

## Supporting Information for

# Isomeric Structure of Pentacoordinate Chiral Spirophosphoranes in Solution by combined use of NMR Experiments and GIAO DFT calculations of NMR parameters

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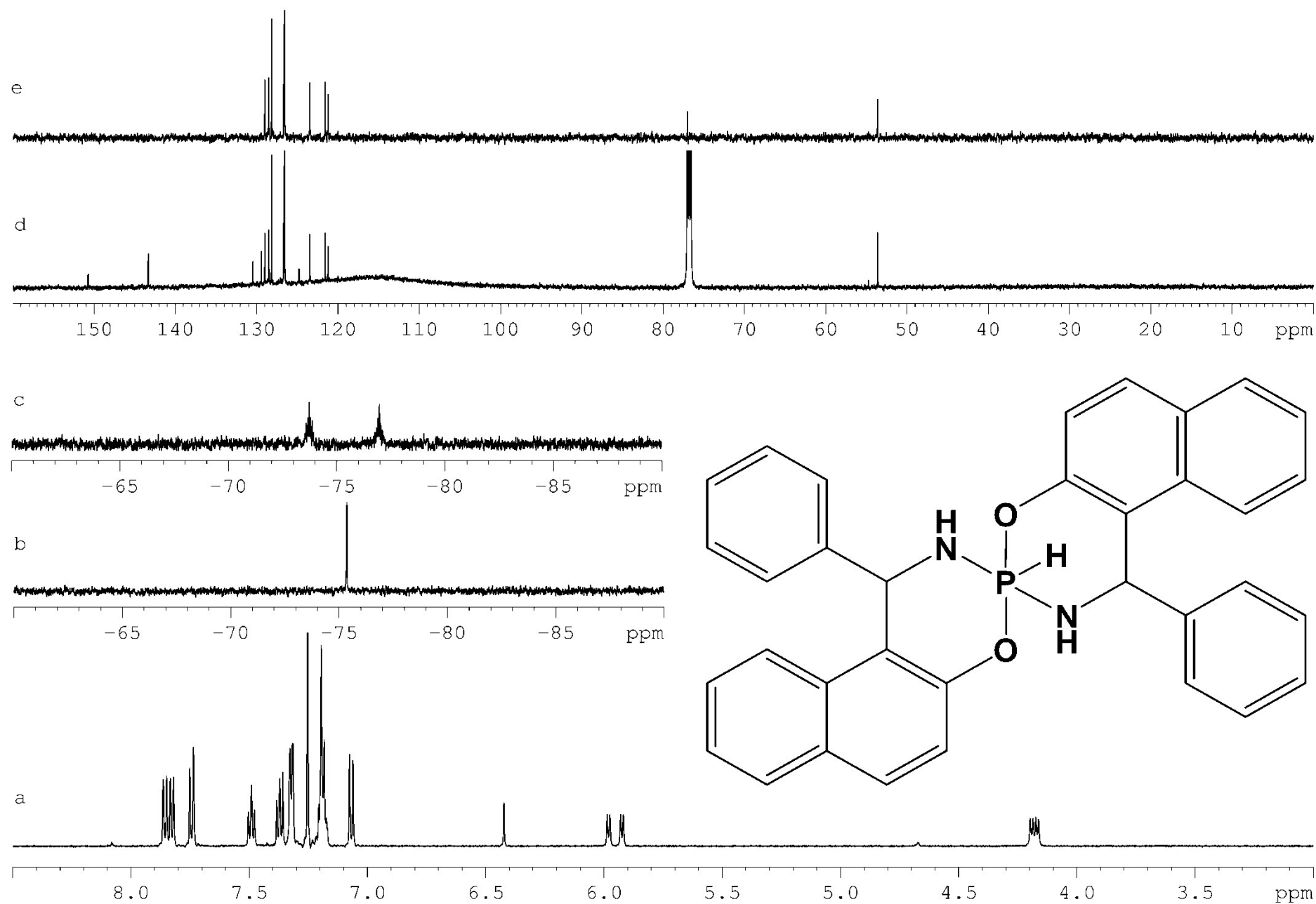
## Experimental Section

**NMR Spectroscopy.** All NMR experiments were performed with a 600, 500 and 400 MHz (600.1, 500.1 and 400.1 MHz for  $^1\text{H}$  NMR; 150.9, 125.8 and 100.6 MHz for  $^{13}\text{C}$  NMR; 242.9, 202.5 and 162.0 MHz for  $^{31}\text{P}$  NMR, 60.81 MHz for  $^{15}\text{N}$  NMR, 376.5 for  $^{19}\text{F}$  respectively) spectrometers equipped with a 5 mm diameter probehead and a pulsed gradient unit capable of producing magnetic field pulse gradients in the z-direction of  $53.5\text{ G}\cdot\text{cm}^{-1}$ . For  $^1\text{H}$ - $^{13}\text{C}$  correlations HSQC experiment optimized for  $J = 145\text{ Hz}$ . For  $^1\text{H}$ - $^{13}\text{C}$  long range correlations HMBC experiment optimized for  $J = 8\text{ Hz}$ . For  $^1\text{H}$ - $^{31}\text{P}$  long range correlations HMBC experiment optimized for  $J = 8\text{ Hz}$ . For  $^1\text{H}$ - $^{15}\text{N}$  correlations HSQC experiment optimized for  $J = 90\text{ Hz}$ . For  $^1\text{H}$ - $^{15}\text{N}$  long range correlations HMBC experiment optimized for  $J = 6\text{ Hz}$ . For  $^{19}\text{F}$ - $^1\text{H}$  long range correlations HETCOR experiment optimized for  $J = 3\text{ Hz}$ . DOSY experiments were performed with ledbpgp2s,<sup>1</sup> using a stimulated echo sequence and two spoil gradients. NOE experiments were performed with 1D DPFNOE techniques.<sup>2</sup> CS's ( $\delta$  in ppm) were referenced to the solvent  $\text{CDCl}_3$  ( $\delta = 7.27\text{ ppm}$  for  $^1\text{H}$  and  $77.0\text{ ppm}$  for  $^{13}\text{C}$  NMR) and to external  $\text{H}_3\text{PO}_4$  ( $0.0\text{ ppm}$ ) for  $^{31}\text{P}$  NMR spectra, to external  $\text{CH}_3\text{CN}$  ( $235.5\text{ ppm}$ ) for  $^{15}\text{N}$  NMR spectra, to external  $\text{C}_6\text{F}_6$  ( $-164.9\text{ ppm}$ ) for  $^{19}\text{F}$  NMR spectra.

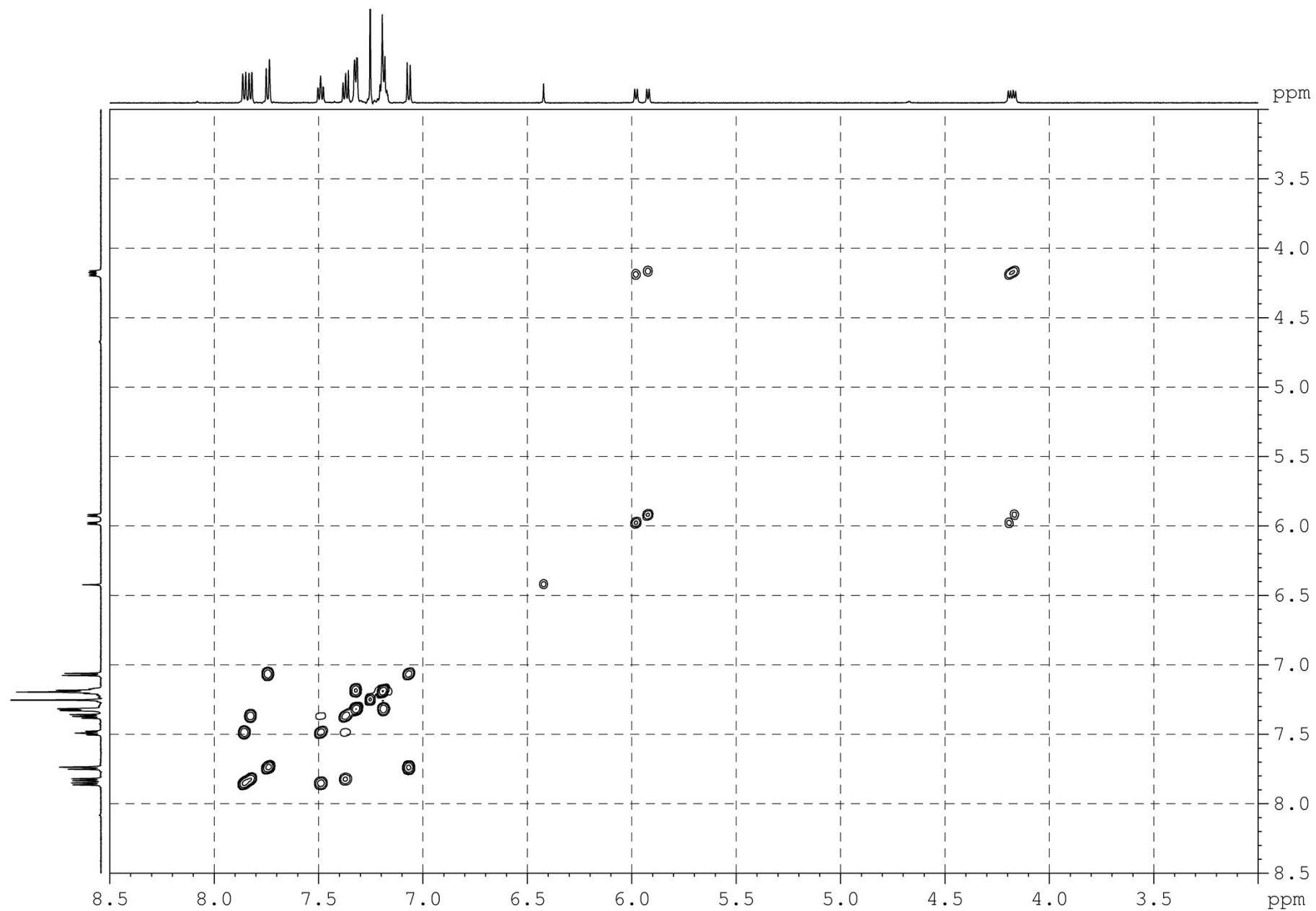
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<sup>1</sup> W. S. Price, *Concepts Magn. Reson.*, 1997, **9**, 299; W. S. Price, *Concepts Magn. Reson.*, 1998, **10**, 197; C. S. Johnson, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1999, **34**, 203.

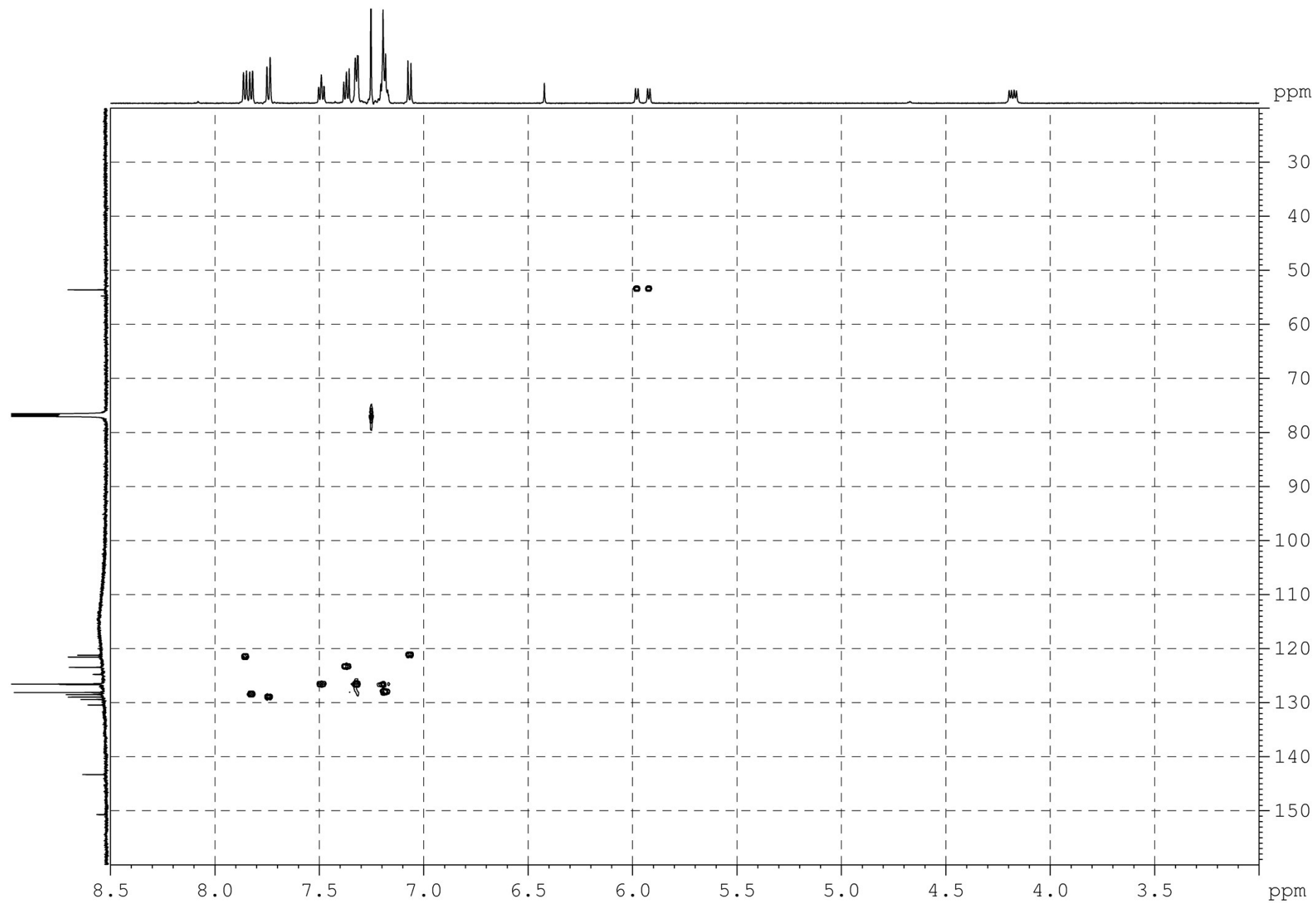
<sup>2</sup> J. Stonehouse, P. Adell, J. Keeler and A.J. Shaka, *J. Am. Chem. Soc.*, 1994, **116**, 6037.



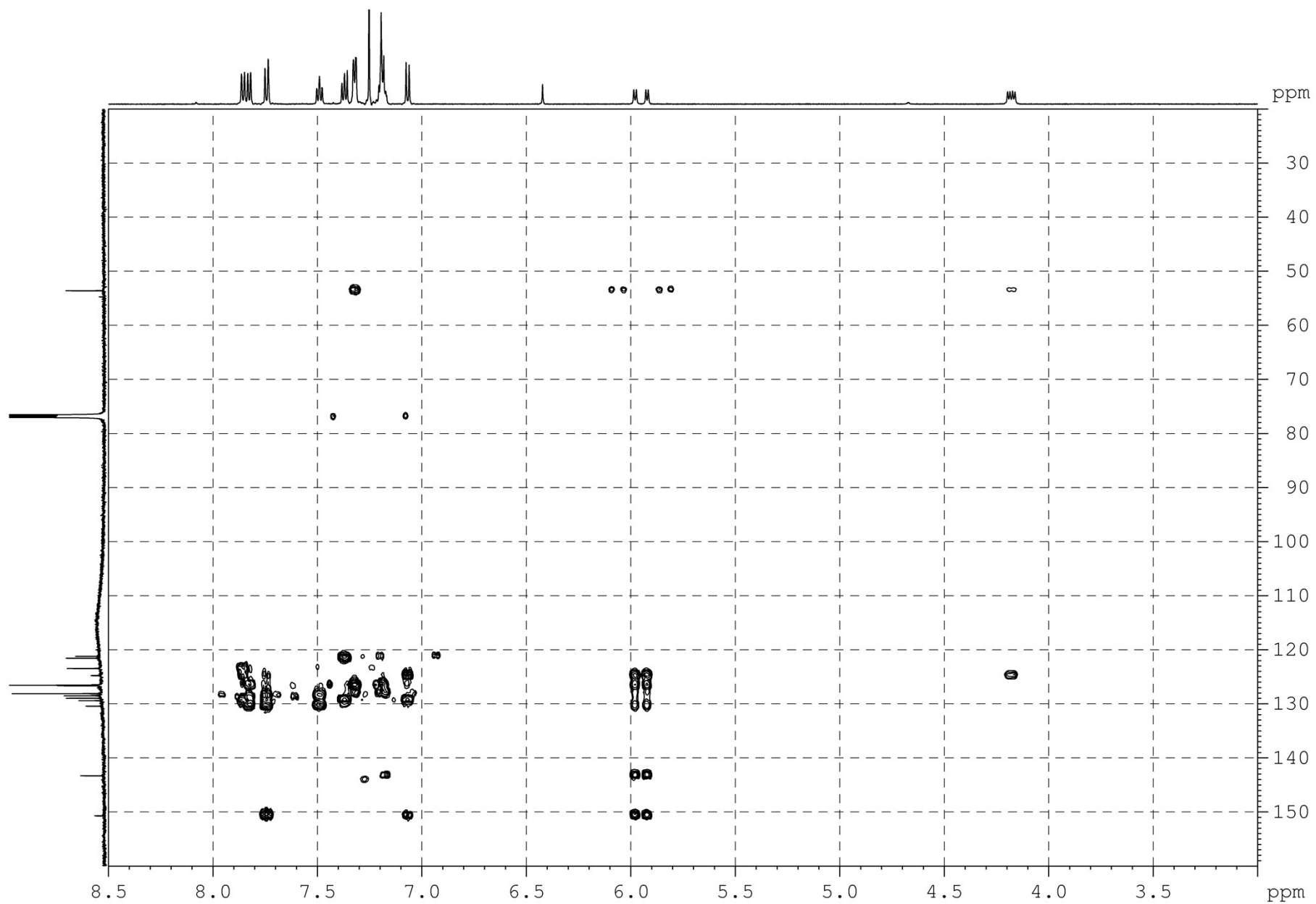
**Figure S1.**  $^1\text{H}$  (a),  $^{31}\text{P}\{^1\text{H}\}$  (b),  $^{31}\text{P}$  (c),  $^{13}\text{C}\{^1\text{H}\}$  (d) and  $^{13}\text{C}$  DEPT (e) spectra of **4a** in  $\text{CDCl}_3$  at  $T = 303\text{ K}$ .



**Figure S2.**  $^1\text{H}$ - $^1\text{H}$  COSY spectra of **4a** in  $\text{CDCl}_3$  at  $T = 303\text{ K}$ .



**Figure S3.**  $^1\text{H}$ - $^{13}\text{C}$  HSQC spectra of **4a** in  $\text{CDCl}_3$  at  $T = 303\text{ K}$ .



**Figure S4.**  $^1\text{H}$ - $^{13}\text{C}$  HMBC spectra of **4a** in  $\text{CDCl}_3$  at  $T = 303\text{ K}$ .

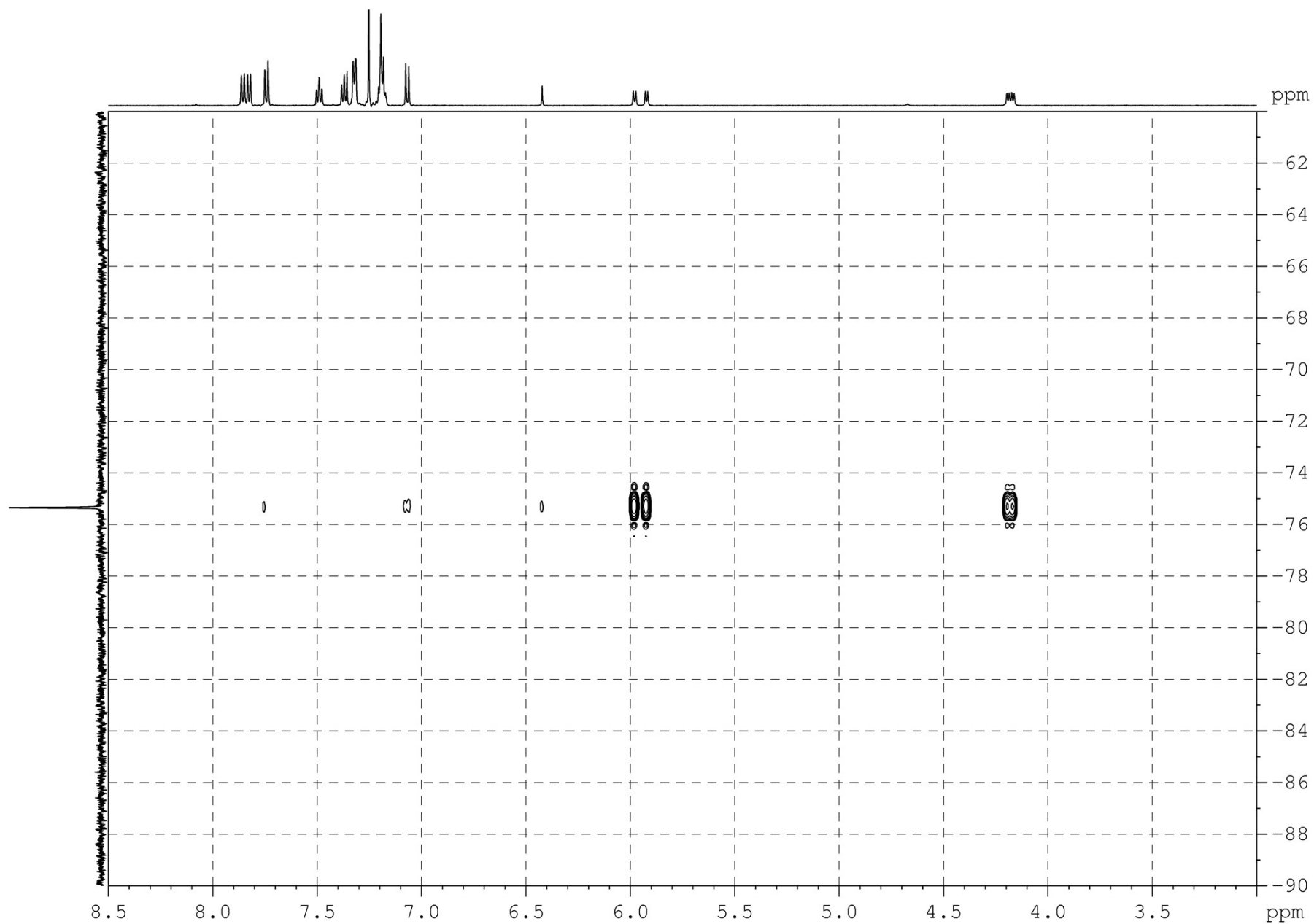
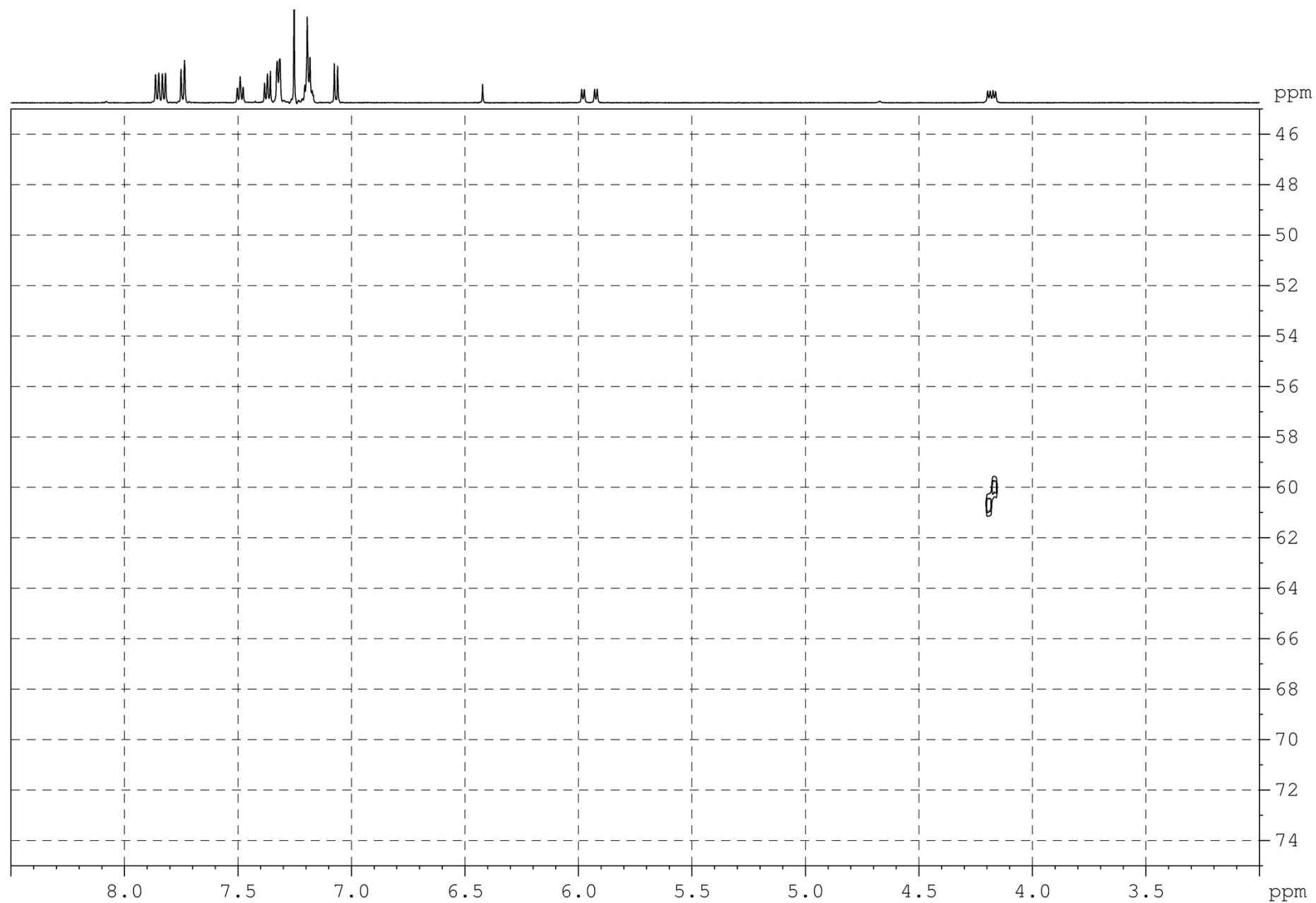
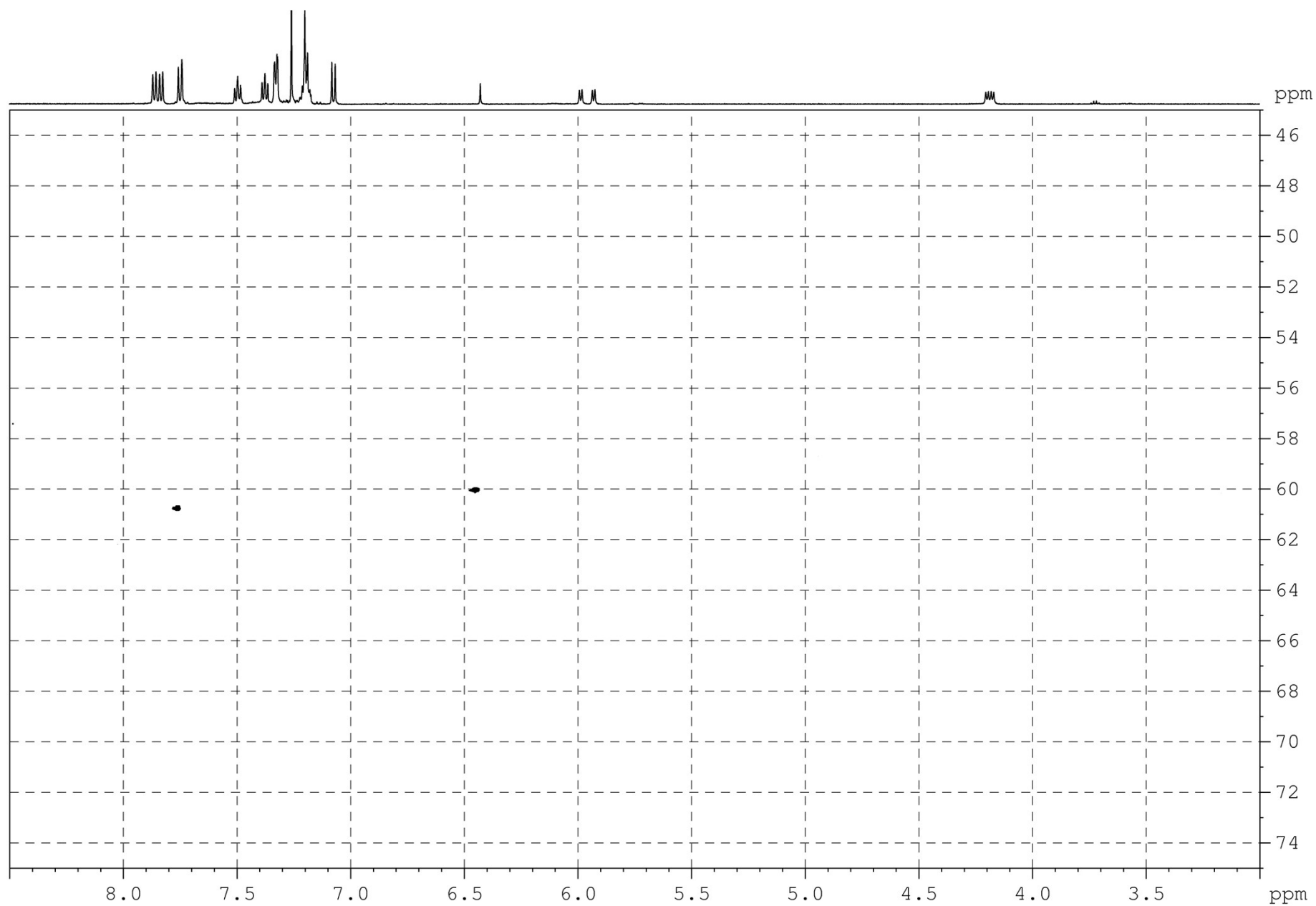


