

**Phosphorus-nitrogen Compounds. Part 73. Dispiromono and Dispirobicyclotetraphosphazene Derivatives: Syntheses, Spectroscopic, Crystallographic and Thermal Studies**

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<sup>a</sup>

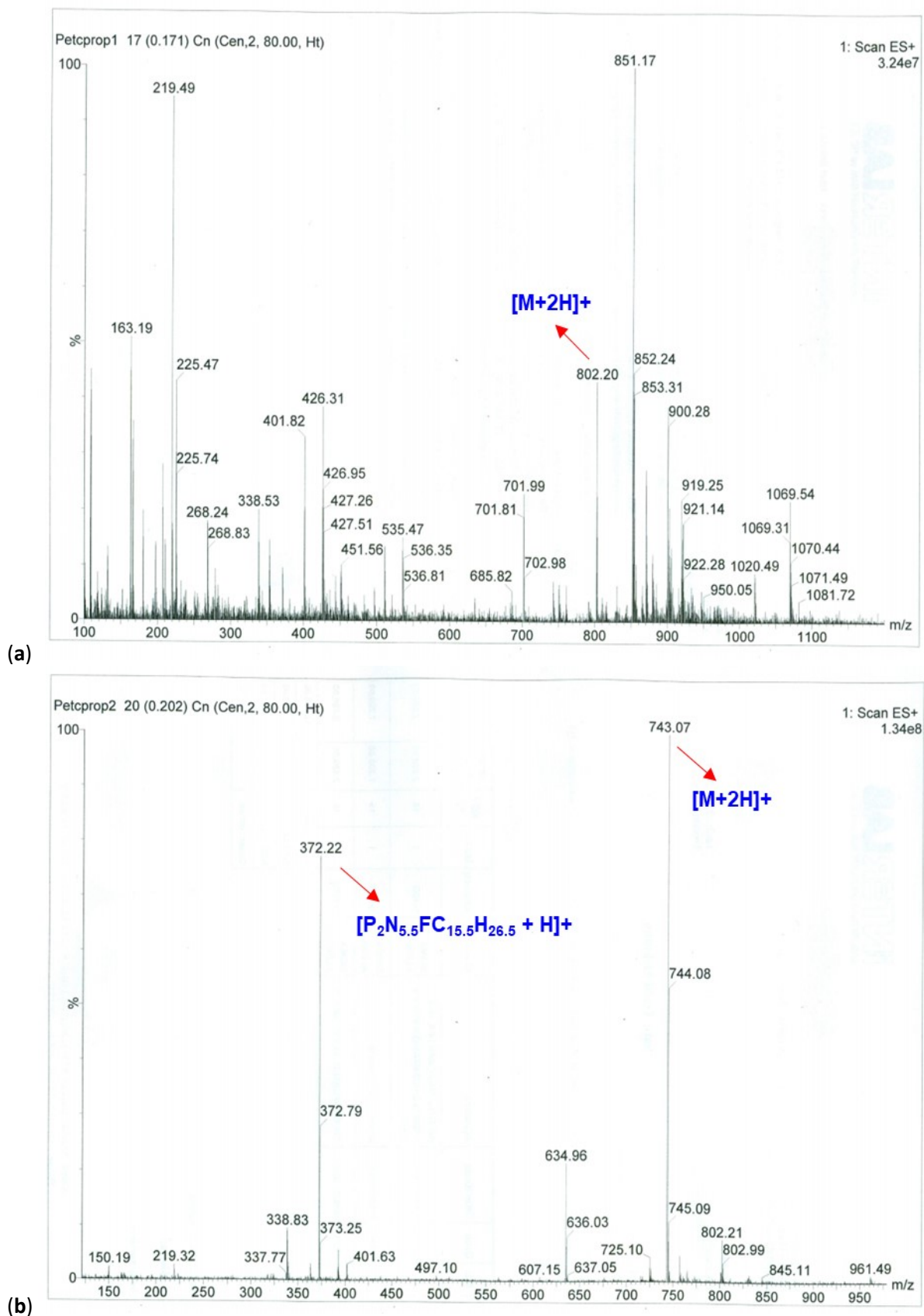
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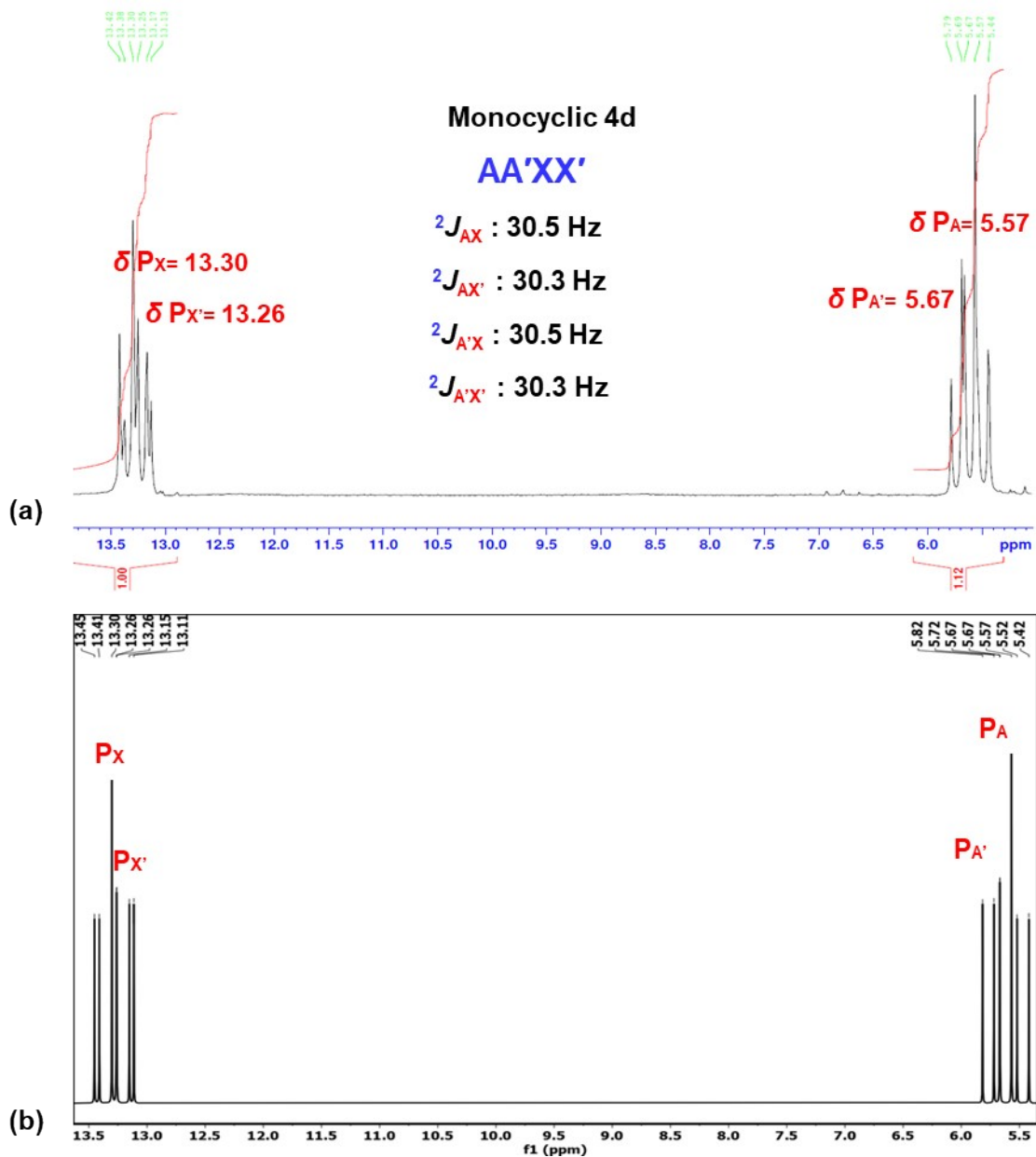
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**Electronic supplementary information (ESI)**

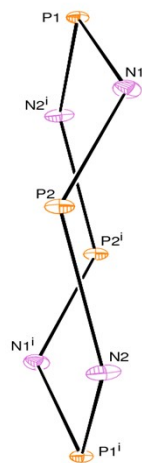
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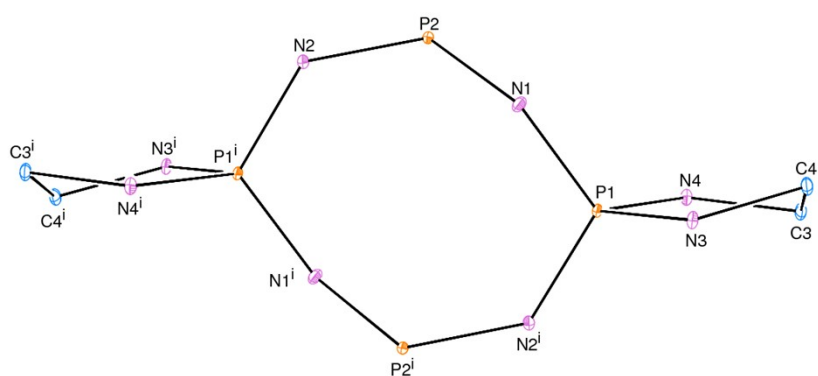




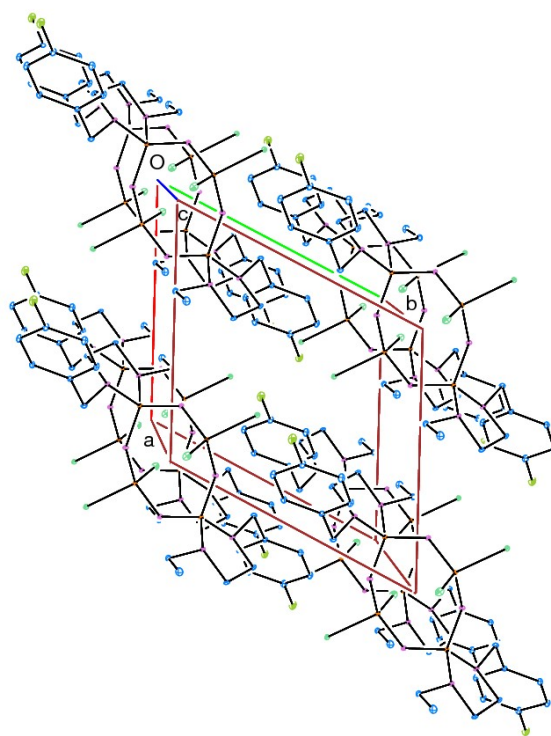
**Figure S2.** (a) In  $\text{CDCl}_3$ , the experimental and (b) simulated  ${}^{31}\text{P} \{^1\text{H}\}$  spectrum of the pure monocyclic **4d**.



(a)

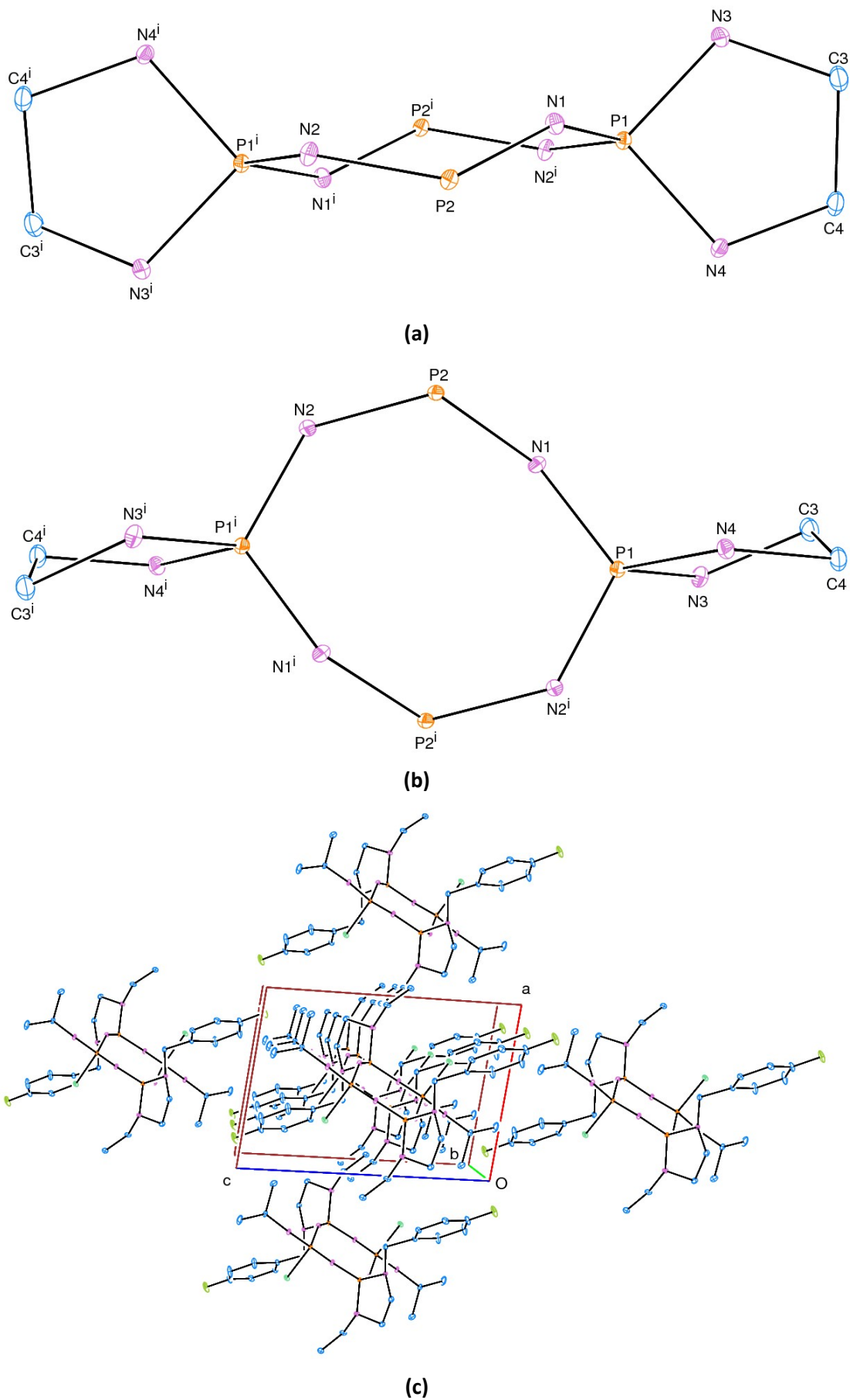


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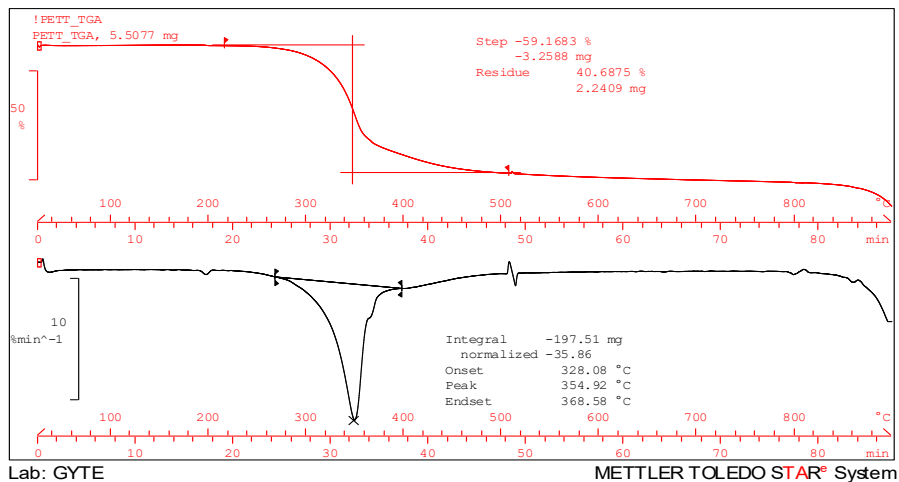


(c)

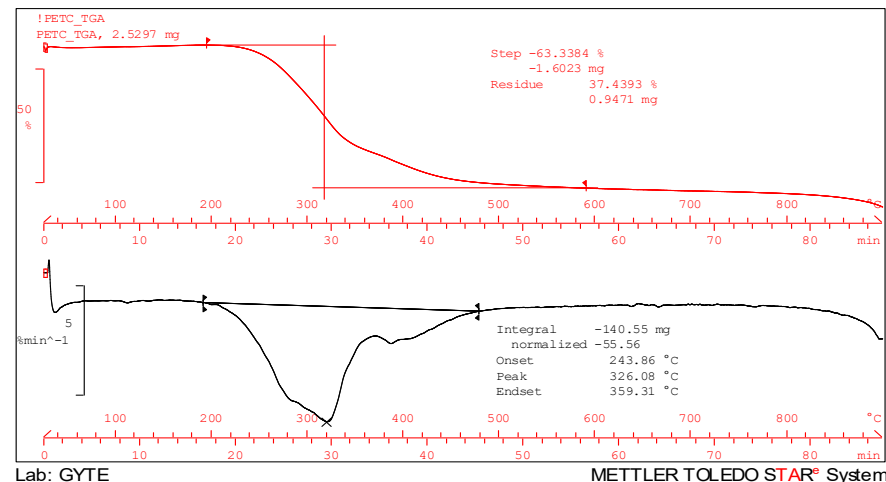
**Figure S3.** The conformations of (a) the tetramer ring, (b) the five-membered spiro ring and (c) packing diagram of **2**.



