

## OCTAHEDRAL IRON (II) PHTHALOCYANINE COMPLEXES: MULTINUCLEAR NMR AND RELEVANCE AS NO<sub>2</sub> CHEMICAL SENSORS

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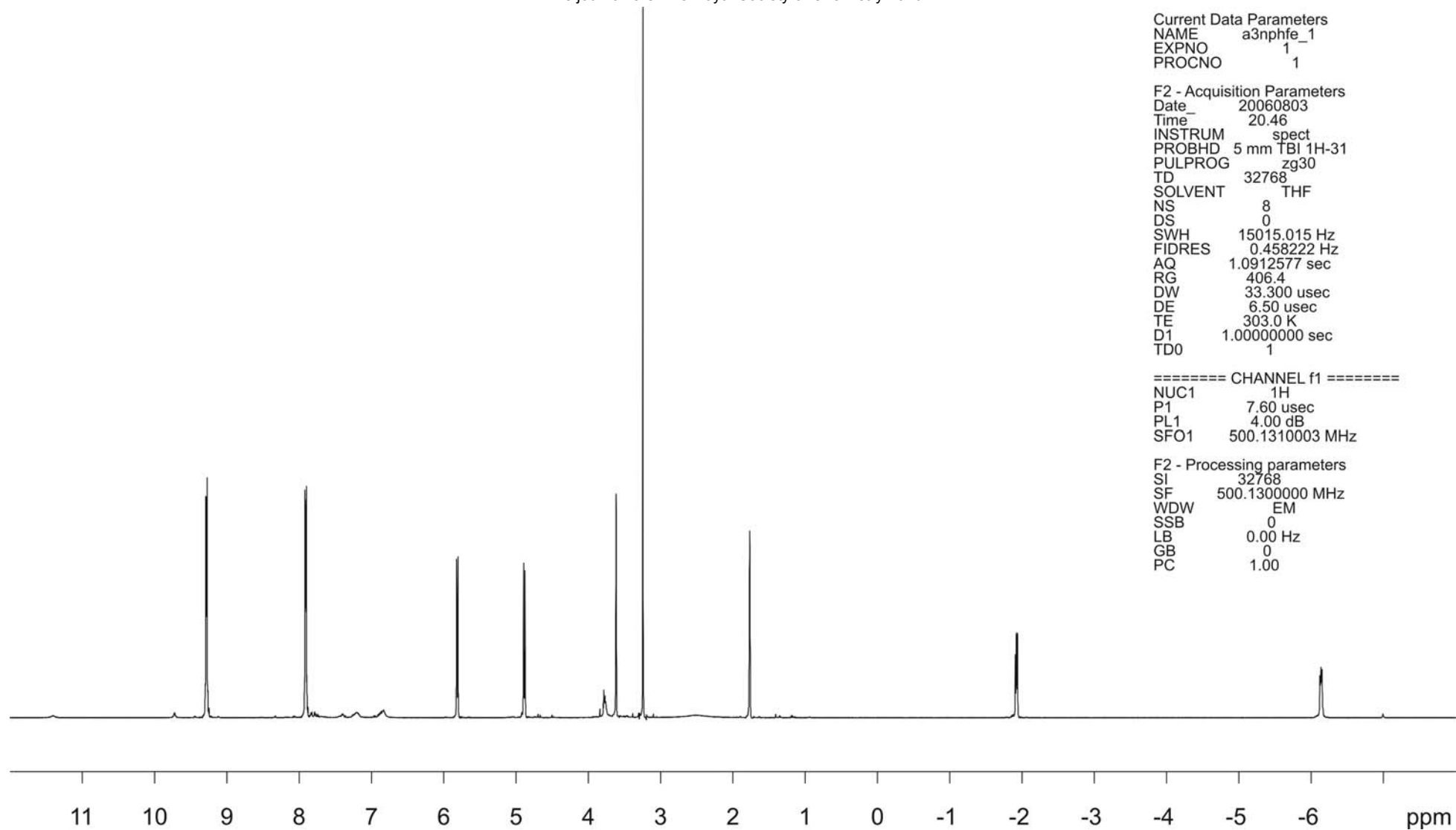


Figure 1.  $^1\text{H}$  NMR (500.13 MHz) spectrum of **4** in  $\text{THF-}d_8$ .

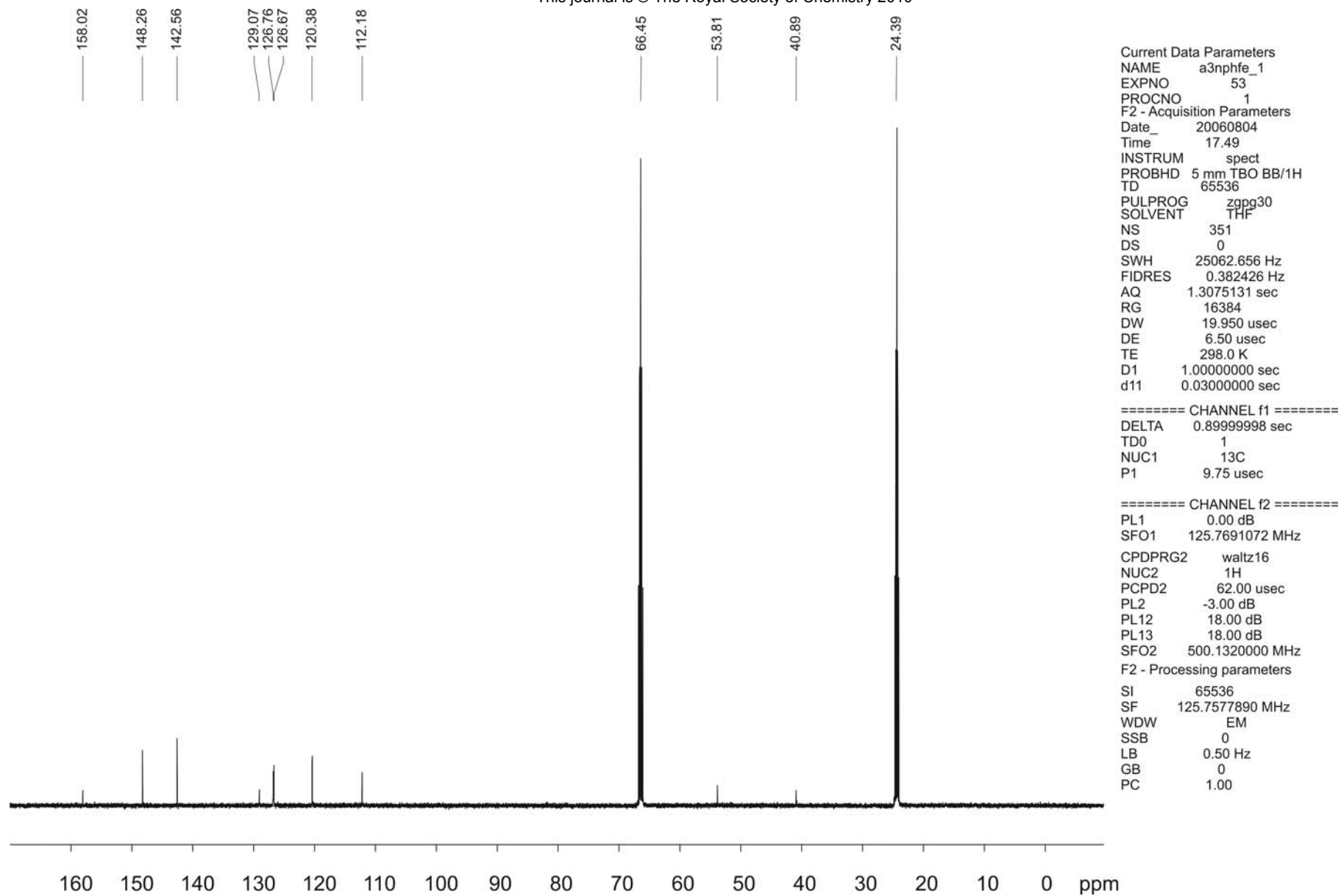


Figure 2.  $^{13}\text{C}$  NMR (125.7 MHz) spectrum of **4** in  $\text{THF-}d_8$ .

