Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information
(32 pages including the cover page)

Room Temperature C–H Bond Activation on a $[Pd^{I}–Pd^{I}]$ Platform

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Contents

Materials and Methods.

All manipulations were carried out under an inert atmosphere with the use of standard Schlenk-line techniques. Glass wares were flame-dried under vacuum prior to use. Solvents were dried by conventional methods prior to use. Pd sponge, $Pd(OAc)_2$ were purchased from Arora Matthey, India. $NOBF_4$, $NaNH_2$ and $B(C_6F_5)_3$ were purchased from Sigma-Aldrich. $Pd(CH_3CN)_4(BF_4)_2$[1], $Pd_2(dba)_3.CHCl_3$[2], $[Pd_2(CH_3CN)_6](BF_4)_2$[3] and 2-aminonicotinaldehyde [4] were synthesized following the literature procedure. 2-Substituted-1,8-Naphthyridine ligands L^1H and L^2H were prepared by Friedlander condensation between 2-aminonicotinaldehyde and corresponding acetyl substituted five membered heterocycles.[5]

^1H and ^{13}C NMR spectra were obtained on a JEOL JNM-LA 500 MHz spectrometer. ^1H NMR chemical shifts were referenced to the residual hydrogen signal of the deuterated solvents. ESI-MS were recorded on a Waters Micro mass Quattro Micro triple-quadruple mass spectrometer using acetonitrile as solvent. Infrared spectra were recorded on a Bruker Vertex 70 FTIR spectrophotometer in the ranges from 400 to 4000 cm^{-1} using KBr pellets. Elemental analyses were performed on a Thermoquest EA1110 CHNS/O analyzer. The crystallized compounds were powdered, washed several times with dry diethyl ether and dried in vacuum for at least 48 h prior to elemental analyses.

X-ray data collection and refinement.

Single crystal X-ray structural studies were performed on a CCD Bruker SMART APEX diffractometer equipped with an Oxford instruments low-temperature attachment. All the data were collected at 100(2) K using graphite-monochromated Mo-Kα radiation (λ_α = 0.71073 Å). The frames were indexed, integrated and scaled using SMART and SAINT software package[6] and the data were corrected for absorption using the SADABS program.[7] The structures were

solved and refined using SHELX suite of programs[8] while additional crystallographic calculations were performed by the programs PLATON.[9] SQUEEZE option in PLATON program was used to remove the disordered water and solvent molecules from the overall intensity data of compounds wherever necessary.[10] Figures were drawn (40 % probability thermal ellipsoids) using ORTEP32.[11] Crystallographic data and pertinent refinement parameters for complexes **1 - 5** are presented in Table S1 and S2. CCDC 940018 – 940020, 952838, 952839 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Complex **1:** A red crystal of dimensions 0.27 × 0.25 × 0.24 mm^3 was covered in paratone oil, mounted on top of a thin glass fiber with silicone grease and placed in a cold stream of nitrogen. All non hydrogen atoms were refined with anisotropic thermal parameters. All H-atoms except those of water molecules were introduced into geometrically calculated positions in the final stages of refinement and were refined according to 'riding model'. Hydrogen atoms of the coordinated water molecules were not located, but were included in the formula sum for the calculation of the intensive properties.

Complex **2:** A red crystal of dimensions 0.31 × 0.23 × 0.21 mm^3 was covered in paratone oil, mounted on top of a thin glass fiber with silicone grease and placed in a cold stream of nitrogen. All non hydrogen atoms were refined with anisotropic thermal parameters. All H-atoms except those of water molecules were introduced into geometrically calculated positions in the final stages of refinement and were refined according to 'riding model'. Hydrogen atoms of the coordinated water molecules were not located, but were included in the formula sum for the calculation of the intensive properties. PLATON/SQUEEZE estimated the solvent-accessible

region to contain 395 (198+197) electrons per unit cell. This amounts to nearly 99 electrons per formula unit. The electron densities are tentatively modeled as to two CH_2Cl_2 and one H_2O molecules per formula unit. These solvent and water molecules were included in the formula sum for the calculation of the intensive properties.

Complex **3:** A red crystal of dimensions 0.25 × 0.22 × 0.16 mm^3 was covered in paratone oil, mounted on top of a thin glass fiber with silicone grease and placed in a cold stream of nitrogen. All H-atoms except those of water molecules were introduced into geometrically calculated positions in the final stages of refinement and were refined according to 'riding model'. Hydrogen atoms of the coordinated water molecules were not located, but were included in the formula sum. SADI and DFIX restraints were applied to model one of the BF_4 and the associated atoms were refined isotropically. Anisotropic treatment of C30, C31, C33, C60, C111, C112, N12 atoms in the main residue and B4A, F16A in the anion resulted in non-positive definite displacement tensors and were therefore subjected to isotropic refinement. Except these, all non-hydrogen atoms were refined with anisotropic thermal parameters. PLATON/SQUEEZE estimated the solvent-accessible region to contain a total of 672 electrons per unit cell. This amounts to 84 electrons per formula unit (z = 8). The electron densities were tentatively modeled as to two C_6H_6 molecules per formula unit. These solvent molecules were included in the molecular formula for the calculation of the intensive properties.

Complex **4:** A red crystal of dimensions 0.38 × 0.32 × 0.22 mm^3 was covered in paratone oil, mounted on top of a thin glass fiber with silicone grease and placed in a cold stream of nitrogen. All non hydrogen atoms were refined with anisotropic thermal parameters. All H-atoms were introduced in calculated positions and refined according to 'riding model', except hydrogens attached to nitrogen atoms in the anion, which were located and refined with restraints.

Complex **5:** An yellow crystal of dimensions 0.36 × 0.20 × 0.18 mm^3 was covered in paratone oil, mounted on top of a thin glass fiber with silicone grease and placed in a cold stream of nitrogen. All non hydrogen atoms were refined with anisotropic thermal parameters. All H-atoms were introduced into geometrically calculated positions in the final stages of the refinement and were refined according to 'riding model'.

General synthesis for 2-Substituted-1,8-Naphthyridines (L^1H, L^2H):

To an ethanolic solution of 2-aminonicotinaldehyde, was added one equivalent of aromatic ketone. The solution was then refluxed under nitrogen for 5 minutes and five drops of freshly prepared saturated methanolic solution of KOH was added. After refluxing for 24 hours, the solvent was evaporated under reduced pressure and the crude product was purified by silica gel column chromatography using ethyl acetate and petroleum ether as eluent.

2-(N-methylpyrrolyl)-1,8-naphthyridine(L^1H): Yield: 82%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.03 (dd, *J* = 4.3 Hz, 1.8 Hz, 1H), 8.08 (dd, *J* = 7.9 Hz, 1.8 Hz, 1H), 8.04 (d, *J* = 8.9 Hz, 1H), 7.80 (d, *J* = 8.9 Hz, 1H), 7.36 – 7.39 (m, 1H), 6.90 (dd, *J* = 3.7 Hz, *J* = 1.6 Hz, 1H), 6.84 (dd, *J* = 2.8 Hz, 1.8 Hz, 1H), 6.23 (dd, *J* = 4.0 Hz, 2.4 Hz, 1H), 4.32 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 155.5, 152.8, 137.3, 136.6, 131.2, 129.4, 121.2, 120.9, 120.7, 114.3, 108.3, 38.8.

2-(2,5-dimethylthiophen-3-yl)-1,8-Naphthyridine (L^2H): Yield: 80%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.09 (dd *J* = 4.2 Hz, 1.8 Hz, 1H), 8.15 (d, *J* = 8.3 Hz, 1H), 8.13 (dd, *J* = 8 Hz, 1.7 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.40–7.43 (m, 1H), 7.20 (s, 1H), 2.81 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 158.8, 155.5, 153.2, 139.8, 137.4, 137.2, 135.9, 135.6, 126.9, 122.2, 121.5, 121.0, 15.9, 15.2.

2-(4-bromo-2,5-dimethylthiophen-3-yl)-1,8-Naphthyridine (L^2Br): To 10 ml of an acetic acid solution containing 2-(2,5-dimethylthiophen-3-yl)-1,8-Naphthyridine (L^3H) was added bromine

at 0ºC in a ratio 1:1.1. The mixture was slowly brought to room temperature and stirred for overnight. A nice yellow precipitate was formed which was filtered, washed with little acetic acid and dried in air. The precipitate was then taken in a beaker containing water and made basic (pH = 8) by addition of saturated sodium carbonate solution. Then it was transferred to a separating funnel and extracted with dichloromethane. The organic layers were combined, dried over anhydrous sodium sulfate and evaporated under reduced pressure to a brown paste. Finally, it was purified by silica gel column chromatography using 30% EtOAc/PE as eluent. Yellowish white powder. Yield: 75%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.21 (dd, J = 4 Hz, 1.7 Hz, 1H), 8.39 (d, J = 8 Hz, 1H), 8.31 (d, J = 8.6 Hz, 1H), 7.82 (d, J = 8.3 Hz, 1H), 7.61–7.63 (m, 1H), 2.58 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 158.6, 155.0, 153.1, 137.9, 136.7, 136.1, 131.2, 124.9, 122.2, 121.7, 109.0, 15.1, 15.0. ESI-MS (CH_3CN), m/z: 320.9887 $[M+H]^+$.

Synthesis of $[Pd_2(C\text{^}N\text{-}L^1)(\mu\text{-}C\text{^}N\text{-}L^1)(L^1H)(H_2O)][(BF_4)_2]$ (1)

$[Pd_2(CH_3CN)_6](BF_4)_2$ (50 mg, 0.079 mmol) was dissolved in 1 mL of dry CH_3CN and added drop-wise to a dichloromethane solution (15 mL) of 2-(1-methyl-1H-pyrrol-2-yl)-1,8-Naphthyridine (L^1H) (66 mg, 0.32 mmol) via cannula at room temperature under N_2 atmosphere. Immediately after the addition, the solution became red. It was then stirred for additional 6 hours at room temperature. After stirring, it was passed through a schlenk frit using a pad of celite to prevent any black particles formed in the reaction mixture. The solution was then concentrated to a small volume under reduced pressure and 10 mL diethyl ether was added while stirring to get a red precipitate. The precipitate was washed with diethyl ether (3 × 10 mL) and dried under vacuum to afford **1** as deep red microcrystalline solid. Block shaped X-ray-quality crystals were grown by layering petroleum ether onto a dichloromethane solution of **1** inside an 8 mm o.d. vacuum-sealed glass tube. Yield: 65 mg (80%).^{1}H NMR (500 MHz, CD_3CN): δ 8.89 (d, 7.6 Hz,

2H), 8.84 (d, 5.2 Hz, 2H), 8.47 (d, 9.2 Hz, 1H), 8.40 (d, 8.9 Hz, 2H), 8.15 (d, 8.9 Hz, 2H), 7.98 (br,m, 1H), 7.92 (d, 8.9 Hz, 1H), 7.83 – 7.87 (m, 2H), 7.26 (br,m, 2H), 7.13 (br,m, 2H), 6.63 – 6.64 (m, 2H), 6.28 – 6.30 (m, 3H), 4.50 (s, 3H), 4.19 (s, 6H). ^{13}C NMR (126 MHz, CD_3CN): δ 207.2, 172.0, 157.3, 156.4, 154.1, 147.4, 144.6, 141.9, 141.2, 137.9, 137.7, 137.1, 133.8, 132.6, 131.4, 130.2, 130.1, 124.3, 123.5, 122.8, 122.3, 120.9, 119.5, 119.1, 118.3, 111.0, 110.0, 109.6, 109.3, 108.6, 40.8, 40.0, 38.7. IR (KBr, cm^{-1}): ν 3453 (br), 3098 (w), 1609 (s), 1531 (s), 1493 (m), 1453 (m), 1427 (s), 1401 (s), 1387 (s), 1324 (m), 1062 (vs, BF_4^-), 840 (m), 743 (m). ESI-MS (CH_3CN), m/z: 924.08 $[Pd_2(L^1)_2(L^1H)(BF_4)]^+$, 523.08 $[Pd_2(L^1)_2(L^1H)^2]^{2+}$, 418.54 $[Pd_2(L^1)_2(L^1H)]^{2+}$. Anal. Calcd for $C_{39}H_{31}N_9B_2F_8Pd_2$: C, 46.28; H, 3.09; N, 12.45. Found: C, 45.78; H, 2.98; N, 13.42.

