

# Supporting Information

## 2-Phenylimidazole—PdCl<sub>2</sub> and 2-Phenylimidazoline—PdCl<sub>2</sub> Complexes; Single Crystal and Powder X-Ray Diffractometry, <sup>1</sup>H NMR Spectra and Comparison of Catalytic Activities in Coupling Reactions

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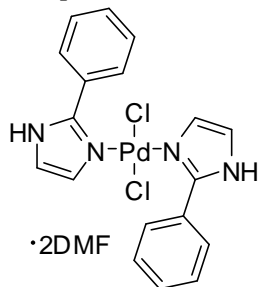
**General Methods and Materials.** All operations were performed under an atmosphere of dry argon using Schlenk and vacuum techniques. All starting materials were obtained from commercial sources and used without further purification unless otherwise stated. Methods A and B were used to grow single crystals of palladium complexes. Method A involves preparing a single crystal by slow diffusion of toluene into a DMF solution of palladium complexes. Method B involves preparing a single crystal by slow evaporation of DMF solution of palladium complexes under vacuum. Melting points were recorded with a Yanaco MP-J3 melting point apparatus, and are uncorrected. Infrared spectra were recorded with a Perkin Elmer FT-IR spectrometer SPECTRUM 1000.  $^1\text{H}$  NMR spectra were recorded with a JEOL JNM-GX-FT NMR 400 spectrometer. Chemical shifts are reported in ppm relative to  $\text{SiMe}_4$  as the internal standard. Spin-spin coupling constants,  $J$ , are given in Hz. Elemental analysis was performed on a Yanaco CHN CORDER MT-5.

## Experimental Procedure and Compound Characterization Data

**Synthesis of dichlorobis(2-phenyl-1*H*-imidazole)palladium( ) (complex 1).** To a suspension of PdCl<sub>2</sub> (177.3 mg, 1.0 mmol) in DMF (5 mL) was added, 2-phenylimidazole (288.4 mg, 2.0 mmol) under argon atmosphere. The mixture was stirred at 50 °C for 2 h until a clear orange yellow solution was formed. After diluting of the resultant solution with DMF (10 mL), toluene (40 mL) was added to precipitate the Pd complex. The Pd complex was isolated as a light yellow powder by filtration, washed with toluene and dried in air. Yield: 438.0 mg (93%). Anal. Calcd. for C<sub>18</sub>H<sub>16</sub>N<sub>4</sub>Cl<sub>2</sub>Pd: C, 46.47; H, 3.46; N, 12.03. Found: C, 46.47; H, 3.53; N, 12.06.

A single crystal of complex 1 [(2-phenylimidazole)<sub>2</sub>PdCl<sub>2</sub>·2DMF] suitable for XRD analysis was obtained by slow diffusion of toluene (2 mL) into a solution containing 60.0 mg of (2-phenylimidazole)<sub>2</sub>PdCl<sub>2</sub> powder in DMF (5 mL) (method A). Yield: 31.7 mg (41%). A single crystal of complex 1 [(2-phenylimidazole)<sub>2</sub>PdCl<sub>2</sub>·2DMF] suitable for XRD analysis was obtained directly by slow evaporation of the resultant solution under vacuum (method B).

*Complex 1·2DMF*



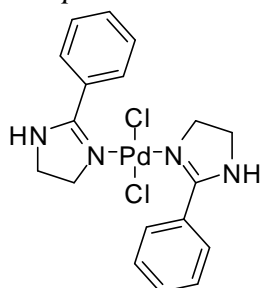
Mp > 300 °C; IR (KBr):  $\nu_{\max}$  (cm<sup>-1</sup>) 3184, 3158, 3117, 1661, 1568, 1506, 1390, 1108, 777, 718, 708, 694, 664; <sup>1</sup>H NMR (400 MHz, DMF-*d*<sub>7</sub>):  $\delta$  13.27 (s, 1H), 8.89 (d, *J* = 7.6 Hz, 2H), 7.67 (dd, *J* = 7.6, 6.4 Hz, 2H); 7.60 (t, *J* = 6.4 Hz, 1H), 7.48 (d, *J* = 1.2 Hz, 2H); Anal. Calc. for C<sub>24</sub>H<sub>30</sub>N<sub>4</sub>O<sub>2</sub>Cl<sub>2</sub>Pd: C, 47.11; H, 4.94; N, 13.74. Found: C, 46.99; H, 4.95; N, 13.61.

**Synthesis of dichlorobis(2-phenyl-4, 5-dihydro-1*H*-imidazole)palladium( ) (complex 2).** To a suspension of PdCl<sub>2</sub> (177.3 mg, 1.0 mmol) in DMF (3 mL) was added 2-phenylimidazoline (292.4 mg,

2.0 mmol) under argon atmosphere. The mixture was stirred at 70 °C for 1 h until a clear orange solution was formed.

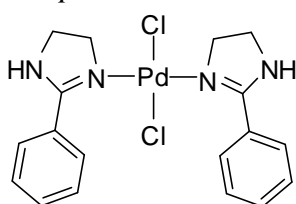
A single crystal of complex **2** suitable for XRD analysis was obtained by slow diffusion of toluene into the resultant solution (method A). After diluting of the resultant solution with DMF (10 mL), toluene (40 mL) was carefully added to the DMF solution of the complex. After three days, orange crystal **2** was obtained by filtration and dried in air. Yield: 329.0 mg (70%). A single crystal of complex **2'** suitable for X-ray diffraction analysis was directly obtained by slow evaporation of the resultant solution under vacuum (method B). A yellow orange crystal was isolated by filtration and dried in air.

*Complex 2*



Mp 239 °C (dec.); IR (KBr):  $\nu_{\max}$  (cm<sup>-1</sup>) 3267, 3242, 2963, 2879, 1616, 1598, 1578, 1511, 1485, 1469, 1274, 1185, 1147, 776, 701; <sup>1</sup>H NMR (400 MHz, DMF-*d*<sub>7</sub>):  $\delta$  8.67 (d, *J* = 7.6 Hz, 2H), 7.96 (s, 1H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.57 (dd, *J* = 7.6, 7.2 Hz, 2H), 4.03 (t, *J* = 10.4 Hz, 2H), 3.63 (t, *J* = 10.4 Hz, 2H); Anal. Calcd. for C<sub>18</sub>H<sub>20</sub>N<sub>4</sub>Cl<sub>2</sub>Pd: C, 46.03; H, 4.29; N, 11.93. Found: C, 45.45; H, 4.41; N, 11.86.