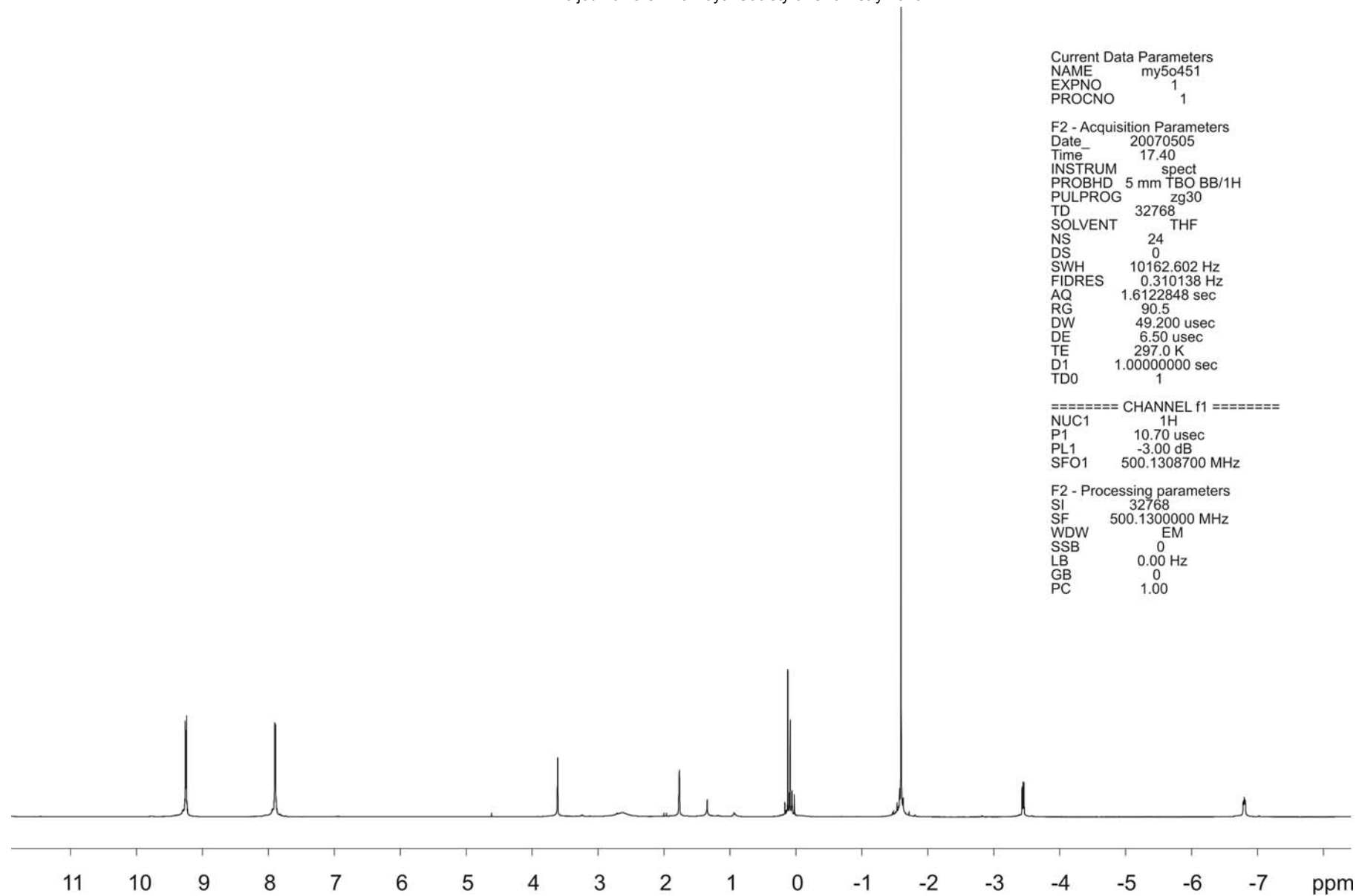


Figure 3.  $^1\text{H}$  NMR (500.13 MHz) spectrum of **5** in  $\text{THF-}d_8$ .

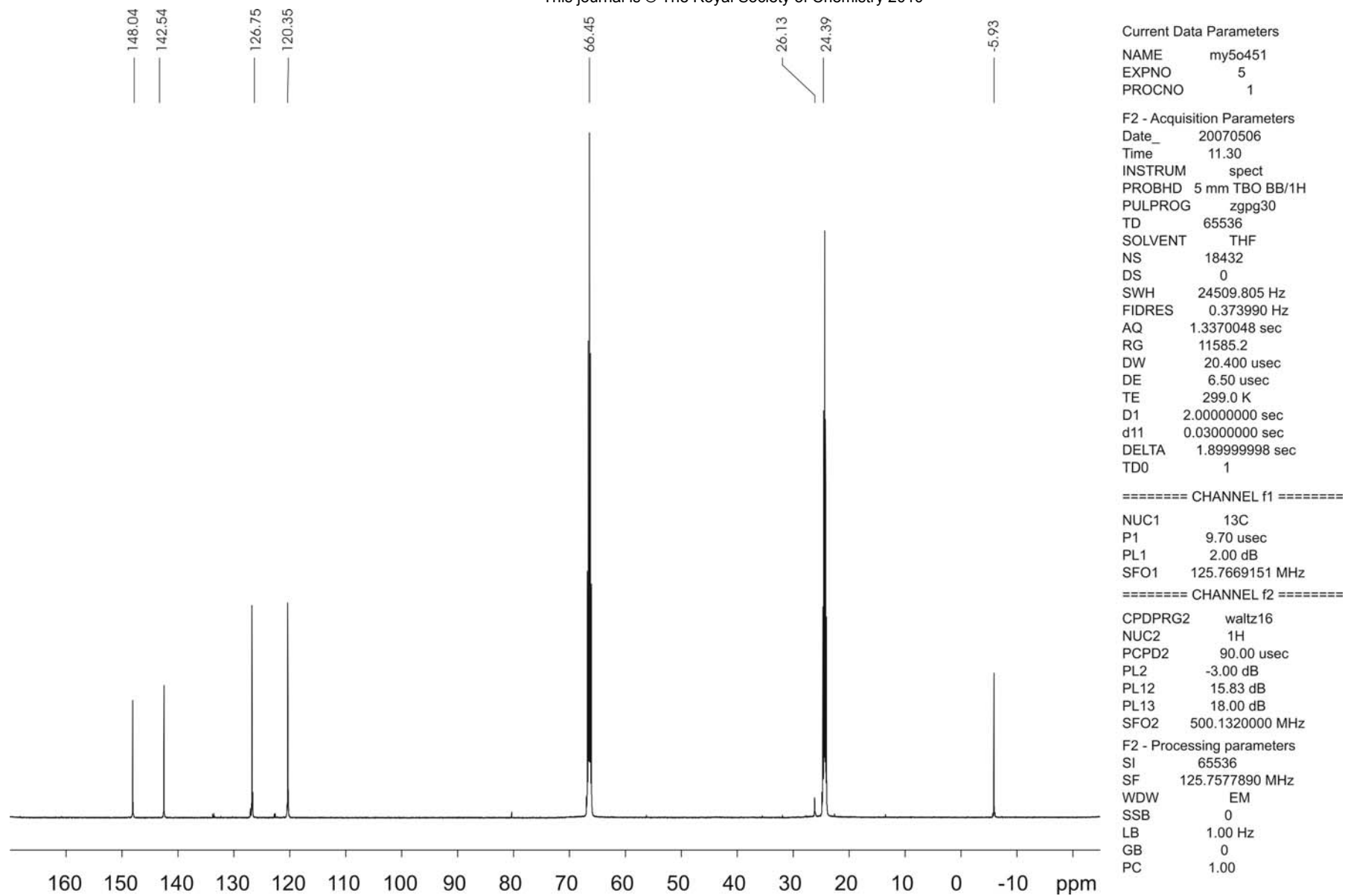


Figure 4.  $^{13}\text{C}$  NMR (125.7 MHz) spectrum of **5** in  $\text{THF-}d_8$ .