Synthesis of $[Pd_3(C^N\text{-}L^2)(\mu\text{-}C^N\text{-}L^2)_2(L^2H)(H_2O)][BF_4]_3$ (2)

Complex **2** was synthesized by the reaction between $[Pd_2(CH_3CN)_6](BF_4)_2$ (50 mg, 0.079 mmol) and 2-(2,5-dimethylthiophen-3-yl)-1,8-Naphthyridine (L^2H) (77 mg, 0.32 mmol) following a procedure similar to that described for the synthesis of **1** except stirring was continued for 12 hours due to gradual change of color of the solution from orange to red. A red powder was obtained. Block shaped X-ray-quality crystals were grown by layering petroleum ether onto a dichloromethane solution of **2** inside an 8 mm o.d. vacuum-sealed glass tube. Yield: 69 mg (56%).^{1}H NMR (500 MHz, CD_3CN): δ 9.01 – 9.04 (m, 4H), 8.88 – 8.92 (m, 1H), 8.65 – 8.67 (m, 2H), 8.51 – 8.55 (m, 1H), 8.45 – 8.47 (m, 1H), 8.34 – 8.40 (m, 1H), 8.25 – 8.30 (m, 1H), 8.15 – 8.16 (m, 2H), 7.95 – 8.02 (m, 4H), 7.63 – 7.67 (m, 1H), 7.41 – 7.47 (m, 1H), 7.32 (br,m, 2H), 2.83 (s, 6H), 2.82 (s, 3H), 2.73 (s, 3H), 2.46 (s, 6H), 2.43 (s, 6H). ^{13}C NMR (126 MHz, CD_3CN): δ 207.0, 202.9, 170.2, 160.0, 159.2, 157.8, 157.6, 154.1, 153.8, 153.0, 147.9, 146.8, 146.7, 146.6, 145.2, 143.3, 142.1, 141.8, 141.5, 139.3, 139.0, 138.9, 138.7, 137.1, 136.6,

135.3, 134.3, 127.4, 127.0, 126.5, 125.4, 124.5, 124.2, 122.7, 122.2, 108.6, 107,0, 102.4, 101.7, 17.2, 15.7, 15.5, 14.3, 14.1. IR (KBr, cm^{-1}): ν 3420 (br), 3080 (w), 2968 (w), 2923 (w), 1631 (s), 1608 (s), 1554 (m), 1523 (m), 1496 (m), 1434 (m), 1381 (m), 1270 (w), 1219 (w), 1061 (vs, BF_4^-), 846 (m), 777 (m). ESI-MS (CH_3CN), m/z: 465 $[Pd_2(L^2)_2(L^2H)]^{2+}$, 386 $[Pd(L^2)(CH_3CN)]^+$, 585.04 $[Pd(L^2)(L^2H)]^+$. Anal. Calcd for $C_{56}H_{45}N_8B_3F_{12}S_4Pd_3$: C, 43.73; H, 2.95; N, 7.29. Found: C, 44.18; H, 2.88; N, 7.08.

Synthesis of $[Pd_3(C\text{^}N\text{-}L^2)(\mu\text{-}C\text{^}N\text{-}L^2)_2(L^2Br)(H_2O)][BF_4]_3$ (3)

Complex **3** was synthesized by the reaction between $[Pd_2(CH_3CN)_6](BF_4)_2$ (50 mg, 0.079 mmol) and 2-(4-bromo-2,5-dimethylthiophen-3-yl)-1,8-Naphthyridine (L^2Br) (102 mg, 0.32 mmol) following a procedure similar to that described for the synthesis of **2**. A red powder was obtained. Needle shaped X-ray-quality crystals were grown by layering petroleum ether onto a dichloromethane solution of **3** inside an 8 mm o.d. vacuum-sealed glass tube. Yield: 100 mg (68%). ^1H NMR (500 MHz, CD_3CN): δ 9.08 – 9.09 (m, 1H), 8.86 – 8.93 (m, 2H), 8.79 (d, 8.8 Hz, 1H), 8.69 (d, 8.3 Hz, 1H), 8.61 (d, 9.5 Hz, 1H), 8.52 (d, 8.5 Hz, 1H), 8.37 – 8.39 (m, 1H), 8.25 – 8.32 (m, 3H), 8.16 – 8.17 (m, 1H), 7.89 – 7.99 (m, 2H), 7.78 – 7.81 (m, 1H), 7.57 – 7.62 (m, 2H), 7.22 – 7.24 (m, 1H), 6.91 – 6.93 (m, 1H), 6.81 – 6.83 (m, 1H), 3.02 (s, 3H), 2.84 (s, 3H) 2.82 (s, 3H), 2.77 (s, 3H), 2.64 (s, 3H), 2.62 (s, 3H), 2.35 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, CD_3CN): δ 209.7, 202.0, 176.9, 162.7, 162.5, 161.8, 160.3, 159.2, 157.4, 157.0, 155.7, 154.9, 154.8, 154.6, 154.3, 152.8, 150.2, 146.1, 144.9, 144.7, 144.3, 143.1, 142.6, 142.2, 142.1, 142.0, 141.7, 141.6, 141.4, 141.0, 140.4, 139.7, 137.9, 137.8, 137.6, 134.5, 128.4, 127.2, 125.1, 124.2, 123.2, 121.6, 121.2, 121.0, 120.6, 108.6, 100.2 15.8, 15.2, 14.5, 14.2, 13.4, 12.7. IR (KBr, cm^{-1}): ν 3465 (br), 3010 (w), 2923 (w), 2855 (w), 1607 (s), 1553 (m), 1527 (s), 1435 (s), 1374 (s), 1058 (vs, BF_4^-), 846 (m), 784 (m). ESI-MS (CH_3CN), m/z: 504 $[Pd_2(L^2)_2(L^2Br)]^{2+}$, 386

$[Pd(L^2)(CH_3CN)]^+$, 662.95 $[Pd(L^2)(L^2Br)]^+$. Anal. Calcd for $C_{56}H_{44}N_8S_4Br_1B_3F_{12}Pd_3$: C, 41.60; H, 2.74; N, 6.93. Found: C, 41.22; H, 2.88; N, 6.33.

Synthesis of $[Pd_2(C\text{^}N\text{-}L^1)(\mu\text{-}C\text{^}N\text{-}L^1)(L^1H)_2][(BNB)_2]$ (4)

$[Pd_2(CH_3CN)_6(BNB)_2]$: $[Pd_2(CH_3CN)_6](BF_4)_2$ (50 mg, 0.079 mmol) was dissolved in 10 mL of dry CH_3CN and to this sodium di-tris(pentafluorophenyl)borane amide ($Na[NH_2\{B(C_6F_5)_3\}_2]$), NaBNB (168 mg, 0.158 mmol) was added. The orange solution was then stirred at room temperature for 30 minutes and passed through a Schlenk frit to prevent $NaBF_4$ formed during the reaction. Then, solvent was removed completely under reduced pressure to get an orange mass. IR (KBr, cm^{-1}): ν 3390 (w, NH_2), 3344 (w, NH_2), 2335 (w, CN), 2310 (w, CN), 2280 (w, CN), 1638 (m, NH_2), 1466 (vs, BNB).

Subsequently, this orange mass was dissolved in 10 mL dry dichloromethane and to this dichloromethane solution (1 mL) of 2-(1-methyl-1H-pyrrol-2-yl)-1,8-naphthyridine (L^1H) (66 mg, 0.32 mmol) was added dropwisely via cannula at room temperature under N_2 atmosphere. Immediately after the addition, the solution became red. It was then stirred for additional 6 hours at room temperature. After stirring, it was passed through a Schlenk frit using a pad of celite to prevent any black particles if formed in the reaction mixture. The solution was then concentrated to a small volume under reduced pressure and 10 mL petroleum ether was added while stirring to get a red precipitate. The precipitate was washed with petroleum ether (3 × 10 mL) and dried under vacuum to afford **4** as deep red microcrystalline solid. Block shaped X-ray-quality crystals were grown by layering petroleum ether onto a dichloromethane solution of **4** inside an 8 mm o.d. vacuum-sealed glass tube. Yield: 173 mg (70%).^{1}H NMR (500 MHz, CD_3CN): δ 8.95 – 8.97 (m, 2H), 8.37 – 8.41 (m, 3H), 8.29 (d, 7.0 Hz, 1H), 8.13 (d, 7.9 Hz, 1H), 8.06 – 8.07 (m, 1H), 7.94 – 7.96 (m, 2H), 7.86 – 7.88 (m, 1H), 7.68 – 7.74 (m, 2H), 7.53 – 7.58 (m, 2H), 7.32 –

