

## Supporting Information

### **Catalytic Aerobic Oxidation of Substituted 8-Methylquinolines in Pd<sup>II</sup> – 2,6-Pyridinedicarboxylic Acid Systems**

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### **References**

**General.** All manipulations were carried out under purified argon using standard Schlenk and glove-box techniques. Solvents were dried and distilled following standard protocols and stored in gas-tight bulbs under argon. All reagents for which a synthesis is not given are commercially available from Aldrich, Acros, Alfa Aesar or Pressure Chemicals and were used as received without further purification. Deuterated solvents from Cambridge Isotope Laboratories were dried, vacuum-transferred and stored in an argon-filled glove box.

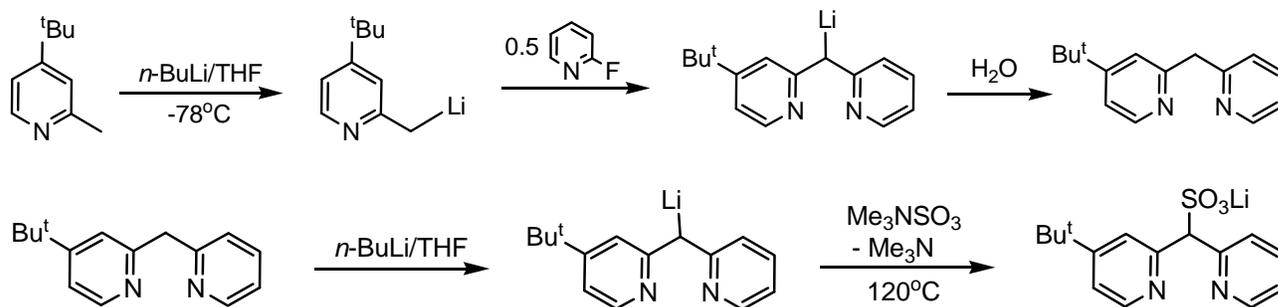
Compounds **1b**,<sup>1</sup> **1c**,<sup>2</sup> **1f**,<sup>2</sup> **1g**,<sup>3</sup> **1h**,<sup>2</sup> **3a**,<sup>4</sup> **3d**<sup>2</sup> were prepared according to published procedures.

<sup>1</sup>H (400.132 MHz) and <sup>13</sup>C NMR (100.625 MHz) spectra were recorded on a Bruker Avance 400 spectrometer. Chemical shifts are reported in ppm and referenced to residual solvent resonance peaks. Elemental analyses were carried out by Chemisar Laboratories Inc., Guelph, Canada.

**Computational details.** Theoretical calculations in this work have been performed using density functional theory (DFT) method,<sup>5</sup> specifically functional PBE,<sup>6</sup> implemented in an original program package “Priroda”.<sup>7</sup> In PBE calculations relativistic Stevens-Basch-Krauss (SBK) effective core potentials (ECP)<sup>8</sup> optimized for DFT-calculations have been used. Basis set was 311-split for main group elements with one additional polarization *p*-function for hydrogen, additional two polarization *d*-functions for elements of higher periods. Full geometry optimization has been performed without constraints on symmetry. For all species under investigation frequency analysis has been carried out. All minima have been checked for the absence of imaginary frequencies. All transition states possessed just one imaginary frequency. Using method of Intrinsic Reaction Coordinate, reactants, products and the corresponding transition states were proven to be connected by a single minimal energy reaction path.

## 1. Synthesis of ligands

### Lithium 4-*tert*-Butylpyridyl-pyridyl methanesulfonate, Li(*t*-Bu-dpms)



**A. 4-*tert*-butyl-2-pyridyl-2-pyridylmethane.** 2-methyl-4-*tert*-butylpyridine was prepared by the method of Ogawa et al.<sup>9</sup> The compound was obtained as a mixture of product and starting material (4-*tert*-butylpyridine) ranging from a 4:1 to a 9:1 ratio and was used without further purification. In the current example, a 87:13 mixture is used and the amount of other reactants was calculated on the basis of 2-methyl-4-*tert*-butylpyridine that was present in the mixture. 3g of the colorless liquid 87:13 mixture (17.5 mmol 2-methyl-4-*tert*-butylpyridine) were placed in a dry reaction flask under Argon and 100 ml. of dry THF were added. The temperature was lowered to  $-78^{\circ}\text{C}$  and 8.74 ml of 2M BuLi solution in cyclohexane (1.75 mmol) were added. The solution was allowed to slowly warm up to room temperature until it turned a dark brown color. The temperature of the reaction was lowered to  $-10^{\circ}\text{C}$  and 0.69 ml of 2-fluoropyridine (8.7 mmol) was slowly added with vigorous stirring while carefully maintaining the temperature at the  $-10^{\circ}\text{C}$  to  $-3^{\circ}\text{C}$  range. After addition, the solution developed a dark, black color and was allowed to warm up to room temperature and stir for 3 hours (or alternatively overnight). The reaction mixture was quenched with water over a cold water bath, extracted with diethyl ether with the extracts washed with water (2 x 100 ml) and saturated NaCl solution (1 x 50 ml). The collected organic extract was dried over  $\text{MgSO}_4$  and concentrated on the rotavap. The product was purified by flash column chromatography (ether/hexane : 3/7), and concentrated to give a light, yellow oil that was > 98% pure by NMR and GC (0.74g., 37.4% yield).

$^1\text{H}$  NMR ( $22^{\circ}\text{C}$ ,  $\text{CDCl}_3$ ),  $\delta$ : 8.39 (d,  $J = 4.80$  Hz, 1H), 8.31 (d,  $J = 5.34$  Hz, 1H), 7.43 (dt,  $J = 7.67$ , 1.82 Hz, 1H), 7.18-7.10 (m, 2H), 6.98 (dd,  $J = 5.33$ , 1.86 Hz, 1H), 6.95 (dd,  $J = 7.41$ , 5.00 Hz, 1H), 4.20 (s, 2H), 1.12 (s, 9H).

$^{13}\text{C}$  NMR (22°C,  $\text{CDCl}_3$ ),  $\delta$ : 160.53, 159.5, 159.0, 149.2, 149.1, 136.4, 123.5, 121.3, 120.5, 118.6, 47.3, 34.5, 30.4.

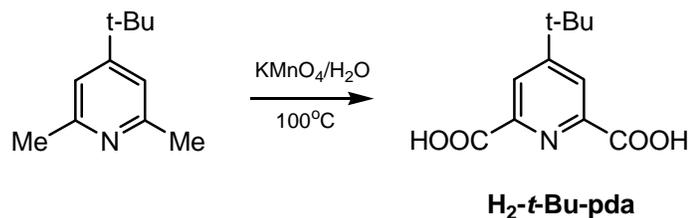
**B. The sulfonation step** was carried out similar to publication.<sup>10</sup> 2.1 g of 4-*tert*-butylpyridyl-pyridyl methane (9.3mmol) were added to a 100ml Schlenk flask filled with 20 mL of dry THF under argon. The solution was cooled to 0°C and 3.71 mL of 2.5M *n*-butyl lithium (9.3 mmol) were added. The solution was allowed to reach room temperature and after half an hour, 1.29 g of trimethyl amine sulfonate complex (9.3 mmol) were added. The Schlenk flask was then closed with a Teflon seal and the mixture heated for 1 day at 120°C. The temperature was then lowered to 5°C and the reaction quenched with water. The product was extracted in water and washed with three 20 mL portions of  $\text{CH}_2\text{Cl}_2$ . The water layer was concentrated and the solid product washed with acetone. Alternatively, acetone can be added to precipitate the sulfonate salt when the volume of water is ~5-10 mL. The product was dissolved in alcohol, filtered through a paper filter and concentrated, then recrystallized from  $\text{H}_2\text{O}$  to obtain 1.5 g of  $\text{Li}(t\text{-Bu-dpms})$  (52% yield) as an analytically pure crystalline, white solid.

$^1\text{H}$  NMR (22°C,  $\text{D}_2\text{O}$ ),  $\delta$ : 8.46 (bd, 1H,  $J=5.2\text{Hz}$ ), 8.33 (d, 1H,  $J=5.2\text{Hz}$ ), 7.96 (d, 1H,  $J=1.9\text{Hz}$ ), 7.86-7.89 (m, 2H), 7.36-7.42 (m, 2H), 5.66 (s, 1H), 1.28 (s, 9H).

$^{13}\text{C}$  NMR (22°C,  $\text{D}_2\text{O}$ ),  $\delta$ : 163.2, 154.5, 154.2, 149.2, 148.9, 138.5, 125.0, 124.1, 122.3, 121.3, 74.4, 34.8, 29.9.

Anal. Calcd for  $\text{C}_{15}\text{H}_{17}\text{LiN}_2\text{O}_3\text{S}$ : C, 57.50; H, 5.50; N, 8.97. Found: C, 57.55; H, 5.13; N, 8.50.

## Synthesis of 4-*tert*-butyl-pyridine-2, 6-dicarboxylic acid, H<sub>2</sub>-*t*-Bu-pda



4-*tert*-butyl-2,6-dimethylpyridine was prepared from 2,6-dimethylpyridine and *tert*-butyl lithium according to the literature.<sup>10</sup>

4-*tert*-butyl-2,6-dimethylpyridine (0.82g, 5 mmol) and KMnO<sub>4</sub> (3.16g, 20 mmol) were mixed in water (25 mL) and refluxed for 18h. The reaction mixture was filtered while hot to remove the brown solid of MnO<sub>2</sub>. The colorless solution was neutralized with 4M aqueous HCl carefully until pH reaches 5. The white solid thus precipitated was filtered off and purified by recrystallization from hot water to give colorless needles of 4-*tert*-butyl-pyridine-2,6-dicarboxylic acid (0.56g, 50%).

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>), δ:

1.34 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 8.17 (s, 2H, py-H3,5), 10.91 (br s, 2H, -COOH);

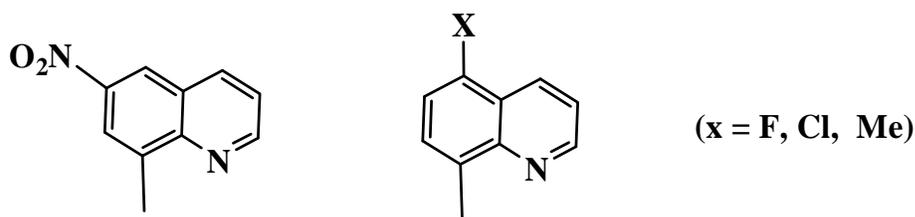
<sup>13</sup>C{<sup>1</sup>H} (100.5 MHz, CD<sub>3</sub>CO<sub>2</sub>D), δ:

30.5 (s, C(CH<sub>3</sub>)<sub>3</sub>), 36.4 (s, C(CH<sub>3</sub>)<sub>3</sub>), 126.1 (s, py-C3,5), 147.8 (s, py-2,6), 167.1 (s, COOH), 167.3 (s, py-C4).

Elem. Analysis, for C<sub>11</sub>H<sub>13</sub>NO<sub>4</sub> (Found (Calc.)): C, 59.32 (59.19); H, 5.42 (5.87); N, 5.96 (6.27).

## 2. Synthesis of 5- or 6-substituted 8-methylquinolines

All quinolines **1a-1i** used in this work are known compounds. 8-Methylquinoline (**1a**) is commercially available. 5,8-dimethyl- (**1b**),<sup>1</sup> 5-methoxy- (**1c**),<sup>2</sup> 5-bromo- (**1f**),<sup>2</sup> 5-iodo- (**1g**),<sup>3</sup> and 5-nitro- (**1h**)<sup>2</sup> 8-methylquinolines were prepared as published before. 5-fluoro- (**1d**) and 5-chloro- (**1e**) and 6-nitro- (**1i**) 8-methylquinolines were prepared following to a procedure similar to that reported for 5,8-dimethylquinoline (**1b**),<sup>1</sup> starting from corresponding substituted 2-methylanilines and glycerin as follows.



### General procedure for the synthesis of 5- or 6- substituted quinolines **1d**, **1e**, **1i**

Glycerin (11.1g, 0.12mol) was added dropwise over a period of 0.5h to a solution of substituted aniline (0.1mol) and NaI (0.2g, 1.3 mmol) in 80% aqueous H<sub>2</sub>SO<sub>4</sub> (55g, 0.45mmol) at 140°C. The mixture was then heated at 140-145°C for 3.5h while distilling the water formed during this period. Upon cooling to room temperature, the dark solution was carefully poured into ice (100g) and then neutralized with 25% NaOH (109.3g, 0.69mol) to basic pH 8~11. The mixture was extracted with benzene (3×50mL). The combined organic solution was washed with water (2×50mL), brine (50mL), and then dried with anhydrous sodium sulfate. After removing benzene, the residue was distilled under vacuum to give the corresponding substituted 8-methyl-quinoline.

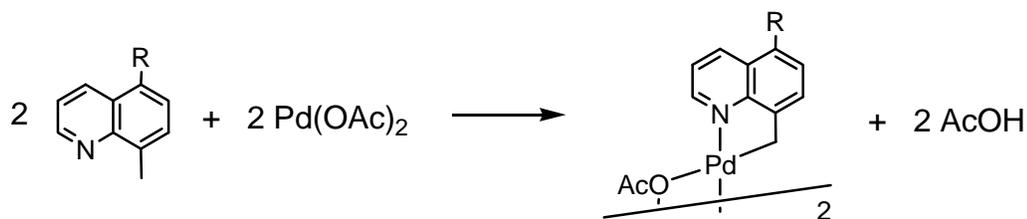
**1d, 5-Fluoro-8-methylquinoline** (colorless liquid, 80%): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 2.74 (s, 3H, -CH<sub>3</sub>), 7.08 (dd, 1H, *J*<sub>HH</sub> = 8.0 Hz, *J*<sub>FH</sub> = 9.6 Hz, quinoline-H6), 7.43 (dd, 1H, *J*<sub>HH</sub> = 8.4 Hz, *J*<sub>HH</sub> = 4.0 Hz, quinoline-H3), 7.44 (br t, 1H, *J*<sub>HH</sub> = *J*<sub>FH</sub> = 6.0 Hz, quinoline-H7), 8.39 (dd, 1H, *J*<sub>HH</sub> = 8.4 Hz, *J*<sub>HH</sub> = 2.0 Hz, quinoline-H4), 8.96 (dd, *J*<sub>HH</sub> = 4.0 Hz, *J*<sub>HH</sub> = 2.0 Hz, quinoline-H2); <sup>13</sup>C{<sup>1</sup>H} (100.5 MHz, CDCl<sub>3</sub>): 17.9 (s, -CH<sub>3</sub>), 109.7 (d, *J*<sub>CF</sub> = 18.5 Hz, quinoline-C6), 119.2 (d, *J*<sub>CF</sub> = 16.3 Hz, quinoline-C10), 121.0 (d, *J*<sub>CF</sub> = 2.9 Hz, quinoline-C3), 128.7 (d, *J*<sub>CF</sub> = 8.3 Hz, quinoline-C7), 129.6 (d, *J*<sub>CF</sub> = 4.7 Hz, quinoline-C4), 133.0 (d, *J*<sub>CF</sub> = 4.3 Hz, quinoline-C8), 147.5 (d, *J*<sub>CF</sub> = 2.4 Hz, quinoline-C9), 150.1 (s, quinoline-C2), 156.9 (d, *J*<sub>CF</sub> = 252.7 Hz, quinoline-C5).

**1e, 5-Chloro-8-methylquinoline** (white solid, 80%):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 2.77 (s, 3H, - $\text{CH}_3$ ), 7.45 (d, 1H,  $J_{\text{HH}} = 8.0$  Hz, quinoline-H6), 7.49 (dd, 1H,  $J_{\text{HH}} = 8.4$  Hz,  $J_{\text{HH}} = 4.0$  Hz, quinoline-H3), 7.50 (d, 1H,  $J_{\text{HH}} = 8.0$  Hz, quinoline-H7), 8.55 (dd, 1H,  $J_{\text{HH}} = 8.4$  Hz,  $J_{\text{HH}} = 1.6$  Hz, quinoline-H4), 8.97 (dd,  $J_{\text{HH}} = 4.0$  Hz,  $J_{\text{HH}} = 1.6$  Hz, quinoline-H2);  $^{13}\text{C}\{^1\text{H}\}$  (100.5 MHz,  $\text{CDCl}_3$ ): 18.2 (s, - $\text{CH}_3$ ), 121.7 (s, quinoline-C3), 126.4 (s, quinoline-C10), 126.5 (s, quinoline-C4), 129.0 (s, quinoline-C5), 129.4 (s, quinoline-C6), 133.3 (s, quinoline-C7), 136.7 (s, quinoline-C8), 147.9 (s, quinoline-C9), 149.9 (s, quinoline-C2).

**1i, 6-Nitro-8-methylquinoline** (pale-yellow solid, 30%):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 2.86 (s, 3H, - $\text{CH}_3$ ), 7.55 (dd, 1H,  $J_{\text{HH}} = 8.4$  Hz,  $J_{\text{HH}} = 4.0$  Hz, quinoline-H3), 8.29 (d, 1H,  $J_{\text{HH}} = 2.4$  Hz, quinoline-H7), 8.30 (dd, 1H,  $J_{\text{HH}} = 8.4$  Hz,  $J_{\text{HH}} = 1.6$  Hz, quinoline-H4), 8.59 (d, 1H,  $J_{\text{HH}} = 2.4$  Hz, quinoline-H5), 9.08 (dd,  $J_{\text{HH}} = 4.0$  Hz,  $J_{\text{HH}} = 1.6$  Hz, quinoline-H2);  $^{13}\text{C}\{^1\text{H}\}$  (100.5 MHz,  $\text{CDCl}_3$ ): 18.5 (s, - $\text{CH}_3$ ), 122.6 (s, quinoline-C3), 122.7 (s, quinoline-C5), 122.8 (s, quinoline-C7), 127.1 (s, quinoline-C10), 138.4 (s, quinoline-C4), 140.3 (s, quinoline-C8), 145.2 (s, quinoline-C6), 149.5 (s, quinoline-C9), 152.7 (s, quinoline-C2).

### 3. Synthesis of cyclopalladated amines **3a** and **3d**

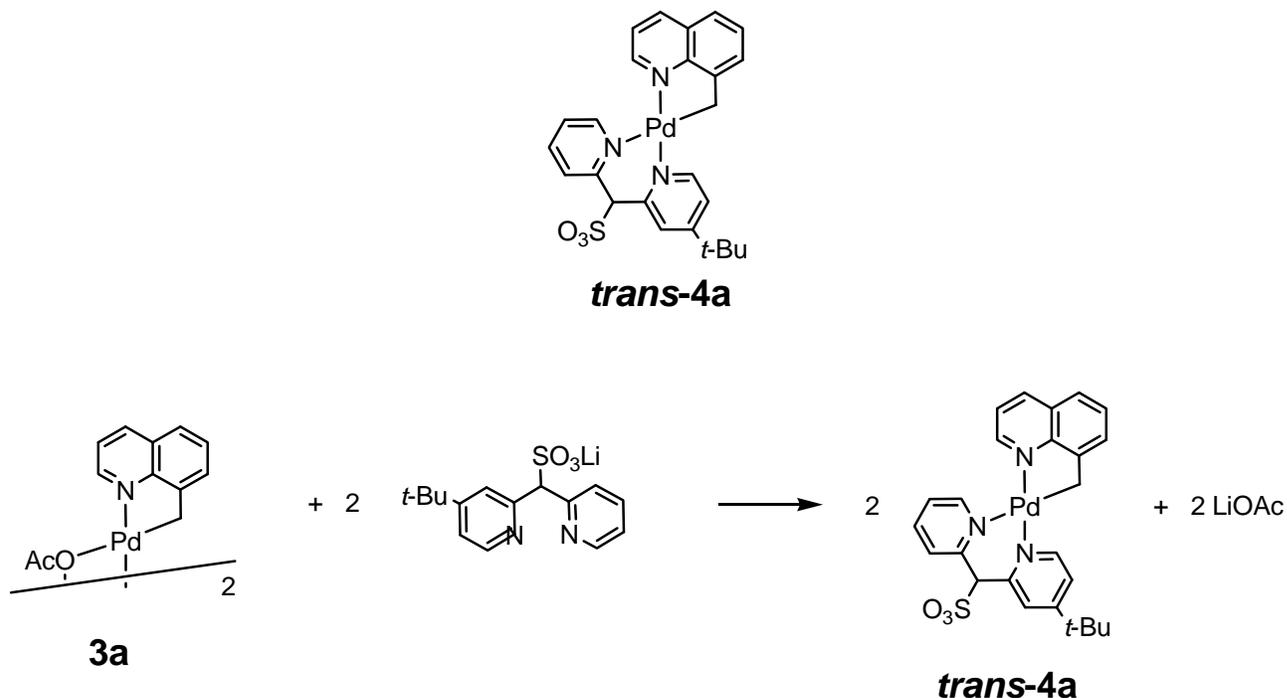
#### General procedure for synthesis of complexes **3**<sup>2,4</sup>



A sample of quinoline **1a** or **1d** (1.0 mmol) was added to a solution of palladium acetate (1.0 mmol) in acetic acid (5 mL) and the reaction mixture was heated at 100 °C for 2h. Upon cooling to room temperature, the solvent was removed under vacuum and the resulting solid was dissolved in methylene chloride (1.5 mL) and filtered through a Celite pad. The filtrate was carefully layered with hexanes (9 mL) and left at -32 °C for 24h. The microcrystalline solid was collected by filtration and dried under vacuum for 12h. Identity of **3a** and **3d** was confirmed by comparing its <sup>1</sup>H NMR and <sup>13</sup>C NMR with those reported in literature.<sup>2,4</sup>

#### 4. Synthesis of *t*-Bu-dpms-supported cyclopalladated amines **4a** and **4d**, Pd(hpda)L (L=H<sub>2</sub>O, DMF), and *t*-Bu-pda and hpda-supported Pd complexes, **7a** and **8a**

##### Synthesis of **4a**



Complex **3a** (0.01 mmol) and Li(*t*-Bu-dpms) (6.4 mg, 0.02 mmol) were dissolved in CD<sub>3</sub>COOD (12 mL), the colorless solution was stirred at room temperature for 1h. <sup>1</sup>H NMR spectra indicated a 100% conversion of **3a** to a 1:1 mixture of *cis*- and *trans*-**4a**.