*Complex 2'*

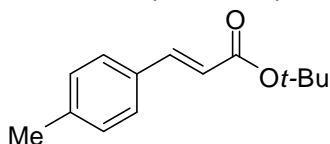


Mp 230 °C (dec.); IR (KBr):  $\nu_{\max}$  (cm<sup>-1</sup>) 3271, 2875, 1610, 1601, 1577, 1512, 1472, 1270, 1187, 775,

698;  $^1\text{H}$  NMR (400 MHz, DMF- $d_7$ ):  $\delta$  8.67 (d,  $J = 7.6$  Hz, 2H), 7.96 (s, 1H), 7.65 (t,  $J = 7.2$  Hz, 1H), 7.57 (dd,  $J = 7.6, 7.2$  Hz, 2H), 4.03 (t,  $J = 10.4$  Hz, 2H), 3.63 (t,  $J = 10.4$  Hz, 2H); Anal. Calcd. For  $\text{C}_{18}\text{H}_{20}\text{N}_4\text{Cl}_2\text{Pd}$ : C, 46.03; H, 4.29; N, 11.93. Found: C, 45.99; H, 4.27; N, 11.88.

**General procedure for Mizoroki-Heck reaction.**  $\text{K}_2\text{CO}_3$  (553 mg, 4.0 mmol) was added to a Schlenk tube equipped with a stirring bar and the tube was dried under vacuum and then filled with argon, 4-bromotoluene (342.0 mg, 2.0 mmol) and *tert*-butyl acrylate (256.4 mg, 2.0 mmol) in DMF (10 mL). Then 1 mL of the solution of 0.02 mmol/mL palladium complex in DMF was added *via* a syringe under argon atmosphere. The mixture was stirred at 120 °C for the indicated reaction time. After the completion of the reaction, the mixture was cooled, the precipitate was removed by filtration and the product was extracted from the filtrate with diethyl ether. The combined organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and filtered. After evaporation, the obtained residue was purified by silica-gel column chromatography to give the Mizoroki-Heck product.

*(E)*-*tert*-Butyl-4-methylcinnamate

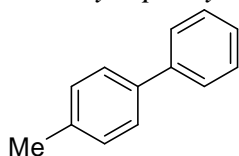


$R_f = 0.71$  (5:1 hexane-ethyl acetate); mp-oil; IR (KBr):  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 2978, 2931, 1708, 1636, 1609, 1514, 1392, 1367, 1324, 1282, 1256, 1207, 1150, 983, 875, 814;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.58 (d,  $J = 16.0$  Hz, 1H), 7.39 (d,  $J = 8.0$  Hz, 2H), 7.16 (d,  $J = 8.0$  Hz, 2H), 6.33 (d,  $J = 16.0$  Hz, 1H), 2.35 (s, 3H), 1.54 (s, 9H);  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.4, 143.4, 140.1, 131.8, 129.4, 127.8, 118.9, 80.1, 28.1, 21.3.

**General procedure for Suzuki coupling reaction.**  $\text{K}_2\text{CO}_3$  (553 mg, 4 mmol) was added to a Schlenk tube equipped with a stirring bar and the tube was dried under vacuum and filled with argon,

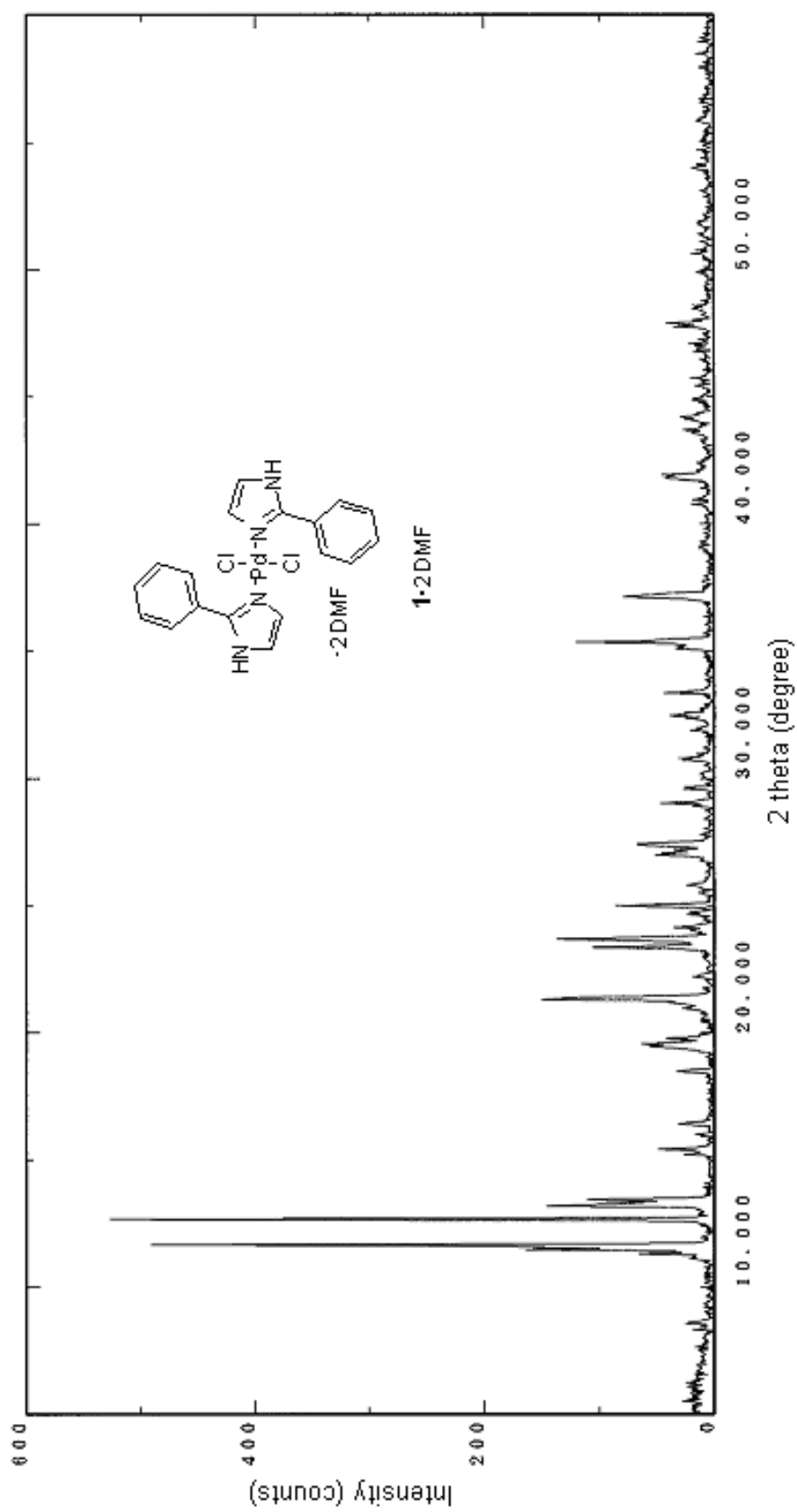
4-bromotoluene (342.0 mg, 2.0 mmol) and dihydroxyphenylborane (244.0 mg, 2.0 mmol) in DMF (10 mL). Then 1 mL of the solution of 0.02 mmol/mL palladium complex in DMF was added *via* a syringe under argon atmosphere. The mixture was stirred at 120 °C for the indicated reaction time. The mixture was cooled and then the precipitate was removed by filtration and the product was extracted from the filtrate with diethyl ether. The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered. After evaporation, the obtained residue was purified by silica-gel column chromatography to give the coupling product.