7.37 (m, 2H), 7.24 – 7.26 (m, 2H), 7.15 (br,s, 1H), 7.06 (d, 2.1 Hz, 1H), 6.92 (s, 1H), 6.83 (s, 1H), 6.81 (s, 1H), 6.71 (br,s, 1H), 6.66 (d, 2.5 Hz, 1H), 6.61 – 6.62 (m, 1H), 6.28 (d, 2.5 Hz, 1H), 6.10 – 6.12 (m, 1H), 6.04 (br,s, 1H), 5.67 (br, 4H), 4.52 (s, 3H), 3.97 (s, 3H), 3.86 (s, 3H), 3.81 (s, 3H). ^{13}C NMR (126 MHz, CD_3CN): δ 207.8, 170.2, 160.2, 157.4, 157.2, 157.1, 155.8, 154.9, 154.7, 154.5, 153.7, 153.4, 153.0, 152.6, 148.8, 146.9, 144.9, 143.5, 142.2, 141.6, 141.2, 140.3, 140.2, 140.1, 139.9, 139.6, 139.5, 138.3, 138.2, 138.1, 137.8, 137.7, 137.6, 137.5, 137.2, 136.5, 136.3, 135.9, 135.8, 135.7, 135.6, 133.6, 133.3, 131.0, 130.6, 130.3, 129.4, 123.9, 122.0, 121.7, 121.4, 121.3, 121.1, 121.0, 120.7, 119.8, 119.2, 116.8, 116.5, 116.3, 116.2, 111.2, 108.6, 108.5, 40.9, 37.9, 36.7, 36.5. ^{19}F NMR (470 MHz, CD_3CN): δ -133.6 (d, 17.8 Hz, 12F), -160.4 (t, 18.3 Hz, 6F), -166.3 (t, 18.3 Hz, 12F). IR (KBr, cm^{-1}): ν 3392 (w, NH_2), 3340 (w, NH_2), 2928 (w), 1645 (m, NH_2), 1613 (m), 1556 (m), 1518 (s), 1466 (vs, BNB), 1427 (m), 1402 (m), 1390 (m), 1379 (m), 1276 (m), 1100 (s), 1084 (s), 986 (s), 978 (s), 957 (m), 837 (m), 780 (m). ESI-MS (CH_3CN), m/z: 418.54 $[Pd_2(L^1)_2(L^1H)]^{2+}$ Anal. Calcd for $C_{124}H_{46}N_{14}B_4F_{60}Pd_2$: C, 47.62; H, 1.48; N, 6.27. Found: C, 47.78; H, 1.38; N, 6.42.

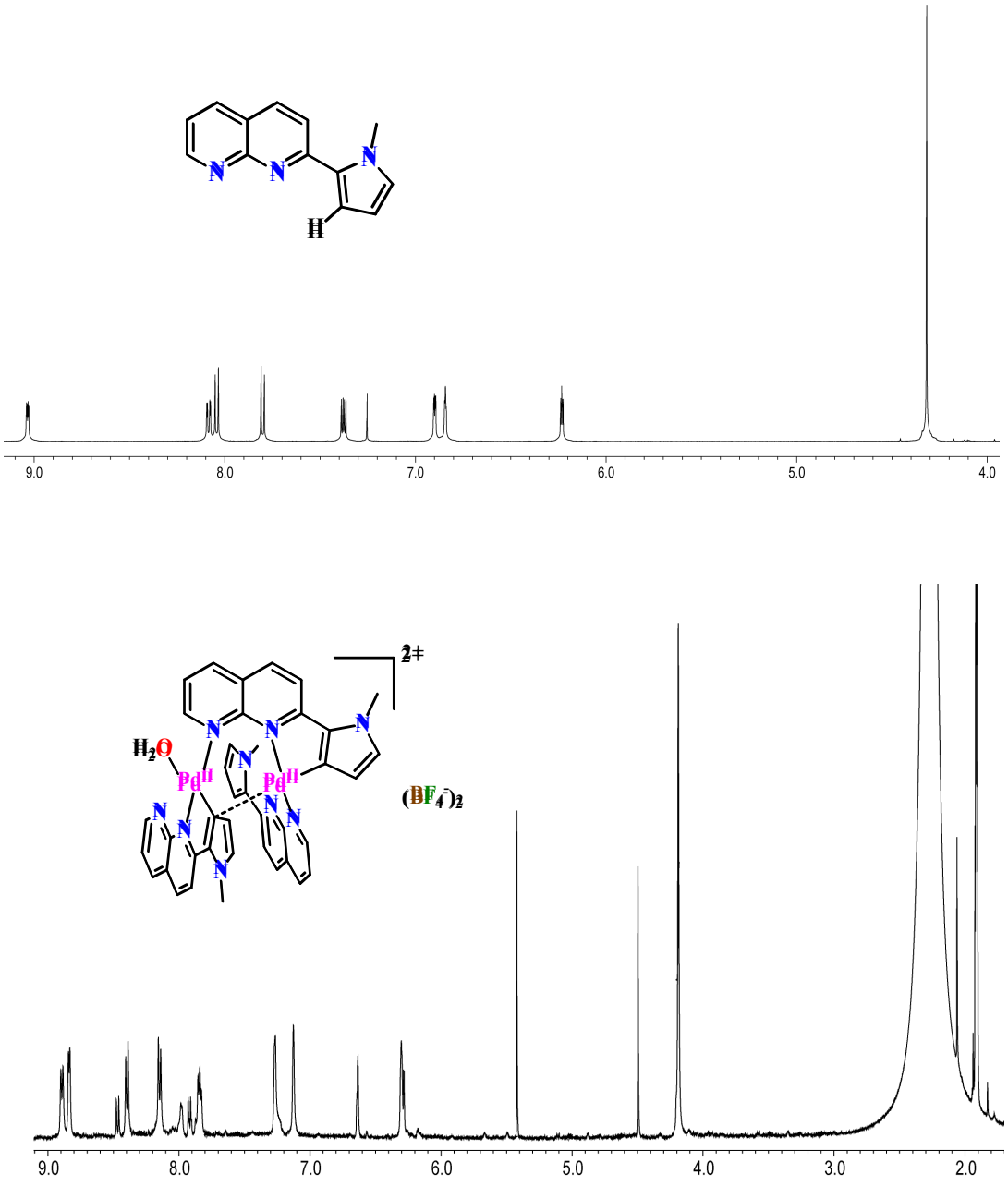

Figure S1. ^{1}H NMR spectra of ligand **L^{1}H** (top) and complex **1** (bellow).

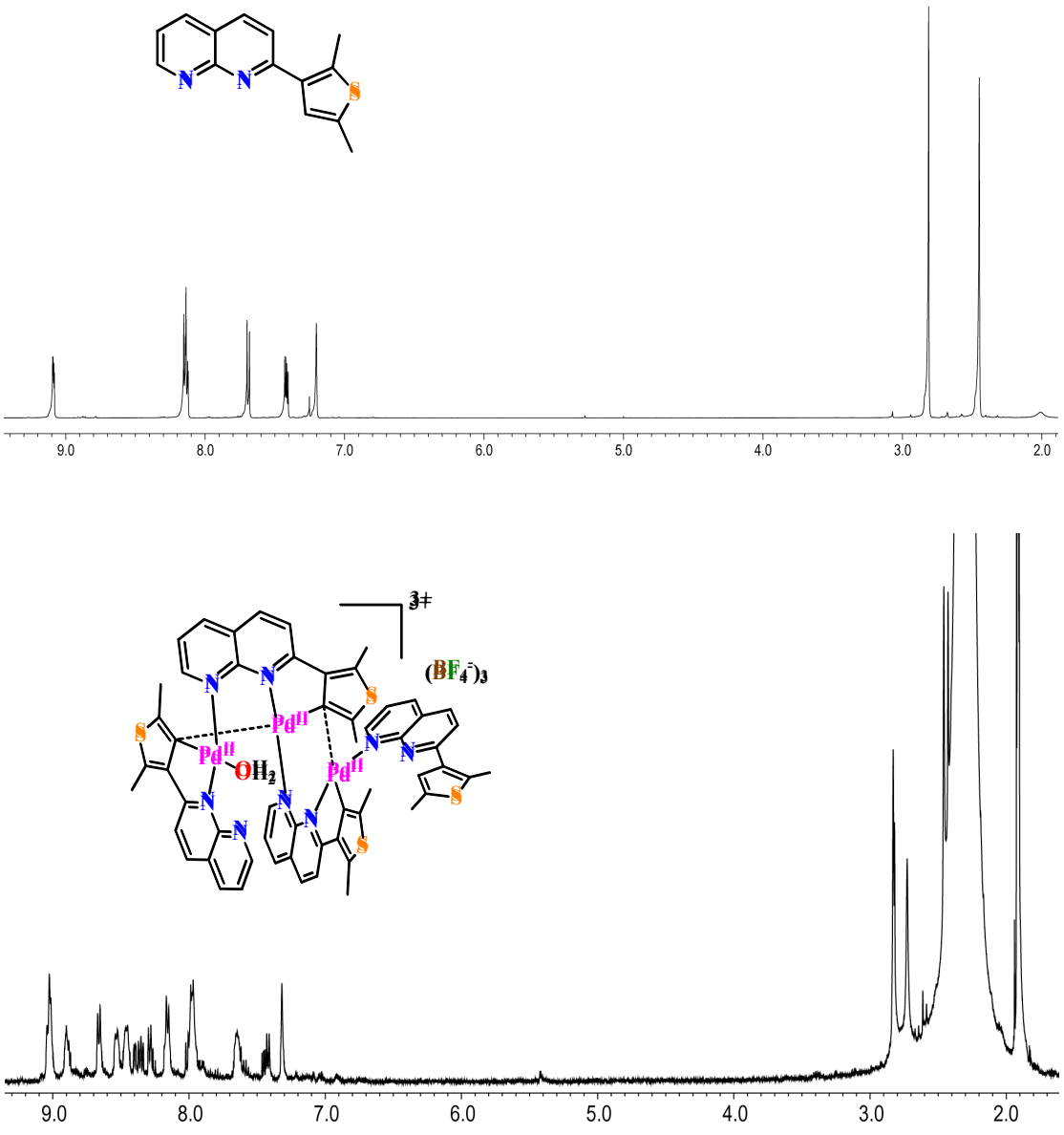

Figure S2. ^{1}H NMR spectra of ligand **L^{2}H** (top) and complex **2** (bellow).

