Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Oxidative Addition of Activated Aryl–Carboxylates to Pd(0): Divergent Reactivity Dependent on Temperature and Structure

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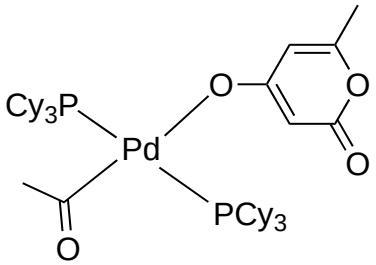
I. General information

All solvents and common reagents are purchased from commercial suppliers and used without further purification. All air-free manipulations are performed under nitrogen-atmosphere using an MBraun glovebox. Palladium(0) bis(tricyclohexylphosphine) is purchased from Strem Chemical and stored under inert atmosphere at -30 °C. 4-acetyloxy-6-methylpyran-2-one (**1a**), 4-acetyloxybenzopyran-2-one (**2a**), and pivalyloxy-6-methylpyran-2-one (**3a**) are prepared by literature procedures.[1] All NMR spectra were acquired on either a Bruker AVANCE 300 MHz spectrometer or a Bruker AVANCE Neo 500 MHz spectrometer. All ^{1}H and ^{13}C chemical shifts are calibrated to residual protio-solvents and all ^{31}P chemical shifts are calibrated to external standards. All data is processed using Bruker TopSpin 4.07. Phase corrections of ^{13}C spectra are performed using automatic phasing with alternative algorithm 2. High-resolution electrospray ionization mass spectrometric analysis was performed using a Thermo Scientific Ultimate 3000 ESI-Orbitrap Exactive Plus at the University of Victoria Mass Spectrometry Facility. Elemental analysis data was obtained at the University of Calgary Department of Chemistry Instrumentation Facility. Single crystal X-ray diffraction was performed on a Bruker APEX-II CCD diffractometer at Temple University. Crystallographic information files (CIFs) for **2c** and **3b** are deposited with the CCDC (1989738-1989739).

II. Synthesis and characterization

acetylpalladium(II)(6-methylpyran-2-one-4-oxy)bis(tricyclohexylphosphine) (1b)



In a nitrogen-atmosphere glovebox, a 4 mL vial is charged with $Pd(PCy_3)_2$ (84 mg, 0.13 mmol) and a solution of 4-acetyloxy-6-methylpyran-2-one (**1a**, 24 mg, 0.15 mmol) in 0.5 mL C_6D_6. The resulting mixture is stirred at 22 °C under inert atmosphere for 24 h. Then, the solution is diluted with 4 mL pentane to precipitate a white solid. The mixture is stirred at 22 °C under inert atmosphere for 1 h. The solid is collected by filtration, rinsed with pentane, and dried under high vacuum. White solid obtained (56 mg, 54% yield).

^{1}H NMR (500 MHz, C_6D_6, 292 K, ppm): δ 5.94 (s, 1H, $C_{Ar}\underline{H}$), 5.64 (s, 1H, $C_{Ar}\underline{H}$), 2.52 (bt, 3H, acyl $C\underline{H}_3$), 2.15–2.03 (m, 6H, PCy_3), 2.00–1.87 (m, 12H, PCy_3), 1.83 (s, 3H, $C\underline{H}_3$), 1.80–1.68 (m, 12H, PCy_3), 1.66–1.50 (m, 18H, PCy_3), 1.30–1.10 (m, 18H, PCy_3).

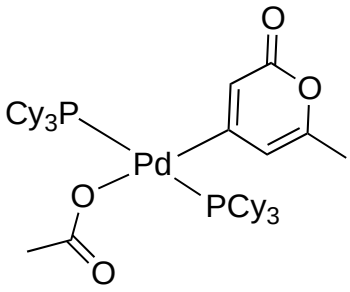
^{13}C NMR (126 MHz, C_6D_6, 292 K, ppm): δ 229.2 (acyl $\underline{C}O$), 179.5, 165.6 ($\underline{C}_{Ar}O$), 159.2 (pyrone $\underline{C}O$), 106.7 ($\underline{C}_{Ar}H$), 89.7 ($\underline{C}_{Ar}H$), 41.9 (t, $^{4}J_{C\text{-}P}$ = 15.9 Hz, acyl $\underline{C}H_3$), 33.7 (t, $^{3}J_{C\text{-}P}$ = 8.4 Hz, PCy_3), 30.0 (br, PCy_3), 27.7 (t, $^{2}J_{C\text{-}P}$ = 5.2 Hz, PCy_3), 26.4 (PCy_3), 19.5 ($\underline{C}H_3$).

^{31}P NMR (202 MHz, C_6D_6, 292 K, ppm): δ 21.3.

HR-MS (ESI): calc'd for $C_{44}H_{74}O_4P_2Pd$, 834.41; calc'd for $C_{38}H_{69}OP_2Pd^+$ (**1b – $C_6H_5O_3$**), 709.38584; found: 709.38689 (most abundant isotopomer)

Elem. Anal.: calc'd for $C_{44}H_{74}O_4P_2Pd$: C, 63.26; H, 8.93; found: C, 63.21; H, 8.68.

(methylpyranone)palladium(II)(acetate)bis(tricyclohexylphosphine) (1c)



In a nitrogen-atmosphere glovebox, a 4 mL vial is charged with $Pd(PCy_3)_2$ (127 mg, 0.19 mmol) and a solution of 4-acetyloxy-6-methylpyran-2-one (**1a**, 46 mg, 0.28 mmol) in 0.7 mL C_6D_6. The resulting mixture is stirred at 80 °C under inert atmosphere for 24 h. Then, the solution is opened to air and diluted with 10 mL hexane. The solution is evaporated to obtain a colorless residue. The residue is triturated with hexane until a white solid is obtained. The solid is collected by filtration, rinsed with pentane, and dried under high vacuum. White solid obtained (62 mg, 39% yield). Isolated as an approximately 10:1 mixture of **1c**:**1d**. Single crystals of **1c** were obtained by recrystallization from a saturated toluene solution with diethyl ether as the anti-solvent. Approximately 2 volume equivalents of diethyl ether were layered on top of the toluene solution in a 4 mL screw-cap vial, which was left to slowly mix at room temperature over several days with no agitation.

^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ 6.66 (s, 1H, $C_{Ar}\underline{H}$), 6.21 (s, 1H, $C_{Ar}\underline{H}$), 2.09 (s, 3H, $C\underline{H}_3$), 2.06–2.00 (m, 6H, PCy_3), 1.99–1.91 (m, 6H, PCy_3), 1.88 (s, 1H, $C\underline{H}_3$), 1.85–1.67 (m, 24H, PCy_3), 1.65–1.55 (m, 6H, PCy_3), 1.54–1.47 (m, 6H, PCy_3), 1.27–1.16 (m, 12H, PCy_3), 1.14–1.04 (m, 6H, PCy_3).

^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm): δ 184.9 (t, $^2J_{C\text{-}P}$ = 7.0 Hz, $\underline{C}_{Ar}$), 175.7 (acetate $\underline{C}$O), 159.2 (pyrone $\underline{C}$O), 152.0 ($\underline{C}_{Ar}$), 118.9 ($\underline{C}_{Ar}$H), 115.9 ($\underline{C}_{Ar}$H), 33.7 (t, $^2J_{C\text{-}P}$ = 9.3 Hz, PCy_3), 30.0 (PCy_3), 29.5 (PCy_3), 27.8 (t, $^3J_{C\text{-}P}$ = 5.4 Hz, PCy_3), 26.5 (PCy_3), 19.1 ($\underline{C}H_3$).

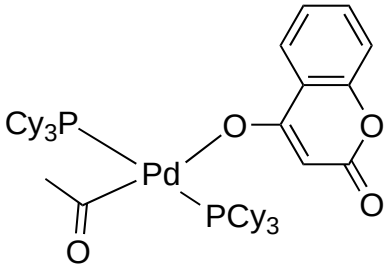
^{31}P NMR (202 MHz, $CDCl_3$, 292 K, ppm): δ 19.7

HR-MS (ESI): calc'd for $C_{44}H_{74}O_4P_2Pd$, 834.41; calc'd for $C_{42}H_{71}O_2P_2Pd^+$ (**1c - OAc**), 775.39641; found: 775.39748 (most abundant isotopomer)

Elem. Anal.: calc'd for $C_{44}H_{74}O_4P_2Pd$: C, 63.26; H, 8.93; found: C, 63.57; H, 9.06.

Elem. Anal.: calc'd for a 10:1 mixture of **1c** ($C_{44}H_{74}O_4P_2Pd$) and **1d** ($C_{48}H_{76}O_5P_2Pd$): C, 63.32; H, 8.89; found: C, 63.57; H, 9.06.

acetylpalladium(II)(oxybenzopyranone)bis(tricyclohexylphosphine)•toluene (2b)



In a nitrogen-atmosphere glovebox, a 20 mL vial is charged with $Pd(PCy_3)_2$ (100 mg, 0.15 mmol) and combined with a solution of 4-acetyloxybenzopyran-2-one (**2a**, 34 mg, 0.16 mmol) in 5 mL toluene. The resulting mixture is stirred at 22 °C under inert atmosphere for 5 h. Then, the solvent volume is removed the resulting solid is rinsed with 10 mL pentane. The solid is collected by filtration, rinsed with pentane, and dried under high vacuum. White solid obtained (104 mg, 80% yield), which is the toluene solvate (by NMR, XRD, and EA). Single crystals of **2b** were obtained by recrystallization from a saturated toluene solution with diethyl ether as the anti-solvent. Approximately 2 volume equivalents of diethyl ether were layered on top of the toluene solution in a 4 mL screw-cap vial, which was left to slowly mix at room temperature over several days with no agitation.

^{1}H NMR (500 MHz, C_6D_6, 292 K, ppm): δ8.09 (d, $^3J_{H\text{-}H}$ = 6.0 Hz, 1H, $C_{Ar}\underline{H}$), 7.24–7.23 (m, 1H, $C_{Ar}\underline{H}$), 7.14–7.10 (m, 2H, $C_{Ar}\underline{H}$), 7.07–7.02 (m, 3H, toluene $C_{Ar}\underline{H}$), 7.02–6.99 (m, 2H, toluene $C_{Ar}\underline{H}$), 6.33 (br s, 1H), 2.51 (br s, 3H), 2.13–2.02 (m, 6H, PCy_3), 2.10 (s, 3H, toluene $C\underline{H}_3$), 2.00–1.82 (m, 12H, PCy_3), 1.78–1.65 (m, 12H, PCy_3), 1.63–1.48 (m, 18H, PCy_3), 1.23–1.01 (m, 18H, PCy_3).

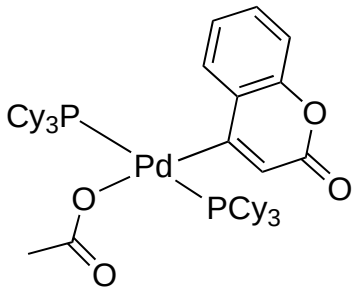
^{13}C NMR (126 MHz, C_6D_6, 292 K, ppm): δ228.8 (acyl $\underline{C}$O), 174.2, 163.9, 155.3, 137.5, 130.3, 129.0, 128.2, 125.3, 124.1, 123.0, 121.5, 116.7, 91.7 (C=$\underline{C}$H), 41.7 (t, $^2J_{C\text{-}P}$ = 16.1 Hz, acyl $\underline{C}H_3$), 33.9 (t, $^3J_{C\text{-}P}$ = 8.1 Hz, PCy_3), 29.9 (d, $^2J_{C\text{-}P}$ = 29.1 Hz, PCy_3), 27.6 (PCy_3), 26.3 (PCy_3), 21.1.

^{31}P NMR (202 MHz, $CDCl_3$, 292 K, ppm): δ21.3

HR-MS (ESI): calc'd for $C_{47}H_{74}O_4P_2Pd$, 870.41; calc'd for $C_{38}H_{69}OP_2Pd^+$ (**2b – $C_9H_5O_3$**), 709.38584; found: 709.38636 (most abundant isotopomer)

Elem. Anal.: calc'd for $C_{54}H_{82}O_4P_2Pd$: C, 67.31; H, 8.58; found: C, 67.29; H, 8.59.

(oxybenzopyranone)palladium(II)(acetate)bis(tricyclohexylphosphine) (2c)



In a nitrogen-atmosphere glovebox, a 4 mL vial is charged with $Pd(PCy_3)_2$ (84.5 mg, 0.13 mmol) and combined with a solution of 4-acetyloxybenzopyran-2-one (**2a**, 30 mg, 0.15 mmol) in 0.5 mL C_6D_6. The resulting mixture is stirred at 80 °C under inert atmosphere for 24 h. Then, the solution is opened to air and diluted with 10 mL hexane. The solution is evaporated to obtain a colorless residue. The residue is triturated with hexane until a white solid is obtained. The solid is collected by filtration, rinsed with hexane, and dried under high vacuum. White solid obtained (61 mg, 56% yield); by NMR spectroscopy, this material is an approximately 10:1 mixture of **2c**:**2d** (Fig. S16).

^{1}H NMR (500 MHz, C_6D_6, 292 K, ppm): δ 9.57 (d, $^3J_{H\text{-}H}$ = 7.8 Hz, $C_{Ar}\underline{H}$), 7.12 (m, $C_{Ar}\underline{H}$), 7.05-7.02 (m, $C_{Ar}\underline{H}$), 7.01–7.97 (m, $C_{Ar}\underline{H}$), 6.86 (s, C=C$\underline{H}$), 2.26–2.21 (m, 6H, PCy_3), 2.21 (s, 3H, OAc C$\underline{H}_3$), 2.14–2.06 (m, 6H, PCy_3), 1.80–1.75 (m, 6H, PCy_3), 1.71–1.63 (m, 6H, PCy_3), 1.61–1.51 (m, 18H, PCy_3), 1.49–1.37 (m, 6H, PCy_3), 1.30–1.19 (m, 6H, PCy_3), 1.16–1.05 (m, 6H, PCy_3), 1.03-0.93 (m, 6H, PCy_3).

^{13}C NMR (126 MHz, C_6D_6, 292 K, ppm): δ 184.3 (t, $^2J_{C\text{-}P}$ = 7.0 Hz, Pd-$\underline{C}$), 175.5 (OAc $\underline{C}$O), 156.9 (pyrone $\underline{C}$O), 151.1 ($\underline{C}_{Ar}$), 136.1 ($\underline{C}_{Ar}$H), 130.9 ($\underline{C}_{Ar}$H), 130.1 ($\underline{C}_{Ar}$) 124.2 ($\underline{C}_{Ar}$H), 123.5 (t, $^3J_{C\text{-}P}$ = 3.1 Hz, C=$\underline{C}$H), 116.4 ($\underline{C}_{Ar}$H), 34.7 (t, $^3J_{C\text{-}P}$ = 9.1 Hz, PCy_3), 30.8 (OAc $\underline{C}H_3$), 29.9 (PCy_3), 28.6–28.5 (m, PCy_3), 27.2 (PCy_3).

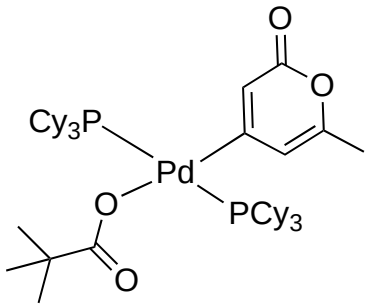
^{31}P NMR (202 MHz, C_6D_6, 292 K, ppm): δ 18.1

HR-MS (ESI): calc'd for $C_{47}H_{74}O_4P_2Pd$, 870.41; calc'd for $C_{45}H_{71}O_2P_2Pd^+$ (**2c – OAc**), 811.39641; found: 811.39715 (most abundant isotopomer)

Elem. Anal.: calc'd for $C_{47}H_{74}O_4P_2Pd$: C, 64.78; H, 8.56; found: C, 65.42; H, 8.67

Elem. Anal.: calc'd for 10:1 mixture of **2c** ($C_{47}H_{74}O_4P_2Pd$) to **2d** ($C_{54}H_{76}O_5P_2Pd$): C, 64.95; H, 8.50; found: C, 65.42; H, 8.67

(methylpyranone)palladium(II)(pivalate)bis(tricyclohexylphosphine) (3c)



In a nitrogen-atmosphere glovebox, a 4 mL vial is charged with $Pd(PCy_3)_2$ (81 mg, 0.12 mmol) and 0.5 mL toluene. This solution is combined with a solution of 4-pivalyloxy-6-methylpyran-2-one (**3a**, 31 mg, 0.15 mmol) in 0.5 mL toluene. The resulting mixture is stirred at 80 °C under inert atmosphere for 24 h. Then, the solution is opened to air and diluted with 10 mL hexane. The solution is evaporated to obtain a colorless residue. The residue is triturated with hexane until a white solid is obtained. The solid is collected by filtration, rinsed with hexane, and dried under high vacuum. White solid obtained (62 mg, 58% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 292 K, ppm): δ6.73 (s, 1H, $C_{Ar}\underline{H}$), 6.20 (s, 1H, $C_{Ar}\underline{H}$), 2.06 (s, 3H, $C\underline{H}_3$), 2.04–1.92 (m, 12H, PCy_3), 1.84–1.67 (m, 24H, PCy_3), 1.66–1.50 (m, 12H, PCy_3), 1.27–1.18 (m, 12H, PCy_3), 1.15 (s, 9H, $C(C\underline{H}_3)_3$) 1.13–1.03 (m, 6H, PCy_3).

^{13}C NMR (126 MHz, $CDCl_3$, 292 K, ppm): δ185.9 (t, $^2J_{C\text{-}P}$ = 6.4 Hz, $\underline{C}_{Ar}$Pd), 181.8 (OPiv $\underline{C}$O), 159.4 (pyrone $\underline{C}$O), 151.6 ($\underline{C}_{Ar}$), 118.8 (t, $^3J_{C\text{-}P}$ = 3.0 Hz, $\underline{C}_{Ar}$H), 115.5 (bt, $\underline{C}_{Ar}$H), 33.5 (t, $^2J_{C\text{-}P}$ = 9.0 Hz, PCy_3), 40.0 ($\underline{C}(CH_3)_3$), 29.9 (PCy_3), 29.7 (PCy_3), 29.2 (PCy_3), 27.7 (q, $^3J_{C\text{-}P}$ = 4.4 Hz, PCy_3), 26.4 ($C(\underline{C}H_3)_3$), 19.1 ($\underline{C}H_3$).

^{31}P NMR (202 MHz, $CDCl_3$, 292 K, ppm): δ17.5.

HR-MS (ESI): calc'd for $C_{47}H_{80}O_4P_2Pd$, 876.46; calc'd for $C_{42}H_{71}O_2P_2Pd^+$ (**3c – OPiv**), 775.39641; found: 775.39741 (most abundant isotopomer)

Elem. Anal.: calc'd for $C_{47}H_{80}O_4P_2Pd$: C, 64.33; H, 9.19; found: C, 64.92; H, 9.29.

Carbon analysis high due to the presence of residual hexanes solvent that could not be removed even after prolonged evacuation (see Fig. S21, S22).

III. Procedure for cross coupling reaction

In a N_2-atmosphere glovebox, a 4 mL vial is charged with $Pd(PCy_3)_2$ (12.5 mg, 0.02 mmol, 9.3 mol %), 6-methyl-4-pivalyloxypyran-2-one (42 mg, 0.2 mmol), phenylboronic acid (52 mg, 0.4 mmol), and 1,3,5-trimethoxybenzene as an internal standard (5.9 mg, 0.035 mmol). The solids are dissolved in 1 mL toluene-d_8 (0.2 M). The vial is sealed with a PTFE lined cap and heated to 100 °C for 20 h. After cooling to rt, the reaction mixture is opened to air and an aliquot is removed and diluted in 0.6 mL $CDCl_3$ for NMR analysis. The solution yield of the product[2] is determined to be 91%.

