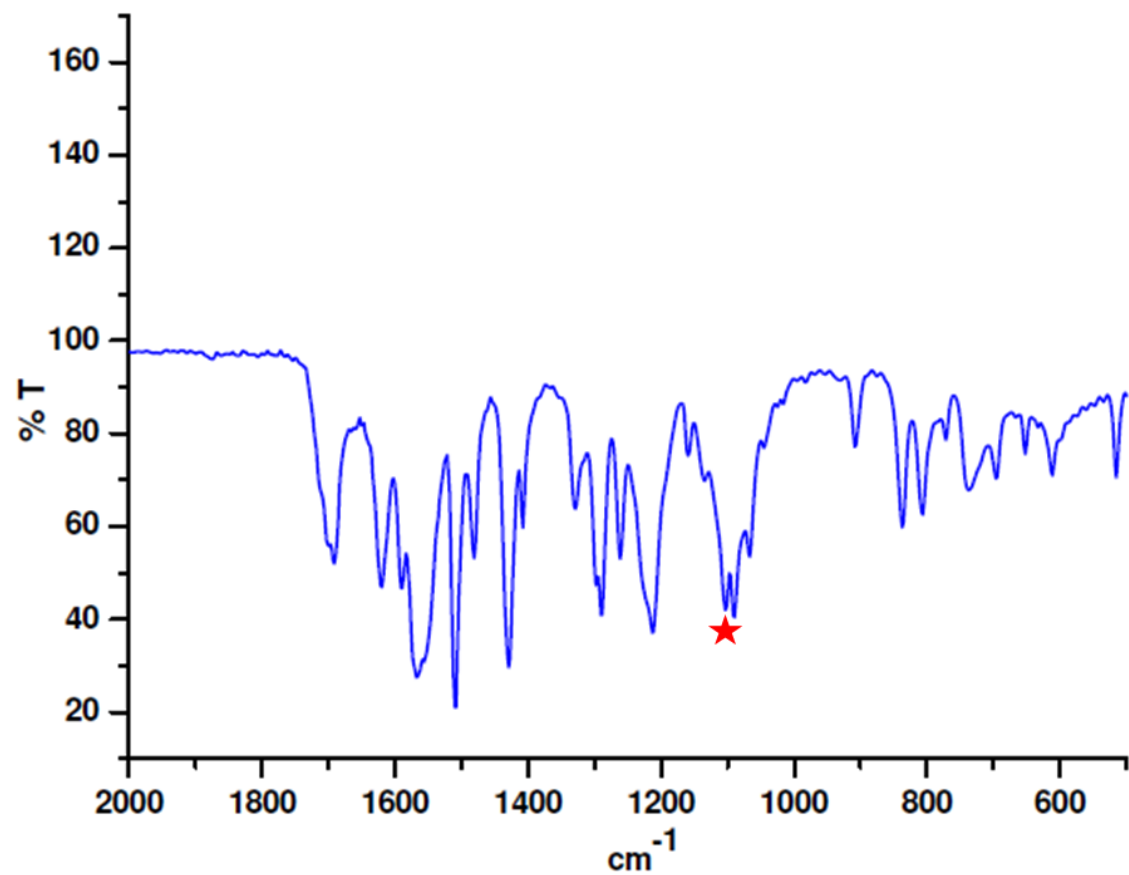


Figure 10S.  $^{13}\text{C}$ -NMR spectrum of  $\text{L}^2$

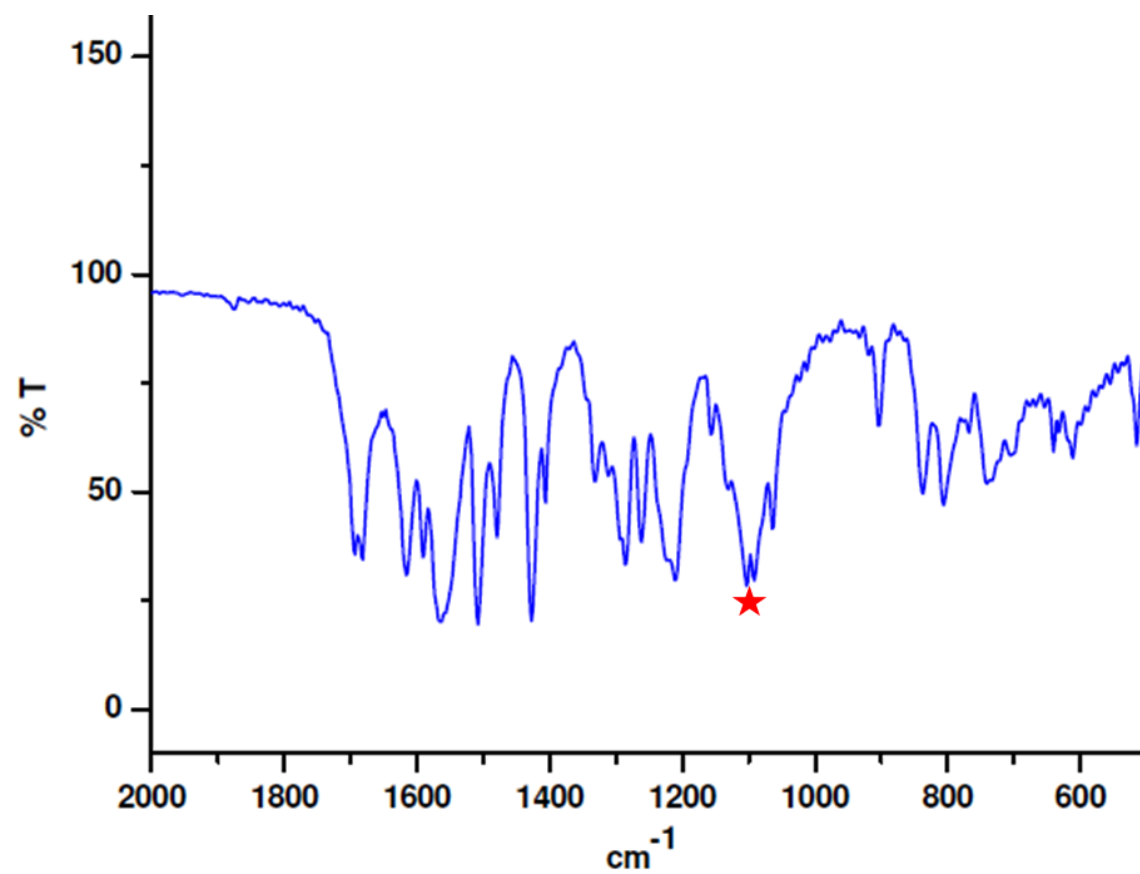


**Figure 11S.** FT-IR spectrum of complex **1**



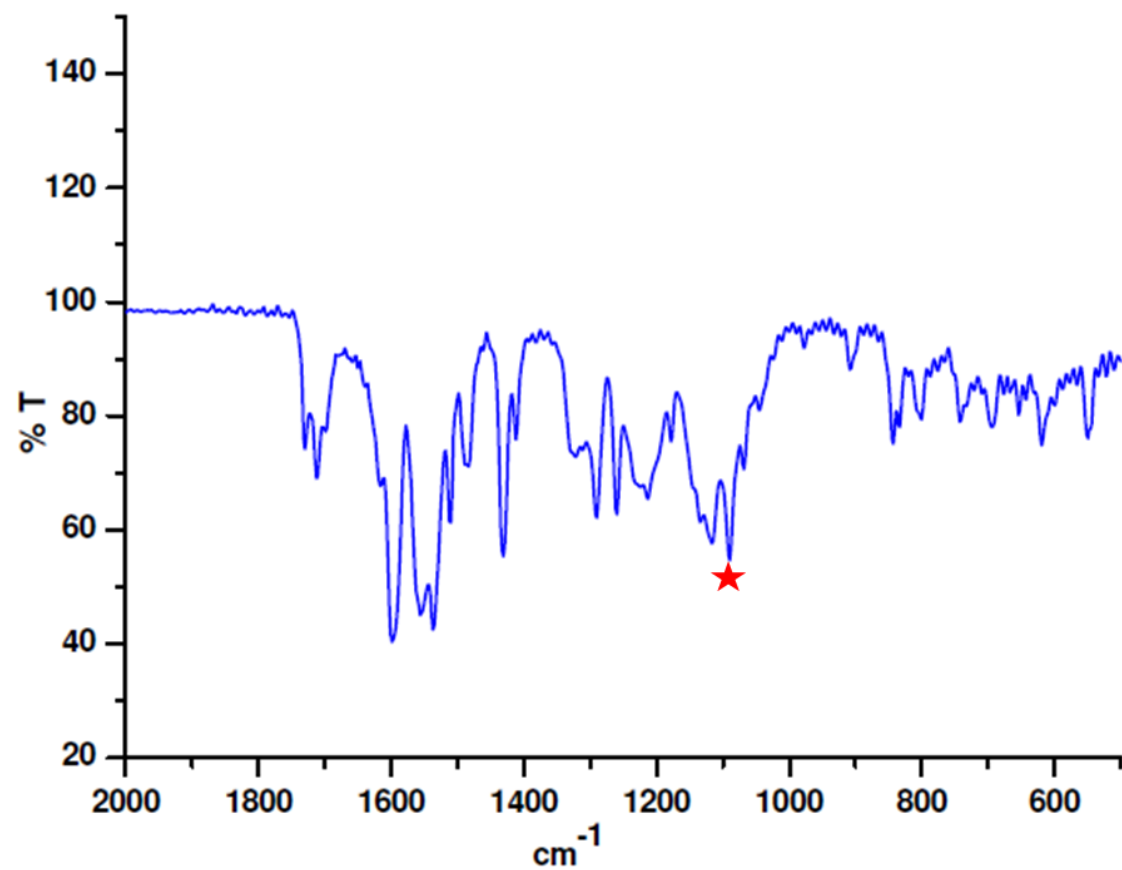
Peak at 1100 cm<sup>-1</sup> (symmetric stretching frequency of SO<sub>4</sub><sup>2-</sup>) indicate the presence of SO<sub>4</sub><sup>2-</sup>.

