

## Supporting Information

# Detection and Differentiation of Neutral Organic Compounds by $^{19}\text{F}$ NMR with a Tungsten Calix[4]arene Imido Complex

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<b>General Methods and Material</b> .....	S2
<b>Preparation of iminophosphorane (<math>\text{Ph}_3\text{P}=\text{NR}</math>) reagent 4</b> .....	S3
<b>Generally Procedure for the preparation of calixarene tungsten imido complexes 1 and 2</b> .....	S4
<b>Additional NMR experiments</b> .....	S6
<b>X-ray structures of complex 1</b> .....	S10
<b>Reference</b> .....	S11
<b><math>^1\text{H}</math>, <math>^{19}\text{F}</math>, and <math>^{13}\text{C}</math> NMR spectrum of all new products</b> .....	S12

**General Methods and Material:**

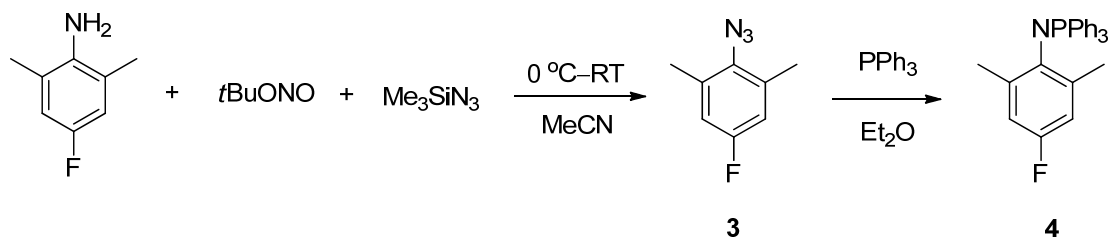
**Material:** All reactions were carried out under argon using standard Schlenk techniques unless otherwise noted. All solvents were of ACS reagent grade or better unless otherwise noted. Anhydrous toluene (PhCH<sub>3</sub>) was obtained from Sigma-Aldrich. Silica gel (40 μm) was purchased from SiliCycle Inc. All reagent grade materials were purchased from Alfa Aesar or Sigma-Aldrich and used without further purification. WOCl<sub>4</sub> was available in Sigma-Aldrich and could also be prepared from WCl<sub>6</sub> according to the procedure described in the literature.<sup>1</sup>

**NMR Spectroscopy:** <sup>1</sup>H, <sup>19</sup>F, and <sup>13</sup>C NMR spectra for all compounds were acquired in CDCl<sub>3</sub> on a Bruker Avance Spectrometer operating at (400 MHz 376MHz, and 100 MHz, respectively). Chemical shifts (δ) are reported in parts per million (ppm) and referenced with TMS for <sup>1</sup>H NMR and CFCl<sub>3</sub> for <sup>19</sup>F NMR.

General procedure for NMR experiment: At ambient temperature, complex **1** (2.07 M in 530 μL of CDCl<sub>3</sub>) was mixed with different analytes (variable concentrations in 20 μL CDCl<sub>3</sub>). The the NMR spectra was recorded on a Bruker Avance Spectrometer with TOPSPIN using autolocking and autoshimming (typically 64 scans).

The obtained NMR data were processed using MestReNova. After phase correction, the spectra were stacked (stacked angle = 0), and the signals between -111.7 ppm to - 113.5 ppm was shown in the manuscript (Figure **1**).

**Mass Spectrometry:** High-resolution mass spectra (HRMS) were obtained at the MIT Department of Chemistry Instrumentation Facility employing electrospray (ESI) as the ionization technique.

**Preparation of iminophosphorane (Ph<sub>3</sub>P=NR) reagent 4:****Scheme S1.** Preparation of iminophosphorane (Ph<sub>3</sub>P=NR) reagent 4.

**Compound 3** was prepared using an analogue procedure described in literature.<sup>2</sup>

4-Fluoro-2,6-dimethylaniline (500 mg, 3.59 mmol) was dissolved in CH<sub>3</sub>CN (8 mL) in a 25 mL flask and cooled to 0 °C. To this mixture, *t*-BuONO (555 mg, 5.39 mmol, 1.5 equiv) was added followed by TMSN<sub>3</sub> (497 mg, 4.32 mmol, 1.2 equiv). The solution was then allowed to warm to room temperature slowly, and stirred at room temperature for 3 h. The reaction mixture was concentrated and the crude product was purified by silica gel chromatography using hexane as the eluent to give product **3** as a colorless oil. (550 mg, Yield:93%) IR (film): 2124, 2101, 1477, 1423, 1278, 1142, 1024, 861, 711, 627 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.74 (d, *J* = 8.9 Hz, 2H), 2.35 (s, 6H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -117.55 (t, *J* = 8.9 Hz, 1F). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 160.05 (d, *J* = 244.3 Hz), 134.16 (d, *J* = 8.5 Hz), 132.88 (d, *J* = 2.8 Hz), 115.21 (d, *J* = 22.4 Hz), 18.27 (s).

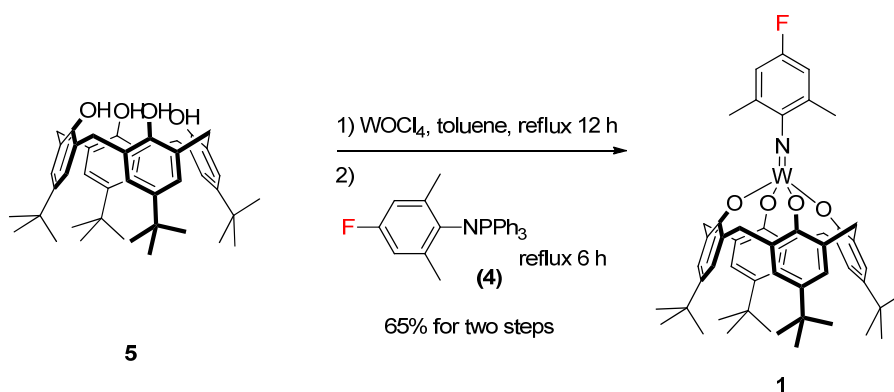
**Compound 4:**

A solution of compound **3** (200 mg, 1.21 mmol) and PPh<sub>3</sub> (317 mg, 1.21 mmol) in Et<sub>2</sub>O (10 mL) was refluxed overnight (10 h). Evaporation of the solvent to give a white solid which was recrystallized from hexane/ether. Colorless crystal (405 mg, Yield:84%).

M.P. 138–140 °C. IR (film): 1471, 1429, 1343, 1281, 1109, 1008, 859, 755, 748, 738, 722, 712, 696, 663 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 7.54 – 7.46 (m, 6H), 7.45 – 7.38 (m, 3H), 7.36 – 7.28 (m, 6H), 6.47 (d, *J* = 10.6 Hz, 2H), 1.80 (d, *J* = 1.8 Hz, 6H). <sup>19</sup>F NMR (376 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ -127.73 (td, *J* = 9.5, 5.4 Hz, 1F). <sup>31</sup>P NMR (162 MHz,

CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  -6.45 (s). <sup>13</sup>C NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  155.74 (dd,  $J$  = 234.4, 4.0 Hz), 143.50 (s), 134.05 (t,  $J$  = 7.4 Hz), 133.05 (d,  $J$  = 100.7 Hz), 132.23 (d,  $J$  = 9.5 Hz), 131.26 (d,  $J$  = 2.8 Hz), 128.31 (d,  $J$  = 11.8 Hz), 113.35 (dd,  $J$  = 21.1, 2.7 Hz), 21.06 (s). HRMS (ESI): calc for C<sub>26</sub>H<sub>24</sub>FNP [M+H]<sup>+</sup> 400.1625, found 400.1607.

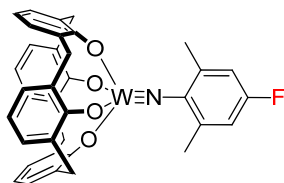
### Generally Procedure for the preparation of calixarene tungsten imido complexes **1** and **2**.



#### Scheme S2. Preparation of calixarene tungsten imido complex **1**.

To a suspension of WOCl<sub>4</sub> (55.3 mg, 0.16 mmol) and *t*Bu-Calixarene **5** (100 mg, 0.15 mmol) were dissolved in 5 mL dry toluene and refluxed for 12 h under an inert atmosphere. Iminophosphorane reagent **4** (80 mg, 0.2 mmol) was added and the mixture was refluxed for additional 6 h. Evaporation of the solvent and the crude product was purified by silica gel chromatography using hexane/dichloromethane (2:1) as the eluent to give product **1** as a yellow solid (97 mg, Yield: 65%).