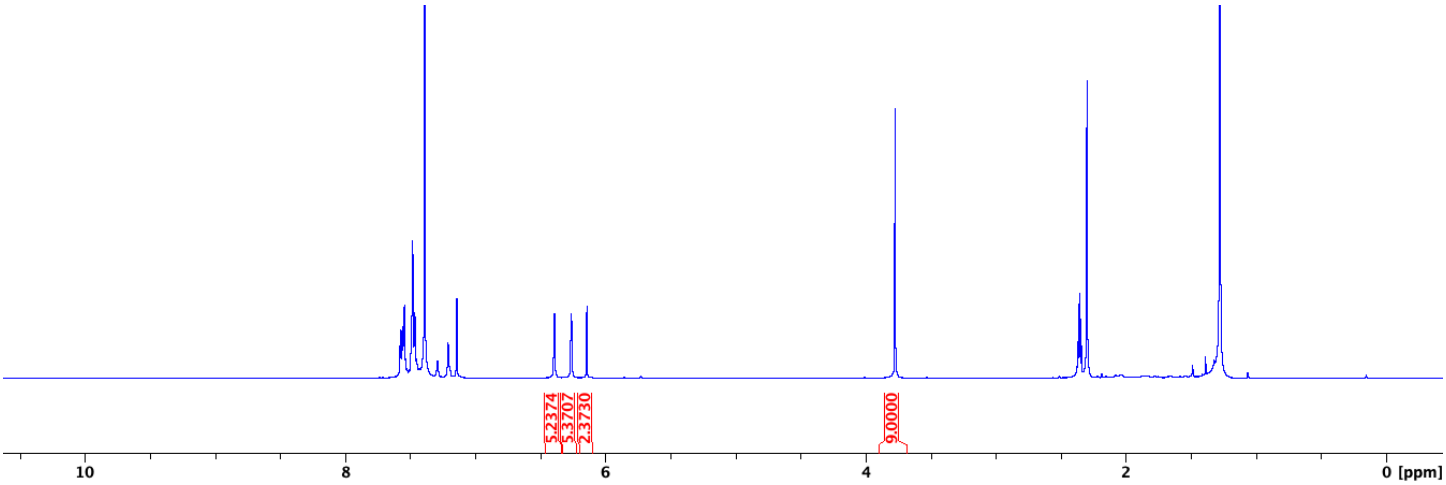
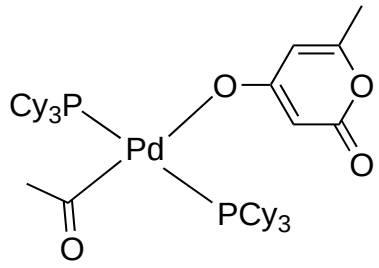


Figure S1. NMR yield determination of 6-methyl-4-phenyloxypyran-2-one

IV. NMR Spectra



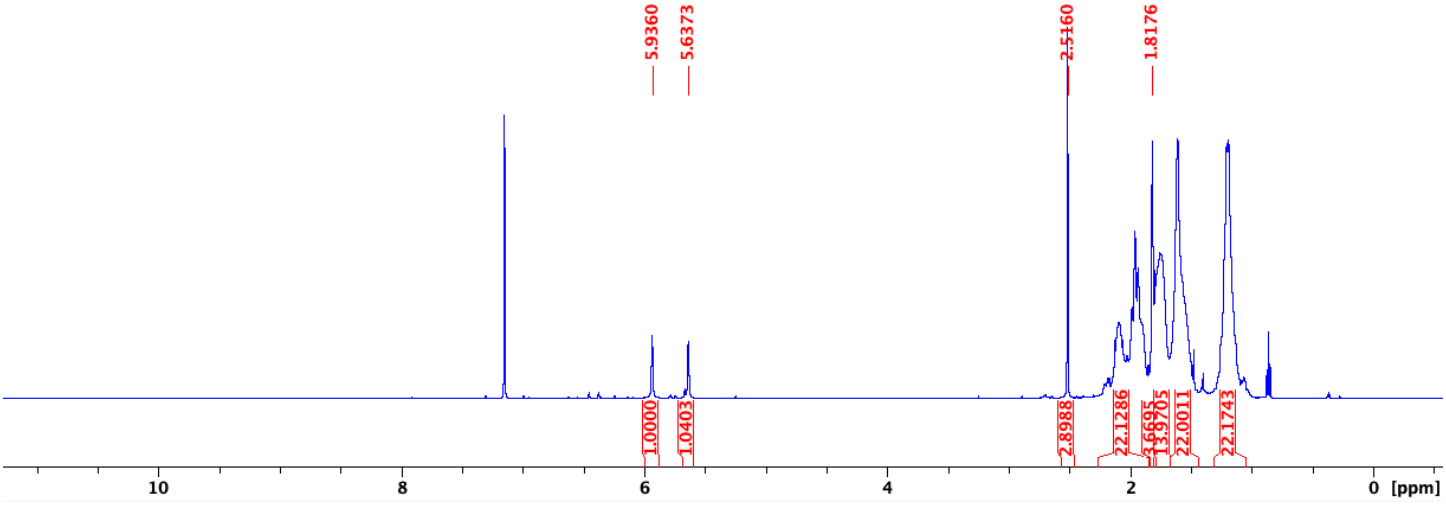


Figure S2. ^{1}H spectra (C_6D_6, 292 K, 500 MHz) of **1b**

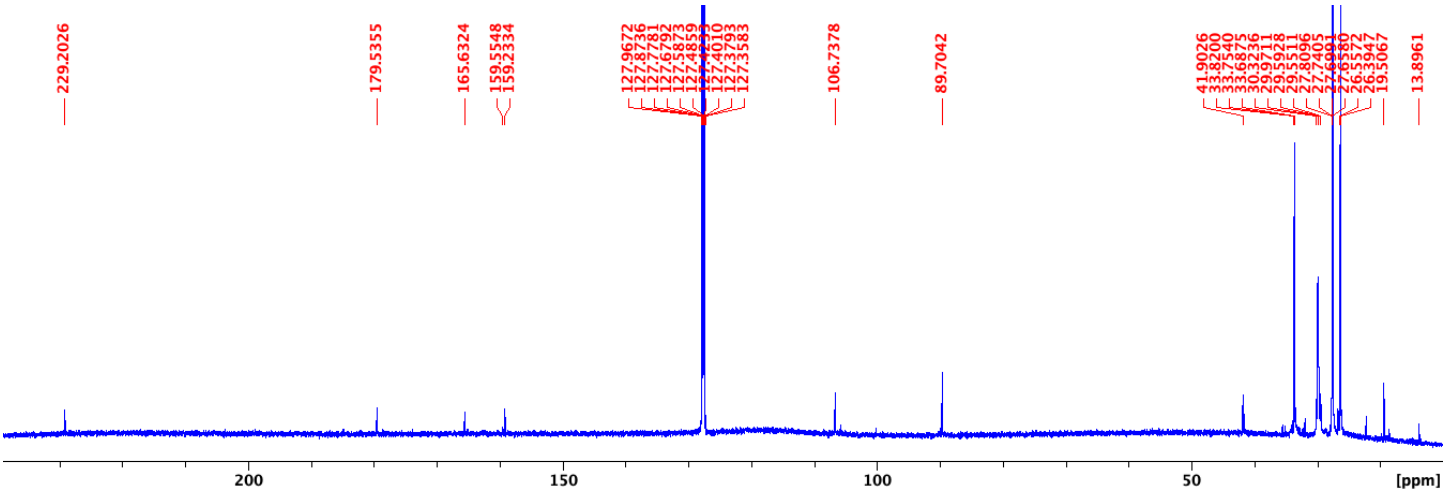


Figure S3. ^{13}C spectra (C_6D_6, 292 K, 126 MHz) of **1b**

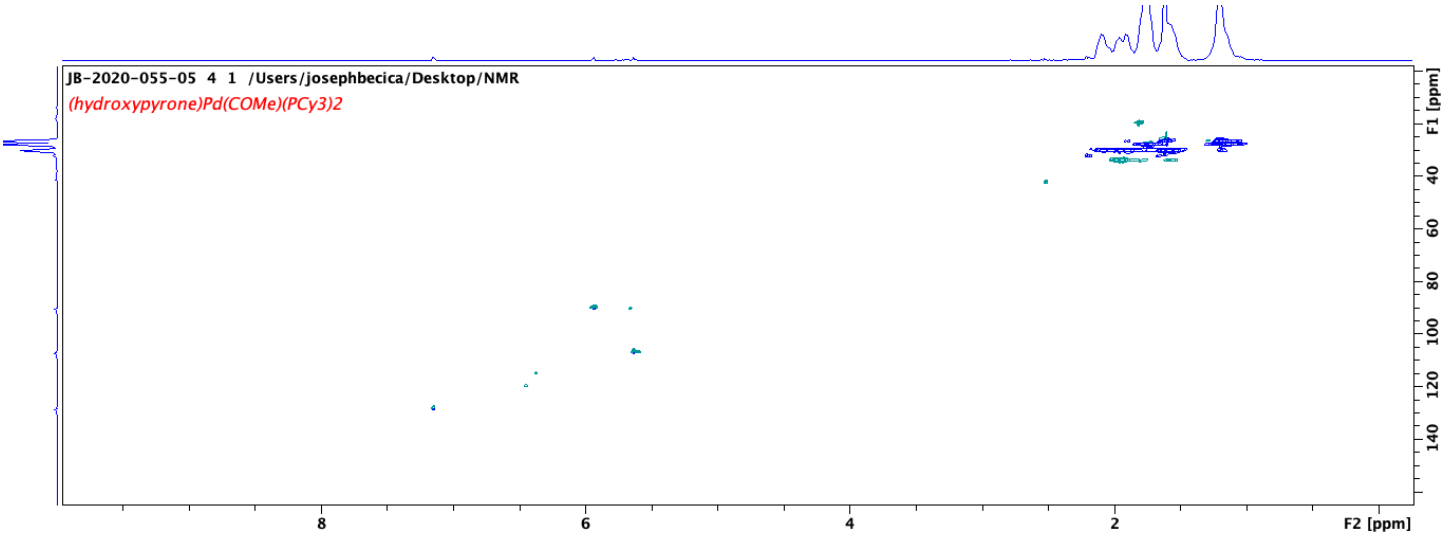


Figure S4. $^{1}H/^{13}C$ HSQC spectra (C_6D_6, 292 K, 500 MHz) of **1b**

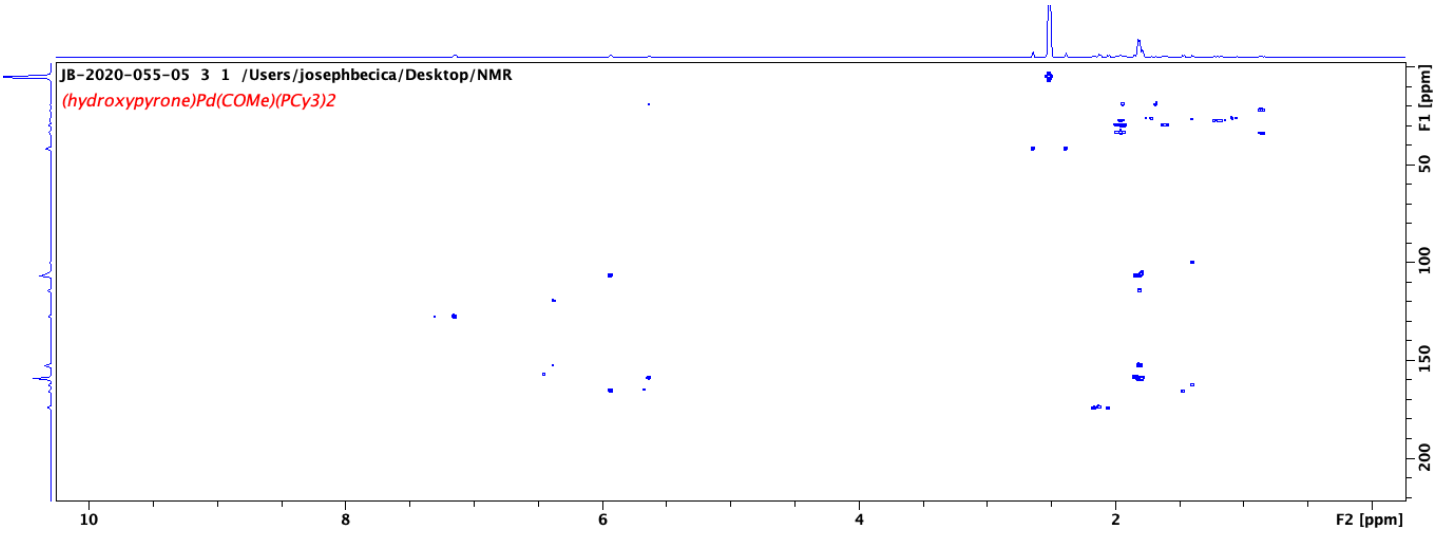


Figure S5. $^{1}H/^{13}C$ HMBC spectra (C_6D_6, 292 K, 500 MHz) of **1b**

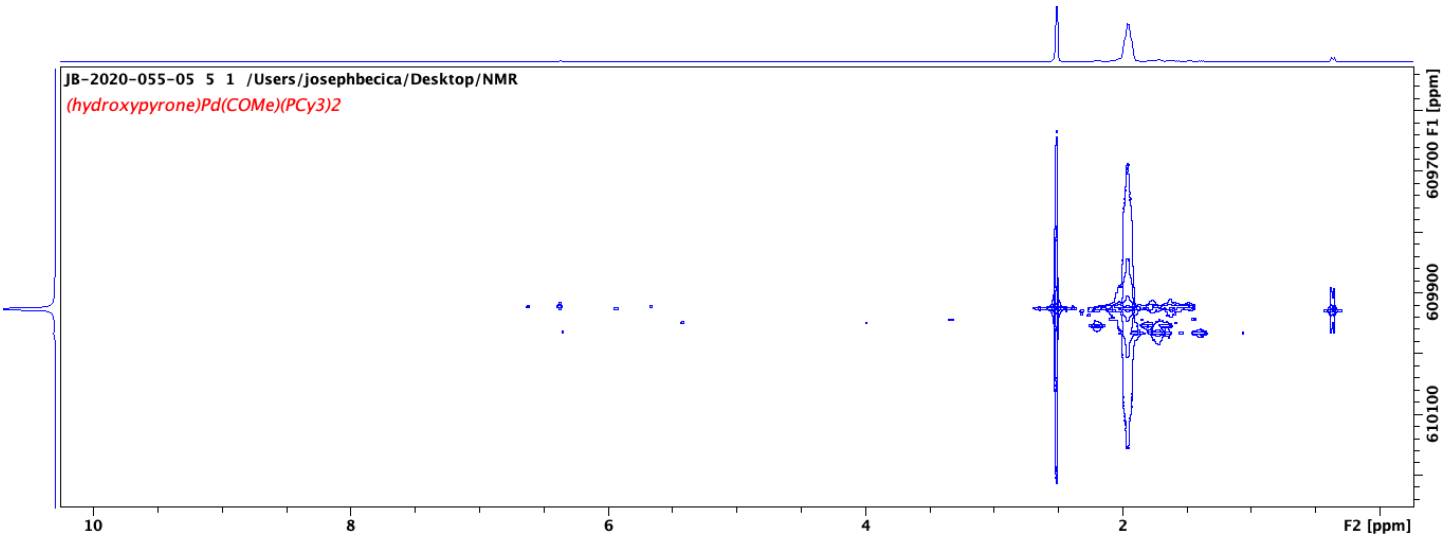
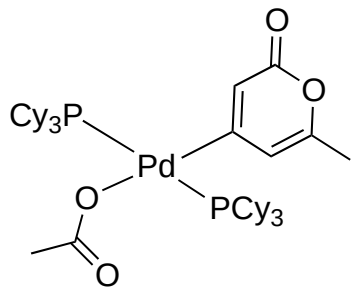


