Supplementary Information

Synthesis, Structure and Palladium Coordination of Ambiphilic, Pyridine and Phosphine-Tethered *N*-Boryl Imine Ligands

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I. General Information

All manipulations were conducted in a glovebox under a nitrogen atmosphere, or using standard Schlenk techniques, unless otherwise noted. Solvents were dried by using a solvent purifier system and stored over activated molecular sieves inside the glovebox. Deuterated chloroform and dichloromethane were stirred over calcium hydride, vacuum transferred, degassed, and stored over 4 Å molecular sieves in the glovebox. 2-(Diphenylphosphanyl)-benzaldehyde and Ph_2BCl were synthesised according to literature procedures.[1,2] Unless otherwise noted, all other reagents were purchased from commercial sources and used without purification. Nuclear magnetic resonance (NMR) characterization data was acquired on 400 and 500 MHz spectrometers for proton, 101 and 126 MHz for carbon, 162 and 203 MHz for phosphorus and 128 and 161 MHz for boron. Mass spectra were

recorded on a high-resolution electrospray ionization quadrupole mass spectrometer in positive and negative ESI mode.

II Synthetic Procedures and Characterization Data

Synthesis of N-(diphenylboryl)-2-benzoylpyridinketimine (1a).

In analogy to the procedure of Hart,[3] 2-benzoylpyridine (0.925 g, 5.0 mmol) was added as a solid to a cold (0 °C) 1 M solution of lithium bis(trimethylsilyl)amide in anhydrous hexane (5.0 mL, 5.0 mmol) in a Schlenk flask under argon over the course of 20 min. A yellow solid precipitated from a brown solution. The reaction mixture was stirred at 0 °C for 0.5 h and then allowed to warm to room temperature. The solution was brought into the glovebox, the solid collected by filtration, and dried under high vacuum overnight to afford **2a** (1.43 g; 4.08 mmol, 82%) as a yellow solid together with 1 equivalent of what is assigned as LiOTMS. NMR data for **2a** are consistent with previous reports of pyridyl N-TMS imines.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ – 0.02 (br s, 5H, SiCH_3), δ 0.02 (s, 9H, SiCH_3), δ 0.06 (br s, 4H, SiCH_3), 7.30-7.43 (m, 4H), 7.50 (dt, J = 6.4, 1.8 Hz, 2H), 7.54 (dt, J = 7.8, 1.0 Hz, 1H), 7.74 (td, J = 7.7, 1.8 Hz, 1H), 8.64 (ddd, J = 4.8, 1.6, 1.0 Hz, 1H). ^{13}C NMR (500 MHz, $CDCl_3$) δ 0.60 (SiCH$_3$), 3.35 (SiCH$_3$), 3.88 (SiCH$_3$), 122.7, 123.7, 127.9, 128.4, 129.8, 136.1, 140.6, 149.1, 158.6, 173.8 LRMS calculated for $C_{15}H_{19}N_2Si$ $[M+H]^+$ 255.1, found: 255.1. This imine was directly converted to **1a**. In a glovebox, a colourless CH_2Cl_2 (6 mL) solution of BPh_2Cl (0.603 g, 3.01 mmol) was added dropwise to a brown CH_2Cl_2 (6.0 mL) solution of *N*-(trimethylsilyl)-2-benzoylpyridinketimine (**2a**) (0.765 g, 3.01 mmol), resulting in a brown solution from which a white solid starts precipitating shortly after the addition of $BPhCl_2$. After stirring for 15 hours, the solid was removed by filtration, and the solution collected. The solvent was removed *in vacuo* to afford **1a** as a pink solid (0.832 g, 2.4 mmol, 80%), together with TMS and trace aromatic impurities.[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (m, 5H), 7.34 (m, 4H), 7.43 (m, 1H), 7.50 (m, 3H), 7.59 (m, 1H), 7.81 (br m, 2H), 8.05 (dt, J = 8.0, 1.0 Hz, 1H), 8.21 (td, J = 7.6, 1.4 Hz, 1H), 8.81 (dt, J = 5.6, 1.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 121.2, 123.4, 126.5, 127.1, 127.6, 128.3, 128.7, 129.9, 132.8, 135.0, 141.8, 143.7, 149.7, 160.3. ^{11}B NMR (161 MHz, $CDCl_3$) δ 10.46 (s, 307 Hz line width at half height). FT-IR (ATR) 1594 cm^{-1}. ESI HRMS *m/z* calculated for $C_{24}H_{20}BN_2$ $[M+H]^+$ 347.1714, found: 347.1717. **1a** is moderately labile at ambient temperature in solution. It was therefore purified and its structure confirmed by coordination to palladium in complex **3a**, and crystallization as a protonated salt.

Synthesis of N-(diphenylboryl)picolinaldimine (1b).

2-Pyridinecarboxaldehyde (0.48 mL, 5.0 mmol) was added dropwise to a cold (0 °C) 1 M solution of lithium bis(trimethylsilyl)amide in anhydrous hexane (5.0 mL, 5.0 mmol) in a 25 mL Schlenk flask under an argon atmosphere, resulting in a brown solution. The reaction mixture was stirred at 0 °C for 0.5 h and then allowed to warm to room temperature. The solution was brought into a glovebox and the brown solid, which started precipitating upon adding 2-pyridinecarboxaldehyde, was collected by filtration, and dried under high vacuum overnight to afford **2b** (0.347 g, 1.26 mmol, 25%) as a brown solid together with 1 equivalent of what is assigned as LiOTMS. **2b** is unstable in solution, precluding its full ^{13}C NMR analysis, but comparison of ^{1}H NMR data to literature data,[4] and subsequent derivatization, confirm its structure. ^{1}H NMR (400 MHz, $CDCl_3$) δ – 0.02 (br s, 5H, SiC*H*$_3$), δ 0.05 (br s, 4H, SiC*H*$_3$), δ 0.28 (s, 9H, SiC*H*$_3$), 7.35 (ddd, J = 7.5, 4.8, 1.3 Hz, 1H), 7.78 (tdd, J = 7.7, 1.7, 0.7 Hz, 1H), 8.01 (dt, J = 7.9, 1.1 Hz, 1H), 8.69 (ddd, J = 4.8, 1.7, 0.9 Hz, 1H), 9.03 (d, J = 0.6 Hz, 1H, C*H*=N). LRMS calculated for $C_9H_{15}N_2Si$ $[M+H]^+$ 179.1, found: 179.2. This imine was directly converted to **1a**. In a glovebox, a colourless CH_2Cl_2 (3.0 mL) solution of BPh_2Cl (99 mg, 0.50 mmol) was added dropwise to a brown CH_2Cl_2 (3.0 mL) solution of *N*-(trimethylsilyl)picolinaldimine (**2b**) (90 mg, 0.50 mmol), resulting in a brown solution from which a white solid starts precipitating shortly after the addition of BPh_2Cl. After stirring for 4 hours, the solid was removed by filtration, and the solution collected. The solvent was removed *in vacuo* to afford **1b** as a brown solid that was dried under high vacuum overnight (118 mg, 0.44 mmol, 86%) together with TMS and aromatic impurities.[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (m, 8H), 7.39 (m, 2H), 7.55 (br t, J = 6.8 Hz, 1H), 7.87 (br d, J = 7.1 Hz, 1H), 8.19 (td, J = 7.7, 1.2 Hz, 1H), 8.72 (br d, J = 5.5 Hz, 1H), 8.86 (s, 1H, C*H*=N^{Im}). ^{11}B NMR (128 MHz, $CDCl_3$) δ 11.76 (s, 208 Hz line width at half height). FT-IR (ATR): 1626 cm^{-1}. ESI HRMS *m/z* calculated for $C_{18}H_{16}BN_2$ $[M+H]^+$ 271.1401, found: 271.1403. **1b** is moderately labile at ambient temperature in solution. It was therefore purified and its structure confirmed by coordination to palladium in complex **3b**.

Synthesis of [Pd{η^1-N^{IM}-[N-(diphenylboryl)-2-benzoylpyridinketimine]}Cl(C_3H_5)] (3a).

In a glovebox, a brown $CDCl_3$ (0.5 mL) solution of *N*-(diphenylboryl)-2-benzoylpyridinketimine (**1a**, 10 mg, 0.029 mmol) was added dropwise to a yellow $CDCl_3$ (0.5 mL) solution of $[PdCl(C_3H_5)]_2$ (5

mg, 0.014 mmol). After the addition was complete, diethyl ether (40 mL) was layered on top of the solution, allowed to diffuse into the resulting yellow solution, leading to the slow precipitation of an orange crystalline powder along with orange, needle-shaped single crystals. The solution was decanted and the residue was washed with diethyl ether (2 × 3 mL) and pentane (2 × 3 mL), and then dried under high vacuum overnight, affording **3a** (12 mg, 0.022 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.76 (d, J = 12.2 Hz, 1H), 2.24 (dd, J = 6.6, 2.2 Hz, 1H), 2.56 (d, J = 12.3 Hz, 1H), 3.72 (dd, J = 6.7, 1.9 Hz, 1H), 4.80 (m, 1H), 7.26 (m, 6H), 7.39 (m, 2H), 7.59 (m, 6H), 7.96 (br d, J = 8.0 Hz, 1H), 8.21 (m, 3H), 8.68 (dt, J = 5.6, 0.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7, 149.9, 143.6, 142.3, 134.8, 134.0, 133.5, 130.9, 128.82, 128.77, 127.62, 127.58, 127.3, 127.2, 124.78, 121.53, 111.70, 60.6, 59.4. ^{11}B{^{1}H} NMR (161 MHz, $CDCl_3$) δ 10.25 (s, 663 Hz line width at half height). FT-IR (ATR): 1611 cm^{-1}. ESI HRMS *m/z* calculated for $C_{27}H_{24}BClN_2PdNa$ $[M+Na]^+$ 551.0648, found: 551.0657. The structure of **3a** was fully determined by X-ray crystallography.

Synthesis of [Pd{η^1-N^{IM}-[N-(diphenylboryl)picolinaldimine]}Cl(C_3H_5)] (3b).

In a glovebox, a colourless $CDCl_3$ (0.5 mL) solution of BPh_2Cl (12 mg, 0.062 mmol) was added dropwise to a brown $CDCl_3$ (0.5 mL) solution of *N*-(trimethylsilyl)picolinaldimine (**2**) (18 mg, 0.10 mmol), resulting in a brown solution from which a white solid starts precipitating shortly after the addition of $BPhCl_2$. After stirring overnight, the solid was removed by filtration, and the solution collected. A $CDCl_3$ (0.5 mL) solution of $[PdCl(C_3H_5)]_2$ (11 mg, 0.030 mmol) was then added. After the addition is complete, the solution was filtered. Diethyl ether (25 mL) then layered onto the $CDCl_3$ solution and was allowed to diffuse into the brown solution, resulting in the slow precipitation of orange, stick-shaped crystals and an orange crystalline powder. The crystals were collected by filtration, washed with diethyl ether (3 × 3 mL) and then dried under high vacuum overnight (22 mg, 0.049 mmol, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (d, J = 12.2 Hz, 1H), 2.83 (d, J = 12.3 Hz, 1H), 3.18 (br d, J = 5.9 Hz, 1H), 3.96 (br d, J = 6.3 Hz, 1H), 5.13 (m, 1H), 7.26 (m, 6H), 7.38 (m, 4H), 7.58 (ddd, J = 7.0, 5.7, 1.0 Hz, 1H), 7.99 (d, J = 7.9 Hz, 1H), 8.22 (td, J = 7.8, 1.2 Hz, 1H), 8.60 (d, J = 5.6 Hz, 1H), 9.60 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 149.3, 143.2, 142.3, 133.44, 133.35, 127.9, 127.39, 127.33, 125.3, 121.6, 112.5, 62.6, 60.2. ^{11}B NMR (161 MHz, $CDCl_3$) δ 10.59 (s, 322 Hz line width at half height). ESI HRMS *m/z* calculated for $C_{21}H_{20}BN_2PdNa$ $[M+Na]^+$ 475.0335 , found: 475.0346. The structure of **3b** was fully determined by X-ray crystallography.

Synthesis of N-(diphenylboryl)-2-diphenylphosphanyl-benzaldimine (4a).

Under a nitrogen atmosphere, a 1M solution of lithium bis(trimethylsilyl)amide in anhydrous hexane (1.97 mL, 1.97 mmol) was added dropwise via syringe to a cold (0 °C) yellow suspension of 2-(diphenylphosphanyl)-benzaldehyde (0.575 g, 1.98 mmol) in pentane (75 mL), resulting in a yellow solution. The reaction mixture was stirred at 0 °C for 0.5 h and then allowed to warm to room temperature. The solvent was removed *in vacuo* and the resulting yellow oil was dried under high vacuum overnight. The product was brought into a glovebox, dissolved in CH_2Cl_2 (10 mL), filtered, and, after solvent removal *in vacuo*, a brown oil of **5a** together with what is assigned as LiOTMS was isolated and dried under high vacuum overnight (58 mg, 1.27 mmol, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.02 (s, 9H, SiCH_3), δ 0.05 (br s, 4H, SiCH_3), δ 0.10 (br s, 5H, SiCH_3), 6.84 (ddd, J = 7.6, 4.9, 1.0 Hz, 1H), 7.25 - 7.33 (m, 11H), 7.40 (br t, J = 7.5 Hz, 1H), 7.92 (ddd, J = 7.6, 3.9, 1.2 Hz, 1H), 9.39 (d, J = 5.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ –1.39 (s, SiCH_3), 1.9 (s, SiCH_3), 3.3 (s, SiCH_3), 3.9 (s, SiCH_3), 4.9 (s, SiCH_3), 128.3 (d, J = 3.6 Hz), 128.5 (d, J = 7.3 Hz), 128.57, 128.60, 130.5 (d, J = 1.2 Hz), 133.1 (d, J = 0.9 Hz), 134.1 (d, J = 20.3 Hz), 137.4 (d, J = 9.6 Hz), 138.4 (d, J = 21.3 Hz), 141.0 (d, J = 13.9 Hz), 167.3 (d, J = 18.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ –10.91. HRMS: calculated for $C_{22}H_{25}NPSi$ $[M+H]^+$ 362.1488; found: 362.1503. This imine was directly converted into **5a**. In a glovebox, a colourless CH_2Cl_2 (2.5 mL) solution of BPh_2Cl (0.196 g, 0.979 mmol) was added dropwise to a dark brown CH_2Cl_2 (4.5 mL) stirring solution of *N*-(trimethylsilyl)-2-diphenylphosphanyl-benzaldimine (**5a**) (0.229 g, 0.635 mmol), resulting in a brown solution, from which a white solid starts precipitating shortly after the addition of $BPhCl_2$. After stirring for 1.5 hours, the solid was removed by filtration, and the solvent was removed *in vacuo* to afford **4a** as a brown oil together with aromatic and TMS impurities (0.235 g; 0.52 mmol 82%).[5] **4a** was fully isolated and its structure confirmed by coordination to palladium in **6a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (ddd, J = 7.7, 4.4, 0.9 Hz, 1H), 6.91 – 7.52 (m, 21H), 7.72 (br t, J = 6.5 Hz, 2H), 9.46 (d, J = 7.3 Hz, 1H, N=CH). ^{13}C NMR (126 MHz, $CDCl_3$): δ 126.0, 126.2, 126.5, 127.0 (d, J = 26.4 Hz), 128.1, 128.63 (d, J = 6.9 Hz), 128.8, 131.5, 132.8, 133.8 (d, J = 19.6 Hz), 134.8, 135.8, 137.1 (d, J = 19.1 Hz), 139.4 (d, J = 19.4 Hz), 162.4 (d, J = 32.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ –17.07. ^{11}B NMR (161 MHz, $CDCl_3$) δ 7.89 (s, 809 Hz line width at half height). FT-IR (ATR): 1632 cm^{-1}. ESI HRMS *m/z* calculated for $C_{31}H_{26}BNP$ $[M+H]^+$ 454.1890; found: 454.1867.

Synthesis of N-(diphenylboryl)-2-di-tert-butyl-phosphanylbenzaldimine (4b).

In a Schlenk flask under nitrogen, a 1 M solution of lithium bis(trimethylsilyl)amide in anhydrous hexane (1.22 mL, 0.0012 mol) was added dropwise to a cold (0 °C) yellow solution of 2-(di-*tert*-butylphosphino)benzaldehyde (0.305 g, 0.0012 mol) in pentane (25 mL), resulting in a yellow solution. The reaction mixture was stirred at 0 °C for 0.5 h and then allowed to warm to room temperature. Solvent removal *in vacuo* afforded **5b** as a yellow oil (0.35 g, 0.84 mmol, 89%) together with what has been assigned as LiOTMS. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ – 0.02 (br s, 5H, SiC*H*$_3$), 0.06 (br s, 4H, SiC*H*$_3$), 0.26 (s, 9H, SiC*H*$_3$), 1.19 (d, J = 12.0 Hz, 18H), 7.39 (m, 2H), 7.79 (m, 1H), 7.99 (m, 1H), 10.10 (d, J = 7.9 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 25 °C) δ –0.9 (s, Si*C*H$_3$), 3.3 (s, Si*C*H$_3$), 3.9 (s, Si*C*H$_3$), 30.6 (d, J = 15.0 Hz), 32.6 (d, J = 23.5 Hz), 126.6 (d, J = 6.3 Hz), 128.9 (d, J = 1.1 Hz), 134.9 (d, J = 3.1 Hz), 138.2 (d, J = 32.1 Hz), 146.0 (d, J = 19.6 Hz), 171.3 (d, J = 36.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C) δ 10.04. HRMS: calculated for $C_{18}H_{33}NPSi$ $[M+H]^+$ 322.2114; found: 322.2116. This imine was directly converted into **5b**. In a glovebox, a colourless CH_2Cl_2 (3.5 mL) solution of BPh_2Cl (0.092 g, 0.046 mmol) was added dropwise to a stirring yellow CH_2Cl_2 (3.5 mL) solution of *N*-(trimethylsilyl)-2-di-*tert*-butyl-phosphanylbenzaldimine (**5b**) (0.146 g, 0.046 mmol), resulting in a yellow solution, from which a white solid starts precipitating shortly after the addition of $BPhCl_2$. After stirring for 2.5 hours, the solid was removed by filtration, and the solvent was removed in vacuo to afford **4b** as a yellow power together with aromatic and TMS impurities (0.131 g, 0.32 mmol, 73%).[5] **4b** was fully isolated and its structure confirmed by coordination to palladium in **6b**. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.04 (d, J = 12.2 Hz, 18H), 1.18 (br d, J = 12.1 Hz, 2H, C*H*$_3$), 6.93 (tt, J = 6.9, 1.1 Hz, 2H), 7.00 (br t, J = 7.3 Hz, 1H), 7.18 - 7.26 (m, 3H), 7.30 (br t, J = 6.8 Hz, 2H), 7.37 - 7.45 (m, 1H), 7.50 (ddd, J = 7.9, 3.9, 1.2 Hz, 1H), 7.62 (dt, J = 6.6, 1.5 Hz, 2H), 7.69 (tt, J = 6.5, 1.5 Hz, 2H), 9.93 (d, J = 7.2 Hz, 1H, N=C*H*). ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) δ 30.4 (d, J = 15.1 Hz), 32.8 (d, J = 23.5 Hz), 126.0 (d, J = 19.4 Hz), 126.9 (d, J = 25.9 Hz), 128.1 (d, J = 1.2 Hz), 129.5, 130.2, 133.0 (t, J = 1.8 Hz), 134.7, 134.8 (d, J = 2.4 Hz), 139.8 (d, J = 30.9 Hz), 140.5 (d, J = 22.6 Hz), 165.2 (d, J = 37.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C) δ 12.08. ^{11}B NMR (161 MHz, $CDCl_3$, 25 °C) δ 7.18 (s, 676 Hz line width at half height). ESI HRMS *m/z* calculated for $C_{27}H_{34}BNP$ $[M+H]^+$ 414.2516; found: 414.2545 ($[M+H]^+$), 416.2703 ($[M+H_2+H]^+$).

Synthesis of bis[(allyl)chloro(N-(diphenylboryl)-2-diphenylphosphanyl-benzaldimine)palladium] (6a).

In a glovebox, a brown toluene (1.5 mL) solution of N-(diphenylboryl)-2-diphenylphosphanyl-benzaldimine (**4a**) (30 mg, 0.067 mmol) was added dropwise to a stirring toluene (1.5 mL) solution of $[PdCl(C_3H_5)]_2$ (8.5 mg, 0.023 mmol), resulting in a brown solution. After stirring for 0.5 hours, solvent removal *in vacuo* led to the isolation of an orange solid that was dried under high vacuum overnight. Washing with diethyl ether (2 × 5 mL) and pentane (2 × 5 mL), the drying under high vacuum overnight afforded **6a** as brown solid with ether impurities (25 mg, 0.020 mmol, 86%). Brown, stick-shaped crystals of **6a** were grown by diffusing diethyl ether into CH_2Cl_2 solution of the isolated solid. ^{1}H NMR (400 MHz, $CDCl_3$, two isomers): δ 2.34 (br t, J = 10.7 Hz, 1H), 2.62 (br dd, J = 7.7, 9.1 Hz, 1H), 3.29 and 3.33 (t, J = 9.2 Hz and t, J = 9.3 Hz; 1H), 4.37 (m, 1H), 4.48 (m, 1H), 6.66 (m, 1H), 6.74 and 6.76 (dt, J = 7.7, 1.4 Hz and dt, J = 7.9, 1.7 Hz; 1H), 6.84 and 6.87 (br t, J = 6.9 Hz and br t, J = 7.4 Hz; 2H), 7.05 (m, 5H), 7.20 (m, 2H), 7.28 (m, 2H), 7.35 (m, 4H), 7.45 (m, 3H), 7.65 (m, 3H), 7.83 (m, 1H), 9.74 and 9.75 (d, J = 3.7 Hz and d, J = 3.7 Hz; 1H, N=C*H*). ^{13}C NMR (126 MHz, $CDCl_3$) δ 61.8 (d, J = 2.2 Hz), 65.8, 105.0, 118.39 (d, J = 24.3 Hz), 118.44 (d, J = 24.8 Hz), 126.9 (d, J = 13.4 Hz), 126.1 (d, J = 15.3 Hz), 127.4 (d, J = 24.0 Hz), 127.6 (d, J = 22.6 Hz), 128.7 (d, J = 11.4 Hz), 128.9 (d, J = 13.7 Hz), 129.0 (d, J = 13.7 Hz), 129.4,, 129.6, 130.5 (d, J = 8.3 Hz), 130.9 (d, J = 8.2 Hz), 131.0 (br d, J = 48.8 Hz), 131.2 (m), 131.6 (d, J = 21.3 Hz), 131.88 (d, J = 42.2 Hz), 131.93 (d, J = 40.6 Hz), 133.14 (d, J = 3.2 Hz), 133.16 (d, J = 3.6 Hz), 133.9 (d, J = 11.6 Hz), 134.0 (m), 134.1 (d, J = 11.8 Hz), 135.2 (d, J = 12.6 Hz), 133.5 (m), 161.1 (d, J = 19.5 Hz), 161.2 (d, J = 19.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.21, 18.31. ^{11}B NMR (161 MHz, $CDCl_3$) δ 6.64 (br s, 1153 Hz line width at half height). **6a** is temperature and moisture sensitive precluding any further characterization, and its structure was fully determined by X-ray crystallography.

Synthesis of bis[(allyl)chloro{η^1-P-[N-(diphenylboryl)-2-di-tert-butyl-phosphanylbenzaldimine]}palladium] (6b).

In a glovebox, a yellow $CDCl_3$ (0.5 mL) solution of *N*-(diphenylboryl)-2-di-*tert*-butyl-phosphanylbenzaldimine (**4b**) (11 mg, 0.027 mmol) was added dropwise to a stirring yellow $CDCl_3$ (0.5 mL) solution of $[PdCl(C_3H_5)]_2$ (5 mg, 0.013 mmol), resulting in a brown solution. In situ ^{1}H ^{11}B,

and ^{31}P NMR analysis reveals the presence of complex **6b** . Yellow, prism-shaped crystals of **6b** were grown by diffusing diethyl ether into the $CDCl_3$ solution of the product. **6b** begins to decompose almost immediately upon NMR analysis. Crude ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81 (d, J = 14.0 Hz, 4H), 0.90 (d, J = 14.2 Hz, 5H), 1.45 (d, J = 14.4 Hz, 9H); 2.50 – 5.20 (5H, C_3H_5): in this range, 2.53 (br t, J = 9.9 Hz, 0.4H), 3.11 – 3.63 (m, 2H), 4.09 (m, 0.4H), 4.50 (m, 0.9H), 5.14 (m, 0.5H); 6.84 - 8.24 (m, 14H), 10.12 (dd, J = 28.0, 4.3 Hz, 0.5H), 10.46 (dd, J = 30.0, 3.7 Hz, 0.5H). Crude ^{31}P NMR (162 MHz, $CDCl_3$) δ 55.0, 55.6. ^{11}B NMR (161 MHz, $CDCl_3$) δ 6.98 (s, 669 Hz line width at half height). Due to its instability, **6b** could not be further analyzed, and its structure was fully determined by X-ray crystallography.

Synthesis of 2-(di-o-tert-butylphosphino)benzaldehyde

As has been previously reported,[6] *t*-butyllithium (1.7 M solution in pentane, 44.0 mL, 0.0748 mol) was added dropwise to a colourless solution of 2-(2-bromophenyl)-[1,3]dioxolane (8.66 g, 0.038 mol) in anhydrous THF (90 mL) at –78 °C in a Schlenk flask under a nitrogen atmosphere,. The yellow reaction mixture was stirred at –78 °C for 1 h. A solution of di-*tert*-butylchlorophosphine (10.64 g, 0.056 mol) in anhydrous THF (20 mL) was then added at –78 °C. The brown reaction mixture was refluxed for 16 h at 78 °C. After cooling the mixture to room temperature, degassed H_2O (100.0 mL) was added. The layers were separated under nitrogen via cannula, the organic layer was collected in a Schlenk flask and the aqueous layer was extracted with degassed diethyl ether (3 × 60 mL). The combined organic layers were dried over $MgSO_4$ (1.0 g) overnight. After filtration, the solvent was removed in vacuo to afford the crude product as an orange oil (13.17 g, 44.7 mmol), which can be further purified flash SiO_2 column chromatography in an inert atmosphere glovebox, but at significant loss in yield (6%). It was therefore used as a crude material for the next step.

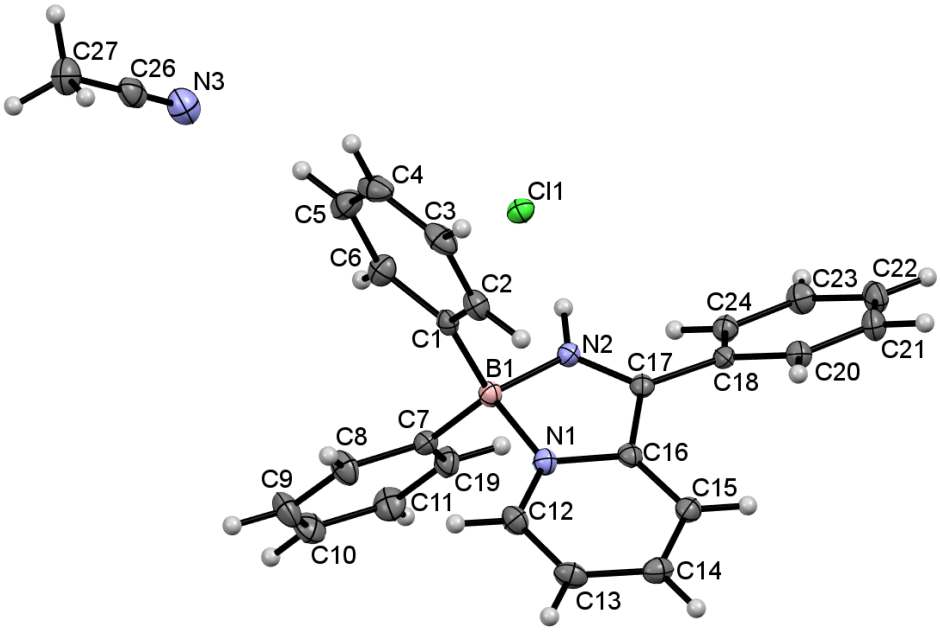
The crude (2-[1,3]dioxolan-2-yl-phenyl)-di-*o*-*tert*-butylphosphine (3.113 g, 0.0125 mol) was added to a schlenk flask in the glovebox and dissolve in acetone (60 mL). The flask was taken out of the glovebox and connected to a Schlenk line, where *p*-toluenesulfonic acid (2.572 g, 0.0145 mol) was added slowly followed by degassed H_2O (6 mL) under a nitrogen atmosphere The resulting brown solution was refluxed for 24 h, at 76 °C. After cooling to room temperature, H_2O (10 mL), saturated $NaHCO_3$ aq (100 mL), and finally ethyl acetate (60 mL) were added by cannula under a nitrogen flow.

After separation of the layers under nitrogen, the organic layer was collected by cannula into a Schlenk flask also under nitrogen. The aqueous phase was extracted with ethyl acetate (3 × 90 mL). The combined organic layer were washed with H_2O (3 × 60 mL) and brine (40.0 mL), both added by cannula, and then dried stirring over $MgSO_4$ (1.000 g) overnight. Filtration and removal of the solvent in vacuo resulted in an orange oil that was dried overnight under high vacuum. The crude material was purified in a glovebox under a nitrogen atmosphere by SiO_2 column chromatography (dichloromethane:hexane 1:1) to afford the product as a yellow oil. (0.97 g, 3.88 mmol, 31%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.21 (d, J = 12.3 Hz, 18H), δ 7.49 (br t, J = 7.7 Hz, 1H), δ 7.55 (td, J = 7.6, 1.7 Hz, 1H), 7.89 (br d, J = 7.9 Hz, 1H), 7.97 (dddd, J = 7.6, 3.7, 1.7, 0.3 Hz, 1H), 11.25 (dd, J = 9.0, 0.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) δ 30.6 (d, J = 14.8 Hz), 32.6 (d, J = 22.2 Hz), 127.4 (d, J = 6.4 Hz), 129.2 (d, J = 1.2 Hz), 131.8, 135.5 (d, J = 3.0 Hz), 140.8 (d, J = 35.4 Hz), 143.1 (d, J = 17.8 Hz), 194.27 (d, J = 41.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C) δ 7.44. HRMS: calculated for $C_{15}H_{24}OP$ $[M+H]^+$ 251.1559; found: 251.1571.

