

## Supporting Information

### Photochemical hydrogen production and cobaloximes: influence of cobalt axial *N*-ligand on the system stability

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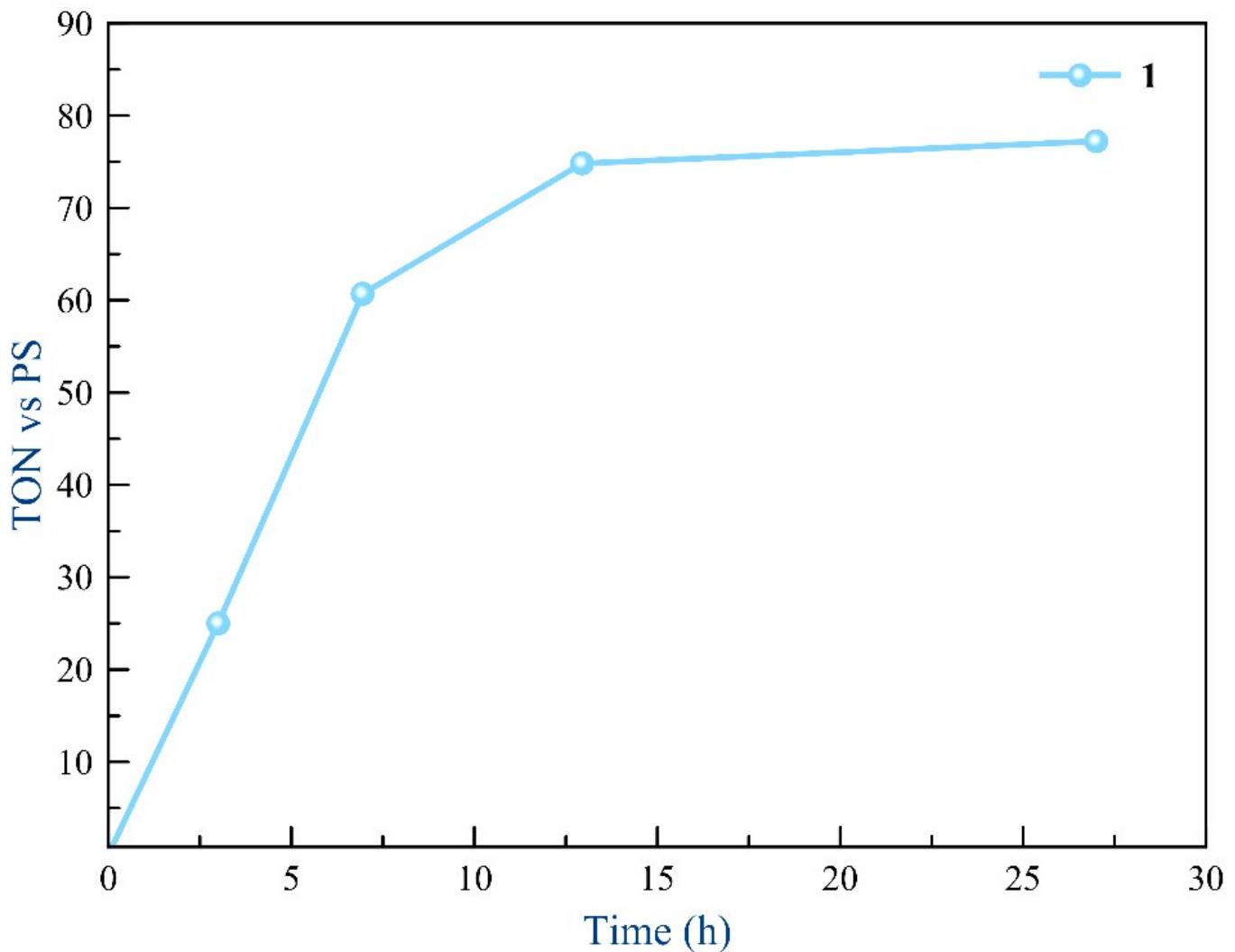
## Table of contents

|  |            |
|--|------------|
| <b>Figure S1.</b> Plot of hydrogen production upon irradiation ( $\lambda > 440$ nm) of solutions (1:1 acetonitrile/water) containing <b>PS</b> ( $4.0 \times 10^{-5}$ M), <b>1</b> ( $4.9 \times 10^{-4}$ M) and TEOA 5% v/v at pH 7 ..                             | <b>S5</b>  |
| <b>Figure S2.</b> Plot of hydrogen production upon irradiation ( $\lambda > 440$ nm) of solutions (1:1 acetonitrile/water) containing <b>PS</b> ( $4.0 \times 10^{-5}$ M), <b>2</b> ( $4.9 \times 10^{-4}$ M) and TEOA 5% v/v at pH 7 ..                             | <b>S6</b>  |
| <b>Figure S3.</b> Plot of hydrogen production upon irradiation ( $\lambda > 440$ nm) of solutions (1:1 acetonitrile/water) containing <b>PS</b> ( $4.0 \times 10^{-5}$ M), <b>2</b> ( $4.9 \times 10^{-4}$ M) and TEOA 5% and 10 mgr TiO <sub>2</sub> v/v at pH 7 .. | <b>S7</b>  |
| <b>Figure S4.</b> Plot of hydrogen production upon irradiation ( $\lambda > 440$ nm) of solutions (1:1 acetonitrile/water) containing <b>PS</b> ( $4.0 \times 10^{-5}$ M), <b>3</b> ( $4.9 \times 10^{-4}$ M) and TEOA 5% v/v at pH 7 ..                             | <b>S8</b>  |
| <b>Figure S5.</b> Plot of hydrogen production upon irradiation ( $\lambda > 440$ nm) of solutions (1:1 acetonitrile/water) containing <b>PS</b> ( $4.0 \times 10^{-5}$ M), <b>4</b> ( $4.9 \times 10^{-4}$ M) and TEOA 5% v/v at pH 7 ..                             | <b>S9</b>  |
| <b>Figure S6.</b> Plot of hydrogen production upon irradiation ( $\lambda > 440$ nm) of solutions (1:1 acetonitrile/water) containing <b>PS</b> ( $4.0 \times 10^{-5}$ M), <b>5</b> ( $4.9 \times 10^{-4}$ M) and TEOA 5% v/v at pH 7 ..                             | <b>S10</b> |
| <b>Figure S7.</b> Plot of hydrogen production upon irradiation ( $\lambda > 440$ nm) of solutions (1:1 acetonitrile/water) containing <b>PS</b> ( $4.0 \times 10^{-5}$ M), <b>8</b> ( $4.9 \times 10^{-4}$ M) and TEOA 5% v/v at pH 7 ..                             | <b>S11</b> |
| <b>Figure S8.</b> Plot of hydrogen production upon irradiation ( $\lambda > 440$ nm) of solutions (1:1 acetonitrile/water) containing <b>PS</b> ( $4.0 \times 10^{-5}$ M), <b>9</b> ( $4.9 \times 10^{-4}$ M) and TEOA 5% v/v at pH 7 ..                             | <b>S12</b> |
| <b>Figure S9.</b> Plot of hydrogen production upon irradiation ( $\lambda > 440$ nm) of solutions (1:1 acetonitrile/water) containing <b>PS</b> ( $4.0 \times 10^{-5}$ M), <b>10</b> ( $4.9 \times 10^{-4}$ M) and TEOA 5% v/v at pH 7 ..                            | <b>S13</b> |
| <b>Figure S10.</b> FT-IR spectrum of complex <b>1</b> ..   | <b>S14</b> |
| <b>Figure S11.</b> FT-IR spectrum of complex <b>2</b> ..   | <b>S15</b> |
| <b>Figure S12.</b> FT-IR spectrum of complex <b>3</b> ..   | <b>S16</b> |
| <b>Figure S13.</b> FT-IR spectrum of complex <b>4</b> ..   | <b>S17</b> |

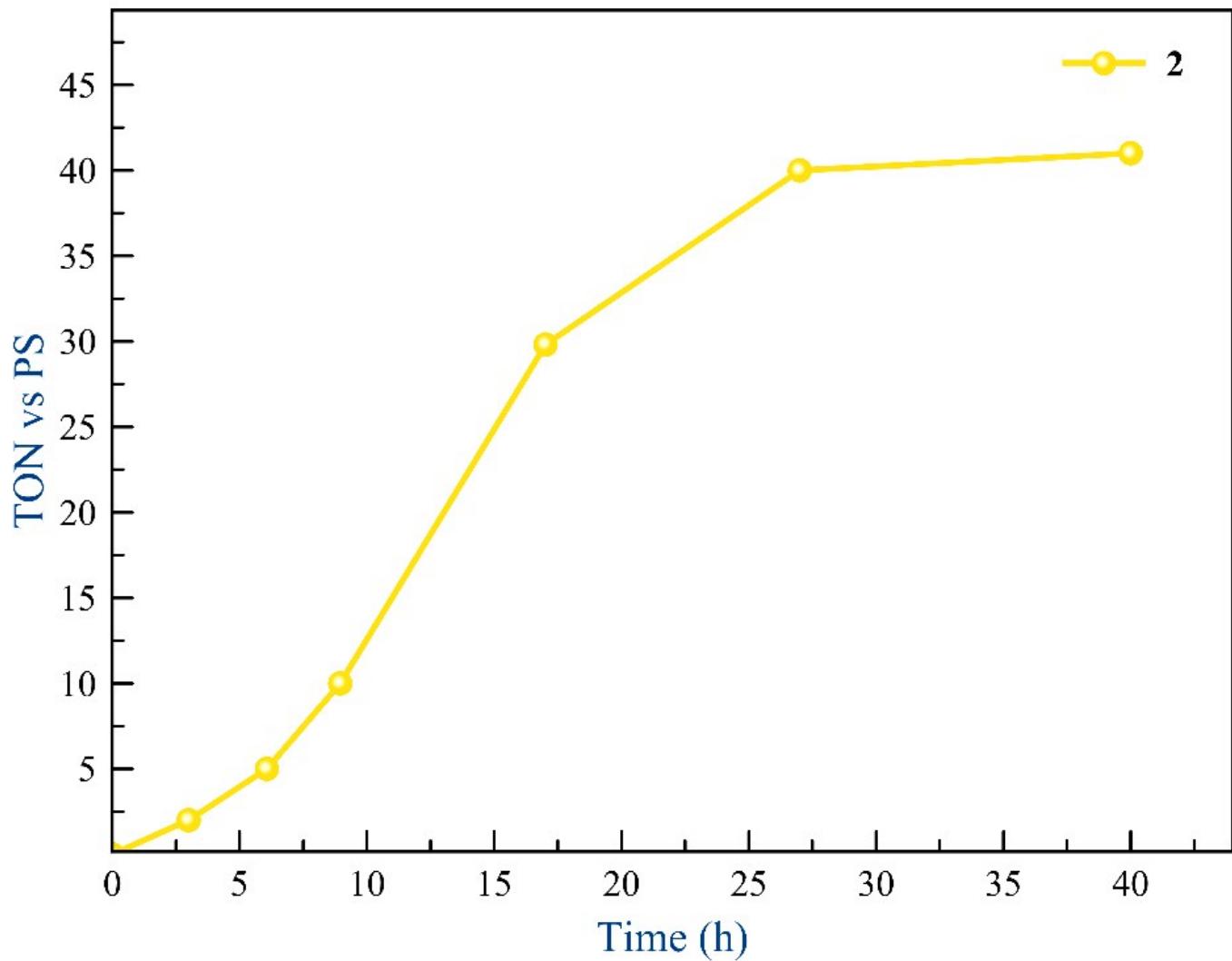
|   |            |
|---|------------|
| <b>Figure S14.</b> FT-IR spectrum of complex <b>5</b> .....   | <b>S18</b> |
| <b>Figure S15.</b> FT-IR spectrum of complex <b>6</b> .....   | <b>S19</b> |
| <b>Figure S16.</b> FT-IR spectrum of complex <b>7</b> .....   | <b>S20</b> |
| <b>Figure S17.</b> FT-IR spectrum of complex <b>8</b> .....   | <b>S21</b> |
| <b>Figure S18.</b> FT-IR spectrum of complex <b>9</b> .....   | <b>S22</b> |
| <b>Figure S19.</b> FT-IR spectrum of complex <b>10</b> .....  | <b>S23</b> |
| <b>Figure S20.</b> UV-Vis spectrum of complex <b>1</b> in solution 1:1 acetonitrile/water containing TEOA 5% v/vat pH 7.....  | <b>S24</b> |
| <b>Figure S21.</b> UV-Vis spectrum of complex <b>2</b> in solution 1:1 acetonitrile/water containing TEOA 5% v/vat pH 7.....  | <b>S25</b> |
| <b>Figure S22.</b> UV-Vis spectrum of complex <b>3</b> in solution 1:1 acetonitrile/water containing TEOA 5% v/vat pH 7.....  | <b>S26</b> |
| <b>Figure S23.</b> UV-Vis spectrum of complex <b>4</b> in solution 1:1 acetonitrile/water containing TEOA 5% v/vat pH 7.....  | <b>S27</b> |
| <b>Figure S24.</b> UV-Vis spectrum of complex <b>5</b> in solution 1:1 acetonitrile/water containing TEOA 5% v/vat pH 7.....  | <b>S28</b> |
| <b>Figure S25.</b> UV-Vis spectrum of complex <b>6</b> in solution 1:1 acetonitrile/water containing TEOA 5% v/vat pH 7.....  | <b>S29</b> |
| <b>Figure S26.</b> UV-Vis spectrum of complex <b>7</b> in solution 1:1 acetonitrile/water containing TEOA 5% v/vat pH 7.....  | <b>S30</b> |
| <b>Figure S27.</b> UV-Vis spectrum of complex <b>8</b> in solution 1:1 acetonitrile/water containing TEOA 5% v/vat pH 7.....  | <b>S31</b> |
| <b>Figure S28.</b> UV-Vis spectrum of complex <b>9</b> in solution 1:1 acetonitrile/water containing TEOA 5% v/vat pH 7.....  | <b>S32</b> |
| <b>Figure S29.</b> UV-Vis spectrum of complex <b>10</b> in solution 1:1 acetonitrile/water containing TEOA 5% v/vat pH 7..... | <b>S33</b> |
| <b>Figure S30.</b> $^1\text{H}$ NMR spectrum of complex <b>1</b> in $\text{CDCl}_3$ . ....                                    | <b>S34</b> |
| <b>Figure S31.</b> $^{13}\text{C}$ NMR spectrum of complex <b>1</b> in $\text{CDCl}_3$ . ....                                 | <b>S35</b> |
| <b>Figure S32.</b> $^1\text{H}$ NMR spectrum of complex <b>2</b> in DMSO. ....  | <b>S36</b> |
| <b>Figure S33.</b> $^{13}\text{C}$ NMR spectrum of complex <b>2</b> in DMSO .....   | <b>S37</b> |
| <b>Figure S34.</b> $^1\text{H}$ NMR spectrum of complex <b>3</b> in $\text{CDCl}_3$ . ....                                    | <b>S38</b> |

|   |            |
|---|------------|
| <b>Figure S35.</b> $^{13}\text{C}$ NMR spectrum of complex <b>3</b> in $\text{CDCl}_3$ .....  | <b>S39</b> |
| <b>Figure S36.</b> $^1\text{H}$ NMR spectrum of complex <b>4</b> in DMSO.. .....              | <b>S40</b> |
| <b>Figure S37.</b> $^{13}\text{C}$ NMR spectrum of complex <b>4</b> in DMSO. ....             | <b>S41</b> |
| <b>Figure S38.</b> $^1\text{H}$ NMR spectrum of complex <b>5</b> in $\text{CDCl}_3$ . ....    | <b>S42</b> |
| <b>Figure S39.</b> $^{13}\text{C}$ NMR spectrum of complex <b>5</b> in $\text{CDCl}_3$ .....  | <b>S43</b> |
| <b>Figure S40.</b> $^1\text{H}$ NMR spectrum of complex <b>6</b> in DMSO.. .....              | <b>S44</b> |
| <b>Figure S41.</b> $^{13}\text{C}$ NMR spectrum of complex <b>6</b> in DMSO .....             | <b>S45</b> |
| <b>Figure S42.</b> $^1\text{H}$ NMR spectrum of complex <b>7</b> in DMSO. ....                | <b>S46</b> |
| <b>Figure S43.</b> $^{13}\text{C}$ NMR spectrum of complex <b>7</b> in DMSO. ....             | <b>S47</b> |
| <b>Figure S44.</b> $^1\text{H}$ NMR spectrum of complex <b>8</b> in DMSO.. .....              | <b>S48</b> |
| <b>Figure S45.</b> $^{13}\text{C}$ NMR spectrum of complex <b>8</b> in DMSO. ....             | <b>S49</b> |
| <b>Figure S46.</b> $^1\text{H}$ NMR spectrum of complex <b>9</b> in $\text{CDCl}_3$ . ....    | <b>S50</b> |
| <b>Figure S47.</b> $^{13}\text{C}$ NMR spectrum of complex <b>9</b> in $\text{CDCl}_3$ . .... | <b>S51</b> |
| <b>Figure S48.</b> $^1\text{H}$ NMR spectrum of complex <b>10</b> in DMSO.. .....             | <b>S52</b> |
| <b>Figure S49.</b> $^{13}\text{C}$ NMR spectrum of complex <b>10</b> in DMSO.. .....          | <b>S53</b> |

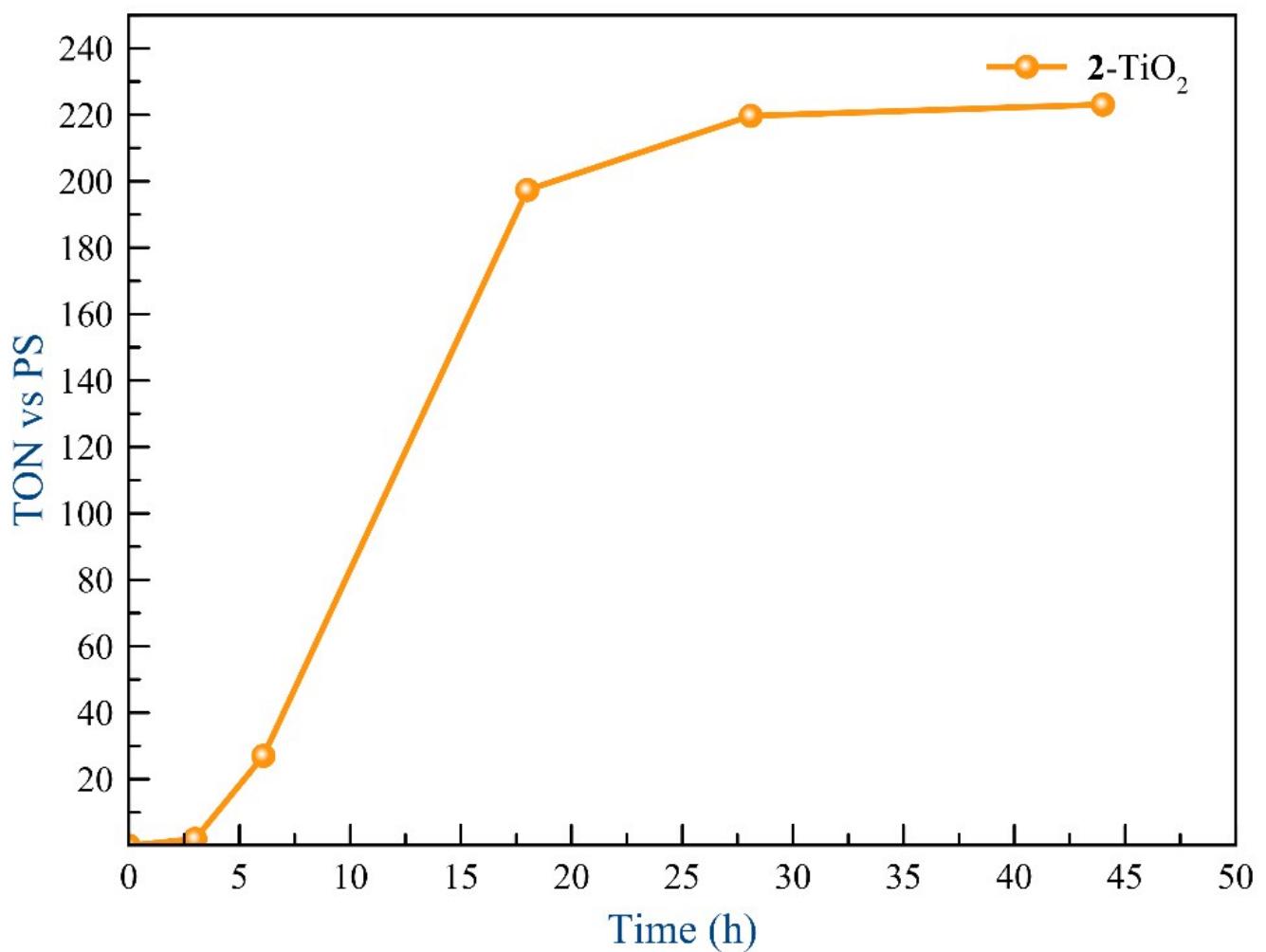
## H<sub>2</sub> Production



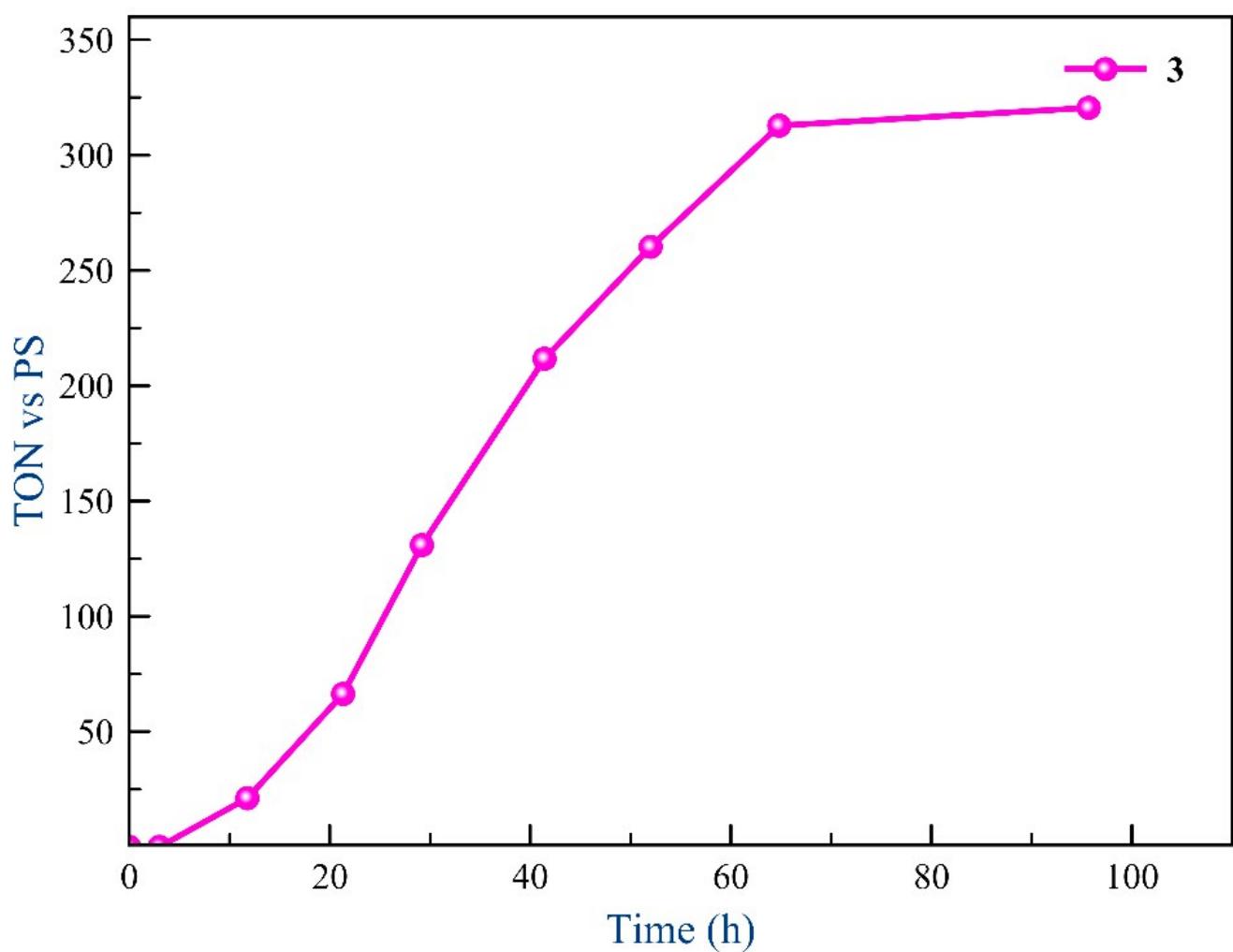
**Figure S1.** Plot of hydrogen production upon irradiation ( $\lambda > 440$  nm) of solutions (1:1 acetonitrile/water) containing **PS** ( $4.0 \times 10^{-5}$ M), **1** ( $4.9 \times 10^{-4}$ M) and TEOA 5% v/v at pH 7.