Figure S6. $^{1}H/^{31}P$ HMBC spectra (C_6D_6, 292 K, 500 MHz) of **1b**



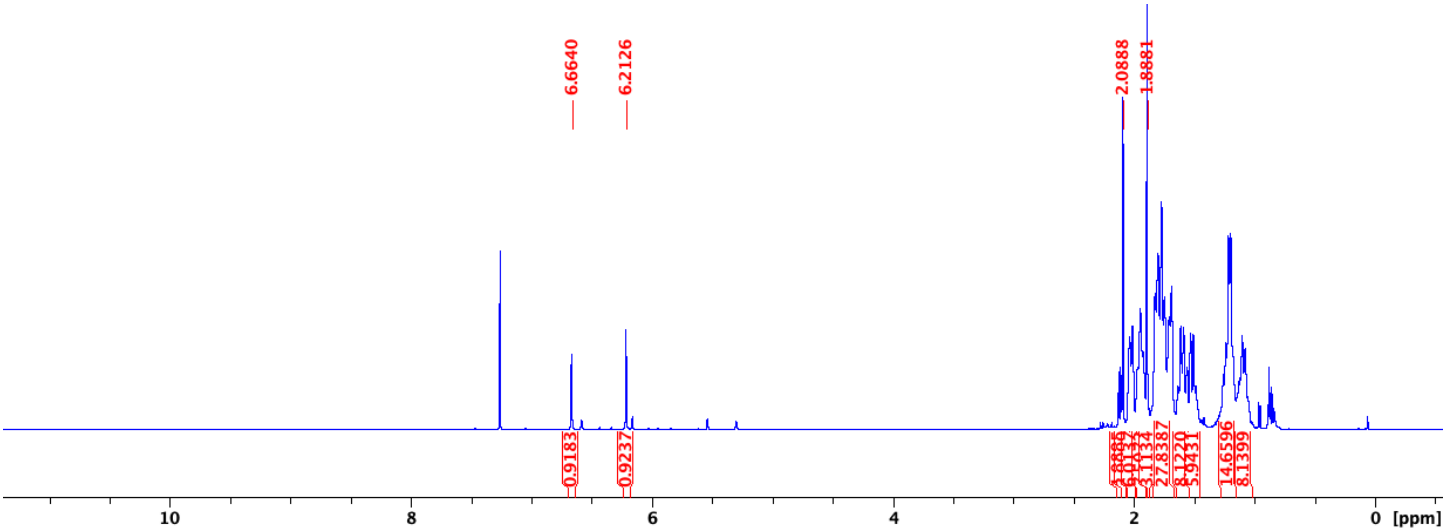


Figure S7. ^{1}H spectra ($CDCl_3$, 292 K, 500 MHz) of **1c**

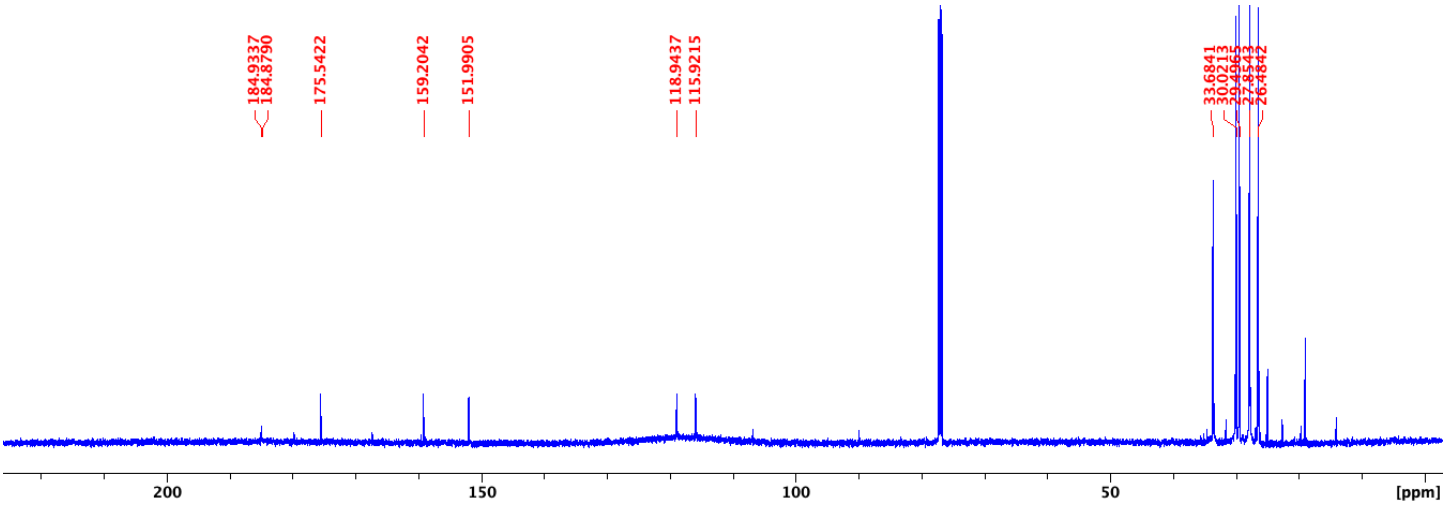


Figure S8. ^{13}C spectra ($CDCl_3$, 292 K, 126 MHz) of **1c**

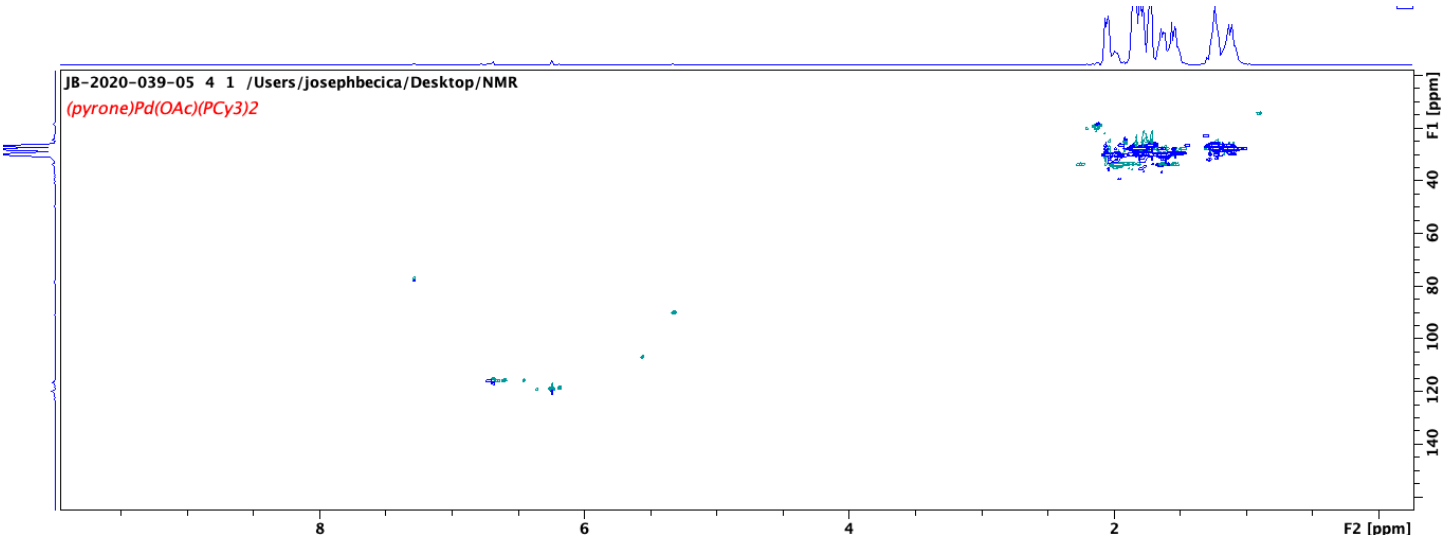


Figure S9. $^{1}H/^{13}C$ HSQC spectra ($CDCl_3$, 292 K, 500 MHz) of **1c**

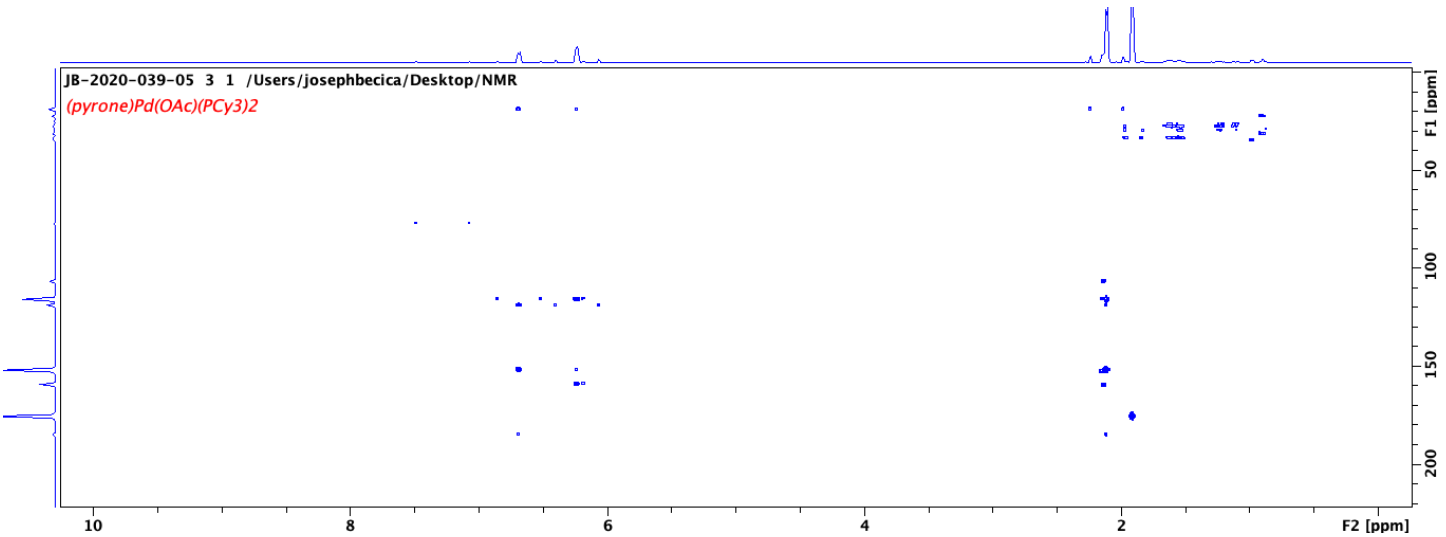


Figure S10. $^{1}H/^{13}C$ HMBC spectra ($CDCl_3$, 292 K, 500 MHz) of **1c**

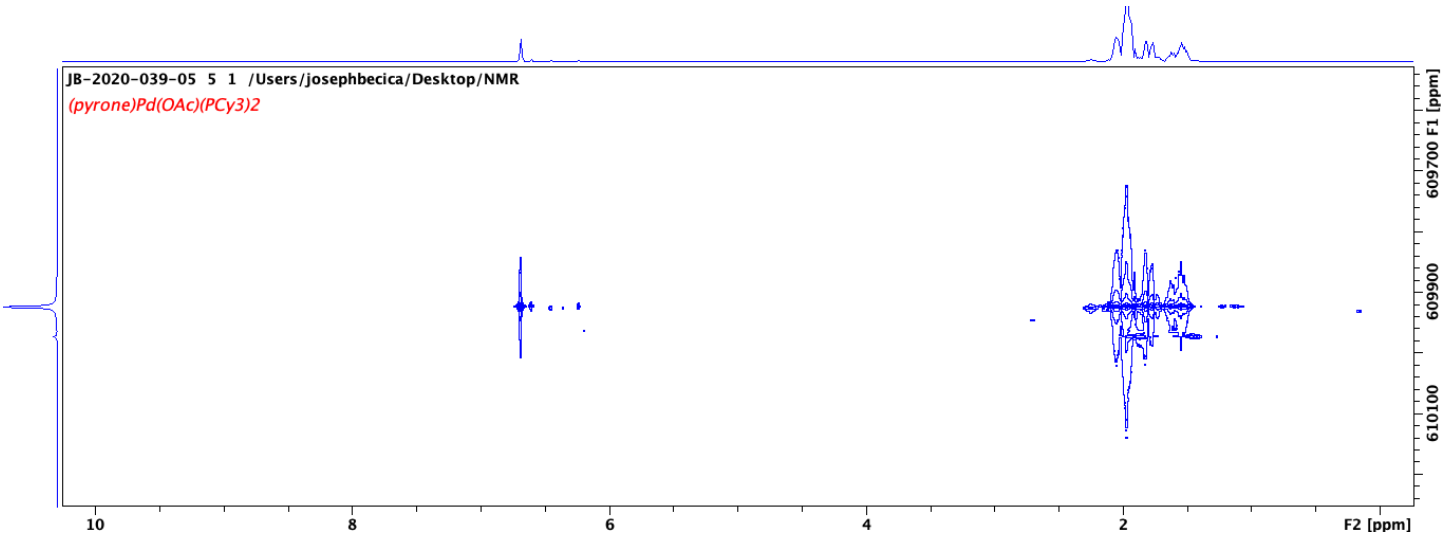


Figure S11. $^{1}H/^{31}P$ HMBC spectra ($CDCl_3$, 292 K, 500 MHz) of **1c**

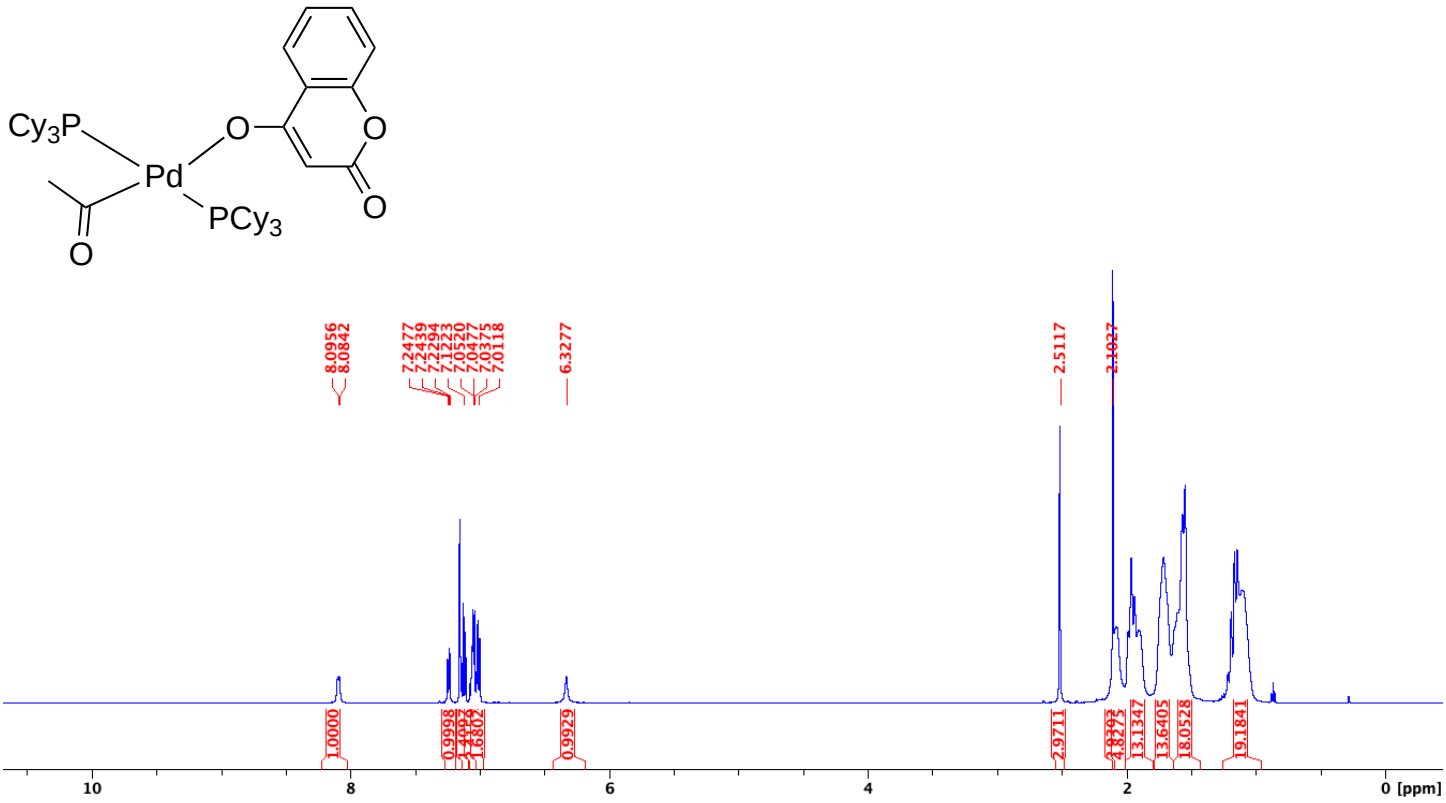


Figure S12. ^{1}H spectra (C_6D_6, 292 K, 500 MHz) of **2b**

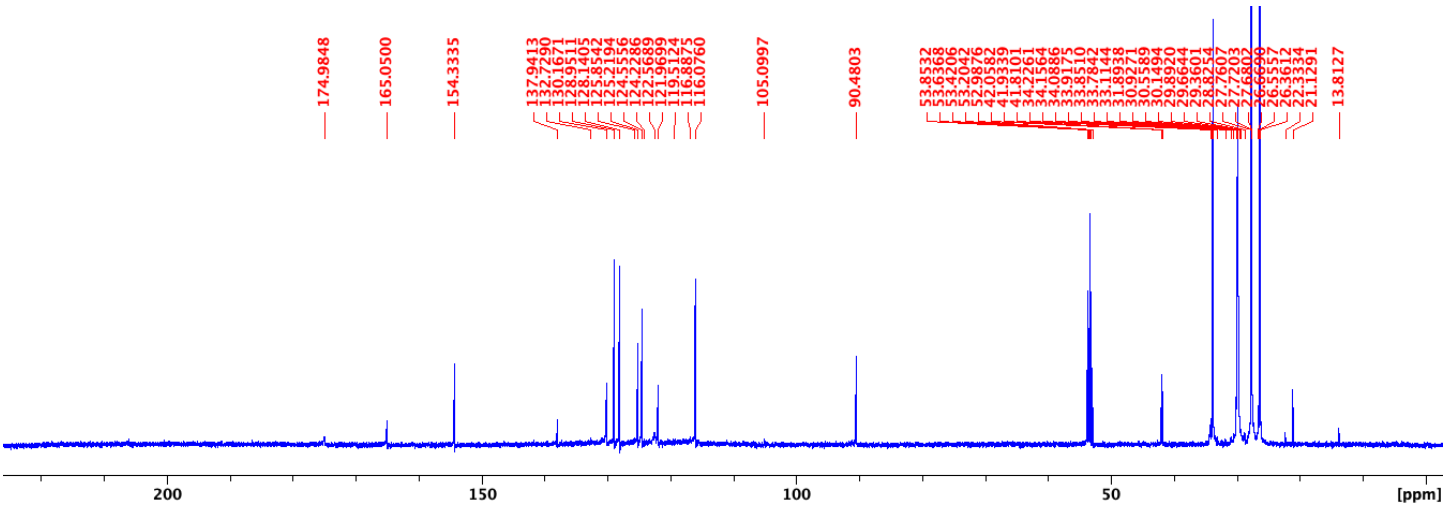


Figure S13. ^{13}C spectra (CD_2Cl_2, 292 K, 126 MHz) of **2b**

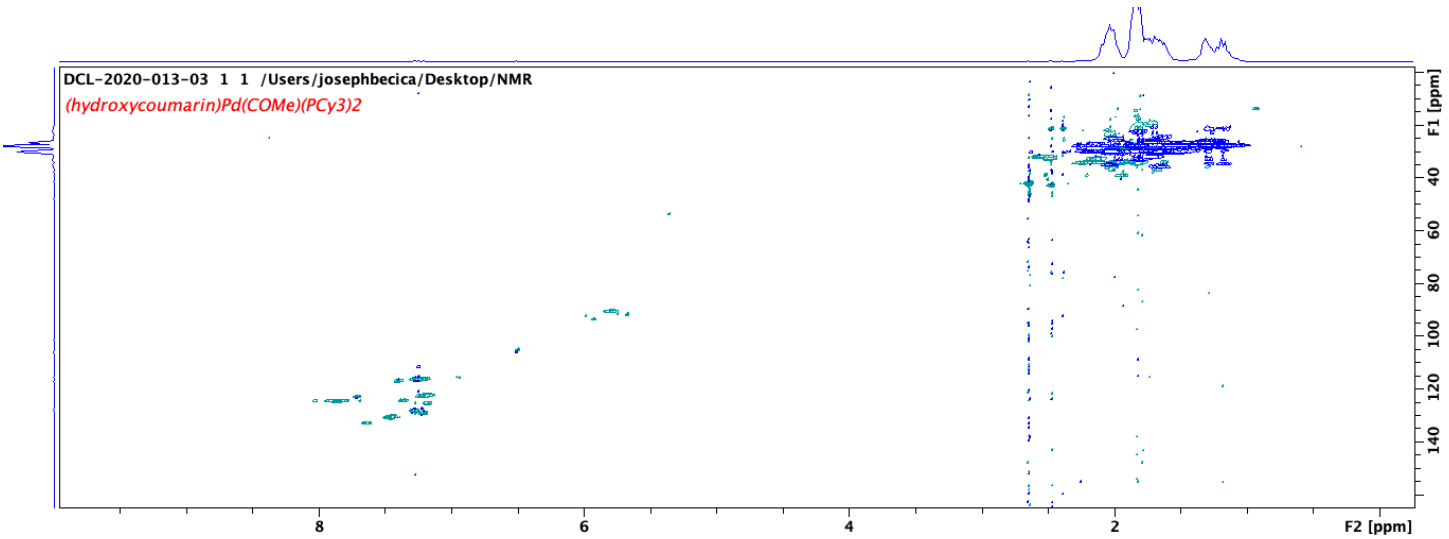


Figure S14. $^{1}H/^{13}C$ HSQC spectra (CD_2Cl_2, 292 K, 500 MHz) of **2b**

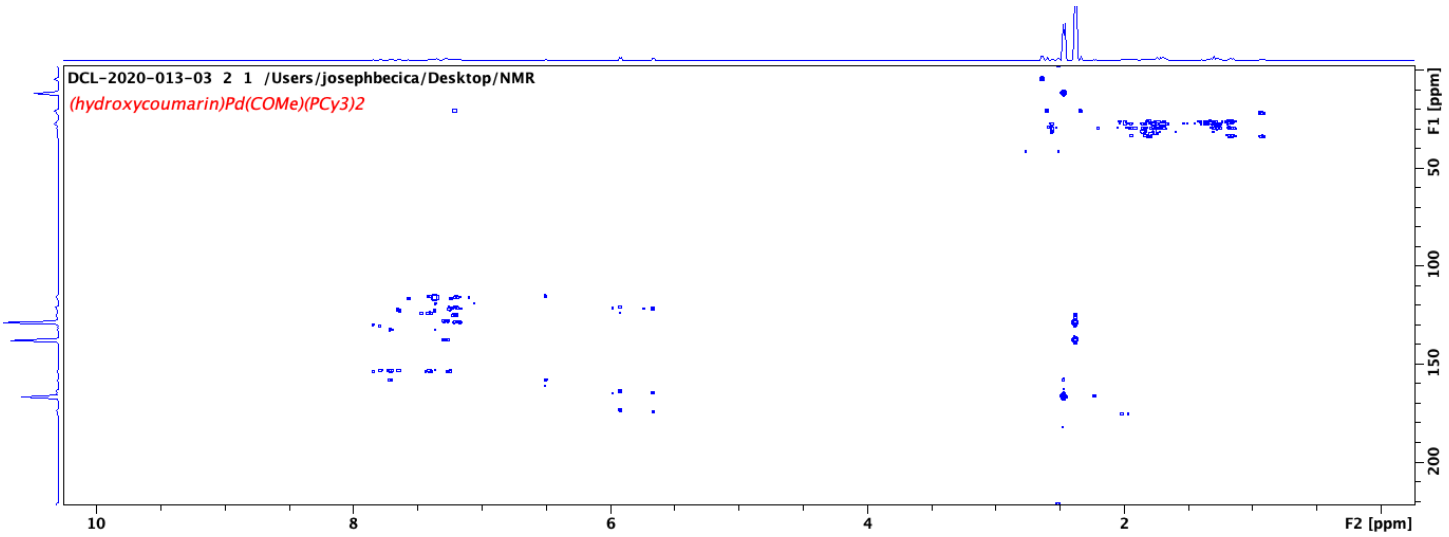


Figure S15. $^{1}H/^{13}C$ HMBC spectra (CD_2Cl_2, 292 K, 500 MHz) of **2b**

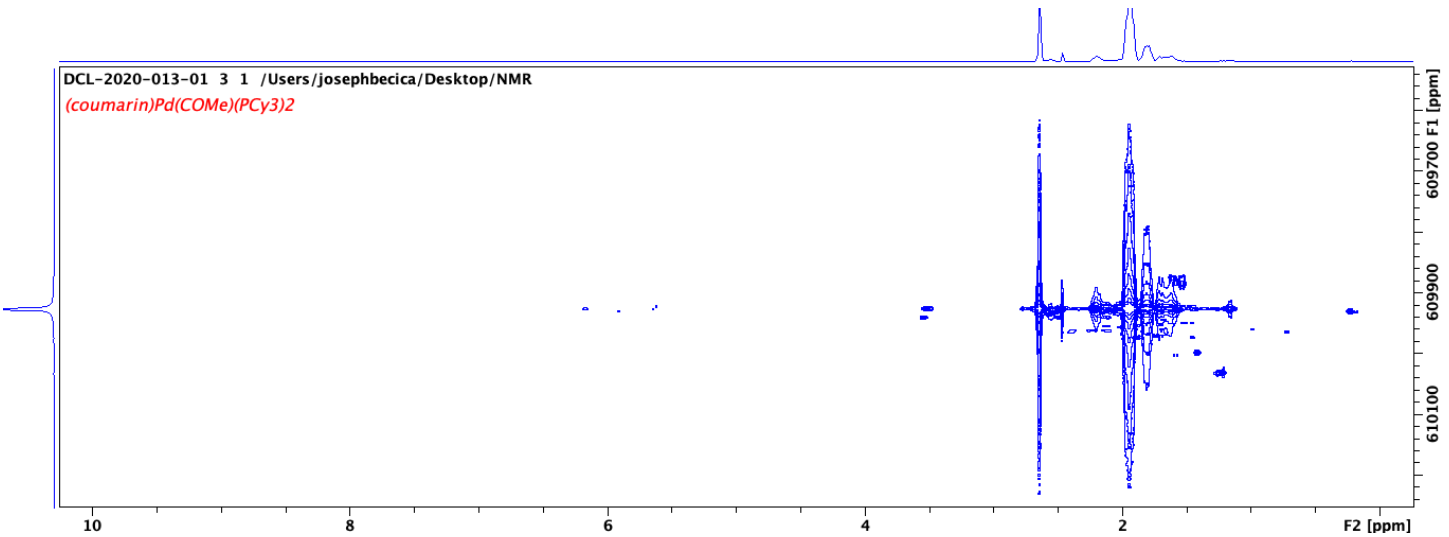
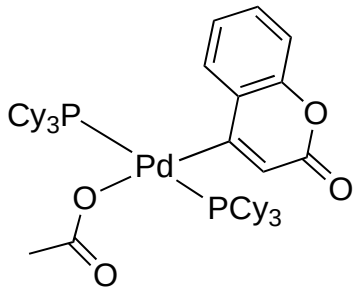