III. X-Ray Structural Data

General: Suitable crystals for x-ray analysis were taken out of a glovebox and submerged in paratone oil, placed onto a mounting loop, and frozen under a dry steam of nitrogen for data collection. Single-crystal X-ray diffraction experiments were carried out with Bruker APEX-II CCD diffractometer by using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and Kryoflex for low-temperature experiments. Data integration, scaling and refinement was performed using SHELXL-2013,[7] and SHELXL-2018.[7] Absorption correction by multi-scan was performed using SADABS.[8] Intrinsic phasing and direct method were used to generate the initial solutions. Final solution refinements were solved by full-matrix least-squares methods on F2 of all data, by using SHELXLE[7,9] software. The hydrogen atoms were placed in calculated positions. SHELX restraints such as, EADP, RIGU, ISOR, SAME, DFIX were applied to disordered compounds **3a**, **3b 6a** and **6b** in order to model the disordered allyl ligands in each structure, and using fractional occupancy when it applies. Measurements for **1aHCl**, **1aHOTf**, **3b**, **6a**, **6b** were performed at -173(2) °C, while compound **3a** measurement was performed at 25(2)°C. Crystal dimensions: **1aHCl**: (0.700 × 0.100 × 0.100 mm^3); **1aHOTf**: (0.40 × 0.40 × 0.07 mm^3); **3a**: (0.20 × 0.20 × 0.10 mm^3); **3b**: (0.160 × 0.130 × 0.120 mm^3); **6a**: (0.40 × 0.20 × 0.10 mm^3); **6b**: (0.20 × 0.10 × 0.10 mm^3). The ORTEP representations of the structures were produced by MERCURY 4.0. Olex2 was used to generate the data tables and report.

Compound 1aHCl



Crystallization: 1a containing residual acetonitrile was dissolved in chloroform in a glovebox and the solvent allowed to slowly evaporate. This led to the precipitation of [*N*-(diphenylboryl)-2-benzoylpyridinketimine]H^+Cl^- (**1aH$^+$Cl$^-$**) as brown, needle-shaped crystals The HCl in this complex was presumably derived from advantageous acid in the chloroform solution

Table 1 Crystal data and structure refinement for compound1aHCl.

Identification code	compound1aHCl
Empirical formula	$C_{26}H_{23}BClN_3$
Formula weight	423.73
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.1188(13)
b/Å	11.1397(11)
c/Å	16.3174(16)
α/°	90
β/°	110.6410(10)
γ/°	90
Volume/Å^3	2231.5(4)
Z	4
ρ_{calc}g/cm^3	1.261
μ/mm^{-1}	0.189
F(000)	888.0
Crystal size/mm^3	0.700 × 0.100 × 0.100
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.446 to 56.776
Index ranges	$-17 \le h \le 17$, $-14 \le k \le 14$, $-21 \le l \le 21$
Reflections collected	25080
Independent reflections	5256 [R_{int} = 0.1293, R_{sigma} = 0.0793]
Data/restraints/parameters	5256/0/285
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0430, wR_2 = 0.1047
Final R indexes [all data]	R_1 = 0.0582, wR_2 = 0.1117
Largest diff. peak/hole / e Å^{-3}	0.45/-0.31

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for compound1aHCl. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
N2	8916.1(9)	776.6(10)	7736.6(7)	15.2(3)
C22	7963.5(13)	1178.6(13)	10475.3(10)	23.8(3)
C11	12217.4(13)	1268.7(14)	7710.5(11)	26.6(4)
C3	6385.2(13)	146.6(14)	4971.7(11)	25.8(4)
C12	9253.5(12)	-2162.1(12)	6868.5(10)	20.1(3)
C4	6467.4(13)	1162.9(14)	4510.8(11)	26.8(4)
C19	11176.7(12)	1017.3(13)	7710.3(10)	21.3(3)
C5	7404.3(14)	1845.2(14)	4817.6(10)	26.0(4)
N1	9092.9(10)	-1158.7(10)	7261.8(8)	16.4(3)
C21	7505.7(13)	133.9(13)	10044.0(10)	22.7(3)
C18	8474.5(11)	399.3(12)	9047.8(9)	15.4(3)
C24	8930.3(12)	1462.4(12)	9483.0(10)	18.5(3)
C17	8729.6(11)	33.8(12)	8273.9(9)	15.2(3)
C2	7231.1(12)	-186.7(13)	5730.2(10)	21.1(3)
C6	8249.1(13)	1514.3(12)	5578.4(10)	21.7(3)
C15	8771.3(11)	-2304.2(12)	8383.2(10)	18.3(3)
C20	7756.7(12)	-261.8(12)	9331.7(10)	18.1(3)
B1	9166.0(14)	193.6(14)	6959.1(11)	16.0(3)
C7	10379.4(11)	500.0(12)	6985.1(9)	16.5(3)
C13	9174.6(12)	-3274.2(13)	7216.7(10)	21.7(3)
C1	8188.7(11)	489.0(12)	6052.2(9)	16.1(3)
C10	12484.2(13)	1006.4(14)	6980.5(11)	27.5(4)
C8	10675.5(13)	248.4(14)	6259.9(10)	24.3(3)
C23	8668.1(12)	1846.2(13)	10189.6(10)	21.8(3)
C14	8935.5(12)	-3349.6(12)	7978.2(11)	20.5(3)
C9	11709.2(13)	498.1(14)	6250.5(11)	28.2(4)
C16	8845.9(11)	-1215.2(12)	8002.2(10)	15.2(3)
Cl1	8894.2(3)	3528.8(3)	7689.9(2)	17.50(11)
N3	10138.8(12)	6602.6(12)	5372.2(10)	32.0(3)
C26	9793.8(13)	6440.7(13)	4630.3(12)	24.4(4)
C27	9367.5(15)	6230.7(14)	3688.3(11)	29.5(4)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for compound1aHCl. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N2	16.1(6)	15.4(6)	13.9(6)	0.8(5)	5.3(5)	1.4(5)
C22	26.3(9)	30.9(8)	17.0(8)	-2.2(6)	10.9(7)	2.6(6)
C11	21.0(8)	35.3(9)	19.9(8)	-2.0(7)	2.6(7)	-2.2(7)
C3	15.6(8)	34.1(9)	27.2(9)	-8.5(7)	7.1(7)	-0.5(6)
C12	22.0(8)	20.8(7)	18.8(8)	-4.2(6)	8.8(6)	0.0(6)
C4	23.8(9)	32.9(9)	18.9(8)	-5.0(7)	1.4(7)	10.4(7)
C19	21.1(8)	27.9(8)	15.3(8)	0.2(6)	6.8(6)	-0.1(6)
C5	33.3(9)	23.1(8)	19.1(8)	1.9(6)	6.2(7)	3.3(7)
N1	17.3(6)	17.4(6)	14.7(6)	-0.3(5)	5.9(5)	-0.1(5)
C21	23.8(8)	26.5(8)	21.9(8)	2.1(6)	13.2(7)	-0.7(6)
C18	15.3(7)	18.8(7)	12.0(7)	2.2(5)	4.8(6)	3.9(5)
C24	18.3(8)	19.9(7)	17.8(8)	1.4(6)	7.0(6)	-0.7(6)
C17	12.0(7)	18.5(7)	14.1(7)	1.0(6)	3.5(6)	0.4(5)
C2	19.0(8)	24.1(7)	22.9(8)	-1.5(6)	10.7(6)	-1.5(6)
C6	24.8(8)	20.7(7)	18.3(8)	-1.3(6)	6.0(6)	-2.1(6)
C15	15.0(7)	20.4(7)	19.2(8)	2.7(6)	5.7(6)	0.3(6)
C20	18.5(8)	18.8(7)	17.4(8)	-0.2(6)	6.7(6)	-0.6(6)
B1	20.4(9)	14.6(7)	14.7(8)	-0.2(6)	8.1(7)	0.7(6)
C7	18.0(7)	16.3(7)	15.3(7)	2.4(6)	6.0(6)	2.6(5)
C13	21.1(8)	16.7(7)	26.5(9)	-4.7(6)	7.4(7)	0.6(6)
C1	18.1(7)	18.7(7)	13.6(7)	-2.1(6)	8.2(6)	1.7(5)
C10	17.2(8)	35.8(9)	30.5(9)	1.7(7)	9.8(7)	1.4(7)
C8	22.7(8)	31.8(8)	19.8(8)	-7.2(7)	9.1(7)	-2.8(6)
C23	24.3(8)	21.5(7)	18.4(8)	-4.5(6)	5.9(6)	-1.3(6)
C14	16.3(8)	16.7(7)	26.7(8)	2.5(6)	5.5(6)	-0.5(6)
C9	25.0(9)	38.9(9)	26.0(9)	-5.9(7)	15.6(7)	0.3(7)
C16	11.8(7)	18.4(7)	14.8(7)	-0.1(6)	4.1(6)	0.5(5)
Cl1	18.7(2)	14.87(17)	17.95(19)	0.50(13)	5.21(14)	0.45(13)
N3	32.6(8)	33.6(8)	34.1(9)	-3.0(7)	17.0(7)	-1.3(6)
C26	21.6(8)	22.3(8)	34.0(10)	0.6(7)	15.6(7)	-1.4(6)
C27	30.6(9)	31.7(9)	29.1(9)	1.0(7)	14.1(8)	-3.9(7)

Table 4 Bond Lengths for compound1aHCl.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N2	C17	1.2902(17)	C18	C24	1.4017(19)
N2	B1	1.5594(19)	C18	C17	1.4732(19)

C22	C21	1.383(2)	C24	C23	1.382(2)
C22	C23	1.389(2)	C17	C16	1.4844(19)
C11	C10	1.386(2)	C2	C1	1.398(2)
C11	C19	1.394(2)	C6	C1	1.3970(19)
C3	C4	1.384(2)	C15	C16	1.3822(19)
C3	C2	1.390(2)	C15	C14	1.393(2)
C12	N1	1.3420(17)	B1	C1	1.614(2)
C12	C13	1.382(2)	B1	C7	1.614(2)
C4	C5	1.380(2)	C7	C8	1.398(2)
C19	C7	1.398(2)	C13	C14	1.387(2)
C5	C6	1.391(2)	C10	C9	1.385(2)
N1	C16	1.3581(19)	C8	C9	1.390(2)
N1	B1	1.5987(19)	N3	C26	1.147(2)
C21	C20	1.387(2)	C26	C27	1.457(2)
C18	C20	1.397(2)			

Table 5 Bond Angles for compound1aHCl.

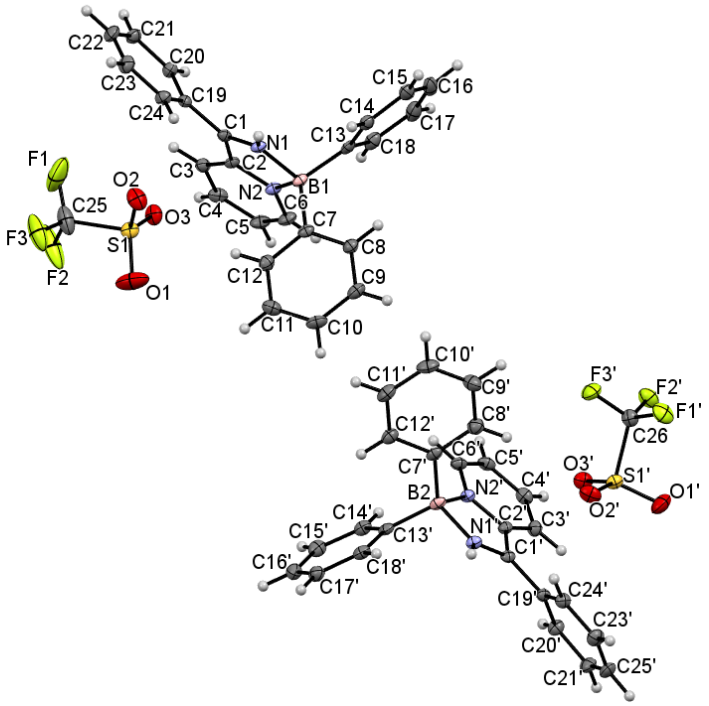
Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C17	N2	B1	115.49(12)	N2	B1	N1	95.07(11)
C21	C22	C23	120.05(14)	N2	B1	C1	109.53(12)
C10	C11	C19	120.11(15)	N1	B1	C1	111.14(11)
C4	C3	C2	120.76(15)	N2	B1	C7	112.26(12)
N1	C12	C13	120.19(14)	N1	B1	C7	110.93(11)
C5	C4	C3	118.91(15)	C1	B1	C7	116.00(12)
C11	C19	C7	121.58(14)	C19	C7	C8	116.81(13)
C4	C5	C6	120.34(15)	C19	C7	B1	123.11(13)
C12	N1	C16	120.91(12)	C8	C7	B1	120.08(13)
C12	N1	B1	126.90(12)	C12	C13	C14	119.73(14)
C16	N1	B1	112.18(11)	C6	C1	C2	116.80(13)
C22	C21	C20	120.34(14)	C6	C1	B1	119.51(13)
C20	C18	C24	119.64(13)	C2	C1	B1	123.56(13)
C20	C18	C17	121.46(13)	C9	C10	C11	119.60(15)
C24	C18	C17	118.85(13)	C9	C8	C7	122.19(15)
C23	C24	C18	119.79(13)	C24	C23	C22	120.34(14)
N2	C17	C18	124.06(12)	C13	C14	C15	119.74(13)
N2	C17	C16	109.51(12)	C10	C9	C8	119.70(15)
C18	C17	C16	126.40(12)	N1	C16	C15	121.18(13)
C3	C2	C1	121.34(14)	N1	C16	C17	107.71(11)
C5	C6	C1	121.85(14)	C15	C16	C17	131.09(14)

C16	C15	C14	118.24(14)	N3	C26	C27	179.36(19)	
C21	C20	C18	119.82(13)					

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for compound1aHCl.

Atom	*x*	*y*	*z*	U(eq)
H22	7795.73	1439.91	10967.4	29
H11	12744.79	1620.52	8211.86	32
H3	5743.34	-328.68	4767.3	31
H12	9422.05	-2107.67	6349.24	24
H4	5888.6	1387.11	3992	32
H19	11005.03	1201.9	8215.22	26
H5	7472.53	2544.39	4507.56	31
H21	7016.85	-315.13	10236.66	27
H24	9417.81	1917.57	9292.78	22
H2	7157.11	-887.8	6036.05	25
H6	8884.94	1999.23	5781.51	26
H15	8612.24	-2338.71	8907.41	22
H20	7441.35	-980.57	9037.6	22
H13	9283.62	-3984.2	6935.61	26
H10	13194.3	1174.15	6980.72	33
H8	10152.74	-104.98	5756.72	29
H23	8971.54	2570.5	10481.41	26
H14	8884.02	-4111.38	8222.48	25
H9	11883.58	321.1	5745.7	34
H27A	9967.33	6248.68	3462.15	44
H27B	8838.13	6857.82	3401.29	44
H27C	9010.52	5444.33	3567.97	44
H1	8871(16)	1643(16)	7804(13)	51(6)

Compound 1aHOTf



Crystallization: 1a was dissolved in chloroform in a glovebox and mixed with an excess of AgOTf. AgCl precipitate immediately formed, and was removed by filtration. The chloroform solvent allowed to slowly evaporate, leading to the precipitation of [*N*-(diphenylboryl)-2-benzoylpyridinketimine]H^+OTf^- (**1aH$^+$OTf$^-$**) as yellow-brown, needle-shaped crystals.

Table 1 Crystal data and structure refinement for Compound1aHOTf.

Identification code	Compound1aHOTf
Empirical formula	$C_{25}H_{20}BF_3N_2O_3S$
Formula weight	496.30
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.2146(6)
b/Å	18.4610(10)
c/Å	22.6386(12)
α/°	90
β/°	102.7270(10)
γ/°	90

Volume/Å^3	4571.8(4)
Z	8
ρ_{calc}g/cm^3	1.442
μ/mm^{-1}	0.198
F(000)	2048.0
Crystal size/mm^3	0.400 × 0.400 × 0.070
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.876 to 56.826
Index ranges	-15 ≤ h ≤ 14, -24 ≤ k ≤ 24, -29 ≤ l ≤ 29
Reflections collected	51660
Independent reflections	10701 [R_{int} = 0.0459, R_{sigma} = 0.0412]
Data/restraints/parameters	10701/0/631
Goodness-of-fit on F^2	1.057
Final R indexes [I>=2σ (I)]	R_1 = 0.0518, wR_2 = 0.1062
Final R indexes [all data]	R_1 = 0.0747, wR_2 = 0.1159
Largest diff. peak/hole / e Å^{-3}	0.52/-0.45

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Compound1aHOTf. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C5'	15540.0(18)	13547.6(10)	6838.5(9)	18.0(4)
C16	6038(2)	6852.0(13)	5116.3(10)	28.7(5)
N2'	16350.8(14)	12394.1(8)	6698.1(7)	14.6(3)
N1	7555.5(14)	6327.1(9)	3194.4(7)	14.6(3)
C13'	17187.3(17)	11822.0(11)	5799.1(9)	16.5(4)
N2	8614.8(15)	7399.4(9)	3491.7(8)	16.1(3)
C2'	17152.7(17)	12455.0(10)	7243.7(9)	14.6(4)
C14'	17158.7(18)	12494.7(11)	5510.0(9)	18.7(4)
N1'	17525.8(14)	11343.9(9)	6903.5(7)	15.1(3)
C3'	17171.6(18)	13061.1(11)	7602.7(9)	18.6(4)
C13	7571.0(17)	6737.7(11)	4285.1(9)	16.6(4)
C14	6949.5(18)	6134.1(11)	4445.4(9)	18.8(4)
C22	4710.3(19)	6407.2(12)	1100.6(9)	23.3(5)
C7	9681.8(17)	6226.3(10)	4004.7(9)	15.4(4)
C12	10484.4(18)	6152.5(11)	3613.6(9)	19.8(4)
C7'	15291.8(17)	11195.8(10)	6178.5(9)	16.2(4)

C24	6328.1(18)	5969.4(11)	1903.1(9)	18.4(4)
C5	9450.9(18)	8563.1(11)	3421.7(10)	21.7(4)
C17'	18313.2(19)	11357.2(12)	5074.1(9)	21.6(4)
B1	8400(2)	6642.6(12)	3791.2(10)	15.3(4)
C16'	18258.9(19)	12030.7(12)	4793.7(10)	23.0(4)
C2	7951.8(17)	7462.0(10)	2916.1(9)	14.5(4)
C3	8023.7(18)	8069.5(11)	2571.3(9)	18.0(4)
C1	7275.5(17)	6777.5(10)	2750.3(9)	14.3(4)
C18	7411(2)	7396.3(12)	4567.1(10)	22.9(5)
C4'	16358.5(19)	13618.9(11)	7389.0(9)	19.2(4)
C8	10062.3(18)	5948.0(11)	4588.3(9)	18.2(4)
C25'	20739.1(19)	11359.2(12)	8878.1(9)	23.8(5)
C12'	14847.7(19)	10945.4(11)	5588.0(9)	20.5(4)
C19	6409.3(17)	6653.2(10)	2174.2(9)	14.6(4)
C24'	18987.7(18)	10948.9(11)	8144.4(9)	17.6(4)
C4	8780.3(18)	8632.5(11)	2835.1(10)	21.1(4)
B2	16539(2)	11661.1(12)	6355.6(10)	16.2(4)
C11	11614.1(19)	5820.1(11)	3800.0(10)	23.4(5)
C19'	18847.5(17)	11643.6(10)	7889.4(9)	14.7(4)
C8'	14597.3(19)	11035.5(11)	6604.1(10)	22.8(4)
C18'	17777.0(17)	11253.4(11)	5564.8(9)	18.5(4)
C6	9370.1(18)	7931.1(11)	3741.3(10)	19.9(4)
C15'	17674.1(19)	12599.2(11)	5012.1(10)	22.9(5)
C10	11975.6(19)	5553.5(11)	4385.7(10)	23.4(5)
C21	4772.0(18)	7083.9(11)	1373.7(9)	20.2(4)
C21'	20613.8(19)	12044.7(12)	8626.6(9)	22.5(4)
C1'	17873.8(17)	11782.6(10)	7352.8(9)	14.1(4)
C6'	15540.5(18)	12920.2(10)	6501.3(9)	17.2(4)
C23'	19921.0(19)	10813.7(12)	8642.5(10)	23.1(5)
C11'	13763(2)	10557.1(12)	5428.9(10)	24.8(5)
C17	6665(2)	7448.9(13)	4983.8(10)	28.2(5)
C20'	19666.3(18)	12192.4(11)	8133.7(9)	18.6(4)
C23	5485(2)	5853.0(12)	1364.5(10)	23.1(5)
C20	5621.5(18)	7208.9(11)	1907.6(9)	16.7(4)
C15	6182.6(19)	6189.2(12)	4848.7(9)	24.0(5)
C10'	13087(2)	10409.4(12)	5856.9(11)	27.1(5)
C9	11192.2(19)	5614.4(11)	4780.0(10)	21.2(4)
C9'	13508(2)	10646.9(12)	6445.9(11)	27.4(5)
S1'	15995.4(5)	10704.5(3)	8444.8(2)	18.50(12)
S1	9663.1(5)	5563.1(3)	1861.2(2)	19.97(12)
O3'	15970.5(13)	11326.8(8)	8059.9(7)	23.0(3)

O3	9271.8(14)	6214.9(8)	2108.9(7)	25.0(3)
F3'	13724.9(12)	10374.2(8)	7913.7(6)	32.5(3)
F2'	13884.8(12)	11159.2(7)	8628.0(6)	30.9(3)
F1'	14271.8(12)	10035.1(7)	8845.2(6)	33.0(3)
O2'	16305.9(14)	10031.6(8)	8183.3(7)	26.0(3)
O2	8872.6(15)	4945.1(8)	1860.7(7)	29.5(4)
O1'	16554.9(15)	10806.3(10)	9071.0(7)	35.1(4)
O1	10942.1(16)	5406.6(10)	2030.9(10)	51.6(6)
C26	14388(2)	10560.6(11)	8457.8(10)	21.6(4)
F3	9721.9(19)	5211.6(8)	745.4(8)	58.3(5)
F2	10083(2)	6332.4(9)	966.3(9)	79.4(7)
F1	8256(2)	5934.8(12)	830.0(8)	73.9(6)
C25	9413(3)	5773.3(13)	1058.4(12)	38.1(6)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for Compound1aHOTf. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C5'	15.6(9)	13.7(9)	25.9(11)	2.9(8)	7.0(8)	3.5(8)
C16	28.8(12)	40.7(14)	17.1(11)	6.3(10)	6.2(9)	15.1(10)
N2'	13.9(8)	13.9(8)	15.3(8)	-0.6(6)	1.5(6)	-0.1(6)
N1	12.9(8)	12.0(8)	17.7(8)	-0.6(6)	0.6(6)	1.0(6)
C13'	12.7(9)	17.9(10)	16.2(10)	-2.8(8)	-2.7(7)	-0.7(7)
N2	13.9(8)	13.5(8)	19.4(9)	0.8(6)	0.1(7)	1.1(6)
C2'	12.8(9)	14.6(9)	16.2(10)	0.3(7)	2.4(7)	-1.2(7)
C14'	18.2(10)	14.6(9)	21.2(11)	-1.3(8)	-0.2(8)	0.4(8)
N1'	14.5(8)	11.4(8)	18.4(8)	-0.7(6)	1.4(6)	1.5(6)
C3'	19.7(10)	18.1(10)	17.9(10)	-2.7(8)	3.7(8)	-0.3(8)
C13	14.2(9)	18.4(10)	14.2(10)	1.9(8)	-3.4(7)	3.6(8)
C14	17.4(10)	20.4(10)	17.0(10)	1.0(8)	-0.1(8)	2.4(8)
C22	22.0(11)	29.3(12)	15.9(10)	-3.1(9)	-1.6(8)	-3.5(9)
C7	14.1(9)	11.4(9)	18.7(10)	-0.9(7)	-0.8(7)	-1.3(7)
C12	20.7(10)	18.5(10)	19.5(11)	2.2(8)	2.9(8)	-0.6(8)
C7'	14.8(9)	12.9(9)	18.6(10)	0.4(7)	-1.4(8)	3.4(7)
C24	18.0(10)	16.5(10)	19.9(10)	-1.1(8)	2.6(8)	1.8(8)
C5	15.2(10)	15.7(10)	31.8(12)	-1.6(9)	0.3(9)	-2.9(8)
C17'	19.3(10)	24.7(11)	19.7(11)	-4.9(8)	2.0(8)	2.7(8)
B1	14.5(10)	12.7(10)	16.8(11)	0.6(8)	-0.9(8)	-1.9(8)
C16'	22.0(11)	28.3(11)	18.4(11)	-1.7(9)	4.1(8)	-2.9(9)
C2	10.6(9)	15.0(9)	16.7(10)	0.4(7)	0.6(7)	2.1(7)

C3	15.0(9)	19.4(10)	19.2(10)	2.8(8)	3.1(8)	0.7(8)
C1	12.1(9)	14.6(9)	16.3(10)	0.3(7)	3.2(7)	2.6(7)
C18	24.9(11)	20.2(10)	20.6(11)	-0.2(8)	-1.4(9)	3.2(9)
C4'	21.9(10)	13.1(9)	24.2(11)	-1.9(8)	8.4(8)	0.1(8)
C8	17.8(10)	17.4(10)	18.3(10)	-0.7(8)	1.7(8)	-1.1(8)
C25'	18.9(10)	32.8(12)	16.7(11)	2.9(9)	-2.6(8)	4.6(9)
C12'	20.5(10)	19.0(10)	19.9(11)	1.9(8)	-0.3(8)	0.6(8)
C19	12.7(9)	16.6(9)	14.8(9)	0.4(7)	3.7(7)	-1.7(7)
C24'	17.3(10)	15.7(9)	19.7(10)	1.9(8)	3.6(8)	-0.1(8)
C4	17.1(10)	15.4(10)	31.0(12)	5.7(8)	5.4(9)	1.0(8)
B2	15.0(11)	12.9(10)	18.7(11)	-1.5(8)	-1.0(9)	4.1(8)
C11	18.3(10)	22.7(11)	30.6(12)	0.8(9)	8.4(9)	0.7(8)
C19'	13.6(9)	15.4(9)	14.9(10)	0.2(7)	2.4(7)	2.2(7)
C8'	21.5(11)	23.8(11)	22.4(11)	-3.7(9)	3.2(9)	-0.2(9)
C18'	15.5(10)	16.9(10)	20.4(10)	-1.2(8)	-1.8(8)	1.0(8)
C6	15.8(10)	16.9(10)	23.6(11)	-2.2(8)	-2.8(8)	-1.7(8)
C15'	23.5(11)	19.8(10)	23.7(11)	2.9(8)	1.3(9)	-3.3(8)
C10	15.0(10)	19.9(11)	32.0(12)	0.8(9)	-2.2(9)	2.9(8)
C21	17.9(10)	22.8(10)	17.9(10)	4.3(8)	-0.1(8)	0.8(8)
C21'	17.5(10)	26.6(11)	21.3(11)	-5.7(9)	-0.4(8)	-3.0(8)
C1'	13.0(9)	12.8(9)	16.4(10)	0.6(7)	2.8(7)	-1.5(7)
C6'	13.2(9)	16.9(10)	20.8(10)	3.4(8)	2.3(8)	2.3(8)
C23'	23.2(11)	21.4(11)	23.9(11)	7.0(9)	3.3(9)	4.7(9)
C11'	24.3(11)	23.3(11)	22.2(11)	-2.2(9)	-5.1(9)	-1.1(9)
C17	34.4(13)	28.9(12)	18.7(11)	-3.2(9)	0.4(9)	13.9(10)
C20'	19.9(10)	15.3(9)	19.4(10)	-0.6(8)	1.9(8)	-1.1(8)
C23	25.6(11)	21.4(11)	21.4(11)	-7.7(8)	3.2(9)	-1.5(9)
C20	18.4(10)	14.9(9)	16.3(10)	0.0(8)	2.6(8)	0.5(8)
C15	21.4(11)	29.7(12)	20.1(11)	7.6(9)	2.9(9)	5.3(9)
C10'	16.4(10)	24.2(11)	37.2(13)	-2.1(10)	-1.8(9)	-3.5(9)
C9	20.1(10)	19.6(10)	20.2(11)	2.0(8)	-3.9(8)	-0.6(8)
C9'	20.5(11)	29.4(12)	34.1(13)	-2.5(10)	10.1(9)	-2.4(9)
S1'	17.4(2)	15.3(2)	21.4(3)	0.91(19)	1.27(19)	0.26(19)
S1	21.3(3)	13.5(2)	24.6(3)	-0.96(19)	4.0(2)	-1.96(19)
O3'	24.5(8)	16.0(7)	28.8(8)	2.9(6)	6.2(6)	1.2(6)
O3	33.9(9)	17.4(7)	24.6(8)	-4.1(6)	8.7(7)	-3.6(6)
F3'	22.8(7)	42.2(8)	29.0(7)	-8.8(6)	-1.8(5)	-5.0(6)
F2'	32.0(7)	26.8(7)	36.8(8)	-3.7(6)	14.0(6)	8.0(6)
F1'	35.6(8)	26.8(7)	40.5(8)	8.5(6)	17.0(6)	-2.7(6)
O2'	25.4(8)	15.3(7)	39.3(9)	0.5(6)	11.2(7)	3.8(6)
O2	40.9(10)	15.8(7)	35.6(9)	-0.7(7)	16.5(8)	-7.1(7)

O1'	32.2(9)	40.6(10)	25.8(9)	1.7(7)	-7.8(7)	-7.3(8)
O1	25.3(9)	39.2(11)	82.1(16)	-11.4(10)	-5.8(10)	6.0(8)
C26	23.9(11)	18.8(10)	22.6(11)	-0.5(8)	5.9(9)	1.1(8)
F3	107.8(15)	34.1(9)	48.7(10)	-18.9(7)	51.2(10)	-19.5(9)
F2	159(2)	33.9(9)	73.2(13)	-13.4(9)	86.3(15)	-37.3(11)
F1	95.9(16)	84.2(15)	29.2(9)	7.2(9)	-12.9(10)	23.9(12)
C25	66.3(19)	24.9(12)	30.9(14)	-5.7(10)	27.4(13)	-11.8(12)

Table 4 Bond Lengths for Compound1aHOTf.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C5'	C4'	1.382(3)	C17'	C18'	1.388(3)
C5'	C6'	1.387(3)	C17'	C16'	1.391(3)
C16	C17	1.375(3)	C16'	C15'	1.385(3)
C16	C15	1.391(3)	C2	C3	1.379(3)
N2'	C6'	1.338(2)	C2	C1	1.479(3)
N2'	C2'	1.363(2)	C3	C4	1.390(3)
N2'	B2	1.597(3)	C1	C19	1.463(3)
N1	C1	1.289(2)	C18	C17	1.395(3)
N1	B1	1.580(3)	C8	C9	1.390(3)
C13'	C14'	1.401(3)	C25'	C21'	1.382(3)
C13'	C18'	1.405(3)	C25'	C23'	1.387(3)
C13'	B2	1.615(3)	C12'	C11'	1.389(3)
N2	C6	1.338(2)	C19	C20	1.401(3)
N2	C2	1.356(2)	C24'	C23'	1.382(3)
N2	B1	1.594(3)	C24'	C19'	1.401(3)
C2'	C3'	1.380(3)	C11	C10	1.389(3)
C2'	C1'	1.472(3)	C19'	C20'	1.397(3)
C14'	C15'	1.389(3)	C19'	C1'	1.466(3)
N1'	C1'	1.291(2)	C8'	C9'	1.394(3)
N1'	B2	1.581(3)	C10	C9	1.388(3)
C3'	C4'	1.390(3)	C21	C20	1.384(3)
C13	C18	1.403(3)	C21'	C20'	1.388(3)
C13	C14	1.404(3)	C11'	C10'	1.382(3)
C13	B1	1.613(3)	C10'	C9'	1.384(3)
C14	C15	1.389(3)	S1'	O1'	1.4308(17)
C22	C21	1.389(3)	S1'	O3'	1.4384(15)
C22	C23	1.389(3)	S1'	O2'	1.4511(15)
C7	C8	1.394(3)	S1'	C26	1.829(2)
C7	C12	1.401(3)	S1	O1	1.4302(18)