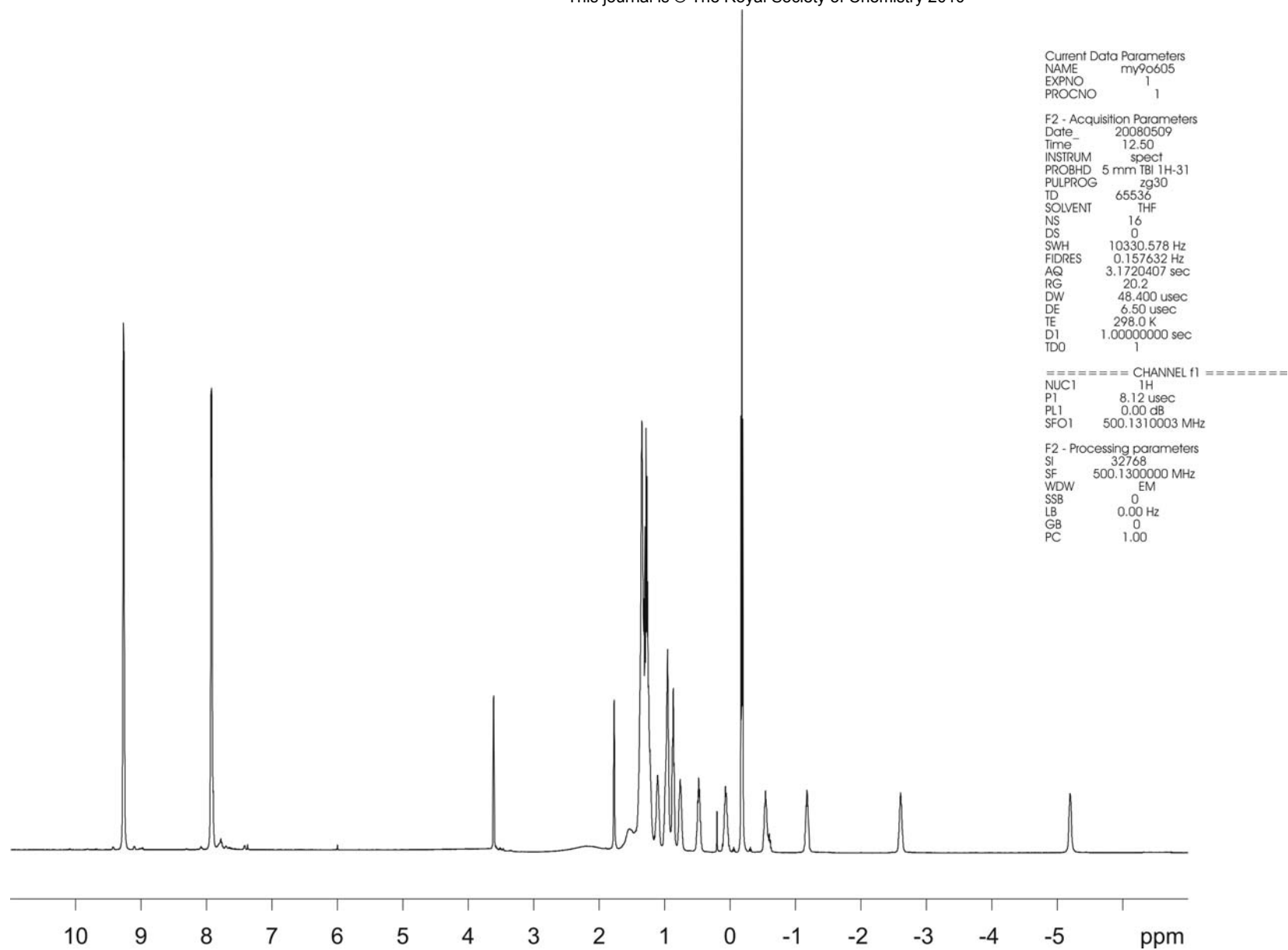


Figure 5.  $^1\text{H}$  NMR (500.13 MHz) spectrum of **6** in  $\text{THF-}d_8$ .

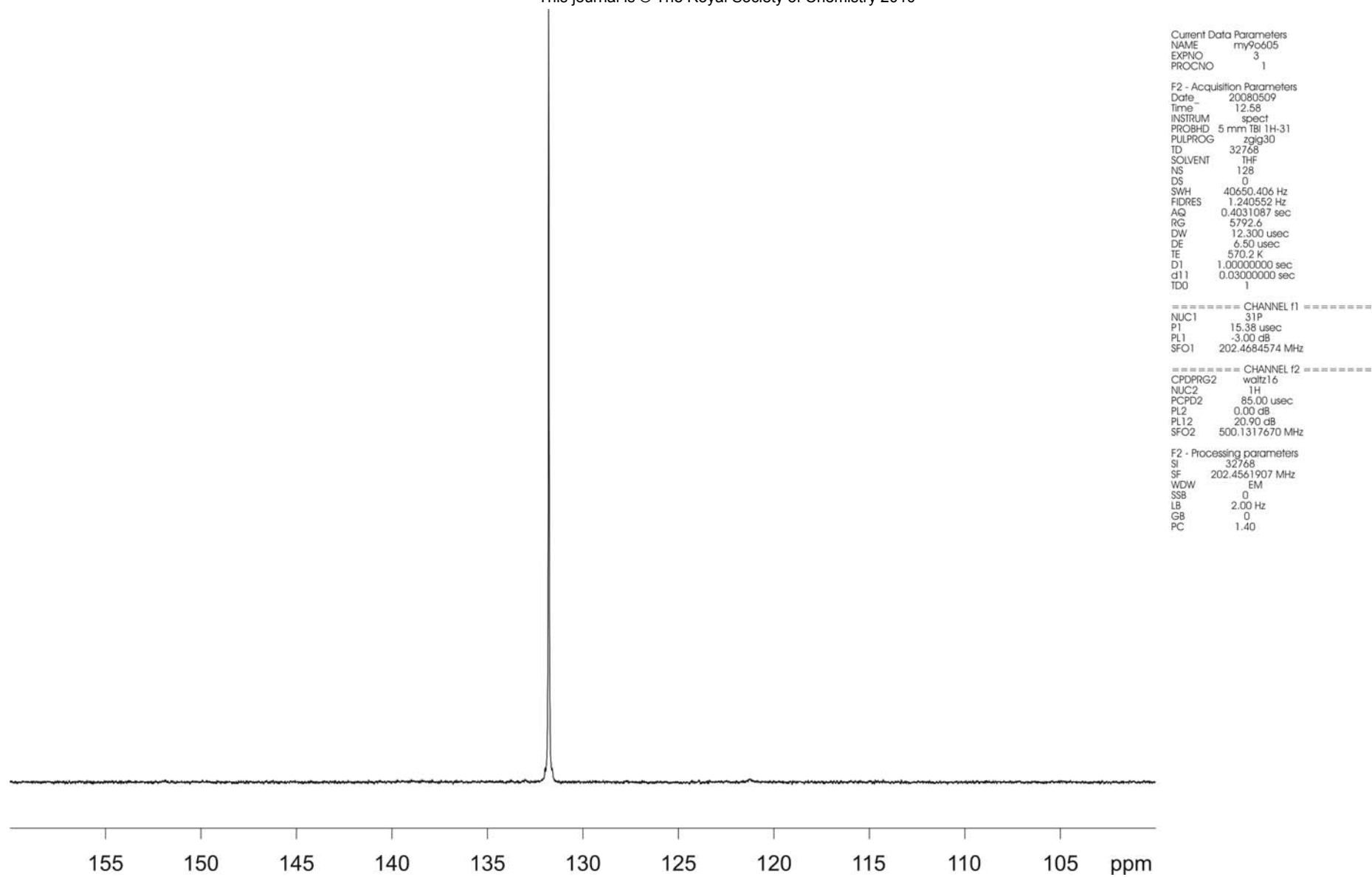


Figure 6.  $^{31}\text{P}$  NMR (202.4 MHz) spectrum of **6** in THF- $d_8$ .

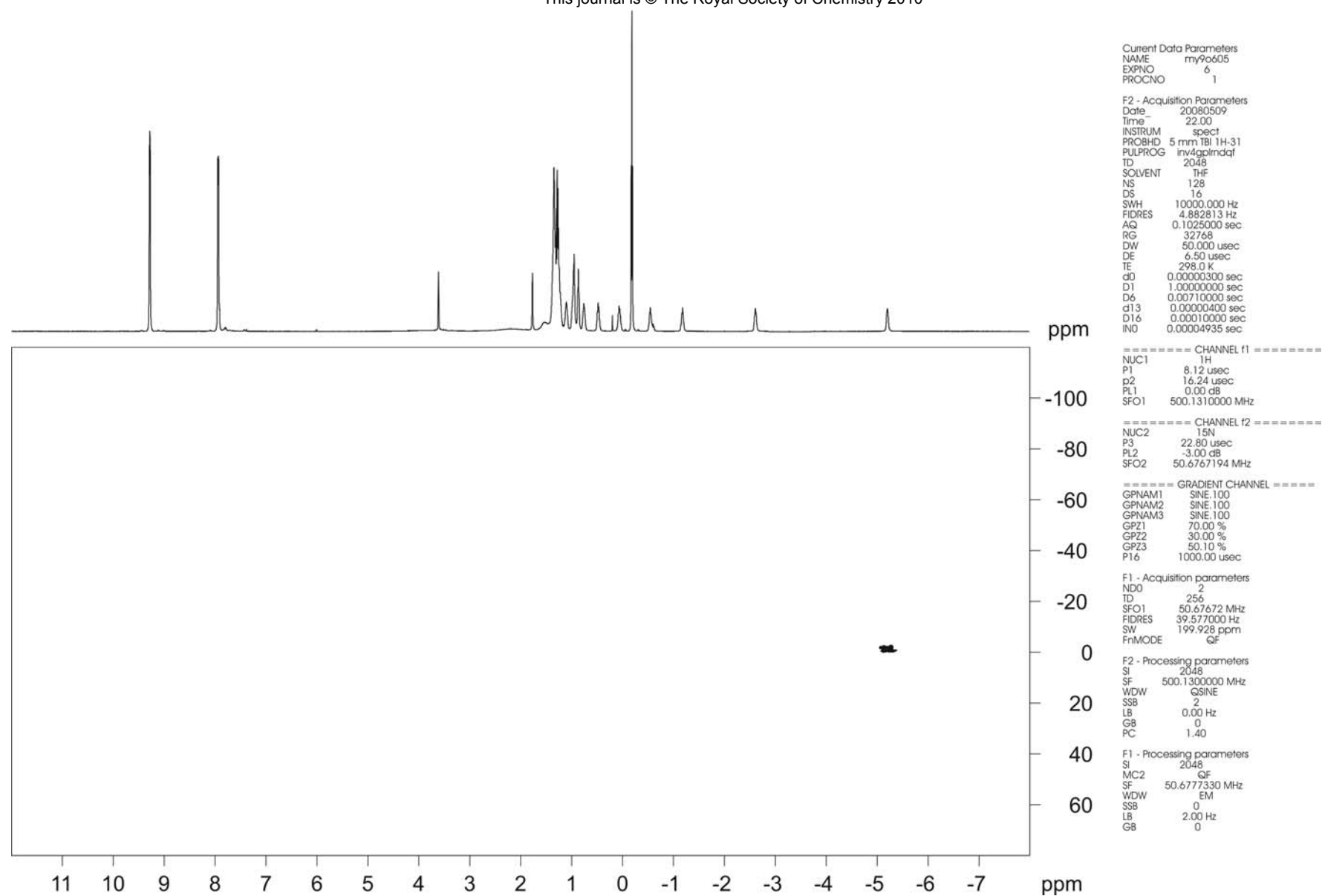


Figure 7.  $^1\text{H}$ ,  $^{15}\text{N}$  gHMQC NMR spectrum of **6** in  $\text{THF-}d_8$ .