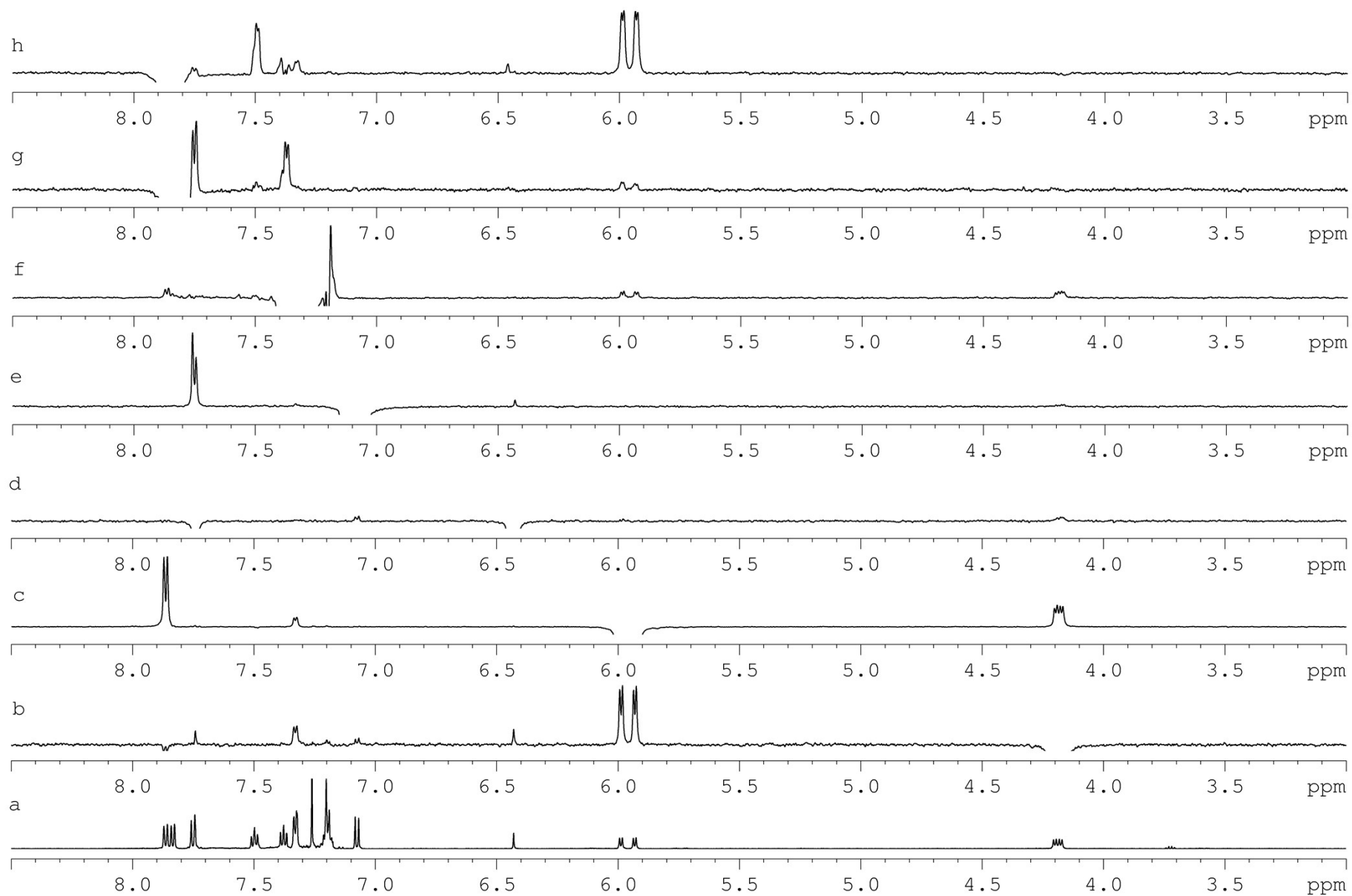
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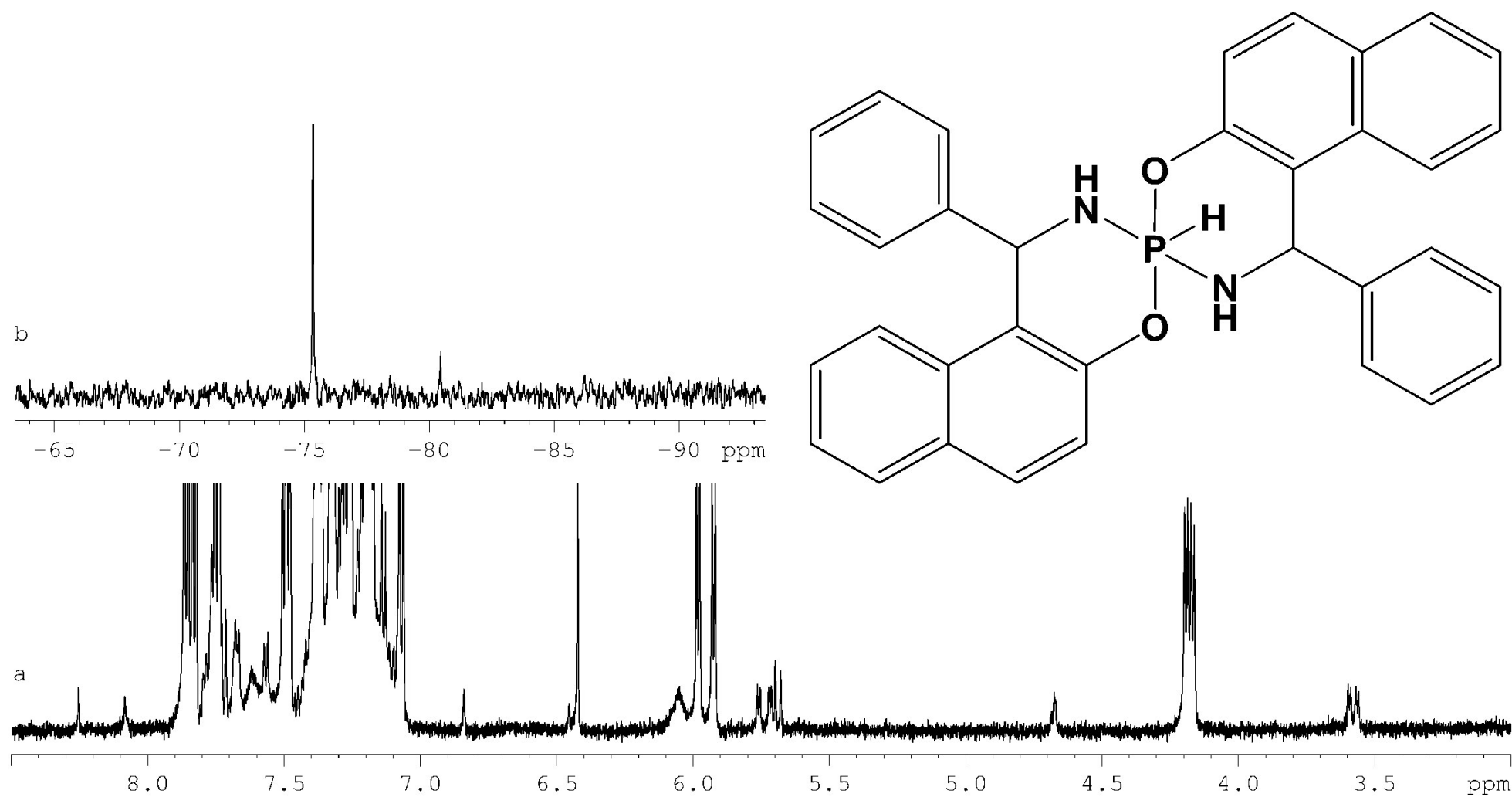
**Figure S6.**  $^1\text{H}$ - $^{15}\text{N}$  HSQC spectra of **4a** in  $\text{CDCl}_3$  at  $T = 303$  K.



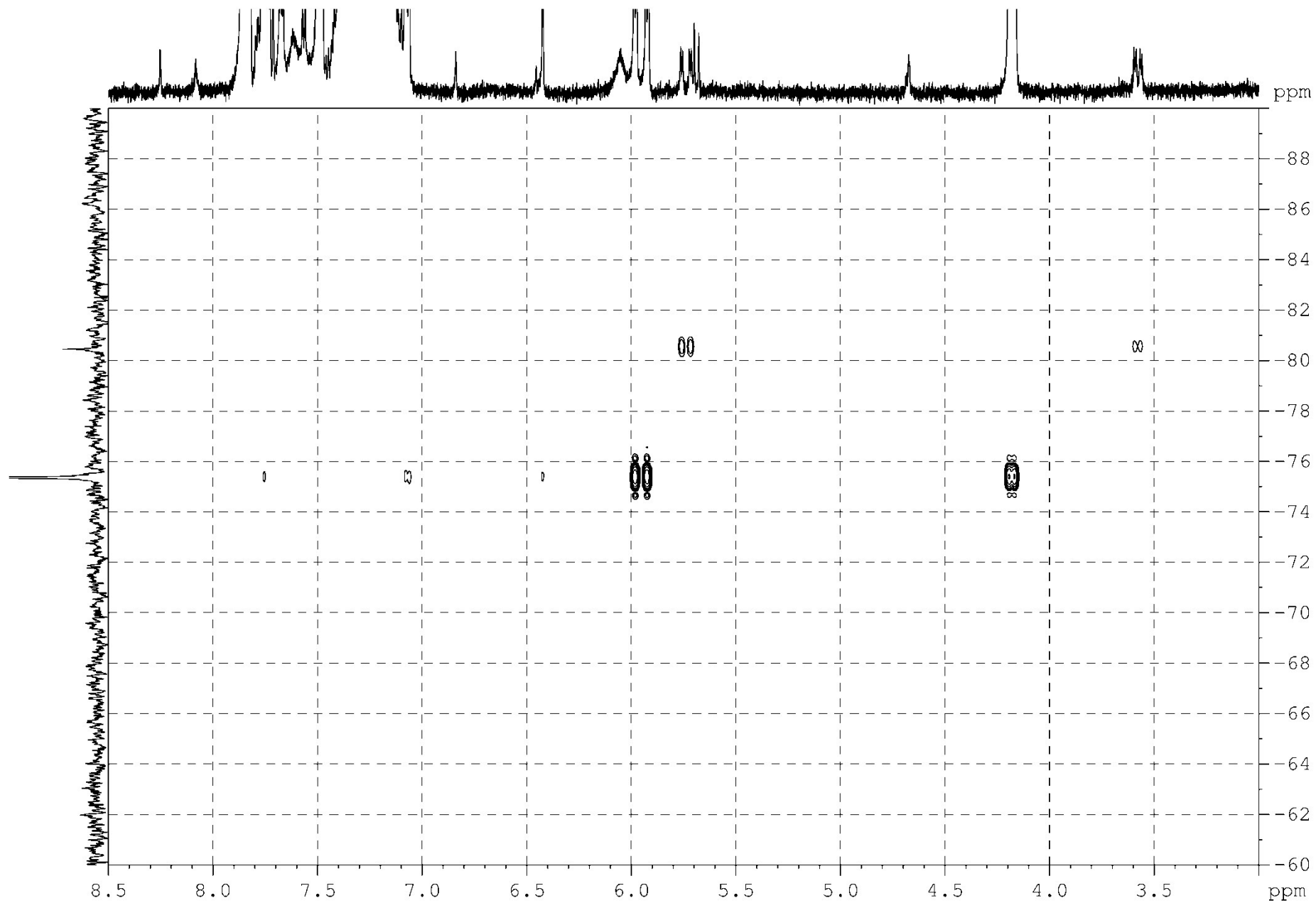
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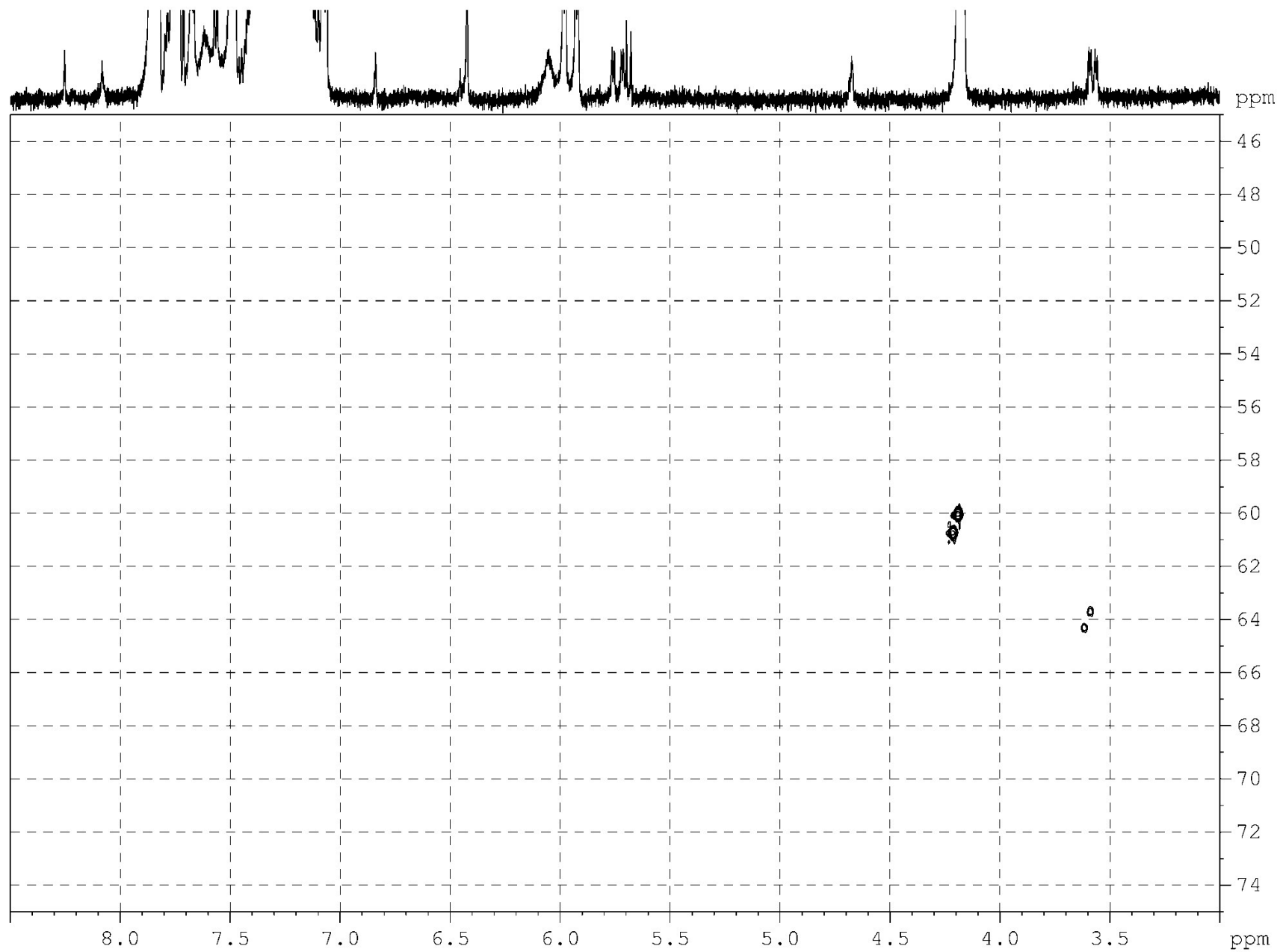
**Figure S8.**  $^1\text{H}$  (a) and 1D NOESY (b-h) spectra of **4a** in  $\text{CDCl}_3$  at  $T = 303\text{ K}$ .



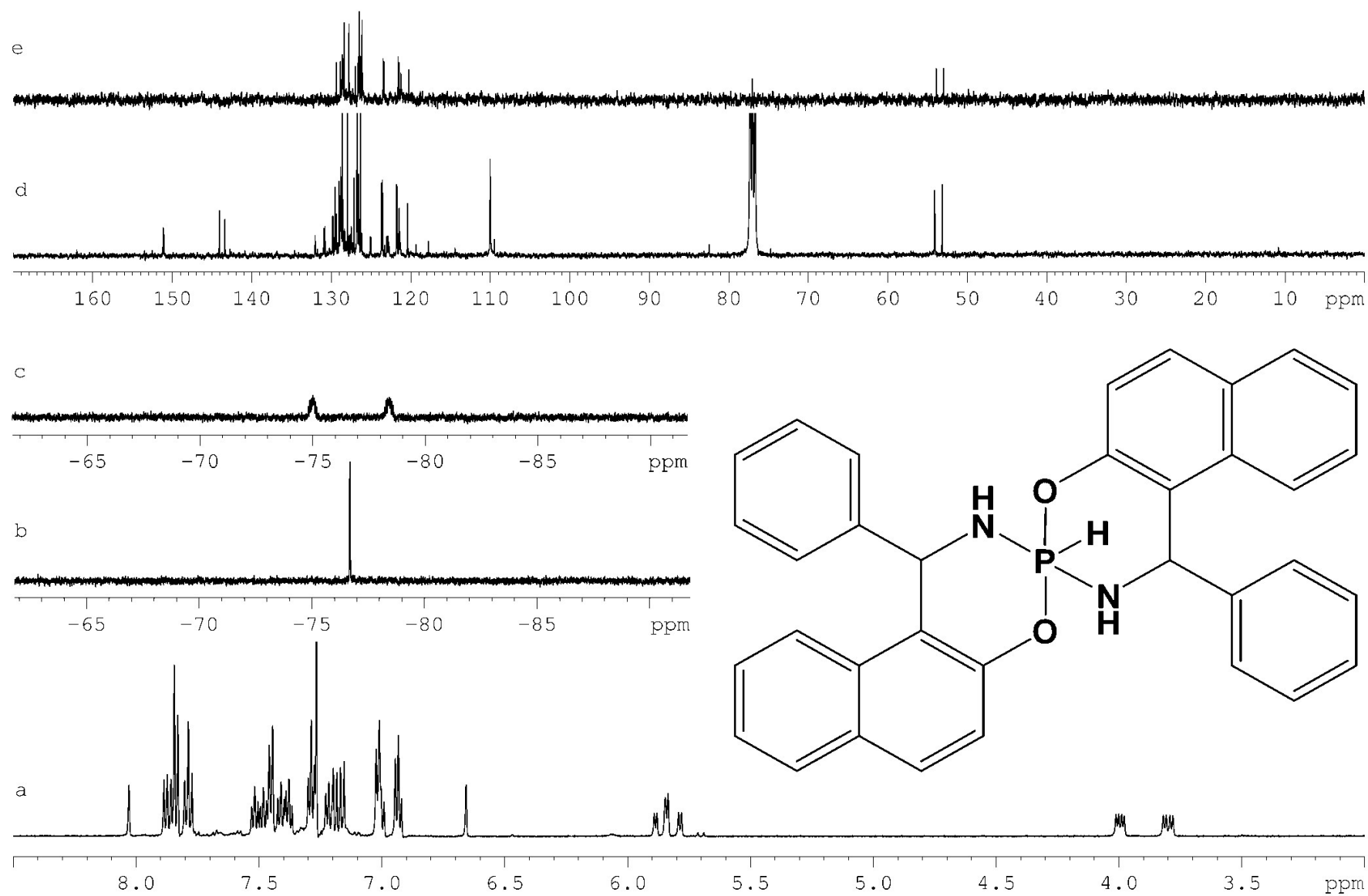
**Figure S9.**  $^1\text{H}$  (a),  $^{31}\text{P}\{^1\text{H}\}$  (b) spectra of **4a** after 24h in  $\text{CDCl}_3$  at  $T = 303\text{ K}$  (**4a** 80 %, **4c** 20 %).



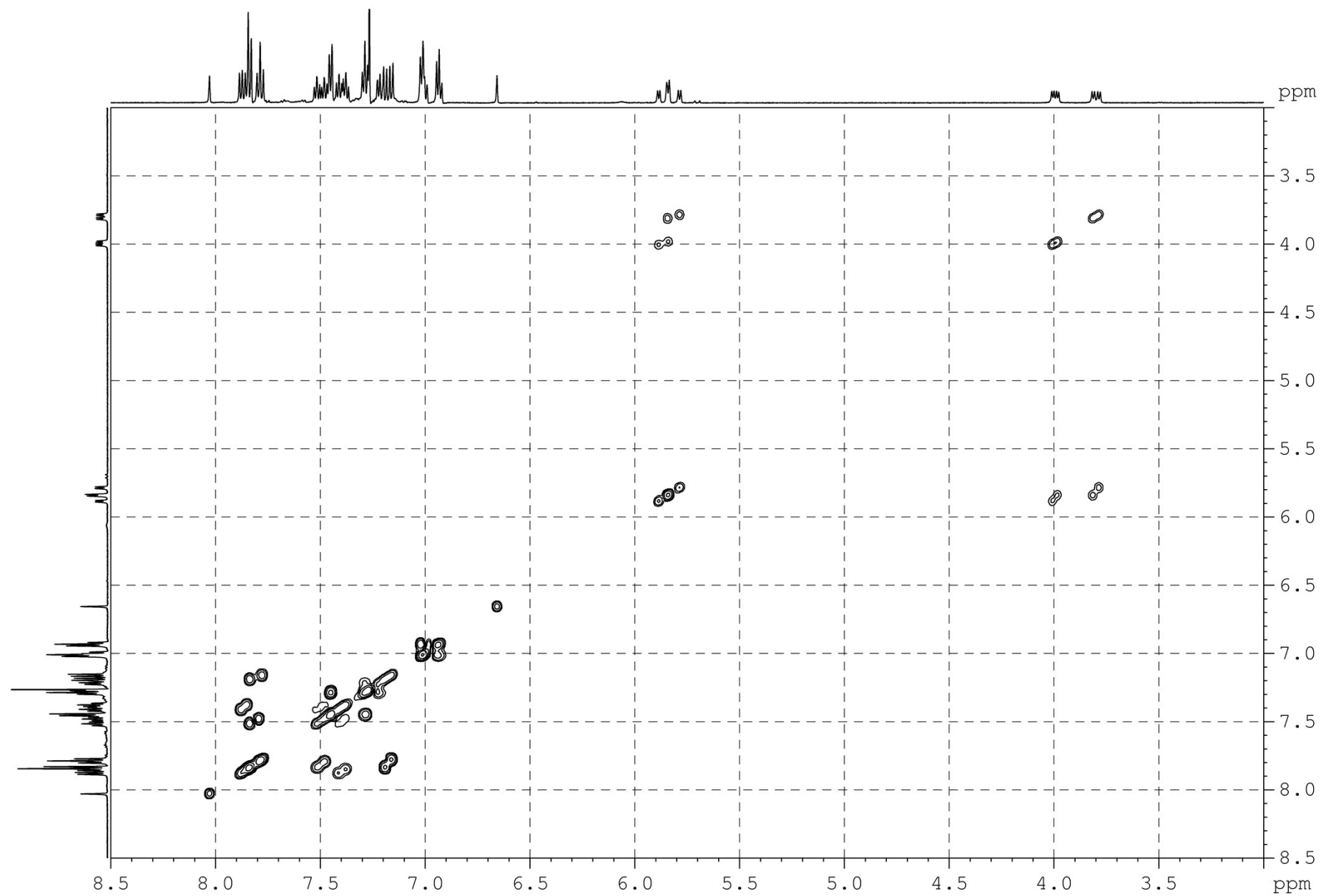
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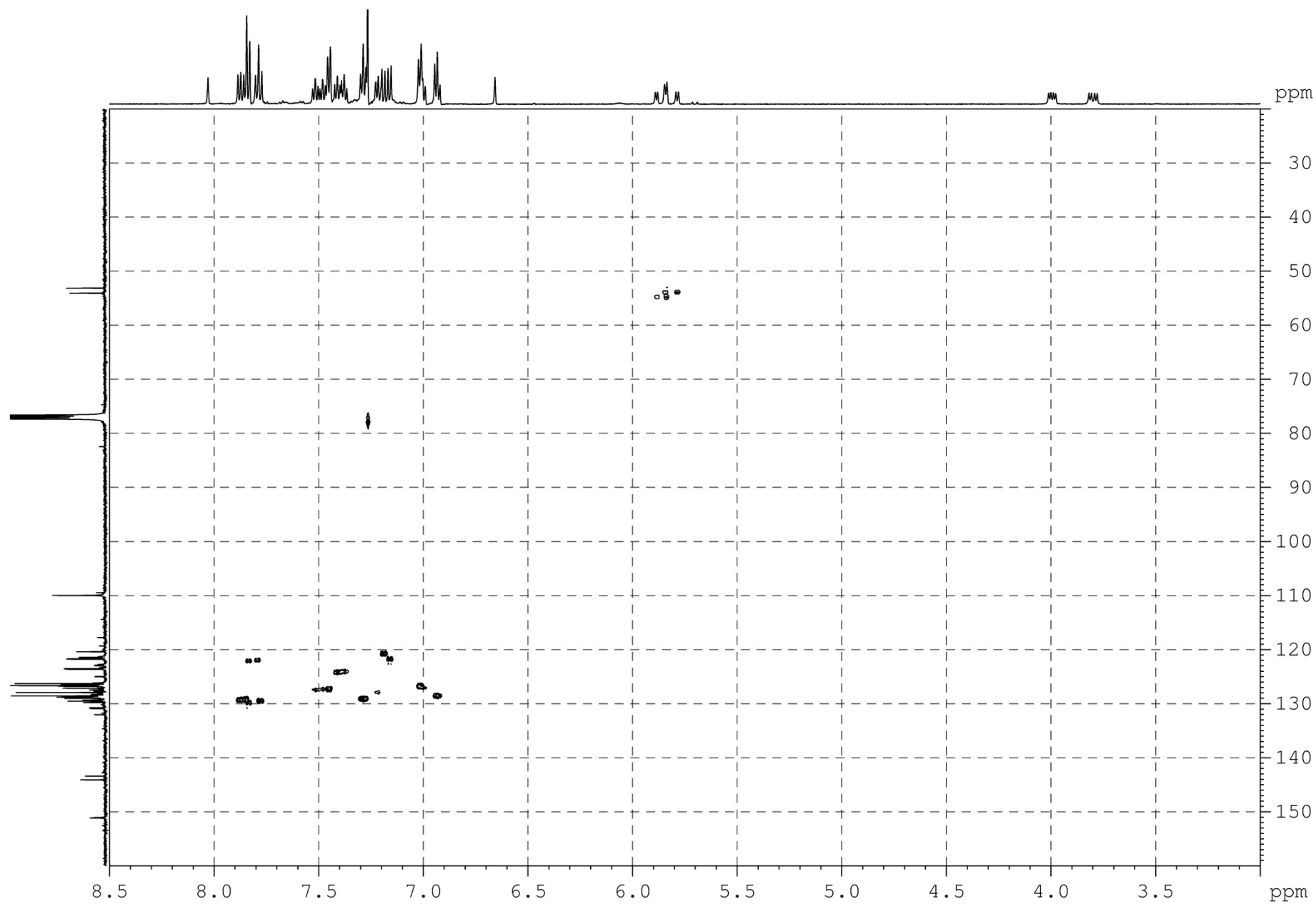
**Figure S11.**  $^1\text{H}$ - $^{15}\text{N}$  HSQC spectra of **4a** after 24h in  $\text{CDCl}_3$  at  $T = 303\text{ K}$  (**4a** 80 %, **4c** 20 %).