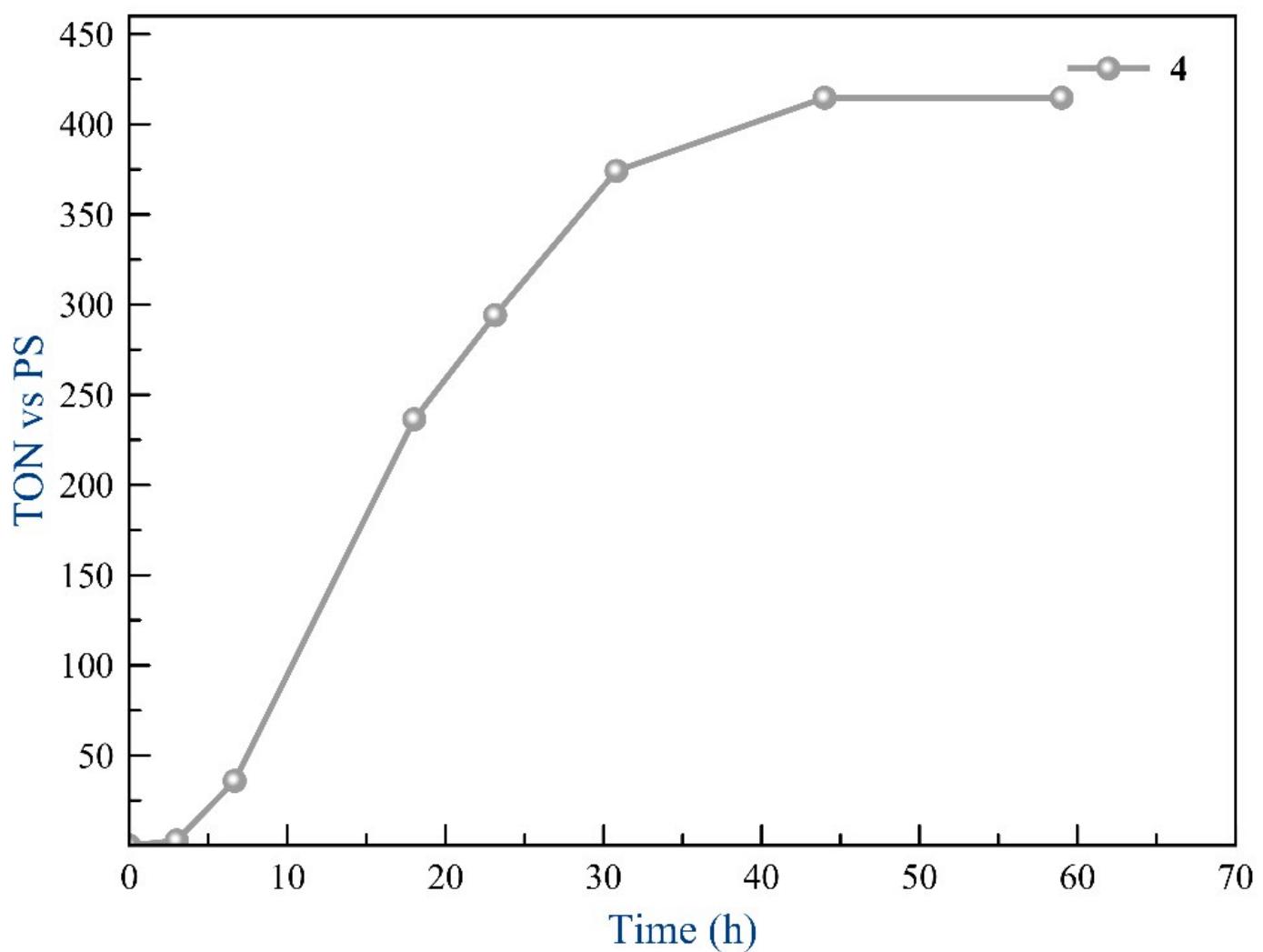
**Figure S2.** Plot of hydrogen production upon irradiation ( $\lambda > 440$  nm) of solutions (1:1 acetonitrile/water) containing **PS** ( $4.0 \times 10^{-5}$ M), **2** ( $4.9 \times 10^{-4}$ M) and TEOA 5% v/v at pH 7.



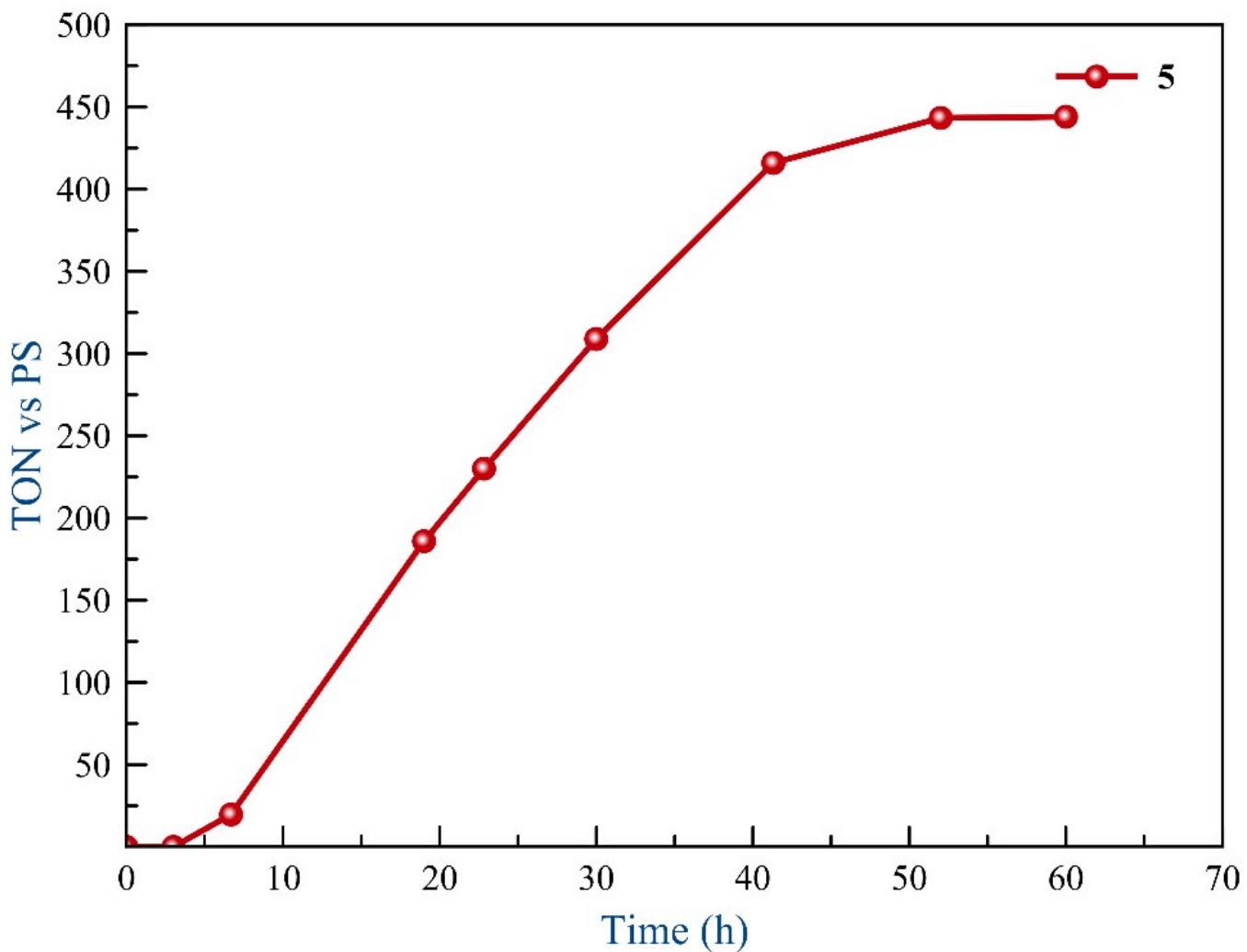
**Figure S3.** Plot of hydrogen production upon irradiation ( $\lambda > 440$  nm) of solutions (1:1 acetonitrile/water) containing **PS** ( $4.0 \times 10^{-5}$ M), **2** ( $4.9 \times 10^{-4}$ M), TEOA 5% v/v and 10 mgr TiO<sub>2</sub> at pH 7.



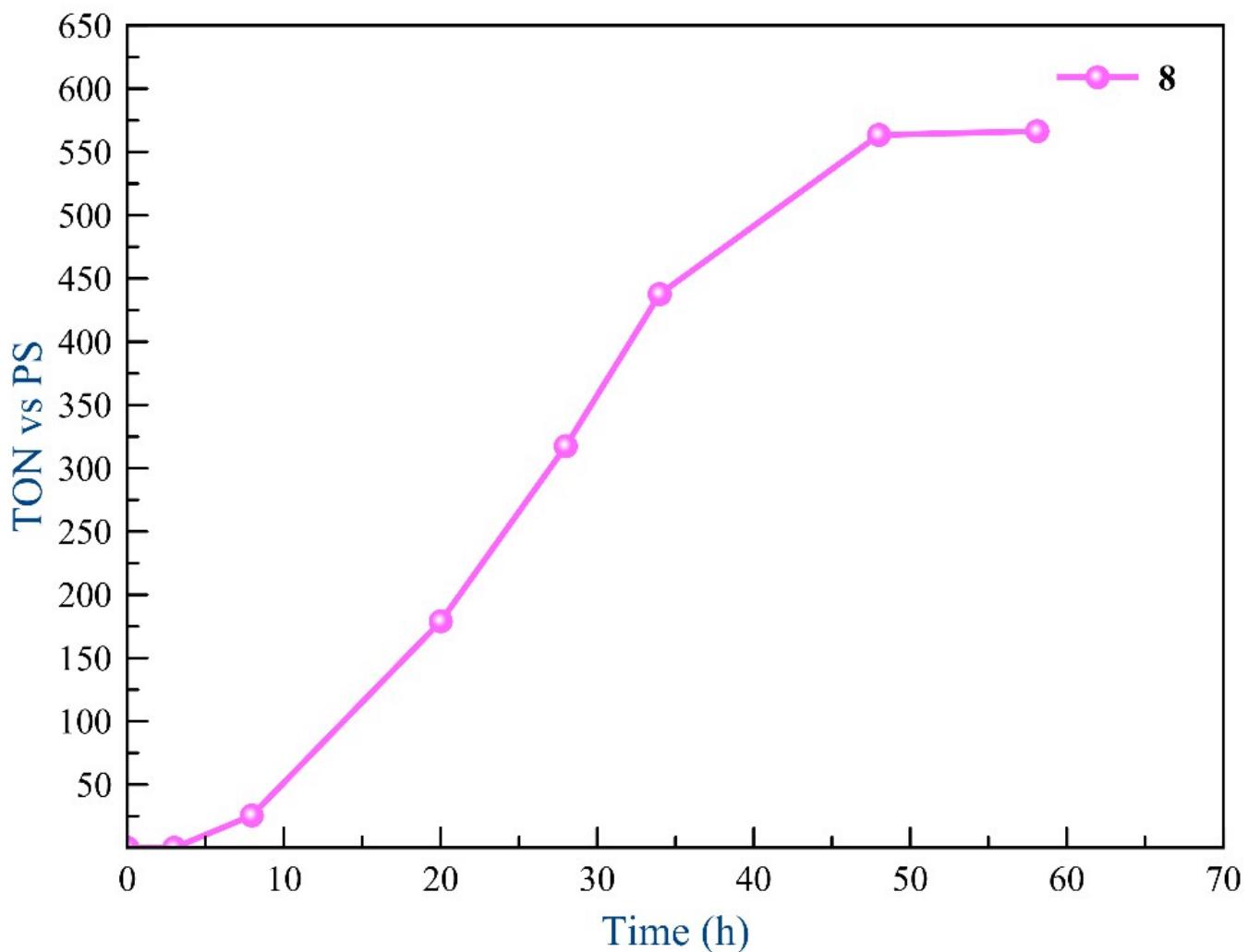
**Figure S4.** Plot of hydrogen production upon irradiation ( $\lambda > 440$  nm) of solutions (1:1 acetonitrile/water) containing **PS** ( $4.0 \times 10^{-5}$ M), **3** ( $4.9 \times 10^{-4}$ M) and TEOA 5% v/v at pH 7.



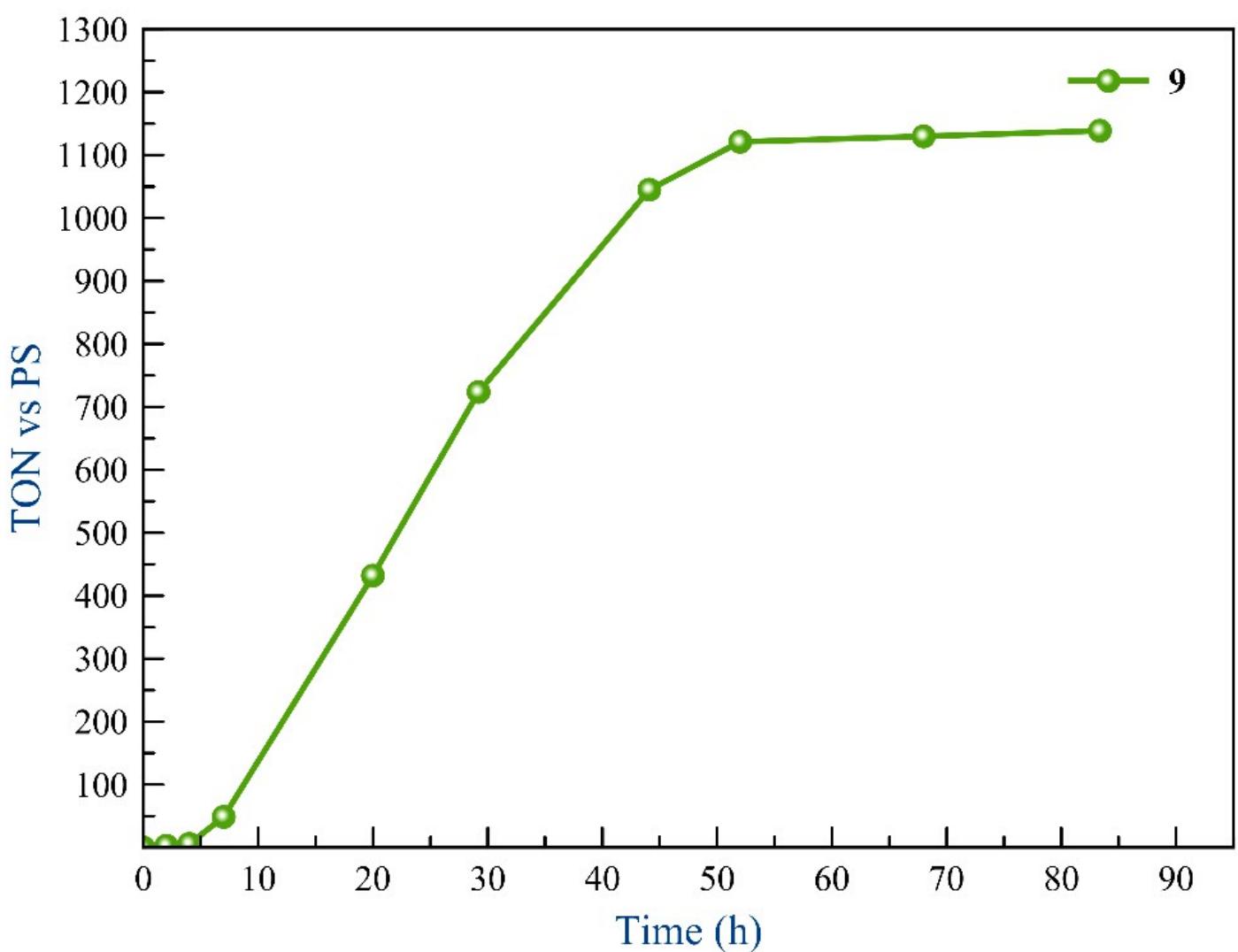
**Figure S5.** Plot of hydrogen production upon irradiation ( $\lambda > 440$  nm) of solutions (1:1 acetonitrile/water) containing **PS** ( $4.0 \times 10^{-5}$ M), **4** ( $4.9 \times 10^{-4}$ M) and TEOA 5% v/v at pH 7.



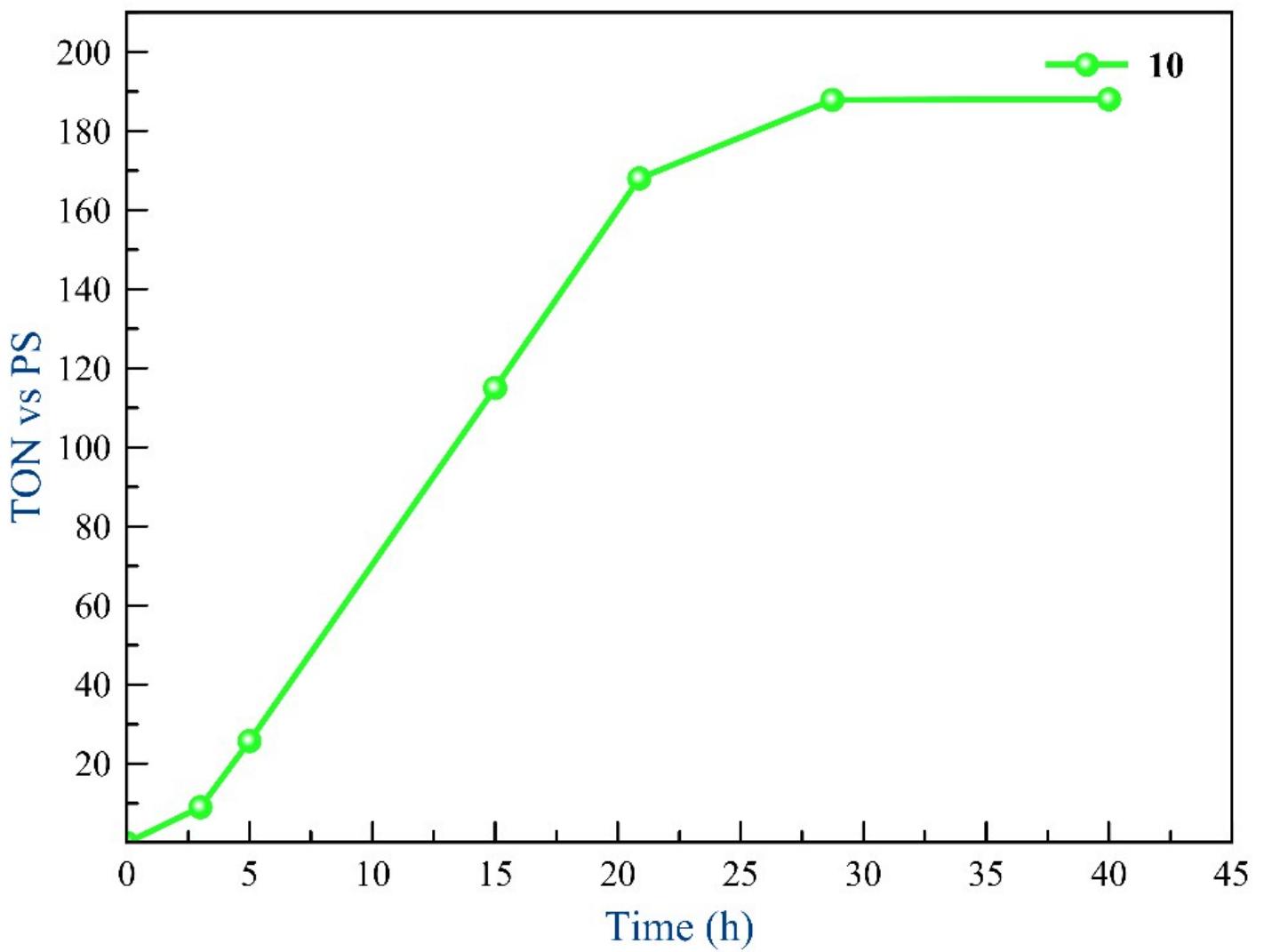
**Figure S6.** Plot of hydrogen production upon irradiation ( $\lambda > 440$  nm) of solutions (1:1 acetonitrile/water) containing **PS** ( $4.0 \times 10^{-5}$ M), **5** ( $4.9 \times 10^{-4}$ M) and TEOA 5% v/v at pH 7.



**Figure S7.** Plot of hydrogen production upon irradiation ( $\lambda > 440$  nm) of solutions (1:1 acetonitrile/water) containing **PS** ( $4.0 \times 10^{-5}$ M), **8** ( $4.9 \times 10^{-4}$ M) and TEOA 5% v/v at pH 7.

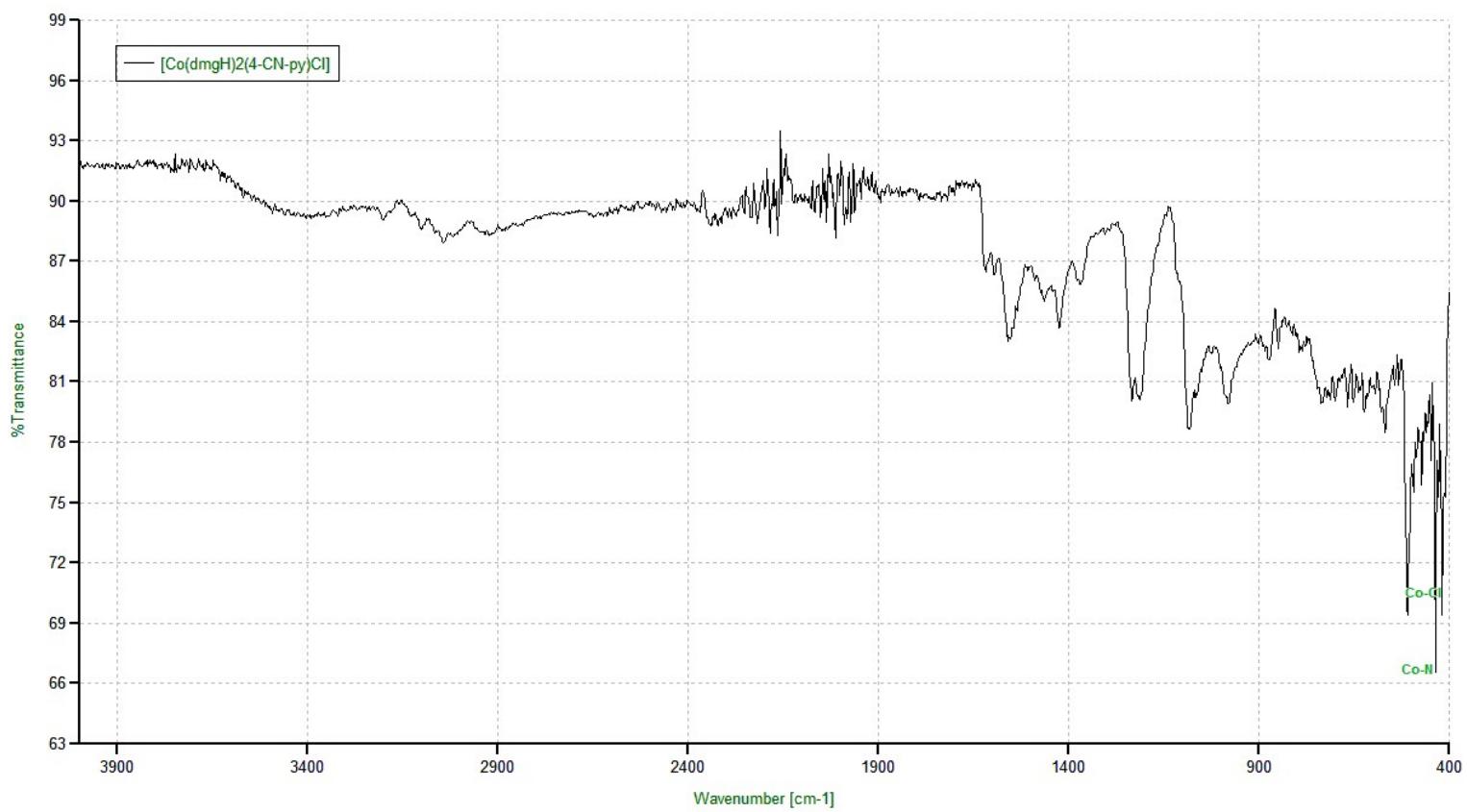


**Figure S8.** Plot of hydrogen production upon irradiation ( $\lambda > 440$  nm) of solutions (1:1 acetonitrile/water) containing **PS** ( $4.0 \times 10^{-5}$ M), **9** ( $4.9 \times 10^{-4}$ M) and TEOA 5% v/v at pH 7.