White solid **4a** was obtained by slow precipitation from a 1/5 acetic acid/diethyl ether solution.

<sup>1</sup>H NMR (CD<sub>3</sub>COOD, 20°C), δ:

1.38 (s, 9H, -C(CH<sub>3</sub>)<sub>3</sub>), 3.52 (br s, 1H, Pd-CHH), 3.81 (br s, 1H, Pd-CHH), 6.44 (s, 1H, CHSO<sub>3</sub>), 7.48 (dd, 1H, *J*<sub>HH</sub> = 8.0 Hz, *J*<sub>HH</sub> = 4.8 Hz), 7.51 (br m, 1H), 7.57 (t, 1H, *J*<sub>HH</sub> = 7.6 Hz), 7.65 (br m, 1H), 7.67 (d, 1H, *J*<sub>HH</sub> = 6.8 Hz), 7.72 (d, 1H, *J*<sub>HH</sub> = 8.0 Hz), 7.98 (t, 1H, *J*<sub>HH</sub> = 7.6 Hz), 7.99 (br m, 1H), 8.06 (br m, 1H), 8.44 (d, *J*<sub>HH</sub> = 8.0 Hz), 8.51 (br s, 1H), 8.67 (br m), 8.80 (br m, 1H), 8.88 (br m). The ratio of intensities of multiplets at 8.67 and 8.88 pm was about 1:1, altogether integrating as 1H.

All signals of 8-quinolylmethyl ligand are sharp. In contrast, downfield signals of *t*-Bu-dpms ligand were broad indicative of fast chemical exchange involving this ligand that may be assigned to a fast *cis-trans*-isomerization of **4a**. That could not be proven by VT NMR experiments because of the high freezing point of CD<sub>3</sub>COOD.

Similar broadening of dpms signals was observed for an analogous complex derived from the parent dpms ligand, (8-quinolylmethyl)Pd<sup>II</sup>(dpms).

In DMSO solution the complex exists presumably as (*t*-Bu-dpms)Pd(dmsO)( $\eta^1$ -quinolylmethyl). Though its <sup>1</sup>H NMR spectrum looks simpler, still, signals of C6-H, C6'-H, C5-H and C5'-H protons of *t*-Bu-dpms are broadened, presumably, due to fast pyridine-for-pyridine ring exchange.

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 25°C),  $\delta$ :

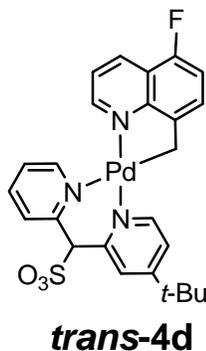
1.33 (s, 9H, -C(CH<sub>3</sub>)<sub>3</sub>), 3.49 (s, 2H, Pd-CH<sub>2</sub>), 6.15 (s, 1H, CHSO<sub>3</sub>), 7.59 (br s, 2H, aryl-H), 7.62 (t, 1H,  $J_{\text{HH}} = 7.6$  Hz, aryl-H), 7.67 (dd, 1H,  $J_{\text{HH}} = 8.0$  Hz,  $J_{\text{HH}} = 5.2$  Hz), 7.70 (d, 1H,  $J_{\text{HH}} = 8.0$  Hz, aryl-H), 7.82 (d, 1H,  $J_{\text{HH}} = 8.0$  Hz, aryl-H), 7.85 (d, 1H,  $J_{\text{HH}} = 8.0$  Hz, aryl-H), 7.93 (d, 1H,  $J_{\text{HH}} = 1.6$  Hz, aryl-H), 8.11 (t, 1H,  $J_{\text{HH}} = 6.8$  Hz, aryl-H), 8.41 (d, 1H,  $J_{\text{HH}} = 4.8$  Hz, aryl-H), 8.65 (d, 1H,  $J_{\text{HH}} = 8.0$  Hz, aryl-H), 8.74 (br m, 1H aryl-H), 8.86 (br m, 1H, aryl-H).

<sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 20°C),  $\delta$ :

28.8 (s, C(CH<sub>3</sub>)<sub>3</sub>), 29.9 (s, C(CH<sub>3</sub>)<sub>3</sub>), 35.0 (s, Pd-CH<sub>2</sub>), 74.9 (s, CHSO<sub>3</sub>), 121.7 (s, aryl-C), 122.4 (s, aryl-C), 124.1 (s, aryl-C), 124.5 (s, aryl-C), 128.4 (s, aryl-C), 128.7 (s, aryl-C), 129.0 (s, aryl-C), 138.6 (s, aryl-C), 139.3 (s, aryl-C), 147.5 (s, aryl-C), 150.1 (s, aryl-C), 151.1 (br s, aryl-C), 152.8 (s, aryl-C), 154.4 (br s, aryl-C), 162.7 (s, aryl-C).

Elemental Analysis, Found (Calc.), C<sub>25</sub>H<sub>25</sub>N<sub>3</sub>O<sub>3</sub>SPd: C, 54.80 (54.20); H, 4.77 (4.55); N, 7.52 (7.59).

## Synthesis of 4d



[Pd(5-fluoro-8-quinolylmethyl)(OAc)]<sub>2</sub> (6.5 mg, 0.01 mmol) and Li(t-Bu-dpms) (6.3 mg, 0.02 mmol) were dissolved in DMSO-*d*<sub>6</sub> (0.7 mL) and the solution was stirred for 1h at room temperature and filtered. The yellow solution was placed in a young-NMR tube under argon and checked by <sup>1</sup>H NMR and <sup>19</sup>F NMR which indicate the existence of two isomers (trans/cis) in a ratio of 2:1.

Major product, <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):

1.32 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 3.41 (s, 2H, Pd-CH<sub>2</sub>-), 6.15 (s, 1H, CHSO<sub>3</sub>), 7.51 (dd, 1H, *J*<sub>FH</sub> = 9.6 Hz, *J*<sub>HH</sub> = 8.4 Hz, quinolone-H6), 7.59 (br s, 1H, aryl-H), 7.67 (m, 1H, aryl-H), 7.75 (dd, 1H, *J*<sub>HH</sub> = 8.4 Hz, *J*<sub>HH</sub> = 5.2 Hz, aryl-H), 7.82 (d, 1H, *J*<sub>HH</sub> = 8.0 Hz, aryl-H), 7.93 (d, 1H, *J*<sub>HH</sub> = 1.6 Hz, aryl-H), 8.12 (t, 1H, *J*<sub>HH</sub> = 7.6 Hz, aryl-H), 8.48 (d, 1H, *J*<sub>HH</sub> = 4.8 Hz, aryl-H), 8.71 (d, 2H, *J*<sub>HH</sub> = 4.4 Hz, aryl-H), 8.73 (brs, 1H, aryl-H), 8.45 (br s, 1H, aryl-H).

<sup>19</sup>F {<sup>1</sup>H} NMR (376.5MHz, DMSO-*d*<sub>6</sub>), δ: -129.3 ppm

Minor product, <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):

1.26 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 3.32 (s, 2H, Pd-CH<sub>2</sub>-), 6.15 (s, 1H, CHSO<sub>3</sub>), 7.51 (dd, 1H, *J*<sub>FH</sub> = 9.6 Hz, *J*<sub>HH</sub> = 8.4 Hz, quinolone-H6), 7.59 (br s, 2H, aryl-H), 7.67 (m, 2H, aryl-H), 7.82 (d, 1H, *J*<sub>HH</sub> = 8.0 Hz, aryl-H), 7.93 (d, 1H, *J*<sub>HH</sub> = 1.6 Hz, aryl-H), 8.12 (t, 1H, *J*<sub>HH</sub> = 7.6Hz, aryl-H), 8.48 (d, 1H, *J*<sub>HH</sub> = 4.8 Hz, aryl-H), 8.72 (d, 2H, *J*<sub>HH</sub> = 4.4 Hz, aryl-H), 8.45 (br s, 1H, aryl-H).

<sup>19</sup>F {<sup>1</sup>H} NMR (376.5MHz, DMSO-*d*<sub>6</sub>), δ: -128.7 ppm.

### Synthesis of Pd(*hpda*)L, L = H<sub>2</sub>O and DMF

4-Hydroxy-pyridine-2,6-dicarboxylic acid(*Hpda*) (92 mg, 0.50 mmol) and Pd(OAc)<sub>2</sub> (112 mg, 0.50 mmol) were mixed in hot water (50 mL) and the mixture was heated at 80 °C for 2h. Upon cooling to room temperature, the yellow solid thus obtained was filtered off and washed with water, ether (3 × 1.5 mL) and then dried under vacuum to give Pd(*Hpda*)(H<sub>2</sub>O) (147mg, 97%). The product is almost insoluble in most common solvents.

Similarly a DMF-adduct can be prepared, Pd(*hpda*)(DMF), DMF should be used as a solvent. Yield 116 mg, 64%.

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): a mixture of dimer and monomer (1/1): dimers: 2.73 (s, 3H, N(CH<sub>3</sub>)(CH<sub>3</sub>), 2.89 (s, 3H, N(CH<sub>3</sub>)(CH<sub>3</sub>)), 6.78 (d, 1H, *J*<sub>HH</sub> = 1.6 Hz, Pyridine-H3 or5), 7.18 (d, 1H, *J*<sub>HH</sub> = 1.6 Hz, Pyridine-H3 or H5), 7.95 (s, 1H, HN(CO)(Me<sub>2</sub>)), 12.62 (br s, 1H, -OH); monomers: 2.73 (s, 3H, N(CH<sub>3</sub>)(CH<sub>3</sub>), 2.89 (s, 3H, N(CH<sub>3</sub>)(CH<sub>3</sub>)), 7.07 (s, 2H, pyridine-H3 and 5), 7.95 (s, 1H, HN(CO)(Me<sub>2</sub>)), 12.62 (br s, 1H, -OH);

Elem. Analysis, Found (Calc.) for C<sub>10</sub>H<sub>10</sub>N<sub>2</sub>O<sub>6</sub>Pd : C, 33.27 (33.31); H, 3.07(2.80); N, 7.60 (7.77).

### Synthesis of Pd(H-*t*-Bu-pda)(CH<sub>2</sub>-8-quinolyl), 7a

To a solution of [Pd(CH<sub>2</sub>-8-quinolyl)(OAc)]<sub>2</sub>, **3a**, (30.7 mg, 0.1 mmol) in acetic acid (2mL) 4-*tert*-butylpyridine-2,6-dicarboxylic acid (H<sub>2</sub>-*t*-Bu-pda) (22.3 mg, 0.1 mmol) in acetic acid (2mL) was added dropwise under argon atmosphere at room temperature. A yellow solid formed after 5 min. The mixture was stirred for further 0.5h. Diethyl ether (8mL) was added slowly to the mixture to allow for more solid to precipitate. The mixture was left at -32 °C for 3h. The yellow solid was filtered off, washed with diethyl ether (2 × 1mL) and dried under vacuum overnight to obtain the title complex (45mg, 95%). The <sup>1</sup>H NMR of this complex in DMSO-d<sub>6</sub> shows very broad signals for all the protons. However in CDCl<sub>3</sub>, two isomers could be detected in 1:10 ratio.

#### Major isomer:

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz, 22°C), δ:

1.33 (s, 9H, -C(CH<sub>3</sub>)<sub>3</sub>), 4.38 (s, 2H, Pd-CH<sub>2</sub>-), 7.53-7.59 (m, 2H, quinolyl-H), 7.74 (d, 2H, *J*<sub>HH</sub> = 8.0 Hz, quinolyl-H), 7.93(s, 2H, pyridine-H), 8.34 (dd, 1H, *J*<sub>HH</sub> = 8.0 Hz, *J*<sub>HH</sub> = 1.6 Hz, quinolyl-H), 9.64 (dd, 1H, *J*<sub>HH</sub> = 5.2 Hz, *J*<sub>HH</sub> = 1.6 Hz, quinolyl-H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125.8MHz, 22°C), δ:

22.7 (s, C(CH<sub>3</sub>)<sub>3</sub>), 31.2 (s, C(CH<sub>3</sub>)<sub>3</sub>), 37.5 (s, Pd-CH<sub>2</sub>), 121.3 (s, aryl-C), 126.4 (s, aryl-C), 128.4 (s, aryl-C), 128.7 (s, aryl-C), 131.0 (s, aryl-C), 134.4 (s, aryl-C), 135.5 (s, aryl-C), 141.9 (s, aryl-C), 146.9 (s, aryl-C), 149.7 (s, aryl-C), 154.7 (s, aryl-C), 168.7 (s, pyridine—C4), 172.3 (s, -COO- and COOH).

#### Minor isomer:

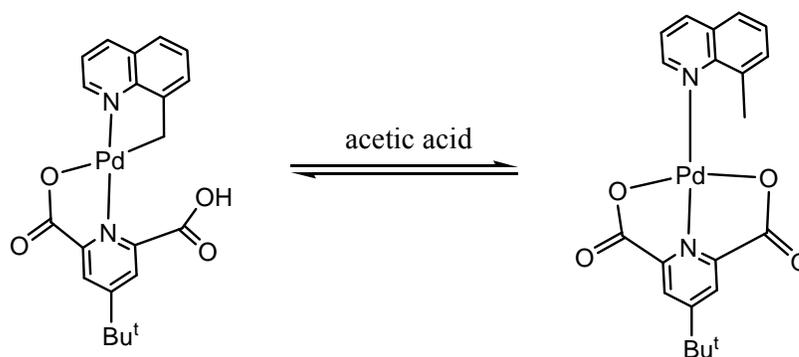
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 22°C) for the minor isomer, δ:

1.34 (s, 9H, -C(CH<sub>3</sub>)<sub>3</sub>), 3.83 (s, 2H, Pd-CH<sub>2</sub>-), 6.84 (dd, 1H, *J*<sub>HH</sub> = 8.0 Hz, *J*<sub>HH</sub> = 8.0 Hz, quinolyl-H), 7.14 (d, 1H, *J*<sub>HH</sub> = 8.0 Hz, quinolyl-H), 7.23 (t, 1H, *J*<sub>HH</sub> = 8.0 Hz, quinolyl-H), 7.30 (d, 1H, *J*<sub>HH</sub> = 6.8 Hz, quinolyl), 7.56 (d, 1H, *J*<sub>HH</sub> = 8.0 Hz, quinolyl-H), 7.71 (br s, 1H, pyridine-H), 7.82 (s, 1H, pyridine-H), 8.84 (d, 1H, *J*<sub>HH</sub> = 4.8 Hz, quinolyl-H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125.8MHz, 22°C), δ:

25.1 (s, C(CH<sub>3</sub>)<sub>3</sub>), 30.8 (s, C(CH<sub>3</sub>)<sub>3</sub>), 36.5 (s, Pd-CH<sub>2</sub>), 121.8 (s, aryl-C), 122.0 (s, aryl-C), 123.8 (s, aryl-C), 126.8 (s, aryl-C), 128.6 (s, aryl-C), 128.7 (s, aryl-C), 129.2 (s, aryl-C), 137.4 (s, aryl-C), 148.8 (s, aryl-C), 150.3 (s, aryl-C), 152.4 (s, aryl-C), 1668.0 (s, pyridine—C4), 172.3 (s, -COO- and COOH).

Elem. Analysis, Found (Calc.) for, C<sub>21</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub>Pd: C, 53.68 (53.57); H, 3.91 (4.28); N, 5.70 (5.95).



**Reversibility of formation of **7a**, Pd(H-*t*-Bu-pda)(CH<sub>2</sub>-8-quinolyl), from Pd(*t*-Bu-dpa)(CH<sub>3</sub>-8-quinolyl)**

Complex Pd(H-*t*-Bu-pda)(CH<sub>2</sub>-8-quinolyl), **7a**, (4.7mg, 0.01mmol) was dissolved in acetic acid-*d*<sub>4</sub> (0.7mL) under argon and then heated at 60 °C for 0.5h. <sup>1</sup>H NMR showed formation of 19% Pd(*t*-Bu-dpa)(8-CH<sub>3</sub>-quinoline).

Further heating caused gradual decrease of the integral intensity of the signals of both PdCH<sub>2</sub> protons in Pd(H-*t*-Bu-dpa)(CH<sub>2</sub>-8-quinolyl) and HQ's methyl protons in Pd(*t*-Bu-dpa)(8-CH<sub>3</sub>-quinoline) due to H/D exchange with the solvent.

**Synthesis of 8a, Pd(Hhpda)(CH<sub>2</sub>-8-quinolyl), in a reaction between 3a and H<sub>2</sub>hpda**

4-Hydroxy-pyridine-2,6-dicarboxylic acid(Hpda) (18.3 mg, 0.1 mmol) and [Pd(OAc)(κ<sup>2</sup>-C,N-CH<sub>2</sub>-C<sub>9</sub>H<sub>6</sub>N)]<sub>2</sub> (30.7mg, 0.05) were mixed in DMF (3mL) and the mixture was stirred at room temperature for 16h under argon atmosphere. To this yellow solution diethyl ether (10mL) was added slowly to precipitate a yellow solid. The yellow solid was filtered and washed with ether (3× 1.5 mL) and then dried under vacuum to give Pd(Hhpda)(CH<sub>2</sub>-C<sub>9</sub>H<sub>6</sub>N-C,N) (39mg, 91%).

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): 3.59 (s, 2H, -Pd-CH<sub>2</sub>-), 7.31 (br s, 2H, aryl-H), 7.63 (br s, 3H, aryl-H), 7.78 (s, 1H, aryl-H), 8.56 (br d, 1H, *J*<sub>HH</sub> = 6.8 Hz, aryl-H), 8.93 (br s, 1H, aryl-H).

Elem. Analysis, Found (Calc.) for C<sub>17</sub>H<sub>12</sub>N<sub>2</sub>O<sub>5</sub>Pd: C, 47.37 (47.41); H, 2.61 (2.81); N, 6.94 (6.50).

**Formation of Pd(Hhpda)(CH<sub>2</sub>-8-quinolyl) in a reaction of 1a with Pd(hpda)(DMF)**

8-Methylquinoline (28.6 mg, 0.2mmol) and Pd(hpda)(DMF) (14.4mg, 0.04 mmol) were mixed in CH<sub>3</sub>COOH (5 mL), the solution was stirred at room temperature for 24h under argon atmosphere. After removing the solvent, the residue was washed with ether (3× 1 mL) and dried. The pale-yellow solid was dissolved in DMSO-*d*<sub>6</sub> According to <sup>1</sup>H NMR, cyclopalladated complex Pd(Hhpda)(CH<sub>2</sub>-C<sub>9</sub>H<sub>6</sub>N-C,N) formed with 50% yield based on Pd(hpda)(DMF); 10 μL anisole additive was used as an internal standard.

## 5. Stoichiometric aerobic oxidation of cyclopalladated complexes

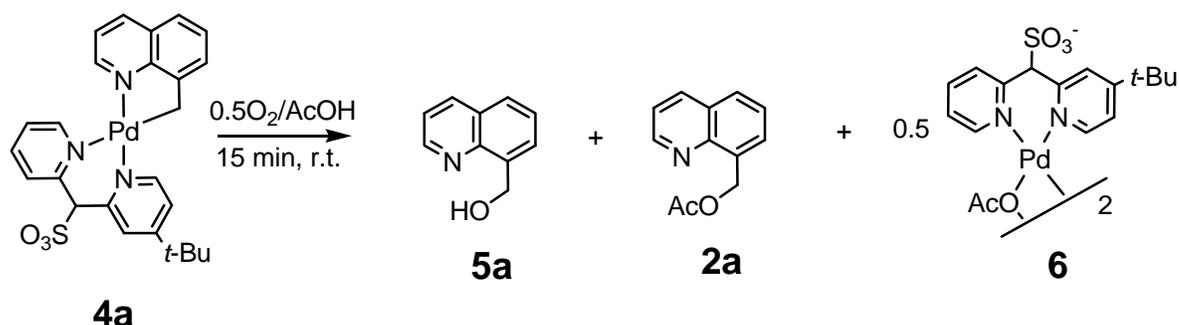
### 5.1. Oxidation of 4a and 4d.

**Volumetric determination of O<sub>2</sub> consumed.**

**Formation of complex 6.**

**Oxidation of cyclopalladated complexes in the presence of metallic Hg**

#### Oxidation of 4a in AcOH solution



*t*-Bu-dpms- supported palladacycle **4a** (0.1 mmol) was dissolved in acetic acid (5mL). The solution was purged with air for 10 min and then stirred at room temperature for 15 min. **No trace of palladium black was detected in the reaction mixture** (visual inspection). After reducing the volume of the mixture to 1 mL, diethyl ether (10 mL) was added slowly to cause formation of a pale-yellow solid. This solid was filtered off and washed with ether (3 × 2 mL), dried under vacuum for 2 hours to obtain pure complex **6** (35.2 mg, 75%). The filtrate obtained as described above was evaporated and purified by a flash chromatography with silica gel to give alcohol **5a** (yield 41%) and acetate **2a** (yield 45%).

