

Supplementary Materials:

***New palladium(II)  $\beta$ -ketoesterates for Focused Electron Beam Induced Deposition: Synthesis, structures, and characterization***

***A. Butrymowicz-Kubiak<sup>1</sup>, T.M. Muziol<sup>1</sup>, A. Kaczmarek-Kędziera<sup>1</sup>, C. S. Jureddy<sup>2</sup>, K. Maćkosz<sup>2</sup>, I. Utke<sup>2</sup>, I. B. Szymańska<sup>1\*</sup>***

<sup>1</sup>*Faculty of Chemistry, Nicolaus Copernicus University in Toruń, Gagarina 7, 87-100 Toruń, Poland*

<sup>2</sup>*Empa - Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Mechanics of Materials and Nanostructures, Feuerwerkerstrasse 39, CH - 3602 Thun, Switzerland*

**X-ray crystal structure determination**

**Table S 1** Crystal data and structure refinement for (1–3).

| Identification code                               | (1)                                                                                                                                 | (2)                                                                                                          | (3)                                                                                                                     |
|---------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------|
| Empirical formula                                 | C16 H26 O6 Pd                                                                                                                       | C14 H22 O6 Pd                                                                                                | C12 H18 O6 Pd                                                                                                           |
| Formula weight                                    | 420.77                                                                                                                              | 392.71                                                                                                       | 364.66                                                                                                                  |
| Temperature [K]                                   | 100(2) K                                                                                                                            | 100(2) K                                                                                                     | 100.15 K                                                                                                                |
| Wavelength [Å]                                    | 1.54184 Å                                                                                                                           | 1.54184 Å                                                                                                    | 1.54184 Å                                                                                                               |
| Crystal system, space group                       | Triclinic, P-1                                                                                                                      | Monoclinic, P2 <sub>1</sub> /n                                                                               | Triclinic, P-1                                                                                                          |
| Unit cell dimensions [Å] and [°]                  | a = 10.23141(11) Å $\alpha$ = 91.9303(9)°<br>b = 12.95320(14) Å $\beta$ = 98.1743(9)°<br>c = 14.56071(17) Å $\gamma$ = 100.3549(9)° | a = 4.35329(10) Å $\alpha$ = 90°<br>b = 10.3794(3) Å $\beta$ = 93.392(2)°<br>c = 17.7657(5) Å $\gamma$ = 90° | a = 7.0247(2) Å $\alpha$ = 89.994(3)°<br>b = 8.6043(3) Å $\beta$ = 80.180(3)°<br>c = 11.5706(4) Å $\gamma$ = 79.606(3)° |
| Volume [Å <sup>3</sup> ]                          | 1875.53(4) Å <sup>3</sup>                                                                                                           | 801.33(4) Å <sup>3</sup>                                                                                     | 677.46(4) Å <sup>3</sup>                                                                                                |
| Z, Calculated density [Mg×m <sup>-3</sup> ]       | 4, 1.490 Mg/m <sup>3</sup>                                                                                                          | 2, 1.628 Mg/m <sup>3</sup>                                                                                   | 2, 1.788 Mg/m <sup>3</sup>                                                                                              |
| Absorption coefficient [mm <sup>-1</sup> ]        | 8.207 mm <sup>-1</sup>                                                                                                              | 9.558 mm <sup>-1</sup>                                                                                       | 11.252 mm <sup>-1</sup>                                                                                                 |
| F(000)                                            | 864                                                                                                                                 | 400                                                                                                          | 368                                                                                                                     |
| Crystal size [mm]                                 | 0.140 x 0.060 x 0.030 mm <sup>3</sup>                                                                                               | 0.130 x 0.040 x 0.020 mm <sup>3</sup>                                                                        | 0.1 x 0.03 x 0.02 mm <sup>3</sup>                                                                                       |
| Theta range for data collection [°]               | 3.072 to 74.503°                                                                                                                    | 4.937 to 74.504°                                                                                             | 3.879 to 74.475°                                                                                                        |
| Limiting indices                                  | -12 ≤ h ≤ 12<br>-16 ≤ k ≤ 16<br>-16 ≤ l ≤ 18                                                                                        | -5 ≤ h ≤ 4<br>-12 ≤ k ≤ 12<br>-17 ≤ l ≤ 22                                                                   | -8 ≤ h ≤ 8<br>-10 ≤ k ≤ 7<br>-14 ≤ l ≤ 14                                                                               |
| Reflections collected/unique                      | 68027                                                                                                                               | 5007                                                                                                         | 8513                                                                                                                    |
| Completeness [%] to theta [°]                     | 99.9 %                                                                                                                              | 98.6 %                                                                                                       | 99.9 %                                                                                                                  |
| Absorption correction                             | Gaussian                                                                                                                            | Gaussian                                                                                                     | Gaussian                                                                                                                |
| Max. and min. transmission                        | 0.908 and 0.490                                                                                                                     | 0.942 and 0.422                                                                                              | 0.920 and 0.433                                                                                                         |
| Refinement method                                 | Full-matrix least-squares on F <sup>2</sup>                                                                                         | Full-matrix least-squares on F <sup>2</sup>                                                                  | Full-matrix least-squares on F <sup>2</sup>                                                                             |
| Data/restraints/parameters                        | 7650 / 0 / 432                                                                                                                      | 1605 / 0 / 100                                                                                               | 2756 / 0 / 179                                                                                                          |
| Goodness-of-fit on F <sup>2</sup>                 | 1.052                                                                                                                               | 1.112                                                                                                        | 1.092                                                                                                                   |
| Final R Indices [I > 2σ(I)]                       | R1 = 0.0184, wR2 = 0.0500                                                                                                           | R1 = 0.0346, wR2 = 0.0948                                                                                    | R1 = 0.0261, wR2 = 0.0746                                                                                               |
| R indices (all data)                              | R1 = 0.0189, wR2 = 0.0503                                                                                                           | R1 = 0.0384, wR2 = 0.0981                                                                                    | R1 = 0.0286, wR2 = 0.0765                                                                                               |
| Largest diff. peak and hole [e. Å <sup>-3</sup> ] | 0.372 and -0.545 e. Å <sup>-3</sup>                                                                                                 | 0.980 and -0.906 e. Å <sup>-3</sup>                                                                          | 0.919 and -0.990 e. Å <sup>-3</sup>                                                                                     |

**Table S 2** Bond lengths [Å] and angles [°] for [Pd(tbaoac)<sub>2</sub>] (**1**).

---

|                   |            |
|-------------------|------------|
| Pd(1)-O(12)       | 1.9657(11) |
| Pd(1)-O(2)        | 1.9710(11) |
| Pd(1)-O(6)        | 1.9947(11) |
| Pd(1)-O(16)       | 1.9978(11) |
| Pd(2)-O(22)       | 1.9628(11) |
| Pd(2)-O(32)       | 1.9660(11) |
| Pd(2)-O(36)       | 1.9972(11) |
| Pd(2)-O(26)       | 2.0010(11) |
| O(12)-Pd(1)-O(2)  | 85.30(5)   |
| O(12)-Pd(1)-O(6)  | 179.55(5)  |
| O(2)-Pd(1)-O(6)   | 94.70(4)   |
| O(12)-Pd(1)-O(16) | 94.88(4)   |
| O(2)-Pd(1)-O(16)  | 179.71(5)  |
| O(6)-Pd(1)-O(16)  | 85.11(4)   |
| C(2)-O(2)-Pd(1)   | 122.69(10) |
| C(4)-O(6)-Pd(1)   | 122.82(10) |
| C(12)-O(12)-Pd(1) | 122.83(10) |
| C(14)-O(16)-Pd(1) | 122.59(10) |
| O(22)-Pd(2)-O(32) | 84.38(5)   |
| O(22)-Pd(2)-O(36) | 178.04(5)  |
| O(32)-Pd(2)-O(36) | 94.34(5)   |
| O(22)-Pd(2)-O(26) | 94.95(5)   |
| O(32)-Pd(2)-O(26) | 175.70(5)  |
| O(36)-Pd(2)-O(26) | 86.44(5)   |
| C(22)-O(22)-Pd(2) | 122.88(10) |
| C(24)-O(26)-Pd(2) | 121.38(10) |
| C(32)-O(32)-Pd(2) | 123.17(10) |
| C(34)-O(36)-Pd(2) | 122.89(10) |

---

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+1

**Table S 3** Bond lengths [Å] and angles [°] for [Pd(ipaoac)<sub>2</sub>] (**2**).

---

|                     |            |
|---------------------|------------|
| Pd(1)-O(1)#1        | 1.9811(19) |
| Pd(1)-O(1)          | 1.9811(19) |
| Pd(1)-O(4)          | 1.999(3)   |
| Pd(1)-O(4)#1        | 1.999(3)   |
| O(1)#1-Pd(1)-O(1)   | 180.00(9)  |
| O(1)#1-Pd(1)-O(4)   | 85.23(8)   |
| O(1)-Pd(1)-O(4)     | 94.77(8)   |
| O(1)#1-Pd(1)-O(4)#1 | 94.78(8)   |
| O(1)-Pd(1)-O(4)#1   | 85.22(8)   |
| O(4)-Pd(1)-O(4)#1   | 180.0      |
| C(2)-O(1)-Pd(1)     | 122.62(18) |
| C(4)-O(4)-Pd(1)     | 122.20(19) |

---

Symmetry transformations used to generate equivalent atoms:  
#1 -x,-y+1,-z+1

**Table S 4** Bond lengths [Å] and angles [°] for [Pd(eaoac)<sub>2</sub>] (**3**).

---

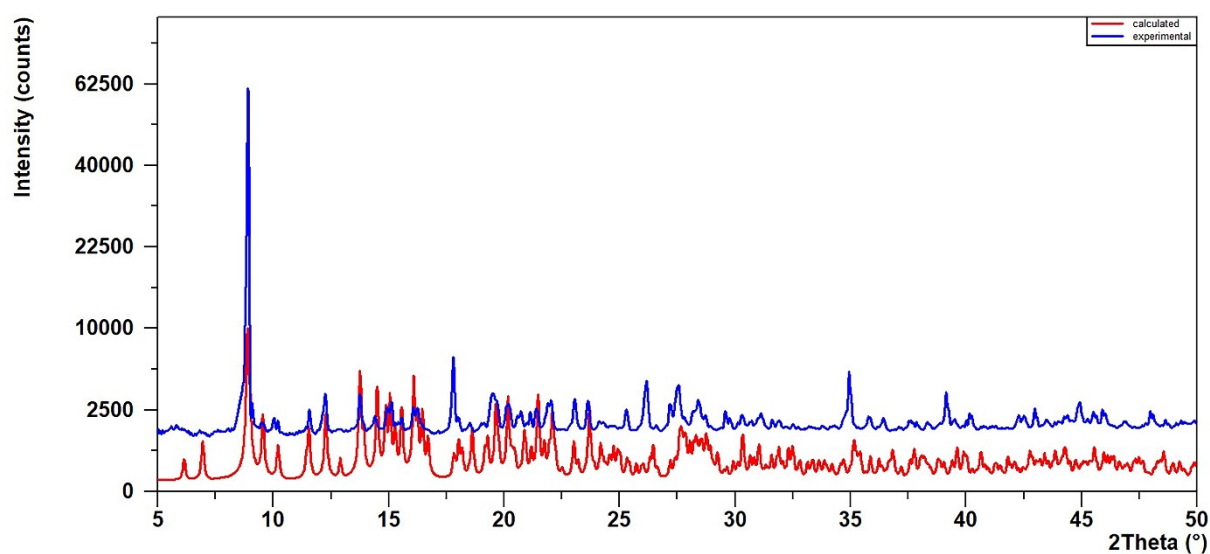
|                        |            |
|------------------------|------------|
| Pd(1)-O(3A)#1          | 1.9923(15) |
| Pd(1)-O(3A)            | 1.9923(15) |
| Pd(1)-O(5)#1           | 1.9833(15) |
| Pd(1)-O(5)             | 1.9833(15) |
| Pd(2)-O(13A)#2         | 1.9917(16) |
| Pd(2)-O(13A)           | 1.9917(16) |
| Pd(2)-O(15)            | 1.9881(15) |
| Pd(2)-O(15)#2          | 1.9881(15) |
| O(3A)#1-Pd(1)-O(3A)    | 180.0      |
| O(5)#1-Pd(1)-O(3A)     | 85.40(6)   |
| O(5)#1-Pd(1)-O(3A)#1   | 94.60(6)   |
| O(5)-Pd(1)-O(3A)#1     | 85.40(6)   |
| O(5)-Pd(1)-O(3A)       | 94.60(6)   |
| O(5)#1-Pd(1)-O(5)      | 180.0      |
| C(3)-O(3A)-Pd(1)       | 122.01(14) |
| C(5)-O(5)-Pd(1)        | 122.94(16) |
| O(13A)#2-Pd(2)-O(13A)  | 180.0      |
| O(15)-Pd(2)-O(13A)     | 94.64(6)   |
| O(15)-Pd(2)-O(13A)#2   | 85.36(6)   |
| O(15)#2-Pd(2)-O(13A)#2 | 94.64(6)   |
| O(15)#2-Pd(2)-O(13A)   | 85.36(6)   |
| O(15)-Pd(2)-O(15)#2    | 180.0      |
| C(13)-O(13A)-Pd(2)     | 122.04(14) |
| C(15)-O(15)-Pd(2)      | 122.60(16) |

---

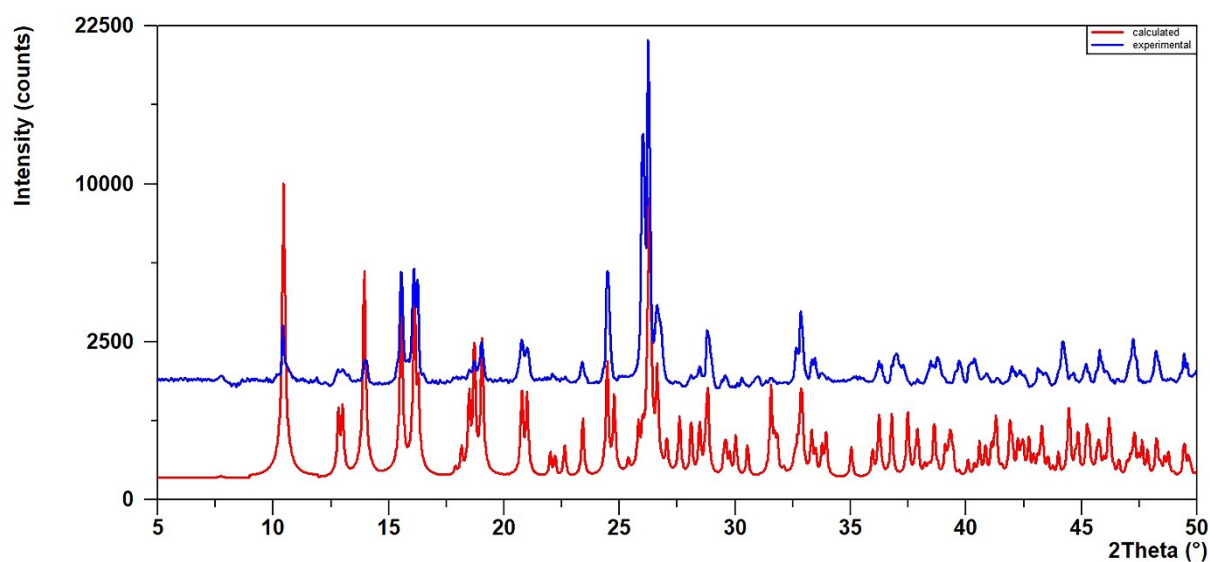
Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1   #2 -x,-y+1,-z+2

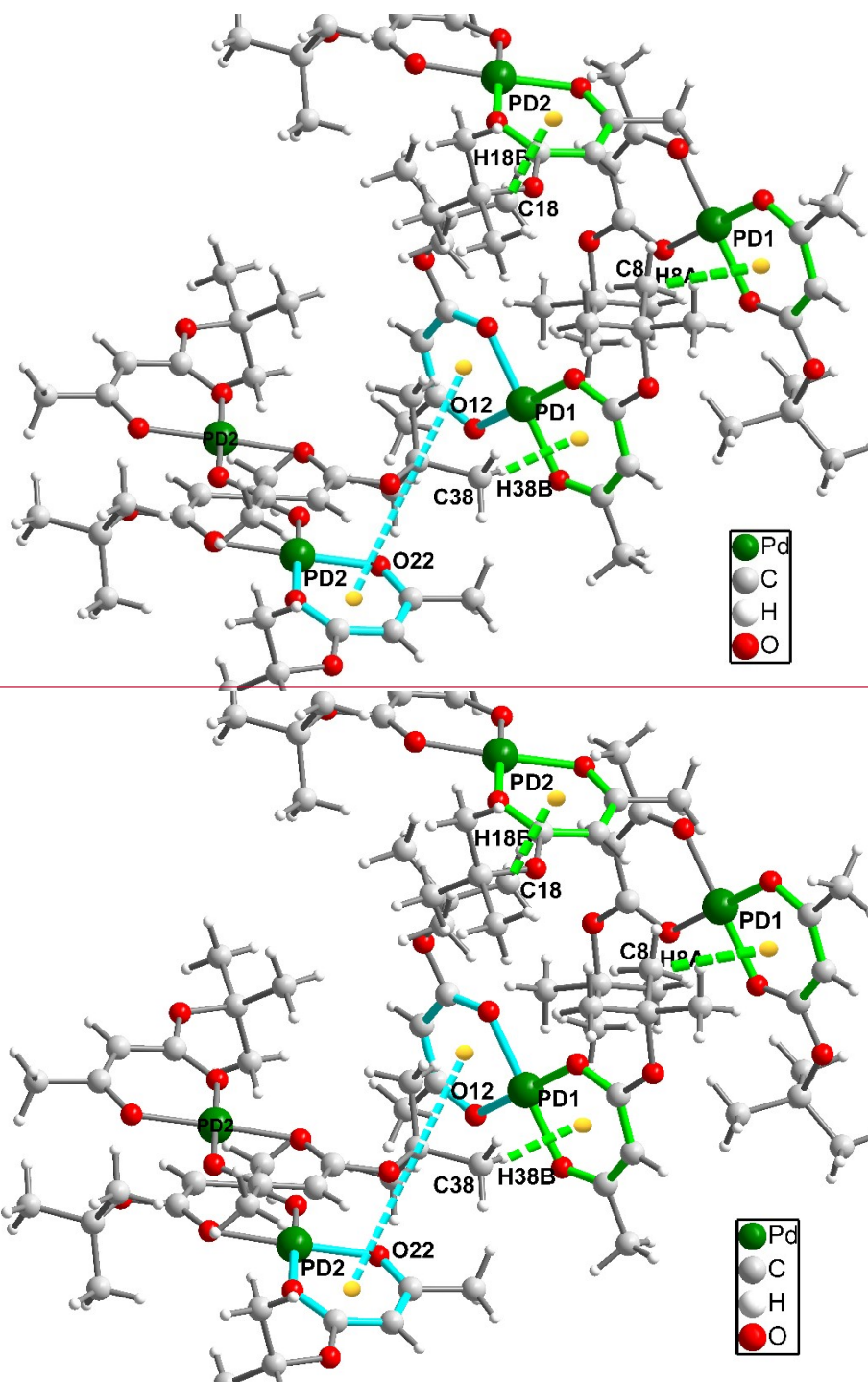




**Figure S 1** Experimental (blue) and calculated (red) XRD patterns of the [Pd(tbaoac)<sub>2</sub>] (1).

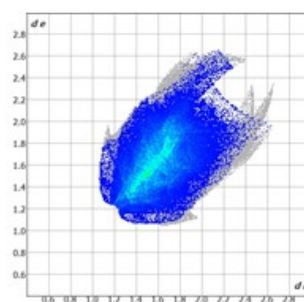
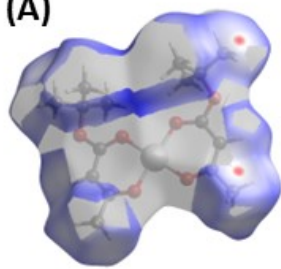


**Figure S 2** Experimental (blue) and calculated (red) XRD patterns of the [Pd(ipaoac)<sub>2</sub>] (2).

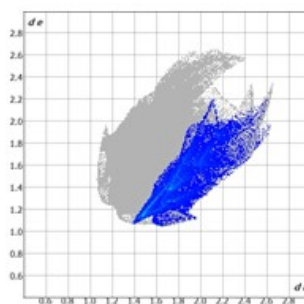
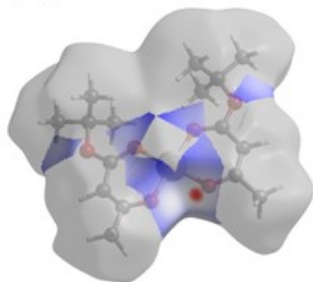


**Figure S 31** C-H... $\pi$  interactions between C8-H8, C23-H23, C38-H38, and chelate ring (green dashed lines) and between chelate rings (blue dashed lines) in the compound [Pd(tbaoac)<sub>2</sub>] (**1**).

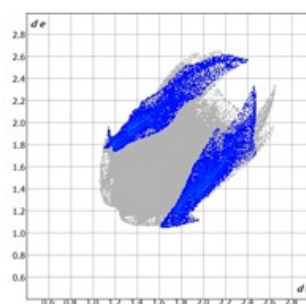
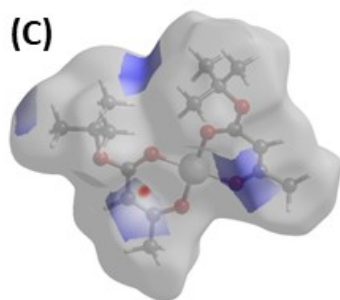
(A)



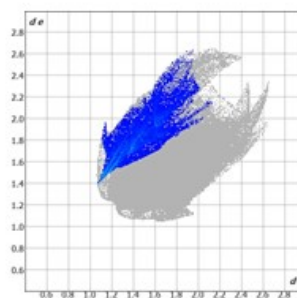
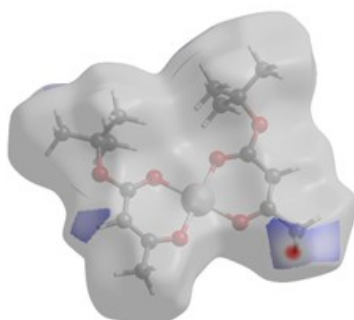
(B)

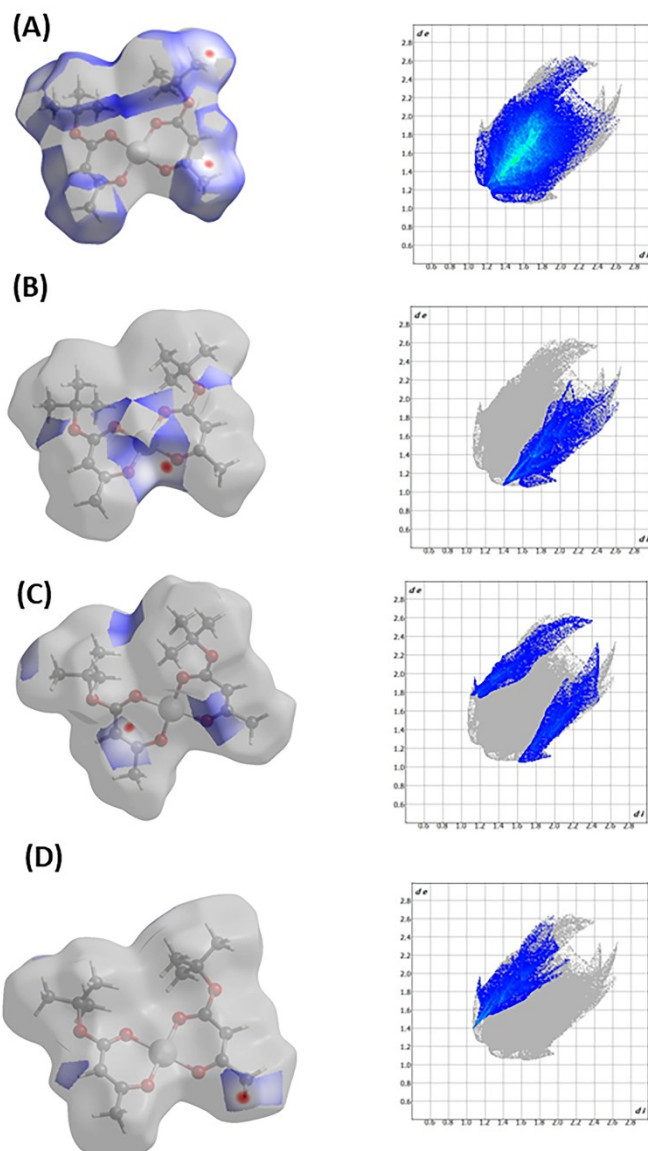


(C)