**Figure 12S.** FT-IR spectrum of complex **2**



Peak at  $1105\text{ cm}^{-1}$  (symmetric stretching frequency of  $\text{SO}_4^{2-}$ ) indicate the presence of  $\text{SO}_4^{2-}$ .

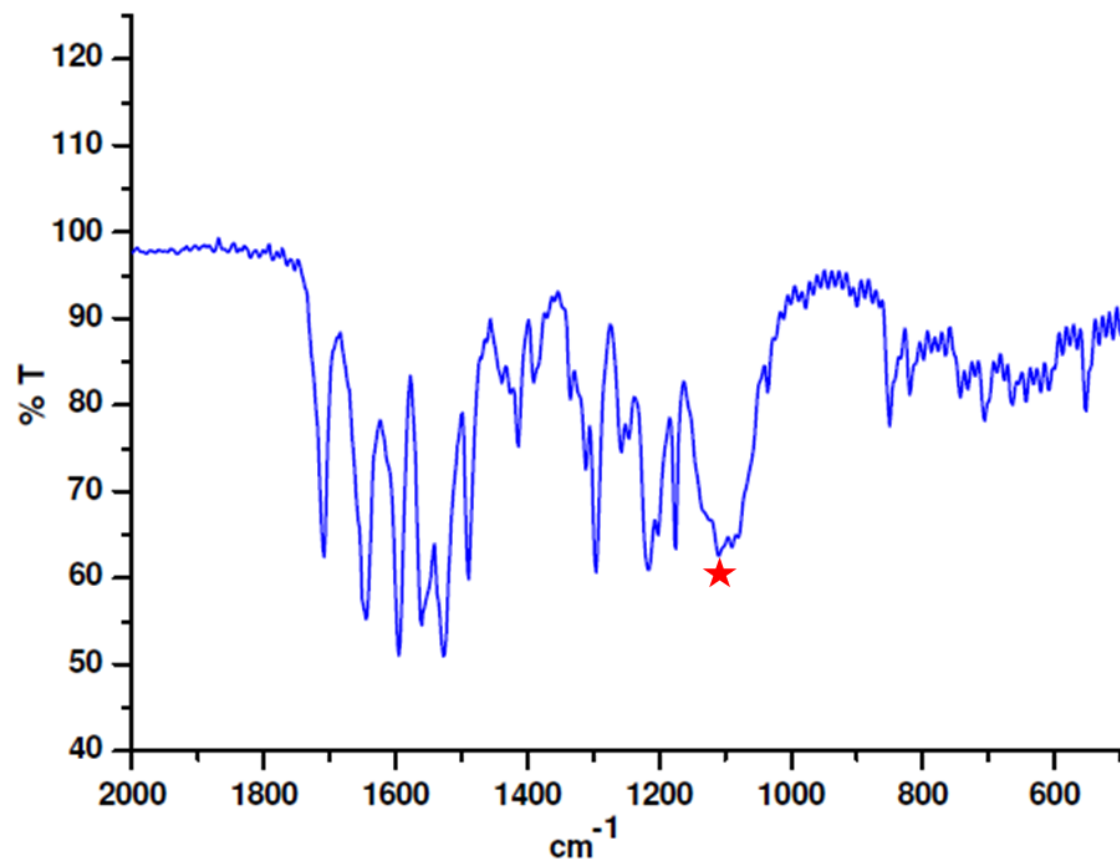
**Figure 13S.** FT-IR spectrum of complex **3**



Peak at  $1116\text{ cm}^{-1}$  (symmetric stretching frequency of  $\text{SO}_4^{2-}$ ) indicate the presence of  $\text{SO}_4^{2-}$ .



**Figure 14S.** FT-IR spectrum of complex **4**



Peak at 1110 cm<sup>-1</sup> (symmetric stretching frequency of SO<sub>4</sub><sup>2-</sup>) indicate the presence of SO<sub>4</sub><sup>2-</sup>.

Figure 15S. Comparison of FT-IR spectra of complexes 1, 1', 1'' and 1'''