#### Oxidation of 4a, 4d in AcOH solution in the presence of 5 equivalents of Ac<sub>2</sub>O

To a complex **4a** or **4d** (0.02 mmol) dissolved in AcOH (1 mL) acetic acid anhydride (0.1mmol) was added. The solution was purged with O<sub>2</sub> and stirred at certain temperature (see the paper) for several hours. The solution was diluted with CD<sub>3</sub>COOD and <sup>1</sup>H NMR spectrum was recorded. **No trace of palladium black was detected in the reaction mixture** (visual inspection). Identity of alcohols **5a**, **5d** and acetates **2a**, **2d** was confirmed by comparing <sup>1</sup>H NMR spectra of these products with spectra of authentic samples of these compounds prepared by other methods and/or with data

reported in literature (**2a**, **5a**, **2d**). The yields were determined by  $^1\text{H}$  NMR integration using 10  $\mu\text{L}$  anisole additive as an internal standard. In all the cases both alcohol **5** and acetate **2** were observed at the early stages of reaction. By the end of reaction acetate was the only organic product detected by NMR.

#### **Volumetric determination of $\text{O}_2$ consumed in reaction between **4a** and $\text{O}_2$**

Complex  $\text{Pd}(\text{CH}_2\text{-8-quinoyl})(t\text{-Bu-dpms})$  (22.2 mg, 0.0400 mmol) **4a** was combined with acetic acid (2.0 mL) and acetic anhydride (0.20 mmol) in a Schlenk flask attached to 1.00 mL gas burette filled with  $\text{O}_2$ . The mixture was stirred at  $17^\circ\text{C}$  under  $\text{O}_2$  atmosphere (1atm). After 9h absorption of  $\text{O}_2$  stopped. The  $\text{O}_2$  consumption was 0.44 mL at 1atm,  $17^\circ\text{C}$  (0.0185 mmol).

The resulting yellow solution was reduced in volume under high vacuum. Dry residue was dissolved in  $\text{DMSO-}d_6$  (1 mL) and analyzed by  $^1\text{H}$  NMR. According to NMR spectroscopy, complex **4a** has reacted completely. 8-acetoxymethylquinoline **2a** was found to be the only quinoline-derived organic product present in solution.

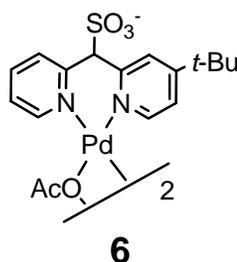
Hence, **4a** and  $\text{O}_2$  reacted in 1:0.5 molar ratio.

### Attempted oxidation of **3a** and **3d** in AcOH solution

The parent palladacycles **3a** and **3d** were inert under the same conditions as described above for **4a** and **4d**. No **2** or **5** were detected by NMR. No palladium black was detected (visual inspection).

**Oxidation of 4a in AcOH solution in the presence of 5 equivalents of Ac<sub>2</sub>O and metallic mercury.** To a solution of **4a** (0.02 mmol) in acetic acid (1mL) acetic anhydride (0.1 mmol) and mercury (0.1 mL) were added. The solution was purged with O<sub>2</sub> for 10 min and then stirred at room temperature for 12 h. The sole organic product **2a** (90%) was identified by <sup>1</sup>H NMR; its yield was determined by <sup>1</sup>H NMR integration using 10 μL anisole additive as an internal standard.

### Complex **6**



The complex crystallizes with one AcOH molecule per Pd atom as it follows from the <sup>1</sup>H NMR and elemental analysis data.

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 22°C), δ:

1.29 (s, 9H, -C(CH<sub>3</sub>)<sub>3</sub>), 1.85 (br s, 6H, OOCCH<sub>3</sub>), 1.92 (br s, 1H, AcOH), 6.27 (s, 1H, CHSO<sub>3</sub>), 7.56 (dt, 1H, *J*<sub>HH</sub> = 6.8 Hz, *J*<sub>HH</sub> = 1.2 Hz, py-H5), 7.61 (dd, 1H, *J*<sub>HH</sub> = 6.8 Hz, *J*<sub>HH</sub> = 2.4 Hz, Bupy-H5'), 7.74 (d, 1H, *J*<sub>HH</sub> = 7.2 Hz, py-H3), 7.85 (d, 1H, *J*<sub>HH</sub> = 1.2 Hz, Bupy-H3'), 8.11 (dt, 1H, *J*<sub>HH</sub> = 8.0 Hz, *J*<sub>HH</sub> = 1.2 Hz, py-H4), 8.29 (d, 1H, *J*<sub>HH</sub> = 5.6 Hz, Bupy-H2'), 8.40 (d, 1H, *J*<sub>HH</sub> = 6.0 Hz, py-H6);

<sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 22°C), δ:

23.4 (s, CH<sub>3</sub>COO), 29.8 (s, C(CH<sub>3</sub>)<sub>3</sub>), 35.0 (s, C(CH<sub>3</sub>)<sub>3</sub>), 74.1 (s, CHSO<sub>3</sub>), 121.8 (s), 124.5 (s), 125.9 (s), 128.9 (s), 140.0 (s), 149.1 (s), 149.7 (s), 150.8 (s), 151.6 (s), 163.63 (s)(aryl-C), 177.7 (s, CH<sub>3</sub>COO).

Elem. Analysis, Found (Calc.) for 7·2AcOH, C<sub>19</sub>H<sub>24</sub>N<sub>2</sub>O<sub>7</sub>SPd: C, 42.95 (42.98); H, 4.47 (4.56); N, 5.65 (5.28).

## 5.2. Oxidation of **3a** with O<sub>2</sub> in the presence of H<sub>2</sub>-*t*-Bu-pda. Volumetric determination of O<sub>2</sub> consumed

Complex [Pd(CH<sub>2</sub>-8-quinoyl)(OAc)]<sub>2</sub> **3a** (12.3 mg, 0.0400 mmol) and *t*-butyl-pyridine-2,6-dicarboxylic acid (H<sub>2</sub>-*t*-Bu-dpa) (8.9 mg, 0.0400 mmol) were combined with acetic acid (2.0 mL) and acetic anhydride (0.20 mmol) ) in a Schlenk flask attached to a 1.00 mL gas burette filled with O<sub>2</sub>. All solids dissolved and resulting yellow solution was stirred at 17°C under O<sub>2</sub> atmosphere (1atm). After nine hours absorption of O<sub>2</sub> stopped. The consumption of O<sub>2</sub> was 0.60 mL (1atm, 17°C, 0.0252 mmol). The yellow solution was reduced in volume under vacuum. Dry residue was dissolved in DMSO-*d*<sub>6</sub> (1 mL) and analyzed by <sup>1</sup>H NMR spectroscopy. According to NMR spectroscopy, all complex **3a** has reacted completely. 8-acetoxymethylquinoline **2a** was found to be the only quinoline-derived organic product present in solution. The yield of 8-acetoxymethylquinoline **2a** determined by <sup>1</sup>H NMR integration using 20 μL dioxane additive as an internal standard was 85%.

Hence, **4a** and O<sub>2</sub> reacted in 1:0.6 ratio.

### 5.3. Oxidation of 3d in the presence of H<sub>2</sub>hpda. Formation of 9d and Pd(5-fluoro-quinoline-8-carboxylate)<sub>2</sub>

Pd(5-fluoro-8-quinolylmethyl)(OAc)<sub>2</sub> (13.0mg, 0.02 mmol) and H<sub>2</sub>hpda·H<sub>2</sub>O (8.1 mg, 0.04 mmol) were mixed in acetic acid (1 mL) and acetic anhydride (20.8 mg, 0.2 mmol). The solution was purged with O<sub>2</sub> for 10 min and then heated at 60 °C for 5h. Upon cooling to room temperature, the solution was diluted with CD<sub>3</sub>COOD and <sup>1</sup>H NMR and <sup>19</sup>F NMR spectra were recorded. **No palladium black was detected in the reaction mixture** (visual inspection). Identity of acetate 8-acetoxymethyl-5-fluoro-quinoline and Pd(5-fluoro-8-quinolinecarboxylate)<sub>2</sub> were confirmed by comparing <sup>1</sup>H NMR spectra of these products with spectra of authentic samples of these compounds prepared by other methods (see below) and the yield of acetate (87%) was determined by <sup>1</sup>H NMR integration using 20 μL anisole additive as an internal standard and Pd(5-fluoro-8-quinolinecarboxylate)<sub>2</sub> was determined by <sup>19</sup>F NMR integration using 10 uL 4-trifluoropyridine as an internal standard.

#### Synthesis of 5-fluoro-quinoline-8-carboxylic acid 7d from 5-fluoro-8-methylquinoline 1d

5-Fluoro-8-methylquinoline (2.42g, 15mmol) was dissolved in sulfuric acid/water (100 mL, 8/5, v/v) and the solution was heated at 90°C. Solid CrO<sub>3</sub> (15g, 150 mmol) was added portion wise at such a rate to keep the temperature below 100°C. Upon cooling to room temperature, ice (200g) and dichloromethane (100mL) were added carefully and the solution was neutralized with 50% NaOH until Ph reached 5. The organic solution was separated and the aqueous phase was extracted with dichloromethane (2× 50mL). The combined organic solution was washed with water (2× 25mL) and dried with anhydrous sodium sulfate. After evaporating the solvent, the off-white solid was purified with flash chromatography with silicon gel to give white solid of 5-fluoro-quinoline-8-carboxylic acid (287mg, 10%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.41 (vt, 1H,  $J_{HH} = J_{FH} = 8.4$  Hz, quinoline-H6), 7.70 (dd, 1H,  $J_{HH} = 8.4$  Hz,  $J_{HH} = 4.4$  Hz, quinoline-H3), 8.66 (dd, 1H,  $J_{HH} = 8.4$  Hz,  $J_{HH} = 1.6$  Hz, quinoline-H4), 8.77 (dd, 1H,  $J_{HH} = 6.0$  Hz,  $J_{HH} = 8.4$  Hz, quinoline-H7), 8.99 (dd,  $J_{HH} = 4.0$  Hz,  $J_{HH} = 1.6$  Hz, quinoline-H2), 15.03 (s, 1H, -COOH); <sup>13</sup>C{<sup>1</sup>H} (100.5 MHz, CDCl<sub>3</sub>): 111.6 (d,  $J_{CF} = 19.4$  Hz, quinoline-C6), 119.2 (d,  $J_{CF} = 17.4$  Hz, quinoline-C10), 121.2 (d,  $J_{CF} = 4.9$  Hz, quinoline-C8), 122.0 (d,  $J_{CF} = 2.6$  Hz, quinoline-C4), 132.5 (d,  $J_{CF} = 4.3$  Hz, quinoline-C3), 136.5 (d,  $J_{CF} = 10.0$  Hz, quinoline-C7), 146.1 (d,  $J_{CF} = 4.1$  Hz, quinoline-C9), 149.8 (s, quinoline-C2), 160.6 (d,  $J_{CF} = 265.1$  Hz, quinoline-C5), 166.3 (s, COO); <sup>19</sup>F{<sup>1</sup>H} NMR (376.47MHz, CDCl<sub>3</sub>): -112.3 ppm.

### **Synthesis of Pd(5-fluoro-quinoline-8-carboxylate)<sub>2</sub>**

5-Fluoro-quinoline-8-carboxylic acid (38.2 mg, 0.2 mmol) and Pd(OAc)<sub>2</sub> (22.4 mg, 0.1 mmol) were mixed in acetic acid (2.5 mL) and then heated at 60 °C for 2h. Upon cooling to room temperature, the white solid thus formed was filtered and washed with ether (3× 1mL) and then dried under vacuum for 12h to give Pd(5-fluoro-quinoline-8-carboxylate)<sub>2</sub> (44mg, 90%). This solid did not dissolved in normal solvents such as THF, water, dichloromethane, acetone, alcohols, DMSO. Elem. Analysis, Found (Calc.) for C<sub>20</sub>H<sub>10</sub>F<sub>2</sub>N<sub>2</sub>O<sub>4</sub>Pd : C, 49.83 (49.35); H, 1.75 (2.07); N, 5.92 (5.76).

## 6. Catalytic oxidation of HQ with O<sub>2</sub> in Pd<sup>II</sup> complex – AcOH – Ac<sub>2</sub>O systems

### General procedure

To a 25 mL Schlenk flask a substituted 8-methylquinoline (1mmol), Pd(acac)<sub>2</sub> (0.05mmol) or Pd(OAc)<sub>2</sub> (0.05mmol), a ligand (0.05mmol) and acetic acid (5mL) were placed. Acetic anhydride (2 mmol) was added and the flask was purged with O<sub>2</sub> for 10 min and then heated at 80°C for 24h. Upon cooling to room temperature, a sample of the mixture was diluted with CD<sub>3</sub>COOD and <sup>1</sup>H NMR spectrum was recorded. Formation of yellowish precipitate of Pd<sup>II</sup> bis(8-quinoline carboxylate) was evident in all cases. Presence of carboxylate groups could be proved by means of IR; presence of corresponding quinoline residue was evident from <sup>1</sup>H NMR spectra of the precipitates in CF<sub>3</sub>COOD. **No palladium black was detected in reaction mixtures** (visual inspection). High ability of H<sub>2</sub>pda to prevent formation of Pd black in various catalytic systems was discussed in the literature before.<sup>11</sup> Identity of acetates was confirmed by comparing <sup>1</sup>H NMR spectra of these products with spectra of authentic samples of these compounds prepared by other methods. Yield of acetates **2** was determined by <sup>1</sup>H NMR integration using 20 μL anisole additive as an internal standard.

The pure acetates could be obtained as follows: after evaporating the solvent, the residue was purified via chromatographic separation using silica gel and ethyl ether/hexane: 10/100 to 40/100 v/v as an eluent. The isolated yields were consistent within 5-8% with those determined by <sup>1</sup>H NMR.

### Blank reactions

A substituted 8-methylquinoline (1mmol), Pd(acac)<sub>2</sub> (0.05mmol) (or Pd(OAc)<sub>2</sub>, 0.05mmol) were mixed with acetic acid (5mL) and acetic anhydride (2 mmol) placed to the 25 mL Schlenk flask. The mixture was purged with O<sub>2</sub> for 10 min and then heated at 80°C for 24h. Upon cooling to room temperature, a sample of the mixture was diluted with CD<sub>3</sub>COOD and <sup>1</sup>H NMR spectrum was recorded. Identity of acetates was confirmed by comparing <sup>1</sup>H NMR spectra of these products with spectra of authentic samples of these compounds prepared by other methods and the yield of acetate was determined by <sup>1</sup>H NMR integration using 20 μL anisole additive as an internal standard.

### Mercury test for the catalytic oxidation of 8-methylquinoline 1a

8-methylquinoline (1mmol), Pd(acac)<sub>2</sub> (0.05mmol) and ligand (0.05mmol) were mixed in acetic acid (5mL). Acetic anhydride (2 mmol) and pure mercury (0.5g) were added and the flask was

purged with O<sub>2</sub> for 10 min and then heated at 80°C for 24h. Upon cooling to room temperature, a sample of the solution was diluted with CD<sub>3</sub>COOD and <sup>1</sup>H NMR spectrum was recorded. The yield of acetate **2a** was determined by <sup>1</sup>H NMR integration using 20 μL anisole additive as an internal standard; 59.3% (the conversion of the 8-methylquinoline is 69%).

#### **Attempted oxidation of 8-acetoxymethyl-5-fluoroquinoline 2d with O<sub>2</sub>**

8-Acetoxymethyl-5-fluoroquinoline (8.8 mg, 0.04 mmol), Pd(acac)<sub>2</sub> (0.01mmol) and 4-hydroxypyridine-2,6-dicarboxylic acid (0,01 mmol) were placed in a 10-mL Schlenk flask. After adding acetic anhydride (0.05 mmol), the flask was purged with O<sub>2</sub> for 10 min and then heated at 80°C for 24 h under oxygen atmosphere. <sup>1</sup>H NMR and <sup>19</sup>F NMR indicated the presence of 100% 8-acetoxymethyl-5-fluoroquinoline remains in the solution.

#### **Oxidation of 5-fluoro-8-methylquinoline with O<sub>2</sub> catalyzed by Pd(acac)<sub>2</sub> - H<sub>2</sub>hpda**

In a 25 mL Schlenk flask 5-fluoro-8-methylquinoline (1mmol), Pd(acac)<sub>2</sub> (0.05mmol) and ligand (0.05mmol) were mixed in acetic acid (5mL). Acetic anhydride (2 mmol) was added and the flask was purged with O<sub>2</sub> for 10 min and then heated at 80°C for 24h. Upon cooling to room temperature, the solution was diluted with CD<sub>3</sub>COOD and <sup>1</sup>H NMR spectrum was recorded. Formation of yellowish precipitate of Pd<sup>II</sup> bis(5-fluoro-8-quinoline carboxylate) was observed. No palladium black was detected in the reaction mixture (visual inspection). Yield of **2d** was determined by <sup>1</sup>H NMR integration using 20 μL anisole additive as an internal standard.

The <sup>19</sup>F NMR was also recorded using 20 μL 4-trifluoropyridine additive as an internal standard.

Identity of acetate **2d** (δ, -122.5 ppm ) was confirmed by comparing a <sup>19</sup>F NMR spectrum of this product with a spectrum of an authentic sample of **2d** prepared as described above.

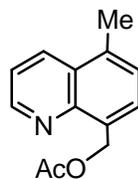
Identity of Pd(5-F-8-quinoline-COO)<sub>2</sub> (4.8%, δ, -112.2 ppm) (δ, -122.5 ppm ) was confirmed by comparing a <sup>19</sup>F NMR spectrum of this product with a spectrum of an authentic sample prepared as described above.

#### **Oxidation of 8-methylquinoline with O<sub>2</sub> catalyzed by Pd(acac)<sub>2</sub> - H<sub>2</sub>hpda**

The experiment was set up as described above for 5-fluoro analogue. <sup>1</sup>H NMR spectrum of Pd<sup>II</sup> dicarboxylate in CF<sub>3</sub>COOD showed the presence of six multiplets of corresponding carboxylic acid: 9.08 (dd, J<sub>HH</sub> = 1.2 Hz, J<sub>HH</sub> = 5.6 Hz, 1H), 9.00 (dd, J<sub>HH</sub> = 7.6 Hz, J<sub>HH</sub> = 1.2 Hz, 1H), 8.66 (dd, J<sub>HH</sub> = 8.4 Hz, J<sub>HH</sub> = 1.2 Hz, 1H), 8.34 (dd, J<sub>HH</sub> = 7.6 Hz, J<sub>HH</sub> = 1.2 Hz, 1H), 7.85 (dd, J<sub>HH</sub> = 8.4 Hz, J<sub>HH</sub> =

7.6 Hz, 1H); 7.79 (dd,  $J_{\text{HH}} = 8.4$  Hz,  $J_{\text{HH}} = 5.6$  Hz, 1H). In IR spectrum of the solid a strong band at  $1653.6\text{ cm}^{-1}$  was observed typical for COOH group.

**8-Acetoxymethyl-5-methyl-quinoline (2b):**<sup>12</sup>



**2b**

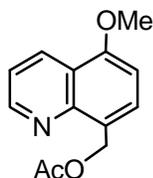
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 20°C), δ:

2.16 (s, 3H, CH<sub>3</sub>COO), 2.70 (s, 3H, -CH<sub>3</sub>), 5.84 (s, 2H, -CH<sub>2</sub>-OAc), 7.38 (d, 1H,  $J_{\text{HH}} = 7.2$  Hz, quinoline-H6), 7.48 (dd, 1H,  $J_{\text{HH}} = 8.4$  Hz,  $J_{\text{HH}} = 4.0$  Hz, quinoline-H3), 7.68 (d, 1H,  $J_{\text{HH}} = 7.2$  Hz, quinoline-7), 8.35 (dd, 1H,  $J_{\text{HH}} = 8.4$  Hz,  $J_{\text{HH}} = 1.6$  Hz, quinoline-H4), 8.984 (dd, 1H,  $J_{\text{HH}} = 4.0$  Hz,  $J_{\text{HH}} = 1.6$  Hz, quinoline-H2);

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 20°C), δ:

18.9 (s, CH<sub>3</sub>-), 21.4 (s, CH<sub>3</sub>COO), 63.1 (s, -CH<sub>2</sub>-OAc), 121.0 (s, quinoline-C3), 126.8 (s, quinoline-C6), 127.7 (s, quinoline-C8), 129.0 (s, quinoline-C7), 132.3 (s, quinoline-C10), 132.8 (s, quinoline-C4), 135.3 (s, quinoline-C5), 146.6 (s, quinoline-C9), 149.6 (s, quinoline-C2), 171.3 (s, -COO-).