*4-Methylbiphenyl*

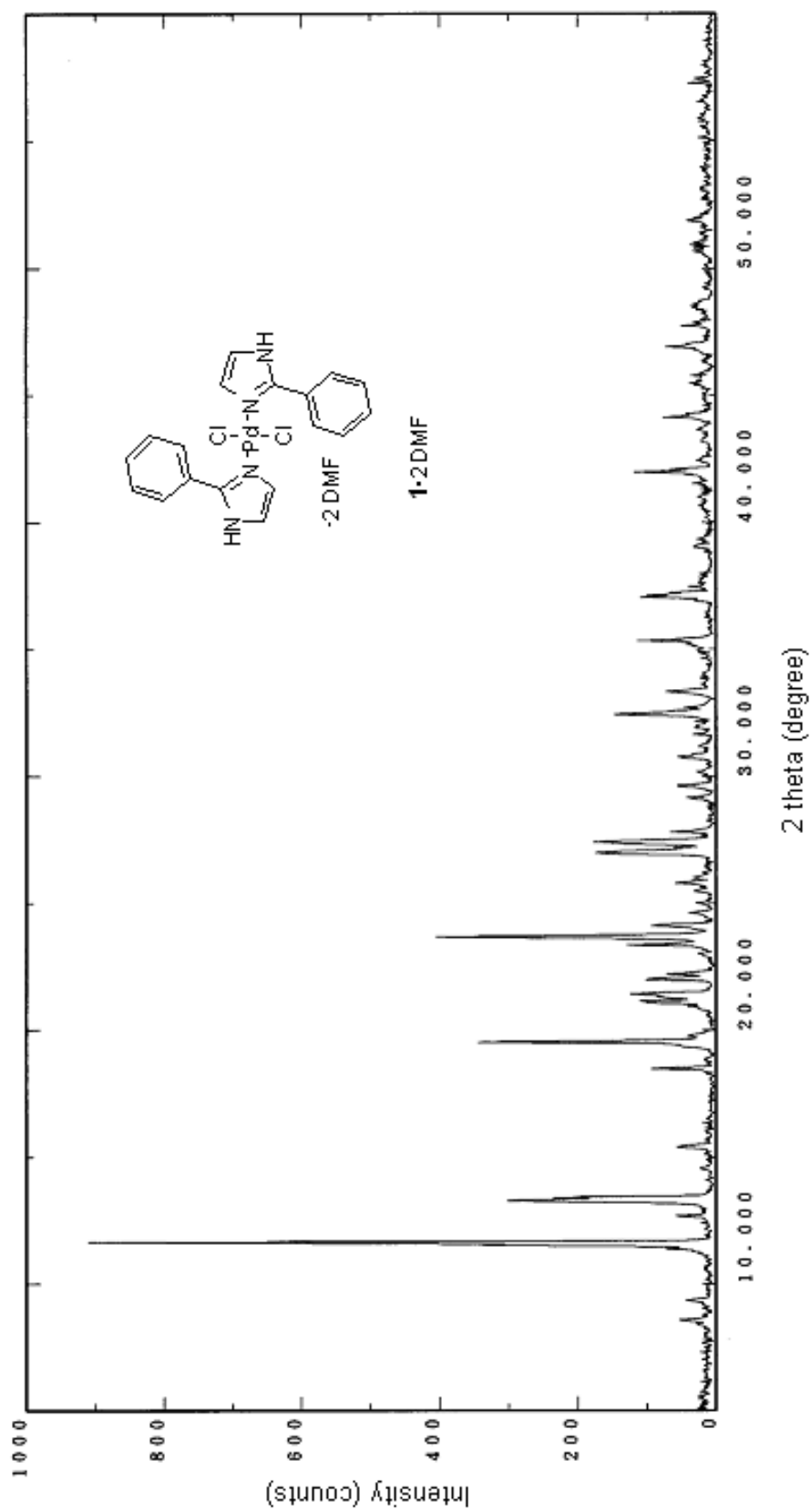


R<sub>f</sub> = 0.78 (5:1 hexane-ethyl acetate); mp 42-44 °C; (KBr):  $\nu_{\max}$  (cm<sup>-1</sup>) 3299, 3183, 2971, 2935, 2871, 1647, 1573, 1490, 1448, 1386, 1360, 1287, 1249, 1186, 971, 940, 689, 559; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.59 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 2H), 2.41 (s, 3H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  141.1, 138.3, 137.0, 129.4, 128.7, 127.0, 126.9, 21.1.