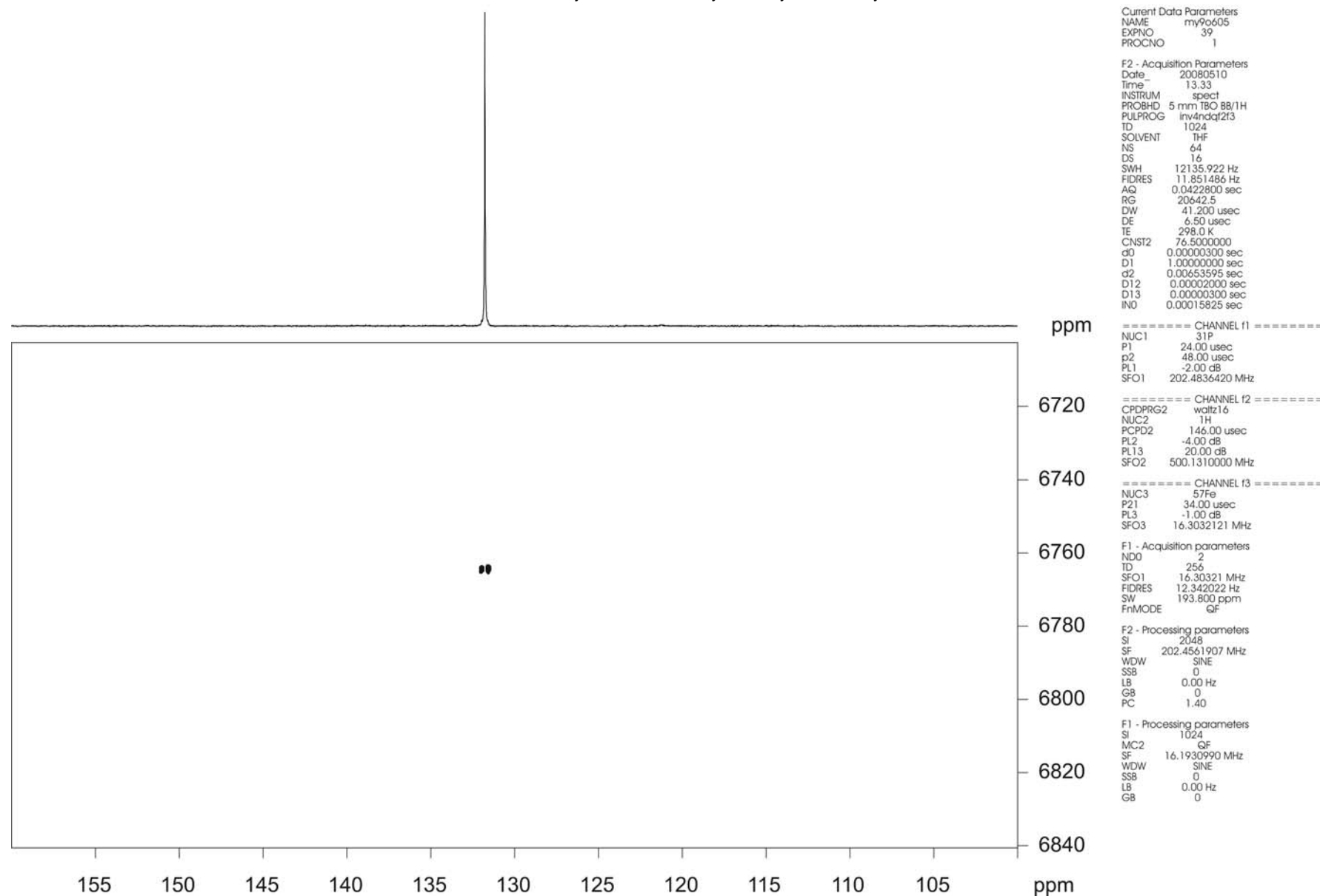


Figure 8.  $^{31}\text{P}$ ,  $^{57}\text{Fe}$  HMQC NMR spectrum of **6** in  $\text{THF-}d_8$ .

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PROCNO 1

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PL1 -3.00 dB  
SFO1 500.1310000 MHz

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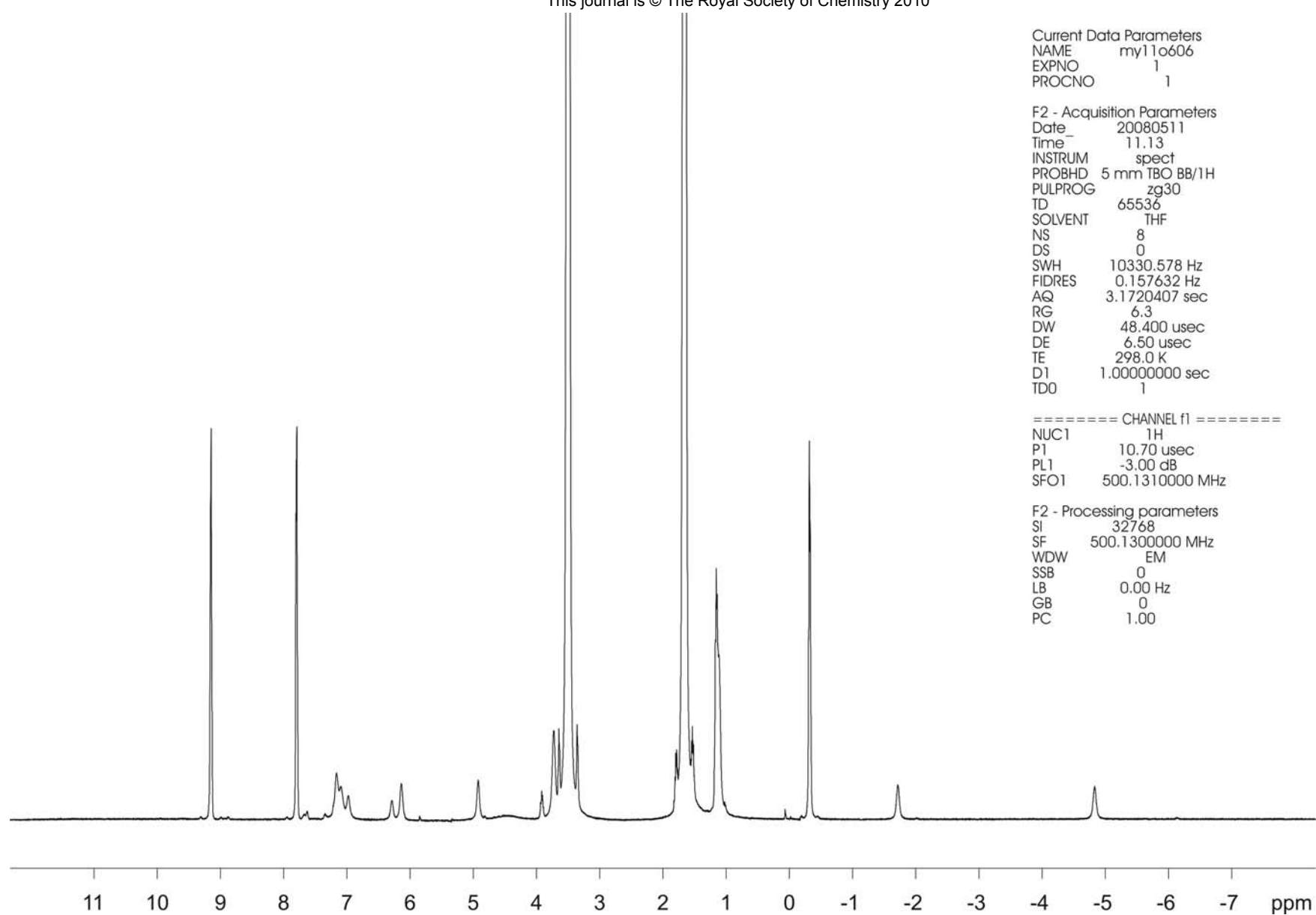


Figure 9.  $^1\text{H}$  NMR (500.13 MHz) spectrum of **7** in THF.