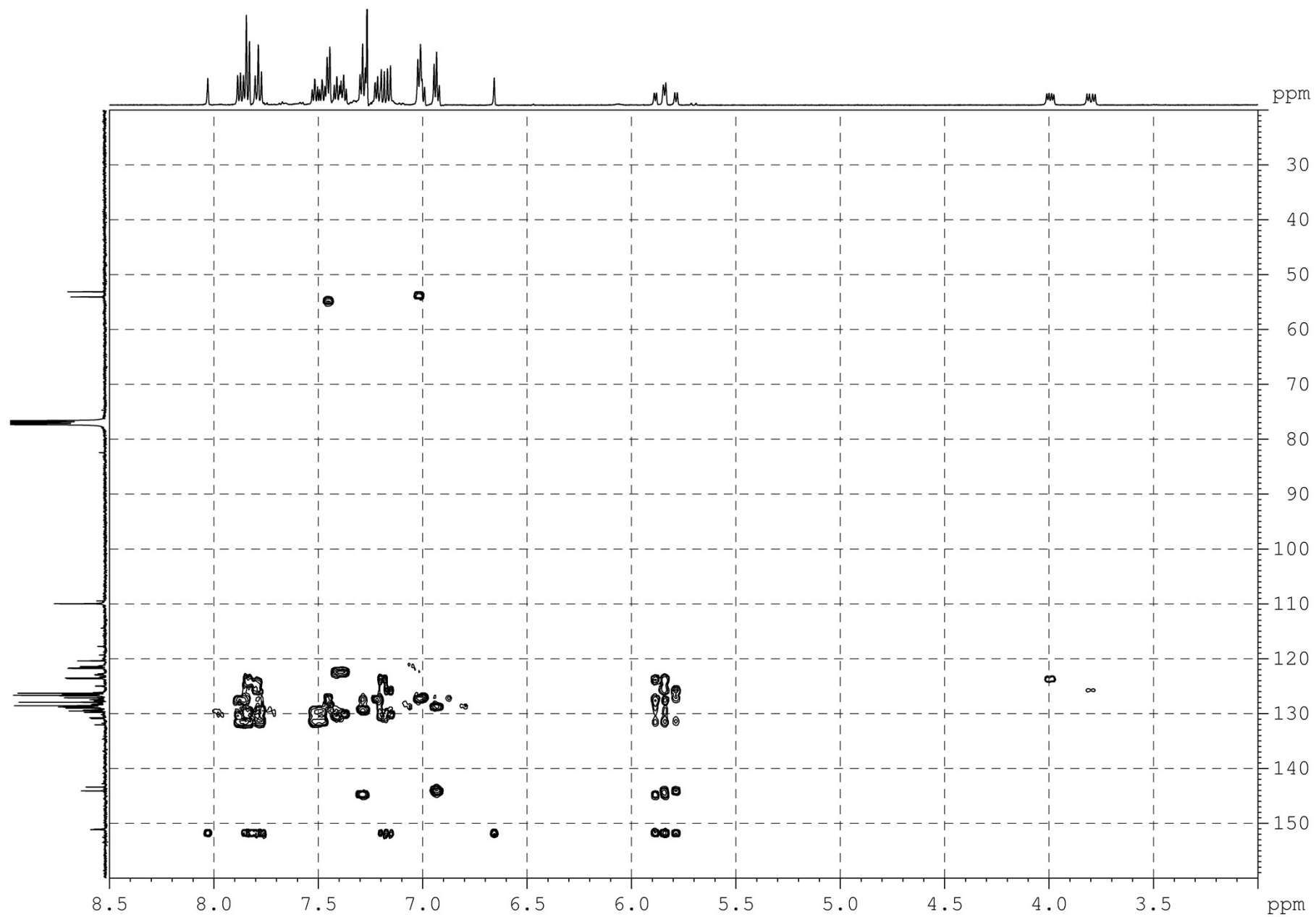
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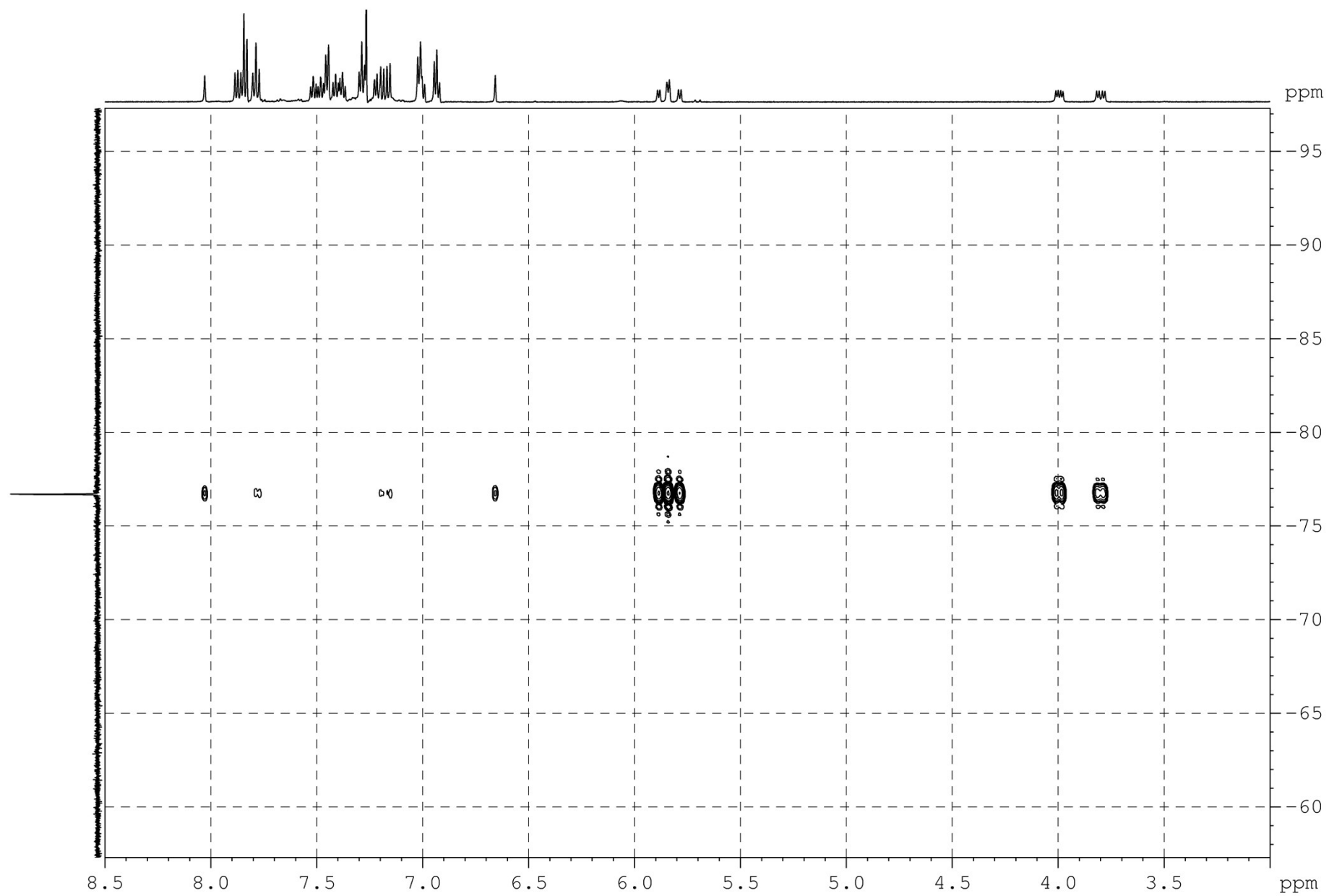
**Figure S13.**  $^1\text{H}$ - $^1\text{H}$  COSY spectra of **4b** in  $\text{CDCl}_3$  at  $T = 303\text{ K}$ .



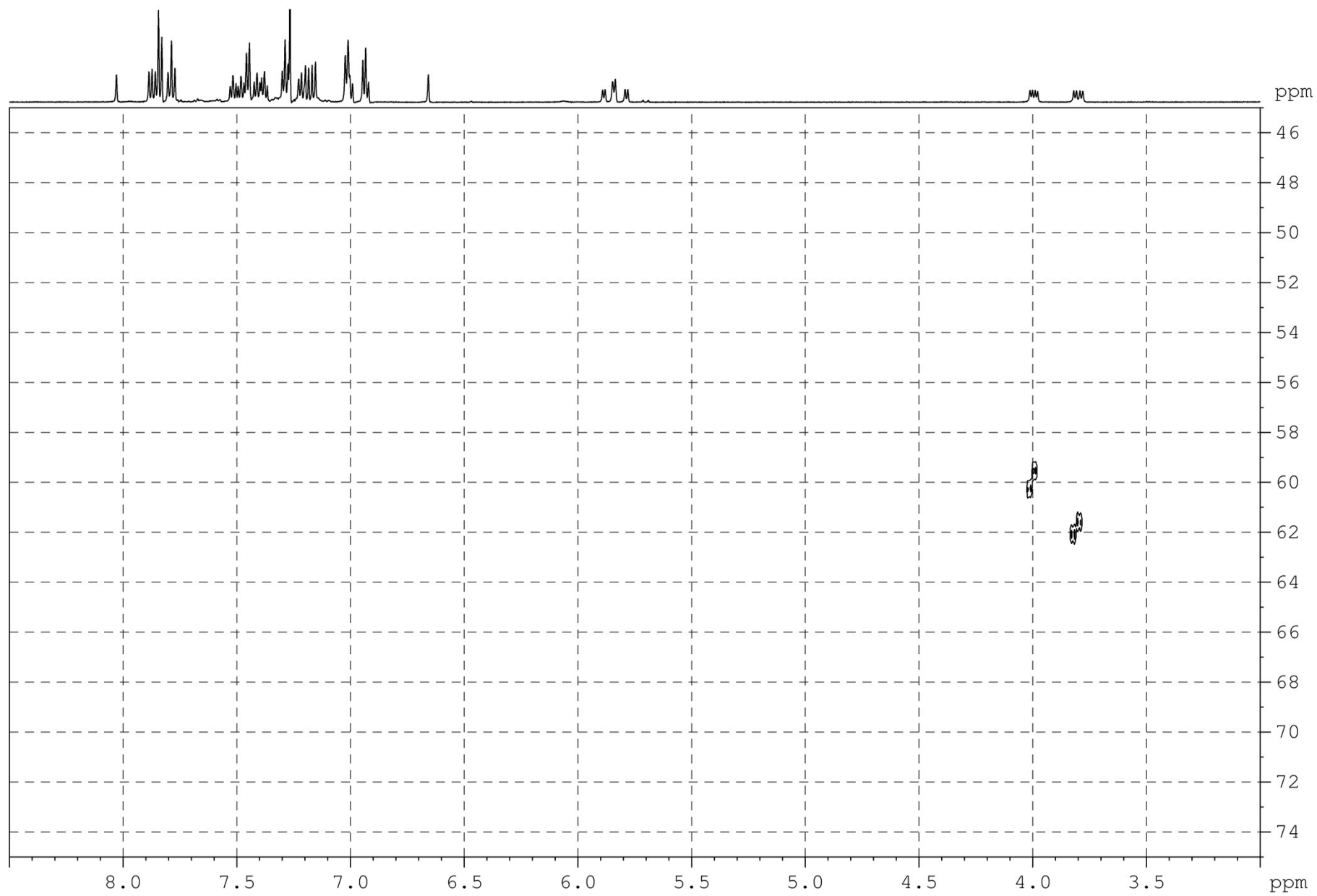
**Figure S14.**  $^1\text{H}$ - $^{13}\text{C}$  HSQC spectra of **4b** in  $\text{CDCl}_3$  at  $T = 303\text{ K}$ .



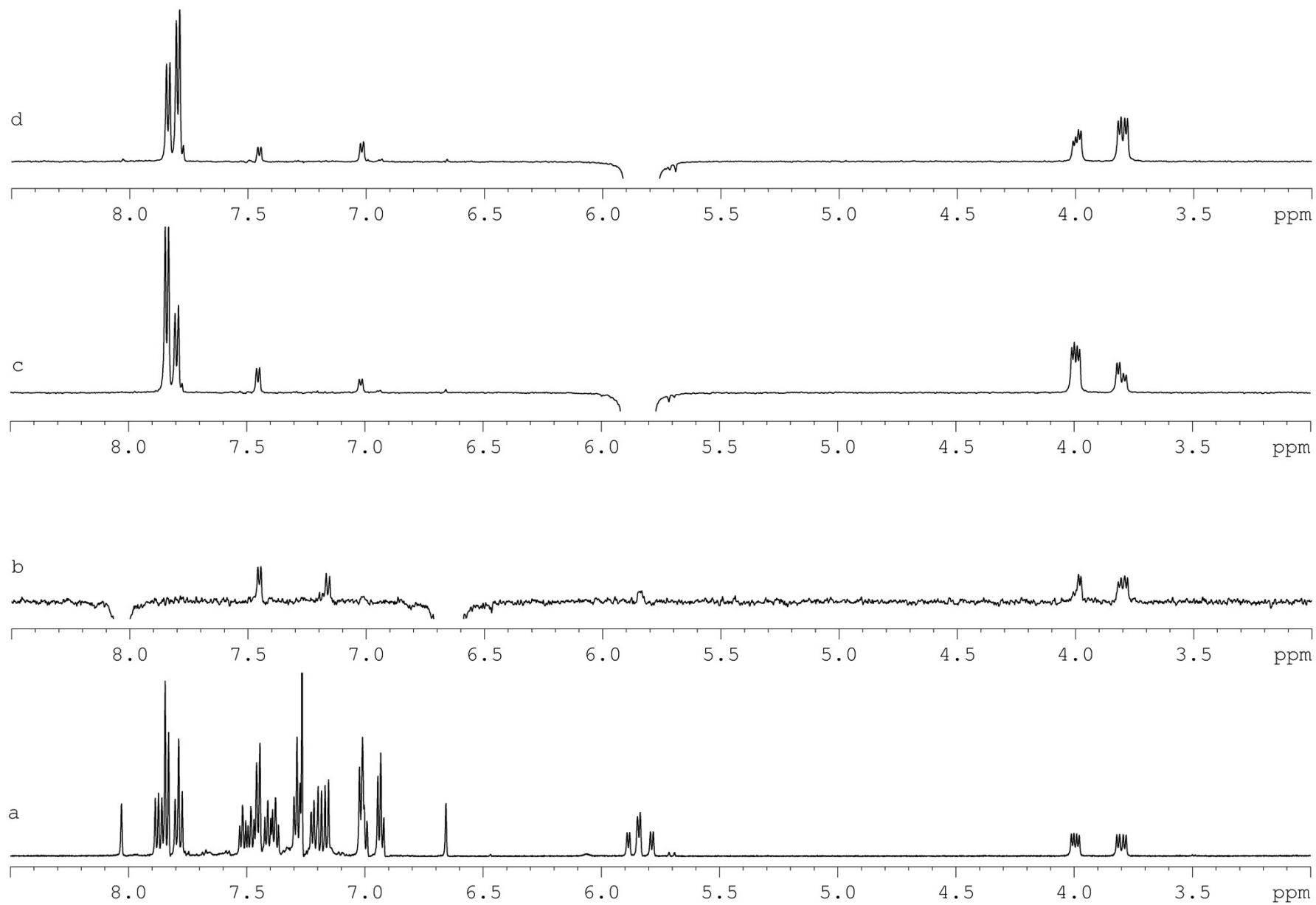
**Figure S15.**  $^1\text{H}$ - $^{13}\text{C}$  HMBC spectra of **4b** in  $\text{CDCl}_3$  at  $T = 303\text{ K}$ .



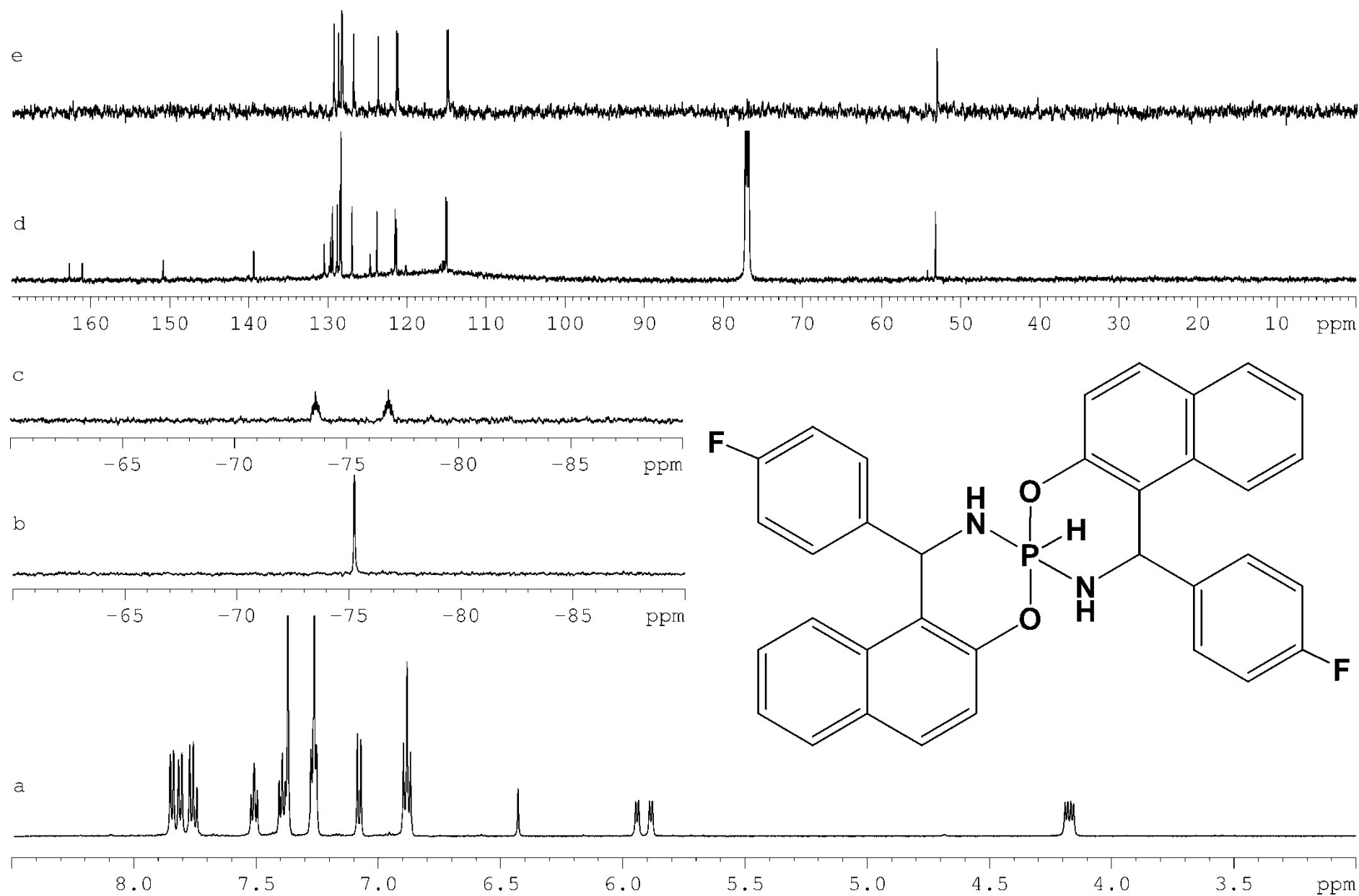
**Figure S16.**  $^1\text{H}$ - $^{31}\text{P}$  HMBC spectra of **4b** in  $\text{CDCl}_3$  at  $T = 303\text{ K}$ .



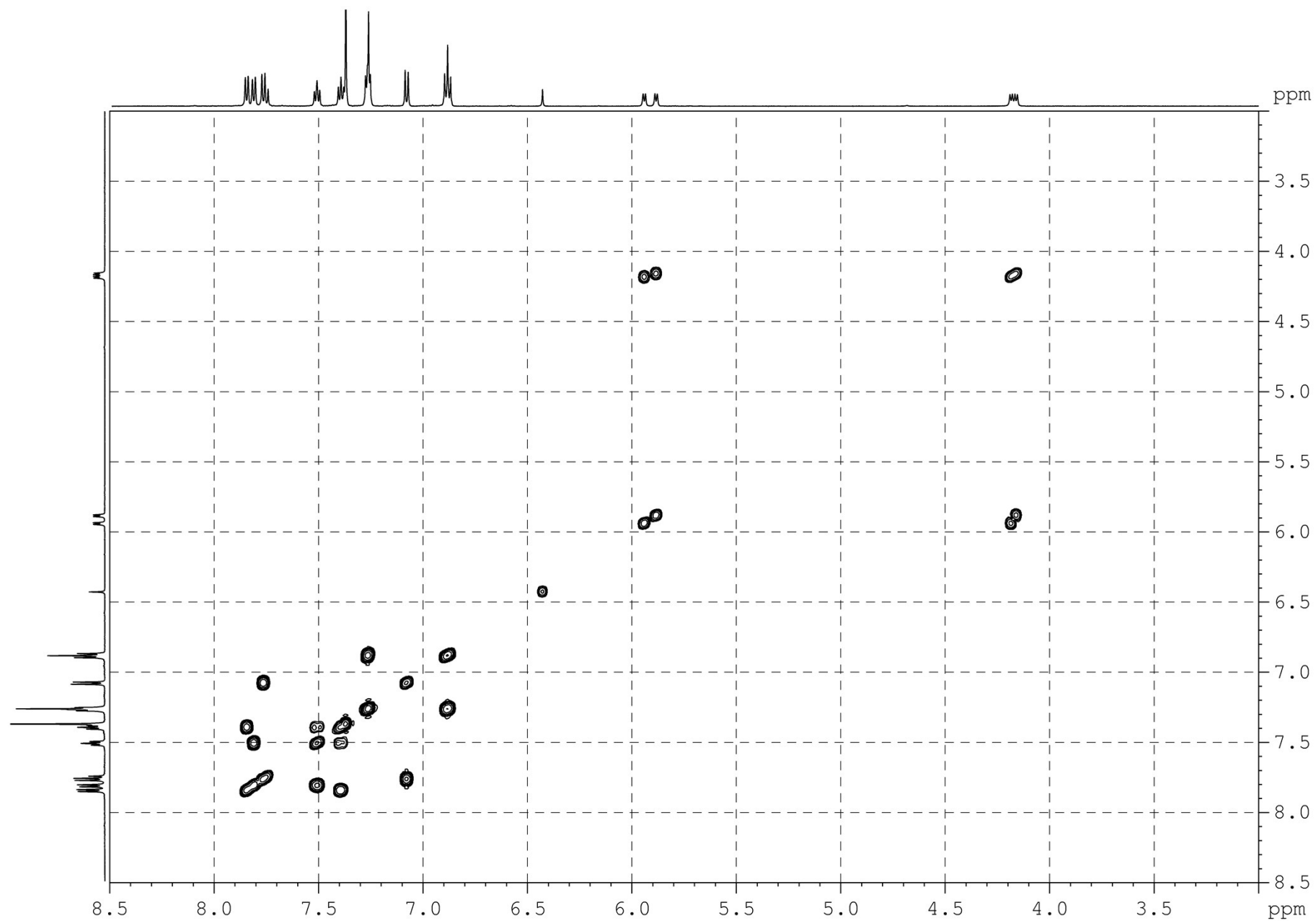
**Figure S17.**  $^1\text{H}$ - $^{15}\text{N}$  HSQC spectra of **4b** in  $\text{CDCl}_3$  at  $T = 303$  K.



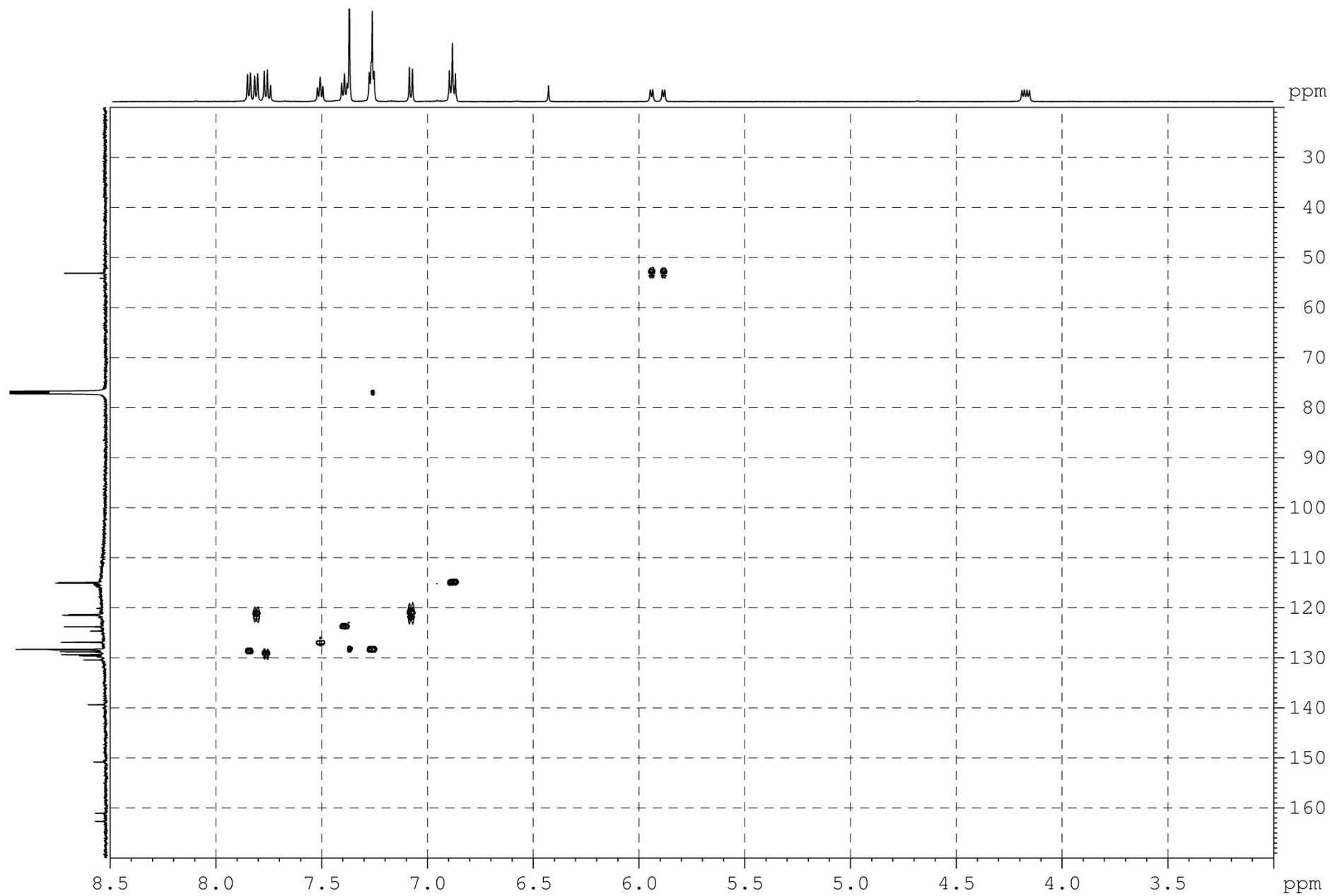
**Figure S18.**  $^1\text{H}$  (a) and 1D NOESY (b-d) spectra of **4b** in  $\text{CDCl}_3$  at  $T = 303\text{ K}$ .



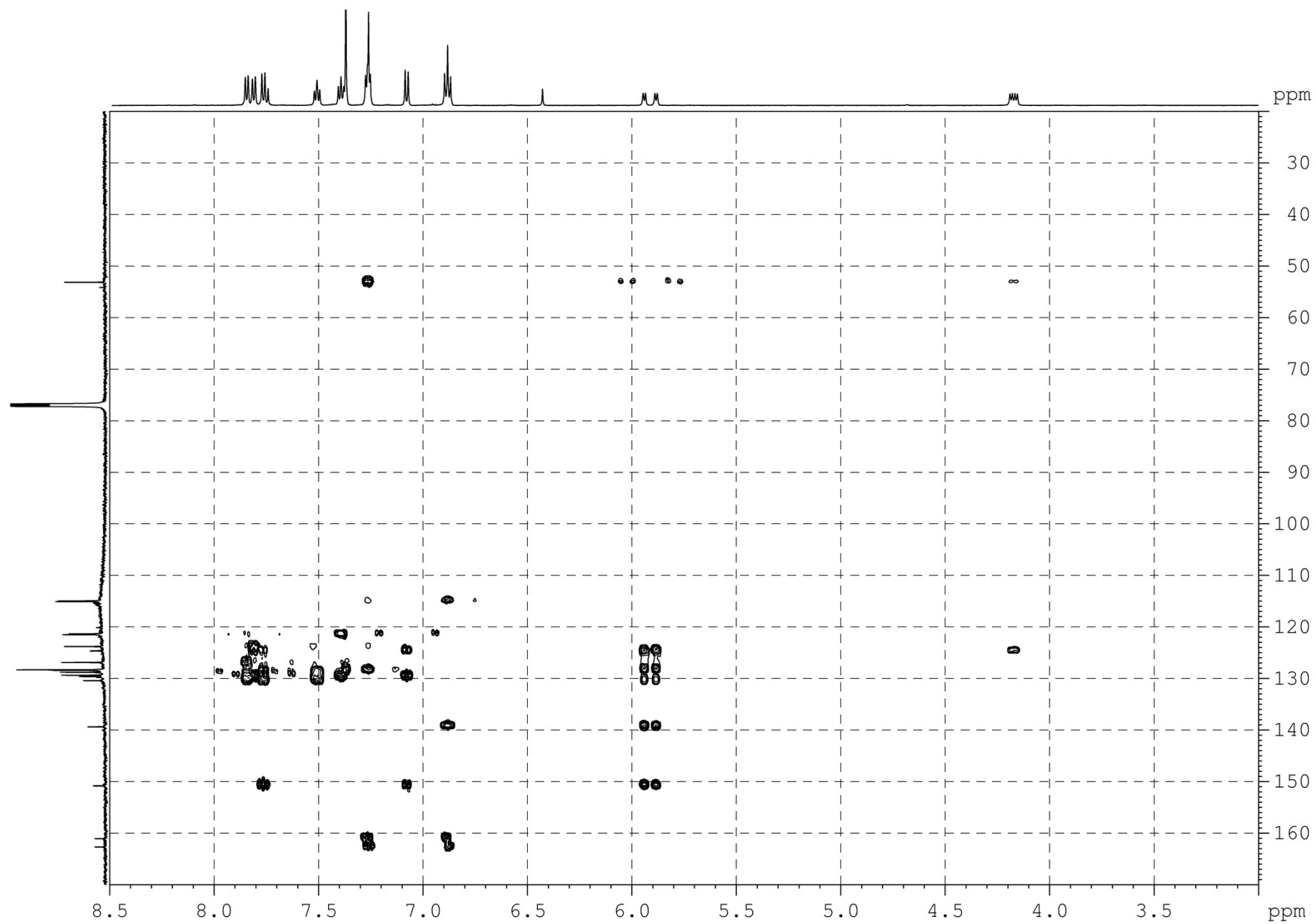
**Figure S19.**  $^1\text{H}$  (a),  $^{31}\text{P}\{^1\text{H}\}$  (b),  $^{31}\text{P}$  (c),  $^{13}\text{C}\{^1\text{H}\}$  (d) and  $^{13}\text{C}$  DEPT (e) spectra of **5a** in  $\text{CDCl}_3$  at  $T = 303$  K.