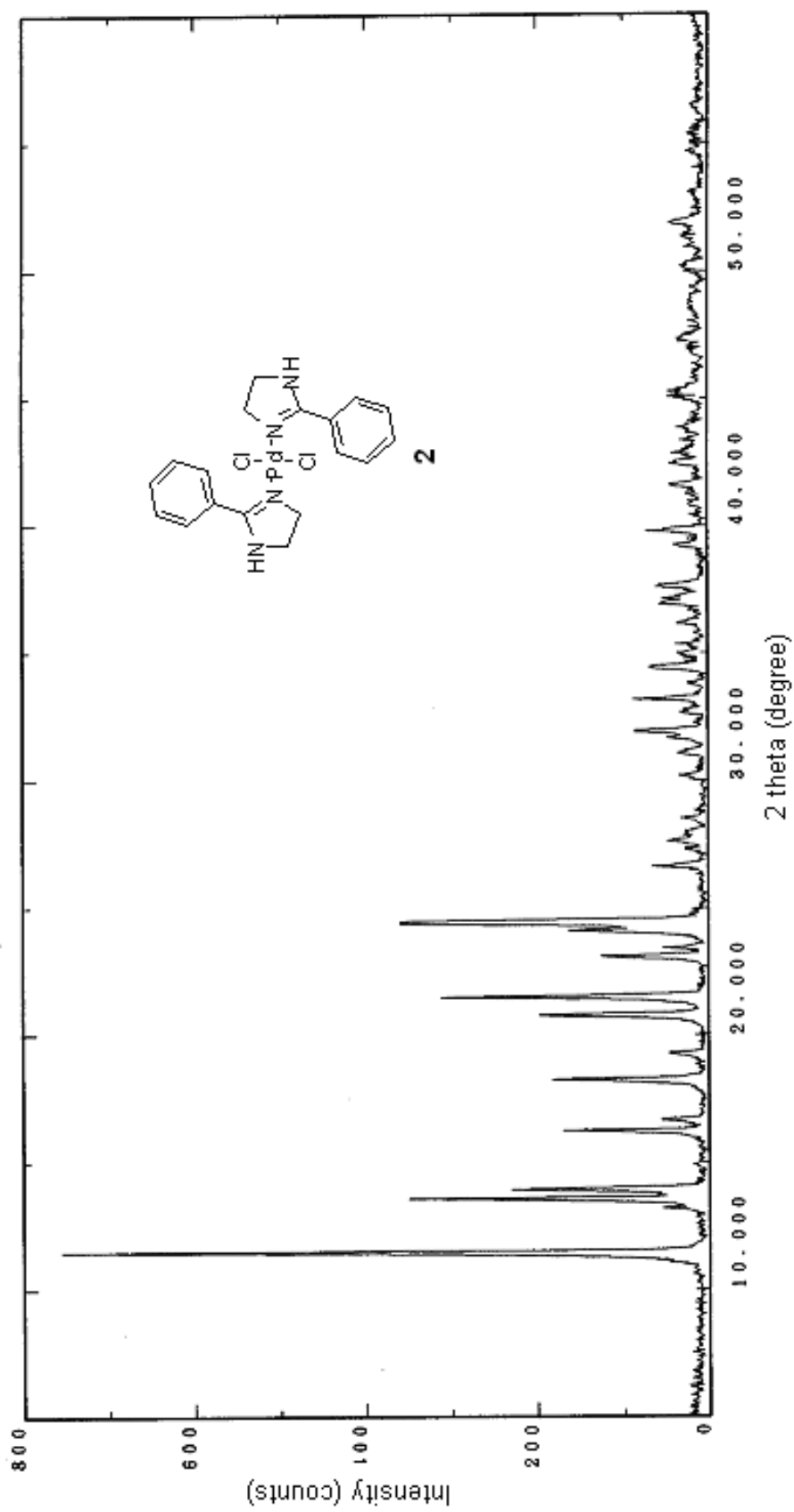
## Powder X-Ray Diffraction Data



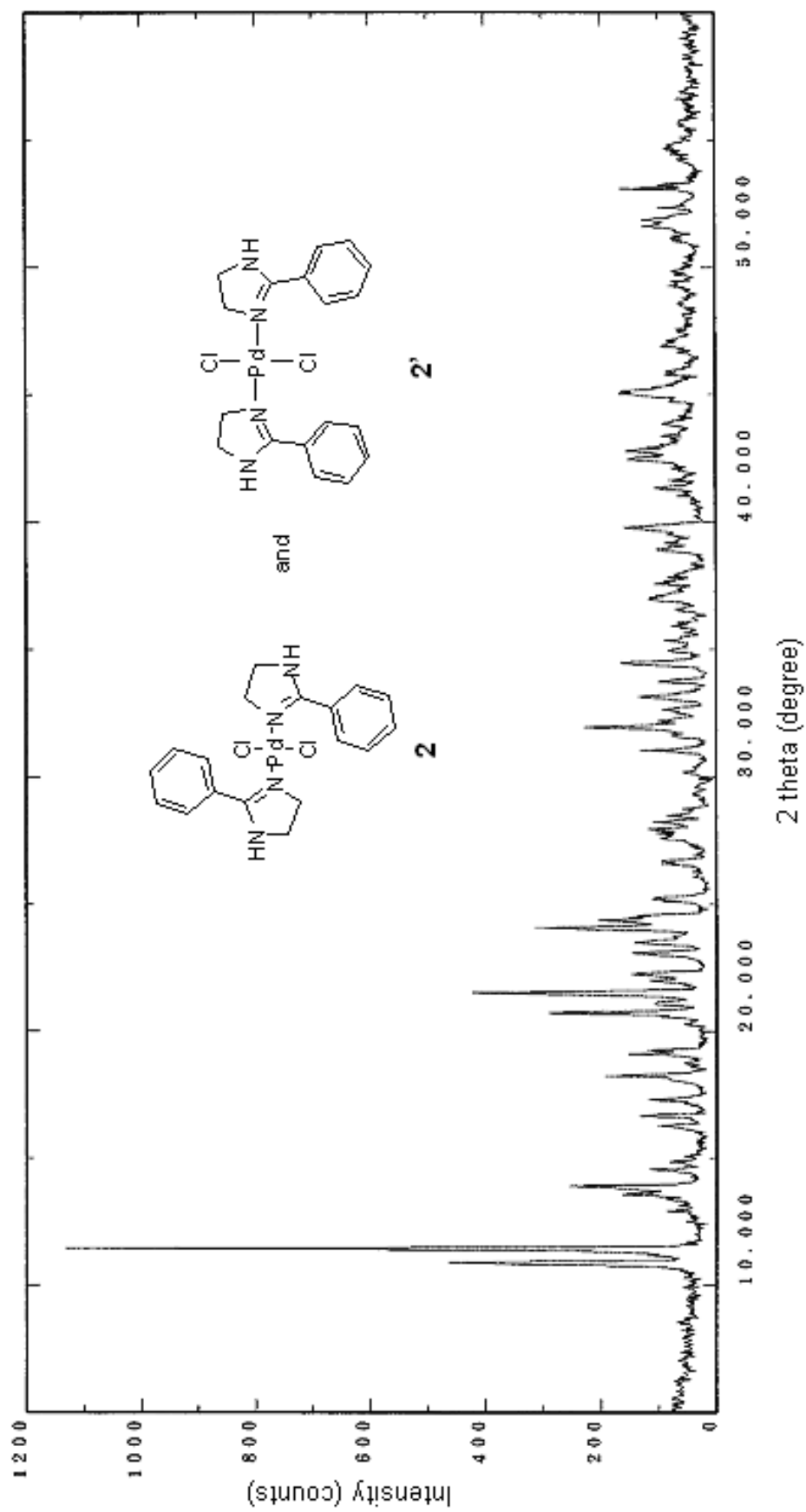
**Figure S1.** Powder XRD chart of complex 1·2DMF (method A).