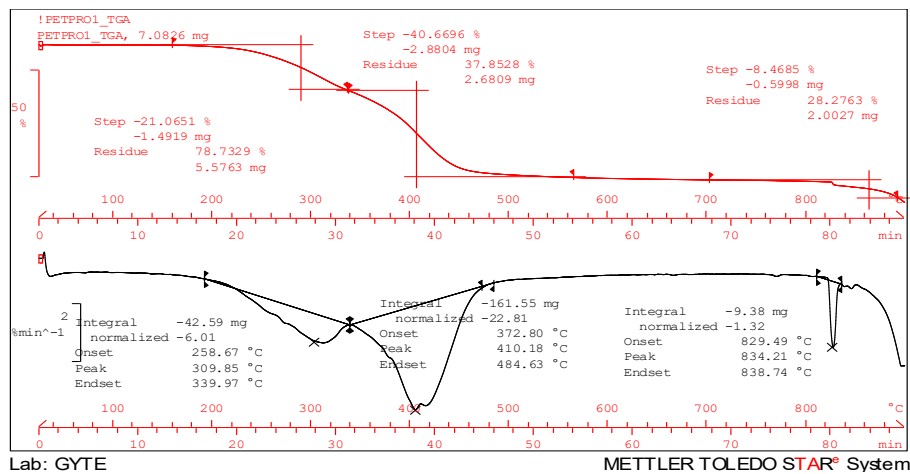
**Figure S4.** The conformations of (a) the tetramer ring, (b) the five-membered spiro ring and (c) packing diagram of **4c**.



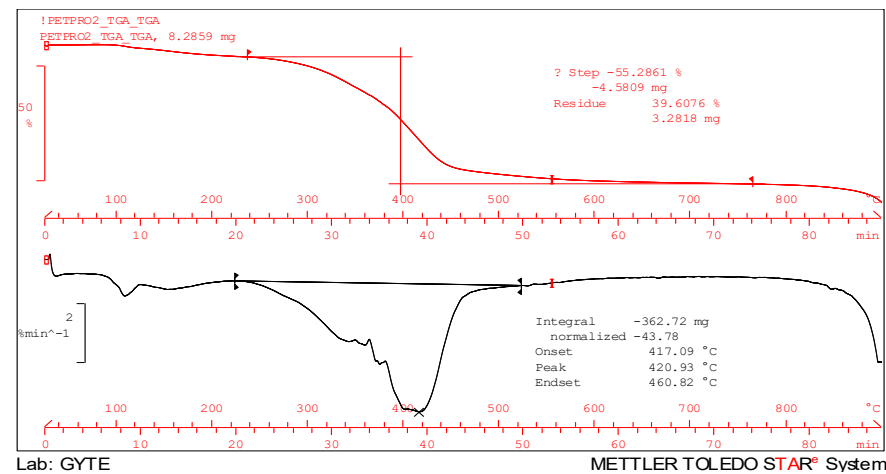
2



3

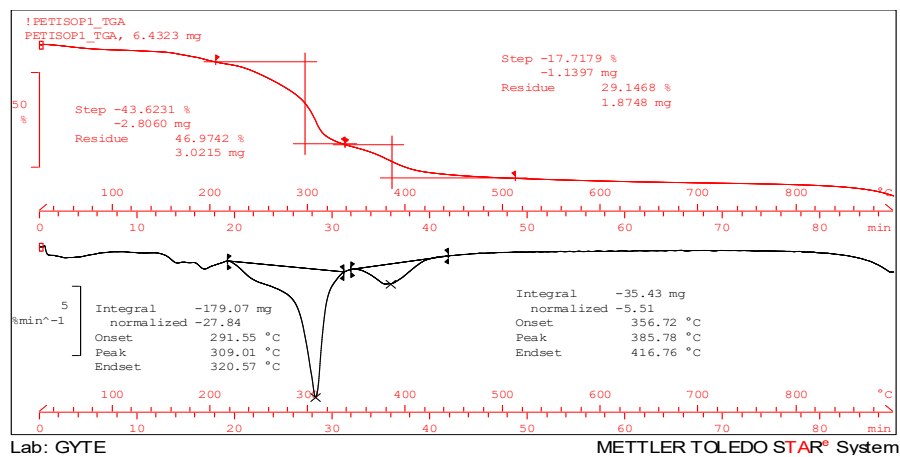


4d

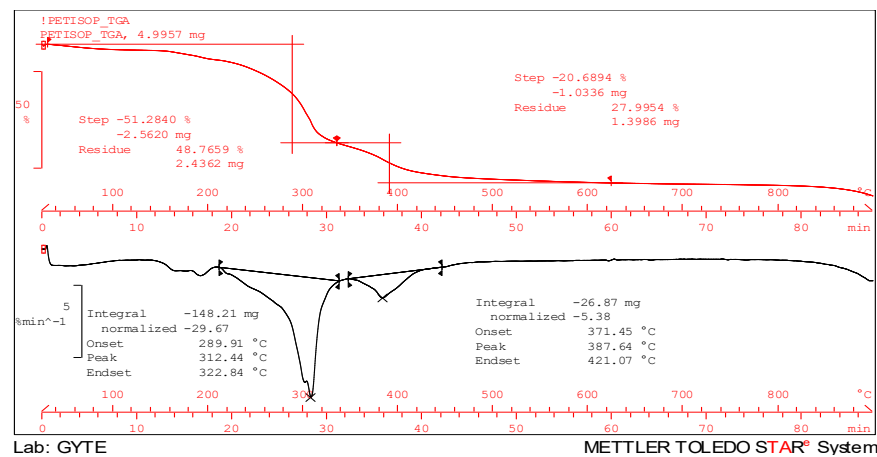


5b

Figure S5. TG curves of the cyclotetraphosphazenes (2, 3, 4d and 5b).



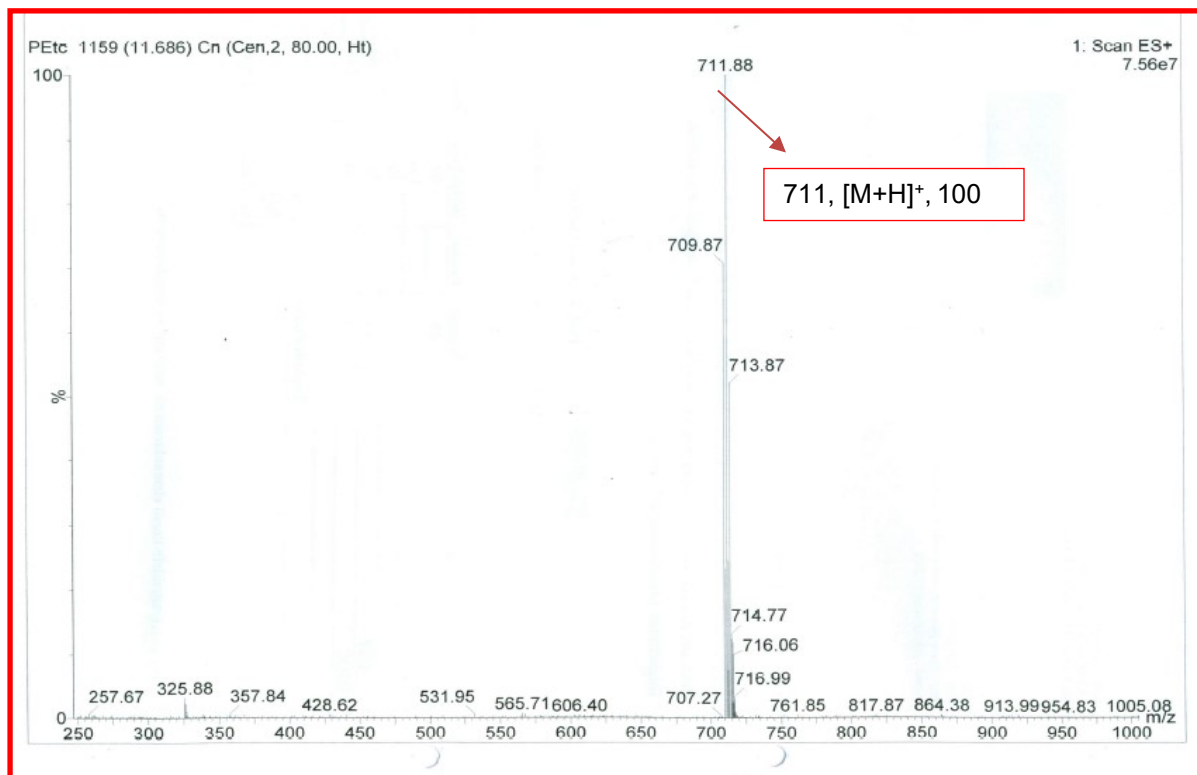
4c



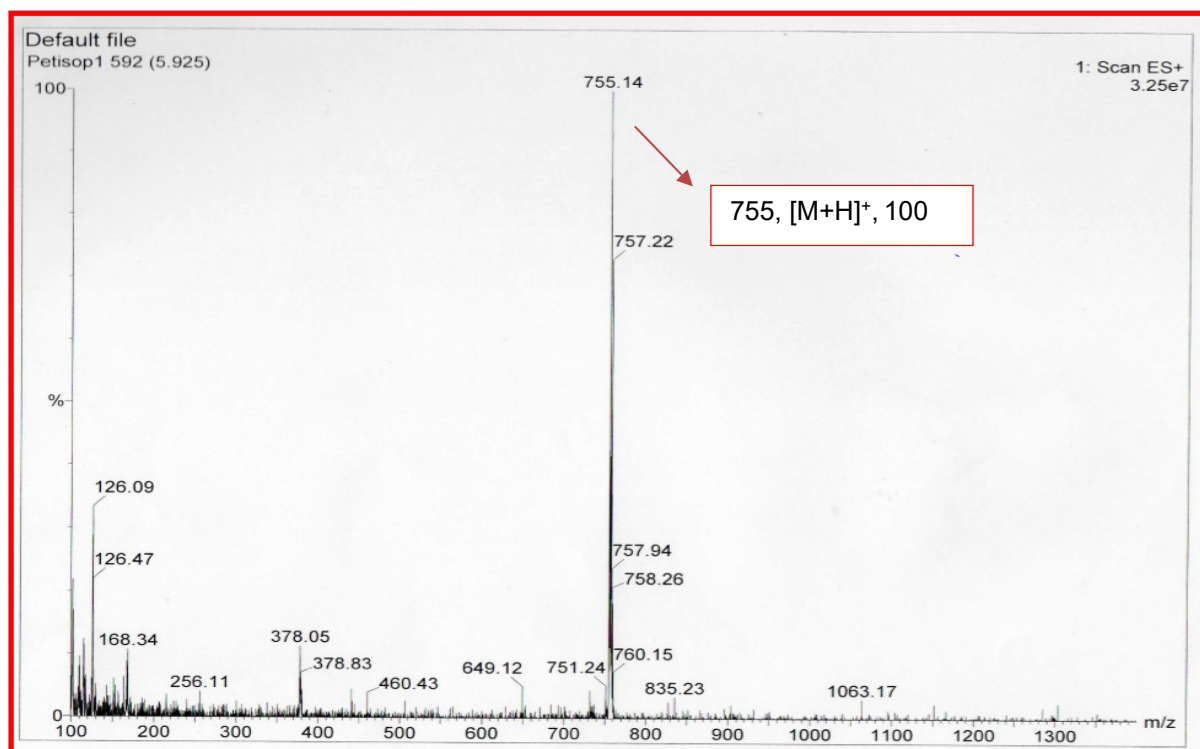
5c

Figure S6. TG curves of the cyclotetraphosphazenes (4c and 5c).

## Section S1. ESI-MS, NMR and FTIR spectra of the compounds

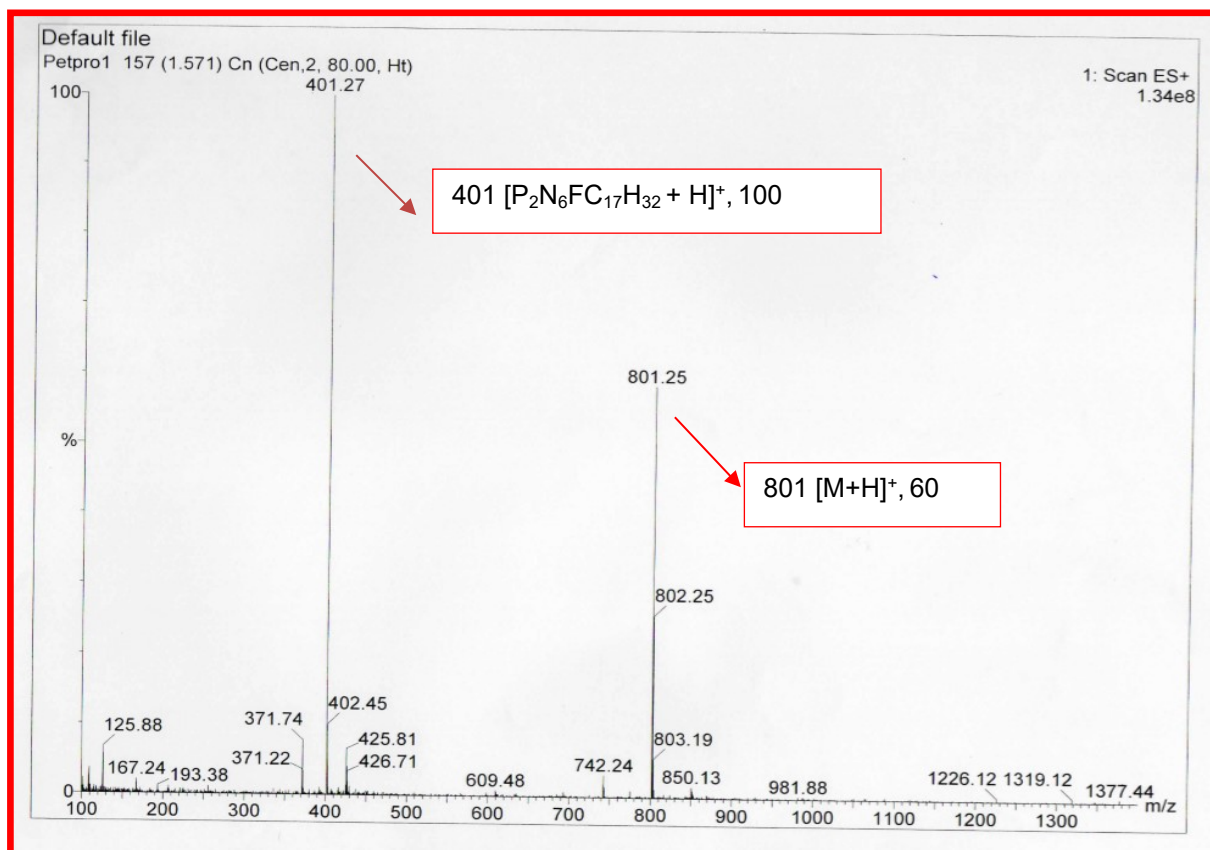


ESI-MS spectra of compound **3**.