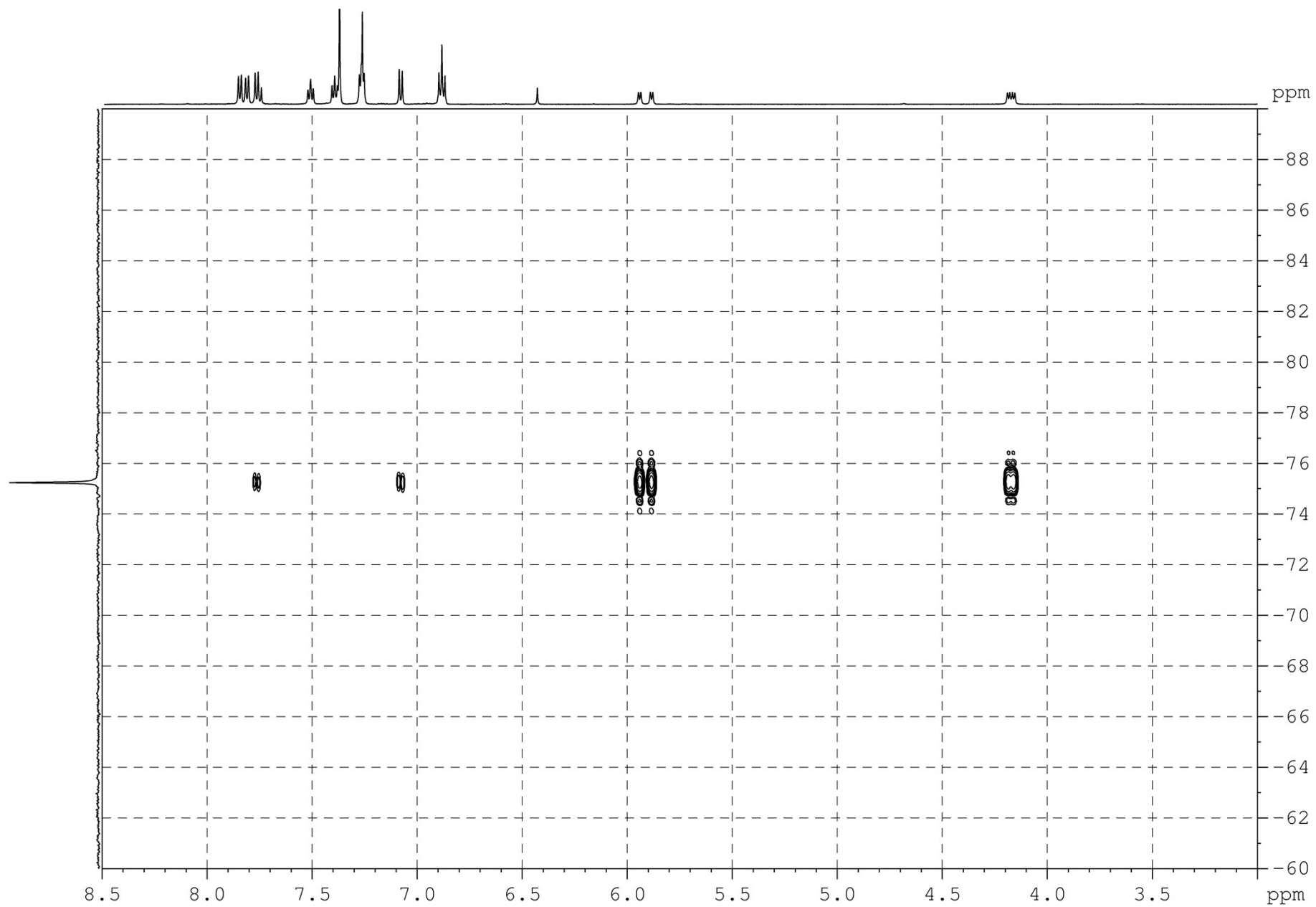
**Figure S20.**  $^1\text{H}$ - $^1\text{H}$  COSY spectra of **5a** in  $\text{CDCl}_3$  at  $T = 303\text{ K}$ .



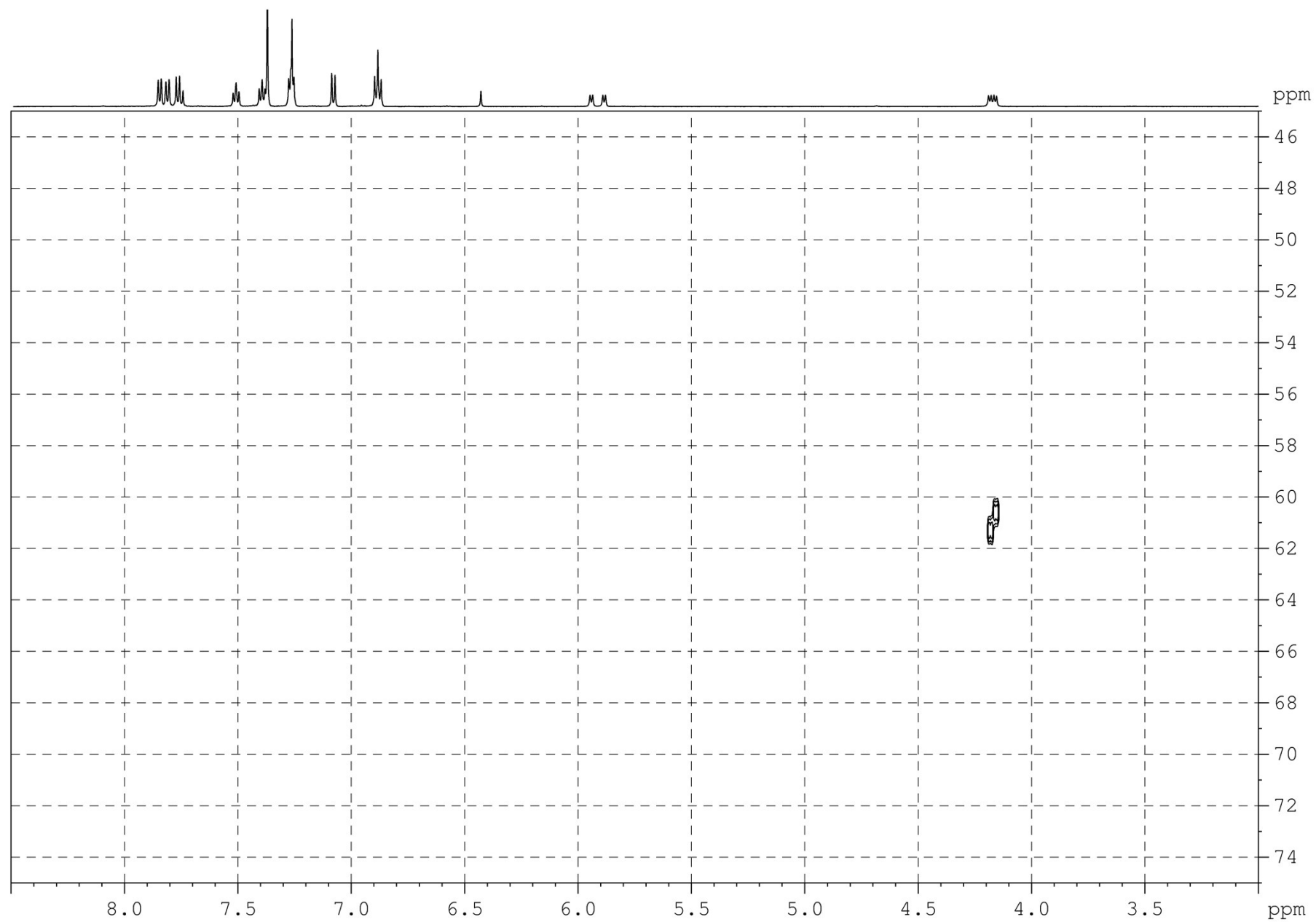
**Figure S21.**  $^1\text{H}$ - $^{13}\text{C}$  HSQC spectra of **5a** in  $\text{CDCl}_3$  at  $T = 303\text{ K}$ .



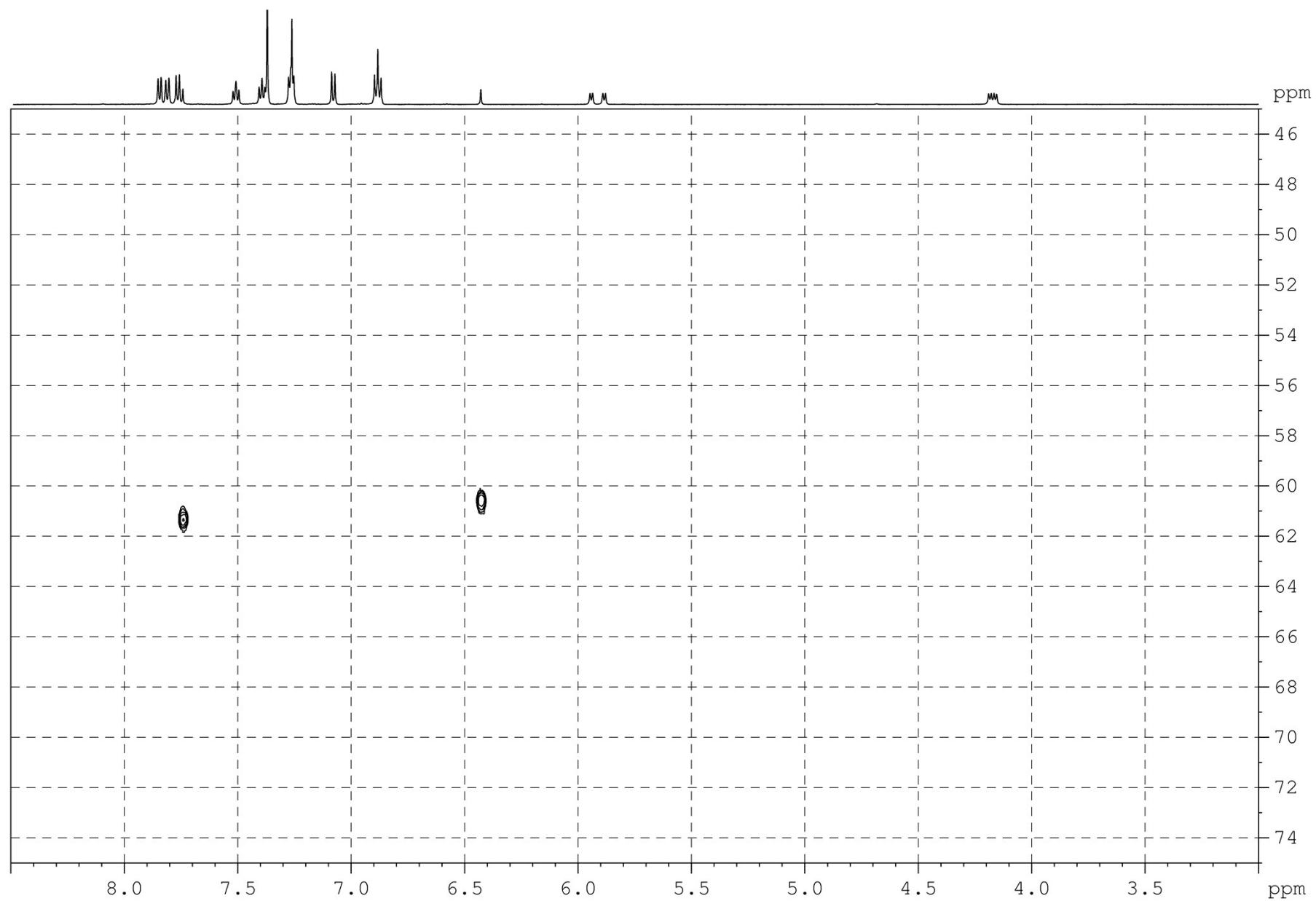
**Figure S22.**  $^1\text{H}$ - $^{13}\text{C}$  HMBC spectra of **5a** in  $\text{CDCl}_3$  at  $T = 303\text{ K}$ .



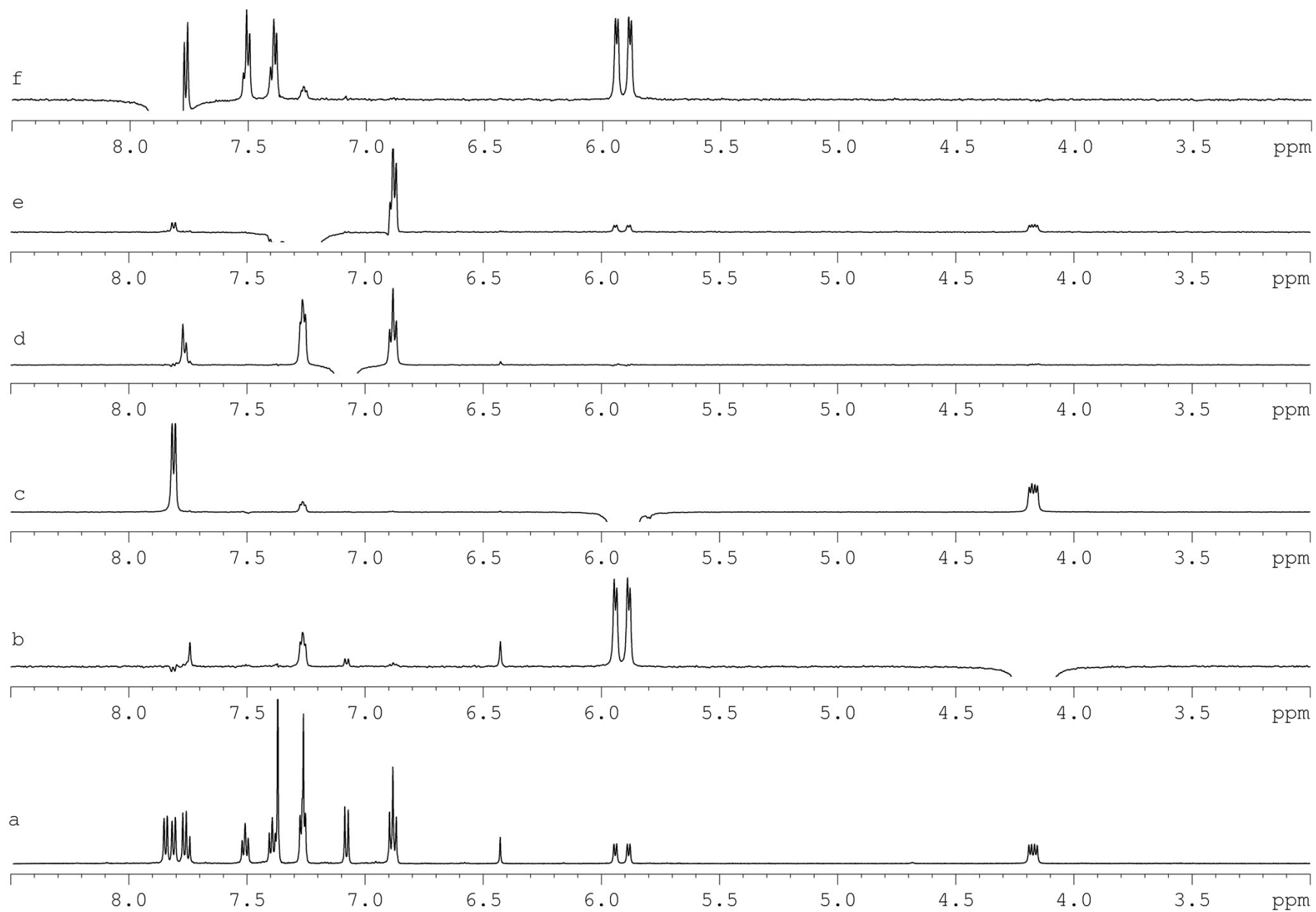
**Figure S23.**  $^1\text{H}$ - $^{31}\text{P}$  HMBC spectra of **5a** in  $\text{CDCl}_3$  at  $T = 303\text{ K}$ .



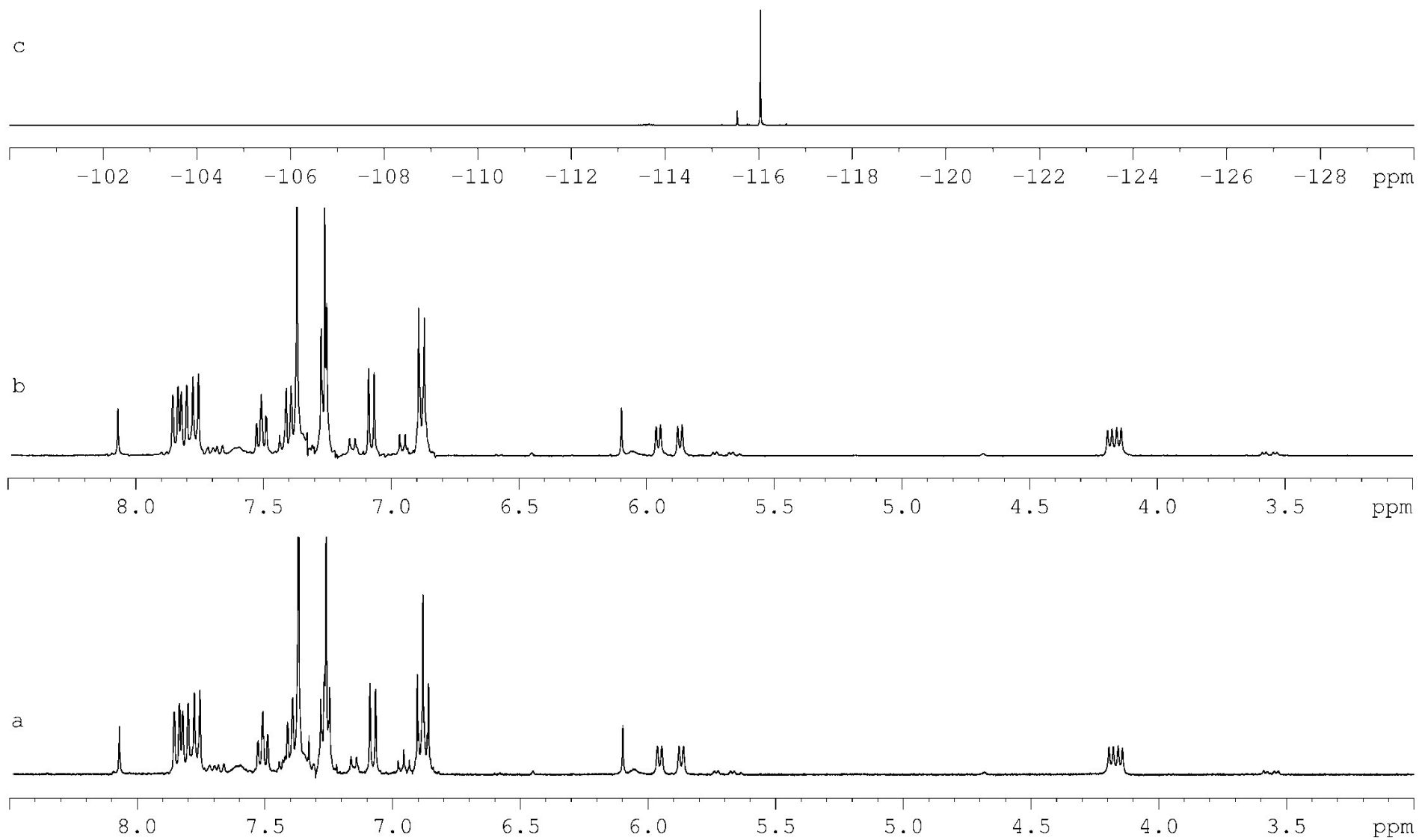
**Figure S24.**  $^1\text{H}$ - $^{15}\text{N}$  HSQC spectra of **5a** in  $\text{CDCl}_3$  at  $T = 303$  K.



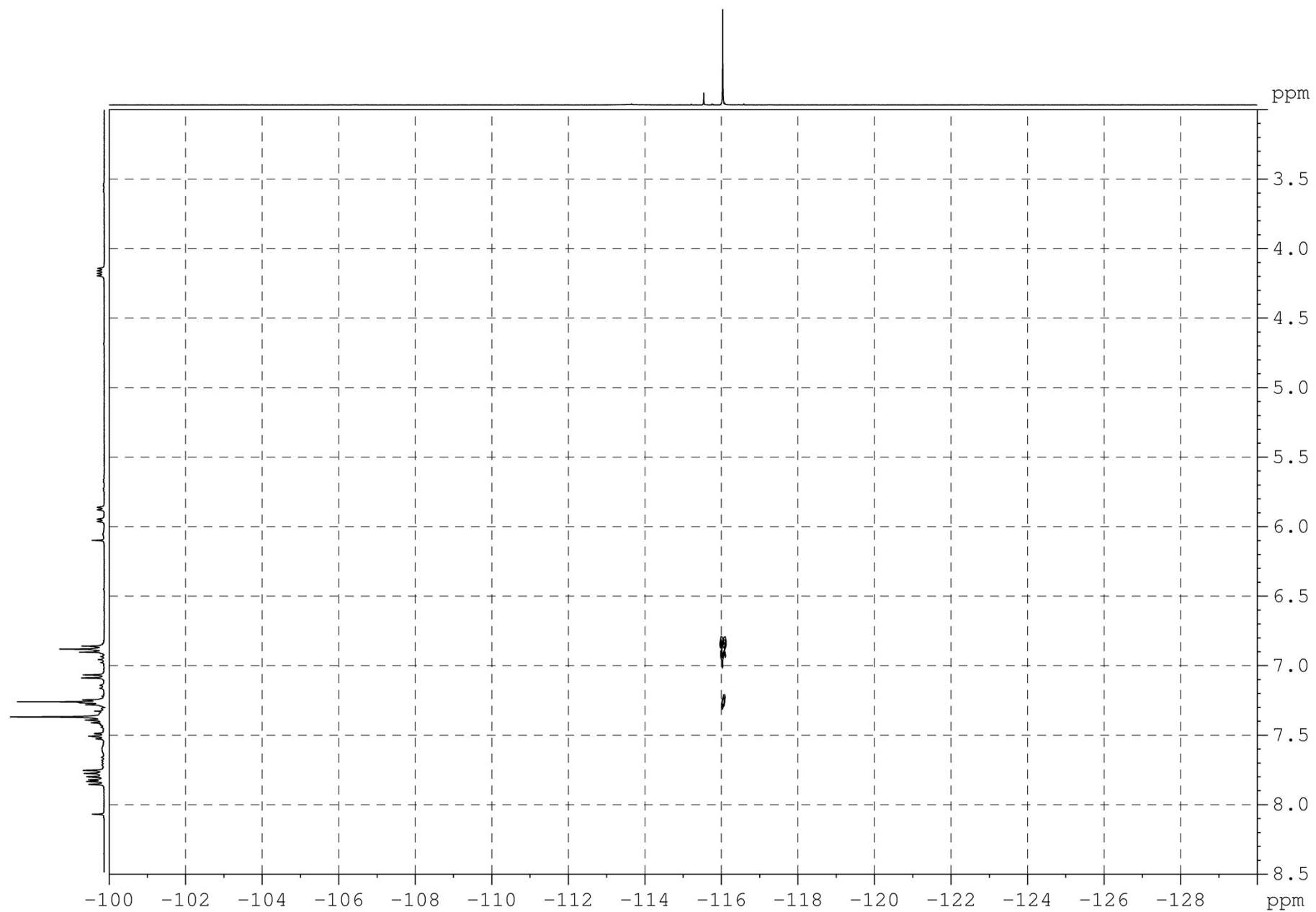
**Figure S25.**  $^1\text{H}$ - $^{15}\text{N}$  HMBC spectra of **5a** in  $\text{CDCl}_3$  at  $T = 303\text{ K}$ .



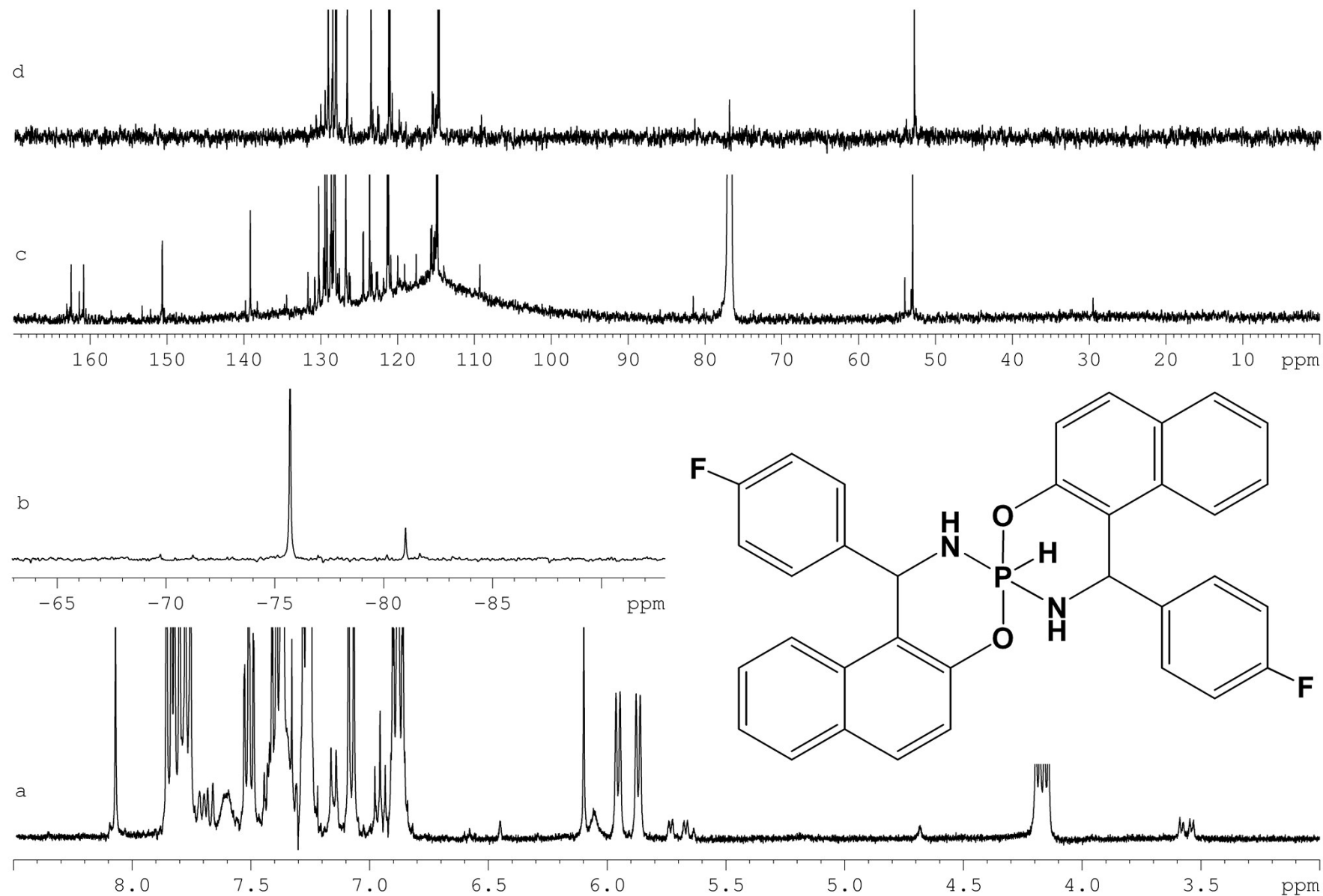
**Figure S26.** <sup>1</sup>H (a) and 1D NOESY (b-f) spectra of **5a** in CDCl<sub>3</sub> at T = 303 K.



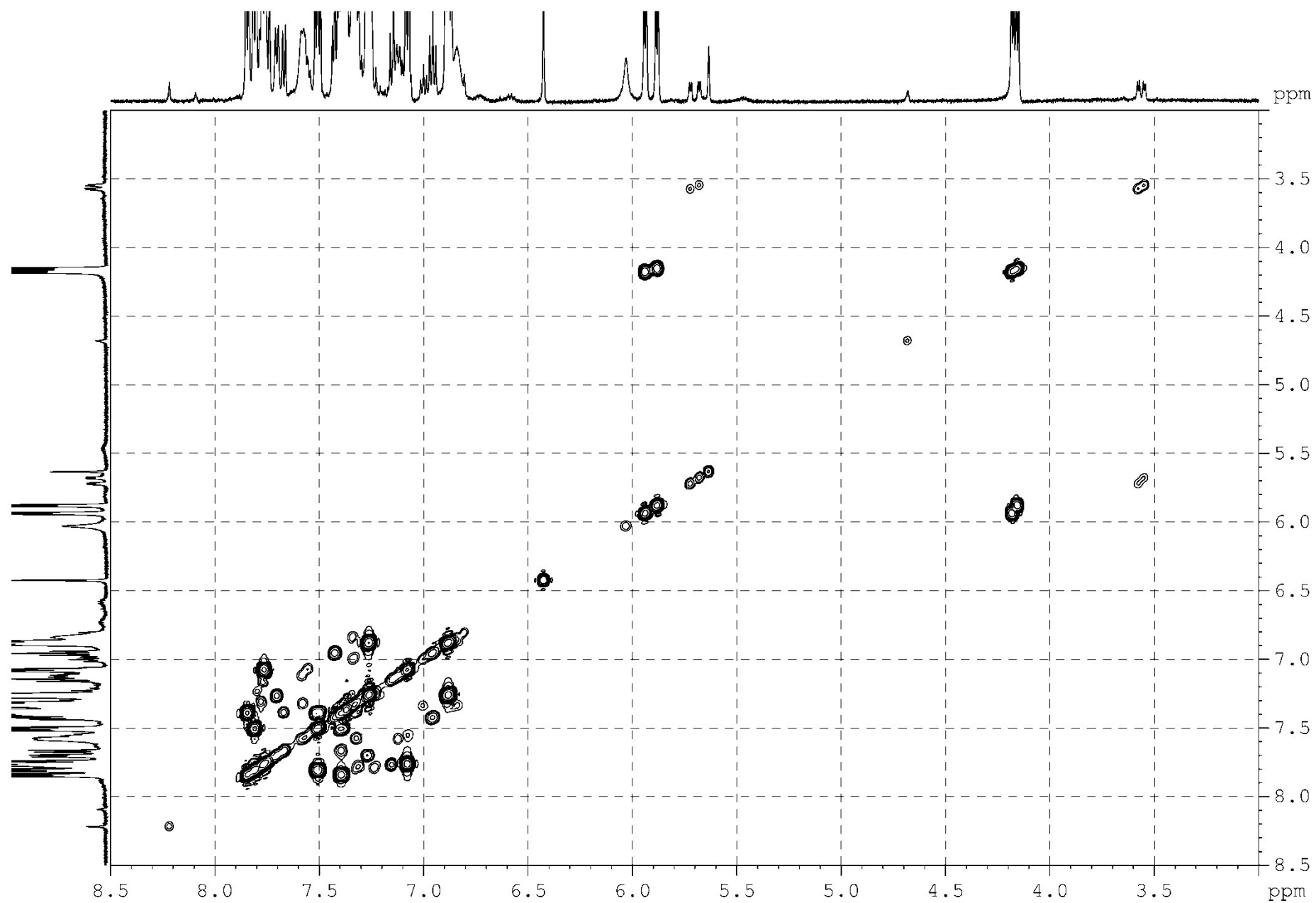
**Figure S27.**  $^1\text{H}$  (a),  $^1\text{H}\{^{19}\text{F}\}$  (b) and  $^{19}\text{F}\{^1\text{H}\}$  (c) spectra of **5a** in  $\text{CDCl}_3$  at  $T = 303 \text{ K}$ .



