Supplementary Information (SI) for Dalton Transactions.
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Electronic Supporting Information

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1. Materials and methods

Unless otherwise noted, all chemicals and starting materials were acquired from Acros, Aldrich and Merck and used without further purification. Solvents were dried using standard procedures. Chloroform (analytical grade) was purchased from Merck and was distilled over CaH_2. Analytical thin-layer chromatography (TLC) was carried out using Merck silica gel 60 plates (precoated sheets, 0.2 mm thick, with the fluorescence indicator F254). Column chromatography purifications were carried out on silica gel (MN Kieselgel 60, 63–200 μm, Macherey-Nagel or Silica 60, 63–200 μm, Aldrich; silica gel for flash chromatography, 40-63 μm, VWR). ^{1}H, ^{13}C, ^{31}P and 2D NMR spectra were acquired on Bruker Avance III (600 MHz), Bruker Avance II (300 MHz) and Bruker Avance III (300 MHz) spectrometers. Chemical shifts are expressed in parts per million (ppm), referenced on the δ scale by using the signals of residual protons of deuterated solvents as an internal reference for ^{1}H and ^{13}C NMR spectroscopies and 80% H_3PO_4 as an external reference for ^{31}P NMR spectroscopy. The coupling constants (J) are expressed in hertz (Hz). Variable-temperature ^{1}H NMR spectra of solutions in D_2O, MeOD, and MeOD/D_2O mixtures were recorded in the range 303--363 K on Bruker Avance III(600 MHz) and Bruker Avance II (300 MHz) spectrometers.

MALDI-TOF mass-spectra were obtained on a Bruker Ultraflex II LRF 2000 mass-spectrometer in positive ion mode with a dithranol matrix. Accurate mass measurements (HRMS) were recorded on a Thermo LTQ Orbitrap XL and a MicrOTOFQ II (Bruker) apparatuses equipped with electrospray ionization (ESI) source. Solutions in $CHCl_3$/methanol (1 : 1) were used for the analysis. The reported m/z values correspond to the most intense peak of the isotopic pattern that were simulated with the Xcalibur software (Thermo). FT-IR spectra were collected at 4 cm^{-1} resolution on either a FT-IR Nexus (Nicolet), a Vertex 70v (Bruker) and FT-IR Perkin Elmer Spectrum 65 spectrophotometers using ATR accessories. The measurements were performed at the Shared Facility Centers of the Frumkin Institute of Physical Chemistry and Electrochemistry, RAS, Kurnakov Institute of General and Inorganic chemistry, RAS, and at the “Plateforme d’Analyses Chimiques et de Synthèse Moléculaire de l’Université de Bourgogne – Pôle Chimie Moléculaire”, the technological platform for chemical analysis and molecular synthesis (http:// www.wpcm.fr).

2. Synthesis of porphyrins

Free-base porphyrins – namely 5,15-bis(diethoxyphosphoryl)-10,20-bis(*p*-tolyl)porphyrin[1] (**$H_2$4d**), 5,15-bis(*p*-carboxyphenyl)-10,20-bis(diethoxyphos-phoryl)porphyrin[2] (**$H_2$6d**) were prepared by published procedures.

Metalloporphyrins – namely [5,15-dibromo-5,15-dimesitylporphyrinato(2–)]zinc,[3] {10-(diethoxyphosphoryl)-5,15-bis[*p*-(methoxycarbonyl)phenyl]porphyrinato(2–)}platinum(II)[4] (**Pt6m**), and {10-(diethoxyphosphoryl)-5,15-bis[*p*-(methoxycarbonyl)phenyl]porphyrinato(2–)}palladium(II) [**Pd6m**][4] were prepared according to the published procedures.

[5,15-Bis(diethoxyphosphoryl)-10,20-dimesitylporphyrinato(2–)]zinc (**Zn5d**). A 50 mL round bottom flask equipped with a reflux condenser and a magnetic bar was charged with [5,15-dibromo-5,15-dimesitylporphyrinato(2–)]zinc (383 mg, 0.50 mmol), $Pd(OAc)_2$ (28 mg, 0.125 mmol) and PPh_3 (98 mg, 0.37 mmol). The reaction vessel was evacuated and purged with N_2 three times. Subsequently, abs. ethanol (15 mL), diethyl phosphite (3.21 mL, 24.9 mmol) and triethylamine (1.05 mL, 0.75 mmol) were added via syringe. The reaction mixture was stirred at reflux until complete conversion of the bromide according to MALDI-TOF (20 h). After cooling, the reaction mixture was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using pentane/ethyl acetate as eluent. The red-purple fraction was collected and evaporated under reduced pressure to give **Zn5d** in 14% yield (65 mg, 93% purity) contaminated with $HPO(OEt)_2$. This mixture was used in the next step without additional purification. Porphyrin **Zn5m**[4] was also isolate in this reaction (226 mg, 61%). ^{1}H NMR (300 MHz, $CDCl_3/CD_3OD$, 2:1 v/v, 25 °C): δ_H 1.38 (t, $^3J_{H,H}$ = 7.1 Hz, 12H, $OCH_2C\underline{H}_3$), 1.79 (s, 12H, Me), 2.63 (s, 6H, Me), 4.19–4.30 (m, 4H, $OC\underline{H}_2CH_3$), 4.45–4.53 (m, 4H, $OC\underline{H}_2CH_3$), 7.28 (s, 4H, *m*-Ph), 8.71 (d, $^3J_{H,H}$ = 5.2 Hz, 4H, Hβ), 10.15 (d, $^3J_{H,H}$ = 5.2 Hz, 4H, Hβ) ppm. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3/CD_3OD$, 2:1 v/v, 25 °C): δ_P 25.04 ppm.

[5,15-Bis(diethoxyphosphoryl)-10,20-dimesitylporphyrinato(2–)]platinum(II) (**$H_2$5d**).
Concentrated hydrochloric acid (2 mL) was added to a solution of **Zn5d** (65 mg, 93% purity; 68 mmol) in $CHCl_3$ (150 mL), and the reaction mixture was stirred at room temperature for 1 h. After washing with aqueous $NaHCO_3$ (2 x 70 mL) and water (50 mL), the reaction mixture was dried over Na_2SO_4, and evaporated under reduced pressure. The residue was chromatographed on silica using the mixture of CH_2Cl_2/CH_3OH (100:0.5) as eluent. The reddish-purple fraction was collected and evaporated under reduced pressure to afford pure **$H_2$5d** (54 mg, 97%). ^{1}H NMR (300 MHz, $CDCl_3/CD_3OD$, 2:1 v/v, 25 °C): δ_H –2.61 (br s, 2H, NH), 1.36 (t, $^3J_{H,H}$ = 7.1 Hz, 12H, $OCH_2C\underline{H}_3$),

1.83 (s, 12H, Me), 2.68 (s, 6H, Me), 4.18–4.29 (m, 4H, OC$\underline{H}_2$CH$_3$), 4.47–4.58 (m, 4H, OC$\underline{H}_2$CH$_3$), 7.33 (s, 4H, *m*-Ph), 8.77 (d, $^3J_{H,H}$ = 5.2 Hz, 4H, Hβ), 10.28 (d, $^3J_{H,H}$ = 5.2 Hz, 4H, Hβ) ppm. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$/CD_3OD, 2:1 v/v, 25 °C): δ_P 21.29 ppm. HRMS (ESI): *m/z* = 819.34136 ([M+H]$^+$, calcd. for $C_{46}H_{53}N_4O_{10}P_2$ *m/z* = 819.34348).

General procedure for preparation of palladium(II) complexes. A 3.9 mM solution of the corresponding free-base porphyrin (**$H_2$4d–$H_2$6d**) in a $CHCl_3$/CH_3CN (4:1, v/v) mixture was stirred and heated. During refluxing $Pd(OAc)_2$ (4–10 equiv) was added into the flask. The reaction mixture was further stirred for 15 minutes. The degree of conversion was monitored by MALDI-TOF mass-spectrometry and UV–vis spectroscopy. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel to afford **Pd4d–Pd6d**.

[**5,15-Bis(diethoxyphosphoryl)-10,20-bis(*p*-tolyl)porphyrinato(2–)]palladium(II) (Pd4d)**. Following the aforementioned general procedure, 40 mg (0.052 mmol) of the free-base porphyrin **$H_2$4d** was treated with 100 mg (0.446 mmol) of $Pd(OAc)_2$. The resulting solid was chromatographed using a CH_2Cl_2/MeOH (96:4 v/v) as eluent to give **Pd4d** as a pink purple crystalline powder in 97% yield (41 mg).^{1}H NMR (300 MHz, $CDCl_3$/CD_3OD, 2:1 v/v, 25 °C): δ_H 1.40 (t, $^3J_{H,H}$ = 7.1 Hz, 12H, OCH$_2$C$\underline{H}_3$), 2.74 (s, 6H, Me), 4.20–4.33 (m, 4H, OC$\underline{H}_2$CH$_3$), 4.48–4.61 (m, 4H, OC$\underline{H}_2$CH$_3$), 7.59 (d, $^3J_{H,H}$ = 8.2 Hz, 4H, *o*-Ph), 8.04 (d, $^3J_{H,H}$ = 8.2 Hz, 4H, *m*-Ph), 8.95 (d, $^3J_{H,H}$ = 5.2 Hz, 4H, Hβ), 10.33 (d, $^3J_{H,H}$ = 5.2 Hz, 4H, Hβ) ppm. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$/CD_3OD, 2:1 v/v, 25 °C): δ_P 21.15 ppm. ^{1}H NMR (75 MHz, $CDCl_3$/CD_3OD, 2:1 v/v, 25 °C): δ_C 16.50 (d, $^3J_{C,P}$ = 7.5 Hz, 2C, CH_3), 21.55 (2C, (Ph)CH_3), 62.93 (d, $^2J_{C,P}$ = 5 Hz, 2C, CH_2), 105.24 (d, $^1J_{C,P}$ = 185.3 Hz, 2C, *meso*-C(P)), 122.90 (2C, *meso*-C(Ph)), 127.67 (4C, CH(Ph)), 132.59 (4C, β-CH), 133.43 (4C, β-CH), 133.94 (4C, CH(Ph)), 137.90 (2C, C(Ph)), 138.16 (2C, C(Ph)), 142.11 (2C, α-C), 143.18 (d, $^2J_{C,P}$ = 16.7 Hz, 2C, α-C).

[5,15-Bis(diethoxyphosphoryl)-10,20-dimesitylporphyrinato(2–)]palladium(II) (Pd5d). Following the aforementioned general procedure, 30 mg (0.037 mmol) of the free-base porphyrin $H_2$4d was treated with 66 mg (0.293 mmol) of $Pd(OAc)_2$. The resulting solid was chromatographed using a CH_2Cl_2/MeOH (97:3 v/v) as eluent to give Pd5d as a pink purple crystalline powder in 98% yield (33 mg).^{1}H NMR (300 MHz, $CDCl_3$/CD_3OD, 2:1 v/v, 25 °C): δ_H 1.38 (t, $^3J_{H,H}$ = 7.1 Hz, 12H, OCH$_2$C$\underline{H}_3$), 1.64 (s, 12H, Me), 2.66 (s, 6H, Me), 4.23–4.36 (m, 4H, OC$\underline{H}_2$CH$_3$), 4.51–4.61 (m, 4H, OC$\underline{H}_2$CH$_3$), 7.31 (s, 4H, *m*-Ph), 8.74 (d, $^3J_{H,H}$ = 5.2 Hz, 4H, Hβ), 10.28 (d, $^3J_{H,H}$ = 5.2 Hz, 4H, Hβ) ppm. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$/CD_3OD, 2:1 v/v, 25 °C): δ_P 21.25 ppm.

{5,15-Bis(diethoxyphosphoryl)-10,20-bis[(*p*-(methoxycarbonyl)phenyl]porphyrinato(2–)}palladium(II) (Pd6d). Following the aforementioned general procedure, 20 mg (0.024 mmol) of

the free-base porphyrin **$H_2$6d** was treated with 21 mg (0.094 mmol) of $Pd(OAc)_2$. The resulting solid was chromatographed using a $CHCl_3$/*n*-hexane (3:2, v/v) as eluent to give **Pd6d** as a pink purple crystalline powder in 98% yield (22 mg). ^{1}H NMR (600 MHz, $CDCl_3/CD_3OD$, 2:1 v/v, 25 °C): δ_H 1.33 (t, $^3J_{H,H}$ = 7.1 Hz, 12H, $OCH_2C\underline{H}_3$), 4.10 (s, 6H, $PhCOOC\underline{H}_3$), 4.14–4.28 (m, 4H, $OC\underline{H}_2CH_3$), 4.38–4.52 (m, 4H, $OC\underline{H}_2CH_3$), 8.19 (d, $^3J_{H,H}$ = 8.2 Hz, 4H, *o*-Ph), 8.42 (d, $^3J_{H,H}$ = 8.2 Hz, 4H, *m*-Ph), 8.79 (d, $^3J_{H,H}$ = 5.2 Hz, 4H, Hβ), 10.22 (d, $^3J_{H,H}$ = 5.2 Hz, 4H, Hβ) ppm. ^{31}P{^{1}H} NMR (242 MHz, $CDCl_3/CD_3OD$, 2:1 v/v, 25 °C): δ_P 20.95 ppm. HRMS (ESI): *m/z* = 955.15076 ($[M+H]^+$, calcd. for $C_{44}H_{43}N_4O_{10}P_2Pd$ *m/z* = 955.14838). UV–vis [$CHCl_3$; λ_{max}, nm (log ε)]: 414 (5.25), 536 (3.94), 578 (4.39). IR (neat, cm^{-1}): ν_{max} 2983 (w), 2923 (w), 2852 (w), 1719 (s, C=O), 1607 (w), 1544 (w), 1433 (m), 1400 (w), 1390 (w), 1347 (w), 1274 (m), 1249 (m), 1206 (w), 1179 (w), 1163 (w), 1095 (m), 1079 (m), 1039 (m), 1001 (s), 926 (s), 892 (s), 862 (s), 797 (s), 764 (m), 736 (m), 707 (m).

General procedure for preparation of platinum(II) complexes. A 5.8 mM solution of the corresponding free-base porphyrin (**$H_2$4d**–**$H_2$6d**) in and $PtCl_2$ (3–13 equiv) were refluxed in benzonitrile for 4h. During the heating, the color of the reaction mixture became orange brown. The degree of conversion was monitored by MALDI-TOF mass-spectrometry and UV–vis spectroscopy. After cooling to room temperature, the reaction mixture was precipitated by *n*-hexane. The resulting solid was filtrated using a glass filter, washed with *n*-hexane (2 × 10 mL) and collected by dissolving it in chloroform. After evaporating the solvent, the residue was purified by column chromatography on silica gel to afford **Pt4d**–**Pt6d**.

[**5,15-Bis(diethoxyphosphoryl)-10,20-bis(*p*-tolyl)porphyrinato(2–)]platinum(II) (Pt4d)**.
Following the aforementioned general procedure, 98 mg (0.128 mmol) of the free-base porphyrin **$H_2$4d** was treated with 248 mg (0.932 mmol) of $PtCl_2$. After 5 h of reflux, the residue obtained as described above was purified by column chromatography on silica gel using CH_2Cl_2/MeOH (96:4 v/v) as eluent to give **Pt4d** as a red orange crystalline powder (31 mg, 25%). ^{1}H NMR (300 MHz, $CDCl_3/CD_3OD$, 2:1 v/v, 25 °C): δ_H 1.37 (t, $^3J_{H,H}$ = 7.1 Hz, 12H, $OCH_2C\underline{H}_3$), 2.74 (s, 6H, Me), 4.15–4.29 (m, 4H, $OC\underline{H}_2CH_3$), 4.44–4.57 (m, 4H, $OC\underline{H}_2CH_3$), 7.58 (d, $^3J_{H,H}$ = 8.2 Hz, 4H, *o*-Ph), 8.01 (d, $^3J_{H,H}$ = 8.2 Hz, 4H, *m*-Ph), 8.90 (d, $^3J_{H,H}$ = 5.2 Hz, 4H, Hβ), 10.32 (d, $^3J_{H,H}$ = 5.2 Hz, 4H, Hβ) ppm. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3/CD_3OD$, 2:1 v/v, 25 °C): δ_P 21.11 ppm. ^{1}H NMR (75 MHz, $CDCl_3/CD_3OD$, 2:1 v/v, 25 °C): δ_C 16.45 (d, $^3J_{C,P}$ = 7.5 Hz, 2C, CH_3), 21.54 (2C, $(Ph)CH_3$), 62.88 (d, $^2J_{C,P}$ = 5 Hz, 2C, CH_2), 105.05 (m, 2C, *meso*-C(P)), 122.85 (d, $^3J_{C,Pt}$ = 32 Hz, 2C, 2C, *meso*-C(Ph)), 127.63 (d, $^6J_{C,Pt}$ = 5.3 Hz, 4C, CH(Ph)), 132.40 (d, $^3J_{C,Pt}$ = 25.5 Hz, 4C, β-CH), 133.30 (d, $^3J_{C,Pt}$ = 14.5 Hz, 4C, β-CH), 133.94 (d, $^5J_{C,Pt}$ = 16.2 Hz, 4C, CH(Ph)), 137.94 (d, $^4J_{C,Pt}$ = 24.5 Hz

2C, C(Ph)), 137.96 (d, $^{7}J_{C,Pt}$ = 4 Hz 2C, C(Ph)), 141.88 (d, $^{3}J_{C,Pt}$ = 30.0 Hz 2C, α-C), 142.48 (dd, $^{3}J_{C,Pt}$ = 78.7 Hz, $^{2}J_{C,P}$ = 17.2 Hz, 2C, α-C).

[5,15-Bis(diethoxyphosphoryl)-10,20-dimesitylporphyrinato(2–)]platinum(II) (**Pt5d**). Following the aforementioned general procedure, 37 mg (0.045 mmol) of the free-base porphyrin **H$_2$5d** was treated with 150 mg (0.564 mmol) of $PtCl_2$. After 8 h of reflux, the residue obtained as described above was purified by column chromatography on silica gel using CH_2Cl_2/MeOH (96:4 v/v) as eluent to give **Pt5d** as a red orange crystalline powder (16 mg, 35%). ^{1}H NMR (300 MHz, $CDCl_3$/CD_3OD, 2:1 v/v, 25 °C): δ_H 1.38 (t, $^{3}J_{H,H}$ = 7.1 Hz, 12H, $OCH_2C\underline{H}_3$), 1.85 (s, 12H, Me), 2.65 (s, 6H, Me), 4.20–4.31 (m, 4H, $OC\underline{H}_2CH_3$), 4.48–4.59 (m, 4H, $OC\underline{H}_2CH_3$), 7.30 (d, $^{3}J_{H,H}$ = 8.2 Hz, 4H, *m*-Ph), 8.70 (m, 4H, Hβ), 10.24 (m, 4H, Hβ) ppm. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$/CD_3OD, 2:1 v/v, 25 °C): δ_P 20.77 ppm. HRMS (ESI): *m/z* = 1011.28857 ([M+H]$^+$, calcd. for $C_{46}H_{51}N_4O_{10}P_2Pt$ *m/z* = 1011.29050).

{5,15-Bis(diethoxyphosphoryl)-10,20-bis[(*p*-(methoxycarbonyl)phenyl]porphyrinato(2–)}platinum(II) (**Pt6d**). Following the aforementioned general procedure, 50 mg (0.059 mmol) of the free-base porphyrin **H$_2$6d** was treated with 47 mg (0.176 mmol) of $PtCl_2$. After 2 h of reflux, the residue obtained as described above was purified by column chromatography on silica gel using CH_2Cl_2/MeOH (99.8:0.2, v/v) as eluent to give **Pt6d** as a red orange crystalline powder (35 mg, 57%). ^{1}H NMR (600 MHz, $CDCl_3$/CD_3OD, 2:1 v/v, 25 °C): δ_H 1.34 (t, $^{3}J_{H,H}$ = 7.0 Hz, 12H, $OCH_2C\underline{H}_3$), 4.10 (s, 6H, $PhCOOC\underline{H}_3$), 4.18–4.26 (m, 4H, $OC\underline{H}_2CH_3$), 4.40–4.51 (m, 4H, $OC\underline{H}_2CH_3$), 8.19 (d, $^{3}J_{H,H}$ = 8.1 Hz, 4H, *o*-Ph), 8.43 (d, $^{3}J_{H,H}$ = 8.1 Hz, 4H, *m*-Ph), 8.77 (d, $^{3}J_{H,H}$ = 5.1 Hz, 4H, Hβ), 10.20 (d, $^{3}J_{H,H}$ = 5.1 Hz, 4H, Hβ) ppm. ^{31}P{^{1}H} NMR (242 MHz, $CDCl_3$/CD_3OD, 2:1 v/v, 25 °C): δ_P 20.46 ppm. HRMS (ESI): *m/z* = 955.15076 ([M+H]$^+$, calcd. for $C_{44}H_{43}N_4O_{10}P_2Pd$ *m/z* = 955.14838), 1911.29805 ([2M + H]$^+$, calcd. for $C_{88}H_{85}N_8O_{20}P_4Pd_2$ *m/z* 1911.31038). UV–vis [CH_2Cl_2; λ_{max}, nm (log ε)]: 400 (5.26), 530 (3.93), 567 (4.40). IR (neat, cm^{-1}): ν_{max} 2981 (w), 2926 (w), 2897 (w), 2852 (w), 1719 (s, C=O), 1607 (m), 1566 (w), 1549 (w), 1535 (w), 1434 (m), 1401 (w), 1390 (w), 1368 (w), 1354 (w), 1277 (s), 1251 (s), 1210 (w), 1191 (w), 1179 (w), 1164 (w), 1110 (m), 1097 (m), 1081 (m), 1037 (m), 1004 (s), 970 (m), 948 (s), 929 (s), 893 (m), 863 (m), 822 (w), 803 (m), 794 (s), 765 (s), 737 (m), 709 (m), 592 (s).

General procedure for the preparation of [10-(ethoxyhydroxyphosphoryl)-5,15-diarylporphyrinato(2−)]palladium(II)/platinum(II) (**Pt3m** and **Pd3m**) *and [10,20-bis(ethoxyhydroxyphosphoryl)-5,15-diarylporphyrinato(2−)]palladium(II)/platinum(II)* (**Pd1d**−**Pd3d** and **Pt1d**−**Pt3d**). To a solution of **M6m** or **M1d**−**M3d** (M = Pt(II), Pd(II)) (1 equiv) in a mixture of THF and EtOH (2:1, v/v, 1.2 mmol/L) was added a 0.5 M aqueous solution of NaOH (150 equiv). The resulting mixture was refluxed for 16 h. The reaction mixture was then cooled to

room temperature, the organic solvents were evaporated, and the remaining aqueous alkaline solution was treated with 0.5 M HCl untill a precipitate formed (pH = 2.5). This solid was filtered and washed with distilled H_2O (2 × 5mL). The subsequent drying under reduced pressure (10 mm Hg) at 25 °C for 24 h afforded the target products **M6m** or **M1d**−**M3d** in almost quantitative yield.

[5,15-Bis(ethoxyhydroxyphosphoryl)-10,20-bis(*p*-tolyl)porphyrinato(2–)]palladium(II) (Pd1d). Following the aforementioned general procedure using 36 mg (0.045 mmol) of porphyrin **Pd4d.** Yield 96% (32 mg).^{1}H NMR (300 MHz, $CDCl_3/CD_3OD$, 2:1 v/v, 25 °C): δ_H 1.26 (t, $^3J_{H,H}$ = 7.1 Hz, 6H, $OCH_2C\underline{H}_3$), 2.71 (s, 6H, Me), 4.05–4.11 (m, 4H, $OC\underline{H}_2CH_3$), 7.57 (d, $^3J_{H,H}$ = 8.0 Hz, 4H, *m*-Ph), 7.97 (d, $^3J_{H,H}$ = 8.0 Hz, 4H, *o*-Ph), 8.82 (d, $^3J_{H,H}$ = 5.2 Hz, 4H, H*β*), 10.30 (d, $^3J_{H,H}$ = 5.2 Hz, 4H, H*β*) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3/CD_3OD$, 2:1 v/v, 25 °C): δ_P 17.84 ppm. HRMS (ESI): *m/z* = 809.09317 ([M-H]$^+$, calcd. for $C_{38}H_{33}N_4O_6P_2Pd$ *m/z* = 809.09156.

[5,15-Bis(ethoxyhydroxyphosphoryl)-10,20-bis(*p*-tolyl)porphyrinato(2–)]platinum(II) (Pt1d). Following the aforementioned general procedure using 31 mg (0.032 mmol) of porphyrin **Pt4d**. Yield 96% (28 mg).^{1}H NMR (300 MHz, $CDCl_3/CD_3OD$, 2:1 v/v, 25 °C): δ_H 1.25 (t, $^3J_{H,H}$ = 7.1 Hz, 6H, $OCH_2C\underline{H}_3$), 2.74 (s, 6H, Me), 4.05–4.11 (m, 4H, $OC\underline{H}_2CH_3$), 7.63 (d, $^3J_{H,H}$ = 8.0 Hz, 4H, *m*-Ph), 7.98 (d, $^3J_{H,H}$ = 8.0 Hz, 4H, *o*-Ph), 8.79 (m, 4H, H*β*), 10.37 (m, 4H, H*β*) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3/CD_3OD$, 2:1 v/v, 25 °C): δ_P 16.49 ppm. HRMS (ESI): *m/z* = 897.15311 ([M-H]$^+$, calcd. for $C_{38}H_{33}N_4O_6P_2Pt$ *m/z* = 897.15074.

[5,15-Bis(ethoxyhydroxyphosphoryl)-10,20-dimesitylporphyrinato(2–)]palladium(II) (**Pd2d**). Following the aforementioned general procedure using 28 mg (0.030 mmol) of porphyrin **Pd5d**. Yield 95% (25 mg).^{1}H NMR (300 MHz, $CDCl_3/CD_3OD$, 1:1 v/v, 25 °C): δ_H 0.98 (t, $^3J_{H,H}$ = 7.1 Hz, 6H, $OCH_2C\underline{H}_3$), 1.54 (s, 12H, Me), 2.47 (s, 6H, Me), 3.87–3.91 (m, 4H, $OC\underline{H}_2CH_3$), 7.06 (s, 4H, Ph), 8.48 (d, $^3J_{H,H}$ = 5.2 Hz, 4H, H*β*), 10.39 (d, $^3J_{H,H}$ = 5.2 Hz, 4H, H*β*) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3/CD_3OD$, 1:1 v/v, 25 °C): δ_P 14.34 ppm. HRMS (ESI): *m/z* = 865.15681 ([M-H]$^+$, calcd. for $C_{42}H_{41}N_4O_6P_2Pd$ *m/z* = 865.15416.

[5,15-Bis(ethoxyhydroxyphosphoryl)-10,20-dimesitylporphyrinato(2–)]platinum(II) (**Pt2d**). Following the aforementioned general procedure using 16 mg (0.016 mmol) of porphyrin Pt4d. Yield 95% (14 mg).^{1}H NMR (300 MHz, $CDCl_3/CD_3OD$ + 1 drop NH_3, 1:1 v/v, 25 °C): δ_H 1.11 (t, $^3J_{H,H}$ = 7.1 Hz, 6H, $OCH_2C\underline{H}_3$), 1.84 (s, 12H, Me), 2.65 (s, 6H, Me), 3.72–3.85 (m, 4H, $OC\underline{H}_2CH_3$), 7.34 (s, 4H, Ph), 8.53 (m, 4H, H*β*), 10.46 (m, 4H, H*β*) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3/CD_3OD$ + 1 drop NH_3, 1:1 v/v, 25 °C): δ_P 13.25 ppm. HRMS (ESI): *m/z* = 953.21692 ([M-H]$^+$, calcd. for $C_{42}H_{41}N_4O_6P_2Pt$ *m/z* = 953.21335.

[10-(ethoxyhydroxyphosphoryl)-5,15-bis(*p*-carboxyphenyl)]porphyrinato(2−)]palladium(II) (Pd3m). The complex was prepared by the reaction of a NaOH (88 mg, 2.20 mmol) solution in 4.2 mL H_2O with a solution of **Pd6m** (12 mg, 0.015 mmol) in 12.6 mL of a THF/EtOH mixture in a

manner similar to that described above as pink crystalline powder. The yield is 98% (11 mg). ^{1}H NMR (600 MHz, $CDCl_3/CD_3OD$, 1:1 v/v, 25 °C): δ_H 1.21 (t, $^{3}J_{H,H}$ = 7.2 Hz, 3H, $OCH_2C\underline{H}_3$), 4.06–4.13 (m, 2H, $OC\underline{H}_2CH_3$), 8.24 (d, $^{3}J_{H,H}$ = 8.1 Hz, 4H, *o*-Ph), 8.46 (d, $^{3}J_{H,H}$ = 8.1 Hz, 4H, *m*-Ph), 8.84 (d, $^{3}J_{H,H}$ = 4.7 Hz, 2H, H*β*), 8.87 (d, $^{3}J_{H,H}$ = 5.0 Hz, 2H, H*β*), 9.28 (d, $^{3}J_{H,H}$ = 5.0 Hz, 2H, H*β*), 10.29 (s, 1H, H*meso*), 10.46 (d, $^{3}J_{H,H}$ = 4.7 Hz, 2H, H*β*) ppm. $^{31}P\{^{1}H\}$ NMR (242 MHz, $CDCl_3/CD_3OD$, 1:1 v/v, 25 °C): δ_P 19.42 ppm. HRMS (ESI): *m/z* = 955.15076 ($[M+H]^+$, calcd. for $C_{44}H_{43}N_4O_{10}P_2Pd$ *m/z* = 955.14838), 1911.29805 ($[2M + H]^+$, calcd. for $C_{88}H_{85}N_8O_{20}P_4Pd_2$ *m/z* 1911.31038).UV–vis [MeOH +1 drop of a saturated solution of NH_4OH in H_2O; λ_{max}, nm (log ε)]: 407 (5.18), 522 (4.26), 553 (4.09). IR (neat, cm^{-1}): ν_{max} 3129 (w), 3047 (w), 2980 (w), 2920 (w), 2851 (w), 1680 (m), 1643 (w), 1604 (m), 1566 (w), 1539 (w), 1404 (m), 1389 (m), 1312 (w), 1275 (m), 1261 (m), 1221 (w), 1176 (m), 1157 (m), 1126 (w), 1086 (m), 1071 (w), 1036 (m), 1010 (s), 943 (br. m), 891 (w), 863 (m), 828 (w), 791 (s), 763 (s), 730 (m), 711 (m), 693 (m), 579 (s), 571(s).

[10-(ethoxyhydroxyphosphoryl)-5,15-bis(*p*-carboxyphenyl)]porphyrinato(2−)]platinum(II) (**Pt3m**). The complex was prepared by the reaction of a NaOH (73 mg, 1.82 mmol) solution in 3.3 mL H_2O with a solution of **Pt6m** (11 mg, 0.012 mmol) in 10 mL of a THF/EtOH mixture in a manner similar to that described above as pink crystalline powder. The yield is 98% (10 mg). ^{1}H NMR (600 MHz, $CDCl_3/CD_3OD$, 1:1 v/v, 25 °C): δ_H 1.26 (t, $^{3}J_{H,H}$ = 7.0 Hz, 3H, $OCH_2C\underline{H}_3$), 4.15–4.21 (m, 2H, $OC\underline{H}_2CH_3$), 8.23 (d, $^{3}J_{H,H}$ = 8.0 Hz, 4H, *o*-Ph), 8.46 (d, $^{3}J_{H,H}$ = 8.0 Hz, 4H, *m*-Ph), 8.79 (d, $^{3}J_{H,H}$ = 4.6 Hz, 2H, H*β*), 8.84 (d, $^{3}J_{H,H}$ = 5.3 Hz, 2H, H*β*), 9.22 (d, $^{3}J_{H,H}$ = 4.6 Hz, 2H, H*β*), 10.20 (s, 1H, H*meso*), 10.37 (d, $^{3}J_{H,H}$ = 5.3 Hz, 2H, H*β*) ppm. $^{31}P\{^{1}H\}$ NMR (242 MHz, $CDCl_3/CD_3OD$, 1:1 v/v, 25 °C): δ_P 19.13 ppm. HRMS (ESI): *m/z* = 955.15076 ($[M+H]^+$, calcd. for $C_{44}H_{43}N_4O_{10}P_2Pd$ *m/z* = 955.14838), 1911.29805 ($[2M + H]^+$, calcd. for $C_{88}H_{85}N_8O_{20}P_4Pd_2$ *m/z* 1911.31038). UV–vis [MeOH +1 drop of a saturated solution of NH_4OH in H_2O; λ_{max}, nm (log ε)]: 395 (5.03), 510 (4.03), 542 (4.01). IR (neat, cm^{-1}): ν_{max} 2923 (w), 2854 (w), 1681 (m), 1605 (m), 1566 (w), 1540 (w), 1415 (m), 1405 (m), 1389 (m), 1335 (w), 1308 (m), 1275 (br. m), 1219 (w), 1175 (m), 1159 (m), 1126 (w), 1087 (m), 1074 (w), 1038 (m), 1014 (s), 938 (br. m), 891 (w), 879 (w), 864 (m), 830 (w), 791 (s), 764 (s), 729 (m), 710 (m), 694 (m), 580 (m), 571(m).

[10,20-bis(ethoxyhydroxyphosphoryl)-5,15-bis(4-carboxyphenyl)]porphyrinato(2−)] palladium(II) (**Pd3d**). The complex was prepared by the reaction of a NaOH (0.188 g, 4.71 mmol) solution in 8.6 mL H_2O with a solution of **Pd6d** (30 mg, 0.031 mmol) in 26 mL of a THF/EtOH mixture in a manner similar to that described above as pink crystalline powder. The yield is 80% (23 mg). ^{1}H NMR (600 MHz, $CDCl_3/CD_3OD$, 1:1 v/v, 25 °C): δ_H 1.26 (t, $^{3}J_{H,H}$ = 7.1 Hz, 6H, $OCH_2C\underline{H}_3$), 4.12–4.18 (m, 4H, $OC\underline{H}_2CH_3$), 8.19 (d, $^{3}J_{H,H}$ = 8.0 Hz, 4H, *o*-Ph), 8.45 (d, $^{3}J_{H,H}$ = 8.0 Hz, 4H, *m*-Ph), 8.78 (d, $^{3}J_{H,H}$ = 5.2 Hz, 4H, H*β*), 10.32 (d, $^{3}J_{H,H}$ = 5.2 Hz, 4H, H*β*) ppm. $^{31}P\{^{1}H\}$ NMR (242 MHz, $CDCl_3/CD_3OD$, 1:1 v/v, 25 °C): δ_P 18.06 ppm. HRMS (ESI, positive ion mode):

m/z = 871.05407 ([M+H]$^+$, calcd. for $C_{38}H_{31}N_4O_{10}P_2Pd$ *m/z* = 871.05590; 893.03635 ([M + Na]$^+$, calcd. for $C_{38}H_{30}N_4O_{10}P_2PdNa$ *m/z* 893.03784. HRMS (ESI, negative ion mode)): *m/z* = 869.04324 ([M-H]$^+$, calcd. for $C_{38}H_{29}N_4O_{10}P_2Pd$ *m/z* = 869.03992. UV–vis [MeOH+1 drop of a saturated solution of NH_4OH in H_2O; λ_{max}, nm (log ε)]: 413 (5.24), 530 (3.99), 568 (4.01). IR (neat, cm^{-1}): ν_{max} 1682 (s), 1605 (m), 1567 (w), 1540 (w), 1512 (w), 1429 (w), 1405 (w), 1391 (w), 1344 (w), 1311 (w), 1254 (m), 1225 (m), 1174 (m), 1123 (w), 1081 (m), 1016 (s), 1000 (s), 941 (s), 891 (s), 862 (s), 788 (s), 766 (s), 731 (s), 704 (s).

[10,20-bis(ethoxyhydroxyphosphoryl)-5,15-bis(4-carboxyphenyl)]porphyrinato(2−)] platinum(II) (**Pt3d**). The complex was prepared by the reaction of a NaOH (86 mg, 2.16 mmol) solution in 4 mL H_2O with a solution of **Pt6d** (15 mg, 0.014 mmol) in 12 mL of a THF/EtOH mixture in a manner similar to that described above as pink crystalline powder. The yield is 100% (14 mg). ^{1}H NMR (600 MHz, $CDCl_3/CD_3OD$, 1:1 v/v, 25 °C): δ_H 1.27 (t, $^3J_{H,H}$ = 7.1 Hz, 6H, $OCH_2C\underline{H}_3$), 4.15–4.21 (m, 4H, $OC\underline{H}_2CH_3$), 8.17 (d, $^3J_{H,H}$ = 8.0 Hz, 4H, *o*-Ph), 8.44 (d, $^3J_{H,H}$ = 8.0 Hz, 4H, *m*-Ph), 8.75 (d, $^3J_{H,H}$ = 5.2 Hz, 4H, Hβ), 10.26 (d, $^3J_{H,H}$ = 5.2 Hz, 4H, Hβ) ppm. ^{31}P{^{1}H} NMR (242 MHz, $CDCl_3/CD_3OD$, 1:1 v/v, 25 °C): δ_P 18.19 ppm. HRMS (ESI, negative ion mode)): *m/z* = 957.10150 ([M-H]$^+$, calcd. for $C_{38}H_{29}N_4O_{10}P_2Pt$ *m/z* = 957.09910. UV–vis [MeOH + 1 drop of a saturated solution of NH_4OH in H_2O; λ_{max}, nm (log ε)]: 400 (4.94), 525 (3.82), 560 (4.40). IR (neat, cm^{-1}): ν_{max} 2982 (w), 2924 (w), 2851 (w), 1683 (m), 1606 (m), 1566 (w), 1546 (w), 1437 (w), 1417 (m), 1393 (w), 1351 (w), 1308 (m), 1275 (br. m), 1256 (br. m), 1226 (m), 1174 (m), 1083 (m), 1035 (s), 1007 (s), 984 (m), 952 (br. s), 892 (m), 863 (s), 831 (m), 789 (s), 768 (s), 730 (m), 705 (m), 678 (m), 593 (s), 577 (s).

3. X-ray crystallography of Pd6d and Pt6d

Table S1. Crystal data and structure refinement.