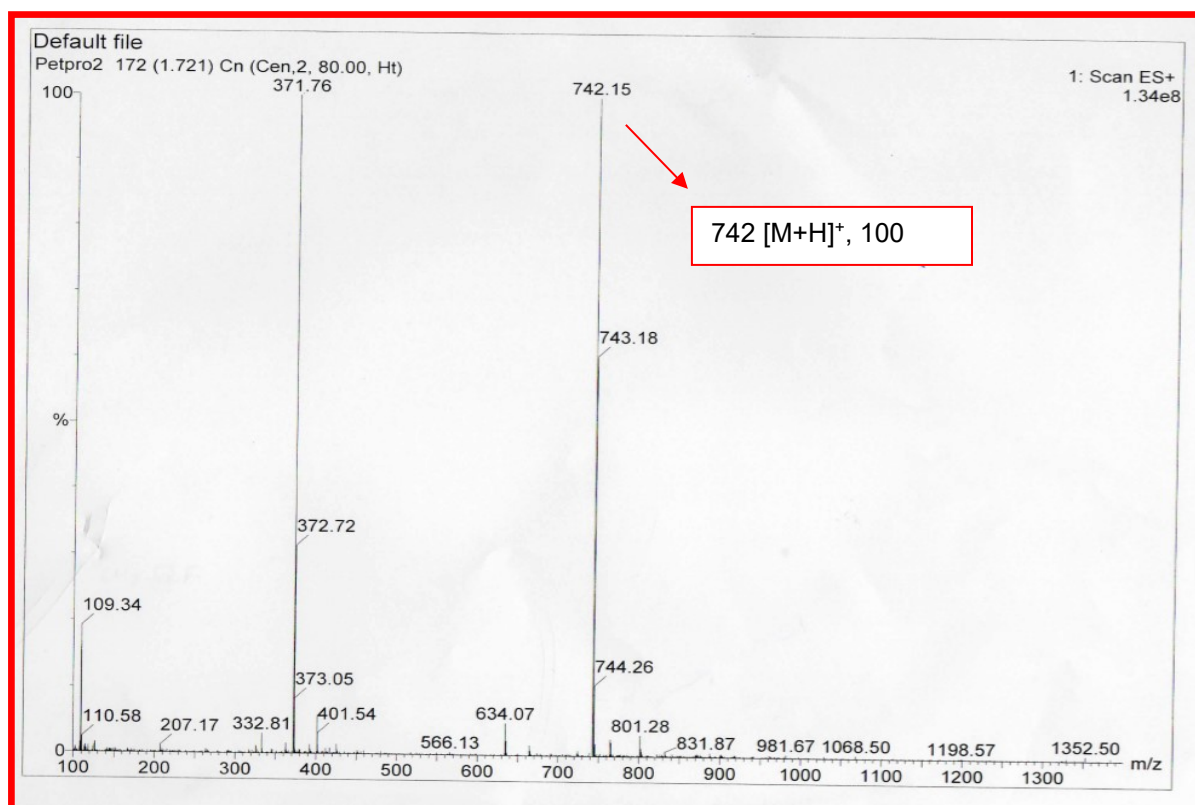


ESI-MS spectra of compound **4c**.

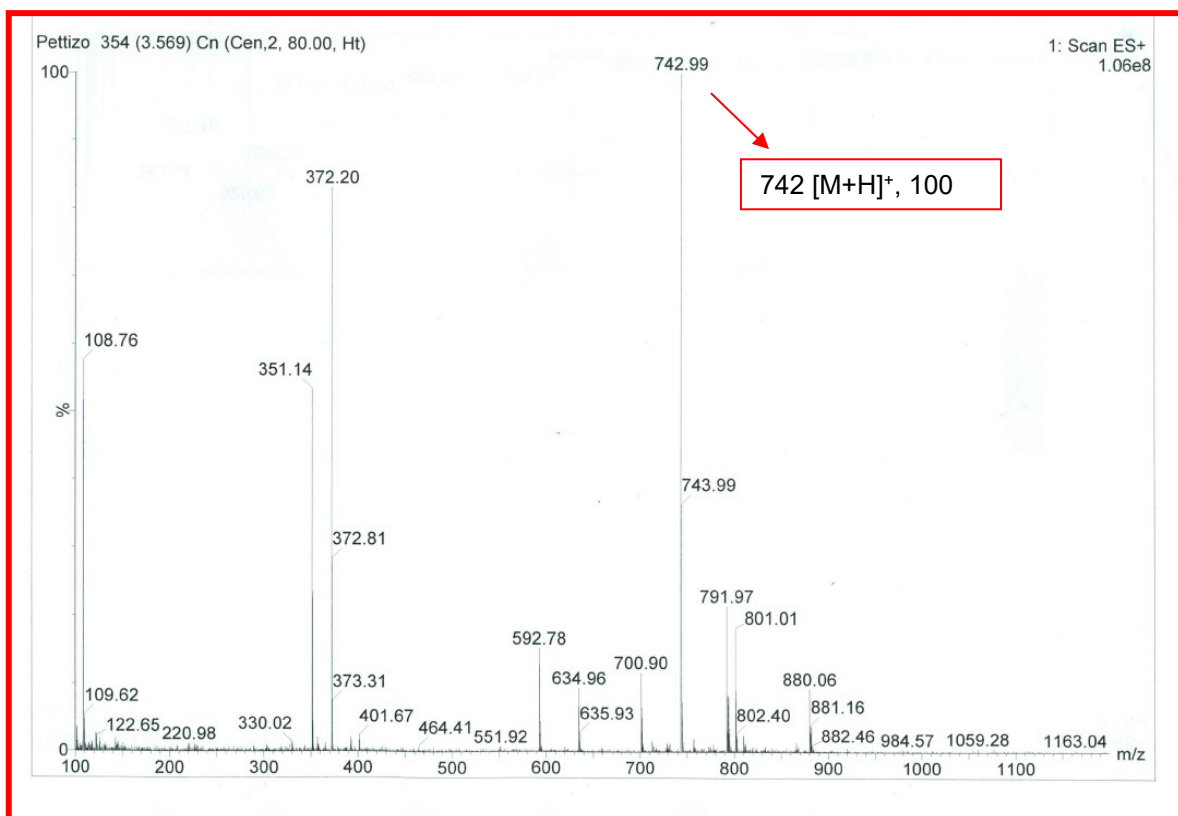




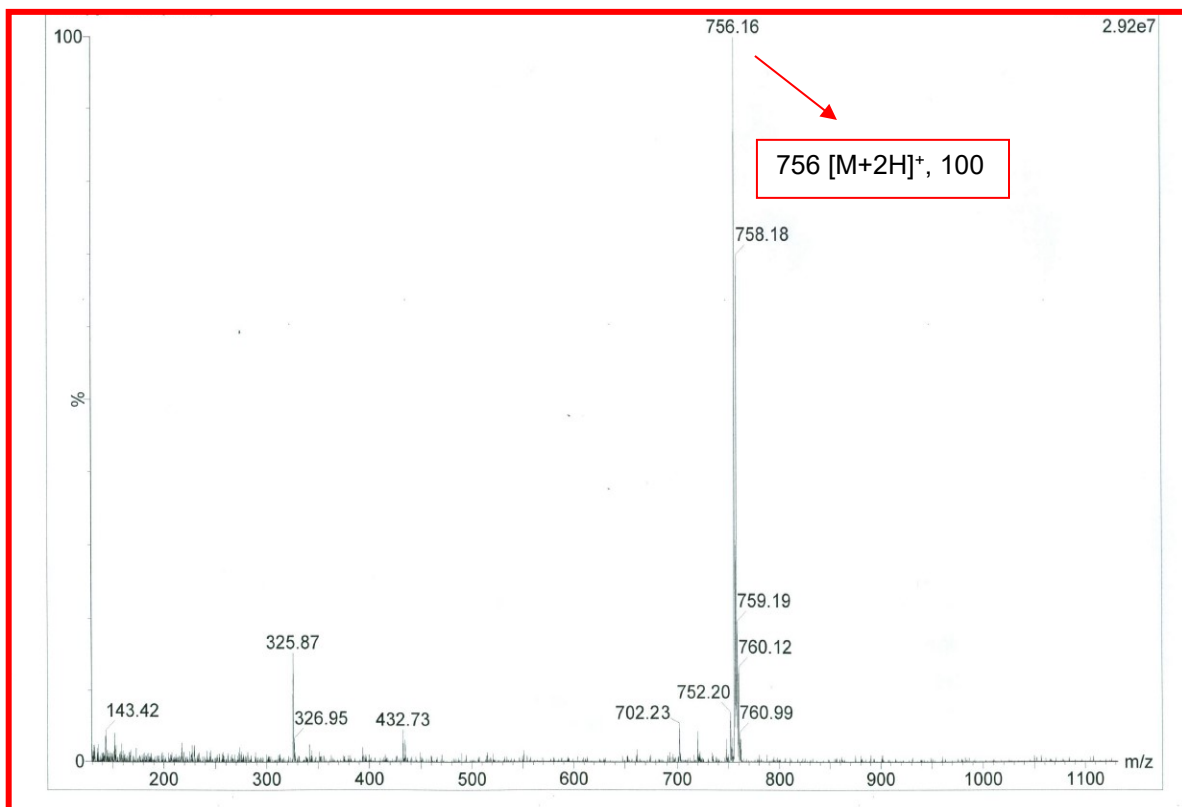
ESI-MS spectra of compound **4d**.



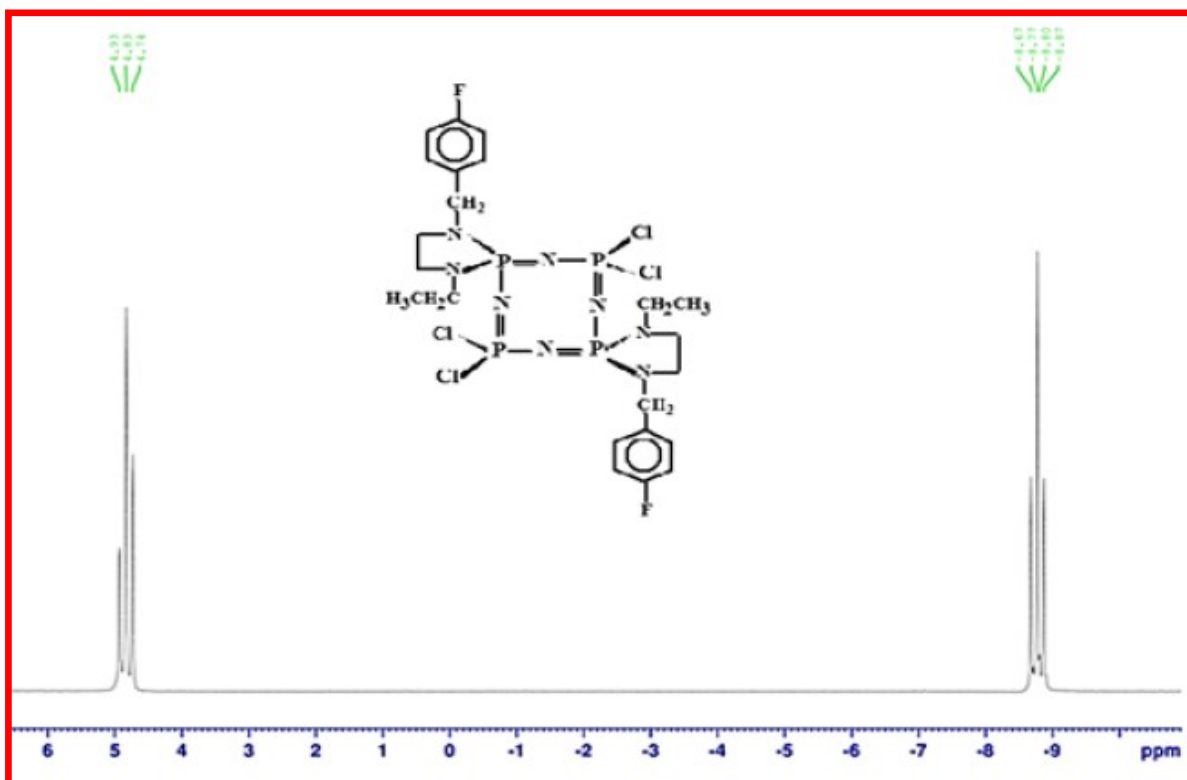
ESI-MS spectra of compound **5b**.



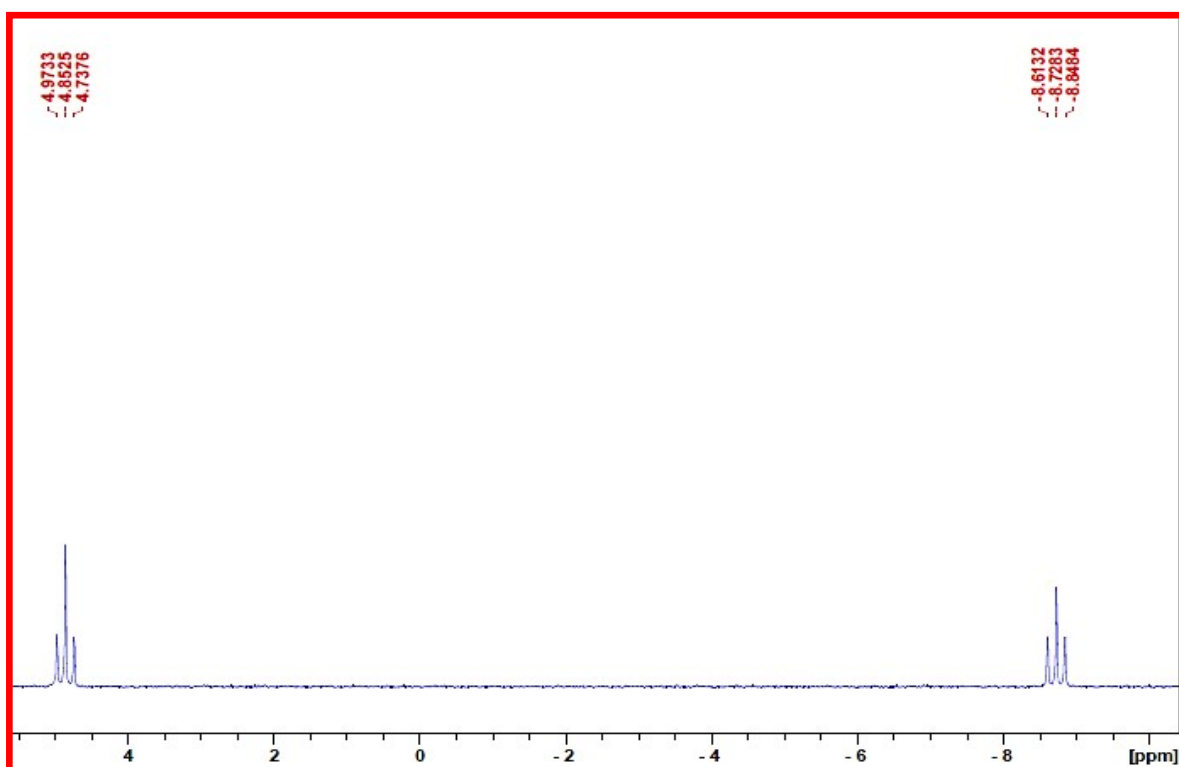
ESI-MS spectra of compound **5c**.