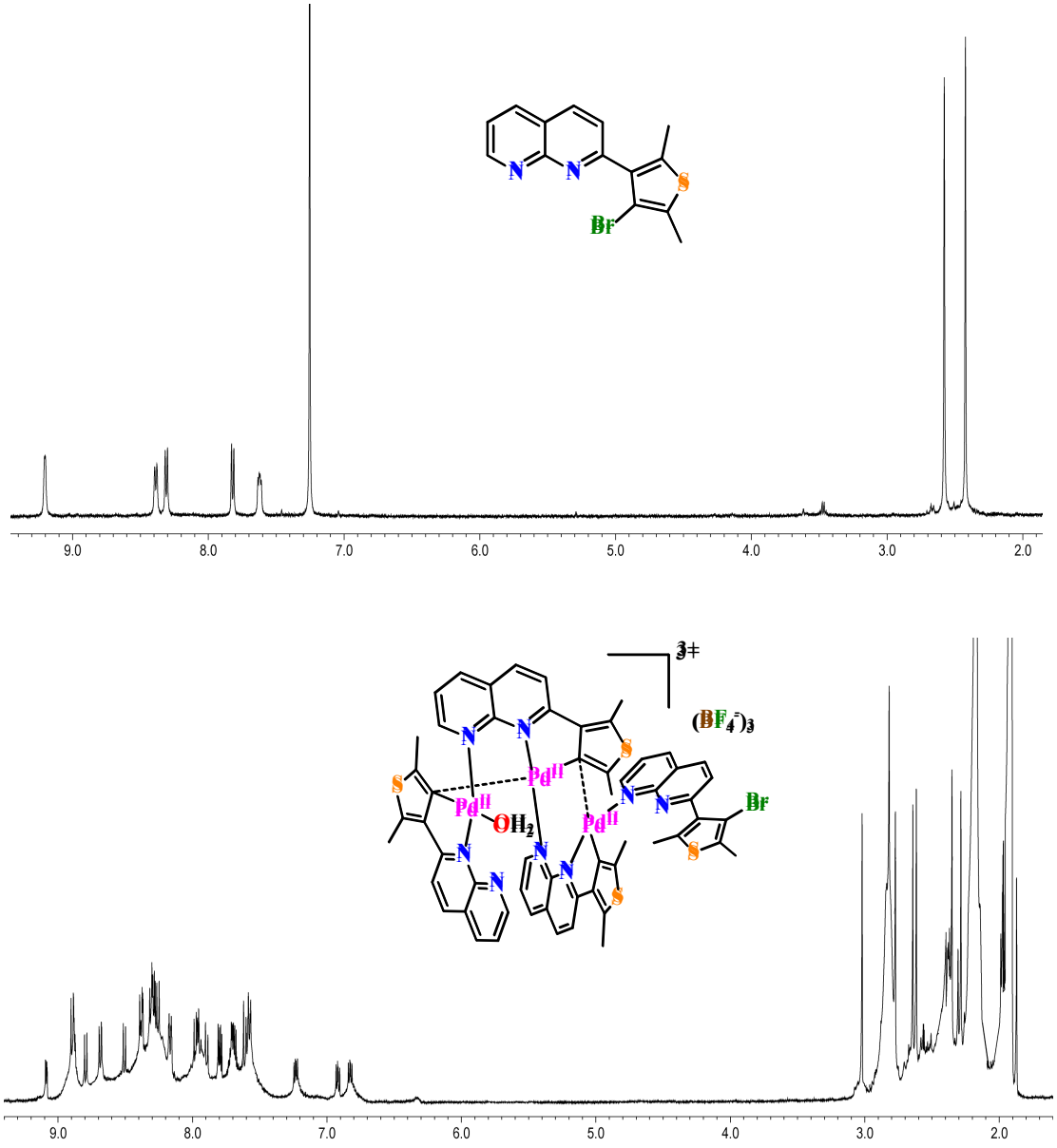

Figure S3. ^{1}H NMR spectra of ligand **L^{2}Br** (top) and complex **3** (bellow).

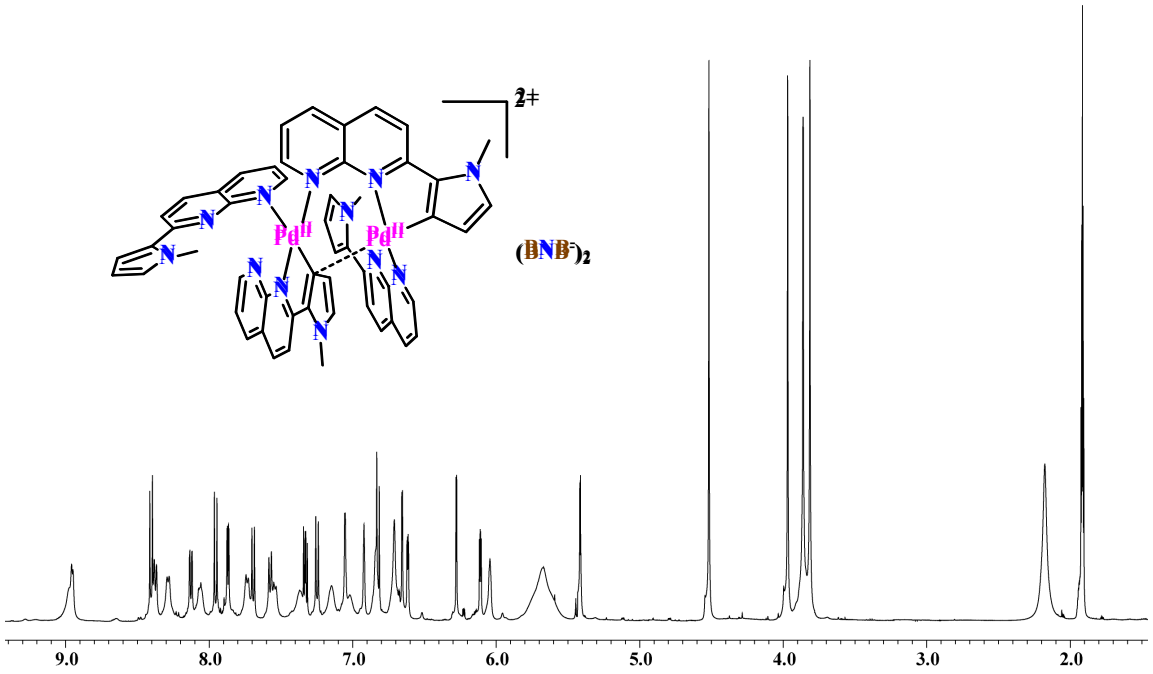

Figure S4. ^{1}H NMR spectrum of complex **4**.

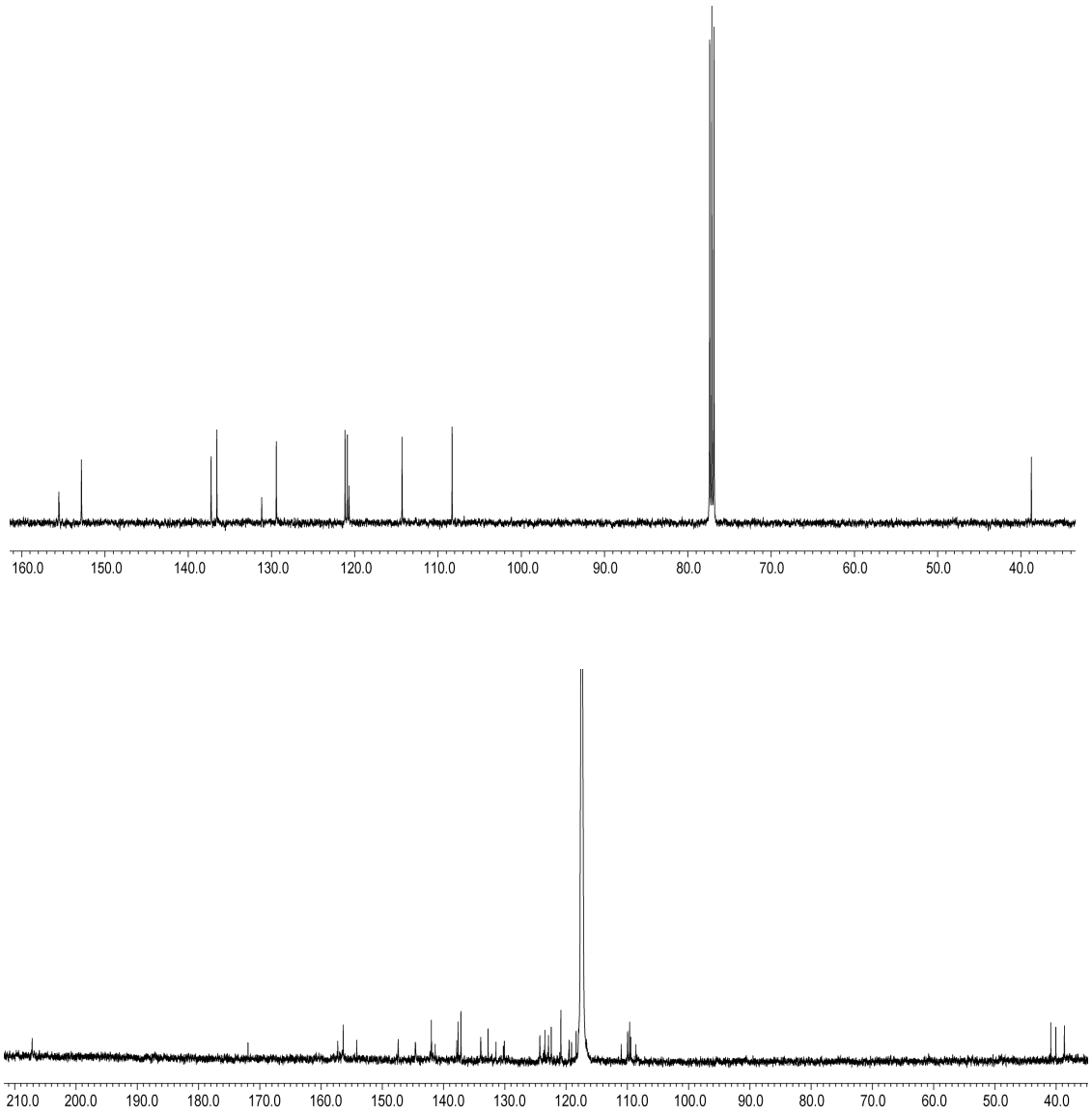

Figure S5. ^{13}C NMR spectra of ligand **L^{1}H** (top) and complex **1** (bellow).