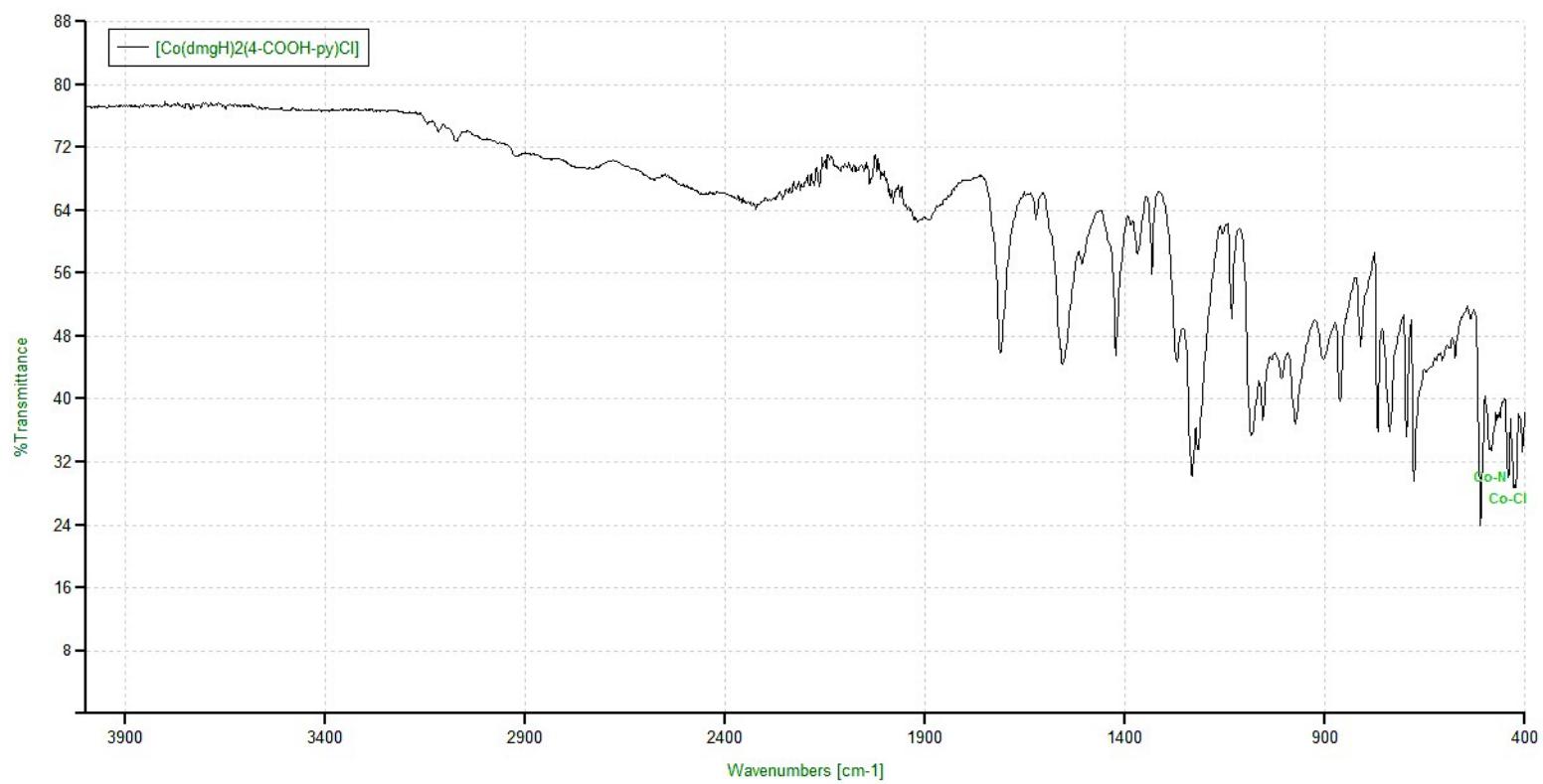


**Figure S9.** Plot of hydrogen production upon irradiation ( $\lambda > 440$  nm) of solutions (1:1 acetonitrile/water) containing **PS** ( $4.0 \times 10^{-5}$ M), **10** ( $4.9 \times 10^{-4}$ M) and TEOA 5% v/v at pH 7.

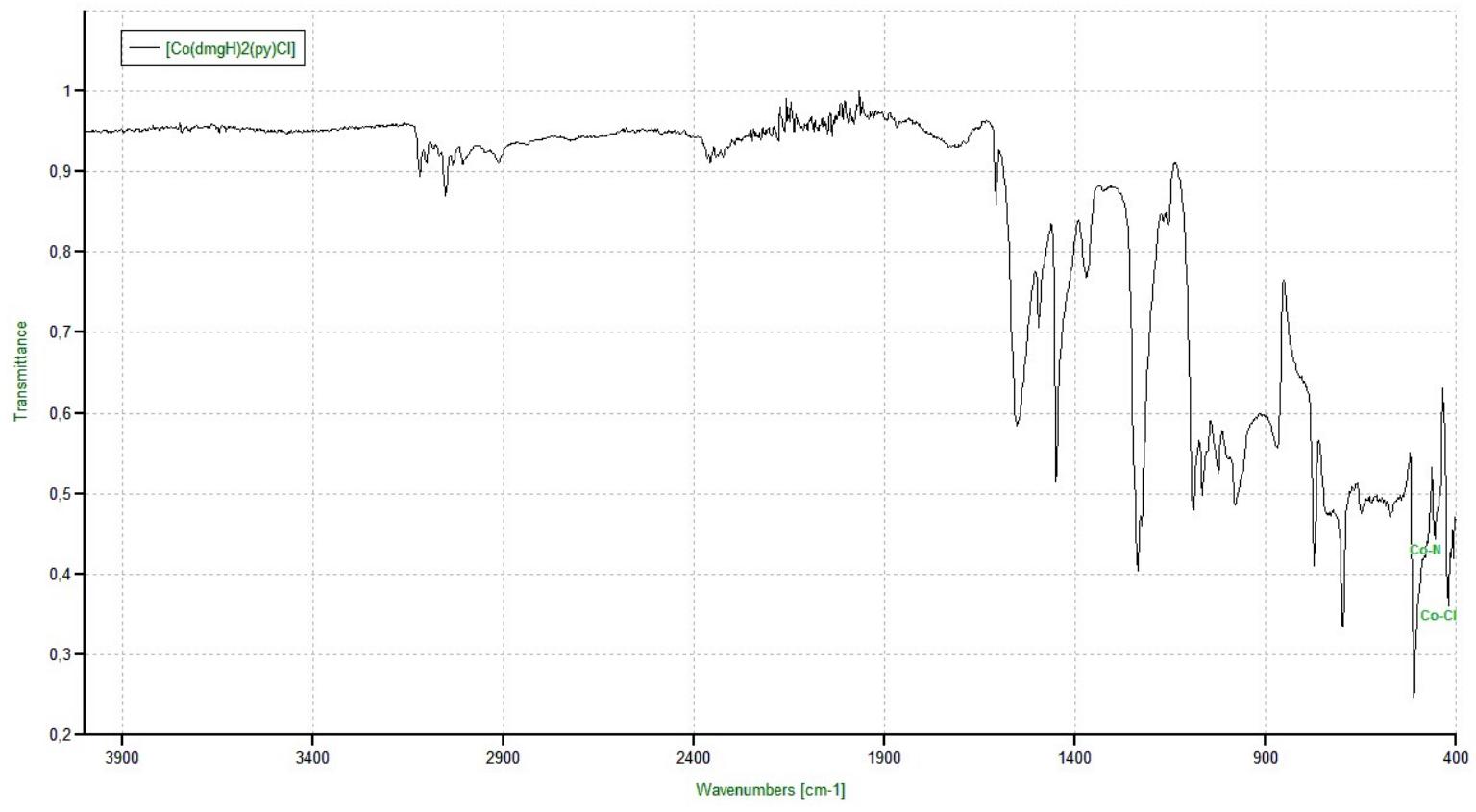
## FT-IR Spectra



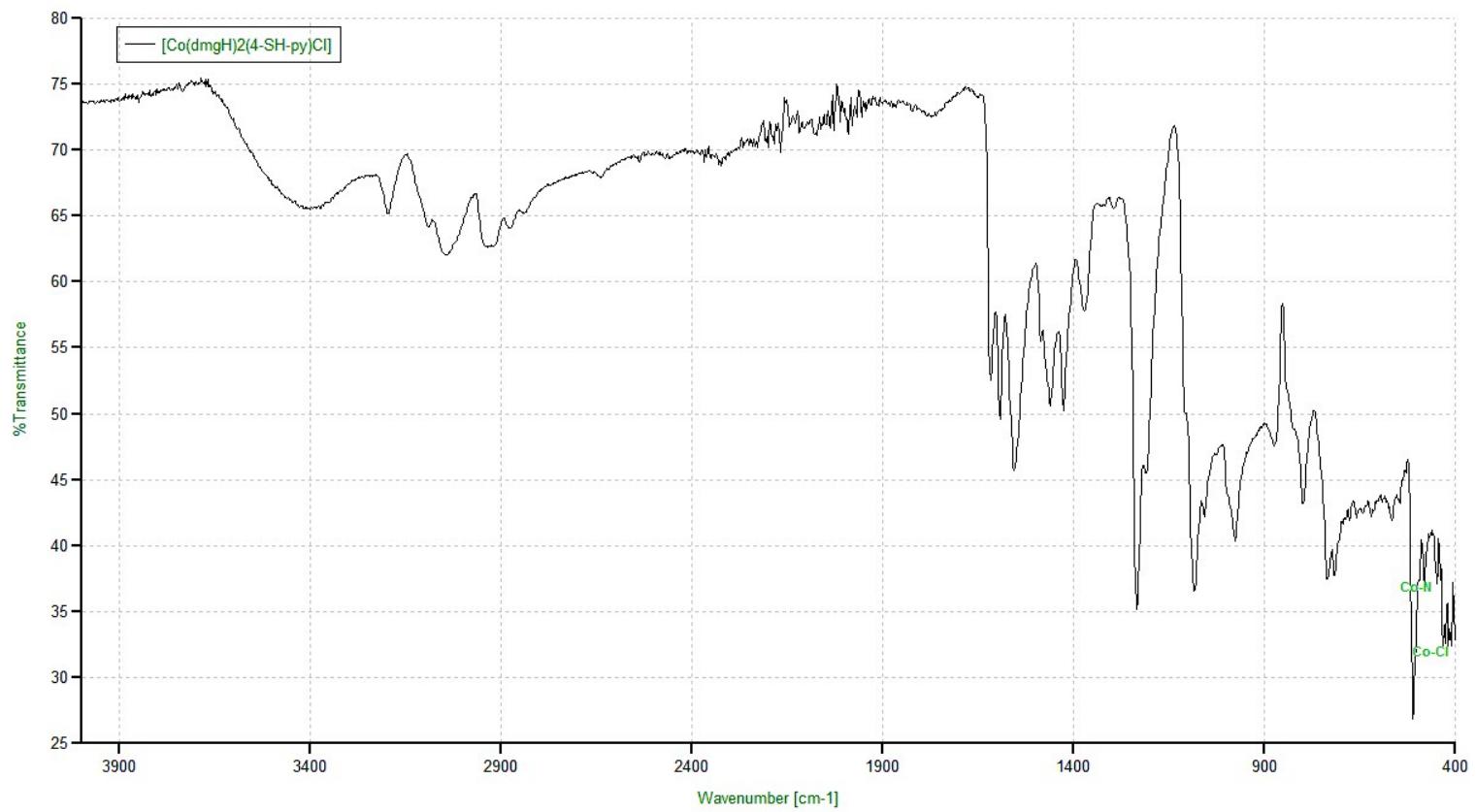
**Figure S10.** FT-IR spectrum of complex **1**.



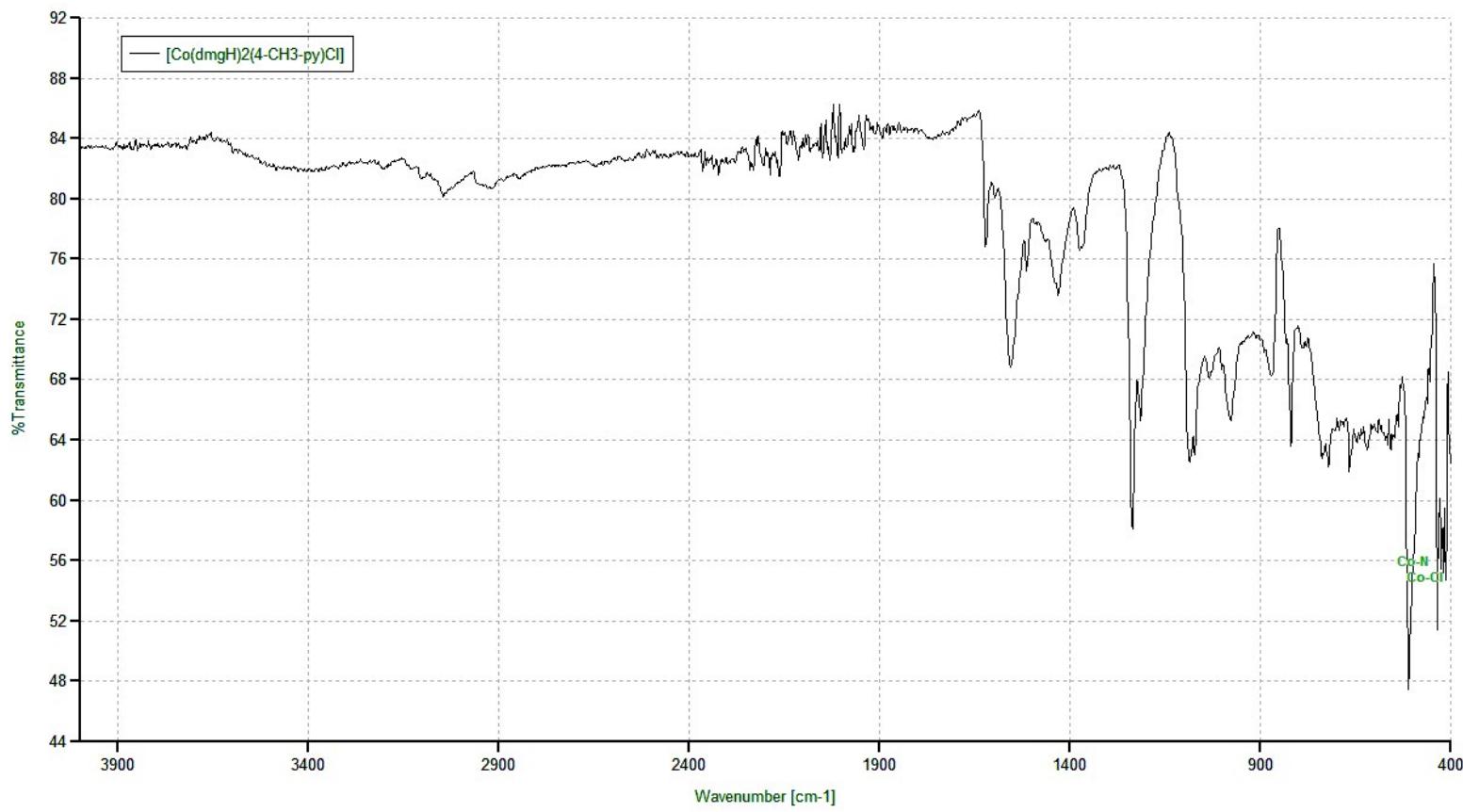
**Figure S11.** FT-IR spectrum of complex **2**.



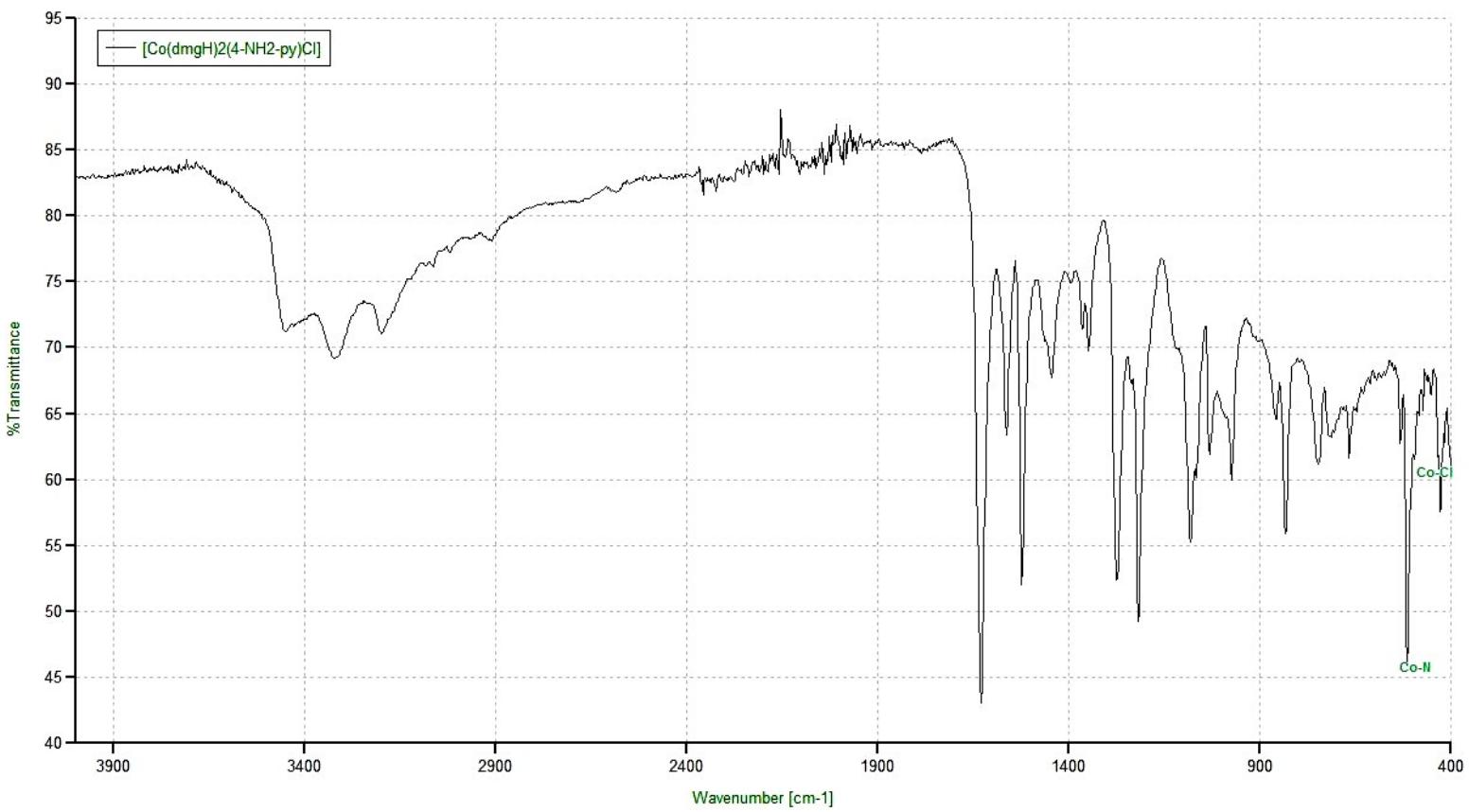
**Figure S12.** FT-IR spectrum of complex **3**.



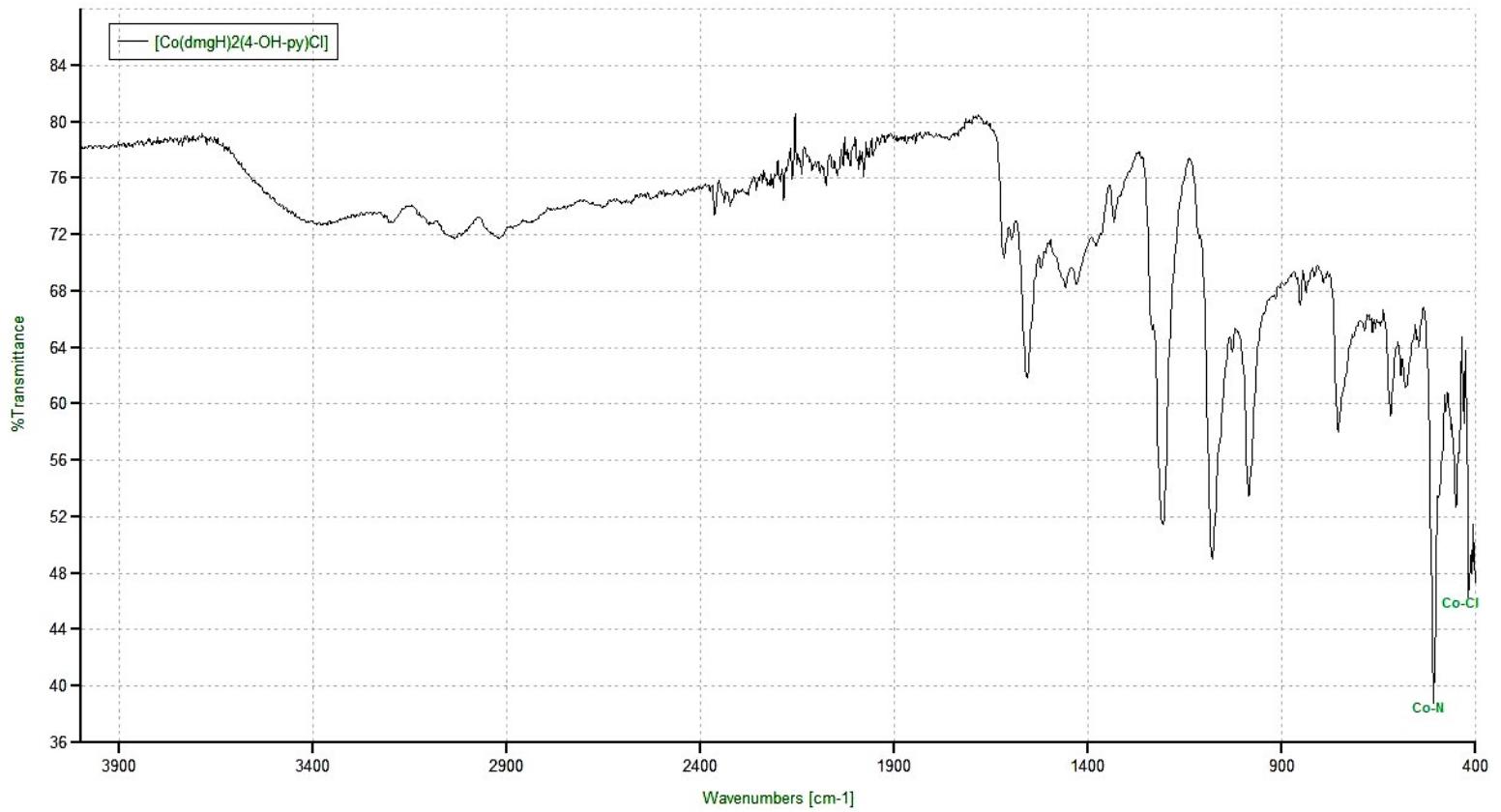
**Figure S13.** FT-IR spectrum of complex 4.



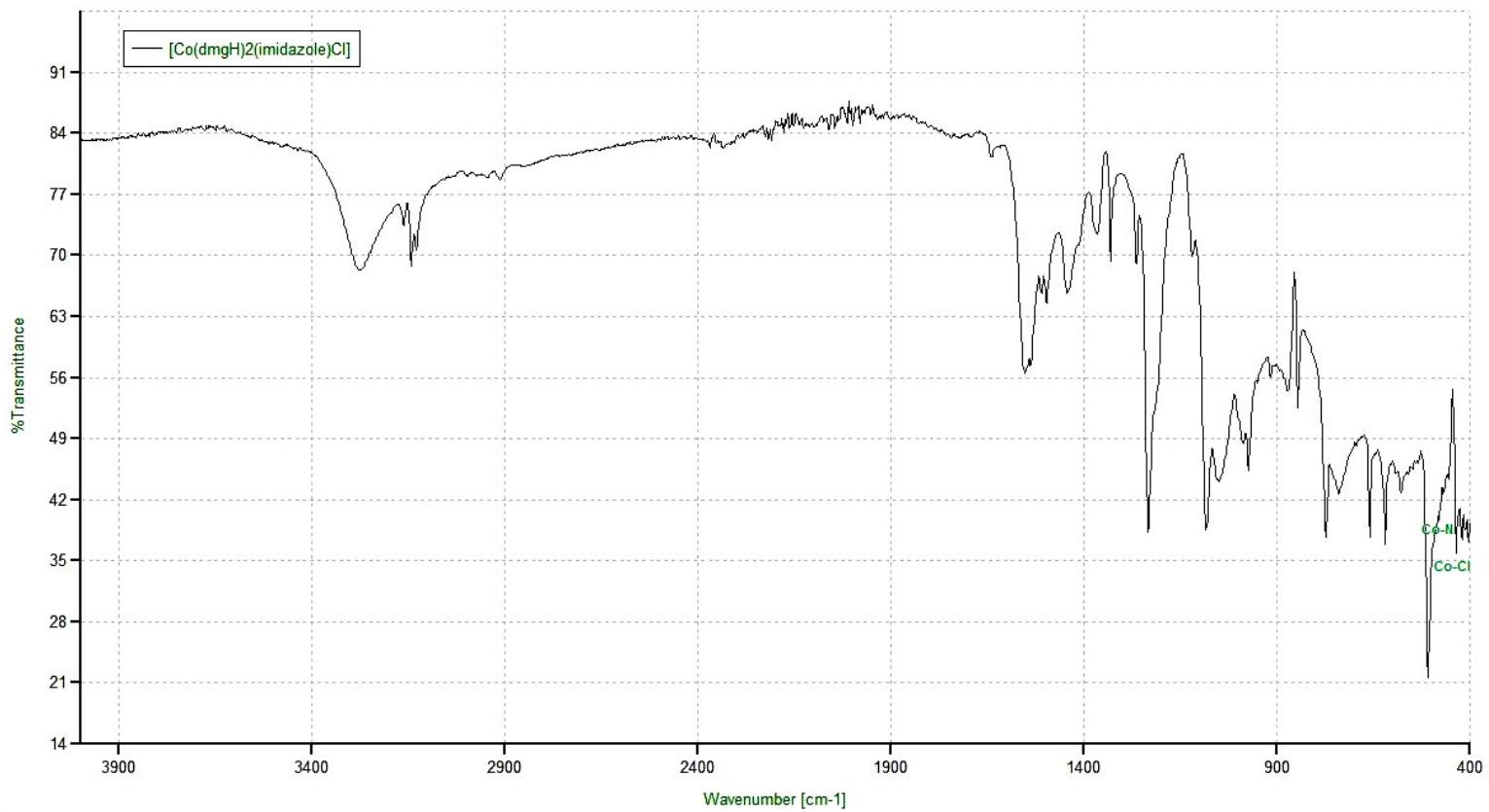
**Figure S14.** FT-IR spectrum of complex 5.