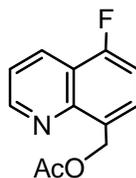
**8-Acetoxymethyl-5-methoxyquinoline (2c):**



**2c**

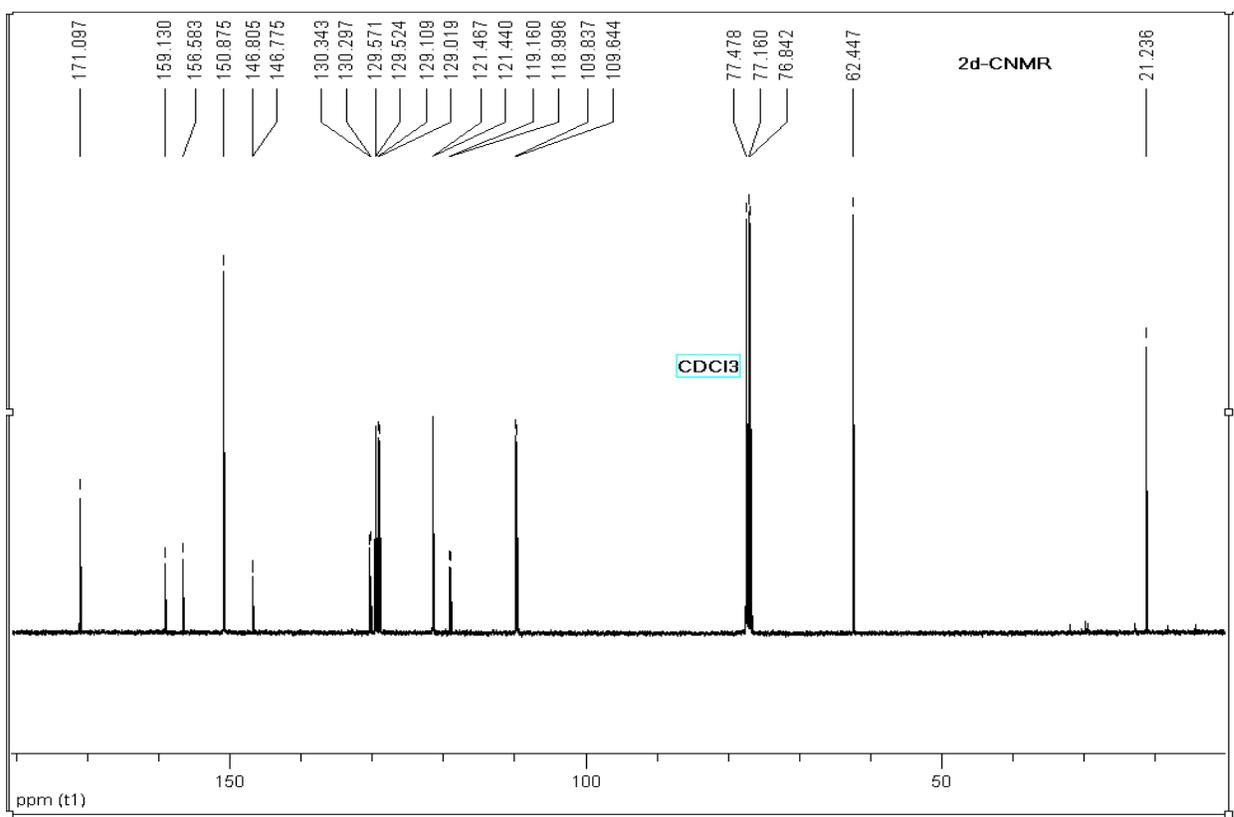
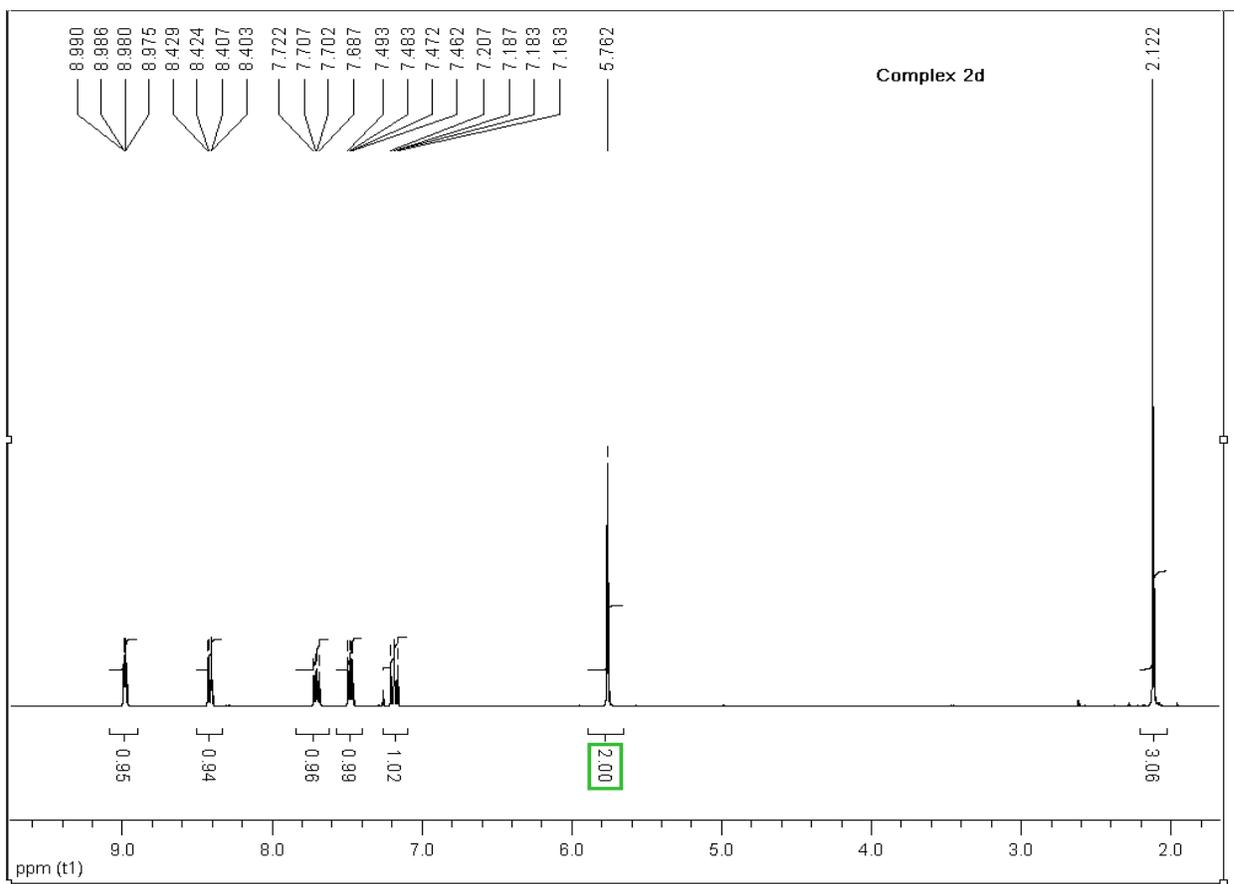
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 2.08 (s, 3H, CH<sub>3</sub>COO), 3.97 (s, 3H, -OCH<sub>3</sub>), 5.70 (s, 2H, -CH<sub>2</sub>-OAc), 6.80 (d, 1H,  $J_{\text{HH}} = 8.0$  Hz, quinoline-H6), 7.38 (dd, 1H,  $J_{\text{HH}} = 8.4$  Hz,  $J_{\text{HH}} = 4.4$  Hz, quinoline-H3), 7.68 (d, 1H,  $J_{\text{HH}} = 8.0$  Hz, quinoline-H7), 8.55 (dd, 1H,  $J_{\text{HH}} = 8.4$  Hz,  $J_{\text{HH}} = 1.6$  Hz, quinoline-H4), 8.93 (dd, 1H,  $J_{\text{HH}} = 4.4$  Hz,  $J_{\text{HH}} = 1.6$  Hz, quinoline-H2); <sup>13</sup>C {<sup>1</sup>H} (100.5 MHz, CDCl<sub>3</sub>): 21.4 (s, CH<sub>3</sub>COO), 55.9 (s, -OCH<sub>3</sub>), 63.0 (s, -CH<sub>2</sub>-OAc), 103.8 (s, quinoline-C6), 120.5 (s, quinoline-C3), 120.9 (s, quinoline-C8), 126.0 (s, quinoline-C10), 130.5 (s, quinoline-C4), 131.1 (s, quinoline-C7), 147.2 (s, quinoline-C9), 150.5 (s, quinoline-C2), 155.7 (s, quinoline-C5), 171.4 (s, -COO-); HR-MS (FAB<sup>+</sup>) for C<sub>13</sub>H<sub>13</sub>NO<sub>3</sub>: 232.0982 (M+H, 100.0%).

**8-Acetoxymethyl-5-fluoroquinoline (2d):<sup>13</sup>**

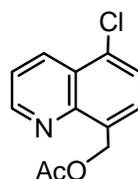


**2d**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 2.12 (s, 3H, CH<sub>3</sub>COO), 2.76 (s, 2H, -CH<sub>2</sub>OAc), 7.18 (dd, 1H, *J*<sub>HH</sub> = 8.0 Hz, *J*<sub>FH</sub> = 9.6 Hz, quinoline-H6), 7.48 (dd, 1H, *J*<sub>HH</sub> = 8.4 Hz, *J*<sub>HH</sub> = 4.0 Hz, quinoline-H3), 7.70 (dd, 1H, *J*<sub>HH</sub> = 8.0 Hz, *J*<sub>FH</sub> = 6.0 Hz, quinoline-H7), 8.42 (dd, 1H, *J*<sub>HH</sub> = 8.4 Hz, *J*<sub>HH</sub> = 2.0 Hz, quinoline-H4), 8.98 (dd, *J*<sub>HH</sub> = 4.0 Hz, *J*<sub>HH</sub> = 2.0 Hz, quinoline-H2); <sup>13</sup>C{<sup>1</sup>H} (100.5 MHz, CDCl<sub>3</sub>): 21.3 (s, -OOCCH<sub>3</sub>), 62.5 (s, CH<sub>2</sub>OAc), 109.8 (d, *J*<sub>CF</sub> = 19.3 Hz, quinoline-C6), 119.1 (d, *J*<sub>CF</sub> = 16.5 Hz, quinoline-C10), 121.5 (d, *J*<sub>CF</sub> = 2.9 Hz, quinoline-C3), 129.1 (d, *J*<sub>CF</sub> = 9.0 Hz, quinoline-C7), 129.6 (d, *J*<sub>CF</sub> = 4.8 Hz, quinoline-C4), 130.4 (d, *J*<sub>CF</sub> = 4.83 Hz, quinoline-C8), 146.9 (d, *J*<sub>CF</sub> = 2.9 Hz, quinoline-C9), 151.0 (s, quinoline-C2), 157.9 (d, *J*<sub>CF</sub> = 256.0 Hz, quinoline-C5), 171.2 (s, -COO-).  
See <sup>1</sup>H and <sup>13</sup>C NMR spectra below.



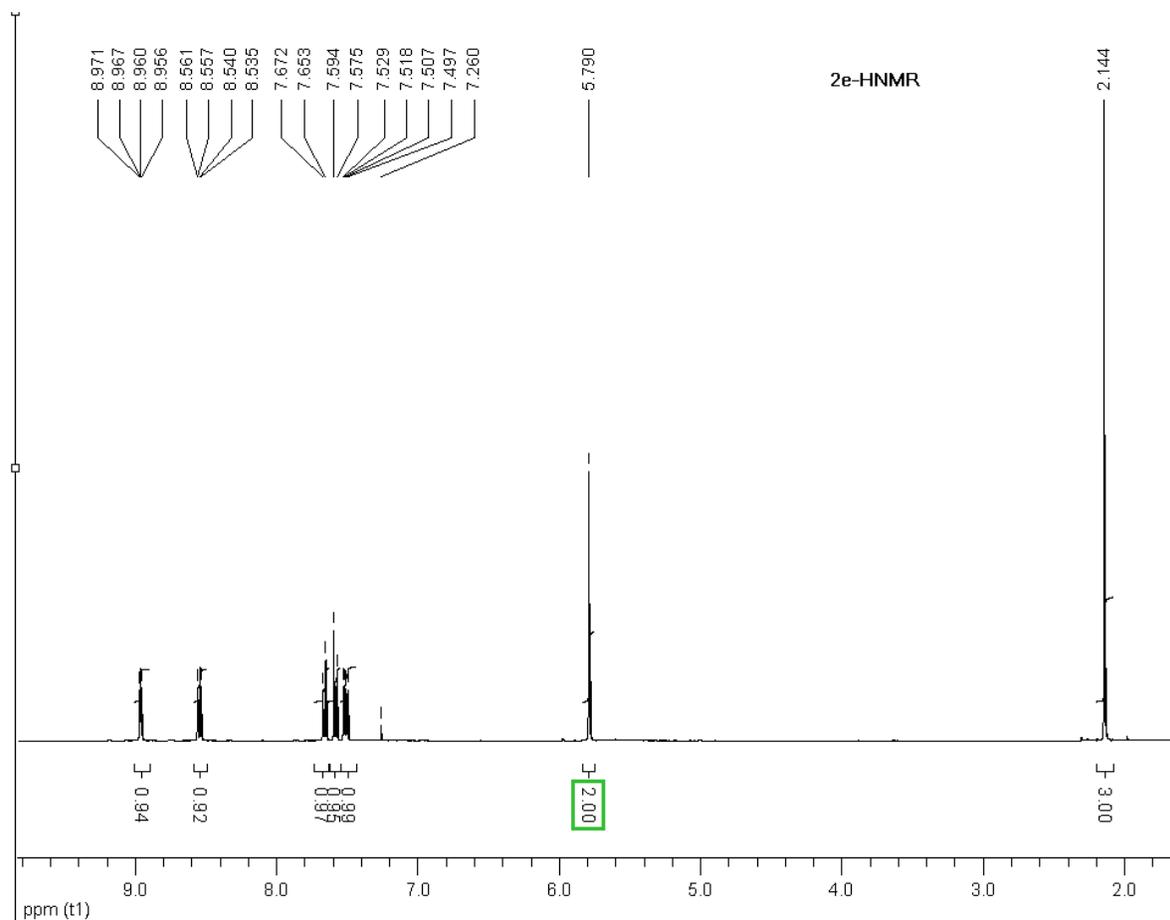
**8-Acetoxymethyl-5-chloroquinoline (2e):**

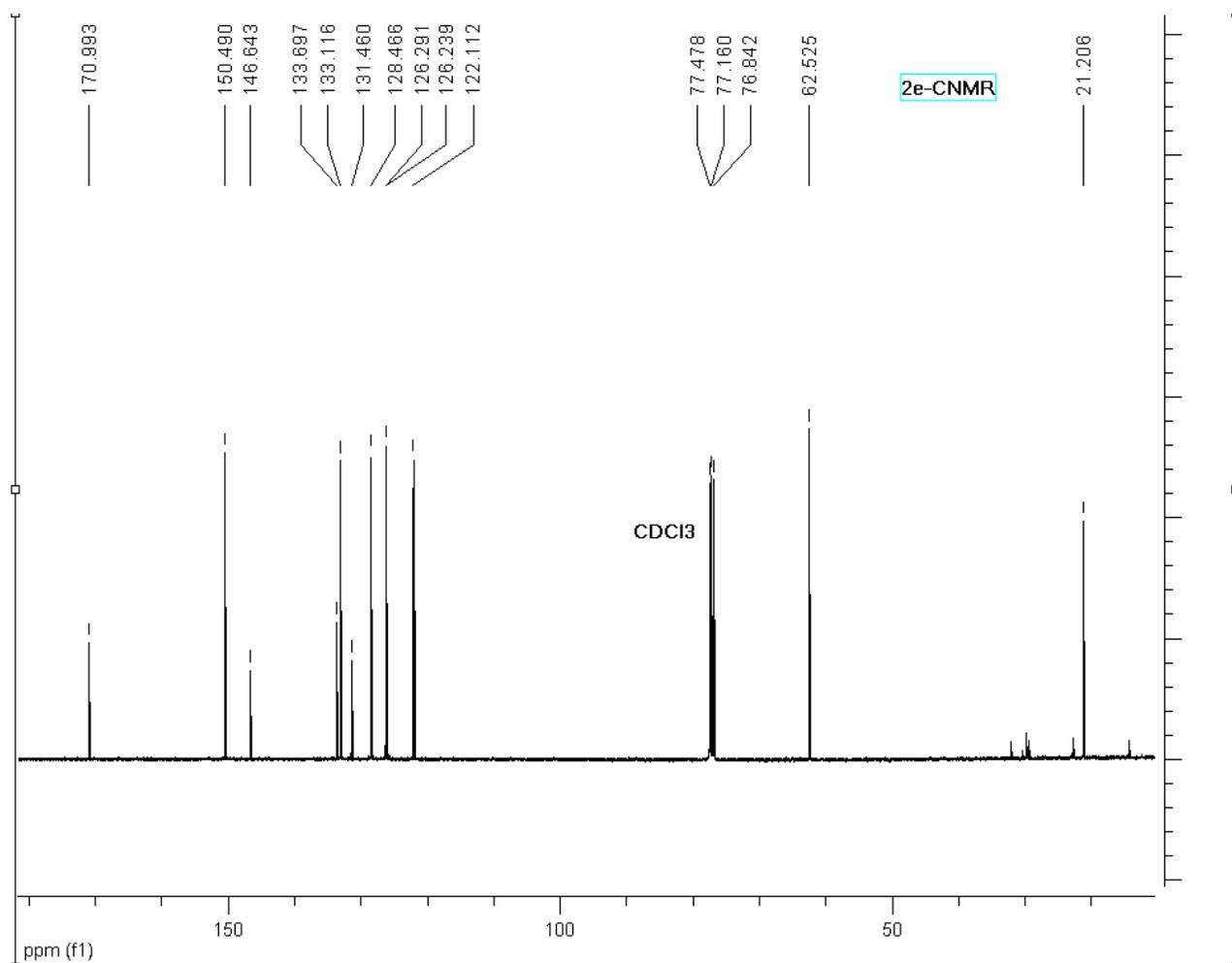


**2e**

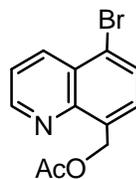
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 2.14 (s, 3H,  $-\text{CH}_3\text{-COO}$ ), 5.79 (s, 2H,  $-\text{CH}_2\text{OAc}$ ), 7.51 (dd, 1H,  $J_{\text{HH}} = 8.4$  Hz,  $J_{\text{HH}} = 4.0$  Hz, quinoline-H3), 7.58 (d, 1H,  $J_{\text{HH}} = 7.6$  Hz, quinoline-H6), 7.66 (d, 1H,  $J_{\text{HH}} = 7.6$  Hz, quinoline-H7), 8.55 (dd, 1H,  $J_{\text{HH}} = 8.4$  Hz  $J_{\text{HH}} = 1.6$  Hz, quinoline-H4), 8.96 (dd,  $J_{\text{HH}} = 4.0$  Hz,  $J_{\text{HH}} = 1.6$  Hz, quinoline-H2);  $^{13}\text{C}\{^1\text{H}\}$  (100.5 MHz,  $\text{CDCl}_3$ ): 21.5 (s,  $-\text{OOCCH}_3$ ), 62.8 (s,  $\text{CH}_2\text{OAc}$ ), 122.4 (s, quinoline-C3), 126.5 (s, quinoline-C10), 126.6 (s, quinoline-C4), 128.8 (s, quinoline-C6), 131.8 (s, quinoline-C5), 133.5 (s, quinoline-C7), 134.0 (s, quinoline-C8), 147.0 (s, quinoline-C9), 150.8 (s, quinoline-C2), 171.3 (s,  $\text{CH}_3\text{COO}$ );

See  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra below.