Identification code	**Pt6d**	**Pd6d**
CCDC number	2027752	2027753
Chemical formula	$C_{44}H_{42}N_4O_{10}P_2Pt$	$C_{44}H_{42}N_4O_{10}P_2Pd$
Formula weight	1043.84	955.15
Temperature, K	100.15	100.15
Crystal system	orthorhombic	orthorhombic
Space group	*Pca*2$_1$	*Pca*2$_1$
a, Å	23.971(5)	23.940(3)
b, Å	7.2177(14)	7.2579(9)
c, Å	23.134(4)	23.162(3)
α, °	90	90
β, °	90	90
γ, °	90	90
Volume, Å^3	4002.5(13)	4024.5(9)
Z	4	4
$\rho_{calc,}$ g cm^{-3}	1.732	1.576
μ, mm^{-1}	3.653	0.608
F(000)	2088.0	1960.0
Crystal size, mm^3	0.38 × 0.1 × 0.04	0.34 × 0.22 × 0.14
Radiation	Mo*Kα* (*λ* = 0.71073)	Mo*Kα* (*λ* = 0.71073)
2*Θ* range for data collection °	8.386 to 69.998	8.368 to 69.998
Index ranges	-38 ≤ h ≤ 38, -11 ≤ k ≤ 9, -37 ≤ l ≤ 37	-38 ≤ h ≤ 38, -11 ≤ k ≤ 11, -37 ≤ l ≤ 37
Reflections collected	102165	132202
Independent reflections	17578 [R_{int} = 0.0768, R_{sigma} = 0.0581]	17666 [R_{int} = 0.0646, R_{sigma} = 0.0411]
Data,restraints,parameters	17578/1/551	17666/1/551
Goodness-of-fit on F^2	1.002	1.015
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0315, wR_2 = 0.0599	R_1 = 0.0271, wR_2 = 0.0601
Final *R* indexes [all data]	R_1 = 0.0672, wR_2 = 0.0697	R_1 = 0.0337, wR_2 = 0.0629
Largest diff. peak/hole, e Å^{-}	1.11/–1.71	0.47/–0.66
Flack parameter	0.470(6)	0.070(15)

Table S2. Bond lengths for **Pt3d**.

Atom	Atom	Length,Å	Atom	Atom	Length,Å
Pt(1)	N(4)	2.019(4)	C(33)	C(24)	1.385(6)
Pt(1)	N(3)	2.009(4)	C(34)	C(35)	1.349(7)
Pt(1)	N(2)	2.017(4)	C(36)	C(35)	1.433(7)
Pt(1)	N(1)	2.011(4)	C(18)	C(17)	1.436(7)
P(2)	O(4)	1.454(4)	O(10)	C(29)	1.339(7)
P(2)	O(5)	1.590(4)	O(10)	C(30)	1.446(6)
P(2)	O(6)	1.558(4)	C(25)	C(32)	1.395(7)
P(2)	C(1)	1.823(6)	C(25)	C(24)	1.495(7)
P(1)	O(3)	1.571(4)	C(25)	C(26)	1.383(8)
P(1)	O(1)	1.467(4)	C(2)	C(3)	1.438(7)
P(1)	O(2)	1.573(4)	C(22)	C(23)	1.438(7)
P(1)	C(19)	1.820(6)	C(22)	C(21)	1.346(7)
O(3)	C(39)	1.440(7)	C(4)	C(3)	1.341(7)
O(5)	C(41)	1.449(7)	C(27)	C(26)	1.384(7)
O(6)	C(43)	1.472(6)	C(27)	C(28)	1.392(7)
O(2)	C(37)	1.457(6)	C(31)	C(32)	1.400(8)
N(4)	C(33)	1.374(7)	C(31)	C(28)	1.376(7)
N(4)	C(36)	1.385(6)	C(15)	C(16)	1.446(7)
N(3)	C(23)	1.374(6)	C(15)	C(6)	1.388(7)
N(3)	C(20)	1.387(6)	C(16)	C(17)	1.345(7)
N(2)	C(18)	1.383(6)	C(24)	C(23)	1.386(7)
N(2)	C(15)	1.378(7)	C(6)	C(7)	1.492(7)
N(1)	C(5)	1.367(6)	C(11)	C(10)	1.486(7)
N(1)	C(2)	1.391(6)	C(11)	O(7)	1.206(8)
C(1)	C(36)	1.400(8)	O(9)	C(29)	1.205(8)
C(1)	C(2)	1.397(8)	C(10)	C(9)	1.397(7)
C(19)	C(18)	1.399(8)	C(9)	C(8)	1.384(7)
C(19)	C(20)	1.391(8)	C(21)	C(20)	1.435(7)
C(5)	C(4)	1.440(7)	C(28)	C(29)	1.495(7)
C(5)	C(6)	1.386(7)	C(7)	C(8)	1.382(8)
O(8)	C(11)	1.327(7)	C(7)	C(14)	1.397(7)
O(8)	C(12)	1.458(6)	C(43)	C(44)	1.489(10)
C(13)	C(10)	1.380(7)	C(38)	C(37)	1.500(8)
C(13)	C(14)	1.392(8)	C(39)	C(40)	1.506(7)
C(33)	C(34)	1.427(7)	C(41)	C(42)	1.527(8)

Table S3. Bond Angles for **Pt3d**.

Atom	Atom	Atom	Angle,°	Atom	Atom	Atom	Angle,°
N(3)	Pt(1)	N(4)	90.98(16	C(29)	O(10)	C(30)	114.4(5
N(3)	Pt(1)	N(2)	88.83(16	C(32)	C(25)	C(24)	119.6(5
N(3)	Pt(1)	N(1)	179.07(18	C(26)	C(25)	C(32)	119.6(5
N(2)	Pt(1)	N(4)	179.63(19	C(26)	C(25)	C(24)	120.8(5
N(1)	Pt(1)	N(4)	88.85(16	N(1)	C(2)	C(1)	125.3(4
N(1)	Pt(1)	N(2)	91.34(16	N(1)	C(2)	C(3)	109.1(4
O(4)	P(2)	O(5)	111.9(2	C(1)	C(2)	C(3)	125.6(4
O(4)	P(2)	O(6)	115.1(2	C(21)	C(22)	C(23)	106.6(4

O(4)	P(2)	C(1)	116.7(3	C(3)	C(4)	C(5)	107.1(5
O(5)	P(2)	C(1)	105.9(2	C(26)	C(27)	C(28)	120.4(5
O(6)	P(2)	O(5)	104.0(2	C(28)	C(31)	C(32)	120.1(5
O(6)	P(2)	C(1)	101.9(3	N(2)	C(15)	C(16)	109.0(4
O(3)	P(1)	O(2)	101.2(2	N(2)	C(15)	C(6)	126.6(4
O(3)	P(1)	C(19)	107.2(3	C(6)	C(15)	C(16)	124.3(5
O(1)	P(1)	O(3)	113.1(2	C(34)	C(35)	C(36)	107.8(4
O(1)	P(1)	O(2)	116.1(3	C(17)	C(16)	C(15)	107.6(5
O(1)	P(1)	C(19)	115.3(2	C(25)	C(32)	C(31)	119.9(5
O(2)	P(1)	C(19)	102.5(2	C(33)	C(24)	C(25)	118.9(5
C(39)	O(3)	P(1)	120.9(4	C(23)	C(24)	C(33)	124.9(5
C(41)	O(5)	P(2)	119.8(4	C(23)	C(24)	C(25)	116.2(4
C(43)	O(6)	P(2)	118.9(3	C(5)	C(6)	C(15)	124.5(5
C(37)	O(2)	P(1)	119.3(4	C(5)	C(6)	C(7)	118.8(4
C(33)	N(4)	Pt(1)	125.7(3	C(15)	C(6)	C(7)	116.6(5
C(33)	N(4)	C(36)	106.2(4	O(8)	C(11)	C(10)	113.5(5
C(36)	N(4)	Pt(1)	128.1(3	O(7)	C(11)	O(8)	122.5(5
C(23)	N(3)	Pt(1)	125.7(3	O(7)	C(11)	C(10)	124.0(5
C(23)	N(3)	C(20)	106.1(4	C(16)	C(17)	C(18)	107.5(4
C(20)	N(3)	Pt(1)	128.1(3	N(3)	C(23)	C(22)	110.1(4
C(18)	N(2)	Pt(1)	128.2(3	N(3)	C(23)	C(24)	126.3(4
C(15)	N(2)	Pt(1)	125.1(3	C(24)	C(23)	C(22)	123.6(5
C(15)	N(2)	C(18)	106.6(4	C(13)	C(10)	C(11)	121.3(5
C(5)	N(1)	Pt(1)	125.6(3	C(13)	C(10)	C(9)	119.6(5
C(5)	N(1)	C(2)	106.0(4	C(9)	C(10)	C(11)	119.0(5
C(2)	N(1)	Pt(1)	128.4(3	C(8)	C(9)	C(10)	120.0(5
C(36)	C(1)	P(2)	117.3(4	C(22)	C(21)	C(20)	108.3(4
C(2)	C(1)	P(2)	118.8(4	C(25)	C(26)	C(27)	120.2(5
C(2)	C(1)	C(36)	123.7(5	N(3)	C(20)	C(19)	125.3(5
C(18)	C(19)	P(1)	118.5(4	N(3)	C(20)	C(21)	108.8(4
C(20)	C(19)	P(1)	117.4(4	C(19)	C(20)	C(21)	125.8(4
C(20)	C(19)	C(18)	124.1(5	C(27)	C(28)	C(29)	118.1(5
N(1)	C(5)	C(4)	110.1(4	C(31)	C(28)	C(27)	119.7(5
N(1)	C(5)	C(6)	126.8(4	C(31)	C(28)	C(29)	122.1(5
C(6)	C(5)	C(4)	123.1(5	C(4)	C(3)	C(2)	107.7(4
C(11)	O(8)	C(12)	115.0(4	C(8)	C(7)	C(6)	121.9(4
C(10)	C(13)	C(14)	120.3(5	C(8)	C(7)	C(14)	119.4(5
N(4)	C(33)	C(34)	110.0(4	C(14)	C(7)	C(6)	118.6(5
N(4)	C(33)	C(24)	126.1(5	O(10)	C(29)	C(28)	112.2(5
C(24)	C(33)	C(34)	123.9(5	O(9)	C(29)	O(10)	124.6(5
C(35)	C(34)	C(33)	107.1(5	O(9)	C(29)	C(28)	123.2(5
N(4)	C(36)	C(1)	125.6(5	C(7)	C(8)	C(9)	120.6(5
N(4)	C(36)	C(35)	108.9(4	O(6)	C(43)	C(44)	109.4(5
C(1)	C(36)	C(35)	125.4(5	C(13)	C(14)	C(7)	120.0(5
N(2)	C(18)	C(19)	125.0(5	O(3)	C(39)	C(40)	108.3(4
N(2)	C(18)	C(17)	109.4(4	O(2)	C(37)	C(38)	107.4(4
C(19)	C(18)	C(17)	125.6(5	O(5)	C(41)	C(42)	110.5(4

Table S4. Bond Lengths for **Pd3d**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd(1)	N(4)	2.0255(17	C(33)	C(24)	1.388(3
Pd(1)	N(3)	2.0154(17	C(34)	C(35)	1.351(3
Pd(1)	N(2)	2.0248(16	C(36)	C(35)	1.444(3
Pd(1)	N(1)	2.0186(17	C(18)	C(17)	1.450(3
P(2)	O(4)	1.4673(17	O(10)	C(29)	1.339(3
P(2)	O(5)	1.5894(17	O(10)	C(30)	1.446(3
P(2)	O(6)	1.5683(16	C(25)	C(32)	1.391(3
P(2)	C(1)	1.823(2	C(25)	C(24)	1.500(3
P(1)	O(3)	1.5774(17	C(25)	C(26)	1.398(3
P(1)	O(1)	1.4677(17	C(2)	C(3)	1.449(3
P(1)	O(2)	1.5803(18	C(22)	C(23)	1.441(3
P(1)	C(19)	1.818(2	C(22)	C(21)	1.351(3
O(3)	C(39)	1.456(3	C(4)	C(3)	1.348(3
O(5)	C(41)	1.459(3	C(27)	C(26)	1.394(3
O(6)	C(43)	1.475(3	C(27)	C(28)	1.391(3
O(2)	C(37)	1.459(3	C(31)	C(32)	1.395(3
N(4)	C(33)	1.378(3	C(31)	C(28)	1.392(3
N(4)	C(36)	1.382(3	C(15)	C(16)	1.439(3
N(3)	C(23)	1.382(3	C(15)	C(6)	1.395(3
N(3)	C(20)	1.377(3	C(16)	C(17)	1.349(3
N(2)	C(18)	1.382(3	C(24)	C(23)	1.389(3
N(2)	C(15)	1.378(3	C(6)	C(7)	1.499(3
N(1)	C(5)	1.375(2	C(11)	C(10)	1.489(3
N(1)	C(2)	1.381(3	C(11)	O(7)	1.207(3
C(1)	C(36)	1.407(3	O(9)	C(29)	1.211(3
C(1)	C(2)	1.408(3	C(10)	C(9)	1.392(3
C(19)	C(18)	1.400(3	C(9)	C(8)	1.388(3
C(19)	C(20)	1.405(3	C(21)	C(20)	1.440(3
C(5)	C(4)	1.443(3	C(28)	C(29)	1.493(3
C(5)	C(6)	1.390(3	C(7)	C(8)	1.403(3
O(8)	C(11)	1.337(3	C(7)	C(14)	1.392(3
O(8)	C(12)	1.448(3	C(43)	C(44)	1.495(4
C(13)	C(10)	1.394(3	C(38)	C(37)	1.504(4
C(13)	C(14)	1.391(3	C(39)	C(40)	1.501(3
C(33)	C(34)	1.440(3	C(41)	C(42)	1.517(3

Table S5. Bond Angles for **Pd3d**.

Atom	Atom	Atom	Angle,°	Atom	Atom	Atom	Angle,°
N(3)	Pd(1)	N(4)	91.08(7	C(29)	O(10)	C(30)	114.86(19
N(3)	Pd(1)	N(2)	88.65(7	C(32)	C(25)	C(24)	119.84(17
N(3)	Pd(1)	N(1)	179.32(7	C(32)	C(25)	C(26)	119.70(19
N(2)	Pd(1)	N(4)	179.55(8	C(26)	C(25)	C(24)	120.42(19
N(1)	Pd(1)	N(4)	88.86(7	N(1)	C(2)	C(1)	125.47(18
N(1)	Pd(1)	N(2)	91.42(7	N(1)	C(2)	C(3)	109.22(17
O(4)	P(2)	O(5)	112.05(9	C(1)	C(2)	C(3)	125.29(18
O(4)	P(2)	O(6)	115.13(10	C(21)	C(22)	C(23)	106.66(18
O(4)	P(2)	C(1)	116.58(10	C(3)	C(4)	C(5)	107.05(18
O(5)	P(2)	C(1)	105.90(9	C(28)	C(27)	C(26)	120.65(19

O(6)	P(2)	O(5)	103.64(9
O(6)	P(2)	C(1)	102.17(9
O(3)	P(1)	O(2)	101.14(10
O(3)	P(1)	C(19)	107.26(10
O(1)	P(1)	O(3)	113.37(10
O(1)	P(1)	O(2)	115.56(10
O(1)	P(1)	C(19)	115.28(10
O(2)	P(1)	C(19)	102.73(10
C(39)	O(3)	P(1)	120.85(15
C(41)	O(5)	P(2)	119.60(14
C(43)	O(6)	P(2)	118.76(15
C(37)	O(2)	P(1)	119.64(16
C(33)	N(4)	Pd(1)	125.59(14
C(33)	N(4)	C(36)	106.32(16
C(36)	N(4)	Pd(1)	128.07(13
C(23)	N(3)	Pd(1)	125.44(14
C(20)	N(3)	Pd(1)	128.30(13
C(20)	N(3)	C(23)	106.24(17
C(18)	N(2)	Pd(1)	128.18(13
C(15)	N(2)	Pd(1)	125.41(13
C(15)	N(2)	C(18)	106.26(16
C(5)	N(1)	Pd(1)	125.25(13
C(5)	N(1)	C(2)	106.30(16
C(2)	N(1)	Pd(1)	128.45(13
C(36)	C(1)	P(2)	117.35(15
C(36)	C(1)	C(2)	123.48(19
C(2)	C(1)	P(2)	119.06(16
C(18)	C(19)	P(1)	118.81(15
C(18)	C(19)	C(20)	123.6(2
C(20)	C(19)	P(1)	117.59(16
N(1)	C(5)	C(4)	109.99(17
N(1)	C(5)	C(6)	127.00(18
C(6)	C(5)	C(4)	123.01(18
C(11)	O(8)	C(12)	114.80(18
C(14)	C(13)	C(10)	119.97(19
N(4)	C(33)	C(34)	109.93(18
N(4)	C(33)	C(24)	126.29(18
C(24)	C(33)	C(34)	123.74(18
C(35)	C(34)	C(33)	106.92(18
N(4)	C(36)	C(1)	125.64(18
N(4)	C(36)	C(35)	109.10(17
C(1)	C(36)	C(35)	125.22(19
N(2)	C(18)	C(19)	125.25(18
N(2)	C(18)	C(17)	109.24(17
C(19)	C(18)	C(17)	125.51(19
C(28)	C(31)	C(32)	119.9(2
N(2)	C(15)	C(16)	109.84(18
N(2)	C(15)	C(6)	126.35(17
C(6)	C(15)	C(16)	123.71(18
C(34)	C(35)	C(36)	107.69(18
C(17)	C(16)	C(15)	107.36(19
C(25)	C(32)	C(31)	120.42(19
C(33)	C(24)	C(25)	118.87(18
C(33)	C(24)	C(23)	124.80(17
C(23)	C(24)	C(25)	116.32(18
C(5)	C(6)	C(15)	124.55(17
C(5)	C(6)	C(7)	118.38(18
C(15)	C(6)	C(7)	116.84(18
O(8)	C(11)	C(10)	113.42(18
O(7)	C(11)	O(8)	122.3(2
O(7)	C(11)	C(10)	124.3(2
C(16)	C(17)	C(18)	107.27(18
N(3)	C(23)	C(22)	109.88(17
N(3)	C(23)	C(24)	126.44(18
C(24)	C(23)	C(22)	123.61(18
C(13)	C(10)	C(11)	121.34(19
C(9)	C(10)	C(13)	119.69(19
C(9)	C(10)	C(11)	118.83(18
C(8)	C(9)	C(10)	120.44(18
C(22)	C(21)	C(20)	107.89(19
C(27)	C(26)	C(25)	119.6(2
N(3)	C(20)	C(19)	125.57(19
N(3)	C(20)	C(21)	109.31(17
C(19)	C(20)	C(21)	125.12(19
C(27)	C(28)	C(31)	119.65(19
C(27)	C(28)	C(29)	118.26(18
C(31)	C(28)	C(29)	122.07(19
C(4)	C(3)	C(2)	107.43(18
C(8)	C(7)	C(6)	121.60(19
C(14)	C(7)	C(6)	118.95(17
C(14)	C(7)	C(8)	119.31(18
O(10)	C(29)	C(28)	112.68(18
O(9)	C(29)	O(10)	123.8(2
O(9)	C(29)	C(28)	123.5(2
C(9)	C(8)	C(7)	120.0(2
O(6)	C(43)	C(44)	109.9(2
C(13)	C(14)	C(7)	120.53(18
O(3)	C(39)	C(40)	108.1(2
O(2)	C(37)	C(38)	107.4(2
O(5)	C(41)	C(42)	110.48(19

Table S6. Short contacts in the crystal packing of **Pt3d** and **Pd3d**.

Atoms D–H···A	D–H distance,Å	H···A distance, Å	D···A distance, Å	D–H···A angle, °	Type of interaction
		Pt3d			
		within the column along [010]			
C8–H8···Pt1[1]	0.95	2.908(1)	3.771(5)	151.9	C_{Ph}–H···Pt contacts
C26[1]–H26[1]···Pt1	0.95	3.200(1)	3.986(5)	141.3	
C14[1]–H14[1]···O7	0.95	2.314(5)	3.184(7)	152.0	CH···O contacts
C32–H32···O9[1]	0.95	2.531(4)	3.272(7)	134.9	
		within the parquet layer in (001)			
C12[2]–H12A[2]···Pt1	0.98	3.185(1)	3.769(5)	119.8	
		between layers			
C39–H39B···O4[3]	0.99	2.490(4)	3.369(6)	147.9	CH···O contacts between
C43–H43B···O1[4]	0.99	2.444(4)	3.422(8)	168.7	phosphoryl groups
		Pd3d			
		within the column along [010]			
C8–H8···Pd1[1]	0.95	2.897(1)	3.761(2)	151.8	C_{Ph}–H···Pd contacts
C26[1]–H26[1]···Pd1	0.95	3.204(1)	3.985(2)	140.7	
C14[1]–H14[1]···O7	0.95	2.337(2)	3.208(3)	152.1	CH···O contacts
C32–H32···O9[1]	0.95	2.568(2)	3.298(3)	133.8	
		within the parquet layer in (001)			
C12[2]–H12A[2]···Pd1	0.98	3.175(1)	3.761(3)	119.9	
		between layers			
C39–H39B···O4[3]	0.99	2.480(2)	3.364(3)	148.5	CH···O contacts between
C43–H43B···O1[4]	0.99	2.445(2)	3.423(3)	169.6	phosphoryl groups

[1]+x,-1+y,+z;[2] 1/2+x,-1-y,+z;[3]3/2-x,+y,-1/2+z;[3]3/2-x,1+y,1/2+z

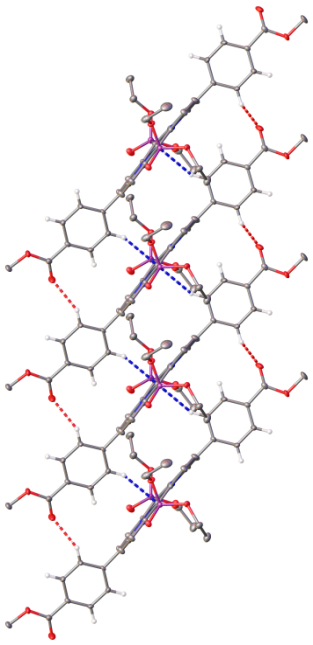


Figure S1. The crystal packing of **M6d** (M = Pt, Pd). (a) View along [011]. Blue dash lines are H_{Ph}···Pt/Pd contacts, red dash lines are H_{Ph}···O contacts. All hydrogen atoms except hydrogens on Ph rings have been omitted for clarity.

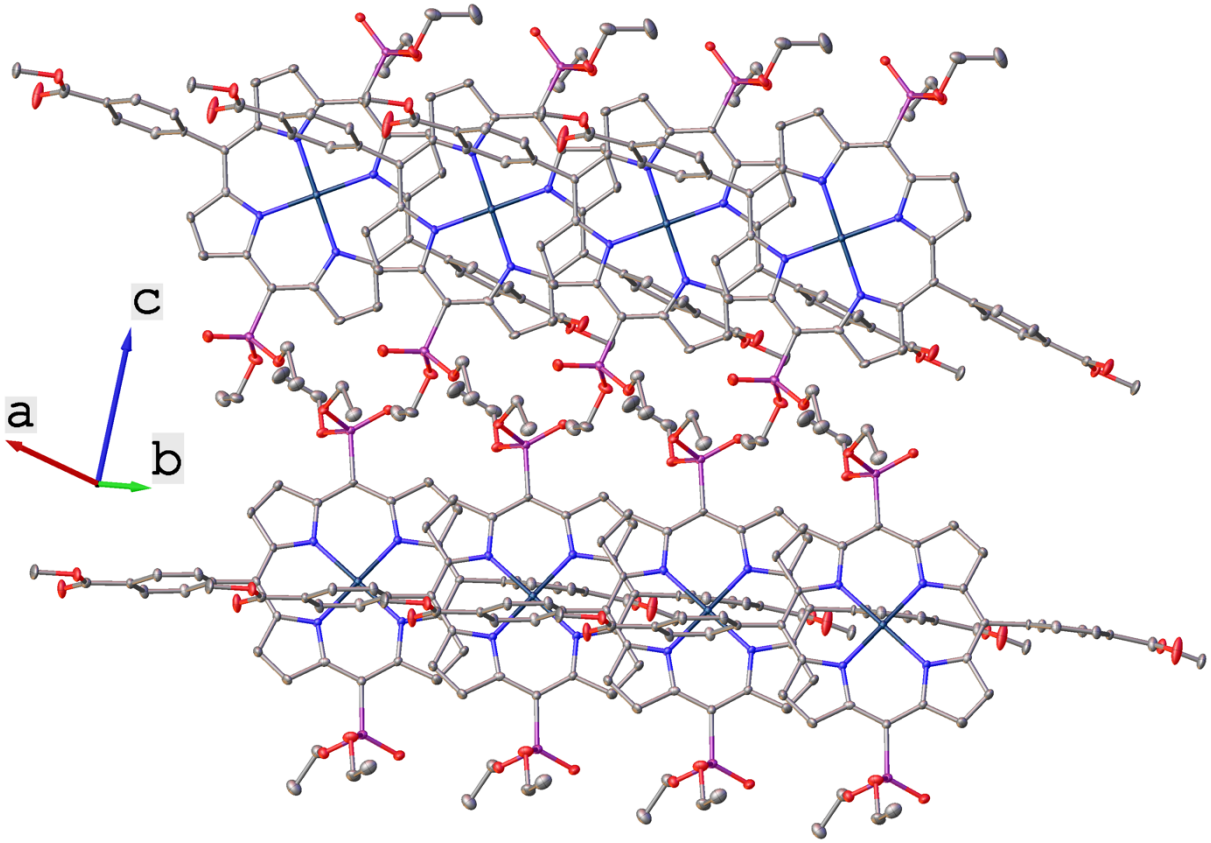


Figure S2. The crystal packing of **M6d** (M = Pt, Pd) showing the deplacement of porphyrin macrocycles in the crystals. All hydrogen atoms have been omitted for clarity.

4. NMR characterization of M3d and NMR studies of their solution aggregation

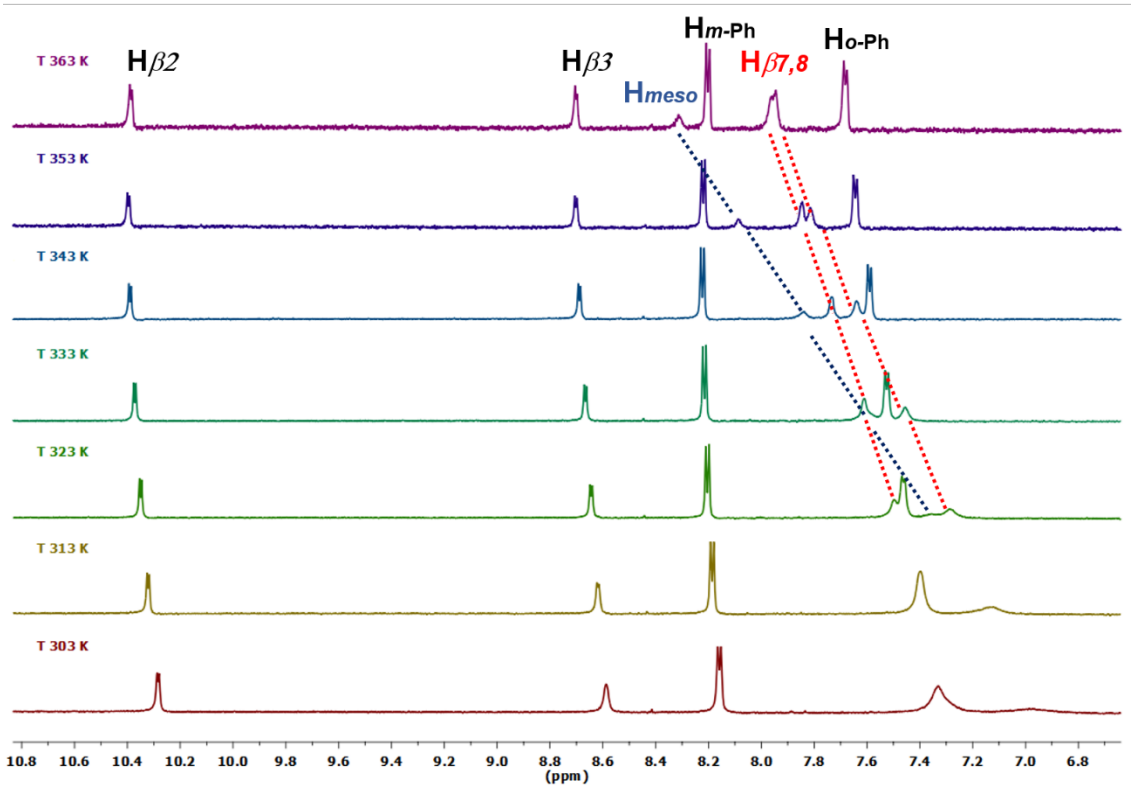


Figure S3. Aromatic region of VT ^{1}H NMR spectra of **Pt3m** in D_2O (C = 1.5 x 10^{-3} M, pD 12).

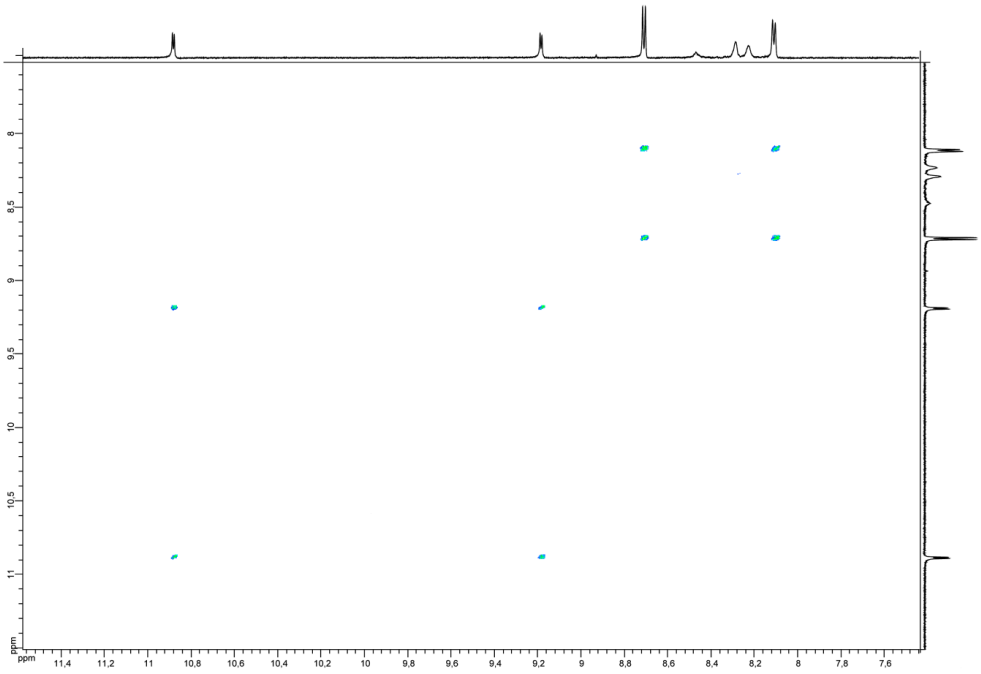


Figure S4. Aromatic region of COSY spectrum of **Pt3m** in D_2O (C= 1.5 × 10^{-3} M, pD 12).

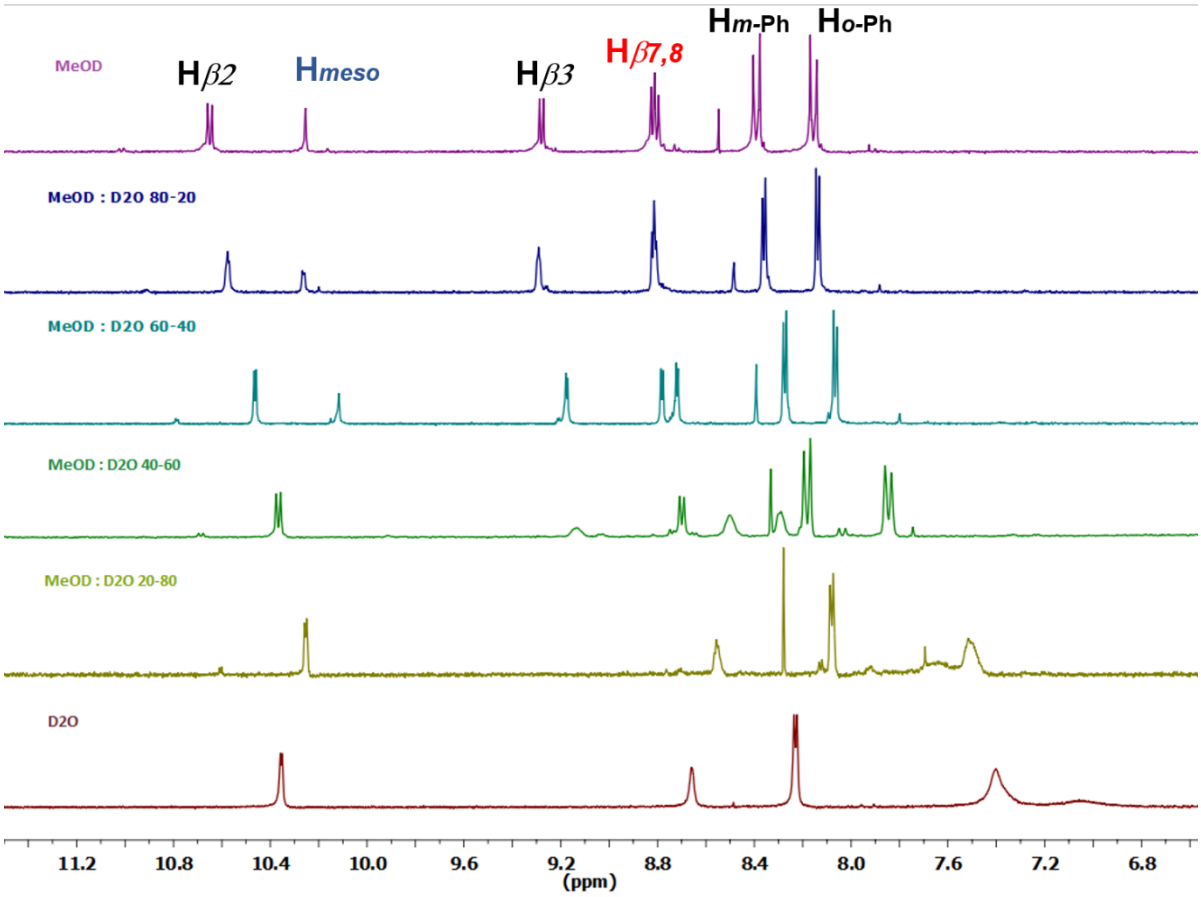


Figure S5. Aromatic region of ^{1}H NMR spectra of **Pt3m** (C = 1.5 × 10^{-3} M) in a D_2O/CD_3OD mixture with a different volume ratio of components at 303 K.

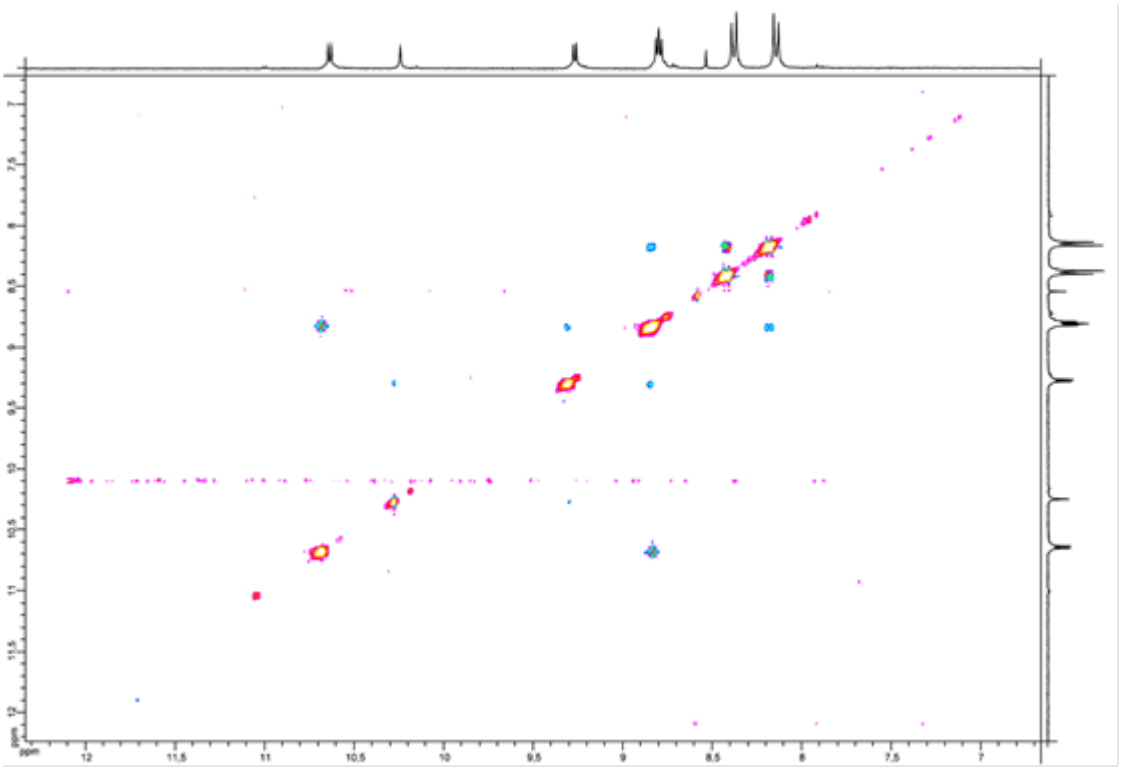


Figure S6. Aromatic region of NOESY spectrum of **Pt3m** (C = 1.5 × 10^{-3} M) at 303 K in CD_3OD.