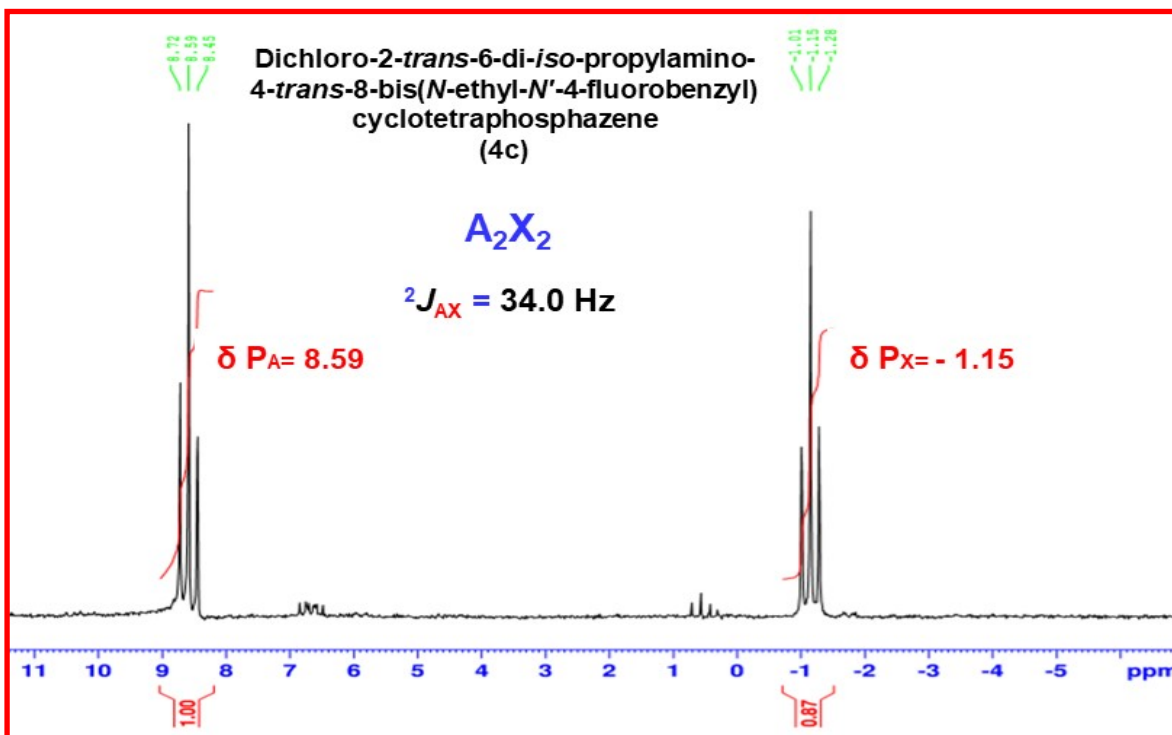
ESI-MS spectra of compound **4b**.



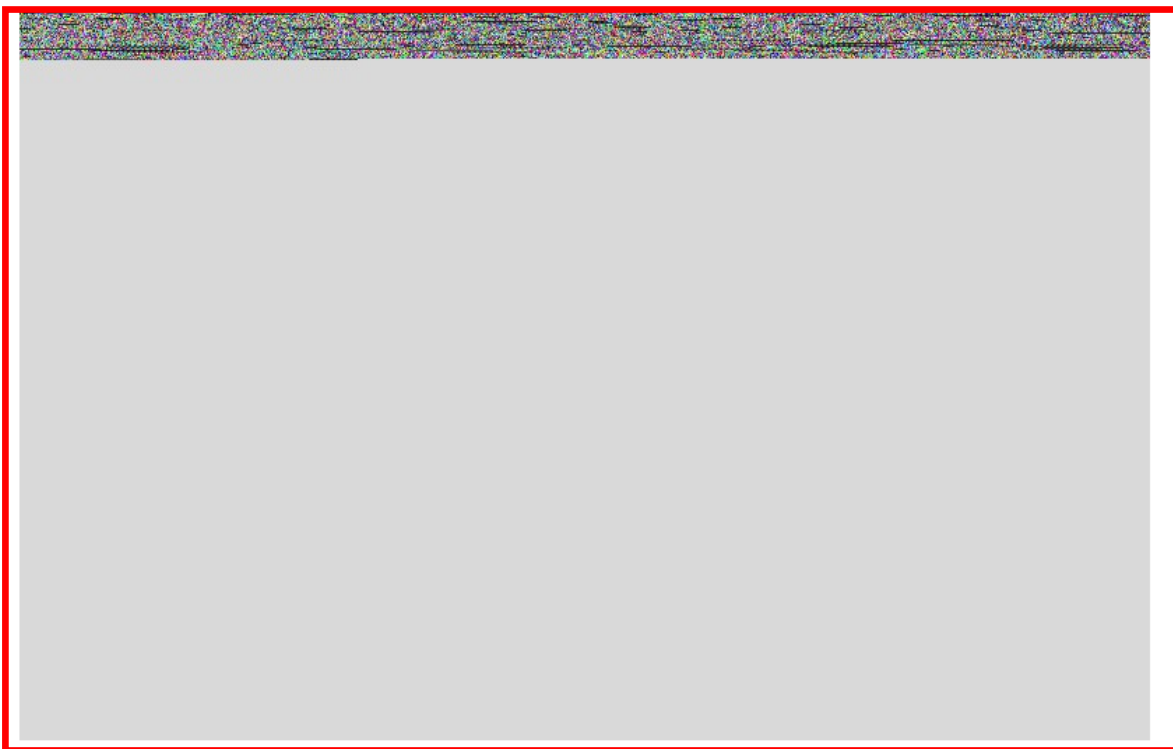
$^{31}\text{P}$  NMR spectrum of compound 2.



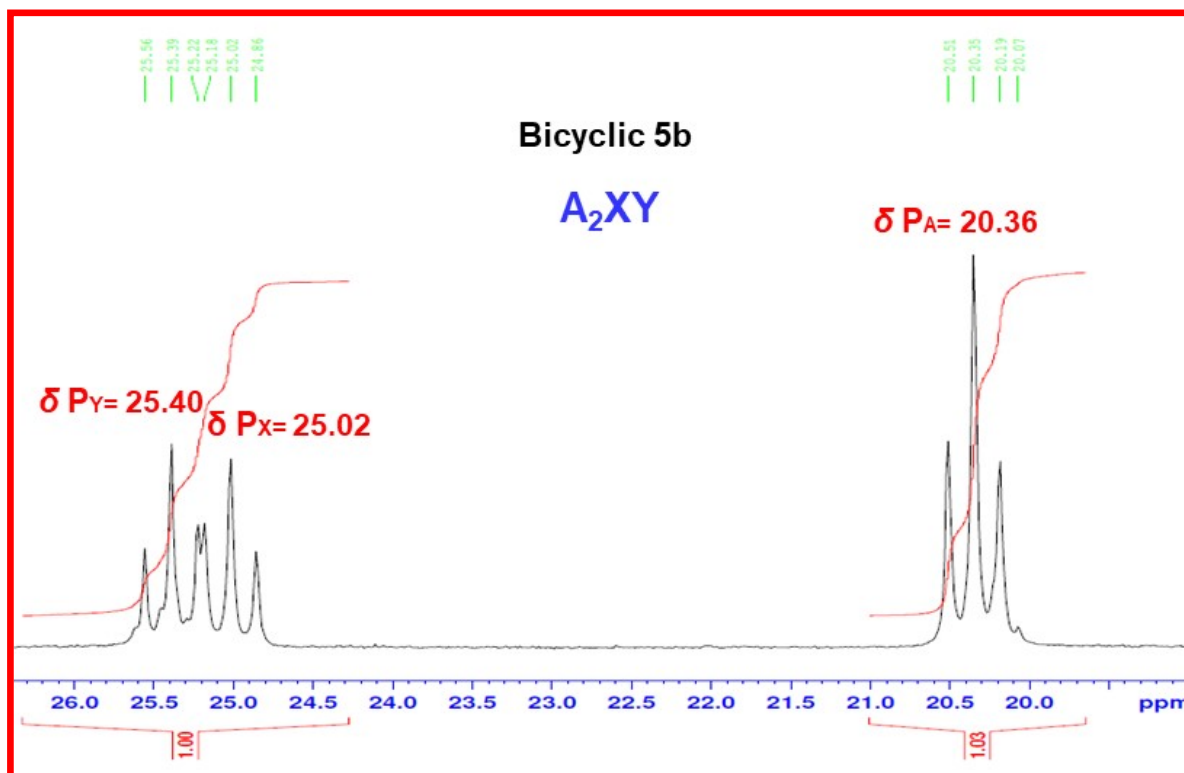
$^{31}\text{P}$  NMR spectrum of compound 3.



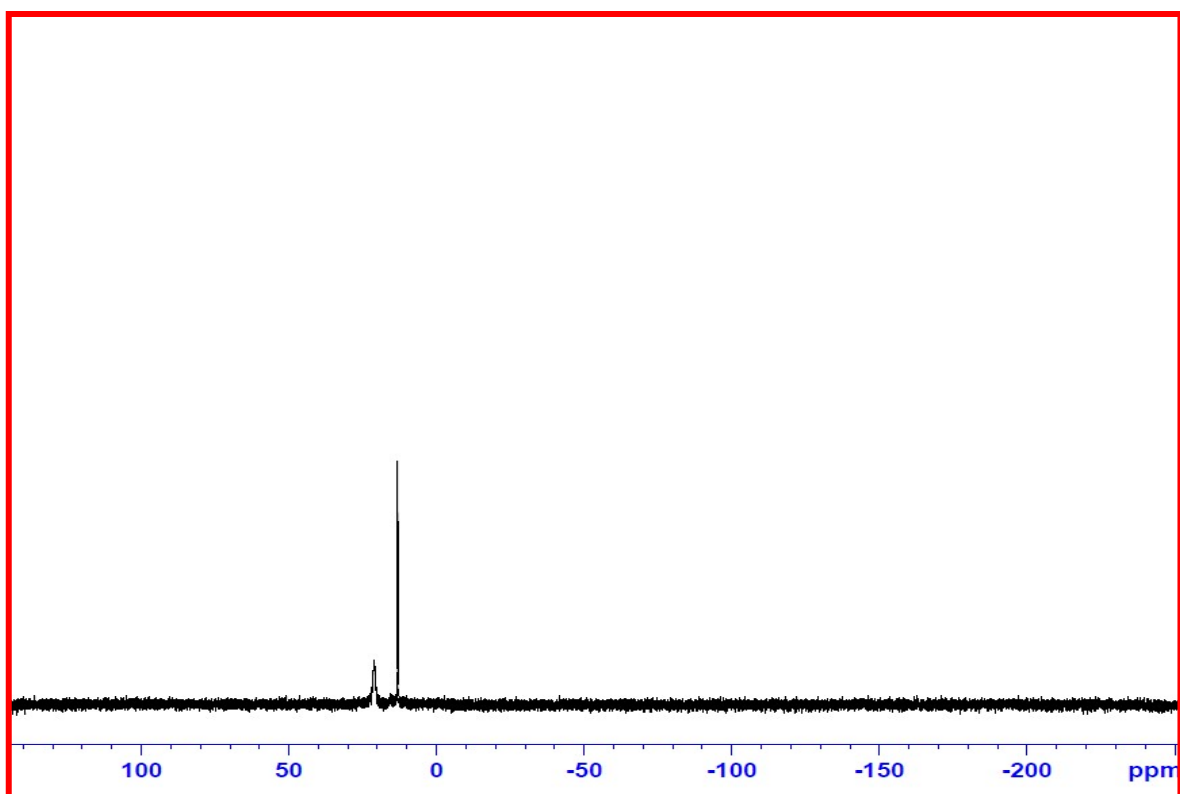
$^{31}\text{P}$  NMR spectrum of compound **4c**.



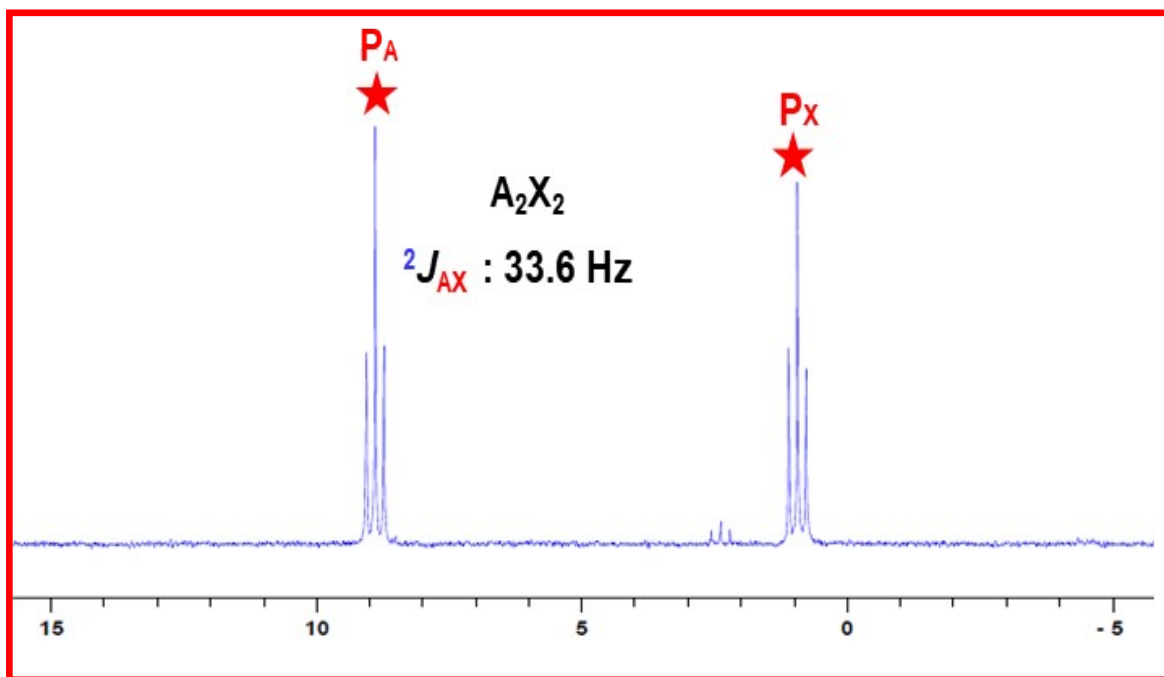
$^{31}\text{P}$  NMR spectrum of compound **4d**.



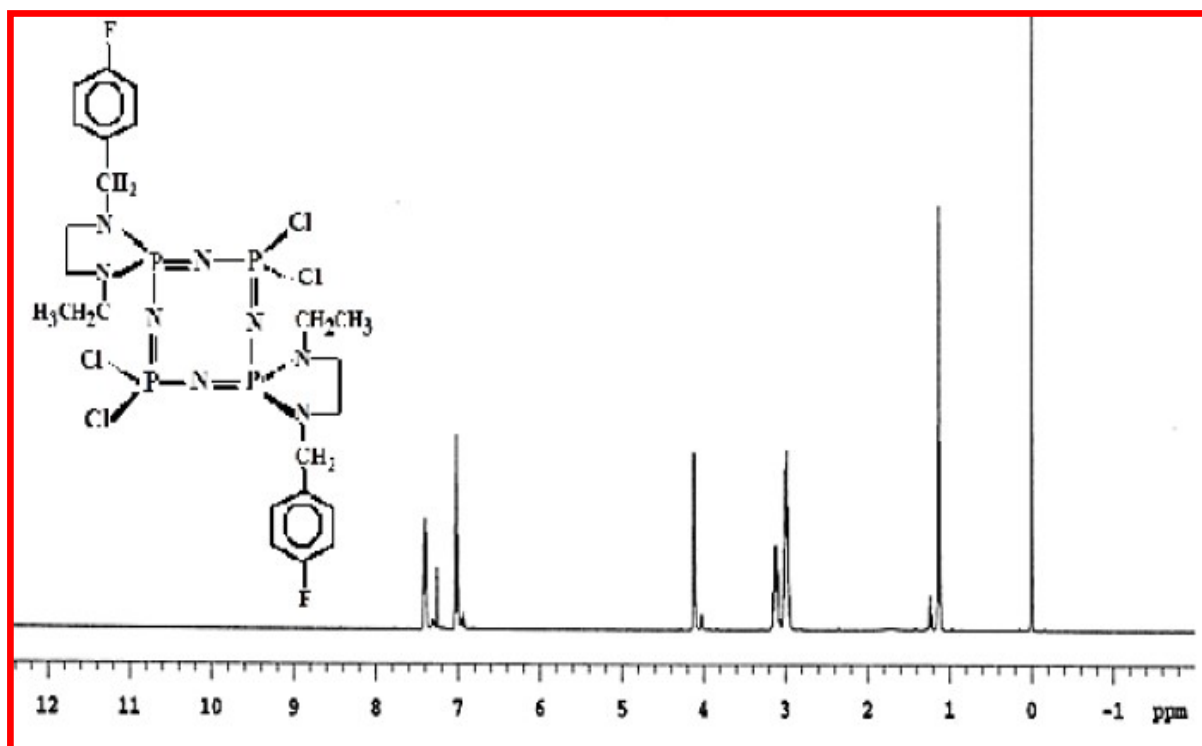
$^{31}\text{P}$  NMR spectrum of compound **5b**.