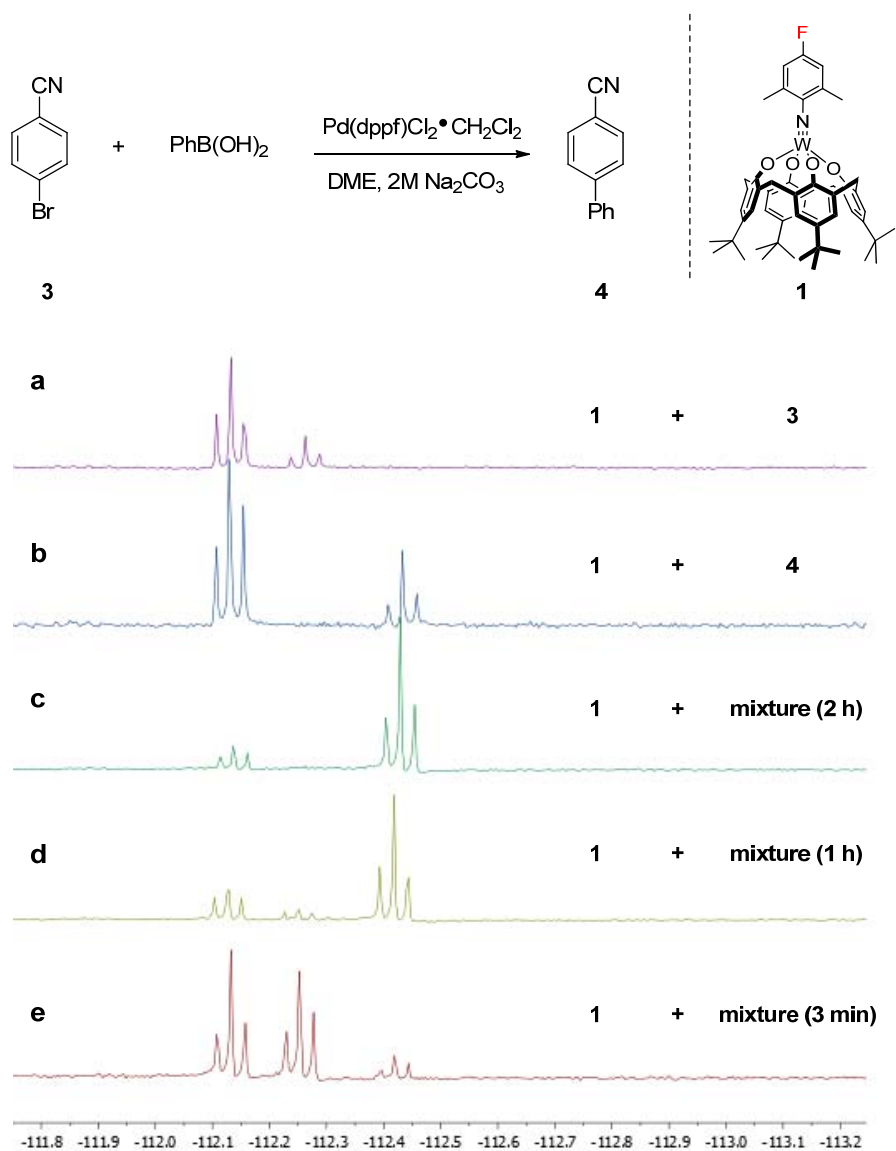
IR (film): 2952, 1461, 1362, 1298, 1244, 1198, 920, 870, 834, 800, 764, 721, 680 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.15 (s, 8H), 6.89 (d,  $J$  = 9.1 Hz, 2H), 4.63 (d,  $J$  = 12.5 Hz, 4H), 3.28 (d,  $J$  = 12.5 Hz, 4H), 3.09 (s, 6H), 1.24 (s, 36H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -112.10 (t,  $J$  = 9.4 Hz, 1F). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  161.28 (d,  $J$  = 248.3 Hz), 155.23 (s), 148.22 (s), 145.06 (s), 142.57 (d,  $J$  = 8.8 Hz), 130.53 (s), 125.13 (s), 113.28 (d,  $J$  = 22.7 Hz), 34.08 (s), 33.07 (s), 31.59 (s), 18.43 (s). HRMS (ESI): calc for C<sub>52</sub>H<sub>61</sub>FNO<sub>4</sub>W [M+H]<sup>+</sup> 966.4088, found 966.4100.

**2****Figure S1.** Structure of tungsten imido complex **2**.

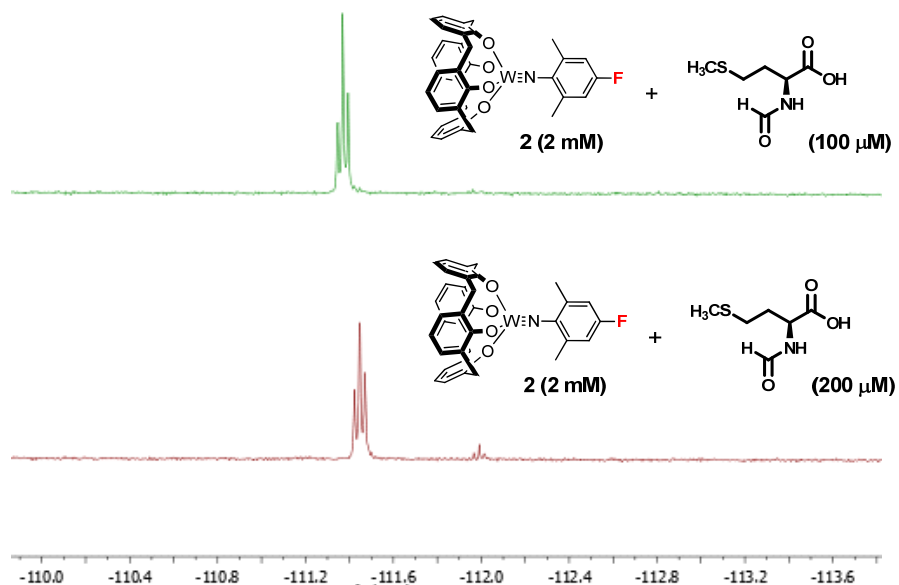
Complex **2** was prepared using the same method. Yellow solid. (Yield: 60%)

IR (film): 2926, 1588, 1448, 1275, 1249, 1222, 1202, 1132, 1078, 919, 895, 856, 812, 765, 714, 640  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.15 (d,  $J = 7.6$  Hz, 8H), 6.92 (d,  $J = 9.0$  Hz, 2H), 6.69 (td,  $J = 7.6, 4.1$  Hz, 4H), 4.64 (d,  $J = 12.5$  Hz, 4H), 3.32 (d,  $J = 12.5$  Hz, 4H), 3.14 (s, 6H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -111.27 (t,  $J = 8.9$  Hz, 1F).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.56 (d,  $J = 248.8$  Hz), 157.38 (s), 142.91 (d,  $J = 9.1$  Hz), 131.15 (s), 128.34 (s), 122.65 (s), 113.39 (d,  $J = 22.8$  Hz), 32.25 (s), 18.49 (d,  $J = 1.2$  Hz). HRMS (ESI): calc for  $\text{C}_{36}\text{H}_{29}\text{FNO}_4\text{W}$   $[\text{M}+\text{H}]^+$  742.1584, found 742.1611.

## Additional NMR experiments:

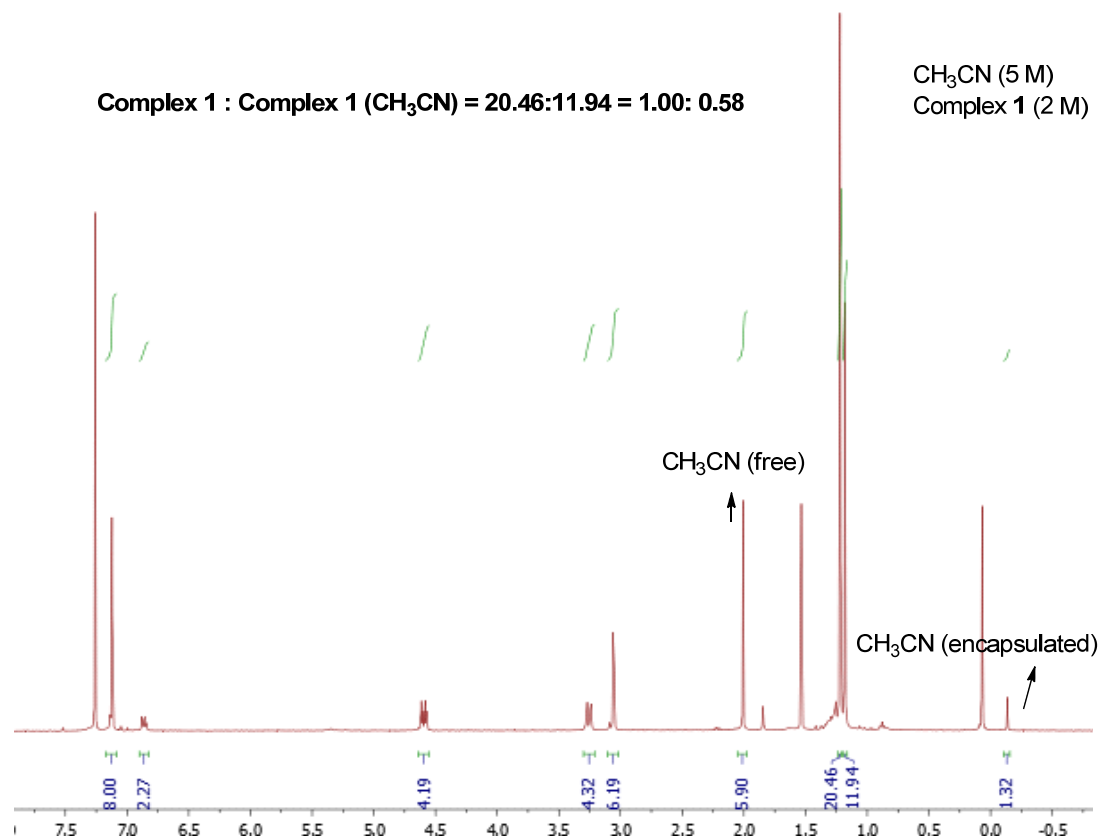


**Figure S2.**  $^{19}\text{F}$  NMR experiments to monitor the reaction process. (a) and (b) showed the identification of the peaks in experiments (d-e).