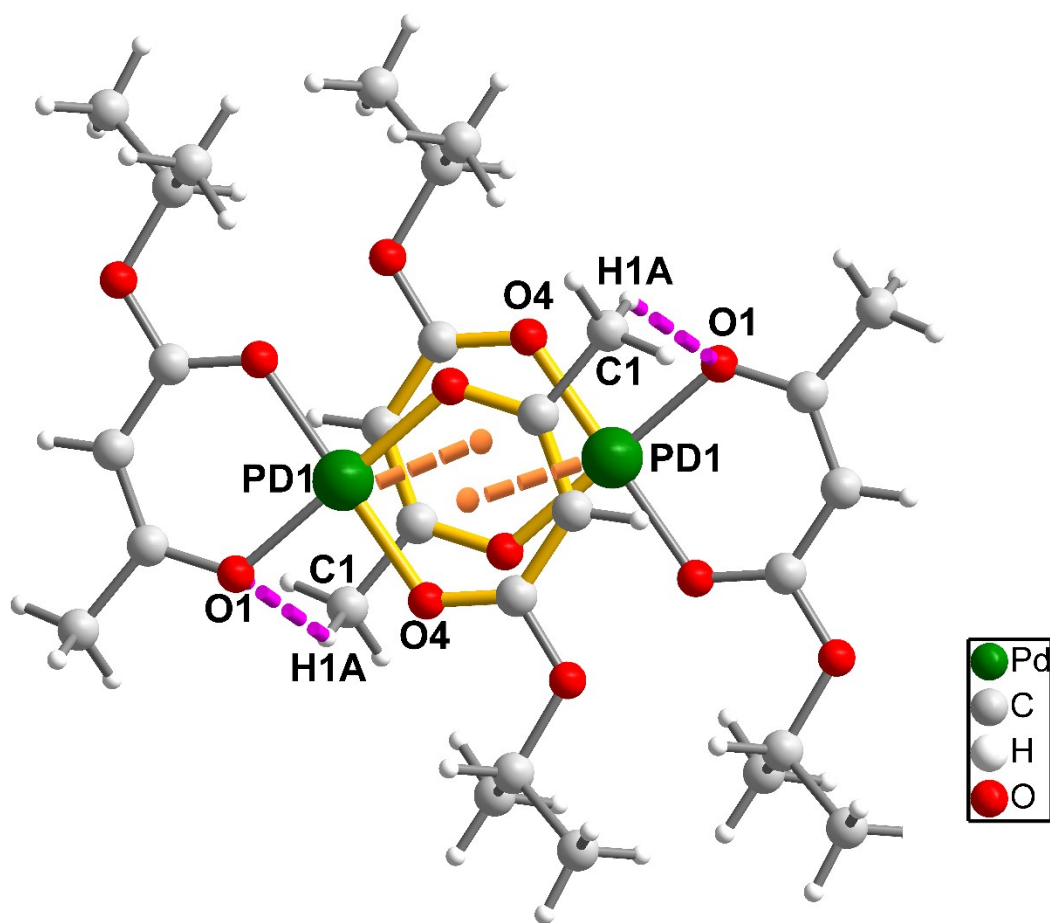
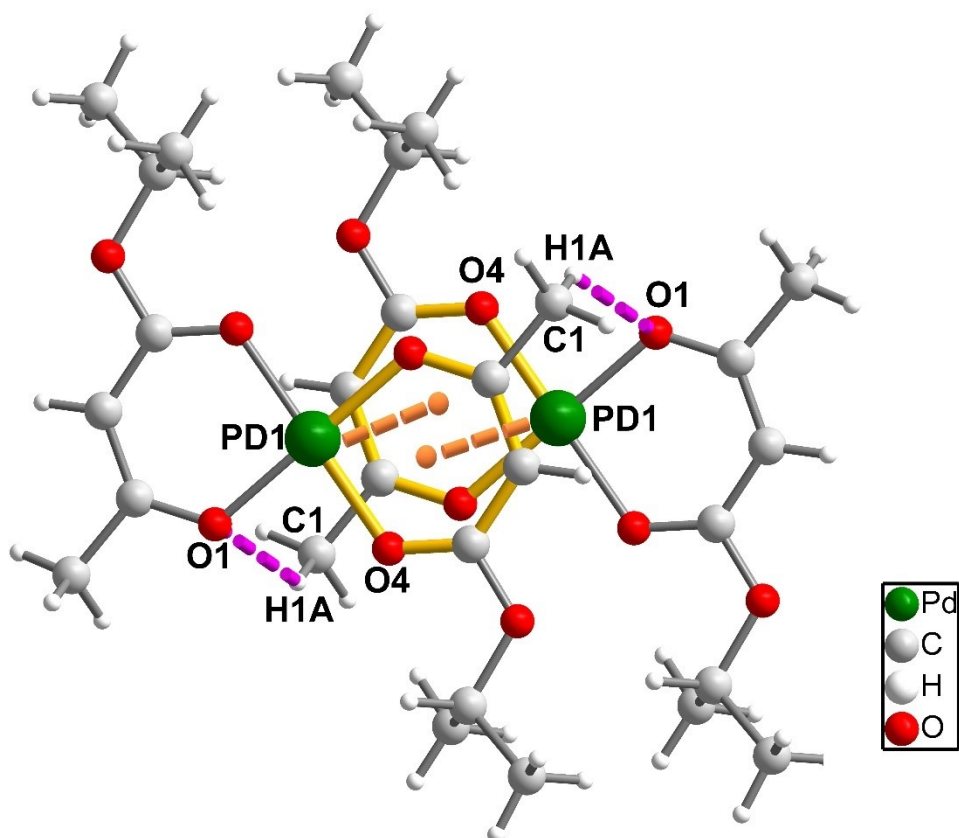


(D)



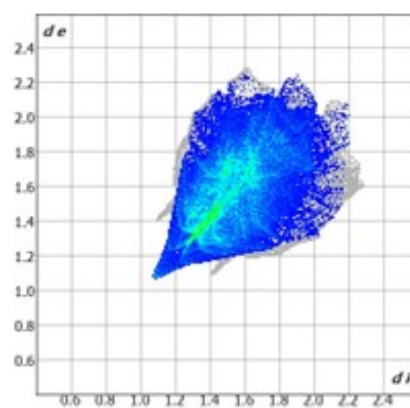
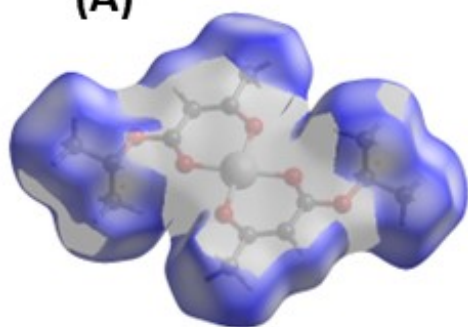


**Figure S 42** Hirshfeld surfaces (left) and fingerprints (right) of selected interactions created in the crystal network of [Pd(tbaoac)<sub>2</sub>] (1) for Pd2 molecule: (A) for H...H (63.5%), (B) for O...H (11.2%), (C) for C...H and H...C (11.1%), and (D) for H...O (10.0%). In brackets, there is a given surface area included as a percentage of the total surface area.

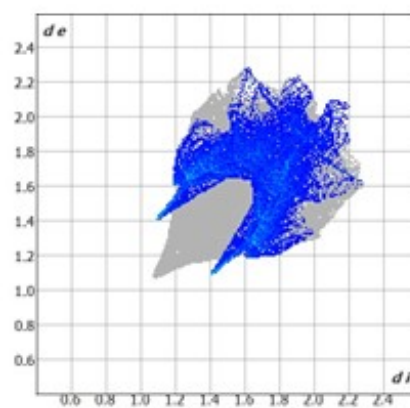
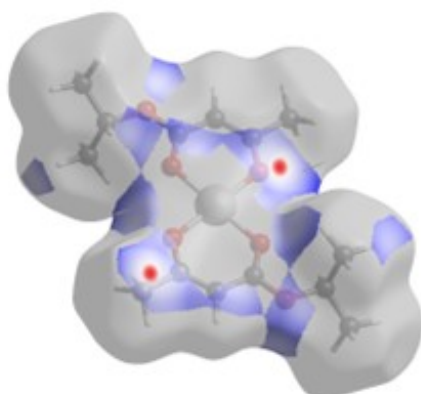


**Figure S 53**  $\pi$ – $\pi$  interactions between palladium ion and chelate ring (orange dashed lines) and O...H hydrogen bonds (magenta dashed lines) in the compound [Pd(ipaoac)<sub>2</sub>] (**2**).

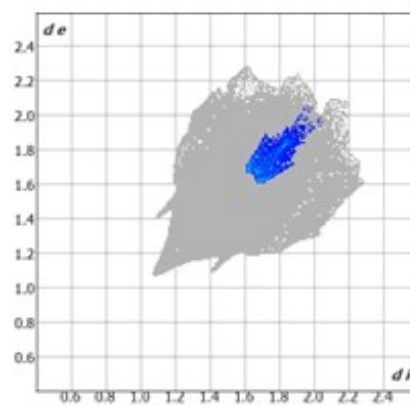
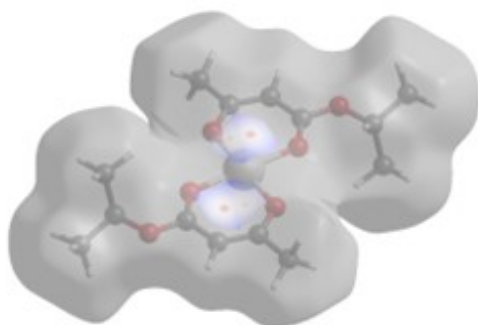
(A)



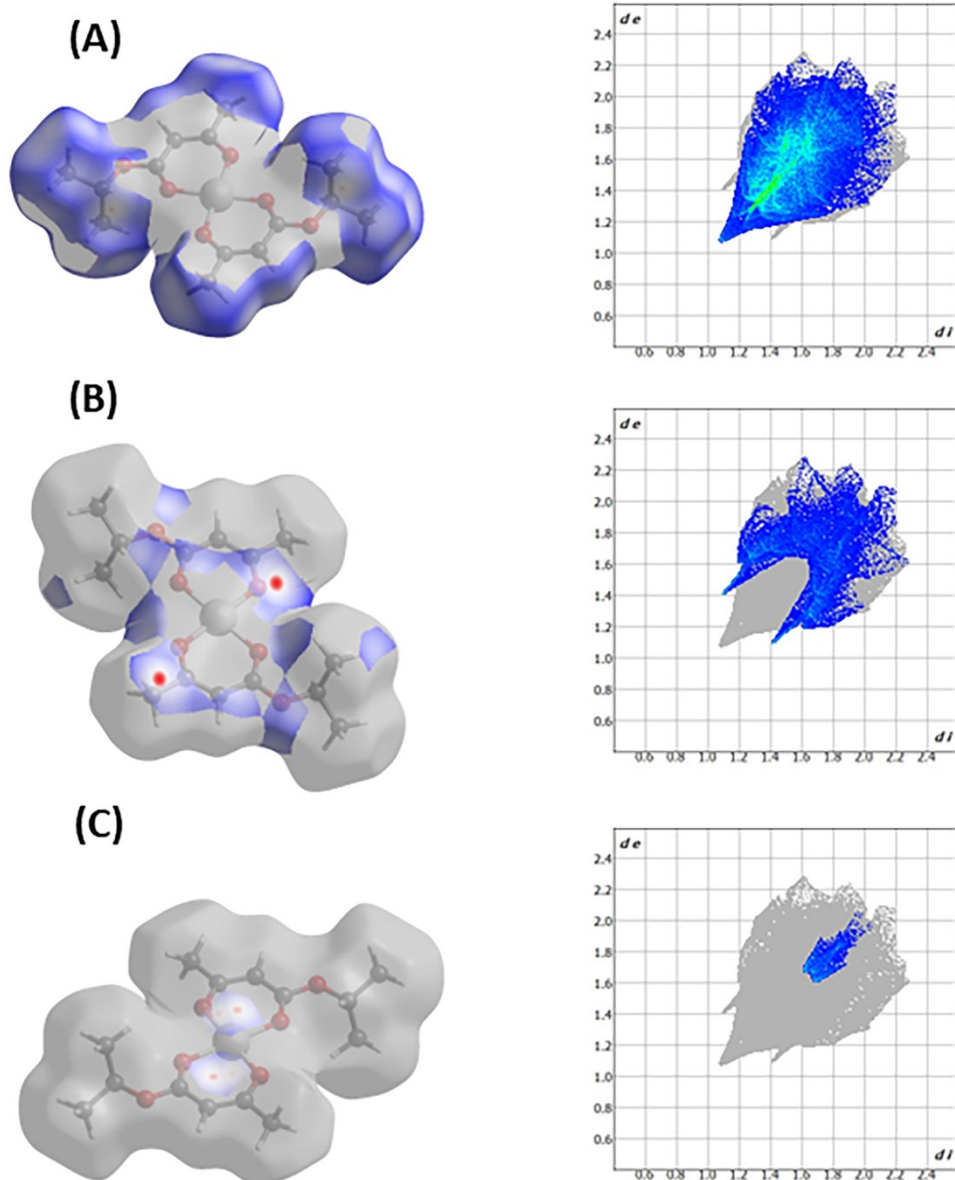
(B)



(C)

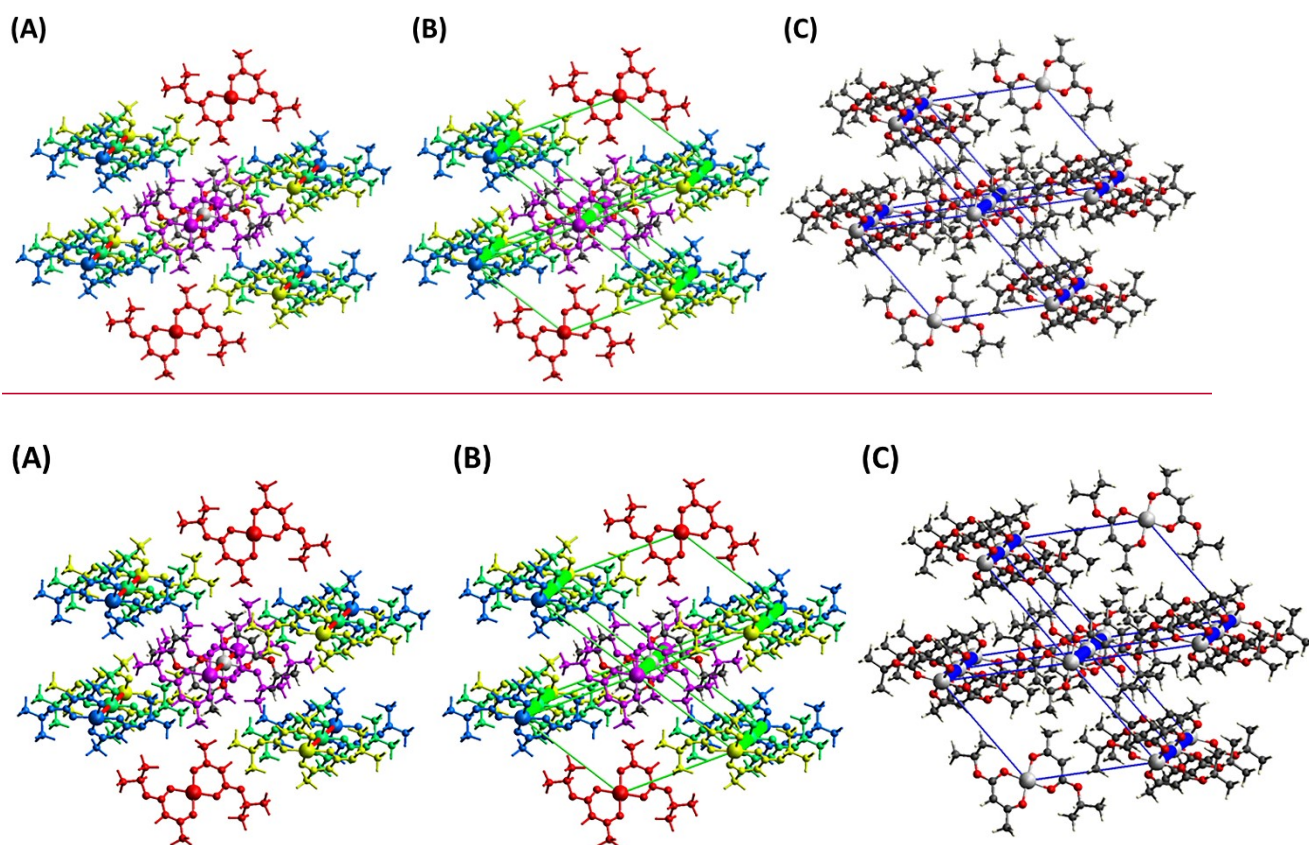




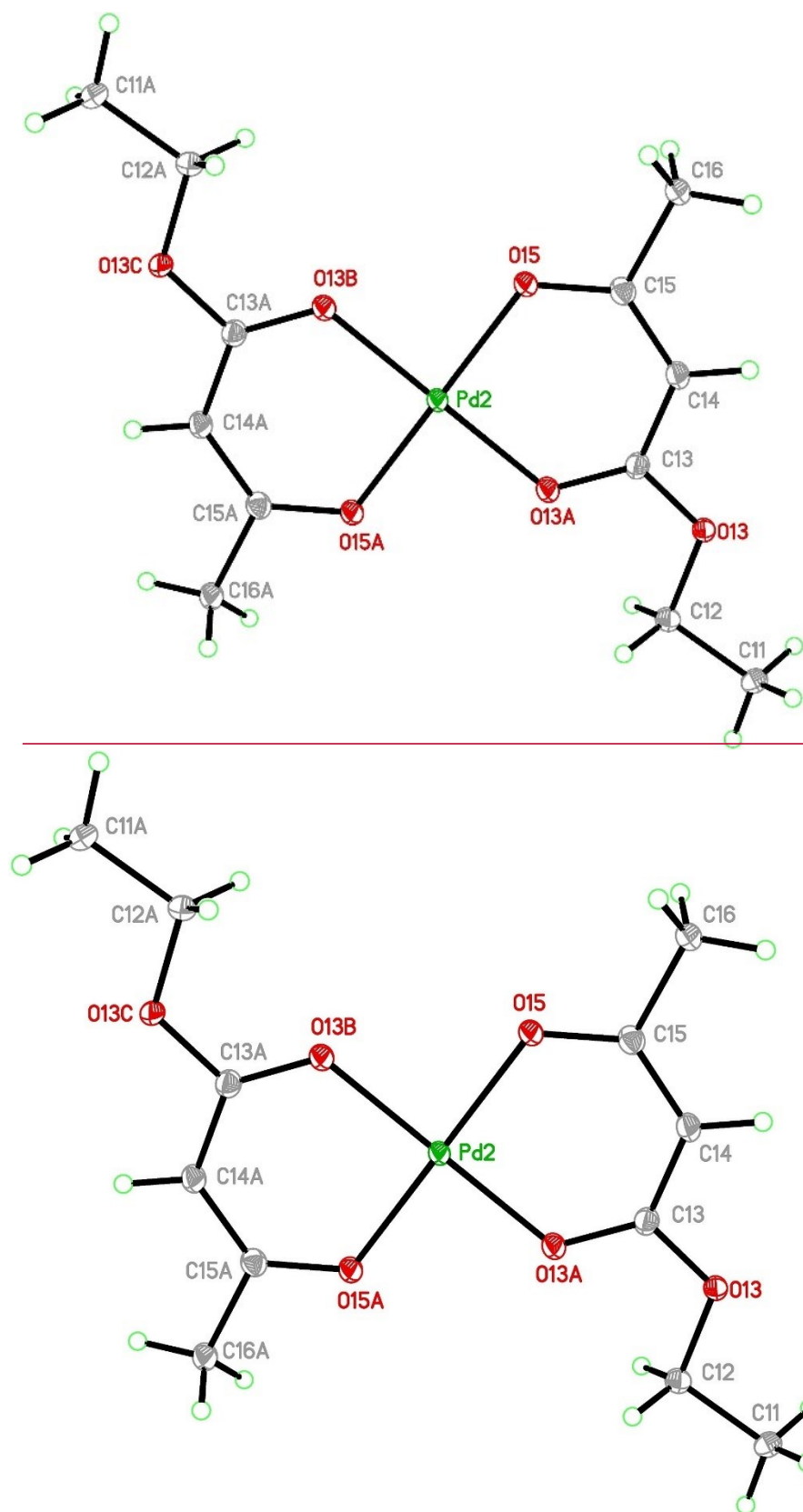


**Figure S 64** Hirshfeld surfaces (left) and fingerprints (right) of selected interactions created in the crystal network of [Pd(ipaoac)<sub>2</sub>] (2): (A) for H...H (67.0%), (B) for H...O (18.1%), and (C) for C...Pd (3.5%). In brackets, there is a given surface area included as a percentage of the total surface area.

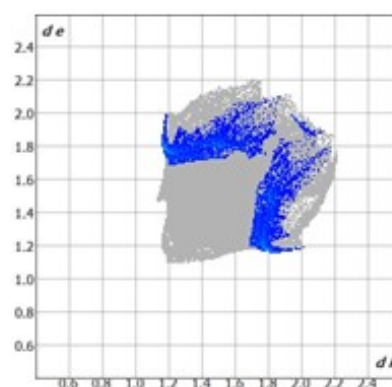
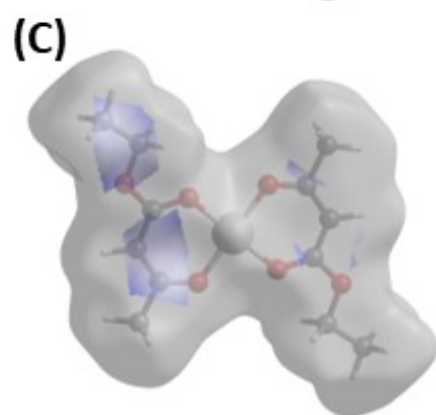
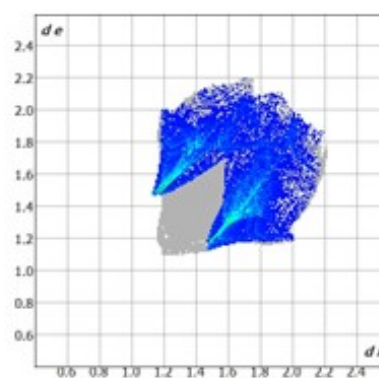
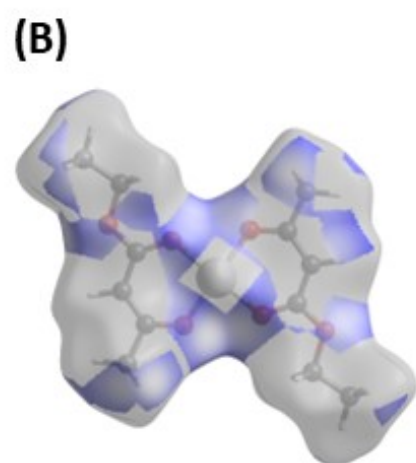
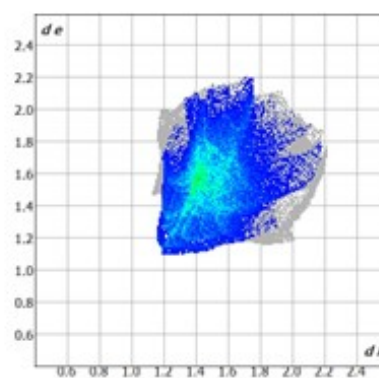
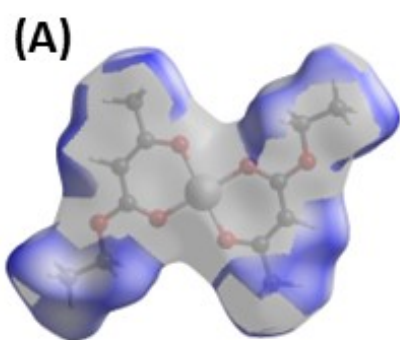


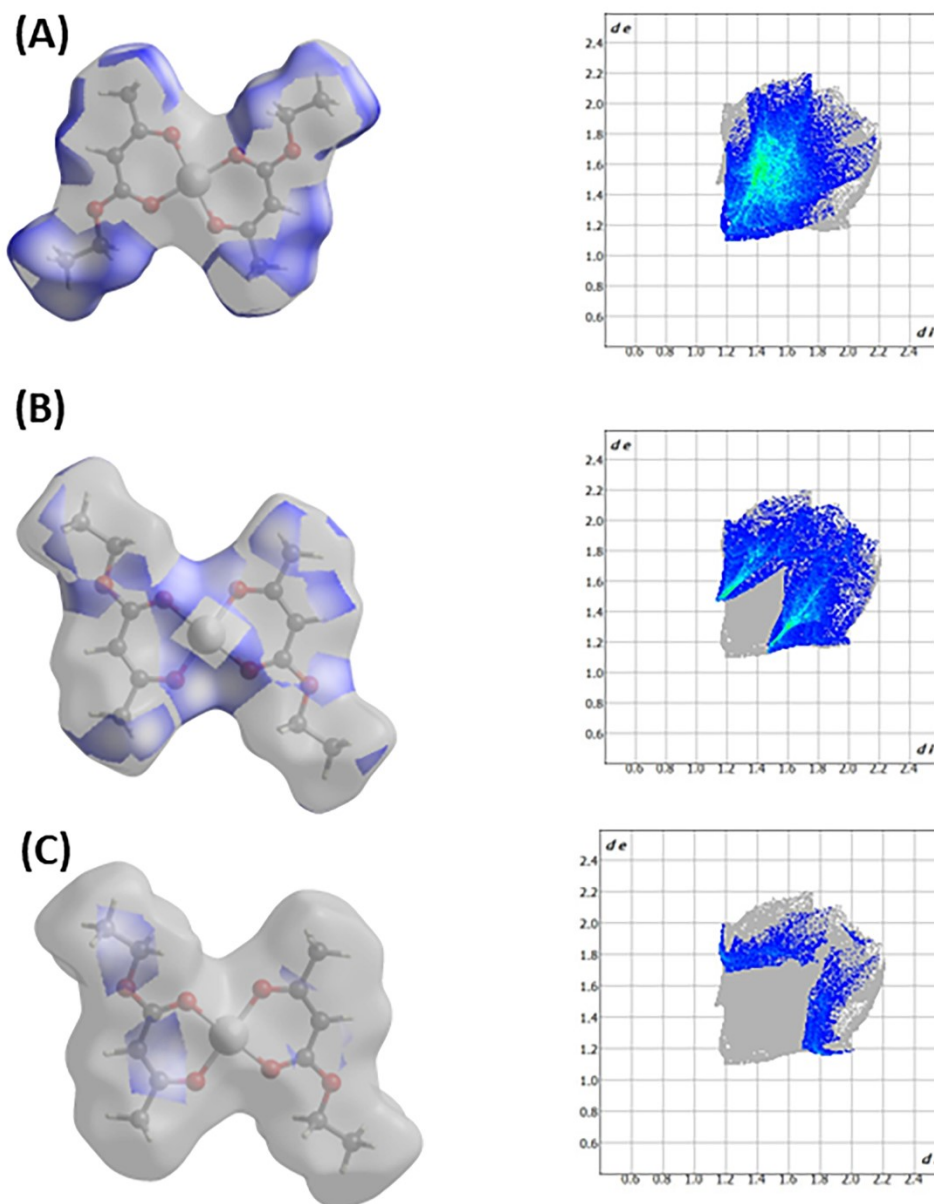


**Figure S 75** Interactions energy: (A) – electrostatic, (B) – van der Waals, and (C) – total in the crystal network of  $[\text{Pd}(\text{ipaoac})_2]$  (**2**).



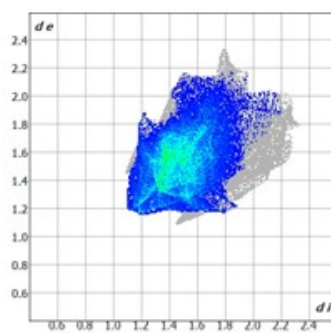
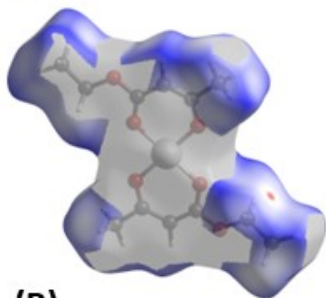
**Figure S 86** The structure of [Pd(eaoac)<sub>2</sub>] (3) with the numbering scheme.



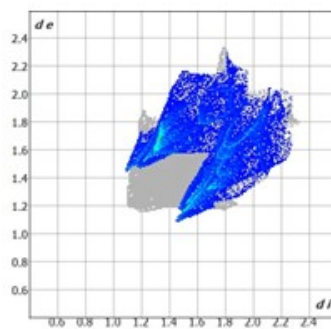
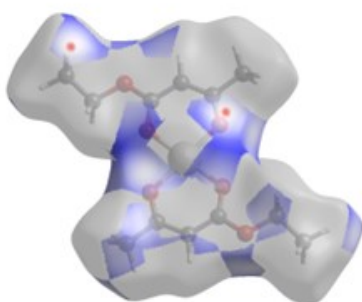


**Figure S 27** Hirshfeld surfaces (left) and fingerprints (right) of selected interactions created in the crystal network of  $[\text{Pd}(\text{eaoac})_2]$  (**3**) for Pd1 molecule: (A) for H...H (53.1%), (B) for O...H (29.7%), and (C) for C...H (7.4%). In brackets, there is a given surface area included as a percentage of the total surface area.