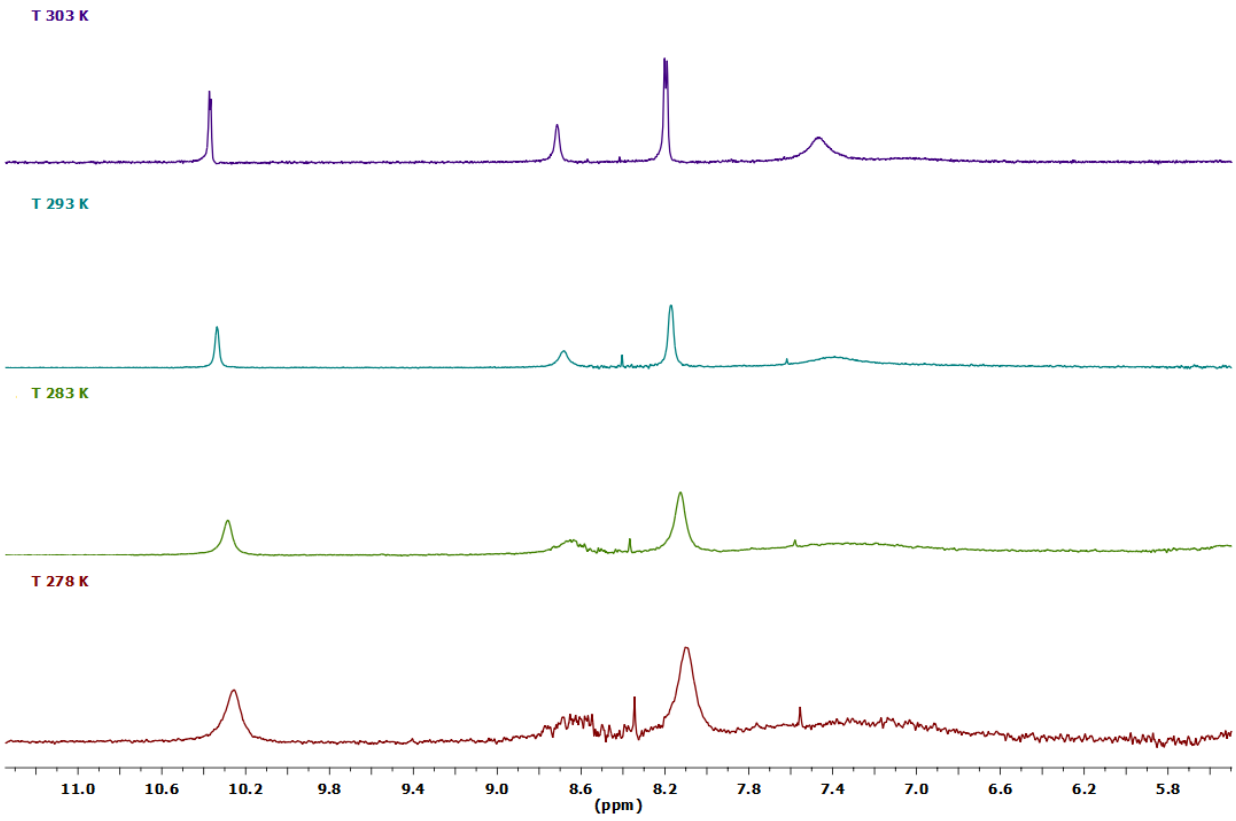


Figure S7. Aromatic region of VT ^{1}H NMR spectra of **Pd3m** in D_2O (C = 1.5 × 10^{-3} M, pD 12).

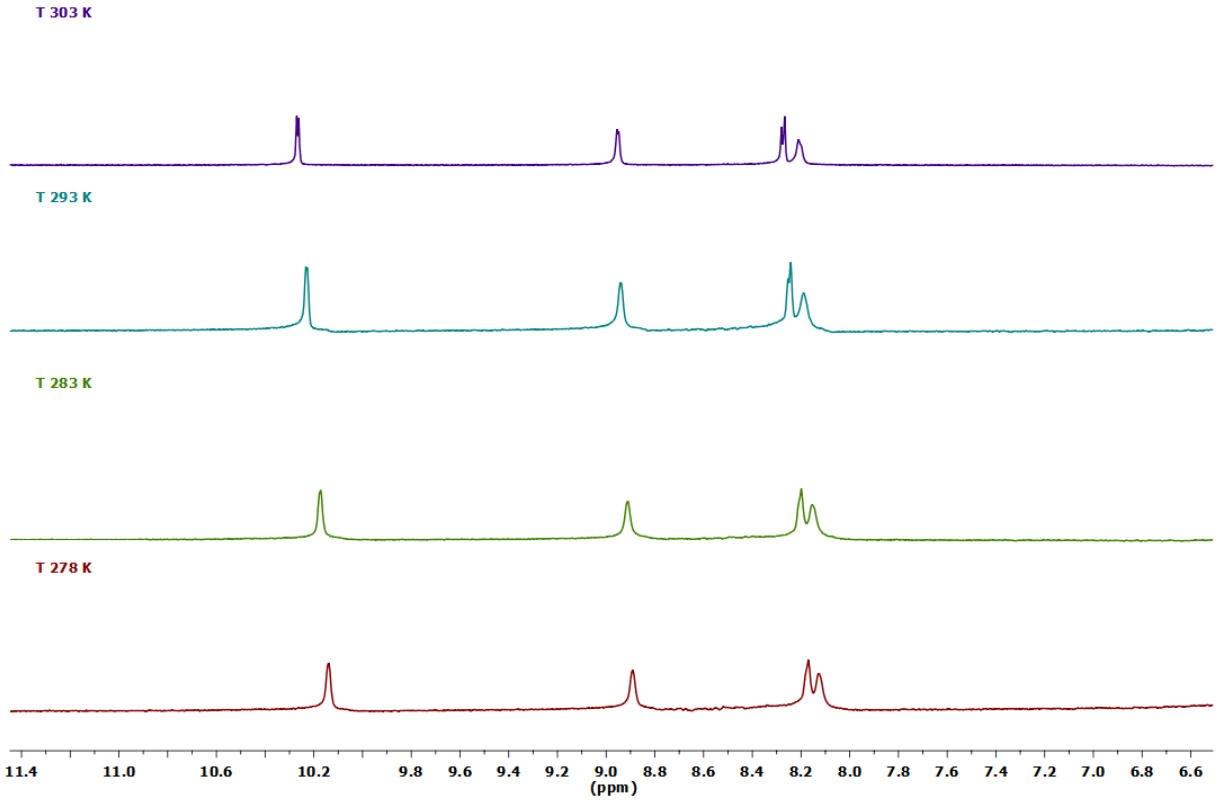


Figure S8. Aromatic region of VT ^{1}H NMR spectra of **Pd3d** in D_2O (C= 1.5 × 10^{-3} M, pD 12).

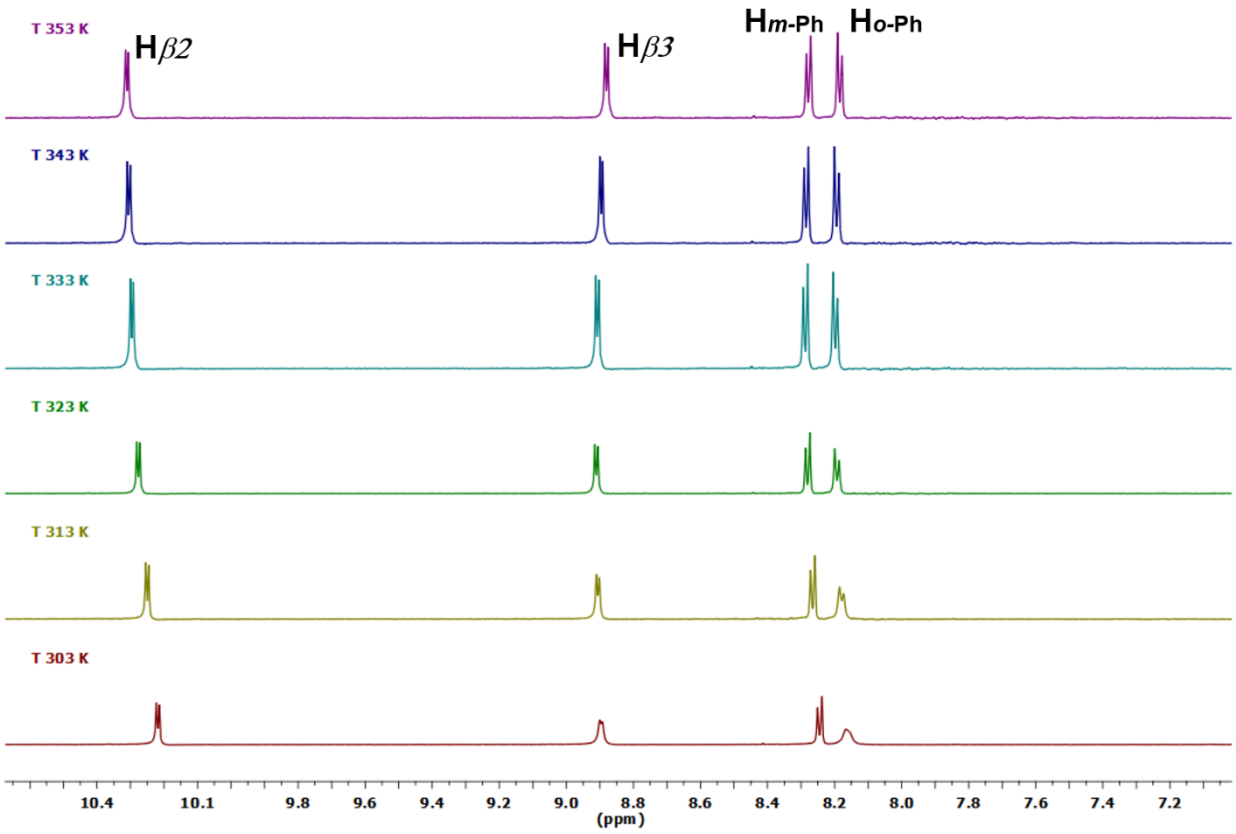
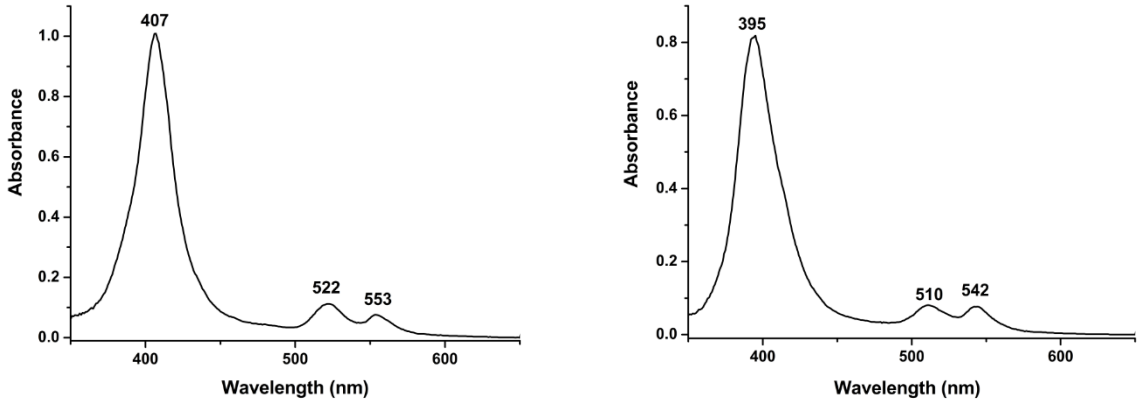


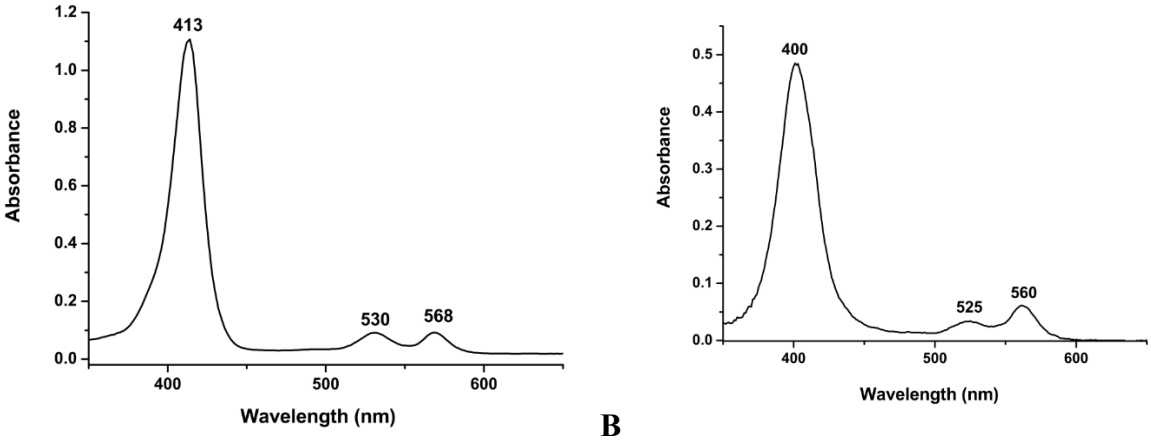
Figure S9. Aromatic region of VT ^{1}H NMR spectra of **Pt3d** in D_2O (C = 1.5 × 10^{-3} M, pD 12).

5. Studies of optical properties and solution aggregation



A **B**

Figure S10. UV–vis absorption spectrum of **Pd3m** (A) and **Pt3m** (B) in MeOH in the presence of one drop of NH_4OH in H_2O at 298 K.



A **B**

Figure S 11. UV–vis absorption spectrum of **Pd3d** (A) and **Pt3d** (B) in MeOH in the presence of one drop of NH_4OH in H_2O at 298 K.

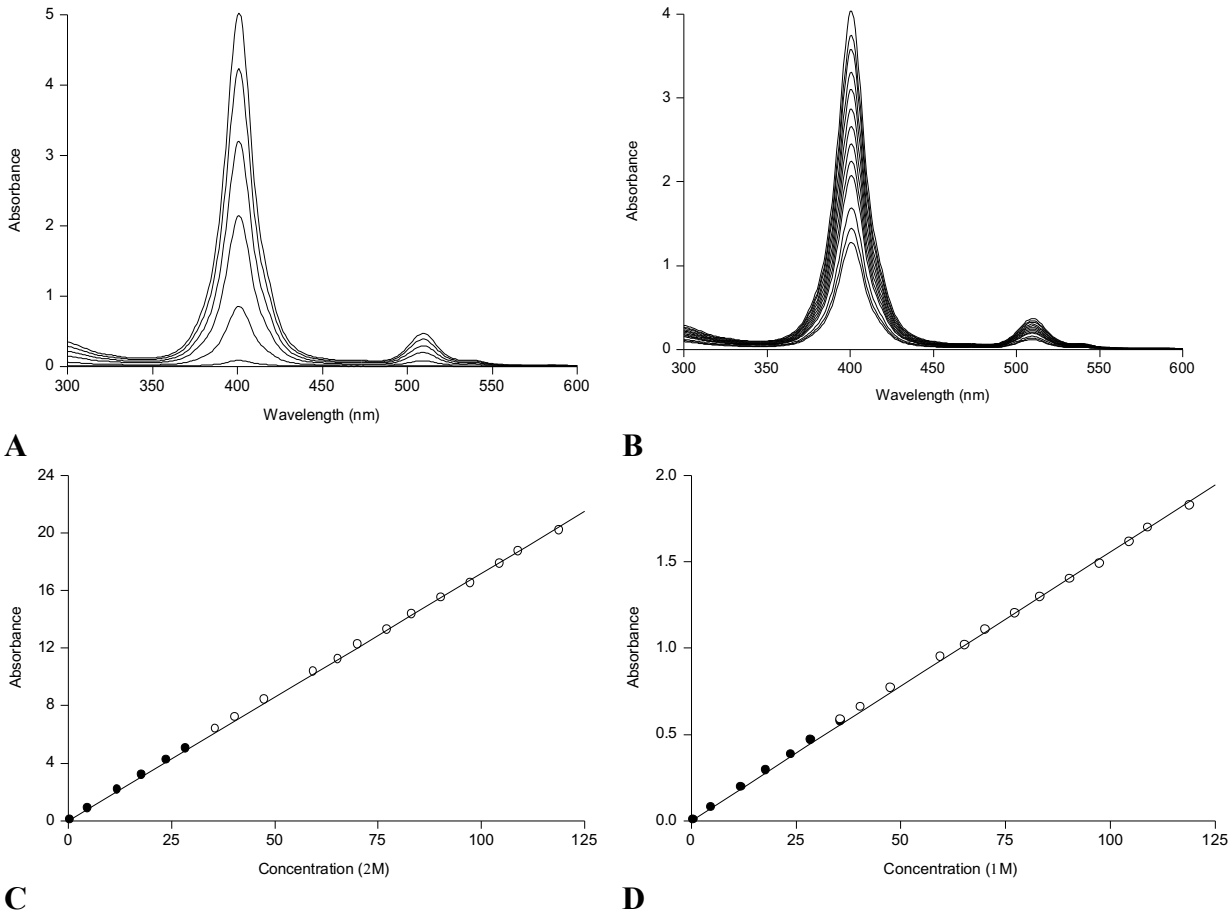


Figure S12. UV–vis absorption spectra of PtTCPP at different concentrations in buffered water/DMF 90:10 v/v mixtures. [MOPS] = 0.05 M, pH = 7.2, I = 0.1 M, [NaCl] = 0.075 M, T = 298.2(2) K, l = 1 cm (A) and 0.2 cm (B); Beer-Lambert plots for Pt(TCPP) at λ_{max} = 401 (C) and 509 nm (D) (l = 1 cm (filled circles) and 0.2 cm (open circles, measured absorbances were multiplied by 5).

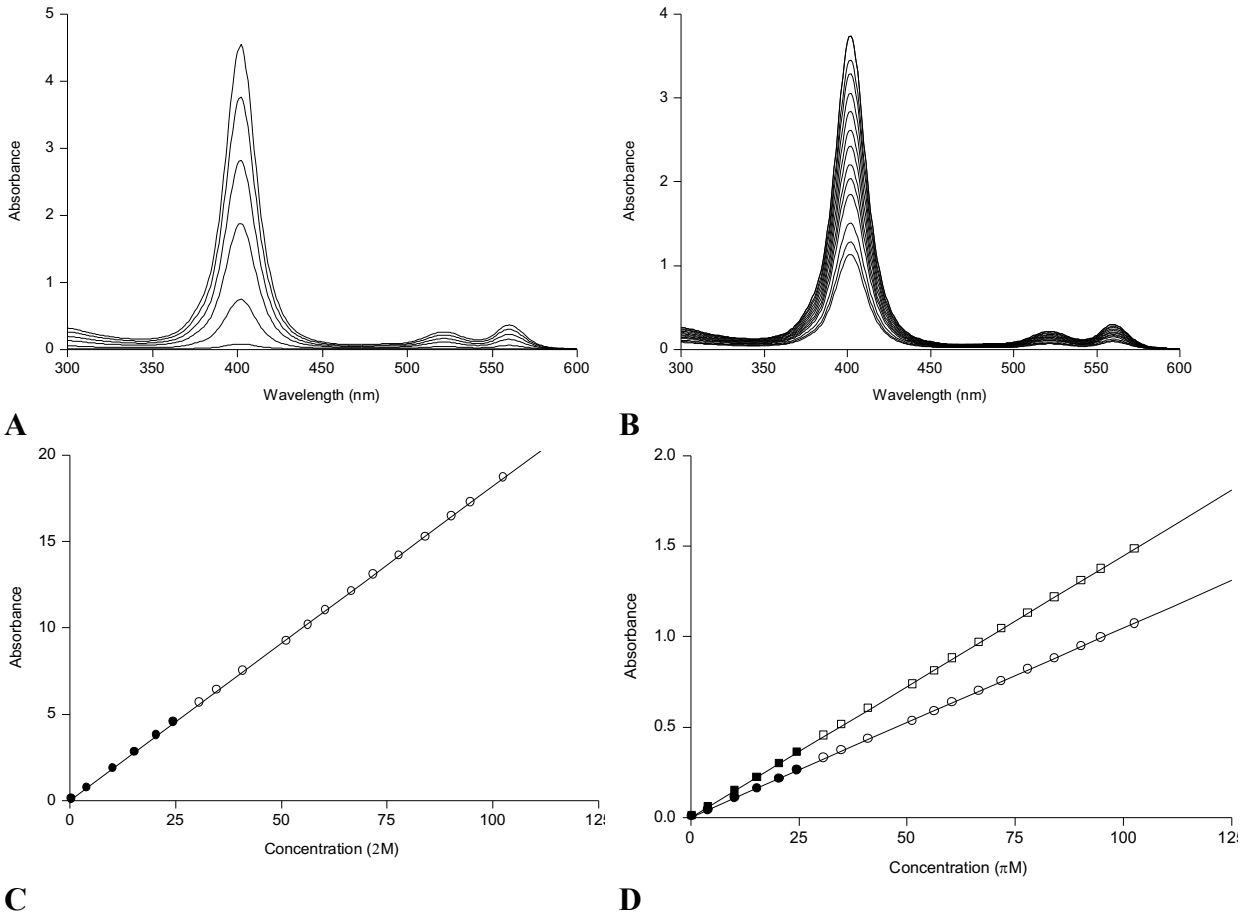


Figure S13. UV–vis absorption spectra of **Pt3d** at different concentrations in buffered water/DMF (9:1 v/v) mixtures. [MOPS] = 0.05 M, pH = 7.2, I = 0.1 M, [NaCl] = 0.075 M, T = 298.2(2) K, l = 1 cm (A) and 0.2 cm (B); Beer-Lambert plots for **Pt3d** at λ_{max} = 402 (C), 522 (D, circles) and 560 nm (D, squares). (l = 1 cm (filled circles) and 0.2 cm (open circles, measured absorbances were multiplied by 5).

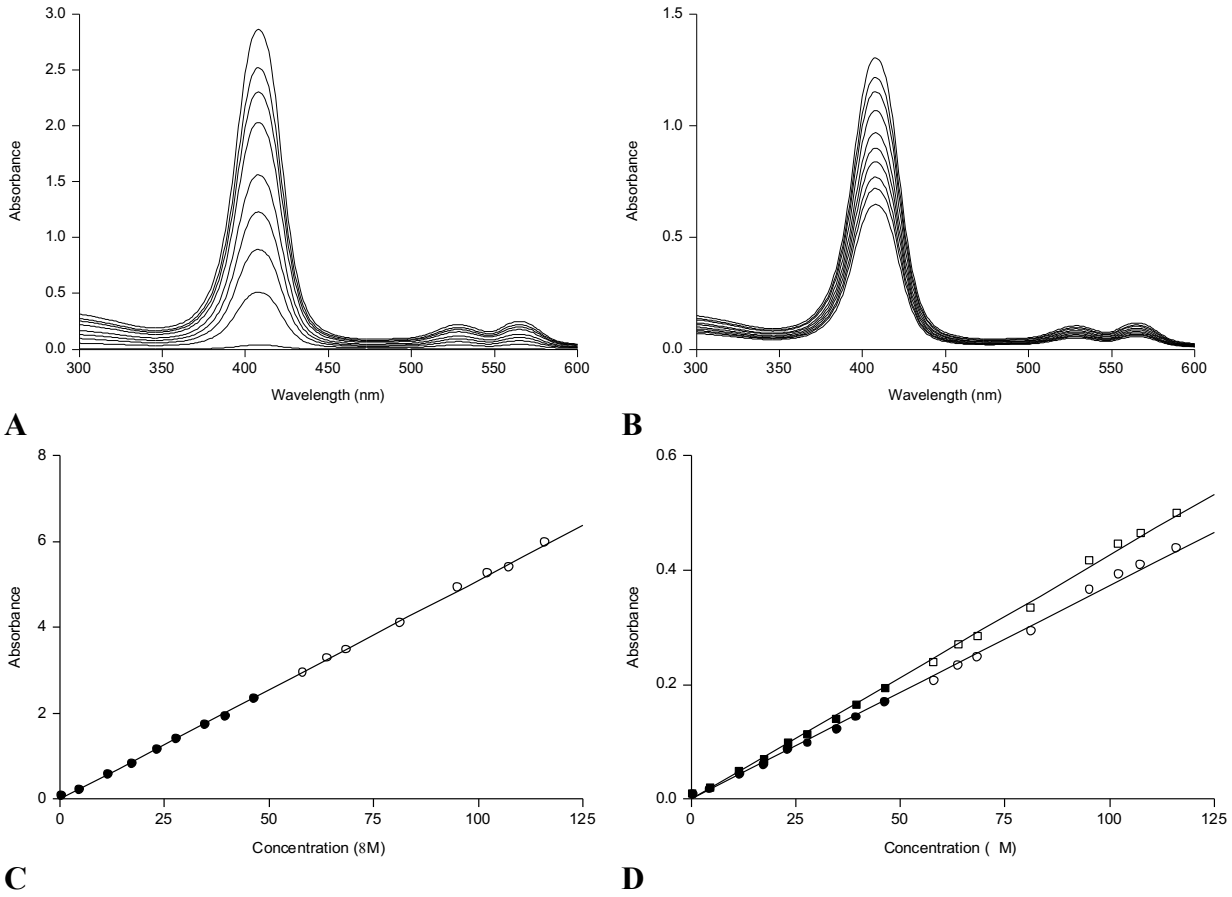


Figure S14. UV–vis absorption spectra of **Pt1d** at different concentrations in buffered water/DMF (9:1 v/v) mixtures. [MOPS] = 0.05 M, pH = 7.2, I = 0.1 M, [NaCl] = 0.075 M, T = 298.2(2) K, l = 1 cm (A) and 0.2 cm (B); Beer-Lambert plots for **Pt1d** at λ_{max} = 408 (C), 529 (D, circles) and 565 nm (D, squares). (l = 1 cm (filled circles) and 0.2 cm (open circles, measured absorbances were multiplied by 5).

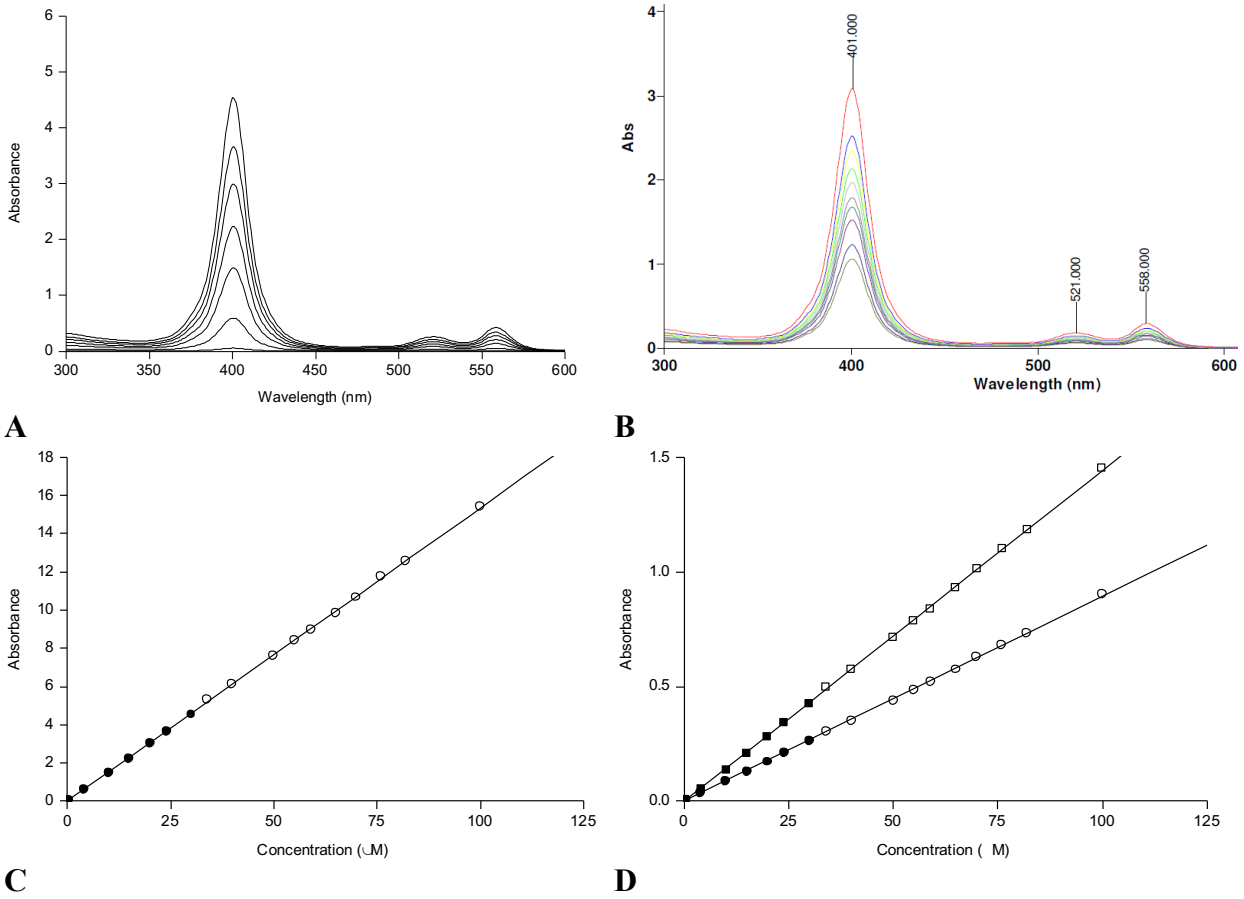


Figure S15. UV–vis absorption spectra of **Pt2d** at different concentrations in buffered water/DMF (9:1 v/v) mixtures. [MOPS] = 0.05 M, pH = 7.2, I = 0.1 M, [NaCl] = 0.075 M, T = 298.2(2) K, l = 1 cm (A) and 0.2 cm (B); Beer-Lambert plots for **Pt2d** at λ_{max} = 401 (C), 521 (D, circles) and 558 nm (D, squares). (l = 1 cm (filled circles) and 0.2 cm (open circles, measured absorbances were multiplied by 5).

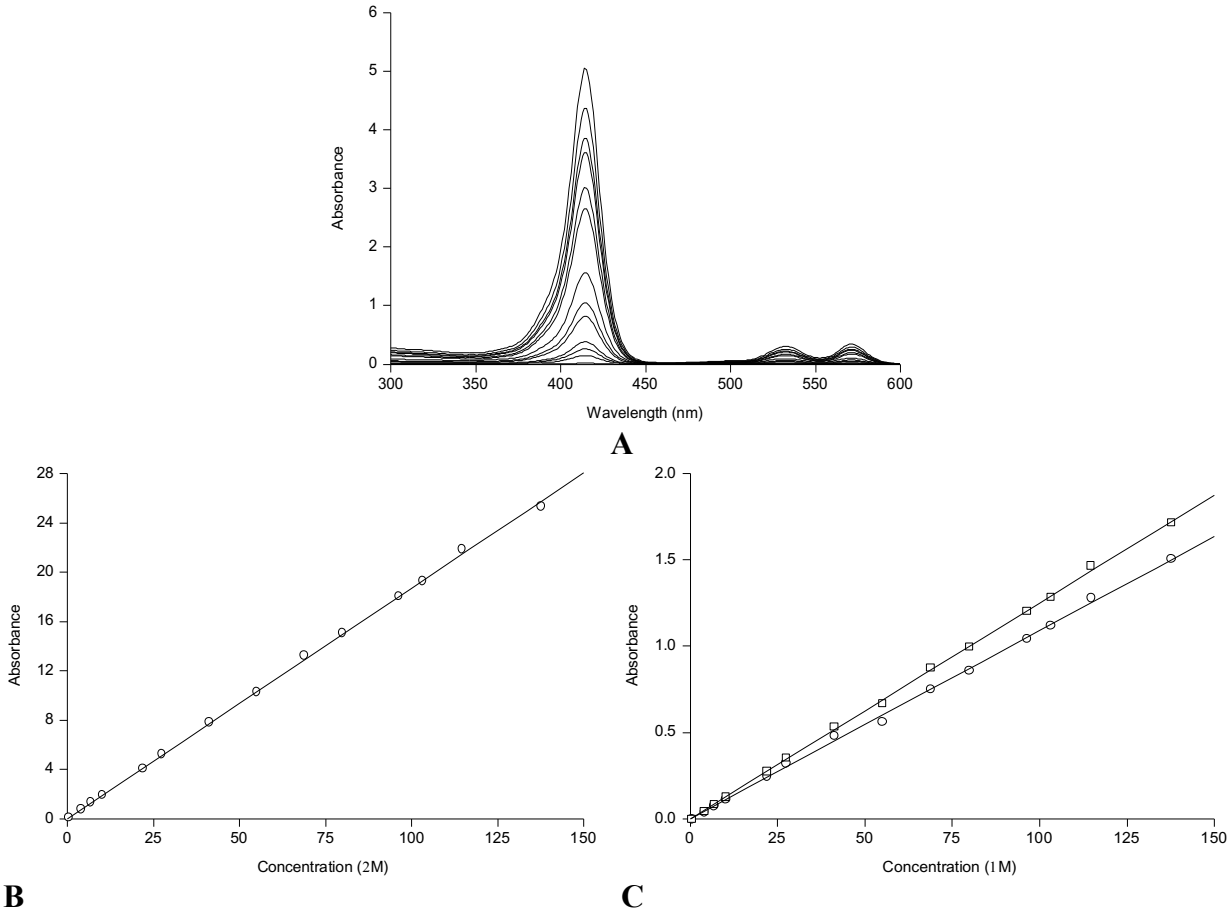


Figure S16. UV–vis absorption spectra of **Pd3d** at different concentrations in buffered water/DMF (9:1 v/v) mixtures. [MOPS] = 0.05 M, pH = 7.2, I = 0.1 M, [NaCl] = 0.075 M, T = 298.2(2) K, l = 0.2 cm (A); Beer-Lambert plots for **Pd3d** at λ_{max} = 414 (B), 532 (C, circles) and 571 nm (C, squares). (l = 0.2 cm (open symbols, measured absorbances were multiplied by 5).

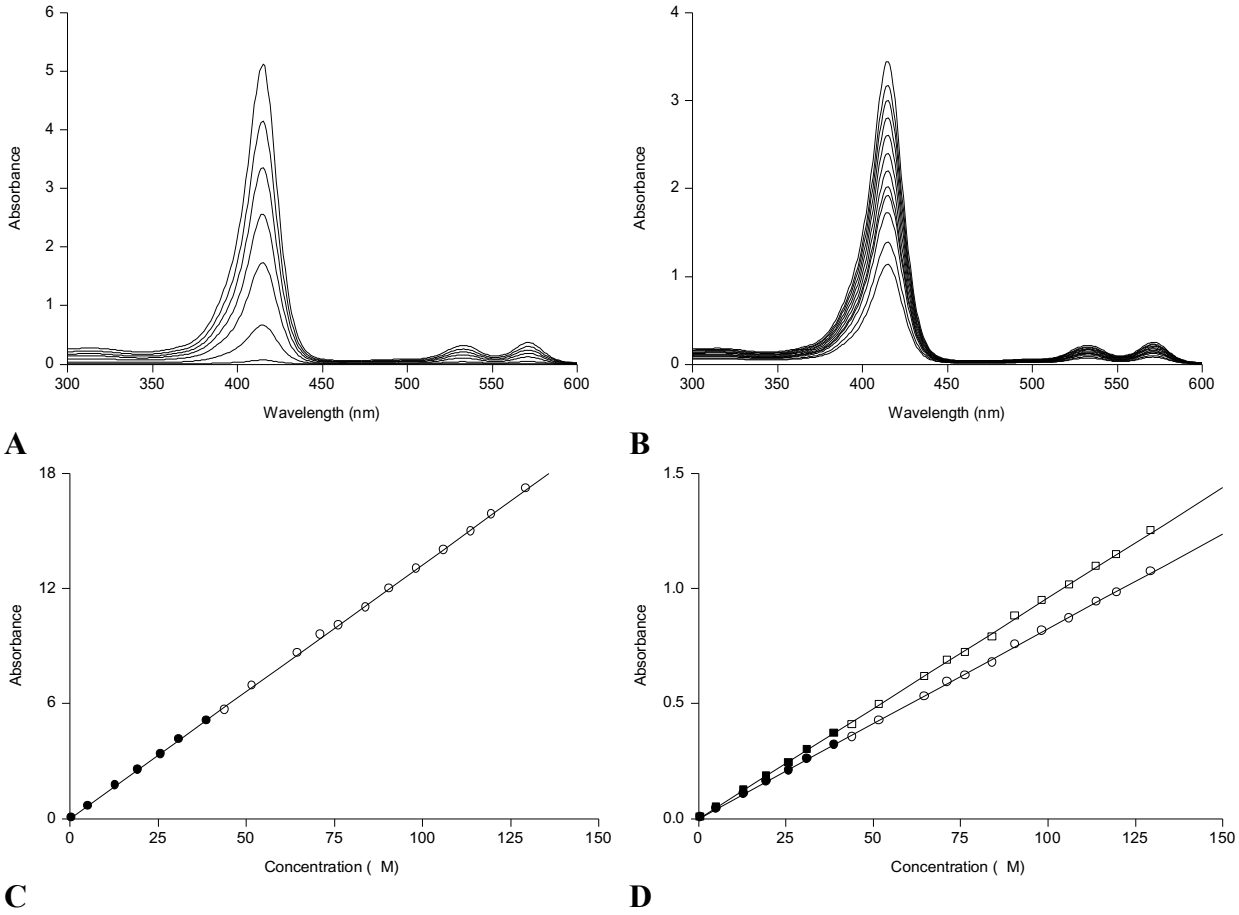


Figure S17. UV–vis absorption spectra of **Pd1d** at different concentrations in buffered water/DMF (9:1 v/v) mixtures. [MOPS] = 0.05 M, pH = 7.2, I = 0.1 M, [NaCl] = 0.075 M, T = 298.2(2) K, l = 1 cm (A) and 0.2 cm (B); Beer-Lambert plots for **Pd1d** at λ_{max} = 415 (C), 533 (D, circles) and 571 nm (D, squares). (l = 1 cm (filled circles) and 0.2 cm (open circles, measured absorbances were multiplied by 5).