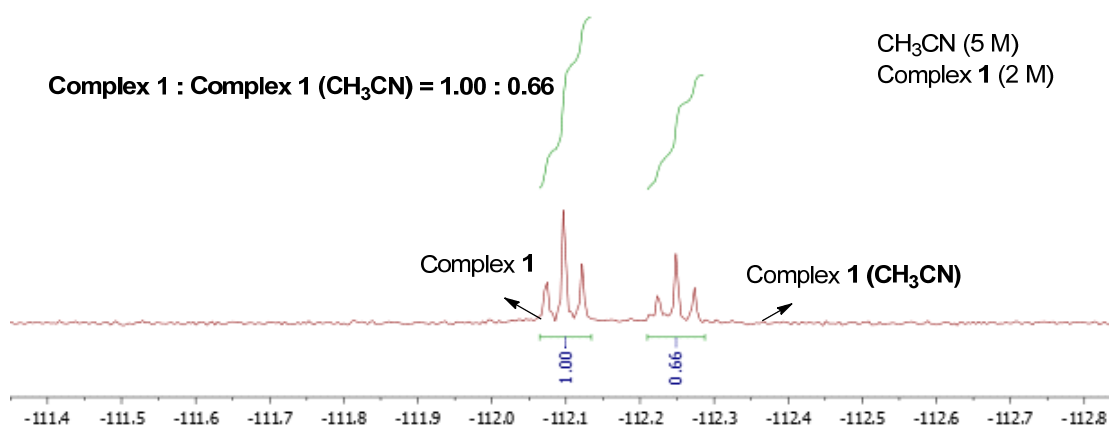


**Figure S3.**  $^{19}\text{F}$  NMR experiments to determine the detection limit of the method.

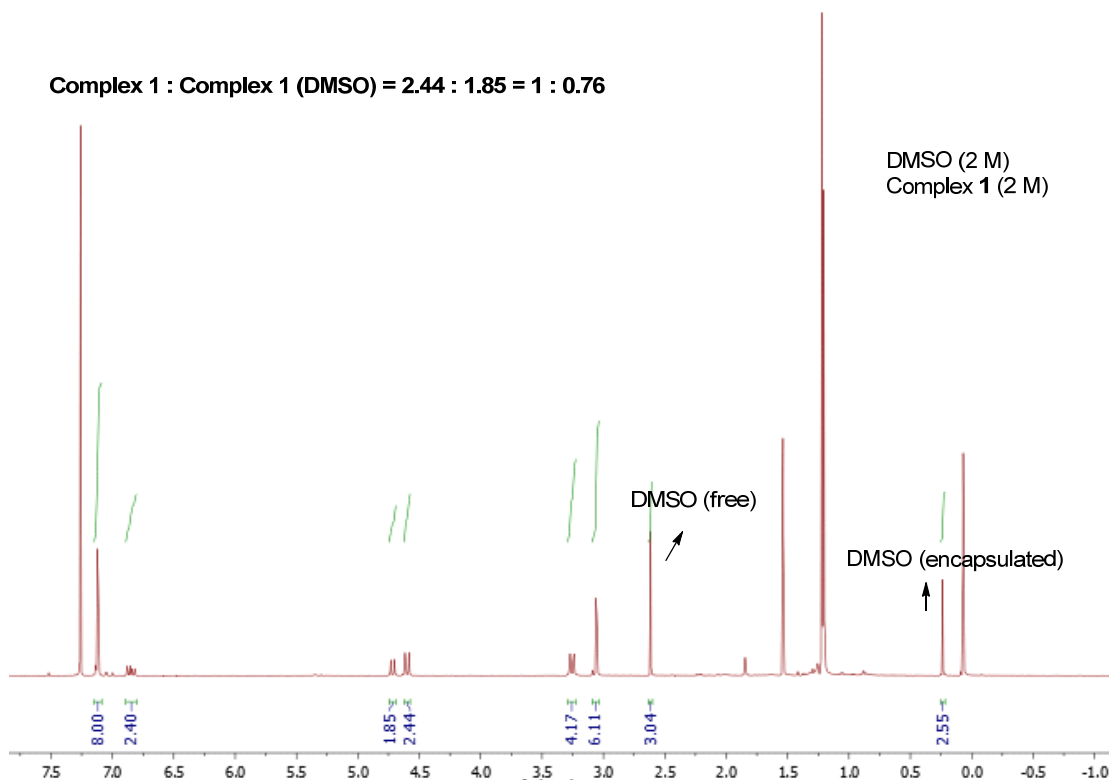
Examples of  $^{19}\text{F}$  NMR and the corresponding  $^1\text{H}$  NMR spectra.



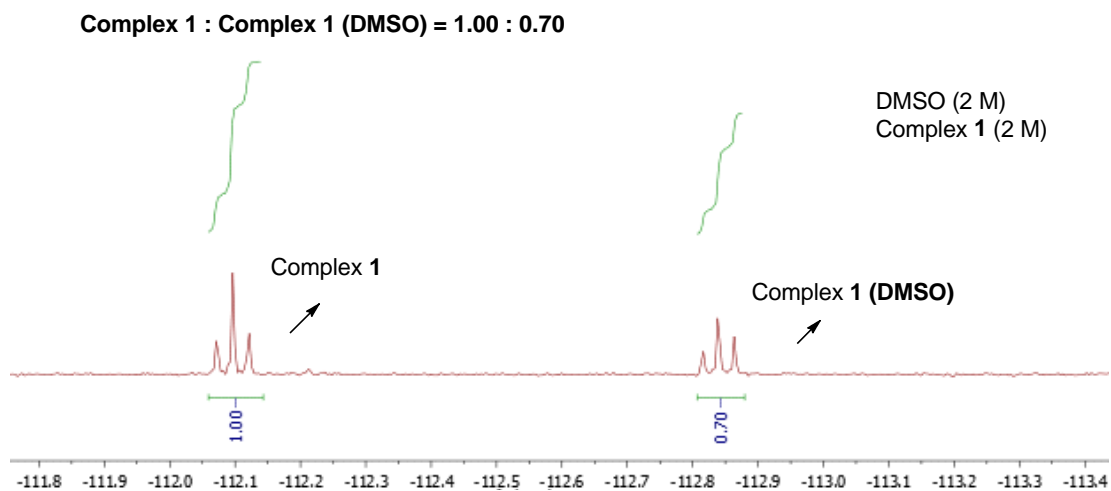
**Figure S4.**  $^1\text{H}$  NMR experiment (32 scans) with complex **1** (2 M) and  $\text{CH}_3\text{CN}$  (5 M).



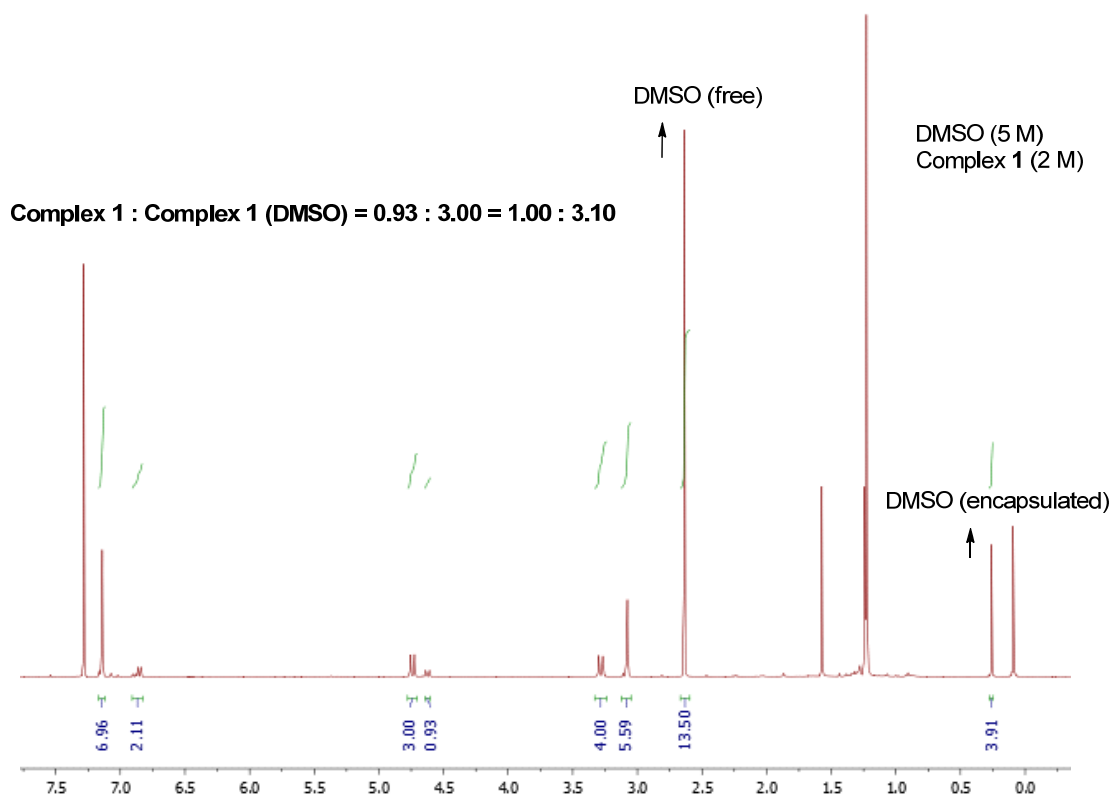
**Figure S5.** <sup>19</sup>F NMR experiment (128 scans) with complex **1** (2 M) and CH<sub>3</sub>CN (5 M).



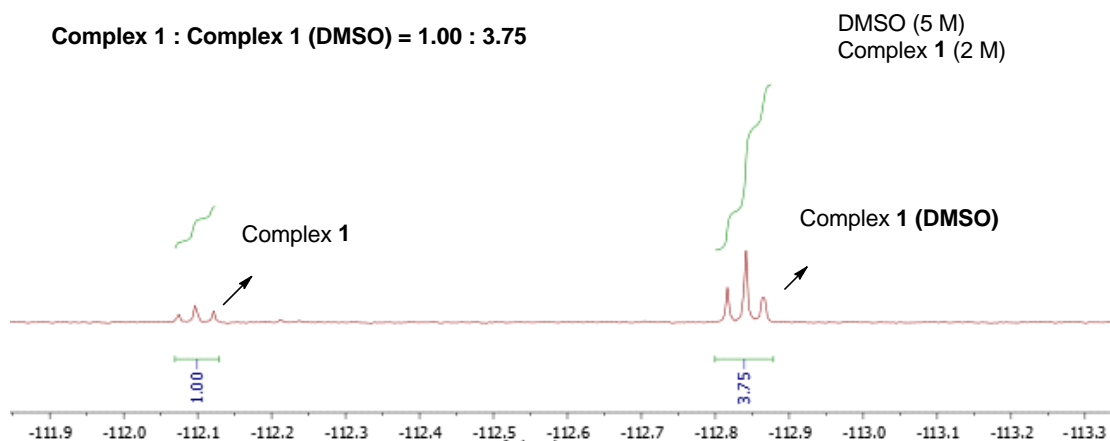
**Figure S6.** <sup>1</sup>H NMR experiment (32 scans) with complex **1** (2 M) and DMSO (2 M).



**Figure S7.**  $^{19}\text{F}$  NMR experiment (128 scans) with complex **1** (2 M) and DMSO (2 M).



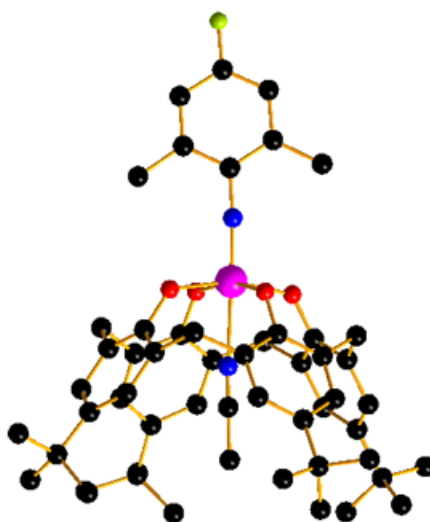
**Figure S8.**  $^1\text{H}$  NMR experiment (32 scans) with complex **1** (2 M) and DMSO (5 M).