**8-Acetoxymethyl-5-bromoquinoline (2f):**<sup>12</sup>



**2f**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 20°C), δ:

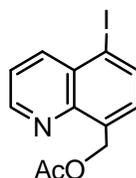
2.14 (s, 3H, CH<sub>3</sub>COO), 5.78 (s, 2H, -CH<sub>2</sub>-OAc), 7.52 (dd, 1H, *J*<sub>HH</sub> = 8.8 Hz, *J*<sub>HH</sub> = 4.0 Hz, quinoline-H3), 7.60 (d, 1H, *J*<sub>HH</sub> = 7.6 Hz, quinoline-H7), 7.80 (d, 1H, *J*<sub>HH</sub> = 7.6 Hz, quinoline-6), 8.53 (dd, 1H, *J*<sub>HH</sub> = 8.8 Hz, *J*<sub>HH</sub> = 1.6 Hz, quinoline-H4), 8.94 (dd, 1H, *J*<sub>HH</sub> = 4.0 Hz, *J*<sub>HH</sub> = 1.6 Hz, quinoline-H2);

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 20°C), δ:

21.3 (s, CH<sub>3</sub>COO), 62.7 (s, -CH<sub>2</sub>-OAc), 122.2 (s, quinoline-C5), 122.6 (s, quinoline-C3), 127.7 (s, quinoline-C8), 129.1 (s, quinoline-C7), 130.2 (s, quinoline-C6), 134.6 (s, quinoline-C10), 135.9 (s, quinoline-C4), 146.9 (s, quinoline-C9), 150.7 (s, quinoline-C2), 171.1 (s, -COO-);

HR-MS (FAB+): 279.9964 (M+H, <sup>79</sup>Br, 100.0%), 281.9946 (M+H, <sup>81</sup>Br, 93.0%). Calculated for C<sub>12</sub>H<sub>11</sub>BrNO<sub>3</sub>: 279.9973 (<sup>79</sup>Br, 100%); 281.9954 (<sup>81</sup>Br, 98.5%)

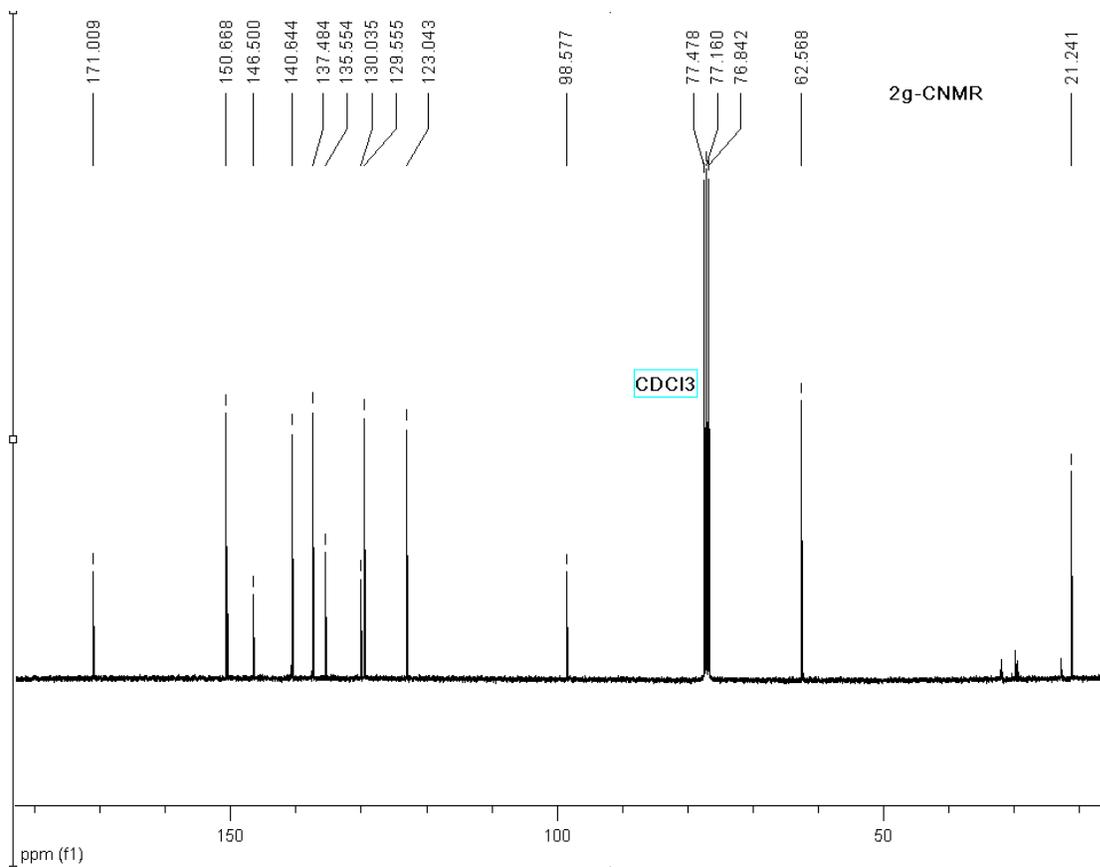
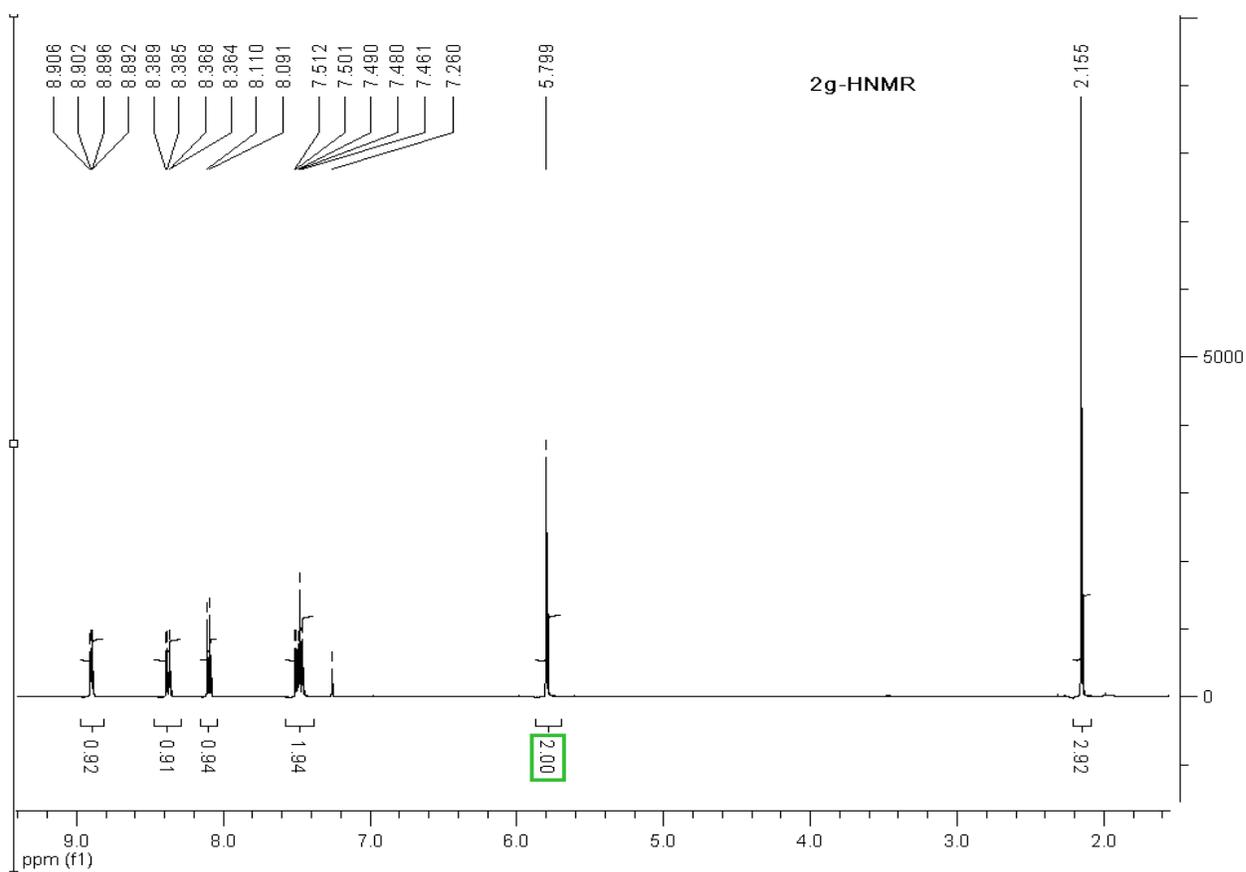
**8-Acetoxymethyl-5-iodoquinoline (2g):**



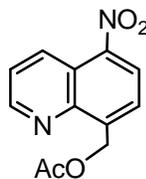
**2g**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 2.16 (s, 3H, -OOCCH<sub>3</sub>), 5.80 (s, 2H, -CH<sub>2</sub>OAc), 7.47 (d, 1H, *J*<sub>HH</sub> = 7.6 Hz, quinoline-H7), 7.50 (dd, 1H, *J*<sub>HH</sub> = 8.4 Hz, *J*<sub>HH</sub> = 4.0 Hz, quinoline-H3), 8.10 (d, 1H, *J*<sub>HH</sub> = 7.6 Hz, quinoline-H6), 8.38 (dd, 1H, *J*<sub>HH</sub> = 8.4 Hz, *J*<sub>HH</sub> = 1.6 Hz, quinoline-H4), 8.90 (dd, *J*<sub>HH</sub> = 4.0 Hz, *J*<sub>HH</sub> = 1.6 Hz, quinoline-H2); <sup>13</sup>C{<sup>1</sup>H} (100.5 MHz, CDCl<sub>3</sub>): 21.5 (s, -OOCCH<sub>3</sub>), 62.9 (s, -CH<sub>2</sub>OAc), 98.9 (s, quinoline-C5), 123.4 (s, quinoline-C3), 129.9 (s, quinoline-C4), 130.3 (s, quinoline-C10), 135.9 (s, quinoline-C8), 137.8 (s, quinoline-C7), 141.0 (s, quinoline-C6), 146.8 (s, quinoline-C9), 151.0 (s, quinoline-C2), 171.3 (s, -COO);

See <sup>1</sup>H and <sup>13</sup>C NMR spectra below.



**8-Acetoxyethyl-5-nitroquinoline (2h):**



**2h**

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $20^\circ\text{C}$ ),  $\delta$ :

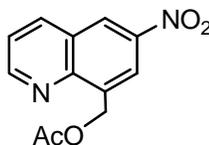
2.07 (s, 3H,  $\text{CH}_3\text{COO}$ ), 5.88 (s, 2H,  $-\text{CH}_2\text{-OAc}$ ), 7.64 – 7.67 (m, 1H, quinoline-H3), 7.81 (d, 1H,  $J_{\text{HH}} = 8.0$  Hz, quinoline-H7), 8.35 (d, 1H,  $J_{\text{HH}} = 8.0$  Hz, quinoline-6), 8.99-9.02 (m, 2H, quinoline-H2 and H4);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $20^\circ\text{C}$ ),  $\delta$ :

21.2 (s,  $\text{CH}_3\text{COO}$ ), 62.8 (s,  $-\text{CH}_2\text{-OAc}$ ), 121.1 (s, quinoline-C10), 124.3 (s, quinoline-C6), 124.6 (s, quinoline-C4), 125.4 (s, quinoline-C3), 132.4 (s, quinoline-C7), 142.6 (s, quinoline-C8), 145.2 (s, quinoline-C9), 145.6 (s, quinoline-C5), 150.9 (s, quinoline-C2), 170.9 (s,  $\text{CH}_3\text{COO}-$ );

HR-MS (FAB+): 247.0724 (M+H, 100.0%). Calculated for  $\text{C}_{12}\text{H}_{11}\text{N}_2\text{O}_4$ : 247.0719

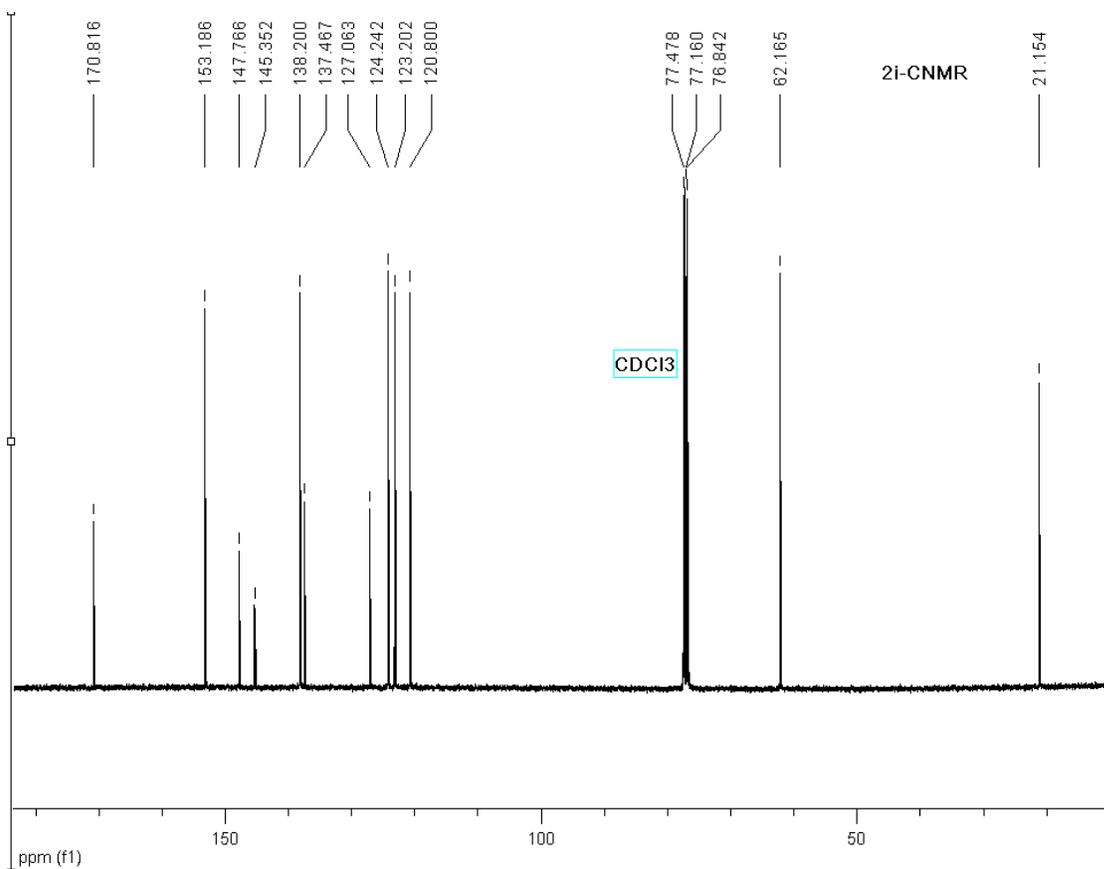
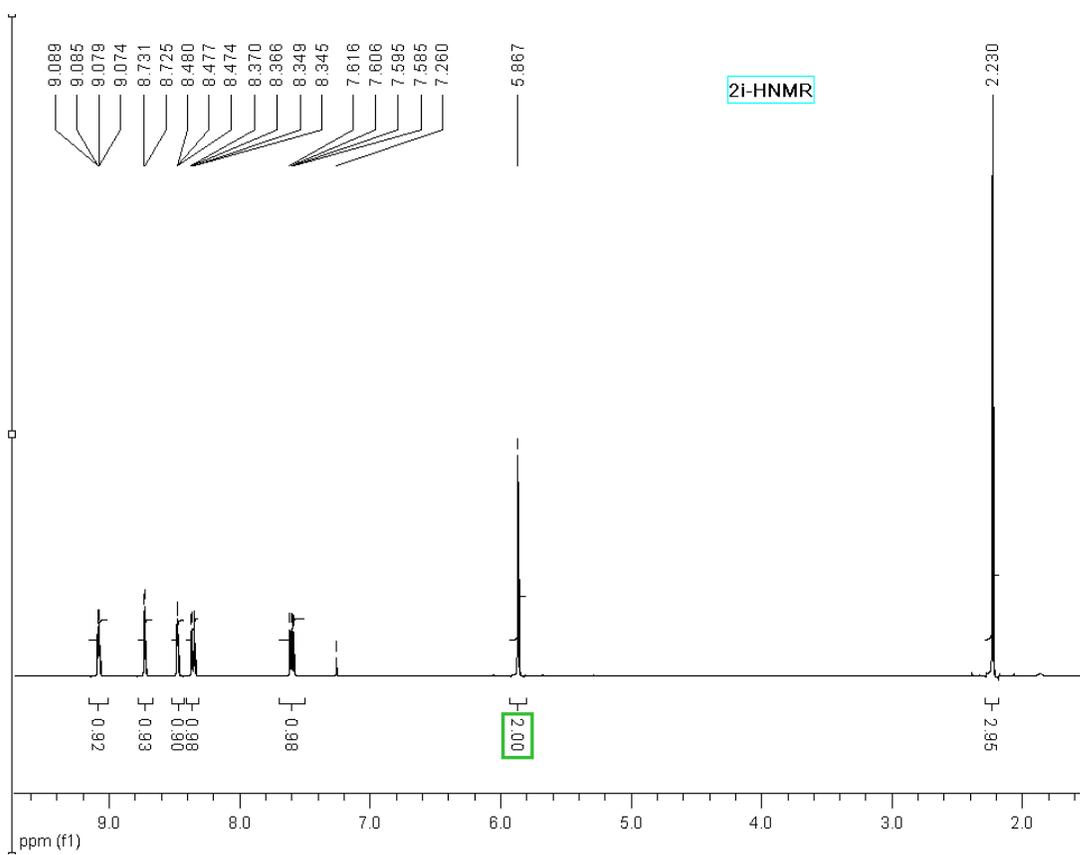
**8-Acetoxyethyl-6-nitroquinoline (2i):**



**2i**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 2.23 (s, 3H,  $-\text{OOCCH}_3$ ), 5.87 (s, 2H,  $\text{CH}_2\text{OAc}$ ), 7.60 (dd, 1H,  $J_{\text{HH}} = 8.4$  Hz,  $J_{\text{HH}} = 4.0$  Hz, quinoline-H3), 8.36 (dd, 1H,  $J_{\text{HH}} = 8.4$  Hz,  $J_{\text{HH}} = 1.6$  Hz, quinoline-H4), 8.48 (d, 1H,  $J_{\text{HH}} = 2.4$  Hz, quinoline-H7), 8.73 (d, 1H,  $J_{\text{HH}} = 2.4$  Hz, quinoline-H5), 9.08 (dd,  $J_{\text{HH}} = 4.0$  Hz,  $J_{\text{HH}} = 1.6$  Hz, quinoline-H2);  $^{13}\text{C}\{^1\text{H}\}$  (100.5 MHz,  $\text{CDCl}_3$ ): 21.2 (s,  $-\text{OOCCH}_3$ ), 62.2 (s,  $\text{CH}_2\text{OAc}$ ), 120.9 (s, quinoline-C3), 123.3 (s, quinoline-C5), 124.3 (s, quinoline-C7), 127.1 (s, quinoline-C10), 137.5 (s, quinoline-C8), 138.3 (s, quinoline-C4), 145.4 (s, quinoline-C6), 147.8 (s, quinoline-C9), 153.3 (s, quinoline-C2), 170.9 (s,  $-\text{COO}$ );

See  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra below.



## 7. Attempted catalytic oxidation of 2-(*p*-tolyl)pyridine and pinacolone oxime in AcOH

### Attempted oxidation of 2-(*p*-tolyl)pyridine and pinacolone oxime with O<sub>2</sub> in the presence of Pd(acac)<sub>2</sub> - H<sub>2</sub>hpda

In a 25 mL Schlenk flask substrates 2-(*p*-tolyl)pyridine or pinacolone oxime (1 mmol), Pd(acac)<sub>2</sub> (0.05mmol) and a ligand (0.05mmol) were mixed with acetic acid (5mL). Acetic anhydride (2 mmol) was added and the flask was purged with O<sub>2</sub> for 10 min and then heated at 80°C for 24h. Upon cooling to room temperature, a sample of the solution was diluted with CD<sub>3</sub>COOD and <sup>1</sup>H NMR spectrum was recorded which indicated that no oxidation products formed and all the substrate remained in the solution.

10 μL anisole additive was used as an internal standard.

### a) Palladation of 2-(*p*-tolyl)pyridine with Pd(hpda)(DMF) in AcOH

Pd(hpda)(DMF) (22mg, 0.06 mmol) and 2-(*p*-tolyl)pyridine (10.2 mg, 0.06 mmol) were mixed in AcOH (2 mL) and the mixture was heated under argon at 60°C for 12h. After cooling to room temperature, the solution was evaporated to dryness. The orange solid was dissolved in acetic acid-*d*<sub>4</sub> (1mL) and the <sup>1</sup>H NMR indicated the formation of Pd(H-hpda)(κ<sup>2</sup>-*C,N*-C<sub>5</sub>H<sub>4</sub>N-(*p*-MeC<sub>6</sub>H<sub>3</sub>)) (49%) which was confirmed by comparing its <sup>1</sup>H NMR spectra with that of authentic sample prepared from [Pd(μ-OAc)(κ<sup>2</sup>-*C,N*-2-(*p*-MeC<sub>6</sub>H<sub>3</sub>)C<sub>5</sub>H<sub>4</sub>N)]<sub>2</sub> and H<sub>2</sub>-hpda in DMF. The yield was determined by <sup>1</sup>H NMR integration using 20 μL anisole additive as an internal standard.

Interestingly, when the above solution was heated under O<sub>2</sub> for 24h at 110°C, formation of 2-(2-acetoxy-4-methylphenyl)pyridine was detected, NMR yield 5%. No palladium black was detected.

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 20°C), δ:

2.24 (s, 3H, CH<sub>3</sub>-Ph), 6.94 (d, 1H, *J*<sub>HH</sub> = 7.2 Hz, aryl-H), 7.24 (br s 1H, aryl-H), 7.46 (br s, 1H, aryl-H), 7.53 (d, 2H, *J*<sub>HH</sub> = 7.2 Hz, aryl-H), 7.95 (br s, 1H, aryl-H), 8.00 (br s, 1H, aryl-H), 8.30 (br s, 1H, aryl-H), 12.7 (brs, 2H, -COOH and -OH).