Figure 13. $^{1}H/^{31}P$ HMBC spectra (CD_2Cl_2, 292 K, 500 MHz) of **2b**



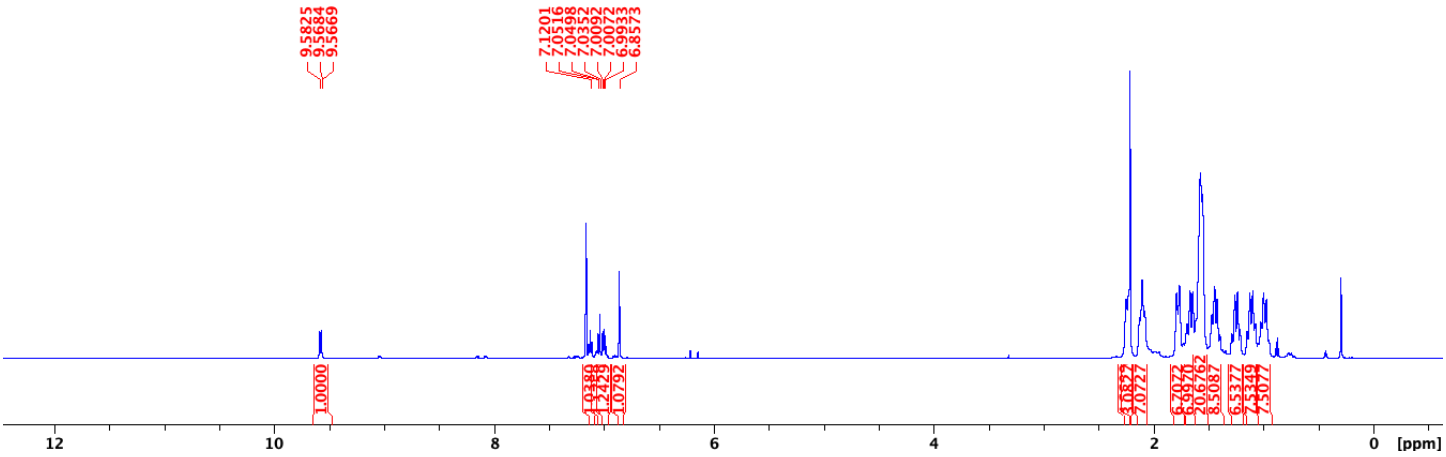


Figure S16. ^{1}H spectra (C_6D_6, 292 K, 500 MHz) of **2c**

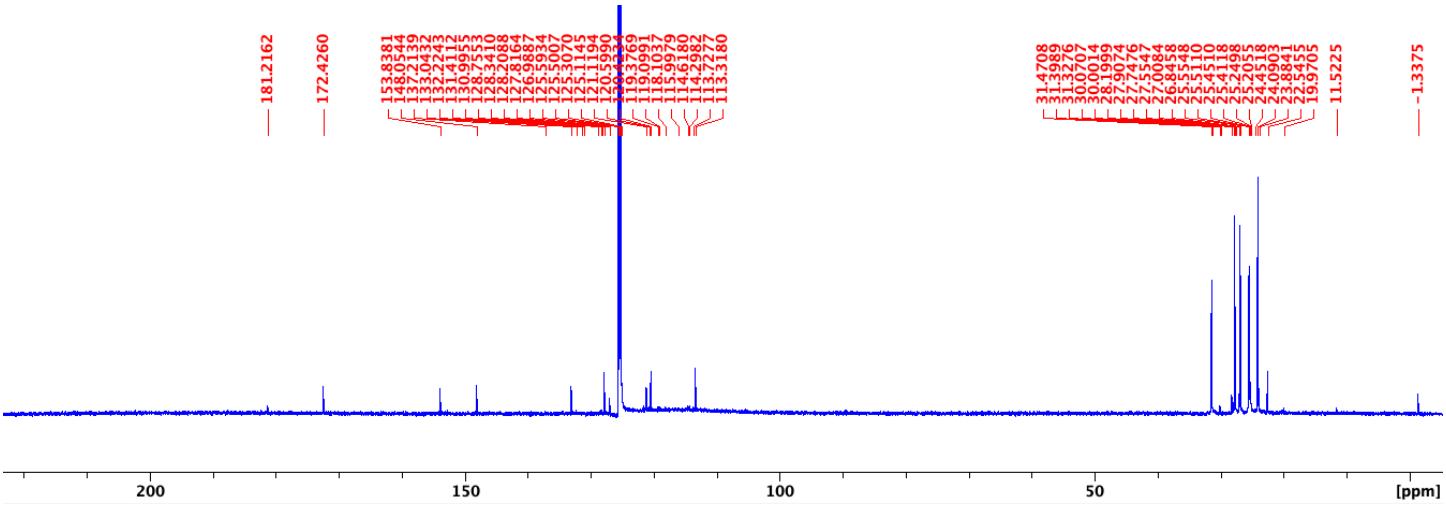


Figure S17. ^{13}C spectra (C_6D_6, 292 K, 126 MHz) of **2c**

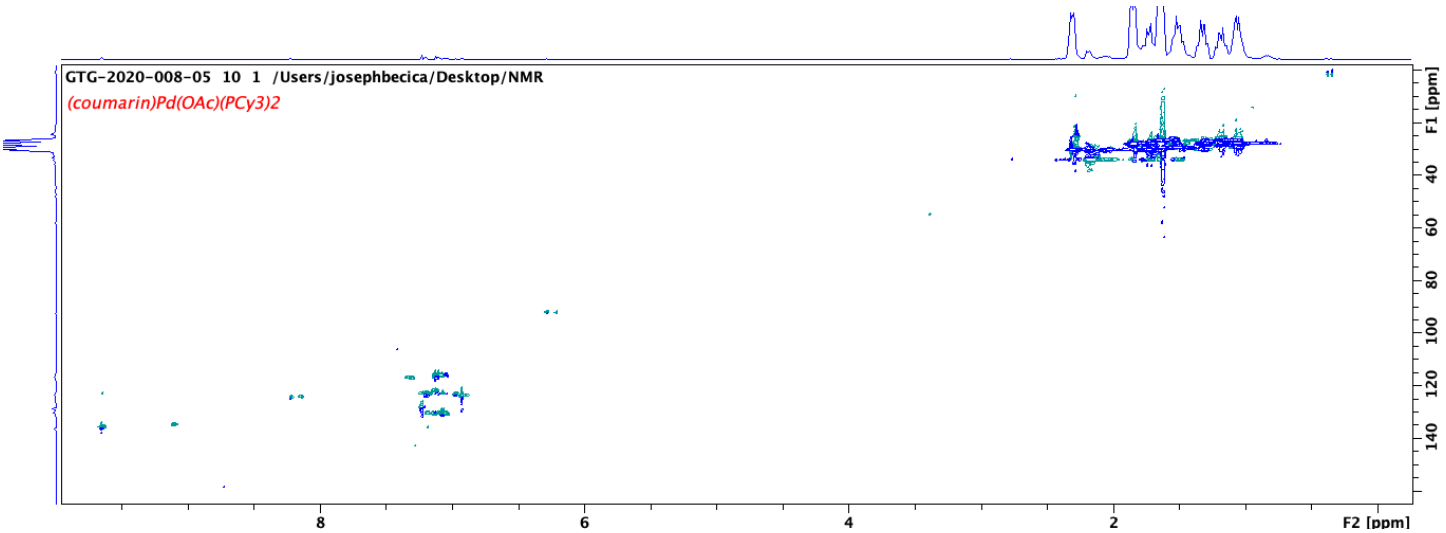


Figure S18. $^{1}H/^{13}C$ HSQC spectra (C_6D_6, 292 K, 500 MHz) of **2c**

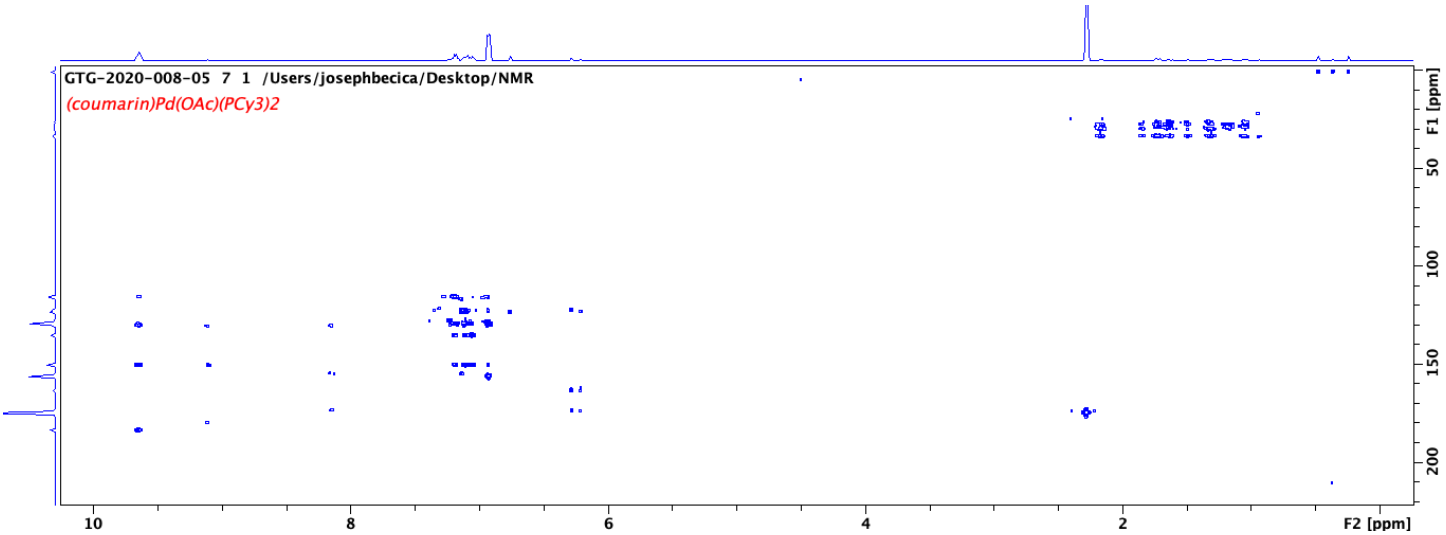


Figure S19. $^{1}H/^{13}C$ HMBC spectra (C_6D_6, 292 K, 500 MHz) of **2c**

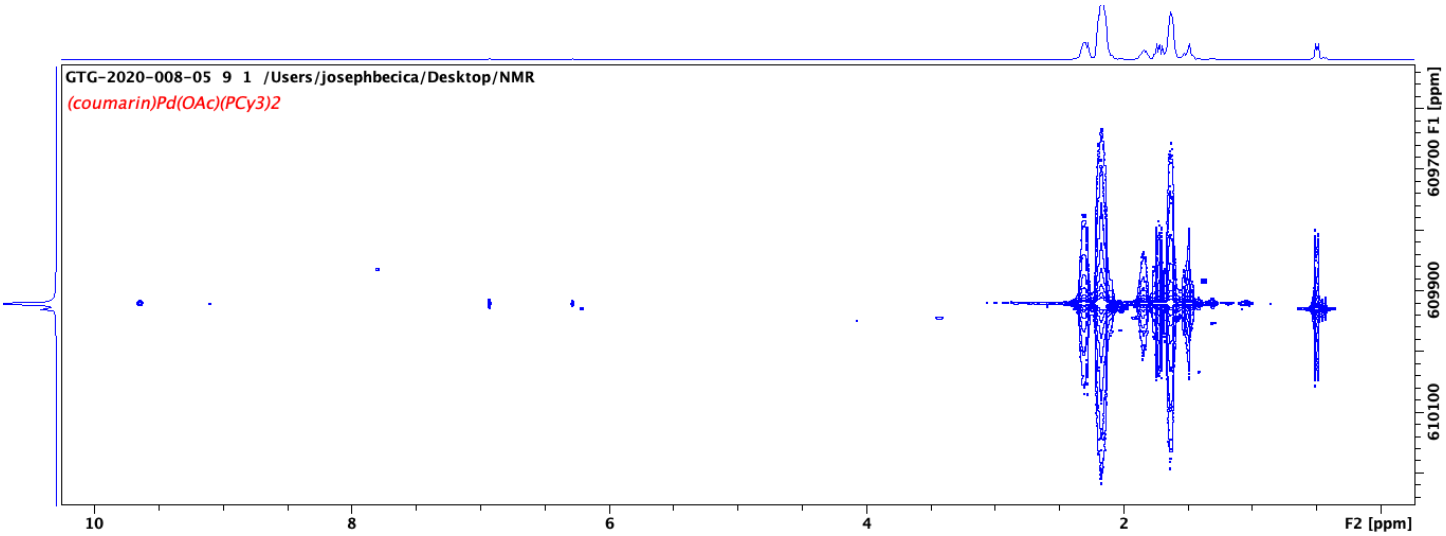
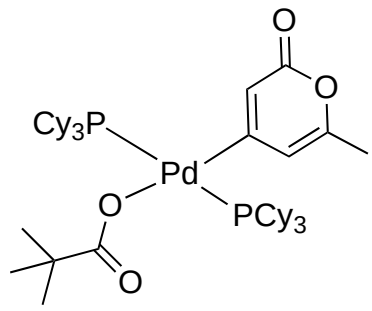


Figure S20. $^{1}H/^{31}P$ HMBC spectra (C_6D_6, 292 K, 500 MHz) of **2c**



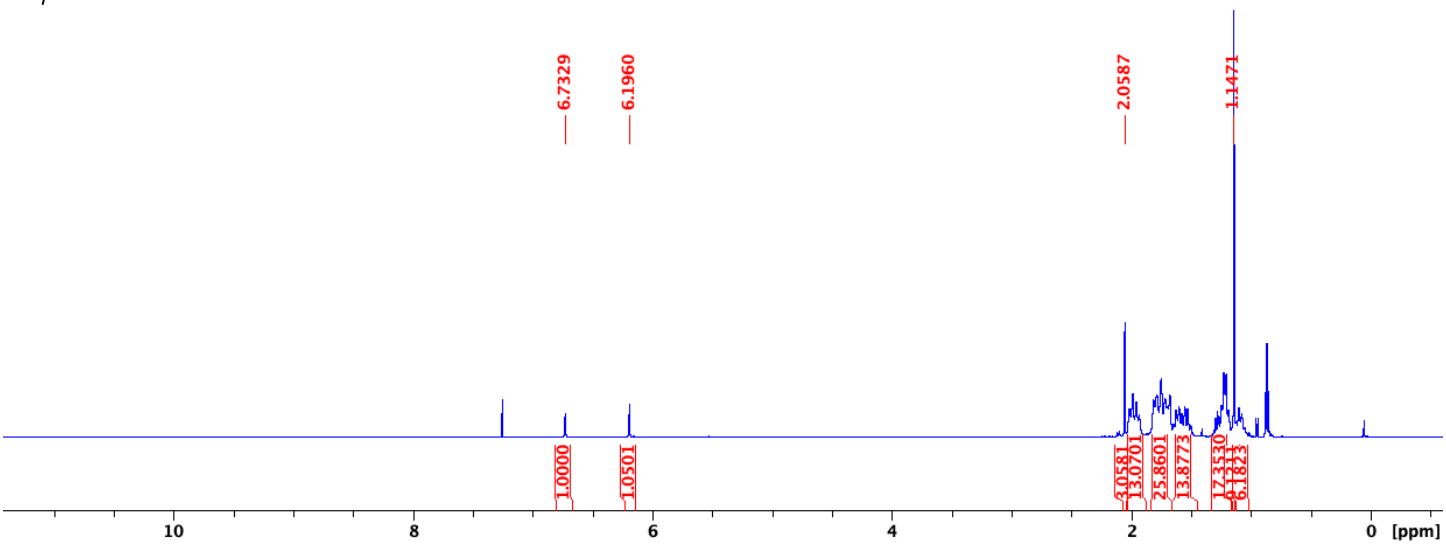


Figure S21. ^{1}H spectra ($CDCl_3$, 292 K, 500 MHz) of **3c**

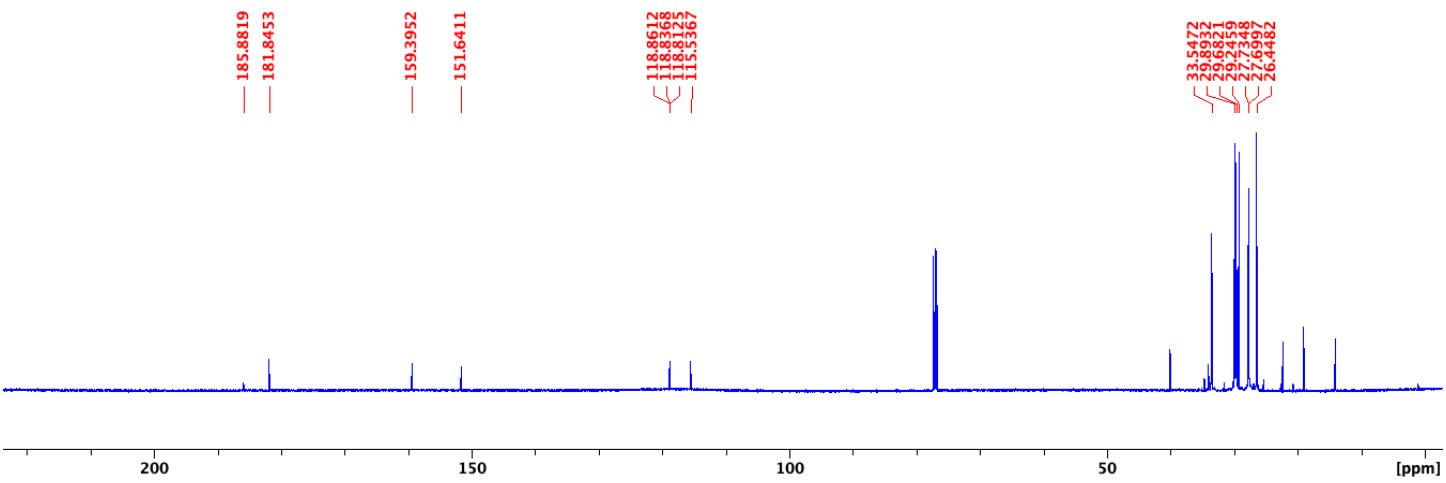


Figure S22. ^{13}C spectra ($CDCl_3$, 292 K, 126 MHz) of **3c**

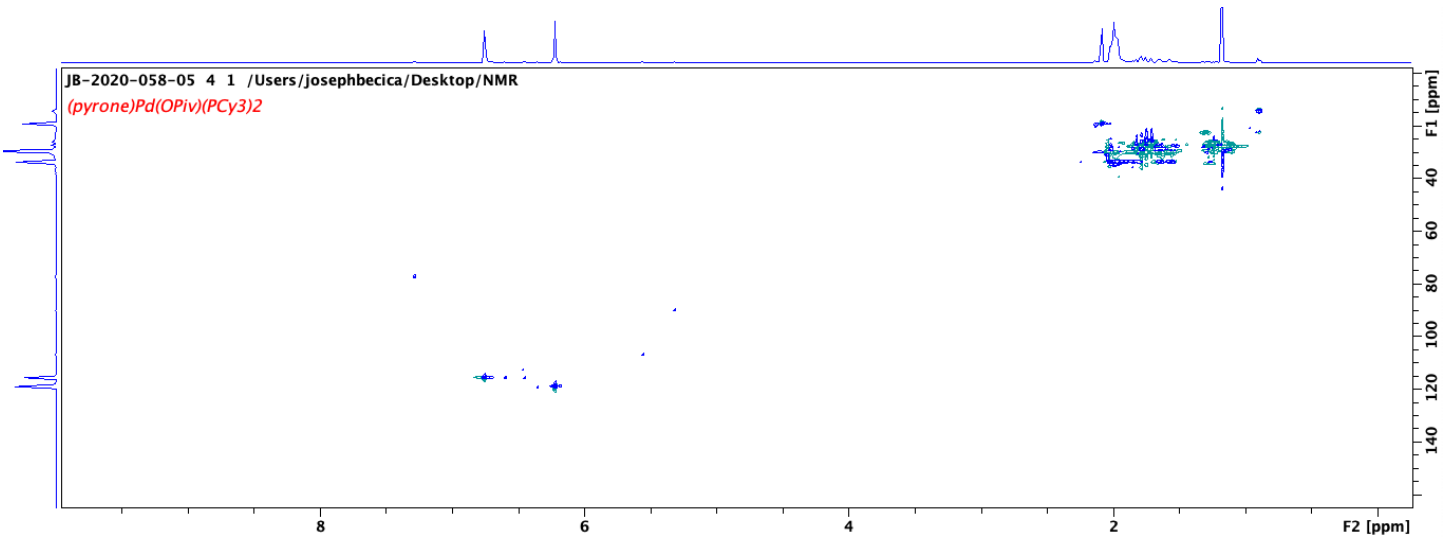


Figure S23. $^{1}H/^{13}C$ HSQC spectra ($CDCl_3$, 292 K, 500 MHz) of **3c**

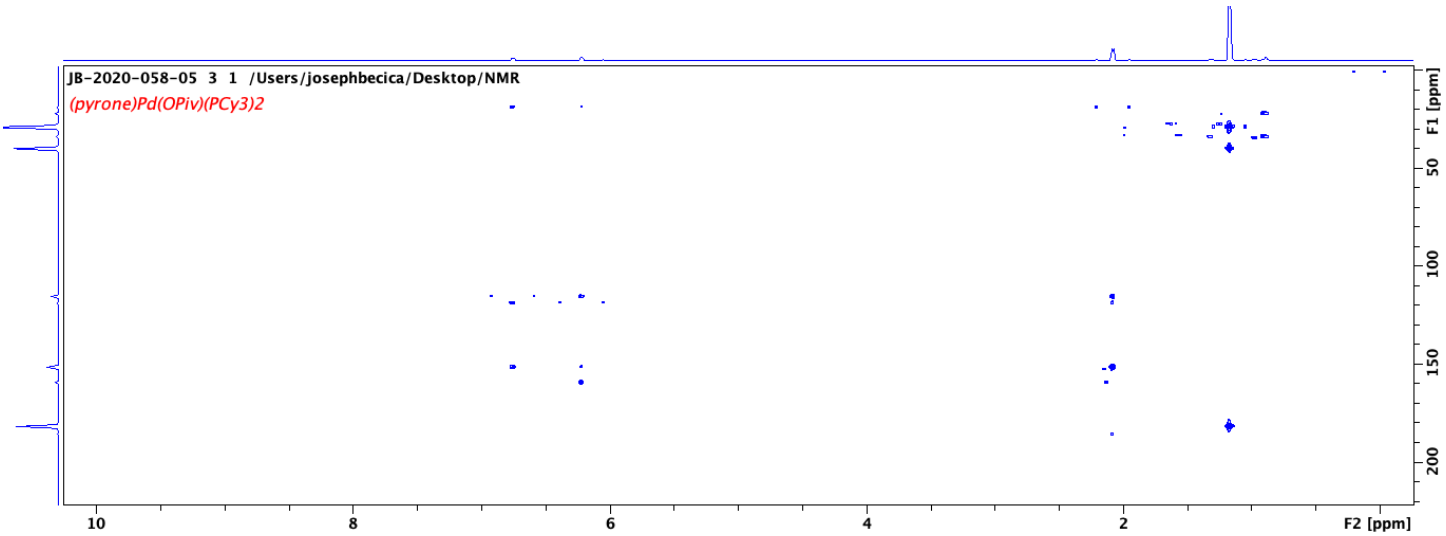


Figure S24. $^{1}H/^{13}C$ HMBC spectra ($CDCl_3$, 292 K, 500 MHz) of **3c**

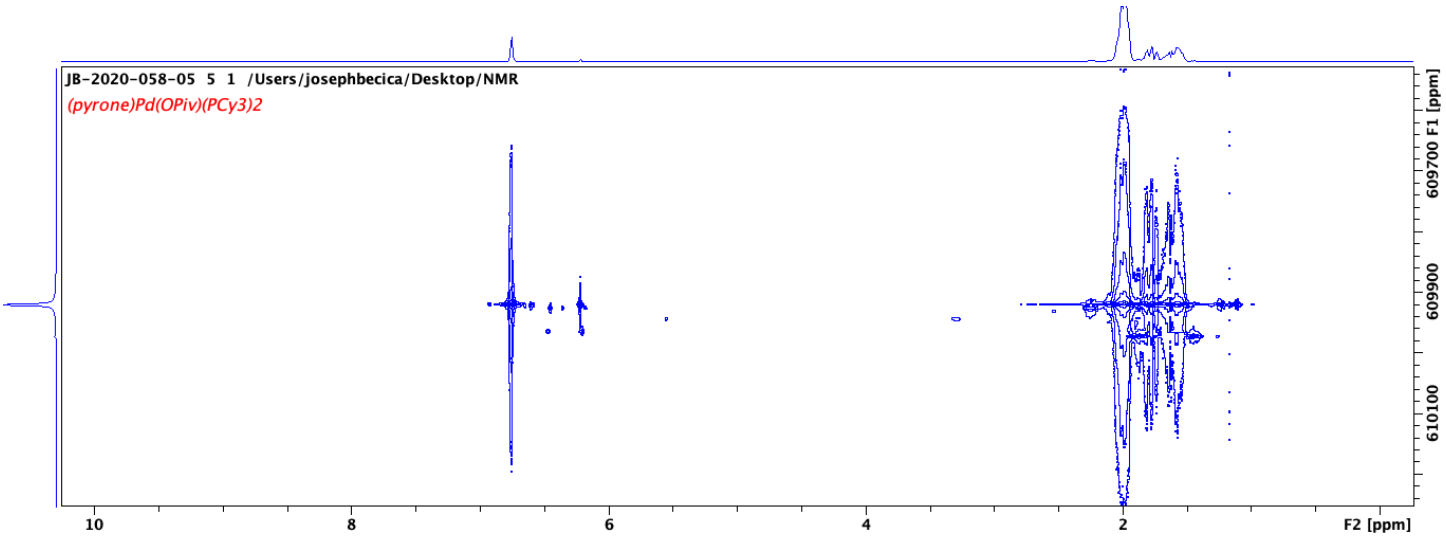


Figure S25. $^{1}H/^{31}P$ HMBC spectra ($CDCl_3$, 292 K, 500 MHz) of **3c**

V. HRMS Spectra

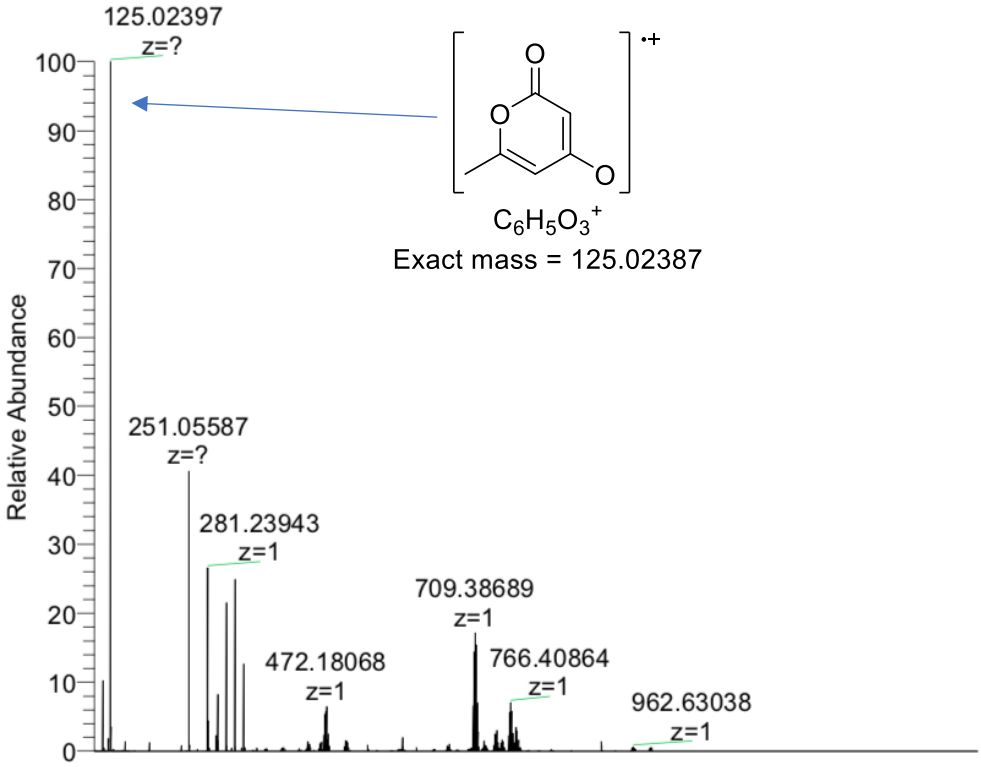


Figure S26. HRMS (ESI) spectrum of **1b**

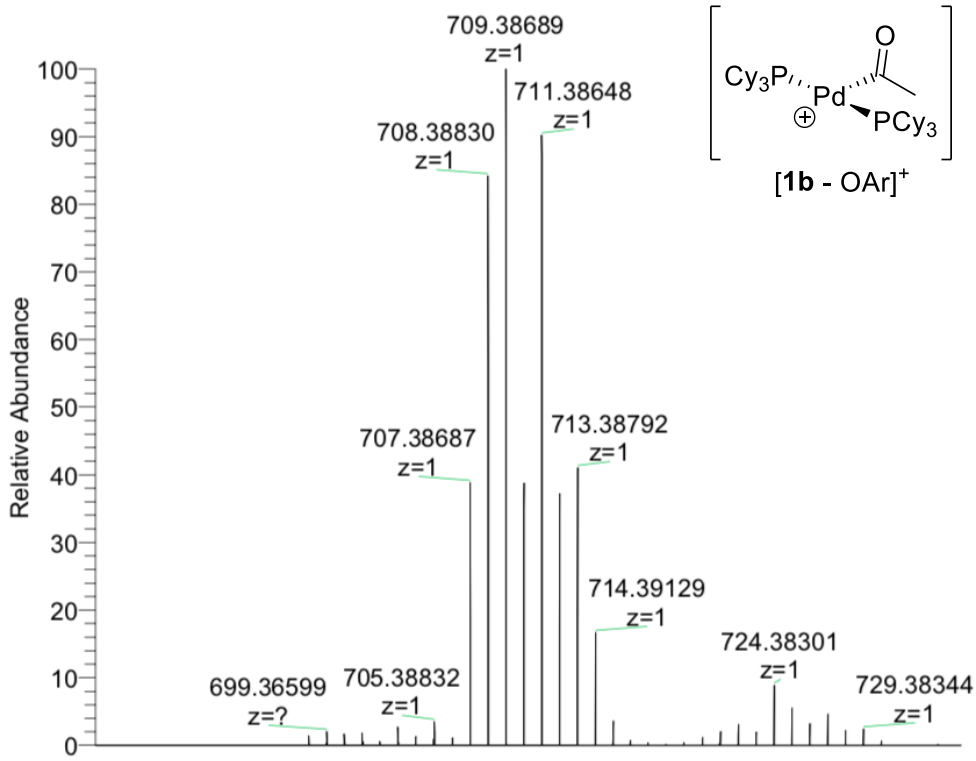


Figure S27. Expansion of HRMS (ESI) spectrum, showing isotope pattern for [**1b** – OAr]$^+$