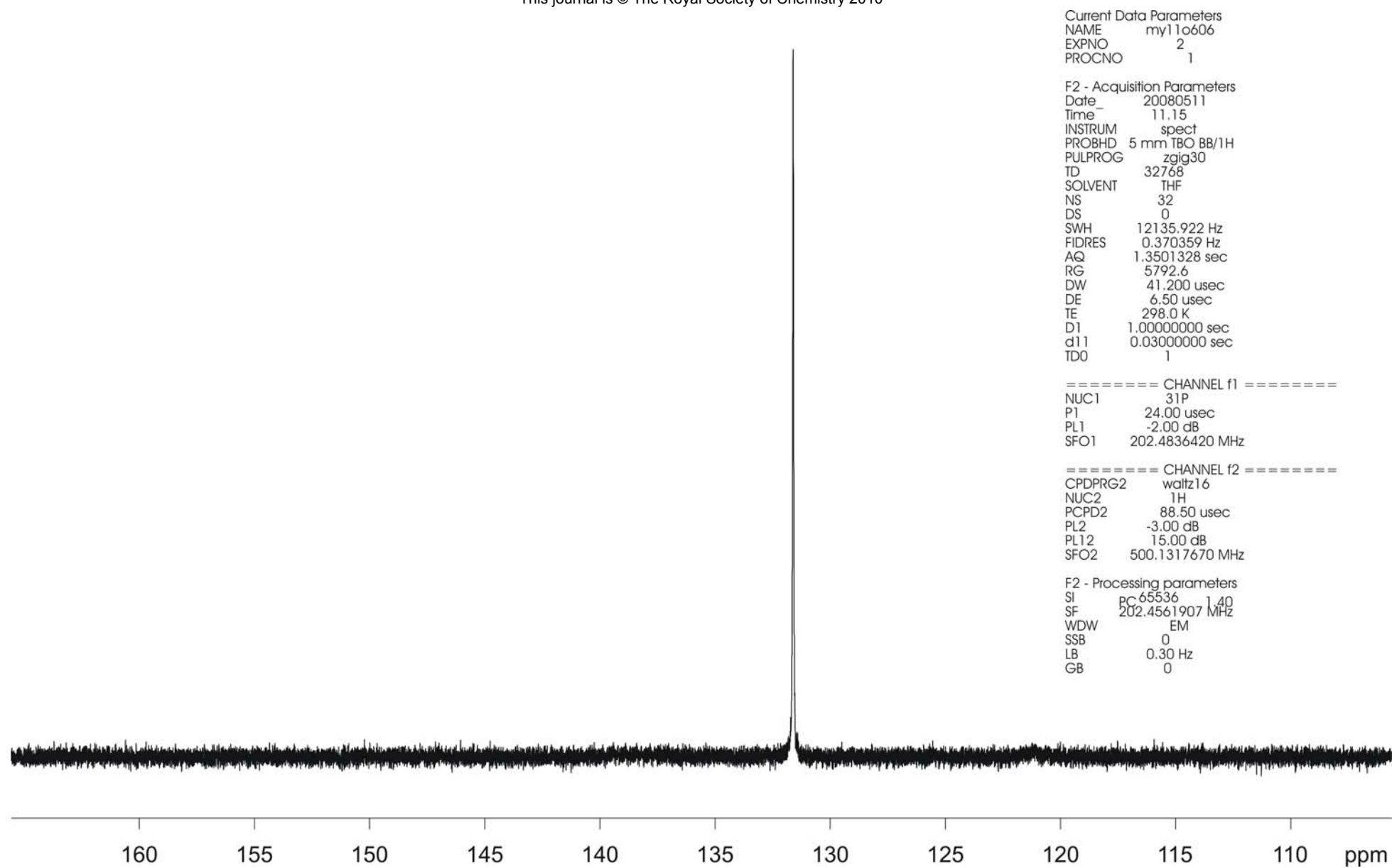


Figure 10.  $^{31}\text{P}$  NMR (202.4 MHz) spectrum of **7** in THF.

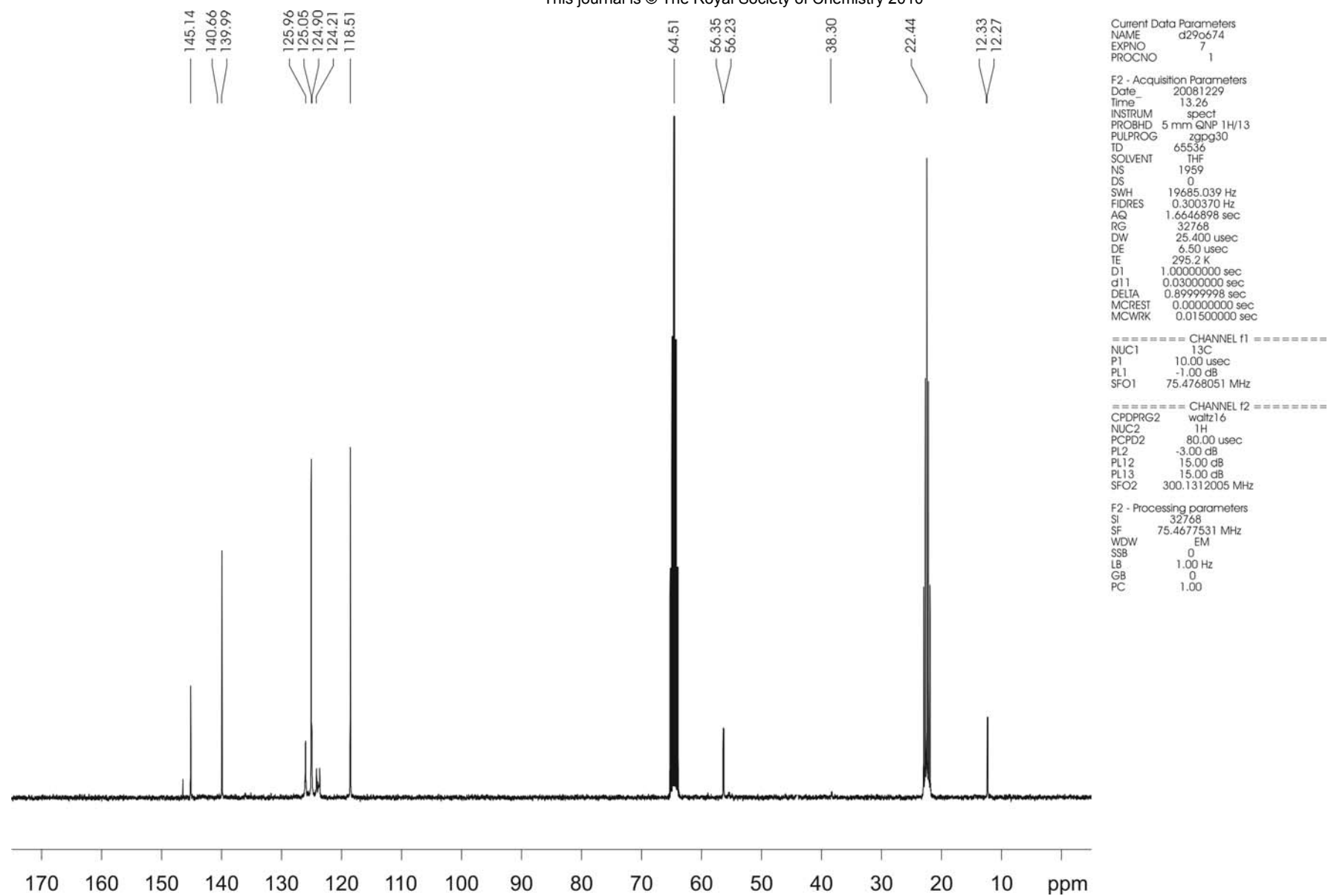


Figure 11.  $^{13}\text{C}$  NMR (75.5 MHz) spectrum of **7** in  $\text{THF-}d_8$ .

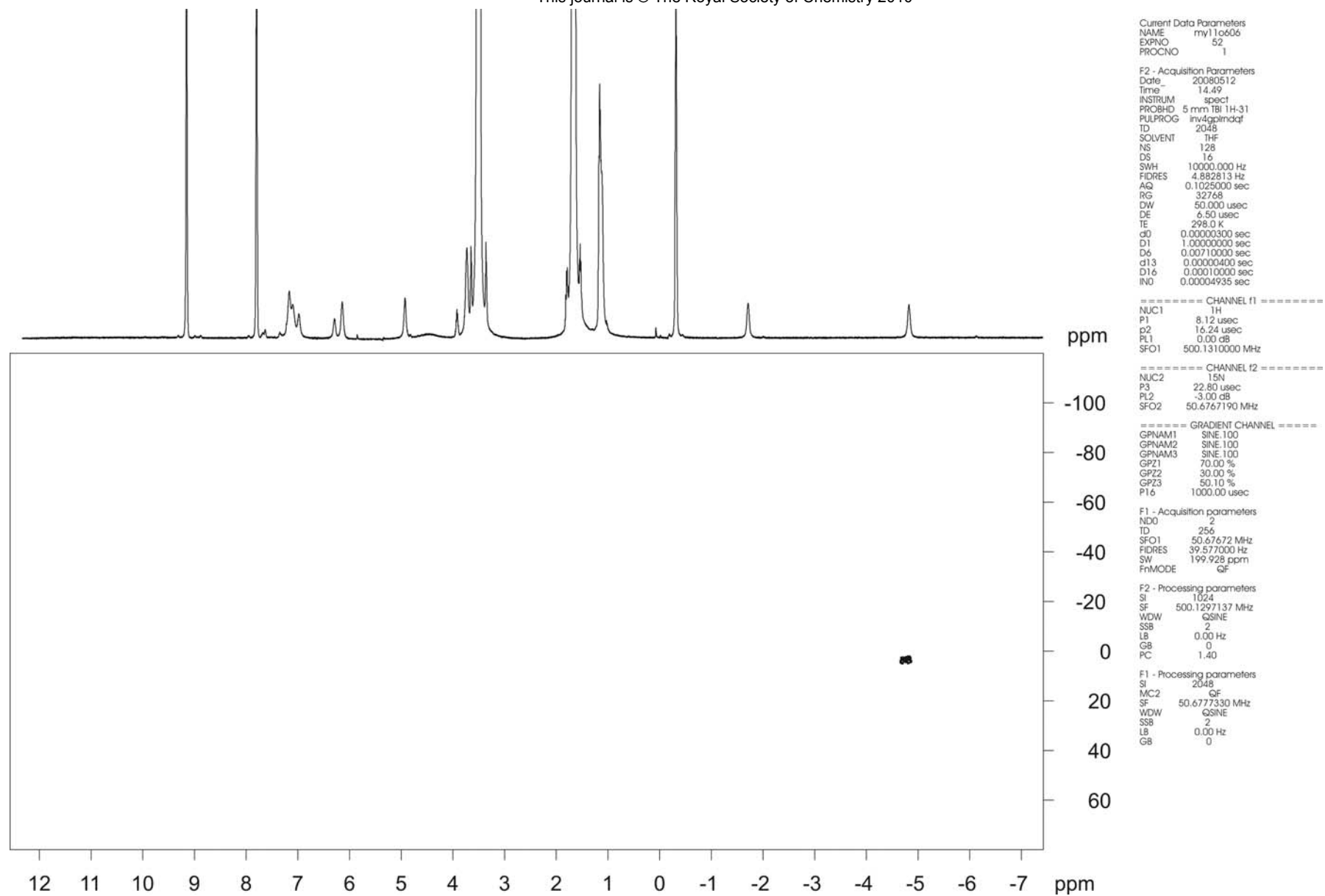


Figure 12.  $^1\text{H}$ ,  $^{15}\text{N}$  gHMQC NMR spectrum of **7** in THF.