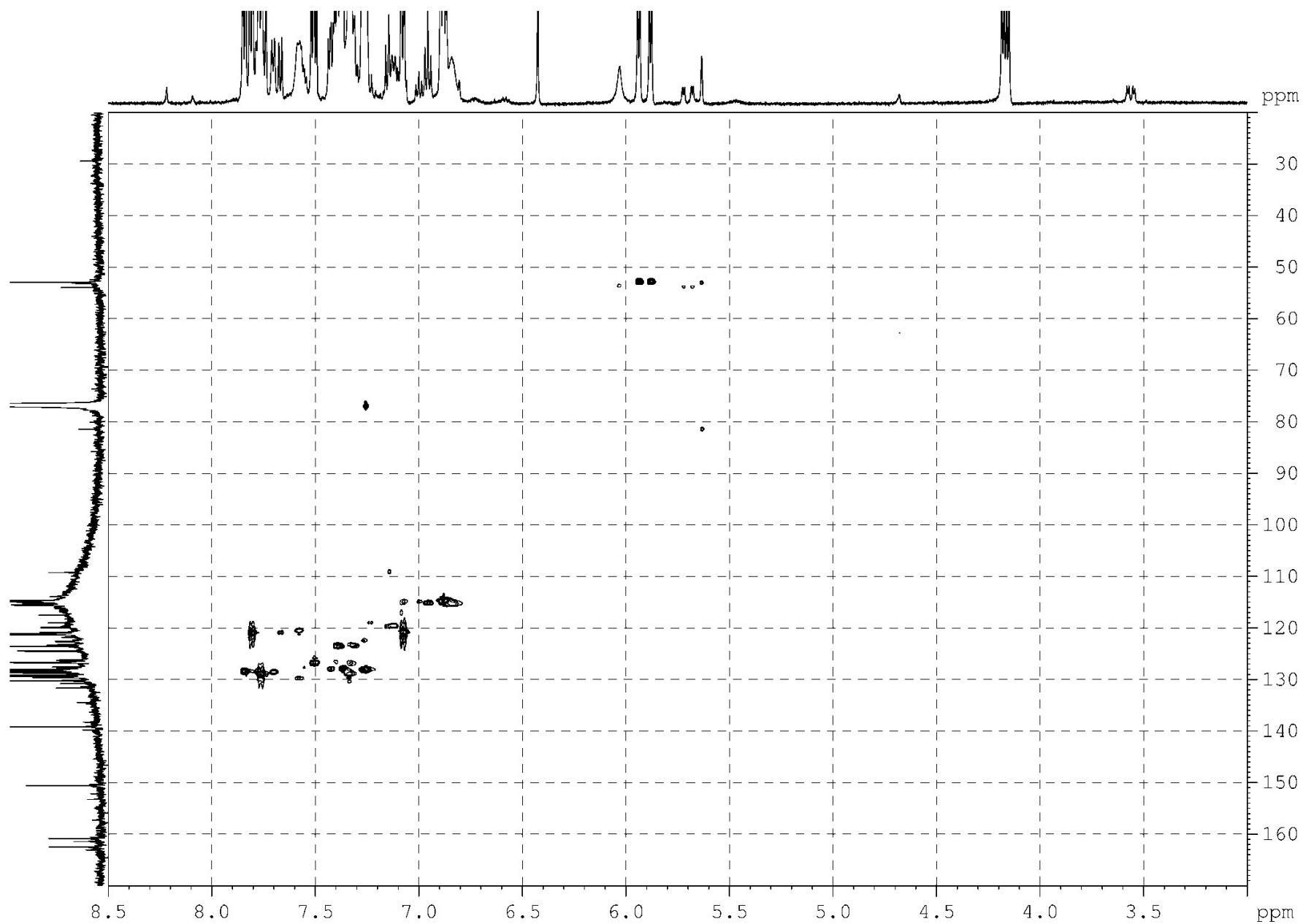
**Figure S28.**  $^{19}\text{F}$ - $^1\text{H}$  HETCOR spectra of **5a** in  $\text{CDCl}_3$  at  $T = 303\text{ K}$ .



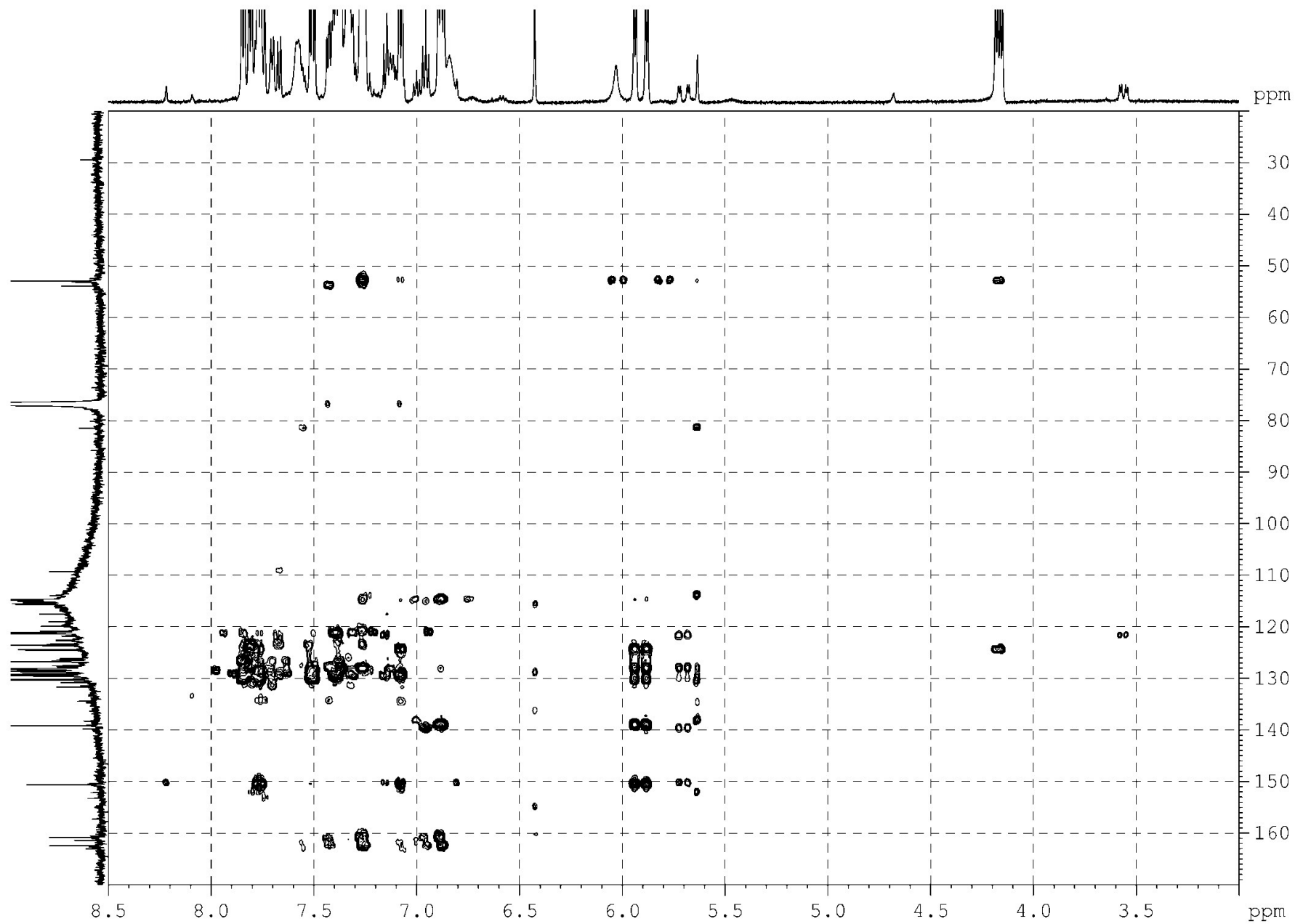
**Figure S29.**  $^1\text{H}$  (a),  $^{31}\text{P}\{^1\text{H}\}$  (b),  $^{13}\text{C}\{^1\text{H}\}$  (c) and  $^{13}\text{C}$  DEPT (d) spectra of **5a** after 5 days in  $\text{CDCl}_3$  at  $T = 303\text{ K}$  (**5a** 87 %, **5c** 13 %).



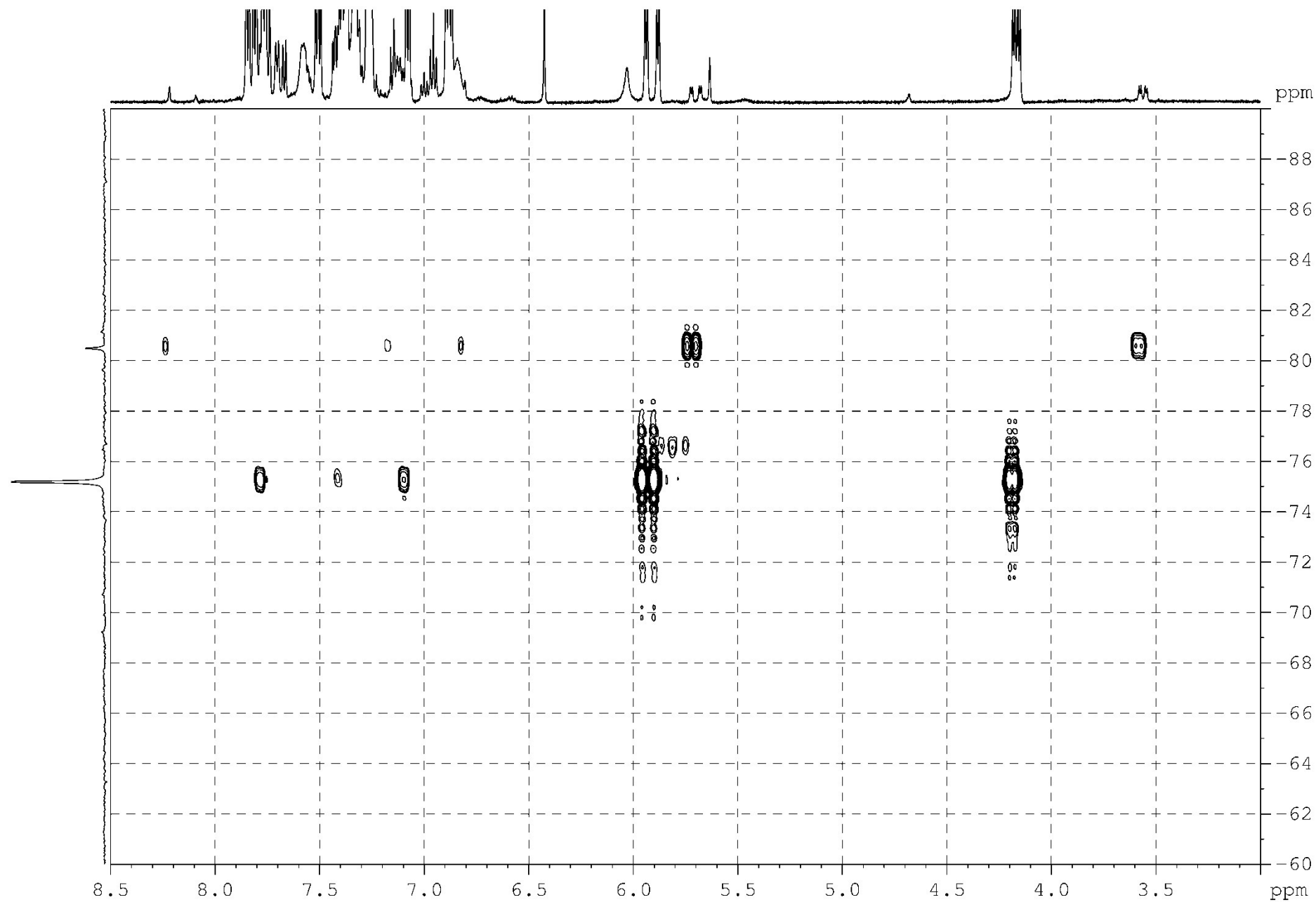
**Figure S30.**  $^1\text{H}$ - $^1\text{H}$  COSY spectra of **5a** after 5 days in  $\text{CDCl}_3$  at  $T = 303\text{ K}$  (**5a** 87 %, **5c** 13 %).



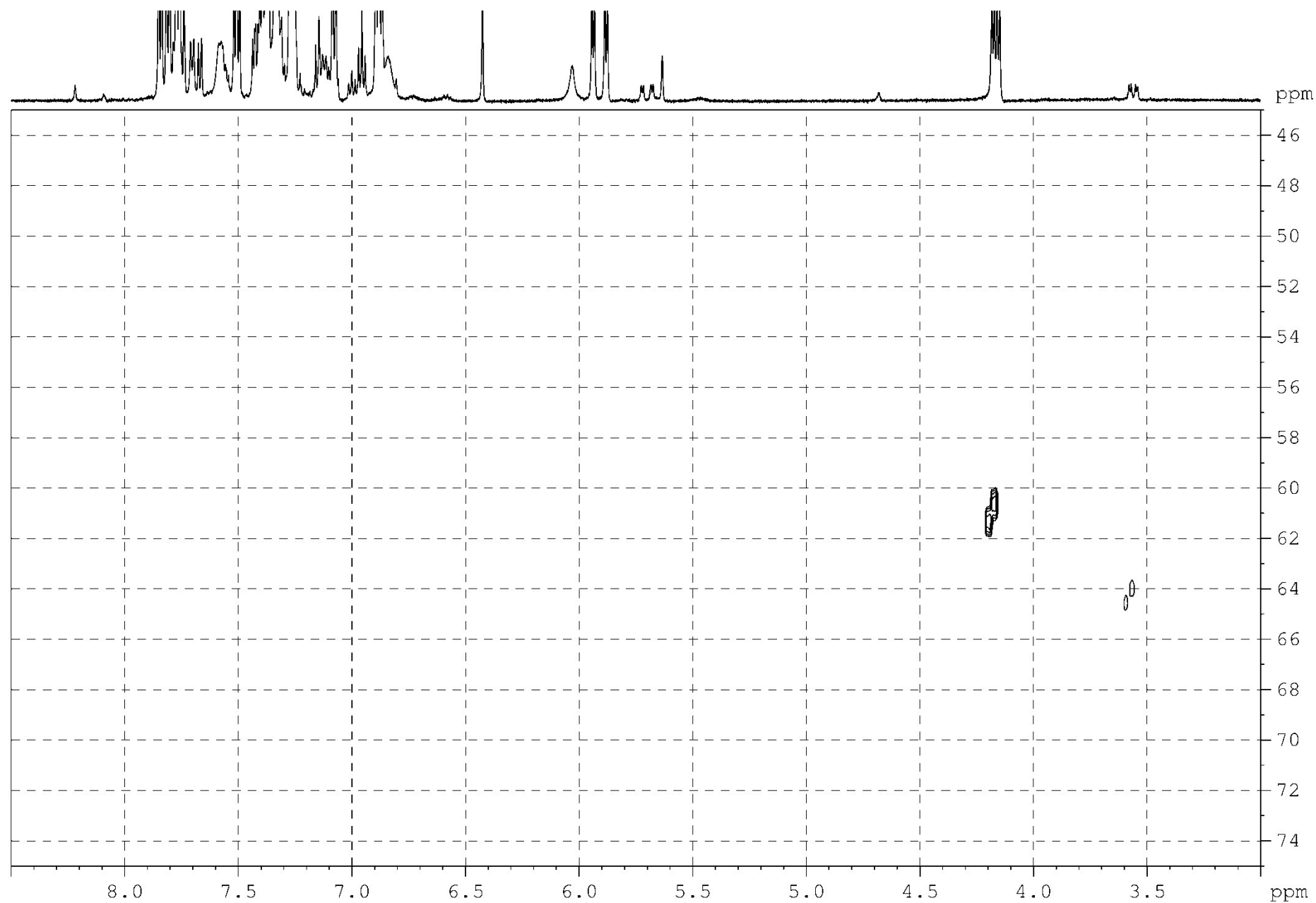
**Figure S31.**  $^1\text{H}$ - $^{13}\text{C}$  HSQC spectra of **5a** after 5 days in  $\text{CDCl}_3$  at  $T = 303\text{ K}$  (**5a** 87 %, **5c** 13 %).



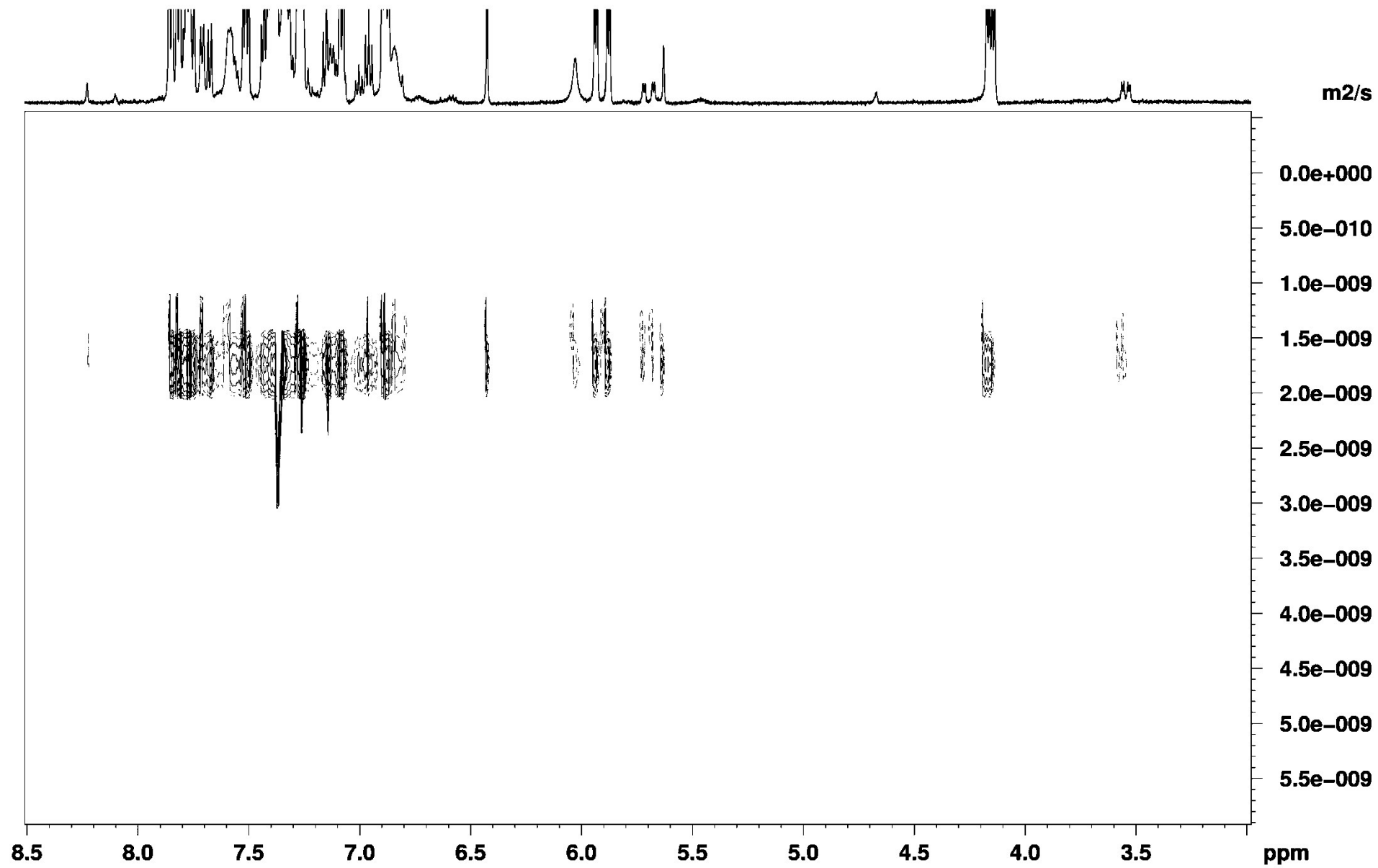
**Figure S32.**  $^1\text{H}$ - $^{13}\text{C}$  HMBC spectra of **5a** after 5 days in  $\text{CDCl}_3$  at  $T = 303\text{ K}$  (**5a** 87 %, **5c** 13 %).



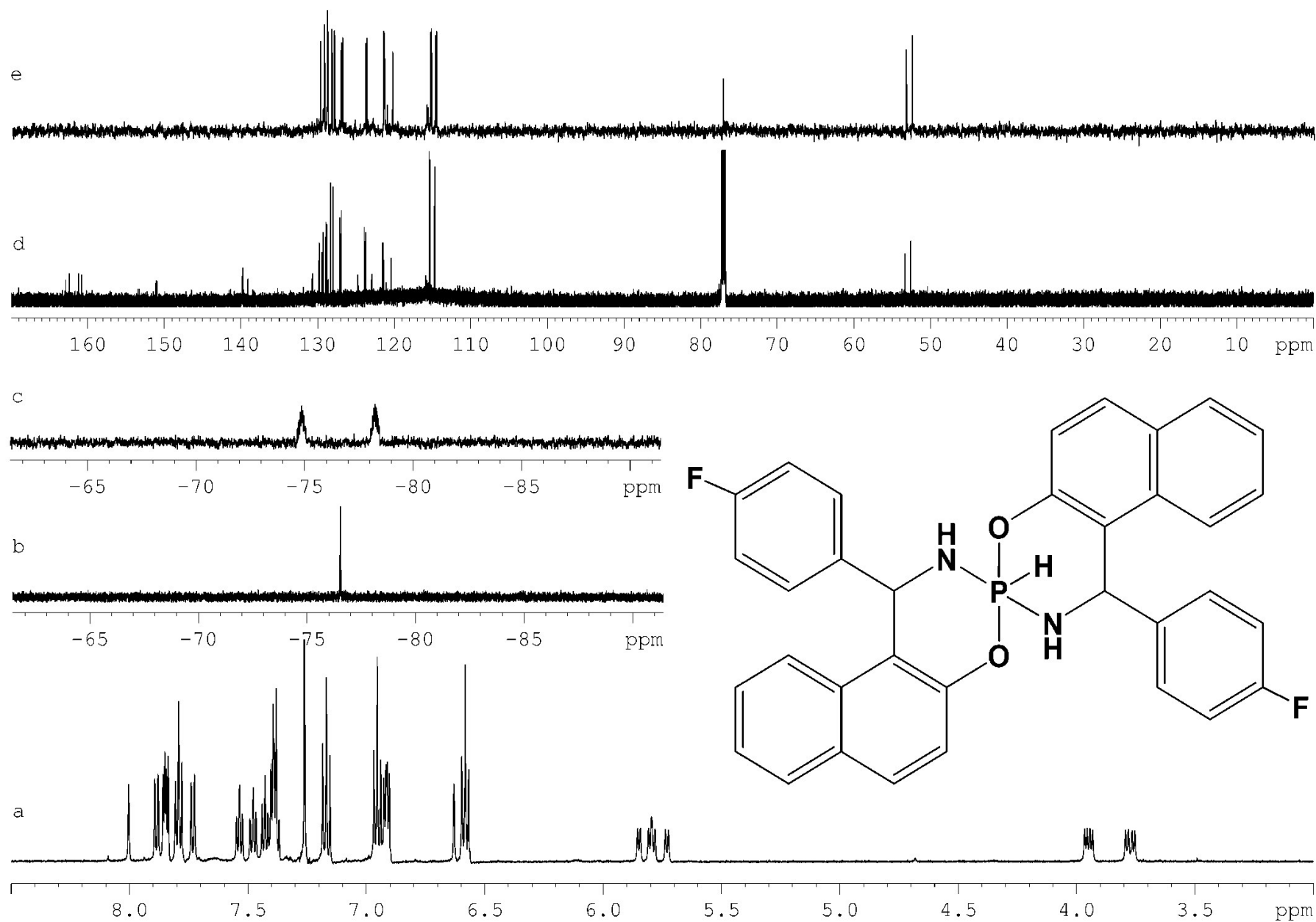
**Figure S33.**  $^1\text{H}$ - $^{31}\text{P}$  HMBC spectra of **5a** after 5 days in  $\text{CDCl}_3$  at  $T = 303\text{ K}$  (**5a** 87 %, **5c** 13 %).



**Figure S34.**  $^1\text{H}$ - $^{15}\text{N}$  HSQC spectra of **5a** after 5 days in  $\text{CDCl}_3$  at  $T = 303\text{ K}$  (**5a** 87 %, **5c** 13 %).



**Figure S35.** 2D DOSY spectra of **5a** after 5 days in CDCl<sub>3</sub> at T = 303 K (**5a** 87 %, **5c** 13 %).



**Figure S36.**  $^1\text{H}$  (a),  $^{31}\text{P}\{^1\text{H}\}$  (b),  $^{31}\text{P}$  (c),  $^{13}\text{C}\{^1\text{H}\}$  (d) and  $^{13}\text{C}$  DEPT (e) spectra of **5b** in  $\text{CDCl}_3$  at  $T = 303$  K.

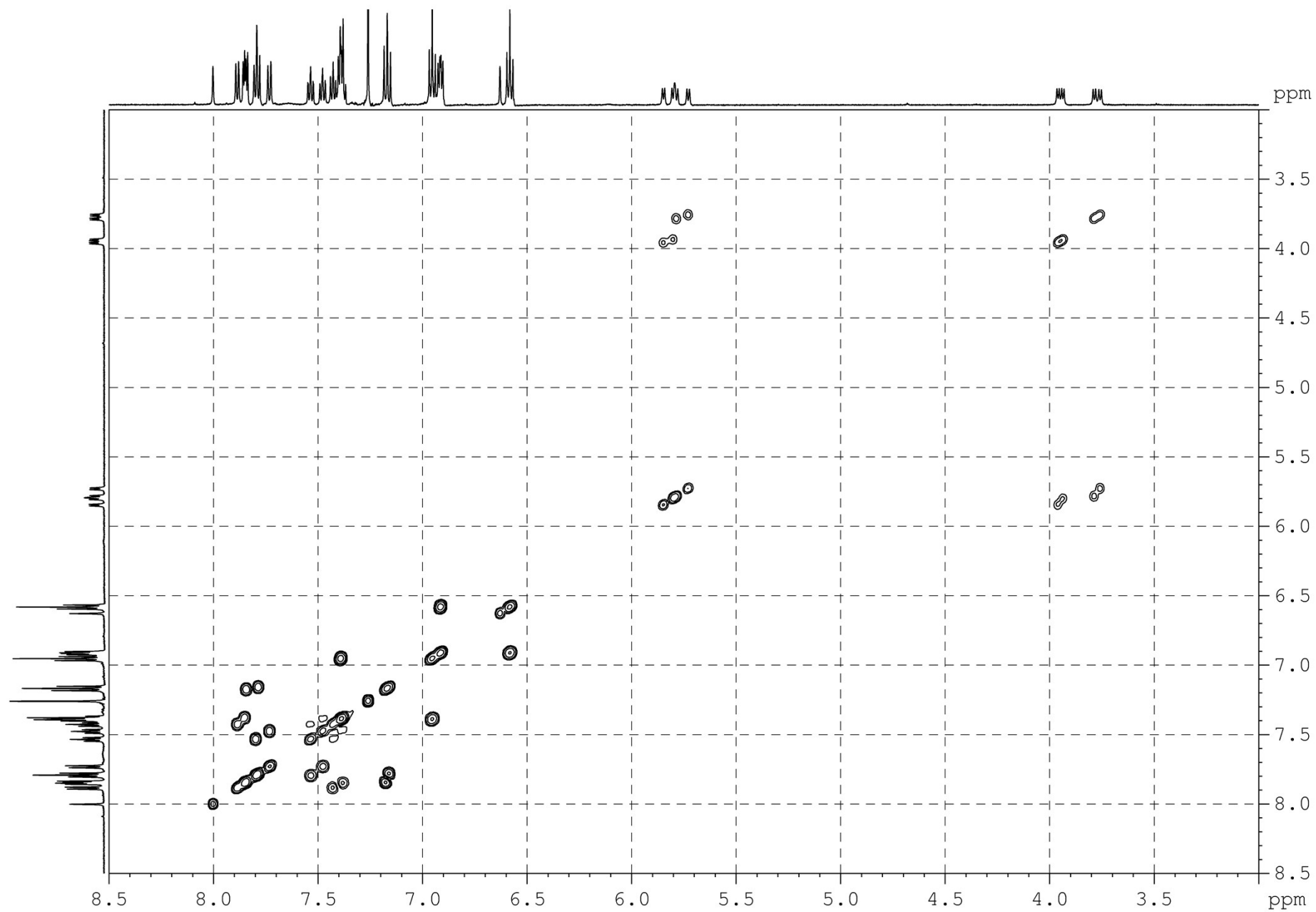
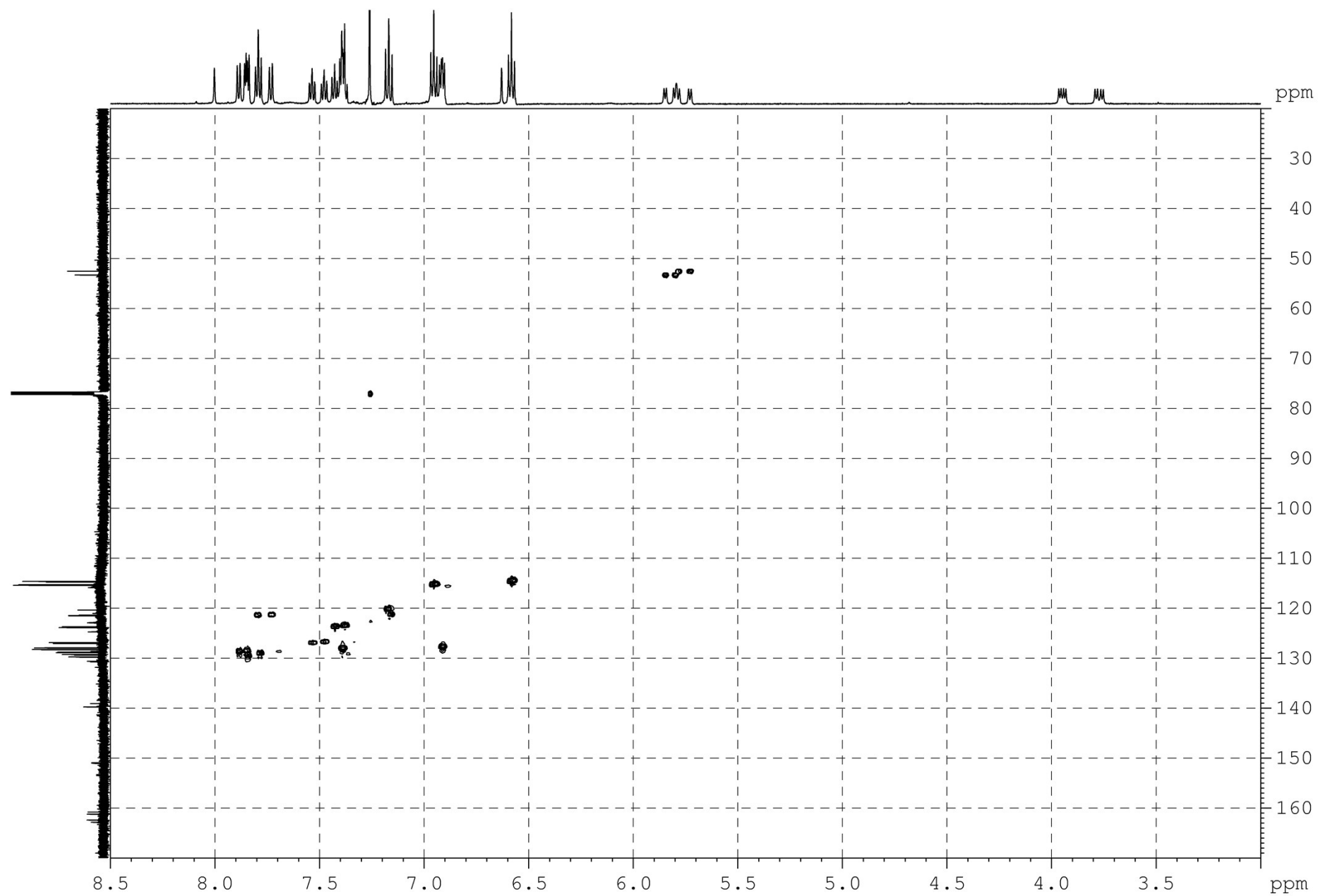
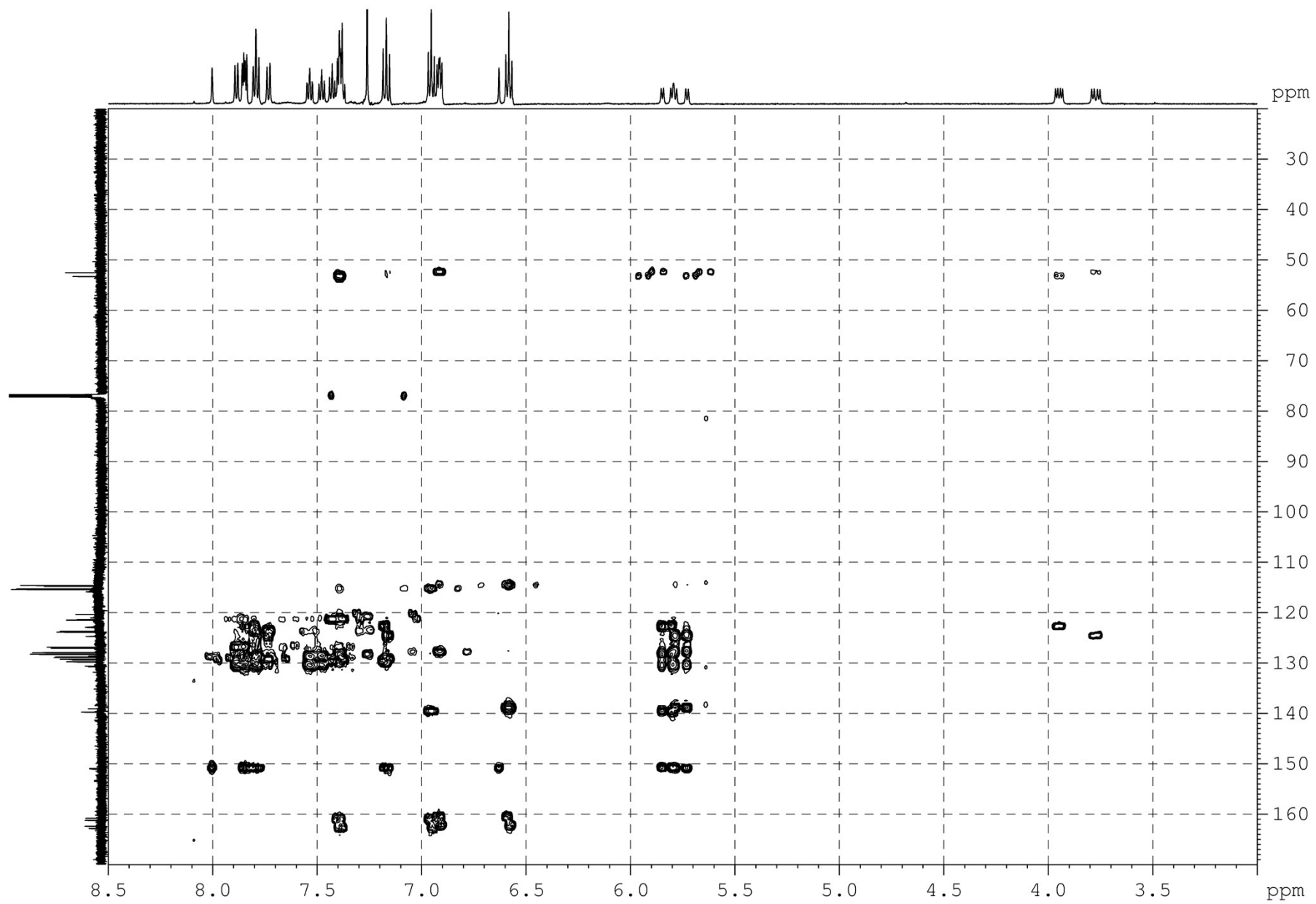