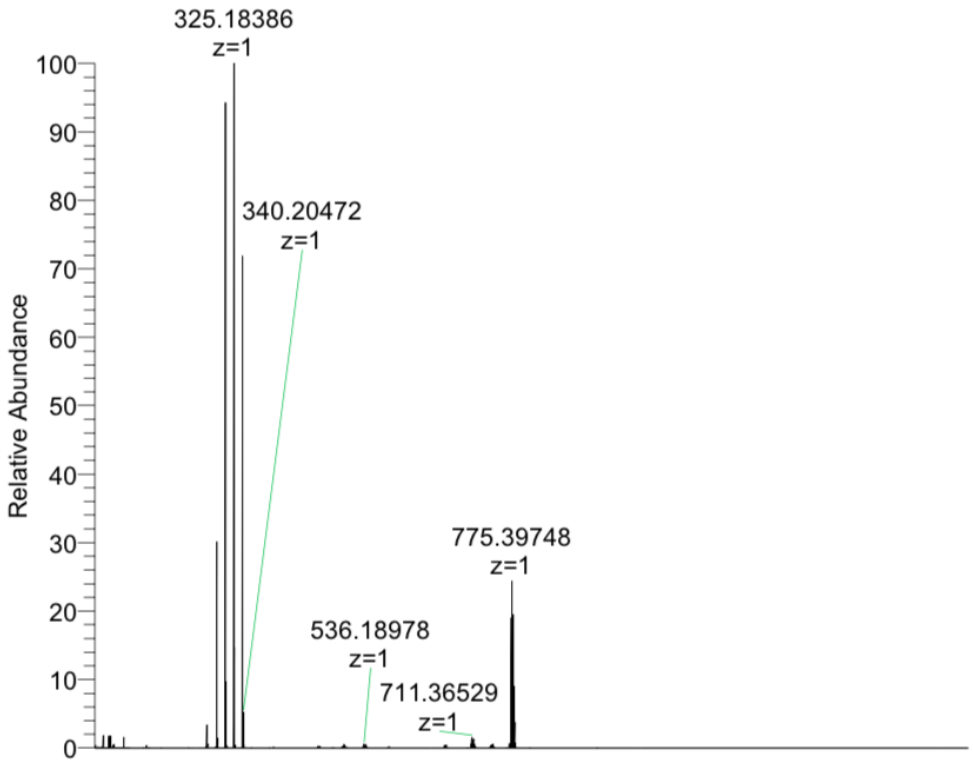


Figure S28. HRMS (ESI) spectrum of **1c**

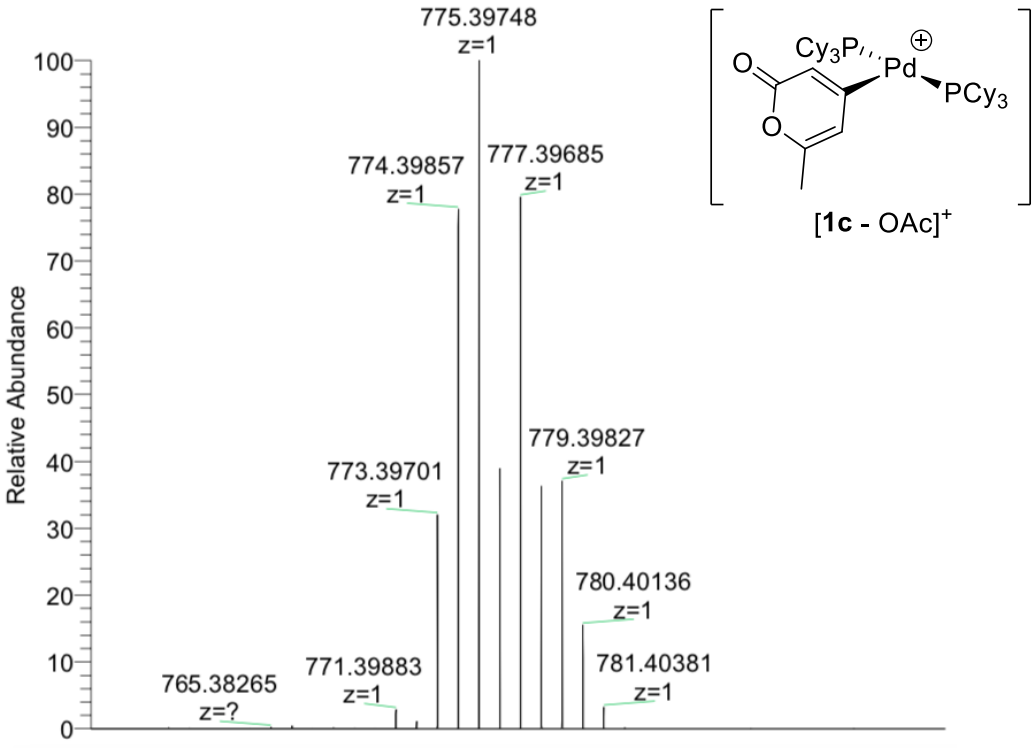


Figure S29. Expansion of HRMS (ESI) spectrum, showing isotope pattern for [**1c** – OAc]$^+$

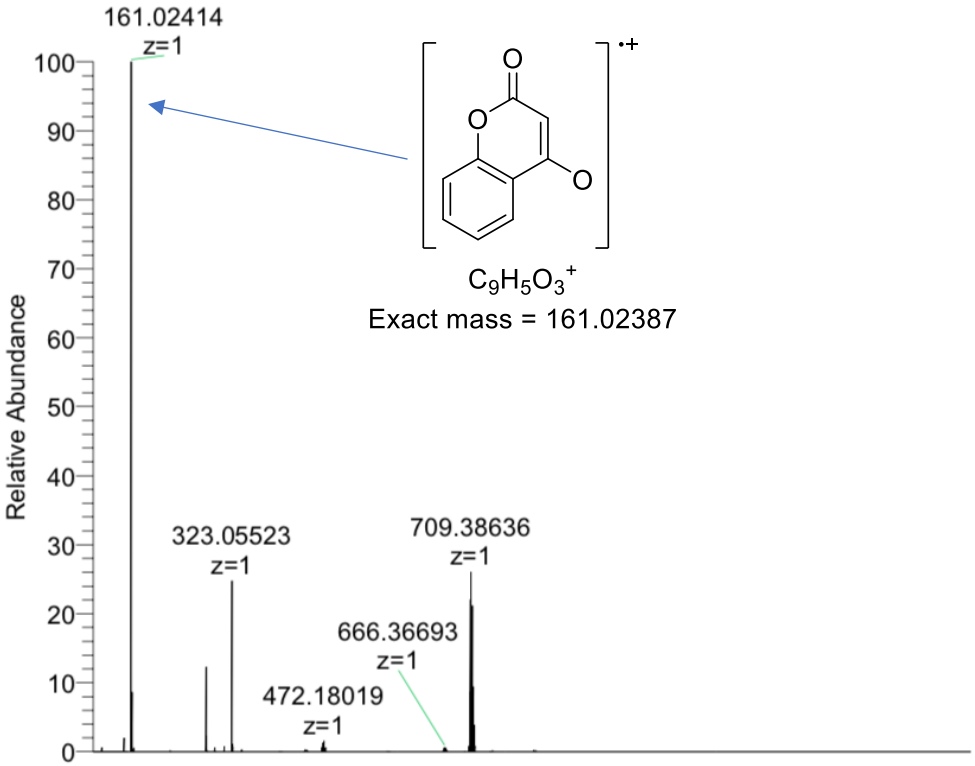


Figure S30. HRMS (ESI) spectrum of **2b**

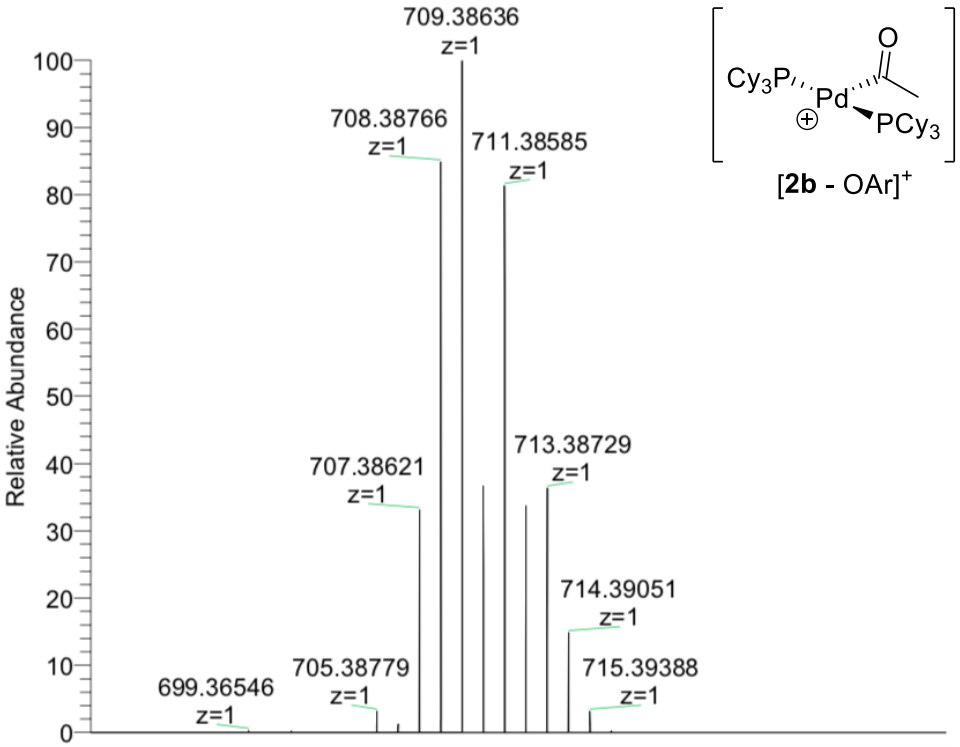


Figure S31. Expansion of HRMS (ESI) spectrum, showing isotope pattern for [**2b** – OAr]$^+$

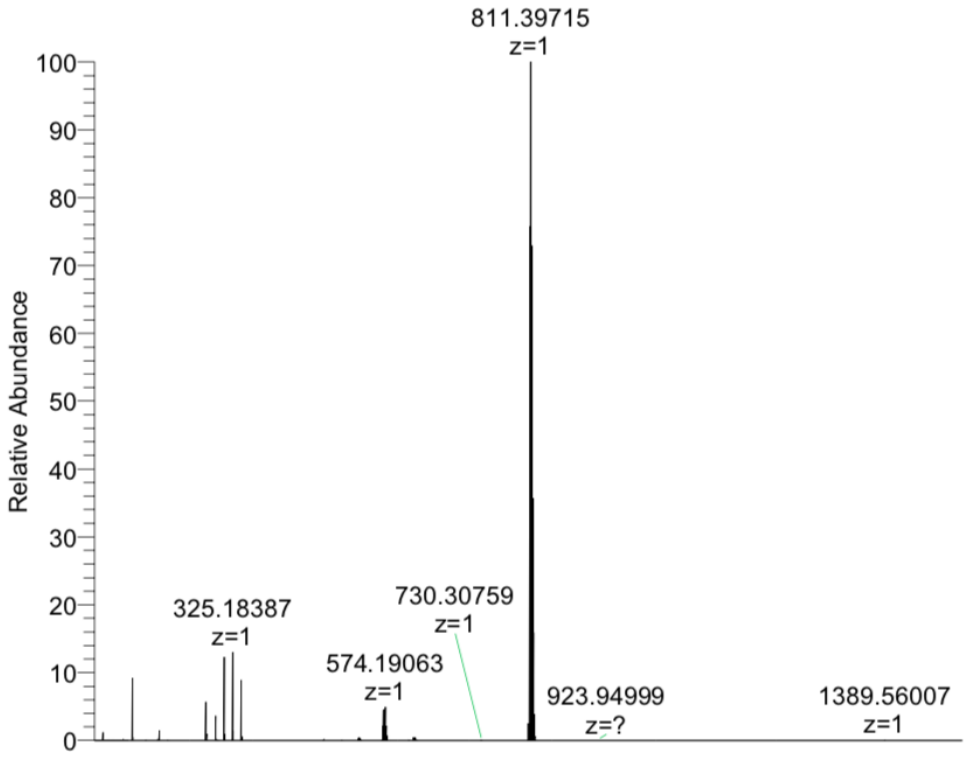


Figure S32. HRMS (ESI) spectrum of **2c**

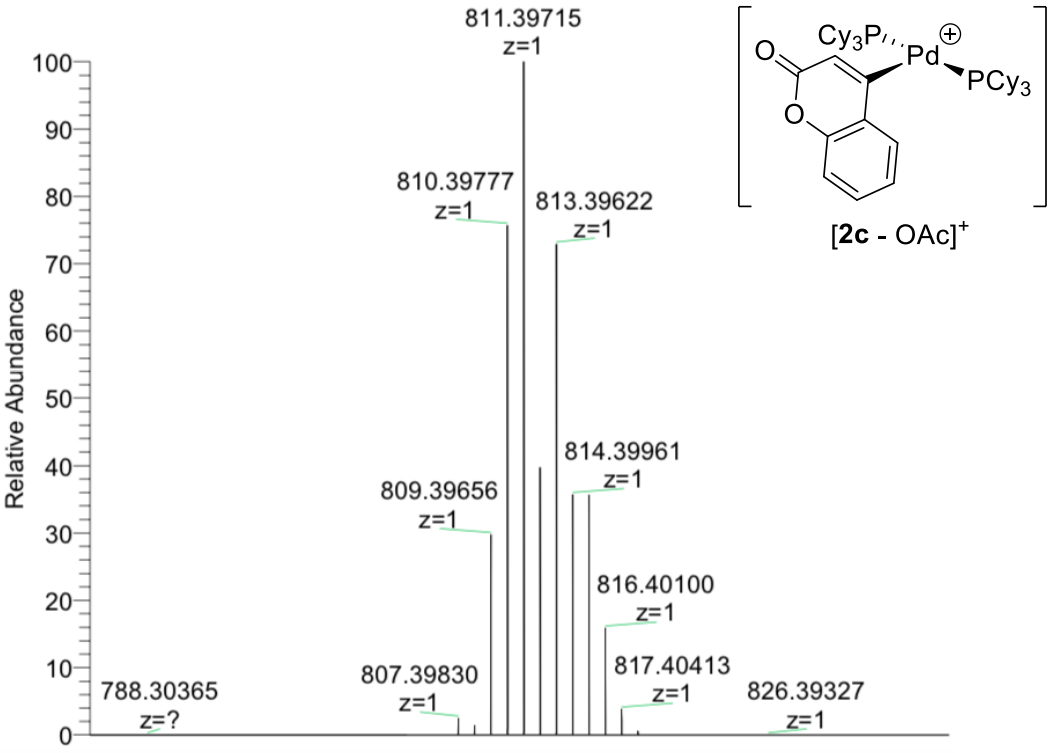


Figure S33. Expansion of HRMS (ESI) spectrum, showing isotope pattern for [**2c** – OAc]$^+$

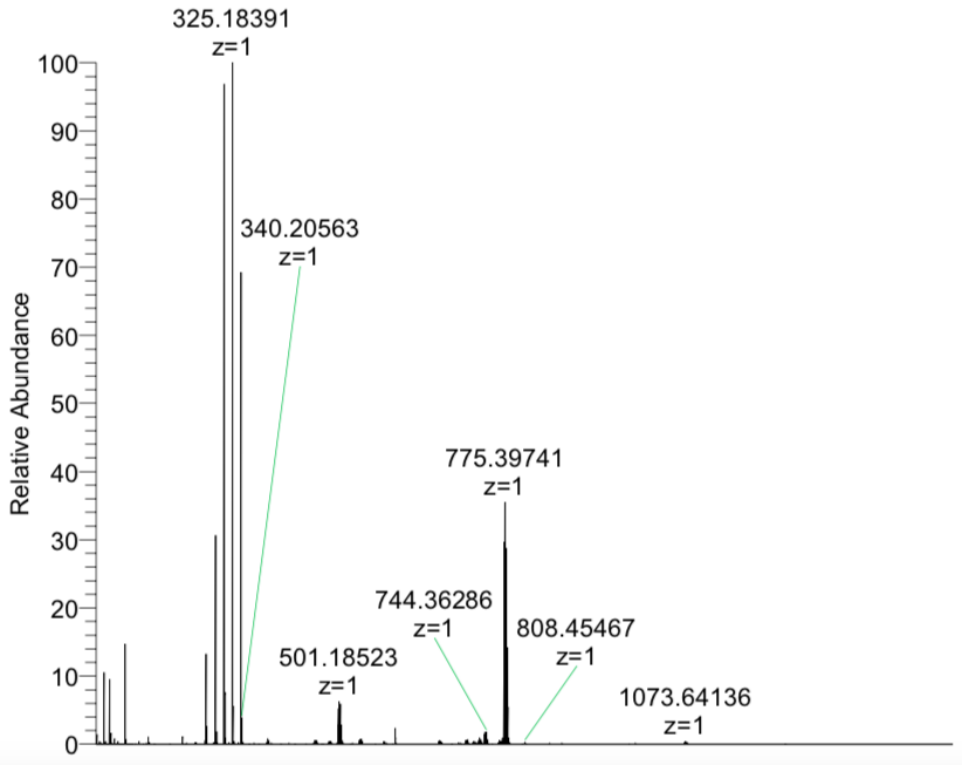


Figure S34. HRMS (ESI) spectrum of **3c**

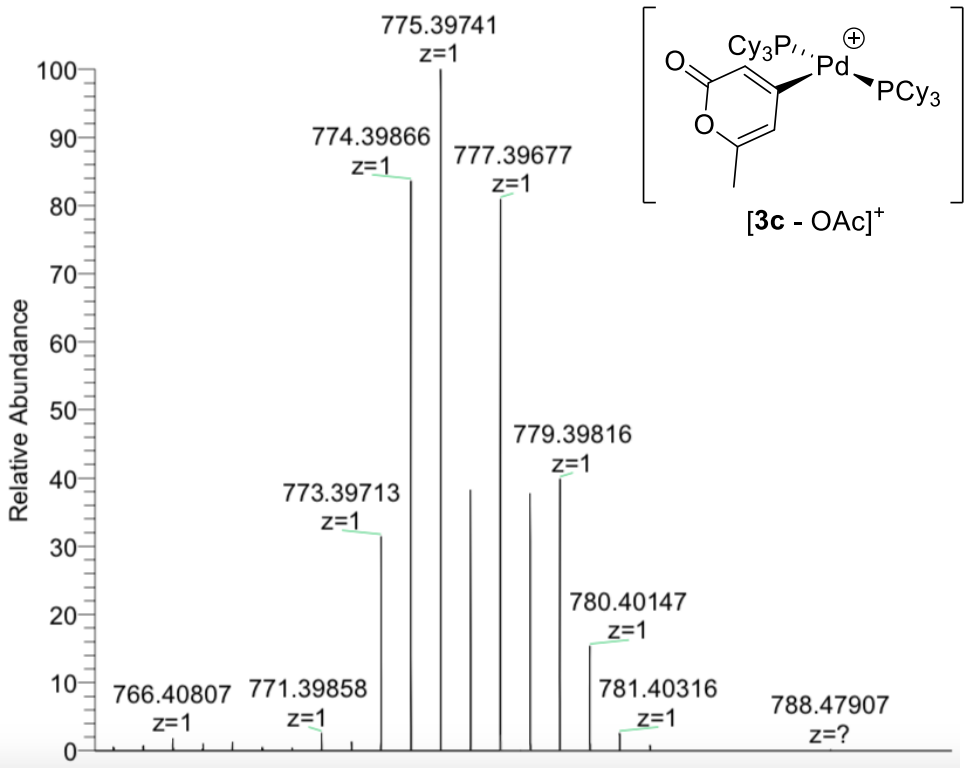


Figure S35. Expansion of HRMS (ESI) spectrum, showing isotope pattern for [**3c** – OAc]$^+$

VI. X-ray crystallography details

Crystal Report for 1c (CCDC 1989738)

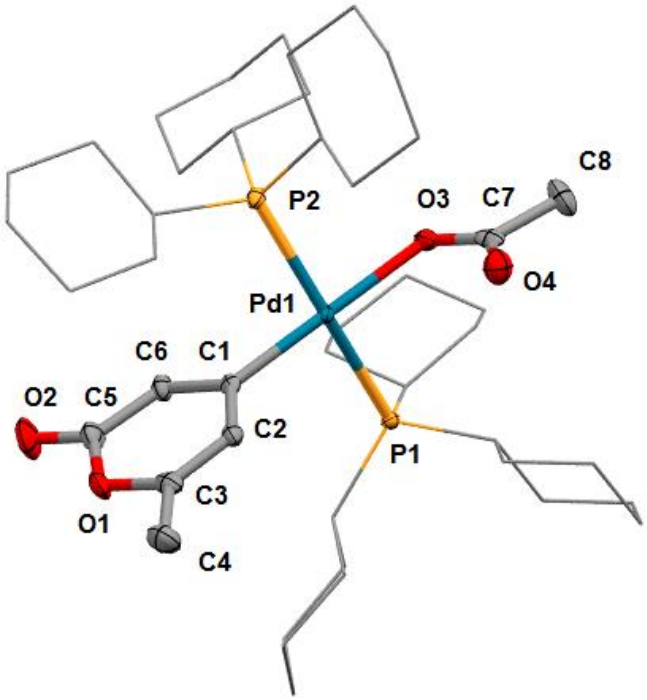


Figure S36. Thermal ellipsoid plot for **1c**. Ellipsoids shown at 50% probability. Cyclohexyl rings are shown in wireframe, and hydrogen atoms are hidden for clarity.