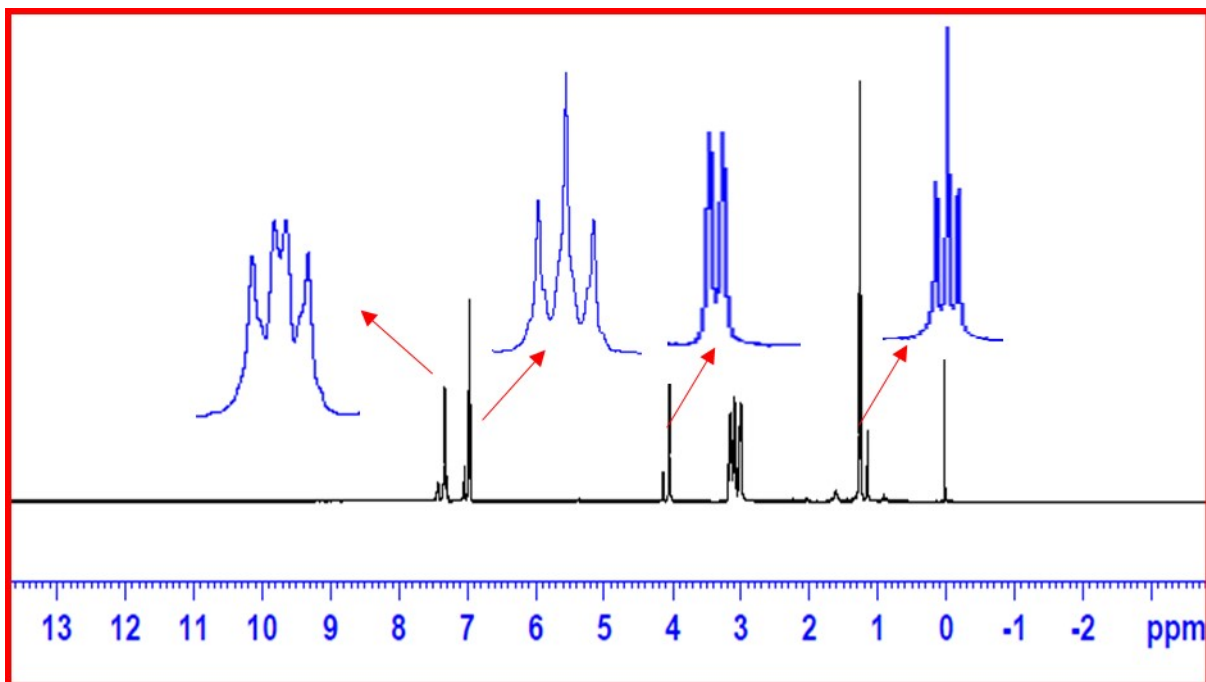
$^{31}\text{P}$  NMR spectrum of compound **5c**.



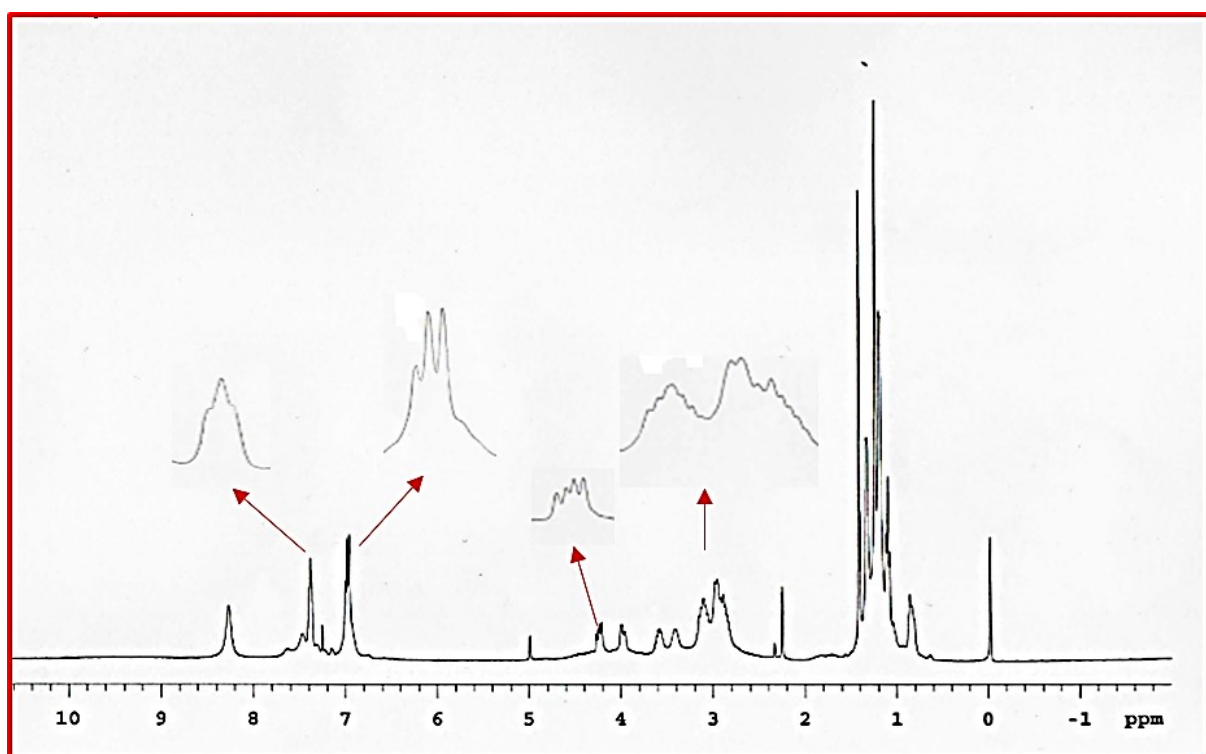
$^{31}\text{P}$  NMR spectrum of compound **4b**.



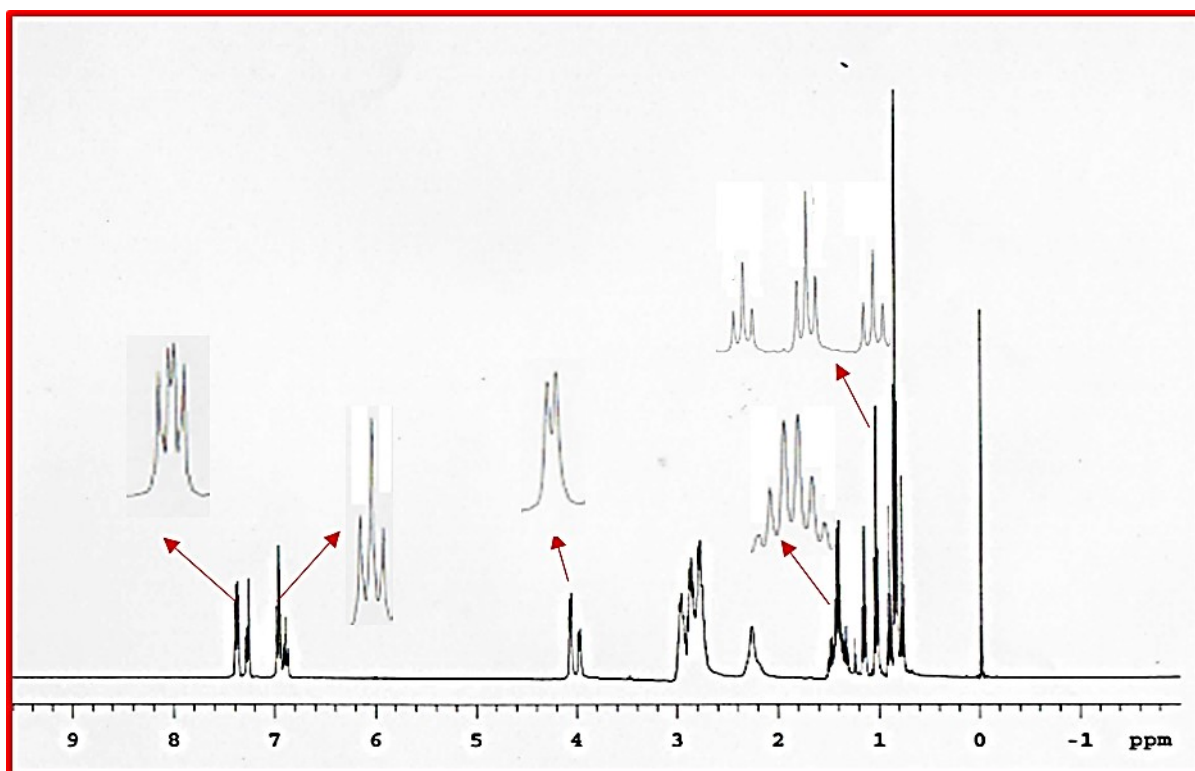
$^1\text{H}$  NMR spectrum of compound **2**.



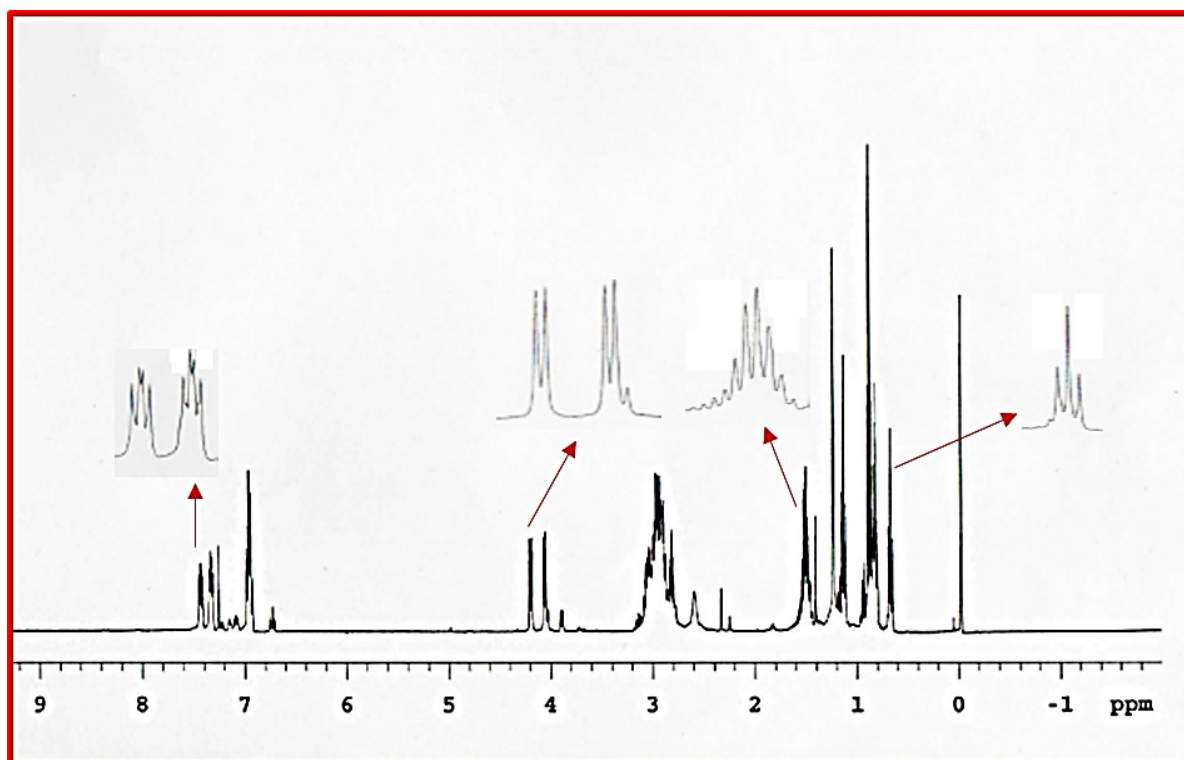
$^1\text{H}$  NMR spectrum of compound 3.



$^1\text{H}$  NMR spectrum of compound 4c.

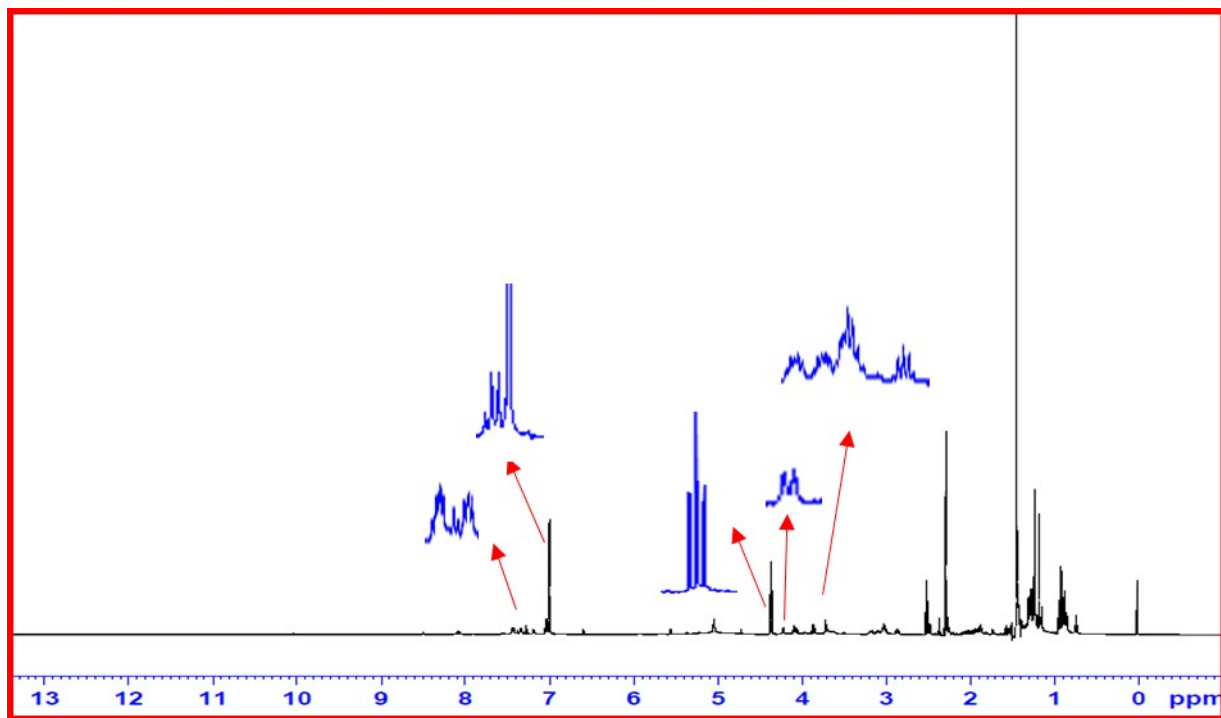


$^1\text{H}$  NMR spectrum of compound **4d**.