**Figure S2.** Powder XRD chart of complex 1·2DMF (method B).

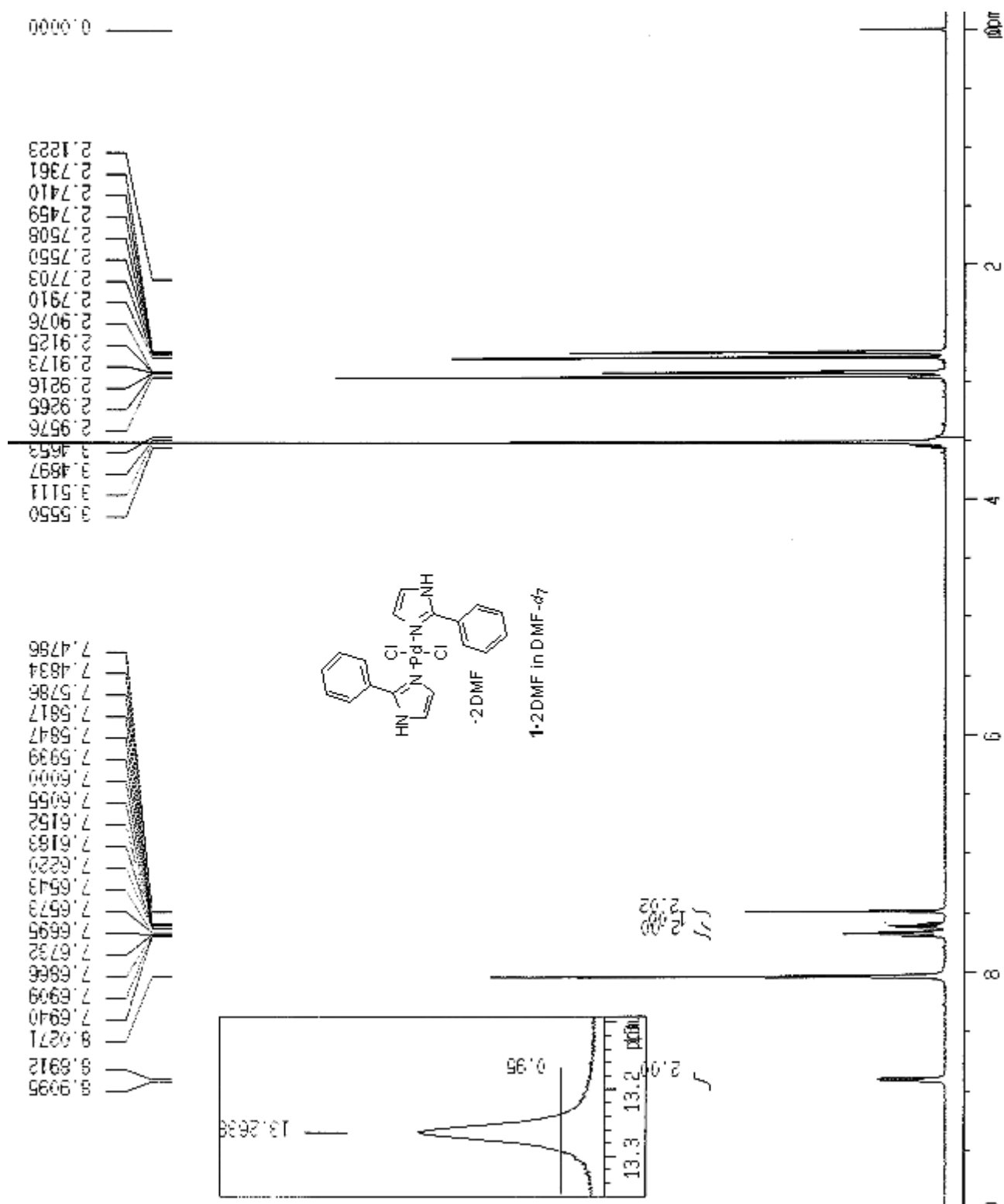


**Figure S3.** Powder XRD chart of complex **2** (method A).

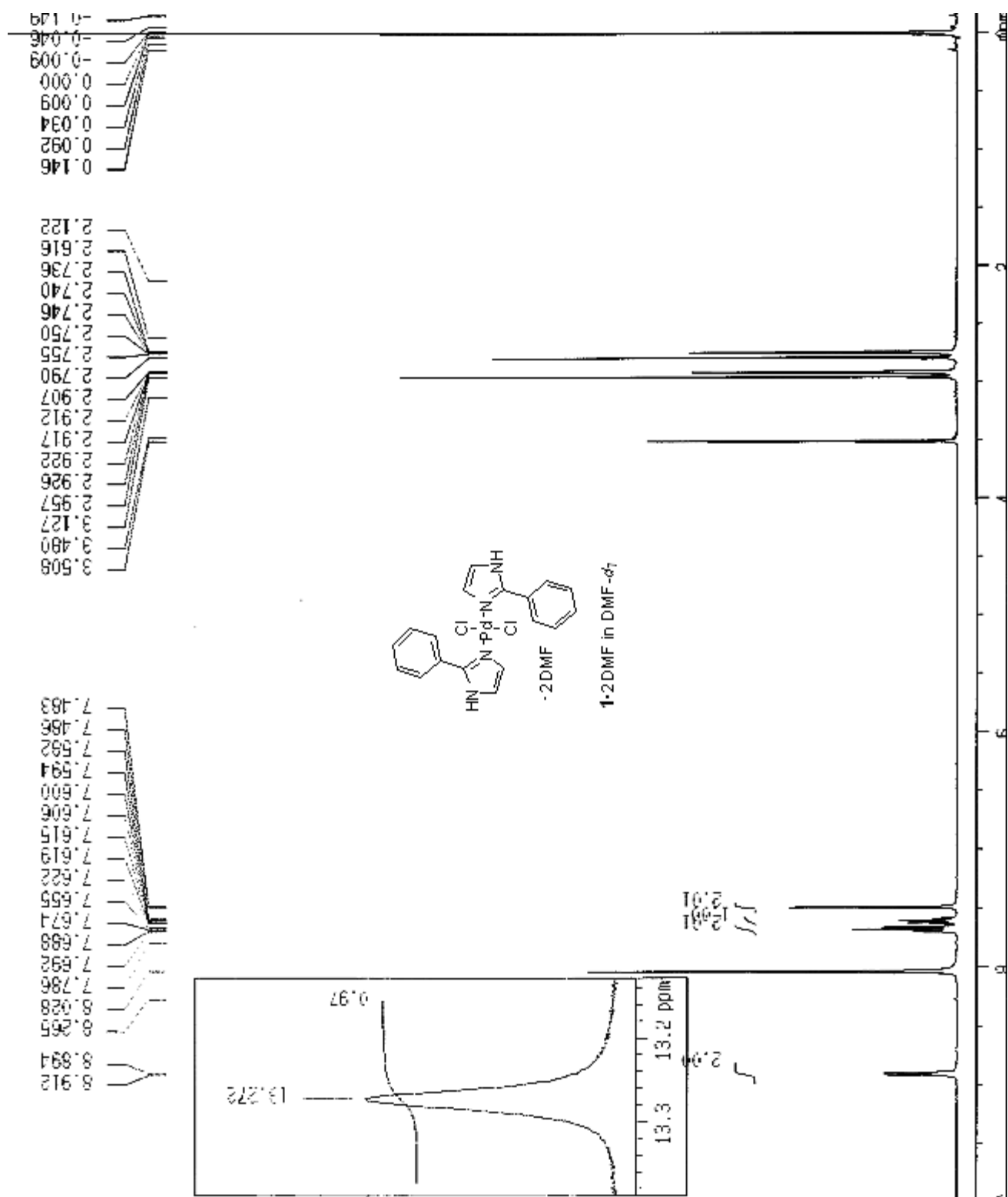