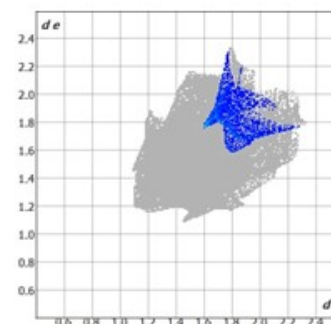
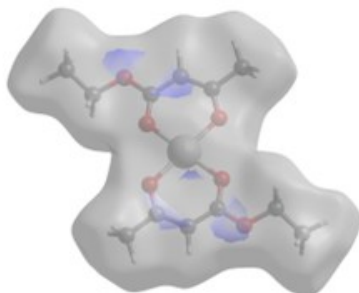
(A)



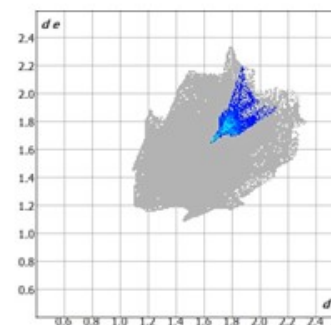
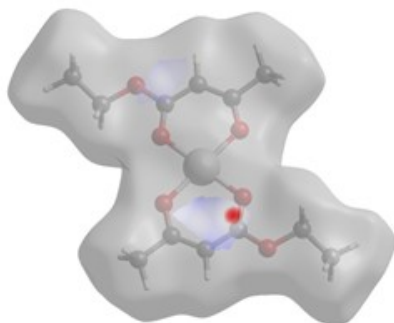
(B)



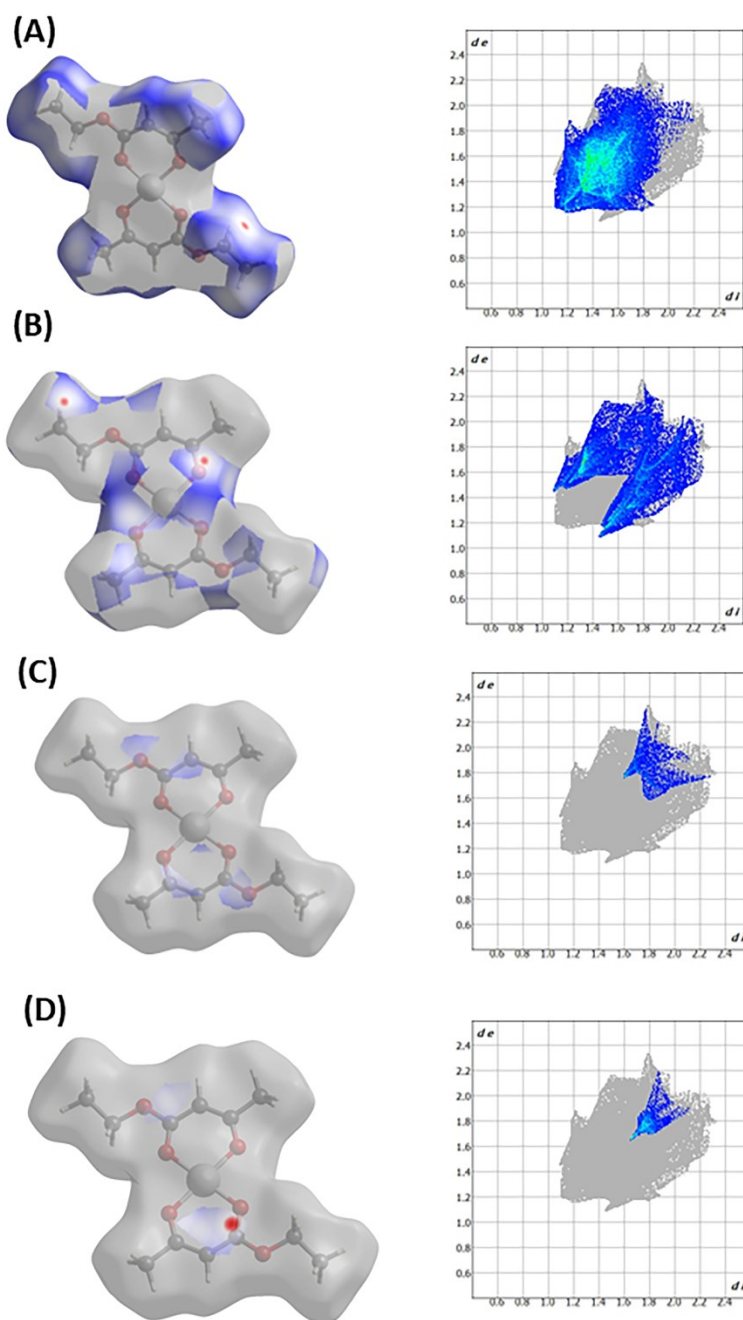
(C)



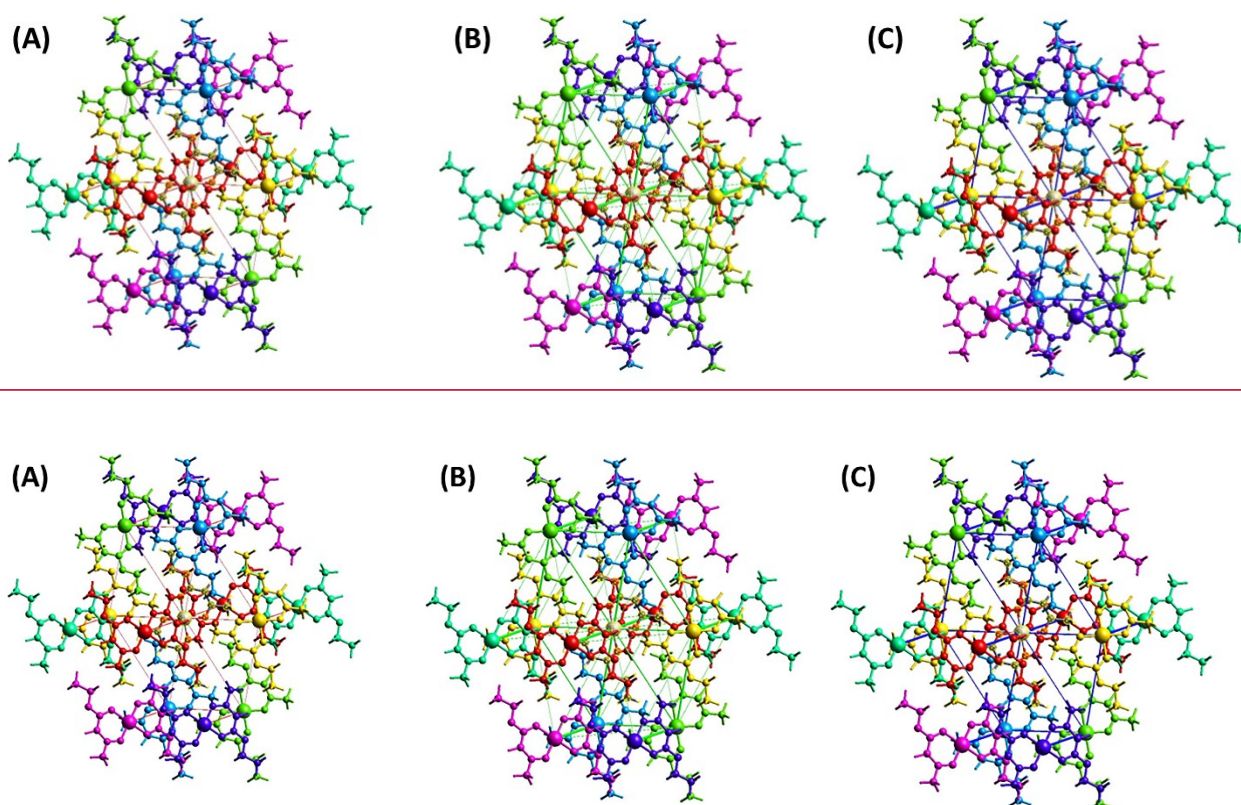
(D)



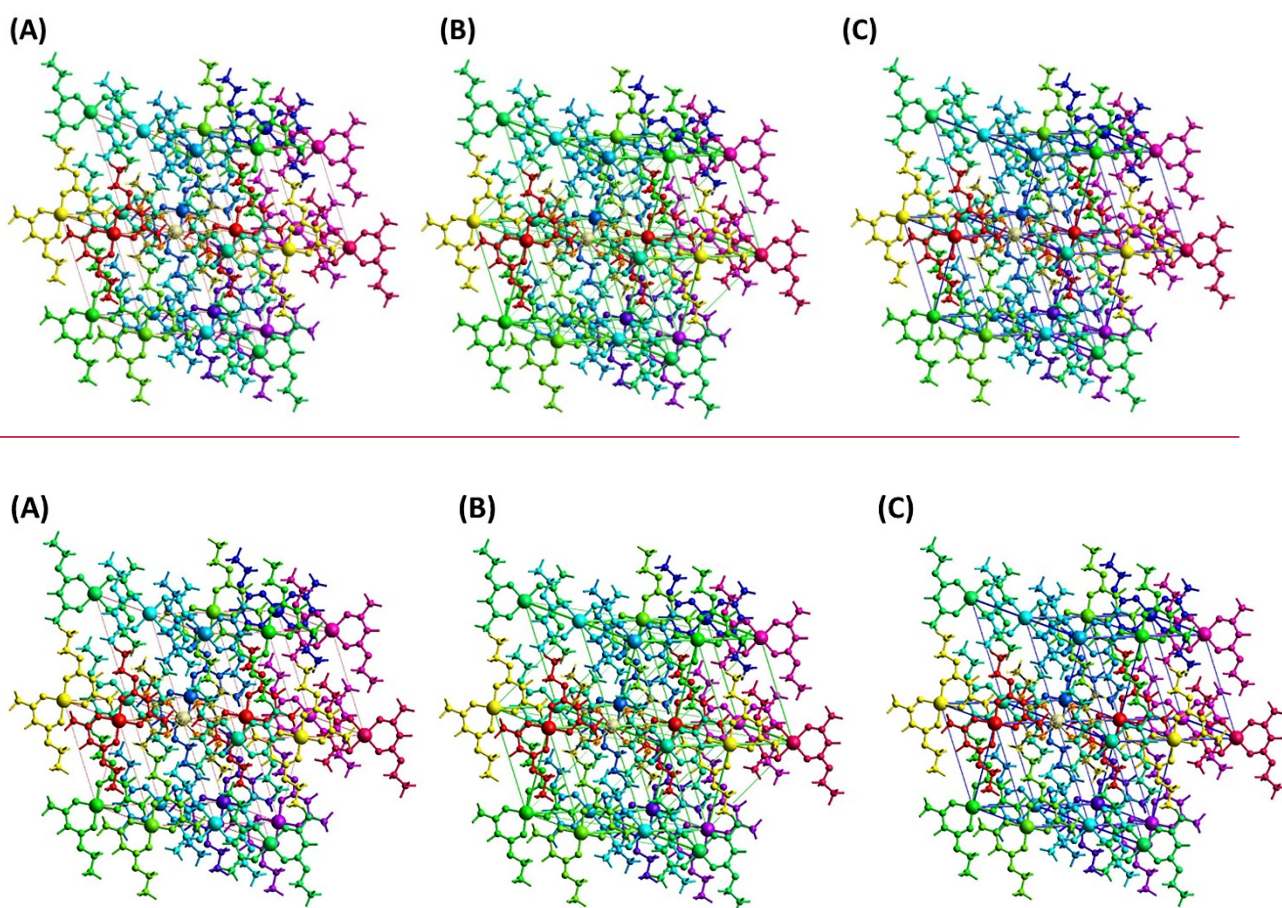




**Figure S 108** Hirshfeld surfaces (left) and fingerprints (right) of selected interactions created in the crystal network of  $[\text{Pd}(\text{eaoac})_2]$  (**3**) for Pd2 molecule: (A) for H...H (58.1%), (B) for H...O (25.9%), (C) for C...O (4.0%), and (D) for C...C (3.6%). In brackets, there is a given surface area included as a percentage of the total surface area.

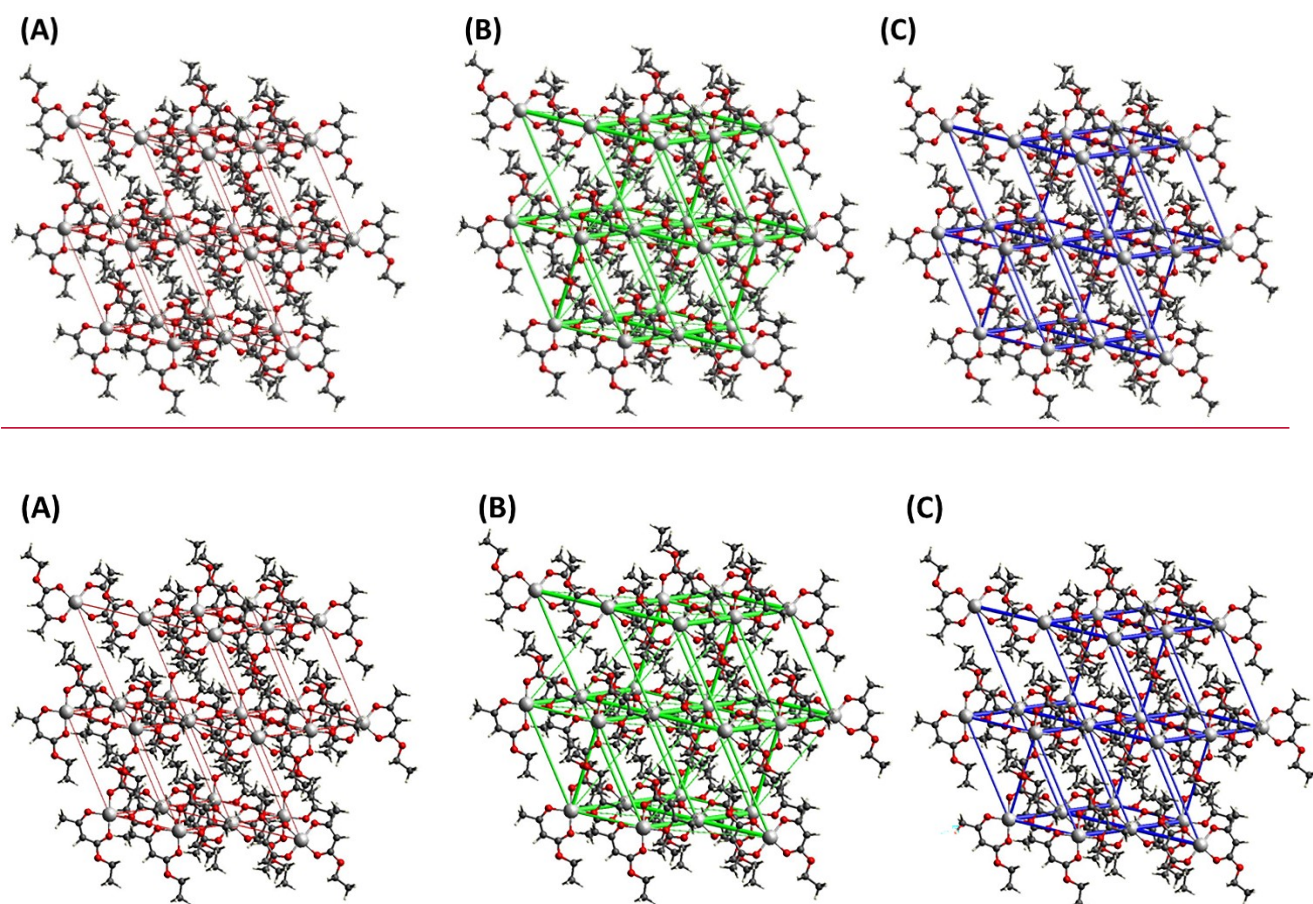


**Figure S 119** Interactions energy: (A) – electrostatic, (B) – van der Waals, and (C) – total in the crystal network of  $[\text{Pd}(\text{eaoac})_2]$  (**3**) for Pd1 molecule.



**Figure S 1240** Interactions energy: (A) – electrostatic, (B) – van der Waals, and (C) – total in the crystal network of [Pd(eaoac)<sub>2</sub>] (3) for Pd<sub>2</sub> molecule.





**Figure S 1311** Interactions energy: (A) – electrostatic, (B) – van der Waals, and (C) – total in the crystal network of  $[\text{Pd}(\text{eaoac})_2]$  (**3**) for Pd1 and Pd2 molecules.

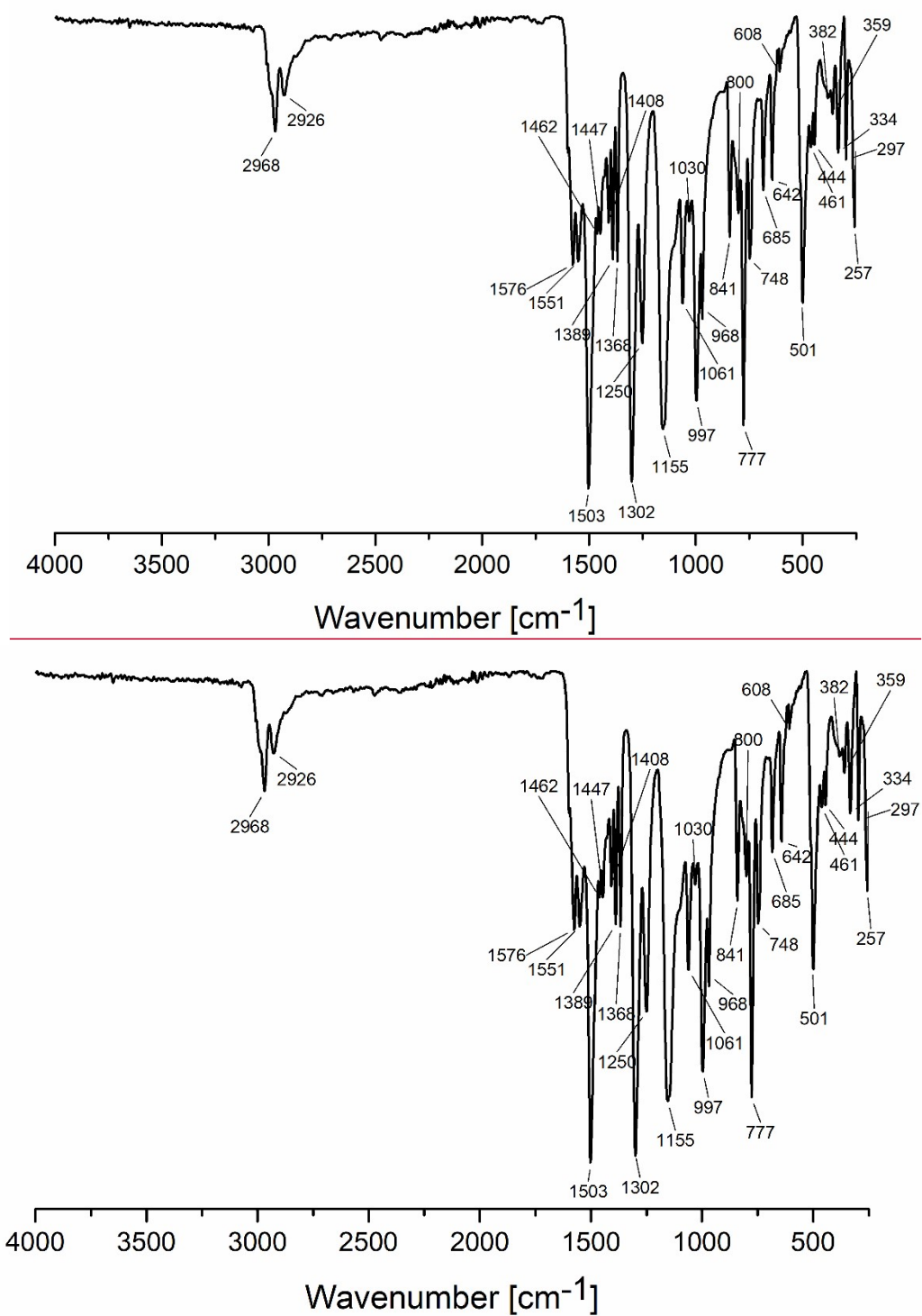


Figure S [1412](#) ATR-IR spectrum for the compound [Pd(tbaoac)<sub>2</sub>] (**1**).

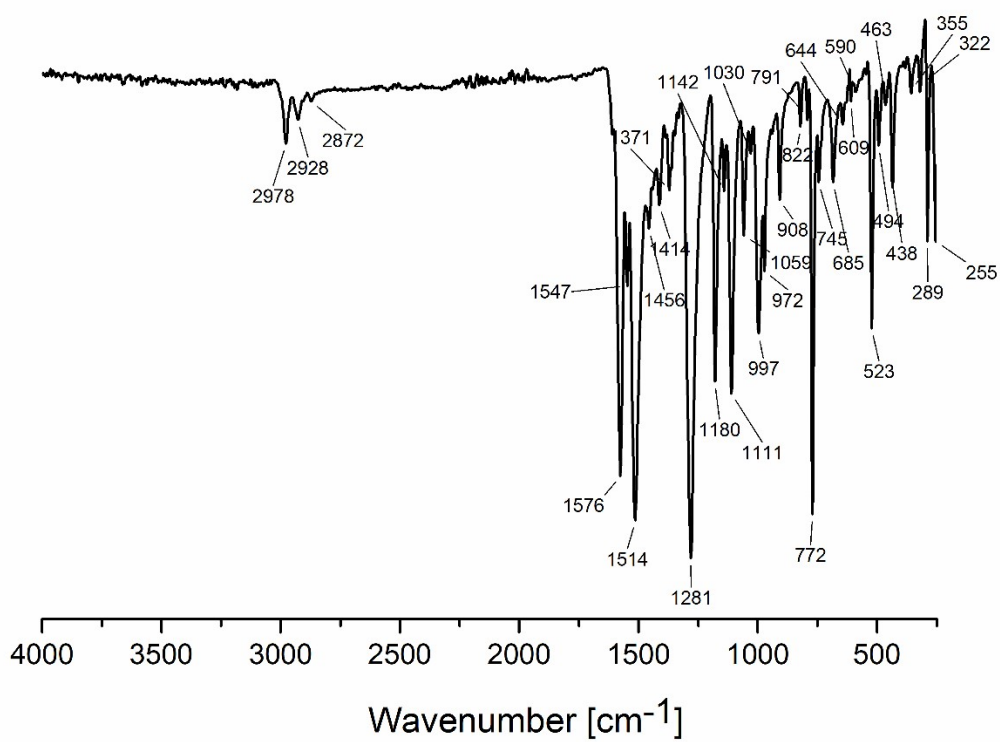
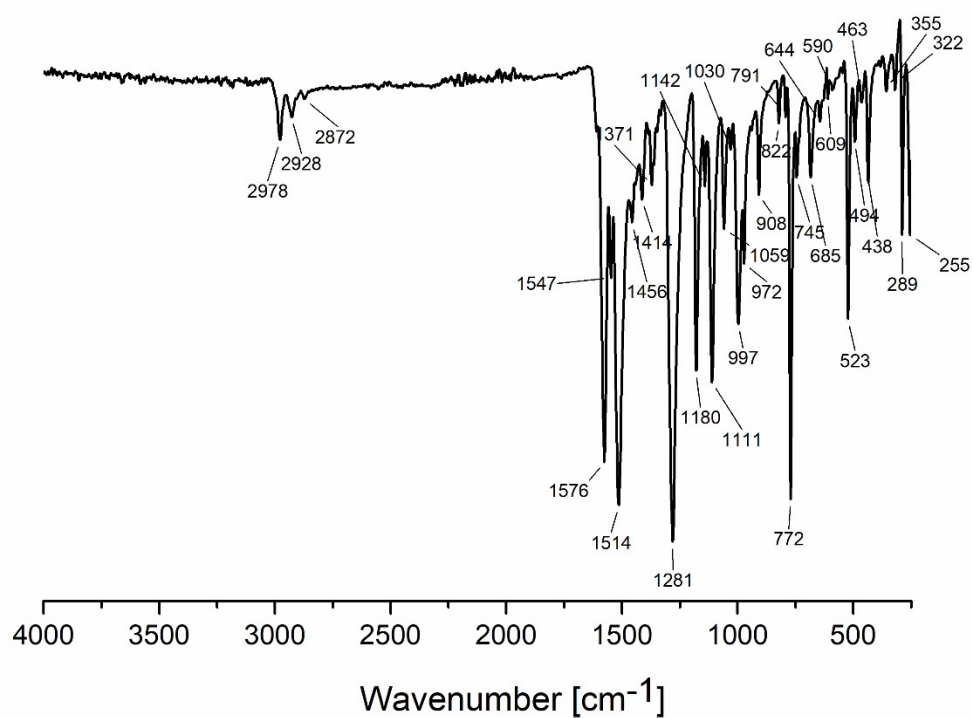


Figure S **1513** ATR-IR spectrum for the compound  $[\text{Pd}(\text{ipaoac})_2]$  (2).