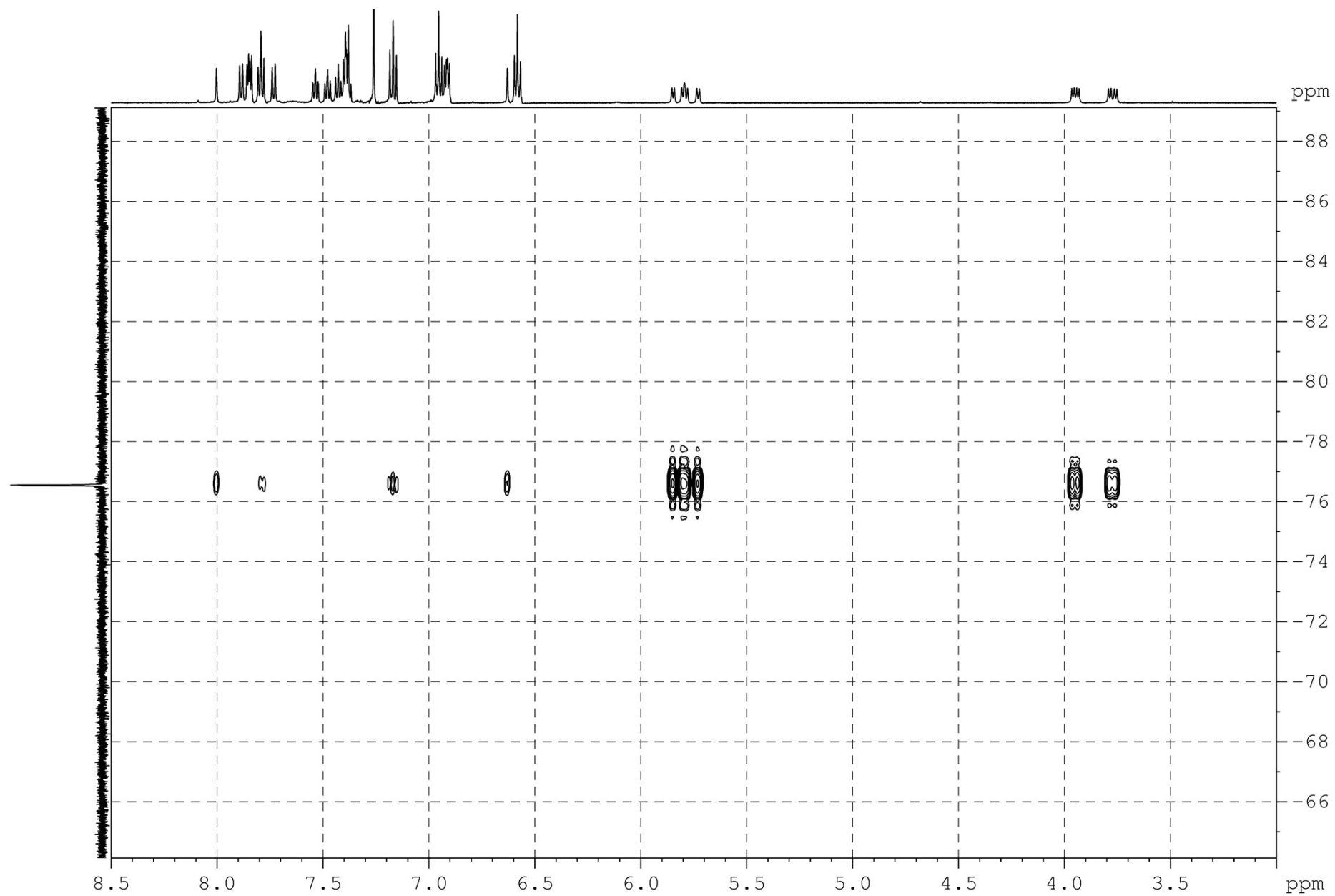
Figure S37.  $^1\text{H}$ - $^1\text{H}$  COSY spectra of **5b** in  $\text{CDCl}_3$  at  $T = 303\text{ K}$ .



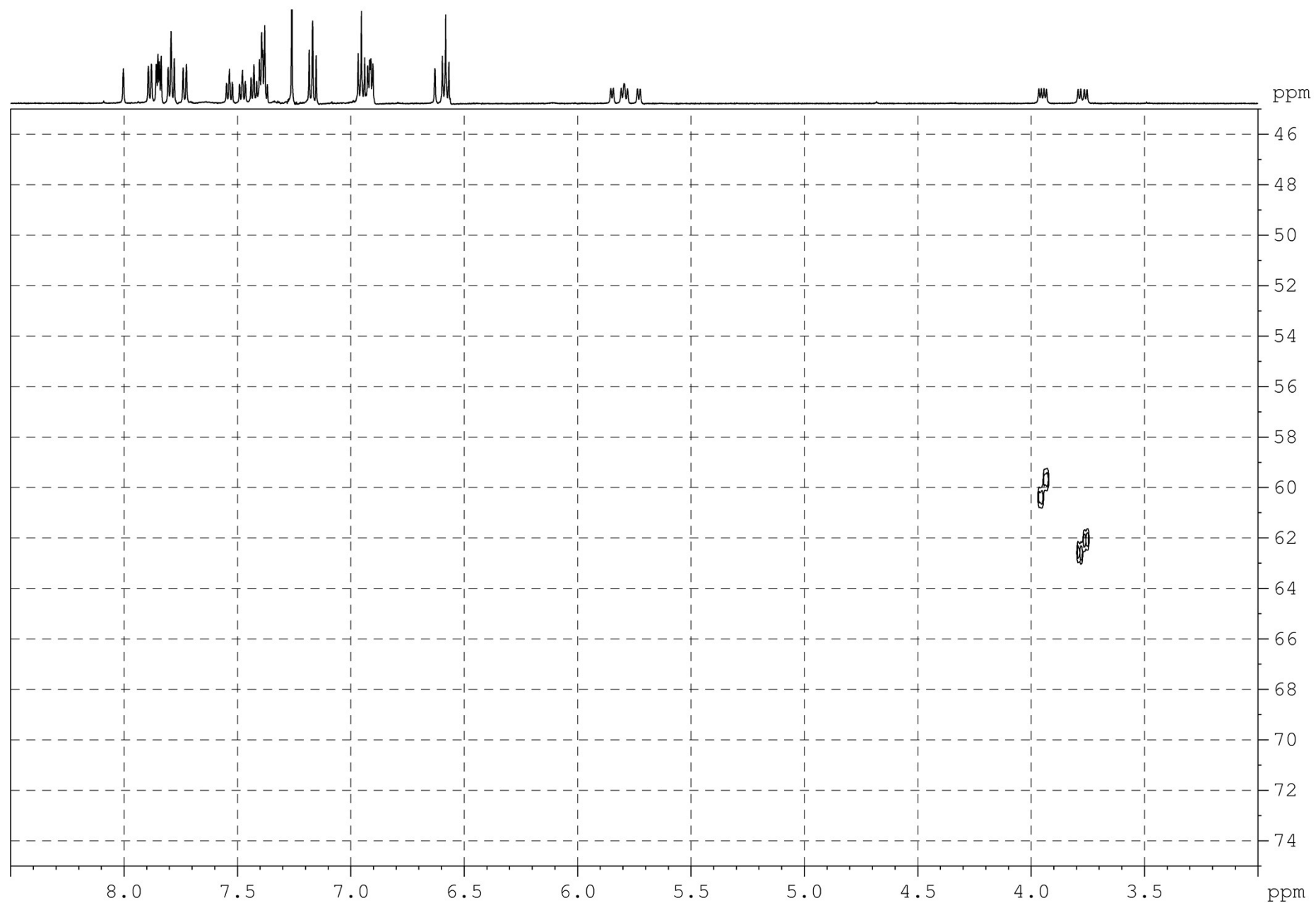
**Figure S38.**  $^1\text{H}$ - $^{13}\text{C}$  HSQC spectra of **5b** in  $\text{CDCl}_3$  at  $T = 303\text{ K}$ .



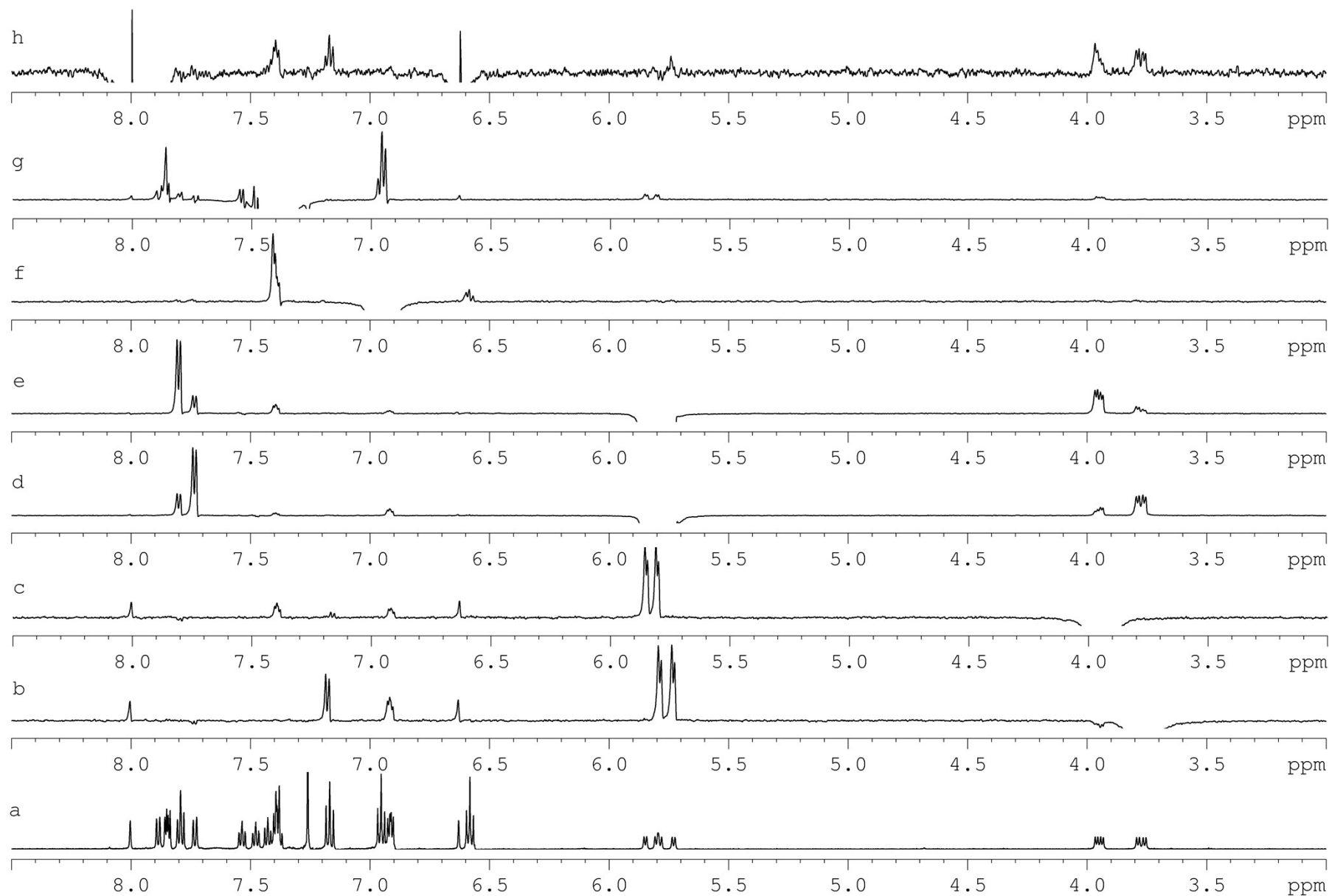
**Figure S39.**  $^1\text{H}$ - $^{13}\text{C}$  HMBC spectra of **5b** in  $\text{CDCl}_3$  at  $T = 303\text{ K}$ .



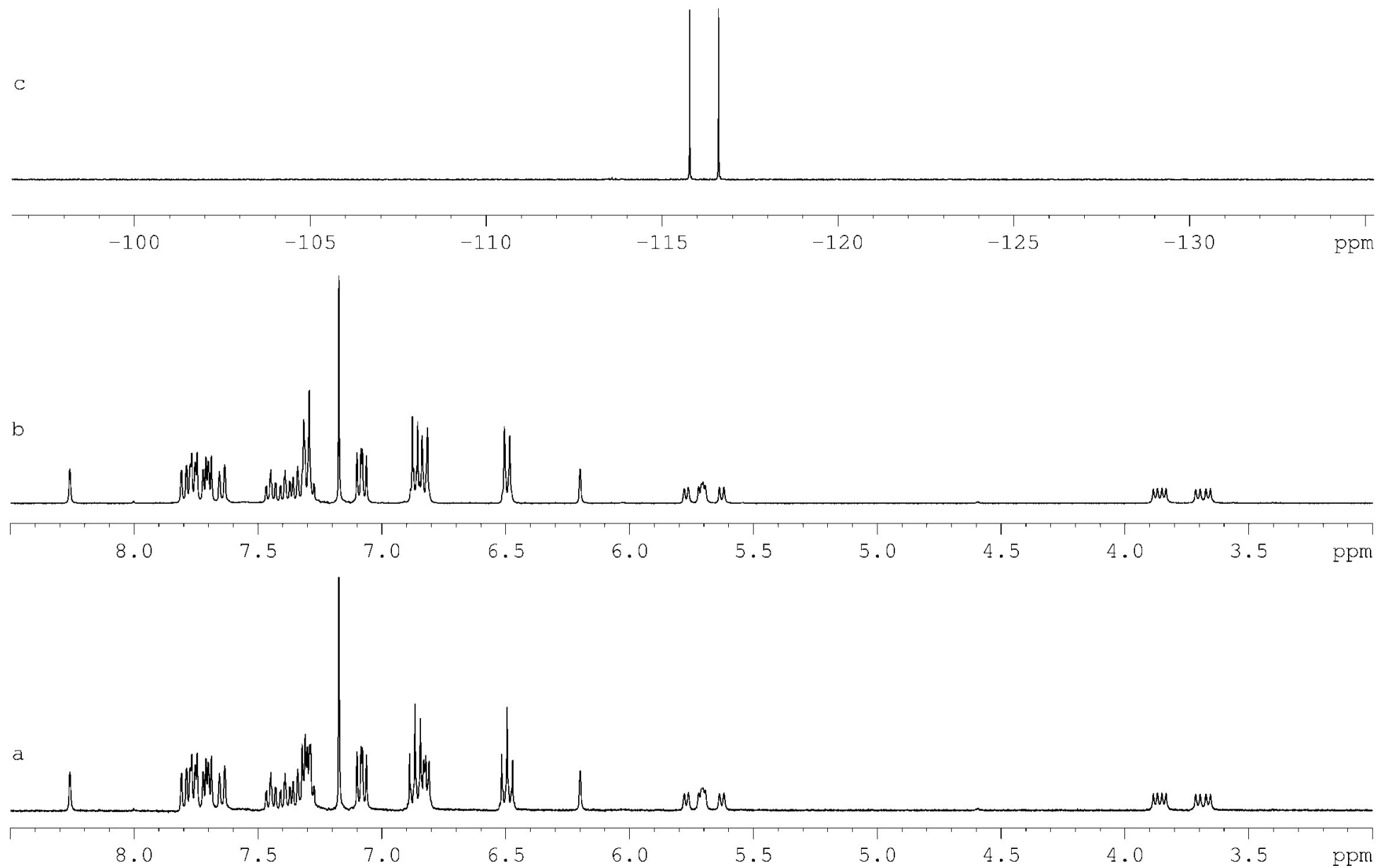
**Figure S40.**  $^1\text{H}$ - $^{31}\text{P}$  HMBC spectra of **5b** in  $\text{CDCl}_3$  at  $T = 303\text{ K}$ .



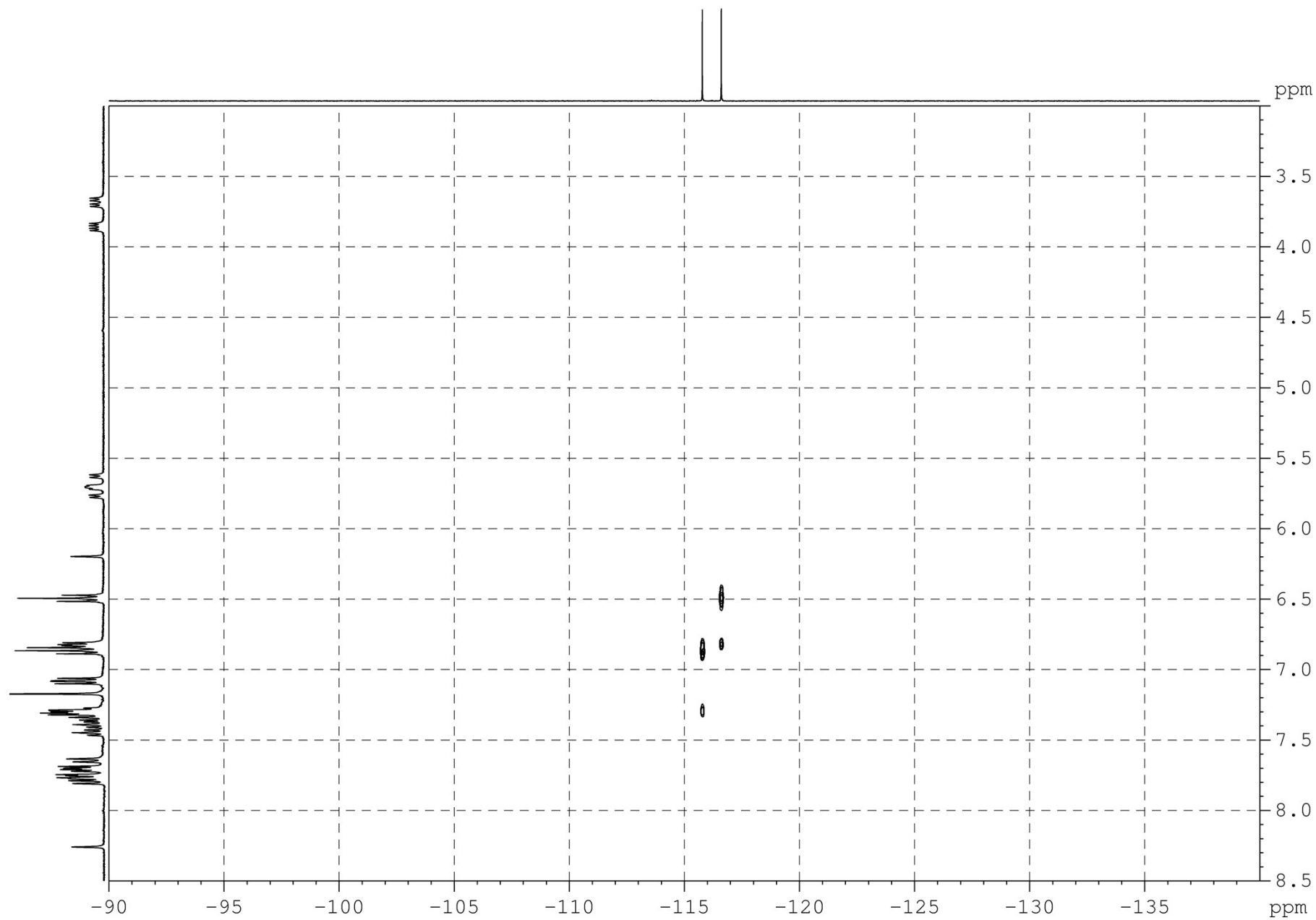
**Figure S41.**  $^1\text{H}$ - $^{15}\text{N}$  HSQC spectra of **5b** in  $\text{CDCl}_3$  at  $T = 303$  K.



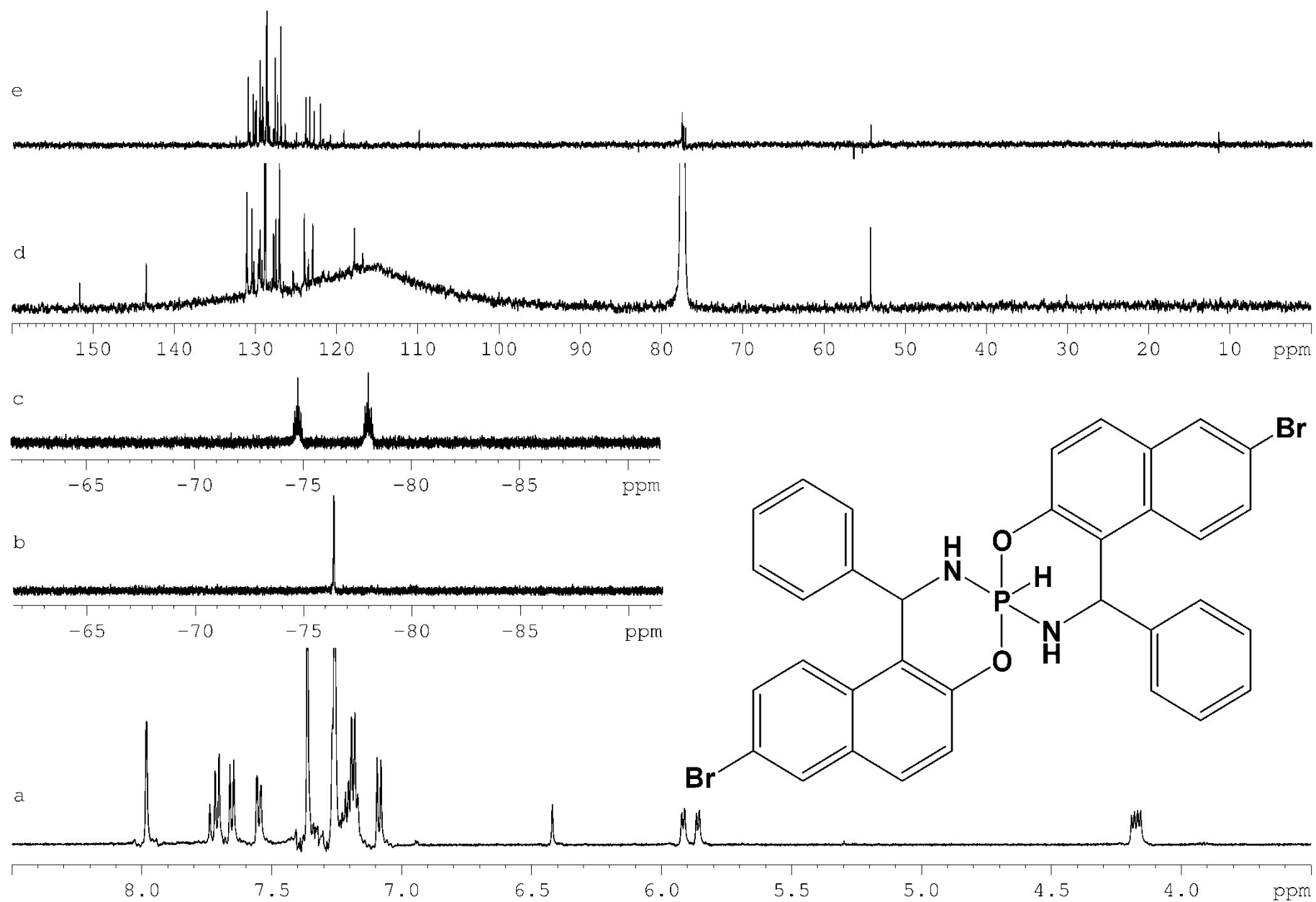
**Figure S42.** <sup>1</sup>H (a) and 1D NOESY (b-h) spectra of **5b** in CDCl<sub>3</sub> at T = 303 K.