C7	B1	1.608(3)	S1	O3	1.4364(15)
C12	C11	1.387(3)	S1	O2	1.4446(15)
C7'	C8'	1.398(3)	S1	C25	1.819(3)
C7'	C12'	1.398(3)	F3'	C26	1.336(2)
C7'	B2	1.615(3)	F2'	C26	1.336(2)
C24	C23	1.385(3)	F1'	C26	1.333(2)
C24	C19	1.398(3)	F3	C25	1.344(3)
C5	C4	1.381(3)	F2	C25	1.321(3)
C5	C6	1.386(3)	F1	C25	1.320(4)

Table 5 Bond Angles for Compound1aHOTf.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C4'	C5'	C6'	119.68(18)	C5	C4	C3	119.69(19)
C17	C16	C15	119.7(2)	N1'	B2	N2'	94.44(14)
C6'	N2'	C2'	120.40(17)	N1'	B2	C13'	108.83(16)
C6'	N2'	B2	127.34(16)	N2'	B2	C13'	110.70(16)
C2'	N2'	B2	112.24(15)	N1'	B2	C7'	114.57(16)
C1	N1	B1	115.23(16)	N2'	B2	C7'	111.80(16)
C14'	C13'	C18'	116.75(19)	C13'	B2	C7'	114.73(17)
C14'	C13'	B2	124.04(18)	C12	C11	C10	120.1(2)
C18'	C13'	B2	119.15(17)	C20'	C19'	C24'	119.77(18)
C6	N2	C2	120.37(17)	C20'	C19'	C1'	120.38(17)
C6	N2	B1	127.20(17)	C24'	C19'	C1'	119.81(17)
C2	N2	B1	112.41(15)	C9'	C8'	C7'	121.5(2)
N2'	C2'	C3'	121.47(18)	C17'	C18'	C13'	121.45(19)
N2'	C2'	C1'	108.11(16)	N2	C6	C5	120.36(19)
C3'	C2'	C1'	130.39(18)	C16'	C15'	C14'	119.9(2)
C15'	C14'	C13'	122.11(19)	C9	C10	C11	119.50(19)
C1'	N1'	B2	115.05(16)	C20	C21	C22	119.74(19)
C2'	C3'	C4'	118.16(19)	C25'	C21'	C20'	120.10(19)
C18	C13	C14	116.73(19)	N1'	C1'	C19'	125.70(17)
C18	C13	B1	124.09(18)	N1'	C1'	C2'	109.70(16)
C14	C13	B1	119.17(17)	C19'	C1'	C2'	124.60(17)
C15	C14	C13	121.8(2)	N2'	C6'	C5'	120.37(19)
C21	C22	C23	120.40(19)	C24'	C23'	C25'	120.0(2)
C8	C7	C12	117.25(18)	C10'	C11'	C12'	120.3(2)
C8	C7	B1	121.85(18)	C16	C17	C18	120.2(2)
C12	C7	B1	120.86(17)	C21'	C20'	C19'	119.73(19)
C11	C12	C7	121.44(19)	C24	C23	C22	120.34(19)

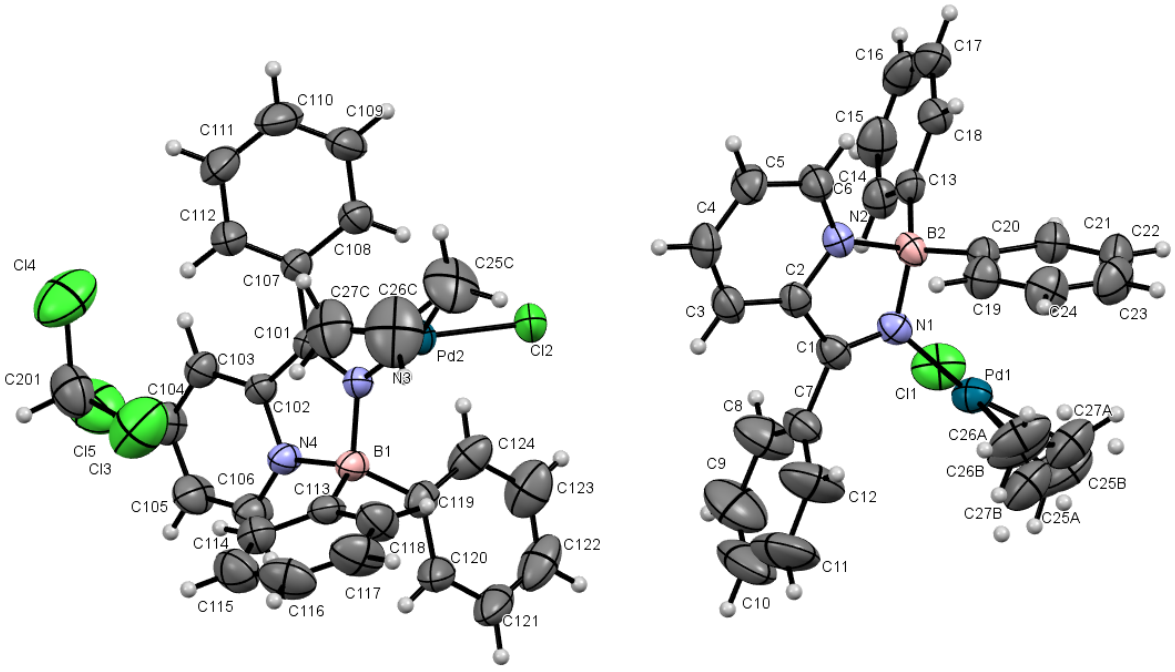
C8'	C7'	C12'	116.99(19)	C21	C20	C19	120.12(18)
C8'	C7'	B2	121.68(18)	C14	C15	C16	119.9(2)
C12'	C7'	B2	121.32(18)	C11'	C10'	C9'	119.3(2)
C23	C24	C19	119.50(19)	C10	C9	C8	119.85(19)
C4	C5	C6	119.72(19)	C10'	C9'	C8'	120.3(2)
C18'	C17'	C16'	120.4(2)	O1'	S1'	O3'	116.18(10)
N1	B1	N2	94.46(14)	O1'	S1'	O2'	115.11(10)
N1	B1	C7	114.10(16)	O3'	S1'	O2'	114.26(9)
N2	B1	C7	109.72(16)	O1'	S1'	C26	102.82(10)
N1	B1	C13	107.74(16)	O3'	S1'	C26	103.78(9)
N2	B1	C13	111.33(16)	O2'	S1'	C26	102.02(9)
C7	B1	C13	117.21(17)	O1	S1	O3	116.03(11)
C15'	C16'	C17'	119.4(2)	O1	S1	O2	114.81(11)
N2	C2	C3	121.70(18)	O3	S1	O2	114.94(9)
N2	C2	C1	108.25(16)	O1	S1	C25	103.68(14)
C3	C2	C1	129.93(18)	O3	S1	C25	102.60(11)
C2	C3	C4	118.10(19)	O2	S1	C25	102.01(11)
N1	C1	C19	126.45(17)	F1'	C26	F2'	107.68(17)
N1	C1	C2	109.26(16)	F1'	C26	F3'	107.70(17)
C19	C1	C2	124.27(17)	F2'	C26	F3'	107.13(17)
C17	C18	C13	121.6(2)	F1'	C26	S1'	110.83(15)
C5'	C4'	C3'	119.86(19)	F2'	C26	S1'	111.40(14)
C9	C8	C7	121.81(19)	F3'	C26	S1'	111.89(15)
C21'	C25'	C23'	120.50(19)	F1	C25	F2	107.8(2)
C11'	C12'	C7'	121.7(2)	F1	C25	F3	108.2(2)
C24	C19	C20	119.89(18)	F2	C25	F3	107.3(2)
C24	C19	C1	119.96(17)	F1	C25	S1	111.20(18)
C20	C19	C1	120.08(17)	F2	C25	S1	110.89(19)
C23'	C24'	C19'	119.85(19)	F3	C25	S1	111.18(19)

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Compound1aHOTf.

Atom	*x*	*y*	*z*	U(eq)
H5'A	14979.58	13926.43	6691.58	22
H16A	5508.49	6892.29	5389.46	34
H1A	7295.09	5876.11	3167.21	18
H14A	16774.54	12892.19	5659.32	22
H1'A	17816.14	10901.18	6902.38	18
H3'A	17725.15	13095.93	7985.17	22

H14B	7056.35	5675.66	4273.55	23
H22A	4134.85	6322.75	731.18	28
H12A	10249.6	6333.94	3212.03	24
H24A	6847.29	5587.48	2086.79	22
H5A	9965.51	8946.88	3605.69	26
H17A	18719.45	10966.2	4928.97	26
H16B	18619.53	12100.15	4455.58	28
H3A	7569.21	8102.48	2165.11	22
H18A	7820.86	7816.51	4472.18	27
H4'A	16365.55	14048.35	7621.01	23
H8A	9534.59	5987.37	4862.43	22
H25A	21390.48	11260.77	9214.93	29
H12B	15299.37	11043.38	5287.91	25
H24B	18442.38	10571.68	7975.26	21
H4A	8835.46	9062.88	2612.57	25
H11A	12141.71	5774.77	3526.31	28
H8'A	14873.89	11194.91	7010.19	27
H18B	17809.37	10787.75	5746.33	22
H6A	9853.76	7875.27	4139.6	24
H15A	17625.56	13060	4821.54	28
H10A	12753.18	5331.15	4515.64	28
H21A	4233.03	7459.5	1194.66	24
H21B	21176.95	12415.4	8791.4	27
H6'A	14962.11	12863.86	6128.56	21
H23A	20002.45	10347.01	8823.77	28
H11B	13484.6	10392.43	5024.39	30
H17B	6589.72	7898.51	5176.47	34
H20A	19575.01	12664.66	7963.02	22
H23B	5436.32	5391.74	1174.59	28
H20B	5670.65	7672.37	2093.72	20
H15B	5757.23	5774.35	4941.65	29
H10B	12341.88	10147.62	5747.87	33
H9A	11427.99	5428.43	5180.07	25
H9'A	13052.51	10544.57	6743.59	33

Compound 3a



Crystallization: 3a was dissolved in $CDCl_3$**,** diethyl ether was layered on top of the solution and allowed to diffuse into the resulting yellow solution, leading to the slow precipitation of an orange crystalline powder along with orange, needle-shaped single crystals of **[**Pd{η^1-N^{IM}-[N-(diphenylboryl)-2-benzoylpyridinketimine]}Cl(C_3H_5)].

Table 1 Crystal data and structure refinement for Compound 3a.

Identification code	Compound3a
Empirical formula	$C_{55}H_{49}B_2Cl_5N_4Pd_2$
Formula weight	1177.65
Temperature/K	298(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.1405(4)
b/Å	16.5696(8)
c/Å	18.1527(9)
α/°	84.1920(10)
β/°	85.2670(10)
γ/°	78.6660(10)

Volume/Å^3	2676.3(2)
Z	2
ρ_{calc}g/cm^3	1.461
μ/mm^{-1}	0.961
F(000)	1188.0
Crystal size/mm^3	0.200 × 0.200 × 0.100
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.232 to 51.398
Index ranges	-11 ≤ h ≤ 11, -20 ≤ k ≤ 20, -22 ≤ l ≤ 22
Reflections collected	27632
Independent reflections	10106 [R_{int} = 0.0266, R_{sigma} = 0.0329]
Data/restraints/parameters	10106/3/623
Goodness-of-fit on F^2	1.013
Final R indexes [I>=2σ (I)]	R_1 = 0.0368, wR_2 = 0.0855
Final R indexes [all data]	R_1 = 0.0515, wR_2 = 0.0945
Largest diff. peak/hole / e Å^{-3}	0.66/-0.47

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Compound3a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Pd2	7262.4(3)	9206.7(2)	8175.3(2)	45.34(9)
Pd1	1506.7(3)	4195.0(2)	6761.2(2)	49.54(9)
Cl2	6323.0(11)	7991.0(7)	8095.7(6)	64.6(3)
Cl1	3627.5(13)	3148.9(7)	6583.2(6)	74.5(3)
Cl5	12653.8(19)	10807.9(9)	7302.6(8)	108.8(5)
Cl4	12208.8(19)	11469.1(12)	8713.6(9)	124.1(6)
Cl3	10047(2)	12042.4(11)	7663.5(11)	126.4(6)
N3	9129(3)	8936.1(15)	7414.9(13)	36.3(6)
N1	2335(3)	4779.2(15)	7574.9(14)	40.1(6)
N2	2595(3)	5391.5(15)	8683.0(14)	38.7(6)
N4	10959(3)	8958.7(17)	6399.7(14)	40.5(6)
C102	11628(3)	8744.1(19)	7042.5(17)	38.1(7)
C101	10451(3)	8739.2(19)	7650.0(16)	36.6(7)
C13	2998(4)	3789.3(19)	8796.1(18)	41.0(7)
C2	3144(3)	5814.4(19)	8083.2(18)	40.7(7)
C113	8531(4)	10128(2)	6396.3(17)	44.7(8)

C19	216(4)	4721(2)	8590.1(17)	40.7(7)
C103	13175(4)	8570(2)	7052.1(19)	47.4(8)
C119	8437(3)	8567(2)	6102.0(18)	45.9(8)
C1	2930(4)	5414.8(19)	7420.7(18)	42.4(7)
C107	10766(3)	8564(2)	8442.9(17)	41.6(7)
C24	-456(4)	4034(2)	8593(2)	51.8(9)
C3	3784(4)	6489(2)	8153(2)	51.1(9)
C6	2662(4)	5621(2)	9361.4(19)	49.4(8)
C20	-739(4)	5483(2)	8628(2)	54.9(9)
C14	4282(4)	3367(2)	8431(2)	52.7(9)
C108	10039(4)	8022(2)	8895.3(19)	49.0(8)
C114	9400(4)	10716(2)	6188(2)	54.4(9)
C18	2662(4)	3487(2)	9524(2)	51.8(9)
C120	7915(4)	8836(3)	5402(2)	67.6(12)
C21	-2278(4)	5556(3)	8656(2)	67.3(11)
C5	3296(4)	6290(2)	9462(2)	55.0(9)
C104	14017(4)	8616(2)	6389(2)	58.2(10)
C105	13304(4)	8827(3)	5737(2)	63.7(11)
C112	11687(4)	8983(2)	8757.5(19)	57.1(10)
C118	6993(4)	10426(3)	6502(2)	64.3(11)
C106	11770(4)	8990(2)	5754.2(19)	53.3(9)
B1	9160(4)	9153(2)	6556(2)	41.6(9)
B2	1992(4)	4619(2)	8432(2)	39.7(8)
C23	-2001(4)	4112(3)	8615(2)	66.7(11)
C7	3354(5)	5754(2)	6661.5(19)	53.5(9)
C124	8319(4)	7766(2)	6359(2)	64.0(11)
C4	3853(4)	6726(2)	8853(2)	55.8(9)
C17	3551(5)	2796(3)	9863(2)	66.9(12)
C16	4795(5)	2395(3)	9486(3)	74.4(13)
C22	-2906(4)	4875(3)	8646(2)	70.0(12)
C109	10238(4)	7909(3)	9649(2)	66.3(11)
C15	5158(4)	2676(2)	8772(3)	69.2(12)
C117	6401(5)	11264(3)	6418(3)	79.8(14)
C116	7293(6)	11821(3)	6217(3)	82.0(14)
C111	11861(5)	8880(3)	9511(2)	72.3(12)
C121	7357(5)	8330(4)	4982(2)	84.7(16)
C110	11131(5)	8344(3)	9952(2)	75.4(13)
C115	8802(6)	11553(3)	6081(2)	76.0(12)
C8	4685(6)	5445(3)	6317(3)	97.8(17)
C201	11960(6)	11694(3)	7778(3)	85.5(14)
C122	7265(5)	7552(4)	5247(3)	84.4(15)

C123	7735(5)	7261(3)	5936(3)	85.0(14)
C12	2416(7)	6388(3)	6303(3)	104.8(19)
C9	5073(8)	5752(5)	5608(3)	125(2)
C10	4131(10)	6357(5)	5246(3)	123(3)
C11	2796(10)	6676(4)	5580(3)	129(2)
C25A	332(17)	3867(8)	5922(10)	85(4)
C26A	-540(40)	5012(15)	6627(12)	92(3)
C27A	-689(7)	4241(5)	6460(4)	86(2)
C25B	-60(70)	3880(20)	6030(30)	85(4)
C26B	-640(130)	5050(50)	6750(40)	92(3)
C27B	-250(20)	4718(16)	6085(15)	86(2)
C25C	5736(6)	9701(4)	9026(3)	98.2(17)
C27C	7811(6)	10296(3)	8503(3)	86.0(15)
C26C	6306(7)	10322(4)	8623(4)	118(2)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for Compound3a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd2	37.12(14)	54.99(17)	42.92(15)	-2.24(12)	2.80(11)	-9.56(12)
Pd1	60.18(18)	44.32(16)	43.65(16)	-6.68(12)	-5.40(13)	-6.46(13)
Cl2	58.6(6)	77.3(7)	65.7(6)	16.6(5)	-16.7(5)	-37.7(5)
Cl1	81.5(7)	66.9(7)	67.8(7)	-20.7(5)	3.1(5)	8.3(5)
Cl5	142.8(13)	97.7(10)	87.9(9)	-27.7(8)	17.9(9)	-27.7(9)
Cl4	116.8(12)	164.5(16)	95.7(10)	-54.0(10)	-21.7(9)	-10.5(11)
Cl3	125.0(13)	110.8(12)	146.9(15)	-21.3(10)	-43.8(11)	-11.0(10)
N3	31.5(13)	41.8(15)	35.6(14)	2.3(11)	-3.1(11)	-9.2(11)
N1	41.2(15)	35.1(14)	41.9(15)	-0.5(11)	-0.9(12)	-4.4(12)
N2	37.8(14)	36.2(14)	42.4(15)	-2.5(11)	0.2(11)	-9.4(11)
N4	32.4(14)	51.8(16)	35.3(14)	0.6(12)	-2.9(11)	-4.8(12)
C102	34.1(16)	41.8(18)	37.1(17)	3.0(13)	-6.1(13)	-6.1(13)
C101	32.9(16)	41.0(17)	36.5(16)	2.6(13)	-5.0(13)	-10.1(13)
C13	43.7(18)	36.4(17)	46.6(19)	-1.2(14)	-10.1(15)	-15.0(14)
C2	36.1(17)	36.1(17)	48.7(19)	1.3(14)	-3.3(14)	-6.7(14)
C113	40.4(18)	58(2)	32.7(17)	5.1(15)	-7.0(14)	-3.8(16)
C19	43.9(18)	42.1(18)	38.1(17)	-3.4(14)	-2.6(14)	-13.0(15)
C103	36.0(18)	57(2)	49(2)	0.9(16)	-7.3(15)	-7.2(15)
C119	30.1(16)	62(2)	44.3(19)	-7.9(16)	-1.2(14)	-5.1(15)
C1	42.6(18)	34.9(17)	47.1(19)	2.0(14)	-0.1(15)	-4.9(14)
C107	34.3(17)	53(2)	37.5(17)	2.8(14)	-5.7(13)	-10.5(15)

C24	49(2)	52(2)	58(2)	-6.9(17)	-4.4(17)	-15.8(17)
C3	50(2)	45(2)	59(2)	5.3(17)	0.0(17)	-17.6(16)
C6	56(2)	50(2)	46(2)	-6.2(16)	2.2(16)	-20.3(17)
C20	52(2)	49(2)	64(2)	-9.8(18)	-3.9(18)	-9.3(17)
C14	46(2)	46(2)	66(2)	-0.7(17)	-4.1(17)	-11.8(16)
C108	40.1(18)	61(2)	45(2)	7.7(16)	-5.6(15)	-11.6(16)
C114	53(2)	58(2)	53(2)	0.5(17)	-6.5(17)	-12.4(18)
C18	59(2)	50(2)	50(2)	2.2(16)	-10.1(17)	-19.7(17)
C120	62(2)	107(3)	41(2)	3(2)	-7.2(18)	-38(2)
C21	50(2)	68(3)	80(3)	-16(2)	-1(2)	1(2)
C5	61(2)	58(2)	52(2)	-14.1(18)	-2.6(18)	-22.2(19)
C104	31.6(18)	74(3)	64(2)	-3(2)	2.9(17)	-3.1(17)
C105	44(2)	93(3)	49(2)	-3(2)	11.1(17)	-9(2)
C112	55(2)	77(3)	44(2)	3.7(18)	-7.7(17)	-27(2)
C118	48(2)	66(3)	70(3)	15(2)	-1.8(19)	-1.9(19)
C106	47(2)	71(2)	38.6(19)	-0.1(17)	1.2(15)	-6.3(18)
B1	30.3(18)	58(2)	34.1(19)	3.1(17)	-2.9(15)	-6.6(17)
B2	45(2)	33.2(19)	42(2)	-1.6(15)	2.1(16)	-13.6(16)
C23	53(2)	81(3)	73(3)	-6(2)	-6(2)	-31(2)
C7	72(3)	46(2)	44(2)	0.4(16)	2.6(18)	-20.7(18)
C124	59(2)	61(3)	72(3)	-21(2)	-21(2)	3.8(19)
C4	55(2)	46(2)	72(3)	-8.8(18)	-4.4(19)	-22.4(17)
C17	87(3)	60(3)	63(3)	16(2)	-31(2)	-34(2)
C16	70(3)	54(3)	103(4)	17(2)	-46(3)	-16(2)
C22	39(2)	90(3)	80(3)	-12(2)	-2.7(19)	-8(2)
C109	54(2)	96(3)	46(2)	21(2)	-3.5(18)	-20(2)
C15	49(2)	50(2)	107(4)	-3(2)	-15(2)	-2.3(18)
C117	62(3)	80(3)	79(3)	14(3)	-1(2)	19(2)
C116	108(4)	55(3)	73(3)	11(2)	-6(3)	2(3)
C111	66(3)	107(4)	52(2)	-7(2)	-17(2)	-33(3)
C121	68(3)	155(5)	44(2)	-16(3)	-5(2)	-50(3)
C110	63(3)	123(4)	38(2)	5(2)	-9.8(19)	-16(3)
C115	96(4)	60(3)	74(3)	5(2)	-6(3)	-23(3)
C8	104(4)	103(4)	72(3)	14(3)	24(3)	-7(3)
C201	95(4)	76(3)	92(4)	-17(3)	10(3)	-35(3)
C122	59(3)	123(4)	82(3)	-59(3)	-2(2)	-19(3)
C123	83(3)	59(3)	116(4)	-33(3)	-20(3)	-2(2)
C12	130(5)	88(4)	77(3)	33(3)	2(3)	3(3)
C9	144(6)	143(6)	80(4)	-1(4)	48(4)	-35(5)
C10	201(8)	126(6)	56(3)	10(3)	18(4)	-82(6)
C11	186(7)	111(5)	80(4)	50(4)	-24(4)	-27(5)

C25A	87(10)	101(4)	72(7)	-31(3)	-27(6)	-7(4)
C26A	91(6)	94(4)	83(9)	-25(4)	-42(7)	29(4)
C27A	66(4)	108(6)	89(5)	-24(4)	-28(4)	-9(4)
C25B	87(10)	101(4)	72(7)	-31(3)	-27(6)	-7(4)
C26B	91(6)	94(4)	83(9)	-25(4)	-42(7)	29(4)
C27B	66(4)	108(6)	89(5)	-24(4)	-28(4)	-9(4)
C25C	86(4)	125(5)	79(3)	-34(3)	39(3)	-14(3)
C27C	94(4)	71(3)	100(4)	-44(3)	10(3)	-23(3)
C26C	106(5)	109(5)	140(6)	-72(4)	30(4)	-7(4)

Table 4 Bond Lengths for Compound3a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd2	C26C	2.095(5)	C119	C120	1.394(5)
Pd2	N3	2.110(2)	C119	B1	1.602(5)
Pd2	C25C	2.111(4)	C1	C7	1.485(5)
Pd2	C27C	2.119(4)	C107	C112	1.381(5)
Pd2	Cl2	2.3612(10)	C107	C108	1.384(4)
Pd1	C27B	2.10(2)	C24	C23	1.390(5)
Pd1	C26A	2.10(3)	C3	C4	1.378(5)
Pd1	C25A	2.106(17)	C6	C5	1.381(5)
Pd1	C27A	2.109(6)	C20	C21	1.385(5)
Pd1	N1	2.110(3)	C14	C15	1.383(5)
Pd1	C26B	2.18(10)	C108	C109	1.384(5)
Pd1	C25B	2.19(6)	C114	C115	1.387(5)
Pd1	Cl1	2.3570(11)	C18	C17	1.387(5)
Cl5	C201	1.762(5)	C120	C121	1.380(6)
Cl4	C201	1.725(5)	C21	C22	1.366(6)
Cl3	C201	1.753(5)	C5	C4	1.376(5)
N3	C101	1.285(4)	C104	C105	1.380(5)
N3	B1	1.563(4)	C105	C106	1.373(5)
N1	C1	1.275(4)	C112	C111	1.380(5)
N1	B2	1.567(4)	C118	C117	1.387(6)
N2	C6	1.335(4)	C23	C22	1.371(6)
N2	C2	1.350(4)	C7	C8	1.352(6)
N2	B2	1.609(4)	C7	C12	1.364(6)
N4	C106	1.336(4)	C124	C123	1.397(6)
N4	C102	1.346(4)	C17	C16	1.368(6)
N4	B1	1.619(4)	C16	C15	1.369(6)
C102	C103	1.387(4)	C109	C110	1.369(6)

C102	C101	1.477(4)	C117	C116	1.352(7)
C101	C107	1.480(4)	C116	C115	1.373(6)
C13	C14	1.397(5)	C111	C110	1.369(6)
C13	C18	1.397(5)	C121	C122	1.346(7)
C13	B2	1.610(5)	C8	C9	1.380(7)
C2	C3	1.380(4)	C122	C123	1.366(7)
C2	C1	1.474(5)	C12	C11	1.391(7)
C113	C114	1.379(5)	C9	C10	1.341(9)
C113	C118	1.399(5)	C10	C11	1.352(9)
C113	B1	1.610(5)	C25A	C27A	1.398(13)
C19	C20	1.391(5)	C26A	C27A	1.38(2)
C19	C24	1.395(5)	C25B	C27B	1.38(2)
C19	B2	1.604(5)	C26B	C27B	1.37(3)
C103	C104	1.378(5)	C25C	C26C	1.365(8)
C119	C124	1.383(5)	C27C	C26C	1.367(7)

Table 5 Bond Angles for Compound3a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C26C	Pd2	N3	129.7(2)	C4	C3	C2	118.5(3)
C26C	Pd2	C25C	37.9(2)	N2	C6	C5	120.8(3)
N3	Pd2	C25C	164.44(18)	C21	C20	C19	121.6(4)
C26C	Pd2	C27C	37.9(2)	C15	C14	C13	121.3(4)
N3	Pd2	C27C	96.00(15)	C109	C108	C107	120.1(3)
C25C	Pd2	C27C	68.9(2)	C113	C114	C115	122.7(4)
C26C	Pd2	Cl2	131.75(19)	C17	C18	C13	121.5(4)
N3	Pd2	Cl2	96.88(7)	C121	C120	C119	122.4(4)
C25C	Pd2	Cl2	97.83(17)	C22	C21	C20	120.6(4)
C27C	Pd2	Cl2	165.94(15)	C4	C5	C6	119.3(3)
C26A	Pd1	C25A	68.5(5)	C103	C104	C105	119.3(3)
C26A	Pd1	C27A	38.2(7)	C106	C105	C104	119.9(3)
C25A	Pd1	C27A	38.7(4)	C111	C112	C107	120.9(4)
C27B	Pd1	N1	126.4(7)	C117	C118	C113	121.3(4)
C26A	Pd1	N1	98.9(5)	N4	C106	C105	120.5(3)
C25A	Pd1	N1	167.0(3)	N3	B1	C119	115.3(3)
C27A	Pd1	N1	131.4(2)	N3	B1	C113	108.4(3)
C27B	Pd1	C26B	37.3(13)	C119	B1	C113	115.3(3)
N1	Pd1	C26B	94.1(17)	N3	B1	N4	97.2(2)
C27B	Pd1	C25B	37.4(9)	C119	B1	N4	109.2(3)
N1	Pd1	C25B	160.2(11)	C113	B1	N4	110.0(3)

C26B	Pd1	C25B	66(2)	N1	B2	C19	108.3(3)
C27B	Pd1	Cl1	132.0(7)	N1	B2	N2	97.7(2)
C26A	Pd1	Cl1	163.1(4)	C19	B2	N2	111.3(3)
C25A	Pd1	Cl1	94.8(3)	N1	B2	C13	113.6(3)
C27A	Pd1	Cl1	128.2(2)	C19	B2	C13	116.8(3)
N1	Pd1	Cl1	97.53(7)	N2	B2	C13	107.5(3)
C26B	Pd1	Cl1	168.4(17)	C22	C23	C24	120.2(4)
C25B	Pd1	Cl1	102.0(10)	C8	C7	C12	118.9(4)
C101	N3	B1	112.0(2)	C8	C7	C1	120.5(4)
C101	N3	Pd2	119.9(2)	C12	C7	C1	120.6(4)
B1	N3	Pd2	126.33(19)	C119	C124	C123	121.8(4)
C1	N1	B2	111.4(3)	C5	C4	C3	119.8(3)
C1	N1	Pd1	122.8(2)	C16	C17	C18	120.2(4)
B2	N1	Pd1	124.5(2)	C17	C16	C15	119.8(4)
C6	N2	C2	120.2(3)	C21	C22	C23	119.5(4)
C6	N2	B2	129.8(3)	C110	C109	C108	120.1(4)
C2	N2	B2	109.9(3)	C16	C15	C14	120.5(4)
C106	N4	C102	120.7(3)	C116	C117	C118	120.9(4)
C106	N4	B1	129.1(3)	C117	C116	C115	119.7(4)
C102	N4	B1	110.2(2)	C110	C111	C112	119.6(4)
N4	C102	C103	120.8(3)	C122	C121	C120	120.5(4)
N4	C102	C101	108.1(2)	C109	C110	C111	120.4(4)
C103	C102	C101	131.1(3)	C116	C115	C114	119.4(4)
N3	C101	C102	112.5(3)	C7	C8	C9	120.6(6)
N3	C101	C107	124.0(3)	Cl4	C201	Cl3	108.4(3)
C102	C101	C107	123.5(3)	Cl4	C201	Cl5	109.9(3)
C14	C13	C18	116.7(3)	Cl3	C201	Cl5	111.0(3)
C14	C13	B2	122.8(3)	C121	C122	C123	119.6(4)
C18	C13	B2	120.4(3)	C122	C123	C124	120.1(5)
N2	C2	C3	121.3(3)	C7	C12	C11	120.1(6)
N2	C2	C1	107.9(3)	C10	C9	C8	120.6(6)
C3	C2	C1	130.8(3)	C9	C10	C11	119.8(6)
C114	C113	C118	116.0(3)	C10	C11	C12	119.9(6)
C114	C113	B1	125.1(3)	C27A	C25A	Pd1	70.7(7)
C118	C113	B1	118.9(3)	C27A	C26A	Pd1	71.3(12)
C20	C19	C24	116.6(3)	C26A	C27A	C25A	117.1(16)
C20	C19	B2	123.4(3)	C26A	C27A	Pd1	70.5(15)
C24	C19	B2	119.4(3)	C25A	C27A	Pd1	70.5(8)
C104	C103	C102	118.7(3)	C27B	C25B	Pd1	68(2)
C124	C119	C120	115.6(4)	C27B	C26B	Pd1	68(4)
C124	C119	B1	123.3(3)	C26B	C27B	C25B	121(4)

C120	C119	B1	121.1(3)	C26B	C27B	Pd1	75(5)
N1	C1	C2	113.1(3)	C25B	C27B	Pd1	75(3)
N1	C1	C7	125.3(3)	C26C	C25C	Pd2	70.4(3)
C2	C1	C7	121.6(3)	C26C	C27C	Pd2	70.1(3)
C112	C107	C108	118.8(3)	C25C	C26C	C27C	122.2(7)
C112	C107	C101	121.0(3)	C25C	C26C	Pd2	71.7(3)
C108	C107	C101	120.0(3)	C27C	C26C	Pd2	72.0(3)
C23	C24	C19	121.5(4)				

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Compound3a.