**Figure S4.** Powder XRD chart of complexes **2** and **2'** (method B).

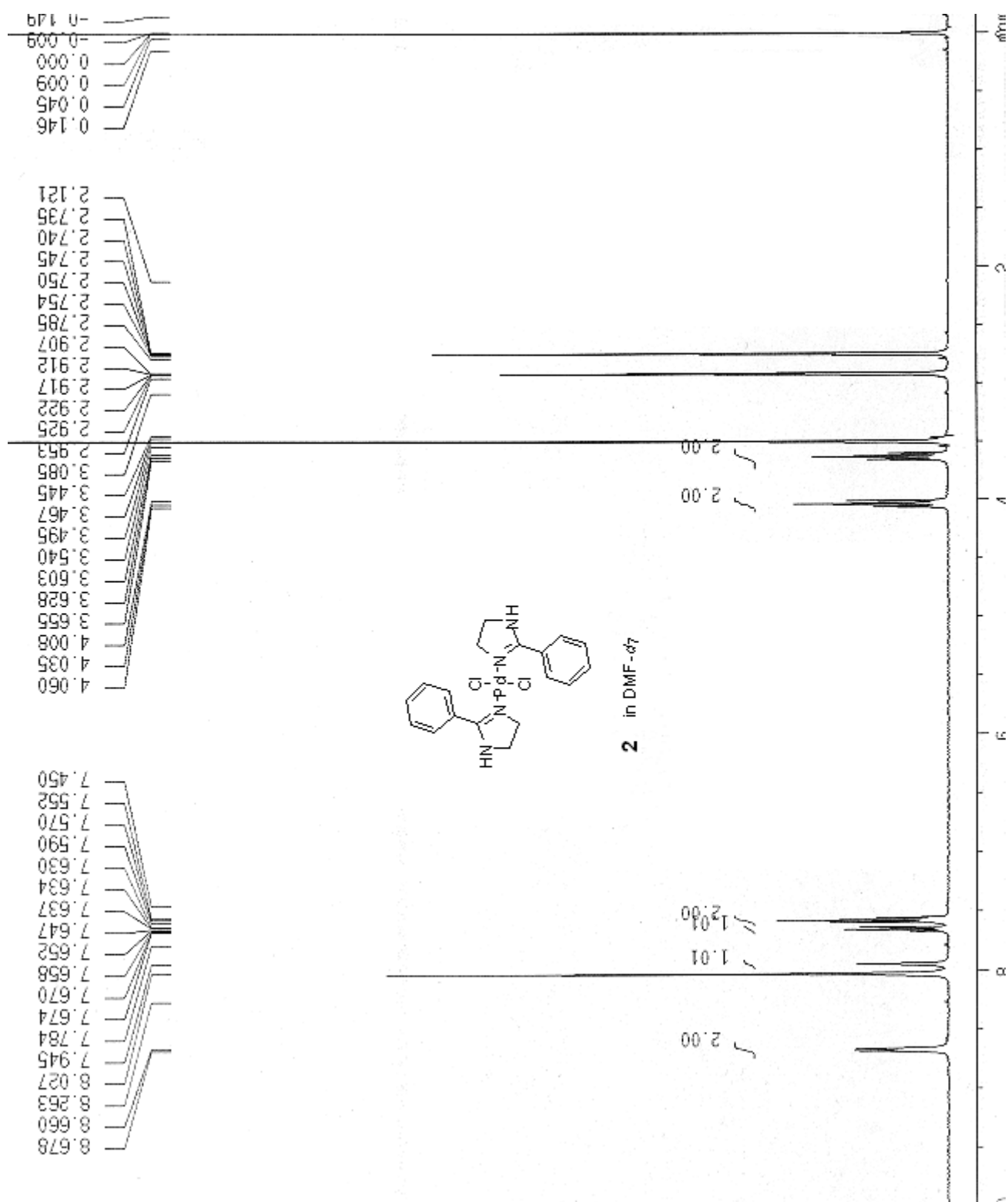
# <sup>1</sup>H NMR Spectra of Palladium Complexes