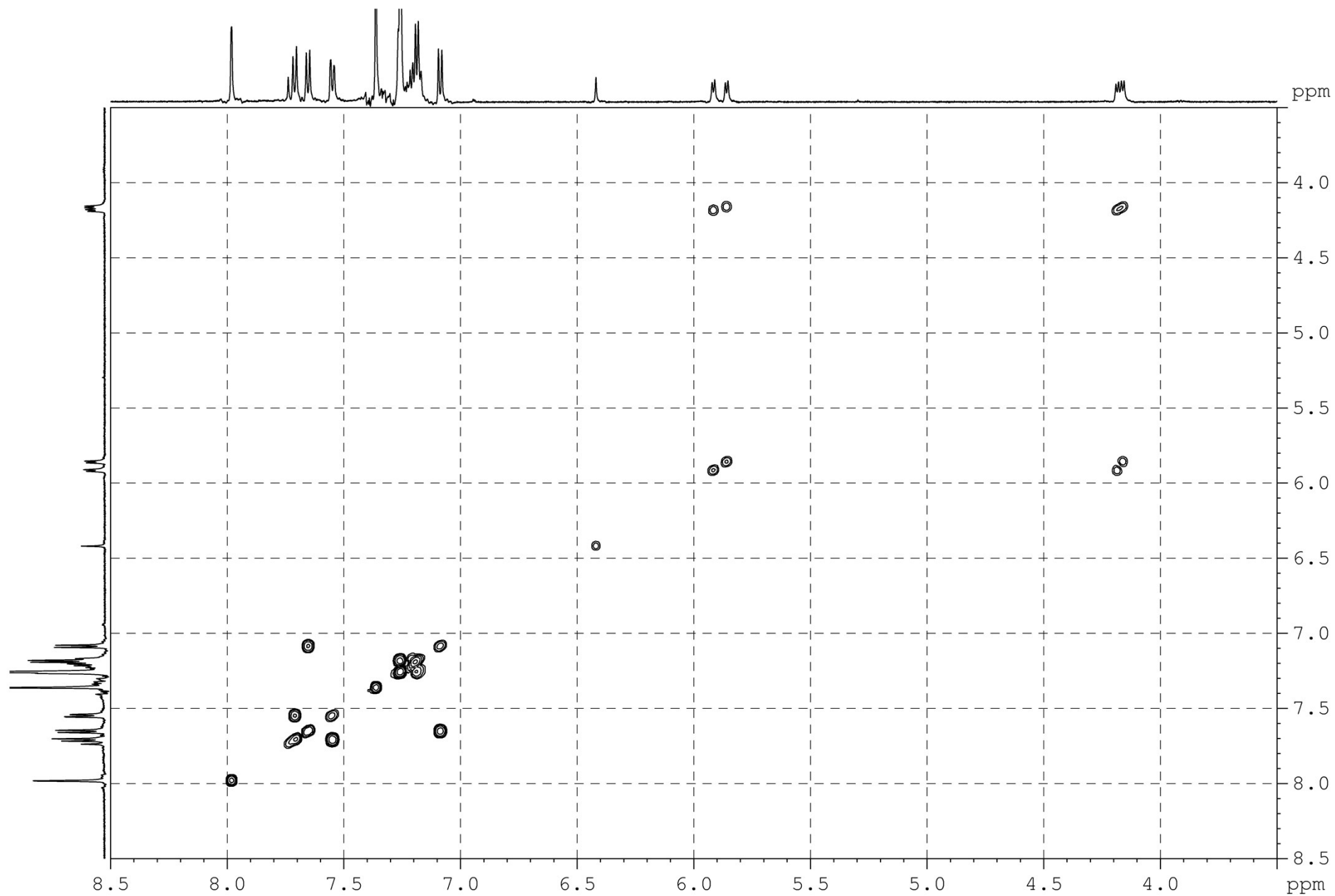
**Figure S43.**  $^1\text{H}$  (a),  $^1\text{H}\{^{19}\text{F}\}$  (b) and  $^{19}\text{F}\{^1\text{H}\}$  (c) spectra of **5b** in  $\text{CDCl}_3$  at  $T = 303 \text{ K}$ .



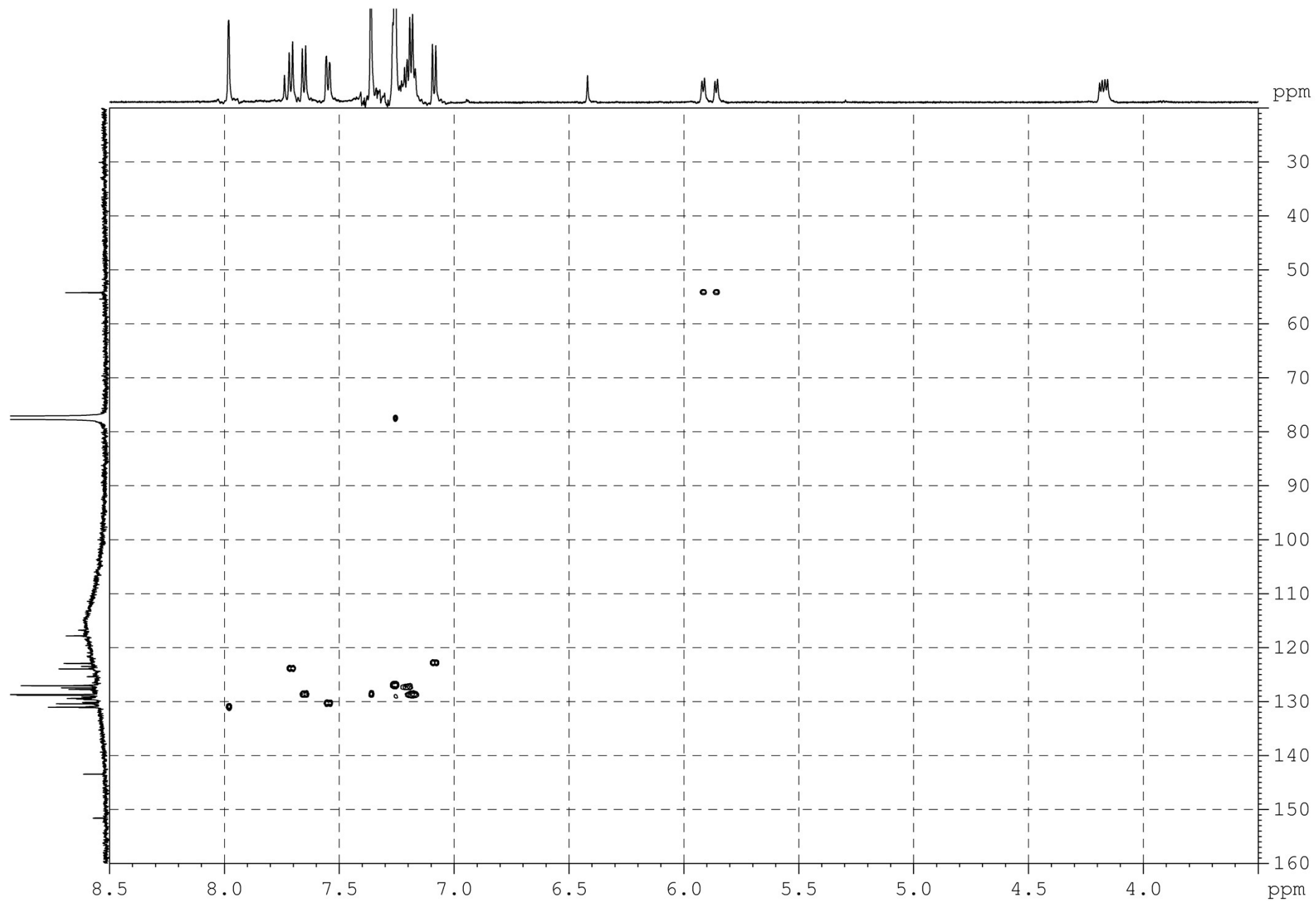
**Figure S44.**  $^{19}\text{F}$ - $^1\text{H}$  HETCOR spectra of **5b** in  $\text{CDCl}_3$  at  $T = 303\text{ K}$ .



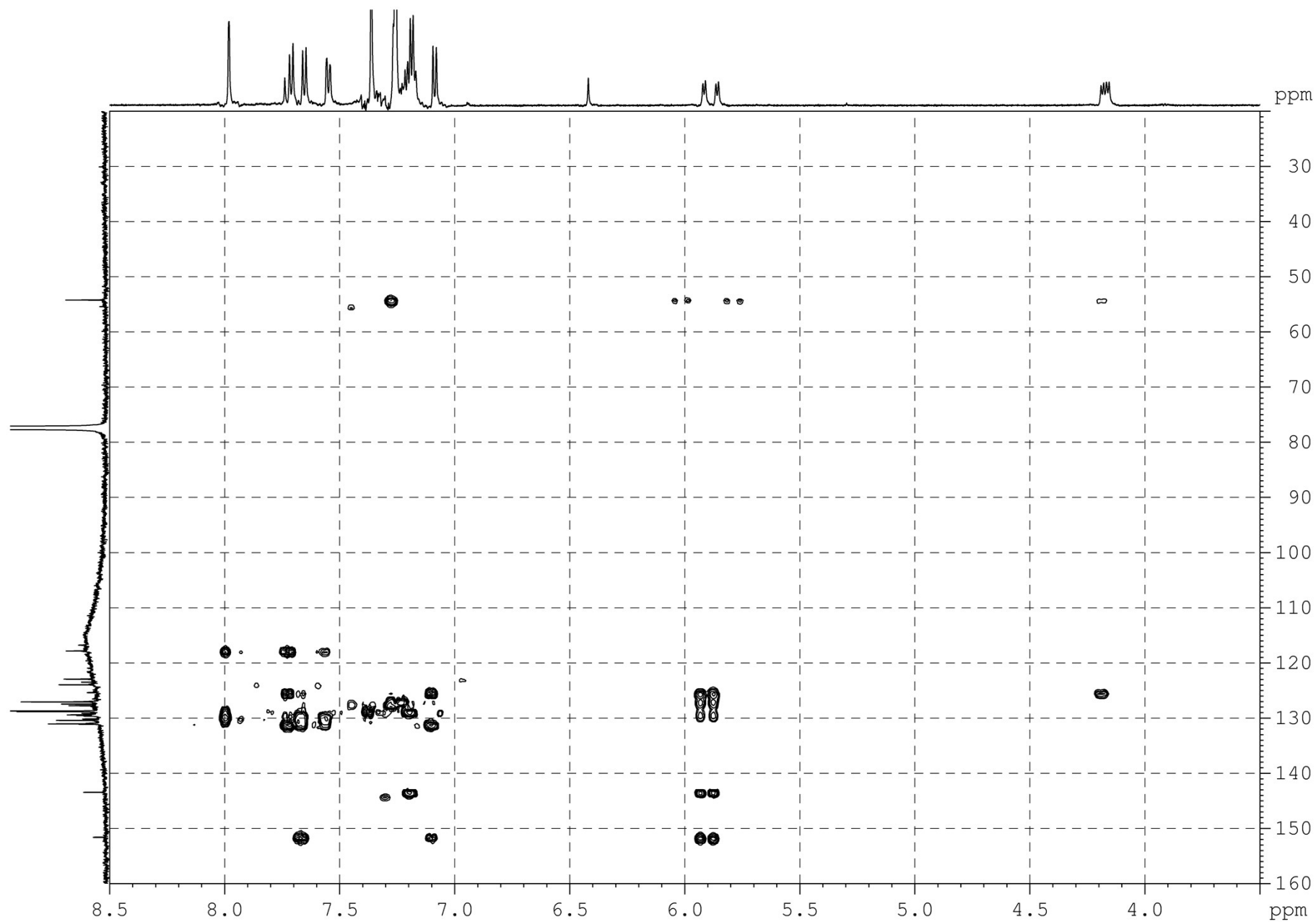
**Figure S45.**  $^1\text{H}$  (a),  $^{31}\text{P}\{^1\text{H}\}$  (b),  $^{31}\text{P}$  (c),  $^{13}\text{C}\{^1\text{H}\}$  (d) and  $^{13}\text{C}$  DEPT (e) spectra of **6a** in  $\text{CDCl}_3$  at  $T = 303\text{ K}$ .



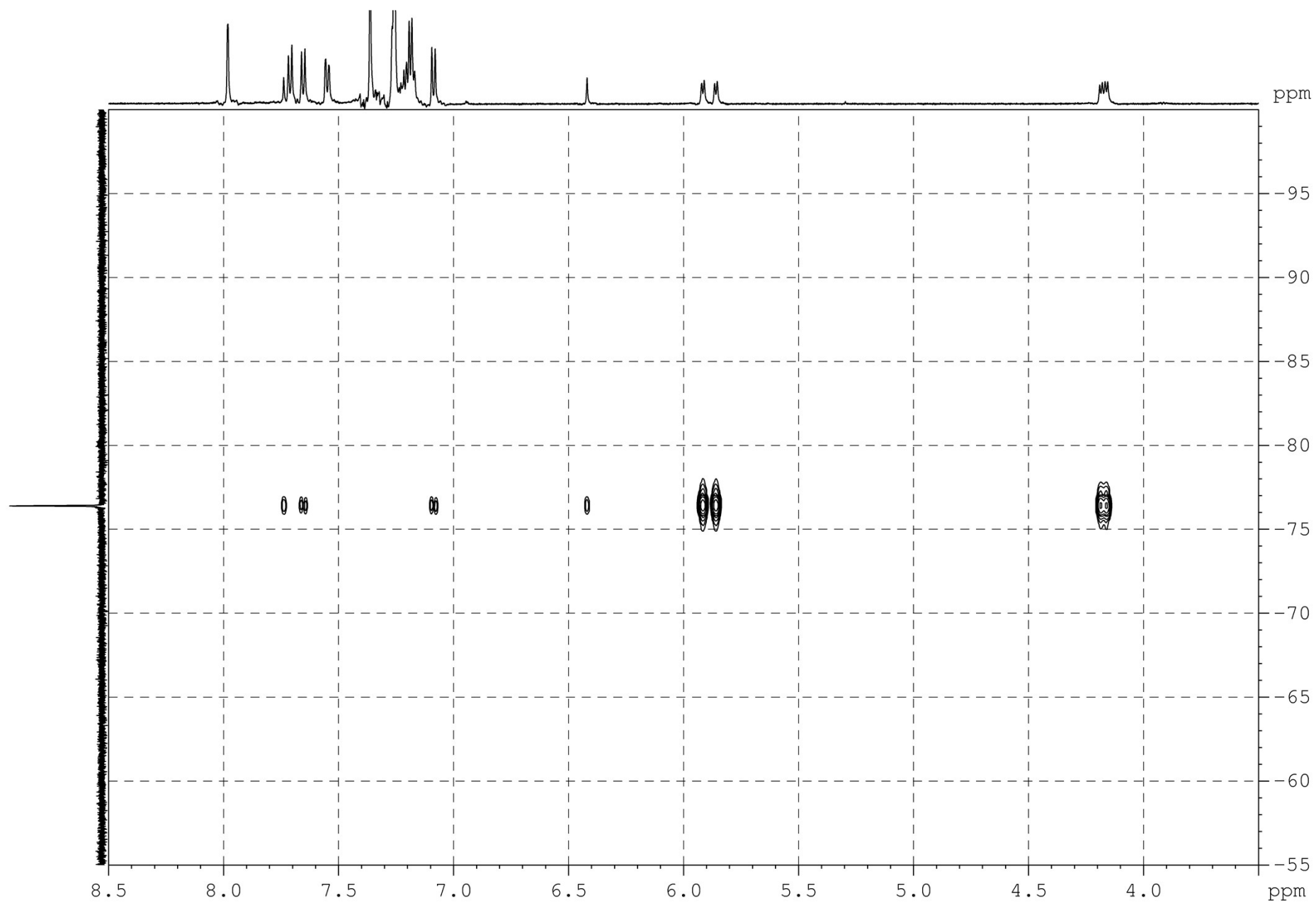
**Figure S46.**  $^1\text{H}$ - $^1\text{H}$  COSY spectra of **6a** in  $\text{CDCl}_3$  at  $T = 303\text{ K}$ .



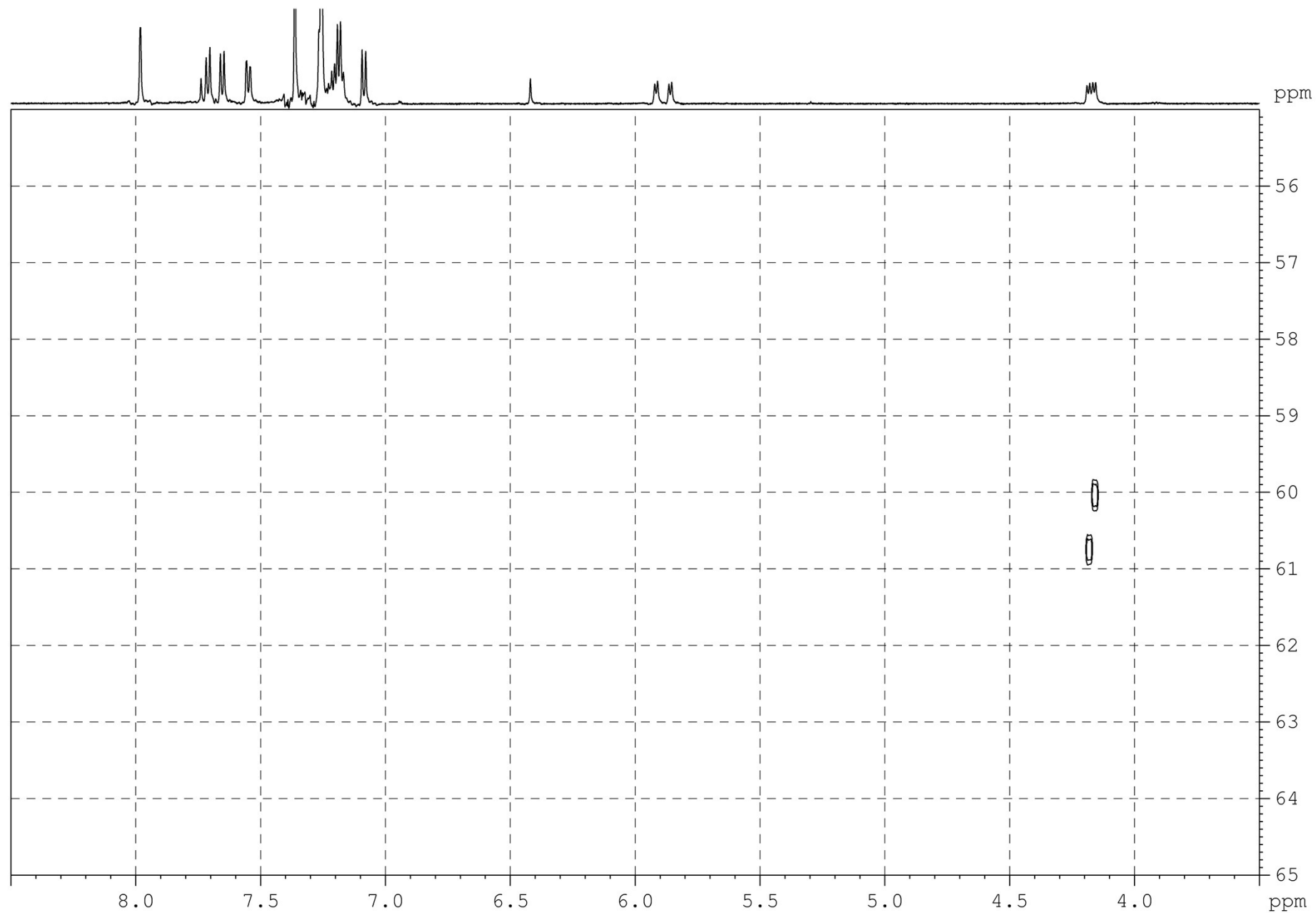
**Figure S47.**  $^1\text{H}$ - $^{13}\text{C}$  HSQC spectra of **6a** in  $\text{CDCl}_3$  at  $T = 303\text{ K}$ .



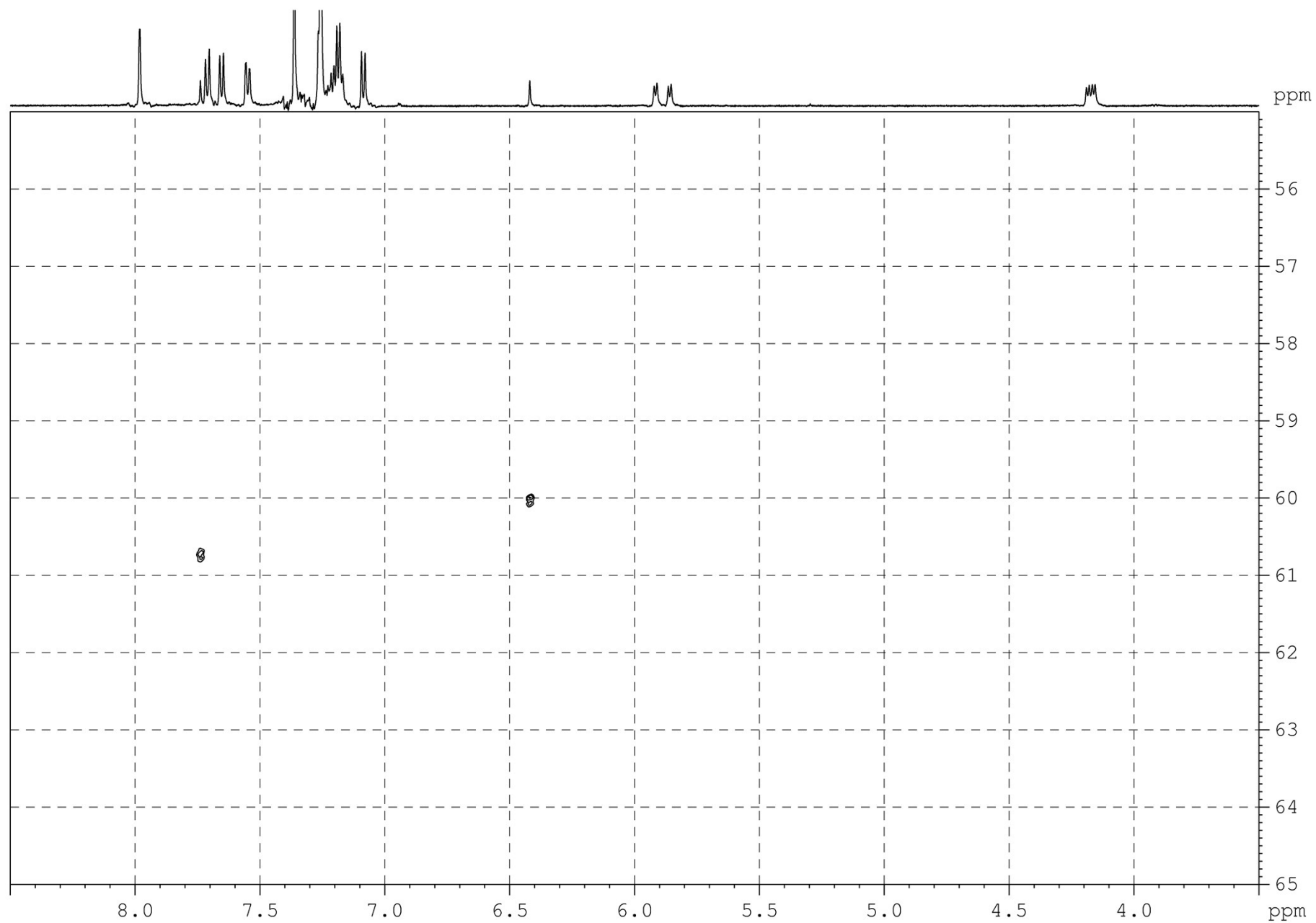
**Figure S48.**  $^1\text{H}$ - $^{13}\text{C}$  HMBC spectra of **6a** in  $\text{CDCl}_3$  at  $T = 303\text{ K}$ .



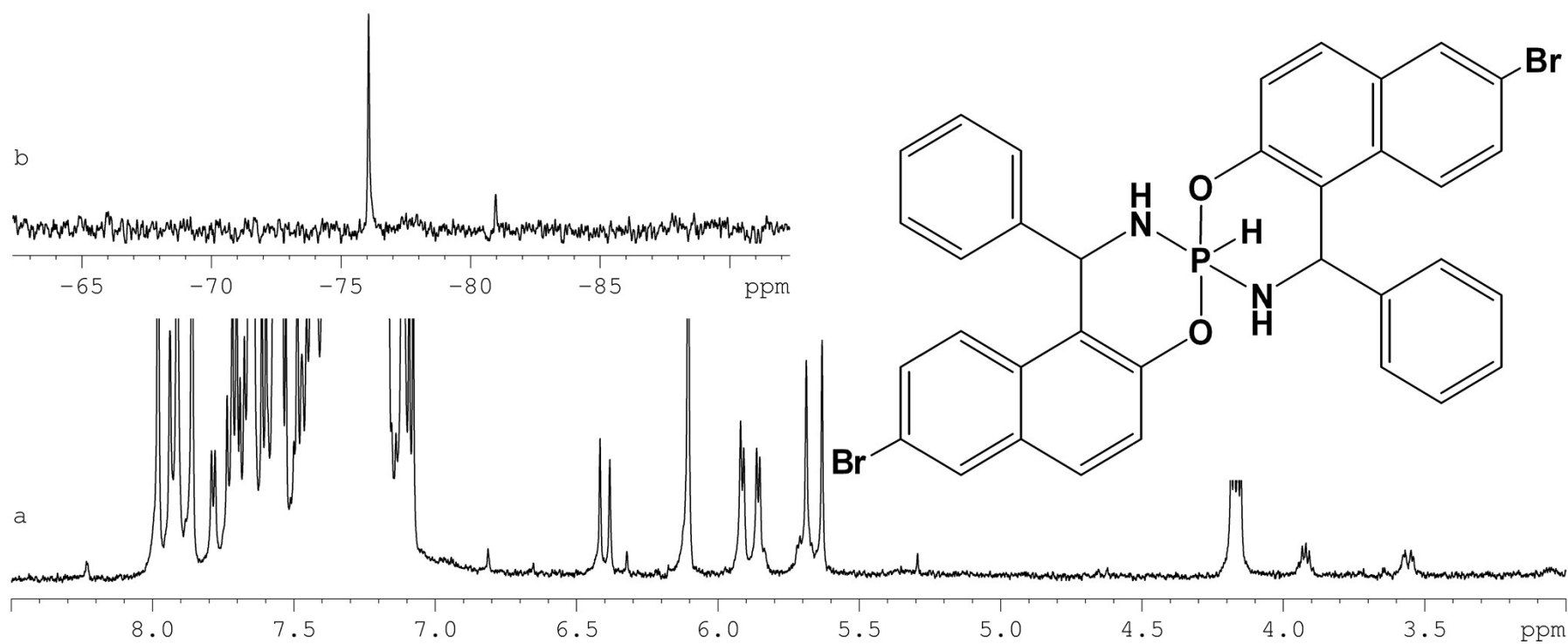
**Figure S49.**  $^1\text{H}$ - $^{31}\text{P}$  HMBC spectra of **6a** in  $\text{CDCl}_3$  at  $T = 303\text{ K}$ .



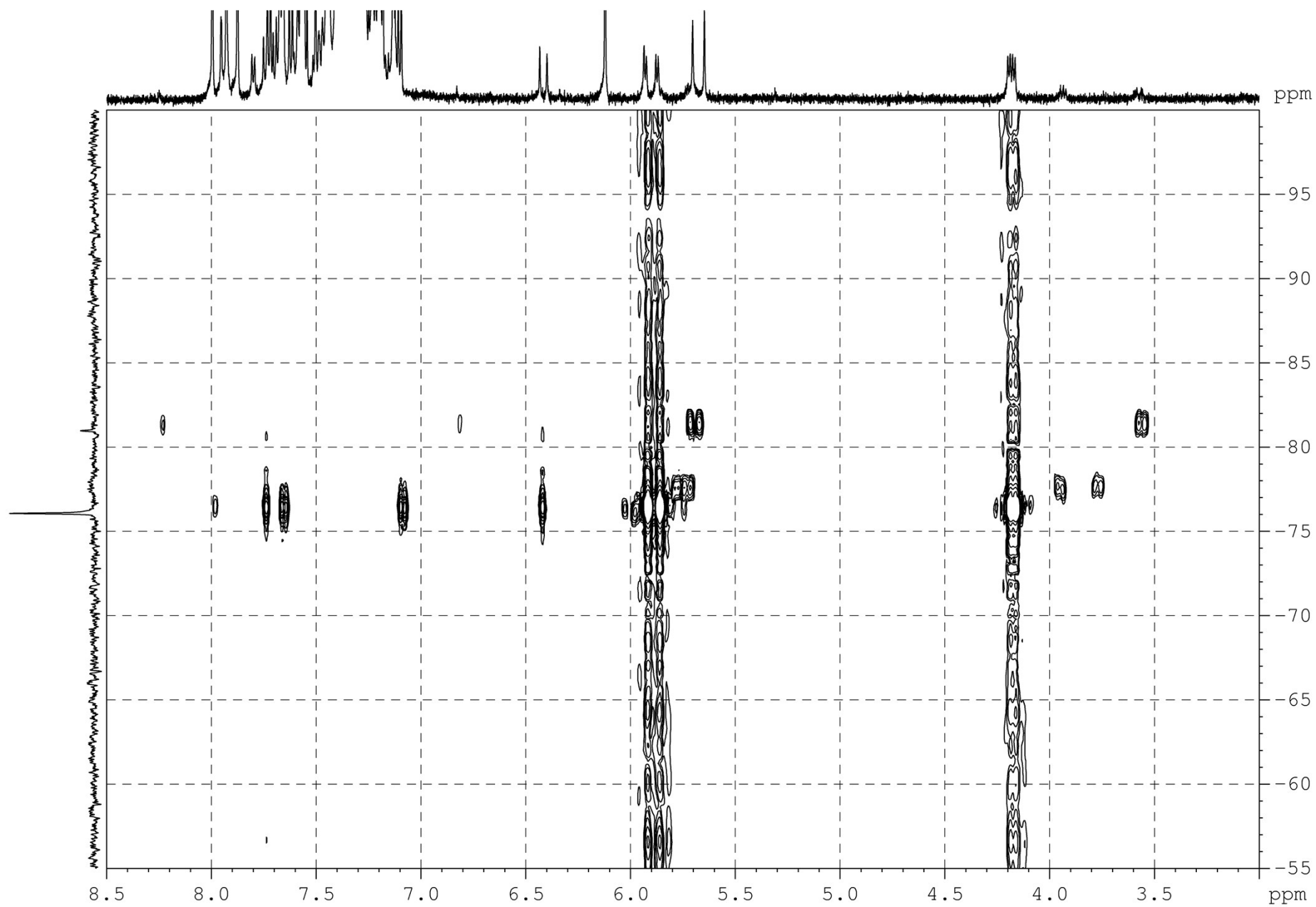
**Figure S50.**  $^1\text{H}$ - $^{15}\text{N}$  HSQC spectra of **6a** in  $\text{CDCl}_3$  at  $T = 303\text{ K}$ .