**Figure S9.**  $^1\text{H}$  NMR experiment (256 scans) with complex **1** (2 M) and DMSO (5 M). Because the concentration of the unbonded complex **1** is very low, 256 scans were employed to obtain accurate integration and a clear signal.

NOTE: Due to the fewer scans and the stack of spectra, the small amount of unbonded complex **1** was not observed in manuscript (Figure 1).

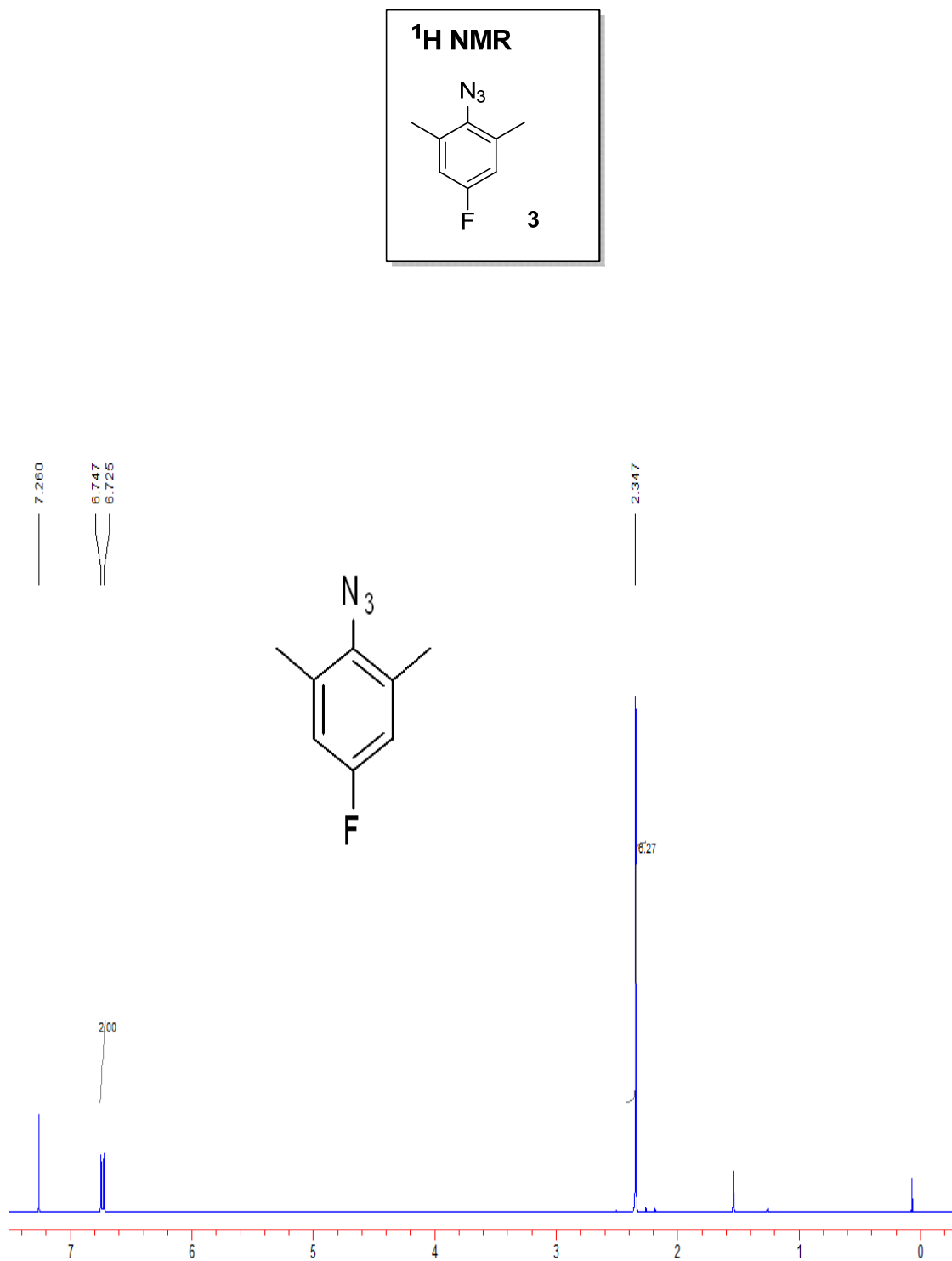
**X-ray structures of complex 1.** (1:1 cocrystal with  $\text{CH}_3\text{CN}$ ) (black = carbon, green = fluorine, blue = nitrogen, red = oxygen, purple = tungsten)