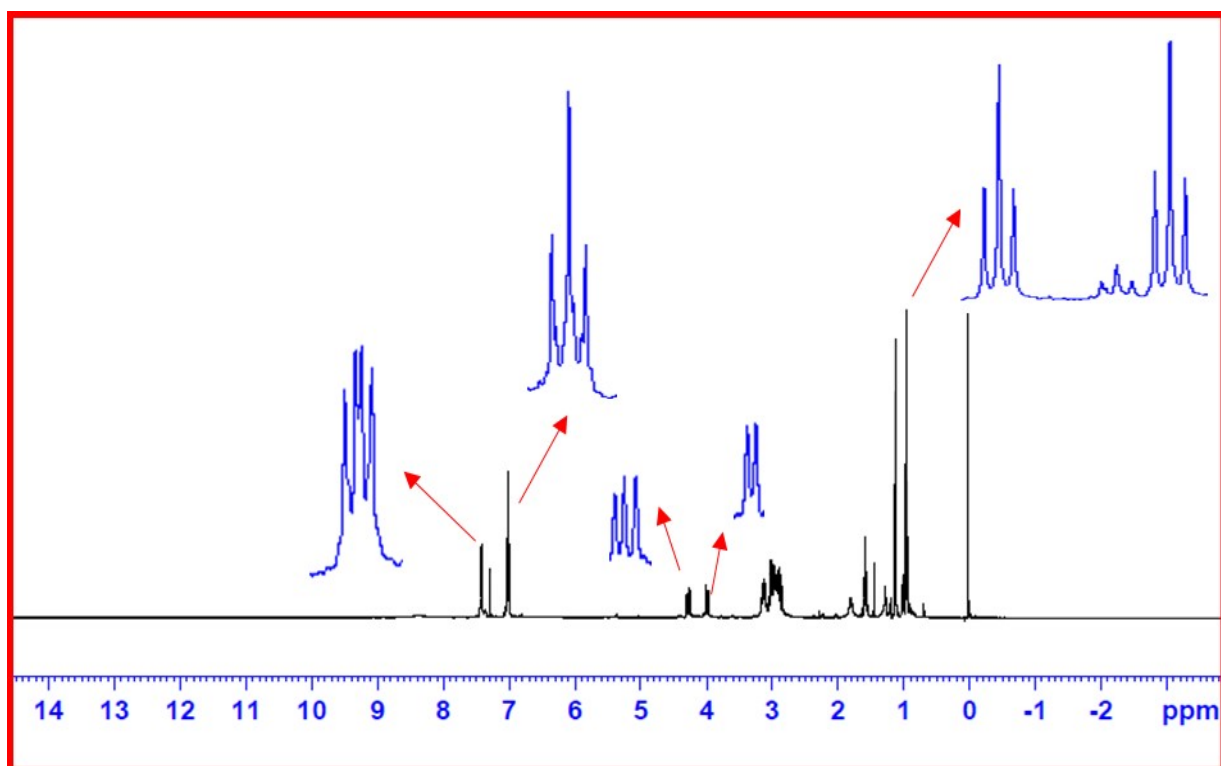


$^1\text{H}$  NMR spectrum of compound **5b**.

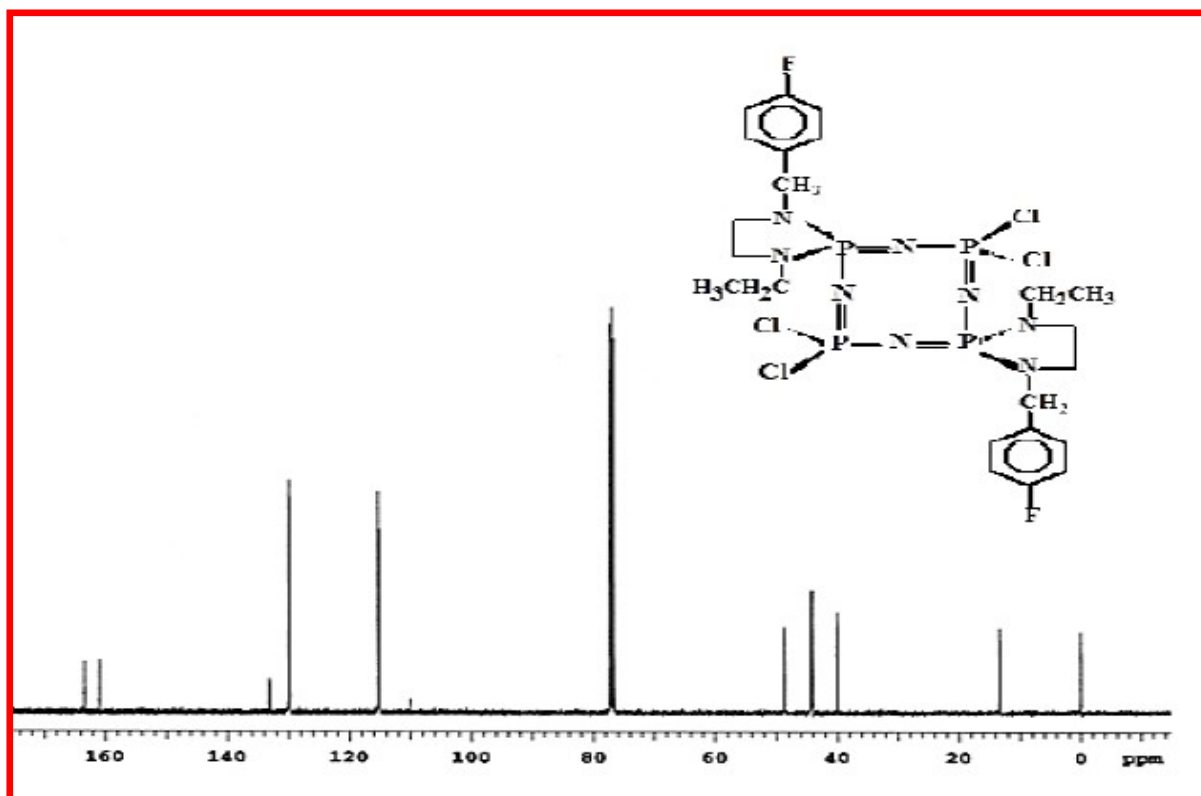




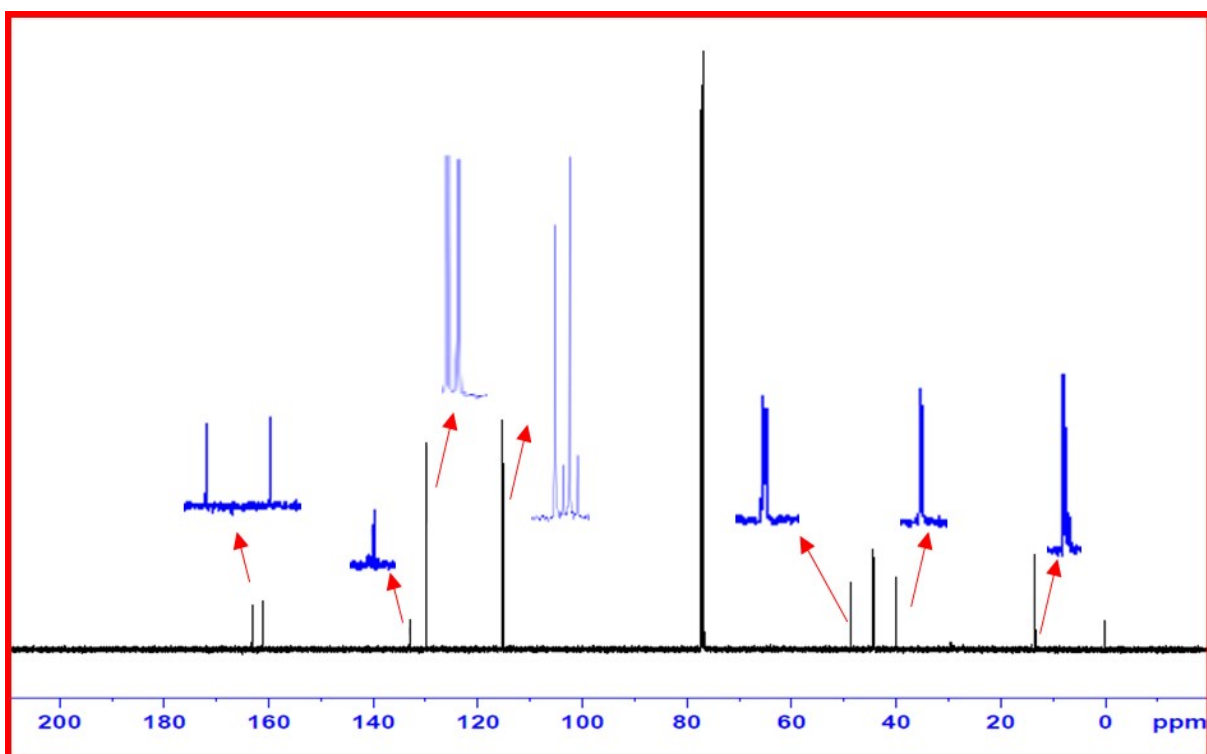
$^1\text{H}$  NMR spectrum of compound **5c**.



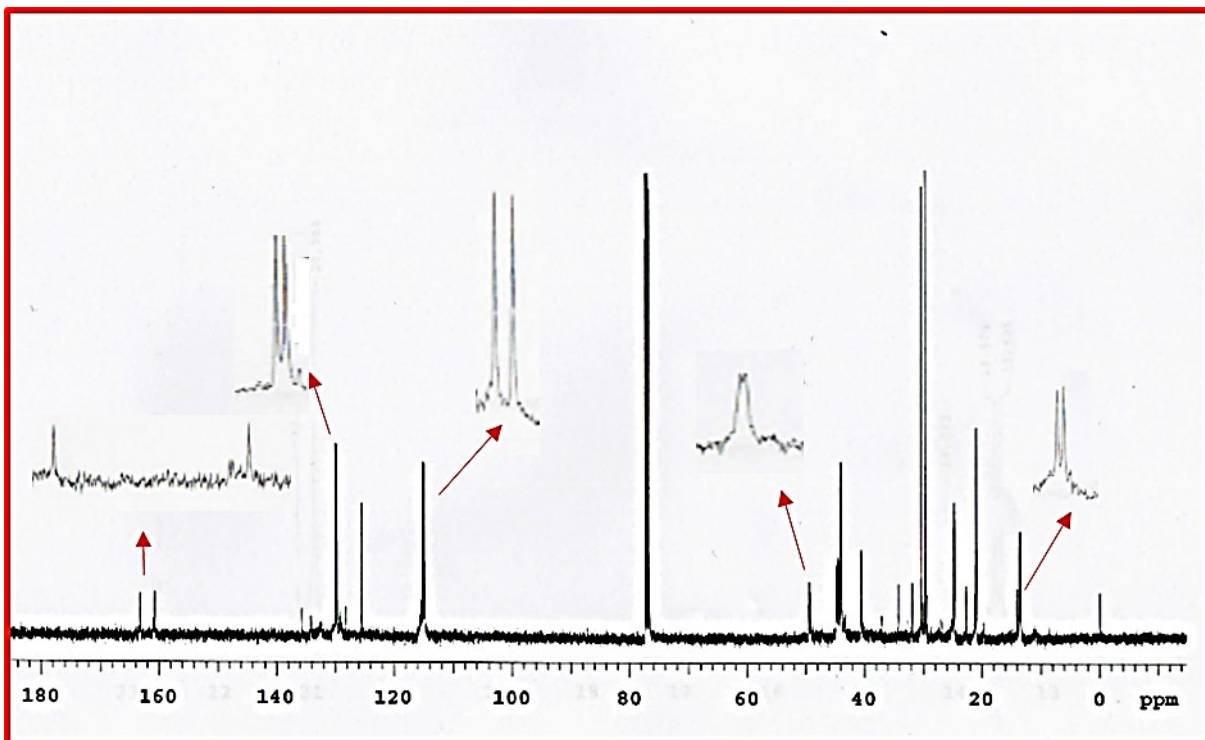
$^1\text{H}$  NMR spectrum of compound **4b**.



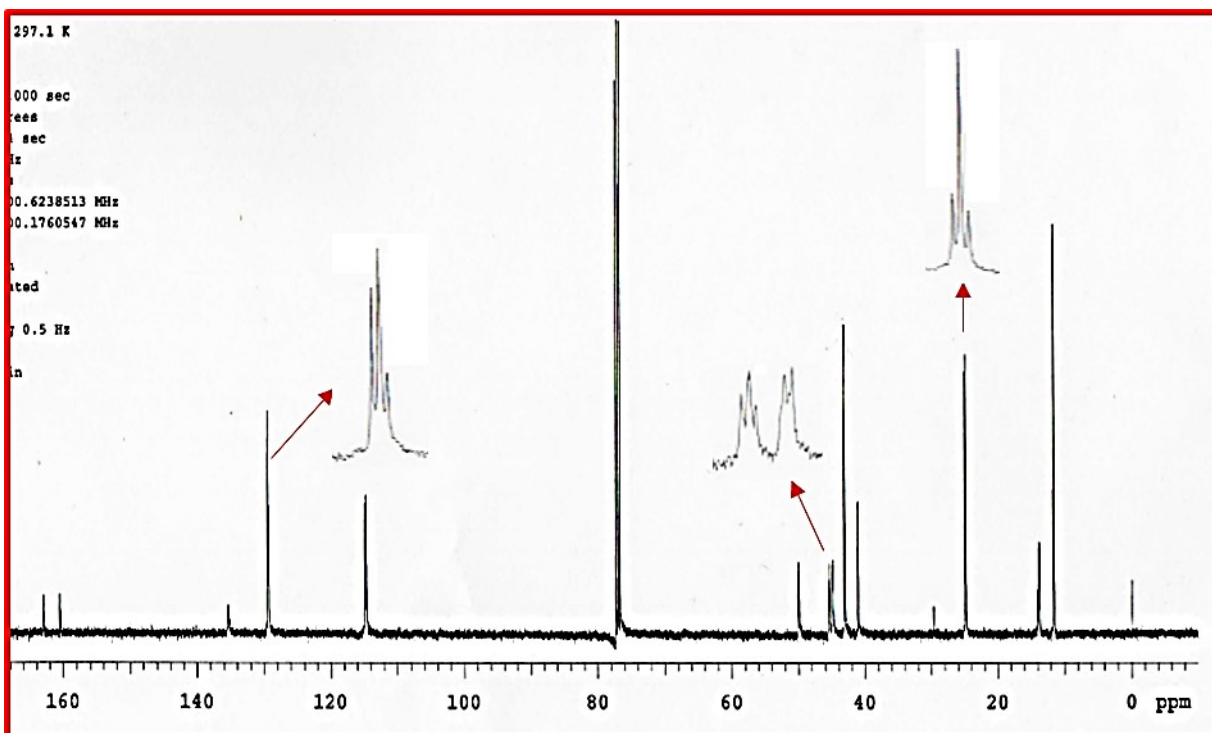
$^{13}\text{C}$  NMR spectrum of compound 2.