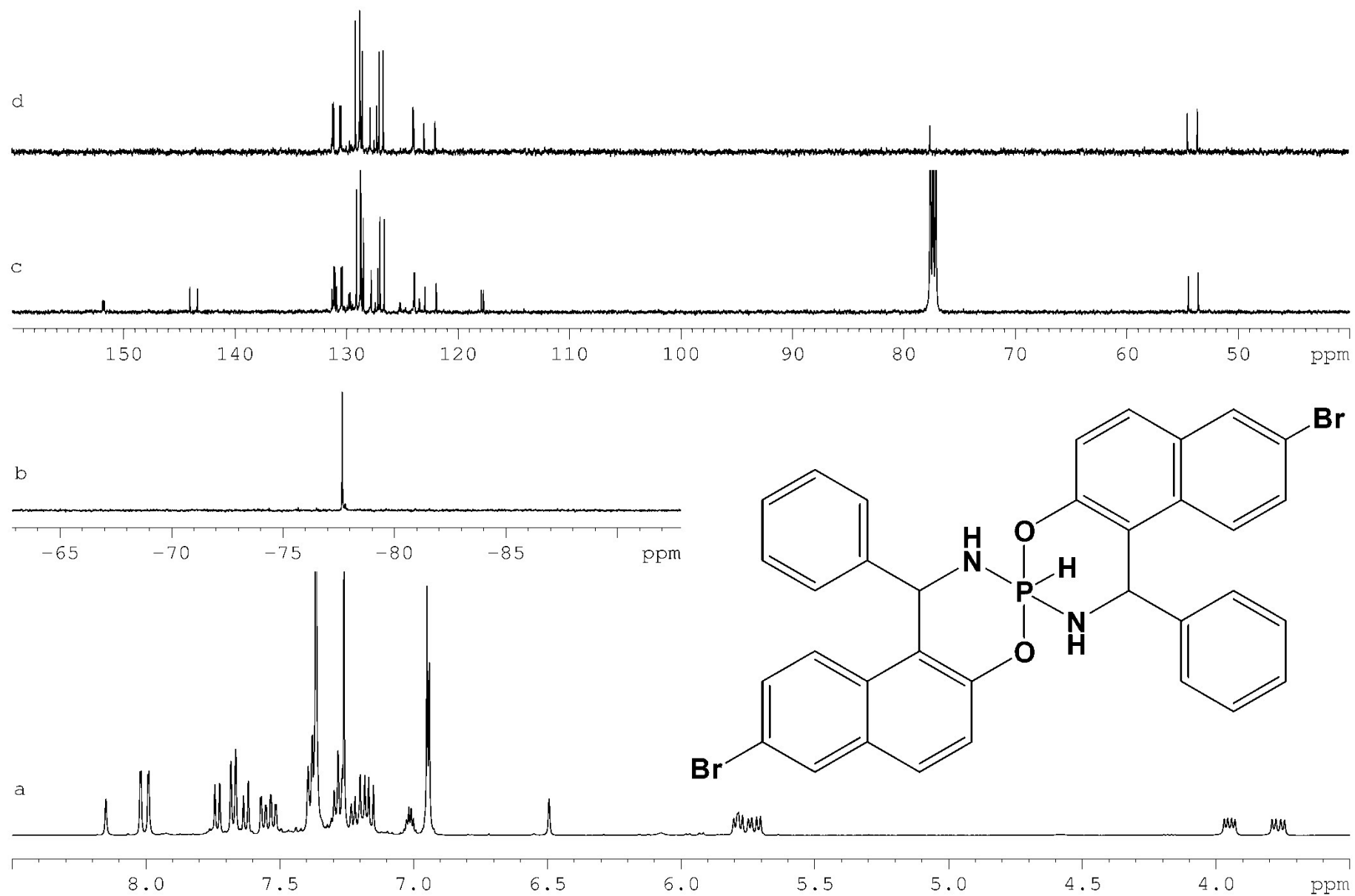
**Figure S51.**  $^1\text{H}$ - $^{15}\text{N}$  HMBC spectra of **6a** in  $\text{CDCl}_3$  at  $T = 303\text{ K}$ .



**Figure S52.**  $^1\text{H}$  (a),  $^{31}\text{P}\{^1\text{H}\}$  (b) spectra of **6a** after 24h in  $\text{CDCl}_3$  at  $T = 303\text{ K}$  (**6a** 86 %, **6c** 14 %).



**Figure S53.**  $^1\text{H}$ - $^{31}\text{P}$  HMBC spectra of **6a** in  $\text{CDCl}_3$  at  $T = 303\text{ K}$  after 24h in  $\text{CDCl}_3$  at  $T = 303\text{ K}$  (**6a** 86 %, **6c** 14 %).



**Figure S54.** <sup>1</sup>H (a), <sup>31</sup>P{<sup>1</sup>H} (b), <sup>13</sup>C{<sup>1</sup>H} (c) and <sup>13</sup>C DEPT (d) spectra of **6b** in CDCl<sub>3</sub> at T = 303 K.

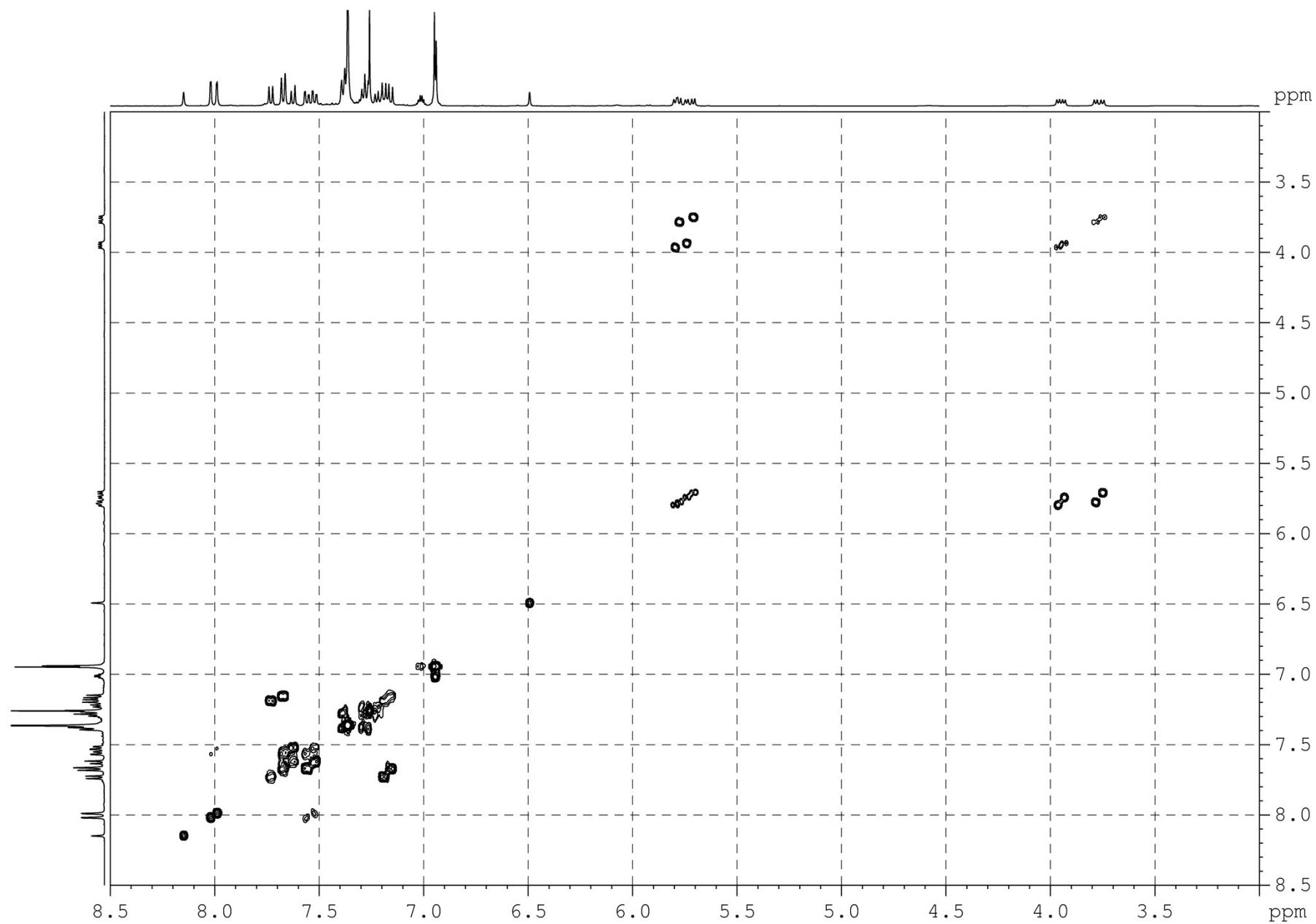
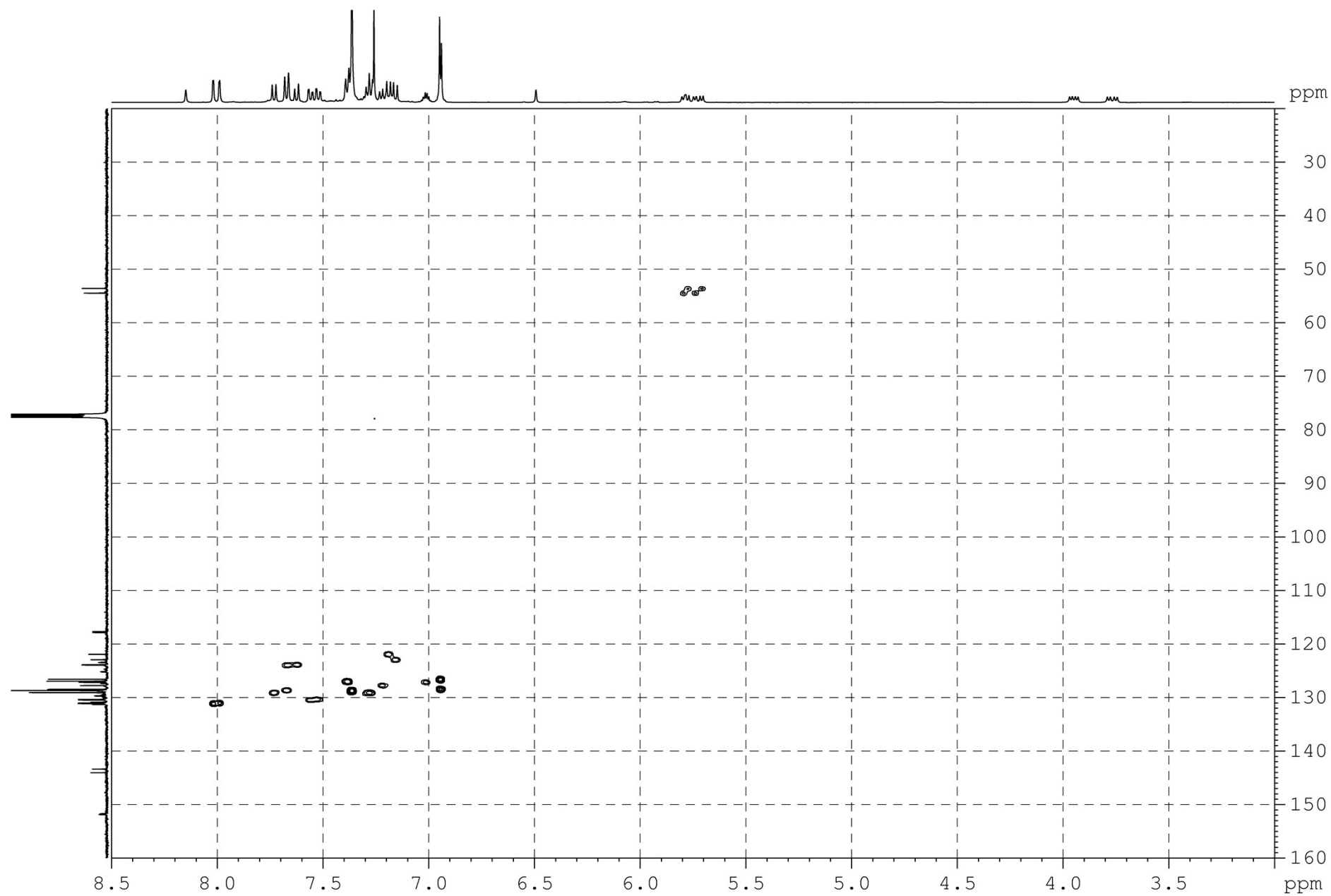


Figure S55.  $^1\text{H}$ - $^1\text{H}$  COSY spectra of **6b** in  $\text{CDCl}_3$  at  $T = 303\text{ K}$ .



**Figure S56.**  $^1\text{H}$ - $^{13}\text{C}$  HSQC spectra of **6b** in  $\text{CDCl}_3$  at  $T = 303\text{ K}$ .

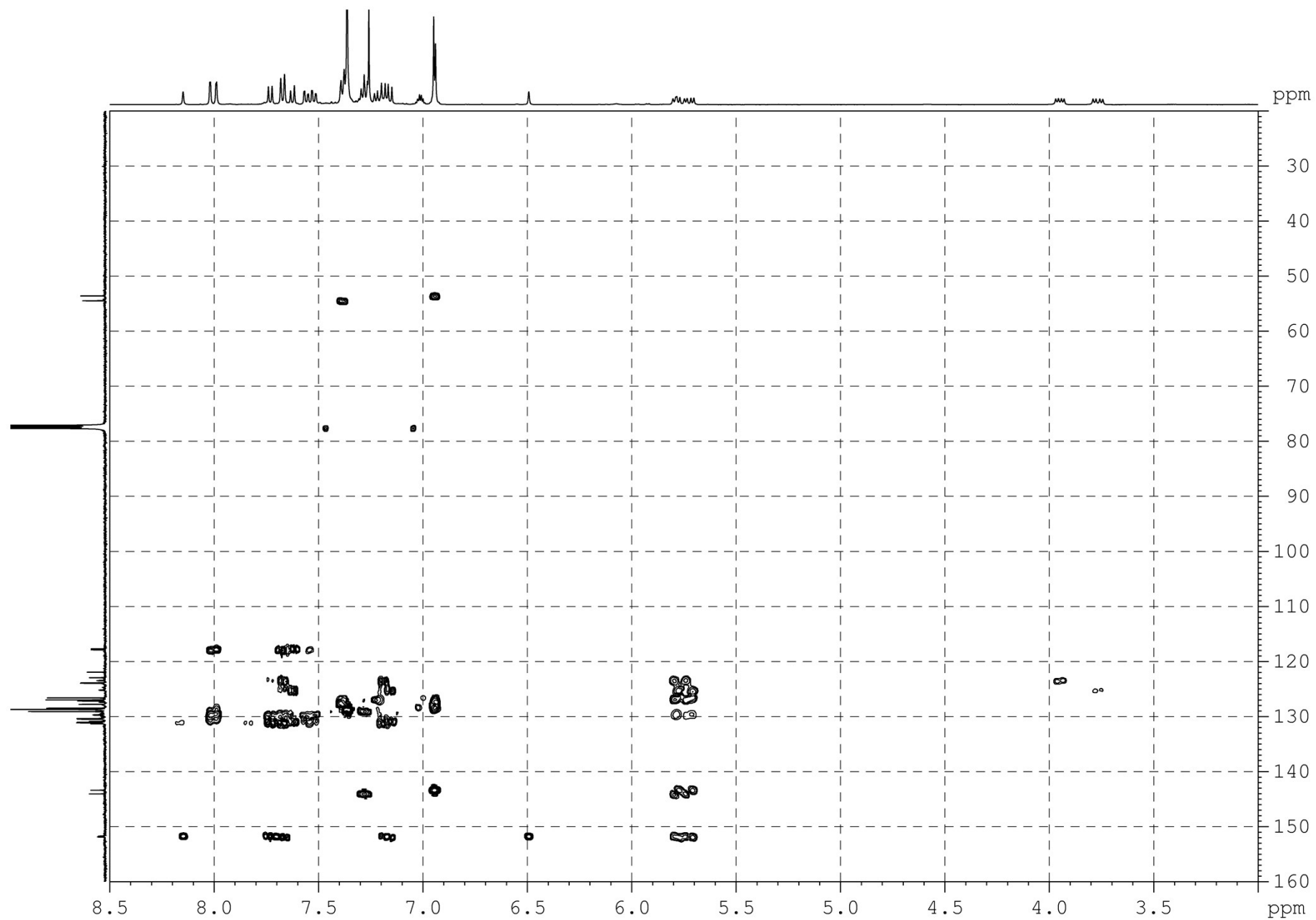
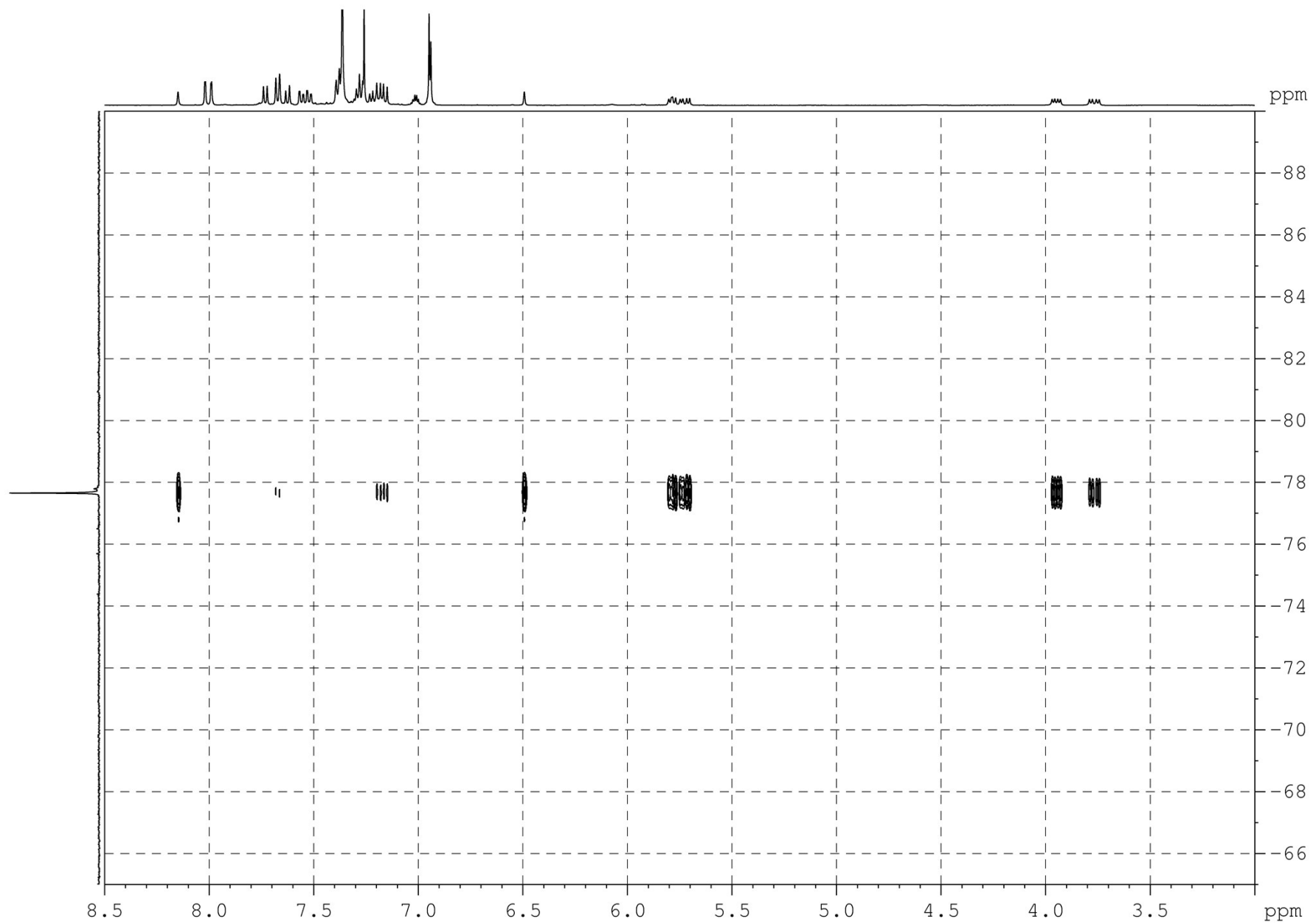
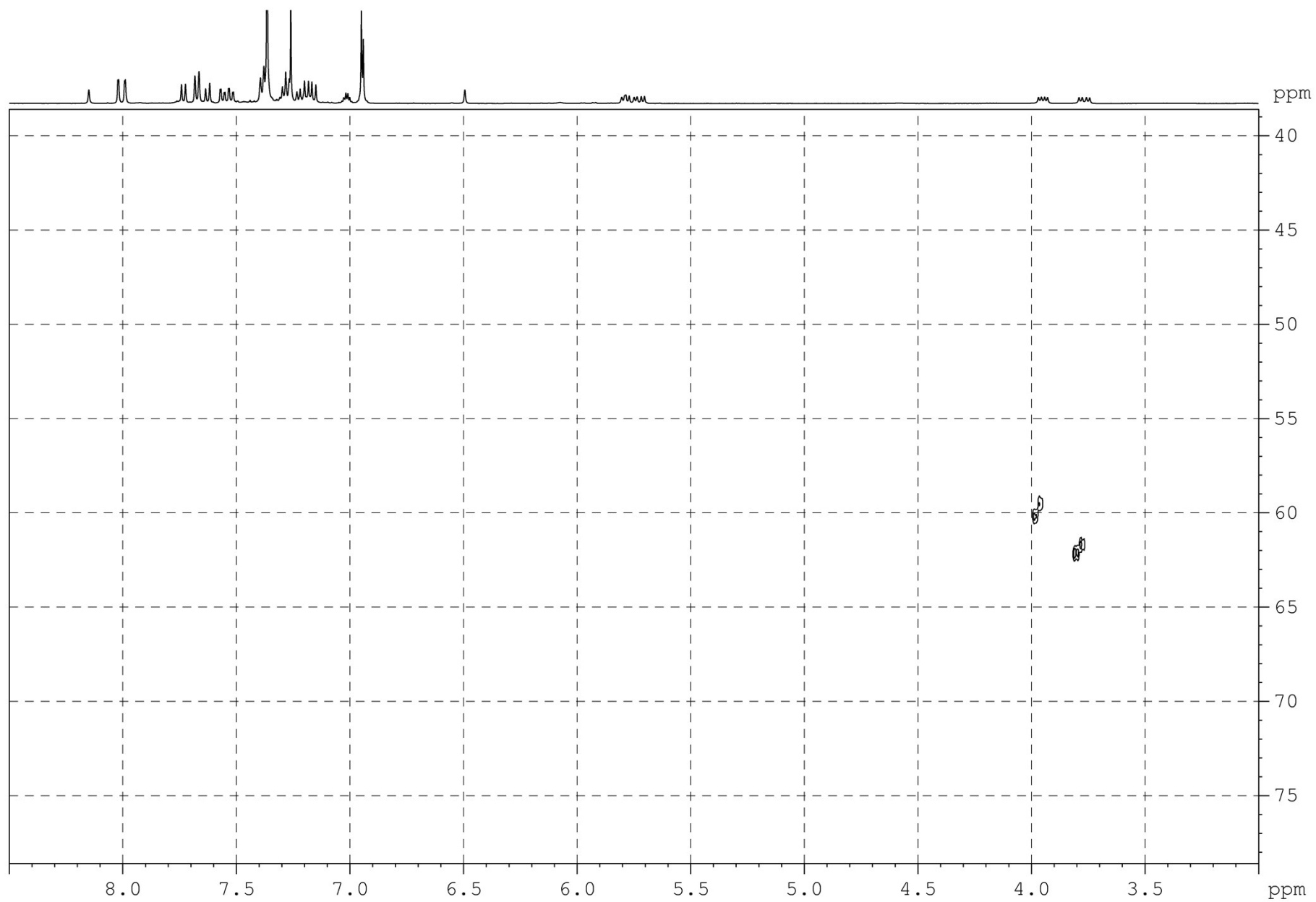


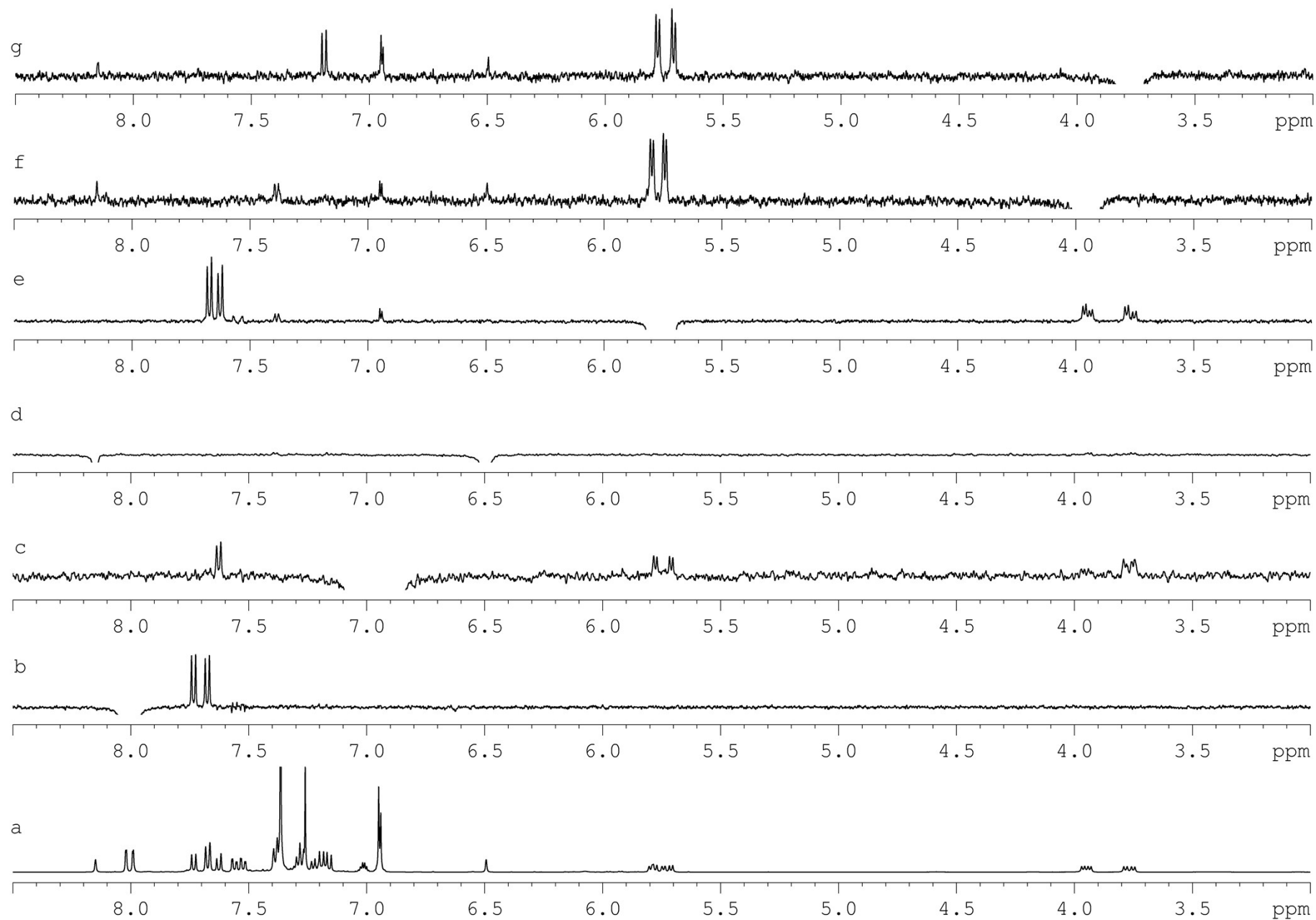
Figure S57.  $^1\text{H}$ - $^{13}\text{C}$  HMBC spectra of **6b** in  $\text{CDCl}_3$  at  $T = 303\text{ K}$ .



**Figure S58.**  $^1\text{H}$ - $^{31}\text{P}$  HMBC spectra of **6b** in  $\text{CDCl}_3$  at  $T = 303\text{ K}$ .



**Figure S59.**  $^1\text{H}$ - $^{15}\text{N}$  HSQC spectra of **6b** in  $\text{CDCl}_3$  at  $T = 303\text{ K}$ .



**Figure S60.**  $^1\text{H}$  (a) and 1D NOESY (b-g) spectra of **6b** in  $\text{CDCl}_3$  at  $T = 303\text{ K}$ .

## Calculations

The quantum chemical calculations were performed using Gaussian 03. Full geometry optimizations have been carried out within the framework of DFT (PBE1PBE) method using 6-31+G(d) basis sets. Chemical shifts (CSs) and SSC were calculated by the GIAO method at the PBE1PBE/6-311G(2d,2p) level of theory.  $^{31}\text{P}$  CSs were referred to  $\text{H}_3\text{PO}_4$  and linear scaling procedure was applied ( $\delta_{\text{scaled}} = (\delta_{\text{unscaled}} - \text{intercept})/\text{slope}$ , where intercept = -14.4 ppm, slope = 1.073).<sup>3</sup>  $^1\text{H}$  CSs were referred to TMS.

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<sup>3</sup> Sh. K. Latypov, F. M. Polyancev, D. G. Yakhvarov and O. G. Sinyashin, *Phys. Chem. Chem. Phys.*, 2015, **17**, 6976.

**Table S1.** Calculated NMR parameters for compound **4** with inclusion of solvent effects in frame of PCM<sup>a</sup>.

| Isomer     | $\Delta E$ | $\delta^{31}\text{P}$ | $\delta\text{H}_6$ | $\delta\text{H}_{16,20}$ | $\delta\text{H}_{17,19}$ | $\delta\text{H}_4$ | $\delta\text{H}_5$ | $^1J_{\text{PH}}$ | $^3J_{\text{PH4}}$ |
|------------|------------|-----------------------|--------------------|--------------------------|--------------------------|--------------------|--------------------|-------------------|--------------------|
| <b>I</b>   | 0          | -76.0                 | 7.64               | 7.59                     | 7.42                     | 5.95               | 3.78               | 716.4             | 36.2               |
| <b>II</b>  | 0.4        | -77.4                 | 7.76               | 7.43, 7.87               | 7.23, 7.59               | 5.80, 5.84         | 3.49, 3.84         | 739.2             | 27.8, 34.9         |
| <b>III</b> | 2.4        | -77.5                 | 7.91               | 7.71                     | 7.53                     | 5.78               | 3.57               | 759.3             | 25.5               |

<sup>a</sup> CS's calculated in frame of PCM (chloroform), chemical shifts in ppm, spin-spin couplings in Hz, relative energy, in kcal/mol.