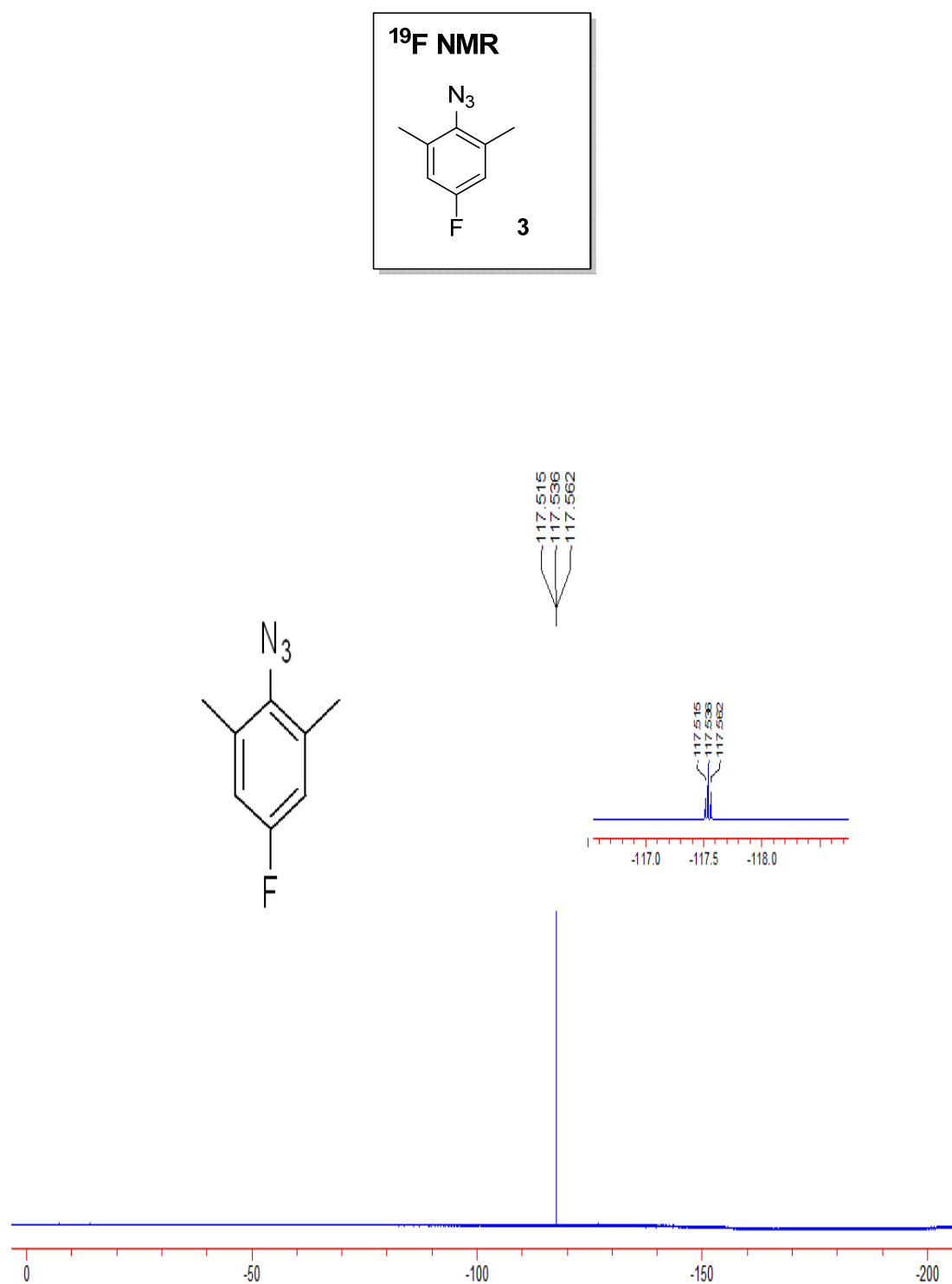


**Figure S10.** X-ray structures of complex **1**.

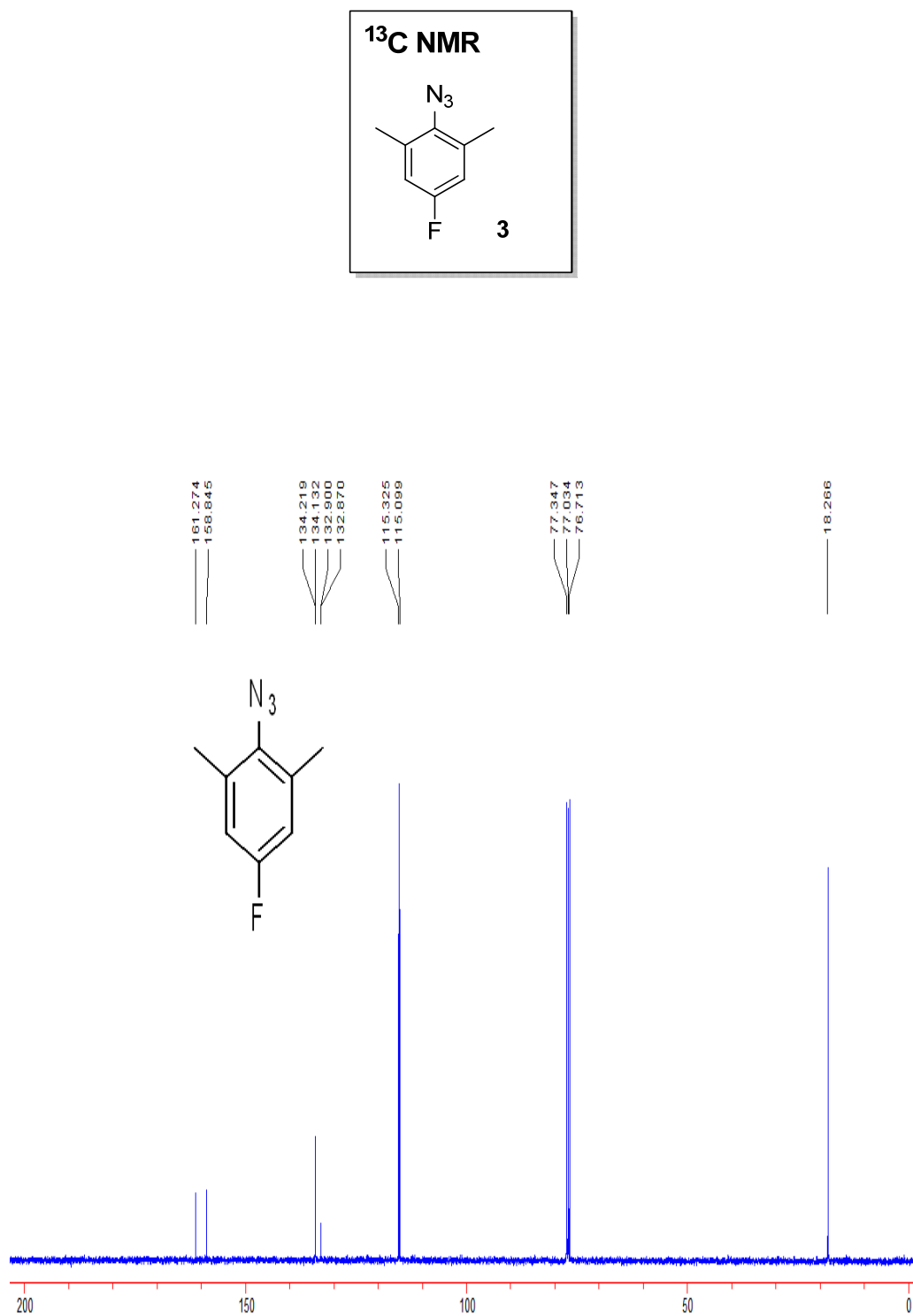
**Reference:**

1. Gibson, V. C.; Kee, T. P.; Shaw, A. *Polyhedron* **1988**, *7*, 579.
2. Barral, K.; Moorhouse, A. D.; Moses, J. E. *Organic Letters* **2007**, *9*, 1809.

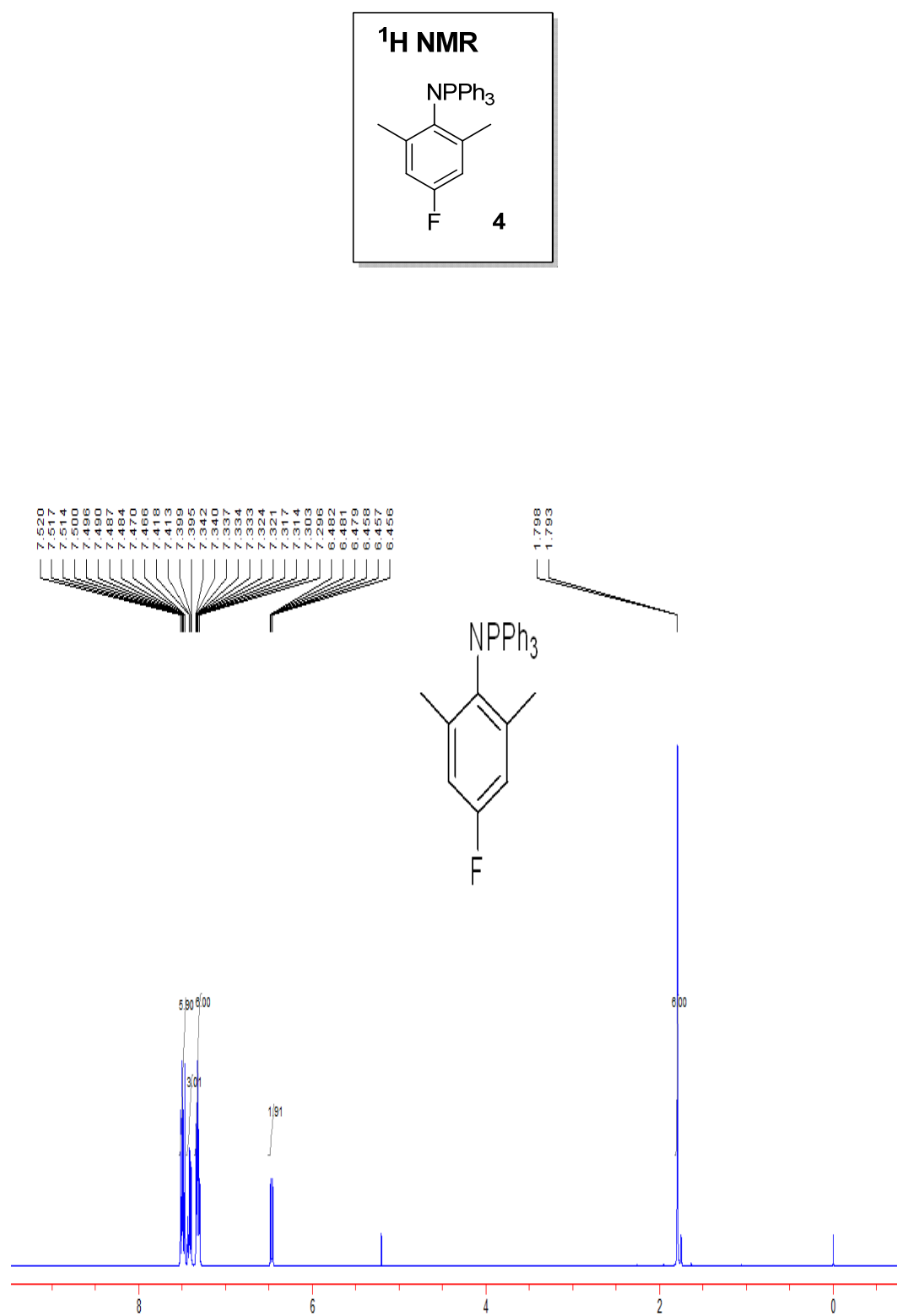
**$^1\text{H}$ ,  $^{19}\text{F}$ , and  $^{13}\text{C}$  NMR spectrum of all new products:****Figure S11.**  $^1\text{H}$  NMR spectrum of compound **3**.



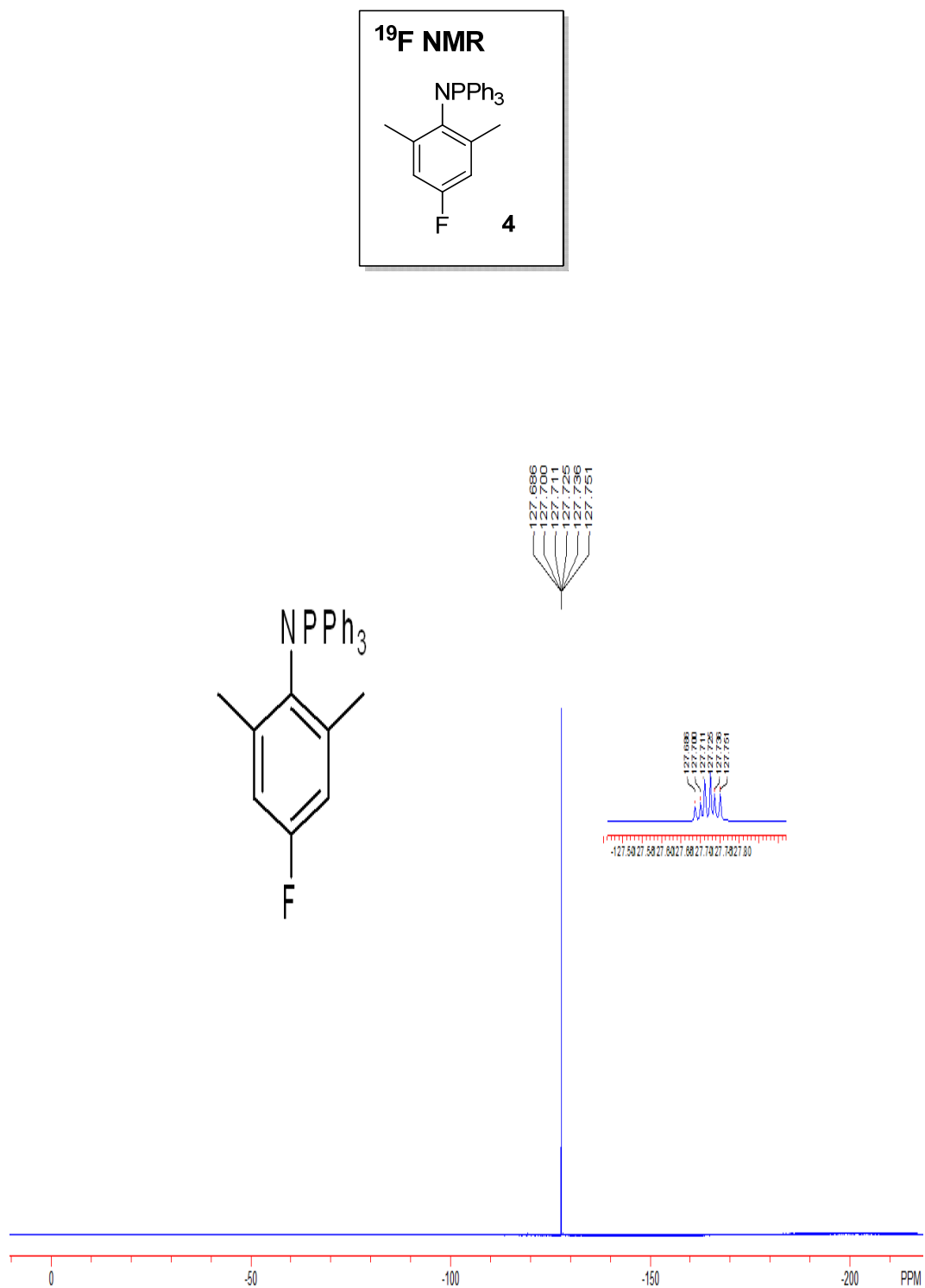
**Figure S12.**  $^{19}\text{F}$  NMR spectrum of compound **3**.