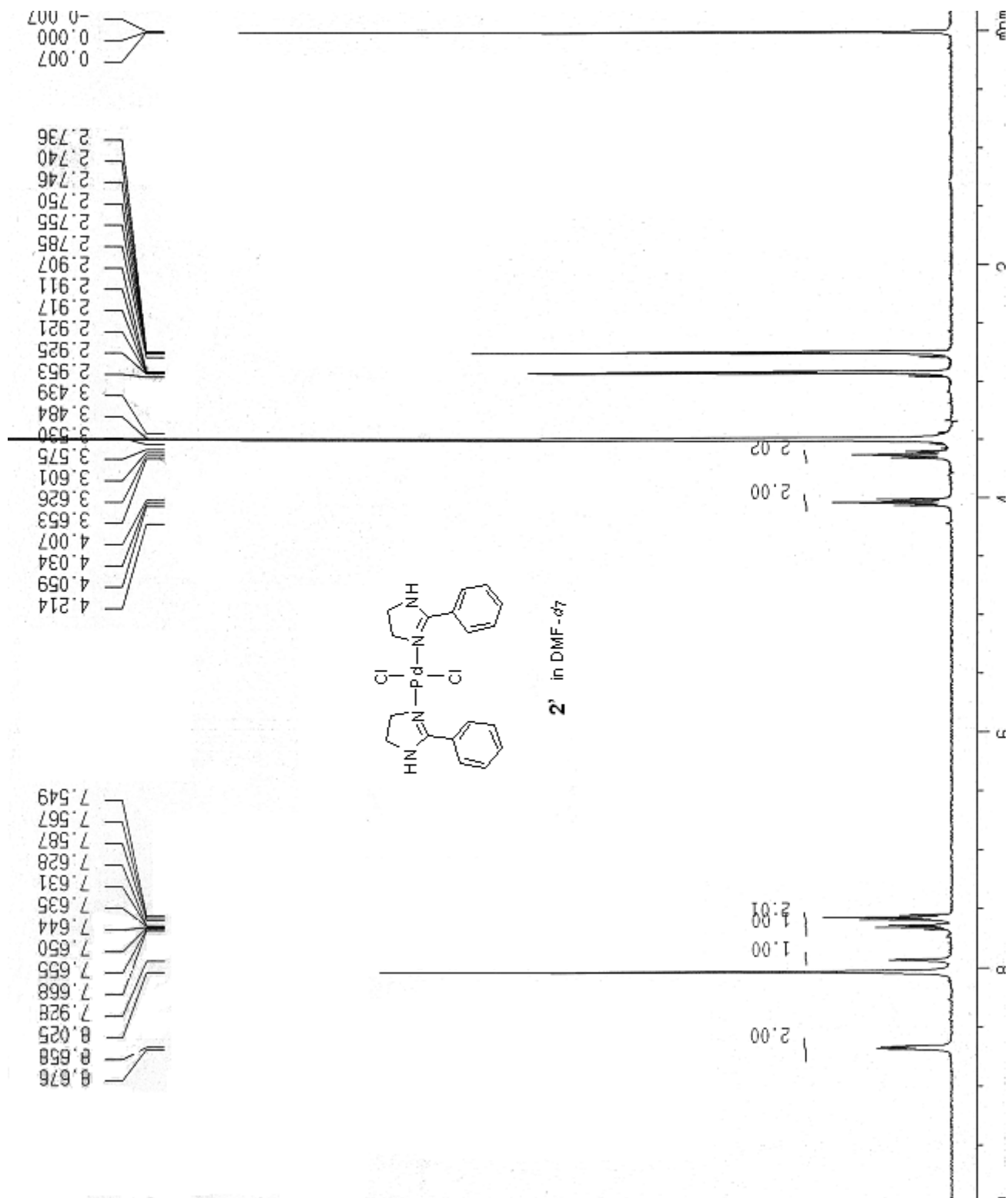
**Figure S5.** <sup>1</sup>H NMR spectrum of complex 1·2DMF in DMF-*d*<sub>7</sub> (The measured sample of the complex 1·2DMF was obtained by method A).



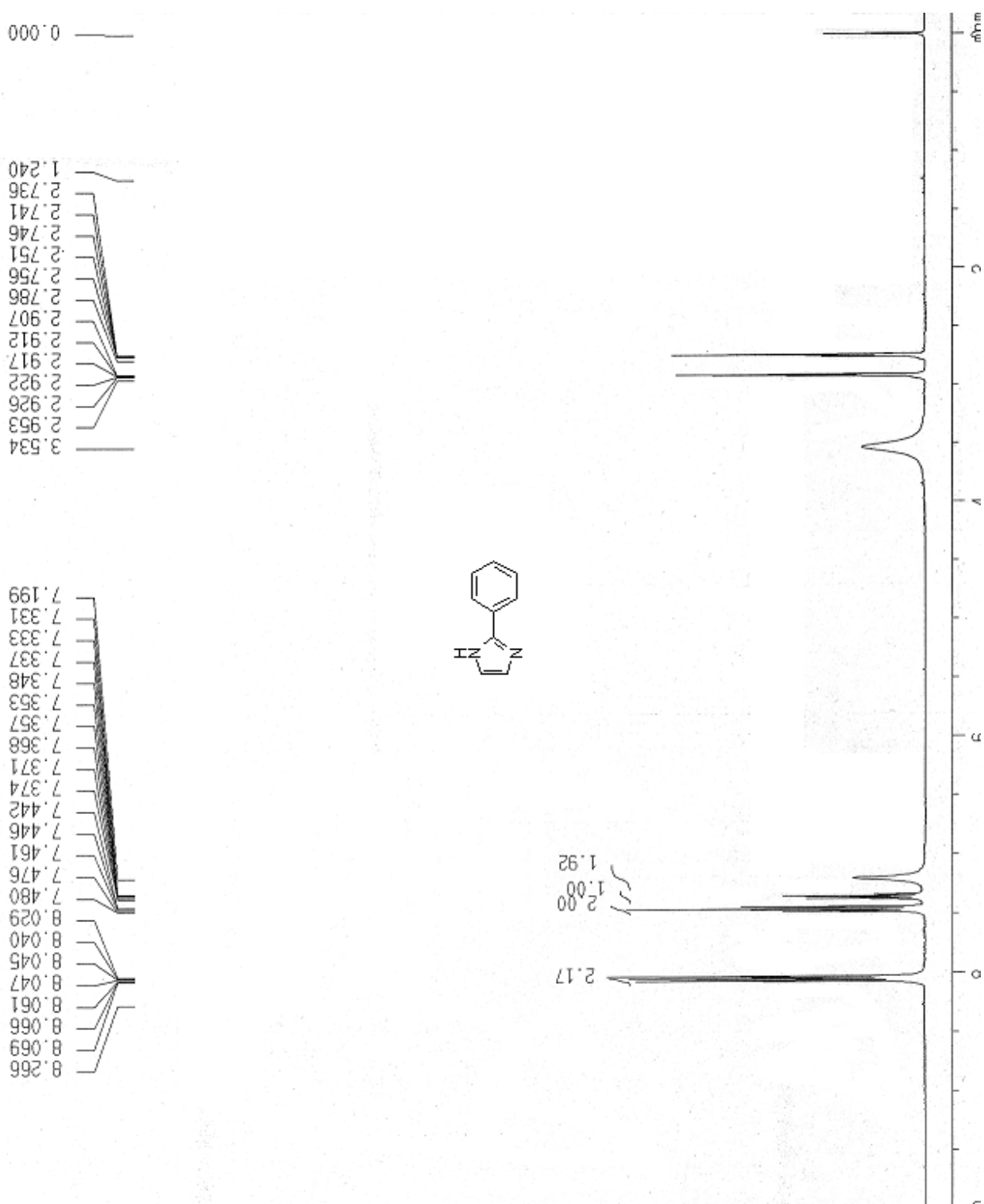
**Figure S6.**  $^1\text{H}$  NMR spectrum of complex **1·2DMF** in  $\text{DMF-}d_7$  (The measured sample of the complex **1·2DMF** was obtained by method B).