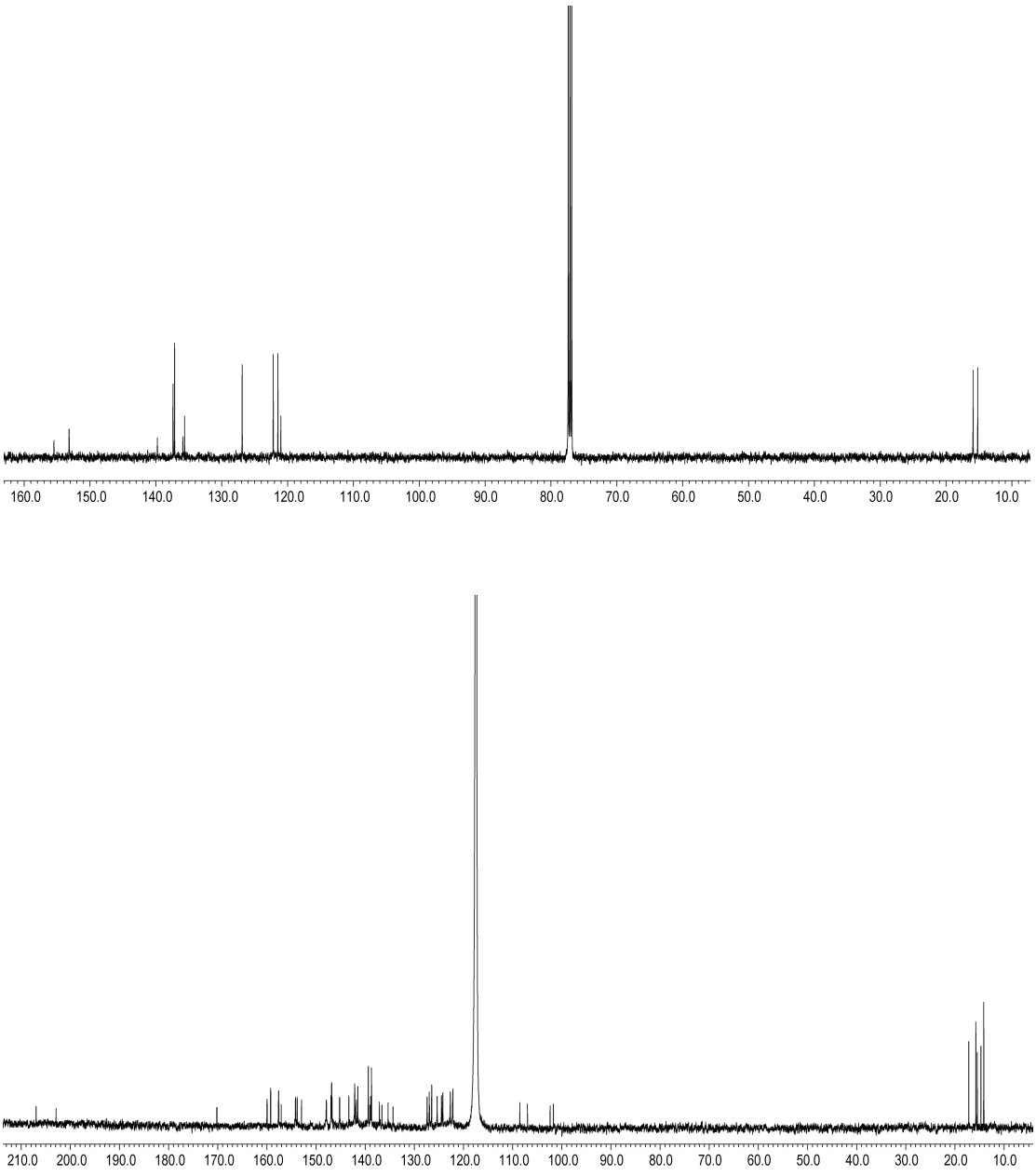

Figure S6. ^{13}C NMR spectra of ligand **L^{2}H** (top) and complex **2** (bellow).

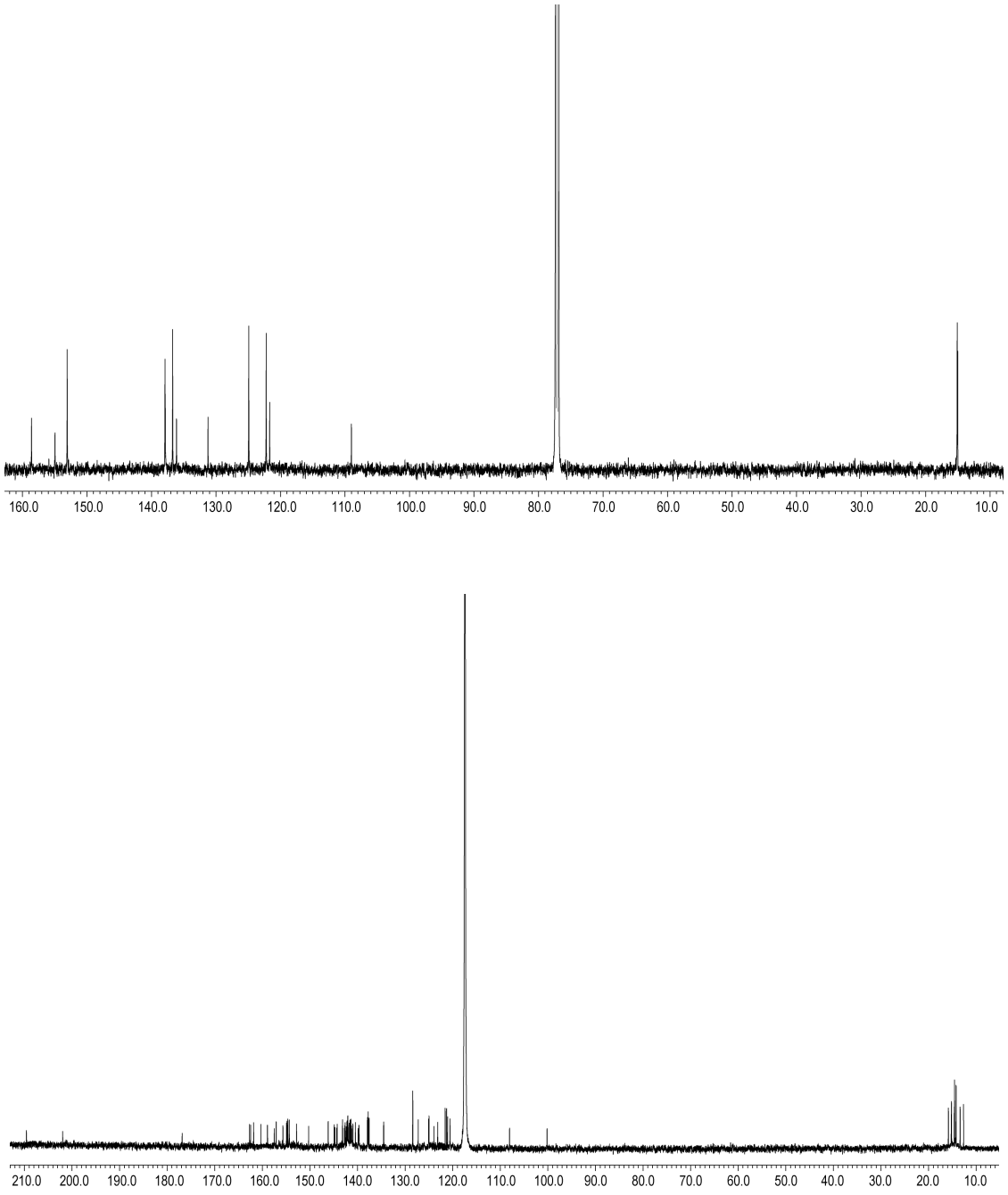

Figure S7. ^{13}C NMR spectra of ligand **L^{2}Br** (top) and complex **3** (bellow).