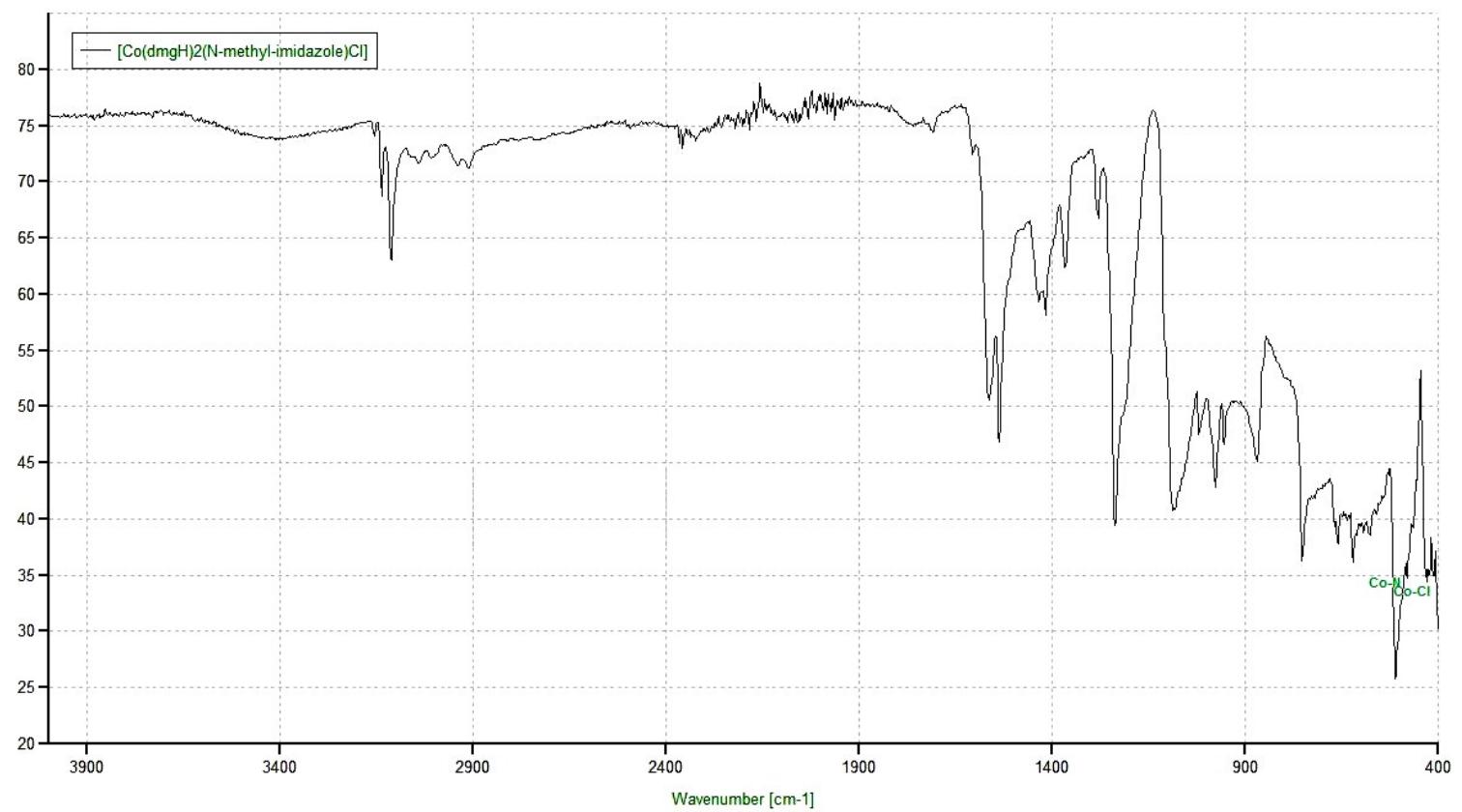
**Figure S15.** FT-IR spectrum of complex **6**.



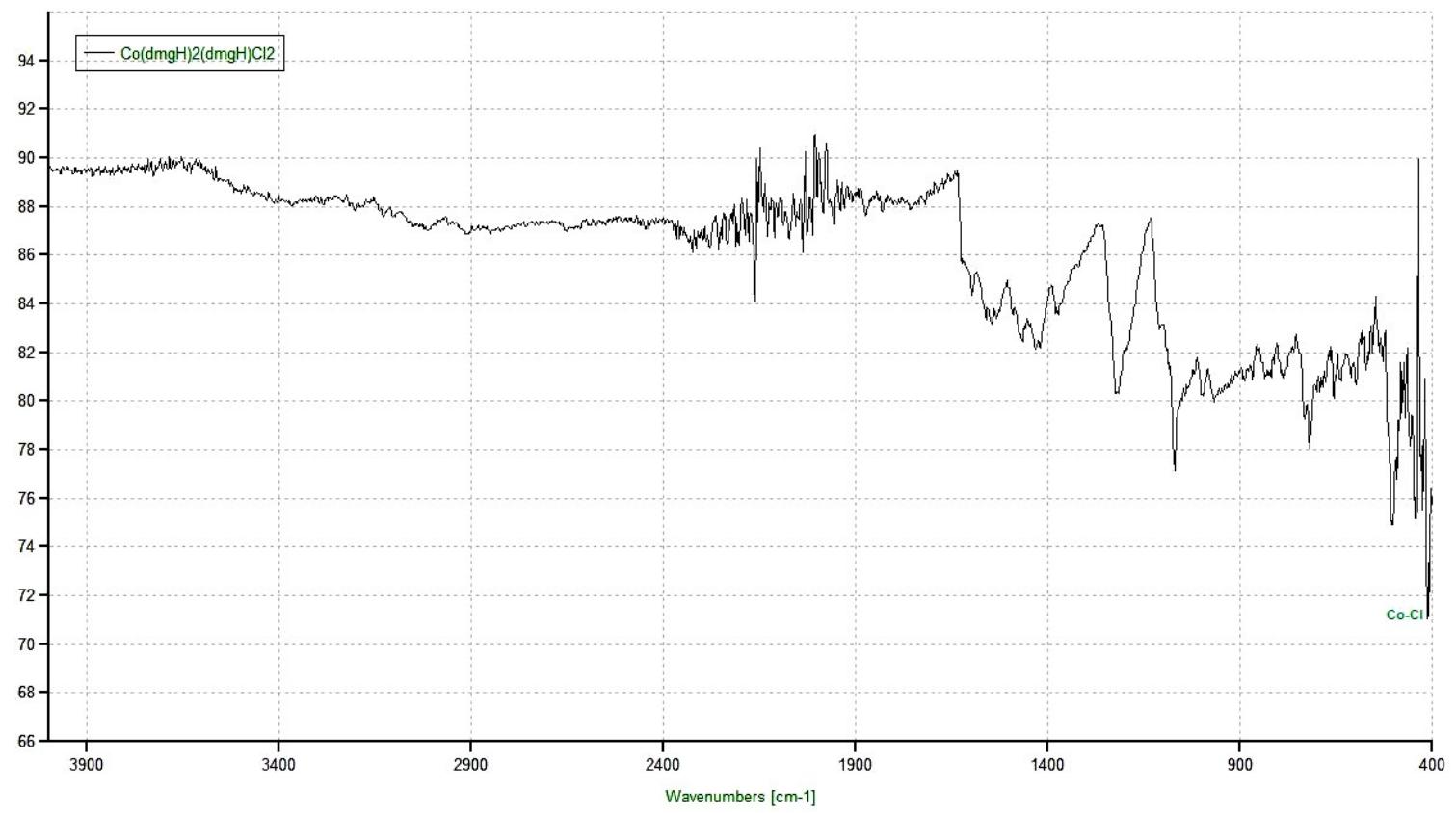
**Figure S16.** FT-IR spectrum of complex 7.



**Figure S17.** FT-IR spectrum of complex **8**.

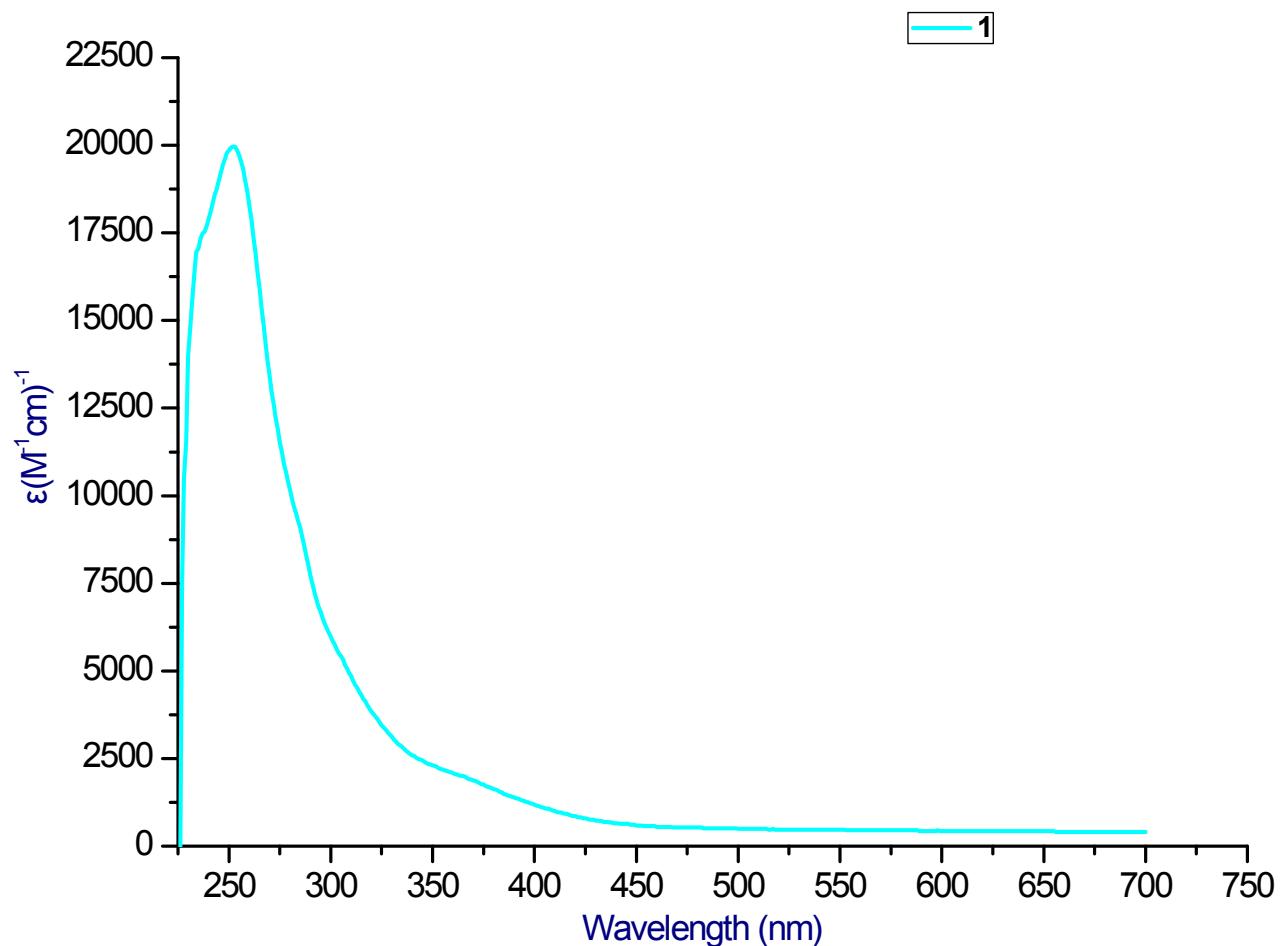


**Figure S18.** FT-IR spectrum of complex **9**.

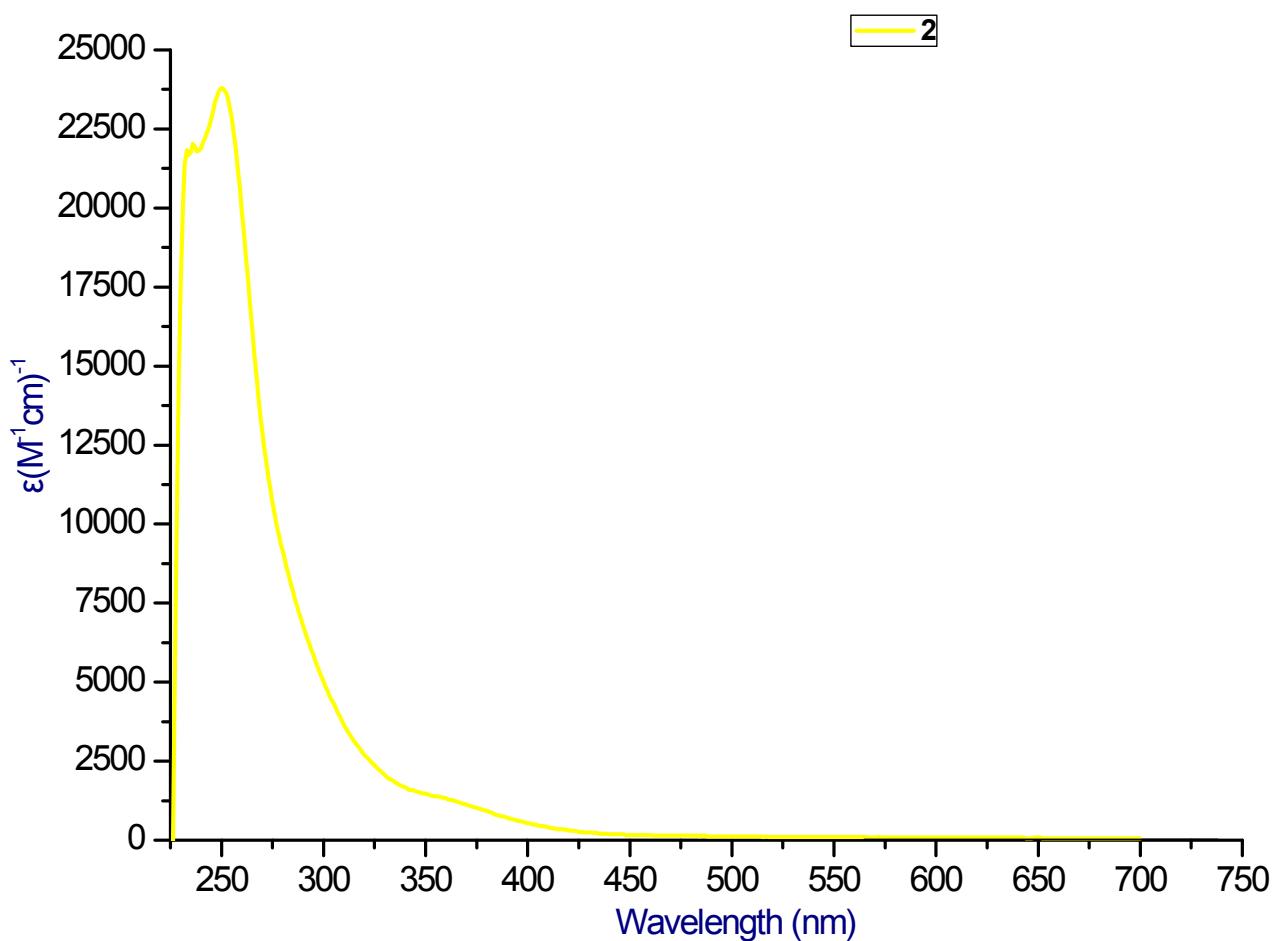


**Figure S19.** FT-IR spectrum of complex **10**.

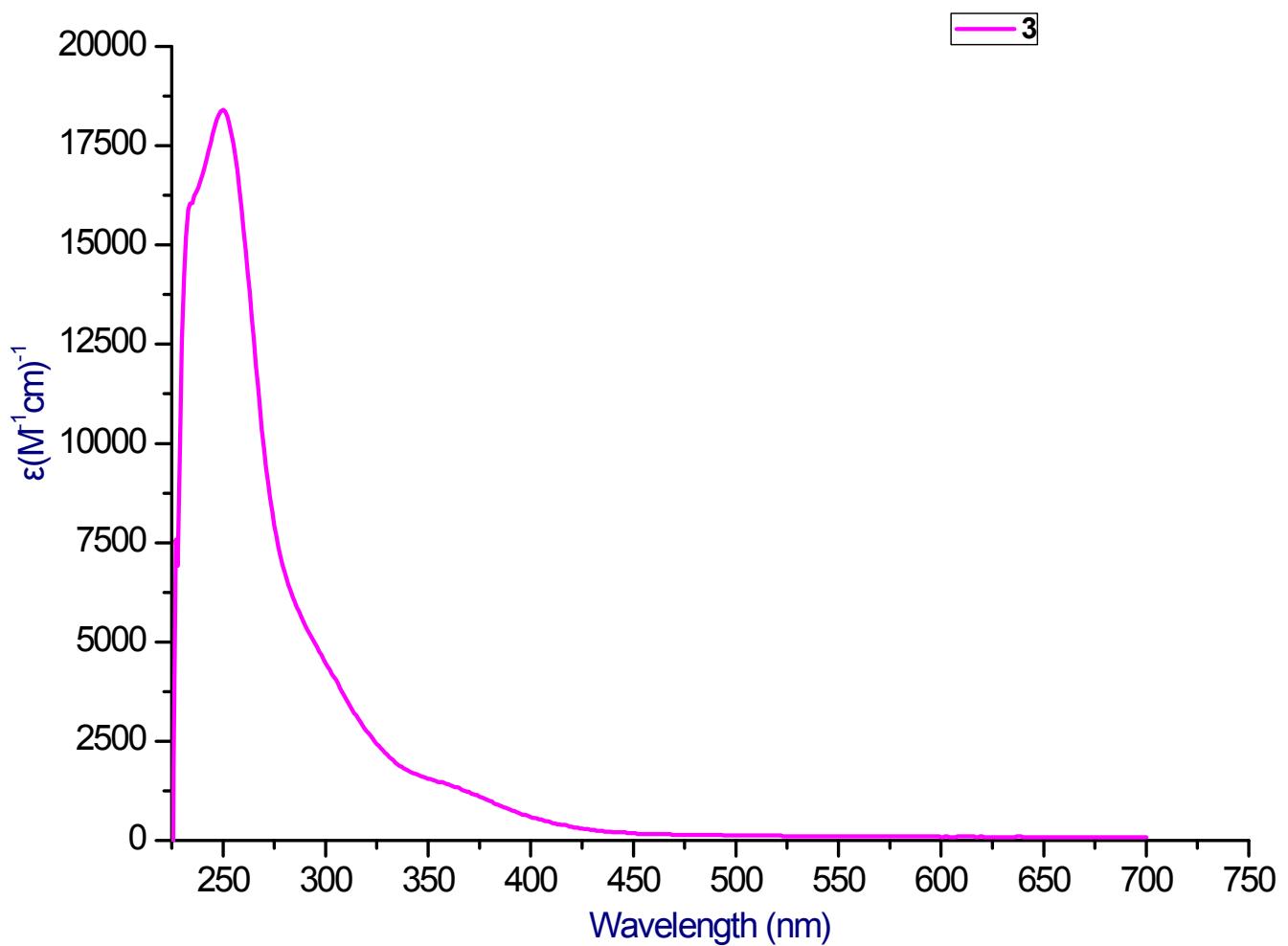
### UV-Vis Spectra



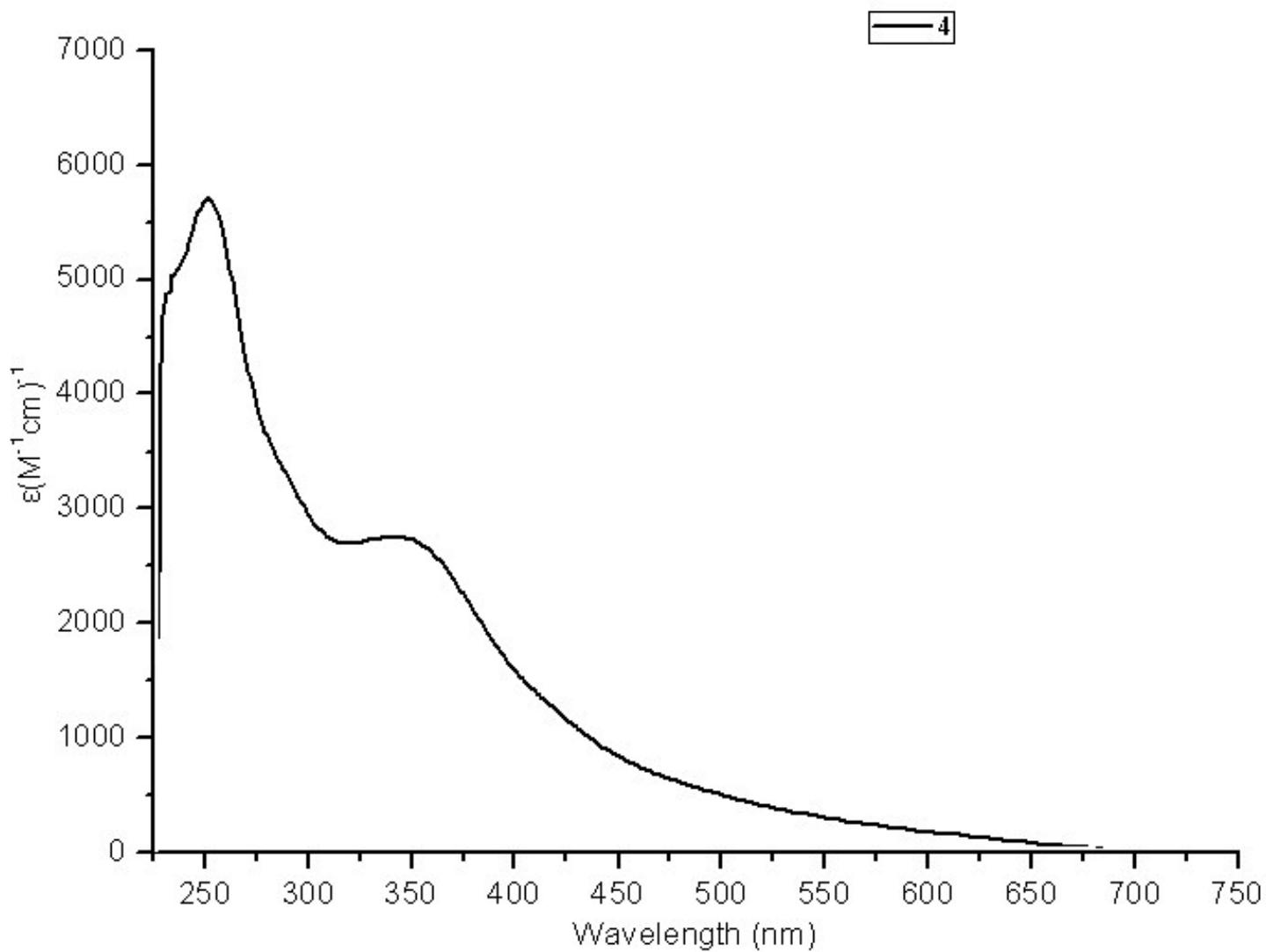
**Figure S20.** UV-Vis spectrum of complex **1** in solution 1:1 acetonitrile/water containing TEOA 5% v/v at pH 7.