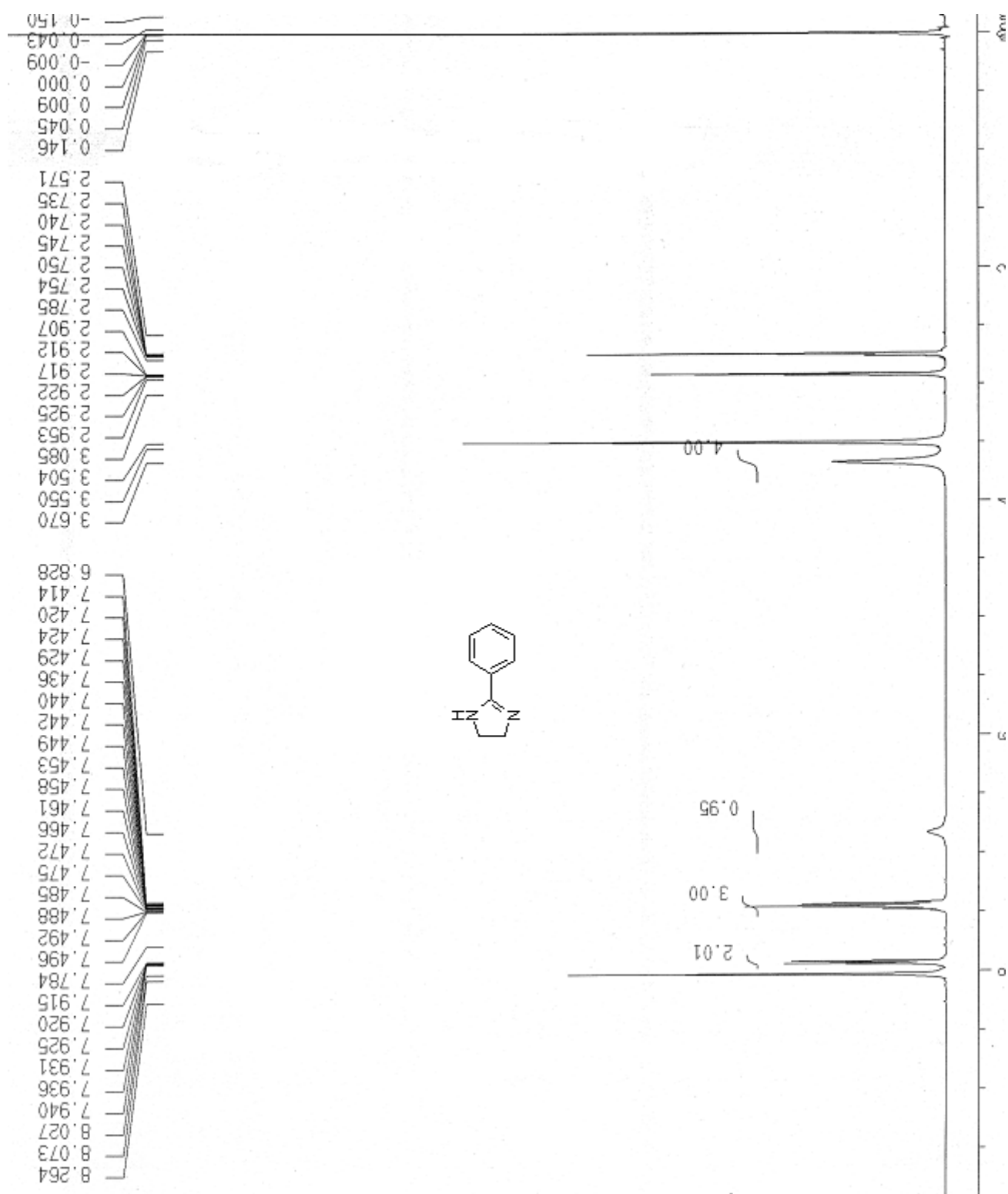
**Figure S7.** <sup>1</sup>H NMR spectrum of complex **2** in DMF-*d*<sub>7</sub> (The measured sample of the complex **2** was obtained by method A).



**Figure S8.**  $^1\text{H}$  NMR spectrum of complex **2'** in  $\text{DMF-}d_7$  (The measured sample of the complex **2'** was obtained by method B and characterized by single crystal X-ray diffraction analysis).



**Figure S9.** <sup>1</sup>H NMR spectrum of 2-phenyl-1*H*-imidazole in DMF-*d*<sub>7</sub>.



**Figure S10.** <sup>1</sup>H NMR spectrum of 2-phenyl-4,5-dihydro-1H-imidazole in DMF-d<sub>7</sub>.