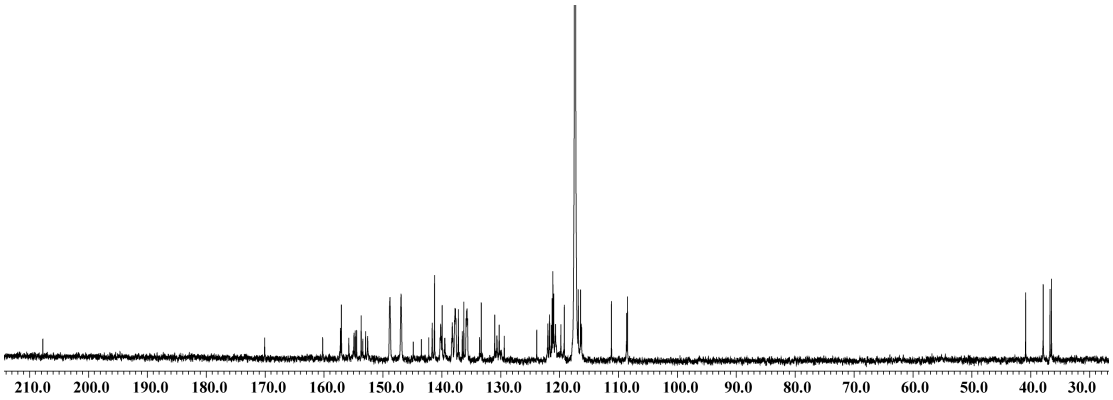

Figure S8. ^{13}C NMR spectrum of complex **4**

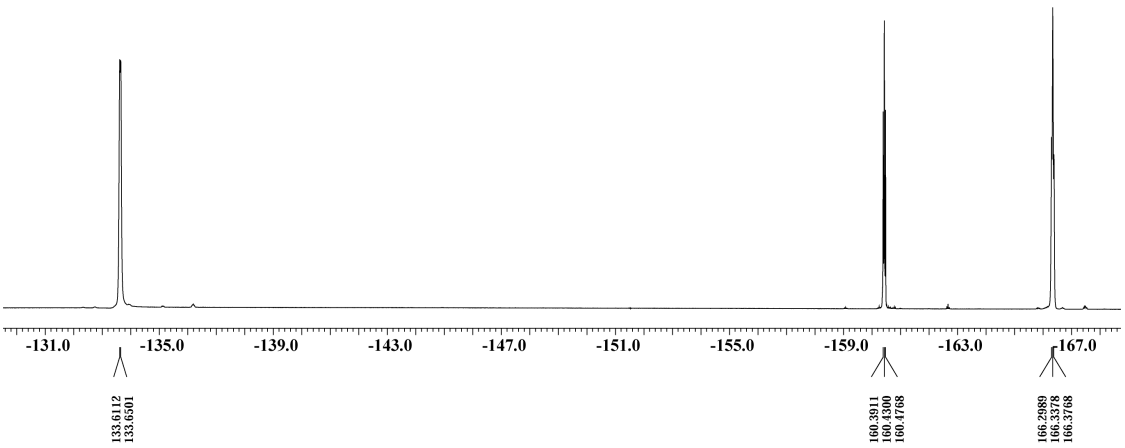

Figure S9. ^{19}F NMR spectrum of complex **4**

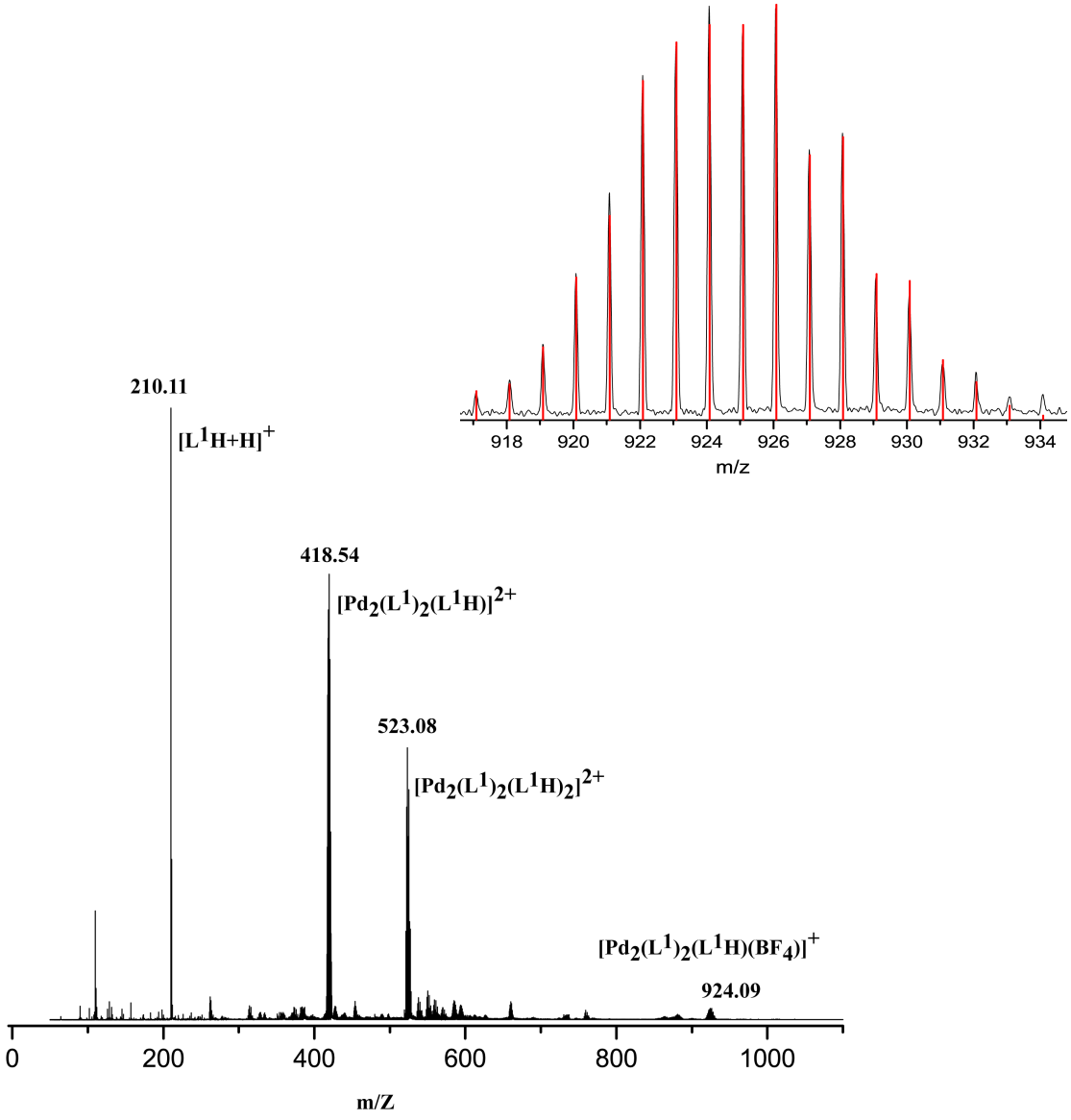

Figure S10: Experimental (black) and simulated (red) ESI-MS Spectrum for $[Pd_2(L^1)_2(L^1H)(BF_4)]^+$ at m/z = 924.08 (z=1) in complex **1**(top) and ESI-MS spectrum in the full range for complex**1**(bellow).

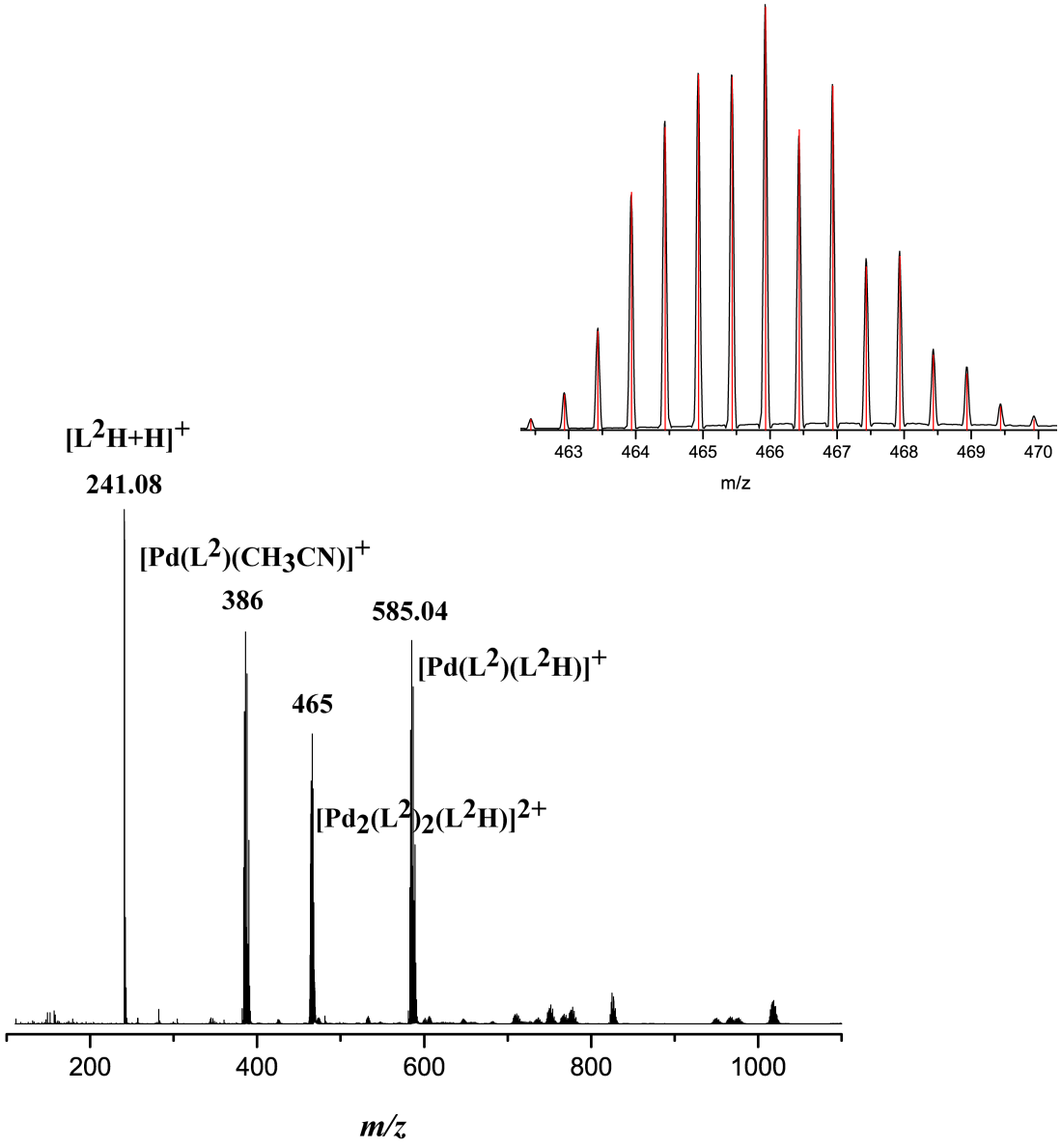

Figure S11: Experimental (black) and simulated (red) ESI-MS Spectrum for $[Pd_2(L^2)_2(L^2H)]^{2+}$ at *m/z* = 465 (*z*=2) in complex **2** (top) and ESI-MS spectrum in the full range for complex **2** (bellow).

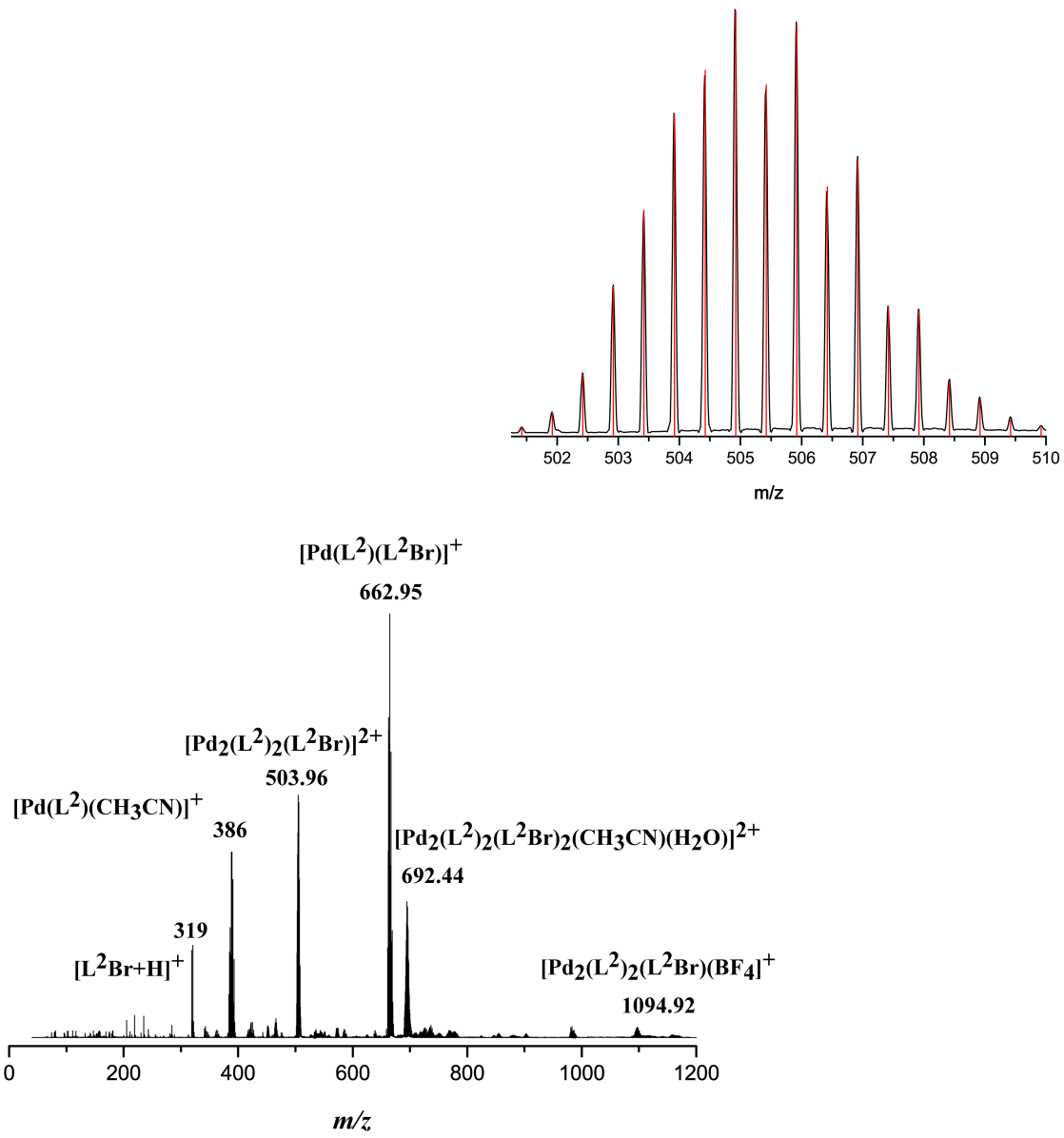

Figure S12: Experimental (black) and simulated (red) ESI-MS Spectrum for $[Pd_2(L^2)_2(L^2Br)]^{2+}$ at *m/z* = 504 (*z*=2) in complex **3** (top) and ESI-MS spectrum in the full range for complex **3** (bellow).