Experimental

A single crystal of $C_{44}H_{74}O_4P_2Pd$ (**1c**) was selected using a MitEGen loop using paratone oil and mounted on a Bruker APEX-II CCD diffractometer. The crystal was kept at 100.04 K during data collection. Using Olex2,[3] the structure was solved with the ShelXS structure solution program using Direct Methods[4] and refined with the XL refinement package using Least Squares minimisation.[5]

Crystal structure determination of 1c

Crystal Data for $C_{44}H_{74}O_4P_2Pd$ (M =835.37 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 11.5817(11) Å, b = 17.9358(17) Å, c = 21.123(2) Å, V = 4387.9(7) Å^3, Z = 4, T = 100.04 K, μ(MoKα) = 0.534 mm^{-1}, $Dcalc$ = 1.265 g/cm^3, 86378 reflections measured (2.978° ≤ 2Θ ≤ 55.738°), 10479 unique (R_{int} = 0.0303, R_{sigma} = 0.0183) which were used in all calculations. The final R_1 was 0.0190 (I > 2σ(I)) and wR_2 was 0.0435 (all data).

Table S1 Crystal data and structure refinement for 1c.

Identification code	1c
Empirical formula	$C_{44}H_{74}O_4P_2Pd$
Formula weight	835.37
Temperature/K	100.04
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	11.5817(11)
b/Å	17.9358(17)
c/Å	21.123(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4387.9(7)
Z	4
ρ_{calc}g/cm^3	1.265
μ/mm^{-1}	0.534
F(000)	1784.0
Crystal size/mm^3	0.2 × 0.15 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.978 to 55.738
Index ranges	-15 ≤ h ≤ 15, -23 ≤ k ≤ 23, -27 ≤ l ≤ 27
Reflections collected	86378
Independent reflections	10479 [R_{int} = 0.0303, R_{sigma} = 0.0183]
Data/restraints/parameters	10479/0/463
Goodness-of-fit on F^2	1.068
Final R indexes [I>=2σ (I)]	R_1 = 0.0190, wR_2 = 0.0428
Final R indexes [all data]	R_1 = 0.0209, wR_2 = 0.0435
Largest diff. peak/hole / e Å^{-3}	0.64/-0.28
Flack parameter	0.410(13)

Table S2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 1c (15). U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Pd1	7234.1(2)	6097.3(2)	5968.8(2)	9.82(4)
P1	7300.8(5)	6936.6(3)	6830.9(2)	10.10(9)
P2	7425.6(4)	5127.9(3)	5220.7(2)	12.26(11)
O1	3520.2(14)	5203.6(10)	6595.6(8)	23.6(4)
O3	8855.2(12)	6506.2(9)	5689.4(8)	17.5(3)
O4	8201.6(15)	7392.6(10)	5033.0(8)	27.8(4)
O2	4289.4(18)	4245.4(11)	7113.3(10)	39.5(5)
C9	8583.2(17)	6712.3(12)	7321.2(10)	11.9(4)
C39	6184.0(19)	4479.2(12)	5128.8(11)	17.1(4)
C1	5727.1(18)	5703.8(12)	6256.4(10)	14.6(4)
C21	6086.7(17)	6892.7(12)	7412.8(10)	12.8(4)
C11	10703.2(18)	6799.6(13)	7541.9(11)	18.7(5)
C15	7576.2(16)	7907.9(11)	6587.9(9)	12.2(4)
C2	4688.1(16)	6071.5(13)	6040.5(10)	15.4(4)
C12	10761.1(18)	5968.0(13)	7694.4(11)	19.4(5)
C14	8620.8(18)	5871.0(12)	7459.2(11)	15.0(4)
C33	7902.2(18)	5498.8(11)	4447.9(9)	13.0(4)
C10	9754.5(17)	6969.1(12)	7056.4(11)	14.9(4)
C20	6703.6(19)	8231.3(12)	6113.1(10)	18.1(5)
C35	8766(2)	5308.3(13)	3368.1(11)	20.7(5)
C22	6353.4(18)	7054.6(13)	8116(1)	17.6(4)
C26	5044.0(17)	7367.9(12)	7203(1)	14.9(4)
C17	8195(2)	9201.5(13)	6894.4(12)	23.6(5)
C5	4482(2)	4804.4(14)	6810.3(12)	23.8(5)
C19	7126(2)	8988.9(12)	5870.7(10)	22.9(5)
C44	5125.0(19)	4836.5(14)	4811.8(11)	20.0(5)
C34	8211.3(19)	4919.3(12)	3939.6(10)	17.1(4)
C40	6398(2)	3699.6(13)	4839.5(12)	23.9(5)
C36	7981(2)	5907.7(12)	3094.9(10)	21.3(5)
C16	7790(2)	8446.8(11)	7141.9(10)	16.0(4)
C6	5589.8(19)	5100.5(13)	6640.1(10)	17.3(4)
C18	7340(2)	9528.1(12)	6420.8(11)	25.8(5)
C38	7081.4(17)	6089.4(13)	4175.9(9)	17.0(4)
C37	7629(2)	6474.5(12)	3602.2(10)	20.7(5)
C13	9589.2(18)	5683.2(13)	7929.9(11)	19.3(5)
C25	3985.1(18)	7192.7(14)	7611.3(12)	20.8(5)
C8	10196(2)	7386.7(17)	5331.4(13)	30.2(6)
C27	8602.2(19)	4487.8(12)	5467.8(11)	18.1(4)
C7	8968.1(18)	7072.3(13)	5341(1)	17.7(5)
C24	4238(2)	7347.7(14)	8309.5(12)	23.4(5)

C23	5286(2)	6897.5(14)	8526.6(11)	22.4(5)
C43	4049(2)	4353.9(16)	4932.4(13)	29.4(6)
C31	10718(2)	4263.4(17)	5664.1(16)	38.0(7)
C3	3639.7(19)	5824.6(14)	6212.0(11)	20.6(5)
C41	5321(2)	3210.7(15)	4937.5(13)	32.3(6)
C32	9805(2)	4846.1(14)	5474.2(13)	26.5(5)
C4	2516.5(18)	6158.1(15)	6033.8(12)	30.0(5)
C28	8328(2)	4145.5(14)	6119.6(11)	25.4(5)
C42	4223(2)	3565.7(16)	4673.8(13)	34.3(7)
C29	9256(3)	3585.3(16)	6322.3(14)	40.3(7)
C30	10459(3)	3927(2)	6307.2(15)	47.0(8)

Table S3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 1c (15). 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	11.17(6)	8.96(6)	9.32(6)	-0.52(6)	0.52(6)	-1.88(6)
P1	9.7(2)	9.5(2)	11.1(2)	-1.02(18)	-0.1(2)	0.5(2)
P2	15.9(3)	10.0(2)	10.8(2)	-1.02(19)	-0.03(18)	-1.60(18)
O1	20.5(8)	25.7(9)	24.7(9)	1.9(7)	7.6(7)	-9.3(7)
O3	13.7(7)	19.3(8)	19.6(8)	-5.5(7)	2.9(6)	-1.8(6)
O4	29.0(9)	26.2(9)	28.3(9)	5.5(8)	-3.0(7)	-1.3(7)
O2	40.1(11)	33.1(11)	45.4(13)	17.9(10)	9.6(9)	-12.9(9)
C9	10.5(9)	13.3(10)	12(1)	-1.6(8)	-1.4(7)	1.4(7)
C39	23.6(11)	15.0(11)	12.6(10)	-2.4(9)	2.3(8)	-7.2(8)
C1	17.5(10)	15.8(11)	10.6(10)	-5.2(8)	1.9(8)	-5.7(8)
C21	11.7(9)	11.8(10)	14.8(10)	-0.9(8)	2.3(8)	0.7(7)
C11	13.0(9)	17.0(11)	26.2(12)	0.6(9)	-5.3(8)	0.5(8)
C15	12.7(10)	9.6(9)	14.4(9)	0.0(7)	0.3(7)	-0.2(7)
C2	16.4(9)	16.7(9)	13.2(10)	-2.3(10)	1.4(7)	-3.5(8)
C12	15.6(9)	19.6(13)	23.0(11)	2.7(9)	-3.8(8)	3.7(8)
C14	14.7(9)	12.9(10)	17.3(11)	2.5(8)	-1.5(8)	0.7(7)
C33	15.4(10)	12.3(9)	11.3(9)	-1.2(7)	1.8(8)	-0.8(8)
C10	12.0(9)	14.4(10)	18.3(11)	2.3(9)	-0.4(8)	0.9(8)
C20	21.4(10)	15.1(11)	17.8(12)	3.8(8)	-4.6(8)	0.6(8)
C35	26.1(11)	19.8(12)	16.3(11)	-3.2(9)	7.3(9)	-0.7(9)
C22	16.4(10)	22.4(12)	13.9(11)	-1.0(9)	1.0(8)	4.4(8)
C26	13.4(9)	13.6(10)	17.7(11)	-1.3(9)	-0.1(8)	0.4(8)
C17	31.6(12)	14.7(11)	24.5(12)	-2.7(10)	-2(1)	-6.6(9)
C5	29.3(12)	22.9(13)	19.2(12)	1.4(10)	6.2(9)	-7.7(10)
C19	31.2(11)	16.4(10)	21.0(11)	6.3(9)	-2.3(9)	-0.2(10)
C44	22.4(11)	23.7(12)	13.9(11)	-2.7(10)	1.5(9)	-7.6(9)
C34	24(1)	14.7(10)	12.5(11)	-2.4(8)	2.1(8)	1.4(8)

C40	35.5(12)	16.4(12)	19.7(12)	-3.0(9)	-1.4(10)	-8.2(9)
C36	32.1(13)	18.2(11)	13.5(10)	2.3(8)	4.5(8)	-4.8(9)
C16	19.6(9)	11.5(9)	17(1)	-3.8(8)	-2.1(9)	1.4(9)
C6	21.6(10)	16.9(11)	13.4(10)	0.6(9)	1.4(8)	-4.8(9)
C18	39.0(13)	11.3(10)	27.2(12)	2.2(9)	0.0(11)	-1.8(10)
C38	22.3(10)	15.4(9)	13.2(9)	1.5(8)	3.1(7)	3.5(9)
C37	31.3(12)	14.2(10)	16.7(10)	3.2(8)	4.3(9)	-0.4(9)
C13	19.2(10)	19.9(12)	18.9(11)	4.5(9)	-1.5(8)	2.9(8)
C25	13(1)	19.2(11)	30.1(13)	2.4(10)	4.2(9)	1.0(8)
C8	23.9(12)	41.9(17)	24.7(14)	6.0(12)	2.9(10)	-13.8(11)
C27	24.9(11)	11.3(10)	18.0(11)	-1.6(9)	-4.2(9)	3.7(8)
C7	17.7(10)	25.5(12)	9.8(10)	-7.5(9)	1.3(8)	0.9(9)
C24	21.3(11)	25.1(13)	23.8(12)	2.1(10)	10.5(9)	6.8(9)
C23	24.8(11)	25.7(13)	16.7(12)	1.1(10)	7.7(9)	5.5(10)
C43	23.8(12)	41.2(16)	23.3(13)	-2.1(12)	-0.4(10)	-13.8(11)
C31	30.5(14)	31.5(15)	51.8(19)	-7.2(14)	-13.9(13)	12.5(12)
C3	17.2(10)	27.0(12)	17.6(11)	-9.4(10)	1.2(8)	-3.5(9)
C41	51.2(17)	19.8(13)	25.9(14)	-1.2(11)	-0.2(12)	-19.9(12)
C32	21.4(11)	21.3(13)	36.9(15)	-2.7(11)	-7.3(10)	4.1(10)
C4	19.6(10)	39.0(14)	31.5(13)	-2.4(13)	4.0(9)	-0.7(9)
C28	43.9(14)	16.5(11)	15.9(12)	1.4(9)	-2.4(10)	6.6(10)
C42	39.9(15)	40.3(16)	22.7(13)	-2.6(12)	-0.2(11)	-27.1(13)
C29	68(2)	27.0(14)	25.4(15)	5.4(12)	-7.3(14)	20.4(14)
C30	55.9(18)	43.0(18)	42.2(17)	-5.1(16)	-24.1(14)	27.7(17)

Table S4 Bond Lengths for 1c (15).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1	P1	2.3639(5)	C14	C13	1.536(3)
Pd1	P2	2.3600(6)	C33	C34	1.537(3)
Pd1	O3	2.1003(15)	C33	C38	1.535(3)
Pd1	C1	1.978(2)	C20	C19	1.532(3)
P1	C9	1.855(2)	C35	C34	1.535(3)
P1	C21	1.869(2)	C35	C36	1.522(3)
P1	C15	1.844(2)	C22	C23	1.537(3)
P2	C39	1.860(2)	C26	C25	1.532(3)
P2	C33	1.847(2)	C17	C16	1.525(3)
P2	C27	1.857(2)	C17	C18	1.525(3)
O1	C5	1.400(3)	C5	C6	1.434(3)
O1	C3	1.384(3)	C19	C18	1.532(3)
O3	C7	1.261(3)	C44	C43	1.539(3)
O4	C7	1.242(3)	C40	C41	1.538(3)
O2	C5	1.210(3)	C36	C37	1.532(3)

C9	C14	1.537(3)	C38	C37	1.532(3)
C9	C10	1.538(3)	C25	C24	1.529(3)
C39	C44	1.537(3)	C8	C7	1.529(3)
C39	C40	1.546(3)	C27	C32	1.534(3)
C1	C2	1.446(3)	C27	C28	1.541(3)
C1	C6	1.361(3)	C24	C23	1.528(3)
C21	C22	1.545(3)	C43	C42	1.529(4)
C21	C26	1.543(3)	C31	C32	1.540(3)
C11	C12	1.527(3)	C31	C30	1.516(5)
C11	C10	1.533(3)	C3	C4	1.481(3)
C15	C20	1.537(3)	C41	C42	1.527(4)
C15	C16	1.538(3)	C28	C29	1.532(4)
C2	C3	1.342(3)	C29	C30	1.522(5)
C12	C13	1.533(3)			

Table S5 Bond Angles for 1c.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
P2	Pd1	P1	169.088(18)	C38	C33	C34	110.46(16)
O3	Pd1	P1	87.99(4)	C11	C10	C9	109.23(18)
O3	Pd1	P2	89.15(4)	C19	C20	C15	110.05(17)
C1	Pd1	P1	91.12(6)	C36	C35	C34	111.67(18)
C1	Pd1	P2	91.47(6)	C23	C22	C21	110.33(18)
C1	Pd1	O3	178.31(8)	C25	C26	C21	110.58(18)
C9	P1	Pd1	108.55(7)	C18	C17	C16	111.47(19)
C9	P1	C21	103.06(9)	O1	C5	C6	116.2(2)
C21	P1	Pd1	117.08(7)	O2	C5	O1	116.6(2)
C15	P1	Pd1	113.13(7)	O2	C5	C6	127.2(2)
C15	P1	C9	102.82(9)	C18	C19	C20	110.97(18)
C15	P1	C21	110.67(9)	C39	C44	C43	109.9(2)
C39	P2	Pd1	117.27(7)	C35	C34	C33	109.85(17)
C33	P2	Pd1	110.76(7)	C41	C40	C39	109.4(2)
C33	P2	C39	111.35(10)	C35	C36	C37	111.25(19)
C33	P2	C27	104.59(10)	C17	C16	C15	110.28(17)
C27	P2	Pd1	109.65(7)	C1	C6	C5	123.2(2)
C27	P2	C39	102.12(10)	C17	C18	C19	111.12(19)
C3	O1	C5	121.44(18)	C37	C38	C33	110.55(17)
C7	O3	Pd1	122.54(14)	C38	C37	C36	111.36(18)
C14	C9	P1	109.96(14)	C12	C13	C14	111.30(18)
C14	C9	C10	109.75(17)	C24	C25	C26	110.64(19)
C10	C9	P1	115.99(15)	C32	C27	P2	114.20(16)
C44	C39	P2	113.67(15)	C32	C27	C28	110.3(2)
C44	C39	C40	109.42(18)	C28	C27	P2	110.27(16)

C40	C39	P2	118.90(16)	O3	C7	C8	113.6(2)
C2	C1	Pd1	118.34(16)	O4	C7	O3	127.2(2)
C6	C1	Pd1	124.71(17)	O4	C7	C8	119.2(2)
C6	C1	C2	116.9(2)	C23	C24	C25	110.21(19)
C22	C21	P1	118.29(14)	C24	C23	C22	111.88(19)
C26	C21	P1	112.12(15)	C42	C43	C44	110.7(2)
C26	C21	C22	109.20(17)	C30	C31	C32	111.6(2)
C12	C11	C10	111.48(18)	O1	C3	C4	112.7(2)
C20	C15	P1	115.11(14)	C2	C3	O1	120.9(2)
C20	C15	C16	111.40(17)	C2	C3	C4	126.4(2)
C16	C15	P1	114.19(14)	C42	C41	C40	112.8(2)
C3	C2	C1	121.1(2)	C27	C32	C31	110.0(2)
C11	C12	C13	110.79(18)	C29	C28	C27	111.5(2)
C13	C14	C9	111.02(18)	C41	C42	C43	111.4(2)
C34	C33	P2	116.32(14)	C30	C29	C28	111.8(2)
C38	C33	P2	113.22(14)	C31	C30	C29	111.1(2)

Table S6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 1c.

Atom	*x*	*y*	*z*	U(eq)
H9	8476	6970	7737	14
H39	5928	4375	5572	20
H21	5810	6365	7401	15
H11A	11458	6965	7372	22
H11B	10549	7082	7935	22
H15	8325	7890	6353	15
H2	4749	6495	5773	19
H12A	11354	5880	8024	23
H12B	10989	5688	7310	23
H14A	7870	5710	7637	18
H14B	8749	5595	7059	18
H33	8638	5770	4537	16
H10A	9920	6705	6655	18
H10B	9732	7511	6968	18
H20A	6610	7884	5753	22
H20B	5943	8291	6321	22
H35A	9506	5537	3500	25
H35B	8936	4933	3037	25
H22A	7003	6737	8258	21
H22B	6586	7583	8165	21
H26A	5238	7903	7242	18
H26B	4866	7263	6753	18
H17A	8288	9550	7254	28

H17B	8957	9143	6688	28
H19A	7850	8920	5629	27
H19B	6541	9204	5582	27
H44A	5260	4882	4351	24
H44B	5001	5343	4985	24
H34A	8756	4549	4118	20
H34B	7505	4653	3804	20
H40A	6564	3748	4382	29
H40B	7073	3464	5045	29
H36A	7280	5671	2917	26
H36B	8386	6169	2747	26
H16A	7068	8511	7387	19
H16B	8383	8236	7428	19
H6	6261	4864	6803	21
H18A	7647	10004	6254	31
H18B	6600	9634	6638	31
H38A	6348	5850	4048	20
H38B	6905	6465	4505	20
H37A	8318	6757	3740	25
H37B	7071	6833	3419	25
H13A	9413	5912	8345	23
H13B	9627	5136	7989	23
H25A	3326	7503	7471	25
H25B	3769	6662	7557	25
H8A	10371	7613	5743	45
H8B	10258	7765	4999	45
H8C	10745	6983	5247	45
H27	8624	4070	5155	22
H24A	4390	7886	8370	28
H24B	3558	7211	8569	28
H23A	5100	6359	8506	27
H23B	5462	7023	8973	27
H43A	3894	4329	5393	35
H43B	3371	4585	4725	35
H31A	10738	3862	5342	46
H31B	11488	4502	5675	46
H41A	5445	2723	4728	39
H41B	5217	3118	5396	39
H32A	9817	5265	5779	32
H32B	9986	5046	5049	32
H4A	2027	5776	5839	45
H4B	2644	6565	5732	45
H4C	2135	6354	6413	45

H28A	8275	4548	6439	31
H28B	7570	3891	6101	31
H42A	3550	3254	4788	41
H42B	4272	3585	4206	41
H29A	9086	3409	6756	48
H29B	9233	3149	6036	48
H30A	10516	4319	6636	56
H30B	11038	3538	6404	56

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

1. Twinned data refinement
Scales: 0.590(13)
0.410(13)

2. Fixed Uiso
At 1.2 times of:
All C(H) groups, All C(H,H) groups
At 1.5 times of:
All C(H,H,H) groups

3.a Ternary CH refined with riding coordinates:
C9(H9), C39(H39), C21(H21), C15(H15), C33(H33), C27(H27)

3.b Secondary CH2 refined with riding coordinates:
C11(H11A,H11B), C12(H12A,H12B), C14(H14A,H14B), C10(H10A,H10B), C20(H20A, H20B), C35(H35A,H35B), C22(H22A,H22B), C26(H26A,H26B), C17(H17A,H17B), C19(H19A,H19B), C44(H44A,H44B), C34(H34A,H34B), C40(H40A,H40B), C36(H36A,H36B), C16(H16A,H16B), C18(H18A,H18B), C38(H38A,H38B), C37(H37A,H37B), C13(H13A, H13B), C25(H25A,H25B), C24(H24A,H24B), C23(H23A,H23B), C43(H43A,H43B), C31(H31A,H31B), C41(H41A,H41B), C32(H32A,H32B), C28(H28A,H28B), C42(H42A,H42B), C29(H29A,H29B), C30(H30A,H30B)

3.c Aromatic/amide H refined with riding coordinates:
C2(H2), C6(H6)

3.d Idealised Me refined as rotating group:
C8(H8A,H8B,H8C), C4(H4A,H4B,H4C)

Crystal report for 2b (CCDC 1989739)

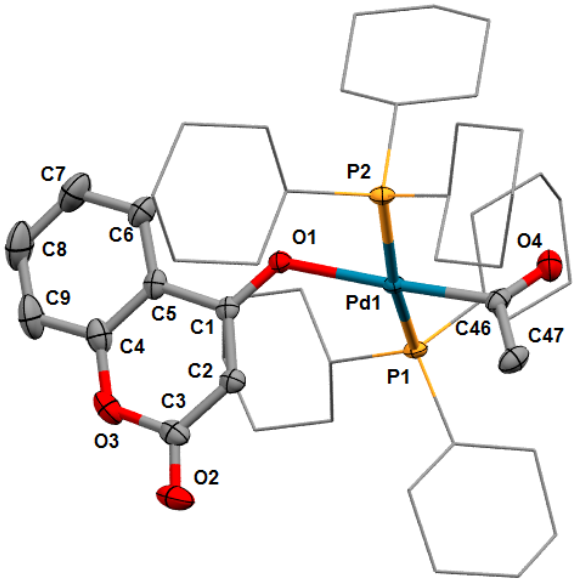


Figure S37. Thermal ellipsoid plot for **2b**. Ellipsoids shown at 50% probability. Cyclohexyl rings are shown in wireframe, hydrogen atoms, and disordered toluene solvent molecule are hidden for clarity. One cyclohexyl ring is disordered, and this figure displays one such configuration.