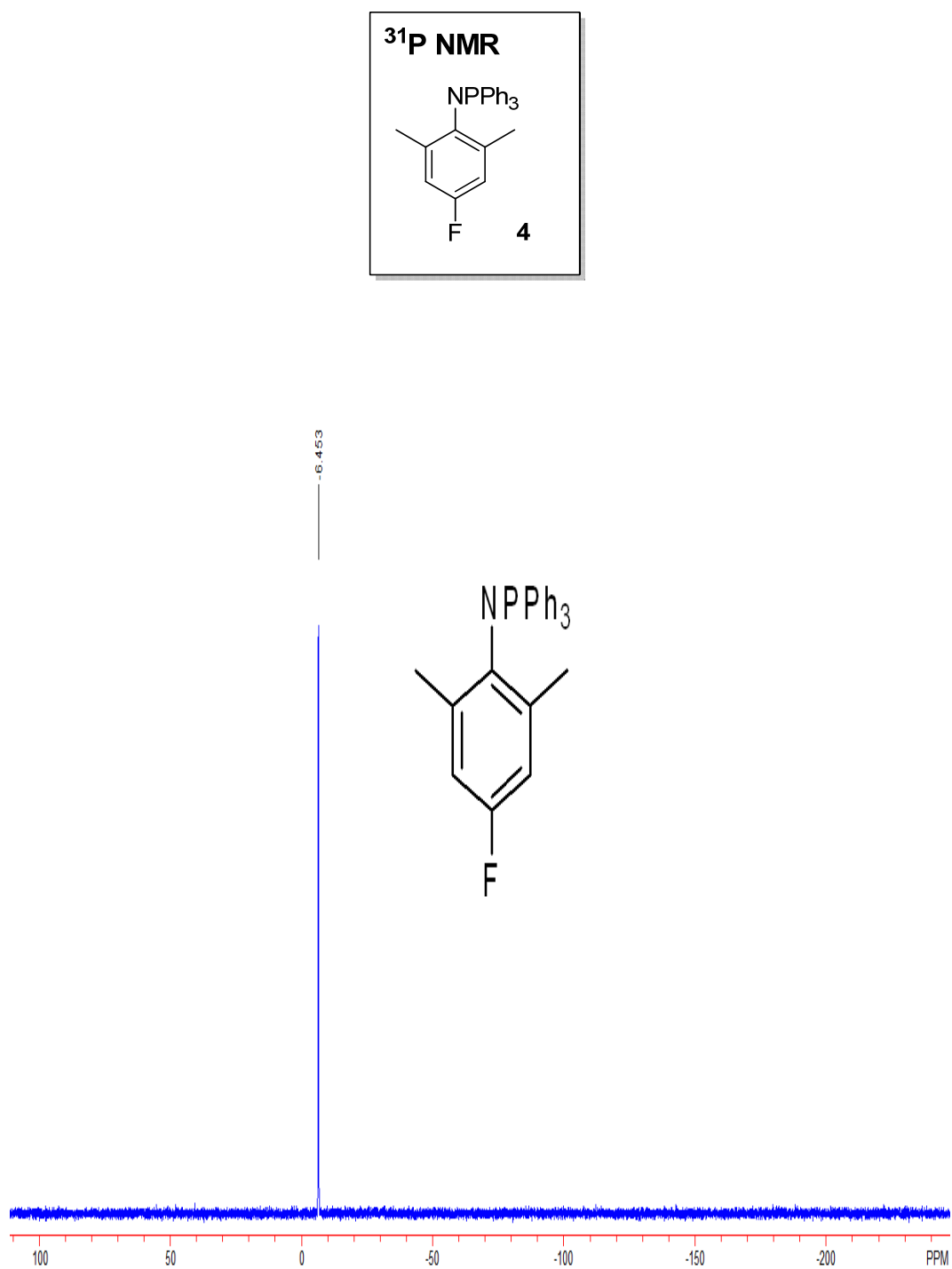
**Figure S13.**  $^{13}\text{C}$  NMR spectrum of compound **3**.



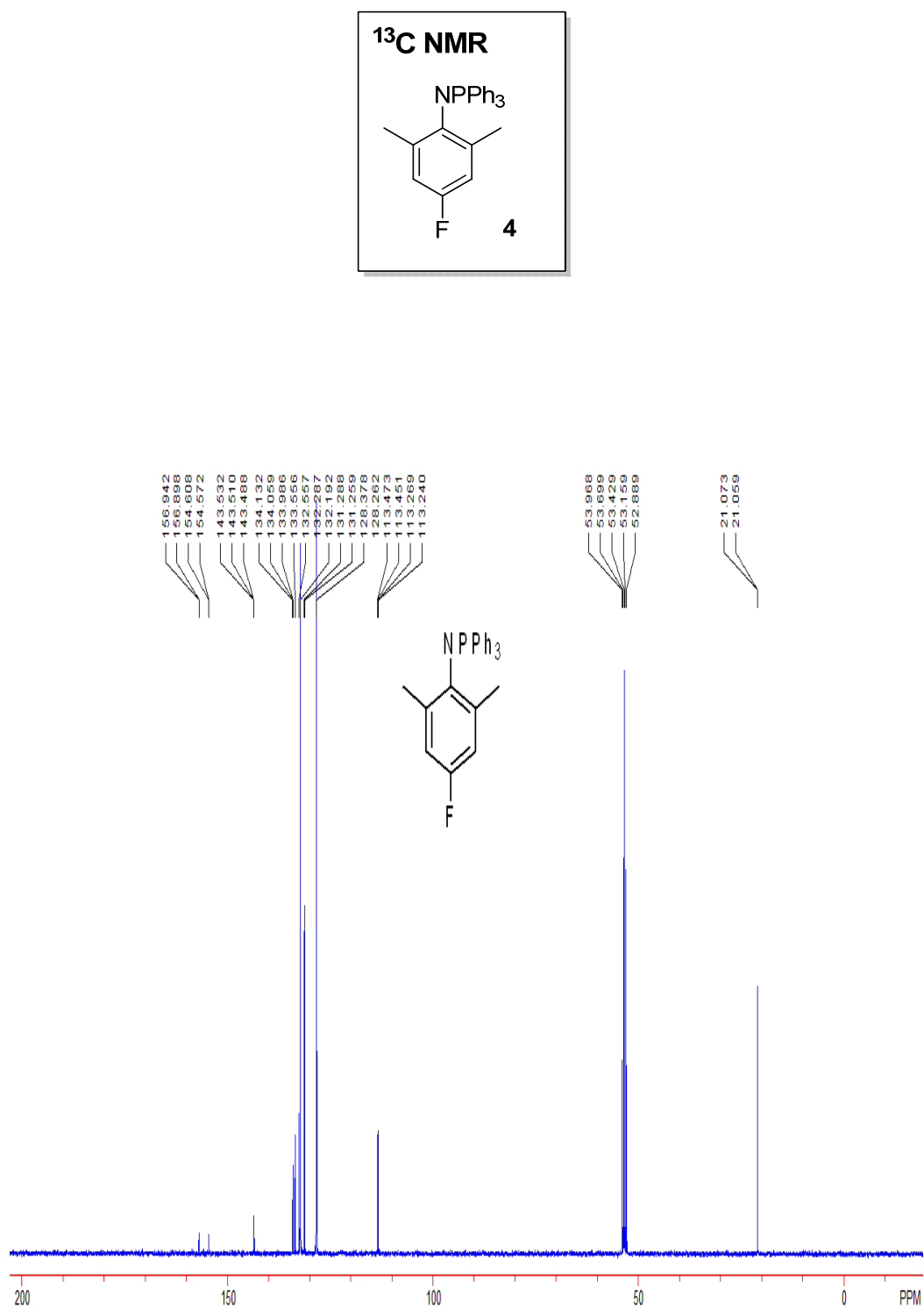
**Figure S14.** <sup>1</sup>H NMR spectrum of compound **4**.



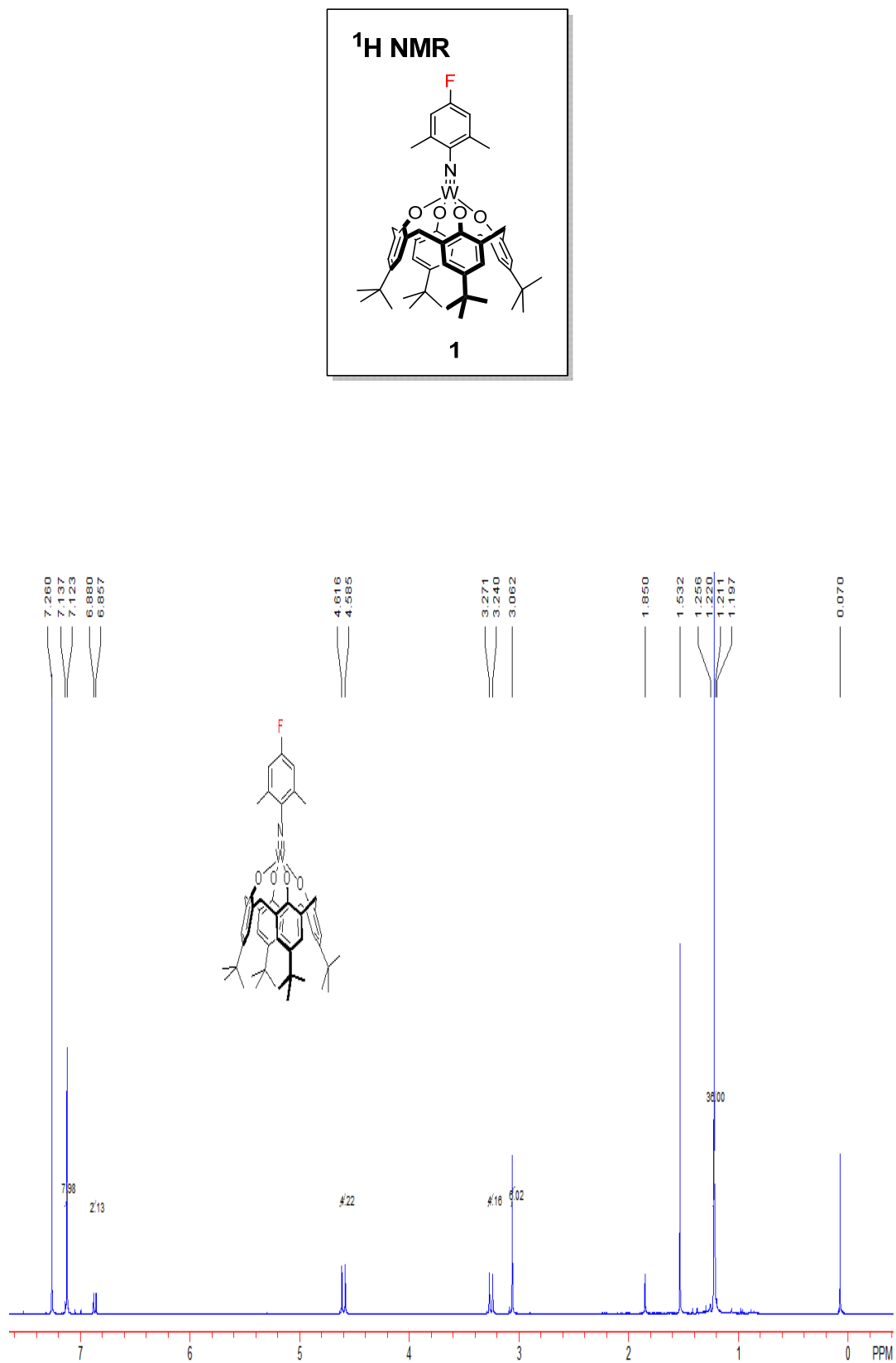
**Figure S15.**  $^{19}\text{F}$  NMR spectrum of compound **4**.