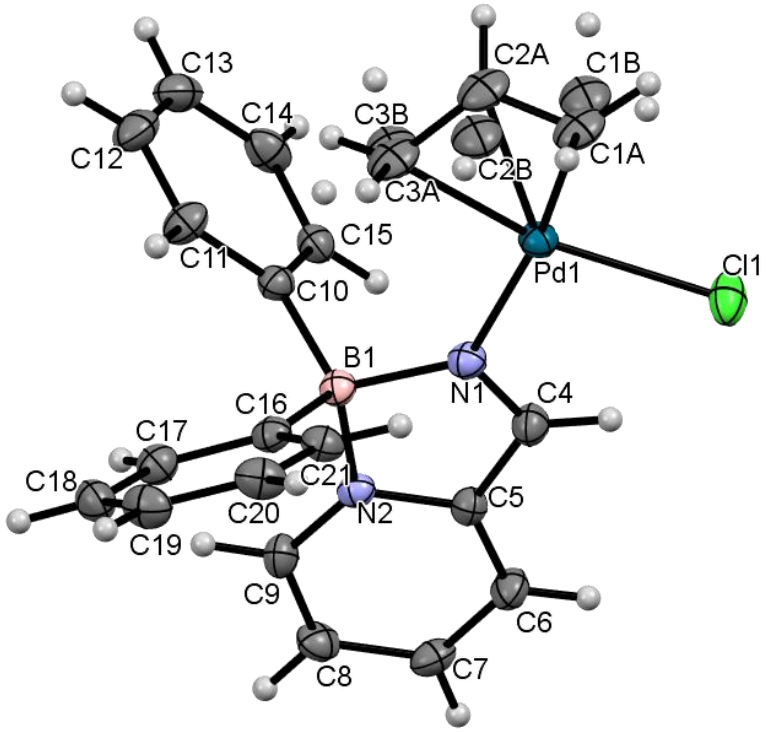
Atom	*x*	*y*	*z*	U(eq)
H5A	13644.39	8420.95	7507.01	57
H00A	155.98	3500.84	8579.6	62
H00B	4168.35	6782.16	7727.57	61
H00C	2269.44	5321.21	9779.99	59
H00D	-325.3	5965.53	8634.47	66
H00E	4559.97	3557.7	7937.42	63
H00F	9402.96	7727.93	8688.07	59
H00G	10450.88	10540.14	6114.57	65
H00H	1803.87	3761.66	9794.05	62
H00I	7945.82	9386.77	5206.54	81
H00J	-2902.51	6084.73	8681.82	81
H00K	3347.03	6447.29	9947.06	66
H00L	15078.03	8504.05	6381.47	70
H00M	13873.44	8860.22	5276.27	76
H00N	12207.64	9347.27	8450.87	69
H01A	6341.15	10045.34	6635.04	77
H01B	11281.72	9125.32	5303.57	64
H01C	-2430.93	3635.77	8609.01	80
H01D	8644.84	7554.32	6836.53	77
H01E	4284	7190.08	8915.2	67
H01F	3294.85	2600.65	10357.67	80
H01G	5406.19	1922.46	9718.46	89
H01H	-3961.35	4928.51	8660.46	84
H01I	9753.1	7528.8	9956.27	80
H01J	6017.51	2394.31	8508.59	83
H01K	5355.05	11450.25	6502.26	96
H01L	6877.92	12394.88	6168.95	98

H01M	12483.64	9178.64	9723.07	87
H01N	7035.05	8533.23	4501.85	102
H01O	11244.96	8273.08	10471.17	91
H01P	9431.49	11937.03	5916.17	91
H01Q	5359.8	5013.49	6565.13	117
H6A	12514.89	12141.7	7580.98	103
H01Z	6875.77	7207.63	4956.53	101
H02A	7665.02	6713.48	6127.05	102
H02B	1501.05	6632.24	6548.08	126
H02C	6014.59	5531.59	5373.4	150
H02E	4402.62	6561.51	4756.18	148
H02F	2117.43	7096.63	5321.84	155
H25A	395.88	4182.92	5431.62	102
H25B	383.22	3268.49	5891.9	102
H26A	-1092.56	5213.62	7085.76	111
H26B	-565.75	5444.26	6207.73	111
H27A	-1380.74	3925.31	6768.73	104
H25C	366.82	3670.71	5554.59	102
H25D	-855.86	3596.95	6275.41	102
H26C	-1485.15	4871.94	7055.02	111
H26D	-612.6	5645	6761.32	111
H27B	-51.96	5087.53	5631.89	104
H25E	4667.69	9694.52	8976.03	118
H25F	6045.92	9560.14	9540.8	118
H27C	8390.77	10233.63	8949.63	103
H27D	8130.8	10687.26	8101.89	103
H26E	5616.7	10742.81	8316.38	142

Table 7 Atomic Occupancy for Compound3a.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
C25A	0.755(9)	H25A	0.755(9)	H25B	0.755(9)
C26A	0.755(9)	H26A	0.755(9)	H26B	0.755(9)
C27A	0.755(9)	H27A	0.755(9)	C25B	0.245(9)
H25C	0.245(9)	H25D	0.245(9)	C26B	0.245(9)
H26C	0.245(9)	H26D	0.245(9)	C27B	0.245(9)
H27B	0.245(9)				

Compound 3b



Crystallization: 3b was dissolved in $CDCl_3$. The brown solution was then layered with diethyl ether and was allowed to diffuse, resulting in the slow precipitation of an orange crystalline powder and orange, stick-shaped crystals of [Pd{η^1-N^{IM}-[N-(diphenylboryl)picolinaldimine]}Cl(C_3H_5)].

Table 1 Crystal data and structure refinement for Compound 3b.

Identification code	Compound3b
Empirical formula	$C_{21}H_{20}BClN_2Pd$
Formula weight	453.05
Temperature/K	100(2)
Crystal system	orthorhombic
Space group	Pbca
a/Å	9.789(6)
b/Å	15.693(9)
c/Å	25.897(15)
α/°	90
β/°	90
γ/°	90

Volume/Å^3	3978(4)
Z	8
ρ_{calc}g/cm^3	1.513
μ/mm^{-1}	1.073
F(000)	1824.0
Crystal size/mm^3	0.16 × 0.13 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.146 to 55.836
Index ranges	-12 ≤ h ≤ 12, -19 ≤ k ≤ 19, -32 ≤ l ≤ 32
Reflections collected	37345
Independent reflections	4425 [R_{int} = 0.0781, R_{sigma} = 0.0457]
Data/restraints/parameters	4425/244/239
Goodness-of-fit on F^2	1.061
Final R indexes [I>=2σ (I)]	R_1 = 0.0378, wR_2 = 0.0746
Final R indexes [all data]	R_1 = 0.0590, wR_2 = 0.0811
Largest diff. peak/hole / e Å^{-3}	1.14/-0.49

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Compound3b. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Pd1	5681.1(2)	1991.9(2)	3659.4(2)	21.52(8)
N1	7308(3)	1724.2(16)	4177.0(10)	21.4(6)
C16	9407(3)	1034.7(19)	3646.3(12)	21.9(6)
C9	10679(3)	1302(2)	4841.8(12)	24.1(6)
C17	10806(3)	955(2)	3519.4(12)	25.5(7)
N2	9416(3)	1443.5(16)	4652.7(9)	19.5(5)
C10	9449(3)	2707.7(19)	3960.2(12)	20.8(6)
C8	10846(3)	1030(2)	5356.4(13)	26.6(7)
C6	8406(3)	1080(2)	5479.2(12)	27.1(7)
C19	10340(4)	-122(2)	2871.6(13)	30.6(8)
C21	8486(3)	501(2)	3376.2(12)	24.2(7)
C5	8290(3)	1334(2)	4961.8(12)	21.9(6)
C11	10064(4)	2959(2)	3492.1(13)	28.4(7)
C20	8947(4)	-68(2)	2990.4(13)	28.4(7)
C18	11278(4)	386(2)	3142.7(13)	27.9(7)
B1	8916(4)	1733(2)	4071.1(13)	20.0(7)

C13	10253(4)	4439(2)	3769.3(15)	32.4(8)
C15	9260(3)	3363(2)	4334.4(12)	22.9(6)
C14	9650(3)	4210(2)	4241.0(14)	29.9(7)
C4	7062(3)	1523(2)	4653.8(12)	24.9(7)
C12	10476(4)	3806(2)	3397.9(14)	33.2(8)
C7	9704(3)	924(2)	5675.7(13)	26.4(7)
Cl1	3923.3(8)	1613.0(6)	4261.7(3)	32.4(2)
C1A	4326(16)	2095(10)	3003(5)	31(3)
C2A	5452(13)	2649(10)	2946(4)	31(3)
C3A	6710(20)	2287(10)	2935(6)	31(3)
C1B	4290(8)	2450(5)	3088(2)	34.9(14)
C2B	5503(6)	2145(5)	2847(2)	34.9(14)
C3B	6805(10)	2494(5)	3022(3)	34.9(14)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for Compound3b. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd1	22.31(13)	24.57(13)	17.69(13)	1.08(10)	-1.82(9)	2.22(10)
N1	23.4(14)	22.1(13)	18.8(13)	0.4(10)	-0.1(10)	0.7(11)
C16	26.2(15)	22.3(14)	17.1(14)	2.3(12)	0.7(13)	0.4(13)
C9	19.1(15)	27.6(16)	25.6(16)	-0.6(13)	1.2(13)	-3.1(13)
C17	27.3(17)	26.0(16)	23.1(16)	0.2(13)	-0.2(13)	-1.1(14)
N2	22.6(13)	18.4(12)	17.4(12)	0.1(10)	0.3(10)	0.5(11)
C10	19.3(15)	21.4(14)	21.6(15)	2.7(11)	-2.3(12)	-0.5(12)
C8	22.3(17)	28.9(17)	28.6(17)	2.9(14)	-7.2(13)	1.1(14)
C6	24.3(16)	35.3(19)	21.6(16)	6.1(14)	2.5(12)	-1.0(14)
C19	40(2)	28.0(17)	23.9(17)	-4.4(14)	1.4(14)	6.8(15)
C21	24.8(16)	23.9(16)	23.8(17)	1.1(13)	-3.6(13)	2.7(13)
C5	20.9(16)	23.4(16)	21.5(15)	0.8(12)	1.9(12)	0.4(12)
C11	35.6(19)	29.9(17)	19.8(16)	2.7(14)	0.9(13)	-4.7(15)
C20	34.5(19)	24.1(17)	26.5(18)	-3.5(13)	-8.1(14)	1.1(14)
C18	25.2(17)	30.9(18)	27.7(18)	0.1(14)	1.9(13)	4.5(14)
B1	19.6(16)	23.9(17)	16.5(16)	1.4(13)	-0.3(13)	-0.2(13)
C13	30.5(18)	24.5(17)	42(2)	8.1(15)	-7.8(15)	-1.2(14)
C15	20.3(15)	26.2(15)	22.1(16)	-0.7(12)	-0.2(13)	3.4(13)
C14	26.6(18)	24.3(16)	39(2)	-6.9(15)	-3.7(14)	2.1(13)
C4	20.0(15)	31.3(17)	23.3(16)	2.5(13)	0.5(12)	-2.0(14)
C12	37(2)	34.3(18)	28.6(18)	11.8(15)	0.1(15)	-5.4(15)
C7	32.6(17)	24.3(16)	22.3(16)	6.1(13)	-3.0(13)	-3.4(14)

Cl1	20.1(4)	51.6(5)	25.3(4)	1.9(4)	-1.5(3)	-4.8(4)
C1A	41(6)	36(5)	15(4)	7(3)	-6(3)	-5(4)
C2A	41(6)	36(5)	15(4)	7(3)	-6(3)	-5(4)
C3A	41(6)	36(5)	15(4)	7(3)	-6(3)	-5(4)
C1B	39(3)	44(3)	21(2)	7.1(18)	-3.8(16)	4(2)
C2B	39(3)	44(3)	21(2)	7.1(18)	-3.8(16)	4(2)
C3B	39(3)	44(3)	21(2)	7.1(18)	-3.8(16)	4(2)

Table 4 Bond Lengths for Compound3b.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1	N1	2.124(3)	C10	C11	1.410(4)
Pd1	C2B	2.125(5)	C10	C15	1.425(5)
Pd1	C2A	2.126(11)	C10	B1	1.642(5)
Pd1	C3B	2.134(10)	C8	C7	1.401(5)
Pd1	C1B	2.136(6)	C6	C7	1.390(5)
Pd1	C1A	2.162(13)	C6	C5	1.403(4)
Pd1	C3A	2.18(2)	C19	C20	1.401(5)
Pd1	Cl1	2.3975(12)	C19	C18	1.404(5)
N1	C4	1.297(4)	C21	C20	1.414(5)
N1	B1	1.597(4)	C5	C4	1.473(4)
C16	C17	1.414(5)	C11	C12	1.411(5)
C16	C21	1.416(5)	C13	C12	1.399(5)
C16	B1	1.626(5)	C13	C14	1.403(5)
C9	N2	1.349(4)	C15	C14	1.404(5)
C9	C8	1.409(5)	C1A	C2A	1.41(2)
C17	C18	1.401(5)	C2A	C3A	1.35(3)
N2	C5	1.373(4)	C1B	C2B	1.424(11)
N2	B1	1.648(4)	C2B	C3B	1.460(12)

Table 5 Bond Angles for Compound3b.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Pd1	C2B	135.14(18)	C7	C8	C9	120.1(3)
N1	Pd1	C2A	136.3(3)	C7	C6	C5	118.3(3)
N1	Pd1	C3B	100.0(2)	C20	C19	C18	119.5(3)
C2B	Pd1	C3B	40.1(3)	C20	C21	C16	121.3(3)
N1	Pd1	C1B	169.2(2)	N2	C5	C6	121.8(3)
C2B	Pd1	C1B	39.1(3)	N2	C5	C4	108.3(3)

C3B	Pd1	C1B	70.7(3)	C6	C5	C4	129.9(3)
N1	Pd1	C1A	166.2(5)	C10	C11	C12	122.3(3)
C2A	Pd1	C1A	38.4(6)	C19	C20	C21	120.2(3)
N1	Pd1	C3A	103.9(5)	C17	C18	C19	119.6(3)
C2A	Pd1	C3A	36.6(7)	N1	B1	C16	113.7(3)
C1A	Pd1	C3A	65.8(6)	N1	B1	C10	110.5(3)
N1	Pd1	Cl1	94.51(8)	C16	B1	C10	114.6(3)
C2B	Pd1	Cl1	127.83(17)	N1	B1	N2	97.7(2)
C2A	Pd1	Cl1	127.5(4)	C16	B1	N2	110.2(2)
C3B	Pd1	Cl1	164.7(2)	C10	B1	N2	108.8(2)
C1B	Pd1	Cl1	94.4(2)	C12	C13	C14	118.8(3)
C1A	Pd1	Cl1	95.1(4)	C14	C15	C10	122.0(3)
C3A	Pd1	Cl1	160.8(5)	C13	C14	C15	120.5(3)
C4	N1	B1	110.4(3)	N1	C4	C5	114.4(3)
C4	N1	Pd1	120.6(2)	C13	C12	C11	120.3(3)
B1	N1	Pd1	128.97(19)	C6	C7	C8	119.5(3)
C17	C16	C21	116.7(3)	C2A	C1A	Pd1	69.4(8)
C17	C16	B1	120.2(3)	C3A	C2A	C1A	117.0(17)
C21	C16	B1	123.0(3)	C3A	C2A	Pd1	73.8(10)
N2	C9	C8	120.0(3)	C1A	C2A	Pd1	72.2(7)
C18	C17	C16	122.5(3)	C2A	C3A	Pd1	69.6(10)
C9	N2	C5	120.3(3)	C2B	C1B	Pd1	70.1(4)
C9	N2	B1	130.5(3)	C1B	C2B	C3B	117.8(8)
C5	N2	B1	109.2(2)	C1B	C2B	Pd1	70.9(4)
C11	C10	C15	116.0(3)	C3B	C2B	Pd1	70.3(4)
C11	C10	B1	123.1(3)	C2B	C3B	Pd1	69.6(5)
C15	C10	B1	120.8(3)				

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Compound3b.

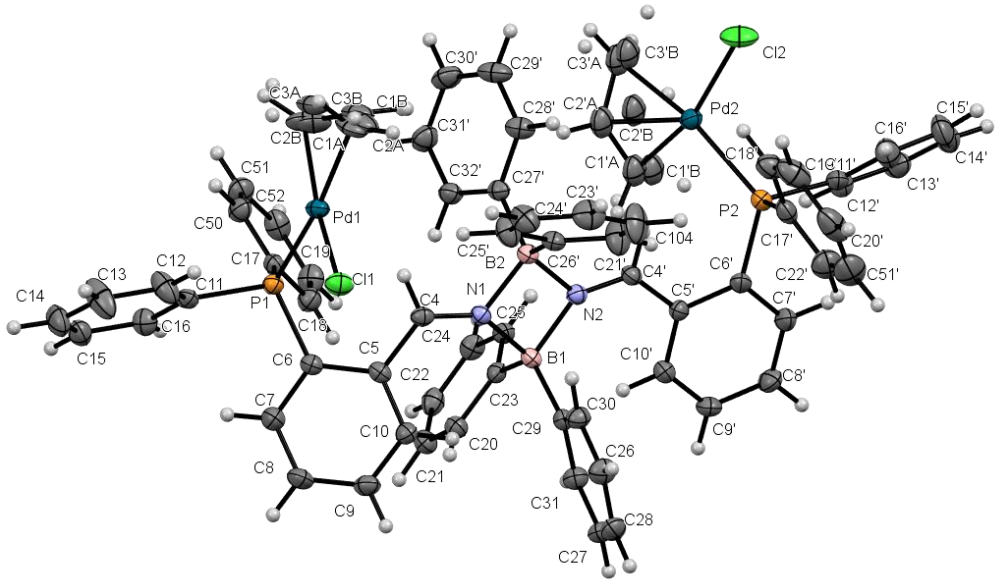
Atom	*x*	*y*	*z*	U(eq)
H9A	11456.12	1385.06	4627.95	29
H17A	11450.97	1300.65	3696.41	31
H8A	11735.39	919.49	5487.22	32
H6A	7618.73	1017.01	5689.99	32
H19A	10648.18	-499.48	2609.53	37
H21A	7539.94	525.11	3455.78	29
H11A	10206.31	2542.76	3231.06	34
H20A	8308.79	-415.41	2810.98	34

H18A	12227.7	344.05	3070.99	34
H13A	10504.11	5012.98	3703.27	39
H15A	8856.84	3221.97	4657.09	27
H14A	9506.12	4630.41	4498.97	36
H4A	6164.67	1499.83	4792.73	30
H12A	10907.25	3948.26	3080.73	40
H7A	9814.9	745.49	6023.77	32
H1A1	4287.61	1599.51	2767.39	37
H1A2	3426.77	2364.57	3065.68	37
H2A	5331.45	3280.95	2933.75	37
H3A1	7498.52	2678.99	2954.47	37
H3A2	6838.49	1809.18	2690.6	37
H1B1	3450.34	2110.22	3032.67	42
H1B2	4134.79	3073.07	3077.92	42
H2B	5475.99	1637.57	2613.77	42
H3B1	6906.96	3121.27	3007.69	42
H3B2	7638.52	2179.86	2919.56	42

Table 7 Atomic Occupancy for Compound3b.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
C1A	0.312(13)	H1A1	0.312(13)	H1A2	0.312(13)
C2A	0.312(13)	H2A	0.312(13)	C3A	0.312(13)
H3A1	0.312(13)	H3A2	0.312(13)	C1B	0.688(13)
H1B1	0.688(13)	H1B2	0.688(13)	C2B	0.688(13)
H2B	0.688(13)	C3B	0.688(13)	H3B1	0.688(13)
H3B2	0.688(13)				

Compound 6a



Crystallization: 6a was dissolved in CH_2Cl_2**,** diethyl ether was layered on top of the solution and allowed to diffuse into the resulting brown solution, leading to the slow precipitation of an orange Brown, stick-shaped crystals of bis[(allyl)chloro(N-(diphenylboryl)-2-diphenylphosphanyl-benzaldimine)palladium].

Table 1 Crystal data and structure refinement for Compound 6a.

Identification code	Compound 6a
Empirical formula	$C_{68}H_{60}B_2Cl_2N_2P_2Pd_2$
Formula weight	1272.44
Temperature/K	100(2)
Crystal system	triclinic
Space group	P-1
a/Å	10.9275(7)
b/Å	15.5825(10)
c/Å	19.4130(13)
α/°	96.5890(10)
β/°	104.4760(10)
γ/°	109.1150(10)
Volume/Å^3	2953.5(3)
Z	2
ρ_{calc}g/cm^3	1.431

μ/mm^{-1}	0.797
F(000)	1296.0
Crystal size/mm^3	0.4 × 0.2 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.832 to 56.912
Index ranges	$-14 \le h \le 14$, $-20 \le k \le 20$, $-25 \le l \le 26$
Reflections collected	33997
Independent reflections	13408 [R_{int} = 0.0334, R_{sigma} = 0.0476]
Data/restraints/parameters	13408/676/709
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0382, wR_2 = 0.0906
Final R indexes [all data]	R_1 = 0.0574, wR_2 = 0.0983
Largest diff. peak/hole / e $Å^{-3}$	1.03/-0.72

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$×10^3) for Compound 6a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Pd1	1402.7(2)	4964.3(2)	1442.2(2)	22.35(7)
Pd2	839.0(2)	373.2(2)	3971.4(2)	23.10(7)
P2	1456.6(7)	-666.2(5)	3335.5(4)	21.85(16)
Cl1	1507.4(7)	4437.6(5)	275.7(4)	29.06(16)
P1	3705.1(7)	5836.1(5)	1918.3(4)	20.10(15)
N1	3528(2)	3024.6(15)	2016.3(11)	18.4(5)
C28'	490(3)	2441(2)	2859.4(16)	27.8(7)
C6	4743(3)	5313.3(19)	1539.9(14)	19.8(6)
Cl2	-1503.7(8)	-528.9(7)	3599.1(5)	42.0(2)
N2	3270(2)	1807.4(15)	2523.6(12)	19.3(5)
C31	6216(3)	1894(2)	1804.2(16)	25.9(6)
C26'	1068(3)	1745.3(19)	1482.6(15)	22.4(6)
C4'	2965(3)	1102.5(18)	2811.6(14)	20.5(6)
C17	4440(3)	6078.0(19)	2907.5(15)	23.1(6)
C5'	3801(3)	577.4(18)	3091.9(15)	20.8(6)
C25	5757(3)	3227.6(19)	3706.5(15)	23.3(6)
C5	4567(3)	4367.6(18)	1508.7(14)	19.1(6)
C24	6846(3)	3852(2)	4280.1(15)	26.4(6)
C11	4136(3)	6987.8(19)	1709.4(15)	21.5(6)

C4	3572(3)	3777.8(19)	1802.8(14)	20.2(6)
C15	5587(3)	8602(2)	1948.2(16)	30.5(7)
C23	5760(3)	3173.7(18)	2981.9(15)	20.3(6)
C30	4005(3)	1524.2(19)	978.2(15)	25.4(6)
C27'	1820(3)	2821.9(19)	2819.6(15)	21.2(6)
C29	4926(3)	1942.8(18)	1679.5(15)	20.2(6)
C22	7983(3)	4441(2)	4145.7(16)	28.5(7)
C9	6107(3)	4507(2)	783.8(16)	28.0(7)
C7'	4042(3)	-758(2)	3542.2(16)	28.6(7)
C10'	5174(3)	885.1(19)	3132.3(15)	24.1(6)
C25'	533(3)	2228(2)	1010.1(16)	32.8(7)
C18	5409(3)	5745(2)	3259.3(16)	26.9(6)
C10	5256(3)	3980(2)	1124.8(15)	22.6(6)
C50	3952(3)	6596(2)	3329.8(16)	27.2(6)
C11'	1288(3)	-1602.5(19)	3834.5(16)	25.2(6)
C51	4413(3)	6769(2)	4078.6(17)	31.9(7)
B2	2302(3)	2338(2)	2218.3(17)	21.1(6)
C6'	3230(3)	-255.3(19)	3321.2(15)	23.4(6)
C9'	5976(3)	389(2)	3376.8(16)	27.4(6)
C52	5361(3)	6417(2)	4421.4(16)	31.7(7)
C21	8021(3)	4402(2)	3435.7(16)	27.4(6)
C20	6921(3)	3784.5(19)	2865.0(16)	24.0(6)
B1	4514(3)	2471(2)	2294.7(17)	20.0(6)
C32'	2686(3)	3644(2)	3329.6(16)	26.0(6)
C28	5674(3)	1089(2)	576.9(17)	31.1(7)
C27	6590(3)	1473(2)	1263.1(16)	28.4(7)
C16	5287(3)	7739(2)	2129.4(16)	28.9(7)
C12	3297(3)	7102(2)	1097.0(18)	38.8(8)
C29'	56(3)	2858(2)	3374.3(17)	35.8(8)
C17'	489(3)	-1272.4(19)	2392.5(16)	27.2(6)
C16'	187(3)	-2430(2)	3556.1(18)	36.2(8)
C12'	2159(3)	-1452(2)	4530.2(17)	30.2(7)
C15'	-32(4)	-3107(2)	3968(2)	44.6(9)
C8	6329(3)	5441(2)	843.2(17)	31.9(7)
C26	4377(3)	1112(2)	437.2(16)	30.2(7)
C19	5854(3)	5914(2)	4012.9(16)	31.3(7)
C22'	951(4)	-1857(2)	2012.6(18)	39.5(8)
C7	5652(3)	5836(2)	1216.4(16)	29.1(7)
C14	4728(3)	8710(2)	1337.9(19)	39.1(8)
C14'	881(4)	-2973(2)	4638(2)	40.6(8)
C24'	-531(3)	1789(2)	379.0(17)	34.8(7)

C23'	-1112(3)	841(2)	194.2(17)	38.1(8)
C21'	476(3)	788(2)	1280.0(19)	40.7(8)
C18'	-744(3)	-1212(2)	2062.7(17)	33.4(7)
C8'	5396(3)	-444(2)	3571.2(17)	29.8(7)
C19'	-1523(4)	-1728(2)	1359.5(18)	42.1(8)
C13	3601(4)	7965(3)	916(2)	53.8(11)
C31'	2269(3)	4069(2)	3848.0(17)	32.3(7)
C30'	944(3)	3672(2)	3867.2(17)	35.5(7)
C13'	1971(4)	-2141(2)	4926.0(19)	37.2(8)
C20'	-1058(4)	-2300(2)	994.6(19)	44.9(9)
C51'	171(4)	-2372(2)	1323.8(19)	47.4(9)
C104	-612(4)	335(2)	649(2)	47.8(10)
C1'A	2755(6)	1393(4)	4502(4)	35.3(7)
C2'A	1950(5)	1787(3)	4537(3)	35.3(7)
C3'A	860(7)	1538(4)	4768(5)	35.3(7)
C1'B	2839(12)	1193(8)	4664(6)	35.3(7)
C2'B	2046(9)	1444(6)	4955(5)	35.3(7)
C3'B	609(12)	1369(8)	4707(8)	35.3(7)
C1A	-743(18)	4286(6)	1167(7)	36(2)
C3A	715(14)	5291(11)	2348(7)	37.3(18)
C2A	-186(4)	4400(4)	1917(3)	36.9(10)
C1B	-870(50)	4139(18)	1190(20)	36(2)
C3B	650(30)	5140(30)	2287(17)	37.3(18)
C2B	-420(11)	4946(9)	1688(6)	36.9(10)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for Compound 6a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd1	20.63(12)	27.59(13)	23.40(12)	8.42(9)	10.72(9)	10.78(10)
Pd2	25.91(13)	24.60(13)	24.58(12)	7.69(9)	11.95(9)	12.76(10)
P2	21.8(4)	19.7(4)	26.0(4)	6.6(3)	11.1(3)	6.9(3)
Cl1	29.8(4)	35.9(4)	22.8(4)	4.8(3)	11.2(3)	12.0(3)
P1	22.8(4)	21.3(4)	20.2(4)	6.8(3)	9.7(3)	10.2(3)
N1	19.7(11)	19.6(12)	16.8(11)	4.8(9)	6.6(9)	7.5(10)
C28'	21.5(15)	38.5(18)	23.1(15)	6.6(13)	7.8(12)	10.2(13)
C6	18.0(13)	21.8(14)	19.0(14)	4.7(11)	6.0(11)	6.3(11)
Cl2	22.3(4)	64.2(6)	41.8(5)	9.4(4)	11.8(3)	18.0(4)
N2	18.2(11)	19.5(12)	19.6(12)	2.4(9)	6.1(9)	6.6(9)
C31	25.7(15)	28.3(16)	25.6(15)	5.3(12)	9.6(12)	11.2(13)