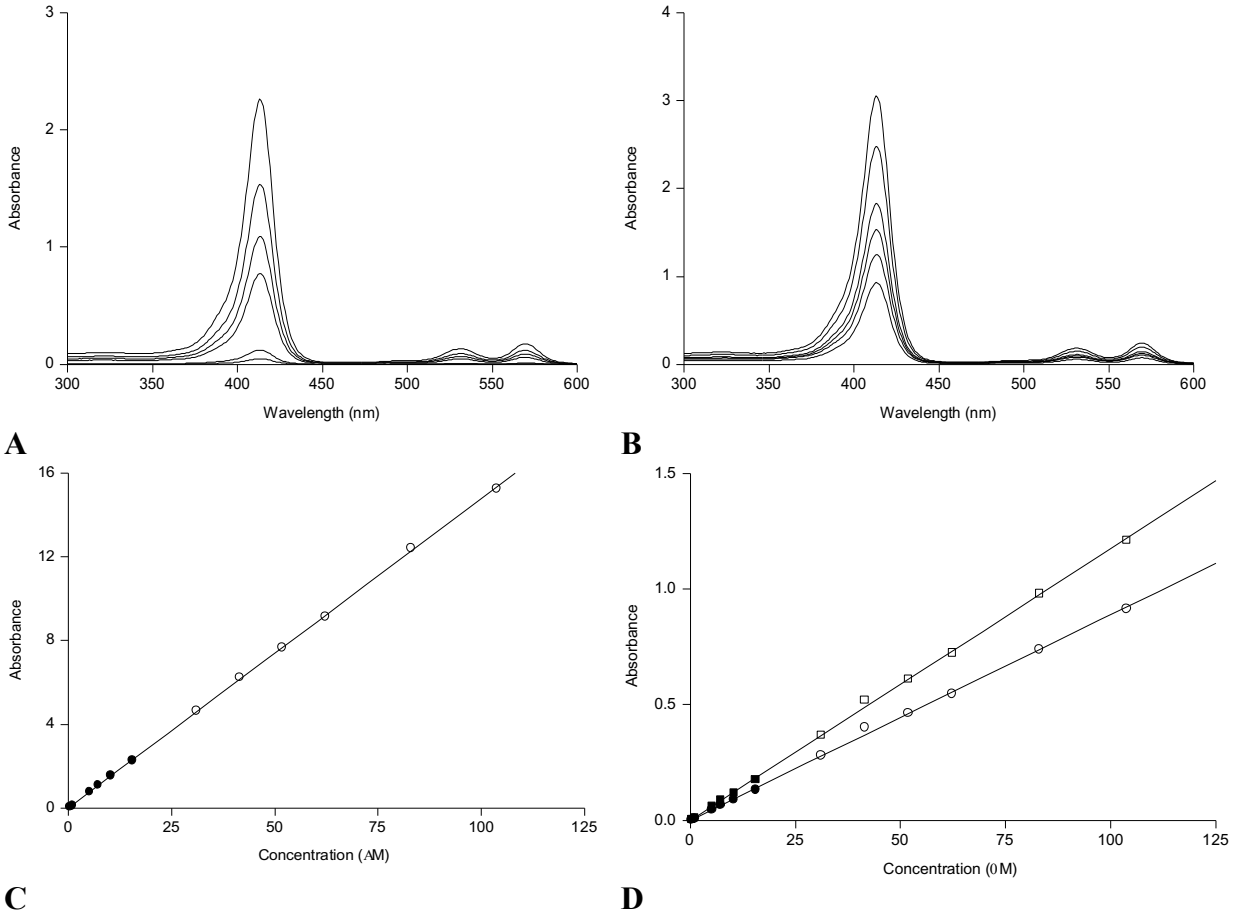
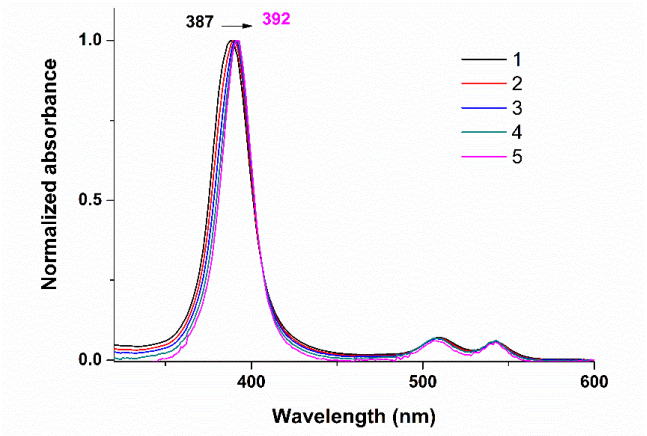
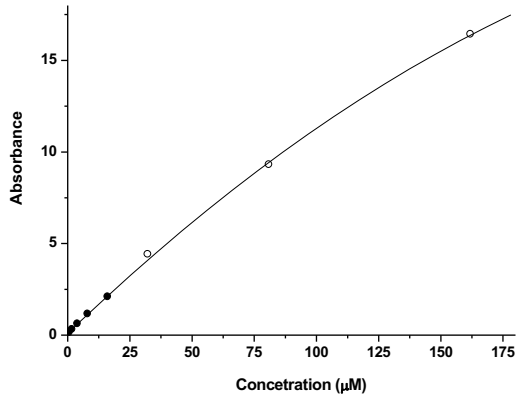


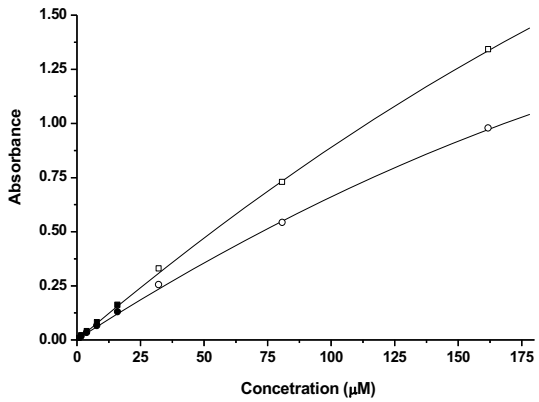
Figure S18. UV–vis absorption spectra of **Pd2d** at different concentrations in buffered water/DMF (9:1 v/v) mixtures. [MOPS] = 0.05 M, pH = 7.2, I = 0.1 M, [NaCl] = 0.075 M, T = 298.2(2) K, l = 1 cm (A) and 0.2 cm (B); Beer-Lambert plots for **Pd2d** at λ_{max} = 415 (C), 533 (D, circles) and 571 nm (D, squares). (l = 1 cm (filled circles) and 0.2 cm (open circles, measured absorbances were multiplied by 5).



A

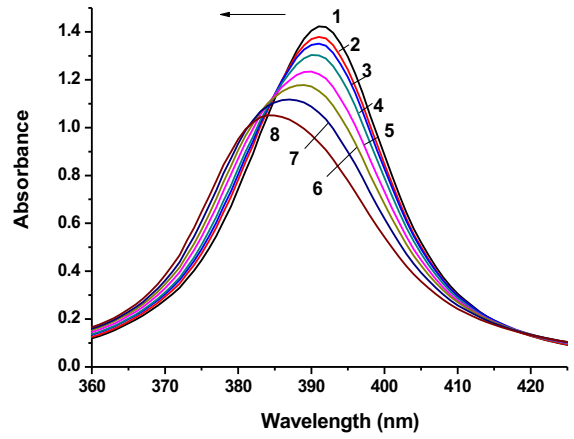


B

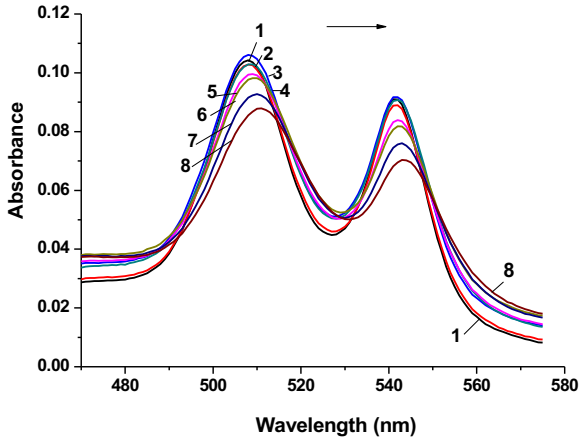


C

Figure S 19. UV–vis absorption spectra of **Pt3m** at different concentrations in buffered water solution. [MOPS] = 0.01 M, pH = 7.2, [NaCl] = 0.1, I = 0.11 M; T = 298 K (A), Beer-Lambert plots for **Pt3m** at λ_{max} = 392 (B), 508 (C, squares) and 541 nm (C, circles), (l = 1 cm (filled circles) and 0.1 cm (open circles, measured absorbances were multiplied by 10).

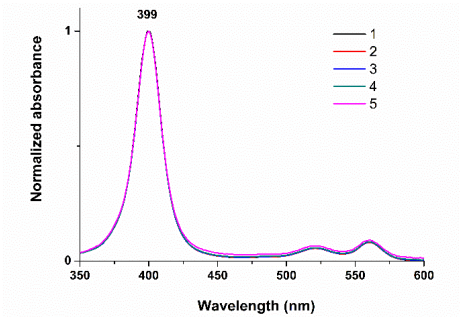


A

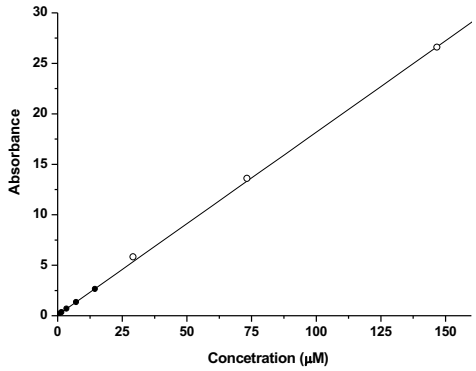


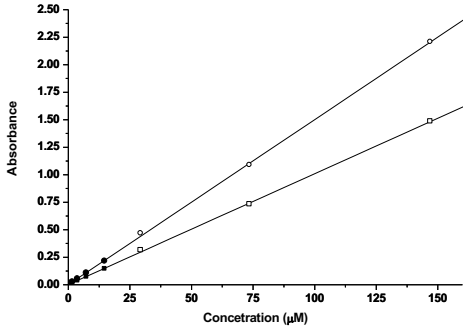
B

Figure S 20. Changes in the UV–vis spectra of **Pt3m** in buffered water. [MOPS] = 0.01 M, pH = 7.2, C = 8.1 10^{-6} M, T = 298 K upon addition of NaCl, I (mmol/L): (1) 10; (2) 20; (3) 30; (4) 50; (5) 110; (6) 210; (7) 410 (8) 810, l = 1 cm, Soret band region (A) and Q bands region (B).



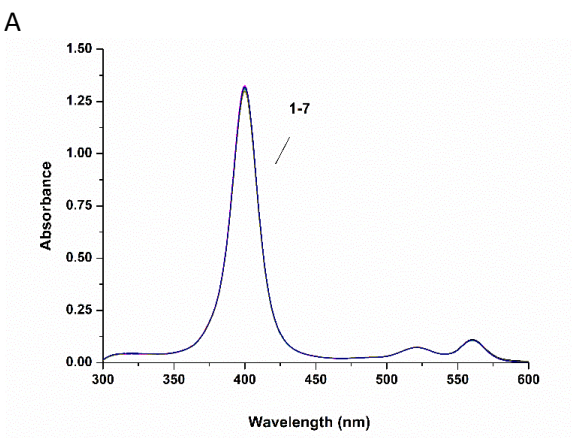
A





B C

Figure S 21. UV–vis absorption spectra of **Pt3d** at different concentrations in buffered water solution. [MOPS] = 0.01 M, pH = 7.2, [NaCl] = 0.1, I = 0.11 M; T = 298 K (A), Beer-Lambert plots for **Pt3d** at λ_{max} = 399 (B), 521 (C, squares) and 560 nm (C circles), (l = 1 cm (filled circles) and 0.1 cm (open circles, measured absorbances were multiplied by 10).



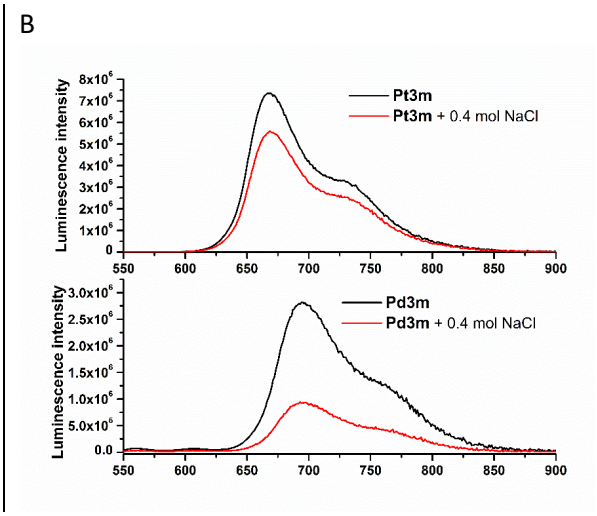


Figure S22. A) Changes in the UV–vis spectra of **Pt3d** in buffered water. [MOPS] = 0.01 M, pH = 7.2, C = 7.3 10^{-6} M, T = 298 K upon addition of NaCl, I (mmol/L): (1) 10; (2) 20; (3) 30; (4) 50; (5) 110; (6) 210; (7) 410 (8) 810, l = 1 cm. B) Phosphorescence spectra of **Pt3m** and **Pd3m** complexes in deaerated buffered water. [MOPS] = 0.01 M, pH = 7.2, T = 298 K in absence and presence of NaCl, μ_{eff} = 0.41 mol L^{-1}; C =1 x 10^{-5} M (for **Pt3m**); C =5 x 10^{-6} M (for **Pd3m**).

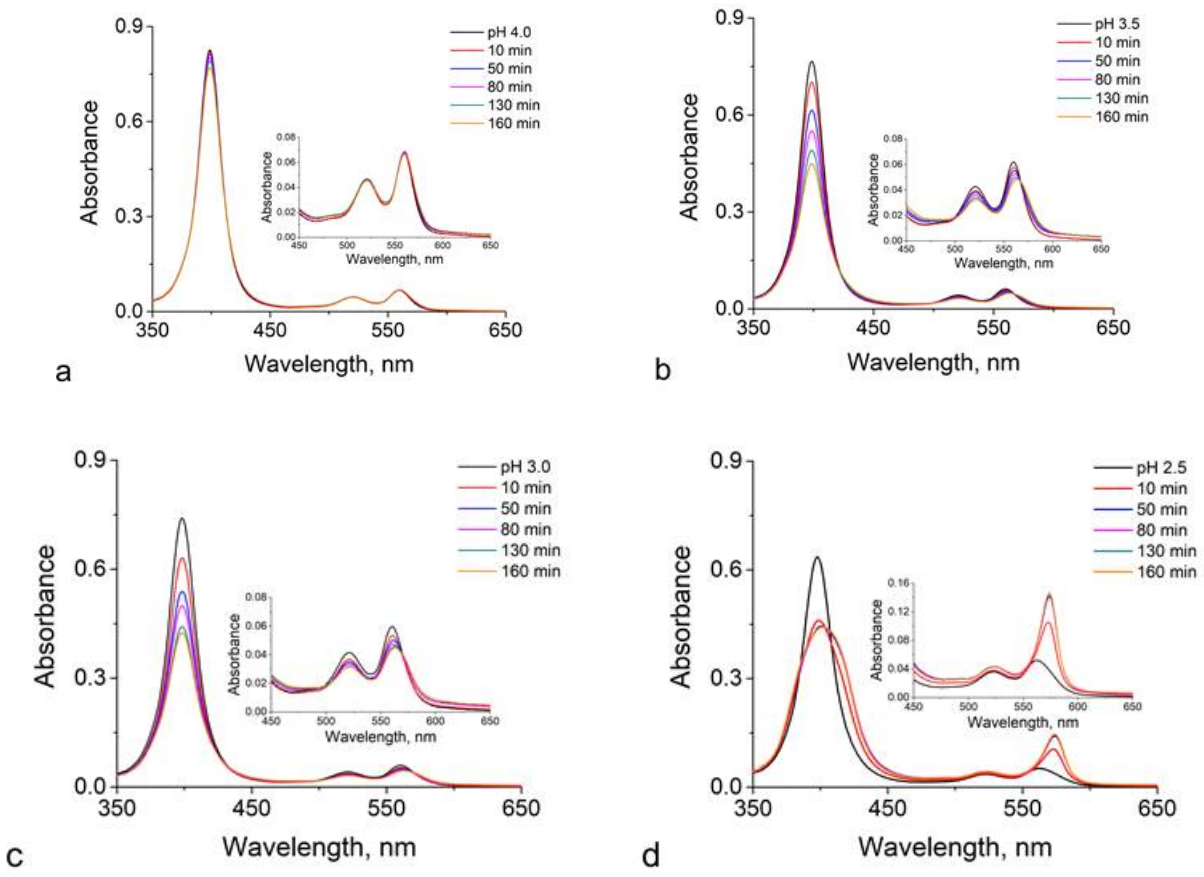


Figure S23. UV–vis spectra of **Pt3d** aqueous solution at pH (a) 4.0, (b) 3.5, (c) 3.0 and (d) 2.5. C = 5.4 μM, μ_{eff} = 0.1 mol L^{-1} NaCl.

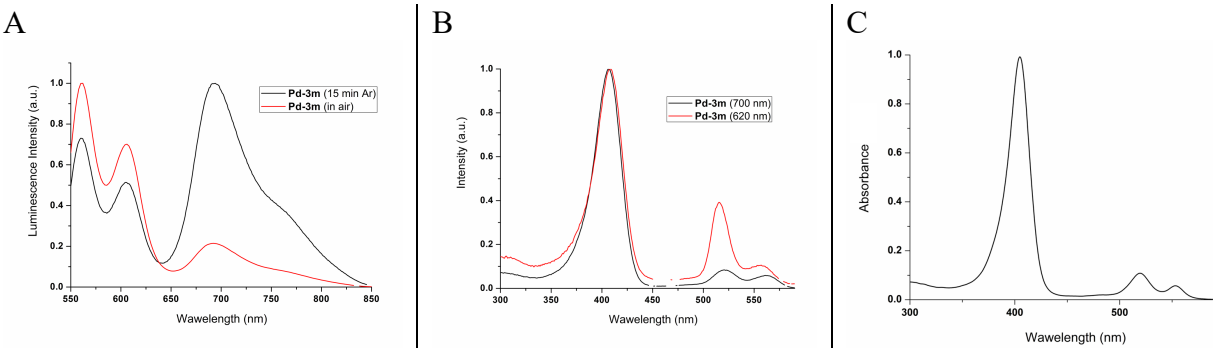


Figure S24. Emission (λ_{ex} = 520 nm) (A), excitation (B, with detection in the fluorescence band (red) and the phosphorescence band (black)) and UV–vis spectra of **Pd3m** in 0.01 M MOPS buffer. pH 7.2 C = $1x10^{-6}$ μM. Emission and excitation spectra were acquired on a Jasco Spectrofluorimeter FP-8300.

6. Spectrophotometric titration of Pt3d

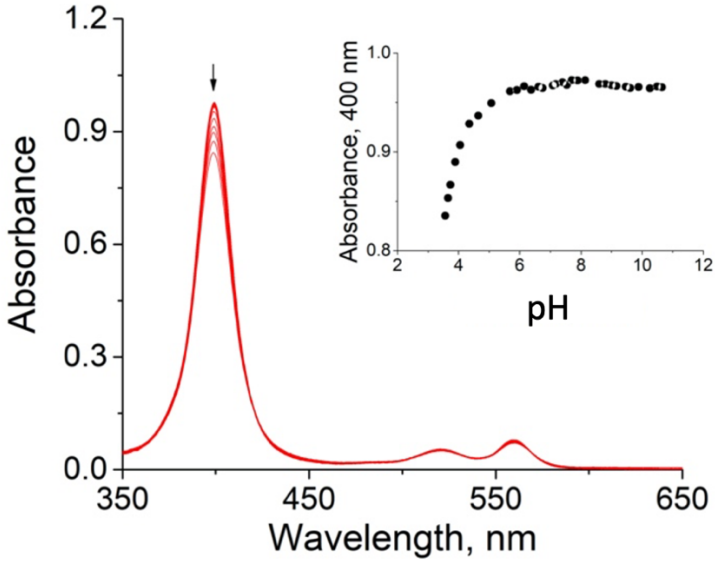


Figure S25. Spectrophotometric titration of **Pt3d** aqueous solution as a function of p[H]. C = 4.6 μM, spectra 1–30 (red): pH = 10.65–3.57; μ_{eff} = 0.1 mol L^{-1} NaCl.

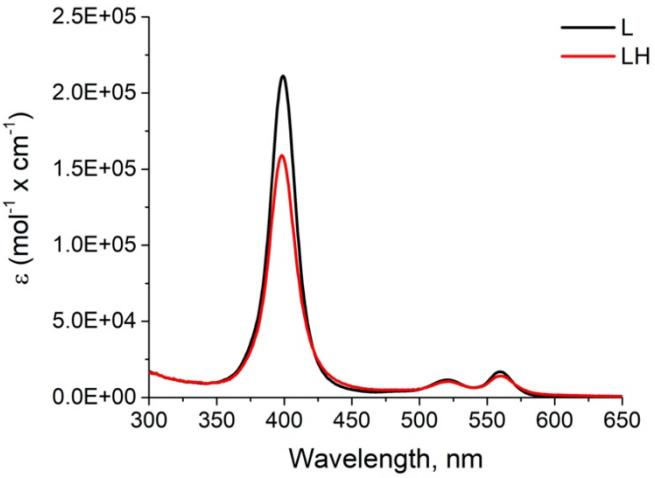


Figure S26. Calculated with the HypSpec program UV–vis spectra of the protonated species of **Pt3d** (L) in aqueous solution.

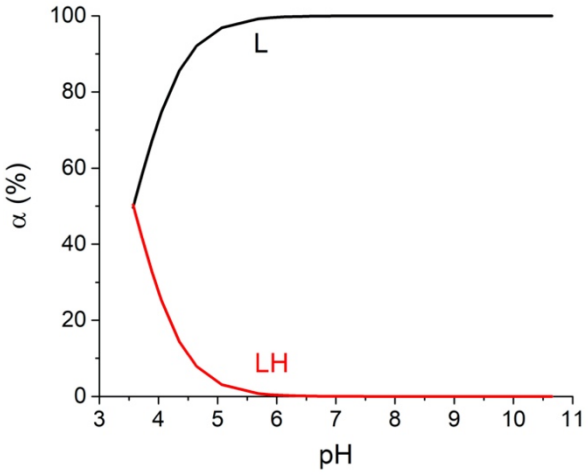


Figure S27. Distribution diagram of the protonated species of **Pt3d** (L) calculated with the HypSpec program based on UV–vis spectra.

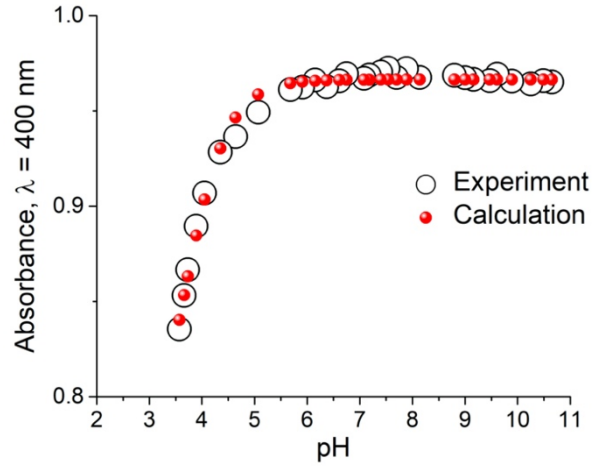


Figure S28. pH-Induced variation of the absorbance intensity corresponding to the absorption maximum 400 nm.

Converged in 1 iterations with sigma = 1.3827E-03

		standard
Log beta	value	deviation
LH	3.5769	0.0055

7. Studies on the single oxygen generation

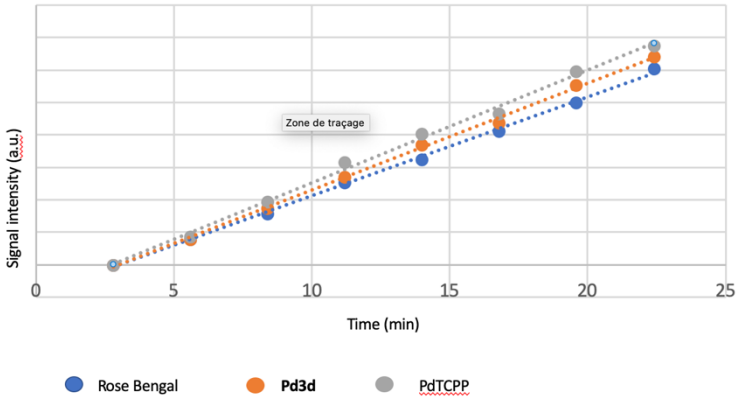


Figure S29. Kinetics of 4-oxo-TEMPO generation in the presence of Pd3d, PdTCPP and Rose Bengal in aqueous solution determined by EPR spectroscopy.

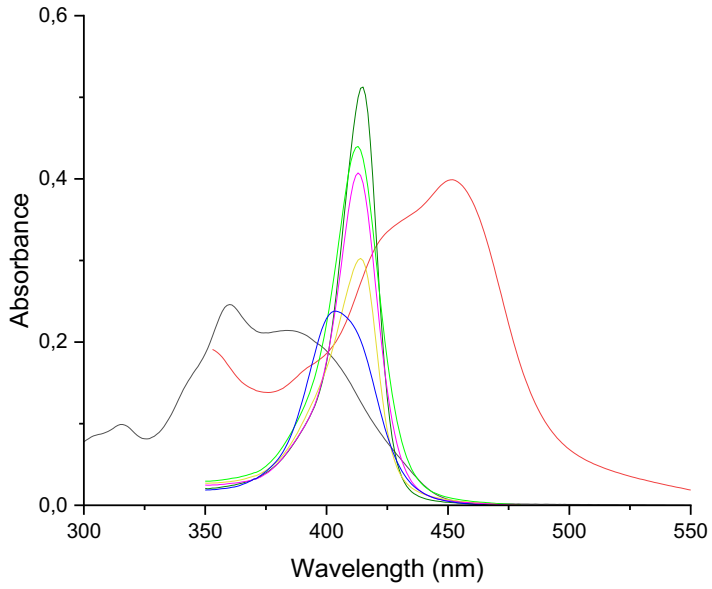


Figure S30. Absorption spectra of the stock-solution in MeCN/H_2O (4:1 v/v) of PSs used in the ADPA photoinduced decay experiments. Phenalenone (**PH**) (black); $[Ru(bpy)_3]Cl_2$ (red); **Pd1d** (blue); **Pd2d** (magenta); **Pd3d**(1) (dark green/olive); **Pd3d**(2) (light green) **PdTCPP** (gold).

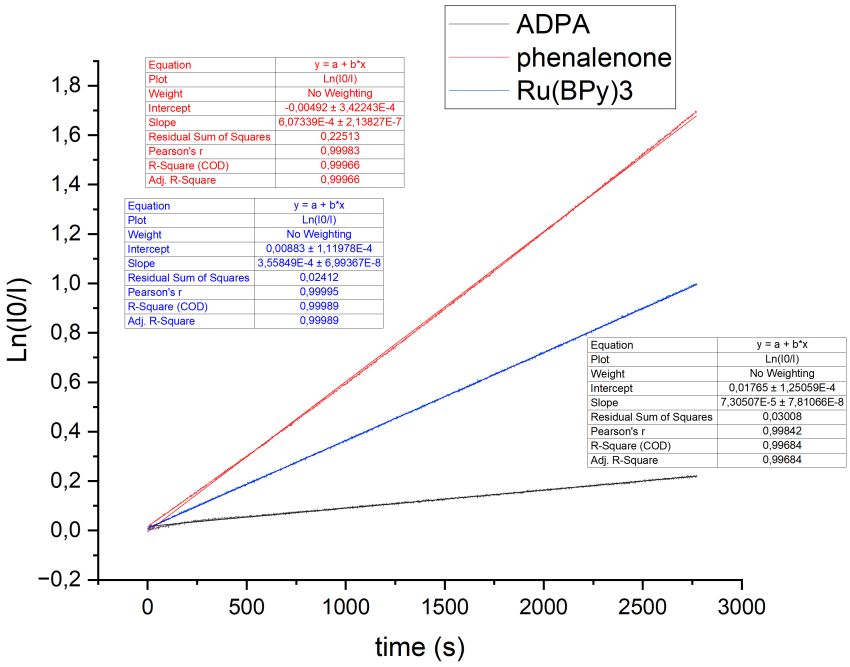


Figure S31. Linear regressions and fits obtained in the kinetic following of ADPA photoinduced oxidation with isoabsorbing solutions of ADPA alone (black), phenalenone (**PH**) (red), $[Ru(bpy)_3]Cl_2$ (blue).

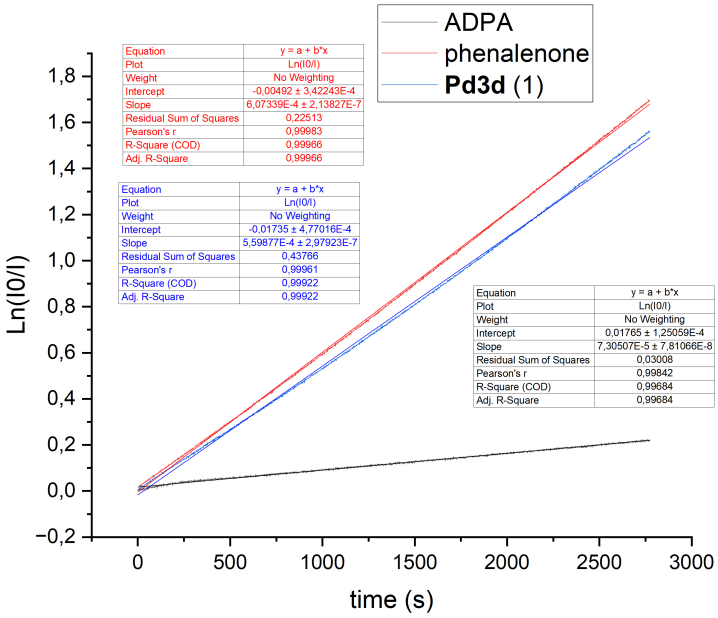


Figure S32. Linear regressions and fits obtained in the kinetic following of ADPA photoinduced oxidation with isoabsorbing solutions of ADPA alone (black), phenalenone (red), **Pd3d** (1) (blue).

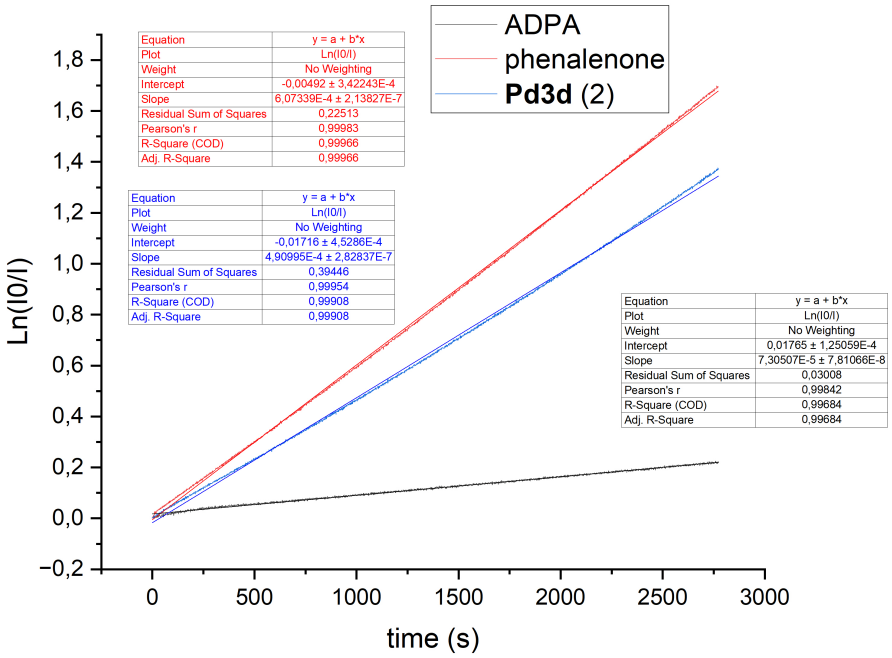


Figure S33. Linear regressions and fits obtained in the kinetic following of ADPA photoinduced oxidation with isoabsorbing solutions of ADPA alone (black), phenalenone (red), **Pd3d** (2) (blue).

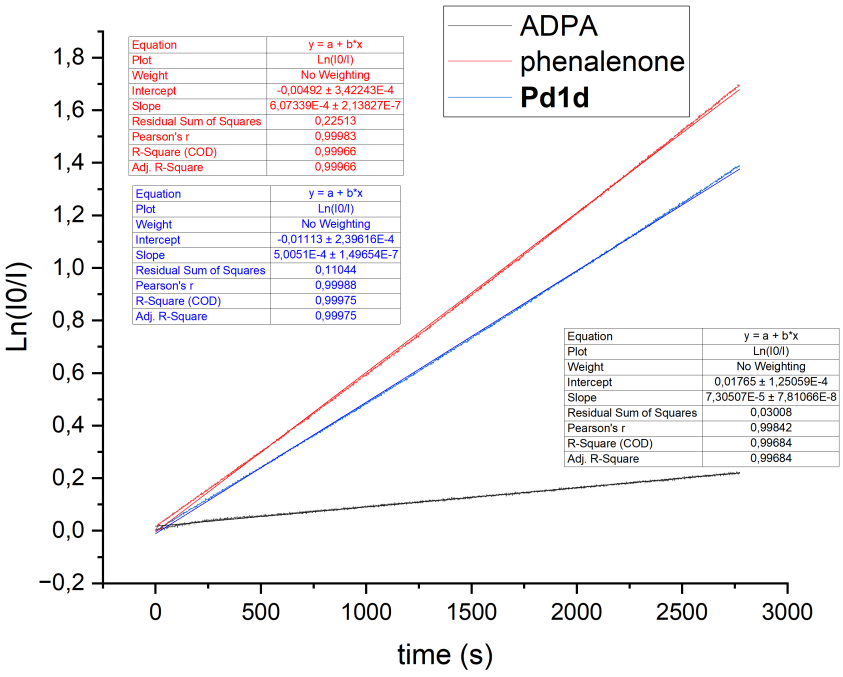


Figure S34. Linear regressions and fits obtained in the kinetic following of ADPA photoinduced oxidation with isoabsorbing solutions of ADPA alone (black), phenalenone (red), **Pd1d** (1) (blue).

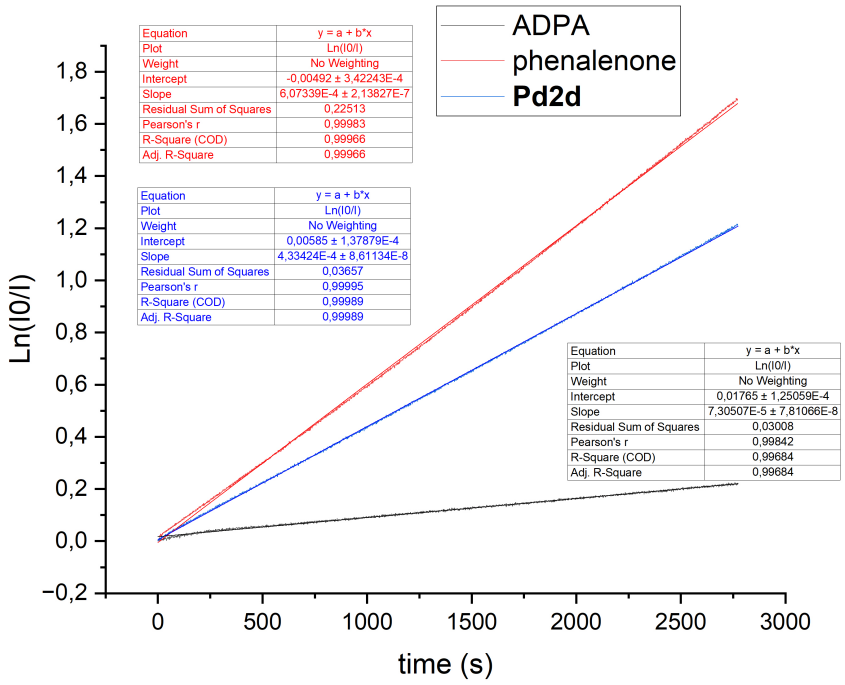


Figure S35. Linear regressions and fits obtained in the kinetic following of ADPA photoinduced oxidation with isoabsorbing solutions of ADPA alone (black), phenalenone (red), **Pd2d** (blue).

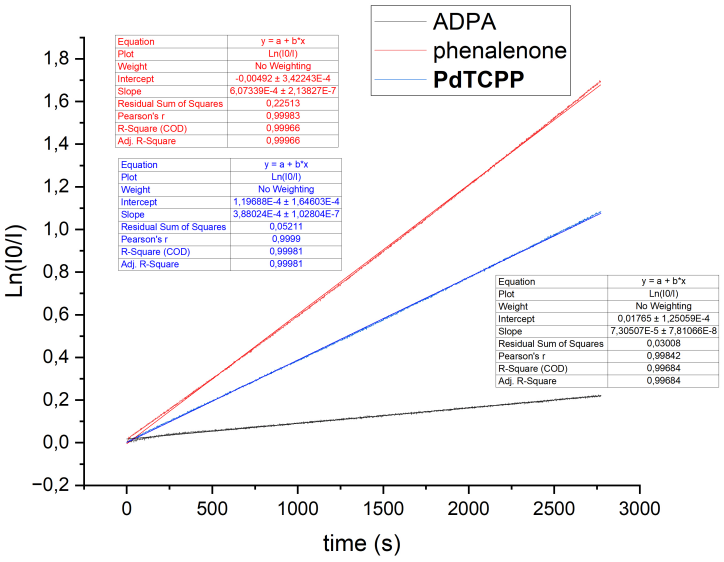


Figure S36. Linear regressions and fits obtained in the kinetic following of ADPA photoinduced oxidation with isoabsorbing solutions of ADPA alone (black), phenalenone (red), **PdTCPP** (blue).

8. Photostability studies

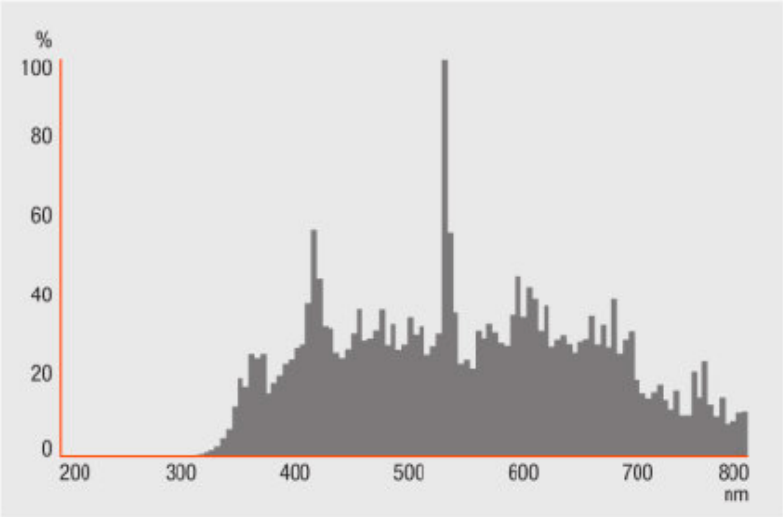


Figure S37. Optical emission spectrum of the 400 W Powerstat HQI BT MM (Osram) tungsten lamp used for the photobleaching studies (picture provided by the courtesy of the manufacturer).