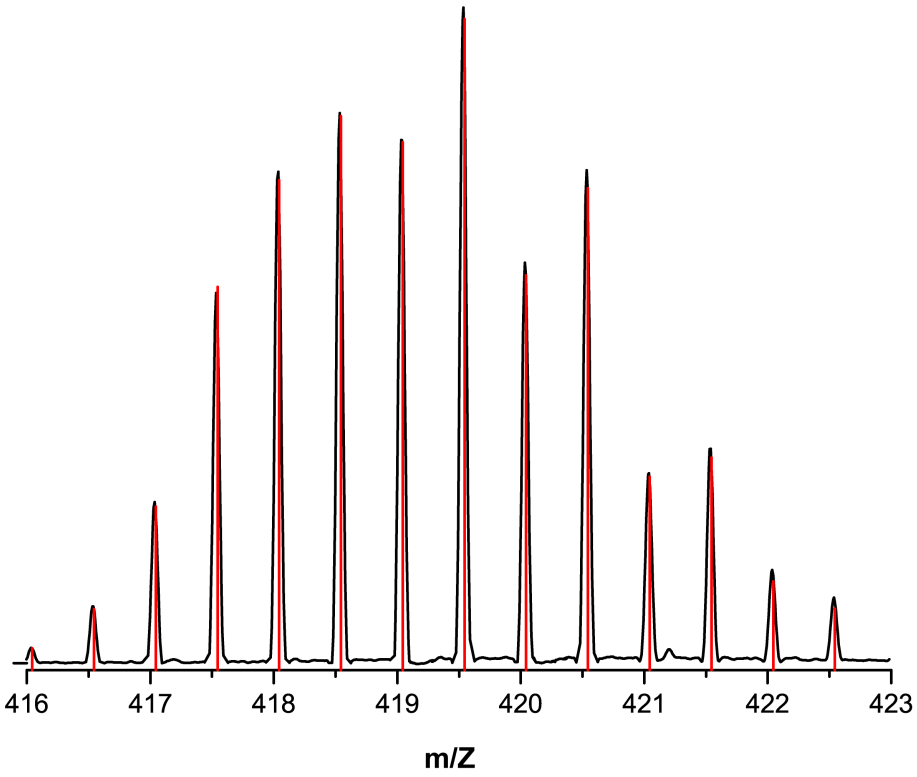

Figure S13: Experimental (black) and simulated (red) ESI-MS Spectrum for $[Pd_2(L^1)_2(L^1H)]^{2+}$ at $m/z = 418.54$ (z=2) in complex **4**

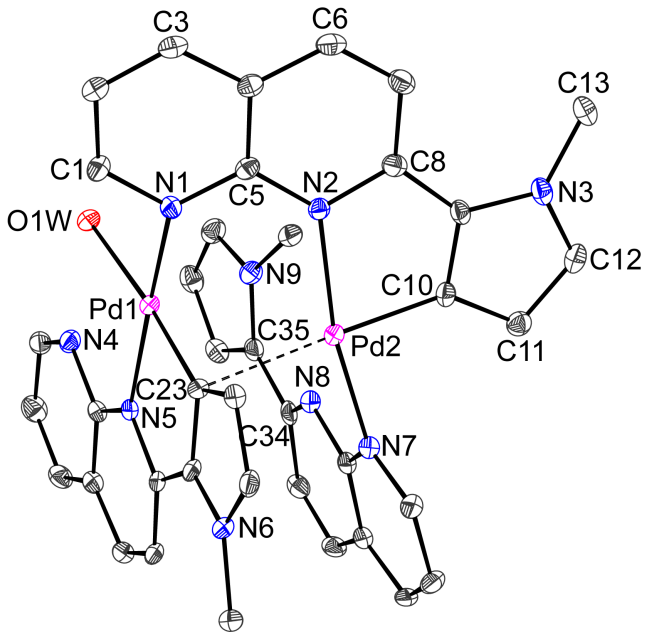

Figure S14. ORTEP diagram (40% probability thermal ellipsoids) of the cationic unit **[Pd$_2$(C^N-L^1)(μ-C^NL^1) (L^{1}H)(H$_2$O)]$^{2+}$** in complex **1** with important atoms labeled. Hydrogen atoms are omitted for the sake of clarity. Selected bond distances (Å) and angles (deg): Pd1···Pd2 = 3.043(1), Pd1–N1 2.032(4), Pd1–N5 2.092(4), Pd2–N2 2.088(4), Pd2–N7 2.026(4), Pd1–C23 1.943(5), Pd2–C10 1.953(5), Pd2–C23 2.410(5), Pd1–C23–Pd2 88.04(2), N1–C5–N2–Pd2 17.1(6), N2–C5–N1–Pd1 14.3(6), N4–C18–N5–Pd1 4.8(6), N2–C8–C9–C10 5.7(6), N5–C21–C22–C23 4.8(6), N8–C34–C35–N9 10.5(7).

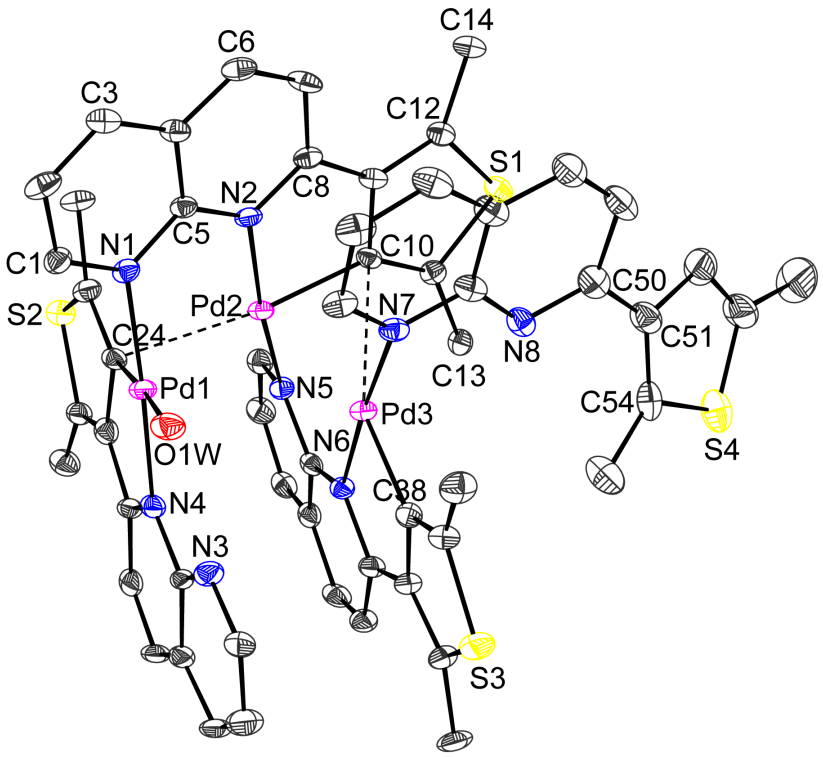

Figure S15. ORTEP diagram (40% probability thermal ellipsoids) of the cationic unit $[Pd_3(C\text{^}N\text{-}L^2)(\mu\text{-}C\text{^}N\text{-}L^2)_2(L^2H)(H_2O)]^{3+}$ in complex **2** with important atoms labeled. Hydrogen atoms are omitted for the sake of clarity. Selected bond distances (Å) and angles (deg): Pd1···Pd2 2.816(1), Pd2···Pd3 2.675(1), Pd1–C24 1.977(8), Pd2–C24 2.518(8), Pd2–C10 1.977(7), Pd3–C10 2.973(7), Pd3–C38 1.963(8), Pd1–C24–Pd2 76.5(3), Pd2–C10–Pd3 61.6(2), N8–C50–C51–C54 27.9(1), N4–C22–C23–C24 2.9(1), N2–C8–C9–C10 1.0(1), N6–C36–C37–C38 1.5(1).

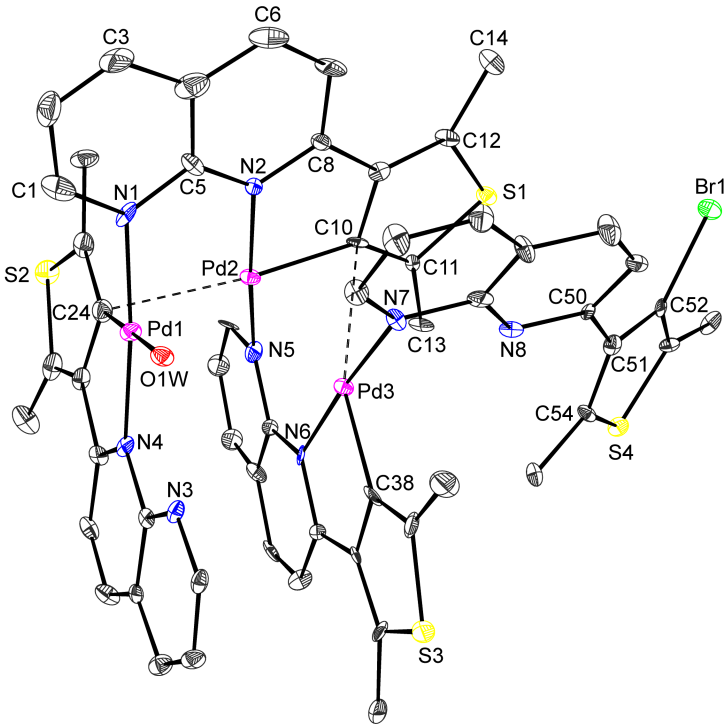

Figure S16. ORTEP diagram (40% probability thermal ellipsoids) of the cationic unit $[Pd_3(C\text{^}N\text{-}L^2)(\mu\text{-}C\text{^}N\text{-}L^2)_2(L^2Br)(H_2O)]^{3+}$ in complex **3** with important atoms labeled. Hydrogen atoms are omitted for the sake of clarity. Selected bond distances (Å) and angles (deg): Pd1···Pd2 2.789(2), Pd2···Pd3 2.705(1), Pd1–C24 1.946(1), Pd2–C24 2.596(1), Pd2–C10 1.979(1), Pd3–C10 2.914(1), Pd3–C38 1.998(1), Pd1–C24–Pd2 74.3(4), Pd2–C10–Pd3 63.8(3), N8–C50–C51–C54 33.5(2), N4–C22–C23–C24 6.4(2), N2–C8–C9–C10 0.9(2), N6–C36–C37–C38 2.5(2).