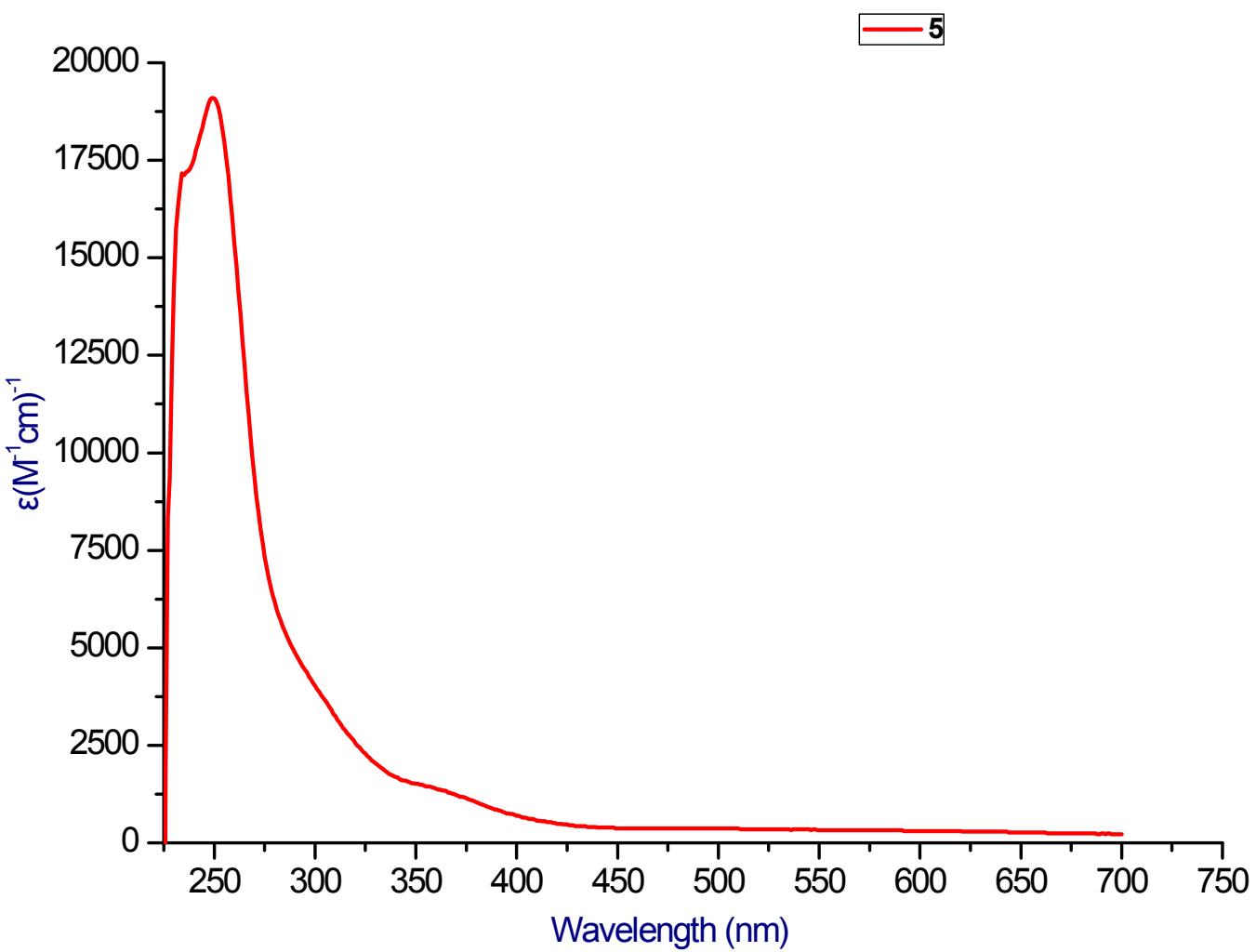
**Figure S21.** UV-Vis spectrum of complex **2** in solution 1:1 acetonitrile/water containing TEOA 5% v/v at pH 7.



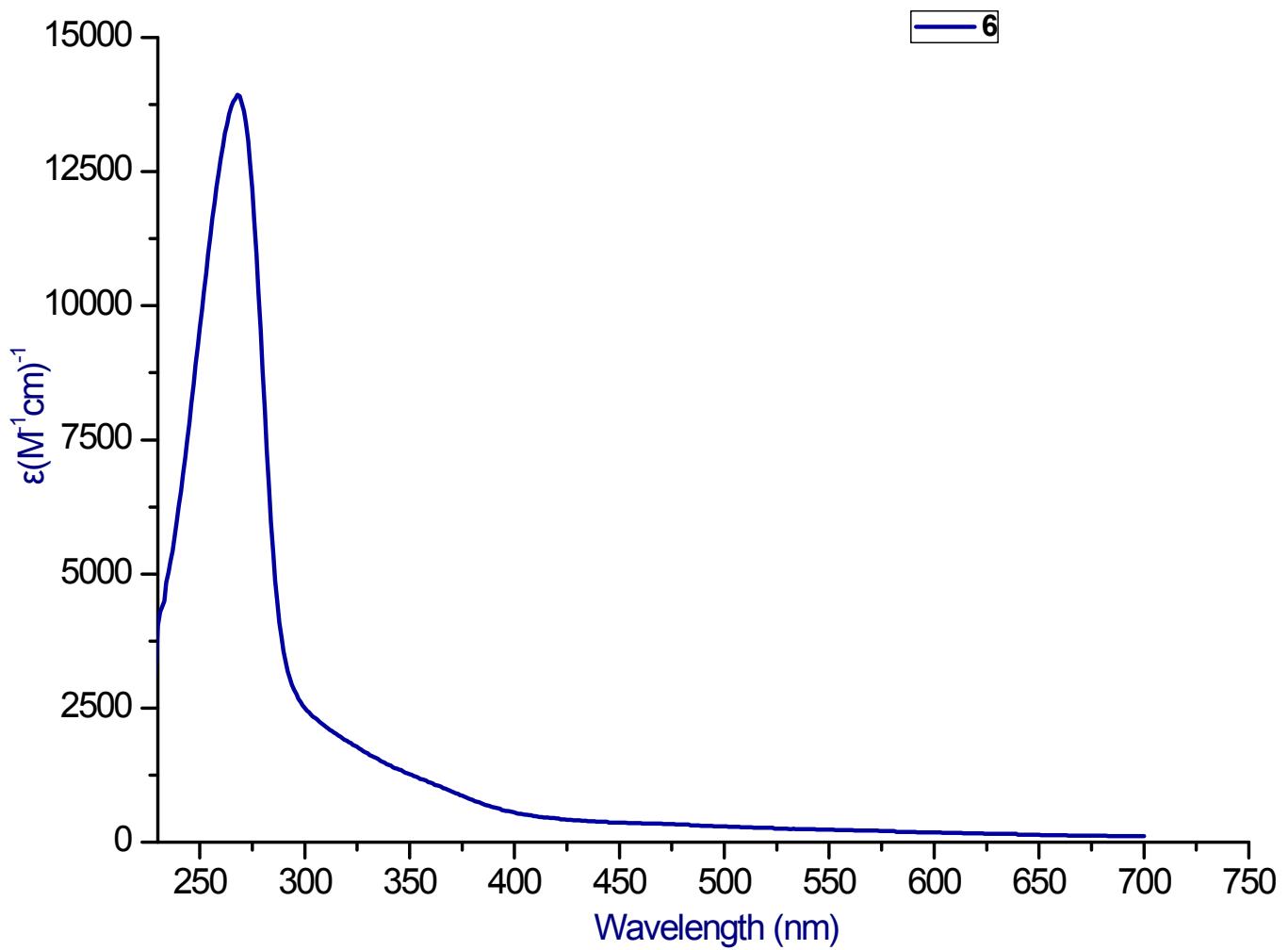
**Figure S22.** UV-Vis spectrum of complex **3** in solution 1:1 acetonitrile/water containing TEOA 5% v/v at pH 7.



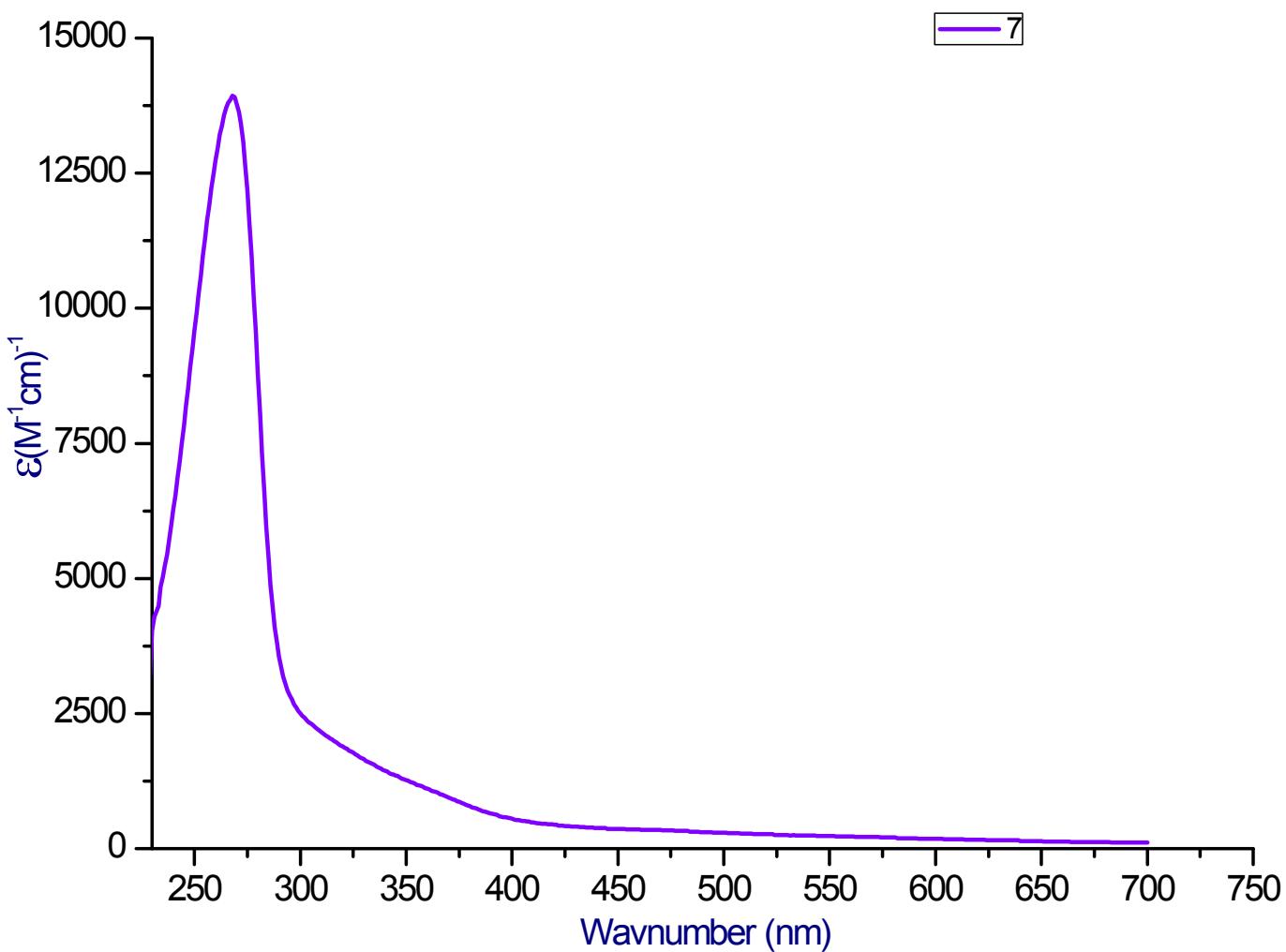
**Figure S23.** UV-Vis spectrum of complex **4** in solution 1:1 acetonitrile/water containing TEOA 5% v/v at pH 7.



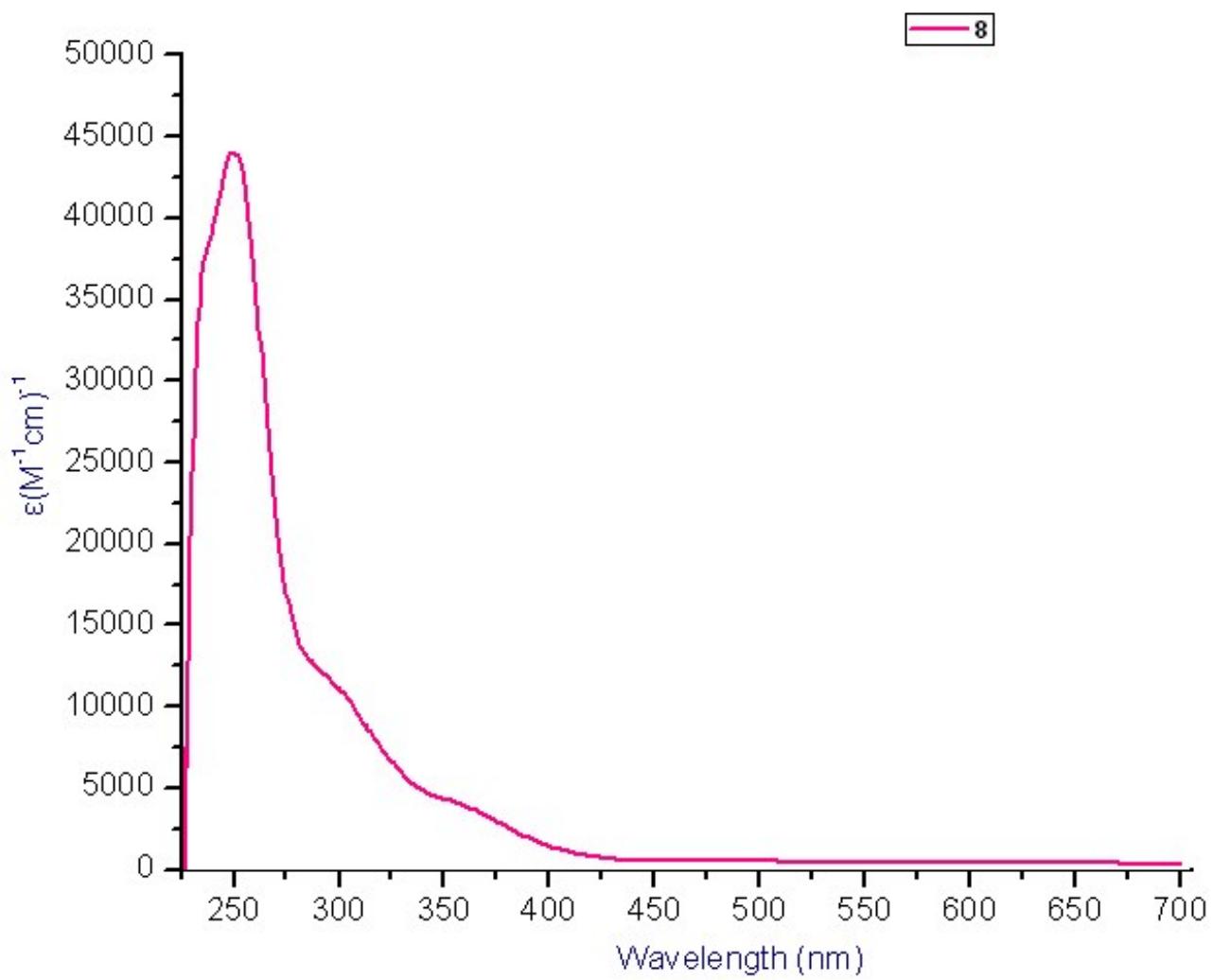
**Figure S24.** UV-Vis spectrum of complex **5** in solution 1:1 acetonitrile/water containing TEOA 5% v/v at pH 7.



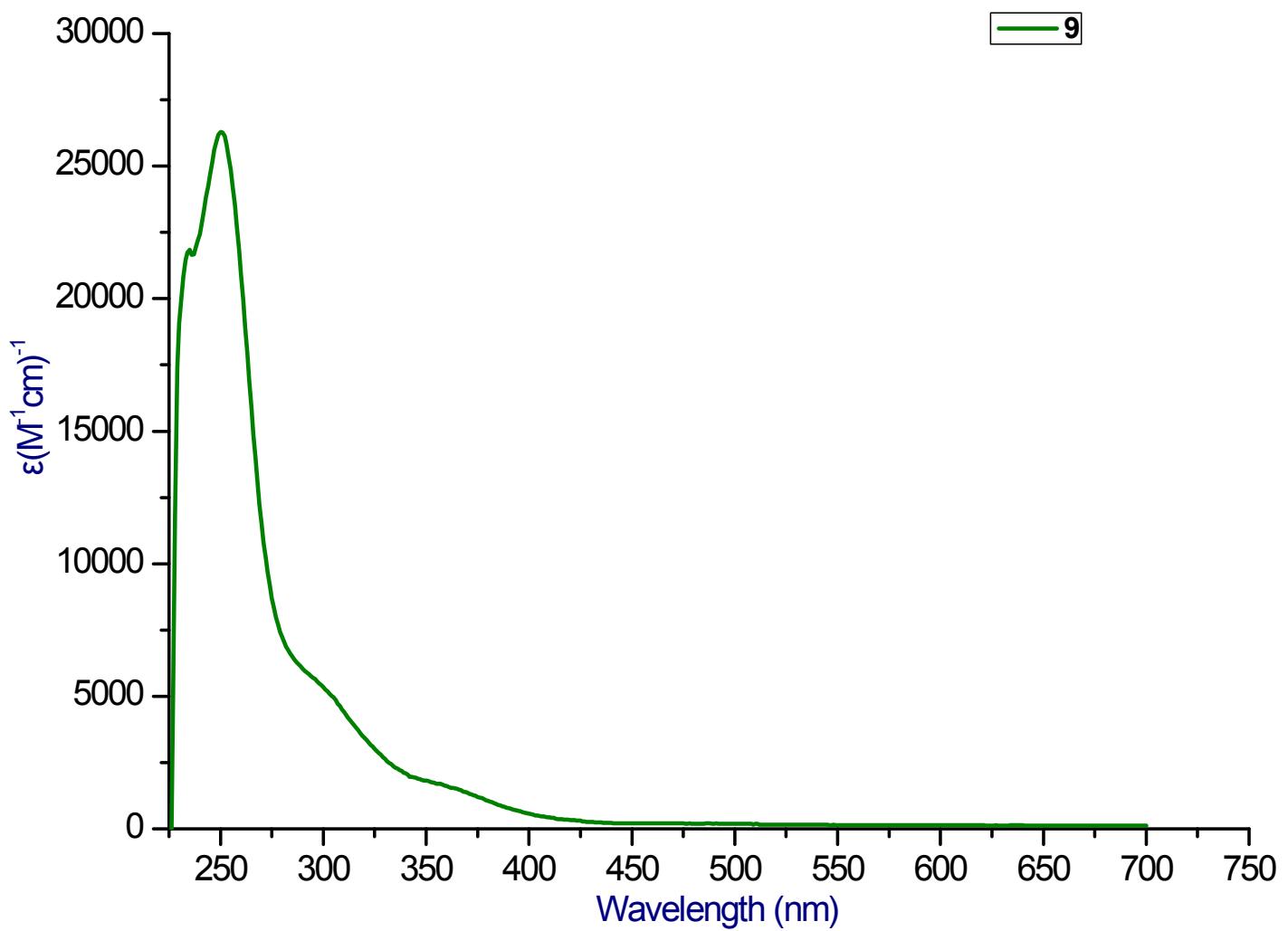
**Figure S25.** UV-Vis spectrum of complex **6** in solution 1:1 acetonitrile/water containing TEOA 5% v/v at pH 7.



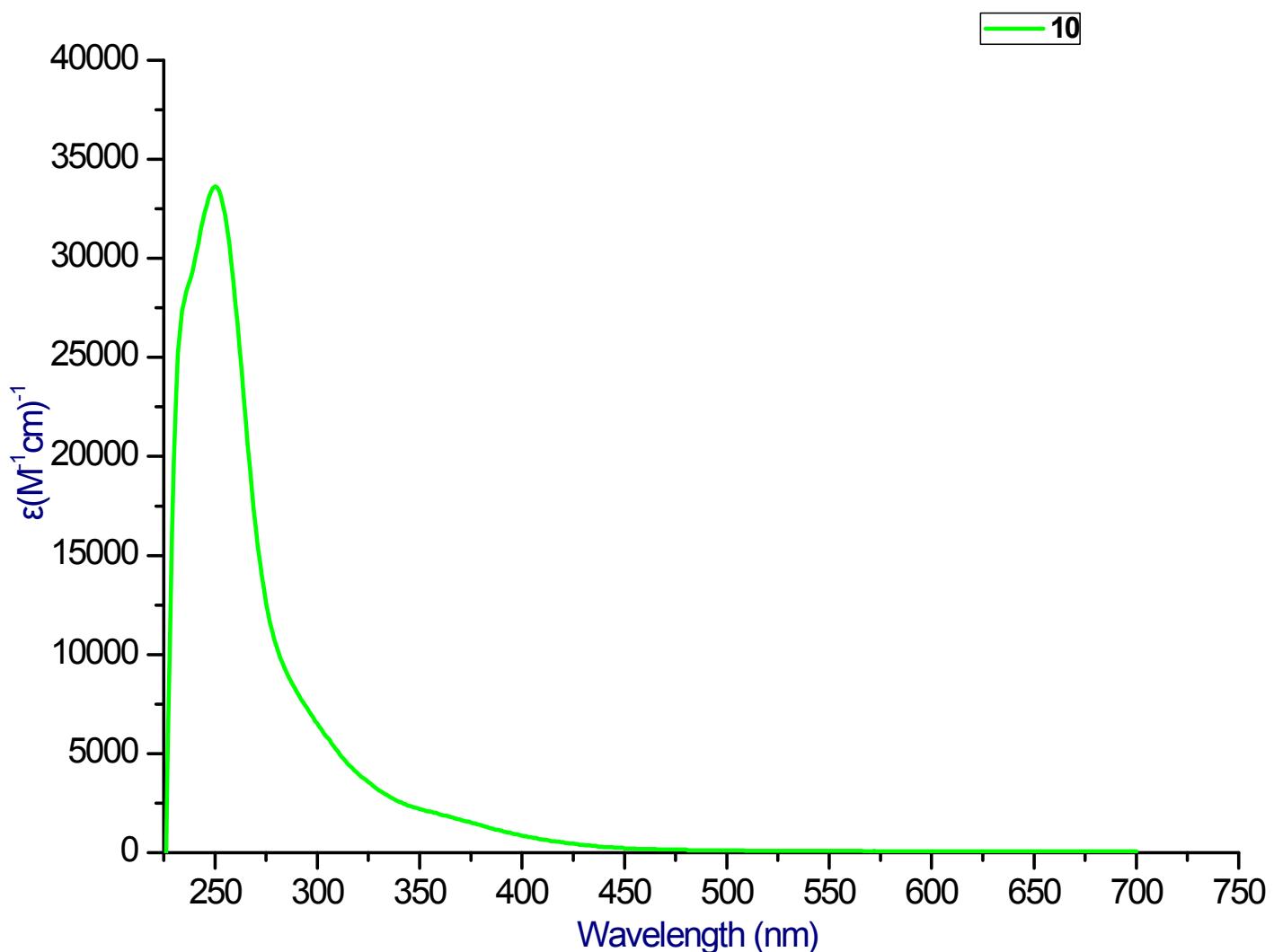
**Figure S26.** UV-Vis spectrum of complex **7** in solution 1:1 acetonitrile/water containing TEOA 5% v/v at pH 7.