### 2) Attempted palladation of pinacolone oxime with Pd(hpda)(DMF) in AcOH

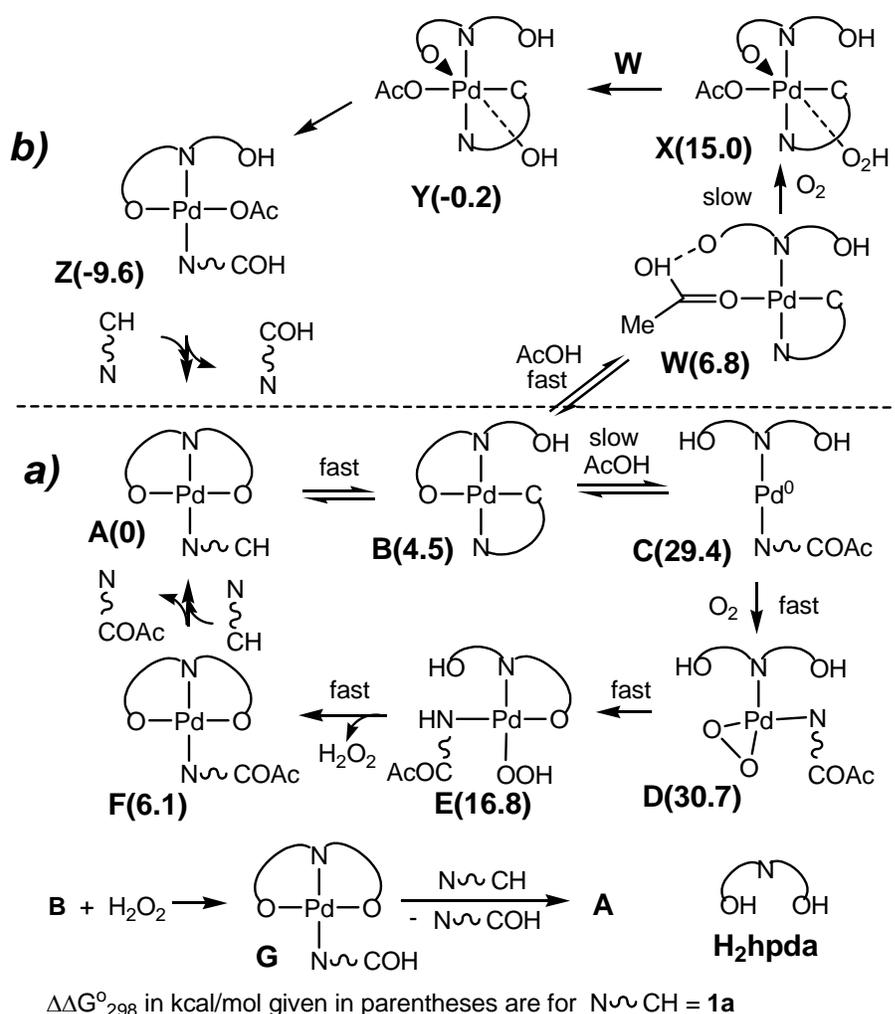
Pd(hpda)(DMF) (22mg, 0.06 mmol) and pinacolone oxime (6.9 mg, 0.06 mmol) were mixed in AcOH (2 mL) and the mixture was heated under argon at 60°C for 12h. After cooling to room temperature, the solution was evaporated to dryness. The orange solid was dissolved in acetic acid-

$d_4$  (1mL) and the  $^1\text{H}$  NMR indicated no formation of the cyclopalladation complex of Pd(H-hpda)( $\kappa^2$ -*N,C*-CH<sub>2</sub>-CMe<sub>2</sub>-C(NO<sub>2</sub>)CH<sub>3</sub>).

#### 8. Oxidation of **3a** – H<sub>2</sub>-*t*-Bu-pda adduct (complex **7**) in AcOH with hydrogen peroxide

Complex **3a** (6.2mg, 0.01mmol) and 4-*tert*-butylpyridine-2,6-dicarboxylic acid (4.5mg, 0.02 mmol) were dissolved in acetic acid- $d_4$  (1mL) and the solution was stirred at room temperature for 0.5h under argon atmosphere. 30% aqueous H<sub>2</sub>O<sub>2</sub> (4.5  $\mu\text{L}$ , 2 equiv) was added and the solution was stirred under argon system for 1.5 h.  $^1\text{H}$  NMR indicates the formation of **2a** (28.7%) and **5a** (13.5%) with 20  $\mu\text{L}$  anisole additive as an internal standard.

**9. DFT calculations: optimized geometries and total energies (Hartree) of intermediates in Scheme 3**



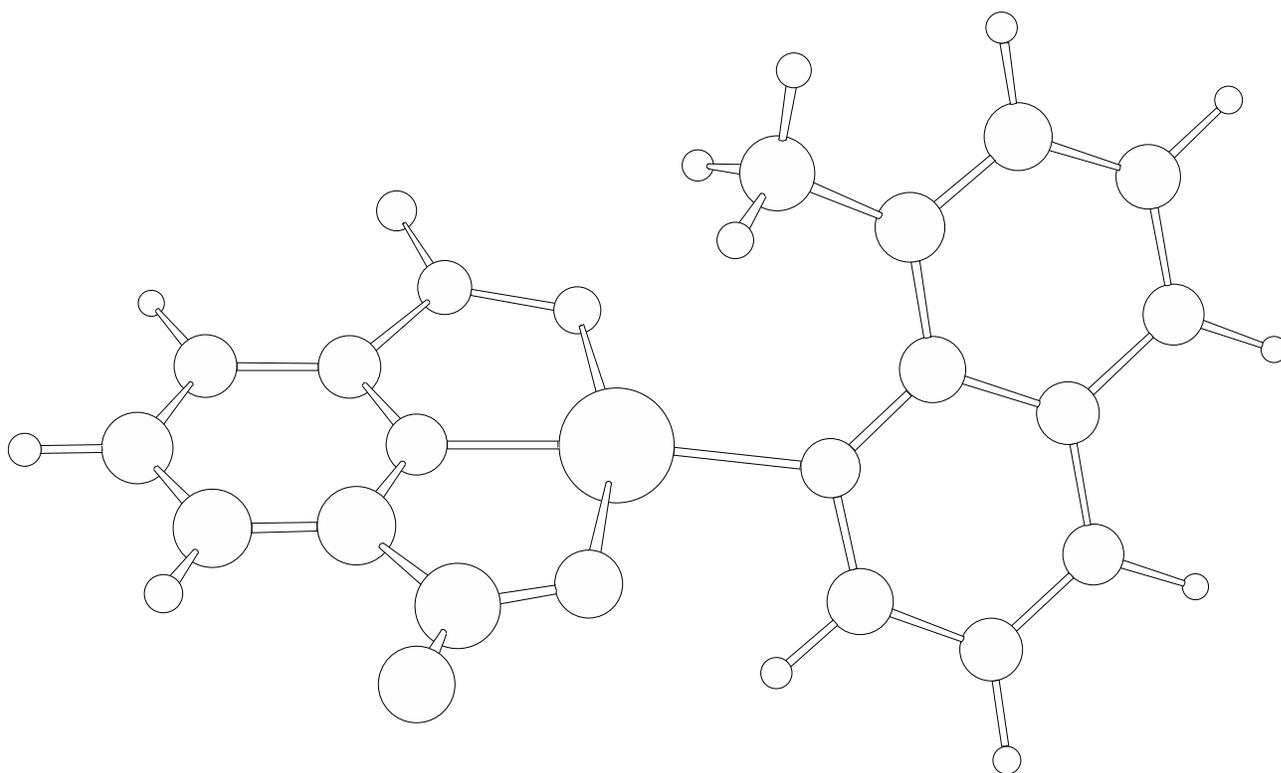
The present preliminary computational analysis lacking some key activation barriers such as one for transformation of **W** to **X** does not allow to discriminate between path a) and b). Importantly, the energy of intermediates and barrier height may be highly solvent-dependent and significantly different in the gas phase and in acetic acid solutions. For instance, our experiments show that **A** and **B** derived from **1a** are of almost the same energy, whereas DFT predicts that **B** is 4.5 kcal/mol less stable. The ability of **B** that has a free COOH group to serve as a strong hydrogen bond donor in AcOH solution allows to account for this discrepancy. A separate computational study may be required to shed light on this and similar problems. In addition, our preliminary computational results show that the transformation of 2-phenylpyridine derived **W** to **X** (N-CH is 2-phenylpyridine in Scheme 3) is about 3 kcal/mol more uphill compared to 8-methylquinoline derivative (N-CH is 8-

methylquinoline in Scheme 3). If we assume that the rate of this transformation is also slower for the aryl palladium(II) complex compared to the 8-methylquinoline analogue, the mechanism shown in Scheme 3b might allow to account for the observed lack of reactivity of the aromatic substrate in reaction (1) under the experimental conditions employed.

Both mechanisms allow to account for the formation of a mixture of alcohols **5** and acetates **2** in stoichiometric aerobic oxidation of 8-methylquinoline – derived complexes **B**. Formation of alcohols and acetate is shown explicitly in Scheme 3a. In the mechanism b) reductive elimination of acetates **2** can occur as a result of an  $S_N2$  attack of AcOH solvent at the benzylic carbon of intermediates **Y** as it was proposed by Stahl for a similar intermediate.<sup>14</sup>

We believe that both mechanisms a) and b) might be operative in our systems. More detailed computational and mechanistic studies will be necessary to support this statement.