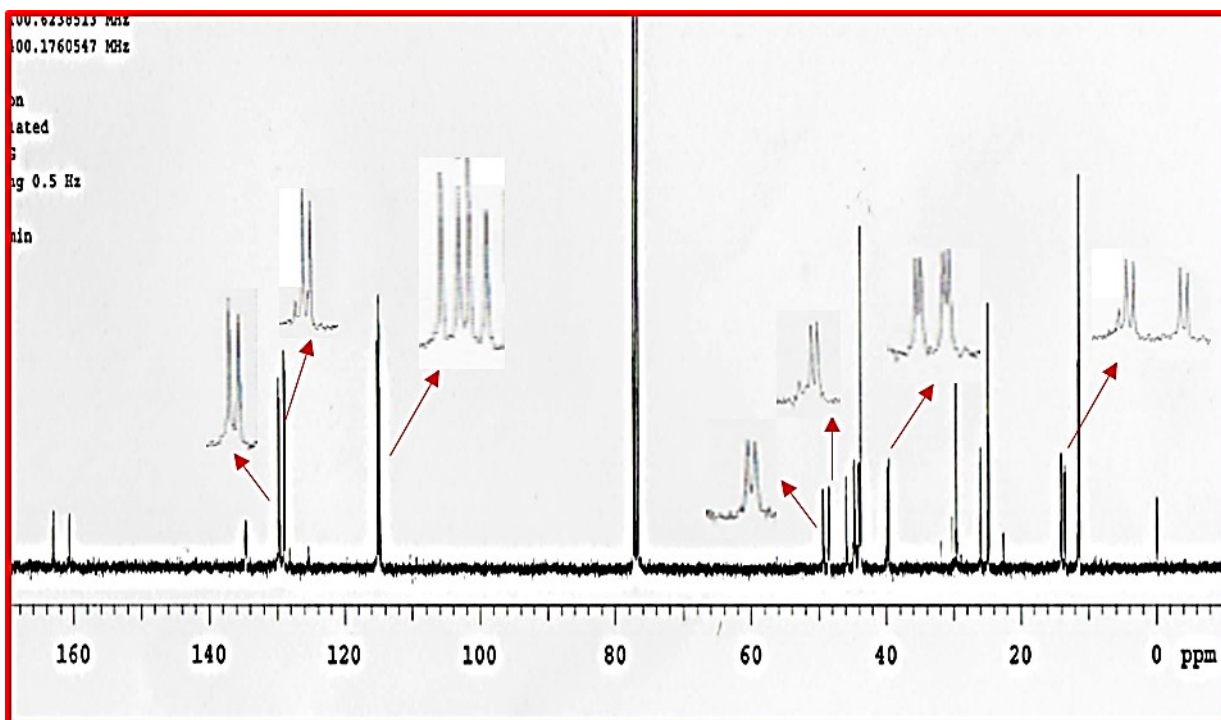
$^{13}\text{C}$  NMR spectrum of compound 3.



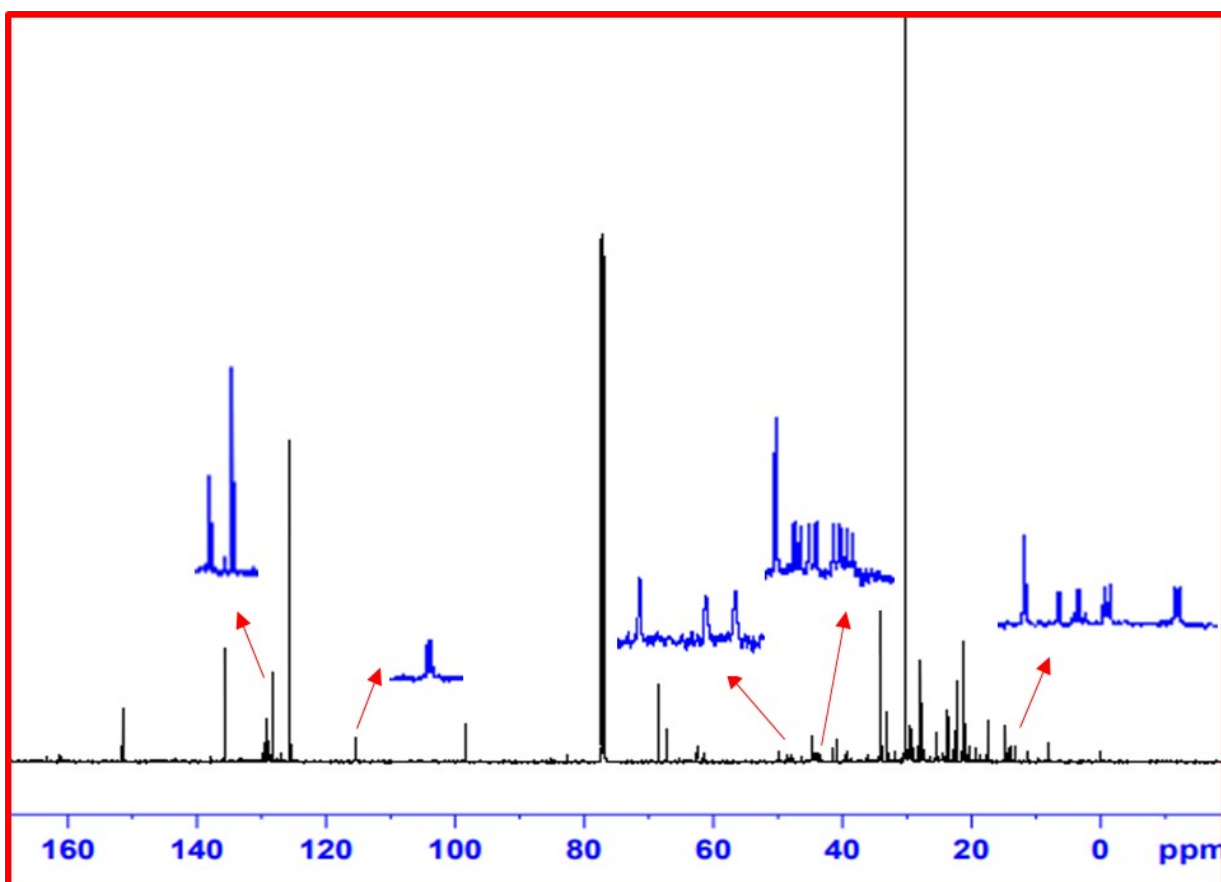
$^{13}\text{C}$  NMR spectrum of compound **4c**.



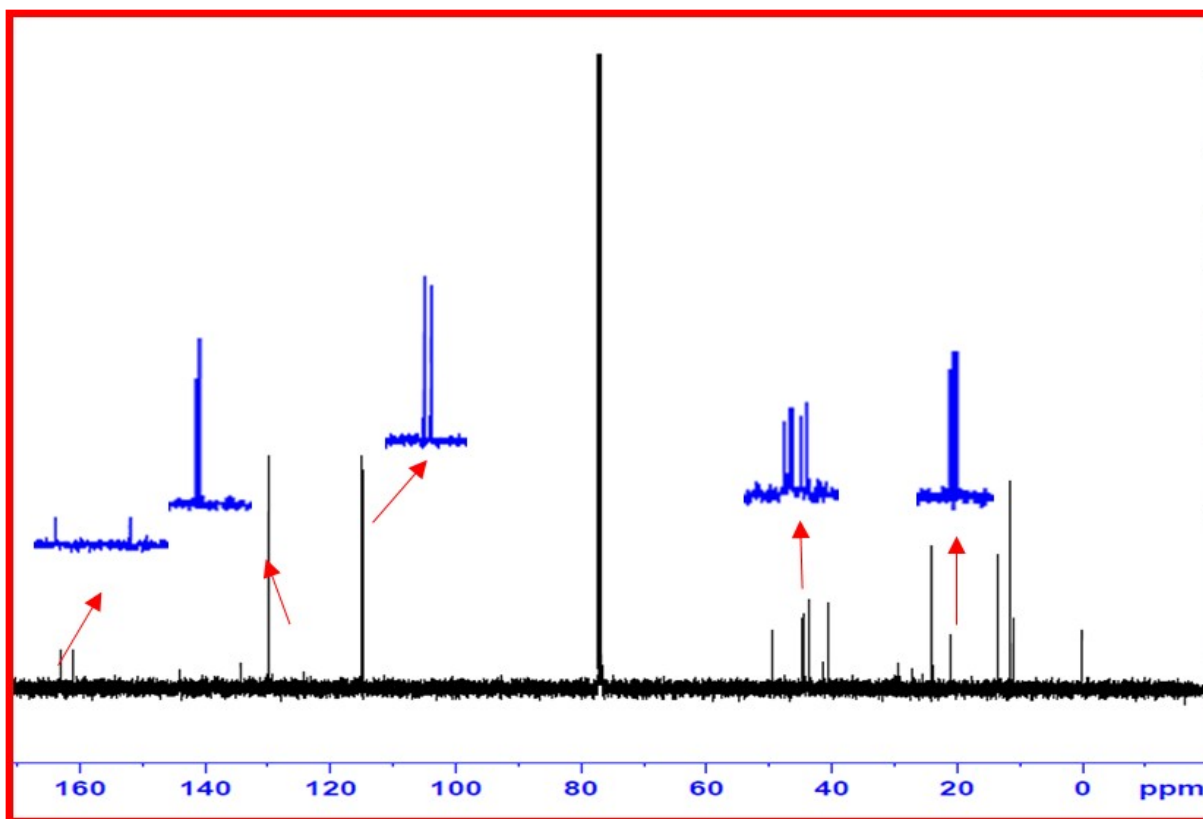
$^{13}\text{C}$  NMR spectrum of compound **4d**.



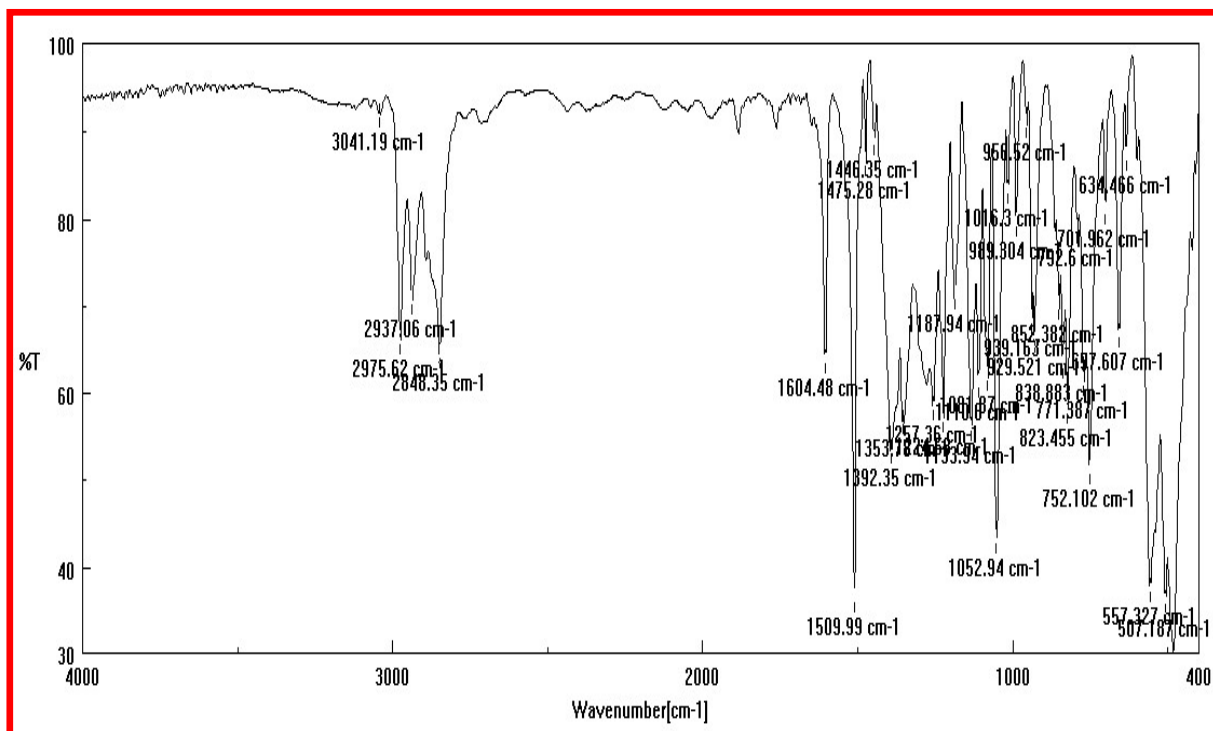
<sup>13</sup>C NMR spectrum of compound **5b**.



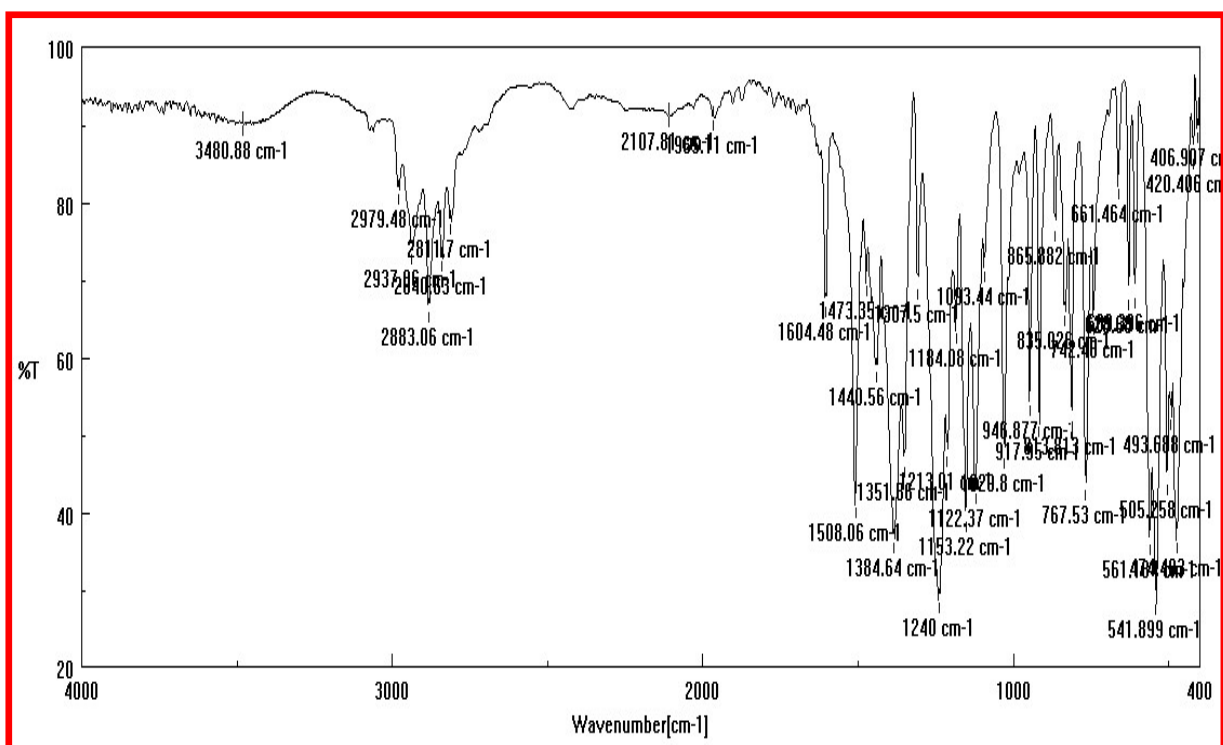
<sup>13</sup>C NMR spectrum of compound **5c**.



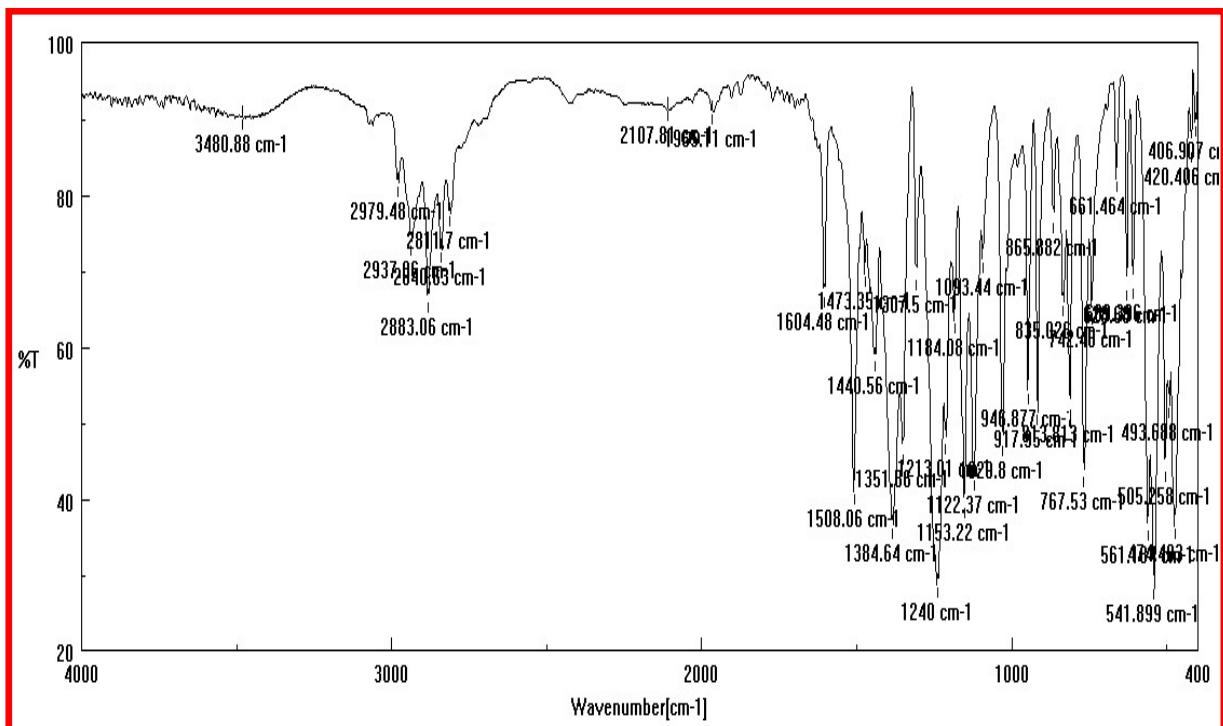
<sup>13</sup>C NMR spectrum of compound **4b**.