C26'	17.7(14)	25.0(15)	25.3(14)	5.9(12)	8.9(11)	6.9(12)
C4'	17.9(13)	19.5(14)	22.5(14)	4.0(11)	7.5(11)	4.1(11)
C17	25.9(15)	21.2(15)	24.0(14)	9.0(12)	10.9(12)	6.9(12)
C5'	20.3(14)	17.6(14)	24.1(14)	2.0(11)	9.0(11)	5.9(11)
C25	25.6(15)	23.4(15)	25.4(14)	6.5(12)	11.9(12)	11.5(12)
C5	17.0(13)	21.4(14)	16.0(13)	4.3(11)	4.3(10)	3.9(11)
C24	31.6(16)	27.5(16)	20.3(14)	4.1(12)	6.2(12)	12.6(13)
C11	24.9(14)	24.1(15)	21.8(14)	9.5(11)	12.8(12)	11.4(12)
C4	19.7(14)	23.3(14)	17.5(13)	2.3(11)	6.5(11)	7.9(12)
C15	37.4(18)	24.1(16)	30.3(16)	6.1(13)	15.6(14)	7.7(14)
C23	21.8(14)	19.3(14)	22.6(14)	4.9(11)	7.5(11)	10.5(12)
C30	21.4(14)	26.3(16)	26.9(15)	2.4(12)	7.2(12)	8.2(12)
C27'	22.2(14)	26.1(15)	21.6(14)	11.4(11)	9.6(11)	12.6(12)
C29	21.7(14)	17.6(14)	23.3(14)	6.1(11)	9.2(11)	7.3(11)
C22	27.4(16)	23.1(15)	29.4(16)	0.9(13)	2.0(13)	8.8(13)
C9	28.7(16)	35.6(17)	28.6(16)	11.4(13)	16.3(13)	16.3(14)
C7'	33.9(17)	26.4(16)	37.2(17)	15.3(13)	19.9(14)	16.5(14)
C10'	24.4(15)	21.3(15)	28.5(15)	7.6(12)	11.5(12)	7.6(12)
C25'	29.7(17)	28.2(17)	31.0(17)	7.7(13)	1.3(13)	4.2(13)
C18	30.5(16)	26.8(16)	27.2(15)	7.1(12)	10.4(13)	13.8(13)
C10	22.3(14)	23.2(15)	25.5(15)	7.0(12)	9.0(12)	10.5(12)
C50	33.1(17)	28.3(16)	26.3(15)	9.2(13)	12.3(13)	15.5(14)
C11'	28.5(15)	23.2(15)	32.6(16)	9.4(12)	18.9(13)	12.1(13)
C51	38.1(18)	29.5(17)	28.7(16)	3.4(13)	13.7(14)	11.6(14)
B2	18.2(15)	20.2(16)	26.0(16)	6.3(13)	8.6(13)	6.4(13)
C6'	28.6(15)	21.4(14)	26.2(15)	7.2(12)	15.7(12)	10.7(12)
C9'	22.0(15)	29.9(16)	35.4(17)	9.1(13)	15.1(13)	10.8(13)
C52	38.2(18)	27.8(17)	20.9(15)	4.2(13)	5.2(13)	5.3(14)
C21	24.1(15)	24.3(16)	32.0(16)	5.3(13)	9.7(13)	6.2(13)
C20	25.1(15)	23.2(15)	24.9(15)	6.7(12)	9.9(12)	8.1(12)
B1	18.5(15)	18.6(16)	23.4(16)	6.5(12)	8.9(12)	5.0(12)
C32'	26.2(15)	28.8(16)	28.9(16)	10.3(12)	14.2(13)	11.9(13)
C28	36.7(17)	27.0(16)	32.6(17)	1.0(13)	18.2(14)	11.8(14)
C27	27.1(16)	29.3(16)	34.0(16)	4.5(13)	16.1(13)	12.8(13)
C16	31.7(16)	29.4(16)	25.1(15)	7.2(13)	7.2(13)	11.3(13)
C12	28.8(17)	37.7(19)	41.3(19)	21.0(16)	2.3(14)	3.5(15)
C29'	25.4(16)	57(2)	33.0(17)	15.5(16)	15.8(14)	18.2(15)
C17'	32.2(16)	20.4(15)	26.6(15)	5.8(12)	13.8(13)	2.9(13)
C16'	40.1(19)	27.4(17)	38.5(18)	7.5(14)	13.2(15)	8.2(14)
C12'	29.9(16)	28.3(16)	35.6(17)	10.3(13)	12.7(14)	11.6(14)
C15'	49(2)	24.5(18)	55(2)	11.0(16)	21.1(18)	2.2(16)

C8	30.9(17)	34.5(17)	40.2(18)	15.5(14)	23.3(15)	12.8(14)
C26	30.4(16)	32.5(17)	23.6(15)	-0.2(13)	6.6(13)	10.0(14)
C19	32.5(17)	31.5(17)	26.3(15)	7.3(13)	1.7(13)	12.5(14)
C22'	49(2)	39(2)	31.7(18)	3.3(15)	16.6(15)	16.3(17)
C7	30.4(16)	26.1(16)	36.6(17)	10.5(13)	17.0(14)	11.7(13)
C14	38.7(19)	30.8(18)	52(2)	23.7(16)	14.0(16)	12.6(15)
C14'	54(2)	34.3(19)	53(2)	26.7(16)	33.1(18)	23.8(17)
C24'	28.0(17)	39.3(18)	32.8(17)	12.0(15)	4.3(13)	9.2(15)
C23'	28.5(17)	45(2)	29.0(17)	-1.0(15)	-0.6(14)	8.5(15)
C21'	36.2(19)	29.2(17)	44(2)	8.7(15)	-3.7(15)	7.7(15)
C18'	29.6(17)	33.1(18)	31.5(17)	0.7(14)	11.5(14)	4.6(14)
C8'	30.8(16)	31.8(17)	37.4(18)	13.8(14)	15.0(14)	19.7(14)
C19'	33.3(18)	48(2)	30.3(18)	2.7(15)	8.5(14)	-1.1(16)
C13	34(2)	54(2)	63(3)	41(2)	-2.8(17)	6.7(17)
C31'	41.0(18)	31.6(17)	29.1(16)	4.9(13)	14.8(14)	17.1(15)
C30'	43.4(19)	48(2)	30.7(17)	13.7(15)	21.8(15)	27.7(16)
C13'	45(2)	42.4(19)	40.4(19)	20.9(15)	22.7(16)	25.5(16)
C20'	50(2)	38(2)	27.6(18)	-1.1(15)	14.3(16)	-6.6(17)
C51'	64(2)	42(2)	34.7(19)	-0.6(16)	24.6(18)	13.7(19)
C104	41(2)	24.0(18)	53(2)	-0.1(16)	-8.0(17)	0.0(15)
C1'A	44.6(17)	22.8(17)	32.7(16)	0.3(11)	10.7(14)	7.8(12)
C2'A	44.6(17)	22.8(17)	32.7(16)	0.3(11)	10.7(14)	7.8(12)
C3'A	44.6(17)	22.8(17)	32.7(16)	0.3(11)	10.7(14)	7.8(12)
C1'B	44.6(17)	22.8(17)	32.7(16)	0.3(11)	10.7(14)	7.8(12)
C2'B	44.6(17)	22.8(17)	32.7(16)	0.3(11)	10.7(14)	7.8(12)
C3'B	44.6(17)	22.8(17)	32.7(16)	0.3(11)	10.7(14)	7.8(12)
C1A	15(4)	49(4)	47(2)	19(3)	14.0(19)	7(3)
C3A	35(2)	56(5)	31(2)	8(3)	21.7(16)	21(3)
C2A	27(2)	53(3)	45(2)	23(2)	23.2(19)	20(2)
C1B	15(4)	49(4)	47(2)	19(3)	14.0(19)	7(3)
C3B	35(2)	56(5)	31(2)	8(3)	21.7(16)	21(3)
C2B	27(2)	53(3)	45(2)	23(2)	23.2(19)	20(2)

Table 4 Bond Lengths for Compound 6a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1	C3B	2.04(5)	C23	C20	1.404(4)
Pd1	C1A	2.127(17)	C23	B1	1.617(4)
Pd1	C3A	2.150(19)	C30	C26	1.383(4)
Pd1	C2A	2.150(4)	C30	C29	1.405(4)

Pd1	C2B	2.153(10)	C27'	C32'	1.401(4)
Pd1	C1B	2.29(5)	C27'	B2	1.605(4)
Pd1	P1	2.3109(8)	C29	B1	1.610(4)
Pd1	Cl1	2.3621(7)	C22	C21	1.384(4)
Pd2	C1'A	2.083(6)	C9	C8	1.382(4)
Pd2	C3'B	2.106(13)	C9	C10	1.382(4)
Pd2	C1'B	2.127(11)	C7'	C8'	1.382(4)
Pd2	C2'A	2.135(4)	C7'	C6'	1.389(4)
Pd2	C2'B	2.176(8)	C10'	C9'	1.382(4)
Pd2	C3'A	2.235(7)	C25'	C24'	1.376(4)
Pd2	P2	2.2970(8)	C18	C19	1.385(4)
Pd2	Cl2	2.3530(8)	C50	C51	1.376(4)
P2	C11'	1.827(3)	C11'	C16'	1.379(4)
P2	C17'	1.828(3)	C11'	C12'	1.387(4)
P2	C6'	1.839(3)	C51	C52	1.389(4)
P1	C11	1.821(3)	C9'	C8'	1.386(4)
P1	C17	1.827(3)	C52	C19	1.371(4)
P1	C6	1.837(3)	C21	C20	1.389(4)
N1	C4	1.279(3)	C32'	C31'	1.390(4)
N1	B2	1.586(4)	C28	C27	1.376(4)
N1	B1	1.619(4)	C28	C26	1.387(4)
C28'	C29'	1.391(4)	C12	C13	1.385(4)
C28'	C27'	1.405(4)	C29'	C30'	1.385(5)
C6	C7	1.394(4)	C17'	C18'	1.379(4)
C6	C5	1.414(4)	C17'	C22'	1.400(4)
N2	C4'	1.274(3)	C16'	C15'	1.390(5)
N2	B2	1.589(4)	C12'	C13'	1.382(4)
N2	B1	1.613(4)	C15'	C14'	1.372(5)
C31	C27	1.391(4)	C8	C7	1.384(4)
C31	C29	1.398(4)	C22'	C51'	1.377(5)
C26'	C21'	1.380(4)	C14	C13	1.370(5)
C26'	C25'	1.388(4)	C14'	C13'	1.378(5)
C26'	B2	1.621(4)	C24'	C23'	1.365(4)
C4'	C5'	1.464(4)	C23'	C104	1.379(5)
C17	C18	1.392(4)	C21'	C104	1.391(4)
C17	C50	1.399(4)	C18'	C19'	1.398(4)
C5'	C10'	1.397(4)	C19'	C20'	1.373(5)
C5'	C6'	1.418(4)	C31'	C30'	1.389(4)
C25	C24	1.391(4)	C20'	C51'	1.383(5)
C25	C23	1.401(4)	C1'A	C2'A	1.237(6)
C5	C10	1.400(4)	C2'A	C3'A	1.332(6)

C5	C4	1.459(4)	C1'B	C2'B	1.279(14)
C24	C22	1.387(4)	C2'B	C3'B	1.483(16)
C11	C12	1.377(4)	C1A	C2A	1.396(15)
C11	C16	1.386(4)	C3A	C2A	1.422(13)
C15	C14	1.381(4)	C1B	C2B	1.350(2)
C15	C16	1.386(4)	C3B	C2B	1.350(2)

Table 5 Bond Angles for Compound 6a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1A	Pd1	C3A	69.6(4)	C28'	C27'	B2	121.3(3)
C1A	Pd1	C2A	38.1(4)	C31	C29	C30	116.5(3)
C3A	Pd1	C2A	38.6(4)	C31	C29	B1	122.4(2)
C3B	Pd1	C2B	37.4(4)	C30	C29	B1	121.1(2)
C3B	Pd1	C1B	65.2(11)	C21	C22	C24	119.4(3)
C2B	Pd1	C1B	35.2(5)	C8	C9	C10	119.8(3)
C3B	Pd1	P1	104.3(7)	C8'	C7'	C6'	121.4(3)
C1A	Pd1	P1	170.2(3)	C9'	C10'	C5'	121.5(3)
C3A	Pd1	P1	100.7(3)	C24'	C25'	C26'	122.7(3)
C2A	Pd1	P1	133.85(13)	C19	C18	C17	120.0(3)
C2B	Pd1	P1	136.5(3)	C9	C10	C5	121.2(3)
C1B	Pd1	P1	169.2(9)	C51	C50	C17	120.8(3)
C3B	Pd1	Cl1	160.9(8)	C16'	C11'	C12'	119.2(3)
C1A	Pd1	Cl1	94.8(3)	C16'	C11'	P2	119.6(2)
C3A	Pd1	Cl1	164.1(2)	C12'	C11'	P2	120.7(2)
C2A	Pd1	Cl1	128.33(14)	C50	C51	C52	119.9(3)
C2B	Pd1	Cl1	125.1(3)	N1	B2	N2	88.00(19)
C1B	Pd1	Cl1	95.7(8)	N1	B2	C27'	114.5(2)
P1	Pd1	Cl1	94.80(3)	N2	B2	C27'	114.7(2)
C3'B	Pd2	C1'B	74.4(5)	N1	B2	C26'	109.9(2)
C1'A	Pd2	C2'A	34.08(16)	N2	B2	C26'	114.1(2)
C3'B	Pd2	C2'B	40.5(4)	C27'	B2	C26'	113.3(2)
C1'B	Pd2	C2'B	34.6(4)	C7'	C6'	C5'	118.6(3)
C1'A	Pd2	C3'A	65.1(3)	C7'	C6'	P2	120.1(2)
C2'A	Pd2	C3'A	35.39(14)	C5'	C6'	P2	121.3(2)
C1'A	Pd2	P2	99.42(18)	C10'	C9'	C8'	119.2(3)
C3'B	Pd2	P2	169.4(4)	C19	C52	C51	119.9(3)
C1'B	Pd2	P2	95.9(3)	C22	C21	C20	120.1(3)
C2'A	Pd2	P2	131.37(12)	C21	C20	C23	122.1(3)
C2'B	Pd2	P2	129.2(2)	C29	B1	N2	114.1(2)

C3'A	Pd2	P2	163.82(19)	C29	B1	C23	116.1(2)
C1'A	Pd2	Cl2	163.86(18)	N2	B1	C23	113.5(2)
C3'B	Pd2	Cl2	91.8(3)	C29	B1	N1	116.4(2)
C1'B	Pd2	Cl2	160.1(3)	N2	B1	N1	86.08(19)
C2'A	Pd2	Cl2	131.22(12)	C23	B1	N1	106.9(2)
C2'B	Pd2	Cl2	128.5(2)	C31'	C32'	C27'	122.6(3)
C3'A	Pd2	Cl2	98.78(18)	C27	C28	C26	119.5(3)
P2	Pd2	Cl2	96.45(3)	C28	C27	C31	119.7(3)
C11'	P2	C17'	103.72(13)	C11	C16	C15	120.9(3)
C11'	P2	C6'	105.52(13)	C11	C12	C13	119.7(3)
C17'	P2	C6'	103.24(13)	C30'	C29'	C28'	120.1(3)
C11'	P2	Pd2	104.08(9)	C18'	C17'	C22'	119.1(3)
C17'	P2	Pd2	122.13(10)	C18'	C17'	P2	120.7(2)
C6'	P2	Pd2	116.41(9)	C22'	C17'	P2	120.1(2)
C11	P1	C17	103.49(13)	C11'	C16'	C15'	120.1(3)
C11	P1	C6	104.83(12)	C13'	C12'	C11'	120.5(3)
C17	P1	C6	105.89(13)	C14'	C15'	C16'	120.1(3)
C11	P1	Pd1	112.04(9)	C9	C8	C7	119.9(3)
C17	P1	Pd1	116.83(9)	C30	C26	C28	120.6(3)
C6	P1	Pd1	112.66(9)	C52	C19	C18	120.8(3)
C4	N1	B2	126.2(2)	C51'	C22'	C17'	120.2(3)
C4	N1	B1	140.3(2)	C8	C7	C6	121.6(3)
B2	N1	B1	92.85(19)	C13	C14	C15	119.9(3)
C29'	C28'	C27'	121.9(3)	C15'	C14'	C13'	120.1(3)
C7	C6	C5	118.4(2)	C23'	C24'	C25'	120.3(3)
C7	C6	P1	119.4(2)	C24'	C23'	C104	118.9(3)
C5	C6	P1	122.0(2)	C26'	C21'	C104	122.0(3)
C4'	N2	B2	126.5(2)	C17'	C18'	C19'	120.4(3)
C4'	N2	B1	140.4(2)	C7'	C8'	C9'	120.3(3)
B2	N2	B1	93.00(19)	C20'	C19'	C18'	119.8(3)
C27	C31	C29	122.3(3)	C14	C13	C12	120.9(3)
C21'	C26'	C25'	115.9(3)	C30'	C31'	C32'	119.4(3)
C21'	C26'	B2	125.8(3)	C29'	C30'	C31'	119.8(3)
C25'	C26'	B2	118.3(3)	C14'	C13'	C12'	119.8(3)
N2	C4'	C5'	129.1(3)	C19'	C20'	C51'	120.2(3)
C18	C17	C50	118.7(3)	C22'	C51'	C20'	120.3(4)
C18	C17	P1	123.7(2)	C23'	C104	C21'	120.1(3)
C50	C17	P1	117.5(2)	C2'A	C1'A	Pd2	75.3(3)
C10'	C5'	C6'	118.8(3)	C1'A	C2'A	C3'A	130.0
C10'	C5'	C4'	120.4(2)	C1'A	C2'A	Pd2	70.6(3)
C6'	C5'	C4'	120.7(2)	C3'A	C2'A	Pd2	76.4(3)

C24	C25	C23	121.8(3)	C2'A	C3'A	Pd2	68.2(3)
C10	C5	C6	119.0(2)	C2'B	C1'B	Pd2	74.8(6)
C10	C5	C4	120.1(2)	C1'B	C2'B	C3'B	135.7(10)
C6	C5	C4	120.5(2)	C1'B	C2'B	Pd2	70.6(6)
C22	C24	C25	120.2(3)	C3'B	C2'B	Pd2	67.2(6)
C12	C11	C16	119.3(3)	C2'B	C3'B	Pd2	72.3(6)
C12	C11	P1	118.1(2)	C2A	C1A	Pd1	71.9(7)
C16	C11	P1	122.6(2)	C2A	C3A	Pd1	70.7(7)
N1	C4	C5	129.0(2)	C1A	C2A	C3A	120.1(9)
C14	C15	C16	119.3(3)	C1A	C2A	Pd1	70.0(7)
C25	C23	C20	116.5(3)	C3A	C2A	Pd1	70.7(8)
C25	C23	B1	123.8(2)	C2B	C1B	Pd1	66.9(17)
C20	C23	B1	119.7(2)	C2B	C3B	Pd1	75.9(19)
C26	C30	C29	121.3(3)	C3B	C2B	C1B	120(3)
C32'	C27'	C28'	116.2(3)	C3B	C2B	Pd1	67(2)
C32'	C27'	B2	122.5(2)	C1B	C2B	Pd1	78(2)

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Compound 6a.

Atom	*x*	*y*	*z*	U(eq)
H28A	−131.74	1882.42	2525.28	33
H31A	6859.37	2158.52	2275.13	31
H4'A	2069.3	887.75	2849.66	25
H25A	4988.86	2826.66	3809	28
H24A	6812	3875.41	4765.84	32
H4A	2857.29	3981.52	1841.01	24
H15A	6375.72	9114.7	2240.56	37
H30A	3107.91	1524.34	873.5	30
H22A	8728.67	4867.57	4537.09	34
H9A	6538.94	4227.34	509.48	34
H7'A	3659.26	−1330.96	3676.23	34
H10A	5566.93	1448.55	2988.44	29
H25B	916.27	2888.09	1127.17	39
H18A	5765.89	5401.26	2982.32	32
H10B	5135.61	3343.68	1098.39	27
H50A	3294.81	6831.54	3097.16	33
H51A	4082.69	7127.47	4360.35	38
H9'A	6913.97	615.81	3411.04	33
H52A	5668.34	6524.61	4937.9	38

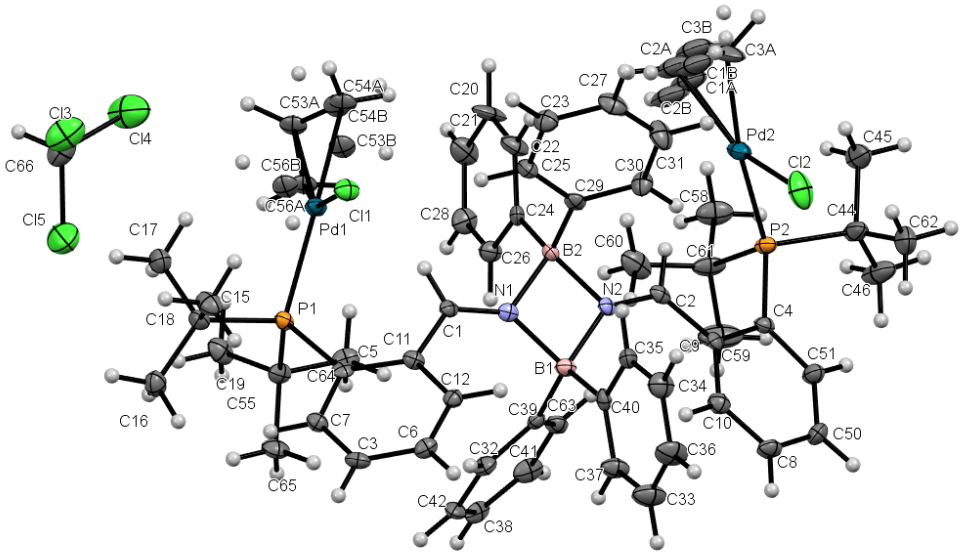
H21A	8799.6	4797.34	3338.7	33
H20A	6956.41	3775.45	2380.23	29
H32A	3594.53	3922.61	3320.57	31
H28B	5926.82	810.75	201.45	37
H27A	7474.7	1449.59	1366.87	34
H16A	5878.04	7660.11	2547.2	35
H12A	2512.2	6590.18	800.03	47
H29A	-850.84	2584.16	3387.61	43
H16B	-422.44	-2537.47	3082.46	43
H12B	2891.56	-871.06	4736.17	36
H15B	-814.8	-3663.98	3784.54	54
H8A	6944.53	5812.21	628.09	38
H26A	3739.3	841.49	-34.67	36
H19A	6507.18	5677.91	4249.66	38
H22B	1805.9	-1897.21	2230.91	47
H7A	5810.21	6479.16	1253.19	35
H14A	4918.58	9300.52	1210.79	47
H14B	760.89	-3453.23	4903.88	49
H24B	-862.66	2147.68	70.73	42
H23A	-1847.05	535.76	-240.39	46
H21B	821.97	427.92	1580.45	49
H18B	-1066.4	-816.55	2315.02	40
H8'A	5932.04	-799.39	3725.12	36
H19B	-2371.95	-1683.26	1134.67	50
H13A	3020.22	8041.51	492.62	65
H31B	2885.91	4625.5	4186.07	39
H30B	646.58	3958.68	4217.52	43
H13B	2590.48	-2042.64	5395.02	45
H20B	-1582.66	-2646.62	514.93	54
H51B	479.04	-2779.59	1073.46	57
H10C	-1011.64	-325.21	531.72	57
H1'1	3257.45	1299.27	4969.33	42
H1'2	3337.94	1604.84	4190.61	42
H2'A	1952.65	2243.21	4214.36	42
H3'1	180	1821.07	4601.02	42
H3'2	1013.13	1472.11	5280.62	42
H1'3	3344.13	854.08	4940	42
H1'4	3406.36	1663.53	4456.04	42
H2'B	2000.35	1054.8	5329.69	42
H3'3	446.19	1897.34	4517	42
H3'4	45.97	1123.95	5020.22	42

H1A1	-1294.02	4662.5	1010.29	44
H1A2	-1138.07	3640.29	876.97	44
H3A1	1287.04	5304.26	2836.09	45
H3A2	350.94	5795.17	2341.55	45
H2A	-232.95	3837.62	2127.03	44
H1B1	-1475.54	4100.94	707.56	44
H1B2	-1133.49	3557.21	1376.03	44
H3B1	582.53	4662.23	2584.32	45
H3B2	1015.8	5781.01	2585.44	45
H2B	-787.6	5439.84	1571.52	44

Table 7 Atomic Occupancy for Compound 6a.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
C1'A	0.623(5)	H1'1	0.623(5)	H1'2	0.623(5)
C2'A	0.623(5)	H2'A	0.623(5)	C3'A	0.623(5)
H3'1	0.623(5)	H3'2	0.623(5)	C1'B	0.377(5)
H1'3	0.377(5)	H1'4	0.377(5)	C2'B	0.377(5)
H2'B	0.377(5)	C3'B	0.377(5)	H3'3	0.377(5)
H3'4	0.377(5)	C1A	0.710(5)	H1A1	0.710(5)
H1A2	0.710(5)	C3A	0.710(5)	H3A1	0.710(5)
H3A2	0.710(5)	C2A	0.710(5)	H2A	0.710(5)
C1B	0.290(5)	H1B1	0.290(5)	H1B2	0.290(5)
C3B	0.290(5)	H3B1	0.290(5)	H3B2	0.290(5)
C2B	0.290(5)	H2B	0.290(5)		

Compound 6b



Crystallization: 6b was dissolved in $CDCl_3$. Yellow, prism-shaped crystals of bis[(allyl)chloro{η^1-P-[N-(diphenylboryl)-2-di-tert-butyl-phosphanylbenzaldimine]}palladium] were grown by diffusing diethyl ether into the solution.

Table 1 Crystal data and structure refinement for Compound 6b.

Identification code	Compound6b
Empirical formula	$C_{61}H_{77}B_2Cl_5N_2P_2Pd_2$
Formula weight	1311.85
Temperature/K	100(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	12.9999(15)
b/Å	13.3865(16)
c/Å	35.007(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	6092.0(12)
Z	4
ρ_{calc}g/cm^3	1.430

μ/mm^{-1}	0.902
F(000)	2696.0
Crystal size/mm^3	0.200 × 0.100 × 0.100
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.258 to 46.474
Index ranges	$-14 \le h \le 14$, $-14 \le k \le 14$, $-38 \le l \le 38$
Reflections collected	51457
Independent reflections	8723 [R_{int} = 0.0519, R_{sigma} = 0.0353]
Data/restraints/parameters	8723/639/675
Goodness-of-fit on F^2	1.015
Final R indexes [I>=2σ (I)]	R_1 = 0.0261, wR_2 = 0.0552
Final R indexes [all data]	R_1 = 0.0296, wR_2 = 0.0565
Largest diff. peak/hole / e $Å^{-3}$	0.46/-0.33
Flack parameter	-0.015(10)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$×10^3) for Compound6b. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Pd1	2893.1(3)	5046.6(3)	9459.2(2)	16.96(10)
Pd2	910.2(3)	6900.2(3)	7125.8(2)	21.76(11)
P2	2308.8(10)	7735.3(10)	6853.9(4)	17.3(3)
Cl1	1442.6(9)	5823.9(9)	9743.4(4)	21.6(3)
P1	4140.4(10)	6103.0(9)	9730.3(4)	15.1(3)
Cl2	33.2(11)	8402.1(12)	7254.8(4)	38.9(4)
C12	2931(4)	8891(3)	9453.9(14)	15.8(10)
C11	3205(3)	7886(3)	9422.3(13)	14.8(11)
C10	2979(3)	9906(4)	7673.8(14)	19.5(11)
C31	-840(4)	7512(4)	8269.9(15)	28.6(13)
C9	2689(4)	8987(4)	7513.6(13)	14.6(11)
C42	6003(4)	8826(4)	8766.5(15)	23.3(12)
C8	3237(4)	10719(4)	7453.4(15)	21.8(12)
C2	2392(3)	8165(4)	7771.2(13)	15.2(11)
C7	4086(4)	8049(4)	10022.8(13)	17.1(10)
N2	2531(3)	8090(3)	8131.8(11)	13.6(9)
C41	5951(4)	8418(4)	8106.7(16)	25.8(12)
C6	3225(4)	9470(4)	9762.1(13)	17.2(11)

C30	213(4)	7598(4)	8215.7(14)	21.1(12)
N1	2736(3)	7703(3)	8743.1(11)	13.0(9)
B2	2153(4)	7187(4)	8396.5(15)	14.5(12)
C29	927(4)	7194(3)	8469.0(13)	15.3(11)
C1	2845(4)	7348(3)	9079.7(13)	14.3(10)
C28	4034(4)	5063(4)	8075.5(14)	26.0(12)
C19	6028(4)	5150(4)	9558.3(15)	26.7(13)
C5	3776(3)	7432(4)	9722.6(14)	14.7(11)
C40	2568(4)	9698(3)	8591.9(13)	15.3(11)
C46	2732(5)	8343(4)	6059.9(15)	41.8(17)
C39	4335(4)	8650(3)	8449.0(14)	14.7(11)
C4	2667(3)	8893(3)	7110.6(14)	16.3(11)
C3	3823(4)	9043(4)	10041.8(14)	18.1(12)
C18	4249(4)	5708(4)	10251.3(14)	19.8(12)
C27	-1220(4)	7041(4)	8594.0(15)	24.0(13)
C38	6499(4)	8606(4)	8433.9(16)	25.1(13)
C50	3231(4)	10631(4)	7061.0(15)	22.1(12)
C26	3642(4)	5960(4)	8205.4(15)	21.9(12)
C25	512(4)	6721(4)	8793.7(14)	19.2(12)
C17	4203(4)	4561(4)	10248.6(15)	27.1(13)
C37	3121(4)	10575(4)	8631.0(15)	23.3(13)
C45	1296(5)	7175(4)	6201.2(15)	40.5(17)
C44	1880(4)	8098(4)	6351.7(14)	29.9(13)
C16	5236(4)	6019(4)	10465.9(15)	24.4(13)
C36	1617(4)	11523(4)	8775.5(17)	33.0(15)
C24	2594(4)	6117(4)	8266.5(13)	15.4(11)
C35	1502(4)	9768(4)	8649.8(14)	18.1(12)
C15	3318(4)	6081(4)	10476.1(15)	27.1(13)
C23	-540(4)	6648(4)	8852.7(14)	22.7(13)
C34	1041(4)	10668(4)	8742.7(15)	27.3(13)
C51	2971(4)	9734(3)	6898.7(14)	21.3(12)
C22	1957(4)	5303(4)	8195.6(15)	25.5(13)
C21	3371(4)	4276(4)	7999.4(16)	31.5(14)
C33	2668(4)	11482(4)	8714.8(17)	34.1(15)
C32	4930(4)	8860(4)	8776.1(14)	21.2(12)
B1	3093(4)	8643(4)	8484.2(16)	16.1(13)
C20	2330(4)	4392(4)	8060.8(17)	34.2(16)
C61	3579(4)	7050(4)	6836.1(16)	26.9(13)
C55	5459(4)	6136(4)	9494.9(15)	19.4(11)
C65	6122(4)	7010(4)	9628.3(15)	24.0(12)
C60	3772(4)	6627(4)	7239.0(16)	34.7(15)