**Figure S27.** UV-Vis spectrum of complex **8** in solution 1:1 acetonitrile/water containing TEOA 5% v/v at pH 7.

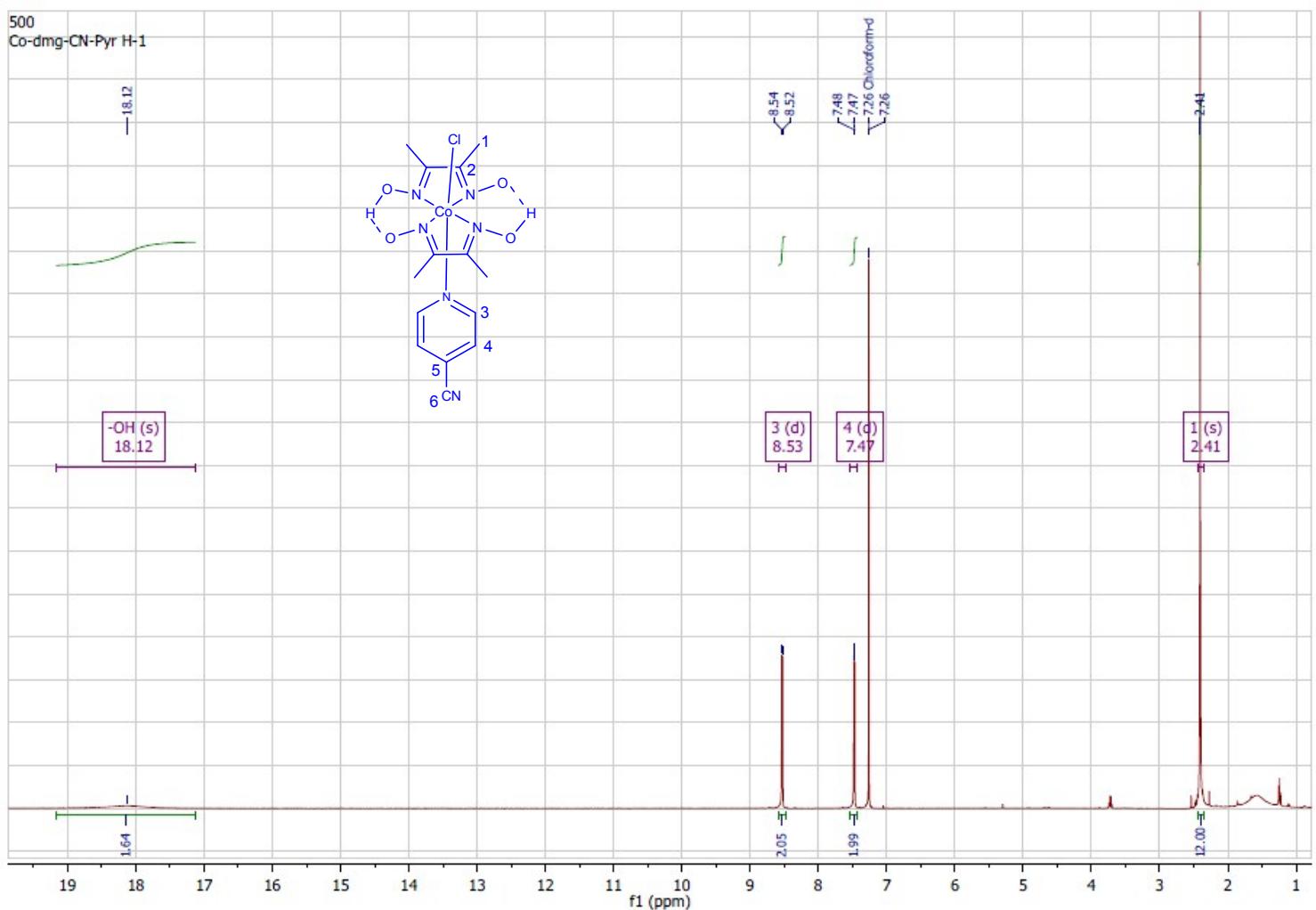


**Figure S28.** UV-Vis spectrum of complex **9** in solution 1:1 acetonitrile/water containing TEOA 5% v/v at pH 7.

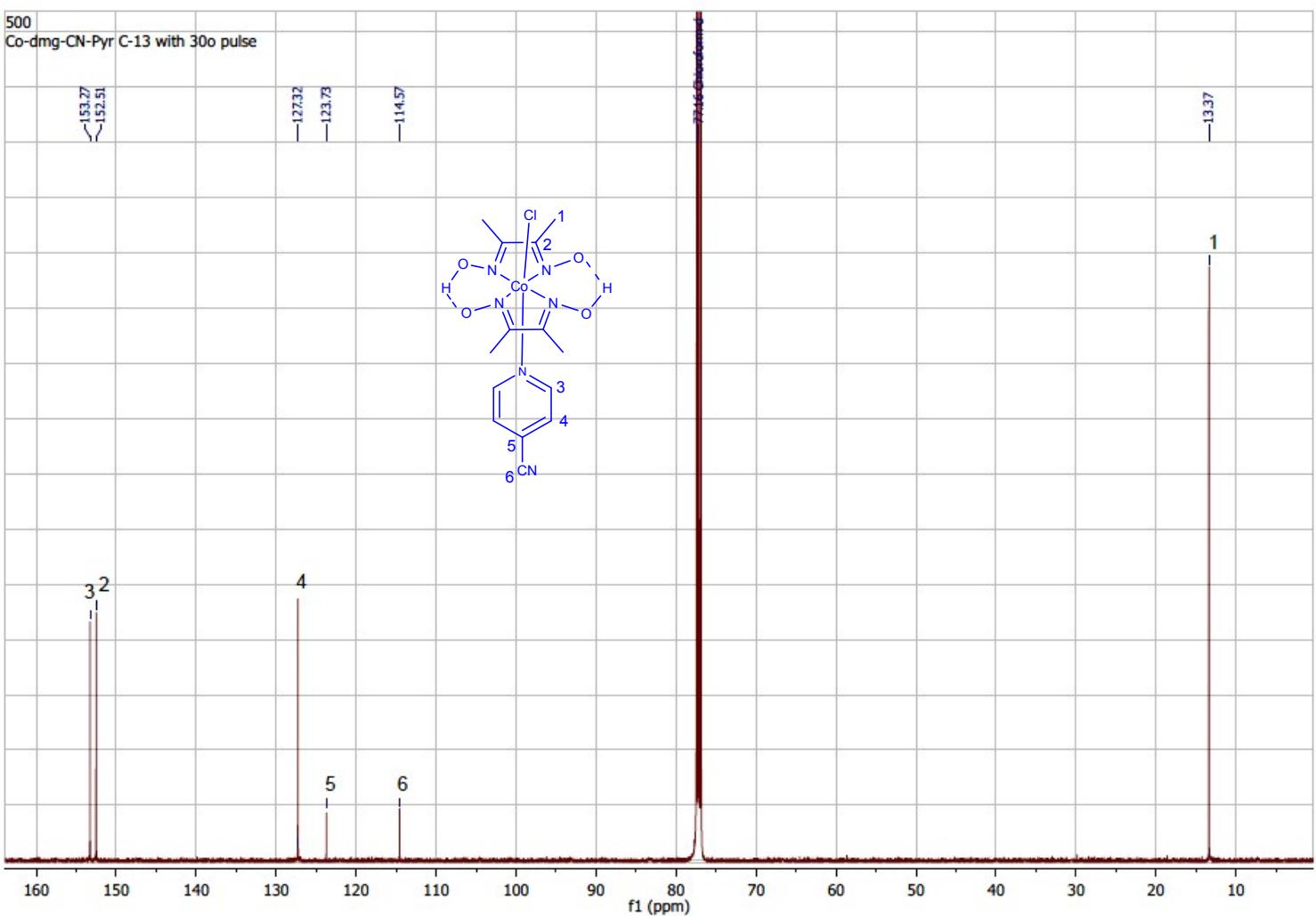


**Figure S29.** UV-Vis spectrum of complex **10** in solution 1:1 acetonitrile/water containing TEOA 5% v/v at pH 7.

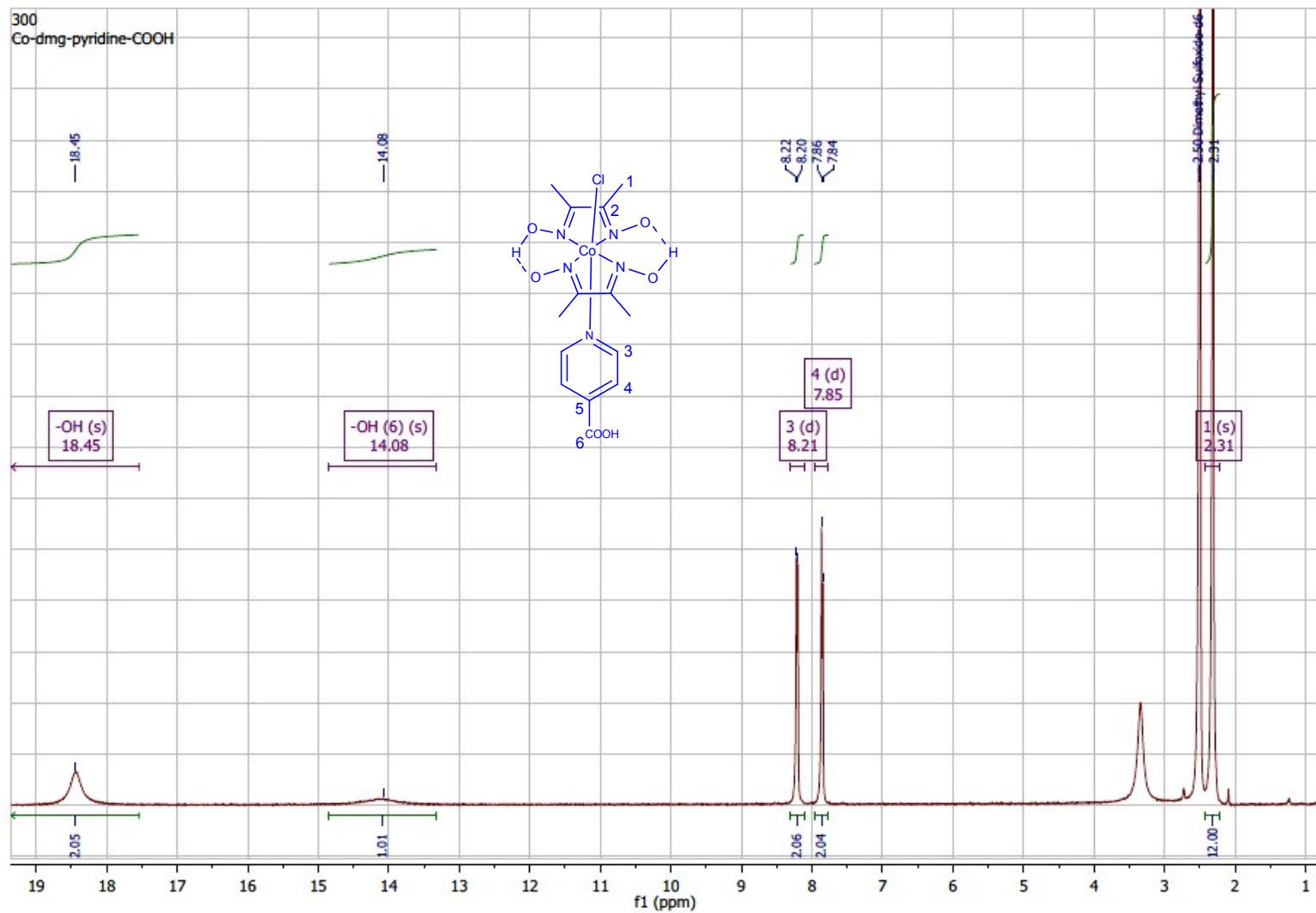
### <sup>1</sup>H & <sup>13</sup>C NMR Spectra



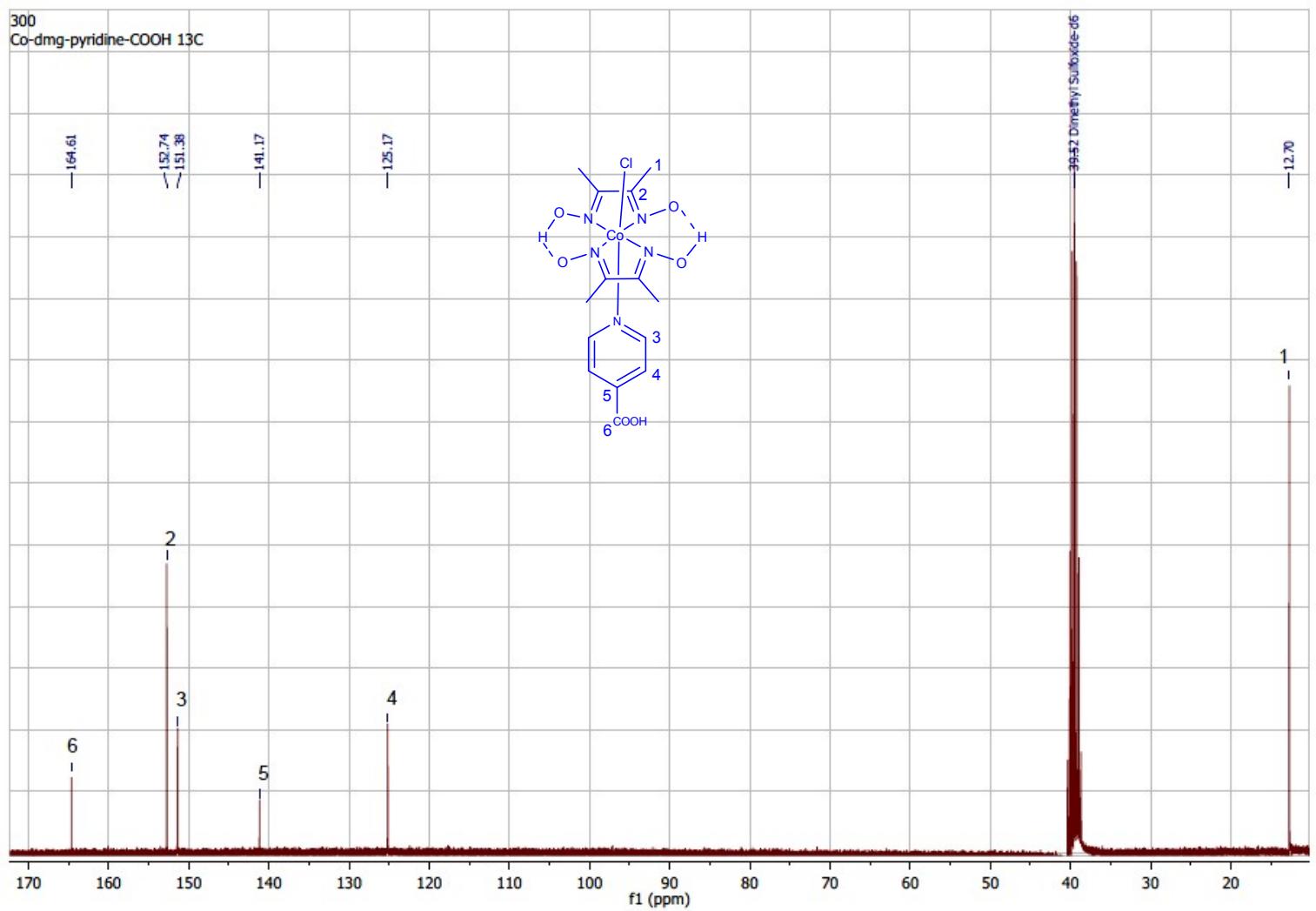
**Figure S30.** <sup>1</sup>H NMR spectrum of complex **1** in CDCl<sub>3</sub>.



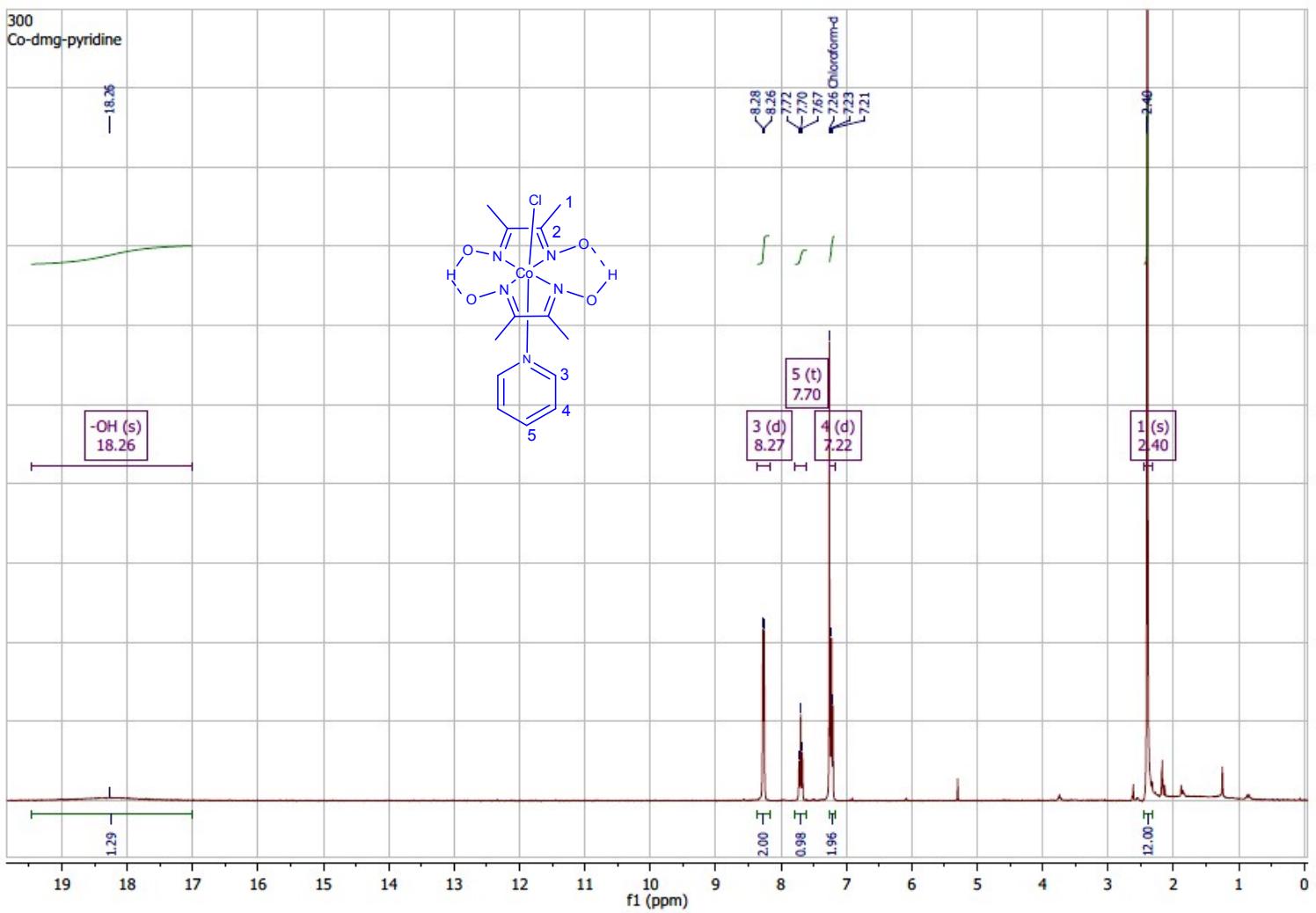
**Figure S31.** <sup>13</sup>C NMR spectrum of complex **1** in CDCl<sub>3</sub>.



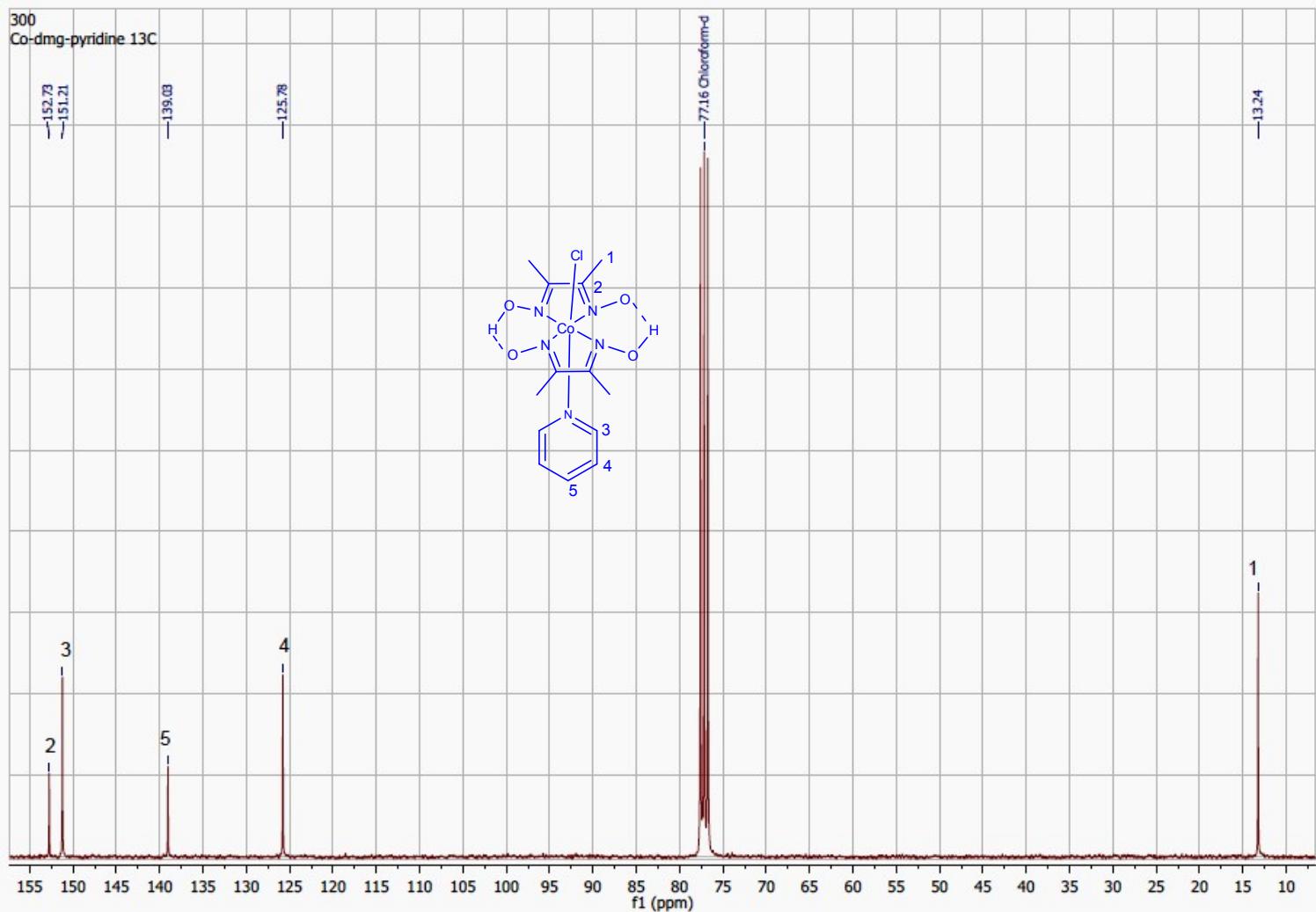
**Figure S32.**  $^1\text{H}$  NMR spectrum of complex **2** in DMSO.



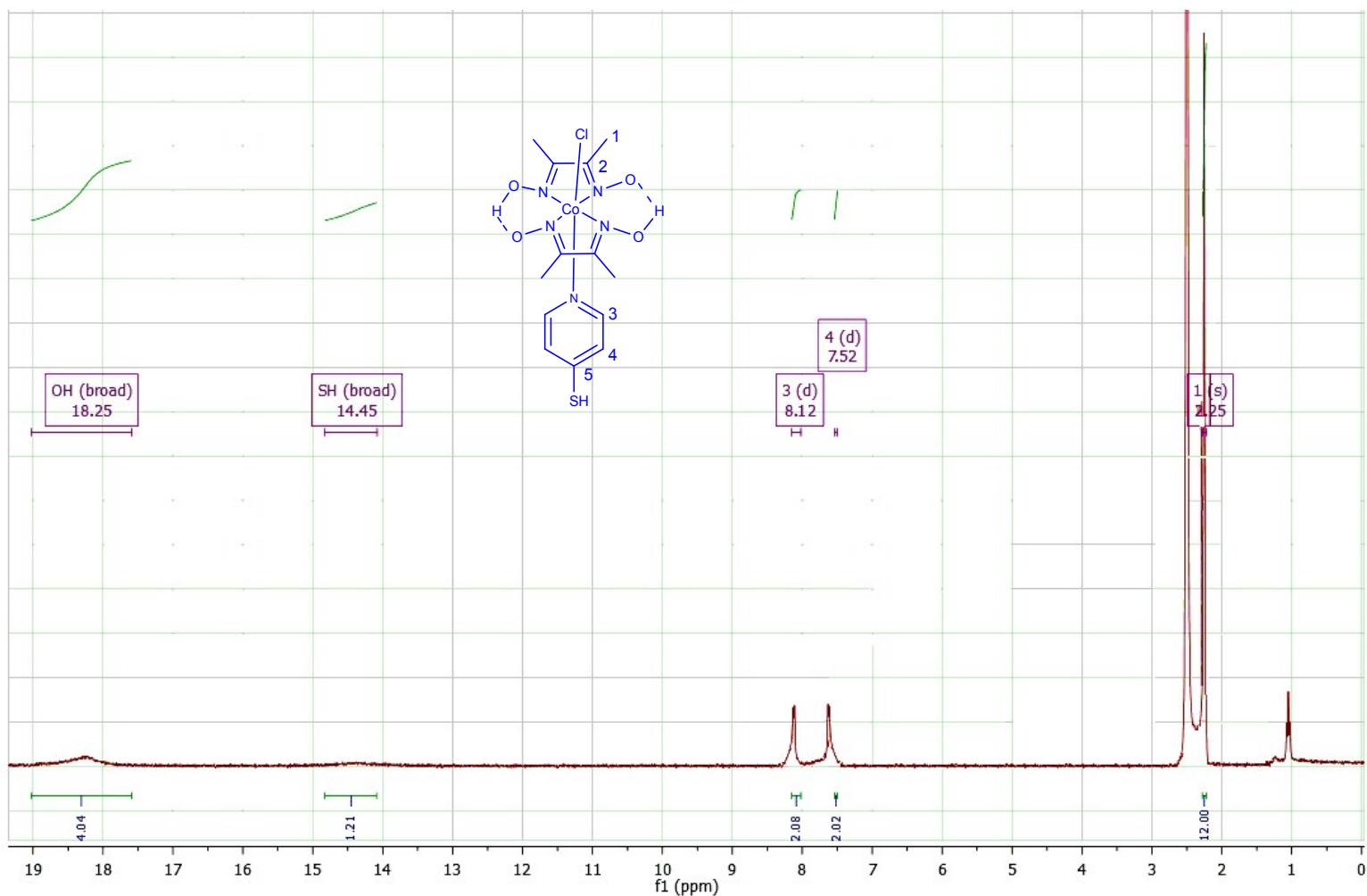
**Figure S33.**  $^{13}\text{C}$  NMR spectrum of complex **2** in DMSO.