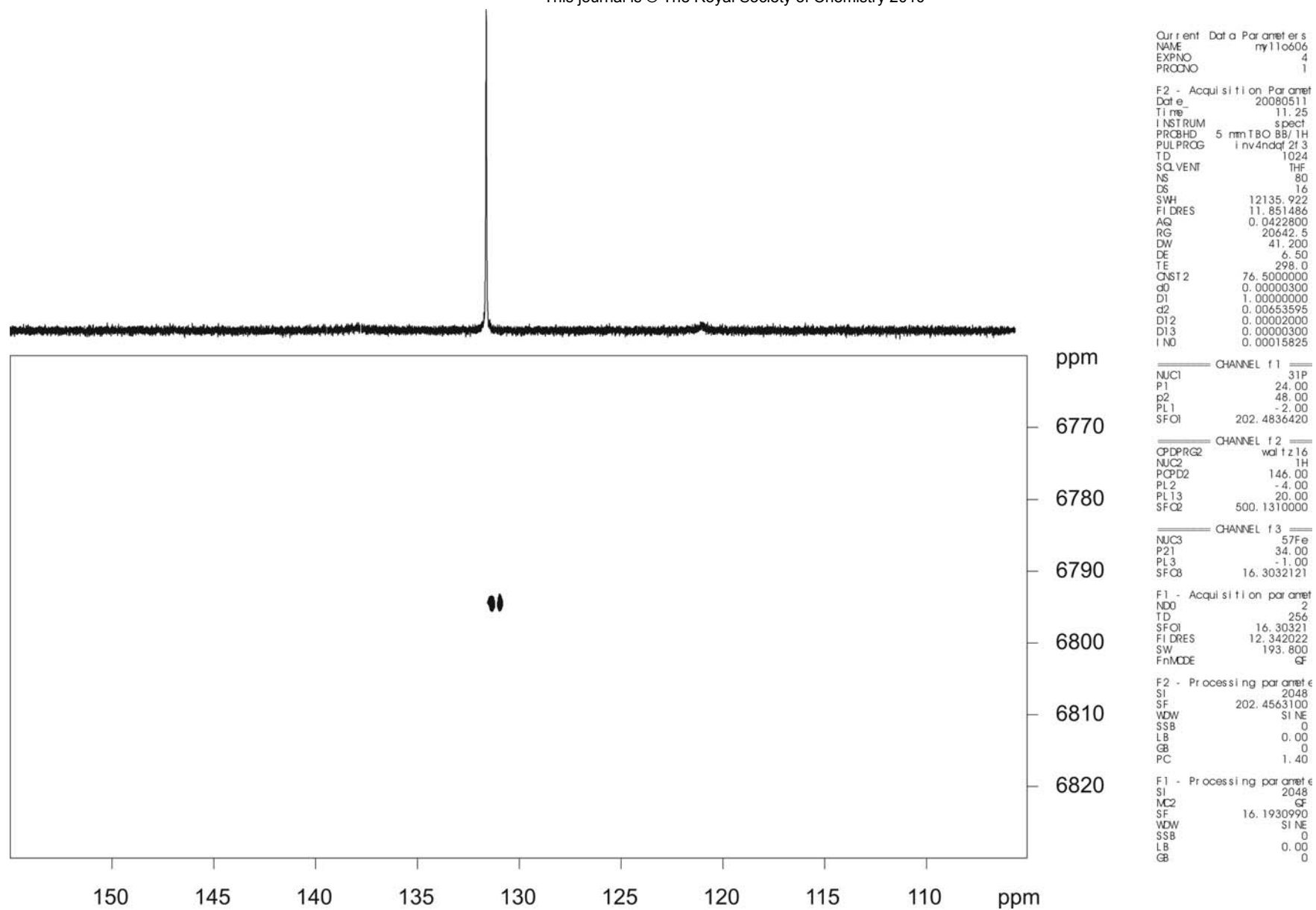


Figure 13.  $^{31}\text{P}$ ,  $^{57}\text{Fe}$  HMQC NMR spectrum of **7** in THF.

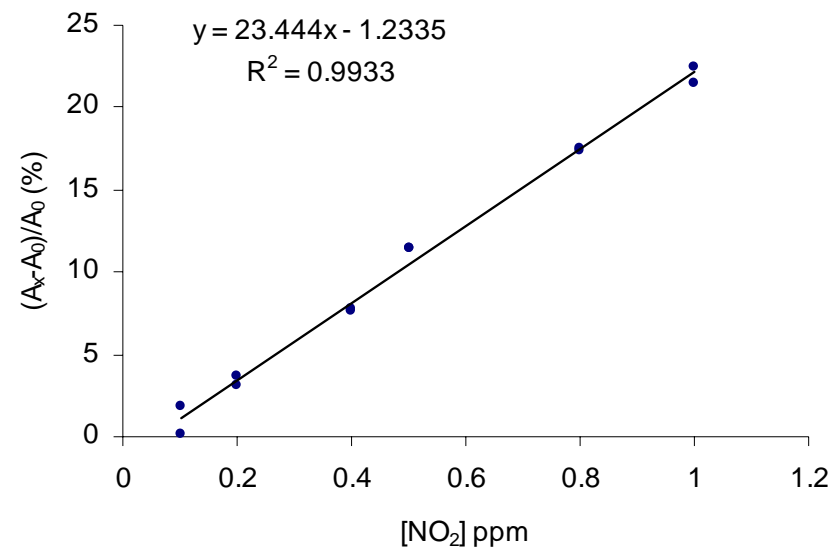


Figure 14. Calibration curve of complex 7 immobilized into AP200/19 for NO<sub>2</sub>; the calculated LOD is 1.2 ppb. A<sub>0</sub> is the absorbance before exposure to NO<sub>2</sub> and A<sub>x</sub> is the absorbance upon exposure to NO<sub>2</sub> for 300 s in air with 50% RH at a flow rate of 200 mL min<sup>-1</sup>.

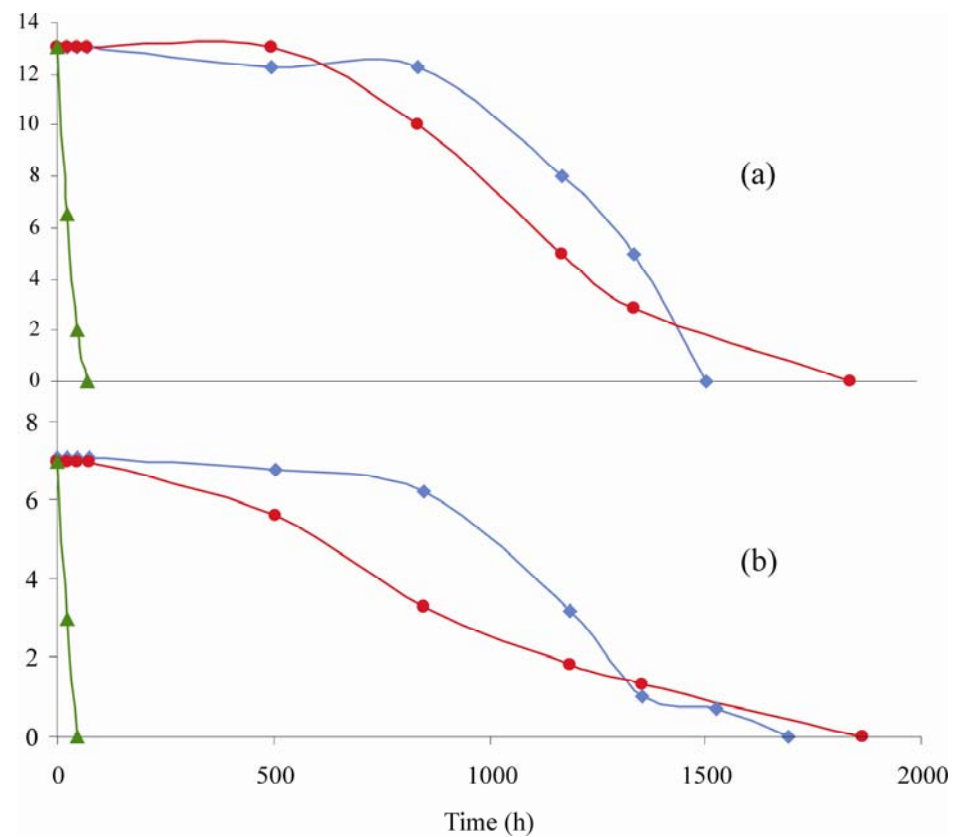


Figure 15. Stability studies at (♦) 4°C, (●) 25°C and (▲) 60°C for sensing layers containing a) complex 4, and b) complex 5, incorporated into AP200/19.  $A_0$  is the absorbance before exposure to  $\text{NO}_2$  and  $A_x$  is the absorbance upon exposure to  $\text{NO}_2$  for 300 s in air with 50% RH.