C63	4874(4)	8430(3)	8117.3(15)	19.0(12)
C64	5261(4)	6266(4)	9064.5(14)	22.1(12)
C59	4497(5)	7714(5)	6734(2)	46.9(18)
C62	1106(5)	8957(4)	6370.4(17)	40.3(16)
C58	3526(5)	6167(4)	6558.8(17)	33.8(15)
Cl3	4479.7(13)	1795.3(12)	10156.9(5)	46.7(4)
Cl4	5048.1(16)	1247.8(14)	9392.8(5)	62.8(6)
Cl5	6504.3(14)	2271.7(14)	9875.5(5)	55.5(5)
C66	5493(5)	1396(4)	9859.7(16)	34.7(15)
C54A	1866(14)	3984(17)	9172(7)	21(3)
C56A	3725(13)	4043(11)	9098(3)	21(3)
C53A	2833(7)	3558(7)	9234(3)	21(3)
C54B	2030(20)	3910(20)	9163(9)	25(4)
C56B	3831(17)	3942(16)	9186(5)	25(4)
C53B	2926(11)	4049(9)	8973(4)	25(4)
C1A	1130(12)	5345(13)	7039(5)	44(2)
C2A	443(10)	5503(10)	7337(5)	44(2)
C3A	-449(9)	6033(10)	7273(5)	43(4)
C1B	-146(19)	5935(14)	7424(5)	44(2)
C2B	1399(10)	5362(19)	7137(8)	44(2)
C3B	325(10)	5347(12)	7168(6)	44(2)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for Compound6b. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd1	17.3(2)	13.2(2)	20.4(2)	-3.80(19)	-2.45(17)	-0.42(18)
Pd2	18.9(2)	25.9(2)	20.4(2)	-0.85(19)	-1.00(19)	-8.6(2)
P2	19.1(7)	15.1(7)	17.7(7)	-2.0(5)	-0.2(6)	-4.8(6)
Cl1	16.4(7)	20.6(7)	27.7(8)	-2.7(6)	1.4(6)	0.4(6)
P1	13.5(7)	13.9(7)	17.7(7)	-2.4(5)	-2.2(6)	1.4(6)
Cl2	28.3(8)	54.2(10)	34.1(8)	1.2(7)	-2.6(7)	20.1(7)
C12	13(2)	15(2)	19(3)	2(2)	1(2)	0(2)
C11	12(2)	16(3)	17(2)	-4(2)	1(2)	1(2)
C10	17(3)	20(3)	22(3)	-2(2)	-1(2)	1(3)
C31	15(3)	41(4)	30(3)	3(3)	-2(3)	7(3)
C9	10(3)	16(3)	18(3)	1(2)	-3(2)	1(2)
C42	13(3)	23(3)	34(3)	7(2)	-8(2)	-6(2)
C8	22(3)	12(3)	31(3)	-4(2)	-2(2)	-1(2)
C2	10(2)	15(3)	20(3)	-5(2)	-2(2)	3(2)

C7	15(2)	19(3)	17(2)	-3(2)	0(2)	0(3)
N2	9(2)	13(2)	19(2)	-0.4(18)	-2.6(16)	2.4(18)
C41	22(3)	17(3)	38(3)	-4(2)	9(3)	4(3)
C6	17(3)	14(3)	21(3)	-1(2)	5(2)	1(2)
C30	17(3)	26(3)	20(3)	5(2)	4(2)	2(2)
N1	10(2)	12(2)	17(2)	-4.1(17)	1.7(17)	3.1(17)
B2	16(3)	14(3)	13(3)	0(2)	-5(2)	-1(2)
C29	17(2)	11(3)	18(3)	-6(2)	-3(2)	1(2)
C1	9(2)	12(2)	22(3)	0(2)	-2(2)	1(2)
C28	19(3)	25(3)	33(3)	-1(3)	3(2)	6(3)
C19	19(3)	28(3)	33(3)	-7(3)	-4(2)	8(3)
C5	7(2)	17(3)	20(3)	0(2)	4(2)	-2(2)
C40	19(3)	18(3)	9(2)	0(2)	-3(2)	3(2)
C46	70(5)	33(4)	22(3)	-3(3)	4(3)	-28(3)
C39	15(3)	9(3)	20(3)	2(2)	-1(2)	-1(2)
C4	12(3)	14(3)	22(3)	-2(2)	-3(2)	-1(2)
C3	15(3)	18(3)	21(3)	-6(2)	1(2)	-5(2)
C18	22(3)	19(3)	18(3)	-1(2)	-4(2)	-2(2)
C27	11(3)	30(3)	31(3)	-7(3)	2(2)	1(2)
C38	11(3)	13(3)	51(4)	7(3)	0(3)	5(2)
C50	27(3)	15(3)	24(3)	6(2)	-3(2)	-2(2)
C26	18(3)	17(3)	31(3)	-2(2)	-3(2)	2(2)
C25	15(3)	22(3)	20(3)	1(2)	-3(2)	-2(2)
C17	32(3)	26(3)	23(3)	3(2)	-6(3)	-3(3)
C37	20(3)	19(3)	31(3)	-9(2)	1(3)	-1(2)
C45	67(5)	37(4)	18(3)	4(3)	-15(3)	-22(3)
C44	47(4)	24(3)	19(3)	2(3)	-8(3)	-17(3)
C16	27(3)	22(3)	25(3)	0(2)	-5(2)	5(2)
C36	30(3)	17(3)	52(4)	-15(3)	-4(3)	5(3)
C24	17(3)	15(3)	14(3)	4(2)	-5(2)	1(2)
C35	19(3)	16(3)	20(3)	2(2)	-6(2)	0(2)
C15	19(3)	38(3)	23(3)	0(3)	1(2)	-4(3)
C23	21(3)	25(3)	22(3)	0(2)	3(2)	-2(2)
C34	20(3)	24(3)	38(3)	-2(3)	-1(3)	6(2)
C51	28(3)	18(3)	19(3)	0(2)	-1(2)	-5(2)
C22	14(3)	26(3)	37(3)	-9(2)	-7(2)	1(2)
C21	29(3)	25(3)	41(4)	-12(3)	-8(3)	10(3)
C33	29(3)	22(3)	51(4)	-11(3)	-1(3)	-3(3)
C32	21(3)	20(3)	23(3)	5(2)	2(2)	-5(2)
B1	16(3)	14(3)	19(3)	-2(2)	-1(2)	-2(2)
C20	15(3)	22(3)	65(4)	-19(3)	-13(3)	-2(2)

C61	24(3)	17(3)	40(3)	-12(3)	7(3)	-3(3)
C55	17(3)	14(3)	27(3)	-4(2)	-2(2)	3(2)
C65	14(3)	26(3)	32(3)	-4(3)	0(2)	-3(2)
C60	26(3)	30(3)	48(4)	-15(3)	-9(3)	12(3)
C63	19(3)	13(3)	25(3)	-4(2)	-4(2)	0(2)
C64	19(3)	21(3)	26(3)	-4(2)	9(2)	1(2)
C59	27(3)	40(4)	73(5)	-20(3)	16(3)	-9(3)
C62	51(4)	38(4)	32(3)	13(3)	-17(3)	-9(3)
C58	32(4)	27(3)	43(4)	-15(3)	12(3)	-3(3)
Cl3	57.3(11)	33.6(9)	49.2(10)	-8.0(8)	19.3(8)	3.3(8)
Cl4	88.4(14)	70.9(13)	29.0(9)	-3.5(9)	9.5(9)	-34.3(11)
Cl5	53.2(11)	61.3(12)	51.9(11)	20.1(9)	-5.2(9)	-18.1(9)
C66	46(4)	27(3)	30(3)	3(3)	8(3)	4(3)
C54A	27(5)	17(4)	21(4)	-10(3)	-1(3)	-3(3)
C56A	27(5)	17(4)	21(4)	-10(3)	-1(3)	-3(3)
C53A	27(5)	17(4)	21(4)	-10(3)	-1(3)	-3(3)
C54B	32(6)	16(5)	25(5)	-10(4)	-3(4)	2(4)
C56B	32(6)	16(5)	25(5)	-10(4)	-3(4)	2(4)
C53B	32(6)	16(5)	25(5)	-10(4)	-3(4)	2(4)
C1A	59(5)	22(3)	51(7)	-1(4)	2(4)	-19(4)
C2A	59(5)	22(3)	51(7)	-1(4)	2(4)	-19(4)
C3A	29(6)	54(8)	47(9)	-7(7)	-4(6)	-28(5)
C1B	59(5)	22(3)	51(7)	-1(4)	2(4)	-19(4)
C2B	59(5)	22(3)	51(7)	-1(4)	2(4)	-19(4)
C3B	59(5)	22(3)	51(7)	-1(4)	2(4)	-19(4)

Table 4 Bond Lengths for Compound6b.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1	C56A	2.138(16)	B2	C24	1.609(7)
Pd1	C56B	2.14(2)	B2	C29	1.614(8)
Pd1	C53A	2.145(8)	C29	C25	1.409(7)
Pd1	C54B	2.16(3)	C28	C26	1.381(7)
Pd1	C53B	2.163(11)	C28	C21	1.387(7)
Pd1	C54A	2.19(2)	C19	C55	1.530(7)
Pd1	P1	2.3517(14)	C40	C37	1.383(7)
Pd1	Cl1	2.3724(13)	C40	C35	1.404(7)
Pd2	C2A	2.101(13)	C40	B1	1.613(7)
Pd2	C1A	2.123(18)	C46	C44	1.542(8)
Pd2	C1B	2.15(2)	C39	C63	1.388(7)

Pd2	C2B	2.16(3)	C39	C32	1.410(7)
Pd2	C3A	2.176(12)	C39	B1	1.620(7)
Pd2	C3B	2.218(16)	C4	C51	1.405(7)
Pd2	P2	2.3369(14)	C18	C15	1.528(7)
Pd2	Cl2	2.3549(15)	C18	C17	1.537(7)
P2	C4	1.851(5)	C18	C16	1.543(7)
P2	C61	1.889(5)	C27	C23	1.370(7)
P2	C44	1.907(5)	C50	C51	1.371(7)
P1	C5	1.841(5)	C26	C24	1.395(7)
P1	C55	1.903(5)	C25	C23	1.386(7)
P1	C18	1.904(5)	C37	C33	1.382(7)
C12	C6	1.382(7)	C45	C44	1.542(7)
C12	C11	1.396(6)	C44	C62	1.529(8)
C11	C5	1.423(6)	C36	C34	1.374(7)
C11	C1	1.476(6)	C36	C33	1.384(8)
C10	C8	1.376(7)	C24	C22	1.391(7)
C10	C9	1.403(7)	C35	C34	1.384(7)
C31	C30	1.388(7)	C22	C20	1.394(7)
C31	C27	1.389(7)	C21	C20	1.379(7)
C9	C4	1.417(7)	C61	C59	1.531(7)
C9	C2	1.474(7)	C61	C58	1.532(7)
C42	C38	1.363(7)	C61	C60	1.540(8)
C42	C32	1.396(7)	C55	C65	1.526(7)
C8	C50	1.379(7)	C55	C64	1.539(7)
C2	N2	1.279(6)	Cl3	C66	1.762(6)
C7	C3	1.375(7)	Cl4	C66	1.745(6)
C7	C5	1.396(6)	Cl5	C66	1.762(6)
N2	B2	1.600(7)	C54A	C53A	1.40(2)
N2	B1	1.613(7)	C56A	C53A	1.411(19)
C41	C38	1.372(7)	C54B	C53B	1.36(3)
C41	C63	1.401(7)	C56B	C53B	1.40(2)
C6	C3	1.375(7)	C1A	C2A	1.39(2)
C30	C29	1.392(7)	C2A	C3A	1.378(18)
N1	C1	1.278(6)	C1B	C3B	1.341(3)
N1	B2	1.589(6)	C2B	C3B	1.400(3)
N1	B1	1.618(7)			

Table 5 Bond Angles for Compound6b.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°

C56A	Pd1	C53A	38.5(5)	C11	C5	P1	123.9(4)
C56B	Pd1	C54B	66.1(8)	C37	C40	C35	116.2(5)
C56B	Pd1	C53B	37.9(6)	C37	C40	B1	123.1(4)
C54B	Pd1	C53B	36.6(8)	C35	C40	B1	120.7(4)
C56A	Pd1	C54A	68.3(6)	C63	C39	C32	116.4(4)
C53A	Pd1	C54A	37.5(5)	C63	C39	B1	124.4(4)
C56A	Pd1	P1	105.5(5)	C32	C39	B1	119.1(4)
C56B	Pd1	P1	101.7(6)	C51	C4	C9	116.7(4)
C53A	Pd1	P1	137.1(3)	C51	C4	P2	119.0(4)
C54B	Pd1	P1	167.8(6)	C9	C4	P2	124.3(4)
C53B	Pd1	P1	132.5(4)	C6	C3	C7	120.6(5)
C54A	Pd1	P1	173.8(4)	C15	C18	C17	107.4(5)
C56A	Pd1	Cl1	157.7(4)	C15	C18	C16	108.7(4)
C56B	Pd1	Cl1	160.5(6)	C17	C18	C16	107.7(4)
C53A	Pd1	Cl1	122.2(3)	C15	C18	P1	110.1(3)
C54B	Pd1	Cl1	95.5(6)	C17	C18	P1	105.6(3)
C53B	Pd1	Cl1	128.0(4)	C16	C18	P1	117.0(4)
C54A	Pd1	Cl1	89.6(4)	C23	C27	C31	119.0(5)
P1	Pd1	Cl1	96.60(5)	C42	C38	C41	120.5(5)
C2A	Pd2	C1A	38.4(5)	C51	C50	C8	119.3(5)
C1B	Pd2	C2B	66.8(8)	C28	C26	C24	122.8(5)
C2A	Pd2	C3A	37.5(5)	C23	C25	C29	122.0(5)
C1A	Pd2	C3A	67.7(6)	C33	C37	C40	123.1(5)
C1B	Pd2	C3B	35.7(2)	C62	C44	C45	107.1(5)
C2B	Pd2	C3B	37.3(2)	C62	C44	C46	109.9(5)
C2A	Pd2	P2	142.6(4)	C45	C44	C46	107.3(4)
C1A	Pd2	P2	107.8(4)	C62	C44	P2	110.1(4)
C1B	Pd2	P2	168.5(7)	C45	C44	P2	104.8(4)
C2B	Pd2	P2	103.6(5)	C46	C44	P2	117.0(4)
C3A	Pd2	P2	169.6(4)	C34	C36	C33	119.6(5)
C3B	Pd2	P2	137.9(4)	C22	C24	C26	115.8(5)
C2A	Pd2	Cl2	123.5(4)	C22	C24	B2	122.4(4)
C1A	Pd2	Cl2	158.4(4)	C26	C24	B2	121.7(5)
C1B	Pd2	Cl2	96.3(5)	C34	C35	C40	121.4(5)
C2B	Pd2	Cl2	162.7(6)	C27	C23	C25	120.7(5)
C3A	Pd2	Cl2	91.0(3)	C36	C34	C35	120.6(5)
C3B	Pd2	Cl2	128.4(3)	C50	C51	C4	123.5(5)
P2	Pd2	Cl2	92.66(5)	C24	C22	C20	122.6(5)
C4	P2	C61	101.7(2)	C20	C21	C28	119.6(5)
C4	P2	C44	107.9(2)	C37	C33	C36	119.2(5)
C61	P2	C44	110.4(3)	C42	C32	C39	121.5(5)

C4	P2	Pd2	113.49(16)	C40	B1	N2	112.9(4)
C61	P2	Pd2	117.45(18)	C40	B1	N1	115.4(4)
C44	P2	Pd2	105.64(17)	N2	B1	N1	86.7(3)
C5	P1	C55	101.7(2)	C40	B1	C39	115.7(4)
C5	P1	C18	107.5(2)	N2	B1	C39	113.3(4)
C55	P1	C18	110.8(2)	N1	B1	C39	109.4(4)
C5	P1	Pd1	113.43(16)	C21	C20	C22	119.5(5)
C55	P1	Pd1	117.42(16)	C59	C61	C58	109.6(4)
C18	P1	Pd1	105.72(16)	C59	C61	C60	107.5(5)
C6	C12	C11	122.1(5)	C58	C61	C60	107.7(5)
C12	C11	C5	119.1(4)	C59	C61	P2	114.0(4)
C12	C11	C1	117.0(4)	C58	C61	P2	110.9(4)
C5	C11	C1	123.8(4)	C60	C61	P2	106.9(4)
C8	C10	C9	122.3(5)	C65	C55	C19	110.1(4)
C30	C31	C27	120.0(5)	C65	C55	C64	107.9(4)
C10	C9	C4	118.8(4)	C19	C55	C64	108.7(4)
C10	C9	C2	118.7(4)	C65	C55	P1	113.2(3)
C4	C9	C2	122.5(4)	C19	C55	P1	110.6(4)
C38	C42	C32	120.0(5)	C64	C55	P1	106.0(3)
C10	C8	C50	119.3(5)	C39	C63	C41	121.9(5)
N2	C2	C9	128.7(5)	Cl4	C66	Cl3	109.9(3)
C3	C7	C5	122.5(5)	Cl4	C66	Cl5	110.6(3)
C2	N2	B2	126.0(4)	Cl3	C66	Cl5	109.7(3)
C2	N2	B1	141.5(4)	C53A	C54A	Pd1	69.3(9)
B2	N2	B1	92.4(3)	C53A	C56A	Pd1	71.1(7)
C38	C41	C63	119.6(5)	C54A	C53A	C56A	120.0(15)
C3	C6	C12	118.6(5)	C54A	C53A	Pd1	73.1(9)
C31	C30	C29	122.6(5)	C56A	C53A	Pd1	70.5(7)
C1	N1	B2	126.5(4)	C53B	C54B	Pd1	71.8(14)
C1	N1	B1	140.7(4)	C53B	C56B	Pd1	71.8(10)
B2	N1	B1	92.7(3)	C54B	C53B	C56B	116.6(17)
N1	B2	N2	88.1(3)	C54B	C53B	Pd1	71.5(13)
N1	B2	C24	115.6(4)	C56B	C53B	Pd1	70.2(10)
N2	B2	C24	113.5(4)	C2A	C1A	Pd2	69.9(10)
N1	B2	C29	110.4(4)	C3A	C2A	C1A	120(2)
N2	B2	C29	113.0(4)	C3A	C2A	Pd2	74.2(8)
C24	B2	C29	113.7(4)	C1A	C2A	Pd2	71.7(10)
C30	C29	C25	115.7(5)	C2A	C3A	Pd2	68.3(7)
C30	C29	B2	124.0(4)	C3B	C1B	Pd2	74.8(11)
C25	C29	B2	120.2(4)	C3B	C2B	Pd2	73.8(14)
N1	C1	C11	127.0(4)	C1B	C3B	C2B	120(2)

C26	C28	C21	119.6(5)	C1B	C3B	Pd2	69.6(12)
C7	C5	C11	117.0(4)	C2B	C3B	Pd2	68.9(14)
C7	C5	P1	119.1(4)				

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Compound6b.

Atom	*x*	*y*	*z*	U(eq)
H12A	2528.92	9186.41	9257.44	19
H10A	2998.02	9968.4	7944.03	23
H31A	-1302.13	7775.11	8085.23	34
H42A	6388.14	8956.69	8991.8	28
H8A	3416.74	11335.22	7570.33	26
H2A	2051.1	7617.55	7653.67	18
H7A	4493.57	7771.54	10221.44	21
H41A	6300.52	8280.52	7874.21	31
H6A	3019.27	10149.2	9780.14	21
H30A	457.6	7945.5	7997.15	25
H1A	2675.27	6662.94	9112.77	17
H28A	4753.53	4986.18	8038.55	31
H19A	5596.03	4593.93	9471.82	40
H19B	6672.36	5153.36	9412.97	40
H19C	6180.32	5069.38	9830.78	40
H46A	3224.35	7789.01	6049.41	63
H46B	2424.38	8440.09	5807.03	63
H46C	3088.72	8954.5	6137.83	63
H3A	4056.63	9437.08	10250.07	22
H27A	-1939.84	6992.05	8635.85	29
H38A	7229.11	8583.35	8428.52	30
H50A	3406.42	11185.54	6904.74	27
H26A	4105.97	6492.69	8255.22	26
H25A	966.16	6443.93	8977.81	23
H17A	4791.82	4297.04	10106.12	41
H17B	4224.17	4312.15	10511.73	41
H17C	3562.92	4343.51	10126.32	41
H37A	3845.85	10551.72	8598.62	28
H45A	1768.4	6606.51	6185.19	61
H45B	730.76	7013.13	6375.79	61
H45C	1017.52	7320.3	5947.02	61
H16A	5839.54	5783.69	10324.46	37

H16B	5260.24	6748.17	10487.81	37
H16C	5233.76	5721.35	10721.71	37
H36A	1296.9	12138.61	8839.33	40
H35A	1088.7	9186.73	8624.63	22
H15A	3323.86	6813.12	10483.38	41
H15B	2685.21	5850.66	10351.92	41
H15C	3346.46	5819.3	10737.33	41
H23A	-792.37	6322.33	9074.82	27
H34A	319.22	10693.47	8784.26	33
H51A	2997.32	9677.62	6628.35	26
H22A	1240.05	5370.17	8240.73	31
H21A	3632.96	3660.77	7905.45	38
H33A	3073.79	12071.49	8730.5	41
H32A	4593.38	9028.66	9008.19	25
H20A	1870.78	3855.54	8011.69	41
H65A	5751.25	7637.46	9586.47	36
H65B	6274.81	6934.31	9900.93	36
H65C	6766.85	7018.28	9483.12	36
H60A	3195.88	6197.18	7313.14	52
H60B	4409.8	6236.54	7238.68	52
H60C	3834.51	7179.16	7421.48	52
H63A	4501.64	8282.33	7890.76	23
H64A	4835.08	5712.56	8971.85	33
H64B	4902.36	6899.6	9019.98	33
H64C	5918.1	6268.94	8927.52	33
H59A	4529.45	8279.31	6911.37	70
H59B	5132.96	7324.46	6751.88	70
H59C	4415.8	7964.66	6472.37	70
H62A	1450.54	9559.38	6465.2	61
H62B	829.86	9084.97	6114.56	61
H62C	543.11	8777.8	6543.34	61
H58A	2937.9	5742.11	6624.75	51
H58B	3444.52	6416.18	6297.41	51
H58C	4161.68	5775.99	6576.93	51
H66A	5752.76	738.43	9954.71	42
H54A	1288.82	3714.1	9325.66	26
H54B	1678.7	4135.65	8904.51	26
H56A	3740.22	4207.87	8822.69	26
H56B	4390.71	3794.77	9197.42	26
H53A	2901.63	2974.77	9410.42	26
H54C	1947.98	3261.19	9297.38	29

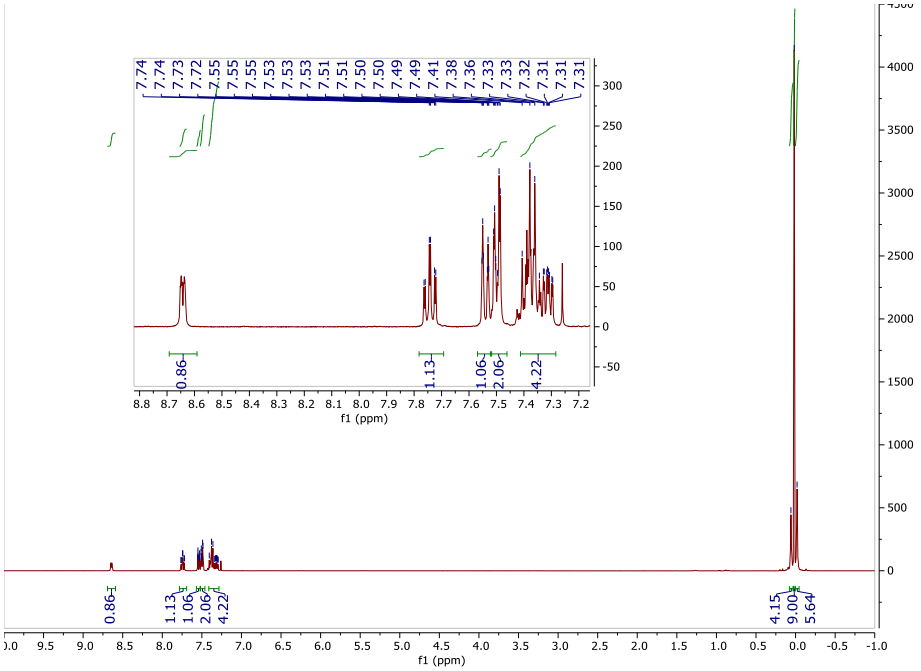
H54D	1394.4	4130.37	9031.42	29
H56C	4471.58	4184.5	9064.27	29
H56D	3918.17	3302.08	9323.83	29
H53B	2937.89	4310.71	8705.63	29
H1A1	841.82	5059.63	6801.02	53
H1A2	1812.15	5071.5	7108.02	53
H2A1	633.16	5299.72	7602.87	53
H3A1	-839.43	6249.88	7501.61	52
H3A2	-888.58	5807.51	7059.21	52
H1B1	16.34	5801.06	7695.44	53
H1B2	-885.79	6063.22	7378.93	53
H2B1	1689.28	5095.27	6896.5	53
H2B2	1785.4	5147.95	7366.74	53
H3B	-86.76	5070.42	6950.97	53

Table 7 Atomic Occupancy for Compound6b.

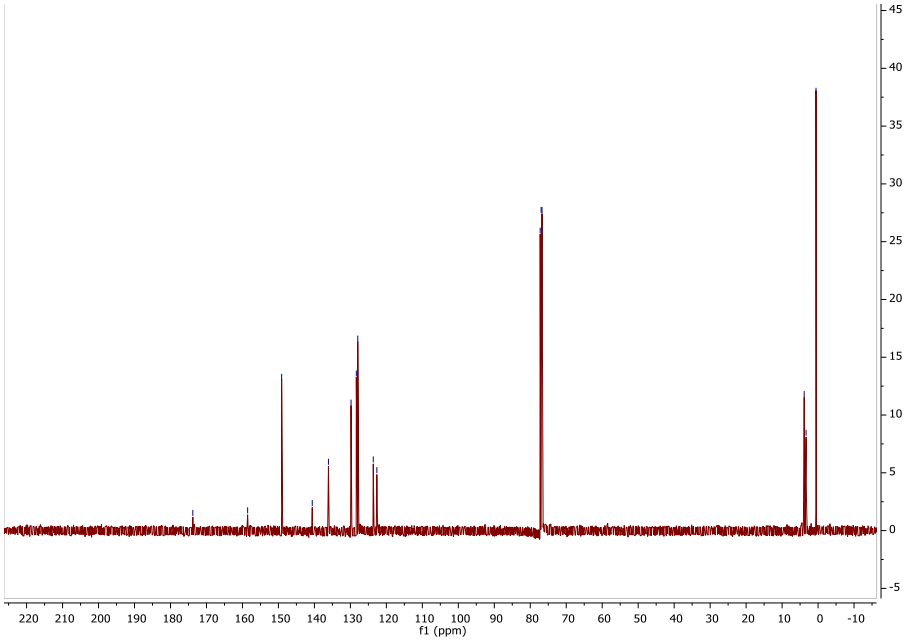
Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
C54A	0.572(14)	H54A	0.572(14)	H54B	0.572(14)
C56A	0.572(14)	H56A	0.572(14)	H56B	0.572(14)
C53A	0.572(14)	H53A	0.572(14)	C54B	0.428(14)
H54C	0.428(14)	H54D	0.428(14)	C56B	0.428(14)
H56C	0.428(14)	H56D	0.428(14)	C53B	0.428(14)
H53B	0.428(14)	C1A	0.583(15)	H1A1	0.583(15)
H1A2	0.583(15)	C2A	0.583(15)	H2A1	0.583(15)
C3A	0.583(15)	H3A1	0.583(15)	H3A2	0.583(15)
C1B	0.417(15)	H1B1	0.417(15)	H1B2	0.417(15)
C2B	0.417(15)	H2B1	0.417(15)	H2B2	0.417(15)
C3B	0.417(15)	H3B	0.417(15)		