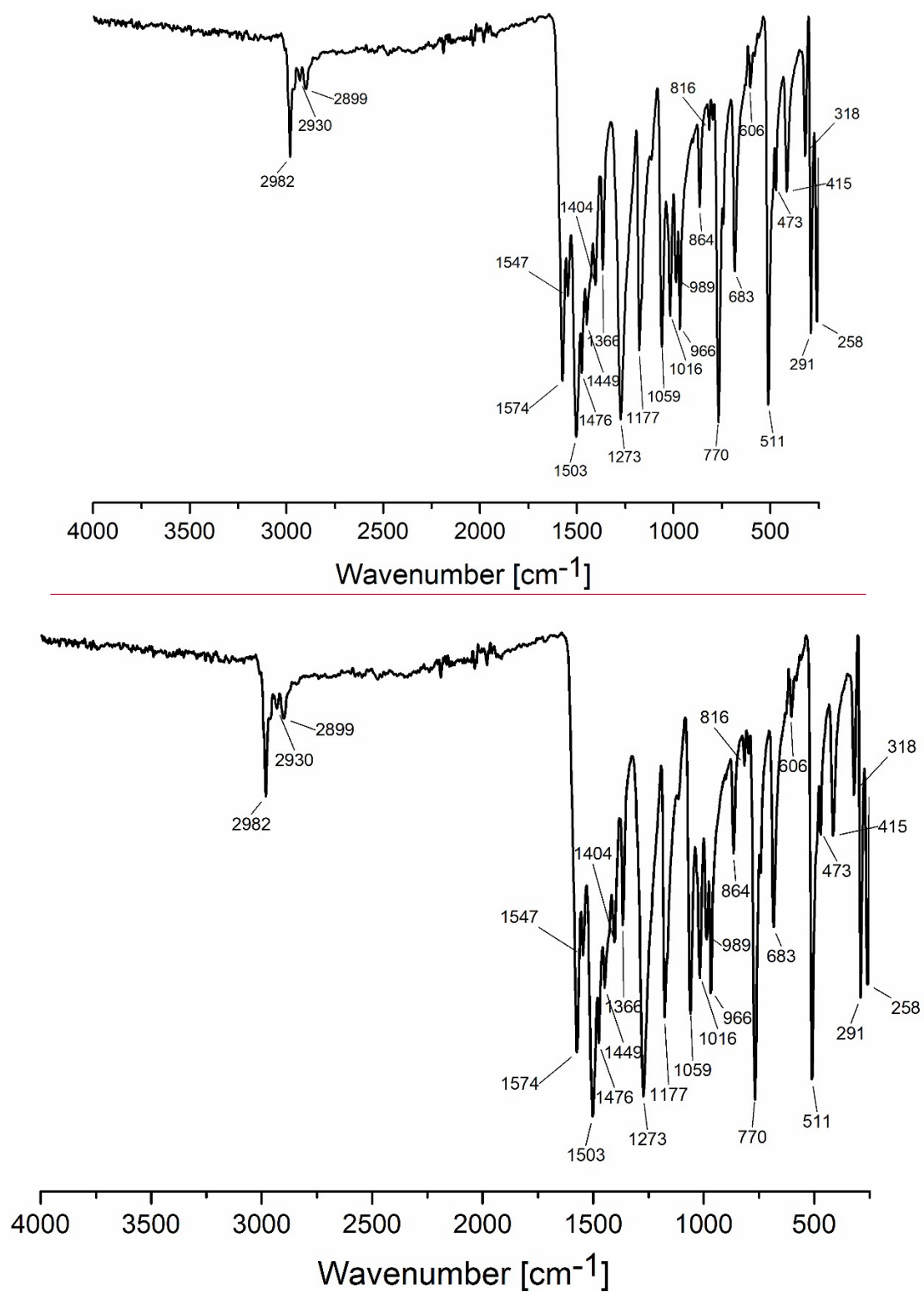
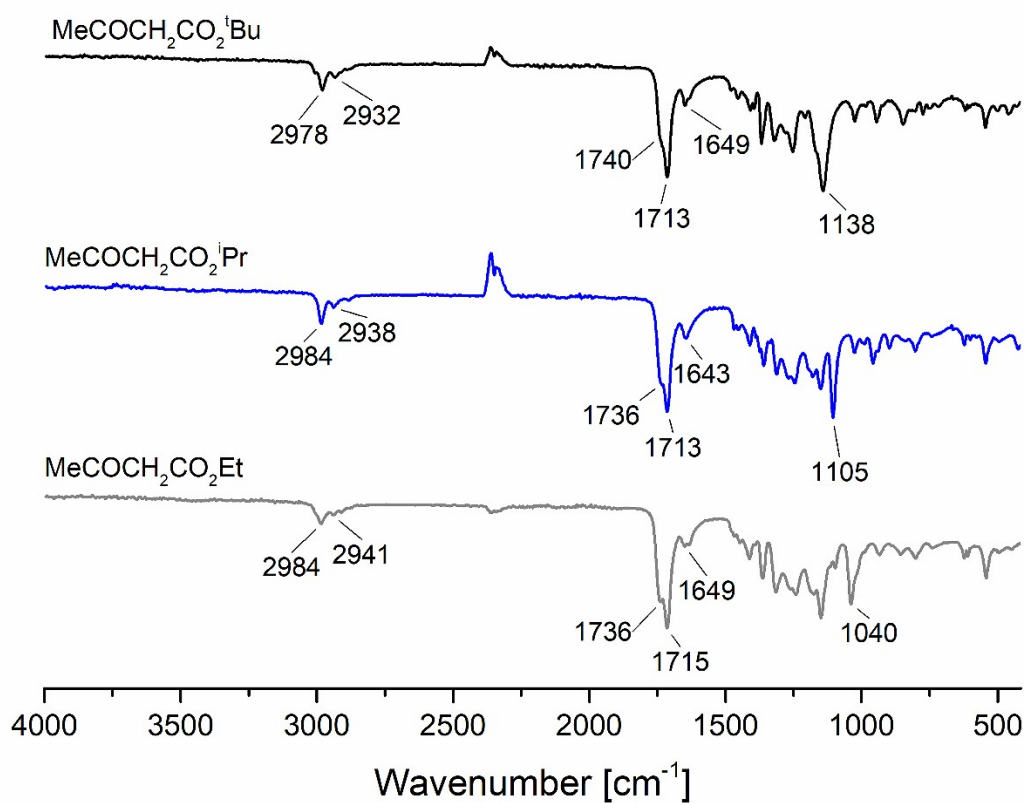
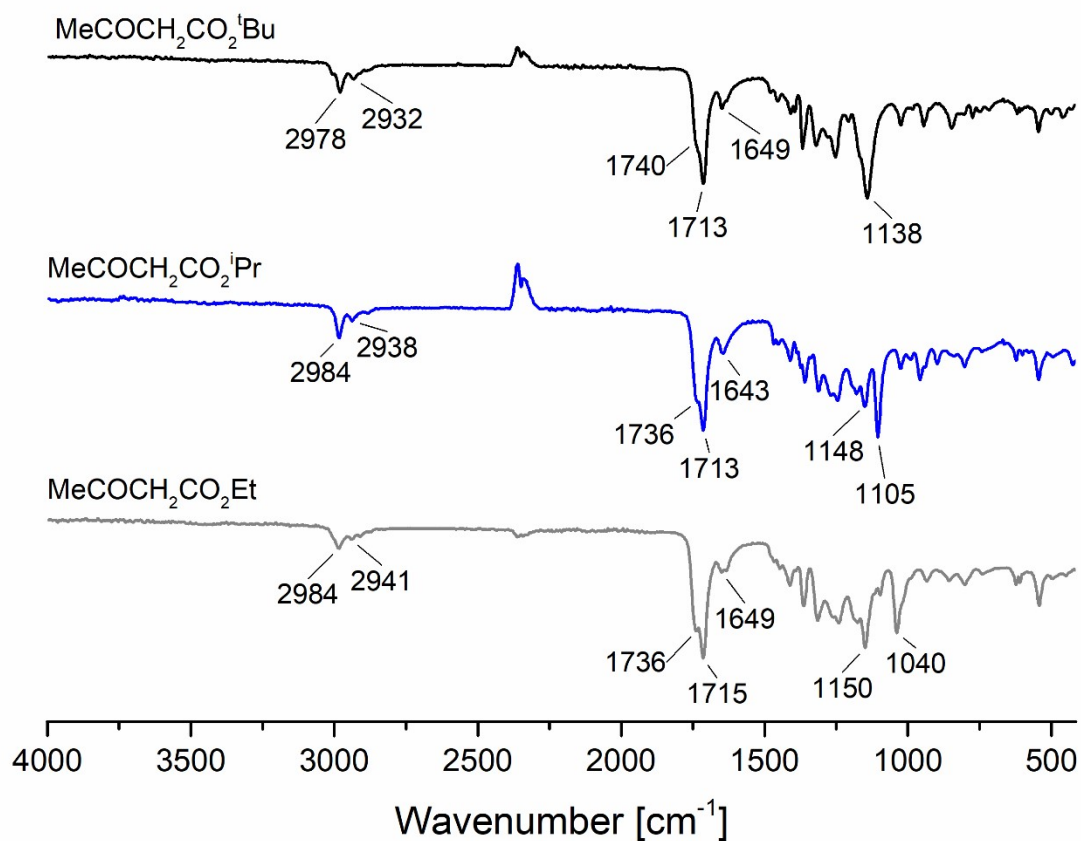
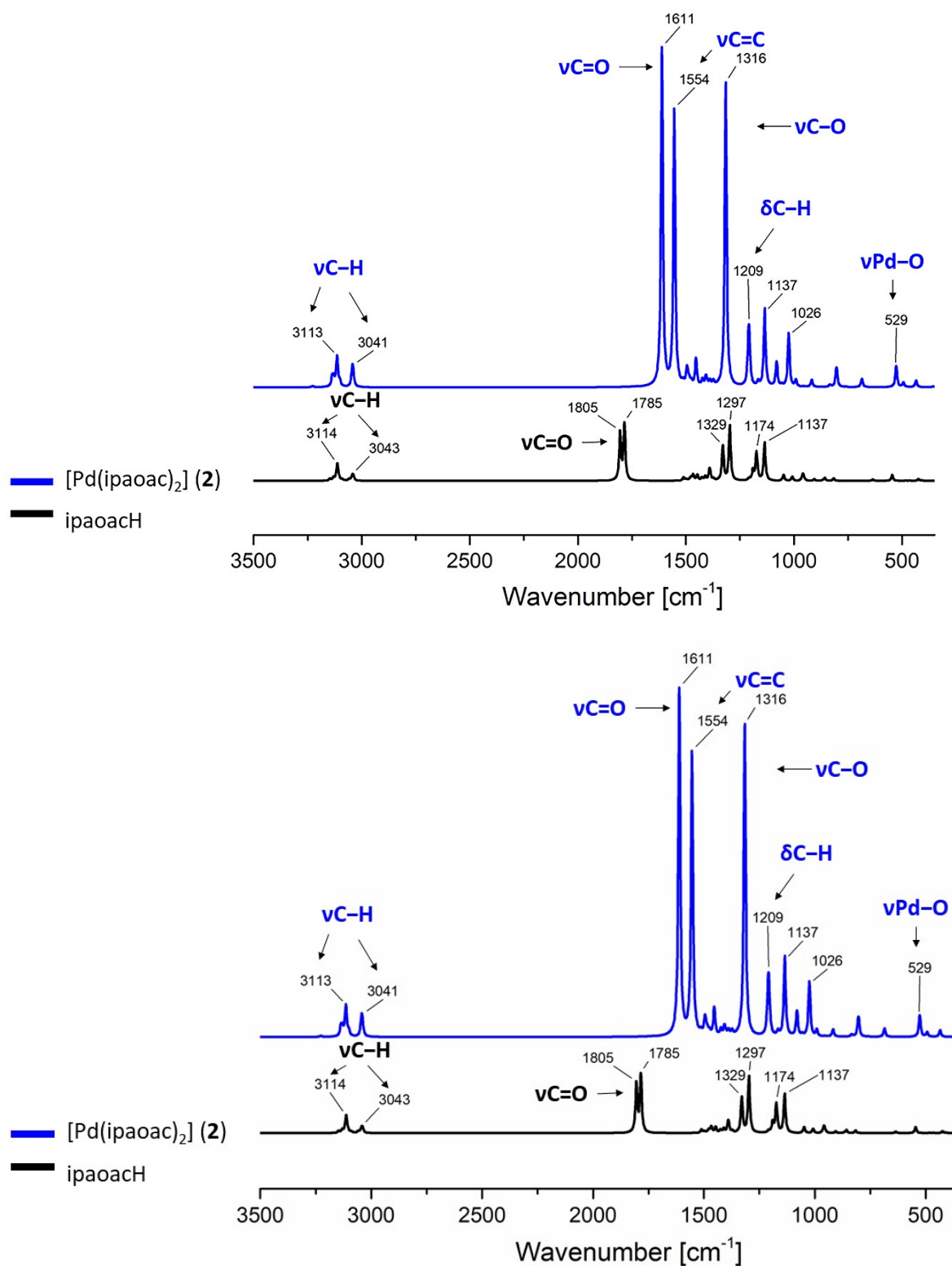


Figure S ~~1614~~ ATR-IR spectrum for the compound  $[\text{Pd}(\text{eaoac})_2]$  (**3**).

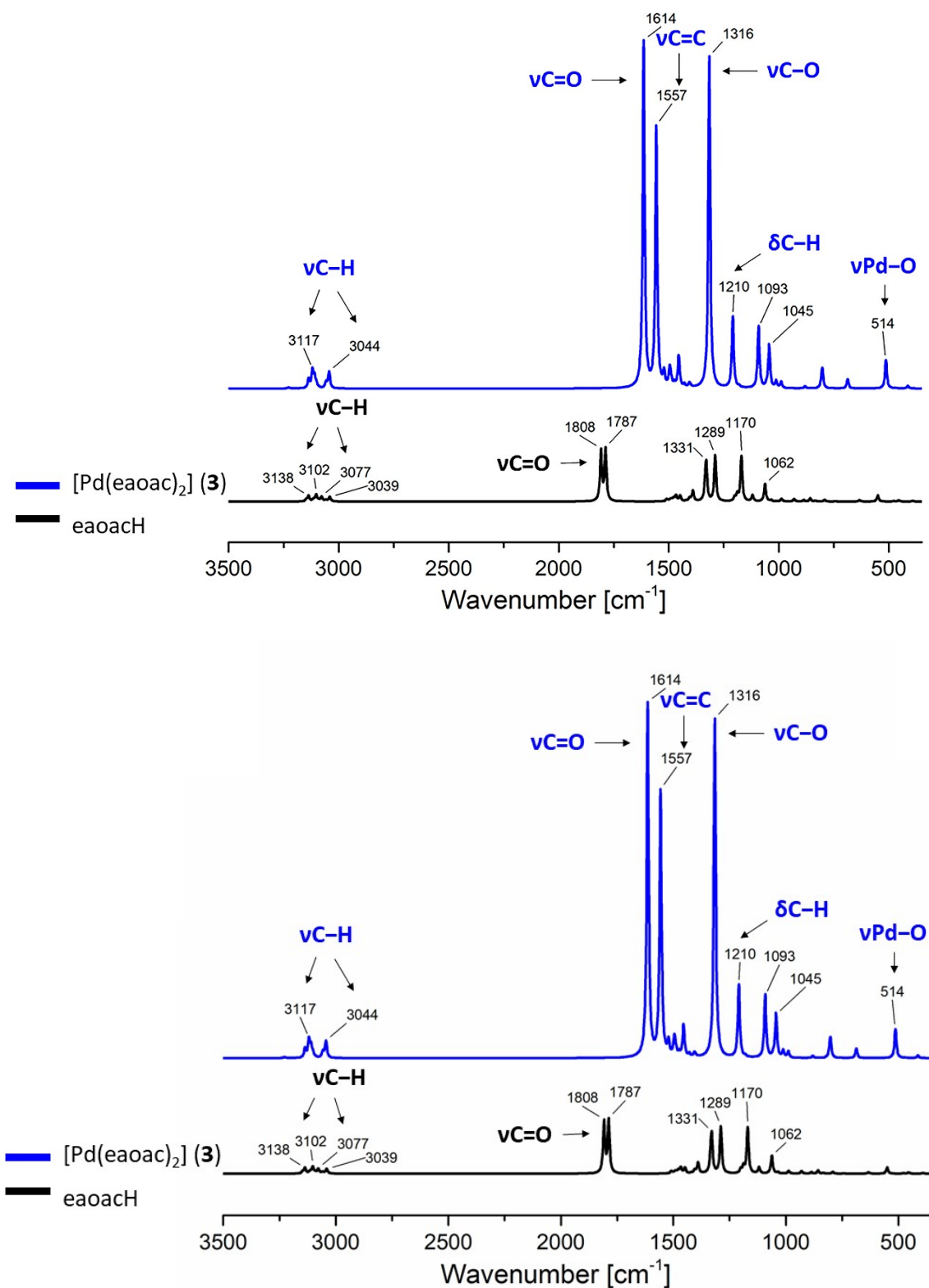


**Figure S 1715** ATR-IR spectra for the protonated ligands: MeCOCH<sub>2</sub>CO<sub>2</sub><sup>t</sup>Bu – tbaoacH (black), MeCOCH<sub>2</sub>CO<sub>2</sub><sup>i</sup>Pr – ipaoacH (blue), and MeCOCH<sub>2</sub>CO<sub>2</sub>Et – eaoacH (grey).

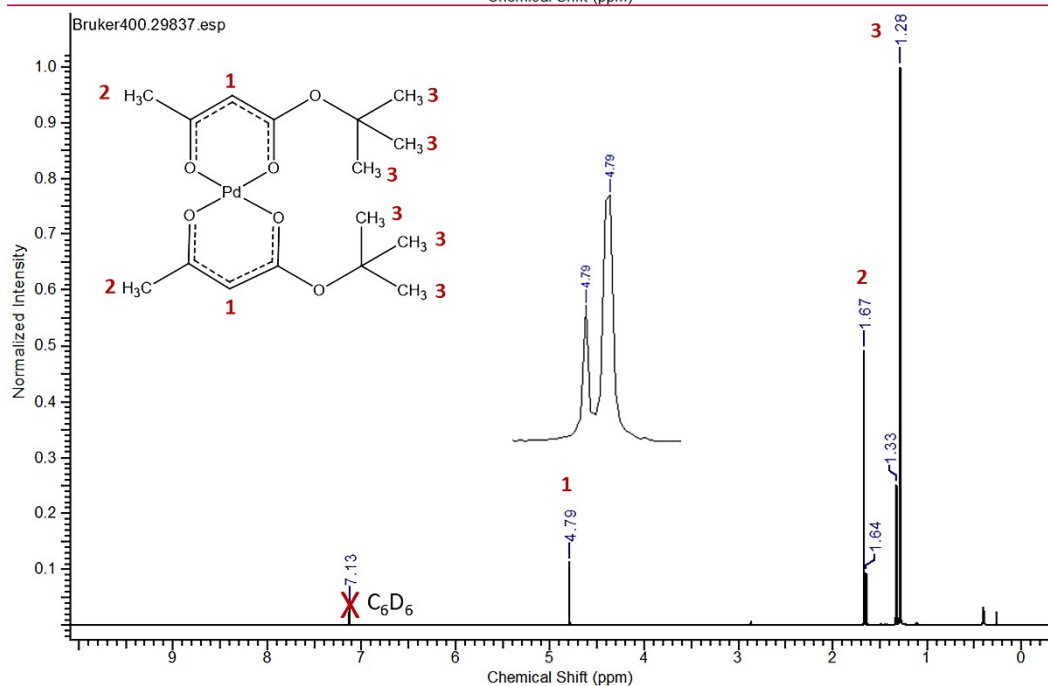
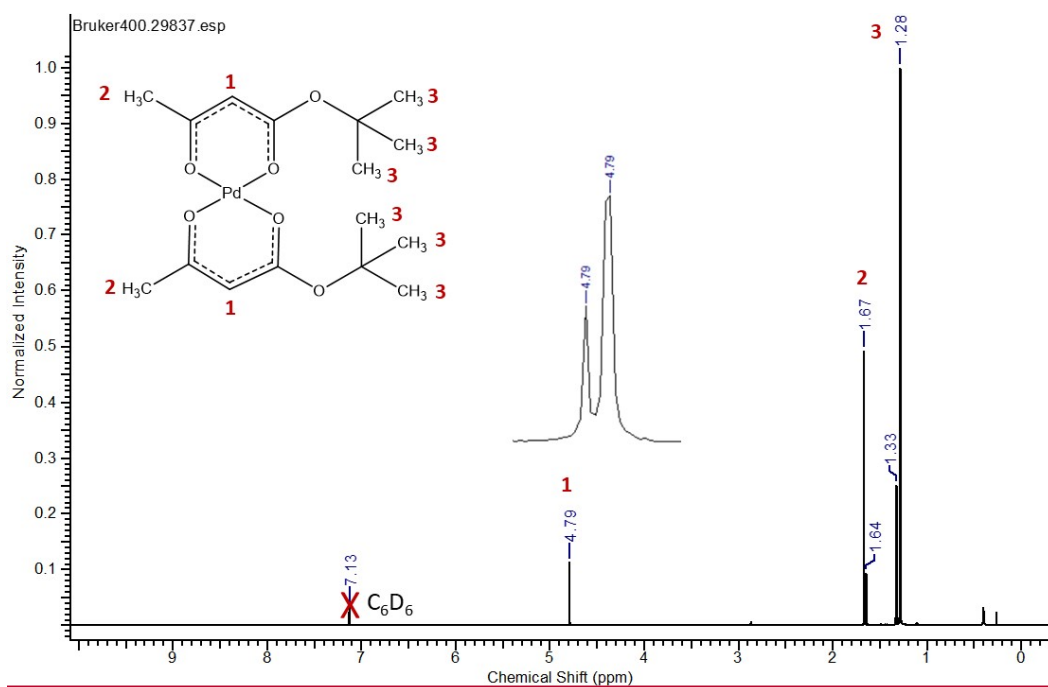


**Figure S 1816** Theoretical infrared spectra calculated by DFT B3LYP-D3/def2-TZVPP for the compound  $[\text{Pd}(\text{ipaoac})_2]$  (**2**) (blue line) and ligand  $\text{ipaoacH}$  (black line).





**Figure S 1917** Theoretical infrared spectra calculated by DFT B3LYP-D3/def2-TZVPP for the compound  $[Pd(eaoac)_2]$  (**3**) (blue line) and ligand eaoach (black line).



**Figure S 2018**  $^1\text{H}$  NMR spectrum of the compound  $[\text{Pd}(\text{tbaoac})_2]$  (1).

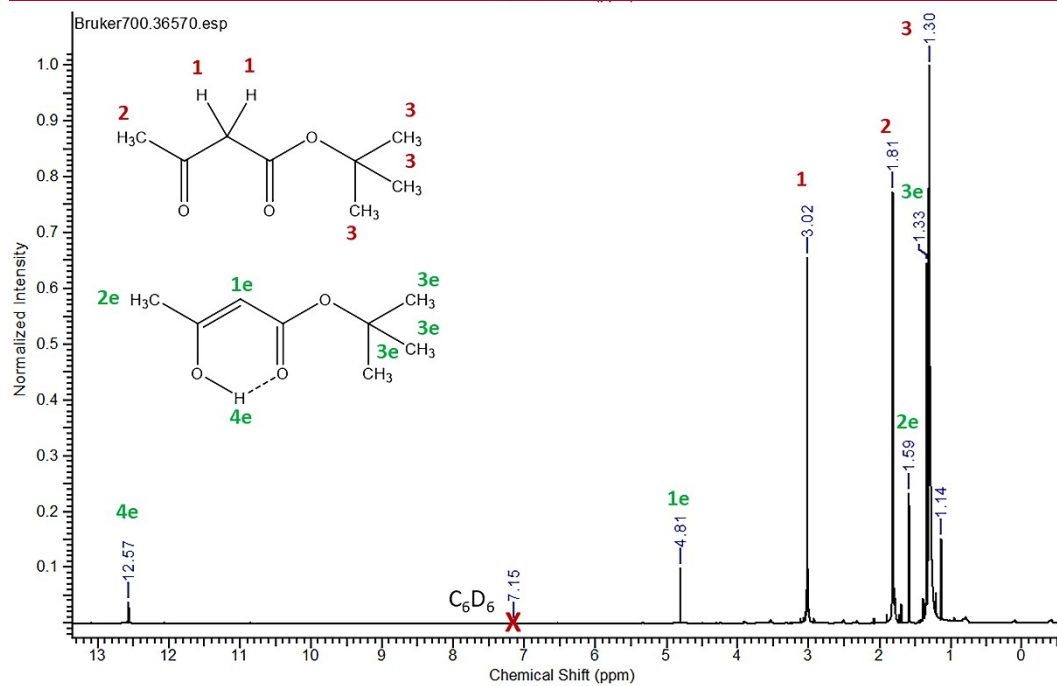
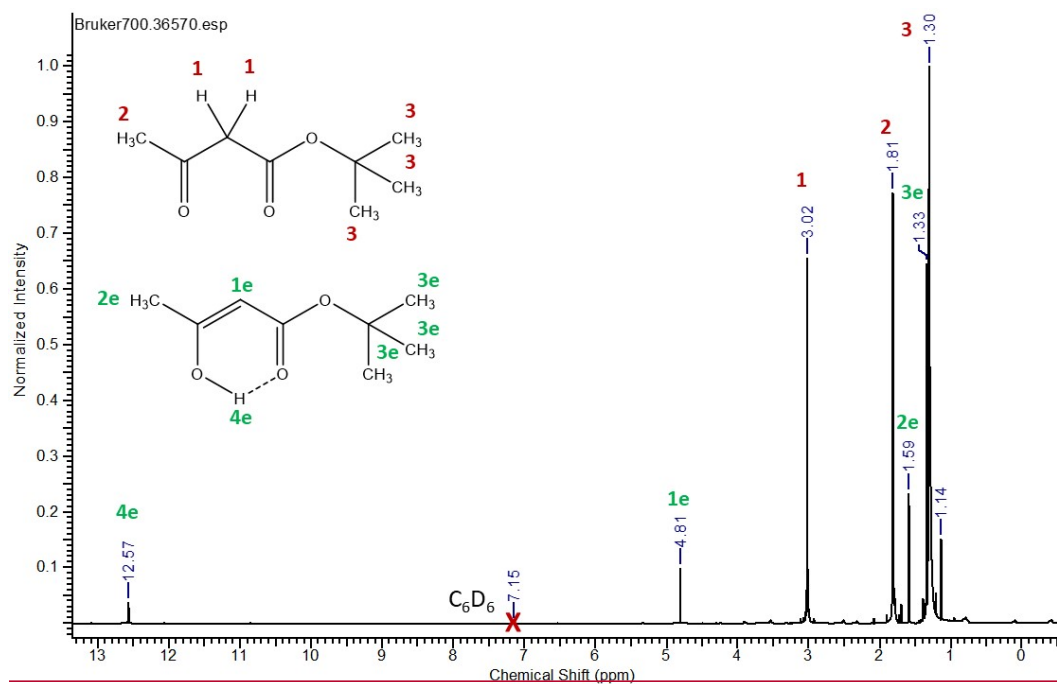


Figure S 2119  $^1\text{H}$  NMR spectrum of the tbaocH –  $\text{MeCOCH}_2\text{CO}_2^t\text{Bu}$ .