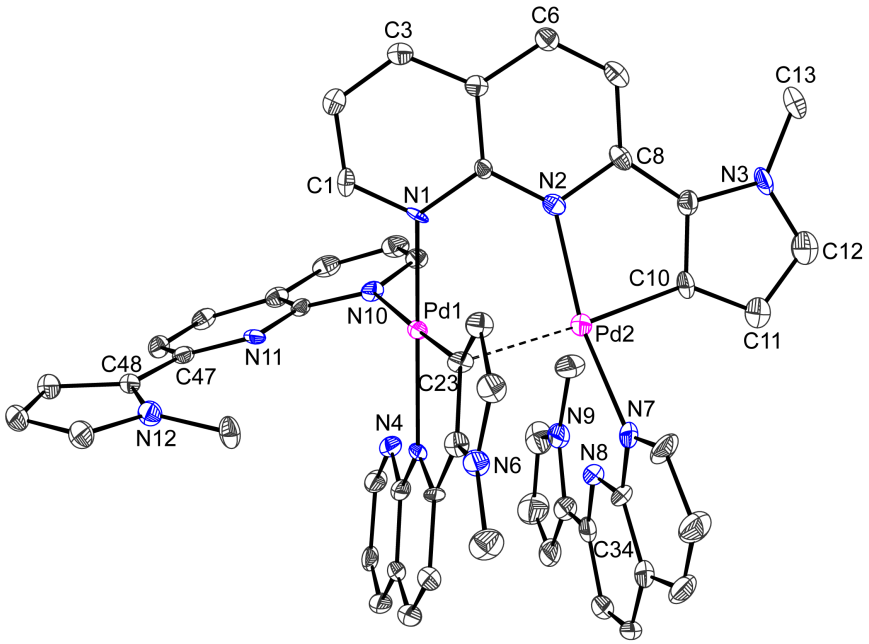

Figure S17. ORTEP diagram (40% probability thermal ellipsoids) of the cationic unit $[Pd_2(C\text{^}N\text{-}L^1)(\mu\text{-}C\text{^}NL^1)\ (L^1H)_2]^{2+}$ in complex **4** with important atoms labeled. Hydrogen atoms are omitted for the sake of clarity. Selected bond distances (Å) and angles (deg): Pd1···Pd2 2.863(1), Pd1–N1 2.025(4), Pd1–N5 2.112(4), Pd2–N2 2.083(4), Pd2–N7 2.054(4), Pd1–C23 1.976(5), Pd2–C10 1.961(5), Pd2–C23 2.407(5), Pd1–C23–Pd2 80.9(2), N1–C5–N2–Pd2 21.9(6), N2–C5–N1–Pd1 4.4(6), N2–C8–C9–C10 7.9(7), N5–C21–C22–C23 0.5(6), N8–C34–C35–N9 8.9(1), N11–C47–C48–N12 16.7(7).

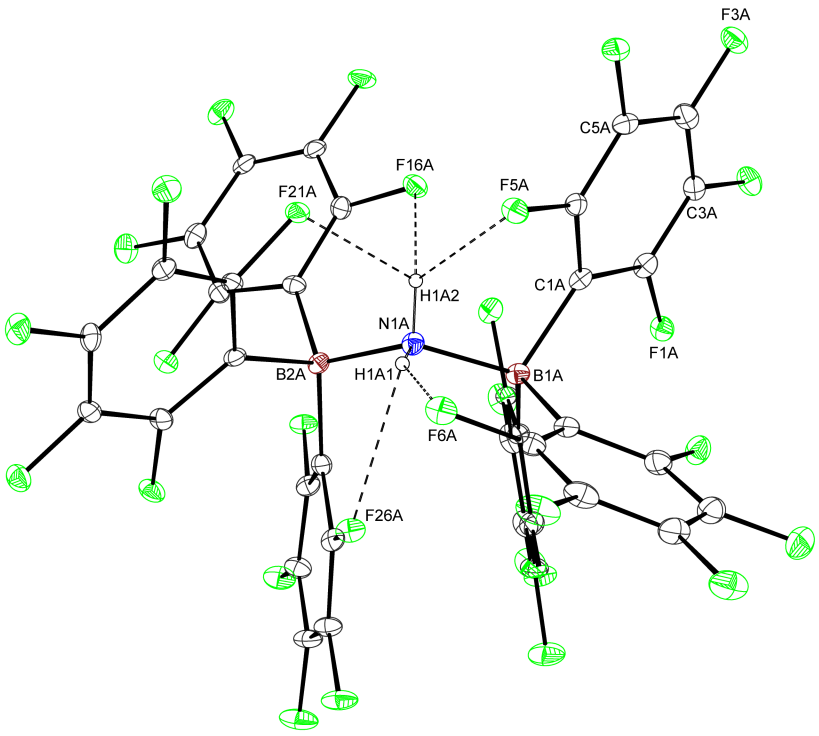

Figure S18. ORTEP diagram (40% probability thermal ellipsoids) of the anionic unit $[NH_2\{B(C_6F_5)_3\}_2]^-$ in complex **4** with important atoms labeled. Dotted lines indicate H···F hydrogen bonding. Selected bond distances (Å): B1A–N1A 1.634(7), B2A–N1A 1.621(6), H1A1···F6A 1.924(4), H1A1···F26A 2.507(4), H1A2···F5A 2.239(4), H1A2···F16A 2.068(4), H1A2···F21A 2.230(3), N1A–(H1A1) –F6A 2.781(7), N1A–(H1A1) –F26A 2.926(8), N1A–(H1A2) –F5A 2.803(7), N1A–(H1A2) –F16A 2.769(8), N1A–(H1A2) –F21A 2.743(6).

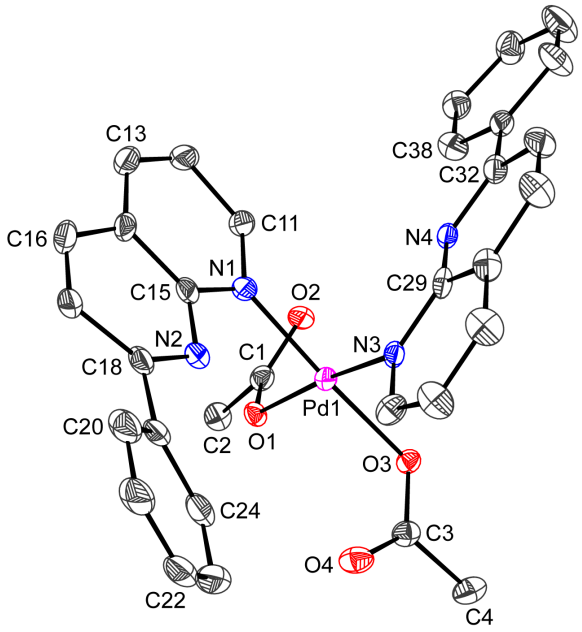

Figure S19. ORTEP diagram (40% probability thermal ellipsoids) of **[Pd(PhNP)$_2$(OAc)$_2$](5)** with important atoms labeled. Hydrogen atoms are omitted for the sake of clarity. Selected bond distances (Å) and angles (deg): Pd1–N1 2.015(5), Pd1–N3 2.021(6), Pd1–O1 2.026(4), Pd1–O3 2.006(4), N2–C18–C19–C24 26.7(1), N4–C32–C33–C38 6.8(9), N2–C15–N1–Pd1 8.7(7), N4–C29–N3–Pd1 7.0(7).

Table S1. Crystallographic data and pertinent refinement parameters for compounds **1 – 5**

	1•2CH_2Cl_2	**2**•2CH_2Cl_2•H_2O	**3**•2.5C_6H_6
Empirical formula	$C_{41}H_{37}B_2Cl_4F_8N_9O_1Pd_2$	$C_{58}H_{53}B_3Cl_4F_{12}N_8O_2Pd_3S_4$	$C_{71}H_{61}B_3Br_1F_{12}N_8O_1Pd_3S_4$
Formula Weight	1200.02	1743.84	1830.14
Crystal System	Triclinic	Monoclinic	Monoclinic
Space Group	*P*-1	*P*2(1)/c	*P*2(1)/n
a (Å)	11.4647(16)	19.485(2)	22.464(4)
b (Å)	14.1481(19)	22.628(3)	22.228(4)
c (Å)	15.650(2)	14.2391(16)	25.760(4)
α (deg)	111.841(2)	90.00	90.00
β (deg)	91.505(2)	100.457(2)	100.596(4)
γ (deg)	108.809(2)	90.00	90.00
V (Å^3)	2199.4(5)	6173.7(12)	12643(4)
Z	2	4	8
ρ (g cm^{-3})	1.812	1.876	1.92
μ (mm^{-1})	1.142	1.262	1.692
F(000)	1192	3464	7288
Reflections Collected	15527	42227	37413
Independent	7459	10510	20264
Observed [I >2σ (I)]	5782	6415	8979
No. of variables	607	792	1585
GooF	1.021	0.933	0.899
Rint	0.0383	0.0775	0.1189
Final R indices [I > 2σ(I)][a]	R1 = 0.0452 wR2 = 0.1090	R1 = 0.0618 wR2 = 0.1489	R1 = 0.0856 wR2 = 0.1776
R indices (all data)[a]	R1 = 0.0606 wR2 = 0.1200	R1 = 0.0987 wR2 = 0.1630	R1 = 0.1871 wR2 = 0.2092
Flack Parameter	–	–	–

[a]$R_1 = \Sigma\ ||F_o| - |F_c||/\Sigma|F_o|$ with $F_o^2 > 2\sigma(F_o^2)$. $wR_2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma|F_o^2|^2]^{1/2}$

Table S1. ….continued.

	4.$2CH_2Cl_2$	**5.**CH_2Cl_2
Empirical formula	$C_{126}H_{50}B_4Cl_4F_{60}N_{14}Pd_2$	$C_{33}H_{28}Cl_2N_4O_4Pd_1$
Formula Weight	3297.64	721.89
Crystal System	Triclinic	Orthorhombic
Space Group	P-1	Pna21
a (Å)	18.389(3)	15.8053(16)
b (Å)	18.555(3)	19.5063(19)
c (Å)	22.215(3)	20.140(2)
α (deg)	100.835(2)	90.00
β (deg)	103.159(2)	90.00
γ (deg)	119.476(2)	90.00
V (Å^3)	6009.7(16)	6209.3(11)
Z	2	8
ρ (g cm^{-3})	1.822	1.544
μ (mm^{-1})	0.543	0.814
F(000)	3248	2928
Reflections Collected	44041	54617
Independent	21075	15248
Observed [I >2σ (I)]	14916	10472
No. of variables	1911	797
GooF	1.047	1.043
Rint	0.0465	0.0631
Final R indices [I > 2σ(I)][a]	R1 = 0.0554	R1 = 0.0582
	wR2 = 0.1356	wR2 = 0.1302
R indices (all data)[a]	R1 = 0.0837	R1 = 0.0942
	wR2 = 0.1590	wR2 = 0.1528
Flack Parameter	–	-0.01(3)

[a] $R_1 = \Sigma ||F_o| - |F_c||/\Sigma|F_o|$ with $F_o^2 > 2\sigma(F_o^2)$. $wR_2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma|F_o^2|^2]^{1/2}$

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