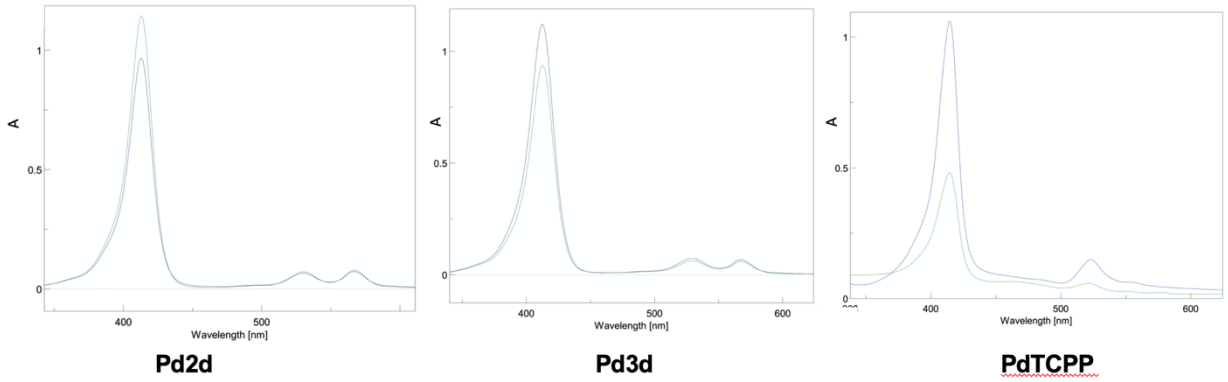
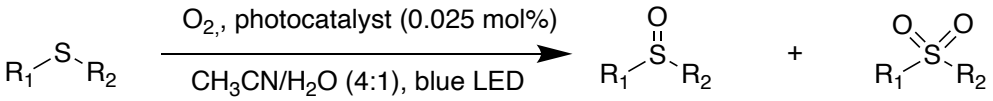
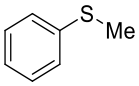
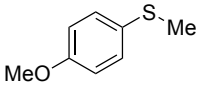
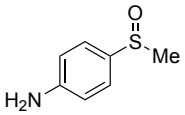
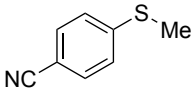
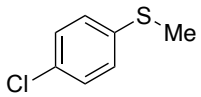
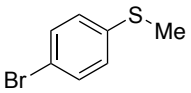
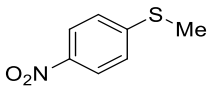


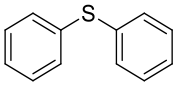
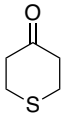
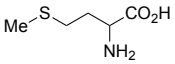
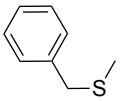
Figure S38. Photodegradation of **Pd2d**, **Pd3d** and PdTCPP in MeCN/H_2O (4:1 v/v) mixture under blue LED (425 nm, 18 W) irradiation in EvoluChem Photoredox box.

9. Photocatalytic oxidation of sulfides

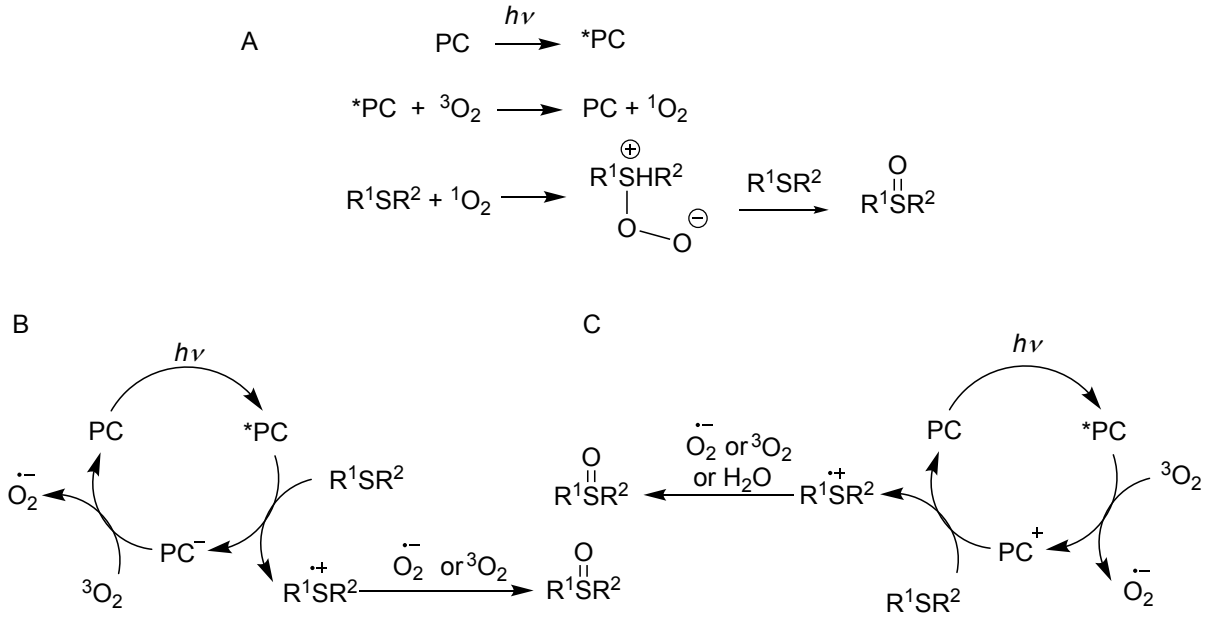
Table S7. Photooxidation of sulfides in the presence of **Pd3d** and PdTCPP.[a]



Entry	Sulfide	Photo-catalyst	Time (h)	Conversion[b] (%)	Yield[b] (%)	
					Sulfoxide	Sulfone
1		**Pd3d**	1	100	98	2
2		PdTCPP	1	100	98	2
						2
3		**Pd3d**	1.25	100	98	2
4		PdTCPP	1.25	95		
			1.5	100	98	2
5		**Pd3d**	2.5	91		
			3.5	100	99	1
6		PdTCPP	2.5	52		
			5	78		
			8	98	97	1
7		**Pd2d**	2.5	77		
			5	100	99	1
8		**Pd3d**	1.5	100	98	2
9		PdTCPP	1.5	100	98	2
10		**Pd2d**	1.5	100	98	2
11		**Pd3d**	1	100	99	1
12		PdTCPP	1	58		
			3.5	100	99	1
13		**Pd3d**	1	100		
14		PdTCPP	1	53		
			3.5	100		
15		**Pd3d**	24	35	33	0
16		PdTCPP	24	20	20	0
17		**Pd3d**	2	98		
			2.5	100	99	1
18		PdTCPP	2	84		
			2.5	95		
			3.5	99	98	1

19		**Pd3d**	1.7	71		
			3.5	100	99	1
20		PdTCPP	1.7	25		
			3.5	66		
			4.5	90		
			8	100	99	1
		Pd2d	1.7	73		
21			3.5	100	99	1
22		**Pd3d**	1.5	81		
23			3.5	100	97	3
		PdTCPP	1.5	100		
24		**Pd3d**	20	42	42	0
25[c]			3.5	100	99	1
26		**Pd3d**	3	100	100	
27		**Pd3d**	2	100	98	2

[a] Reaction conditions: 0.5 mmol of sulfide and PS (0.025 mol%) were stirred and irradiated by blue LED (425 nm, 18 W) in MeCN/H_2O mixture (2.5 mL, 4:1, v/v) under di-oxygen (balloon, V = 1L) in EvoluChem Photoredox box. [b] Conversion and selectivity were determined by ^1H NMR analysis of reaction mixtures using biphenyl as an internal standard. [c] 0.09 mol% of PS



Scheme S1. Representation of mechanisms of photocatalytic oxidation of sulfides by molecular oxygen proceeding through energy transfer (A) and electron transfer (B and C).

10. Spectral characterization of porphyrins

a. NMR spectra

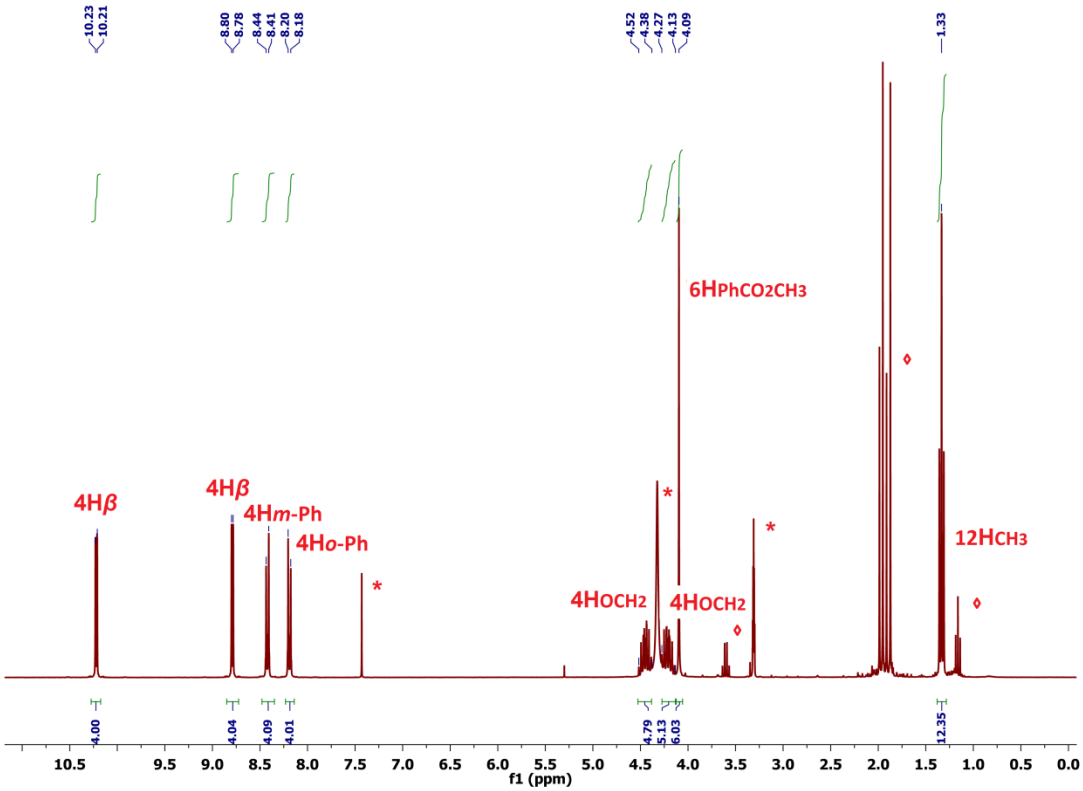


Figure S39. ^{1}H NMR spectrum of **Pd3d** in the mixture of $CDCl_3/CD_3OD$ (2:1, v/v). Solvent peaks are indicated with * (δ_H 7.43 ppm – $CHCl_3$, δ_H 5.32 ppm – CH_2Cl_2, δ_H 4.32 ppm –DOH and H_2O, δ_H 3.33 ppm – CHD_2OD). Solvent impurity peaks are indicated with ◊.

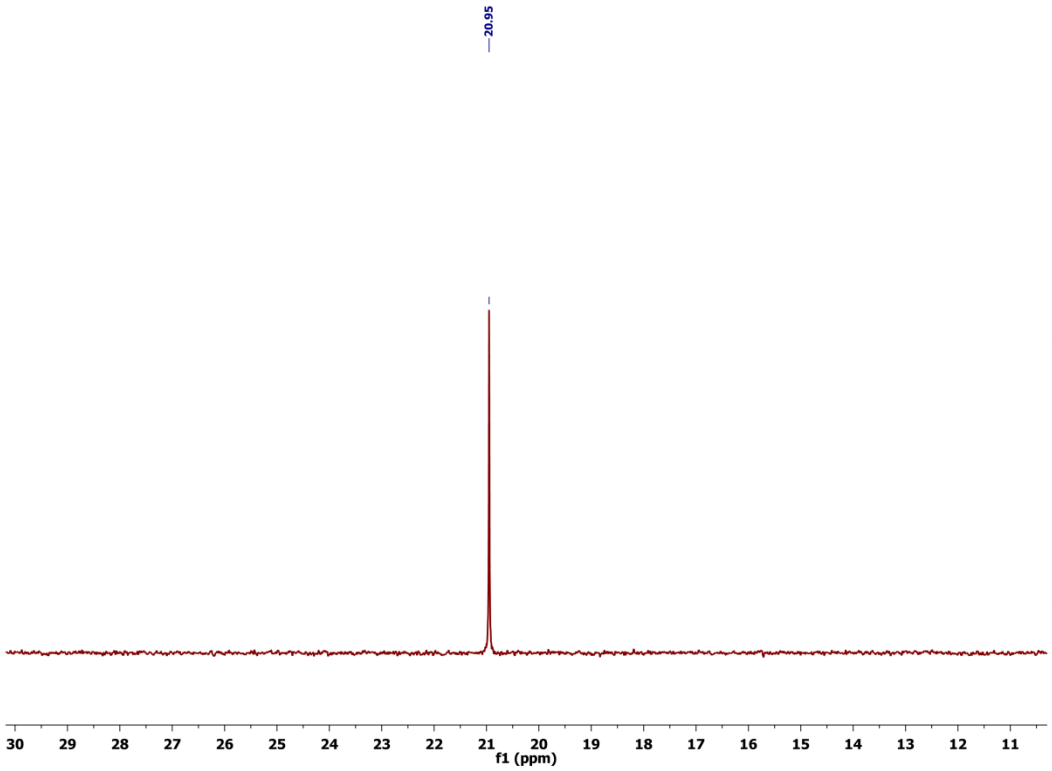


Figure S40. ^{31}P NMR spectrum of **Pd3d** in the mixture of $CDCl_3/CD_3OD$ (2:1, v/v).

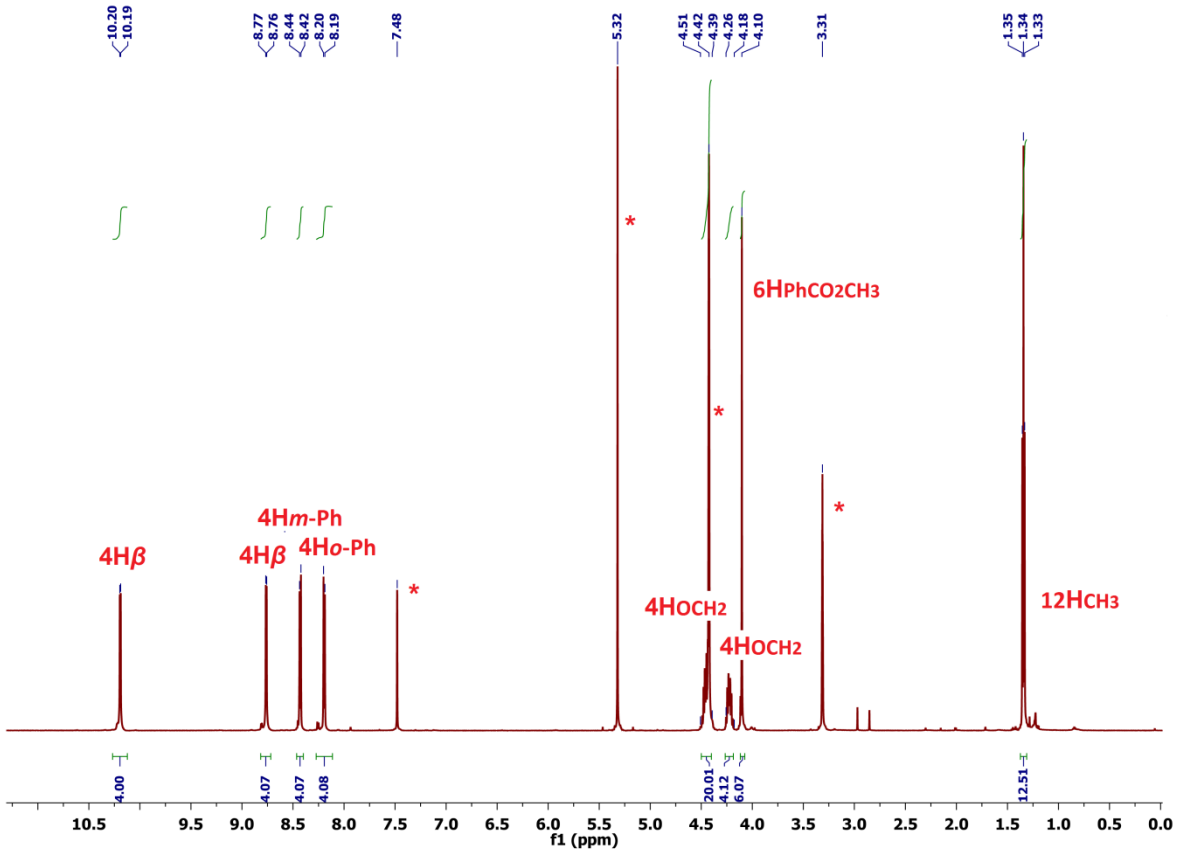


Figure S41. ^{1}H NMR spectrum of **Pt3d** in the mixture of $CDCl_3/CD_3OD$ (2:1, v/v). Solvent peaks are indicated with * (δ_H 7.48 ppm – $CHCl_3$, δ_H 5.32 ppm – CH_2Cl_2, δ_H 4.2 ppm –DOH and H_2O, δ_H 3.33 ppm – CHD_2OD).

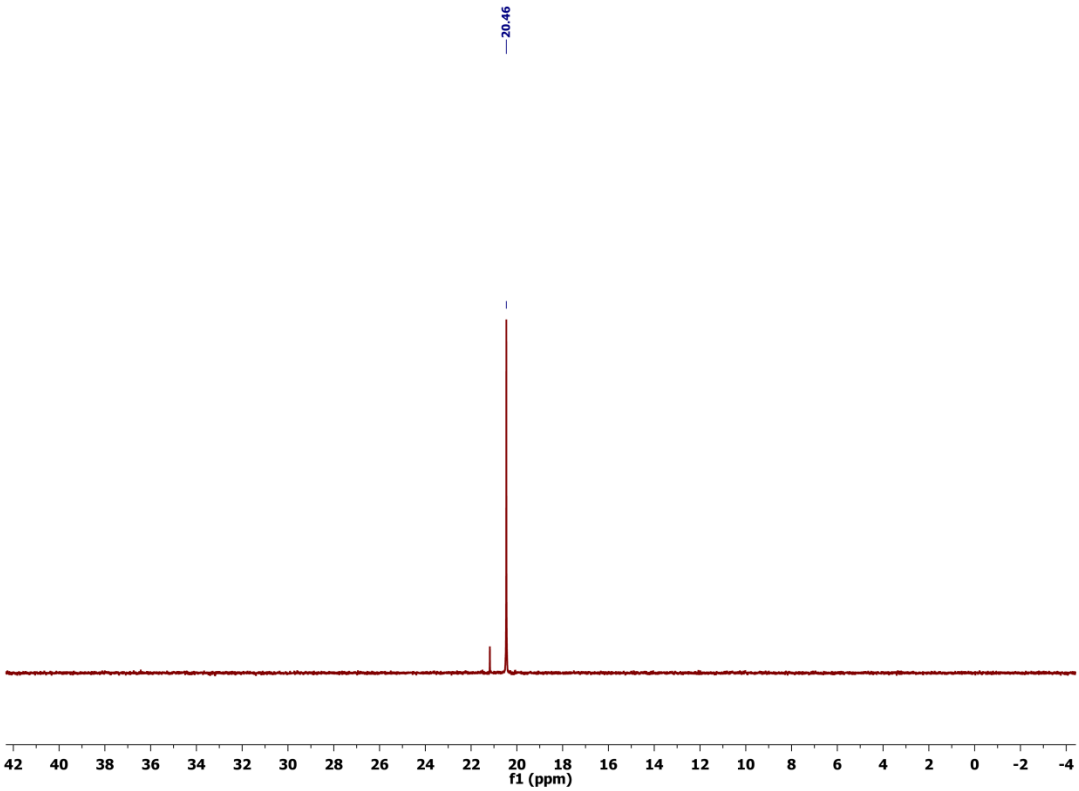


Figure S42. ^{31}P NMR spectrum of **Pt3d** in the mixture of $CDCl_3/CD_3OD$ (2:1, v/v).

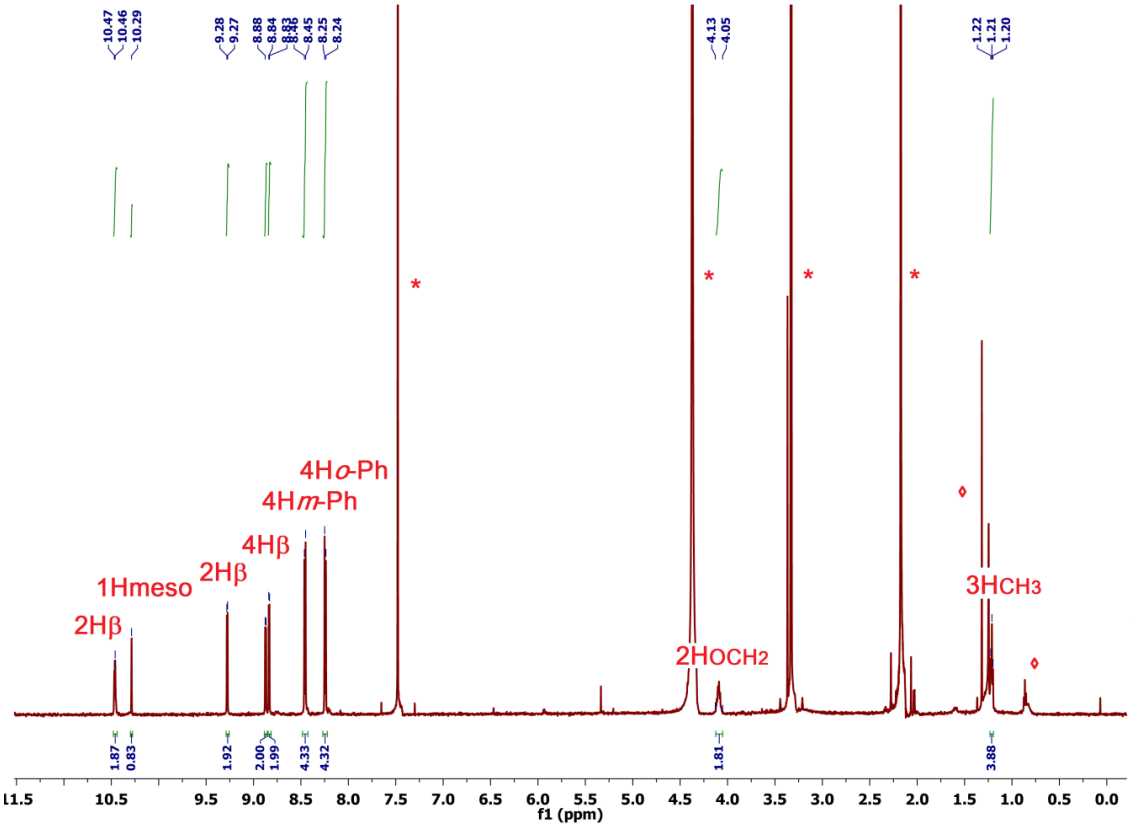


Figure S43. ^{1}H NMR spectrum of **Pd3m** in the mixture of $CDCl_3/CD_3OD$ (1:1, v/v). Solvent peaks are indicated with * (δ_H 7.48 ppm – $CHCl_3$, δ_H 5.32 ppm – CH_2Cl_2, δ_H 4.37 ppm –DOH and H_2O, δ_H 3.33 ppm – CHD_2OD, δ_H 2.17 ppm –C_2H_5OH). Solvent impurity peaks are indicated with ◊.

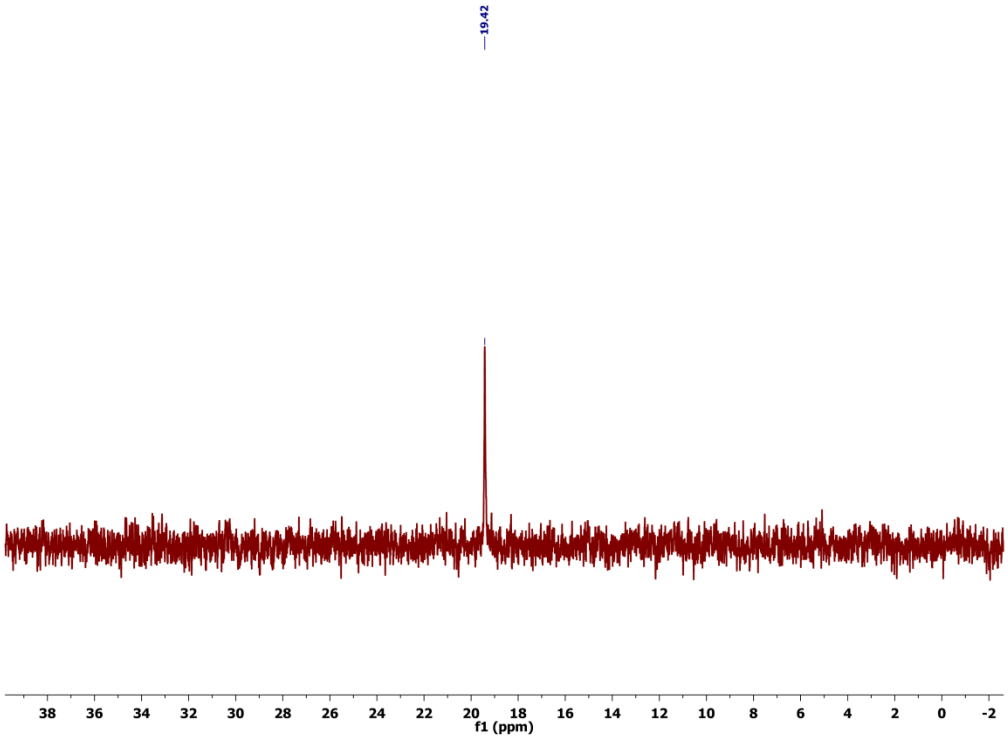


Figure S44. ^{31}P NMR spectrum of **Pd3m** in the mixture of $CDCl_3/CD_3OD$ (1:1, v/v).

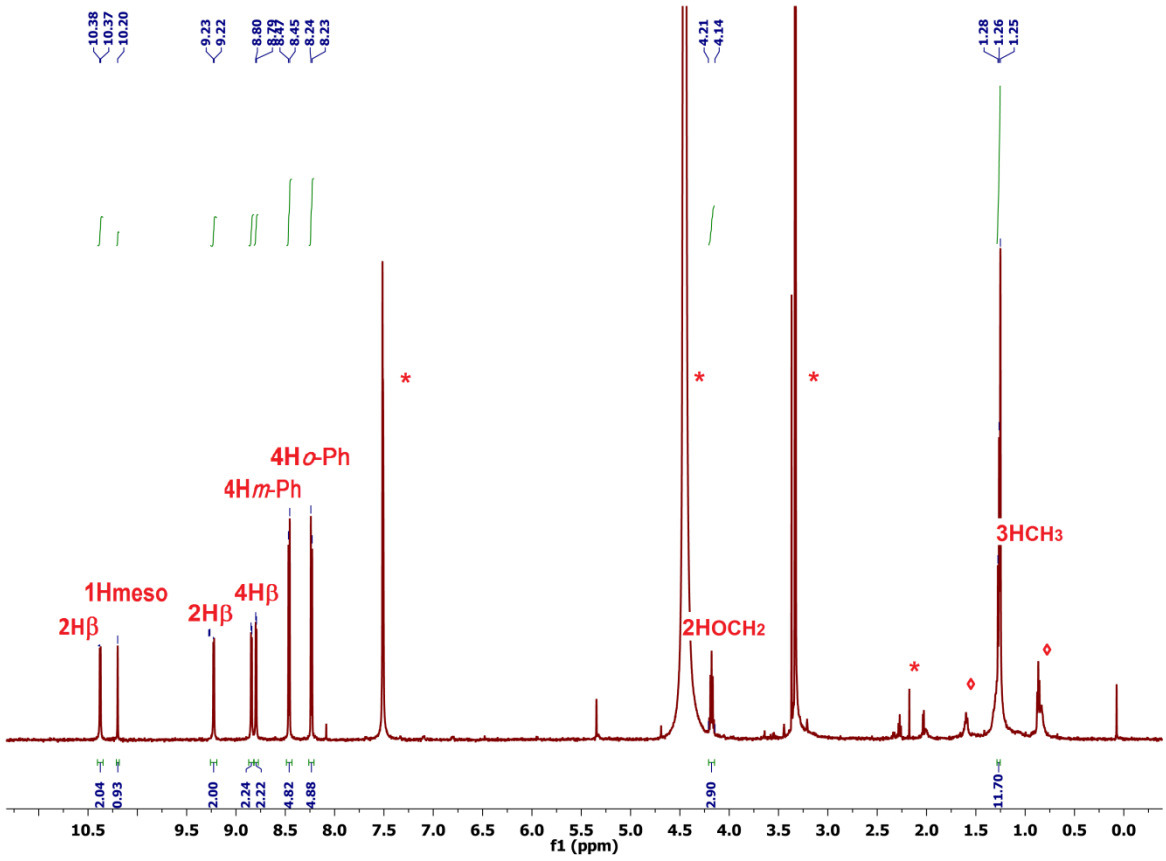


Figure S45. ^{1}H NMR spectrum of **Pt3m** in the mixture of $CDCl_3/CD_3OD$ (1:1, v/v). Solvent peaks are indicated with * (δ_H 7.51 ppm – $CHCl_3$, δ_H 5.32 ppm – CH_2Cl_2, δ_H 4.46 ppm –DOH and H_2O, δ_H 3.33 ppm – CHD_2OD, δ_H 2.17 ppm –C_2H_5OH). Solvent impurity peaks are indicated with ◊.

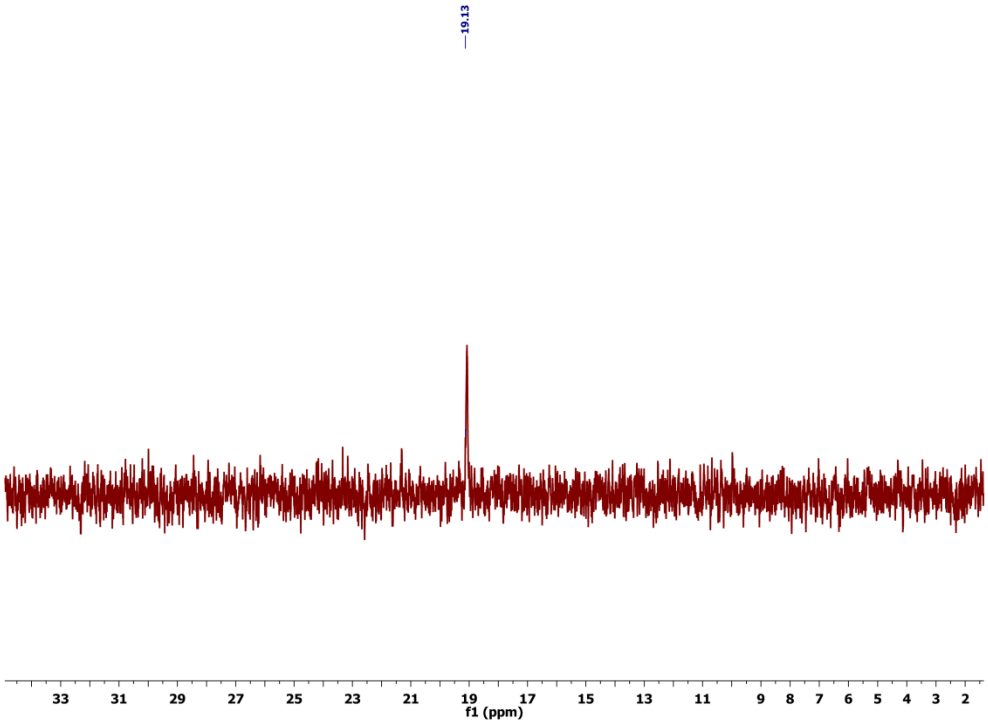


Figure S46. ^{31}P NMR spectrum of **Pt3m** in the mixture of $CDCl_3/CD_3OD$ (1:1, v/v).

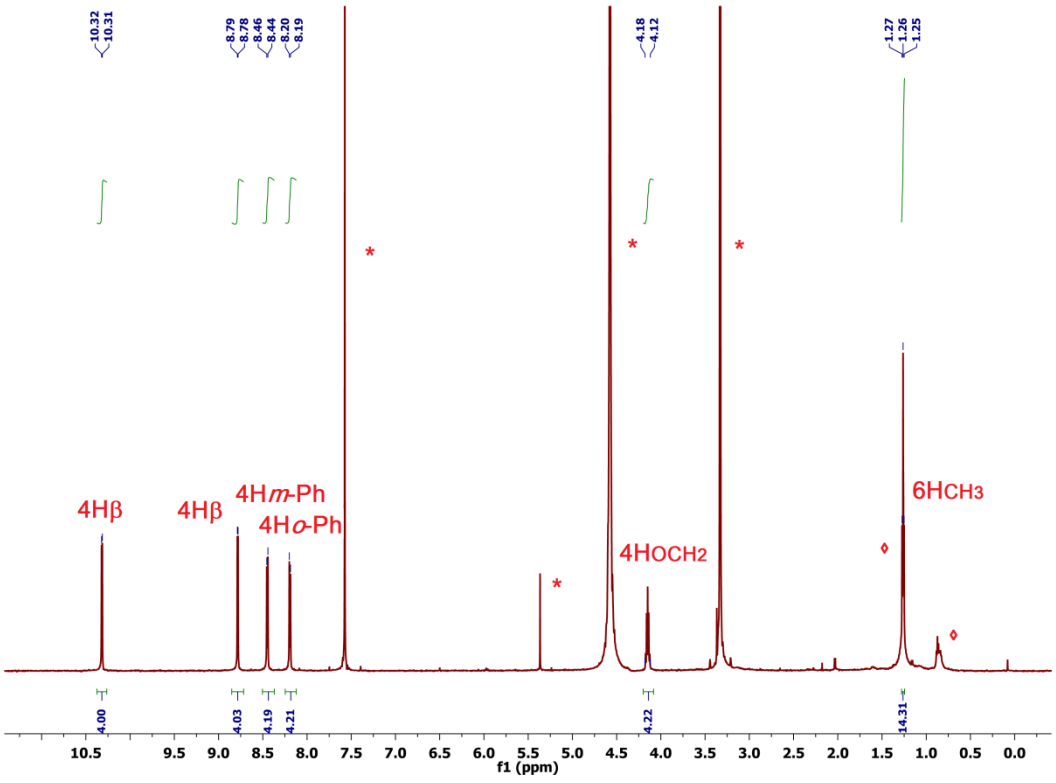


Figure S47. ^{1}H NMR spectrum of **Pd3d** in the mixture of $CDCl_3/CD_3OD$ (1:1, v/v). Solvent peaks are indicated with * (δ_H 7.57 ppm – $CHCl_3$, δ_H 5.37 ppm – CH_2Cl_2, δ_H 4.58 ppm –DOH and H_2O, δ_H 3.33 ppm – CHD_2OD, δ_H 1.25 ppm –DOH and H_2O). Solvent impurity peaks are indicated with ◊.

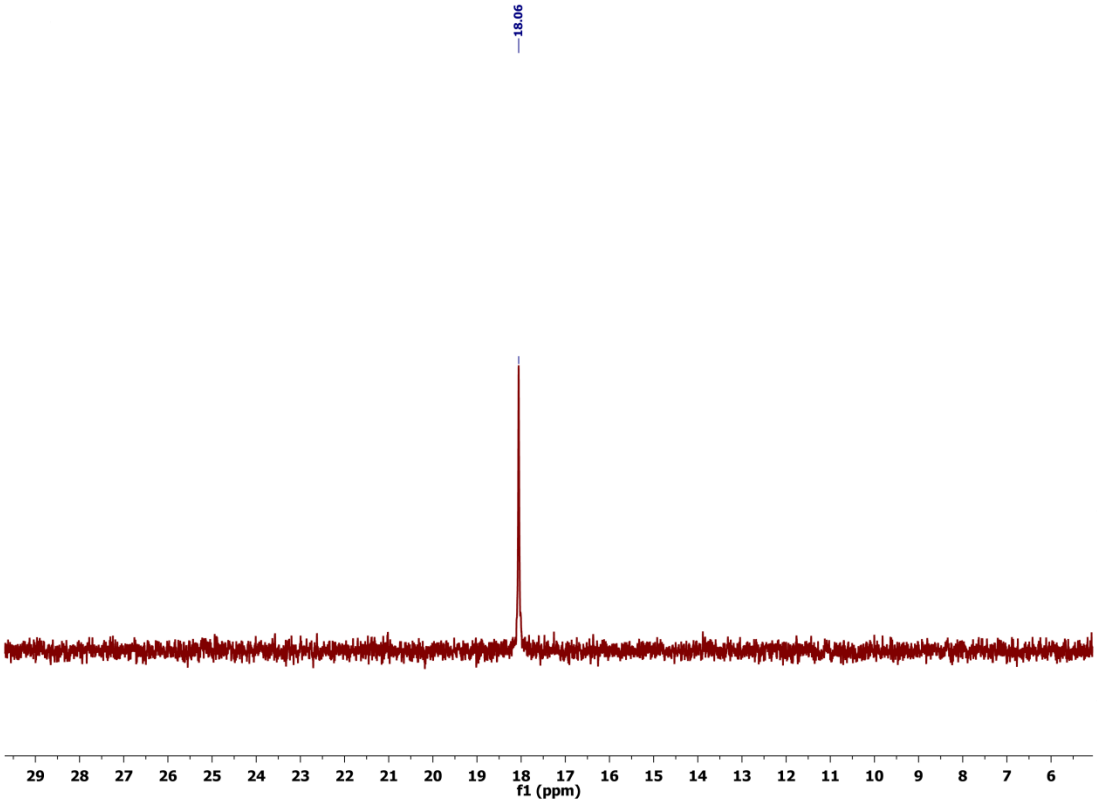


Figure S48. ^{31}P NMR spectrum of **Pd3d** in the mixture of $CDCl_3/CD_3OD$ (1:1, v/v).

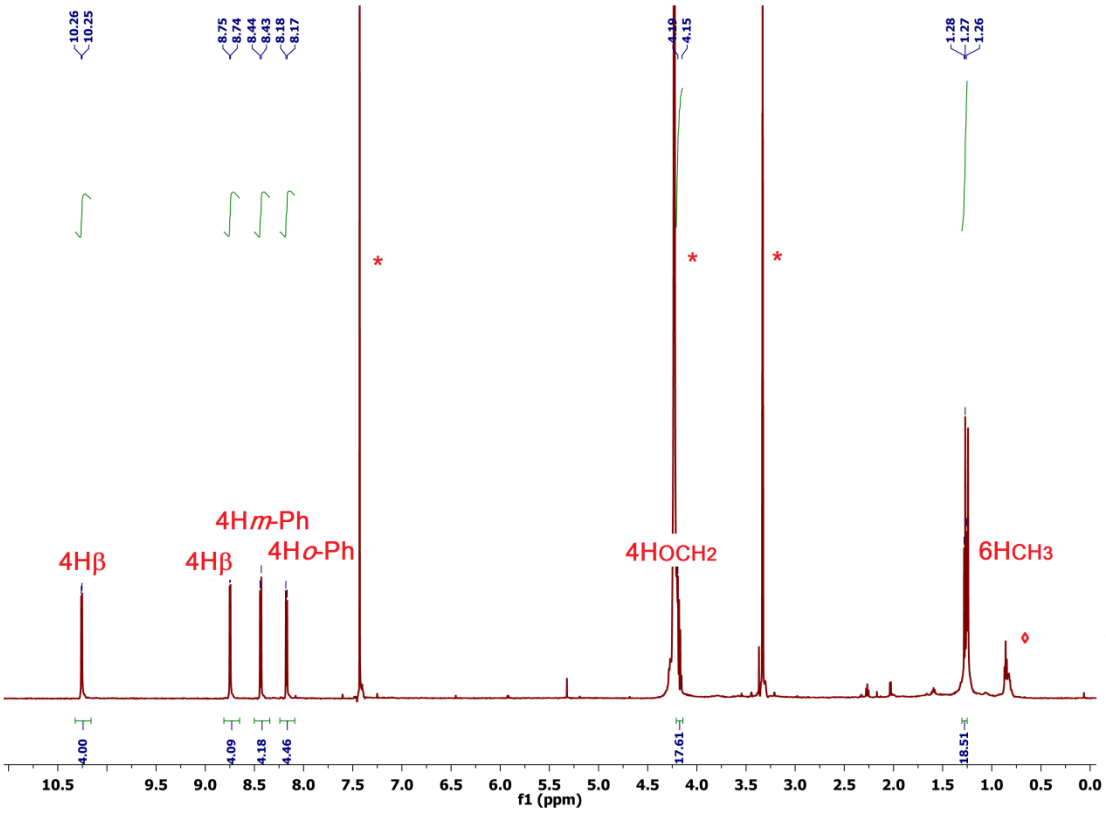


Figure S49. ^{1}H NMR spectrum of **Pt3d** in the mixture of $CDCl_3/CD_3OD$ (1:1, v/v). Solvent peaks are indicated with * (δ_H 7.43 ppm – $CHCl_3$, δ_H 5.32 ppm – CH_2Cl_2, δ_H 4.23 ppm –DOH and H_2O, δ_H 3.33 ppm – CHD_2OD, δ_H 1.24 ppm –DOH and H_2O). Solvent impurity peaks are indicated with ◊.