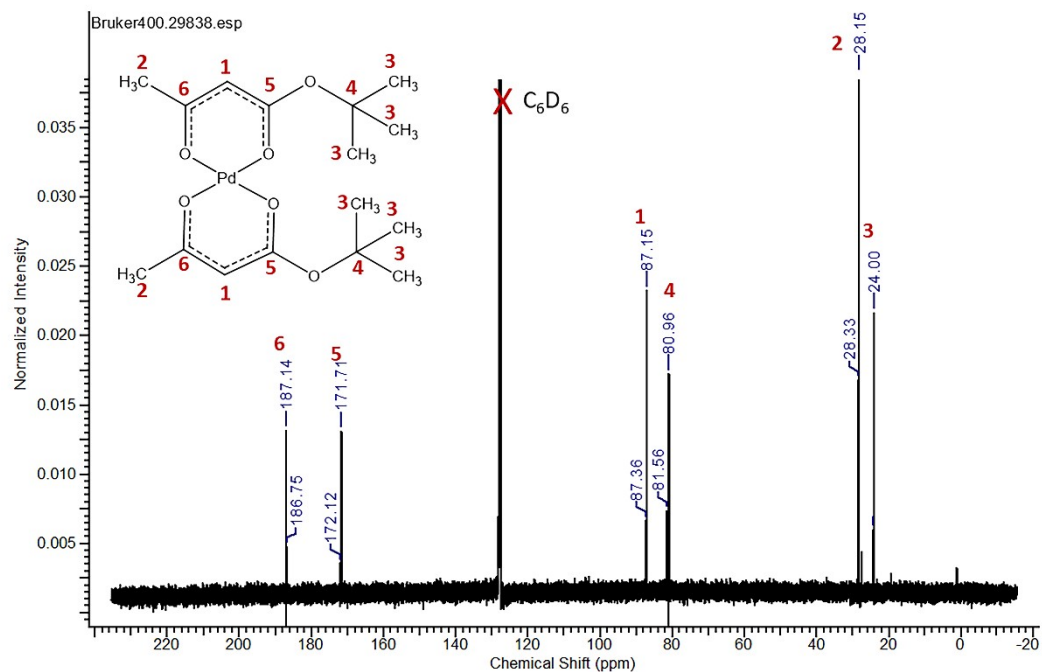
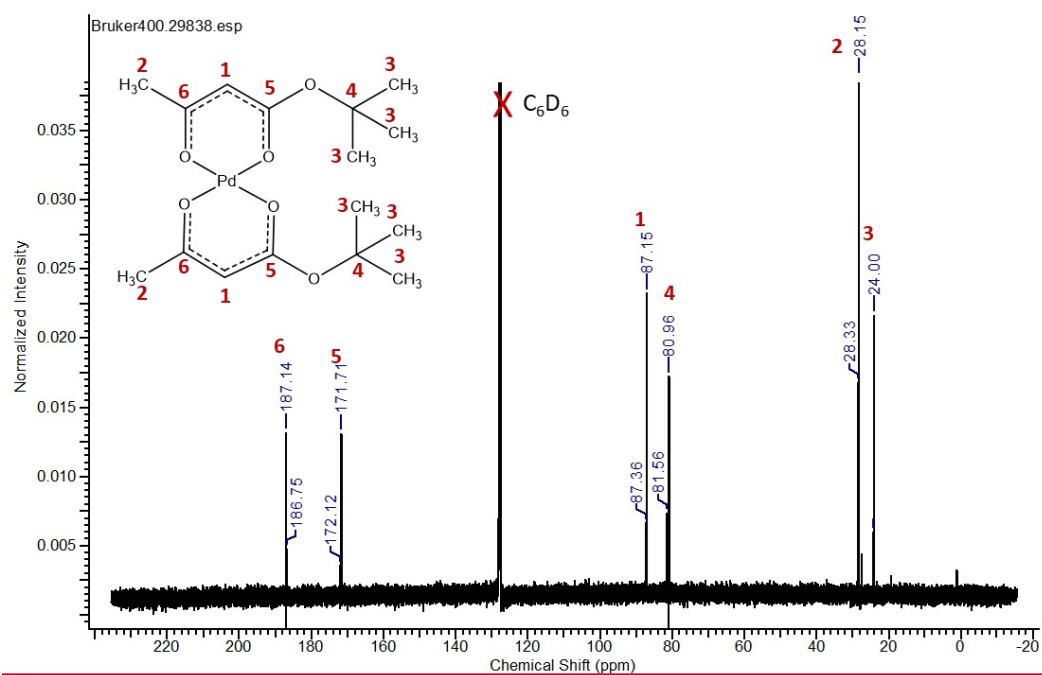
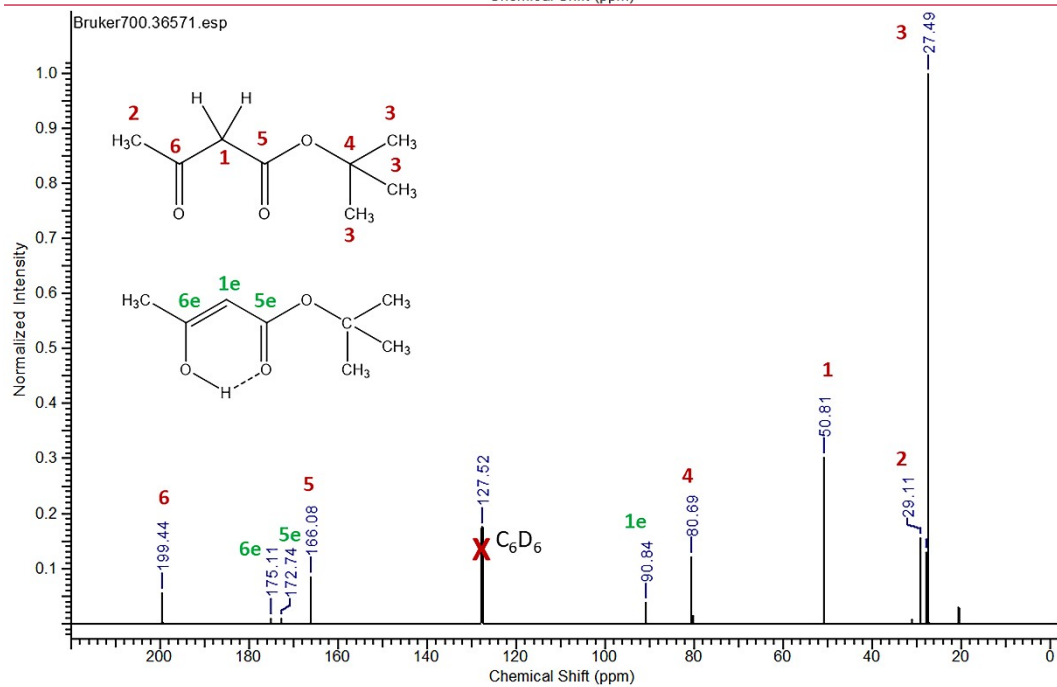
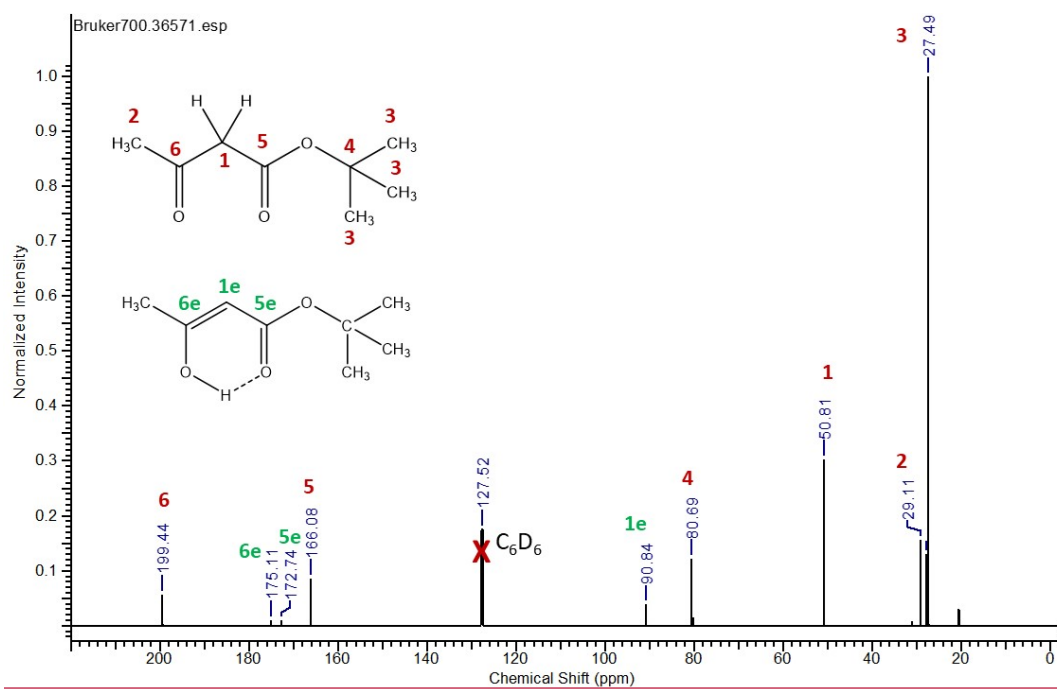


Figure S 2220  $^{13}\text{C}$  NMR spectrum of the compound  $[\text{Pd}(\text{tbaoc})_2]$  (1).



**Figure S 2321**  $^{13}\text{C}$  NMR spectrum of the tbaocH –  $\text{MeCOCH}_2\text{CO}_2^t\text{Bu}$ .

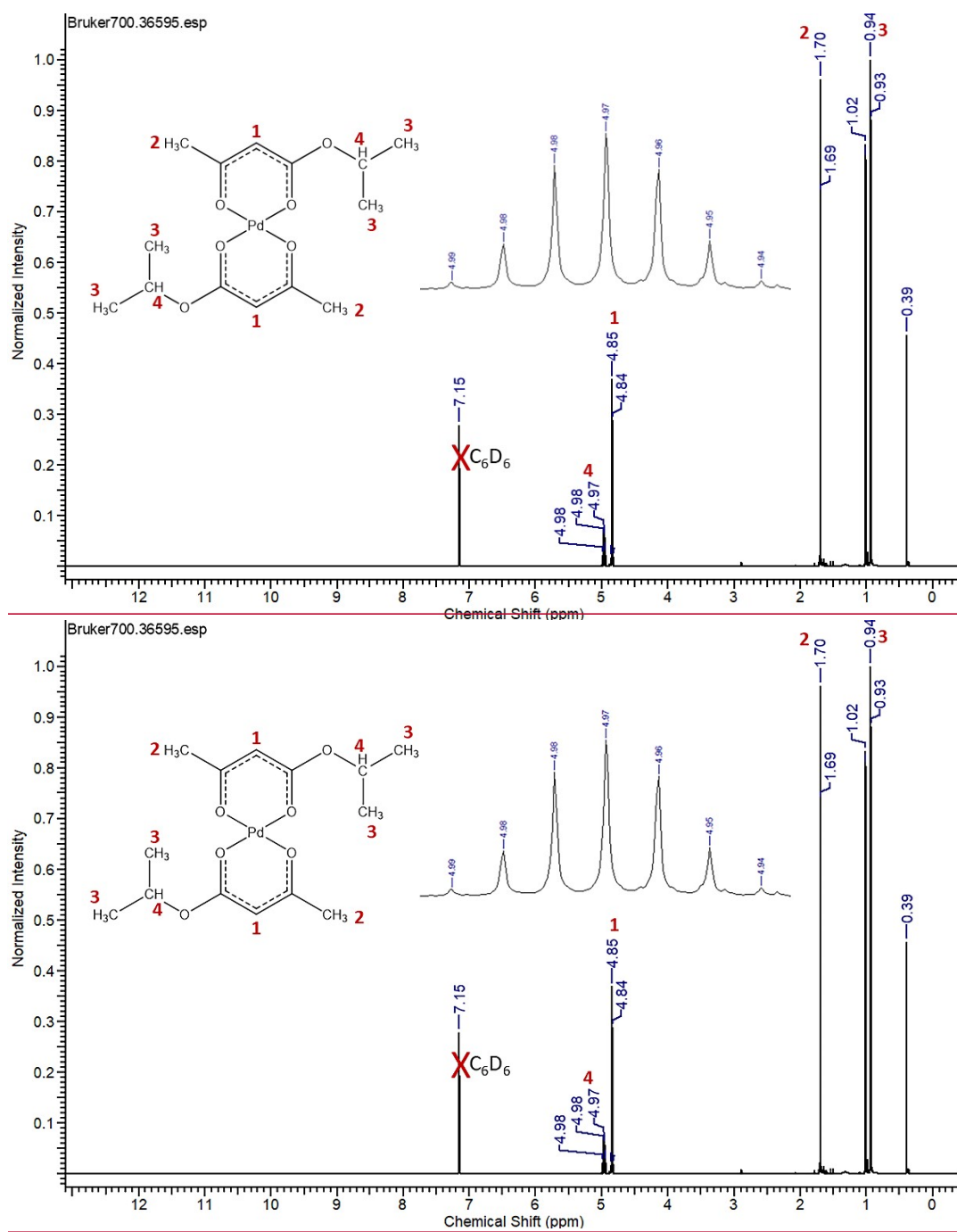


Figure S 2422  $^1\text{H}$  NMR spectrum of the compound  $[\text{Pd}(\text{ipaoac})_2]$  (2).



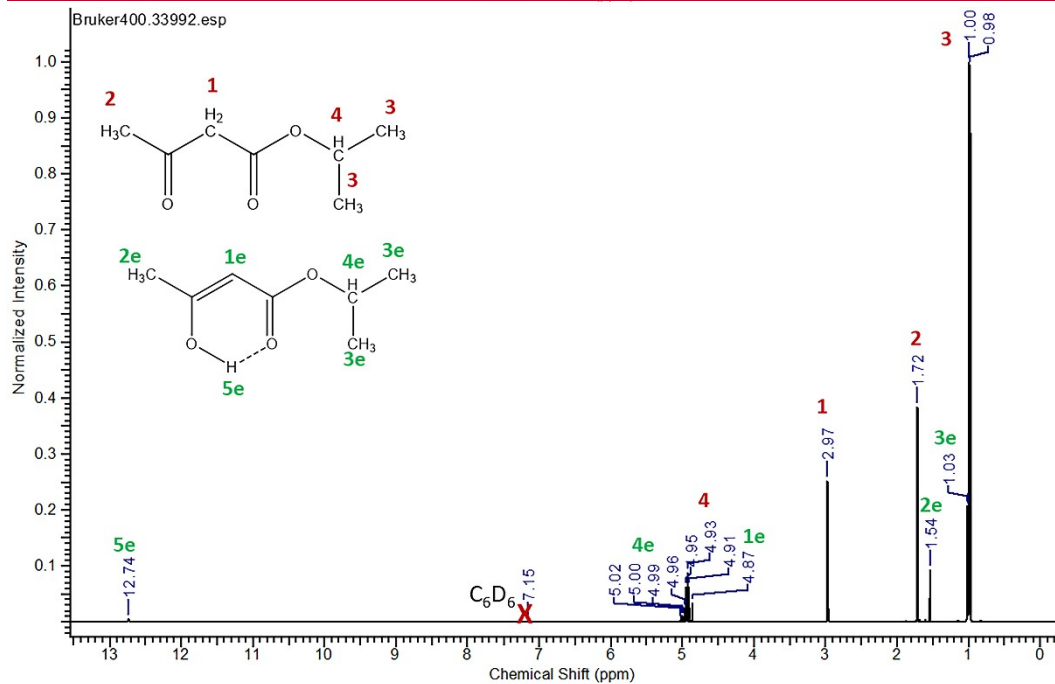
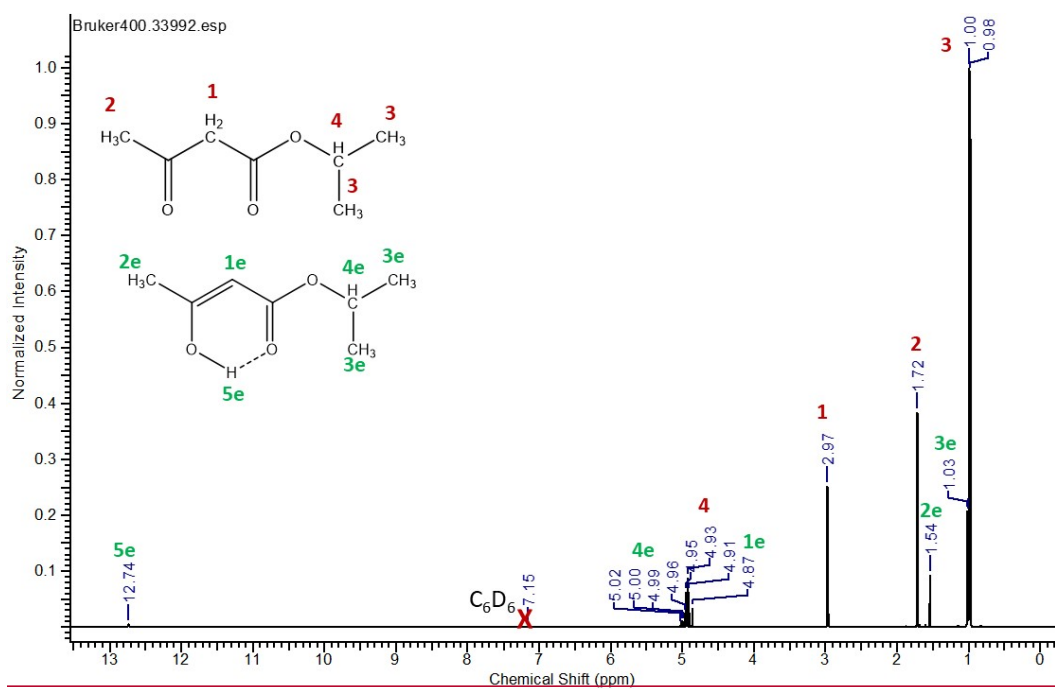


Figure S 2523  $^1\text{H}$  NMR spectrum of the ipaoacH –  $\text{MeCOCH}_2\text{CO}_2^i\text{Pr}$ .

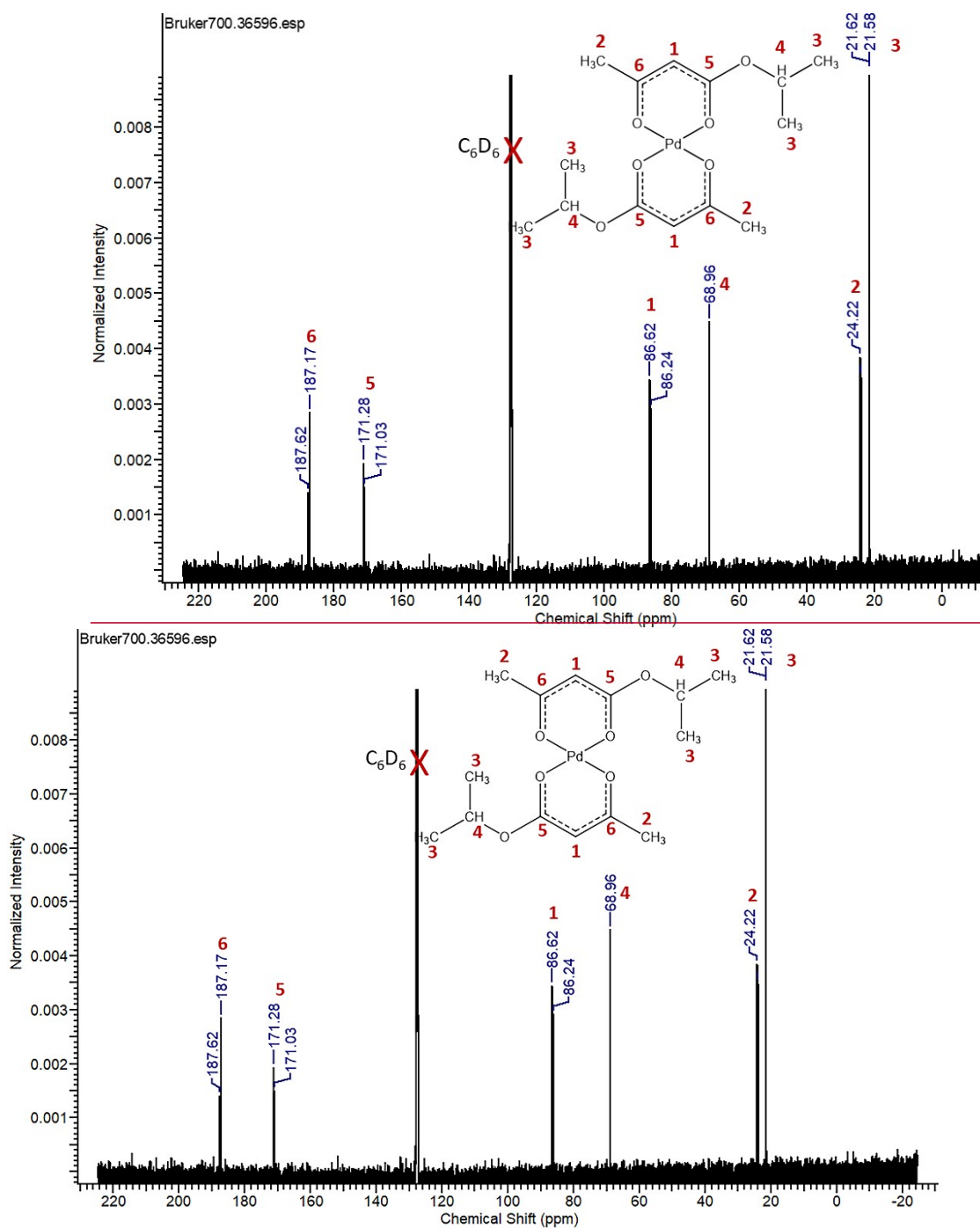


Figure S 2624  $^{13}\text{C}$  NMR spectrum of the compound  $[\text{Pd}(\text{ipaoac})_2]$  (2).

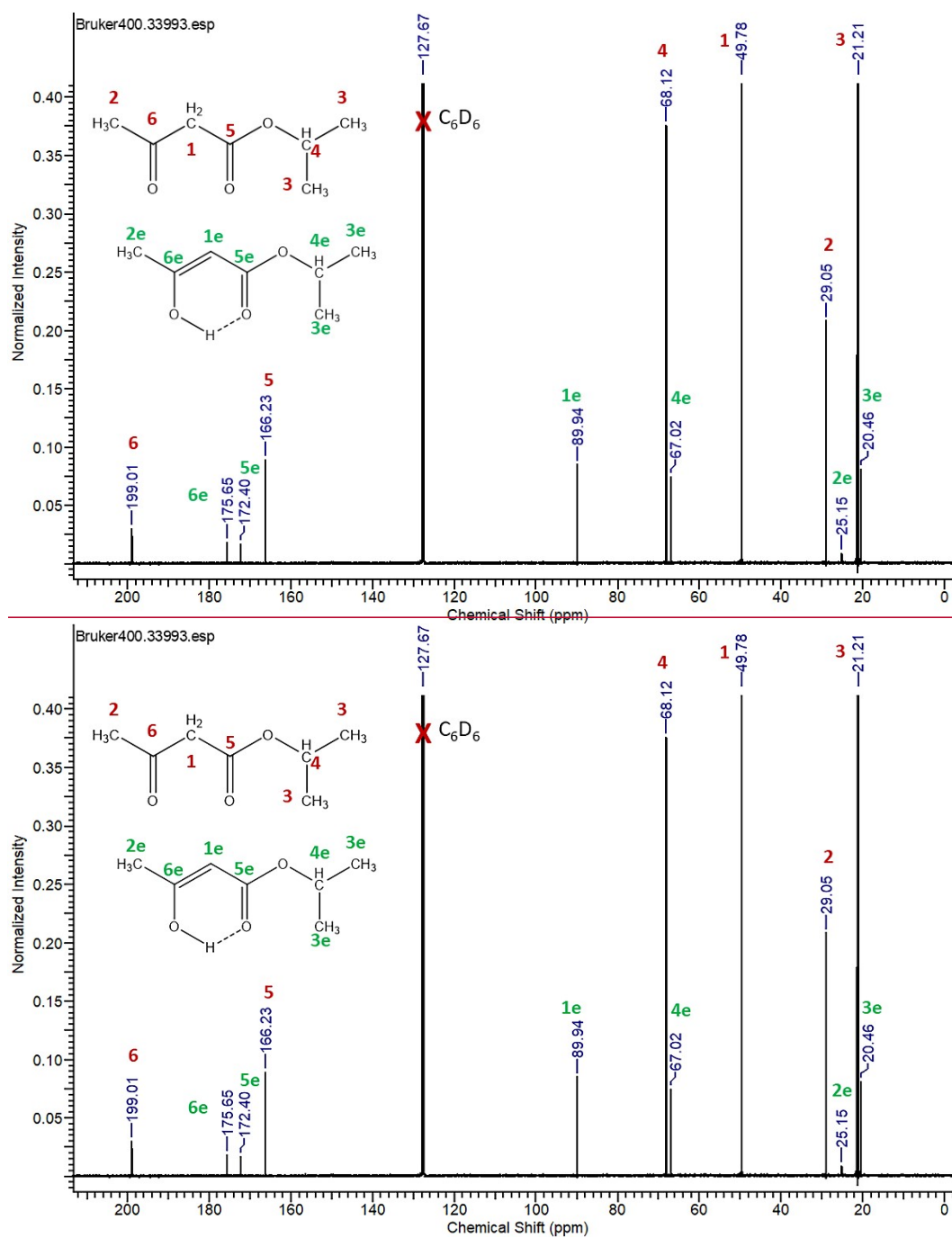
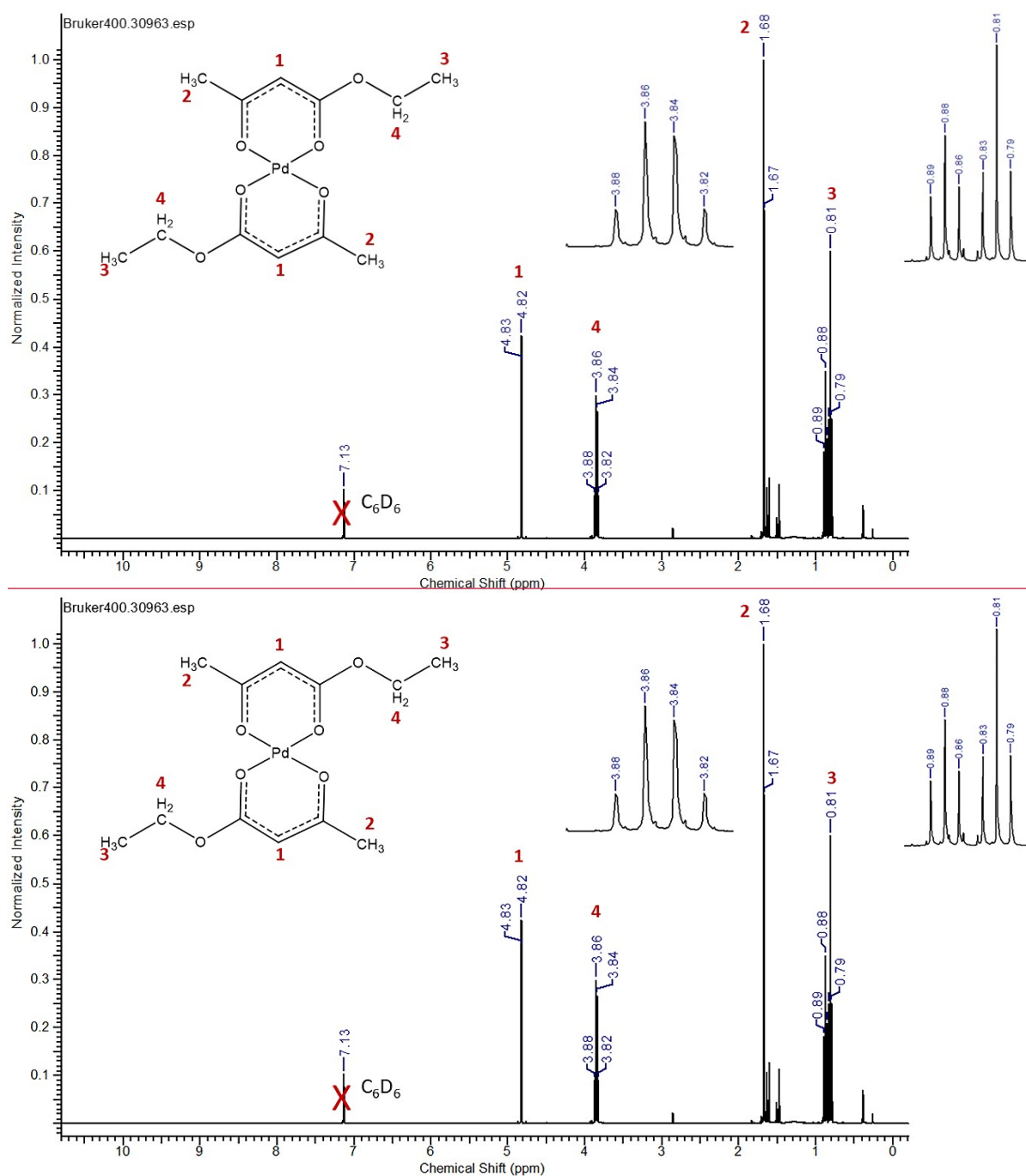


Figure S 2725  $^{13}\text{C}$  NMR spectrum of the ipaoacH –  $\text{MeCOCH}_2\text{CO}_2^i\text{Pr}$ .