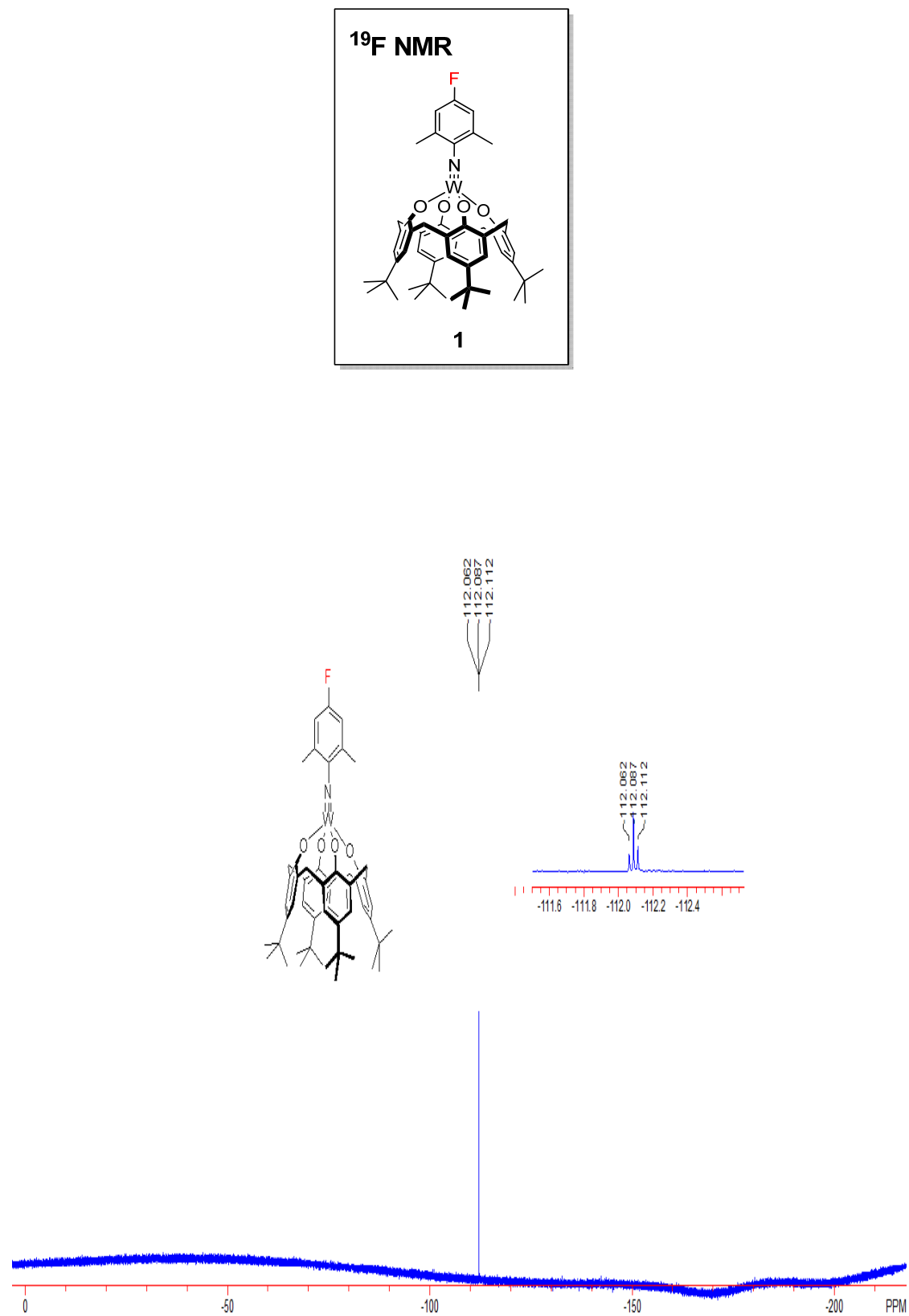
**Figure S16.**  $^{31}\text{P}$  NMR spectrum of compound **4**.



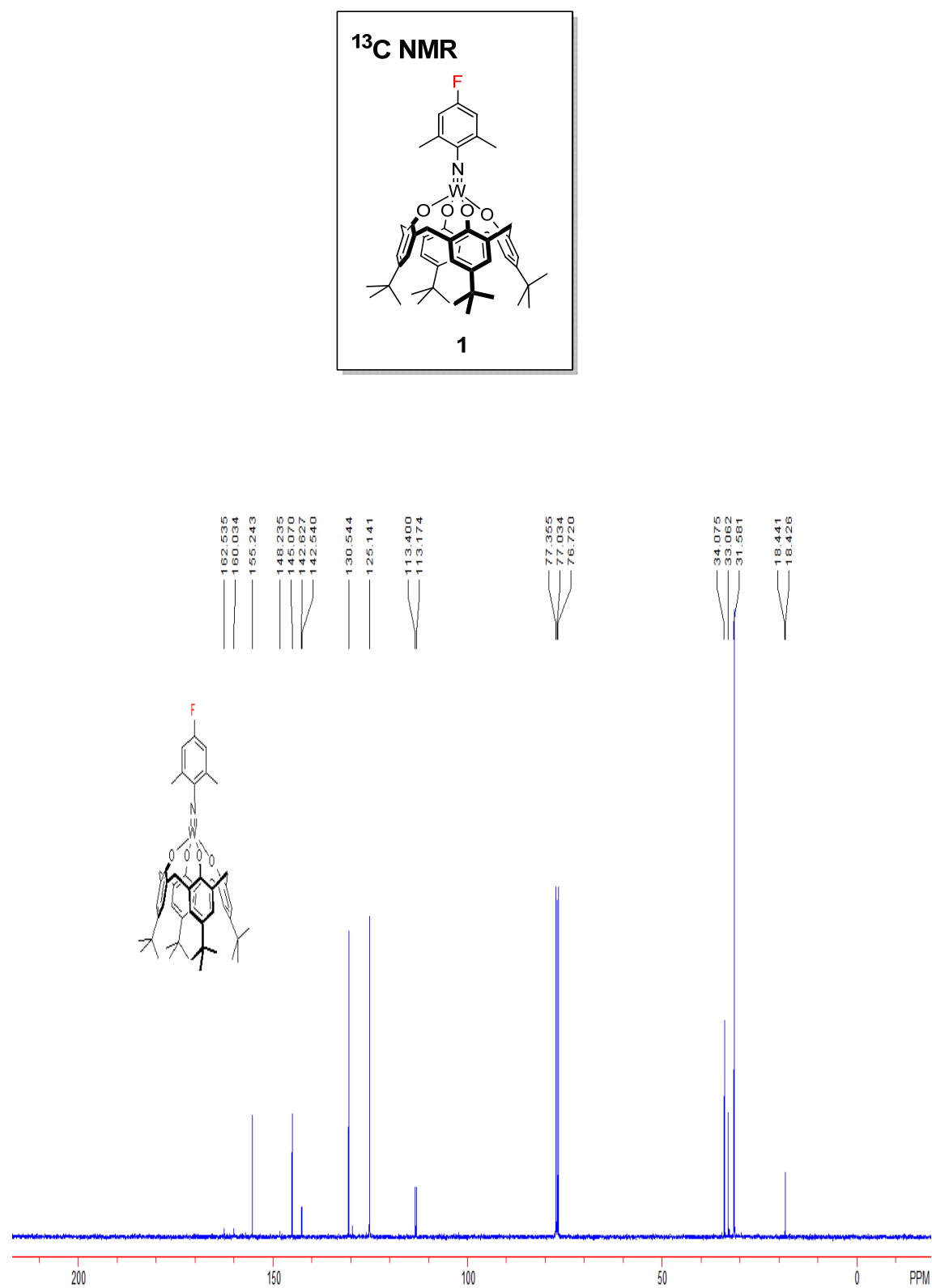
**Figure S17.** <sup>13</sup>C NMR spectrum of compound **4**.