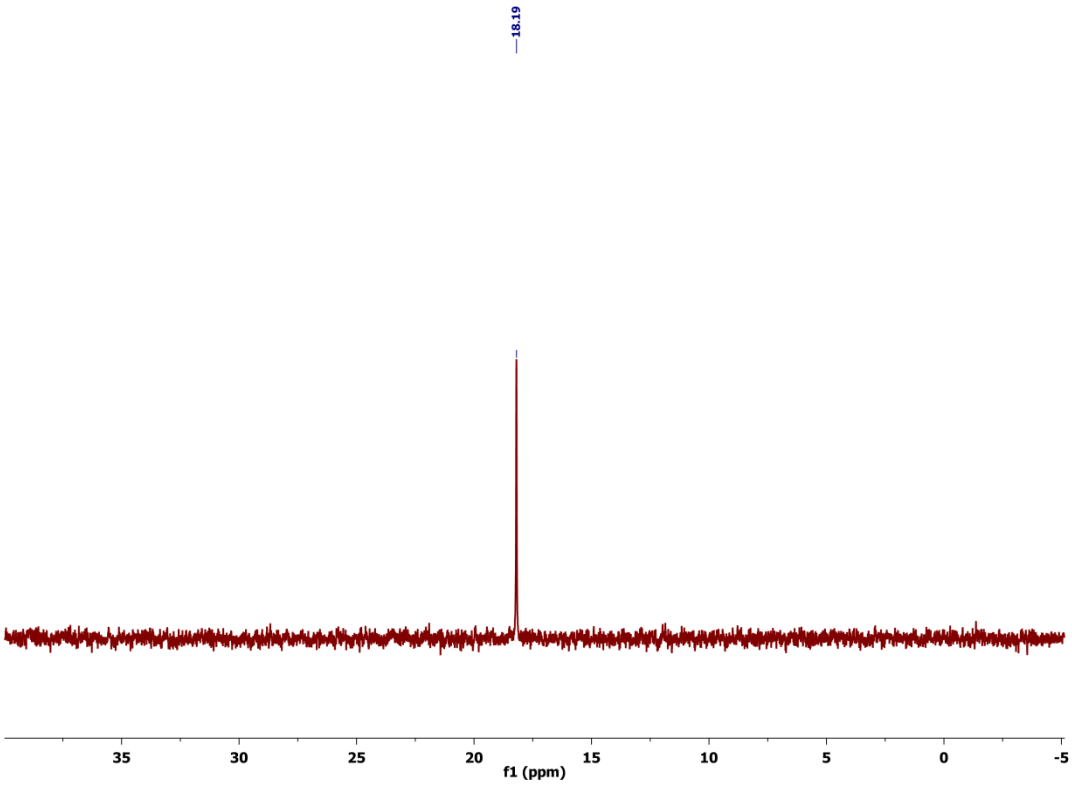


Figure S50. ^{31}P NMR spectrum of **Pt3d** in the mixture of $CDCl_3/CD_3OD$ (1:1, v/v).

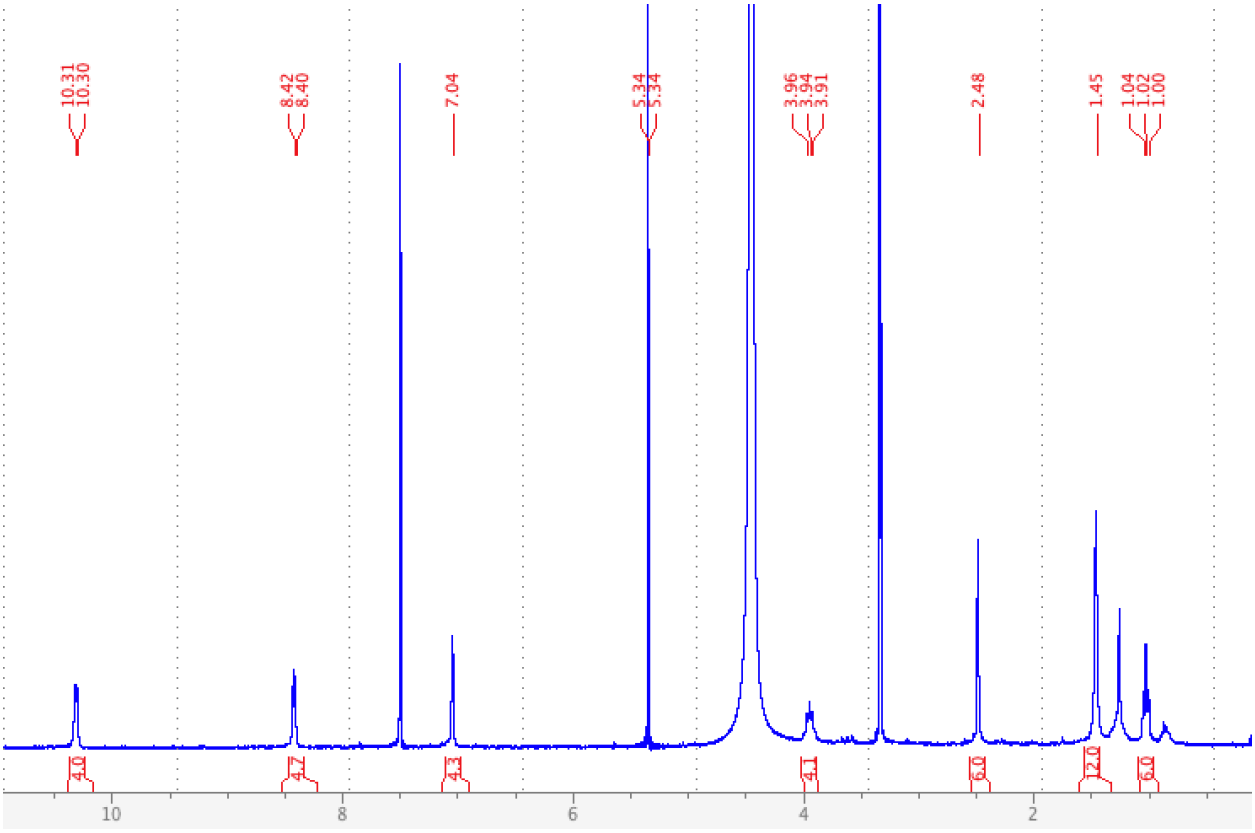


Figure S51. ^{1}H NMR spectrum of **Pd2d** in the mixture of $CDCl_3/CD_3OD$ (1:1, v/v).

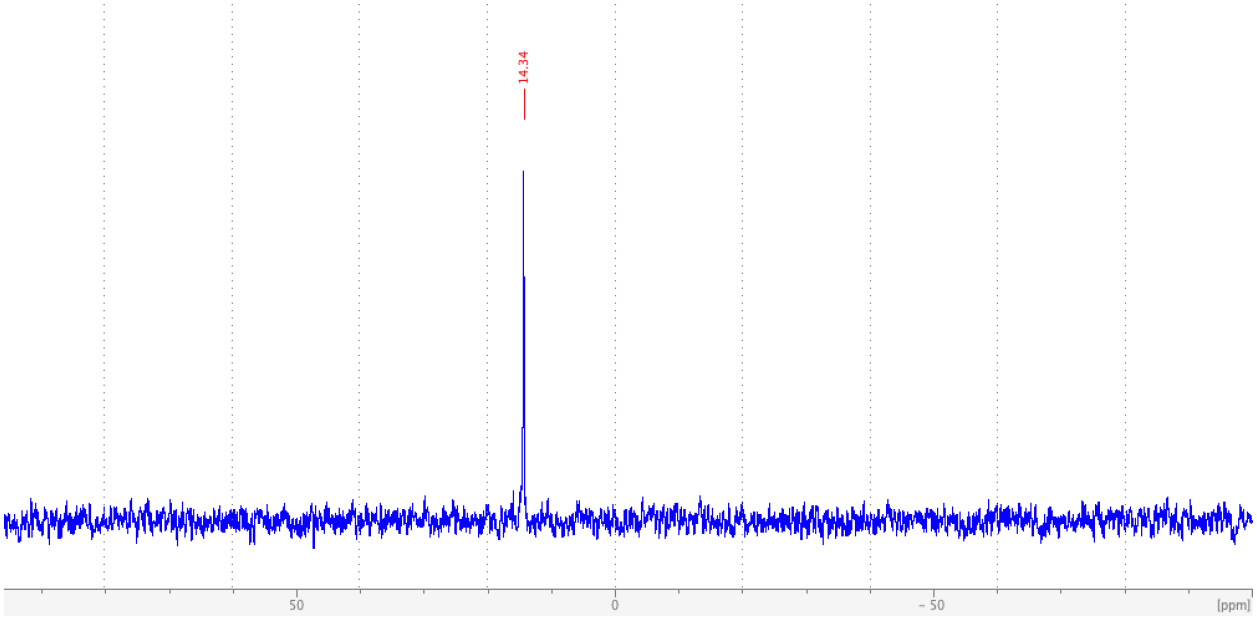


Figure S52. ^{31}P NMR spectrum of **Pd2d** in the mixture of $CDCl_3$/CD_3OD (1:1, v/v).

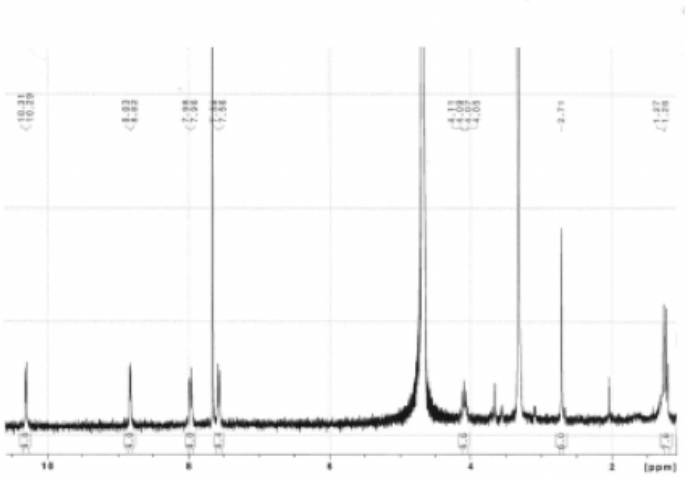


Figure S53. ^{1}H NMR spectrum of **Pd1d** in the mixture of $CDCl_3$/CD_3OD (1:1, v/v).

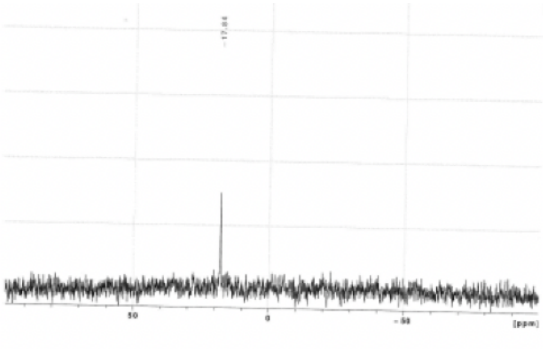


Figure S54. ^{31}P NMR spectrum of **Pd1d** in the mixture of $CDCl_3$/CD_3OD (1:1, v/v).

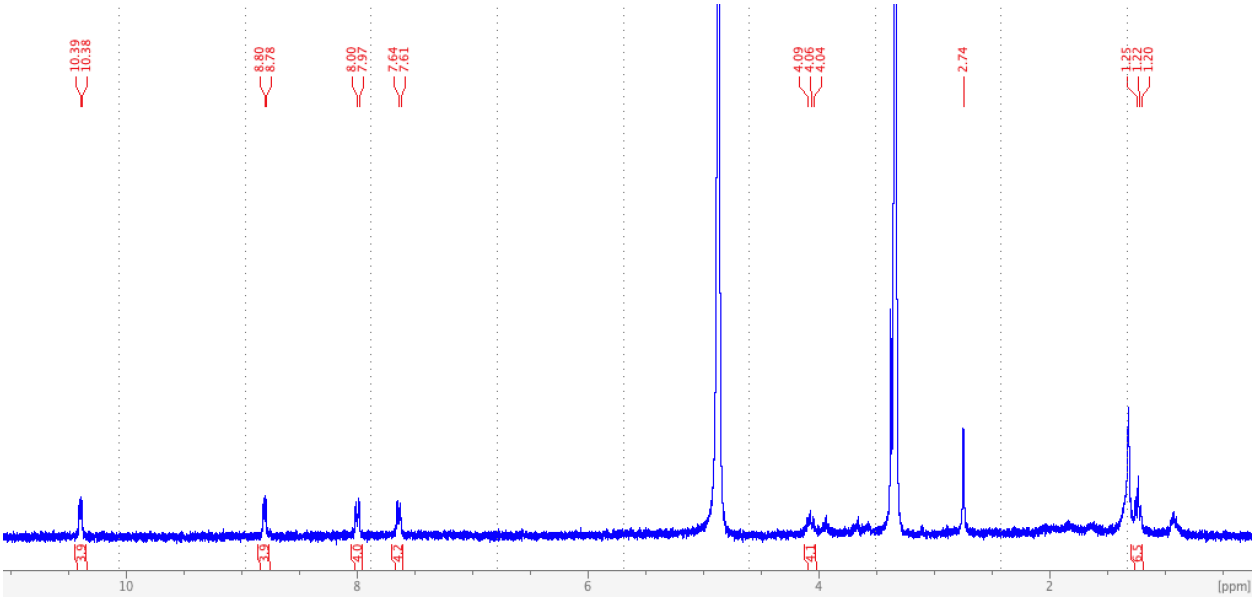


Figure S55. ^{1}H NMR spectrum of **Pt1d** in the mixture of $CDCl_3$/CD_3OD (1:1, v/v).

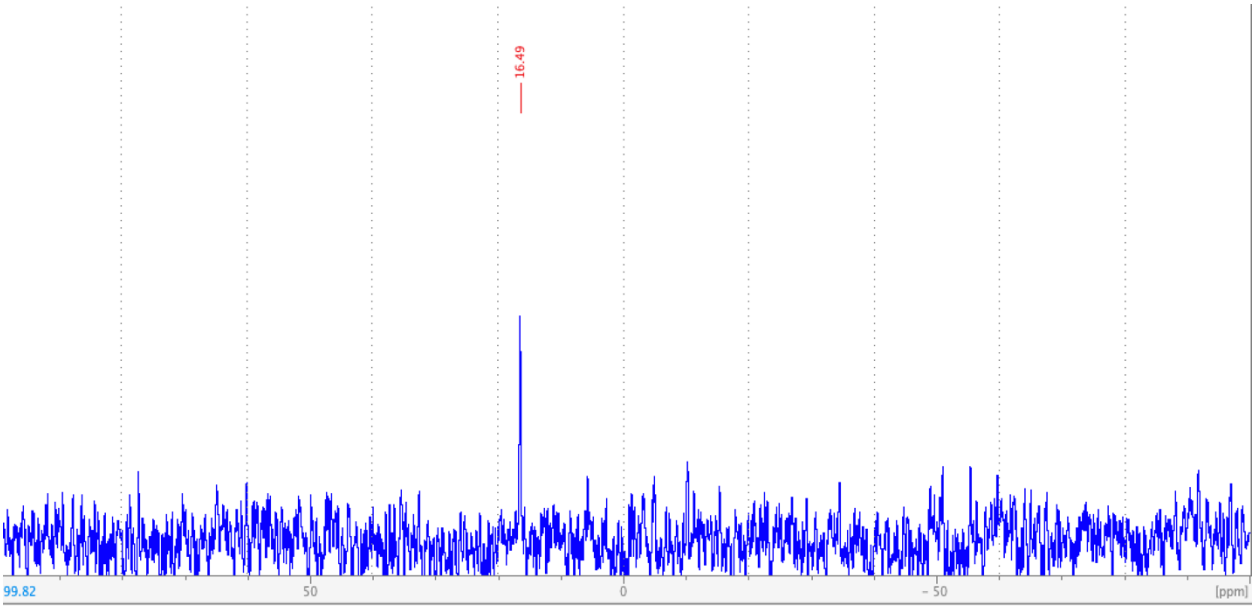


Figure S56. ^{31}P NMR spectrum of **Pt1d** in the mixture of $CDCl_3$/CD_3OD (1:1, v/v).

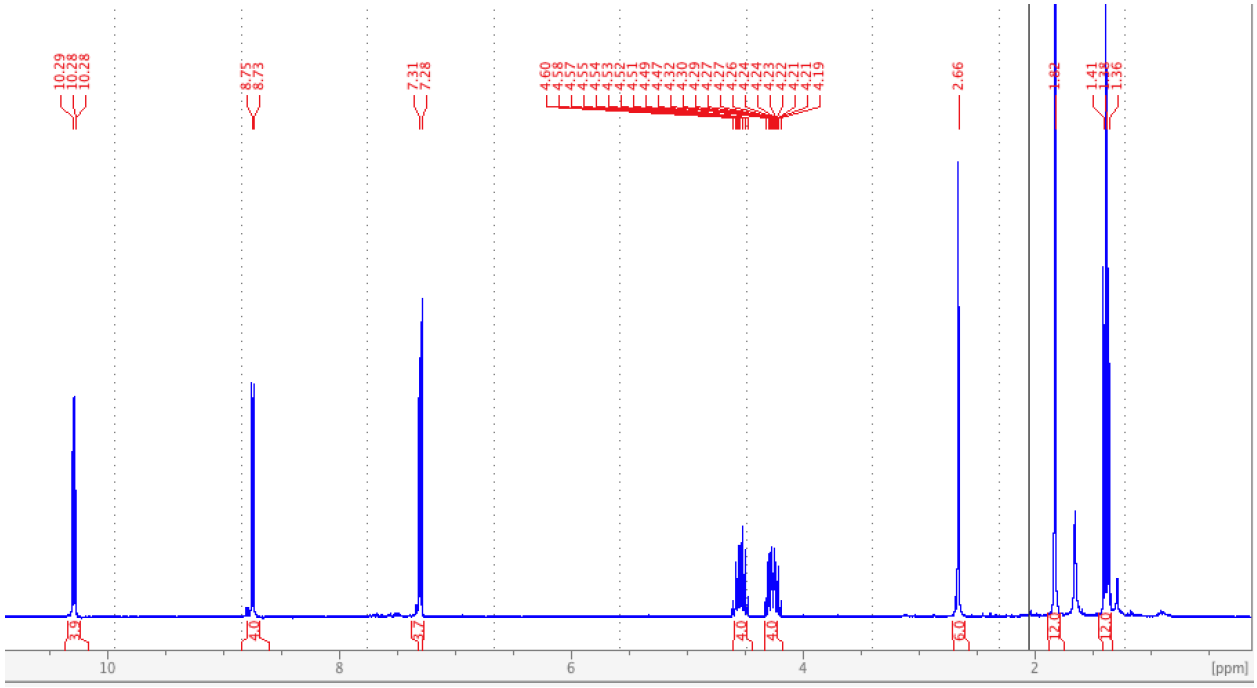


Figure S57. ^{1}H NMR spectrum of **Pd5d** in the mixture of $CDCl_3$/CD_3OD (2:1, v/v).

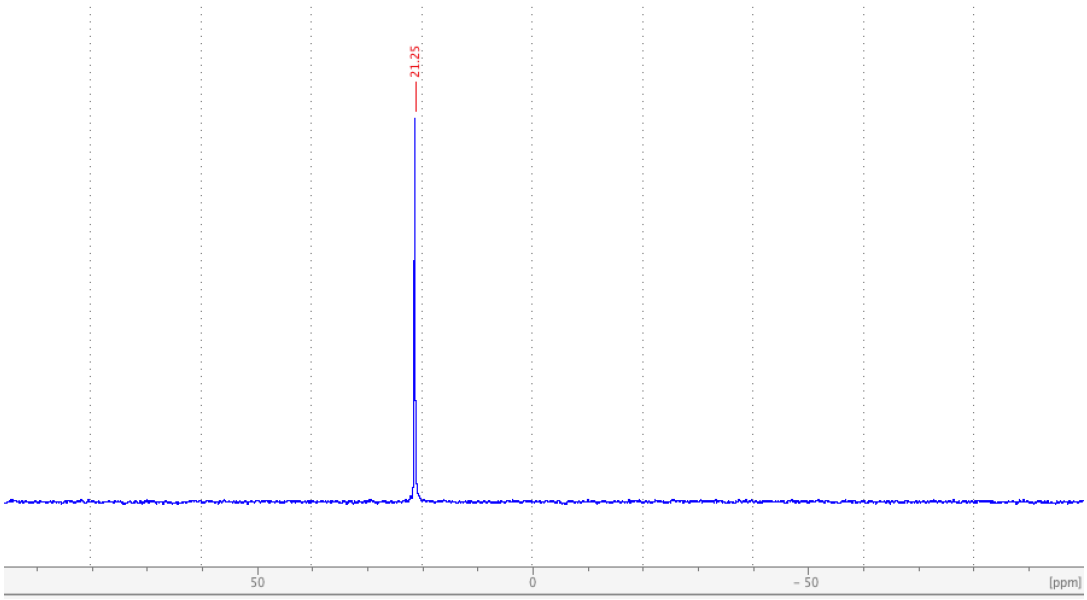


Figure S58. ^{31}P NMR spectrum of **Pd5d** in the mixture of $CDCl_3$/CD_3OD (2:1, v/v).

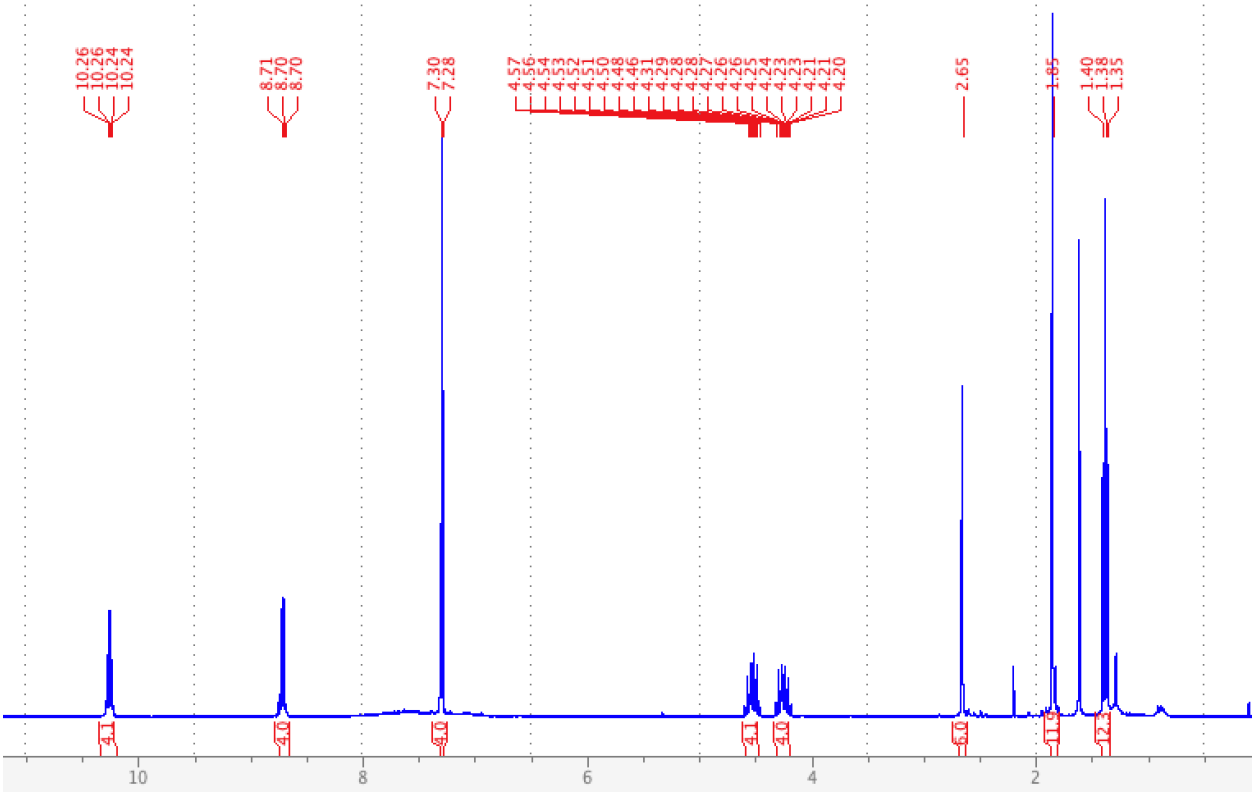


Figure S59. ^{1}H NMR spectrum of **Pt5d** in the mixture of $CDCl_3/CD_3OD$ (2:1, v/v).

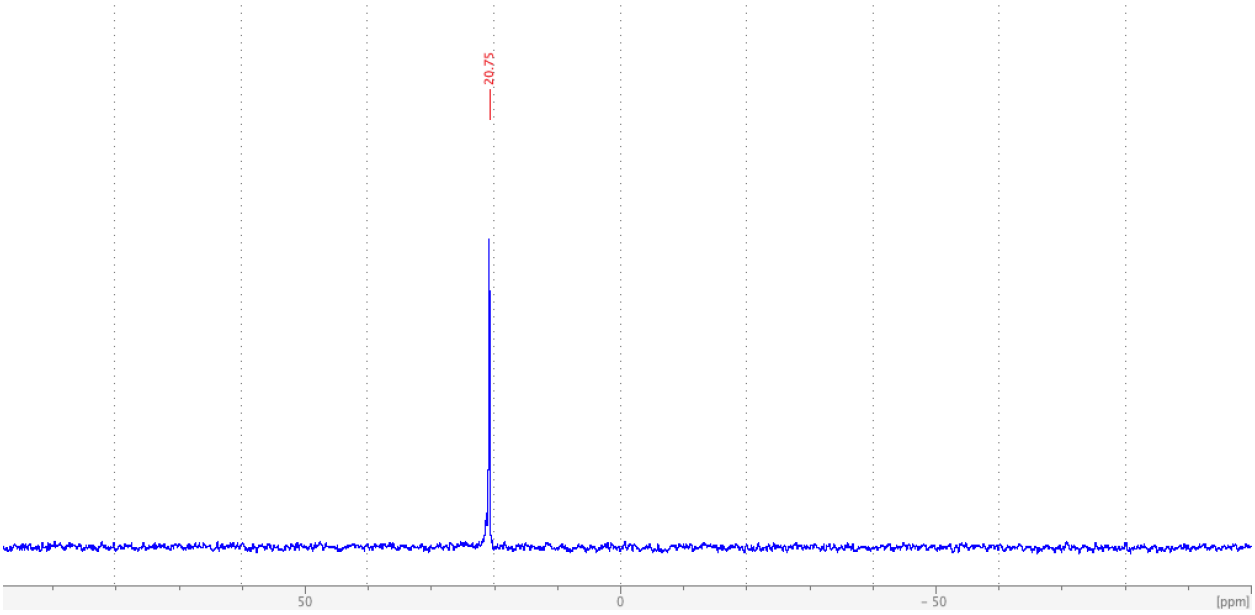


Figure S60. ^{31}P NMR spectrum of **Pt5d** in the mixture of $CDCl_3/CD_3OD$ (2:1, v/v).

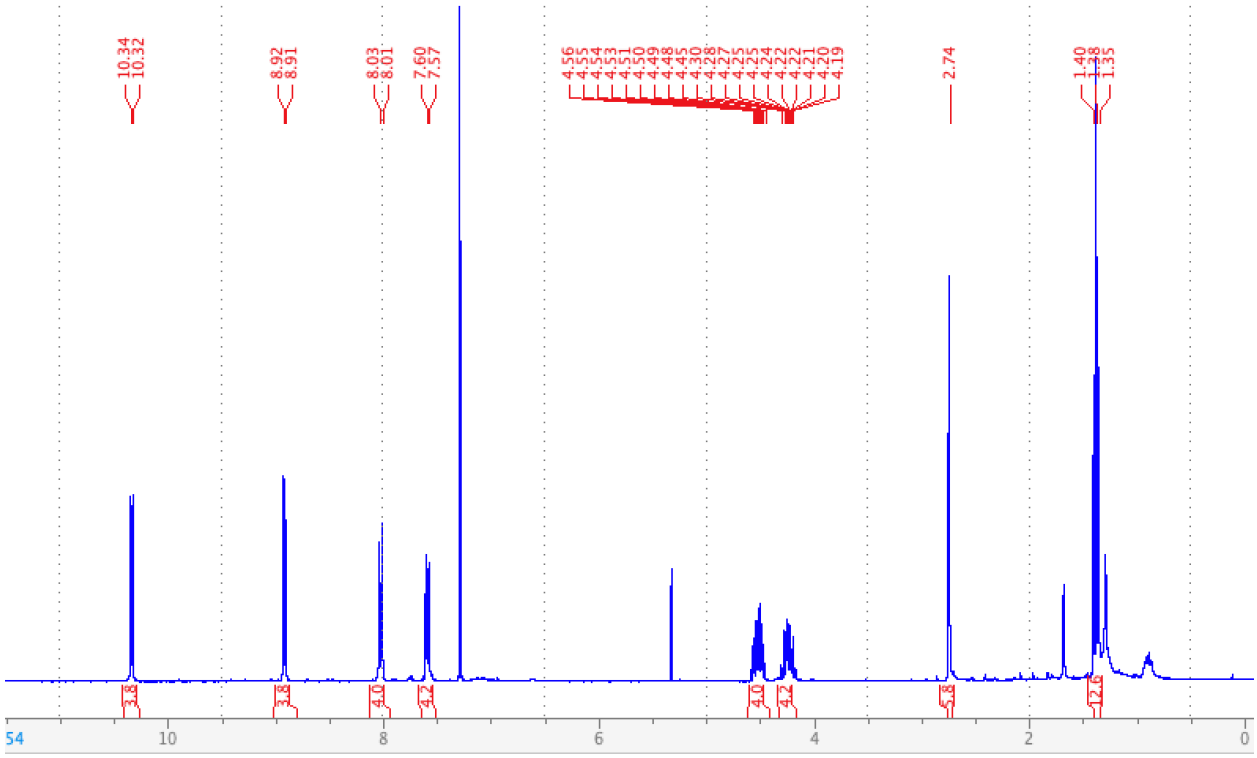


Figure S61. ^{1}H NMR spectrum of **Pd4d** in the mixture of $CDCl_3$/CD_3OD (2:1, v/v).

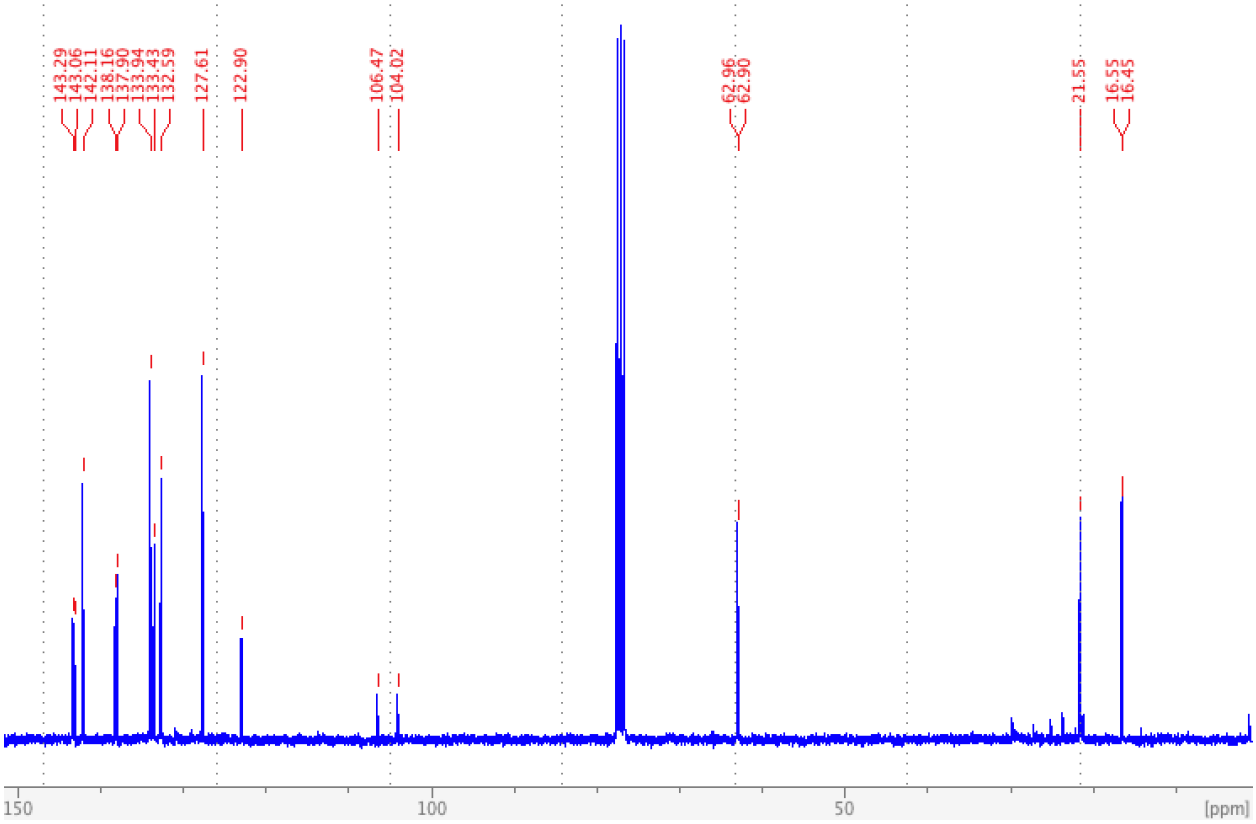


Figure S62. ^{13}C NMR spectrum of **Pd4d** in the mixture of $CDCl_3$/CD_3OD (2:1, v/v).

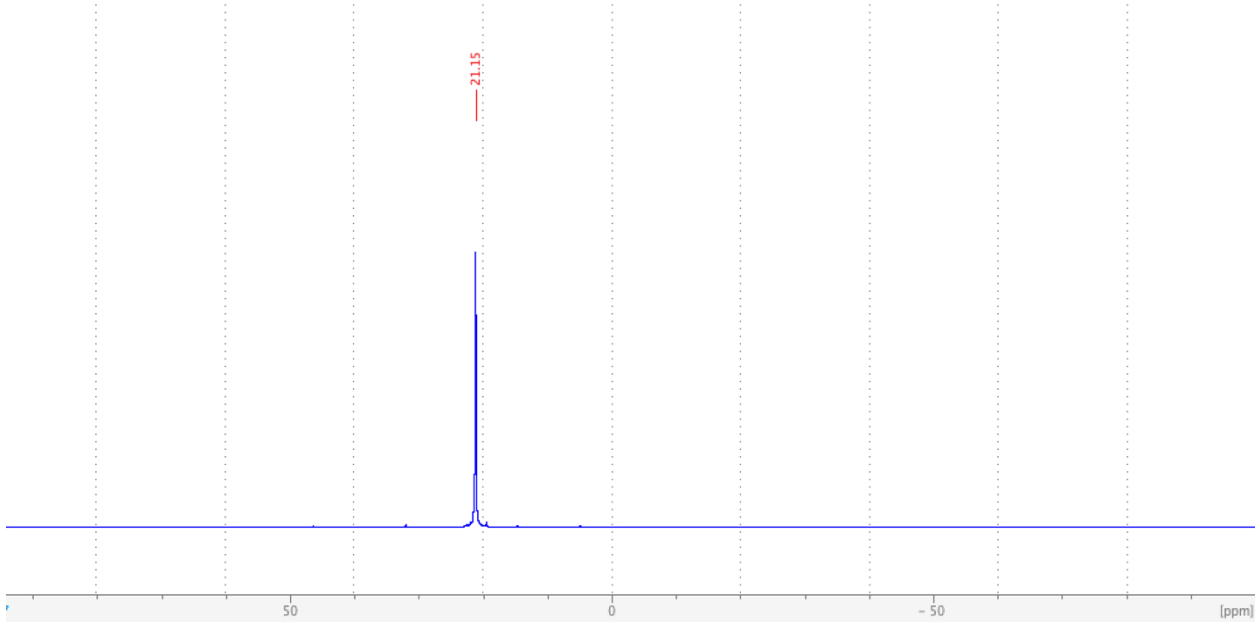


Figure S63. ^{31}P NMR spectrum of **Pd4d** in the mixture of $CDCl_3$/CD_3OD (2:1, v/v).