A

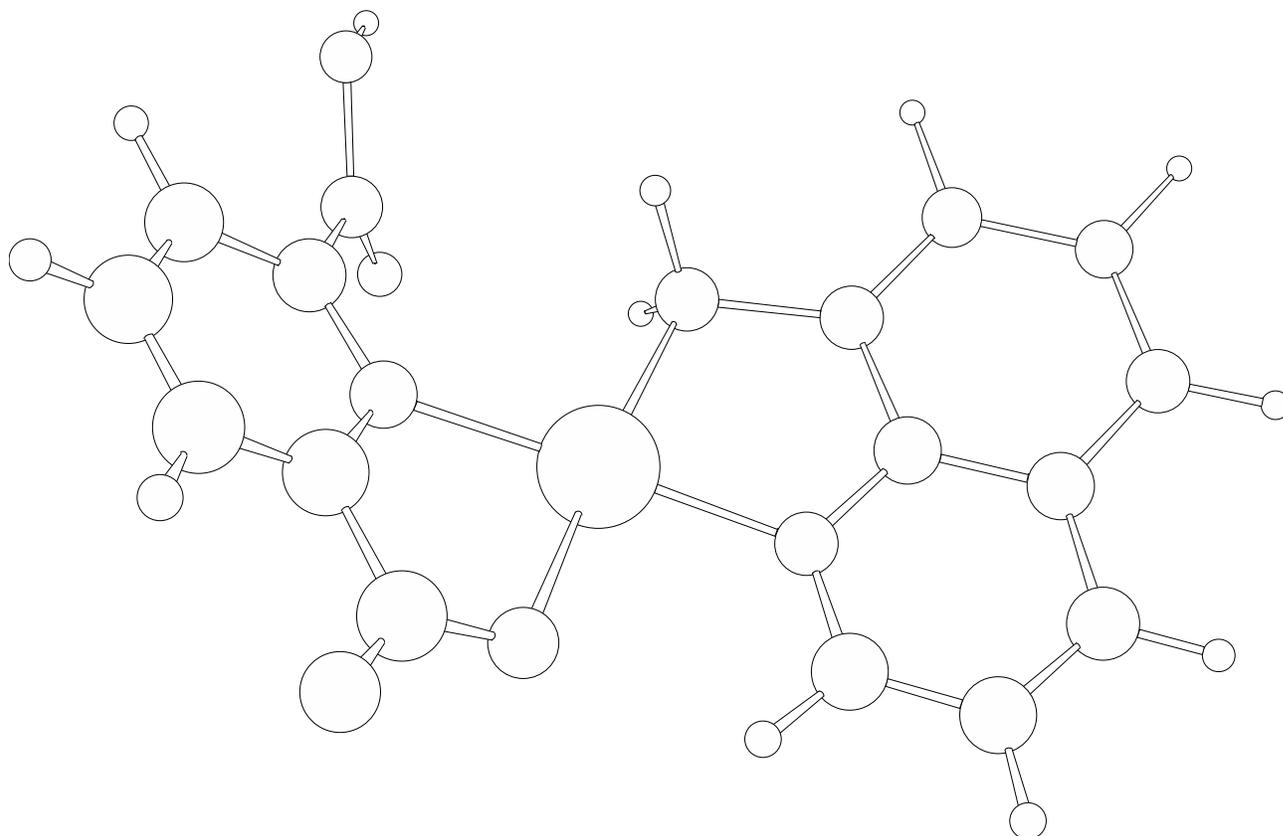


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**B**

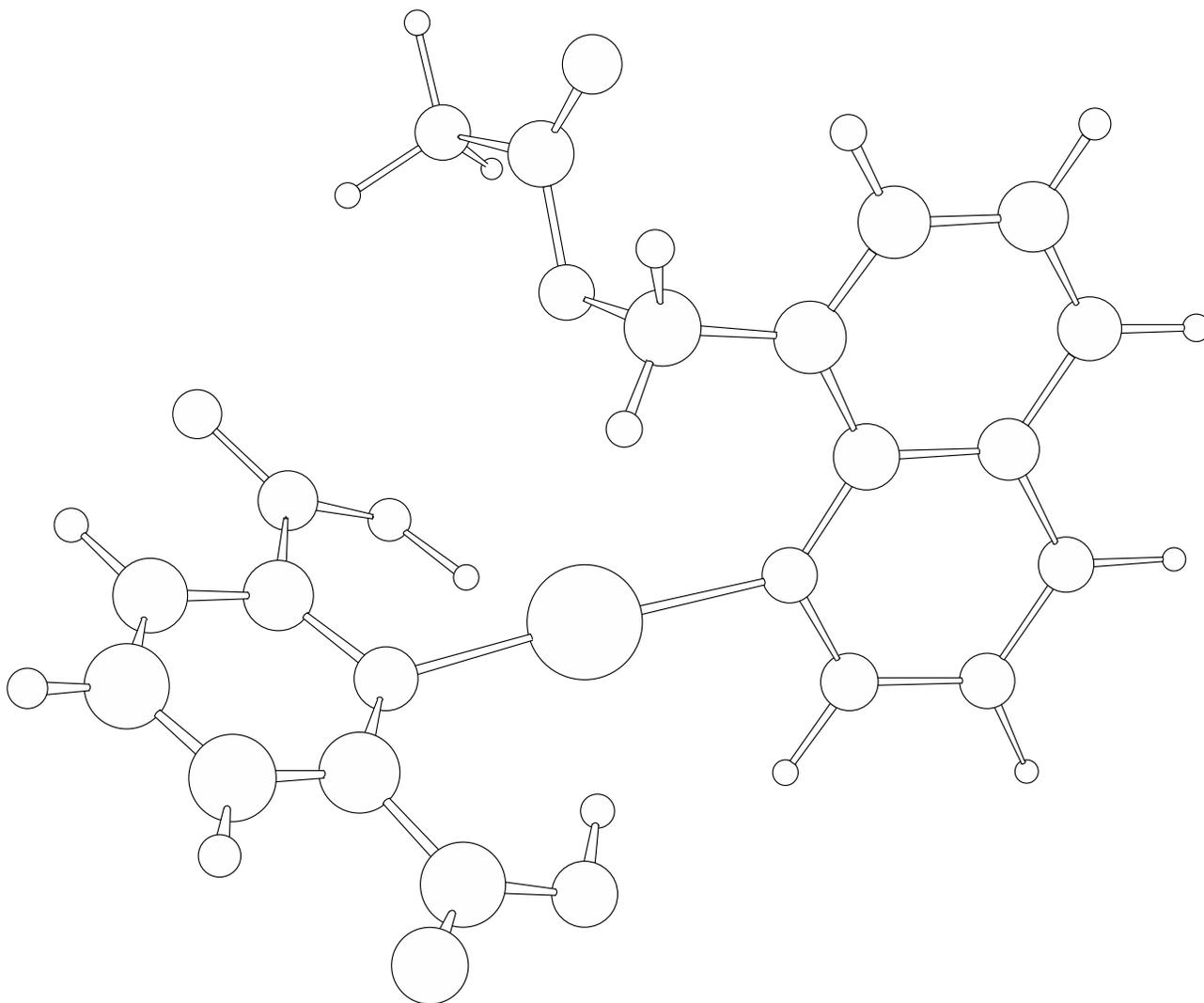


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C

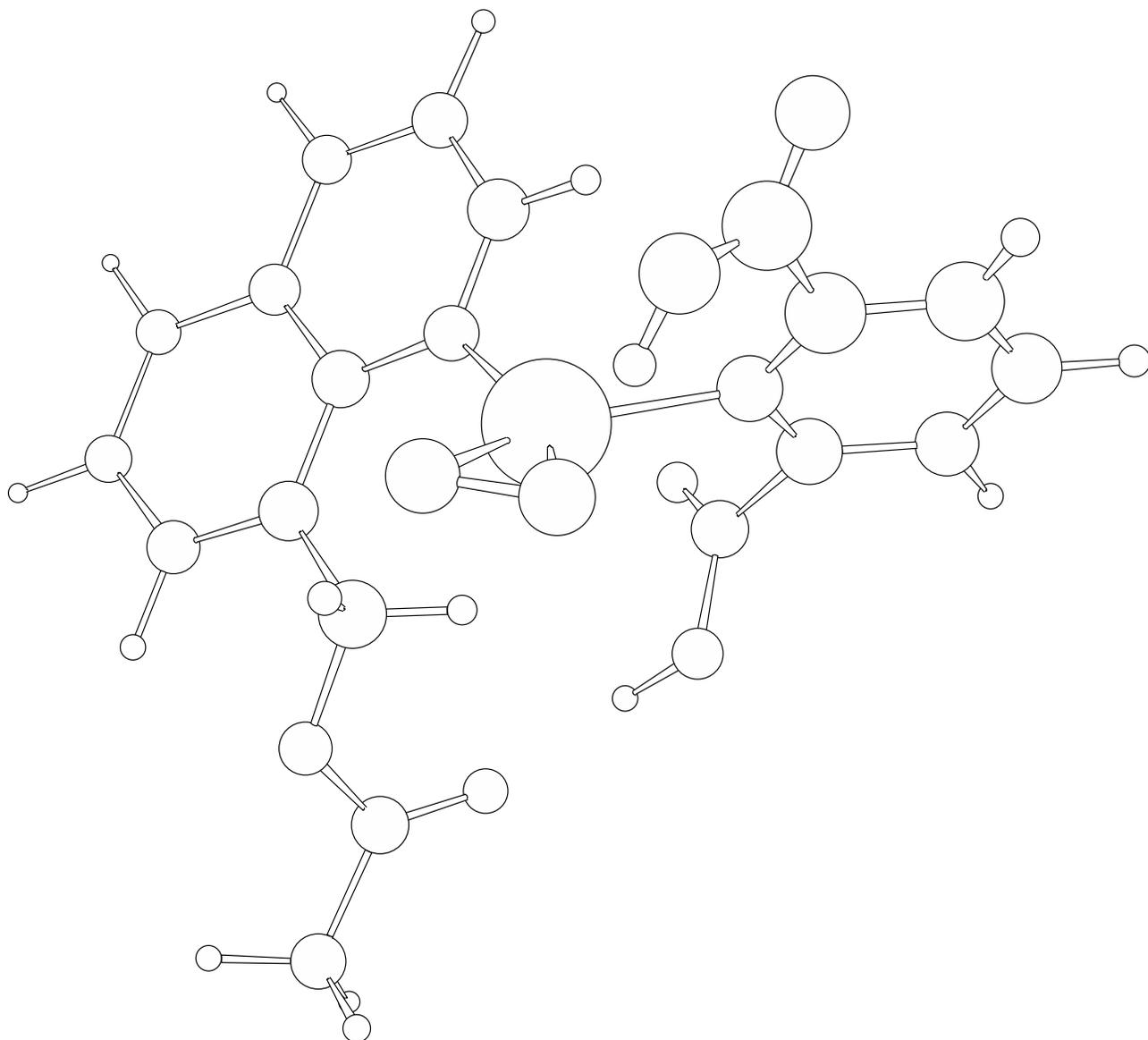


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**D**

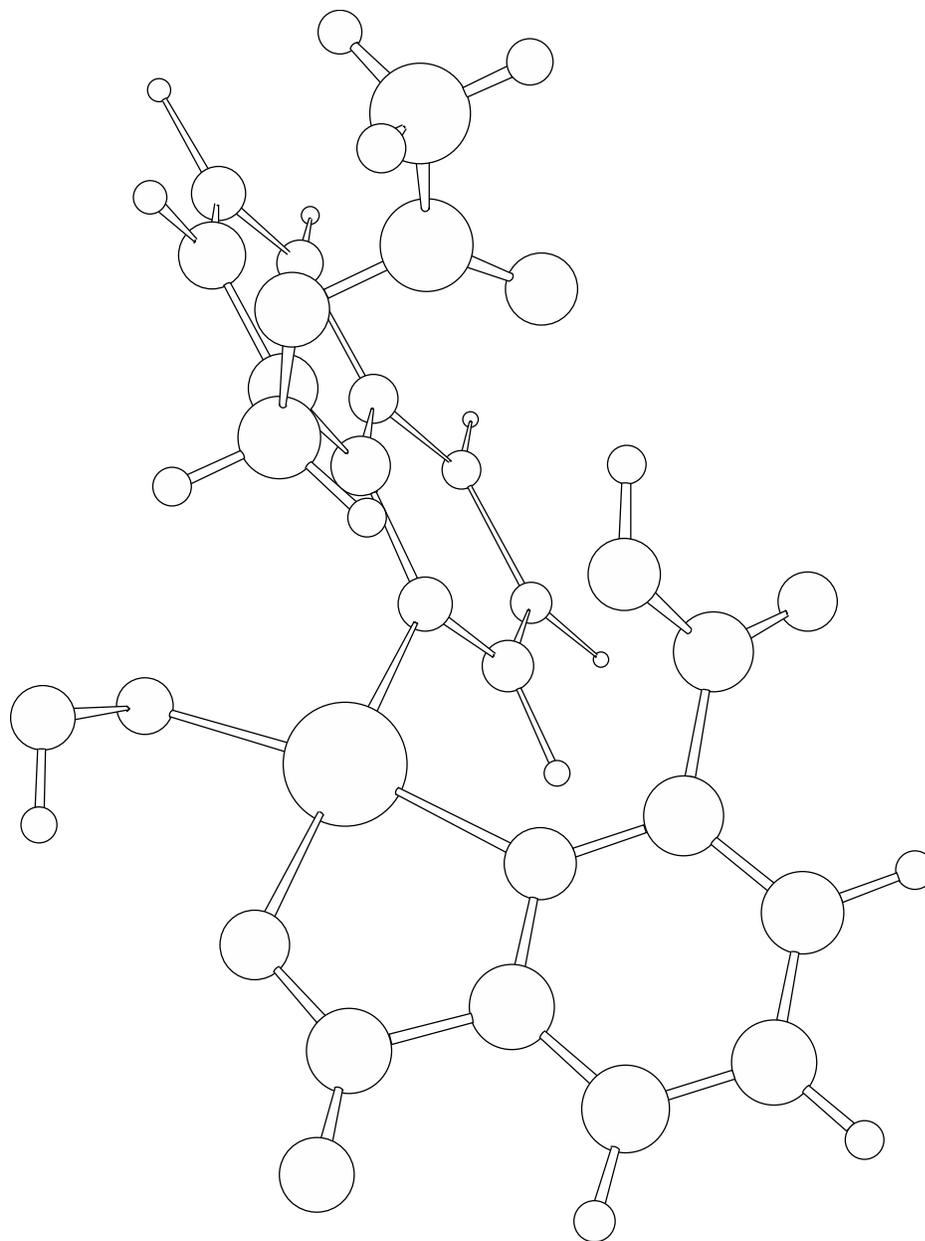


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**E**

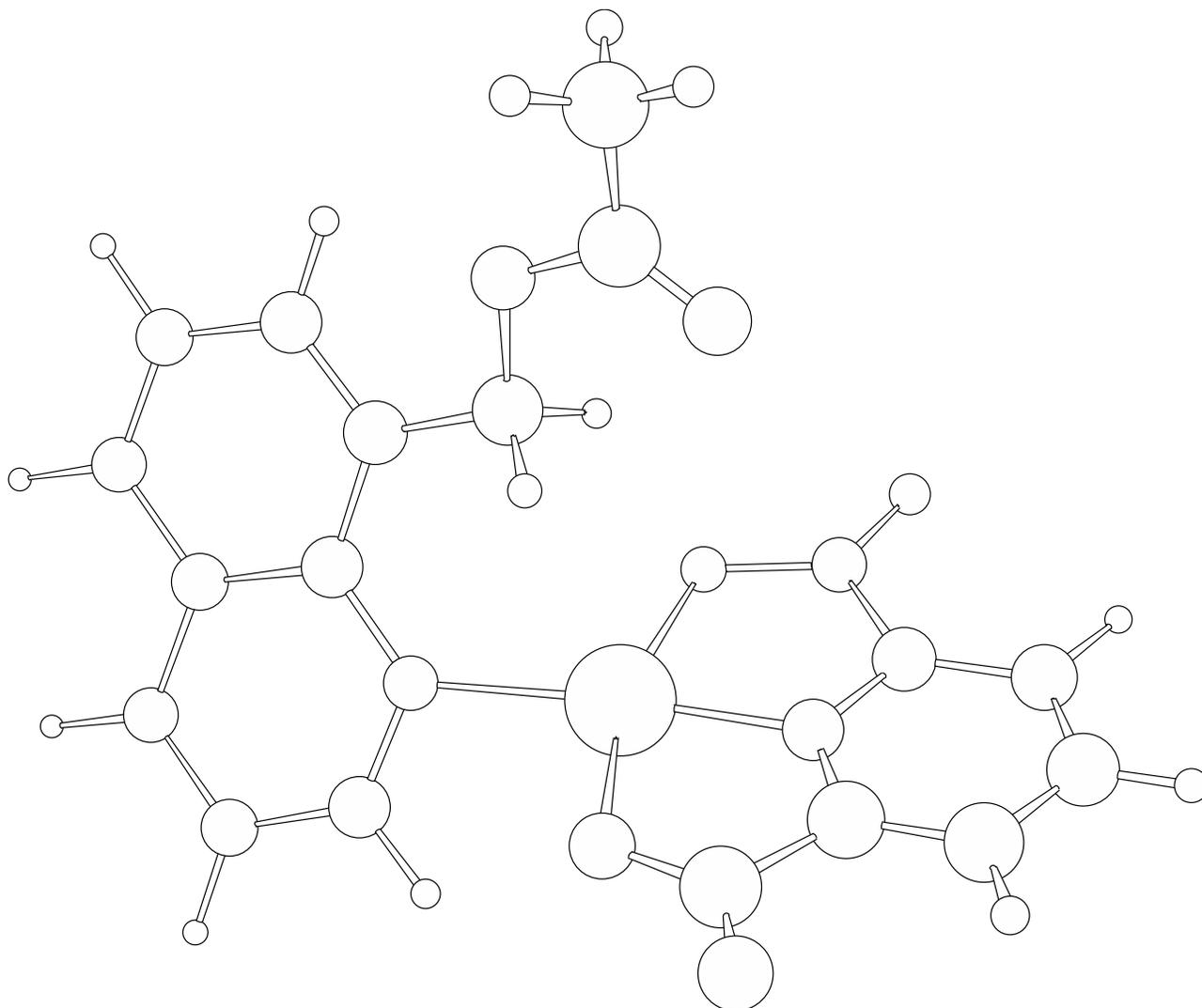


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**F**

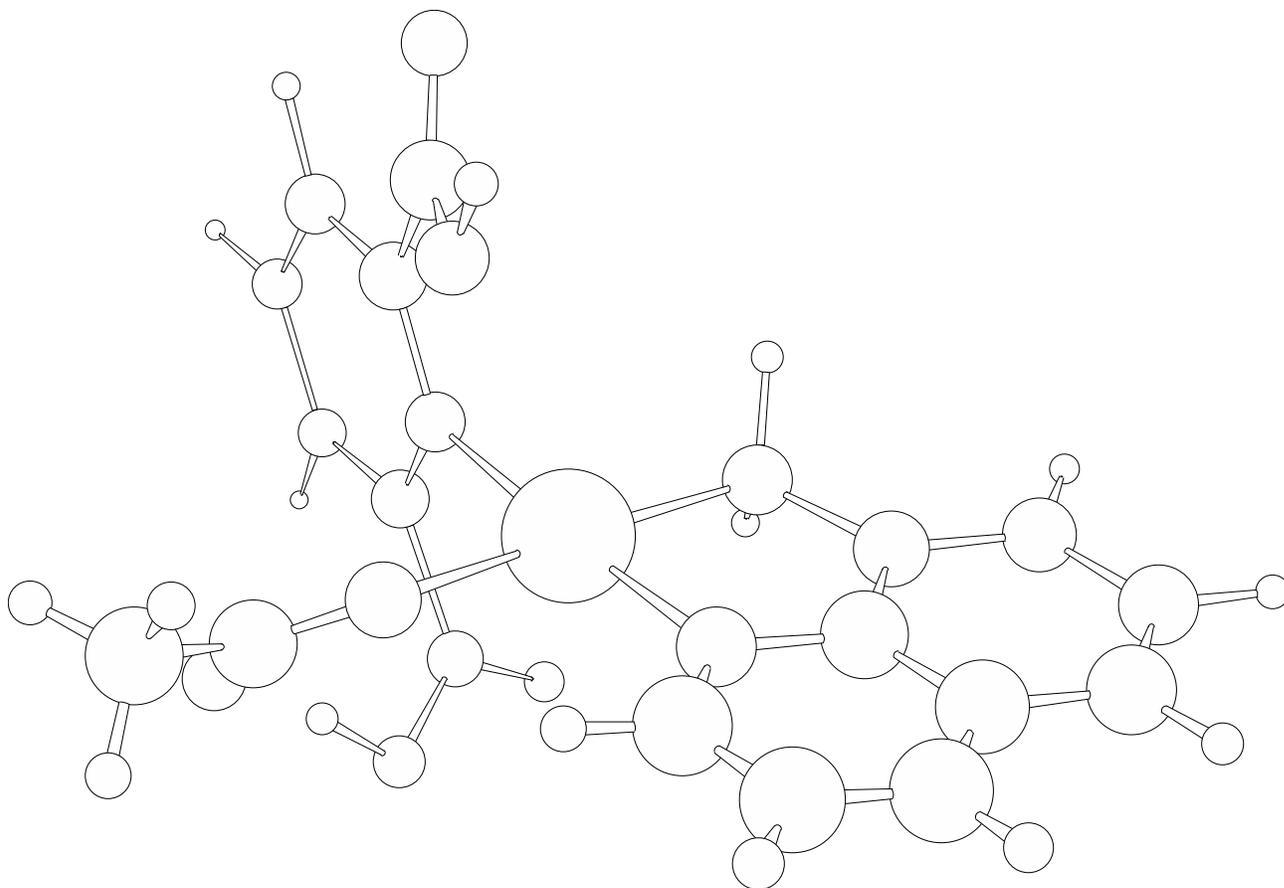


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W

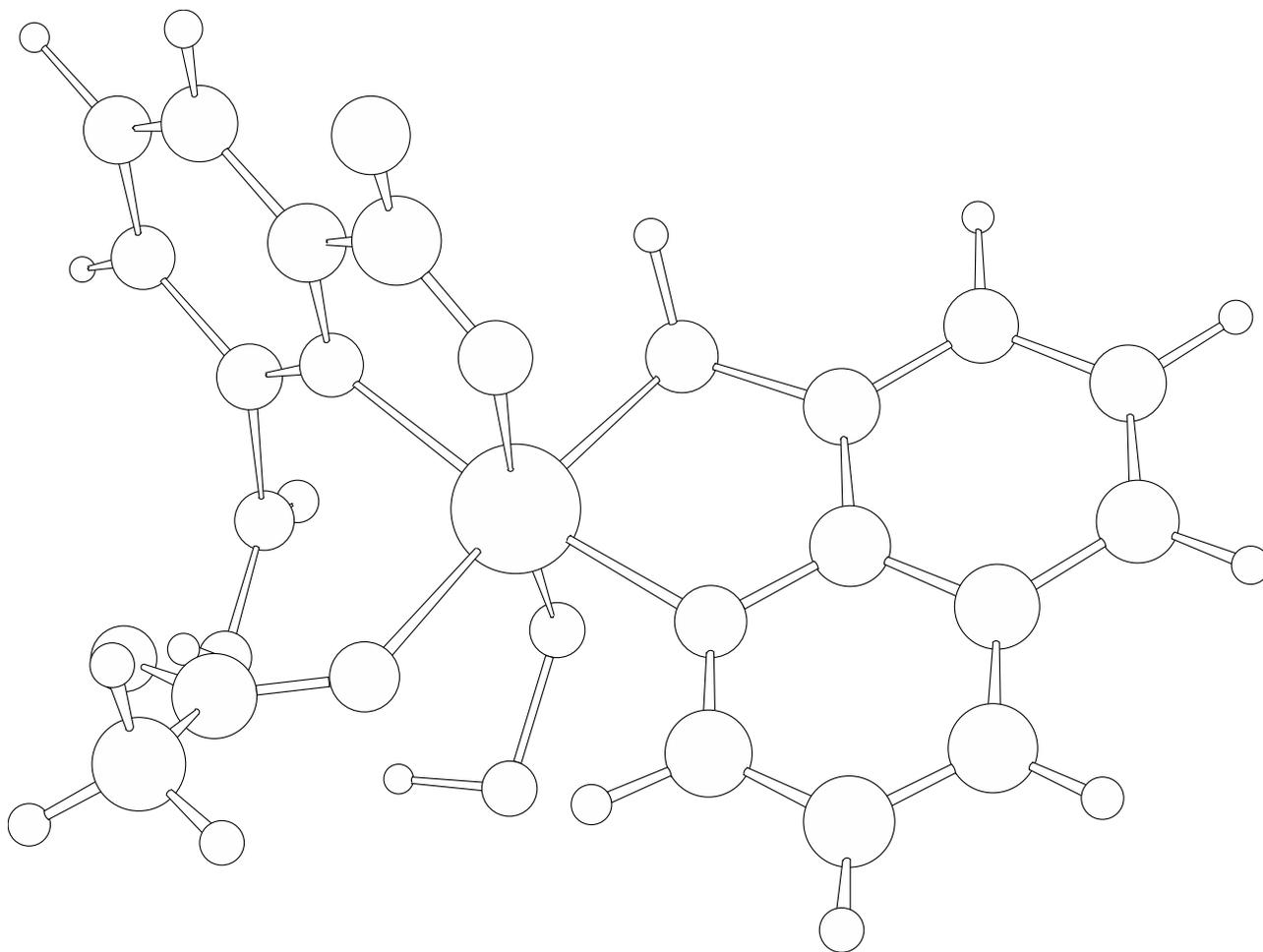


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**X**

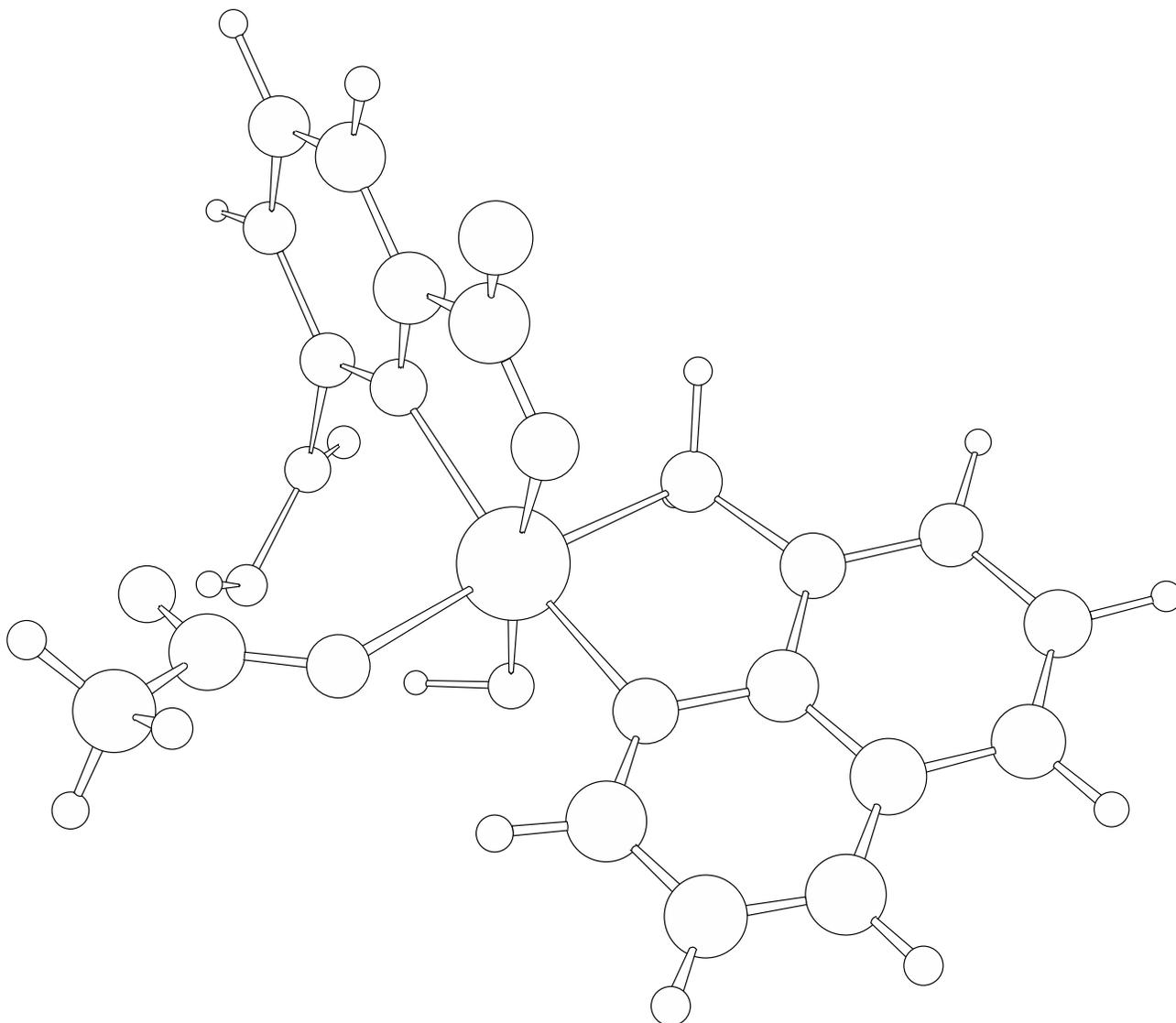


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Y

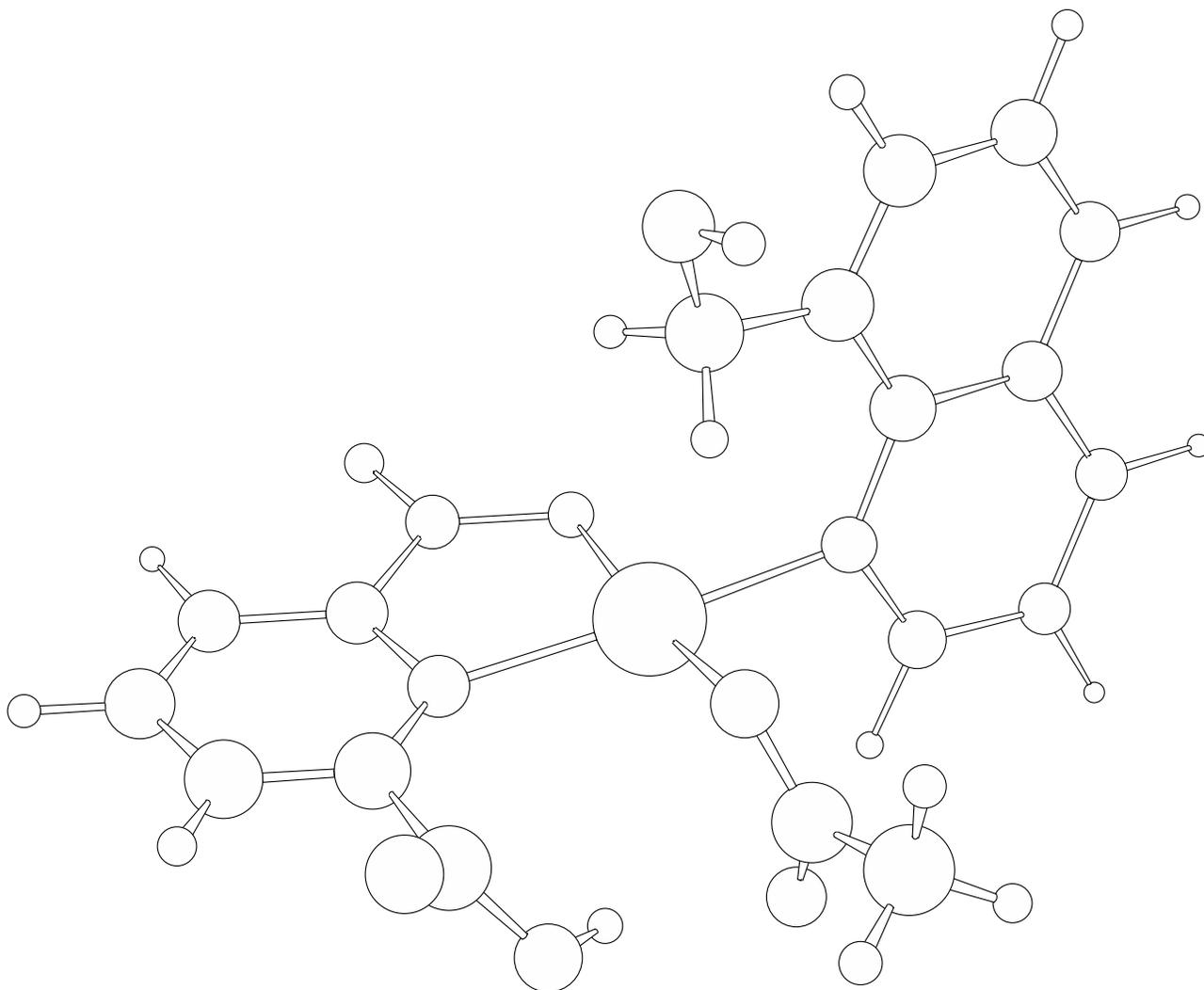


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**Z**

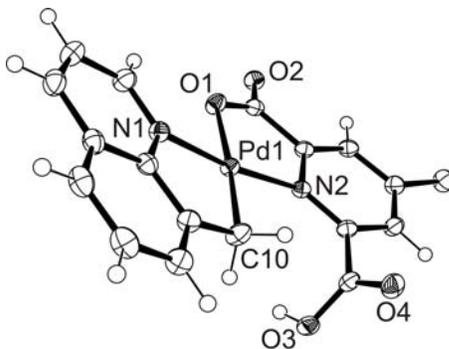


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## 10. X-Ray crystal structure determination of complex $7a \cdot \text{CH}_2\text{Cl}_2$



A colorless prism of  $(\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_4\text{Pd}) \cdot \text{CH}_2\text{Cl}_2$ , approximate dimensions  $0.075 \times 0.075 \times 0.185 \text{ mm}^3$ , was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 150(2) K on a three-circle diffractometer system equipped with Bruker Smart Apex II CCD area detector using a graphite monochromator and a  $\text{MoK}\alpha$  fine-focus sealed tube ( $\lambda = 0.71073 \text{ \AA}$ ). The detector was placed at a distance of 5.2 cm from the crystal.

A total of 4230 frames were collected with a scan width of  $0.3^\circ$  an exposure time of 10 sec/frame using Apex2 (Bruker, 2005). The total data collection time was 18.8 hours. The frames were integrated with Apex2 software package using a narrow-frame integration algorithm. The integration of the data using a Triclinic unit cell yielded a total of 22144 reflections to a maximum  $\theta$  angle of  $30.00^\circ$ , of which 6360 were independent (completeness = 99.2%,  $R_{\text{int}} = 2.09\%$ ,  $R_{\text{sig}} = 2.10\%$ ) and 5880 were greater than  $2\sigma(I)$ .