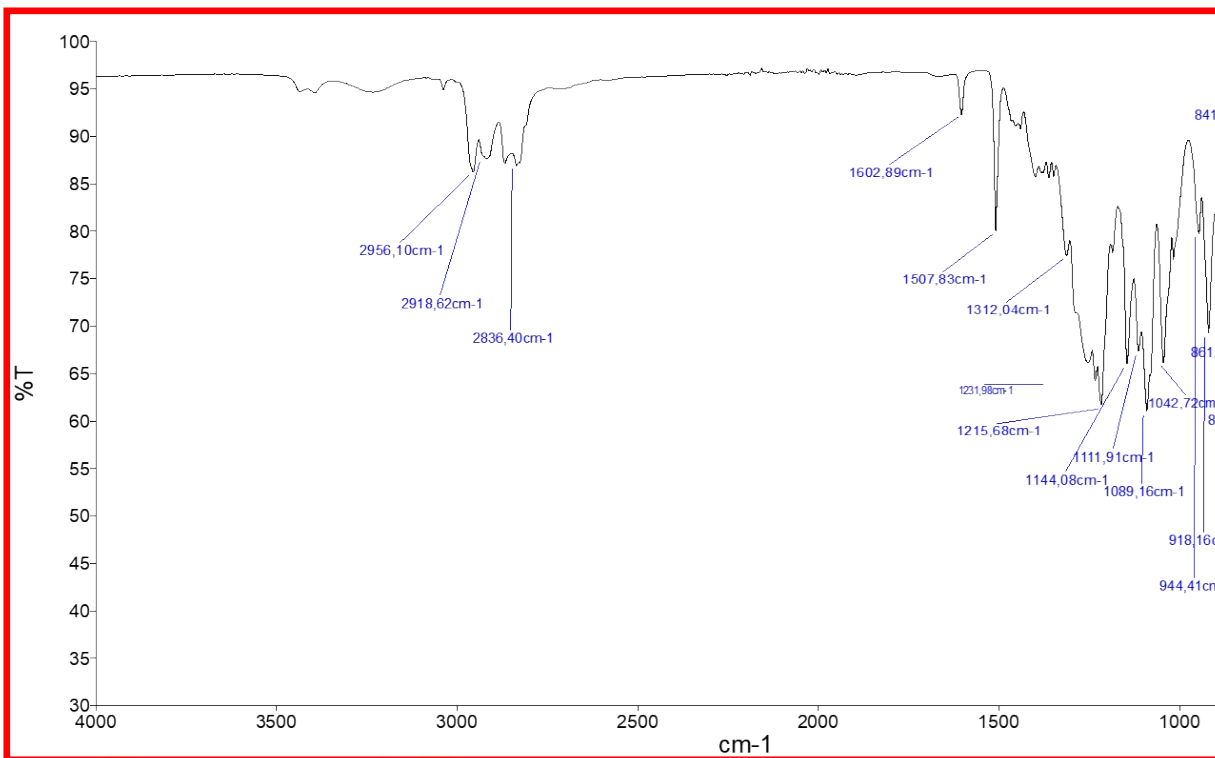
IR spectrum of compound **2**.



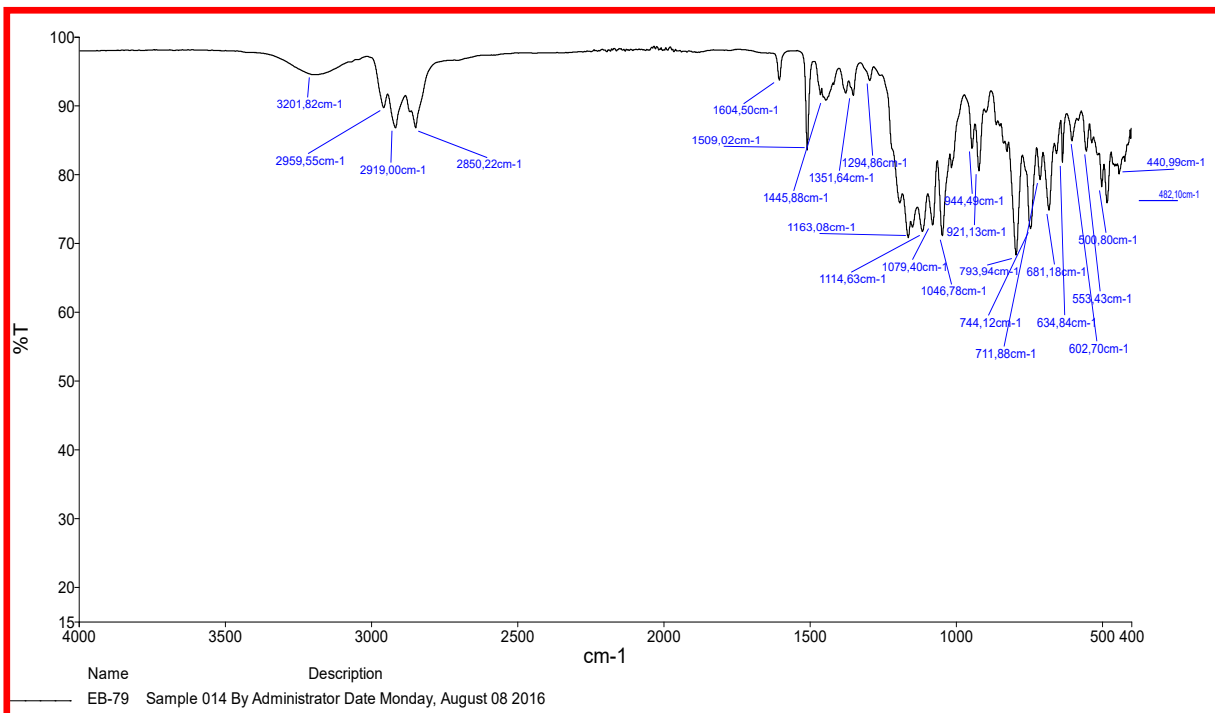
IR spectrum of compound 3.



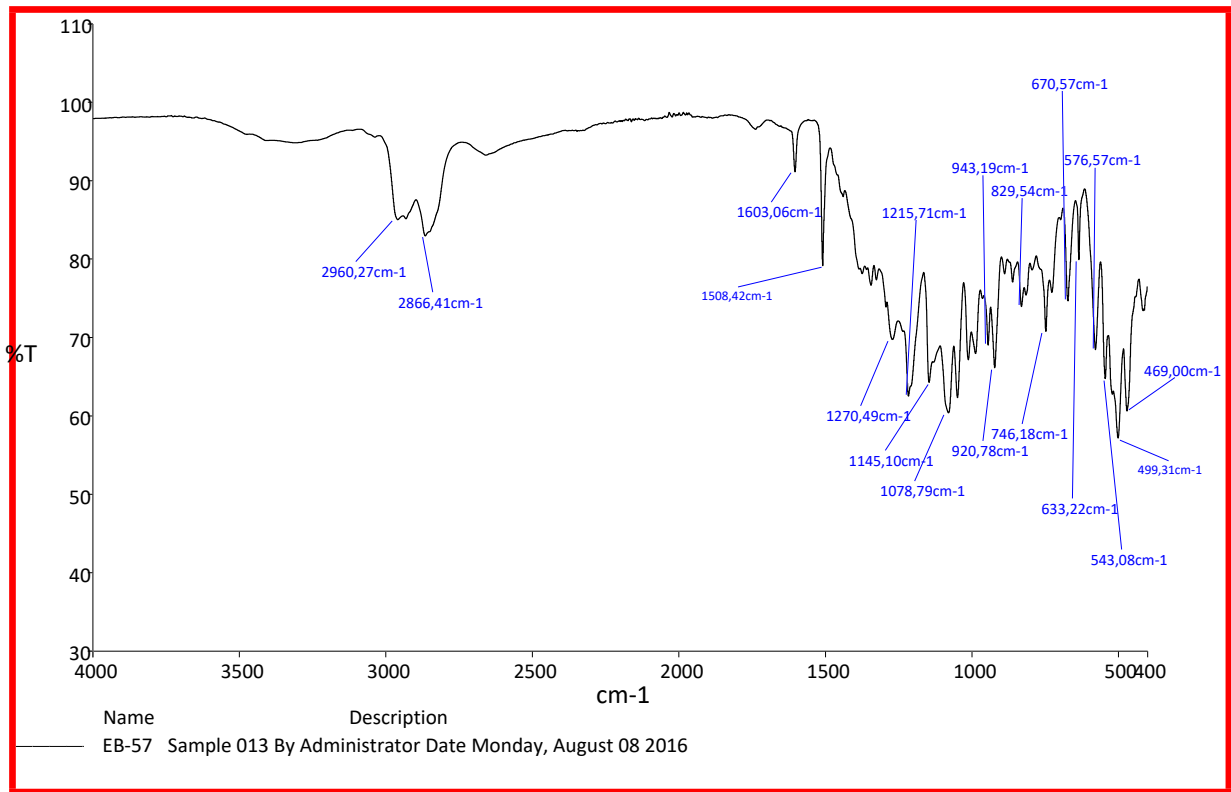
IR spectrum of compound 4c.



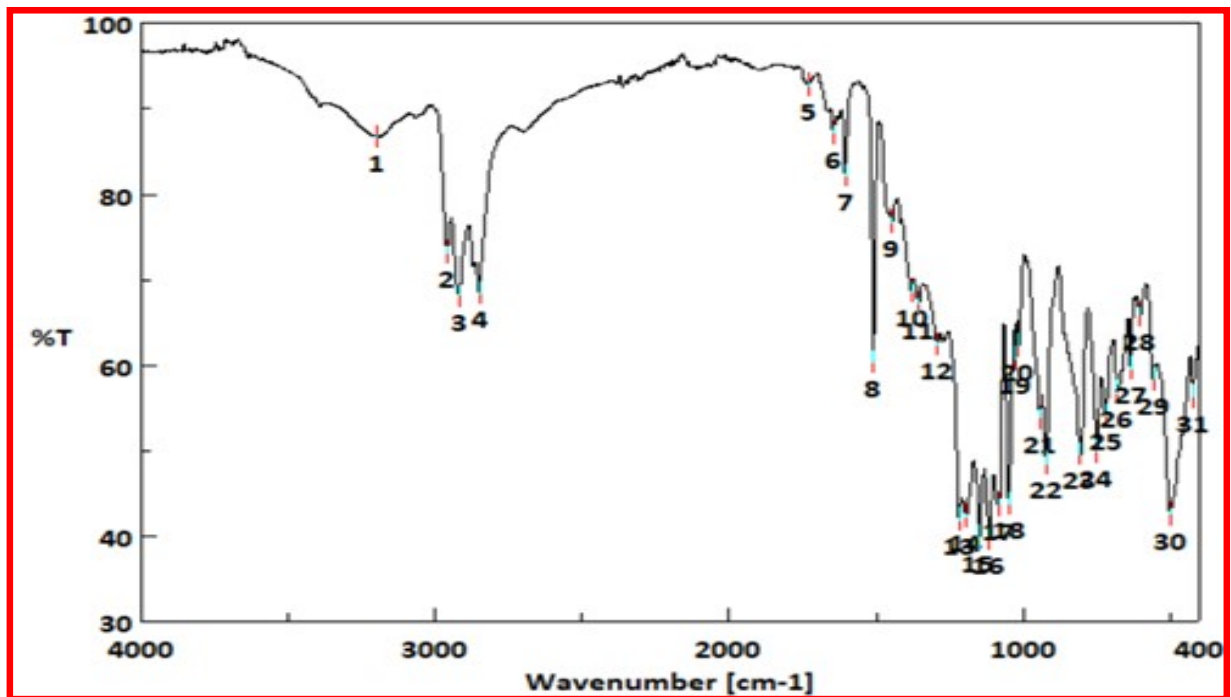
IR spectrum of compound **4d**.



IR spectrum of compound **5b**.



IR spectrum of compound **5c**.





[ Result of Peak Picking ]					
No.	Position	Intensity	No.	Position	Intensity
1	3196.43	86.7038	2	2959.23	73.1876
3	2917.77	68.121	4	2849.31	68.4145
5	1729.83	92.7712	6	1645.95	87.2157
7	1603.52	82.1488	8	1508.06	60.2675
9	1445.39	76.7794	10	1377.89	68.6557
11	1352.82	67.1778	12	1291.11	62.3416
13	1216.86	41.8935	14	1193.72	42.2143
15	1148.4	39.8204	16	1113.69	39.6788
17	1080.91	43.6013	18	1047.16	43.6733
19	1027.87	60.7533	20	1014.37	62.2738
21	941.092	53.7664	22	919.879	48.4704
23	804.171	49.5277	24	747.281	49.8641
25	717.39	54.0891	26	678.82	56.7481
27	633.501	59.5565	28	600.717	65.9007
29	556.363	58.3373	30	498.509	42.4557
31	419.442	56.2487			

IR spectrum of compound **4b**.

## Section S2. Single Crystal X-ray Structure Determinations

The crystallographic data were collected on a Bruker APEX II QUAZAR three-circle diffractometer by Mo K $\alpha$  radiation ( $\lambda=0.71073$  Å) at T = 173(2) K (for **2**) and 125(2) K (for **4c**). No absorption correction was applied. The structures of **2** and **4c** were solved using direct methods<sup>1</sup> and refined by full-matrix least-squares against F<sup>2</sup> using all data.<sup>2</sup> All non-H atoms were refined anisotropically. The molecular and packing diagrams together with the ring conformations of **2** and **4c** were drawn by the ORTEP-3 program incorporated in the WinGX package.<sup>3</sup> The H atom positions were calculated geometrically at distances of 0.93 Å (aromatic CH), 0.97 Å (CH<sub>2</sub>) and 0.96 Å (CH<sub>3</sub>) (in **2**) and 0.95 Å (aromatic CH), 1.00 Å (methine CH), 0.99 Å (CH<sub>2</sub>) and 0.98 Å (CH<sub>3</sub>) (in **4c**) from the parent C atoms; a riding model was used during the refinement process and the U<sub>iso</sub>(H) values were constrained to be xU<sub>eq</sub>(carrier atom), where x = 1.2 (for CH and CH<sub>2</sub>) and x = 1.5 (for CH<sub>3</sub>). In **4c**, the NH hydrogen (H5) atom is located in a difference Fourier map, and refined freely.

### References

- (1) G. M. Sheldrick, *Acta Crystallogr. Sect. A.*, 2015a, **71**, 3-8.
- (2) G. M. Sheldrick, *Acta Crystallogr. Sect. C.*, 2015b, **71**, 3-8.
- (3) L. J. Farrugia, *J. Appl. Cryst.*, 2012, **45**, 849-854.