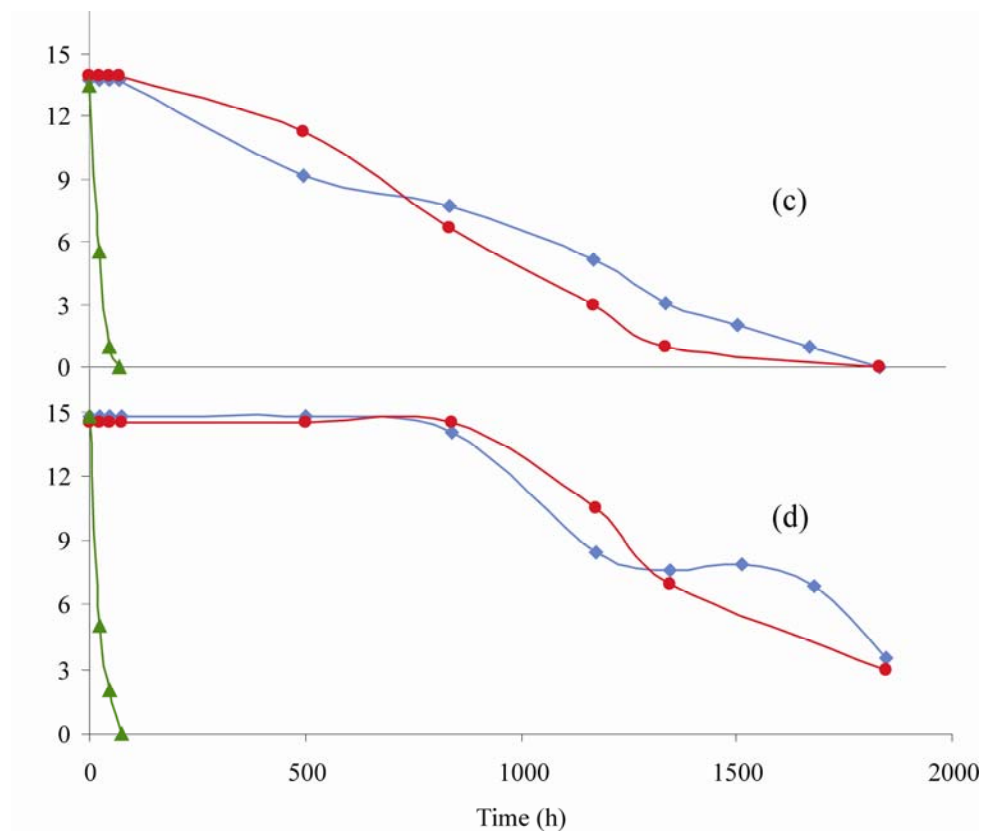


Figure 16. Stability studies at (◆) 4°C, (●) 25°C and (▲) 60°C for sensing layers containing a) complex 6, and b) complex 7, incorporated into AP200/19.  $A_0$  is the absorbance before exposure to  $\text{NO}_2$  and  $A_x$  is the absorbance upon exposure to  $\text{NO}_2$  for 300 s in air with 50% RH.

<sup>1</sup>H, j23mt+b, 1:30

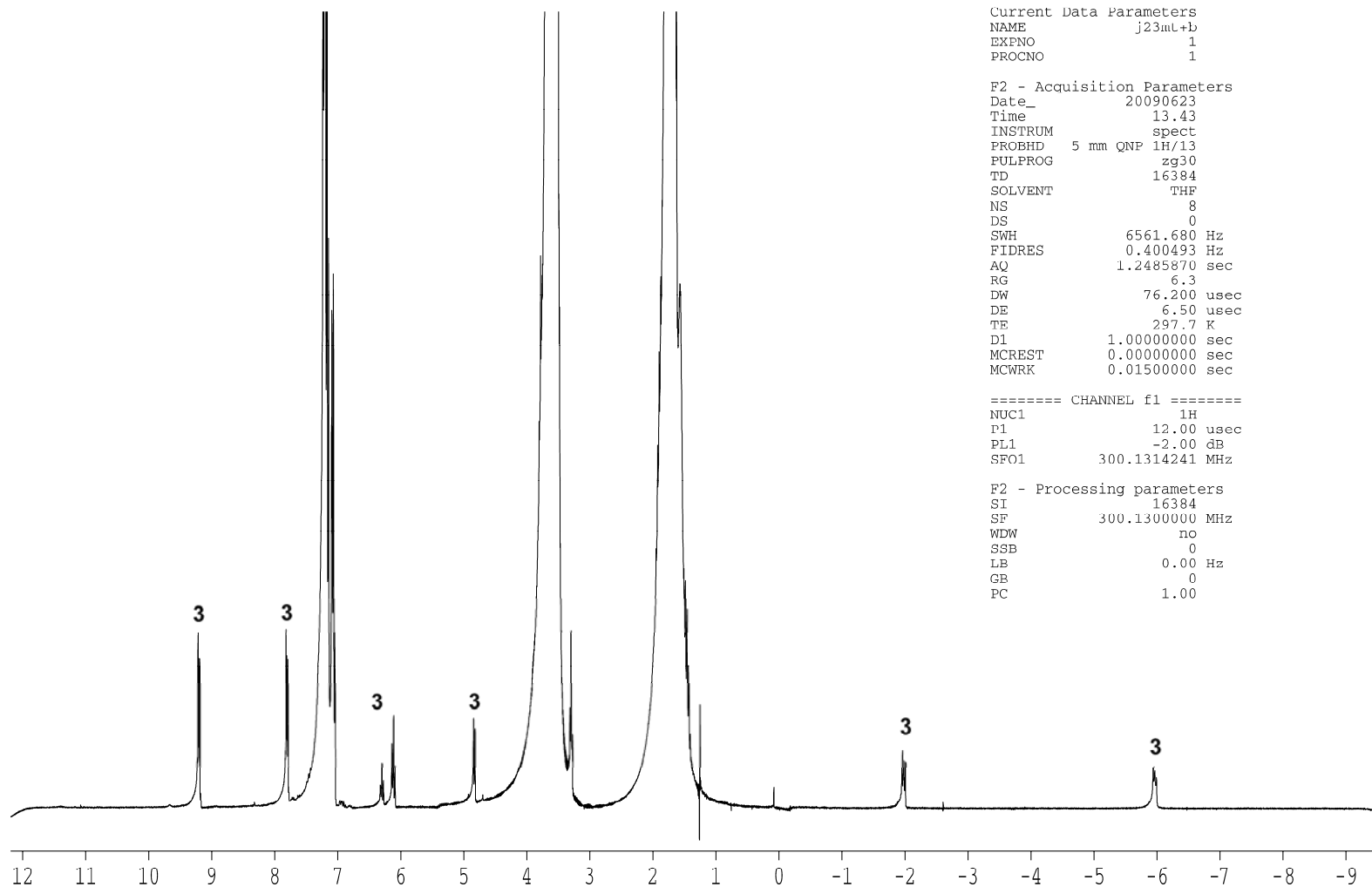


Figure 17. <sup>1</sup>H NMR of the THF cocktail based on **1**:benzylamine, in the ratio 1:30. Complex **3** can be clearly identified among THF and benzylamine signals.