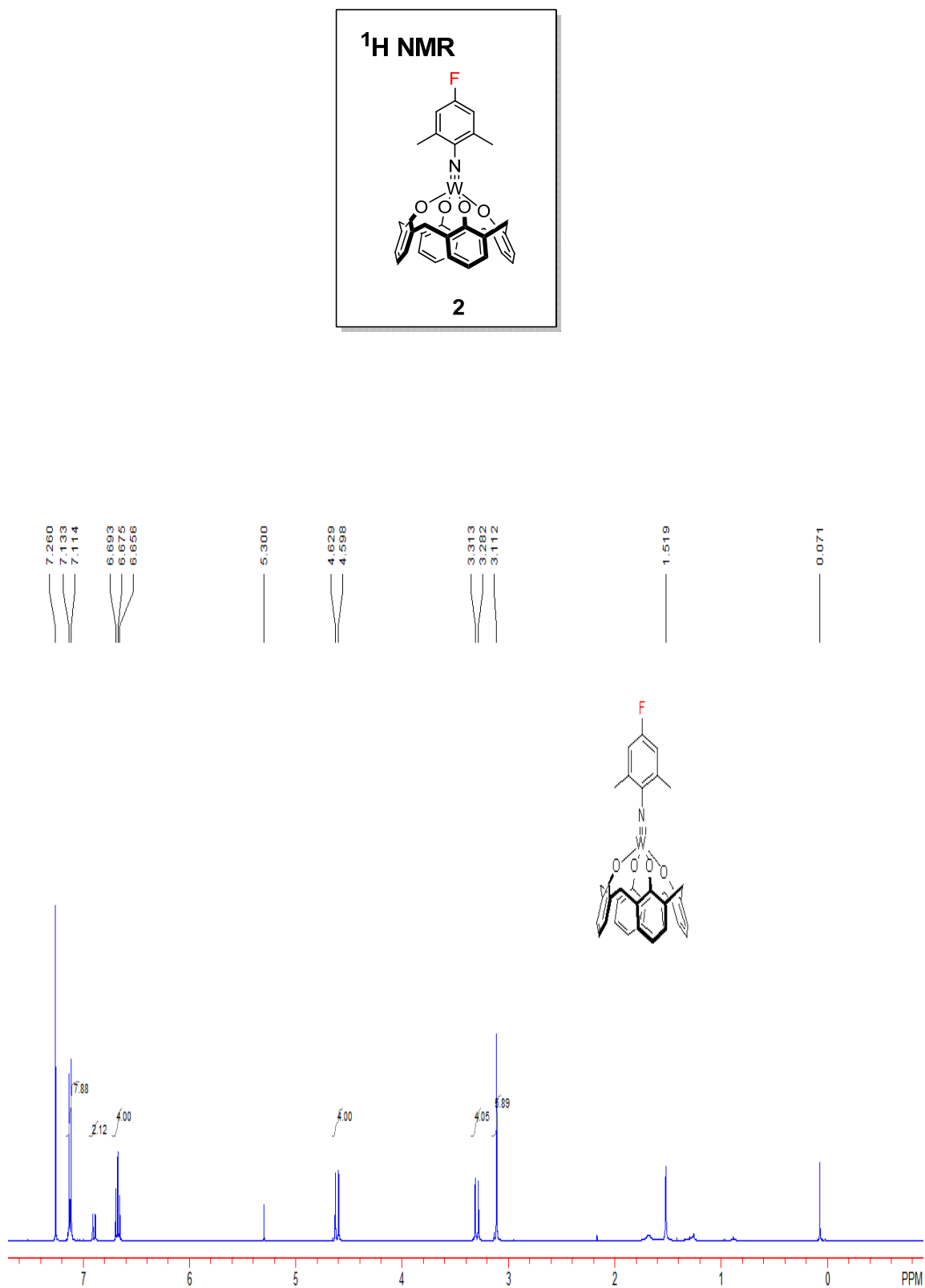
**Figure S18.**  $^1\text{H}$  NMR spectrum of compound **1**.



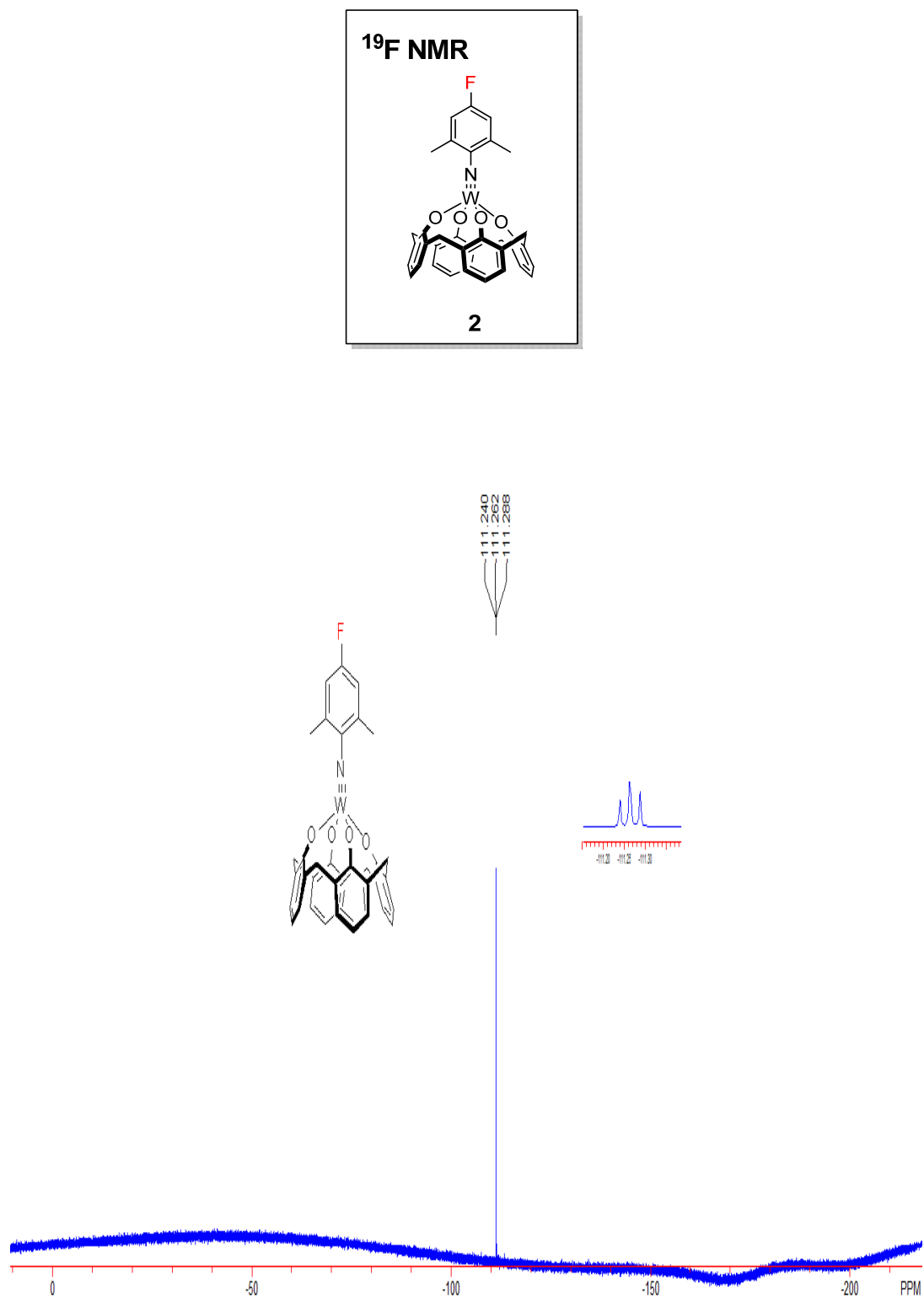
**Figure S19.** <sup>19</sup>F NMR spectrum of compound **1**.



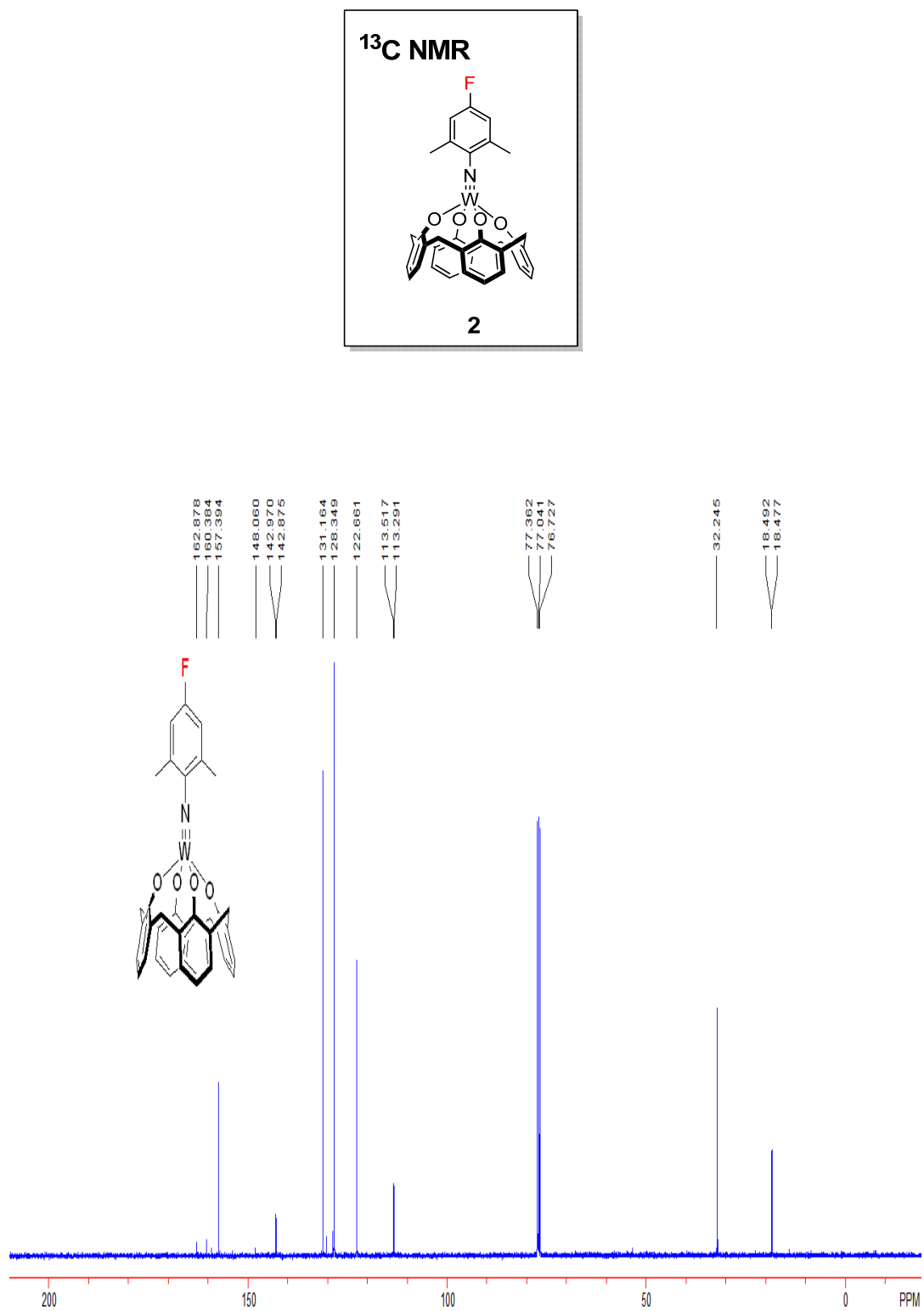
**Figure S20.** <sup>13</sup>C NMR spectrum of compound **1**.



**Figure S21.**  $^1\text{H}$  NMR spectrum of compound 2.



**Figure S22.** <sup>19</sup>F NMR spectrum of compound **2**.



**Figure S23.**  $^{13}\text{C}$  NMR spectrum of compound 2.