**Figure S 2826**  $^1\text{H}$  NMR spectrum of the compound  $[\text{Pd}(\text{eaoac})_2]$  (3).

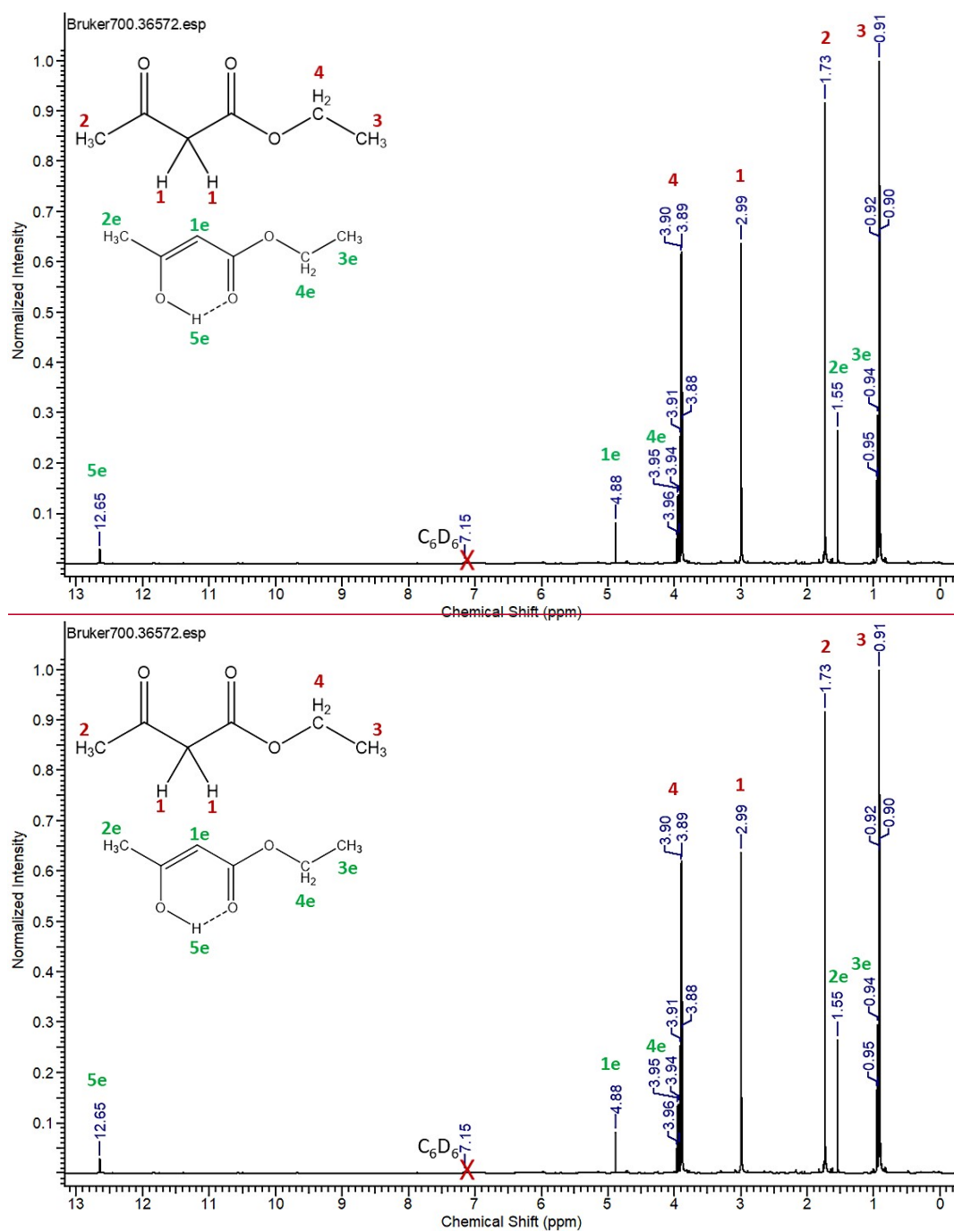
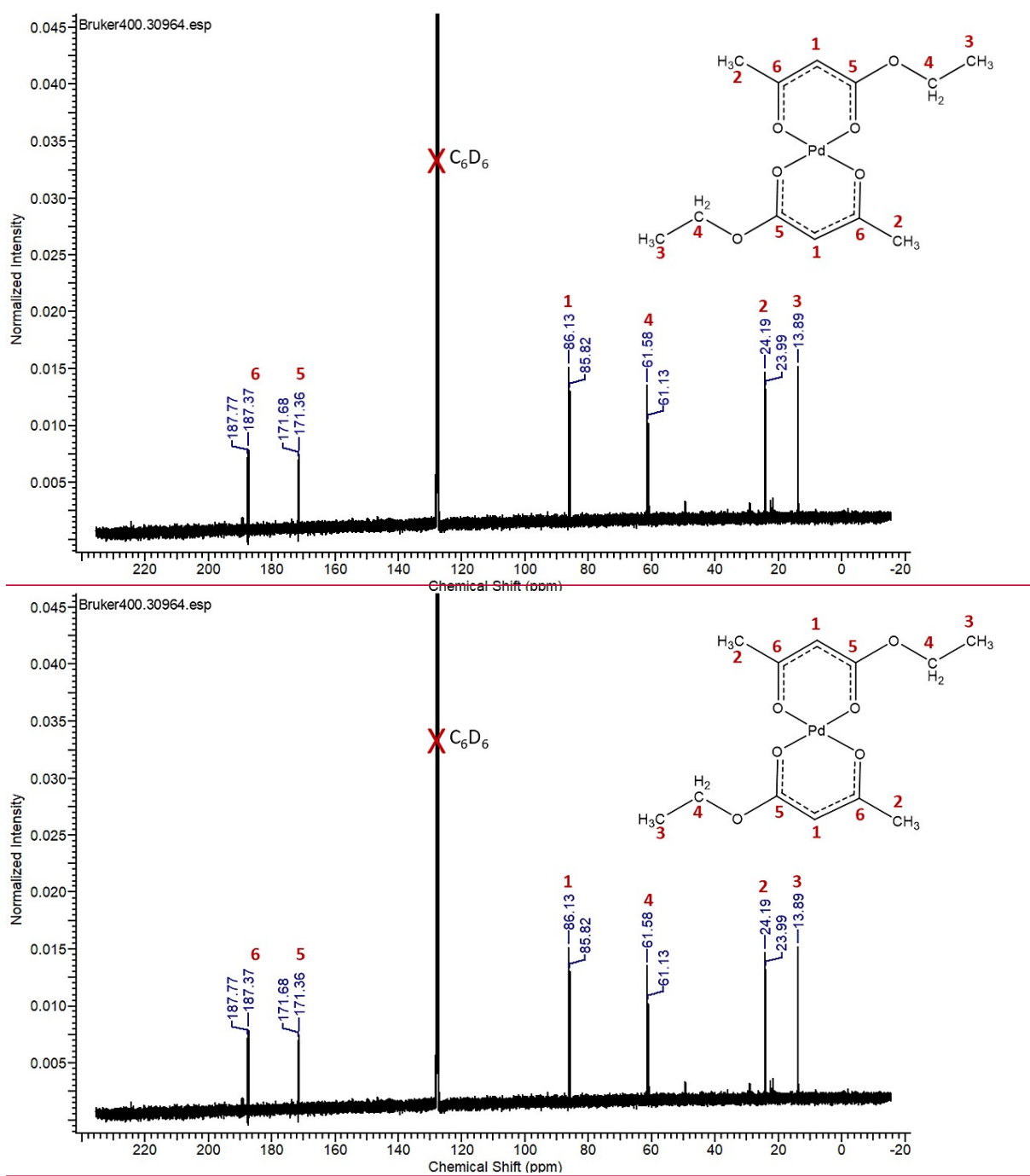


Figure S 2927  $^1\text{H}$  NMR spectrum of the compound eaoacH –  $\text{MeCOCH}_2\text{CO}_2\text{Et}$ .



**Figure S 3028**  $^{13}\text{C}$  NMR spectrum of the compound  $[\text{Pd}(\text{eaoac})_2]$  (3).



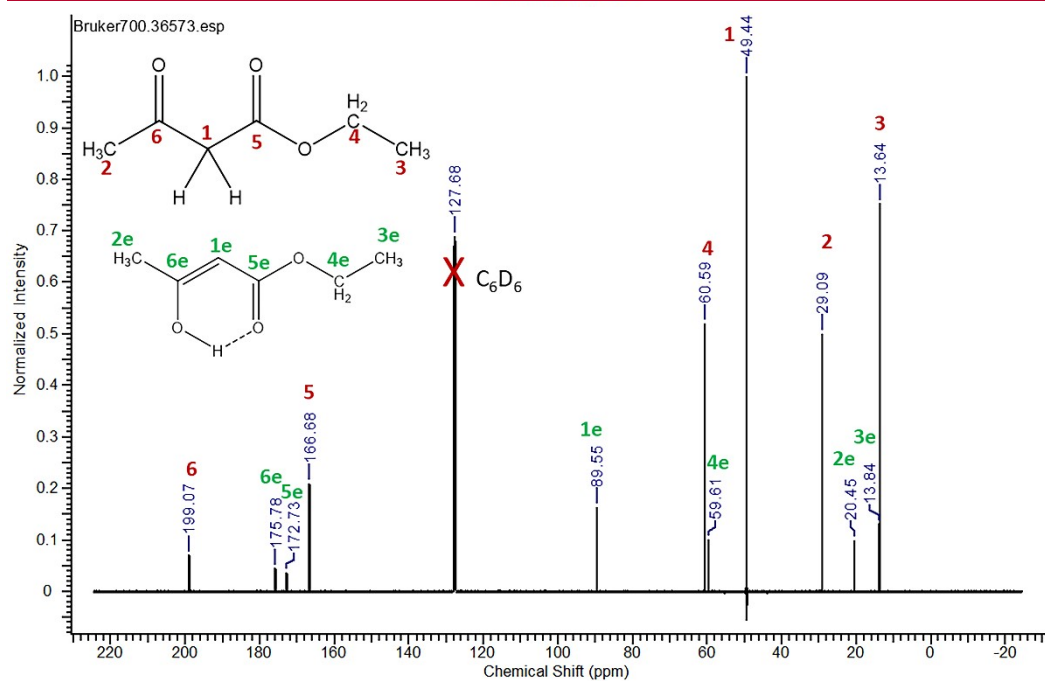
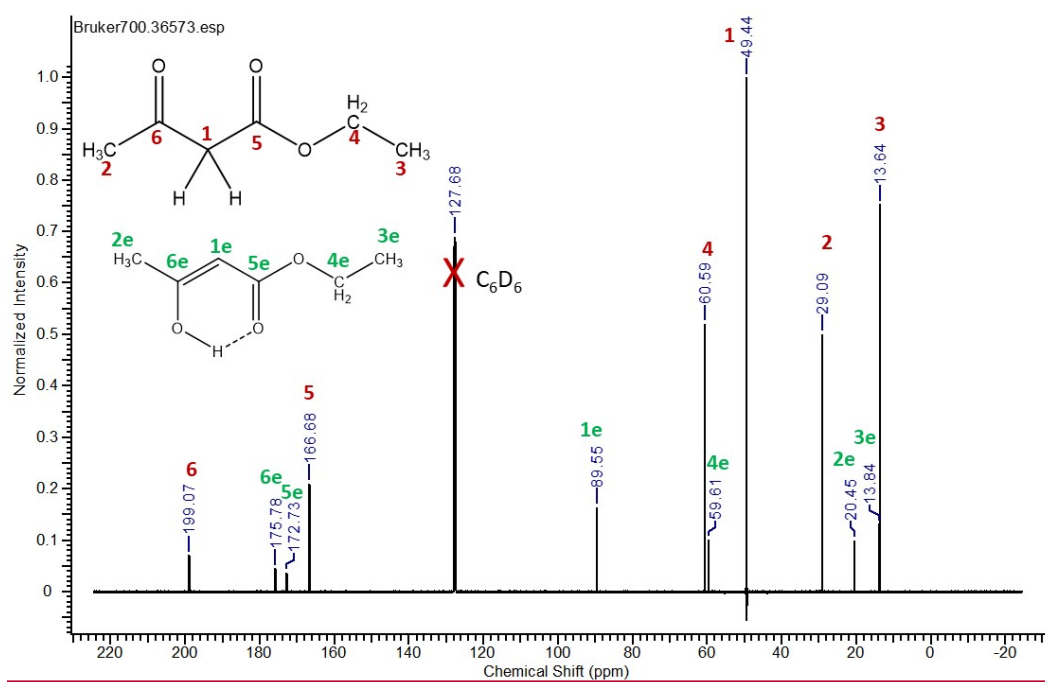
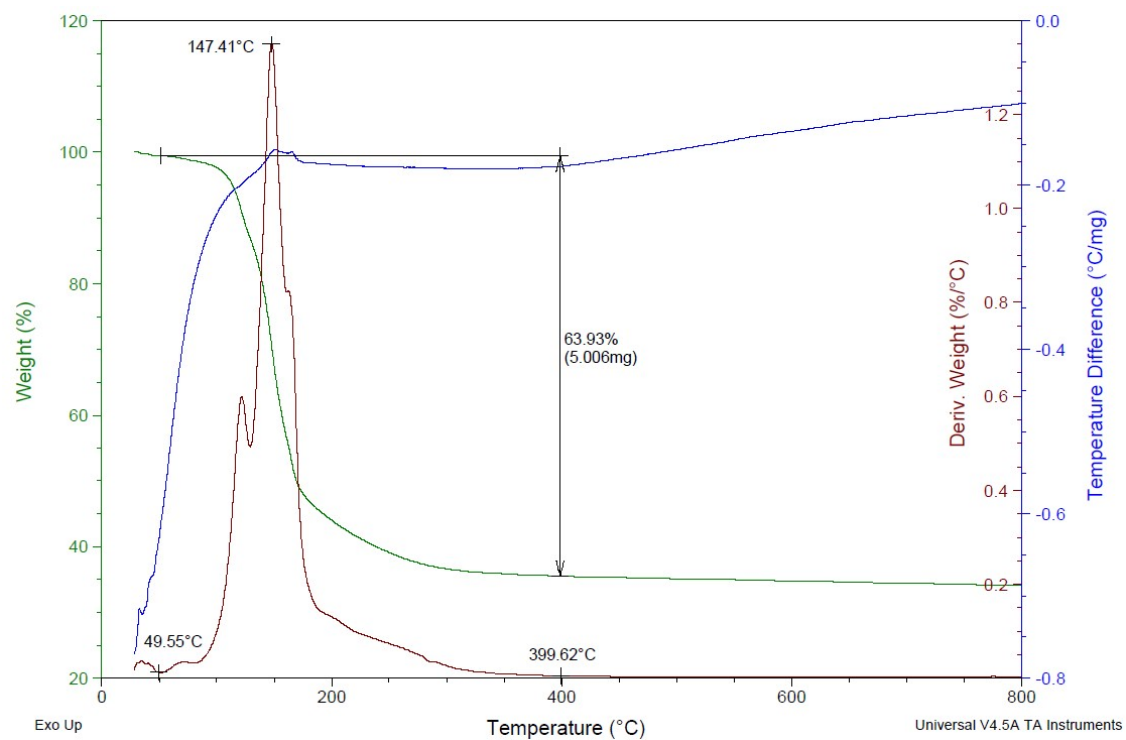
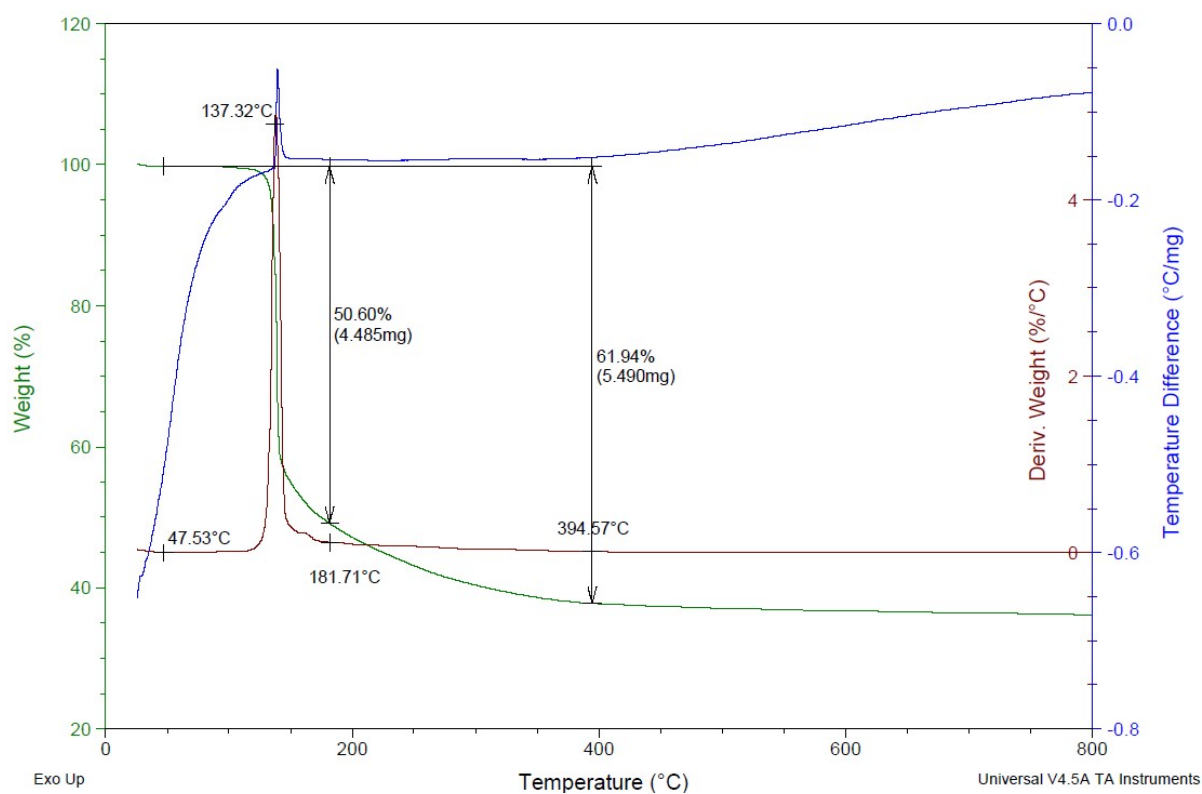


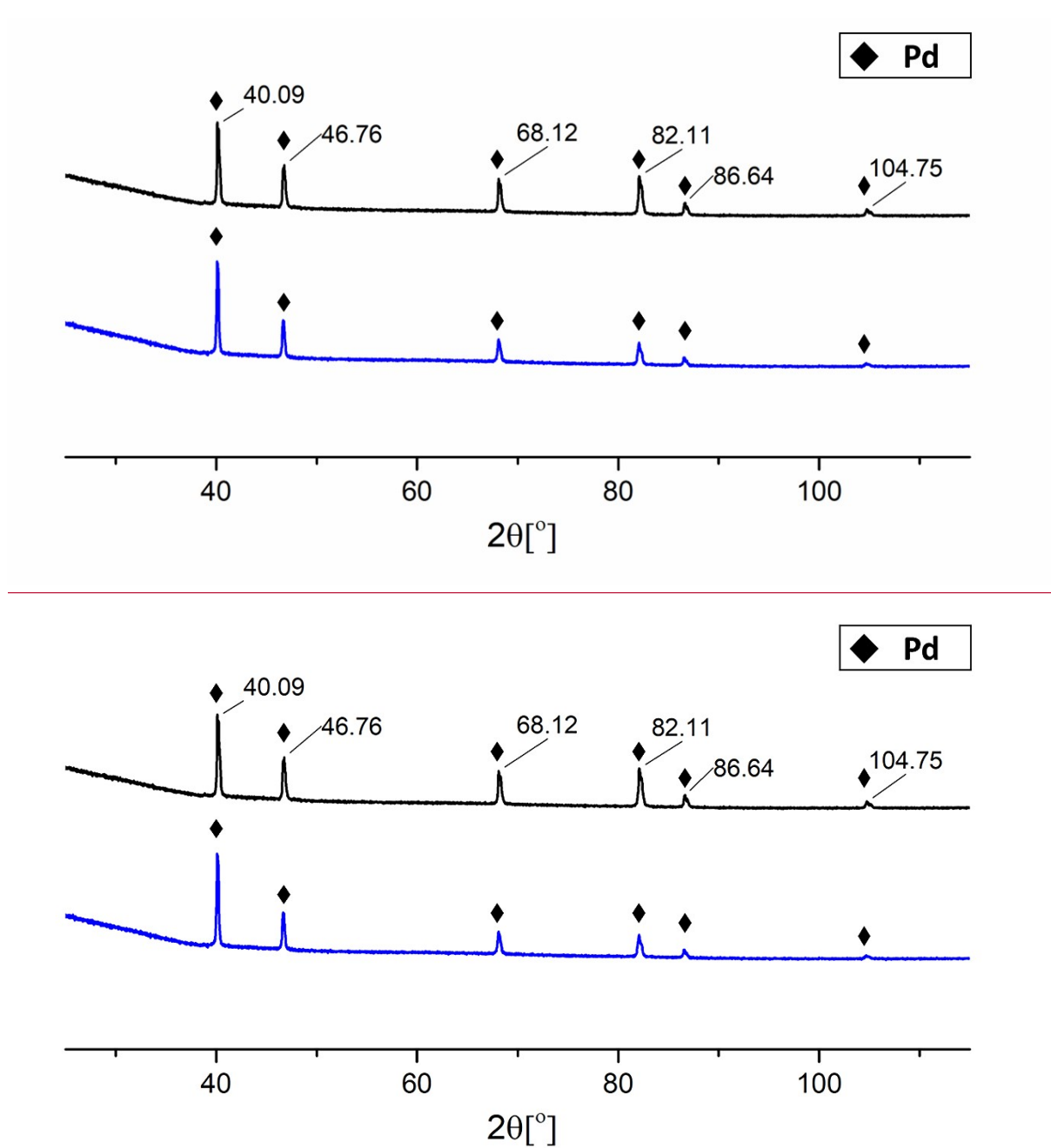
Figure S 3129  $^{13}\text{C}$  NMR spectrum of the eaoach –  $\text{MeCOCH}_2\text{CO}_2\text{Et}$ .



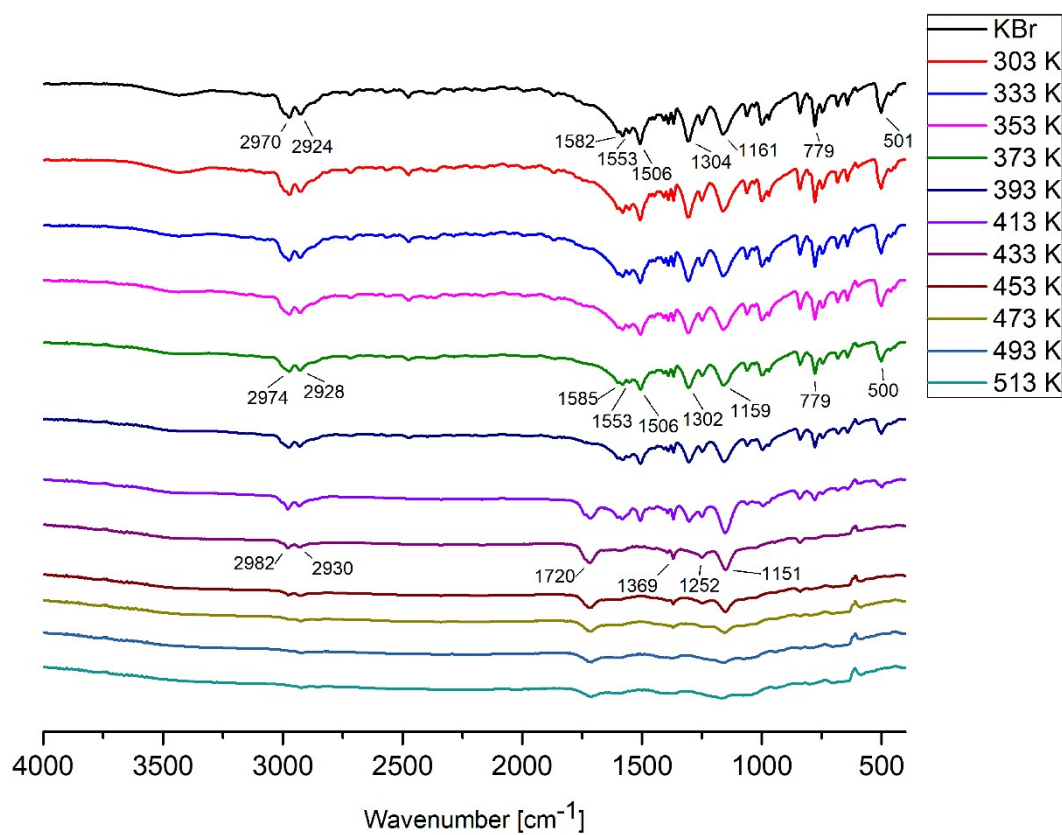
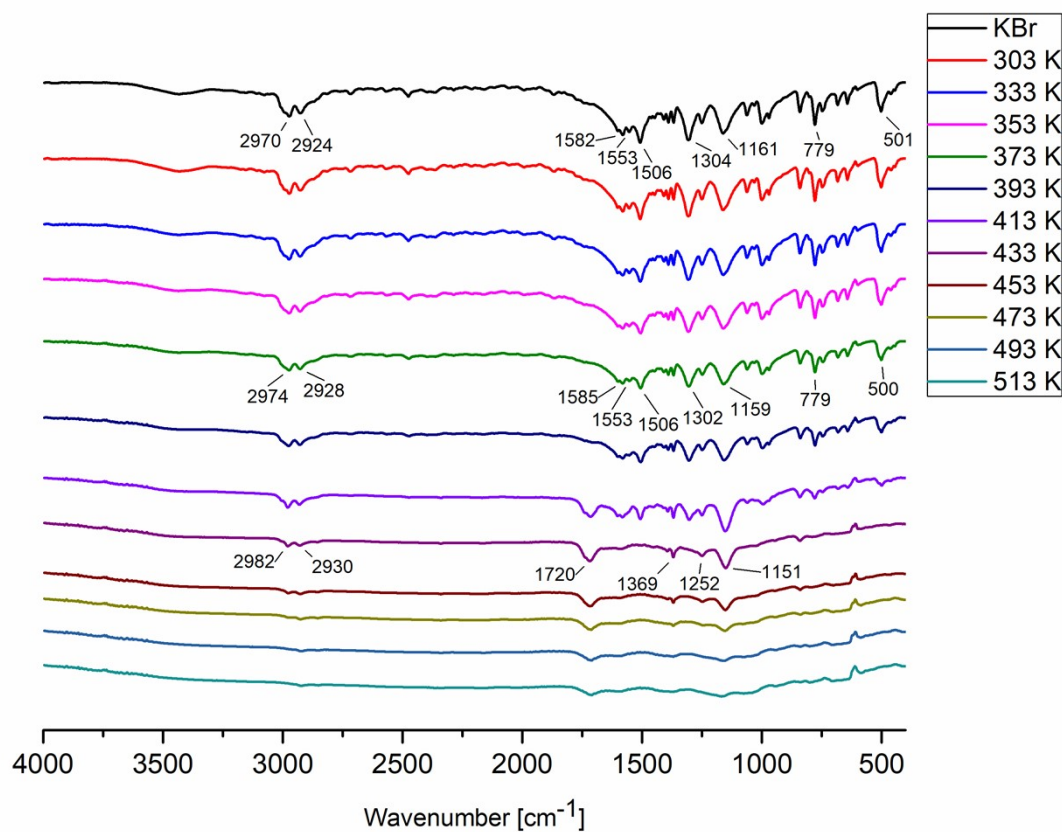
**Figure S 3230** Thermogram of  $[\text{Pd}(\text{ipaoac})_2]$  (2) (TG, DTG, DTA curves).