III. NMR Spectra

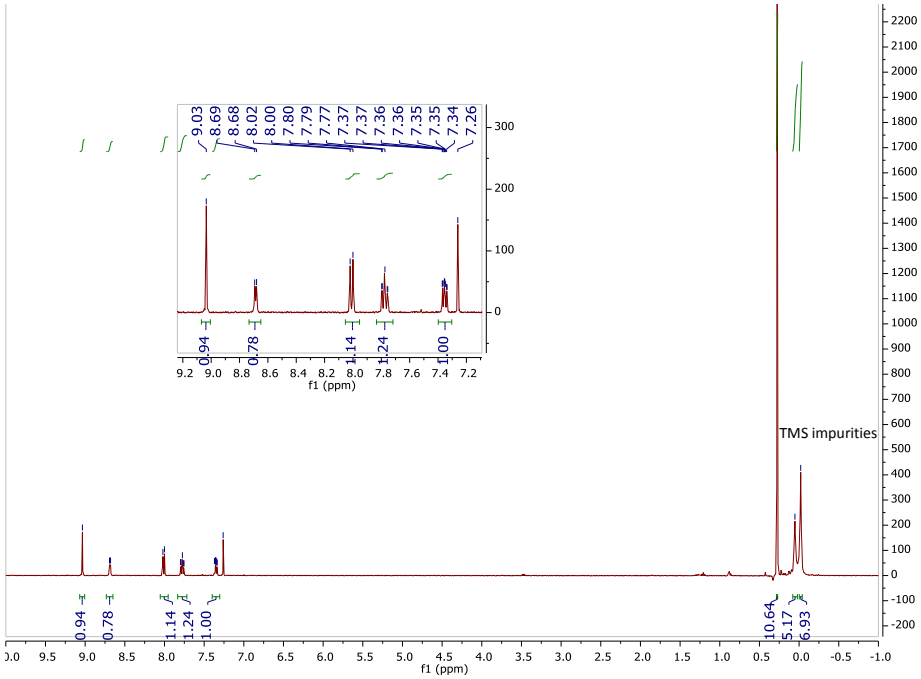
^{1}H NMR ($CDCl_3$) **2a**



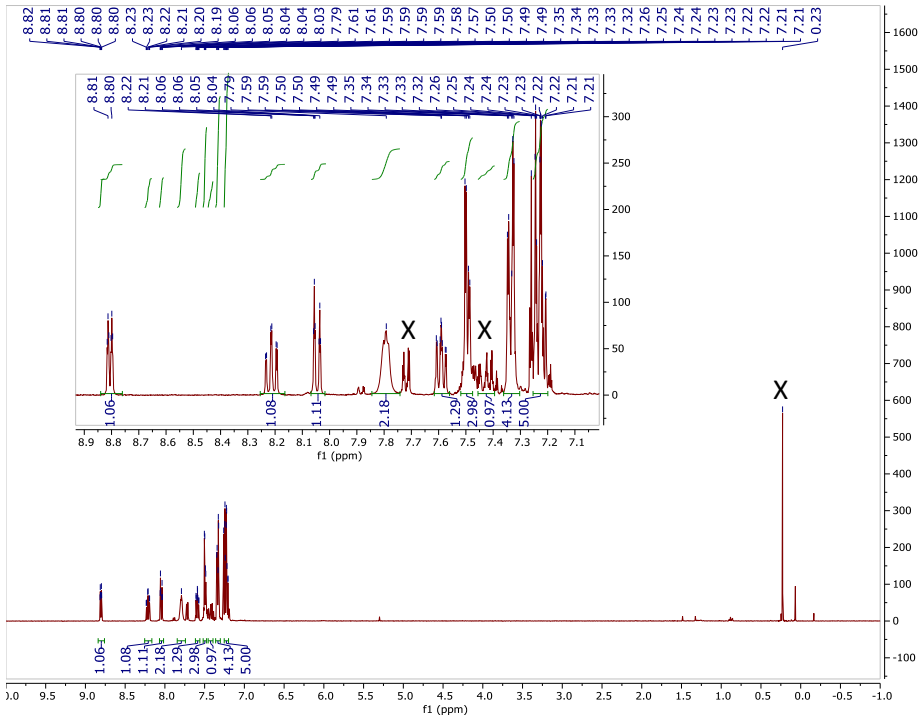
^{13}C NMR ($CDCl_3$) **2a**



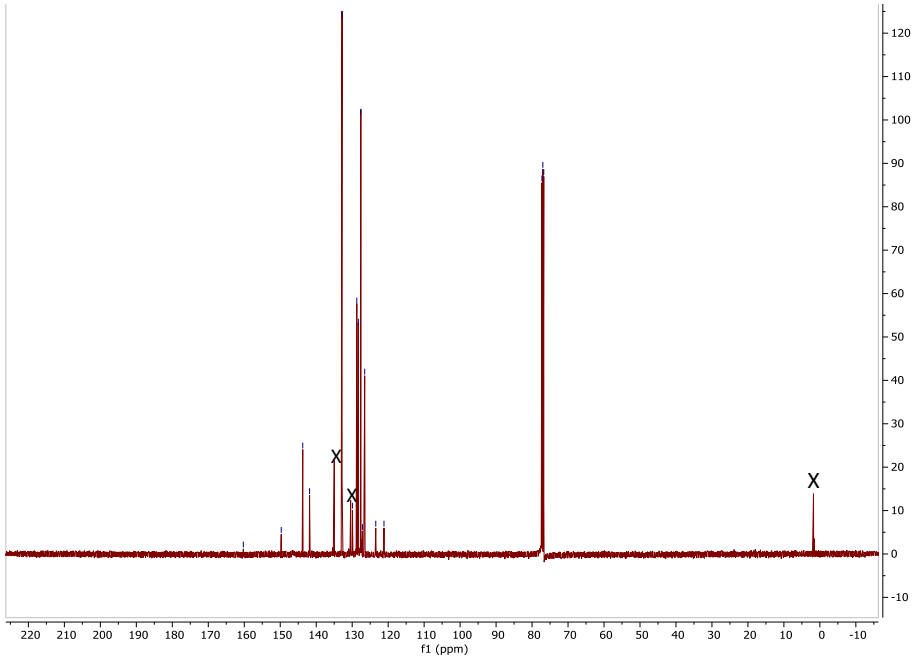
^{1}H NMR ($CDCl_3$) **2b**



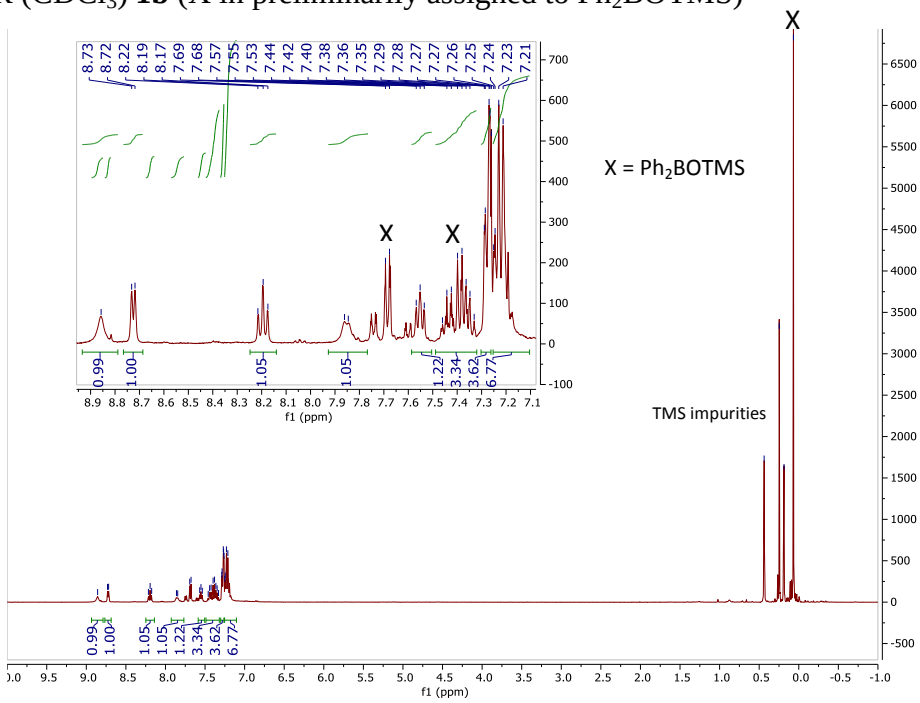
^{1}H NMR ($CDCl_3$) **1a** (X is preliminarily assigned to Ph_2BOTMS)[5]



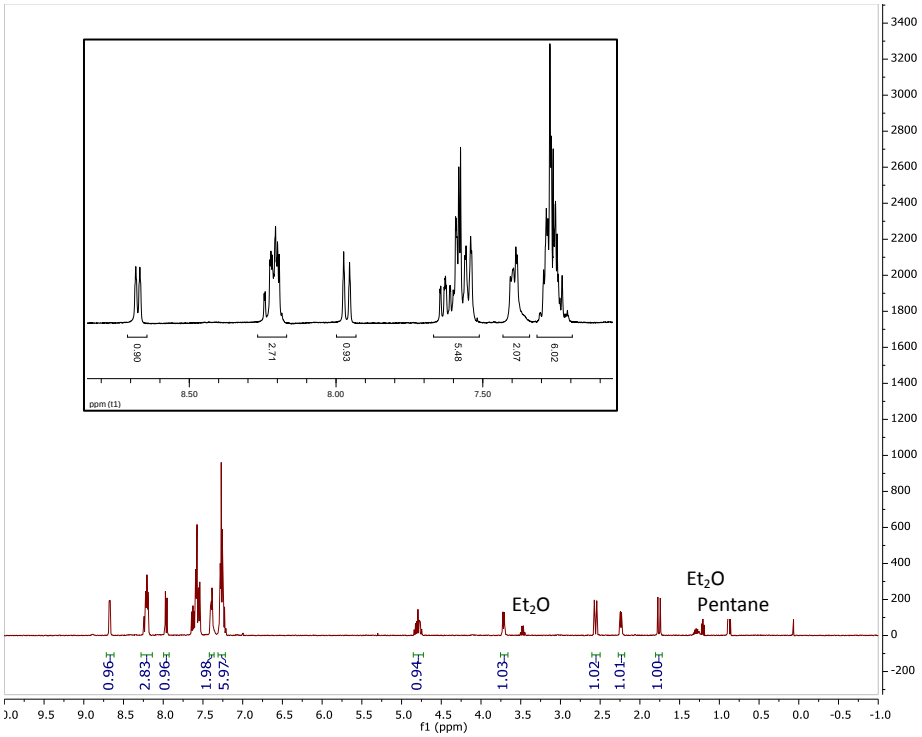
^{13}C NMR ($CDCl_3$) **1a** (X in preliminarily assigned to Ph_2BOTMS)[5]



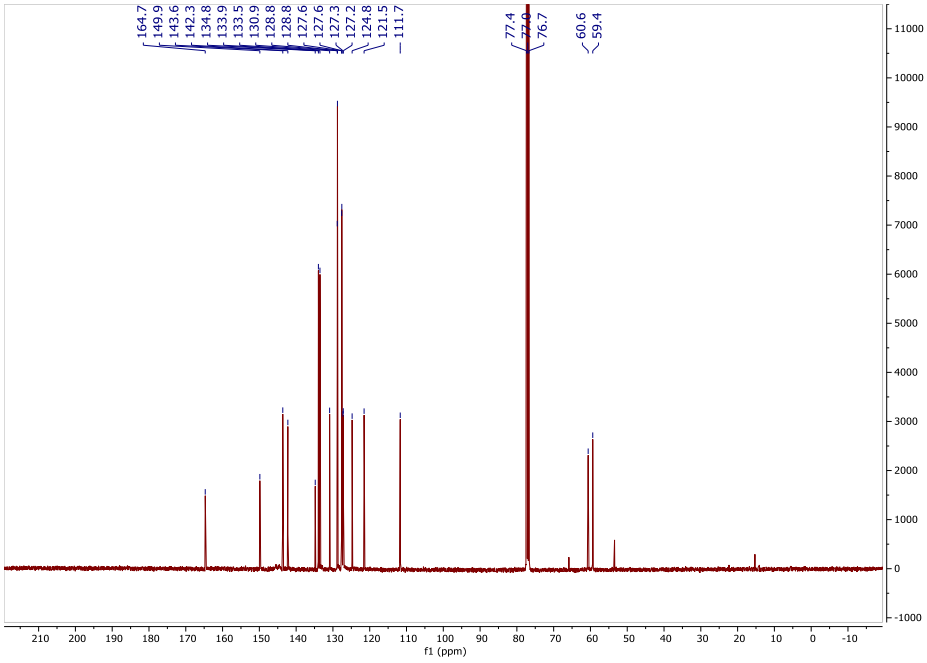
Crude ^1H NMR ($CDCl_3$) **1b** (X in preliminarily assigned to Ph_2BOTMS)[5]