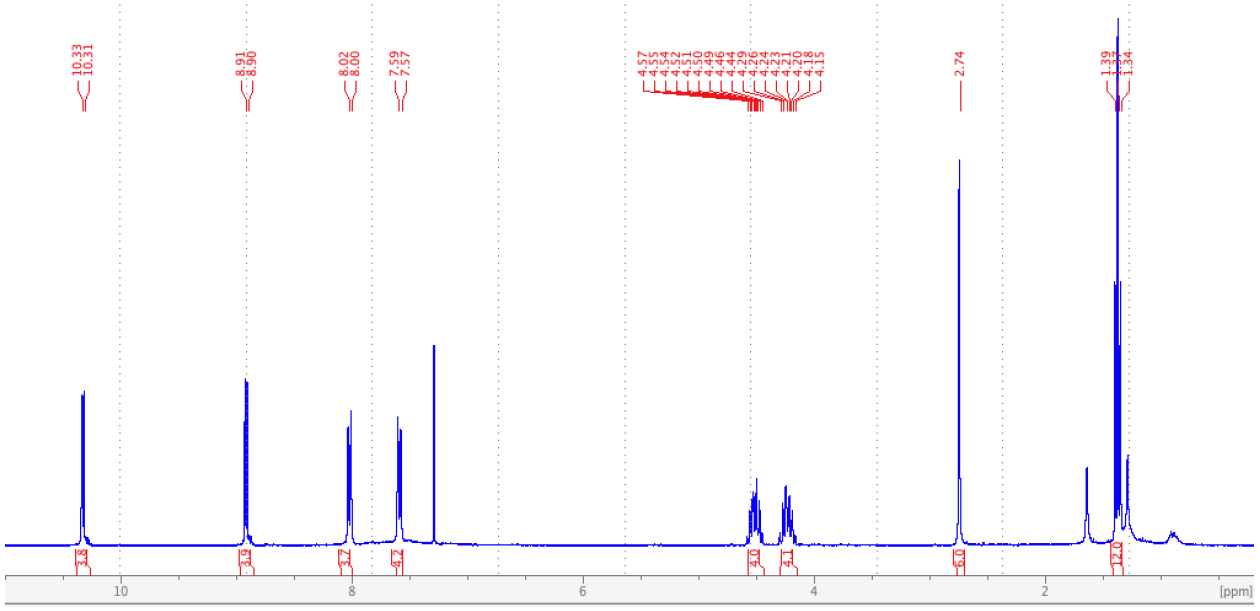


Figure S64. ^{1}H NMR spectrum of **Pt4d** in the mixture of $CDCl_3$/CD_3OD (2:1, v/v).

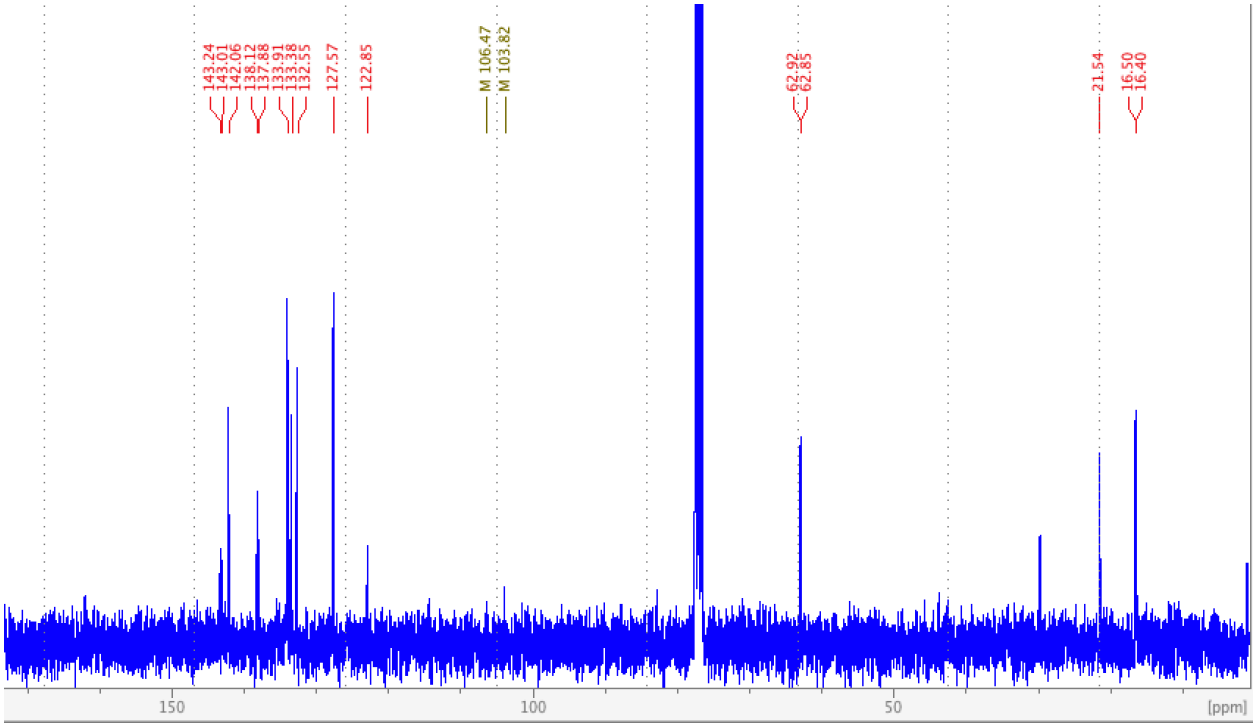


Figure S65. ^{13}C NMR spectrum of **Pt4d** in the mixture of $CDCl_3/CD_3OD$ (2:1, v/v).

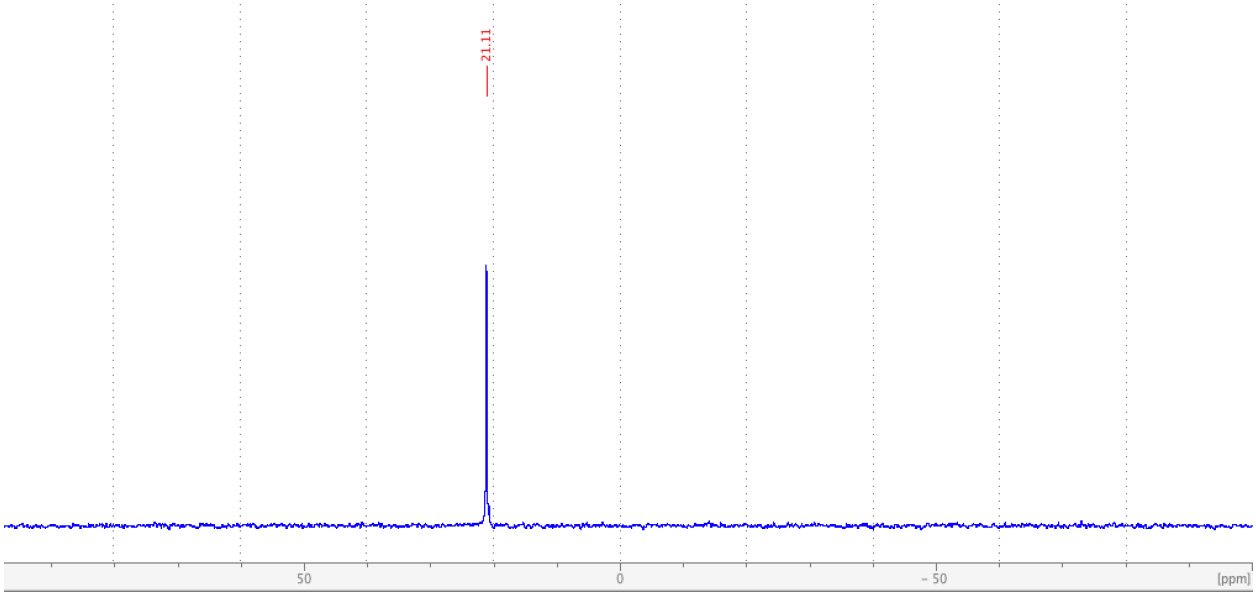


Figure S66. ^{31}P NMR spectrum of **Pt4d** in the mixture of $CDCl_3/CD_3OD$ (2:1, v/v).

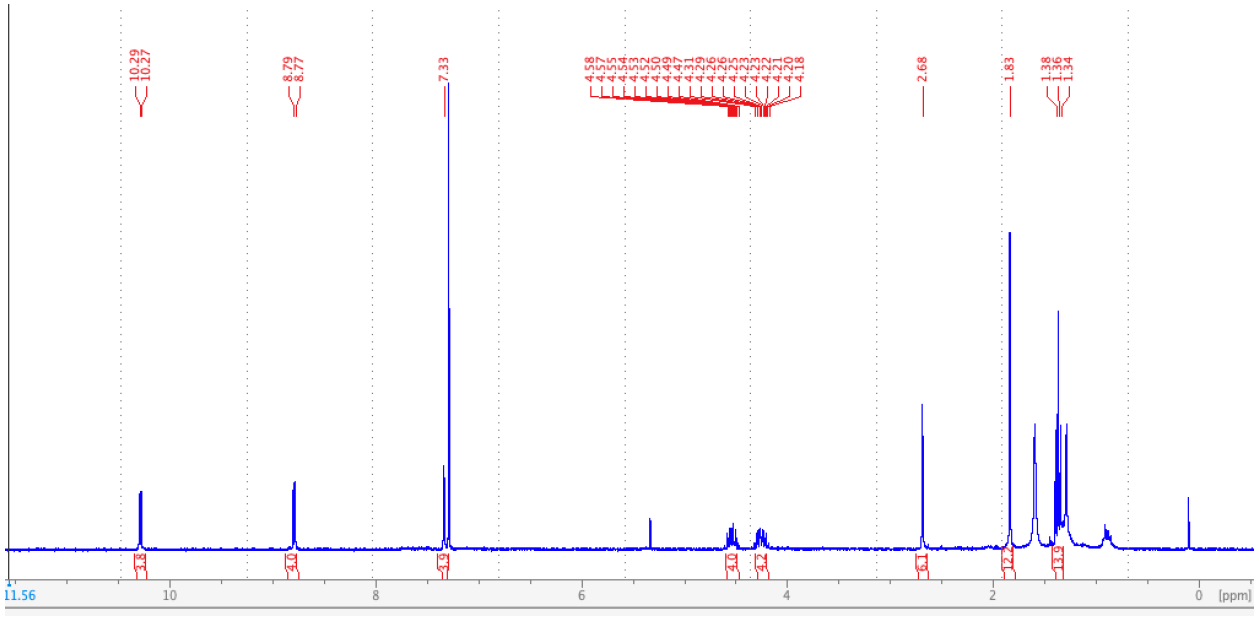


Figure S67. ^{1}H NMR spectrum of **$H_2$5d** in the mixture of $CDCl_3$/CD_3OD (2:1, v/v).

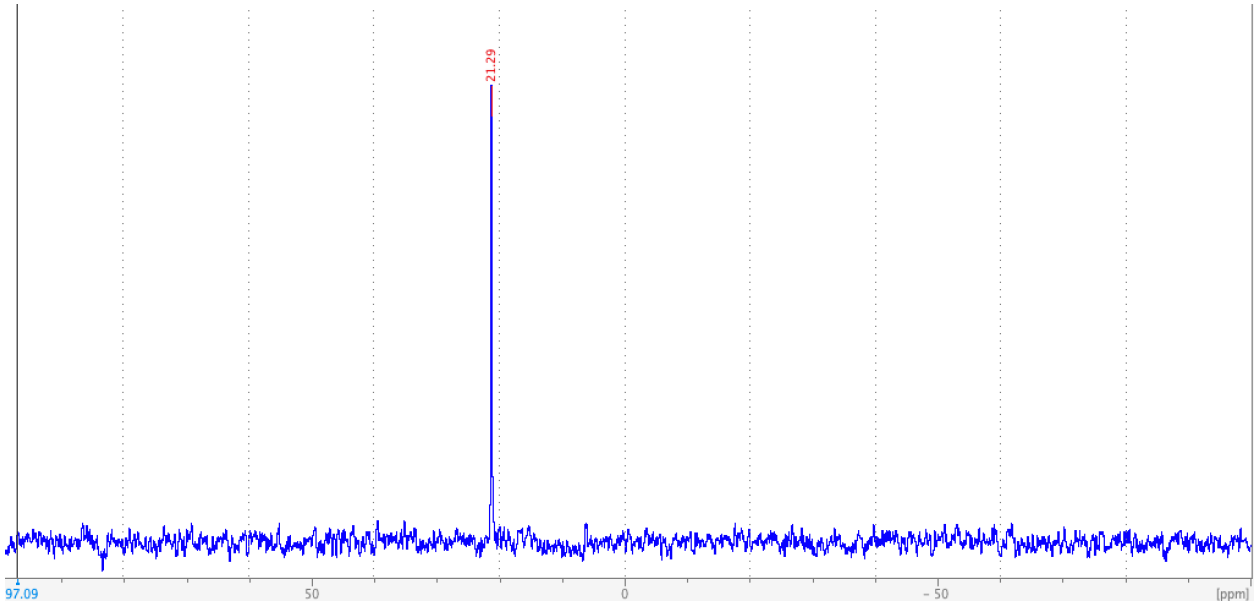


Figure S68. ^{31}P NMR spectrum of **$H_2$5d** in the mixture of $CDCl_3$/CD_3OD (2:1, v/v).

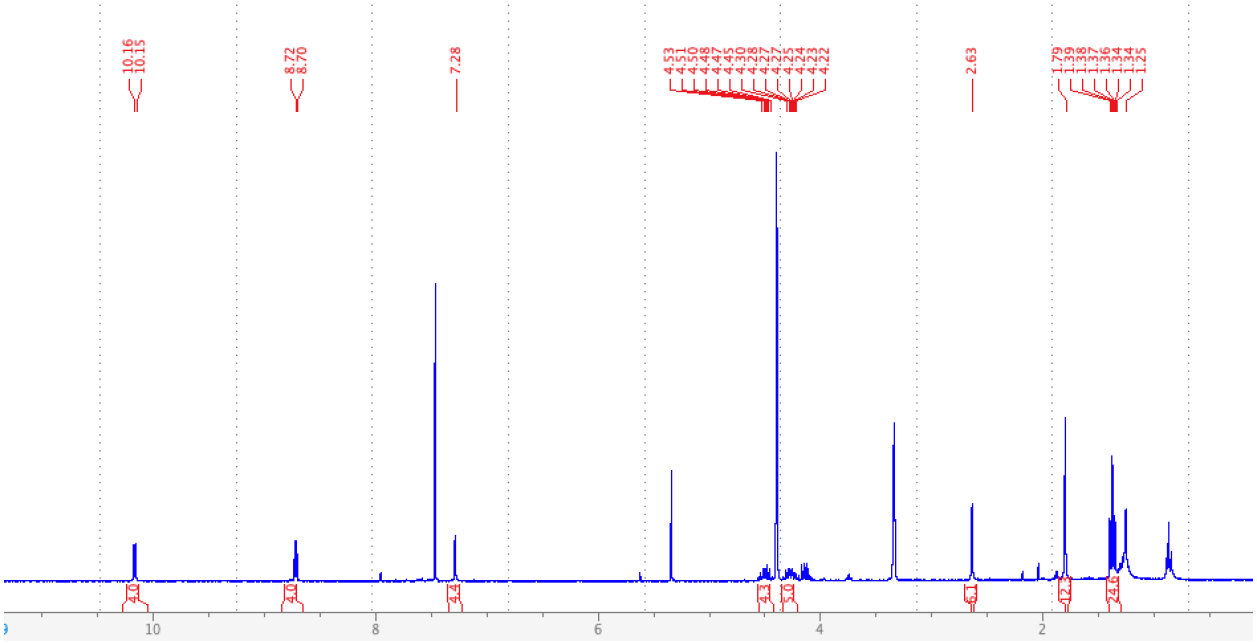


Figure S69. ^{1}H NMR spectrum of **Zn5d** in the mixture of $CDCl_3/CD_3OD$ (2:1, v/v).

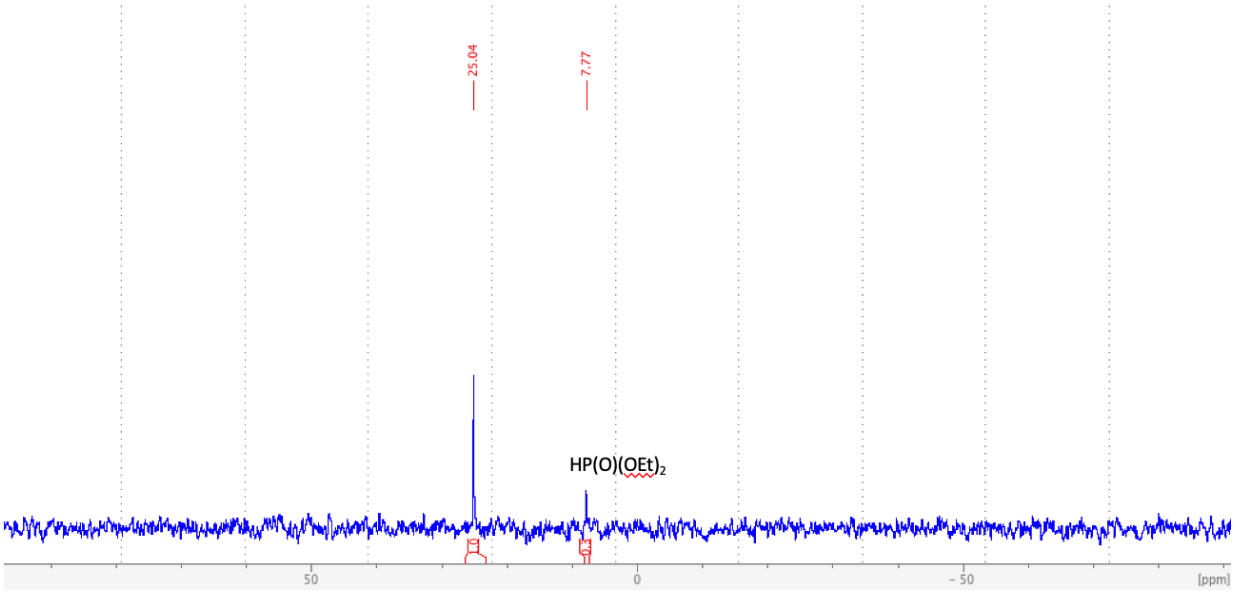


Figure S70. ^{31}P NMR spectrum of **Zn5d** in the mixture of $CDCl_3/CD_3OD$ (2:1, v/v).

b. HRMS (ESI) spectra

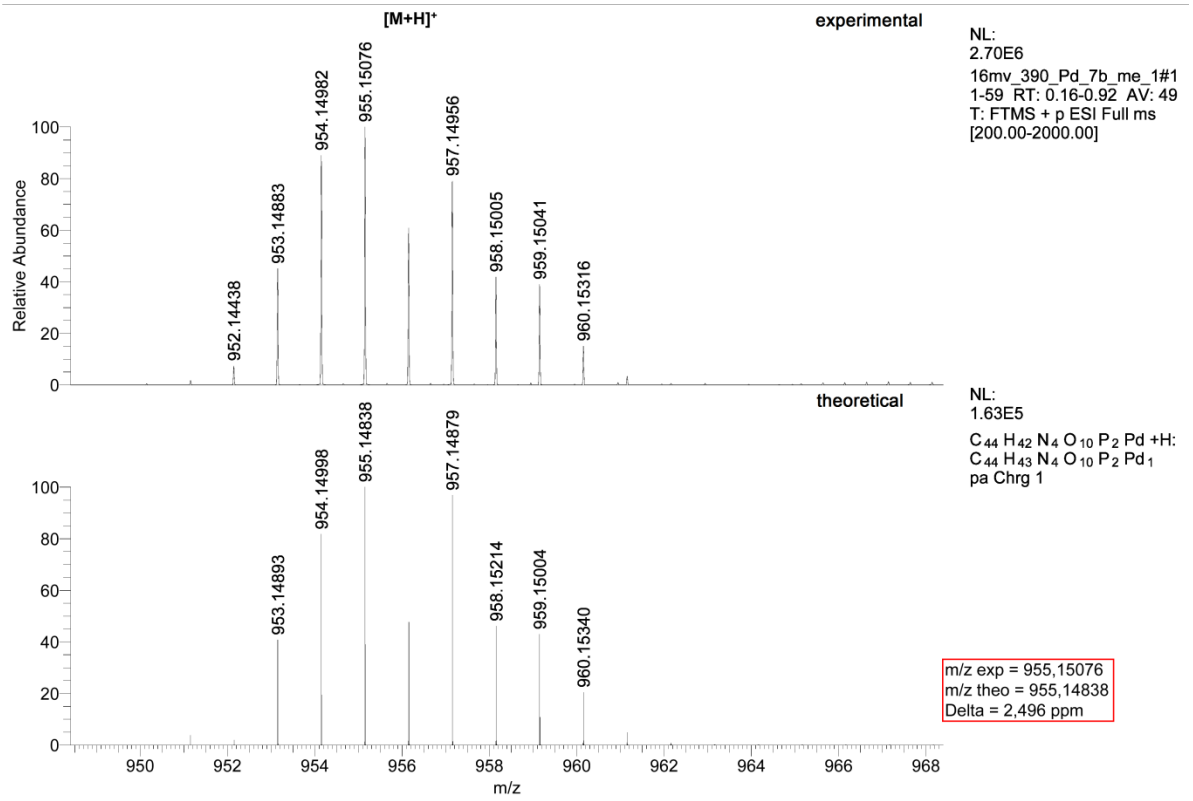


Figure S71. HRMS (ESI) spectrum of **Pd3d**.

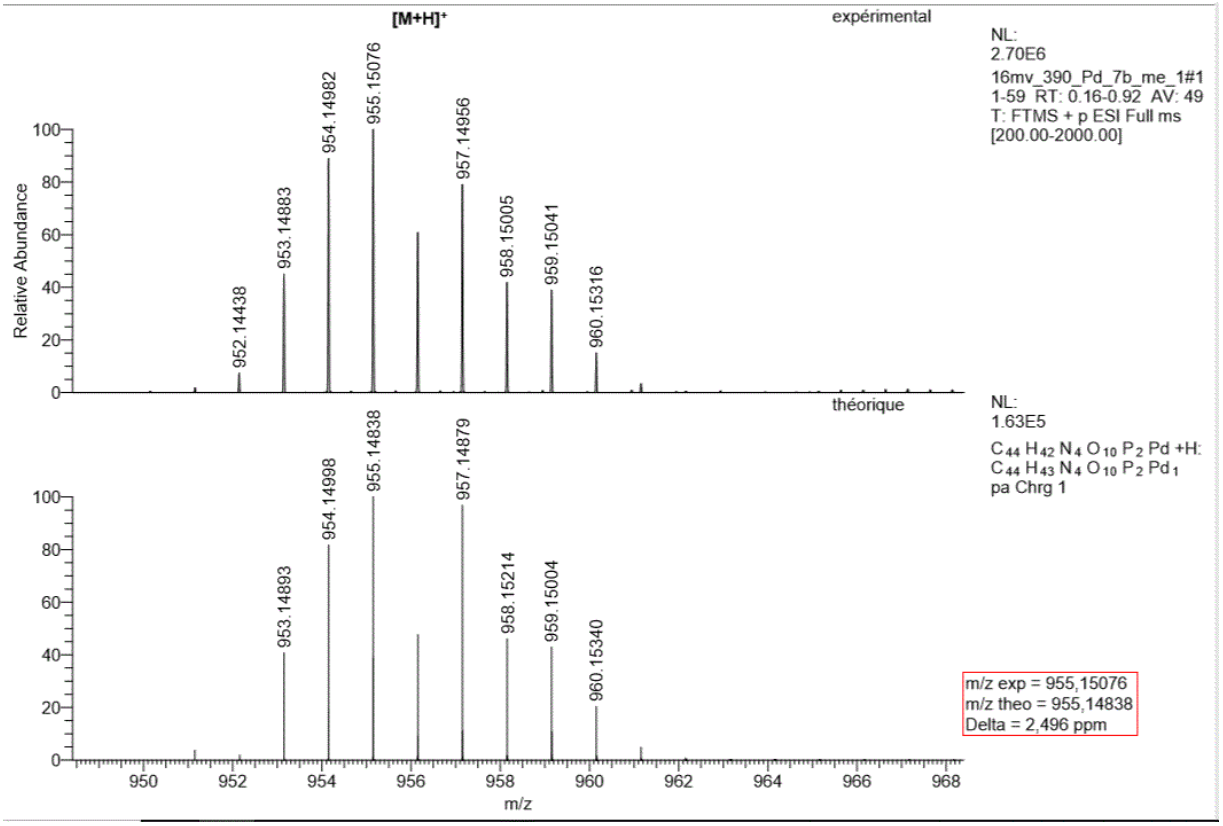


Figure S72. HRMS (ESI) spectrum of **Pt3d**.

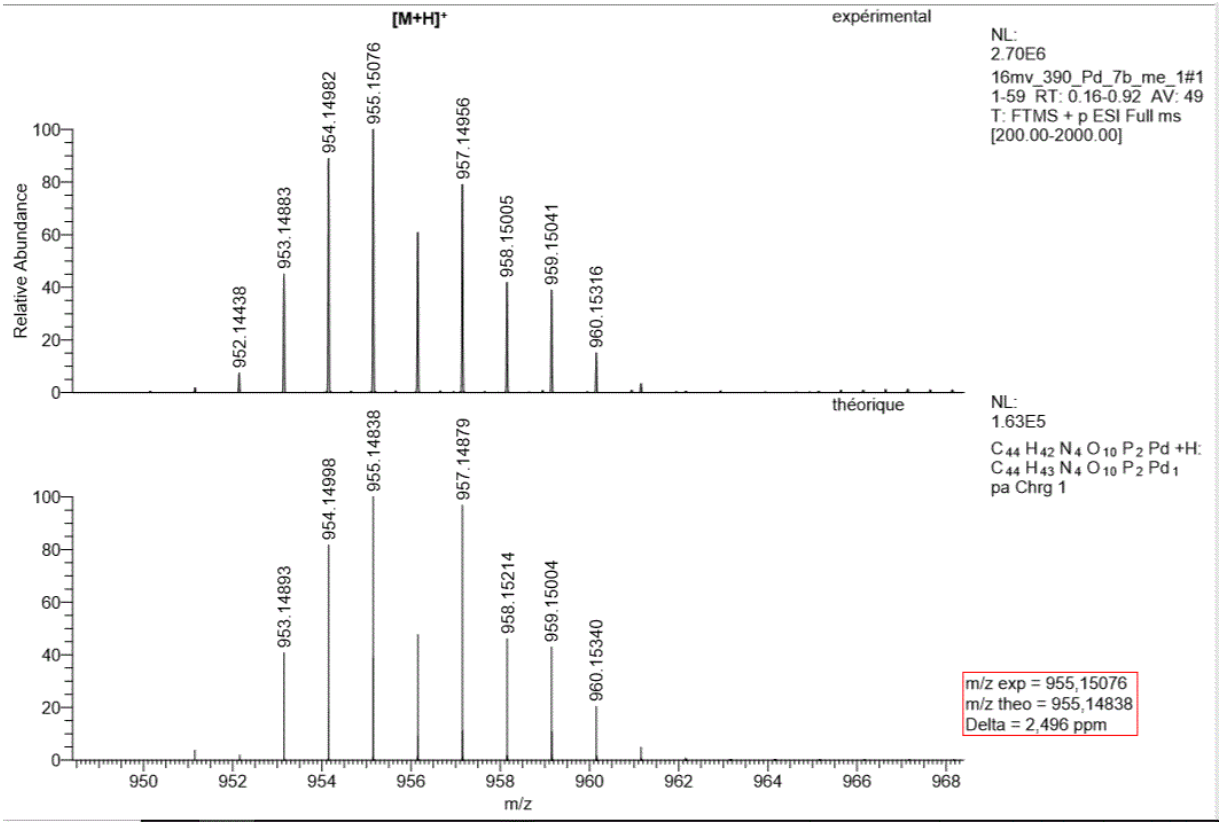


Figure S73. HRMS (ESI) spectrum of **Pd3m**.

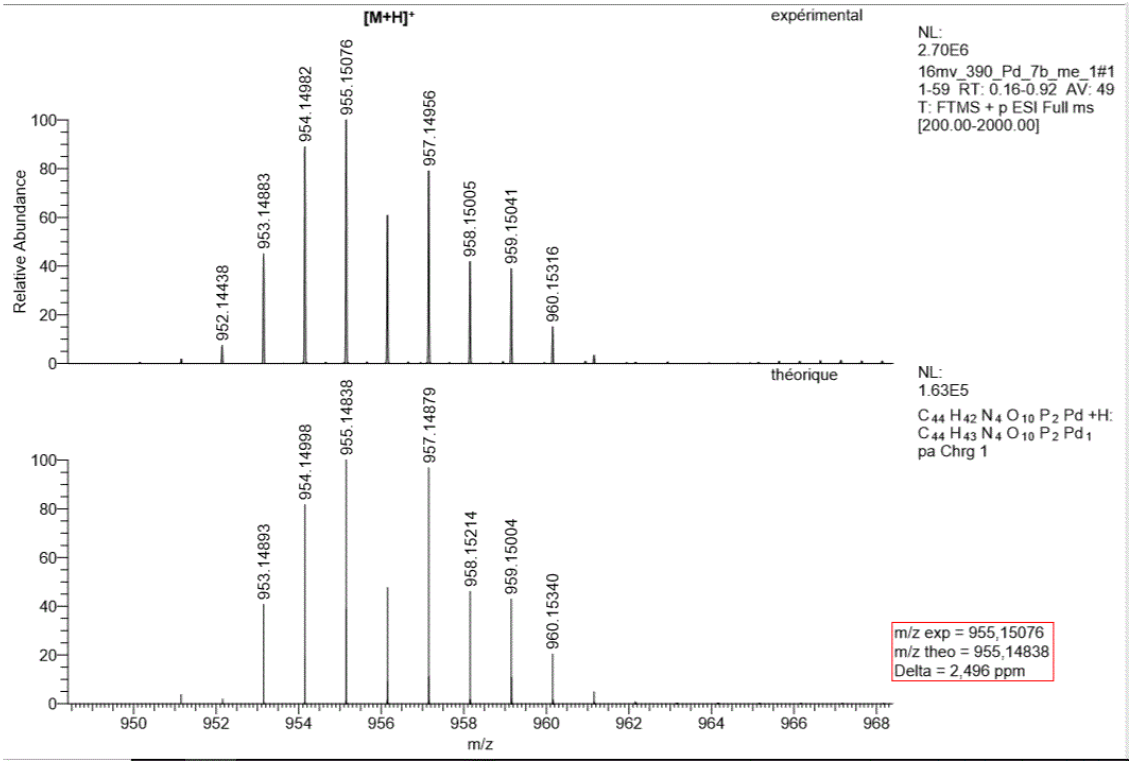


Figure S74. HRMS (ESI) spectrum of **Pt3m**.

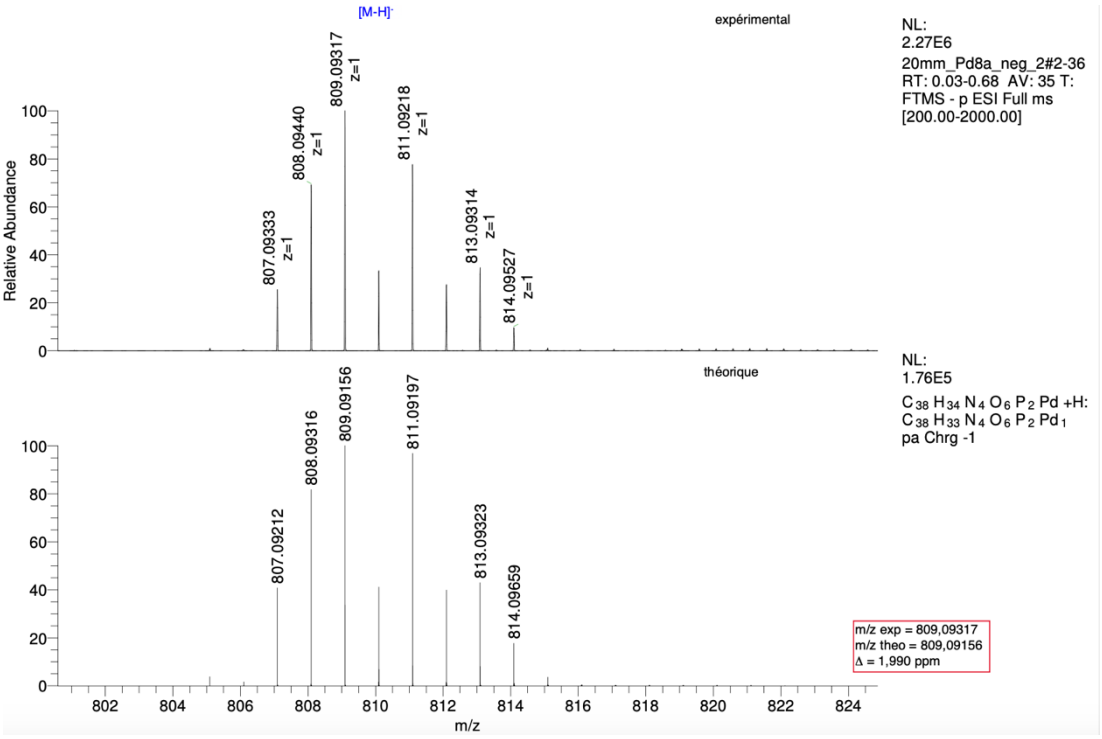


Figure S75. HRMS (ESI) spectrum of **Pd1d.**

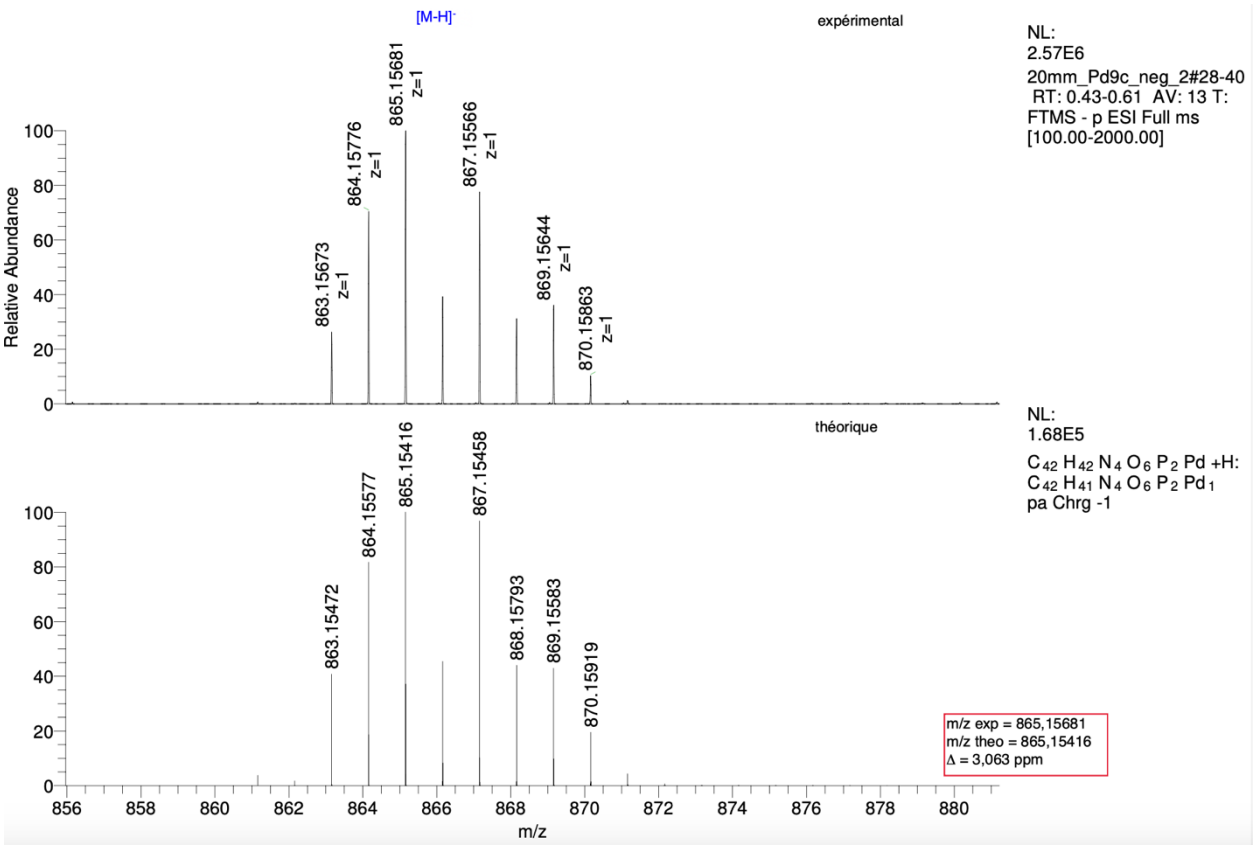
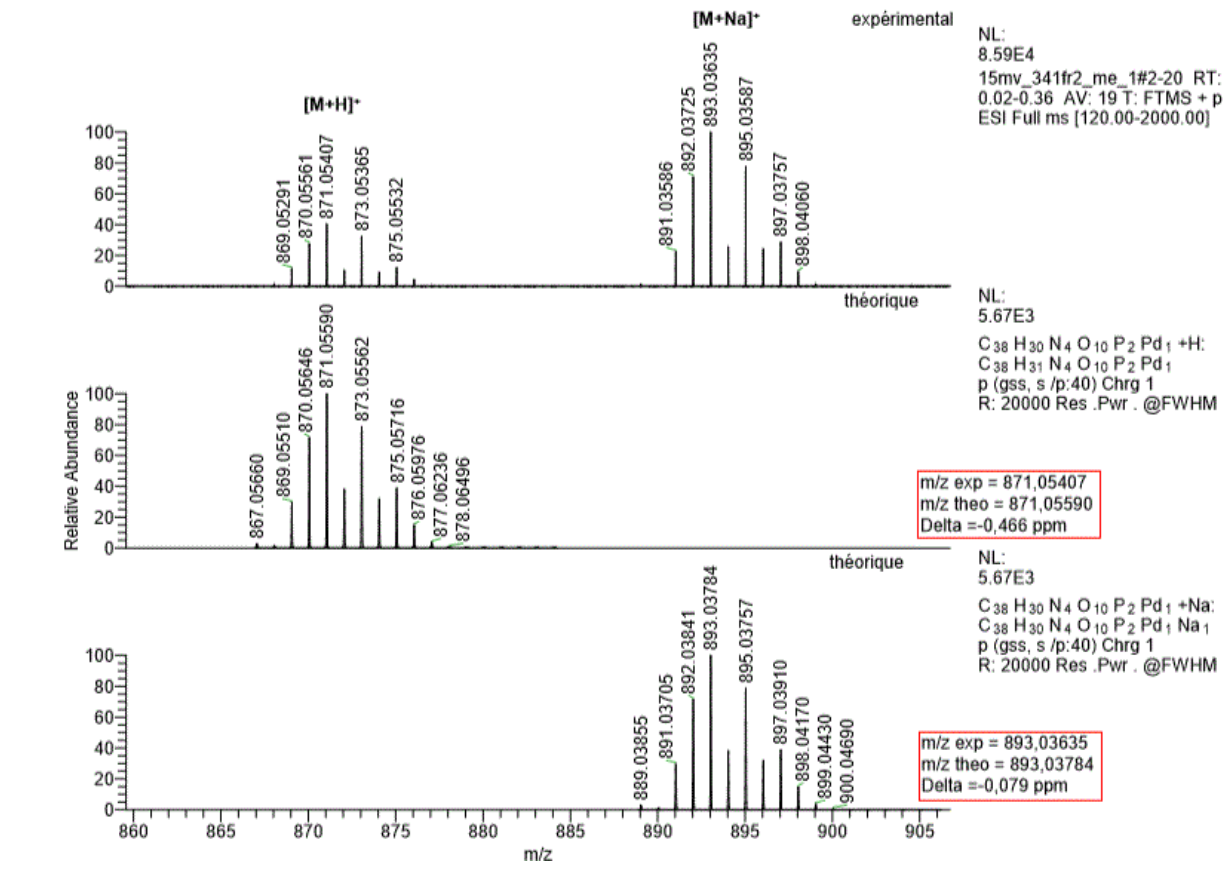


Figure S76. HRMS (ESI) spectrum of **Pd2d.**

A



B

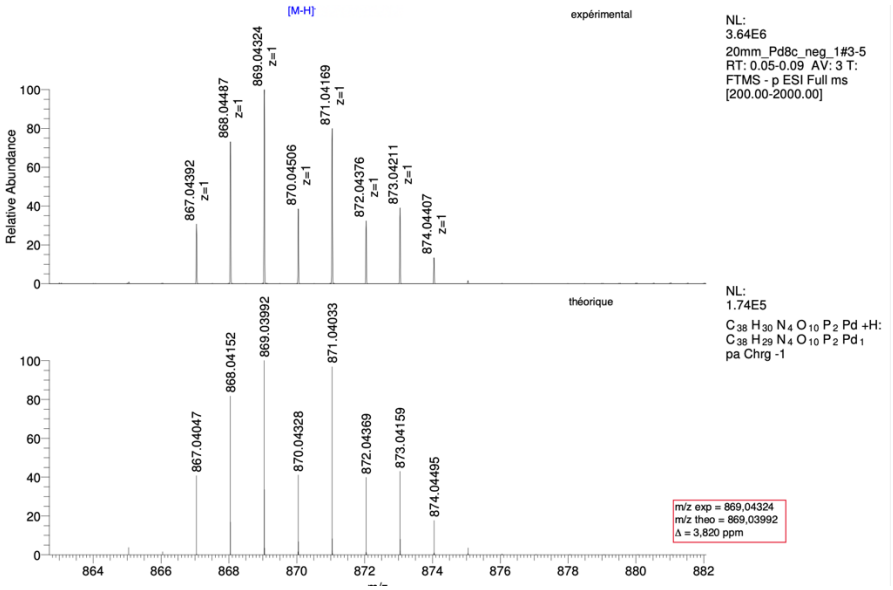


Figure S77. HRMS (ESI) spectrum of **Pd3d** in the positive ion mode (A) and the negative ion mode (B).