<sup>1</sup>H, j23mt+b+f, 1:30:15

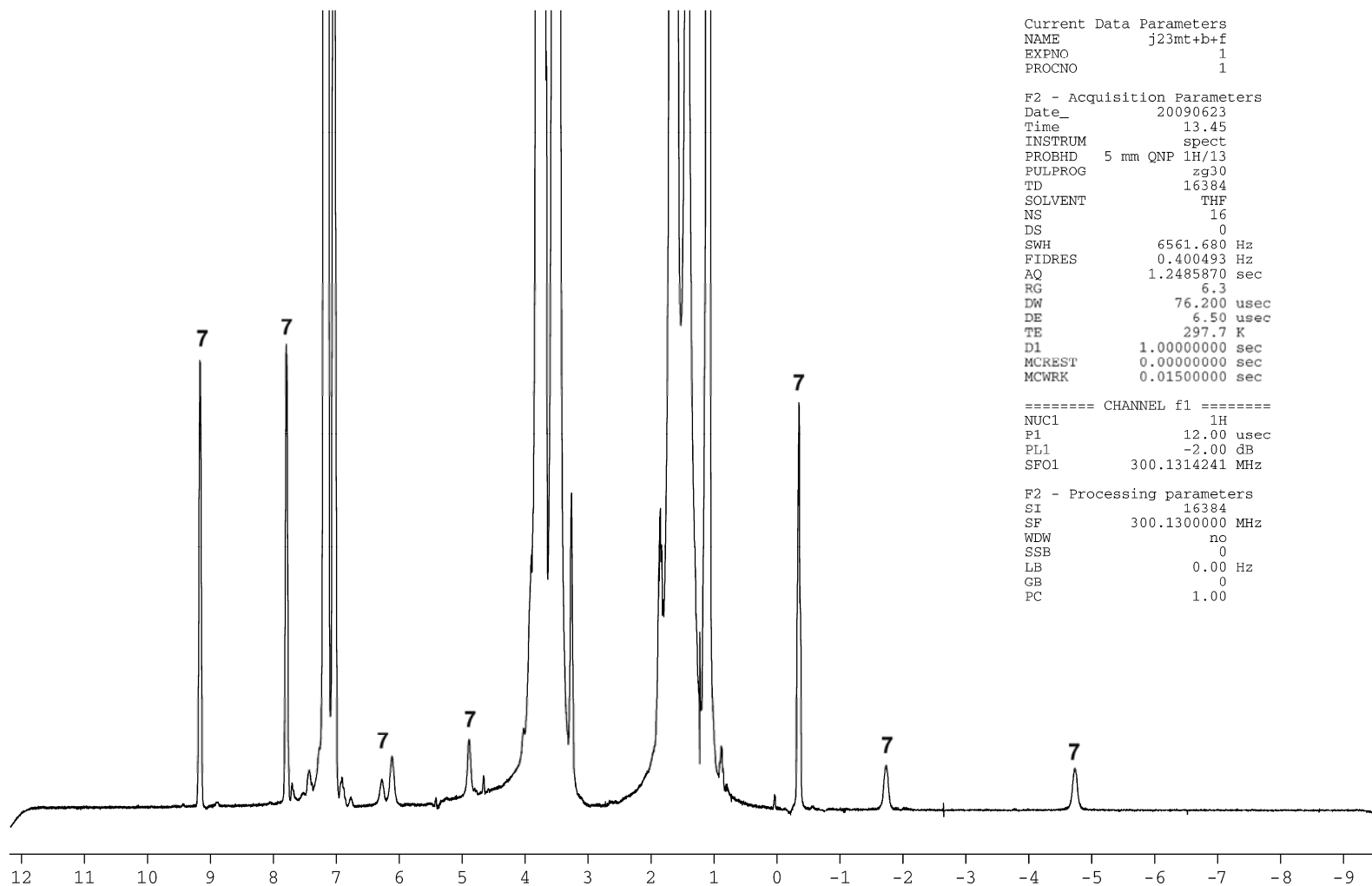


Figure 18. <sup>1</sup>H NMR of the THF cocktail based on **1**:benzylamine:P(EtO)<sub>3</sub>, in the ratio 1:30:15. Complex **7** can be clearly identified among THF, benzylamine, and triethylphosphite signals.

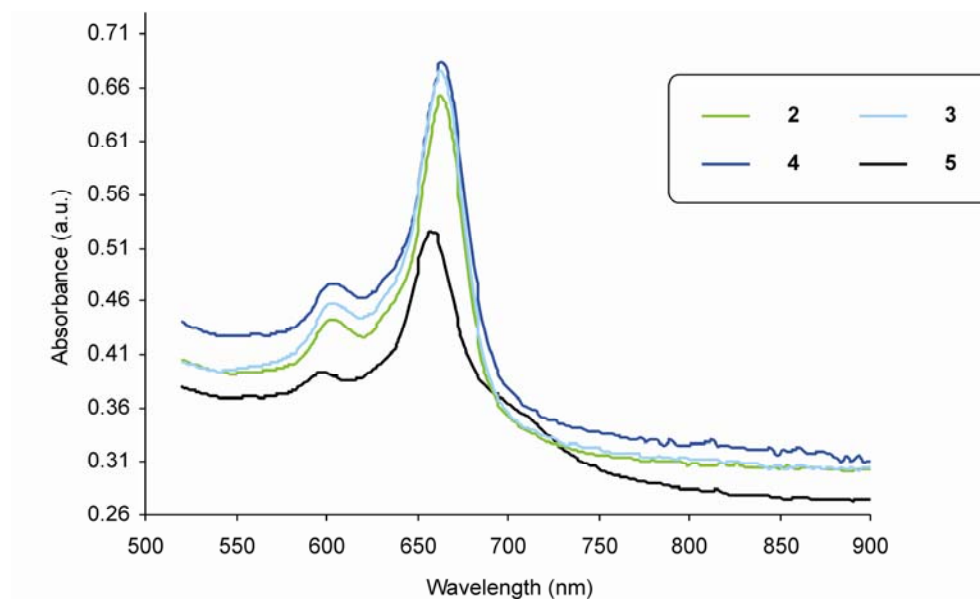


Figure 19. Absorption spectra of complexes **2-5** (FePc:amine molar ratio 1:30) immobilized into AP200/19 in air with 50% RH and at flow-rate of 200 mL min<sup>-1</sup>.

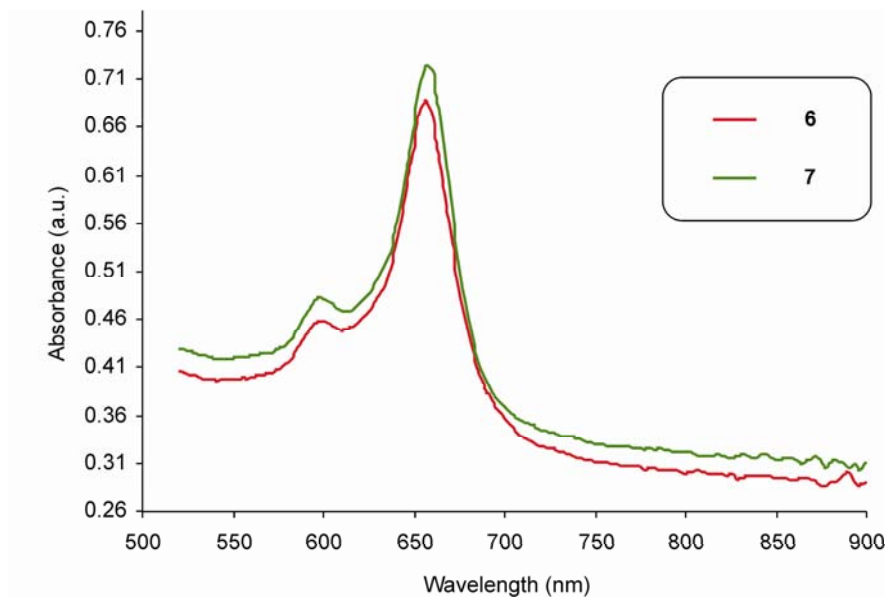


Figure 20. Absorption spectra of the cocktails for complexes **6** and **7** formation (FePc:amine:P(OEt)<sub>3</sub> molar ratio 1:30:15) immobilized into AP200/19 in air with 50% RH and at flow-rate of 200 mL min<sup>-1</sup>.

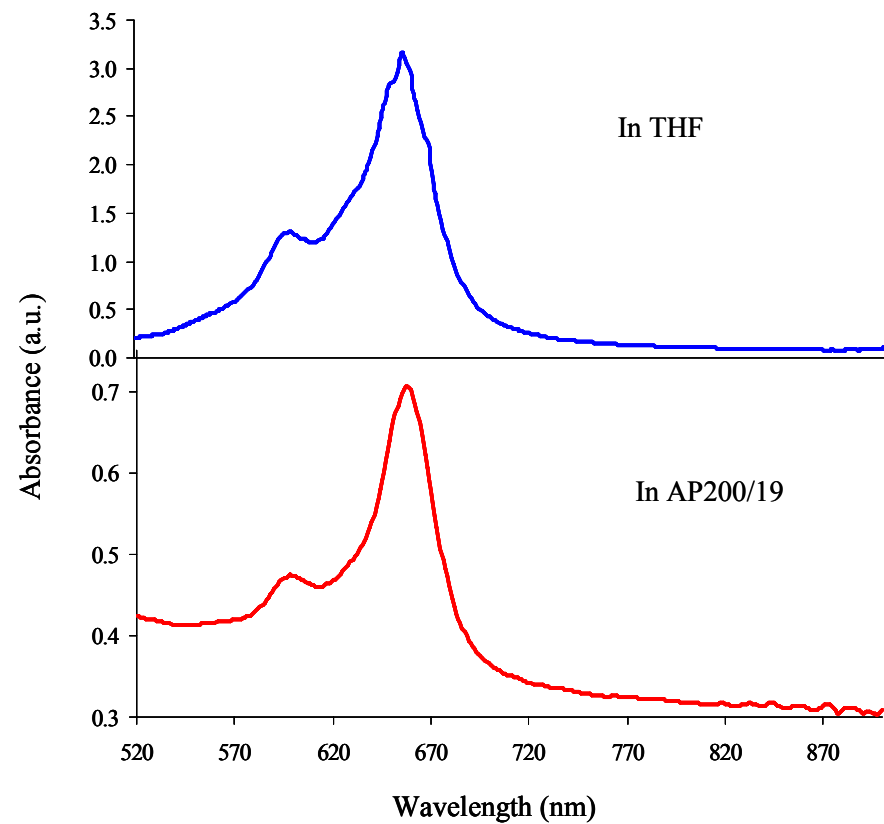


Figure 21. Absorption spectra of complex **7** in THF solution (top) and incorporated into AP200/19 (bottom).