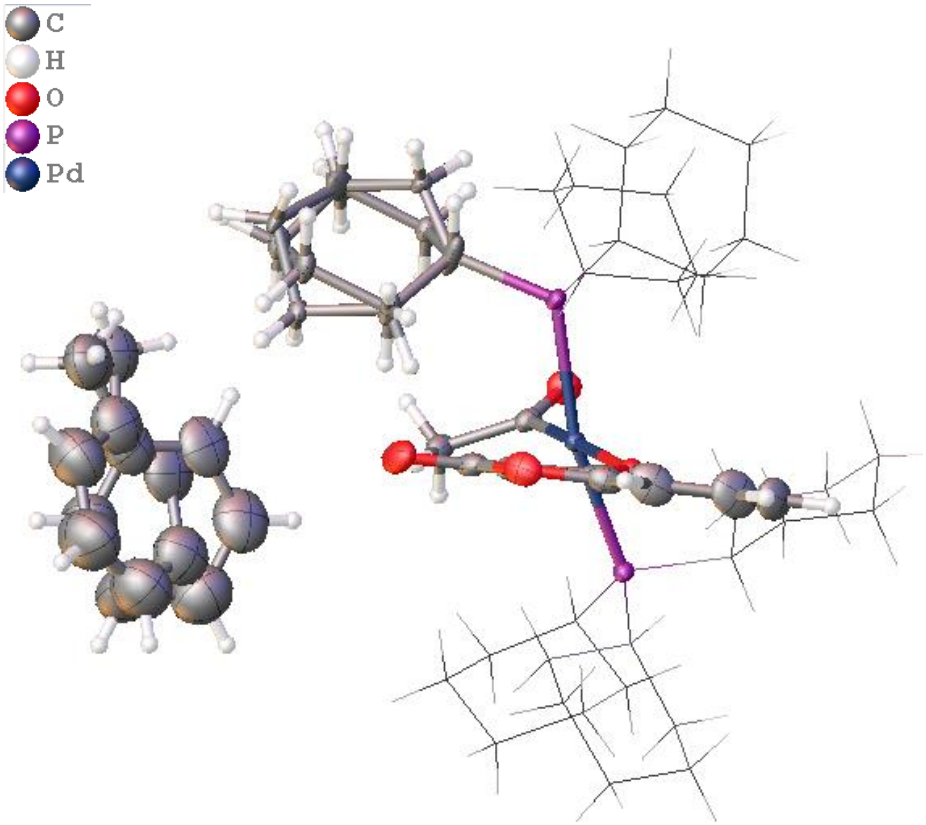


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Figure S38. Olex thermal ellipsoid plot of **2b** displaying modelled disorder for cyclohexyl ring (C22-C27) and disordered toluene solvent molecule. Ellipsoids shown at 50% probability. Other cyclohexyl rings are shown in wireframe

Experimental

Single crystals of $C_{54}H_{81.98}O_4P_2Pd$ (**2b**) were selected using a MitEGen loop using paratone oil. A suitable crystal was selected and mounted on a Bruker APEX-II CCD diffractometer. The crystal was kept at 99.95 K during data collection. Using Olex2,[3] the structure was solved with the SIR2004 structure solution program using Direct Methods[4] and refined with the XL refinement package using Least Squares minimisation.[5]

Crystal structure determination of 2b

Crystal Data for $C_{54}H_{81.98}O_4P_2Pd$ (*M* =963.51 g/mol): triclinic, space group P-1 (no. 2), *a* = 13.5548(9) Å, *b* = 13.7277(10) Å, *c* = 14.8809(10) Å, *α* = 67.8780(10)°, *β* = 74.0210(10)°, *γ* = 86.400(2)°, *V* = 2463.4(3) Å^3, *Z* = 2, *T* = 99.95 K, μ(MoKα) = 0.486 mm^{-1}, *Dcalc* = 1.299 g/cm^3, 52734 reflections measured (3.07° ≤ 2Θ ≤ 55.928°), 11753 unique (R_{int} = 0.0274, R_{sigma} = 0.0244) which were used in all calculations. The final R_1 was 0.0342 (I > 2σ(I)) and wR_2 was 0.0912 (all data).

Table S7 Crystal data and structure refinement for 2b.

Identification code	2b
Empirical formula	$C_{54}H_{81.98}O_4P_2Pd$
Formula weight	963.51
Temperature/K	99.95
Crystal system	triclinic
Space group	P-1
a/Å	13.5548(9)
b/Å	13.7277(10)
c/Å	14.8809(10)
α/°	67.8780(10)
β/°	74.0210(10)
γ/°	86.400(2)
Volume/Å^3	2463.4(3)
Z	2
ρ_{calc}g/cm^3	1.299
μ/mm^{-1}	0.486
F(000)	1028.0
Crystal size/mm^3	0.3 × 0.2 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.07 to 55.928
Index ranges	-17 ≤ h ≤ 17, -18 ≤ k ≤ 18, -19 ≤ l ≤ 17
Reflections collected	52734
Independent reflections	11753 [R_{int} = 0.0274, R_{sigma} = 0.0244]
Data/restraints/parameters	11753/276/623
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0342, wR_2 = 0.0865
Final R indexes [all data]	R_1 = 0.0419, wR_2 = 0.0912
Largest diff. peak/hole / e Å^{-3}	1.63/-0.85

Table S8 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 2b. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Pd1	7121.5(2)	2948.1(2)	3252.0(2)	13.91(5)
P1	8825.4(4)	3145.1(4)	3330.8(4)	15.42(10)
P2	5550.6(4)	3093.4(4)	2806.7(4)	16.05(11)
O1	7491.6(11)	1827.1(11)	2533.2(11)	17.9(3)
O4	6882.3(14)	4941.7(13)	3441.7(14)	30.6(4)
O3	8389.8(14)	-1199.0(13)	3690.8(15)	33.5(4)
O2	7978.0(15)	-1193.2(15)	5232.6(15)	38.4(5)
C20	10397.1(16)	4828.9(16)	2374.9(16)	18.3(4)
C36	4981.1(18)	-116.0(18)	3525.5(18)	25.0(5)
C46	6715.0(16)	3999.4(18)	3879.1(17)	20.9(4)
C35	5037.7(17)	894.9(17)	3718.7(16)	20.3(4)
C34	5181.5(16)	1858.9(16)	2729.5(16)	17.5(4)
C10	9717.7(15)	2238.9(17)	2884.6(16)	18.1(4)
C16	9272.4(16)	4527.5(16)	2557.1(16)	17.3(4)
C40	5802.2(16)	4057.0(17)	1490.6(16)	19.1(4)
C11	9912.7(16)	2504.6(17)	1748.9(16)	20.1(4)
C19	10256.5(18)	6481.8(18)	913.3(18)	25.1(5)
C18	9138.8(19)	6150.9(18)	1080.1(18)	26.1(5)
C1	7707.2(15)	866.4(16)	2946.9(16)	17.5(4)
C17	8980.8(18)	4952.0(18)	1553.5(17)	23.8(5)
C28	4436.3(16)	3618.2(17)	3497.1(16)	19.4(4)
C41	6666.5(17)	3726.8(18)	765.1(16)	22.7(4)
C5	8075.3(16)	270.5(17)	2288.2(18)	21.8(4)
C12	10488.5(17)	1629.5(18)	1443.9(18)	23.0(4)
C39	4285.5(17)	1886.6(18)	2276.4(18)	22.8(4)
C38	4234.4(18)	877.9(19)	2080.5(18)	26.2(5)
C33	3943.7(17)	2822.9(18)	4568.3(17)	23.5(5)
C29	3586.8(18)	4068(2)	2970.6(19)	27.0(5)
C42	6849.1(18)	4535.3(19)	-312.7(17)	25.8(5)
C21	10557.0(17)	6031.6(17)	1901.5(17)	21.3(4)
C2	7641.0(16)	341.4(17)	3956.8(17)	20.8(4)
C43	7097.9(18)	5633(2)	-383.2(18)	28.8(5)
C30	2804.7(18)	4602(2)	3573(2)	30.2(5)
C6	8139.3(19)	697(2)	1258.1(19)	29.9(5)
C45	6040.1(18)	5168.7(18)	1422.8(17)	23.8(5)
C37	4119.0(19)	-99.1(19)	3040.9(19)	27.4(5)
C47	6134.3(18)	3563(2)	4991.7(18)	27.4(5)
C27	8513(2)	1869.4(17)	5355.5(17)	24.8(5)
C13	11494.8(18)	1427.6(19)	1734.3(19)	27.3(5)
C4	8419.6(18)	-736.1(19)	2695(2)	29.5(5)

C15	10742.2(17)	2066.1(19)	3163.3(19)	25.6(5)
C3	7984.4(18)	-689.8(18)	4359.3(19)	26.5(5)
C31	2341.2(19)	3844(2)	4657(2)	35.3(6)
C44	6253.0(19)	5973.1(19)	339.4(18)	27.8(5)
C32	3179.1(19)	3366(2)	5174.2(19)	30.4(5)
C7	8543(3)	128(3)	661(2)	46.4(7)
C14	11307.7(18)	1194(2)	2853(2)	28.7(5)
C22	9035(3)	2927.5(19)	4565.8(19)	37.6(7)
C26	8799(4)	1630(3)	6354(2)	25.2(11)
C24	9188(2)	3495(3)	5924(2)	40.9(7)
C9	8827(2)	-1307(2)	2094(3)	47.1(8)
C8	8883(3)	-871(3)	1087(3)	55.0(9)
C25	8569(3)	2548(3)	6702(2)	24.5(10)
C23	8859(2)	3819(2)	4907(2)	19.4(8)
C53	5467(3)	1901(4)	8800(3)	79.1(10)
C52	5450(3)	2712(3)	7897(3)	78(1)
C51	4594(4)	2814(3)	7531(3)	95.0(13)
C50	3755(3)	2105(4)	8069(4)	108.7(15)
C49	3772(3)	1294(4)	8971(4)	111.9(15)
C48	4628(4)	1192(3)	9337(3)	99.3(13)
C54	6462(6)	1782(7)	9191(5)	88.9(13)
C23A	9628(6)	3396(6)	4891(6)	17(2)
C26A	8121(8)	1747(6)	6499(6)	17(2)
C25A	9066(7)	2099(7)	6691(6)	19(2)
C54A	6382(18)	2455(19)	8903(18)	83.9(17)
C53A	5780(11)	1738(13)	8910(12)	87.9(14)
C52A	5119(12)	2299(10)	8350(11)	80.4(14)
C51A	4329(11)	1771(13)	8263(11)	91.8(15)
C50A	4201(12)	682(13)	8735(14)	114.4(18)
C49A	4862(15)	121(10)	9295(13)	119.1(19)
C48A	5652(13)	649(13)	9382(11)	105.8(17)

Table S9 Anisotropic Displacement Parameters ($Å^2×10^3$) for 2b. 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	12.48(8)	16.18(8)	12.97(8)	-4.82(6)	-4.14(5)	0.33(5)
P1	15.7(2)	18.1(2)	13.0(2)	-4.0(2)	-6.77(19)	-1.51(19)
P2	12.6(2)	20.3(2)	13.6(2)	-3.9(2)	-4.37(19)	0.48(19)
O1	17.2(7)	19.0(7)	18.9(7)	-7.4(6)	-6.9(6)	1.3(5)
O4	34.7(10)	25.1(8)	35.3(10)	-15.4(8)	-9.4(8)	3.5(7)
O3	29.8(9)	21.8(8)	44.2(11)	-7.4(8)	-11.1(8)	7.0(7)
O2	41.0(11)	32.1(10)	37.3(11)	2.2(8)	-23.8(9)	-2.3(8)

C20	15.8(9)	21.2(10)	18.4(10)	-7.0(8)	-5.3(8)	-2.3(8)
C36	26.6(11)	23.5(11)	24.4(12)	-7.4(9)	-8.1(9)	0.6(9)
C46	16.8(10)	29.0(11)	22.4(11)	-13.8(9)	-8.4(8)	4.0(8)
C35	20(1)	22.2(10)	17.2(10)	-4.8(8)	-6.1(8)	-0.2(8)
C34	14.8(9)	21.2(10)	15.7(10)	-4.6(8)	-5.2(8)	-1.8(7)
C10	13.5(9)	20.5(10)	19.2(10)	-4.5(8)	-6.9(8)	0.9(7)
C16	16.5(9)	18.3(9)	15.7(10)	-1.9(8)	-7.8(8)	-2.2(7)
C40	15.2(9)	23.6(10)	14(1)	-1.1(8)	-5.4(8)	-0.1(8)
C11	18.2(10)	23(1)	18.5(10)	-5.8(8)	-6.8(8)	0.2(8)
C19	28.6(12)	21.6(10)	22.0(11)	-3.3(9)	-7.4(9)	-6.8(9)
C18	30.4(12)	23.4(11)	21.7(11)	0.1(9)	-14(1)	-3.4(9)
C1	11.6(9)	20.1(10)	22.6(11)	-9.2(8)	-5.6(8)	-0.8(7)
C17	25.9(11)	23.7(11)	19.8(11)	0.3(9)	-13.4(9)	-6.5(9)
C28	13.4(9)	23.7(10)	19.2(10)	-5.7(8)	-4.9(8)	2.7(8)
C41	19.6(10)	27.9(11)	16.1(10)	-3.5(9)	-4.1(8)	0.6(8)
C5	15(1)	23.5(10)	28.4(12)	-13.1(9)	-3.0(8)	-2.1(8)
C12	22.1(11)	22.3(10)	23.6(11)	-7.9(9)	-5.2(9)	-0.2(8)
C39	19.4(10)	26.4(11)	22.7(11)	-5.4(9)	-10.8(9)	-0.8(8)
C38	23.5(11)	33.9(12)	25.7(12)	-12.3(10)	-11.6(9)	-1.6(9)
C33	20.2(10)	23.2(11)	21.5(11)	-5.5(9)	-1.0(9)	0.7(8)
C29	20.5(11)	34.3(12)	28.7(12)	-12.3(10)	-11.6(9)	8.5(9)
C42	20.9(11)	34.8(12)	14.8(10)	-2.0(9)	-3.5(8)	-2.5(9)
C21	20(1)	22.5(10)	22.6(11)	-8.6(9)	-6.5(8)	-3.0(8)
C2	17.8(10)	21.6(10)	22.8(11)	-6.8(9)	-6.7(8)	-1.3(8)
C43	22.8(11)	33.9(13)	19.3(11)	2.3(10)	-5.4(9)	-6.8(9)
C30	18.8(11)	33.8(13)	37.5(14)	-12.4(11)	-9.8(10)	7.3(9)
C6	29.6(12)	35.9(13)	28.2(13)	-17.9(11)	-5.7(10)	1(1)
C45	23.6(11)	23.9(11)	20.1(11)	-3.0(9)	-7.3(9)	0.5(8)
C37	26.1(12)	27.3(11)	30.1(13)	-11(1)	-8.1(10)	-3.7(9)
C47	20.7(11)	41.1(14)	24.8(12)	-17.5(11)	-5.9(9)	2.9(10)
C27	41.9(14)	18.2(10)	16.4(10)	-5.6(8)	-12.1(10)	-0.5(9)
C13	18.5(11)	26.3(11)	33.5(13)	-9.4(10)	-4.4(9)	1.1(9)
C4	22.0(11)	25.7(11)	39.9(15)	-14.6(11)	-3.8(10)	1.0(9)
C15	17.5(10)	32.0(12)	31.0(13)	-11(1)	-14.1(9)	3.8(9)
C3	19.9(11)	25.2(11)	33.1(13)	-5.2(10)	-12.5(10)	-1.6(9)
C31	20.3(12)	34.8(13)	42.4(16)	-13.1(12)	2.4(11)	2.7(10)
C44	26.8(12)	24.9(11)	24.8(12)	1.2(9)	-10.1(10)	-2.6(9)
C32	27.6(12)	30.0(12)	24.8(12)	-8.1(10)	3.6(10)	0.2(10)
C7	52.5(19)	57.4(19)	36.7(16)	-30.7(15)	-4.3(14)	0.1(15)
C14	18.4(11)	31.9(12)	35.9(14)	-10.6(11)	-11.7(10)	6.9(9)
C22	73(2)	22.6(11)	21.0(12)	-0.5(10)	-26.6(13)	-12.6(12)
C26	38(3)	21.1(15)	15.6(15)	-3.8(12)	-10.1(15)	-0.1(14)
C24	47.9(16)	57.6(18)	21.8(13)	-21.8(13)	-0.2(11)	-26.7(14)

C9	45.7(17)	34.2(15)	63(2)	-28.5(15)	-5.5(15)	11.0(13)
C8	60(2)	53.9(19)	59(2)	-43.8(18)	1.3(17)	8.1(16)
C25	31(2)	28.2(19)	15.3(15)	-9.4(13)	-6.8(13)	3.0(16)
C23	20.6(15)	21.9(14)	16.3(14)	-6.9(11)	-6.3(11)	1.0(11)
C53	82.4(15)	80(2)	75.2(18)	-43.4(14)	-3.0(12)	8.2(14)
C52	82.1(16)	80(2)	70.9(19)	-47.7(13)	3.7(13)	21.8(16)
C51	88.8(19)	107(3)	86(2)	-47.9(17)	-8.1(13)	32.5(18)
C50	109(2)	115(3)	114(3)	-52(2)	-37.1(17)	9.6(19)
C49	119.6(19)	119(3)	107(3)	-44.7(18)	-36.5(16)	-23(2)
C48	109.6(17)	97(3)	92(2)	-34.0(17)	-25.6(13)	-19.0(16)
C54	90.0(17)	108(4)	67(2)	-42(2)	-4.2(14)	-8(2)
C23A	15(4)	23(4)	15(4)	-7(3)	-7(3)	-3(3)
C26A	16(5)	21(4)	12(4)	-4(3)	-4(3)	2(3)
C25A	21(4)	27(5)	12(4)	-9(3)	-10(3)	7(4)
C54A	89(3)	94(2)	71(4)	-45(3)	-8(2)	14(2)
C53A	92(2)	93.4(14)	76(3)	-40(2)	-7.6(15)	8.2(16)
C52A	91(2)	94(2)	67(3)	-55(2)	-5.5(15)	17.2(15)
C51A	94(2)	99.8(19)	87(3)	-50(2)	-11.2(16)	9.1(18)
C50A	114(2)	104.6(18)	115(4)	-33(3)	-26.4(18)	-8(2)
C49A	120(3)	100.6(19)	118(4)	-20(2)	-28(2)	-13.3(17)
C48A	107(2)	97.7(14)	96(4)	-23(2)	-16.7(18)	-5.1(19)

Table S10 Bond Lengths for 2b.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1	P1	2.3817(5)	C13	C14	1.521(4)
Pd1	P2	2.3743(5)	C4	C9	1.386(4)
Pd1	O1	2.1475(15)	C15	C14	1.530(3)
Pd1	C46	1.972(2)	C31	C32	1.523(4)
P1	C10	1.855(2)	C7	C8	1.387(5)
P1	C16	1.846(2)	C22	C23	1.476(4)
P1	C22	1.847(2)	C22	C23A	1.344(7)
P2	C34	1.849(2)	C26	C25	1.519(5)
P2	C40	1.855(2)	C24	C25	1.484(4)
P2	C28	1.850(2)	C24	C23	1.590(4)
O1	C1	1.282(3)	C24	C23A	1.543(8)
O4	C46	1.212(3)	C24	C25A	1.815(9)
O3	C4	1.365(3)	C9	C8	1.370(5)
O3	C3	1.398(3)	C53	C52	1.3900
O2	C3	1.218(3)	C53	C48	1.3900
C20	C16	1.528(3)	C53	C54	1.586(8)
C20	C21	1.534(3)	C53	C54A	1.57(2)
C36	C35	1.530(3)	C53	C53A	0.505(15)
C36	C37	1.528(3)	C53	C52A	0.915(16)

C46	C47	1.521(3)	C53	C51A	1.968(14)
C35	C34	1.537(3)	C53	C48A	1.646(16)
C34	C39	1.535(3)	C52	C51	1.3900
C10	C11	1.537(3)	C52	C53A	1.742(17)
C10	C15	1.536(3)	C52	C52A	0.745(14)
C16	C17	1.538(3)	C52	C51A	1.881(17)
C40	C41	1.533(3)	C51	C50	1.3900
C40	C45	1.540(3)	C51	C52A	1.501(16)
C11	C12	1.535(3)	C51	C51A	1.428(17)
C19	C18	1.536(3)	C50	C49	1.3900
C19	C21	1.524(3)	C50	C51A	0.937(13)
C18	C17	1.529(3)	C50	C50A	1.972(19)
C1	C5	1.471(3)	C49	C48	1.3900
C1	C2	1.380(3)	C49	C51A	1.102(17)
C28	C33	1.541(3)	C49	C50A	1.102(18)
C28	C29	1.538(3)	C48	C53A	1.626(15)
C41	C42	1.530(3)	C48	C52A	1.678(13)
C5	C6	1.399(3)	C48	C51A	1.647(14)
C5	C4	1.392(3)	C48	C50A	1.560(15)
C12	C13	1.520(3)	C48	C49A	1.504(15)
C39	C38	1.528(3)	C48	C48A	1.539(15)
C38	C37	1.525(3)	C54	C54A	0.87(2)
C33	C32	1.529(3)	C54	C53A	1.128(14)
C29	C30	1.530(3)	C54	C48A	1.85(2)
C42	C43	1.523(4)	C26A	C25A	1.530(12)
C2	C3	1.418(3)	C54A	C53A	1.31(3)
C43	C44	1.523(4)	C53A	C52A	1.3900
C30	C31	1.529(4)	C53A	C48A	1.3900
C6	C7	1.378(4)	C52A	C51A	1.3900
C45	C44	1.531(3)	C51A	C50A	1.3900
C27	C22	1.542(3)	C50A	C49A	1.3900
C27	C26	1.549(4)	C49A	C48A	1.3900
C27	C26A	1.582(8)			