The final cell dimensions of  $a = 9.8530(3) \text{ \AA}$ ,  $b = 10.5424(3) \text{ \AA}$ ,  $c = 10.9053(3) \text{ \AA}$ ,  $\alpha = 95.7794(4)^\circ$ ,  $\beta = 96.0116(4)^\circ$ ,  $\gamma = 100.7455(4)^\circ$ ,  $V = 1098.39(5) \text{ \AA}^3$ , are based upon the refinement of the XYZ-centroids of 13725 reflections with  $2.6 < \theta < 30.9^\circ$  using Apex2 software. Analysis of the data showed 0 % decay during data collection. Data were corrected for absorption effects with the Semi-empirical from equivalents method using SADABS (Sheldrick, 1996). The minimum and maximum transmission coefficients were 0.814 and 0.919.

The structure was solved and refined using the SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997) software in the space group  $P-1$  with  $Z = 2$  for the formula unit  $(\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_4\text{Pd}) \cdot \text{CH}_2\text{Cl}_2$ . The final anisotropic full-matrix least-squares refinement on  $F^2$  with 303 variables converged at  $R_1 = 2.40\%$  for the observed data and  $wR_2 = 5.23\%$  for all data. The goodness-of-fit was 1.000. The largest peak on the final difference map was  $0.691 \text{ e}/\text{\AA}^3$  and the largest hole was  $-0.593 \text{ e}/\text{\AA}^3$ . On the basis of the final model, the calculated density was  $1.680 \text{ g}/\text{cm}^3$  and  $F(000)$ ,  $560 \text{ e}$ .

**Table 1.** Crystal data and structure refinement for UM#1596.

X-ray lab book No.	1596	
Empirical formula	(C <sub>21</sub> H <sub>20</sub> N <sub>2</sub> O <sub>4</sub> Pd)·CH <sub>2</sub> Cl <sub>2</sub>	
Formula weight	555.72	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal size	0.185×0.075×0.075 mm <sup>3</sup>	
Crystal habit	colorless prism	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	$a = 9.8530(3) \text{ \AA}$	$\alpha = 95.7794(4)^\circ$
	$b = 10.5424(3) \text{ \AA}$	$\beta = 96.0116(4)^\circ$
	$c = 10.9053(3) \text{ \AA}$	$\gamma = 100.7455(4)^\circ$
Volume	1098.39(5) Å <sup>3</sup>	
Z	2	
Density, $\rho_{\text{calc}}$	1.680 g/cm <sup>3</sup>	
Absorption coefficient, $\mu$	1.120 mm <sup>-1</sup>	
F(000)	560 e <sup>-</sup>	
Diffractometer	Bruker Smart Apex II CCD area detector	
Radiation source	fine-focus sealed tube, MoK $\alpha$	
Detector distance	5.2 cm	
Data collection method	$\omega$ and $\phi$ scans	
Total frames	4230	
Frame size	512 pixels	
Frame width	0.3°	
Exposure per frame	10 sec	
Total measurement time	18.8 hours	
$\theta$ range for data collection	1.89 to 30.00°	
Index ranges	$-13 \leq h \leq 13, -14 \leq k \leq 14, -15 \leq l \leq 15$	
Reflections collected	22144	
Independent reflections	6360	
Observed reflection, $I > 2\sigma(I)$	5880	
Coverage of independent reflections	99.2 %	
Variation in check reflections	0 %	
Absorption correction	Semi-empirical from equivalents SADABS (Sheldrick, 1996)	
Max. and min. transmission	0.919 and 0.814	
Structure solution technique	direct	
Structure solution program	SHELXS-97 (Sheldrick, 1990)	
Refinement technique	Full-matrix least-squares on F <sup>2</sup>	
Refinement program	SHELXL-97 (Sheldrick, 1997)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	6360 / 6 / 303	
Goodness-of-fit on F <sup>2</sup>	1.000	
$\Delta/\sigma_{\text{max}}$	0.001	
Final R indices:	R <sub>1</sub> , $I > 2\sigma(I)$	0.0240
	wR <sub>2</sub> , all data	0.0523
	R <sub>int</sub>	0.0209
	R <sub>sig</sub>	0.0210
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.01P)^2 + 1.462P]$ , $P = [\max(F_o^2, 0) + 2F_o^2]/3$	
Largest diff. peak and hole	0.691 and -0.593 e <sup>-</sup> /Å <sup>3</sup>	

$$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|, \quad wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$$

**Table 2.** Atomic coordinates and equivalent\* isotropic atomic displacement parameters ( $\text{\AA}^2$ ) for UM#1596.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	$U_{eq}$
Pd1	0.248127(13)	0.444647(12)	0.452622(11)	0.01600(4)
N1	0.38860(14)	0.36307(13)	0.54569(13)	0.0188(3)
C10	0.27885(19)	0.32214(18)	0.30782(16)	0.0235(3)
C11	0.43614(19)	0.39366(18)	0.66515(16)	0.0238(3)
C12	0.5385(2)	0.33479(19)	0.72353(17)	0.0271(4)
C13	0.59186(19)	0.24344(18)	0.65657(17)	0.0252(4)
C14	0.54519(17)	0.20971(16)	0.52813(16)	0.0208(3)
C15	0.59381(19)	0.11842(17)	0.44805(18)	0.0251(4)
C16	0.5392(2)	0.09237(18)	0.32555(18)	0.0266(4)
C17	0.43550(19)	0.15559(18)	0.27591(17)	0.0250(4)
C18	0.38688(18)	0.24687(16)	0.34987(16)	0.0204(3)
C19	0.44212(17)	0.27237(16)	0.47573(15)	0.0184(3)
O1	0.21353(13)	0.56376(12)	0.61164(11)	0.0217(2)
O2	0.10053(13)	0.72284(12)	0.66225(11)	0.0215(2)
O3	0.00873(13)	0.33520(12)	0.14463(11)	0.0218(2)
O4	0.15883(14)	0.47812(13)	0.06620(11)	0.0263(3)
N2	0.11720(14)	0.55279(13)	0.36700(12)	0.0162(2)
C21	0.14017(17)	0.64570(16)	0.58544(15)	0.0182(3)
C22	0.09384(16)	0.64997(15)	0.44917(15)	0.0171(3)
C23	0.02942(17)	0.74870(16)	0.41382(15)	0.0194(3)
C24	-0.01133(18)	0.75648(16)	0.28868(16)	0.0204(3)
C25	0.01091(18)	0.65565(17)	0.20537(15)	0.0214(3)
C26	0.07189(17)	0.55668(16)	0.24666(15)	0.0182(3)
C27	0.08620(18)	0.45138(16)	0.14662(15)	0.0195(3)
C28	-0.0697(2)	0.87054(18)	0.24455(18)	0.0266(4)
C29**	-0.1577(5)	0.9221(5)	0.3383(3)	0.0342(8)
C30**	0.0548(4)	0.9795(4)	0.2376(8)	0.0745(19)
C31**	-0.1633(6)	0.8326(6)	0.1203(4)	0.0719(17)
C28A**	-0.0697(2)	0.87054(18)	0.24455(18)	0.0266(4)
C29A**	-0.119(2)	0.9596(16)	0.3409(13)	0.0342(8)
C30A**	0.047(2)	0.949(2)	0.186(3)	0.0745(19)
C31A**	-0.1943(19)	0.810(2)	0.147(2)	0.0719(17)
C1	0.3252(2)	0.7045(2)	0.9200(2)	0.0343(4)
Cl1	0.47693(6)	0.63945(6)	0.94085(5)	0.04269(13)
Cl2	0.34858(9)	0.86023(7)	1.00256(7)	0.06165(19)

\*  $U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

\*\* Occupation factors for C28 - C31 is 0.820(14) and for C28A - C31A is 0.180(14).

**Table 3.** Anisotropic atomic displacement parameters\* ( $\text{\AA}^2$ ) for UM#1596.

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Pd1	0.01675(6)	0.01678(6)	0.01496(6)	0.00032(4)	0.00242(4)	0.00525(4)
N1	0.0185(7)	0.0185(6)	0.0193(6)	0.0019(5)	0.0021(5)	0.0041(5)
C10	0.0261(9)	0.0267(9)	0.0187(8)	-0.0031(6)	0.0002(6)	0.0126(7)
C11	0.0254(9)	0.0255(9)	0.0204(8)	0.0012(6)	0.0013(6)	0.0064(7)
C12	0.0281(9)	0.0321(10)	0.0208(8)	0.0048(7)	-0.0015(7)	0.0070(7)
C13	0.0207(8)	0.0275(9)	0.0284(9)	0.0100(7)	0.0002(7)	0.0051(7)
C14	0.0170(8)	0.0196(8)	0.0268(8)	0.0070(6)	0.0037(6)	0.0035(6)
C15	0.0213(8)	0.0227(8)	0.0346(10)	0.0080(7)	0.0074(7)	0.0087(6)
C16	0.0276(9)	0.0225(8)	0.0333(10)	0.0028(7)	0.0110(7)	0.0107(7)
C17	0.0264(9)	0.0254(9)	0.0246(8)	0.0006(7)	0.0060(7)	0.0087(7)
C18	0.0204(8)	0.0199(8)	0.0212(8)	0.0010(6)	0.0036(6)	0.0053(6)
C19	0.0166(7)	0.0173(7)	0.0216(8)	0.0031(6)	0.0039(6)	0.0032(6)
O1	0.0265(6)	0.0235(6)	0.0163(5)	0.0001(4)	0.0022(4)	0.0099(5)
O2	0.0268(6)	0.0205(6)	0.0176(5)	-0.0019(4)	0.0058(5)	0.0061(5)
O3	0.0262(6)	0.0222(6)	0.0163(5)	-0.0029(4)	0.0035(5)	0.0051(5)
O4	0.0325(7)	0.0287(7)	0.0191(6)	0.0017(5)	0.0085(5)	0.0079(5)
N2	0.0156(6)	0.0165(6)	0.0164(6)	-0.0002(5)	0.0030(5)	0.0033(5)
C21	0.0177(7)	0.0178(7)	0.0175(7)	-0.0004(6)	0.0035(6)	0.0001(6)
C22	0.0164(7)	0.0169(7)	0.0173(7)	-0.0007(6)	0.0030(5)	0.0028(5)
C23	0.0203(8)	0.0175(7)	0.0200(7)	-0.0024(6)	0.0024(6)	0.0054(6)
C24	0.0202(8)	0.0189(8)	0.0226(8)	0.0013(6)	0.0014(6)	0.0063(6)
C25	0.0255(8)	0.0218(8)	0.0168(7)	0.0006(6)	-0.0007(6)	0.0069(6)
C26	0.0186(7)	0.0186(7)	0.0168(7)	-0.0010(6)	0.0023(6)	0.0040(6)
C27	0.0233(8)	0.0217(8)	0.0143(7)	-0.0003(6)	-0.0001(6)	0.0094(6)
C28	0.0312(10)	0.0227(8)	0.0288(9)	0.0043(7)	0.0023(7)	0.0128(7)
C29	0.042(2)	0.0261(18)	0.0388(12)	0.0037(12)	0.0052(13)	0.0180(15)
C30	0.0532(19)	0.039(2)	0.154(6)	0.051(3)	0.051(3)	0.0245(16)
C31	0.131(4)	0.064(3)	0.0296(19)	-0.0093(19)	-0.030(2)	0.072(3)
C28A	0.0312(10)	0.0227(8)	0.0288(9)	0.0043(7)	0.0023(7)	0.0128(7)
C29A	0.042(2)	0.0261(18)	0.0388(12)	0.0037(12)	0.0052(13)	0.0180(15)
C30A	0.0532(19)	0.039(2)	0.154(6)	0.051(3)	0.051(3)	0.0245(16)
C31A	0.131(4)	0.064(3)	0.0296(19)	-0.0093(19)	-0.030(2)	0.072(3)
C1	0.0319(11)	0.0395(11)	0.0306(10)	0.0083(8)	0.0006(8)	0.0043(9)
Cl1	0.0515(3)	0.0547(3)	0.0289(2)	0.0089(2)	0.0077(2)	0.0250(3)
Cl2	0.0823(5)	0.0467(4)	0.0599(4)	-0.0020(3)	0.0083(4)	0.0279(4)

\* The anisotropic atomic displacement factor exponent takes the form:  $-2\pi^2 [ h^2a^2U_{11} + \dots + 2hka*b*U_{12} ]$

**Table 4.** Hydrogen atom coordinates and isotropic atomic displacement parameters ( $\text{\AA}^2$ ) for UM#1596.

Atom	$x/a$	$y/b$	$z/c$	$U_{\text{iso}}$
H10A	0.1904	0.2613	0.2749	0.034(6)
H10B	0.3103	0.3724	0.2405	0.035(6)
H11	0.4002	0.4572	0.7129	0.026(5)
H12	0.5703	0.3587	0.8095	0.027(6)
H13	0.6599	0.2028	0.6960	0.027(6)
H15	0.6642	0.0754	0.4794	0.027(6)
H16	0.5717	0.0304	0.2727	0.028(6)
H17	0.3988	0.1351	0.1906	0.031(6)
H3	-0.0213	0.3287	0.2135	0.054(8)
H23	0.0126	0.8122	0.4756	0.019(5)
H25	-0.0161	0.6546	0.1190	0.025(5)
H29A	-0.1856	1.0009	0.3126	0.051
H29B	-0.1029	0.9425	0.4206	0.051
H29C	-0.2410	0.8558	0.3416	0.051
H30A	0.1045	0.9548	0.1685	0.112
H30B	0.1178	0.9936	0.3156	0.112
H30C	0.0218	1.0597	0.2242	0.112
H31A	-0.1070	0.8473	0.0522	0.108
H31B	-0.2349	0.8858	0.1164	0.108
H31C	-0.2079	0.7405	0.1127	0.108
H29D	-0.1536	0.9097	0.4063	0.051
H29E	-0.1942	0.9965	0.3013	0.051
H29F	-0.0414	1.0300	0.3774	0.051
H30D	0.1364	0.9271	0.2155	0.112
H30E	0.0517	1.0423	0.2083	0.112
H30F	0.0294	0.9285	0.0949	0.112
H31D	-0.1801	0.7265	0.1077	0.108
H31E	-0.2034	0.8687	0.0840	0.108
H31F	-0.2794	0.7957	0.1874	0.108
H1A	0.3005	0.7094	0.8304	0.049(8)
H1B	0.2472	0.6461	0.9486	0.050(8)

**Table 5.** Bond lengths (Å), valence and torsion angles (°) for UM#1596.

Pd1-N1	2.0027(14)	Pd1-C10	2.0220(16)	Pd1-N2	2.0848(13)
Pd1-O1	2.1319(12)	N1-C11	1.324(2)	N1-C19	1.378(2)
C10-C18	1.503(2)	C11-C12	1.409(2)	C12-C13	1.366(3)
C13-C14	1.416(3)	C14-C19	1.414(2)	C14-C15	1.417(2)
C15-C16	1.368(3)	C16-C17	1.411(3)	C17-C18	1.379(2)
C18-C19	1.402(2)	O1-C21	1.261(2)	O2-C21	1.2510(19)
O3-C27	1.314(2)	O4-C27	1.211(2)	N2-C26	1.348(2) N2-
C22	1.361(2)	C21-C22	1.516(2)	C22-C23	1.382(2)
C23-C24	1.397(2)	C24-C25	1.392(2)	C24-C28	1.525(2)
C25-C26	1.387(2)	C26-C27	1.513(2)	C28-C31	1.529(3)
C28-C30	1.530(4)	C28-C29	1.530(3)	C1-C12	1.754(2) C1-
C11	1.761(2)				
N1-Pd1-C10	82.90(6)	N1-Pd1-N2	172.51(5)	C10-Pd1-N2	102.15(6) N1-
Pd1-O1	94.89(5)	C10-Pd1-O1	176.45(6)	N2-Pd1-O1	80.33(5)
C11-N1-C19	119.12(15)	C11-N1-Pd1	125.16(12)	C19-N1-Pd1	115.66(11)
C18-C10-Pd1	109.59(11)	N1-C11-C12	121.96(17)	C13-C12-C11	120.04(17)
C12-C13-C14	119.63(16)	C19-C14-C13	117.30(16)	C19-C14-C15	117.52(16)
C13-C14-C15	125.18(16)	C16-C15-C14	119.87(16)	C15-C16-C17	121.42(16)
C18-C17-C16	120.72(17)	C17-C18-C19	117.70(16)	C17-C18-C10	125.79(16)
C19-C18-C10	116.50(14)	N1-C19-C18	115.30(14)	N1-C19-C14	121.94(15)
C18-C19-C14	122.75(15)	C21-O1-Pd1	113.37(10)	C26-N2-C22	115.93(14)
C26-N2-Pd1	132.14(11)	C22-N2-Pd1	110.98(10)	O2-C21-O1	125.70(15) O2-
C21-C22	116.97(15)	O1-C21-C22	117.32(14)	N2-C22-C23	123.17(15) N2-
C22-C21	116.96(14)	C23-C22-C21	119.87(14)	C22-C23-C24	120.96(15)
C25-C24-C23	115.48(15)	C25-C24-C28	121.70(15)	C23-C24-C28	122.75(15)
C26-C25-C24	120.95(15)	N2-C26-C25	123.39(15)	N2-C26-C27	121.17(14)
C25-C26-C27	115.43(14)	O4-C27-O3	122.08(15)	O4-C27-C26	119.89(16) O3-
C27-C26	117.77(14)	C24-C28-C31	112.2(2)	C24-C28-C30	107.0(2)
C31-C28-C30	112.0(3)	C24-C28-C29	110.9(2)	C31-C28-C29	107.0(2)
C30-C28-C29	107.6(2)	C12-C1-C11	111.39(12)		
C10-Pd1-N1-C11	179.18(16)	O1-Pd1-N1-C11	-3.61(15)	C10-Pd1-N1-C19	2.10(12)
O1-Pd1-N1-C19	179.31(11)	N1-Pd1-C10-C18	-1.58(12)	N2-Pd1-C10-C18	172.81(12)
C19-N1-C11-C12	-1.0(3)	Pd1-N1-C11-C12	-177.97(13)	N1-C11-C12-C13	0.2(3)
C11-C12-C13-C14	0.8(3)	C12-C13-C14-C19	-1.0(3)	C12-C13-C14-C15	178.87(17)
C19-C14-C15-C16	-1.1(3)	C13-C14-C15-C16	179.02(17)	C14-C15-C16-C17	0.6(3)
C15-C16-C17-C18	0.6(3)	C16-C17-C18-C19	-1.2(3)	C16-C17-C18-C10	178.99(17)
Pd1-C10-C18-C17	-179.17(15)	Pd1-C10-C18-C19	1.0(2)	C11-N1-C19-C18	-179.36(16)
Pd1-N1-C19-C18	-2.09(19)	C11-N1-C19-C14	0.8(2)	Pd1-N1-C19-C14	178.07(12)
C17-C18-C19-N1	-179.18(15)	C10-C18-C19-N1	0.7(2)	C17-C18-C19-C14	0.7(3)
C10-C18-C19-C14	-179.49(16)	C13-C14-C19-N1	0.2(2)	C15-C14-C19-N1	-179.69(15)
C13-C14-C19-C18	-179.65(16)	C15-C14-C19-C18	0.5(2)	N1-Pd1-O1-C21	171.09(12)
N2-Pd1-O1-C21	-3.10(11)	C10-Pd1-N2-C26	-6.58(16)	O1-Pd1-N2-C26	176.01(15)
C10-Pd1-N2-C22	-174.68(11)	O1-Pd1-N2-C22	7.91(10)	Pd1-O1-C21-O2	176.89(13)
Pd1-O1-C21-C22	-2.08(18)	C26-N2-C22-C23	-0.8(2)	Pd1-N2-C22-C23	169.43(13)
C26-N2-C22-C21	178.34(14)	Pd1-N2-C22-C21	-11.45(17)	O2-C21-C22-N2	-169.58(14)
O1-C21-C22-N2	9.5(2)	O2-C21-C22-C23	9.6(2)	O1-C21-C22-C23	-171.36(15)
N2-C22-C23-C24	-2.4(3)	C21-C22-C23-C24	178.52(15)	C22-C23-C24-C25	3.2(2)
C22-C23-C24-C28	-173.88(16)	C23-C24-C25-C26	-1.0(3)	C28-C24-C25-C26	176.05(17)
C22-N2-C26-C25	3.0(2)	Pd1-N2-C26-C25	-164.60(13)	C22-N2-C26-C27	-177.50(14)
Pd1-N2-C26-C27	14.9(2)	C24-C25-C26-N2	-2.2(3)	C24-C25-C26-C27	178.35(16)
N2-C26-C27-O4	-116.37(18)	C25-C26-C27-O4	63.1(2)	N2-C26-C27-O3	69.4(2)
C25-C26-C27-O3	-111.10(18)	C25-C24-C28-C31	28.5(4)	C23-C24-C28-C31	-154.6(3)
C25-C24-C28-C30	-94.8(4)	C23-C24-C28-C30	82.1(4)	C25-C24-C28-C29	148.1(3)
C23-C24-C28-C29	-35.0(3)				

**Table 7.** Hydrogen bond information for UM#1596 (Å and °).

D—H...A*	d(D—H)	d(H...A)	d(D...A)	∠(DHA)
O3—H3...O2#1	0.84	1.72	2.5412(17)	165.9

\* D - donor atom, H - hydrogen, A - acceptor. Symmetry transformation codes: #1 -x,-y+1,-z+1

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