**Figure S 3331** Thermogram of  $[\text{Pd}(\text{eaoac})_2]$  (3) (TG, DTG, DTA curves).

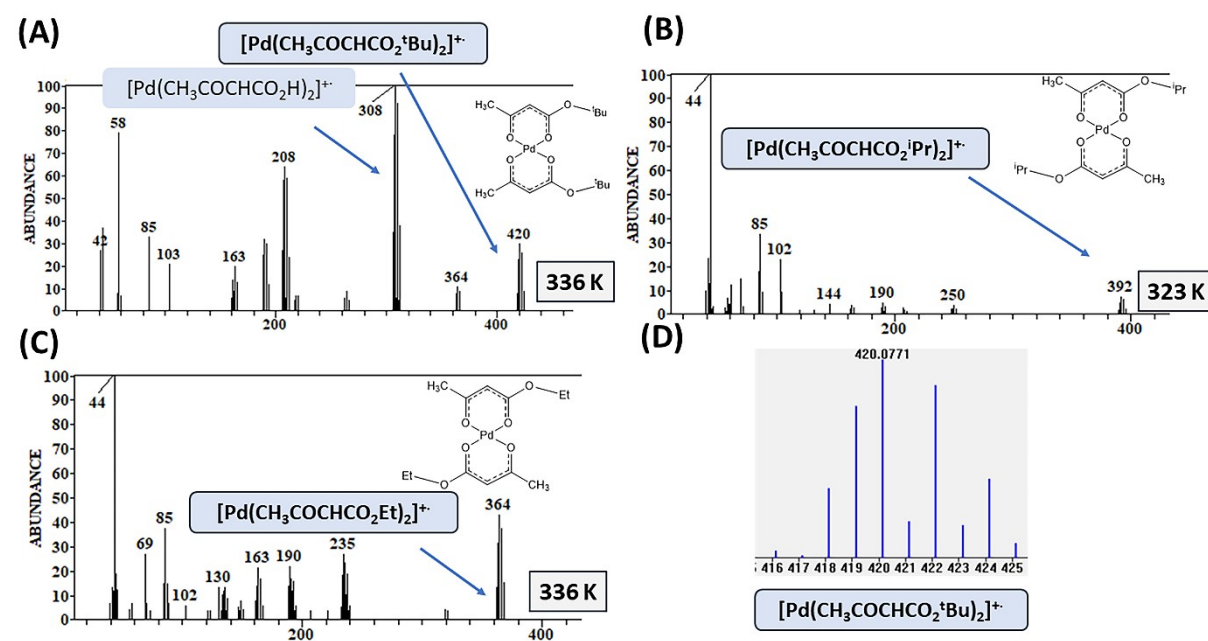
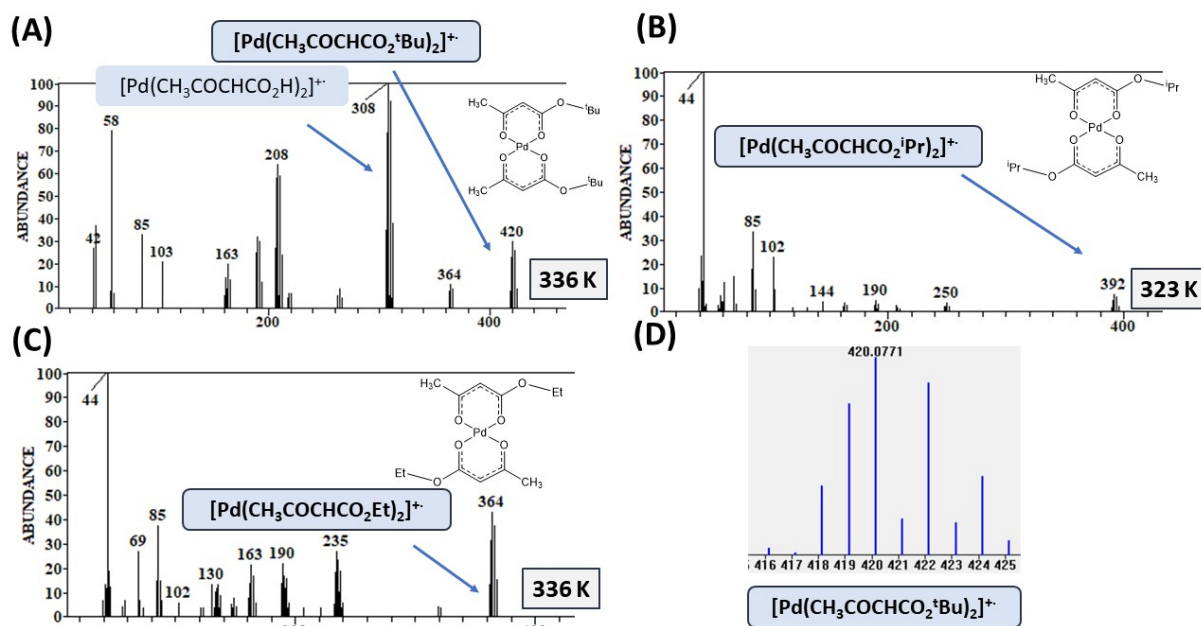


**Figure S 3432** XRD analysis of the residue after thermal analysis of  $[\text{Pd}(\text{ipaoac})_2]$  (**2**) and  $[\text{Pd}(\text{eaoac})_2]$  (**3**).

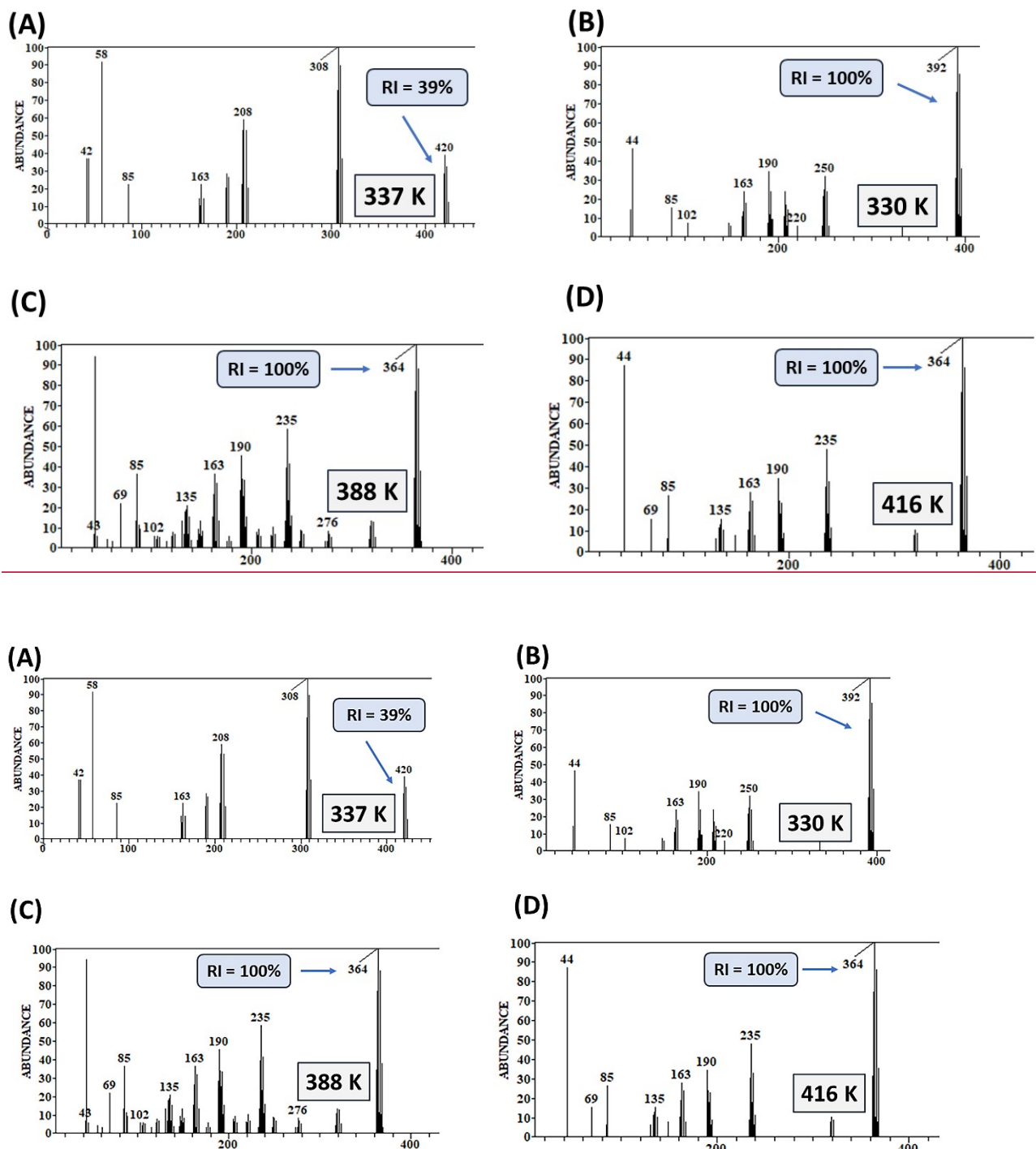


**Figure S 3533** VT IR spectra in the solid state for the compound  $[\text{Pd}(\text{tbaoac})_2]$  (1) in the temperature range 303–513 K.





**Figure S 3634** EI MS spectra, where the molecular ions appeared: (A) –  $[\text{Pd}(\text{tbaoc})_2]$  (1) at the temperature 336 K, (B) –  $[\text{Pd}(\text{ipaoac})_2]$  (2) at 323 K and (C) –  $[\text{Pd}(\text{eaoac})_2]$  (3) at 336 K, and (D) – isotopic pattern simulation for the molecular ion  $[\text{Pd}(\text{tbaoc})_2]^+$ .



**Figure S 3735** EI MS spectra, where the molecular ions achieved the highest relative intensity: (A) –  $[\text{Pd}(\text{tbaoac})_2]$  (1) at the temperature 337 K, (B) –  $[\text{Pd}(\text{ipaoac})_2]$  (2) at 330 K and (C) –  $[\text{Pd}(\text{eaoac})_2]$  (3) at 388 K, and (D) – at 416 K.



**Table S 5** EI MS results for the complex [Pd(tbaoac)<sub>2</sub>] (**1**).

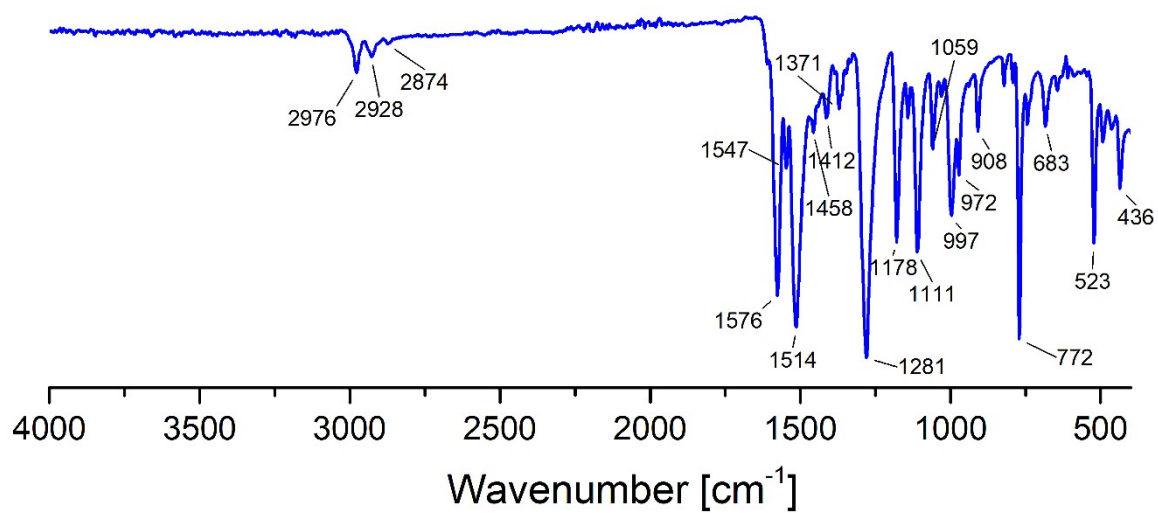
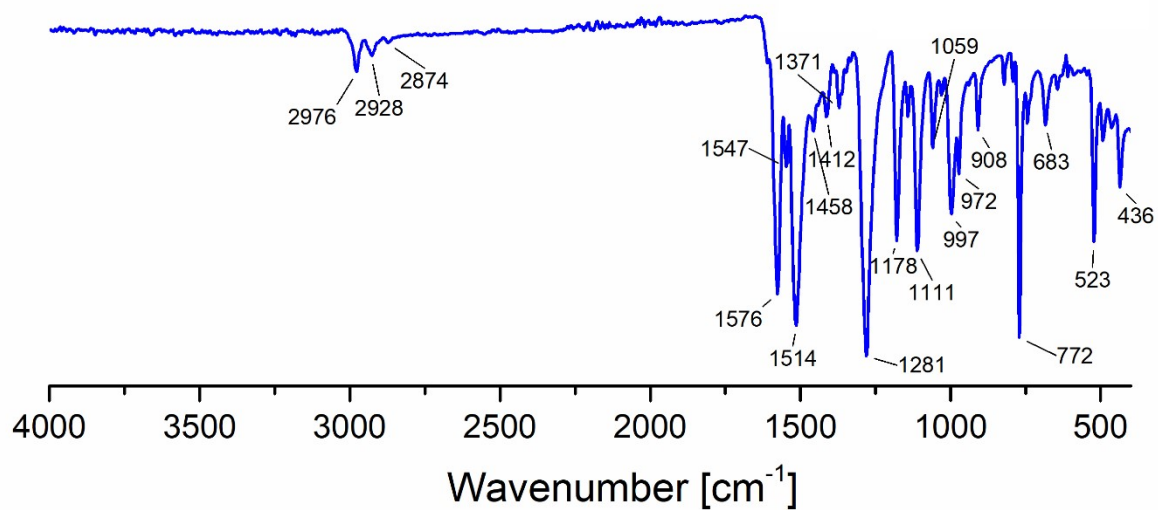
| Fragments                                                                                                                  | m/z | Relative Intensity (RI) [%] |       |       |       |
|----------------------------------------------------------------------------------------------------------------------------|-----|-----------------------------|-------|-------|-------|
|                                                                                                                            |     | 336 K                       | 342 K | 349 K | 365 K |
| [CHCO] <sup>+</sup>                                                                                                        | 41  | —                           | 2     | 1     | 1     |
| [CH <sub>2</sub> =CO] <sup>+</sup>                                                                                         | 42  | 27                          | 48    | 4     | 4     |
| [CH <sub>3</sub> CO] <sup>+</sup>                                                                                          | 43  | —                           | 6     | 14    | 11    |
| [CH <sub>3</sub> CHO] <sup>+</sup> /[CO <sub>2</sub> ] <sup>+</sup>                                                        | 44  | 37                          | 51    | 100   | 100   |
| [CO <sub>2</sub> H] <sup>+</sup>                                                                                           | 45  | —                           | 2     | 11    | 7     |
| [HCOOH] <sup>+</sup>                                                                                                       | 46  | —                           | 3     | 64    | 37    |
| [CH <sub>3</sub> COCH] <sup>+</sup> /[(CH <sub>3</sub> ) <sub>2</sub> C=CH <sub>2</sub> ] <sup>+</sup>                     | 56  | —                           | 4     | 1     | <1    |
| [CH <sub>3</sub> COCH <sub>2</sub> ] <sup>+</sup> /[ <sup>t</sup> Bu] <sup>+</sup>                                         | 57  | 8                           | 8     | 1     | 1     |
| [(CH <sub>3</sub> ) <sub>2</sub> CO] <sup>+</sup> /[C <sub>4</sub> H <sub>10</sub> ] <sup>+</sup>                          | 58  | 79                          | 100   | 1     | 1     |
| [CH <sub>3</sub> CO <sub>2</sub> H] <sup>+</sup>                                                                           | 60  | 7                           | 9     | 38    | 20    |
| [CH <sub>3</sub> COCH <sub>2</sub> C] <sup>+</sup> /[ <sup>t</sup> BuC] <sup>+</sup>                                       | 69  | —                           | 2     | —     | —     |
| [CH <sub>3</sub> COCH <sub>2</sub> CO] <sup>+</sup> /[ <sup>t</sup> BuCO] <sup>+</sup>                                     | 85  | 33                          | 23    | —     | —     |
| [CH <sub>3</sub> COCH <sub>2</sub> CO <sub>2</sub> H] <sup>+</sup> /[ <sup>t</sup> BuOCHO] <sup>+</sup>                    | 102 | —                           | 2     | —     | —     |
| [CH <sub>3</sub> COCH <sub>2</sub> C(OH) <sub>2</sub> ] <sup>+</sup> /[ <sup>t</sup> BuOCHOH] <sup>+</sup>                 | 103 | 21                          | 33    | —     | —     |
| [Pd(CH <sub>3</sub> COCH <sub>2</sub> )] <sup>+</sup>                                                                      | 163 | 20                          | 6     | —     | —     |
| [Pd(CH <sub>3</sub> COCHCO)] <sup>+</sup>                                                                                  | 190 | 32                          | 5     | —     | —     |
| [Pd(CH <sub>3</sub> COCH <sub>2</sub> CO <sub>2</sub> H)] <sup>+</sup>                                                     | 208 | 64                          | 7     | —     | —     |
| [Pd(CH <sub>3</sub> COCH <sub>2</sub> CO <sub>2</sub> <sup>t</sup> Bu)] <sup>+</sup>                                       | 264 | 9                           | 1     | —     | —     |
| [Pd(CH <sub>3</sub> COCH <sub>2</sub> CO <sub>2</sub> ) <sub>2</sub> ] <sup>+</sup>                                        | 308 | 100                         | 5     | —     | —     |
| [Pd(CH <sub>3</sub> COCHCO <sub>2</sub> <sup>t</sup> Bu)(CH <sub>3</sub> COCH <sub>2</sub> CO <sub>2</sub> )] <sup>+</sup> | 364 | 11                          | 1     | —     | —     |
| [Pd(CH <sub>3</sub> COCHCO <sub>2</sub> <sup>t</sup> Bu) <sub>2</sub> ] <sup>+</sup>                                       | 420 | 30                          | 2     | —     | —     |

**Table S 6** EI MS results for the complex [Pd(ipaoac)<sub>2</sub>] (**2**).

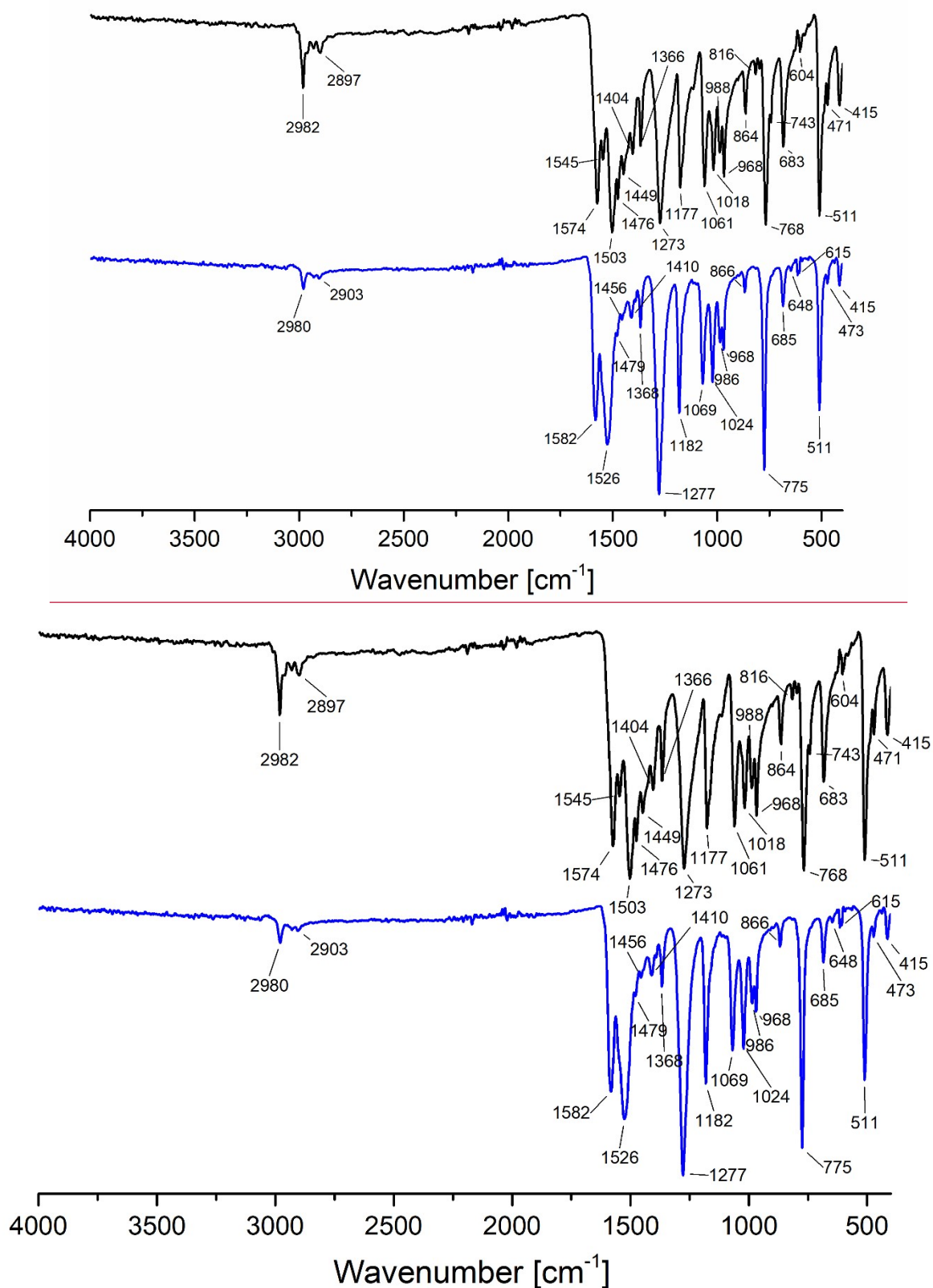
| Fragments                                                                                      | m/z | Relative Intensity (RI) [%] |       |       |       |
|------------------------------------------------------------------------------------------------|-----|-----------------------------|-------|-------|-------|
|                                                                                                |     | 323 K                       | 328 K | 332 K | 349 K |
| [CHCO] <sup>+</sup>                                                                            | 41  | —                           | —     | —     | —     |
| [CH <sub>2</sub> =CO] <sup>+</sup>                                                             | 42  | 23                          | 18    | 22    | 30    |
| [CH <sub>3</sub> CO] <sup>+</sup>                                                              | 43  | 12                          | 9     | 17    | 9     |
| [CH <sub>3</sub> CHO] <sup>+</sup> /[CO <sub>2</sub> ] <sup>+</sup>                            | 44  | 100                         | 100   | 100   | 100   |
| [CO <sub>2</sub> H] <sup>+</sup>                                                               | 45  | 2                           | 2     | —     | 12    |
| [HCOOH] <sup>+</sup>                                                                           | 46  | 3                           | 3     | —     | 32    |
| [CH <sub>3</sub> COCH] <sup>+</sup>                                                            | 56  | 3                           | 2     | —     | —     |
| [CH <sub>3</sub> COCH <sub>2</sub> ] <sup>+</sup>                                              | 57  | 2                           | 2     | —     | —     |
| [(CH <sub>3</sub> ) <sub>2</sub> CO] <sup>+</sup>                                              | 58  | 7                           | 5     | —     | 9     |
| [CH <sub>3</sub> CO <sub>2</sub> H] <sup>+</sup>                                               | 60  | 4                           | 22    | —     | 9     |
| [CH <sub>3</sub> COCH <sub>2</sub> C] <sup>+</sup>                                             | 69  | 15                          | 12    | —     | 45    |
| [CH <sub>3</sub> COCH <sub>2</sub> CO] <sup>+</sup>                                            | 85  | 33                          | 82    | 24    | 19    |
| [ <sup>i</sup> PrCO <sub>2</sub> ] <sup>+</sup>                                                | 87  | 9                           | 23    | —     | —     |
| [CH <sub>3</sub> COCH <sub>2</sub> CO <sub>2</sub> H] <sup>+</sup>                             | 102 | 23                          | 75    | —     | 15    |
| [CH <sub>3</sub> COCH <sub>2</sub> C(OH) <sub>2</sub> ] <sup>+</sup>                           | 103 | 9                           | 37    | —     | —     |
| [CH <sub>3</sub> COCH <sub>2</sub> CO <sub>2</sub> <sup>i</sup> Pr] <sup>+</sup>               | 144 | 4                           | 22    | —     | —     |
| [Pd(CH <sub>3</sub> COCH <sub>2</sub> )] <sup>+</sup>                                          | 163 | 4                           | 29    | —     | —     |
| [Pd(CH <sub>3</sub> COCHCO)] <sup>+</sup>                                                      | 190 | 2                           | 43    | —     | —     |
| [Pd(CH <sub>3</sub> COCH <sub>2</sub> CO <sub>2</sub> <sup>i</sup> Pr)] <sup>+</sup>           | 250 | 4                           | 35    | —     | —     |
| [Pd(CH <sub>3</sub> COCHCO <sub>2</sub> <sup>i</sup> Pr)(CH <sub>3</sub> COCHCO)] <sup>+</sup> | 333 | —                           | 5     | —     | —     |
| [Pd(CH <sub>3</sub> COCHCO <sub>2</sub> <sup>i</sup> Pr) <sub>2</sub> ] <sup>+</sup>           | 392 | 7                           | 49    | 98    | —     |