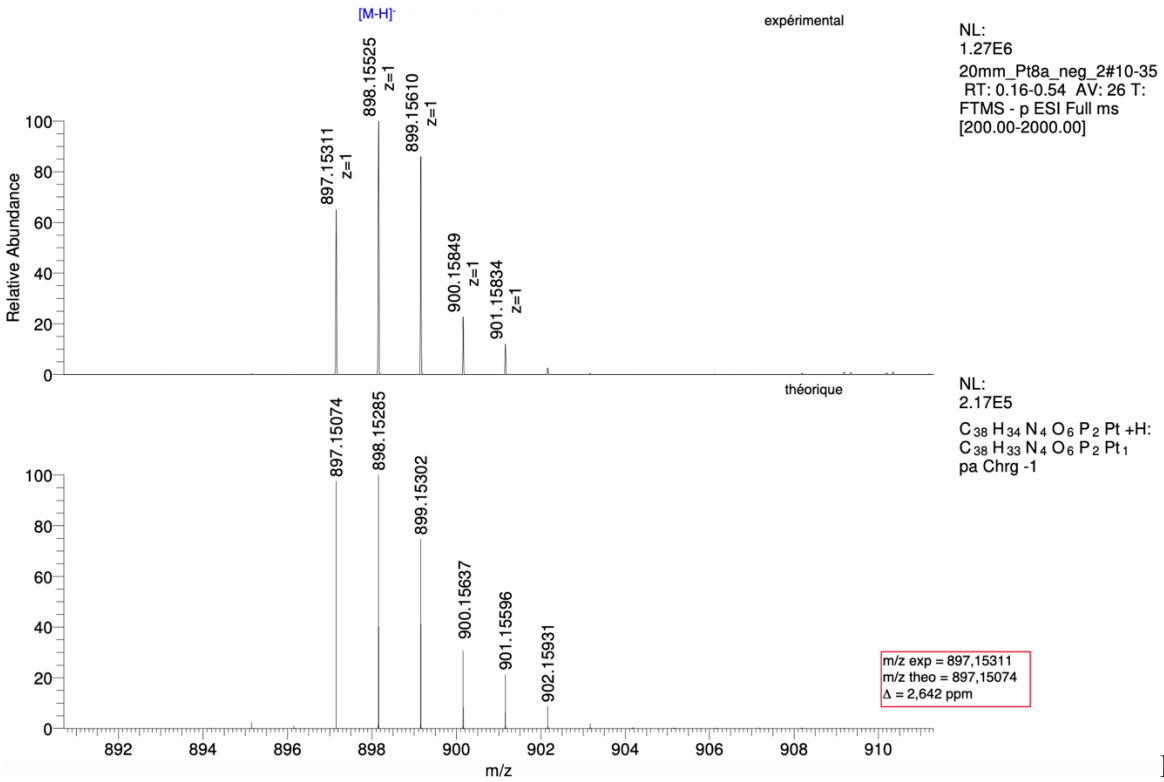


Figure S78. HRMS (ESI) spectrum of **Pt1d**.

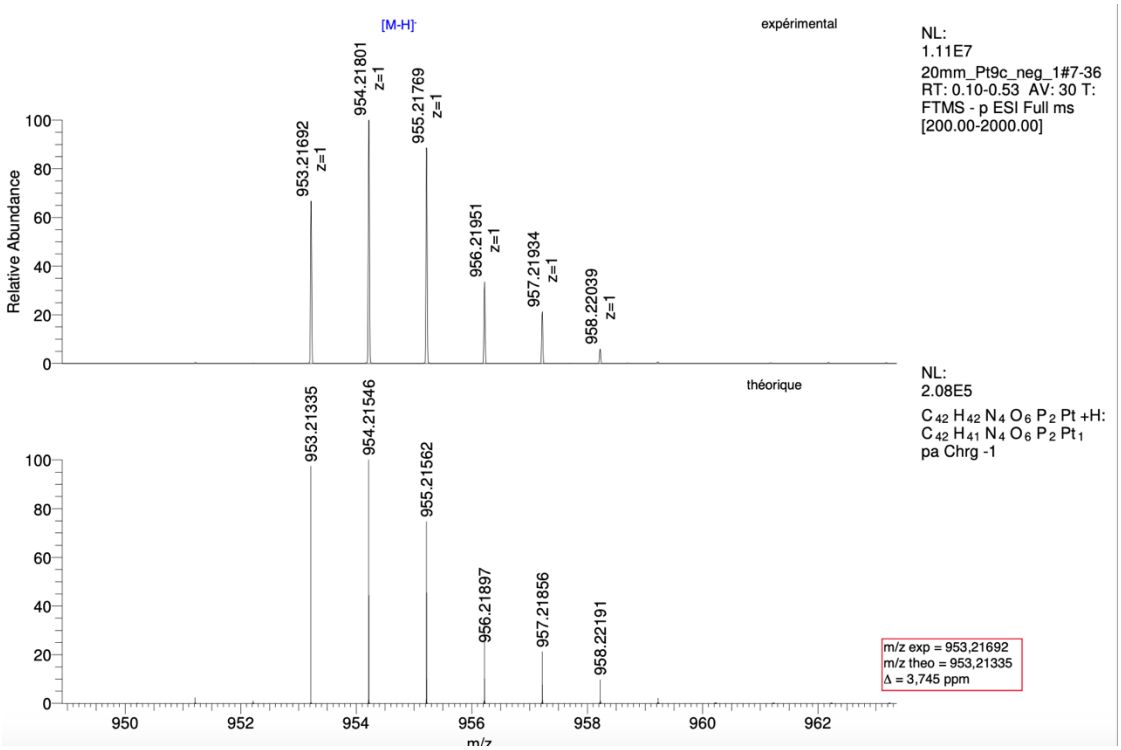


Figure S79. HRMS (ESI) spectrum of **Pt2d.**

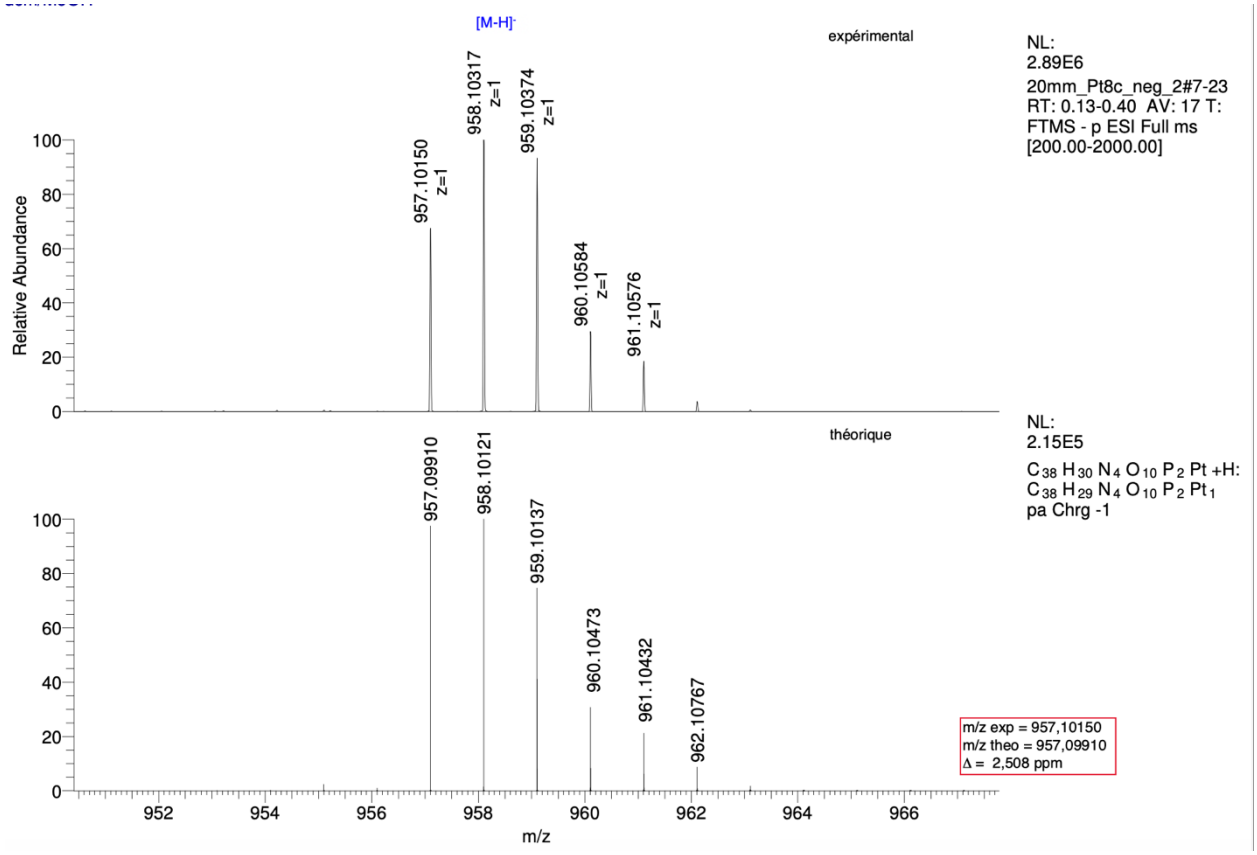


Figure S80. HRMS (ESI) spectrum of **Pt3d**.

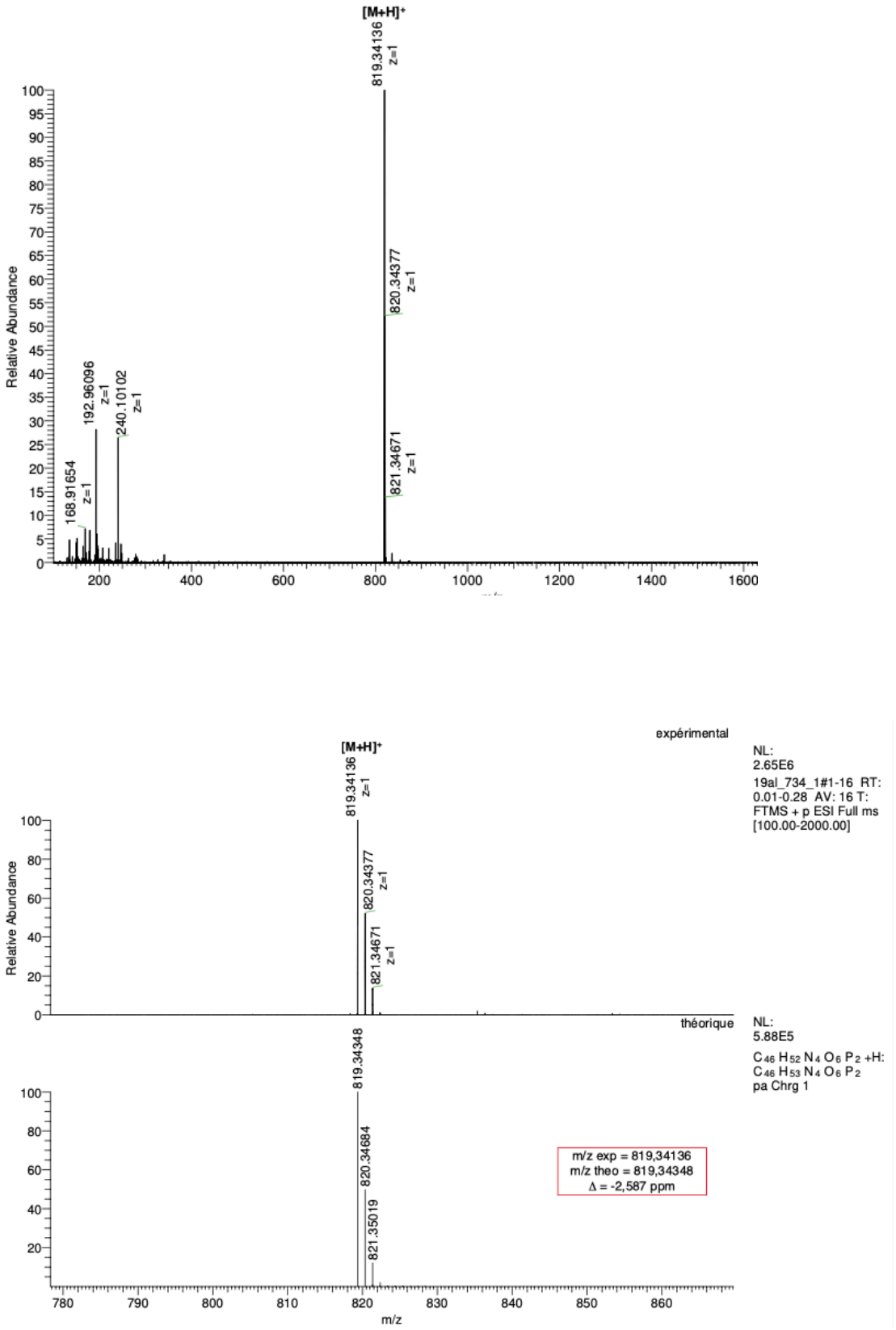


Figure S81. HRMS (ESI) spectrum of **$H_2$5d**.

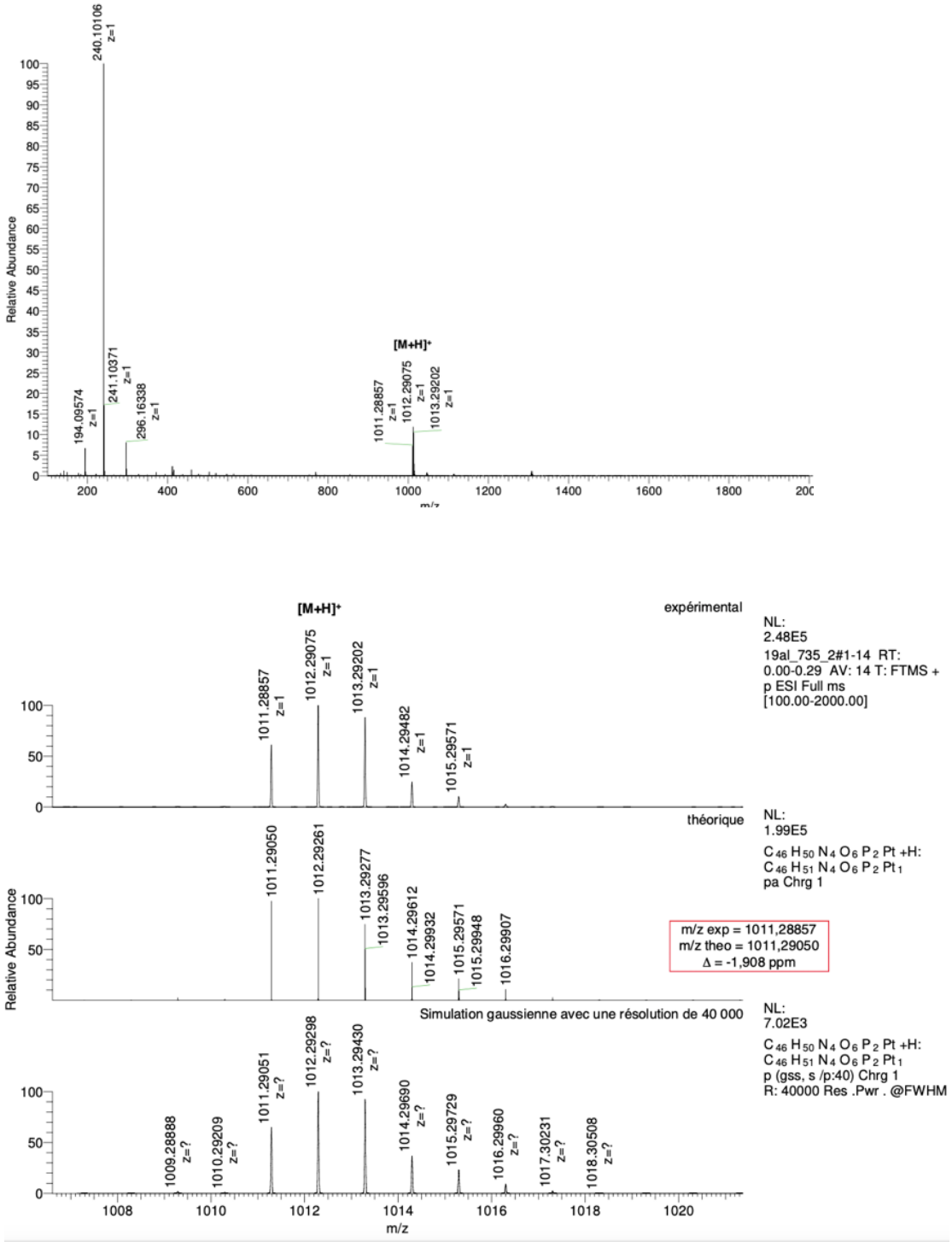


Figure S82. HRMS (ESI) spectrum of **Pt5d**.

c. IR spectra

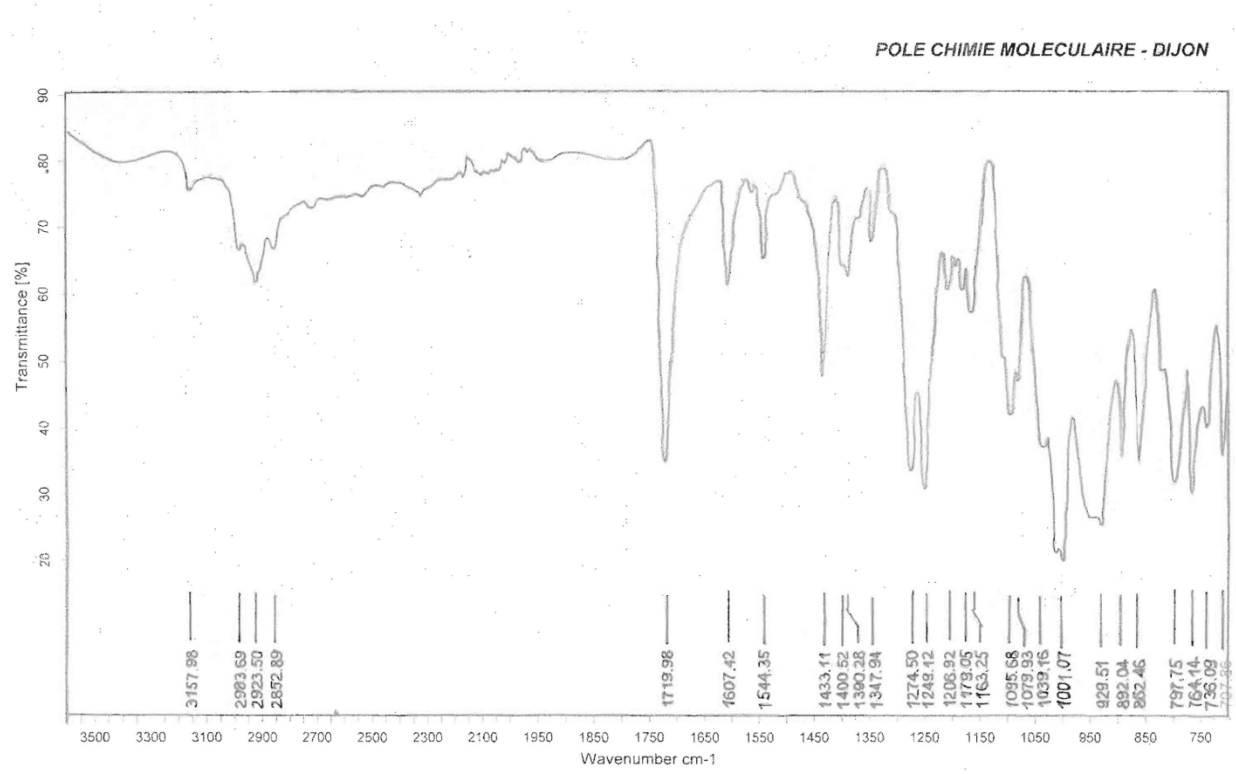


Figure S83. IR spectrum of **Pd3d.**

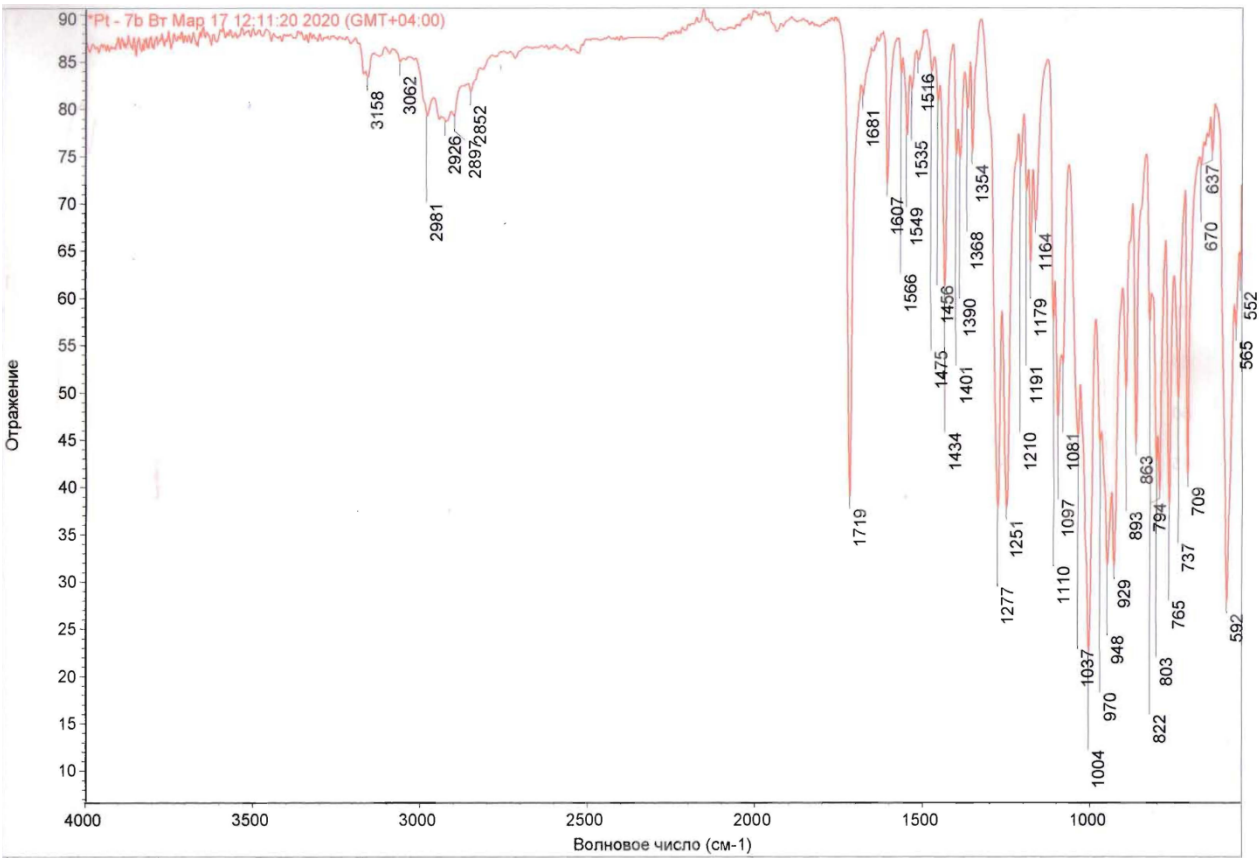


Figure S84. IR spectrum of **Pt3d**.

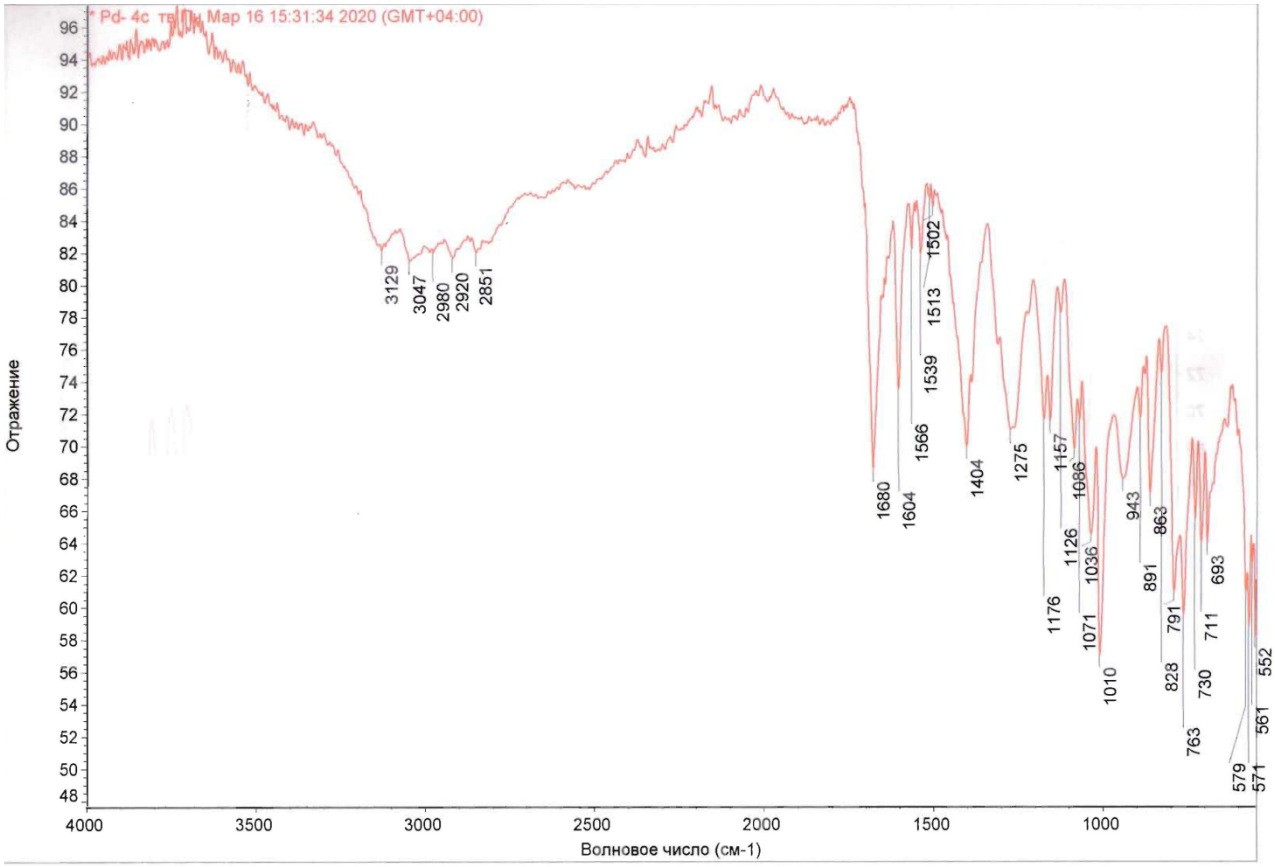


Figure S85. IR spectrum of **Pd3m**.

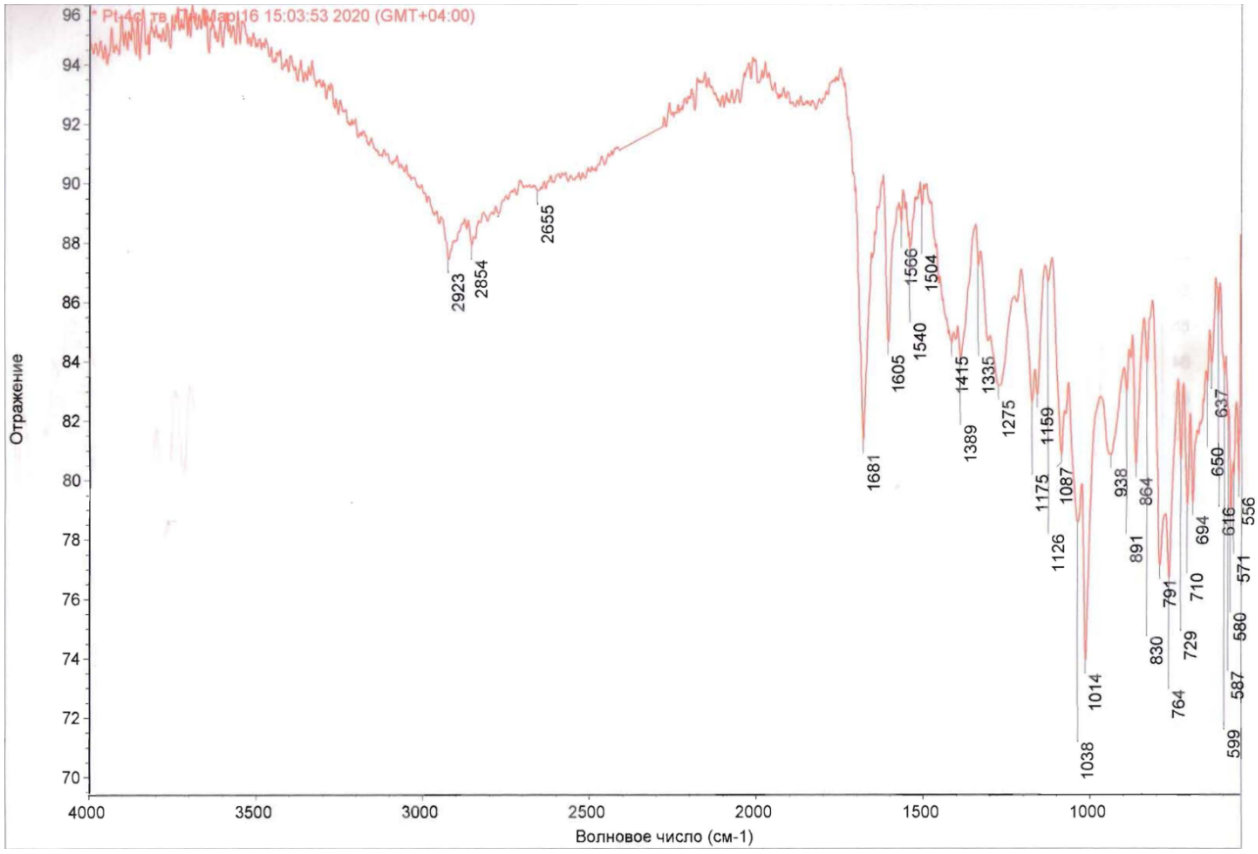


Figure S86. IR spectrum of **Pt3m**.

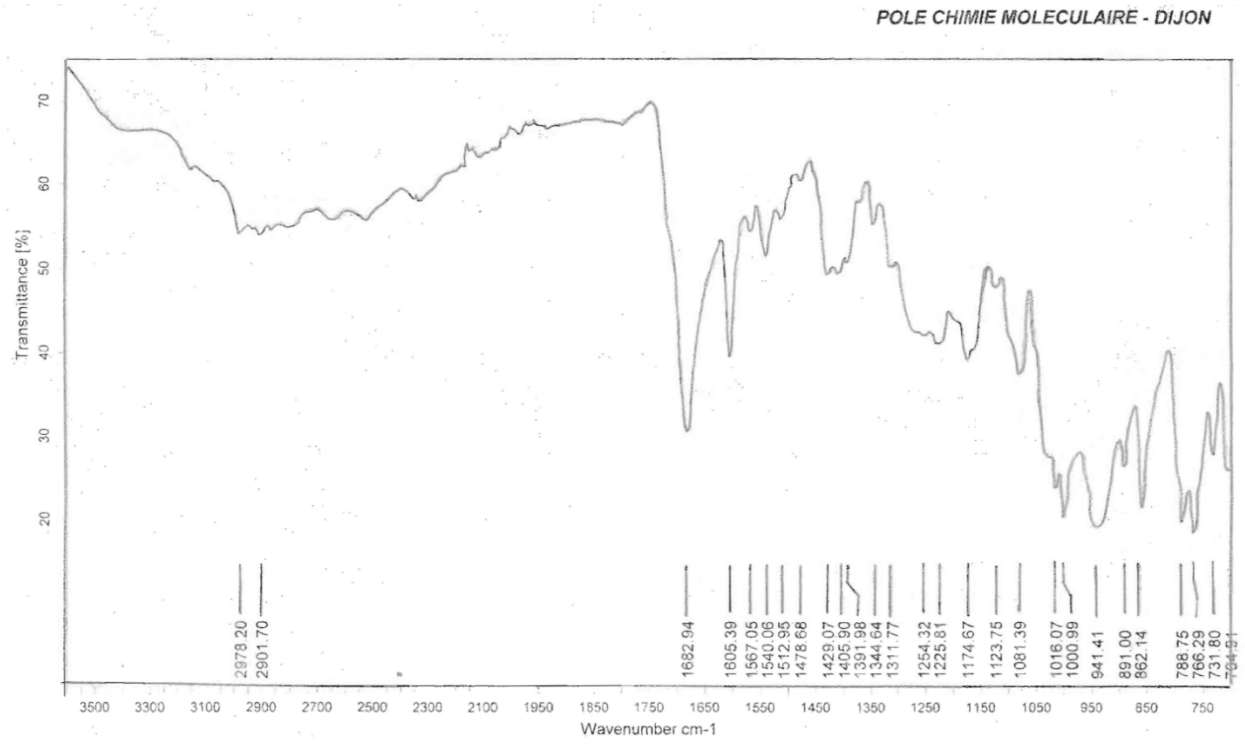


Figure S87. IR spectrum of **Pd3d.**

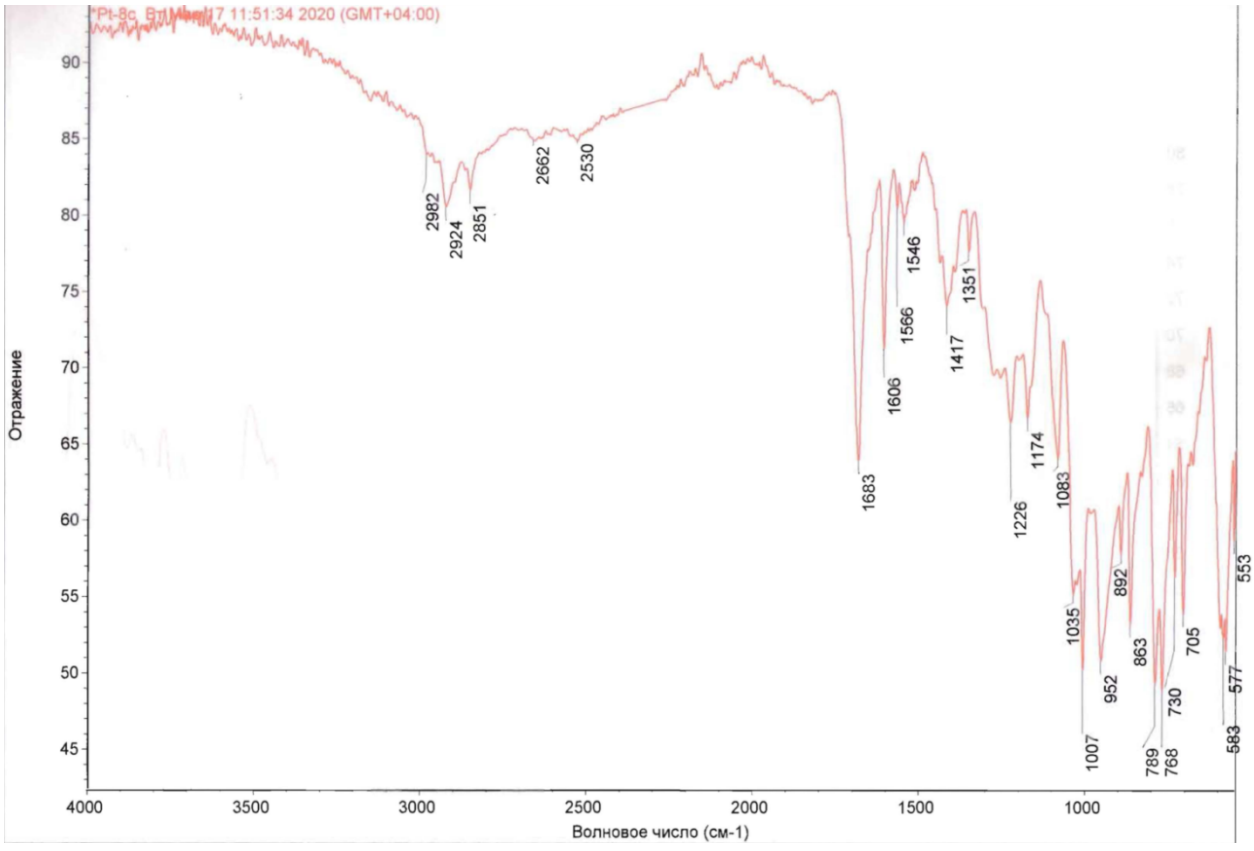


Figure S88. IR spectrum of **Pt3d**.

11. References

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