Table S11 Bond Angles for 2b.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
P2	Pd1	P1	166.469(19)	C49	C50	C50A	32.9(5)
O1	Pd1	P1	94.92(4)	C51A	C50	C51	72.8(11)
O1	Pd1	P2	85.67(4)	C51A	C50	C49	52.2(10)
C46	Pd1	P1	88.03(6)	C51A	C50	C50A	39.9(10)
C46	Pd1	P2	91.14(6)	C50	C49	C48	120.0
C46	Pd1	O1	176.75(7)	C51A	C49	C50	42.2(7)

C10	P1	Pd1	112.82(7)	C51A	C49	C48	81.8(7)
C16	P1	Pd1	107.43(7)	C51A	C49	C50A	78.2(10)
C16	P1	C10	110.43(10)	C50A	C49	C50	104.0(10)
C16	P1	C22	104.07(10)	C50A	C49	C48	76.6(8)
C22	P1	Pd1	118.58(11)	C53	C48	C53A	17.1(6)
C22	P1	C10	103.09(12)	C53	C48	C52A	33.0(6)
C34	P2	Pd1	111.33(7)	C53	C48	C51A	80.3(6)
C34	P2	C40	103.72(10)	C53	C48	C50A	116.9(6)
C34	P2	C28	111.00(10)	C53	C48	C49A	111.7(7)
C40	P2	Pd1	106.78(7)	C53	C48	C48A	68.2(7)
C28	P2	Pd1	119.07(7)	C49	C48	C53	120.0
C28	P2	C40	103.36(10)	C49	C48	C53A	135.8(6)
C1	O1	Pd1	126.08(14)	C49	C48	C52A	87.1(6)
C4	O3	C3	121.23(18)	C49	C48	C51A	41.5(6)
C16	C20	C21	109.38(17)	C49	C48	C50A	43.4(7)
C37	C36	C35	111.29(19)	C49	C48	C49A	94.4(8)
O4	C46	Pd1	124.91(18)	C49	C48	C48A	145.3(8)
O4	C46	C47	119.4(2)	C53A	C48	C52A	49.7(4)
C47	C46	Pd1	115.65(16)	C53A	C48	C51A	94.7(6)
C36	C35	C34	110.14(18)	C51A	C48	C52A	49.4(4)
C35	C34	P2	113.96(15)	C50A	C48	C53A	121.5(7)
C39	C34	P2	117.45(15)	C50A	C48	C52A	96.0(7)
C39	C34	C35	109.93(17)	C50A	C48	C51A	51.3(4)
C11	C10	P1	112.36(14)	C49A	C48	C53A	100.5(8)
C15	C10	P1	117.65(16)	C49A	C48	C52A	121.6(7)
C15	C10	C11	109.83(18)	C49A	C48	C51A	99.5(8)
C20	C16	P1	117.81(14)	C49A	C48	C50A	53.9(5)
C20	C16	C17	109.91(17)	C49A	C48	C48A	54.3(5)
C17	C16	P1	113.16(14)	C48A	C48	C53A	52.0(5)
C41	C40	P2	112.01(15)	C48A	C48	C52A	96.8(7)
C41	C40	C45	110.69(18)	C48A	C48	C51A	121.5(7)
C45	C40	P2	111.07(15)	C48A	C48	C50A	101.9(8)
C12	C11	C10	110.84(18)	C53	C54	C48A	56.7(5)
C21	C19	C18	110.48(18)	C54A	C54	C53	72.6(18)
C17	C18	C19	110.61(19)	C54A	C54	C53A	80.9(19)
O1	C1	C5	117.41(19)	C54A	C54	C48A	129.3(19)
O1	C1	C2	125.9(2)	C53A	C54	C53	9.1(9)
C2	C1	C5	116.73(19)	C53A	C54	C48A	48.6(8)
C18	C17	C16	109.93(18)	C22	C23A	C24	118.6(5)
C33	C28	P2	112.52(15)	C25A	C26A	C27	103.0(6)
C29	C28	P2	117.08(16)	C26A	C25A	C24	102.0(6)
C29	C28	C33	108.96(18)	C54	C54A	C53	75.2(18)
C42	C41	C40	110.59(19)	C54	C54A	C53A	58.0(17)

C6	C5	C1	122.4(2)	C53A	C54A	C53	17.5(8)
C4	C5	C1	118.7(2)	C53	C53A	C52	39.4(16)
C4	C5	C6	118.8(2)	C53	C53A	C48	53.9(15)
C13	C12	C11	111.61(19)	C53	C53A	C54	150(3)
C38	C39	C34	109.71(18)	C53	C53A	C54A	111(3)
C37	C38	C39	111.61(19)	C53	C53A	C52A	15.9(18)
C32	C33	C28	110.14(18)	C53	C53A	C48A	111.8(16)
C30	C29	C28	110.2(2)	C48	C53A	C52	91.2(7)
C43	C42	C41	111.7(2)	C54	C53A	C52	125.6(12)
C19	C21	C20	111.24(18)	C54	C53A	C48	139.4(14)
C1	C2	C3	123.5(2)	C54	C53A	C54A	41.1(11)
C44	C43	C42	110.98(19)	C54	C53A	C52A	146.2(13)
C31	C30	C29	111.5(2)	C54	C53A	C48A	93.8(13)
C7	C6	C5	120.2(3)	C54A	C53A	C52	87.3(15)
C44	C45	C40	111.69(19)	C54A	C53A	C48	145.9(16)
C38	C37	C36	110.94(19)	C54A	C53A	C52A	105.2(16)
C22	C27	C26	109.7(2)	C54A	C53A	C48A	134.7(16)
C22	C27	C26A	118.6(3)	C52A	C53A	C52	24.4(6)
C12	C13	C14	110.45(19)	C52A	C53A	C48	67.1(5)
O3	C4	C5	122.1(2)	C52A	C53A	C48A	120.0
O3	C4	C9	117.0(2)	C48A	C53A	C52	136.8(6)
C9	C4	C5	121.0(3)	C48A	C53A	C48	60.8(5)
C14	C15	C10	110.06(19)	C53	C52A	C51	170.2(15)
O3	C3	C2	117.5(2)	C53	C52A	C48	55.9(7)
O2	C3	O3	115.1(2)	C53	C52A	C53A	8.7(10)
O2	C3	C2	127.4(2)	C53	C52A	C51A	115.7(9)
C32	C31	C30	111.0(2)	C52	C52A	C53	113.3(19)
C43	C44	C45	111.7(2)	C52	C52A	C51	66.9(11)
C31	C32	C33	110.6(2)	C52	C52A	C48	165.8(17)
C6	C7	C8	119.7(3)	C52	C52A	C53A	105.4(16)
C13	C14	C15	112.4(2)	C52	C52A	C51A	120.5(17)
C27	C22	P1	110.04(16)	C51	C52A	C48	121.9(10)
C23	C22	P1	116.93(19)	C53A	C52A	C51	164.5(9)
C23	C22	C27	114.9(2)	C53A	C52A	C48	63.2(5)
C23A	C22	P1	135.1(4)	C53A	C52A	C51A	120.0
C23A	C22	C27	114.2(4)	C51A	C52A	C51	59.1(9)
C25	C26	C27	111.0(3)	C51A	C52A	C48	64.1(5)
C25	C24	C23	109.9(2)	C52	C51A	C53	42.3(3)
C23A	C24	C25A	97.2(4)	C51	C51A	C53	88.8(8)
C8	C9	C4	119.1(3)	C51	C51A	C52	47.3(5)
C9	C8	C7	121.2(3)	C51	C51A	C48	129.3(11)
C24	C25	C26	109.2(3)	C50	C51A	C53	143.8(15)
C22	C23	C24	108.2(2)	C50	C51A	C52	113.1(13)

C52	C53	C48	120.0	C50	C51A	C51	68.4(9)
C52	C53	C54	119.2(4)	C50	C51A	C49	85.6(12)
C52	C53	C54A	92.1(10)	C50	C51A	C48	135.6(14)
C52	C53	C51A	65.5(5)	C50	C51A	C52A	123.1(15)
C52	C53	C48A	147.5(7)	C50	C51A	C50A	114.4(15)
C48	C53	C54	120.8(4)	C49	C51A	C53	99.4(9)
C48	C53	C54A	144.0(9)	C49	C51A	C52	135.9(12)
C48	C53	C51A	55.6(5)	C49	C51A	C51	143.9(13)
C48	C53	C48A	60.2(6)	C49	C51A	C48	56.7(6)
C54	C53	C51A	167.7(6)	C49	C51A	C52A	116.5(10)
C54	C53	C48A	69.7(6)	C49	C51A	C50A	50.9(10)
C54A	C53	C54	32.2(8)	C48	C51A	C53	44.1(3)
C54A	C53	C51A	157.0(11)	C48	C51A	C52	85.8(7)
C54A	C53	C48A	101.9(11)	C52A	C51A	C53	24.8(4)
C53A	C53	C52	127(2)	C52A	C51A	C52	20.0(6)
C53A	C53	C48	109.0(19)	C52A	C51A	C51	64.3(9)
C53A	C53	C54	20.7(18)	C52A	C51A	C48	66.5(5)
C53A	C53	C54A	52(2)	C52A	C51A	C50A	120.0
C53A	C53	C52A	155(3)	C50A	C51A	C53	95.5(4)
C53A	C53	C51A	147(2)	C50A	C51A	C52	132.5(6)
C53A	C53	C48A	51.6(14)	C50A	C51A	C51	163.6(9)
C52A	C53	C52	29.5(9)	C50A	C51A	C48	61.2(6)
C52A	C53	C48	91.1(9)	C49	C50A	C50	43.2(7)
C52A	C53	C54	147.9(10)	C49	C50A	C48	60.0(7)
C52A	C53	C54A	117.5(14)	C49	C50A	C51A	50.9(9)
C52A	C53	C51A	39.5(6)	C49	C50A	C49A	116.5(10)
C52A	C53	C48A	138.4(13)	C48	C50A	C50	85.1(7)
C48A	C53	C51A	100.2(7)	C51A	C50A	C50	25.6(6)
C53	C52	C51	120.0	C51A	C50A	C48	67.6(5)
C53	C52	C53A	13.3(5)	C49A	C50A	C50	143.9(6)
C53	C52	C51A	72.2(4)	C49A	C50A	C48	61.0(6)
C51	C52	C53A	132.0(5)	C49A	C50A	C51A	120.0
C51	C52	C51A	49.0(4)	C50A	C49A	C48	65.1(6)
C53A	C52	C51A	83.2(5)	C50A	C49A	C48A	120.0
C52A	C52	C53	37.2(13)	C48A	C49A	C48	64.1(6)
C52A	C52	C51	83.5(13)	C53	C48A	C54	53.6(6)
C52A	C52	C53A	50.3(12)	C48	C48A	C53	51.6(4)
C52A	C52	C51A	39.6(12)	C48	C48A	C54	99.3(9)
C52	C51	C52A	29.6(6)	C53A	C48A	C53	16.5(5)
C52	C51	C51A	83.7(6)	C53A	C48A	C48	67.2(5)
C50	C51	C52	120.0	C53A	C48A	C54	37.5(7)
C50	C51	C52A	90.6(6)	C49A	C48A	C53	104.0(5)
C50	C51	C51A	38.8(6)	C49A	C48A	C48	61.6(6)

C51A	C51	C52A	56.6(5)	C49A	C48A	C54	157.5(7)
C51	C50	C50A	111.0(5)	C49A	C48A	C53A	120.0
C49	C50	C51	120.0				

Table S12 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2b.

Atom	*x*	*y*	*z*	U(eq)
H20A	10845.03	4512.86	1918.46	22
H20B	10583.14	4556.04	3021.57	22
H36A	5644.75	-196.2	3076.27	30
H36B	4861.25	-728.54	4171.57	30
H35A	5620.23	877.06	4004.74	24
H35B	4397.72	947.07	4213.58	24
H34	5792.63	1709.42	2250.56	21
H10	9343.79	1534.42	3221.7	22
H16	8871.15	4941.81	2951.21	21
H40	5161.63	4083.09	1274.32	23
H11A	9248.38	2593.11	1577.36	24
H11B	10322.56	3177.46	1366.7	24
H19A	10717.58	6224.87	414.42	30
H19B	10336.57	7259.45	640.62	30
H18A	8672.99	6465	1528.4	31
H18B	8966.55	6417.26	426.72	31
H17A	9412.26	4638.47	1086.5	29
H17B	8253.27	4751.59	1673.82	29
H28	4718.59	4220.25	3587.96	23
H41A	7305.96	3664.07	977.79	27
H41B	6480.83	3029.9	788.42	27
H12A	10049.03	973.52	1777.98	28
H12B	10630.86	1832.54	706.04	28
H39A	3632.47	1952.67	2747.97	27
H39B	4383.71	2504.52	1636.42	27
H38A	3644.24	892.33	1805.39	31
H38B	4868.42	843.14	1570.26	31
H33A	3584.84	2240.22	4528.69	28
H33B	4485.36	2521.36	4911.42	28
H29A	3894.75	4585.52	2283.2	32
H29B	3236.91	3493.14	2909.91	32
H42A	7425.16	4320.27	-764.34	31
H42B	6227.45	4551.15	-543.66	31
H21A	10137.08	6340.05	2378.11	26
H21B	11287.52	6226.53	1774.79	26
H2	7349.97	689.12	4406.34	25

H43A	7757.54	5636.14	-219.43	35
H43B	7175.55	6140.43	-1081.56	35
H30A	3145.22	5214.84	3581.23	36
H30B	2248.78	4863.1	3240.22	36
H6	7903.64	1381.12	969.11	36
H45A	5449.73	5386.73	1858.11	29
H45B	6646.42	5154.64	1675.52	29
H37A	4133.79	-737.26	2878.91	33
H37B	3447.43	-106.98	3523.64	33
H47A	5416.56	3758.53	5071.95	41
H47B	6450.34	3853.88	5360.27	41
H47C	6161.79	2793.8	5259.61	41
H27A	8739.43	1298.99	5100.9	30
H27B	7757.93	1903.53	5476.71	30
H27C	9003.54	1312.35	5314.27	30
H27D	7916.55	1725.19	5154.02	30
H13A	11970.41	2053.15	1336.57	33
H13B	11819.03	823.02	1577.41	33
H15A	11173.68	2727.39	2817.09	31
H15B	10612.19	1868.33	3899.34	31
H31A	1877.21	4226.8	5038.32	42
H31B	1929.64	3275.32	4653.84	42
H44A	5615.78	6059.96	119.81	33
H44B	6458.86	6662.81	317.34	33
H32A	2864.14	2848.38	5859.51	36
H32B	3545.21	3926.78	5240.62	36
H7	8588.61	419.7	-38.41	56
H14A	11975.55	1107.66	3016.95	34
H14B	10898.26	522.35	3246.1	34
H22	9787.22	2815.5	4468.47	45
H26A	8404.6	991.29	6879.98	30
H26B	9539.38	1490.94	6253.05	30
H24A	9926.52	3345.35	5798.64	49
H24B	9079.21	4083.9	6166.31	49
H24C	8516.3	3829.16	5980.36	49
H24D	9671.41	3878.54	6080.19	49
H9	9065.56	-1990.95	2376.38	56
H8	9158.72	-1261.25	673.07	66
H25A	7828.81	2687.05	6810.17	29
H25B	8741.12	2374.73	7348.44	29
H23A	8124.06	3986.33	5024.06	23
H23B	9270.56	4450.5	4385.89	23
H52	6023.85	3196.36	7530.03	94

H51	4582.58	3368.46	6914.54	114
H50	3169.99	2175.13	7818.68	130
H49	3198.66	809.7	9338.34	134
H48	4639.92	637.6	9953.86	119
H54A	6878.02	2443.98	8848.03	133
H54B	6865.33	1214.5	9047	133
H54C	6256.63	1615.3	9919.66	133
H23C	9826.65	4113.68	4378.32	20
H23D	10265.56	3005.16	4911.17	20
H26C	7540.21	2202.02	6603.78	21
H26D	7904.25	1006.97	6944.15	21
H25C	9682.43	1732.09	6469.17	23
H25D	8952.24	1973.57	7412.92	23
H54D	6522.88	3042.47	8248.37	126
H54E	7029.03	2146.02	9017.7	126
H54F	6042.51	2713.32	9437.81	126
H52A	5206.03	3042.86	8026.83	96
H51A	3876.95	2154.05	7880	110
H50A	3661.36	321.3	8675.72	137
H49A	4774.84	-622.66	9618.27	143
H48A	6103.93	266.13	9765.12	127

Table S13 Atomic Occupancy for 2b.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
H27A	0.725(10)	H27B	0.725(10)	H27C	0.275(10)
H27D	0.275(10)	C26	0.725(10)	H26A	0.725(10)
H26B	0.725(10)	H24A	0.720(10)	H24B	0.720(10)
H24C	0.270(7)	H24D	0.270(7)	C25	0.720(10)
H25A	0.720(10)	H25B	0.720(10)	C23	0.730(7)
H23A	0.730(7)	H23B	0.730(7)	C53	0.764(4)
C52	0.764(4)	H52	0.764(4)	C51	0.764(4)
H51	0.764(4)	C50	0.764(4)	H50	0.764(4)
C49	0.764(4)	H49	0.764(4)	C48	0.764(4)
H48	0.764(4)	C54	0.764(4)	H54A	0.764(4)
H54B	0.764(4)	H54C	0.764(4)	C23A	0.270(7)
H23C	0.270(7)	H23D	0.270(7)	C26A	0.275(10)
H26C	0.275(10)	H26D	0.275(10)	C25A	0.280(10)
H25C	0.280(10)	H25D	0.280(10)	C54A	0.236(4)
H54D	0.236(4)	H54E	0.236(4)	H54F	0.236(4)
C53A	0.236(4)	C52A	0.236(4)	H52A	0.236(4)
C51A	0.236(4)	H51A	0.236(4)	C50A	0.236(4)
H50A	0.236(4)	C49A	0.236(4)	H49A	0.236(4)

C48A 0.236(4) H48A 0.236(4)

Refinement model description

Number of restraints - 276, number of constraints - unknown.
Details:
1. Fixed Uiso
At 1.2 times of:
All C(H) groups, All C(H,H) groups, All C(H,H,H,H) groups
At 1.5 times of:
All C(H,H,H) groups
2. Restrained distances
C53-C54 = C53A-C54A
0.01 with sigma of 1.5
C54-C53 = C53A-C54A
0.02 with sigma of 2.5
C48-C53 = C49A-C53A
0.02 with sigma of 2.5
3. Rigid bond restraints
C54, C53, C48, C49, C50, C51, C52, C54A, C53A, C48A, C49A, C50A, C51A, C52A
with sigma for 1-2 distances of 0.0001 and sigma for 1-3 distances of 0.0001
C25A, C25
with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01
4. Uiso/Uaniso restraints and constraints
C25A ≈ C25: within 1.7A with sigma of 0.04 and sigma for terminal atoms of
0.08
C54 ≈ C53 ≈ C48 ≈ C49 ≈ C50 ≈ C51 ≈ C52 ≈ C54A
≈ C53A ≈ C48A ≈ C49A ≈ C50A ≈ C51A ≈ C52A: within 2A
with sigma of 0.01 and sigma for terminal atoms of 0.02
Uanis(C25A) ≈ Ueq, Uanis(C25) ≈ Ueq: with sigma of 0.1 and sigma for
terminal atoms of 0.2
5. Others
Sof(H24C)=Sof(H24D)=Sof(C23A)=Sof(H23C)=Sof(H23D)=1-FVAR(1)
Sof(C23)=Sof(H23A)=Sof(H23B)=FVAR(1)
Sof(H27C)=Sof(H27D)=Sof(C26A)=Sof(H26C)=Sof(H26D)=1-FVAR(2)
Sof(H27A)=Sof(H27B)=Sof(C26)=Sof(H26A)=Sof(H26B)=FVAR(2)
Sof(C25A)=Sof(H25C)=Sof(H25D)=1-FVAR(3)
Sof(H24A)=Sof(H24B)=Sof(C25)=Sof(H25A)=Sof(H25B)=FVAR(3)
Sof(C54A)=Sof(H54D)=Sof(H54E)=Sof(H54F)=Sof(C53A)=Sof(C52A)=Sof(H52A)=
Sof(C51A)=Sof(H51A)=Sof(C50A)=Sof(H50A)=Sof(C49A)=Sof(H49A)=Sof(C48A)=
Sof(H48A)=1-FVAR(4)
Sof(C53)=Sof(C52)=Sof(H52)=Sof(C51)=Sof(H51)=Sof(C50)=Sof(H50)=Sof(C49)=
Sof(H49)=Sof(C48)=Sof(H48)=Sof(C54)=Sof(H54A)=Sof(H54B)=Sof(H54C)=FVAR(4)
6.a Ternary CH refined with riding coordinates:
C34(H34), C10(H10), C16(H16), C40(H40), C28(H28), C22(H22)
6.b Secondary CH2 refined with riding coordinates:
C20(H20A,H20B), C36(H36A,H36B), C35(H35A,H35B), C11(H11A,H11B), C19(H19A,
H19B), C18(H18A,H18B), C17(H17A,H17B), C41(H41A,H41B), C12(H12A,H12B),

C39(H39A,H39B), C38(H38A,H38B), C33(H33A,H33B), C29(H29A,H29B), C42(H42A,H42B), C21(H21A,H21B), C43(H43A,H43B), C30(H30A,H30B), C45(H45A,H45B), C37(H37A, H37B), C27(H27A,H27B), C27(H27C,H27D), C13(H13A,H13B), C15(H15A,H15B), C31(H31A,H31B), C44(H44A,H44B), C32(H32A,H32B), C14(H14A,H14B), C26(H26A,H26B), C24(H24A,H24B), C24(H24C,H24D), C25(H25A,H25B), C23(H23A,H23B), C23A(H23C, H23D), C26A(H26C,H26D), C25A(H25C,H25D)

6.c Aromatic/amide H refined with riding coordinates:
C2(H2), C6(H6), C7(H7), C9(H9), C8(H8), C52(H52), C51(H51), C50(H50), C49(H49), C48(H48), C52A(H52A), C51A(H51A), C50A(H50A), C49A(H49A), C48A(H48A)

6.d Fitted hexagon refined as free rotating group:
C53(C52,C51,C50,C49,C48), C53A(C52A,C51A,C50A,C49A,C48A)

6.e Idealised Me refined as rotating group:
C47(H47A,H47B,H47C), C54(H54A,H54B,H54C), C54A(H54D,H54E,H54F)

VII. References

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