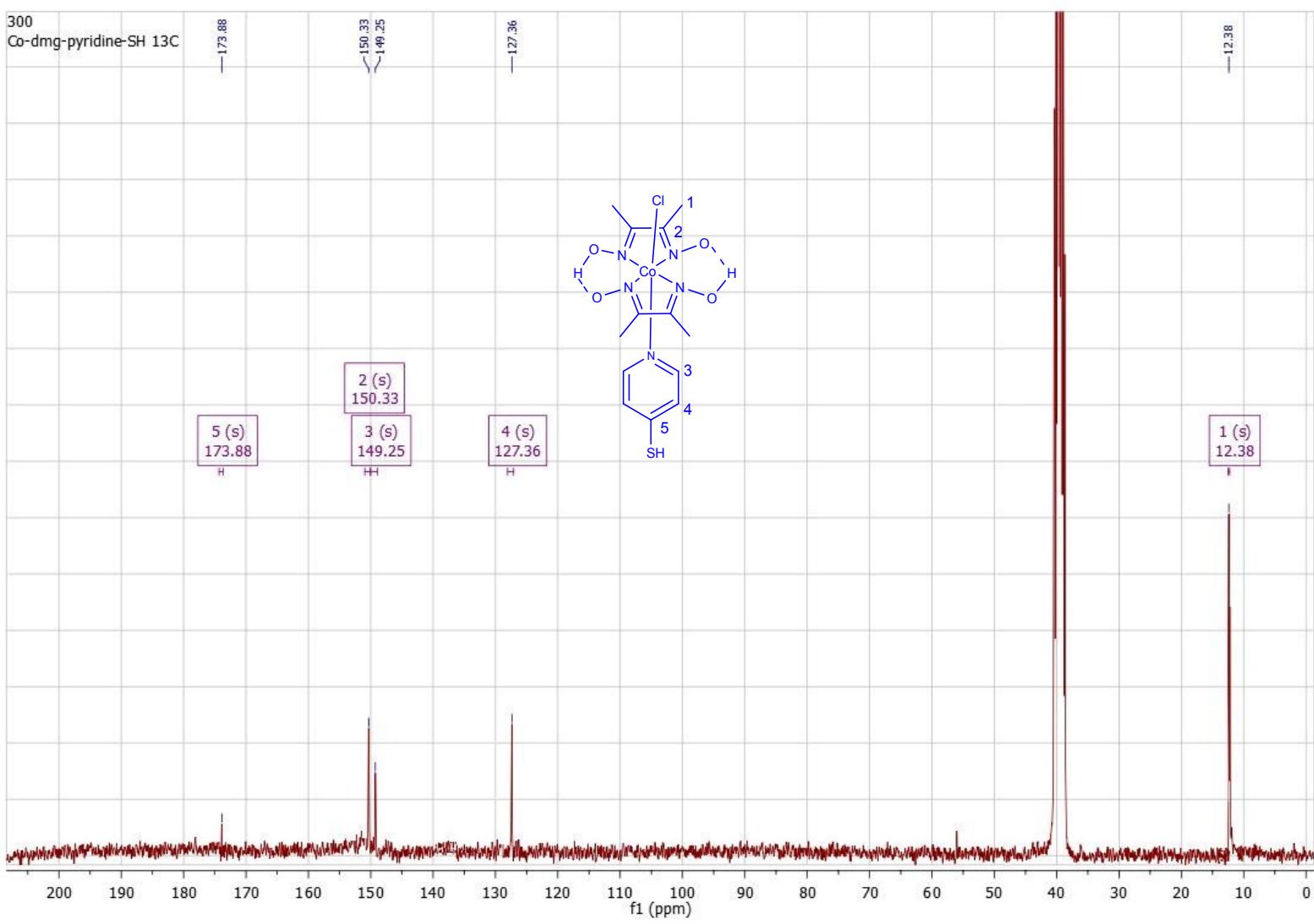
**Figure S34.**  $^1\text{H}$  NMR spectrum of complex **3** in  $\text{CDCl}_3$ .



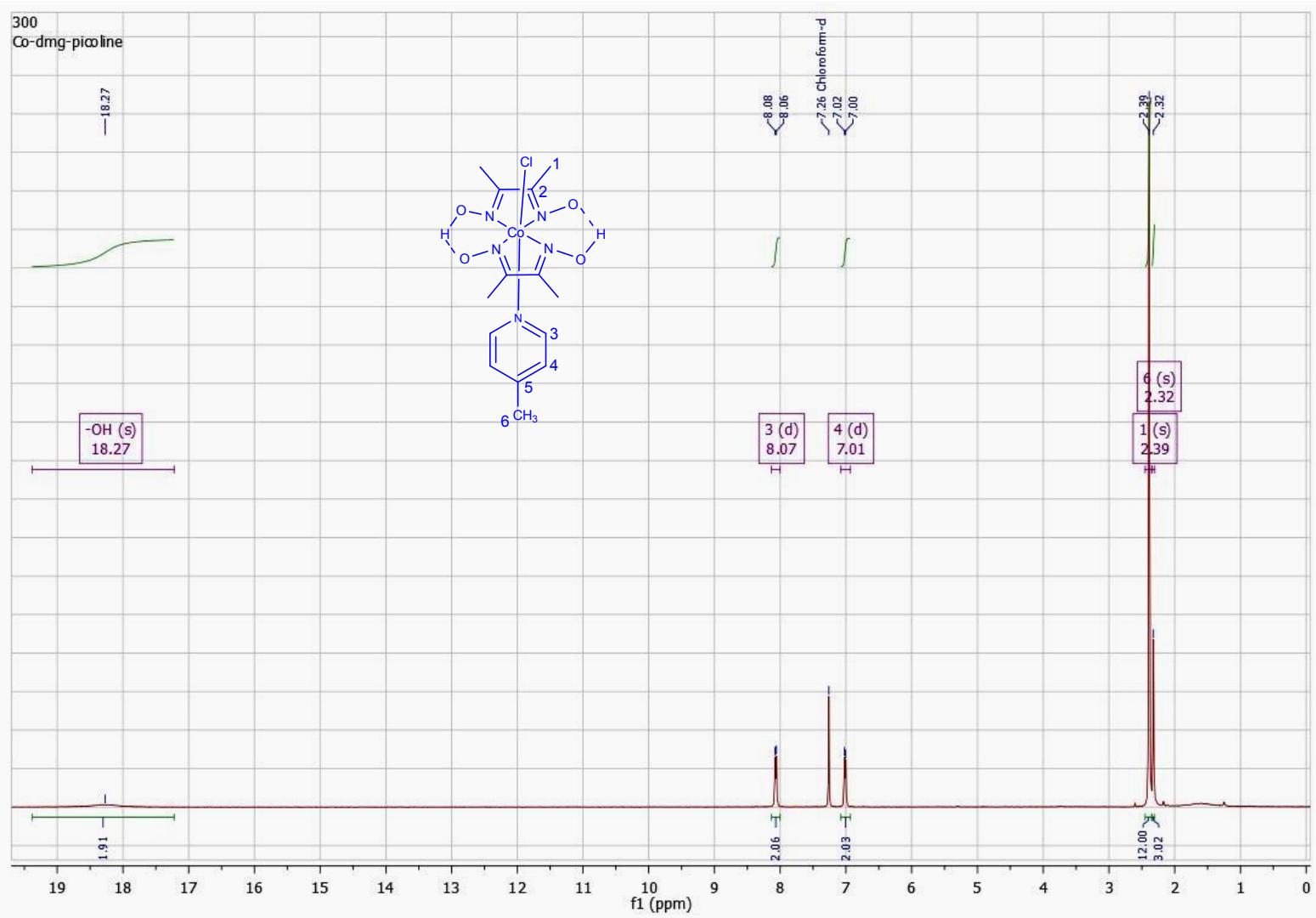
**Figure S35.**  $^{13}\text{C}$  NMR spectrum of complex **3** in  $\text{CDCl}_3$ .



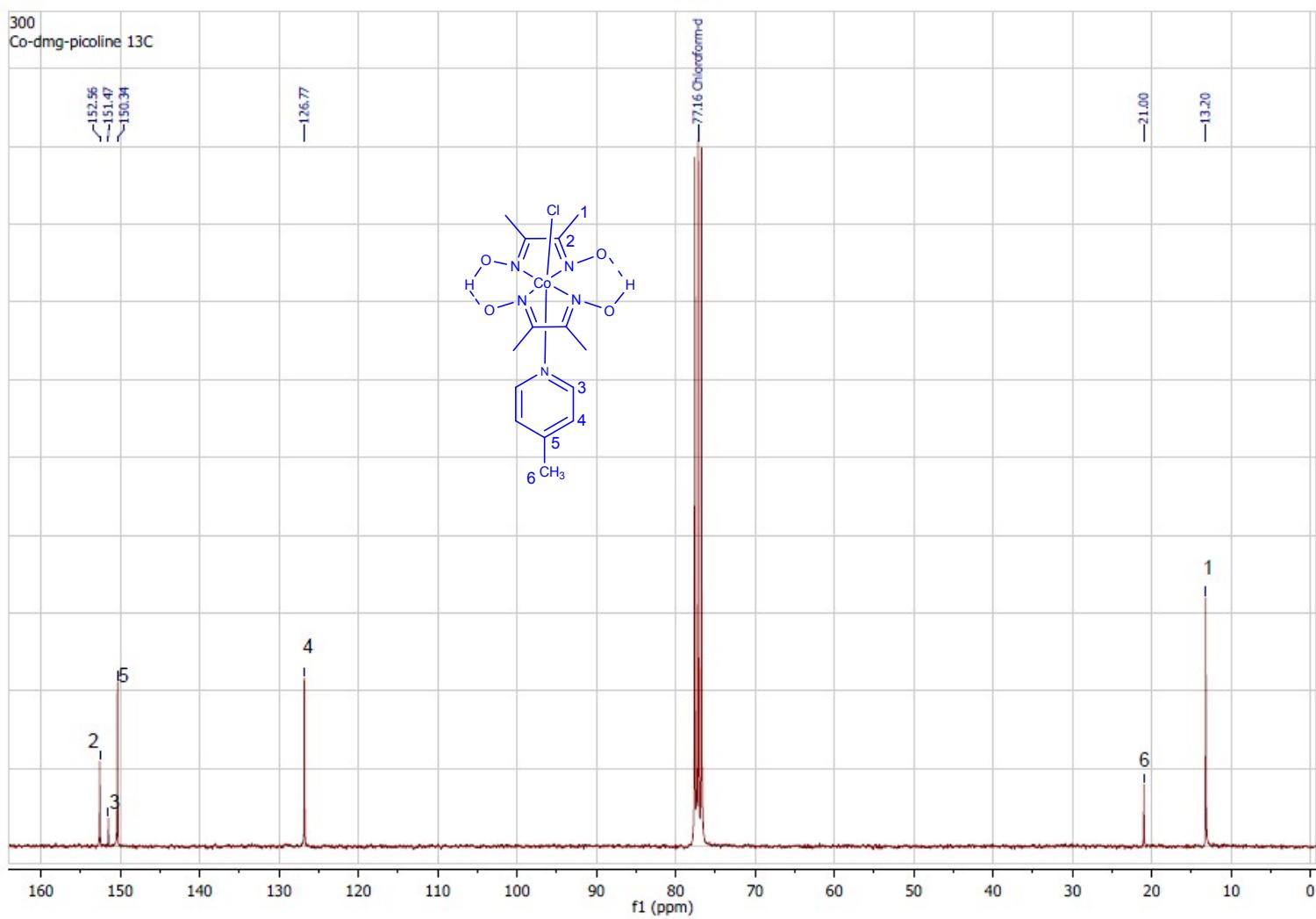
**Figure S36.**  $^1\text{H}$  NMR spectrum of complex 4 in DMSO.



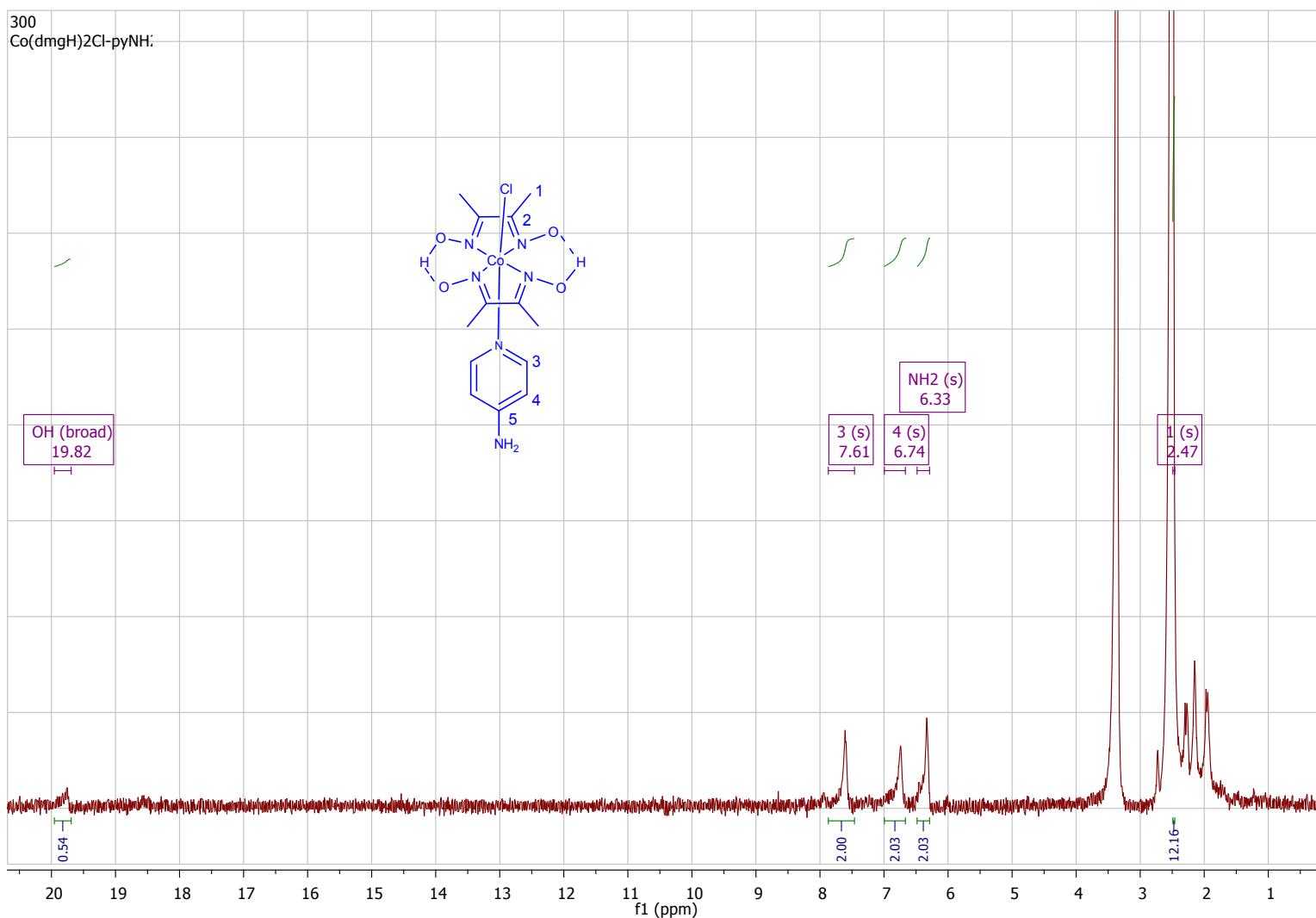
**Figure S37.** <sup>13</sup>C NMR spectrum of complex 4 in DMSO.



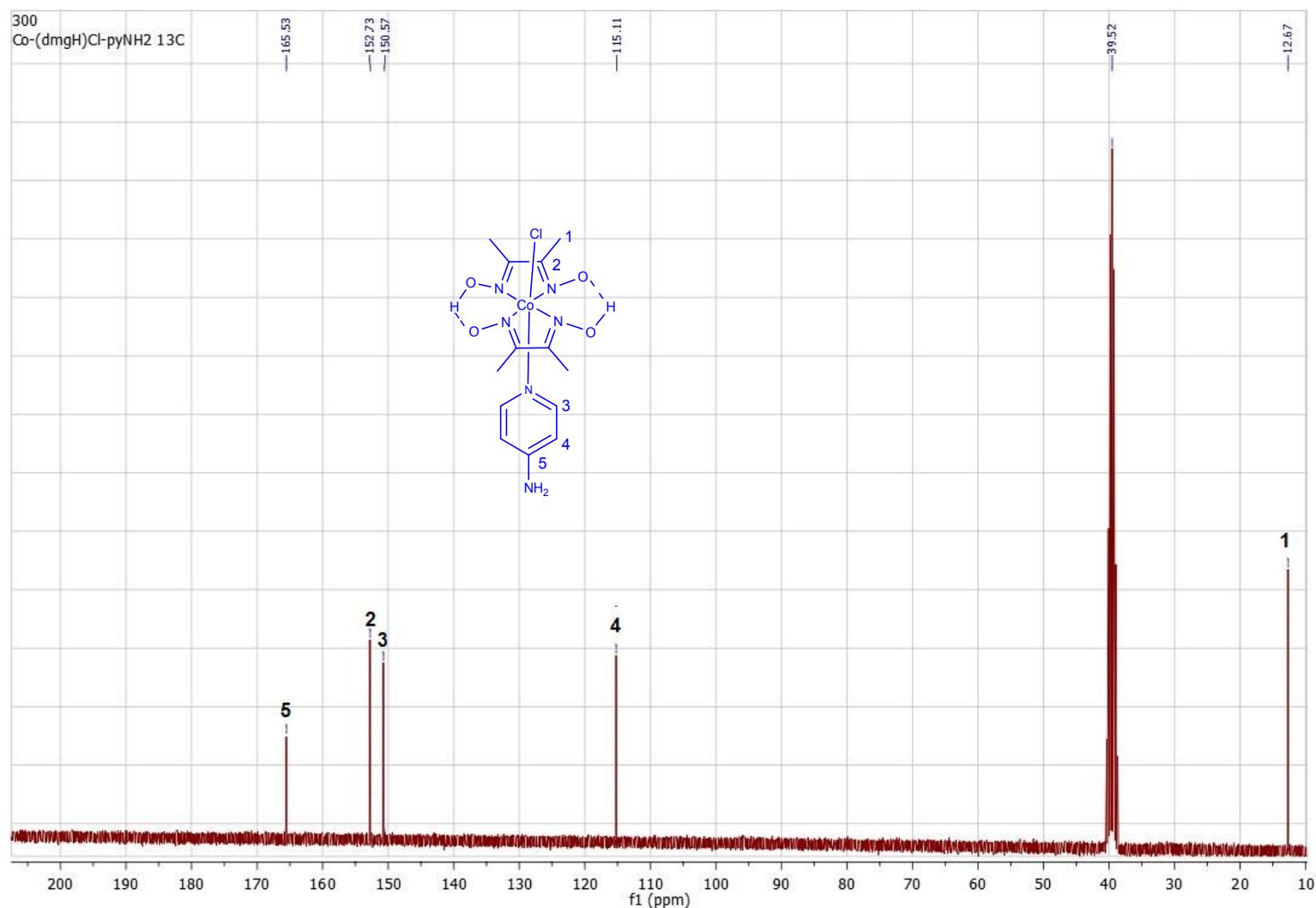
**Figure S38.**  $^1\text{H}$  NMR spectrum of complex **5** in  $\text{CDCl}_3$ .



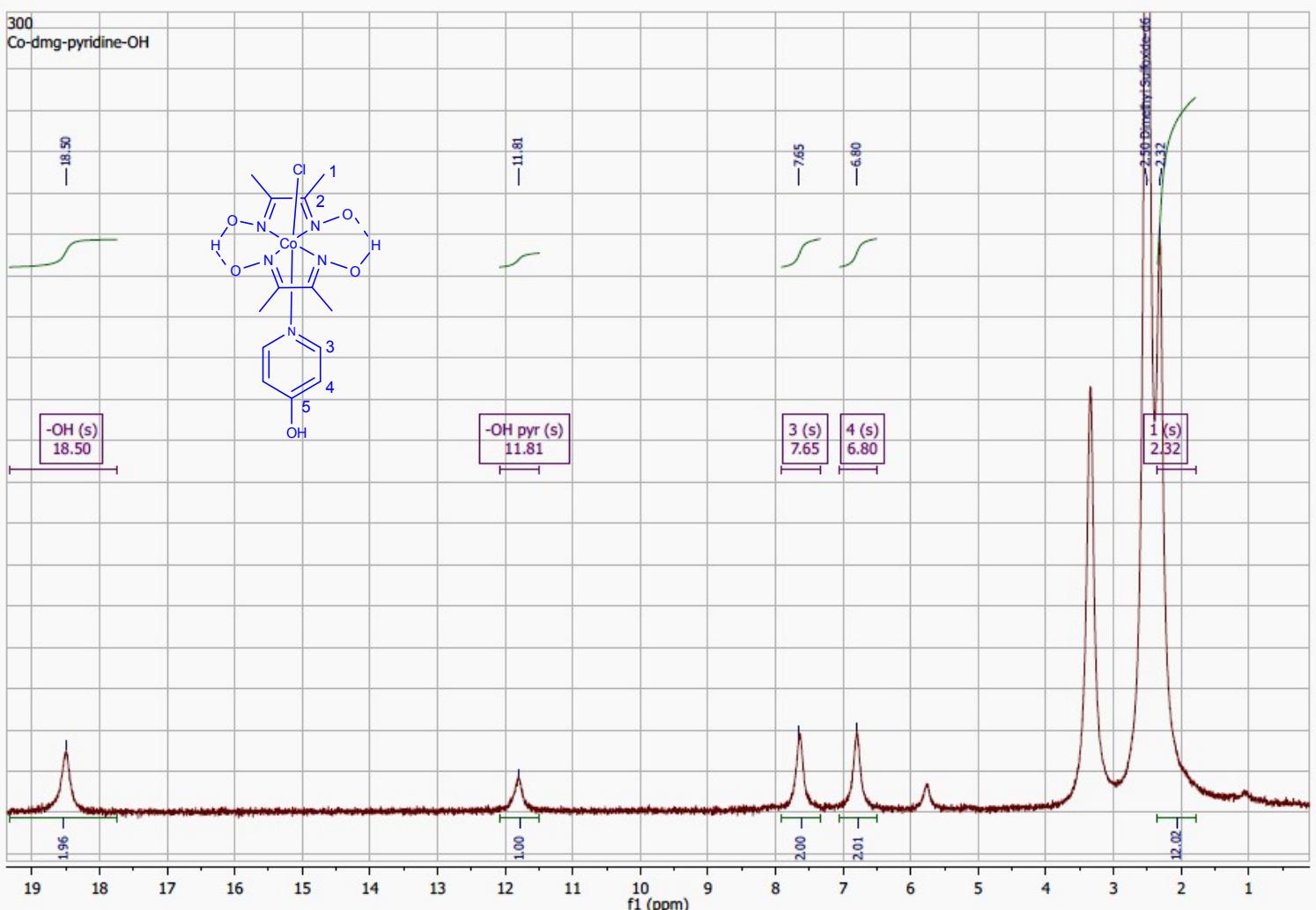
**Figure S39.** <sup>13</sup>C NMR spectrum of complex **5** in CDCl<sub>3</sub>.



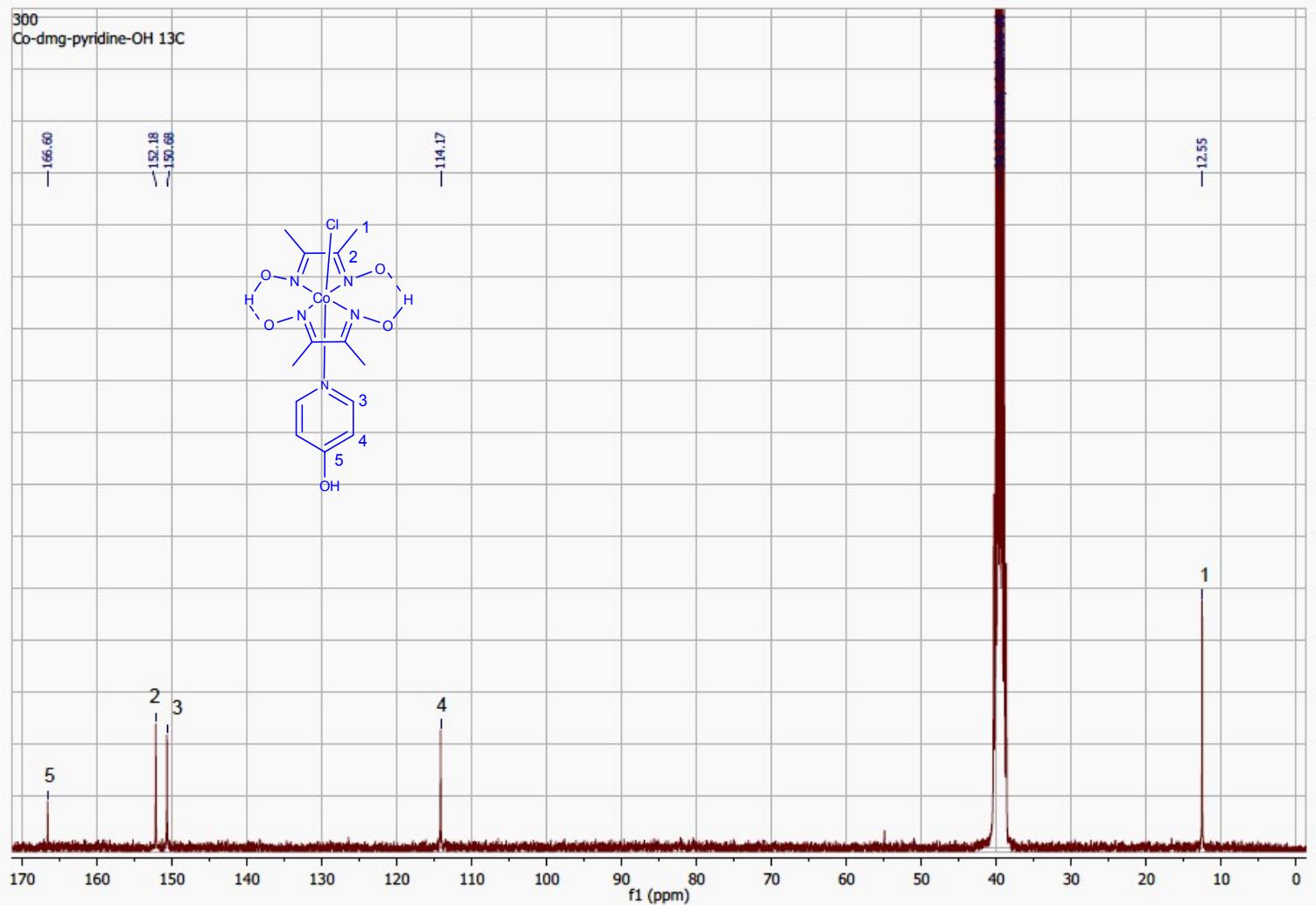
**Figure S40.** <sup>1</sup>H NMR spectrum of complex 6 in DMSO.