**Table S 7** EI MS results for the complex [Pd(eaoac)<sub>2</sub>] (**3**).

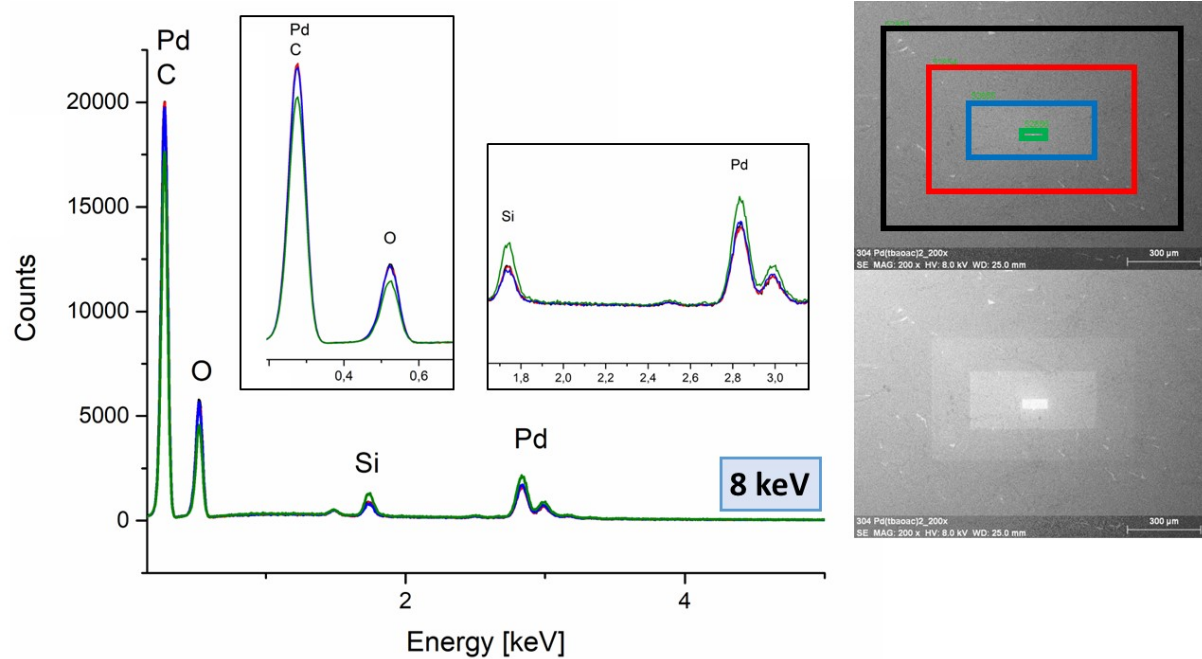
| Fragments                                                                                                | m/z | Relative Intensity (RI) [%] |       |       |       |       |
|----------------------------------------------------------------------------------------------------------|-----|-----------------------------|-------|-------|-------|-------|
|                                                                                                          |     | 336 K                       | 339 K | 375 K | 419 K | 422 K |
| [CHCO] <sup>+</sup>                                                                                      | 41  | —                           | 4     | —     | —     | —     |
| [CH <sub>2</sub> CO] <sup>+</sup>                                                                        | 42  | 13                          | 24    | —     | 3     | —     |
| [CH <sub>3</sub> CO] <sup>+</sup>                                                                        | 43  | 12                          | 13    | 12    | 16    | 14    |
| [CH <sub>3</sub> CHO] <sup>+</sup> /[CO <sub>2</sub> ] <sup>+</sup>                                      | 44  | 100                         | 100   | 100   | 100   | 100   |
| [CO <sub>2</sub> H] <sup>+</sup>                                                                         | 45  | 19                          | 64    | —     | 4     | 6     |
| [HCOOH] <sup>+</sup>                                                                                     | 46  | 12                          | 16    | 6     | 6     | 5     |
| [CH <sub>3</sub> COCH] <sup>+</sup>                                                                      | 56  | 4                           | 8     | 5     | 4     | —     |
| [CH <sub>3</sub> COCH <sub>2</sub> ] <sup>+</sup>                                                        | 57  | —                           | —     | —     | 4     | —     |
| [(CH <sub>3</sub> ) <sub>2</sub> CO] <sup>+</sup>                                                        | 58  | 7                           | 9     | —     | —     | —     |
| [CH <sub>3</sub> CO <sub>2</sub> H] <sup>+</sup>                                                         | 60  | —                           | 8     | —     | 7     | 8     |
| [CH <sub>3</sub> COCH <sub>2</sub> C] <sup>+</sup>                                                       | 69  | 27                          | 25    | 27    | 22    | 18    |
| [CH <sub>3</sub> COCH <sub>2</sub> CO] <sup>+</sup>                                                      | 85  | 37                          | 34    | 36    | 32    | 24    |
| [CH <sub>3</sub> COCH <sub>2</sub> CO <sub>2</sub> H] <sup>+</sup> /[OCHCO <sub>2</sub> Et] <sup>+</sup> | 102 | 6                           | 6     | 5     | 6     | —     |
| [CH <sub>3</sub> COCH <sub>2</sub> CO <sub>2</sub> Et] <sup>+</sup>                                      | 130 | 13                          | 14    | 12    | 13    | 9     |
| [Pd(CH <sub>3</sub> COCH <sub>2</sub> )] <sup>+</sup>                                                    | 163 | 21                          | 19    | 29    | 20    | —     |
| [Pd(CH <sub>3</sub> COCHCO)] <sup>+</sup>                                                                | 190 | 22                          | 22    | 32    | 23    | —     |
| [Pd(CH <sub>3</sub> COCHCOOEt)] <sup>+</sup>                                                             | 235 | 27                          | 29    | 40    | 30    | —     |
| [Pd(CH <sub>3</sub> COCHCO <sub>2</sub> Et)(CH <sub>3</sub> COCHCO)] <sup>+</sup>                        | 319 | 4                           | 5     | 7     | 7     | —     |
| [Pd(CH <sub>3</sub> COCHCO <sub>2</sub> Et) <sub>2</sub> ] <sup>+</sup>                                  | 364 | 43                          | 58    | 66    | 57    | —     |



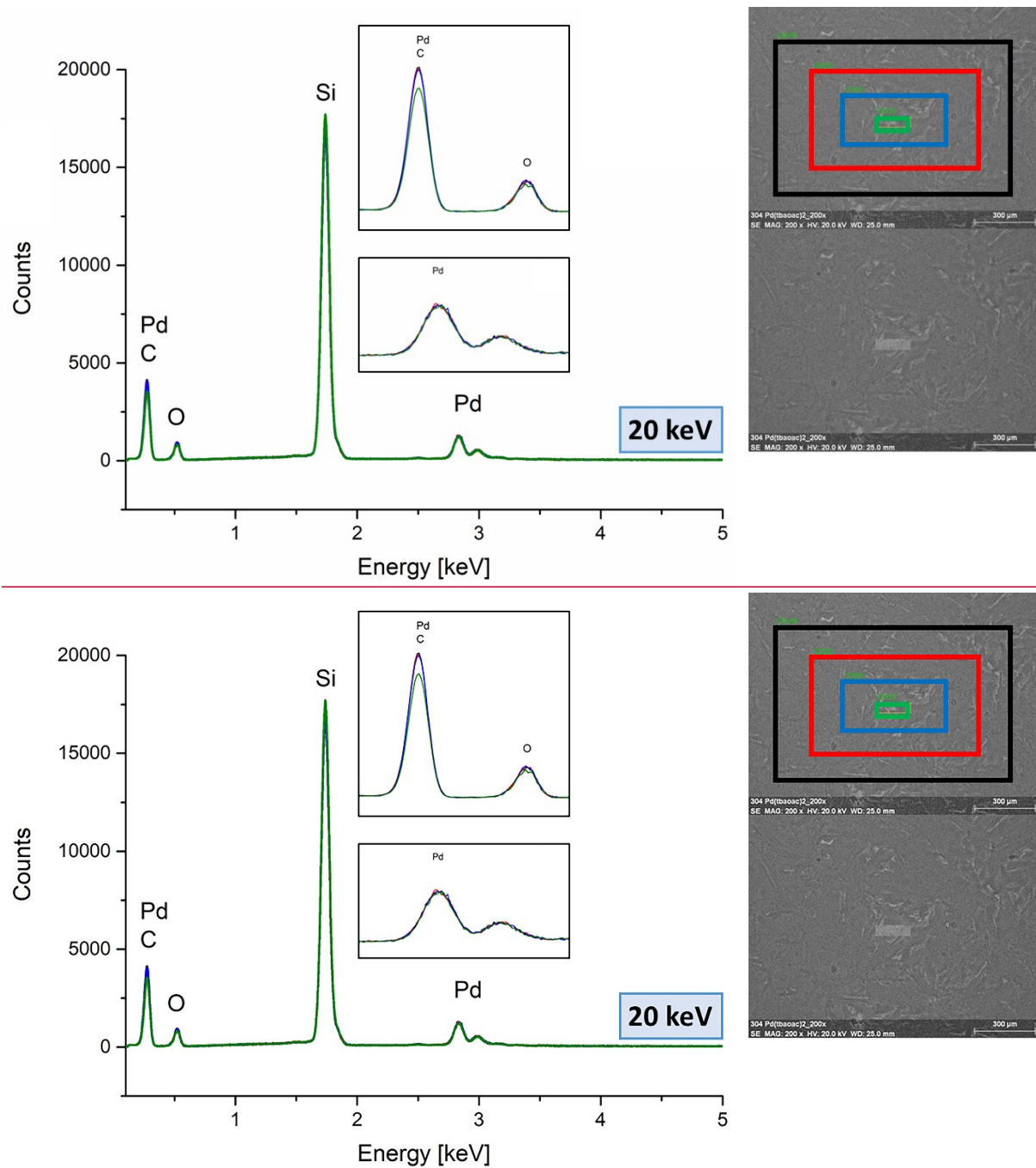
**Figure S 3836** Infrared spectrum for the compound [Pd(ipaoac)<sub>2</sub>] (**2**) after sublimation (blue) at 353 K ( $p = 10^{-2}$  mbar).



**Figure S 3937** Infrared spectra for the compound  $[\text{Pd}(\text{eaoac})_2]$  (**3**) before (black) and after sublimation (blue) at 353 K ( $p = 10^{-2}$  mbar).

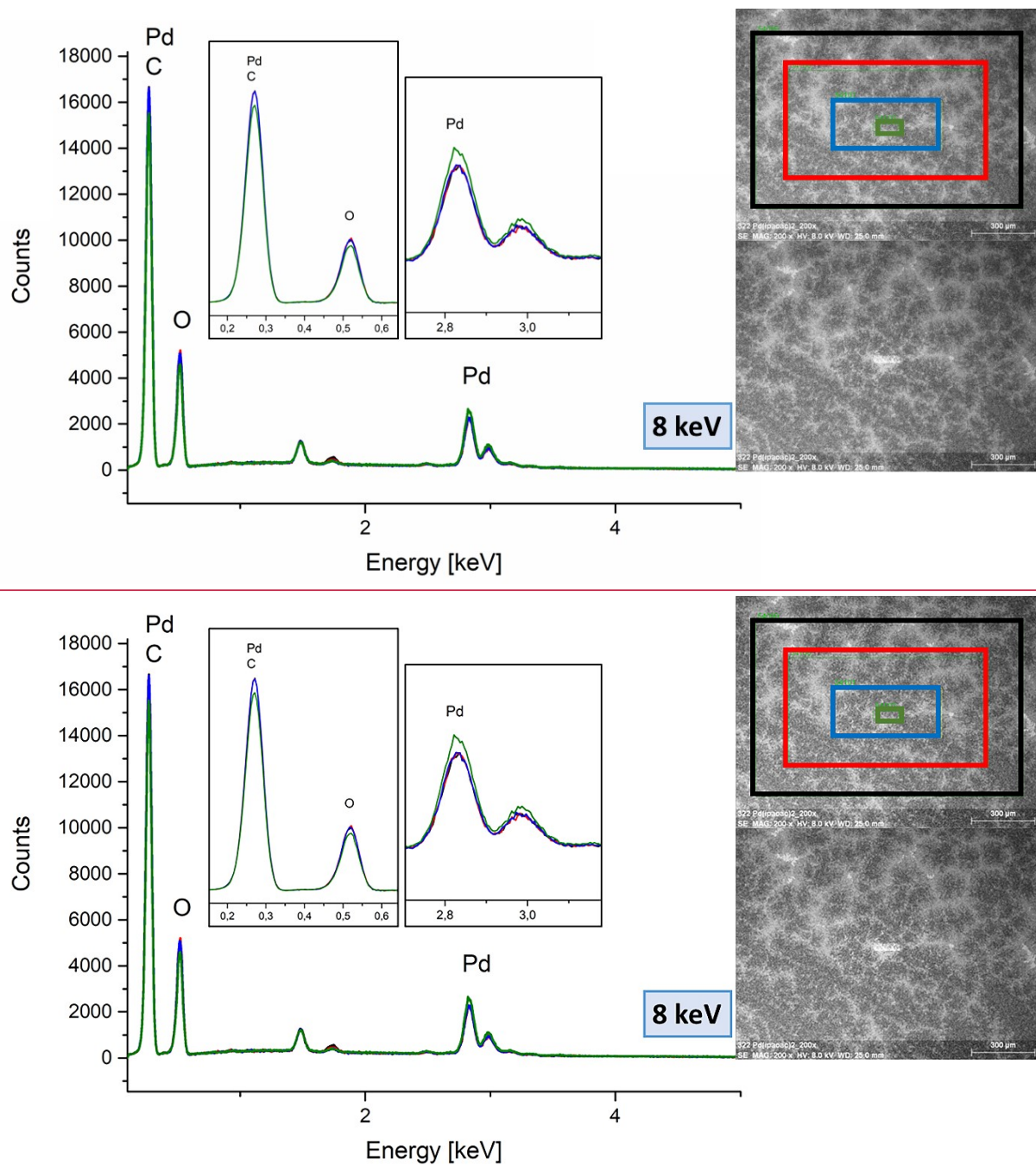


**Figure S 38** Examined scan areas' EDX spectra (8 keV) for the  $[\text{Pd}(\text{tbaoac})_2]$  (1) layer deposited on a Si(111) substrate (Mag = 200x).

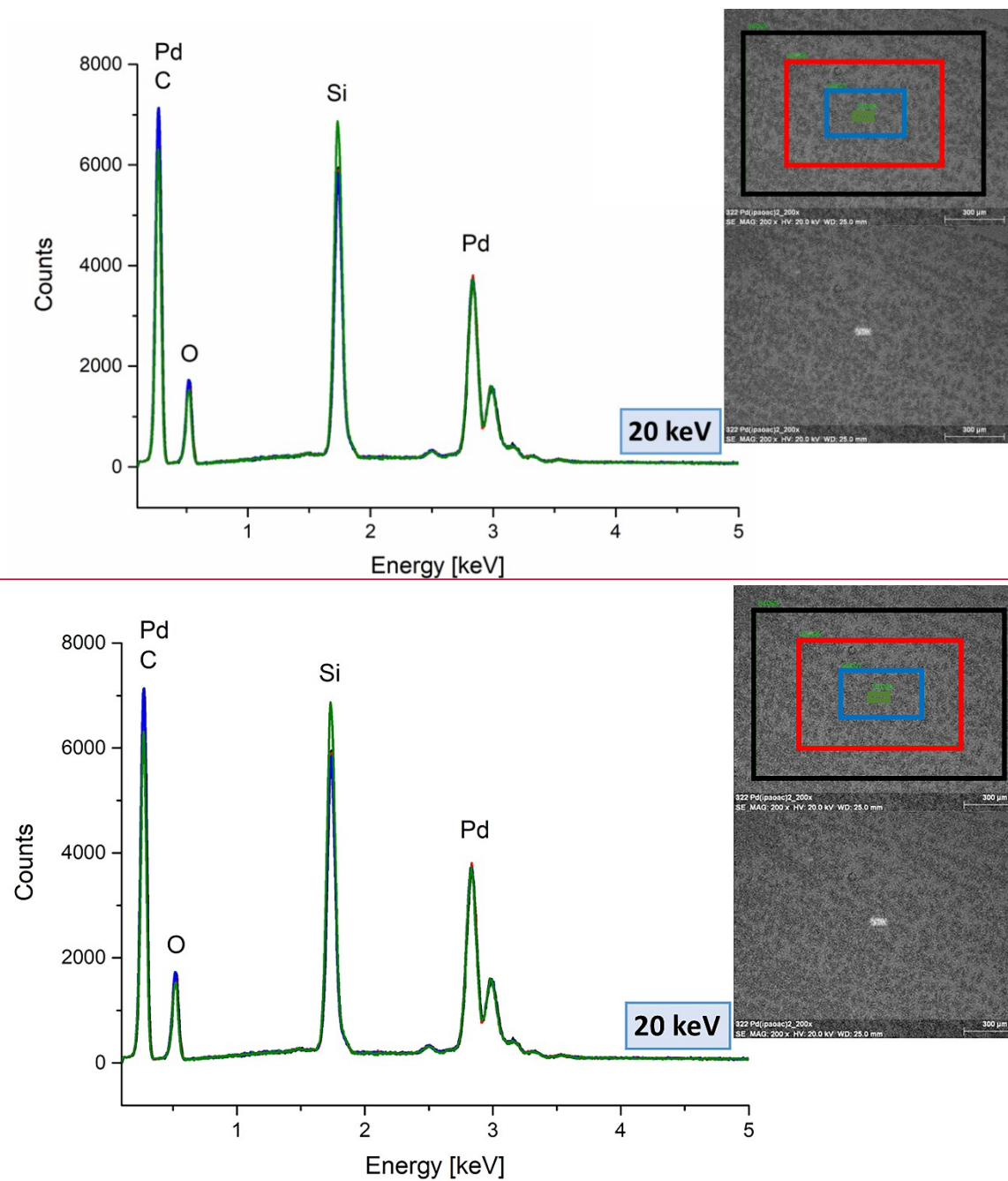


**Figure S 4039** Examined scan areas' EDX spectra (20 keV) for the [Pd(tbaoac)<sub>2</sub>] (1) layer deposited on a Si(111) substrate (Mag = 200x).

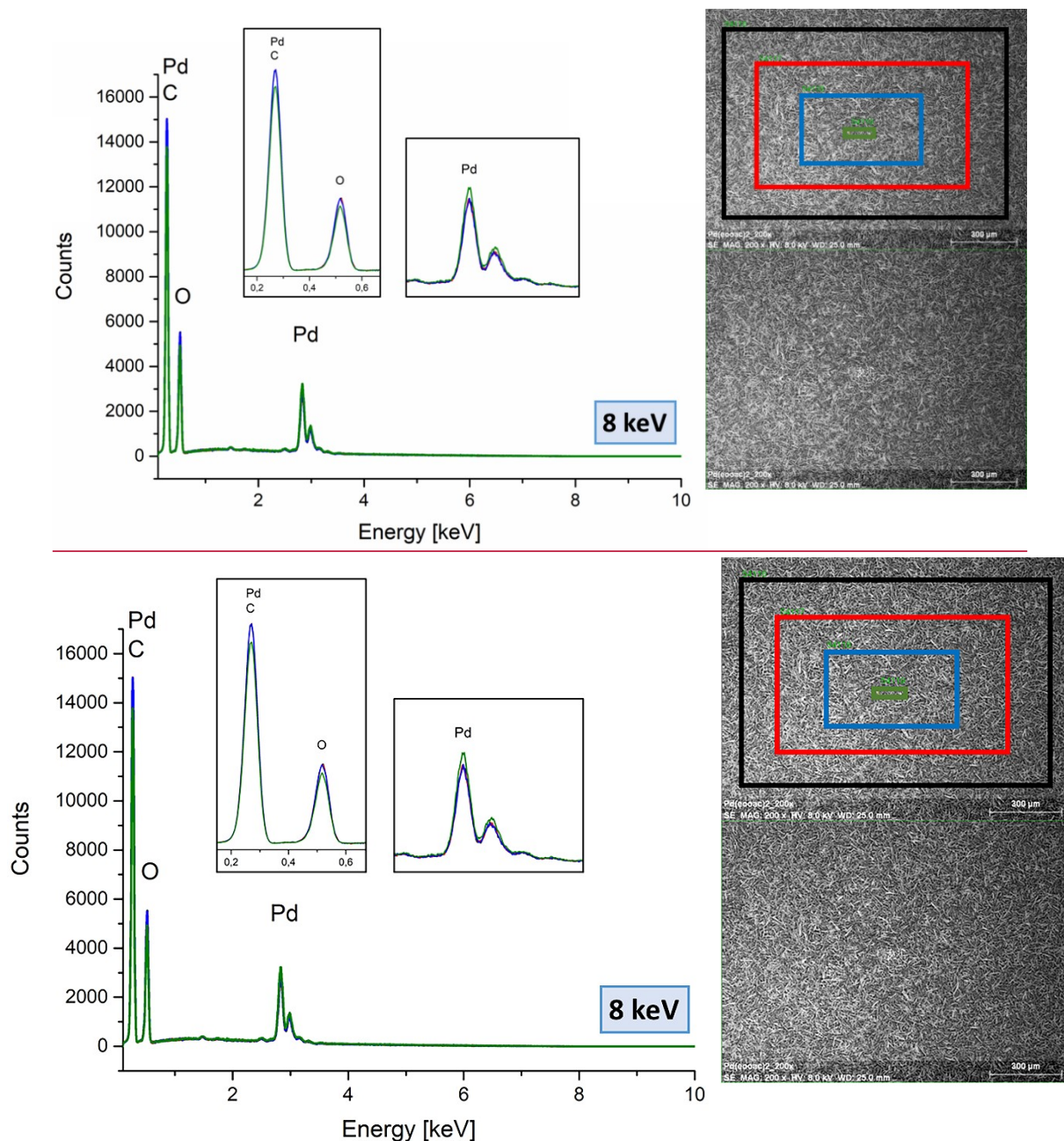




**Figure S 4140** Examined scan areas' EDX spectra (8 keV) for the  $[\text{Pd}(\text{ipaoac})_2]$  (**2**) layer deposited on a Si(111) substrate (Mag = 200x).

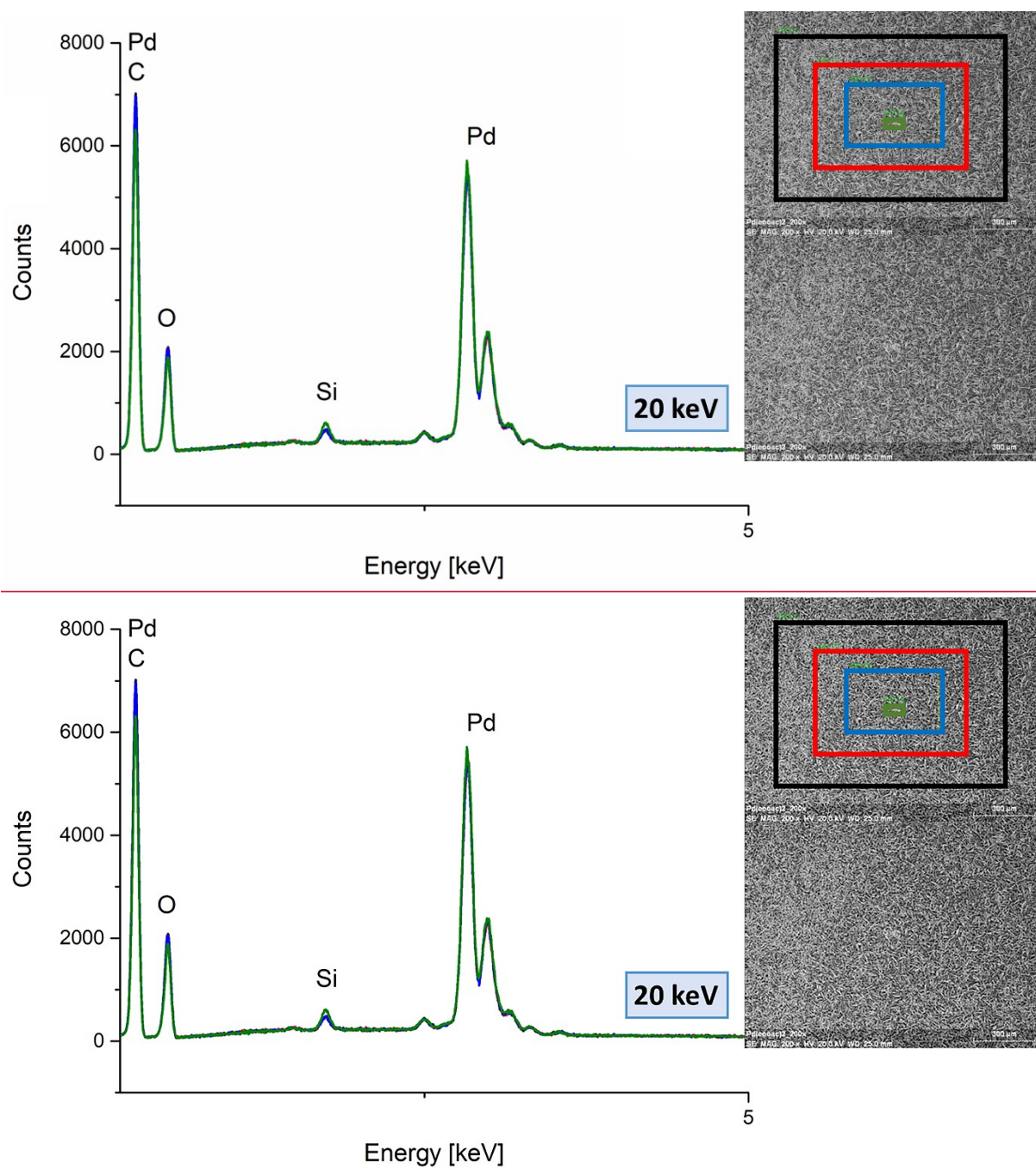


**Figure S 4241** Examined scan areas' EDX spectra (20 keV) for the  $[\text{Pd}(\text{ipaoac})_2]$  (2) layer deposited on a Si(111) substrate (Mag = 200x).



**Figure S 4342** Examined scan areas' EDX spectra (8 keV) for the [Pd(eaoac)<sub>2</sub>] (3) layer deposited on a Si(111) substrate (Mag = 200x).





**Figure S 4443** Examined scan areas' EDX spectra (20 keV) for the [Pd(eaoac)<sub>2</sub>] (3) layer deposited on a Si(111) substrate (Mag = 200x).