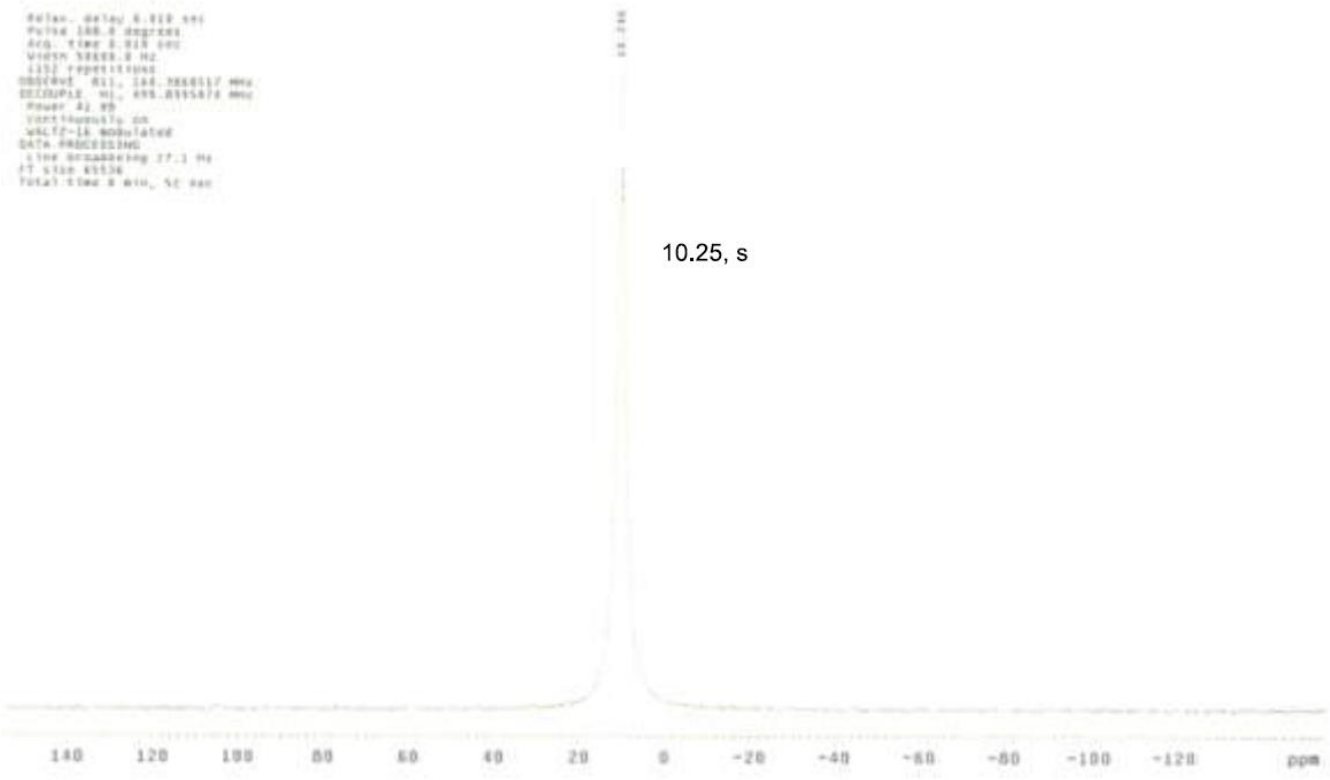
^{1}H NMR ($CDCl_3$) **3a**



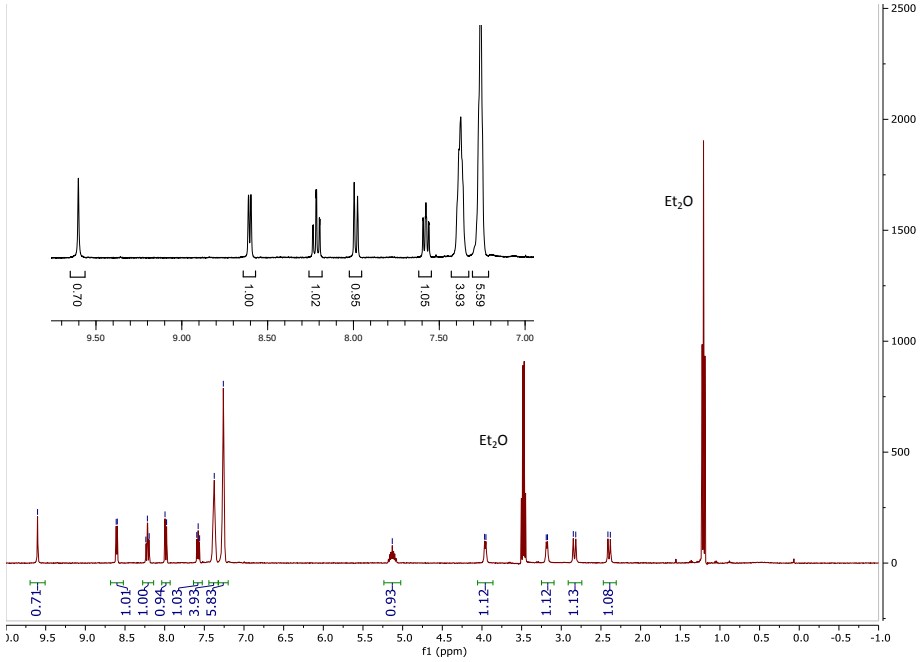
^{13}C NMR ($CDCl_3$) **3a**



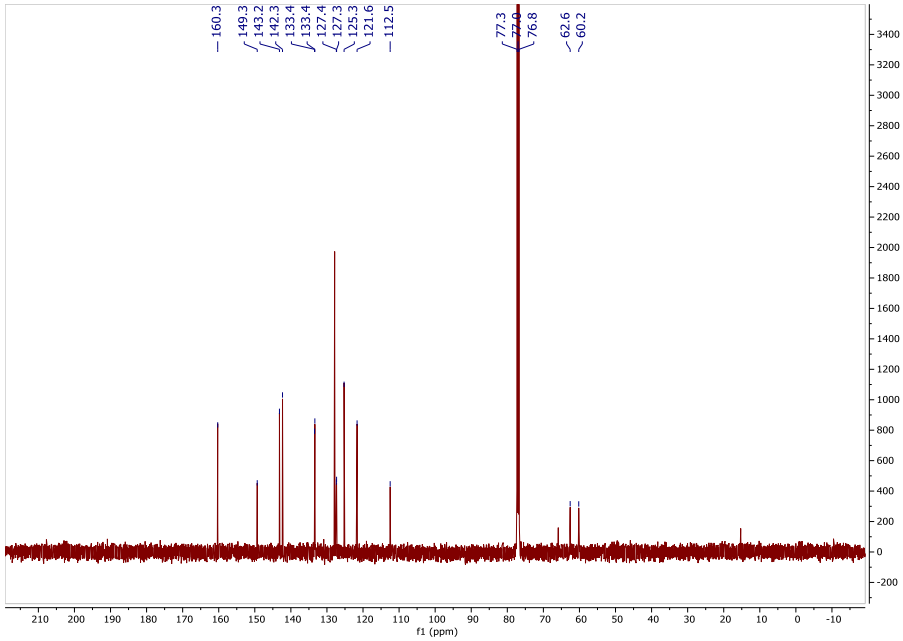
^{11}B NMR ($CDCl_3$) **3a**



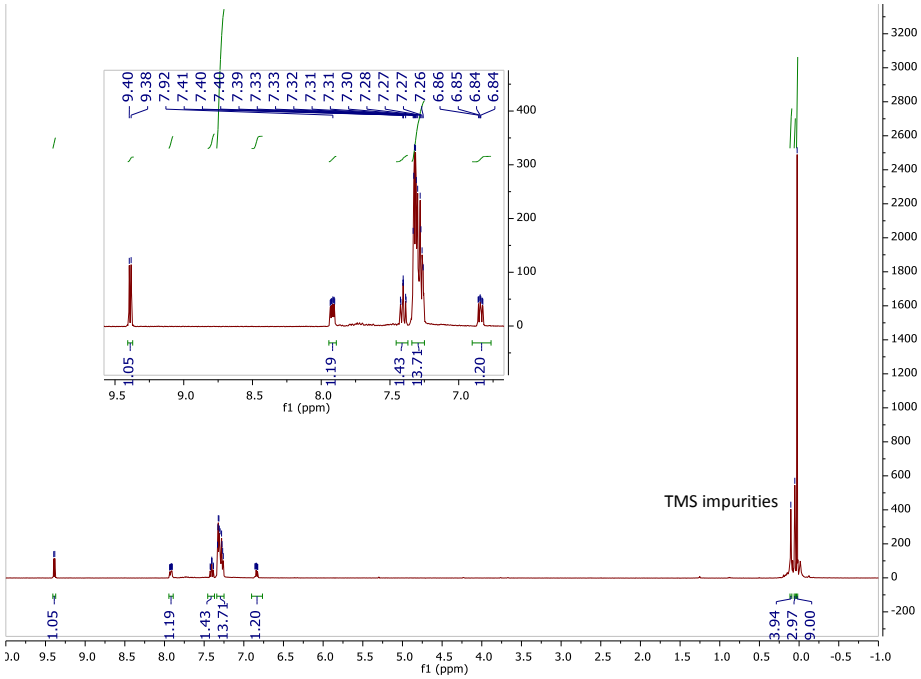
^{1}H NMR ($CDCl_3$) **3b**



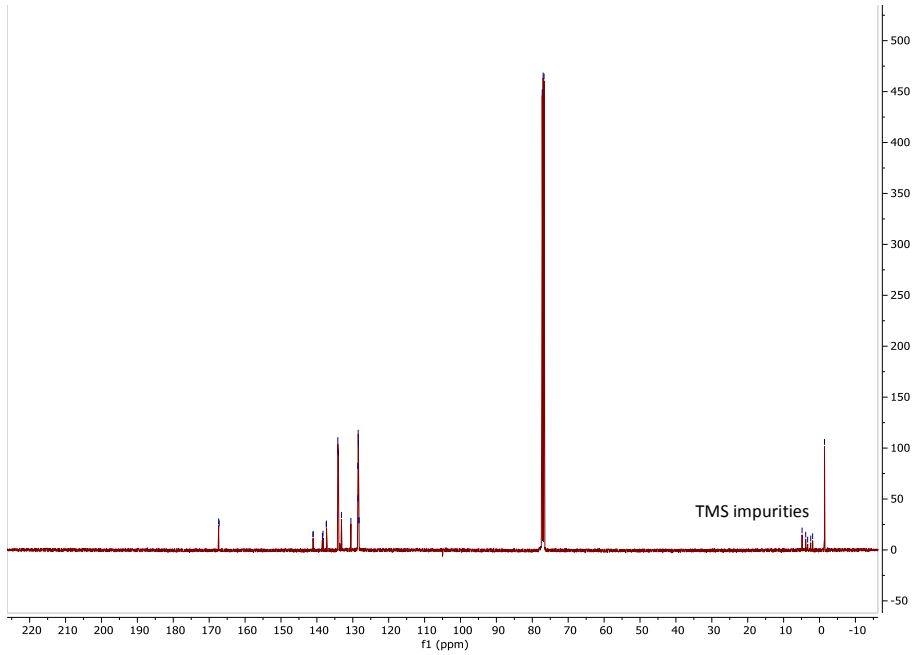
^{13}C NMR ($CDCl_3$) **3b**



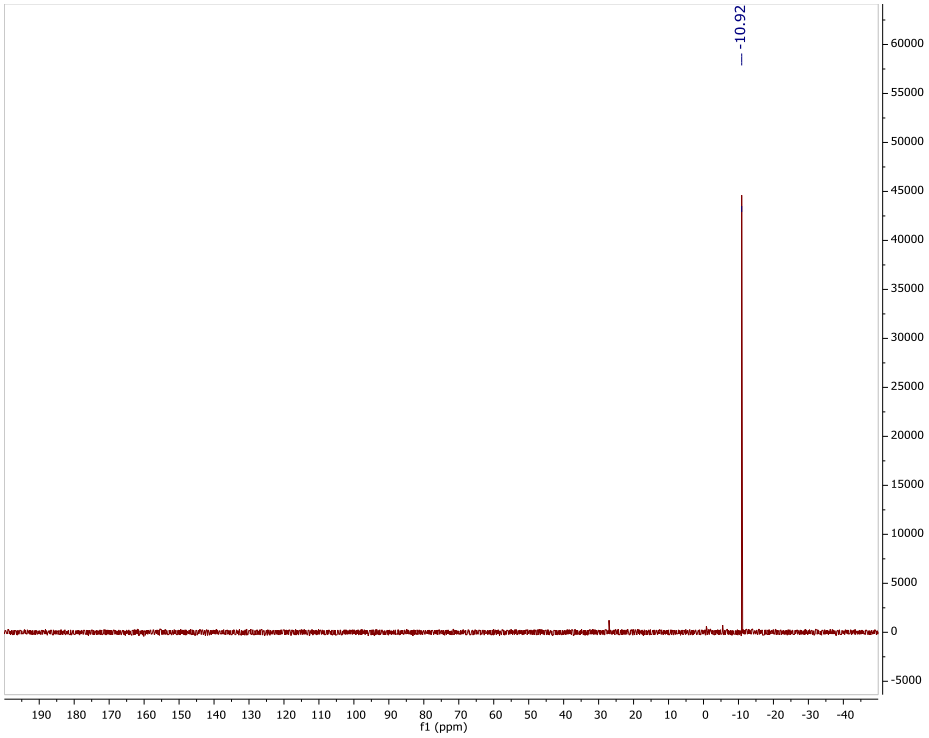
^{1}H NMR ($CDCl_3$) **5a**



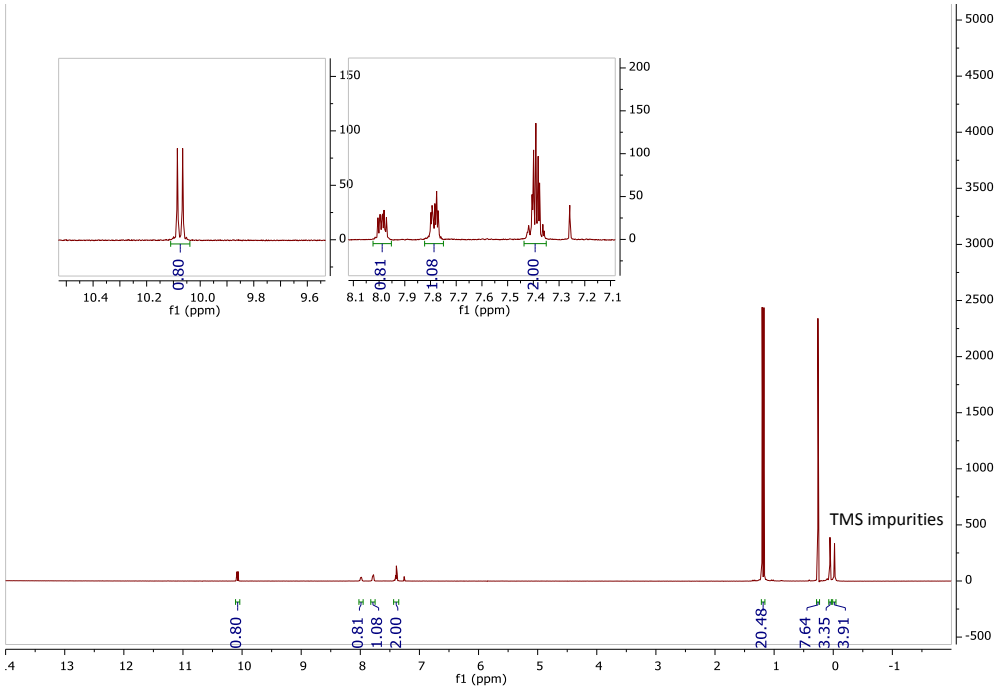
^{13}C NMR ($CDCl_3$) **5a**



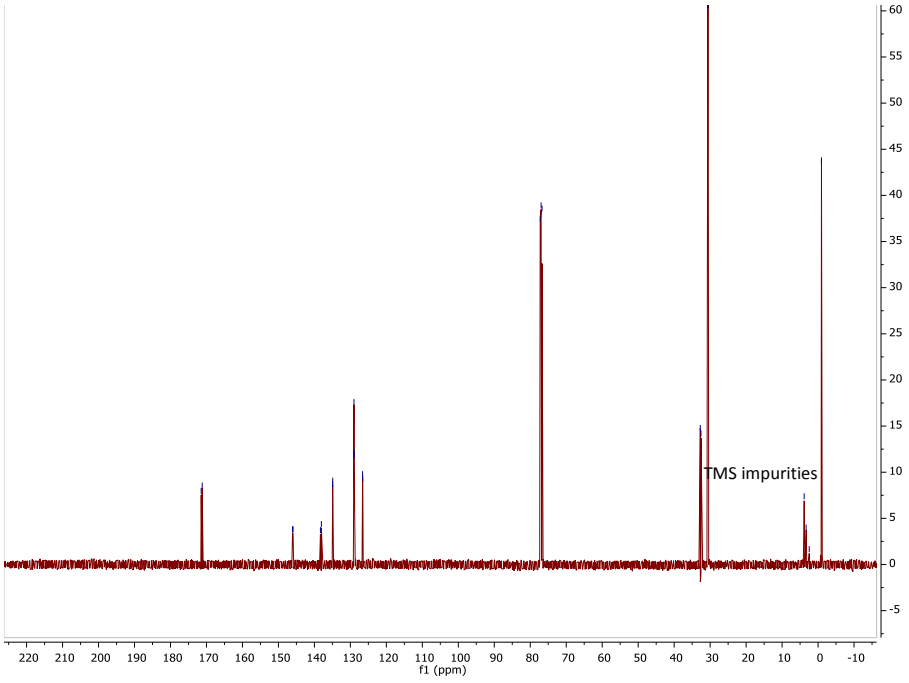
^{31}P NMR ($CDCl_3$) **5a**



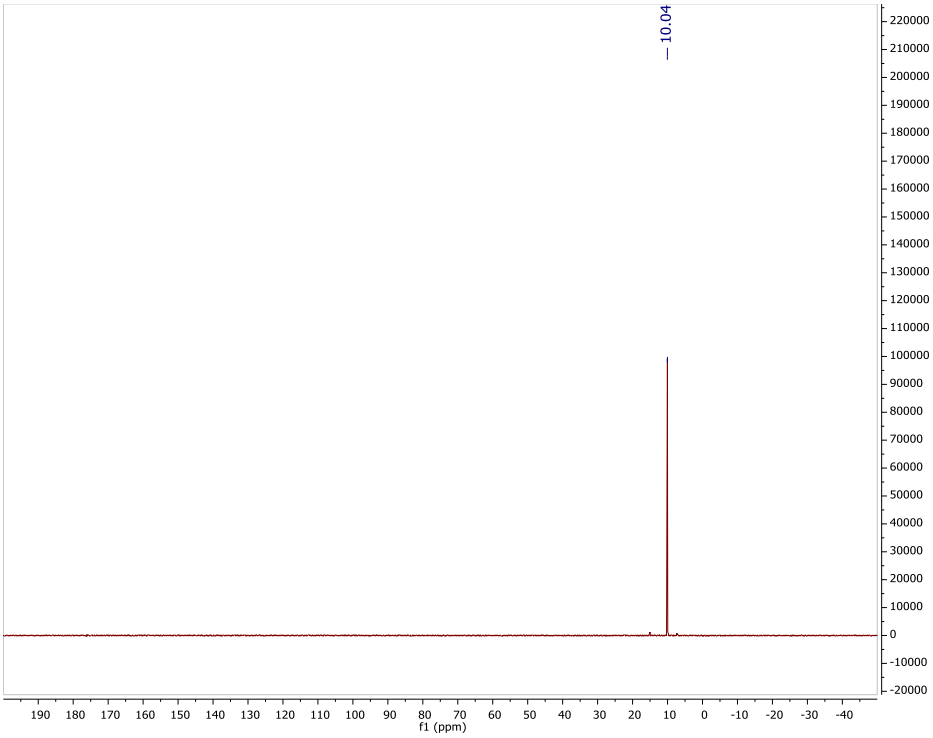
^{1}H NMR ($CDCl_3$) **5b**



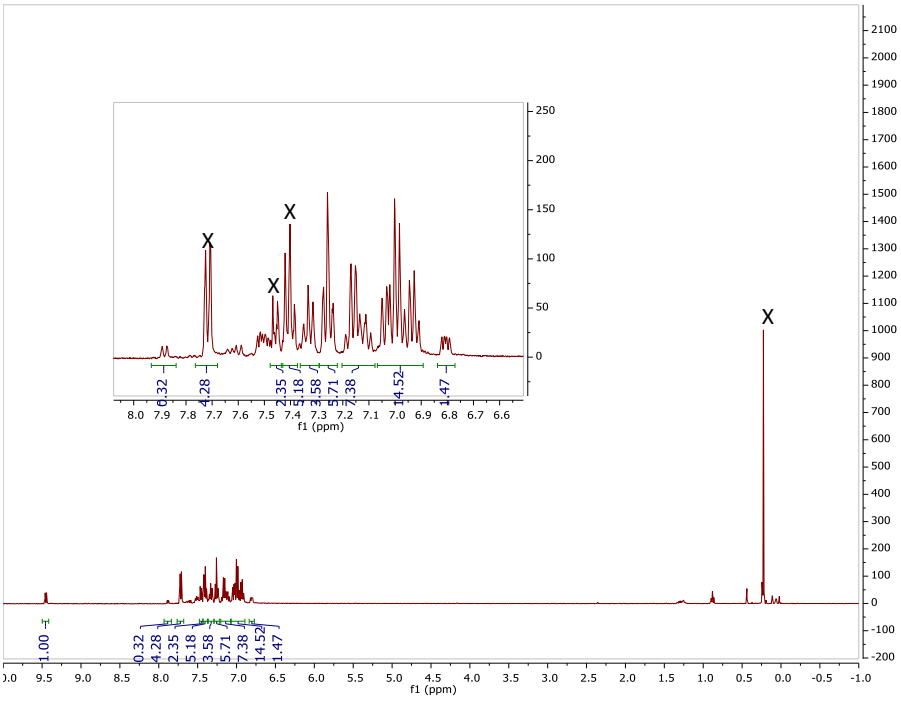
^{13}C NMR ($CDCl_3$) **5b**



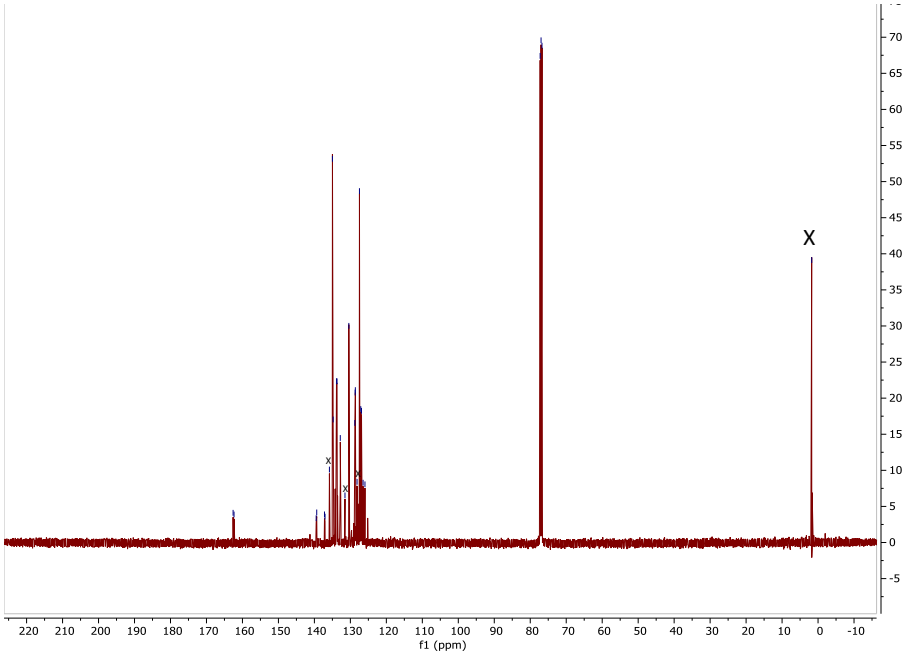
^{31}P NMR ($CDCl_3$) **5b**



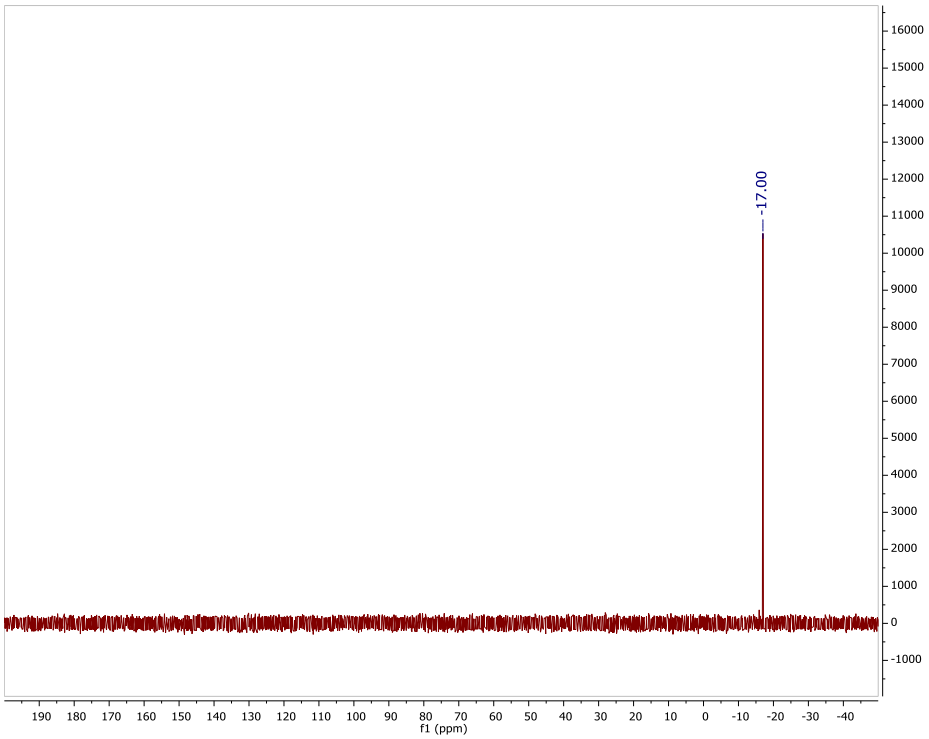
^{1}H NMR ($CDCl_3$) **4a** (X in preliminarily assigned to Ph_2BOTMS)[5]



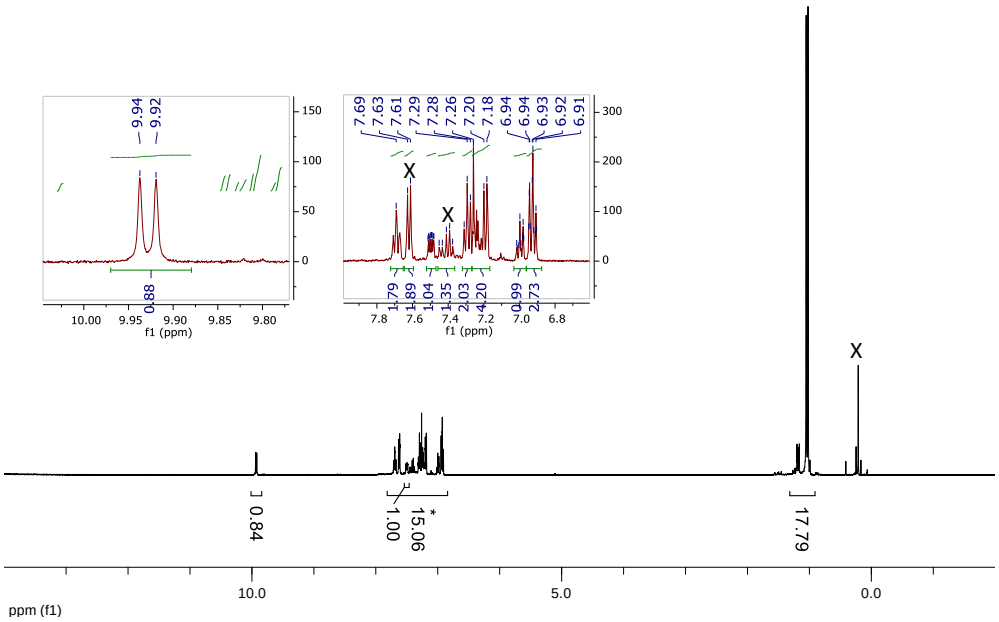
^{13}C NMR ($CDCl_3$) **4a** (X in preliminarily assigned to Ph_2BOTMS)[5]



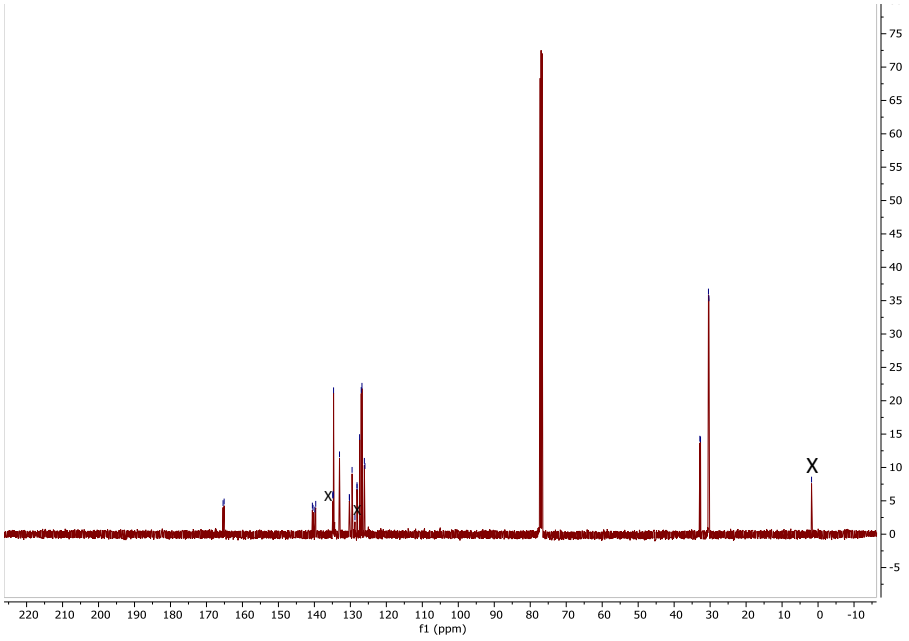
^{31}P NMR ($CDCl_3$) **4a**



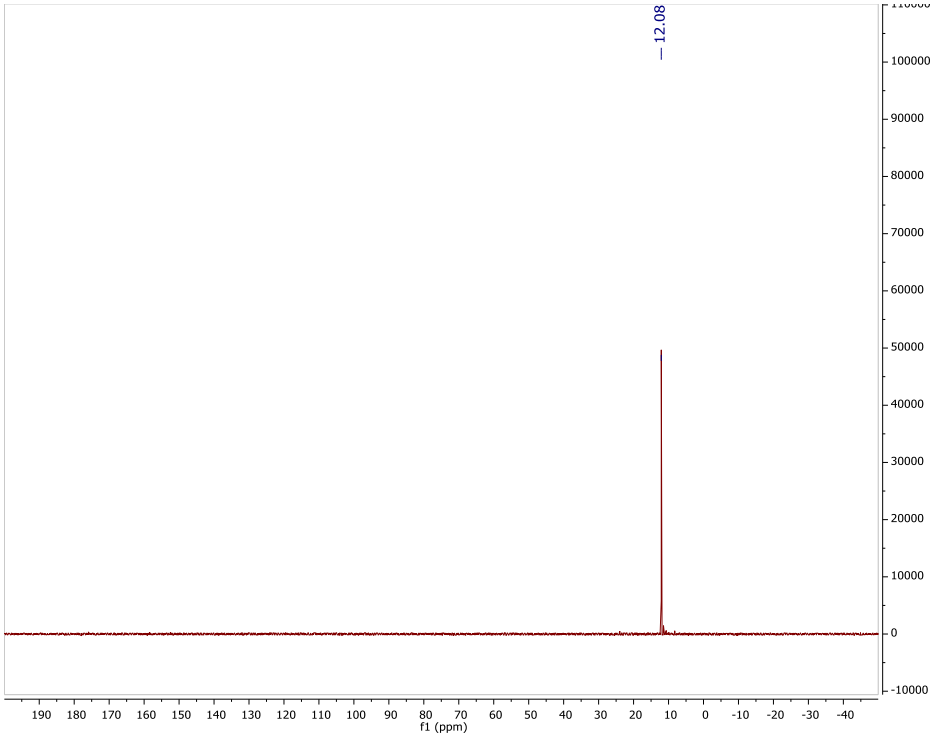
^{1}H NMR ($CDCl_3$) **4b** (X in preliminarily assigned to Ph_2BOTMS)[5]



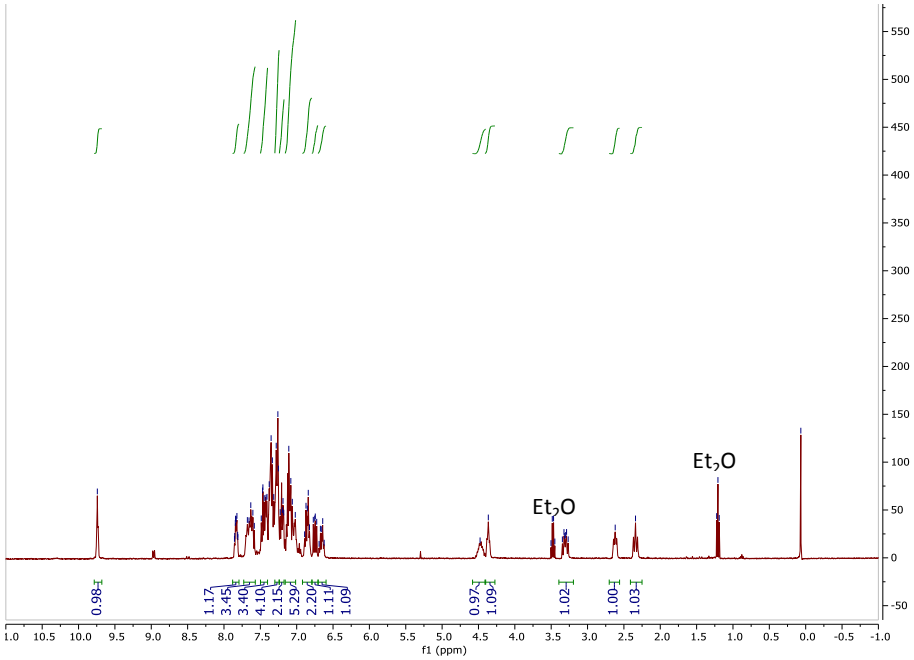
^{13}C NMR ($CDCl_3$) **4b** (X in preliminarily assigned to Ph_2BOTMS)[5]



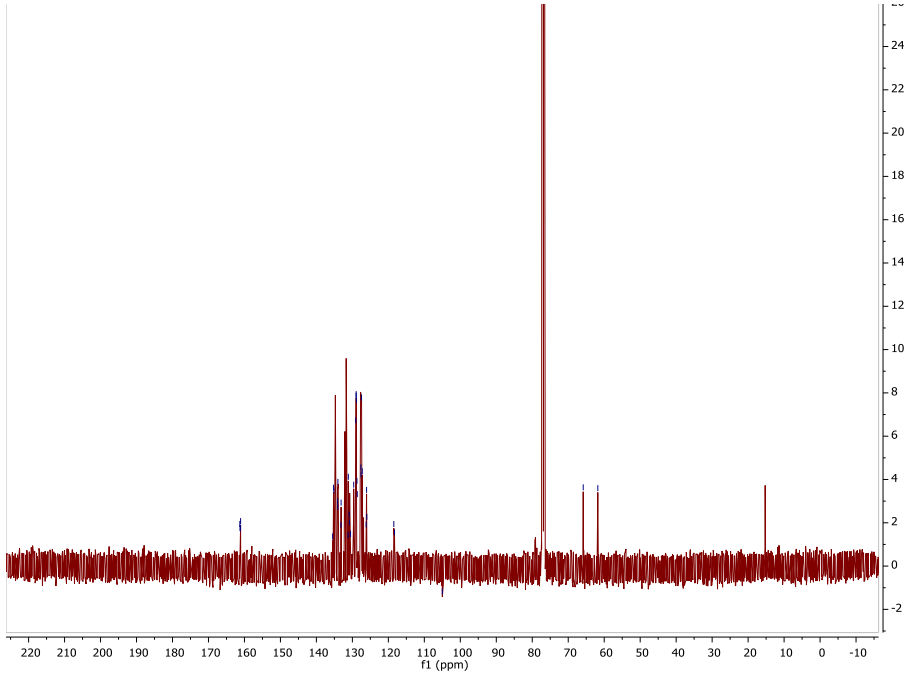
^{31}P NMR ($CDCl_3$) **4b**



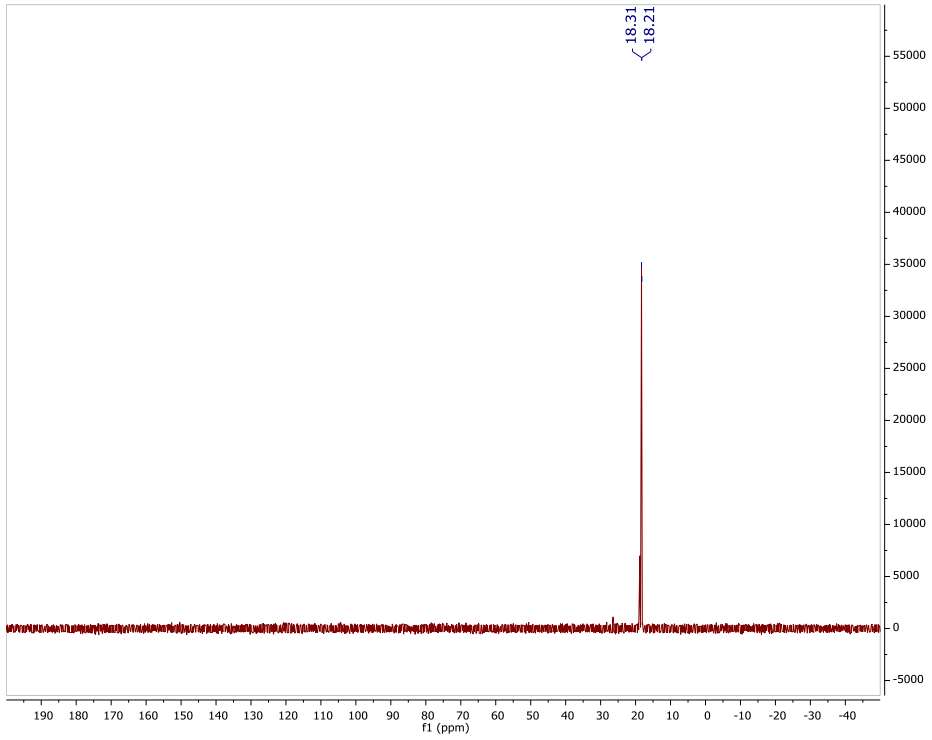
^{1}H NMR ($CDCl_3$) **6a**



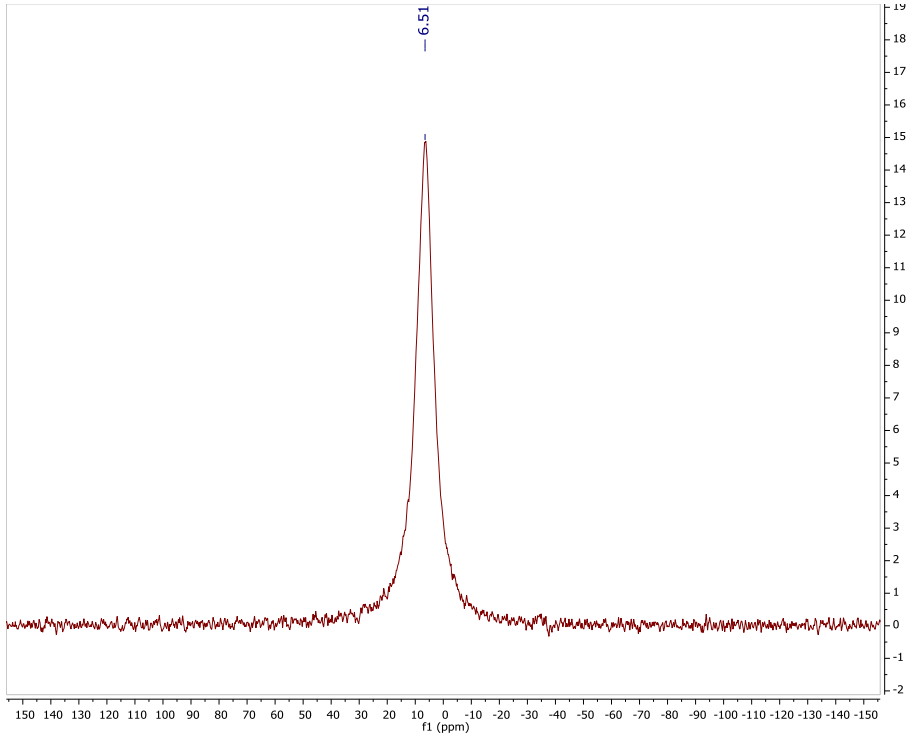
^{13}C NMR ($CDCl_3$) **6a**



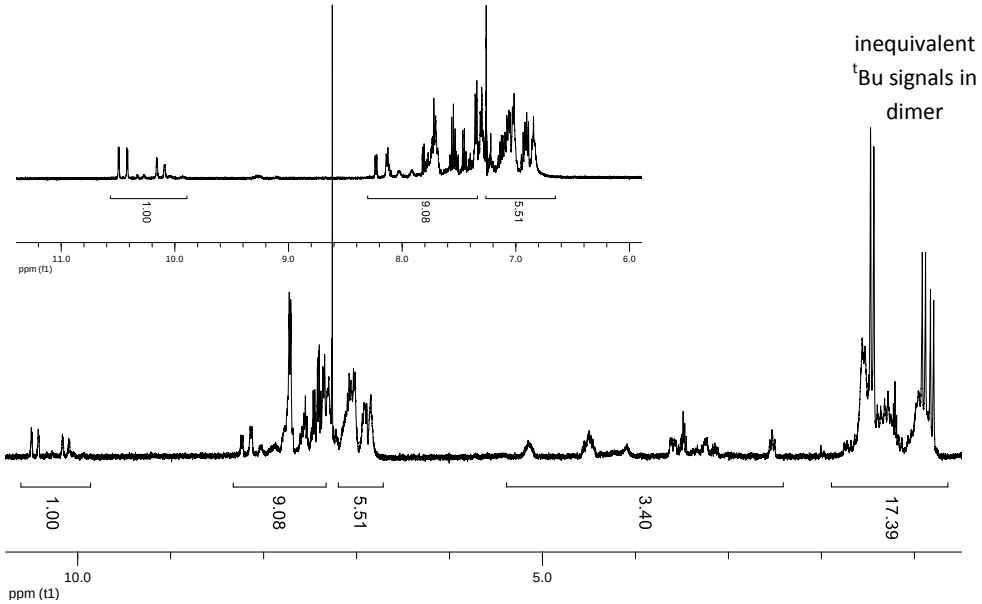
^{31}P NMR ($CDCl_3$) **6a**



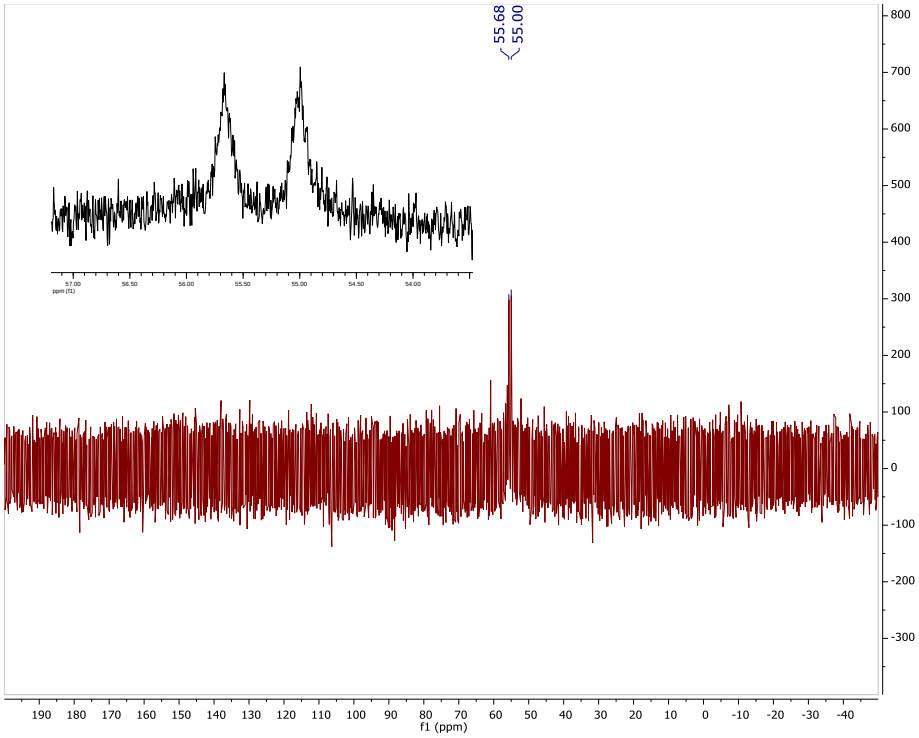
^{11}B NMR ($CDCl_3$) **6a**



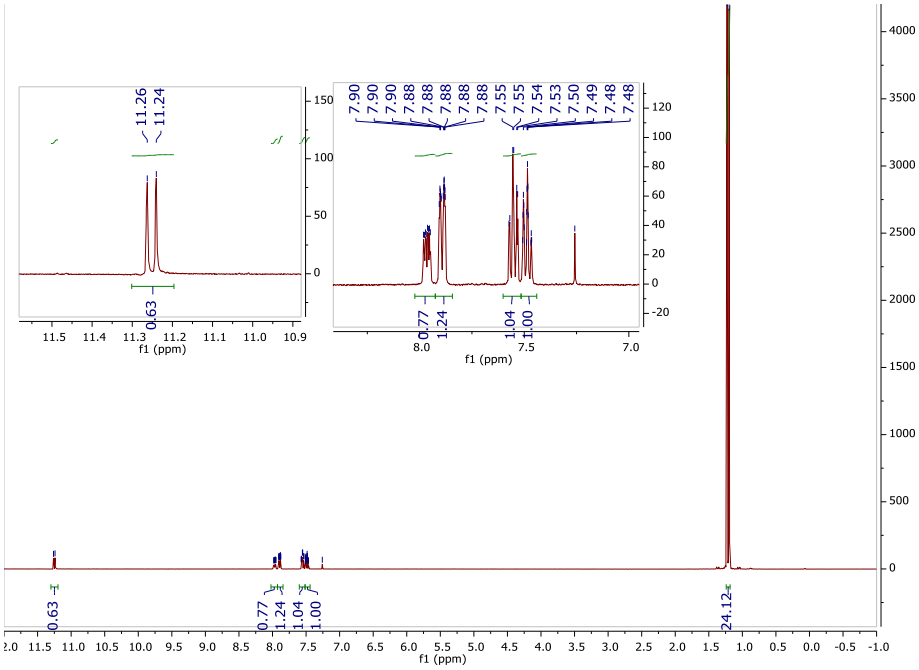
In situ ^{1}H NMR ($CDCl_3$) of **6b** (with partial decomposition)



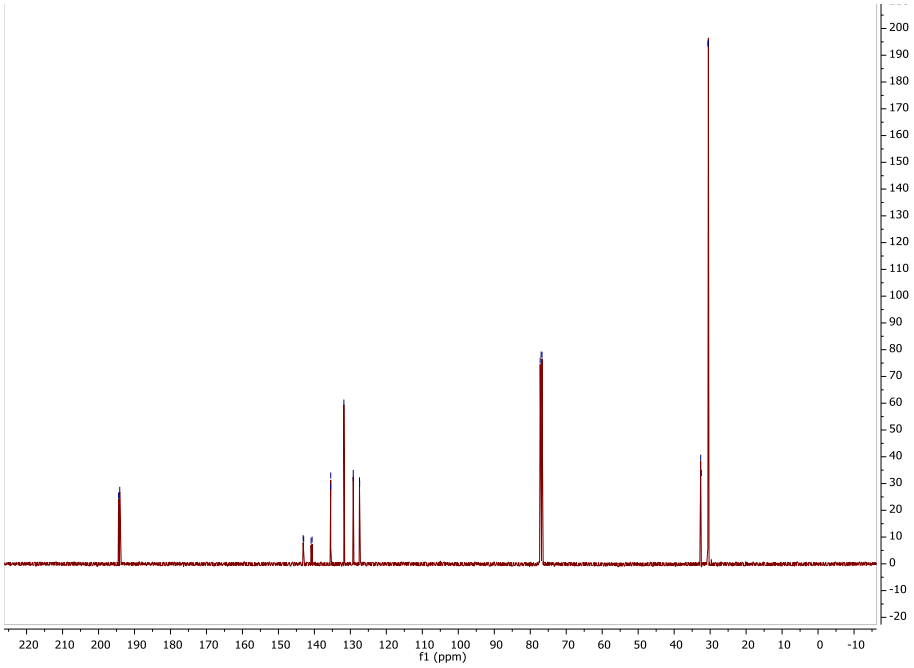
In situ ^{31}P NMR ($CDCl_3$) of **6b**



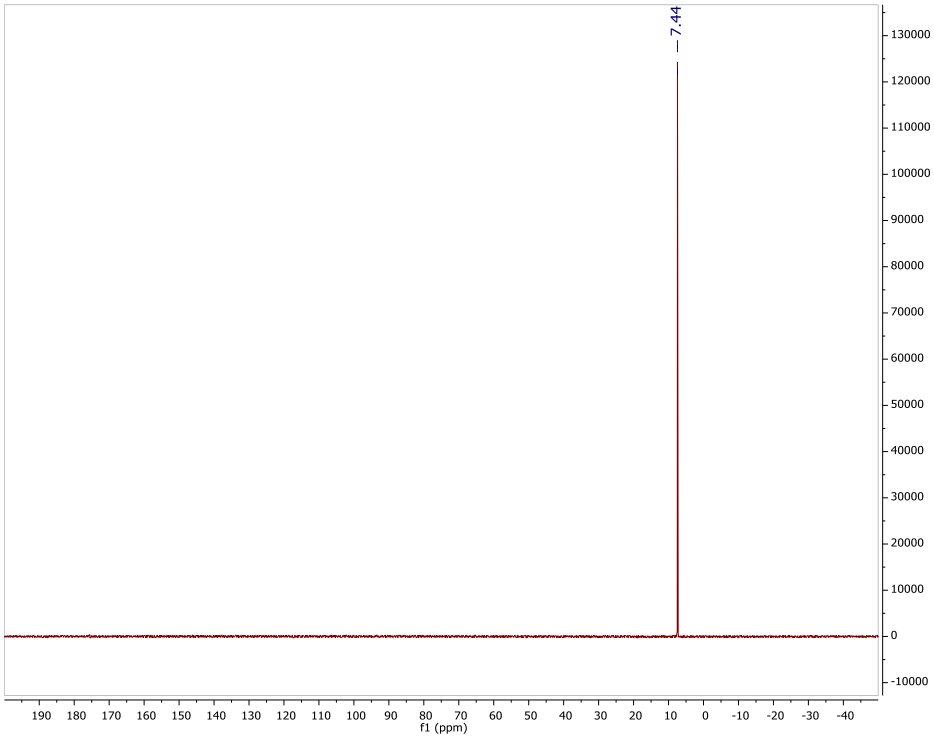
^{1}H NMR ($CDCl_3$) 2-(di-o-tert-butylphosphino)benzaldehyde



^{13}C NMR ($CDCl_3$) 2-(di-o-tert-butylphosphino)benzaldehyde



^{31}P NMR ($CDCl_3$) 2-(di-o-tert-butylphosphino)benzaldehyde



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5) We preliminarily assign these impurities to the formation of Ph_2BOTMS, and show analogous NMR signals to that formed in the in situ reaction of Ph_2BCl and LiOTMS in ^1H NMR (500 MHz, $CDCl_3$) δ 0.23 (s, 2H), 7.41 (dtt, *J* = 12.6, 7.3, 6.8, 1.5 Hz, 1H), 7.46 (td, *J* = 3.7, 1.9 Hz, 1H), 7.72 (dt, *J* = 6.9, 1.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 1.8, 127.5, 130.5, 135.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ 44.82.
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