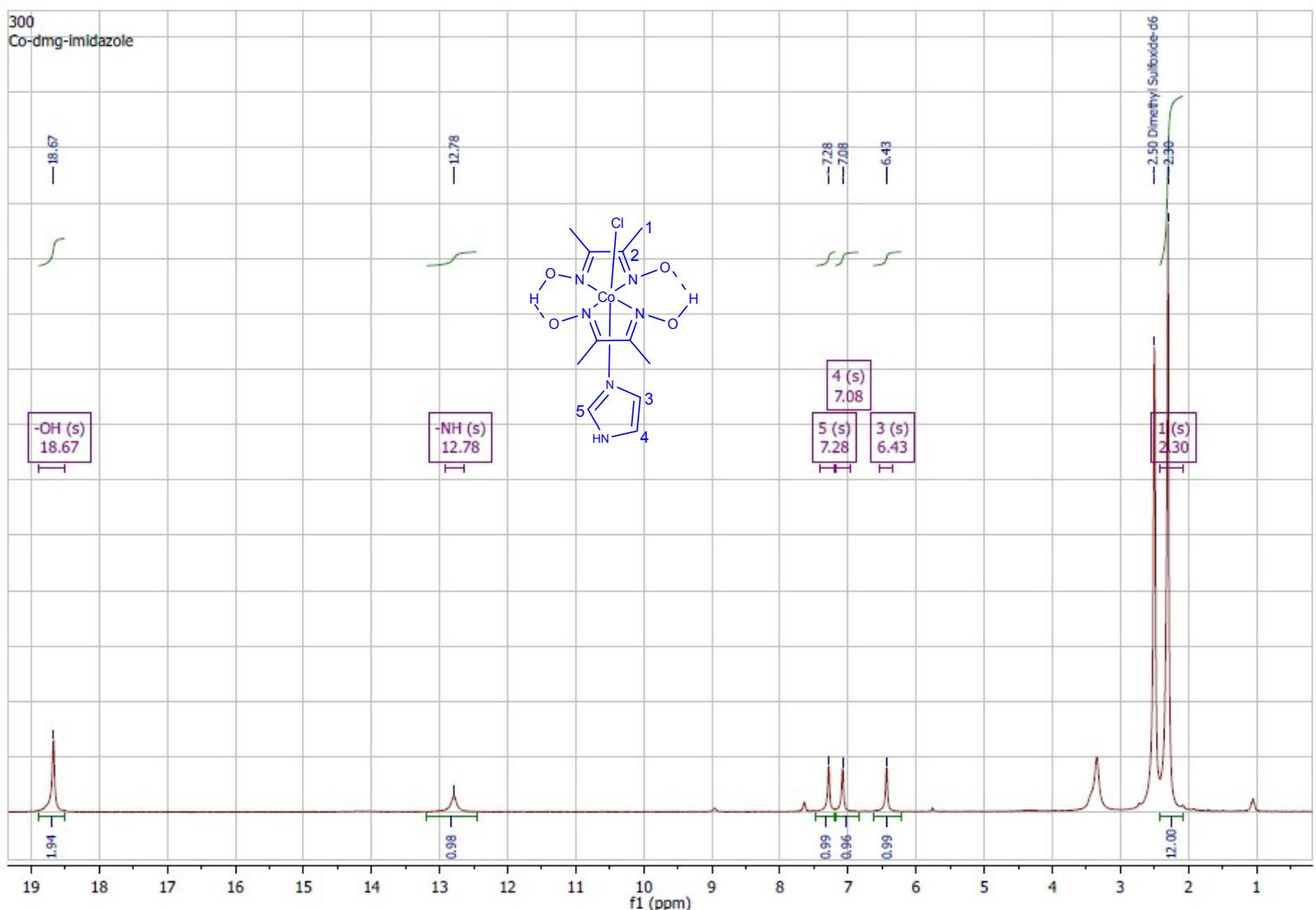
**Figure S41.** <sup>13</sup>C NMR spectrum of complex **6** in DMSO.



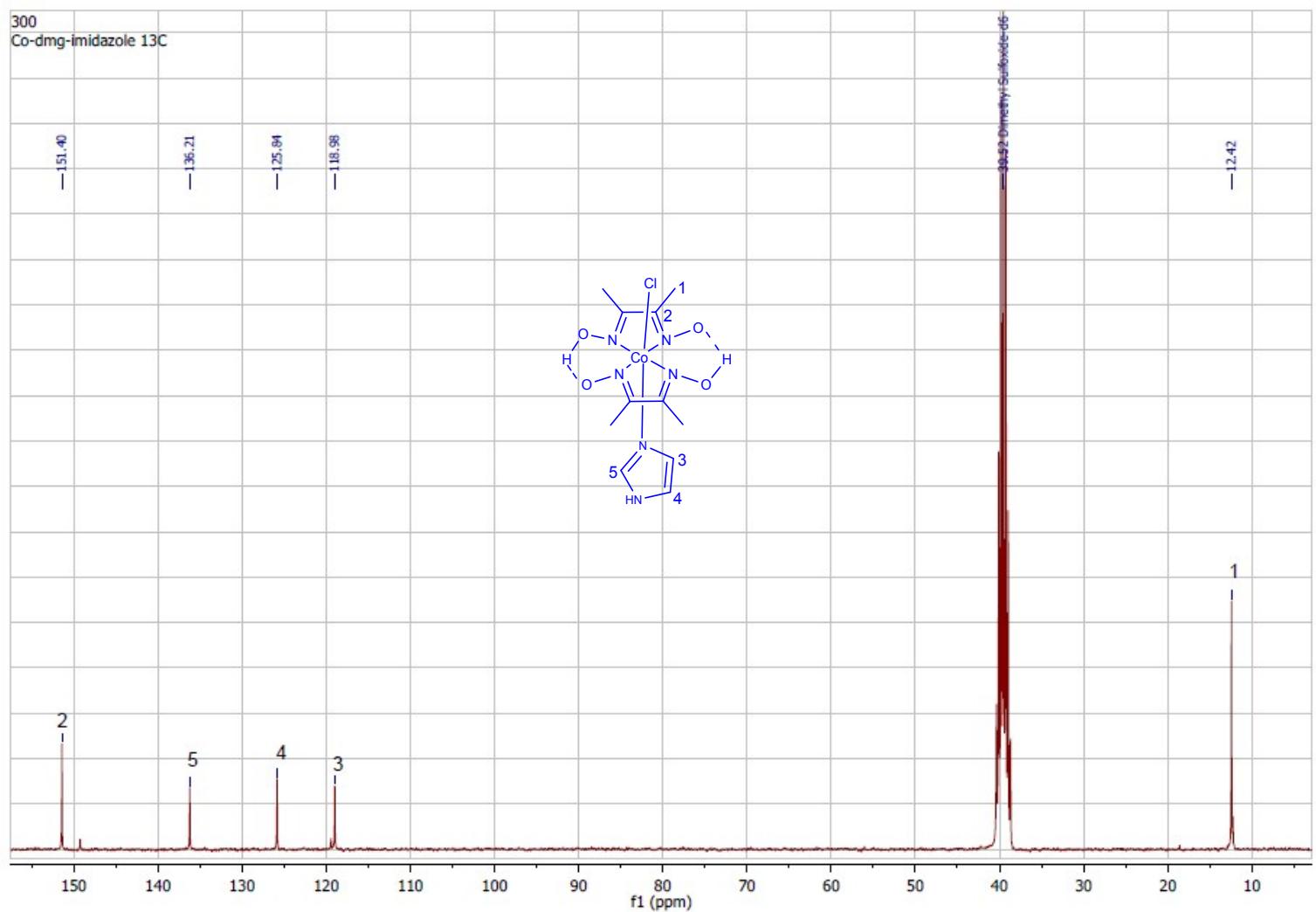
**Figure S42.**  $^1\text{H}$  NMR spectrum of complex 7 in DMSO.



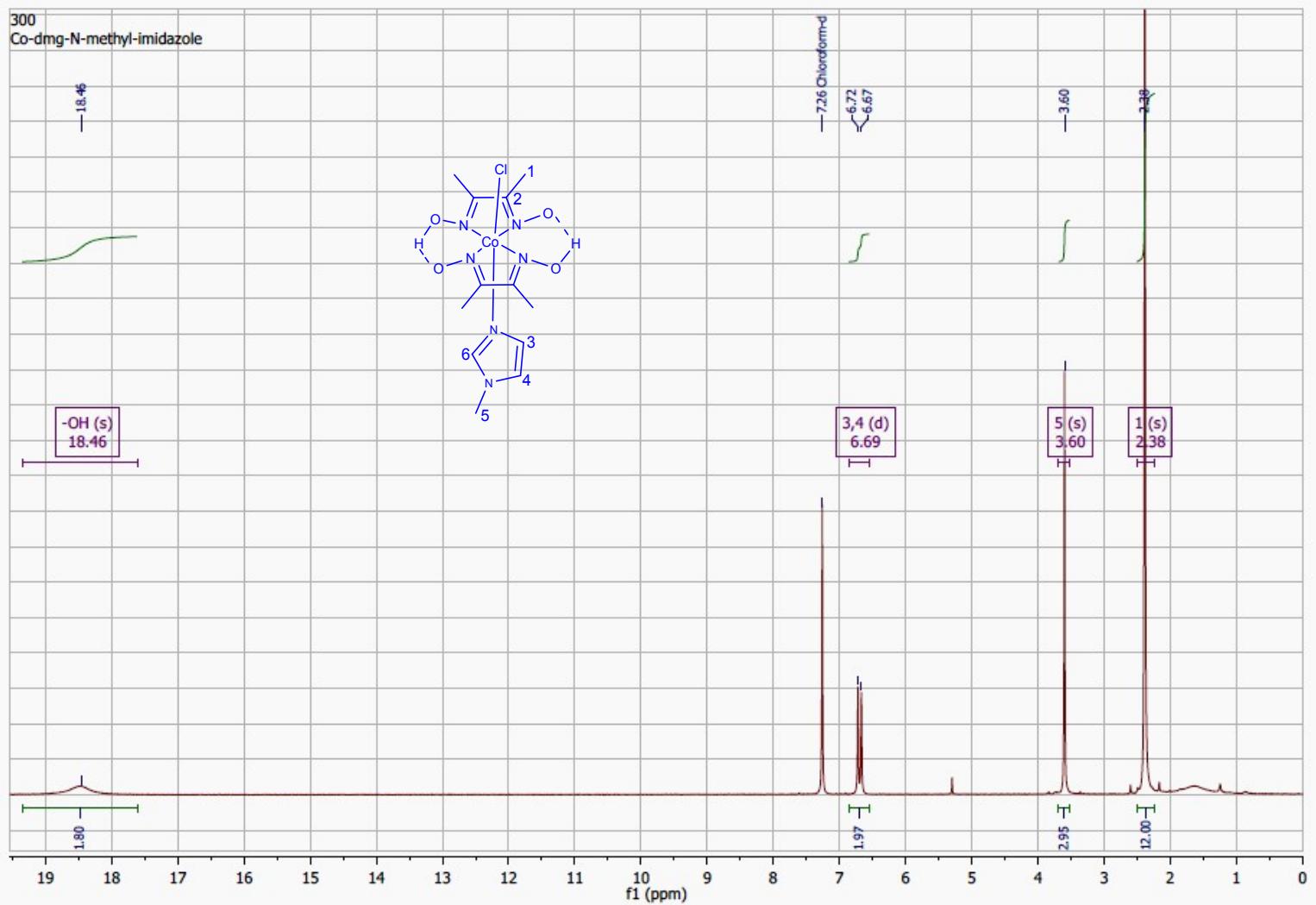
**Figure S43.**  $^{13}\text{C}$  NMR spectrum of complex 7 in DMSO.



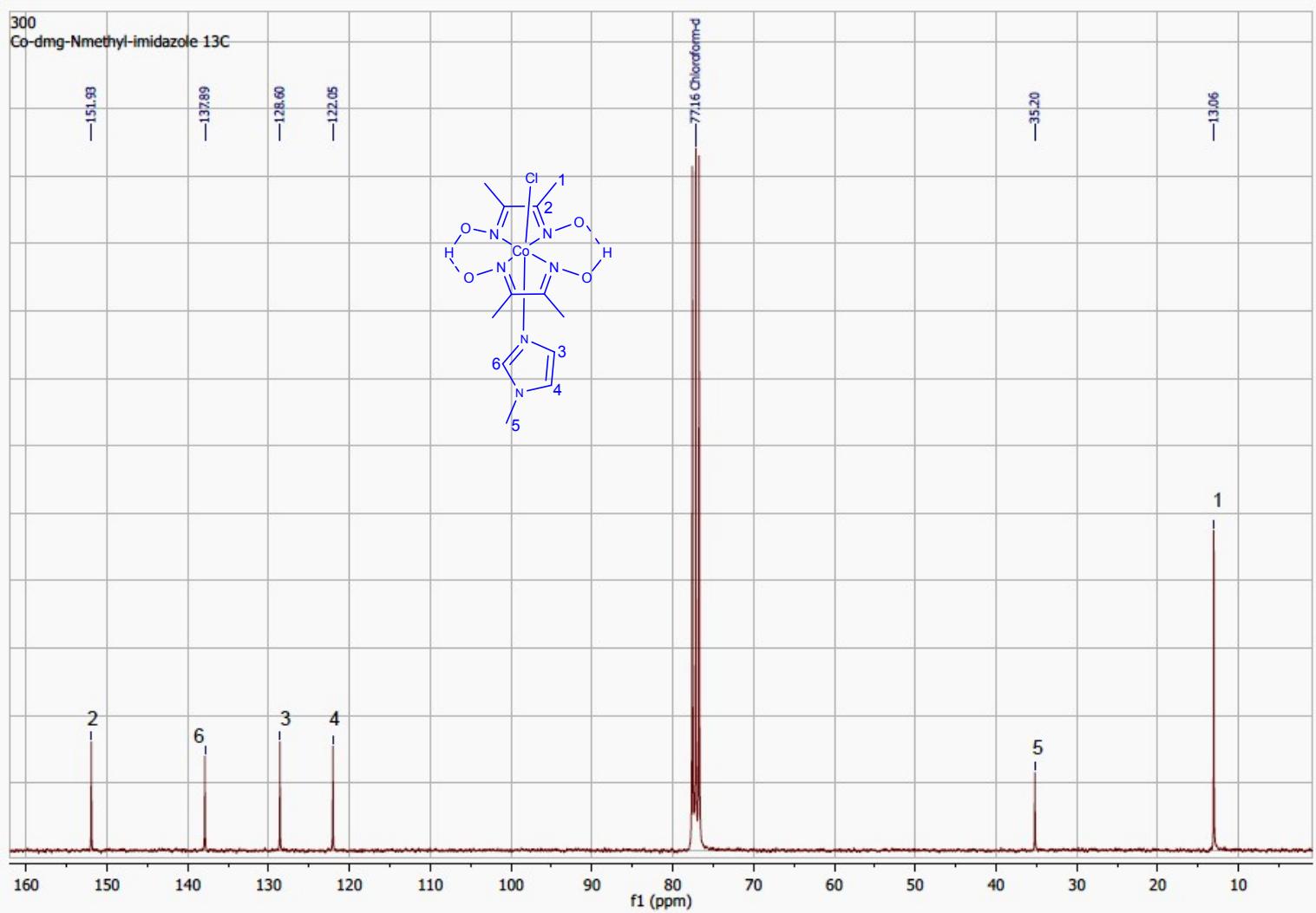
**Figure S44.**  $^1\text{H}$  NMR spectrum of complex **8** in DMSO.



**Figure S45.**  $^{13}\text{C}$  NMR spectrum of complex **8** in DMSO.

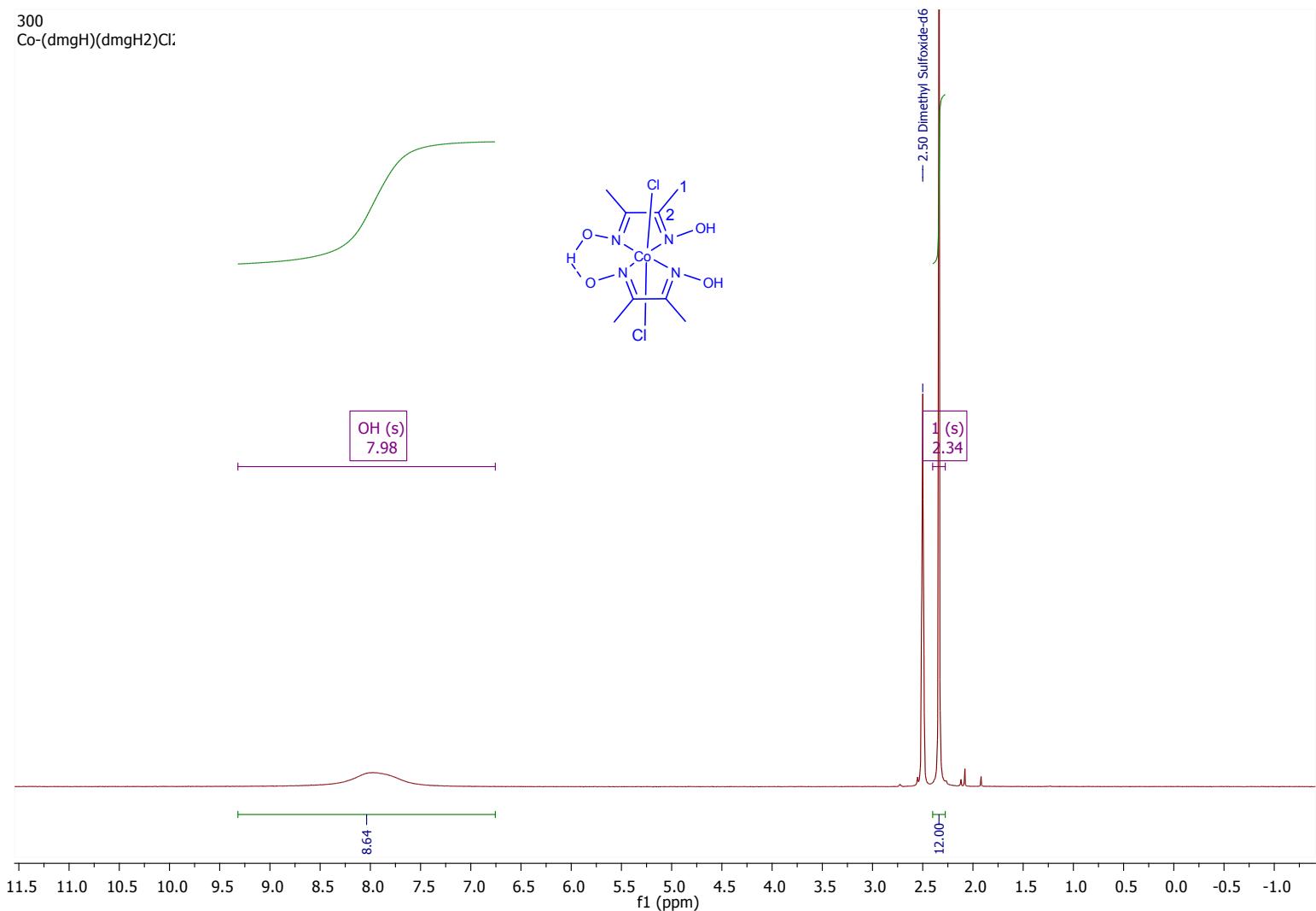


**Figure S46.**  $^1\text{H}$  NMR spectrum of complex **9** in  $\text{CDCl}_3$ .

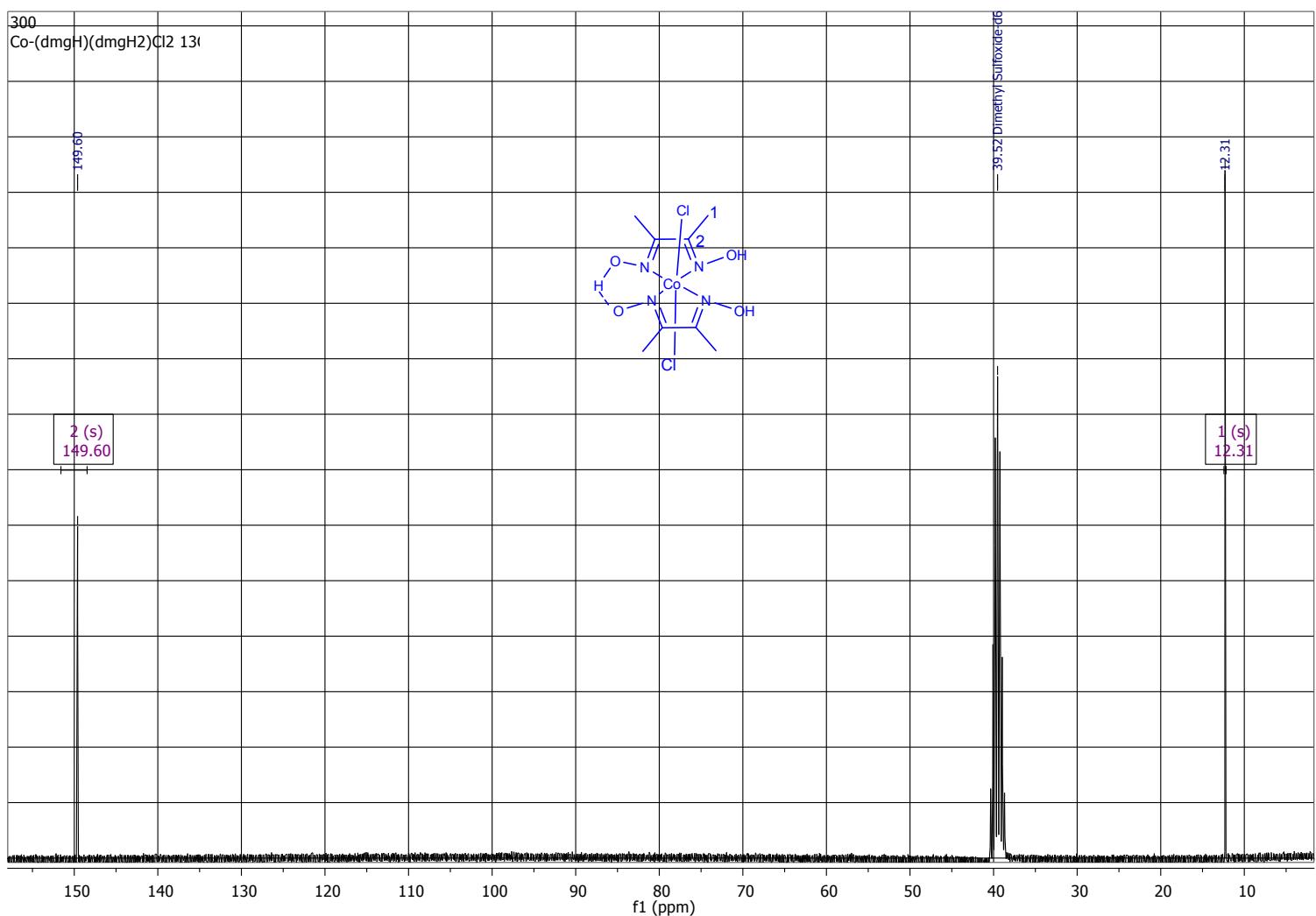


**Figure S47.**  $^{13}\text{C}$  NMR spectrum of complex **9** in  $\text{CDCl}_3$ .

300  
Co-(dmgh)(dmgh<sub>2</sub>)Cl:



**Figure S48.** <sup>1</sup>H NMR spectrum of complex **10** in DMSO.



**Figure S49.** <sup>13</sup>C NMR spectrum of complex **10** in DMSO.